

Photoconductivity in Donor–Acceptor Polyferrocenylsilane–Fullerene Composite Films

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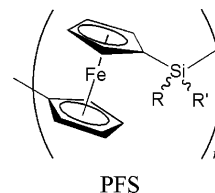
Organometallic polymer-based solid-state photoconductive and photovoltaic devices using thin films of blends of poly(ferrocenylmethylphenylsilane) (PFMPS) and fullerenes as the active layers were fabricated. Buckminsterfullerene C₆₀ and [6,6]-phenyl C₆₁ butyric acid methyl ester (PCBM) fullerene derivative were investigated as electron acceptors in the devices, in the range of 5–18 mol % relative to the ferrocenyl electron donor in PFMPS. The devices show a predominantly UV spectral response. The short circuit currents were on the order of nanoamperes under white light illumination of ca. 160 mW/cm², and the open circuit voltage was found to vary from ca. 0.3 V for devices with C₆₀ to ca. 0.45 V for devices with PCBM.

Introduction

Metal-containing polymers are a topic of much current research interest due to the potential for combining the characteristics of transition metals with the favorable processing and mechanical properties of polymers within one material.^{1–3} These so-called metallopolymers can demonstrate a variety of promising traits, such as potentially useful electrical, optical, magnetic, and catalytic properties, which may not be readily realized within the organic polymer class. Polyferrocenylsilanes (PFSs, see Scheme 1) are a representative class of metallopolymer that possesses numerous properties of interest for a variety of materials science applications.⁴

The optical and electrical properties of PFSs arise mainly due to the presence of the ferrocenyl moiety in the polymer backbone, and these properties have been a topic of investigation recently. For example, PFSs and related polyferrocenes have been shown to possess relatively high refractive indices for polymers.⁵ In addition, they have been examined as sensitizing materials in optical fiber probes for detection of gases.⁶ The electrical and redox properties of PFSs have also been studied in some detail. Cyclic voltammetry studies have shown that PFSs possess two redox waves, proposed to be due to electronic communication between neighboring iron centers.^{7–9} While the intrinsic

Scheme 1. Structure of Polyferrocenylsilanes (PFSs)



conductivity of PFSs are typically on the order of 10⁻¹¹ S cm⁻¹, chemical oxidative doping of the polymer with I₂ results in an increase in conductivity, and values in the range 10⁻⁸ to 10⁻⁴ S cm⁻¹ have been reported.^{10–12} PFSs have attracted attention as charge dissipation coatings,¹³ and in the doped state have been shown to be moderate hole transport materials.¹⁰

We have undertaken a research effort focused on the optoelectronic properties of PFS materials. Recently, we reported on the use of a photoinduced charge-transfer reaction involving PFSs that could be used to control the electrical properties of the polymer.¹⁴ Central to this process was the well-known photoreaction of ferrocene with halocarbons, such as CHCl₃, to yield the oxidized ferrocenium species.^{15–17}

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This reaction was used to controllably oxidize PFS samples, either in solution or in thin films. It was shown to allow optical control of the electrical conductivity of films of PFS over several orders of magnitude. In addition, the resulting photooxidized materials demonstrated photoconductivity.^{14,18}

Photoinduced electron transfer (PET) involving a ferrocenyl moiety as the donor and a fullerene group as the acceptor has been shown recently, particularly in work by Guldi and co-workers,^{19,20} to give a rapid charge transfer to create a relatively long-lived charge separated state possessing the ferrocenium cation and a fulleride radical anion. These types of complexes have been investigated in terms of artificial photosynthesis and photocurrent generation.^{21–24} In the majority of these cases, the materials were studied in solution, or in thin films incorporated into photoelectrochemical cells containing electrolytic solutions. Examples of solid-state photoconducting devices based on metal-containing polymers are limited and involve transition metal species incorporated into conjugated polymer systems. Platinum poly-yne systems bearing conjugated spacer units in the main chain have been demonstrated as photocells in sandwich-type diode structures.^{25–28} An enhanced photocurrent response in related systems by mixing with C₆₀ fullerene has also been described.²⁹ Recently, a layer-by-layer electrostatic self-assembled photovoltaic device employing a cationic poly(*p*-phenylenevinylene) species bearing ruthenium–polypyridyl complexes in the backbone was reported.³⁰ Photoconductivity in thin films of oxidized oligomeric and polymeric ferrocene-based materials has been reported recently in lateral conduction modes.^{14,18,31,32} Herein, we report photoconductive and photovoltaic effects in solid-state devices made with PFS/fullerene composite thin films.

