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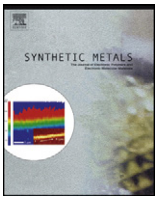

Investigation of novel PCBM analogs containing thienyl groups for organic photovoltaic devices

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ABSTRACT

Novel [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) analogs containing benzo[b]thiophene and thieno[3,2-b]thiophene were used as electron acceptors in bulk heterojunction thin layer organic photovoltaic devices. The solubility of the novel methanofullerenes in dichloromethane significantly varied, and es-TThCBM, which was 1.4 times as soluble as PCBM, exhibited maximum solubility. The morphology of the thin films prepared from the mixtures of these methanofullerenes with regioregular poly(3-hexylthiophene) (P3HT) was investigated by XRD, AFM, and UV–vis absorption spectroscopy. Devices containing the novel methanofullerenes exhibited nearly the same performance as those containing PCBM.

1. Introduction

The demand for inexpensive, renewable energy sources has led to the development of new approaches for the production of efficient, low-cost photovoltaic (PV) devices [1–3]. In particular, the use of polymers for PV cell fabrication can be considerably advantageous from the viewpoint of the low-cost production of large-area, flexible, and light solar cells [4–7]. Recently, bulk heterojunction solar cells comprising conjugated polymers (donors) and fullerene derivatives (acceptors) have inspired significant scientific interest [8,9]. The high efficiency and considerable overall promise of a PV cell based on regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT, Fig. 1) and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM, Fig. 1) has been demonstrated [10]. Considerable attention has been focused on improving device efficiency, for example, by changing the solvent used for spin coating the active layer [11,12], by annealing the device for improving the polymer crystallinity [13,14], and by controlling the growth rate of the organic film [15,16]. These studies revealed that the morphology of the active layer is a critical factor in determining the device efficiency. Moreover, it is essential to investigate the development of new materials in order to achieve a significant improvement in PV cell efficiency. New donor materials have been developed for use in bulk heterojunction PV devices, such as poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b*′]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)](PCPDTBT) [17], poly[3,6-bis-(4′-dodecyl-[2,2′]bithiophenyl-5-yl)-2,5-bis-(2-ethyl-hexyl)-2,5-dihydropyrrolo[3,4–]pyrrole-1,4-dione](pBBTDPP2) [18], etc. However, the development of new acceptor materials other than PCBM has not been sufficiently investigated [19–22].

Little is known about how the structure of fullerene derivatives affects the morphology of the active layer of a PV cell. Recently, Hummelen et al. fabricated a device using a thienyl analog [1-(3-methoxycarbonyl)propyl-1-thienyl-6,6-methanofullerene, ThCBM, Fig. 1] for achieving improved miscibility with P3HT [23]. However, the reasons for ThCBM being superior to PCBM are not entirely clear. In a previous study, we synthesized novel PCBM analogs incorporating various types of thienyl groups [24]. In this research, we report in detail the structural effect of fullerene derivatives on the morphology of P3HT films. The performance of PV devices comprising novel PCBM analogs is also investigated. The structures of the fullerene derivatives used in this research are illustrated in Fig. 1.

2. Experimental

2.1. Materials

PCBM and ThCBM were synthesized in accordance with the methods described in the corresponding literature [23,25]. The syntheses of 2-BThCBM and es-TThCBM are described in our previous study [24]. All the other solvents and materials are commercially available and were purified before use.

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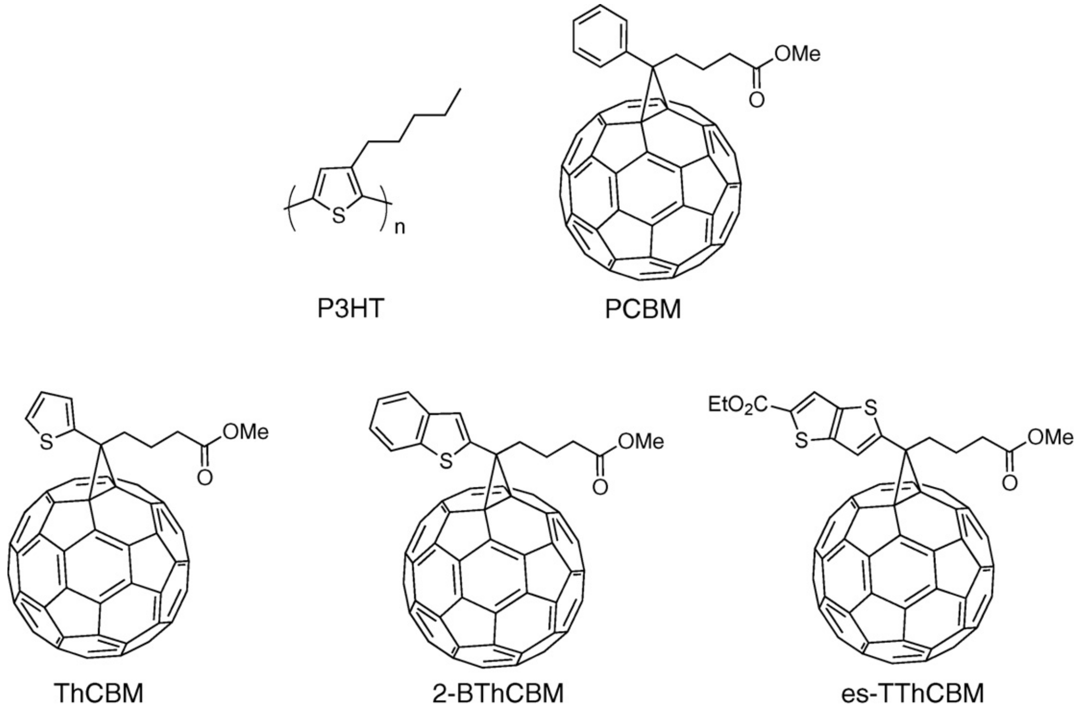

