



The preparation and properties of bulk-heterojunction organic solar cells with indole-containing fulleropyrrolidine derivatives as acceptors



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ABSTRACT

Two indole-containing fullerene derivatives, *N*-hydrogen-2-[3-(*N*-2-ethylhexylindolyl)][60]fulleropyrrolidine (EHIHC60P), and *N*-(2-ethylhexylindolyl)-2-[3-(*N*-2-ethylhexylindolyl)][60]fulleropyrrolidine (DEHIC60P) were synthesized by the typical Prato reaction. The absorption spectra, electrochemical properties of the two compounds were measured. Inverted solar cells were fabricated with the structure of ITO/ZnO/poly(3-hexylthiophene) (P3HT):fullerene derivatives/MoO₃/Ag. The highest power conversion efficiencies (PCEs) of 3.32% and 3.23% were obtained for P3HT/EHIHC60P and P3HT/DEHIC60P based solar cells at the composite ratio of 1:1 after the active layers were annealed at 150 °C under inert atmosphere, with a open-circuit voltage (*V*_{oc}) of 0.66 V and 0.74 V, respectively. For comparison, the device based on P3HT/PCBM at the same conditions showed the PCE of 3.28%, with a *V*_{oc} of 0.61 V. The influence on the photovoltaic property of the fullerene derivatives, which was induced by some subtle changes in the chemical structure was compared and discussed.

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1. Introduction

Organic photovoltaic devices (OPVs) have been widely regarded as one of the candidates to solve the energy crisis, and attract an extensive attention due to their light weight, low cost, and flexible features.^{1–4} Since the introduction of bulk-heterojunction (BHJ) concept in 1995,⁵ organic solar cells with the BHJ active layer, which consists of conjugated polymer as donor and fullerene derivative as acceptor, have been extensively studied.^{6–10} Recently, the power conversion efficiency (PCE) of OPVs has exceeded 10%.¹¹ The donor–acceptor (D–A) type conjugated copolymers, which have broad range of light absorption, significantly enhance the light-harvesting ability of the active layers in the photovoltaic devices.¹² In the past decades, considerable efforts have been made on the design and preparation of novel D–A type conjugated donor materials. The innovation on the structure of D–A conjugated copolymers has become the main driving force to improve the efficiency of the photovoltaic device.¹³ In contrast, researches on the

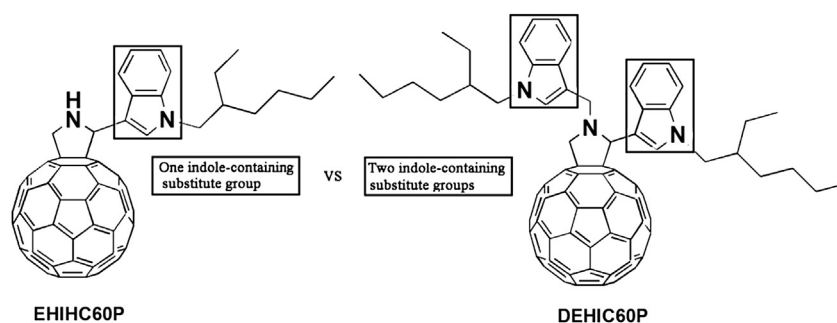
structure–property relationship of the acceptor materials are limited. Until now, the most widely used acceptor material is still phenyl-C61-butyrac acid methyl ester (PCBM),^{14,15} which offers good solubility in organic solvents, but also suffers from the drawbacks such as weak absorption in the visible region, relatively low lowest unoccupied molecular orbital (LUMO) energy, and large scale aggregation.^{16,17} Recently, more attentions have been paid on the development of new fullerene derivatives other than PCBM to further improve the performance of OPVs through the pathway of the acceptor materials.^{18–23} For instance, Li et al. reported a remarkable indene substituted fullerene bisadduct (ICBA).²⁴ OPVs based on poly(3-hexylthiophene) (P3HT)/ICBA showed PCE of 5.44% with *V*_{oc} of 0.84 V, and the PCE can be up to 6.5% after further device optimization.²⁵ Matsuo and co-workers reported OPVs with silylmethylfullerene (SIMEF) as acceptor, which showed higher PCE than that using PCBM.²⁶ Lately, a 54π-electron fullerene acceptor, called bis-TOQMF, has been developed and given the PCE of 4.56% when applied in OPVs by Ding et al.²⁷ Other fullerene derivatives, such as indolinone-substituted methanofullerene,²⁸ thieno-*o*-quinodimethane fullerene multi-adducts,²⁹ diarylmethanofullerene,³⁰ dibenzosuberane-substituted fullerene derivatives,³¹ 2-benzyl-1,2-dihydro[60]fullerenes,¹⁸ methanofullerene derivative,³² and alkoxy-substituted dihydronaphthyl-based [60]fullerene bisadduct derivatives,³³ were prepared and used as acceptors in the active

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layer of the photovoltaic devices. All the above reports indicated that new fullerene derivatives with proper energy levels, mobility, and compatibility also play a pivotal role in improving the performance of OPVs, and the photovoltaic properties of the fullerene derivatives could be tuned and optimized by altering the substitute groups on the fullerene derivatives.^{19,34}

