Octa, deca, and dodeca(4-nitrophenyl) cage silsesquioxanes *via* 4-trimethylsilylphenyl derivatives

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Pure octa, deca, and dodeca(4-nitrophenyl) cage silsesquioxanes were obtained by regio-selective 4-nitration of octa, deca, and dodeca(4-trimethylsilylphenyl) cage silsesquioxanes *via ipso*-substitution of trimethylsilyl-phenyl bonds by fuming nitric acid. 3-Nitration of octa(4-methylphenyl)-octasilesquioxane was also described. The starting octa(4-methyl-, 4-isopropyl- and 4-trimethylsilylphenyl)octasilsesquioxanes were selectively formed in 9–21% isolated yield in the presence of hydrochloric acid. Mixtures of octa, deca and dodecasilsesquioxanes, with decasilsesquioxane as the main component, were formed in the presence of tetrabutylammmonium fluoride as a catalyst. All the cage compounds could be separated mainly by crystallization.

Introduction

An increasing need has been noted for the introduction of functional groups to polyhedral oligomeric silsesquioxanes (POSS), such as cage octa-, deca-, and dodecasilsesquioxane, [$(RSiO_{1.5})_n$, R-T_8, R-T_{10} and R-T_{12}] to be used as the building blocks to construct a variety of nano-hybrid materials with precise structure.[1-12] Phenyl derivatives, to which functional groups can be introduced by a variety of reactions, are the most convenient for the purpose. However, it is normally very difficult to directly synthesize functionalized phenyl-substituted cages, and thus functionalization of phenyl groups attached to cage silicon atoms has been long desired.

The amino group is one of the versatile functional groups used to construct new structures by condensation or addition reactions, and introduction of the nitro group is the key to introducing the amino group to an aromatic group. Laine and Olson reported the nitration of Ph-T_8 (R = phenyl, Ph) by fuming nitric acid and further reduction and application of the product.[13] However, the multi-, but incomplete functionalization of the phenyl ring often made it difficult to correlate the properties of the system with the structure. Recently, Zhang reported an improved synthesis of octa-nitrated Ph-T_8, but the position of the nitration was not controlled. Nitration at the 2-, 3- and 4- positions had occurred.[14] We also confirmed their result.

Meanwhile, it has been well recognized that the aromatic–silicon bonds are susceptible to electrophilic cleavage. For example, we reported the synthesis of an optically active bromosilane by the cleavage of the naphthyl–silicon bond of optically active silane by bromine.[15] Eaborn reported that treatment of 1,4-bis(trimethylsilyl)benzene by fuming nitric acid resulted in the substitution of one trimethylsilyl (TMS) group by a nitro group.[16] It would be interesting to establish the selective cleavage and substitution of the phenyl–silicon linkage of phenyl–TMS by a nitro group over phenyl–silsesquioxane silicon linkage in cage 4-TMSPh-oligosilsesquioxanes.

Here, we firstly report the synthesis and separation of octa[4-methyl (4-M), 4-isopropyl (4-P)- and 4-TMS-Ph]-T_8, and deca-, and dodeca- analogues, namely [4-MPh-T_{10}, 4-TMSPh-T_{10}, and 4-TMSPh-T_{12}]. Next, regio-selective 3-nitration of 4-MPh-T_8, and selective nitration of 4-TMSPh-T_8, -T_{10}, and -T_{12} at the 4-position *via ipso*-substitution of TMS–phenyl bonds were described.

Results and discussion

4-Methylphenyl(4-MPh)-T_8, 4-PPh-T_8 and 4-TMSPh-T_8 were obtained in moderate yield by direct acidic hydrolysis of (4-MPh)triethoxysilane, (4-PPh)triethoxysilane, and (4-TMSPh)triethoxysilane in the presence of hydrochloric acid (HCl). Simple washing with ethanol gave pure 4-MPh-T_8 and 4-PPh-T_8. Passage through a short silica gel column with hexane as an eluent gave pure 4-TMSPh-T_8. Hydrolysis of 4-substituted-phenyltriethoxysilane in the presence of tetrabutylammmonium fluoride (TBAF) gave a mixture of T_8, T_{10} and T_{12} cages with T_{10} as the major fraction. 4-Methylphenyl-T_{10} was obtained from the mixture by crystallization using acetonitrile–THF (1 : 1). Treatment of the mixture of 4-TMSPh cages firstly with hexane removed 4-TMSPh-T_8 (11%) as a crystalline material. Following crystallization using ethanol–hexane (1 : 4), crystalline 4-TMSPh-T_{12} was obtained in 7% yield. Final crystallization using acetonitrile–THF (1 : 3) gave crystalline 4-TMSPh-T_{10} in 30% yield. Each fraction was purified by further recrystallization.

