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Synthesis and Characterization of Poly(ferrocenylsilane)s and Their Charge Transfer Salts

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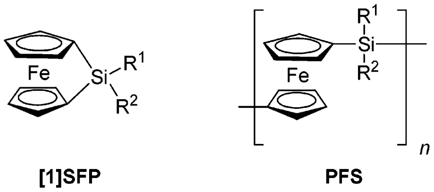
ABSTRACT: A novel series of poly(ferrocenylsilane)s (PFSs), i.e., poly(ferrocenylmethyl(*N*-ethyl-*N*-phenyl)-propylsilane) (**4a**), poly(ferrocenylmethyl(3-(4-methoxylphenyl)propylsilane)) (**4b**), and poly(ferrocenylmethyl(3-(9-carbazolyl)propylsilane)) (**4c**), were synthesized by transition-metal-catalyzed ring-opening polymerization (ROP) of the corresponding substituted [1]silaferrocenophanes (**3a**−**c**). They were characterized by ^{1}H and ^{13}C NMR, FT-IR, elemental analysis, GPC, DSC, TGA, and cyclic voltammetry. Attempts have been made to dope PFSs **4** with 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), chloranil (CA), tetracyanoethylene (TCNE), and iodine. Only iodine and TCNE were able to form charge transfer salts **5a**−**c** and **6a**−**c**, respectively. FT-IR, elemental analysis, and Mössbauer spectra results showed partially oxidized states for **5a**−**c** and **6a**−**c**, and magnetic measurements by a SQUID magnetometer demonstrated paramagnetic behavior with significant antiferromagnetic interactions for these complexes over a wide temperature range.

Introduction

The research for organic or polymeric magnets constitutes a challenge in material sciences research. Since the first molecular ferromagnet, a charge transfer salt between decamethylferrocene and tetracyanoethylene (TCNE), was discovered,[1] metallocene charge transfer salts have been intensively studied partially due to their attractive d-spin electrons.[2] So far, many of such organic−organometallic magnets have been developed, and some structure−property relationships have been established.[2] To extend such a charge transfer salt strategy, it is worthwhile to investigate the polymer system and to explore structure−property relationships further. To this aim, we center our attention on a new type of ferrocene polymer, poly(ferrocenylsilane) (PFS).

High molecular weight PFSs, polymers with ferrocene and silicon alteratively arranged along the polymer chain, were first prepared by Manners in the early 1990s through thermal ring-opening polymerization (ROP) of [1]silaferrocenophane ([1]SFP).[3] Many interesting properties have been observed, such as the unique electronic, optical, and magnetic properties associated with the metal centers in the backbone.[4] As an emerging new material, PFSs have been studied in many fields such as optical crystals, semiconductors, redox-active gels, components of sensors, etching resists, liquid crystal, and nonlinear optics.[5−11] Because of its rich iron loading, high ceramic yield, and good processability, PFS was also investigated intensively as precursors for shaped magnetic ceramics.[12]The oxidation of iron centers in PFSs with electron acceptors to form a charge-transfer salt provides an alterative approach to realize their magnetic properties. Strong Fe−Fe interactions in PFSs, as evidenced by cyclic voltammetry (CV) with two reversible redox waves,[13] may favor the interaction between iron spin centers in the main chain. In fact, after oxidizing oligoferrocenylsilanes ($R^1 = R^2$ = methyl, M_w ca. 1500) with TCNE, Garnier reported its magnetic behavior in which an obvious strong ferromagnetic interaction existed, and the Currie temperature was about 20 K.[14] Subsequently, Manners[15] tried to oxidize high-molecular-weight PFS ($R^1 = R^2 =$ methyl) and the model linear trimetallocene ($(Fe(\eta\text{-}C_5H_4\text{-}SiMe_2Fc)_2$ ($Fc = Fe(\eta\text{-}C_5H_4)(\eta\text{-}C_5H_5)$)) with TCNE, but no oxidized product was obtained. Therefore, he studied the electrochemical behavior of a series of PFSs with one or more methyl groups on the cyclopentadienyl rings which would make them more readily oxidized. The magnetic behavior of their TCNE oxidized products indicated that all of them were paramagnets. Structural analysis indicated that most of Fe^{II} centers were partially oxidized to Fe^{III}.

Chart 1



The manipulation of substituents on the silicon atoms opens another opportunity to tune the properties of PFSs. PFSs with different substituents, such as hydrogen, chlorine, alkyl, aryl, trifluoropropyl, alkyoxyl, aryoxyl, and ferrocenyl groups, have been prepared for

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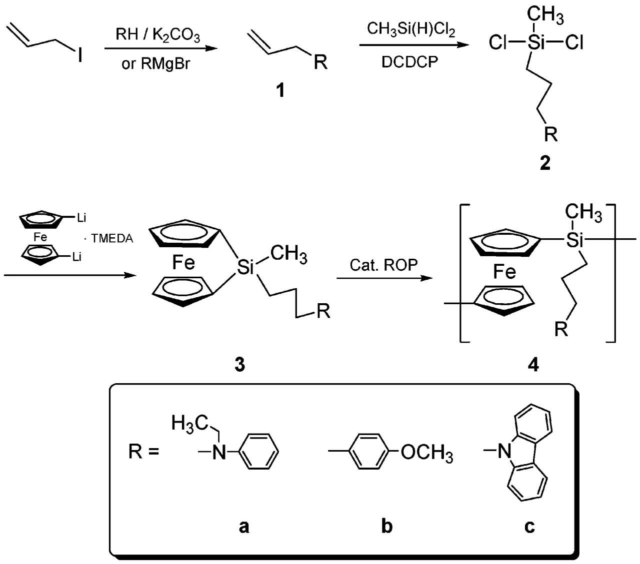
Scheme 1



different application purposes.[16] However, few studies addressed magnetic properties of PFSs, and the substituents on silicon were limited to the dimethyl group for this purpose. There is still much room to modulate their properties by changing the substituent on silicon and to study the structure−property relationships. Electron-rich organic compounds have been widely used for charge-transfer complex research.[17] Introducing electron-rich substituents such as phenylamine or carbazole groups onto silicon as a side chain may render some promising properties. With this aim in mind, we reported a brief communication on the magnetic properties of the charge transfer complex of carbazole-functionalized oligoferrocenylsilane with TCNE and found that it showed paramagnetic property with weak antiferromagnetic interactions.[18] Herein, we present in detail the synthesis and characterization of a novel series of PFSs **4a**−**c** with different electron-rich substituents at silicon (Scheme 1) and the magnetic properties of their charge-transfer complexes **5** and **6** obtained by doping **4** with iodine and TCNE.

