Synthesis and characterization of bis(trialkoxysilymethyl)arenes from related bis(trichlorosilylmethyl)arenes. Comparisons between some organosilicate xerogel materials derived from both

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A series of bis(trialkoxysilylmethyl)aryl compounds **1–17** {$[(RO)_3SiCH_2]_2Ar$, R = Me, Et, Pr, Bu, Ar = 1,4-C_6H_4; R = Et, Pr, Bu, Ar = 1,4-$C_6H_2Me_2$-2,6; R = Et, Pr, Bu, Ar = 1,4-C_6Me_4-2,3,5,6; R = Et, Pr, Bu, Ar = 1,3-C_6H_4; R = Bu, Ar = 1,2-C_6H_4; R = Et, Pr, Bu, Ar = 9,10-$C_{14}H_8$} prepared from the related bis(trichlorosilylmethyl)aryl compounds and characterised by ^1H, ^{13}C and ^{29}Si NMR and IR spectroscopy, and high resolution mass spectrometry. The X-ray crystal structures of two of the bis(trichlorosilylmethyl)aryl precursor compounds are reported. Organosilicate xerogels prepared from the precursors **2**, **7** and **12** are discussed.

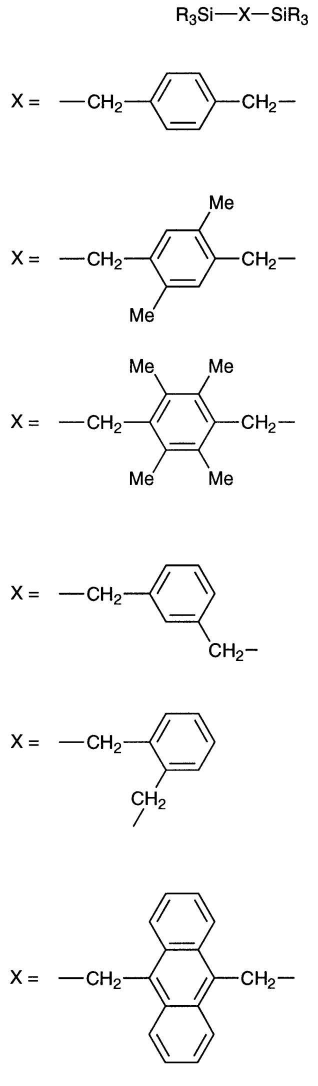
These have been studied by a combination of solid state NMR spectroscopy, scanning electron microscopy (one case) and nitrogen sorption porosimetry and their properties compared with those of xerogels derived from related bis(trichlorosilylmethyl)arenes.

The idea of tailoring the internal structures of organosilicate xerogels by inserting organic spacers into the siloxane network through the sol–gel processing of compounds with organobridged trifunctional silyl groups, $X_3Si—R—SiX_3$ was originally reported by Shea.[1] A number of studies have focused on the relationship between the nature of the organic group and the microarchitecture of the derived glassy xerogel materials.[2–4] One of our aims was to gauge the extent to which the nature of the functional groups in such organobridged precursors affect properties such as distribution of T^n environments, overall % condensation and surface area in derived gels. We have recently synthesised a series of bis(trichlorosilylmethyl)arenes,[5] from which we prepared and characterised the corresponding monolithic transparent xerogels. In this paper we report on the related series of bis(trialkoxysilylmethyl)arenes, their conversion to xerogels and some of the properties of these materials, *e.g.* local chemical structure, by ^{13}C and ^{29}Si CP MAS NMR spectroscopy, morphology, by scanning electron microscopy (SEM) and surface area, by nitrogen sorption porosimetry.

Results and Discussion

There are numerous reported methods for the synthesis of organoalkoxysilane compounds, $RSi(OR)_3$. In addition to direct reactions of organotrichlorosilanes with alcohols[6] organylation of alkoxychlorosilanes such as $(EtO)_3SiCl$ using lithium[7] or sodium[8] or Grignard[1,7,9] reagents as well as hexachloroplatinic acid promoted organylation[2,3] are commonly used. We tried without success to use the *p*-xylenediyl dianion 1,4-$[CH_2]_2C_6H_4^{2-}$, as the Grignard reagent in conjunction with $Si(OEt)_4$ or $(Et_3O)_3SiCl$ to obtain 1,4-$[(EtO)_3SiCH_2]_2C_6H_4$. Only diethyl ether-insoluble polymer like materials were obtained. Direct reaction of bis(trichlorosilylmethyl)arenes[5] with alcohol gave the series of bis(trialkoxysilylmethyl)arenes **1–17**. The reactions were performed at room temperature and were quantitative. These compounds broadly follow the properties noted for other organotrialkoxysilanes, and are all readily hydrolysed in moist air and soluble in most organic solvents. Unlike the chloride starting materials these compounds are liquids reflecting weaker intermolecular interactions in the alkoxides and are mostly colourless, apart from **6**, **11** and **17**. They are deep orange–brown, and are derived from the similarly coloured solid bis(trichlorosilylmethyl)anthracene.

We previously reported on the molecular structure of



1 R = OMe
2 R = OEt
7 R = OPr
12 R = OBu

3 R = OEt
8 R = OPr
13 R = OBu

4 R = OEt
9 R = OPr
14 R = OBu

5 R = OEt
10 R = OPr
15 R = OBu

16 R = OBu

6 R = OEt
11 R = OPr
17 R = OBu

2,5-bis(trichlorosilylmethyl)-*p*-xylene, **A**,[5] and have since completed X-ray studies on the related compounds 1,4-bis(trichlorosilylmethyl)benzene, **B**, and 1,3-bis(trichlorosilylmethyl)benzene, **C** (molecular structures are shown in Fig. 1 and Fig. 2, along with the corresponding structural data). The bond lengths and angles are all within expected ranges and there are no short inter- or intra-molecular contacts. Both the distances Cl_3Si-CH_2 and the angles $Cl_3Si-CH_2-C(Ar)$ are similar in **A**, **B** and **C**. As with **A** the CH_2SiCl_3 groups in **B** and **C** are mutually *trans* about the plane of the arene bridge. Thus there are no obvious structural consequences associated with the additional steric effect of the methyl substituents in **A** compared to **B** and the different substitution pattern in **B** compared to **C**. To the best of our knowledge these are the only compounds with CH_2SiCl_3 functions to be structurally characterised.

