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Self-organization of a tetrasubstituted tetrathiafulvalene (TTF) in a silica based hybrid organic–inorganic material

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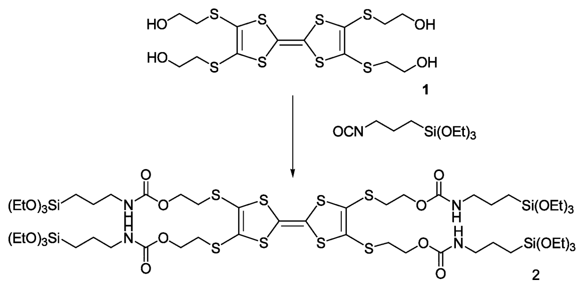
A hybrid organic inorganic nanostructured material containing a TTF core substituted by four arms exhibited a high level of both condensation at silicon (96%) and self-organization as evidenced by X-ray diffraction and an unprecedented birefringent behaviour.

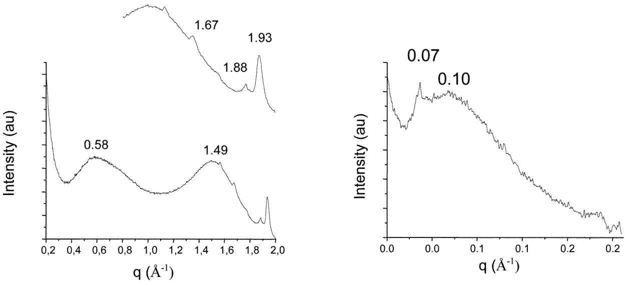
Sol–gel polycondensation is a very convenient method for the preparation of hybrid organic–inorganic silicon-based materials.[1] The choice of the precursor is extensive and several organic groups have been introduced into matrices by hydrolytic polycondensation of polyalkoxysilyl precursors.[2] The solids obtained are particularly attractive since they maintain the properties of the organic units. Moreover, besides the self-organization introduced by hydrogen bonding[3] these materials exhibit an anisotropic organization at the nanometric scale evidenced by their chemical reactivity,[4–6] and X-ray diffraction data.[7] A micrometric scale anisotropic order has also been observed by birefringence measurements.[8,9] These observations show that the hybrid materials are very good models for studying organization induced by weak van der Waals type interactions occurring between organic units during polycondensation as evidenced in the case of rigid or semi-flexible linear rod organic spacers and linear molecules with flexible arms.[10] In this paper we describe the same studies performed on a planar mesogenic structure corresponding to a tetrathiafulvalene unit (TTF) substituted by four flexible arms including the possibility of hydrogen bonding. The tetrasubstituted(trialkoxysilyl) TTF derivative **2** was obtained from the tetra-hydroxyethylthio TTF **1**[11] upon reaction with γ-isocyanatopropyltriethoxysilane in the presence of triethylamine (Scheme 1).† The hydrolysis of **2** was performed in THF with TBAF (tetrabutylammonium fluoride) as catalyst and a stoichiometric amount of H_2O.‡ The sol–gel transition was observed after 1–2 min. The gel was aged 6 days and then treated as usual to give a non-porous xerogel **X2** ($S_{BET} < 10$ m^2 g^{-1}).

