



The effect of thiophene substituents of fulleropyrrolidine acceptors on the performance of inverted organic solar cells[☆]



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ABSTRACT

A series of tailored fulleropyrrolidine derivatives with thiophene substituents was synthesized and studied as electron acceptor materials in inverted organic bulk heterojunction (BHJ) solar cells. The study concentrated on seeking correlation between the molecular structure of the acceptor and its capability to form a photovoltaic BHJ film with the used electron donor material poly(3-hexylthiophene), P3HT. Atomic force and scanning electron microscopy imaging showed that the sensitivity of the BHJ morphology is tied to the molecular structure of the acceptor, which was further studied by photovoltaic characterization of the model solar cells. The photovoltaic performance clearly depended on the molecular structure of the fulleropyrrolidine substituents although there was only slight difference in the BHJ surface morphology. Fulleropyrrolidine derivatives with one or two thiophene units performed better as acceptor materials than those with three or four thiophene units. Additionally, hexyl side chains attached to the four thiophene unit increased the compatibility of a fulleropyrrolidine derivative with P3HT compared to a similar derivative without of the hexyl groups. The results provide new knowledge of the effect of the molecular structure of fulleropyrrolidine derivatives on the BHJ morphology in organic photovoltaics.

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1. Introduction

Organic photovoltaic (OPV) devices are promising candidates for low cost solar energy conversion technology and have faced extensive research during the past years [1–5]. Large area OPVs are potentially light weight, flexible, and inexpensive as they can be fabricated over large areas using, e.g. roll-to-roll printing and coating techniques on various ductile materials [6–8]. Bulk heterojunction (BHJ) is the most studied OPV architecture, in which

electron donor and acceptor materials are blended together to form interpenetrating network structure. It was introduced to improve the low efficiencies exhibited by planar structures due to the short exciton diffusion length of the organic semiconducting polymers. In BHJ, interpenetrating donor–acceptor network is achieved at the nanoscale by blending the donor and acceptor in solution, and allowing the formation of a film with the network structure during evaporation of the solvent [9–12].

The BHJ cells are typically composed of a conjugated polymer donor, such as poly(3-hexylthiophene) (P3HT), and a soluble fullerene derivative acceptor, such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM). The energy levels and miscibility of the donor and the acceptor can be tuned through the design of their molecular structure. The matching of the energy level of the donor material to that of the acceptor compound is one of the key steps to improve the total efficiency of the cell. Using low-band gap polymers power conversion efficiencies (PCEs) of 8% have been achieved for organic tandem solar cells [13–30].

The thermodynamic limit of the open-circuit voltage (V_{oc}) is proportional to the difference between the highest occupied

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molecular orbital (HOMO) energy of a donor and the lowest unoccupied molecular orbital (LUMO) energy of an acceptor. In addition, sufficient HOMO–HOMO and LUMO–LUMO offsets of the donor and the acceptor are needed to exceed the Coulombic attraction of the hole–electron pair to overcome the exciton binding energy in order to avoid the back charge transfer and thus increase photocurrent. Therefore, the best performance is always a compromise between high short-circuit current (I_{sc}) and high V_{oc} .

The morphology at molecular level in the interpenetrating electron donor–acceptor network of the photoactive layer affects strongly on the performance of a polymer solar cell. The short living exciton must reach the donor–acceptor interface in few nanoseconds. This corresponds to diffusion length of approximately 10–20 nm. To increase the probability for the exciton to reach the interface, the donor–acceptor contact area must be as large as possible. Furthermore, after the exciton dissociation, free hole and the electron must drift to the electrodes thorough the interpenetrating network within their lifetimes. To fulfill these criteria is the basic idea of a BHJ cell. The cell performance can be increased by several physical treatments such as thermal annealing, white light or microwave irradiation, or by “solvent” and “solvent vapor” annealing [11,31–46].

The synthetic efforts to produce higher I_{sc} and/or V_{oc} have been concentrated mainly on the modification of donor molecules. Same time the effect of acceptor design has not been considered with same emphasis. However, acceptors have significant role in cell performance, as the excitons are created also in the acceptor phase and their molecular structure affects the film morphology and electron transfer properties. Therefore, an alternative way to enhance photovoltaic performance is to widen absorption range of an acceptor and to alter its structure to achieve better miscibility and energy level alignment between a donor and an acceptor by tailored synthetic modification. The most well-known and used electron acceptor materials in BHJ based OPVs are still PCBM and its C71 counterpart [47–50]. However, a wide variety of other functionalized analogs and hetero analogs have been proposed to improve their processability or HOMO–LUMO levels [51–66]. A variety of molecular structures, in which the electron donor and acceptor moieties are covalently linked to each other are also synthesized and studied for applications in photovoltaic devices. In most cases functionalized fullerene is linked to a single molecule, or to conjugated oligomeric or polymeric structures [67–73].

Eight fulleropyrrolidine derivatives with thiophene substituents ranging from 1 to 4 thiophene units were synthesized and used as electron acceptors in inverted BHJ based OPVs in the present study with P3HT as the electron donor material. The substituents were designed both to widen absorption spectra of the acceptor and to resemble molecular structure of P3HT to assist in formation of the interpenetrating network structure. Similar molecular entity in the acceptor and donor compounds is assumed to improve phase separation in the BHJ and photophysical interaction between the networks. This is expected to enhance photovoltaic efficiency of the OPVs. An additional phenyl substituent for PhC₆₀M, PhC₆₀Bi, PhC₆₀Ter was introduced to mimic PCBM. The fullerene derivatives were blended with P3HT to form BHJ structures similar to the P3HT:PCBM architecture. The photoactive film structures were studied by atomic force microscopy (AFM) and scanning electron microscope (SEM) imaging to clarify the effect of the thiophene chain on the film forming nature with P3HT. Finally, photovoltaic characteristics of the model solar cells were determined with an aim to establish correlation between the film structure and photovoltaic efficiency.

