

Final Report

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**Photo-induced Electron Transfer from a Conducting Polymer to
Buckminsterfullerene:
A Molecular Approach to High Efficiency Photovoltaic Cells**

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The recognized need to develop inexpensive and renewable energy sources continues to stimulate new approaches directed toward efficient, low cost photovoltaic devices. Due to the potential advantages which would be realized with polymer-based photovoltaic materials (e.g. low cost fabrication in large sizes and in desired shapes), efficient "plastic" solar cells would have major impact.

For photovoltaic cells made with pure conjugated polymers, energy conversion efficiencies were typically 10^{-3} - $10^{-2}\%$,¹ too low to be used in practical applications. The recent discovery of photoinduced electron transfer in composites of conducting polymers (as donors) and buckminsterfullerene, C₆₀, and its derivatives (as acceptors)²⁻⁶ provided a molecular approach to high efficiency photovoltaic conversion. Since the time scale for photoinduced charge transfer is subpicosecond, more than 10³ times faster than the radiative or nonradiative decay of photo-excitations,² the quantum efficiency for charge transfer and charge separation from donor to acceptor is close to unity. Thus, photoinduced charge transfer across a donor/acceptor (D/A) interface provides an effective method to overcome early time carrier recombination in organic systems and thus to enhance the optoelectronic response of these materials. For example, with the addition of only 1% C₆₀, the photoconductivity of MEH-PPV:C₆₀ increases by an order of magnitude over that of pure MEH-PPV.^{3,6}

Although the quantum efficiency for photoinduced charge separation is near unity for a D/A pair, the conversion efficiency in a bilayer heterojunction device is limited⁷:

- (i) Due to the molecular nature of the charge separation process, efficient charge separation occurs only at the D/A interface; thus, photoexcitations created far from the D/A junction recombine prior to diffusing to the heterojunction.
- (ii) Even if charges are separated at the D/A interface, the photovoltaic conversion efficiency is limited by the carrier collection efficiency; i.e. the separated charges must be collected with high efficiency.

Consequently, *interpenetrating phase separated D/A network composites would appear to be ideal photovoltaic materials.^{8,9} Through control of the morphology of the phase separation into an interpenetrating network, one can achieve a high interfacial area within a bulk material. Since any point in the composite is within a few nanometers of a D/A interface, such a composite is a "bulk D/A heterojunction" material. Because of the interfacial potential barrier (as demonstrated by the built-in potential in the bilayer D/A heterojunction diode⁷), ultrafast photoinduced charge transfer and charge separation will occur with quantum efficiency approaching unity, leaving holes in the donor phase and electrons in the acceptor phase. This process is illustrated in the upper portion of Fig. 1a. If the network is bicontinuous, (as shown schematically in Fig. 1b, the collection efficiency can be equally efficient.⁸*

Such a bicontinuous D/A network material is promising for use in thin film solar cells. In addition to the high quantum efficiency of charge separation, the electronic structure of such a bicontinuous D/A network allows one to choose contact electrodes with work-functions which optimize the carrier collection efficiencies of holes from the donor phase and electrons from the acceptor phase. Thus, thin film sandwich devices with bicontinuous D/A composites as the active material promise to function as efficient solar cells with high η_c and η_e .

During the period of this DOE funding, we made significant progress toward creating "bulk D/A heterojunction" materials. This progress is summarized briefly in the following paragraphs. Reprints of publications which resulted from this research are attached.

I. "Plastic" Photovoltaic Cells Made with Donor-Acceptor Composites: Enhanced Carrier Collection Efficiency via a Network of Internal Heterojunctions⁹

The carrier collection efficiency (η_c) and energy conversion efficiency (η_e) of polymer photovoltaic cells has been improved by blending the semiconducting polymer with C₆₀ or its functionalized derivatives. Using composite films of MEH-PPV, poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene), and fullerenes, η_c ~7.4 % electrons/photon and η_e ~1.2 % (20 mW/cm² at 430 nm), 100 times better than in devices made with pure MEH-PPV. At low illumination ($\mu\text{W}/\text{cm}^2$), the efficiencies are even higher, η_c ~15% and η_e ~1.7 %. A two-step process is involved:

- (i) The efficient charge separation results from photoinduced electron transfer from the MEH-PPV (as donor) to C₆₀ (as acceptor);
- (ii) The high collection efficiency results from a bicontinuous network of internal donor/acceptor heterojunctions.

II. Charge Separation and Photovoltaic Conversion in Polymer Composites with Internal Donor/Acceptor Heterojunctions¹⁰

The photosensitivity of semiconducting polymers can be enhanced by blending donor and acceptor polymers to optimize photoinduced charge separation. We have studied the photovoltaic response of devices fabricated from a novel phase-separated polymer blend (composite) made with poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene), MEH-PPV, as donor and cyano-PPV, CN-PPV, as acceptor. The photoluminescence and electroluminescence of both component polymers are quenched in the blend, indicative of rapid and efficient separation of photogenerated electron-hole pairs with electrons on the acceptor and holes on the donor. Diodes made with such a composite semiconducting polymer as the photosensitive medium show promising photovoltaic characteristics with carrier collection efficiency of 5 % electrons/photon and energy conversion efficiency of 0.9 %, ~ 20 times larger than in diodes made with pure MEH-PPV and ~100 times larger than in diodes made with CN-PPV. The photosensitivity and the quantum yield increase with reverse bias voltage, to 0.3 A/Watt and 80% electrons/photon respectively at -10 V, comparable to results obtained from photodiodes made with inorganic semiconductors.

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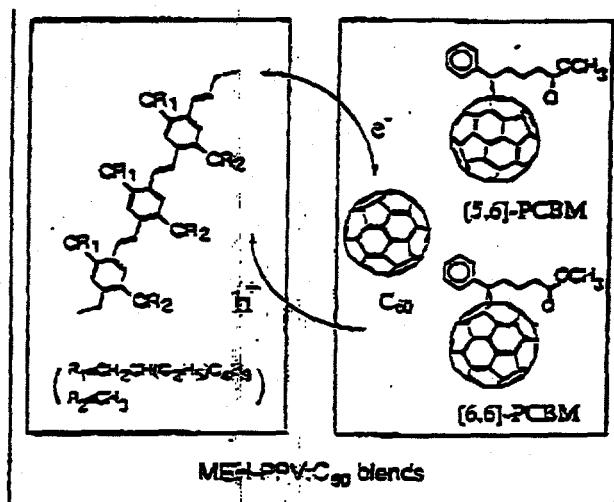


Figure 1a:

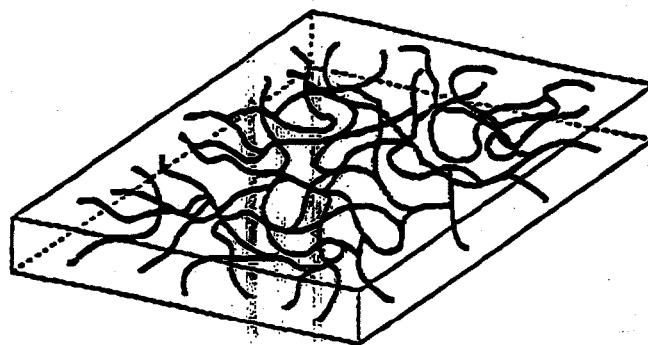


Figure 1b: