

Donor–Acceptor C₆₀-Containing Polyferrocenylsilanes: Synthesis, Characterization, and Applications in Photodiode Devices**

By Masato Nanjo, Paul W. Cyr, Kun Liu, Edward H. Sargent,* and Ian Manners**

A series of polyferrocenylsilane (PFS) random copolymers containing covalently bound pendant [C₆₀]fullerene groups, the first well-characterized metallopolymers with pendant C₆₀ units, have been prepared and characterized. The fullerene content of the prepared copolymers ranges from 7 to 24% relative to monomer unit. The desired copolymers were synthesized in three steps: metal-catalyzed ring opening polymerization of sila[1]ferrocenophanes was performed to synthesize random copolymers of poly(ferrocenylmethylphenylsilane-co-ferrocenylchloromethylsilane); the resulting random PFSs were then functionalized by reaction with 11-azido-1-undecanol to give PFSs with pendant azide groups; the desired donor–acceptor C₆₀-containing PFSs were then synthesized by the reaction of the azide group in the side chains with C₆₀ in toluene at 110 °C. The resulting C₆₀-containing PFSs are air-stable and soluble in aromatic solvents, chloroform, or THF. The UV-vis spectra of these materials show broad absorption up to 800 nm. Thin films of these materials were examined as the active layer in rare examples of all solid-state sandwich-type diode devices based on ferrocene-fullerene dyads. The devices exhibit photoconducting and photovoltaic responses, with an open circuit potential of ca. 0.3 V under white light illumination.

1. Introduction

Metal-containing polymers^[1–3] are attracting increased attention as luminescent,^[4,5] redox-active,^[6–10] conductive,^[11] catalytic,^[12,13] etch resistant^[14,15] and self-assembled supramolecular materials.^[16,17] Polyferrocenylsilanes (PFSs) are a representative class of metallopolymers that possess numerous properties of interest for a variety of materials science applications.^[18–20] Because of the presence of the ferrocenyl moiety in the polymer backbone, electrical properties of PFSs are of particular interest. PFSs have two reversible redox

potentials due to electronic communications between neighboring iron centers.^[21–23] Although their intrinsic conductivities classify them as insulators, chemical oxidative doping of PFSs with iodine leads to an increase in conductivity of several orders of magnitude, into the range of 10^{−4} to 10^{−8} S·cm^{−1} similar to semiconductors, and the doped materials possess p-type charge carriers.^[24–27] Photo-oxidation of PFS films can also be achieved by near-UV light irradiation in the presence of chloroform vapor, and the photo-oxidized PFSs show a conductive nature (~10^{−8} S·cm^{−1}) in the dark and a photoconductive response under illumination.^[28]

Charge transfer complexes containing ferrocenes have been well investigated in the context of conducting and magnetic materials.^[29] However, Guldi and co-workers recently reported intramolecular photo-induced electron transfer in ferrocene (donor)/fullerene (acceptor) dyads, and the photo-excited dyads consisting of a ferrocene radical cation and fullerene radical anion reveal relatively long-lived charge separation dynamics (on the order of microseconds).^[30] These phenomena are very interesting for potential applications as photo-active materials.^[31–37] However, such applications have most often been studied in solution or in thin films incorporated into photoelectrochemical cells containing electrolytic solutions. Very recently, we have described photoconductive and photovoltaic properties in solid-state devices made with PFS/fullerene composite thin films.^[38] Although some platinum- or ruthenium-containing conjugated polymers have been synthesized and demonstrate photoluminescent,^[39–41] photoconductive,^[39] and photovoltaic properties,^[42,43] examples of such devices based on metal-containing polymers are limited. Furthermore, while varieties of polymers incorporating fullerenes into backbones, side-chains, and end-groups have been reported,^[44] linear metallopolymers bearing fullerene groups are unexplored. We report herein the synthesis of PFS- containing covalently bound C₆₀ units and their application in photodiode devices.

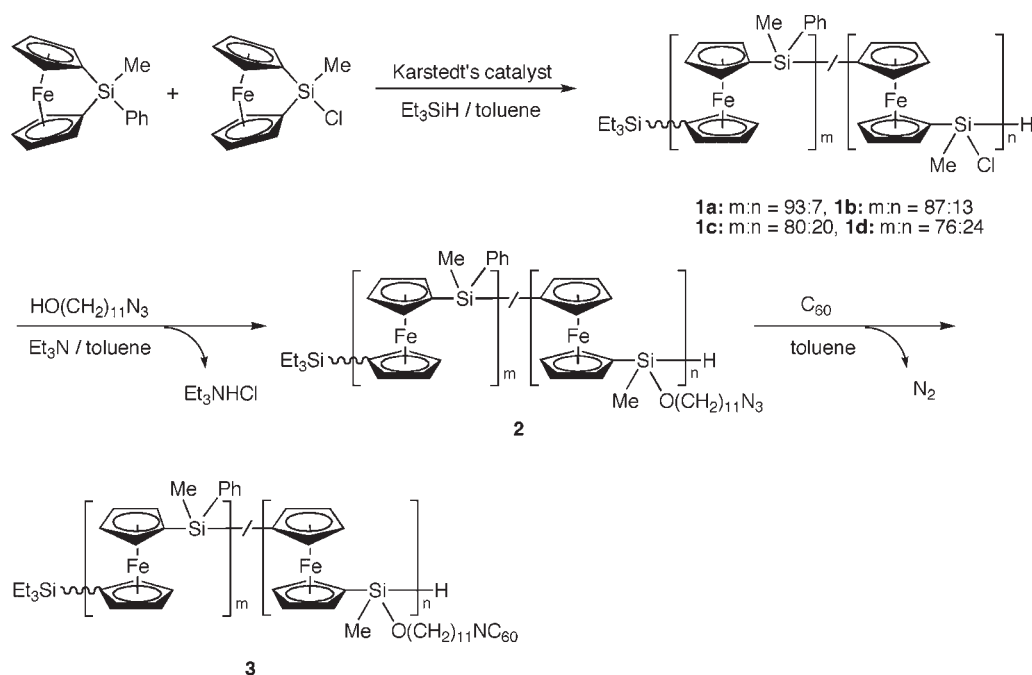
[*] Prof. E. H. Sargent, Dr. P. W. Cyr
Department of Electrical and Computer Engineering
University of Toronto
10 King's College Road, Toronto, ON M5S 3G6 (Canada)
E-mail: ted.sargent@utoronto.ca

Prof. I. Manners
School of Chemistry
University of Bristol
Bristol, BS81TS (UK)
E-mail: ian.manners@bristol.ac.uk

Prof. I. Manners, Dr. M. Nanjo,^[+] K. Liu
Department of Chemistry
University of Toronto
80 St. George Street, Toronto, ON M5S 3H6 (Canada)

[+] Present address: Department of Materials Science, Faculty of Engineering, Tottori University, Japan.

