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Nanostructuring organo-silicas: combination of intermolecular interactions and molecular recognition properties to generate self-assembled hybrids with phenylene or adenine···thymine bridging units†

Joël J. E. Moreau,* Benoît P. Pichon, Guilhem Arrachart, Michel Wong Chi Man and Catherine Bied

Laboratoire de Hétérochimie Moléculaire et Macromoléculaire (CNRS UMR 5076), Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296 Montpellier cedex 05, France. E-mail: jmoreau@cit.enscm.fr; Fax: +33 (0)4 67 14 72 12; Tel: +33 (0)4 67 14 72 11

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Owing to hydrophobic interactions, silyl linkers containing long alkylene chains allowed the synthesis of self-organised hybrids. Lamellar organo-silicas with phenylene or a hydrogen-bonded adenine···thymine complex as the bridging units are reported.

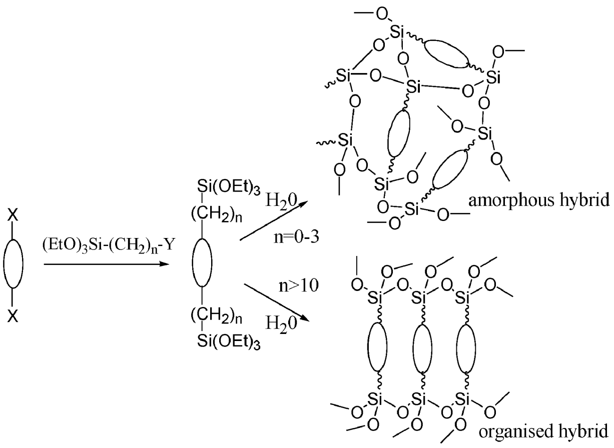
Since the first report of bridged organo-polysilsesquioxanes,[1,2] the hydrolysis-condensation of bis(trialkoxysilyl) organic molecules has led to a variety of silica hybrids with covalent linkages between the organic and the silicate network.[3,4] Materials with unique functionalities have resulted from mixing organic and inorganic substructures at the molecular level.[5,6] A step beyond the synthesis of new hybrids consists in structuring the solid on the nanoscopic scale in order to ensure appropriate tuning of the properties.[7] The creation of hybrids with well-ordered mesopore structures was obtained by using external organic surfactant templates,[8] first applied in the synthesis of a silica mesophase.[9]

Hybrid silsesquioxanes offer unique synthetic routes since the organic component can itself exhibit self-assembling properties and may direct the formation of the three-dimensional hybrid network by a self-organisation process. In connection to this, the use of hydrophobic trialkoxysilyl alkanes was first shown to allow the synthesis of layered or hexagonal silica-based materials.[10] Interestingly, weak interactions between aromatic units led to birefringent anisotropic or nanostructured hybrids.[11,12] We recently reported the use of H-bonding interactions for nanostructuring hybrids.[13,14] For the first time, a self-organised hybrid silica with a long-range ordered structure was obtained. The synthesis of lamellar hybrid solids with a crystalline arrangement of the organic substructures was achieved by combining H-bonding with π-stacking or hydrophobic interactions in the solid state.[14,15]

To obtain hybrid silsesquioxanes with targeted properties, the attachment of a trialkoxysilyl group (Scheme 1) to an organic molecule with appropriate properties is required. It is usually achieved by direct linkage through an hydrolytically stable Si–C bond or by use of readily available two- or three-carbon linkers.[1–5] We were interested in exploring the use of long hydrocarbon chains, which may play a double role in the material's synthesis: (i) as a linker, to ensure the covalent attachment between the organic and the inorganic components, and (ii) as a structure-directing motif, owing to its hydrophobic properties for the nanostructuring of the hybrid (Scheme 1).

We report here the use of C_{10} and C_{11} alkylenes to self-direct the organisation of organic substructures in a hybrid network (Scheme 1). First we chose a simple phenylene bridging unit since it was shown to give amorphous or short-range ordered hybrids in the absence of a structure-directing agent except for reactions in the solid state.[1,2,11,12,16] Additionally, the use of C_{10} or C_{11} alkylene chains should allow to generate nanostructured materials by combining self-organisation properties, resulting from the presence of a long hydrocarbon chains, with molecular recognition properties based on H-bonding interactions.[17]

The phenylene unit was linked to a functional $Si(OEt)_3$ group through a long alkylene spacer using three different procedures, according to Scheme 2. The intermolecular interactions in **1** and **2** combine hydrogen bonding and hydrophobic self-association. Interactions between two molecules of **2**, forming two intermolecular H-bonds, are expected to be weaker than between two molecules of **1**, which can give four intermolecular H-bonds. Bis(silylated) linker **3**, which has no H-bonding group,[16] was synthesised for comparison. The IR spectrum of **1** showed vibrations at 1633 (ν_{CO}) and 1582 (δ_{NH})



Scheme 1 Synthesis of organised *versus* amorphous hybrids.

