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PAPER

# Further studies of fluoride ion entrapment in octasilsesquioxane cages; X-ray crystal structure studies and factors that affect their formation<sup>†</sup>

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A range of fluoride-encapsulated octasilsesquioxane cage compounds have been prepared using the TBAF route. Our studies suggest that whilst it is relatively straightforward to prepare fluoride-encapsulated octasilsesquioxane cage compounds with adjacent sp<sup>2</sup> carbons, leading to a range of aryl and vinyl substituted compounds, the corresponding sp<sup>3</sup> carbon derivatives are more capricious, requiring an electron withdrawing group that can stabilize the cage whilst not acting as a leaving group. Analysis by X-ray crystallography and solution <sup>19</sup>F/<sup>29</sup>Si NMR spectroscopy of R<sub>8</sub>T<sub>8</sub>@F<sup>-</sup> reveal very similar environments for the encapsulated fluoride octasilsesquioxane cages. Migration of a fluoride ion

from inside the cage to outside the cage without breaking the T<sub>8</sub> framework and the possibility of

encapsulating other anions within silsesquioxane cages have been also investigated.

#### Introduction

Spherosilicates (the so called  $T_8$  and  $Q_8$  cages) have found a wide range of uses from models for catalytic supports in organometallic chemistry<sup>1-4</sup> to providing a scaffold for the synthesis of dendrimers.<sup>5-8</sup> We have developed a novel synthetic strategy using *n*-butylammonium fluoride (TBAF) as a catalyst in the presence of scarce water giving significantly improved yields of the corresponding octasilsesquioxane cage with isolated yields of up to 95%.9 Whilst attempting to refine this synthesis we found that by careful control of temperature, pressure and TBAF concentration during the reaction work-up a completely new class of cage compound was formed. The X-ray crystal structure of these materials showed that a fluoride ion was perfectly centred within the octaphenyl-octasilsesquioxane cage and its <sup>19</sup>F NMR chemical shift ( $\delta$  –26.4) indicated that it essentially resembles a "naked" uncoordinated fluoride ion. Many parallels can be drawn between the cavity in these fluoride-encapsulated octasilsesquioxane cage compounds and the environments that exist in zeolites<sup>10</sup> meaning the former can be used as a simple model for zeolites as the basis for future studies.

It is well known that fluoride anions play at least two important roles in zeolites synthesis. Besides its mineralizing role that catalyzes the breaking and formation of Si–O–T (T = Si, Al) bonds, fluoride anions can act as templates, being found inside

the small double four-membered ring (D4R) cages.<sup>11</sup> Fluoride ion also acts as a stabilizing agent for the zeolite building unit *via* electron density transfer into the framework of silicon atoms<sup>12,13</sup> through pentacoordination.<sup>14</sup>

The fluoride anion has been widely reported as being encapsulated in the double four-ring (D4R) units, analogous to a silicon  $T_8$  cage, of the framework from octadecasil synthesis and in some gallophosphates such as GaPO<sub>4</sub>. Morris et *al.*<sup>15</sup> have reported fluoride anion encapsulation within the double four ring analogues 'D<sub>4</sub>R–GeO<sub>2</sub>' of composition [Ge<sub>8</sub>O<sub>12</sub>(OH)<sub>8</sub>F]<sub>2</sub>.

Haddad and coworkers have synthesized the corresponding fluoride-encapsulated octasilsesquioxane cages with an associated tetramethyl ammonium ion.<sup>16</sup> Their route involves starting with the preformed  $T_8$  cage and stirring with tetramethyl ammonium fluoride in THF for 16 h. As well as the corresponding vinyl and phenyl fluoride-encapsulated octasilsesquioxane cages they also obtained styryl, and perfluoralkyl derivatives. MALDI ToF mass spectrometry was used to calculate the collision cross sections which agreed with the known X-ray crystallographic structures together with those calculated using a modified projection model.

There have been numerous theoretical calculations of silsesquioxane cages and encapsulated cages. High level of theory (B3LYP/6-311++G(d,p)) calculations have shown that for aromatic systems attached to the cage, the HOMO and LUMO are outside the cage<sup>16-19</sup> primarily centered on the organic ligands. This leads to a more positive charge in the centre of the cage that can act as a host for the fluoride anion. Electron donating alkyl groups lead to a HOMO associated with the cage atoms which interacts unfavorably with fluoride ion inside the cage.

In this paper we report the preparation and crystal structures of further aryl and vinyl fluoride encapsulated octasilsesquioxane cage compounds, we examine the preparation of  $sp_3$ 

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Aryl group	Compound	<sup>19</sup> F NMR chemical shift	<sup>29</sup> Si NMR chemical shift		
Phenyl	1	-26.4	-80.6		
Tolyl	2	-26.8	-80.4		
<i>p</i> -Chlorophenyl	3	-27.2	-80.7		
<i>p</i> -Bromophenyl	4	-27.2	-80.5		
<i>p</i> -Methoxyphenyl	5	-27.6	-80.2		

Table 1 <sup>19</sup>F and <sup>29</sup>Si chemical shifts for a range of aryl fluoride encapsulated octasilsesquioxane cages

substituted fluoride encapsulated octasilsesquioxane cages using a range of strategies and examine the crystal structures of the perfluoroalkyl fluoride encapsulated octasilsesquioxane cage first synthesized by Haddad and coworkers. We also report an examination of fluoride ion exchange by other anions, the possibility of encapsulating other halides and the migration of a fluoride anion through the face of the cage without breaking its structure.

#### **Results and discussion**

#### (a) Aryl substituted encapsulated cages

Based on our successful synthesis of the phenyl and tolyl fluoride encapsulated octasilsesquioxane cages we have made a range of substituted aromatic derivatives.<sup>20,21</sup> In each case the corresponding aryltrialkoxysilane 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. Purification by flash chromatography on silica gel and/or recrystallisation often led to crystals of sufficient quality for single crystal X-ray crystallographic analysis. The relevant <sup>19</sup>F and <sup>29</sup>Si NMR spectroscopic chemical shifts are given in Table 1.

The <sup>19</sup>F chemical shifts only vary by a small amount, within a range of  $-27.1 \pm 0.7$  ppm, suggesting the aromatic substituent has little effect on the "naked" fluorine ion. Interestingly other small peaks were seen in the <sup>19</sup>F NMR spectrum within the range -25 to -30 ppm (up to 10% in some cases). These could arise from larger  $T_{10}$  cages that encapsulate the fluorine and/or from  $T_8$ cages where one of the organic substituents has been substituted for fluorine, leading to another Si-F peak of equal intensity at about -132 ppm.<sup>22</sup> The <sup>29</sup>Si NMR chemical shifts were also fairly constant,  $-80.8 \pm 0.6$  ppm, again suggesting similar environments that are hardly affected by the variation of substituent. These values are slightly, ~1 ppm, lower than those of the corresponding empty cages, as shown in Table 2 which also vary only slightly with any substitution,  $-79.0 \pm 0.6$  ppm. Unlike the 4-substuted phenyltrimethylsilanes the 29Si NMR chemical shift of the cages did not follow a Hammet plot.23

Table 2 <sup>29</sup>Si NMR data for substituted empty aryl cages T<sub>8</sub>[RSi–Csp<sup>2</sup>]<sub>8</sub>

Aryl group	<sup>29</sup> Si NMR chemical shift	Reference	
<i>p</i> -Bromophenyl	-79.39	24	
<i>N</i> , <i>N</i> -Dimethylbenzenamine	-79.50	25	
<i>p</i> -Chloromethylphenyl	-78.40	26	
<i>p</i> -Hydroxymethylphenyl	-78.50	26	



**Fig. 1** X-ray crystal structure of the fluoride encapsulated octa-*p*-chlorophenyl octasilsesquioxane (tetrabutylammonium salt) with thermal ellipsoids drawn at the 50% probability level. H atoms and TBAF are omitted for clarity.



Fig. 2 X-ray crystal structure of the fluoride encapsulated octa-*p*-methoxyphenyl octasilsesquioxane (tetrabutylammonium salt) with thermal ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

A similar variation is seen for the corresponding aryl trialkoxysilanes which have a <sup>29</sup>Si NMR chemical shift of  $57.5 \pm 1$  ppm. Fig. 1 and 2 show the crystal structures of the fluoride encapsulated *p*-chloro- and *p*-methoxyoctaphenylsilsesquioxane cages. Selected bond distances and angles one shown in Table 3.

Table 3 shows that the key bond angles and distances of the silsesquioxane cage vary very little with aryl substitution. A comparison of the crystal structural data of **3** and **5** with their nonencapsulated analogue  $T_8(p-IC_6H_4)_8$  **6**<sup>27</sup> (Table 3) which is the only substituted aryl cage with a crystal structure reported,

	Crystal structure								
Compound	Mean Si · · · F (/Å)	Mean Si– $R(C_{sp2})$ (/Å)	Mean O–Si–O (/°)	Mean trans Si–Si (a) (/Å)	Mean Si–O (/Å)	Mean Si–O–Si (/°)			
1	2.65	1.86	112.8	5.31	1.62	141.2			
2	2.66	1.86	112.8	5.31	1.63	141.2			
3	2.65	1.85	112.9	5.30	1.62	141.0			
5	2.66	1.86	112.7	5.32	1.63	141.4			
6	_	1.82	108.9	5.38	1.61	149.6			

 Table 3
 Selected bond distances and angles for compounds 1–3, 5 and 6

shows that fluoride ion entrapment inside the octasilsesquioxane cage causes the  $Si_sO_{12}$  cage framework to contract slighty in the fluoride-containing cage. This slight contraction of the framework is illustrated by the shrinkage of the mean Si–O–Si bond angle, which may be due to repulsion of the oxygen and fluoride atoms. The average O–Si–O bond angle also increases and there is a slight lengthing of the Si–Csp<sup>2</sup> bond length, which is consistent with a weak silicon–fluoride ion interaction. The fluorine atom is a centre of inversion for the octa-*p*-chlorophenyl octasilsesquioxane (tetrabutylammonium salt).