Herein, two fulleropyrrolidine derivatives EHIHC60P and DEHIC60P were designed and prepared (the structures were shown in Scheme 1). In the case of EHIHC60P, 3-(*N*-2-ethylhexylindolyl) group was connected to the pyrrolidine ring. The indole-containing substitute group was selected due to its excellent electron-donating property.^{23,28} To further improve the photovoltaic performance of the indole-containing fulleropyrrolidine derivatives, the second indole-containing substituted group ((1-(2-ethylhexyl)-1*H*-indol-3-yl)methyl group) was introduced to the N atom of the pyrrolidine ring, thus the LUMO level of the fullerene derivative DEHIC60P (Scheme 1) could be further raised in some extent, which would result in higher V_{oc} values of photovoltaic devices.¹² Compared to the previously reports of the multi-adduct fullerene derivatives, our strategy has the advantage of avoiding the isomers and energy disorder while controllable enhancing the LUMO level of the acceptors.^{14,15,24,29–33} Meanwhile, ethylhexyl alkyl chain on nitrogen atom in the indole ring could improve the solubility of fulleropyrrolidine derivatives and miscibility with the donor polymers.³⁵ The structure–property relationship of fullerene derivatives was investigated. The influence on the photovoltaic property, which was induced by some subtle changes in the chemical structure such as the amount and connection mode of the electron-donating groups, was carefully compared and discussed.



Scheme 1. The design strategy and the structures of fulleropyrrolidine derivatives with one (EHIHC60P) or two (DEHIC60P) indole substitute groups.

2. Results and discussion

2.1. Synthesis

Indole-containing fullerene derivatives EHIHC60P and DEHIC60P were synthesized conveniently via a 1,3-dipolar cycloaddition reaction³⁶ (as shown in Scheme 2). The reaction time was optimized to avoid the multi-addition adducts, which could lead to a relative low yield of the target compound. EHIHC60P and DEHIC60P have good solubility in the common organic solvents such as chloroform, toluene, chlorobenzene, and *o*-dichlorobenzene. They are readily purified by column chromatography to give the target product in high purity.

2.2. Optical properties

Fig. 1 shows the ultraviolet–visible (UV–vis) absorption spectra of EHIHC60P and DEHIC60P in chloroform (10^{-5} mol/L). The absorption band in the region of 300–800 nm is similar for each derivative. As shown in the inset of Fig. 1, there is a sharp peak at

about 430 nm and a weak peak at about 700 nm, which is consistent with the literature.³⁷ These results clearly indicate that the absorption characteristics of the functionalized fullerene derivatives are governed by the π system of the fullerene. It is obvious that the absorption intensity of EHIHC60P and DEHIC60P is much stronger than that of PCBM at the same concentration, which could be due to the contribution of the indole functional groups. Meanwhile, DEHIC60P shows stronger absorption than EHIHC60P, which is expected to be beneficial to their application in OPVs. As shown in Table 1, the optical bandgaps estimated from the absorption edges of EHIHC60P and DEHIC60P are both 1.71 eV, which are almost same as that of PCBM (1.73 eV). The energy bandgaps did not show obvious change when the indole substitute groups were conjugation-interruptedly linked on fulleropyrrolidine ring.

2.3. Electrochemical properties

Electronic energy levels (especially the LUMO levels) of the fullerene derivatives are crucial for their application in OPVs as acceptors. To evaluate the redox behaviors of the synthesized fullerene derivatives, the electrochemical properties of EHIHC60P, DEHIC60P, and PCBM were measured by cyclic voltammetry (CV) in *o*-dichlorobenzene with 0.04 M Bu_4NPF_6 as the supporting electrolyte. Both fullerene derivatives exhibited three quasi-reversible reduction waves in the negative potential range from 0 to -2.5 V (vs Ag/AgCl) as shown in Fig. 2. The onset reduction potentials ($E_{\text{red}}^{\text{onset}}$) of EHIHC60P and DEHIC60P were slightly shifted to negative region, indicating higher LUMO en-

ergy levels than that of PCBM. It could be attributed to the electron-donating effect from the substituted indole groups on the fullerene ring, which raise the LUMO energy level. The LUMO energy levels of the fullerene derivatives were estimated from their onset reduction potentials according to the equation $\text{LUMO} = -[(E_{\text{red}}^{\text{onset}} - E_{\text{Fc}}) + E_{\text{ref}}]$ (eV), where E_{Fc} is the potential of the external standard, the ferrocene/ferrocenium ion (Fc/Fc^+) couple, and E_{ref} is the reference energy level of ferrocene (4.8 eV below the vacuum level; the vacuum level is defined as zero). The experimental values of EHIHC60P, DEHIC60P, and PCBM are summarized in Table 1, which also contains the theoretical energy levels calculated from the density functional theory (DFT) for comparison. As shown in Table 1, the LUMO energy levels of EHIHC60P and DEHIC60P are -3.65 and -3.60 eV, which are raised by 0.08 and 0.13 eV in comparison with that of PCBM (-3.73 eV), respectively. The experimental LUMO levels of the acceptors were in reasonable agreement with the calculated results. The higher LUMO energy levels are desirable for higher open-circuit voltages of OPVs. Frontier molecular orbital (HOMO and LUMO) for the acceptors is shown in Table S1.

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