Cyclopentadienyl-functionalised polyhedral silsesquioxanes as building blocks for new nanostructured materials

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Abstract

This work is to design new organosilicon precursors, which contain both siloxane and cyclopentadienyl functionalities and use these compounds as building blocks for new nanomaterials. Polyhedral silsesquioxanes, $(RSiO_{1.5})_n$ ($n = 8$ and 10) with cyclopentadienyl (R = $-C_5H_5$ or $-(CH_2)_3-C_5H_5$) functionalities have been prepared by hydrolytic condensation of the correspondent silicon organic precursors $RSiCl_3$ or $RSi(OC_2H_5)_3$. The products with cyclopentadienyl groups have been used to prepare new cross-linked 3D polymeric materials by Diels–Alder reaction. The compounds have been characterised by multinuclear (^1H and ^{29}Si) NMR, ESI MS and IR spectroscopy, UV/Vis spectrometry, gel permeation chromatography and scanning electron microscopy. The approach above seems to be very promising for the preparation of new nanostructured materials.
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1. Introduction

Controlled pore inorganic and organic solids play a key role in modern chemical technology as heterogeneous catalysts, adsorbents, porous membranes, and as a host-matrix for pharmacology, bio- and nanotechnology. Although over the last decade there has been some progress in the development of new porous materials, there exists an unsatisfied demand for new still better materials. Polyhedral silsesquioxanes $(RSiO_{1.5})_n$ ($n = 6$, 8, 10, etc.) are very promising as building blocks for new materials with controlled pore size. Several silsesquioxane-based approaches to polymeric materials have been reported [1,2]. Most of these approaches are based on the reactivity of the silanol groups, which enable the preparation of polymers through the formation of bridging siloxane units [1].

The main objective of our work is to develop new cyclopentadienyl–silsesquioxane hybrids as building blocks for new nanoporous materials. These materials would combine advantages of both the cyclopentadienyl- and the siloxane – functions in one.

It is well known that cyclopentadienyls are among the most important ligands in metallorganic chemistry, because they form a wide range of stable complexes whose steric and electronic properties can be easily tailored by varying the ring substituents. The η^5-cyclopentadienyl transition metal derivatives have played an important role in structural, synthetic and catalytic chemistry. They have found applications in many areas such as reagents in organic chemistry, as Ziegler–Natta catalysts and even as cancerostatic compounds [3].

Thus the introduction of cyclopentadienyl–siloxane hybrids, could open up fundamental new approaches in both siloxane and cyclopentadienyl chemistry. However, there are a number of serious problems in the preparation of these materials. The Cp-fragment has been found to be quite sensitive to temperature (e.g. dimerisation)

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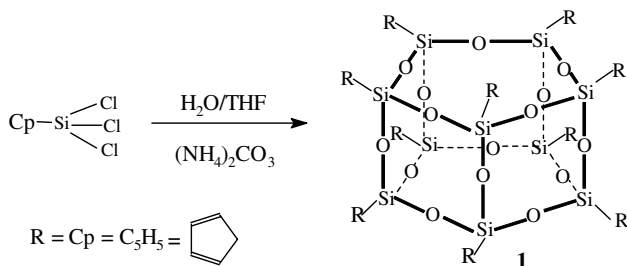*E-mail addresses:* bentma@tcd.ie (M. Bent), igounko@TCD.IE (Y. Gun'ko).

and to other conditions (e.g. acids). This makes the work with Cp-functionalised siloxanes very difficult and challenging. There are only a few publications on the immobilisation of substituted Cp-ligands on siloxanes and polysiloxanes [4,5].

Here we report a development of new cyclopentadienyl-functionalised silsesquioxanes and their use for the preparation of new nanostructured polymeric materials.

