The characterization of rectifying heterojunctions (diodes) fabricated from a semiconducting polymer, a soluble derivative of poly(phenylene-vinylene), and buckminsterfullerene, C60, are reported. Rectification ratios in the current versus voltage characteristics exceed 10^6. When illuminated, the devices exhibit a large photoresponse as a result of photoinduced electron transfer across the heterojunction interface from the semiconducting polymer (donor) onto C60 (acceptor). The photodiode and photovoltaic responses are characterized. Photoinduced electron transfer across the donor-acceptor rectifying heterojunction offers potential for photodetector and for solar cell applications.

Photoinduced electron transfer with a subpicosecond transfer rate has been demonstrated in composites of the semiconducting polymer, poly[2-methoxy,5-(2’-ethylhexyloxy)-1,4-phenylene-vinylene], MEH-PPV, and buckminsterfullerene, C60. The observation of photoinduced electron transfer between the donor, MEH-PPV, and the acceptor, C60, suggests the possibility of utilizing this phenomenon at the interface between MEH-PPV and C60 in a thin film heterojunction bilayer.

In this letter, we report the fabrication and characterization of heterojunction diodes fabricated from MEH-PPV and C60. Rectification ratios in excess of 10^6 are obtained. A large photoresponse is observed in the current vs voltage characteristics, resulting from photoinduced electron transfer across the interface.

The utility of MEH-PPV as a processible polymer with the electronic and optical properties of a semiconductor has already been demonstrated in Schottky-type light emitting devices which exhibit relatively high efficiency electroluminescence. MEH-PPV is a member of the family of conjugated polymers; these quasi-one-dimensional conducting polymers have relatively broad \( \pi \) (valence) and \( \pi^* \) (conduction) bands, and they can be doped, with resulting properties that span the full range from insulator to metal. MEH-PPV is a weak donor (as are many other conjugated polymers) which can be oxidized with relative ease. Buckminsterfullerene has been demonstrated to be an \( n \)-type semiconductor which acts as a relatively strong acceptor.

Comparison of the energies of the lowest unoccupied states of C60 with the energies of the highest occupied states of semiconducting polymers suggests that partial charge transfer can occur in the ground state. Studies of the MEH-PPV/C60 composites have shown, however, that although charge transfer between the donor and the acceptor does not occur in the ground state, charge separation can be photoinduced with high efficiency.

The heterojunction diodes consist of successive layers of MEH-PPV, C60, and gold deposited onto indium/tin-oxide (ITO) coated glass substrates. The MEH-PPV layer was spin-cast onto the ITO-glass substrate from 1% xylene solution at 2000 rpm. The C60 was subsequently vacuum evaporated to form the heterojunction. Typical thicknesses are 1000 Å for both the MEH-PPV and the C60. The metal (gold or aluminum) contacts were deposited on top of the devices by vacuum evaporation at pressures below 1X 10^-6 Torr and patterned with a shadow mask to define active areas of 0.1 cm^2. All processing steps are carried out in nitrogen atmosphere or under vacuum, except the transfers to and from the vacuum chamber for C60 deposition.

Electrical data were obtained with a Keithley 236 Source-Measure Unit. The 514.5 nm line of an argon ion laser was used as the light source in measurements of the intensity dependence of the photocurrent. A tungsten lamp with a single-grating monochromator was used for the photoreponse measurement. The light was mechanically chopped at the exit slit and a lock-in amplifier was used to detect the photocurrent. All spectra have been corrected for the spectral response of the lamp and monochromator by normalization to the response of a calibrated silicon photodiode.

Figure 1 shows the current-voltage characteristics of the heterojunction device consisting of ITO/MEH-PPV/ C60/Au. Positive bias is defined as positive voltage applied to the ITO contact. Exponential turn-on up to 500 mV in forward bias is clearly observable; the rectification ratio is approximately 10^6.

In order to test if the ITO or the gold electrodes form blocking (or rectifying) contacts, the following three layer devices were prepared: gold/MEH-PPV/gold, gold/MEH-
PPV/ITO, gold/C$_{60}$/gold, and gold/C$_{60}$/ITO. since all such devices have completely symmetric and linear current-voltage characteristics, we conclude that gold and ITO form non-rectifying contacts both to MEH-PPV and to C$_{60}$, in agreement with the reported absence of rectification in Au/C$_{60}$/ITO devices.$^{13}$ We, therefore, attribute the rectifying behavior of the four layer device to the interface of the heterojunction between the semiconducting polymer and C$_{60}$.

The current-voltage characteristic of the device changes dramatically upon illumination with visible light. Figure 2 shows the current-voltage data, with the ITO/MEH-PPV/C$_{60}$/Au device in the dark and with the device illuminated with 514.5 nm light with intensity ($P_{in}$) of $\approx 1$ mW/cm$^2$. The open circuit voltage ($V_{oc}$) is 0.44 V which saturates to around 0.53 V under stronger illumination. The short circuit current density ($J_{sc}$) is $2.08 \times 10^{-6}$ A/cm$^2$, and the fill factor (FF) can be obtained from the relation

$$\text{FF} = \frac{\int V_{oc} J \, dV}{J_{sc} V_{oc}}.$$ 

The data of Fig. 2 give a fill factor of 0.48 and a power conversion efficiency of 0.04%.$^{14}$ An open circuit voltage of about 0.5 V appears to be characteristic of the MEH-PPV/C$_{60}$ interface. Similar values were obtained with ITO/MEH-PPV/C$_{60}$/Al devices and with Al/MEH-PPV/C$_{60}$/ITO devices.$^{13}$

As expected from the observation of fast photoinduced electron transfer from MEH-PPV to C$_{60}$,$^{1,2}$ a remarkable increase in both forward and reverse bias current is observed to result from photoinduced charge separation at the heterojunction interface. The jump in the current by nearly four orders of magnitude (from $1 \times 10^{-9}$ to $6 \times 10^{-6}$ A/cm$^2$) upon illumination at $-1$ V (reverse) bias demonstrates that the heterojunction serves as a relatively sensitive photodiode.

Figure 3 shows the dependence of the short circuit current and the photocurrent at $-1$ V (reverse) bias as a function of the illumination intensity (514.5 nm). The data in Fig. 3 show no indication of saturation at light intensities up to approximately 1 W/cm$^2$; i.e., one order of magnitude greater than the terrestrial solar intensity.

The spectral dependence of the photoreponse of these heterojunction devices is displayed in Fig. 4. The onset of
The demonstration of a rectifying heterojunction between a semiconducting polymer and buckminsterfullerene has potentially important scientific and technological implications. The heterojunction is quite sensitive as a photodetector with a dark current below 100 μA/cm². Moreover, there is potential for using such devices in photovoltaic energy conversion. To be efficient, however, one must use a semiconducting polymer with band gap limitations which result in separated charge carriers occurs at the heterojunction interface.

For an Al/MEH-PPV/ITO device without C₆₀, we find that Vₑₑₑ saturates at 1.4 V, but Jₑₑ is a factor of 20 smaller than in the heterojunction devices. Recently reported Al/AIO₃/C₆₀/MIS junctions have a higher photoconversion efficiency, but Jₑₑ and Vₑₑ were not reported.

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