Synthesis and properties of polysilanes with tetrathiafulvalene as pendant group

Yibo Liu,[a] Chengyun Wang,*[a] Meijiang Li,[b] Guoqiao Lai[b] and Yongjia Shen*[a]

Received (in Durham, UK) 11th September 2007, Accepted 19th November 2007
First published as an Advance Article on the web 4th December 2007
DOI: 10.1039/b713819a

Two polysilanes with tetrathiafulvalene (TTF) as pendant groups were synthesized by reaction of 2-cyanoethyl substituted TTF **1** with (chloromethylphenyl)dimethyl(phenyl)polysilane, or reaction of 4-vinylphenyl-TTF **2** with poly[methylsilane-*co*-methyl(phenyl)silane]. The structures and properties of TTF-polysilanes and their intermediates were characterized by ^{1}H NMR, mass, GPC, UV/Vis, IR and cyclic voltammetry (CV). The results of UV/Vis and CV of these polysilanes indicated interaction between the TTF moieties and σ-electron delocalized Si–Si chain in the ground states. These polysilanes doped by I_2 exhibited high conductivities (10^{-2} S cm^{-1}).

Introduction

Polysilanes comprising Si–Si bonds have attracted much attention for their potential applications as functional polymers,[1] such as photoconducting materials,[2] conductors and semiconductors,[3,4] photoresists,[5] Si–C ceramic precursors[6] and NLO materials.[7] Some of their intriguing electrical pro perties are related to the specific σ-electron delocalization, which endows polysilanes with a directional conductivity that is strongest along the axis of the chain. Meanwhile, tetrathiafulvalene (TTF) and its derivatives are also of interest because they have large electron donating properties and can form highly conducting charge-transfer complexes.[8] Especially, crystals of TTF CT-complexes have metallic conductivity because of the regular formation of segregated stacks of donors and acceptors and a certain degree of charge transfer between the stacks. Despite the inherent electronic advantages, crystals of TTF CT-complexes tend to be brittle and unprocessable. The polymers of TTF can overcome this problem for their good processability, however, they possess lower conductivity than that of crystalline TTF CT-complexes. There have been several attempts to integrate TTF moieties into some polymers in recent decades,[9–12] and it is a potential direction in conducting polymers.

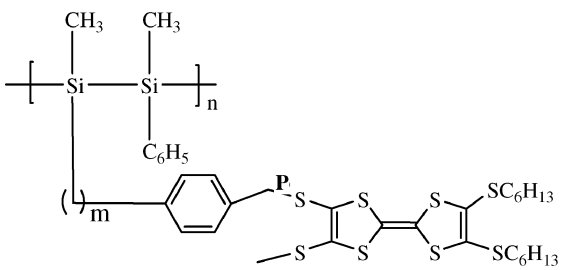
In this paper, we report two polysilanes with TTF moiety as pendant group (Fig. 1). Such polymers would possess an advantage of both conjugated polymer chain and electron-donating side chain.

Results and discussion

Synthesis

Two different synthetic routes lead to polysilanes with TTF moieties as pendant groups (Scheme 1). The first one is a classical synthetic reaction of cyanoethyl-TTF and an active halide, *i.e.*, deprotection of the 2-cyanoethyl group in TTF **1** with the aid of CsOH followed by the reaction with (chloromethylphenyl)dimethyl(phenyl)polysilane afforded polymer **P1**. The second one is the addition reaction of 4-vinylphenyl-TTF **2** to poly[methylsilane-*co*-methylphenylsilane] in the presence of a catalytic amount of hexachloroplatinic acid giving polymer **2**. TTF **1** was synthesized according to a literature procedure.[13] The key intermediate TTF **2** and **3** were synthesized by the reaction of TTF **1** and 4-(bromomethyl)-1-vinylbenzene or benzyl bromide in the presence of CsOH·H_2O. Poly(hydrosilane)copolymer (PHMS), Methylphenylpolysilane (PMPS) and (chloromethylphenyl)dimethylphenylpolysilane (CMPMPS) were synthesized according to the reported procedures.[14–16]

