Low bandgap carbazole copolymers containing an electron-withdrawing side chain for solar cell applications

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ABSTRACT

A new series of low bandgap carbazole copolymers containing an electron-withdrawing moiety as a side chain, via Suzuki, Yamamoto, and Stille polymerization reactions has been synthesized. Their bandgaps and molecular energy levels can be tuned by copolymerizing with different conjugated electron-donating units. The resulting copolymers have low optical and electrochemical bandgaps. The optical bandgaps of the copolymers range from 1.79 to 1.24 eV. In order to investigate their photovoltaic properties, polymer solar cell devices based on low bandgap copolymers were fabricated with a structure of ITO/PEDOT:PSS/copolymers:PCBM/Al, under the illumination of AM 1.5 G, 100 mW/cm^2. The power conversion efficiencies (PCE) of the polymer solar cells based on these low bandgap copolymers were measured. The best performance was obtained by using PC-CARB as the electron donor and 6,6-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) as the electron acceptor. The PCE of the solar cell based on PC-CARB/$P_{71}CBM$ (1:4) was 1.27% with an open-circuit voltage (V_{oc}) of 0.65 V, and a short-circuit current (J_{sc}) of 6.69 mA/cm^2.

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1. Introduction

Polymer solar cells have attracted a lot of attention in recent years due to their potential use for new generation renewable energy sources [1–4]. They have the advantages of low cost, light weight, flexibility, and easy manufacture [5–8]. The most commonly used polymer solar cell device structure is the bulk heterojunction (BHJ) structure due to its high efficiency [9–14]. In this structure, an electron-donating conjugated polymer blends with an electron acceptor, such as 6,6-biphenylC61-butyric acid methyl ester (PCBM), as the active layer. After photoexcitation, electrons transfer from the excited conjugated polymer chains to the electron acceptor molecules (PCBM). The donor–acceptor (D–A) BHJ structure has been considered ideal for efficient and fast exciton dissociation, and charge transport can be enhanced by the increase in interfacial area between the donor and acceptor [15–17]. The D–A BHJ solar cells give power conversion efficiencies in the range of 4–7% [18–21]. Compared to inorganic solar cells, the PCE of polymer solar cells is still too low for commercial application. For the conjugated polymer part, further improvement of PCE demands the development of new materials with

higher carrier mobility and broader absorption of the solar spectrum [22–24].

Intramolecular donor–acceptor systems typically consist of electron-donating groups (electron rich segments), and electron acceptors (electron deficient segments) [25–28]. The incorporation of electron-withdrawing moieties as side chains of a conjugated polymer can widen the absorption spectrum. After photoexcitation, the charge separation occurs through transfer of electrons from the main chains to the side chains, and then to PCBM. Electrons can transfer at PCBM by hopping, and holes can transfer at the main chains of the polymer by hopping and delocalization. Therefore, conjugated polymers containing electron-withdrawing acceptors as side chains not only exhibit enhanced charge transfer ability, but also absorb light more effectively [29].

In this paper, we report the synthesis of a new donor–acceptor monomer (Br$_2$-CARB-NAP) with an electron-withdrawing moiety as a side chain. It was copolymerized with different kinds of electron-donating monomers containing an alkyl side chain to prepare a new series of low bandgap copolymers. In the donor–acceptor monomer, the donor is the electron rich carbazole, and the acceptor is the electron deficient 14H-benzo[4,5]isoquino[2,1-a]perimidin-14-one. In this work, we selected typical conjugated building blocks to tune the absorption spectra and molecular energy levels to match the requirements of an ideal donor polymer [30]. The highest occupied

molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of an ideal donor polymer are −5.4 and −3.9 eV, respectively [30]. Several commonly used conjugated blocks such as 9-(4-n-octyl-phenyl)-9H-carbazole, 9,9-dioctylfluorene, 3-hexyl-thiophene, and ethene were copolymerized with Br$_2$-CARB-NAP to investigate the relationships between their structures and properties [18,31–35]. The optical and electrochemical properties of the low band gap copolymers and the performance of the solar cells based on the copolymers were evaluated.

2. Experimental

2.1. Materials

Pd(OAc)$_2$, 1,8-diaminonaphthalene, 4-bromo-1,8-naphthali-canhydride, bis(1,5-cyclooctadiene)nickel(0), methane-sulfonic acid (MSA), and 9,9-dioctyl- fluorene-2,7-diboronic acid bis(1,3-propanediol) ester were obtained from Aldrich Chemicals. Toluene, chloroform, dichlorobenzene, tetrahydrofuran (THF), acetone and 1-methyl-2-pyrrolidinone (NMP) were purchased from TEDIA. PBu$_3^t$ was obtained from Strem Chemicals. PEDOT:PSS was purchased form Bayer. 6.6-Phenyl C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) and 6.6-Phenyl C$_{71}$-butyric acid methyl ester (PC$_{71}$BM) were obtained from FEM Technology Co., Inc. Tetrakis (triphenyl-phosphine)Pd(0), Aliquat 336, 2,2-dipyridyl, and N-bromo-succinimide (NBS) were purchased from Acros Organics. (E)-1,2-bis(tributylstannyl) ethane were purchased from TCI Organics. All other chemicals were purchased from Aldrich and used as received.