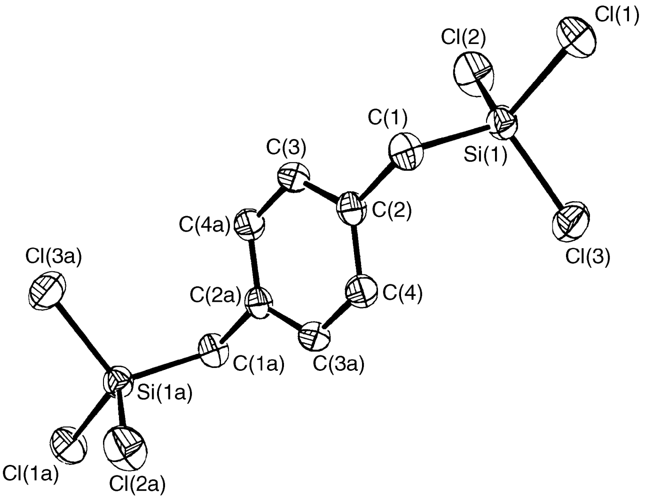


Fig. 1 Molecular structure of compound **B** (ellipsoids at the 50% probability level). Selected bond lengths (Å) and angles (°) for compound **B**: Cl(1)–Si(1) 2.022(1), Cl(2)–Si(1) 2.014(1), Cl(3)–Si(1) 2.022(1), Cl(4)–Si(2) 2.019(1), Cl(5)–Si(2) 2.018(2), Cl(6)–Si(2) 2.013(2), Si(1)–C(1) 1.842(4), Si(2)–C(5) 1.816(4), C(1)–Si(1)–Cl(2) 110.9(2), C(1)–Si(1)–Cl(3) 111.0(2), Cl(2)–Si(1)–Cl(3) 107.67(7), C(1)–Si(1)–Cl(1) 111.2(1), Cl(2)–Si(1)–Cl(1) 108.49(7), Cl(3)–Si(1)–Cl(1) 107.43(6), C(5)–Si(2)–Cl(6) 112.4(2), C(5)–Si(2)–Cl(5) 109.7(2), Cl(6)–Si(2)–Cl(5) 106.59(8), C(5)–Si(2)–Cl(4) 111.4(1), Cl(6)–Si(2)–Cl(4) 108.29(7), Cl(5)–Si(2)–Cl(4) 108.28(7), C(2)–C(1)–Si(1) 113.7(3).

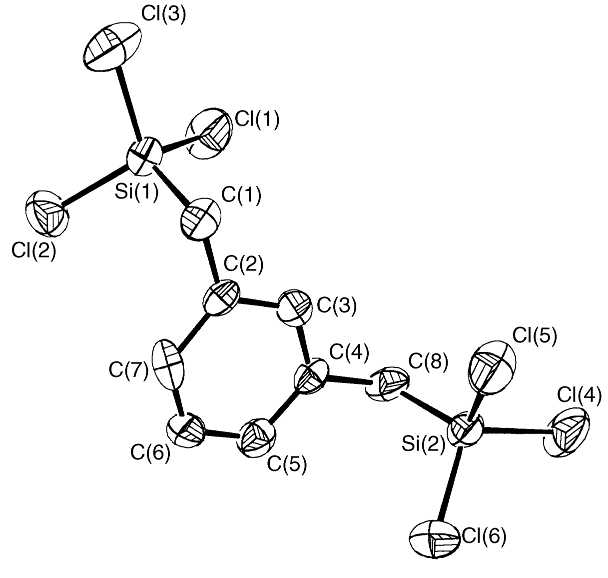


Fig. 2 Molecular structure of compound **B** (ellipsoids at the 50% probability level). Selected bond lengths (Å) and angles (°) for compound **C**: Si(1)–C(1) 1.857(10), Si(1)–Cl(2) 1.993(4), Si(1)–Cl(1) 2.009(5), Si(1)–Cl(3) 2.011(4), Si(2)–C(8) 1.836(10), Si(2)–Cl(5) 1.990(4), Si(2)–Cl(6) 2.003(4), Si(2)–Cl(4) 2.013(4), C(1)–Si(1)–Cl(2) 109.8(4), C(1)–Si(1)–Cl(1) 111.4(4), Cl(2)–Si(1)–Cl(1) 109.0(2), C(1)–Si(1)–Cl(3) 112.3(4), Cl(2)–Si(1)–Cl(3) 107.0(2), Cl(1)–Si(1)–Cl(3) 107.3(2), C(8)–Si(2)–Cl(5) 110.7(4), C(8)–Si(2)–Cl(6) 112.0(4), Cl(5)–Si(2)–Cl(6) 107.4(2), C(8)–Si(2)–Cl(4) 111.2(4), Cl(5)–Si(2)–Cl(4) 107.7(2), Cl(6)–Si(2)–Cl(4) 107.5(2), C(2)–C(1)–Si(1) 112.4(7).

Spectroscopic data for compounds 1–17

Analytical and spectroscopic data for compounds **1**–**17** (^1H, ^{13}C and ^{29}Si NMR, IR and *m/z*) are assembled in Tables 1–11. The spectroscopic data confirm the expected structural features. Correlation data[10] were used for the assignment of arene proton and ^{13}C resonances. In the ^1H NMR spectra, Tables 1, 4 and 7, the chemical shifts of the methylene protons in the alkoxysilylmethylanthracene derivatives are *ca.* 1 ppm downfield of the other compounds and the ^{13}C chemical shifts for the methylene carbons in the anthrancene derivatives are 6 ppm upfield of those of the other aralkyl bridges. These relative shifts follow the patterns observed for related xylene and 9,10-dimethylanthracene compounds.[11] The ^{29}Si NMR chemical shifts of anthrancene derivatives **6**, **11** and **17**, Table 10, occurred at lower field than in other aralkyl bridged species.

The chemical shifts of the methylene protons in the trialkoxysilylmethylbenzenes were *ca.* 1 ppm upfield of those of the corresponding trichloride starting materials as expected on grounds of likely electronegativity differences between alkoxy and chloride groups. The methylene carbons of the aralkyl bridges were shifted *ca.* 10 ppm upfield from the corresponding trichlorosilyl compounds. In all of the durene derivatives, the signals due to the methylene and the methyl protons of the aralkyl fragment were coincident. Changing the aryl bridge had no effect on the chemical shifts of the alkoxy protons or carbons (Tables 1–9) and these were similar to those of the corresponding alcohols.[12] Similarities between the coupling constants $^3J_{CH_3\text{-}CH_2}$ and $^3J_{CH_2\text{-}CH_2}$ greatly simplified the multiplicity associated with protons on the alkyl chains of the alkoxy groups in many cases. Thus the total number of lines seen for any given set of equivalent protons followed from the total number, *n*, of proton neighbours to which they are coupled[10] (see Tables 1, 4, 7). The ^{29}Si NMR chemical shifts, Table 10, were in the range from $\delta -47.54$ to -53.36, as expected for $-Si(OR)_3$ containing compounds.[13] The ^{29}Si NMR chemical shift of compound **1** occurred at lower field than those of the others.