[**] I.M. thanks the European Union for a Marie Curie Chair and the Royal Society for a Wolfson Research Merit Award. E.H.S. thanks the Canadian Government for a Canada Research Chair. M.N. thanks the Ministry of Education, Culture, Sports, Science and Technology Japan for Overseas Advanced Educational Research Practice Support Program. We are also grateful to Ethan J. D. Klem, Dr. Tim Burrow, Georgeta Masson, Kyoung Taek Kim, and Hai Wang for their contributions to the characterization of the described materials.



Scheme 1. Syntheses of random copolymers of C₆₀-containing PFS.

2. Results and Discussion

2.1. Synthesis of C₆₀-Containing PFS

Random copolymers of PFS (**1a–d**) were synthesized by the Pt-catalyzed ring opening polymerization of methylphenylsila-

la[1]ferrocenophane and chloromethylsila[1]ferrocenophane monomers in the presence of triethylsilane in toluene (Scheme 1).^[45,46] The copolymers **1a–d** were purified by reprecipitation into hexanes and were obtained as yellow-orange powders. The resulting copolymers were functionalized by 11-azido-1-undecanol in the presence of triethylamine. After removal of ammonium salt by filtration the azide-attached polymers (**2a–d**) were isolated as orange powders by reprecipitation into hexanes. Based on the GPC data the molecular weights of the azide-attached PFS were: **2a**, $M_n = 25100$; $M_w = 63400$; $PDI = 2.53$; **2b**, $M_n = 27300$; $M_w = 67600$; $PDI = 2.48$; **2c**, $M_n = 32600$; $M_w = 70000$; $PDI = 2.15$; **2d**, $M_n = 23800$; $M_w = 66900$; $PDI = 2.81$. The azide group content in these polymers was determined by comparisons of ¹H NMR signal integrations between CH₂–O in the side chains and phenyl protons in the main chain. In the IR spectra of **2a–d** the characteristic absorption of the azide groups was clearly observed at 2095 cm⁻¹ as shown in Figure 1A.

The syntheses of C₆₀-containing PFSs were performed by the 1,3-dipolar cycloaddition reaction of the azide group to C₆₀ and the subsequent nitrogen elimination reaction.^[47] The azide-functionalized PFSs **2a–d** were mixed with an excess of C₆₀ in toluene at 110 °C. The progress of the reactions could be checked by the diminishing azide absorption in the IR spectra. After 21 h the azide IR absorption completely disappeared in the reaction mixture (Figure 1B), suggesting that all azide groups were converted into the aziridine adducts of C₆₀. As well a new absorption was observed at 527 cm⁻¹ assigned to the attached C₆₀,^[48] however, the other characteristic IR absorptions for the C₆₀ moiety were not detected due to an overlap with absorptions of PFS. The

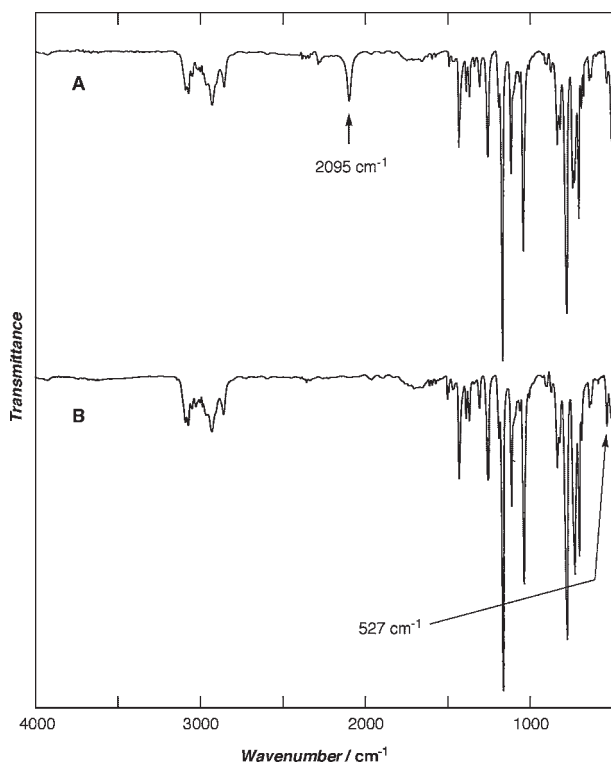


Figure 1. IR spectra for A) **2b** and B) **3b**.

Table 1. Molecular masses and thermal parameters for 3 [fcSiMePh]_m-/[fcSiMeO(CH₂)₁₁NC₆₀]_n.

Polymer	m:n[a]	M _n [b]	M _w [b]	PDI[b]	T _g /°C[c]	Td ₁₀ /°C[d]	CY (%) [e]
3a	93:7	20100	47100	2.34	97	430	34
3b	87:13	21200	52200	2.47	101	429	42
3c	80:20	25000	50700	2.03	101	406	36
3d	76:24	15700	38500	2.46	100	426	39

[a] Determined by ¹H NMR; [b] Estimated by GPC in THF using polystyrene standards, $PDI = M_w/M_n$; [c] The glass transition temperatures were measured at a heating rate of 10 °C/min; [d] The 10% weight loss temperatures were measured at a heating rate of 10 °C/min under N₂; [e] The ceramic yields were determined at 900 °C.

resulting C₆₀-containing PFSs (**3a–d**) were purified by iterative reprecipitations into hexanes to remove unreacted C₆₀ and were obtained as brown powders in 52–63% isolated yields. PFSs **3a–d** are air-stable and readily soluble in aromatic solvents, dichloromethane, chloroform, or THF.

2.2. Characterization of C₆₀-Containing PFS

The molecular masses of C₆₀-containing PFSs **3a–d** are summarized in Table 1 together with their glass transition temperatures (T_g), 10% degradation temperatures (Td₁₀), and

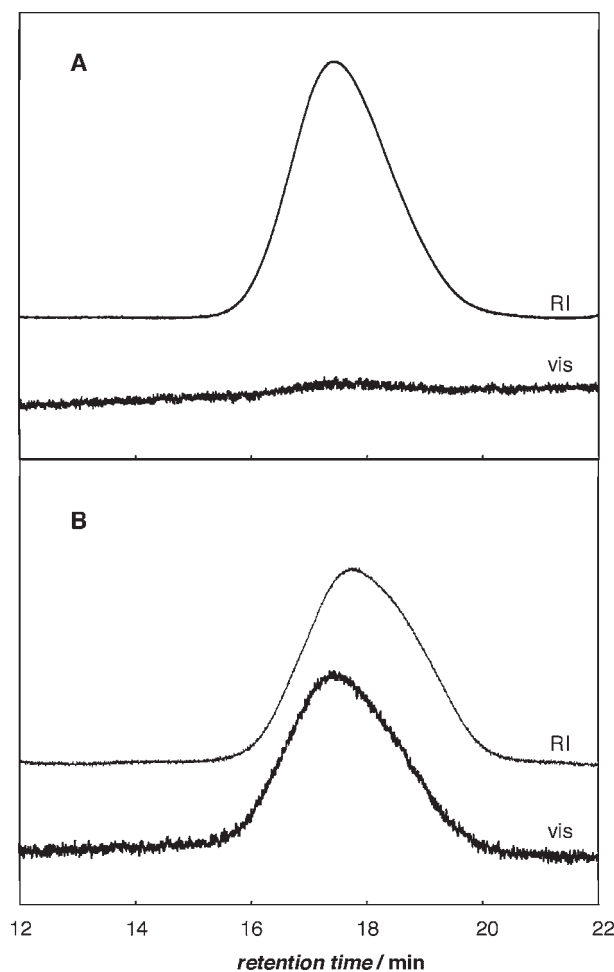


Figure 2. GPC profiles for A) **2b** and B) **3b** detected by RI and visible light (600 nm) detectors.

