(Trialkoxysilyl)tetrathiafulvalenes: Precursors of Organized Organic-Inorganic Hybrid Materials by Sol-Gel Chemistry

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The synthesis, characterization and electrochemical behaviour of novel monomers for use in sol-gel processes are described. These new compounds include a rigid tetrathiafulvalene (TTF) core substituted by one or two spacers, to which a triethoxysilyl group is covalently bonded. The synthesis is based on the preparation of various cyanoethyl-protected TTF thiolates, deprotection and alkylation of thiolate with 2-bromoethanol, and subsequent condensation of the alcohol function with 3-(triethoxysilyl)propyl isocyanate. The donor ability of the title compounds has been investigated by electrochemical studies. The hydrolytic polycondensation of these new precursors was performed in THF solution in the presence of nucleophile (tetrabutylammonium fluoride, TBAF) or acid (HCl) catalysts. The resulting hybrid solids are highly polycondensed and present organization at both the nanometric (X-ray diffraction) and micrometric (birefringence) scales.

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Introduction

Among the various possibilities used to form hybrid organic-inorganic materials, sol-gel polycondensation has attracted attention as it is an easy procedure to implement, under very mild conditions, to afford polysilsesquioxanes.[1−6] Sol-gel chemistry is thus expanding very rapidly, as it allows the preparation of a wide variety of hybrid organic-inorganic silicon based materials, in which the distribution of the organic group is homogeneous within the material. Moreover, thanks to the mild conditions used to form these polysilsesquioxanes (essentially hydrolysis of the polyalkoxysilyl precursor at room temperature), various organic fragments have been introduced into inorganic matrices. The organic moiety can be varied in length, rigidity, functionality and/or geometry of substitution. As examples, hybrid materials have been prepared from rigid molecules such as acetylenic,[7] thiophene,[8,9] or polyphenylene[10,11] moieties, or from flexible structures such as alkyl groups.[12,13] All the precursors contain an organic moiety covalently bonded to one or more hydrolysable trialkoxysilyl groups through a non-hydrolysable Si−C bond (general formula $R[Si(OR')_3]_n$, where R is the organic moiety). In the case of precursors substituted with one alkoxysilyl group ($n = 1$), the hydrolytic polycondensation gives rise to small macromolecules (mainly eight- and 12-unit oligomers) in which the organic parts are located at the surface of the macromolecules, which opens the way to functionalized surfaces.[14] On the other hand, when several alkoxysilyl groups are present on the organic fragment ($n>1$), their hydrolytic polycondensation affords three-dimensional hybrid polymers generally regarded as amorphous materials, like all inorganic solids prepared by sol-gel chemistry. However, it has been shown that self-organization in these monophasic hybrid materials occurs spontaneously during the hydrolytic polycondensation of bis-trialkoxysilylated precursors $R[Si(OR')_3]_n$ ($n = 2$).[15−17] (Scheme 1). In most cases the organic units present organization at the nanometric scale, evidenced by X-ray powder diffraction, and also at the micrometric scale, as shown by birefringence experiments in cross-polarized light microscopy.[15−17] However, the birefringence depends on several parameters: experimental conditions (kinetic control)[15] and the nature of the organic group.[15−17]

In the last few years, efforts have been devoted to directing the organization of the organic units within these materials. It has recently been shown, for instance, that weak interactions between aromatic units[17,18] or hydrogen bonding provided by urea groups[19] allowed the preparation of new anisotropic nanostructured hybrid materials through self-assembly of the molecular precursor. We have recently obtained the first self-organized tetrathiafulvalene (TTF) in a silica-based hybrid organic-inorganic material

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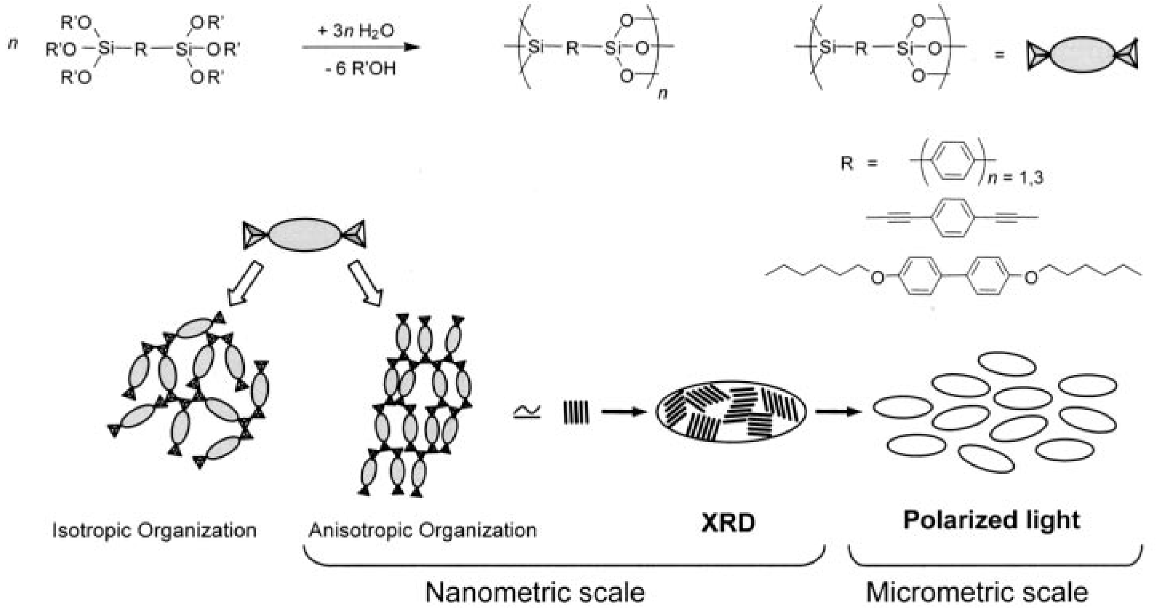
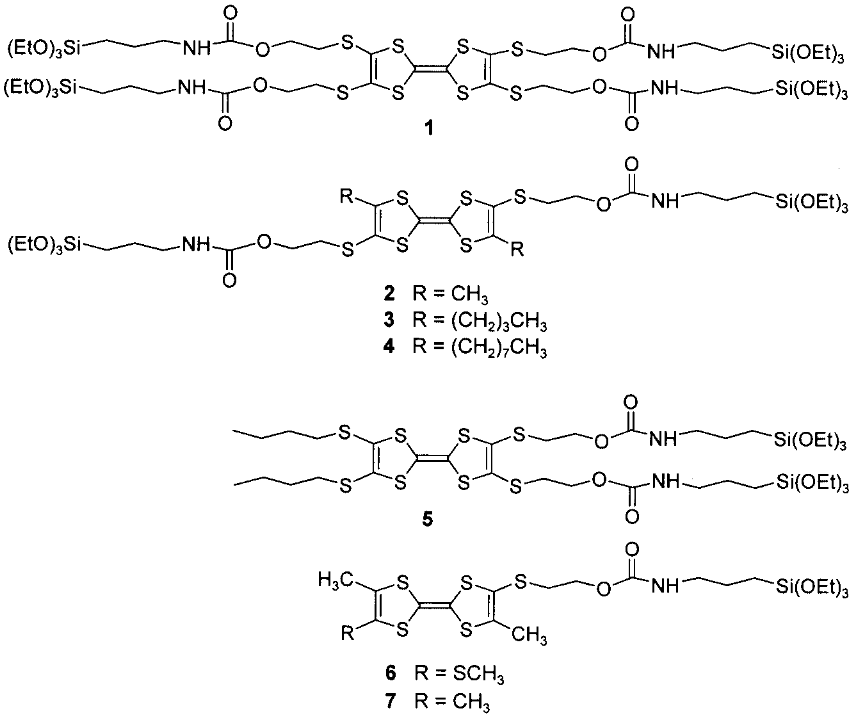


Scheme 1

prepared by sol-gel chemistry.[20] TTFs have provided the foundations of many organic materials[21−23] in which a wealth of attractive electronic properties (conductivity,[24] supraconductivity,[25,26] magnetism[27] …) has been observed, arising from specific organization and intermolecular interactions of these π-donor molecules in the solid state, mainly due to overlap interactions between open-shell species and weaker interactions (van der Waals interactions, hydrogen bonding...). It was thus attractive to extend this study to other TTF precursors.

In a preliminary communication we reported a route to the tetrakis-substituted(trialkoxysilyl) TTF derivative **1**, containing a carbamate moiety in the side chains.[20] It was therefore of interest to investigate the potential to extend this route to bis- and monosubstituted(trialkoxysilyl) TTFs (**2**−**7**), in order to evaluate the self-organization of TTF

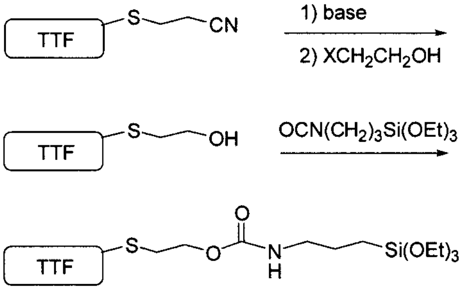


Scheme 2

cores with fewer side chains. Moreover, we also modified two parameters for the bis-substituted TTF: the positions of the triethoxysilyl groups, either on two different (**2**–**4**) or on the same dithiole ring (**5**) of the TTF core, and the length of the alkyl chain (R = Me, Bu, Oct) directly linked on the dithiole ring (**2**–**4**). In this article we report full experimental details on the synthesis of these TTFs (Scheme 2), analysis of their electron-donating properties and their sol-gel hydrolytic polycondensation. The auto-organization of the resulting organic-inorganic hybrid materials is evidenced by X-ray and birefringence experiments.

