Trialkoxysilyl Mono-, Bi-, and Terthiophenes as Molecular Precursors of Hybrid Organic–Inorganic Materials

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Silica gel containing thiophene units have been obtained from molecular organosilicon precursors, and the properties associated to the electron rich thiophene moieties have been explored. The sol–gel polymerization of 2,5-bis(trimethoxysilyl)mono-, bi-, and terthiophene quantitatively led to thiophenylene bridged silsesquioxane network: $[O_{1.5}Si\text{–}(C_4H_2S)_p\text{–}SiO_{1.5}]_n$ (p = 1–3). The derived xerogels were characterized by IR and ^{13}C and ^{29}Si CP MAS NMR spectroscopies. The major environment of the Si atom corresponded to a T^2:$CSi(OR)(OSi)_2$ substructure. The gels are microporous with N_2 BET surface area up to 685 m^2g^{-1}. A charge-transfer complex containing gel was also obtained upon cohydrolysis and condensation of $Si(OMe)_4$ with 5,5″-bis(trimethoxysilyl)terthiophene/TCNQ charge-transfer (CT) complex. The CT units and the siloxane network in the hybrid material were respectively characterized in the electronic spectrum exhibiting an absorption band of the $[TCNQ^{-}]$ radical anion and in the ^{29}Si CP MAS NMR spectrum showing $CSiO_3$ and SiO_4 substructures. The electrochemical oxidation of thiophenylene-bridged gels led to the polymerization of the thiophene units. ^{29}Si CP MAS NMR of the oxidized materials revealed the cleavage of the Si–C bond in the solid. The formation of polythiophene within the inorganic matrix was established on the basis of Raman spectroscopy. It was further confirmed by the isolation of some soluble oligomers upon oxidation of a related monosilylthiophene gel. The polymerization, which occurred in the solid, gave a composite material containing polythiophene chains and a silica network.

Introduction

The sol–gel process has been proved to offer unique possibilities to prepare metal oxide materials under very smooth conditions.[1] Nanocomposite and new mixed organic–inorganic materials also resulted from the sol–gel polymerization of silicon alkoxides.[2–4] Recent work has for example led to the preparation of organically modified composites for nonlinear optics and photonics.[5] The use of molecular or macromolecular building blocks was also studied as a possibility to control the morphology of silica-based materials.[6,7]

The hydrolysis and polycondensation of organosilicon alkoxides $RSi(OR')_3$, containing a stable nonhydrolyzable Si–C bond, is of particular interest since it allows the formation of a hybrid network at the molecular level[4,8–10] (eq 1). The properties and the morphology of the resulting

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$$n\mathrm{RSi(OR')_3} \xrightarrow[\text{(-R'OH)}]{\mathrm{H_2O}} (\mathrm{RSiO_{1.5}})_n \qquad (1)$$

silsesquioxanes $(\mathrm{RSiO_{1.5}})_n$, with organic substituents at regular intervals in the silicate framework, have been explored.[8–10] The use of bis(trialkoxy)silylated organic molecules led to a variety of amorphous microporous hybrid materials generally presenting high surface area.[8,9]

The introduction of an appropriate organic fragment linked to the inorganic silica network by a covalent Si–C bond can lead to hybrid materials with intrinsic properties. Although it allows a general formation of molecularly defined materials, only some examples have been given, including materials with nonlinear optical properties,[11] ionic conductivity materials,[12] and materials with catalytic properties.[13,14]

Our interest in mixed inorganic–organic silsesquioxane materials led us to study thiophene-containing gels. The versatile chemical reactivity of thiophene can allow the preparation of molecular precursors with various structures. Thiophene is an electron-rich conjugated molecule which upon polymerization leads to highly electroactive materials. Thiophene oligomers or polymers exhibit nonlinear optical properties[15] and upon oxidative doping lead to material with electrochromic, charge-transport, and electrochemical properties.[16]

We wish to report here the preparation and some properties of molecularly defined silica gels containing thiophene units.

Results and Discussion

Preparation and Characterization of Silsesquioxane Gels Containing Thiophene Units. The bis(trimethoxysilyl)thiophene precursors **1–3** were prepared upon silylation of the corresponding mono-, bi-, and terthiophenes (Scheme 1). Whereas **1** was prepared via a direct silylation as described earlier,[9] **2** and **3** were obtained upon successive lithiation and silylation with $\mathrm{ClSi(OMe)_3}$. The formation of thiophenylene-bridged polysilsesquioxane gels was then achieved upon hydrolysis in the presence of $\mathrm{NH_4F}$ (0.1 mol %) as catalyst.[17] Owing to a low solubility of the monomeric precursors **2** and **3** in MeOH, the sol–gel polymerization was performed in THF. Transparent gels formed in all cases within a short period of time (Table 1) and were allowed to stand at 20 °C for 2 days. After air drying and washing with ether, the solids were collected and dried in vacuo at 150 °C.

The hybrid gels **4–6** deviated from the ideal stoichiometry $[\mathrm{O_{1.5}Si(C_4H_2S)_pSiO_{1.5}}]_n$ and contained un-cross-linked units with residual hydroxy and methoxy groups. The spectroscopic characteristics of the materials (IR, CP MAS NMR) were similar to those obtained for related amorphous *p*-phenylene silsesquioxane gels.[8,9] In particular the ^{29}Si NMR analysis clearly established that the Si–C bond was retained within the gel. As shown in Figure 1, a set of three resonances was observed in the ^{29}Si CP MAS NMR of the xerogels **4–6**. The major resonances at −72 ppm correspond to a substructure of type $\mathrm{T^2{:}C{-}\mathit{Si}(OR)(OSi)_2}$ with two directions of condensation. Two minor resonances, at −64 and −81 ppm, also appeared and can be assigned respectively to $\mathrm{T^1{:}C{-}\mathit{Si}(OR)_2(OSi)}$ and $\mathrm{T^3{:}C{-}\mathit{Si}(OSi)_3}$. Although quantitative conclusions are not valid for CP MAS NMR, the spectra are consistent with the mean structure presented in Figure 2. The network mainly consisted of siloxane chains with bridging mono-, di-, and terthiophene units. The relative intensities of the NMR lines varied from gel **4** to **6**. The intensity of the resonance at −81 ppm increased from mono- to bi- and terthiophene-containing materials. This is indicative of an increase in the degree of condensation of the three-dimensional network. The probably reduced mobility of the siloxane chains in the network containing a rigid monothiophene bridge resulted in a reduced degree of condensation, when compared to the longer and more flexible di- and terthiophene bridges. The properties of the gels were partially examined. The X-ray powder diffraction pattern of samples **4–6** showed no crystallinity. The amorphous materials are microporous with a mean pore diameter below 20–30 Å. The $\mathrm{N_2}$ BET measurements gave surface areas which vary widely according to the structure of the precursor and the experimental conditions, especially the nature of the solvent (Table 1, lines 2, 4, 6, 8). For xerogels prepared under identical conditions, the $\mathrm{N_2}$ BET surface areas appeared to increase from mono- to di- and terthiophene-derived materials. The formation of highly porous materials does not seem here to be associated to the presence of a rigid-rod spacer[8] or to a reduced degree of condensation of the polymeric network. In the case of thiophene-bridged hybrid gels, the porosity and $\mathrm{N_2}$ BET surface area increased with the flexibility of the spacer and with the degree of condensation of the material. This further confirmed[9] that the solid morphology is the result of several directing factors (reaction conditions, precursor structure, etc.).

Properties of Thiophenylene-Bridged Gels 4–6. We then decided to explore the properties of the molecularly defined gels **4–6** which contained electron-rich thiophenylene fragments.

