Cage octaphenylsilsesquioxane from cyclic tetrasiloxanetetraol and its sodium salt

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ABSTRACT

Cage octasilsesquioxane with various substituents were obtained by the condensation reaction of various all-*cis* cyclic tetrasiloxanetetraol (R-T_4-tetraol, R = phenyl, *p*-tolyl, *i*-butyl, naphthyl) with benzyltrimethylammonium hydroxide or tetrabutylammonium fluoride as a catalyst. Co-condensation of phenyl-T_4-tetraol with phenyl-d_5-T_4-tetraol or with *p*-tolyl-T_4-tetraol were found to proceed through reshuffling process evidenced by scrambling of the substituents. Pure octa(4-bromo-substituted phenyl)octasilsesquioxane was synthesized for the first time from tetra(4-bromo-substituted phenyl)tetrasiloxanetetraol sodium salt.

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1. Introduction

Scott initially discovered completely condensed methyl-substituted oligomeric silsesquioxanes in 1946 [1]. Later, Barry showed the cubic or hexagonal prismatic shape of the completely condensed molecules [2]. Brown reported the formation of cubic "cage"-structured octahedral octaphenylsilsesquioxane [(PhSiO$_{1.5}$)$_8$; Ph-T_8, Ph = phenyl] [3]. The structure of formed cages depends on the reaction conditions, and can be even incompletely condensed [4,5]. While, incompletely condensed cages have been paid much interest as a model for silica surface [6], completely condensed cages, [(RSiO$_{1.5}$)$_n$; R-T_8, R-T_{10}, R-T_{12}, where n = 8, 10, 12], especially Ph-T_8 have attracted much attention as precursors for organic–inorganic nano-hybrid functional materials [7]. The Ph-T_8 is usually obtained from phenyltrichlorosilane or phenyltrialkoxysilane under acidic or basic condition in high yield. Benzyltrimethylammonium hydroxide [BzTMAH] is a typical catalyst for the formation of T_8 [8]. Tetrabutylammonium fluoride [TBAF] is another effective catalyst for the formation of the cages [9]. Meanwhile, silsesquioxane-based compounds can be also used as the starting materials for the cages [10]. Kabe et al. reported the amine-catalyzed formation of the mixture of T_8, T_{10}, T_{12} including vinyl derivative in acetone in moderate yield from various silsesquioxane derivatives. In some cases, Ph-T_8 and *o*-tolyl-T_8 could be selectively obtained by the reaction [10a,b]. Formation of completely or incompletely condensed POSS is not a simple reaction, but includes many steps of equilibration depending on the reaction

conditions [5c,9,11]. Scrambling of the cages has been also noticed during functional transformation of the cage compounds [12].

Tetraphenyltetrasiloxanetetraol (Ph-T_4-tetraol) is another possible interesting starting material for the synthesis of Ph-T_8 cage. Brown originally reported the formation of all-*cis*-Ph-T_4-tetraol from phenyltrichlorosilane, and commented on the possibility of the compound being an intermediate for Ph-T_8 [3c]. We reported the formation and isolation of all stereo-isomers of Ph-T_4-tetraol [5b,13]. Shchegolikhina et al. reported the formation of the all-*cis*-Ph-T_4-tetraol from phenyltributoxysilane [14]. It should be commented that all-*cis* cyclic tetrasiloxanetetraol, namely all-*cis* T_4-tetraol, or its alkali metal salt is actually often selectively formed under acidic, or under basic condition.

In this report, we firstly demonstrated the formation of T_8 from T_4-tetraol. To apply this reaction in the synthesis of T_8 with functional group, functionalized T_4-tetraol is needed. However, selective synthesis and isolation of functionalized Ph-T_4-tetraol is not an easy task. Functionalized T_4-tetraol can be sometimes isolated as alkaline salt, but treatment of the salt with acid to isolate free silanol gives further condensed products. This fact has limited the possible synthesis of functionalized Ph-T_8 from Ph-T_4-tetraol. Meanwhile, direct synthesis of functionalized Ph-T_8, or introduction of functional groups to the phenyl moiety, in which functional group can act as the scaffold to build nano-hybrid materials, has not been well established, either. For examples, Laine reported the bromination and nitration of Ph-T_8, but the number and position of the functional groups were not well-controlled [15].