2. Results and discussion

The main approach for the preparation of the oligosilsesquioxanes is kinetically controlled hydrolysis of the appropriate silicon organic precursors. In this work the precursors have been prepared using standard organometallic approaches. $CpSiCl_3$ was synthesised by the reaction of $SiCl_4$ with NaCp in THF [6]. Hydrolysis of $CpSiCl_3$ in THF in the presence of ammonium carbonate gave the completely condensed oligosilsesquioxane $Cp_{10}Si_{10}O_{15}$ [T_{10}] (1) as a major product (Scheme 1). The compound was characterised by C and H elemental analysis, ^{1}H and ^{29}Si NMR, IR, ES MS spectra. ^{1}H NMR (Fig. 1) has shown very broad peaks of cyclopentadienyl group at 5.71 (H–C=) and 3.22 (H–C–) ppm with an appropriate 4:1 ratio and some residual solvent (THF and Et_2O) peaks. ^{29}Si NMR contained three signals at -71.50, -74.39 and -77.04 ppm. The presence of 3 signals in ^{29}Si NMR can be explained by the different positions of Si substituents in the Cp-rings (Fig. 2). IR spectra of the compound (in KBr) contained characteristic C–H bands and also a very broad band of Si–O–Si stretching with the maximum at 1105 cm^{-1}. The ES MS spectrum has shown a maximum M$^+$ peak of 1170, which is correspondent to $Cp_{10}Si_{10}O_{12}(T_{10})$ fragment. Cryoscopic determination of the molecular weight for 1 in c-hexane gave an average value of 1193 (out of 5 measurements). This is very close to ES MS data considering the experimental error, which might be up to 5% for cryoscopic techniques.

The oligosilsesquioxane 1 was found to be unstable and temperature sensitive. Dimerisation via Diels–Alder reaction of monosubstituted cyclopentadienyl–siloxane
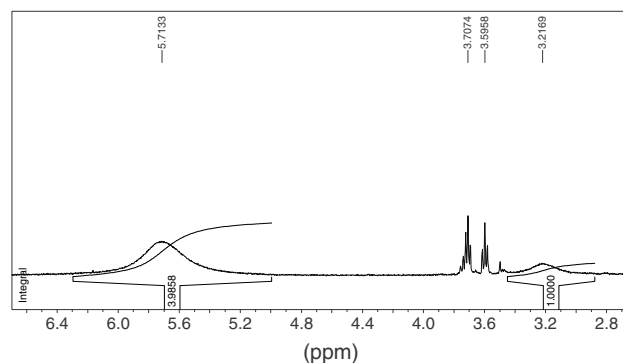

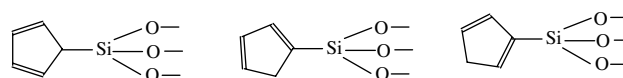Fig. 1. ^{1}H NMR of $Cp_{10}Si_{10}O_{15}$ (1) in CDCl$_3$.

Fig. 2. Possible positions of Si substituents in Cp-rings.

derivatives has been noticed before as an obstacle for the preparation of Cp-functionalised polysiloxanes and gels [5]. In this work we decided to use this property for the preparation of branched silsesquioxane oligomers or dendrimers. The polymerisation of 1 was achieved via the Diels–Alder reaction by stirring the mixture in THF at room temperature and then by heating it under reflux (Scheme 2). The products were studied by ^{1}H and ^{29}Si NMR, IR and MS spectra and gel permeation chromatography (GPC). The ^{1}H NMR spectrum has shown a very broad series of multiplets from 6.65 to 5.45 ppm and from 3.55 to 1.7 ppm attributed to cyclopentadienyl ligands and Diels–Alder adducts. The ^{29}Si NMR spectrum contained a number of signals between -71.50 and -78.73 ppm. The IR spectra of the these products (in KBr) contained characteristic C–H bands at 2962 and 1446 cm^{-1} and also a very strong and broad band of Si–O–Si stretching, with the maximum at 1089 cm^{-1}. The GPC chromatogram shows a broad distribution of molar masses with $M_p = 1335$ g/mol and an average molar mass of the product of $M_w = 2761$ g/mol. The average mass lies between the mass of $(T_{10})_2$ (theoretical mass 2340) and $(T_{10})_3$ (theoretically 3510). The number average molar mass (M_n) is 1859 g/mol. The heterogeneity index M_w/M_n is 1.485.

