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# Fluoride Ion Entrapment in Octasilsesquioxane Cages as Models for Ion Entrapment in Zeolites. Further Examples, X-ray Crystal Structure Studies, and Investigations into How and Why They May Be Formed

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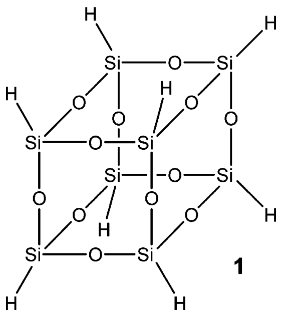
Two fluoride-encapsulated octasilsesquioxane cage compounds have been prepared using the TBAF route as important molecular models for studying ion entrapment in siliceous zeolites. Analyses by X-ray crystal structure and solution $^{19}F/^{29}Si$ NMR spectroscopy reveal very similar environments for the encapsulated fluoride ion perfectly centered within each cage with evidence of weak silicon−fluoride ion interactions. By comparing our NMR and X-ray data with those of nonencapsulated cage analogues from the literature, we observe the effect the fluoride ion has on the geometry of the cage and use the findings of related studies in the literature to suggest reasons fluoride ion may be becoming entrapped in the silsesquioxane core.

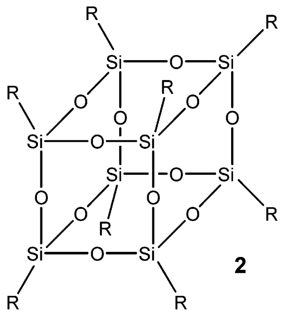
## 1. Introduction

Monofunctionalized octasilsesquioxane cages (the so-called $T_8$ and $Q_8$ cages) are a well-known class of spherosilicates and have found a wide use from models for catalytic supports in organometallic chemistry[1−3] to providing a scaffold for the synthesis of dendrimers.[4−7] With such important applications in surface and materials chemistry high-yielding and selective synthetic routes to prepare them have long been sought. Initial studies by Barry,[8] Martynova,[9] and Feher[10] centered on the hydrolysis of alkyl, allyl, or aryl trichlorosilanes. While formation of the alkyl, allyl, or aryl cage was completed in a single reaction step, mixed product formation meant that reported yields never exceeded 30%.

Müller et al.[11] were the first to report the preparation of the simplest octasilsesquioxane, octahydrosilsesquioxane (**1**), by a similar hydrolytic route and then prepared functionalized cages **2** by a second hydrosilylation step to attach the required functionality to the preformed cage. While the hydrosilylation reactions were found to occur quantitatively, low yields of the octahydro precursor remained an unresolved barrier to full synthetic exploitation.



**1**



**2**

Our group has recently developed a new synthetic strategy in the synthesis of silsesquioxane cages of various sizes and also studied their interconversion, cage opening, and selective cage expansion routes[12] based on reactions catalyzed by tetra-*n*-butylammonium fluoride (TBAF) in the presence of scarce water. We have shown that the reaction of TBAF with functionalized triethoxysilanes gives significantly improved yields of the corresponding octasilsesquioxane cage, with isolated yields of up to 95% having been demonstrated.[13]

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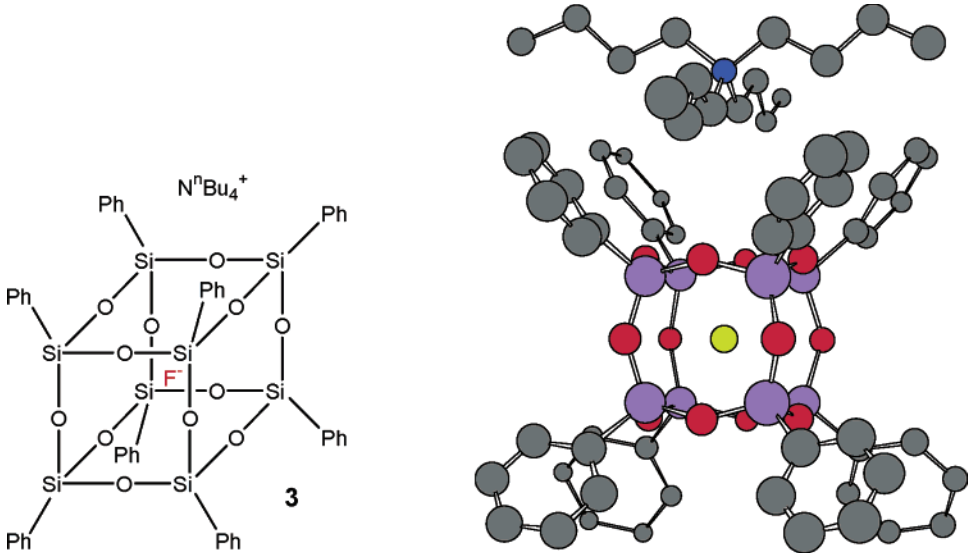