Experimental Section

Materials. The solvents used except for CH_2Cl_2 were dried over Na−K alloy and distilled under an argon atmosphere before use. Dichloromethane was dried over CaH_2 and distilled under an argon atmosphere before use. Ferrocene was purified by sublimation twice. Butyllithium was prepared by reacting lithium with butyl chloride in petroleum ether, and the concentration was determined according to the reported method.[19] *N,N,N′,N′*-Tetramethyldiamine (TMEDA) was purified by refluxing with sodium and distilling before use. Dichloromethylsilane was fractional distilled in the presence of molecular sieves (4 Å) before use. Dicyclopentadienedichloroplatinum (DCDCP) was synthesized using the method of Doyle.[20] Dilithioferrocene−TMEDA was prepared according to the literature procedure.[21] Tetracyanoethylene (TCNE) was purified by sublimation in a vacuum and recrystallization from chlorobenzene.

Equipments. ^{1}H NMR and ^{13}C NMR spectra were obtained with Varian Mercury 300 and Bruker 400 spectrometers in $CDCl_3$ with TMS as inner standard. FT-IR spectra were recorded on a Testscan Shimadzu FT-IR 3000 series in the region of 4000−450 cm^{-1} on KBr pellets. Microanalysis was performed on a MOD1106 elemental antianalyzer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were measured using a Rigaku thermoflex DSC8131 and TG8110, respectively, at a scan rate of 10 °C/min in nitrogen. Molecular weights were determined by GPC using THF and a Waters 2410 refractive index detector relative to polystyrene standards.

Electrochemical experiments were carried out under N_2 in CH_2Cl_2 solution of **4a**−**c** and 0.1 M Bu_4NPF_6 using a CHI 660A electrochemical workstation (CH Instruments, Shanghai) and a Pt working electrode and Ag/AgCl as reference electrode with a sweep rate of 100 mV/s.

Iron-57 Mössbauer spectroscopy was performed on Oxford Ins. MS 500 Mössbauer instrument with Co/RT as the radioactive source and intensity as 25 mC. Isomers were reported relative to iron metal. Computer fittings of the data to Lorentenzian lines were carried out with $X^2 < 1.5$.

Solid-state magnetic properties were measured using a Quantum Design MPMS-5s SQUID magnetometer. Data were corrected for the diamagnetism of the sample holder by extrapolation of χ vs $1/T$ to infinite temperature.

All reactions and manipulations were carried out under an argon atmosphere using standard Schlenk techniques except when otherwise stated.

Synthesis of Allylic Aromatic Compounds 1. Compounds **1a** and **1c** were prepared by *N*-ethylaniline or carbazole with allyl iodide in the presence of potassium carbonate in DMF.[22,23]

*Preparation of 4-Allylmethoxylbenzene (**1b**).* 4-Allylmethoxylbenzene (**1b**) was synthesized following the literature procedure.[24] The Grignard reagent, prepared by *p*-methoxylbromobenzene (9.35 g, 50 mmmol), magnesium (1.2 g, 50 mmol) in dried THF (100 mL), was added to the allyl iodide solution (5.5 mL in 10 mL of THF, ca. 55 mmol) in an ice−salt bath (−20 °C). After stirring at room temperature overnight and filtering off precipitates, the filtrate was washed with water three times and dried by pellet KOH. Distillation gave 5.66 g of colorless oil in 76.4% yield. FAB MS *m/z* 149.1 ([M + 1]$^+$) (100%). ^{1}H NMR ($CDCl_3$): 7.2 (d, 2H, Ar−*H*), 6.8 (d, 2H, Ar−*H*), 6.1 (m, br, 1H, =C*H*−), 5.2 (t, 2H, =C*H*$_2$), 3.9 (s, 3H, −O−C*H*$_3$), 3.4 (d, 2H, Ar−C*H*$_2$−). ^{13}C NMR ($CDCl_3$): 157.9 (Ar), 137.8 (CH_2=*C*H−), 132.0 (Ar), 129.4 (Ar), 115.3- (*C*H$_2$=CH−), 113.8 (Ar), 55.2 (O*C*H$_3$), 39.3 (−*C*H$_2$−).

Substituted Dichlorosilane (2). 2a−**c** were synthesized following a previously reported procedure.[22] **2a** was purified by fractional distillation, and **2b** and **2c** were used directly in the next step.