ceramic yields at 900 °C. The T_gs of **3a–d** were observed at around 100 °C; these values are similar to that found in polyferrocenylmethylphenylsilane (90 °C).^[20] The molecular masses of **3a–d** were estimated by GPC to be lower than those of their corresponding azide-functionalized PFS precursors, however, the polydispersity indices (PDI) of **3a–d** showed similar values to those of the corresponding starting materials and products. Thus, this is probably not a result of chain cleavage during the reaction of **2a–d** with C₆₀, but rather contraction in the hydrodynamic radius as a consequence of the insolubility of C₆₀ in THF (the solubility of C₆₀ itself in THF has been estimated as 5 μg mL⁻¹).^[49] Additionally, two or three azide groups in **2** may react with a single molecule of C₆₀ to form two or three azide adducts of C₆₀, though an excess of C₆₀ was employed in the course of the reaction in order to minimize formation of multiple adducts. The attachment of C₆₀ to PFS was confirmed by GPC profiles using a visible light absorption (vis) detector and a refractive index (RI) detector (Figure 2). Although no significant GPC profiles monitored at 600 nm were observed in azide-functionalized PFSs **2a–d**, C₆₀-containing PFSs **3a–d** showed the same profiles in both vis and RI detectors, indicating that **3a–d** contain covalently attached C₆₀ in the side chains. The UV-vis absorption spectra of **2b** and **3b** are shown in Figure 3. The *d–d* transition band for the ferrocene moiety was observed at 447 nm for **2b**, however, no significant absorption occurred at wavelengths longer than 600 nm. In contrast, PFS **3b** has a

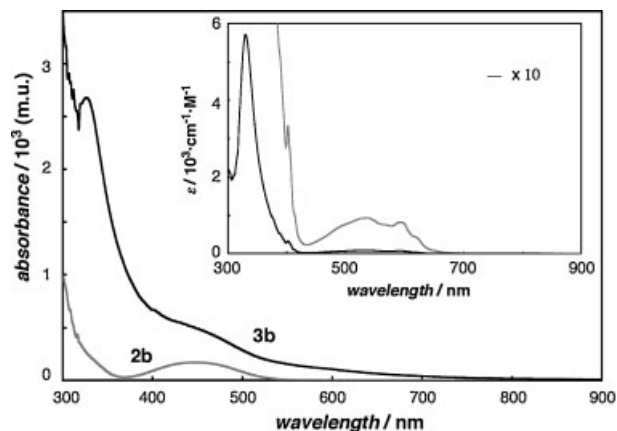


Figure 3. UV-vis spectra of **2b** (gray) and **3b** (black) in toluene. The absorbance is normalized based on monomer units. The absorption spectrum of C₆₀ in toluene is shown as an inset.

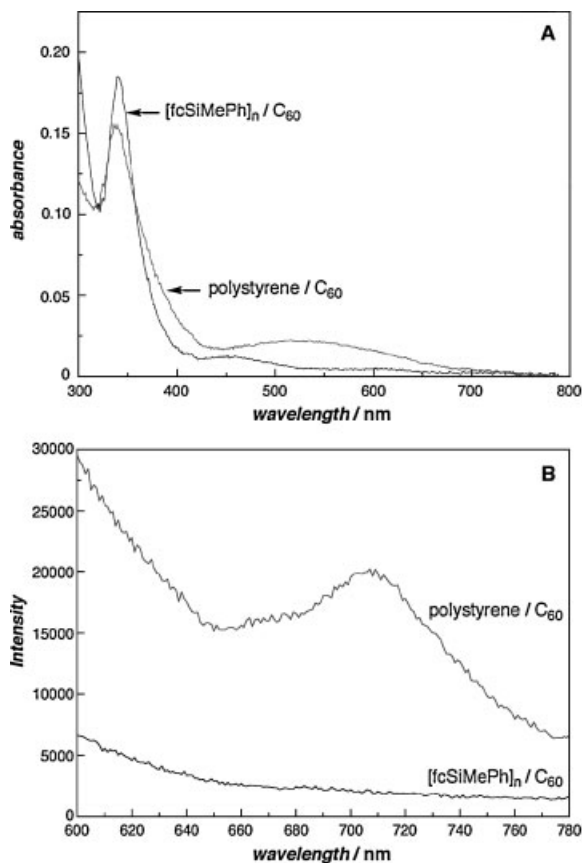


Figure 4. A) UV-vis spectra of polystyrene/C₆₀ thin film (gray) and [fcSiMePh]_n/C₆₀ thin film (black). B) Fluorescence spectra of polystyrene/C₆₀ thin film (gray) and [fcSiMePh]_n/C₆₀ thin film (black) with an excitation wavelength of 380 nm.

broad tailing absorption up to 800 nm due to the presence of C₆₀ in the PFS side-chain. These electronic spectra are fully consistent with the GPC analyses of the azide- and C₆₀-functionalized PFSs. The characteristic UV absorption and shoulder for **3b** were also observed at 326 nm and 402 nm, respectively.^[48] These absorptions originate from the C₆₀ moiety as shown in the inset of Figure 3, which shows the UV-vis spectrum for C₆₀ in toluene. PFS **3b** was also characterized by ¹H, ¹³C, and ²⁹Si NMR in benzene-*d*₆. In the ¹³C NMR spectrum, a very broad signal was observed ranging from 80 to 180 ppm, which is assigned to the attached C₆₀ moiety.^[50]