**Figure 1.** Structure of tetrabutylammonium octaphenyloctasilsesquioxane fluoride (**3**).

Further studies into the reaction's mechanism have allowed us to propose the role aqueous fluoride ion plays in catalyzing cage formation and observe from the X-ray crystal structures of many of our octasilsesquioxane cages the role the pendant group substituent has on both the geometry of the cage to which it is attached and in some instances observe evidence of the potential liquid crystalline properties of individual cages.[14] In particular, we have identified the role water plays in providing the oxygens for cage formation.

While attempting to refine our synthesis of octaphenyloctasilsesquioxane using TBAF and phenyltriethoxysilane, we found that by careful control of temperature, pressure, and TBAF concentration during the reaction workup the first example of a completely new class of cage compound was formed,[15] whereby a fluoride ion becomes encapsulated within the cage, and that this charged moiety then precipitates as its tetra-*n*-butylammonium salt from the reaction solution (**3**; Figure 1). The X-ray crystal structure of the recrystallized material confirmed that a fluoride ion was perfectly centered within the octaphenyloctasilsesquioxane cage, and its $^{19}$F NMR chemical shift ($\delta$ $-26.4$) indicated that it essentially resembles a naked fluoride ion. Such a chemical shift is in keeping with a value we had previously and independently predicted for a naked fluoride ion.[16] Attempts to remove the fluoride ion from the cage by refluxing in a variety of solvents was unsuccessful and suggested the faces of the silsesquioxane cage cannot provide a sufficiently large opening for the fluoride ion to pass through. The work of Catlow et al.[17,18] studying fluoride ion containment in siliceous zeolites such as octadecasil allows many parallels to be drawn between the cavity environments that exist in zeolites and octasilisesquioxanes, meaning the latter can be used as a simple model for the former as the basis for future studies. In this paper we report the preparation and crystal structures of further fluoride-encapsulated octasilsesquioxane cage compounds, compare their structures with their nonfluoride encapsulated analogues, and discuss how and why fluoride ion entrapment may be occurring.

## 2. Results and Discussion

Following our initial success, we now report the preparation of further compounds of the same structural type by a similar route. When vinyltriethoxysilane was reacted with TBAF (containing 5% water as purchased) for 24 h with stirring at the room temperature, followed by removal of the solvent with warming under reduced pressure, a brown gel was obtained. By the addition of chloroform and stirring, a white powder, **4**, could be separated with an isolated yield of 60% and recrystallized from acetone (Figure 2). The structure of **4** was confirmed by single-crystal X-ray crystallography, as shown in Figure 3. A similar reaction starting from *p*-tolyltriethoxysilane afforded the corresponding fluoride-encapsulated cage, **5**, in 55% isolated yield, with its structure also being confirmed by single-crystal X-ray crystallography, as shown in Figure 4.

In both new structures the fluoride ion is perfectly centered inside the silsesquioxane cage with a silicon fluorine distance of no less than 2.63 Å, meaning that each fluoride ion's interaction with its surrounding silicons is best described as electrostatic. The arrangement of the tetra-*n*-butylammonium cation in **4** with respect to the cage is complex, with the shortest nitrogen−fluorine distance being 6.68 Å and there being three other contacts of less than 10 Å. In **5** the tetra-*n*-butylammonium groups sit slightly skewed over one face of the cage above a cleft formed by the *p*-tolyl groups in a manner reminiscent of that seen in the crystal structure of **3**,[15] with a nitrogen fluorine distance of 8.95 Å.