The typical reaction scheme is shown for 4-TMSPh POSS cages in Scheme 1, and the results of the synthesis of 4-TMSPh-cages are shown in Table 1.

Formation of T_{10} and T_{12} cages should be the result of the decomposition of the T_8 cage and re-assembly to thermodynamically more stable cages, which are commonly observed under various reaction conditions.[8,9b,11b,11c,17] For example, Yokozawa reported the formation of T_8, T_{10} and T_{12} in the hydrolysis of cyclic hexasiloxanehexaol or dodecasiloxaneodecaol, phenylsilanetriol, or trialkoxysilanes by amines.[9b] Bassindale reported the formation of a mixture of cages from cyclic tetrasiloxanetetraol in the presence

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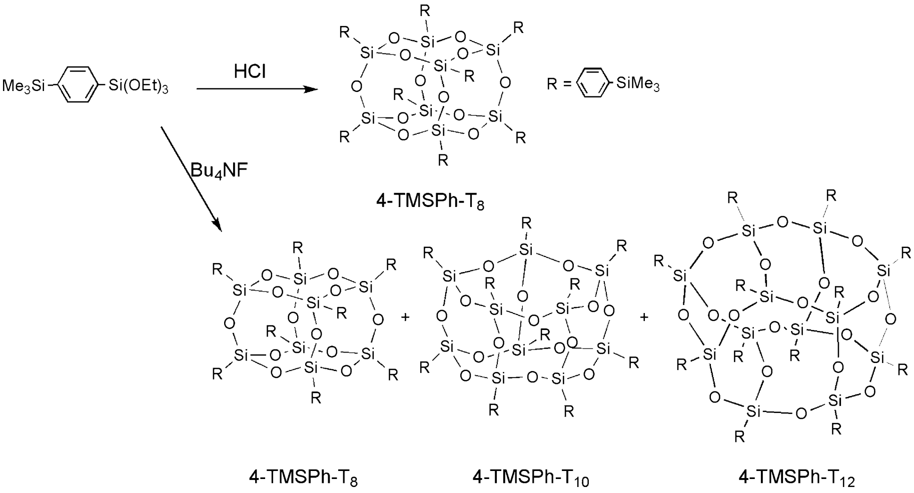
Table 1 Synthesis of 4-substituted Ph-POSS cages

Triethoxysilane	Catalyst	Solvent	T_8 (Yield, %)	T_{10} (Yield, %)	T_{12} (Yield, %)
4-TMSPh	HCl	EtOH	21	[b]	[b]
4-TMSPh	TBAF	CH_2Cl_2	11	30	7
4-MePh	HCl	EtOH	21	[b]	[b]
4-MePh	TBAF	CH_2Cl_2	10	41	[a]
4-PPh	HCl	EtOH	9	[b]	[b]

[a] Not isolated. [b] Not detected by NMR.



Scheme 1 Synthesis of 4-TMSPh-T_8, T_{10} and T_{12}.

of TBAF.[8] We noticed extensive rearrangement of the T_8 cage under azidation of octakis(3-chloropropyl)octasilsesquioxane to produce a thermodynamically more stable mixture of octakis(3-azidopropyl)-, deca(3-azidopropyl)-, and dodeca(3-azidopropyl)-silsesquioxanes.[18] Such cage rearrangement was also reported by Rikowski.[19]