We attempted the synthesis of the octa-*p*-pentafluorophenyloctasilsesquioxane and octanaphthyloctasilsesquioxane (tetrabutylammonium salt) however, an insoluble gel was obtained. Further analysis suggested the cleavage of the Si–C bond by the fluoride ion to give the relatively stable pentafluorophenyl and naphthyl anions. As will be discussed later, there is a delicate balance between the electron withdrawing effect of the aryl group in stabilizing fluoride encapsulated cage formation and its ability to act as a leaving group.

#### (b) Vinyl substituted encapsulated cages

Recently Haddad and coworkers published a synthesis of the tetramethylammonium fluoride-encapsulated octastyrenylsilsesquioxane cage.<sup>16</sup> Independently we have produced the tetrabutylammonium fluoride-encapsulated octastyrenyloctasilsesquioxane cage, 7, whose X-ray crystal structure is shown in Fig. 3. Selected bond distances and angles are reported in Table 4.



Fig. 3 X-ray crystal structure of the fluoride encapsulated octa-styrenyloctasilsesquioxane (tetrabutylammonium salt) with thermal ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

The crystal structure of 7 could only be obtained when it contained toluene as solvate. In the absence of toluene, the crystals rapidly turned amorphous, indicating that this solvent is necessary for lattice stabilization. This compound has a <sup>19</sup>F NMR chemical shift of -23.3 ppm and a <sup>29</sup>Si NMR chemical shift of -81.9 ppm similar to the values obtained by Haddad, -24.5 and -81.0 ppm respectively. The bond lengths and bond angles when compared to the empty octastyrenyloctasilsesquioxane cage **8**<sup>28</sup> follow a similar pattern to that observed previously. Again the fluorine atom is a centre of inversion for the octa-styrenyloctasilsesquioxane (tetrabutylammonium salt).

Substituted vinyl silsesquioxane cages have been prepared from the corresponding vinyl cage using a cross metathesis reaction catalyzed by Grubbs catalyst.<sup>29</sup> Whilst we found that this reaction worked perfectly well in our hands for the empty cages we were unable to carry out the cross metathesis reaction using the fluorideencapsulated octavinyloctasilsesquioxane cage with a range of alkenes. Subsequent cross metathesis reactions in the presence of tetrabutylammonium salts suggest that they deactivate the Grubbs catalyst and prevent further reaction.

We have also prepared the (E)-3-phenylprop-1enyltriethoxysilane,30,31 (E)-2-(naphthalen-2-yl)vinyltriethoxysilane and biphenylethenyltriethoxysilane from the corresponding 3-phenylprop-1-ene, 2-ethenylnaphthalene and 4-ethynylbiphenyl by reaction with triethoxysilane in the presence of a 3%solution of Karstedt's catalyst in xylene. Reaction of these trialkoxysilanes with tetrabutylammonium fluoride gave no cage compound but only 3-phenylpropene, 2-ethenylnaphthalene and 4-ethenylbiphenyl respectively, and fluorotriethoxysilane, suggesting that the 1-phenylpropene, 2-ethynylnaphthalene and 4-ethenylbiphenyl are too good a leaving group under the condition of nucleophilic substitution.

We also used Haddad's route<sup>16</sup> to try to synthesise  $T_8(4-vinylbiphenyl)_8TMAF$  (11) and  $T_8(2-vinylnaphthyl)_8TMAF$  (12). Firstly, we synthesized the  $T_8(4-vinylbiphenyl)_8$  (9) and the  $T_8(2-vinylnaphthyl)_8$  (10) using a cross-metathesis reaction. The cross-metathesis reactions were carried out using  $T_8(vinyl)_8$  and a 1st generation Grubbs catalyst, ([RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)<sub>2</sub>]) in DCM with 2-ethenylnaphthalene and 4-ethenylbiphenyl respectively (Scheme 1). The solvent was removed and the crude product was subjected to flash column chromatography. The products (9) and (10) were isolated in good yields, 78% and 75% respectively.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of these compounds confirm their complete conversion from the parent  $T_8(vinyl)_8$  compound. The <sup>29</sup>Si NMR spectra revealed a single peak for both compounds with chemical shifts of -78.02 ppm for **9** and -77.93 ppm for **10**.

These spectra confirm that all eight vinyl groups had been exchanged and this was further confirmed by MALDI ToF mass

 Table 4
 Selected bond distances and angles for compounds 7 and 8

	Crystal structure					
Compound	Mean Si · · · F (/Å)	Mean Si– $R(C_{sp2})$ (/Å)	Mean O–Si–O (/°)	Mean trans Si–Si (a) (/Å)	Mean Si–O (/Å)	Mean Si–O–Si (/°)
7	2.65	1.86	112.8	5.31	1.62	141.20
8	_	1.81	109.0	5.38	1.61	148.51
		$\begin{array}{c} 0 & -5i \\ 0 & -5i \\ 0 & 0 \\ 0 &$	$R = \frac{H_2C_2^2CH_2}{Grubbs Catalor Scheme Catalor$	$\begin{array}{c} & & & & \\ & & & \\ alyst \\ ion \\ R \end{array} \xrightarrow{R} \begin{array}{c} & & & \\$	$rac{1}{6}$	

Scheme 1 Synthesis of 9 and 10 by cross-metathesis.

spectrometry. The MALDI ToF mass spectra of **9** and **10** exhibit ions at m/z = 1849.5 and 1641.3 which correspond to the molecular mass of **9** and **10**.

The synthesis of compounds  $T_8(4$ -vinylbiphenyl)<sub>8</sub>TMAF (11) and  $T_8(2$ -vinylnaphthyl)<sub>8</sub>TMAF (12) was carried out in the same manner as that described by Haddad *et al.*<sup>16</sup> Unfortunately, both reactions led to insoluble resins after 5 min of stirring. The similar results obtained using both TBAF and TMAF highlight the delicate balance in substituent properties between the need to stabilize the cage and the weakening of the Si–C bond to substitution.

#### (c) sp<sup>3</sup> Alkyl substituted encapsulated cages

As reported previously we have tried to prepare fluorideencapsulated octaalkyloctasilsesquioxane<sup>20,21</sup> cage compounds from the corresponding alkyltriethoxysilane using tetrabutylammonium fluoride. In all cases we either obtained resin or empty cages. Interestingly when we used benzyltriethoxysilane the only product isolable was toluene *via* substitution at silicon by fluoride ion, again highlighting the balance of electronic properties.

An alternative approach is to start with the fluorideencapsulated octavinyl octasilsesquioxane cage and carry out a reaction that converts the  $sp^2$  carbon to an  $sp^3$  carbon. The three reactions we tried were bromination, hydrosilylation and cycloaddition. Bromination was carried out using bromine in carbon tetrachloride. We believe that the bromination led to an  $sp^3$ carbon adjacent to the silsesquioxane cage containing a fluoride ion which under the conditions of the reaction was not stable. Specifically, the fluoride ion attacks one of the cage silicon atoms leading to cage reorganization and resin formation.

The reaction of the empty octavinyloctasilsesquioxane cage under the same conditions gave the expected product. Hydrosilylation with triethylsilane and Speier's catalyst gave only resin. The reaction of the empty octavinyloctasilsesquioxane cage under the same conditions gave the expected product. The empty octavinyloctasilsesquioxane cage underwent cycloaddition with cyclopentadiene readily to give a complex mixture of stereoisomers of  $T_8[exo/endo-2-bicycloheptyl]_8$ a compound we have previously synthesized by reaction of *exo/endo-5-*(bicycloheptenyl)triethoxysilane with tetrabutylammonium fluoride.<sup>9</sup> However, reaction of the fluoride-encapsulated octavinyloctasilsesquioxane cage with cyclopentadiene gave no reaction suggesting that the cage deactivated the alkene dienophile to cycloaddition. Additionally, monofunctionalization of  $T_8[CH=CH_2]_8$ TBAF was performed using one equivalent of trifluoromethanesulfonic acid TfOH but gave only  $T_8[CH=CH_2]_8$ . The acid enabled the migration of the fluoride anion to the outside of the  $T_8[CH=CH]_8$  cage without breaking its framework. The reaction of the empty octavinyloctasilsesquioxane cage under the same conditions gave the addition product in good agreement with that reported by Feher *et al.*<sup>32</sup>

Haddad and coworkers<sup>16</sup> have prepared the fluorideencapsulated octaperfluorooctasilsesquioxane cages by treating the empty cage with tetramethylammonium fluoride. We carried out a similar synthesis based on our tetrabutyl ammonium fluoride strategy. Reaction with the corresponding perfluorotriethoxysilane gave the fluoride-encapsulated octaperfluorooctasilsesquioxane cages in good yield (90%). In fact these compounds were formed readily in solution and did not need the careful work up conditions typical of the aryl derivatives. Table 5 gives the NMR data of these compounds together with those reported by Haddad. Fig. 4 shows the crystal structure of the fluoride encapsulated octa(3,3,3-trifluoropropyl)octasilsesquioxane cage.

Selected structural data of the tetra-*n*-butylammonium octa-(3,3,3-trifluoropropyl)octasilsesquioxane fluoride T<sub>8</sub> cage and the corresponding empty cage, octa-(3,3,3-trifluoropropyl)octasilsesquioxane<sup>33,34</sup> are given in Table 6. The Si–O interatomic distances range from 1.62 to 1.63 Å. The O–Si–O angles indicate an almost regular tetrahedral coordination about silicon, ranging from 111.71° to 113.70° and the Si–O–Si angles from 139.57° to 141.71°.

A comparison of the crystal data of **13** with its non-encapsulated analogue which has been reported in the literature<sup>33,34</sup> as a THF solvate shows how fluoride ion entrapment inside the octasilsesquioxane cage causes the Si<sub>8</sub>O<sub>12</sub> cage framework to contract

Table 5 <sup>19</sup>F and <sup>29</sup>Si chemical shifts for a range of fluoride encapsulated perfluoroalkyloctasilsesquioxane cages

Alkyl group	Compound No	<sup>19</sup> F NMR chemical shift <sup><i>a</i>,<i>b</i></sup>	<sup>29</sup> Si NMR chemical shift <sup><i>a</i>, <i>c</i></sup>
CH <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub>	13	-28.4 (-28.7)	-70.9 (-66.7)
CH <sub>2</sub> CH <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	14	-28.2(-28,7)	-70.2(-66.9)
CH <sub>2</sub> CH <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	15	-28.4(-28,8)	-70.5 (-67.0)
CH <sub>2</sub> CH <sub>2</sub> CF	16	-28.3	-70.5

<sup>*a*</sup> Literature data<sup>16</sup> given in brackets. <sup>*b*</sup> Referenced to external CFCl<sub>3</sub> at 0 ppm. <sup>*c*</sup> The <sup>29</sup>Si NMR in acetone-d<sub>6</sub>.