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† Electronic supplementary information (ESI) available: ^{13}C solid state NMR spectrum of **L2**; ^{29}Si solid state NMR spectra of **L1** and **L2**; IR spectra of **L1** and **L4**. See http://www.rsc.org/suppdata/nj/b4/b419376h/

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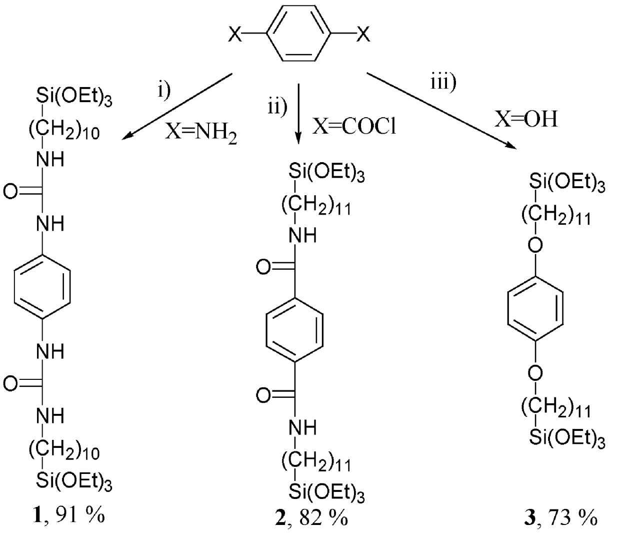


Scheme 2 Synthesis of hydrophobic precursors **1–3**: (i) 10-isocyanatodecyltriethoxysilane, CH_2Cl_2; (ii) 11-aminoundecyltriethoxysilane, CH_2Cl_2; (iii) 11-bromoundecene, K_2CO_3, CH_3CN then $HSi(OEt)_3$, Pt, THF.

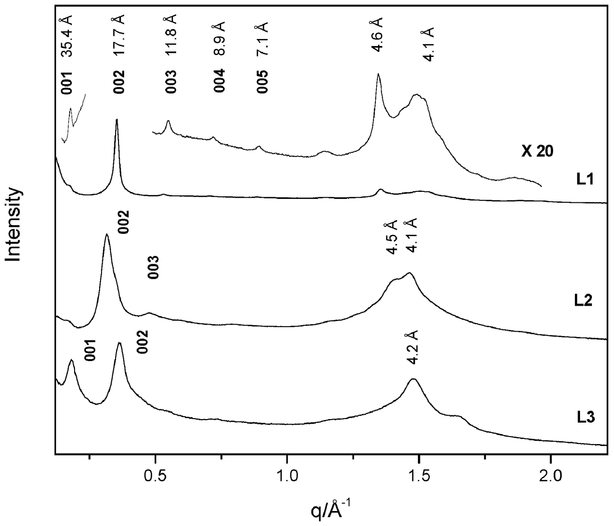
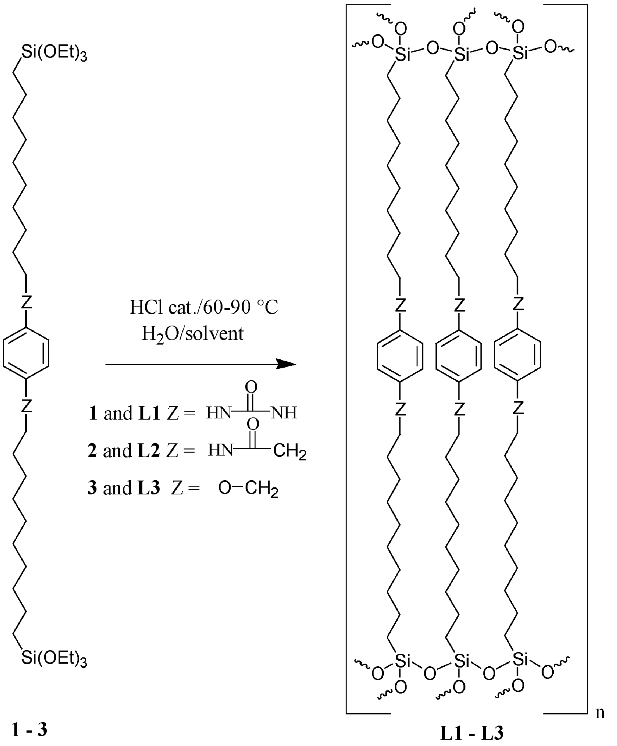


Fig. 1 Powder X-ray diffraction diagrams of hybrids **L1–L3**.

cm^{-1}. The observed low $\Delta\nu$ value ($\nu_{CO} - \delta_{NH}$) of 51 cm^{-1} is evidence for strong intermolecular H-bonding.[18] Interestingly, this value is much lower than the one observed for a similar molecule having a C_3 instead of a C_{10} carbon chain ($\Delta\nu = 60$ cm^{-1}).[15] The hydrophobic interactions between the long alkyl chains of **1** provide a synergetic effect and a significant reinforcement of the H-bonds. The IR spectrum of **2** is also consistent with H-bonding association ($\nu_{CO} = 1637$ cm^{-1}, $\delta_{NH} = 1548$ cm^{-1}).

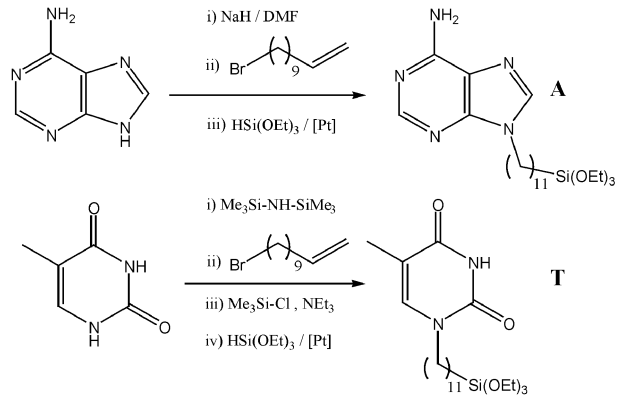
The hydrolysis-condensation of **1–3** to form silsesquioxane hybrids **L1–L3** was achieved in water to favour self-organisation by hydrophobic interactions (Scheme 3).[19] After 3 days at 60–80 °C, the white solids, which formed quantitatively, were collected after drying at 110 °C. Solid state ^{13}C and ^{29}Si NMR showed the expected resonances in agreement with the compositions described in Scheme 3 (see electronic supplementary information, ESI). ^{29}Si NMR spectra exhibited T^2 [$C–Si(OSi)_2(OH)$] and T^3 [$C–Si(OSi)_3$] units with a majority of T^2. The degree of condensation of the silicate networks varied from 72% to 79–80% for materials **L1–L3**, respectively. Confirming strong interactions between the organic substructures, the IR spectra showed H-bonded urea in **L1**: $\nu_{CO} = 1634$; $\delta_{NH} = 1581$ cm^{-1} ($\Delta\nu = 53$ cm^{-1}, see ESI) and amide in **L2**: $\nu_{CO} = 1644$; $\delta_{NH} = 1552$ cm^{-1}.



Scheme 3 Acid-catalysed hydrolysis-condensation[19] of **1–3** giving lamellar hybrids **L1–L3**, respectively.

Evidence of the lamellar structure of the materials was obtained upon examination of the X-ray powder diffraction diagram of **L1–L3** (Fig. 1). **L1** showed several sharp Bragg diffraction peaks. The one at the low q value of 0.177 $Å^{-1}$ corresponds to a characteristic distance $d = 35.4$ Å, compatible with the length of the organic spacer. Other peaks at higher q values corresponding to d values of 17.7, 11.8, 8.9 and 7.1 Å can be associated to the second, third, fourth and fifth orders of the first peak. These peaks correspond to the X-ray reflections of a unique family of reticular planes, indicating that the structure of **L1** appears to be mainly characterised by a periodicity in one direction. A similar long-range ordered lamellar structure can be proposed for **L2** and **L3** (Fig. 1). The observed main characteristic distances of 38.4 and 34.8 Å are also compatible with the length of the organic spacer. As already observed for related lamellar hybrids, the intensities of the XRD peaks due to the spacing 002 are larger than those of the 001 and other diffraction peaks. The diffraction peaks at 4.5–4.6 Å are associated to characteristic distances of H-bonded functional groups.[15] The peaks in the diffraction spectrum of **L2** appeared broader than those observed for **L1**. This is indicative of a decrease of the correlation length:[20] ξ(**L1**) = 369 Å, ξ(**L2**) = 103 Å, and of the ordering. This is in agreement with a decrease of the interactions between the organic spacers in **L2** containing H-bonded amido groups compared to **L1** with stronger H-bonded urea groups.

The most interesting feature came from the examination of the Bragg peaks in the diffraction diagram of **L3**. A related material with C5 alkylene spacer generated in a thin Teflon-coated cell exhibited birefringent properties.[16] Here, peaks for d values of 34.8 and 17.4 Å can be assigned to 001 and 002 reflection planes of an ordered lamellar structure. The interactions between spacer, only arising from the hydrophobic eleven-carbon chains, are directing the formation of the layered hybrid material **L3**. The calculated correlation length for **L3** ($\xi = 216$ Å) is higher than that for **L2**. This shows that the long chain organic linker without an H-bonding motif, as in **3**, can direct the organisation of the hybrid network



Scheme 4 Synthesis of the adenine (**A**) and thymine (**T**) precursors.

This led us to explore whether we would be able to combine these structuring properties by use of interactions between long hydrocarbon chain with molecular recognition properties involving H-bonding interactions in order to assemble and to organise two different organosilicon precursors. We first synthesised the silylated derivatives of adenine and thymine (Scheme 4).