Synthesis of [1]SFPs (3). The strained [1]silaferrocenophanes **3** were prepared following literature procedure,[21] and the typical preparation procedure for [1]methyl(3-(*N*-ethyl-*N*-phenyl)amino-1-propyl)silaferrocenophane (**3a**) is illustrated as follows: *N*-(3-methyldichlorosilylpropyl)-*N*-ethylbenzeneamine (2.6 g, 9.4 mmol) in 5 mL of petroleum ether was added dropwise into the slurry of dilithioferrocene/TMEDA in 100 mL of petroleum ether (prepared from 1.8 g of ferrocene treated with 17.0 mL of 1.29 M butyllithium), and then the resulting mixture was stirred for 24 h at room temperature. After the LiCl was filtered off, the solvent was removed in a vacuum, and the red-orange needle crystals (1.4 g) were obtained through crystallization at −30 °C in dried petroleum ether. Yield: 38% by ferrocene. ^{1}H NMR ($CDCl_3$): 7.2 (t, 2H, Ar−*H*), 6.6 (m, 3H, Ar−*H*), 4.4−3.9 (m, 8H, Cp−*H*), 3.4−3.2 (m, 4H, N−C*H*$_2$−), 1.6−1.3 (m, 2H, N−C−C*H*$_2$−C−), 1.1 (t, 3H, −C−C*H*$_3$), 0.6 (t, 2H, Si−C*H*$_2$−C), 0.3 (s, 3H, Si−C*H*$_3$).

[1]Silaferrocenophanes **3b** and **3c** were recrystallized in cold petroleum ether (−30 °C) and were used directly in transition-metal-catalyzed ROP without further characterization.

Preparation of 4 via Transition-Metal-Catalyzed ROP of 3. The typical procedure for the preparation of **4a** through transition-metal-catalyzed ROP was as follows: **3a** (1.2 g, 3.1 mmol) and DCDCP (20 mg) were dissolved in 10 mL of dry THF, and then the solution was stirred at room temperature for 48 h. The color of the solution turned red-orange to orange with the polymerization proceeding. The solution was concentrated and then poured into excess methanol, which gave a yellow polymer **4a**. Purified **4a** (1.0 g) was obtained in 83% yield by reprecipitating twice in THF/methanol and dried in a vacuum. ^{1}H NMR (400 MHz, $CDCl_3$): 7.2 (br, 2H, Ar−*H*), 6.6 (m, 3H, Ar−*H*), 4.2−4.0 (m, br, 8H, Cp), 3.4−3.2 (br, 4H, NCH_2), 1.6 (br, 2H, NCH_2CH_2C−), 1.1 (t, 3H, CH_2CH_3), 0.8 (br, 2H, $SiCH_2CH_2$), 0.5 (s, 3H, $SiCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): 149.1 (Ar), 129.1 (Ar), 115.9 (Ar), 111.8 (Ar), 73.7, 72.3 (Cp), 68.7 (ipso-Cp), 55.8 (NCH_2CH_2), 49.1 (NCH_2CH_3), 28.3 ($SiCH_2CH_2$) 15.2 ($SiCH_2$), 14.0 (CH_2CH_3), −2.1 ($SiCH_3$). FT-IR (KBr, cm^{-1}): 3431, 3089, 2962, 2926, 2870, 1594, 1502, 1359, 1247, 1160, 1032, 833, 772, 742, 685, 486. Anal. Calcd for $(C_{22}H_{27}NFeSi)_n$: C, 67.87; H, 6.94; N, 3.60. Found: C, 67.68; H, 6.91; N, 3.54.

4b: yellow fibrous powder. Yield: 26% based on the *p*-allylmethoxylbenzene. ^1H NMR ($CDCl_3$): 7.1 (br, 2H, Ar−H), 6.8 (m, 2H, Ar−H), 4.2−4.0 (m, br, 8H, Cp), 3.8 (br, 3H, OCH_3), 2.6 (br, 2H, $ArCH_2$), 1.7 (br, 2H, $CH_2CH_2CH_2$), 0.9 (br, 2H, $SiCH_2$), 0.4 (s, 3H, $SiCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): 158.4 (Ar), 134.4 (Ar), 129.2 (Ar), 113.9 (Ar), 73.5, 72.2 (Cp), 68.9 (ipso-Cp), 55.4 (OCH_3), 39.8 ($-CH_2CH_2CH_2Si-$), 29.4 ($-CH_2CH_2Si-$), 14.8 ($SiCH_2$), −2.3 ($SiCH_3$). FT-IR (KBr, cm^{-1}): 3410, 3086, 2925, 2856, 1611, 1511, 1300, 1247, 1163, 1036, 821, 774, 486. Anal. Calcd for $(C_{21}H_{24}OFeSi)_n$: C, 67.02; H, 6.38. Found: C, 66.89; H, 6.90.

4c: yellow fibrous powder. Yield: 40% based on the 9-allylcarbazole. ^1H NMR ($CDCl_3$): 8.1 (br, 2H, Ar), 7.4−7.2 (m, 6H, Ar), 4.2−3.8 (m, br, 8H, Cp), 3.4 (br, 2H, NCH_2), 1.9 (br, 2H, $SiCH_2CH_2$), 0.8 (br, 2H, $SiCH_2$), 0.3 (s, 3H, $SiCH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): 140.3 (Ar), 125.6 (Ar), 122.7 (Ar), 120.3 (Ar), 118.7 (Ar), 108.6 (Ar), 73.6 (Cp), 72.0 (Cp), 69.1 (ipso-Cp), 62.7 (NCH_2), 26.9 ($SiCH_2CH_2$), 16.3 ($SiCH_2$), −2.1 ($SiCH_3$). FT-IR (KBr, cm^{-1}): 3435, 3049, 2929, 2872, 1595, 1484, 1455, 1326, 1229, 1164, 1034, 808, 776, 749, 723, 486. Anal. Calcd for $(C_{26}H_{25}NFeSi)_n$: C, 71.72; H, 5.75; N, 3.22. Found: C, 71.45; H, 6.34; N, 3.50.