Experimental Section

Materials and General Equipment. Poly(ferrocenylmethylphenylsilane) (PFMPS), with $M_n = 180\,000$ and PDI = 3.35, was synthesized by transition-metal-catalyzed ROP as previously

described.³³ Buckminsterfullerene C₆₀ (>99% purity), purchased from Bucky USA, and PCBM (>99%), purchased from American Dye Source, Inc., were used as received. Absorption spectra were obtained using a Cary 500 spectrophotometer.

Device Fabrication. Solutions of fullerene and PFMPS were prepared by dissolving the polymer in solutions with known concentrations of fullerene. The active layer of the devices was deposited by spin coating of 5–10 wt % polymer (relative to solvent) solutions, in either chlorobenzene or 1,2-dichlorobenzene, onto precleaned ITO-coated glass slides (Delta Technologies Ltd., $R_s < 100\ \Omega$). The films were dried in a vacuum and then metal contacts ($\sim 3\ \text{mm}^2$) were deposited on the top surface via thermal evaporation through a mask to give a 150 nm Mg/100 nm Ag/10 nm Au metal stack. Mg was used as the work function difference between Mg and ITO (ca. 1.2 eV) should create a local field within the device to aid in extraction of charge carriers. This top metal contact was then covered with Ag and Au to provide protection against oxidation of Mg, and to endow mechanical robustness to the device when electrically probing. The active layer of the devices was typically 300–600 nm thick, as measured using a Veeco Dektak3 surface step profiler.

Device Characterization. Electrical characterization of the devices was performed using an Agilent Technologies 4155C Semiconductor Parameter Analyzer and microprobe station. Optical illumination was achieved through the ITO side of the device using a Cole-Parmer fiber optic illuminator (Model 09745-00) with the output beam focused to a diameter of $\sim 1\ \text{cm}$. The total spectral power output was measured as 160 mW. To obtain the photocurrent spectrum, the light from a white light source was dispersed by a monochromator (Triax 320), passed through a band-pass filter to remove harmonics, and focused on the device. A bias of $-1\ \text{V}$ was applied and the current at various wavelengths was measured using a Keithley 6430 source-measure unit. The light intensity at each wavelength was separately measured so the photocurrent at each wavelength could be scaled to the same incident light intensity by assuming the photocurrent was linearly proportional to the light power in the low-intensity region used.

Results and Discussion

The use of ferrocene–fullerene dyads in photoactive films made from layer-by-layer electrostatic deposition has been reported.^{21,22} However, in these cases the films were studied in a photoelectrochemical cell using an electrolytic solution. We wished to explore the potential for a solid-state photodiode device which used the photoinduced electron transfer (PET) reaction of ferrocene and fullerene. Polyferrocenylsilanes are an ideal class of material for such a device as the polymers are highly processible, possess a large ferrocenyl unit content, and demonstrate electrical conductivity in thin films. The devices were prepared by spin-coating solutions of poly(ferrocenylmethylphenylsilane) (PFMPS) with varying fullerene content onto ITO-coated slides, and then top metal contacts were thermally evaporated onto the film to give a sandwich structure diode device with an active area of $\sim 3\ \text{mm}^2$. The devices show asymmetric I – V curves due to the work function differences of the metal electrodes, and a representative I – V plot is shown in Figure 1. An increase in dark current in the devices is observed with the presence of fullerene. The increase in dark current with the presence

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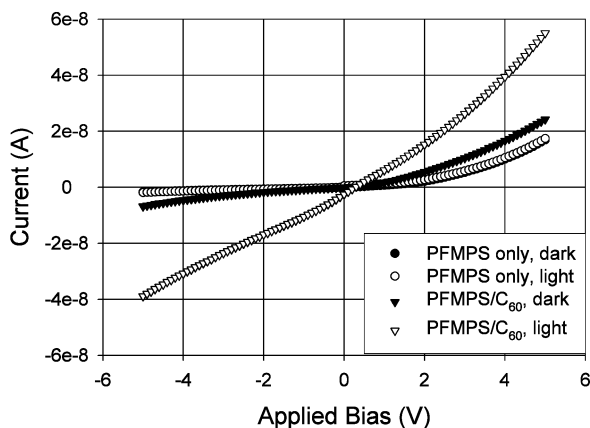


Figure 1. I - V plots for devices with 0 mol % (PFMPS only, circles) and 5 mol % C_{60} (PFMPS/ C_{60} , triangles) under dark (filled symbols) and illuminated (open symbols) conditions. mol % is relative to ferrocene content in the polymer.

of C_{60} in the film implies improved charge transport properties in the composite. PFSs are very poor conductors in the intrinsic state, as seen by the low currents in the PFMPS only device (Figure 1). The inclusion of C_{60} could presumably improve the transport properties in the composite due to the excellent electron-conducting properties of C_{60} .