The monosilylation of these compounds was achieved by alkenylation[21] with bromoundecene, followed by the hydrosilylation of the terminal double bond with $HSi(OEt)_3$ in the presence of a Pt catalyst to give functional derivatives **A** and **T**. In chloroform solution, the two precursors **A** and **T**, with complementary nucleic bases, formed the 1 : 1 complex **A**· · ·**T**. Evidence for the formation of a 1 : 1 complex of the silylated derivatives containing adenine and thymine nucleic bases was obtained from liquid ^{1}H NMR examination of $CDCl_3$ solutions (6×10^{-2} M) of pure **A**, pure **T** and a 1 : 1 mixture of **A** and **T**. In comparison with the solutions of the pure **A** and **T** compounds, the 1 : 1 mixture showed significant upfield shifts of the NH_2 protons of the adenine fragment (from 5.8 to 6.2 ppm) and of the N_3–H proton of the thymine mooiety (from 8.8 to 11.2 ppm). These upfield shifts are characteristic of a 1 : 1 adenine· · ·thymine complex[22] and reveal the existence of strong hydrogen bonding between **A** and **T** in solution. The hydrolysis of this 1 : 1 **A**· · ·**T** complex was achieved at 65 °C for 3.5 days in water with NaOH as catalyst (Scheme 5).

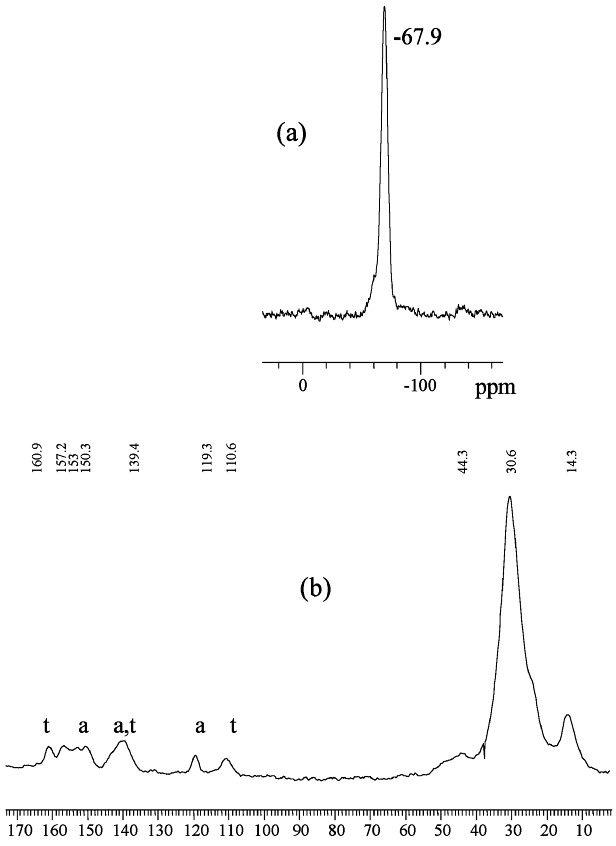
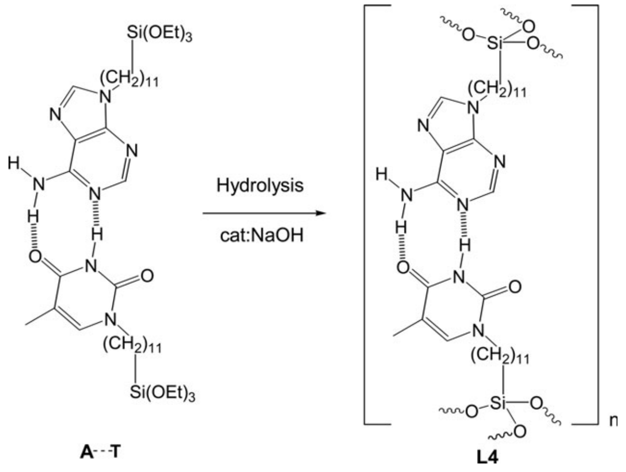


Fig. 2 ^{29}Si (a) and ^{13}C (b) solid state NMR of the adenine· · ·thymine bridged silsesquioxane **L4**.

The resulting hybrid **L4** was analysed by solid state NMR spectroscopy. ^{29}Si solid state NMR [Fig. 2(a)] exhibited a single signal at −67.9 ppm, indicative of a high degree of condensation of the hybrid siloxane network. ^{13}C solid state NMR [Fig. 2(b)] showed signals in the region 110–161 ppm, which are characteristic of the sp^2 carbons of the adenine (labelled a in the spectrum) and of the thymine (labelled t in the spectrum) units and are consistent with the existence of the **A**· · ·**T** complex in the solid material.

The X-ray powder diffraction of **L4** showed Bragg peaks (Fig. 3). The first two peaks at 0.195 and 0.386 Å^{-1} could be assigned as the first and second order peaks, respectively, of reticular planes of a lamellar form. The first peak corresponds to a characteristic distance of 32.2 Å, which is consistent with the length of the organic spacer in the (**A**· · ·**T**) complex. It is shorter than the similar distances in **L1–L3**, probably due to a



Scheme 5 Schematic representation of the formation of a thymine· · ·adenine bridged silsesquioxane.