In the IR spectra, the characteristic bands,[10,14] of $Si-C$, $Si-OR$ and $C=C$, $C-H$ of the phenyl groups were observed. As with the organotrichlorosilane, the $Si-C$ vibrations occured between 1200 and 1262 cm^{-1} as expected. The $Si-OR$ vibrations of ethoxy compounds appear as two close bands at *ca.* 1100 cm^{-1} (ref. 7). The other alkoxy compounds showed one sharp band in this region. Also as with the organotrichlorosilane, no $C=C$ vibrations were observed in durene derivatives. The aromatic ring $C-H$ out of plane deformations generally appeared as a strong band at *ca.* 800 cm^{-1}. In all of the anthracene derivatives, and the ethoxy compounds, the aromatic $C-H$ out of plane vibrations occurred below 800 cm^{-1}, whilst in the others, including 1,3- and 1,2-disubstitued benzenes, this band appeared above 800 cm^{-1}.

The mass spectra fragmentation patterns of compounds **1**–**17** are assembled in Table 11. $[M]^+$ and $[M-2Si(OR)_3]^+$ fragments appear for compounds **1**–**17**. In addition the $[Si(OR)_3]^+$ fragments were observed for the methoxy compound **1**, ethoxy compound **4** and all of the propoxy and butoxy compounds. $[M-Si(OR)_3]^+$ fragments appeared in most of the compounds apart from **1**, **10**, **15**, **16**, that is those compounds where the two trialkoxylsilylmethyl groups occupy mutual *ortho* or *meta* positions on the phenyl ring.

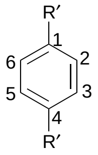
Table 1 ^1H NMR assignments in compounds **1**–**6** ($CDCl_3$)

	1	1 2 3 $CH_2Si(OCH_2CH_3)_3$ 2	3	4	5	6
OCH_3	3.49(s, 18H)*					
CH_3			2.23(s, 6H)	2.23(12H)		
aromatic ring	7.03(s, 4H)	7.09(s, 4H)	6.90(s, 2H)		7.14–7.28(m, 4H)	7.43–7.55(m, 4H)
H1	2.18(s, 4H)	2.20(s, 4H)	2.10(s, 4H)	2.23(s, 4H)	2.14(s, 4H)	3.21(s, 4H)
H2		3.67–3.93(q, 12H)	3.60–3.86(q, 12H)	3.53–3.80(q, 12H)	3.64–3.89(q, 12H)	3.46–3.73(q, 12H)
H3		1.12–1.30(t, 18)	1.07–1.24(t, 18H)	1.04–1.21(t, 18H)	1.08–1.26(t, 18H)	0.94–1.11(t, 18H)

Table 2 ^{13}C NMR assignments in compounds **1**–**6** ($CDCl_3$, 150.90 MHz)

	1 2 3 $CH_2Si(OCH_2CH_3)_3$ 1	2	3	4	5	6
OCH_3	50.61					
CH_3			16.76	16.72		
C1	18.23	19.55	19.35	19.23	20.47	14.46
C2		58.29	58.42	58.26	58.47	58.54
C3		18.20	17.90	17.32	18.04	17.93

Table 3 ^{13}C NMR assignments of ring carbons in compounds **1**–**6** ($CDCl_3$, 150.9 MHz)[a]



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	1	2	3	4	5	6
C1	132.93	133.58	131.49	130.73	136.98	129.29
C2	128.58	128.56	132.42	131.70	129.50	125.02
C3	128.58	128.56	130.79	131.70	136.98	126.01
C4	132.93	133.58	131.49	130.73	125.12	124.10
C5	128.58	128.56	132.42	131.70	127.80	
C6	128.58	128.56	130.79	131.70	125.12	

[a] $R' = CH_2Si(OCH_3)_3$; $R = CH_2Si(OCH_2CH_3)_3$.

Sol–gel processing of 1,4-bis(trialkoxysilylmethyl)arenes

We have already reported on the synthesis and properties of a range of organosilicate xerogel materials, **XCl**, derived through sol–gel processing of 1,4-bis(trichlorosilylmethyl)-arene compounds,[5] and we were interested to compare the properties of similar materials derived from related alkoxy precursors. The conditions used for sol–gel processing of 1,4-$[(RO)_3SiCH_2]_2C_6H_4$ compounds **2** (R = Et), **7** (R = Pr) and **12** (R = Bu) to xerogels **X1**, **X2**, **X3a** and **X3b** respectively, are summarised in Table 12 with further details given in the Experimental section, and involve HCl acid catalysis. The molar ratio of Si—OR functions to HCl in these sol–gel mixtures are 40–100 and it is possible that some intermediate Si—Cl is formed (Si—OR/H_2O ratios were between 0.5 and 1). Nonetheless times to gelation for the alkoxy compounds were generally longer than previously found for the related chlorosilane compounds. A slower rate of hydrolysis is expected for the alkoxy species.[15] In each case a transparent monolith was formed.

The xerogels **X1**–**X3**, Table 12, were studied by both ^{13}C and ^{29}Si CPMAS NMR spectroscopy. Chemical shift data are given in Tables 13 and 14. The relative peak areas associated with T^n environments (obtained using GAUSSIAN simulation of the ^{29}Si spectra and where $n = 0$–3 refers to the number of Si—O—Si bonds associated with particular Si sites) in xerogels **X1**–**X3** are given in Table 13. A comparison of the data with those for the related xerogel **XCl** derived from the chlorosilane, in each case reveals an increase (*ca.* 10%) in the T^2 component at the expense of T^3. The absence of any T^0 peak for **X1** and **X3b**, both of which were processed in ethanol, is noteworthy. The overall percentage condensation in each case, Table 13, was calculated as previously described,[4] and is slightly lower than that achieved for the related **XCl** material.

Peak assignments for the ^{13}C and CPMAS NMR spectra are given in Table 14. Peaks associated with the organic bridges in the organosilicate framework are close to those previously assigned to the **XCl** xerogel and assignments were confirmed by non-quaternary suppression techniques as previously described.[4] Other peaks present in these spectra are associated with residual alkoxy groups both as the alcohol and associated with T^n environments. The intensity of these peaks decreased substantially when materials were heated to 200 °C at 0.001 Torr for 48 h.

The solvent-free xerogels **X1**–**X3** were found to have BET surface areas $<2\ m^2\ g^{-1}$ when examined by nitrogen sorption porosimetry. This contrasts with the **XCl** material having the same organic bridge but which was microporous with a surface area 600 $m^2\ g^{-1}$ (ref. 4). It is noteworthy that other bis(trialkoxysilyl)arylenes and alkylenes also gave low surface area materials and this was thought to be a consequence of the non-rigidity of the bridging group in these cases.[16] The different distributions in T^n environments compared to those of **XCl** coupled with the presence of residual T^n alkoxy groups in **X1**–**X3** represent differences in the local chemical environments which may have effected pore structure although we are not aware of previous correlations of this type. A high resolution SEM (Fig. 3) on a relatively thick film of **X3a** cast on a glass slide reveals an apparently more densely packed nanoparticulate surface texture than found for the related **XCl** material.[4]

Further work concerning the use of these materials as confinement matrices for a variety of guest species is in hand. This work illustrates that the formation of xerogels is controlled by a number of factors and that properties can be adjusted by altering the nature of the precursors.