Nitration of 4-TMS-POSS cages was examined. For comparison, nitration of (4-MPh)- and (4-PPh)-T_8 were also carried out. Nitration of 4-MPh-T_8 by fuming nitric acid (added at −30 °C), or by copper(II) nitrate trihydrate (copper(II) nitrate/octasilsesquioxane = 1.2/0.125 mol/mol) at room temperature gave clean 3-nitration. When the starting material peak in the ^{1}H-NMR disappeared, three aromatic protons at δ = 8.32, 7.88 and 7.45 and one CH_3Ph at 2.64 ppm appeared, which strongly indicated the formation of a 4-methyl-3-nitrophenyl group. There were no symmetrical doublet pairs of protons assignable to 3- and 2-protons of 4-nitrophenyl derivatives, which might be produced by *ipso* substitution. The accurate position of nitration was confirmed by the help of NOE of the product in NMR (Fig. 1). On irradiation of methyl protons, only one peak at δ = 7.88 ppm assigned to the 2-proton appeared as a positive signal. Other correlation was also consistent with the 3-nitration. Thus, the NOE analysis of the product confirmed the 3-nitration of 4-MPh-T_8.

^{29}Si NMR showed only one peak at δ = −79.2 ppm assignable to the T^3 structure.

MALDI-TOF MS showed an interesting phenomenon. The highest mass of 1528 Da could be octa(4-methyl-3-nitrophenyl)octasilsesquioxane with one 3-nitro group on each phenyl group of the T_8 cage [$(CH_3NO_2PhSiO_{1.5})_8$-Na^+], and the MS spectrum showed arrays of peaks differing in molar mass by 15 (Fig. 2). The difference of 15 in the molar mass can be explained by the disappearance of a methyl group, and the removal of a methyl group can occur at the nitration stage *via ipso* substitution, or at the ionization stage in MS analysis. Considering the consistent and thoroughly assigned NMR of octa(4-methyl-3-nitrophenyl)octasilsesquioxane shown in Fig. 1, these arrays of peaks seemed to appear under ionization conditions of the compound by eliminating a methyl group, and not by *ipso* substitution.

Ipso substitution might be possible in the nitration of 4-PPh-T_8. However, the reaction gave the product with broadened proton signals at around δ = 8.1, 7.7 (2 : 1). Slow 3-nitration and scrambling of the cage seemed to have occurred.

Although some decomposed products were formed when fuming nitric acid was added to 4-TMSPh-T_8 at room temperature, almost completely pure nitrated products were obtained from 4-TMSPh-T_8, T_{10}, and T_{12}, if the addition of the acid was carried out at −30 °C followed by reaction at room temperature for 10 h as shown in Scheme 2.

^{1}H, ^{13}C, ^{29}Si-NMR and IR data also support the formation of the 4-nitrated product.

IR spectra of the 4-nitrophenyl-T_8, T_{10}, and T_{12} (4-NPh-T_8, T_{10}, and T_{12}) are shown in Fig. 3.

The spectra showed two strong peaks at 1345, 1515 (NPh-T_8), 1349, 1520 (NPh-T_{10}) and 1348, 1518 cm^{-1} (NPh-T_{12}) assignable to symmetric and antisymmetric stretching of the N=O band.

^{29}Si-NMR showed the disappearance of the singlet of the trimethylsilyl groups of TMSPh-T_8, T_{10} and T_{12} at δ = −3.83, −3.98 and −4.06, −4.13 ppm, and the appearance of about