Since, all-*cis*-Ph-T_4-tetraol might be a possible key intermediate for the formation of various Ph-T_8 derivatives, and stereochemistry of the formed Ph-T_4-tetraol can be controlled by the reaction

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condition, elucidation of stereochemistry of the T_8, possibly formed from the cyclic tetramer, will give some information about the reaction mechanism. We demonstrated the scrambling of stereochemistry and substituents in T_8 formation from T_4-tetraol. We further demonstrate the formation of pure 4-bromo-substituted phenyl-T_8 as a new building block from the condensed products in the acidification of the sodium salt of 4-bromo-substituted phenyl-T_4-tetraol.
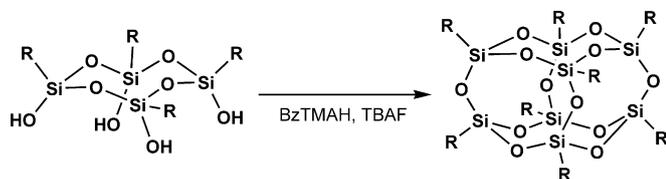
2. Results and discussion

2.1. Formation of cage octasilsesquioxane, T_8 from cyclic tetrasiloxane, T_4-tetraol

When all-*cis*-R-T_4-tetraol was treated with BzTMAH, T_8 cage was obtained as confirmed by NMR and TOF-MS, and shown in Scheme 1.

Another effective catalyst was TBAF. The results under various reaction conditions are summarized in Table 1.

It is interesting to comment that benzene is the best choice as the solvent to produce T_8 from T_4-tetraol as is the same with direct synthesis of T_8 from phenyltri(ethoxy)silane [8] in the presence of BzTMAH (24.0 mol%). Even the use of such high concentration of the catalyst did not give the scrambled cages. The low solubility of the product, Ph-T_8 seems important to prevent further scrambling of the cages to give T_{10} or T_{12}. TBAF showed higher reactivity than BzTMAH in benzene. Lower concentration of 0.14 M of the catalyst (1 mol%) was enough to obtain T_8 in high yield. Acetone is another choice of solvent when TBAF is used as the catalyst as reported by Bassindale, where mixture of cages was obtained [9c]. Importance of the amounts of water in the effective synthesis of cages by TBAF was also pointed out [9b]. Use of lower concentration of 0.14 M of the catalyst was essential to selectively obtain T_8 in reasonable yield under mild reaction condition (Table 1). Chloroform can be also used as a solvent. When higher concentration of TBAF was used, mixture of cages was formed [9c]. Under such condition, kinetic rate of the formation and further scrambling and decomposition, described later, seems competitively occurring [9b]. Solubility of the products in the solvent is another important

factor to determine the products. The less soluble crystalline T_8 seems to precipitate out from the solution. When the yield is low, the T_4-tetraol was changed into randomized oligomeric unidentified products. The reaction with TBAF was applied to *p*-tolyl-(*p*-Tol-), *i*-butyl-(*i*-Bu-), naphthyl-(Np-)-T_4-tetraol derivatives, and the results are shown in Table 2.

p-Tolyl-T_4-tetraol gave randomized products with identifiable T_8 and T_{10} in most of the cases. In chloroform, T_{10} was formed in rather low yield. In ethanol, T_8 could be produced from *p*-Tol-Si(OEt)$_3$ under refluxing condition for 4 days with hydrochloric acid. In case of *p*-anisyl-T_4-tetraol, *p*-anisyl-T_8 could be identifiable in the reaction mixture, although the yield was really poor.