According to this data the most plausible composition of the material is a mixture of several linked T_{10} oligomers similar to the one shown in Scheme 2. ESI/MS has been shown to be a very good technique in the analysis of functionalised silsesquioxanes [7], certain dendrimers [8] and polymers [9]. ESI TOF MS spectra of our materials were quite informative. The MS spectrum of products has shown several peaks assigned to doubly and triply charged oligomeric species: 1592.5

Scheme 1. Preparation of $Cp_{10}Si_{10}O_{15}$ (1) oligosilsesquioxane.
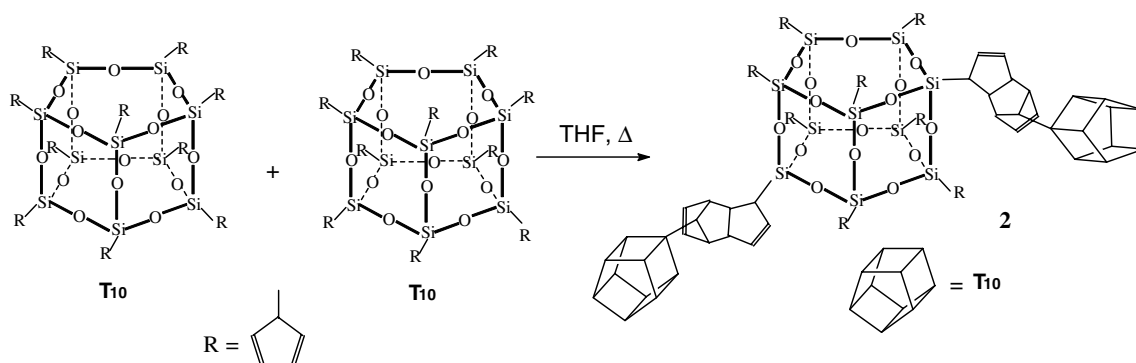
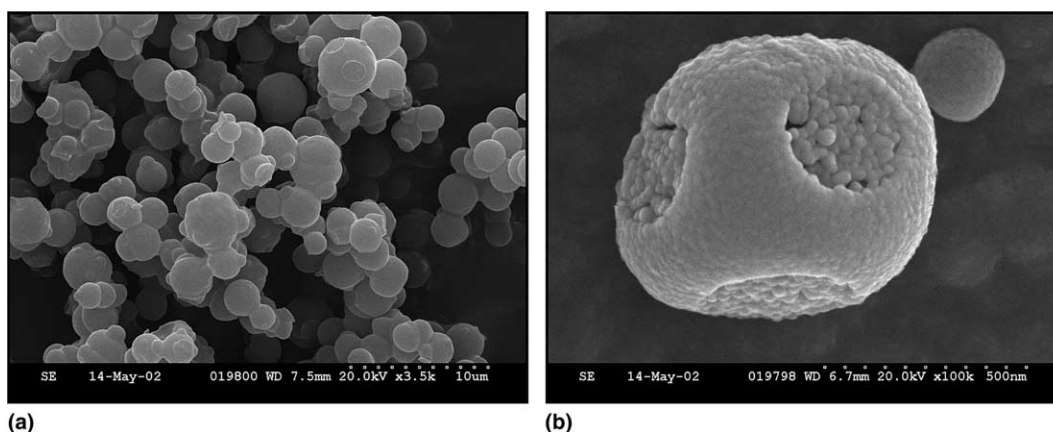Scheme 2. Schematic presentation of polymerisation of $Cp_{10}Si_{10}O_{15}$ fragments via Diels–Alder reaction.

$[(T_{10})_3 - 5Cp]^{2+}$, 1517 $[(T_{10})_4 - 2Cp]^{3+}$, 1451 $[(T_{10})_4 - 5Cp]^{3+}$, 1148.3 $[(T_{10})_3 - Cp]^{3+}$, 1083 $[(T_{10})_3 - 4Cp]^{3+}$, 780 $[(T_{10})_2]^{3+}$. This data demonstrates the clear presence of $(T_{10})_2$, $(T_{10})_3$ and $(T_{10})_4$ oligomers, which is quite consistent with the GPC results. According to these results the degree of polymerisation in the product **2** is not very high ($4T_{10}$ maximum).