The devices also demonstrate noticeable photocurrent when C_{60} is present. However, no photocurrent generation was observed in the devices without fullerene present. At an applied bias of -1 V, a photocurrent to dark current ratio of 15 is observed in the device with 5 mol % C_{60} . The photocurrent generation is proposed to occur via an intermolecular PET from the ferrocene units of PFMPS to the fullerene. Under an applied bias, subsequent charge transport within the device occurs such that the charges are collected at the appropriate electrodes. The charge transport could be via hole conduction within the PFS phase and electron conduction within the C_{60} phase, similar to the situation in bulk heterojunction plastic solar cells based on conjugated polymers and fullerene derivatives that have been reported recently.^{34,35}

A weak photovoltaic effect was also observed in the PFMPS/fullerene composite devices, as shown in Figure 2. The devices typically showed low short circuit currents (I_{sc}) on the order of nanoamperes, open circuit potentials (V_{oc}) of 0.31–0.34 V, and fill factors (FF) of 0.25–0.27. The device shown in Figure 2 had $I_{sc} = 2.62$ nA, $V_{oc} = 0.31$ V, and a FF of 0.25. While devices with up to 18 mol % C_{60} relative to ferrocene content were prepared and demonstrated photocurrent and photovoltaic behavior, phase separation on the microscale was readily observed by optical microscopy in the films when the C_{60} content exceeded about 8 mol %, with large (hundreds of micrometers in length) crystallites of fullerene present. The dark and photocurrents were higher in these devices; however, while the fill factors were typically the same as those for the devices with 5 mol % C_{60} content, the V_{oc} values were markedly reduced, to ca. 200 mV generally.

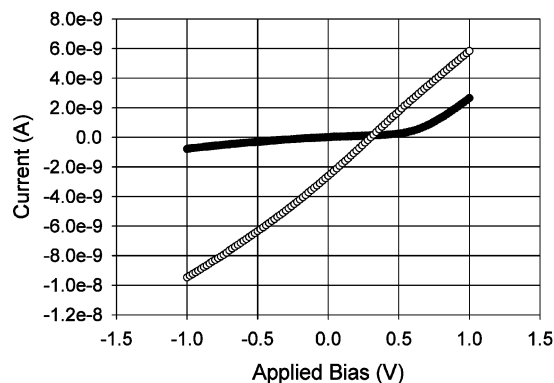


Figure 2. I - V plot for a PFMPS/ C_{60} device in the region near zero bias in the dark (filled circles) and under illumination (open circles).

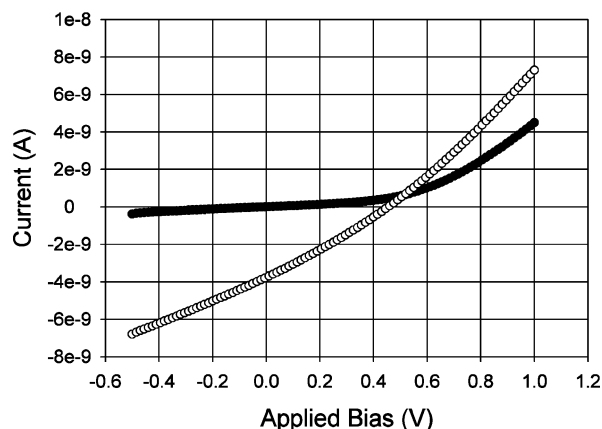


Figure 3. I - V curve for a PFMPS/PCBM device with 12 mol % PCBM showing dark (filled circles) and illuminated (open circles) conditions.

In an attempt to increase the fullerene content without inducing phase separation, the use of the [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) fullerene derivative was also investigated. This material has shown much promise in plastic solar cells based on fullerene/conjugated polymer composites due to its relatively high solubility, and excellent electron accepting and transport properties.³⁵ Devices containing 12 mol % PCBM relative to ferrocene were prepared, and these demonstrated no observable macrophase separation on the micrometer scale. A representative I - V plot in the region near zero bias is shown in Figure 3 for such a device. Again a photovoltaic response is observed, with $I_{sc} = 3.8$ nA, $V_{oc} = 440$ mV, and a FF of 0.28. The use of higher fullerene content, without phase separation, is achieved using PCBM and gives rise to a higher short circuit current, an increase in open circuit potential, and a slightly larger fill factor compared to those with 5 mol % C_{60} discussed above. In addition, higher photocurrent response was obtained in these devices, with a photo- to dark current ratio of 40 at -1 V bias, compared to 15 for the devices with 5 mol % C_{60} .

