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Polymer Photovoltaic Cells: Enhanced Efficiencies via a Network of Internal Donor-Acceptor Heterojunctions

G. Yu,* J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger

The carrier collection efficiency ($\eta_c$) and energy conversion efficiency ($\eta_e$) of polymer photovoltaic cells were improved by blending of the semiconducting polymer with $C_{60}$ or its functionalized derivatives. Composite films of poly(2-methoxy-5-(2’-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV) and fullerenes exhibit $\eta_c$ of about 29 percent of electrons per photon and $\eta_e$ of about 2.9 percent, efficiencies that are better by more than two orders of magnitude than those that have been achieved with devices made with pure MEH-PPV. The efficient charge separation results from photoinduced electron transfer from the MEH-PPV (as donor) to $C_{60}$ (as acceptor); the high collection efficiency results from a bicontinuous network of internal donor-acceptor heterojunctions.

The need to develop inexpensive renewable energy sources continues to stimulate new approaches to production of efficient, low-cost photovoltaic devices. Although inorganic semiconductors (silicon, amorphous silicon, gallium arsenide, and sulfide salts) have been the primary focus, the photosensitivity and the photovoltaic effects in devices made with organic materials have also been explored, including conjugated polymers (1), organic molecules (2), stacked discotic liquid crystals (3), and self-assembling organic semiconductors (4). Because of the advantages that would be realized with polymer-based photovoltaics (such as low-cost fabrication in large sizes and in desired shapes), efficient "plastic" solar cells would have a major impact.

Energy conversion efficiencies of photovoltaic cells made with pure conjugated polymers were typically $10^{-2}$ to $10^{-3} \%$, (1), too low to be used in applications. The discovery of photoinduced electron transfer in composites of conducting polymers as donors and buckminsterfullerene ($C_{60}$) (5) provided a molecular approach to high-efficiency photovoltaic conversion (6, 7). Because the time scale for photoinduced electron transfer is subpicosecond, more than $10^3$ times faster than the radiative or nonradiative decay of photoexcitations (5), the quantum efficiency of charge separation from donor to acceptor is close to unity. Thus, photoinduced charge transfer across a donor-acceptor (D-A) interface provides an effective way to overcome early time-carrier recombination in organic systems and thus to enhance their optoelectronic response. For example, with the addition of only 1% $C_{60}$, the photoconductivity increases by an order of magnitude over that of pure MEH-PPV (6, 7).

Although the quantum efficiency for

\[ \eta_e \]

\[ \text{polymer photovoltaic cell fabricated with this bulk heterojunction material is sketched at the bottom.} \]
MEH-PPV devices (Fig. 2B) exhibit three
remains clean and trap-free. No indication of
those of pure MEH-PPV devices (indepen-
dent of Ca. Capacitance measurements of
shifts to lower voltage by ~0.8 V. Thus, the
ITO device, the exponential current turn-on
physics. In the Ca/MEH-PPV:[6,6]PCBM/
vices shown in Fig. 2 imply similar device
approximately 10^17 A/cm^2 for
increase by more than four orders of mag-
nitude between 1.3 and 1.8 V, and "current
increase by more than four orders of mag-
itude (Fig. 2A) and a Ca/MEH-PPV/ITO de-
function difference between Ca and ITO.

The similar I-V characteristics of the de-
vice shown in Fig. 2 imply similar device
physics. In the Ca/MEH-PPV-[6,6]PCBM/
ITO device, the exponential current turn-on
shifts to lower voltage by ~ 0.8 V. Thus, the
lower unoccupied molecular orbital of
[6,6]PCBM is ~ 0.8 eV below the Fermi en-
ergy of Ca. Capacitance measurements of
the blend devices yield values similar to
those of pure MEH-PPV devices (indepen-
dent of bias), implying that the energy gap
remains clean and trap-free. No indication of
ground-state charge transfer was observed.

The forward I-V characteristics of the
MEH-PPV devices (Fig. 2B) exhibit three
regions: a small shunt current (< 10^15
A/cm^2) for V < 1.2 V, an exponential
increase by more than four orders of mag-
nitude between 1.3 and 1.8 V, and "current
saturation" at higher voltages (the current
increases, but at a less than exponential
rate). In reverse bias, the current saturates at
approximately 10^15 mA/cm^2 for |V| < 3 V.
The I-V characteristics at high fields have
been interpreted in terms of tunneling (15)
into a thin-film semiconductor deplet-
ed of carriers. Capacitance-voltage and al-
ternating current conductivity experiments
provide evidence in support of this model
(16). The exponential current turn-on and
the V sc under strong illumination corre-
pond to the flat band condition.

Because photoinduced electrons in
MEH-PPV will lower their energy by trans-
ferring to the C sc, and photoinduced holes
in C sc will lower their energy by transferring
to the MEH-PPV, the photosensitivity (PS)
is substantially enhanced in the phase-
separated composite (as shown in Fig. 2).
The short-circuit current (I sc) in the MEH-
PPV-[6,6]PCBM device is I sc = 0.5
mA/cm^2; under 20 mW/cm^2, corresponding
to PS = 25 mA/W and \( \eta_e = 7.4\% \) electrons
per photon (e/ph), both of which are ap-
proximately two orders of magnitude higher
than those of MEH-PPV devices (Fig. 2B).
The electroluminescence quantum efficiency
of the blend device was ~ 3 \times 10^{-7}
photons per electron, 10^2 to 10^3 times less
than in pure MEH-PPV devices, which is
consistent with ultrafast photoinduced
charge separation (5).

The carrier collection and energy con-
version efficiencies of the bicontinuous D-
A network material are critically dependent
on the network's morphology and chemical
composition. By changing the solvent from
xylene to 1,2-dichlorobenzene we have
been able to cast high-quality MEH-
PPV-[6,6]PCBM films with methano-
fullerene compositions up to 1.4 weight
ratio (approximately one acceptor for every
polymer repeat unit). For devices made from
this blend, \( I_{sc} = 2 \text{ mA/cm}^2, \) PS = 100
mW/W, and \( \eta_e = 29\% \) e/ph under 20 mW/
cm^2 at 430 nm.

Figure 3 shows \( \eta_e \) (Fig. 3A) and \( \eta_c \) (Fig.
3B) as a function of illumination intensity
for several blend devices and for pure MEH-
PPV devices. The blend weight ratios are 3:1
for the MEH-PPV:C_sc device, and 1:1 and
1:4 for the devices using the functionalized
fullerenes. For Ca/MEH-PPV-[6,6]PCBM
(1:4)/ITO devices, the photosensitivity is
substantially sublinear with light intensity (I):
\( \eta_e = 29\% \) e/ph and \( \eta_c = 2.9\% \) at 20
mW/cm^2; \( \eta_e = 45\% \) e/ph and \( \eta_c = 3.2\% \)
at 10 \mu W/cm^2 (17). In reverse bias, these
device are excellent photodetectors; for
example, at -2 V, PS > 200 mW/A and \( \eta_c >
60\% \) e/ph at 20 mW/cm^2, a substantial
improvement over earlier results and better
than ultraviolet-enhanced silicon photodi-
odes at 430 nm (7).

The spectral response of these photovol-
talic devices is similar to that obtained from
photocative cells made from MEH-
PPV:C_sc blends (6). The photovoltaic re-
response turns on at approximately 1.5 eV and
is relatively flat for photon energy > 2.5 eV.
The PS and the \( \eta_c \) are nearly the same
when Al is substituted for Ca as the cathode,
although V oc decreases slightly from 0.82 V
to 0.68 V at 20 mW/cm^2. Typical data from
A/MEH-PPV-[6,6]PCBM/ITO devices are also
included in Fig. 3. Thus, stable metals
with work functions as high as 4.3 eV can be
used as the cadmium electrode to collect elec-
trons effectively from the acceptor phase.

Ideally, the work function of the anode
metal should be close to the donor highest
occupied molecular orbital (HOMO) and
the work function of the cathode should be
close to the acceptor lowest unoccupied
molecular orbital (LUMO). An "ohmic" con-
tact would then form selectively at each
interface, being ohmic for holes at the in-
terface between the donor and the high-
work-function metal contact but blocking
for electrons at the same interface, and vice
versa. The built-in potential would be the
difference between the acceptor LUMO and
the donor HOMO.

The bulk D-A heterojunction material
provides an automatic selection of electrons
from the acceptor component and holes from
the donor component. The use of Ca (or Al)
as the cathode and ITO as the anode
creates a large internal field (for a given film
thickness, the internal field is larger with
Ca). These two contact materials automatically extract electrons from C_sc and
holes from MEH-PPV. Even though the low-
work-function metal is in direct contact with
the donor, holes will not be extracted at this
interface, because the internal field forces
the holes toward the

Fig. 2. (A) I-V characteristics of a Ca/MEH-PPV:
[6,6]PCBM/ITO device in the dark (open circles)
and under 20 mW/cm^2 of illumination at 430 nm
(solid circles). (B) The corresponding data from a
Ca/MEH-PPV/ITO device. Currents were plotted as absolute values.

Fig. 3. \( \eta_e \) (A) and \( \eta_c \) (B) of Ca/MEH-PPV:
[6,6]PCBM(1:4)/ITO (solid squares); Ca/MEH-
PPV-[6,6]PCBM(1:1)/ITO (open squares); Al/
MEH-PPV-[6,6]PCBM(1:1)/ITO (diamonds); Ca/
MEH-PPV-[6,6]PCBM(1:1)/ITO (open circles); Ca/
MEH-PPV:C_60(3:1)/ITO (triangles); and Ca/MEH-
PPV/ITO (solid circles).
high-work-function contact. For the same reason, electrons are extracted from C60 at the Ca/M EH-PPV:C60 interface. The result, then, is that separated carriers are not “wasted”; they are automatically collected by the proper electrode so that external work can be done.

The substantial enhancement in ϵc achieved with the bicontinuous D-A network material results from the large increase in the interfacial area over that in a D-A bilayer and from the relatively short distance from any point in the polymer to a charge-separating interface. Moreover, the internal D-A junctions inhibit carrier recombination and thereby improve the lifetime of the photoinduced carriers (6), so that the separated charge carriers can be efficiently collected by the built-in field from the asymmetric electrodes. Similar effects have been observed in MEH-PPV:Cyano-PPV polymer blends (10, 11).

The device efficiencies are not yet optimized. Because only ~60% of the incident power was absorbed at 430 nm in the thin-film devices used for obtaining the data in Fig. 3, the internal carrier collection efficiency and energy conversion efficiency are approximately 1.7 times larger; that is, ϵc ≈ 90% e/ph and ϵη ≈ 5.5% at 10 μW/cm2. Although nearly 100% absorption can be achieved by using thicker films, ϵc is currently limited in thick-film devices by internal resistive losses. Further improvements in device efficiencies are expected when the blend composition and the network morphology are optimized.

REFERENCES AND NOTES


12. Electrical measurements were performed with a

Keithley 236 Source-Measure Unit. The excitation source was a tungsten-halogen lamp with a band-pass filter (centered at 430 nm, with a bandwidth of 100 nm). The maximum optical power at the sample was ~20 mW/cm2.


17. ϵc was calculated from the relation ϵc = FFc(Voc/Pc) using the following definition of filling factor:

\[
FF = \int_0^{V_m} \frac{V}{V_m} dV
\]

[see (8)]. In engineering applications, another definition of FF is sometimes used \( FF = I_m/V_m/V_c \) where \( I_m \) and \( V_m \) are current and voltage for maximum power output. The FF and the ϵc following this definition are approximately half of the values shown in the text.

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