Isobutyl derivative gave good yield of T_8 in various solvents. Reaction in tetrahydrofuran gave 91% yield. Shorter reaction time of one day was sufficient in acetone. Not only acetone or tetrahydrofuran, but also acetonitrile and ethyl acetate were the good solvents. Addition to these solvents, hydrocarbon solvents, ethers and even alcohols can be used. In case of naphthyl-T_4-tetraol, the reaction was slower than the case of isobutyl derivative, and higher concentration of the reagents and longer reaction time were applied. Reasonable yield of T_8 was attained in various solvents. Heating in acetone seemed too vigorous. The ratio of T_4-tetraol to TBAF and the concentration of the reagents do not seem important factors to obtain high yield.

2.2. Scrambling reaction in the formation of T_8

The formation of T_8 from T_4-tetraol was originally intended to synthesize unsymmetrical T_8 from the combination of two different T_4-tetraols.

The interesting fact in the formation of Ph-T_8 from Ph-T_4-tetraol lies at the points that Ph-T_8 could be also obtained from the stereoisomeric mixture of Ph-T_4-tetraol, and that the scrambling of the component of T_4-tetraol in produced Ph-T_8 had occurred. To study the situation, the mixture of Ph-T_4-tetraol and Ph-d_5-T_4-tetraol, and *p*-Tol-T_4-tetraol and Ph-T_4-tetraol were treated under the same reaction condition. The MS of the product shown in Fig. 1 clearly indicates the random distribution of each component in the produced T_8.

Both Ph and Ph-d_5 units are distributed statistically in T_8 cage. Decomposition of T_4-tetraol and reassembling T_8 are simultaneously occurring in the reaction system [5c]. This reaction can

Scheme 1. Formation of R-T_8 from all-*cis*-R-T_4-tetraol.

Table 1
Formation of Ph-T_8 from all-*cis*-Ph-T_4-tetraol (0.25 M) by ammonium catalysts.

Catalyst	mol% cat.	Solvent	Temperature	Time (h)	Yield (%)
BzTMAH	24.0	Acetone	Reflux	2	1.5
	24.0	Methanol	Reflux	2	Randomized
	24.0	Chloroform	Reflux	2	16
	24.0	Benzene	Reflux	2	95
TBAF	1.0	Benzene	Reflux	2	82
	1.0	Acetone[a]	r.t.	72	85
	58.8	Acetone[b]	r.t.	24	>95 (T_8 and T_{10})
	1.0	Methanol[a]	r.t.	72	Randomized[c]
	1.0	Chloroform[a]	r.t.	72	61

[a] 0.14 M.
[b] 1.7 M, Ref. [9c].
[c] With identifiable T_8.

Table 2
Yield (%) of R-T_8 from all-*cis*-R-T_4-tetraol (0.14 M) in various solvents by TBAF 1 mol% at room temperature for 3 days.

Solvent	R = *p*-Tol	*i*-Bu	Np
Acetone	Mix	93[a]	86[b]
	–	–44[c,d]	21[e]
Acetonitrile	Mix	91[c]	80[b]
Ethylacetate	Mix	93[c,f]	63[b]
Chloroform	17[g]	88[c]	80[b]
Hexane	Mix	88[c]	94[b]
Benzene	Trace[g]	74[c]	45[b]
Toluene	Mix	67[c]	10[b]
Ether	–	77[c]	89[b]
Tetrahydrofuran	Mix	91	77[b]
Methanol	Mix	91[c]	83[b]
Ethanol	18[h]	–	–
2-Propanol	1–2	–	–

