

## Bulk Heterojunction Organic Photovoltaic Cell Fabricated with a p-Type Conjugated Star-shaped Molecule

Tae Wan Lee,<sup>1</sup> Dae Cheol Kim,<sup>1</sup> Nam Su Kang,<sup>2</sup> Jae Woong Yu,<sup>\*2</sup> Min Ju Cho,<sup>1</sup>  
Kyung Hwan Kim,<sup>1</sup> and Dong Hoon Choi<sup>\*1</sup>

<sup>1</sup>Department of Chemistry, Advanced Materials Chemistry Research Center, Korea University,  
5 Anam-dong, Sungbuk-gu, Seoul 136-701, Korea

<sup>2</sup>Korea Institute of Science & Technology, Center for Energy Materials Research,  
39-1 Hawolkok-dong, Sungbuk-gu, Seoul 136-791, Korea

(Received May 26, 2008; CL-080533; E-mail: dhchoi8803@korea.ac.kr, jwyu@kist.re.kr)

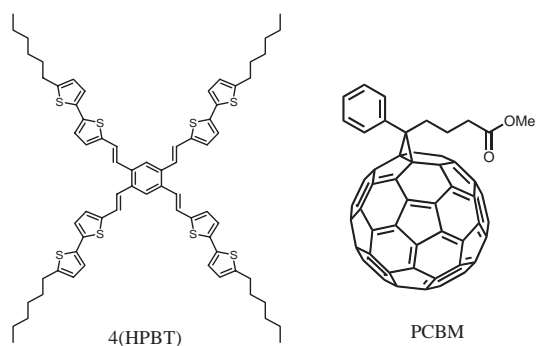
A new multibranch crystalline molecule was synthesized through Horner–Emmons reactions using hexyl-substituted thiophene-based carbaldehydes as dendrons and benzene-1,2,4,5-tetramethylphosphonic acid octaethyl ester as the core unit. The molecule was employed to fabricate organic photovoltaic (OPV) cells with methanofullerene [6,6]-phenyl C61-butyric acid methyl ester (PCBM). Poly(3-hexylthiophene) (P3HT) was also used as a dopant to improve the film quality and power conversion efficiency. As a result, the short-circuit current density and open circuit voltage were increased when P3HT was added into 4(HPBT) and PCBM dyad, resulting in a higher power conversion efficiency of around 0.6%.

Organic semiconductor materials based on extended linear  $\pi$ -conjugated systems have been very intriguing and significantly developed over the past several years.<sup>1–3</sup> With regard to the application of organic semiconductors in electronic and optoelectronic devices, the organic photovoltaic cell (OPV) is an important device for developing future energy resources.<sup>4–9</sup>

Recently, organic photovoltaic devices employing conjugated polymer–fullerene heterojunctions have been shown to have a power conversion efficiency approaching 6.0–6.1%, this range of value is obtained by introducing variations in the processing techniques. However, a problem in the synthesis of conjugated polymers is their poor solubility due to their rigid backbone. In that sense, oligothiophene has advantages over polythiophene. The former is well known as a good hole-transport material, and by changing the number of thiophene rings and making chemical modifications or substitutions, its characteristics relevant to PV applications (such as carrier mobility, energy level, and structure) can be controlled. However, most of the linear oligothiophenes are not well soluble in organic solvents either.

We recently reported the facile and high-yield synthesis of new p-type thiophene-based multibranch semiconducting molecules.<sup>10</sup> Figure 1 illustrates the structure of the p-type multibranch semiconducting molecule, 4(HPBT). The four-armed crystalline star-shaped molecule contains bithiophene as the dendritic wedge and a hexyl chain group at the periphery. The Horner–Emmons coupling of benzene-1,2,4,5-tetramethylphosphonic acid octaethyl ester and thiophene-based carbaldehyde produces the conjugated star-shaped molecule with a yield of 70–78%.

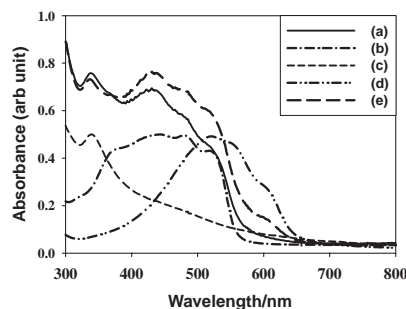
When we employ the star-shaped molecule for the fabrication of OPV devices, its thermal stability and dynamic behavior are important. The thermal properties of 4(HPBT) are characterized by differential scanning calorimetry (DSC). The molecule



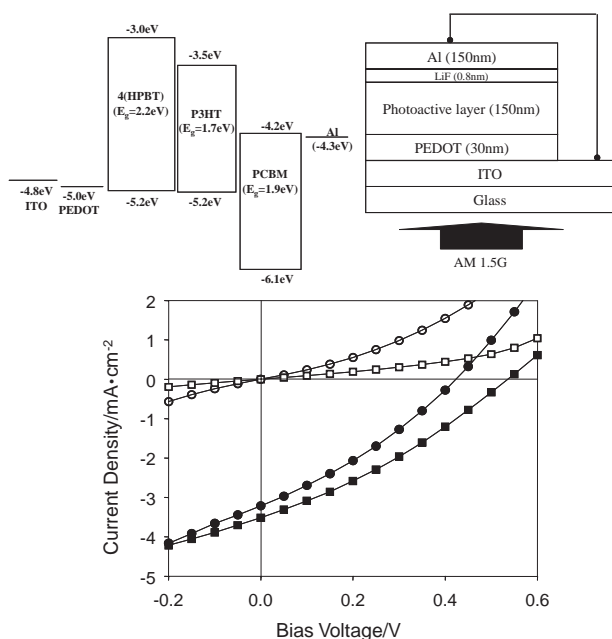
**Figure 1.** Structures of 4(HPBT) and PCBM used for bulk heterojunctions.