2.3. Fabrication of Photodiode Devices

The successful synthesis of C₆₀-containing PFSs bearing [60] fullerene covalently linked to the PFS backbone through saturated hydrocarbon side chains provides a novel material for study in photoactivated electronic devices. It is well-known that ferrocene is a good electron donor and fullerene is an excellent electron acceptor. Guldi and Prato have reported and reviewed work on photo-induced intramolecular electron transfer systems that use ferrocene-fullerene dyad derivatives.^[30] The charge separated states of the ferrocenium ion and fullerene radical anion in these dyads have relatively long half lives, on the order of 10⁻³ s, and an especially long half life of 0.38 s has been observed in a ferrocene–porphyrin–fullerene triad system.^[51] Furthermore, the rate constants for the charge separation process have been estimated to be on the order of ~10¹⁰ s⁻¹, and quantum yields have been calculated to be >90%.^[52] These studies have indicated that the ferrocene-

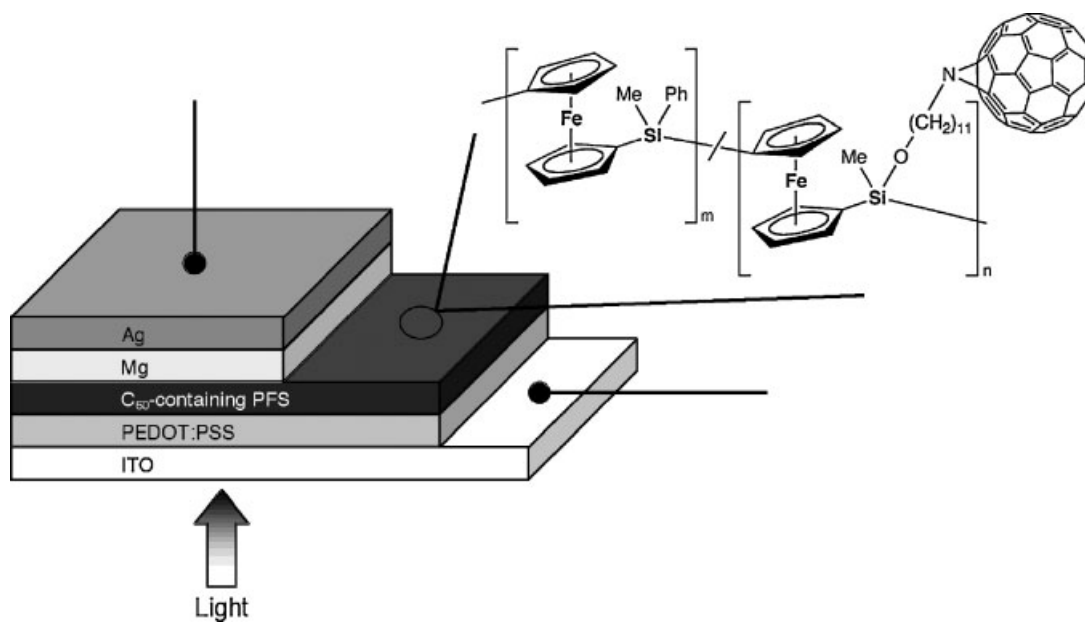


Figure 5. Schematic representation of a photodiode device using random copolymers of C₆₀-containing PFS as an active layer.

fullerene dyad system is promising for applications in photoconductive devices. However, such systems have generally been investigated in solution, and the devices have been composed of thin films in electrolyte-containing photoelectrochemical cells. An all-solid-state device may offer fabrication, development and stability advantages with the use of the ferrocene-fullerene dyad photoactive system. In this paper we demonstrate that such devices can be realized using C₆₀-containing PFSs. Since C₆₀-containing PFSs are stable and readily soluble in some common solvents, they have the advantage of solution processing and handling in device fabrication. Furthermore, thermogravimetric analyses for C₆₀-containing PFSs **3a–d** provided information on their thermal stabilities as shown in Table 1 (temperature for 10% weight loss, *T*_{d10}, is more than 400 °C in all cases), suggesting that C₆₀-containing PFSs have sufficient thermal stability for use in a photoactive device.

To demonstrate the potential for photo-induced charge separation, two thin films of PFS and polystyrene containing the same concentration of C₆₀ were made by spin-coating on a quartz substrate. The absorption bands of C₆₀ in both films were observed as shown in Figure 4A. Although the emission spectrum of C₆₀ in the polystyrene thin film was observed at 710 nm as a broad signal ($\lambda_{\text{ex}} = 380 \text{ nm}$) virtually no emission was detected in the case of the corresponding PFS-C₆₀ film (Figure 4B). This indicates that the fluorescence from C₆₀ was substantially quenched by PFS.

Solid-state diode devices were prepared by spin-coating chlorobenzene solutions of **3b** or **3c** (~10 wt %) onto PEDOT:PSS/ITO coated glass slides, and then top metal contacts of Mg with a protective layer of Ag were thermally evaporated onto the film through a shadow mask to give a sandwich structure diode device with an active area of ~3 mm² (Figure 5). Since Mg is a sufficiently low-work-function metal (3.7 eV) against ITO (4.7 eV), it should create a local field within the device to support extraction of charge carriers. The devices showed asymmetric *I–V* curves due to the work function differences of the metal electrodes, and a weak but clear photovoltaic effect was observed in both devices of **3b** and **3c** under white light illumination condition. *I–V* curves for **3c** in the region near zero bias are shown in Figure 6. This device had a short circuit current (*I*_{sc}) of 3.08 nA, an open circuit potential (*V*_{oc}) of 0.30 V, and a fill factor (FF) of 0.27. A photovoltaic effect was also observed in a device of **3b** under illumination (*I*_{sc} = 1.96 nA, *V*_{oc} = 0.26 V, FF = 0.27). At an applied bias of –0.5 V, a higher photocurrent response was obtained in the device of **3c** with a photocurrent to dark current ratio of 45, compared to 22 for the device of **3b**. The photovoltaic effect derives from a photo-induced electron transfer from a ferrocene moiety as an electron donor in the polymer backbone to the fullerene as the electron acceptor in the polymer side chains.

C₆₀-containing PFSs function as an active layer in the all-solid-state photodiode devices. The observed photocurrents were relatively small and showed similar values to those found in related devices using PFS/C₆₀ or PFS/PCBM ([6,6]-