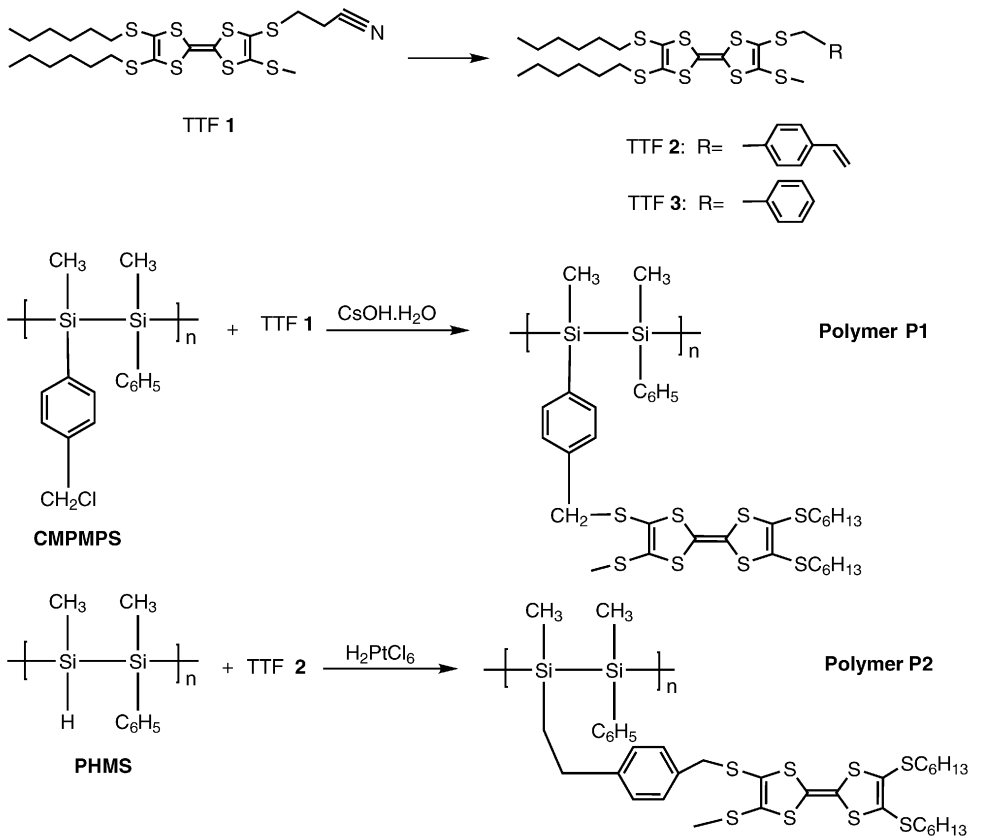
The ^{1}H NMR spectra of polymers **P1** and **P2** are shown in Fig. 2. In polymer **P1**, the methyl protons of the Si–CH_3 groups appeared as a broad peak at δ 0.01–0.46 ppm, those of the phenyl groups gave a broad peak at δ 7.40–6.97 ppm, and the methylene protons (PhCH_2–TTF and PhCH_2Cl) in polymer **P1** gave a peak at δ 4.57. S–CH_2–, –CH_2– and –CH_3 protons of TTF groups in polymer **P1** gave broad peaks at δ 2.79–2.98, 1.20–2.03 and 0.89–1.02, respectively. The numbers in Fig. 2 denote the integrated intensities for –CH_3 and Ph protons in polymers **P1** and **P2**. These two peaks were chosen for the integration calculation. On the other hand, the



m=0, Polymer P1
m=2, Polymer P2

Fig. 1

[a] *Laboratory of Advanced Materials and Institute of Fine Chemicals, East China University of Science & Technology, Shanghai 200237, P. R. China. E-mail: yjshen@ecust.edu.cn, cywang@ecust.edu.cn*
[b] *Key Lab of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, P. R. China*

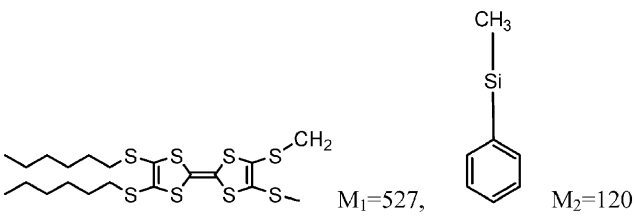


Scheme 1

following moieties were chosen as calculated models for polymers **P1** and **P2**.