The ^{29}Si CP MAS NMR spectrum of **X2** exhibited T^2 [C–Si(OR)(OSi)$_2$, δ −58.5 ppm (13%)] and T^3 [C–Si(OSi)$_3$, δ −66.5 ppm (87%)] substructures corresponding to a level of condensation estimated at 96%.[12] This very high level of condensation is surprising compared with other hybrid solids (usual range 61–80%)[13] and could be attributed to a favourable organization induced by the TTF units. The powder X-ray diffraction diagram of **X2** exhibited two broad signals centred at 1.49 Å^{-1} (4.20 Å) and 0.58 Å^{-1} (10.79 Å) when analysed from 0.2 to 2.0 Å^{-1} (Fig. 1(a)). This behaviour is similar to that of other polysilsesquioxane materials with a short-range order in the solid.[7,14] The signal centred at 1.49 Å^{-1} was attributed to the contribution of the Si–O–Si units.[7] Interestingly other rather sharp signals were observed at 1.56 Å^{-1} (4.01 Å), 1.67 Å^{-1} (3.75 Å), 1.88 Å^{-1} (3.34 Å) and 1.93 Å^{-1} (3.25 Å). These peaks are not observed in the case of linear spacers. They cannot be interpreted, however they evidence a higher periodicity and an organization of the solid on a longer range order than usually exhibited by these materials.[15] The more intense peak at 3.25 Å should correspond to the distance between two planes of TTF as already reported in the literature (3.43 Å).[16] More information has been obtained between 0.04 and 0.24 Å^{-1}, two signals were observed, a sharp one at 0.07 Å^{-1} (91.06 Å) and a broad one at 0.10 Å^{-1} (65.45 Å) (Fig. 1(b)). Taking into account the distance of 3.25 Å between the TTF units, these distances of 91.06 and 65.45 Å could roughly correspond to a stacking of respectively 28 and 20 TTF units.

A small part of the homogeneous solution containing precursor, THF, catalyst and H_2O, was introduced by capillarity in a thin Teflon-coated glass cell which was then sealed.[9] The sol–gel transition was observed in the cell after 30 min (absence of hydrodynamic movement after a gentle pressure on one cell glass plate). The cell was analysed by microscopy in polarized light. At the beginning the sol did not exhibit any birefringence property, indicating an isotropic medium. Immediately after the gel formation, a very weak birefringence appeared without any cracks in the gel. After a while the birefringence increased and the images in the plates were very different from the previous observations. For the first time some circular isotropic regions are observed (Fig. 2). Fig. 3(a) shows a magnified image of one of these isotropic regions. From moving off the centre of the circular isotropic region (A) a strongly bright ring (B) is observed followed by a black ring (C) and finally four extinction branches (D). To characterise these different



Scheme 1 Synthesis of the TTF precursor **2**.



a) b)

Fig. 1 X-Ray powder diagrams of the xerogel **X2**.

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birefringent regions, we first tilted the plate by 30° with respect to the light incidence direction. The central region (A) remains black. This fact suggests that (A) is free of matter since the material is almost fully polycondensed (96%). Moreover it is not possible to observe free oligomers as evidenced by the absence of T^0 and T^1 signals in the ^{29}Si CP MAS NMR spectrum. Furthermore this is confirmed by high magnifying microscopic experiments which reveal the Teflon layers used for coating the glass plates. In contrast the black ring (C) becomes bright when the cell is tilted suggesting that the gel is anisotropic in the region (C) with a slow optical axis ***s*** oriented perpendicular to the glass plates. In the other two birefringent regions (B) and (D) the slow optical axis ***s*** was measured using a Bereck compensator. Fig. 3(b) shows the slow axis field around the central isotropic region. The slow optical axis ***s*** is oriented radially close to the circular isotropic region (bright region (B) in Fig. 3(a)), it becomes normal to the cell plates (black ring (C) in Fig. 3(a)) and is finally oriented tangential to the circular isotropic region (four extinction branches region (D) in Fig. 3(a)). It is interesting to point out that this highly unusual birefringent behaviour has never been observed in either hybrid materials or the field of liquid crystals.

The value of birefringence increased with the length of ageing as previously observed with other precursors.[17] After several days, the birefringence (Δn) was evaluated at $\sim 5 \times 10^{-3}$. No changes were observed after several months. The birefringence measured in the solid is the signature of a micrometric organization. It has been reported that the nature of the organic unit is one of the key parameters for the formation of anisotropic organized materials.[9b] When the organic spacer is linear with more or less flexibility, the birefringence generally appears after the formation of cracks in the gel, indicating that the anisotropic organization at the mesoscopic level is closely linked to the cracking process.[14,15] In the present case the gel resulting from the hydrolysis–condensation of the TTF derivative **2** is birefringent without cracks. This difference could be explained by the nature of the organic unit, which presents a mesogen structure with a planar discotic core connected to four flexible arms. Probably the nature of the rigid and flexible parts and their ratio in the organic spacer are key factors for both short- and long-range order organization.