A summary of key crystal data and solution $^{19}$F and $^{29}$Si NMR spectral data for **3**−**5**, together with equiva-

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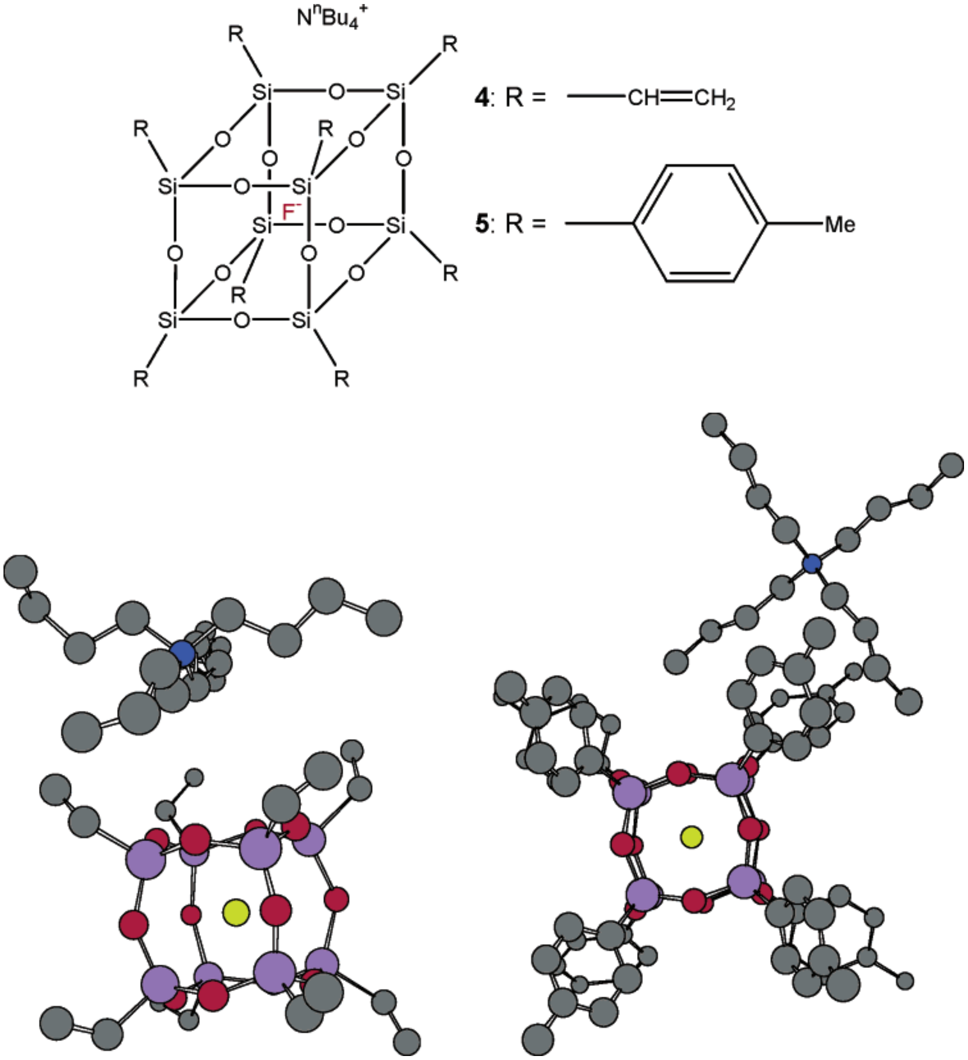

**Figure 2.** Structure of tetrabutylammonium octavinyloctasilsesquioxane fluoride (**4**) and tetrabutylammonium octa-*p*-tolyloctasilsesquioxane fluoride (**5**).

lent information for the non-fluoride-encapsulated analogues of **3** and **4** (**6** and **7**, respectively), is presented in Table 1. While octa-*p*-tolyloctasilsesquioxane (**8**) is a known compound and preliminary X-ray studies of its structure have been carried out,[19,20] full structure solution has not been completed to date. Figure 5 illustrates the cage dimension whose mean value, *a*, appears in Table 1 for compounds **3**−**7**.