As an example, the calculation of TTF content in the polymer **P1** is given as:

$$\text{TTF content in polymer } \mathbf{P1} = (1.76/6)M_1/[(1.76/6)M_1 + (8.68/5)M_2] \times 100\% = 42.6\%$$



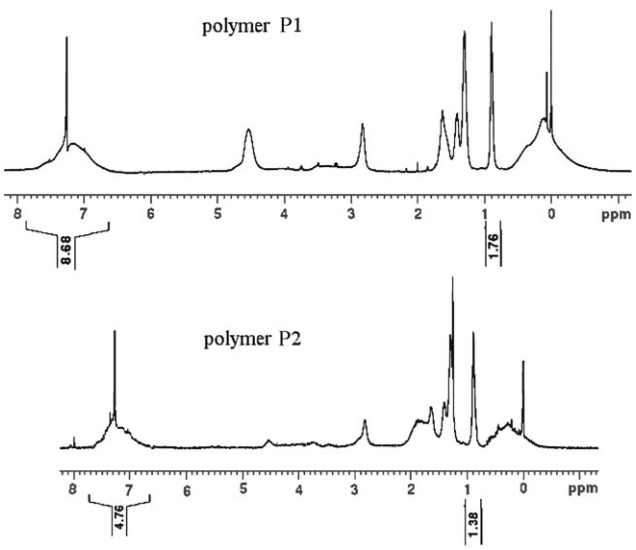


Fig. 2 ^{1}H NMR spectra of polymers **P1** and **P2** in $CDCl_3$. The numbers denote the integrated intensities for $-CH_3$ protons in the bis(hexylthio) moieties and Ph protons.

The chemical shifts of the TTF moiety in polymer **P2** were similar to those of polymer **P1**. The TTF content in polymer **P2** was calculated to be 51.7% based on ^{1}H NMR.

GPC analysis of polymer **P1** showed M_n = 10 238, which corresponds to a 45.1% content of TTF segments. The GPC analysis of polymer **P2** showed M_n = 7253, corresponding to a 56.6% content of TTF segments.

The elemental analyses data of polymers **P1** and **P2** are also listed in Table 1, the TTF content based on elemental analysis were 40.66% and 55.13%, respectively, which were close to the values based on ^{1}H-NMR and GPC.

Thermogravimetric analysis (TGA) was performed in air within a range of 20–600 °C with a heating rate of 10 °C min^{-1}. The thermal decomposition of the polymers **P1** and **P2** presented a single stage of decomposition (see Fig. 3). At almost 35% weight loss was observed upon increasing the temperature from 200 to 420 °C, which increased to about 50% at 500 °C. The decomposition process was essentially complete around 700 °C, with 58% weight lost at this stage.

Table 1 The composition of CMPMPS, PHMS, polymers **P1** and **P2**

Polymer	TTF content[a] (wt%)	TTF content (wt%)[b]	M_n	M_w/M_n	Elemental analysis (%) H	C	S	TTF content[c] (wt%)	TTF moieties : Si atoms (mol)[a]
CMPMPS	—	—	5631	2.29	—	—	—	—	—
PHMS	—	—	3147	1.87	—	—	—	—	—
Polymer **P1**	42.6	45.1	10238	2.20	6.25	57.39	19.75	40.66	1:6
Polymer **P2**	51.7	56.6	7253	2.03	6.48	56.49	26.78	55.13	1:4.2

[a] Based on ^{1}H NMR. [b] Based on GPC. [c] Based on elemental analysis.

The IR spectrum displayed the specific absorption band of the Si–CH_3 group at 1246 cm^{-1}, C–H (phenyl) group at 3066 cm^{-1}, the peaks at 540, 510 and 420 cm^{-1} were related to Si–Si stretching absorption in the polymers **P1** and **P2**. The absorption band of the Si–H group in the polymer **P2** at 2150 cm^{-1} still remained, which indicated that some of the Si–H groups were retained, because of steric hindrances.[3] These residual Si–H groups are useful for immobilization in the polysilane and play an important role in the charge-generating process.