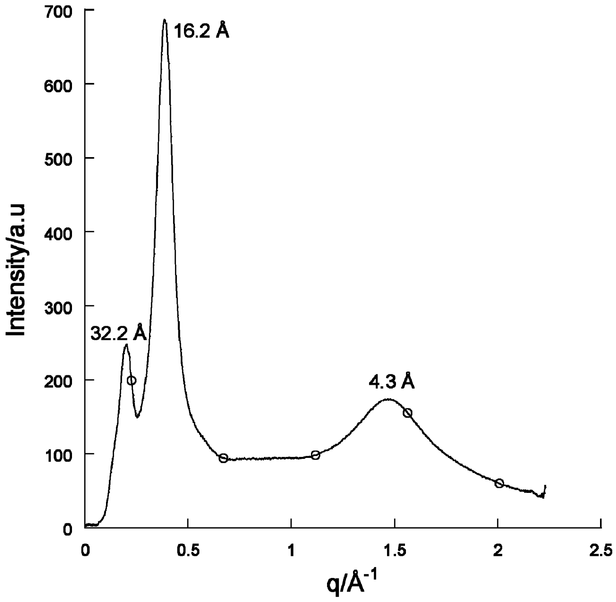


Fig. 3 Powder X-ray diffraction of the adenine· · ·thymine-bridged silsesquioxane **L4**.

different arrangement of the organic units with a bent or a tilted angle in the layered structure.

These preliminary results indicate that H-bonding interactions between adenine and thymine moieties allow association into a 1 : 1 complex and its organisation into a lamellar solid, owing to the structure-directing effects of the long hydrocarbon linkers. It is interesting to note that a variety of nanostructured materials may result from the combination of molecular recognition and self-assembling properties.

In conclusion, the use of silylated linkers containing C_{10} or C_{11} alkylene chains has been shown here to generate nanostructured bridged silsesquioxanes by a self-organisation process. It should allow the attachment of bridging organic substructures with various functionalities. Organic units not able to self-assemble could be used, provided the linker contains a hydrophobic segment as structure-directing motif. It appears that similarly organised solids can be created by using H-bonding interactions between urea groups or hydrophobic interactions between long hydrocarbon chains. Compared to H-bonding linkers,[13–15] long hydrocarbon linkers have the advantage to give soluble and easy-to-handle precursors. The hydrolysis-condensation can be easily achieved upon dispersion of the precursor in water to give nanostructured hybrids. Moreover, the introduction of nucleic acid base pairs in bridged silsesquioxanes shows that, in association with structure-directing motives, molecular recognition properties can lead to nanostructured materials incorporating two different organic subunits. Molecular recognition properties based on hydrogen-bonding interactions having a high potential to associate organic substructures, this approach offers interesting possibility to generate bio-inspired materials. We are currently investigating the generation of self-organised solids with anisotropic properties. For example, these may find uses as materials for electronics, optics or biosensors.[6,7]

Experimental

Powder X-ray diffraction (PXRD) measurements were performed at 20 °C at the "Groupe de Dynamique des Phases Condensées" in Montpellier (France) in glass capillaries with a copper rotating anode X-ray source (4 kW). $\Lambda_{K\alpha} = 1.542$ Å. Collection range of 2θ: 0–17° for the wide angle and 0.35–4° for the small angle.

Precursor synthesis

1,4-Bis[(triethoxysilyl)decylureido]benzene (1). In a Schlenk tube, 1,4-diaminobenzene (550 mg, 5.09 mmol) was dissolved in CH_2Cl_2 (40 ml) under nitrogen atmosphere. 3-(Triethoxysilyl)propylisocyanate (4.09 g, 11.86 mmol) was added and the mixture was stirred overnight at room temperature. The solvent was evaporated and the precipitate was washed with pentane. The solution was filtered to remove the solvent and excess 3-(triethoxysilyl)propylisocyanate. The resulting brown solid was dried *in vacuo* to give **1**. Yield: 91%; m.p.: 244 °C; IR (KBr, cm^{-1}): 1582 (δ_{NH}), 1633 (ν_{CO}), 3325 (ν_{NH}); ^1H NMR (DMSO d^6, δ): 0.53 (t, 4H, CH_2Si), 1.13 (t, 18H, CH_3), 1.2 at 1.4 (m, 36H, CH_2), 3.72 (qd, 12H, OCH_2), 5.97 (t, 2H, NH), 7.20 (s, 4H, H_{ar}), 8.13 (s, 2H, NH); ^{13}C NMR (50 MHz, DMSO d^6, δ): 9.8 (CH_2Si), 18.1 (CH_3), 22.3, 26.3, 28.6, 28.7, 28.8, 28.9, 29.8 and 32.3 (CH_2), 39.7 (CH_2N), 57.5 (CH_2O), 118.2 (CH_{ar}) and 134.2 (C_{ar}), 155.3 (CO); ^{29}Si NMR (50 MHz, DMSO d^6, δ): −45.1; FAB-MS: 799 $[M+1]^+$ (51%); anal. calcd for $C_{40}H_{78}N_4O_8Si_2$ (%): C 60.11, H 9.84, N 7.01; found: C 59.56, H 9.83, N 7.44.