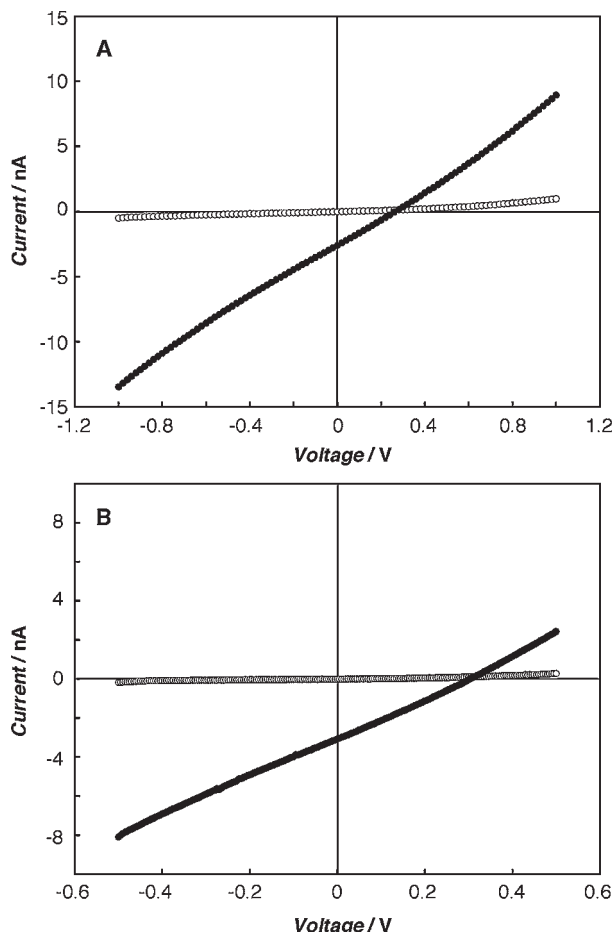


Figure 6. *I–V* plot for an ITO/PEDOTPSS/**3c**/Mg device in the dark (open circles) and under illumination (filled circles). A) In the region from –1 to 1 V bias with 100 ms delay time. B) In the region from –0.5 to 0.5 V bias with 500 ms delay time.

phenyl C₆₁ butyric acid methyl ester) composite thin films.^[38] One reason for the low photocurrents is the weak absorption in C₆₀-containing PFSs throughout much of the visible spectrum, especially beyond ca. 500 nm. However, the C₆₀-containing PFS system has large synthetic versatility and flexibility due to the possibility to introduce various substituents at the silicon and/or ferrocene centers. Thus, increased absorption could be achieved by using a suitable dye as a sensitizer, either by blending in or binding to C₆₀-containing PFSs.^[53] The C₆₀-containing PFS system thus presents a new area with much potential, particularly for the use of ferrocene-fullerene systems for all-solid-state photoactive devices.

3. Conclusions

The new donor–acceptor C₆₀-containing PFSs were synthesized by the reaction of azide-functionalized PFSs with C₆₀ in toluene. The C₆₀-containing PFSs are air-stable and soluble in

aromatic solvents, dichloromethane, chloroform, and THF. GPC measurements clearly show that C₆₀ is covalently bound to the side chains of the PFSs. In UV-vis absorption spectra, a very broad absorption was observed due to the presence of pendant C₆₀ units. The C₆₀-containing PFSs were explored as an active layer for a rare example of an all-solid-state photodiode device based on ferrocene–fullerene dyads. The device demonstrated photoconductive and photovoltaic responses under white light illumination. The open circuit potential was 0.30 V and the short circuit current was on the order of nanoamperes. Although the photocurrent generation was relatively modest in such devices, the C₆₀-containing PFSs provide a novel solid-state material for photodiode devices as a functional metal-containing polymer without any blending or doping. Furthermore, although the initial results we report are relatively modest, considerable scope exists for logical modifications and future optimization of device performance.

4. Experimental

Equipment and Materials: Buckminsterfullerene C₆₀ (>99% purity) was obtained from Bucky USA. Karstedt's catalyst (2.1–2.4 wt % of Pt in xylene) and triethylsilane were purchased from Gelest Inc. and were used as received. Toluene, hexane, and tetrahydrofuran (THF) were reagent grade (>99.5%), used from freshly opened bottles. Chlorobenzene was obtained commercially and distilled prior to use. PEDOT:PSS [poly(styrenesulfonate)/poly(2,3-dihydrothieno(3,4-b)-1,4-dioxin)] (dispersion, 1.3 wt % in water) was obtained from Aldrich. ITO-coated glass plates (25 × 25 × 0.9 mm, R_s < 100 Ω) were purchased from Delta Technologies Ltd. Methylphenylsila[1]ferrocenophane, [54] methylchlorosila[1]ferrocenophane, [55] and 11-azido-1-undecanol [56] were synthesized according to the literature. The ¹H, ¹³C, and ²⁹Si NMR spectra were obtained using Varian Mercury 300, Varian Mercury 400, and Unity 500 spectrometers. Molecular weights were determined by gel-permeation chromatography (GPC) using a Viscotek GPCmax VE2001 liquid chromatograph equipped with a Viscotek TDA 302 differential refractometer and a Viscotek UV-Vis detector model 2501. Absorption spectra were obtained using a Perkin Elmer UV/vis/NIR spectrometer model Lambda 900. The glass-transition temperature was determined by differential scanning calorimetry (DSC) measurement at a heating rate of 10 °C min⁻¹ using a TA Instruments DSC 2920. Thermogravimetric analysis (TGA) was performed on a TA Instruments SDT Q600 under nitrogen atmosphere at a heating rate of 10 °C min⁻¹.

Synthesis of Random Copolymer of Poly(ferrocenylmethylphenylsilane) and Poly(ferrocenylchloromethylsilane), [fcSiMePh]_m-/[fcSiClMe]_n (1): A representative random copolymerization of **1b** (*m:n* = 87:13) is described. In a nitrogen atmosphere glove box, methylphenylsila[1]ferrocenophane (1.037 g, 3.41 mmol) and chloromethylsila[1]ferrocenophane (0.130 g, 0.495 mmol) were dissolved in 30 mL of toluene to which was added 80 μL (0.004 mmol) of Karstedt's catalyst and 60 μL (0.38 mmol) of triethylsilane. The polymerization was allowed to proceed overnight at ambient temperature. Subsequent precipitation of the polymer solution into rapidly stirring hexanes followed by overnight drying under vacuum (~10⁻² mm Hg) afforded the title polymer **1b** as an orange powder (1.087 g, 93%). ¹H NMR (C₆D₆, δ): 0.72–0.81 (br-m, 3.39H), 3.97–4.40 (br-m, 9.27H), 7.26 (br, 3.00H), 7.72 (br, 2H).

[fcSiMePh]_m-/[fcSiClMe]_n where *m:n* = 93:7 (1a): An orange powder. 84%. ¹H NMR (C₆D₆, δ) 0.66–0.83 (br-m, 3.24H), 3.95–4.41 (br-m, 8.94H), 7.26 (br, 3.00H), 7.71 (br, 2H).

[fcSiMePh]_m-/[fcSiClMe]_n where *m:n* = 80:20 (1c): An orange powder. 91%. ¹H NMR (C₆D₆, δ): 0.70–0.84 (br-m, 3.53H, Me), 3.98–4.40 (br-m, 9.94H, Cp), 7.26 (br, 3.00H, Ph), 7.72 (br, 2H, Ph).

[fcSiMePh]_m-/[fcSiClMe]_n where *m:n* = 76:24 (1d): An orange powder. 72%. ¹H NMR (C₆D₆, δ): 0.70–0.84 (br-m, 3.90H), 3.95–4.42 (br-m, 10.79H), 7.27 (br, 3.00H), 7.73 (br, 2H).