Reaction of Polymers 4 with I_2 and TCNE. *Treatment of Polymers **4** with I_2 To Prepare Complexes **5**.* The typical procedure for the preparation of **5a** is as follows: A solution of 215.3 mg (0.848 mmol) of iodine in 40 mL of dry CH_2Cl_2 was added dropwise to a stirred solution of 100 mg of **4a** (0.257 mmol of monomer units) in 10 mL of dry CH_2Cl_2; stirring was performed at room temperature for an additional 10 h. The precipitate was collected and repeatedly washed with CH_2Cl_2 sufficiently until the filtrate was colorless and then dried in a vacuum to give 246 mg of black solid **5a**. FT-IR (KBr, pellet): 3438, 3080, 2932, 2871, 1637, 1593, 1483, 1439, 1379, 1252, 1158, 1032, 1004, 856, 833, 767, 685, 547, 470. Anal. Calcd for $[\mathbf{4a}]^{nx+}[I_{6.06}{}^{x-}]_n$: C, 22.1; H, 2.26; N, 1.17. Found: C, 22.1; H, 2.40; N, 1.20.

5b. FT-IR (KBr, pellet): 3417, 2923, 2852, 1612, 1511, 1455, 1408, 1382, 1256, 1160, 1027, 1001, 845, 775. Anal. Calcd for $[\mathbf{4c}]^{nx+}[I_{3.23}{}^{x-}]_n$. C, 32.1; H, 3.05. Found: C, 31.9; H, 3.98.

5c. FT-IR (KBr, pellet): 3434, 3092, 2924, 2874, 1625, 1592, 1482, 1451, 1325, 1228, 1153, 1037, 1020, 1005, 846, 772, 752, 724. Anal. Calcd for $[\mathbf{4d}]^{nx+}[I_{4.78}{}^{x-}]_n$: C, 29.9; H, 2.40; N, 1.34. Found: C, 29.9; H, 2.34; N, 1.17.

*Treatment of Polymers **4** with TCNE To Prepare Complexes **6**.* The typical procedure for the preparation of **6a** is given below: A solution of 72.5 mg (0.66 mmol) of TCNE in 30 mL of dry CH_2Cl_2 was added dropwise to a stirred solution of 100 mg of **4a** (0.257 mmol of monomer units) in 10 mL of dry CH_2Cl_2; stirring was performed at room temperature for an additional 10 h. The precipitate was collected and repeatedly washed with CH_2Cl_2 and then dried in a vacuum to give 110 mg of black solid **6a**. FT-IR (KBr, pellet): 3437, 3090, 2931, 2870, 2199, 1604, 1505, 1252, 1158, 1032, 866, 811, 773, 734, 668, 530. Anal. Calcd for $[\mathbf{4a}]^{n+}[TCNE^{-}]_n$: C, 65.0; H, 5.22; N, 13.54. Found: C, 63.1; H, 4.80; N, 16.20.

6b. FT-IR (KBr, pellet): 3445, 3221, 2926, 2204, 1637, 1607, 1579, 1509, 1248, 1176, 1035, 827, 781. Anal. Calcd for $[\mathbf{4c}]^{n+}$-$[TCNE^{-}]_n$ $\{(C_{27}H_{24}N_4OFeSi)_n\}$: C, 64.3; H, 4.76; N, 11.11. Found: C, 59.4; H, 5.33; N, 18.95.

6c. FT-IR (KBr, pellet): 3435, 3050, 2929, 2873, 2199, 1594, 1484, 1452, 1326, 1229, 1155, 1037, 863, 832, 751, 724. Anal. Calcd for $[\mathbf{4d}]^{n+}[TCNE^{-}]_n$ $\{(C_{32}H_{25}N_5FeSi)_n\}$: C, 68.2; H, 4.44; N, 12.43. Found: C, 61.9; H, 4.31; N, 19.84.

Results and Discussion

1. Synthesis and Characterization of PFSs 4. ROP, including thermal,[3] anion,[25] and transition-metal-catalyzed ROP,[26] afforded a convenient route to prepare PFSs. To get functionalized PFSs, two synthetic methods could be chosen. In the first strategy, functionalized PFS could be prepared by postpolymerization functionalization with reactive groups on PFS such as hydrosilyl,[10] chlorosilyl,[8,11] and haloalkylsilyl.[27] Because chlorosilanes and strained [1]SFPs in the first step were commercially available or could be easily prepared, it is a convenient and commonly utilized method to synthesize PFSs for different purposes. The direct ROP of functionalized strained [1]SFP provides an alterative strategy. This method could provide well-defined polymer structure with a limitation of the groups on the silicon because of the lithium reagent conditions in the preparation of [1]SFPs. To obtain the defined PFS structures for well understanding the structure−property relationships of their oxidized complexes, in this paper, the second strategy was adopted to synthesize three different substituted PFSs. First, as shown in Scheme 1, three allylic aromatic compounds **1** were prepared and characterized following the previously reported method.[22−24] Subsequent hydrosilylation reaction between allylic compounds **1** and dichloromethylsilane in the presence of DCDCP afforded substituted dichlorosilanes **2**. Compound **2a** was purified by fractional distillation, and its structure was confirmed by proton NMR spectroscopy. The strained [1]silaferrocenophanes **3** were prepared according to a literature procedure.[21] High-vacuum sublimation, a method commonly used for the purification of cyclic [1]SFPs, failed to give pure compounds for our monomers. Therefore, recrystallization was used to give very nice red-orange needle crystals. The structure of **3a** was confirmed by its proton NMR spectrum. After recrystallization in petroleum ether at −30 °C, [1]SFPs **3b** and **3c** were directly used for ROP without any characterization.

Transition-metal-catalyzed ROP of [1]SFPs **3** afforded polymers **4**. All of them have very good solubility in common solvents such as CH_2Cl_2 and THF. The characterization of polymers **4** was performed by ^1H and ^{13}C NMR, FT-IR, and microanalysis. The ^1H NMR spectra and the assignments of PFS **4a** are illustrated in Figure 1.