Results and Discussion

The general strategy used for the synthesis of the bis- and monosubstituted trialkoxysilyl-TTFs (**2**–**7**) is depicted in Scheme 3. The common approach consists first of the preparation of the various substituted cyanoethyl-TTFs, it having been shown that a cyanoethyl-protected TTF thiolate is an efficient building block for the preparation of a wide range of TTF derivatives.[28–31] Thiolate is easily regenerated in the presence of a strong base under inert atmosphere and is then allowed to react with various electrophiles such as 2-bromoethanol. By this approach, we prepared six new TTFs functionalized with hydroxyethylthio groups. The introduction of the alkoxysilane function was achieved through the reaction between the hydroxy group and the isocyanate function of the commercially available (triethoxysilyl)propyl isocyanate to afford six new silylated TTFs (Scheme 3).

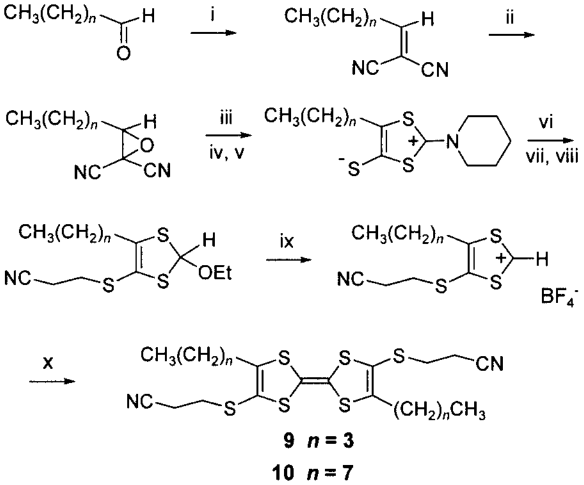


2-7

Scheme 3. General strategy for the synthesis of TTF derivatives (**2**–**7**)

It is worth noting that the synthetic pathway we have used for the synthesis of the title compounds allowed us to incorporate a carbamate function within the spacer between the TTF core and the trialkoxysilyl group. Carbamate functions are of great interest as they may influence the organization of the hybrid materials through hydrogen-bonding interactions. We also wish to point out that the alkoxysilyl substituents have to be introduced in the last stage of the synthesis, due to their high sensitivity towards the acidic, nucleophilic and basic conditions used to induce the hydrolytic polycondensation. To improve the solubility of the TTF derivatives, TTF **3** and TTF **4** were substituted with butyl and octyl chains, respectively. In the case of TTF **5**, the triethoxysilyl groups are on the same dithiole ring. Indeed, we set out to study the influence of the position of the alkoxysilane functions on the rigid organic block on the organization in the solid state after gelation.

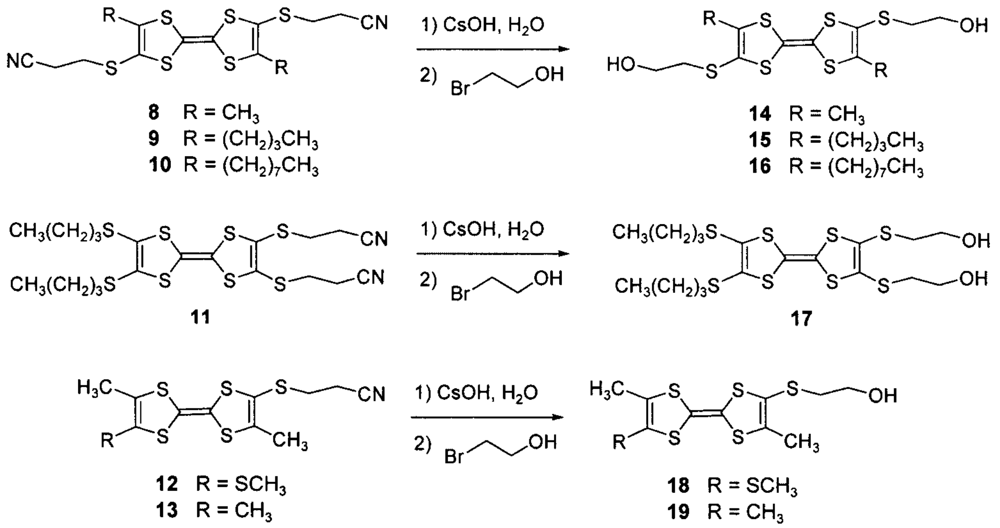
Among the different cyanoethylthio-functionalized TTFs **8**–**13** used as starting compounds, only the bis-cyanoethylthio-TTFs **9** and **10** were not mentioned in the literature, while we had previously reported the TTFs **8**, **12** and **13** as precursors of other TTF derivatives.[32–34] The synthetic pathway used to reach the TTFs **9** and **10**, substituted with two lipophilic groups (R = Bu, Oct), is outlined in Scheme 4. Their preparation was achieved according to this multistep synthesis by adjusting literature procedures.[35] A Knoevenagel condensation followed by epoxidation and treatment with dithiocarbamate salt opened the way to mesoionic-1,3-dithioles with alkyl chains (R = Bu, Oct). Alkylation with bromopropionitrile followed by reduction and acidic hydrolysis allowed the formation of the 2-ethoxy-1,3-dithiole derivatives. 1,3-Dithiolium salts were obtained in the presence of $HBF_4{\cdot}Et_2O$ and were converted, in basic medium, into TTFs **9** and **10**.



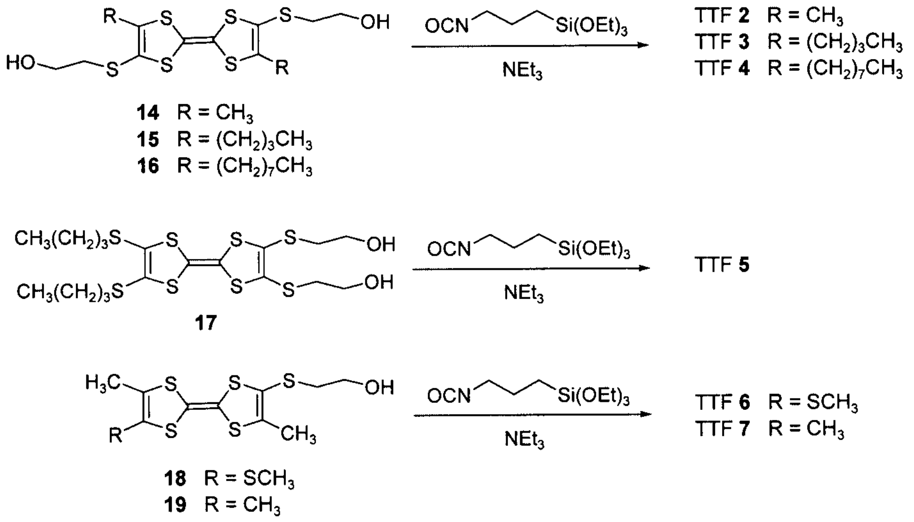
Scheme 4. Reaction conditions: i) $CH_2(CN)_2$, basic Al_2O_3; ii) NaClO, CH_3CN; iii) dithiocarbamate salt; iv) H_2SO_4; v) Ac_2O, CS_2, NEt_3; vi) bromopropionitrile; vii) $NaBH_4$, EtOH; viii) HCl, EtOH; ix) $HBF_4{\cdot}Et_2O$; x) NEt_3

As shown in Scheme 5, deprotection of the bis(cyanoethylthio)-substituted TTFs **8**–**11** and the cyanoethylthio-substituted TTF **12**–**13** with the appropriate amount of caesium hydroxide at room temperature, followed by alkylation with one or two equivalents of 2-bromoethanol, afforded the hydroxyethylthio-substituted TTFs **14**–**19** in good to excellent yields (70–92%) after column chromatography.

The trialkoxysilylated TTFs **2**–**7** (Scheme 6) were prepared by treatment of the hydroxyethylthio-substituted TTFs **14**–**19** with 3-(triethoxysilyl)propyl isocyanate in the presence of triethylamine and purified by column chromatography. Yields are moderate to good (26–76%), as silylated TTFs are sensitive to the presence of acid and/or trace water. They must be kept in a dry and cold atmosphere to limit uncontrolled polymerisation reactions.



Scheme 5



Scheme 6

Electrochemical Behaviour

The redox properties of these new TTF derivatives were investigated by cyclic voltammetry, and the results are summarized in Table 1. Each of the TTFs exhibits two reversible monoelectronic waves, as usually observed for TTF derivatives. It may be noted that the electron-donating capabilities of these new compounds are influenced by the presence of the thioalkyl groups linked to the donor core.