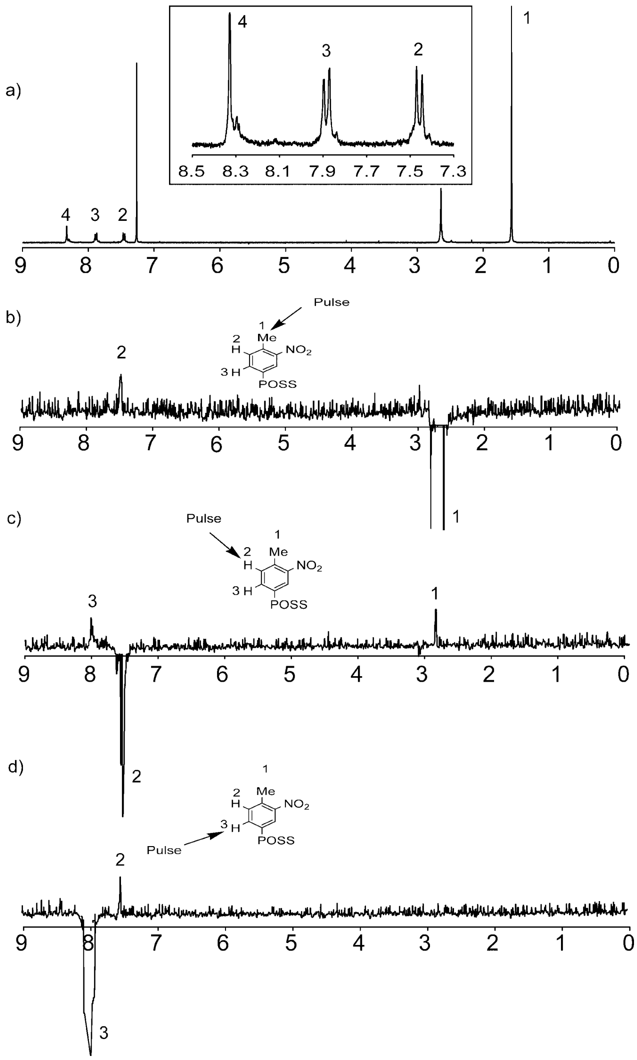


Fig. 1 NOE spectrum of octa(4-methyl-3-nitrophenyl)octasilsesquioxane. a) ^{1}H-NMR of octa(4-methyl-3-nitrophenyl)silsesquioxane. b) NOE enhancement of 2-proton upon irradiation of 1-proton. c) NOE enhancement of 1- and 3-protons upon irradiation of 2-proton. d) NOE enhancement of 2-proton upon irradiation of 3-proton.

1–2 ppm shifted cage peaks of NPh-T_8, T_{10}, and T_{12} at $\delta = -79.2$ (NPh-T_8), -80.9 (NPh-T_{10}) and $\delta = -80.3, -82.2$ ppm, respectively (Fig. 4).

The T_{12} cage is composed of four 8-membered rings and four 10-membered rings, and two kinds of silicon atom are located at the corners formed by two 10-memberd rings and one 8-membered ring, or at the corners formed by two 8-membered rings (indicated by purple in graphical abstract) and one 10-membered ring (indicated by bold in graphical abstract). The ratio is 2 : 1. Consistent with this consideration, contrary to the fact that only one signal was observed for T_8 and T_{10}, two singlet signals were observed for T_{12}.

This is the first report on the effective formation of 4-nitrophenyl cage POSS derivatives. These pure nitro compounds, 4-nitroPh-T_8 (NPh-T_8), 4-nitroPh-T_{10} (NPh-T_{10}), and 4-nitroPh-T_{12} (NPh-T_{12}) will find applications in designing new nano-hybrid materials with precise structure.

Conclusion

Nitration of 4-trimethylsilylphenyl T_n (n = 8, 10, 12) cages by fuming nitric acid under controlled conditions gave clean 4-nitration through *ipso* substitution in good yield.

Contrarily, nitration of 4-methylphenyl-T_8 by copper(II) nitrate trihydrate/acetic anhydride system and fuming nitric acid gave clean 3-nitration.

Experimental

All reagents used were of analytical grade. ^{1}H (500 MHz),^{13}C (125 MHz) and ^{29}Si (99 MHz) NMR spectra were measured on a Varian NMR spectrometer model Unity INOVA 500. Chemical shifts were given in ppm (δ). FT-IR spectra were measured with a Perkin Elmer Spectrum One at room temperature. MALDI-TOF MS spectra were recorded on a Voyager DE RP.

Octa(4-substituted-phenyl)octasilsesquioxanes

To ethanol (13 ml) solution of HCl (0.16 g, 4.6 mmol, HCl 35%) in a 30 ml round-bottom flask, 4-substituted-phenyltriethoxysilane (3.0 mmol), was added under vigorous stirring, and kept under refluxing temperature of the solvent for 4 days. After cooling to room temperature, the formed precipitate was filtered and washed with ethanol. Pure enough compounds could be obtained for 4-methyl and 4-isopropyl derivatives. Simple passage through a silica gel column with hexane as an eluent gave pure 4-trimethylsilylphenyl-T_8. The obtained white powder was dried under vacuum.

