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Polymer solar cells based on poly(3-hexylthiophene) and fullerene: Pyrene acceptor systems

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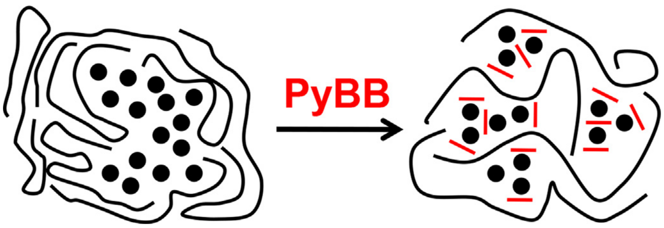
HIGHLIGHTS

- Pyrene derivatives favour the dispersion of unfunctionalized fullerenes.
- Polymer solar cells with pyrene: C60 adduct as acceptor have efficiencies of 1.54%.
- When C60 is substituted with C70 the efficiency is increased to 2.50%.
- DFT calculations support the plausibility of the formation of pyrene: fullerene adducts.
- The use of unfunctionalized fullerenes may decrease the costs of polymer solar cells.

GRAPHICAL ABSTRACT



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ABSTRACT

The replacement of widely used fullerene derivatives, e.g. [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), with unfunctionalized C60 and C70 is an effective approach to reduce the costs of organic photovoltaics. However, solubility issues of these compounds have always represented an obstacle to their use. In this study, bulk-heterojunction solar cells made of poly(3-hexylthiophene) donor polymer, C60 or C70 acceptors and a pyrene derivative (1-pyrenebutiric acid butyl ester) are reported. Butyl 1-pyrenebutirate limits the aggregation of fullerenes and improves the active layer morphology, plausibly due to the formation of pyrene-fullerene complexes which, in the case of pyrene-C70, were also obtained in a crystalline form. Maximum power conversion efficiencies of 1.54% and 2.50% have been obtained using, respectively, C60 or C70 as acceptor. Quantum mechanical modeling provides additional insight into the formation of plausible supermolecular structures *via* π-π interactions and on the redox behaviour of pyrene-fullerene systems.

1. Introduction

The literature on novel materials for polymer solar cells [1–3] deals mainly with the development of the donor components of the active layer [4–9], while much fewer papers are devoted to novel acceptors [10,11]. [6,6]-phenyl-C61-butyric acid methyl ester

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(PCBM) is the oldest [12], the most used [13] and, to date, still one of the most effective acceptors for bulk heterojunction polymer solar cells. The popularity of PCBM, aside from its unique electronic properties, is mainly due to its good solubility in many organic solvents and easy processability of its blends. The methyl phenylbutyrate substituent imparts to PCBM – and to its C70 homologue (PC71BM) – proper miscibility with poly(3-hexylthiophene) (P3HT), as well as with other donor polymers, able to form the peculiar nanostructured percolating morphology required by the photoactive film. Alternative acceptors to PCBM and PC71BM exist, but are scarce. The indene-C60 bis adduct (ICBA) [14], indene-C60 mono adduct (ICMA) [15] and indene-C70 bis adduct [16,17] are very effective, also in tandem cells. Bis-PCBM [18] and endohedral fullerenes [19] showed some promises, but their high cost does not justify a possible use in large-area devices; other non-fullerene acceptors, e.g. peryleneimides [20] or vinazenes [21], did not achieve high performances to date.

On the other hand, unfunctionalized C60 and C70, which would be advantageous for their availability and relatively low cost, have been seldom used in bulk heterojunction solar cells, because of their low solubility [22–24] that causes aggregation and poor film morphology. Rait et al. reported power conversion efficiencies up to 2.1% for P3HT:C60 solar cells, by using trichlorobenzene as a solvent [25], but according to other authors [26] – and to our experience - the devices are scarcely reproducible. Motaung et al. reported P3HT:C60 solar cells with 0.029% efficiency [27]; prolonged annealing leads to larger C60 domains and lower efficiency. By using 1,2,4-trimethylbenzene solvent, Tada et al. obtained efficiencies of 0.87% and 1.47% for P3HT:C60 [27] and P3HT:C70 [28] solar cells, respectively. Better performances have been reported by Tang et al., who attained a good morphology control in P3HT:C70 blends by using a heptane/*o*-dichlorobenzene mixture as solvent and achieved a 2.24% efficiency [29], and by Chan et al. [30], who reported a P3HT:C60 device with 2.56% efficiency by using an alkyl thiophene/fullerene-substituted thiophene block copolymer as interfacial agent. In the latter paper, however, the preparations of the comonomer and the polymer are quite laborious. Finally, Lu et al. [31] engineered the morphology of C60, by creating a nanorod network in the P3HT matrix by CS_2 vapor treatment, and were able to increase the efficiency of the devices from 0.40% to 2.50%.

Here, we report a new and simple approach for P3HT:C60 and P3HT:C70 bulk heterojunction solar cells fabrication, by exploiting π-π interactions between fullerenes and pyrene to promote fullerene dispersion in the active blend.

2. Experimental part

2.1. Materials

P3HT (OS2100, Plextronics Inc.), C60 (Sigma–Aldrich), C70 (Sigma–Aldrich), 1-pyrenebutyric acid (Sigma Aldrich), n-butanol (Sigma Aldrich) were purchased in high purity grade and used as received.