When the $^{29}$Si NMR chemical shifts of fluoride-encapsulated cages are compared with those of their nonencapsulated analogues, it is noted that the chemical shift of the silicon moves slightly upfield with entrapment, which may be considered due to a weak interaction of the fluoride ion with the eight equivalent silicons surrounding it and so slightly increasing its coordination number.[21] As previously observed for compound **3**, we also observe sharp singlets in the silicon spectra of **4** and **5**, confirming consistently weak fluorine−silicon interactions. The $^{19}$F NMR chemical shifts of **4** and **5** are almost identical with that of **3** and, since they are among the lowest field measurements for a fluoride ion known, point to the fluoride ion of each being essentially naked. The $^{19}$F NMR chemical shifts measured are comparable with those of similarly encapsulated fluoride ions in germanium oxide D4R cages prepared by Morris et al.[22]

The similarity of the $^{19}$F and $^{29}$Si NMR chemical shift data of **3**−**5** suggests that the silicon and fluoride environments in each are very alike. This is further corroborated by the similarity of the summarized cage crystal structure data in Table 1. Such an observation is in line with the observed rigidity in the solid-state cage geometry of nonencapsulated octasilsesquioxanes already reported in the literature.[14,23]

A comparison of the crystal structure data of the fluoride-containing cages with their nonencapsulated analogues, however, shows how fluoride ion entrapment in each causes the $Si_8O_{12}$ framework to contract slightly, presumably due to the small interactions of the fluoride ion with its surrounding silicon atoms. The contraction also has the effect of decreasing the mean Si−O−Si bond angle, which may also be due to the repulsion of the oxygen atoms in the cage by the fluoride ion. The increase in the mean sum of the O−Si−O bond angles

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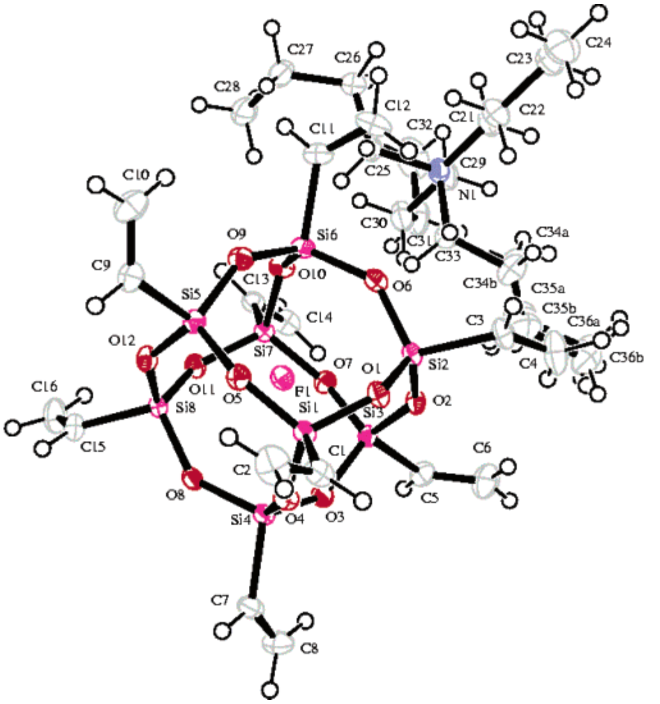

**Figure 3.** X-ray crystal structure of fluoride-encapsulated octavinyloctasilsesquioxane (tetrabutylammonium salt) with thermal ellipsoids drawn at the 30% probability level.

