



Research paper

Synthesis and characterizations of carbazole–isoindigo–carbazole oligomers for photovoltaic application



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ABSTRACT

6,6'-Dibromo-*N,N'*-(2-octyldodecanyl)isoindigo was coupled to either 4-(*N*-carbazolyl)phenyl boronic acid or 9-phenyl-9H-carbazole-3-boronic acid to give two different conjugated molecules of P-II-P and C-II-C, respectively. The optical band gap/HOMO levels of P-II-P and C-II-C were 1.90/–5.60 eV and 1.85/–5.39 eV, respectively. Based on the experimental and calculation data, C-II-C is more highly conjugated than P-II-P. The performances of C-II-C-based photovoltaic devices were better than those of P-II-P-based devices, with the best power conversion efficiency of 0.44%.

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1. Introduction

During the last two decades, conjugated polymer-based organic solar cells have been actively investigated [1,2], and the world champion organic cells reported a power conversion efficiency (PCE) greater than 11% [3]. Development of new low bandgap polymers to further enhance the PCE of single solar cells is still a challenge [4–6]. However, development of *p*-type polymers for organic solar cells has been limited by several factors, such as complex synthetic procedures, broad molecular weight distribution and difficult purification [7,8]. In contrast, *p*-type small molecules or oligomers have advantages that include relatively simple and reproducible synthetic procedures, a well-defined chemical structure, and high purity, resulting in PCEs over 6% [9–11].

For maximized solar energy harvest, the *p*-type materials are required to exhibit a high absorbance (high absorption coefficient) and broad absorption range (small band gap). In addition, a nanostructured morphology is also required in the presence of an *n*-type material, such as [6,6]-phenyl C₇₁ butyric acid methyl ester (PC₇₁-BM), for efficient charge separation and charge transfer in the photoactive layer of solar cells. The *p*-type material should also have appropriate energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for efficient separation of excitons into holes and electrons in photoactive

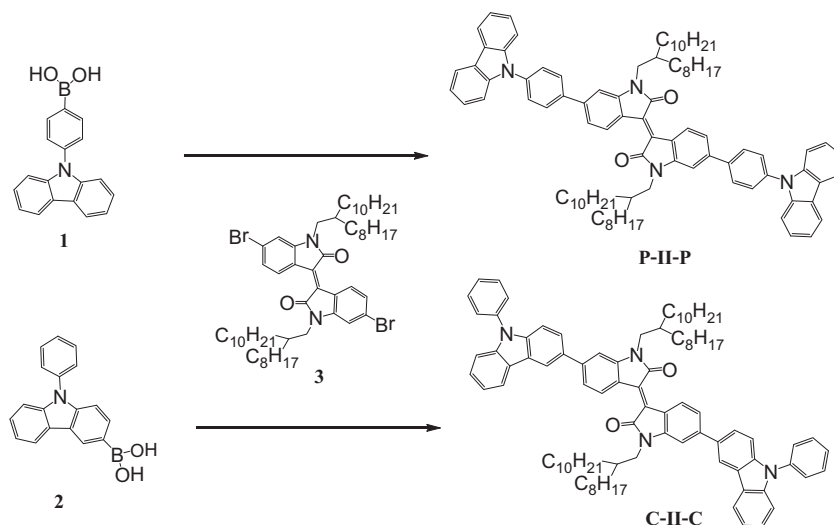
layers, as well as high open-circuit voltage (V_{oc}) of the resulting solar cells. One of the synthetic strategies to synthesize such *p*-type organic molecules is a suitable combination of an electron-donor with an electron-acceptor [12–14].

The PCE of organic photovoltaics is well-known to be proportional to three parameters: V_{oc} , short circuit current (J_{sc}), and fill factor (FF). The V_{oc} is closely related to the energy difference between the HOMO of the *p*-type material and the LUMO of the *n*-type material in a cell. The J_{sc} is highly dependent on the bandgap of donor materials, corresponding to the energy difference of the HOMO and LUMO of a compound [15], which can be generally increased by reducing the bandgap of the *p*-type materials due to extending the absorption to a longer wavelength range.

Isoindigo is a strong electron-acceptor that can cause the HOMO level of the resulting *p*-type material to be sufficiently deep, similar to diketopyrrolopyrrole [16–18]. Isoindigo is well known to be easily prepared in bulk quantities. Furthermore, its optical and electrochemical properties can be changed with substitution [19]. On the other hand, carbazole is well known as an electron-donor with a low-lying HOMO energy level and has been used in the synthesis of *p*-type materials [20–24]. PCEs of a fluorinated isoindigo–dithienocarbazole polymer and isoindigo–dithienocarbazole–isoindigo oligomer based solar cells were reported to be 7.5% [23] and 1.13% [21], respectively. Thus, it is interesting to study conjugated compounds consisting of isoindigo and carbazole units, but such chemical structures have not been reported yet in the literature.

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Scheme 1. Synthetic routes to P-II-P and C-II-C.

In this work, we attempted to synthesize two different conjugated compounds by connecting two identical carbazoles to (2-octyldodecanyl)isoindio (II) via Suzuki coupling: (1) two identical carbazole (C) units are linked to II through *N*-phenyl rings (P-II-P), and (2) two identical C moieties are directly linked to II (C-II-C) (Scheme 1). This paper describes the synthesis and basic characterizations, including thermal, optical, electrochemical properties, and performances in photovoltaic devices.