2.2. Synthesis of butyl 1-pyrenebutyrate (PyBB)

To a 100 mL two-necked round bottom flask equipped with a magnetic stirrer, 879 mg of 1-pyrenebutyric acid, 50 mL of n-butanol and 1 mL of concentrated sulphuric acid were added, forming a suspension which became a solution upon heating to reflux temperature. After 3 h the solution was cooled to room temperature, and 200 mL of brine and 200 mL of ethyl acetate were added. The aqueous fraction was removed and the organic fraction was extracted three times (250 mL) with distilled water. The organic fraction was dried over anhydrous sodium sulphate, filtered, and the solvent was distilled under reduced pressure. 1.03 g (yield 84%) of a pale yellow oil were obtained, which became a white solid after 24 h of storage at +4 °C in a refrigerator. T_m = 37.4 °C (DSC). ^{1}H-NMR (CD_2Cl_2): 8.31 ppm (1H, H1′, d, $J_{1',2'} = 9.3$ Hz), 8.17 ppm (1H, H7′, d, $J_{7',8'} = 7.9$ Hz), 8.16 ppm (1H, H9′, d, $J_{9',8'} = 7.9$ Hz), 8.12 ppm (1H, H2′, d, $J_{2',1'} = 9.3$ Hz), 8.11 ppm (1H, H5′, d, $J_{5',6'} = 7.6$ Hz), 8.03 ppm (2H, H3′ e H4′, s br.), 7.99 ppm (1H, H8′, t, $J_{8',7,9'} = 7.6$ Hz), 7.87 ppm (1H, H6′, d, $J_{6',5'} = 7.7$ Hz), 4.11 ppm (2H, H1, t, $J_{1,2} = 6.7$ Hz), 3.40 ppm (2H, H5, t, $J_{5,6} = 7.7$ Hz), 2.46 ppm (2H, H7, t, $J_{7,6} = 7.3$ Hz), 2.20 ppm (2H, H2, m), 1.62 ppm (2H, H6, m), 1.39 ppm (2H, H3, m), 0.94 ppm (3H, H4, t, $J_{4,3} = 7.4$ ppm). The full spectrum is reported in Supporting Information (Figures S1 and S2).

2.3. Electrochemical analysis

The cyclovoltammetric (CV) characterizations were carried out with an Autolab PGSTAT 12 potentiostat, run by a PC with GPES software. The working cell included a Glassy Carbon (GC) disk embedded in Teflon® (Amel, surface 0.071 cm^2) as the working electrode, a Platinum counter electrode (Metrohm), and an aqueous saturated calomel electrode (SCE, Amel) as the reference electrode. Dissolved sample analysis: a solution of the sample ($\approx 2 \cdot 10^{-4}$ M) in 0.1 M tetrabutylammonium tetrafluoroborate TBATFB (Fluka, electrochemical grade) acetonitrile:*o*-dichlorobenzene 1:4, was purged with argon and analysed in the electrochemical cell. Film analysis: the sample was dissolved in chlorobenzene ($\approx$1 mg/ml) and drop coated from a capillary on the GC electrode. The electrolytic solution was acetonitrile (Carlo Erba, HPLC grade) with 0.1 M tetrabutylammonium tetrafluoroborate TBATFB (Fluka, electrochemical grade). The solution was degassed by argon purging. The scan rate was 200 mV s^{-1}. According to IUPAC recommendations, data have been referred to the Fc$^+$/Fc redox couple (ferricinium/ferrocene) [32]. E_{HOMO} and E_{LUMO} values were extrapolated from the onset peaks potential, according to the following semiempirical equation [33]:

$$E_{HOMO/LUMO} = \left[- e\left(E_{onset(vs \cdot SCE)} - E_{onset(Fc/Fc+vs\ SCE)} \right) \right] - 5.1 eV.$$

2.4. Optical spectroscopy

UV–Vis absorption spectra of thin films spin–coated onto quartz substrates were acquired in transmission mode with a double beam double monochromator Perkin Elmer λ 950 spectrophotometer in the range 200–850 nm, with a bandwidth of 1 nm and stepwise of 1 nm.

2.5. Fabrication of photovoltaic devices

Standard solar cells were fabricated by first spin-coating 30 nm of PEDOT:PSS (Clevios P AI 4083, Heraeus GmbH) as buffer layer, filtered through a 0.45 μm filter, on top of ITO-coated glass substrates (15 Ω/sq, Kintec Co., Hong Kong) at 3000 rpm for 90 s and annealed at 120 °C for 10 min. The active layer (100 nm) was spin-coated at 600 rpm for 90 s on top of PEDOT:PSS from solution in chlorobenzene heated at 35 °C. The concentration of P3HT (Plexcore OS 2100, Plextronics Inc., Pittsburgh) was 10 mg/mL. The blend component ratios are given in Table 2. The devices were completed by the cathode deposition consisting either of 100 nm of aluminium or 15 nm of calcium and 100 nm of aluminium in a thermal evaporator in a 10^{-6} Torr vacuum. C70 based solar cells were post-annealed on a hot plate at 150 °C for 30 min under nitrogen atmosphere. Each substrate contained 3 cells, each with a nominal active area of 25 mm^2. The effective active area of each cell was measured with an optical microscope.