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Recent Developments in the Chemistry of Cubic Polyhedral Oligosilsesquioxanes

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1. Introduction

The study of the chemistry of compounds containing Si−O bonds has for many years been dominated by both silica and minerals for which the formula unit SiO_2 is important, or by the silicones field in which the R_2SiO unit dominates. However, within the last 10−15 years, the field of silsesquioxane chemistry, based on compounds with $RSiO_{3/2}$ repeat units, has grown dramatically. These compounds thus have a formula unit between that of the inorganic ceramic materials and the more organic silicone polymers and have often been described as having "hybrid" properties, that is, some from the chemically inert and thermally stable inorganic Si−O−Si fragment and some from the potentially reactive and readily modified R−Si fragment. A variety of polymeric structures based on the $RSiO_{3/2}$ backbone may be readily prepared, from random polymers through ladder polymers to more highly ordered discrete molecular species with the general formula $(RSiO_{3/2})_n$ where n is commonly 6, 8, or 10. This review focuses on those compounds based on the $(RSiO_{3/2})_8$ formula, and in particular the significant growth in studies since 2003; earlier work in this area has been reviewed.[1]

The general structure of $(RSiO_{3/2})_8$ compounds (Figure 1) shows some of the important features of these molecules including the siloxane cage size and the distribution of the eight pendant arms from the cube in a three-dimensional arrangement. These cubic siloxane cages with readily functionalized substituents have thus become very popular as nanometer-scale building blocks in a wide range of polymeric materials. These compounds have become known as polyhedral oligosilsesquioxanes and the name POSS has been trademarked by Hybrid Plastics.[2] One of the main reasons for the rapid growth of POSS applications is the recent commercial availability of a range of useful precursors. The full nomenclature for these polyhedral structures is complicated, but fortunately, the nomenclature used for siloxane polymers can be applied, thus a silicon atom bearing three oxygen atoms also connected to silicon is denoted by "T", and therefore in Figure 1, for $R = X = H$ the structure can be abbreviated as T_8H_8 and many structures of the general type T_8R_8 (R = alkyl, aryl, alkoxy, siloxy, etc.) are known.

This review will focus on the synthesis, properties, and applications of molecular T_8R_8 compounds rather than on their properties and applications within polymeric materials.

David B. Cordes studied chemistry at the University of Otago, New Zealand, obtaining a BSc(Hons) in 2002 and PhD in 2006, working with Professor L. R. Hanton on the synthesis and characterization of coordination polymeric materials. He moved to The University of Alabama in 2007 for a postdoctoral position with Professor R. D. Rogers, looking at materials and crystal engineering applications for ionic liquid systems. He joined the Lickiss group in 2008 as a postdoctoral research associate, and is working on the preparation of metal-organic frameworks for hydrogen storage, and the chemistry of silsesquioxanes. His interests are in self-assembled materials in the solid state, crystal engineering and X-ray crystallography.

Paul Lickiss is Reader in Organometallic Chemistry in the Chemistry Department at Imperial College London. He obtained both his BSc. (1980) and DPhil. (1983) from the University of Sussex, where his DPhil. was supervised by Professor C. Eaborn, FRS. He left Sussex to work as a postdoctoral fellow with Professor A. G. Brook in Toronto where he prepared some of the first compounds to contain silicon to carbon double bonds. He returned to Sussex and was awarded one of the new Royal Society University Research Fellowships. In 1989 he took up a lectureship at the University of Salford and after four years he moved to London to take up a lectureship at Imperial College where he was made a Senior Lecturer in 1999 and a Reader in 2001. The Lickiss research group has a range of interests in the field of main-group chemistry, particularly organosilicon chemistry. The main areas of interest have been the chemistry of bulky organosilicon compounds and reactive intermediates derived from them such as silyl cations. Silanols and siloxanes have also been a continuing area of interest as has the use of ultrasound for chemical synthesis. More recently the chemistry of silsesquioxanes has been a focus in the group together with the synthesis and characterization of metal-organic frameworks as materials for gas storage. Apart from chemistry, Paul enjoys playing badminton, origami, and collecting books.

Franck Rataboul graduated in Chemistry from the University of Toulouse working for his research project with B. Chaudret. He obtained his PhD from the University of Lyon (France) working with J.M. Basset on heterogeneous catalysis for alkane transformations. After one year of postdoctoral research with M. Beller (Rostock, Germany) on homogeneous catalysis, he spent two years as a research associate at Imperial College London in the group of P. D. Lickiss, working on POSS-based metal organic frameworks. In October 2007, he joined the Institute for Research on Catalysis and Environment at the University of Lyon with a permanent CNRS research position. His current projects include the transformation of polysaccharides using heterogeneous catalysis.

However, some discussion of how molecular POSS compounds can be applied in composites and other polymeric materials and the effects that the POSS species have is provided in the Properties and Applications sections (section 4). The applications of POSS-containing materials have previously been reviewed extensively. Thus, general reviews on the incorporation and effects of POSS on polymeric material properties have been published,[3–24] as well as more specialized reviews on cross-linked resins containing POSS species,[25–27] the flammability of POSS-containing nanocomposites,[28–34] modification of polyolefins using POSS species,[35] viscoelastic and thermal properties of POSS-filled nanocomposites,[36–38] silsesquioxane-based catalysts,[39,40] synthesis of POSS compounds,[37,41] POSS-substituted polyurethanes used for high-performance applications,[42] POSS nanocomposites for biomedical applications,[43] POSS materials for dental nanocomposites,[44] POSS compounds as additives in cosmetics,[45] POSS cages as building blocks for zeolite-like materials,[46] the presence of POSS cages in the wider field of sol−gel processing of polysilsesquioxanes,[47] optical properties of POSS-containing materials,[48,49] flow properties of polymers,[50] and the effects of aryl-substituted POSS species on the reinforcement of composite materials.[51] Earlier studies on polymers and copolymers containing POSS polyhedra have been reviewed.[52]

It should also be noted that the use of incompletely condensed silsesquioxanes such as $T_7R_7(OH)_3$ and related metallasiloxanes as mimics for silica surfaces and catalyst supports has also been reviewed.[53–59]

2. Synthesis of POSS Compounds

This section is focused on the synthesis of T_8 POSS, both previously unknown species and new syntheses of known species. The wide variety of polymeric and composite materials with POSS species as components will be discussed in section 4, while this section will concentrate primarily on discrete molecular species. For older synthetic routes to T_8 POSS species, see ref 1.

While there are many specific routes for the synthesis of POSS compounds, they can be simplified to two types of reactions, making POSS species by preparing a T_8 core from precursors containing fewer than eight silicon atoms and chemically modifying the functional groups of an already existing T_8 core to give a new POSS derivative. Each of these types of reaction can then be broken down further into two subcategories (Scheme 1). Within the making of T_8

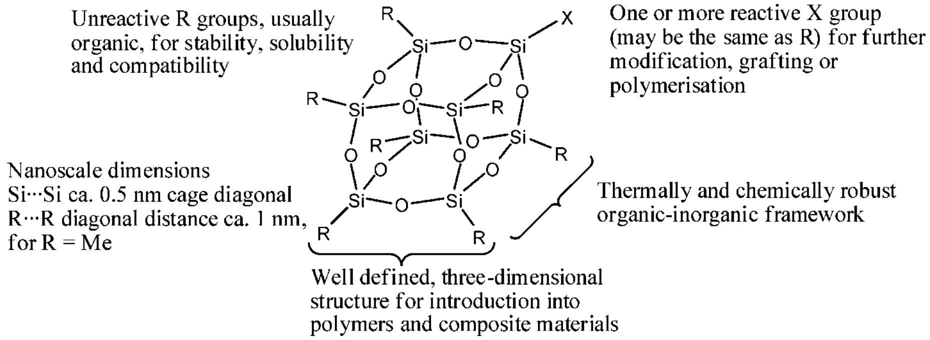


Figure 1. The general features of a cubic polyhedral silsesquioxane.

Scheme 1

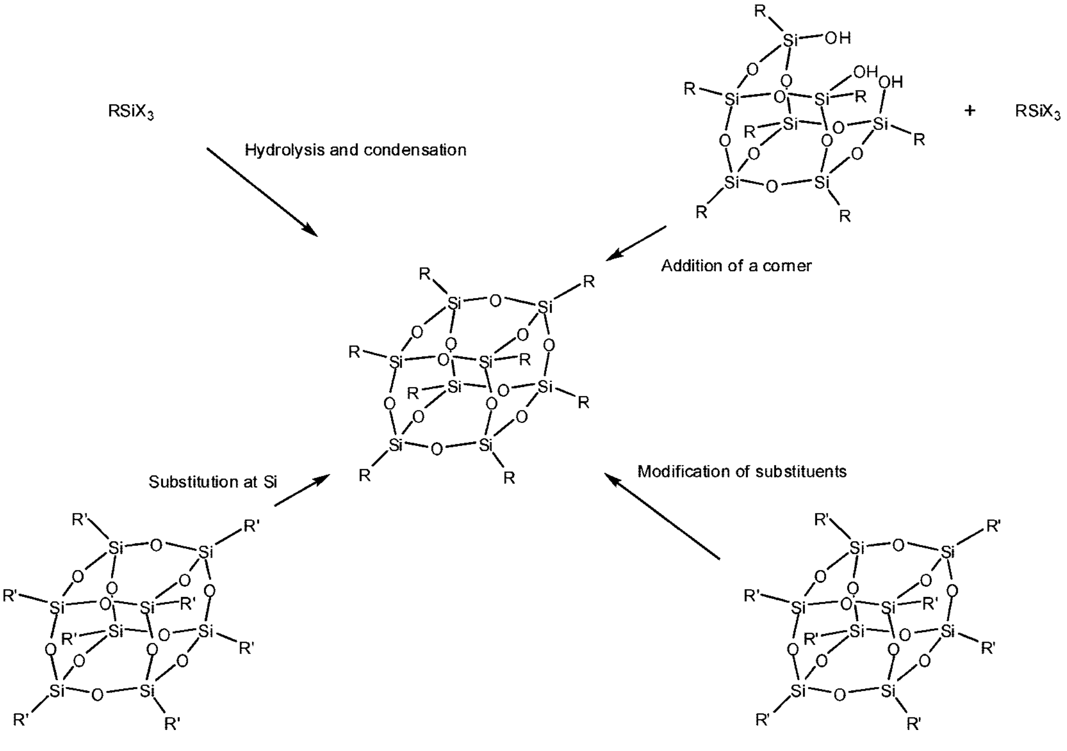
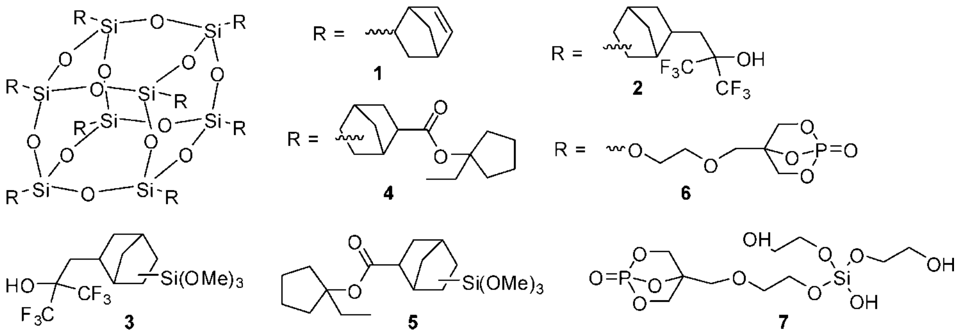


Chart 1



cores, there is the hydrolysis and condensation of simple chloro- or alkoxysilanes, or the addition of a chloro- or alkoxysilane to a corner-truncated cube species $R_7Si_7O_9(OH)_3$ (or a metalated derivative), while for the modification of functionalities on a T_8 core, there is the substitution of functional groups at one or more of the corner Si atoms or the modification of one or more of the functional groups. A certain degree of variation on these is possible for the synthesis of T_8 species with differing substitutions, T_8R_7R' being the most common, and $T_8R_6R'_2$, $T_8R_6R'R''$, $T_8R_5R'_3$, and $T_8R_4R'_4$ also being known. However, there is to date no way to control or direct the formation of particular substitutional isomers of the T_8 cage when introducing two or more different substituents.

2.1. Synthesis of POSS Compounds by Hydrolysis and Condensation

2.1.1. T_8R_8 Compounds

Syntheses of T_8-type POSS have been known for over 60 years now, with much of the early preparative work involving the spontaneous formation of cubic T_8 species from the hydrolysis and condensation reactions of chloro- or alkoxysilanes. This preferential formation of the cubic species over the T_{10}, T_{12}, and other POSS species is likely due to the stability of the Si_4O_4 ring structure. While a significant proportion of the simpler T_8 POSS derivatives have been prepared by the hydrolysis/condensation route, it does have certain inherent disadvantages. These include the often long reaction times, up to three months in some cases, and their often less than 50% yields. These low yields are one of the biggest problems inherent in the hydrolysis/condensation route to POSS species and are due to the formation of mixtures of products: first with byproduct of ladder and other nonpolyhedral silsesquioxane polymers, followed by the formation of other higher oligomers of the desired POSS species, such as the T_{10} and T_{12} derivatives. Even after the optimization of reaction conditions, separation of the desired T_8 product from the byproducts can lead to much lower than ideal yields. In order to improve the yields of these simple preparations, work is ongoing with changes in solvent systems, type of hydrolysis, and addition of other compounds to the reactions. The hydrolysis of $RSiX_3$ route also, necessarily, usually affords symmetrical T_8R_8 compounds; attempts to prepare compounds bearing two or more substituents by hydrolysis of mixtures of precursors invariably lead to complicated mixtures that are difficult to separate, see section 2.1.2. Those new octasubstituted T_8 POSS prepared since 2003 and those prepared by improved methods are presented in Table 1 and Chart 1, while those with differing substitution patterns are presented in Table 2 and Chart 2.

Some of the simplest T_8 POSS, such as T_8H_8 and T_8Me_8, have been among those with the poorest synthetic yields, starting from simple silanes.[1] One of the most common current preparations of T_8H_8 is a scarce-water hydrolysis of $HSiCl_3$ in a biphasic system, in the presence of partially hydrated $FeCl_3$, which proceeds to give a 17.5% yield of T_8H_8, after separation of the $T_{10}H_{10}$ byproduct.[60] This yield has been improved slightly by the use of a modified solvent system in a 1997 preparation[61] and by making further small changes in preparative methods to give a current best T_8H_8 yield of 23% (Table 1, entries 1−3). Although T_8H_8 is potentially a very useful precursor to other T_8 derivatives, the low yield of its synthesis has frustrated its widespread use. In the case of T_8Me_8, early syntheses focused on the controlled heating of the product from the hydrolysis/condensation reaction of $MeSi(OEt)_3$, which resulted in a great variation in synthetic yields. More recent work looked at carrying out the hydrolysis in poly(2-hydroxyethyl methacrylate), which while not showing a high yield did provide a more reliable route (Table 1, entries 4 and 5). However, an alternative method published around the same time showed a significantly improved yield, resulting from the use of a complicated hydrolysis medium (Table 1, entry 8). This has been followed by attempts to further optimize reaction conditions; however no improvement in yield has been reported (Table 1, entries 6 and 7). There have been recent SEM and TEM studies into the growth mechanism of microcrystalline particles of both T_8Me_8 and T_8Et_8, which showed that the growth process of cubic crystals started from an initial assembly of spherical particles, which then formed one-dimensional rods, followed by the rods forming bundles before assembling of the bundles to form crystals.[62]

The syntheses of various other simple alkyl-substituted POSS have also been improved upon in recent years, with one of the often useful techniques being the addition of NBu_4F to the hydrolysis mixture,[63] which has been seen to lead, in some cases, to significant improvements in yield (Table 1, entries 22, 44, 45, 47−49, 53, 54, 57, 58, 63, and 75). In addition to preparation of conventional POSS species by this technique, variation in reaction conditions also allows for the formation of POSS species encapsulating F^- anions (see section 2.4).

Another commonly used POSS material, $T_8[(CH_2)_3NH_2]_8$ and its hydrochloride salt, has also seen development in its synthesis. The most common route to $T_8[(CH_2)_3NH_2]_8$ is the acid-catalyzed hydrolysis of $H_2N(CH_2)_3Si(OEt)_3$, which forms the hydrochloride salt in up to 35% yield as a stable white solid after 1−6 weeks depending on method.[64−66] This salt can then be converted to the free amine in quantitative yield by passing a methanolic solution of it over a basic Amberlite IRA-400 exchange resin.[65,66] However, there have

Table 1. T_8R_8 Derivatives Prepared by Solvolysis of Alkoxy- or Chlorosilanes

entry	R, T_8R_8, or compound number	starting materials	yield (%)	refs
1	-H	$HSiCl_3$ + $FeCl_3$, HCl, K_2CO_3, $CaCl_2$, MeOH, hexane	18	69, 70
2	-H	$HSiCl_3$ + $FeCl_3$, HCl, K_2CO_3, $CaCl_2$, MeOH, petroleum ether, toluene	20	71, 72
3	-H	$HSiCl_3$ + $FeCl_3$, HCl, K_2CO_3, $CaCl_2$, MeOH, hexane, toluene	23	73–75
4	-Me	$MeSi(OEt)_3$ + poly(2-hydroxyethyl methacrylate), NH_3, H_2O, MeOH	23	76
5	-Me	$MeSi(OEt)_3$ + poly(2-hydroxyethyl methacrylate), HCl, H_2O, MeOH	23	76
6	-Me	$MeSi(OEt)_3$ + NEt_4OH, H_2O, MeOH, toluene, ether	66	77
7	-Me	$MeSi(OMe)_3$ + NEt_4OH, H_2O, MeOH, toluene, ether	84	77
8	-Me	$MeSi(OEt)_3$ + NEt_3, HCl, AcOH, H_2O, acetone, MeCN	88	78
9	-CH_2Ph	$PhCH_2SiCl_3$ + basic Amberlite, EtOH	68	79
10	-CH_2NHPh	$PhNHCH_2Si(OMe)_3$ + HCl, NEt_3		80
11	-$CH{=}CH_2$	$CH_2{=}CHSi(OEt)_3$ + HCl, H_2O, EtOH	18	81–84
12	-$CH{=}CH_2$	$CH_2{=}CHSiCl_3$ + acid Amberlite, MeOH	24	79
13	-$CH{=}CH_2$	$CH_2{=}CHSiCl_3$ + $FeCl_3$, HCl, H_2O, MeOH, CH_2Cl_2, petroleum ether	35	85
14	-$CH{=}CH_2$	$CH_2{=}CHSi(OEt)_3$ + NMe_4OH, MeOH	80	86
15	-*n*-Pr	*n*-$PrSiCl_3$ + HCl, MeOH		87
16	-$(CH_2)_2CF_3$	$CF_3(CH_2)_2Si(OEt)_3$ + KOH, H_2O, EtOH		88
17	-$(CH_2)_2CF_3$	$CF_3(CH_2)_2SiCl_3$ + H_2O, acetone	10	89
18	-$(CH_2)_2C_6F_5$	$C_6F_5(CH_2)_2Si(OEt)_3$ + KOH, H_2O, EtOH		88
19	-$CH_2CH{=}CH_2$	$CH_2{=}CHCH_2Si(OMe)_3$ + HNO_3, H_2O, DMSO	2	90
20	-*i*-Bu	*i*-$BuSi(OMe)_3$ + KOH, H_2O, acetone	96	91–93
21	-$(CH_2)_3Cp$	$Cp(CH_2)_3Si(OEt)_3$ + HCl, H_2O, acetone	59	94, 95
22	-$(CH_2)_3C_6H_4$-4-OMe	$MeOC_6H_4$-4-$(CH_2)_3Si(OEt)_3$ + NBu_4F, H_2O, $CHCl_3$	17	96
23	$T_8[1$-$(CH_2)_3$-2-Me-1,2-*closo*-$C_2B_{10}H_{10}]_8$	1-$Cl_3Si(CH_2)_3$-2-Me-*closo*-$C_2B_{10}H_{10}$ + DMSO, $CHCl_3$	23	97
24	$T_8[1$-$(CH_2)_3$-2-Me-1,2-*closo*-$C_2B_{10}H_{10}]_8$	1-$(EtO)_3Si(CH_2)_3$-2-Me-*closo*-$C_2B_{10}H_{10}$ + NBu_4F, H_2O, THF	70	97
25	$T_8[1$-$(CH_2)_3$-2-Me-1,2-*closo*-$C_2B_{10}H_{10}]_8$	1-$(EtO)_3Si(CH_2)_3$-2-Me-*closo*-$C_2B_{10}H_{10}$ + NaOH, H_2O, THF	55	97
26	$T_8[1$-$(CH_2)_3$-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}]_8$	1-$Cl_3Si(CH_2)_3$-2-Ph-*closo*-$C_2B_{10}H_{10}$ + DMSO, $CHCl_3$	21	97
27	$T_8[1$-$(CH_2)_3$-2-Ph-1,2-*closo*-$C_2B_{10}H_{10}]_8$	1-$(EtO)_3Si(CH_2)_3$-2-Ph-*closo*-$C_2B_{10}H_{10}$ + NBu_4F, H_2O, THF	28	97
28	-$(CH_2)_3NH_2$	$H_2N(CH_2)_3Si(OEt)_3$ + NEt_4OH, H_2O, *n*-PrOH, MeCN	72	98, 99
29	-$(CH_2)_3NH_2$	$H_2N(CH_2)_3Si(OEt)_3$ + NMe_4OH, MeOH	93	100
30	-$(CH_2)_3NH_2$	$H_2N(CH_2)_3Si(OEt)_3$ + NEt_4OH, *n*-PrOH, H_2O, MeCN		101
31	$\{T_8[(CH_2)_3NH_3]_8\}Cl_8$	$H_2N(CH_2)_3Si(OEt)_3$ + HCl, $PtCl_4$, MeOH	30	102, 103
32	$\{T_8[(CH_2)_3NH_3]_8\}Cl_8$	$H_2N(CH_2)_3Si(OEt)_3$ + HCl, MeOH	30	68, 104–109
33	$\{T_8[(CH_2)_3NH_3]_8\}[ZnCl_4]_{2.8}Cl_{2.4}$	$H_2N(CH_2)_3Si(OEt)_3$ + $ZnCl_2$, HCl, MeOH	4	110
34	-$(CH_2)_3NHCH_2CH(OH)CH_2OPh$	$PhOCH_2CH(OH)CH_2NH(CH_2)_3Si(OEt)_3$ + NaOH, H_2O, THF		111
35	-$(CH_2)_3N[CH_2CH(OH)CH_2OPh]_2$	$[PhOCH_2CH(OH)CH_2]_2N(CH_2)_3Si(OEt)_3$ + NaOH, H_2O, THF		111
36	-$(CH_2)_3N[CH_2CH(OH)CH_2OPh]_2$	$[PhOCH_2CH(OH)CH_2]_2N(CH_2)_3Si(OEt)_3$ + catalyst, H_2O, THF		112
37	-$(CH_2)_3N[CH_2CH(OH)CH_2OPh]\{(CH_2)_2N[CH_2CH(OH)CH_2OPh]_2\}$	$\{[PhOCH_2CH(OH)CH_2]_2N(CH_2)_2\}[PhOCH_2CH(OH)CH_2]N(CH_2)_3Si(OMe)_3$ + NaOH, THF		113
38	-$(CH_2)_3OCH_2CH(O)CH_2$	$CH_2(O)CHCH_2O(CH_2)_3Si(OMe)_3$ + NEt_4OH, H_2O, Ac-*i*-Bu		114
39	-$(CH_2)_3SH$	$HS(CH_2)_3Si(OEt)_3$ + HCl, H_2O		115
40	-$(CH_2)_3Cl$	$Cl(CH_2)_3Si(OMe)_3$ + HCl, $PtCl_4$, MeOH		103
41	-$(CH_2)_3Cl$	$Cl(CH_2)_3Si(OMe)_3$ + HCl, MeOH	31	116–118
42	-$(CH_2)_3Cl$	$Cl(CH_2)_3Si(OMe)_3$ + HCl, $Sn(n\text{-}Bu)_2[O_2C(CH_2)_{10}Me]_2$, MeOH	35	119, 120
43	-$(CH_2)_3Cl$	$Cl(CH_2)_3Si(OEt)_3$ + HCl, MeOH	37	121–124
44	-$(CH_2)_2CHMe_2$	$Me_2CH(CH_2)_2Si(OEt)_3$ + NBu_4F, H_2O, CH_2Cl_2, THF	26	63
45	-$(CH_2)_2CMe_2CO_2Me$	$MeOC({=}O)CMe_2(CH_2)_2Si(OEt)_3$ + NBu_4F, H_2O, CH_2Cl_2, THF	20	63
46	-$(CH_2)_2(CF_2)_3CF_3$	$CF_3(CF_2)_3(CH_2)_2Si(OEt)_3$ + KOH, H_2O, EtOH	99	125
47	-*n*-C_6H_{13}	*n*-$C_6H_{13}Si(OEt)_3$ + NBu_4F, H_2O, CH_2Cl_2, THF	44	63
48	-$CH_2CH(Et)(CH_2)_3Me$	$Me(CH_2)_3CH(Et)CH_2Si(OMe)_3$ + NBu_4F, H_2O, CH_2Cl_2	43	96
49	-*n*-Oct	*n*-$C_8H_{17}Si(OEt)_3$ + NBu_4F, H_2O, CH_2Cl_2, THF	65	63
50	-$(CH_2)_2(CF_2)_5CF_3$	$CF_3(CF_2)_5(CH_2)_2Si(OEt)_3$ + KOH, H_2O, EtOH		88, 125
51	-$(CH_2)_2(CF_2)_7CF_3$	$CF_3(CF_2)_7(CH_2)_2Si(OEt)_3$ + KOH, H_2O, EtOH		88, 125
52	-*c*-C_5H_9	*c*-$C_5H_9Si(OEt)_3$ + NMe_3, HCl, AcOH, H_2O, *n*-PrCN, acetone,	86	78
53	-*c*-C_5H_9	*c*-$C_5H_9Si(OEt)_3$ + NBu_4F, H_2O, CH_2Cl_2, THF	95	63
54	-Cy	$CySi(OEt)_3$ + NBu_4F, H_2O, CH_2Cl_2, THF	84	63
55	-Cy	$CySi(OEt)_3$ + NEt_3, HCl, D-aspartic acid, H_2O, MeCN, Ac-*n*-Pr	87	78
56	-Cy	$CySi(OEt)_3$ + HCl, H_2O, MeC(=O)-*i*-Bu, EtOH	43	126
57	*exo*-**1**[a]	*exo*-2-bicyclo[2.2.1]hept-5-en-2-yltriethoxysilane + NBu_4F, H_2O, CH_2Cl_2	47	63
58	*endo*-**1**[a]	*endo*-2-bicyclo[2.2.1]hept-5-en-2-yltriethoxysilane + NBu_4F, H_2O, CH_2Cl_2	56	63
59	**2**	**3** + KOH, $(COOH)_2$, H_2O		127
60	**4**	**5** + KOH, $(COOH)_2$, H_2O		127
61	-Ph	$PhSi(OMe)_3$ + $PhCH_2NMe_3OH$, H_2O, benzene		128
62	-Ph	$PhSi(OEt)_3$ + NEt_4OH, H_2O, MeOH, toluene, ether	30	77
63	-Ph	$PhSi(OEt)_3$ + NBu_4F, H_2O, CH_2Cl_2, THF	49	63
64	-Ph	$PhSiCl_3$ + H_2O, EtOAc	70	129
65	-Ph	$PhSi(OMe)_3$ + NEt_4OH, H_2O, MeOH, toluene, ether	70	77
66	-Ph	$PhSiCl_3$ + basic Amberlite, EtOH	74	79
67	-Ph	$PhSiCl_3$ + KOH, H_2O, EtOH	80	130
68	-Ph	$PhSiCl_3$ + H_2O, trace KOH	$\sim$90	131
69	-Ph	$PhSiCl_3$ + $PhCH_2NMe_3OH$, H_2O, benzene	98	132–134
70	-C_6H_4-2-Me	MeC_6H_4-2-$Si(OMe)_3$ + $PhCH_2NMe_3OH$, H_2O, benzene	82	135
71	-C_6H_4-3-Me	MeC_6H_4-3-$SiCl_3$ + H_2O, EtOH	6	135
72	-C_6H_4-4-Me	MeC_6H_4-4-$SiCl_3$ + H_2O, EtOH	7	135
73	-C_6H_4-4-Cl	ClC_6H_4-4-$SiCl_3$ + $PhCH_2NMe_3OH$, H_2O, benzene		136
74	-C_6H_4-2-Et	EtC_6H_4-2-$Si(OMe)_3$ + $PhCH_2NMe_3OH$ H_2O, benzene	73	135
75	-C_6H_4-2-NHNHPh	$O(SiH_2C_6H_4\text{-}2\text{-}N{=}NPh)_2$ + NBu_4F, H_2O, $CHCl_3$	90	137
76	$[NMe_4]_8[T_8O_8]$	$Si(OEt)_4$ + NMe_4OH, H_2O		138
77	$[NMe_4]_8[T_8O_8]$	$Si(OEt)_4$ + NMe_4OH, MeOH, H_2O	99	139–144
78	**6**	**7** + NMe_4OH, H_2O	71	145

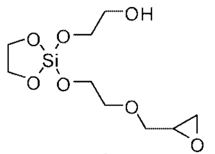
[a] These compounds were referred to in ref 63 as octa(*exo*- and *endo*-2-bicycloheptyl)silsesquioxane; however the presented ^1H and ^{13}C NMR indicate the bicycloheptenyl structure to be the correct one.

Table 2. T_8 Derivatives with Two or More Different Substituents Prepared from Alkoxy- Or Chlorosilanes

entry	T_8 derivative	starting materials	yield (%)[a]	refs
1	$T_8Me_6(CH{=}CH_2)_2$	$CH_2{=}CHSi(OAc)_3 + MeSi(OMe)_3$, TfOH, $NH_3(aq)$, $[NMe_3C_{16}H_{33}]Cl$, toluene, H_2O	95−98	148
2	$T_8(i\text{-}Bu)_6(CH{=}CH_2)_2$	$CH_2{=}CHSi(OAc)_3 + i\text{-}BuSi(OEt)_3$, TfOH, $NH_3(aq)$, NMe_4OH, xylene, toluene, H_2O	75−95	148
3	$T_8(n\text{-}Oct)_6(CH{=}CH_2)_2$	$CH_2{=}CHSi(OAc)_3 + n\text{-}OctSi(OEt)_3$, TfOH, $NH_3(aq)$, NMe_4OH, xylene, toluene, H_2O	55	148
4	$T_8(i\text{-}Oct)_6[(CH_2)_3NH_2]_2$	$H_2N(CH_2)_3Si(OMe)_3 + i\text{-}OctSi(OMe)_3$, $NH_3(aq)$, H_2O	82	149
5	$T_8Ph_6(CH{=}CH_2)_2$	$CH_2{=}CHSi(OAc)_3 + PhSi(OEt)_3$, TfOH, $NH_3(aq)$, NMe_4OH, xylene, toluene, H_2O	90	148
6	$[NMe_4]_6T_8(O)_6(OH)O(CH_2)_2OCH_2CH(O)CH_2$	$Si(OEt)_4$ + **8**, Me_4NOH		150
7	$T_8Me_4[(CH_2)_3OCH_2CH(O)CH_2]_4$ and $T_8Me_2[(CH_2)_3OCH_2CH(O)CH_2]_6$	$MeSi(OEt)_3 + CH_2(O)CHCH_2O(CH_2)_3Si(OMe)_3$, NMe_4OH, H_2O, i-PrOH	>90[b]	151

[a] All products exist as an unknown mixture of substitutional isomers. [b] Consists of a mixture of these T_8 species and other T_9 and T_{10} derivatives.

Chart 2



8

been two recent reports claiming the synthesis of the free amine directly from the starting silane in yields ranging from 72−93%, depending on conditions (Table 1, entries 28−30). In contrast to previous reports on the instability of the free amine prepared by neutralization of the hydrochloride,[66] most of these direct preparations of the free amine claim to lead to a much more stable material. Experimental modification of the preparative route to the hydrochloride salt has not led to a significantly improved yield of the product (Table 1, entries 30−32). There has been a study carried out on the hydrolysis and condensation reaction, looking at the other non-T_8 silsesquioxane products produced.[67] Some work has been done on the preparation of $T_8[(CH_2)_3NH_3]_8^{8+}$ salts with different anions. The chloride has been exchanged with dodecylbenzenesulfonate, giving rise to a lamellar hybrid material,[68] and a mixed nonstoichiometric anion system, comprising both Cl^- and $[ZnCl_4]^{2-}$, has been prepared by the hydrolysis of $H_2N(CH_2)_3Si(OEt)_3$, carried out in the presence of $ZnCl_2$ (Table 1, entry 33).

The syntheses of phenyl and substituted aryl POSS derivatives have been investigated. T_8Ph_8 can now be prepared in good yield, by any of several methods (Table 1, entries 61−69); however there has been less work carried out on the direct synthesis of substituted aromatic species, despite the problems associated with preparing specifically substituted compounds from T_8Ph_8 itself. Most of the known POSS compounds with substituted aromatic substituents have been prepared by modifications of the known substituted aromatic species (see section 2.7). While a range of both simple and more complex substituted aromatic species have been reported in the older literature,[1] a more limited number of new syntheses from chloro- or alkoxysilanes have been developed recently (Table 1, entries 70−75).

2.1.2. $T_8R_{(8-n)}R'_n$ Compounds

The synthesis of T_8 POSS with different substituents by the cohydrolysis and condensation of chloro- or alkoxysilanes has not proven very successful, due to the formation of a wide variety of POSS and other silsesquioxane products from a single reaction and the difficulty of separating a desired single product. There are, however, a very limited number of cases where particular products could be separated from a mixture. The products with different values of n in the formation of $T_8R_{(8-n)}R'_n$ [$n = 0, 1, 2$ (three isomers); R = Pr, R′ = $(CH_2)_3Cl$, $(CH_2)_3I$, $(CH_2)_3SH$, or $CH_2CH{=}CH_2$ and R = Et, R′ = $CH{=}CH_2$] from the corresponding chloro- or methoxysilanes[146] were able to be separated by HPLC. Another recent report shows the preparation of four $T_8(CH{=}CH_2)_2R_6$ POSS derivatives from the acid-catalyzed cohydrolysis of $CH_2{=}CHSi(OAc)_3$ with the corresponding alkoxysilane (Table 2, entries 1−3, 5). A similar type of reaction, although base-catalyzed, was seen for the cohydrolysis of $H_2N(CH_2)_3Si(OMe)_3$ with i-$OctSi(OMe)_3$, which resulted in the formation of $T_8[(CH_2)_3NH_2]_2(i\text{-}Oct)_6$ (Table 2, entry 4). An inseparable mixture of two different products, $T_8Me_4[(CH_2)_3OCH_2CH(O)CH_2]_4$ and $T_8Me_2[(CH_2)_3OCH_2CH(O)CH_2]_6$, was formed by the reaction of $MeSi(OEt)_3$ and $CH_2(O)CHCH_2O(CH_2)_3Si(OMe)_3$ (Table 2, entry 7). In all of these systems, no analysis of the isomers formed was undertaken. Another recently prepared POSS derivative with differing substituents can be seen in Table 2, entry 6. This POSS species is related to the previously known $[DMPI]_6[T_8(O)_6(OH)_2]$;[147] however this new compound may prove able to be incorporated into polymer systems by reaction of its epoxide ring. Once again, the precise isomer or mixture of isomers formed could not be identified, although powder X-ray diffraction did suggest the presence of a moderately crystalline product.

All of these preparations illustrate the most significant problem in trying to prepare differently substituted POSS species from simple silane derivatives: that without some sort of templating or directing agent, there is nothing to limit how many different isomers are going to form, and it may be very difficult to separate those that do. Further complicating the matter is that there is no way to determine beforehand either what mixture of products of varying substitution will form or whether they will be separable. More successful ways to prepare POSS derivatives with different types of substituents use either the corner-capping method or synthetic modification of a pre-existing T_8R_8 compound.

2.2. Synthesis of POSS Compounds by Corner Capping of Partially Condensed Silsesquioxanes, $T_7R_7(OH)_3$

The syntheses of T_8R_7R' derivatives from partially condensed silsesquioxanes all follow the same general reaction

Table 3. T_8R_7R' Derivatives Prepared by Corner Capping of Partially Condensed Silsesquioxanes, $T_7R_7(OH)_3$

	substituents or compound number				
entry	R	R′	starting materials	yield (%)	refs
1	-Et	$-(CH_2)_2OAc$	$Et_7Si_7O_9(OH)_3 + AcO(CH_2)_2SiCl_3$, NEt_3, THF		157
2	**9**		$Et_7Si_7O_9(OH)_3$ + 2-(bicyclo[2.2.1]hept-5-en-2-yl)ethyltrimethoxysilane, phosphazine suberbase, MeOH		158
3	-Et	$-(CH_2)_2C_6H_4$-4-SO_2Cl	$Et_7Si_7O_9(OH)_3 + ClSO_2C_6H_4$-4-$(CH_2)_2SiCl_3$, NEt_3, THF, CH_2Cl_2		159
4	-Et	$-(CH_2)_3OCH_2CH(O)CH_2$	$Et_7Si_7O_9(OH)_3 + CH_2(O)CHCH_2O(CH_2)_3Si(OMe)_3$, phosphazine superbase, MeOH	87	158
5	-Et	$-(CH_2)_3OAc$	$Et_7Si_7O_9(OH)_3 + AcO(CH_2)_3SiCl_3$, NEt_3, THF		157
6	-*i*-Bu	-H	$(i\text{-Bu})_7Si_7O_9(OH)_3 + HSiCl_3$, NEt_3, THF	67	160
7	-*i*-Bu	$-CH{=}CH_2$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + CH_2{=}CHSi(OMe)_3$, NMe_4OH	60	91, 92
8	-*i*-Bu	$-(CH_2)_2OAc$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + AcO(CH_2)_2SiCl_3$, NEt_3, THF	88	157, 161, 162
9	-*i*-Bu	$-(CH_2)_2C_6H_4$-4-SO_2Cl	$(i\text{-Bu})_7Si_7O_9(OH)_3 + ClSO_2C_6H_4$-4-$(CH_2)_2SiCl_3$, NEt_3, THF, CH_2Cl_2		159
10	-*i*-Bu	$-(CH_2)_3NH_2$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + NH_2(CH_2)_3Si(OEt)_3$, NEt_4OH, H_2O, THF	77	91, 93, 163
11	-*i*-Bu	$-(CH_2)_3NH_2$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + NH_2(CH_2)_3Si(OEt)_3$, H_2O, THF	87	164
12	-*i*-Bu	$-(CH_2)_3NH(CH_2)_2NH_2$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + NH_2(CH_2)_2NH(CH_2)_3Si(OMe)_3$, NEt_4OH, H_2O, THF	7	91, 163
13	-*i*-Bu	$-(CH_2)_3NH(CH_2)_2NH_2$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + NH_2(CH_2)_2NH(CH_2)_3Si(OMe)_3$, THF, EtOH	87	164
14	-*i*-Bu	$-(CH_2)_3Cl$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + Cl(CH_2)_3Si(OMe)_3$, NEt_4OH, THF	60	91, 163
15	-*i*-Bu	$-(CH_2)_3Cl$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + Cl(CH_2)_3SiCl_3$, NEt_3, THF	73	165
16	-*i*-Bu	$-(CH_2)_3OAc$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + AcO(CH_2)_3SiCl_3$, NEt_3, THF		157
17	-*i*-Bu	$-(CH_2)_3OC({=}O)C({=}CH_2)Me$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + MeC({=}CH_2)CO_2(CH_2)_3Si(OMe)_3$, NEt_4OH, H_2O, THF	40	91, 163
18	-*i*-Bu	$-(CH_2)_3OC({=}O)C({=}CH_2)Me$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + MeC({=}CH_2)CO_2(CH_2)_3Si(OMe)_3$, phosphazine superbase, THF	75	158
19	-*i*-Bu	-*i*-Bu	$(i\text{-Bu})_7Si_7O_9(OH)_3 + i\text{-BuSi(OMe)}_3$, NEt_4OH, H_2O, THF	40	91, 163
20	-*i*-Bu	-Ph	$(i\text{-Bu})_7Si_7O_9(OH)_3 + PhSi(OMe)_3 + NEt_3$, THF, EtOH		166
21	-*i*-Bu	$-C_6H_4$-4-Me	$(i\text{-Bu})_7Si_7O_9(OH)_3 + MeC_6H_4$-4-$SiCl_3$, pyridine, THF	92	167
22	-*i*-Bu	$-C_6H_4$-4-CH_2Cl	$(i\text{-Bu})_7Si_7O_9(OH)_3 + ClCH_2C_6H_4$-4-$SiCl_3$, NEt_3, THF	80	168, 169
23	-*i*-Bu	$-C_6H_4$-4-CH_2Br	$(i\text{-Bu})_7Si_7O_9(OH)_3 + BrCH_2C_6H_4$-4-$SiCl_3$, pyridine, THF	91	167
24	-*i*-Bu	$-C_6H_4$-4-CBr_3	$(i\text{-Bu})_7Si_7O_9(OH)_3 + Br_3CC_6H_4$-4-$SiCl_3$, pyridine, THF	80	167
25	-*i*-Bu	$-OCH_2CH(O)CH_2$	$(i\text{-Bu})_7Si_7O_9(OH)_3 + CH_2(O)CHCH_2OSi(OEt)_3$, NEt_4OH, H_2O, THF	78	93
26	-*i*-Bu	-Cl	$(i\text{-Bu})_7Si_7O_9(OH)_3 + SiCl_4$, NEt_3, THF		170
27	-*i*-Oct	$-(CH_2)_2OAc$	$(i\text{-Oct})_7Si_7O_9(OH)_3 + AcO(CH_2)_2SiCl_3$, NEt_3, THF		157
28	-*i*-Oct	$-(CH_2)_2C_6H_4$-4-SO_2Cl	$(i\text{-Oct})_7Si_7O_9(OH)_3 + ClSO_2C_6H_4$-4-$(CH_2)_2SiCl_3$, NEt_3, THF, CH_2Cl_2		159
29	-*i*-Oct	$-(CH_2)_3NH(CH_2)_2NH_2$	$(i\text{-Oct})_7Si_7O_9(OH)_3 + NH_2(CH_2)_2NH(CH_2)_3Si(OMe)_3$, THF, EtOH		164
30	-*i*-Oct	$-(CH_2)_3OAc$	$(i\text{-Oct})_7Si_7O_9(OH)_3 + AcO(CH_2)_3SiCl_3$, NEt_3, THF		157
31	$-(CH_2)_2CF_3$	-H	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + HSiCl_3$, NEt_3, THF	76	171, 172
32	$-(CH_2)_2CF_3$	-Me	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + MeSiCl_3$, NEt_3, THF	72	173
33	$-(CH_2)_2CF_3$	$-(CH_2)_2CF_3$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + CF_3(CH_2)_2SiCl_3$, NEt_3, THF	76	173
34	$-(CH_2)_2CF_3$	$-(CH_2)_2(CF_2)_5CF_3$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + CF_3(CF_2)_5(CH_2)_2SiCl_3$, NEt_3, THF	82	173
35	$-(CH_2)_2CF_3$	$-(CH_2)_2(CF_2)_7CF_3$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + CF_3(CF_2)_7\ (CH_2)_2SiCl_3$, NEt_3, THF	80	173
36	$-(CH_2)_2CF_3$	$-(CH_2)_2(CF_2)_9CF_3$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + CF_3(CF_2)_9(CH_2)_2SiCl_3$, NEt_3, THF	73	173
37	$-(CH_2)_2CF_3$	$-(CH_2)_2OAc$	$[CF_3(CH_2)_2]_7Si_7O_9(OH)_3 + AcO(CH_2)_2SiCl_3$, NEt_3, THF		157
38	$-(CH_2)_2CF_3$	$-(CH_2)_2OAc$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + AcO(CH_2)_2SiCl_3$, NEt_3, THF	66	174
39	$-(CH_2)_2CF_3$	$-(CH_2)_2Ph$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + Ph(CH_2)_2SiCl_3$, NEt_3, THF	54	173
40	$-(CH_2)_2CF_3$	$-(CH_2)_2C_6H_4$-4-SO_2Cl	$[CF_3(CH_2)_2]_7Si_7O_9(OH)_3 + ClSO_2C_6H_4$-4-$(CH_2)_2SiCl_3$, NEt_3, THF, CH_2Cl_2		159
41	$-(CH_2)_2CF_3$	$-(CH_2)_2CH(CF_3)_2$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + (CF_3)_2CH(CH_2)_2SiCl_3$, NEt_3, THF	73	173
42	$-(CH_2)_2CF_3$	$-(CH_2)_3OCF(CF_3)_2$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + (CF_3)_2CFO(CH_2)_3SiCl_3$, NEt_3, THF	75	173
43	$-(CH_2)_2CF_3$	$-(CH_2)_3OAc$	$[CF_3(CH_2)_2]_7Si_7O_9(OH)_3 + AcO(CH_2)_3SiCl_3$, NEt_3, THF		157
44	$-(CH_2)_2CF_3$	$-(CH_2)_3OC({=}O)C({=}CH_2)Me$	$[CF_3(CH_2)_2]_7Si_7O_9(OH)_3 + MeC({=}CH_2)CO_2(CH_2)_3SiCl_3$, NEt_3, THF	61	175
45	$-(CH_2)_2CF_3$	$-(CH_2)_3Cl$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + Cl(CH_2)_3SiCl_3$, NEt_3, THF	73	176
46	$-(CH_2)_2CF_3$	$-(CH_2)_3Br$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + Br(CH_2)_3SiCl_3$, NEt_3, THF	76	177
47	$-(CH_2)_2CF_3$	$-C_6H_4$-4-$OCF{=}CF_2$	$Na_3\{[CF_3(CH_2)_2]_7Si_7O_9(O)_3\} + CF_2{=}CFOC_6H_4$-4-$SiCl_3$, NEt_3, THF	18	178
48	$-(CH_2)_2(CF_2)_3CF_3$	$-(CH_2)_3OC({=}O)C({=}CH_2)Me$	$[CF_3(CF_2)_3(CH_2)_2]_7Si_7O_9(OH)_3 + MeC({=}CH_2)CO_2(CH_2)_3SiCl_3$, NEt_3, THF	60	175
49	$-(CH_2)_2(CF_2)_5CF_3$	$-(CH_2)_2OAc$	$[CF_3(CF_2)_5(CH_2)_2]_7Si_7O_9(OH)_3 + AcO(CH_2)_2SiCl_3$, NEt_3, $CF_3CF_2CHCl_2$, Cl_2FCCF_2CHFCl		157
50	$-(CH_2)_2(CF_2)_5CF_3$	$-(CH_2)_3OAc$	$[CF_3(CF_2)_5(CH_2)_2]_7Si_7O_9(OH)_3 + AcO(CH_2)_3SiCl_3$, NEt_3, $CF_3CF_2CHCl_2$, Cl_2FCCF_2CHFCl		157
51	-*c*-C_5H_9	$-CH_2Cl$	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + ClCH_2SiCl_3$, NEt_3, THF	78	179
52	**10**		$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ + (9*H*-fluoren-9-yl)methyltriethoxysilane, THF	59	179
53	-*c*-C_5H_9	$-(CH_2)_2(CF_2)_7CF_3$	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + CF_3(CF_2)_7(CH_2)_2SiCl_3$, NEt_3, THF	81	180
54	-*c*-C_5H_9	$-(CH_2)_2OAc$	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + AcO(CH_2)_2SiCl_3$, NEt_3, THF	94	157, 162
55	-*c*-C_5H_9	$-(CH_2)_2C_6H_4$-4-SO_2Cl	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + ClSO_2C_6H_4$-4-$(CH_2)_2SiCl_3$, NEt_3, THF, CH_2Cl_2		159
56	**11**		$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ + 3-(9*H*-fluoren-9-yl)propyltrichlorosilane, NEt_3, THF	74	179
57	**11**		$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3$ + 3-(9*H*-fluoren-9-yl)propyltriethoxysilane, NEt_3, THF	57	179
58	-*c*-C_5H_9	$-(CH_2)_3Cl$	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + Cl(CH_2)_3SiCl_3$, THF	82	179, 181

Table 3. Continued

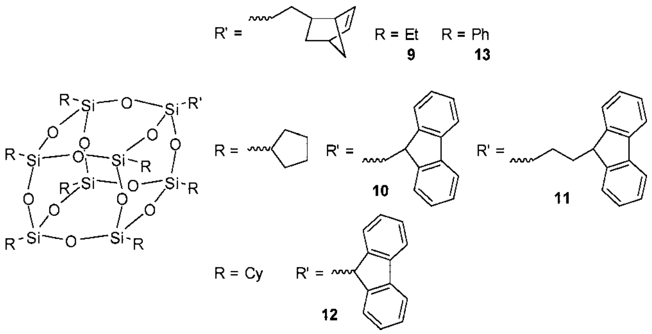
entry	substituents or compound number R	R′	starting materials	yield (%)	refs
59	-c-C_5H_9	-$(CH_2)_3NH_2$	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + NH_2(CH_2)_3Si(OMe)_3$, THF	78	182
60	-c-C_5H_9	-$(CH_2)_3OAc$	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + AcO(CH_2)_3SiCl_3$, NEt_3, THF		157
61	-c-C_5H_9	-$(CH_2)_3OC({=}O)CH{=}CH_2$	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + CH_2{=}CHCO_2(CH_2)_3SiCl_3$, NEt_3, THF	68	183
62	-c-C_5H_9	-$(CH_2)_3SiMe_2C_6H_4$-4-$SiMe_2H$	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + HSiMe_2C_6H_4\text{-}4\text{-}SiMe_2(CH_2)_3SiCl_3$, NEt_3, THF	83	184
63	-c-C_5H_9	-C_6H_4-4-CH_2Cl	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + ClCH_2C_6H_4\text{-}4\text{-}SiCl_3$, NEt_3, THF	80	179, 185, 186
64	-c-C_5H_9	-C_6H_4-4-CH_2Cl	$(c\text{-}C_5H_9)_7Si_7O_9(OH)_3 + ClCH_2C_6H_4\text{-}4\text{-}SiCl_3$, pyridine, THF	90	187
65	**12**		$Cy_7Si_7O_9(OH)_3$ + 9*H*-fluoren-9-yltrichlorosilane, NEt_3, THF	80	179
66	-Cy	-$(CH_2)_2OAc$	$Cy_7Si_7O_9(OH)_3 + AcO(CH_2)_2SiCl_3$, NEt_3, THF		157
67	-Cy	-$(CH_2)_2C_6H_4$-4-SO_2Cl	$Cy_7Si_7O_9(OH)_3 + ClSO_2C_6H_4\text{-}4\text{-}(CH_2)_2SiCl_3$, NEt_3, THF, CH_2Cl_2		159
68	-Cy	-$(CH_2)_3NH(CH_2)_2NH_2$	$Cy_7Si_7O_9(OH)_3 + NH_2(CH_2)_2NH(CH_2)_3Si(OMe)_3$, THF, EtOH	95	164
69	-Cy	-$(CH_2)_3NH(CH_2)_2NH_2$	$Cy_7Si_7O_9(OH)_3 + NH_2(CH_2)_2NH(CH_2)_3Si(OMe)_3$, phosphazine superbase, THF	62	158
70	-Cy	-$(CH_2)_3OAc$	$Cy_7Si_7O_9(OH)_3 + AcO(CH_2)_3SiCl_3$, NEt_3, THF		157
71	-Cy	-$(CH_2)_3SiMe_2C_6H_4$-4-$SiMe_2H$	$Cy_7Si_7O_9(OH)_3 + HSiMe_2C_6H_4\text{-}4\text{-}SiMe_2(CH_2)_3SiCl_3$, NEt_3, THF	88	184
72	-Cy	-C_6H_4-4-CH_2Cl	$Cy_7Si_7O_9(OH)_3 + ClCH_2C_6H_4\text{-}4\text{-}SiCl_3$, NEt_3, THF	80	188
73	-Cy	-$OSiCl_3$	$Cy_7Si_7O_9(OH)_3 + O(SiCl_3)_2$, NEt_3, toluene	62	156
74	-Cy	-$SiCl_3$	$Cy_7Si_7O_9(OH)_3 + Si_2Cl_6$, NEt_3, toluene	43	156
75	-c-C_6H_9	-$(CH_2)_3SiMe_2C_6H_4$-4-$SiMe_2H$	$(c\text{-}C_6H_9)_7Si_7O_9(OH)_3 + HSiMe_2C_6H_4\text{-}4\text{-}SiMe_2(CH_2)_3SiCl_3$, NEt_3, THF	82	184
76	**13**		$Ph_7Si_7O_9(OH)_3$ + 2-(bicyclo[2.2.1]hept-5-en-2-yl)ethyltrichlorosilane, NEt_3, THF	75	189
77	-Ph	-$(CH_2)_2CN$	$Na_3[Ph_7Si_7O_9(O)_3] + NC(CH_2)_2SiCl_3$, NEt_3, THF		190
78	-Ph	-$(CH_2)_2OAc$	$Ph_7Si_7O_9(OH)_3 + AcO(CH_2)_2SiCl_3$, NEt_3, THF	47	157
79	-Ph	-$(CH_2)_2OAc$	$Na_3[Ph_7Si_7O_9(O)_3] + AcO(CH_2)_2SiCl_3$, NEt_3, THF	66	191
80	-Ph	-$(CH_2)_2C_6H_4$-4-SO_2Cl	$Ph_7Si_7O_9(OH)_3 + ClSO_2C_6H_4\text{-}4\text{-}(CH_2)_2SiCl_3$, NEt_3, THF, CH_2Cl_2	10	159
81	-Ph	-$(CH_2)_3Cl$	$Na_3[Ph_7Si_7O_9(O)_3] + Cl(CH_2)_3SiCl_3$, NEt_3, THF		190
82	-Ph	-$(CH_2)_3Cl$	$Na_3[Ph_7Si_7O_9(O)_3] + Cl(CH_2)_3SiCl_3$, THF	45	192, 193
83	-Ph	-$(CH_2)_3NH_2$	$Ph_7Si_7O_9(OH)_3 + NH_2(CH_2)_3Si(OMe)_3$, toluene	68	158, 194
84	-Ph	-$(CH_2)_3NH(CH_2)_2NH_2$	$Ph_7Si_7O_9(OH)_3 + NH_2(CH_2)_2NH(CH_2)_3Si(OMe)_3$, THF, EtOH	89	164
85	-Ph	-$(CH_2)_3OAc$	$Ph_7Si_7O_9(OH)_3 + AcO(CH_2)_3SiCl_3$, NEt_3, THF		157
86	-Ph	-$(CH_2)_3SiMe_2C_6H_4$-4-$SiMe_2H$	$Ph_7Si_7O_9(OH)_3 + HSiMe_2C_6H_4\text{-}4\text{-}SiMe_2(CH_2)_3SiCl_3$, NEt_3, THF	84	184

scheme (eq 1), where a partially condensed silsesquioxane, $R_7Si_7O_9(OH)_3$, or its sodium salt, $Na_3[R_7Si_7O_9(O)_3]$, reacts with a chloro- or alkoxysilane, often in the presence of a base such as NEt_3 or a tetraalkylammonium hydroxide (Table 3 and Chart 3). The partially condensed trisilanol species have been known since 1965,[152] and while the methods of preparing such precursors have evolved somewhat, the methods used for the preparation of T_8R_7R' derivatives from them generally has not. Much of the early work on these differently substituted POSS species was conducted by Feher et al.,[153–155] who were looking to use such systems as models for catalysts and other materials on a silica surface. While there is still significant interest in this field (see section 4.3), much of the current direction for the syntheses of such new POSS is their integration into other materials, either as a property-changing monomer in a polymeric system or as a component in a nanocomposite or similar material. As can be seen from Table 3, yields from this type of reaction are generally good.

$$R_7Si_7O_9(OH)_3 + R'SiX_3 \xrightarrow{\text{base}} T_8R_7R' \quad X = Cl, O\text{-alkyl} \tag{1}$$

One of the key advantages to the use of such T_8R_7R' derivatives is that with a sufficiently bulky R group, the reactivity of an R′ group may be reduced so that it is more stable and more readily handled than the $T_8R'_8$ analogue. This is illustrated by the preparation of $T_8R_7(CH_2)_3NH_2$ species (R = *i*-Bu, *c*-C_5H_9 or Ph; Table 3, entries 10, 11, 59 and 83), because the $T_8[(CH_2)_3NH_2]_8$ derivative is commonly reported as being only stable at −30 °C in methanolic solution.[66] Similarly, the $T_8(i\text{-}Bu)_7Cl$, $T_8Cy_7OSiCl_3$, and $T_8Cy_7SiCl_3$ have also been successfully prepared (Table 3, entries 26, 73 and 74).

Chart 3

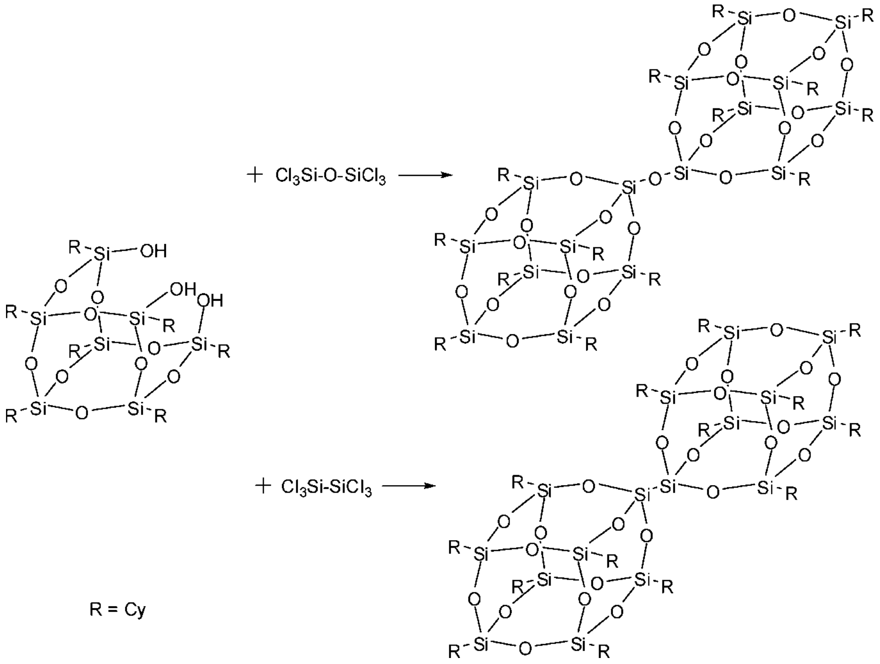


There have also been two bridged systems prepared by addition of an appropriate chlorosilane to 2 equiv of partially condensed silsesquioxane. Thus the bis-T_8 compounds $O(T_8Cy_7)_2$ and $(T_8Cy_7)_2$ were prepared in reasonable yield by the reaction of $Cy_7Si_7O_9(OH)_3$ with hexachlorodisiloxane and hexachlorodisilane, respectively (Scheme 2).[156]

2.3. Miscellaneous Syntheses of POSS Compounds

Several unusual preparations of T_8 derivatives involving the direct formation of the T_8 POSS core from novel silicon precursors have been reported. Some of these are related to the traditional hydrolysis and condensation reaction used with chloro- or alkoxysilanes. The first of these involves the hydrolysis and condensation, under basic conditions, of the silica

Scheme 2



that can be extracted from rice hull ash leading to the formation of the anionic $[T_8O_8]^{8-}$ POSS core.[195] This reaction has the potential to provide a cheap and readily accessible route to T_8 POSS derivatives, because huge quantities of rice hull ash are produced by the burning of rice hulls for power generation, and this material currently has limited utility. In a similar manner, the use of industrially produced silica as a silicon source for the synthesis of POSS species has also been investigated as a cost-effective route to certain POSS species.[196]

A more recent and unusual hydrolytic route to a T_8 POSS compound is the hydrolysis and condensation of tetramethyltetramethoxycyclotetrasiloxane.[197,198] This cyclic siloxane behaves as half of a T_8 cube and, on reaction with tetrabutylammonium fluoride, produces T_8Me_8 in 52% yield, one of the better yields for the preparation of this compound. It should also be noted that earlier studies have found that the use of dicyclohexylcarbodiimide as a dehydrating agent can effect the dehydration of the disiloxane $[Cy(OH)_2Si]_2O$ to give T_8Cy_8[199] and of the cyclotetrasiloxane $[i\text{-Pr}(OH)OSi]_4$ to give $T_8(i\text{-Pr})_8$.[200]

Another reaction of less practical use for POSS synthesis involves the oxidation of an octa-*t*-butyl functionalized silacubane by MCPBA to form the corresponding $T_8(SiMe_2\text{-}t\text{-Bu})_8$.[201] The yield of this reaction is high; however, the necessity of preparing a silacubane as a precursor will likely limit its utility.

2.4. Synthesis of Endohedral POSS Compounds

An unusual group of T_8 POSS derivatives are those in which the T_8 cage encapsulates an atom or ion thus forming an endohedral complex. While the central cavity of the molecule is not large, it has proven possible to introduce sufficiently small monatomic species, either during the initial synthesis of the T_8 cube or as a postsynthetic modification. Fluoride anions are among the most commonly introduced species and can be introduced by both methods. Under appropriate synthetic conditions, rather than just making the expected T_8 derivative, the presence of tetrabutylammonium fluoride in the hydrolysis/condensation reactions of the silanes may lead to the endohedral species $[NBu_4][F@T_8(CH{=}CH_2)_8]$, $[NBu_4][F@T_8Ph_8]$, and $[NBu_4][F@T_8(C_6H_4\text{-}4\text{-}Me)_8]$.[202,203] The presence of these endohedral species rather than the usual T_8 derivative was initially noted due to the differing solubilites of the products. The presence of the fluoride anion within the T_8 cage has been confirmed both by ^{19}F NMR spectroscopy and single-crystal X-ray diffraction studies (see section 3.4.1).

Similar endohedral complexes have also been prepared by the reaction of T_8R_8 compounds with tetrabutylammonium fluoride, with varying results.[204,205] For the reaction of T_8 species with electron-withdrawing functional groups, the endohedral complexes $[NMe_4][F@T_8Ph_8]$, $[NMe_4][F@T_8(CH{=}CH_2)_8]$, $[NMe_4][F@T_8(CH{=}CHPh)_8]$, $[NMe_4]\{F@T_8[(CH_2)_2CF_3]_8\}$, $[NMe_4]\{F@T_8[(CH_2)_2(CF_2)_3CF_3]_8]$, and $[NMe_4][F@T_8[(CH_2)_2(CF_2)_5CF_3]_8]$ could be prepared and isolated, whereas for T_8 species containing solely electron-donating functional groups, such as T_8Me_8, T_8Et_8, T_8Cy_8, and $T_8(i\text{-Bu})_8$, no reaction was observed.[204,205] When T_8 compounds with mixtures of electron-donating and -withdrawing groups were reacted with tetrabutylammonium fluoride, the only products obtained were found to result from cage opening and rearrangement to give a range of endohedral species.[204,205]

Atomic hydrogen has also been encapsulated within the T_8 cage, forming the endohedral complex $H@T_8(OSiMe_3)_8$, by γ-irradiation of the empty $T_8(OSiMe_3)_8$ cage in air.[206] This endohedral species is stable in both solid and solution, and its interactions with rare earth and d-block acetylacetonate complexes were studied by EPR. A magnetic interaction was seen between the complexes and the endohedral T_8 species; however, the rare earth acetylacetonate complexes caused the hydrogen atom to leave the cage.[206] Studies of the trapping and detrapping of H atoms in a variety of POSS cages, including T_8, T_{10}, and T_{12} species, and ESR spectra of the endohedral complexes have recently been reviewed.[207]

Table 4. T_8R_8 Derivatives Prepared by Hydrosilylation

entry	R or compound number	starting materials	yield (%)	refs
1	$-(CH_2)_2O(CH_2)_2Cl$	$T_8H_8 + CH_2{=}CHO(CH_2)_2Cl$, H_2PtCl_6	98	69, 208
2	$-(CH_2)_2Cy$	$T_8H_8 + CH_2{=}CHC_6H_{11}$, H_2PtCl_6, hexane	74	208
3	$-(CH_2)_2C_6H_4$-4-Br	$T_8H_8 + CH_2{=}CHC_6H_4$-4-Br, H_2PtCl_6	67	209
4	$-(CH_2)_2C_6H_4$-4-Br	$T_8H_8 + CH_2{=}CHC_6H_4$-4-Br, Pt(dvs), toluene	81	210
5	$-(CH_2)_2C_6H_4$-4-CH_2Cl and -$CHMeC_6H_4$-4-CH_2Cl	$T_8H_8 + CH_2{=}CHC_6H_4$-4-CH_2Cl, H_2PtCl_6, $Cl(CH_2)_2Cl$	85^a	211
6	$-(CH_2)_2SiMe_2(CH_2)_2SiCl_3$	$T_8(CH_2)_2SiMe_2CH{=}CH_2 + HSiCl_3$, Pt(dvs), ether	91	212
7	$-(CH_2)_2SiMe_2C_6H_4$-4-$SiMe_2H$	$T_8(CH{=}CH_2)_8 + HSiMe_2C_6H_4$-4-$SiMe_2H$, Pt(dvs), toluene		213
8	**13**	$T_8[(CH_2)_2SiMe_2C_6H_4$-4-$SiMe_2H]_8$ + 7-allyloxy coumarin, Pt(dvs), toluene	97	213
9	$-(CH_2)_2SiMe_2C_6H_4$-4-Br	$T_8(CH{=}CH_2)_8 + HSiMe_2C_6H_4$-4-Br, Pt(dvs), ether	67	214
10	$-(CH_2)_2SiMe_2C_6H_3$-3,5-Br_2	$T_8(CH{=}CH_2)_8 + HSiMe_2C_6H_3$-3,5-$Br_2$, Pt(dvs), ether	73	214
11	$-(CH_2)_2SiMe[(CH_2)_2SiMe_2Cl]_2$	$T_8(CH_2)_2SiMe(CH{=}CH_2)_2 + HSiMe_2Cl$, Pt(dvs), ether	88	212
12	$-(CH_2)_2SiMe[(CH_2)_2SiMeCl_2]_2$	$T_8(CH_2)_2SiMe(CH{=}CH_2)_2 + HSiMeCl_2$, Pt(dvs), ether	92	212
13	$-CH_2CHMeC_6H_4$-3-CMe_2NCO	$T_8H_8 + CH_2{=}CMeC_6H_4$-3-$CMe_2NCO$, Pt(dvs)		170
14	$-(CH_2)_3Cy$	$T_8H_8 + CH_2{=}CHCH_2Cy$, H_2PtCl_6, $Cl(CH_2)_2Cl$, $MeO(CH_2)_2OMe$	94	215
15	$-(CH_2)_3Ph$	$T_8H_8 + CH_2{=}CHCH_2Ph$, H_2PtCl_6, $Cl(CH_2)_2Cl$, $MeO(CH_2)_2OMe$	69	215
16	$-(CH_2)_3CN$	$T_8H_8 + CH_2{=}CHCH_2CN$, H_2PtCl_6, 1,2-dichloroethane		216
17	$-(CH_2)_3(OCH_2CH_2)_3Me$	$T_8H_8 + CH_2{=}CHCH_2(OCH_2CH_2)_3Me$, Pt(dvs)		70
18	$-(CH_2)_3(OCH_2CH_2)_2OH$	$T_8H_8 + CH_2{=}CHCH_2(OCH_2CH_2)_2OH$, Pt(dvs), toluene		217
19	$-(CH_2)_3(OCH_2CH_2)_3OH$	$T_8H_8 + CH_2{=}CHCH_2(OCH_2CH_2)_3OH$, Pt(dvs), toluene		217
20	$-(CH_2)_3(OCH_2CH_2)_4OH$	$T_8H_8 + CH_2{=}CHCH_2(OCH_2CH_2)_4OH$, Pt(dvs), toluene		217
21	$-(CH_2)_3(OCH_2CH_2)_6OH$	$T_8H_8 + CH_2{=}CHCH_2(OCH_2CH_2)_6OH$, Pt(dvs), toluene		217
22	$-(CH_2)_3OCH_2CH(O)CH_2$	$T_8H_8 + CH_2{=}CHCH_2OCH_2CH(O)CH_2$, Pt(dvs), toluene	94	71, 72, 218
23	**14**	T_8H_8 + 2-(4-allyloxyphenyl)-5-(4-octyloxyphenyl)-1,3,4-oxadiazole, Pt(dcp), dichloroethane	52	219
24	$-(CH_2)_3SiCl_3$	$T_8H_8 + CH_2{=}CHCH_2SiCl_3$, H_2PtCl_6, toluene		220
25	$-(CH_2)_4Br$	$T_8H_8 + CH_2{=}CH(CH_2)_2Br$, H_2PtCl_6	88	208
26	$-(CH_2)_5Br$	$T_8H_8 + CH_2{=}CH(CH_2)_3Br$, H_2PtCl_6	100	208
27	$-(CH_2)_6Cl$	$T_8H_8 + CH_2{=}CH(CH_2)_4Cl$, H_2PtCl_6	94	208
28	$-(CH_2)_7Br$	$T_8H_8 + CH_2{=}CH(CH_2)_5Br$, H_2PtCl_6, toluene	90	208
29	$-(CH_2)_8Br$	$T_8H_8 + CH_2{=}CH(CH_2)_6Br$, H_2PtCl_6	96	208
30	$-CH{=}CHCMe_2OH$ and $-OCMe_2C{\equiv}CH$	$T_8H_8 + CH{\equiv}CCMe_2OH$, H_2PtCl_6, toluene	*b*	220
31	$-CH{=}CHCH_2C_6H_4$-4-$CO_2C_6H_4$-4-$N{=}NC_6H_4$-4-OMe and $-C({=}CH_2)CH_2C_6H_4$-4-$CO_2C_6H_4$-4-$N{=}NC_6H_4$-4-OMe	$T_8H_8 + CH{\equiv}CCH_2C_6H_4$-4-$CO_2C_6H_4$-4-$N{=}NC_6H_4$-4-OMe, Pt(dcp), dichloroethane	51^a	221
32	$-CH{=}CH(CH_2)_4Cl$ and $-C({=}CH_2)(CH_2)_4Cl$	$T_8H_8 + CH{\equiv}C(CH_2)_4Cl$, H_2PtCl_6, toluene	79^a	208
33	$-OSiMe_2(CH_2)_2CO_2$-*t*-Bu	$T_8(OSiMe_2H)_8 + CH_2{=}CHCO_2$-*t*-Bu, H_2PtCl_6, THF		222
34	**15**	$T_8(OSiMe_2H)_8$ + 4-vinylcyclohexene, Pt(dcp)	97	142
35	**16**	$T_8(OSiMe_2H)_8$ + 4-vinylcyclohexene epoxide, Pt(dcp)		223
36	**16**	$T_8(OSiMe_2H)_8$ + 4-vinylcyclohexene epoxide, Pt(dvs), toluene	96	224, 225
37	$-OSiMe_2(CH_2)_2Ph$ and $-OSiMe_2CH(Me)Ph$	$T_8(OSiMe_2H)_8 + CH_2{=}CHPh$, Pt(dvs), toluene	63^a	226, 227
38	$-OSiMe_2(CH_2)_2C_6H_4$-3-$C(CF_3)_2OH$	$T_8(OSiMe_2H)_8 + CH_2{=}CHC_6H_4$-3-$C(CF_3)_2OH$, Pt(dvs), toluene	99	228
39	$-OSiMe_2(CH_2)_2C_6H_4$-4-OAc	$T_8(OSiMe_2H)_8$, $+ CH_2{=}CHC_6H_4$-4-OAc, Pt(dvs), hexane		229
40	$-OSiMe_2(CH_2)_2C_6H_4$-4-OAc	$T_8(OSiMe_2H)_8 + CH_2{=}CHC_6H_4$-4-OAc, Pt(dvs), toluene	93	230–232
41	$-OSiMe_2(CH_2)_2C_6H_4$-4-OAc and $-OSiMe_2CH(Me)C_6H_4$-4-OAc	$T_8(OSiMe_2H)_8 + CH_2{=}CHC_6H_4$-4-OAc, Pt(dvs), toluene	56^a	226, 227
42	**17**	$T_8(OSiMe_2H)_8$ + 9-vinyl-9*H*-carbazole, Pt(dvs), toluene	70	233–235
43	$-OSiMe_2(CH_2)_2SiMe_2OSi_7O_9(OH)_2(c\text{-}C_5H_9)_7$	$T_8(OSiMe_2H)_8 + CH_2{=}CHSiMe_2OSi_7O_9(OH)_2(c\text{-}C_5H_9)_7$, Pt(dvs), toluene	83	236
44	$-OSiMe_2(CH_2)_2SiMe_2OSi_7O_9[OSiMe_2(CH_2)_2SiMe_2OSi_7O_9(OH)_2(c\text{-}C_5H_9)_7]_2(c\text{-}C_5H_9)_7$	$T_8[OSiMe_2(CH_2)_2SiMe_2OSi_7O_9(OSiMe_2H)_2(c\text{-}C_5H_9)_7]_8 + CH_2{=}CHSiMe_2OSi_7O_9(OH)_2(c\text{-}C_5H_9)_7$, Pt(dvs), toluene	63	236
45	$-OSiMe_2(CH_2)_3Cl$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2Cl$, H_2PtCl_6, ether	48	237
46	$-OSiMe_2(CH_2)_3CN$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2CN$, H_2PtCl_6, ether	43	238
47	**18**	$T_8(OSiMe_2H)_8$ + **19**, Pt(dvs), toluene	47	239
48	$-OSiMe_2(CH_2)_3NMe_2$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2NMe_2$, Pt(dvs), THF		240
49	**20**	$T_8(OSiMe_2H)_8$ + 3-allyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine, Pt(dvs), toluene	*a*	241
50	$-OSiMe_2(CH_2)_3OH$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2OH$, Pt(dvs), toluene	99	242, 243
51	$-OSiMe_2(CH_2)_3O(CH_2)_2Me$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2)_2Me$, Pt(dvs), toluene		244
52	$-OSiMe_2(CH_2)_3OCH_2CH(O)CH_2$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2OCH_2CH(O)CH_2$, Pt(dvs), toluene	95	225, 245, 246
53	$-OSiMe_2(CH_2)_3OCH_2CH(O)CH_2$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2OCH_2CH(O)CH_2$, Pt(dcp), toluene	91	139, 140, 247
54	**21**	$T_8(OSiMe_2H)_8$ + **22**, Pt(dvs), toluene		248
55	$-OSiMe_2(CH_2)_3O(CH_2CH_2O)_2H$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_2H$, Pt(dvs), toluene		217, 249–251
56	$-OSiMe_2(CH_2)_3O(CH_2CH_2O)_2Me$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_2Me$, Pt(dvs), toluene		250–253
57	$-OSiMe_2(CH_2)_3O(CH_2CH_2O)_2C({=}O)C({=}CH_2)Me$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_2C({=}O)C({=}CH_2)Me$, Pt(dvs), toluene		254
58	$-OSiMe_2(CH_2)_3O(CH_2CH_2O)_3H$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_3H$, Pt(dvs), toluene		217, 249–251
59	$-OSiMe_2(CH_2)_3O(CH_2CH_2O)_3Me$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_3Me$, Pt(dvs), toluene		250, 251, 255
60	$-OSiMe_2(CH_2)_3O(CH_2CH_2O)_4H$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_4H$, Pt(dvs), toluene		217, 249–251, 256

Table 4. Continued

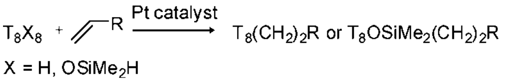
entry	R or compound number	starting materials	yield (%)	refs
61	$\mathrm{-OSiMe_2(CH_2)_3O(CH_2CH_2O)_4Me}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_4Me}$, Pt(dvs), toluene		250–253, 255, 257
62	$\mathrm{-OSiMe_2(CH_2)_3O(CH_2CH_2O)_6H}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_6H}$, Pt(dvs), toluene		217, 250, 251
63	$\mathrm{-OSiMe_2(CH_2)_3O(CH_2CH_2O)_6Me}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_6Me}$, Pt(dvs), toluene		250, 251, 255
64	$\mathrm{-OSiMe_2(CH_2)_3O(CH_2CH_2O)_8Me}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_8Me}$, Pt(dvs), toluene		250–253, 255
65	$\mathrm{-OSiMe_2(CH_2)_3O(CH_2CH_2O)_{12.5}Me}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2CH_2O)_{12.5}Me}$, Pt(dvs), toluene		250–253
66	$\mathrm{-OSiMe_2(CH_2)_3O[(CH_2)_3O]_2C({=}O)CH_2\text{-}C({=}CH_2)Me}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O[(CH_2)_3O]_2C({=}O)CH_2C({=}CH_2)Me}$, Pt(dvs), toluene	95	141, 258
67	$\mathrm{-OSiMe_2(CH_2)_3OCF_2CHFCF_3}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2OCF_2CHFCF_3}$, Pt(dvs), toluene	90	244, 259
68	$\mathrm{-OSiMe_2(CH_2)_3O(CH_2)_6OC_6H_4\text{-}4\text{-}C_6H_4\text{-}4\text{-}CN}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2O(CH_2)_6OC_6H_4\text{-}4\text{-}C_6H_4\text{-}4\text{-}CN}$, Pt(dvs), toluene	43[c]	260
69	$\mathrm{-OSiMe_2(CH_2)_3OSiMe_2\text{-}}t\mathrm{\text{-}Bu}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2OSiMe_2\text{-}}t\mathrm{\text{-}Bu}$, Pt(dvs), toluene	88	261
70	$\mathrm{-OSiMe_2CH_2CHMeC_6H_4\text{-}3\text{-}CMe_2NCO}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CMeC_6H_4\text{-}3\text{-}CMe_2NCO}$, Pt(dvs), THF	94	170
71	$\mathrm{-OSiMe_2(CH_2)_3C_6H_4\text{-}2\text{-}OH}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2C_6H_4\text{-}2\text{-}OH}$, Pt(dvs), toluene	99	228
72	$\mathrm{-OSiMe_2(CH_2)_3C_6H_3\text{-}2\text{-}OH\text{-}5\text{-}C(CF_3)_2C_6H_4\text{-}4\text{-}OH}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2C_6H_3\text{-}2\text{-}OH\text{-}5\text{-}C(CF_3)_2C_6H_4\text{-}4\text{-}OH}$, Pt(dvs), toluene	99	228
73	**23**	$\mathrm{T_8(OSiMe_2H)_8}$ + **24**, Pt(dvs), toluene	54	262
74	**25**	$\mathrm{T_8(OSiMe_2H)_8}$ + triallyl isocyanurate, $\mathrm{H_2PtCl_6}$, toluene	66	160
75	$\mathrm{-OSiMe_2CH{=}CHCH_2OC({=}O)C({=}CH_2)Me}$	$\mathrm{T_8(OSiMe_2H)_8 + CH{\equiv}CCH_2OC({=}O)C({=}CH_2)Me}$, Pt(dvs), toluene	91	141, 254
76	$\mathrm{-OSiMe_2(CH_2)_4CH(O)CH_2}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CH(CH_2)_2CH(O)CH_2}$, Pt(dvs), toluene	>95	224, 263, 264
77	**26**	$\mathrm{T_8(OSiMe_2H)_8}$ + 2,7-bis(2,2-diphenylvinyl)-9-(hex-5-enyl)-9-methyl-9*H*-fluorene, Pt(dvs), toluene	60	239
78	$\mathrm{-OSiMe_2(CH_2)_2CMe_2(CH_2)_2OC({=}O)CMe_2Br}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CHCMe_2(CH_2)_2OC({=}O)CMe_2Br}$, Pt(dvs), $\mathrm{CH_2Cl_2}$, toluene	75	265
79	**27**	$\mathrm{T_8(OSiMe_2H)_8}$ + **28**, Pt(dvs), toluene	61	239
80	$\mathrm{-OSiMe_2(CH_2)_9Me}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CH(CH_2)_7Me}$, Pt(dvs), toluene		266
81	$\mathrm{-OSiMe_2(CH_2)_{11}OC_6H_4\text{-}4\text{-}CO_2C_6H_4\text{-}4\text{-}C_6H_4\text{-}3\text{-}OC({=}O)C_6H_4\text{-}4\text{-}OC({=}O)C_6H_4\text{-}4\text{-}O(CH_2)_{11}Me}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CH(CH_2)_9OC_6H_4\text{-}4\text{-}CO_2C_6H_4\text{-}4\text{-}C_6H_4\text{-}3\text{-}OC({=}O)C_6H_4\text{-}4\text{-}OC({=}O)C_6H_4\text{-}4\text{-}O(CH_2)_{11}Me}$, Pt(dvs), toluene	91	267
82	$\mathrm{-OSiMe_2(CH_2)_{11}OC_6H_2\text{-}2,5\text{-}[CH{=}CHC_6H_4\text{-}4\text{-}N(C_6H_4\text{-}4\text{-}Me)_2]_2\text{-}4\text{-}O(CH_2)_5Me}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CH(CH_2)_9OC_6H_2\text{-}2,5\text{-}[CH{=}CHC_6H_4\text{-}4\text{-}N(C_6H_4\text{-}4\text{-}Me)_2]_2\text{-}4\text{-}O(CH_2)_5Me}$, Pt(dvs), toluene	20	262
83	$\mathrm{-OSiMe_2(CH_2)_{12}OC_6H_4\text{-}4\text{-}CO_2C_6H_4\text{-}4\text{-}C_6H_4\text{-}3\text{-}OC({=}O)C_6H_4\text{-}4\text{-}OC({=}O)C_6H_4\text{-}4\text{-}O(CH_2)_{11}Me}$	$\mathrm{T_8(OSiMe_2H)_8 + CH_2{=}CH(CH_2)_{10}OC_6H_4\text{-}4\text{-}CO_2C_6H_4\text{-}4\text{-}C_6H_4\text{-}3\text{-}OC({=}O)C_6H_4\text{-}4\text{-}OC({=}O)C_6H_4\text{-}4\text{-}O(CH_2)_{11}Me}$, Pt(dvs), toluene	13	268
84	**29**	$\mathrm{T_8(OSiMe_2H)_8}$ + **30**, Pt(dvs), toluene	33	262
85	**31**	$\mathrm{T_8(OSiMe_2H)_8}$ + 2-bicyclo[2.2.1]hept-5-en-2-ylmethyl-1,1,1,3,3,3-hexafluoropropan-2-yl acetate, Pt(dvs), hexane	*a*	229, 269
86	**32**	$\mathrm{T_8(OSiMe_2H)_8}$ + 2-tetrahydropyranyltetracyclo[4.4.0.$1^{2,5}$.$1^{7,12}$]dodec-3-ene-5-carboxylic acid, Pt(dvs), THF	*a*	269, 270
87	**33**	$\mathrm{T_8(OSiMe_2H)_8}$ + **34**, Pt(dvs), THF	*a*	269, 270
88	**35**	$\mathrm{T_8(OSiMe_2H)_8}$ + **36**, Pt(dvs), hexane	*a*	269, 270
89	**37**	$\mathrm{T_8(OSiMe_2H)_8}$ + **38**, Pt(dvs), hexane	*a*	269, 270
90	$\mathrm{-OSiMe_2OSiMe_2(CH_2)_{11}OC_6H_4\text{-}4\text{-}CO_2C_6H_4\text{-}4\text{-}C_6H_4\text{-}3\text{-}OC({=}O)C_6H_4\text{-}4\text{-}OC({=}O)C_6H_4\text{-}4\text{-}O(CH_2)_{11}Me}$	$\mathrm{T_8(CH{=}CH_2)_8 + HSiMe_2OSiMe_2(CH_2)_{11}OC_6H_4\text{-}4\text{-}CO_2C_6H_4\text{-}4\text{-}C_6H_4\text{-}3\text{-}OC({=}O)C_6H_4\text{-}4\text{-}OC({=}O)C_6H_4\text{-}4\text{-}O(CH_2)_{11}Me}$, Pt(dvs), toluene	79	267

[a] Contains a mixture of α- and *β*-isomers. [b] Consists of a mixture of these products. [c] Average of 5.5 arms substituted.