**Fig. 4** X-ray crystal structure of the fluoride encapsulated octa-3,3,3-trifluoropropyloctasilsesquioxane (tetrabutylammonium salt) with thermal ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity.

slightly in the fluoride-containing cage. This slight contraction of the framework is illustrated by the shrinkage of the mean Si–O– Si bond angle as shown in Table 6, which is probably due to the repulsion of oxygen and fluoride atoms.

The O–Si–O bonds also increases and there is a slight lengthening of the Si–Csp<sup>3</sup> bond lengh, which is consistent with a weak silicon–fluoride interaction.

The symmetric unit of trifluoropropyl<sub>8</sub>T<sub>8</sub> contains two silicon atoms, Si(1) and Si(2), which are interconnected *via* an oxygen atom O(1). The fluoropropyl chain ( $\mathbf{R} = CH_2CH_2CF_3$ ) bonded to the Si(1) shows perfect ordering, while the other fluoropropyl chain bonded to the Si(2) shows two disordered positions. However, the symmetric unit for the trifluoropropyl<sub>8</sub>T<sub>8</sub>TBAF contains four silicon atoms, Si(1), Si(2), Si(3) and Si(4), which are interconnected *via* oxygen atoms O(1), O(3), O(5) and O(6). The fluoropropyl chain ( $\mathbf{R} = CH_2CH_2CF_3$ ) bonded to Si(1), Si(2), Si(3) and Si(4) all show perfect ordering. Again the fluorine atom is a centre of inversion for the octa-3,3,3-trifluoropropyl octasilsesquioxane (tetrabutylammonium salt). The crystal packing of the trifluoropropyl<sub>8</sub> $T_8$  showed an interesting long range Si  $\cdots$  F interaction (Fig. 5A). Each of the four symmetry-generated chains forms a dimeric contact with a neighbouring POSS molecule, with an intermolecular Si(1)  $\cdots$  F(3) distance of 3.48 Å. These contacts significantly influence the melting point properties (234–237 °C).

The crystal packing of the trifluoropropyl<sub>8</sub> $T_8TBAF$  (14) also show an interesting complex Si ··· F interaction (Fig. 5B). The intermolecular Si ··· F distance with the neighbouring POSS molecule is 3.55–4.37 Å. These contacts again significantly influence the melting point properties (143 °C).

### (d) Fluoride ion encapsulation within a $T_8$ cage using a tetraethylammonium fluoride

Another source of fluoride ion which is suitable for our cage synthesis and which is commercially available is tetraethylammonium fluoride (TEAF). We thus performed two separate experiments with different monomers, vinyltriethoxysilane and 1H, 1H, 2H, 2H-nonafluorohexyltriethoxysilane in toluene and in the presence of tetraethylammonium fluoride (Scheme 2). The two reactions were stirred for 24 h at room temperature. The compounds vinyl<sub>8</sub>T<sub>8</sub>TEAF (17) and nonafluorohexyl<sub>8</sub>T<sub>8</sub>TEAF (18) were obtained in 30 and 81% yield respectively.



**Scheme 2** The synthetic route to  $T_8R_8TEAF$ .

Table 6	Selected bond	distances and	angles for	compounds	T <sub>8</sub> (CH <sub>2</sub>	CH <sub>2</sub> CF <sub>3</sub>	) <sub>8</sub> TBAF	(13) and	T <sub>8</sub> (CH <sub>2</sub>	$CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$	$CF_3$
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	Si–O (Å)		0–Si–O (°)		Si–O–Si (°)	
Compound	Range	Mean	Range	Mean	Range	Mean
T <sub>8</sub> (CH <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub> ) <sub>8</sub> TBAF ( <b>13</b> ) T <sub>8</sub> (CH <sub>2</sub> CH <sub>2</sub> CF <sub>3</sub> ) <sub>8</sub>	1.62–1.63 1.61–1.62	1.625 1.615	111.71–113.70 108.59–110.06	112.7 109.32	139.57–141.71 144.29–154.95	140.64 149.62



**Fig. 5** (A) Packing diagram of trifluoropropyl<sub>8</sub> $T_8$  and (B) trifluoropropyl<sub>8</sub> $T_8$ TBAF along the *c*-axis showing the dimeric nature of the intermolecular Si  $\cdots$  F contacts. THF, TBAF and hydrogen molecules are omitted for clarity.

<sup>29</sup>Si-NMR and <sup>19</sup>F-NMR spectroscopy have been used to characterize the species formed. The <sup>29</sup>Si-NMR spectra of 17 and 18 both exhibited single sharp peaks with a chemical shift at -82.8ppm for 17 and at -72.2 ppm for 18. Additionally, the <sup>19</sup>F-NMR spectra of 17 and 18 displayed a peak corresponding to a fluoride ion encapsulated within a  $T_8$  cage. A small single peak at -28.17ppm probably corresponds to T<sub>8</sub>[CH<sub>2</sub>CH<sub>2</sub>(CF<sub>2</sub>)<sub>3</sub>CF<sub>3</sub>]<sub>7</sub>FTEAF due to nucleophilic attack of F- anion on a silicon atom. A small peak at -114.8 ppm can be attributed to free TBAF and the small peak at -132.0 ppm can be assigned to the Si-F related to the  $T_8[CH_2CH_2(CF_2)_3CF_3]_7FTEAF$  species. The compound T<sub>8</sub>[CH<sub>2</sub>CH<sub>2</sub>(CF<sub>2</sub>)<sub>7</sub>CF<sub>3</sub>]<sub>8</sub>TBAF has also been analyzed by MALDI mass spectrometry. The MALDI mass spectrum of  $T_8[CH_2CH_2(CF_2)_7CF_3]_8TEAF$  confirms the identity of the proposed compound. Unfortunately we could not obtain a single crystal X-ray structure of these two samples.

# (e) Migration of a fluoride ion from inside the cage to outside the cage without breaking the $T_8$ framework and the possibility of encapsulating other anions or cations within silsesquioxanes cages

**Reaction of T<sub>8</sub>[CH=CH]<sub>8</sub>TBAF and T<sub>8</sub>Ph<sub>8</sub>TBAF with triffic acid.** In principle the monofunctionalization<sup>32</sup> of T<sub>8</sub>[CH=CH<sub>2</sub>]<sub>8</sub> provides access to a wide range of potentially useful compounds. The T<sub>8</sub>[CH=CH<sub>2</sub>]<sub>8</sub>TBAF was reacted with one equivalent of triffic acid in a DCM/THF mixture to ensure the complete solubility of the cage. After 12 h, we expected to observe the monofunctionalization of one of the vinyl groups or cleavage of the Si–O–Si linkages and/or Si–C bonds. Surprisingly the <sup>1</sup>H, <sup>13</sup>C and <sup>29</sup>Si–NMR spectroscopy confirmed the structure of the product to be T<sub>8</sub>[CH=CH<sub>2</sub>]<sub>8</sub> and the <sup>19</sup>F-NMR confirmed the loss of the fluoride anion without apparent breaking of the Si<sub>8</sub>O<sub>12</sub> cage framework as suggested by Hossain, Pitmann and co-workers.<sup>35</sup> This was confirmed by the disappearance of the peak at –25 ppm in the <sup>19</sup>F-NMR spectrum.

The reaction of  $T_8Ph_8TBAF$  was carried out using similar conditions. The  $T_8Ph_8TBAF$  in THF was reacted with one equivalent of acid. After 12 h the solution became cloudy and a white solid precipitated. The solvent was removed leaving a

white insoluble solid. The <sup>19</sup>F-NMR spectrum (in acetone-d<sub>6</sub>) displayed peaks at -79.02 ppm (CF<sub>3</sub>, CF<sub>3</sub>SO<sub>3</sub>H), -134.44 and -134.73 ppm which correspond to free TBAF. However, the peak at -25 ppm corresponding to isolated fluoride ion within the T<sub>8</sub> cage, had disappeared. The <sup>29</sup>Si-NMR gave a peak at -79.6 ppm corresponding to the formation of T<sub>8</sub>Ph<sub>8</sub>.

**Reaction of T<sub>8</sub>[CH=CH<sub>2]8</sub>TBAF with** *p***-toluenesulfonic acid monohydrate. We also examined the effect of a weaker acid than triflic acid (pK\_a \sim -15), that is** *p***-toluenesulfonic acid monohydrate (TsOH·H<sub>2</sub>O, pK\_a = -2.8) on T<sub>8</sub>[CH=CH<sub>2</sub>]<sub>8</sub>TBAF. The T<sub>8</sub>[CH=CH<sub>2</sub>]<sub>8</sub>TBAF in THF was reacted with one equivalent of TsOH·H<sub>2</sub>O. The reaction was stirred at room temperature for 12 h. After the solvent was removed, the <sup>29</sup>Si-NMR spectrum showed two peaks at -79.82 (integration: 11) which corresponds to T<sub>8</sub>Vi<sub>8</sub> and at -82.83 ppm (integration: 89) which corresponds to T<sub>8</sub>Vi<sub>8</sub>TBAF. The <sup>19</sup>F-NMR spectrum displayed a very intense single sharp peak at -25.95 ppm corresponding to T<sub>8</sub>Vi<sub>8</sub>TBAF.** 

The mechanism governing this migration is not yet clearly understood. A possible mechanism for this unusual migration involves the proton complexing with the  $F^-$  ion and pulling it out of the cage as shown in (Scheme 3).