Mix: randomized products with identifiable T_8 and T_{10}.
[a] 1 day.
[b] 0.25 M, 5 days.
[c] 10 mol% cat.
[D] Reflux, 4 h.
[e] 0.25 M, reflux, 4 h.
[f] 1 day.
[g] *p*-Tol-T_{10}.
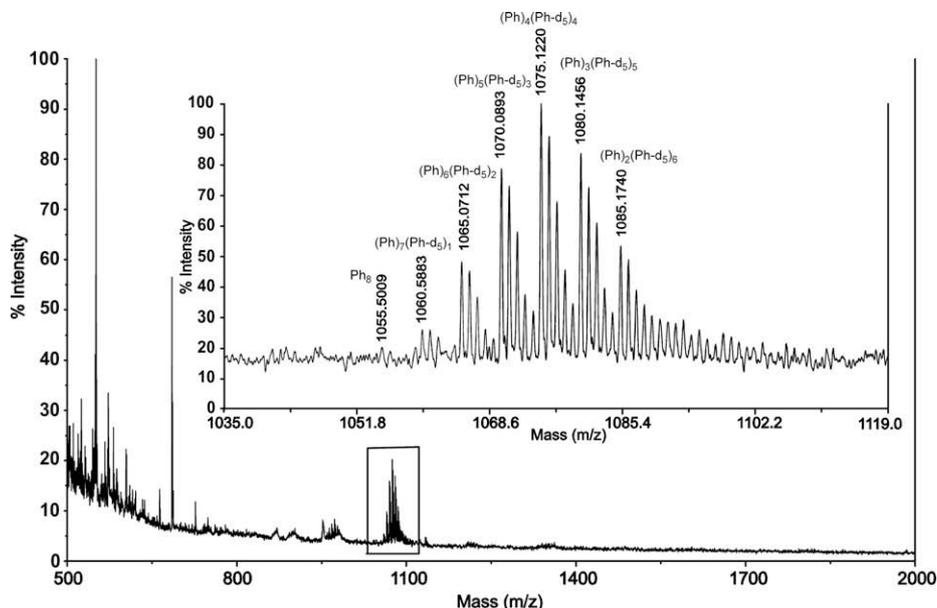[h] From *p*-Tol Si(OEt)$_3$ with 150 mol% HCl, reflux for 4 days.

Fig. 1. MS of the product Ph-T_8 from the mixture of Ph- and Ph-d_5-T_4-tetraols.

be applied to synthesize T_8 with mixed substituent in the cage. When p-Tol-T_4-tetraol and Ph-T_4-tetraol were treated with BzT-MAH in benzene for 24 h, a mixture of crystalline products was obtained in 30% yield. This product has the arrays of mass ranging from 1069 [peak of (p-Tol)$_1$(Ph)$_7$-T_8 with Na$^+$] to 1125 [peak of (p-Tol)$_5$(Ph)$_3$-T_8 with (Na$^+$)] indicating the cage products composed of mixed substituents of p-Tol and Ph. By proton NMR shown in Fig. 2-a, the ratio was determined to be 4:1.

Relatively low yield of mixed cages (30% compared to >90% from Ph-T_8 itself) and absence of p-Tol-T_8 cage may indicate that scrambling of substituents had occurred, and at least 5 to 6-phenyl substituents are needed to make the cage crystalline to precipitate from the reaction mixture.

2.3. Octa(4-bromo-substituted phenyl)-T_8 from condensate

As already discussed, Olsson and Laine have reported the preparation of a mixture of functionalized T_8 compounds through electrophilic substitution reactions like nitration or bromination of phenyl rings [15,16]. However, the selectivity was not well-controlled. To widen the applicability of the POSS derivatives, func-

tionalization of phenyl group directly attached to the core silicon atom has been desired, but there was no report on the direct synthesis of selectively 4-functionalized-phenyl-T_8.

There are some cases where the T_4-tetraol cannot be isolated as pure tetraol, or neutralization of the alkali metal salt with acid gives complex product mixture. Typical example is the 4-bromo-substituted phenyl derivative [17]. Alkali metal salt of 4-bromo-substituted phenyl-T_4-tetraol could be isolated as solid crystalline material, but neutralization gave complex oligomeric condensed products. However, we found that when the condensed product was treated with BzTMAH, 4-bromo-substituted phenyl-T_8 was obtained as the pure crystalline material in reasonable yield (58%) as shown in Scheme 2. The compound showed a pair of doublet at δ 7.55 and 7.58 assigned to meta and ortho protons of 1,4-bromo and silyl substituted benzene. The molar mass (1687.4) by MAL-DI-TOF MS well coincided with the calculated value (1686.4). This is the first report on the direct synthesis of pure 4-bromo-substituted phenyl-T_8. The brominated T_8 can be used in the synthesis of new POSS systems.