2.5. Synthesis of POSS Compounds by Hydrosilylation

2.5.1. T_8R_8 Compounds

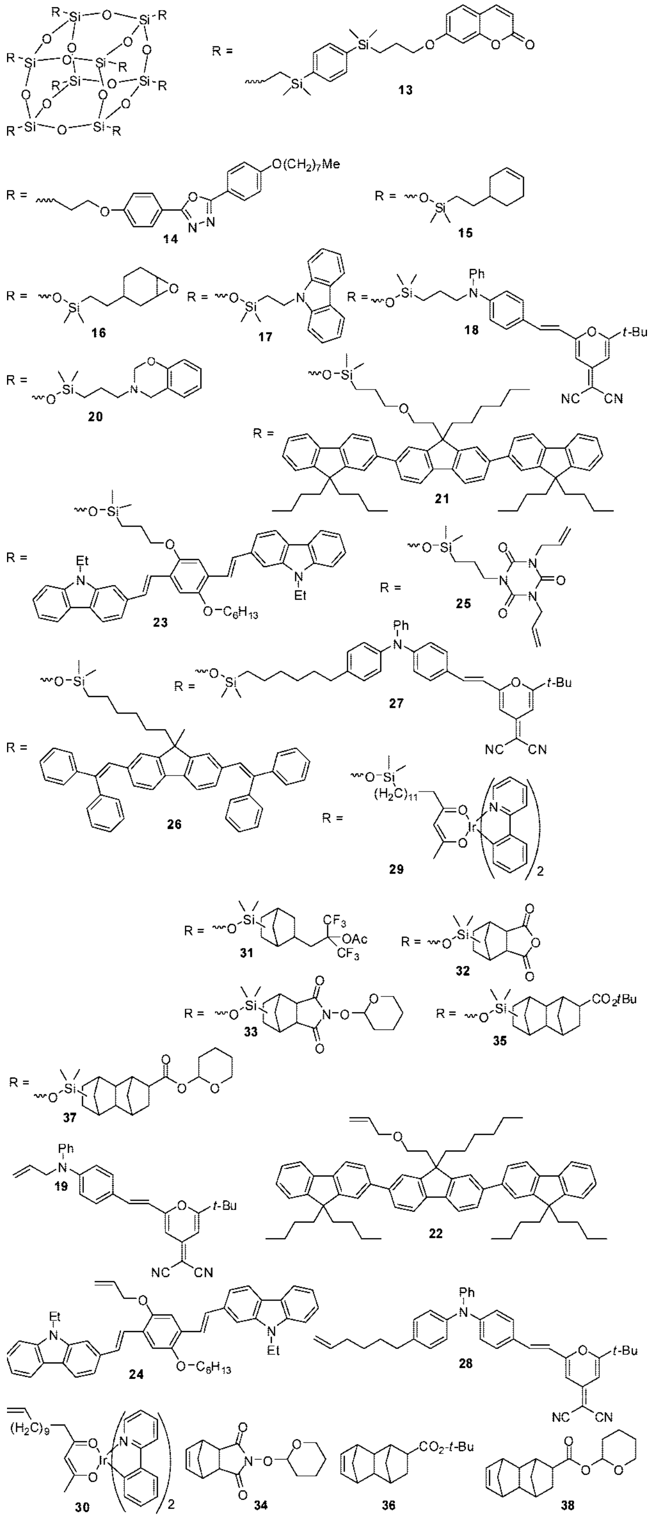
Hydrosilylation is a simple, often platinum-catalyzed, reaction allowing the addition of a Si−H to an unsaturated compound such as an alkene or alkyne. In the case of T_8 derivatives, the general reaction can be summarized in eq 2, with the T_8 starting material usually being either T_8H_8 or $T_8(OSiMe_2H)_8$, and the syntheses of specific T_8R_8 derivatives are presented in Table 4 and Chart 4. While the yields of such a reaction are often high, especially in the cases of simple alkyl-functionalized alkenes,[1] there are potentially two general problems with this reaction. The first of these, and the most general, is the problem of forming either the α- or the *β*-isomer of the product. Due to the strong directing effect of silicon, this is not often a problem, with usually solely the α-product being formed. In no case does the *β*-product form exclusively, and only in a limited number of cases is a mixture of isomers reported (Table 4, entries 5, 31, 32, 37, 41, 84−88). The second problem, reaction at an oxygen center, rather than the carbon−carbon double or triple bond, may occur when there is an alcohol or carbonyl functionality present in the alkene or alkyne. While there are few reports of this occurring in reactions with T_8 POSS, it has been reported for a system with a terminal alcohol functional group (Table 4, entry 30), suggesting that it may occur in others, albeit at low levels. Depending on the desired use of the POSS-based material in question, the formation of isomeric mixtures in these reactions may be a problem. For uses as property modifiers in polymeric systems or nanocomposites, small proportions of such "impurities" will likely be of little consequence. However, where further chemical reaction is required or if specific pure products are desired, then separation of the isomers may prove necessary.



(2)

Following the discovery of a practical synthetic route to T_8H_8, hydrosilylation became one of the most common

Chart 4



methods for producing T_8 POSS species with octa-alkyl substitution due to its simplicity and the often high yield of hydrosilylated products. Similarly, the use of $T_8(OSiMe_2H)_8$ as a starting material in hydrosilylation reactions (Table 4, entries 33−90) allows a similarly wide range of compounds to be prepared in which the new substituent is removed from the immediate effects of the POSS cage through a Si−O−Si linkage. The substituents in both these systems range from simple alkyl or substituted alkyl systems (Table 4, entries 14, 25−29, 45, 46, 48, 50, and 80) to aromatic species (Table 4, entries 5, 7−10, 13, 15, 23, 31, 37−42, 47, 49, 54, 68, 70−73, 77, 79, 81−84, and 90), or functionalities useable for polymerization reactions (Table 4, entries 13, 22, 35, 36, 53, 57, 66, 70, 75, 76, and 78) among others. Further, the use of hydrosilylation to prepare T_8 POSS derivatives allows for the incorporation of functionalities such as C−OH or Si−Cl in the product that would likely react in a synthesis by hydrolysis and condensation. In this way, functionalities such as potentially reactive silicon-containing species (Table 4, entries 6, 11, 12, 24, 43, and 44), halogens (Table 4, entries 1, 3−5, 9, 10, 25−29, 32, 45, and 78), and alcohols (Table 4, entries 18−21, 30, 38, 43, 44, 50, 55, 58, 60, 62, 71, and 72) may be incorporated into T_8 POSS systems.

While the majority of the hydrosilylation reactions occur between T_8 derivatives containing the Si−H group and an unsaturated organic compound, there are a few reactions that have been reported for the opposite, namely, the reaction between a T_8 derivative containing an unsaturated hydrocarbon functional group and an added Si−H species (Table 4, entries 6, 7, 9−12, and 90). While some of these reactions involve the comparatively simple $T_8(CH{=}CH_2)_8$ being reacted with more complicated organosilicon derivatives (Table 4, entries 7, 9, 10, and 90), three start from more complex alkene-containing POSS derivatives (Table 4, entries 6, 11, and 12). In all of these compounds, the reported yields are reasonable.

2.5.2. T_8R_7R' Compounds

The syntheses using hydrosilylation of a variety of T_8 POSS derivatives containing two different substituents are presented in Tables 5 and 6 and Charts 5 and 6. Again, there are only a limited number of syntheses where β-substitution is preferred over α or where isomeric mixtures form through reactions with oxygen functions as well as carbon−carbon multiple bonds (Table 5, entries 5, 10 and 12). In the case of two of these reactions; Table 5, entries 10 and 12, modification of the conditions led to the ability to produce the desired hydrosilylation product and not the unwanted oxygen-substituted isomer (Table 5, entries 11 and 13). As was the case for the T_8R_8 hydrosilylation reactions, the majority of those presented here are between T_8 derivatives containing a Si−H group and an added unsaturated organic compound. The exceptions for these reactions are for two $T_8R_7CH_2CH{=}CH_2$ compounds (Table 5, entries 15 and 19) and two $T_8R_7CH{=}CH_2$ compounds (Table 6, entries 2 and 3). These reactions appear to proceed in as favorable a manner as those involving a T_8-silyl species.

Four highly unusual reactions are entries 1−4 in Table 5. In these, T_8H_8 is treated with unsubstituted alkyl derivatives in an appropriate ratio to give solely the T_8H_7R product. While the yields of these reactions are not as high as many other hydrosilylations, the opportunities arising for further functionalization of such products are significant, allowing for a greater variety of T_8R_7R' derivatives to be prepared and potentially allowing for the controlled introduction of more types of substituents on a single T_8 POSS cube.

Four further cases of hydrosilylation reactions of T_8 derivatives with differing functionalities are presented in Table 6. These reactions are of the type that would typically produce conventional T_8R_7R' derivatives; however, in this case there is one significant feature that sets them apart from the other hydrosilylations presented. In all four of the reactions, the added organic (Table 6, entries 1 and 4) or organometallic (Table 6, entries 2 and 3) compound is

Table 5. T_8R_7R' Derivatives Prepared by Hydrosilylation

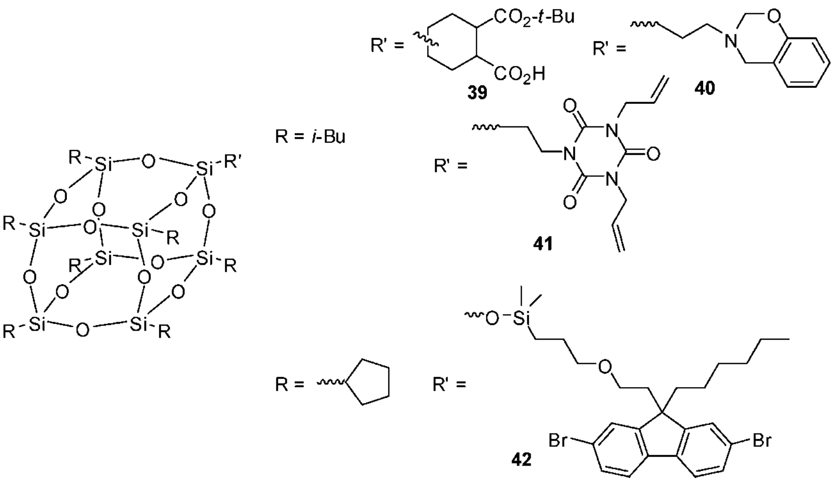
entry	substituents or compound number R	 R′	starting materials	yield (%)	refs
1	-H	$-(CH_2)_3CO_2$-*n*-$C_{16}H_{33}$	$T_8H_8 + CH_2{=}CHCH_2CO_2$-*n*-$C_{16}H_{33}$, H_2PtCl_6, toluene	30	271
2	-H	*n*-$C_{19}H_{39}$	$T_8H_8 + CH_2{=}CH$-*n*-$C_{17}H_{35}$, H_2PtCl_6, toluene	40	272
3	-H	*n*-$C_{21}H_{43}$	$T_8H_8 + CH_2{=}CH$-*n*-$C_{19}H_{39}$, H_2PtCl_6, toluene	40	272
4	-H	*n*-$C_{23}H_{47}$	$T_8H_8 + CH_2{=}CH$-*n*-$C_{21}H_{43}$, H_2PtCl_6, toluene	40	272
5	**39**		$T_8(i\text{-Bu})_7H$ + 6-(*tert*-butoxycarbonyl)cyclohex-3-enecarboxylic acid, Pt(dvs), THF	*a*	270
6	**40**		$T_8(i\text{-Bu})_7H$ + 3-allyl-3,4-dihydro-2*H*-benzo[*e*][1,3]oxazine, Pt(dvs), toluene	53	273
7	-*i*-Bu	$-(CH_2)_3C_6H_3$-2-OH-5-$CMe_2C_6H_4$-4-OH	$T_8(i\text{-Bu})_7H + CH_2{=}CHCH_2C_6H_3$-2-OH-5-$CMe_2C_6H_4$-3-$CH_2CH{=}CH_2$-4-OH, Pt(dvs), toluene		228
8	**41**		$T_8(i\text{-Bu})_7H$ + triallyl isocyanurate, H_2PtCl_6, toluene	69	160
9	-*i*-Bu	$-OC_6H_4$-4-$CMe_2C_6H_4$-4-OH	$T_8(i\text{-Bu})_7H + CH_2{=}CHCH_2C_6H_3$-2-OH-5-$CMe_2C_6H_4$-3-$CH_2CH{=}CH_2$-4-OH, Pt(dvs), toluene		228
10	-*i*-Bu	$-OSiMe_2(CH_2)_3OH$ and $-OSiMe_2OCH_2CH{=}CH_2$	$T_8(i\text{-Bu})_7OSiMe_2H + H_2C{=}CHCH_2OH$, Pt(dvs), THF	*a*	274
11	-*i*-Bu	$-OSiMe_2(CH_2)_3OH$	$T_8(i\text{-Bu})_7OSiMe_2H$+ $H_2C{=}CHCH_2OH$, Pt(dvs), toluene		274
12	-*i*-Bu	$-OSiMe_2(CH_2)_5OH$ and $-OSiMe_2O(CH_2)_3CH{=}CH_2$	$T_8(i\text{-Bu})_7OSiMe_2H + H_2C{=}CH(CH_2)_3OH$, Pt(dvs), THF	*a*	274
13	-*i*-Bu	$-OSiMe_2(CH_2)_5OH$	$T_8(i\text{-Bu})_7OSiMe_2H + H_2C{=}CH(CH_2)_3OH$, Pt(dvs), toluene		274
14	-*i*-Bu	$-OSiMe_2CH_2CHMeC_6H_4$-3-CMe_2NCO	$T_8(i\text{-Bu})_7OSiMe_2H + CH_2{=}CMeC_6H_4$-3-$CMe_2NCO$, Pt(dvs)		170
15	$-(CH_2)_2CF_3$	$-(CH_2)_3SiCl_3$	$T_8[(CH_2)_2CF_3]_7CH_2CH{=}CH_2 + HSiCl_3$, Pt catalyst, THF	98	275
16	$-(CH_2)_2CF_3$	$-(CH_2)_3OCH_2C(O)CH_2$	$T_8[(CH_2)_2CF_3]_7H + CH_2{=}CHCH_2OC(O)CH_2$, Pt(dvs), THF	90	172
17	-*c*-C_5H_9	$-(CH_2)_3C_6H_4$-4-$OCF{=}CF_2$	$T_8(c\text{-}C_5H_9)_7H + CH_2{=}CHCH_2C_6H_4$-4-$OCF{=}CF_2$, Pt(dvs), CH_2Cl_2		276
18	**12**		$T_8(c\text{-}C_5H_9)_7H$ + 9-allyl-9*H*-fluorene, H_2PtCl_4, toluene	71	179
19	-*c*-C_5H_9	$-(CH_2)_3SiMe_2C_6H_4$-4-$SiMe_2H$	$T_8(c\text{-}C_5H_9)_7CH_2CH{=}CH_2 + HMe_2SiC_6H_4$-4-$SiMe_2H$, Pt(dvs), toluene	72	277
20	-*c*-C_5H_9	$-OSiMe_2(CH_2)_3OC_6H_4$-4-OMe	$T_8(c\text{-}C_5H_9)_7OSiMe_2H + CH_2{=}CHCH_2OC_6H_4$-4-OMe, Pt(dvs), toluene	90	278
21	**42**		$T_8(c\text{-}C_5H_9)_7OSiMe_2H$ + 9-(2-allyloxyethyl)-2,7-dibromo-9-hexyl-9*H*-fluorene, Pt(dvs), toluene	79	279
22	$-OSiMe_3$	$-OSiMe_2(CH_2)_3$-NH-$Si(i\text{-Pr})_3$	$T_8(OSiMe_3)_7OSiMe_2H + CH_2{=}CHCH_2NHSi(i\text{-Pr})_3$, Pt(dvs), toluene	89	280
23	$-OSiMe_3$	$-OSiMe_2(CH_2)_3N(SiMe_3)_2$	$T_8(OSiMe_3)_7OSiMe_2H + CH_2{=}CHCH_2N(SiMe_3)_2$, Pt(dvs), toluene	87	280

[a] Contains a mixture of α- and β-isomers.

Table 6. Multi-T_8 Derivatives Prepared by Hydrosilylation

entry	T_8 derivative or compound number	starting materials	yield (%)	refs
1	**43**	$T_8(c\text{-}C_5H_9)_7OSiMe_2H$ + 9,9-bis(2-allyloxyethyl)-2,7-dibromo-9*H*-fluorene, Pt(dvs), toluene	67	281
2	$Si[OSiMe_2(CH_2)_2T_8Cy_7]_4$	$T_8Cy_7CH{=}CH_2 + Si(OSiMe_2H)_4$, $PtCl_2(SEt_2)_2$, toluene		282
3	$O(SiMe_2OSiMe_2(CH_2)_2T_8Ph_7)_2$	$T_8Ph_7CH{=}CH_2 + O(SiMe_2OSiMe_2H)_2$, H_2PtCl_6, THF		283
4	$CMe_2[C_6H_3\text{-}3\text{-}(CH_2)_3T_8(i\text{-Bu})_7\text{-}4\text{-}OT_8(i\text{-Bu})_7]_2$	$T_8(i\text{-Bu})_7H + CMe_2(C_6H_4\text{-}3\text{-}CH_2CH{=}CH_2\text{-}4\text{-}OH)_2$, Pt(dvs), toluene		228

Chart 5

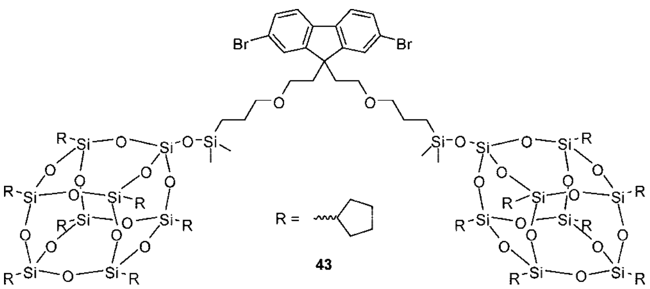


designed to bridge between multiple T_8 cores, resulting in the formation of multi-T_8 species. Three of these new compounds (Table 6, entries 1, 3, and 4) are bis-T_8 compounds, while the other (Table 6, entry 2) is a tetrakis-T_8 compound.

2.5.3. $T_8R_{(8-n)}R'_n$ Compounds

The syntheses of several unusual POSS derivatives are presented in Table 7 and Chart 7. These hydrosilylation reactions use specific ratios of two different reactants plus a

Chart 6



43

T_8R_8 species, leading to the formation of $T_8R_{(8-n)}R'_n$ POSS compounds. Most of these reactions again show little preference for β-substitution over α, the exception being entry 22, which produces a reported mixture of isomers. Furthermore, all except two of the reactions (Table 7, entries 3 and 4) start from $T_8(OSiMe_2H)_8$ rather than a vinyl-T_8 compound.

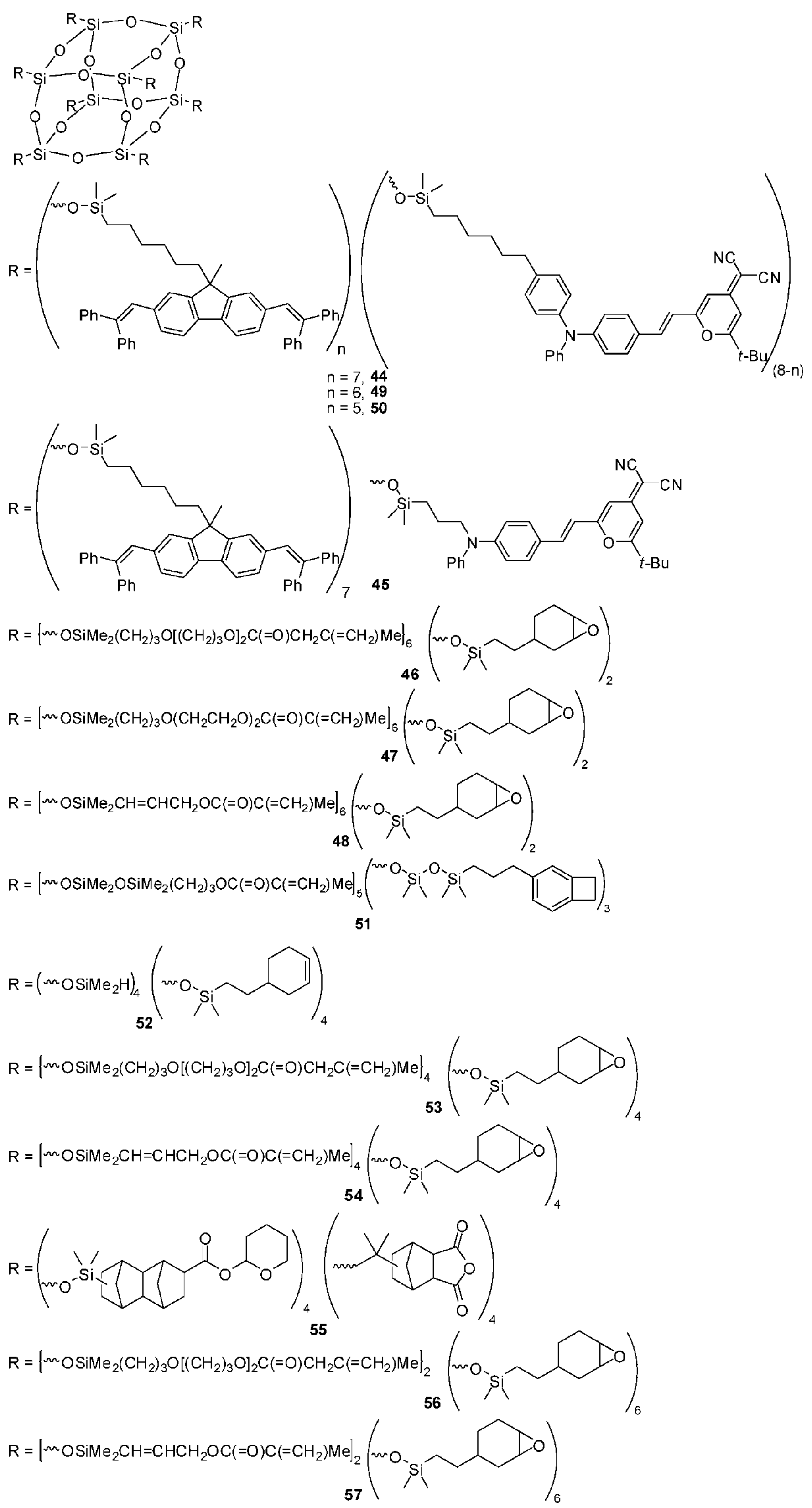
While it is possible to determine the resulting ratios of differing functional groups at the POSS core, it is likely that a variety of varying substitutional isomers will be formed, even for a single $T_8R_{(8-n)}R'_n$ product. One study has looked in more detail into the substitution patterns present on the T_8 core from the reaction of T_8H_8 with varying molar ratios of either phenol and undec-1-ene or phenol and 3,3-dimethylpent-4-enoate.[284] While complex mixtures of products were clearly formed, patterns observed in the ^{29}Si NMR spectra of the product mixtures suggest that identification of particular substitutional isomers may be possible. While most of the compounds presented in Table 7 are claimed to consist of a product with a single combination of functional groups, the fact that two of them (Table 7, entries 11 and 23) show products with either varying substitution ratios or noninteger ratios of substituents, respectively, suggests that many of the other compounds may likewise consist of complicated mixtures. Depending on the intended use of such a product, this could be a significant drawback to such syntheses, unless the unwanted products could be separated.

Table 7. $T_8R_{(8-n)}R'_n$ Derivatives Prepared by Hydrosilylation

	substituents, compound or compound number				
entry	R	R′	starting materials	yield (%)	refs
1	**44**		$T_8(OSiMe_2H)_8$ + 2,7-bis(2,2-diphenylvinyl)-9-methyl-9-(pent-4-enyl)-9*H*-fluorene, **27**, Pt(dvs), toluene	26[a]	239
2	**45**		$T_8(OSiMe_2H)_8$ + 2,7-bis(2,2-diphenylvinyl)-9-methyl-9-(pent-4-enyl)-9*H*-fluorene, **18**, Pt(dvs), toluene	20	239
3	$-[(CH_2)_2Si(OEt)_3]_6$	$-(CH{=}CH_2)_2$	$T_8(CH{=}CH_2)_8 + HSi(EtO)_3$, Pt(dvs), toluene		285, 286
4	$-[(CH_2)_2SiMe_2C_6H_4\text{-}4\text{-}NPh_2]_6$	$-(CH{=}CH_2)_2$	$T_8(CH{=}CH_2)_8 + HSiMe_2C_6H_4\text{-}4\text{-}NPh_2$, Pt(dvs), ether		287
5	$-[OSiMe_2(CH_2)_3Ph]_6$	$-[OSiMe_2(CH_2)_4CH{=}CH_2]_2$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2Ph$, $CH_2{=}CH(CH_2)_2CH{=}CH_2$, Pt(dvs), toluene	65	288
6	**46**		$T_8(OSiMe_2H)_8$ + $CH_2{=}CHCH_2O[(CH_2)_3O]_2C({=}O)CH_2C({=}CH_2)Me$, 4-vinylcyclohexene epoxide, Pt(dcp), toluene	88	141, 258
7	**47**		$T_8(OSiMe_2H)_8$ + $CH_2{=}CHCH_2O(CH_2CH_2O)_2C({=}O)C({=}CH_2)Me$, 4-vinylcyclohexene epoxide, Pt(dcp), toluene		254
8	**48**		$T_8(OSiMe_2H)_8 + CH{\equiv}CCH_2OC({=}O)C({=}CH_2)Me$, 4-vinylcyclohexene epoxide, Pt(dcp), toluene	87	141, 254
9	$-[OSiMe_2(CH_2)_5Me]_6$	$-[OSiMe_2(CH_2)_4CH(O)CH_2]_2$	$T_8(OSiMe_2H)_8 + CH_2{=}CH\text{-}n\text{-}Bu$, $CH_2{=}CH(CH_2)_2CH(O)CH_2$, Pt(dvs)		264
10	**49**		$T_8(OSiMe_2H)_8$ + 2,7-bis(2,2-diphenylvinyl)-9-methyl-9-(pent-4-enyl)-9*H*-fluorene, **27**, Pt(dvs), toluene	18[a]	239
11	$Li_{1-3}\{T_8[OSiMe_2(CH_2)_3O(CH_2CH_2O)_4Me]_{5-7}[OSiMe_2(CH_2)_3O(CF_2)_2SO_3]_{1-3}\}$		$T_8(OSiMe_2H)_8 + Li[CH_2{=}CHCH_2O(CF_2)SO_3]$, $CH_2{=}CHCH_2O(CH_2CH_2O)_4H$, Pt(dvs), THF		250, 251
12	$-[OSiMe_2(CH_2)_3Ph]_5$	$-[OSiMe_2(CH_2)_4CH{=}CH_2]_3$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2Ph$, $CH_2{=}CH(CH_2)_2CH{=}CH_2$, Pt(dvs), toluene	54	288
13	**50**		$T_8(OSiMe_2H)_8$ + 2,7-bis(2,2-diphenylvinyl)-9-methyl-9-(pent-4-enyl)-9*H*-fluorene, **27**, Pt(dvs), toluene	9[a]	239
14	$-[OSiMe_2(CH_2)_{11}OC_6H_4\text{-}4\text{-}CO_2C_6H_4\text{-}4\text{-}C_6H_4\text{-}3\text{-}OC({=}O)C_6H_4\text{-}4\text{-}OC({=}O)C_6H_4\text{-}4\text{-}O(CH_2)_{11}Me]_5$	$-(OSiMe_2H)_3$	$T_8(OSiMe_2H)_8 + CH_2{=}CH(CH_2)_9OC_6H_4\text{-}4\text{-}CO_2C_6H_4\text{-}4\text{-}C_6H_4\text{-}3\text{-}OC({=}O)C_6H_4\text{-}4\text{-}OC({=}O)C_6H_4\text{-}4\text{-}O(CH_2)_{11}Me$, Pt(dvs), toluene	77	267
15	**51**		$T_8(OSiMe_2OSiMe_2H)_8 + CH_2{=}CHCH_2OC({=}O)C({=}CH_2)Me$, 4-allyl-1,2-dihydrocyclobutabenzene, Pt catalyst		289
16	**52**		$T_8(OSiMe_2H)_8$ + 4-vinylcyclohexene, Pt(dcp), toluene	94	142, 290, 291
17	$-[OSiMe_2(CH_2)_3Ph]_4$	$-[OSiMe_2(CH_2)_4CH{=}CH_2]_4$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2Ph$, $CH_2{=}CH(CH_2)_2CH{=}CH_2$, Pt(dvs), toluene	42	288
18	**53**		$T_8(OSiMe_2H)_8$ + $CH_2{=}CHCH_2O[(CH_2)_3O]_2OC({=}O)CH_2C({=}CH_2)Me$, 4-vinylcyclohexene epoxide, Pt(dcp), toluene		141, 258
19	$-[OSiMe_2(CH_2)_3OCF_2CHFCF_3]_4$	$-[OSiMe_2(CH_2)_3OCH_2CH(O)CH_2]_4$	$T_8(OSiMe_2H)_8 + CH_2{=}CHCH_2OCF_2CHFCF_3$, $CH_2{=}CHCH_2OCH_2CH(O)CH_2$, Pt(dvs), toluene	90	292
20	**54**		$T_8(OSiMe_2H)_8 + CH{\equiv}CCH_2OC({=}O)C({=}CH_2)Me$, 4-vinylcyclohexene epoxide, Pt(dcp), toluene		141
21	$-[OSiMe_2(CH_2)_6]_4$	$-[OSiMe_2(CH_2)_4CH(O)CH_2]_4$	$T_8(OSiMe_2H)_8 + CH_2{=}CH\text{-}n\text{-}Bu$, $CH_2{=}CH(CH_2)_2CH(O)CH_2$, Pt(dvs)		264
22	**55**		$T_8(OSiMe_2H)_8$ + **37**, 2-tetrahydropyranyltetracyclo[4.4.0.1^{2,5}.1^{7,12}]-dodec-3-ene-5-carboxylic acid, Pt(dvs), THF	[b]	270
23	$-[OSiMe_2(CH_2)_{11}OC_6H_4\text{-}4\text{-}CO_2C_6H_4\text{-}4\text{-}C_6H_4\text{-}3\text{-}OC({=}O)C_6H_4\text{-}4\text{-}OC({=}O)C_6H_4\text{-}4\text{-}O(CH_2)_{11}Me]_{3.5}$	$-(OSiMe_2H)_{4.5}$	$T_8(OSiMe_2H)_8 + CH_2{=}CH(CH_2)_9OC_6H_4\text{-}4\text{-}CO_2C_6H_4\text{-}4\text{-}C_6H_4\text{-}3\text{-}OC({=}O)C_6H_4\text{-}4\text{-}OC({=}O)C_6H_4\text{-}4\text{-}O(CH_2)_{11}Me$, Pt(dvs), toluene	70	267
24	**56**		$T_8(OSiMe_2H)_8$ + $CH_2{=}CHCH_2O[(CH_2)_3O]_2OC({=}O)CH_2C({=}CH_2)Me$, 4-vinylcyclohexene epoxide, Pt(dcp), toluene		141, 258
25	**57**		$T_8(OSiMe_2H)_8 + CH{\equiv}CCH_2OC({=}O)C({=}CH_2)Me$, 4-vinylcyclohexene epoxide, Pt(dcp), toluene		141

[a] Three separable products from the same reaction. [b] Contains a mixture of α- and β-isomers.

Chart 7



One rather unusual hydrosilylation reaction of T_8H_8 has recently been investigated. It involves the reaction of T_8H_8 with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane.[75] The reaction proceeds in an α/β ratio of 3.4:1, but it also shows signs of creating a certain number of linkages between adjacent T_8 cages.

2.6. Synthesis of POSS Compounds by Reactions at Silicon Other than Hydrosilylation

While hydrosilylation is one of the most common methods for synthesis of T_8 POSS species, there are a variety of other reactions used, where the transformation

Table 8. T_8R_8 Derivatives Prepared by Reactions at Silicon Centers Other than Hydrosilylation

entry	R, T_8R_8, or compound number	starting materials	yield (%)	refs
1	$-(CH_2)_2SiMe_2OMe$	$T_8[(CH_2)_2SiMe_2Cl]_8 + NEt_3$, MeOH, THF		294
2	$-(CH_2)_2SiMe_2OMe$	$T_8[(CH_2)_2SiMe_2Cl]_8 + NEt_3$, MeOH, THF	87	295
3	$-(CH_2)_2SiMe(OMe)_2$	$T_8[(CH_2)_2SiMeCl_2]_8 + NEt_3$, MeOH, THF		294
4	$-(CH_2)_2Si(OMe)_3$	$T_8[(CH_2)_2SiCl_3]_8 + NEt_3$, MeOH, THF		294
5	**58**	$T_8[(CH_2)_2SiMe_2Cl]_8$ + cholic acid trimethoxysilylpropyl ester, NEt_3, THF	74	296
6	**59**	$T_8[(CH_2)_2SiMe_2Cl]_8$ + cholic acid 3-diazo-4-ethoxy-2,4-dioxobutyl ester, THF	93	297
7	$[T_8O_8]^{8-}$	$T_8(OSiMe_2H)_8 + H_2O$, MeOH		298
8	-OEt	T_8H_8 + EtOH, NEt_2OH, benzene	54	74
9	-O-*i*-Pr	T_8H_8 + *i*-PrOH, NEt_2OH, benzene	87	74
10	-O-*t*-Bu	T_8H_8 + *t*-BuOH, NEt_2OH, benzene	83	74
11	-O-Oct	T_8H_8 + OctOH, NEt_2OH, benzene	80	74
12	-OCy	T_8H_8 + CyOH, NEt_2OH, benzene	80	74
13	$-OSiMe_2H$	$[NMe_4]_8[T_8O_8] + HMe_2SiCl$, hexane	85	139, 140, 142, 225
14	$-OSiMe_2H$	$[NMe_4]_8[T_8O_8] + HMe_2SiCl$, toluene	85	141
15	$-OSiMe_3$	$T_8(OSiMe_2H)_8 + Me_3SiCl$, AcOH, hexane	98	299
16	$-OSiMe_3$	$T_8H_8 + Me_3SiOH$, NEt_2OH, benzene	54	74
17	$-OSiMe_2CH_2Cl$	$T_8(OSiMe_2H)_8 + ClCH_2Me_2SiCl$, AcOH, hexane	94	299
18	$-OSiMe_2CH_2Br$	$T_8(OSiMe_2H)_8 + BrCH_2Me_2SiCl$, AcOH, hexane	90	299
19	$-OSiMe_2(CH_2)_2SiMe_2OSi_7O_9(OSiMe_2H)_2(c\text{-}C_5H_9)_7$	$T_8[OSiMe_2(CH_2)_2SiMe_2OSi_7O_9(OH)_2(c\text{-}C_5H_9)_7]_8 + HMe_2SiCl$, NEt_3, benzene	70	236
20	$-OSiMe_2(CH_2)_3OH$	$T_8[OSiMe_2(CH_2)_3OSiMe_2\text{-}t\text{-}Bu]_8 + NBu_4F$, THF, AcOH	81	261
21	$-OSiMe_2CH{=}CH_2$	$[NMe_4]_8[T_8O_8] + CH_2{=}CHMe_2SiCl$, THF		144
22	$-OSiMe_2C_6H_4\text{-}4\text{-}Me$	$[NMe_4]_8[T_8O_8] + Me\text{-}4\text{-}C_6H_4Me_2SiCl$, hexane	40	143
23	$-OSiMe_2OH$	$T_8(OSiMe_2H)_8$ + Pd/C, H_2O		289
24	$-OSiMe_2OEt$	$[NMe_4]_8[T_8O_8] + EtOMe_2SiCl$, pyridine, THF		300
25	$-OSiMe_2OSiMe_2H$	$T_8(OSiMe_2OH)_8 + HMe_2SiCl$, pyridine, THF		289
26	$-OSiMe_2OSiMe_3$	$T_8(OSiMe_2H)_8 + (Me_3Si)_2O$, cyclohexane, HCl	97	298
27	$-OSiMe(OEt)_2$	$[NMe_4]_8[T_8O_8] + (EtO)_2MeSiCl$, pyridine, THF		300
28	$-OSi(OEt)_3$	$[NMe_4]_8[T_8O_8] + (EtO)_3SiCl$, pyridine, THF		300

Table 9. T_8R_7R' Derivatives Prepared by Reactions at Silicon Centers Other than Hydrosilylation

	substituents or compound number				
entry	R	R′	starting materials	yield (%)	refs
1	-*i*-Bu	$-OSiMe_2H$	$T_8(i\text{-}Bu)_7OH + HMe_2SiCl$, NEt_3, THF		170
2	-*i*-Bu	$-OSiMe(C_6H_4\text{-}4\text{-}OCF{=}CF_2)_2$	$T_8(i\text{-}Bu)_7OH + (CF_2{=}CFO\text{-}4\text{-}C_6H_4)_2MeSiCl$	29	301, 302
3	$-(CH_2)_2CF_3$	$-(CH_2)_3OSiMe_3$	$T_8[(CH_2)_2CF_3]_7(CH_2)_3OH + Me_3SiCl$, NEt_3, THF	90	176
4	$-c\text{-}C_5H_9$	$-OSiMe_2C{\equiv}CH$	$T_8(c\text{-}C_5H_9)_7(OH) + HC{\equiv}CMe_2SiOEt$, $Me\text{-}C_6H_4\text{-}4\text{-}SO_2OH$, toluene	99	303
5	$-c\text{-}C_5H_9$	$-OSiMe_2(CH_2)_3NH_2$	$T_8(c\text{-}C_5H_9)_7(OH) + H_2N(CH_2)_3Me_2SiOMe$, hexane or THF		304
6	$-c\text{-}C_5H_9$	$-OSiMe(C_6H_4\text{-}4\text{-}OCF{=}CF_2)_2$	$T_8(c\text{-}C_5H_9)_7OH + (CF_2{=}CFO\text{-}4\text{-}C_6H_4)_2MeSiCl$,	28	301, 302
7	-Ph	$-(CH_2)_3OSiMe_3$	$T_8Ph_7(CH_2)_3OH + Me_3SiCl$, NEt_3, THF	92	192
8	-OEt	$-(CH_2)_3CO_2\text{-}n\text{-}C_{16}H_{33}$	$T_8H_7(CH_2)_3CO_2\text{-}n\text{-}C_{16}H_{33}$ + EtOH, NEt_2OH, toluene	70	271
9	-OEt	$-n\text{-}C_{19}H_{39}$	$T_8H_7(n\text{-}C_{19}H_{39})$ + EtOH, NEt_2OH, toluene	70	272
10	-OEt	$-n\text{-}C_{21}H_{43}$	$T_8H_7(n\text{-}C_{21}H_{43})$ + EtOH, NEt_2OH, toluene	70	272
11	-OEt	$-n\text{-}C_{23}H_{47}$	$T_8H_7(n\text{-}C_{23}H_{47})$ + EtOH, NEt_2OH, toluene	70	272
12	$-OSiMe_3$	$-OSiMe_2H$	$T_8(OSiMe_3)_7OH + HMe_2SiCl$, NEt_3, toluene	89	305
13	**60**		$T_8(OSiMe_3)_7OSiMe_2(CH_2)_3NHC({=}O)C_6H_4\text{-}2\text{-}CO_2Si(i\text{-}Pr)_3$	80	306
14	$-OSiMe_3$	$-OSiMe_2(CH_2)_3NHC({=}O)C_6H_4\text{-}2\text{-}CO_2Si(i\text{-}Pr)_3$	$T_8(OSiMe_3)_7OSiMe_2(CH_2)_3NHSi(i\text{-}Pr)_3$ + phthalic anhydride, THF	99	306
15	$-OSi(OSiMe_3)_3$	$-OSi(OSiMe_3)_2OH$	$T_8[OSi(OEt)_3]_8 + Me_3SiCl$, H_2O, THF	75	293

occurs at silicon centers, as shown in Tables 8−10 and Charts 8 and 9. Most of these reactions are variants on substitution reactions (Scheme 3), ranging from simple substitution at silicon, such as alkoxide/chloride or alkoxide/alkoxide exchange (Table 8, entries 1−6) to the exchange of protons at silicon for oxygen species (Table 8, entries 8−12, 16, 23, and 26; Table 9, entries 8−11) or the introduction of di- or trimethylsilyl species (Table 8, entries 13, 14, 21, 22, 24, 27, and 28; Table 9, entries 1−7, 12). In the case of the T_8R_7R' systems (Scheme 4), where the seven nonreactive groups are able to shield the silsesquioxane core, more forcing conditions, such as lithiation, may be used to bring about the substitution (Table 10, entries 1, 3, and 4). Such reactions have been used to form linked multi-T_8 species, both in cases with simple oxygen bridges between two T_8 derivatives (Table 10, entries 1 and 3) and in cases with more complicated, partially condensed silsesquioxane bridges (Table 10, entry 4).

Attempts have been made to produce highly silylated T_8 derivatives by silylation of simple T_8 compounds such as $[T_8O_8]^{8-}$ and T_8H_8 with either $(Me_3SiO)_3SiCl$ or $(Me_3SiO)_3SiOH$. Both showed silylation to proceed, but neither reaction went to completion, with two or three corners of the cube not substituted.[293] This was thought to be due to the steric bulk of the silylating agents used. A

Table 10. Bridged $(T_8R_7)_2R'$ Derivatives Prepared by Reactions at Silicon Centers Other than Hydrosilylation

entry	R	R′	starting materials	yield (%)	refs
1	-*c*-C_5H_9	-O-	$T_8(c\text{-}C_5H_9)_7OH + T_8(c\text{-}C_5H_9)_7Cl$, *n*-BuLi, THF	65	307
2	-Cy	-O-	T_8Cy_7Cl +NEt_3, ether	56	308
3	-Cy	-O-	$T_8Cy_7OH + T_8Cy_7Cl$, *n*-BuLi, THF	67	307
4	-Cy	-$Si_8O_{11}Cy_8$	$T_8Cy_7Cl + Si_8O_{11}Cy_8(OH)_2$, *n*-BuLi, THF	73	307

Chart 8

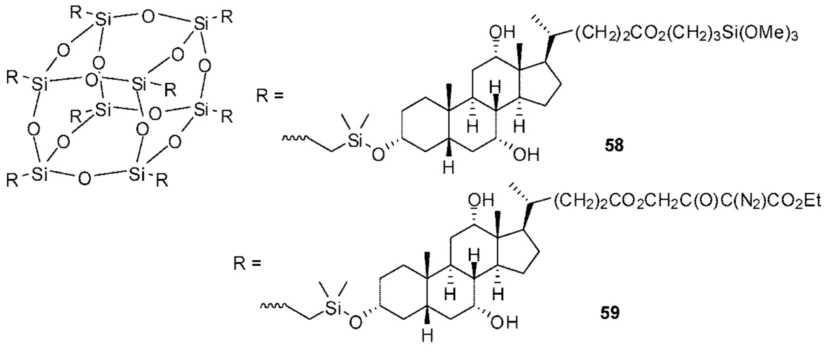


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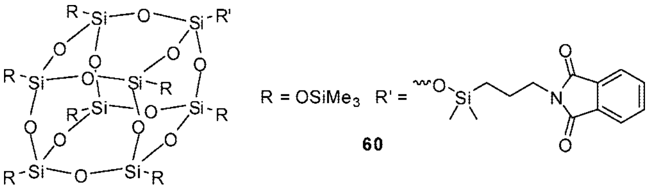
Chart 9



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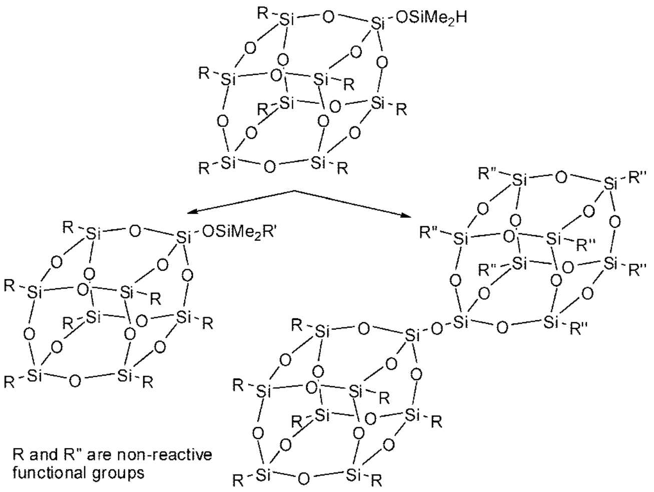
more practical route was found to be achievable by silylation of $T_8[OSi(OEt)_3]_8$ with chlorotrimethylsilane, which produced a product much closer to the desired $T_8[OSi(OSiMe_3)_3]_8$ (Table 9, entry 15).

In addition to reactions where new functionalities are added to the T_8 core, reactions at a T_8 vertex silicon resulting in the removal of part or all of a substituent are known (Scheme 3). Cleavage of part of a substituent at a vertex of a POSS cage was found to occur by desilylation (Table 8, entry 19; Table 9, entry 13), while removal of a complete substituent was found to occur by alcoholysis in the case of the preparation of $[T_8O_8]^{8-}$ from $T_8(OSiMe_2H)_8$ (Table 8, entry 7).

Scheme 4



2.7. Modification of Substituents To Prepare POSS Compounds

While the range of T_8 POSS derivatives that can be prepared by the reactions described above is large, it can

Scheme 3

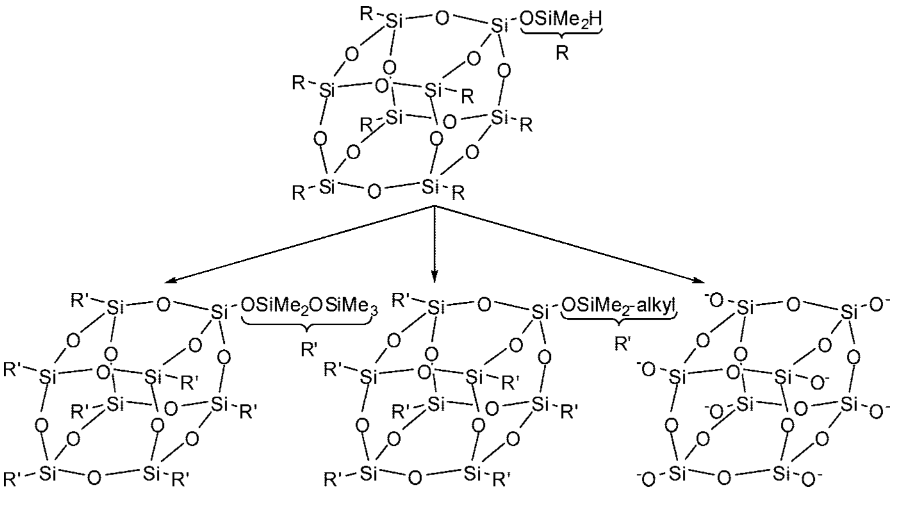


Table 11. T$_8$R$_8$ Derivatives Prepared by Organic Substitution Reactions of T$_8$ POSS Compounds

entry	R, T$_8$R$_8$ or compound number	starting materials	yield (%)	refs
1	-(CH$_2$)$_2$SiMe$_2$C$_6$H$_4$-4-C≡CSiMe$_3$	T$_8$[(CH$_2$)$_2$SiMe$_2$C$_6$H$_4$-4-Br]$_8$ + HC≡CSiMe$_3$, [Pd(PPh$_3$)$_2$Cl$_2$], CuI, PPh$_3$, NEt$_3$, THF	47	214
2	-(CH$_2$)$_2$SiMe$_2$C$_6$H$_4$-3-P(NMe$_2$)$_2$	T$_8$[(CH$_2$)$_2$SiMe$_2$Cl]$_8$ + BrC$_6$H$_4$-3-P(NMe$_2$)$_2$, *n*-BuLi, NaHCO$_3$, ether, THF, CH$_2$Cl$_2$		319
3	**61**	T$_8$[(CH$_2$)$_2$SiMe$_2$C$_6$H$_4$-3-P(NMe$_2$)$_2$]$_8$ + (*S*)-2-(phenylaminomethyl)pyrrolidine, toluene	63^{a}	212, 319
4	-(CH$_2$)$_2$SiMe[C$_6$H$_4$-3-P(NMe$_2$)$_2$]$_2$	T$_8$[(CH$_2$)$_2$SiMeCl$_2$]$_8$ + BrC$_6$H$_4$-3-P(NMe$_2$)$_2$, *n*-BuLi, NaHCO$_3$, THF, CH$_2$Cl$_2$		212, 319
5	**62**	T$_8${(CH$_2$)$_2$SiMe[C$_6$H$_4$-3-P(NMe$_2$)$_2$]$_2$}$_8$ + (*S*)-2-(phenylaminomethyl)pyrrolidine, toluene	72^{a}	212, 319
6	-(CH$_2$)$_2$Si[C$_6$H$_4$-3-P(NMe$_2$)$_2$]$_3$	T$_8$[(CH$_2$)$_2$SiCl$_3$]$_8$ + BrC$_6$H$_4$-3-P(NMe$_2$)$_2$, *n*-BuLi, NaHCO$_3$, ether, THF, CH$_2$Cl$_2$		212, 319
7	**63**	T$_8${(CH$_2$)$_2$Si[C$_6$H$_4$-3-P(NMe$_2$)$_2$]$_3$}$_8$ + (*S*)-2-(phenylaminomethyl)pyrrolidine, toluene	60^{a}	212, 319
8	-(CH$_2$)$_2$P(=O)(OH)$_2$	T$_8$[(CH$_2$)$_2$P(=O)(OEt)$_2$]$_8$ + BrSiMe$_3$, H$_2$O, MeOH		320
9	-(CH$_2$)$_2$P(=O)(OEt)$_2$	T$_8$(CH$_2$)$_2$Br + P(OEt)$_3$,		320
10	-(CH$_2$)$_2$SO$_2$C$_6$H$_4$-4-CH$_2$I	T$_8$[(CH$_2$)$_2$SO$_2$C$_6$H$_4$-4-CH$_2$Cl]$_8$ + NaI, MeCN	12	211
11	-CH=CHPh	T$_8$(CH=CH$_2$)$_8$ + PhI, [Pd(OAc)$_2$], PPh$_3$, NEt$_3$, THF	51	214
12	-CH=CHC$_6$H$_4$-4-CH=CHPh	T$_8$(CH=CHC$_6$H$_4$-4-Br)$_8$ + CH$_2$=CHPh, Pd[P(*t*-Bu)$_3$]$_2$, Pd$_2$(dba)$_3$, NCy$_2$Me, 1,4-dioxane	79	321, 322
13	-CH=CHC$_6$H$_4$-4-CH=CHC$_6$H$_4$-4-Me	T$_8$(CH=CHC$_6$H$_4$-4-Br)$_8$ + CH$_2$=CHC$_6$H$_4$-4-Me, Pd[P(*t*-Bu)$_3$]$_2$, Pd$_2$(dba)$_3$, NCy$_2$Me, 1,4-dioxane	74	321, 322
14	-CH=CHC$_6$H$_4$-4-CH=CHC$_6$H$_4$-4-NH$_2$	T$_8$(CH=CHC$_6$H$_4$-4-Br)$_8$ + CH$_2$=CHC$_6$H$_4$-4-NH$_2$, Pd[P(*t*-Bu)$_3$]$_2$, Pd$_2$(dba)$_3$, NCy$_2$Me, 1,4-dioxane	73	321, 322
15	-CH=CHC$_6$H$_4$-4-CH=CHC$_6$H$_4$-4-OMe	T$_8$(CH=CHC$_6$H$_4$-4-Br)$_8$ + CH$_2$=CHC$_6$H$_4$-4-OMe, Pd[P(*t*-Bu)$_3$]$_2$, Pd$_2$(dba)$_3$, NCy$_2$Me, 1,4-dioxane	81	321, 322
16	**64**	T$_8$(CH=CH$_2$)$_8$ + 9-bromoanthracene, Pd[P(*t*-Bu)$_3$]$_2$, NCy$_2$Me, toluene	>85^{b}	323, 324
17	**65**	T$_8$(CH=CH$_2$)$_8$ + 2-bromonaphthalene, Pd[P(*t*-Bu)$_3$]$_2$, NCy$_2$Me, toluene	>85^{b}	323, 324
18	**66**	T$_8$(CH=CH$_2$)$_8$ + 2-bromo-9,9-dimethyl-9*H*-fluorene, Pd[P(*t*-Bu)$_3$]$_2$, NCy$_2$Me, toluene	>85^{b}	323, 324
19	**67**	T$_8$(CH=CH$_2$)$_8$ + 1-bromopyrene, Pd[P(*t*-Bu)$_3$]$_2$, NCy$_2$Me, toluene	>85^{b}	323–325
20	**68**	T$_8$(CH=CH$_2$)$_8$ + 2-(4-bromophenyl)-5-(naphthalene-1-yl)-1,3,4-oxadiazole, Pd[P(*t*-Bu)$_3$]$_2$, NCy$_2$Me, toluene	>85^{b}	323, 324
21	-CH=CHC$_6$H$_4$-4-N(Ph)C$_6$H$_4$-4-NPh$_2$	T$_8$(CH=CH$_2$)$_8$ + BrC$_6$H$_4$-4-N(Ph)C$_6$H$_4$-4-NPh$_2$, Pd[P(*t*-Bu)$_3$]$_2$, NCy$_2$Me, toluene	>85^{b}	323, 324
22	-CH=CHC$_6$H$_4$-4-C≡CSiMe$_3$	T$_8$(CH=CHC$_6$H$_4$-4-Br)$_8$ + HC≡CSiMe$_3$, [Pd(PPh$_3$)$_2$Cl$_2$], CuI, PPh$_3$, NEt$_3$, THF	37	214
23	[NMe$_4$]$_8${T$_8$[7-(CH$_2$)$_3$-8-Me-7,8-*nido*-C$_2$B$_9$H$_{10}$]$_8$}	T$_8$[1-(CH$_2$)$_3$-2-Me-1,2-*closo*-C$_2$B$_{10}$H$_{10}$]$_8$ + KOH, NMe$_4$Cl, EtOH, THF	42	97
24	[T$_8$(CH$_2$)$_3$N(*n*-C$_8$H$_{17}$)Me$_2$]Cl$_8$	T$_8$[(CH$_2$)$_3$Cl]$_8$ + NMe$_2$-*n*-C$_8$H$_{17}$, DMF		117
25	-(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OH][CH$_2$CH(OH)CH$_2$OC(=O)NH-*n*-C$_{18}$H$_{38}$]	T$_8$[(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OH]$_2$ + OCN-*n*-C$_{18}$H$_{38}$, DMF	90	326
26	-(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OC(=O)NH-*n*-C$_{18}$H$_{38}$]$_2$	T$_8$[(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OH]$_2$ + OCN-*n*-C$_{18}$H$_{38}$, DMF	86	326
27	-(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OC(=O)NH-*n*-C$_{18}$H$_{38}$]{CH$_2$CH[OC(=O)NH-*n*-C$_{18}$H$_{38}$]CH$_2$OC(=O)NH-*n*-C$_{18}$H$_{38}$}	T$_8$[(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OH]$_2$ + OCN-*n*-C$_{18}$H$_{38}$, DMF	91	326
28	-(CH$_2$)$_3$N{CH$_2$CH[OC(=O)NH-*n*-C$_{18}$H$_{38}$]CH$_2$OC(=O)NH-*n*-C$_{18}$H$_{38}$}$_2$	T$_8$[(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OH]$_2$ + OCN-*n*-C$_{18}$H$_{38}$, DMF	86	326
29	-(CH$_2$)$_3$N{CH$_2$CH[OC(=O)C$_6$H$_4$-2-CO$_2$H]CH$_2$OC(=O)C$_6$H$_4$-2-CO$_2$H}{CH$_2$CH[OC(=O)C$_6$H$_4$-2-CO$_2$H]CH$_2$OC(=O)NH-*n*-C$_{18}$H$_{38}$}	T$_8$[(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OH]$_2$ + OCN-*n*-C$_{18}$H$_{38}$, phthalic anhydride, DMF, benzene	60	326
30	-(CH$_2$)$_3$N{CH$_2$CH[OC(=O)C$_6$H$_4$-2-CO$_2$H]CH$_2$OC(=O)NH-*n*-C$_{18}$H$_{38}$}$_2$	T$_8$[(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OH]$_2$ + OCN-*n*-C$_{18}$H$_{38}$, phthalic anhydride, DMF, benzene	65	326
31	-(CH$_2$)$_3$N{CH$_2$CH[OC(=O)NH-*n*-C$_{18}$H$_{38}$]CH$_2$OC(=O)NH-*n*-C$_{18}$H$_{38}$}{CH$_2$CH[OC(=O)C$_6$H$_4$-2-CO$_2$H]CH$_2$OC(=O)NH-*n*-C$_{18}$H$_{38}$}	T$_8$[(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OH]$_2$ + OCN-*n*-C$_{18}$H$_{38}$, phthalic anhydride, DMF, benzene	71	326
32	**69**	T$_8$(CH$_2$)$_3$Cl + 3-amino-1,2,4-triazole, DMF	80	121–124
33	-(CH$_2$)$_3$N$_3$	T$_8$(CH$_2$)$_3$Cl + NaN$_3$, DMF	79	118, 165
34	-(CH$_2$)$_3$OH	T$_8$[(CH$_2$)$_3$Cl]$_8$ + Ag$_2$O, H$_2$O, EtOH, THF	91	116
35	-(CH$_2$)$_3$OCH$_2$CH(OH)CH$_2$OC$_6$H$_4$SO$_3$H	T$_8$[(CH$_2$)$_3$OCH$_2$CH(O)CH$_2$]$_8$ + HOC$_6$H$_4$SO$_3$H, THF		327
36	-(CH$_2$)$_3$OCH$_2$CH(OH)CH$_2$OC$_6$H$_3$-2-6-Me$_2$	T$_8$[(CH$_2$)$_3$OCH$_2$CH(O)CH$_2$]$_8$ + HOC$_6$H$_3$-2-6-Me$_2$	90	328
37	-(CH$_2$)$_3$SO$_2$C$_6$H$_4$-4-Me	T$_8$[(CH$_2$)$_3$Cl]$_8$ + Ag(MeC$_6$H$_4$-4-SO$_3$), MeCN		211
38	-C$_6$H$_4$-3-(CH$_2$)$_{17}$Me	T$_8$Ph$_8$ + Me(CH$_2$)$_{17}$Cl, AlCl$_3$, CH$_2$Cl$_2$	68	329
39	-C$_6$H$_4$-3-(CH$_2$)$_{17}$Me-5-SO$_3$H	T$_8$[C$_6$H$_4$-3-(CH$_2$)$_{17}$Me]$_8$ + H$_2$SO$_4$, CH$_2$Cl$_2$	82	329
40	-C$_6$H$_4$-4-CH=CH-2-C$_5$H$_4$N	T$_8$(C$_6$H$_4$-4-I)$_8$ + CH$_2$=CH-2-C$_5$H$_4$N, Pd$_2$dba$_3$, tri*o*-tolylphosphine, H$_2$CuSn, NEt$_3$, dioxane	50	316, 317
41	-C$_6$H$_4$-4-CH=CH-4-C$_5$H$_4$N	T$_8$(C$_6$H$_4$-4-I)$_8$ + CH$_2$=CH-4-C$_5$H$_4$N, Pd$_2$dba$_3$, tri-*o*-tolylphosphine, H$_2$CuSn, NEt$_3$, dioxane	48	316, 317
42	-C$_6$H$_4$-4-CH=CHC$_6$H$_4$-4-Me	T$_8$(C$_6$H$_4$-4-I)$_8$ + CH$_2$=CHC$_6$H$_4$-4-Me, Pd$_2$dba$_3$, tri-*o*-tolylphosphine, Cu, NCy$_2$Me, dioxane	87	316, 317
43	-C$_6$H$_4$-4-C≡CCO$_2$Me	T$_8$(C$_6$H$_4$-4-I)$_8$ + HC≡CCO$_2$Me, CuI, Pd(PPh$_3$)$_4$, NEt$_3$, dioxane	67	318
44	-C$_6$H$_4$-4-C≡CPh	T$_8$(C$_6$H$_4$-4-I)$_8$ + HC≡CPh, CuI, Pd(PPh$_3$)$_4$, NEt$_3$, dioxane	90	316–318
45	-C$_6$H$_4$-4-C≡CC$_6$H$_4$-4-Me	T$_8$(C$_6$H$_4$-4-I)$_8$ + HC≡CC$_6$H$_4$-4-Me, CuI, Pd(PPh$_3$)$_4$, NEt$_3$, dioxane	89	318
46	-C$_6$H$_4$-4-C≡CC$_6$H$_4$-4-OMe	T$_8$(C$_6$H$_4$-4-I)$_8$ + HC≡CC$_6$H$_4$-4-OMe, CuI, Pd(PPh$_3$)$_4$, NEt$_3$, dioxane	90	318
47	-C$_6$H$_4$-4-C≡CC$_6$H$_4$-4-CF$_3$	T$_8$(C$_6$H$_4$-4-I)$_8$ + HC≡CC$_6$H$_4$-4-CF$_3$, CuI, Pd(PPh$_3$)$_4$, NEt$_3$, dioxane	70	318
48	-C$_6$H$_4$-4-C≡CSiMe$_3$	T$_8$(C$_6$H$_4$-4-I)$_8$ + HC≡CSiMe$_3$, CuI, Pd(PPh$_3$)$_4$, NEt$_3$, dioxane	89	318
49	-C$_6$H$_4$-4-Ph	T$_8$(C$_6$H$_4$-4-I)$_8$ + PhB(OH)$_2$, Pd$_2$dba$_3$, tri-*o*-tolylphosphine, Ag$_2$O, THF	83	316, 317
50	-C$_6$H$_4$C$_6$Me$_4$-4-*i*-Bu	T$_8$(C$_6$H$_4$Br)$_8$ + 4-*i*-BuC$_6$Me$_4$MgBr, Pd(PPh$_3$)$_4$, THF	*c*	313
51	-C$_6$H$_4$C$_6$H$_2$-2,6-Me$_2$-4-C$_6$Me$_4$-4-*i*-Bu	T$_8$(C$_6$H$_4$Br)$_8$ + 4-*i*-BuC$_6$Me$_4$-4-C$_6$H$_2$-2,6-Me$_2$MgBr, Pd(PPh$_3$)$_4$, THF	*b*,*c*	313
52	-C$_6$H$_4$C$_6$H$_2$-2,5-Me$_2$-4-OCH$_2$CH(Et)(CH$_2$)$_3$Me	T$_8$(C$_6$H$_4$Br)$_8$ + Me(CH$_2$)$_3$CH(Et)CH$_2$OC$_6$H$_2$-2,5-Me$_2$-4-MgBr, Pd(PPh$_3$)$_4$, THF	60^{c}	330

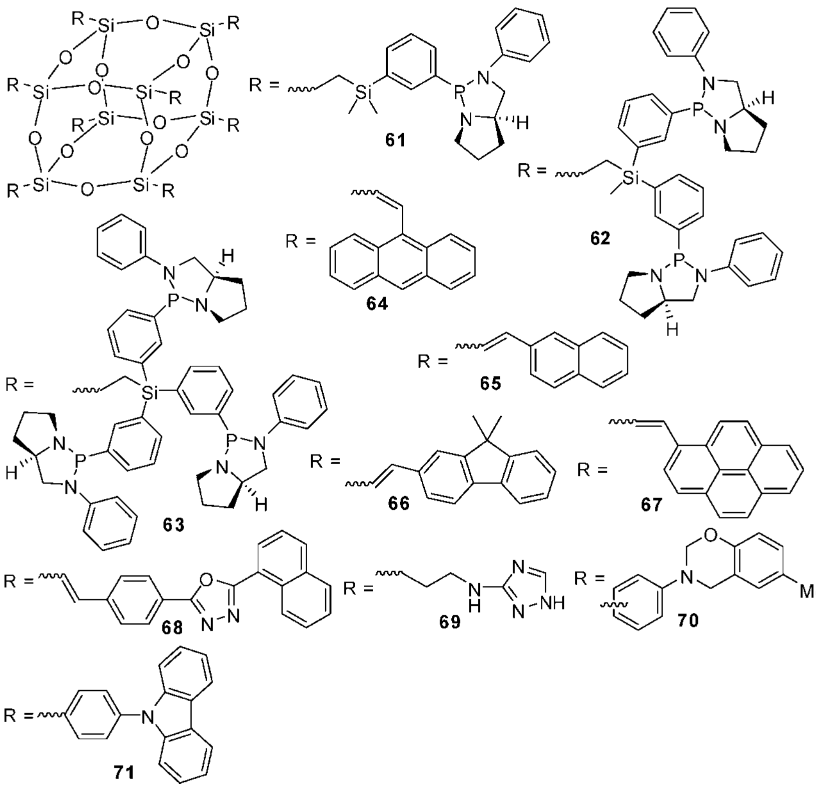
Table 11. Continued

entry	R, T_8R_8 or compound number	starting materials	yield (%)	refs
53	$-C_6H_4C_6H_4-4-C_6H_2-2,5-Me_2-4-OCH_2CH(Et)(CH_2)_3Me$	$T_8(C_6H_4Br)_8 + Me(CH_2)_3CH(Et)CH_2OC_6H_2-2,5-Me_2-4-C_6H_4-4-MgBr$, $Pd(PPh_3)_4$, THF	51^c	330
54	$-C_6H_4C_6H_2-2,5-Me_2-4-C_6H_4-4-CH_2CH(Et)(CH_2)_3Me$	$T_8(C_6H_4Br)_8 + Me(CH_2)_3CH(Et)CH_2C_6H_4-4-C_6H_2-2,5-Me_2-4-MgBr$, $Pd(PPh_3)_4$, THF	55^c	330
55	$-C_6H_4C_6H_2-2,5-Me_2-4-C_6H_4-4-OCH_2CH(Et)(CH_2)_3Me$	$T_8(C_6H_4Br)_8 + Me(CH_2)_3CH(Et)CH_2OC_6H_4-4-C_6H_2-2,5-Me_2-4-MgBr$, $Pd(PPh_3)_4$, THF	55^c	330
56	$-C_6H_4C_6H_2-2,5-(OMe)_2-4-C_6H_4-4-OCH_2CH(Et)(CH_2)_3Me$	$T_8(C_6H_4Br)_8 + Me(CH_2)_3CH(Et)CH_2OC_6H_4-4-C_6H_2-2,5-(OMe)_2-4-MgBr$, $Pd(PPh_3)_4$, THF	48^c	330
57	$-C_6H_4C_6H_4-4-C_6H_4-4-C_6H_2-2,5-Me_2-4-OCH_2CH(Et)(CH_2)_3Me$	$T_8(C_6H_4Br)_8 + Me(CH_2)_3CH(Et)CH_2OC_6H_2-2,5-Me_2-4-C_6H_4-4-C_6H_4-4-MgBr$, $Pd(PPh_3)_4$, THF	42^c	330
58	$-C_6H_4NH_2$	$T_8(C_6H_4NO_2)_8 + FeCl_3$, C, $N_2H_4 \cdot H_2O$, THF	93^c	132, 331, 332
59	$-C_6H_4NH_2$	$T_8(C_6H_4NO_2)_8 +$ Pd/C, NEt_3, $HCO_2H, \cdot H_2O$, THF	82^c	128, 133, 312, 333–335
60	$-C_6H_4NH_2$	$T_8(C_6H_4NO_2)_8 +$ Pd/C, $N_2H_4 \cdot H_2O$, THF	62^c	336
61	$-C_6H_4N_3$	$T_8C_6H_4NH_2 + H_2SO_4$, $NaNO_2$, NaN_3, H_2O	*c*	337
62	$-C_6H_4NO_2$	$T_8Ph_8 + HNO_3$	92^c	128, 132, 133, 312, 331, 333–336
63	$-C_6H_4N[CH_2CO_2Me]_2$	$T_8(C_6H_4NH_2)_8 + ClCH_2CO_2Me$, K_2CO_3, KI, acetone	*c*	338
64	**70**	$T_8(C_6H_4NH_2)_8 + HOC_6H_4-4-Me$, CH_2O	68^c	257
65	**71**	$T_8(C_6H_4-4-I)_8 +$ carbazole, Cu_2O, $AcNMe_2$	76	316, 317
66	$-C_6H_3(NH_2)_2$	$T_8[C_6H_3(NO_2)_2]_8 + HCOOH$, Pd/C, NEt_3, THF	70^c	129
67	$-C_6H_3(NO_2)_2$	$T_8Ph_8 + HNO_3$, H_2SO_4	78^c	129
68	$-C_6H_3-2,4-(NO_2)_2$	$T_8Ph_8 + HNO_3$, H_2SO_4	82	130, 339
69	$-C_6H_4-4-P(=O)(OEt)_2$	$T_8(C_6H_4-4-I)_8 + NiP(=O)(OEt)_3$, $P(=O)(OEt)_3$, *m*-xylene	68	316, 317
70	$-C_6H_4-3-SO_3H$	$T_8Ph_8 + ClSO_2OH$	99	329
71	$Na_8[T_8(C_6H_4SO_3)_8]$	$T_8Ph_8 + ClSO_2OH$, NaOH, H_2O	*c*	340
72	$-C_6H_4Br$	$T_8Ph_8 + Br_2$, $FeCl_3$, $CHCl_3$	60^c	313
73	$-C_6H_4-4-I$	$T_8Ph_8 + ICl$, CH_2Cl_2	90	316, 317
74	$T_8Ph_8Br_{5.3}$	$T_8Ph_8 + Br_2$, Fe, CH_2Cl_2	87^b	314
75	methacrylate derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + CH_2=C(Me)CO_2Me$, $Pd[P(t-Bu)_3]_2$, Pd_2dba_3, dioxane, NCy_2Me	58^b	314
76	methylstyrene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + CH_2=CHC_6H_4-4-Me$, $Pd[P(t-Bu)_3]_2$, Pd_2dba_3, dioxane, NCy_2Me	78^b	314
77	methyl propiolate derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + CH\equiv CCO_2Me$, CuI, $Pd_2(dba)_3$, $Pd[P(t-Bu)_3]_2$, NEt_3, dioxane	56^b	318
78	phenylacetylene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + CH\equiv CPh$, CuI, $Pd_2(dba)_3$, $Pd[P(t-Bu)_3]_2$, NEt_3, dioxane	85^b	318
79	4-ethynyltoluene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + CH\equiv CC_6H_4-4Me$, CuI, $Pd_2(dba)_3$, $Pd[P(t-Bu)_3]_2$, NEt_3, dioxane	86^b	318
80	4-ethynylanisole derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + CH\equiv CC_6H_4-4-OMe$, CuI, $Pd_2(dba)_3$, $Pd[P(t-Bu)_3]_2$, NEt_3, dioxane	87^b	318
81	4-ethynyl-α,α,α-trifluorotoluene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + CH\equiv CC_6H_4-4-CF_3$, CuI, $Pd_2(dba)_3$, $Pd[P(t-Bu)_3]_2$, NEt_3, dioxane	64^b	318
82	trimethylsilylacetylene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + CH\equiv CSiMe_3$, CuI, $Pd_2(dba)_3$, $Pd[P(t-Bu)_3]_2$, NEt_3, dioxane	80^b	318
83	amine derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + NH_2C_6H_4-3-NH_2$, $Fc(PPh_2)_2$, Pd_2dba_3, toluene, *t*-BuONa	75^b	314
84	thiophene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + C_4H_3S-2-B(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, Aliquat 336, H_2O, toluene	52^b	341
85	phenyl derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + Na(BPh_4)$, $Pd(PPh_3)_4$, dioxane	*b*	314
86	phenyl derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + PhB(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, Aliquat 336, H_2O, toluene	49^b	341
87	4-butylbenzene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + n-BuC_6H_4-4-B(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, Aliquat 336, H_2O, toluene	41^b	341
88	biphenyl derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + PhC_6H_4-4-B(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, Aliquat 336, H_2O, toluene	38^b	341
89	naphthalene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + C_{12}H_7-2-B(OH)_2$, $Pd(PPh_3)_4$, K_2CO_3, Aliquat 336, H_2O, toluene	28^b	341
90	9,9-dimethylfluorene derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} +$ 9,9-dimethylfluorene-2-boronic acid, $Pd(PPh_3)_4$, K_2CO_3, Aliquat 336, H_2O, toluene	59^b	341
91	phosphonic phenylester derivatives of $T_8Ph_8Br_{5.3}$	$T_8Ph_8Br_{5.3} + P(=O)(OPh)_2Cl$, *n*-BuLi, THF	78^b	329
92	phosphonic half-phenylester derivatives of $T_8Ph_8Br_{5.3}$	phosphonic phenylester derivatives of $T_8Ph_8Br_{5.3}$ + NaOH, HCl, THF, H_2O	*b*	329
93	$-OSiMe_2(CH_2)_2SiMe_2OSi_7O_9(O_2BPh)-(c-C_5H_9)_7$	$T_8[OSiMe_2(CH_2)_2SiMe_2OSi_7O_9(OH)_2(c-C_5H_9)_7]_8 + PhBCl_2$, NEt_3, benzene	53	236
94	$-OSiMe_2C_6H_4-4-CBr_3$	$T_8(OSiMe_2C_6H_4-4-Me)_8 +$ NBS, AIBN, CCl_4	86^d	143
95	$-OSiMe_2C_6H_4-4-CO_2H$	$T_8(OSiMe_2C_6H_4-4-CBr_3)_8 + AgNO_3$, HCO_2H, H_2O, acetone	90	143

[a] Overall yield from starting $T_8[(CH_2)_2SiMe_{(3-n)}Cl_n]_8$. [b] Contains a mixture of substitutions. [c] Contains a mixture of isomers. [d] Contains a mixture of products with varying degrees of bromination.

be significantly expanded by the use of conventional organic synthesis techniques to modify functionalities remote from the POSS core. There is, however, a significant downside to this approach to the synthesis of new T_8 POSS species. This is the issue of stability of the POSS core in the presence of the reagents necessary to carry out the organic transformation. This is a problem for strong bases, which can readily cleave the Si−O bonds

Chart 10



of the POSS core. However, under controlled reaction conditions or in the presence of bulky substituents, T_8 cores can remain stable through the course of many synthetic procedures.