UV/Vis spectra and cyclic voltammetry

The UV absorption maxima of the model compound TTF **3**, polymer PMPS, PHMS and polymers **P1** and **P2** together with a mixture consisting of TTF **3** and PMPS with the equivalent molar ratio of TTF moieties : Si atoms in CH_2Cl_2 are summarized in Table 2. The absorption curves of the polymer **3**, for example, are shown in Fig. 4. Polymer PMPS, PHMS and TTF **3** showed absorption peaks at 338, 337 and 335 nm, respectively. The maximum of the absorption curve of polymer **P1** was found at 316 nm, which suggests that the absorption of the polysilane moiety and TTF moiety in polymer **P1** were overlapped. Surprisingly it was remarkably blue shifted compared to those of TTF **3** and PMPS, and it was the same for polymer **P2**. These results probably indicated an intramolecular interaction between Si–Si system and TTF moiety due to the unique σ-electron delocalization.[8] On the other hand, the UV/Vis absorption curve of a physical mixture consisting of TTF **3** and PMPS exhibited neither a new peak nor any peak shift on the whole wavelength range. It may be concluded that there was no distinct intermolecular interaction between TTF **3** and PMPS in the mixture.

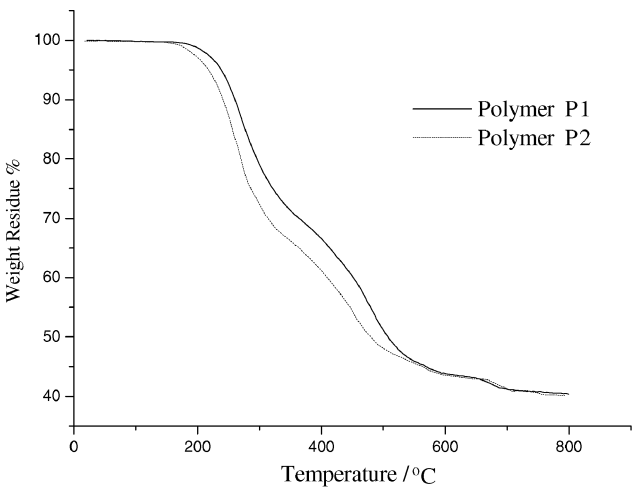


Fig. 3 TGA curves of polymers **P1** and **P2**.

The electrochemical properties of TTF **3**, polymers **P1** and **P2** together with the mixture consisting of TTF **3** and PMPS with the equivalent molar ratio of TTF moieties : Si atoms were obtained by cyclic voltammetry. The CV curves of polymer **P1** and TTF **3** are shown in Fig. 5. The voltammetric data were collected in Table 2.

As shown in Table 2, TTF **3** showed two one-electron reversible oxidation waves at 0.56 and 0.96 V, respectively, corresponding to the radical cation TTF^+ and dication TTF^{2+}. The polymers **P1** and **P2** also showed two reversible oxidation waves at 0.66, 1.14 V and 0.67 and 1.16 V, respectively. It was clear that the TTF moiety retained its electrochemical activity in polymers **P1** and **P2**. Significant enhancement of the oxidation potentials compared to TTF **3** suggested that though polymers **P1** and **P2** preserved the electrochemical character of the TTF moiety, they have higher oxidation potentials than those of TTF **3**, probably indicating an intramolecular interaction between the Si–Si system and TTF moiety in the ground state, due to the unique σ-electron delocalization similarly to some D–σ-A compounds containing the TTF unit.[8] The CV curve of a mixture consisting of TTF **3** and PMPS was coincident with that of TTF **3**, this result also indicated that there was no distinct intermolecular interaction between TTF **3** and PMPS.

Polysilane comprising Si–Si chain possesses unique σ-electron delocalization, which endowed the polysilane with electron-accepting properties. The same situation also occurs for poly(aryleneethynylene) species.[17,18] Therefore, as for many D–σ-A compounds containing the TTF unit,[8] the bridge (alkylene and phenyl) between the Si–Si chain and TTF moiety did not block the interaction between them. Actually, the results of UV/Vis spectra and cyclic voltammetry of polymers **P2** exhibited that there were intramolecular interactions

Table 2 UV peaks and voltammetric data of polymers **P1** and **P2**, PMPS, PHMS and TTF **3**

Compound	λ_{max}/nm (25 °C) in CH_2Cl_2	CV ($E_{1/2}$/V)
PMPS	270, 338	—
PHMS	274, 337	—
TTF **3**	263, 335	0.56, 0.96
Polymer **P1**	266, 316	0.66, 1.14
Polymer **P2**	265, 314	0.67, 1.16
Mixture[a]	262, 270, 336	0.56, 0.97

[a] Mixture consisting of TTF **3** and PMPS with the equivalent molar ratio of TTF : Si atoms.