Formation of a Polymeric Charge-Transfer (CT) Complex. Ter- and quaterthiophene have been shown to form charge-transfer complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ).[18] Whereas an organogel exhibited doping, when immersed in a DMF solution containing TCNQ, to give a polymeric CT complex,[19] the reaction of a large electron-acceptor molecule with the highly cross-linked gel **6** seemed difficult. Therefore the preparation of a polymeric charge-transfer complex network was considered starting from a CT complex precursor. Upon reaction of the silylated terthiophene **3** with 1 mol equiv

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Scheme 1. Preparation of Thiophenylene Silsesquioxane Gels

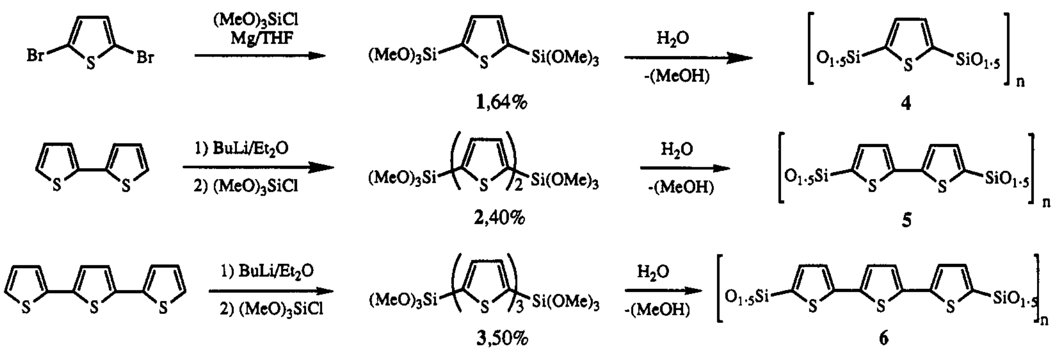
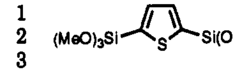
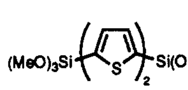
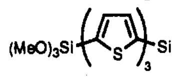
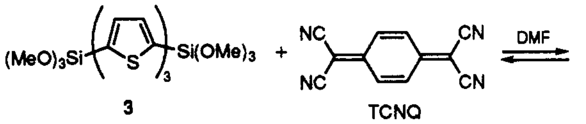


Table 1. Hydrolysis and Polycondensation of Silylthiophenes 1-3[a]

entry	precursor	precursor concn, mol L^{-1}	solvent	gel time (min)	surface area[b] (m^2 g^{-1})
1		3	MeOH	10^{-1}	*c*
2		1	MeOH	15	685
3		0.3	MeOH	3×10^3	*c*
4		1	THF	15	19
5		3	THF	20	*c*
6		1	THF	30	65
7		0.3	THF	240	398
8		1	THF	15	188
9		0.3	THF	600	*c*

[a] All reactions were performed at 20 °C using 3 mol equiv of H_2O in the presence of 10^{-3} mol equiv of NH_4F catalyst. [b] BET surface from multipoint analysis of N_2 adsorption isotherm. [c] Not determined.

of TCNQ in DMF, a dark-green color developed instantaneously (eq 2).



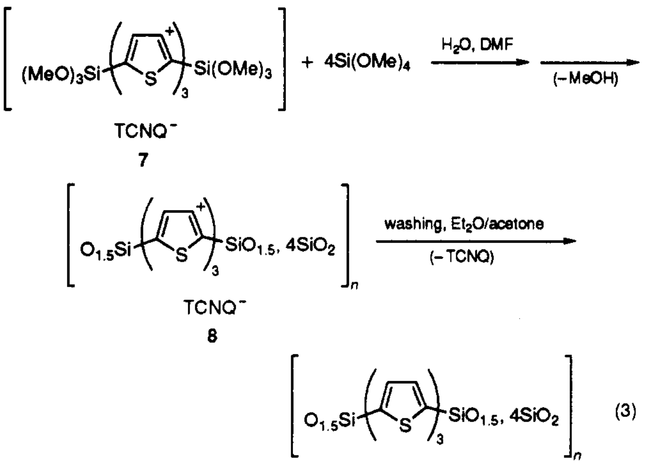
3 TCNQ

$[3^+, TCNQ^-]$ (2)

7

Attempted crystallization of the CT complex 7 failed; only neutral TCNQ was crystallized out of the reaction mixtures. Evidence for the formation of [3$^+$, TCNQ$^-$] complex 7 was obtained from the electronic spectrum of the DMF solutions. The dominant peaks around 375 nm arise from the π–π^* transition of the neutral 3 and TCNQ moieties. Well-resolved bands assigned to the TCNQ anion radical (TCNQ$^-$) were observed at 847 (ϵ = 4170), 749 (ϵ = 3590), and 647 nm (ϵ = 1970) (Figure 3). The relatively low absorption coefficients for these bands, although higher than the reported values for unsilylated terthiophene CT complex,[18] mean a weak charge transfer. The formation of 7 was also supported by ^{29}Si NMR analysis of the reaction mixture. In addition to a signal at −58.15 ppm corresponding to the neutral molecule 3, two new resonances with similar intensities appeared at −67.03 and −67.27 ppm. The latter may be assigned to the two Si atoms with different environments in the CT complex. A nonsymmetric structure was reported for crystalline CT complex of terthiophene.[18]

Although pure crystalline CT complex 7 was not isolated, the DMF solutions were treated with H_2O. From the diluted DMF solutions of 7 no gel formation was observed. This contrasts with the rapid gelation which occurred in the absence of TCNQ. Gelation however occurred upon hydrolyzing a mixture of 7 with 4 mol of $(MeO)_4Si$ (eq 3).



A dark green gel 8 resulted from the cocondensation of 7 and $Si(OMe)_4$. The gel 8, which expelled some solvent, was dried in vacuo to give quantitatively a powder. Elemental analyses revealed a N/Si ratio value of 0.54 (calculated 0.67), indicating that 80% of the TCNQ was retained in the solid. The CP MAS NMR analysis showed the expected resonances for the hybrid gel 8. ^{29}Si NMR exhibited signals corresponding to the different substructures arising from an uncomplete condensation of the material: −75 and −81 ppm respectively assigned to T^2: C*Si*(OR)(OSi)$_2$ and T^3:C*Si*(OSi)$_3$, as well as −89.9, −99.9, and −110 ppm for SiO_4 (Q^2, Q^3, Q^4) substructures.[20] The electronic spectrum of the solid 8 revealed absorption bands at 855, 752, and 684 nm, characteristic of the TCNQ$^-$ radical anion (Figure 4). The hybrid polymeric network 8 therefore contained CT complex species of type 7. The solid-state properties of 8 have been partially examined. It showed no crystallinity by examination of its X-ray powder diffraction pattern. N_2 BET measurement gave a small surface area (6 m^2 g^{-1}) for this CT complex gel. The electrical conductivity was determined on a pressed disk by the four points technique. A relatively low value

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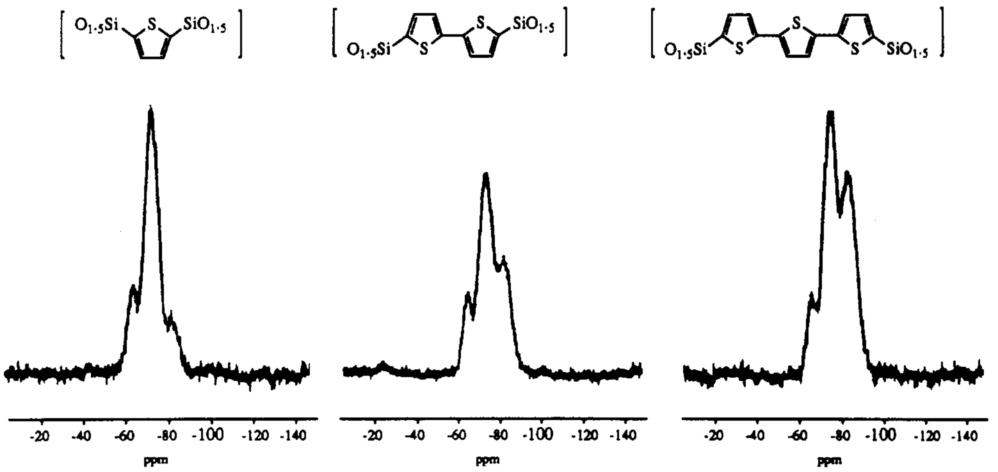


Figure 1. ^{29}Si CP MAS NMR spectra of the xerogels 4–6.