Experimental details

All reactions and manipulations involving moisture sensitive compounds were carried out under purified nitrogen. The bis(trichlorosilylmethyl)arene starting materials were made as previously described.[5] The alcohols used were purified by distillation from the corresponding magnesium alkoxides. The bis(trialkoxysilylmethyl)arenes were purified by Schlenk flask to Schlenk flask distillation *via* a connecting glass tube. A dynamic vacuum was applied through the receiver Schlenk and, with the distillation Schlenk immersed in an oil bath products were collected at 150–180 °C in the liquid nitrogen cooled receiver Schlenk and subsequently stored under nitrogen. Solution phase NMR spectra were recorded on Bruker AW-250 (^{13}C, 62.89 MHz; ^{29}Si, 49.66 MHz), Bruker AW-400, Bruker AMX-600 (^{13}C, 150.90 MHz; ^{29}Si, 119.23 MHz) and Bruker WP-80 (^1H, 80 MHz) NMR spectrometers. Spectra were recorded on samples dissolved in dried deuteriated $CDCl_3$

Table 4 ^{1}H NMR assignments in compounds **7–11** ($CDCl_3$).

			2 3 4 $CH_2Si(OCH_2CH_2CH_3)_3$		
	7	**8**	**9**	**10**	**11**
CH_3	—	2.25(s, 6H)	2.24(12H)		
aromatic ring	7.04(s, 4H)	6.90(s, 4H)		6.90–6.98(s, 4H)	7.43–7.58(m, 4H) 8.33–8.46(m, 4H)
H1	2.15(s, 4H)	2.10(s, 4H)	2.24(s, 4H)	2.14(s, 4H)	3.21(s, 4H)
H2	3.55–3.72(t, 12H)	3.60–3.65(t, 12H)	3.50–3.66(t, 12H)	3.60–3.66(t, 12H)	3.43–3.58(t, 12H)
H3	1.40–1.57(sxt, 12H)	1.46–1.61(sxt, 12H)	1.39–1.64(m, 12H)	1.45–1.60(sxt, 12H)	1.29–1.54(m, 12H)
H4	0.78–0.96(t, 18H)	0.86–0.93(t, 18H)	0.86–1.11(t, 18H)	0.84–0.90(t, 18H)	0.66–0.82(t, 18H)

Table 5 ^{13}C NMR assignments in compounds **7–11** ($CDCl_3$, 150.90 MHz)

		2 3 4 $CH_2Si(OCH_2CH_2CH_3)_3$			
	7	**8**	**9**	**10**	**11**
CH_3		16.87	16.77		
C1	19.42	19.43	19.28	19.97	14.18
C2	64.48	64.45	64.32	64.49	64.42
C3	25.51	25.51	25.48	25.49	25.33
C4	10.08	10.05	11.17	10.06	9.94

and kept under nitrogen atmosphere. All chemical shifts (δ in ppm) were referenced to appropriate nuclei in tetramethylsilane. IR spectra were recorded on a Perkin-Elmer FTIR 1720X spectrophotometer, using neat liquids between two KBr plates. Mass spectra were obtained on a Kratos MS 50RF mass spectrometer. The samples were sealed in nitrogen-filled Pyrex capillary tubes. The capillaries were opened and mounted in the probe under a nitrogen atmosphere. A summary of the observed fragmentation patterns is given in Table 11. Elemental analysis (C,H) was obtained from University College London Analytical Service. The samples were sealed under nitrogen in a glass tube.

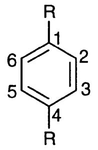
Crystallographic measurements were made using a CAD-4 diffractometer in ω-2θ scan mode, on selected single crystals mounted inside 0.7 mm glass capillaries, which were flame sealed under nitrogen. The structures were solved by direct methods and refined by least-squares analysis.

The solid state ^{13}C and ^{29}Si NMR spectra were acquired using cross polarization (CP) magic angle spinning (MAS), and high-power proton decoupling on a Bruker MSL-300 spectrometer. Typical conditions were 2 ms contact time, 1 s recycle delay, a 90° pulse length of 4.07 μs and a spinning speed of 4.5 kHz. The ^{13}C and ^{29}Si frequencies were 75.5 and 59.6 MHz, respectively. All spectra were recorded at room temperature and chemical shifts are quoted relative to $SiMe_4$. Scanning electron micrographs were obtained using a JEOL JC6300 Scanning Electron Microscope.

Surface area measurements were obtained using a Micromeritics ASAP 2400 instrument.

Preparation of 1,4-bis(trimethoxysilylmethyl)benzene 1. 1,4-Bis(trichlorosilylmethyl)benzene (2.30 g, 6.2 mmol) was dissolved in methanol (40 cm^3) and stirred overnight. Removal of the excess methanol afforded the product as a colourless liquid (1.82 g, yield 85%). δ_H (80 MHz, $CDCl_3$): 2.18(s, 4H), 3.49(s, 18H), 7.03(s, 4H). δ_{Si} (119.23 MHz, $CDCl_3$) −47.54. δ_C (150.9 MHz, $CDCl_3$): 18.23, 50.61, 128.58, 132.93. ν/cm^{-1} (KBr): 2944(s), 2842(s), 1904(w), 1512(s), 1462(m), 1422(m), 1401(m), 1192(s), 1088(s, b), 1023(m), 849(s), 804(s), 747(m), 730(m), 664(w), 641(w), 563(w), 522(m), 478(m). *m/z* (% relative intensity) theoretical *m/z*: $C_{14}H_{26}Si_2O_6$, 346.1280(66.2)-346.1268. $C_3H_9O_3Si$, 121.0321(100)121.0321. C_8H_8, 104.0639-(45.0)104.0626.

Table 6 ^{13}C NMR assignments of ring carbons in compounds **7–11** ($CDCl_3$, 150.90 MHz)^a



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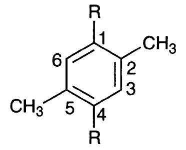

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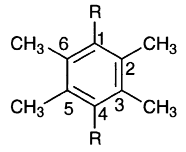

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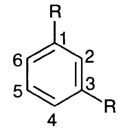

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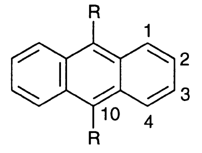

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	7	**8**	**9**	**10**	**11**
C1	133.27	131.78	130.81	137.11	129.22
C2	128.62	132.46	131.10	129.57	124.63
C3	128.62	131.35	131.10	137.11	125.97
C4	133.27	131.78	130.81	125.07	123.97
C5	128.62	132.46	131.10	127.75	
C6	128.62	131.35	131.10	125.07	

^{a}R = $CH_2Si(OCH_2CH_2CH_3)_3$.