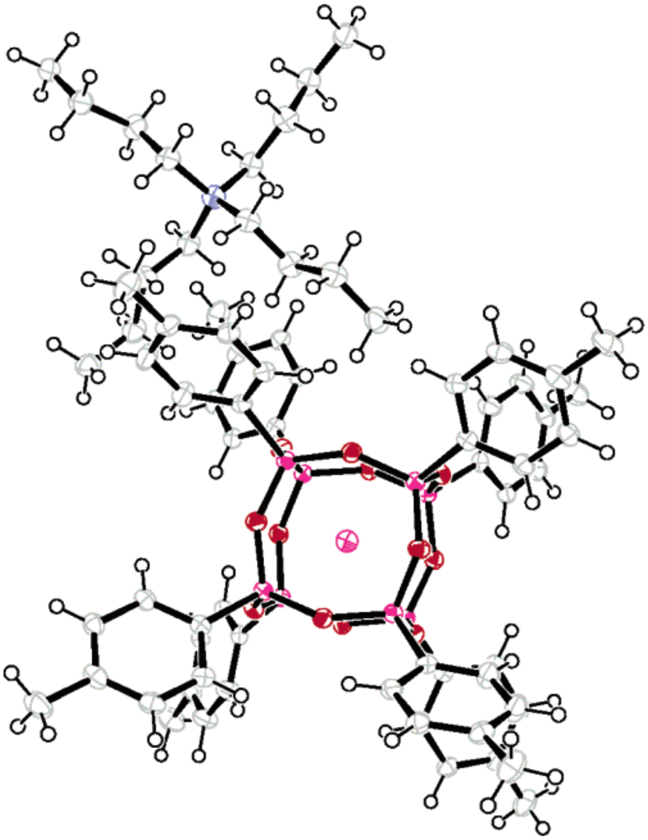

**Figure 4.** X-ray crystal structure of fluoride-encapsulated octa-*p*-tolyloctasilsesquioxane (tetrabutylammonium salt) with thermal ellipsoids drawn at the 30% probability level.

around each silicon, resulting in a more planar $SiO_3$ moiety and a slight lengthening of the $Si-C_{sp2}$ bond length, are also consistent with their being a weak silicon−fluoride ion interaction.[24]

While fluoride ion entrapment within an isolated silsesquioxane cage was first reported by us,[15] such a discovery is not without precedent. Fluoride entrapment within siliceous zeolites has long been known and various compounds have been characterized by X-ray diffraction[25−27] with fluoride ion environments comparable to our own. The silicate octadecasil, which contains similarly encapsulated fluoride ions, has been revealed using REDOR NMR spectroscopy by Hirschinger et al.[28,29]

The repeated central positioning of the fluoride ion in our octasilsesquioxane cages forces us to conclude that it is highly unlikely to be located there by chance. From the crystal structure data we also have evidence that a weak Si···F interaction is occurring. However, it is perhaps less straightforward to explain why fluoride ion appears to act as a template for cage formation and consequently how under optimized conditions it becomes trapped inside. That said, similar behavior attributed to a templating effect has been observed with fluoride ion, which increases the rate of mineralization of aluminophosphate microporus materials and also results in their incorporation into the D4R units of the zeolite framework.[30]

A computational study by George and Catlow[17] into the stability of fluoride ions encapsulated within octadecasil calculated migration energy barriers for fluoride ions, out of the D4R siloxane units containing them, as high as 3.15 eV, compared to 0.62 eV for similarly sized hydroxide ions. Such stability suggests why the fluoride ion was not easily removed from our octasilsesquioxane cages by the non-cage-destructive methods employed. The theoretical studies of Pandey et al.[31] into the electronic properties of methylsilsesquioxanes have critically suggested that the LUMO of hexamethylhexasilsesquioxane lies inside the cage itself. If a similar arrangement occurred for the octasilsesquioxane analogue, this could explain why the fluoride ion can act as a template and provide a reason the fluoride ion appears and is stable at the center of the cage.

While repeated attempts have been made to prepare fluoride-encapsulated cages where the R group at silicon is bound by a $sp^3$ carbon, such as a benzyl group, we have only ever isolated the conventional octasilisesquioxane cage without a fluoride ion inside from such reactions. This persistent observation could be explained by orbital energy level differences between encapsulated cages with $sp^2$- and $sp^3$-bound pendant groups at silicon.