The solution absorption spectra for both PFMPS and PCBM are shown in Figure 4a. The polymer shows much lower absorption coefficients at virtually all wavelengths relative to the fullerene derivative. Blends of the two materials in various molar ratios have absorption spectra, in solution and in films, that are simply superpositions of the respective components (see inset in Figure 4b), indicating no ground state interaction between the polyferrocene and

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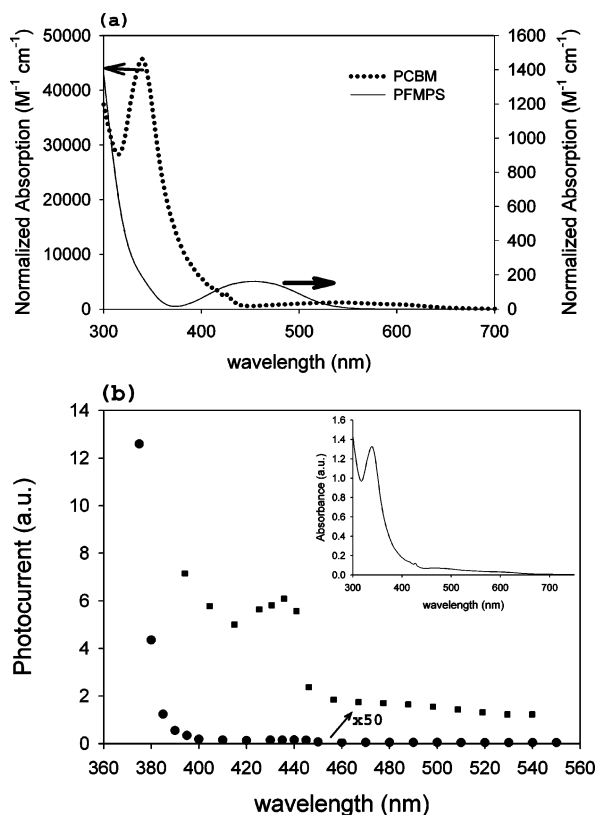


Figure 4. (a) Absorption spectra for PFMPS and PCBM in chlorobenzene solution. Note the different scales. (b) Spectral response of photocurrent at -1 V bias for a device with 12 mol % PCBM. The region between 400 and 540 nm is also shown expanded (50 \times on vertical scale) for further detail. The absorption spectrum of the film is shown as an inset.

PCBM, consistent with that previously reported in molecular dyads of ferrocene and fullerene.^{19,22} The photoaction spectrum of a device, shown in Figure 4b, demonstrates that appreciable photocurrent generation only occurs for wavelengths less than ca. 400 nm. This is similar to that observed for Pt poly-yne organometallic polymer-based photocells reported previously.^{25–27,29} The spectral response of the device corresponds closely to the absorption spectrum of the film, shown in the inset of Figure 4. This is consistent with the previously observed photoresponses in ferrocene–fullerene dyad layer-by-layer films studied in photoelectrochemical cells.^{21,22}

The exact nature of the origin of the V_{oc} in the PFS/fullerene devices studied here is not presently known. The origin of the open circuit potential in fullerene/conjugated polymer composites has been examined in some detail, and although it is not yet entirely understood, a dependence upon the relative difference between the oxidation potential of the polymer (donor) and the reduction potential of the fullerene (acceptor) has been established.^{36,37} It is not clear if this

relationship also applies to the PFMPS/fullerene devices, as PFSs are not semiconducting conjugated polymers. The V_{oc} does not depend exclusively on the work function offsets of the metal electrodes as this is the same in all devices studied in this work. However, the devices made with the PCBM derivative were found to exhibit larger V_{oc} values (by >100 mV) than those made with C_{60} . The first reduction potential of PCBM is reported to be ca. 90 mV higher than C_{60} ,³⁶ and thus a larger open circuit potential could be expected. That is, given a constant polymer oxidation potential, the greater the reduction potential of the acceptor (fullerene), the larger the observed V_{oc} .³⁶ The low fill factor of the devices could be a result of high series or low shunt resistances, possibly due to poor charge carrier transport properties in the blends or the presence of nanoscopic pinholes. In addition, the lifetimes of the photogenerated carriers may be low.

Current efforts are underway to prepare more responsive devices, including the use of photosensitizers to create a triad-like system²⁴ to enable visible region photoconductive response of the devices and possibly higher photovoltaic power conversion efficiencies. The phase separation and fullerene crystallization detected at higher C_{60} loadings suggest that the covalent attachment of fullerenes to PFSs, to prepare so-called double-cable³⁸ materials, may lead to improved device performance. Studies directed toward this end are in progress.

Conclusion

Composite films of fullerenes and PFS were used as the active layers in solid-state photodiode devices. These devices possessed photoconducting and photovoltaic responses. The results are consistent with a photoinduced electron-transfer reaction whereby the polymer acts as an electron donor and the fullerene as the electron acceptor. Although the system described has not been optimized, the results provide a rare example of an all-solid-state photoconducting and photovoltaic device based on a functional metal-containing polymer. Current work is focused on polyferrocenes with covalently bound C_{60} units and improvement in device performance.

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