Table 1. Cyclic voltammetry data of TTF; *E* given in Volt vs. SCE, Pt working electrode with 0.1 M $n\mathrm{Bu_4NPF_6}$ in $\mathrm{CH_2Cl_2}$, scan rate100 mV/s

	E^1	E^2	ΔE (mV)
TTF **2**	0.41	0.84	430
TTF **3**	0.47	0.88	410
TTF **4**	0.41	0.83[a]	420
TTF **5**	0.50	0.82	320
TTF **6**	0.40	0.80	400
TTF **7**	0.32	0.79	470

[a] Quasi-reversible wave.

Indeed, with only one alkylthio substituent, the first oxidation wave is observed at lower oxidation potential (E^1 = 0.32V vs. SCE in **7**) than for two (0.40V < E^1 < 0.47V vs. SCE, in **2–4** and **6**) or four (E^1 = 0.50V vs. SCE, in **5**). As can be seen, the presence of silyloxy groups does not affect the redox behaviour of the TTF core; the donating ability of these new compounds is similar to that seen in, for example, a dimethyldimethylthio-TTF study under similar conditions (E^1 = 0.40 V, E^2 = 0.78 V vs. SCE, ΔE = 380 mV). The cation radical states of most of these new TTFs are stable over a wide potential range (ΔE = 320–470 mV). This result is of importance, as the physical properties are linked to the interaction between the radical species.

Preparation and Characterization of Hybrid Silsesquioxane Materials from TTFs 2−5

The hydrolysis-polycondensation of precursors **2**−**5** was performed under mild conditions in THF in the presence of 2% molar of catalyst (TBAF or HCl) and 1.5 equivalents of H_2O by $Si(OEt)_3$ group (stoichiometric amount) at room temperature. In the cases of **2**−**4**, gelation occurred within a few minutes (2−3 min) in the presence of the nucleophilic catalyst while needing a longer time in that of the acid catalyst (Table 2). No gel had formed after several weeks in the case of **5**. The gels were aged for six days and were then powdered and washed with ethanol, acetone and diethyl ether to give the xerogels, which were dried in vacuo (10^{-2} Torr) at 120 °C for two hours. They were used for porosimetry, NMR analyses and X-ray diffraction analysis. With regard to the textures of the solids, nitrogen BET measurements[36−37] gave no significant specific surface area for all the samples. All the solids were non-porous ($S_{BET} < 10\ m^2/g^{-1}$).

^{29}Si CP MAS NMR of the xerogels **2X**−**4X** displayed different distributions of signals according to the catalyst used. The main trend emerging from these results is the influence of the catalyst on the amounts of the different T^x substructures and on the level of polycondensation. Indeed, in the presence of the nucleophilic catalyst TBAF (xerogels **XA**), only one resonance − assigned to $T^3[C\text{-}Si(OSi)_3]$ units (δ = −68.2 ppm for **2XA**, − 67.7 ppm for **3XA** and −69 ppm for **4XA**) − was observed, while for the xerogels **XB**, generated with the acid catalyst HCl, resonances assigned to substructures $T^1[C\text{-}Si(OR)_2(OSi))$ at about −49 ppm, $T^2[C\text{-}Si(OR)(OSi)_2]$ at about −58 ppm and $T^3[C\text{-}Si(OSi)_3]$ units at about − 68 ppm were found (see Exp. Sect.). CP MAS is not generally quantitative, but no significant variation in relative peak intensity was observed in the case of such alkylene or arylene hybrid solids on comparison with single-pulse experiments that allow for quantitative determination.[38−39] Moreover, since materials produced from similar precursors are being compared, it can be assumed that relative peak intensity can be used to indicate variation of the level of condensation between them. The levels of condensation, estimated by deconvolution of spectra[38−39] are reported in Table 2. Interestingly, all the xerogels **XA** presented very high levels of condensation (100% with allowance for the accuracy of NMR), while moderately polycondensed siloxane networks were observed in the case of the xerogels **XB** (73%). This unusually high level of condensation is close to that of the first gel we described from the tetrakis-silylated TTF **1**, which was attributed to favourable organization induced by the TTF and carbamate units. With regard to the xerogels obtained with the aid of the acid catalyst, it is necessary to bear in mind that in the presence of protic acid such as HCl, protonation of the donor core could occur, inducing firstly a diminution of the catalyst necessary for the overall process and secondly a distortion of the donor core, as the protonated TTF is now not fully planar.[40,41]

X-ray powder diffraction analysis of these materials was performed; the diagrams are given in Figure 1. As with all the other nanostructured hybrid materials,[42] the X-ray diffraction diagrams did not exhibit any sharp Bragg's signals. However, broad signals, too large to be interpreted in terms of crystalline periodicity, were observed in all cases and were, as already shown, indicative of organization at the nanometric scale. As a first approximation, with a priori assumption of Bragg's law, the distances associated with the q values were determined ($d = 2\pi/q$). As can be seen in Figure 1, the nature of the catalyst used for the hydrolysis-polycondensation reaction had no influence on the organization at the nanometric scale, since the X-ray diffraction patterns of the corresponding solids (**XA** and **XB**) presented signals located at the same q values. The only difference observed was in the relative intensities of the peaks for the solids prepared under nucleophilic or acidic conditions. Each X-ray diffraction diagram exhibited three signals: two main, broad signals at similar distances in all the diagrams and another signal, the location of which is a function of the R substituent (Me, Bu, Oct) on the TTF core. The first broad signal, observed at 1.31 Å^{-1} (4.8 Å) for solids **2X** and at 1.50 Å^{-1} (4.2 Å) for xerogels **3X** and **4X**, and also observed in other nanostructured silica-based hybrid materials presenting non-linear geometry, is at present difficult to interpret. The second broad signal, observed at 0.67 Å^{-1} (9.4 Å) for **2X**, 0.57 Å^{-1} (11.0 Å) for **3X** and 0.54 Å^{-1} (11.7 Å) for **4X**, could be attributable to the contribution of the rigid TTF core, since, for instance, the distance between the two outer sulfur atoms of the same molecule amounts to approximately 9.6 Å for a *cis* configuration and 10.4 Å for a *trans* one.

Table 2. Characteristics of gels and xerogels

Xerogel	Precursor	Catalyst	Gel time (min)	Birefringence Δn ($\times 10^3$)	^{29}Si CP MAS NMR (%)				L. C.[a]
					T^0	T^1	T^2	T^3	(%)
1XA	1	TBAF	1−2	5	0	0	14	86	95
2XA	2	TBAF	2	1	0	0	0	100	100
2XB	2	HCl	15	1.1	0	16	49	35	73
3XA	3	TBAF	2	1.5	0	0	0	100	100
3XB	3	HCl	15	1.5	0	18	45	37	73
4XA	4	TBAF	3	2.5	0	0	0	100	100
4XB	4	HCl	165	2.7	0	16	52	32	72

[a] Level of condensation.

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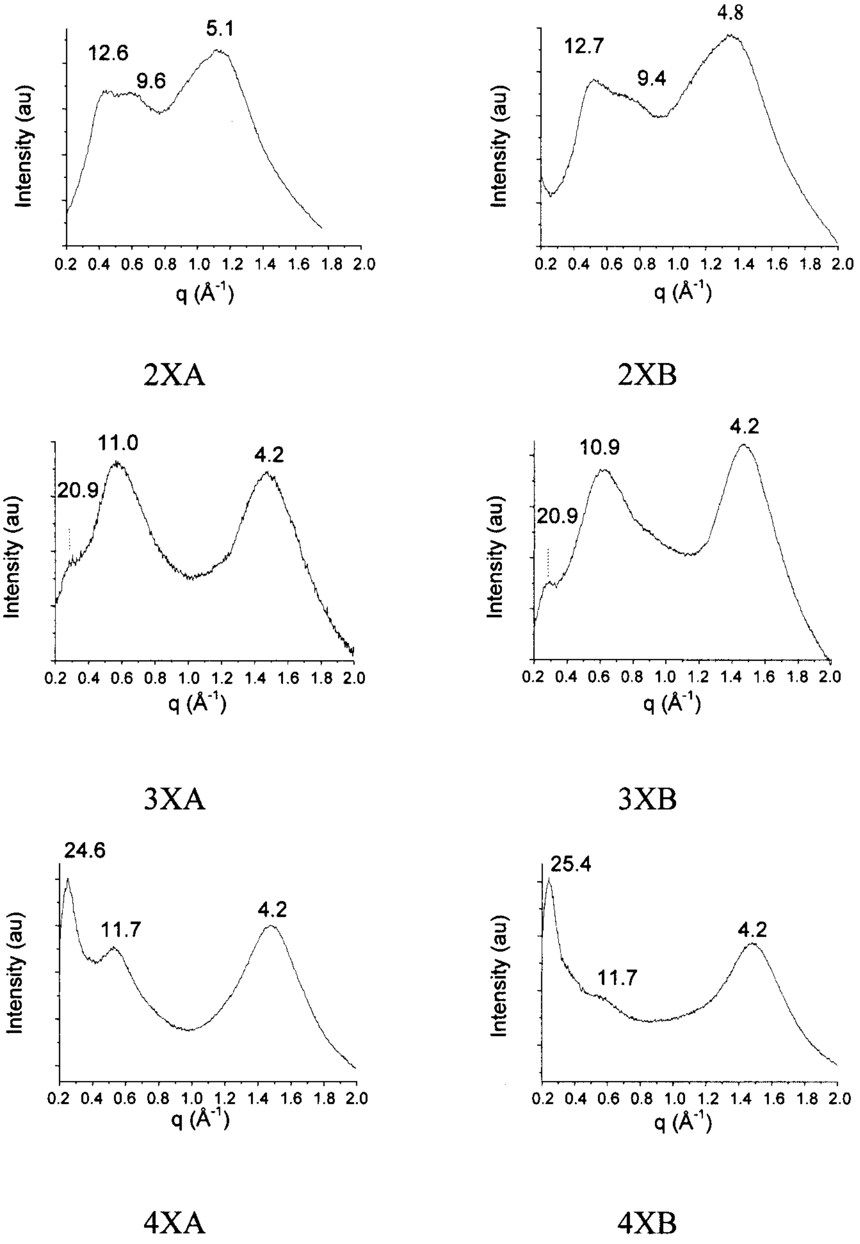