The product **2** was also examined by scanning electron microscopy (SEM). As can be clearly seen from Fig. 3 the product consists of spherical or dice-like particles with an average diameter of 3.5 μm. These spheres in turn appear to be composed of even smaller several nanometer-sized spheres as shown in Fig. 3(B). This shape is consistent with the nature of dendritic growth of the monomer units via the Diels–Alder reaction as shown in Scheme 2.

We have also noticed that Cp–Si bond in the $(Cp_{10}Si_{10}O_{12})_n$ oligomers are quite sensitive to acids that lead to Cp-loss. For this reason it was decided to investigate presumably more stable similar systems based on (3-cyclopentadienylpropyl)triethoxysiloxane. (3-Cyclopenta dienylpropyl)triethoxysilane was prepared from (3-chloropropyl)-triethoxysilane and CpNa. The hydrolytic condensation of (3-cyclopentadienylpropyl)-trieth-

oxysilane with water in acetone yielded mostly T_8 silsesquioxane $(CpC_3H_6)_8Si_8O_{12}$ (**3**) (Scheme 3). The compound was characterised by ^1H and ^{29}Si NMR, IR and MS spectra. ^1H NMR spectrum has shown very broad peaks for Cp-ligands from 6.4 to 5.99 ppm and at 3.51 ppm and CH_2 groups from 1.85 to 0.77 ppm. The ^{29}Si NMR contained only a broad signal at -68.51 ppm. IR spectra have shown a very broad band at 1155 cm^{-1} assigned to Si–O–Si vibrations. The MS (ESI TOF) spectrum in CH_3CN contained the $[M]^+$ peak at 1272 and peaks of several fragments formed due to Cp- or CpC_3H_6-elimination. Cryoscopy of **3** in *c*-hexane gave an average molecular weight of 1297 (out of 5 measurements). This value is close to the weight of $(CpC_3H_6)_8Si_8O_{12}$ within the experimental error.

Compound **3** can be easily polymerised by heating via the Diels–Alder reaction in THF giving again soluble and insoluble T_8 based polymers $(CpC_3H_6)_8Si_8O_{12}]_n$ (**4**) (Scheme 4). The products have been characterised by C and H elemental analysis, ^1H and ^{29}Si NMR, IR and MS spectra. ^1H NMR spectra of the soluble compounds in DMSO-d_6 contained very broad peaks of for Cp-ligands from 6.4 to 5.99 ppm, Cp-dimer-ligands

Fig. 3. SEM images of polymeric product **2**.
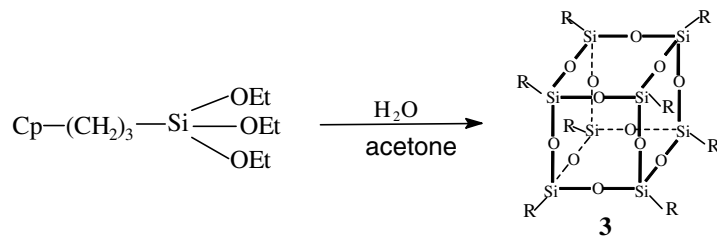
Scheme 3. Synthesis of $(CpC_3H_6)_8Si_8O_{12}$ (**3**) T_8–oligosilsesquioxane (R = CpC_3H_6-).
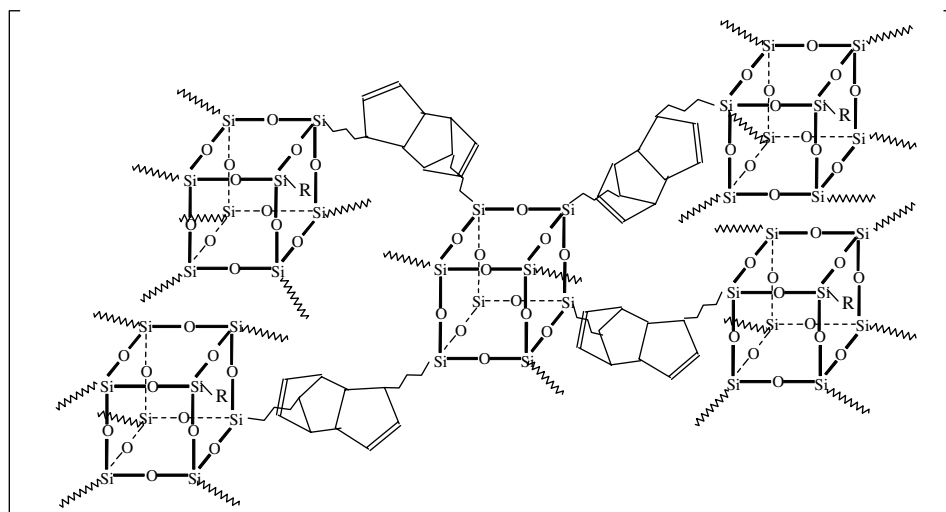
Scheme 4. Schematic presentation of $[(CpC_3H_6)_8Si_8O_{12}]_n$ (**4**).

