

Photoinduced Electron Transfer and Photovoltaic Devices of a Conjugated Polymer with Pendant Fullerenes

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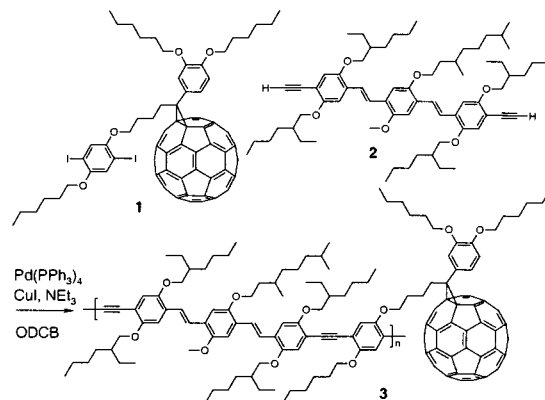
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Photoinduced electron transfer from a donor to an acceptor is widely studied to mimic the natural photosynthetic reaction center and to investigate the prospects of molecular materials in photovoltaic energy conversion.¹ Promising conversion efficiencies have been obtained in so-called bulk-heterojunction solar cells in which the active layer is a composite film of a conjugated donor polymer and an acceptor polymer or a fullerene derivative.^{2,3} In these blends charges are preferentially formed at the donor–acceptor interface, and intimate mixing of donor and acceptor is therefore beneficial for charge generation. For efficient transport of the positive charge carriers through the donor phase and of electrons via the acceptor phase to the electrodes, a phase-segregated bicontinuous network is required. A convenient route to obtain a predefined nanoscopic phase-segregated network is linking donor and acceptor via a covalent bond.^{4,5} We intend to achieve the desired nanoscopic bicontinuous networks by synthesizing π -conjugated polymers with pendant fullerenes. The preparation of well-defined polymers incorporating fullerenes has remained a challenge over the years, and only a few synthetic routes have ensured full structural homogeneity of the final polymer.⁶ Conjugated polymers incorporating fullerenes have previously been prepared by electrochemical polymerization of oligothiophene–fullerene dyads or by grafting C₆₀ on precursor polymers, but these materials have not been incorporated in electrooptical devices.⁷

Here we report the synthesis of a novel processable π -conjugated polymer **3** (Scheme 1) with covalently linked methanofullerenes using a palladium-catalyzed cross-coupling reaction to overcome these limitations. We demonstrate that photoexcitation of **3** results in an electron-transfer reaction from the conjugated backbone to the pendant C₆₀ moiety and that **3** can be applied via spin coating to form the active layer of the first polymer solar cell based on a covalently linked donor–acceptor bulk-heterojunction.

Scheme 1



Polymer **3** was synthesized via a palladium-catalyzed cross-coupling reaction of diiodobenzene **1**, carrying a pendant methanofullerene, and oligo(*p*-phenylene vinylene) **2**, end-capped with two reactive ethynyles, under inert conditions in 1,2-dichlorobenzene/triethylamine (7:3 v/v) (Scheme 1). This polymerization can be performed under mild conditions and is one of the reactions developed in recent years for the synthesis of electronic polymer materials, which ensures the alternation of the two monomers.⁸ The synthetic details of the preparation and characterization of the two monomers are provided in the Supporting Information. The presence of both double and triple bonds in the backbone make **3** a hybrid polymer of poly(*p*-phenylene vinylene) and poly(*p*-phenylene ethynylene), similar to those recently reported.⁹

The polymerization reaction was followed by absorption spectroscopy, as a red-shift in time of the π – π^* transition of the polymer with respect to that of monomer **2** ($\lambda_{\text{max}} = 428$ nm). The three hexyloxy chains ensure that **1** is a highly soluble C₆₀ derivative, but its reactivity toward **2** under these conditions is less than that of 1,4-diiodo-2,5-bis(2'-ethylhexyloxy)benzene (**4**). Reaction of **2** and **4** was performed to obtain polymer **5**, which is similar to **3** but lacks the pendant methanofullerene and is used as a reference in the spectroscopic studies described below. After 24 h of polymerization, the effective conjugation length of **3**, as inferred from $\lambda_{\text{max}} = 468$ nm, approaches that of **5** ($\lambda_{\text{max}} = 474$ nm) (Figure 1a).

The molecular weight of the polymers determined by size-exclusion chromatography (SEC, Figure 1b) shows that **3** ($M_w = 16.2$ kg/mol, PDI = 2.82) has a lower degree of polymerization than **5** ($M_w = 35.8$ kg/mol, PDI = 2.32), consistent with the small 6 nm hypsochromic shift. The difference in SEC molecular

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weights might not reflect the actual situation accurately; for monomer **2** the molecular weight determined by SEC corresponds to the actual value (SEC: $M_w = 1172$ g/mol, PDI = 1.02; MALDI-TOF $M_w = 1029.46$ g/mol), but there is a significant underestimation for **1** by a factor of 3 (SEC: $M_w = 555$ g/mol, PDI = 1.02; MALDI-TOF $M_w = 1510.6$ g/mol) (Figure 1b).

