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Reducible fabrication cost for P3HT-based organic solar cells by using one-step synthesized novel fullerene derivative

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ABSTRACT

The cyclohexanone-containing fullerene mono-adduct, abbreviated as $CHOC_{60}$, was efficiently prepared through single-step Diels-Alder reaction with 2-(trimethylsilyloxy)-l,3-butadiene and fullerenes. After reduction and esterification, $CHOC_{60}$ was further converted into cyclohexyl acetate functional fullerene mono-adduct, named as $CHAC_{60}$, which showed excellent solubility in common organic solvents. P3HT-based bulk heterojunction organic solar cells (OSCs) were fabricated through a typical structure of ITO/PEDOT:PSS/P3HT:($CHOC_{60}$ or $CHAC_{60}$)/Ca/Al. The composite ratios of P3HT and the fullerene derivatives were modified such as 1:0.5, 1:1 and 1:1.5 (w/w). The devices fabricated using $CHOC_{60}$ or $CHAC_{60}$ as acceptors achieved the power conversion efficiencies (PCEs) of 2.97% and 3.15%, respectively, which exhibited comparative photovoltaic performances with commercial $PC_{61}BM$. Moreover, $CHOC_{60}$-based devices significantly reduced the manufacturing cost by the simplified synthesis of $CHOC_{60}$ with high yield and low fullerene consumption. The non-aromatic side chain radical $CHOC_{60}$ and $CHAC_{60}$ provide a new idea for the design of fullerene derivative acceptors.

1. Introduction

Energy crisis is one of the most important global issues which mankind has faced over the last few decades. Depletion of traditional energy sources such as coal and oil demands the development of new energy systems for the producing and storage of electricity. Organic solar cells (OSCs) based on electron donors (D) and electron acceptors (A) heterojunction [1,2] have attracted much attention owing to the advantages which include low cost, light weight, and the capability to fabricate flexible large-area modules [3–8]. OSCs have already broken through the bottle neck of power conversion efficiency (PCE) above 10% owing to the rapid development of donors and interfacial materials [9–12]. However, the kinds of electron acceptors are relatively limited. To date, fullerene and their derivatives, particularly 6,6-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) and its C_{70}-based homologue ($PC_{71}BM$), are still the most successful electron acceptor materials for OSCs since fullerene derivatives possess unique advantages such as high electron affinity, small reorganization energy and good charge transport ability and even 3D electron transport property [13].

Although the fullerene-free OSCs exhibited dramatic improvement of PCEs during the past two years [14], the evolution of high performance nonfullerene acceptors is still a huge challenge. Generally, fullerene-free acceptors need proper solubility, crystallinity and reasonable energy levels. Furthermore, they should possess a rigid extended fused-ring backbone to decrease the reorganization energy and have wave functions in the lowest unoccupied molecular orbital (LUMO) that are delocalized to afford the opportunity for significant intermolecular electronic coupling. However, materials with fused-ring backbone usually demand complicated synthesis and purification procedures which increase the costs. Moreover, because of the lack of desirable stability for most of the high performance low-band gap polymer donors and non-fullerene acceptors, scientists still selected more suitable P3HT-$PC_{61}BM$ system for fabricating large-area roll-to-roll printable plastic OSCs [15–17]. Hence, in order to further reduce the costs of P3HT-based OSCs, the research of novel and easily synthesized fullerene acceptors with desirable yields, high purities and excellent photovoltaic performances remain indispensable [18–22].