from 6.61 to 2.17 ppm and broad multiplets of CH_2 groups from 1.85 to 0.77 ppm.

The ^{29}Si NMR spectrum contained a number of signals between -67.88 and -70.04 ppm. The IR spectrum showed a very broad Si–O–Si band at 1142 cm^{-1}. The MS (ESI TOF) spectrum in CH_3CN contained the $[M]^+$ peak at 1272 and peaks of several fragments formed due to Cp- or CpC_3H_6–elimination. GPC showed a very broad distribution of molar masses with $M_p = 1960$ g/mol. The average mass (M_w) of 5156 g/mol is close to that for the $(T_8)_4$ (theoretically 5088) fragment. The number average molar mass (M_n) is 2471 g/mol. The heterogeneity index M_w/M_n of 2.086 is quite high. After the analysis of all data we come to the conclusion that the product is most likely a mixture of polymers based on the linked T_8 fragments with a broad mass distribution and a high heterogeneity. Surprisingly ESI TOF MS spectra of **4** in CH_3CN have shown only peaks characteristic to the monomeric T_8 unit. As can be seen from the SEM images (Fig. 4) this material also is composed of spherical particles (with an average diameter of 4 μm) joined together into branched assemblies.

In conclusion, we have prepared new Cp-functionalised polyhedral silsesquioxanes and have demonstrated their possible application as building blocks for new pol-

ymeric nanostructured materials. These compounds could also be potentially modified into different metal-containing products by metallation of the free C_5H_5-groups. This may open up a fundamentally new approach for the preparation of new controlled pore size metal-containing materials.

3. Experimental

3.1. General procedures

Trichloro-cyclopenta-2,4-dienyl-silane ($CpSiCl_3$) was prepared from $SiCl_4$ and CpNa according to published procedure [6]. (3-Chloropropyl) triethoxysilane was obtained from Aldrich. All manipulations on the preparation and handling of trichloro-cyclopenta-2,4-dienyl-silane and (3-cyclopenta dienyl propyl)-triethoxysilane were carried out under vacuum or argon by Schlenk techniques. Solvents were dried and distilled over sodium–potassium alloy under argon prior to use and then condensed into a reaction flask under vacuum shortly before use. GPC was performed with a Waters 600 E differential spectrometer provided with 7.810 mm styragel columns HT3 (500–3000 Å), HT5 (50000–4106 Å) and
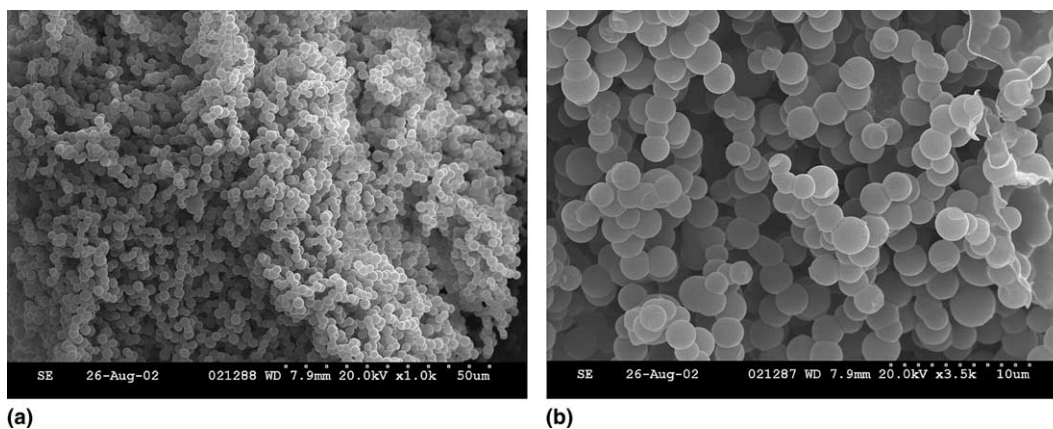
Fig. 4. SEM images of polymeric product **4**.