Octa(4-methylphenyl)octasilsesquioxane (4-MPh-T_8). δ: ^{1}H ($CDCl_3$) 7.63 [d, 2H, $J_{HH} = 7.8$ Hz, 2-H], 7.16 (d, 2H, $J_{HH} = 7.8$ Hz, 3-H to methyl), 2.34 [s, 3H, 4-CH_3]; ^{13}C ($CDCl_3$) 140.6, 134.3, 128.6, 127.0 [C_6H_4], 21.62 [CH_3]; ^{29}Si [$CDCl_3$] −78.0. MALDI-TOF MS m/z $[M+Na]^+$: 1167. Calcd. for $C_{56}H_{56}O_{12}Si_8$: 1144. (Yield 21%).

Octa(4-isopropylphenyl)octasilsesquioxane (4-PPh-T_8). δ: ^{1}H (Acetone-d_6) 7.68 [d, 2H, $J_{HH} = 8.0$ Hz, 2-H], 7.16 [d, 2H, $J_{HH} = 8.0$ Hz, 3-H to isopropyl], 2.89 [m, 1H, 4-$CH(CH_3)_2$], 1.24 [d, 6H, 4-$CH(CH_3)_2$]. ^{13}C ($CDCl_3$) 151.4, 134.4, 127.6, 126.0 [C_6H_4], 34.2 [$CH(CH_3)_2$], 24.0 [$CH(CH_3)_2$]. ^{29}Si ($CDCl_3$): -78.2. MALDI-TOF MS m/z $[M+Na]^+$: 1392. Calcd. for $C_{72}H_{88}O_{12}Si_8$: 1368. (Yield 9%).

Octa(4-trimethylsilylphenyl)octasilsesquioxane (4-TMSPh-T_8). δ: ^{1}H ($CDCl_3$) 7.72 [d, 2H, $J_{HH} = 8.0$ Hz, 2-H], 7.52 [d, 2H, $J_{HH} = 8.0$ Hz, 3-H to trimethylsilyl], 0.254 [s, 9H, 4-$(CH_3)_3Si$]. ^{13}C ($CDCl_3$) 143.4, 133.3, 132.7, 130.5 [C_6H_4], -1.29 [$(CH_3)_3Si$]. ^{29}Si ($CDCl_3$): −78.4, −3.83. MALDI-TOF MS m/z $[M+Na]^+$: 1631. Calcd. for $C_{72}H_{104}O_{12}Si_{16}$: 1608. (Yield 21%).

Formation of a mixture of cages by TBAF

To a dichloromethane (1 L) solution of TBAF (3 ml of a 1 mol L^{-1} solution in THF) and water (80 mmol) in a 2 L flask, 4-substituted-phenyltriethoxysilane (50 mmol), was added under vigorous stirring at room temperature for 24 h. After the reaction solution was washed with 5 × 100 ml water, the organic layer

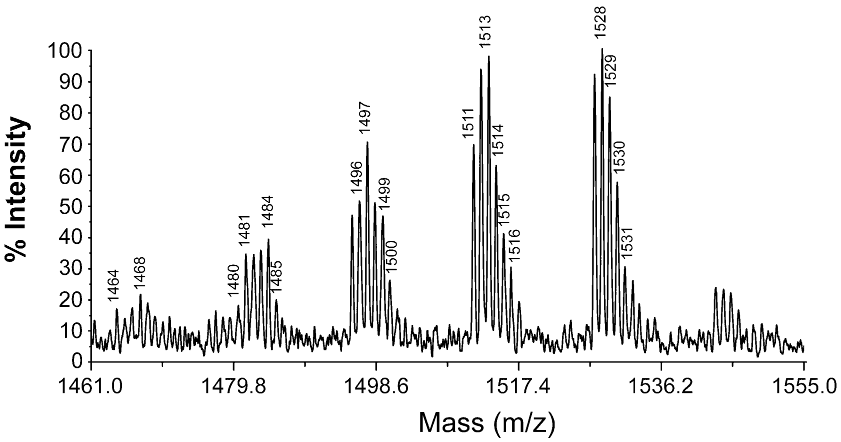
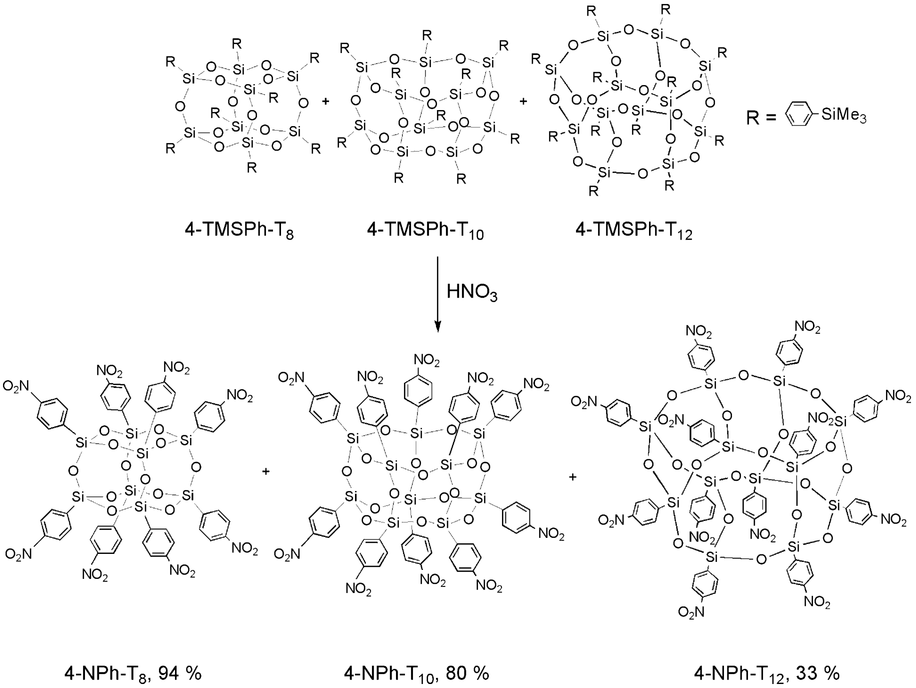