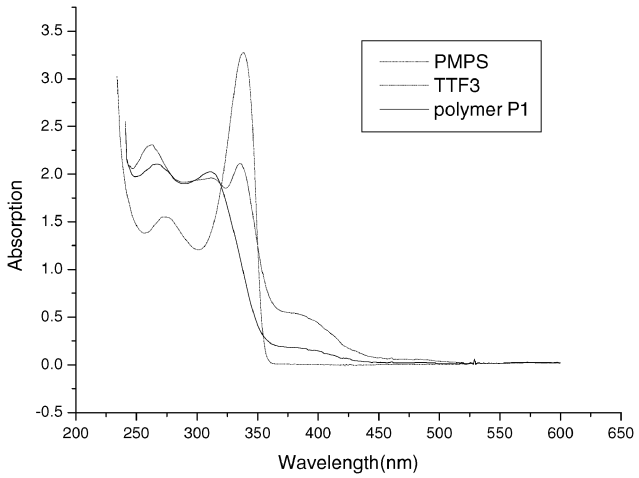


Fig. 4 UV/Vis curves of polymer **P1**, PMPS and TTF **3** in CH_2Cl_2.

between the Si–Si chain and TTF moieties due to such unique σ-electron delocalization in the Si–Si chain.

Doping and electrical conductivity

Polymer films were prepared by spin-coating their THF solutions onto a ITO glass plate, followed by drying in vacuum at 30 °C for 2 h. The average thickness of the polymer films determined by a surface stepper was 500–800 μm. After exposure of the polymers to an iodine atmosphere and removal of the excess iodine *in vacuo*, the polymer appearance changed from brown to black, the conductivity was measured using a four-probe technique with SZ85 apparatus. The content of iodine was determined by gravimetric analysis. The conductivity, which depended on the time of exposure and content of iodine, increased rapidly and reached a plateau (4 h) as shown in Fig. 6, when the content of iodine in polymers **P1** and **P2** were 55 and 61%, respectively.

The conductivities of polymers **P1** and **P2**, methylpolysilane and some different TTF polymers doped by I_2 were summarized in Table 3.

The conductivities of polymers **P1** and **P2** with TTF moieties as pendant groups were found to be one to three orders of magnitude higher than those of non-conjugated TTF polymers (backbone non-conjugation or pendant groups) and methylpolysilanes. Polymers **P1** and **P2** were oxidized by an equivalent of TCNQ (tetracyanoquinodimethane) using the solution-phase doping method with acetonitrile as solvent, and their conductivities were slightly lower than those of polymers **P1** and **P2** doped by I_2. Polymers **P1** and **P2** possessed higher conductivities for two reasons. On the one hand, for the polysilane, σ-electrons of the Si–Si backbone can participate and facilitate the mobilization of the charges along the polysilane main chain, thus causing an increase in the conductivity. On the other hand, TTF and its derivatives would form charge-transfer (CT) complexes with an electron acceptor, such as iodine, and in the frame of TTF-based conductors, such a combination could also contribute to increase the charges and the dimensionality of the conduction process. This combination might eventually lead to materials presenting hybrid conduction. In general, the ionization potentials

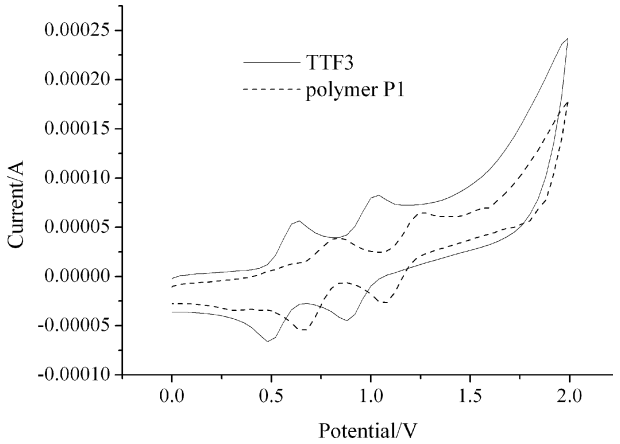


Fig. 5 CV curves of TTF **3** (10^{-3} M) and a cast film of polymer **P1** in MeCN.

(5.4 eV) of polysilane is lower than the TTF group (6.7 eV).[19] This suggested that charges were first generated from TTF–iodine complexes, and transferred from the TTF groups to the Si–Si backbone, finally charge transport occurred by hopping between the σ-electron conjugated Si–Si backbone. Therefore, the σ-electron Si–Si backbone gave the polymer systems exceptional charge carrying ability and higher conductivity. Polysilanes with TTF moieties as pendant groups can be regarded as a new type of polysilane having both charge generation sites and charge transport sites.