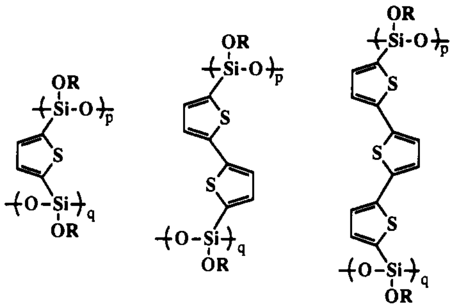


Figure 2. Mean structure of thiophenylene-bridged gels 4–6.

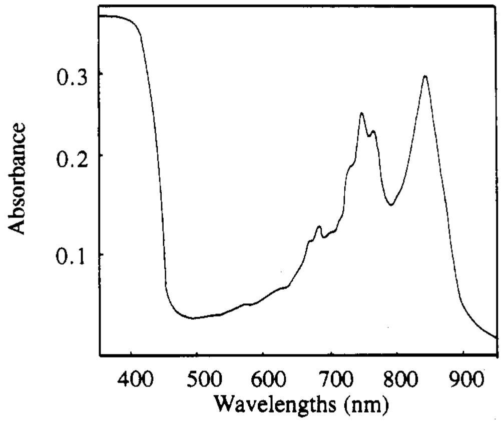


Figure 3. Electronic spectrum of [5,5″-bis(trimethoxysilyl)-terthiophene TCNQ] charge-transfer complex 7 (7×10^{-5} M solution in DMF).

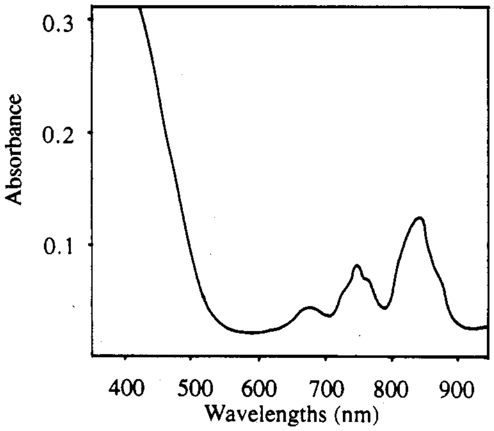
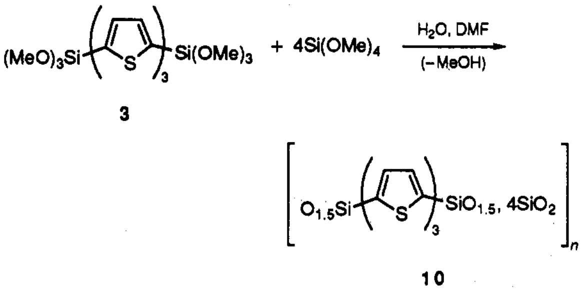


Figure 4. Electronic spectrum of charge-transfer complex containing gel 8 (diffuse reflectance spectroscopy).



(4)

(ca. 10^{-7} S cm^{-1}) was found, although higher than the observed conductivity (10^{-10} S cm^{-1}) for related solid terthiophene/TCNQ charge-transfer complex.[18]

It is interesting to note that the CT complex in 8 appeared quite labile. Upon washing with Et_2O and acetone, almost all the neutral TCNQ could be removed from the gel to give 9 (eq 3). The elemental analysis gave a N/Si ratio of 0.05 indicating that only 7% of the original TCNQ molecule remained in 9. Consistently the ^{13}C and ^{29}Si CP MAS NMR only showed signals corresponding to a network containing $C\mathit{Si}O_3$ (T^2, T^3) and SiO_4 (Q^2, Q^3, Q^4) substructures. After elimination of TCNQ, gel 9 was amorphous and almost the same value (9 m^2 g^{-1}) was determined for the N_2 BET surface area.

For comparison a hybrid gel 10, with a stoichiometry similar to 9, was also prepared upon co-gelation of terthiophene 3 and $Si(OMe)_4$ (eq 4). The hydrolysis and condensation under reaction conditions identical to those used in eq 3, produced the thiophene-containing gel 10. Although the gels 9 and 10 exhibited similar spectroscopic (IR, CP MAS NMR) characteristics, the gel 10 presented a very high N_2 BET surface area (566 m^2 g^{-1}), about 60 times higher than that of gel 9. We already emphasized that the morphology of silsesquioxane gel can vary widely according to the reaction conditions and according to the structure of the precursors.[9] It appeared that the intermolecular interaction introduced during the sol–gel polymerization, via a CT complex formation, also influenced greatly the surface area of the material. Similar observation have been made with hybrid gel obtained from unsaturated organosilicon precursor via the formation of a transitory transition-metal complex.[21]

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(21) Corriu, R. J. P.; Moreau, J. J. E.; Thépot, Ph.; Wong Chi Man, M., to be published.

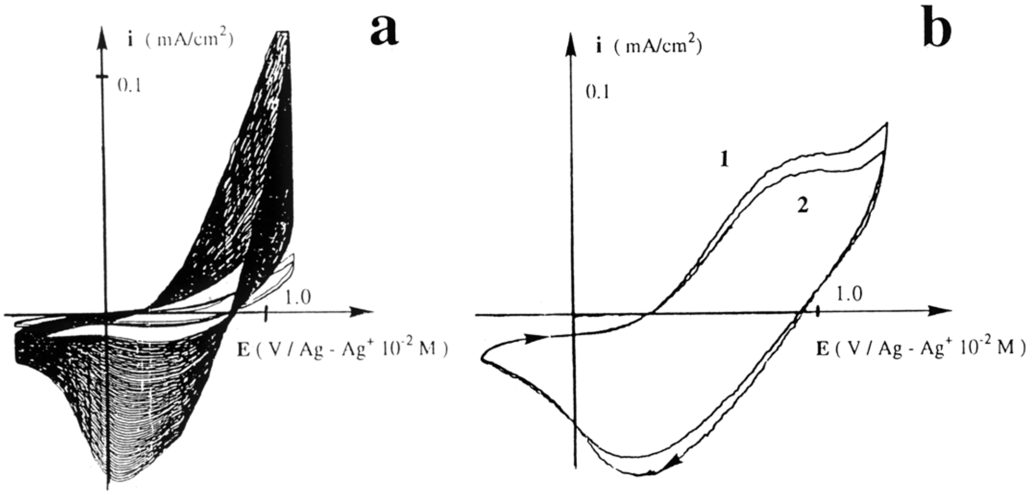

Figure 5. (a) Cyclic voltamograms between −0.4 and 1.3 V (vs Ag–Ag$^+$, 10^{-2} M) corresponding to the electropolymerization of gels **5** and **6** (scan rate: 200 mV/s^{-1}). (b) Final cyclic voltamogram of the polythiophene-containing gels **11**: (1) gel prepared from **5**; (2) gel prepared from **6**.

*Electrochemical Behavior of Hybrid Gels **5** and **6**.* Samples of gels prepared from the silyl precursors **2** and **3** were deposited on a Pt electrode. The electrochemical behavior of gels **5** and **6** was then studied by cyclic voltametry between −0.4 and 1.3 V (vs Ag–Ag$^+$, 10^{-2} M) at a rate of 200 mV s^{-1}. The intensity of the voltamogram increased with time to reach a maximum value after ca. 10 scans (Figure 5). This behavior is usually observed in electropolymerization reactions. The values of the oxidation and reduction peaks ($E_p{}^a$ = 0.86 V, $E_p{}^c$ = 0.26 V), together with the observed blue-red electrochromism of the sample, are consistent with the formation of polythiophene within the gel. It seemed that the silylthiophene substructures in the polymeric gel could undergo oxidative coupling to polythiophene. Such anodic oxidation with cleavage of the Si–C bond was reported earlier in the electrolysis of silylthiophene solutions.[22-26] A similar oxidative coupling occurred here in the solid state (eq 5).