Fig. 2 MALDI-TOF MS spectra of octa(4-methyl-3-nitrophenyl)silsesquioxane.



Scheme 2 Synthesis of 4-nitrophenyl (4-NPh)-T_8, T_{10} and T_{12}.

was separated and dried with Na_2SO_4, and concentrated to give a colorless solid of the mixture of T_8, T_{10} and T_{12} cages.

Deca(4-methylphenyl)decasilsesquioxane (4-MPh-T_{10}). Treatment of the product mixture firstly with acetonitrile–THF (1 : 1) removed the T_{10} cage as a crystalline material (Yield 41%). Following this, crystallization using acetone gave crystals of T_8 cage (Yield 10%). δ: ^{1}H ($CDCl_3$): 7.48 [d, 2H, J_{HH} = 7.8 Hz, 2-*H*], 7.05 [d, 2H, J_{HH} = 7.8 Hz, 3-*H* to trimethylsilyl], 2.30 [s, 3H, 4-CH_3]. ^{13}C ($CDCl_3$): 140.2, 134.2, 128.4. 127.5 [C_6H_4], 21.6 [CH_3]. ^{29}Si ($CDCl_3$): –79.5. MALDI-TOF MS *m/z* [M+Na]$^+$: 1453. Calcd. for $C_{70}H_{70}O_{15}Si_{10}$: 1430. (Yield 41%).

Hydrolysis of 4-trimethylsilylphenyltriethoxysilane in the presence of TBAF gave a mixture of 4-TMSPh-T_8, 4-TMSPh-T_{10} and 4-TMSPh-T_{12} with 4-TMSPh-T_{10} as the major fraction.

Treatment of the mixture firstly with hexane removed the T_8 cage as a crystalline material (Yield 11%). Following this, crystallization using ethanol–hexane (1 : 4) gave T_{12} cage as crystals (Yield 7%). Final crystallization using acetonitrile–THF (1 : 3) gave T_{10} cage as crystals (Yield 30%).

Deca(4-trimethylsilylphenyl)decasilsesquioxane (4-TMSPh-T_{10}). δ: ^{1}H ($CDCl_3$): 7.55 [d, 2H, J_{HH} = 8.0 Hz, 2-*H*], 7.39 [d, 2H, J_{HH} = 8.0 Hz, 3-*H*], 0.23 [s, 9H, 4-(CH_3)$_3$Si]. ^{13}C ($CDCl_3$): 143.1, 133.3, 132.4, 131.0 [C_6H_4], -1.29 [(CH_3)$_3$Si]. ^{29}Si ($CDCl_3$): –79.6, –3.98. MALDI-TOF MS *m/z* [M+Na]$^+$: 2033. Calcd. for $C_{90}H_{130}O_{15}Si_{20}$: 2010. (Yield 30%).