3. Conclusions

Condensation to obtain cage octasilsesquioxanes from cyclic tetrasiloxanetetraols was performed in the presence of ammonium catalysts. Reaction condition was established to selectively obtain T_8 cage for both catalysts. It was shown that the cyclic tetrasiloxanetetraol is really a possible starting material in the formation of T_8 cage. The reaction using deuterated starting material unambiguously confirmed the scrambling of the starting components in the reaction. The reaction conditions which do not include scrambling will be reported soon. Pure octa(4-bromo-substituted phenyl)octasilsesquioxane was synthesized for the first time. The compound will find an important role in development of both basic study and application of POSS in the future.

4. Experimental

4.1. Analysis

High resolution NMR spectra (^{1}H at 500 MHz, ^{29}Si at 99 MHz) were obtained on a Varian NMR spectrometer model Unity INOVA

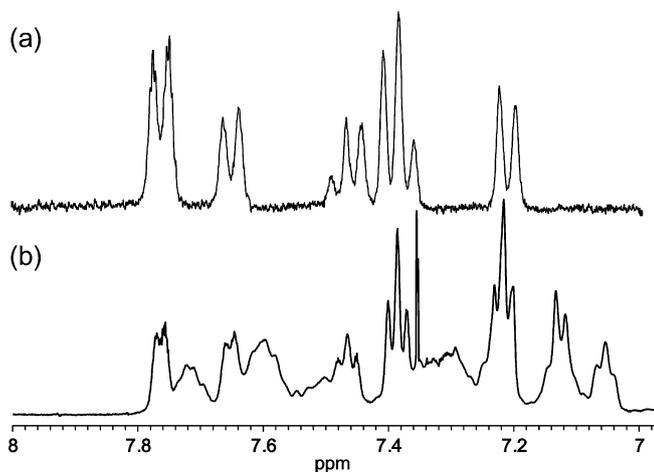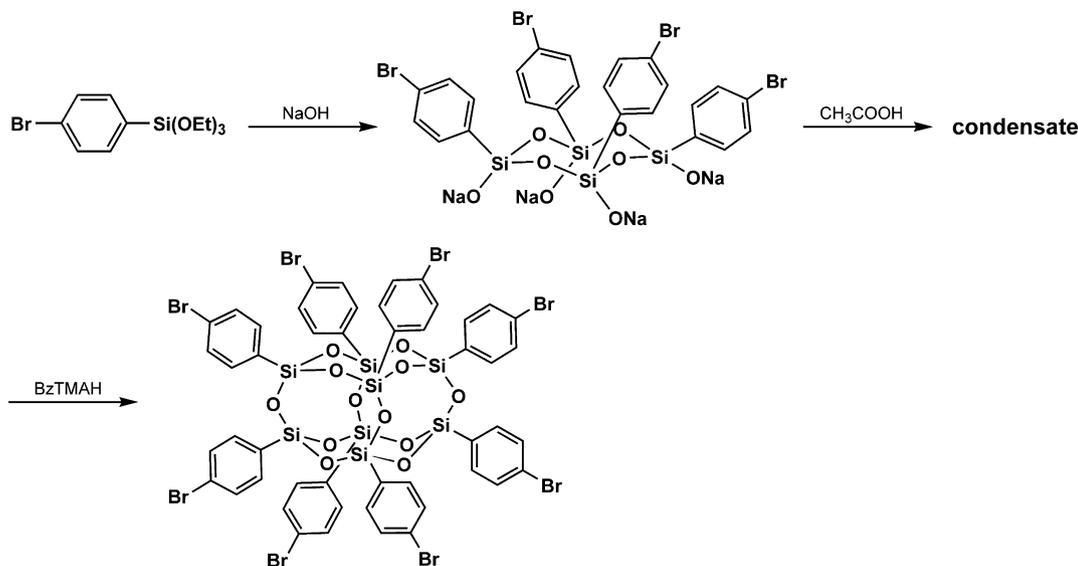**Fig. 2.** ^{1}H NMR of the product T_8 from the mixture of Ph- and p-Tol-T_4-tetraol. (a) Isolated crystalline product, (b) as produced.