#### (f) Ion exchange

Having developed a methodology for the migration of a fluoride anion through the face of the cage without breaking its structure, based on the proton, we decided to examine different cations. Specifically, we examined the reaction with lithium tetraphenylborate (LiPh<sub>4</sub>B), lithium iodide (LiI), caesium iodide (CsI), potassium iodide (KI) and sodium iodide (NaI).

**T<sub>8</sub>[CH=CH<sub>2</sub>]<sub>8</sub>TBAF reaction with lithium tetraphenylborate.** The T<sub>8</sub>[CH=CH<sub>2</sub>]<sub>8</sub>TBAF was dissolved in THF, and an excess of lithium tetraphenylborate was added to the solution. The reaction was stirred at room temperature for 12 h. The solution became cloudy and a white precipitate was observed due to the formation of LiF. After removing the solvent, the <sup>29</sup>Si-NMR spectrum (acetone-d<sub>6</sub>) revealed two sharp peaks, one at



Scheme 3 The proposed mechanism of migration of the  $F^-$  ion outside of the  $T_8$  cage.

-79.85 ppm, which can be attributed to T<sub>8</sub>Vi<sub>8</sub>, and another at -82.86 ppm, corresponding to the T<sub>8</sub>Vi<sub>8</sub>-TBAF cage.

The <sup>19</sup>F-NMR (acetone-d<sub>6</sub>) spectrum exhibited a single sharp peak at -25.94 ppm which can be assigned to the unchanged T<sub>8</sub>[CH=CH<sub>2</sub>]<sub>8</sub>TBAF.

Clearly, the lithium tetraphenylborate can cause the migration of the fluoride ion through the face of the  $T_8$  cage. The lithium iodide gave the same result as lithium tetraphenylborate. However, sodium, caesium or potassium iodide did not cause fluoride migration from inside the cage as confirmed by the <sup>29</sup>Si-NMR and <sup>19</sup>F-NMR spectra.

The mechanism governing this migration is not yet clearly understood, but probably involves the lithium complexing with the  $F^-$  ion and pulling it out of the cage.

### (g) The possibility of encapsulating another anion within a silsesquioxanes cage

Numerous analogues of TBAF are available, such as tetra*n*-butylammonium bromide (TBABr), tetra-*n*-butylammonium chloride (TBACl) and tetra-*n*-butylammonium hydroxide (TBAOH). We chose phenyltriethoxysilane as the monomer and TBABr, TBAI, TBACl and tetraethylammonium hydroxide (TEAOH, with 35% by weight of water) as sources of anions. We conducted the reactions of phenyltriethoxysilane with these different anions in toluene, apart from TBAOH·3H<sub>2</sub>O which was carried out with vinyltriethoxysilane in toluene. After stirring for 24 h, the reactions were stopped and the solvent removed at 80 °C under a vacuum of 70 mbar (Scheme 4). The crude products of the reactions were analyzed by <sup>29</sup>Si-NMR spectroscopy.



**Scheme 4** The attempted synthetic route to  $X^-@T_8R_8$ .

The <sup>29</sup>Si-NMR spectra of the TBABr, TBAI, TBACl reactions revealed only the peak for phenyltriethoxysilane (-58.7 ppm). The <sup>29</sup>Si-NMR spectrum (in CDCl<sub>3</sub>) of the reaction of vinyltriethoxysilane with TBAOH.3H<sub>2</sub>O exhibited a number of peaks in the Si–T region. However, there are three major peaks with chemical shifts at -72.0, -73.3 and -82.5 ppm. Unfortunately, we could not obtain a single crystal X-ray structure or MS data for this sample as we observed its quick degradation to a resin like material. Thus, it is not possible to confirm the presence of a hydroxide encapsulated T<sub>8</sub> cage.

#### Conclusion

We have shown the utility of our TBAF synthesis of fluoride encapsulated cages and expanded the repertoire of substituted aryl cages. We have synthesized and obtained the crystal structure of the styrenyl derivative and shown the limitation of other methods of synthesis of vinyl fluoride encapsulated cages such as cross metathesis. In the past, we have been unable to synthesize an encapsulated fluoride ion within a silsesquioxane cage in which the pendant groups attached to the cage silicon atoms are connected via an sp<sup>3</sup> hybridized carbon atom. We have described a facile, single step, preparation of a fluoride ion encapsulated within a fluorinated polyhedral oligomeric silsesquioxane (F-POSS@F-) in which the silicon atoms of the pendant groups are connected *via* an sp<sup>3</sup> hybridized carbon atom. We have also demonstrated the capricious nature of sp<sup>3</sup> substituents and the need for a balance between an electron withdrawing group to stabilize the cage whilst not acting as a good leaving group. Further work will involve looking at other electron withdrawing groups, their properties and their synthetic utility. We demonstrated that a strong acid and lithium salt can lead to the migration of a fluoride ion through the face of the  $T_8$  cage without breaking the Si<sub>8</sub>O<sub>12</sub> structure. An attempt to remove the fluoride ion with different cationic salts such as LiI, NaI, LiPh<sub>4</sub>B was unsuccessful. We also failed to encapsulate anions such as bromide, chloride and iodide, within an octasilsesquioxane cage.

#### Experimental

#### Synthesis of tetra-*n*-butylammonium octa(*para*-chlorophenyl)octasilsesquioxane fluoride (3)

4-Chlorophenyltriethoxysilane (1 g, 3.63 mmol, 2 equiv) was dissolved in dry toluene (20 cm<sup>3</sup>) then tetra-*n*-butylammonium fluoride (1.82 cm<sup>3</sup> of 1 M solution in THF with 5% water, 1 equiv)

was added. The mixture was stirred at room temperature for 24 h, the reaction was stopped and the solvent removed on a rotary evaporator with a temperature gradient from 30 °C to 80 °C over 10 min, then leaving at 80 °C and a vacuum of 80 mbar for 15 min. A yellow solid gel was obtained. The solid was subjected to flash column chromatography on silica gel, eluting with acetone/hexane: 3/7 ( $R_{\rm f}$  0.42). The compound was obtained as a white solid. Recrystallization from acetone/hexane offered colourless crystals (0.4 g, 56%). Mp > 400 °C. (Found: C, 48.72; H, 4.47. Calcd. for  $C_{64}H_{68}Cl_8FNO_{12}Si_8$ : C, 48.94; H, 4.59%).  $\delta_{\rm H}$  $(300 \text{ MHz}; \text{ acetone-d}_6; \text{ Me}_4\text{Si}) 7.73 \text{ (d, }^3J_{\text{HH}} = 8.4 \text{ Hz}, 16\text{H}, \text{Ar-}H),$ 7.35 (d,  ${}^{3}J_{HH} = 8.22$  Hz, 16H, Ar-H), 3.46–3.40 (m, 8H, N-CH<sub>2</sub>), 1.87–1.76 (m, 8H,  $CH_{2}$ ), 1.49–1.28 (m, 8H,  $CH_{2}$ ), 0.97 (t,  ${}^{3}J_{HH} =$ 7.32 Hz, 12H, CH<sub>3</sub>). δ<sub>C</sub> (75.5 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 136.4 (*i*-C), 136.1 (o-CH of Ar), 135.9 (p-C of Ar), 128.5 (m-CH of Ar), 59.4 (*N*-*C*H<sub>2</sub>), 24.4 (*C*H<sub>2</sub>), 20.4 (*C*H<sub>2</sub>), 13.8 (*C*H<sub>3</sub>). δ<sub>si</sub> (79.3 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -80.7.  $\delta_{\rm F}$  (376 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -27.2  $(89\% \text{ integration ratio})[(4-ClC_6H_4)_8T_8-TBAF], -26.34 \text{ ppm}(11\%)$ [ $(4-ClC_6H_4)_{8-n}F_nT_8-TBAF$ ].

m/z (MALDI-TOF): 1326.6 ([M-TBA]<sup>-</sup>, 100%), 1230.6 ([T<sub>8</sub>(4-ClC<sub>6</sub>H<sub>4</sub>)<sub>7</sub>F-TBA], 18%). X-ray data are given in the supporting materials.

#### Synthesis of 4-bromophenyltriethoxysilane

A three-necked 500 cm<sup>3</sup> round bottomed flask equipped with a pressure-equalizing dropping funnel, a reflux condenser, and a magnetic stir bar was charged with magnesium turnings (2.02 g, 84.78 mmol, 1 equiv) and was flame-dried in vacuo under vigorous stirring (3 times). After back filling with argon, THF (100 cm<sup>3</sup>) were added followed by dropwise addition of a solution of 1,4dibromobenzene (20 g, 84.78 mmol) in THF (100 cm<sup>3</sup>). Ice-cooling was needed at the beginning of the Grignard reaction in order to ensure a gentle reflux. After complete addition, the reaction was maintained for 30 min at ambient temperature. The highly viscous suspension was decanted from the excess of magnesium and transferred to a pressure-equalizing dropping funnel. A second three-necked 500 cm<sup>3</sup> round bottomed flask equipped with the above pressure-equalizing dropping funnel, a reflux condenser and a magnetic stir bar was charged with tetraethyl orthosilicate (35.32 cm<sup>3</sup>, 169.56 mmol, 2 equiv). The Grignard reagent was added dropwise and the resulting reaction mixture maintained for 18 h at 66 °C. The reaction mixture was allowed to return to ambient temperature and filtered using a sinter funnel. The filter cake was washed with n-pentene and the organic solvent was evaporated off under reduced pressure. The crude product was distilled (94 °C at 0.1 mmHg) affording (14 g, 52%) as colourless liquid.  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.55–7.48 (m, 5H, Ar-H), 3.86 (t,  ${}^{3}J_{HH} =$ 7.14 Hz, 6H, O-C $H_2$ ), 1.23 (t,  ${}^{3}J_{\rm HH}$  = 6.96 Hz, 9H, C $H_3$ ).  $\delta_{\rm C}$  (75.5 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 136.4 (*i*-C of Ar), 131.2 (*o*-C of Ar), 127.9 (m-C of Ar), 125.4 (p-C of Ar), 58.8  $(O-CH_2)$ , 18.3  $(CH_3)$ .  $\delta_{Si}$  (79.3 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): – 58.4 (lit.<sup>36</sup>)