The average molecular weights of polymers **4** (Table 1) were estimated by gel permeation chromatography (GPC) with polystyrene as the relative standard. Among them, PFSs **4a** and **4b** showed high molecular weight (M_n as high as 10^4); however, PFSs **4c** has a relative low average molecular weight (DP is about 13). Thus, the molecular weights of PFSs via ROP procedure strongly depend on the properties of substituents on silicon. [1]SFP **3b** with *p*-methoxylphenyl substituent afforded **4b** with the largest average molecular weight (M_n is about 5.7×10^4 Da), but **3c** with a bulk carbazolyl only gave an oligoferrocenylsilane **4d** (M_n is about 5.5×10^3 Da). A plausible reason is that the [1]SFP with a bulky substituent such as carbazolyl on silicon was more readily to form cyclic compounds in transition-metal-catalyzed ROP in comparison to that with a relatively smaller substituent, and this directly influenced the degree of polymerization.

The substituents on silicon also affected the thermal behaviors of PFSs. Generally, symmetric substituents on PFSs favor crystallization, while asymmetric ones

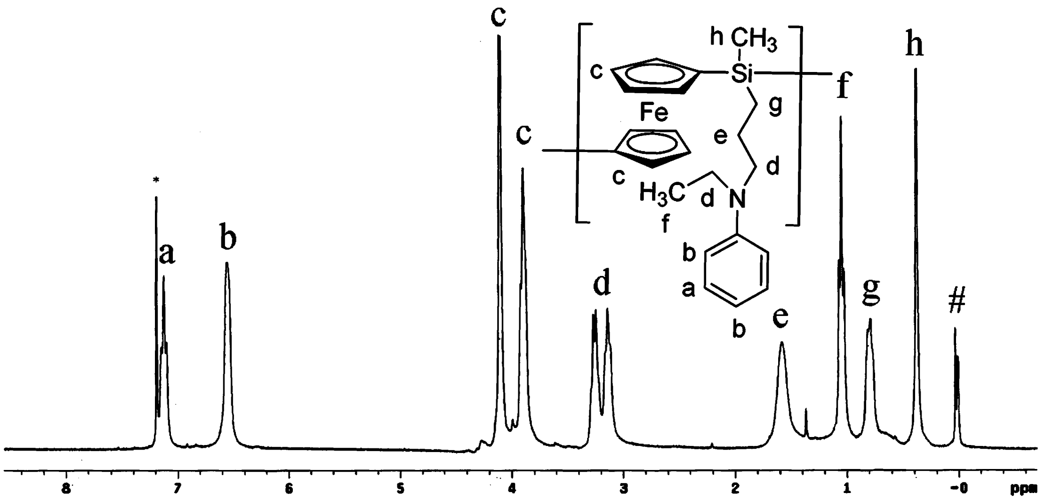


Figure 1. ^{1}H (300 MHz) NMR spectrum and assignment of **4a** in $CDCl_3$ (*, solvent; #, TMS).

Table 1. Molecular Weight and Thermal Analysis Data for 4a–c

	M_w ($\times10^4$)	M_n ($\times10^4$)	PDI (M_w/M_n)	T_g (°C)	T_d[a] (°C)
4a	9.1	3.0	3.0	26	350
4b	10.8	5.7	1.9	62	322
4c	1.2	0.55	2.2	68	320

[a] The decomposed temperature T_d referred to the temperature of 5% weight loss.

Table 2. Cyclic Voltammetry Data for PFSs 4a–c and Ferrocene[a]

polymer	$^1E_{1/2}$ (mV)[b]	$^2E_{1/2}$ (mV)[b]	ΔE (mV)[c]
4a	459	708	249
4b	410	654	244
4c	509	760	251
ferrocene	430		

[a] Data obtained from the analysis of polymers in 0.1 M Bu_4NPF_6 CH_2Cl_2 solution at a scan rate of 100 mV/s. [b] $^1E_{1/2}$ and $^2E_{1/2}$ refer to the half-wave potentials for the first and second oxidation waves, respectively, and are relative to the Ag/AgCl reference electrode. [c] $\Delta E = {}^2E_{1/2} - {}^1E_{1/2}$.

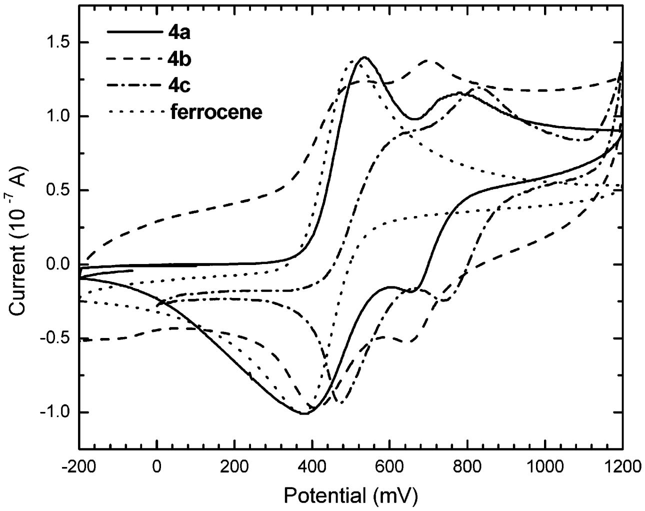


Figure 2. Cyclic voltammogram of **4a–c** and ferrocene in CH_2Cl_2 solution referenced to Ag/AgCl electrode.

are amorphous.[16] All the polymers **4a–c** were glassy polymers with clear T_gs by differential scanning calorimetry (DSC). PFS **4c** had the highest T_g, which may be attributed to the bulky carbazolyl side groups. No melting transitions were observed in the DSC analysis of **4a–c**. The thermal stability of **4** was also investigated by thermogravimetric analysis (Table 1). Polymers **4a–c** had rather good thermal stability and were stable up to 320 °C.