The molecules tested here resemble the fullerene derivatives studied in OPVs by Saravanan et al. [74] and Yoshimura et al. [75] who observed several advantages for substituting fullerene core

with a thiophene chain resembling the donor polymer. These studies are referenced in results analysis having many similarities with the results obtained here.

2. Experimental

2.1. Synthesis of fulleropyrrolidines

Fullerene C₆₀ was tailored with thiophene substituents to influence photoelectric properties of the compound and morphology of the BHJ (P3HT:C₆₀ derivative). The chemical structures of the newly synthesized fulleropyrrolidines are presented in Fig. 1. The syntheses were carried out according to Prato's standard fulleropyrrolidine synthetic method [76], described below.

2,2':5',2'':5'':2'''-Quaterthiophene-carboxaldehyde: a solution of 2,2':5',2'':5'':2'''-quaterthiophene (500 mg, 1.51 mmol) in 2.32 ml of DMF was added to Vilsmeier complex which was prepared by mixing of DMF (2.32 ml, 30 mmol) and POCl₃ (0.141 ml, 1.51 mmol) at 0 °C for 30 min in 100 ml RB flask and then heated at 90 °C for 3 h. Then the mixture was cooled at room temperature and kept on an ice bath. A saturated solution of NaOH was added into the flask to maintain the pH of the solution between 7 and 8. Then the mixture was filtered and yellow colored residue was collected and purified by silica column. The desired compound was obtained as a yellow solid eluted by hexane: chloroform (50:50 v/v) yield-47%. ¹H NMR (CDCl₃, 400 MHz), 7.10 ppm (m, 2H, Ar–H), 7.20 ppm (m, 2H, Ar–H), 7.25 ppm (t, 1H, Ar–H), 7.35 ppm (d, 1H, Ar–H), 7.50 ppm (d, 1H, Ar–H), 7.62 ppm (d, 2H, Ar–H), 10.02 ppm (s, 1H, –CHO).

3,3'''-Dihexyl-2,2':5',2'':5'':2'''-quaterthiophene-carboxaldehyde: 3,3'''-dihexyl-2,2':5',2'':5'':2'''-quaterthiophene (1.51 mmol) was taken and followed the same procedure as for 1 yield-45%. ¹H NMR (CDCl₃, 400 MHz), 0.90 ppm (m, 7H, alkyl H's), 1.20 ppm (m, 7H, alkyl H's), 1.70 ppm (m, 12H, alkyl H's), 6.95 ppm (d, 1H, Ar–H), 7.10 ppm (d, 1H, Ar–H), 7.15 ppm (d, 1H, Ar–H), 7.20 ppm (m, 1H, Ar–H), 7.28 ppm (m, 2H, Ar–H), 7.32 ppm (s, 1H, Ar–H), 10.05 ppm (s, 1H, –CHO).

Thiophene fulleropyrrolidine (C₆₀M): 2-thiophene carboxaldehyde (120 mg, 1.07 mmol), sarcosine (190 mg, 2.14 mmol) and fullerene 1.55 g (2.14 mmol) were kept in 250 ml RB flask then the mixture was refluxed for 16 h in 120 ml of toluene. Then the mixture was cooled at room temperature, and the solvent was evaporated. A black colored crude product was obtained and purified by silica column. The desired compound was obtained as a brown colored solid eluted by hot solvent of hexane: toluene (60:40 v/v) yield-43%. ¹H NMR (CDCl₃, 400 MHz), 2.98 ppm (s, 3H, –CH₃), 4.25 ppm (d, 1H, –CH₂), 5.01 ppm (d, 1H, –CH₂), 5.25 ppm (s, 1H, –CH), 7.10 ppm (t, 1H, Ar–H), 7.20 ppm (d, 1H, Ar–H), 7.40 ppm (d, 1H, Ar–H). ESI mass cald. 859.86, found 860.2.

Bithiophene fulleropyrrolidine (C₆₀Bi): 2,2'-bithiophene-5-carboxaldehyde (1.07 mmol) was taken and followed the same procedure as C₆₀M yield-41%. ¹H NMR (CDCl₃, 400 MHz), 2.98 ppm (s, 3H, –CH₃), 4.20 ppm (d, 1H, –CH₂), 4.98 ppm (d, 1H, –CH₂), 5.20 ppm (s, 1H, –CH), 7.00 ppm (t, 1H, Ar–H), 7.10 ppm (d, 1H, Ar–H), 7.20 ppm (m, 2H, Ar–H), 7.30 ppm (m, 1H, Ar–H) yield-130 mg (30%). ESI mass cald. 941.98, found 942.8.

Terthiophene fulleropyrrolidine (C₆₀Ter): 5-carboxaldehyde-2,2':5',2''-terthiophene (1.07 mmol) was taken and followed the same procedure as C₆₀M yield-38%. ¹H NMR (CDCl₃, 400 MHz), 2.98 ppm (s, 3H, –CH₃), 4.20 ppm (d, 1H, –CH₂), 5.00 ppm (d, 1H, –CH₂), 5.22 ppm (s, 1H, –CH), 7.00–7.20 ppm (m, 4H, Ar–H), 7.22 ppm (m, 2H, Ar–H), 7.24 ppm (m, 1H, Ar–H). ESI mass cald. 1024.1, found 1025.0.

Quaterthiophene fulleropyrrolidine (C₆₀TTh): 2,2':5',2'':5'':2'''-quaterthiophene-carboxaldehyde (1.07 mmol) was taken and the same procedure was followed as C₆₀M yield-39%. ¹H NMR (CDCl₃,

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