Dodeca(4-trimethylsilylphenyl)dodecasilsesquioxane (4-TMSPh-T_{12}). δ: ^{1}H ($CDCl_3$): 7.54 [d, 2H, J_{HH} = 8.0 Hz, 2-*H*], 7.45 [d, 4H, J_HH=8.0 Hz, 2-*H*], 7.39 (d, 2H, J_{HH} = 8.0 Hz, 3-*H*), 7.31 (d, 4H, J_{HH} = 8.0 Hz, 3-*H*), 0.22 [s, 13H, 4-(CH_3)$_3$Si]. ^{13}C ($CDCl_3$): 142.9, 142.7, 133.4, 132.4, 132.3, 131.5, 131.2 [C_6H_4], –1.28, –1.31 [(CH_3)$_3$Si]. ^{29}Si ($CDCl_3$): –81.5, –79.4, –4.13, –4.06. MALDI-TOF

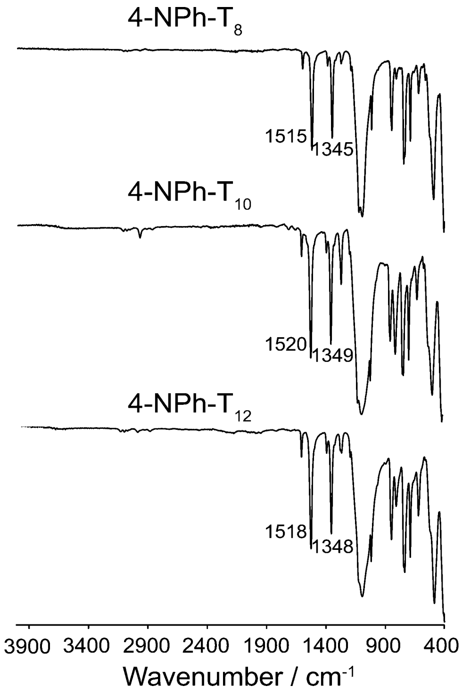


Fig. 3 FT-IR spectra of 4-NPh-T_8, T_{10}, and T_{12}.

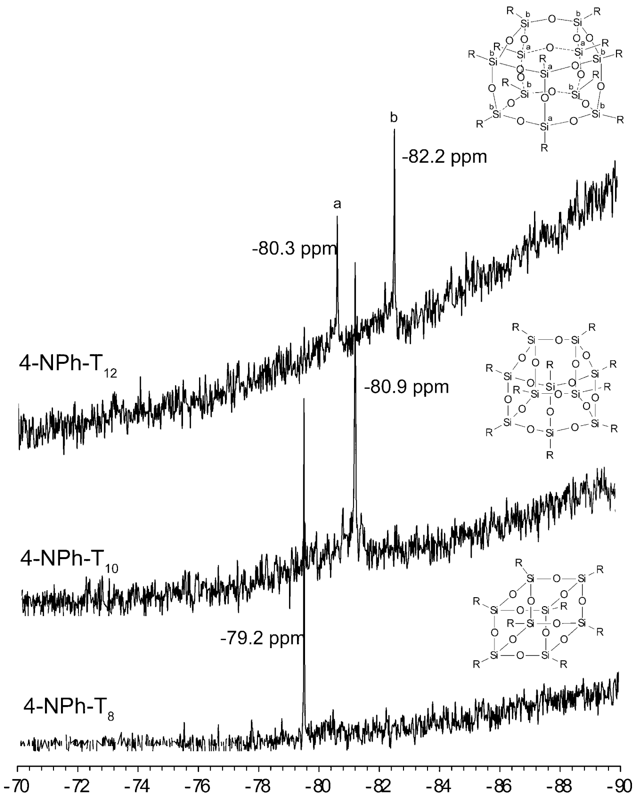


Fig. 4 ^{29}Si-NMR of 4-NPh-T_8, T_{10} and T_{12}.

MS *m/z* $[M+Na]^+$: 2435. Calcd. for $C_{108}H_{156}O_{18}Si_{24}$: 2412. (Yield 7%).