In this work, two novel fullerene derivatives containing cyclohexyl group, $CHOC_{60}$ and $CHAC_{60}$, were reported. $CHOC_{60}$ was synthesized as electron acceptor through one-step Diels-Alder reaction with high purity (up to 99%) and high yield (up to 46%), making the fabrication costs of $CHOC_{60}$ much less than that of

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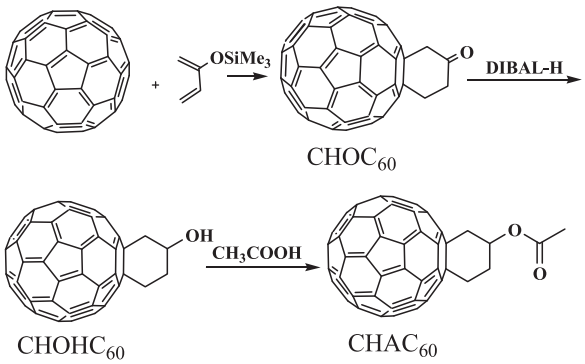

Scheme 1. Synthetic routes and chemical structures of $CHOC_{60}$ and $CHAC_{60}$.

commercially available $PC_{61}BM$ which was usually prepared in a three-step process [23]. After modification of $CHOC_{60}$ through reduction and esterification, $CHAC_{60}$ was formed which exhibited better solubility in common organic solvents. $CHOC_{60}$ and $CHAC_{60}$ showed similar frontier molecular orbital energy levels (especially LUMO energy level) and higher light-harvesting abilities in visible region compared with $PC_{61}BM$. Both of P3HT/$CHOC_{60}$-based OSCs and P3HT/$CHAC_{60}$-based OSCs exhibited nice photovoltaic performances. The chemical structures of fullerene acceptors used in this study and their synthetic routes are illustrated in Scheme 1.

2. Experiments

2.1. Materials

P3HT was synthesized according to the published literature [24]. $PC_{61}BM$ was purchased from American Dye Source and used as received. The ITO glasses ($\leq 15\ \Omega$/square, transmittance $> 85\%$) were purchased from Nippon Sheet Glass Company, Ltd, and cleaned sequentially with deionized water, acetone and isopropanol for 40 min each, then treated with UV-ozone for 20 min. PEDOT: PSS (Baytron□ P VP Al 4083) was purchased from Baytron Company.

2.2. Characterization and measurement

^1H and ^{13}C NMR spectra were collected with a Bruker DMX-400 Spectrometer. Elemental Analyzation was measured via PerkinElmer PE2400II Elemental Analyzer. Mass spectra were collected through Bruker Autoflex III MALDI-TOF-MS spectrometer. The UV–vis absorption spectra were measured by a Perkin-Elmer Lambda 950 spectrophotometer. Surface images and the roughness were conducted on a Veeco Dimension 3100V atomic force microscope. The cyclic voltammetry (CV) measurements were performed on a CHI 660D electrochemical workstation with a solution of tetrabutylammonium hexafluorophosphate (0.10 M) as the supporting electrolyte and material (10^{-3} M) in *O*-dichlorobenzene/acetonitrile (5:1) at a scan rate of 100 mV/s under argon atmosphere. A Pt electrode was used as working electrode. A Pt wire and an Ag/Ag^+ electrode were used as the counter electrode and reference electrode. XRD data were collected on Bruker AXS (D8 Discover) diffractometer.

Current density-voltage (*J-V*) characteristics of the devices were measured under the simulated solar light (100 mW/cm^2; AM 1.5G) provided by a Newport-Oriel® Sol3A 450W solar simulator and stored in Ar atmosphere without encapsulation. The device parameters were recorded with a Keithley 2440 Source Measure Unit. The intensity of the simulated solar light was calibrated by a standard Si photodiode detector (PV measurements Inc.), which was calibrated at National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) spectra were determined using a Newport-Oriel® IQE 200TM which was calibrated by standard Si/Ge solar cell under illumination with monochromatic light from a Xe lamp at room temperature in air. The thickness of films was measured on a surface profiler (Dektak 150).

2.3. Device fabrication

Organic photovoltaic devices with a typical sandwich structure of ITO/PEDOT:PSS/P3HT:Acceptor/Ca/Al were fabricated. PEDOT:PSS aqueous solution was filtered through 0.45 μm filter and spin-coated at 4000 rpm for 1 min onto the treated ITO substrate and baked on the hot plate at 120 °C for 20 min. The pre-dissolved composite solution was filtered by using 0.22 μm syringe filters, and the active layer was spin-cast from the filtered solution (P3HT concentration of 20 mg mL^{-1}) at 800 rpm for 60 s and thermally annealed at 110 °C for 10 min. Finally, the top electrodes consisting of Ca (20 nm) and Al electrode (100 nm) were evaporated under a vacuum as high as 3×10^{-6} Torr in vacuum chamber through a shadow mask to define the active area of the devices (12.57 mm^2).