Cyclic voltammetry (CV) is one of the most useful tools to investigate metal–metal interactions in metallocene systems, especially in understanding the electrochemical behavior of compounds in solution.[28] The CV curves of **4a–c** in CH_2Cl_2 are illustrated in Figure 2, and the half-wave potentials ($E_{1/2}$) are summarized in Table 2. For comparison, the data of ferrocene at the same condition were also presented. It was shown that ferrocene only had one reversible redox couple, but **4a–c** each had two couples of reversible oxidation waves with equal intensity, providing a clear evidence for the existence of strong communication between the iron centers along the PFS main chains.[13] The oxidation of alternating iron centers along PFS backbones at the first potential was followed by the oxidation of the iron centers in between at a relatively higher potential.[13] As seen from Table 2, **4b** had the lowest first oxidation half-wave potential ($^1E_{1/2}$), while **4c** had the highest. Thus, **4b** was easiest to be oxidized, followed by ferrocene and **4a**, and **4c** was the most difficult. The lowest oxidization potential ($^1E_{1/2} = 410$ mV vs Ag/AgCl) appeared in PFS **4b**, most likely because this smallest *p*-methoxylphenyl group was favorable to yielding stronger interaction with ferrocene mainchain. The separation of the two waves ($\Delta E = {}^1E_{1/2} - {}^2E_{1/2}$) is an important parameter to evaluate the electronic interaction between the iron centers in the chain. Generally, modifying the substituents on silicon induced modest changes in the PFSs' $^1E_{1/2}$ and ΔE values. These three materials had nearly equal ΔE values. The relatively larger ΔE values (250 mV) in comparison to the literature values (220 mV)[13] demonstrated that the electron-rich substituents introduced altered the electrochemical behavior of the PFS main chain. This phenomenon has also been observed in electron-rich side-chain functionalized polysilane systems.[29]

2. Preparation and Structural Characterization of the Charge-Transfer Complexes. Ferrocene compounds may exhibit magnetism only after one electron is transferred to an electron acceptor. The degree of such transfer has a critical influence on its magnetic properties. Hence, the acceptors (oxidants) play a key role in forming charge transfer complexes and have to be selected on the basis of properties of both donors and acceptors. As a series of important oxidants, 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and chloranil (CA) were attempted to oxidize **4a**−**c**. But there was no precipitate or color change in the doping experiments with **4a**−**c**. Iodine, known as one of the most powerful oxidants and extensively used to dope organic compounds in organic solid materials research, was selected as the electron acceptor in this study. In fact, iodine had been used to oxidize PFS for semiconductor research,[6] and the electronic conductivity experiments showed that conductivity increased by 8 orders of magnitude in comparison to the undoped precursor PFS.[6] More recent doping research of PFS with iodine found that iodine could partially oxidize the iron centers in PFSs.[30] TCNE was also chosen as an acceptor associated with its electrochemical preference to accepting an electron from ferrocene and forming a stabilized and persistent radical anion TCNE$^{\bullet-}$.[1,31] The black charge-transfer complexes **5** and **6** were obtained by adding an excess of a CH_2Cl_2 solution of iodine and a TCNE CH_2Cl_2 solution to **4** in CH_2Cl_2. The doping procedure was much faster in the iodine doping system in which the precipitate appeared immediately after the iodine solution was added dropwise. While in the case of TCNE as oxidant, the doping was obviously slower, and the precipitate could not appear until an overnight stirring at room temperature. To get rid of any residual iodine and TCNE, precipitates were washed sufficiently with CH_2Cl_2 until the filtrate was colorless or until no TCNE point was observed by TLC. It is worthwhile to note that precipitates **5** and **6** are not soluble in CH_2Cl_2, $CHCl_3$, and THF but very soluble in strongly polar solvents such as DMF, DMSO, and NMP.

The characterizations of **5** and **6** were carried out by means of FT-IR, microanalysis, and Mössbauer spectroscopy. FT-IR spectroscopy has been a very useful tool to determinate the degree of oxidation of ferrocene compounds.[28,32] When a ferrocene is oxidized to a ferrocenium ion, there is a large change observed by FT-IR spectroscopy. It has been shown that the perpendicular C−H bending band of ferrocene is the most diagnostic of the oxidized state. This band may be seen at 805−815 cm^{-1} for ferrocene and at 850−860 cm^{-1} for ferrocenium triiodide. If the cation is delocalized (no barrier), only a bending band located at 830 cm^{-1} appears. When there is a barrier existing in the cationic ferrocenium and ferrocene, FT-IR spectroscopy gives the separated perpendicular bending bands of ferrocene and ferrocenium ion.[28,32] The absorption peaks obtained from the FT-IR spectra of **4** and the charge transfer complexes **5** and **6** are listed in the experimental part. Polymer **4b** showed strong C−H bending of ferrocene at 821 cm^{-1}. After doping with TCNE, this absorption band shifted slightly to 827 cm $^{-1}$. However, after it was doped with iodine, this absorption band was substituted by a sharp absorption peak located at 845 cm^{-1}, which may be attributed to the formation of the ferrocenium ion. This trend was more obvious in the **4c** series. A strong C−H bending band of ferrocene located at 821 cm^{-1} in **4c** shifted slightly to 832 cm^{-1} in **6d** but a larger shift to a new peak at 846 cm^{-1} in **5c**. So iodine was more powerful than TCNE to oxidize Fe^{II} centers in **4b** and **4c** to ferrocenium ions.