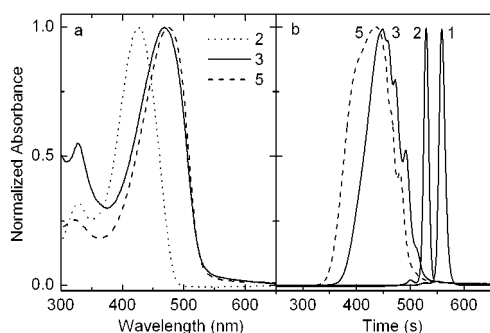


Figure 1. (a) UV-vis spectra of **2**, **3**, and **5** in chloroform. (b) SEC traces of monomers **1** and **2**, and polymers **3** and **5** in chloroform.

Excitation of **3** in dilute toluene solution at 486 nm reveals that the photoluminescence (PL) of **3** is quenched by 2 orders of magnitude in comparison with the emission of **5**. The PL quenching in solution confirms unambiguously the covalent linkage of the C_{60} moieties to the polymer backbone in **3**. The nature of the PL quenching mechanism in this apolar solvent involves a singlet-singlet energy transfer from the photoexcited conjugated backbone to the methanofullerene.^{5,10}

PL quenching is also observed in thin films of **3**. In this case, however, a photoinduced charge-transfer reaction occurs as inferred from modulated cw photoinduced absorption (PIA) spectroscopy. The PIA spectrum of a thin film of **3** exhibits a characteristic band at 1.20 eV of the methanofullerene radical anion and the two distinctive strong bands of cation radicals (polarons) generated on the conjugated polymer at 0.62 and 1.53 eV together with a bleaching band at 2.45 eV (Figure 2).⁵ All PIA bands of **3** increase with the pump intensity (I) following a square-root power law ($-\Delta T \approx I^{0.5}$). This suggests nongeminate bimolecular recombination of the photoinduced charges, which indicates the migration of opposite charges to different sites in the film. The lifetime of the photoinduced charges extends into the millisecond time domain, similar to that observed in polymer-fullerene blends.

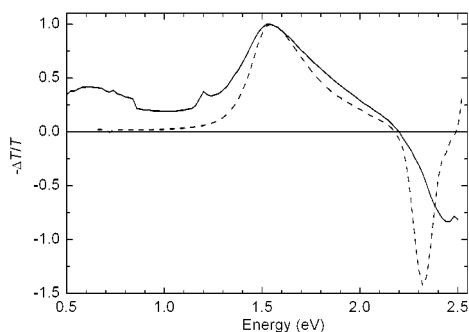


Figure 2. Photoinduced absorption spectra of thin films of polymer **3** (solid line) and **5** (dashed line) on quartz recorded at 80 K.

The PIA spectrum of a film of reference polymer **5** exhibits a single band at 1.55 eV of the triplet excited state. The lifetime of

this triplet state is 860 μ s. The near coincidence of the triplet absorption of **5** and the high-energy radical cation absorption of **3** at 1.53 eV, is often encountered in π -conjugated polymers.¹¹ The low-energy radical cation band at 0.62 eV and the methanofullerene anion band at 1.20 eV for **3**, and their absence in the PIA spectrum of **5**, give direct spectral evidence of a photoinduced electron transfer in **3** between the conjugated chain and the pendant methanofullerene.

Photovoltaic cells were prepared by spin coating **3** from chloroform onto a transparent ITO front electrode covered with a conducting layer of polyethylenedioxythiophene polystyrenesulfonate (PEDOT:PSS) and depositing an aluminum back electrode in a vacuum. The film thickness is around 30 nm with a surface roughness of less than 5 nm. The dark current and photocurrent of the device under white-light illumination (100 mW/cm², AM1.5) reveal promising characteristics (Figure 3): A short circuit current of $I_{sc} = 0.42$ mA/cm², an open circuit voltage of $V_{oc} = 0.83$ V, and a fill factor of 0.29 characterize the depicted cell. The rather low rectification ratio of 36 of the cell at ± 2 V in the dark is related to the low film thickness. The incident monochromatic photon-to-current efficiency (IPCE) has an onset at 550 nm and exhibits a maximum of 6% at 480 nm. The values of I_{sc} and V_{oc} have improved compared to previously reported π -conjugated polymer/fullerene solar cells,¹² although there has been substantial progress recently using improved processing and introduction of an interfacial layer at the Al electrode.³

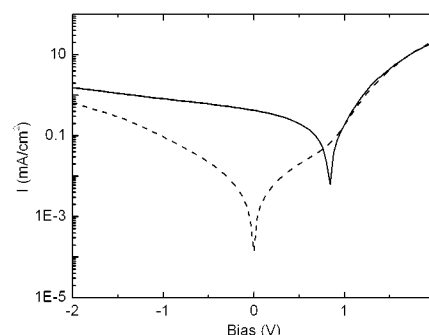


Figure 3. I/V curves of an ITO/PEDOT:PSS/3/Al device in the dark (dashed line) and under white-light illumination (solid line).

In conclusion, we have synthesized the first conjugated polymer with pendant methanofullerenes that exhibits a photoinduced electron-transfer reaction and has been used as the active layer of a photovoltaic cell. The results indicate that a bicontinuous network of donor and acceptors, confined to a molecular scale, is an attractive approach to new materials for photovoltaic applications.

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Supporting Information Available: Synthetic procedures and full characterization of all new molecules together with details concerning PIA spectroscopy, device preparation, and IPCE (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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