Syntheses of [fcSiMePh]_m-/[fcSiMe{O(CH₂)₁₁N₃}]_n (2): A representative functionalization of **2b** (*m:n* = 87:13) is described. In a nitrogen atmosphere glove box, **1b** (1.087 g, 0.44 mmol for Cl group) were dissolved in 5 mL of toluene to which was added 200 μL (1.46 mmol) of triethylamine and 1.0 mL (1.0 mmol) of a stock solution of 11-azido-1-undecanol in toluene (1.02 M). The reaction was allowed to proceed overnight. After removal of the resulting ammonium salt by filtration, precipitation of the polymer solution into rapidly stirring hexanes followed by overnight drying under vacuum (~10⁻² mm Hg) afforded the title polymer **2b** as an orange powder (1.056 g, 90%). ¹H NMR (C₆D₆, δ): 0.58–0.85 (br-m, 3.49H, Me), 1.00–1.72 (br-m, 3.11H, CH₂-chain), 2.71 (br, 0.28H, CH₂-N), 3.73 (br, 0.28H, CH₂-O), 3.97–4.48 (br-m, 9.38H, Cp), 7.27 (br, 3.00H, Ph), 7.75 (br, 2.00H, Ph). ¹³C NMR (C₆D₆, δ): -3.3 (br, Me), -2.8 (br, Me), 26.4, 26.9, 29.0, 29.4, 29.9 (br), 33.3, 51.3 (CH₂-N), 63.3 (CH₂-O), 70.2 (Cp), 72.0 (Cp), 72.4 (Cp), 74.2 (Cp), 74.4 (Cp), 129.3 (Ph), 134.6 (Ph), 138.9 (Ph). ²⁹Si NMR (C₆D₆, δ): -10.9, 2.6. IR (film on NaCl) 2094 cm⁻¹ (-N₃). GPC analysis: *M*_n = 27300, *M*_w = 67600, *PDI* = 2.48.

[fcSiMePh]_m-/[fcSiMe{O(CH₂)₁₁N₃}]_n where *m:n* = 93:7 (2a): An orange powder. 82%. ¹H NMR (C₆D₆, δ): 0.58–0.85 (br-m, 3.21H, Me), 1.00–1.82 (br-m, 2.79H, CH₂-chain), 2.72 (br, 0.24H, CH₂-N), 3.76 (br, 0.24H, CH₂-O), 3.95–4.50 (br-m, 8.70H, Cp), 7.30 (br, 3.00H, Ph), 7.72 (br, 2.00H, Ph). IR (film on NaCl) 2094 cm⁻¹ (-N₃). GPC analysis: *M*_n = 25100, *M*_w = 63400, *PDI* = 2.53.

[fcSiMePh]_m-/[fcSiMe{O(CH₂)₁₁N₃}]_n where *m:n* = 80:20 (2c): An orange powder. 91%. ¹H NMR (C₆D₆, δ): 0.65–1.00 (br-m, 3.45H, Me), 1.00–1.80 (br-m, 3.44H, CH₂-chain), 2.71 (br, 0.30H, CH₂-N), 3.76 (br, 0.30H, CH₂-O), 3.95–4.50 (br-m, 10.63H, Cp), 7.30 (br, 3.00H, Ph), 7.72 (br, 2H, Ph). IR (film on NaCl) 2094 cm⁻¹ (-N₃). GPC analysis: *M*_n = 32600, *M*_w = 70000, *PDI* = 2.15.

[fcSiMePh]_m-/[fcSiMe{O(CH₂)₁₁N₃}]_n where *m:n* = 76:24 (2d): An orange powder. 74%. ¹H NMR (C₆D₆, δ): 0.49–0.87 (br-m, 3.93H, Me), 1.00–1.77 (br-m, 4.93H, CH₂-chain), 2.72 (br, 0.54H, CH₂-N), 3.73 (br, 0.54H, CH₂-O), 3.97–4.48 (br-m, 10.54H, Cp), 7.27 (br, 3.00H, Ph), 7.75 (br, 2.00H, Ph). IR (film on NaCl) 2094 cm⁻¹ (-N₃). GPC analysis: *M*_n = 23800, *M*_w = 66900, *PDI* = 2.82.

Syntheses of [fcSiMePh]_m-/[fcSiMe{O(CH₂)₁₁NC₆₀}]_n (3): A representative synthesis of **3b** (*m:n* = 87:13) is described. **2b** (199 mg, 0.081 mmol for azide group) and C₆₀ (129 mg, 0.179 mmol) were dissolved in toluene (80 mL) and the mixture was heated at 110 °C with vigorous stirring for 21 h. The reaction mixture was then concentrated by evaporation and excessive C₆₀ was removed by filtration. The filtrate was precipitated into hexanes, however, the supernatant was still colored purple due to a contamination of C₆₀. The precipitate was dissolved in toluene (~5 mL), and then reprecipitations were repeated until the color of the supernatant completely disappeared. The precipitate was dried overnight under dynamic vacuum (~10⁻² mm Hg) to give the title polymer **3b** as a brown powder (0.161 g, 63%). ¹H NMR (C₆D₆, δ): 0.50–0.85 (br-m, 3.80H, Me), 1.00–1.77 (br-m, 3.36H, CH₂-chain), 3.76 (br, 0.41H, CH₂-O), 3.95–4.55 (br-m, 9.05H, Cp), 7.27 (br, 3.00H, Ph), 7.75 (br, 2.00H, Ph). ¹³C NMR (C₆D₆, δ): -3.3 (br, Me), -1.68 (br, Me), 5.0, 8.2, 20.8, 25.7, 26.4 (br), 30.0 (br), 33.3 (br), 34.8, 52.0 (br, CH₂-N), 63.3 (br, CH₂-O), 70.3 (Cp), 72.4 (Cp), 74.2 (Cp), 74.5 (Cp), 129.3 (Ph), 134.6 (Ph), 138.9 (Ph). ²⁹Si NMR (C₆D₆, δ): -10.9, 0.1. *T*_g = 101 °C. GPC analysis: *M*_n = 21200, *M*_w = 52200, *PDI* = 2.47.

[fcSiMePh]_m-/[fcSiMe{O(CH₂)₁₁NC₆₀}]_n where *m:n* = 93:7 (3a): A brown powder. 58%. ¹H NMR (C₆D₆, δ): 0.50–0.85 (br-m, 3.22H, Me), 0.98–1.85 (br-m, 2.86H, CH₂-chain), 3.66–3.85 (br, 0.26H, CH₂-O), 3.92–4.58 (br-m, 8.94H, Cp), 7.27 (br, 3.00H, Ph), 7.75 (br, 2H, Ph). *T*_g = 97 °C. GPC analysis: *M*_n = 20100, *M*_w = 47100, *PDI* = 2.34.