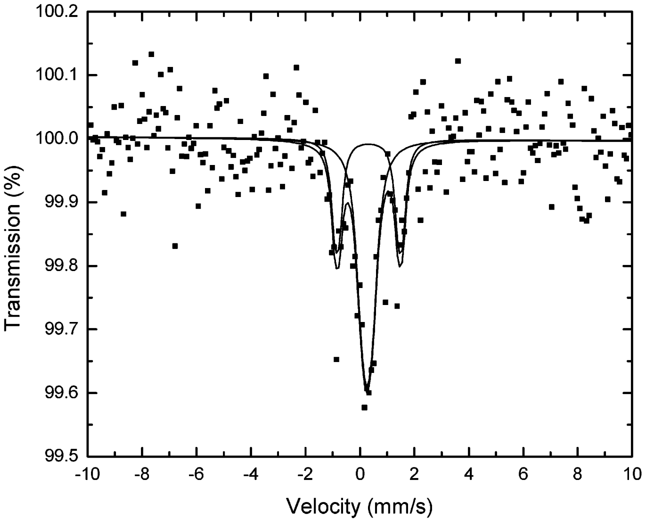


Figure 3. ^{57}Fe Mössbauer spectrum of **5a** at room temperature.

Iron-57 Mössbauer spectroscopy is a powerful technique to determine the oxidizing process and estimate the content of Fe^{II} and Fe^{III} in ferrocene compounds, in which Fe^{II} shows a doublet with a quadrupole splitting Qs of 2.4 mm/s and Fe^{III} ferrocenium ion exhibits a second inner doublet with a quadrupole splitting Qs of 0−0.8 mm/s.[33] The iron-57 Mössbauer spectrum of **5a** is shown as a representative in Figure 3. As seen from Figure 3, an outer, single, symmetrical quadrupole doublet at $\delta = 0.26$ mm/s with Qs = 2.33 mm/s resulted from the Fe^{II} of ferrocene. Besides this outer doublet, there was also an inner singlet at $\delta = 0.28$ mm/s with Qs = 0.31 mm/s, which is characteristic of the Fe^{III} of ferrocinium ion. Therefore, not all the iron centers in PFS had been oxidized, and ferrocene and ferrocenium ion coexisted in **5a**. The content of ferrocenium ion was estimated to be 64% and ferrocene to be 36% based on the calculation of the ratio from corresponding peak areas. The iron-57 Mössbauer results of **5b,c** and **6b** are listed in Table 3. As seen from Table 3, all the doped complexes were ferrocene/ferrocenium ion coexisted systems, and the iodine-doped materials had a relatively high Fe(III) content.

Iodine favors the formation of polyiodide anions such as I_3^- and I_5^- when it oxidizes ferrocene compounds[33a,34] or aromatic compounds.[17d] Manners' group[13b] and Pannell's group[30] studied the iodine doping of oligoferrocenylsilane and 1,1′-bistrimethylsilylferrocene and found that only triiodide counteranions were formed. To date, the form of iodine in **5** has not been clarified although the vibration peak at 846 cm^{-1} in the FT-IR spectra could be attributed to the combinational effect of ferrocenium ion and I_3^-, implying the existence of I_3^-. Elemental analysis is another useful tool to analyze the composition of oxidized products. The microanalysis results showed that the content of iodine was much larger than that of the expected polyiodides. The reason could be that the charge transfer complex between iodine and the electron-rich aromatic ring were formed in addition to the formation of charge transfer salts between iodine and ferrocene.[17] Similar cases appeared in TCNE doping systems. TCNE has many possible forms in its charge transfer salts, such as the free form TCNE, [TCNE]$^-$, [TCNE]$^{\bullet-}$, $[TCNE]_2^{2-}$, [TCNE]$^{2-}$, pentacyanopropendide, and tricyanoethanolate ions resulting from the decomposition of [TCNE]$^{\bullet-}$.[15,31] However, there was no characteristic vibration of [TCNE]$^{\bullet-}$ in FT-IR spectra at 2144 and 2183 cm^{-1}, and only a single −C≡N band at 2199 cm^{-1} appeared which is not

Table 3. Mössbauer Results and Magnetic Properties Data of 5a−c and 6a−c

	Fe^{2+}			Fe^{3+}				
	δ (mm/s)	*Qs* (mm/s)	%[a]	δ (mm/s)	*Qs* (mm/s)	%[a]	θ[b] (K)	*C*[b] (emu/g)
5a	0.26	2.33	36	0.28	0.31	64	−1.3	1.54E−3[d]
5b	0.23	2.28	32	0.26	0.41	68	−20.1	6.27E−3
5c	0.27	2.31	43	0.28	0.34	57	−6.3	2.65E−3
6a	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	−18.6	6.12E−4
6b	0.25	2.31	44	0.24	0.32	56	−10.1	3.23E−3
6c	–[c]	–[c]	–[c]	–[c]	–[c]	–[c]	1.3	1.83E−3

[a] The ratio of Fe^{3+} to Fe^{2+} was based on the integration of Mössbauer spectra of complexes. [b] The Weiss constants and *C* were obtained by fitting their susceptibility data to the Curie−Weiss law from 120 to 300 K for **5a−c** and **6b,c** and from 80 to 130 K for **6a**. [c] Data unavailable. [d] Read as 1.54×10^{-3}.

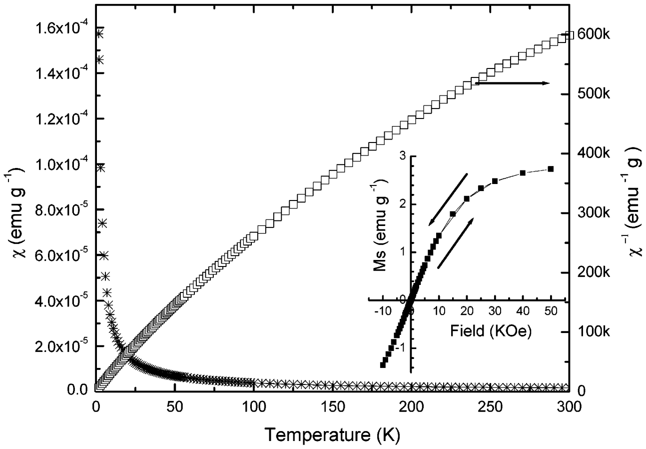


Figure 4. Magnetic susceptibility (χ) and reciprocal magnetic susceptibility (χ^{-1}), measured in a field of 500 Oe, and magnetization (*Ms*) with field (*H*) at 1.85 K (inner) of **5a**.