As shown in Fig. 6, the conductivity reached a plateau and remained unchanged even when the polymers were exposed in iodine atmosphere for longer times, which indicated that the structures of polymers **P1** and **P2** were stable and Si–Si bonds were not broken under the oxidative doping conditions. The fact probably resulted from the carriers in polymers, which were stabilized by the reversible transfer between the polysilane main chain and TTF moieties, even transferring intermolecularly through the TTF moieties and iodine.[4]

The conductivity of polymer **P2** was higher than that of polymer **P1**. Although they were synthesized by two different routes, their chemical structures were similar to each other.

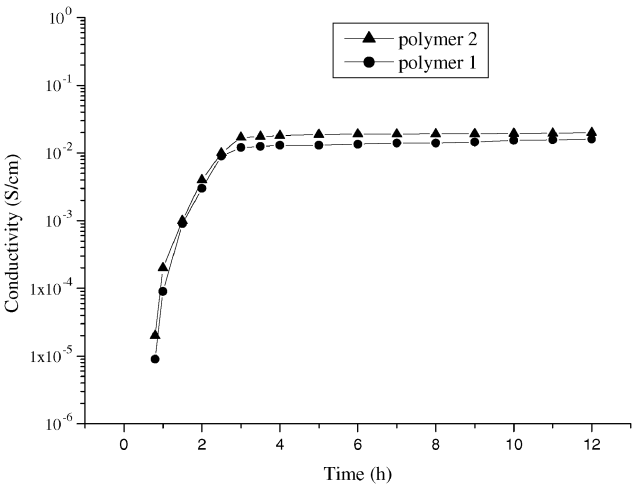


Fig. 6 Time dependence of conductivity of polymers **P1** and **P2** doped by I_2.

Table 3 The conductivity of iodine-doped polysilanes and some TTF polymers

Polymer	Conductivity (25 °C)/S cm^{-1}	Ref.
PMPS	1.3×10^{-6}	This work
Methylpolysilane (pendant group: dimethylbenzenamine)	1×10^{-3}	4
Methylpolysilane (pendant group: carbazole)	1×10^{-3}	4
TTF polymer (pendant group)	5.0×10^{-7}	9
TTF polymer (backbone)	2.0×10^{-6} (non-conjugation)	10
	5.5×10^{-1}, 1.5×10^{-2} (conjugation)	11
Polymer **P1**	1.6×10^{-2} (I_2)	This work
Polymer **P1**	7.8×10^{-3} (TCNQ)	This work
Polymer **P2**	1.9×10^{-2} (I_2)	This work
Polymer **P2**	9.1×10^{-3} (TCNQ)	This work

The differences could be the result of different content of TTF moieties in the polymer chain, because the conductivity of iodine-doped TTF-polysilane was increased with an increase of TTF content. More TTF moieties in the polymer would generate more charges, which can transfer to the Si–Si chain and facilitate the π–π interaction between neighboring TTF units (intra- and inter-molecular reactions) just as in other conducting TTF polymers.[20]

Some TTF polymers with π-conjugation were reported to possess similar or higher conductivity, but they were sparingly soluble and difficult to process. In contrast, polymers **P1** and **P2** possess reasonable solubility in THF, $CHCl_3$, toluene and DMF.

Conclusions

Novel polysilanes, polymers **P1** and **P2**, with tetrathiafulvalene as pendant groups were synthesized by two different routes. The results of UV/Vis and cyclic voltammetry of the polymers indicated interaction between the TTF moieties and Si–Si chain in the ground states. Both polymers exhibited higher conductivities when doped by I_2, and could be regarded as a new type of polysilane having both charge generation sites and charge transport sites. The conductivity depended on the TTF content in the polymers. Polymers **P1** and **P2** are promising as good potential conducting materials.

Experimental

All the reagents and solvents were of commercial quality and were distilled or dried, if necessary, using the standard procedures.