2.7.1. Substitution Reactions

Despite these limitations, there has been significant research effort involved in systematically investigating the modification of T_8 POSS compounds by organic synthetic reactions. For examples of substitution reactions of T_8R_8 POSS, see Table 11 and Chart 10, for reactions carried out on T_8R_7R' derivatives see Table 12 and Charts 11 and 12, for reactions leading to $T_8R_{(8-n)}R'_n$ compounds, see Table 13 and Chart 13, and multi-T_8 species may be found in Table 14 and Chart 14. A wide range of substitution reactions has been attempted with T_8 POSS compounds. Some of these reactions have been conventional and highly specific in their substitution, such as nucleophilic substitutions (Table 11, entries 2, 4, 6, 8–10, 25–34, 37, 63, 69, 91, and 93; Table 12, entries 1, 2, 7, 9, 17, 19–21, 23, 25–32, 34, 36–38, 43, 48, and 49; Table 14), Heck reactions (Table 11, entries 11–21, 40–42, 75, and 76; Table 13, entries 2 and 3), Suzuki

Chart 11

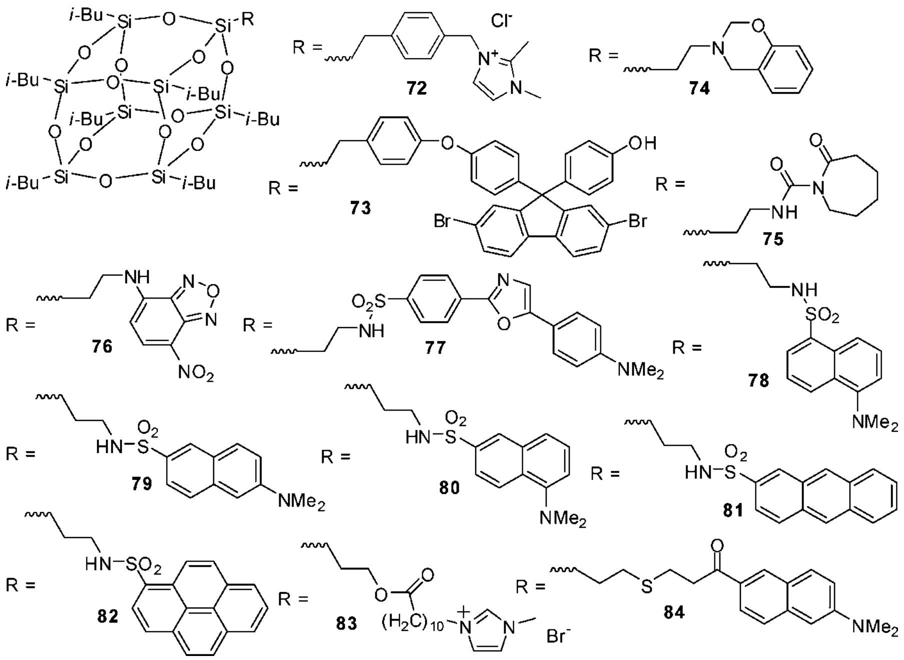
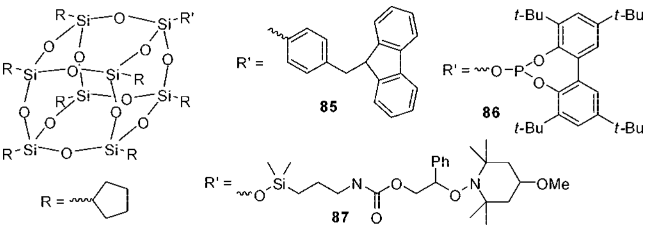


Chart 12



reactions (Table 11, entries 49 and 84−90), and Sonogashira reactions (Table 11, entries 1, 22, 43−48, and 77−82; Table 12, entry 45). There have also been a variety of less directed substitutions, such as nitration (Table 11, entries 62 and 67) or other substitution at an aromatic ring (Table 11, entries 71, 72, and 74). Given the previously noted instability of the T_8 cage in the presence of strong base, it is surprising to see the preparation of several T_8 POSS derivatives by reaction with Grignard reagents (Table 11, entries 50−57), although the reported yields are moderate and the degree of substitution of the T_8 system is not always complete.

One of the more unusual substitution reactions reported is that between $T_8[(CH_2)_3NH_2]_8$ and catechin, which is carried out enzymatically using horseradish peroxidase.[309] The product appears to be a disubstituted system, with two

Table 12. T_8R_7R' Derivatives Prepared by Organic Substitution Reactions of T_8 POSS Compounds

	substituents, compound, or compound number				
entry	R	R′	starting materials	yield (%)	refs
1	-i-Bu	-OH	$T_8(i\text{-Bu})_7(CH_2)_2Cl + H_2O$, THF		170
2	**72**		$T_8(i\text{-Bu})_7(CH_2)_2C_6H_4CH_2Cl$ + 1,2-dimethylimidazole, THF	*a*	342
3	**73**		$T_8(i\text{-Bu})_7(CH_2)_2C_6H_4CH_2Cl$ + 4,4′-(2,7-dibromo-9*H*-fluorene-9,9-diyl)diphenol, NaI, K_2CO_3, THF	21[a]	343
4	-i-Bu	$-CH{=}CHCH_2C(CF_3)_2OH$	$T_8(i\text{-Bu})_7CH_2CH{=}CH_2 + CF_3C({=}O)CF_3$		228
5	**74**		$T_8(i\text{-Bu})_7(CH_2)_3NH_2$ + PhOH, $H_2C({=}O)$, THF	56	273
6	-i-Bu	$-(CH_2)_3NHC({=}O)C_6H_3\text{-3,5-}(OH)_2$	$T_8(i\text{-Bu})_7(CH_2)_3NHC({=}O)C_6H_3\text{-3,5-}(O\text{-}CH_2\text{-}Ph)_2$ + Pd/C, H_2, THF	95	344
7	-i-Bu	$-(CH_2)_3NHC({=}O)C_6H_3\text{-3,5-}(OCN)_2$	$T_8(i\text{-Bu})_7(CH_2)_3NHC({=}O)C_6H_3\text{-3,5-}(OH)_2$ + BrCN, NEt_3, ether	78	344
8	**75**		$T_8(i\text{-Bu})_7(CH_2)_3NH_2$ + 1,1′-carbonyldiazepan-2-one, toluene		345
9	**76**		$T_8(i\text{-Bu})_7(CH_2)_3NH_2$ + 4-chloro-7-nitrobenzo[*c*][1,2,5]oxadiazole, $CHCl_3$	53	346
10	**77**		$T_8(i\text{-Bu})_7(CH_2)_3NH_2$ + 4-[5-(4-dimethylaminophenyl)oxazol-2-yl]benzene-1-sulfonyl chloride, $CHCl_3$	91	346
11	**78**		$T_8(i\text{-Bu})_7(CH_2)_3NH_2$ + 5-dimethylaminonaphthalene-1-sulfonyl chloride, $CHCl_3$	69	346
12	**79**		$T_8(i\text{-Bu})_7(CH_2)_3NH_2$ + 6-dimethylaminonaphthalene-2-sulfonyl chloride, $CHCl_3$	67	346
13	**80**		$T_8(i\text{-Bu})_7(CH_2)_3NH_2$ + 5-dimethylaminonaphthalene-2-sulfonyl chloride, $CHCl_3$	89	346
14	**81**		$T_8(i\text{-Bu})_7(CH_2)_3NH_2$ + anthracene-2-sulfonyl chloride, $CHCl_3$		346
15	**82**		$T_8(i\text{-Bu})_7(CH_2)_3NH_2$ + pyrene-1-sulfonyl chloride, $CHCl_3$	53	346
16	-i-Bu	$-(CH_2)_3N_3$	$T_8(i\text{-Bu})_7(CH_2)_3Cl + NaN_3$, DMF, THF	93	165
17	-i-Bu	$-(CH_2)_3OCH_2CH(OH)CH_2N_3$	$T_8(i\text{-Bu})_7(CH_2)_3OCH_2CH({=}O)CH_2$, NaN_3, $CeCl_3\cdot 7H_2O$, DMF, THF	69	347
18	**83**		$T_8(i\text{-Bu})_7(CH_2)_3OC({=}O)(CH_2)_{10}Br$ + methylimidazole	65	348
19	**84**		$T_8(i\text{-Bu})_7(CH_2)_3SH$ + 1-(6-dimethylaminonaphthalen-2-yl)prop-2-en-1-one, $CHCl_3$	73	346
20	$[T_8(i\text{-Bu})_7C_6H_4\text{-4-}CH_2N(n\text{-}C_{18}H_{37})Me_2]Cl$		$T_8(i\text{-Bu})_7C_6H_4\text{-4-}CH_2Cl + N(n\text{-}C_{18}H_{37})Me_2$		169
21	-i-Bu	$-C_6H_4\text{-4-}CH_2OH$	$T_8(i\text{-Bu})_7C_6H_4\text{-4-}CH_2Br + AgClO_4\cdot H_2O$, acetone, H_2O	88	167
22	-i-Bu	$-C_6H_4\text{-4-}CO_2H$	$T_8(i\text{-Bu})_7C_6H_4\text{-4-}CBr_3 + AgNO_3$, HCO_2H acetone, H_2O	86	167
23	-i-Bu	$-OSiMe_2(CH_2)_3NHCO_2(CH_2CH_2O)_{23}\text{-}(CH_2CH_2)_{38}Me$	$T_8(i\text{-Bu})_7OSiMe_2(CH_2)_3NCO + HO(CH_2CH_2O)_{23}(CH_2CH_2)_{38}Me$, $Sn(n\text{-Bu})_2[OC({=}O)(CH_2)_{10}Me]_2$, toluene	60	349
24	$-(CH_2)_3CF_3$	$-(CH_2)_3OH$	$T_8[(CH_2)_3CF_3]_7(CH_2)_3Cl + Ag_2O$, H_2O, THF	85	176
25	$-(CH_2)_3CF_3$	$-(CH_2)_3N_3$	$T_8[(CH_2)_3CF_3]_7(CH_2)_3Br + NaN_3$, DMF	90	177
26	$-c\text{-}C_5H_9$	$-CH_2CH(OH)CH_2OH$	$T_8(c\text{-}C_5H_9)_7CH_2CH(O)CH_2 + H_2SO_4$, H_2O, THF	81	180
27	**10**		$T_8(c\text{-}C_5H_9)_7CH_2Cl$ + fluorene, n-BuLi, THF, EtOH	82	179
28	$-c\text{-}C_5H_9$	$-(CH_2)_2C_6H_4CH_2N_3$	$T_8(c\text{-}C_5H_9)_7(CH_2)_2C_6H_4CH_2Cl + NaN_3$, DMF, THF	98[a]	347, 350
29	**12**		$T_8(c\text{-}C_5H_9)_7(CH_2)_3Cl$ + fluorene, n-BuLi, THF, EtOH	53	179
30	$-c\text{-}C_5H_9$	$-(CH_2)_3OC_6H_4\text{-4-}CHO$	$T_8(c\text{-}C_5H_9)_7(CH_2)_3I + HOC_6H_4\text{-4-}CHO$, K_2CO_3, THF, acetone	80	351
31	$-c\text{-}C_5H_9$	$-(CH_2)_3OC_6H_2\text{-2,5-}Br_2\text{-4-}O(CH_2)_{11}Me$	$T_8(c\text{-}C_5H_9)_7(CH_2)_3I + HOC_6H_2\text{-2,5-}Br_2\text{-4-}O(CH_2)_{11}Me$, K_2CO_3, THF, acetone	70	352
32	$-c\text{-}C_5H_9$	$-(CH_2)_3I$	$T_8(c\text{-}C_5H_9)_7(CH_2)_3Cl$ + NaI, acetone, THF	58	181
33	**85**		$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-4-}CH_2Cl$ + fluorene, n-BuLi, THF, EtOH	62	179
34	$[T_8(c\text{-}C_5H_9)_7C_6H_4\text{-4-}CH_2PPh_3]Cl$		$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-4-}CH_2Cl + PPh_3$, toluene	96	353
35	$-c\text{-}C_5H_9$	$-C_6H_4\text{-4-}CH_2OC_6H_4\text{-4-}CHO$	$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-4-}CH_2Cl + HOC_6H_4\text{-4-}CHO$, K_2CO_3, NaI, toluene	97	185
36	$-c\text{-}C_5H_9$	$-C_6H_4\text{-4-}CH_2OC_6H_4\text{-4-}CH(C_6H_4\text{-4-}NH_2)_2$	$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-4-}CH_2OC_6H_4\text{-4-}CHO + C_6H_5NH_2$, $C_6H_5NH_2\cdot HCl$, HCl, NaOH	50	185
37	$-c\text{-}C_5H_9$	$-C_6H_4\text{-4-}CH_2OC_6H_3\text{-2,5-}Me_2$	$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-4-}CH_2Cl + HOC_6H_3\text{-2,5-}Me_2$, K_2CO_3, KI, DMF, THF	81	354
38	$-c\text{-}C_5H_9$	$-C_6H_4\text{-4-}CH_2OC_6H_3\text{-2,5-}(CH_2Br)_2$	$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-4-}CH_2OC_6H_3\text{-2,5-}Me_2$ + NBS, AIBN, CCl_4		354
39	$[T_8(c\text{-}C_5H_9)_7C_6H_4\text{-4-}CH_2PPh_3]Cl$		$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-4-}CH_2Cl + PPh_3$, toluene		187
40	$-c\text{-}C_5H_9$	$-OPPh_2$	$T_8(c\text{-}C_5H_9)_7OTl + ClPPh_2$, toluene	82	355
41	**86**		$T_8(c\text{-}C_5H_9)_7OTl$ + 2,4,8,10-tetra-*t*-butyl-6-chlorodibenzo[*d,f*][1,3,2]dioxaphosphepine, toluene	79	355
42	**87**		$T_8(c\text{-}C_5H_9)_7OSiMe_2(CH_2)_3NCO$ + 2-(4-methoxy-2,2,6,6-tetramethylpiperidin-1-yloxy)-2-phenylethanol, $Sn(n\text{-Bu})_2[OC({=}O)(CH_2)_{10}Me]_2$, toluene	62	356, 357
43	$-c\text{-}C_5H_9$	$-OSiMe_2(CH_2)_3NHCO_2(CH_2CH_2O)_{23}\text{-}(CH_2CH_2)_{38}Me$	$T_8(i\text{-Bu})_7OSiMe_2(CH_2)_3NCO + HO(CH_2CH_2O)_{23}(CH_2CH_2)_{38}Me$, $Sn(n\text{-Bu})_2[O({=}O)C(CH_2)_{10}Me]_2$, toluene	60	349
44	$-c\text{-}C_5H_9$	$-OSiMe_2(CH_2)_3OC_6H_2\text{-4-}OMe\text{-2,5-}(CH_2Cl)_2$	$T_8(c\text{-}C_5H_9)_7OSiMe_2(CH_2)_3OC_6H_4\text{-4-}OMe$ + HCl, H_2CO, H_2O, 1,4-dioxane	81	278
45	$-c\text{-}C_5H_9$	$-OSiMe_2C{\equiv}C\text{-2-}C_5H_4N$	$T_8(c\text{-}C_5H_9)_7OSiMe_2C{\equiv}CH + C_5H_4N\text{-2-}Br$, CuI, $PdCl_2(PPh_3)_2$, NEt_3	54	303
46	-Cy	$-C_6H_4\text{-4-}CH_2OC_6H_4\text{-4-}NO_2$	$T_8Cy_7C_6H_4\text{-4-}CH_2Cl + HOC_6H_4\text{-4-}NO_2$, Cs_2CO_3, NaI, DMF, THF	97	188
47	-Cy	$-C_6H_4\text{-4-}CH_2OC_6H_4\text{-4-}NH_2$	$T_8Cy_7C_6H_4\text{-4-}CH_2OC_6H_4\text{-4-}NO_2 + NH_4Cl$, Zn(s), THF, MeOH	63	188
48	-Cy	$-OP(NMe_2)_2$	$T_8Cy_7OH + P(NMe)_3$, CH_2Cl_2	99	358
49	-Ph	$-(CH_2)_3OH$	$T_8Ph_7(CH_2)_3Cl + Ag_2O$, H_2O, EtOH, THF	88	192, 193

[a] Contains a mixture of isomers.

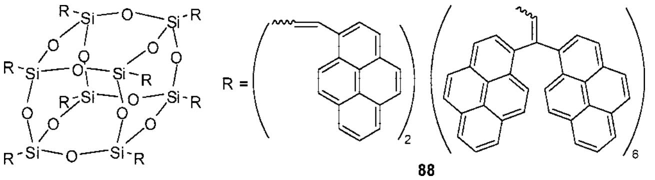
Table 13. $T_8R_{(8-n)}R'_n$ Derivatives Prepared by Organic Substitution Reactions of T_8 POSS Compounds

entry	substituents or compound number R	 R′	starting materials	yield (%)	refs
1	-(*i*-Oct)$_6$	-[$(CH_2)_3NHC(=O)NH(CH_2)_3Si(OEt)_3$]$_2$	T_8(*i*-Oct)$_6$[$(CH_2)_3NH_2$]$_2$ + $OCN(CH_2)_3Si(OEt)_3$, THF		149
2	-$(CH=CH_2)_2$	-[$CH=CHC_6H_4$-4-N(Ph)C_6H_4-4-C_6H_4-4-(Ph)C_6H_4-3-Me]$_6$	$T_8(CH=CH_2)_8$ + $BrCHC_6H_4$-4-N(Ph)C_6H_4-4-C_6H_4-4-(Ph)C_6H_4-3-Me, Pd[P(*t*-Bu)$_3$]$_2$, NCy_2Me, toluene, 1,4-dioxane	>85	359
3	**88**		$T_8(CH=CH_2)_8$ + 1-bromopyrene, Pd[P(*t*-Bu)$_3$]$_2$, NCy_2Me, toluene	>80	325

equivalents of catechin bound to the amine group of the POSS derivative as either an imide or secondary amine (Scheme 5). As might be expected for such a reaction, the substitution pattern on the POSS cube is unknown.

A series of quaternization reactions of the amino-POSS derivative $T_8[OSiMe_2(CH_2)_3NMe_2]_8$ have recently been carried out to prepare potentially antimicrobial POSS derivatives.[240,310]

Chart 13



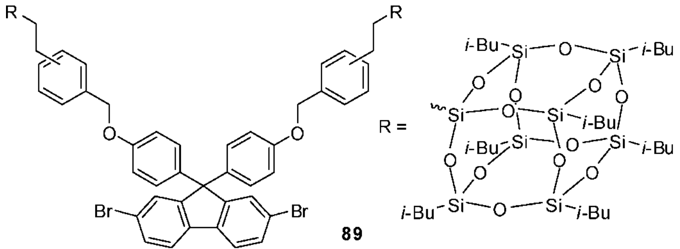
88

Table 14. Bridged $(T_8R_7)_2R'$ Derivatives Prepared by Organic Substitution Reactions of T_8 POSS Compounds

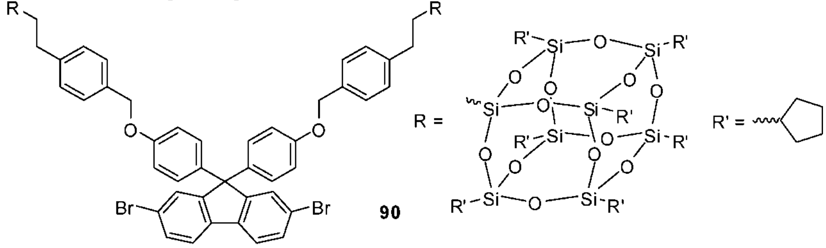
entry	substituents or compound number R	 R′	starting materials	yield (%)	refs
1	**89**		T_8(*i*-Bu)$_7(CH_2)_2C_6H_4CH_2Cl$ + 4,4′-(2,7-dibromo-9*H*-fluorene-9,9-diyl)diphenol, NaI, K_2CO_3, THF	7[a]	343
2	-*i*-Bu	1,2-$(CN)_2C_6H_2$-4,5-[$S(CH_2)_3$-]$_2$	T_8(*i*-Bu)$_7(CH_2)_3SH$ + 1,2-$(CN)_2$-C_6H_2-4,5-Cl_2, K_2CO_3, THF	94	360
3	**90**		T_8(*c*-C_5H_9)$_7(CH_2)_2C_6H_4$-4-CH_2Cl + 4,4′-(2,7-dibromo-9*H*-fluorene-9,9-diyl)diphenol, NaI, K_2CO_3, THF, DMF		361
4	**91**		T_8(*c*-C_5H_9)$_7(CH_2)_3I$ + (*R*)-6,6′-dibromo-1,1′-binaphthyl-2,2′-diol, K_2CO_3, acetone, THF	29	362
5	-*c*-C_5H_9	-$(CH_2)_3OC_6H_2$-2,5-Br_2-4-$O(CH_2)_3$-	T_8(*c*-C_5H_9)$_7(CH_2)_3I$ + HOC_6H_2-2,5-Br_2-4-OH, K_2CO_3, THF, acetone	15	352
6	**92**		T_8(*c*-C_5H_9)$_7C_6H_4$-4-CH_2Cl + 4,4′-(2,7-dibromo-9*H*-fluorene-9,9-diyl)dianiline, K_2CO_3, KI, DMF, THF	68	363

[a] Contains a mixture of isomers.

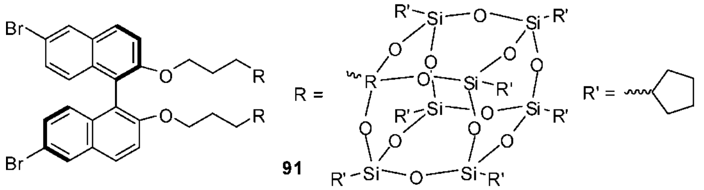
Chart 14



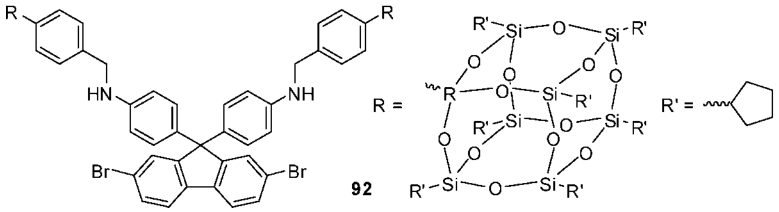
89



90

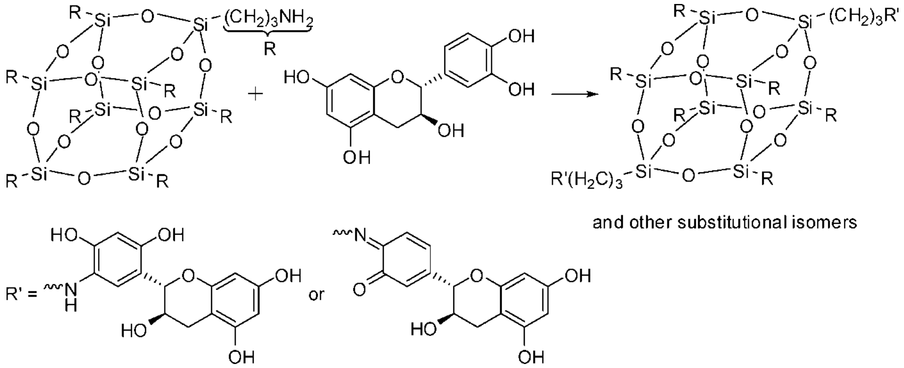


91



92

Scheme 5



These were carried out by treating the POSS derivative with a series of alkyl iodides, $Me(CH_2)_nI$ ($n = 0$, 3, 7, 11, 15, and 17), using different ratios of POSS to iodide to produce products with varying levels of quaternization. These quaternary ammonium salts were tested for antimicrobial activity both in solution and as components in polysiloxane coatings and were found to be effective against both *Staphylococcus aureus* and *Candida albicans* with longer alkyl chain lengths and relatively low levels of quaternization causing the biggest effect.

For the nondirected substitution of the aromatic rings of POSS such as T_8Ph_8, a large body of work has been compiled looking at the different reactions and whether it is possible to achieve a uniform substitution of the phenyl rings.[1] However, with a few exceptions, most of these attempts have not given rise to a single product. While the mononitration of T_8Ph_8 does not show a strong preference for 2-, 3-, or 4-substitution,[311] the dinitration, under the appropriate reaction conditions, can give rise to a majority of 2,4-dinitrated product (Table 11, entry 67). This then allows for the conversion of the nitro groups to amines, giving the octakis-2,4-diamine. For these nitration reactions, and especially for the reduction of the nitrates to amines, a number of minor synthetic variations have been investigated (Table 11, entries 58−60, 62, and 66−68). Further reaction of the $T_8(C_6H_4NH_2)_8$ isomeric mixture has not often been attempted, although there have been three recent modifications reported (Table 11, entries 61, 63, and 64). In addition, the octahydrochloride salt of the T_8 derivative has recently been prepared for use in DNA-detection experiments in which it is found that resonance light scattering signals are enhanced by the POSS−DNA interaction.[312]

Bromination of T_8Ph_8 has been undertaken using several methods to generate different brominated products (Table 11, entries 72 and 74). The monobrominated T_8 product is reported as comprising a mixture of predominantly 3- and 4-substituted phenyl rings.[313] Under almost identical conditions, a variety of brominated products have been reported, depending on the starting concentration of bromine.[314] The various isomers produced using differing starting conditions have been analyzed, and the $T_8Ph_8Br_{5.3}$ derivative was chosen as the best of those produced for further reaction. This is because it contains the smallest amount of multiply brominated aromatic rings and the highest proportion of 4-brominated product.[314] Because it does not substitute every phenyl ring of the parent T_8 compound, any further reactions will result in highly complicated mixtures of products. More highly brominated derivatives are also produced by this method, including up to an average of 15.7 bromines per T_8Ph_8.[314]

Sulfonation of T_8Ph_8 has also been reported to give a variety of products with varying substitutions, depending on reaction conditions. There have been reported preparations of two different products containing predominantly 3-sulfonated phenyl rings; one being the octa-sulfonated product (Table 11, entry 70) and the other being a partially sulfonated material, with an average of 40% of the phenyl rings having a sulfonic acid group.[315] Another report, however, with similar initial reaction conditions (Table 11, entry 71) but a workup leading to the sodium salt of the sulfonic acids is not reported to give any preference for one substitutional isomer over another.

While the bromination of T_8Ph_8 has not been successfully carried out to produce a single isomer, there has been a recent report of the specific iodination of T_8Ph_8, affording $T_8(C_6H_4\text{-}4\text{-}I)_8$ POSS in good yield (Table 11, entry 73). This has subsequently enabled the synthesis of a number of specifically substituted derivatives, by the use of a variety of substitution chemistries (Table 11, entries 40−49, 65, and 69). This synthesis of $T_8(C_6H_4\text{-}4\text{-}I)_8$ now opens up a wide range of possibilities for the synthesis of specifically functionalized nanoscale molecular building blocks.[316-318]

Similar chemistries to those used on the T_8R_8 systems can also been applied to the T_8R_7R' systems. This produces an equally wide variety of products with varying substitutions (Tables 12 and 14). Reaction of a starting T_8R_7R' with an appropriate bridging group has led to the synthesis of several bis-T_8 derivatives (Table 14). Of equal interest are the $T_8R_{(8-n)}R'_n$ compounds, which are presented in Table 13. While one of these has a comparatively conventional synthetic route starting from an existing $T_8R_{(8-n)}R'_n$ compound (Table 13, entry 1), the other two are more unusual. Both of these T_8 derivatives are synthesized by the incomplete Heck reaction of $T_8(CH{=}CH_2)_8$ with aromatic bromide derivatives. The reported yields of these compounds are good, although it is apparent that other Heck products were also produced by the reaction, if in lower yield.

2.7.2. Reactions Involving Acid Derivatives

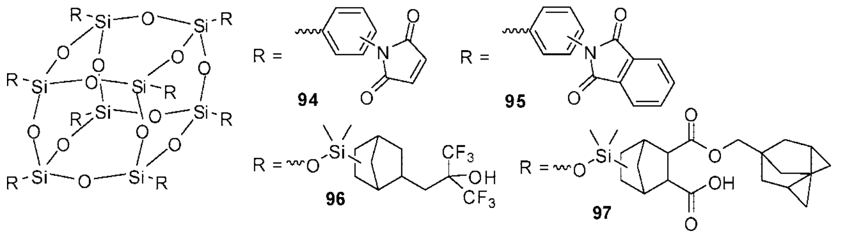
Reactions of POSS compounds involving carboxylic acid functionalities are straightforward, both for those involving T_8R_8 systems (Table 15 and Chart 15) and also for those involving T_8R_7R' (Table 16 and Charts 16 and 17), and fall into two categories, those involving addition of an acid derivative to a functionalized T_8 species and those involving the hydrolysis of a T_8 acid derivative. Those reactions involving addition of an acid derivative break down fairly evenly between those forming amides (Table 15, entries 1, 2, 4−8, 10, 12−14, and 16−21; Table

Table 15. T$_8$R$_8$ Derivatives Prepared by Reactions Involving Carboxylic Acid Derivatives

entry	R or compound number	starting materials	yield (%)	refs
1	-CH=CHC$_6$H$_4$-4-CH=CHC$_6$H$_4$-4-NHC(=O)C$_6$H$_3$-3,5-(NO$_2$)$_2$	T$_8$(CH=CHC$_6$H$_4$-4-CH=CHC$_6$H$_4$-4-NH$_2$)$_8$ + ClC(=O)C$_6$H$_3$-3,5-(NO$_2$)$_2$, NEt$_3$, THF	90	322
2	-CH=CHC$_6$H$_4$-4-CH=CHC$_6$H$_4$-4-NHC(=O)C$_6$H$_3$-3,5-Br$_2$	T$_8$(CH=CHC$_6$H$_4$-4-CH=CHC$_6$H$_4$-4-NH$_2$)$_8$ + ClC(=O)C$_6$H$_3$-3,5-Br$_2$, NEt$_3$, THF	92	322
3	-CH=CHC$_6$H$_4$-4-C$_6$H$_3$-3,5-(CH$_2$OH)$_2$	T$_8$[CH=CHC$_6$H$_4$-4-C$_6$H$_3$-3,5-(CHO)$_2$]$_8$ + NaBH$_4$, THF, MeOH	71	364
4	-(CH$_2$)$_3$NH(L-Lys) TFA salt	T$_8$[(CH$_2$)$_3$NH$_3$]$_8$Cl$_8$ + BLDCH, HBTU, HOBT, N(*i*-Pr)$_2$Et, citric acid, CF$_3$CO$_2$H, H$_2$O, DMF	47	365
5	-(CH$_2$)$_3$NH(L-Lys)(L-Lys)$_2$ TFA salt	T$_8$[(CH$_2$)$_3$NH(L-Lys)]$_8$ TFA salt + BLDCH, HBTU, HOBT, N(*i*-Pr)$_2$Et, citric acid, CF$_3$CO$_2$H, H$_2$O, DMF	80	365
6	-(CH$_2$)$_3$NH(L-Lys)(L-Lys)$_2$(L-Lys)$_4$ TFA salt	T$_8$[(CH$_2$)$_3$NH(L-Lys)(L-Lys)$_2$]$_8$ TFA salt + BLDCH, HBTU, HOBT, N(*i*-Pr)$_2$Et, citric acid, CF$_3$CO$_2$H, H$_2$O, DMF	61	365
7	-(CH$_2$)$_3$NH(L-Lys)(L-Lys)$_2$(L-Lys)$_4$(L-Lys)$_8$ TFA salt	T$_8$[(CH$_2$)$_3$NH(L-Lys)(L-Lys)$_2$(L-Lys)$_4$]$_8$ TFA salt + BLDCH, HBTU, HOBT, N(*i*-Pr)$_2$Et, citric acid, CF$_3$CO$_2$H, H$_2$O, DMF	70	365
8	-(CH$_2$)$_3$NHC(=O)(CH$_2$)$_2$CO$_2$H	T$_8$[(CH$_2$)$_3$NH$_2$]$_8$ + succinic anhydride, NEt$_3$, MeOH	79	108
9	-(CH$_2$)$_3$N[(CH$_2$)$_2$CO$_2$H]$_2$	T$_8${(CH$_2$)$_3$N[(CH$_2$)$_2$CO$_2$-*t*-Bu]$_2$}$_8$ + HCO$_2$H,	99	104
10	-(CH$_2$)$_3$N[(CH$_2$)$_2$C(=O)NH(CH$_2$)$_2$NH$_2$]$_2$	T$_8${(CH$_2$)$_3$N[(CH$_2$)$_2$CO$_2$Me]$_2$}$_8$ + H$_2$N(CH$_2$)$_2$NH$_2$	92	105
11	-(CH$_2$)$_3$N{CH$_2$CH[OC(=O)NHC$_6$H$_4$-4-Me]CH$_2$OPh}(CH$_2$)$_2$N{CH$_2$CH[OC(=O)NHC$_6$H$_4$-4-Me]CH$_2$OPh}$_2$	T$_8${(CH$_2$)$_3$N[CH$_2$CH(OH)CH$_2$OPh](CH$_2$)$_2$N[CH$_2$CH(OH)CH$_2$OPh]$_2$}$_8$ + MeC$_6$H$_4$-4-NCO		113, 366
12	-(CH$_2$)$_3$NAc$_2$	T$_8$[(CH$_2$)$_3$NH$_3$]$_8$Cl$_8$ + Ac$_2$O	59	110
13	-C$_6$H$_4$NHC(=O)CMe$_2$Br	T$_8$(C$_6$H$_4$NH$_2$)$_8$ + BrC(=O)CMe$_2$Br, NEt$_3$, THF	[a]	367, 368
14	-C$_6$H$_4$NHC(=O)C$_6$H$_4$-4-CF=CF$_2$	T$_8$(C$_6$H$_4$NH$_2$)$_8$ + ClC(=O)C$_6$H$_4$-4-CF=CF$_2$, NEt$_3$, THF	73[a]	369
15	-C$_6$H$_4$N[CH$_2$CO$_2$H]$_2$	T$_8${C$_6$H$_4$N[CH$_2$CO$_2$Me]$_2$}$_8$ + HCl, EtOH, H$_2$O		338
16	**94**	T$_8$(C$_6$H$_4$NH$_2$)$_8$ + maleic anhydride, NEt$_3$, Ac$_2$O, AcNMe$_2$, EtOAc	86[a]	133, 134
17	**94**	T$_8$(C$_6$H$_4$NH$_2$)$_8$ + maleic anhydride, MeC$_6$H$_4$-4-SO$_3$H, DMF, toluene		370
18	**94**	T$_8$(C$_6$H$_4$NH$_2$)$_8$ + maleic anhydride, NaOAc, Ac$_2$O, DMF, EtOAc	75	371
19	**94**	T$_8$(C$_6$H$_4$NH$_2$)$_8$ + maleic anhydride, Ac$_2$O, NEt$_3$, DMF, EtOAc, THF	76	372
20	**95**	T$_8$(C$_6$H$_4$NH$_2$)$_8$ + phthalic anhydride, *N*-methylpyrrolidone	80[a]	373
21	**95**	T$_8$(C$_6$H$_4$NH$_2$)$_8$ + phthalic anhydride, PhNH$_2$, *N*-methylpyrrolidone	*a*	374
22	-OSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OH	T$_8$[OSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OAc]$_8$ + NH$_4$OH, HCl, MeOH		229
23	-OSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OH	T$_8$[OSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OAc]$_8$ + NaOH, HCl, H$_2$O, THF, ether		375
24	-OSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OH	T$_8$[OSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OAc]$_8$ + N$_2$H$_4$·H$_2$O, 1,4-dioxane	87[a]	226
25	**96**	**31** + NH$_4$OH, HCl, MeOH	*a*	229
26	**97**	**32** + 1-adamantylmethanol, DMAP, THF	*a*	270
27	-OSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OH	T$_8$[SiOMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OAc]$_8$, HCl, acetone		270
28	-OSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OH	T$_8$[OSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OAc]$_8$ + NaOH, HCl, H$_2$O, THF, ether	82	231, 232
29	-OSiMe$_2$(CH$_2$)$_3$OC(=O)CMe$_2$Br	T$_8$[OSiMe$_2$(CH$_2$)$_3$OH]$_8$ + BrC(=O)CMe$_2$Br, NEt$_3$, THF	*a*	367
30	-OSiMe$_2$(CH$_2$)$_3$O(CH$_2$CH$_2$O)$_2$OC(=O)C(=CH$_2$)Me	T$_8$[OSiMe$_2$(CH$_2$)$_3$O(CH$_2$CH$_2$O)$_2$H]$_8$ + CH$_2$=CMeCOCl, NEt$_3$, CH$_2$Cl$_2$		376
31	-OSiMe$_2$(CH$_2$)$_3$O(CH$_2$CH$_2$O)$_3$OC(=O)C(=CH$_2$)Me	T$_8$[OSiMe$_2$(CH$_2$)$_3$O(CH$_2$CH$_2$O)$_3$H]$_8$ + CH$_2$=CMeCOCl, NEt$_3$, CH$_2$Cl$_2$		376
32	-OSiMe$_2$(CH$_2$)$_3$O(CH$_2$CH$_2$O)$_4$OC(=O)C(=CH$_2$)Me	T$_8$[OSiMe$_2$(CH$_2$)$_3$O(CH$_2$CH$_2$O)$_4$H]$_8$ + CH$_2$=CMeCOCl, NEt$_3$, CH$_2$Cl$_2$		376
33	-OSiMe$_2$(CH$_2$)$_3$O(CH$_2$CH$_2$O)$_6$OC(=O)C(=CH$_2$)Me	T$_8$[OSiMe$_2$(CH$_2$)$_3$O(CH$_2$CH$_2$O)$_6$H]$_8$ + CH$_2$=CMeCOCl, NEt$_3$, CH$_2$Cl$_2$		376

[a] Product contains a mixture of isomers.

Chart 15



16, entries 4−7, 17, 18, 21, and 22) and those forming esters (Table 15, entries 26 and 29−33; Table 16, entries 3, 8−13, 15, 16, 20, 24, and 26); however the hydrolysis reactions have only been investigated for esters (Table 15, entries 9, 15, 22−25, 28, and 29; Table 16, entries 1, 2, 14, 19, 23, and 25), where they have usually been used as a protecting group for an alcohol. Perhaps somewhat surprisingly, all the reactions involving formation of an ester or amide except two (Table 15, entries 10 and 26) took place between an amine- or alcohol-functionalized POSS compound and an added acid derivative. This is likely due to the potential difficulty in introducing unprotected acid functionalities into POSS species.

The majority of the substitution reactions have been carried out in the presence of an amine base such as DMAP or triethylamine, even when reactive acid derivatives such as acid halides or anhydrides were being used. However, in a limited number of cases the reactions were seen to proceed in good yield without requiring a base. These reactions were between T$_8$(*i*-Bu)$_7$R derivatives and acryloyl chloride (Table 16, entries 12 and 13) and between T$_8$R$_8$ amine derivatives and maleic or phthalic

Table 16. T_8R_7R' Derivatives Prepared by Reactions Involving Carboxylic Acid Derivatives

entry	substituents or compound number: R	substituents or compound number: R′	starting materials	yield (%)	refs
1	-*i*-Bu	$-(CH_2)_2OH$	$T_8(i\text{-Bu})_7(CH_2)_2OAc$ + NaOH, dioxane	71	161
2	-*i*-Bu	$-(CH_2)_2OH$	$T_8(i\text{-Bu})_7(CH_2)_2OAc + H_2SO_4$, MeOH, $CHCl_3$	80	162
3	-*i*-Bu	$-(CH_2)_2OC(=O)C_6H_4\text{-}4\text{-}OCF=CF_2$	$T_8(i\text{-Bu})_7(CH_2)_2OH + CF_2=CFOC_6H_4\text{-}4\text{-}CO_2H$, DCC, DPTS, CH_2Cl_2	73	162
4	-*i*-Bu	$-(CH_2)_3NH(CH_2)_2NHC(=O)C_6H_4\text{-}4\text{-}C\equiv CH$	$T_8(i\text{-Bu})_7(CH_2)_3NH(CH_2)_2NH_2 + HC\equiv CC_6H_4\text{-}4\text{-}COCl$, NEt_3, $CHCl_3$	55	347
5	-*i*-Bu	$-(CH_2)_3NHC(=O)(CH_2)_2SC(=S)SCH_2Ph$	$T_8(i\text{-Bu})_7(CH_2)_3NH_2 + ClC(=O)(CH_2)_2SC(=S)SCH_2Ph$, pyridine, THF	85	377–379
6	-*i*-Bu	$-(CH_2)_3NHC(=O)C_6H_3\text{-}3,5\text{-}(OCH_2Ph)_2$	$T_8(i\text{-Bu})_7(CH_2)_3NH_2 + HOC(=O)C_6H_3\text{-}3,5\text{-}(OCH_2Ph)_2$, oxalyl chloride, DMF, NEt_3 CH_2Cl_2	99	344
7	**98**		$T_8(i\text{-Bu})_7(CH_2)_3NH_2$ + **99**, $CHCl_3$	42	346
8	**100**		$T_8(i\text{-Bu})_7(CH_2)_3OCH_2CH(CH_2OH)OH$ + 4-(pyren-1-yl)butanoic acid, DMAP, DCC, CH_2Cl_2		380
9	-*i*-Bu	$-(CH_2)_3OC(=O)C(CH_2)_{10}Br$	$T_8(i\text{-Bu})_7(CH_2)_3OH + Br(CH_2)_{10}CO_2H$, DMAP, DCC, CH_2Cl_2	67	381
10	-*i*-Bu	$-(CH_2)_3OC(=O)(CH_2)_{10}Br$	$T_8(i\text{-Bu})_7(CH_2)_3OH + Br(CH_2)_{10}COCl$, pyridine, THF	70	348
11	**101**		$T_8(i\text{-Bu})_7(CH_2)_3OH$ + 11-(3,6,7,10,11-pentakis(pentyloxy)triphenylen-2-yloxy)undecanoic acid, DMAP, DCC, CH_2Cl_2	42	381, 382
12	-*i*-Bu	$-OSiMe_2(CH_2)_3OC(=O)C(=CH_2)Me$	$T_8(i\text{-Bu})_7OSiMe_2(CH_2)_3OH + ClC(=O)C(=CH_2)Me$, THF or toluene	75	274
13	-*i*-Bu	$-OSiMe_2(CH_2)_5OC(=O)C(=CH_2)Me$	$T_8(i\text{-Bu})_7OSiMe_2(CH_2)_5-OH + ClC(=O)C(=CH_2)Me$, THF or toluene	75	274
14	$-(CH_2)_2CF_3$	$-(CH_2)_2OH$	$T_8[(CH_2)_2CF_3]_7(CH_2)_2OAc + H_2SO_4$, MeOH, $CF_3CF_2CHCl_2$, Cl_2FCCF_2CHFCl	90	157, 174
15	$-(CH_2)_2CF_3$	$-(CH_2)_2OC(=O)CMe_2Br$	$T_8[(CH_2)_2CF_3]_7(CH_2)_2OH + BrMe_2CCOBr$, NEt_3, CH_2Cl_2	70	157, 174
16	$-(CH_2)_2CF_3$	$-(CH_2)_2OC(=O)C_6H_4\text{-}4\text{-}OCF=CF_2$	$T_8[(CH_2)_2CF_3]_7(CH_2)_2OH + CF_2=CFOC_6H_4\text{-}4\text{-}CO_2H$, DCC, DPTS, CH_2Cl_2	40	162
17	$-(CH_2)_3NHC(=O)CF_3$	$-(CH_2)_3NH_2$	$\{T_8[(CH_2)_3NH_3]_8Cl_8\} + CF_3CO_2Et$, NEt_3, MeOH		106
18	**102**		$T_8[(CH_2)_3NHC(=O)CF_3]_7(CH_2)_3NH_2$ + (*E*)-2-cyano-3-(1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinolin-9-yl)acrylic acid, 4-(4,6-dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride, MeOH	23	106
19	-*c*-C_5H_9	$-(CH_2)_2OH$	$T_8(c\text{-}C_5H_9)_7(CH_2)_2OAc + H_2SO_4$, MeOH, $CHCl_3$	97	162
20	-*c*-C_5H_9	$-(CH_2)_2OC(=O)C_6H_4\text{-}4\text{-}OCF=CF_2$	$T_8(c\text{-}C_5H_9)_7(CH_2)_2OH + CF_2=CFOC_6H_4\text{-}4\text{-}CO_2H$, DCC, DPTS, CH_2Cl_2	83	162
21	**103**		$T_8(c\text{-}C_5H_9)_7(CH_2)_3NH_2$ + 3,4-dimethylcyclohex-3-enecarboxylic acid, 3,4-dimethylcyclohex-3-enecarbonyl chloride, NEt_3, CH_2Cl_2	68	182
22	**104**		$T_8Cy_7C_6H_4\text{-}4\text{-}CH_2OC_6H_4\text{-}4\text{-}NH_2$ + phthalic anhydride, $AcNMe_2$, THF		188
23	-Ph	$-(CH_2)_2OH$	$T_8Ph_7(CH_2)_2OAc + H_2SO_4$, MeOH, $CHCl_3$	91	157, 191
24	-Ph	$-(CH_2)_2OC(=O)CMe_2Br$	$T_8Ph_7(CH_2)_2OH + BrCMe_2COBr$, NEt_3, CH_2Cl_2	81	157, 191
25	-Ph	$-(CH_2)_3OH$	$T_8Ph_7(CH_2)_3OAc + H_2SO_4$, MeOH, $CHCl_3$	53	157
26	-Ph	$-(CH_2)_3OC(=O)CMe_2Br$	$T_8Ph_7(CH_2)_3OH + BrCMe_2COBr$, NEt_3, CH_2Cl_2	48	157

Chart 16

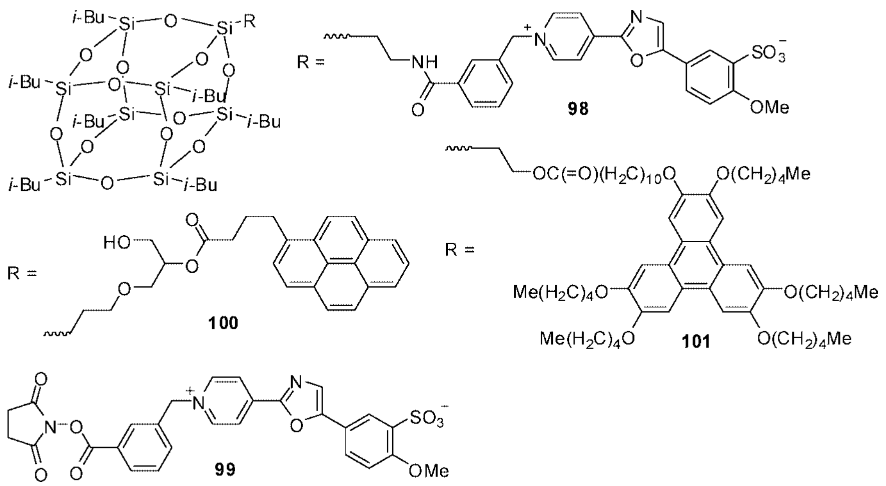
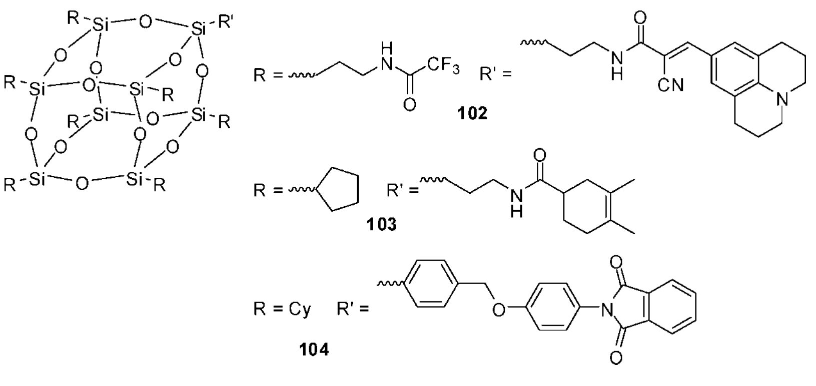


Chart 17



anhydride (Table 15, entries 17 and 20). One other reaction between a methyl ester T_8 derivative and ethylenediamine was also seen to proceed in good yield without the addition of any other base (Table 15, entry 10). In this case, the ethylene diamine reagent allowed for the hydrolysis of the ester and formation of the amide.

Most of the hydrolysis reactions were seen to be acid catalyzed, with a few exceptions using sodium hydroxide (Table 15, entries 23 and 28; Table 16, entry 1), ammonium hydroxide (Table 15, entries 22 and 25), or hydrazine hydrate (Table 15, entry 24). Despite the use of the base, these reactions did not result in the hydrolysis of the T_8 cage, presumably because of the steric hindrance imposed by the tether between the reacting center and the T_8 core. Most of the hydrolyses observed for T_8 compounds may be viewed as the removal of an acetate protecting group from an alcohol. Two reactions, however, showed the formation of carboxylic acid functional groups by hydrolysis of the parent methyl esters. In all cases, the protected derivatives would have been used to allow for a cleaner synthetic route to the parent compound.

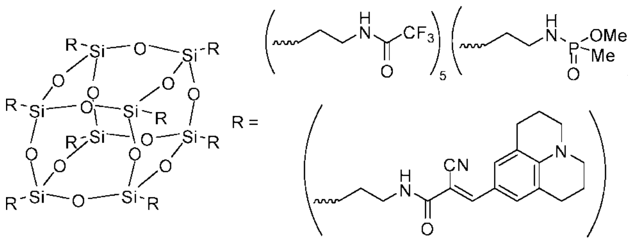
A group of compounds with biological applications have recently been prepared using reactions of carboxylic acid derivatives. These comprise a dendrimeric series of compounds prepared by the addition of suitable protected lysine residues to $T_8[(CH_2)_3NH_2]_8$ (Table 15, entries 4−7).[365] Subsequent reaction of these with 1,2,7,10-tetraazacyclododecane derivatives produced POSS compounds with an outer surface of the tetraaza macrocycles, suitable for coordination to metals. Unfortunately, no apparent attempt was made to determine with which of the potential terminal amine sites in the dendrimeric parent POSS compounds the macrocycle had reacted. These multimacrocyclic POSS species were further treated with Gd(III), to produce gadolinium-containing POSS compounds potentially suitable for use as MRI contrast agents.[383]

Several POSS compounds with an unusually diverse range of substituents have recently been prepared from $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$.[106] These include the highly unusual T_8R_7R' derivative $T_8[(CH_2)_3NHC({=}O)CF_3]_7(CH_2)_3NH_2$, prepared by reaction of $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ with ethyl trifluoroacetate (Table 16, entry 17). This has subsequently been reacted with (*E*)-2-cyano-3-(1,2,3,5,6,7-hexahydropyrido-[3,2,1-*ij*]quinolin-9-yl)acrylic acid (Table 16, entry 18) to give a difunctional T_8R_7R' compound. A more complicated product has also been prepared by the reaction of $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ with a mixture of ethyl trifluoroacetate, (*E*)-2-cyano-3-(1,2,3,5,6,7-hexahydropyrido[3,2,1-*ij*]quinolin-9-yl)acrylic acid, and methylphosphinic dichloride to give **93** in 30% yield (Chart 18).[106] This product has been used as a multimodal chemosensor for the detection of solvent polarity. In a related system, reaction of $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ with further ethyl trifluoroacetate gave rise to a mixture of $T_8[(CH_2)_3NHC({=}O)CF_3]_n[(CH_2)_3NH_2]_{(8-n)}$ products ($n = 3$, 4, or 5).[107] These were subsequently attached to silica nanoparticles and used as a ^{19}F NMR probe for monitoring enzyme activity.

2.7.3. Metathesis Reactions of POSS−Alkenes

Early work on the synthesis of unsaturated derivatives of T_8 POSS compounds was conducted by Feher et al. looking at the cross-metathesis of $T_8(CH{=}CH_2)_8$ with a variety of simple and substituted alkenes and using either the first generation Grubbs' catalyst, $[RuCl_2({=}CHPh)(PCy_3)_2]$, or

Chart 18



93

Shrock's catalyst, $\{Mo[{=}NC_6H_3\text{-}2,6\text{-}(i\text{-}Pr)_2]({=}CHCMe_2Ph)[OCMe(CF_3)_2]_2\}$.[384] This early work has been followed by the work of Itami et al., who have investigated the formation of unsaturated T_8 species by either cross-metathesis using the first or second generation Grubbs' catalysts or silylative coupling using $[RuHCl(CO)(PCy_3)_2]$. Details of their syntheses and those of other groups preparing unsaturated derivatives of T_8 POSS compounds are presented in Table 17 and Chart 19. They found that the reactions proceeded in similar yields with either catalyst for 1-hexene (Table 17, entries 2 and 3), allyltrimethylsilane (Table 17, entries 4 and 5), and styrene (Table 17, entries 6 and 7), although the silylative couplings for 1-hexene and allyltrimethylsilane give a complicated mixture of isomers, rather than the majority *trans* product formed in the other reactions. However, in the reactions of vinyltrimethylsilane (Table 17, entry 1), 1-vinyl-2-pyrrolidinone (Table 17, entry 19), butylvinyl ether (Table 17, entry 20), *tert*-butyl vinyl ether (Table 17, entry 21), and trimethylsilyl vinyl ether (Table 17, entry 22), only the silylative coupling catalyst led to a reaction, although in these reactions, both vinyltrimethylsilane and 1-vinyl-2-pyrrolidinone gave mostly *trans* products. For the reaction of *tert*-butyl vinyl sulfide (Table 17, entry 23), neither the first generation Grubbs' catalyst nor the silylative coupling catalyst produced a reaction; however, the reaction was successfully carried out using the second generation Grubbs cross-metathesis catalyst.

The area has also been investigated by other groups, looking at using $T_8(CH{=}CH_2)_8$ as either a dendrimeric core by coupling it with a variety of styrenyl derivatives (Table 17, entries 7−11 and 15−18) or a photoluminescent system by decorating it with vinylbiphenyl derivatives (Table 17, entries 12−14). The reactions were carried out using the first generation Grubbs catalyst, except in one case where it was not specified (Table 17, entry 11), and all products were described as being successfully prepared. However, no report was made of the formation of *cis* or *trans* isomers, of the products, nor of the effectiveness of the catalyst used.

2.7.4. Addition Reactions

Besides metathesis and silylative coupling, addition to a carbon−carbon double bond may also be used to prepare POSS derivatives. Examples of this reaction are presented in Table 18 and Chart 20 and Table 19 for T_8R_8, and $T_8R_{(8-n)}R'_n$ species, respectively. Most of these reactions take

Chart 19

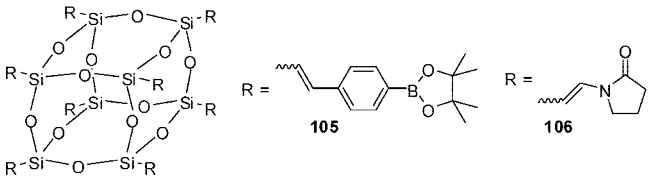


Table 17. T_8R_8 Derivatives Prepared by Cross-Metathesis or Silylative Coupling

entry	R or compound number	starting materials	yield (%)	refs
1	$-CH{=}CHSiMe_3$	$T_8(CH{=}CH_2)_8 + H_2C{=}CHSiMe_3$, $[RuHCl(CO)(PCy_3)_2]$, toluene	95	385
2	$-CH{=}CH(CH_2)_3Me$	$T_8(CH{=}CH_2)_8 + CH_2{=}CH(CH_2)_3Me$, $[RuHCl(CO)(PCy_3)_2]$, toluene	74	385
3	$-CH{=}CH(CH_2)_3Me$	$T_8(CH{=}CH_2)_8 + CH_2{=}CH(CH_2)_3Me$, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	72	385
4	$-CH{=}CHCH_2SiMe_3$	$T_8(CH{=}CH_2)_8 + CH_2{=}CHCH_2SiMe_3$, $[RuHCl(CO)(PCy_3)_2]$, toluene	69	385
5	$-CH{=}CHCH_2SiMe_3$	$T_8(CH{=}CH_2)_8 + CH_2{=}CHCH_2SiMe_3$ $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	89	385
6	$-CH{=}CHPh$	$T_8(CH{=}CH_2)_8 + CH_2{=}CHPh$, $[RuHCl(CO)(PCy_3)_2]$, toluene	92	385
7	$-CH{=}CHPh$	$T_8(CH{=}CH_2)_8 + CH_2{=}CHPh$, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	96	321, 322, 385
8	**105**	$T_8(CH{=}CH_2)_8$ + 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	51	214
9	$-CH{=}CHC_6H_4$-4-Me	$T_8(CH{=}CH_2)_8 + CH_2{=}CHC_6H_4$-4-Me, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	75	321, 322
10	$-CH{=}CHC_6H_4$-4-CH_2Cl	$T_8(CH{=}CH_2)_8 + CH_2{=}CHC_6H_4$-4-$CH_2Cl$, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	65	214
11	$-CH{=}CHC_6H_4$-4-Ph	$T_8(CH{=}CH_2)_8 + CH_2{=}CHC_6H_4$-4-Ph, Grubbs' catalyst		386
12	$-CH{=}CHC_6H_4$-4-C_6H_3-3,5-$(CHO)_2$	$T_8(CH{=}CH_2)_8 + CH_2{=}CHC_6H_4$-4-$C_6H_3$-3,5-$(CHO)_2$, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	78	364
13	$-CH{=}CHC_6H_4$-4-C_6H_3-3,5-$(CO_2Me)_2$	$T_8(CH{=}CH_2)_8 + CH_2{=}CHC_6H_4$-4-$C_6H_3$-3,5-$(CO_2Me)_2$, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	62	387
14	$-CH{=}CHC_6H_4$-4-C_6H_3-3,4-$(OMe)_2$	$T_8(CH{=}CH_2)_8 + CH_2{=}CHC_6H_4$-4-$C_6H_3$-3,4-$(OMe)_2$, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	69	387
15	$-CH{=}CHC_6H_4$-3-NO_2	$T_8(CH{=}CH_2)_8 + CH_2{=}CHC_6H_4$-3-$NO_2$, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	81	321, 322
16	$-CH{=}CHC_6H_4$-4-OMe	$T_8(CH{=}CH_2)_8 + CH_2{=}CHC_6H_4$-4-OMe, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	84	321, 322
17	$-CH{=}CHC_6H_4$-4-Cl	$T_8(CH{=}CH_2)_8 + CH_2{=}CHC_6H_4$-4-Cl, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	76	321, 322
18	$-CH{=}CHC_6H_4$-4-Br	$T_8(CH{=}CH_2)_8 + CH_2{=}CHC_6H_4$-4-Br, $[RuCl_2({=}CHPh)(PCy_3)_2]$, CH_2Cl_2	90	214, 321, 322
19	**106**	$T_8(CH{=}CH_2)_8$ +1-vinyl-2-pyrrolidinone, $[RuHCl(CO)(PCy_3)_2]$, toluene	69	385
20	$-CH{=}CHOBu$	$T_8(CH{=}CH_2)_8 + H_2C{=}CHOBu$, $[RuHCl(CO)(PCy_3)_2]$, toluene	86	385
21	$-CH{=}CHO$-*t*-Bu	$T_8(CH{=}CH_2)_8 + H_2C{=}CHO$-*t*-Bu, $[RuHCl(CO)(PCy_3)_2]$, toluene	91	385
22	$-CH{=}CHOSiMe_3$	$T_8(CH{=}CH_2)_8 + H_2C{=}CHOSiMe_3$, $[RuHCl(CO)(PCy_3)_2]$, toluene	81	385
23	$-CH{=}CHS$-*t*-Bu	$T_8(CH{=}CH_2)_8 + H_2C{=}CHS$-*t*-Bu, $[(H_2IMes)RuCl_2({=}CHPh)(PCy_3)]$, CH_2Cl_2[a]	91	385

[a] H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene.

Table 18. T_8R_8 Derivatives Prepared by Addition Reactions to POSS−Alkene Derivatives

entry	R or compound number	starting materials	yield (%)	refs
1	-Et	$T_8(CH{=}CH_2)_8 + H_2$, Pd/C, toluene	89	390
2	$-CHDCH_{1.14}D_{1.86}$	$T_8(CH{=}CH_2)_8 + D_2$, Pd/C, toluene		390
3	$-(CH_2)_2CHO$	$T_8(CH{=}CH_2)_8 + CO/H_2$, $PtCl_2$(sixantphos), $SnCl_2$		92
4	$-(CH_2)_2CO_2Me$	$T_8(CH{=}CH_2)_8$ + CO + MeOH, $MeSO_2OH$, Pd_2dba_3, C_6H_4-1,2-$[CH_2P$-(*t*-$Bu_2)]_2$, toluene	43	391
5	$-(CH_2)_2Ph$	$T_8(CH{=}CH_2)_8 + C_6H_6 + AlCl_3$	73	392
6	$-(CH_2)_2P({=}O)(OEt)_2$	$T_8(CH{=}CH_2)_8 + (EtO)_2P({=}O)H$, AIBN, cyclohexane		320
7	$-(CH_2)_2S(CH_2)_2(CF_2)_5CF_3$	$T_8(CH{=}CH_2)_8 + HS(CH_2)_2(CF_2)_5CF_3$, AIBN	90	393
8	$-(CH_2)_2S(CH_2)_2(CF_2)_7CF_3$	$T_8(CH{=}CH_2)_8 + HS(CH_2)_2(CF_2)_7CF_3$, AIBN	91	393
9	$-(CH_2)_2SCy$	$T_8(CH{=}CH_2)_8$ + HSCy, AIBN		394
10	$-(CH_2)_2SPh$	$T_8(CH{=}CH_2)_8$ + PhSH, AIBN		394
11	$-(CH_2)_2S$-2-C_5H_5N	$T_8(CH{=}CH_2)_8$ + HS-2-C_5H_5N, AIBN		394
12	**107**	$T_8(CH{=}CH_2)_8$ + **108**, AIBN, H_2O, THF	70	395
13	**109**	$T_8(CH{=}CH_2)_8$ + **110**, AIBN, H_2O, THF	66	395
14	**111**	$T_8(CH{=}CH_2)_8$ + **112**, AIBN, H_2O, THF	73	395
15	$-(CH_2)_2Br$	$T_8(CH{=}CH_2)_8$ + HBr(g), $(BzO)_2$, toluene	65	320, 391
16	$-CH_2CH(O)CH_2$	$T_8(CH_2CH{=}CH_2)_8$ + MCPBA, $CHCl_3$	75	90
17	$-(CH_2)_3N[(CH_2)_2CO_2Me]_2$	$T_8[(CH_2)_2NH_2]_8 + CH_2{=}CHCO_2Me$	63	105
18	$-(CH_2)_3N[(CH_2)_2CO_2$-*t*-$Bu]_2$	$T_8[(CH_2)_2NH_2]_8 + CH_2{=}CHCO_2$-*t*-Bu	61	104
19	$-(CH_2)_3OC({=}O)(CH_2)_2N[(CH_2)_3NMe_2]$ $(CH_2)_2CO_2(CH_2)_2NMe_2$	$T_8[(CH_2)_3OC({=}O)CH{=}CH_2]_8 + H_2N(CH_2)_3NMe_2$, $CH_2{=}CHCO_2(CH_2)_2NMe_2$, THF	85[a]	396
20	$-(CH_2)_3OC({=}O)CMeBrCH_2Br$	$T_8[(CH_2)_3OC({=}O)CH{=}CH_2]_8 + Br_2$, $CHCl_3$	[a]	397
21	$-(CH_2)_3OC({=}O)CHMe_2$	$T_8[(CH_2)_3OC({=}O)C({=}CH_2)Me]_8 + H_2$, Pd/C, toluene	[a]	398
22	−2,2-Cl_2-*c*-C_3H_3	$T_8(CH{=}CH_2)_8 + HCCl_3$, NaOH, H_2O, Bu_4NBr	44	392
23	$-OSiMe_2(CH_2)_2S(CH_2)_2(CF_2)_5CF_3$	$T_8(OSiMe_2CH{=}CH_2)_8 + HS(CH_2)_2(CF_2)_5CF_3$, AIBN	89	393
24	$-OSiMe_2(CH_2)_2S(CH_2)_2(CF_2)_7CF_3$	$T_8(OSiMe_2CH{=}CH_2)_8 + HS(CH_2)_2(CF_2)_7CF_3$, AIBN	88	393
25	**113**	$T_8[SiOMe_2(CH_2)_2C_6H_4$-4-$OH]_8$ + 1-methoxycyclohex-1-ene, $(CO_2H)_2$, PGMEA		270
26	**114**	**97** + $CH_2{=}CHOEt$, CF_3CO_2H, PGMEA		270

[a] Both reactants and products consist of a mixture of T_8, T_{10}, T_{12}, and T_{14} POSS derivatives.