2XA 2XB

3XA 3XB

4XA 4XB

Figure 1. X-ray powder diagrams of the xerogels; values indicated for each peak are in Å

Interestingly, the position of the third signal in the X-ray powder diagrams differs according to the nature of the side chain on the TTF core in **2**–**4**. For instance, it corresponds to 0.49 Å^{-1} (12.7 Å) for xerogels **2X** with two methyl substituents, 0.30 Å^{-1} (20.9 Å) for xerogels **3X** with two butyl substituents, and 0.25 Å^{-1} (25.4 Å) for xerogels **4X** with two octyl substituents. This could be attributable to better organization of the TTF cores in the solid thanks to these longer lipophilic chains. Indeed, increased pre-organization of the TTFs could be due to hydrophilic interactions (alkyl chains bearing the silyloxy group) and segregation with the hydrophobic chain (octyl chain) favouring a "short-medium" range order organization. Moreover, the higher intensity of this peak at low q value in **4X** in relation to that of the signal at 4.2 Å can also be noted. In this case, the better organization could originate from the presence of the octyl group, inducing discotic behaviour of the TTF cores. This can be correlated to the previously made observation in the case of **1**,[20] so the signal at 25.4 Å could roughly correspond to a stacking of eight TTF units with allowance for a spacing of 3.25 Å between the units[43,44]

Observation by microscopy under polarized light gives information about the micrometric-scale order in the solids. A small part of the gelation mixture was introduced separately into thin Teflon-coated cells.[45] The initial solutions were completely dark when analysed by polarized optical microscopy, an observation characteristic of an isotropic medium. Transparent gels had formed, as evidenced by the absence of hydrodynamic movement, allowing a clear observation and measurements of the birefringence. Birefringence was observed for all the gels (**2X**−**4X**), and no significant influence of the catalyst on the value of birefringence was noticed (Table 2). The lowest birefringence was obtained for the TTF substituted with methyl groups **2X** ($1-1.1\times10^{-3}$) and the highest for the TTF substituted with octyl groups **4X** ($2.5-2.7\times10^{-3}$). These values reveal the presence of an anisotropic organized material. Interestingly, the value of birefringence increased with the length of the alkyl chain linked to the donor core, which was consistent with the differences observed in the X-ray powder diffractograms. However, two different morphologies were obtained for the birefringence pictures (Figure 2).

In the case of solids **2XA**, **4XA** and **4XB**, the birefringence appeared with formation of cracks after ageing of the gel during one day and its intensity had stabilized after one week. The morphology of the cracks was different in all cases. Parallel linear cracks were observed in the case of **2XA** (Me group), whereas a spiral was observed for **4XA** and irregular chunks for **4XB** (octyl group). These changes might originate from the presence of a longer lipophile chain in the case of **4X**. The orientation of the optical axis in the solids was determined with the aid of a Berek compensator and was found to be parallel to the propagation of the cracks in the case of **2XA** and perpendicular to the edges of the chunks in the case of **4XA** and **4XB** (Figure 3), and represents the average orientation of the organic moieties. In the case of **2X** and **3X**, because of the shortness of the methyl or butyl groups, the organic units can be compared to small rods and so the optical axis is oriented in the same direction as the organic group. The organic units inside the micrometric sized aggregates were therefore parallel, and the aggregates were thus oriented parallel to the propagation of the cracks (Figure 3).

A similar observation has previously been reported in the case of rigid-rod precursors.[46] In the case of solids **4X**, with allowance for the discotic behaviour of the TTFs, the optical axis is perpendicular to the core and so the organic units are parallel to the cracks. A similar observation has recently been reported in the case of planar precursors.[47]

In contrast, in the case of solids **2XB**, **3XA** and **3XB** the birefringence appeared after ageing during three weeks and its intensity was stable after four weeks. It did not present any cracking.

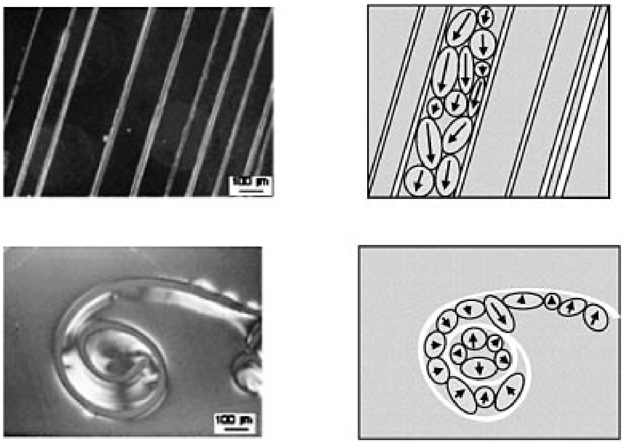
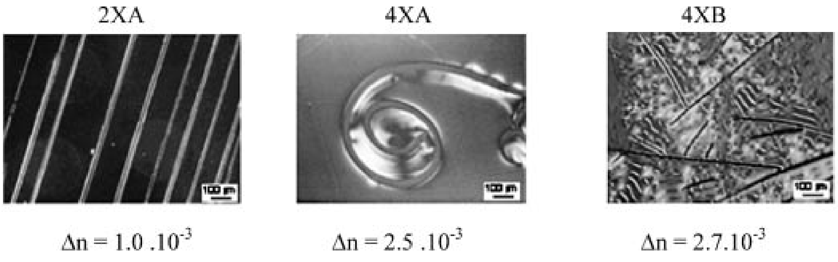


Figure 3. Orientation of the optical axis in the case of solids **2XA** (top) and **4XA** (bottom)

Conclusion

In conclusion, we present a two-step synthesis of new functionalized tetrathiafulvalene derivatives starting from preformed TTFs. They are substituted through the use of a spacer group (nine-atom chain) to one or two trialkoxysilyl functions. A carbamate function is part of the spacer, which may influence the organization of the materials by hydrogen-bonding. These compounds were fully characterized by ^{1}H and ^{13}C NMR spectroscopy and HR mass spectrometry, and analytically pure samples were prepared. Their electrochemical behaviour is very close to what is usually observed for such electron-rich olefins. A whole range of novel hybrid organic-inorganic materials emerge from these new precursors. The resulting non-porous solids are highly polycondensed and present organization at both the nanometric and the micrometric scales. These results strengthen the view that the auto-organization observed during the hydrolytic process is induced by the weak interactions (van der Waals, London, π-π stacking, hydrogen bonding) existing between the organic units during the polycondensation.



2XA 4XA 4XB

$\Delta n = 1.0 .10^{-3}$ $\Delta n = 2.5 .10^{-3}$ $\Delta n = 2.7.10^{-3}$

Figure 2. Birefringence pictures for the solids **2XA**, **4XA** and **4XB**

Experimental Section

General: THF was distilled from sodium-benzophenone prior to use. DMF was stirred over CaO overnight and distilled prior to use. All reagents were commercially available and were used without purification. Bis-cyanoethylthio-substituted TTFs **8**[32,33] and **11**[48] and mono-cyanoethylthio-substituted TTFs **12**[32,33] and **13**[33,34] were synthesized by literature procedures. We had previously mentioned the TTFs **8** and **13** as precursors of other TTF derivatives without giving their data, so their characterization is described in this Exp. Sect. Melting points were measured on a Kofler hot-stage apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker ARX 200 spectrometer, and ^{29}Si NMR were registered on a Bruker AM 300 spectrometer. Chemical shifts are quoted in parts per million (ppm) referenced to tetramethylsilane. The ^{29}Si CP MAS NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 60 MHz with use of a recycling delay of 10 s and a contact time of 5 ms. The spinning rate was 5 kHz. Chemical shifts are given relative to tetramethylsilane. Mass spectra were recorded on a Varian MAT 311 instrument at the Centre Régional de Mesures Physiques de l′Ouest, Rennes. Elemental analysis were performed at the Laboratoire Central de Microanalyse du CNRS, Lyon. TLC was performed with Merck Kieselgel 60 F_{254} plates, with viewing under ultraviolet light (254 nm). Chromatography was performed on Merck 60 silica gel (70−260 mesh). Cyclic voltammetry was carried out on a 10^{-3} M solution of TTF derivative in CH_2Cl_2 containing 0.1 M nBu_4NPF_6 as supporting electrolyte. Voltammograms were recorded at 0.1 Vs^{-1} on a platinum disk electrode (1 mm^2). Potentials were measured versus Standard Calomel Electrode (SCE). The nitrogen adsorption-desorption isotherms at 77.35 K were recorded on a Micromeritics Gemini III 2375 apparatus. The specific surface area was determined by use of the BET equation. The X-ray experiments were performed on powders of solids in a Lindeman tube with an imaging plate two-dimensional detector (Marresearch 2D "Image-Plate") with a rotating anode apparatus (Rigaku RU 200). The radiation used was Cu-K_α (λ = 1.5418 Å). Optical properties of the materials were observed with a Laborlux12POLS polarizing microscope. Photographs were taken with 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 µm). Δl was measured by use of a Berek compensator.