#### Synthesis of tetra-*n*-butylammonium octa(*para*-bromophenyl)octasilsesquioxane fluoride (4)

4-Bromophenyltriethoxysilane (1.59 g, 5 mmol, 2 equiv) was dissolved in dry toluene (20 cm<sup>3</sup>) then tetra-*n*-butlyammonium fluoride (2.5 cm<sup>3</sup> of 1 M solution in THF with 5% water, 1 equiv)

was added. The mixture was stirred at room temperature for 24 h, the reaction was stopped and the solvent removed on a rotary evaporator with a temperature gradient from 30 °C to 80 °C over 10 min, then leaving at 80 °C and a vacuum of 70 mbar for 15 min. A yellow solid gel was obtained. The solid was subjected to flash chromatography column on silica gel, eluting with acetone/hexane: 3/7 (retention factor  $R_{\rm f}$  0.42). Recrystallization from acetone/hexane gave 0.2 g (17% yield) of a white crystalling material. Mp > 400 °C. (Found: C, 39.92; H, 3.48. Calcd. for C<sub>64</sub>H<sub>68</sub>Br<sub>8</sub>FNO<sub>12</sub>Si<sub>8</sub>: C, 40.20; H, 3.58%). δ<sub>H</sub> (300 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 7.66 (d,  ${}^{3}J_{HH} = 8.4$  Hz, 16H, Ar-H), 7.08 (d,  ${}^{3}J_{HH} = 8.4$  Hz, 16H, Ar-H), 3.47-3.43 (m, 8H, N-CH<sub>3</sub>), 1.90–1.79 (m, 8H, CH<sub>2</sub>), 1.50–1.40 (m, 8H, CH<sub>2</sub>), 0.98 (t,  ${}^{3}J_{\rm HH}$  = 7.32 Hz, 12H, CH<sub>3</sub>).  $\delta_{\rm C}$  (75.5 MHz; acetoned<sub>6</sub>; Me<sub>4</sub>Si): 136.8 (i-C of Ar), 136.4 (o-CH of Ar), 131.4 (m-CH of Ar), 127.1 (p-C of Ar), 59.3 (N-CH<sub>2</sub>), 24.3 (CH<sub>2</sub>), 20.4  $(CH_2)$ , 13.8  $(CH_3)$ .  $\delta_{si}$  (79.3 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -80.6 ppm.  $\delta_{\rm F}$  (376 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -26.9 (12% integration) [(4-BrPh)<sub>8-n</sub>F<sub>n</sub>T<sub>8</sub>-TBAF], -27.1 (10%) [(4-BrPh)<sub>8-n</sub>F<sub>n</sub>T<sub>8</sub>-TBAF], -27.2 (67% integration) [(4-BrlPh)<sub>8</sub>T<sub>8</sub>-TBAF], -28.6 ppm (11%) [(4- $BrPh_{10-n}F_nT_{10}-TBAF$ ]. *m*/*z* (MALDI-TOF): 1682.3 ([M-TBA]<sup>-</sup>, 100%) 1546.4 ([T<sub>8</sub>(4-BrC<sub>6</sub>H<sub>4</sub>)<sub>7</sub>F-TBA]<sup>-</sup>, 8%).

#### Synthesis of tetra-*n*-butylammonium octa(*para*-methoxyphenyl)octasilsesquioxane fluoride (5)

Methoxyphenyltriethoxysilane (1.01 g, 3.73 mmol, 1.49 equiv) was dissolved in dry toluene (20 cm<sup>3</sup>) then tetra-n-butlyammonium fluoride (2.5 cm<sup>3</sup> of 1 M solution in THF with 5% water, 1 equiv) was added. The mixture was stirred at room temperature for 24 h. The reaction was stopped and the solvent removed on a rotary evaporator with a temperature gradient from 30 °C to 80 °C over 10 min, then leaving at 80 °C and a vacuum of 70 mbar for 15 min. A yellow solid gel was obtained. The solid was subjected to flash chromatography column on silica gel, eluting with (acetone/hexane: 2/1) ( $R_{\rm f}$  0.67). The product was obtained as a white solid. Recrystallization from CH<sub>3</sub>CN/CHCl<sub>3</sub> gave (0.4 g, 56%). Mp > 350 °C. (Found: C, 56.53; H, 5.96. Calc. for C<sub>72</sub>H<sub>92</sub>FNO<sub>20</sub>Si<sub>8</sub>: C, 56.33; H, 5.87%). v<sub>max</sub> (Nujol)/cm<sup>-1</sup>: 2921  $(v_{\text{C-H}})$ , 2852  $(v_{\text{C-H}})$ , 1595, 1537, 1503, 1280  $(v_{\text{C-O}})$ , 1249, 1098  $(v_{as(Si-O-Si)}), 1003, 797(v_{C-H}), 691(v_{C-H}), 674. \delta_{H} (300 \text{ MHz}; \text{CD}_{3}\text{CN};$ Me<sub>4</sub>Si): 7.61 (d,  ${}^{3}J_{HH} = 8.61$  Hz, 16H, Ar-H), 6.87 (d,  ${}^{3}J_{HH} =$ 8.79 Hz, 16H, Ar-H), 3.09-3.03 (m, 8H, N-CH<sub>3</sub>), 2.14 (s, 24H, Ar-O-CH<sub>3</sub>), 1.64–1.53 (m, 8H, CH<sub>2</sub>), 1.40–1.28 (m, 8H, CH<sub>2</sub>), 0.96 (t,  ${}^{3}J_{HH} = 7.32$  Hz, 12H, CH<sub>3</sub>).  $\delta_{C}$  (75.5 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si):161.7 (p-C of Ar), 136.4 (i-C of Ar), 131.0 (m-CH of Ar), 113.7 (o-CH of Ar), 59.1 (N-CH<sub>2</sub>), 24.5 (Ar-O-CH<sub>3</sub>), 24.3 (CH<sub>2</sub>), 20.2 (CH<sub>2</sub>), 13.7 (CH<sub>3</sub>).  $\delta_{si}$  (79.3 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -80.2.  $\delta_{\rm F}$  (376 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -27.6. *m/z* (MALDI-TOF): 1292.2 ([M-TBA]<sup>-</sup>, 100%). X-ray data are given in the supporting materials.

#### Synthesis of β-(*trans*)-styryltriethoxysilane

Phenylacetylene (11.80 g, 115.52 mmol) was added to triethoxysilane (27.60 g, 168.06 mmol, 1.45 equiv) in dry toluene (60 cm3) together with 0.5 cm3 of a 3% solution of Karstedt's catalyst (Ptdivinyltetramethyldisiloxane complex) in xylene, the mixture was refluxed for 12 h under argon. The solvent was removed under vacuum. A yellow oil was obtained (28 g, 91%) as a mixture of  $\beta$ -(*trans*)-styryltriethoxysilane and  $\alpha$ -(*cis*)-styryltriethoxysilane. The mixture was distilled under vacuum (96 °C at 0.1mmHg) gave  $\beta$ -(*trans*)-styryltriethoxysilane (20 g, 65%) as colourless liquid.  $\delta_{\rm H}$ (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.84–7.25 (m, 5H; Ph), 7.21 (d, 3JH,H = 19.41 Hz, 16H; SiCH=CHPh), 6.17 (d, 3JH,H = 9.41 Hz, 8H, PhCH=CHSi), 3.88 (q, 3JH,H = 6.6 Hz, 6H, O-CH2), 1.27 (t, 3JH,H = 7.5 Hz, 9H, CH3).

 $δ_{\rm C}$  (75.5 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 149.2 (PhCH=CHSi). 137.7 (*i*-C of Ar), 128.76 (*m*-CH of Ar), 128.6 (*p*-Cof Ar), 126.8 (*o*-CH of Ar), 117.8 (SiCH=CHPh), 50.6 (*O*-CH2), 18.3 (CH3).  $\delta_{\rm Si}$  (79.3 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): -56.5 (β-*trans*-addition), -59.7 (α-*cis*). (lit.37–38)

#### Synthesis of tetra-*n*-butylammonium octa-(β-styryl)octasilsesquioxane fluoride (7)

β-Styryltriethoxysilane (1.33 g, 5 mmol, 2 equiv) was dissolved in dry toluene (20 cm<sup>3</sup>) then tetra-n-butylammonium fluoride (2.5 cm<sup>3</sup> of 1 M solution in THF with 5% water, 1 equiv) was added. The mixture was stirred at room temperature for 24 h and the solvent removed on a rotary evaporator with a temperature gradient from 30 °C to 80 °C over 10 min, then leaving at 80 °C and a vacuum of 80 mbar for 15 min. A yellow solid gel was obtained (1.76 g). Recrystallization from solvent chloroform/toluene gave a colourless crystalline solid (0.10 g, 11%).  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>;  $Me_4Si$ ) 6.35 (d,  ${}^{3}J_{H,H}$  = 19.05 Hz, 8H; CH=CH-Si), 7.22 (d,  ${}^{3}J_{H,H}$  = 18.84 Hz, 8H; CH=CH-Ph), 7.38-7.27 (m, 24H; Ph-H), 7.51 (d,  ${}^{3}J_{H,H} = 7.32$  Hz, 16H; Ph-H), 3.19–3.13 (t,  ${}^{3}J_{H,H} = 8.04$  Hz, 2H, N-CH<sub>2</sub>) 1.62–152 (m, 12H, CH<sub>2</sub>) 1.36–1.31 (m, 12H, CH<sub>2</sub>), 0.95 (t,  ${}^{3}J_{HH} = 7.35$  Hz, 3H, CH<sub>3</sub>).  $\delta_{C}$  (75.5 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 144.7 (i-C of Ph), 138.8 (m-CH of Ph), 128.4 (p-C of Ph), 127.7 (o-CH of Ph), 126.6 (PhCH=CHSi), 125.5 (SiCH=CHPh), 58.7  $(N-CH_2)$ , 24.8  $(CH_2)$ , 19.7  $(CH_2)$ , 13.7  $(CH_3)$ .  $\delta_{si}$  (79.3 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): -81.3.  $\delta_F$  (376 MHz; CD<sub>2</sub>Cl<sub>2</sub>; Me<sub>4</sub>Si): -23.2, -23.3, -30.3. m/z (MALDI-TOF): 1070.3 ([styryl<sub>6</sub>F<sub>2</sub>T<sub>8</sub>-TBA]<sup>-</sup>, 15%), 1178.1 ([styryl<sub>7</sub>FT<sub>8</sub>-TBA]<sup>-</sup>, 25%), 1261.2 ([styryl<sub>8</sub>T<sub>8</sub>-TBA]<sup>-</sup>, 100%), 1486.2 ([styryl<sub>2</sub>FT<sub>10</sub>-TBA]<sup>-</sup>, 7%). X-ray data are given in the supporting materials.