Chart 20

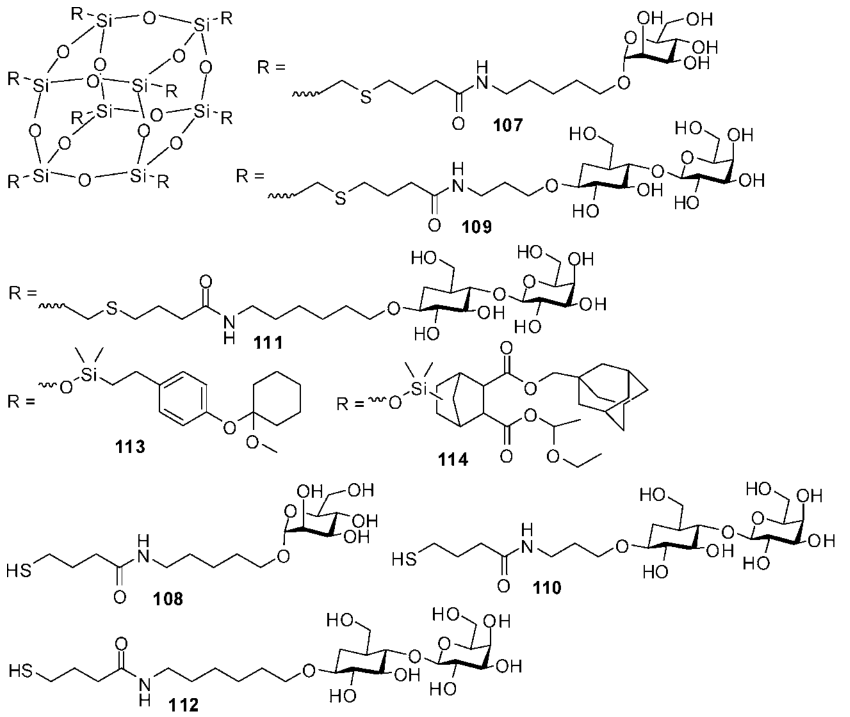


Table 19. $T_8R_{(8-n)}R'_n$ Derivatives Prepared by Addition Reactions to POSS Involving Alkene Derivatives

	functional groups				
entry	R_7	R'	starting materials	yield (%)	refs
1	-Pr	$-CH_2CH_2SPh$	$T_8(Pr)_7CH{=}CH_2 + PhSH$, AIBN		394
2	-Pr	$-CH_2CH_2SCy$	$T_8(Pr)_7CH{=}CH_2 + HSCy$, AIBN		394
3	-Pr	$-CH_2CH_2S\text{-}2\text{-}C_5H_5N$	$T_8(Pr)_7CH{=}CH_2 + HS\text{-}2\text{-}C_5H_5N$, AIBN		394
4	$-i$-Bu	$-(CH_2)_2CHO$	$T_8(i\text{-}Bu)_7CH{=}CH_2 + CO/H_2$, $PtCl_2$(sixantphos), $SnCl_2$		92
5	$-i$-Bu	$-(CH_2)_3NH(CH_2)_2N[(CH_2)_2CO_2CH_2CH(OH)CH_2\text{-}OC({=}O)C({=}CH_2)Me]_2$	$T_8(i\text{-}Bu)_7(CH_2)_3NH(CH_2)_2NH_2 + CH_2{=}CHCO_2CH_2CH(OH)CH_2OC({=}O)C({=}CH_2)Me$, CH_2Cl_2	76[a]	194
6	$-c\text{-}C_5H_9$	$-OSi[(CH_2)_2CHO]_3$	$T_8(c\text{-}C_5H_9)_7OSi(CH{=}CH_2)_3 + CO/H_2$, $PtCl_2$(sixantphos), $SnCl_2$		92
7	-Ph	$-(CH_2)_3NH(CH_2)_2CO_2CH_2CH(OH)CH_2\text{-}OC({=}O)C({=}CH_2)Me$	$T_8Ph_7(CH_2)_3NH_2 + CH_2{=}CHCO_2CH_2CH(OH)CH_2OC({=}O)C({=}CH_2)Me$, CH_2Cl_2	99	194

	functional groups				
entry	R_6 or R_4	R'_2 or R'_4	starting materials	yield (%)	refs
8	$-(CH{=}CH_2)_6$	$-[CH(O)CH_2]_2$	$T_8(CH{=}CH_2)_8$ + MCPBA, CH_2Cl_2	55[b]	81
9	$-(CH{=}CH_2)_4$	$-(2,2\text{-}Cl_2\text{-}c\text{-}C_3H_3)_4$	$T_8(CH{=}CH_2)_8 + HCCl_3$, CH_2Cl_2, *t*-BuOK, 18-crown-6	44	392

[a] Product also contains a small percentage of addition product involving the secondary amine. [b] Product is a mixture of epoxidation products.

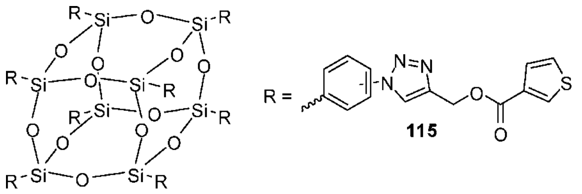
place between a POSS derivative containing a carbon−carbon double bond and an appropriate reagent; however, there are six reported reactions between an appropriately substituted T_8 POSS derivative and alkene reagent (Table 18, entries 17, 18, 25, and 26; Table 19, entries 5 and 7). Furthermore, there is one reaction that shows two additions, first of an amine-containing compound to a POSS derivative containing a carbon−carbon double bond followed by the addition of this POSS derivative to an alkene reagent (Table 18, entry 19).

A wide range of addition reactions to double bonds in POSS derivatives have been shown to occur, ranging from the simplest example of hydrogen or deuterium gas (Table 18, entries 1, 2, and 21) to carbon monoxide (Table 18, entries 3 and 4; Table 19, entries 4 and 6), thiols (Table 18, entries 7−14, 23, and 24; Table 19, entries 1−3), and halogen derivatives (Table 18, entry 15).

Rather surprisingly, the reaction described in Table 19, entry 9, shows the reaction of $T_8(CH{=}CH_2)_8$ with chloroform in the presence of potassium *tert*-butoxide and 18-crown-6 giving rise to the tetra-substituted derivative $T_8(CH{=}CH_2)_4(2,2\text{-}Cl_2\text{-}c\text{-}C_3H_3)_4$ in modest yield, without any indication of cleavage of the T_8 cage by the base. A similar reaction to these, between $T_8(CH{=}CH_2)_8$ and chloroform in the presence of sodium hydroxide and tetrabutylammonium bromide, likewise does not show cage cleavage but leads instead to the formation of the octasubstituted $T_8(2,2\text{-}Cl_2\text{-}c\text{-}C_3H_3)_8$ (Table 18, entry 19). A related reaction was seen for the partial epoxidation of $T_8(CH{=}CH_2)_8$ using MCPBA, resulting in the formation of $T_8(CH{=}CH_2)_6[CH(O)CH_2]_4$ (Table 19, entry 8).

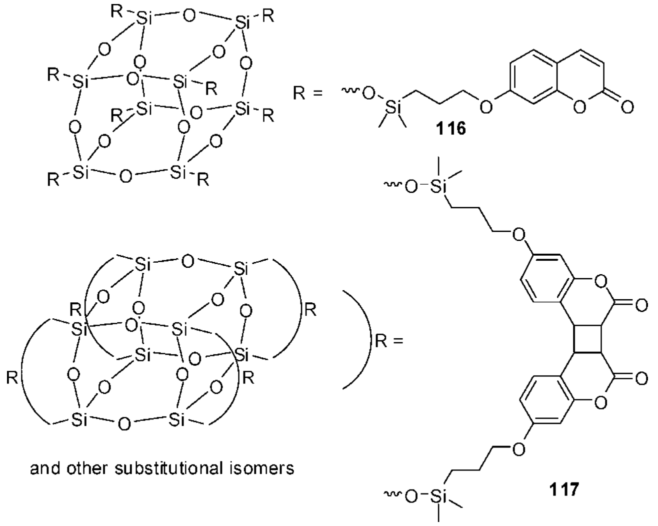
Two further and rather surprising sets of radical-mediated addition reactions of thiol-substituted POSS to alkenes or alkynes have been recently observed for the POSS derivative $T_8(i\text{-}Bu)_7(CH_2)_3SH$.[388,389] The first of these was a thiol−yne reaction between this thiol-POSS and the tetra-alkyne $C[CH_2OC({=}O)(CH_2)_3S(CH_2)_2CO_2CH_2C{\equiv}CH]_4$.[388] Spectroscopic data of the product in comparison to the starting POSS indicated that the reaction had proceeded successfully to give the octa-POSS derivative $C\{CH_2OC({=}O)(CH_2)_3S(CH_2)_2\text{-}CO_2CH_2C[S(CH_2)_3T_8(i\text{-}Bu)_7]CH_2S(CH_2)_3T_8(i\text{-}Bu)_7\}_4$. The sec-

Chart 21



115

Chart 22



116

117

ond set of reactions was between the thiol-POSS and polymers of *N*-isopropylacrylamide with two different end-group modifications to give either an alkene or an alkyne functionality.[389] Analyses of the products indicated the formation of the mono-POSS and di-POSS polymers from the alkene- and alkyne-modified starting materials, respectively, although the thiol−yne reaction was seen not to go fully to completion.

2.7.5. Cycloaddition Reactions

The number of POSS derivatives so far prepared via cycloaddition reactions is small and, surprisingly, only one of these syntheses is claimed to give a symmetric T_8R_8 species. Compound **115** (Chart 21) was prepared by the "click" reaction between octakis(azidophenyl) T_8 derivatives and propynylthiophene-3-carboxylate.[337]

The only other symmetric T_8 derivative prepared by cycloaddition is a very unusual T_8R_4 compound (**117**), where the R groups bridge between the corners of the T_8 cage (Chart 22). This compound was prepared by the intramolecular photocycloaddition of an octasubstituted T_8R_8 derivative containing coumarin functional groups (**116**) in excellent yield, although it is not known whether a single substitutional isomer was formed.[399] This intramolecular cycloaddition reaction was found to be partially reversible, and further study on this system has also shown that when the dimerization is carried out in concentrated solution, an apparent three-dimensional polymer is formed by photodimerizations between adjacent POSS derivatives.

All of the other cycloaddition products are $T_8(c\text{-}C_5H_9)_7R$ derivatives (Table 20 and Chart 23). The most simple of the studies involved the reaction of a POSS−azide derivative with phenylacetylene to form a 1,2,3-triazene derivative by a click reaction (Table 20, entry 1). The second study was a comprehensive investigation of a series of cycloadditions, looking at microwave-assisted and conventional syntheses (Table 20, entries 2−14). The results show the formation of a series of isoxazolidine- and isoxazoline-containing POSS derivatives. The microwave-assisted reactions often performed better, resulting in higher yields, and product mixtures that could be separated to give individual isomers. In addition, one of these isoxazolidine-containing ester derivatives (**127**) could be deprotected to leave the free acid (**128**).

2.8. Synthesis of Metal Complexes of POSS Compounds

The chemistry of metal complexes of silsesquioxanes has been of interest since 1986, when Feher et al. started publishing a series of papers on the use of metal complexes of T_8 POSS moieties as either models of metal catalysts bound to a silica surface or catalysts themselves.[153−155] However, these materials generally consisted of a metalated T_7 system, $R_7Si_7O_{12}M$, often with further ligands coordinated to the metal. Since then, interest has broadened to include T_8 systems with a variety of metals coordinated to functional groups outside the cubic POSS core. The T_8 compounds containing metals may be divided into two groups, those with octasubstitution of metals and those with a single metalated site and seven inert substituents. While most of the POSS−metal complexes are prepared either by the reaction of a POSS directly with a metal salt or by a metal exchange reaction, there is a more limited group of complexes prepared by reacting functionalized POSS species in the presence of a metal to make a more complicated ligand system, still coordinated to the metal. A series of such complexes have been prepared by the metal-templated macrocyclization of bis-T_8 substituted benzene derivatives to form octa-POSS substituted phthalocyanines (Table 22, entries 2−6).

Both octa-metalated (Table 21) and monometalated (Table 22 and Charts 24 and 25) classes of POSS compounds have continued to be prepared, with a greater recent emphasis on the monometalated species, often for catalyst modeling. There have been two groups of new octa-metal substituted species prepared, the first from the reaction of $T_8[(CH_2)_3NH_2]_8$ and its HCl salt with a selection of metal salts and from the formation of the $\{T_8[(CH_2)_3NH_3]_8\}^{8+}$ cationic species with a mixture of Cl^- and $[ZnCl_4]^{2-}$ anions by hydrolysis of the parent silane in the presence of $ZnCl_2$ (Table 21, entries 1−11) and the second from the stepwise reaction of T_8H_8 with tin and titanium compounds (Table 21, entries 12, 14−16).

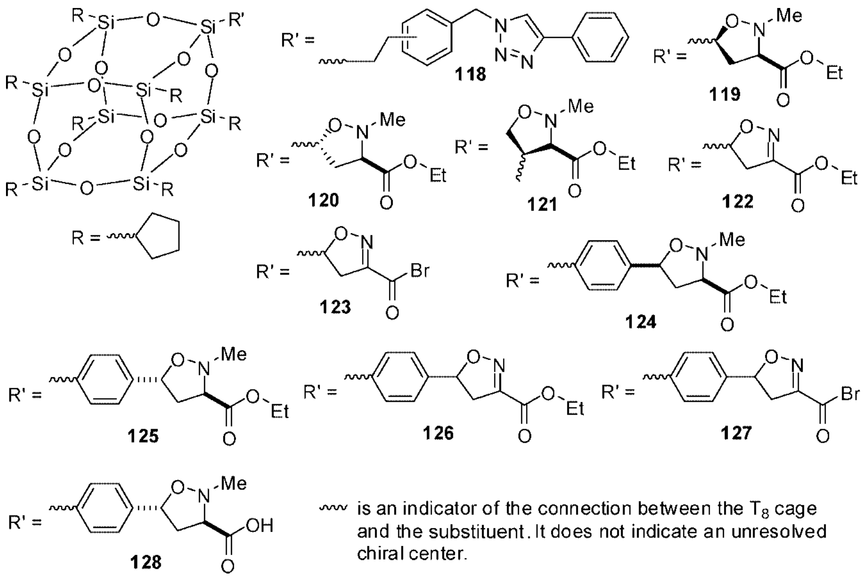
While monometallic T_8 POSS species are most commonly prepared as catalysts or silica-anchored catalyst model systems, these are not the only possible uses for such complexes. The metal centers incorporated into such catalyst models range from first row transition metals such as titanium and manganese (Table 22, entries 21−25) through the second row metals zirconium and molybdenum (Table 22, entries 9−12, 26−28, and 33) and heavier third row metals tungsten, rhenium, and osmium (Table 22, entries 13, 14, 20, and 29−32) to precious metals such as palladium and platinum (Table 22, entries 1, 19, and 34). This variety of metals incorporated into POSS systems has allowed for the modeling of a large variety of silica-anchored catalysts, and from this a better understanding of the mechanism of catalyst action and the potential for the specific design of future catalysts is possible.

Table 20. T_8R_7R' Derivatives Prepared by Cycloaddition Reactions

entry	compound number	starting materials	yield (%)	refs
1	**118**	$T_8(c\text{-}C_5H_9)_7(CH_2)_2C_6H_4CH_2N_3$ + $PhC{\equiv}H$, bis(benzyl-1,2,3-triazolylmethyl)amine, $[Cu(MeCN)_4]PF_6$, toluene	56[a]	347, 350
2	**119**	$T_8(c\text{-}C_5H_9)_7CH{=}CH_2$ + $MeN^+(O^-){=}CHCO_2Et$, toluene, microwave	11[b]	400
3	**120**	$T_8(c\text{-}C_5H_9)_7CH{=}CH_2$ + $MeN^+(O^-){=}CHCO_2Et$, toluene, microwave	60[b]	400
4	**121**	$T_8(c\text{-}C_5H_9)_7CH{=}CH_2$ + $MeN^+(O^-){=}CHCO_2Et$, toluene, microwave	3[b]	400
5	**122**	$T_8(c\text{-}C_5H_9)_7CH{=}CH_2$ + $HON{=}CHCO_2Et$, NaOCl, CH_2Cl_2	15	400
6	**122**	$T_8(c\text{-}C_5H_9)_7CH{=}CH_2$ + $HON{=}CHCO_2Et$, Al_2O_3, $CHCl_3$, microwave	70	400
7	**122**	$T_8(c\text{-}C_5H_9)_7CH{=}CH_2$ + $HON{=}CHCO_2Et$, NBS, CH_2Cl_2	11[b]	400
8	**123**	$T_8(c\text{-}C_5H_9)_7CH{=}CH_2$ + $HON{=}CHCO_2Et$, NBS, CH_2Cl_2	39[b]	400
9	**124**	$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$ + $MeN^+(O^-){=}CHCO_2Et$, toluene, microwave	4[b]	400
10	**125**	$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$ + $MeN^+(O^-){=}CHCO_2Et$, toluene, microwave	86[b]	400
11	**126**	$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$ + $HON{=}CHCO_2Et$, NaOCl, CH_2Cl_2	15	400
12	**126**	$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$ + $HON{=}CHCO_2Et$, Al_2O_3, $CHCl_3$, microwave	75	400
13	**126**	$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$ + $HON{=}CHCO_2Et$, NBS, NEt_3, CH_2Cl_2	14[b]	400
14	**127**	$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$ + $HON{=}CHCO_2Et$, NBS, NEt_3, CH_2Cl_2	46[b]	400

[a] Contains a mixture of isomers. [b] Reaction produces a separable mixture of these products.

Chart 23



~~ is an indicator of the connection between the T_8 cage and the substituent. It does not indicate an unresolved chiral center.

Table 21. T_8-Derived Metal Complexes and Salts

entry	T_8 derivative or compound number	starting materials	yield (%)	refs
1	$T_8[(CH_2)_3NH_2]_8Ni_2(NO_3)_4$	$T_8[(CH_2)_3NH_2]_8$ + $Ni(NO_3)_2{\cdot}6H_2O$, MeOH	60	110
2	$T_8[(CH_2)_3NH_2]_8Cu_2(NO_3)_4$	$T_8[(CH_2)_3NH_2]_8$ + $Cu(NO_3)_2{\cdot}3H_2O$, MeOH	60	110
3	$T_8[(CH_2)_3NH_2]_8Cu_2Br_4$	$T_8[(CH_2)_3NH_2]_8$ + $CuBr_2$, MeOH	90	110
4	$T_8[(CH_2)_3NH_2]_8Zn_2(NO_3)_4$	$T_8[(CH_2)_3NH_2]_8$ + $Zn(NO_3)_2{\cdot}6H_2O$, MeOH	77	110
5	$T_8[(CH_2)_3NH_2]_8Zn_2I_4$	$T_8[(CH_2)_3NH_2]_8$ + ZnI_2, MeOH	87	110
6	$T_8[(CH_2)_3NH_2]_8Cd_2(BF_4)_4$	$T_8[(CH_2)_3NH_2]_8$ + $Cd(BF_4)_2{\cdot}6H_2O$, MeOH	86	110
7	$T_8[(CH_2)_3NH_2]_8Cd_2(NO_3)_4$	$T_8[(CH_2)_3NH_2]_8$ + $Cd(NO_3)_2{\cdot}4H_2O$, MeOH	81	110
8	$T_8[(CH_2)_3NH_3]_8[CoCl_4]_4$	$T_8[(CH_2)_3NH_3]_8Cl_8$ + $CoCl_2{\cdot}6H_2O$, MeOH	27	110
9	$T_8[(CH_2)_3NH_3]_8[CuCl_4]_4$	$T_8[(CH_2)_3NH_3]_8Cl_8$ + $CuCl_2{\cdot}2H_2O$, MeOH	82	110
10	$T_8[(CH_2)_3NH_3]_8[CdCl_4]_4$	$T_8[(CH_2)_3NH_3]_8Cl_8$ + $CdCl_2$, MeOH	74	110
11	$\{T_8[(CH_2)_3NH_3]_8\}[ZnCl_4]_{2.8}Cl_{2.4}$	$H_2N(CH_2)_3Si(OEt)_3$ + $ZnCl_2$, HCl, MeOH	4	110
12	$T_8(OSnBu_3)_8$	T_8H_8 + $O(SnBu_3)_2$	95	402
13	**29**	$T_8(OSiMe_2H)_8$ + **28**, Pt(dvs), toluene	33	262
14	$T_8(OSnBu_3)_8$	$T_8(OSnBu_3)_8{\cdot}4H_2O$		403
15	$T_8(OSnBu_3)_8{\cdot}4H_2O$	T_8H_8 + $O(SnBu_3)_2$, toluene	91	402
16	$T_8(OTiClCp_2)_8$	$T_8(OSnMe_3)_8$ + Cp_2TiCl_2, CH_2Cl_2	84	402

However, catalyst studies are not the only uses for such metallo-POSS compounds. Metal complexes containing T_8 POSS cages have been prepared as materials with optical limiting properties (Table 22, entries 2−4), as

Table 22. T$_8$-Derived Metal Complexes with Differing Substitutions

entry	T$_8$ derivative or compound number	starting materials	yield (%)	refs
1	**129**	T$_8$(*i*-Bu)$_7$(CH$_2$)$_3$OC(=O)CH=CH$_2$ + **130**, CH$_2$Cl$_2$, ether	40	404
2	**131**	1,2-(CN)$_2$C$_6$H$_2$-4,5-[S(CH$_2$)$_3$T$_8$(*i*-Bu)$_7$]$_2$ + CoCl$_2$·6H$_2$O, ethylene glycol	59	360
3	**132**	1,2-(CN)$_2$C$_6$H$_2$-4,5-[S(CH$_2$)$_3$T$_8$(*i*-Bu)$_7$]$_2$ + CuCl, urea	71	360
4	**133**	1,2-(CN)$_2$C$_6$H$_2$-4,5-[S(CH$_2$)$_3$T$_8$(*i*-Bu)$_7$]$_2$ + Zn(OAc)$_2$·2H$_2$O, DMF	33	360
5	**134**	1,2-(CN)$_2$C$_6$H$_2$-4,5-[S(CH$_2$)$_3$T$_8$(*i*-Bu)$_7$]$_2$ + Lu(OAc)$_3$·6H$_2$O, Li, *n*-C$_5$H$_{11}$OH	2	405
6	**135**	1,2-(CN)$_2$C$_6$H$_2$-4,5-[S(CH$_2$)$_3$T$_8$(*i*-Bu)$_7$]$_2$ + Gd(OAc)$_3$·6H$_2$O, Li, *n*-C$_5$H$_{11}$OH	17	405
7	**136**	**10** + Me$_3$SiCl, *n*-BuLi, THF	74	179
8	**137**	**10** + Me$_3$SiCl, *n*-BuLi, THF	74	179
9	**138**	**10** + Zr(Cp*)Cl$_3$, *n*-BuLi, THF, toluene	83	179
10	**139**	**10** + Zr(Cp″)Cl$_3$, *n*-BuLi, THF, toluene	73	179
11	**140**	**10**+ ZrCl$_4$, *n*-BuLi, THF, toluene	43	179
12	**141**	**11** + Zr(Cp*)Cl$_3$, *n*-BuLi, THF, toluene	42	179
13	**142**	**103** + K$_2$OsO$_2$(OH)$_4$, *N*-methylmorpholine-*N*-oxide, H$_2$O, *t*-BuOH, cyclohexene, CH$_2$Cl$_2$	42^a	182
14	**143**	**103** + K$_2$OsO$_2$(OH)$_4$, *N*-methylmorpholine-*N*-oxide, H$_2$O, *t*-BuOH, cyclohexene, CH$_2$Cl$_2$	42^a	182
15	**144**	**85** + [Zr(Cp*)Cl$_3$], *n*-BuLi, THF, toluene	83	179
16	T$_8$(*c*-C$_5$H$_9$)C$_6$H$_4$-4-CH=CHFc	T$_8$(*c*-C$_5$H$_9$)$_7$C$_6$H$_4$-4-CH$_2$PPh$_3^+$ Cl$^-$ + FcCHO, NaOEt, CHCl$_3$	89^b	187, 353
17	**145**	T$_8$(*c*-C$_5$H$_9$)$_7$OH + **146**, pyridine	63	406
18	**147**	T$_8$(*c*-C$_5$H$_9$)$_7$OH + **148**, pyridine	63	406
19	**149**	**86** + Pt(cod)Cl$_2$, CH$_2$Cl$_2$		355
20	T$_8$(*c*-C$_5$H$_9$)$_7$ORe(CH$_2$-*t*-Bu)(=CH-*t*-Bu)(≡C-*t*-Bu)	T$_8$(*c*-C$_5$H$_9$)$_7$OH + Re(CH$_2$-*t*-Bu)$_2$(=CH-*t*-Bu)(≡C-*t*-Bu), C$_6$D$_6$	95	407
21	T$_8$(*c*-C$_5$H$_9$)$_7$OTi(CH$_2$Ph)$_2$C$_5$H$_3$-1,3-(SiMe$_3$)$_2$	T$_8$(*c*-C$_5$H$_9$)$_7$OH + Ti(CH$_2$Ph)$_3$C$_5$H$_3$-1,3-(SiMe$_3$)$_2$, C$_6$D$_6$		408
22	T$_8$(*c*-C$_5$H$_9$)$_7$OTi(O-*i*-Pr)$_3$	T$_8$(*c*-C$_5$H$_9$)$_7$OH + Ti(O-*i*-Pr)$_4$, ether	80	409
23	**150**	T$_8$(*c*-C$_5$H$_9$)$_7$OH + **151**, THF		410
24	**152**	T$_8$(*c*-C$_5$H$_9$)$_7$OH + **153**, THF		410
25	[T$_8$(*c*-C$_5$H$_9$)$_7$O]$_2$[Mn(TMEDA)$_2$]	T$_8$(*c*-C$_5$H$_9$)$_7$OH + [Mn(CH$_2$-*t*-Bu)$_2$(TMEDA)], benzene	54	411
26	T$_8$(*c*-C$_5$H$_9$)$_7$OMo(=NH)(CH$_2$*t*-Bu)$_3$	T$_8$(*c*-C$_5$H$_9$)$_7$OH + Mo(≡N)(CH$_2$-*t*-Bu)$_3$, benzene	76	412
27	T$_8$(*c*-C$_5$H$_9$)$_7$OMo(=NC$_6$H$_3$-2,6-*i*-Pr$_2$)(CH$_2$-*t*-Bu)(=CH-*t*-Bu)	T$_8$(*c*-C$_5$H$_9$)$_7$OH + Mo(=NC$_6$H$_3$-2,6-*i*-Pr$_2$)(CH$_2$-*t*-Bu)$_2$(=CH-*t*-Bu), C$_6$D$_6$ or pentane	100	413
28	[T$_8$(*c*-C$_5$H$_9$)$_7$O]$_2$Mo[NH(*t*-Bu)C$_6$H$_3$-3,5-(*i*-Pr)$_2$][N(*t*-Bu)C$_6$H$_3$-3,5-(*i*-Pr$_2$)](≡CEt)	T$_8$(*c*-C$_5$H$_9$)$_7$OH + Mo[N(*t*-Bu)C$_6$H$_3$-3,5-(*i*-Pr)$_2$]$_3$(≡C-Et), pentane	60	414
29	T$_8$(*c*-C$_5$H$_9$)$_7$OW[=NC$_6$H$_3$-2,6-(*i*-Pr$_2$)](CH$_2$-*t*-Bu)(=CH-*t*-Bu)	T$_8$(*c*-C$_5$H$_9$)$_7$OH + W[=NC$_6$H$_3$-2,6-(*i*-Pr$_2$)](CH$_2$-*t*-Bu)$_2$(=CH-*t*-Bu), C$_6$D$_6$		415, 416
30	[T$_8$(*c*-C$_5$H$_9$)$_7$O]$_2$W[=NC$_6$H$_3$-2,6-(*i*-Pr$_2$)](CH$_2$-*t*-Bu)$_2$	T$_8$(*c*-C$_5$H$_9$)$_7$OH + W[=NC$_6$H$_3$-2,6-(*i*-Pr$_2$)](CH$_2$-*t*-Bu)$_2$(=CH-*t*-Bu), C$_6$D$_6$		415
31	T$_8$Cy$_7$ORe(CO)$_5$	T$_8$Cy$_7$OH + *n*-BuLi, Re(CO)$_5$CF$_3$SO$_3$, CO, CH$_2$Cl$_2$		417
32	[T$_8$Cy$_7$(μ-O)Re(CO)$_4$]$_2$	T$_8$Cy$_7$ORe(CO)$_5$, CH$_2$Cl$_2$		417
33	[T$_8$Cy$_7$OP(NMe$_2$)$_2$]$_2$Mo(CO)$_4$	T$_8$Cy$_7$OP(NMe$_2$)$_2$ + norbornadienemolybdenumtetracarbonyl, CH$_2$Cl$_2$	95	358
34	[T$_8$Cy$_7$OP(NMe$_2$)$_2$]$_2$PtCl$_2$	T$_8$Cy$_7$OP(NMe$_2$)$_2$ + Pt(cod)Cl$_2$, CH$_2$Cl$_2$	96	358

[a] Combined yield for both related products. [b] Mixture of *E* and *Z* isomers.

nanocomposite materials (Table 22, entry 16), or as species containing novel chromophores (Table 22, entries 17 and 18). A series of monometalated iridium-POSS complexes has recently been prepared for potential use in light-emitting devices.[401] The complexes are prepared by the hydrosilylation of the suitably functionalized iridium complexes with either T$_8$(*c*-C$_5$H$_9$)$_7$OSiMe$_2$H or T$_8$(OSiMe$_2$H)$_8$ and *N*-allylcarbazole. Light-emitting devices were prepared by blending the iridium complexes with suitable organic polymeric materials.

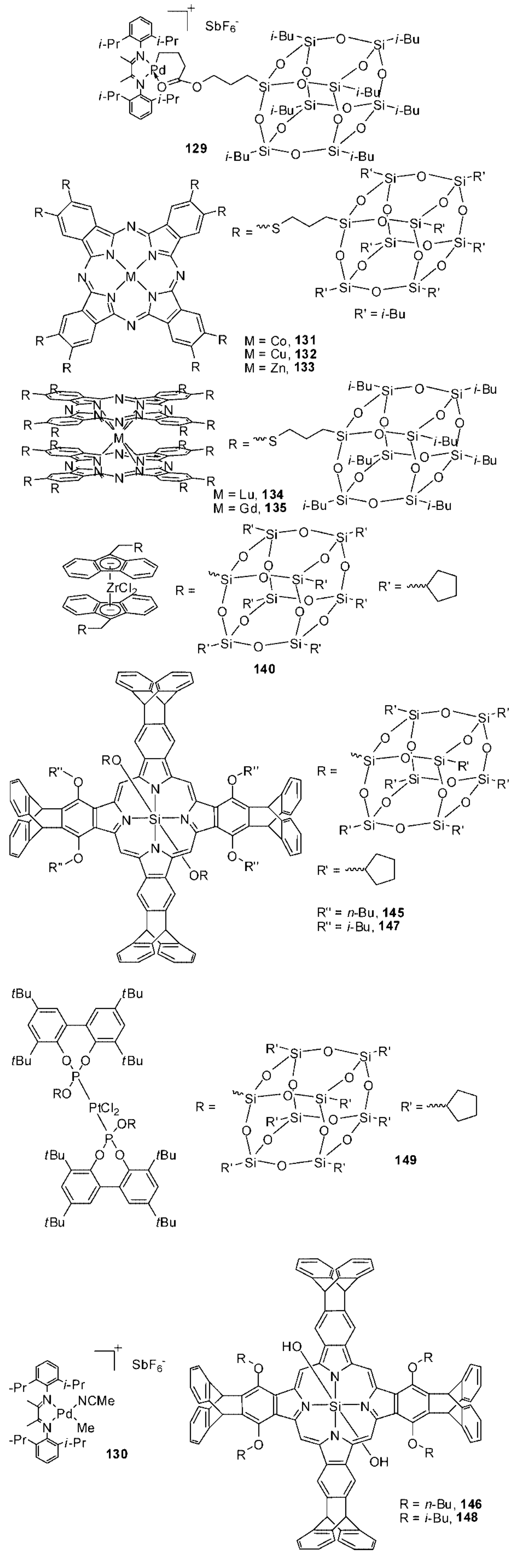
In addition to these metalated T$_8$ POSS species, a large body of work also exists on the incompletely condensed metalated species, the successors to Feher's early work. These silsesquioxanes include both open cage type, where metals are coordinated *exo* to the silsesquioxane core, and metal-capped derivatives, where a R$_7$Si$_7$O$_9$(OH)$_3$ derivative has been treated with an appropriate metal species to form the T$_8$-like metallasilsesquioxane, R$_7$Si$_7$O$_{12}$ML$_n$ (Chart 26). Depending on its nature, the introduced metal site may be further functionalized. For recent reviews of these and other metallasilsesquioxanes, see refs 53–57.

2.9. Synthesis of Incompletely Condensed POSS Compounds

The controlled synthesis of incompletely condensed POSS derivatives is a key area for those interested in the synthesis of further T$_8$R$_7$R′ POSS species, as well as those interested in modeling the silica surface and the interaction of small molecules with it. The most commonly used incompletely condensed POSS derivatives are the trisilanols R$_7$Si$_7$O$_9$(OH)$_3$, while the disilanols, R$_8$Si$_8$O$_{11}$(OH)$_2$, although less common, are also known and have been used in model systems.[54,57,418] While there are a limited number of R$_7$Si$_7$O$_9$(OH)$_3$ species that can be prepared directly from a chloro- or alkoxysilane, it is more common to prepare such derivatives by the controlled base hydrolysis of a T$_8$R$_8$ precursor.[1] It is clear from the reactions of R$_7$Si$_7$O$_9$(OH)$_3$ species (see section 2.2) to produce T$_8$R$_7$R′ species that a wide range of these derivatives is now available.

There have been few recent literature reports of the conversion of T$_8$R$_8$ species to R$_7$Si$_7$O$_9$(OH)$_3$, with examples of such studies including the preparation of (*i*-Bu)$_7$Si$_7$O$_9$(OH)$_3$ from T$_8$(*i*-Bu)$_8$,[91–93] and the synthesis of a series of varying partially condensed derivatives from T$_8$R$_8$

Chart 24



species, where R = Me, Et, CH=CH$_2$, c-C$_5$H$_9$, Cy, or C$_6$H$_4$-4-Me.[419] In a similar manner, the disilanol R$_8$Si$_8$O$_{11}$(OH)$_2$, where R = Me, CH=CH$_2$, i-Bu, c-C$_5$H$_9$, or Cy, is likewise usually prepared by the controlled hydrolysis, under either acidic or basic conditions, of the parent T$_8$ POSS compound.[57,418,420,421]

A more complex partially condensed POSS species has been prepared by the hydrolysis of T$_8$(i-Bu)$_7$(CH$_2$)$_3$NH$_2$ to give (i-Bu)$_6$[H$_2$N(CH$_2$)$_3$]Si$_7$O$_9$(OH)$_3$.[422] This reaction is not fully selective but has been seen to result in about 88% of the obtained material being the desired (i-Bu)$_6$[H$_2$N(CH$_2$)$_3$]-Si$_7$O$_9$(OH)$_3$, although it is present as a mixture of isomeric products. Such a material opens up possibilities for preparing difunctional T$_8$R$_6$R′R″ in a somewhat controlled fashion. Another unusual cage-opened POSS derivative has recently been prepared by the reaction of T$_8$Me$_8$ with boron trifluoride diethyletherate. This led to the formation in low yield of the edge-opened POSS derivative Me$_8$F$_2$Si$_8$O$_{11}$,[423] which, in contrast to most of the other cage-opened POSS species, does not contain any silanol groups.

3. Physical Properties of POSS Compounds

3.1. Physical Properties − Introduction

The discussion in this section concentrates on the properties of molecular POSS species; for a description of the properties of polymeric materials containing POSS groups see the applications section below. The majority of simple T$_8$R$_8$ compounds are white or off-white powders, colorless crystals, or oils, and the lower molecular weight compounds may be sublimed. The T$_8$ cube has an electron-withdrawing effect similar to that of the CF$_3$ group as determined by ^{13}C NMR chemical shift measurements[424] and this has an effect on reactions taking place at aromatic POSS rings, see section 2.7.1. While this section concentrates on the physical properties, the chemical properties can be found in either the preparations section, for the case of simple modifications of the pendant arms on the POSS core, or in the applications section, for the incorporation of POSS species into polymeric materials.

3.2. Computational and Gas-Phase Studies on the Structures of T$_8$ Compounds

The structure of T$_8$H$_8$ has been the subject of numerous computational studies, which have been summarized and the results of which have been tabulated recently.[1,425–429] Ab initio methods generally give results in reasonable agreement with an earlier neutron diffraction study,[430] which found values of 162.6(2) pm (Si−O), 146.1(5) pm (Si−H), and 147.35(12)° (Si−O−Si angle). Comparisons between solid-state structures and calculations are often hampered by the lattice effects in the solid state causing distortions away from ideal structures (see section 3.4.1), in this case from O_h symmetry. However, the structure of T$_8$H$_8$ has recently been determined in the gas phase by electron diffraction methods where it was found to have O_h symmetry and 161.41(3) pm (Si−O), 145.4(8) pm (Si−H), and 147.9(2)° (Si−O−Si) in good agreement with MP2/6-311++G(3df,3pd) calculations giving respective values of 162.9 pm, 145.3 pm, and 147.8°.[429] Both T$_8$H$_8$ and T$_8$Me$_8$ have also been used as models to develop a molecular dynamics method to enable experimental equilibrium structures to be obtained from gas-phase electron diffraction measurements.[431]

Chart 25

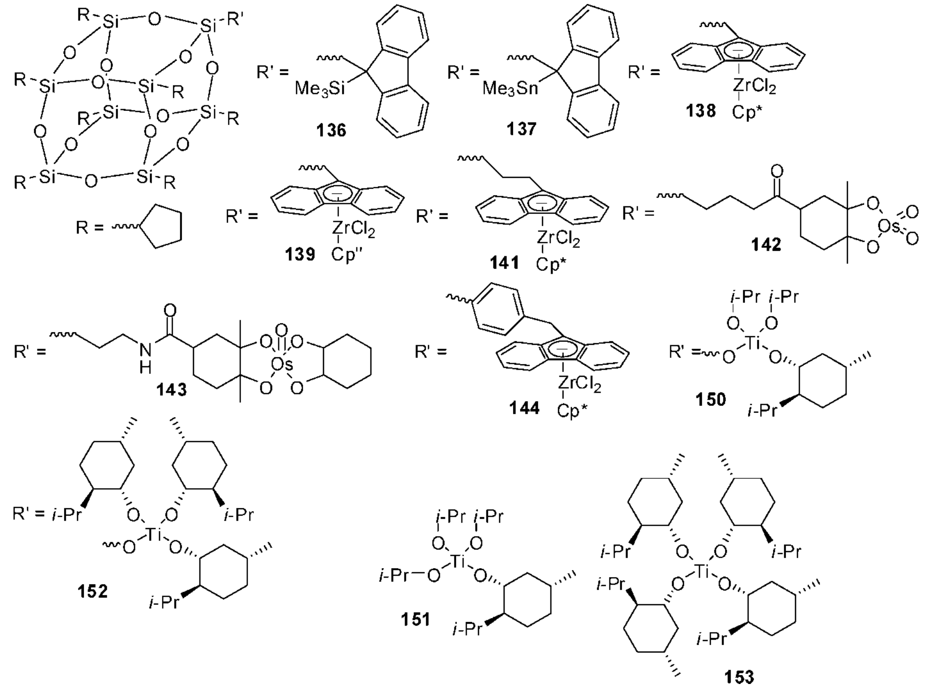
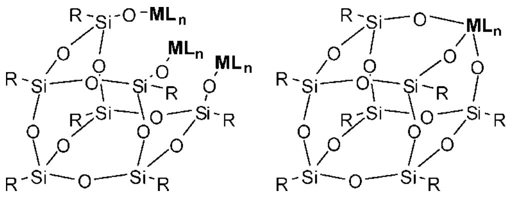


Chart 26



Calculations on the three biradicals (at "ortho", "meta" or "para" Si positions on the POSS cube) derived from removal of two hydrogen atoms from T_8H_8 show that for the "meta" and "para" cases the unpaired spins are relatively isolated but in the "ortho" biradical case there is some weak electronic coupling.[432] The IR and Raman spectra for T_8H_8 have both been calculated using molecular dynamics methods and give reasonable agreement with experimental values, the calculated Si−O−Si frequencies in the Raman spectrum being 1113, 687.84, and 613.62 cm^{-1} and the experimental values being 1117, 697, and 610 cm^{-1} respectively,[433] (see section 3.10). The MM3* force field has been used to calculate properties of T_8H_8 using the generalized Born/surface area model for $CHCl_3$ and H_2O. The calculations indicate that there is significant fluxional motion for the POSS cage and that solvation free energies for T_8H_8 in $CHCl_3$ and H_2O are −28.9 and 7.6 kJ mol^{-1} respectively.[434] This is consistent with the experimental observation that T_8H_8 has poor solubility in water.

The interaction of T_8H_8 with a model Si(100) surface has been modeled using Hartree−Fock, DFT and multiconfiguration self-consistent field methods, which predict that there are two possible addition products, one that is thermodynamically favored in which a Si−Si bond is formed between the POSS and the surface, and a second that is kinetically favored in which a cage Si−O bond breaks to give a POSS cage bound to the surface via both a silicon and oxygen atom.[435] The complicated mechanism by which $HSi(OH)_3$ condenses to give T_8H_8 has been the subject of a detailed computational study, which shows that the reaction is overall exothermic by 48.3 kJ mol^{-1} and that hydrogen bonding is, as would be expected, important in determining the relative stabilities of the intermediates and transition structures and the mechanistic route.[436] The structure and catalytic activity of $(HTiO_{1.5})_8$[437] and the stabilities and structures of other mixed metal cubic cages $H_8M_nSi_{8-n}O_{12}$ (M = Ge, Sn, or Zr; $n = 0-8$) have been calculated using Hartree−Fock and MP2 levels of theory with $H_8Si_8O_{12}$ (T_8H_8) being found the most stable of the compounds.[438] It should be noted that most of the possible structures available in the $R_8M_nSi_{8-n}O_{12}$ system (M = C, Ge, or Sn; $n = 0-8$) other than for M = Si are either unknown or very rare.

The structures of a range of T_8H_7R cages (R = Et, *n*-Pr, *n*-Bu, Cy) have been calculated using Hartree−Fock and MP2 methods in order to determine the effects of substituents on the cage structure. The results show that only small changes occur when one of the corners of the cage is substituted by an alkyl group compared with the parent T_8H_8 and that combination of an atomistic force field specific to silsesquioxanes with an independent one designed for hydrocarbon chains might remove the need to develop specific force fields for each individual POSS compound.[425,427] A force field has also been developed to simulate POSS/hydrocarbon systems, which has been applied to T_8H_7Cy showing good agreement between calculated and experimental values for both structure and vibrational properties.[439] Related calculations also show that the POSS cage is very stable toward attack by atomic oxygen.[427]

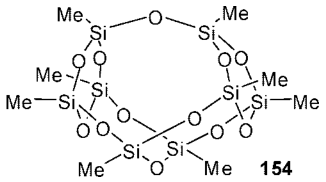
The electronic natures of T_8H_8, T_8H_7Ph, $T_8H_6Ph_2$, $T_8H_7(C_6H_4\text{-}4\text{-}Ph)$, and T_8Ph_8 and crystalline T_8H_8 and $T_8Ph_8\cdot$acetone have been studied by a range of theoretical methods, which show that, in contrast to T_8H_8, which has a HOMO localized at the lone pairs on the oxygen atoms, the aryl-substituted compounds have HOMO and LUMO orbitals localized on the aromatic rings.[440,441] The HOMO for $T_8(CH_2CH_2CF_3)_8$ is calculated by DFT methods to comprise oxygen lone pairs, while the LUMO comprises oxygen centered σ^* orbitals.[204] Molecular simulations of $T_8H_7(n\text{-}C_9H_{19})$ show that it forms lamellar structures rather than cylindrical ones, driven by packing involving strong face-to-face interactions promoted by the shape and size of the POSS core and the effect of a poor solvent. However, if a solvent is chosen that is good for the POSS cage but poor for the alkyl group then ordered cylinders form.[442,443] Similar simulations using a POSS cube with four substituents around one face show that hexagonally arranged cylinders are formed via self-assembly.[443]

Molecular dynamics simulations of T_8H_8 and T_8Me_8 in *n*-$C_{16}H_{34}$ and in poly(dimethylsiloxane) have been used to calculate thermodynamic and transport properties of these small POSS compounds such that the mean force between pairs of POSS molecules can be investigated. The osmotic second virial coefficients for T_8H_8 were found to be negative in both solvents at a range of temperatures, whereas for T_8Me_8 above 600 K the value becomes positive suggesting that at these temperatures both solvents are good.[444] Related calculations show that pairs of T_8H_8 or T_8Me_8 molecules in poly(dimethylsiloxane) solution attract each other and that diffusion of these POSS molecules occurs via a "hopping" mechanism.[445] Molecular dynamics simulations show that T_8Me_8 molecules in *n*-hexane exhibit attraction at short distances between them but for the related $T_8Me_7(CH_2)_8Me$, there is a short-range repulsion between the POSS molecules.[446] The attraction between POSS cages in solution has been modeled using molecuar dynamics simulations for molecules in which two T_8Me_7 fragments are connected by a hydrocarbon chain. Both cages move together through a solution when the chain is short, but when the chain is long, they are able to move independently.[447]

Atomistic molecular dynamics simulations of nanocomposites comprising polyimide and either T_8H_8 or $T_8(C_6H_4NH_2)_8$ indicate that the glass transition temperature of the composite increases with the incorporation of $T_8(C_6H_4NH_2)_8$ but that it decreases on incorporation of T_8H_8.[448] Several different force fields have been evaluated for their ability to simulate physical properties of small POSS molecules. The charge-transfer reactive and universal force fields together with COMPASS and Hybrid-COMPASS force fields give good agreement between theory and experiment for fractional coordinates and crystal packing data for both T_8H_8 and T_8Me_8. CTR and Hybrid-COMPASS methods also give good agreement with experiment for the melting point of T_8H_8.[426]

Calculations using the MM3 force field and the generalized Born/surface area continuum model on the hypothetical $T_8H_{8-n}(OH)_n$ (where $n = 1-8$) species indicate, as expected, that the hydroxylated species have increasing solubility in water as the number of OH groups increases.[434] $T_8(OH)_8$ has additionally been used as a model for the silica surface in computational studies of the interaction of polyoxometallates with silica.[449] The $T_8H_7(OH)$ molecule has been used as a computational model for a silica surface Si−OH group catalyzed formation of imidazole[1,2-*a*]pyrazine-3,6-diones[450] and as a test system for comparison of the results from a QM/QM electronic embedding method with those from SCF−HF, DFT−HF, and DFT−DFT methods. The results compare well, and the deprotonation energy for $T_8H_7(OH)$ to give $T_8H_7(O^-)$ is found to be about 1440 kJ mol^{-1}.[451] DFT calculations have been carried out on the condensation reactions of $Si(OH)_4$ including chain, ring, and $T_8(OH)_8$ cage formation for which the activation barrier for formation is 117.6 kJ mol^{-1} under neutral conditions.[452] The reaction between $T_8(c\text{-}C_5H_9)_7OH$ and $Me_2Si(OMe)(CH_2)_3NH_2$ has been studied by ab initio and DFT methods, which show that the reaction is slower in THF than in hexane and that the reaction is second-order with respect to $Me_2Si(OMe)(CH_2)_3NH_2$, one of the $Me_2Si(OMe)(CH_2)_3NH_2$ molecules acting as a catalyst.[453]

Chart 27



The calculated heats of formation and ionization potentials using both semiempirical and ab initio methods for $[T_8O_8]^{8-}$ and $Li_8[T_8O_8]$ are −105.40 and −3895.80 kJ mol^{-1} and −15.35 and 6.62 eV, respectively, while the HOMO energies are 15.3538 and −6.6218 eV, respectively.[454] The role of Me_4N^+ cations on the stability of $[T_8O_8]^{8-}$ in aqueous solution has been found to be more important than in just balancing the charge. Molecular dynamics calculations on relatively concentrated $[T_8O_8]^{8-}/[NMe_4]^+/H_2O$ solutions [1:16:450] show that the $[NMe_4]^+$ ions are situated over each face of the POSS core forming a coordination sphere that excludes water molecules from the surface of the cage, thus reducing the ease of hydrolysis of the siloxane polyhedron.[455] This effect is much less marked for the related $[T_6O_6]^{6-}$ ion, and the octameric cage is found to be the more stable in aqueous solution by ca. 290 kJ mol^{-1}.[456] T_8-like cages are also found to be present as important species in calculations on the lowest energy structures of $(SiO_2)_8O_2$ and $(SiO_2)_8O_2H_4$ clusters.[457]

The structure of T_8Me_8 has also been the subject of computational studies; RHF/6-31G** calculations give values of 162.9 pm (Si−O), 185.3 pm (Si−C), and 149.9° (Si−O−Si),[458] and MP2/6-311++G(3df,3pd) calculations give values of 163.2 pm, 183.7 pm, and 148.6°, respectively.[429] These values agree well with those of 161.74(5) pm, 182.9(3) pm, and 148.9(2)° from a gas-phase electron diffraction study.[429] In addition to the O_h symmetry structure of T_8Me_8, there is also a C_{2v} isomer, **154** (Chart 27), containing tri-, tetra-, and pentasiloxane rings, which has calculated Si−O−Si bond angles ranging from 163.39° for the oxygen atoms solely within tetrasiloxane rings to 131.42° for oxygen atoms involved solely within trisiloxane rings.[458] Although organic derivatives of this cage system do not appear to have been isolated, an anionic silicate cage with this structure has been found in aqueous alkaline solution (see, for example, ref 459) The geometric parameters (Si−O distance 165.6 pm, Si−O−Si angle 142.0°) and total energy for $T_8(CH{=}CH_2)_8$ have also been calculated.[460]

The sizes and shapes of dendrimer molecules T_8R_8 (R = $CH_2CH_2SiMe(CH_2CH_2PPh_2)_2$, $CH_2CH_2SiMe(OCH_2PPh_2)_2$, $CH_2CH_2SiMe[(CH_2)_3PPh_2]_2$, and $CH_2CH_2SiMe[O(CH_2)_2PPh_2]_2$) have been determined by molecular dynamics modeling and were found to be relatively isotropic in shape with aspect ratios of 1.06−1.21, the oxygen-containing species having smaller aspect ratios. The presence of oxygen also leads to a smaller radius of gyration, values for molecules T_8R_8, R = $CH_2CH_2SiMe(CH_2CH_2PPh_2)_2$ and $CH_2CH_2SiMe[O(CH_2)_2PPh_2]_2$, being 9.526 and 9.227 Å, respectively.[461] These POSS dendrimers act as polydentate ligands at transition metal centers and their P−M−P bite angles have also been calculated using molecuar dynamics methods for coordination to $[HRh(CO)_2]$ centers giving, for example, a bite angle of 108.7° for the $CH_2CH_2SiMe(CH_2CH_2PPh_2)_2$ derivative.[462] Density functional theory calculations on $T_8H_n(C_5H_4)_{8-n}$ ($n = 0-7$) complexes with transition metals such as Sc show that these complexes could bind hydrogen molecules and act as potential hydrogen storage materials.[463] The sizes and distribution of pores within POSS-derived networks have been studied by Monte Carlo methods. The intercube pore size and the degree of cross-linking is increased on using longer linkers, but the larger mesopores present become smaller with longer linkers. Rigid tethers lead to low cross-linking density in these systems due to the presence of many free linking sites (unlike many metal–organic frameworks) and narrow pore size distribution.[464]

The effects of binding cations (Li^+, Na^+, K^+), anions (F^-, Cl^-, Br^-), and noble gases (He, Ne, Ar) to T_8H_8 and its carbon and germanium analogues have been studied by calculations at the B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) levels. Exohedral binding is preferred for the neutral and cationic species but endohedral for the anions. For the endohedral complexes of T_8H_8 with He, Ne, Ar, and K^+, the cage expands, but for Li^+ and Na^+ complexes, the cage contracts.[465] One face of a POSS cube can be seen as structurally similar to 12-crown-4, and DFT calculations show that the binding of Li^+ to T_8R_8 (where R = H, Cy) is significant, about $80kT$ and $120kT$, respectively.[466] Such interactions may be of importance in polymer nanocomposites because they hinder agglomeration.

The structures of a range of exohedral and endohedral transition metal complexes with T_8H_8 have been calculated using ab initio DFT methods. It was found that the insertion of a metal into the cage reduces the HOMO–LUMO gap from 8.1 eV for the empty cage to between 1.2 and 4.96 eV for the endohedral species. The endohedral complexes $M@T_8H_8$ for M = Cr, Fe, Co, Ni, Cu, Ru, and Os are more stable than the separate components, and such species may be potential targets for synthesis.[467] Molecular species containing endohedral F^- have been characterized experimentally, see Table 24, but molecular T_8 cages containing endohedral cations have yet to be prepared.[110] MP2 calculations of endohedral ions $[F@T_8R_8]^-$ (R = Me, CF_3, $CH{=}CH_2$, or $CH_2CH_2CF_3$) show that the binding energy for the fluoride within the POSS cage ranges from 293 to 1130 kJ mol^{-1}.[204] Calculations using MP2 methods on the insertion reaction of H_2 into a range of polyhedra, including the mixed metal cubic cages $H_8M_nSi_{8-n}O_{12}$ (M = Si, Ge, Ti, or Zr; $n = 0-8$), show that the energy barrier for insertion into T_8H_8 is about 303 kJ mol^{-1} and that the reaction is endothermic by about 71 kJ mol^{-1}.[468] T_8H_8 has been used as a cage in which to constrain ethane in computational studies (B3LYP hybrid funtional and 6-31G(d) basis set) designed to find species with short C–C bonds. In the $[C_2H_6@T_8H_8]$ case, the C–C bond is indeed short, having a length of 1.40 Å, but the effect on the POSS cage was not reported.[469] DFT studies on the association of T_8Me_8 with hydrogen show that $H^{\bullet}$ forms an initial weak interaction with the outside of the POSS cage but can enter the cage in a slightly endothermic, ΔE = ca. 21 kJ mol^{-1}, reaction with an energy barrier of 121 kJ mol^{-1} to give $H^{\bullet}@T_8Me_8$; this process can be repeated to give $H_2@T_8Me_8$, but the barrier to the diffusion of the H_2 molecule from inside the cage is then large at 254 kJ mol^{-1}.[470]

Atomistic simulations of $T_8(c\text{-}C_5H_9)_8$ in a polyethylene matrix show that the POSS species quickly tend to aggregate within the polymer and that the deformations that these aggregates cause to the polymer backbone are similar to those found for a rigid surface.[471] Aggregation of $T_8(i\text{-Bu})_8$ in poly(methyl methacrylate) occurs above about 21% loading, but for the case below ca. 15% loading, molecular dynamics calculations show that the POSS species is homogeneously dispersed and that gas diffusivity for O_2 and N_2 is increased compared with pristine poly(methyl methacrylate).[472] Such aggregation is often seen in POSS–polymer composite materials, see section 3.4.2.

Monte Carlo calculations on organic–inorganic hybrid networks comprising POSS cages linked by alkyl chains of various lengths predict, in agreement with experimental observations,[473] that the porosity decreases as the chain length increases and that the distance between the POSS cages increases as the linker length increases. The degree of cross-linking achieved depends on the length of the linker unit and the greatest degree is calculated to be when using a $-(CH_2)_6-$ chain.[474]

A range of physical properties (T_g, X-ray scattering curves, and solubility parameters) for copolymers of styrene and of methyl methacrylate with POSS monomers have been calculated using molecular dynamics methods. The T_g values are found to increase for the styrene copolymers compared with polystyrene but not for the methyl methacrylate copolymers.[475] Molecular dynamics simulations of the cross-linking of $T_8[(CH_2)_3OCH_2C(O)CH_2]_8$ with diglycidyl ether bisphenol A using a 5 wt % incorporation of POSS molecules lowers the coefficient of volume thermal expansion slightly but leads to no apparent change in T_g.[476] Molecular dynamics simulations of $T_8(n\text{-Bu})_8$ dispersed in poly(dimethylsiloxane) with varying degrees of cross-linking show that the shear modulus is significantly increased with high loadings of the POSS species together with two or more cross-links between the POSS and the siloxane.[477]

3.3. Solid-State NMR Studies

Solid-state ^{29}Si NMR spectroscopy has become a widely used tool for the analysis of POSS species, both as discrete molecules and when incorporated into polymeric materials. The chemical shifts for a range of T_8R_8 and T_8R_7R' compounds published since 2003 are shown in Table 23. Relatively narrow chemical shift ranges for alkyl (−65 to −70 ppm), aryl (−75 to −81 ppm), and siloxy (−95 to −120 ppm) substituted POSS cages account for most of the data recorded, and the data are generally in good agreement with those recorded in solution (see section 3.9.1). These well-defined chemical shifts for simple molecules are useful for comparison with spectra recorded of polymeric materials containing POSS cages when confirmation is needed that the POSS cage has not been degraded during the polymerization process.

Solid-state ^{29}Si NMR spectra have been used to confirm the integrity of the T_8 cage on the formation of organic–inorganic hybrid materials. For example, on reaction of $T_8[CH_2CH(O)CH_2]_8$ with diamines[90] and in the radical induced polymerization of $T_8(OSiMe_2H)_8$ with methyl methacrylate, the signals at −68.56 and −67.46 for the reaction of the former with two different diamines and at −108.6 and 13.3 ppm for the latter, corresponding to the POSS core and the $OSiMe_2CH_2$- groups, respectively, are both observed, and only a small signal attributable to rearrangement product is present.[478] Similarly, solid state ^{29}Si NMR data for nanocomposites derived from $T_8[OSiMe_2(CH_2)_4CH(O)CH_2]_8$ or from $T_8(C_6H_4NH_2)_8$ indicate that the POSS cores remain largely intact.[479]

Table 23. Solid-State ^{29}Si NMR Data for T_8R_8 and T_8R_7R' Compounds

R or R′, or T_8 derivative, or compound number	^{29}Si NMR chemical shift (ppm from Me_4Si)	refs
-H	−84; −85.5; −83.1	72, 483, 484
-Me	−65.3; −65.8; −65.97; −65.9, −66.4 (3:1 ratio)	77, 197, 423, 485
-$CH{=}CH_2$	−81.7; −79.5; −79.5; −79.23; −79.68	82–85, 485
-$CH_2CH(O)CH_2$	−69.76	90
-$(CH_2)_3Cl$	−66.0, −67.1; −65.6, −66.3	116, 117
-$(CH_2)_3OH$	−67.2	116
-$(CH_2)_2CF_3$	−67.558, −68.418 (from HMDS)	89
-$(CH_2)_2(CF_2)_5CF_3$	−66.7, −67.4	486
-$(CH_2)_2SiMe_2C(SiMe_3)_3$	2.7 ($SiMe_2$), −1.4 ($SiMe_3$), ca. −65 (SiO_3)	487
$T_8[1\text{-}(CH_2)_3\text{-}2\text{-}Me\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_{10}]_8$	−66.1	97
$[NMe_4]_8\{T_8[7\text{-}(CH_2)_3\text{-}8\text{-}Me\text{-}7,8\text{-}\textit{nido}\text{-}C_2B_9H_{10}]_8\}$	−66.2	97
$T_8[1\text{-}(CH_2)_3\text{-}2\text{-}Ph\text{-}1,2\text{-}\textit{closo}\text{-}C_2B_{10}H_{10}]_8$	−66.0	97
-$(CH_2)_3NH_2$	−66.4; −68	99, 100
$\{T_8[(CH_2)_3NH_3]_8\}Cl_8$	−67.0; −67.2	68, 488
$\{T_8[(CH_2)_3NH_3]_8\}[SO_3C_6H_4C_{12}H_{25}]_8$	−67.4	68
$\{T_8[(CH_2)_3NMe_2C_8H_{17}]_8\}Cl_8$	−60 to −75, max. −68.42	117
-CH_2CHMe_2	−76.9	485
-*c*-C_5H_9	−64, −68	489
-Ph	−76.82; −80.40; −76.5; −75.9; −76.5; −77.7; −78.74; −71.3; −65.2; −77.3, −78.5 (3:1 ratio)	63, 77, 132, 333, 340, 490–495
-C_6H_4-2-Me	−75 to −80	135
-C_6H_4-3-Me	−75 to −80	135
-C_6H_4-4-Me	−75 to −80	135
-C_6H_4-2-Et	−78.8	135
-$C_6H_4NO_2$	−78.5, −81.3; −77.3, −79.7; −79.5, −82.8; −80.1; −81.1; −67.1, −70.8	132, 312, 331, 333, 336, 491, 492
-C_6H_4-3-NO_2	−79.5	493
-C_6H_4-4-NO_2	−82.6	493
-$C_6H_4NH_2$	−71.9, −77.1; −70.0, −77.5; −75.0; −76; −75.8, −79.4; −63.1, −66.7	132, 331, 333, 336, 372, 491, 492, 496, 497
-$C_6H_4NHC({=}O)CH{=}CHPh$	−72.0, −77.6	491
94	−67.6, −78.2, −81.4	133, 371
95	−66.2	374
6	−102	145
-$OSiMe_2H$	−108.69, −2.89 ($SiMe_2$)	140
-$OSiMe_3$	−106.0, 14.2 ($SiMe_3$)	485
16	−96.9, 26.0	479
-$OSiMe_2(CH_2)_3OH$	−108.3 (POSS cage), 13.0 ($SiMe_2$)	243
-$OSiMe_2(CH_2)_3OCH_2CH(O)CH_2$	−129.4, −7.3	140
-$OSiMe_2(CH_2)_3CN$	−118[a]	238
-$OSi(OSiMe_3)_3$	−111.9 (POSS cage), −107.5 [O*Si*($OSiMe_3)_3$], 9.0 ($SiMe_3$)	293
$[NMe_4]_8[T_8O_8]$	−96.5, −99.4	140, 485
-$SiMe_2$-*t*-Bu	−70.76, −11.20, −12.90	201
-$(CH_2CH_2CF_3)_7$, H	−68.6, −58.3 (SiH)	171, 172
-(*i*-Bu)$_7$, C_6H_4-4-$CH{=}CH_2$	−67.8 (Si-*i*-Bu), ca. −80 (Si-styryl)	498
-Ph_7, -$(CH_2)_3OH$	−64.06, −77.02	192, 193
-Ph_7, -$(CH_2)_3Cl$	−64.06, −77.02	192

[a] $SiMe_2$ signal not observed.

Detailed solid-state ^{13}C and ^{29}Si NMR studies of epoxy networks reinforced with POSS cages show that the POSS cages aggregate in domains ranging from 1 to 20 nm across depending on the nanocomposite composition. Most of these results are consistent with the domain size measured by SAXS or electron microscopy, but for one example the domain size measured by NMR spectroscopy was much smaller suggesting the presence of “broken domains”.[480] Solid-state ^{29}Si NMR has also been used to determine the degree of substitution in the reaction between $T_8(OSnMe_3)_8$ and chlorosilanes to give materials in which the POSS cages are cross-linked by Si−O−Si linkages.[481] The solid-state ^{29}Si NMR signal from $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ in the presence of Pd nanoparticles is broadened, but the chemical shift is not significantly altered indicating that the cage is not cleaved by the particles and that there is a weak interaction between the POSS species and the Pd. The supported Pd particles can be used for the catalytic dehydrogenation of 1,4-diphenylbutadiyne.[482]

Solid-state ^{13}C NMR spectra have been recorded for few T_8 derivatives, but the spectrum of T_8Me_8 shows a single sharp resonance at −4.01 ppm[197] and the solid-state ^{13}C NMR spectrum of $T_8(CH{=}CH_2)_8$ has been found to be useful for setting up the Hartmann−Hahn conditions for magic angle spinning $^{29}Si \rightarrow {}^{13}C$ cross-polarization transfer, the $^1J_{Si-C}$ coupling constant being found to be 136 Hz.[499] The solid-state ^{13}C spectra for $T_8[OSiMe_2(CH_2)_3CN]_8$ and $T_8(SiMe_2$-*t*-Bu$)_8$ have also been recorded.[201,238] Solid-state ^{13}C spectra of star polymers comprising a T_8 core and poly(ε-caprolactone) substituents show that they can form inclusion complexes with cyclodextrins.[261] A comparison of the solid-state ^{13}C NMR spectrum of $T_8(i\text{-}Bu)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$ and its copolymers with vinylpyrrolidine demonstrate that the POSS cage is indeed incorporated into the polymer.[498] The solid-

Table 24. Selected Structural Data for T_8R_8 Compounds (2003−2009) together with Some Earlier Data for Comparison

R or compound formula	Si−O (Å) within T_8 cage[a]		Si−O−Si (deg) within T_8 cage[a]		refs
	range	avg	range	avg	
-H	1.6168(11)−1.6195(7)	1.618	147.49(6)−147.60(7)	147.54	504
-H[b]	1.6143(3)	[b]	147.9(2)	[b]	429
-Cl	1.595(4)−1.610(4)	1.601	148.0(3)−148.8(3)	148.4	505
-CH_3	1.610(2)−1.617(2)	1.614	148.9(1)−149.6(5)	149.3	506
-CH_3[b]	1.6174(5)	[b]	148.9(2)	[b]	429
-CH_3[c]	1.612(1)−1.618(1)	1.615	149.6(1)	149.6	198
-$CH{=}CH_2$	1.577−1.623	1.600	148.58 and 151.58	150.08	507
-$CH{=}CH_2$	1.596(6)−1.617(7)	1.605	150.0(5) and 150.5(5)	150.3	508
-$CH{=}CH_2$[d]	1.6184(13)−1.6295(13)	1.6232	138.67(9)−143.06(9)	141.06	203
-$(CH_2)_2O(CH_2)_2Cl$	1.605(3)−1.632(3)	1.616	142.9(2)−159.3(3)	149.2	69, 208
-$(CH_2)_2Br$	1.603(10)−1.629(10)	1.615	145.9(7)−152.8(7)	149.2	391
-$(CH_2)_2CO_2Me$	1.601(10)−1.650(10)	1.627	143.7(8)−148.7(8)	148.2	391
-$(CH_2)_3C_6H_4$-4-OMe	1.604(5)−1.627(4)	1.615	145.6(3)−156.6(3)	149.5	96
-$(CH_2)_3Cl$	1.606(4)−1.631(4)	1.619	147.7(3)−151.5(3)	149.8	119
$T_8(CH_2CH_2CF_3)_8\cdot THF$	1.6164(10)−1.6232(10)	1.6185	144.29(7)−154.95(8)	148.69	173
-$CH_2CH{=}CH_2$	1.607−1.618	[e]	145.0−152.7	[e]	90
-CH_2CHMe_2	1.611(5)−1.622(5)	1.617	143.7(3)−152.3(3)	149.6	63
-$CH{=}CHPh$	1.598(4)−1.627(3)	1.614	142.52(17)−153.15(19)	148.69	385
	1.617(2)−1.626(2)	1.621	145.89(12)−150.31(15)	147.55	
-$CH{=}CHCH_2SiMe_3$	1.620(3)−1.629(3)	1.624	142.43(17)−154.58(18)	148.75	385
$\{Si_8O_{12}[(CH_2)_3NH_3]_8\}[ZnCl_4]_{2.8}Cl_{2.4}$	1.605(6)−1.636(7)	1.618	144.0(5)−157.2(5)	149.3	110
-$(CH_2)_2(CF_2)_3CF_3$	1.6150(17)−1.6212(18)	1.6188	146.52(10)−150.81(11)	148.53	125
-$(CH_2)_2CMe_2CH_2CO_2Me$	1.611(2)−1.632(2)	1.621	139.63(14)−155.88(15)	149.14	63
	1.613(2)−1.628(2)	1.620	143.48(14)−153.24(14)	148.24	
-$(CH_2)_2(CF_2)_7CF_3$	1.614(2)−1.626(2)	1.620	144.30(15)−149.94(14)	147.39	125
	1.615(2)−1.627(2)	1.620	141.80(14)−150.81(15)	147.44	
-*n*-Oct	1.615(3)−1.628(3)	1.621	141.1(2)−159.8(2)	149.3	96
-*c*-C_5H_9	1.615(3)−1.630(3)	1.623	140.5(2)−156.04(19)	148.5	63
-Cy	1.586(6)−1.635(6)	1.603	149.9(4)−151.7(4)	150.8	96
-Cy	1.539(2)−1.6705(17)	1.613	140.76(8)−160.68(11)	150.52	96
-Cy	1.613(2)−1.625(2)	1.618	144.82(16)−151.82(17)	149.32	96
$T_8Ph_8\cdot Me_2CO$	1.607−1.617	1.612	144.63−151.53	149.21	509
$T_8Ph_8\cdot C_5H_4N\cdot C_6H_4$-1,2-$Cl_2$	1.602−1.624	1.613	144.09−155.68	149.17	510
-C_6H_5[d]	1.6199(15)−1.6294(16)	1.6241	138.57(10)−143.87(10)	141.18	202
-C_6H_4-2-Me	1.6119(15)−1.6257(15)	1.6188	139.01(11)−163.34(11)	149.22	511
-C_6H_4-4-Me	1.610(2)−1.629(4)	1.616	144.0(2)−151.60(17)	148.0	512
-C_6H_4-4-Me[d]	1.6234(19)−1.628(2)	1.625	140.50(13)−142.47(13)	141.17	203
-C_6H_4-4-CH_2Cl	1.600(4)−1.634(4)	1.619	139.0(3)−164.3(3)	148.8	512
$T_8(C_6H_4\text{-4-I})_8\cdot EtOAc$	1.603(4)−1.616(4)	1.610	144.7(4)−152.0(3)	148.0	317
-$OSi(CH{=}CH_2)_3$[f]	1.588(3)−1.617(3)	1.608	142.8(2)−151.8(2)	148.5	503
-$OSi(CH{=}CH_2)_3$[g]	1.597(7)−1.617(7)	1.607	146.6(4)−150.7(3)	148.7	503
-$OSnMe_3$	1.580(3)−1.629(4)	1.608	148.8(2)−161.2(2)	149.3	402, 403
$T_8(OSnMe_3)_8\cdot 4H_2O$	1.5872(16)−1.6277(17)	1.6121	136.35(10)−172.13(12)	149.50	402, 403
$T_8(OTiClCp_2)_8\cdot 3CH_2Cl_2$	1.579(2)−1.612(2)	1.601	145.36(14)−151.21(16)	148.70	402
$[NMe_3CH_2CH_2OH]_8[T_8O_8]\cdot 24H_2O$	1.614(3)−1.633(3)	1.625	144.70(17)−148.03(17)	146.60	195
-$SiMe_2$-*t*-Bu	1.620(7)−1.630(6)	1.625	148.5(4)−152.2(4)	150.2	201
-$Co(CO)_4$	1.610(4)−1.637(4)	1.623	147.6(2)−154.1(3)	150.8	513

[a] Bond distances, angles, and ESDs determined using PLATON[515] on data obtained from the CCDC (version 5.30).[516] [b] Data from GED study, symmetry leads to single values for Si−O bond lengths and Si−O−Si angles. [c] Data from PXRD study. [d] Anionic endohedral fluoride with $[NBu_4]^+$ cation. [e] Bond lengths and angles from a table in the paper. [f] Crystallized from CCl_4. [g] Crystallized from toluene.

state ^1H and ^2H NMR spectra for T_8Et_8 and its partially deuterated derivatives have been recorded and are consistent with X-ray and calorimetry measurements showing that phase changes typical of plastic crystals occur, a rhombohedral phase being present at high temperature and a triclinic one at low temperature.[390]

3.4. X-ray Diffraction Studies

3.4.1. Single-Crystal Structures

Over 100 T_8 derivatives have had their structures determined by X-ray crystallography; early structures and comparisons with other silsesquioxane structures have been reviewed.[1] Selected structural data for recently determined structures of symmetrically substituted T_8R_8 compounds are given in Table 24 and those for T_8R_7R' compounds in Table 25, showing both the range of compounds characterized and bond lengths and angles for the POSS core. The Si−O bond lengths are generally unexceptional and most fall in the range 1.60−1.63 Å, as found in other siloxanes.[500] The Si−O−Si angles in the POSS core may vary significantly within a single structure, for example from 136.35° to 172.13° in $T_8(OSnMe_3)_8\cdot 4H_2O$[402,403] and from 140.76° to 160.68° in one of the structures of T_8Cy_8,[96] but despite this, the average values fall in the narrow range of ca. 147.5°−150.8°. A plot of the nonbonded Si···Si distance versus the Si−O−Si angle for a wide range of T_8 derivatives shows that the majority of bond angles fall in the range 140°−160° and distances in the range 3.05−3.2 Å, the most notable outlier on the plot being $T_8(OSnMe_3)_8\cdot 4H_2O$ as mentioned above (Figure 2).[402] EXAFS and XANES data have been collected on the metallosilicates derived from reaction of $T_8(OSnMe_3)_8$ with metal chlorides.[501] The wide ranging angles are due to the propensity of many of the structures containing larger, more flexible substituents to deform and adopt conformations that minimize the spaces that would occur in the lattice if they

Table 25. Selected Structural Data for Miscellaneous T_8 Derivatives

compound	Si−O (Å)[a] range	Si−O (Å)[a] average	Si−O−Si (deg)[a] range	Si−O−Si (deg)[a] average	refs
$T_8(CH_2CH_2CF_3)_7Me$	1.584(14)−1.633(18)	1.611	144.9(3)−152.9(4)	148.6	173
137·$^1/_2$*n*-C_6H_{14}	1.606(6)−1.634(6)	1.618	145.6(4)−154.2(4)	148.9	179
	1.606(5)−1.635(7)	1.616	147.2(4)−152.2(4)	149.3	
139·$2^1/_2CH_2Cl_2$	1.608(3)−1.626(3)	1.616	144.55(19)−151.8(2)	149.2	179
$[T_8(c\text{-}C_5H_9)_7]_2Mo(\equiv CEt)[N(t\text{-}Bu)(2,6\text{-}Me_2\text{-}C_6H_3)]_2$	1.43(3)−1.52(3)	1.63	127.6(16)−169(3)	144	414
	1.52(3)−1.82(3)	1.63	137.8(16)−168.2(18)	151.5	
$[T_8(c\text{-}C_5H_9)_7O]Mo(CH_2\text{-}t\text{-}Bu)_3(=NH)$	1.615(2)−1.6242(19)	1.619	145.48(12)−152.15(13)	149.09	412
$[T_8(c\text{-}C_5H_9)_7O]_2Mn(TMEDA)_2$	1.608(2)−1.641(3)	1.621	143.95(17)−152.58(17)	148.76	411
149	1.584(9)−1.656(10)	1.616	145.1(6)−153.6(6)	149.0	355
	1.603(7)−1.648(9)	1.621	140.6(4)−156.1(5)	148.2	
12	1.596(3)−1.632(3)	1.619	142.8(2)−161.3(2)	149.0	179
$(T_8Cy_7)_2O$	1.6050(19)−1.6250(17)	1.6172	143.37(11)−157.73(14)	149.19	308
	1.6057(19)−1.6291(15)	1.6201	140.54(11)−160.91(14)	148.68	
$(T_8Cy_7)_2O$	1.6060(15)−1.6314(14)	1.6213	137.88(9)−168.09(11)	148.53	307
	1.6056(15)−1.6293(12)	1.6190	142.43(9)−157.89(10)	148.93	
$[T_8Cy_7(\mu\text{-}O)Re(CO)_4]_2\cdot 3CH_2Cl_2$	1.594(8)−1.638(8)	1.613	138.5(5)−164.2(5)	148.5	417
	1.589(7)−1.640(7)	1.613	139.1(5)−160.8(5)	149.0	
$[T_8Cy_7(\mu\text{-}O)Re(CO)_4]_2\cdot n\text{-}C_5H_{12}$[b]					417
T_8Cy_6-*p*-Me_2	1.585(11)−1.617(10)	1.605	149.1(8)−151.9(7)	150.5	516
T_8Cy_6-*p*-$(CH_2CH=CH_2)_2$	1.590(5)−1.623(6)	1.603	151.0(4) and 149.3(4)	150.2	517

[a] Bond distances, angles, and ESDs determined using PLATON[515] on data obtained from the CCDC (version 5.30).[516] [b] No coordinates presented in CCDC data for this structure, nor details within ref 417.

were to point ideally toward the vertices of a cube. The larger POSS molecules distort either to form a disk-like structure through substituents on two opposite faces of the core closing up toward each other or to give a rod-like geometry through the substituents around a pair of opposite faces closing up around these faces. Examples of these deformations are discussed in more detail in ref 1.