The entrapment of ions in this way suggests an important potential use of such materials in biochemical ion transport applications where ions could be carried, for example, across solution-phase boundaries or cell

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**Table 1. Selected NMR Resonances and Bond Distances and Angles for Compounds 3−8**

| | solution NMR | | crystal structure | | | | | |
|---|---|---|---|---|---|---|---|---|
| compd | $\delta(^{29}Si)$ (ppm) | $\delta(^{19}F)$ (ppm) | mean Si···F (Å) | mean Si−R($C_{sp^2}$) (Å) | mean O−Si−O (deg) | mean trans Si−Si (*a*) (Å) | mean Si−O (Å) | mean Si−O−Si (deg) |
| **3** | −80.6 | −26.4 | 2.65 | 1.86 | 338.5 | 5.31 | 1.62 | 141.2 |
| **4** | −82.9 | −25.3 | 2.65 | 1.85 | 338.5 | 5.30 | 1.62 | 141.1 |
| **5** | −80.4 | −26.8 | 2.66 | 1.86 | 338.5 | 5.31 | 1.63 | 141.2 |
| **6** | −79.7 | | | 1.83 | 327.2 | 5.38 | 1.61 | 149.2 |
| **7** | −80.2 | | | 1.82 | 325.6 | 5.37 | 1.61 | 150.3 |
| **8** | −79.5 | | | n/m[a] | n/m | n/m | n/m | n/m |

[a] n/m = not measured.

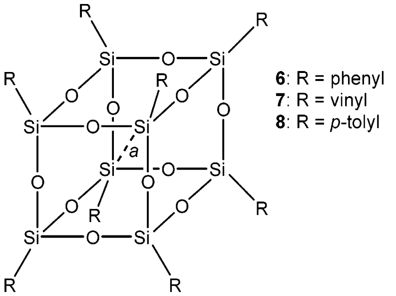

**Figure 5.** Representation of cage dimension *a* that appears in Table 1.

membranes and then chemically released in situ by opening the containing cage framework. Our simple model for the study of siliceous zeolite structures presented here is now being developed further within the group to look at the scope of ion entrapment in other silsesquioxane cage systems, to investigate the possibility of encapsulating anions other than fluoride, and also to find routes for the containment of metal cations in a similar manner.

## 3. Conclusion

We have successfully prepared two further fluoride-encapsulated octasilsesquioxane cage compounds using the same TBAF and scarce water-catalyzed route as for our previously reported example. Analyses of the three compounds' solution $^{19}F$ and $^{29}Si$ NMR spectra and X-ray crystal structures reveal that the environments of the encapsulated fluoride ion are very similar in each case, being perfectly centered within the cage. By comparison of $^{29}Si$ NMR chemical shift and X-ray cage dimensional data of the encapsulated cage with data from its unencapsulated analogue, slight contraction of the cage and increased pentacoordination at each silicon is observed when fluoride ion is placed inside the cage, consistent with there being a weak fluoride ion−silicon coordination. The nature of the R group at silicon would seem to be highly important to the fluoride ion's stability at the center of the cage in the octasilsesquioxanes, since attempts to prepare them with $C_{sp^3}$ instead of $C_{sp^2}$ bound R groups was universally unsuccessful.

A review of the literature reveals a strong similarity between the fluoride environment inside our octasilsesquioxane cages with that of fluoride ions in siliceous zeolites, and thus, we intend to exploit our model of zeolite structure to undertake further extensive ion entrapment studies. The literature relating to fluoride ions in such zeolites provides several possible reinforcing explanations as to why the fluoride ion may be becoming encapsulated in our octasilsesquioxane cages, suggesting that it is occurring more than just by chance. For example, under the right conditions, a templating effect by the fluoride ion may be aiding cage self-assembly, eventually leading to it becoming entrapped, while energetic and molecular orbital calculations suggest that the center of the cage may be a real potential energy minimum for the stabilization of contained ions.