3,3′-[[5,5′-Dimethyl-2,2′-bi-1,3-dithiolylidene-4,4′-diyl]bis(thio)]bis-(propanenitrile) (8): Triethylamine (1 mL, 7 mmol) was added to a solution of 5-(2-cyanoethylthio)-4-methyl-1,3-dithiolium tetrafluoroborate (1.73 g, 6 mmol) in acetonitrile (20 mL). The mixture was stirred at room temperature for 1 h. The precipitate was filtered and washed with ethanol. Chromatography over silica gel (CH_2Cl_2) afforded **8** (0.80 g, 66%) as an orange powder. M.p. 151−152. °C. R_f = 0.56 (CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ = 2.20 (s, 6 H, CH_3), 2.66 (t, J = 6.8 Hz, 4 H, CH_2), 2.95 (t, J = 6.8 Hz, 4 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ = 16.2, 19.1, 31.5, 109.4, 116.9, 118.3, 139.1. HRMS: calculated for $C_{14}H_{14}N_2S_6$: 401.9481; found 401.9477. $C_{14}H_{14}N_2S_6$: calcd. C 41.76, H 3.50, N 6.96, S 47.78 ; found C 42.18, H 3.34, N 7.14, S 47.78%.

3,3′-[[5,5′-Dibutyl-2,2′-bi-1,3-dithiolylidene-4,4′-diyl]bis(thio)]bis-(propanenitrile) (9): The procedure was the same as had been used for TTF **8**, but starting from 4-butyl-5-(2-cyanoethylthio)-1,3-dithiolium tetrafluoroborate (1.90 g, 6 mmol). Chromatography over silica gel (CH_2Cl_2) afforded **9** (0.61 g, 42%) as an pale orange powder. M.p. 164−165 °C. R_f = 0.66 (CH_2Cl_2). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ = 0.97 (t, J = 7.1 Hz, 6 H, CH_3), 1.30−1.65 (m, 8 H, CH_2), 2.66 (t, J = 7.3 Hz, 4 H, $=CCH_2$), 2.70 (t, J = 7.0 Hz, 4 H, SCH_2), 2.99 (t, J = 7.0 Hz, 4 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ = 14.2, 18.9, 22.6, 30.4, 31.3, 32.3, 109.1, 116.0, 118.0, 144.6. HRMS: calculated for $C_{20}H_{26}N_2S_6$: 486.0420; found 486.0424. $C_{20}H_{26}N_2S_6$: calcd. C 49.38, H 5.35, N 5.76, S 39.51 ; found C 49.18, H 5.27, N 5.79, S 40.03%.

3,3′-[[5,5′-Dioctyl-2,2′-bi-1,3-dithiolylidene-4,4′-diyl]bis(thio)]bis-(propanenitrile) (10): The procedure was the same as had been used for TTF **8**, but starting from 5-(2-cyanoethylthio)-4-octyl-1,3-dithiolium tetrafluoroborate (2.24 g, 6 mmol). Chromatography over silica gel (CH_2Cl_2/EP, 2:1) afforded **10** (1.42 g, 79%) as an orange powder. M.p. 110−112 °C. R_f = 0.68 and 0.48 (CH_2Cl_2/EP, 2:1), *cis*/*trans* isomers. ^1H NMR (200 MHz, $CDCl_3$, ppm): δ = 0.92 (t, J = 6.4 Hz, 6 H, CH_3), 1.31 (m, 24 H, CH_2), 1.56 (m, 4 H, CH_2), 2.52−2.75 (m, 4 H, CH_2), 2.98 (t, J = 6.9 Hz, 4 H, SCH_2). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ = 14.5, 18.9, 23.1, 29.4, 29.5, 29.6, 30.2, 30.7, 31.3, 32.2, 109.1, 116.0, 118.0, 144.7. HRMS [ESI]: calculated for $C_{28}H_{42}N_2S_6$: 598.1672; found 598.1671. $C_{28}H_{42}N_2S_6$: calcd. C 56.14, H 7.07, N 4.68 ; found C 55.78, H 6.95, N 4.63%.

3-[(4,4′,5′-Trimethyl-2,2′-bi-1,3-dithiolyliden-4-yl)thio]propanenitrile (13): Triethylamine (1 mL, 7 mmol) was added to a solution of 5-(2-cyanoethylthio)-4-methyl-1,3-dithiolium tetrafluoroborate (0.87 g, 3 mmol) and 4,5-dimethyl-1,3-dithiolium hexafluorophosphate (0.83 g, 3 mmol) in acetonitrile (40 mL). The mixture was stirred at room temperature for 1 h. Solvent was removed by rotary evaporation, and the residue was extracted with CH_2Cl_2 and washed with water. Chromatography over silica gel (CH_2Cl_2/EP, 2:1) afforded TTF **13** (0.25 g, 25%) as an orange powder. M.p. 129−130 °C. R_f = 0.61 (CH_2Cl_2/EP, 2:1). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ = 1.99 (s, 6 H, CH_3), 2.22 (s, 3 H, CH_3), 2.69 (t, J = 6.9 Hz, 2 H, CH_2), 2.98 (t, J = 6.9 Hz, 2 H, CH_2). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): δ = 14.2, 16.0, 18.8, 31.2, 104.8, 112.4, 116.5, 118.1, 123.3, 139.0. HRMS: calculated for $C_{12}H_{13}NS_5$: 330.9652; found 330.9652. $C_{12}H_{13}NS_5$: calcd. C 43.50, H 3.93, S 48.34 ; found C 43.32, H 3.79, S, 48.05%.

General Procedure for the Synthesis of Mono- or Bis(hydroxyethylthio)-TTFs: A solution of CsOH, H_2O (1.5 mmol for **12** and **13**; 3 mmol for **8**−**11**) in MeOH (5 mL) was slowly added under argon to a solution of the mono- or bis(cyanoethylthio)-TTF **8**−**13** (1.5 mmol) in 40 mL of DMF. The mixture was stirred for 30 min at room temperature, after which 2-bromoethanol (1.5 mmol for **12** and **13**; 3 mmol for **8**−**11**) was added. Stirring was continued for 2 h at room temperature. Solvents were removed under vacuum, and the residue was extracted with CH_2Cl_2 and washed with water. Chromatography over silica gel afforded the corresponding mono- or bis(hydroxyethylthio) TTF **14**−**19**.

2,2′-[(5,5′-Dimethyl-2,2′-bi-1,3-dithiolylidene-4,4′-diyl)bis(thio)]bis-(ethanol) (14): Chromatography over silica gel (CH_2Cl_2/Et_2O, 1:1) afforded **14** (0.4 g, 70%) as an orange powder. M.p. 97−98 °C. R_f = 0.47 (CH_2Cl_2/Et_2O, 1:1). ^1H NMR (200 MHz, $[D_6]$DMSO, ppm): δ = 2.15 (s, 6 H, CH_3), 2.82 (t, J = 6.1 Hz, 4 H, SCH_2), 3.54 (dt, J = J = 6.1 Hz, 4 H, OCH_2), 4.98 (t, J = 6.1 Hz, 2 H, OH). ^{13}C NMR (50 MHz, $[D_6]$DMSO, ppm): δ = 15.5, 38.3, 60.2, 107.9, 118.8, 135.7. HRMS: calculated for $C_{12}H_{16}O_2S_6$: 383.94746, found 383.9475.

2,2′-[(5,5′-Dibutyl-2,2′-bi-1,3-dithiolylidene-4,4′-diyl)bis(thio)]bis-(ethanol) (15): Chromatography over silica gel (CH_2Cl_2/Et_2O, 4:1) afforded **15** (0.52 g, 74%) as an orange powder. M.p. 109−110 °C. R_f = 0.64 (CH_2Cl_2/Et_2O, 4:1). ^1H NMR (200 MHz, $CDCl_3$, ppm): δ = 0.95 (t, J = 7.1 Hz, 6 H, CH_3), 1.30−1.60 (m, 8 H, CH_2), 2.18

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(bd s, 2 H, OH), 2.62 (t, J = 7.3 Hz, 4 H, =CCH$_2$), 2.93 (t, J = 6.1 Hz, 4 H, SCH$_2$), 3.79 (t, J = 6.1 Hz, 4 H, OCH$_2$). ^{13}C NMR (50 MHz, CDCl$_3$, ppm): δ = 14.2, 22.6, 30.3, 32.2, 39.1, 61.3, 108.9, 117.8, 142.3. HRMS: calculated for $C_{18}H_{28}O_2S_6$: 468.0414; found 468.0411.