HT6E (5000–1107 Å). The positive-ion electrospray ionisation time-of-flight mass spectrometry (ESI TOF MS) was performed using a Micromass LCT time of flight mass spectrometer with a Waters 2690 separation module with a Waters 996 photodiode array detector. The MS spectra were acquired by directly infusing the oligomers solution (0.0004 mg/ml in CH_3CN) into the ESI ion source. The m/z range of the mass spectrometer was 200–3000 Da. Acetonitrile was used as a solvent stream. The spray tip potential was 3000.0 V, the nozzle potential was 20.0 V and extraction cone voltage was 5.0 V. Desolvation temperature was 120.0 °C, source temperature was 110 °C. The nitrogen flow rate was 3 l/h. The NMR spectra were recorded using a Bruker DPX 300 (^{1}H, 300 MHz) or a Varian −400 (^{1}H, 400 MHz) instruments in $CDCl_3$ or DMSO-d_6 at ambient temperature unless stated otherwise and referenced for ^{1}H internally to residual solvent resonances; IR spectra (500–4000 cm^{-1}) were recorded in KBr using a Perkin–Elmer instrument. All SEM images were recorded on S-4300 PC field emission scanning electron microscope.

3.2. Synthesis of $Cp_{10}Si_{10}O_{15}$ (**1**)

Freshly prepared trichloro-cyclopenta-2,4-dienyl-silane (21.9 g, 0.11 M) in 100 ml of THF was carefully hydrolysed by the drop wise addition of a solution of $(NH_4)_2CO_3$ (2.97 g) in distilled water (70 ml) at 0 °C. The mixture was stirred for one day. The product was extracted with diethyl ether and the organic layer was separated and dried with anhydrous magnesium sulphate. The solution was concentrated in vacuum. A pale yellow solid **1** was precipitated. The precipitate was washed with diethyl ether and dried in vacuum to give 8.6 g (67%) of **1**. Anal. Calc. for $C_{50}H_{50}Si_{10}O_{15}$: C, 51.28; H, 4.27. Found: C, 52.03; H, 4.34%. ^{1}H NMR (400 MHz, $CDCl_3$, 22 °C), 5.71 (40H, vbr, Cp, H–C=), 3.22 (10H, vbr, Cp, H–C–). ^{29}Si NMR (99 MHz, $CDCl_3$, 22 °C) δ: −71.50(s), −74.39(s), −77.04(s). IR

(KBr, cm^{-1}): 2962(m), 1709(m), 1446(m), 1261(m), 1105(w sh), 845(w), 801(w) 757(m), 431(w). MS (ESI TOF, CH_3CN): 1171 [M + H$^+$]$^+$, 1105 [M–Cp]$^+$, 846 [M–5Cp + H$^+$]$^+$, 371 [M–Cp + 2H$^+$]$^{2+}$. Cryoscopy in *c*-hexane: average (out of 5) M.w. 1193.