#### Synthesis of biphenylethenyltriethoxysilane

4-Ethynylbiphenyl (10 g, 56.11 mmol), was dissolved in dry toluene (40 ml) added to triethoxysilane (9.67 g, 58.91 mmol, M = 164.27 g mol<sup>-1</sup>, 1.05 equiv) and 200 µl of a 3% solution of Karstedt's catalyst (Pt-divinyltetramethyldisiloxane complex) in xylene. The mixture was refluxed for one day under argon. The solvent was removed under vacuum. Yellow oil was obtained (22.13 g). The crude product was distilled (196 °C at 0.4mmHg) to afford a colourless liquid (13.45 g, 70% of β-*trans*-addition).

(Found C, 70.10; H, 7.59; O, 14.13; Si, 8.20 calcd for  $C_{20}H_{26}O_3Si$ C, 70.13; H, 7.65; O, 14.01; Si, 8.20%).  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.49–7.44 (m, 10H; C<sub>6</sub>H<sub>4</sub>-Ph), 7.21 (d, <sup>3</sup>J<sub>H,H</sub> = 19.23 Hz, 16H; CH=CH C<sub>6</sub>H<sub>4</sub>), 6.12 (d, <sup>3</sup>J<sub>H,H</sub> = 19.23 Hz, 8H, CH=CHSi), 3.80 (q, <sup>3</sup>J<sub>H,H</sub> = 6.96 Hz, 6H, O-CH<sub>2</sub>), 1.18 (t, <sup>3</sup>J<sub>H,H</sub> = 7.5 Hz, 9H, CH<sub>3</sub>).  $\delta_{\rm C}$  (75.5 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 148.50, 142.65, 141.39, 136.61, 128.70, 127.36, 127.15, 127.14, 126.59, 117.69, 58.65, 18.06.  $\delta_{\rm Si}$  (79.3 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): -56.5 (β-*trans*-addition). m/z (ESI): 342.20.

#### Synthesis of T<sub>8</sub>(biphenylethyl)<sub>8</sub> (9)

Octavinyloctasilsesquioxane (Vi<sub>8</sub>T<sub>8</sub>) (0.5 g, 0.79 mmol) and 4vinylbiphenyl (2.56 g, 14.21 mmol, 18 equiv), in a 1:24 ratio were added to a solution of [RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)<sub>2</sub>](Grubbs Catalyst, 1st generation) (26 mg,  $M = 822.96 \text{ g mol}^{-1}$ , 0.5 mol% per vinyl silyl group) in CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred under gentle reflux for 6 days. The reactions were performed under an argon atmosphere. After the disappearance of the signal assigned to Vi<sub>8</sub>T<sub>8</sub> was confirmed by <sup>1</sup>H NMR spectroscopy, the volatiles were evaporated and the residue was subjected to short column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub>). The volatiles were evaporated and the residue dried in vacuum to give a white powder (1.14 g, 78% yield). Mp > 400 °C. (Found C, 72.56; H, 5.00.calcd for  $C_{112}H_{88}O_{12}Si_8$ : C, 72.69; H, 4.79%).  $v_{max}(Nujol)/cm^{-1}$ : 2725, 1604, 1567, 1306, 1270, 1203, 1148, 1074 (Vas(Si-O-Si)), 985, 889, 849, 797, 722 ( $v_{s(Si=O-Si)}$ ).  $\delta_{H}$  (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.66–7.15 (m, 80H, Ph-CH=CHSi +  $C_6H_5$ ), 6.40 (d,  ${}^{3}J_{HH} = 19.23$  Hz, 8H, CH=CH-Si).  $\delta_{C}$  (75.5 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 148.8, 141.7, 140.5, 136.4, 128.8, 127.46, 127.3, 127.0, 117.5.  $\delta_{si}$  (79.3 MHz; dichloromethane-d<sub>2</sub>; Me<sub>4</sub>Si): -78.0. m/z (MALDI-TOF): 1856.5 ([M+Li]<sup>+</sup>, 65%), 1849.5 ([M<sup>+</sup>]; 100%), 1671.4 ([M-vinylbiphenyl]<sup>+</sup>, 77%).

#### Synthesis of T<sub>8</sub>(2-naphthylvinyl)<sub>8</sub> (10)

Octavinyloctasilsesquioxane (0.5 g, 0.79 mmol) and 2vinylnaphthalene (2.92 g, 18.96 mmol, 24 equiv) were added to a solution of [RuCl<sub>2</sub>(=CHPh)(PCy<sub>3</sub>)<sub>2</sub>] (Grubbs Catalyst, 1st generation) (32 mg, 0.5 mol% per vinyl silyl group) in CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred under gentle reflux for 6 days and the reactions were performed under an argon atmosphere. After the disappearance of the signal assigned to  $Vi_8T_8$  was confirmed by <sup>1</sup>H NMR spectroscopy, the volatiles were evaporated and the residue was subjected to short column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub>). The volatiles were evaporated and the residue dried in vacuum to afford white powder, (0.79 g, 75%). Mp 267-270 °C. (Found: C, 70.31; H, 4.40. Calc. for C<sub>112</sub>H<sub>88</sub>O<sub>12</sub>Si<sub>8</sub>: C, 70.21; H, 4.42%). *v*<sub>max</sub> (Nujol)/cm<sup>-1</sup>: 2852, 1602, 1201, 1096 (*v*<sub>as(Si-O-Si)</sub>), 988, 829, 755 ( $v_{s(Si-O-Si)}$ ).  $\delta_{H}$  (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.86–7.71 (m, 4H, Ar-*H*), 7.65 (d,  ${}^{3}J_{HH}$  = 19.24 Hz, 1H, Ar-*H*), 7.51–7.42 (m, 3H, Ar-*H*), 6.54 (d, 1H,  ${}^{3}J_{HH}$  = 19.24 Hz, Ar-*H*).  $\delta_{\rm C}$  (75.5 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 149.7, 133.7, 128.4, 128.3, 128.0, 127, 126.3, 123.3, 117.7.  $\delta_{s_i}$  (79.3 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): -77.93 ppm. m/z (MALDI-TOF): 1641.3 ([M<sup>+</sup>], 100%), 1488.3 ([M-vinylnaphthalene]<sup>+</sup>, 75%).

#### Synthesis of octa(exo/endo-2-(bicycloheptenyl)silsesquioxane

In a 250 cm<sup>3</sup> round bottom flask connected to a condenser were placed freshly distilled cyclopentadiene (from cracking dicyclopentadiene) (10 g, 151.28 mmol) and  $T_8Vi_8$  (0.5 g, 0.79 mmol). After standing for 30 min at room temperature, the mixture was heated at reflux for 4 h, during which time the reaction temperature rose to 170 °C. The cyclopentadiene appeared to be consumed. As confirmed by the disappearance of the signal assigned to  $Vi_8T_8$  in the <sup>1</sup>H NMR spectrum. Two-thirds of the cyclopentadiene was removed by distillation and the residual solution cooled to room temperature. The product was precipitated from the solution by the addition of excess alcohol, and dried at 60 °C. The product was purified by column chromatography (SiO<sub>2</sub>-hexane) (0.64 g, 70% yield).  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 1.07 (2H, m, SiCHCH<sub>2</sub>), 1.30 (1H, m, SiCHCH<sub>2</sub>CH), 1.83 (1H, m, SiCH), 2.81 (1H, m, SiCHCHCH<sub>2</sub>), 2.9 (1H, m, SiCHCHCH<sub>2</sub>), 5.93 (2H, m, CH=CH).  $\delta_{\rm C}$  (75.5 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 21.5 (SiCH), 26.8 (SiCHCH<sub>2</sub>), 42.4 (SiCHCH), 44.2 (SiCHCH<sub>2</sub>CH), 50.7 (SiCHCHCH<sub>2</sub>), 133.8 (CH=CH), 135.6 (CH = CH).  $\delta_{\rm Si}$  (79.3 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): -66.6, -66.7, -67.2, -67.4, -68.0, -68.3, -68.6, -68.8, -68.9 (lit.<sup>9</sup>).