[*fcSiMePh*]_m-/[*fcSiMe*{O(CH₂)₁₁NC₆₀}]_n where *m:n* = 80:20 (**3c**): A brown powder. 52%. ¹H NMR (C₆D₆, δ): 0.40–1.00 (br-m, 4.06H, Me), 1.00–2.05 (br-m, 3.34H, CH₂-chain), 3.77 (br, 0.43H, CH₂-O), 3.96–4.60 (br-m, 10.19H, Cp), 7.27 (br, 3.00H, Ph), 7.75 (br, 2.00H, Ph). T_g = 101 °C. GPC analysis: M_n = 25 000, M_w = 50 700, PDI = 2.03.

[*fcSiMePh*]_m-/[*fcSiMe*{O(CH₂)₁₁NC₆₀}]_n where *m:n* = 76:24 (**3d**): A brown powder. 54%. ¹H NMR (C₆D₆, δ): 0.50–0.98 (br-m, 4.09H, Me), 1.00–2.07 (br-m, 4.27H, CH₂-chain), 3.78 (br, 0.78H, CH₂-O), 3.90–4.65 (br-m, 11.05H, Cp), 7.27 (br, 3.00H, Ph), 7.75 (br, 2.00H, Ph). T_g = 101 °C. GPC analysis: M_n = 15 700, M_w = 38 500, PDI = 2.46.

Device Fabrication: A thin layer of PEDOT:PSS was coated onto a pre-cleaned ITO-coated glass plate by spin-coating (1600 rpm, 180 sec) and subsequent drying at 130 °C under vacuum (~10⁻² mm Hg) for 1 h. The active layer of C₆₀-containing PFS **3** was deposited by spin coating (1000 rpm, 90 sec) a 10 wt % solution of **3** in chlorobenzene onto the PEDOT:PSS layer. The films were dried under vacuum and then metal contacts (~3 mm²) were deposited on the top surface by thermal evaporation through a shadow mask to give a 125 nm Mg/100 nm Ag metal stack.

Device Characterization: Electrical measurement of the devices was carried out using an Agilent Technologies 4155C Semiconductor Parameter Analyzer and microprobe station. Optical illumination was performed through the ITO side of the device using a Cole-Parmer fiber optic illuminator model EW-09745-00 with the output beam focused to a diameter of ~1 cm. The spectral power output was measured to be 160 mW.

Measurement of UV and Fluorescence Spectra for PFS/C₆₀ and Polystyrene/C₆₀ Thin Films: C₆₀ (2.3 mg) and [*fcSiMePh*]_n (7.7 mg) were dissolved in chlorobenzene (100 mL) to make a total 10 wt % solution (mole ratio of C₆₀: [*fcSiMePh*]_n = 13:100). This solution was identical to the one that was used for fabricating the device. The PFS-C₆₀ film was prepared by spin-coating (1000 rpm, 60 sec) using this solution onto a quartz slide. An analogous polystyrene-C₆₀ thin film was also prepared under the same conditions (2.3 mg of C₆₀, and 7.7 mg of polystyrene). The emission spectra were measured with an excitation wavelength of 380 nm. Although the emission spectrum of C₆₀ in the polystyrene thin film was readily observed at 710 nm as a broad signal (λ_{ex} = 380 nm) virtually no emission was detected in the case of the corresponding PFS-C₆₀ film.

Received: March 15, 2007
Revised: October 10, 2007

[1] *Metal-Coordination Polymers* (Eds: A. S. Abd-El-Aziz, C. E. Carraher, Jr., C. U. Pittman, Jr., M. Zeldin), Wiley, Hoboken **2005**.
[2] I. Manners, *Synthetic Metal-Containing Polymers*, Wiley-VCH, Weinheim **2004**.
[3] *Macromolecules Containing Metal and Metal-Like Elements*, Vol. 2 (Eds: A. S. Abd-El-Aziz, C. E. Carraher, Jr., C. U. Pittman, Jr., J. E. Sheats, M. Zeldin), Wiley, Hoboken **2004**.
[4] R. Shunmugam, G. N. Tew, *J. Am. Chem. Soc.* **2005**, *127*, 13567.
[5] Z. Wang, A. R. McWilliams, C. E. B. Evans, X. Lu, S. Chung, M. A. Winnik, I. Manners, *Adv. Funct. Mater.* **2002**, *12*, 415.
[6] J. A. Barron, S. Glazier, S. Bernhard, K. Takada, P. L. Houston, H. D. Abreuña, *Inorg. Chem.* **2003**, *42*, 1448.
[7] K. Kulbaba, M. J. MacLachlan, C. E. B. Evans, I. Manners, *Macromol. Chem. Phys.* **2001**, *202*, 1768.
[8] M. Sykora, K. A. Maxwell, T. J. Meyer, *Inorg. Chem.* **1999**, *38*, 3596.
[9] A. C. Arsenault, H. Míguez, V. Kitaev, G. A. Ozin, I. Manners, *Adv. Mater.* **2003**, *15*, 503.
[10] S. Zou, M. A. Hempenius, H. Schönherr, G. J. Vancso, *Macromol. Rapid Commun.* **2006**, *27*, 103.