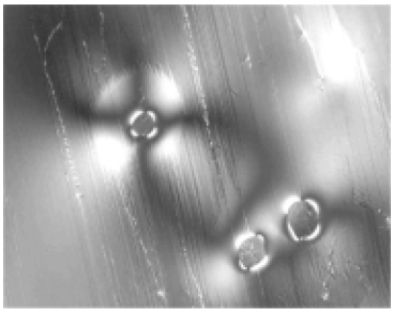

Fig. 2 **X2** Observed by polarizing optical microscopy.

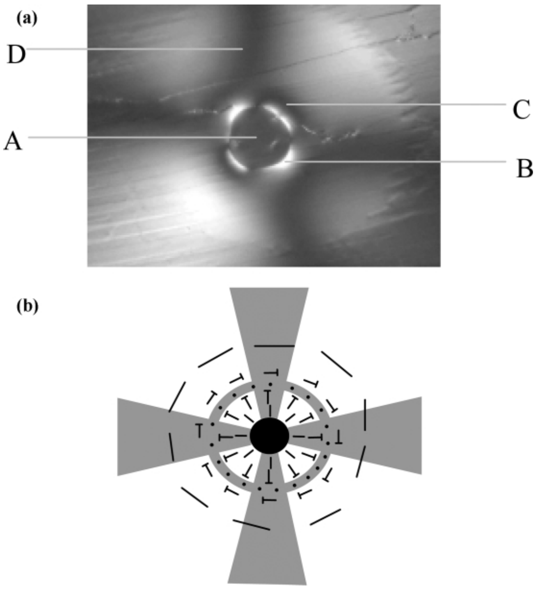

Fig. 3 (a) Magnified image of one isotropic region of **X2** and (b) orientation of the optical slow axis ***s***.

Notes and references

† *Selected data* for **2**: orange thick oil. ^1H NMR ($CDCl_3$): δ 0.66 (t, *J* 8.2 Hz, 8H), 1.26 (t, *J* 7.0 Hz, 36H), 1.65 (tt, *J* 6.3 Hz, *J* 8.2 Hz, 8H), 3.09 (t, *J* 6.3 Hz, 8H), 3.19 (q, *J* 6.3 Hz, 8H), 3.85 (q, *J* 7.0 Hz, 24 H), 4.26 (t, *J* 6.3 Hz, 8H), 5.33 (br t, *J* 6.3 Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 8.02, 18.68, 23.61, 35.55, 43.87, 58.84, 63.33, 111.13, 128.46, 156.45; ^{29}Si NMR ($CDCl_3$): δ -45.70; FAB $[C_{54}H_{105}O_{20}N_4S_8Si_4 + H]^+$, *m/z*: calc. 1497.4165, found 1497.4134; elemental analysis: calc. for $C_{54}H_{105}O_{20}N_4S_8Si_4$: C 43.30, H 7.00, N 3.74, S 17.09. Found: C 43.84, H 7.09, N 3.80, S 17.04%.

‡ In a Schlenk tube, 1.75 g (1.17 mmol) of **2** and 1.67 mL of dried THF were introduced. 1.67 mL of solution containing 24 μL (24 μmol) of TBAF (1 mol L^{-1} in THF), 127 μL (7.02 mmol) of H_2O and 1.52 mL of dried THF, were added. After homogenization, a part of this mixture was introduced by capillarity into the cell, and the remaining solution was kept in the Schlenk tube. In the two cases, after the sol–gel transition, the gel was aged for 6 days. Then, the gel obtained in the Schlenk tube was crushed and washed twice with acetone, ethanol and diethyl ether, and the resulting powder was dried at 120 °C *in vacuo* for 3 h yielding an orange xerogel. The gel obtained in the cell was observed using a Laborlux 12POLS polarizing microscope. Photographs were taken using a Leica wild MPS28 camera. The birefringence Δn of the gels was obtained from the expression $\Delta l = (\Delta n)d$, where Δl is the optical path difference and d is the cell thickness which is evaluated by UV-vis spectroscopy (15 ± 2 μm); Δl was measured by a Berek compensator.

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