X-ray diffraction studies on $T_8(CH_2CH_2R)_8$ [R = CF_3, $(CF_2)_3CF_3$, or $(CF_2)_7CF_3$] show that the CF_3 derivative[125,173] has the substituents at the POSS core radiating diagonally from the Si atoms but that the compounds with longer chains have a near parallel orientation for the chains (Figure 3). POSS derivatives with flexible substituents are also prone to disorder within the lattice leading to poor quality X-ray data being obtained, sometimes such that only a T_8 core is located with any certainty.[391] The unit cell data for a range of alkyl-substituted POSS species have been tabulated and shows that packing of the molecules within hexagonal planes is closer than the separation between the planes. The *c*/*a* ratio is roughly constant at ca. 1.03, despite variation in the size and nature of the alkyl groups including both compounds of the type T_8R_8 and T_8R_7R', implying a similar molecular arrangement for such compounds. However, the parent silane T_8H_8 has a *c*/*a* ratio of 1.68, and aryl-substituted species do not seem to follow this trend.[502] XRD data for materials prepared by cohydrolysis of $H_2N(CH_2)_2Si(OEt)_3$, *n*-octadecylisocyanate, and phthalic anhydride are consistent with either rhombohedral-centered hexagonal or primitive hexagonal lattices with unit cell dimensions similar to those for T_8 POSS compounds containing shorter substituents. These smaller than expected unit cells are thought to be due to significant interdigitation of the substituents.[326] A single-crystal X-ray study of partially deuterated T_8Et_8 has been conducted over the temperature range 290−110 K. Four phases are observed, one rhombohedral at 290 K and three triclinic at 250, 230, and 210 K.[390] The density of all of the phases of T_8Et_8 is higher than that of $T_8(n\text{-}Pr)_8$, which is thought to be due to the shorter alkyl chain enabling a closer packing of molecules.[390] The crystal structure of $T_8[OSi(CH=CH_2)_3]_8$ differs depending on the solvent used for crystallization; from CCl_4, a tetragonal cell containing four molecules is found, but from toluene, tetragonal crystals with cells containing one molecule are formed.[503]

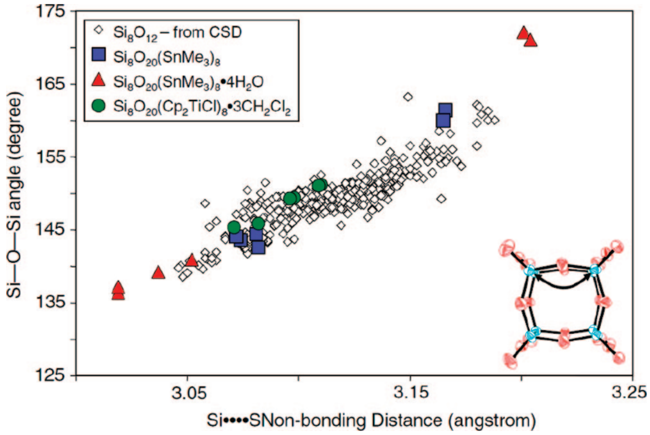


Figure 2. Plot of Si−O−Si angles as a function of nonbonding Si···Si distances for selected T_8R_8 and $T_8(OR)_8$. Reprinted from Clark, J. C.; Saengkerdsub, S.; Eldridge, G. T.; Campana, C.; Barnes, C. E. Synthesis and structure of functional spherosilicate building block molecules for materials synthesis. *J. Organomet. Chem.* **2006**, *691*, 3213−3222,[402] Copyright 2006, with permission from Elsevier.

Much has been made of the potential of POSS derivatives as nanosized building blocks for the construction of more elaborate materials. This potential derives from both the high symmetry of the cage and the size of the cage with Si···Si distances being ca. 3.11, 4.40, and 5.39 Å for distances along an edge, across a face, and across the body diagonal of a typical cage. These distances vary little over a wide range of POSS derivatives, and their values have been tabulated for comparison.[96] A notable subset of the structures in Table 24 are those containing an endohedral fluoride ion, in which the Si−O−Si angles are close to 141.2°. The presence of the fluoride causes the POSS framework to contract slightly, the low value of the Si−O−Si angles presumably being due to repulsions between the fluoride and the cage oxygen atoms.[203]

The unit cell parameters for T_8H_8, $T_8(c\text{-}C_5H_9)_8$, and $T_8H_7n\text{-}C_6H_{13}$ have been calculated and give results in close

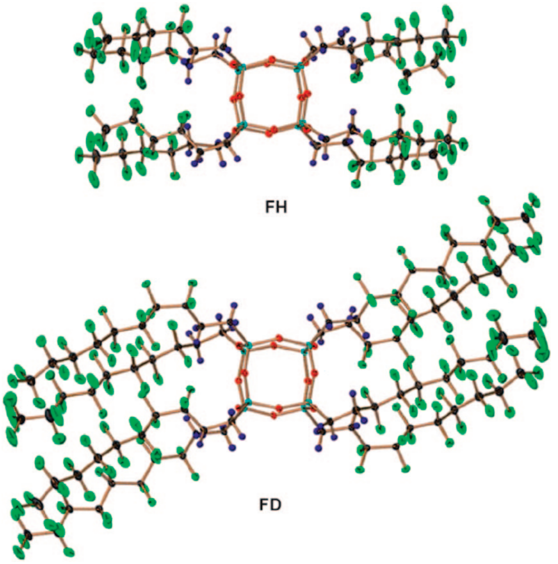


Figure 3. Views of the single-crystal X-ray structures of $T_8[(CH_2)_2(CF_2)_3CF_3]_8$ (FH) and $T_8[(CH_2)_2(CF_2)_7CF_3]_8$ (FD) showing near-parallel orientation of the fluoroalkyl substituents. Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, B. D. Fluorinated polyhedral oligomeric silsesquioxanes (F-POSS). *Angew. Chem., Int. Ed.* **2008**, *47*, 4137−4140.[125] Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

agreement with the experimentally determined values.[433,439] The solid-state structure of T_8H_7n-C_6H_{13} is bilayered due to the preference for hydrocarbon−hydrocarbon and POSS−POSS interactions rather than hydrocarbon−POSS interactions.[439] This tendency for POSS−POSS interactions is also often found in more complicated polymeric materials (see WAXS and SAXS studies in section 3.4.2) and is also found to occur in molecular simulations of blends of $T_8(c\text{-}C_5H_9)_8$ and oligoethylene.[518] The melting behavior for T_8H_7n-C_6H_{13} has also been studied, a melting point of 430 K being calculated using molecular dynamics simulations.[439]

3.4.2. Diffraction Studies on Powders, Thin Films, and Solutions

A variety of diffraction techniques applicable to powders and films have been extensively used to determine the nature of POSS particles and domains in nanocomposites, polymers, blends, and other materials. The similarity between features in the XRD pattern of monomeric POSS species and those in polymeric materials can thus be used to show that the POSS cage has remained intact during the polymerization process. These studies are usually based on knowledge of the diffraction pattern for the discrete molecular species used as monomers or fillers in materials synthesis. Many reports of such data make no comment about the details of the XRD pattern, only that there are common features attributable to the POSS species in spectra recorded both before and after processing. Here, again, the emphasis of this review is on data for molecular species, rather than the polymers formed, which have been the subject of several reviews.[3−7,9−14,28,29,36,42,43,46,50−52]

There are several features that are commonly seen in many of the XRD spectra of POSS-containing compounds. Diffraction peaks at 2θ values of ca. 8.3°, 18.9°, and 24.4° corresponding to *d*-spacings of ca. 11, 5, and 3 Å are typical and have been attributed to the overall dimensions of the POSS molecule, the body diagonal of the POSS cage, and the distance between opposite Si_4O_4 faces, respectively.[142]

It should be noted that the ideal cubic nature of the POSS cage is often distorted (see section 3.4.1) and that the body diagonal, face diagonal, and face-to-face distances across the POSS cage vary significantly, and thus the reported positions of diffraction peaks for these parameters can vary significantly. Detailed comparisons between XRD data reports are also complicated by *d*-spacing values sometimes being omitted, together with a lack of reporting of the wavelength of the radiation used, although this is commonly Cu Kα with a wavelength of 1.542 Å. Waddon and Coughlin[502] have provided a detailed analysis of the diffraction patterns of several alkyl-substituted POSS compounds, including indexing the reflections, and have shown that they can be regarded as spheres that pack in a hexagonal ABCA fashion to give a hexagonal or rhomobohedral cell and that they give structures with similar lattice parameter ratios (see section 3.4.1).

Although the rhombohedral nature of T_8 POSS crystal structures is mentioned in many publications, often referring back to the work of Waddon and Coughlin, it should be noted that an analysis of the 119 single-crystal structures deposited in the Cambridge Crystallographic Database reveals that almost half (55) are in fact triclinic, 26 are monoclinic, and only 23 are rhombohedral. The *apparent* preponderance of rhombohedral structures commonly cited in the literature probably derives largely from the fact that several of the most widely studied T_8 POSS deviatives such as $T_8(CH{=}CH_2)_8$[507,508] and $T_8(OSiMe_2H)_8$[519,520] do have rhombohedral structures and that several other simple, relatively frequently used compounds such as T_8Et_8 and T_8Cy_8 can be found in rhombohedral,[96,521,522] triclinic,[96,523] and tetragonal[96] modifications.

3.4.2.1. T_8R_8 Compounds. The XRD pattern for T_8Me_8 has been determined experimentally by X-ray powder methods and by electron diffraction and computationally and used for a Rietveld analysis of the structure showing a rhombohedral crystalline structure.[76,198,524] This is in line with the many other POSS species also having been found to contain a rhombohedral or hexagonal cell, see preceding paragraph. WAXS has been used to show that the nanocrystal size of T_8Me_8 in nanocomposites with isotactic polypropylene is ca. 35 ± 3 nm,[525] while in ethylene−propylene copolymers the crystal size is ca. 50 nm,[526] and in HDPE the size is 25 nm.[527] The X-ray diffraction pattern of T_8Me_8 has a dominant characteristic peak at ca. $2\theta = 10.8°$,[197] which is also present in spectra of POSS polyethylene nanocomposites containing over 1% by weight POSS, indicating that the T_8Me_8 crystallizes when dispersed in the polyethylene matrix.[524,528,529] The powder X-ray diffraction pattern for T_8H_8 has been shown to have characteristic peaks at $2\theta = 7.9°$, 8.4°, 11.04°, 18.9°, and 24.13°[122] and at $2\theta = 12.5°$, 25.3°, and 26.1°.[484]

The temperature dependence of the WAXD pattern for T_8Me_8 has been studied from 26 to 200 °C with little change being seen over this range. The peaks are still strong and distinct when the POSS is blended with ethylene−propylene copolymer[526] and in nanocomposites with isotactic polypropylene.[525] The XRD patterns for both T_8Me_8 and T_8Et_8 for cubic crystalline samples show sharp peaks, whereas spherical particles that are precursors to cubic crystals in the growth of T_8Me_8 show broad features.[62]

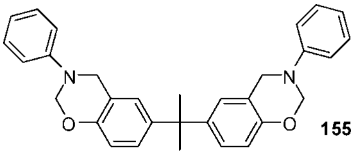
Small-angle neutron scattering patterns for $T_8(n\text{-}Pr)_8$ in toluene solutions of polystyrene show that there is a tendency for POSS-rich domains to form in which polymer is excluded.[87] The XRD pattern for $T_8(i\text{-}Bu)_8$ shows two characteristic peaks at $2\theta = 8.0°$ and $8.8°$,[530] while WAXD shows it to be crystalline with numerous sharp peaks, for example, at ca. $2\theta = 7.96°$, $8.84°$, and $10.86°$ corresponding to *d*-spacings of 11.1, 10.0, and 8.1 Å, which are also seen in blends with poly(methyl methacrylate) and with phenolic resin,[528,531,532] in blends with silicone rubber,[533] and also in POSS–epoxy-cyanate composites showing that the POSS is phase segregated and not bonded to the resin.[534] The WAXD peaks for T_8Cy_8 corresponding to *d*-spacings of 11.6, 8.7, 7.8, and 5.0 Å are also seen in blends with poly(methyl methacrylate),[531] and SEM has been used to show the presence of phase-separated T_8Cy_8 crystallites of up to micrometer dimensions when blended with poly(methyl methacrylate).[535]

WAXD diffraction patterns for $T_8(i\text{-Oct})_8$, which is sold commercially as a viscous liquid mixture including other cage sizes, have been reported,[528] and the XRD pattern of $T_8(i\text{-Oct})_8$ in polysiloxane composites shows sharp peaks at $2\theta = 7.9°$ and $8.8°$, which are also present in the pure compound and so are consistent with the presence of POSS crystallites in the matrix.[536] These peaks are present in the pure compound up to 180 °C but broaden significantly at 230 °C as the material becomes amorphous.[537] The XRD pattern for $T_8(CH{=}CH_2)_8$ shows several sharp peaks at $2\theta = 9.8°$, $20.1°$, and $29.9°$,[538,539] and the powder X-ray pattern for $T_8(CH_2CH{=}CH_2)_8$ shows the compound to be polycrystalline but crystals suitable for single-crystal X-ray studies have proven hard to obtain.[90] The XRD pattern for as-prepared $T_8(CH{=}CHPh)_8$ shows numerous relatively sharp peaks, but after heating it shows a pattern indicative of an amorphous structure, suggesting that polymerization has occurred.[322] The XRD of $T_8(CH_2CH_2Ph)_8$ shows a single intense peak at $2\theta = 7.3°$, corresponding to a *d*-spacing of 12.1 Å.[540]

The XRD pattern of $T_8[(CH_2)_3NH_2]_8$ shows numerous sharp peaks indicative of the crystalline nature of the compound that are consistent with a rhombohedral unit cell with $a = 11.57$ Å and $\alpha = 95.1°$.[98,101–103] Wide-angle X-ray diffraction has also been used to show that the presence of POSS cages, derived from $T_8[(CH_2)_3OH]_8$, as cores in star poly(caprolactone) materials did not alter the crystalline structure of the polymer.[116] The WAXD pattern of mixtures of $T_n[(CH_2)_3OC(O)C({=}CH_2)Me]_n$ and of its hydrogenated derivatives $T_n[(CH_2)_3OC(O)CHMe_2]_n$ ($n = 8$, 10, 12, and 14) show similar features and have peaks at $2\theta = 6.56°$ and $19.3°$ for the acrylate and $2\theta = 6.40°$ and $19.3°$ for the reduced compound.[398] The XRD powder pattern for $T_8[(CH_2)_3SH]_8$ shows peaks at $2\theta = 8.3°$, $11.1°$, $12.1°$, and $19.3°$ corresponding to *d*-spacings of 10.7, 8.0, 7.3, and 4.6 Å.[541] The X-ray powder pattern for $T_8[(CH_2)_3Cl]_8$ is characteristic of a rhombohedral structure,[103] and the powder XRD pattern of $T_8[(CH_2)_3I]_8$ shows a sharp diffraction pattern between 20° and 30°, aspects of which are still apparent when $T_8[(CH_2)_3I]_8$ is polymerized with 2-ethynylpyridine, indicating that the polyacetylene gel formed contains crystallinity derived from the POSS sections.[542]

The WAXD pattern for T_8Ph_8 shows sharp diffraction peaks as expected for a highly crystalline compound,[543] but the WAXD pattern for a mixture of the isomers of **94** gives a broad peak at $2\theta = 5.3°$ and a very broad amorphous halo at $2\theta = 20°$, the broadening being due to the different isomers present.[133] PXRD of **94** shows diffraction peaks at $2\theta = 5.64°$ and $19.44°$ with *d*-spacing of 1.57 and 0.46 nm attributable to the size of the POSS molecules and the presence of different isomers (*o*, *m*, *p*), respectively.[370] The XRD pattern for $T_8(C_6H_4NH_2)_8$ has a peak at $2\theta = 7.8°$ corresponding to a *d*-spacing of 10 Å, but on reaction with 4-(trifluorovinyloxy)benzoyl chloride the long-range order is lost.[369] Similarly, a clear peak recorded at $2\theta = 8°$ in the XRD pattern of $T_8(C_6H_4NH_2)_8$, indicative of crystallinity, is missing when it is used to form nanocomposites with bismaleimide–diamine resins.[331] Similar effects are seen for $T_8(C_6H_4NH_2)_8$ in cyanate ester composites[544] and in $T_8(C_6H_4NH_2)_8$ used in formation of phenolic resins, although in this case a broad peak at $2\theta = 5.8°$ does indicate some order in the resin.[545] SAXS and TEM studies of $[NMe_3C_{16}H_{33}][T_8(C_6H_4SO_3)_8]$ show the formation of a self-assembled layer structure with a *d*-spacing of 4.53 nm.[340] The XRD pattern for the benzoxazinyl derivative **70** exhibits a single crystalline peak at $2\theta = 5.3°$, but unlike the case with many polymers containing POSS fragments, this peak is lost when the compound is copolymerized with benzoxazine derivative **155** (Chart 28).[546]

Chart 28

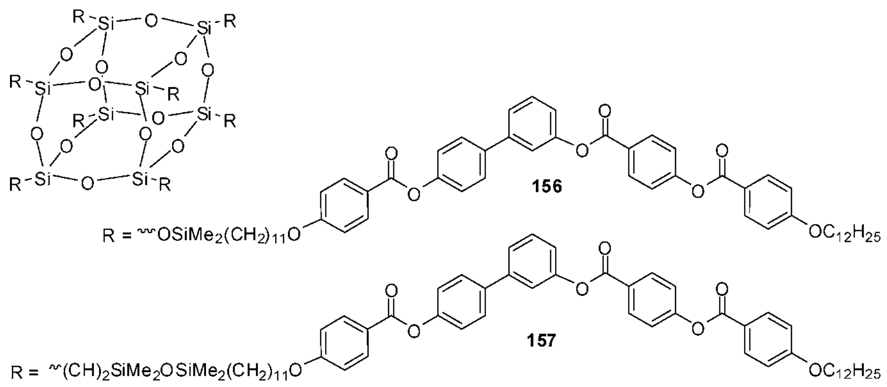


155

Few compounds containing alkoxy substituents at the corners of a T_8 cube have been prepared, but the XRD pattern of compound **6** has been reported to show intense sharp diffraction peaks at 6.1°, 12.2°, and 23.8° corresponding to *d*-spacings of 14.48, 7.25, and 3.72 Å.[145] The XRD pattern for $T_8(OSiMe_2H)_8$ shows several sharp peaks, for example, at ca. $2\theta = 8.3°$, $18.9°$, and $24.4°$ corresponding to *d*-spacings of 11, 5, and 3 Å and appropriate to a rhombohedral crystal structure. The 3 Å spacing is attributable to the distance between opposite Si_4O_4 faces of the POSS core, the 5 Å spacing attributable to the POSS cage diagonal distance, while the 11 Å spacing is related to the size of the POSS molecule.[142,226,237,547] WAXS studies on $T_8(OSiMe_2H)_8$[263,548] and $T_8[OSiMe_2(CH_2)_4CH(O)CH_2]_8$[263] show the former to be crystalline, with a rhombohedral unit, whereas in the latter the alkyl chains are thought to disrupt the lattice and a pattern attributable to an amorphous material is observed. WAXD studies of PEG derivatives of $T_8(OSiMe_2H)_8$ provide evidence for the presence of small disordered POSS domains,[547] but sharp diffraction peaks due to POSS cages are not observed when it is incorporated into poly(dimethylsiloxane urethane) nanocomposite membranes.[549] Although the powder X-ray diffraction pattern for $T_8(OSiMe_2H)_8$ shows the presence of crystalline material, the related acrylonitrile derivative $T_8[OSiMe_2(CH_2)_3CN]_8$ shows a loss of crystallinity,[238] as does **69**, which shows only broad peaks at $2\theta = 6.0°$ and $21.01°$,[122] while the WAXS patterns for both $T_8[OSiMe_2(CH_2)_3O(CH_2)_2CH_3]_8$ and $T_8[OSiMe_2(CH_2)_3OCF_2CHFCF_3]_8$ show that the compounds are amorphous.[244] Loss of crystallinity has also been seen when $T_8[OSiMe_2(CH_2)_2\text{-}4\text{-}C_6H_4]_8$ groups are used to terminate light-emitting polyfluorene derivatives via hydrosilylation reactions.[210] However, loss of POSS crystallinity in light-emitting materials does not necessarily occur, see section 4.4.2.

Layers of $T_8(OSiMe_3)_8$ deposited onto Si or other supports by vapor deposition were found by X-ray diffraction to be ideally orientated polycrystalline films, aligned in the [001]

Chart 29

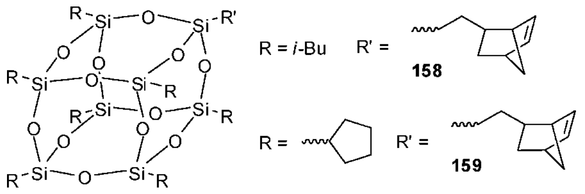


direction in the space group $P\bar{1}$.[550,551] The XRD pattern for $T_8[OSiMe_2(CH_2)_3OH]_8$ shows it to be highly crystalline, but on incorporation into a POSS−polyimide film, the crystallinity is lost.[242,552] The X-ray powder pattern for freshly prepared **17** also shows a high degree of crystallinity, but after the material is melted and solidified, it becomes glassy and amorphous.[233] The X-ray powder pattern for **16** shows a pattern characteristic of a rhombohedral structure,[479] and the powder XRD pattern for $T_8[OSi(OSiMe_3)_3]_8$ shows reflections corresponding to *d*-spacings of 15.3 and 13.1 Å.[293] WAXD studies of **156** at different temperatures show diffractions corresponding to *d*-spacings of 4.7, 7.3, 8.0, and 10.8 Å due to the crystalline hexagonal POSS core and that on cooling from the melt, a change from isotropic to smectic phase occurs at 145 °C; the DSC trace for **156** also shows several transitions.[267] WAXD patterns for **157** (Chart 29) also indicate the presence of a smectic C phase.[267]

3.4.2.2. T_8R_7R' Compounds. The use of diffraction techniques in studying T_8R_7R' compounds is extensive. As for T_8R_8 compounds, these studies concentrate on whether the POSS cage remains intact during polymerization or other processing and whether domains of POSS cages are formed. A peak in X-ray diffraction patterns at ca. $2\theta = 7.9°-8.3°$ is often observed in these compounds and can be attributed to the overall dimensions of the POSS molecule, see section 3.4.2. For a detailed analysis of the assignment of individual reflections in XRD patterns, see ref 502.

The WAXD patterns for a range of ethylene−propylene−POSS polymers containing T_8Et_7 pendant groups shows POSS domains 1.1 nm in size corresponding to only one POSS unit per domain.[189] The X-ray powder patterns for Langmuir−Blodgett films of poly{*N*-dodecylacrylamide-*co*-[3-methacryloxypropylhepta(trifluoropropyl]POSS} and its heptaphenyl analogue show an ordered periodic structure and an average center-to-center for the POSS cages of 1.5 nm.[553] The peaks in the powder X-ray diffraction pattern of $T_8(i\text{-Bu})_7(CH_2)_2C_6H_4CH_2Cl$ at $2\theta = 8.3°$ and 11.0° are characteristic of the POSS hexagonal structure. These peaks are retained when the POSS compound is tethered to a dimethylimidazolium center and also when this species is subsequently exchanged into a montmorillonite clay, again demonstrating the propensity of POSS species to self-assemble into crystalline domains.[342] In a similar fashion, a characteristic broad peak at ca. 7.2°, attributable to aggregation of the POSS, in the diffraction pattern of $T_8(i\text{-Oct})_7(CH_2)_3NH_2$ is still observable when this compound is exchanged into sodium montmorillonite, where it modifies the interlayer spacing.[554] However, the sharp diffration peaks found for pure $T_8(i\text{-Bu})_7CH_2CH{=}CH_2$ are not found in a nanocomposite formed by melt compounding it with cycloolefin copolymers.[555]

Chart 30



The solid-state structure of compound **101** has been investigated in detail by 2D SAXS, WAXD, and TEM, both as a single compound and as a blend with $T_8(i\text{-Bu})_7(CH_2)_3OH$. The phenylene moieties in the pure compound form lamellar bilayers that fit between the adjacent POSS cages, and the compound has a rhombohedral unit cell of dimensions $a = 1.63$ nm, $c = 1.73$ nm, and $\alpha = 120°$. The POSS polyhedra stack in a four layer lamella with an ABCA arrangement similar to the rhombohedral arrangement in simple POSS single-crystal structures.[381,382] For $T_8(i\text{-Bu})_7(CH_2)_3OC({=}O)(CH_2)_{10}Br$, the rhombohedral unit cell dimensions are $a = 1.63$ nm, $c = 1.71$ nm, and $\alpha = 120°$, and for $T_8(i\text{-Bu})_7(CH_2)_3OH$, there are two component crystals, the major one having a rhombohedral cell with unit dimensions $a = 1.65$ nm, $c = 1.75$ nm, and $\alpha = 120°$.[381,382]

WAXS for $T_8(i\text{-Bu})_7OSiMe_2(CH_2)_3OCH_2CEt_3$ has its most intense reflection at $2\theta = 8.1°$ indexed as the (101) reflection of the POSS, and hexagonal cell parameters calculated at $a = 16.30$ and $c = 17.24$ Å.[556] The WAXD patterns for a range of ethylene−propylene−POSS polymers containing pendant $T_8(i\text{-Bu})_7$ groups shows POSS domains from 1.3 to 2.7 nm in size corresponding to one to two POSS units per domain.[189] XRD of polyethylene chains with end-tethered $T_8(i\text{-Bu})_7$ substituents shows a broad and weak diffraction peak at ca. 9.5° (*d*-spacing of ca. 10.8 Å) attributed to aggregation of the POSS nanoparticles to form crystallites but, surprisingly, none of the sharp peaks usually observed for the POSS cage itself.[404] WAXD of **158** (Chart 30) shows a sharp peak at $2\theta = 8.2°$ corresponding to a *d*-spacing of 10.8 Å.[557,558] The WAXS pattern of $T_8(i\text{-Bu})_7(CH_2)_3NH_2$ has been recorded for comparison with POSS-modified polyamide-6 materials,[559] and the WAXS pattern of $T_8(i\text{-Bu})_7(CH_2)_3NHCH_2CH_2NH_2$ shows well-defined reflections at $2\theta = 8.1°$, 10.8°, 12.1°, and 18.8°, which are not found in polyurethane nanocomposites derived from it.[560,561]

The WAXD pattern of $T_8(i\text{-Bu})_7(CH_2)_3OC({=}O)C({=}CH_2)Me$ shows strong sharp peaks at $2\theta = 9.5°$, 12.9°, and 22.4° corresponding to *d*-spacings of 10.8, 8.0, and 4.6 Å;[562] these are largely lost on incorporation of the POSS cages into dimethacrylate,[563,564] isobornyl methacrylate, and di(ethylene glycol) dimethacrylate networks,[565] but at high loadings in copolymers with poly(octafluoropentyl acrylate), a peak at ca. $2\theta = 8°$ is prominent and indicative of POSS aggregation.[566] In contrast, the WAXS pattern of $T_8(i\text{-Oct})_7(CH_2)_3OC(=O)C(=CH_2)Me$ is broad as a pure compound and shows no aggregation in copolymers.[566] The WAXS pattern of $T_8(i\text{-Bu})_7(CH_2)_3OC(=O)C(=CH_2)Me$ has also been reported to show significant peaks at $2\theta = 7.40°$, 8.04°, 8.37°, 8.61°, 9.14°, 9.64°, 10.14°, 10.98°, 12.05°, 17.95°, 18.93°, 20.95°, and 24.61°, and some crystallinity is retained even at 5% loading in nanocomposites prepared with a dimethacrylate derivative of bisphenol A.[567] WAXS and SAXS have been used to show that after annealing, a regular array of sheets of POSS cages with a *d*-spacing of 4.9 nm is formed in poly(methyl methacrylate) containing pendant $T_8(i\text{-Bu})_7$ cages.[568] The PXRD pattern of $T_8(i\text{-Bu})_7(CH_2)_3SH$ shows a series of characteristic peaks at $2\theta = 8.03°$, 10.78°, 11.92°, and 18.73° and indexes to give a hexagonal unit cell with lattice parameters $a = b = 16.4$ Å, $c = 17.4$ Å.[569] WAXS of $T_8(i\text{-Bu})_7(CH_2)_3SH$ shows the most intense peak at $2\theta = 8.15°$, and although this is also seen in compounds containing short poly(methyl methacrylate) chains connected via the sulfur atom, with longer chains the formation of POSS crystallites, as evidenced by WAXS, is suppressed.[570]

WAXD studies of $T_8(i\text{-Bu})_7(CH_2)_3OCH_2CH(O)CH_2$ show a complicated diffractogram possibly indicative of the presence of two crystalline phases.[571,572] A significant peak at $2\theta = 8.4°$, which is also present in networks formed from $T_8(i\text{-Bu})_7(CH_2)_3OCH_2CH(O)CH_2$ in epoxy-amine materials, is indicative of POSS-rich domains in these materials.[573] Similar effects are seen for $T_8Ph_7(CH_2)_3OCH_2CH(O)CH_2$ in epoxy-amine networks.[573] The WAXS patterns of $T_8(R)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$ (R = *i*-Bu, *c*-C_5H_9, or Cy) contain many sharp diffraction peaks, the main peak in each case corresponding to a *d*-spacing of 11.0, 10.8, and 11.2 Å. In contrast to many copolymers containing POSS species, diffraction peaks corresponding to a rhombohedral lattice are not observed in $T_8(R)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$−styrene (R = *i*-Bu, *c*-C_5H_9, or Cy) copolymers.[574,575] The XRD pattern for the diamine derivative $T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH_2OC_6H_4\text{-}4\text{-}CH(C_6H_4\text{-}4\text{-}NH_2)_2$ shows peaks at $2\theta = 8.3°$, 11.3°, 19.1°, and 25.9° corresponding to *d*-spacings of 10.5, 7.2, 4.6, and 3.3 Å, the 10.5 Å spacing being due to the POSS cages and the others due to the rhombohedral crystal structure.[185]

WAXD for $T_8(i\text{-Bu})_7OSiMe_2(CH_2)_3OCH_2CEt(CH_2OH)_2$ has its main reflections at ca. $2\theta = 7.9°$, 10.52°, and 18.6° corresponding to *d*-spacing of 11.2, 8.3, and 4.8 Å, respectively, and a rhombohedral or equivalent hexagonal unit cell. The diffraction peaks are also seen for some polycaprolactone networks containing this POSS system suggesting that the cage survives the polymerization reaction and that a crystalline POSS phase is present in the materials produced.[576] The $2\theta = 7.9°$ peak is also observed in $T_8(i\text{-Bu})_7OSiMe_2(CH_2)_3OCEt(CH_2OH)_2$−polyurethane copolymers and is attributable to POSS crystals (of rhombohedral unit cell, $a = 11.0$ Å, $\alpha = 104°$) in the polymer, rather than the cages being dispersed at a molecular level.[577–580]

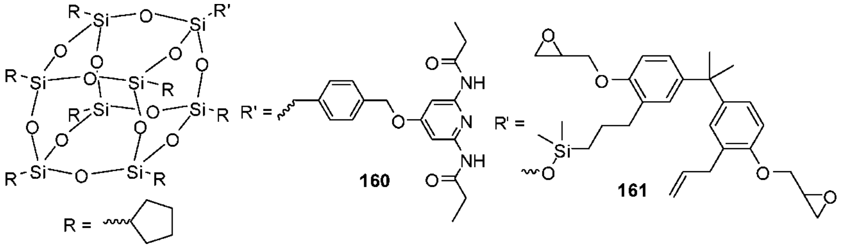
The XRD pattern for $[T_8(i\text{-Bu})_7(CH_2)_3NH_3]Cl$ shows reflections at $2\theta = 7.9°$ and 8.8°,[581] while for $T_8(i\text{-Bu})_7(CH_2)_3NH_2$, the highest intensity peak is seen at $2\theta = 8.3°$.[530] The WAXD diffraction pattern of $T_8(i\text{-Bu})_7(CH_2)_3NH(CH_2)_2NH_2$ shows peaks at $2\theta = 8.1°$, 10.8°, 12.1°, and 18.8°, and although there is a reflection at $2\theta = 8.6°$ in a polyurethane−$T_8(i\text{-Bu})_7(CH_2)_3NH(CH_2)_2NH_2$ hybrid film, it is thought that this may be due to unreacted POSS monomer in the matrix.[582]

A WAXD pattern with reflections at $2\theta = 8.22°$ and 18.2° corresponding to *d*-spacing of 10.76 and 4.72 Å has been found for $T_8(c\text{-}C_5H_9)_7H$,[583] but sharp diffraction peaks for the same compound have also been reported at $2\theta = 9.45°$ and ca. 22°, and these peaks are also present when the compound is used to terminate poly(propylene oxide) chains.[584] X-ray diffraction, electron microscopy, and electron diffraction of **159** (Chart 30) have been used to study its crystal structure and morphology. It is found that the POSS molecules can be treated as spheres, and the structure can be described as hexagonal or rhombohedral with an ABCA arrangement of layers.[502] For example, powder diffraction patterns of **159** show four main reflections at 8.2°, 11.0°, 12.1°, and 19.0°, corresponding to *d*-spacings of 10.8, 8.03, 7.31, and 4.66 Å, respectively[502] The WAXS pattern for **160** (Chart 31) shows peaks at $2\theta = 8.1°$, 11.0°, 12.2°, 19.1°, and 24.8° corresponding to *d*-spacings of 10.65, 7.95, 7.20, 4.60 and 3.55 Å respectively. The peaks due to shorter range ordering are also seen when **160** forms a nanocomposite with a thymine-functionalized polystyrene, showing that small POSS crystallites are still present.[585]

The WAXD pattern for $T_8(c\text{-}C_5H_9)_7(CH_2)_2C_6H_4\text{-}4\text{-}CH_2Cl$ shows peaks at ca. $2\theta = 8.3°$, 11.3°, 12.0°, 19.1°, and 25.9° corresponding to *d*-spacings of 10.5, 7.2, 6.9, 4.6, and 3.3 Å, respectively, the 10.5 Å spacing being due to the POSS molecule and the others being due to a rhombohedral crystal structure[361,586] The WAXD pattern for **159** shows reflections at $2\theta = 8.2°$, 11.0°, 12.1°, and 19.0° corresponding to *d*-spacings of 10.8, 8.03, 7.31, and 4.66 Å and a hexagonal unit cell with $a = 16.06$ and $c = 17.14$ Å. These peaks are also seen in the material produced on copolymerization of this monomer with polybutadiene (Figure 4).[587] The XRD pattern for $T_8(c\text{-}C_5H_9)_7(CH_2)_3CN$ shows sharp peaks including an intense one at $2\theta = 8.2°$ corresponding to a *d*-spacing of 10.2 Å, which is also seen in cyanate ester composite materials derived from this POSS species.[544] The XRD pattern for $T_8(c\text{-}C_5H_9)_7(CH_2)_3OC(=O)C(=CH_2)Me$ shows peaks at $2\theta = 8.2°$, 11.1°, 12.3°, 19.2°, and 24.9° corresponding to *d*-spacings of 10.7, 7.9, 7.1, 4.6, and 3.6 Å, respectively, the 10.7 Å peak being attributed to the size of the POSS molecule and the remaining peaks being attributed to the rhombohedral crystal structure.[588–592]

X-ray powder diffraction plots of a blend of $T_8(c\text{-}C_5H_9)_7(CH_2)_3SiMe_2C_6H_4\text{-}4\text{-}SiMe_2H$ with polystyrene−polybutadiene−polystyrene cast from a toluene solution show the POSS compound to have a crystalline nature and a distinct peak at $2\theta = 8.1°$.[277] SAXS has been used to investigate the *d*-spacing and segregation of the phases in styrene−butadiene−styrene triblock copolymers with pendant T_8R_7 groups (R = *c*-C_5H_9, Cy, cyclohexenyl, or Ph) derived from $T_8R_7(CH_2)_3SiMe_2C_6H_4\text{-}4\text{-}SiMe_2H$ precursors and grafted on to the butadiene block.[184,593] The unit cell data for $T_8(R)_7(CH_2)_3NCO$ (R = *i*-Bu or *c*-C_5H_9) were found to be identical, being trigonal $R\bar{3}m$ with $a = 16.2$ and $c = 17.2$ Å. Lamellar crystals of these POSS units crystallize in poly[ethylene-*b*-(ethylene oxide)-*b*-POSS]compounds to give units with similar dimensions to the simple molecular species.[349] WAXS for $T_8(c\text{-}C_5H_9)_7(CH_2)_3OCH_2CH(OH)CH_2OH$ has its most intense reflection at $2\theta = 8.3°$ assigned to the 101 reflections of the POSS cage.[594] WAXS

Chart 31



has also been carried out on $T_8(c\text{-}C_5H_9)_7OSiMe_2(CH_2)_3NCO$ and on polystyrene terminated by this POSS derivative via an amide linkage. A peak at 2θ = ca. 8.6° corresponding to a *d*-spacing of ca. 10.8 Å is present in both.[595] WAXS of **161** (Chart 31) shows peaks at 8°, 10.8°, and 18.8°.[264]

WAXD has been used to show the dispersion of POSS additives $T_8(c\text{-}C_5H_9)_7R$ [$R = (CH_2)_2(CF_2)_7CF_3$ or $CH_2CH(OH)CH_2OH$] in polystyrene and shows that the POSS molecules segregate at the surface, forming crystallites of 10 and 19 nm sizes, respectively.[180] The XRD pattern of $T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$ has characteristic peaks at 2θ = 7.9°, 10.8°, 11.9°, and 19.3°, which can be seen in styrene−$T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH{=}CH_2$ copolymers containing several percent of the POSS monomer,[596] and WAXD of $T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}(E)\text{-}CH{=}CHFc$ has been used to show that it does not occur as a separated phase in nanocomposites with polystyrene.[353] The XRD pattern of $T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH_2Cl$ shows peaks at 2θ = 8.3°, 19.1°, and 26.1° corresponding to *d*-spacings of 10.5, 4.6, and 3.3 Å, the first one of which is attributable to the size of the POSS molecule and the other two, again, to a rhombohedral lattice.[186,354,363] The peak at 8.3° is also seen in polyfluorenes incorporating $T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH_2\text{-}$ groups[363] and similarly in POSS−poly(phenylene methylene) materials,[186] and POSS−poly(phenylene vinylene) copolymers.[354]

WAXD of $T_8Cy_7OSiMe_2(CH_2)_3NCO$ and polymers derived from the reaction of this with poly(ethylene glycol) shows strong characteristic reflections at 2θ = 7.8°, 10.62°, and 18.20° and corresponding rhombohedral unit cell parameters of a = 11.57 Å and α = 95.5° associated with crystalline POSS phases in both the monomeric compound and the polymers.[597] The XRD pattern of $T_8Cy_7(CH_2)_3OC({=}O)C({=}CH_2)Me$ shows sharp reflections at 2θ = 7.83°, 10.46°, 11.61°, 18.14°, and 18.80°; copolymers of this monomer with *n*-$BuOC({=}O)C(C{=}CH_2)Me$ show a reflection at 2θ = 7.2° indicative of crystallinity in the polymer.[598] WAXS patterns show that incorporation of $T_8Cy_7(CH_2)_3OC(O)C({=}CH_2)Me$ into dimethacrylate networks leads to a loss of crystallinity.[563] The WAXS pattern of $T_8Ph_7(CH_2)_3OCH_2CH(O)CH_2$ shows intense peaks at 2θ = 8.4°, 9.1°, and 19°,[264] while that for $T_8Ph_7(CH_2)_3OC(O)C({=}CH_2)Me$ shows sharp peaks that are retained in copolymers with poly(octafluoropentyl acrylate), again indicative of POSS aggregation.[566] The WAXD pattern for a POSS-capped poly(ε-caprolactone) derived from $T_8Ph_7(CH_2)_3OH$ shows a peak at 2θ = 7.28° attributable to aggregation of POSS cores.[543] The WAXD patterns for a range of ethylene−propylene−POSS polymers containing T_8Ph_7 groups shows POSS domains from 1.3 to 9.5 nm in size corresponding to three to seven POSS units per domain.[189]

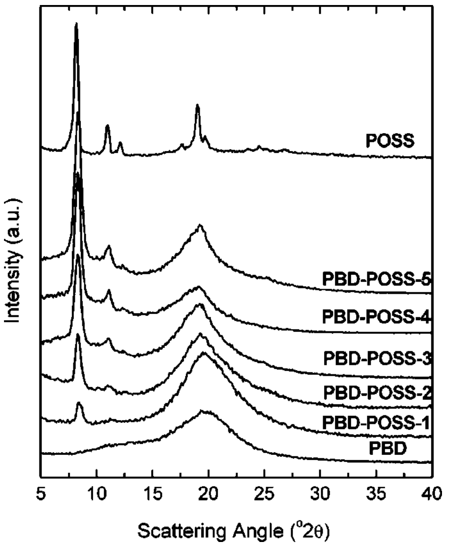


Figure 4. WAXD of **159** (top), polybutadiene (bottom), and a series of copolymers of **159** and polybutadiene, varying from 50% **159** by weight (PBD−POSS-5) to 10% **159** by weight (PBD−POSS-1). Reproduced with permission from ref 587. Copyright 2004 American Chemical Society.

3.5. Microscopy Studies of T_8 POSS Compounds

3.5.1. T_8R_8 Compounds

STM has been used to provide images of individual molecules of T_8H_8 chemisorbed on a Si(100)-2 × 1 surface. Comparison of the experimental and simulated images indicates that the preferred mode of chemisorption is via one of the Si vertices rather than through an arrangement in which the cage opens up along one edge to bind via both Si and O.[599] STM has also been used to show that chemisorbed T_8H_8 molecules on a gold surface are readily displaced by *n*-$C_8H_{17}SiH_3$[600] and that a mixed monolayer of these species contains 60% *n*-$C_8H_{17}SiH_3$ and 40% T_8H_8.[601] STM has also been used to image T_8H_8 on highly oriented pyrolytic graphite showing that it can adopt two different types of monolayers, one in which the face of the POSS is in contact with the graphite and a second in which an edge contacts the surface (Figure 5).[441]

STM, XPS, and RAIRS have been used to show that T_8H_8 behaves differently when deposited on different silicon surfaces. When deposited on a Si(100)-2 × 1 surface, the POSS cage attaches to the surface via a single vertex, but on Si(111)-7 × 7, it seems that the cage breaks open along one edge to bind as a "cracked cluster". This difference in reactivity may be due to the proximity of Si surface diradicals,[602] the opening of one edge of the cube being reminiscent of bulk reactions in which this has been achieved (see section 2.9). High-resolution TEM has been used to image T_8H_8 in both single and multiwalled carbon nanotubes (Figure 6) and shows that the molecules are disordered within the tubes.[603]

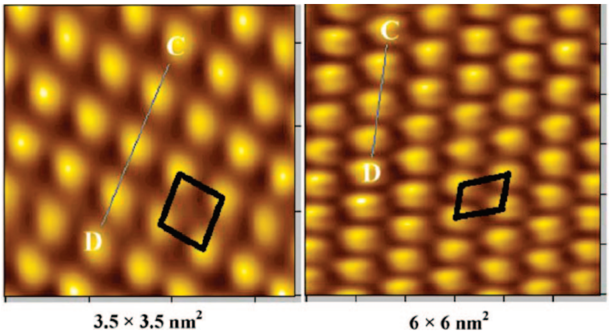


Figure 5. High-resolution STM images of monolayers of T_8H_8 on highly oriented pyrolytic graphite showing (left) the face of the POSS cube in contact and (right) the edge of the cube in contact. Reprinted from Shieh, D.-L.; Chen, F.-C.; Lin, J.-L. Investigation of orientation and packing of $H_8Si_8O_{12}$ arrays on graphite by scanning tunneling microscopy. *Appl. Surf. Sci.* **2006**, *252*, 2171−2177.[441] Copyright 2006, with permission from Elsevier.

Further studies of T_8H_8 encapsulated in both single and double walled carbon nanotubes have been carried out, using an alternative method to prepare the encapsulated species.[604] HR-TEM images of a series of encapsulated compounds showed that the T_8H_8 had reacted to form a double-ladder polymeric species, $Si_{4n}O_{8n-4}H_8$, when the nanotube diameter was in the range 1.14−1.31 or 1.15−1.37 nm for single- and double-walled nanotubes, respectively. However, in single-walled nanotubes of diameter greater than 1.7 nm, a disordered structure of discrete T_8H_8 molecules is observed.[604] The TEM images were found to be in good agreement with those obtained from simulation of $Si_{4n}O_{8n-4}H_8$ encapsulated within nanotubes, and the double-ladder structure was more likely than the related single-ladder structure $Si_{2n}O_{3n-2}H_{2n+4}$ (Figure 7). It was concluded that the reaction was not caused by the electron beam, because spectroscopic data collected prior to TEM also indicated the necessary structural changes.

SEM of T_8Me_8 has shown the compound to have regular cubic crystals smaller than ca. 5 μm,[62,197,198] whereas SEM of T_8Me_8 prepared from swollen poly(2-hydroxyethyl methacrylate) shows that cubic crystals having clean surfaces and edges up to 20−30 μm long may be formed.[76] SEM and TEM have also been used to image the progress of product formation on hydrolysis of $MeSi(OEt)_3$ and $EtSi(OEt)_3$ and show that self-assembly of the final cubic crystalline material occurs via initial spherical particle formation, followed by chains of spherical particles and bundles of rod-like structures.[62]

TEM of the $T_8(i\text{-Bu})_8$−epoxy-cyanate composites shows that the POSS is not evenly distributed in the resin but forms particles of 50 nm to micrometer size, consistent with XRD patterns.[534] Brewster angle microscopy of $T_8(i\text{-Bu})_8$ shows that it forms aggregates at the air/water interface at all concentrations, but when blended with poly(dimethylsiloxane), the degree of POSS aggregation is significantly reduced,[605] and AFM of $T_8(i\text{-Bu})_8$ blended in phenolic resins shows that evenly dispersed POSS particles occur at 20% POSS content while at 60% POSS content macrophase separation occurs.[532] SEM-EDXS and TEM-EDXS methods have been used to show the dispersion of $T_8(i\text{-Bu})_8$ in POSS/polypropylene nanocomposites and that at the surface there is POSS enrichment.[606] SEM of poly(ε-caprolactam) blended with T_8Ph_8 or $T_8(i\text{-Bu})_8$ shows that the POSS molecules adhere poorly to the polymer and instead form POSS domains of 1−20 μm in the T_8Ph_8 case and ca. 500 nm in the $T_8(i\text{-Bu})_8$ case.[345] TEM and XRD of polystyrene thin films incorporating $T_8(c\text{-}C_5H_9)_8$ show smooth surfaces with no obvious POSS crystallites, but after annealing at 413 K crystallites are observed that roughen the surface, and a new diffraction peak for POSS crystallites is also observed.[607]

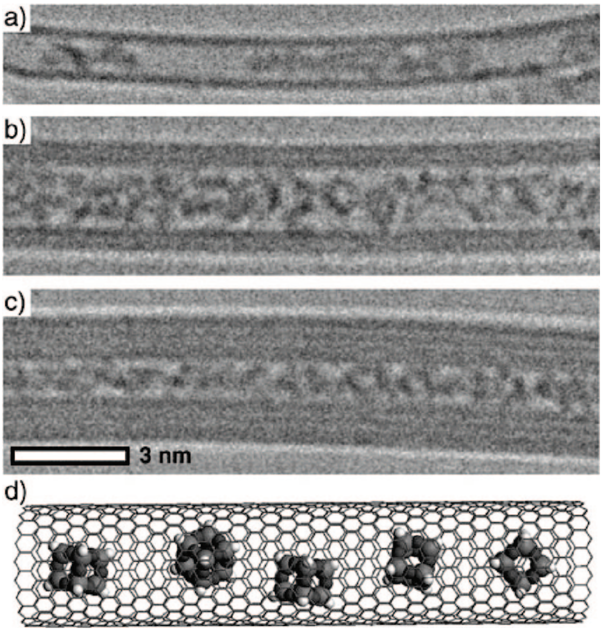


Figure 6. High-resolution TEM images of T_8H_8 inside various nanotubes: (a) inside a single-walled nanotube; (b) inside a multiwalled nanotube; (c) inside a narrow multiwalled nanotube; (d) schematic representation of T_8H_8 inside a nanotube. Wang, J.; Kuimova, M. K.; Poliakoff, M.; Briggs, G. A. D.; Khlobystov, A. N. Encapsulation and IR probing of cube-shaped octasilasesquioxane $H_8Si_8O_{12}$ in carbon nanotubes. *Angew. Chem., Int. Ed.* **2006**, *45*, 5188−5191.[603] Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

SEM, TEM, and EDXS methods have been used to show the distribution of Au, Pd, and Si in metal nanoparticles with $T_8[(CH_2)_3NH_2]_8$ as a core.[608] TEM and scanning force microscopy show a narrow size distribution of particles (containing $T_8\{(CH_2)_3N[CH_2CH(OH)CH_2OH]_2\}_8$ units) with average size 3 nm resulting from the hydrolysis of $[HOCH_2CH(OH)CH_2]_2N(CH_2)_3Si(OEt)_3$,[609] and AFM and SAXS show that when these are used to modify poly(ether urethane)s they aggregate to form a hexagonal lattice in domains 30−60 nm across.[610] SEM of $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ shows it to form crystalline microrods and particles ranging in size from 1 to 80 μm, and energy-dispersive X-ray spectroscopy has been used to show the presence of Cl and Si in the correct ratio.[611] SAXS, SEM, and TEM studies of nanocomposites formed from $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ and carboxyl-functionalized gold nanoparticles show a narrow range of interparticle spacings with a mean value of 1.12 ± 0.12 nm, commensurate with the size of a $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ species and the formation of a porous network structure[612–614] SAXS and TEM of $\{T_8[(CH_2)_3NH_3]_8\}[n\text{-}C_{12}H_{25}SO_3]_8$ show that a lamellar structure is formed with an interlayer spacing of 3.1 nm.[68]

SEM of $T_8(OSiMe_2H)_8$ shows that well-defined cubic particles with a porous structure of ca. 100 μm size may be formed from the silylation of $[T_8O_8]^{8-}$ with HMe_2SiCl,[237,238] while the related derivatives $T_8[OSiMe_2(CH_2)_3CN]_8$ and $T_8[OSiMe_2(CH_2)_3Cl]_8$ show a much lower degree of porosity.[238,615] TEM of $T_8(OSiMe_2H)_8$−poly(methyl methacrylate) nanocomposites shows that phase separation can

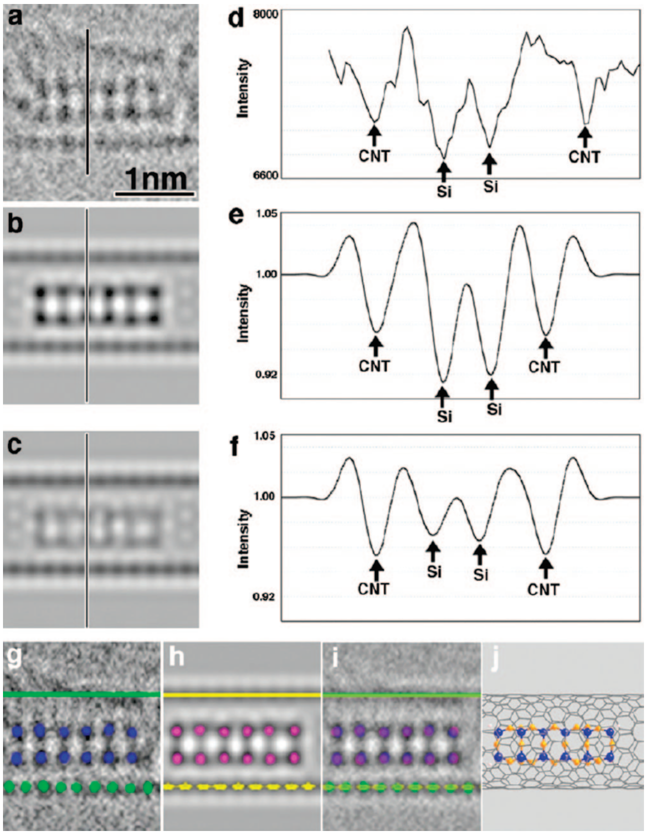


Figure 7. $Si_{4n}O_{8n-4}H_8$ encapsulated within the single-walled (14,2) carbon nanotube: (a) HR-TEM image; (b) simulated image of the encapsulated double-ladder $Si_{4n}O_{8n-4}H_8$; (c) simulated image of the encapsulated single-ladder $Si_{2n}O_{3n-2}H_{2n+4}$; (d−f) line profiles of panels a−c, respectively; (g, h) images of panels a and b, respectively, with Si atoms and nanotube walls highlighted; (i) overlay of panels g and h; (j) framework model of the encapsulated $Si_{4n}O_{8n-4}H_8$. Reproduced with permission from ref 604. Copyright 2008 American Chemical Society.

occur giving cube-like aggregates of POSS species up to 500 nm in size.[616] TEM images have also been used to show that $[T_8O_8]^{8-}$ can be used as a linker between PbSe nanocrystal quantum dots and γ-Fe_2O_3 nanoparticles to form a conjugated structure.[617]

3.5.2. T_8R_7R' Compounds

TEM has been used to show that the POSS cages in polyurethane networks, where they are used to cross-link the polymer rather than being pendant groups, are dispersed homogeneously within the polymer matrix at the nanometer scale.[618] This is in contrast to materials in which the POSS fragments are pendant groups, in which agglomeration of the POSS cages tends to occur.

AFM of $T_8(i\text{-Bu})_7(CH_2)_3OCH_2CH(O)CH_2$ has been used to image crystals of size 9−10 μm.[619] AFM studies of polyurethanes containing pendant $T_8(i\text{-Bu})_7$ groups connected via a cyclohexanediol linkage show that the surface of the polymer is much rougher than when no POSS species are present.[620] TEM and EDXS mapping have also been used to show that the $T_8(i\text{-Bu})_7$ segments, bound via CH_2CH_2−cyclohexanediol linkers, in POSS−poly(carbonate-urea)urethane nanocomposites form hard crystalline areas.[621] The attachment of $T_8(i\text{-Oct})_7$ cages to single-walled carbon nanotubes via a propylamide linkage was confirmed by the observation of the Si−O−Si stretch at 1111 cm^{-1}, by the appearance of the nanotubes in TEM images, and by EELS where the silicon distribution showed that the POSS was grafted along the length of the tubes and not just at the tips.[622]

TEM of polyimide tethered POSS derived from the benzyl derivative $T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH_2Cl$ show a layered structure with POSS crystallites of about 10 nm thick (Figure 8).[361,586]

SEM coupled with energy-dispersive X-ray mapping shows that use of a short curing molecule such as diethylphosphite or dicyandiamide for preparation of epoxy−POSS hybrid prevents macrophase separation and that the POSS cages are well dispersed in the polymer matrix.[623,624] In contrast, SEM of methacryloxypropyl functionalized POSS species in nanocomposites derived from free-radical polymerization with polyarylacetylenes shows that the POSS is well dispersed within the matrix.[625] SEM has also been used to show that addition of methacryloxypropyl POSS derivatives to layered clays can lead to the formation of aerogels with a “house of cards” structure.[626] It has been noted that the $T_8(c\text{-}C_5H_9)_7$-containing blocks in block copolymers of poly(*n*-butyl acrylate) and poly(propyl methacrylate) are selectively stained by RuO_4 for imaging in TEM studies.[590]

Specular X-ray reflectivity studies on Langmuir−Blodgett multilayer films of polymers containing a pair of $T_8Cy_7OSiMe_2(CH_2)_3NHC({=}O)$- groups separated by poly(ethylene glycol) chains show that the films have a double layer structure with a thickness of 17.6 Å.[627] X-ray reflectivity of LB multilayer films of the type POSS−PEG−POSS (where POSS is T_8Cy_7) show that double layers are formed with a calculated POSS diameter for each POSS cage of ca. 12.4 Å.[628]

3.6. TGA, DSC, and Related Studies

3.6.1. T_8R_8 Compounds (R = H, Alkyl, Vinyl, Aryl, or Silyl Derivatives)

There have been numerous studies on the thermal stability and decomposition pathways for T_8R_8 compounds (R = H, Me, *i*-Bu, *i*-Oct, Ph) and other POSS species by TGA. Such studies can be complicated by the ready sublimation of many simple POSS compounds under nitrogen and the potential for some to be stable enough to sublime, at least partially, in air. If sublimation does occur, then the heating rate and air or gas flow rates will affect the sublimation rate. Further complications when comparing relative stabilites of POSS compounds and ceramic yields derived from heating them are that the gas atmosphere used in a TGA study is sometimes not reported, and the assumed residue (presumably usually SiO_2 for these compounds) is not given.

For T_8H_8 and T_8Me_8, incomplete evaporation has been reported to occur both in air and in a N_2 atmosphere, but for $T_8(i\text{-Bu})_8$ and $T_8(i\text{-Oct})_8$ near complete evaporation occurs in an inert atmosphere, at approximately 265 °C for $T_8(i\text{-Bu})_8$,[530] whereas oxidation occurs in air to give silica. For T_8Ph_8, the thermal stability is greater, giving a high ceramic residue of silica containing carbon, see below.[135,629] However, TGA of T_8Me_8 and T_8Et_8 in N_2 has also been reported to show almost 100% evaporation at ca. 250−260 °C.[62,197] TGA of T_8H_8 shows rapid, near complete mass loss at temperatures over ca. 200 °C due to its sublimation.[484] The TGA trace for T_8Me_8 has been reported to show decomposition under nitrogen starting at ca. 230 °C, but in the light of other studies described above, the mass loss observed was actually likely to be due to sublimation.[525] When blended with isotactic polypropylene T_8Me_8 forms a nanocomposite having a decomposition onset at 320−348 °C.[525] The significant

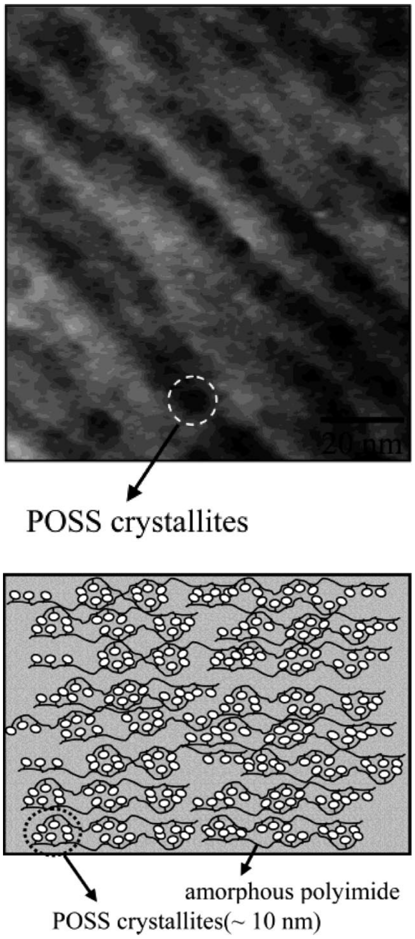


Figure 8. (top) TEM of a cross section of a composite film comprising polyimide and $T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}CH_2Cl$ showing domains of POSS crystallites. (bottom) Schematic representation of the POSS-polyimide composite. Reproduced with permission from ref 586. Copyright 2003 American Chemical Society.

volatility of both T_8H_8 and T_8Me_8 has enabled gas-phase structural analysis of both compounds by electron diffraction methods at 127−136 and 220−240 °C respectively.[429]

The DSC traces for both T_8Et_8 and its partially deuterated derivatives show that several phase transitions occur over the temperature range of −150 to 0 °C, the main transition occurring at slightly lower temperature for the fully protonated compound.[390] The DSC of $T_8(i\text{-Bu})_8$ shows two endotherms, a sharp one at 60 °C and a broader one at 261 °C.[531] The melting point of $T_8(i\text{-Bu})_8$ determined by DSC in N_2 is reported at ca. 265 °C (presumably corresponding to the endothermic peak previously reported[531]), while TGA shows that maximum evaporation occurs at 285 °C,[630] and that complete mass loss occurs at ca. 375 °C due to evaporation of the sample, but in air a ceramic residue of 26% is formed as oxidation competes with evaporation.[630–632] DSC shows a melting point for $T_8(i\text{-Oct})_8$ of 268 °C.[536,537]

The more complicated alkyl substituted cages, T_8R_8 [R = $(CH_2)_5Br$, CH_2CH_2Cy, and $(CH_2)_2O(CH_2)_2Cl$], lose no mass on heating to 381, 442, and 338 °C respectively,[208,633] but significant mass loss is seen for R = CH_2CH_2Cy at 460 °C,[634] for R = $(CH_2)_3Br$ at 380 °C,[634] and for R = $(CH_2)_2O(CH_2)_2Cl$ above 350 °C,[69] as shown by TGA. TGA DTA analysis of $T_8(CH_2CH_2Ph)_8$ in a N_2 atmosphere shows the onset of decomposition to occur at ca. 350 °C, with a maximum rate of decomposition occurring at 359 °C.[540] The DSC trace of $T_8(CH_2CH_2Ph)_8$ shows a glass transition at −13 °C.[635] The DSC trace of $T_8(c\text{-}C_5H_9)_8$ shows no significant thermal transitions between 30 and 140 °C, consistent with its thermal stability,[636] and the decomposition temperature for T_8Cy_8 has been reported as about 310 °C[637] and at ca. 343 °C.[126] The TGA of $T_8(CH{=}CH_2)_8$ under a N_2 atmosphere shows it to be stable to ca. 280 °C,[85,638] but sublimation appears to compete with decomposition, because the residual mass is significantly lower than would be expected for complete conversion to silica.[639] The related compounds $T_8(CH{=}CHC_6H_4\text{-}4\text{-}CH{=}CHC_6H_4\text{-}4\text{-}R)_8$ (R = H, Me, OMe, or NH_2) are stable to 300 °C, except for the aniline derivative, which gains mass, presumably via oxidation of the NH_2 group, at ca. 250 °C.[322] The $T_8(CH{=}CHC_6H_4\text{-}R)_8$ (R = H, 4-Me, 4-OMe, 4-Cl, 4-Br, or 4- or 3-NO_2) are also stable to ca. 300 °C except for the tolyl derivative, which also seems to oxidize.[321,322]

TGA of $T_8[(CH_2)_3NH_2]_8$ shows a two-step decomposition process, the first at ca. 150 °C attributable to loss of water from the hygroscopic compound and the second at between 425−500 °C due to degradation of the POSS species itself. The char yield at 800 °C is significantly higher than expected for just SiO_2 formation, but it is not clear to what the extra mass is due.[98]

TGA of $T_8[(CH_2)_3NH_2]_8$ under a N_2 atmosphere has also been reported to show that decomposition starts at ca. 320 °C[101] and that rapid initial mass loss occurs at ca. 350 °C followed by steady mass loss up to 700 °C.[102] TGA and DTA data for $T_8[(CH_2)_3NH_2]_8$ and $T_8[(CH_2)_3Cl]_8$ have been used to determine the activation energy for crystallization of each compound,[103] and DSC studies of $T_8[(CH_2)_3NH_2]_8$ show a melting point of 196.6 °C and an onset for decomposition of 242 °C, that is, somewhat lower than those determined by TGA.[100] TGA of $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ under a flow of N_2 shows a two-step decomposition corresponding to initial breakdown of the alkylammonium chloride group between 305 and 420 °C and a second step at 420−650 °C due to degradation of the propyl chains.[68] More specifically, it has been shown to have an initial onset of 5% decomposition at 322 °C.[611]

TGA of $T_8[(CH_2)_3SH]_8$ in oxygen shows initial decomposition at 300 °C and a ceramic yield at 650 °C of 52.8%, consistent with the formation of SiO_2, while DSC shows a small endotherm at 23.5 °C and melting at 257 °C.[541] DSC studies of $T_8(CH_2CH{=}CH_2)_8$ show a melting point endotherm at 71 °C, and the heat of melting is estimated to be 36.5 J g^{-1}, while DSC of the related epoxide $T_8[CH_2CH(O)CH_2]_8$ exhibits evidence of polycrystallinity.[90] The decomposition temperatures for $T_8(CH_2CH{=}CH_2)_8$ and $T_8[CH_2CH(O)CH_2]_8$ are estimated to be 190 and 252 °C, respectively, by DSC.[90] TGA of the fluorinated alkyl derivatives, $T_8(CH_2CH_2R)_8$ [R = CF_3, $(CF_2)_3CF_3$, $(CF_2)_5CF_3$, or $(CF_2)_7CF_3$], in air shows that all of the compounds evaporate, the $(CF_2)_7CF_3$ derivative subliming at over 300 °C[640] and being stable up to about 350 °C in nitrogen.[88] The TGA of a POSS cage with eight cholic acid derivatized substituents connected to the cage via -$CH_2CH_2SiMe_2O$- linkages (**58**) shows that thermal degradation starts at 148 °C under a N_2 atmosphere.[296] TGA studies of $T_8(SiMe_2\text{-}t\text{-Bu})_8$ show it to be thermally stable up to about 300 °C in an argon atmosphere.[201]

The temperature dependence of the heat capacity of crystalline T_8Ph_8 has been measured using a calorimeter, and from these data enthalpy, entropy, and Gibbs function values over the range 0−300 K were calculated.[641] TGA of the aryl-POSS derivatives T_8R_8 (R = Ph, $C_6H_4\text{-}2\text{-}Me$, $C_6H_4\text{-}3\text{-}Me$,

C_6H_4-4-Me) show melting temperatures of 472, 385, 424, and 407 °C, respectively, and onset of decomposition occurs at 486, 435, 431, and 413 °C, respectively in flowing N_2.[135] The octaphenyl derivative, T_8Ph_8, is reported to be stable to about 480 °C by TGA/DTA and gives SiO_2 at higher temperatures, but the nitrated derivative, $T_8[C_6H_3(NO_2)_2]_8$, detonates at 420 °C in synthetic air.[129,339] However, the derivative thermogravimetry traces of T_8Ph_8 and $T_8(C_6H_4NO_2)_8$ have both been reported to indicate rapid decomposition at 420 and 380 °C, respectively, and $T_8(C_6H_4NH_2)_8$ undergoes a slow decomposition from 300 to 650 °C in an N_2 atmosphere.[335] A 5% mass loss for T_8Ph_8 determined by TGA has also been reported at 436.8 °C.[131] TGA of $T_8(C_6H_4NH_2)_8$ in nitrogen shows 5% mass loss at 330 °C and 20% loss at 489 °C, with a ceramic yield of 41.1% at 1000 °C in air.[332,497] DSC experiments indicate that the presence of **94** greatly reduces the curing temperature and accelerates the curing in reactions forming bismaleimide−triazine resins.[496] TGA of heavily brominated T_8Ph_8 derivatives in dry air shows that significant decomposition only occurs above about 420 °C.[314]

3.6.2. T_8R_8 Compounds (R = Alkoxy or Siloxy Derivative)

TGA of anhydrous $[NMe_4]_8[T_8O_8]$ shows a sharp decomposition at 200 °C, and the compound gives a ceramic yield, 48.3%, consistent with the theoretical value for SiO_2 as residue, 47.9%, above 500 °C. This is thought to retard the combustion of $[NMe_4]_8[T_8O_8]$−polystyrene composites.[138] The TGA and DTA traces for series of alkoxy-substituted POSS compounds $T_8(OR)_8$ (R = Et, *n*-Oct, *i*-Pr, *t*-Bu, and Cy) have also been reported.[74] TGA of $T_8(OSiMe_2H)_8$, $T_8[OSiMe_2(CH_2)_3CN]_8$, and $T_8[OSiMe_2(CH_2)_3Cl]_8$ show a tendency for the compounds to sublime and to form SiO_2 as their residue at high temperatures.[238,615] In contrast, under nitrogen, $T_8(OSiMe_2H)_8$ is found to sublime between 188 and 280 °C.[238,615,642] In synthetic air, the TGA of $T_8[OSiMe_2H]_8$ shows 24.5% mass loss between 172 and 281 °C attributable to loss of the $SiMe_2H$ groups and formation of SiO_2 at 1200 C.[237] In studies of this type where sublimation will occur as well as decomposition, detailed discussion of TGA data is difficult.