Preparation of 1,4-bis(triethoxysilylmethyl)benzene 2. Prepared as described for **1** from 1,4-bis(trichlorosilylmethyl)benzene (2.00 g, 5.36 mmol) and ethanol (40 cm^3); after further distillation, yield, 1.84 g (80%). ν/cm^{-1} (KBr): 2975(s), 2927(s), 2890(s), 1512(m), 1483(w), 1443(w), 1422(w), 1391(m), 1366(w), 1295(w), 1262(w), 1222(m), 1170(s), 1104(s), 1083(s), 960(s), 839(m), 799(s), 723(w), 565(w), 528(w), 483(w). *m/z* (% relative intensity) theoretical *m/z*: $C_{20}H_{38}Si_2O_6$,

Table 7 ^1H NMR assignments in compounds **12–17** ($CDCl_3$)

		1 2 3 4 5 $CH_2Si(OCH_2CH_2CH_2CH_3)_3$				
	12	**13**	**14**	**15**	**16**	**17**
CH_3		2.21(s, 6H)	2.35(s, 12H)			
aromatic ring	7.03(s, 4H)	6.90(s, 2H)		6.90–6.98(m, 4H)	7.05–7.12(m, 4H)	7.45–7.57(m, 4H) 8.33–8.45(m, 4H)
H1	2.14(s, 4H)	2.09(s, 4H)	2.35(s, 4H)	2.13(s, 4H)	2.27(s, 4H)	3.21(s, 4H)
H2	3.65–3.70(t, 12H)	3.61–3.75(t, 12H)		3.65–3.70(t, 12H)	3.58–3.68(t, 12H)	3.48–3.63(t, 12H)
H3	1.44–1.55(p, 12H)	1.15–1.59(m, 24H)	1.27–1.71(m, 24H)	1.42–1.55(p, 12H)	1.26–1.69(m, 24H)	1.11–1.57(m, 24H)
H4	1.27–1.41(sxt, 12H)			1.26–1.41(sxt, 12H)		
H5	0.87–0.93(t, 18H)	0.82–1.00(t, 18H)	0.81–1.00(t, 18H)	0.87–0.92(t, 18H)	0.80–0.98(t, 18H)	0.70–0.96(t, 18H)

Table 8 ^{13}C NMR assignments in compounds **12–17** ($CDCl_3$, 150.90 MHz)

		1 2 3 4 5 $CH_2Si(OCH_2CH_2CH_2CH_3)_3$				
	12	**13**	**14**	**15**	**16**	**17**
CH_3		16.74	16.06			
C1	19.59	19.51	19.44	20.02	20.31	14.30
C2	62.74	62.52	62.42	62.60	62.55	62.59
C3	34.61	34.47	34.47	34.47	34.47	34.20
C4	18.93	18.80	18.81	18.79	18.79	18.69
C5	13.89	13.89	13.83	13.66	13.64	13.62

430.2196(76.2)430.2207. $C_{14}H_{23}O_3Si$, 267.1359(5.4)267.1417. C_8H_8, 104.0661(100)104.0626. Calc. for $C_{20}H_{38}Si_2O_6$: C, 55.76; H, 8.89. Found: C, 54.68; H: 8.77%

Preparation of 2,5-bis(triethoxysilylmethyl)-*p*-xylene 3. Prepared as described for **1** from **2**, 5-bis(trichlorosilylmethyl)-*p*-xylene (2.60 g, 6.48 mmol) and ethanol (40 cm^3). Yield, 2.73 g (92%). ν/cm^{-1} (KBr): 2973(s), 2927(s), 2884(s), 1559(m), 1541(m), 1506(m), 1457(m), 1390(s), 1201(s), 1169(s), 1083(s), 960(s), 885(w), 838(m), 797(s), 761(s), 669(w), 507(w), 471(m). m/z (% relative intensity) theoretical m/z. $C_{22}H_{42}Si_2O_6$, 458.2535(36.1)458.2520. $C_{16}H_{27}O_3Si$, 295.1662(8.3)295.1729. $C_{10}H_{12}$,132.0949(100)132.0939.

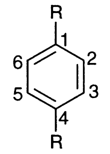
Preparation of 1,4-bis(triethoxysilylmethyl)durene 4. Prepared as described for **1** from 1,4-bis(trichlorosilylmethyl)-durene (2.4 g, 5.59 mmol) and ethanol (40 cm^3). Yield, 2.12 g (78%). ν/cm^{-1} (KBr): 2974(s), 2926(s), 2887(s), 1481(w), 1442(m), 1391(s), 1366(w), 1295(w), 1250(w), 1169(s), 1083(s), 960(s), 855(m), 789(s), 755(w), 554(w). m/z (% relative intensity) theoretical m/z. $C_{24}H_{46}Si_2O_6$,486.2829(39.6)486.2833. $C_{18}H_{31}O_3Si$, 323.2012(4.0%)320.2042. $C_{12}H_{16}$, 160.1264(9.8)-160.1252.

Preparation of 1,3-bis(triethoxysilylmethyl)benzene 5. Prepared as described for **1** from 1,3-bis(trichlorosilylmethyl)-benzene (2.6 g, 6.97 mmol) and ethanol (40 cm^3). Yield, 2.52 g (84%). m/z (% relative intensity) theoretical m/z. $C_{20}H_{38}Si_2O_6$, 430.2189(2.5)430.2207. $C_{14}H_{23}O_3Si$,267.1437(1.0)267.1417. C_8H_8, 104.0600(13.4)104.0626.

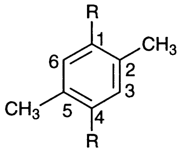
Preparation of 9,10-bis(triethoxysilylmethyl)anthracene 6. Prepared as described for **1** from 9,10-bis(trichlorosilylmethyl)-anthracene (2.0 g, 4.23 mmol) and ethanol (40 cm^3). Yield, 1.91 g (85%). ν/cm^{-1} (KBr): 2974(s), 2926(s), 2888(s), 1457(w), 1447(s), 1389(s), 1367(s), 1294(w), 1261(w), 1168(s), 1083(s), 1026(s), 962(s), 870(w), 794(s), 753(s), 664(w), 459(w). m/z (% relative intensity) theoretical m/z. $C_{28}H_{42}Si_2O_6$, 530.2514-(100%)530.2520. $C_{22}H_{27}O_3Si$, 367.1655(2.0)367.1729. $C_{16}H_{12}$, 204.0961(8.6)204.0939.