1,4-Bis[(triethoxysilyl)undecylamido]benzene (2). In a Schlenk tube, 11-(amino)undecyltriethoxysilane (734 mg, 2.20 mmol) was dissolved in dry CH_2Cl_2 (15 ml), under nitrogen atmosphere, followed by addition of triethylamine (404 mg, 4 mmol). After 5 min, terephthaloyle chloride (231 mg, 1 mmol) dissolved in CH_2Cl_2 (5 ml) was added dropwise. After standing overnight at room temperature, the solvent was evaporated and the precipitate was washed with pentane. The powder was then dissolved in cyclohexane and the hot solution was filtered. The solvent was evaporated to give **2** as a white powder. Yield: 82%; m.p.: 134–137 °C; IR (KBr, cm^{-1}): 1548 (δ_{NH}), 1637 (ν_{CO}), 3301 (ν_{NH}); ^1H NMR (DMSO d^6, δ): 0.62 (t, 4H, CH_2Si), 1.15–1.45 (m, 50H, CH_3 and CH_2), 1.6 (m, 4H, CH_2), 3.19 (qd, 4H, CH_2), 3.54 (s, 4H, CH_2), 3.8 (qd, 12H, OCH_2), 5.37 (m, 2H, NH), 7.24 (s, 4H, H_{ar}); ^{13}C NMR (DMSO d^6, δ): 9.8 (CH_2Si), 18.1 (CH_3), 22.2, 26.3, 28.5, 28.6, 28.7, 28.8, 28.9, 29.0, 33.2, 42.0 (CH_2), 57.5 (CH_2O), 128.6 (CH_{ar}) and 134.4 (C_{ar}), 169.8 (CO); ^{29}Si NMR (50 MHz, DMSO d^6, δ): −45.2; FAB-MS: 779 $[M - EtO]^+$ (44%); anal. calcd for $C_{44}H_{84}N_2O_8Si_2$ (%): C 64.03, H 10.26, N 3.39, found: C 62.28, H 10.32, N 3.53.

1,4-Bis(11-undeceneoxy)benzene. Hydroquinone (550 mg, 5 mmol) was dissolved under nitrogen in CH_3CN (50 ml). Then, potassium carbonate (1.52 g, 11 mmol) was added, followed, after 5 min, by 11-bromoundecene (2.4 ml, 11 mmol). The mixture was left under reflux for 24 h and was then added to a solution of NaOH (0.1 N). The precipitate was filtered, then crystallised in methanol. Yield: 82%; m.p.: 59 °C; IR ($CHCl_3$, cm^{-1}): 1514 ($\nu_{C=C}$), 2851 ($\nu_{s\ CH_2}$), 2921 ($\nu_{as\ CH_2}$); ^1H NMR ($CDCl_3$, δ): 1.3–1.4 (m, 24H, CH_2), 1.78 (qt, 4H, CH_2), 2.07 (qd, 4H, CH_2), 3.92 (t, 4H, OCH_2), 4.98 (m, 4H, $CH_2{=}$), 5.85 (m, 2H, $CH{=}$), 6.84 (s, 4H, CH_{ar}); ^{13}C NMR ($CDCl_3$, δ): 26.0 (CH_2), 28.9, 29.1, 29.3 at 29.6 (4 CH_2), 33.8 (CH_2), 68.6 (CH_2O), 114.1 ($C{=}$), 115.4 (CH_{ar}), 139.2 ($C{=}$), 153.2 (C_{ar}). FAB-MS: 414 $[M+1]^+$ (63%); anal. calcd for $C_{28}H_{46}O_2$ (%): C 81.10, H 11.18; found: C 79.62, H 11.18

1,4-Bis[(triethoxysilyl)undecyloxy]benzene (3). This compound was obtained following synthetic procedures for related precursors with C5 alkylene chains.[16] 1,4-Bis(11-undeceneoxy)benzene (500 mg, 1.2 mmol) was dissolved in dry THF (20 ml). Triethoxysilylane (1.33 ml, 7.2 mmol) and Karstedt catalysis (53 µl, 1%) were added. After one night at room temperature, the solvent was evaporated, giving **3** as a colourless oil. Yield: 89%; IR (KBr, cm^{-1}): 1075–1101 (ν_{SiO}), 1508 ($\nu_{C=C}$), 2856–2976 (ν_{CH_2,CH_3}); ^1H NMR ($CDCl_3$, δ): 0.60 (t, 4H, CH_2Si), 1.21 (t, 4H, CH_3), 1.1–1.5 (m, 36H, CH_2), 1.71 (qt, 4H, CH_2), 3.78 (qd, 12H, OCH_2), 6.77 (s, 4H, H_{ar}); ^{13}C NMR ($CDCl_3$, δ): 10.3 (CH_2Si), 18.3 (CH_3), 22.7, 26.0, 29.2 and 29.4 (CH_2), 29.5 at 29.6 (5 CH_2) and 33.1 (CH_2), 58.2 (CH_2O), 115.3 (CH_{ar}) and 153.3 (C_{ar}); ^{29}Si NMR (50 MHz, $CDCl_3$, δ): −45.2; FAB-MS: 742 $[M+1]^+$ (14%).