(5)

5, $p = 2$
6, $p = 3$

11

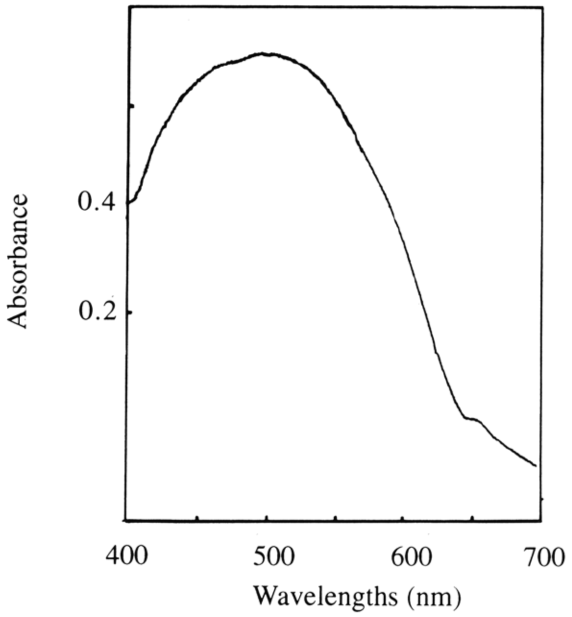

Figure 6. Electronic spectrum of **11** (diffuse reflectance spectroscopy).

Further evidence for the formation of polythiophene within the solid material was obtained upon spectroscopic analysis of oxidized samples of gels **5** and **6**. Oxidized films of gels **5** and **6** on a Pt electrode were reduced at −0.2 V for 15 min. The samples were then undoped with MeOH to give a red film containing polythiophene. Examination of the gels **5** and **6** by scanning electron microscopy (SEM) showed that their granular morphology was not modified after oxidation to give **11**. The X-ray-dispersive fluorescence spectroscopy (EDAX) revealed no significative variation of the Si/S ratio in the gel before and after oxidation (**5**, Si/S = 0.94, **6** Si/S = 0.66). The IR absorption spectroscopy of **11** showed an absorption in the region of 1460 cm^{-1}. However, it did not appear very useful owing to large overlaps of the absorption bands of the thiophenylene silsesquioxane gel **3** and bands which would be characteristic of a silica gel containing polythiophene. An evidence for the formation of polythiophene was obtained upon analyzing the electronic spectra. Whereas the spectra of **5** and **6** before oxidation showed a band with a maximum at 420 nm, the recorded diffused reflexion spectra of **11** in the visible region (Figure 6) showed a large absorption band at 490 nm, close to the value of 510 nm generally observed for polythiophene. The strongest evidence for the formation of polythiophene within the silica matrix came from the analysis of the Raman resonance spectra (RRS). This technique causes a strong exaltation of the Raman diffusion band upon excitation of the sample at a wavelength within the absorption region of poly-

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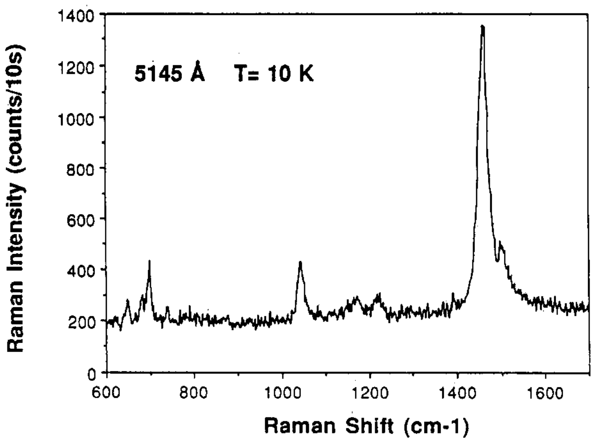
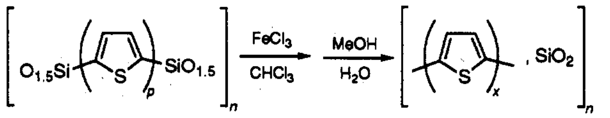


Figure 7. Raman resonance spectrum of polythiophene-containing gel **11**.

thiophene. The diffusion bands characteristic of polythiophene[27] at 652, 682, 700, 1047, 1171, 1220, and 1458 cm^{-1} clearly emerged from the Raman resonance spectrum (Figure 7). The obtained spectrum allowed an evaluation of the "quality" of the polythiophene according to Furukawa et al.[28] These correlations have been used to evaluate the mean conjugation length in polythiophene by Raman spectroscopy. It revealed highly structured and conjugated polymer when prepared by anodic electropolymerization of silylthiophene monomers in solution.[26] In the case of polythiophene resulting from the oxidation of gels **5** and **6**, the diffusion bands at 700 and 682 cm^{-1}, assigned to a C–H bending vibration respectively in a planar and nonplanar conformation, are relatively high. This is indicative of the presence of nonplanar segments in the chain and of a relatively low mean conjugation length. This result is consistent with the above observation of the $\pi-\pi^*$ absorption at a relatively low wavelength in the electronic spectra. It is in fact not surprising that the solid-state oxidation of gels **5** and **6** to form polythiophene gave polymer chain with distorted conformations. Whereas in solution the polymerization gave regular and more conjugated chains.

The observed easy reaction in the solid state may be attributed to kinetic and structural factors. The kinetic factor is due to the silyl groups. The high activity of the silylthiophene units toward oxidative coupling[22,26] may allow a more facile polycondensation. On the other hand, concerning reactions which occur in the solid state, structural factors are certainly important. The sol–gel polycondensation of the thiophene precursors could result in some partial structural arrangement of the organic moieties, in the amorphous silica network. The partially cross-linked gel, with thiophene units at regular intervals in the inorganic network, may allow the coupling reaction between proximal thiophene bridging fragments, without a too large reorganization of the silica framework. The observed facile polythiophene formation may be indicative of such a favorable structural arrangement of the organic units within the silica framework. Related observations have been made in the case of organosilicon polymers. The facility of poly-addition reactions between chain units of various poly(silanylene–diynes) have been correlated to the mean distances between the reactive diyne fragments in a solid material.[29] A similar high reactivity of diyne units was found in related silica gel materials.[30]

Chemical Oxidation of Thiophene-Bridged Silsesquioxane Gels. The electrochemical oxidation allowed to characterize the formation of polythiophene via a polymerization reaction within the amorphous solid. We tried to extend the scope of this reaction by examining the chemical oxidation of the thiophene reactive units in three different gels. The monothiophenylene-bridged gels **4a** (with high porosity and high surface area, Table 1, entry 2), **4b** (with a low surface area, Table 1, entry 4), and the terthiophenylene-bridged gel **6** (Table 1, entry 8) were powdered and stirred with 3 mol of $FeCl_3$ in $CHCl_3$ for 4 days (eq 6). MeOH was then added to the deep blue mixture, and the resulting red solids were collected, washed, and dried. The elemental analyses did not show significant variation of the Si/S ratio before and after treatment with $FeCl_3$. Hybrid materials **12** and **14** with similar characteristics were produced by oxidation of **4a** and **6**, respectively. The formation of polythiophene in **12** and **14** was established on the basis of spectroscopic analysis. The UV–visible spectra exhibited a band at 510 nm. The Raman spectra also showed the characteristic diffusion lines.[27] However, these were not observed in the case of the solid **13** recovered after treatment of the low-porosity gel **4b**.