2,2′-[(5,5′-Dioctyl-2,2′-bi-1,3-dithiolylidene-4,4′-diyl)bis(thio)]bis(ethanol) (16): Chromatography over silica gel (CH$_2$Cl$_2$/Et$_2$O, 6:1) afforded **16** (0.7 g, 80%) as a red oil. R_f = 0.67 and 0.44 (CH$_2$Cl$_2$/Et$_2$O, 6:1), *cis*/*trans* isomers. ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ = 0.90 (t, J = 6.4 Hz, 6 H, CH$_3$), 1.29 (m, 20 H, CH$_2$), 1.53 (m, 4 H, CH$_2$), 2.02 (bd s, 2 H, OH), 2.58 (t, J = 7.5 Hz, 4 H, =CCH$_2$), 2.91 (t, J = 6.0 Hz, 4 H, SCH$_2$), 3.77 (t, J = 6.0 Hz, 4 H, OCH$_2$). ^{13}C NMR (50 MHz, CDCl$_3$, ppm): δ = 14.1, 22.6, 29.0, 29.1, 29.2, 29.6, 30.2, 31.8, 38.8, 60.9, 108.5, 117.2, 142.0. HRMS [ESI]: calculated for $C_{26}H_{44}O_2S_6$: 580.1665; found 580.1665.

2,2′-[[4′,5′-Bis(butylthio)-2,2′-bi-1,3-dithiolylidene-4,5-diyl]bis(thio)]bis(ethanol) (17): Chromatography over silica gel (CH$_2$Cl$_2$/Et$_2$O, 3:1) afforded **17** (0.73 g, 92%) as an orange powder. M.p. 79−80 °C. R_f = 0.42 (CH$_2$Cl$_2$/Et$_2$O, 3:1). ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ = 0.95 (t, J = 7.2 Hz, 6 H, CH$_3$), 1.37−1.54 (m, 4 H, CH$_2$), 1.55−1.71 (m, 4 H, CH$_2$), 2.84 (t, J = 7.2 Hz, 4 H, =CCH$_2$), 3.02 (t, J = 5.5 Hz, 4 H, SCH$_2$), 3.78 (t, J = 5.5 Hz, 4 H, OCH$_2$). ^{13}C NMR (50 MHz, [D$_6$]DMSO, ppm): δ = 13.8, 21.3, 31.7, 35.5, 38.4, 60.6, 109.7, 109.8, 127.3, 127.4. HRMS: calculated for $C_{18}H_{28}O_2S_8$: 531.9855; found 531.9852.

2-{[4′,5-Dimethyl-5′-(methylthio)-2,2′-bi-1,3-dithiolyliden-4-yl]thio}-ethanol (18): Chromatography over silica gel (CH$_2$Cl$_2$) afforded **18** (0.42 g, 79%) as an orange powder. M.p. 69−71 °C. R_f = 0.34 (CH$_2$Cl$_2$). ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ = 2.14 (s, 3 H, CH$_3$), 2.16 (s, 3 H, CH$_3$), 2.33 (s, 3 H, SCH$_3$), 2.90 (t, J = 6.1 Hz, 2 H, SCH$_2$), 3.76 (t, J = 6.1 Hz, 2 H, OCH$_2$). ^{13}C NMR (50 MHz, CDCl$_3$, ppm): δ = 15.8, 16.0, 19.9, 39.1, 61.4, 108.6, 109.9, 118.5, 121.3, 134.3, 136.7. HRMS: calculated for $C_{11}H_{14}OS_6$: 353.9369; found 353.9367.

2-[(4′,5,5′-Trimethyl-2,2′-bi-1,3-dithiolyliden-4-yl)thio]ethanol (19): Chromatography over silica gel (CH$_2$Cl$_2$/Et$_2$O, 3:1) afforded **19** (0.44 g, 92%) as an orange powder. M.p. 101−102 °C. R_f = 0.60 (CH$_2$Cl$_2$/Et$_2$O, 3:1). ^{1}H NMR (200 MHz, [D$_6$]DMSO, ppm): δ = 1.88 (s, 6 H, CH$_3$), 2.01 (s, 3 H, CH$_3$), 2.73 (t, J = 6.1 Hz, 2 H, SCH$_2$), 3.46 (dt, J = J = 6.1 Hz, 2 H, OCH$_2$), 4.90 (t, J = 6.1 Hz, 1 H, OH). ^{13}C NMR (50 MHz, [D$_6$]DMSO, ppm): δ = 13.8 (2C), 15.5, 38.3, 60.3, 104.7, 109.8, 118.8, 123.1, 123.2, 135.7. HRMS: calculated for $C_{11}H_{14}OS_5$: 321.9648; found 321.9645.

General Procedure for the Synthesis of Mono- or Bis(alkoxysilyl)-TTF: 3-(Triethoxysilyl)propyl isocyanate (1.1 mmol for **18** and **19**; 2.2 mmol for **14**−**17**) and triethylamine (1.1 mmol for **18** and **19**; 2.2 mmol for **14**−**17**) were added under argon to a solution of the mono- or bis-TTF **14**−**19** (1 mmol) in anhydrous THF (10 mL). The mixture was heated at reflux for 12 h and concentrated to 4/5 of its original volume. Heating at reflux was continued for another 6 h. Evaporation of the solvent followed by chromatography over silica gel afforded the mono- or bis-alkoxysilyl TTFs **2**−**7**.

(5,5′-Dimethyl-2,2′-bi-1,3-dithiolylidene-4,4′-diyl)bis(thio)bis(ethane-2,1-diyl) Bis{*N*-[3-(triethoxysilyl)propyl]carbamate} (2): Chromatography over silica gel (CH$_2$Cl$_2$/Et$_2$O, 3:1) afforded **2** (0.23 g, 26%) as an orange powder. M.p. 150−151 °C. R_f = 0.63 (CH$_2$Cl$_2$/Et$_2$O, 3:1). ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ = 0.62 (m, 4 H, SiCH$_2$), 1.23 (t, J = 7.0 Hz, 18 H, CH$_3$), 1.62 (tt, J = J = 6.8 Hz, 4 H, CH$_2$), 2.13 (s, 6 H, CH$_3$), 2.92 (t, J = 6.1 Hz, 4 H, SCH$_2$), 3.17 (dt, J = J = 6.8 Hz, 4 H, NCH$_2$), 3.82 (q, J = 7.0 Hz, 12 H, CH$_2$), 4.18 (t, J = 6.1 Hz, 4 H, OCH$_2$), 5.00 (t, J = 6.8 Hz, 2 H, NH). ^{13}C NMR (50 MHz, CDCl$_3$, ppm): δ = 8.3, 16.0, 18.9, 23.9, 35.3, 44.0, 59.1, 63.5, 109.1, 118.7, 137.1, 158.7. ^{29}Si NMR (60 MHz, CDCl$_3$, ppm): δ = −45.70 and −45.80 (s, *cis*/*trans* isomers). HRMS: calculated for $C_{32}H_{58}N_2O_{10}S_6Si_2$: 878.1954, found 878.1955. $C_{32}H_{58}N_2O_{10}S_6Si_2$: calcd. C 43.71, H 6.65, N 3.19, S 21.88 ; found C 43.42, H 6.57, N 3.16, S 21.80%.

Compound 3: Chromatography over silica gel (CH$_2$Cl$_2$/Et$_2$O, 3:1) afforded **3** (0.71 g, 74%) as a thick orange oil. R_f = 0.78 (CH$_2$Cl$_2$/Et$_2$O, 3:1). ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ = 0.65 (m, 4 H, SiCH$_2$), 0.95 (t, J = 7.1 Hz, 6 H, CH$_3$), 1.25 (t, J = 7.1 Hz, 18 H, CH$_3$), 1.38−1.72 (m, 12 H, CH$_2$), 2.60 (t, J = 6.9 Hz, 4 H, =CCH$_2$), 2.95 (t, J = 6.3 Hz, 4 H, SCH$_2$), 3.19 (dt, J = J = 6.3 Hz, 4 H, NCH$_2$), 3.84 (q, J = 7.1 Hz, 12 H, CH$_2$), 4.20 (t, J = 6.3 Hz, 4 H, OCH$_2$), 5.02 (m, 2 H, NH). ^{13}C NMR (50 MHz, CDCl$_3$, ppm): δ = 8.0, 14.1, 15.0, 18.6, 22.5, 23.6, 32.1, 35.1, 43.8, 58.8, 63.3, 108.9, 118.0, 142.4, 156.4. ^{29}Si NMR (60 MHz, CDCl$_3$, ppm): δ = −45.60 and −45.65 (s, *cis*/*trans* isomers). HRMS: calculated for $C_{38}H_{70}O_{10}N_2S_6Si_2$: 962.2893, found 962.2888. $C_{38}H_{70}O_{10}N_2S_6Si_2$: calcd. C 47.40, H 7.28, N 2.91, S 19.96, Si 5.82; found C 47.29, H 7.30, N 2.81, S 20.37, Si 6.00%.