***N*-9-Undecenyladenine.** A suspension of sodium adenine in dry DMF (150 ml), prepared from adenine (2 g, 14.8 mmol) and sodium hydride (0.355 g, 14.8 mmol), was stirred for 2 h. 11-Bromo-1-undecene (5.1 g, 22 mmol) was added dropwise and the mixture was heated to 70 °C for 8 h, giving a clear solution. The clear reaction mixture was concentrated to dryness under reduced pressure; the remaining solid was washed with dichloromethane and filtered. The solvent was eliminated *in vacuo* leading to an oil. *N*-9-Undecenyladenine was separated from *N*-7-undecenyl adenine by silica gel column chromatography (eluent: $CHCl_3$–EtOH, 6 : 1 v/v). A white solid was obtained. Yield: 65%; m.p.: 105 °C; ^1H NMR ($CDCl_3$, δ): 1.18 (m, 12H, 6 CH_2), 1.8–1.9 (m, 4H, 2CH_2), 4.12 (t, 2H, NCH_2), 4.86 (m, 2H, $CH_2{=}$), 5.5–5.8 (m, 1H, $CH{=}$), 6.78 (s, 2H, NH_2), 7.7 (s, 1H, C_2H), 8.3 (s, 1H, C_8H); ^{13}C NMR (CDC_{l3}, δ): 26.5–33.5, 43.78, 114, 119.5, 138.9, 140.1, 149.9, 155.8.

***N*-9-(Triethoxysilylundecyl)adenine (A).** To a stirred solution of *N*-9-undecenyladenine (0.84 g, 2.9 mmol) in anhydrous THF (10 ml) heated to reflux was added triethoxysilane (1.34 ml, 7.25 mmol) under nitrogen atmosphere, followed by the Karstedt catalyst (50 µl, 10.4% Pt). The reflux was pursued overnight, then the solvent was evaporated and the white precipitate obtained was washed several times with pentane. The white powder, which was filtered off, was dried *in vacuo*. Yield: 85%; m.p: 64 °C. ^{1}H NMR ($CDCl_3$, δ): 0.55 (t, 2H, CH_2Si), 1.16 (m, 25H, 3 CH_3 and 8 CH_2), 1.8 (m, 2H, CH_2), 3.7 (q, 6H, OCH_2), 4.09 (t, 2H, NCH_2), 6.78 (s, 2H, NH_2), 7.7 (s, 1H, C_2H), 8.2 (s, 1H, C_8H). ^{13}C NMR ($CDCl_3$, δ): 10.3, 18.2, 22–33, 43.9, 119.6, 140.2, 149.9, 155.8. ^{29}Si NMR ($CDCl_3$, δ): −44.48 (CH_2–Si). FAB-MS: 452 $[M+1]^+$ (100%). IR (KBr, cm^{-1}): 3500–3000, 2976, 2926, 2854, 1640, 1614, 1416, 1309, 1105, 1079, 956, 795; anal. calcd for $C_{14}H_{25}N_5O_3Si$ (%): C 58.50, H 9.15, N 15.51; found: C 58.11, H 9.02, N 15.8.

***N*-1-Undecenylthymine.** In a Schlenk tube, a mixture of thymine (2.24 g, 17.8 mmol), 1,1,1,3,3,3-hexamethyldisilazane (HMDS, 11.4 ml, 54 mmol), and trimethylchlorosilane (TMSCl, 1.1 ml, 8.9 mmol) was refluxed under nitrogen atmosphere until a clear solution was obtained. The excess of HMDS was evaporated. To the resulting 2,4-bis(trimethylsilyl)thymine were added dry DMF (15 ml) and 11-bromo-1-undecene (5 g, 21.4 mmol). The mixture was stirred for 11 days at 80 °C under an inert atmosphere. After removal of the solvent, the remaining oil was chromatographed (CH_2Cl_2–EtOH 10 : 1 v/v) giving a solid recrystallised from toluene (yield: 70%). M.p: 97.5 °C; ^{1}H NMR ($CDCl_3$, δ): 1.24 (m, 12H, 6 CH_2), 1.62 (m, 2H, CH_2), 1.9–2 (m, 5H, CH_2 and CH_3), 3.65 (t, 2H, NCH_2), 4.9 (m, 2H, $CH_2{=}$), 5.7–5.9 (m, 1H, $CH{=}$), 6.97 (s, 1H, C_6H), 9.9 (br s, 1H, NH);^{13}C NMR ($CDCl_3$, δ): 12.3, 26–33, 48.5, 110.5, 114.1, 139, 140.4, 151.16, 164.7.