(6)

4a, $p = 1$ (685 $m^2\,g^{-1}$) **12**
4b, $p = 1$ (19 $m^2\,g^{-1}$) **13**
6, $p = 3$ (188 $m^2\,g^{-1}$) **14**

The polymerization via C–C bond coupling of the thiophene units resulted in Si–C bond breaking in the solid. Evidence for Si–C bond cleavage was obtained from the solid-state NMR analysis of the samples before and after treatment with $FeCl_3$. The ^{29}Si CP MAS NMR of gels **4a**, **4b**, and **6** as well as those of the oxidized solids **12–14** are shown in Figure 8. The signals at −64, −72, and −81 ppm corresponding to $C\mathit{Si}O_3$ (T^1, T^2, T^3) substructures in the original material **4a** were replaced by signals at −90, −100, and −110 ppm corresponding to $\mathit{Si}O_4$ (Q^2, Q^3, Q^4) substructures in the oxidized materials. **12**. It clearly showed that Si–C bond cleavage occurred upon treatment with $FeCl_3$. The gel **4b** was however unaffected by treatment with $FeCl_3$, as indicated by the ^{29}Si CP MAS NMR spectra of **4b** and **13**. The behavior of gel **6** was similar to that of **4a**; nevertheless, the presence of a line at −81 ppm in the spectrum of **14** (Figure 7) is indicative of an incomplete Si–C bond cleavage in the solid produced by oxidation of **6**. Therefore, the solid morphology has a clear influence on the reactivity of the Si–C bond. Whereas a complete cleavage was established for gel **4a** (with a 685 $m^2\,g^{-1}$ surface area), uncomplete cleavage occurred for gel

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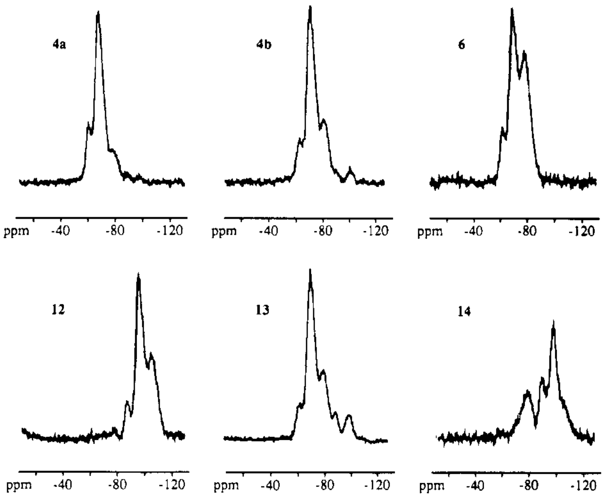
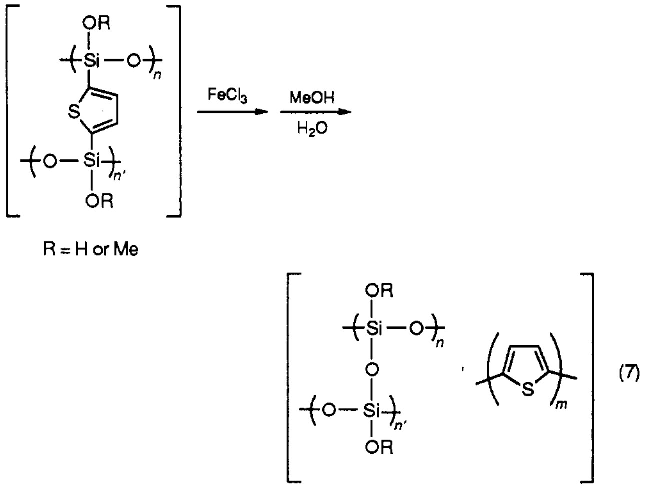


Figure 8. ^{29}Si CP MAS NMR of mono- and terthiophene gels before (**4a**, **4b**, **6**) and after treatment with $FeCl_3$ (**12**–**14**).

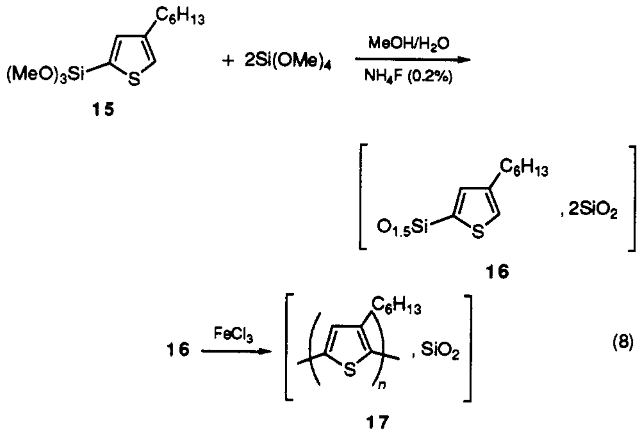
6 (188 m^2 g^{-1}) and very few cleavage was observed in the case of **4b** (19 m^2 g^{-1}). The reactivity of the Si–C bond is related to ability of the oxidizing reagent to diffuse within the solid.

It is also worth noting that the relative intensities of the signals assigned to T ($CSiO_3$) substructures and Q (SiO_4) substructures presented strong similarities. The coupling of thiophene units within the gel is associated to the conversion of a major T^2 [$C\mathit{Si}(OSi)_2(OR)$] to a major Q^3 [$\mathit{Si}(OSi)_3(OR)$] substructure in the silicate framework. In average, the Si–C bond in the thiophenylene bridge is replaced by a Si–O–Si bridge (eq 7). This produced an amorphous composite material made of an organic polythiophene and an inorganic siloxane network. The X-ray diffraction pattern showed no crystallinity for the polythiophene formed under these conditions.[31]



(7)

To obtain some chemical evidence for the formation of polythiophene, the oxidation of a silsesquioxane containing thiophene was also carried out in the case of a related gel **16**. The latter was prepared upon cocondensation of monomer **15** containing an *n*-hexylthiophene substituent and $Si(OMe)_4$ (eq 8). The ^{29}Si CP MAS NMR of gel **16** presented two sets of signals corresponding to the expected mixture of $C\mathit{Si}O_3$ and $\mathit{Si}O_4$ substructures with various degrees of condensation (cf. Experimental Section). The thienyl unit with a C_6 substituent is linked through one Si–C bond to the silicate framework. The gel **16** showed a N_2 BET surface area of 3.8 m^2 g^{-1}.



(8)

Upon oxidation with $FeCl_3$, a red solid **17** was produced. The formation of poly(hexylthiophene) was established on the basis of Raman spectroscopic analysis. The ^{29}Si NMR also showed extensive cleavage of Si–C bonds in the oxidized material **17**. Little $C\mathit{Si}O_3$ resonances remained after treatment with $FeCl_3$. The poly(hexylthiophene) which formed was further characterized after partial isolation. A Soxhlet extraction of the solid **17** allowed the recovery of about 40% of the hexylthiophene units, as a soluble polymer which was identified upon elemental and spectroscopic analysis. The gel permeation chromatography analysis of the soluble poly(hexylthiophene) revealed low molecular weight material ($M_n = 15 \times 10^3$, $M_w/M_n = 37$). The partial separation of the poly(hexylthiophene) from the silica framework is indicative of the formation of the polymer at the surface of the solid. The presence of many thiophene units at the surface of the hybrid material **16** is consistent with its formation from a monomer containing only one $Si(OMe)_3$ functional group and in which the organic moiety has a C_6 hydrophobic substituent.[32]

The use of bisilylated monomers with two $Si(OMe)_3$ functional groups gave gels with alternating thiophene and siloxane units, in which the organic fragment lies in the bulk of the material rather than at the surface. The oxidative coupling of the thiophene moieties occurred between neighboring fragments as proposed in the mechanistic Scheme 2. The thiophene radical cations formed initially upon reaction of $FeCl_3$[26,33] then duplicate to β-silyl dicationic intermediates. The Si–C bond cleavage can then occur by nucleophilic attack of the chlorine anion at the silicon atom. The resulting chlorosilane then leads to SiO_4 substructures by reaction with a residual Si–OH group. A direct nucleophilic reaction of the hydroxyl groups at the silicon in the β-silyl cationic species is also possible and