^{1}H and ^{13}C NMR spectra were recorded on a BRUKER 400 instrument. Mass spectra were measured on a TRACE DSQ MS. Elemental analyses were performed on a Vario EL III. Absorption spectra were measured with a Nicolet evolution 300 UV/Vis spectrophotometer. Gel permeation chromatography (GPC) was carried out using toluene as a solvent. Thermogravimetric analysis was performed on a MOM Paulik–Pauli–Erdey derivatograph at 10 °C min^{-1} heating rate in air. All the electrochemical experiments were performed in dichloromethane or acetonitrile with *n*-Bu_4NPF_6 as the supporting electrolyte, platinum as the working and counter electrodes, and Ag/AgCl as the reference electrode. The scan rate was 100 mV s^{-1}.

Synthesis of 2-(2-cyanoethylthio)-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene (TTF 1)

TTF **1** was synthesized according to the literature.[13] Yield: 51%. ^{1}H NMR [400 MHz, $CDCl_3$] δ: 3.03 (2H, t, J = 4 Hz, SCH_2CH_2CN), 2.83 (4H, t, J = 4 Hz, SCH_2–), 2.78 (3H, s, SCH_3), 2.71 (2H, t, J = 4 Hz, SCH_2CH_2CN), 1.24–1.89 (16H, m, –CH_2–, SCH_3), 0.88 (6H, t, J = 6.7 Hz, –CH_3). MS (EI, m/z): 567.02. Anal. Calc. for $C_{22}H_{33}NS_8$: C, 46.52; H, 5.86. Found: C, 46.51, H, 5.88%.

Synthesis of 2-(4-vinylbenzylthio)-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene (TTF 2)

To a solution of 2-(2-cyanoethylthio)-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene (1.0 g, 1.76 mmol) in anhydrous degassed THF (50 ml) was added a solution of CsOH·H_2O (320 mg, 1.9 mmol) in anhydrous degassed MeOH (5 ml) over a period of 30 min. The mixture was stirred for an additional 30 min, then a solution of 1-(bromomethyl)-4-vinylbenzene (431 mg, 2.2 mmol) in anhydrous degassed THF (5 ml) was added. The reaction mixture was stirred overnight. After removing solvent under reduced pressure and separation by column chromatography on silica gel with CH_2Cl_2–hexane (1 : 6, v/v) as eluent, 2-(4-vinylbenzylthio)-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene **2** was obtained as brown oil, yield: 68% (754 mg).

^{1}H NMR [400 MHz, $CDCl_3$] δ: 7.35 (2H, d, J = 8 Hz, Ar–H), 7.24 (2H, d, J = 8 Hz, Ar–H), 6.69 (H, q, J = 4 Hz, –CH═), 5.75 (H, d, J = 8 Hz, ═CH–H), 5.26 (H, d, J = 4 Hz, ═CH–H), 3.92 (2H, s, SCH_2Ph), 2.81 (4H, t, J = 4 Hz, SCH_2–), 2.78 (3H, s, SCH_3), 1.24–1.89 (16H, m, –CH_2–, SCH_3), 0.88 (6H, t, J = 6.7 Hz, –CH_3). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 135.0, 134.7, 134.2, 127.8, 127.5, 126.9, 117.2, 113.5, 45.4, 31.3, 29.7, 28.2, 27.3, 19.1, 16.8, 15.0. MS (EI, m/z): 630.12. Anal. Calc. for $C_{28}H_{38}S_8$: C, 53.29; H, 6.07. Found: C, 53.30, H, 6.09%.

Synthesis of 2-benzylthio-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene (TTF 3)

TTF **3** was synthesized with the same procedure as TTF **2**, benzyl bromide was used to replace 1-(bromomethyl)-4-vinylbenzene. 2-(benzylthio)-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene (TTF **3**) was obtained as red–black solid, yield: 81%.

^{1}H NMR [400 MHz, $CDCl_3$] δ: 7.37 (2H, d, J = 8 Hz, Ar–H), 7.20 (2H, d, J = 8 Hz, Ar–H), 7.18 (2H, d, Ar–H), 3.91 (2H, s, SCH_2Ph), 2.82 (4H, t, J = 4 Hz, SCH_2–), 2.78

(3H, s, SCH_3), 1.24–1.88 (16H, m, $-CH_2-$, SCH_3), 0.88 (6H, t, J = 6.7 Hz, $-CH_3$). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 135.1, 134.3, 127.8, 127.2, 126.9, 116.8, 117.2, 44.5, 31.3, 29.7, 28.2, 27.3, 19.1, 16.8, 15.0. MS (EI, m/z): 604.11. Anal. Calc. for $C_{26}H_{36}S_8$: C, 51.61; H, 6.00. Found: C, 51.60, H, 6.02%.