Preparation of 1,4-bis(tripropoxysilylmethyl)benzene 7. Prepared as described for **1** from 1,4-bis(trichlorosilylmethyl)-

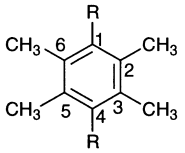
Table 9 ^{13}C NMR assignments of ring carbons in compounds **12–17** ($CDCl_3$, 150.90 MHz)



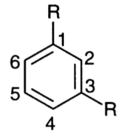
12



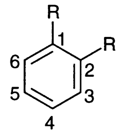
13



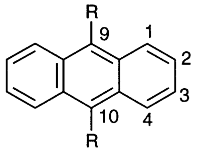
14



15



16



17

	12	**13**	**14**	**15**	**16**	**17**
C1	133.44	131.79	130.86	137.14	129.58	129.31
C2	128.79	132.50	131.10	129.61	135.33	125.00
C3	128.79	130.93	131.10	137.14	135.33	126.03
C4	133.44	131.79	130.86	125.07	129.58	124.01
C5	128.79	132.50	131.10	127.77	124.44	
C6	128.79	130.93	131.10	125.07	124.44	

[a] $R = CH_2Si(OCH_2CH_2CH_2CH_3)_3$.

Table 10 ^{29}Si chemical shifts of compounds **1–17** in $CDCl_3$

compound	chemical shift δ
1	−17.51
2	−50.78
3	−51.67
4	−51.69
5	−50.90
6	−53.36
7	−51.06
8	−51.00
9	−51.83
10	−51.18
11	−53.20
12	−50.68
13	−50.61
14	−50.80
15	−51.05
16	−50.78
17	−52.16

benzene (1.8 g, 4.83 mmol) and propanol (40 cm^3). Yield, 2.36 g (95%). ν/cm^{-1} (KBr): 2962(s), 2936(s), 2877(s), 1512(m), 1463(m), 1422(w), 1391(m), 1261(m), 1221(m), 1171(m), 1154(m), 1088(s,b), 1017(s), 916(w), 899(w), 878(w), 850(s), 757(m), 567(w), 528(w), 419(m). *m/z* (% relative intensity) theoretical *m/z*. $C_{26}H_{50}Si_2O_6$, 514.3146(45.3)514.3146. $C_{17}H_{29}O_3Si$, 309.1829(4.7)309.1886. $C_9H_{21}O_3Si$, 205.1266-(99.4)205.1260. C_8H_8, 104.0639(100)104.0626.

Preparation of 2,5-bis(tripropoxysilylmethyl)-*p*-xylene 8. Prepared as described for **1** from 2,5-bis(trichlorosilylmethyl)-*p*-xylene (2.60 g, 6.48 mmol) and ethanol (40 cm^3). Yield, 2.35 g (90%). ν/cm^{-1} (KBr): 2962(s), 2936(s), 2877(s), 1504(m), 1463(m), 1391(m), 1262(m), 1201(m), 1169(m), 1154(m), 1087(s, b), 1017(s), 885(m), 850(s), 802(w), 767(m), 466(w). *m/z* (% relative intensity) theoretical *m/z*. $C_{28}H_{54}Si_2O_6$, 542.3481-(48.1)542.3459. $C_{19}H_{33}O_3Si$, 337.2199(6.0)337.2199. $C_9H_{21}O_3Si$, 205.1317(89.3)205.1260. $C_{10}H_{12}$, 132.0968-(100)132.0939.

Table 13 ^{29}Si CPMAS chemical shift data (δ), relative areas of T^n environments and overall % condensation

xerogel	δ,T^0	δ,T^1	δ,T^2	δ,T^3	% condensation
XCl	−18.0, 5.2	−53.5, 5.3	−62.0, 51.3	−71.0, 38.2	74.2
X1		−53.0,8.3	−61.9,73.2	−70.7, 18.6	70.4
X2	−17.5, 5.9	−53.9, 9.5	−62.3, 57.9	−70.2, 26.6	68.5
X3a	−18.4, 4.3	−53.4, 4.7	−61.7, 61.4	−70.1, 29.6	72.3
X3b		−53.8, 8.8	−62.2, 66.6	−70.8, 24.6	72.1

Table 14 ^{13}C CP MAS chemical shift data and chemical shift assignments

xerogel	arene carbons	$-CH_2$ (T^1–T^3)	$-CH_2$ (T^0)	residual-SiOR/ROH
XCl	129.6, 134.1	22.5	0.8	
X1	129.5, 133.9	22.0		58.7, 18.1
X2	129.5, 133.8	22.4	0.5	64.8, 26.1, 10.8
X3a	129.6, 133.8	22.5	1.4	62.7, 35.0, 19.7, 14.3
X3b	129.5, 134.0	21.9		62.4, 34.9, 19.6, 14.5

Preparation of 1,4-bis(tripropoxysilylmethyl)durene 9. Prepared as described for **1** from 1,4-bis(trichloroxylsilylmethyl)durene (2.4 g, 5.59 mmol) and propanol (40 cm^3). Yield, 2.96 g (93%). δ_H (80 MHz, $CDCl_3$): 0.86–1.11(t, 18H), 1.39–1.64(m, 12H), 2.24(s, 16H), 3.50–3.66(q, 12H). ν/cm^{-1} (KBr): 2962(s), 2935(s), 2876(s), 1458(m), 1437(w), 1420(w), 1391(m), 1261(m), 1173(w), 1153(w), 1087(s,b), 1017(s), 899(w), 863(m), 830(m), 754(m), 555(w). *m/z* (% relative intensity) theoretical *m/z*. $C_{30}H_{58}Si_2O_6$, 570.3771(100)570.3772. $C_{21}H_{37}O_3Si$, 365.2438(5.0)365.2512. $C_9H_{21}O_3Si$, 205.0530-(22.6)205.1260. $C_{12}H_{16}$, 160.1226(3.3)160.1252.