#### Synthesis of T<sub>8</sub> (CH<sub>2</sub>CH<sub>2</sub>SiEt<sub>3</sub>)<sub>8</sub>

Vi<sub>8</sub>T<sub>8</sub> (200 mg, 0.31 mmol) and triethylsilane (295.73 mg, 2.54 mmol, 8.05 equiv) in toluene (20 cm<sup>3</sup>) were added to a 250 cm<sup>3</sup> round bottom flask together with 200 µl of a 3% solution of Karstedt's catalyst (Pt-divinyltetramethyldisiloxane complex) in xylene. The mixture was stirred and heated at 80 °C for 16 h. The reaction was followed by <sup>1</sup>H NMR spectroscopy and the reaction was stopped after the disappearance of the signal assigned to the vinyl group of the  $Vi_8T_8$ . The solvent was removed under vacuum. The product was purified using a silica gel column with hexane/AcOEt (9/1) as eluent to obtain the title compound as a waxy solid (0.44 g, 90%). Mp 229-231. (Found C, 49.14; H, 9.90.calcd for C<sub>64</sub>H<sub>152</sub>O<sub>12</sub>Si<sub>16</sub>: C, 49.17; H, 9.80%). *v*<sub>max</sub> (Nujol)/cm<sup>-1</sup>: 2923, 2853, 1463, 1415, 1377, 1120 (*v*<sub>as(Si-O-Si)</sub>), 1014, 752 ( $v_{s(Si-O-Si)}$ ), 713.  $\delta_{H}$  (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 0.98-0.87(m, 80H, CH<sub>2</sub>), 0.61–0.45 (m, 72H, CH<sub>3</sub>).  $\delta_{\rm C}$  (75.5 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 7.5 (Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 4.5 (SiCH<sub>2</sub>CH<sub>2</sub>SiEt<sub>3</sub>), 2.9  $(Si(CH_2CH_3)_3)$ , 2.3  $(SiCH_2CH_2SiEt_3)$ .  $\delta_{Si}$  (79.3 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 8.9 (CH<sub>2</sub>CH<sub>2</sub>SiEt), -65.8 (Si-T<sub>8</sub>). m/z (MALDI-TOF): 1670.7 ([M+Ag]<sup>+</sup>), 1533.7 7 ([M-CH<sub>2</sub>CH<sub>3</sub>]<sup>+</sup>)

#### Synthesis of octa(1,2-dibromoethyl)octasilsesquioxane

A solution of (0.86 g, 5.37 mmol, 8.1 equiv) of bromine in carbon tetrachloride (5 cm<sup>3</sup>) was added dropwise to a solution of Vi<sub>8</sub>T<sub>8</sub> (0.42 g, 0.66 mmol) in (10 cm<sup>3</sup>) carbon tetrachloride cooled in an ice bath. After addition the reaction was stirred overnight at room temperature under argon. The reaction mixture was evaporated to dryness, and the residue was washed with cold pentane to give a yellow solid (1.10 g, 88%). Mp 289–292 °C. (Found: C, 10.39; H, 1.73. Calc. for C<sub>16</sub>H<sub>16</sub>Br<sub>16</sub>O<sub>12</sub>Si<sub>8</sub>: C, 10.10; H, 1.85%). $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 3.98–3.94 (m, 1H; CH<sub>2</sub>-Br), 3.84–3.79 (m, 1H; CH<sub>2</sub>-Br), 3.60–3.56 (m, 1H; Si-CH-Br).  $\delta_{\rm C}$  (75.5 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): 31.6 (s, CH<sub>2</sub>-Br), 29.9, 29.9, 29.8, 29.7 (m, Si-CH-Br).  $\delta_{\rm Si}$  (79.3 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si): -78.7.

#### Synthesis of tetra-*n*-butylammonium octa(3,3,3-trifluoropropyl)octasilsesquioxane fluoride (13)

To a stirred solution of (3,3,3-trifluoropropyl)trimethoxysilane (1.05 g, 4.81 mmol, 2 equiv) in dry toluene (20 cm<sup>3</sup>) was added TBAF (2.40 cm<sup>3</sup>, 2.40 mmol of 1 M solution in THF with 5% water, 1 equiv) at room temperature. The mixture was stirred at reflux for 16 h under argon, the reaction was stopped and hexane (150 cm<sup>3</sup>) was added to the mixture. The cloudy solution was transferred to the freezer (-20 °C). A colourless oil was obtained and the hexane phase was separated from it. The oil was subjected to flash chromatography on a silica gel column, eluting with (acetone/hexane: 3/7) ( $R_{\rm f}$  0.11). Recrystallization from chloroform–acetone afforded colourless crystals (0.71 g, 81%)

yield). Mp 142–143 °C (from chloroform). (Found: C, 33.09; H, 4.60. Calcd. for  $C_{24}H_{32}F_{25}O_{12}Si_8$ : C, 33.03; H, 4.71%).  $v_{max}$  (Nujol)/cm<sup>-1</sup>: 2920, 2852, 1462, 1454, 13763, 1313, 1267, 1209, 1102, 1061 ( $v_{as(Si-O-Si)}$ ), 1033, 899, 834, 834, 740 ( $v_{s(Si-O-Si)}$ ), 711, 712, 648.  $\delta_{H}$  (300 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 3.48–3.43 (m, 8H, N-CH<sub>3</sub>), .27–2.10 (m, 16H), 1.88–1.78 (m, 8H, CH<sub>2</sub>), 1.50–1.40 (m, 8H, CH<sub>2</sub>), 0.98 (t, <sup>3</sup> $J_{HH}$  = 7.14 Hz, 12H, CH<sub>3</sub>), 0.69–0.63 (m, 16H).  $\delta_{C}$  (75.5 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 128.2 (q, <sup>3</sup>J = 274.93 Hz), 59.1 (*N*-CH<sub>2</sub>), 27.4 (q, <sup>3</sup>J = 30.2 Hz), 24.4 (CH<sub>2</sub>), 20.4 (CH<sub>2</sub>), 13.8 (CH<sub>3</sub>), 6.72 (t, <sup>3</sup>J = 25.5 Hz).  $\delta_{Si}$  (79.3 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -70.9.  $\delta_{F}$  (376 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -28.4 (F<sup>-</sup>), -69.3 (24F, CF<sub>3</sub>). *m*/*z* (MALDI-TOF): 1211.0 ([M-TBA]<sup>-</sup>, 100%). X-ray data are given in the supporting materials.

### Synthesis of tetra-*n*-butylammonium octa(1*H*, 1*H*,2*H*,2*H*-nonafluorohexyl) octasilsesquioxane fluoride (14)

1H,1H,2H,2H-nonafluorohexyltriethoxysilane (4.10 g, 10 mmol, 2 equiv) was dissolved in dry toluene (20 cm<sup>3</sup>) then tetra-nbutylammonium fluoride (5 cm<sup>3</sup> of 1 M solution in THF with 5% water, 1 equiv) was added. The mixture was stirred at room temperature under argon for 16 h, the reaction was stopped and hexane (150 cm<sup>3</sup>) was added to the mixture. The cloudy solution was transferred to the freezer (-20 °C). Colourless oil was obtained and the hexane phase was separated from the oil. The oil was subjected to flash chromatography on a silica gel column, eluting with acetone/hexane:  $3/7 (R_f 0.3)$ . A white solid was obtained (2.82 g, 85% yield). TGA mp 83-84 °C. (Found: C, 28.83; H, 2.41. Calcd. for C<sub>64</sub>H<sub>68</sub>F<sub>73</sub>NO<sub>12</sub>Si<sub>8</sub>: C, 28.95; H, 2.58%). v<sub>max</sub> (Nujol)/cm<sup>-1</sup>: 2920, 2851, 1462, 1375, 1313, 1268, 1203, 1146, 1079 ( $v_{as(Si-O-Si)}$ ), 1035, 897, 741 ( $v_{s(Si-O-Si)}$ ).  $\delta_{H}$  (300 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 3.48-3.44 (m, 8H, N-CH<sub>3</sub>), 2.33-2.10 (m, 16H, CH<sub>2</sub>), 1.90–1.78 (m, 8H, CH<sub>2</sub>), 1.50–1.40 (m, 8H, CH<sub>2</sub>), 1.01 (t,  ${}^{3}J_{HH} = 7.12$  Hz, 12H, CH<sub>3</sub>), 0.80–0.68 (m, 16H, CH<sub>2</sub>).  $\delta_{\rm C}$  (75.5 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 129.5 (CF<sub>2</sub>), 129.3 (CF<sub>2</sub>), 58.5 (NCH<sub>2</sub>), 23.6 (CH<sub>2</sub>), 19.5 (CH<sub>2</sub>), 12.94(CH<sub>3</sub>), 3.4 (CH<sub>2</sub>Si).  $\delta_{Si}$ (79.3 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -70.2.  $\delta_{\rm F}$  (376 MHz; acetone-d<sub>6</sub>;  $Me_4Si$ : -27.3 (F<sup>-</sup> for  $T_8(CH_2CH_2R_f)_7F$ -TBAF), -28.2 (1F) (F<sup>-</sup> for T<sub>8</sub>(CH<sub>2</sub>CH<sub>2</sub>R<sub>f</sub>)<sub>8</sub>-TBAF), -81.3 (24F), -116.3 (16F), -125.2 (16F), -126.9 (16F)). m/z (MALDI-TOF) : 2410.9 ([M-TBA]<sup>-</sup>, 100%)

#### Synthesis of tetra-*n*-butylammonium octa(1*H*,1*H*,2*H*, 2*H*-tridecafluorooctyl) octasilsesquioxane fluoride (15)

1*H*,1*H*,2*H*,2*H*-tridecafluorooctyltriethoxysilane (1.5 g, 2.94 mmol, 2 equiv) was dissolved in dry toluene (20 cm<sup>3</sup>) then tetra-*n*-butylammonium fluoride (1.47 cm<sup>3</sup> of 1 M solution in THF with 5% water, 1eq) was added. The mixture was stirred at reflux under argon for 16 h, the reaction was stopped and hexane (150 cm<sup>3</sup>) was added to the mixture. The cloudy solution was transferred to the freezer (-20 °C). A colourless oil was obtained, and the hexane phase was separated from the oil. The oil was subjected to flash chromatography on a silica gel column, eluting with (acetone/hexane: 3/7) ( $R_f$  0.3). A white solid was obtained after removal of the solvent. Recrystallization from acetone/chloroform gave a colourless crystal (1.1 g, 87%). Mp 56–57 °C.  $v_{max}$  (Nujol)/cm<sup>-1</sup>: 2921, 2852, 1642, 1376, 1237, 1207, 1143, 1100, 896, 806, 810, 707.  $\delta_H$  (300 MHz; acetone- $d_6$ ; Me<sub>4</sub>Si): 3.49–3.43 (m, 8H, N-CH<sub>3</sub>), 2.31–2.20 (m, 16H), 1.89–1.78 (m, 8H,

 Table 7
 Crystallographic data for the four crystalline systems investigated by X-ray diffraction analysis