Fig. 1. Molecular structures of P3HT and [6,6]-methanofullerenes.

2.2. Instrumentation

X-ray diffraction (XRD) measurements were performed with a Rigaku RINT 2000 diffractometer using Cu $K\alpha$ radiation at wavelength $\lambda = 0.154$ nm. The thin films were studied using grazing incidence diffraction geometry in order to increase the length of the XRD beam path in the film. The angle between the film surface and the incident beam was fixed at 0.3°. The detector scans the films at angle 2θ in a plane defined by the incident beam and the surface normal. AFM images were taken with a Digital Instruments Nanoscope IIIa at a scan rate of 1.0 Hz in the tapping mode. UV–vis absorption spectra were recorded using a Shimadzu UV-3100A spectrometer. Reduction potentials were determined by cyclic voltammetry (CV) using an ALS Electrochemical Analyzer 630A equipped with a platinum working electrode (1.6 mm diameter), platinum wire counter electrode, and Ag/Ag$^+$ reference electrode. Measurements were performed using a 5-mL one-compartment cell under Ar gas; an *ortho*-dichlorobenzene solution containing tetrabutylammonium perchlorate (0.1 M) was used as a supporting electrolyte, and the scan rate was 20 mV/s at room temperature.

2.3. Solubility determination

Solubility data were obtained as follows: *ca.* 1.5 mL of CH_2Cl_2 was added to an excess of methanofullerene solids. The mixture was sonicated at room temperature for 15 min and then centrifuged for 15 min. The solution phase was passed through a 0.45-mm syringe filter. A 1.0-mL sample of this saturated solution was then diluted to 50 mL with CH_2Cl_2. The solubilities of the methanofullerenes were calculated from the absorbance value at 430 nm by measuring the absorbance of a standard solution of the methanofullerenes (0.1 g/L) in CH_2Cl_2.

2.4. Device fabrication

Indium tin oxide (ITO) substrates were first cleaned by sonication sequentially in detergent, water, acetone, and methanol, followed by treatment with ultraviolet (UV) ozone. The cleaned ITO substrates were spin coated with an aqueous solution of poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonic acid (PEDOT:PSS; Baytron P) at 5000 rpm for 50 s. The resulting thin layer was dried in a vacuum oven at 120 °C for 10 min. Samples of P3HT (Mw 17,500) and different fullerene derivatives were dissolved in chlorobenzene at a ratio of 1:0.8 (2.25 wt.%). The active layer was obtained by spin coating the blend at 800 rpm for 50 s and drying under an N_2 atmosphere for 12 h. Thermal evaporation and a shadow mask were used to deposit the LiF (0.5 nm) and Al

Table 1
Solubility of methanofullerenes.[a]

Solubility	PCBM	ThCBM	2-BThCBM	es-TThCBM
mmol/L	17.6	10.4	13.2	23.8
g/L	16.0	9.56	13.1	24.9

[a] Maximum solubility in dichloromethane at room temperature.

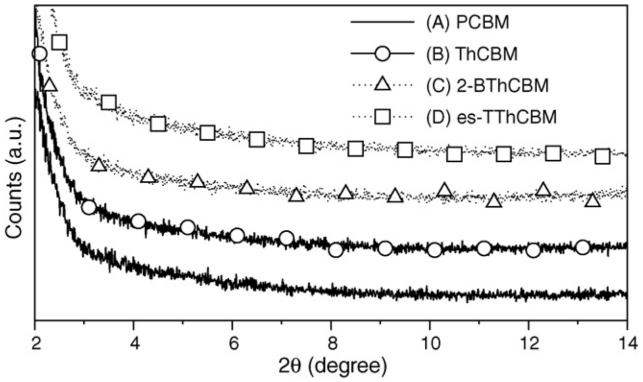

Fig. 2. Diffractogram (grazing incidence) of pristine P3HT/fullerene composite films containing (A) PCBM, (B) ThCBM, (C) 2-BThCBM, and (D) es-TThCBM.