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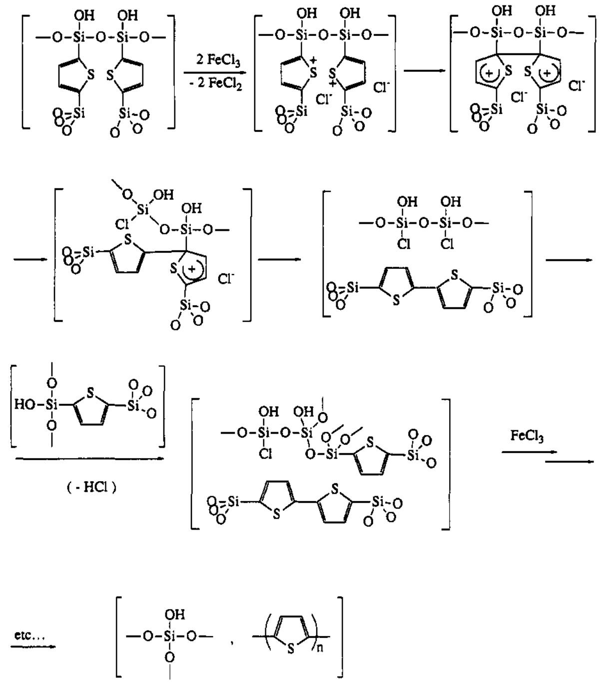
Scheme 2. Proposed Mechanism for the Chemical Oxidation of Thiophenylene-bridged Silsesquioxane Gels



will lead to the same SiO_4 unit with elimination of HCl. Further step-by-step oxidation similarly leads to polymerization of the thiophene units within the solid to produce a poly or oligothiophene chain and a siloxane network. The complete substitution of SiCl bond occurred during the hydrolytic workup of the solid.

Conclusion

Thiophenylene-bridged silsesquioxanes appeared as interesting new mixed organic–inorganic materials. The electron-rich properties of thiophene units interspaced at regular intervals within the silicate framework were used to form new classes of hybrid materials. Silyl terthiophene monomers reacted with TCNQ and subsequent sol–gel polymerization gave rise to a charge-transfer complex gel. On the other hand, the oxidative coupling of the thiophene units led to silica gel containing polythiophene. Related glass-conducting polymer composite have been prepared by gelation of a sol containing a polymer.[34] Here, the observed polymer formation in hybrid gels constitutes an interesting approach to composite materials. Such a reaction in the amorphous solid, starting with a network made of perfectly alternating organic and siloxane fragments is of potential interest for the preparation of composite materials at the molecular level.

Experimental Section

Manipulations were performed under a nitrogen atmosphere using a vacuum line and Schlenk tube techniques. All solvents were dried and distilled before use. Melting points were obtained with a Gallenkamp apparatus and are uncorrected. ^1H NMR spectra were obtained with a Bruker AW-80 spectrometer, ^{13}C and ^{29}Si NMR spectra, in solution and in the solid state with Bruker WP 250 SY and FT AM 300 apparatus, respectively. Solvents and chemical shifts (δ relative to Me_4Si) are indicated. X-ray powder diffraction measurements were obtained with a Seifert MZ4 apparatus. Mass spectra were performed with a JEOL JMS-D 100 or JMS-DX 300 mass spectrometer (ionization energy, 70 eV). BET measurements were obtained with a Micromeritic using N_2 gas. Elemental analyses were performed by the "Service Central de Micro-analyse du CNRS". Electronic spectra were performed on a Beckman Acta V apparatus for samples in solution and on a Carry 2300 for diffuse reflectance spectroscopy of solid samples. Gel permeation chromatography was performed with a Waters 510 apparatus equipped with UV and refractive index detection. Energy-dispersive X-ray spectroscopy (EDAX) measurements were carried out using a Cambridge 515 SEM with a PV 9600 EDAX attachment. The data were collected by a standard analytical procedure and corrected for ZAF. (We checked that the Si/S ratio measured according to this technique were in agreement with those obtained upon elemental analysis.)

Electrochemical Experiments. Gels for electrochemical experiments were deposited on polished Pt plates (1 × 1 cm). Experiments were carried out using a one-compartment cell (10 cm^3) with Pt plate as a counter electrode and a Ag–$AgNO_3$ (10^{-2} M) electrode as the reference. Electrolytic medium was prepared by dissolving the $N(Bu)_4ClO_4$ (0.02 M) in nitrobenzene and was degassed using dry nitrogen. Cyclic voltametry was performed with a EG & G 362 potentiostat. Plots were obtained on a Philips recorder.

Raman and FTIR Experiments. Raman spectra were recorded on a "Coderg T 800" triple monochromator spectrometer. The 514.5 nm (2.41 eV) of an argon ion laser was used as a light source. To avoid local heating and degradation of the samples, the incident light power was kept below 10 mW and the incident beam was defocused. A backscattering configuration was used, and the instrumental resolution was of about 6 cm^{-1}. To obtain the best resolution for the Raman and photoluminescence spectra all the experiments have been performed at low temperature (T = 10 K). The samples were mounted in a cryostat and cooled by helium gas.

IR spectra have been collected using a Bomen DA-8 spectrometer with a microscope attachment. For the gel deposited on platinum electrode and electrochemically oxidized, the IR spectra have been recorded using the microscope attachment under reflexion procedure. Other compounds have been examined on KBr pellets.

2,5-Bis(trimethoxysilyl)thiophene (1) was prepared according to a procedure reported earlier.[9]

5,5′-Bis(trimethoxysilyl)bithiophene (2). To a solution of 10.7 g (6.42 × 10^{-2} mol) of bithiophene dissolved in 250 mL of ether cooled to 0 °C was added dropwise 64.2 mL (0.14 mol) of n-BuLi (2.2 M solution in hexane). After stirring for 3 h, the mixture was cooled to −80 °C and a solution of 22.1 g (0.141 mol) of chlorotrimethoxysilane in 50 mL of ether was slowly added. The solution was then allowed to warm and was stirred for 15 h at room temperature. After filtration, ether was pumped off and the mixture was extracted with pentane. The solvent was evaporated under vacuum and the residue distilled at 165 °C (0.9 mmHg) to afford 10.44 g (40% yield) of compound **3**. ^1H NMR (CCl_4, δ, ppm) 3.60 (18H, s), 7.25 (4H, m); ^{13}C NMR ($CDCl_3$, δ, ppm) 51.44, 126.05, 127.61, 138.37, 144.00; ^{29}Si NMR ($CDCl_3$, δ, ppm) −58.32. Mass spectrum (rel intensity, assignment) m/e 406 (100, M^+), 375 (8, M^+ − MeO), 286 (20, M^+ − $Si(OMe)_3$ + H), 166 (20, M^+ − $2Si(OMe)_3$ + 2H), 121 (72, $Si(OMe)_3$). Anal. Calcd for $C_{14}H_{22}O_6S_2Si_2$: C, 41.32; H, 5.45; Si, 13.81. Found: C, 41.84; H, 5.46; Si, 14.00.

5,5″-Bis(trimethoxysilyl)terthiophene (3). To a solution of terthiophene (9 g, 3.62 × 10^{-2} mol) in 150 mL of ether was added dropwise 31.8 mL of n-BuLi (2.5 M solution in hexane). The mixture was then cooled to −78 °C and an ethereal solution of chlorotrimethoxysilane (12.46 g, 7.96 × 10^{-2} mol) was added. After stirring for 15 h at room temperature, the resulting solution was filtered and the solvents were pumped off. The mixture was then extracted with hexane. The solvent was evaporated in vacuo and the residue distilled at 230 °C (0.04 mmHg) to give 8.80 g

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(50% yield) of a green viscous liquid. ^{1}H NMR (CCl_4, δ, ppm) 3.77 (18H, s), 7.33 (2H, s), 7.51 (4H, dd). ^{13}C NMR($CDCl_3$, δ, ppm) 51.39, 125.46, 127.34, 128.30, 136.59, 138.37, 144.13. ^{29}Si ($CDCl_3$, δ, ppm) −58.35. Mass spectrum (rel intensity, assignment) *m/e* 488 (100, M^+), 457 (5, $M^+ - MeO$), 368 (29, $M^+ - Si(OMe_3) + H$), 248 (11, $M^+ - 2Si(OMe)_3 + 2H$), 121 (23, Si, $(OMe)_3$). Anal. Calcd for $C_{18}H_{24}O_6S_3Si_2$: C, 44.24; H, 4.95; Si, 11.49. Found: C, 43.98; H, 4.90; Si, 11.59.