Synthesis of poly(hydrosilane)copolymer (PHMS)

The poly(hydrosilane)copolymer was obtained by the homogeneous reductive coupling between methyldichlorosilane and methylphenyldichlorosilane.[14] The mole ratio of methylphenylsilylene unit to methylhydrosilylene units in the PHMS was about 0.54 : 0.46, based on ^1H NMR spectroscopy, which is similar to the feeding ratio (1 : 1) of the monomers, yield 11%. M_n = 3147, M_w/M_n = 1.87.

Synthesis of the methylphenylpolysilane (PMPS)

Methylphenylpolysilane was obtained by Wurtz coupling reaction,[15] yield: 41%, M_n = 25 630, M_w/M_n = 2.36.

Synthesis of the chloromethyl methylphenylpolysilane (CMPMPS)

The chloromethyl methylphenylpolysilane was synthesized according to Ban's report.[16] The content of chloromethylene moieties in the CMPMPS was about 40% of the polysilane chain, based on ^1H NMR, yield: 46%, M_n = 5631, M_w/M_n = 2.29.

Synthesis of polymer P1

To a solution of 2-(2-cyanoethylthio)-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene (1.62 g, 2.86 mmol) in anhydrous degassed $CHCl_3$ (30 ml) was added a solution of $CsOH\cdot H_2O$ (480 mg, 2.86 mmol) in anhydrous degassed MeOH (5 ml) over a period of 30 min. The mixture was stirred for an additional 30 min, and slowly added to the solution of (chloromethylphenyl)methylphenylpolysilane (1.0 g, 0.22 mmol) in anhydrous degassed $CHCl_3$ (30 ml). The reaction mixture was stirred overnight, the reaction product was washed with deionized water and dried over $MgSO_4$ and filtered. The filtrate was concentrated to 10 ml and poured into 200 ml methanol and the brown solid formed was washed several times with hexane and dried in vacuum at 30 °C for 5 h, yield: 39% (0.95 g). M_n = 10 238, M_w/M_n = 2.20. ^1H NMR [400 MHz, $CDCl_3$] δ: 7.40–6.97 (Si–Ph), 4.48–4.62 ($PhCH_2S$), 2.79–2.98 (TTF: SCH_2-, SCH_3), 0.89–1.89 (TTF: $-CH_2-$, $-CH_3$). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 135.1–127.2 (Ph–C and TTF ring-C), 116.9–117.3 (TTF ring-C), 46.5, 31.3, 29.9, 28.4, 27.3, 19.1, 16.7, 15.0, −6.3 (Si–CH_3). Anal. for polymer **P1**: C, 6.25, H, 57.39, S, 19.75%.

Synthesis of polymer P2

A mixture of 2-(4-vinylbenzylthio)-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene (3.16 g, 5 mmol), polyhydrosilane copolymer (1.00 g, 0.47 mmol), and hexachloroplatinic acid solution in isopropanol (0.1 ml, 0.1 mol l^{-1}) dissolved in freshly dried THF (30 ml) was stirred for 1 h at room temperature and then refluxed for another 48 h. Then the reaction mixture was cooled to room temperature and filtered. The filtrate was concentrated to 10 ml and poured into 200 ml methanol and the brown solid formed was washed several times with hexane and dried in vacuum at 30 °C for 5 h, yield: 42% (1.92 g). M_n = 7253. M_w/M_n = 2.03. ^1H NMR [400 MHz, $CDCl_3$] δ: 7.42–6.98 (SiPh), 4.47–4.61 ($PhCH_2S$), 2.78–2.99 (TTF: SCH_2-, SCH_3), 0.88–2.14 ($SiCH_2CH_2Ph$ and TTF: $-CH_2-$, $-CH_3$). ^{13}C NMR [100 MHz, $CDCl_3$]: δ 135.1–126.9 (Ph–C and TTF ring-C), 116.9–117.2 (TTF ring-C), 46.3, 33.2, 31.4, 29.6, 28.2, 27.5, 19.1, 16.2, 15.1, 12.2, −6.3 ($SiCH_3$). Anal. for polymer **P2**: C, 6.48, H, 56.49, S, 26.78%.

Acknowledgements

This work was supported by National Science Foundation of China (No. 20676036), the Key Project of the Ministry of Education of China (No. 03053) and the foundation of East China University of Science & Technology.

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