The DSC scans of $T_8(OSiMe_2H)_8$ and $T_8[OSiMe_2(CH_2)_2C_6H_4$-4-OAc$]_8$ have been compared, and while the latter shows a single glass transition at −15 °C, its $T_8(OSiMe_2H)_8$ precursor shows no glass transition.[230,252] DSC studies also show that star-shaped POSS−poly(ethylene oxide) materials with $T_8(OSiMe_2)_8$ centers have lower crystallization temperatures and narrower melting temperatures compared with poly(ethylene oxide) in the absence of the POSS.[548] TGA of **16** has been reported to show a 5% mass loss in argon at ca. 335 °C,[643] as well as an onset of degradation at 404 °C in argon and 361 °C in oxygen.[644] DSC of **16** shows two melting points, at 112 and 124 °C, presumably due to the two different morphologies (one with much more jagged features than the other) of this compound that are seen by SEM.[644] The melting point has also been reported as 123.4 °C on a first heating scan and ca.110 °C on a second heating scan.[643] TGA of $T_8[OSiMe_2(CH_2)_3OCF_2CHFCF_3]_8$ under N_2 shows a 5% mass loss at ca. 281 °C, and it decomposes in three steps.[259] TGA of mixed hydrosilylation products $T_8(OSiMe_2CH_2CH_2Ph)_8/T_8(OSiMe_2CHMePh)_8$, $T_8(OSiMe_2CH_2CH_2C_6H_4$-4-OAc$)_8/T_8(OSiMe_2CHMeC_6H_4$-4-OAc$)_8$, and $T_8(OSiMe_2CH_2CH_2C_6H_4$-4-OH$)_8/T_8(OSiMe_2CHMeC_6H_4$-4-OH$)_8$ shows that decomposition starts at ca. 431, 384, and 358 °C respectively.[226] TGA of $T_8(OSiMe_2C_6H_4$-4-R$)_8$ (R = Me, CBr_3, or CO_2H) in air shows temperatures for loss of 5% mass at 370, 164, and 180 °C, respectively, and the expected ceramic yields.[143] DSC of **17** shows a sharp melting point at 166 °C, and TGA shows it to be stable in air and nitrogen to 400 and 450 °C respectively.[233–235]

Methacrylate and epoxide POSS monomers are popular precursors for incorporation into polymer materials and have good thermal stability as monomers. Thus, TGA of $T_8(OSiMe_2R)_8$ [R = $(CH_2)_3(OCH_2CH_2CH_2)_2OC({=}O)C({=}CH_2)Me$ or $CH{=}CH_2CH_2OC({=}O)C({=}CH_2)Me$] shows 5% decomposition to occur in dry air at ca. 257 and 302 °C, respectively,[141] and TGA of $T_8[OSiMe_2(CH_2)_3OCH_2CH(O)CH_2]_8$ shows decomposition under nitrogen starting at ca. 350 °C,[645] with acid impurities being found to lower the decomposition temperature to ca. 190 °C.[646] TGA of a range of macromonomers $T_8[OSiMe_2(CH_2)_3(OCH_2CH_2)_nOC({=}O)CMe({=}CH_2)]_8$ and $T_8[OSiMe_2(CH_2)_3(OCH_2CH_2)_nOH]_8$ (n = 2, 3, 4, or 6) showed that decomposition takes place in two steps and that the expected ceramic yield of SiO_2 is close to that found experimentally. T_g values for the methacrylate derivatives are ca. 10−20 °C higher than those for the corresponding ethylene glycol derivatives.[376]

3.6.3. T_8R_7R' Compounds (R = i-Bu)

The DSC trace of $T_8(i\text{-Bu})_7(CH_2)_3OCH_2CH(O)CH_2$ shows two melting peaks at 112 and 132 °C, and on cooling, crystallization peaks at 138 and 118 °C, the two melting points possibly being caused by the presence of two different crystalline phases. AFM shows that the higher melting seems to be associated with the center of a crystal and the lower one the periphery of the crystal.[571,647] DSC of $T_8(i\text{-Bu})_7(CH_2)_3OCH_2CH(O)CH_2$ has also been reported to give melting peaks at ca. 112 and 133 °C with a total melting heat of ca. 26 J g^{-1} and crystallization peaks at ca. 119 and 139 °C with a total crystallization heat of ca. 15 J g^{-1}.[619,648] TGA of $T_8(i\text{-Bu})_7(CH_2)_3OCH_2CH(O)CH_2$ in an inert atmosphere and in oxygen show residue yields of 24.4% and 42.7%, respectively, at 600 °C, the onset of decomposition being slightly less than 300 °C in each case.[619] The TGA of $T_8(i\text{-Bu})_7(CH_2)_3OCH_2CH(O)CH_2$ has also been reported to show significant decomposition at 220 °C under argon[647] and to show about 20% decomposition over 300 min at 200 °C, with rapid decomposition above ca. 250 °C.[649] TGA of **158** in air shows it to start decomposition at ca. 200 °C and have about 20% mass loss at ca. 250 °C.[557,558] TGA of $T_8(i\text{-Bu})_7(CH_2)_3OC({=}O)C({=}CH_2)Me$ shows 5% decomposition in air and in nitrogen at 265 and 282 °C, respectively,[562] while DSC shows that at ca. 110 °C, it melts (ΔH = 15.6 J g^{-1}) without decomposing but that at 140 °C it exhibits an exotherm attributable to self-polymerization.[650]

DSC studies of the $T_8(i\text{-Bu})_7$ derivative **101** show two transitions, one at 36 °C attributed to formation of a liquid crystalline phase for the triphenylene pendant group and one at 42 °C attributable to crystallization of POSS cages,[381] while DSC of $T_8(i\text{-Bu})_7CH_2CH{=}CH_2$ shows a first scan melting point of ca. 49 °C.[555] DSC studies also show that poly(methyl methacrylate)−POSS homopolymers containing $T_8(i\text{-Bu})_7$ groups bound via a Si−C_6H_4-4-CH_2 linkage are fully miscible with phenolic blends of various molecular weights.[168] DSC of $T_8(i\text{-Bu})_7(CH_2)_3NH_2$ shows two melting points, at ca. 61 and 266 °C, thought to be due to two different morphologies of the amine being present. TGA shows the amine to start decomposition at ca. 277 °C in Ar and at ca. 265 °C in O_2,[651] with rapid mass loss, possibly due to evaporation, at 293 °C.[530] The DSC of $T_8(i\text{-}Bu)_7(CH_2)_3OH$ shows a melting point at ca. 56 °C, while TGA shows that thermal degradation starts at ca. 220 °C[652] and that decomposition of $T_8(i\text{-}Bu)_7OSiMe_2H$ starts at 300 and 325 °C in air and argon, respectively.[274]

3.6.4. T_8R_7R' Compounds ($R = Et$, $c\text{-}C_5H_9$, or Cy)

Although studies on T_8R_7R'compounds have been mainly concerned with compounds where $R = i\text{-}Bu$, there are a few studies on related compounds where $R = Et$, $c\text{-}C_5H_9$, or Cy. Thus, the T_g values for $T_8R_7(CH_2)_3OC({=}O)C({=}CH_2)Me$ compounds have been found to be 251 and 350 °C for $R = Et$ and $c\text{-}C_5H_9$, respectively.[653] TGA of $T_8(c\text{-}C_5H_9)_7OSiMe_2(CH_2)_3NCO$ in air or in nitrogen shows decomposition starting at ca. 250 °C.[595] TGA and DSC thermograms of $T_8Cy_7(CH_2)_3OC({=}O)C(Me){=}CH_2$ show that it decomposes in two stages under flowing N_2, the first at 350 °C and the second starting at 533 °C. The residual mass is significantly less than that expected for formation of SiO_2, which is though to be due to the partial sublimation of the sample.[654]

3.7. Mass Spectra of POSS Compounds

The application of mass spectrometry in the analysis of many simple POSS compounds has been widespread, the π-electron density and electronegative atoms in the substituents on the POSS core binding alkali metals or protons readily to give positive ions. High power lasers may induce POSS cage fragmentation, but this seems not to be a problem that prevents observation of a molecular ion.[204] Bowers and co-workers[204] have highlighted the difficulties in generating large ions derived from oligomers or polymers containing POSS components without fragmentation. This is thought to be due to low ionization efficiency because the POSS cage is good at delocalizing electron density; it may be possible to overcome this by preparing endohedral fluoride complexes with higher ionization efficiency (see below for examples).[204]

The ability of mass spectrometric techniques to analyze complicated mixtures has been important in many studies on POSS compounds, for two main reasons. The first is that, as is described in section 2.1.2, cohydrolysis of mixtures of simple monomers to give silsesquioxanes often gives complicated mixtures, both of polyhedral species and of polymeric compounds. Such mixtures are hard to characterize by many methods but their widely differing masses, dependent on how many "T" units are present, usually makes them relatively easy to identify by mass spectrometry. Although simple chemical ionization spectra may be obtained from low molecular weight compounds such as $T_8[(CH_2)_3Cl]_8$,[117] the high molecular weights of many T_8R_8 compounds means that more modern techniques such as MALDI and electrospray ionization are often required for sample analysis and in conjunction with ion mobility mass spectrometry. As is the case for other types of compounds, the ease of ionization is a factor in determining the MALDI data intensity, and so comparisons of POSS isomer ratios need to take this into account. A second important area has been in the analysis of products from reactions involving an octafunctional precursor, T_8R_8, that may not give complete reaction to afford a $T_8R'_8$ product. In such cases, the differing masses of R groups in $T_8R_nR'_{8-n}$ ($n = 0-8$) mean that the degree of substitution is conveniently assessed, although the distribution of the R and R′ groups for $n = 2-6$ around a T_8 cube is better investigated by ^{29}Si NMR spectroscopy.

Mass spectrometry has also been used to determine the behavior of POSS cages toward electron impact. In most symmetrically substituted compounds, T_8R_8 (R is organic or inorganic substituents), the cage is resistant to electron impact up to 3 keV.[89] However, in $T_8(CH_2CH_2CF_3)_8$, the cage is cleaved much more readily, possibly via intramolecular transfer of F to a silicon atom.[89] Cryoscopy in cyclohexane has also been used to confirm the structure of $T_8[(CH_2)_3Cp]_8$ in solution and is consistent with the ESIMS.[94] FABMS has been used to characterize simple monomeric POSS species such as $T_8(CH_2CH_2R)_8$ [$R = Ph$;[392] $R = Cy$, $(CH_2)_3Br$, or $(CH_2)_4Cl$[634]]. Time of flight secondary ion mass spectrometry of polycarbonate with $T_8(CH_2Ph)_8$ as an additive has been used to show that the POSS species is not found uniformly across the polycarbonate but is enriched in domains.[655] The collision cross sections for T_8Ph_8 and $T_8(CH_2Ph)_8$ have been measured experimentally using electrospray ionization, MALDI, and ion mobility methods. These results, when compared with calculated data and those determined from X-ray data for crystalline samples, show good agreement between the methods suggesting that the cage structure is not significantly deformed in the gas phase compared with the solid state and that the sodium ion does not cause fragmentation of the cage in Na^+POSS ions.[656] Similar studies have been carried out for the styryl and phenylethyl derivatives, $T_8(CH{=}CHPh)_8$ and $T_8(CH_2CH_2Ph)_8$, for which MALDI was used to generate $Na^+T_8(CH{=}CHPh)_8$ and $Na^+T_8(CH_2CH_2Ph)_8$ ions and their collision cross section was measured using ion mobility based methods. For $Na^+T_8(CH{=}CHPh)_8$, five different conformers were observed arising from the Na^+ binding to four oxygen atoms on one face of the cage and the styryl groups then pairing up in different ways. Again calculated values for the collision cross sections were very similar to the experimental values.[204,657] The related epoxide derivatives, $Na^+T_8(CH{=}CHPh)_x[CH(O)CHPh]_{8-x}$ (where $x = 5$, 6, or 7) have been analyzed using similar methods. As might be expected, the epoxystyryl groups may be distributed about the cage to give isomers for $x = 5$ and 6 and the aryl rings may also be in different orientations with respect to each other to give a family of isomers. Again, calculated collision cross sections for these species agree well with the experimental values.[658]

The collision cross sections for $(T_8R_7)_2R'$, $Na^+(T_8Cy_7)_2O$, $Na^+[T_8(c\text{-}C_5H_9)_7]_2O$, and $Na^+(T_8Cy_7O)_2Si_8O_{11}Cy_8$ have been measured using ion mobility and computational methods. MALDI was used to generate the ions, which were found to have a low-energy staggered structure in the case of the cyclopentyl derivative, the Cy groups interconverting between axial and equatorial conformations in the case of the Cy dimer, and an exo-exo stereochemistry for the trimeric species. The experimentally determined cross sections were in good agreement with those calculated by molecular modeling.[307] The collision cross sections for a range of negative POSS ions $F^-@T_8R_8$ ($R = CH{=}CH_2$, Ph, $CH{=}CHPh$, $CH_2CH_2CF_3$, etc.) have been determined both experimentally by ESI and computationally, and the results from both methods are in good agreement. The related sodiated species $H^+[F^-@T_8R_8]Na^+$ give similar good agreement for collision cross sections from MALDI data and calculation.[204]

Fourier transform ion cyclotron resonance mass spectrometry has also been used to investigate the POSS products derived from hydrolysis of triethoxysilanes $(EtO)_3SiR$ [$R =$

$(CH_2)_3C_6H_4$-4-OMe, *i*-Oct, *c*-C_5H_9, or Cy] in the presence of Bu_4NF and ^{18}O-labeled water,[96] and MALDI-TOF experiments have been used to characterize the complicated mixture formed on hydrolysis of $CH_2{=}CHSiCl_3$, compounds containing from five to twenty "T" units being assigned to masses in the spectrum.[460] In a similar manner, MALDI-TOF has been used to analyze the complex mixture formed on the hydrolysis of $(Me_3Si)_3CSiMe_2CHCH_2Si(OEt)_3$ in the presence of N(*n*-Bu)$_4$F in a variety of solvents. Thus, the POSS compound $T_8[CH_2CH_2SiMe_2C(SiMe_3)_3]_8$ can be identified, as can other partially condensed POSS-related products.[659] MALDI-TOF methods have also been used to determine the ratios of $T_8/T_{10}/T_{12}$ cages produced on the amine-catalyzed condensation of silanols such as $PhSi(OH)_3$ or $[Ph(HO)Si]_6$ and siloxane resins derived from hydrolysis of $(MeO)_3SiR$ (R = $CH{=}CH_2$, Ph, or C_6H_4-2-Me).[511] UV-MALDI-TOF mass spectrometry has been used to characterize the many products, including T_8 derivatives, obtained by hydrolysis of $(EtO)_3Si(CH_2)_3NH_2$ in the presence of phenylglycidylether[660] and also to show that T_8 derivatives are formed in the complicated mixture produced on hydrolysis of $(EtO)_3SiR\{R = (CH_2)_3NHCH_2CH(OH)CH_2OPh$ and $(CH_2)_3N[CH_2CH(OH)CH_2OPh]_2\}$.[111]

Capillary electrophoresis-ion-trap mass spectrometry has been used to characterize the products arising from hydrolysis of $MeC({=}CH_2)C({=}O)O(CH_2)_3Si(OMe)_3$ showing that a range of incompletely condensed siloxanes are present along with T_8-type species.[661] MALDI-TOF methods have also been used to investigate the identity and relative stabilities of the components of the complicated mixture formed on hydrolysis of $CH_2(O)CHCH_2O(CH_2)_3Si(OMe)_3$. Together with IR and NMR studies, the cage species present in the mixture, including T_8 derivatives, were proposed to be more stable than the ladder structures formed.[662] LC/MS has been used to characterize the products obtained from cohydrolysis of $MeSi(OEt)_3$ and $CH_2(O)CHCH_2O(CH_2)_3Si(MeO)_3$ and shows that T_8 derivatives $T_8Me_{8-n}[(CH_2)_3OCH_2CH(O)CH_2]_n$ (where n = 4 or 6) are formed along with T_9 and T_{10} compounds.[151] Electrospray mass spectrometry has also been used in a detailed study of how $T_8(OH)_8$ and other silicate polyhedra are built up in solution from smaller silicate fragments.[663–665] Methoxylation of the cube to give $T_8(OH)_7OMe$ can be observed to occur either by reaction with the methanol solvent or by breakdown of the Me_4N^+ template ion.[664] This is a much faster method than ^{29}Si NMR spectroscopy for identifying silicate species in solution but care needs to be taken or equipment modifications may be necessary not to cause solid precipitation inside the spectrometer.[664]

Electrospray mass spectrometry has been used to characterize the mixtures obtained on Ru-catalyzed cross-metathesis or silylative coupling reactions of $T_8(CH{=}CH_2)_8$,[385] and MALDI has been used to determine the octasubstituted nature of a range of styryl POSS derivatives $T_8(CH_2CH_2Ar)_8$ (Ar = Ph, C_6H_4-4-Me, C_6H_4-4-OMe, C_6H_4-4-Cl, C_6H_4-4-Br, or C_6H_4-4-NO_2) derived from Ru-catalyzed metathesis reactions with $T_8(CH{=}CH_2)_8$.[321] MALDI-TOF has also been used to determine the degree of substitution in the platinum-catalyzed hydrosilylation reaction between $T_8(CH{=}CH_2)_8$ and $(EtO)_3SiH$[285] and in determining the degree of substitution in the hydrosilylation reaction between $T_8(OSiMe_2H)_8$ and various combinations of allylbenzene and 1,5-hexadiene, which afford a mixture of isomers of $T_8[OSiMe_2(CH_2)_3Ph]_{8-n}(OSiMe_2C_6H_{11})_n$ (n = 0−8).[288] MALDI-TOF has also been used to characterize chromatographically separated, individual POSS species $T_8(OSiMe_2R)_n(OSiMe_2R')_{8-n}$ (R, R′ = photoluminescent substituents; n = 1, 2, or 3) (**18**, **26**, **27**, **44**, **45**, **49**, and **50**) derived from Pt-catalyzed hydrosilylation reactions of $T_8(OSiMe_2H)_8$.[239] ESI TOF mass spectrometry has been used to show that all eight of the Si−H groups in the precursor had been substituted in a Pt-catalyzed hydrosilylation of $T_8(OSiMe_2H)_8$ to give **16**[479] and also gives M^+ ions for $T_8[(CH_2)_3Cp]_8$.[94]

High molecular weight POSS derivatives may be readily characterized by MALDI-TOF mass spectrometry,[63,666] including glycoclusters derived from $T_8(CH{=}CH_2)_8$,[395] bis-POSS derivatives of phthalocyanines,[406] octakis-POSS substituted metallophthalocyanines,[360,405] luminescent aryl derivatives of $T_8(CH{=}CH_2)_8$,[323] polypyrene substituted POSS species, containing up to 14 pyrene groups, derived from Heck coupling of $T_8(CH{=}CH_2)_8$ with 1-bromopyrene,[325] an octafunctional dendrimer precursor $T_8[OSiMe_2(CH_2)_2CMe_2(CH_2)_2OC({=}O)CMe_2Br]_8$,[265] and polyfluorene POSS substituted compounds with potential as a hole-transporting group for use in OLED devices, derived from Heck coupling of $T_8(CH{=}CH_2)_8$ with a bromofluorene.[667] However, as mentioned above, there are difficulties in generating large ions derived from POSS oligomers or polymers (rather than large single POSS cage derivatives) containing POSS components without fragmentation. MALDI-TOF has also been used to characterize dendrimer drug carriers based on $T_8[(CH_2)_3NH]_8$ cores. Thus, masses of up to 16 314 for $T_8[(CH_2)_3NH(\text{L-Lys})(\text{L-Lys})_2(\text{L-Lys})_4(\text{L-Lys})_8]_8$ were measured, indicating complete surface reaction.[365] MALDI-TOF using $AgNO_3$ or AgO_2CCF_3 as ion source has been used to determine the extent of bromination of T_8Ph_8 using a variety of bromination methods, up to 17 bromines per POSS molecule being identified.[314,668] Some of these bromides, mixtures of $T_8Ph_n(C_6H_4Br)_{8-n}$ (n = 2, 3, 4, or 5) isomers with an average of 5.3 bromines per POSS molecule have been subjected to Suzuki coupling with $ArB(OH)_2$ (Ar = Ph, biphenyl, naphthyl, 9,9-dimethylfluorenyl, etc.), and the resulting polyaromatic compounds have also been characterized by MALDI methods.[341]

Mass spectrometry has also been used to characterize compounds of the type T_8R_7R' in which the T_8R_7 unit is an inert pendant with a reactive R′ group or is within a polymeric species. Ion mobility mass spectrometry has been used in conjunction with molecular mechanics to investigate the structures and cross sections of propyl methacrylate (PMA) oligomers of the type $[T_8(c\text{-}C_5H_9)_7(PMA)]_n$. These compounds can be sodiated using MALDI methods, and the experimental results indicate that there is only one conformer for both $[T_8(c\text{-}C_5H_9)_7(PMA)]Na^+$ and $[T_8(c\text{-}C_5H_9)_7(PMA)]_3Na^+$ but several for $[T_8(c\text{-}C_5H_9)_7(PMA)]_2Na^+$, these results being in good general agreement with the computational studies. For longer chains such as $[T_8(c\text{-}C_5H_9)_7(PMA)]_8Na^+$, the POSS cages group together and may hinder further extension of the chain.[669] FABMS has also been used to characterize monomeric POSS species such as $T_8(c\text{-}C_5H_9)_7OTi(O\text{-}i\text{-}Pr)$,[409] and electrospray mass spectrometry has been used to characterize Os-containing POSS species **142** and **143**, for which the isotope pattern for Os can be seen.[182]

MALDI methods have also been used to confirm that the tetra-POSS compound $[T_8(i\text{-}Bu)_7(CH_2CH_2SiMe_2O)]_4Si$ (m/z = 3821.91) is formed via the Pt-catalyzed reaction between $(HSiMe_2O)_4Si$ and $T_8(i\text{-}Bu)_7(CH{=}CH_2)$[282] and to characterize a series of fluorophore-containing $T_8(i\text{-Bu})_7$ derivatives that can be used as sensors for a variety of toxic chemicals.[346] MALDI-TOF can also be used in conjunction with size-exclusion chromatography to distinguish between the components in silsesquioxane mixtures containing $[(n\text{-Oct})_7T_8]_2O$ and $[(n\text{-Oct})_7T_8O]_2[(n\text{-Oct})_6T_8]$ as well as larger silsesquioxanes $[T_n(n\text{-}C_7H_{15})_n]$ with values of n up to 28.[670] Furthermore, POSS derivatives $T_8(n\text{-Oct})_8$, $[(n\text{-Oct})_7T_8]_2O$, and $[(n\text{-Oct})_7T_8O]_2[(n\text{-octyl})_6T_8]$ have also been characterized by coupled HPLC−MALDI-TOF methods.[666]

3.8. Electronic Spectra of POSS Compounds

The electronic spectra of T_8 POSS derivatives have not been widely studied until relatively recently when their importance as tethers for an extensive range of organic species, including photoluminescent and fluorescent fragments, has been realized. Some of the fundamental electronic properties of the T_8 cage have also been reinvestigated recently. The absorption and emission spectra for stilbene derivatives $T_8(CH{=}CHC_6H_4\text{-}4\text{-}CH{=}CHC_6H_4\text{-}4\text{-}R)_8$ (R = H, Me, OMe or NH_2) have been recorded and compared with their simple organic counterparts bearing no POSS cage. Surprisingly, the emission for the 4-NH_2 derivative shows a bathochromic shift of 119 to 507 nm (in MeCN) from the 388 nm for the 4-H compound. The reason for this dramatic effect is not clear, but because calculations on the nature of the HOMO and LUMO for a T_8 core show it to be highly electrophilic, it is thought that the LUMO may act as an acceptor for charge transfer from the NH_2 group. Because the POSS core is symmetrical, this would suggest a three-dimensional conjugation and that the T_8 core does not act as a traditional silica-like insulator (Figure 9).[322] Further work on this aspect of POSS cage electronic structure should prove very interesting.

Fluorescence and photoluminescence studies on related biphenyl derivatives, $T_8(CH{=}CHC_6H_4\text{-}4\text{-}Ph)_8$, **162** and **163** (Chart 32), show that although the POSS cage has relatively little effect on the photophysical properties of the chromophores when the biphenyl is unsubstituted, when a bulky functional group is added to the biphenyl, the restricted molecular freedom allows tuning of the photophysical properties.[386] The aldehyde $T_8[CH{=}CHC_6H_4\text{-}4\text{-}C_6H_3\text{-}3,5(CHO)_2]_8$ is not fluorescent but the related alcohol, $T_8[CH{=}CHC_6H_4\text{-}4\text{-}C_6H_3\text{-}3,5(OH)_2]_8$, has a photoluminescent quantum yield of 10% at saturation and a bathochromic emission shift compared with $CH_2{=}CHC_6H_4\text{-}4\text{-}C_6H_3\text{-}3,5(OH)_2$.[364] The UV spectrum of $T_8(SiMe_2\text{-}t\text{-Bu})_8$ shows a significant bathochromic shift with a lowest transition energy absorption at 285 nm compared with simple hexa-alkyl substituted disilanes, which have corresponding absorptions at ca. 200 nm. The reasons for this difference are not well understood.[201] The search for materials with low dielectric constant, k, for use in electronic devices has led to investigation of the potential of methyl silsesquioxanes (k ca. 2.6−2.8) for this purpose. Thus, the electronic absorption spectra, excited-state properties, and third-order polarizabilities have been calculated for both the O_h and C_{2v} isomers of T_8Me_8.[458]

The UV spectrum of $T_8(c\text{-}C_5H_9)_7OTi(O\text{-}i\text{-Pr})_3$ at 10^{-5} M in hexane shows a λ_{max} value of 247 nm, while the diffuse reflectance UV spectrum shows two bands, a sharper, weaker one at 229 nm and a stronger, broader one at 286 nm,[409] while λ_{max} for $T_8[C_6H_4NHC({=}O)CH{=}CHPh]_8$ in acetone is 337 nm.[491] The absorption spectrum for $T_8\{(CH_2)_3N[(CH_2)_2\text{-}CO_2Na]_2\}_8$ in the presence of Cu^{2+} gives a λ_{max} at 714 nm and a Job's plot indicates a 4:1 stoichiometry for the POSS/Cu^{2+} complex.[104] The UV spectrum of a transparent film made from a poly(carbazole) derivative as electron donor and a dinitrobenzyl-substituted POSS compound as electron acceptor showed that each POSS molecule forms about four charge complex interactions.[671] A range of polypyrene POSS derivatives formed by Heck coupling of $T_8(CH{=}CH_2)_8$ and 1-bromopyrene show solution photoluminescence bathochromic shifts of ca. 50 nm from molecular pyrene itself, presumably due to the extra conjugation provided by the Si-$CH{=}CH_2$ linkage.[325] The high density of pyrene groups in compounds containing eight such groups leads to a high fluorescent efficiency but lower efficiencies are found if too many (up to 14) pyrene groups are present, probably due to luminescent quenching.[325] A range of aryl-substituted POSS species **164**−**171** (Chart 33) have been shown by photoluminescence excitation spectra, UV, micro-Raman, and TEM to be novel examples of quantum dot materials in which the organic arms are isolated by the POSS cage. The photoluminescence spectra indicate that the emissive centers are the pendent arms on the cage and not the cage itself.[313,330,672] These compounds are soluble and readily processed and the photoluminescent yields are increased when the conjugated arms are attached to the POSS core.

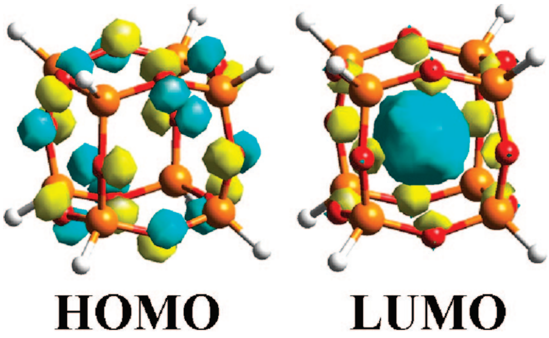
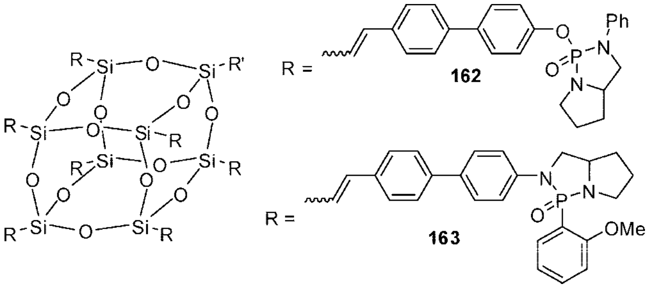


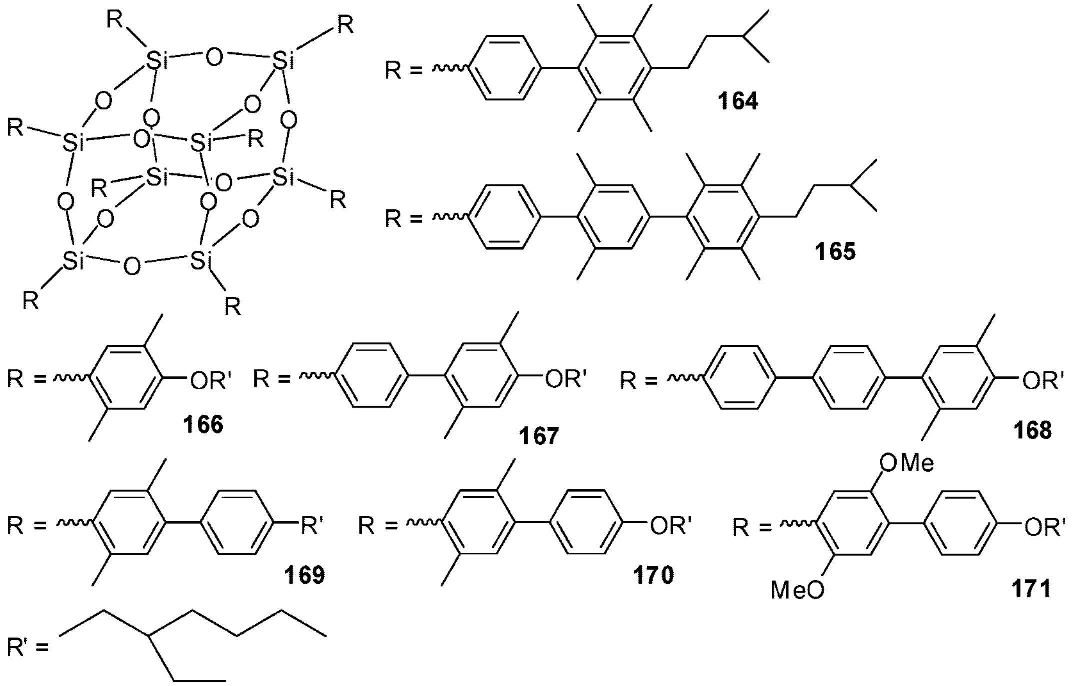
Figure 9. HOMO and LUMO of T_8R_8. Reproduced with permission from ref 322. Copyright 2008 American Chemical Society.

Chart 32



The incorporation of a POSS core into a polymer matrix tends to reduce the aggregation of the polymer chains and to improve emission, reducing the formation of exciplexes and excimers. When a cyclopentyl POSS fragment was attached at the C-9 position to a polyfluorene via an $OSiMe_2$ linker, electroluminescent devices fabricated from the polyfluorene gave a deep blue emission and showed no evidence of aggregation or excimer formation.[279] Similarly, terfluorene chromophores attached to a T_8 cage via an $OSiMe_2$ group gave an electroluminescent nanoparticle with good solubility and a higher external quantum yield compared with poly(dihexylfluorene) devices,[248] and $T_8(c\text{-}C_5H_9)_7(CH_2)_3$- substituents on π-conjugated polymers promote uniform dispersion and reduce aggregation, even in concentrated (5.0×10^{-4} M) solution in $CHCl_3$.[673]

Chart 33



The absorption and photoluminescence spectra of a $T_8(i\text{-}Bu)_7$-terminated polyfluorene have been recorded for comparison with doping materials used to make white-light-emitting diodes and show that there is good overlap between the POSS polymer emission and the dopant absorption band.[674] The electroluminescence spectrum of T_8Ph_7-terminated poly(9,9-dioctylfluorene) blended with poly(*p*-phenylene vinylene) shows both blue and green emission bands.[675] Photoluminescence studies also show that similar polyfluorene derivatives containing $T_8(c\text{-}C_5H_9)_7$ cages attached via $OSiMe_2$ linkages have increased fluorescence quantum yields, the POSS cages being thought to reduce fluorescence quenching.[676] The UV−vis and photoluminescence spectra of a range of $T_8Ph_n(C_6H_4Ar)_{8-n}$ ($n = 2, 3, 4$, or 5) isomers (Ar = Ph, biphenyl, naphthyl, 9,9-dimethylfluorenyl, etc.) have been recorded and show spectra similar to those for the simple untethered aromatic but with a small bathochromic shift of about 20−30 nm.[341] Polyfluorenes bearing one or two $T_8(c\text{-}C_5H_9)_7$ groups per fluorene unit emit blue light with high quantum efficiency in solution,[281,343] while those with only $T_8(c\text{-}C_5H_9)_7$ groups as termini exhibit green emission.[677,678] A range of poly(phenylene vinylene)s with pendant $T_8(c\text{-}C_5H_9)_7$ groups attached via an $OSiMe_2(CH_2)_3O$ linkage were found to have UV−vis absorption and photoluminescent emission maxima with increasing hypsochromic shifts as the POSS content increased.[278] LED devices fabricated using these polymers show increased brightness and electroluminescent efficiency compared with related materials without the POSS content.[278]

The photoluminescence spectra of a range of POSS compounds, **18**, **26**, **27**, **44**, **45**, **49**, and **50**, in which there are either one or two types of emitting dye substituents linked to the POSS core via $OSiMe_2$ linkages have been recorded in an attempt to prepare single processable molecules that emit at multiple wavelengths. The photoluminescence from the blue-emitting substituents is dominated by lower energy emission from yellow or orange emitters.[239] Similarly, introduction of $T_8[OSiMe_2(CH_2)_2C_6H_4\text{-}4\text{-}CH_2-]_8$ units, derived from the parent benzyl chloride, as cross-linkers into poly(phenylene vinylene) materials gives highly efficient green-emitting materials.[679] The electronic absorption and photoluminescence spectra of dilute solutions of the carbazole derivative **17** and the PL spectrum of a thin film of the compound suggest that the electronic properties of the carbazole are little affected and that formation of excimers is suppressed.[233,235]

Photoluminescence spectra have also been used to demonstrate that polymers containing $T_8(i\text{-}Bu)_7$ groups bound to poly(*n*-butyl methacrylate) via a propyl methacryl chain can be used as sensors for water vapor.[680] The UV−vis spectrum of methacrylate copolymers containing pendant $T_8(i\text{-}Bu)_7$ groups shows that incorporation of the POSS fragment causes a slight decrease in the transparency, but the resist sensitivity and photopolymerization rates are enhanced as the POSS content increases.[681]

Transient absorption spectrometry has been applied to POSS derivatives of phthalocyanines in order to determine the rate constants of triplet-state quenching for comparison with less bulky derivatives.[406] POSS cages labeled with a boron-based fluorescent dye have been investigated as biocompatible drug carriers and have been used to give fluorescence confocal images, which show that the dye-labeled POSS species is localized in intracellular regions.[682] Fluorescence spectroscopy has also been used to monitor solvent polarity using POSS species partially substituted with a chromaphore.[106]

3.9. NMR and EPR Spectroscopies

3.9.1. Solution ^{29}Si NMR Studies

NMR spectroscopy is, as might be expected, one of the most powerful tools for investigating the structures of T_8 POSS compounds. The organic derivatives of T_8 cages are generally quite soluble in common NMR solvents, which renders them convenient for analysis by multinuclear NMR spectroscopy. ^1H and ^{13}C spectra of organic substituents are little perturbed by the T_8 cage but the ^{29}Si chemical shifts of

Table 26. ^{29}Si NMR Data for T_8R_8 Compounds in Solution

R, T_8 derivative, or compound number	^{29}Si NMR chemical shift (ppm from Me_4Si)	solvent[a]	refs
-H	−84.8; −84.12; −84.5	$CDCl_3$	170, 209, 217
-H	−84.8		75
-H	−84.47		73
-CH_2CH_3	−65.5	$CDCl_3$	390
-$CHDCH_2D$[b]	−65.4 (broad multiplet)	$CDCl_3$	390
-$CH_2CH_2S(CH_2)_2(CF_2)_5CF_3$	−68.65	$CDCl_3$	393
-$CH_2CH_2S(CH_2)_2(CF_2)_7CF_3$	−68.54	$CDCl_3$	393
-CH_2CH_2Br	−70.45	$CDCl_3$	391
-$CH_2CH_2C_6H_4$-4-Br	−66.5	$CDCl_3$	209
-$CH{=}CH_2$	−80.2	$(CD_3)_2CO$	203
-$CH{=}CH_2$	−80.2	$CDCl_3$ or CD_2Cl_2	334
-$CH{=}CH_2$	−79.8, −80.6; −79; −87	$CDCl_3$	79, 684, 685
-$CH{=}CH_2$	−80.0	THF-d_8	204, 205
-$CH{=}CH_2$[c]	−83.0	THF-d_8	204, 205
-$CH{=}CH_2$[c]	−82.9	$(CD_3)_2CO$	203
-$CH{=}CHPh$	−78.35; −78.23	$CDCl_3$	322, 385
-$CH{=}CHPh$	−78.2	THF-d_8	204, 205
-$CH{=}CHPh$[c]	−81.0	THF-d_8	204, 205
-$CH{=}CHC_6H_4$-4-Cl	−78.9	C_6D_6	214
-$CH{=}CHC_6H_4$-4-Br	−78.45	$CDCl_3$	322
-$CH{=}CHC_6H_4$-3-NO_2	−78.96	$CDCl_3$	322
-$CH{=}CHC_6H_4$-4-$CH{=}CHPh$	−78.15	$CDCl_3$	322
-$CH{=}CHC_6H_4$-4-$CH{=}CHC_6H_4$-4-OMe	−78.12	$CDCl_3$	322
-$CH{=}CHC_6H_4$-4-$CH{=}CHC_6H_4$-4-NH_2	−78.06	$CDCl_3$	322
-$CH{=}CHC_6H_4$-4-C_6H_3-3,5-$(CO_2Me)_2$	−78.5	$CDCl_3$	387
-$CH{=}CHC_6H_4$-4-C_6H_3-3,4-$(OMe)_2$	−78.3	$CDCl_3$	387
105	−78.37	C_6D_6	214
-$CH_2CH{=}CH_2$	−70.77	$CDCl_3$	90
-$CH_2CH_2SiMe_2OMe$	−65.91, 18.62 ($SiMe_2OMe$)	$(CD_3)_2CO$	295
-$CH_2CH_2SiMe_2CH_2CH_2SiCl_3$	−67.4, 6.5 ($SiMe_2$), 13.5 ($SiCl_3$)	$CDCl_3$	212
-$CH_2CH_2SiMe(CH_2CH_2SiMe_2Cl)_2$	−67.4, 8.3 (SiMe), 32.5 (SiCl)	$CDCl_3$	212
-$CH_2CH_2SiMe(CH_2CH_2SiMeCl_2)_2$	−66.7, 8.8 (SiMe), 33.3 ($SiCl_2$)	$CDCl_3$	212
-$CH_2CH_2SiMe_2C_6H_3$-3,5-Br_2	−66.0, 1.4 ($SiMe_2$)	$CDCl_3$	214
61	−66.9, −1.3 ($SiMe_2$)	$CDCl_3$	212, 319
62	−66.1, −6.3 (SiMe)	$CDCl_3$	212, 319
63	−66.7, −10.1 (SiAr)	$CDCl_3$	212, 319
-$(CH_2)_3Cy$	−66.7	$CDCl_3$	215
-$(CH_2)_3Ph$	−66.8	$CDCl_3$	215
-$(CH_2)_3NH_2$	−66.5	$CDCl_3$	98
$\{T_8[(CH_2)_3NH_3]_8\}Cl_8$	−66.4	$(CD_3)_2SO$	104–109
-$(CH_2)_3NHC({=}O)(CH_2)_2CO_2H$	−65.3	D_2O	108
-$[(CH_2)_3NMe_2(CH_2CH_2OH)]Cl$	−67.31	D_2O	120
-$(CH_2)_3N[(CH_2)_2CO_2\text{-}t\text{-}Bu]_2$	−66.6	$CDCl_3$	104
-$(CH_2)_3N[(CH_2)_2CO_2H]_2$	−41.2	$CDCl_3$	104
-$(CH_2)_3N(CH_2CO_2H)_2$	−67.2	D_2O	109
-$(CH_2)_3N[CH_2C(O)NH(CH_2)_2NH_2]_2$	−67.4	D_2O	109
-$(CH_2)_3NHPh$	−67.11	$CDCl_3$	120
-$(CH_2)_3N_3$	−69.1	$CDCl_3$	118
-$(CH_2)_3OC({=}O)Me$	−68.69	$CDCl_3$	120
-$(CH_2)_3OC({=}O)CHMe_2$	−66.6	$CDCl_3$	218
-$(CH_2)_3OC({=}O)C({=}CH_2)Me$	−68.69	$CDCl_3$	120
-$(CH_2)_3OCH_2CH(O)CH_2$	−65.2	$CDCl_3$	71, 139, 236
-$CHMeCH_2OCH_2CH(O)CH_2$	−67.6	$CDCl_3$	71, 139, 236
-$(CH_2)_3SH$	−66.80	$CDCl_3$	115
-$(CH_2)_3Cl$	−66.2; −67.28; −68.0; −67.1	$CDCl_3$	118–120, 122, 123, 686
-$(CH_2)_3I$	−66.2	$CDCl_3$	686
-$(CH_2)_2CF_3$	−66.7	THF-d_8	204, 205
-$(CH_2)_2CF_3$	−67.3	$(CD_3)_2CO$	173
-$(CH_2)_2CF_3$[c]	−70.4	THF-d_8	204, 205
-$(CH_2)_2(CF_2)_3CF_3$	−66.9	$(CD_3)_2CO$	125
-$(CH_2)_2(CF_2)_3CF_3$	−66.4	THF-d_8	204, 205
-$(CH_2)_2(CF_2)_3CF_3$[c]	−70.1	THF-d_8	204, 205
-$(CH_2)_2(CF_2)_5CF_3$	−67.0	$(CD_3)_2CO$	125
-$(CH_2)_2(CF_2)_7CF_3$	−67.0	$(CD_3)_2CO$	125
-$(CH_2)_2(CF_2)_7CF_3$	−66.6	THF-d_8	204, 205
-$(CH_2)_2(CF_2)_7CF_3$[c]	−70.7	THF-d_8	204, 205
-$(CH_2)_3Cp$	−68.51	$CDCl_3$	94
-$(CH_2)_3C_6H_4$-4-OMe	−66.77	$CDCl_3$	96
-$(CH_2)_3(OCH_2CH_2)_2OH$	−83.27		217
-$(CH_2)_3(OCH_2CH_2)_3OMe$	ca. −66.5	$CDCl_3$	70
-$CH{=}CHCMe_2OH$	−64.2	$(CD_3)_2CO$	220
69	−68.50		121–123
-$CH_2CH(O)CH_2$	−69.7	$CDCl_3$	90
-$(CH_2)_2CO_2Me$	−67	$CDCl_3$	391
-*i*-Bu	−67.9	$CDCl_3$	63
-$(CH_2)_2CMe_2CH_2CO_2Me$	−65.9	$CDCl_3$	63
-*c*-C_5H_9	−66.6; −66.54	$CDCl_3$	63, 90
-Cy	−68.7; −71.53; −71.23	$CDCl_3$	63, 126, 637
-$CH{=}CH_2(CH_2)_3Me$	−79.10	$CDCl_3$	385

Table 26. Continued

R, T_8 derivative, or compound number	^{29}Si NMR chemical shift (ppm from Me_4Si)	solvent[a]	refs
-n-C_6H_{13}	−66.6	$CDCl_3$	63
endo-**1**	−68.72	$CDCl_3$	63
exo-**1**	−66.93	$CDCl_3$	63
n-Oct	−67.16		670
n-Oct	−66.6	$CDCl_3$	63
i-Oct	−68.20	$CDCl_3$	96
-CH_2Ph	−71.44	$CDCl_3$	79
-Ph	−78.3	$CDCl_3$	128
-Ph	−79.7	$(CD_3)_2CO$	203
-Ph	−78.1	THF-d_8	204
-Ph[c]	−80.6	$CDCl_3$	202
-Ph[c]	−80.7	THF-d_8	204, 205
-C_6H_4-4-Me	−79.5	$(CD_3)_2CO$	203
-C_6H_4-4-Me[c]	−80.4	$(CD_3)_2CO$	203
-$C_6H_4NO_2$[b]	−79.1, −83.0	$(CD_3)_2CO$	330
-$C_6H_4NO_2$[b]	−79.39, −83.18;	$CDCl_3$	128
-$C_6H_4NO_2$[b]	−69, −71	THF	134
-$C_6H_4NH_2$[b]	−73.3, −77.2; −71.9, −76.4	$(CD_3)_2CO$, THF	330, 398
-$C_6H_4NH_2$[b]	−68.2, −78.9	$CDCl_3$	128
-C_6H_4-2-NHNHPh	−71.3		137
94[b]	−82	$(CD_3)_2SO$	370
95[b]	−80.8 br	CH_2Cl_2, $(CD_3)_2CO$	373
166	−69.245	$CDCl_3$	117
167	−69.289	$CDCl_3$	117
168	−69.248	$CDCl_3$	117
169	−69.408	$CDCl_3$	117
170	−69.804	$CDCl_3$	117
171	−68.316	$CDCl_3$	117
$[NMe_4]_8[T_8O_8]$	−99.4	$MeOH/H_2O$	139, 687
$[NMe_4]_8[T_8O_8]$[d]	−98.122	$H_2O/D_2O/KOH$	459
OEt	−103	$CDCl_3$	74
O-n-Oct	−103	$CDCl_3$	74
O-i-Pr	−103	$CDCl_3$	74
O-t-Bu	−108	$CDCl_3$	74
O-Cy	−103	$CDCl_3$	74
-$OSiMe_2H$	−110.34, −3.00 ($SiMe_2$)	THF-d_8	688
-$OSiMe_2H$	−108.7, −2.1 ($SiMe_2$); −108.697, −1.26 (d, J = 234 Hz, $SiMe_2H$)	$CDCl_3$	141, 142
-$OSiMe_2H$	−108.697, −2.897 ($SiMe_2$)		139, 687
-$OSiMe_2OEt$	−109.8, −9.9 ($SiMe_2$)	$CDCl_3$	300
-$OSiMe(OEt)_2$	−110, −50.1 (SiMe)	$CDCl_3$	300
-$OSi(OEt)_3$	−110, −89.4 [$Si(OEt)_3$]; −110.8, −89.4 [$Si(OEt)_3$]	$CDCl_3$	293, 300
-$OSiMe_2OSiMe_3$	−108.986, −21.990 ($SiMe_2O$), 12.469 ($SiMe_3$)	THF-d_8	298
15	−108.86, 13.49 ($SiMe_2$)	$CDCl_3$	142
16	−100.9, 21.0		224
-$OSiMe_2CH_2CHMe$-C_6H_4-4-CMe_2NCO	−108.5, 20.0 ($SiMe_2$)	$CDCl_3$	243
-$OSiMe_2(CH_2)_3OC({=}O)$-C_6H_4-4-NH_2	−108.05, 13.60 ($SiMe_2$)	$(CD_3)_2SO$	689
-$OSiMe_2(CH_2)_3OCH_2CH_2OC({=}O)C_6H_4$-4-$NH_2$	−108.52, 13.60 ($SiMe_2$)	$CDCl_3$	689
-$OSiMe_2CH{=}CH_2$	−100.4, 8.58, 9.026 ($SiMe_2$)	$CDCl_3$	144
-$OSiMe_2CH_2CH_2S(CH_2)_2(CF_2)_5CF_3$	−108.89, 11.80 ($SiMe_2$)	$CDCl_3$	393
-$OSiMe_2CH_2CH_2S(CH_2)_2(CF_2)_7CF_3$	−108.87, 11.79 ($SiMe_2$)	$CDCl_3$	393
-$OSiMe_2(CH_2)_3NMe_2$	−107.3, 14.9 ($SiMe_2$)	$(CD_3)_2CO$	240
-$OSiMe_2(CH_2)_3OH$	−100.4, 8.6 ($SiMe_2$)	$CDCl_3$	242
-$OSiMe_2CH{=}CHCH_2OC({=}O)C({=}CH_2)Me$	−109.4, 1.39, 1.04 (α, β isomers)	$CDCl_3$	141
-$OSiMe_2(CH_2)_4CH(O)CH_2$	−101, 21.3 ($SiMe_2$); −100.4, 20.9 ($SiMe_2$)	$CDCl_3$	224, 263, 690
-$OSiMe_2(CH_2)_3OCH_2CH(O)CH_2$	−108, 13.6 ($SiMe_2$)	$CDCl_3$	263
-$OSiMe_2(CH_2)_3OCH_2CH(O)CH_2$	−129.4, −7.3 ($SiMe_2$)	C_6D_6	139, 247, 687
-$OSiMe_2(CH_2)_3OC({=}O)CMe_2Br$	−109.8, 12.0 ($SiMe_2$)	$CHCl_3$	691
-$OSiMe_2(CH_2)_3C_6H_4$-2-OH	15.6 ($SiMe_2$)	$CDCl_3$	228
-$OSiMe_2(CH_2)_3(OCH_2CH_2)_2OH$	−109.27, 12.72 ($SiMe_2$)		217
-$OSiMe_2(CH_2)_3(OCH_2CH_2)_nOH$	−108.5, 13.0 ($SiMe_2$)	$CDCl_3$	692
-$OSiMe_2(CH_2)_3(OCH_2CH_2)_2OC({=}O)CMe({=}CH_2)$	−109.22, 13.24 ($SiMe_2$)		376
-$OSiMe_2(CH_2)_3[O(CH_2)_3]_2O{-}C({=}O)CMe({=}CH_2)$	−108.8, 13.0 ($SiMe_2$)	$CDCl_3$	141
17	−108.88, 12.04 ($SiMe_2$)	$CDCl_3$	233–235
-$OSiMe_2CH_2Cl$	−109.31, 7.36 ($SiMe_2$)	THF-d_8	299
-$OSiMe_2CH_2Br$	−109.36, 7.02 ($SiMe_2$)	THF-d_8	299
-$OSiMe_3$	−108.95, 12.53 ($SiMe_3$)	THF-d_8	688
-$OSiMe_3$	−109, 13 ($SiMe_3$)	$CDCl_3$	74
-$OSiMe_2C_6H_4$-4-Me	−104.4, 6.8 ($SiMe_2$)	$CDCl_3$	143
-$OSiMe_2C_6H_4$-4-CBr_3	−104.7, 6.92 ($SiMe_2$)	$CDCl_3$	143
-$OSiMe_2C_6H_4$-4-CO_2H	−108.8, 3.4 ($SiMe_2$)	$(CD_3)_2CO$	143
-$OSnMe_3$	−110.144		402
-OSn-n-Bu_3	−101.0		402
-$O[TiClCp_2]$	−101.9		402
-$SiMe_2$-t-Bu	−71.31, −12.67 ($SiMe_2$-t-Bu)	$CDCl_3$	201

[a] Where no solvent is listed, none was given in the reference in question. [b] Contains a mixture of isomers. [c] Anionic endohedral fluoride, $[NBu_4]^+$ cation. [d] Enriched in ^{29}Si.

the POSS cage silicon atoms are sensitive to changes in their substituents and thus ^{29}Si NMR spectroscopy has become a powerful technique both for checking the purity of POSS compounds and in their identification. Characteristic ^{29}Si chemical shifts for T_8(alkyl)$_8$ compounds come in the range of ca. −65 to −70 ppm, as shown in Table 26, and similar shifts are found for the POSS cages when such precursors are incorporated into polymeric materials. The chemical shifts for T_8(aryl)$_8$ are found in the range ca. −77 to −83 ppm although for the substituted compounds such as $T_8(C_6H_4NH_2)_8$, many of these spectra are complicated by the presence of several isomers. Again, the presence of this characteristic shift range in polymeric materials is taken to indicate that the cage has not been degraded during a polymerization process. The chemical shift range for T_8 compounds with siloxy substituents is usually observed at ca. −110 ppm, as is seen in Table 26.

The ^{29}Si spectrum of the product obtained from free radical polymerization of $T_8(CH{=}CH_2)_8$ and acetoxystyrene was used to distinguish the degree of reaction because the $\mathit{Si}CH{=}CH_2$ signal and the $\mathit{Si}CH_2CH_2$ signal are distinctly different at −79 and −66 ppm, respectively.[683] Similarly the ^{29}Si NMR chemical shift has been used to show that the product from hydrosilylation of T_8H_8 with $HC{\equiv}CCMe_2OH$ is predominantly the C-substituted $T_8(CH{=}CHCMe_2OH)_8$ and not the O-substituted $T_8(OCMe_2C{\equiv}CH)_8$.[220]

An interesting series of compounds shown in Table 26 are those containing a fluoride ion within the cage,[204,205] for example, $[NBu_4][F@T_8(CH{=}CH_2)_8]$ (δ ca. −83 ppm), which show an upfield shift of a few ppm compared with their empty cage counterparts. Only a single chemical shift is seen for the endohedral complexes suggesting that the fluoride interacts equally with all the Si atoms in the cage.

As discussed in sections 2.1.2 and 2.5.3, the synthesis of T_8 cages containing two or more different substituents, other than by corner-capping $Si_7O_9(OH)_3R_7$ and related compounds, remains a challenge, with one of the best ways of investigating the mixtures of isomers often formed in these attempted syntheses being ^{29}Si NMR spectroscopy. Table 27 shows ^{29}Si NMR data for T_8R_7R' compounds (Chart 34), the chemical shifts being, as expected, similar to those found for the corresponding TR or TR′ groups in T_8R_8 and $T_8R'_8$ compounds. Ideally, three different TR Si environments in a 3:3:1 ratio are observed for a T_8R_7R' compound, together with the TR′ signal, but the three signals are often difficult to distinguish and appear as a single broad signal. A detailed study of the ^{29}Si NMR spectra of $T_8(OPh)_n(R)_{8-n}$ [$n = 0-8$; R = n-$C_{11}H_{23}$ or $(CH_2)_2CMe_2CH_2CO_2Me$] prepared from T_8H_8 showed that complicated mixtures of all possible isomers were formed. Mathematical modeling of the spectra shows that they are consistent with the predominant isomers formed being those bearing dissimilar substituents on adjacent Si atoms.[284]

The ^{29}Si NMR spectrum of the isomers of **52**, derived from hydrosilylation of $T_8(OSiMe_2H)_8$ with vinylcyclohexane, show two different SiO_4 silicon environments at −108.6 and −108.94 attributed to $\mathit{Si}OSiMe_2H$ and $\mathit{Si}OSiMe_2CH_2$, respectively, and at 13.78 and −2.86 for $OSiMe_2H$ and $OSiMe_2CH_2$, respectively.[142] Hydrosilylation of $T_8(OSiMe_2H)_8$ with a 6:2 mixture of allylbenzene and 1,5-hexadiene gives products having ^{29}Si NMR signals at −108.84 ($\mathit{Si}O_4$), 12.67 [$Ph(CH_2)_3\mathit{Si}Me_2O$], and 12.78 ppm ($C_6H_{11}\mathit{Si}Me_2O$) corresponding to a mixture of isomers of $T_8[OSiMe_2(CH_2)_3Ph]_{8-n}(OSiMe_2C_6H_{11})_n$ (n = 0−6).[288]

The presence of two signals at −67.3 and −69.2 ppm in the ^{29}Si NMR spectrum of a product obtained from the cohydrolysis of $NH_2(CH_2)_3Si(OEt)_3$ and (i-Oct)$Si(OMe)_3$ has been used as evidence for the formation of compound **172** (Chart 35). However, this structure has three different Si environments (although two signals may of course be coincident) and other isomers may also be present.[149] The presence of $[NMe_3(CH_2CH_2OH)]^+$ in silicate solutions promotes the formation of the unusual silicate anion $[T_8(O)_4(OT)_4]^{16-}$ in which the exocyclic T-units are distributed symmetrically at alternate corners of the T_8 cage and has ^{29}Si NMR chemical shifts at −82, −99, and −109 ppm ascribed to the exocyclic Si, the cage T−O-Si, and the cage SiO^- silicon atoms, respectively.[694]

3.9.2. Other Heteronuclear NMR Studies

The change in the ^{11}B NMR spectrum has been used to show that $T_8(c\text{-}C_5H_9)_7(OH)$ interacts with $(C_6F_5)_3B$ via B···OH coordination,[695] while an analysis of the ^{119}Sn NMR chemical shift tensors in crystalline samples of $T_8(OSnMe_3)_8$ and $T_8(OSnMe_3)_8 \cdot 4H_2O$ shows that the tensors change significantly with change in tin atom coordination number. This change has been used to infer the nature of the tin coordination in an amorphous sample of $T_8(OSnMe_3)_8$.[403] The high number of fluorine nuclei in POSS species derived from $T_8[(CH_2)_3NH_2]_{8-n}[(CH_2)_3NHC({=}O)CF_3]_n$ (where n = 3−5) and attached to the surface of silica nanoparticles has enabled monitoring of enzymatic activity by ^{19}F NMR spectroscopy.[107] Dendrimers based on a $T_8[(CH_2)_3NH]_8$ core encased in L-lysine with a shell containing chelating groups can be used to prepare Gd(III)-based contrast agents for magnetic resonance angiography. These agents are readily excreted, show size-dependent contrast enhancement, and may reduce the toxic side effects of such agents by allowing reduction in the dose.[383] Related dendrimers derived from $T_8[(CH_2)_3N(CH_2CO_2H)_2]_8$ have also been prepared as contrast agents for magnetic resonance imaging.[109]

3.9.3. EPR Spectra

The use of EPR spectroscopy in the characterization of T_8 derivatives has been sparse but the increasing interest in using the T_8 cage to encapsulate a range of species has prompted several recent studies. The EPR spectrum for a mixture of the endohedral POSS complexes $H@T_8(n\text{-}Pr)_8$ and $D@T_8(n\text{-}Pr)_8$ in toluene has been recorded in order to determine the temperature dependence of the ^{29}Si superhyperfine coupling constant, which was found to exhibit a negative temperature coefficient.[428] The EPR spectra of the POSS series $H@T_8[(CH_2)_nH]_8$ (where n = 0−3) have also been recorded as solids and in solution in which isotropic hyperfine interactions with ^{29}Si can be observed.[696] The rate of detrapping of H or D from POSS cages such as $H@T_8(n\text{-}Pr)_8$ has been measured in the solid state and in solution and is found to vary little with changes to cage substituent, to be independent of other free radicals or oxygen, and to have activation energies, E_a, for detrapping of H and D from T_8Me_8 of 126.7 ± 1.2 and 127.4 ± 1.2 kJ mol^{-1}, respectively. A difference in zero-point energies of trapped H and D is thought to give rise to the observed kinetic isotope effect for detrapping H and D from T_8Me_8.[428] The g-value and hyperfine splitting constant for the hydrogen atom in the cage in $H@T_8(OSiMe_3)_8$ are 2.0032 and 1418.6 MHz, respectively, and the excitation energy of decay is 110−117 kJ

Table 27. ^{29}Si NMR Data for T_8R_7R' Compounds in Solution

R and R′, T_8 derivative, or compound no.				
R	R′	^{29}Si NMR Chemical shift (ppm from Me_4Si)	solvent[a]	refs.
-$(CH_2)_2CF_3$	-Me	−64.8, −67.5, −68.0	$(CD_3)_2CO/CDCl_3$	173
-$(CH_2)_2CF_3$	-$(CH_2)_2OH$	−67.65, −67.66, −67.84	$CDCl_3$	174
-$(CH_2)_2CF_3$	-$(CH_2)_2OC(=O)Me$	−67.62, −67.72, −68.66	$CDCl_3$	174
-$(CH_2)_2CF_3$	-$(CH_2)_2OC(=O)CMe_2Br$	−67.67, −67.73, −69.02	$CDCl_3$	174
-$(CH_2)_2CF_3$	-$(CH_2)_2Ph$	−66.4, −67.4, −67.7	$(CD_3)_2CO$	173
-$(CH_2)_2CF_3$	-$(CH_2)_2(CF_2)_5CF_3$	−67.2, −67.4	$(CD_3)_2CO$/THF	174
-$(CH_2)_2CF_3$	-$(CH_2)_2(CF_2)_7CF_3$	−67.2, −67.3	$(CD_3)_2CO$	174
-$(CH_2)_2CF_3$	-$(CH_2)_2(CF_2)_9CF_3$	−67.2, −67.3	$(CD_3)_2CO$	174
-$(CH_2)_2CF_3$	-$(CH_2)_2CH(CF_3)_2$	−67.3, −70.6	$(CD_3)_2CO$	174
-$(CH_2)_2CF_3$	-$(CH_2)_2OC(=O)C_6H_4$-4-$OCF=CF_2$	−67.5, −67.6, −68.6 (4:3:1)	$CDCl_3$	162
-$(CH_2)_2CF_3$	-$(CH_2)_2OCF(CF_3)_2$	−66.1, −67.3, −67.5	$(CD_3)_2CO$	174
-$(CH_2)_2CF_3$	-$(CH_2)_3OH$	−69.4, −68.4, −67.0, −66.1 (3:1:3:1)	$(CD_3)_2CO$	176
-$(CH_2)_2CF_3$	-$(CH_2)_3Cl$	−70.1, −69.2, −66.7, −65.9 (1:3:3:1)	$(CD_3)_2CO$	176
-$(CH_2)_2CF_3$	-$(CH_2)_3Br$	−65.8, −66.8, −67.0	$(CD_3)_2CO$	177
-$(CH_2)_2CF_3$	-C_6H_4-4-$OCF=CF_2$	−68, −71.5	$(CD_3)_2CO$	178
-*i*-Bu	-$(CH_2)_2OC(=O)Me$	−67.0, −67.4, −70.0 (3:4:1)	$CDCl_3$	162
-*i*-Bu	-$(CH_2)_2OH$	−67.1, −67.3, −69.1 (3:4:1)	$CDCl_3$	162
-*i*-Bu	-$(CH_2)_2OC(=O)C_6H_4$-4-$OCF=CF_2$	−67.0, −67.3, −69.9 (3:4:1)	$CDCl_3$	162
-*i*-Bu	-$(CH_2)_3NH_2$	−66.8, −67.2, −67.4	$CDCl_3$	422
-*i*-Bu	-$(CH_2)_3N_3$	−67.57, −67.86, −68.12 (3:4:1)	$CDCl_3$	165
-*i*-Bu	-$(CH_2)_3Cl$	−67.57, −67.87, −68.10 (3:4:1)	$CDCl_3$	165
-*i*-Bu	-$CH=CHCH_2C(CF_3)_2OH$	−61.4, −64.6	$CDCl_3$	228
173		−63.0, −61.0	$CDCl_3$	228
-*i*-Bu	-$(CH_2)_3OCH_2CH(O)CH_2$	−67.32, −67.64, −67.86; −67.29, −67.61, −67.83 (1:3:4)	$CDCl_3$	573, 647
-*i*-Bu	-$(CH_2)_3OCH_2CH(OH)CH_2N_3$	−66.25, −67.29	$CDCl_3$	347
-*i*-Bu	-$(CH_2)_3NHCH_2CH_2NH_2$	−67.34, −6.59,[b] −67.65	$CDCl_3$	347
-*i*-Bu	-$(CH_2)_3NHC(=O)C_6H_3$-3,5-$(OCN)_2$	−65.5, −67.8, −68.1	$CDCl_3$	344
-*i*-Bu	-C_6H_4-4-Me	−79.5, −67.3, −66.7	$CDCl_3$	167
-*i*-Bu	-C_6H_4-4-CH_2Br	−76.3, −63.3, −62.6	$CDCl_3$	167
-*i*-Bu	-C_6H_4-4-CH_2OH	−76.3, −63.3, −62.6	$CDCl_3$	167
-*i*-Bu	-C_6H_4-4-CBr_3	−63.27, −62.59, −62.55	$CDCl_3$	167
-*i*-Bu	-C_6H_4-4-CO_2H	−77.0, −63.3, −62.5	$CDCl_3$	167
-*i*-Bu	-$OSiMe_2H$	−2.98, −66.84, −67.76, −67.79, −108.97	$CDCl_3$	274
-*i*-Bu	-$OSiMe(C_6H_4$-4-$OCF=CF_2)_2$	−9.6, −66.3, −67.3, −109.0 (1:3:4:1)	$CDCl_3$	302
174		−64.0, −62.0, −104	$CDCl_3$	228
175		−65, −63, −104	$CDCl_3$	228
-*c*-C_5H_9	-H	−66.47 (SiCH), −83.90 (Si−H)	$CDCl_3$	584
-*c*-C_5H_9	-$OSiMe(C_6H_4$-4-$OCF=CF_2)_2$	−9.8, −65.3, −65.9, −107.9 (1:3:4:1)	$CDCl_3$	302
-*c*-C_5H_9	-Cl	−65.74, −66.32, −66.36 (3:3:1), −89.53 (SiCl)	$CDCl_3$	307
11		−65.83, −66.41, −77.01 (3:4:1)	$CDCl_3$	179
-*c*-C_5H_9	-$(CH_2)_2OC(=O)Me$	−65.9, −66.0, −69.2 (3:4:1)	$CDCl_3$	162
-*c*-C_5H_9	-$(CH_2)_3OC(=O)CH=CH_2$	−66.53, −67.00	$CDCl_3$	183
-*c*-C_5H_9	-$(CH_2)_2OH$	−65.9, −68.1 (7:1)	$CDCl_3$	162
-*c*-C_5H_9	-$(CH_2)_2OC(=O)C_6H_4$-4-$OCF=CF_2$	−65.9, −68.0, −69.1 (4:3:1)	$CDCl_3$	162
-*c*-C_5H_9	-$(CH_2)_3OC_6H_4$-4-CHO	−66.2, −66.7	$CDCl_3$	351
-*c*-C_5H_9	-$(CH_2)_3Cl$	−66.52, −67.11	$CDCl_3$	181
-*c*-C_5H_9	-$(CH_2)_3I$	−65.52, −67.93 (7:1)	$CDCl_3$	181
91		−66.50, −66.60, −67.72	$CDCl_3$	362
-*c*-C_5H_9	-$(CH_2)_3SiMe_2C_6H_4$-4-$SiMe_2H$	−3.40 ($SiMe_2$), −17.02 ($SiMe_2H$), −66.25 (4 SiC_5H_9), −66.41 (3 SiC_5H_9), −66.57 ($SiCH_2$)		184, 277
176		−66.47, −66.77	$CDCl_3$	352
177		−66.40, −66.69	$CDCl_3$	352
120		−65.99, −66.56 [3:4, Si(*c*-C_5H_9)], −77.41	$CDCl_3$	400
121		−65.76, −66.19 [3:4, Si(*c*-C_5H_9)], −71.34	$CDCl_3$	400
119		−71.06, −71.67 [3:4, Si(*c*-C_5H_9)], −81.92	$CDCl_3$	400
123		−65.70, −66.26 [3:4, Si(*c*-C_5H_9)], −78.34	$CDCl_3$	400
122		−66.56, −66.37 [3:4, Si(*c*-C_5H_9)], −78.61	$CDCl_3$	400
124		−66.03, −66.36 [3:4, Si(*c*-C_5H_9)], −79.84	$CDCl_3$	400
125		−66.03, −66.36 [3:4, Si(*c*-C_5H_9)], −79.84	$CDCl_3$	400
126		−66.56, −66.37 [3:4, Si(*c*-C_5H_9)], −78.61	$CDCl_3$	400
127		−66.07, −66.46 [3:4, Si(*c*-C_5H_9)], −80.40	$CDCl_3$	400
128		−66.31, −66.39 [3:4, Si(*c*-C_5H_9)], −79.81	$CDCl_3$	400
-*c*-C_5H_9	-C_6H_4-4-CH_2Cl	−67.8, −68.2, −79.6	THF	354, 363, 586
-*c*-C_5H_9	-C_6H_4-4-$CH_2OC_6H_4$-4-CHO	−67.9, −68.2, −79.6	THF	185
-*c*-C_5H_9	-C_6H_4-4-$CH_2OC_6H_2$-4-Me-2,6-$(OMe)_2$	−66.5, −66.6	$CDCl_3$	186
178		−67.9, −68.2, −79.6	THF	185
-*c*-C_5H_9	-C_6H_4-4-(*E*)-$CH=CHFc$	−66.15, −66.49, −79.62	$CDCl_3$	187, 353
-*c*-C_5H_9	-C_6H_4-4-(*Z*)-$CH=CHFc$	−66.15, −66.49, −79.62	$CDCl_3$	187, 353
-*c*-C_5H_9	-OT_8(*c*-$C_5H_9)_7$	−65.71, −66.47, −110.00 (3:4:1)	$CDCl_3$	307
-*c*-C_5H_9	-$OSiMe_2C\equiv CH$	−15.79, −65.58, −66.24, −108.13 (1:3:4:1)	$CDCl_3$	303
-*c*-C_5H_9	-$OSiMe_2C\equiv C$-2-C_5H_4N	−15.12, −65.58, −66.27, −108.18 (1:3:4:1)	$CDCl_3$	303
150		−65.94, −66.65, −112.20 (3:4:1)	$CDCl_3$	410
152		−66.37, −66.72, −110.86 (3:4:1)	$CDCl_3$	410
-*c*-C_5H_9	-$OMo(CH_2$-*t*-$Bu)_3(=NH)$	−105.11, −65.72, −65.68, −65.63 (1:3:1:3)	C_6D_6	412
-*c*-C_5H_9	-$OMo(PMe_3)_2(\equiv N)(=CH$-*t*-Bu)	−100.79, −66.21, −65.64 (1:3:4)	C_6D_6	412
-*c*-C_5H_9	-$ORe(CH_2$-*t*-Bu)(=CH-*t*-Bu)($\equiv$C-*t*-Bu)	−99.9, −65.7, −65.2 (1:4:3)	C_6D_6	407
-*c*-C_6H_9	-$(CH_2)_3SiMe_2C_6H_4$-4-$SiMe_2H$	−3.45 ($SiMe_2$), −17.02 ($SiMe_2H$), −67.65 (4 SiC_6H_9), −67.89 (3 SiC_6H_9), −66.16 ($SiCH_2$)	$CDCl_3$	184
-*c*-C_6H_9	-Cl	−67.89, −68.47, −68.53 (3:3:1), −89.28 (SiCl)	$CDCl_3$	307

Table 27. Continued

R and R′, T_8 derivative, or compound no.				
R	R′	^{29}Si NMR Chemical shift (ppm from Me_4Si)	solvent[a]	refs.
-Cy	-$(CH_2)_3SiMe_2C_6H_4$-4-$SiMe_2H$	−3.43 ($SiMe_2$), −17.03 ($SiMe_2H$), −68.38 (4 SiCy), −68.56 (3 SiCy), −66.47 ($SiCH_2$)	$CDCl_3$	184
-Cy	-C_6H_4-4-CH_2Cl	−67.8, −68.2, −79.6	THF	188
-Cy	-C_6H_4-4-$CH_2OC_6H_4$-4-NO_2	−67.9, −68.2, −79.6	THF	188
-Cy	-C_6H_4-4-$CH_2OC_6H_4$-4-NH_2	−67.9, −68.2, −79.3	THF	188
104		−67.9, −68.2, −79.5	THF	188
-Cy	-$SiCl_3$	−62.0 (*Si*$SiCl_3$), −31.4 ($SiCl_3$), −67.7, −67.8, −67.9, −68.4	$CDCl_3$	156
-Cy	-$OSiCl_3$	−66.0 (*Si*$OSiCl_3$), −56.6 ($OSiCl_3$), −67.8, −68.0, −68.6, −69.0, −69.6, −69.8, −70.2	$CDCl_3$	156
-Cy	T_8Cy_7	−68.1, −68.6, −68.8, −69.0, −69.5	$CDCl_3$	156
-Cy	T_8Cy_7O	−92.4 (SiO_4), −67.6, −67.8, −68.7, −69.5, −71.7; −67.67, −68.46, −68.49, −109.77 (3:3:1:1)	$CDCl_3$	156, 307
$(T_8Cy_7)_2$(*exo*,*exo*-$Si_8O_{13}Cy_8$)		−65.67, −65.57, −67.81, −67.88, −68.37, −68.40, −68.88, −110.09 (1:1:3:1:3:1:1:1)	$CDCl_3$	307
-Cy	-$O[Re(CO)_5]$	−68.06, −68.66, −99.40 (1:6:1)	CD_2Cl_2	417
$[T_8Cy_7(\mu\text{-}O)Re(CO)_4]_2$		−67.87, −68.55, −68.61, −101.92 (3:1:3:1)	CD_2Cl_2	417
$[T_8(n\text{-}Oct)_7]_2O$		ca. −67, −111.0,		670
-Ph	-$(CH_2)_2C_6H_4$-4-SO_2Cl	−66.69 ($SiCH_2$), −78.35, −78.41, −78.67	$CDCl_3$	191
-Ph	-$(CH_2)_2OC({=}O)Me$	−67.97 ($SiCH_2$), −78.36, −78.67	$CDCl_3$	191
-Ph	-$(CH_2)_2OH$	−67.31 ($SiCH_2$), −78.42, −78.79	$CDCl_3$	191
-Ph	-$(CH_2)_2OC({=}O)CMe_2Br$	−68.27 ($SiCH_2$), −78.4, −78.7	$CDCl_3$	191
13		−65, −78	$(Cl_2DC)_2$	189
-Ph	-$(CH_2)_3OCH_2CH(O)CH_2$	−64.86, −78.23, −78.66 (1:3:4)	$CDCl_3$	573
-Ph	-$(CH_2)_3SiMe_2C_6H_4$-4-$SiMe_2H$	−3.61 ($SiMe_2$), −17.22 ($SiMe_2H$), −78.23 (4 SiPh), −78.71 (3 SiPh), −65.25 ($SiCH_2$)	$CDCl_3$	184
-Ph	-$(CH_2)_3NH_2$	−64.76, −78.30, −78.78 (1:4:3)	$CDCl_3$	194
-OEt	-$(CH_2)_2CO_2C_{16}H_{33}$	−102.80, −102.75, −102.72, −65.26 ($SiCH_2$)	$CDCl_3$	271
-OEt	-$C_{16}H_{33}$	−102.56, −102.63, −102.69, −64.12 ($SiCH_2$)	$CDCl_3$	272
-OEt	-$C_{18}H_{37}$	−102.58, −102.60, −102.69, −64.17 ($SiCH_2$)	$CDCl_3$	272
-OEt	-$C_{20}H_{41}$	−102.58, −102.60, −102.69, −64.17 ($SiCH_2$)	$CDCl_3$	272
179		−108.84 (SiO_4), 13.30, 12.07 ($SiMe_2$), −67.44, −66.35, −65.59, −56.72	$CDCl_3$	693
180		−108.87 (SiO_4), 13.20, 9.83 ($SiMe_2$), −5.39 ($SiMe_2H$), −66.18, −67.29, −67.95	$CDCl_3$	693
181		−108.42 (SiO_4), 13.12, 12.28, 9.54 ($SiMe_2$); −56.39, −65.38, −66.12, −67.18, −67.65	$CDCl_3$	693
182		−108.94 (SiO_4), 13.08, 10.10 ($SiMe_2$), −63.67, −64.88, −66.97, −67.76	$CDCl_3$	693