Preparation of 1,3-bis(tripropoxysilylmethyl)benzene 10. Prepared as described for **1** from 1,3-bis(trichlorosilylmethyl)-benzene (2.60 g, 6.97 mmol) and propanol (40 cm^3). Yield, 3.40 g (95%). ν/cm^{-1} (KBr): 2962(s), 2936(s), 2877(s), 1604(w),

Table 11 Typical fragments in mass spectrum of compounds **1–17**

compound	typical fragments
1	$[M]^+$, $[M-2Si(OR)_3]^+$, $[Si(OR)_3]^+$
2	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$
3	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$
4	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$, $[Si(OR)_3]^+$
5	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$
6	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$
7	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$, $[Si(OR)_3]^+$
8	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$, $[Si(OR)_3]^+$
9	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$, $[Si(OR)_3]^+$
10	$[M]^+$, $[M-2Si(OR)_3]^+$, $[Si(OR)_3]^+$
11	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$, $[Si(OR)_3]^+$
12	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$, $[Si(OR)_3]^+$
13	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$, $[Si(OR)_3]^+$
14	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$, $[Si(OR)_3]^+$
15	$[M]^+$, $[M-2Si(OR)_3]^+$, $[Si(OR)_3]^+$
16	$[M]^+$, $[M-2Si(OR)_3]^+$, $[Si(OR)_3]^+$
17	$[M]^+$, $[M-2Si(OR)_3]^+$, $[M-Si(OR)_3]^+$, $[M-Si(OR)_3]^+$, $[Si(OR)_3]^+$

Table 12 Conditions for formation of xerogels

xerogel	precursor(mass/g)	solvent (volume/cm^3)	catalyst	time to gelation/d
XCl	$1,4\text{-}\{Cl_3SiCH_2\}_2C_6H_4$ (1.0)	THF(10)	0.11 cm^3 of 0.1 M HCl	1
X1	$1,4\text{-}\{(EtO)_3SiCH_2\}_2C_6H_4$ (2.0)	EtOH(10)	0.4 cm^3 of 0.1 M HCl	6
X2	$1,4\text{-}\{(PrO)_3SiCH_2\}_2C_6H_4$(1.89)	PrOH(10)	0.35 cm^3 of 0.1 M HCl	60
X3a	$1,4\text{-}\{(BuO)_3SiCH_2\}_2C_6H_4$(2.35)	BuOH(10)	1.0 cm^3 of 0.1 M HCl	21
X3b	$1,4\text{-}\{(BuO)_3SiCH_2\}_2C_6H_4$(2.1)	EtOH(5)	0.35 cm^3 of 0.1 M HCl	4

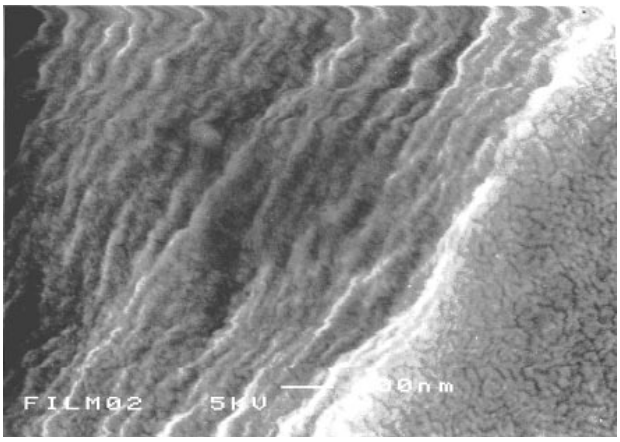


Fig. 3 Scanning electron micrograph showing nanoparticulate surface of film of **X3a**

1559(w), 1507(w), 1474(w), 1458(m), 1438(w), 1392(m), 1260(m), 1170(m), 1154(m), 1087(s,b), 1017(s), 930(w), 899(w), 847(s), 800(m), 755(w), 703(w), 472(w). *m*/*z* (% relative intensity) theoretical *m*/*z*. $C_{26}H_{50}Si_2O_6$, 514.3142(20.1)514.3146. $C_9H_{21}O_3Si$, 205.1252(100),205.1260. C_8H_8, 104.0613(6.6)-104.0626.

Preparation of 9,10-bis(tripropoxysilylmethyl)anthracene 11. Prepared as described for (1) from 9,10-bis(trichlorosilyl methyl)anthracene (2.00 g, 4.23 mmol) and propanol (40 cm^3). Yield, 2.39 g (92%). ν/cm^{-1} (KBr): 2961(s), 2934(s), 2876(s), 1473(w), 1457(m), 1387(w), 1369(m), 1261(m), 1169(m), 1087(s,b), 1018(s), 881(m), 840(m), 808(m), 746(s), 670(w), 420(w). *m*/*z* (% relative intensity) theoretical *m*/*z*. $C_{34}H_{54}Si_2O_6$, 614.3434(41.9)614.3459. $C_{25}H_{33}O_3Si$, 409.2172(1.7)409.2199. $C_9H_{21}O_3Si$, 205.1145(100)205.1260. $C_{16}H_{12}$, 204.0897(16.1)-204.0939.

Preparation of 1,4-bis(tributoxysilylmethyl)benzene 12. Prepared as described for **1** from 1,4-bis(trichlorosilylmethyl)-benzene (4.00 g, 10.72 mmol) and butanol (50 cm^3). After further distillation 5.45 g (85%) colourless liquid was obtained. δ_C (62.90 MHz, CDCl$_3$): 13.89, 18.93, 19.59, 34.61, 62.74, 128.79, 133.44. ν/cm^{-1} (KBr): 2959(s), 2934(s), 2874(s), 1512(m), 1465(m), 1385(m), 1301(w), 1262(w), 1222(w), 1171(w), 1093(s), 1041(s), 988(m), 899(m), 841(m), 801(m), 746(w), 567(w), 532(w). *m*/*z* (% relative intensity) theoretical *m*/*z*. $C_{32}H_{62}Si_2O_6$, 598.4085(100)598.4085. $C_{20}H_{35}O_3Si$, 351.2366(1.3)351.2356. $C_{12}H_{27}O_3Si$, 247.1708(48.5)247.1729. C_8H_8, 104.0633 (19.7)104.0626. Calc. for $C_{32}H_{62}Si_2O_6$: C, 64.16; H, 10.43. Found: C, 63.13; H: 10.70.

Preparation of 2,5-bis(tributoxysilylmethyl)-*p*-xylene 13. Prepared as described for **1** from 2,5-bis(trichlorosilylmethyl)-*p*-xylene (2.60 g, 6.48 mmol) and butanol (40 cm^3). Yield, 3.49 g (86%). ν/cm^{-1} (KBr): 2959(s), 2933(s), 2874(s), 1559(w), 1541(w), 1506(s), 1459(s), 1386(s), 1261(s), 1234(w), 1201(w), 1168(s), 1093(s,b), 1041(s), 988(s), 898(s), 837(w), 801(s), 734(w), 462(w), 442(w). *m*/*z* (% relative intensity) theoretical *m*/*z*: $C_{34}H_{66}Si_2O_6$, 626.4395(41.0)626.4397. $C_{22}H_{39}O_3Si$, 379.2733-(6.4)379.2668. $C_{12}H_{27}O_3Si$, 247.1721(34.2)247.1729. $C_{10}H_{12}$, 132.0937(82.4)132.0939.