Compound reference	3	5	7	13	
Chemical formula	C64H68Cl8FNO12Si8	C <sub>72</sub> H <sub>92</sub> FNO <sub>20</sub> Si <sub>8</sub>	$C_{94}H_{108}FNO_{12}Si_8$	C40H68F25NO12Si8	
Formula mass	1570.51	1535.19	1687.53	1454.67	
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	
a/Å	27.2513(11)	12.6188(5)	13.5940(3)	14.5495(4)	
b/Å	21.4772(9)	12.8071(5)	15.2028(3)	15.8583(4)	
c/Å	12.7007(5)	46.5571(19)	22.2570(4)	16.7260(4)	
$\alpha$ (°)	90.00	90.00	86.9340(10)	93.1750(10)	
$\beta$ (°)	103.431(2)	92.2580(10)	85.9290(10)	108.8610(10)	
$\gamma$ (°)	90.00	90.00	75.9750(10)	114.5910(10)	
Unit cell volume/Å <sup>3</sup>	7230.2(5)	7518.3(5)	4448.28(15)	3238.86(14)	
T/K	120(2)	120(2)	120(2)	120(2)	
Space group	$P2_1/c$	$P2_1/n$	$P\overline{1}$	PĪ	
No. of formula units per unit	4	4	2	2	
cell, Z					
Absorption coefficient, $\mu/\text{mm}^{-1}$	0.506	0.217	0.184	0.289	
No. of reflections measured	39431	50830	66463	64160	
No. of unique reflections	12430	16108	20347	14825	
$R_{\rm int}$	0.0938	0.0535	0.0498	0.0889	
Final $R_1$ values $(I > 2\sigma(I))$	0.1427	0.0680	0.0783	0.0717	
Final w $R_2$ values $(I > 2\sigma(I))$	0.2307	0.2001	0.1559	0.1681	
Final $R_1$ values (all data)	0.2399	0.1206	0.1162	0.1203	
Final w $R_2$ values (all data)	0.2777	0.2543	0.1782	0.1942	
Goodness of fit on $F_2$	1.073	1.035	1.040	1.028	

CH<sub>2</sub>), 1.50–1.40 (m, 8H, CH<sub>2</sub>), 0.98 (t, <sup>3</sup>J<sub>HH</sub> = 7.14 Hz, 12H, CH<sub>3</sub>), 0.75–0.70 (m, 16H).  $\delta_{\rm C}$  (75.5 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 69.6 (CH<sub>2</sub>), 59.1 (*N*-CH<sub>2</sub>), 31.7, 29.5, 29.4, 26.2 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 19.7 (CH<sub>2</sub>), 13.3 (CH<sub>3</sub>), 3.8 (SiCH<sub>2</sub>).  $\delta_{\rm Si}$  (79.3 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): −70.5.  $\delta_{\rm F}$  (376 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): −28.4 (1F) (F<sup>-</sup>), −81.9 (24F), −116.9 (t, <sup>3</sup>J<sub>F-F</sub> = 19.68, <sup>3</sup>J<sub>F-F</sub> = 14.7, 16F), −122.6 (16F), −123.6 (16F), −124.3 (16F), −127.1 (16F). *m/z* (MALDI-TOF): 3211.7 ([M-TBA]<sup>-</sup>, 100%).

## Synthesis of tetra-*n*-butylammonium octa(1*H*,1*H*,2*H*,2*H*-heptadecafluorodecyl) octasilsesquioxane fluoride (16)

(1H,1H,2H,2H-heptadecafluorodecyl)triethoxysilane (2 g. 3.27 mmol, 2 equiv) was dissolved in dry toluene (20 cm<sup>3</sup>) then tetra-n-butylammonium fluoride (1.63 cm<sup>3</sup> of 1 M solution in THF with 5% water, 1 equiv) was added. The mixture was stirred at reflux under argon for 16 h, the reaction was stopped and hexane (150 cm<sup>3</sup>) was added to the mixture. The cloudy solution was transferred to the freezer (-20 °C). Colourless oil was obtained and the hexane phase was separated from the oil. The oil was subjected to flash chromatography on a silica gel column, eluting with (acetone/hexane: 3/7) ( $R_f$  0.28) to obtain the title compound as white solid (1.60 g, 91%). Mp 90–91 °C.  $v_{\rm max}$ (Nujol)/cm<sup>-1</sup>: 2920, 1462, 1375, 1202, 1146, 970, 896, 709.  $\delta_{\rm H}$  (300 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 3.49–3.43 (m, 8H, N-CH<sub>3</sub>), 2.30–2.18 (m, 16H, CH<sub>2</sub>-CF<sub>3</sub>), 1.89–1.78 (m, 8H, CH<sub>2)</sub>, 1.50–1.39 (m, 8H, CH<sub>2</sub>), 0.98 (t,  ${}^{3}J_{HH} = 7.14$  Hz, 12H, CH<sub>3</sub>), 0.76–0.70 (m, 16H, CH<sub>2</sub>-Si).  $\delta_{\rm C}$  (75.5 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 59.4 (N-CH<sub>2</sub>), 24.4 (CH<sub>2</sub>), 20.4(CH<sub>2</sub>), 13.8 (CH<sub>3</sub>), 4.2 (Si-CH<sub>2</sub>).  $\delta_{Si}$  (79.3 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -70.5.  $\delta_{F}$  (376 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -27.48 (F<sup>-</sup> for T<sub>8</sub>(CH<sub>2</sub>CH<sub>2</sub>R<sub>F</sub>)<sub>7</sub>F-TBAF), -28.3 (F<sup>-</sup> for T<sub>8</sub>(CH<sub>2</sub>CH<sub>2</sub>R<sub>F</sub>)<sub>8</sub>-TBAF), -81.9 (24F), -116.9 (16F), -122.4 and -122 (48F), -123.45 (16F), -124.3 (16F), -127.0 (16F). m/z (MALDI-TOF): 4011.7 ([M-TBA]<sup>-</sup>, 100%), 3584.7  $[T_8(CH_2CH_2R_f)_7F-TBA]^-$ , 28%).

# Synthesis of tetra-*n*-ethylammonium octavinyloctasilsesquioxane fluoride (17)

Vinyltriethoxysilane (1.20 g, 6.30 mmol, 1 eq) was dissolved in dry acetone (20 cm<sup>3</sup>) then tetraethylammonium fluoride (2.5 cm<sup>3</sup> of 1 M solution in THF with 5% water, 2 equiv) was added. The mixture was stirred at room temperature for 24 h, the reaction was stopped and the solvent removed on a rotary evaporator at 400 mbar and at 55 °C. A yellow solid gel was obtained which was difficult to purify.  $\delta_{\rm H}$  (300 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 5.85 ppm (s, 24H, vinyl-H), 3.5 (m, 8H, N-CH<sub>2</sub>), 1.06 ppm (t, <sup>3</sup>J<sub>HH</sub> = 7.51 Hz, 12 H, CH<sub>3</sub>).  $\delta_{\rm C}$  (75.5 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 136.7 (Si-CH=CH<sub>2</sub>), 132.5 (Si-CH = CH<sub>2</sub>), 57.0 (s, N-CH<sub>2</sub>), 19.3 (CH<sub>3</sub>).  $\delta_{\rm si}$  (79.3 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -25.1.

## Synthesis of tetra-*n*-ethylammonium octa(1*H*,1*H*,2*H*,2*H*-nonafluorohexyl)octasilsesquioxane fluoride (18)

1H,1H,2H,2H-nonafluorohexyltriethoxysilane (2 g, 4.87 mmol, 2 equiv) was dissolved in dry toluene (20 cm<sup>3</sup>) then tetraethylammonium fluoride hydrate (TEAF, H<sub>2</sub>O) (0.36 g, 2.44 mmol, 1 equiv) was added. The mixture was stirred at reflux under argon for 16 h. The reaction was stopped and hexane (150 cm<sup>3</sup>) was added to the mixture. The cloudy solution was transferred to the freezer (-20 °C). A colourless oil was obtained and the hexane phase was separated from the oil. The oil was subjected to flash chromatography on a silica gel column, eluting with (acetone/hexane: 3/7) to obtain the title compound as a white solid (1.25 g, 81%). Mp 79–81 °C.  $v_{\text{max}}$  (Nujol)/cm<sup>-1</sup>: 2925 ( $v_{\text{C-H}}$ ), 2850, 1465, 1380, 1309, 1569, 1206, 1147, 1080 (V<sub>as(Si-O-Si)</sub>), 1037, 895, 743 ( $v_{s(Si-O-Si)}$ ).  $\delta_{H}$  (300 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 3.48 (q,  ${}^{3}J_{HH} = 7.16$  Hz, 2H, N-CH<sub>2</sub>), 3.51–3.47 (m, 8H, CF<sub>2</sub>-CH<sub>2</sub>), 2.30-2.09 (m, 16H), 1.35 (t, 12H, CH<sub>3</sub>), 0.73-0.66 (m, 8H, CH<sub>2</sub>, SiCH<sub>2</sub>).  $\delta_{\rm C}$  (75.5 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): 3.8 (Si–CH<sub>2</sub>), 7.2(Si-CH<sub>2</sub>CH<sub>2</sub>), 26.1 (N-CH<sub>2</sub>CH<sub>2</sub>), 52.9 (N-CH<sub>2</sub>), 109.0 (CF<sub>2</sub>), 118.5  $(CF_2)$ , 119.1 $(CF_2)$ , 123.1 $(CF_2)$ .  $\delta_{Si}$  (79.3 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si):  $-70.2. \delta_{\rm F}$  (376 MHz; acetone-d<sub>6</sub>; Me<sub>4</sub>Si): -28.2, -29.1, -82.8 (24F), -117.7 (16F), -125.9 (16F), -127.6 (16F), -132.0. m/z (MALDI-TOF): 2411.0 ([M-TBA]<sup>-</sup>, 100%).

#### X-ray crystallography experimental

The crystallographic data collection of compounds **3**, **5**, **7** and **13** were performed using a Nonius Kappa CCD diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) controlled by the Collect<sup>39</sup> software package at 120(2) K. The data were processed using Denzo<sup>40</sup> and semi-empirical absorption corrections were applied using SADABS.<sup>41</sup> Crystallographic data are in Table 7. The structures were solved by direct methods and refined by full-matrix least-square procedures on  $F^2$  using SHELXS-97 and SHELXL-97,<sup>42</sup> respectively. All non-hydrogen atoms were refined anisotropically. For compound **3**, the tetrabutylammonium cation was disordered over two positions, and loose geometrical (SAME) and thermal (SIMU) restraints were used.

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