## 4. Experimental Section

**General Experimental Details.** All NMR spectra were obtained using either a JEOL EX 400 NMR or a JEOL Lambda 300 NMR spectrometer with the pulse delay for $^{29}Si$ NMR spectra standardized at 20 s. All spectra were recorded at room temperature (25 °C) using deuterated [$D_6$]acetone dried over 4 Å molecular sieves as solvent unless stated otherwise. The NMR external reference compound was tetramethylsilane (TMS) for $^1H$, $^{13}C$, and $^{29}Si$ NMR spectra and $CFCl_3$ for $^{19}F$ NMR spectra. The spectral data point positions of these compounds were accurately located before data acquisition. $^1H-^1H$ and $^1H-^{13}C$ COSY and DEPT programs were frequently used to help the assignment of $^1H$ and $^{13}C$ NMR spectra. MALDI-TOF experiments were performed using a Voyager-DE-STR instrument. The organic solvent, matrix, and cationization reagent for sample preparation were chloroform, dithranol, and silver trifluoroacetate (AgTFA), respectively. ESI experiments were performed using a Waters ZQ4000 instrument, and FAB experiments were performed using a Finnigan MAT 95 XP instrument.

**Tetrabutylammonium Octavinyloctasilsesquioxane Fluoride (4).** Vinyltriethoxysilane (1.24 g, 6.52 mmol) was dissolved in dried toluene (20 mL), and then tetrabutylammonium fluoride (2.5 mL of a 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature for 24 h. The solvent was removed on a rotary evaporator at 130 mmHg and 70 °C, and a brown gel was obtained. Recrystallization from acetone afforded colorless crystals of **4** (0.46 g, 60%).

$^1H$ NMR (300 MHz, [$D_6$]acetone): $\delta$ 5.98 (m, 24H; vinyl H), 3.47−3.41 (m, 8H; N−$CH_2$), 1.80−1.70 (m, 8H; $CH_2$), 1.50−1.38 (m, 8H; $CH_2$), 0.98 (t, $^3J_{HH} = 7.4$ Hz, 12H, $CH_3$). $^{13}C$ NMR (75.5 MHz, [$D_6$]acetone): $\delta$ 136.7 (Si−$CH_{vinyl}$), 132.0 ($H_2C_{vinyl}$), 59.3 (N−$CH_2$), 24.4 ($CH_2$), 20.3 ($CH_2$), 13.8 ($CH_3$). $^{19}F$ NMR (376 MHz, [$D_6$]acetone): $\delta$ −25.3. $^{29}Si$ NMR (79.30 MHz, [$D_6$]-acetone): $\delta$ −82.9. Anal. Calcd for $C_{32}H_{60}FNO_{12}Si_8$: C, 42.97; H, 6.76; N, 1.57. Found: C, 43.19; H, 6.70; N, 1.54. MS (ESI): *m*/*z* (%) calculated for $C_{16}H_{24}FO_{12}Si_8^-$ 650.9 and for $TBA^+$ 242.3; found [$M^-$] 651.0 (100%), [$M^+$] 242.3 (100%). Temperature of decomposition (determined by TGA measurement): 150 °C.

**Tetrabutylammonium Octa-*p*-tolyloctasilsesquioxane Fluoride (5).** *p*-Tolyltriethoxysilane (1.05 g, 4.13 mmol) was dissolved in dried toluene (20 mL), and then tetrabutylammonium fluoride (2.5 mL of a 1 M solution in THF with 5% water) was added. The mixture was stirred at room temperature for 24 h. The solvent was removed on a rotary evaporator at 74 mmHg and 87 °C and a brown gel obtained. Recrystallization from acetone afforded colorless crystals of **5** (0.56 g, 55%).

$^1$H NMR (300 MHz, [D$_6$]acetone): $\delta$ 7.60 (d, $^3J_{HH} = 7.8$ Hz, 16H; Ar H), 7.02 (d, $^3J_{HH} = 7.8$ Hz, 16H; Ar H), 3.40−3.35 (m, 8H; N−CH$_2$), 2.20 (s, 24H; Ar−CH$_3$), 1.80−1.70 (m, 8H; CH$_2$), 1.43−1.30 (m, 8H; CH$_2$), 0.91 (t, $^3J_{HH} = 7.3$ Hz, 12H; CH$_3$). $^{13}$C NMR (75.5 MHz, [D$_6$]acetone): $\delta$ 139.0 (*p*-C), 135.2 (*i*-C), 135.0 (*m*-CH), 128.7 (*o*-CH), 59.3 (N−CH$_2$), 24.4 (CH$_2$), 21.5 (Ar−CH$_3$), 20.4 (CH$_2$), 13.8 (CH$_3$). $^{19}$F NMR (376 MHz, [D$_6$]-acetone): $\delta$ −26.8. $^{29}$Si NMR (79.30 MHz, [D$_6$]acetone): $\delta$ −80.4. Anal. Calcd for $C_{72}H_{92}FNO_{12}Si_8$: C, 61.45; H, 6.59; N, 1.00. Found: C, 61.75; H, 6.83; N, 0.86. MS (MALDI-TOF): *m*/*z* (%) calculated for $C_{56}H_{56}FO_{12}Si_8^-$ 1164.2 and for TBA$^+$ 242.3; found [M$^-$] 1164.4 (100%), [M$^+$] 242.3 (100%). Temperature of decomposition (determined by TGA measurement): range of 340−345 °C.