Preparation of 1,4-bis(tributoxysilylmethyl)durene 14. Prepared as described for **1** from 1,4-bis(trichlorosilylmethyl)-durene (2.4 g, 5.59 mmol) and propanol (40 cm^3). Yield, 3.44 g (94%). ν/cm^{-1}(KBr): 2959(s), 2933(s), 2874(s), 1464(s), 1433(w), 1384(s), 1298(w), 1262(m), 1235(w), 1172(w), 1093(s,b), 1041(s), 1010(w), 987(s), 900(s), 831(w), 798(m), 773(w), 735(s), 428(w). *m*/*z* (% relative intensity) theoretical *m*/*z*: $C_{36}H_{70}Si_2O6$, 654.4712(4.7)654.4711. $C_{24}H_{43}O_3Si$, 407.2929(13.3)407.2982. $C_{12}H_{27}O_3Si$, 247.1688(30.3)247.1729. $C_{12}H_{16}$, 160.1231-(100)160.1252.

Preparation of 1,3-bis(tributoxysilylmethyl)benzene 15. Prepared as described for **1** from 1,3-bis(trichlorosilylmethyl)-benzene (2.60 g, 6.97 mmol) and butanol (40 cm^3). Yield, 3.96 g (95%). ν/cm^{-1} (KBr): 2959(s), 2933(s), 2874(s), 1604(m), 1585(w), 1465(s), 1386(s), 1300(w), 1261(w), 1235(w), 1170(w), 1152(w), 1093(s) 1041(s), 1010(w), 988(s), 930(m), 899(s), 835(w), 806(s), 736(m), 702(w), 455(w). *m*/*z* (% relative intensity) theoretical *m*/*z* $C_{32}H_{62}Si_2O_6$, 598.4080(14.0)598.4085. $C_{12}H_{27}O_3Si$, 247.1653(100)247.1729. C_8H_8, 104.0636(56.1)-104.0626. Calc. for $C_{32}H_{62}Si_2O_6$: C, 64.16; H, 10.43. Found: C, 63.04; H: 10.38%.

Preparation of 1,2-bis(tributoxysilylmethyl)benzene 16. Prepared as described for **1** from 1,2-bis(trichlorosilylmethyl)-benzene (2.50 g, 6.70 mmol) and butanol (40 cm^3). Yield, 3.73g (93%). ν/cm^{-1} (KBr): 2959(s), 2873(s), 2741(s), 1601(m), 1576(w), 1488(s), 1465(s), 1434(w), 1387(s), 1300(s), 1265(m), 1234(w), 1222(m), 1167(s), 1093(s), 1040(s), 1010(w), 988(s), 957(w), 938(w), 898(s), 801(s), 776(w), 758(m), 728(m), 673(m), 616(s), 562(w), 595(s), 471(s), 417(s). *m*/*z* (% relative intensity) theoretical *m*/*z* $C_{32}H_{62}Si_2O_6$, 598.4083(8.0)598.4085. $C_{12}H_{27}O_3Si$, 247.1641(100)247.1729. C_8H_8, 104.0641(26.2)-104.0626.

Preparation of 9,10-bis(tributoxysilylmethyl)anthracene 17. Prepared as described for **1** from 9, 10-bis(trichlorosilylmethyl)-anthracene (2.00 g, 4.23 mmol) and butanol (40cm^3). Yield, 2.80 g (95%). *m*/*z* (% relative intensity) theoretical *m*/*z* $C_{40}H_{66}Si_2O_6$, 698.4403(100)698.4398. $C_{28}H_{39}O_3Si$, 451.2728(10.8)451.2669. $C_{12}H_{27}O_3Si$, 247.1726(57.8)247.1729. $C_{16}H_{12}$, 204.0936(37.9)204.0939.

General procedure for the preparation of xerogels X1, X2, X3a, X3b. In general a clear solution of the alkoxy compound, 1,4-bis(RO$_3$SiCH$_2$)$_2$C$_6$H$_4$ (R = Et, Pr, Bu) in the appropriate solvent (see Table 12) was prepared under nitrogen in a Pyrex round-bottomed flask and subsequently treated with aqueous HCl (0.11 cm^3). This mixture was vigorously stirred to a clear sol, and left to gel in a static nitrogen atmosphere. No precipitation was observed and clear transparent gels subsequently formed. Gelation occured within 1–60 d. The wet gels were left to age for a further 24 h after which drying commenced through two small (diameter *ca.* 1 mm) pin-holes for several days. Subsequently, the whole sample was exposed to air for further slow drying for three weeks. The dried xerogels were obtained as transparent orange coloured monoliths. Precise experimental quantities used are given in Table 12.

X-Ray crystallography

Crystal data for compound **B**, $C_8H_8Cl_6Si_2$, $M = 373.02$, monoclinic space group $P2_1/c$; with $a = 8.9956(10)$, $b = 13.035(2)$, $c = 13.460(2)$ Å, $\beta = 103.85(1)°$, $V = 532.3(4)$ Å^3 , $Z = 4$, D_c 1.617 g cm^{-3}, $F = 1.249$ mm^{-1}, (000) = 744, 3087 reflections were measured using Mo-Kα ($\lambda = 0.71069$ Å) radiation. 2684 independent reflections were measured, θ range 2.21 $< \theta < 24.97°$. The structure was solved by direct methods and difference Fourier technique (SHELXS-86).[17] Refinement was carried out with full-matrix least-squares analysis on F^2(SHELXL-93)[18]. $R = \sum|F_o - F_c|/\sum F_o = 0.0406$ [1710 reflections with $I > 2\sigma(I)$]. $wR2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2] \sum[w(F_o{}^2)^2]\}^{1/2} = 0.0928$; $w = 1/[\sigma^2(F_o{}^2) + (0.0458P)^2 + 0.0.34P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$, and residual electron density 0.411/−0.327 e Å^3.

Crystal data for compound **C**, $C_8 H_8 Cl_6 Si_2$, $M = 373.02$, triclinic, space group $P\bar{1}$; with $a = 9.895(1)$, $b = 10.305(1)$, $c = 15.778(2)$ Å, $\alpha = 89.6(1)$, $\beta = 101.98(2)$, $\gamma = 91.29(1)°$, $V = 1573.4(3)$ Å^3, $Z = 4$, $D_c = 1.617$ g cm^{-3}, $\mu = 1.216$ mm^{-1}, $F(000) = 744$, 4774 reflections were measured using Mo-Kα ($\lambda = 0.71069$ Å) radiation. 4378 independent reflections were measured, θ range $1.98° < \theta < 22.99°$). The structure was solved by direct methods and difference Fourier technique (SHELXS-86).[13] Refinement was carried out with full-matrix least-squares analysis on F^2(SHELXL-93).[14] $R = \sum/F_o - F_c F_o = 0.0824$ [2198 reflections with $I > 2\sigma(I)$]. $wR2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]\sum[w(F_o{}^2)^2]/\}^{1/2} = 0.0928$; $w = 1/[\sigma^2(F_o{}^2) + (0.1546P)^2 + 0.00P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$, and residual electron density 0.489/–0.369 e Å^3.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater, Chem.,* 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/33.

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