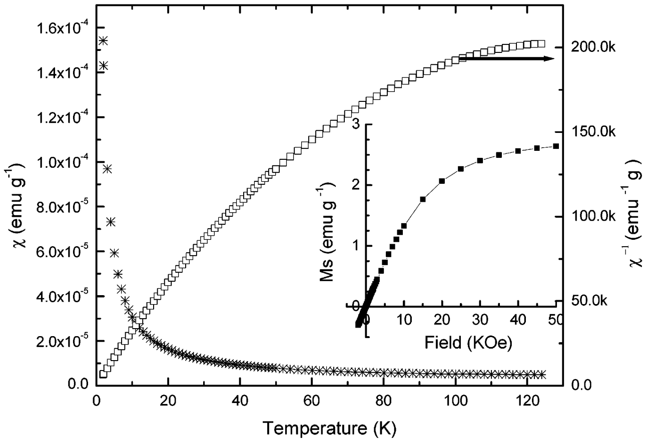


Figure 5. Magnetic susceptibility (χ) and reciprocal magnetic susceptibility (χ^{-1}), measured in a field of 500 Oe, and magnetization (*Ms*) with field (*H*) at 1.85 K (inner) of **6a**.

characteristic stretching frequency of TCNE, $[TCNE]^-$, $[TCNE]^{\bullet-}$, $[TCNE]_2^{2-}$, or $[TCNE]^{2-}$, such a phenomenon was similar to the report by Manners.[15] Meanwhile, the microanalysis results were far away from calculated values based on the expected 1:1 ratios of iron and acceptor molecules in all of **5** and **6**. The reason was, possibly, that the charge transfer complex between TCNE and the electron-rich aromatic rings was formed accompanying the first iron center being oxidized. It seems likely that the introduction of electron-rich substituents complicated the doping process. It is hard to get the accurate composition of these kinds of charge transfer complexes. The combination of FT-IR and Mössbauer spectra indicated that some of iron centers in polymers **4** were oxidized to ferrocenium ion, and polyiodide and cyano-carbon ions were formed.

3. Measurements of Magnetic Properties of 5 and 6. The solid-state magnetic properties of all the oxidized products **5** and **6** were studied with a SQUID magnetometer. The susceptibility of **5** and **6** at the external field 500 Oe increased slowly with the temperature dropped at a high-temperature region (60−300 K), while it increased sharply when the temperature dropped down below 20 K, demonstrating that the moments of all the individual spin centers were aligned with the external field and were trapped in the low temperature. The relationships of magnetic susceptibility (χ) vs temperature (*T*), reciprocal magnetic susceptibility (χ^{-1}) vs temperature, and the magnetization (*Ms*) vs field (*H*) at 1.85 K (inner) are illustrated in Figure 4 for **5a** and in Figure 5 for **6a**. The Weiss constant (θ) fitted by the data of **5a** was about −1.3 K with $C = 1.5 \times 10^{-3}$ emu g^{-1}, indicating that a relatively weak antiferromagnetic interaction between magnetic ions existed in **5a**. Magnetization (*Ms*) vs field (*H*) of **5a** at 1.85 K (Figure 4 inner) showed that saturation magnetization could be reached at very high magnetic field, but no clear hysteresis loop was observed. All of these properties characterized **5a** as a paramagnet. A similar result was also observed in **6a**, which had a cycanocarbon counterion different from the polyiodide in **5a**. Although a relative larger minus Weiss constant (−18.6 K) implied a more significant antiferromagnetic interaction, magnetization of **6a** at 1.85 K (Figure 5 inner) also only reached a saturation at very high magnetic field. The susceptibility data of **5b**,**c** and **6b**,**c** were also fitted to the Curie−Weiss law (60−300 K), and the Weiss constants are listed in Table 3. All of the PFS complexes exhibited antimagnetic interactions. Manners studied the magnetic behavior of TCNE oxidized polyferrocenylethylene and found significant antiferromagnetic interactions in this material.[35] Substituting the ethylene with silylene afforded a communicating PFS backbone to exchange magnetic ions, and both ferromagnetic and antiferromagnetic materials based on their oxidized products were observed.[14,15] All of these results show that it seems that antiferromagnetic interaction is easy to form in this type of materials; however, it was still difficult to yield an antiferromagntic phase change to afford bulk ferromagnetic materials.

Summary

In summary, [1]SFPs **3a−c** were prepared and underwent a transition-metal-catalyzed ROP to give three PFSs **4a−c** with different electron-rich substituents on silicon. Studies showed that substituents on silicon had a moderate effect on polymer average molecular weight, glass transition temperature, and electrochemical behaviors.

Significant Fe–Fe interactions in **4a**–**c** were confirmed by the two reversible redox couples in their cyclic voltammograms. A series of oxidants such as TCNQ, CA, TCNE, and iodine were chosen to oxidize **4a**–**c**. Only the reactions between **4a**–**c** and iodine or TCNE gave charge transfer salts. The resulting **5a**–**c** and **6a**–**c** are soluble in polar solvents such as DMF and DMSO. FT-IR, microanalysis, and iron-57 Mössbauer spectroscopy results showed that all of the PFSs were partially oxidized. The magnetic behavior studies showed that **5a**–**c** and **6a**–**c** obeyed the Curie–Weiss law with significant antiferromagnetic interactions. It seems that antiferromagnetic interactions readily appear in these doped PFSs systems, but it is hard to yield antiferromagnetic phase changes to exhibit bulk ferromagnetic properties. To obtain a magnet is a complicated process and is a combination of many factors, such as the choice of electron acceptors, the process of preparation and the change of substitutents on silicon or ferrocene, etc. Future work will be focused on how to enhance these combinations to get bulk magnetic materials.

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