[a] Where no solvent is listed, none was given in the reference in question. [b] This reported value seems to be an error and should presumably be −67.59 ppm.

mol^{-1}.[207] The effect of rare earth complexes such as $Gd(acac)_3$ on encapsulated hydrogen in $H@T_8(OSiMe_2H)_8$ has also been investigated by EPR.[206]

3.10. Vibrational Spectra of POSS Compounds

Vibrational spectroscopy has been used extensively for the characterization of T_8 compounds, particularly for checking that the characteristic Si−O−Si band in the IR spectrum of a monomeric T_8 compound is present in a material in which the monomer is incorporated, which is usually taken to indicate that the processing of the monomer has not destroyed the T_8 cage. The ν_{as} band due to the Si−O−Si linkages is usually strong and occurs at ca. 1100 cm^{-1}, but it is also broad, and this has led to a range of values being quoted for the same compound by different authors. IR data for a wide range of POSS derivatives are given in Table 28. The analogous bands in ladder silsesquioxanes also occur in the region of 1030−1055 cm^{-1},[697,698] so they may be used to distinguish cage from ladder compounds. Much of the early work on the fundamental vibrational properties of T_8 POSS cages was reported prior to 2003 and can be found reviewed elsewhere.[1]

For a single molecule of T_8H_8, there are 78 normal modes of vibration but only six triply degenerate modes are predicted to be IR active[483,699] The solid-state IR spectrum of T_8H_8 has been described in detail and shows that there are significant solid-state effects when compared with solution spectra. This is in contrast to the Raman spectra in which there is little difference between the two types of spectrum, the difference being attributed to the fact that the POSS cage is distorted in the solid state[483] The IR and the Raman spectra for T_8H_8 have also been calculated giving reasonable agreement with experimental values.[433] A detailed study of the solid-state effects on the IR spectrum of T_8H_8 has shown some older assignments to be incorrect, such that δ_s(O−Si−O) is at 557.9 and δ_{as}(O−Si−O) at 389.5 cm^{-1}.[483] The Si−H stretch in T_8H_8 has also been reported at 2144 cm^{-1},[139] at 2150 cm^{-1},[209] and at 2275 cm^{-1}[171] and the Si−O−Si stretch at 1120 cm^{-1}[209] and 1121 cm^{-1}.[72] The reflection−absorption IR spectrum of T_8H_8 chemisorbed on a gold surface shows bands at 1181, 1111, and 1075 cm^{-1}, all of which are attributable to ν_{as}(Si−O−Si),[600] and coherent anti-Stokes Raman scattering microscopy has used the decay of the O−Si−O bending band (attributable to the cage structure) to monitor cage cross-linking on a heated glass surface.[700] A study of the Si−H stretching frequency in T_8H_8 in various environments has been carried out. In CCl_4 solution and in the solid, KBr and CsI pellet, ν(Si−H) is found at 2277, 2294, and 2300 cm^{-1}, respectively.[603] However, when it is constrained within single or multiwalled nanotubes of diameters 1.0−3 nm, a red shift of 15−19 cm^{-1} for the ν(Si−H) band occurs, which is thought to be due to the Si−H groups interacting not with each other, as in the crystal, but mainly with the walls of the nanotube. The ν(Si−H) band is also significantly broader for molecules within a nanotube, consistent with the high degree of disorder present when compared with the solid T_8H_8.[603] The Si−H stretching frequency in $T_8(OSiMe_2H)_8$ has been reported at

Chart 34

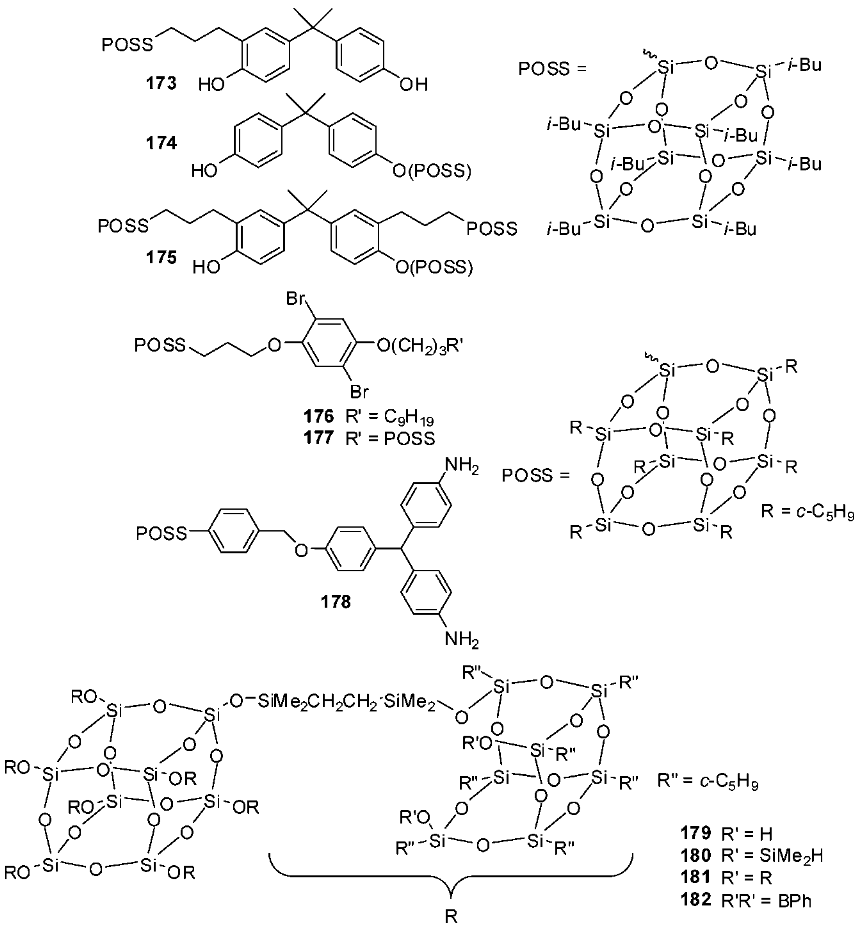
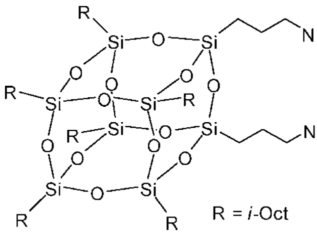


Chart 35



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2250 cm^{-1},[210] 2142 cm^{-1},[254] and 2140 cm^{-1}.[701] The IR and Raman spectra for T_8Me_8 have been determined experimentally and compared with calculated spectra; the experimental IR values are at ca. ν_{as}(Si−O−Si) 1115, 1192, ν_s(Si−O−Si) 517, and δ(O−Si−O) 465, 379 cm^{-1}.[198,697]

The Si−O−Si stretch in $T_8[(CH_2)_3OCH_2CH(O)CH_2]_8$ is at 1103−1110 cm^{-1}, which can also be seen in the interpenetrating network formed from this POSS and $CMe_2(C_6H_4\text{-}4\text{-}OH)_2$ in the presence of poly(ethylene oxide),[71,72,218,702] in cross-linked polymers with poly(*N*-isopropylacrylamide),[703] in cross-linked polymers with poly(4-vinylpyridine),[218] and in poly(ethylene imine) hybrids[172] The FT photoacoustic IR and the Raman spectra of **183** and **184** (Chart 36) have been described, together with complexes derived from their reaction with Cp_2ZrCl_2, but little information about the siloxane cage is reported.[113,366,704]

The vibrational spectra of molecular species such as $T_8(OH)_8$ have been calculated and compared with more complicated three-dimensional structures of selected zeolites and silicalites. There are significant similarities in the spectra, the all in-phase Si−O−Si mode for $T_8(OH)_8$ being calculated to be at 495 cm^{-1}.[705] For $H_8[T_8O_8]$ the ν_{as}Si−O−Si, ν_sSi−O−Si, $\nu_{s,as}$Si−O−(H), and δO−Si−O values are 1114; 736, 611, 555; 926; and 461 and 375 cm^{-1} respectively, with a fully symmetric, breathing, or pore-opening vibration at 371 cm^{-1}. These calculations and calculated IR frequencies for cages in which one or more Si atoms are replaced by Al suggest that such isolated small clusters can act as good models for aluminosilicate materials.[706] Ab initio calculations have also been used to determine the Raman spectrum for $Na_8[T_8O_8]$,[707] and the Si−O−Si stretch in $[NMe_4]_8[T_8O_8]$ is 1037 cm^{-1}.[708]

The Si−O−Si asymmetric stretching frequencies for $T_8(OSiMe_2R)_8$, R = H, $(CH_2)_3OH$, and $(CH_2)_3OC(O)C({=}CH_2)Me$ fall in the range 1085−1100 cm^{-1}, while the Si−O−Si bending frequencies fall in the range 550−560 cm^{-1}.[230,262,478] The polarized Raman spectra of layers of $T_8(OSiMe_3)_8$ deposited by CVD methods show the films to be oriented,[550] and the Raman spectrum of $T_8(OSiMe_2H)_8$ shows a Si−H stetch of 2141 cm^{-1}.[246] The extreme Si−O−Si bond angles (136.35°−172.13°) in $T_8(OSnMe_3)_8 \cdot 4H_2O$ lead to significant splitting of both the symmetric and antisymmetric Si−O−Si stretches.[402]

The characteristic IR bands for T_8R_7R' compounds are, as would be expected, similar to those for the related T_8R_8 species. Again, detailed analysis of the IR spectrum of this type of compound is not given in many publications, the broad Si−O stretch being of most interest in both simple molecular species and composite materials where data similar to molecular species are taken to indicate that the POSS cage has not been fragmented during any processing. Typical IR data for T_8R_7R' compounds are given in Table 29. Molecular

Table 28. Typical IR Frequencies Associated with the Si−O−Si Bonds in T_8R_8 Compounds

R, T_8 derivative, or compound number	Si−O frequencies (cm^{-1})	refs
-H	1120	209
-H	1121	72
-H	ν_{as}(Si−O−Si) 1117	604
-Me	ν_{as}(Si−O−Si) 1115, 1192, ν_s(Si−O−Si) 517, and δ(O−Si−O) 465, 379	198
-Me	1113.1	423
-Me	1144	62
-Et	1144	62
-CH═CH$_2$	1109	82–84, 538, 684
-CH═CH$_2$	1099, 585	685
-CH═CH$_2$	1115.94	85
-CH$_2$CH═CH$_2$	1105	90
-CH$_2$CH(O)CH$_2$	1107	90
-(CH$_2$)$_3$Cl	ν_{as}(Si−O) 1230−940, δ(O−Si−O) 552	373
-(CH$_2$)$_2$O(CH$_2$)$_2$Cl	1118.3	69
-Cy	1110	126
-(CH$_2$)$_3$NH$_2$	1120	98
-(CH$_2$)$_3$NH$_2$	1130	99
-(CH$_2$)$_3$NH$_2$	1134, 1037	100
{T$_8$[(CH$_2$)$_3$NH$_3$]$_8$}Cl$_8$	1105	488
-(CH$_2$)$_3$OCH$_2$CH(O)CH$_2$	1103−1110	71, 72, 172, 218, 702, 703
-(CH$_2$)$_3$Cp	1155	94
-(CH$_2$)$_5$Br	1118.9	634
-(CH$_2$)$_6$Cl	1117.2	634
T$_8$[1-(CH$_2$)$_3$-2-Me-1,2-*closo*-C$_2$B$_{10}$H$_{10}$]$_8$	1119	97
T$_8$[1-(CH$_2$)$_3$-2-Ph-1,2-*closo*-C$_2$B$_{10}$H$_{10}$]$_8$	1103	97
[NMe$_4$]$_8${T$_8$[7-(CH$_2$)$_3$-8-Me-7,8-*nido*-C$_2$B$_9$H$_{10}$]$_8$}	1111	97
-Ph	ν_{as}(Si−O) 1137, δ(O−Si−O) 509	339
-Ph	1160	709
-Ph	1124	492
-Ph	1117	134
-Ph	1115	493
-Ph	1136.2 and 1113.2	495
-Ph	ca. 1100	335, 710
-Ph	1106.3, 1137.5	131
-C$_6$H$_4$NO$_2$^{a}	ca. 1100	335, 710
-C$_6$H$_4$NO$_2$^{a}	1159	134
-C$_6$H$_4$NH$_2$^{a}	1100	335, 710
-C$_6$H$_4$NH$_2$^{a}	1119	546
-C$_6$H$_4$NH$_2$^{a}	1120, 1126	372, 496
-C$_6$H$_4$NH$_2$^{a}	1125	134
-C$_6$H$_4$NH$_2$^{a}	1138	371
94	1138	371
94	1128	134
[NMe$_4$]$_8$[T$_8$O$_8$]	1037	708
-OSiMe$_2$H	1100	237
-OSiMe$_2$H	1096	142
-OSiMe$_2$(CH$_2$)$_3$OCF$_2$CHFCF$_3$	ca. 1100	259
-OSiMe$_2$(CH$_2$)$_3$OCH$_2$CH(O)CH$_2$	1103	328
-OSiMe$_2$(CH$_2$)$_3$OCH$_2$CH(O)CH$_2$	1100	645
15	1096	142
16	1100	479
-OSiMe$_2$C$_6$H$_4$-4-CO$_2$H	1100	143
-OSiMe$_2$(CH$_2$)$_2$C$_6$H$_4$-4-OAc	1065	375
-OSiMe$_2$(CH$_2$)$_2$Ph	1100	711
17	1089	233–235

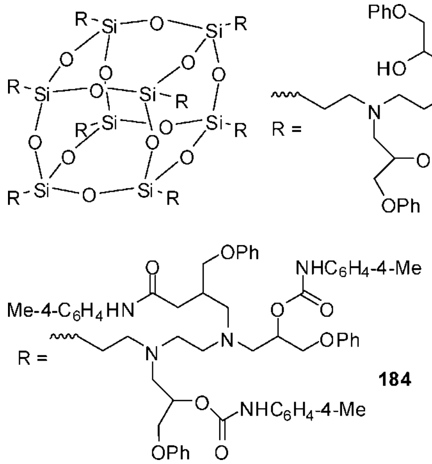
[a] Contains a mixture of isomers.

dynamics simulations have been used to calculate the Si−O−Si and Si−H stretches in $T_8H_7(n\text{-}C_6H_{13})$ for comparison with experimental data. Overall the calculated and experimental data are in excellent agreement although the calculated and experimental values for the Si−H stretch of 2350 and 2274 cm^{-1}, respectively, are significantly different,[439] while the experimentally determined Si−H stretch in $T_8(i\text{-Bu})_7H$ is at 2215 cm^{-1}.[712]

The characteristic Si−O−Si stretches of $T_8(i\text{-Bu})_7(CH_2)_3$-NH- end-capped poly($\varepsilon$-caprolactone) and poly(L,L-lactide) are reported to be 1099 cm^{-1} and show that the polymerization process has not caused cleavage of the POSS cage.[713] The Si−O−Si stretch in $T_8(i\text{-Bu})_7C_6H_4$-4-CH═CH$_2$ occurs at 1109 cm^{-1}, and this characteristic band is also seen in copolymers of this POSS monomer with vinylpyrrolidone, indicating that the POSS cage is retained following the polymerization process.[498]

The IR spectrum of $T_8(i\text{-Bu})_7OH$ in a solid KBr matrix shows a ν_{as} Si−O−Si stretch at 1113 cm^{-1} and the ν_s Si−O−Si stretch at 815 cm^{-1}, together with a broad hydrogen bonded SiOH band in the 3425 cm^{-1} region.[714] However, the IR spectrum of $T_8(i\text{-Bu})_7OH$ in KBr has also been reported to show both a sharp band due to free SiOH groups at ca. 3680 cm^{-1} and a broad band at ca. 3500 cm^{-1} attributed to a hydrogen-bonded dimeric silanol species.[715] Differences in the degree of hydrogen bonding seen in these

Chart 36



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IR spectra may be due to differences in sample concentration and preparation. The IR spectrum of a 0.1 M solution of $T_8(i\text{-}Bu)_7OH$ in CCl_4 surprisingly shows only a single sharp band due to SiOH at ca. 3680 cm^{-1} indicating that there is no hydrogen bonding present,[715] whereas most silanols show strong hydrogen bonding to each other.[716,717] The disappearance of the silanol stretching frequency at ca. 3715 cm^{-1} in $T_8(c\text{-}C_5H_9)_7OH$ in hexane solution has been used to monitor its rate of reaction with $Me_2Si(OMe)(CH_2)_3NH_2$ and shows that the apparent rate constant is greatest at 245 K.[453]

The Si−O−Si stretch for $T_8Cy_7(CH_2)_3OC(=O)C(Me)=CH_2$ is reported at 1110 cm^{-1},[654] and characteristic Si−O−Si stretches from such precursor-derived groups in elastomeric nanocomposites formed by copolymerization with 2-ethylhexyl acrylate and divinylbenzene have also been found at 1110 cm^{-1}.[718] The Si−O−Si asymmetric and symmetric stretches in $T_8(i\text{-}Oct)_7(CH_2)_3NH_2$ are reported to be 1118 and 486 cm^{-1}, respectively, which has been used to argue for the T_8 POSS structure rather than a ladder siloxane product (Si−O−Si stretches at 1030−1055 cm^{-1}).[149]

The IR spectrum of the POSS core in the copolymer poly(*N*-dodecylacrylamide-*co*-3-methacryloxypropylheptaphenyl POSS) has a sharp peak at 1130 cm^{-1}, but on photooxidation, this absorption is lost and replaced by one at 1065 cm^{-1}, due to breakdown of the cage and formation of a conventional SiO_2 film.[719] IR spectroscopy has also been used to show that after reaction with oxygen plasmas, a "SiO_2-like" layer is formed on the surface of a range of polymers with pendent T_8Et_7 cages.[720]

3.11. X-ray Photoelectron Spectra of POSS Compounds

XPS has not been widely used in POSS chemistry, but the interest in T_8 and other silsesquioxane polyhedra has produced a small number of studies, mostly to determine the presence and distribution of POSS cages within nanocomposite materials. The Si 2p photoemission spectrum of T_8H_8 chemisorbed on a gold surface has been recorded and shows two peaks in a 1:7 ratio, which has been used as evidence to show that the POSS cages bond to the surface via a single vertex.[600] The Si 2p core level XPS spectrum of $T_8(OSiMe_2H)_8$ has been recorded in order to make comparisons with platinum derivatives of the silane formed via hydrosilylation reactions.[723] The Si 2s and Si 2p signals in the XPS spectrum of POSS-capped poly(ethylene oxide) in an epoxy resin have been used to show that the POSS is enriched at the surface of the thermoset material.[171] Similarly, XPS shows that the POSS cages have a higher than expected concentration at the surface of acrylate copolymers with a pendant T_8R_7 group (R = Et or $c\text{-}C_5H_9$)[724] and has been used to determine the elemental composition of $T_8R_7(CH_2)_3OC(=O)C(=CH_2)Me$ (R = Et or $c\text{-}C_5H_9$) precursors and a range of copolymers derived from them with, for example, *tert*-butyl methacrylate[653] or methyl methacrylate with $T_8(i\text{-}Bu)_7(CH_2)_3OC(=O)C(=CH_2)Me$.[725]

XPS has also been used to determine the composition of POSS methacrylate materials grafted onto silicon wafers,[726] to determine the Si content in polyurethane networks crosslinked via POSS cages,[618] and to show the presence of Si in thermoset polymers derived from $T_8Ph_7(CH_2)_3OH$ and caprolactone.[543] XPS has also been used to characterize the supported catalysts formed on reaction between **178** and Cp_2ZrCl_2, giving a core level Si 2p peak at 102.8 eV.[113]

3.12. Chromatographic Methods Applied to T_8 POSS Compounds

3.12.1. Gel Permeation Chromatography Analysis

The relatively high molecular weights of even relatively simple T_8 derivatives, the tendency of mixtures to be formed in their synthesis, and the incorporation of POSS species into polymeric materials have meant that GPC and other more sophisticated chromatographic methods have been applied widely in their analysis. GPC studies of materials that may contain mixtures of compounds containing eight or fewer reacted substituents at a POSS cage are complicated by the possibility of the hydrodynamic radii of species containing from four to eight similar substituents overlapping. Similarly, the choice of standard is also important because POSS materials tend to be relativley globular when compared, for example, with polystyrene. GPC analysis has been used to assess the nature of both polymeric materials containing POSS cages and the purity of monomeric POSS compounds such as $T_8(C_6H_4NO_2)_8$ and $T_8(C_6H_4NH_2)_8$,[492] **69**,[121] $T_8(c\text{-}C_5H_9)_7OSiMe_2(CH_2)_3NCO$,[595] **16**,[479] and $T_8[OSiMe_2(CH_2)_3OCH_2CH(O)CH_2]_8$.[223] GPC has also been used to show that the reaction between $T_8(C_6H_4NH_2)_8$ and $Me_2BrCC(=O)Br$ gives not only $T_8[C_6H_4NHC(=O)CMe_2Br]_8$ but also higher molecular weight products.[367]

GPC has been used to determine that the Pt-catalyzed hydrosilylation of $T_8(OSiMe_2H)_8$ with allyl-poly(ethylene oxide) species leads to reaction of only about five of the Si−H groups per T_8 cage[727] and also to show the probable monodisperse nature of a product derived from hydrosilylation of the silane with allyl-terminated poly(ethylene oxide).[728] GPC has also been used to characterize the different isomers formed from the hydrosilylation reaction between $T_8(OSiMe_2H)_8$ and a mixture of di(propylene glycol)allylethermethacrylate and 4-vinyl-cyclohexene-epoxide[141] and to determine the extent of bromination of T_8Ph_8, where it is possible to introduce up to ca. 16 bromines to each POSS molecule.[314] Starburst dendritic POSS species such as **179** with molecular weights of up to 12 000 with a polydispersity of 1.2 have also been characterized using GPC.[236]

3.12.2. Size-Exclusion Chromatography

SEC methods have been used to determine the purity of products derived from substitution reactions of T_8 compounds

Table 29. Typical IR Frequencies Associated with the Si−O−Si Bonds in T_8R_7R' Compounds

R	R′	Si−O frequencies (cm^{-1})	refs
-H	-n-C_6H_{13}	1139	439
-i-Bu	-$(CH_2)_2OH$	1082	161
-i-Bu	-$(CH_2)_2OC(=O)Me$	1082	161
-i-Bu	-$(CH_2)_3NH_2$	1100	721
-i-Bu	-$(CH_2)_3NH_2$	1104	377
-i-Bu	-$(CH_2)_3NHC(=O)(CH_2)_2SC(=S)SCH_2Ph$	1104	377
-i-Bu	-$(CH_2)_3NHCH_2CH_2NH_2$	1123	722
-i-Bu	-$(CH_2)_3OCH_2CH(OH)CH_2OH$	1100	594
-i-Bu	-$(CH_2)_3SH$	ca. 1107	570
-i-Bu	-C_6H_4-4-$CH=CH_2$	1109	498
-i-Bu	-OH	1113	714
-Cy	-$(CH_2)_3OC(=O)C(Me)=CH_2$	1110	654
-i-Oct	-$(CH_2)_3NH_2$	1118, 486	149
-Ph	-$(CH_2)_3OH$	1134	192, 193

and also to show that T_8 products are formed in the hydrolytic condensation reaction of trialkoxysilanes. Preparative SEC has been used to purify carbazole derivative **17**,[233] and SEC has been used to show the monomodal mass distribution of the polymer formed on hydrosilylation between $T_8(OSiMe_2H)_8$ and undecenyl polystyrene macromonomers.[729] SEC has also been used to show the purity of the isomeric T_8R_8 (R = C_6H_4-2-Me, C_6H_4-3-Me, or C_6H_4-4-Me) species and to show that the para-isomer occupies the largest volume.[135] SEC analysis has also proved useful in the determination of the purity of the phenylene derivative **101**,[381] for monitoring the condensation reactions of $CH_2(O)CHCH_2O(CH_2)_3Si(OMe)_3$ and the formation of T_8 species in the resulting mixture,[730] and in showing the presence of $T_8[(CH_2)_3Cl]_8$ in the hydrolytic polycondensation reaction of $Cl(CH_2)_3Si(OMe)_3$.[117] Characterization of the different generations of dendrimers formed in the preparation of globular contrast agents used for MRI based on $T_8[(CH_2)_3NH]_8$ cores surrounded by L-lysine has also been carried out using SEC analysis.[383]

3.13. Electrochemistry

There are few electrochemical studies on simple molecular T_8 derivatives, but the presence of a T_8 core has been concluded to have little effect on the electrochemical properties of carbazole centers, because the redox features of the carbazole derivative **17** are similar to those of ethylcarbazole.[233,234] Polymers containing ferrocenyl-substituted T_8 cages have been used in the detection of glucose via amperometric enzyme electrodes.[731] Cyclic voltammetry shows that the monomer **115** has initial electroactivity (E_{ox} = 1.45 V in $[NBu_4][BF_4]/CH_2Cl_2$) but that current decreases with repeated cycling. Cyclic voltammetry measurements on films cast from the phthalocyanatolutetium(III) complex **134** show it to be electrochromic, having a green−blue transition, with possible applications in electrochromic devices.[405]

Electrochemical polymerization of **115** with pyrrole gives a polypyrrole that contains POSS cages and shows optical contrast (transmittance change from 17% to 30% at 730 nm), switching time (0.4 versus 1.1 s), and color properties (four different colors in oxidized and neutral states) superior to those for the polypyrrole itself. These improvements are thought to be due to the structure becoming more loosely packed due to the presence of the POSS cages leading to easier injection and extraction of ions.[337]

3.14. Other Spectroscopic and Physical Properties

The solubility of a range of aryl POSS derivatives T_8R_8 (R = Ph, C_6H_4-2-Me, C_6H_4-3-Me, C_6H_4-4-Me, or C_6H_4-2-Et) in common organic solvents has been investigated; the best solvents in all cases were CH_2Cl_2 and THF, and the least soluble compounds were the Ph and the C_6H_4-2-Me derivatives.[135] The mechanical properties of $T_8(c\text{-}C_5H_9)_8$ have been calculated in order to assess how a POSS cage should be considered when in a rubbery matrix. The averaged bulk modulus, the averaged Young's modulus, and an isotropic averaged shear modulus for $T_8(c\text{-}C_5H_9)_8$ were found to be anisotropic with values of ca. 7.5, 11.8, and 4.7 GPa. These results indicate that as crystalline aggregates the POSS can be modeled as a "rigid" entity when in a rubbery matrix.[433] The hardness of $T_8(C_6H_4\text{-}2\text{-}Et)_8$ has been measured after the solidification of a molten sample, and it was found to have a Vickers hardness of 249 HV using 0.25 N.[135] The mechanical properties of thin films of $T_8(c\text{-}C_5H_9)_7CH_2CH_2C(=O)OMe$ have been investigated using irradiation by Si ions. The pristine film has a hardness and elastic modulus of 0.11 and 5 GPa, respectively, but as the film decomposes under irradiation, it forms amorphous silicate-like material with a hardness and elastic modulus of 6 and 65 GPa, respectively.[732]

The kinematic viscosity of several POSS species that are viscous liquids T_8R_8 [R = $(CH_2)_7Br$, $(CH_2)_8Br$, $(CH_2)_6Cl$, and CH_2CH_2Ph] have been determined and found to be 35, 38, ca. 42, and 48 cSt, respectively. These compounds additionally showed onsets for solidification of 0, +8, −5, and −20 °C, respectively. The properties are thought to show that these compounds have the potential to be used in hydraulic fluid formulations.[220] The viscosity of $T_8(OSiMe_2R)_8$ compounds, where R = $(CH_2)_3OCH_2CH(O)CH_2$, $(CH_2)_2C(=O)C(=CH_2)Me$, and $OSiMe_2OSiMe_2H$ have been measured and found to be ca. 600, 220, and 200 mPa s. These values are similar to some engine oils, but the compounds are not chemically robust enough for such use.[646,733] The relative viscosity as a function of concentration in hexane for $T_8(i\text{-}Bu)_7(CH_2)_3NHC(=O)C_6H_3\text{-}3,5\text{-}(OCN)_2$ has been plotted and the extrapolated intrinsic viscosity found to be 0.005 ± 0.002 dL g^{-1}, which is consistent with a size of ca. 1 nm for the molecule.[344]

The viscosities of several amphiphilic telechelic species containing a pair of $T_8Cy_7OSiMe_2(CH_2)_3NHC(=O)$ groups separated by poly(ethylene glycol) chains have been measured. The solution viscosity was strongly influenced by the water content in THF/water solutions, the water causing polyelectrolyte effects to occur.[734] The water contact angles for $T_8R_7(CH_2)_3OC(=O)C(=CH_2)Me$ (R = Et or c-C_5H_9) are 101° and 116°, respectively,[653] and similar contact angle measurements show that POSS−poly(carbonate-urea)urethane nanocomposites show contact angle hysteresis, which is in contrast to conventional polyurethanes and which is thought to be due to the changes in surface topography caused by the tendency of POSS species to form hard crystalline areas in nanocomposites.[621] Contact angle studies using water and CH_2I_2 on polyurethane networks cross-linked by POSS cages show an enhanced surface hydrophobicity and reduction in surface free energy compared with related materials with no POSS content.[618]

For the fluorinated POSS derivatives T_8R_8 [where R = $(CH_2)_2(CF_2)_7CF_3$, $(CH_2)_2(CF_2)_5CF_3$, or $(CH_2)_2(CF_2)_3CF_3$], the surface energy decreases as the fluoroalkyl chain length increases, and the water contact angle for the compound with R = $(CH_2)_2(CF_2)_7CF_3$, 154°, is higher than that of PTFE.[125,162,640,735–737] The heptadecafluorodecyl derivative $T_8[(CH_2)_2(CF_2)_7CF_3]_8$ has a very low solid-surface energy of ca. 10 mN m^{-1} (cf. ca. 18 mN m^{-1} for Teflon) and has been used to give a very low surface energy flexible coating on surfaces such as feathers or fabrics.[738] The related sulfur-containing POSS species, $T_8[OSiMe_2CH_2CH_2S(CH_2)_2(CF_2)_nCF_3]_8$ and $T_8[CH_2CH_2S(CH_2)_2(CF_2)_nCF_3]_8$ (where $n = 5$ or 7), when blended with poly(methyl methacrylate), can give materials with water contact angles of 114°−124°, much higher than the value of 71° for poly(methyl methacrylate) itself.[393]

Polymers containing two $T_8Cy_7OSiMe_2(CH_2)_3NHC(=O)$ groups separated by poly(ethylene glycol) chains show irregular birefringence, but conventional PEG homopolymers show regular "Maltese Cross" birefringence. This change is thought to be due to the tendency of the POSS cage to nucleate to form crystalline areas[597] as shown by other methods described above. Studies on the reactivity ratio of styrene and $T_8R_7C_6H_4$-4-$CH=CH_2$ (where R = i-Bu or Cy) in copolymerization reactions suggest that the often observed aggregation of POSS cages in copolymers is caused by self-assembly rather than by block copolymerization.[739]

$T_8(c\text{-}C_5H_9)_7C_6H_4$-4-($E$)-$CH=CHFc$ has paramagnetic properties at room temperature with a remnant magnetization of 0.035 emu g^{-1} and a hysteresis coercive force of 0 Oe, indicative of soft magnetic properties.[353] The dielectric loss for $T_8[(CH_2)_2Ph]_8$ as a function of temperature and frequency has been plotted and shows one dielectrically active relaxation process attributable to dynamic glass transition or α-relaxation.[740] The dielectric loss features of $T_8[(CH_2)_2Ph]_8$ blended with polystyrene and with poly(bisphenol A carbonate) have similar features,[740,741] and POSS modification of polymers tends to lead to reduction in dielectric constant.[185,586,588,589] For example, the reduction in dielectric constant of nanocomposites of maleimide-containing polyamides with $T_8(i\text{-}Bu)_7(CH_2)_3NH_2$ increases as the POSS content increases.[721] The conductivity, permittivity, and capacitance of poly(propyl methacryl-heptaisobutyl-POSS-*co*-*N*-butyl methacrylate) containing 15−25% of POSS cage by weight have been measured in order to assess the suitability of such materials as humidity sensors. Pores within the material that can host water molecules are thought to increase the conductivity.[742,743] The triazole derivative, **69**, has also been found to be highly porous having a surface area, as measured using the BET method, variously measured at 1200[121] and 862 m^2 g^{-1}.[124] Such measurements are prone to variable results, often due to differences in sample preparation, but in either case, a high surface area may lead to applications in gas capture or storage or capture of metal ions.[124]

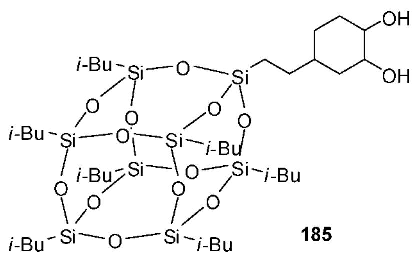
Dielectric relaxation spectroscopy and dynamic mechanical spectroscopy studies of $T_8[OSiMe_2(CH_2)_3OCH_2CH(O)CH_2]_8$ and of compound **16** show that both undergo two relaxation processes, which both increase in frequency as the temperature is increased. The dielectric strength increases for one of the processes with increasing temperature but decreases for the other process.[744] Rutherford backscattering spectra have been used for surface depth profiling of nanocomposites derived from $T_8(OSiMe_2H)_8$ and poly(methyl methacrylate), the Si atom distribution showing that the POSS component of the material accumulates near the surface.[616]

3.15. Biological Properties and Medical Uses of POSS

The increasing number of investigations into the physical properties of both simple molecular T_8 derivatives and materials incorporating them has led to studies of their potential in medical applications. Silicone materials based on the well-known linear and branched siloxanes have many uses in the biomedical field, and it is likely that polymers derived from POSS units will have similar applications. The cationic POSS species $[T_8(C_6H_4NH_3)_8]Cl_8$ can be used as a probe for DNA by using resonance light scattering, such that nucleic acids from calf thymus DNA could be detected in the 0.35−42.82 μg mL^{-1} concentration range.[312] Complexes of DNA and cationic lipids containing pendent $T_8(i\text{-}Bu)_7$ groups have been shown to form a different phase from those containing triphenylene or cyanobiphenyl tails.[745] Dendrimers of the type $T_8[(CH_2)_3NH(\text{L-Lys})(\text{L-Lys})_2(\text{L-Lys})_4(\text{L-Lys})_8]_8$ show good biocompatibility and were found to bind and slow the migration of DNA, as well as being capable of in vitro gene delivery as shown by increased (compared with a SuperFect control) transfection efficiency in MDA-MB-231 breast carcinoma cells.[365] Cytotoxicity studies using mouse muscle and human osteoblast cell lines on $T_8[OSiMe_2(CH_2)_3OH]_8$ and lactide or caprolactone polymers derived from it show good cell viability as determined by measuring the numbers of living and dead cells in test versus control samples. The polycaprolactone derived materials showed up to 95% cell viability, and their potential for use in tissue engineering is being studied.[746]

Polyurethanes modified with POSS cages derived from $T_8(CH=CH_2)_8$ have a comparatively low surface free energy and a large water contact angle hysteresis and have been shown to have a lower platelet absorption than polyurethane or PTFE.[684] Copolymerization of methyl methacrylate and $T_8(CH=CH_2)_8$ leads to POSS-reinforced composite resins, which showed good biocompatibility as determined by an agar overlay test and mutagenesis assay.[747] Cells may be attached to and grown on porous inorganic solids derived from the pyrolysis of nanocomposites that have been prepared from copolymerization of $T_8Cy_7(CH_2)_3OC(=O)C(=CH_2)Me$, 2-ethylhexyl acrylate, and divinylbenzene.[748] The surface modification of a nanocomposite prepared from **185** (Chart 37) and poly(carbonate-urea)urethane using UV light in an ammonia atmosphere gives a material having a surface with improved cell adhesion and proliferation leading to a 400% increase in cell numbers when compared with the unmodified nanocomposite; this may have applications in tissue engineering and hybrid medical devices.[749]

Chart 37



185

Poly(carbonate-POSS-urea)urethane polymers have been investigated to see whether they might be useful polymers in medical devices. Exposure of endothelial cells to the polymer does not result in significant damage to the cells, and the polymer may be seeded with such cells to give viable cells on the material.[750] POSS−poly(carbonate-urea)urethane nanocomposites containing $T_8(i\text{-Bu})_7$ groups are found to be compatible with endothelial cells showing no difference in cell viability when compared with standard media and to be of potential use in cell seeding (good cell proliferation was found at 14 days even at low cell seeding densities of 1.0×10^3 cells cm^{-2}) and in cardiovascular devices,[751] including synthetic heart-valve leaflets[752] and small caliber cardiovascular bypass prostheses.[753]

POSS cages have been incorporated into bioactive nanocomposites that can be used for coronary, vascular, and bypass grafts and promote endothelialization.[754,755] A synthesis of a POSS−catechin conjugate, catalyzed by horseradish peroxidase, derived from $T_8[(CH_2)_3NH_2]_8$ shows the stability of the POSS core toward the enzyme and hydrogen peroxide. The conjugate product exhibited greater superoxide scavenging than the catechin monomer.[309] An in vitro study of the stability of a polyurethane incorporating $T_8(i\text{-Bu})_7$ units via (cylohexanediol)ethyl linkages shows that the POSS cages seem to provide some shielding to the soft phase of the nanocomposite, which helps to preserve its elasticity and pliability.[756] This type of polymer has also been shown to have enhanced biological stability when compared with conventional silicone materials and to inhibit inflammation.[620,757,758] This is thought to be due to adsorption and inactivation of fibrinogen on the surface, as indicated by the large contact angle hysteresis and amphilicity.[757] This suggests that there will be potential for the use of POSS cages to strengthen polymer matrices for use in biomedical devices. Nanoparticles containing a T_8Cy_7 core linked to a poly(vinyl alcohol) outer shell via an $OSiMe_2(CH_2)_3NC(O)$ linkage can be used to improve the controlled release of the anticancer drug paclitaxel giving continuous release over 40 days.[759] Such particles would seem to have significant potential for drug delivery. Similarly, stent coatings based on POSS/polyurethane polymers containing polylactide/caprolactone, poly(ethylene glycol), and $T_8(i\text{-Bu})_7$ components can be used to modulate release of paclitaxel for 90% release in 12 h to 90 days.[760] An in vitro study of the reproductive toxicity of poly(ethylene glycol)-substituted POSS cage has been carried out, and the cages were found to be cytotoxic at concentrations of $\geq 0.1\ \mu g\ mL^{-1}$, but human chorionic gonadotropin reduced cytotoxicity to $\geq 1000\ \mu g\ mL^{-1}$.[256] See section 4.4.1 for a further description of the uses of POSS-containing materials with biological applications.

4. Applications of T_8 POSS Derivatives

4.1. Introduction

Early studies on the synthesis and characterization of T_8 POSS derivatives were often carried out in order to investigate their interesting structures, optimize syntheses, and discover the extent of chemical interconversions that could be achieved at the substituents without degradation of the POSS cage. More recently, there has been considerable growth in the use of molecular POSS species in materials chemistry, significant applications being found in polymers and in nanocomposite materials. Thus, T_8R_8 and T_8R_7R' POSS species have been found to modify polymeric materials in many useful ways; this section describes these applications.

The size of a typical POSS monomer such as $T_8(CH{=}CH_2)_8$ is about 1.1 nm (between $=CH_2$ carbons in "para" positions) and so is compatible with the size of polymers and can be seen as among the smallest discrete particles of silica. Organic/inorganic nanocomposites of the organic polymer/POSS type can thus be regarded as intermediates between traditional organic polymers and ceramic materials.

There are four main ways of using POSS molecules to form hybrid polymers and nanocomposites. The first method consists of a copolymerization of an organic monomer, such as styrene, propylene, or methyl methacrylate, with POSS molecules bearing the same or similar functional group in one or all of their pendant arms. Covalent bonds are thereby formed between the polymer matrix and the POSS derivative. Depending on whether the POSS species has one or eight polymerizable functional groups, it can act here either as a pendant group or a cross-linker, respectively (Figure 10). Depending on the reaction conditions, the POSS species can be dispersed at a molecular level or aggregated together as either crystalline or amorphous phases (see section 3.5). Furthermore, the POSS molecule may also act as the polymerization initiator if it contains α-halo-ester groups, as, for example, in $T_8[SiMe_2(CH_2)_2\text{-}CMe_2(CH_2)_2OC(=O)CMe_2Br]_8$ and $T_8Ph_7(CH_2)_3\text{-}OC(=O)CMe_2Br$.[157,265,761]

A second method consists of either the polymerization of classical monomers in the presence of POSS molecules bearing unreactive groups, commonly alkyl groups, or of the introduction of POSS molecules into the already prepared polymer matrix by physical mixing. This method does not produce covalent bonds between the polymer matrix and the POSS molecules, the latter being "trapped" or "blended" into the organic matrix (Figure 10).

The third method can be considered a variation on the first, because it consists of the grafting of a POSS unit bearing a single reactive function onto a preprepared polymer by the formation of covalent bonds. This method can produce either polymers with many pendant POSS cages grafted along the polymer backbone, the same type of structure as shown formed from reactive monomers shown in Figure 10, or POSS-terminated polymers, depending on the nature of the polymer precursor. However, the penetration of the POSS species into the polymer and its even distribution through the polymer depends on the solubility of preprepared polymer in the chosen solvent system.

The fourth method consists in the direct cross-linking of POSS units without using an additional polymer, either directly by reaction of appropriate POSS derivatives with each other[473] or by covalent binding to small organic molecules to form a three-dimensional network. In this case,

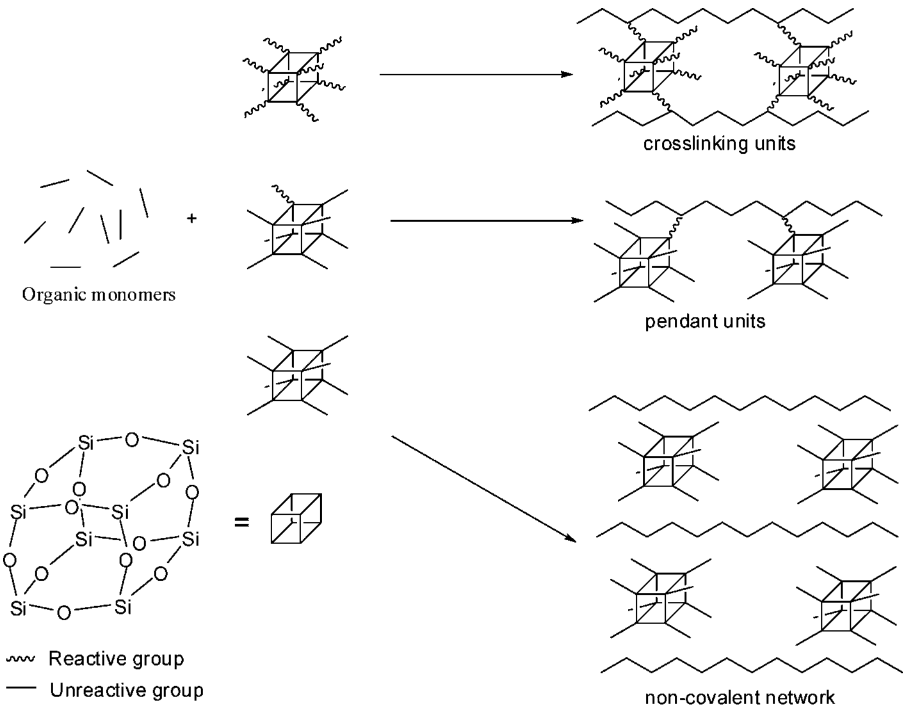


Figure 10. Methods for the incorporation of POSS components into polymeric materials.

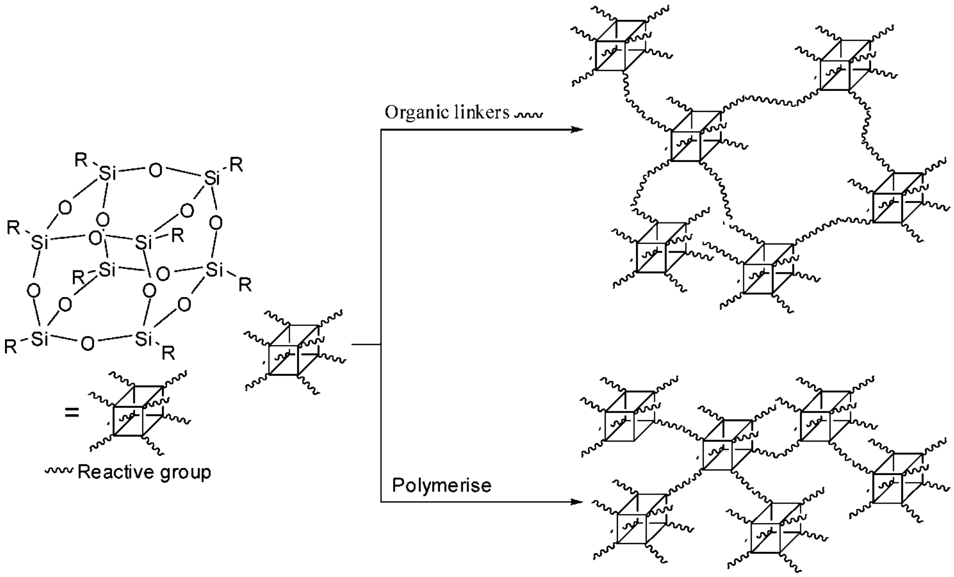


Figure 11. Schematic representation of cross-linked polymeric networks of POSS cages.

the POSS units need to bear reactive functions such as amines or epoxides (Figure 11).

For all of these methods, the resulting materials are often referred to as organic−inorganic hybrid nanocomposites, because they arise from a mixture of an organic component (the starting monomers or polymers) and an inorganic one (the POSS molecules). In this situation, “nano” refers to the nanoscale dimensions of the T_8 POSS core (see section 1). The POSS-containing materials have found uses in elastomers, thermosets, thermoplastics, liquid crystalline polymers, dendrimers, low dielectric materials, electrolytes, holographic gratings, laser materials, cosmetics, dental and other medical materials, magnetic resonance imaging agents, fire retardant materials, photonics, biology, fuel cells, space-resistant materials, resists, and other applications as described below.

The properties conferred by the addition of POSS components to novel materials depend greatly on their method of incorporation (copolymerization, grafting, blending), the chemical and physical properties of the substituents at the POSS core, and the degree of loading of the POSS material. Perhaps unsurprisingly, the thermal and mechanical properties are usually most enhanced if the POSS component is chemically bound to the polymer rather than being blended with it. The high thermal stability of many POSS compounds is important if they are to be used in blends with polymers, because the polymer melting point is often high and so processing temperatures for melt blending with POSS are high. The organic substituents on the POSS core can also be modified to ensure miscibility with the polymer for blending purposes or copolymerization. There are a wide range of functional groups available on POSS substituents, for example, alkenyl, amine, epoxy, methacryloyl, isocyanate, hydrido, and alkyl halide. This range enables polymerization with a variety of polymers such as polyimides, polymethacrylates, polyurethanes, poly[1-(trimethylsilyl)-1-propyne], poly(ε-caprolactone), polycarbonate, and Nafion.

The hybrid nature of these materials means that the improved properties are not bought at the price of a loss in processability, a problem often found when using more traditional methods of achieving these improvements. Generally mechanical properties are improved, flammability is reduced, T_g values increase, and thermal stability increases as a cross-linked POSS core acts as an anchor point within a polymer matrix. Depending on the mode of POSS incorporation and the formation and the percentage loading of the POSS, crystalline domains of POSS may form in the materials and may also be significant. This crystallization of POSS cages when pendant on polymer chains or in blends may reduce the degree of polymer crystallization and reinforce small polymer crystallites. One possible problem with the incorporation of POSS species into polymeric materials is the potential for breakdown of the POSS cage and thus loss of the desirable features of the symmetrical octameric polyhedron. This often does not happen due to the chemically and thermally robust nature of the cage, but it can be monitored by the presence of the cage features in the IR spectrum, ^{29}Si NMR spectroscopy, and X-ray diffraction methods. A second potential problem when processing POSS monomers is that they may sublime at high temperature unless there are polymerizable or other reactive groups present.

Calculations on the effect of the incorporation of POSS cages on the mechanical properties of polymeric materials show that the greatest effects are seen when significant cross-linking occurs via many of the eight pendant arms on the POSS core, followed by lesser effects if the POSS cages are joined via pairs of edges, with smallest effects being seen for pendant T_8R_7 groups within the material.[762]

The thermal stability of composite materials is often improved by the addition of POSS units because their degradation leads to initial reaction of organic substituents followed by breakdown of the POSS core to give an insulating SiO_2-containing char at the surface, which retards further combustion. T_g may decrease on addition of POSS if the molecules of POSS are individually distributed (via blending) because they may act as molecular lubricants allowing for chain slippage in a polymeric material. If compatibility between the polymer and POSS is poor, then domains form and T_g is less affected or increased.[763] Other unusual properties such as swelling in both hydrocarbon and water for POSS−PEG−PDMS cross-linked membranes may also be found on the introduction of POSS units.[764]

One further useful property of POSS-containing materials is that their degradation by oxygen gives a passivating surface layer of SiO_2, which can grow and resist further attack by oxygen. The resistance to degradation by oxygen is thought to be due to an initial reaction of C−H bonds and loss of organic groups in POSS derivatives, which leads to increased Si−O bond formation and then eventual production of a glass-like silica outer layer. Continued reaction to break Si−O bonds at the surface then offers no thermodynamic advantage, and there is a concomitant change in the surface properties from hydrophobic to hydrophilic.[765,766]

The specific applications of POSS compounds in polymers and materials are described in detail below, those properties being significantly affected are mechanical properties (refs 112, 115, 139, 185, 189, 247, 295, 333, 374, 494, 539, 546, 557, 559, 593, 606, 687, 767–788), tensile modulus (refs 140, 577, 638, 687, 762, 770, 775, 788, 789), shear modulus (refs 555, 762, 790–792), storage modulus (refs 71, 72, 189, 224, 225, 246, 291, 333, 357, 496, 524, 526, 531, 537, 545, 546, 555, 558, 561, 572, 582, 606, 624, 687, 710, 712, 721, 737, 767, 768, 773, 774, 777, 780, 790, 793–804), Young’s modulus (refs 276, 526, 616, 721, 770, 783, 805), loss modulus (refs 767, 803), flexural strength (refs 638, 794, 805), compressive strength (refs 373, 806), hardness (refs 112, 224, 258, 606, 807, 808), stiffness (refs 217, 546, 783, 809, 810), sheer thinning behavior (ref 594), peel strength (refs 709, 811–814), shear strength (ref 813), lap sheer (ref 709), contact angle (refs 326, 368, 561, 815, 816), crystallization (refs 193, 217, 524, 527, 577, 580, 598, 812, 813, 817–820), glass transition temperature (refs 72, 82, 83, 128, 132, 134, 168, 169, 216, 224, 225, 232, 241, 250, 251, 253, 255, 257, 278, 291, 301, 328, 359, 371, 498, 538, 564, 579, 582, 594, 595, 618, 624, 635, 681, 685, 690, 718, 740, 742, 767, 782, 788, 797, 801, 802, 811−813, 817, 821−834), melting behavior (refs 50, 193, 835, 836), interfacial properties (refs 172, 807, 810, 837), liquid crystal properties (refs 260, 268, 838), swelling behavior (refs 144, 172, 183, 642, 703, 764, 784, 796), water absorption (refs 327, 374, 779), rheological behavior (refs 357, 495, 526, 537, 547, 562, 566, 574, 580, 590, 730, 773, 778, 804, 839−842), dewetting behavior (refs 357, 607, 636, 843−846), density (ref 779), gel formation (refs 562, 847, 848), lithographic properties (refs 128, 269, 296, 297, 849− 851), electrochromic contrast (ref 852), laser action, (refs 853, 854), surface area, roughness, porosity, and permeability (refs 181, 185, 286, 327, 464, 549, 635, 806, 814, 855−866), surface free energy (ref 867), aggregation behavior (refs 362, 864, 868, 869), conductivity (refs 140, 231, 250−252, 255, 257, 327, 329, 679, 852, 870−872), dielectric characteristics (refs 75, 101, 130, 139, 144, 185, 242, 244, 245, 247, 259, 289, 295, 372, 374, 496, 588, 591, 592, 635, 645, 721, 728, 740, 742, 744, 827, 873− 879), electrochemical stability (ref 871), anion exchange behavior (ref 857), coefficient of thermal expansion (refs 225, 645, 794, 880), viscosity (refs 555, 778, 789, 791, 795), shrinkage (refs 141, 258, 561), transparency (refs 181, 215, 216, 291, 369, 552, 763, 823), refractive index (refs 881, 882), optical limiting properties (ref 221), resist behavior (refs 127, 174, 297, 653, 724, 851, 858, 883− 889), excimer formation (refs 380, 890), color tenability (ref 891), catalytic activity (refs 319, 404), thermal expansion coefficient (refs 169, 892, 893), viscoelastic properties (refs 561, 572, 645, 767, 780, 791, 793, 894− 899), morphology (refs 115, 132, 232, 242, 243, 264, 329, 370, 525, 588, 597, 647, 702, 711, 773, 786, 810, 816, 823, 855, 863, 872, 879, 895, 900−903), oleophobicity (ref 904), water repellency (refs 125, 171, 173, 301, 302, 328, 543, 628, 640, 845, 904), formation of inclusion complexes (refs 161, 692), hydrothermal stability (refs 286, 905), biodegradability (ref 577), stabilization of metal nanoparticles (refs 266, 338), corrosion resistance (refs 859, 906), thermal stability (refs 29, 71, 81−83, 115, 134, 162, 169, 216, 227, 232, 239, 241, 245, 273, 289, 290, 328, 329, 331, 333, 342, 362, 368, 370−373, 375, 494, 495, 524, 542, 546, 552, 581, 598, 618, 619, 631, 649, 650, 676, 678, 681, 685, 702, 714, 722, 768, 769, 772, 773, 776, 785, 788, 795, 797, 798, 800, 807, 822, 824, 825, 829, 833, 835, 836, 839, 862, 891, 893, 905, 907−915), combustion rate (refs 29, 30, 32, 34, 138, 291, 331, 546, 638, 708, 907, 912, 916−920), living polymerization properties (ref 921), and oxygen barrier properties (refs 162, 290, 625, 642, 766, 781, 851, 887, 922−924), and POSS confers some of the oxidative stability (i.e., better environmental stability)[765] associated with ceramic materials.

For polymer and nanocomposite applications, there are about 20 T_8 POSS compounds that are commonly used, commercially available from Hybrid Plastics[2] and other suppliers, as well as the many other derivatives prepared for specific applications (see section 2).

4.2. Hybrid Nanocomposite Materials

An important feature of the application of POSS species into nanocomposites is the degree of chemical modification that can be achieved and that, unlike many more conventional nanocomposites, the POSS cage may either be chemically bonded to the polymer matrix as a reactive nanofiller or present as an unreactive filler, as described in section 4.1. Advantages of the use of POSS molecules as fillers over other fillers such as clays, carbon fibers and carbon nanotubes is that they are much smaller than traditional fillers, they have a monodisperse size, they have low density, and they can be readily chemically modified to generate a range of reactive substituents to suit a particular application. On incorporation of a POSS component the processability of a polymeric material is often retained, and many of the useful materials properties described below occur at POSS loadings below 10%. Because the POSS species have dimensions similar to those of polymer chain segments, they may restrict motion at the molecular level, thus increasing T_g. However, because their shape is nearly spherical, they may reduce polymer viscosity and act as a plasticizer. POSS filled polymers can wet fibers well, reduce polymer shrinkage, and increase toughness. The viscoelastic properties are modified by the hindering of molecular chain relaxation through the large mass and size of the POSS changing the microstructure. The dimensions of T_8 POSS derivatives means that they are good at reinforcing polymer chains and control chain motion at a molecular level by maximizing the interactions with the polymer by up to eight chemical linkages.

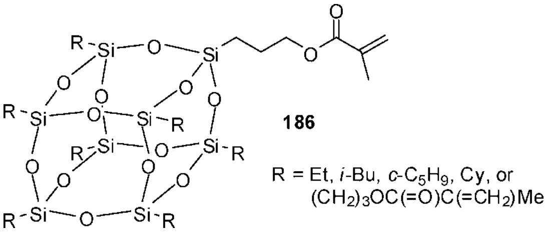
For reactive, polymerizable functions, groups such as oxetane, epoxy, methyl methacrylate, styryl, amine, or glycol are used, as well as the α-halo esters. When nonreactive substituents are required, alkyl and aryl groups are often used, with methyl, isobutyl, cyclopentyl and -hexyl, and phenyl groups being the most common. More specialized applications have used other nonreactive functionalities including longer chain alkyl species, and fluoroalkyl chains. Examples of the chemistry and applications of POSS compounds reported over the past seven years with these compounds are described below.

4.2.1. Nanocomposites Involving POSS Derivatives with Reactive Functionalities

4.2.1.1. Propyl Methacrylate Functionalized POSS. The most popular acrylate-functionalized POSS monomers are those bearing the propyl methacrylate function (Chart 38), which have been widely used due to the high transparency to visible light of the corresponding poly(methyl methacrylate) polymers.

Many reports of the incorporation of such POSS species in poly(methyl methacrylate)-based networks have been published. In general, it has been shown that there is a better dispersion of the POSS molecule in the polymer network if it possesses more than one functionalized arm [e.g., **186**, R = $(CH_2)_3OC({=}O)C({=}CH_2)Me$] and is cross-linked into the matrix rather than being pendant. Additionally, the rubbery modulus increases with the amount of incorporated POSS,[563] and the glass transition temperature T_g also increases.[398] However, some studies have shown that the bulkiness of the POSS groups can create free volume and chain separation in the hybrid material leading to a reduction in T_g.[376] The octafunctional methacrylate monomer, **186** R = $(CH_2)_3OC({=}O)C({=}CH_2)Me$, has been polymerized with a dimethacrylate monomer in situ in a montmorillonite aerogel lattice to give a low density thermoresponsive organic−inorganic composite[779] and the monofunctional compounds **186**, R = c-C_5H_9 or i-Bu, have been attached as pendant units to triblock copolymers creating POSS domains that affect the morphology and properties of the final material.[590] The monomethacrylate **186**, R = c-C_5H_9, has been self-polymerized on flat silicon wafers by surface-initiated polymerization to give hydrophobic surface layers.[726] Theoretical studies have been performed on the effect of the introduction of **186**, R = Cy or i-Bu, as pendant groups in poly(methyl methacrylate) polymer by atomistic molecular dynamics calculation. The effect of POSS loading and of the alkyl substituent was studied, and it was shown that T_g increased in case of R = Cy while it decreased in case of R = i-Bu.[925] Further molecular dynamic simulation studies on the grafting of **186**, R = c-C_5H_9, Cy, Ph, or i-Bu, onto poly(methyl methacrylate) to evaluate the effect of POSS on the T_g showed no real impact due to the difference in polarities of the polymer backbone and the POSS hydrocarbyl substituents. A different effect was calculated when the polymer was polystyrene.[475]

Chart 38



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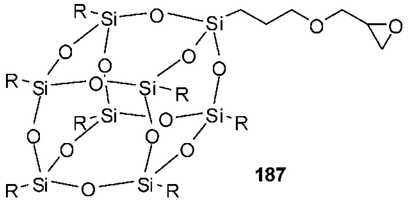
Incorporation of methacrylate-functionalized POSS into other acrylate-based polymers has been reported to give high resolution and sensitivity lithography resists[653,886,887,926,927] or devices,[849] dental composite materials with improved mechanical properties,[805,928] thermosetting matrices,[567] or fluorinated materials.[862] A POSS−methacrylate polymer has also been used in photosensitive paints as a binder for the luminescent dye, replacing the silica normally used and adding properties such as transparency, permeability to oxygen, and thermal resistance.[929] The use of such materials has also been reported in various nanocomposites and nanostructures for which properties such as viscosity, glass transition, and swelling were assessed,[718,895,930] in electrical insulating resins with good heat and mechanical resistance,[931] and in films with good transparency[932] or controlled hydrophilicity when supporting remote oxygen plasma.[766]

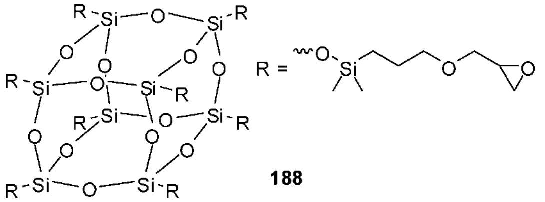
Methacrylate-functionalized POSS derivatives including both octamethacrylate and monomethacrylate compounds have also been introduced into other polymeric materials such as poly(vinyl chloride) to replace the usual organic volatile plasticizer,[782] into acetoxystyrene by copolymerization,[933] and

Chart 39



187

R = *i*-Pr, *i*-Bu, *i*-Oct, Ph or $(CH_2)_3OCH_2CH(O)CH_2$



188

in silicon-containing resins for electronic, semiconductor, or lithography applications.[591,743,884,885,902,913,934–952] Their incorporation into polyimide nanocomposites with lower dielectric constants than classical poly(imides)[588,589,592] and in polyurethane dispersions with enhanced surface properties[953] have also been reported, as have polyamide−POSS hybrid materials.[831]

There has also been study into the use and applications of derivatives of the type **186** with R groups other than ethyl, isobutyl, cyclopentyl, and cyclohexyl. This has included examinations of such materials for uses in ophthalmic devices (R = H),[954] multilayer resists (R = Me[945] or Ph[945]), photosensitive resins (R = Me),[955] carbon coating (R = Me),[809,956] polystyrene-based hybrids (R = Ph),[475] dental resins (R = Ph),[194] and chemically amplified resists (R = Ph).[851]

4.2.1.2. Other Acrylate-Based Functionalities. The acrylate derivative $T_8R_7(CH_2)_3OC({=}O)CH{=}CH_2$, R = *c*-$C_5H_9$, has been studied for use in preparing hybrid gels,[183] while that with R = Ph has been investigated for use in the preparation of pattern forming materials.[957] Composite materials for dental applications have been investigated using $T_8[OSiMe_2CH{=}CHCH_2OC({=}O)C({=}CH_2)Me]_8$[141] or $T_8(c\text{-}C_5H_9)_7[OSiMe_2(CH_2)_3OC({=}O)C({=}CH_2)Me]$.[958] Two related POSS derivatives, $T_8(i\text{-}Bu)_7[OSiMe_2(CH_2)_nOC({=}O)C({=}CH_2)Me]$ (n = 3 or 5), have also been studied as nano-building-block components.[274] Composite materials containing $T_8(i\text{-}Bu)_7(CH_2)_3OCH_2CH[OC({=}O)CH{=}CH_2]CH_2OC({=}O)\text{-}CH{=}CH_2$ have also been developed for use in liquid-crystalline panels or as photocurable sealants,[959] while $T_8[OSiMe_2(CH_2)_3OC({=}O)C({=}CH_2)Me]_8$ has been used in the preparation of imprint materials.[960]

Two further POSS derivatives containing fluorinated methacrylate substituents, $T_8(c\text{-}C_5H_9)_7(CH_2)_2OC({=}O)C(CF_3){=}CF_2$ and $T_8(i\text{-}Bu)_7(CH_2)_3OC({=}O)C(CF_3){=}CH_2$, have also been developed and used in fluoropolymer lithography resists.[850,961] Another POSS derivative related to the acrylate species, the acrylamide $T_8[(CH_2)_3NHC({=}O)C({=}CH_2)Me]_8$ has also been tested for use as a component in heat-developable photographic films.[962]

4.2.1.3. Epoxy-Based Substituents. Another reactive substituent widely used for the preparation of POSS-based nanocomposites is the epoxide group, commonly found in POSS precursors either at the end of a functionalized chain, for example, Chart 39, or as a cyclohexylepoxide, for example, **16** (Chart 4).

Epoxy resins themselves are the most commonly used thermosets due to their properties such as high modulus and strength, chemical resistance, and easy processing. They are used as adhesives and coatings and in other high-performance materials. The incorporation of POSS units leads to epoxy-based nanocomposites with features such as enhanced oxidative and thermal resistances, improved flame retardance, and improved dielectric properties. The reaction of the POSS species occurs via the epoxide ring opening with a reactive organic function of a polymer or a monomer, sometimes in the presence of an organic epoxy resin such as the diglycidyl ether of bisphenol A (DGEBA), a commercial epoxy resin component. The POSS precursors commonly used in such nanocomposite materials are shown in Chart 39, while the most commonly used reactive function group used in the organic monomer or polymer is the amine group.

Several examples of nanocomposites with different amines showing improved physical properties have been reported.[140,218,619,647,648,687,703,773] For example, the copolymerization of epoxide **188** with 4,4′-diaminodiphenylmethane in the presence of DGEBA gave a material with lower T_g, better thermal stability, and higher modulus, thought to be arising from the reinforcement effect due to the POSS units.[71] The lifetime of such a system has been calculated, and it was found to be theoretically thermally stable for more than 30 years at 100 °C in the absence of other reagents.[649] Structure−property relationships were assessed, including the influence of the organic moiety on the final material. For example, it was shown that the aromatic character of part of the tether improves the thermomechanical properties.[223,497] A similar reaction of epoxide **188** with phenylenediamine gave a material with higher T_g and lower dielectric constant than in the case when DGEBA was used.[245] Both $T_8[OSiMe_2(CH_2)_4CH(O)CH_2]_8$ and **188** have been treated with a commercial Ciba LY5210 epoxy resin in the presence of the epoxy hardening agent 3,3′-dimethyl-4,4′-diaminodicyclohexylmethane. Better mechanical and thermal stabilities were observed compared with preparations of the commercial resin. When high ratios of POSS were used no T_g was observed, indicating the high density of cross-links arising from the presence of the POSS species.[263]

The use of monofunctional POSS in preparing epoxide-derived nanocomposites has also been reported. For example, the reaction of **187**, R = *i*-Oct, *i*-Pr, or Ph, with poly(oxopropylene) diamine (also known as Jeffamine D) gave epoxides with pendant POSS units. A comparison with DGEBA showed that the POSS monomers were less reactive toward the amine due to the steric demand imposed by the nonreactive alkyl groups.[847] The influence of the alkyl substituent and the synthetic procedure on the final epoxides was studied using **187**, R = *i*-Bu or Ph, and 4,4′-methylenebis(2,6-diethylaniline) in the presence of DGEBA. For R = Ph, there were found to be more POSS−POSS interactions, which gave rise to POSS-rich domains within the material. In this situation, a prereaction of the POSS unit was necessary to produce its dissolution in the reaction mixture.[573] Recently, solid-state ^1H NMR has been used to study the size of domains in poly(propylene oxide)/DGEBA composites with **187**, R = *i*-Oct or Ph, making it possible to distinguish between primary domains and aggregates.[480]

Organic compounds containing functions other than amines have also been treated with epoxy−POSS precursors, for example, hydroxyl-containing species, through temperature-catalyzed ring-opening polymerization of benzoxazines,[72,702,963]

Chart 40

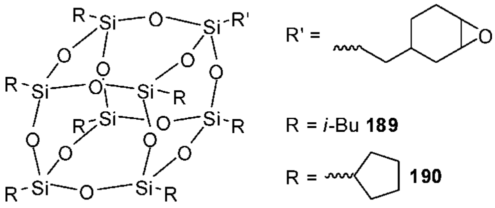
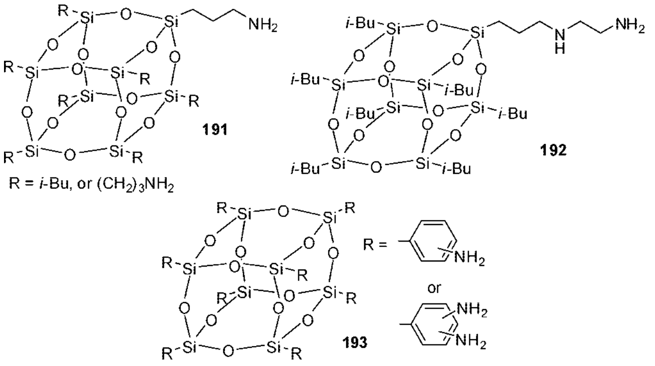


Chart 41



acid groups from poly(amic acid),[224,479] diethylphosphite or dicyandiamide groups in the presence of DGEBA,[624] and cyanate groups from a polyurethane polymer or from the dicyanate ester resin of bisphenol A, to form cyanate/epoxy composites.[114,618] Furthermore, epoxide **187**, R = *i*-Bu, has been copolymerized with epoxidized linseed oils to form bionanocomposites. These materials also showed improved properties due to the presence of POSS units.[571]

The use of a variety of other POSS monomers in the preparation of epoxide-derived nanocomposites has also been reported. These include the derivatives $T_8[CH_2CH(O)CH_2]_8$,[90,964,965] $T_8[CH_2CH(O)CH\text{-}Ph]_8$,[658] $T_8[OSiMe_2CH_2CH(O)CH_2]_8$,[645] $T_8[OSiMe_2(CH_2)_4CH(O)CH_2]_8$,[263,264,790] $T_8(R)_7CH_2CH(O)CH_2$ (R = *i*-Bu or $c\text{-}C_5H_9$),[966,69] **189** and **190** (Chart 40),[811,943,969,970] $T_8(c\text{-}C_5H_9)_7OSiMe_2(CH_2)_3OCH_2CH(O)CH_2$,[811] $T_8Ph_7(CH_2)_3OCH_2CH(O)CH_2$,[264,573,847,790,877] $T_8(OSiMe_2C_5H_{11})_6[OSiMe_2(CH_2)_4CH(O)CH_2]_2$,[264,790] $T_8[CH(O)CH_2]_6(CH{=}CH_2)_2$,[81] and $T_8(OSiMe_2C_5H_{11})_4[OSiMe_2(CH_2)_4CH(O)CH_2]_4$.[264,790]

There have been several patented applications for POSS-epoxy nanocomposites in the fields of antireflective hard masks for lithography applications,[971] integrated circuits and flip chip underfill,[880,972,973] and inks.[974] For other applications of epoxy-POSS composite materials, see section 4.2.3.

4.2.1.4. Other Reactive Functional Groups. A variety of amine-functionalized compounds, Chart 41, have also been used to prepare hybrid nanostructures involving covalently bound POSS species.

For example, the amine derivatives **191**, R = $(CH_2)_3NH_2$, and **193**, R = $C_6H_4NH_2$ or $C_6H_3(NH_2)_2$, have been cross-linked with dianhydrides such as pyromellitic dianhydride (PMDA) or oxidiphthalic dianhydride (ODPA) to form POSS-based hyperbranched poly(imides) with thermal stability up to 500 °C.[102,373,492,710] Similarly, **193**, R = $C_6H_4NH_2$, reacts with DGEBA to form epoxy-nanocomposites with increased glass-transition temperature.[780,798] The hydrochloride salt $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ has been used to prepare transparent composites by reaction with polymers such as poly(vinylpyrrolidone).[216] It has also been used as an intercalating agent to modify the clay sodium montmorillonite, giving expanded galleries in the material, while further reaction with DGEBA in the presence of 4,4′-diaminodiphenylmethane formed epoxy-nanocomposites.[488] In a similar fashion, $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ has been used to form POSS-modified epoxy networks in conjunction with DGEBA and Jeffamine T403, a polyetheramine.[611] Furthermore, an application has been patented for the introduction of $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ as a biocidal agent in cellulose-reinforced thermoplastic polymers such as HDPE.[975]

The monoamine derivative **191**, R = *i*-Bu, has been treated with formaldehyde and phenol to prepare benzoxazine-based POSS derivatives, subsequently used to form poly(benzoxazine) nanocomposites with pendant POSS units,[273] and with benzoic acid derivatives to prepare biscyanate ester-based POSS species. These biscyanate ester species are able to react further to form micellar structures with an organic core and an inorganic shell, which have been named “POSS nanoplanets” and which may have potential for the inclusion of guest species in the inorganic core during the cure process.[344] The same monoamine POSS derivative has also been introduced during the polymerization of caprolactam to prepare semicrystalline hybrid polyamide 6 (PA6)[345] and introduced to maleimide-containing poly(amides) giving composites with lower T_g and dielectric constants.[721] It has also been treated with DGEBA to form epoxy nanocomposites, which have subsequently been cured with further amines, amides, or phosphates to give materials with good transparency and thermal properties,[623] and introduced as pendant units in fluoro-containing poly(imides) to form coatings.[976] Its use has also been studied as a surfactant for the preparation of polystyrene/clay nanocomposites from montmorillonite,[581] as a component in polyurethane aqueous dispersions for transparent coatings,[977] and in poly(ethylene terephthalate) nanocomposite fibers with excellent initial and high-temperature modulus.[978]

In a similar manner, the diamine, **192**, has been introduced in polyamide nanocomposites, where it increased the viscosity but not the thermal stability.[722] It has been incorporated into polyurethane-based adhesives[709,812] and epoxy-based adhesives in which it was found to enhance the peel strength from 0.19 to 0.38 N mm^{-1},[811] and used to reinforce polyurethane−urea[791] or polyurethane films changing their viscoelastic behavior.[560,561,894] Other amino-functionalized POSS derivatives that have been used for the preparation of resins or nanocomposites include $T_8Cy_7(CH_2)_3NH(CH_2)_2NH_2$,[158] $T_8Cy_7C_6H_4\text{-}4\text{-}(CH_2)OC_6H_4\text{-}4\text{-}NH_2$,[188] $T_8(c\text{-}C_5H_9)_7C_6H_4\text{-}4\text{-}(CH_2)OC_6H_4\text{-}4\text{-}CH(C_6H_4\text{-}4\text{-}NH_2)_2$[185,979] and $T_8Ph_7(CH_2)_3NH_2$.[158,194]

Amine-functionalized POSS derivatives have also been used for the stabilization of metallic nanoparticles. The octaamine hydrochloride POSS species, $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$, has been used to separate and stabilize Au nanoparticles prepared in situ from $HAuCl_4$.[980] In a similar manner, it has been used to prepare nanocomposites from Au nanoparticles protected with dodecanethiol and 11-mercaptoundecanoic acid. In the presence of a base, deprotonation occurs and amide bonds are formed between the surfactants and the POSS molecules leading to stabilized nanocomposites (Figure 12).[613,981]

In a similar way, aggregates of Pd nanoparticles stabilized with $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ were linked to Au nanoparticles stabilized by dodecanethiol and 11-mercaptoundecanoic acid to form a bimetallic Pd−Au nanocomposite.[608,982] It may be further noted here that several studies describe the use of other POSS molecules as stabilizers of nanoparticles or colloids, giving rise to systems that can be considered as

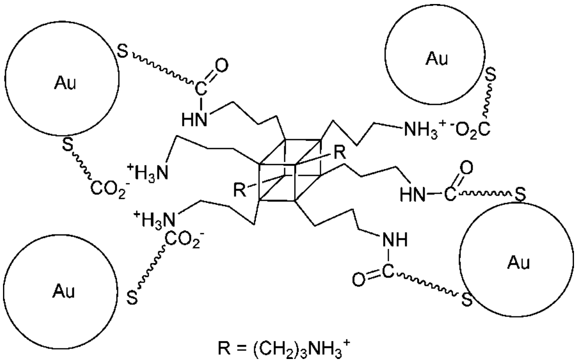
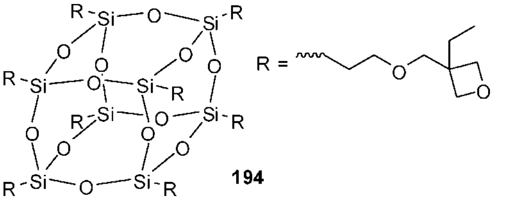


Figure 12. Schematic representation of $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ cross-linking Au nanoparticles protected with 11-mercaptoundecanoic acid.