2.4. Synthesis of $CHOC_{60}$ and $CHAC_{60}$

2.4.1. Synthesis of $CHOC_{60}$

A solution of 236.7 mg (1.67 mmol) of 2-(trimethylsilyloxy)-l,3-butadiene in 30 mL of dry toluene was added over 1 h via a syringe pump to a refluxing solution of 1.00 g (1.39 mmol) of C_{60} in 350 mL of dry toluene under argon. After complete addition, the reaction mixture was continued to stir for 24 h at 110 °C. The solvent was evaporated and the crude product was loaded on the top of a column packed with silica gel in hexanes and elution with hexanes/CS_2 (1:1) afforded unconsumed C_{60}. Further elution with toluene gave 510 mg (46%) of $CHOC_{60}$ as a shiny black crystalline material. ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ (ppm) 4.44 (bs, 2H), 3.94 (bs, 2H), 3.62 (t, 2H). ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ (ppm) 155.41, 155.25, 147.84, 146.64, 146.46, 146.43, 145.87, 145.77, 145.71, 145.64, 145.62, 145.27, 144.82, 144.78, 143.35, 142.80, 142.77, 142.25, 142.16, 142.16, 141.99, 141.91, 141.833, 140.59, 140.52, 135.19, 129.14, 128.39, 125.50, 63.13, 62.64, 52.02, 39.94, 37.88, 30.22. Elemental analysis for $C_{64}H_6O$: calculated: C, 97.21; H, 0.76; O, 2.02; found: C, 97.32, H, 7.95 (purity: 99.89%). MALDI-TOF MS: calculated for $C_{64}H_6O$, 791; found: 790.5 (M^+).

2.4.2. Synthesis of $CHOHC_{60}$

A solution of 300 mg (0.38 mmol) of $CHOC_{60}$ in 100 mL of dry toluene was added dropwise 1 mL (1 mmol) of a 1.0 M solution of diisobutylaluminum hydride in hexane at 25 °C. The reaction mixture was stirred for 5 h at 25 °C and then treated with 50 mL of saturated NH_4C1 for 3 h. The organic layer was separated and the aqueous layer was extracted with toluene (2×50 mL). The combined organic phases were dried over Na_2SO_4 followed by evaporation of the solvent. Flash chromatography on silica gel with toluene afforded 280 mg (93%) of $CHOHC_{60}$ as a black solid. ^1H NMR (400 MHz, $CDCl_3/CS_2$) δ (ppm) 5.21 (m, 1H), 3.78 (m, 1H), 3.68 (m, 1H), 3.55 (m, 1H), 3.35 (m, 1H), 3.26 (m, 1H), 2.68 (m, 1H), 1.99 (bs, 1H, OH). ^{13}C NMR (100 MHz, $CDCl_3/CS_2$) δ (ppm) 158.64, 157.65, 157.61, 157.35, 148.09, 146.87, 146.70, 146.44, 146.35, 146.16, 146.01, 145.92, 145.89, 145.85, 145.83, 145.28, 145.22, 145.14, 143.70, 143.06, 143.03, 143.00, 142.67, 142.55, 142.52, 142.47, 142.15, 142.13, 142.08, 142.05, 140.79, 140.74, 140.70, 136.32, 135.94, 135.72, 135.44, 66.87, 64.40, 63.18, 45.03, 35.94, 33.54. Elemental analysis for $C_{64}H_8O$: calculated: C, 96.96; H, 1.02; O, 2.02; found: C, 96.37, H, 6.95 (purity: 99.39%). MALDI-TOF MS: calculated for $C_{64}H_8O$, 793; found: 792.5 (M^+).