3.3. Synthesis of $[Cp_{10}Si_{10}O_{15}]_n$ (**2**)

$Cp_{10}Si_{10}O_{12}$ (8.2 g, 0.007 M) was stirred in THF (150 ml) at ambient temperature for 2 h and then heated under reflux for 10 h. The mixture was then filtered and the yellow-brown precipitate was washed several times with diethyl ether and dried in vacuum to give 7.3 g of the product **2**. Anal. Calc. for $C_{50}H_{50}Si_{10}O_{15}$: C, 51.28; H, 4.27. Found: C, 51.93; H, 4.30%. ^{1}H NMR (400 MHz, DMSO-d_6, 22 °C), 6.65–5.45 (ms, vbr, Cp+ Cp−dimer), 3.55–1.7 (ms,vbr, Cp+Cp−dimer). ^{29}Si NMR (99 MHz, DMSO-d_6, 22 °C) δ: from −71.50 to −78.73 (br). MS (ESI TOF, CH_3CN): 1592.5 [(T$_{10}$)$_3$ − 5Cp]$^{2+}$, 1517 [(T$_{10}$)$_4$ − 2Cp]$^{3+}$, 1451 [(T$_{10}$)$_4$ − 5Cp]$^{3+}$, 1148.3 [(T$_{10}$)$_3$ − Cp]$^{3+}$, 1083 [(T$_{10}$)$_3$ − 4Cp]$^{3+}$, 780 [(T$_{10}$)$_2$]$^{3+}$. IR (KBr, cm^{-1}): 2954(w), 1650(w), 1594(w), 1430(m), 1089(w m), 944(w), 737(w), 714(m), 491(w). UV/Vis (λ_{max}, nm): 208 (br), 246 (br).

3.4. Synthesis of $(CpC_3H_6)_8Si_8O_{12}$ (**3**)

(3-Cyclopentadienylpropyl)triethoxysilane was prepared from (3-chloropropyl)-triethoxysilane (60.20 g, 0.25 M) and CpNa in THF and was purified by vacuum distillation (b.p. 90–91 °C/1 mm, 41 g, 61%). The hydrolytic condensation of (3-cyclopentadienylpropyl)triethoxysilane (20 g, 0.074 M) in acetone (170 ml) was performed by the addition of distilled water (25 ml), with the traces of conc. HCl (0.5 ml) at 0 °C. The mixture was stirred for one day at ambient temperature. The solvent was removed in vacuum to give a pale yellow precipitate. The product was washed with hexane and dried in vacuum (6.94 g, 59%). Anal. Calc. for

$C_{64}H_{88}Si_8O_{12}$: C, 60.38; H, 6.92. Found: C, 60.63; H, 6.98%. ^{1}H NMR (400 MHz, CDCl$_3$, 22 °C) δ: 6.4–5.99 (32H, br m, Cp), 3.51 (8H, br m, Cp), 1.85–0.77 (48H, vbr m, CH$_2$). ^{29}Si NMR (99 MHz, CDCl$_3$, 22 °C) δ: −68.51 (br s). IR (KBr, cm^{-1}): 2933(w), 1713(m), 1455(m), 1383(w), 1155(w m), 1050(w), 799(w), 700(m), 467(w sh). MS (ESI TOF, CH$_3$CN): 1272 [M]$^+$, 1207 [M–Cp]$^+$, 844 [M$-$4CpC$_3$H$_6$]$^+$. Cryoscopy in *c*-hexane: average (out of 5) M.w. 1297.

3.5. Preparation of $(CpC_3H_6)_8Si_8O_{12}]_n$ (**4**)

(CpC$_3$H$_6$)$_8$Si$_8$O$_{12}$ (6.2 g, 0.0048 M) was stirred in THF (100 ml) at ambient temperature for 2 h and then the mixture was heated under reflux for 10 h. A yellow precipitate appeared on the bottom of the flask. The mixture was filtered and the yellow product was washed several times with diethyl ether and dried in vacuum to give 5.3 g of **4**. Anal. Calc. for $C_{64}H_{88}Si_8O_{12}$: C, 60.38; H, 6.92. Found: C, 60.43; H, 6.96%. ^{1}H NMR (400 MHz, DMSO-d$_6$, 22 °C) δ: 6.61–5.84 (vbr m, Cp), 5.24–5.01 (vbr m, Cp +Cp−dimer), 2.62–2.17 (br m, Cp-dimer), 1.87–0.90(vbr m, CH$_2$), ^{29}Si NMR (99MHz, DMSO-d$_6$, 22 °C) δ: from −67.88 to −70.04 (br). IR (KBr, cm^{-1}): 2976(w), 1704(w), 1446(w), 1379(w), 1260, 1142(w), 568(w m).

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