2.2. Measurements and characterization

^{1}H NMR spectra were collected on a Brucker Advance 400 spectrometer. Molecular weight determination was obtained by using a Waters GPC 2414 in tetrahydrofuran (THF) via a calibration curve of polystyrene standards. Fourier Transform Infared Spectra (FTIR) were collected on a Jasco Model–460 Spectrometer. Thermal stability was analyzed using a TA Instrument Thermogravi-metric Analyzer (TGA) Model 2050 at a heating rate of 10 °C/min under nitrogen. The glass transition temperature (T_g) was determined on a TA Instruments Model 2920 Differential Scanning Calorimeter (DSC) at a heating rate of 10 °C/min under nitrogen. Ultraviolet–visible (UV/vis) absorption spectra were recorded on a Hitachi U-2001 spectrophotometer. The electrochemical measurements of the copolymer were carried out on a potentiostat/galvanostat Autolab PGSTAT30 with a platinum electrode at a scan rate of 50 mV/s against an Ag/AgCl reference electrode with a nitrogen-saturated solution of 0.1 M tetra-butylammonium hexafluorophosphate (TBAPF) in acet-onitrile. The polymer film electrode was prepared by first dissolving the copolymers in 1,2-dichlorobenzene, and then drop-casting a film onto a glassy carbon disc electrode. The electrode was allowed to dry for 30 min at room temperature. The transmission electron micro-scopy (TEM) images of the polymer/PC$_{61}$BM films were obtained with a JEOL JEM-1200EX transmission electron microscope. The thickness of the polymer films were measured with a KLA-Tencor/AS-IQ new Alpha-Step Profilometer.

2.3. Synthesis of monomers

2.3.1. 11-Bromo-14H-benzo[4,5]isoquino[2,1-a]perimidin-14-one (BNI-NAP)

To a 100 mL round-bottom flask containing 1 g (3.6 mmol) of 4-bromo-1,8-naphthalic anhydride in 30 ml of NMP, 0.57 g (3.6 mmol) of 1,8-diamino-naphthalene was added. Two drops of methanesulfonic acid (MSA) were added as a catalyst. The mixture was slowly heated to 100 °C, and kept at that tempera-ture for half an hour. Then, the mixture was heated to reflux for 24 h. After 24 h, the dark-red reaction mixture was cooled to room temperature, and an orange product precipitated out from the reaction mixture. The product was isolated by filtration, and washed with a minimum amount of NMP followed by recrystalli-zation from NMP. The solid was dried in vacuum at 130 °C for 24 h. A brown powder (BNI-NAP) was obtained. The yield was 88%; mp: 247 °C. The synthetic route is shown in Scheme 1. FT-IR: 1682 cm^{-1} (C=O). ^{1}H NMR (400 MHz, DMSO-d$_6$, ppm): 7.55 ppm (t, 2H), 8.06–8.12 ppm (m, 4H), 8.31 ppm (t, 1H), 8.41 ppm (s, 1H), 8.54–8.8 ppm (m, 2H), 8.9 ppm (m, 1H).

2.3.2. 11-Carbazol-14H-benzo[4,5]isoquino[2,1-a]perimidin-14-one (CARB-NAP)

Pd(OAc)$_2$ (23 mg, 0.1 mmol), PBu$_3^t$ (1.6 ml, 0.25 M in o-xylene, 0.4 mmol), BNI-NAP (1 g, 2.5 mmol), carbazole (0.434 g, 2.6 mmol), sodium tertiary butoxide (0.306 g, 3.2 mmol), and o-xylene (40 ml) were mixed at room temperature in a three neck round-bottom flask, and heated to reflux for 12 h under argon. After addition of water and extractive work-up with chloroform, o-xylene was stripped off in vacuum. The residue was recrystallized from methanol: chloroform (2:8) to give CARB-NAP. The synthetic route is shown in Scheme 1.
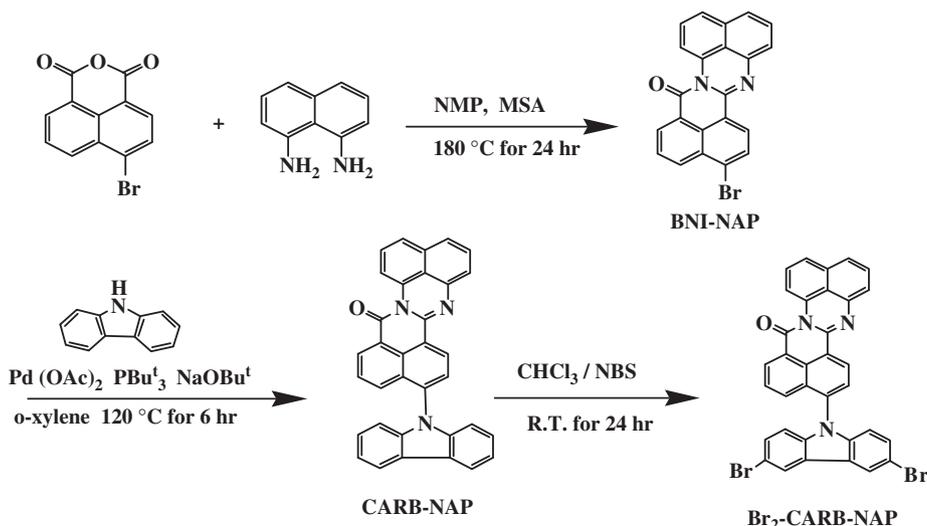
Scheme 1. Synthesis of Br$_2$-CARB-NAP.