Nitration of cages by fuming nitric acid

A 4-TMSphenyl POSS cage (0.06 mmol) was added to 1 ml of fuming nitric acid with stirring at −30 °C. After addition was complete, the solution was stirred for an additional 30 min, and then stirred at room temperature for 10 h. The solution was poured into 50 ml ice-water. The precipitates were filtered, washed with water and ethanol. The obtained yellow powder was dried under vacuum at room temperature.

Octa(4-nitrophenyl)octasilsesquioxane (4-NPh-T_8). δ: ^{1}H (THF-d_8): 8.31 [2H, d, J_{HH} = 8.7 Hz, 3-*H*], 8.06 [2H, d, J_{HH} = 8.7 Hz, 2-*H*]; ^{13}C (Acetone-d_6): 151.4, 136.7, 136.2, 123.7 [C_6H_4].^{29}Si (Acetone-d_6): −79.22; FT-IR: 1089 cm^{-1} [Si–O–Si], 1515 cm^{-1}, 1345 cm^{-1} [N=O$_2$]. (Yield 94%).

Deca(4-nitrophenyl)decasilsesquioxane (4-NPh-T_{10}). δ: ^{1}H (THF-d_8): 8.23 [2H, d, J_{HH} = 8.7 Hz, 3-*H*], 8.12 [2H, d, J_{HH} = 8.7 Hz, 2-*H*]; ^{13}C (Acetone-d_6): 150.7, 137.8, 136.3, 123.4 [C_6H_4]. ^{29}Si (Acetone-d_6): −80.92. FT-IR: 1095 cm^{-1} [Si–O–Si], 1520 cm^{-1}, 1349 cm^{-1} [N=O$_2$]. (Yield 80%).

Dodeca(4-nitrophenyl)dodecasilsesquioxane (4-NPh-T_{12}). δ: ^{1}H (THF-d_8): 8.21 [1H, d, J_{HH} = 8.7 Hz, 3-*H*], 8.13 [2H, d, J_{HH} = 8.7 Hz, 3-*H*], 7.92 [1H, d, J_{HH} = 8.7 Hz, 2-*H*], 7.79 [2H, d, J_{HH} = 8.7 Hz, 2-*H*], ^{29}Si (Acetone-d_6): −80.34, −82.24. FT-IR: 1102 cm^{-1} [Si–O–Si], 1518 cm^{-1}, 1348 cm^{-1} [N=O$_2$]. (Yield 33%).

Octa(4-methylphenyl)octasilsesquioxane (0.13 g, 0.1 mmol) was similarly treated with fuming nitric acid. After reaction, the solution was poured into 40 ml ice water. The precipitates were filtered, washed with water and ethanol. The obtained yellow powder was dried under vacuum. (0.12 g, 70%). δ: ^{1}H (Acetone-d_6): 8.32 [1H, s, 2-*H* to nitro], 7.88 [1H, d, J_{HH} = 7.8 Hz, 2-*H*], 7.45 [1H, d, J_{HH} = 7.8 Hz, 3-*H*)], 2.64 (3H, s, C*H*$_3$). ^{29}Si (CDCl$_3$): −79.17. FT-IR: 1087 cm^{-1} [Si–O–Si], 1518 cm^{-1}, 1348 cm^{-1} [unti symmmetric and symmetric stretching of nitro].

Nitration of cages by copper(II) nitrate trihydrate

Copper(II) nitrate trihydrate (15.0 mg, 1.2 mmol) was dissolved in acetic anhydride (0.8 mL) followed by stirring in an ice bath for 10 min, and the system was left to warm to room temperature for one hour. A solution of octa(4-methylphenyl)octasilsesquioxane (0.14 g, 0.12 mmol) in chloroform (2 mL) was added to the $Cu(NO_3)_2$/acetic anhydride solution under nitrogen atmosphere. Stirring was continued for 10 h. The progress of the reaction was monitored by NMR. Chloroform (10 mL) and water (10 mL) were added to the reaction system, and stirred for a while until the chloroform phase changed to colorless and the water phase became blue. The separated chloroform phase was washed with excess aqueous 5 wt% sodium carbonate solution, and stirred vigorously for 1.3 h. The organic solution was dried on magnesium sulfate overnight, and then filtered. Evaporation of the solvent gave a yellow product. (0.178 g, 99%).

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