

# Hyperbranched Conjugated Polymers for Photovoltaic Applications

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**ABSTRACT:** Three hyperbranched phenylene vinylenes (HPVs)—H-mn, H-es, and H-py—were used in fabricating polymer photovoltaic cells (PVCs). PVCs with photoactive layers composed of pure HPV, a blend of HPV and C<sub>60</sub>, and a blend of HPV, poly(2-methoxy-5,2'-ethylhexyloxy-1,4-phenylene vinylene) (MEH-PPV), and C<sub>60</sub>, were fabricated, and their current–voltage characteristics were measured and investigated. The PVC with photoactive layers composed of H-es and C<sub>60</sub> showed promising photovoltaic characteristics, with an energy-conversion efficiency of 0.035%, when

illuminated under 85 mW/cm<sup>2</sup> white light. The short-circuit current and energy-conversion efficiency of the PVCs based on H-mn/C<sub>60</sub> and H-py/C<sub>60</sub> were greatly improved when they were blended with a small amount of MEH-PPV. The incident photon-to-collected-electron efficiency of the HPV/MEH-PPV/C<sub>60</sub> PVCs indicated that both HPVs and MEH-PPV contributed to the photocurrent. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1459–1466, 2004

**Key words:** hyperbranched; charge transfer

## INTRODUCTION

Photovoltaic cells (PVCs) based on blends of a conjugated polymer and C<sub>60</sub> have drawn considerable attention in recent years because of their easy fabrication and low cost and the good possibility of obtaining flexible devices in comparison with traditional inorganic solar cells.<sup>1,2</sup> Polymer PVCs are created through the sandwiching of a photoactive layer of a conjugated polymer/C<sub>60</sub> blend between an indium tin oxide (ITO) anode and a metal (e.g., Al) cathode. When polymer PVCs are irradiated, the conjugated polymer in the blend layer absorbs the light to excite an electron in the highest occupied molecular orbital (HOMO) energy level of the conjugated polymer to the lowest unoccupied molecular weight (LUMO) energy level and leave a hole in the HOMO energy level; in this way, an exciton is formed. When the exciton is transferred to the interface of the conjugated polymer and C<sub>60</sub>, the excited electron transfers to the LUMO energy level of C<sub>60</sub>, and so the charge is separated on the interface between the electron donor of the conjugated polymer and the electron acceptor C<sub>60</sub>. The separated electrons move along with C<sub>60</sub> toward the cathode, the holes move along with the conjugated polymer chains

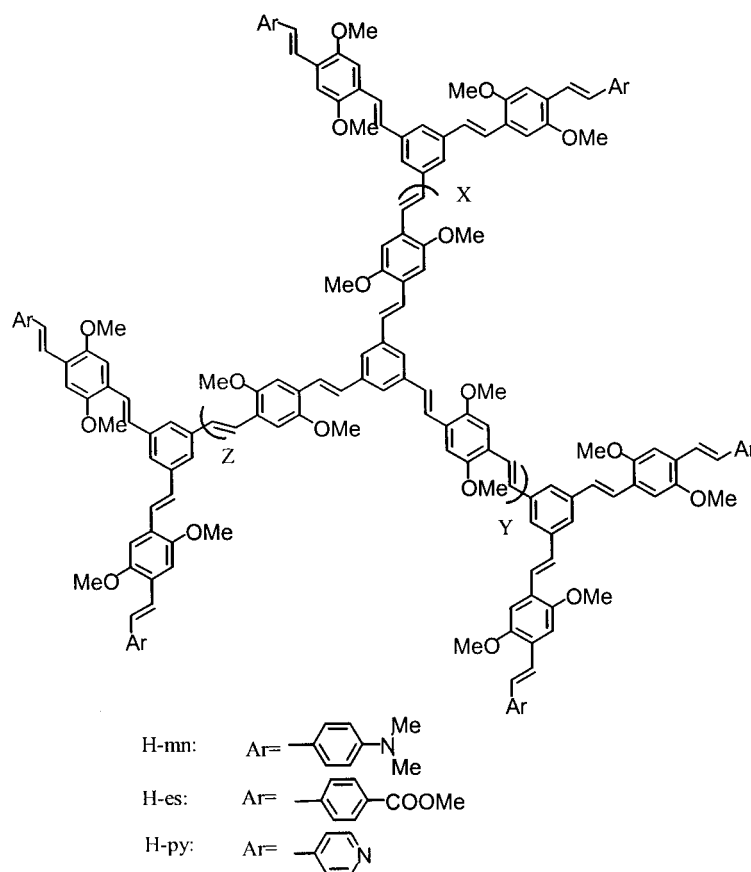
toward the anode, and they produce the photocurrent and photovoltage. Because charge separation occurs on the interface between the conjugated polymer and C<sub>60</sub>, this kind of PVC is often called a bulk heterojunction PVC. Efficient charge separation and rapid charge transportation are crucial for the high performance of PVCs. Although the efficiency for photoinduced charge separation is near unity for a donor/acceptor pair, the overall device efficiency is limited because of the charge collection efficiency; that is, the separated charge must be collected before recombination, and efficient charge separation occurs only at a donor/acceptor interface. Thus, the bulk heterojunction structure appears to be an ideal structure.<sup>3</sup>