Scheme 2. Synthesis of octa(4-bromo-substituted phenyl)octasilsesquioxane from tetra(4-bromo-substituted phenyl)tetrasiloxanetetraol sodium salt.

in CDCl$_3$, THF-d_8 or CD$_2$Cl$_2$. For MALDI-TOF MS (Shimadzu-Kratos Kompact MALDI III) analysis, the matrix 2,5-dihydroxybenzoic acid 98% (DHBA) was dissolved in THF (50 mg/mL), and mixed with the sample solution (0.1 mg/mL in THF) in 1:1 v/v ratio. The samples were dried in air at least for 30 min. The spectra were calibrated by the use of bradykinin.

4.2. Reagents

BzTMAH (40 wt.% methanol solution) and TBAF (1 M THF solution) were purchased from Aldrich and used without further purification. The content of water was determined by ^{1}H NMR in THF-d_8 to be 2.3% and 3.0%, respectively. Acetone, acetonitrile, ethylacetate, chloroform, hexane, benzene, toluene, ether, tetrahydrofuran, methanol, ethanol and 2-propanol were purchased from Kanto Chemical and distilled before use.

4.3. Synthesis of octasilsesquioxane (R-T$_8$) from cyclic tetrasiloxanetetraol (R-T$_4$-tetraol)

Typical examples of the synthesis of T$_8$ from T$_4$-tetraol is given for the synthesis of Ph-T$_8$ POSS from Ph-T$_4$-tetraol.

By BzTMAH: To all-cis-Ph-T$_4$-tetraol (1.38 g, 2.5 mmol) placed in a flask under nitrogen atmosphere, benzene (10 mL) and BzTMAH (0.28 mL, 40 wt.% methanol solution, 0.6 mmol) were added. After the reaction mixture was stirred for 12 h at room temperature, formed solid was filtered, and washed successively with benzene and methanol (15 mL each). The product was pure enough for further analysis, and was determined to be phenyl-T$_8$ (1.22 g, 95% yield) by MALDI-TOF MS and NMR analysis. The data were well coincided with the reported values [8]. p-Tolyl-T$_8$ (p-Tol-T$_8$), i-butyl-T$_8$ (i-Bu-T$_8$) and naphthyl-T$_8$ (Np-T$_8$) were similarly synthesized. Synthesis of substituted-T$_4$ (p-Tol-T$_4$, i-Bu-T$_4$, Np-T$_4$) were previously reported [13].

By TBAF: To all-cis-Ph-T$_4$-tetraol (0.55 g, 1.0 mmol) placed in a flask under nitrogen atmosphere, acetone (7 mL) and TBAF (0.01 mL, 1 M THF solution, 0.01 mmol) were added. After the reaction mixture was stirred for 72 h at room temperature, formed solid was filtered, and washed successively with benzene and methanol (15 mL each). The product was pure enough for further analysis, and was determined to be phenyl-T$_8$ (1.10 g, 85% yield) by MALDI-TOF MS and NMR analysis.