**X-ray Crystallography.** All structures were measured on a *Nonius Kappa CCD* diffractometer ($\phi$ scans and $\omega$ scans to fill *asymmetric unit* or *Ewald* sphere) using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). The data collection was performed in a $\psi$ rotation mode. A list of crystal data, data collection, structure solution and refinement parameters is provided in Table 2. The raw intensity data was corrected for Lorentz and polarization effects as well as absorption correction (SORTAV).[32] Structure solutions were searched and refined by direct methods[33] (SHELXS 97_2) and difference Fourier analyses (SHELXL 97_2),[34] respectively, based on $F^2$. Atom form factors for neutral atoms were taken from the literature.[35] Second- and third-row elements were refined anisotropically with hydrogen atoms assumed in idealized positions riding on their pivot atoms.

**Table 2. Crystal Data and Data Collection and Refinement Parameters for Compounds 4 and 5**

| | **4** | **5** |
|---|---|---|
| formula | $C_{32}H_{60}FNO_{12}Si_8$ | $C_{72}H_{92}FNO_{12}Si_8$ |
| mol wt | 894.53 | 1407.19 |
| color | colorless | colorless |
| morphology | block | shard |
| cryst size (mm) | 0.80 × 0.60 × 0.30 | 0.30 × 0.22 × 0.08 |
| cryst syst | monoclinic | tetragonal |
| space group | $P2_1/n$ | $I\bar{4}$ |
| unit cell dimens | | |
| *a* (Å) | 12.1509(1) | 12.6476(1) |
| *b* (Å) | 18.2072(2) | 12.6476(1) |
| *c* (Å) | 20.6679(2) | 22.6513(6) |
| α (deg) | 90 | 90 |
| $\beta$ (deg) | 96.9900(10) | 90 |
| $\gamma$ (deg) | 90 | 90 |
| *V* (Å$^3$) | 4538.45(8) | 3623.34(10) |
| *Z* | 4 | 2 |
| $D_{calcd}$ (g cm$^3$) | 1.309 | 1.290 |
| *F*(000) | 1904 | 1496 |
| temp (K) | 120(2) | 120(2) |
| no. of rflns collected | 48 660 | 10 458 |
| no. of indep rflns | 10 632 | 4040 |
| abs cor | semiempirical from equivalents | |
| $R_{int}$ | 0.0603 | 0.0697 |
| $\theta$ range (deg) | 2.98−27.47 | 3.14−27.49 |
| *h* range | −15 to +15 | −16 to +16 |
| *k* range | −23 to +21 | −16 to +16 |
| *l* range | −26 to +26 | −29 to +25 |
| final *R* indices ($F^2 > 2\sigma(F^2)$) | R1 = 0.0403,<br>wR2 = 0.1041 | R1 = 0.0489,<br>wR2 = 0.1141 |
| *R* indices (all data) | R1 = 0.0578,<br>wR2 = 0.1124 | R1 = 0.0632,<br>wR2 = 0.1242 |
| *S* (goodness of fit on $F^2$) | 1.027 | 1.039 |
| $N_{ref}$ | 10 362 | 4040 |
| $N_{par}$ | 502 | 216 |

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC 229788 and 229789. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. Fax: (+44) 1223-336-033. E-mail: data_request@ccdc.cam.ac.uk.

**Supporting Information Available:** Crystallographic data as CIF files for compounds **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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