Chart 42



194

hybrid nanocomposites.[617,723,983,984] For example, Pt nanoparticles were formed and stabilized in situ during the preparation of $T_8[OSiMe_2C_{10}H_{21}]_8$ from $T_8[OSiMe_2H]_8$ by Pt hydrosilylation of 1-decene. It was shown that the nature of the interaction between capping agent and nanoparticle depends on the stoichiometry of the reagents.[266] The preparation of monodisperse Pt/Pd and Pt/Au nanoparticles stabilized by the aldehyde-containing POSS derivative $T_8[C_6H_4N(CHO)_2]_8$ has been reported, as well as their ability to form reusable catalysts for the hydrogenation of phenylaldehydes into alcohols under mild conditions.[985]

Another reactive functionality used in POSS derivatives for the preparation of nanocomposites is the oxetane ring group in compound **194** (Chart 42). The similarities of the oxetane ring to the epoxide ring mean that it should be possible to integrate it into organic polymeric materials in a similar manner to epoxide-containing POSS species.

Reports of the use of oxetane **194** are limited and only relate to the patent literature where applications have been reported in the fields of transparent polymers with shock and penetration resistance,[986,987] insulating coatings for magnetic materials,[988] and transparent sheets, polymers, or resins with good heat resistance for applications such as imaging devices,[989–995] optical waveguides,[996,997] and various other optical materials such as lenses and optical cards.[998]

4.2.2. Nanocomposites and Other Materials Involving POSS Derivatives with Unreactive Substituents

There are two POSS derivatives containing unreactive substituents that have been commonly used in the formation of polymer blends, T_8Me_8 and $T_8(i\text{-Bu})_8$. The incorporation of T_8Me_8 into HDPE was studied, showing the influence of the POSS content on the properties (viscosity, modulus) of the resulting composite. It was found that increasing the POSS content in the polymer resulted in crystallization and agglomeration of POSS units in the matrix while lowering the polymer crystallinity and increasing its viscosity.[529] More recently, it has been shown that when prepared by isothermal crystallization, the POSS units affect the rate of crystallization of HDPE only if well dispersed in the matrix, acting as a nucleating agent.[527] Nonisothermal crystallization studies have also been reported, where with increasing amounts of POSS derivative present, the amount of supercooling required to crystallize the composite decreased.[818]

Nanocomposites prepared by melt-mixing of T_8Me_8 and linear low-density polyethylene show that incorporation of the POSS molecule improves both thermal stability and storage and loss moduli.[524] Similarly, when T_8Me_8 is blended with poly(ethylene terephthalate) a material with significantly improved fire retardancy is formed.[912] When T_8Me_8 is incorporated in polypropylene, it has been shown that an increase of the modulus and a reduction of the yield strength can be obtained; a reverse effect was observed if $T_8(i\text{-Bu})_8$ or $T_8(i\text{-Oct})_8$ were used.[783] The tensile properties of polypropylene blended with 1−5% T_8Me_8 are also enhanced.[770] The crystallization behavior has been studied at very low POSS loading; crystallization rate increased with POSS content, while the thermal stability decreased due to weak bonding forces between POSS units and the polymer matrix.[525,820]

A comparison to other POSS on the influence of the alkyl chain length on material properties has been carried out. SEM, TEM, and XRD studies showed that a better dispersion is obtained with longer alkyl chain, when Me is compared with *i*-Bu or *i*-Oct, due to better compatibility between the two components of the hybrid.[528,999] HDPE composite materials involving T_8Me_8 have had a number of practical applications investigated and, in some cases, patented, for example, their use in medical device materials for internal use[1000] and in the preparation of electrically charged plastic films.[1001]

If used in ethylene−polypropylene copolymers, the POSS units induce a physical gelation in the composite as shown by their rheological behavior being solid-like rather than liquid-like as in the neat resin, the rheological behavior being controlled by interactions between the POSS moieties and nanocrystals in the material, rather than POSS−polymer interactions.[526] This behavior has been shown to enhance the mechanical properties of the material by acting as a physical cross-linker.[1002] The incorporation of T_8Me_8 into poly(methacrylate) polymers[1003] and also into transparent cellulose acylate films has been reported,[1004] where it acted as a flame retardant. Treatment of the usually inert T_8Me_8 with $BF_3 \cdot OEt_2$ leads to one edge of the POSS cage being opened and a difluoride to be formed. This has been copolymerized with the di-Grignard $C_6H_4\text{-}1,3\text{-}(C{\equiv}CMgBr)_2$ to give a novel arylacetylene polymer with good oxidative and thermal properties.[423,1005]

In a similar manner to T_8Me_8, $T_8(i\text{-Bu})_8$ has been introduced into a polypropylene matrix, and the changes in properties such as tensile strength and crystallization have been studied.[528,789,783,999,1006] Another study showed changes in the surface properties of the resulting nanocomposite, with a reduction in the relative surface friction coefficient corresponding to an increase in the relative surface roughness.[860] Kinetic studies of the crystallization of the polymer have been performed by DSC, indicating that the crystallization temperature and rate could be improved by the addition of a suitable amount of the POSS derivative.[1006] $T_8(i\text{-Bu})_8$ has also been introduced into polybutadiene and the effect of the added POSS derivative on the mechanical response and morphological dynamics when under tensile deformation were studied by in situ SAXS.[593] The effects of $T_8(i\text{-Bu})_8$ on thermal degradation and combustion of polypropylene have been investigated and show that the POSS molecules aggregate at the surface and give a silica-like phase on heating.[916]

The isobutyl POSS derivative, $T_8(i\text{-Bu})_8$, has also been blended with functionalized polymers such as poly(methyl methacrylate),[531] phenolic resins,[1007] poly(lactic acid),[1008] and nylon-6.[345] These materials generally showed a good dispersion of the POSS species at low content and aggregation of POSS molecules above its solubility limit,[531] except for the nylon-6 nanocomposite prepared by the in situ polymerization of caprolactam, which showed no dispersion of the POSS derivative at all.[345] When $T_8(i\text{-Bu})_8$ was blended with epoxy-cyanate esters, the resulting materials showed an increase in the glass-transition temperature.[534] Surface analysis of POSS−nylon 6 nanocomposites containing $T_8(i\text{-Oct})_8$ show significant improvements in hardness and modulus coupled with reductions in friction and highly hydrophobic surface formation.[1009] For polyamide nanocomposites based around polymers such as various forms of nylon, special application has been found in the food packaging industry.[1010] Poly(hydroxybutyrate) has been shown to have increased thermal stability when melt blended with the larger inert POSS species $T_8(i\text{-Oct})_8$.[839] The aryl-POSS compound, T_8Ph_8, has been blended with polyimide to give nanocomposite films, but this appeared to give materials with poor interfacial interactions.[335] T_8Ph_8 has also been blended with polystyrene to give composites with improved thermal stability and flame retardance,[495] and with acrylate-based dental composites.[866]

POSS derivatives such as $T_8(i\text{-Bu})_8$ have also been introduced into several silicone rubber polymers. In the case of poly(methylvinylsiloxane), elastomers were formed by melt mixing, and the influence of the reaction temperature (mixing and vulcanization) on the final composition was demonstrated.[533,537] In poly(dimethylsiloxane)[605] or silicone oil based on octamethylcyclotetrasiloxane, nanocomposites were formed showing good fluidity and dispersibility of the POSS species.[1011] The effects of blending $T_8(i\text{-Bu})_8$ with silicone rubber have also been investigated by both XRD methods and TEM.[533]

4.2.3. Other Hybrid Nanocomposites and Polymeric Materials Containing POSS Compounds

A wide range of other hybrid POSS nanocomposites and polymers have been prepared and investigated. Examples of these are given in Tables 30−34 and Charts 43 and 44 and are arranged according to the structure of the POSS precursor.

4.3. Applications in Catalysis

Over the past seven years, there have been a wide variety of reports on the use of POSS compounds in the field of catalysis, as models for silica surfaces, as models for silica-bound catalyst systems, and as catalysts in their own right.[53–57] In the area of heterogeneous catalysis, POSS compounds have been developed as models for silica-supported heterogeneous catalysts. Here, such “homogeneous” models can give important information on the environment of the catalytic site and potentially on reaction mechanism and can therefore provide a better understanding of the structure−activity relationships. In a similar manner, POSS species are able to be used as models for a silica surface acting as a catalyst.

4.3.1. Heterogeneous Catalyst Models

A series of silica-based catalyst models where the metal is directly bonded to the corner of the POSS cage via a M−O−Si linkage, Chart 45, have been reported as products from the reaction of $T_8(c\text{-}C_5H_9)_7OH$ with metal alkyl complexes. Applications for these catalysts and their model systems are found in olefin metathesis reactions, for example.[407,411–413,415,416]

In a similar manner, titanium-based POSS compounds have also been used as structural models of silica-supported titanium-containing epoxidation catalysts. Thus the reaction of $T_8(c\text{-}C_5H_9)_7OH$ with $Ti(O\text{-}i\text{-}Pr)_4$ affords $T_8(c\text{-}C_5H_9)_7OTi(O\text{-}i\text{-}Pr)_3$.[409] The silanol $T_8(c\text{-}C_5H_9)_7OH$ has been used as a precatalyst for alkyne metathesis and polymerization reactions in the presence of $Mo(\equiv CEt)[N(C_6H_3\text{-}3,5\text{-}Me_2)t\text{-}Bu]_3$. It has been shown that the actual active species formed during the reaction was the dimeric complex $(c\text{-}C_5H_9)_7T_8\{OMo(\equiv CHEt)[N(C_6H_3\text{-}3,5\text{-}Me_2)(t\text{-}Bu)][NH(C_6H_3\text{-}3,5\text{-}Me_2)(t\text{-}Bu)]O\}T_8(c\text{-}C_5H_9)_7$ and that it had similar activity to the more traditional silica-supported Mo catalysts.[414]

Computational modeling by DFT has been carried out on the rhenium complexes $T_8(Me)_7[ORe(CH_2\text{-}t\text{-}Bu)({=}CH\text{-}t\text{-}Bu)(\equiv C\text{-}t\text{-}Bu)]$ and $T_8(Me)_7[ORe(Et)({=}CHMe)(\equiv CMe)]$, and this has confirmed that POSS species can be considered as good models for catalysts bound to silica surfaces, due to similarities in their calculated structural and electronic properties.[1093]

4.3.2. Silica Surface Modeling for Catalysis

In a study of the catalytic effect of the silica surface, the silanol T_8H_7OH has been used as a theoretical model of silica for computational studies looking at the catalytic role of the silica surface in the coupling of amino acids to more complex molecules.[450] This study had the more general goal of attempting to mimic the start of terrestrial life and determining whether external catalysts or other species were needed for these basic reactions.

4.3.3. Supported Homogeneous Catalyst Models

In these systems, where a ligand binding the transition metal catalyst is grafted onto the support, appropriately functionalized POSS derivatives provide useful models for small areas of silica support having grafted organic species. POSS species containing fluorenyl groups have been prepared and coordinated to Cp^*ZrCl_2 or $Cp''ZrCl_2$ fragments to give compounds **138**−**141** and **144** that are models for zirconium-based olefin polymerization catalysts. The model systems have been shown to be catalytically active in ethylene polymerization when activated with MAO.[179]

Another ethylene polymerization catalyst, the POSS-supported cationic Pd−diimine complex **129** allows “living” polymerization and copolymerization with functional olefins to give branched polymers with low polydispersities.[404]

An osmium-based dihydroxylation catalyst, **143**, has been prepared by coordination of OsO_4 to a cyclic olefin precursor. This compound is a model of the analogous silica-supported catalyst for the dihydroxylation of cyclopentene and cyclohexene.[182]

Table 30. Nanocomposites and Other Polymeric Materials Formed Involving Reactive T_8R_8 Precursors

R, T_8R_8, or compound number	applications	refs
-H	polyurethane hybrids	170
	copolymers formed with $T_8\{(CH_2)_2SiMe[(CH_2)_2Si(CH{=}CH_2)_3]_2\}_8$ to prepare dielectric films	1012
	formation of polymers with $(CH_2{=}CHMe_2Si)_2O$	75
	nanocomposite with $HC{\equiv}CCH_2O$-C_6H_4-4-N=N−C_6H_4-4-OMe	221
	precursor to soluble electron transport hybrid materials	219
	precursor to heterosubstituted POSS compounds for use as binders	1013
	formation of highly thermally stable polymers with low dielectric constant on reaction with 4,4′-bis(allyloxybenzoyloxy)benzene	484
	precursor to silicon nanocrystals in silica via spin coating and thermal processing	700, 1014–1016
195	resins for light-emitting diodes	965
$-CH_2Ph$	polycarbonate hybrids	655
	transparent hybrids with poly(vinyl chloride)	1017
$-(CH_2)_2(CF_2)_nCF_3$ (n = 0, 3, 5, or 7)	hydrophobic fluoropolymers	88, 301, 736, 737, 1018
$-(CH_2)_2(CF_2)_5CF_3$	poly(dimethylsiloxane) nanocomposites as antibacterial coatings for cotton fabrics	486
196	antioxidant stabilizer for polymers	963
197	antioxidant stabilizer for polymers	963
$-(CH_2)_2$-*c*-C_6H_{11}	formation of nanocomposite with polystyrene	215
198	photopolymerization followed by heating to give structured silicates	1019
	formation of epoxy nanocomposite showing increased thermal stability and tensile strength	788
	effect of POSS on the morphology of poly(2,6-dimethyl-1,4-phenylene oxide)/polyamide 6 blends	816
$-(CH_2)_2Ph$	poly(biphenol A carbonate) hybrids	740
	stabilization of polystyrene thin films and dewetting behavior	180
	formation of nanocomposite with polystyrene	215
	melt-mixed polycarbonate nanocomposites	540
$-(CH_2)_2C_6H_4$-4-CH_2Cl	star-shaped poly(oxazoline)	211
$-(CH_2)_2C_6H_4$-4-Br	poly(fluorene)-based light-emitting polymers	209, 1020
199	antioxidant stabilizer for polymers	963
$-(CH_2)_2OSiMe_2Cl$	component of cholic acid based molecular resist	296
$-(CH_2)_2SiMe_2OMe$	conducting polymers	1021
59	bilayer resists for 193 nm lithography	297
$-(CH_2)_2SiMe[(CH_2)_2Si(CH{=}CH_2)_3]_2$	copolymers formed with T_8H_8 to prepare dielectric films	1012
$-(CH_2)_2Si(CH{=}CH_2)_3$	formation of homopolymers to give insulating films	1012
$-(CH_2)_2SiMe(OMe)_2$	resins for insulating films	294
$-(CH_2)_2Si(OMe)_3$	resins for insulating films	294
$-CH{=}CH_2$	polypropylene hybrids for flame retardancy	34
	poly(acetoxystyrene) hybrids	683
	poly(acrylate) dental composites	747
	poly(methyl methacrylate) hybrids	685
	rheology modifier for low-density polyethylene	778
	nanocomposites with vinyl pyrollidine	84
	component of POSS mixture for surface modification of biomaterial polyurethane	684
	preparation of POSS-grafted polypropylene by reactive blending	539, 638, 819, 841
	thermoset polymers containing carborane groups	1022
	nanocomposite with polyurethane acrylate showing enhanced thermal stability and T_g	1023
	composite formation with low-density polyethylene	879
	composites formed by melt blending with nylon 1010 had greater thermal stability than nylon 1010 alone	639
$-(CH_2)_3Ph$	polystyrene hybrids	215
$-(CH_2)_3NH_2$	core for star polyamides for low-κ dielectric materials	101
$\{T_8[(CH_2)_3NH_3]_8\}Cl_8$	component of POSS−palladium nanocomposites for hydrogen sensing	881
	formation of composites with polystyrene	708
	component of surface coating for silica nanoparticles use as NMR probe	107
	stabilization of Pd nanoparticles	608
	precursor to dendritic poly(amino acid) derivatives	1024
	precursor to water-soluble network polymers	108
	formation of nanohybrids with $-S(CH_2)_3CO_2H$-capped Mn-doped quantum dots for detecting DNA	1025
	source of cations in formation of photocatalytically active TiO_2 coatings	1026
$-(CH_2)_3NHC({=}O)(CH_2)_2CO_2H$	precursor to water-soluble network polymers	108
$-(CH_2)_3N[CH_2CH(OH)CH_2OH]_2$	component of POSS-based nanoparticles; hybrid polyurethane polymers	609, 610
69	solid phase sorbent for copper	123
$-(CH_2)_3NH(\text{L-Lys})_8$-$(\text{L-Lys})_{16}$-$(\text{L-Lys})_{32}$	Gd(III) derivative as contrast agent for magnetic resonance angiography	383
$-(CH_2)_3OH$	star-shaped poly(caprolactam) hybrids	116

Table 30. Continued

R, T_8R_8, or compound number	applications	refs
-$(CH_2)_3OCH_2CH(O)CH_2$	preparation of reinforced epoxy matrices	767
	POSS-substituted poly(hydroxybutyrate)	839
	preparation of poly(ethylene imine) hybrids	172
-$(CH_2)_3OC(=O)CH(=CH_2)$	preparation of polypropylene nanocomposites by γ-irradiation	1027
-$(CH_2)_3OC(=O)C(=CH_2)Me$	cured with unsaturated polyester resins	1028
	hybrid dye-doped poly(methyl methacrylate) materials for laser applications	853, 854
	UV curing with methacrylic oligomers to give hybrid coatings	823
	filler in fatty acid vinyl ester fire retardant	917
	reinforcement of methylsilicone resins	769
	nonlinear optical films from reaction with a chromophore bonded to allyl glycidyl ether	1029
	radiation processing of POSS and polypropylene to give nanocomposites	1027
	ultralow dielectric constant materials from reaction with furfuryl glycidyl ether derivatives	1030
	component in methacrylate/silica matrix for nonlinear optical films	1029
-$(CH_2)_3OC(=O)CBr(CH_2Br)Me$	polymerization initiator for acrylonitrile to form starburst nanoparticles for embedding in sulfonic perfluoropolymers such as Nafion	397
-$(CH_2)_3SH$	reinforcement for epoxy amine networks	115
-$(CH_2)_3Cl$	precursor to porous chelating resins for heavy metals via reaction with 3-amino-1,2,4-tetrazole	124
-$(CH_2)_3I$	hybrid poly(acetylene) gels, star-shaped poly(2-methyloxazoline)	542, 686
-Cy	hybrids with poly(vinyl chloride)	1017
-C_6H_4-4-C_6H_4-4-$OCF=CF_2$	electro-optical devices	1031
94	modifier for epoxy resins	134
	modification of thermal and dielectric properties in bismaleimide−triazine resins	372, 496
-$C_6H_4NO_2$	porous thin films based on poly(phenyl siloxane) matrix	130
-$C_6H_4NH_2$	hybrid bismaleimide resins with good processability	493
	nanocomposite films by blending with polyimide	335
	component in star polymers of 2,2,3,4,4,4-hexafluorobutyl methacrylate	368
	cores for star polymers with polyaniline	871
	precursor to benzoxazine derivatives for making nanocomposites	1032
	electrochromic devices by tethering to polyaniline	1033
	hybrid cellulose composite materials with improved thermal properties	1034
	POSS-functionalized carbon nanofibers	1035
-$C_6H_4NHC(=O)CMe_2Br$	nanocomposite with poly(methyl methacrylate)	367
115	enhanced electrochromic properties of polypyrrole	337
-$C_6H_4OCF=CF_2$	electro-optical devices	1031
-C_6H_4X (X = SO_3H or PO(OH)OPh	additives in sulfonated polyphenylsulfone hydrogen fuel cell proton exchange membranes	329
-$C_6H_4Br^a$	precursor to phosphonylated compounds for polymer formulation	1036
$[NMe_4]_8[T_8O_8]$	precursor to multifunctional silsesquioxanes for coatings	1037
	precursor to multiarm or star polymers	1038
	formation of a hexagonal mesophase composite material from nonaethylene glycol dodecyl ether and water	1039
-$OSiMe_2H$	poly(methyl methacrylate) hybrids with improved T_g and toughness	367, 616
	fluorinated polymers	1040
	nonconjugated diene-based hybrid gels	1041
	nanocomposite with poly(ethylene glycol) for in vitro screening of pharmaceuticals	256
	precursor to water-soluble star polyacrylamides	265
	POSS/polystyrene hybrid material with donor−acceptor interactions	671
	precursor to hybrid bent-core liquid crystals with POSS cores	267
	molecular resist precursor for 193-nm lithography	269
	thermoset polymers and dendritic networks containing carborane groups	701, 1022
	hybrid resin formation with diethynylbenzene	1042, 1043
	precursor to dendritic networks using $(CH_2=CHSiMe_2C\equiv C)_2$-derived linkers	804
	precursor to nanocomposites for cosmetic use	1044
	precursor to discoloration-resistant resins for optical applications	1045
	precursor to colored silsesquioxanes for use as pigments and dyes	1046
	precursor to films with good thermal properties	1047
	reacted with **15** to give resin sheets with useful optical properties	1048
	reacted with *N*-(9-ethyl-carbazol-3-yl)undec-10-enamide to give a organic/inorganic electroluminescent material	1049
	nanocomposite formation with polydimethylsioxane	792
	nanocomposite membranes with poly(dimethylsiloxane-urethane)	549
	hybrid gels via $Pt(acac)_2$ catalyzed photohydrosilylation with 1,5-hexadiene or 1,9-decadiene	1050

Table 30. Continued

R, T_8R_8, or compound number	applications	refs
	phosphorescent POSS species containing anchored iridium complexes	401
-$OSiMe_3$	modifier of cross-linked poly[1-(trimethylsilyl)-1-propyne] to decrease permeability	856
15	hybrid polymers with UV and IR transmittance	1051
	poly(phenylene ether) resins	1052
	reacted with $T_8(OSiMe_2H)_8$ to give resin sheets with useful optical properties	1048
200	component in cellulose acylate films in optical imaging devices	1004
16	nanonetworks with polypropylene	821
	nanocomposites with epoxy-amine systems	644
	formation of PEGylated POSS using poly(propylene oxide)/poly(ethylene oxide) copolymers	1053
-$OSiMe_2(CH_2)_2Ph$	electroluminescent nanocomposites	711
	blended with polystyrene to give nanocomposite	226
	blends formed with poly(ethylene oxide)	227
-$OSiMe_2(CH_2)_2C_6H_4$-3-$C(CF_3)_2OH$	polymer coatings for surface acoustic wave sensor platforms	228
-$OSiMe_2(CH_2)_2C_6H_4$-4-OH	phenolic nanocomposites	375
	blended with poly(4-vinylpyridine) to give nanocomposite	226
	polymer blends with poly(methyl methacrylate) and poly(vinyl pyrrolidine)	231
	$LiClO_4$-doped polymer blend with poly(methyl methacrylate)	232
	blends formed with poly(ethylene oxide)	227
-$OSiMe_2(CH_2)_2C_6H_4$-4-CH_2COMe	blends formed with poly(ethylene oxide)	227
-$OSiMe_2(CH_2)_2C_6H_4$-4-OAc	phenolic nanocomposites	230
	blended with poly(4-acetoxystyrene) to give nanocomposite	226
-$OSiMe_2(CH_2)_2C_6H_4$-4-Cl	precursor to poly(phenylene vinylene) hybrid materials for use in efficient organic light-emitting diodes	679
-$OSiMe_2(CH_2)_2C_6H_4$-4-Br	poly(fluorene)-based light-emitting polymers	210
-$OSiMe_2(CH_2)_2SiMe(OMe)_2$	precursor to films with good transparency and thermal properties	1054
-$OSiMe_2CH{=}CH_2$	hybrid polymers with UV and IR transmittance	1051
	poly(phenylene ether) resins	1052
	materials formed by cross-linking other POSS (computational studies)	464
	implantation in a Nafion matrix for fuel cell applications	144
	precursor to polysiloxanes with useful transparency, dielectric and processability properties	1055
-$OSiMe_2CH{=}CHCH_2OC({=}O)C({=}CH_2)Me$	component in dental nanocomposites	254
-$OSiMe_2[(CH_2)_3O]_3C({=}O)C({=}CH_2)Me$	component in dental nanocomposites	254
-$OSiMe_2(CH_2)_3C_6H_4$-2-OH	phenolic nanocomposites	228
	chemical sensor compositions	1056
20	benzoxazine-based polymers	241
-$OSiMe_2(CH_2)_3OH$	star polymers with caprolactone	261
	polymers with poly(methyl methacrylate)	478
	polymer hybrid materials with random styrene/*N*,*N*-dimethylacrylamide copolymers	552
	preparation of low-κ nanocomposite films with polyimide	242
	formation of polyurethanes with $HO(CH_2)_6OH$	243
	formation of polyurethane hybrid materials with $T_8(OSiMe_2CH_2CHMe$-C_6H_4-4-$CMe_2NCO)_8$	243
-$OSiMe_2(CH_2)_3OC({=}O)$-C_6H_4-4-NH_2	precursor to polyurethane networks containing polysiloxane chains	689
-$OSiMe_2(CH_2)_3OCH_2CH_2OC({=}O)$-$C_6H_4$-4-$NH_2$	precursor to polyurethane networks containing polysiloxane chains	689
-$OSiMe_2CH_2CHMe$-C_6H_4-4-CMe_2NCO	formation of polyurethane hybrid materials with $T_8[OSiMe_2(CH_2)_3OH]_8$	243
-$OSiMe_2(CH_2)_3OCH_2CH(O)CH_2$	nanonetworks with polypropylene	821, 1057
	hybrid coatings formed with polythiourethane	733
	epoxy-POSS nanocomposites by photopolymerization with diglycidyl ether of bisphenol A	246
-$OSiMe_2(CH_2)_3O(CH_2)_2[O(CH_2)_2]_nOH$	poly(ethylene glycol) hybrids	217, 249, 547, 548
	POSS−methyl methacrylate hybrid materials	376
-$OSiMe_2(CH_2)_3O(CH_2)_2[O(CH_2)_2]_nMe$	poly(ethylene glycol) hybrids	217, 249, 547, 548
	POSS−methyl methacrylate hybrid materials	376
-$OSiMe_2(CH_2)_3OCF_2CHFCF_3$	epoxy composites with low dielectric constant	259
	polyimide nanocomposites with low dielectric constant	244
116	hybrid three-dimensional materials prepared by photopolymerization	213, 399
-$OSiMe_2C(SiMe_3){=}CHSiMe_3$	hybrid polymers with UV and IR transmittance	1051
-$OSiMe_{3-n}(OEt)_n$ ($n = 1, 2,$ or 3)	nanobuilding blocks for xerogels	300
-$OSiMe_2OSiMe_2H$	precursor to mixed acrylate and benzocyclobutane derivatives for imprint lithography	1058
-$OSnMe_3$	precursor to amorphous porous silica	481
	precursor to metallosilicate catalysts	501

[a] Contains multiple isomers.

Table 31. Nanocomposites and Polymeric Materials Formed Involving $T_8(i\text{-Bu})_7R$ Precursors

R or compound number	applications	refs
-H	poly(benzoxazine) hybrids	273
-CH$_2$Cl	hyperbranched polyimide−POSS nanocomposites	878
-CH(Pr)OCH$_2$CH(OH)CH$_2$OH	polyurethane hybrids	834
158	poly(dicyclopentadiene) hybrids	558, 1059
	POSS-substituted ethylene−propylene thermoplastic elastomers	189
189	modifier for nanocomposite poly(*N*-vinyl-2-pyrrolidine/itaconic acid) hydrogels	796
185	shape memory polyurethane hybrids	1060, 1061
	biocompatible poly(carbonate urea) urethane hybrids	621, 749–751
	POSS-modified polyurethane for medical devices	620, 755
	POSS-modified polyurethanes for corrosion protection	906
72	modifier for montmorillonite	342
-(CH$_2$)$_2$OH	poly(caprolactone) hybrids	161
-(CH$_2$)$_2$OAc	poly(caprolactone) hybrids	161
-(CH$_2$)$_2$SiMeCl$_2$	phenolic hybrid resins	1007
-CH=CH$_2$	hybrids involving polyolefins, polyamides, polyesters, polyacrylates, polycarbonates, polyurethanes, poly(dimethylsiloxanes), polysilanes, poly(vinyl chloride), polystyrene, phenol resins, epoxide resins	163
	hybrids involving poly(norbornene)	1062
	hybrids involving polysiloxanes	282, 792
	formation of POSS−propylene copolymer using Zr catalyst	836
-CH$_2$CH=CH$_2$	formation of copolymer with propylene	836
	formation of nanocomposites with bicyclo[2.2.1]hept-2-ene−ethylene copolymer	555
-CH=CHCH$_2$C(CF$_3$)$_2$OH	poly(carbosilane) hybrids for surface acoustic wave sensors	228
-(CH$_2$)$_3$C$_6$H$_3$-2-OH-5-CMe$_2$C$_6$H$_4$-4-OH	polymer coatings for surface acoustic wave sensor platforms	228
-(CH$_2$)$_3$NH$_2$	POSS/poly(ethylene terephthalate) nanocomposites with improved mechanical properties	795, 978
	precursor to POSS-terminated poly(*N*-isopropylacrylamide)	377
	precursor to fluorescent colorants	1063
	helical polypeptides terminated by POSS from ring-opening polymerization of γ-benzyl-L-glutamate-*N*-carboxyanhydride	1064
	hybrid material from reactive blending with maleic anhydride-grafted polypropylene	530
	composite material with poorer thermal stability and mechanical properties from nonreactive blending with $T_8(i\text{-Bu})_8$	530
	formation of surface-modified silica nanoparticles	1065
	precursor to amphiphilic POSS−dendron nanohybrids	1066
	precursor to polystyrene−poly(ethylene oxide) block copolymers with the POSS species at the junction of the two blocks	1067
-(CH$_2$)$_3$NH(CH$_2$)$_2$NH$_2$	component of poly(phenylene ether)-based resin films	1068, 1069
	component in polyethylene terephthalate nanocomposites	978
	resin additives	1070
	component in electric wire covering materials	1071, 1072
-(CH$_2$)$_3$NCO	polyurethane hybrid resins	1073
-(CH$_2$)$_3$N$_3$	modifier for poly(ε-caprolactone) by end-capping	652
-(CH$_2$)$_3$NHC(=O)(CH$_2$)$_2$SC(=S)SCH$_2$Ph	use as chain-transfer agent in polymerization of *tert*-butyl acrylate, leading to formation of tadpole-shaped organic/inorganic hybrid materials	378
	use as chain-transfer agent in polymerization of styrene, leading to formation of organic/inorganic hybrid	379
-(CH$_2$)$_3$NHC(=O)C$_6$H$_3$-3,5-(OCN)$_2$	hybrid micelles	344
201	photosensitive hybrid resins	1074
-(CH$_2$)$_3$OH	modifier for poly(ε-caprolactone) by end-capping	652
	precursor to fluoropolymer resists	850
-(CH$_2$)$_3$OCH$_2$CH(OH)CH$_2$OH	polyurethane hybrids with thermo(oxidative) stability	579, 594, 815, 822
100	films containing pyrenyl excimers for sensing applications	380
-(CH$_2$)$_3$OCH$_2$CH(O)CH$_2$	reinforcement of epoxy adhesives	572, 803
-(CH$_2$)$_3$OC(=O)C(=CH$_2$)Me	copolymer with *n*-butyl methacrylate to give films for humidity sensing	742
	nanocomposite with *n*-butyl methacrylate for gas sensing applications	680
	filler in fatty acid vinyl ester fire retardant	917
	nanocomposite with polypropylene via radiation induced grafting methods	771
	block copolymers with poly(methyl methacrylate) forming layered films	568
	component of negative-type photoresists	883
	preparation of nanocomposite particles with methyl methacrylate	725
	formation of POSS-substituted fluoroelastomers	566
	formation of copolymers with methyl methacrylate	564
	preparation of POSS-terminated polyethylene	404
	linear polymers with isobornyl methacrylate and cross-linked polymers with di(ethylene glycol) dimethacrylate, both with low surface energies	565
	formation of copolymers with styrene	899
-(CH$_2$)$_3$OC(=O)C(=CH$_2$)F	precursor to fluoropolymer resists	850
-(CH$_2$)$_3$OC(=O)C(=CH$_2$)CF$_3$	precursor to fluoropolymer resists	850
131, **132**, **133**	optical limiting materials	360
-(CH$_2$)$_3$SH	POSS−poly(methyl methacrylate) hybrids	570
	preparation of stabilized gold nanoparticles	569, 1075
	precursor to multifunctional thioethers	388
	precursor to POSS-terminated poly(*N*-isopropylacrylamide)	389
-C$_6$H$_4$-4-CH=CH$_2$	copolymers with styrene	574, 575, 842
[T$_8$(C$_6$H$_4$-4-CH$_2$NMe$_2$C$_{18}$H$_{37}$)$_8$]Cl$_8$	POSS-treated clay for preparation of polystyrene nanocomposites	169
-OCH$_2$CH(OH)CH$_2$OH	polyurethane hybrid aqueous dispersions	560
-OC$_6$H$_4$-4-CMe$_2$C$_6$H$_4$-4-OH	polymer coatings for surface acoustic wave sensor platforms	228
-OSiMe$_2$(CH$_2$)$_3$NCO	poly(amidoamine) hybrids	825
-OSiMe$_2$(CH$_2$)$_3$OCH$_2$-C(Et)(CH$_2$OH)$_2$	hydrophobic and biodegradable polyurethane hybrids	556, 577, 845
	biodegradable polycaprolactone network materials with shape memory	576
	formation of a polyethylene glycol-based multiblock polyurethane-containing POSS units	580
	component in biodegradable stent coatings for drug release	760

Table 32. Nanocomposites and Polymeric Materials Formed Involving $T_8(c\text{-}C_5H_9)_7R$ Precursors

R or compound number	applications	refs
-H	poly(siloxane) hybrids	583
	POSS-terminated poly(propylene oxide) nanocomposites	584
	styrene−isoprene copolymer hybrids	858
-CH=CH_2	formation of copolymer with propylene	836
159	polybutadiene hybrids	587
	ethylene−propylene copolymer hybrids	829
$\text{-CH}_2\text{CH(OH)CH}_2\text{OH}$	stabilization of polystyrene thin films and dewetting behavior	180
$\text{-(CH}_2)_2(\text{CF}_2)_7\text{CF}_3$	stabilization of polystyrene thin films and dewetting behavior	180
$\text{-(CH}_2)_2\text{C}_6\text{H}_4\text{-4-CH=CH}_2$	poly(isobutylene) hybrids	908
$\text{-(CH}_2)_3\text{C}_6\text{H}_4\text{-4-OCF=CF}_2$	fluorinated copolymers to form optical films	276
$\text{-CH}_2\text{CH=CH}_2$	silicone compositions	1076
$\text{-(CH}_2)_3\text{CN}$	cyanate ester hybrid resins	544
$\text{-(CH}_2)_3\text{OC(=O)C(=CH}_2)\text{Me}$	fluorinated polyimide/POSS nanocomposites with low dielectric constant	592
	resins with good heat resistance	931, 1077, 1078
$\text{-(CH}_2)_3\text{OC}_6\text{H}_4\text{-4-CHO}$	precursor to POSS-terminated poly(azomethine)s via aza-Wittig polymerizations	351
$\text{-(CH}_2)_3\text{I}$	poly(oxazoline) hybrids	181
	precursor to binaphthyl-based hybrid chiral polyarylene materials	362
	precursor to POSS-modified poly(*p*-phenylene)s with enhanced photoluminescent stability	352
	POSS-modified poly(phenylene−ethynylene) luminescent polymers	891
$\text{-(CH}_2)_3\text{SiMe}_2\text{C}_6\text{H}_4\text{-4-SiMe}_2\text{H}$	polystyrene−butadiene−polystyrene hybrids	184, 277
$\text{-C}_6\text{H}_4\text{Cl}^a$	precursor to POSS-terminated polyfluorenes polymers for light-emitting diodes	1079
$\text{-C}_6\text{H}_4\text{-4-CH}_2\text{OC}_6\text{H}_3\text{-2,5-(CH}_2\text{Br)}_2$	luminescent poly(phenylene vinylene) hybrids	354
202	thymine-functionalized polystyrene hybrids	585
$\text{-C}_6\text{H}_4\text{-4-CH}_2\text{Cl}$	polyimide hybrids	586
	luminescent poly(fluorene) hybrids	363
	poly(ether imide) hybrids	901
$\text{-C}_6\text{H}_4\text{-4-CH=CH}_2$	poly(methyl methacrylate-co-*n*-butylacrylate) hybrids	1080
	poly(methyl methacrylate) hybrids	867
	formation of copolymers with styrene	574, 575, 596
$\text{-C}_6\text{H}_4\text{-4-CH}_2\text{OC}_6\text{H}_2\text{-4-Me-2,6-(OMe)}_2$	formation of hybrid poly(phenylene−methylene) polymers	186
$\text{-C}_6\text{H}_4\text{-4-CH=CHFc}$	magnetic polystyrene hybrids	187, 353
$\text{-C}_6\text{H}_4\text{-4-Cl}$	semiconducting poly(fluorene) hybrids	677, 678
$\text{-OSiMe}_2\text{H}$	luminescent poly(fluorene) hybrids	281
	DGEBA-based hybrids	824
	phosphorescent POSS-based materials containing anchored iridium complexes	401
87	polystyrene hybrids	356, 846
$\text{-OSiMe}_2(\text{CH}_2)_3\text{NCO}$	polyurethane hybrid adhesives	709
	poly(styrene−isoprene) hybrids	903
	polystyrene hybrids	356, 595
	epoxy hybrid adhesives	811
42	poly(fluorene) hybrids	279
161	component in rubbery networks containing poly(oxypropylene)diamine and diglycidyl ether of bisphenol A	1081
$\text{-OSiMe}_2(\text{CH}_2)_3\text{OC}_6\text{H}_2\text{-2,5-(CH}_2\text{Cl)}_2\text{-4-OMe}$	luminescent poly(phenylene vinylene) hybrids	278
$\text{-OSiMe(C}_6\text{H}_4\text{-4-OCF=CF}_2)_2$	fluorinated hybrid polymers	301

[a] Contains multiple isomers.

4.3.4. Homogeneous Catalyst Systems

The phosphite compound, **86**, containing a POSS substituent, forms the platinum bis-T_8 complex **149**.[355] This complex and a rhodium complex of **86** have been tested for the catalyzed hydroformylation of 1-octene. The results suggested that this ligand has potential in this area of catalysis, because its complexes showed better performance than some other electron-withdrawing monophosphite species such as $P(OCH_2CF_3)_3$, although its performance was not as good as the related 2,4,8,10-tetra-*tert*-butyl-6-phenoxydibenzo[*d,f*][1,3,2]dioxaphosphepine.

Other phosphorus-containing POSS derivatives have also been used in catalyst systems. Three POSS phosphines, $T_8(CH_2CH_2PPh_2)_8$, $T_8[CH_2CH_2SiMe(CH_2PPh_2)_2]_8$, and $T_8\{CH_2CH_2SiMe[(CH_2)_2PPh_2]_2\}_8$, have been tested as ligands in the palladium-catalyzed methoxycarbonylation of ethene.[1094] The three POSS compounds were seen to lead to different ratios of methyl propanoate to polyketone depending on the spacing of the phosphines from the adjacent silicon atoms and hence their likelihood of being able to chelate to the palladium.

A POSS-based compound bearing a single pyridyl function on one corner, **204** (Chart 46), was prepared from $T_8(c\text{-}C_5H_9)_7OH$ and used in the aerobic Pd-catalyzed oxidation of benzylic alcohols into benzaldehydes.[303] The POSS species behaved well as a catalyst, producing a high turnover, and with the presence of the POSS portion of the molecule apparently suppressing the precipitation of Pd(0) species.

A quite different series of catalysts with a dendrimeric structure terminated by a titanium-alkoxy group such as $Ti(O\text{-}i\text{-}Pr)_3$ have been prepared and patented, showing the catalytic effect of dendrimeric and other bulky ligands.[320] These catalysts include $T_8\{(CH_2)_2Si[(CH_2)_3OTi(O\text{-}i\text{-}Pr)_3]\}_8$ and compounds prepared from phosphonate-containing POSS species, which, although not fully characterized, were thought to include $T_8[(CH_2)_2P(=O)(\mu\text{-}O)_2Ti(O\text{-}i\text{-}Pr)_2]_8$, $T_8[(CH_2)_2SiMe_2$-

Table 33. Nanocomposites and Polymeric Materials Formed Involving Miscellaneous T_8R_7R' Precursors

substituents or compound number			
R	R′	applications	refs
-H	-*i*-Bu	polymers for ophthalmic devices	954
-H	-$CH{=}CH_2$	polymers for ophthalmic devices	954
-H	-*n*-C_9H_{19}	theoretical study on self-assembly to give nanostructures	442, 443
9		poly(norbornene) hybrids	1059
		POSS-substituted ethylene−propylene thermoplastic elastomers	189
-Et	-$(CH_2)_3OCH_2CH(O)CH_2$	nanocomposites with poly(propylene oxide)	1057
-$CH{=}CH_2$	-$(CH_2)_3OCH_2CH(OH)CH_2OH$	component of POSS mixture for surface modification of biomaterial polyurethane	684
-*i*-Pr	-$OSiMe(C_6H_4\text{-}4\text{-}OCF{=}CF_2)_2$	low surface energy copolymers	301
-CH_2CMe_2-*i*-Bu	-$(CH_2)_3OCH_2CH(O)CH_2$	epoxy hybrids	264, 790, 847
-$(CH_2)_2CF_3$	-$(CH_2)_2OC({=}O)CMe_2Br$	fluorinated poly(methacrylate)-based hybrids	174
-$(CH_2)_2CF_3$	-$(CH_2)_2OC({=}O)C_6H_4\text{-}3,5\text{-}(NH_2)_2$	various hybrids with low dielectric constants	1082
-$(CH_2)_2CF_3$	-$(CH_2)_2SiCl_3$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2CF_3$	-$CH{=}CH_2$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2CF_3$	-$(CH_2)_3N_3$	formation of POSS-terminated polyrotaxanes	177
-$(CH_2)_2CF_3$	-$(CH_2)_3OH$	formation of POSS-end-capped poly(ε-caprolactone) for embedding in epoxy resin to form nanocomposites	176
-$(CH_2)_2CF_3$	-$(CH_2)_3OC({=}O)Me{=}CH_2$	fluorinated hybrids for transparent films	175, 1084, 1085
		copolymer with *N*-dodecylacrylamide for preparation of ultrathin films	553, 1086
		precursor to release films	1087
		in resin compositions for surface modifiers	1088, 1089
		as component in compositions for nanoimprinting	1090
		as component in films and release paper	1091
		in films for improving adhesion of inks	1092
		precursor to copolymers useful as films and coatings	1085
-$(CH_2)_2CF_3$	-$(CH_2)_3OCH_2CH(O)CH_2$	preparation of poly(ethylene imine) hybrids	172
-$(CH_2)_2CF_3$	-$(CH_2)_3SiCl_3$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2CF_3$	-$(CH_2)_4CH{=}CH_2$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2CF_3$	-$(CH_2)_6SiCl_3$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2CF_3$	-$C_6H_4\text{-}4\text{-}OCF{=}CF_2$	fluorinated hybrids	178
-$(CH_2)_2(CF_2)_3CF_3$	-$(CH_2)_2SiCl_3$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2(CF_2)_3CF_3$	-$CH{=}CH_2$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2(CF_2)_3CF_3$	-$(CH_2)_3OC({=}O)C({=}CH_2)Me$	fluorinated polymer hybrids as coupling agent for coatings	175
-$(CH_2)_2(CF_2)_3CF_3$	-$(CH_2)_3SiCl_3$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2(CF_2)_3CF_3$	-$CH_2CH{=}CH_2$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2(CF_2)_3CF_3$	-$(CH_2)_3CH{=}CH_2$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2(CF_2)_3CF_3$	-$(CH_2)_6SiCl_3$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2(CF_2)_5CF_3$	-$(CH_2)_2SiCl_3$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2(CF_2)_5CF_3$	-$CH{=}CH_2$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2(CF_2)_5CF_3$	-$CH_2CH{=}CH_2$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-$(CH_2)_2(CF_2)_5CF_3$	-$(CH_2)_6SiCl_3$	fluorinated polymer hybrids used as coupling agent for coatings	275, 1083
-*c*-C_6H_9	-$(CH_2)_3SiMe_2C_6H_4\text{-}4\text{-}SiMe_2H$	styrene−butadiene−styrene hybrid copolymers	184
-*c*-C_5H_5	-$C_6H_4\text{-}4\text{-}CH_2Cl$	low-dielectric constant polyimide films	586
203		molecular dynamic simulations on the preparation of nanohybrid materials	762
-Cy	-$(CH_2)_3O(C{=}O)C({=}CH_2)Me$	synthesis of elastomer nanocomposites by copolymerization with 2-ethylhexyl acrylate and divinylbenzene	718
-Cy	-$(CH_2)_3SiMe_2C_6H_4\text{-}4\text{-}SiMe_2H$	styrene−butadiene−styrene copolymer hybrids	184
-Cy	-$C_6H_4\text{-}4\text{-}CH{=}CH_2$	formation of copolymers with styrene	575
-Cy	-$OSiMe_2(CH_2)_3NCO$	poly(ethylene glycol) hybrids	734
		poly(vinyl alcohol) with pendant POSS groups	759
-Cy	-Cl	poly(phenylene vinylene)-based hybrids	872
i-Oct	-$(CH_2)_3NH_2$	POSS/poly(ethylene terephthalate) nanocomposites with improved mechanical properties	795, 978
		surface modification of montmorillonite clay	863
i-Oct	-$(CH_2)_3OC({=}O)C({=}CH_2)Me$	POSS-substituted fluoroelastomers	566
13		POSS-substituted ethylene−propylene thermoplastic elastomers	189
-Ph	-$(CH_2)_2C_6H_4\text{-}4\text{-}SO_2Cl$	initiator and component of polystyrene and poly(methyl methacrylate) hybrids	191
-Ph	-$(CH_2)_2OC({=}O)CMe_2Br$	initiator and component of polystyrene and poly(methyl methacrylate) hybrids	191
-Ph	-$(CH_2)_3OH$	poly(caprolactone) hybrids for supramolecular chemistry	192
-Ph	-$(CH_2)_3OC({=}O)C({=}CH_2)Me$	copolymer with poly(*N*-dodecylacrylamide) as precursor to ultrathin SiO_2 films	553, 719
		POSS-substituted fluoroelastomers	566
		nanocomposite photoresists derived from POSS, 4-hydroxy styrene. and *tert*-butyl methacrylate precursors	851
-OEt	-$(CH_2)_2C({=}O)O(CH_2)_{17}CH_3$	hydrolysis to give mesoporous materials	271
-OEt	-$(CH_2)_nCH_3$ (n = 15, 17, or 19)	mesostructured siloxane−organic hybrids and mesoporous silica	272

Table 34. Nanocomposites and Polymeric Materials Formed Involving $T_8R_{(8-n)}R'_n$ Precursors

	substituents or compound number			
n	R	R′	applications	refs
0−8	-Me	-$(CH_2)_3OCH_2CH(O)CH_2$	nanocomposite formation with bisphenol A epoxy resin	151
2.4	-CH=CH_2	-$(CH_2)_2Si(OEt)_3$	supermicroporous silica precursor	286
2	-CH=CH_2	-$(CH_2)_3OCH_2CH(OH)CH_2OH$	component of POSS mixture for surface modification of biomaterial polyurethane	684
2	-*i*-Oct	-$(CH_2)_3NHC(=O)NH(CH_2)_3Si(OEt)_3$	hydrolyzed to give corrosion-inhibiting coating on Al alloy	149
	47		component of dental nanocomposites	254
	48		component of dental nanocomposites	254
4	-$C_6H_4SO_3H$	Ph	component in Nafion reinforced proton-exchange membrane	315
4	-$OSiMe_2(CH_2)_3OCF_2$=CHF	-$OSiMe_2(CH_2)_3OCHCH(O)CH_2$	poly(imides) with low dielectric constant	292

Chart 43

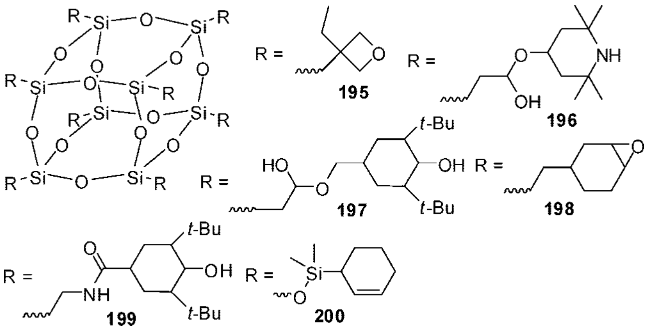


Chart 44

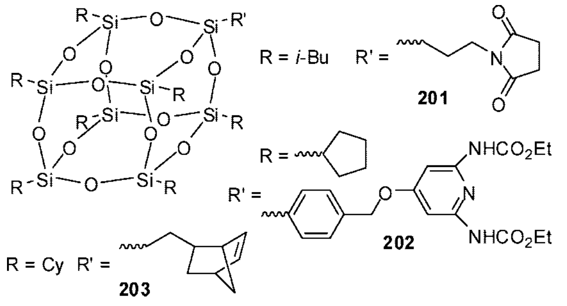


Chart 45

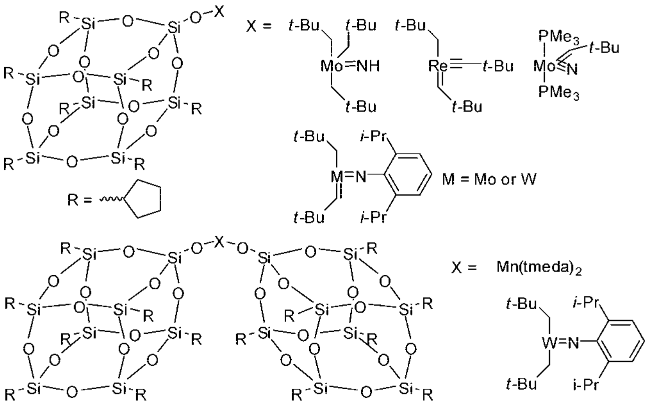


Chart 46

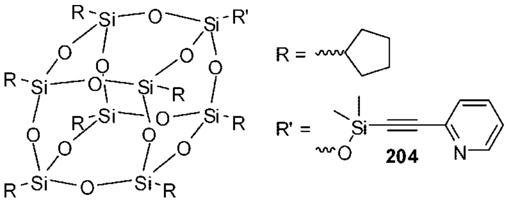


Chart 47

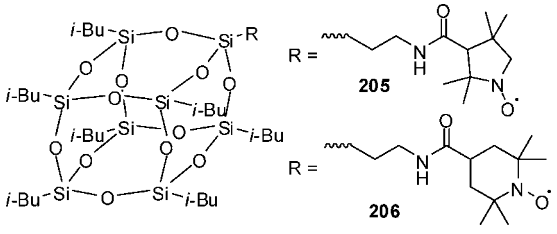
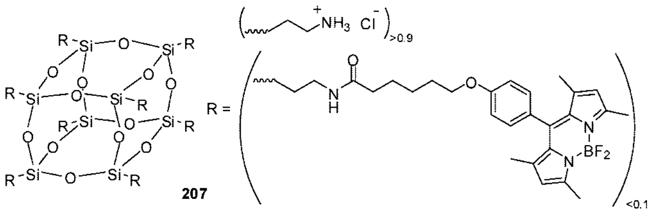


Chart 48



$(CH_2)_3OTi(O\text{-}i\text{-}Pr)_3]_8$, and $T_8\{(CH_2)_2Si[(CH_2)_3OTi(O\text{-}i\text{-}Pr)_3]_3\}_8$ or alternatively species with titanium cross-linking between POSS.[320] The basis of the dendrimeric complexes are a previously reported series of dendrimeric POSS compounds, prepared by a series of hydrophosphonation or hydrosilylation reactions from $T_8[CH=CH_2]_8$.[1095−1097]

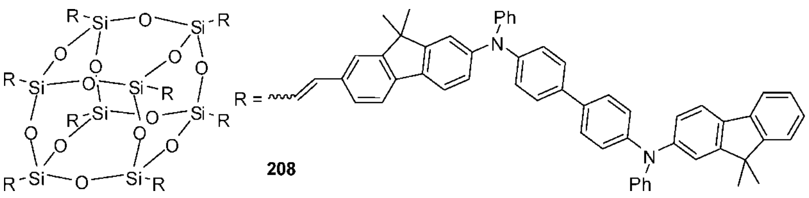
A few POSS compounds have also been used as catalyst systems without the presence of additional transition metals. A number of functionalized POSS derivatives containing either tetramethylpiperidine- or tetramethylpyrrolidine-*N*-oxide, **205** and **206** (Chart 47), have been prepared and also patented for the aerobic oxidation of compounds such as cumene or other hydrocarbons to their hydroperoxides.[93]

4.4. Other Applications for POSS Derivatives

4.4.1. Biomaterials

The biocompatibility of many silicon-based materials has prompted investigations into the applications of POSS derivatives in the field of biomaterials chemistry. Recently, $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ has been partially functionalized with a succinimidyl ester derivative of a BODIPY (boron dipyrromethane) dye to form a potential drug delivery system, **207** (Chart 48).[682] The presence of the BODIPY function gave fluorescent properties to the molecule, the remaining ammonium groups allowing its solubility in aqueous media, thereby favoring cellular uptake by diffusion. Results showed localization of the fluorescent species in the cytosol of the cells and also that the POSS−BODIPY species showed little cellular toxicity.

Chart 49



208

When treated with catechin in the presence of the *Myceliophthora* laccase, $T_8[(CH_2)_3NH_2]_8$ formed polyphenol hybrids encapsulating the enzymes. These systems showed increased reactivity for superoxide anion (O_2^-) generation with oxidase systems, in comparison to the catechin without the POSS species.[1098] A series of $\{T_8[(CH_2)_3Cl]_{(8-n)}[(CH_2)_3NMe_2Oct]_n\}Cl_n$ derivatives have been prepared from $T_8[(CH_2)_3Cl]_8$ and $NMe_2C_8H_{17}$ and tested for their antibacterial behavior, resulting from the presence of the quaternary ammonium groups, against both Gram-positive and Gram-negative bacteria; they are less effective against the Gram-negative than Gram-positive bacteria.[117] For example, minimum inhibitory concentrations of 8 and 62.5 μg mL^{-1} could be achieved for activity against *Staphylococcus aureus* and *Escherichia coli*, respectively. Silsesquioxane cages have also been used to form conjugates with polylactides for use as biocompatible materials.[1099] The POSS derivative $T_8[OSiMe_2(CH_2)_3NMe_2]_8$ has also been tested for its antimicrobial activity, following partial quaternization with alkyl iodides such as n-$C_{12}H_{25}I$ and n-$C_{18}H_{37}I$. The resulting products were found to be suitable for use as antimicrobial coatings.[240]

POSS derivatives with appropriate substituents have been seen to interact with specific biomolecules. The binding affinity of a phage library of peptides to silicone surfaces was evaluated by exposing them to POSS species such as T_8H_8, T_8Me_8, and T_8Ph_8, acting as silicone surface models.[1100,1101] Differences in the binding selectivity were observed depending on the pendant group of the POSS cage; T_8Me_8 and T_8Ph_8 bind strongly but nonspecifically via the protein coat of the phage, while T_8H_8 and $T_8[(CH_2)_2CF_3)]_8$ are bound specifically by the phages. In a study on more specific interactions with biological systems, a cationic imidazolium-functionalized POSS, **83**, was found to induce a mesophase transition from a lamellar phase, formed by complexes of DNA with cationic lipids, to an inverted hexagonal phase of lipoplexes on binding of this POSS compound to double-stranded DNA. The corresponding hybrid materials were thought possibly to be useful as components in bio-organic microelectronics.[348,745]

Nanocomposites of POSS−poly(carbonate-urea)urethane containing $T_8(i\text{-}Bu)_7$ pendant groups have greater thromboresistance than either poly(carbonate-urea)urethane or PTFE and so may be useful materials for bypass grafts or microvessels.[621] The problems of shrinkage and leaching of monomer from dental nanocomposites has led to study of acrylate-based POSS composite resins for use as such materials.[44,141,258,866] See section 3.15 for a further description of POSS interactions with biological systems.

4.4.2. Molecular Optics and Electrical Systems

Numerous examples of the application of POSS molecules or materials have been published in the fields of optics and electronics. For example, a series of polyaromatic substituted POSS, **64**−**67**, were prepared from $T_8(CH{=}CH_2)_8$ through Heck coupling. They were shown both to be photoluminescent and to have charge transport abilities.[323,324] Another photoluminescent POSS compound, **17**, having a carbazole-based substituent, has been prepared from $T_8(OSiMe_2H)_8$. It has been shown that the presence of the POSS core did not affect the electronic properties inherent to the carbazole species.[233–235] The photoluminescence of products has additionally been used to analyze the purity of potentially photoluminescent POSS compounds, such as $T_8[CH{=}CHC_6H_4\text{-}4\text{-}C_6H_3\text{-}3,5\text{-}(CO_2Me)_2]_8$ and $T_8[CH{=}CHC_6H_4\text{-}4\text{-}C_6H_3\text{-}3,4\text{-}(OMe)_2]_8$.[387]

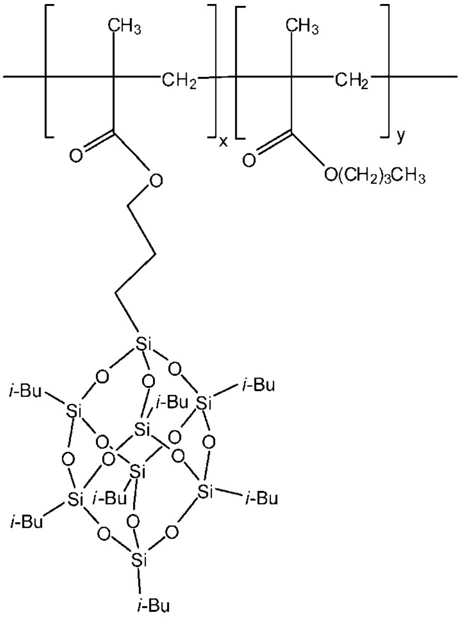
A POSS species has been used in the preparation of a material reported to show quantum dot-like properties, but this has not yet been followed up by more comprehensive studies.[313,672] Two derivatives with multiaryl functional groups, **164** and **165**, were seen to behave in the same manner in the solid state as inorganic quantum dot materials, including showing the necessary quantum confinement effect. The cubic T_8 core of the materials appears to isolate the organic arms of the molecule sufficiently from each other to attain quantum confinement.

The POSS compound $T_8(CH_2SiMe_2C_6H_4\text{-}4\text{-}NPh_2)_8$ is one example of a series prepared for use in organic light-emitting diodes (OLEDs), the preparation of which has been patented.[287] The POSS materials are included in the devices in a carrier transport layer intercalated between the two electrodes and the light-emitting layer of the system. In these devices, the POSS component controlled the transport of electrons and holes. Improvements in brightness and efficiency were claimed over devices made without the POSS species. A compound with somewhat similar functional groups, **208**, has been prepared by Heck coupling for use as an electroluminescent film precursor for OLED applications (Chart 49).[667] The material showed a significant improvement over the parent molecular counterparts in these applications.

The POSS−pyrene derivatives **67** and **88** have also been tried for application in OLED technology as the light-emitting portion of an OLED device.[325] The POSS species in this application were able to be applied by spin-coating onto glass substrates, potentially offering an advantage over other systems, which require vacuum deposition or have possible problems with purity. Initial results suggested that these materials showed promise, although synthetic modification would likely be required. Other POSS with chromophore substituents (**21**, **23**, and **29**) have also been prepared and showed good film-forming and luminescence properties.[248,262] They have been used as emitting material in double-layer OLEDS[262] or deposited on quartz or indium tin oxide plates for use as electroluminescent nanoparticles.[248]

In addition, simpler POSS derivatives have been used in materials where they do not contribute directly to the electrical or luminescent properties, although their presence results in changes in behavior of the systems. For instance, $\{T_8[(CH_2)_3NH_3]_8\}Cl_8$ has been introduced into photoluminescent materials to pack between poly(electrolyte) multilayers and thereby stop the diffusion of the quantum dot

Chart 50



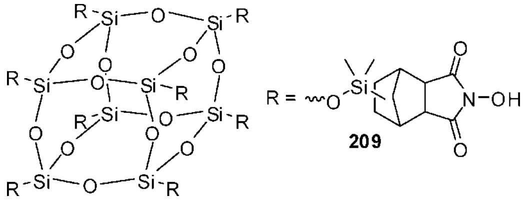
materials into the film.[1102] In an electrochemical system, thermolysis of $T_8(OSiMe_2H)_8$ in pyridine afforded a three-dimensional network where the POSS units are linked through -$OSiMe_2O$- bridges. Adsorption of toluidine blue O, a phenothiazine stain and electrochemical mediator, into the cross-linked POSS species gave a material that showed redox behavior by square-wave voltammetry.[237] The synthesis of Si-based phthalocyanines with $[T_8(c\text{-}C_5H_9)_7O]^-$ groups as axial ligands (**145** and **147**) has been reported.[406] Comparison of the properties of these derivatives to a varied set of related phthalocyanines having various axial ligands or peripheral substitutions showed the importance of the steric hindrance in the photo- and electrochemical properties of the molecules.

In a different area of electrochemistry, nonaqueous electrolysis solutions have been prepared containing POSS compounds that include ion-conductive organic groups, such as PEO. The PEO−POSS derivatives $T_8\{(CH_2)_3[O(CH_2)_2]_nOMe\}_8$ and $T_8\{OSiMe_2(CH_2)_3[O(CH_2)_2]_nOMe\}_8$ were found to give electrolyte materials with improved chemical and thermal stabilities in the presence of lithium salts.[1103] In addition, $T_8\{OSiMe_2(CH_2)_3[O(CH_2)_2]_nOMe\}_8$ ($n = 4-8$) has been used to prepare lithium-based electrolytes both with[255,257] and without[252] blending with PEO, with in some cases a greater conductivity observed than that for pure PEO. The compound $T_8[OSiMe_2(CH_2)_3CN]_8$ has been treated with $Na_2[Fe(CN)_5NH_3]$ to form a composite material[238] that has been incorporated into a carbon paste electrode and used for preliminary electrochemical studies.

A hybrid butyl methacrylate copolymer with pendant POSS units (Chart 50) has been used to prepare amperometric chemical sensors that give a good response to water vapor for humidity sensing. The phenomenon is explained in terms of a resonant charge transfer within POSS cages enhanced by the presence of water.[680]

Recently, a series of metallophthalocyanine complexes substituted with $T_8(i\text{-}Bu)_7(CH_2)_3S$- units were prepared, and their optical properties were assessed.[360,1104] Here the advantage of having POSS substituents is to increase the solubility of the phthalocyanine complexes by preventing their aggregation. Complexes with Cu(II) coordinated to the phthalocyanine showed very high nonlinear absorption and could be used for optical limiting applications. A series of POSS $T_8(i\text{-}Bu)_7R$ compounds, **76−84**, which showed a change in their wavelength of fluorescence emission in response to their chemical environment, have been prepared from $T_8(i\text{-}Bu)_7(CH_2)_3SH$ or $T_8(i\text{-}Bu)_7(CH_2)_3NH_2$.[346] For further applications of POSS compounds in materials with useful optical and electrical properties, see section 4.2.3.

Chart 51


209

4.4.3. POSS Deposition and Coatings

Derivatives of POSS species have been used as components in coatings for a variety of uses, ranging from lithography to insulating layers. The POSS species **209**, shown in Chart 51, is an example of compounds patented for a use as nonpolymeric topcoats for photoresists in immersion lithography systems.[1105] Here the hydrophobic character of the POSS prevents the dissolution of the photoresist in the immersion film of the prepared devices by preventing the resist and film from interacting and thereby limits their degradation. For further applications of POSS compounds in coatings and films, see section 4.2.3.

Insulating materials with low dielectric constant have been prepared by spin-coating onto a silicon substrate a solution of a POSS derivative having hydrolyzable alkoxy groups, such as $T_8[(CH_2)_2Si(OEt)_3]_8$, $T_8[OSiMe_2(CH_2)_2Si(OEt)_3]_8$, or $T_8[OSiMe_2(CH_2)_2SiMe(OEt)_2]_8$.[1106] Other POSS derivatives have been deposited onto various surfaces, and their properties have been studied using a variety of techniques. Polycrystalline films of $T_8(OSiMe_3)_8$ were prepared by chemical vapor deposition on supports, such as silicon surfaces or quartz plates.[550,551] X-ray diffraction and Raman spectroscopy showed that the polycrystals are oriented in one crystallographic direction. $T_8(c\text{-}C_5H_9)_7(CH_2)_2COMe$ has been deposited by spin-coating onto silicon wafers. The hardness and elastic modulus of the resulting POSS films after irradiation were assessed using the nanoindentation technique.[732] A process concerning the covering of poly(olefin) surfaces using POSS compounds has been described, allowing an easier use or processing of the resulting materials.[974]

T_8H_8 and $T_8H_7(n\text{-}_6H_{13})$ have been successively chemisorbed onto Au(111) surfaces by vacuum deposition through Si−H activation as previously reported.[1107] More recent scanning tunneling microscopy studies of these same surfaces showed that a composite monolayer surface formed with well-defined domain regions of the individual components.[600,601] This composite layer was found to act as a chemical imaging agent for the gold surface.

Scanning tunneling microscopy has been also used to study the interaction of T_8H_8 on highly oriented pyrolytic graphite.[441] The resulting images showed two different ordered monolayers of the T_8 cubes, one where the face of the cube is in contact with the surface and the second one with the cube adopting a tilted orientation. In both cases, the POSS species were physisorbed onto the surface, rather than being chemisorbed. The reactivity of T_8H_8 with two different Si surfaces, Si(110)-2 × 1 and Si(111)-7 × 7, was studied using microscopy and spectroscopy experiments. On the Si(110) surface, chemisorption via single vertices was observed, whereas it was shown that the POSS undergoes decomposition in the case of the Si(111) surface.[599,602]

Carbon nanotubes of different diameters (1−3 nm) have been filled with T_8H_8 by heat-vacuum deposition or using supercritical carbon dioxide.[603] It has been shown that the interaction of the POSS molecules with the nanotubes depends on the diameter of the latter. If the nanotubes were too large, only a weak interaction was observed and the POSS molecules were not retained in the nanotubes. If they slightly exceeded the size of the POSS, efficient electrostatic interactions were present, holding them in place. However, if the nanotube diameter was close to the size of the POSS, a pressure was exerted on the adsorbate. T_8H_8 may also be encapsulated in single- and double-walled nanotubes using solution and ultrasonic methods.[604] When the nanotube diameters were 1.14−1.31 or 1.15−1.37 nm for single- and double-walled nanotubes, respectively, HR-TEM images showed that the T_8H_8 had reacted to form a double-ladder polymeric species, $Si_{4n}O_{8n-4}H_8$. A disordered structure of discrete T_8H_8 molecules was seen in nanotubes of greater diameter than this. Another study involving carbon nanotubes was recently reported, where multiwalled carbon nanotubes having acid chloride groups were functionalized by the external grafting of $T_8[(CH_2)_3NH_2]_8$ via amide linkages.[622] The resulting materials were blended with poly(lactic acid) with a better dispersion in the matrix due to the presence of the POSS components.

As well as acting as a component in composite materials, T_8Me_8 has also been used as a surface-treatment agent to good effect. Its use as a coating for carbon fibers to improve surface roughness and interface adhesiveness, while retaining the mechanical strength of the carbon fibers, has been described.[956] Additionally, general applications in the formation of surfaces with desired properties such as hydrophobicity, abrasion, and self-cleaning,[1108] as well as their use in low-dielectric constant films,[1109,1110] have been patented. Another use for POSS derivatives in coatings can be as a porogen. $T_8\{(CH_2)_3OC({=}O)(CH_2)_2N[(CH_2)_3NMe_2](CH_2)_2CO_2(CH_2)_2NMe_2\}_8$ has been used as a sacrificial porogen in the preparation of nanoporous poly(methyl silsesquioxane) films.[396]

4.4.4. Varnishes

A varnish is, in its simplest form, a formulation of a polymer and a solvent. For liquid crystal device applications, varnishes are used for forming liquid crystal alignment layers. Such layers normally comprise organic or inorganic polymers such as silicon dioxide, which show high heat and light resistance. In the case of silicon dioxide, a drawback is its hygroscopic character, because water can cause damage to the device. The use of T_8 POSS compounds with organic arms has been reported as additives to varnishes to replace silicon dioxide, in order to minimize the hygroscopic properties of the material. For example, the POSS compounds $T_8Cy_7(CH_2)_3SH$, $T_8Cy_7(CH_2)_3OC({=}O)C({=}CH_2)Me$, $T_8(i\text{-Bu})_7(CH_2)_3CN$, $T_8(i\text{-Bu})_7(CH_2)_3NH_2$, $T_8(i\text{-Bu})_7(CH_2)_3OCH_2CH(OH)CH_2OH$, $T_8Ph_7(n\text{-Pr})$, $T_8Ph_7(CH_2)_3O(CH_2)_2OC({=}O)(CH_2)_2COOH$, $T_8Ph_7(CH_2)_3C_6H_3\text{-}3,5\text{-}(NH_2)_2$, and two malonic anhydride POSS derivatives have been added to basic varnish compositions.[1111,1112]

4.4.5. Inks

An ink is a formulation of many components with varying roles to play, depending on the nature of the ink. Thus, specifically functionalized POSS species have been shown to play particular roles in certain inks. For example, $T_8[(CH_2)_2Cl]_8$ has been used as a leveling agent in ink compositions to help the formation of insulating thin films[1113] and $T_8(i\text{-Bu})_7(CH_2)_2Si(OEt)_3$ has been used as an additive in both inks and other coatings to improve properties such as hydrophobicity, abrasion, or self-cleaning characteristics.[1108]

5. Conclusions

The rapid growth in the number of publications concerning POSS compounds and their applications continues. This is especially true for the patent literature; this seems due to the relatively well understood routes to simple POSS compounds and the commercial availability of a range of POSS precursors to polymeric materials. The fundamental nature of the POSS T_8 cage, having high symmetry, good chemical and thermal stability and ready manipulation of the substituents at the corners of the cage, mean that novel compounds and new materials derived from them are usually readily prepared. Thus, applications of POSS-containing materials in areas such as medical polymers, high-temperature composites, dendrimers, liquid crystals, and coatings for spacecraft continue to be explored, and many new applications can be anticipated. Perhaps the main synthetic challenges remaining to the synthesis of simple POSS compounds are a simple high-yield route to T_8H_8, and the precise control of the substitution pattern of different substituents around a POSS cage, for example, in isomers of $T_8R_4R'_4$. If these challenges can be met, then even more rapid growth in this exciting field can be foreseen.

6. Definitions

AIBN	2,2′-azobisisobutyronitrile
BLDCH	$N_\alpha N_\varepsilon$-di-(t-BOC)$_2$-L-Lys dicyclohexylammonium salt
t-BOC	*t*-butyloxycarbonyl
COMPASS	condensed-phase optimized molecular potentials of atomistic simulation studies
Cp*	pentamethylcyclopentadienyl
Cp″	1,3-bis(trimethylsilyl)cyclopentadienyl
dba	dibenzylideneacetone
DCC	1,3-dicyclohexylcarbodiimide
dcp	dicyclopentadiene
DGEBA	diglycidyl ether of bisphenol A
DMAP	4-dimethylaminopyridine
DMPI	1,1-dimethylpiperidinium
DPTS	4-dimethylaminopyridinium 4-toluenesulfonate
dvs	divinyltetramethyldisiloxane
Fc	ferrocenyl
GED	gas electron diffraction
HBTU	2-(1*H*-benzotriazole-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate
HDPE	high-density polyethylene
HOBT	1-hydroxybenzotriazole hydrate
HV	Vickers hardness
LB	Langmuir−Blodgett
MCPBA	*meta*-chloroperoxybenzoic acid
MM3	molecular mechanics force field 3
Oct	octyl
OLED	organic light-emitting diode
PGMEA	propylene glycol methyl ether acetate

POSS	polyhedral oligosilsesquioxane
RAIRS	reflection−absorption infrared spectroscopy
RHF	restricted Hartree−Fock
sixantphos	bis-4,6-diphenylphosphino-10,10-dimethylphenoxasilin
Tf	trifluoromethylsulfonyl
TMEDA	tetramethylethylenediamine

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