exhibits distinct crystalline–isotropic transitions at 178 °C. A cold crystallization temperature appeared at 90 °C as an endothermic peak. TGA measurement at a heating rate of 10 °C/min under nitrogen reveals that the molecule has good thermal stability. Compared to the onset decomposition temperature of the well-known  $\alpha,\alpha'$ -dihexylsexithiophene (DH-6T), which is around 309 °C, 4(HPBT) has higher onset decomposition temperatures (ca. 350–380 °C).

The absorption spectra of organic blended or homogeneous films were recorded by using an HP8453 absorption spectrophotometer. The organic films were deposited on precleaned quartz plates. The absorption spectra of 4(HPBT), PCBM, and their blend samples in the film state are illustrated in Figure 2. The compositions of two of the blend samples were (a) 4(HPBT):PCBM = 1:0.6 and (e) 4(HPBT):P3HT:PCBM = 1:0.2:0.6. The absorption maxima of 4(HPBT) in the solution state were



**Figure 2.** Absorption spectra of 4(HPBT), PCBM, P3HT, and their mixtures. Films containing (a) 4(HPBT):PCBM = 1:0.6, (b) 4(HPBT), (c) PCBM, (d) P3HT, and (e) 4(HPBT):P3HT:PCBM = 1:0.2:0.6.



**Figure 3.** Energy diagram, multilayered PV device structure, and  $J$ - $V$  characteristics of Al/PEDOT/4(HPBT):PCBM/LiF/Al (circle) and Al/PEDOT/4(HPBT):P3HT:PCBM/LiF/Al (square). \*Open symbol: dark current density, \*Closed symbol: photocurrent density.

located at 422 nm. We observed a drastic spectral change in the film states of 4(HPBT), which is attributed to a high degree of intermolecular interaction. When mixing PCBM with 4(HPBT), we observed a slight spectral broadening at around 565 nm. When we mixed 20% of P3HT with the 4(HPBT) matrix, a small increase in the absorbance was observed around 600 nm and the HOMO–LUMO energy gap was observed at a longer wavelength ( $\lambda_{\text{cutoff}} = 650$  nm).

All the OPV devices were fabricated on glass substrates pre-coated with a 300-Å-thick ITO anode (with a sheet resistance of 20  $\Omega/\text{cm}$ ). PCBM was purchased from Acros Co. and was used as received without purification. First, PEDOT:PSS (Baytron Co.) layers were deposited onto the ITO-coated glass substrate in series. Subsequently, a solution containing photoactive materials was spin coated.

0.8-nm-thick LiF which served as a buffer layer, was vacuum deposited on top of the active layer and 150-nm-thick aluminum was evaporated, and the prepared device was post annealed at 120 °C for 10 min. The active area of the OPV cells is 0.16 cm<sup>2</sup>. Current–voltage characteristics were measured with a Keithley 2400 source-measure unit. A 300-W Xe lamp was used as a light source to produce intensity of 100 mW/cm<sup>2</sup>. To mimic sun light, an AM 1.5 (Oriel) neutral density filter was used to reduce intensity as necessary. Intensity of incoming light power was measured with a calibrated broadband optical power meter (Spectra Physics model 404).

**Table 1.** Summary of PV device performance

	$J_{\text{sc}}/\text{mA}\cdot\text{cm}^{-2}$	$V_{\text{oc}}/\text{V}$	FF	PCE/%
4(HPBT):PCBM	3.21	0.42	0.31	0.43
4(HPBT):P3HT:PCBM	3.51	0.54	0.31	0.59

Figure 3 demonstrates the energy diagram, device configuration, and current density–voltage characteristics of the most effective 4(HPBT)-based devices in dark and under illumination. The binary sample with 4(HPBT) and PCBM involves an open-circuit photovoltage of 0.42 V and a short-circuit current density of 3.21 mA cm<sup>2</sup>. The fill factor, a measure of the squareness of the  $J$ - $V$  characteristics, is equal to 0.31. On the basis of these data, the monochromatic power conversion efficiency of the 4(HPBT):PCBM (1:0.6) device is evaluated as 0.43%, which is reasonably high. When we mix 20 wt % of P3HT with the above-mentioned matrix, the  $V_{\text{oc}}$  value increases slightly, which is due to improvement of the interfacial contact between the photoactive layer and the electrode. PCE also increases to a quite high value (around 0.59%), which indicates that holes can be transported through the extra P3HT dopant easily and collected by the anode and by the spectral broadening effect that extends the spectrum to longer wavelengths.

In conclusion, we have demonstrated that the 4(HPBT):PCBM dyad and 4(HPBT):P3HT:PCBM triad are efficient materials for photovoltaic cells. The generation of high photocurrents is ascribable to the photoinduced charge separation of the compound and the good thiophene-based multibranched molecular network for hole transport. When a conjugated polymer, P3HT is employed as a dopant, the bulk heterojunction device exhibits a more promising power conversion efficiency.

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