Compound 4: Chromatography over silica gel (CH$_2$Cl$_2$/Et$_2$O, 6:1) afforded **4** (0.91 g, 85%) as a thick red oil. R_f = 0.76 and 0.67 (CH$_2$Cl$_2$/Et$_2$O, 6:1), *cis*/*trans* isomers. ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ = 0.64 (m, 4 H, SiCH$_2$), 0.90 (t, J = 6.5 Hz, 6 H, CH$_3$), 1.24 (t, J = 6.9 Hz, 18 H, CH$_3$), 1.29 (m, 20 H, CH$_2$), 1.52 (m, 4 H, CH$_2$), 1.64 (tt, J = J = 6.3 Hz, 4 H, CH$_2$), 2.58 (t, J = 7.5 Hz, 4 H, =CCH$_2$), 2.93 (t, J = 6.3 Hz, 4 H, SCH$_2$), 3.18 (dt, J = J = 6.3 Hz, 4 H, NCH$_2$), 3.83 (q, J = 6.9 Hz, 12 H, CH$_2$), 4.19 (t, J = 6.3 Hz, 4 H, OCH$_2$), 4.95 (m, 2 H, NH). ^{13}C NMR (50 MHz, CDCl$_3$, ppm): δ = 7.9, 14.4, 14.9, 18.5, 22.9, 23.6, 29.3, 29.5, 29.9, 30.4, 32.1, 35.0, 43.7, 58.7, 63.2, 108.7, 117.9, 142.4, 156.3. ^{29}Si NMR (60 MHz, CDCl$_3$, ppm): δ = −45.65 and −45.77 (s, *cis*/*trans* isomers). HRMS (ESI): calculated for $C_{46}H_{86}N_2O_{10}NaS_6Si_2$ [M + Na$^+$]: 1097.4043, found 1097.4047. $C_{46}H_{86}N_2O_{10}S_6Si_2$: calcd. C 51.36, H 8.06, N 2.60, S 17.88, Si 5.22 ; found C 51.03, H 7.87, N 2.63, S 17.40, Si 5.73%.

Compound 5: Chromatography over silica gel (CH$_2$Cl$_2$/Et$_2$O, 4:1) afforded **5** (0.78 g, 76%) as an orange solid. M.p. 59−60 °C. R_f = 0.80 (CH$_2$Cl$_2$/Et$_2$O, 4:1). ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ = 0.65 (m, 4 H, SiCH$_2$), 0.95 (t, J = 7.1 Hz, 6 H, CH$_3$), 1.25 (t, J = 7.0 Hz, 18 H, CH$_3$), 1.30−1.70 (m, 12 H, CH$_2$), 2.85 (t, J = 7.2 Hz, 4 H, CH$_2$), 3.07 (t, J = 6.4 Hz, 4 H, SCH$_2$), 3.18 (dt, J = J = 6.6 Hz, 4 H, NCH$_2$), 3.83 (q, J = 7.0 Hz, 12 H, CH$_2$), 4.25 (t, J = 6.4 Hz, 4 H, OCH$_2$), 5.33 (br t, J = 6.6 Hz, 2 H, NH). ^{13}C NMR (50 MHz, [D$_6$]DMSO, ppm): δ = 7.5, 13.7, 18.5, 21.3, 23.3, 31.7, 35.1, 35.5, 43.4, 58.0, 62.5, 109.3, 110.1, 127.4, 127.5, 156.0. ^{29}Si NMR (60 MHz, CDCl$_3$, ppm): δ = −45.66 (s). HRMS: calculated for $C_{38}H_{70}N_2O_{10}S_8Si_2$: 1026.2335; found 1026.2329. $C_{38}H_{70}N_2O_{10}S_8Si_2$: calcd. C 44.44, H 6.82, N 2.73, S 24.95, Si 5.46; found C 44.66, H 6.91, N 2.73, S 25.01, Si 5.60%.

2-[(5,5′-Dimethyl-4′-(methylthio)-2,2′-bi-1,3-dithiolyliden-4-yl)thio]-ethyl *N*-[3-(Triethoxysilyl)propyl]carbamate 6: Chromatography over silica gel (CH$_2$Cl$_2$/Et$_2$O, 4:1) afforded **6** (0.32 g, 54%) as an orange powder. M.p. 123−124 °C. R_f = 0.69 (CH$_2$Cl$_2$/Et$_2$O, 4:1). ^{1}H NMR (200 MHz, CDCl$_3$, ppm): δ = 0.53 (m, 2 H, SiCH$_2$), 1.14 (t, J = 7.0 Hz, 9 H, CH$_3$), 1.53 (tt, J = J = 6.9 Hz, 2 H, CH$_2$), 2.05 (s, 6 H, CH$_3$), 2.23 (s, 3 H, SCH$_3$), 2.83 (t, J = 6.1 Hz, 2 H, SCH$_2$), 3.07 (dt, J = J = 6.9 Hz, 2 H, NCH$_2$), 3.72 (q, J = 7.0 Hz, 6 H, CH$_2$), 4.08 (t, J = 6.1 Hz, 2 H, OCH$_2$), 5.12 (t, J = 6.9 Hz, 1 H, NH). ^{13}C NMR (50 MHz, CDCl$_3$, ppm): δ = 8.0, 15.5, 15.8, 18.7, 19.7, 23.6, 35.0, 43.8, 58.8, 63.3, 108.5, 109.1, 118.5, 121.1, 134.0, 136.8, 156.4. ^{29}Si NMR (60 MHz, $CDCl_3$, ppm): $\delta = -45.71$ and -45.81 (s, *cis/trans* isomers). HRMS: calculated for $C_{21}H_{35}NO_5S_6Si$: 601.0609; found 601.0609. $C_{21}H_{35}NO_5S_6Si$: calcd. C 41.90, H 5.86, N 2.33, S 31.96, Si 4.65 ; found C 42.24, H 5.88, N 2.18, S 31.72, Si 4.92%.

2-[(4′,5,5′-Trimethyl-2,2′-bi-1,3-dithiolyliden-4-yl)thio]ethyl *N*-[3-(Triethoxysilyl)propyl]carbamate (7): Chromatography over silica gel (CH_2Cl_2/Et_2O, 4:1) afforded **7** (0.34 g, 60%) as an orange powder. M.p. 81−82 °C. R_f = 0.77 (CH_2Cl_2/Et_2O, 4:1). ^{1}H NMR (200 MHz, $CDCl_3$, ppm): $\delta = 0.63$ (m, 2 H, $SiCH_2$), 1.23 (t, J = 7.0 Hz, 9 H, CH_3), 1.63 (tt, $J = J$ = 6.9 Hz, 2 H, CH_2), 1.95 (s, 6 H, CH_3), 2.13 (s, 3 H, CH_3), 2.92 (t, J = 6.0 Hz, 2 H, SCH_2), 3.17 (dt, $J = J$ = 6.9 Hz, 2 H, NCH_2), 3.83 (q, J = 7.0 Hz, 6 H, CH_2), 4.18 (t, J = 6.0 Hz, 2 H, OCH_2), 5.05 (t, J = 6.9 Hz, 1 H, NH). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): $\delta = 8.0$, 14.1, 15.8, 18.7, 23.6, 35.0, 43.8, 58.8, 63.4, 118.5, 118.5, 123.1, 123.2, 136.8, 156.4. ^{29}Si NMR (60 MHz, $CDCl_3$, ppm): $\delta = -45.65$ (s). HRMS: calculated for $C_{21}H_{35}NO_5S_5Si$: 569.0888; found 569.0888. $C_{21}H_{35}NO_5S_5Si$: calcd. C 44.26, H 6.19, N 2.46, S 28.13, Si 4.93 ; found C 44.10, H 6.17, N 2.45, S 28.36, Si 4.95%.

General Procedure for the Synthesis of the Gels and the Xerogels: The preparation of the xerogels was carried out by the following general procedure. The preparation of the xerogel **2XA** is given as an example: compound **2** (0.5 g, 0.585 mmol) and dried THF (835 μL) were introduced into a Schlenk tube, and 835 μL of a solution containing TBAF (12 μL 1 mol·L^{-1} in THF, 12 μmoles), H_2O (31 μL, 1.75 mmol) and dried THF (792 μL) were added. After homogenization, part of this mixture was introduced into the cell by capillarity, and the remaining solution was kept in the Schlenk tube. In the two cases, after the sol-gel transition, the orange gel was allowed to age for 6 days. The gel obtained in the Schlenk tube was then crushed and washed twice with acetone, ethanol and diethyl ether, and the resulting powder was dried at 120 °C in vacuo for 3 hours to yield an orange xerogel. The gel times and the characteristics data of each orange xerogel are given in Table 2.

2XA: (370 mg, 0.58 mmol); yield 100%. ^{29}Si CP MAS NMR (δ, ppm, 60 MHz): −68.2 (T^3). $S_{BET} < 10$ m^2·g^{-1}.

2XB: Compound **2** (0.5 g, 0.585 mmol) in THF (835 μL) together with 792 μL of THF containing 12 μL of HCl and 31 μL of H_2O gave a gel after 15 min. **2XB**: orange powder (365 mg, 0.58 mmol); yield 99%. ^{29}Si CP MAS NMR (60 MHz, ppm): $\delta = -48.9$ (T^1); −57.5 (T^2); 65.6 (T^3). $S_{BET} < 10$ m^2·g^{-1}.