[11] B. J. Holliday, T. M. Swager, *Chem. Commun.* **2005**, 23.
[12] D. A. Durkee, H. B. Eitouni, E. D. Gomez, M. W. Ellsworth, A. T. Bell, N. P. Balsara, *Adv. Mater.* **2005**, *17*, 2003.
[13] S. Lastella, Y. J. Jung, H. Yang, R. Vajtai, P. M. Ajayan, C. Y. Ryu, D. A. Rider, I. Manners, *J. Mater. Chem.* **2004**, *14*, 1791.
[14] S. B. Clendinning, S. Aouba, M. S. Rayat, D. Grozea, J. B. Sorge, P. M. Brodersen, R. N. S. Sodhi, Z.-H. Lu, C. M. Yip, M. R. Freeman, H. E. Ruda, I. Manners, *Adv. Mater.* **2004**, *16*, 215.
[15] I. Korczagin, S. Golze, M. A. Hempenius, G. J. Vancso, *Chem. Mater.* **2003**, *15*, 3663.
[16] K. Temple, K. Kulbaba, K. N. Power-Billard, I. Manners, K. A. Leach, T. Xu, T. P. Russell, C. J. Hawker, *Adv. Mater.* **2003**, *15*, 297.
[17] J. L. Bender, P. S. Corbin, C. L. Fraser, D. H. Metcalf, F. S. Richardson, E. L. Thomas, A. M. Urbas, *J. Am. Chem. Soc.* **2002**, *124*, 8526.
[18] M. Tanabe, G. W. M. Vandermeulen, W. Y. Chan, P. W. Cyr, L. Vanderark, D. A. Rider, I. Manners, *Nat. Mater.* **2006**, *5*, 467.
[19] I. Manners, *Science* **2001**, *294*, 1664.
[20] K. Kulbaba, I. Manners, *Macromol. Rapid Commun.* **2001**, *22*, 711.
[21] D. A. Foucher, B.-Z. Tang, I. Manners, *J. Am. Chem. Soc.* **1992**, *114*, 6246.
[22] R. Rulkens, A. J. Lough, I. Manners, S. R. Lovelace, C. Grant, W. E. Geiger, *J. Am. Chem. Soc.* **1996**, *118*, 12683.
[23] M. T. Nguyen, A. F. Diaz, V. V. Dement'ev, K. H. Pannell, *Chem. Mater.* **1993**, *5*, 1389.
[24] L. Espada, K. H. Pannell, V. Papkov, L. Leites, S. Bukalov, I. Suzdalev, M. Tanaka, T. Hayashi, *Organometallics* **2002**, *21*, 3758.
[25] L. Bakueva, E. H. Sargent, R. Resendes, A. Bartole, I. Manners, *J. Mater. Sci. Mater. Electron.* **2001**, *12*, 21.
[26] R. Rulkens, R. Resendes, A. Verma, I. Manners, K. Murti, E. Fossum, P. Miller, K. Matyjaszewski, *Macromolecules* **1997**, *30*, 8165.
[27] M. Tanaka, T. Hayashi, *Bull. Chem. Soc. Jpn.* **1993**, *66*, 334.
[28] P. W. Cyr, M. Tzolov, I. Manners, E. H. Sargent, *Macromol. Chem. Phys.* **2003**, *204*, 915.
[29] A. Togni, in *Ferrocenes* (Eds: A. Togni, T. Hayashi), VCH, Weinheim **1995**, pp. 433–466.
[30] D. M. Guldi, M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* **1997**, *119*, 974.
[31] H. Imahori, S. Fukuzumi, *Adv. Funct. Mater.* **2004**, *14*, 525.
[32] D. M. Guldi, H. Imahori, K. Tamaki, Y. Kashiwagi, H. Yamada, Y. Sakata, S. Fukuzumi, *J. Phys. Chem. A* **2004**, *108*, 541.
[33] D. M. Guldi, C. Luo, D. Koktysh, N. A. Kotov, T. Da Ros, S. Bosi, M. Prato, *Nano Lett.* **2002**, *2*, 775.
[34] C. Luo, D. M. Guldi, M. Maggini, E. Menna, S. Mondini, N. A. Kotov, M. Prato, *Angew. Chem. Int. Ed.* **2000**, *39*, 3905.
[35] D. M. Guldi, M. Prato, *Acc. Chem. Res.* **2000**, *33*, 695.
[36] D. M. Guldi, *Chem. Commun.* **2000**, 321.
[37] M. Prato, M. Maggini, *Acc. Chem. Res.* **1998**, *31*, 519.
[38] P. W. Cyr, E. J. D. Klem, E. H. Sargent, I. Manners, *Chem. Mater.* **2005**, *17*, 5770.
[39] W.-Y. Wong, G.-L. Lu, K.-H. Choi, J.-X. Shi, *Macromolecules* **2002**, *35*, 3506.
[40] N. Chawdhury, A. Köhler, R. H. Friend, W.-Y. Wong, J. Lewis, M. Younus, P. R. Raithby, T. C. Corcoran, M. R. A. Al-Mandhary, M. S. Khan, *J. Chem. Phys.* **1999**, *110*, 4963.
[41] M. Younus, A. Köhler, S. Cron, N. Chawdhury, M. R. A. Al-Mandhary, M. S. Khan, J. Lewis, N. J. Long, R. H. Friend, P. R. Raithby, *Angew. Chem. Int. Ed.* **1998**, *37*, 3036.
[42] K. Y. K. Man, H. L. Wong, W. K. Chan, C. Y. Kwong, A. B. Djuricic, *Chem. Mater.* **2004**, *16*, 365.
[43] A. Köhler, H. F. Wittmann, R. H. Friend, M. S. Khan, J. Lewis, *Synth. Met.* **1994**, *67*, 245.
[44] See, for example: a) A. Cravino, N. S. Sariciftci, *J. Mater. Chem.* **2002**, *12*, 1931. b) J. L. Segura, N. Martín, D. M. Guldi, *Chem. Soc. Rev.* **2005**,

- 34, 31. c) T. Otsubo, Y. Aso, K. Takimiya, *Pure Appl. Chem.* **2005**, *77*, 2003. d) C. Wang, Z. X. Guo, S. Fu, W. Wu, D. Zhu, *Prog. Polym. Sci.* **2004**, *29*, 1079. e) M. Even, B. Heinrich, D. Guillon, D. M. Guldi, M. Prato, R. Deschenaux, *Chem. Eur. J.* **2001**, *7*, 2595.
- [45] P. Gómez-Elipé, P. M. Macdonald, I. Manners, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 762.
- [46] P. Gómez-Elipé, R. Resendes, P. M. Macdonald, I. Manners, *J. Am. Chem. Soc.* **1998**, *120*, 8348.
- [47] M. Prate, Q. Chan Li, F. Wudl, V. Lucchini, *J. Am. Chem. Soc.* **1993**, *115*, 1148.
- [48] M. R. Banks, J. I. G. Cadogan, I. Gosney, P. K. G. Hodgson, P. R. R. Langridge-Smith, J. R. A. Millara, A. T. Tylora, *J. Chem. Soc. Chem. Commun.* **1995**, 885.
- [49] T. Yoshihara, M. Murai, Y. Tamaki, A. Furube, R. Katoh, *Chem. Phys. Lett.* **2004**, *394*, 161.
- [50] Y. Chen, R.-F. Cai, L.-X. Xiao, Z.-E. Huan, D. Pan, *J. Mater. Sci.* **1998**, *33*, 4633.
- [51] H. Imahori, D. M. Guldi, K. Tamaki, Y. Yoshida, C. Luo, Y. Sakata, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 6617.
- [52] M. Fujitsuka, N. Tsuboya, R. Hamasaki, M. Ito, S. Onodera, O. Ito, Y. Yamamoto, *J. Phys. Chem. A* **2003**, *107*, 1452.
- [53] M. Grätzel, *Inorg. Chem.* **2005**, *44*, 6841.
- [54] D. Foucher, R. Ziembinski, R. Peterson, J. Pudelski, M. Edwards, Y. Ni, J. Massey, C. R. Jaeger, G. J. Vancso, I. Manners, *Macromolecules* **1994**, *27*, 3992.
- [55] D. L. Zechel, K. C. Hultszch, R. Rulkens, D. Balashis, Y. Ni, J. K. Pudelski, A. J. Lough, I. Manners, D. A. Foucher, *Organometallics* **1996**, *15*, 1972.
- [56] S. M. Andersen, C.-C. Ling, P. Zhang, K. Townson, H. J. Willison, D. R. Bundle, *Org. Biomol. Chem.* **2004**, *2*, 1199.