***N*-1-(Triethoxysilylundecyl)thymine (T).** In a Schlenk tube, a mixture of *N*-1-undecenylthymine (0.835 g, 3 mmol) and TMSCl (0.77 ml, 6 mmol) in dry toluene (40 ml) was stirred under nitrogen atmosphere. A solution of triethylamine (0.84 ml, 6 mmol) in dry toluene (10 ml) was added dropwise. The mixture was stirred at room temperature for 12 h, then the precipitate obtained was filtered; the filtrate was concentrated under reduce pressure. To the protected undecenylthymine was added anhydrous THF (5 ml), triethoxysilane (1.7 ml, 9 mmol), and platinum Karstedt catalyst (2.4% Pt, 70 µl). The stirring was continued overnight, then the solvent was evaporated and the white precipitate obtained was washed several times with pentane. The white powder, which was filtered off, was dried *in vacuo*. Yield: 85%; m.p.: 87 °C; ^{1}H NMR (CDC_{l3}, δ): 0.57 (t, 2H, CH_2Si), 1.19 (m, 25H, 3 CH_3 et 8 CH_2), 1.57 (m, 2H, CH_2), 1.86 (s, 3H, CH_3), 3.63 (t, 2H, NCH_2), 3.77 (q, 6H, OCH_2), 6.9 (s, 1H, C_6H), 9.9 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$, δ): 10.3, 12.2, 18.2, 22–33, 48.5, 58.2, 110.4, 140, 151, 164.7; ^{29}Si NMR ($CDCl_3$, δ): −44.5; FAB-MS: 443 $[M+1]^+$ (32%); IR (KBr, cm^{-1}): 3414, 3223, 2926, 2854, 1690, 1642, 1479, 1422, 1360, 1220, 1105, 1080, 948, 764; anal. calcd for $C_{22}H_{42}N_2O_5Si$ (%): C 59.69, H 9.56, N 6.33; found: C 59.25, H 9.54, N 6.85.

Materials synthesis

L1. In a 12 ml tube, 1,4-bis[(triethoxysilyl)decylureido] benzene (**1**; 125 mg, 0.17 mmol) was completely dissolved in DMSO (2.8 ml) by heating. A gel was obtained at room temperature. Distilled water (1.7 ml) was added while stirring and a white precipitate formed. Then a 1 M solution of HCl (31.3 µl) was added. The tube was sealed and after 4.5 days reaction at 60 °C, the precipitate was filtered, then washed successively with water, ethanol and acetone. The solid was dried for one night at 110 °C, yielding **L1** as a brown powder. The characteristics of **L1** are the following: IR (KBr, cm^{-1}): 1581 (δ_{NH}), 1634 (ν_{CO}) and 3330 (ν_{NH}); ^{13}C CPMAS NMR δ: 11.4, 31.8 (7C), 40.1, 58.2, 125.0, 133.0, 158.7; ^{29}Si CPMAS NMR δ: −47.7, −57.7, −67.6 (T^1, T^2 and T^3); anal. found (%): C 55.29, H 8.45, N 9.22, Si 10.60.

L2. Following the procedure for **L1** above with 1,4-bis[(triethoxysilyl)undecylamidomethyl]benzene (**2**; 140 mg, 0.17 mmol), **L2** was obtained as a yellow powder. The characteristics of **L2** are the following: IR (KBr, cm^{-1}): 1552 (δ_{NH}), 1644 (ν_{CO}) and 3299 (ν_{NH}); ^{13}C CPMAS NMR δ: 14.5, 31.3 (9C), 40.4, 53.6, 129.9, 132.9, 172.6; ^{29}Si CPMAS NMR δ: −57.7, −66.7, (T^2 and T^3); anal. found (%): C 55.68, H 8.23, N 4.11, Si 11.82.

L3. Following the procedure for **L1** above (but omitting the DMSO) with 1,4-bis[(triethoxysilyl)undecyloxy]benzene (**3**; 125 mg, 0.17 mmol), **L3** was obtained as a yellow powder. The characteristics of **L3** are the following: IR (KBr, cm^{-1}): 1039–1111 (ν_{SiO}), 1511 ($\delta_{C=C}$), 2853–2925 (ν_{CH_2}) and 3431 (ν_{SiOH}); ^{13}C CPMAS NMR δ: 11.4, 31.8 (8C), 40.1, 58.2, 125.0, 133.0; ^{29}Si CPMAS NMR δ: −47.9, −57.5, −66.9 (T^1, T^2 and T^3); anal. found (%): C 44.36, H 6.42, N 10.81, Si 15.40.

L4. *N*-9-(Triethoxysilylundecyl)adenine (113 mg, 0.25 mmol) and *N*-1-(triethoxysilylundecyl)thymine (111 mg, 0.25 mmol) were completely dissolved in dry THF (0.25 ml) to facilitate the formation of the **A**···**T** complex. After concentrating the mixture, the residue was dissolved in an aqueous sodium hydroxide solution (40 mg NaOH in 2.5 ml H_2O). The solution was left to stand for 3.5 days at 65 °C. The resulting gel was filtered, washed successively with water, ethanol and acetone. The solid **L4** was collected, after drying, as a colourless powder. The characteristics of **L4** are the following: IR (KBr, cm^{-1}, see ESI): 3400–3200, 2923, 2852, 1660, 1603, 1510, 1466, 1142, 1020; ^{13}C CPMAS NMR δ: 14.3, 30.6, 44.3, 110.6, 119.3, 139.4, 150.3, 153, 157.2 160.9; ^{29}Si CPMAS NMR δ: −67.9 (T^3).

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