Most of the reported work on polymer PVCs has been focused on linear one-dimensional materials, such as poly(2-methoxy-5,2'-ethylhexyloxy-1,4-phenylene vinylene) (MEH-PPV) and MDMO-PPV. Although a few multidimensional conjugated polymers, such as hyperbranched conjugated polymers, have been reported to have charge-transport and processing properties comparable to those of their linear counterparts,<sup>4–6</sup> and some dendritic polymers have been used in photodetectors,<sup>7,8</sup> as far as we know, there has been no report on PVCs based on hyperbranched conjugated polymers.

Hyperbranched conjugated polymers have certain advantages over conventional linear conjugated polymers because of their unique structure.<sup>9–11</sup> These polymers deserve attention in the field of photoelectronic devices, not only because of their amorphous properties and good solubility in common organic

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**Figure 1** Molecular structure of the three HPVs.

solvents but also because of their twisted intramolecular charge transfer (TICT) properties. Twisting in hyperbranched conjugated polymers contributes to the efficiency of charge separation and irreversible photoinduced charge transfer, and this reduces the possibility of charge recombination and enhances the quantum efficiency of the nonradiative process.<sup>12,13</sup> Thus, it may be suitable for applications in polymer PVCs.

In this study, we used three hyperbranched phenylene vinylenes (HPVs)—H-mn, H-es, and H-py (Fig. 1)—blended with  $C_{60}$  to fabricate polymer PVCs. The effect of adding a small amount of MEH-PPV to a blend on the performance of the PVCs was also investigated.

## EXPERIMENTAL

The HPVs used and investigated in this work were synthesized via the Wittig reaction in a one-pot process, as described elsewhere.<sup>14,15</sup> The length of the branches in a single polymer molecule of the HPVs was not exactly the same because of the synthesis of the one-pot reaction.

Absorption and photoluminescence (PL) spectra were obtained for thin films on quartz and for diluted

toluene solutions. The ultraviolet–visible (UV–vis) absorption spectra were taken with a Hitachi U-3010 UV–vis spectrometer. The PL spectra were taken with a Hitachi F-4500 fluorescence spectrometer. Cyclic voltammetry was performed, for the determination of the energy gap and HOMO and LUMO energy levels of the HPVs, on an EG&G PARC 283 potentiostat/galvanostat with a glassy carbon electrode as the working electrode, Pt wire as the counter electrode, and  $\text{Ag}/\text{Ag}^+$  as the reference electrode.

The polymer PVCs were fabricated through the spin casting of the polymer or polymer blend from 1,2-dichlorobenzene solutions onto ITO glass substrates coated with a conducting layer of poly(3,4-ethylene dioxothiophene)–poly(styrene sulfonate) (PEDOT–PSS; Bayer), followed by the vacuum deposition of aluminum metal on the polymer layer. ITO/PEDOT–PSS acted as anode, and the aluminum layer acted as a cathode. The effective area of the electrode was approximately  $10 \text{ mm}^2$ . Polymer blends were made through the mingling of HPV (as a donor) and  $C_{60}$  (as an acceptor) in a 1:1 (w/w) ratio of HPV to  $C_{60}$  at the maximum solubility of the HPVs (solution 1) or through the addition of a small amount of MEH-PPV (25 wt % HPV) into HPV/ $C_{60}$  blends in a 0.5:0.125:0.5 (w/w/w) ratio of HPV to MEH-PPV to  $C_{60}$  (solution

TABLE I  
Molecular Weights, ( $M_n$  and  $M_w$ ) Energy Gap ( $E_g$ ) and HOMO and LUMO of HPVs

HPV	$M_n$	$M_w$	Polydispersity index	$E_g$	HOMO	LUMO
H-mm	3559	17368	4.88	2.54	-5.26	-2.72
H-es	5112	19576	3.83	2.72	-5.46	-2.74
H-py	7076	28714	4.06	2.65	-5.42	-2.77

2). A halogen lamp simulated a white-light source at different light intensities of 85–13 mW/cm<sup>2</sup>, and the light intensity was justified with a single-crystal Si photocell. The light was illuminated from the ITO side. The current–voltage (I–V) curve measurements of the PVC devices were conducted on a Keithley 236 computer-controlled source measurement system. The incident photon-to-collected-electron efficiency (IPCE) spectrum was measured with a Keithley 195 DMM system coupled with a WDG3 monochromator and a 500-W xenon lamp.

## RESULTS AND DISCUSSION

### Properties of the HPVs

The three HPVs studied in this work—H-mn, H-es, and H-py—have the same periphery conjugated core structure and different functional ending units. For H-mn, dimethylaniline acts as an electron-rich ending group; for H-py, pyridine acts as an electron-withdrawing ending group; and for H-es, ester alkyl acts as a neutral ending group. The different electronegativities of their ending units may affect the charge-transfer ability in the polymer blends and thus may affect the performance of the devices.

The number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of the HPVs are listed in Table I. Because of their synthesis via the Wittig reaction in a one-pot process, they have broad molecular weight distributions. The energy gap and HOMO and LUMO energy levels of the three HPVs, calculated from their turn-on redox potentials measured by cyclic voltammetry, are also given in Table I. These three HPVs are yellow-green polymers with fairly broad band gaps; these may be related to their low molecular weight and short conjugated chain length.

The HPVs have good solubility in common organic solvents such as chloroform, toluene, chlorobenzene, and cyclohexone, which is crucial for the spin-casting fabrication of polymer devices. The good solubility may benefit from their weak intermolecular interactions due to their multidimensional structure and low solvation energy.

Figure 2 shows the absorption spectra of the three HPVs in toluene solutions. Because the three HPVs have the same core structure and their different ending units constitute only a small portion of the entire molecule, they have similar absorption peak positions. The three absorption spectra all show two absorption

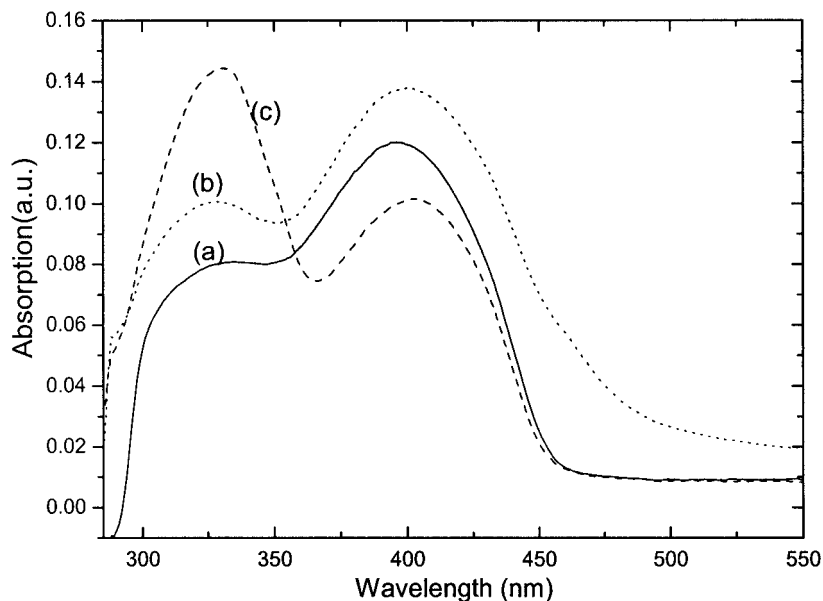


Figure 2 Absorption spectra of (a) H-mn, (b) H-py, and (c) H-es in toluene solutions.

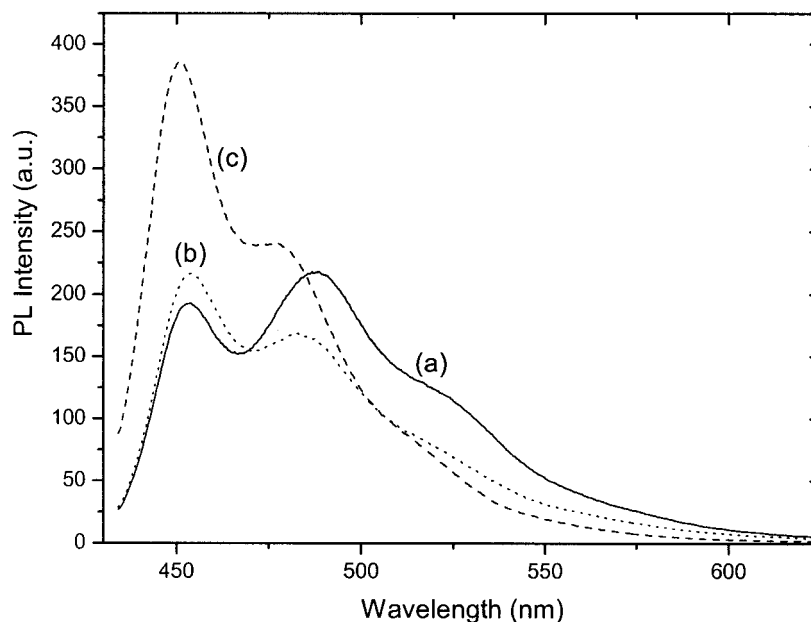


Figure 3 PL spectra of (a) H-mn, (b) H-py, and (c) H-es in toluene solutions.

peaks with absorption maxima at 331 and 402 nm, respectively. However, the relative intensities of the two peaks are different for the different HPVs, and they should be affected by the functional ending groups. For H-es, the peak at 331 nm is stronger than that at 402 nm, whereas for H-mn and H-py, the stronger peak is that at 402 nm. Upon excitation by the light at 430 nm, the solutions exhibit intense fluorescence, with two maxima between 450 and 500 nm, as shown in Figure 3.

In the solid state, the absorption of H-py is slightly blueshifted from that in solution, with the two maxima at 326 and 388 nm, whereas the maximum PL emission is redshifted to 508 nm with a shoulder at 540 nm, as shown in Figure 4. These differences suggest a large change in the intermolecular and intramolecular interactions from the solution to the solid film. One possible explanation is that the dendritic structure of the HPVs causes significant hindrance in the solid state. Thus, the  $\pi$ - $\pi$  stacking of the polymer backbone

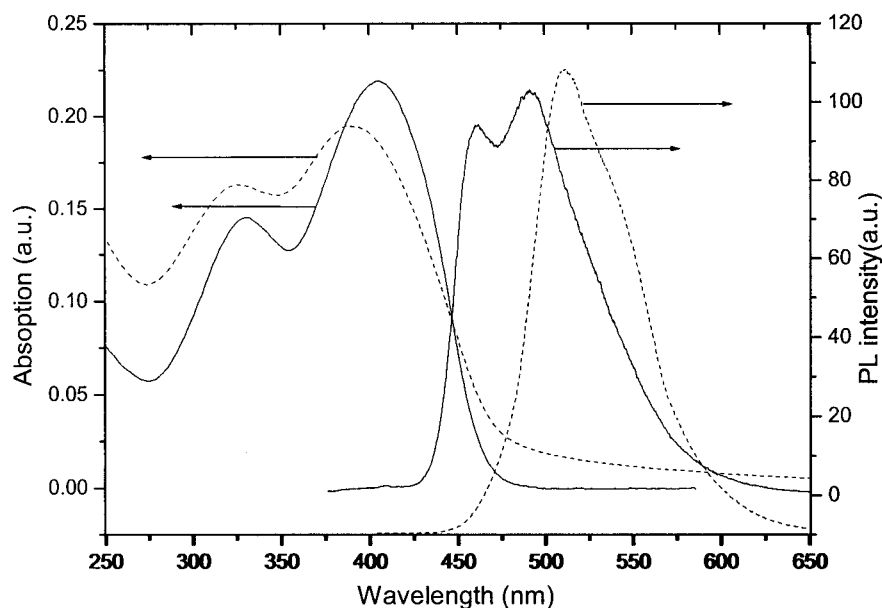
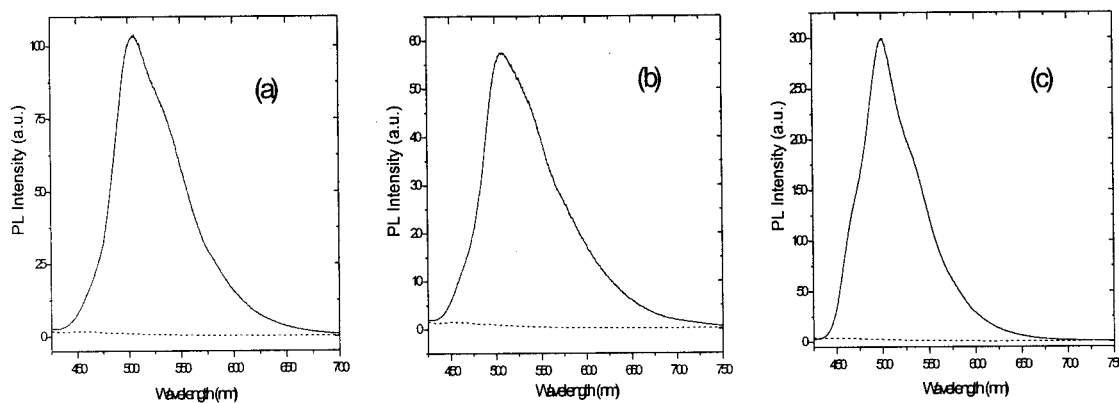


Figure 4 Absorption and PL spectra of H-py in (—) toluene solutions and (---) solid films.



**Figure 5** PL spectra of films of (—) HPVs and (---) 1:1 (w/w) HPV/ $C_{60}$  blends: (a) H-mn and H-mn/ $C_{60}$  blend, (b) H-py and H-py/ $C_{60}$  blend, and (c) H-es and H-es/ $C_{60}$  blend.

is hindered and the conjugated length is reduced in the ground state, and so blueshifting of absorption is observed. In the excited state of the solid film, a low-energy excimer is formed after energy absorption, and the PL spectra are redshifted. Because the structure of the excimer is complicated, the PL spectrum of the solid film of H-py deviates from typical double-peak spectra (see Fig. 4). A detailed discussion can be found in other articles.<sup>16,17</sup>

The concept of TICT was introduced by Grobowski et al. in 1973.<sup>18</sup> TICT phenomena have been found in various organic molecules containing an electron-acceptor group and an electron-donor group; photoinduced intramolecular charge transfer occurs with a twist of the molecular conformation. Yang et al.<sup>19</sup> proved that H-mn would be in the TICT state under photoexcitation. The lower peak in the PL spectra is attributed to a locally excited state; the higher peak is attributed to the TICT state. We hope that this TICT property may have some positive effect on the device performance of the polymer PVCs.

To investigate the charge-transfer property between the HPVs and  $C_{60}$ , we studied the effect of  $C_{60}$  on PL of the HPVs. Because there was very little absorption of  $C_{60}$  at 430 nm, this wavelength was selected to excite polymers for the study on the interactions between the polymers and  $C_{60}$ . Figure 5 shows the PL spectra of the HPVs without and with  $C_{60}$ . The fluorescence of all three polymers is quenched by  $C_{60}$  dramatically; this is a direct indication of a photoinduced charge-transfer process from the photoexcited polymers to the quencher molecule  $C_{60}$ . This efficient photoinduced charge transfer indicates the promising applications of the HPVs for polymer PVCs.

### PVCs based on the HPVs

First, we fabricated polymer PVCs with pure HPVs as the active layers. The device structure was ITO/PE-

DOT-PSS/HPV/Al, and the HPV layer was spin-cast from a 1,2-dichlorobenzene solution with the highest concentration of the polymers. The short-circuit current ( $J_{sc}$ ) and open-circuit voltage ( $V_{oc}$ ) values of the polymer PVCs under 85 mW/cm<sup>2</sup> white-light irradiation (halogen lamp) are listed in Table II. The  $J_{sc}$  values of the devices based on the HPVs are  $10^{-3}$ – $10^{-4}$  mA/cm<sup>2</sup>, which are comparable to the  $J_{sc}$  values of the PVCs with pure MEH-PPV as the active layer.<sup>20</sup> The  $V_{oc}$  values of the PVCs based on the HPVs is about 0.5 V, which agrees with the energy-level difference between the ITO anode and the Al cathode.

The bulk heterojunction PVCs based on the HPVs were fabricated with the ITO/PEDOT-PSS/HPV+ $C_{60}$  (1:1 w/w)/Al device structure. Also, the concentration of the HPV solutions for the device fabrication was at their highest solubility, and the weight ratio of HPV to  $C_{60}$  was 1:1. The dark I-V and photo I-V characteristics of the PVC device based on H-es under different illumination intensities are plotted in Figure 6. The performance parameters of the PVC devices based on the three HPVs under 85 mW/cm<sup>2</sup> white-light irradiation are collected in Table III. The devices have fairly high fill factors (FFs): 0.39 for the PVC based on H-es and about 0.3 for those PVCs based on H-mn and H-py. FF is related to charge transport and recombination.<sup>2</sup> The TICT property of HPVs may help to improve charge separation and reduce charge recombination, and this improves FF. For the best device

**TABLE II**  
Performance Parameters of the ITO/HPV/Al PVC devices

Active layer	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)
H-mn (0.6 wt %)	$1.33 \times 10^{-3}$	0.46
H-es (1 wt %)	$1.1 \times 10^{-3}$	0.5
H-py (0.8 wt %)	$5.83 \times 10^{-4}$	0.55

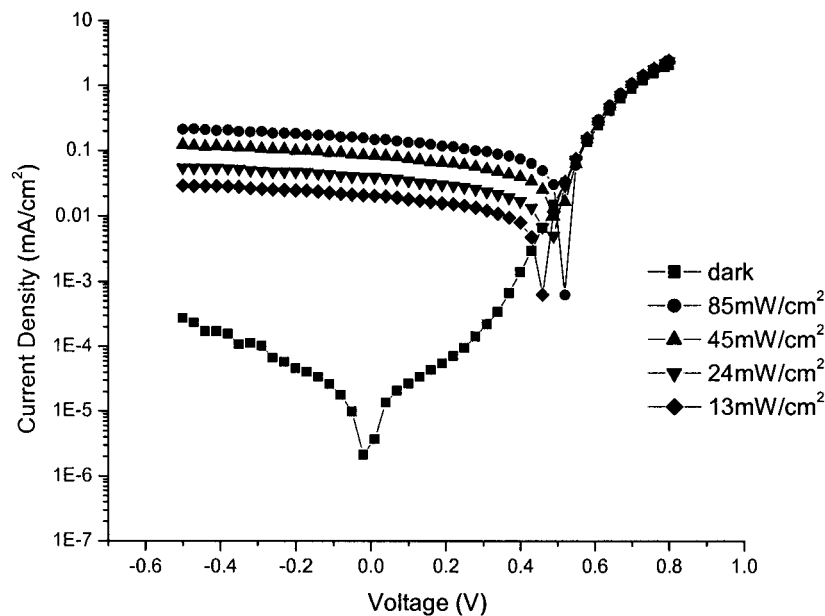


Figure 6 I-V characteristics of an ITO/PEDOT-PSS/H-es+C<sub>60</sub>/Al PVC device.

based on H-es/C<sub>60</sub> within the three PVCs,  $J_{sc}$  is 0.15 mA/cm<sup>2</sup>, and the energy-conversion efficiency ( $\eta_e$ ) is 0.035%. The relatively low efficiency may be caused by poor light absorption or charge transportation, although the charge separation is good in the hyper-branched polymer/C<sub>60</sub> system. The thickness of the photoactive polymer film in the PVCs is quite thin (ca. 30 nm) because of the low viscosity of the blend solutions of the HPVs and C<sub>60</sub>, which limits the photoabsorption. In addition, the absorption of the three HPVs in the visible region is quite narrow: they only absorb the light with wavelengths of 300–450 nm (see Fig. 2). Thus, most of the irradiation light (visible light) is transmitted or reflected; that is, the utility of the photoenergy is fairly low. The poor light absorption is the main reason for the lower  $\eta_e$  values of the PVCs.

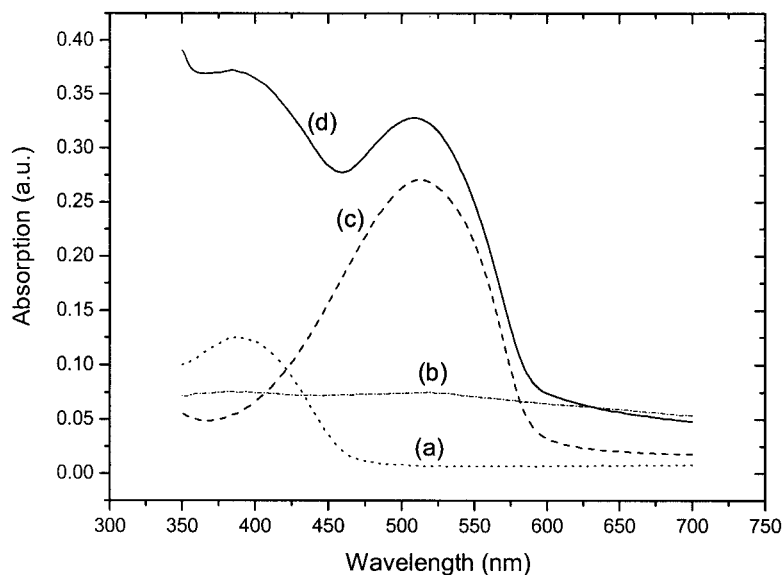
To improve the performance of the PVCs based on the HPVs, we added small amounts of MEH-PPV to blend solutions of the HPVs and C<sub>60</sub> with a weight ratio of 25:1 (w/w) MEH-PPV/HPV. The purpose of

adding MEH-PPV was to produce more uniform and thicker films and to use the optical absorption of both the HPVs and MEH-PPV. The improvement of the film-forming property after the addition of MEH-PPV benefited from the high molecular weight of MEH-PPV and the higher viscosity of the polymer blend solution with MEH-PPV. Figure 7 shows the absorption spectra of HPV/MEH-PPV/C<sub>60</sub>, which overlap those of HPV, MEH-PPV, and C<sub>60</sub> absorption. The absorption spectra also indicate that there is no ground-state charge transfer when MEH-PPV is mixed with a blend of HPV and C<sub>60</sub>. Figure 8 shows the I-V curves of the ITO/PEDOT-PSS/H-py+MEH-PPV+C<sub>60</sub>/Al PVC device, and Table III lists the performance parameters of the three devices based on the blends of the HPVs, C<sub>60</sub>, and MEH-PPV.  $J_{sc}$  and  $\eta_e$  for the devices based on H-py and H-mn improve greatly after MEH-PPV is added. Figure 9 shows IPCE of the PVC devices based on the blends of the HPVs, MEH-PPV, and C<sub>60</sub>. For the PVC based on H-mn, a maxi-

TABLE III  
Performance Parameters of the PVC Devices with HPV/C<sub>60</sub> and HPV/MEH-PPV/C<sub>60</sub>

Devices with HPV/C <sub>60</sub>	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{OC}$ (V)	FF	$\eta_e$ (%)
H-mn/C <sub>60</sub> = 0.6:0.6 w/w <sup>a</sup>	0.075	0.52	0.29	0.0134
H-es/C <sub>60</sub> = 1:1 w/w	0.15	0.50	0.39	0.035
H-py/C <sub>60</sub> = 0.8:0.8 w/w	0.134	0.53	0.31	0.026
HPV/MEH-PPV/C <sub>60</sub> = 0.5:0.125:0.5 w/w/w				
H-mn	0.38	0.58	0.37	0.09
H-es	0.14	0.52	0.39	0.03
H-py	0.47	0.57	0.36	0.11

<sup>a</sup> The weight ratio indicates the solution concentration used in the fabrication of the PVCs.



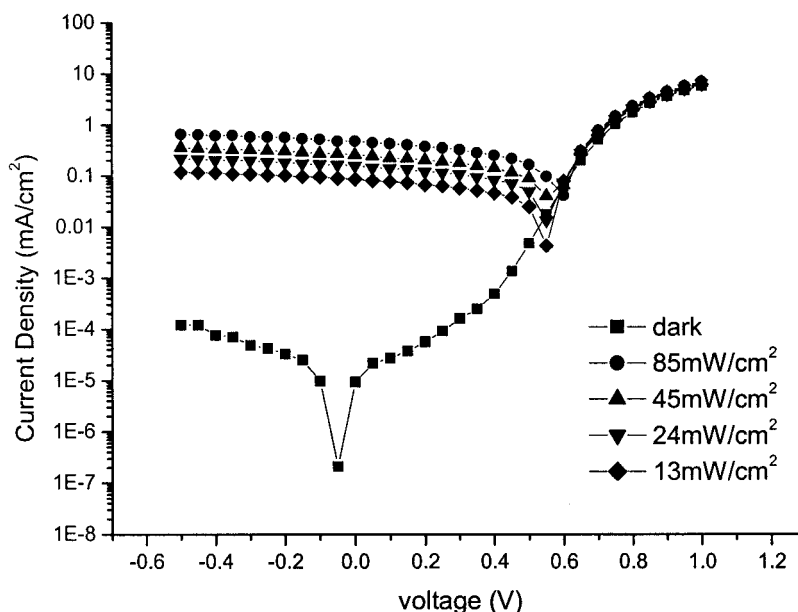
**Figure 7** Absorption spectra of films of (a) H-py, (b)  $C_{60}$ , (c) MEH-PPV, and (d) 1:1:1 (w/w/w) H-py/MHE-PPV/ $C_{60}$  blends.

imum of 7.5% at 400 nm for the quantum efficiency was reached, corresponding to the absorption maximum of H-mn, and a second peak of 2.0% was located at 510 nm, corresponding to the absorption maximum of MEH-PPV; this showed the utility of the optical absorption of both the HPVs and MEH-PPV.

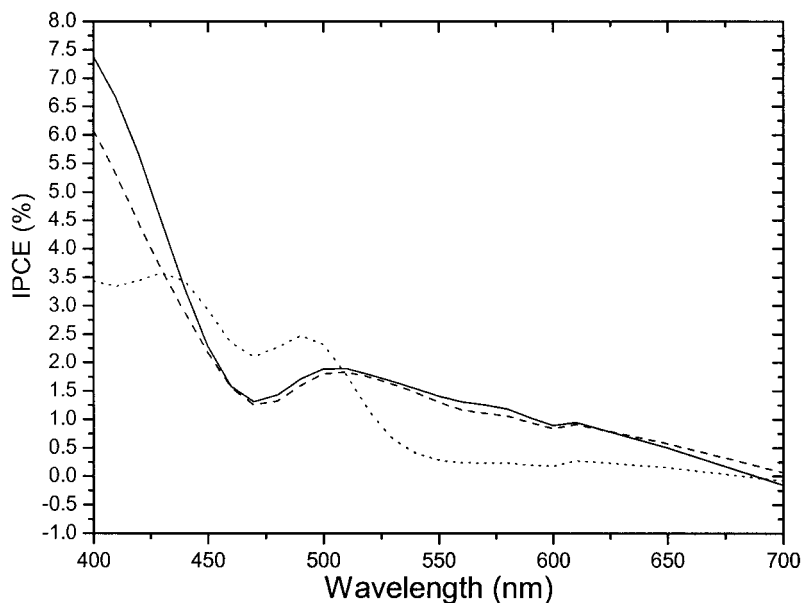
### CONCLUSIONS

Novel hyperbranched conjugated polymers, HPVs, with some special properties were used in making

PVCs. The absorption and PL spectra of the HPVs were inspected. PL of the HPVs was quenched dramatically with  $C_{60}$ , and this was a direct indication of charge transfer between HPVs and  $C_{60}$ . Three kinds of PVCs were fabricated with HPVs, blends of HPVs and  $C_{60}$ , and blends of HPVs and MEH-PPV with  $C_{60}$  as an active layer.  $J_{sc}$  under irradiation and  $\eta_e$  of the PVC based on the H-es/ $C_{60}$  blend were comparable to those of the common polymer PVCs based on linear conjugated polymers. Adding small amounts of MEH-PPV to the H-mn/ $C_{60}$  and H-py/ $C_{60}$  blends improved



**Figure 8** I-V characteristics of an ITO/PEDOT-PSS/H-py/MEH-PPV/ $C_{60}$ /Al PVC device (0.5:0.125:0.5 weight ratio of ITO/PEDOT-PSS/H-py to MEH-PPV to  $C_{60}$ ).



**Figure 9** IPCE of ITO/HPV/MEH-PPV/C<sub>60</sub>/Al PVC devices (0.5:0.5:0.5 weight ratio of ITO/HPV to MEH-PPV to C<sub>60</sub>): (—) H-mn, (---) H-es, and (····) H-py.

the device performance greatly. Further optimizing the ratio of the blend may improve the efficiency, which is under investigation in our laboratory.

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