Octaphenylsilsesquioxane (Ph-T$_8$): ^{1}H NMR (500 MHz, THF-d_8): δ 7.34 (t, 2H, J = 7.3 Hz, m-C$_6$H$_5$Si), 7.42 (t, 1H, J = 7.3 Hz, p-C$_6$H$_6$Si), 7.76 (d, 2H, J = 7.3 Hz, o-C$_6$H$_5$Si); ^{29}Si NMR (99 MHz, THF-d_8): δ −77.9. MALDI-TOF MS (m/z): 1055.1 ([M+Na]$^+$, calc.: 1055.1).

Octa(p-tolyl)silsesquioxane (p-Tol-T$_8$): ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.16 (d, 2H, J = 7.8 Hz, m-C$_6$H$_4$Si), 7.63 (d, 2H, J = 7.8 Hz, o-C$_6$H$_4$Si), 2.34 (s, 3H, CH$_3$); ^{29}Si NMR (99 MHz, CDCl$_3$): δ −78.05; MALDI-TOF MS (m/z): 1168.3 ([M+Na]$^+$, calc.: 1167.2).

Octa(i-butyl)silsesquioxane (i-Bu-T$_8$): ^{1}H NMR (500 MHz, CDCl$_3$): δ 0.59 (d, 2H, J = 6.9 Hz, SiCH$_2$CH(CH$_3$)$_2$), 0.95 (d, 6H, J = 7.3 Hz, SiCH$_2$CH(CH$_3$)$_2$), 1.85 (m, 1H, SiCH$_2$CH(CH$_3$)$_2$); ^{29}Si NMR (99 MHz, CDCl$_3$): δ −67.90; MALDI-TOF MS (m/z): 895.4 ([M+Na]$^+$, calc.: 895.3).

Octanaphthylsilsesquioxane (Np-T$_8$): ^{1}H NMR (500 MHz, THF-d_8): δ 7.15 (t, 1H, J = 7.8 Hz, ArH), 7.42 (t, 1H, J = 7.8 Hz, ArH), 7.48 (t, 1H, J = 7.8 Hz, ArH), 7.83 (d, 1H, J = 8.2 Hz, ArH), 7.91 (m, 2H, ArH), 8.75 (d, 1H, J = 8.2 Hz, ArH); ^{29}Si NMR (99 MHz, THF-d_8): δ −77.02; MALDI-TOF MS (m/z) 1456.8 ([M+Na]$^+$, calc.: 1455.2).

4.4. Synthesis of 4-bromo-substituted phenyl-T$_8$ from sodium hydroxide catalyzed condensate

Acetic acid (0.37 g, 6.24 mmol) was added dropwise to THF (30 mL) dispersion of sodium 4-bromo-substituted phenylcyclotetrasiloxanolate (1.0 g, 1.04 mmol), reported by Pizzotti et al. [16]. After stirring for 2 h, water (200 mL) and ether (100 mL) were added to the reaction mixture. The organic layer was separated and dried over anhydrous sodium sulfate. The solvent was evaporated after filtration. The condensate was obtained as white solid (0.81 g, 90%).

To the condensate of 4-bromo-substituted phenyl-T$_4$ (0.52 g, 2.43 mmol) placed in a flask under nitrogen atmosphere, benzene (2.5 mL) and benzyltrimethylammonium hydroxide (BzTMAH, 0.07 mL, 0.15 mmol) were added. After the reaction mixture was stirred for 24 h at room temperature, meantime the starting solid went into solution, and crystalline product was formed. The formed solid was filtered, and washed successively with benzene and methanol (5 mL each). The product was pure enough for further analysis, and was determined to be 4-bromo-substituted phenyl-T$_8$ (0.29 g, 58% yield). ^{1}H NMR (500 MHz, CD$_2$Cl$_2$): δ 7.55 (d, 2H, J = 8.7 Hz, m-C$_6$H$_4$Si), 7.58 (d, 2H, J = 8.7 Hz, o-C$_6$H$_4$Si); ^{29}Si NMR

(99 MHz, CD$_2$Cl$_2$): δ −78.3; MALDI-TOF MS (m/z): 1687.4 ([M+Na]$^+$, calc.: 1686.4).

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