3XA: Compound **3** (0.2 g, 0.213 mmol) in THF (304 μL) together with 185 μL of THF containing 4 μL of TBAF and 115 μL of H_2O gave a gel after 2 min. **3XA:** (150 mg, 0.21 mmol); yield 98%. ^{29}Si CP MAS NMR (60 MHz, ppm): $\delta = -67.7$ (T^3). $S_{BET} < 10$ m^2·g^{-1}.

3XB: Compound **3** (0.2 g, 0.213 mmol) in THF (304 μL) together with 185 μL of THF containing 4 μL of HCl and 115 μL of H_2O gave a gel after 15 min. **3XB**: (155 mg, 0.22 mmol); yield 100%. ^{29}Si CP MAS NMR (60 MHz, ppm): $\delta = -49.1$ (T^1); −57.2 (T^2); −65.5 (T^3). $S_{BET} < 10$ m^2·g^{-1}.

4XA: Compound **4** (0.3 g, 0.28 mmol) in THF (398 μL) together with 377 μL of THF containing 6 μL of TBAF and 15 μL of H_2O gave a gel after 3 min. 4**XA:** (238 mg, 0.28 mmol); yield 100%. ^{29}Si CP MAS NMR (60 MHz, ppm): $\delta = -69.0$ (T^3). $S_{BET} < 10$ m^2·g^{-1}.

4XB: Compound **4** (0.3 g, 0.28 mmol) in THF (398 μL) together with 982 μL of THF containing 0.6 μL of HCl and 15 μL of H_2O gave a gel after 165 min. 4**XB**: (230 mg, 0.27 mmol); yield 98%. ^{29}Si CP MAS NMR (60 MHz, ppm): $\delta = -49.8$ (T^1); −59.3 (T^2); −68.5 (T^3). $S_{BET} < 10$ m^2·g^{-1}.

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[1] K. J. Shea, D. A. Loy, *Acc. Chem. Res.* **2001**, *34*, 707.

[2] K. J. Shea, D. A. Loy, *Chem. Mater.* **2001**, *13*, 3306.

[3] G. Cerveau, R. J. P. Corriu, *Coord. Chem. Rev.* **1998**, *178−180*, 1051.

[4] D. A. Loy, K. J. Shea, *Chem. Rev.* **1995**, *95*, 1431.

[5] R. J. P. Corriu, *Angew. Chem. Int. Ed.* **2000**, *39*, 1376.

[6] C. J. Brinker, G. W. Scherer, *Sol-Gel Science: The physics and Chemistry of Sol-Gel Processing,* Academic Press, New York, **1990**.

[7] R. J. P. Corriu, P. Thépot, J. J. E. Moreau, M. Wong Chi Man, *Chem. Mater.* **1996**, *8*, 100.

[8] R. J. P. Corriu, J. J. E. Moreau, P. Thépot, M. Wong Chi Man, *Chem. Mater.* **1992**, *4*, 1217.

[9] J. H Small, K. J. Shea, D. A. Loy, *J. Non-Cryst. Solids* **1993**, *160*, 234.

[10] K. J. Shea, D. A. Loy, O. W. Webster, *Chem. Mater.* **1989**, *1*, 572.

[11] K. J. Shea, D. A. Loy, O. W. Webster, *J. Am. Chem. Soc.* **1992**, *114*, 6700.

[12] H.W. Oviatt, K. J. Shea, J. H. Small, *Chem. Mater.* **1993**, *5*, 943.

[13] J. J. E. Moreau, L. Vellutini, M. Wong Chi Man, C. Bied, J.-L. Bantignies, P. Dieudonné, J.-L. Sauvajol, *J. Am. Chem. Soc.* **2001**, *123*, 7957.

[14] F. J. Feher, D. A. Newmann, J. F. Walzer, *J. Am. Chem. Soc.* **1989**, *111*, 1741.

[15] B. Boury, F. Ben, R. J. P. Corriu, P. Delord, M. Nobili, *Chem. Mater.* **2002**, *14*, 730.

[16] B. Boury, R. J. P. Corriu, *Chemical Record* **2003**, *3*, 120 and references cited therein.

[17] B. Boury, R. J. P. Corriu, *Chem. Commun.* **2002**, 795 and references cited therein.

[18] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* **2002**, *416*, 304.

[19] J. J. E. Moreau, B. Pichon, M. Wong Chi Man, C. Bied, H. Pritzkow, J.-L. Bantignies, P. Dieudonné, J.-L. Sauvajol, *Angew. Chem. Int. Ed.* **2004**, *43*, 203.

[20] G. Cerveau, R. J. P. Corriu, F. Lerouge, N. Bellec, D. Lorcy, M. Nobili, *Chem. Commun.* **2004**, 396.

[21] M. R. Bryce, *Chem. Soc., Rev.* **1991**, *20*, 355.

[22] T. Otsubo, K. Takimiya, Y. Aso, *Phosphorus Sulfur Silicon* **2001**, *171*, 231.

[23] J. M. Fabre, *J. Solid State Chem.* **2002**, *168*, 367.

[24] J. Ferraris, D. O. Cowan, V. V. Walatka, J. H. Perlstein, *J. Am. Chem. Soc.* **1973**, *95*, 948.

[25] A. Andrieux, C. Duroure, D. Jérôme, K. Bechgaard, *J. Phys. Lett.* **1979**, *40*, 381.

[26] D. Jérôme, A. Mazaud, M. Ribault, K. Bechgaard, *J. Phys. Lett.* **1980**, *41*, L195.

[27] E. Coronado, C. J. Gomez-Garcia, *Chem. Rev.* **1998**, *98*, 273.

[28] J. Lau, O. Simonsen, J. Becher, *Synthesis* **1995**, 521.

[29] K. B. Simonsen, N. Sventrup, J. Lau, O. Simonsen, P. Mork, G. J. Kristensen, J. Becher, *Synthesis* **1996**, 407.

[30] J. Lau, P. Blanchard, A. Riou, M. Jubault, M. P. Cava, J. Becher, *J. Org. Chem.* **1997**, *62*, 4936.

[31] K. B. Simonsen, J. Becher, *Synlett* **1997**, *62*, 1211.

[32] P. Pellon, E. Brulé, N. Bellec, K. Chamontin, D. Lorcy, *J. Chem. Soc., Perkin Trans. 1* **2000**, 4409.

[33] N. Bellec, D. Lorcy, *Tetrahedron Lett.* **2001**, 3189.

[34] P. Pellon, G. Gachot, J. Le Bris, S. Marchin, R. Carlier, D. Lorcy, *Inorg. Chem.* **2003**, *6*, 2056.

[35] F. Bertho, A. Robert, P. Batail, P. Robin, *Tetrahedron* **1990**, *46*, 433.

[36] S. J. Gregg, S.W. Sing, *Adsorption, Surface Area and Porosity*; Academic Press: London, **1982**.
[37] S. Brunauer, P. H. Emmett, E. J. Teller, *J. Am. Chem. Soc.* **1938**, *60*, 309.
[38] G. Cerveau, R. J. P. Corriu, C. Lepeytre, P. H. Mutin, *J. Mater. Chem.* **1998**, *8*, 2707.
[39] H.W. Oviatt, K. J. Shea, J. H. Small, *Chem. Mater.* **1993**, *5*, 943.
[40] M. Giffard, P. Alonso, J. Garin, A. Gorgues, T. P. Nguyen, P. Richomme, A. Robert, J. Roncali, S. Uriel, *Adv. Mater.* **1994**, *6*, 298.
[41] M. Giffard, A. Gorgues, A. Riou, J. Roncali, P. Alonso, S. Uriel, J. Garin, T. P. Nguyen, *Synth. Metals* **1995**, *70*, 1133.
[42] B. Boury, R. J. P. Corriu, in *Supplement Si: The Chemistry of Organic Silicon Compounds* (Z. Rappoport, Y. Apeloig, Eds.), Wiley, Chichester, **2001**; chapter 10, p. 565.
[43] H. Kobayashi, A. Kobayashi, Y. Sasaki, G. Saito, H. Inokuchi, *Bull. Chem. Soc., Jpn.* **1986**, *59*, 301.
[44] S. Matsumiya, A. Izuoka, T. Sugawara, T. Taruishi, Y. Kawada, *Bull. Chem. Soc., Jpn.* **1993**, *66*, 513.
[45] B. Boury, R. J. P. Corriu, P. Delord, M. Nobili, V. Le Strat, *Angew. Chem. Int. Ed.* **1999**, *38*, 3172.
[46] A. Vergnes, M. Nobili, P. Delord, L. Cipelletti, R. J. P. Corriu, B. Boury, *J. Sol-gel Science and Technol.* **2003**, *26*, 621.
[47] G. Cerveau, R. J. P. Corriu, E. Framery, F. Lerouge, *J. Mater. Chem.* **2004**, in press.
[48] N. Le Narvor, N. Robertson, E. Wallace, J. D. Kilburn, A. E. Underhill, P. N. Bartlett, M. Webster, *J. Chem. Soc., Dalton Trans.* **1996**, 823.

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