2-(Trimethoxysilyl)-4-hexylthiophene (15). 3-Hexylthiophene was first prepared via a cross-coupling reaction. The Grignard reagent of 1-bromohexane (0.18 mol, 1 M in THF) was added dropwise at room temperature to a mixture of 3-bromothiophene (29.3 g, 0.18 mol) and 2% of [1,3-bis(diphenylphosphino)propane]nickel(II) chloride ($Ni(d_{ppp})_2Cl_2$) (2 g, 3.68×10^{-3} mol). After stirring at 50 °C for 15 h, the THF was removed by distillation under atmospheric pressure. The salts were extracted with pentane which was distilled at 760 mmHg after filtration of the mixture. Distillation of the residue thus obtained afforded 23.3 g (75% yield) of 3-hexylthiophene. To 8 g (4.76×10^{-2} mol) of the latter compound in 150 mL of THF cooled at 0 °C were added dropwise 23 mL (5.7×10^{-2} mol) of *n*-BuLi (2.5 M solution in hexane). After stirring for 4 h at room temperature, this mixture was added dropwise to 8.9 g (5.7×10^{-2} mol) of chlorotrimethoxysilane in 50 mL of THF cooled at −60 °C. The solution was then allowed to warm and was stirred for 15 h at room temperature before being filtered. The THF was pumped off and the mixture was extracted with pentane. The solvent was evaporated under vacuum and the residue thus obtained distilled at 160 °C (1.6 mmHg) to afford 9.60 g (70% yield) of compound **15**. ^{1}H NMR (CCl_4, δ, ppm) 0.81 (3H, t); 1.22 (8H, m); 1.55 (2H, m); 7.19 (2H, m). ^{13}C NMR ($CDCl_3$, δ, ppm) 14.45, 22.98, 29.40, 3024, 31.00, 32.04, 51.34, 127.44, 127.65, 138.90, 145.18. ^{29}Si NMR ($CDCl_3$, δ, ppm) −57.37. Anal. Calcd for $C_{13}H_{24}O_3SSi$: C, 54.16; H, 8.33; S, 11.11. Found: C, 54.27; H, 8.38; S, 11.78.

Charge-Transfer Complex 5,5″-Bis(trimethoxysilyl)terthiophene/TCNQ (7). This complex was prepared and characterized in solution. 5,5″-Bis(trimethoxysilyl)terthiophene (0.049 g, 10^{-4} mol) and TCNQ (0.02 g, 10^{-4} mol) were dissolved separately in respectively 2 and 6 mL of *N,N*-dimethylformamide at 60 °C. As soon as the two solutions were mixed, the solution turned dark-green. Attempts to crystallize the complex were unsuccessful; only TCNQ crystals were obtained. ^{13}C NMR spectrum of the solution appeared identical to that of 5,5″-bis(trimethoxysilyl)terthiophene. ^{29}Si NMR spectrum exhibited three signals at −58.14 ppm for the free precursor and at −67.03 and −67.23 ppm for the charge-transfer complex. Electronic spectrum of a 7×10^{-5} molar solution in DMF revealed the presence of several transitions. Bands located at 847 ($\epsilon = 4170$), 749 ($\epsilon = 3590$), and 684 nm ($\epsilon = 1970$) are attributable to the TCNQ anion radical ($TCNQ^-$) and the peak around 375 nm results from the $\pi-\pi^*$ transition of both free components of the charge-transfer complex.

Hydrolysis and Polycondensation of 2,5-Bis(trimethoxysilyl)thiophene (1). This polymerization has already been reported.[9]

Hydrolysis and Polycondensation of 5,5′Bis(trimethoxysilyl)bithiophene (2). To 3, 1, an 0.3 M THF solutions of **2** (1.52 g, 3.74×10^{-3} mol) were added 0.20 mL (0.011 mol) of water and 0.1% (3.74×10^{-6} mol) of NH_4F. Gelation occurred respectively after 20, 30, and 240 min. The gels obtained were allowed to cure for 48 h. After washing with ether and drying under vacuum at 150 °C, about 1 g of colorless powder was collected. All samples showed identical spectroscopic characteristics: ^{13}C CP MAS NMR 49.6, 125.0, 137.4, 143.9, ppm. ^{29}Si CP MAS NMR −65.7, −73.9, −81.9 ppm. Anal. Calcd for $C_8H_4O_3S_2Si_2$: C, 35.82; H, 1.49; O, 17.91; S, 23.88; Si, 20.90. Carbon to silicon ratio: C/Si = 4; found: C/Si = 4.4. X-ray powder diffraction showed two broad bands, *d* spacing 4.4 and 11.9 Å. The gel obtained from a 1 M solution exhibited a specific surface area of 65 $m^2\ g^{-1}$, while the one obtained from a 0.3 M solution showed a surface area of 398 $m^2\ g^{-1}$.

Hydrolysis and Polycondensation of 5,5″-Bis(trimethoxysilyl)terthiophene (3). To 1 and 0.3 M THF solution of **3** (2.1 g, 4.3×10^{-3} mol) were added 0.1% (4.3×10^{-6} mol) of NH_4F and 0.23 mL (1.3×10^{-2} mol) of water. The colored gels which formed in respectively 15 min and 10 h were allowed to cure for 48 h. After washing with ether and drying in vacuo at 150 °C, about 1.5 g of green powder was collected. Both samples showed identical spectroscopic characteristics: ^{13}C CP MAS NMR 51.1, 125.3, 137.6 (large), 145.1 (large) ppm. ^{29}Si CP MAS NMR −64.5, −73.3, −80.7 ppm. Anal. Calcd for $C_{12}H_6O_3S_3Si_2$: C, 41.14; H, 1.71; O, 13.71; S, 27.43; Si, 16.00. Carbon-to-silicon ratio: C/Si = 6; found: C/Si = 6.8. X-ray powder diffraction: one very broad and weak band, *d* spacing 3.80 Å. N_2 BET surface area of the gel obtained from the 1 M solution: 188 $m^2\ g^{-1}$.

Hydrolysis and Polycondensation of the Charge-Transfer Complex 5,5″-Bis(trimethoxysilyl)terthiophene/TCNQ (7) in Presence of 4 equiv of TMOS. A 0.05 complex solution was prepared in DMF as described above from 1 g (2.05×10^{-3} mol) of 5,5″-bis(trimethoxysilyl)terthiophene and 0.42 g (2.05×10^{-3} mol) of TCNQ. TMOS (1.25 g, 8.2×10^{-3} mol) was added to the mixture at 60 °C, as well as NH_4F (1.23×10^{-5} mol, 0.1%) and water (0.40 mL, 2.2×10^{-2} mol). A temperature of 60 °C was maintained, and the dark-green gel **8** formed after 3 days. It was then separated in two parts. The first one was washed with acetone and ether, powdered and then dried under vacuum at 100 °C to afford 1.36 g of a practically colorless powder. ^{13}C CP MAS NMR 125.3, 136.8, 143.9 ppm. ^{29}Si NMR −74.9, −80.7, −90.0, −99.9, −110.0 ppm. Anal. Calcd for $C_{12}H_6O_{11}S_3Si_6$: Carbon-to-silicon ratio: C/Si = 2. Found: C/Si = 2.35, N/Si = 0.05. N_2 BET surface area: 9 $m^2\ g^{-1}$. The second part was not washed with solvent. The gel was powdered and DMF was pumped off under vacuum at 60 °C. About 1.5 g of green powder was collected. Electronic spectrum: three bands attributable to $TCNQ^-$ at 855, 752, and 684 nm; one broad band at 472 nm. ^{13}C CP MAS NMR 126.5, 136.5, 144.0 ppm. ^{29}Si CP MAS NMR −74.8, −81.3, −89.9, −99.9, 110.0 ppm. Anal. Calcd for $C_{24}H_{10}N_4O_{11}S_3Si_6$. Carbon-to-silicon and nitrogen-to-silicon ratios: C/Si = 4, N/Si = 0.67; found: C/Si = 4.4, N/Si = 0.54. X-ray powder diffraction: one broad band, *d* spacing 3.92 Å. N_2 BET surface area: 5.9 $m^2\ g^{-1}$. Electrical conductivity determined on a pressed disk by the four-points technique: 10^{-6} S cm^{-1}.

Hydrolysis and Polycondensation of 5,5″-Bis(trimethoxysilyl)terthiophene (3) in the presence of 4 equiv of TMOS. To 0.5 g (1.01×10^{-3} mol) of **3** in 20 mL of DMF at 60 °C were added successively 0.62 g (4.04×10^{-3} mol) of TMOS, 6.06×10^{-5} mol (0.1%) of NH_4F and 2.20 mL (1.11×10^{-2} mol) of water. A yellow gel was obtained after 4 min. After washing with ether, the gel was powdered and then dried under vacuum at 100 °C. About 0.6 g of yellow powder was collected. ^{13}C CP MAS NMR: 124.7, 136.8, 143.9. 29Si CP MAS NMR −75.0, −82.9, 90.0, −100.4, −108.5. Anal. Calcd for $C_{12}H_6O_{11}S_3Si_6$. Carbon-to-silicon ratio: C/Si = 2; found: C/Si = 2.2. N_2 BET surface area: 566 $m^2\ g^{-1}$.

Hydrolysis and Polycondensation of 2-(Trimethoxysilyl)-4-hexylthiophene (15) in the presence of 2 equiv of TMOS. To a 3 M solution of **15** (1.5 g, 5.21×10^{-3} mol) in MeOH were added 2 equiv (1.58 g, 1.04×10^{-2} mol) of TMOS, 0.52 mL (2.86×10^{-2} mol) of water and 3.13×10^{-5} mol (0.2%) of NH_4F. The gel obtained after 12 days was allowed to stand at room temperature for 48 h. After washing with ether and drying in vacuo at 150 °C, about 1.5 g of solid **16** was collected. ^{13}C CP MAS NMR: 14.4, 23.0, 28.4, 30.1, 51.0, 128.5, 139.3, 144.7 ppm. ^{29}Si CP MAS NMR −73.3, −81.5, −91.3, −100.5, −108.5 ppm. Anal. Calcd for $C_{10}H_{15}O_{5.5}SSi_3$. Carbon to silicon ratio: C/Si = 3.3; found: C/Si = 2.8.

Electrochemical Oxidation of Gels 5 and 6. Deposits of gels **5** and **6** were obtained by hydrolysis and polycondensation of precursors **2** and **3** on a platinum electrode. The platinum surface was covered with a few drops of the THF solutions of **2** and **3** prepared above and the solvent was allowed to evaporate. After heating the electrode for 1 h at 50 °C, a homogeneous transparent deposit was obtained. Cyclic voltammetry was then performed between −0.4 and 1.3 V at a rate of 200 mV s^{-1}. After 10 scans, the intensity reached its maximum value, and the voltammogram exhibited the following values for anodic and cathodic peak potentials: $E_p^a = 0.86$ V, $E_p^c = 0.26$ V. IR spectra: 1460 cm^{-1}. Electronic spectra of undoped samples: broad band at 490 nm. Raman resonance spectra exhibit the characteristic diffusion bands of polythiophene at 652, 682, 700, 1047, 1171, 1220, and 1458 cm^{-1}.

General Procedure for Chemical Oxidation of Gels. $FeCl_3$ (3 equiv) was introduced in a Schlenk tube and dried in vacuo at about 100 °C. Dry distilled chloroform and powdered gel were added to the metal halogenide. After this stirred for 4 days at room temperature, methanol was added to the mixture. The precipitate obtained was filtered, washed with water and MeOH and then cleansed with methanol in a Soxhlet extractor for 24 h before being dried in vacuo at 50 °C.

Chemical Oxidation of Gel 6. The reaction was performed with 0.6 g (1.7×10^{-3} mol) of **6**, 0.83 g (5.1×10^{-3} mol) of $FeCl_3$ and 11 mL of chloroform. After usual workup, 0.58 g of red powder **14** was collected. ^{29}Si CP MAS NMR −81.8 (T^3), −92.0 (Q^2), −100.5 (Q^3), −110.0 (Q^4). ^{13}C CP MAS NMR 50.2, 124.3 135.9, 145.0. Electronic spectrum: broad band centered at 510 nm. Raman spectroscopy: characteristic diffusion bands of polythiophene identical to those described above for **11**.

Chemical Oxidation of Gel 4a. 4a (0.6 g, 3.2×10^{-3} mol) $FeCl_3$ (1.57 g, 9.7×10^{-3} mol), and chloroform (20 mL) were stirred for 4 days at room temperature. Following the procedure described above, 0.61 g of red powder **12** was collected. ^{29}Si CP MAS NMR −90.7 (Q^2), −100.8 (Q^3), −108.6 (Q^4). ^{13}C CP MAS NMR 51.4, 131.5 (large). Electronic spectrum: broad band centered at 510 nm. Raman spectrum is nearly identical to the one obtained for solid **14**.

Chemical Oxidation of Gel 4b. The reaction was carried out following the general procedure, using the same amounts as above. After filtering, washing, and drying, about 0.6 g of brown powder **13** was obtained. ^{29}Si CP MAS NMR −65.6 (T^1), −73.7 (T^2), −82.5 (T^3). ^{13}C CP MAS NMR 52.4, 137.3. Electronic and Raman spectra: absence of the characteristic bands of polythiophene.

Chemical Oxidation of Cogel 16. Cogel **16** (1 g, 2.9×10^{-3} mol) $FeCl_3$ (1.44 g, 8.8×10^{-3} mol), and chloroform (17 mL) were stirred at room temperature for 4 days. Usual workup led to about 1 g of red solid. This solid was then extracted with THF in an ultrasonic bath and then in a Soxhlet extractor. The solution was filtered and evaporation of the solvent led to 0.21 g (43% yield) of poly(hexylthiophene) which was characterized as well as the orange solid (0.83 g) obtained by filtration which exhibited the following characteristics: ^{29}Si CP MAS NMR −81.5 (T^3), −91.3 (Q^2), −100.5 (Q^3), −108.5 (Q^4). ^{13}C CP MAS NMR 13.7, 23.3, 31.0, 50.8, 129.0, 140.0 (large). Anal. Calcd for SiO_2: O, 53.33; Si, 46.67. Oxygen-to-silicon ratio: O/Si = 2. Found: O/Si = 2.5, C/Si = 2.0. N_2 BET surface area: 24 $m^2\ g^{-1}$. Poly(hexylthiophene): Electronic spectrum in CH_2Cl_2: characteristic band at λ_{max} = 427 nm which disappears upon oxydation with $NOBF_4$. Raman spectrum: only the more intense characteristic band of poly(hexylthiophene) could be seen at 1458 cm^{-1}. Gel permeation chromatography: $M_w = 5.5 \times 10^4$, $M_n = 1.5 \times 10^3$, $M_w/M_n = 37$. This average molecular weight corresponds to an average of 9–10 rings/chain. Anal. Calcd for $(C_{10}H_{14}S)_n$: C, 79.29; H, 8.43; S, 19.28. Found: C, 63.26; H, 7.77; S, 15.84; Si, 4.40 corresponding to $(C_{10.6}H_{15.7}SSi_{0.3})_n$.