2. Experimental

2.1. Synthesis

4-(9H-Carbazole-9-yl)phenylboronic acid (1). Compound **1** was prepared from 9-(4-bromophenyl)carbazole, according to a reported procedure [25]. $^1\text{H NMR}$ (CDCl_3 , 500 MHz, ppm): 8.57 (d, 2H), 8.18 (d, 2H), 7.80 (d, 2H), 7.57 (d, 2H), 7.46 (m, 2H), 7.34 (m, 2H).

9-Phenyl-9H-carbazole-3-boronic acid (2). Compound **2** was prepared from 3-bromo-9-phenyl-9H-carbazole, according to a reported procedure [26]. $^1\text{H NMR}$ (CDCl_3 , 500 MHz, ppm): 9.12 (s, 1H), 8.37 (d, 2H), 7.60–7.66 (m, 4H), 7.52 (m, 2H), 7.45 (m, 2H), 7.39 (m, 1H).

6,6'-Dibromo-*N,N'*-(2-octyldodecanyl)-isoindigo (3). Compound **3** was prepared from furan-2-carbonitrile, according to a reported procedure [27]. $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): 8.62 (d, 2H), 7.22 (d, 2H), 3.91 (d, 4H), 1.88 (m, 2H), 1.21 (m, 64H), 0.86 (m, 12H); Anal. Calculated for $\text{C}_{54}\text{H}_{86}\text{Br}_2\text{N}_2\text{O}_2\text{S}_2$: C, 63.64; H, 8.50; N, 2.75; S, 6.29. Found: C, 63.67; H, 8.62; N, 3.19; S, 6.97.

P-II-P. Compound **3** (300 mg, 0.255 mmol), compound **1** (219 mg, 0.764 mmol), $\text{Pd}(\text{PPh}_3)_4$ (41 mg, 0.0255 mmol), and potassium carbonate (350 mg, 2.55 mmol) were dissolved in THF (25 mL). The solution was refluxed at 75 °C for 26 h. The reaction was quenched by adding water and the organic phase was extracted with dichloromethane. The combined organic solution was washed with a saturated aqueous sodium chloride solution, dried over magnesium sulfate, and concentrated under a reduced pressure. The crude product was purified by column chromatography (silica gel, hexane/dichloromethane = 4/1), to give a red solid (0.18 g, yield: 50%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): 9.40 (d, 2H), 9.23 (s, 2H), 8.26 (d, 2H), 7.68–7.63 (dd, 2H), 7.60–7.50 (b, 9H), 7.46–7.34 (b, 11H), 7.30–7.24 (b, 2H), 7.10 (s, 2H), 3.75–3.71 (d, 4H), 1.99–1.93 (b, 2H), 1.39–1.09 (b, 78H), 0.79–0.72 (b, 15H). Anal.

Calculated for $\text{C}_{75}\text{H}_{102}\text{N}_2\text{O}_2$: C 83.62; H 8.58; N 4.29. Found: C 83.54; H 9.26; N 4.19.

C-II-C. Compound **3** (250 mg, 0.255 mmol), compound **2** (219 mg, 0.764 mmol), $\text{Pd}(\text{PPh}_3)_4$ (30 mg, 0.0255 mmol), and potassium carbonate (350 mg, 2.54 mmol) were dissolved in 15 mL THF. The solution was refluxed at 75 °C for 26 h. The reaction mixture was separated by the same procedure as above to yield a red solid (0.18 g, 55%). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): 9.23 (d, 2H), 8.35 (s, 2H), 8.16 (d, 2H), 7.67–7.63 (dd, 2H), 7.60–7.51 (b, 9H), 7.46–7.34 (b, 11H), 7.29–7.24 (b, 2H), 7.07 (s, 2H), 3.75–3.71 (d, 4H), 1.99–1.93 (b, 2H), 1.39–1.09 (b, 78H), 0.79–0.72 (b, 15H). Anal. Calculated for $\text{C}_{75}\text{H}_{102}\text{N}_2\text{O}_2$, C 83.62; H 8.58; N 4.29. Found: C 83.43; H 8.94; N 4.12.

2.2. Measurement

$^1\text{H NMR}$ spectra were recorded on a JEOL FT-NMR (400 MHz) spectrophotometer in CDCl_3 . UV–visible spectra were obtained using a V-670 (JASCO) spectrophotometer. Elemental analyses were performed using a CE Instruments Flash EA 1112 series element analyzer. Thermogravimetric analysis (TGA) was performed on a TA Q-50 at a scanning rate of 10 °C min^{-1} under nitrogen. Differential scanning calorimetry (DSC) experiments were carried out on a TA Instrument (DSC2910) at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Cyclic voltammetry (CV) for films deposited on ITO glass in an acetonitrile solution of 0.1 M *n*- Bu_4NPF_6 was performed on a VersaSTAT3 (METEK) cyclic voltammeter at a scanning rate of 50 mV s^{-1} under argon at room temperature. Atomic force microscopy (AFM) was carried out on a MultiMode + BioScope (Digital Instruments) in tapping mode.

2.3. Fabrication of photovoltaic devices

Photovoltaic devices with active areas of 9 mm^2 were fabricated with the configuration ITO/PEDOT:PSS/P-II-P(or C-II-C): PC_{71}BM /LiF/Al. Patterned indium tin oxide (ITO) glass was prepared by ultrasonic cleaning with deionized water, acetone, and isopropyl alcohol, and then treated with UV and ozone. PEDOT:PSS was spin-coated onto the prepared ITO glass (30 nm) and dried at 140 °C for 20 min under nitrogen. Blends of P-II-P (or C-II-C) with PC_{71}BM (110 nm) in chlorobenzene (20 mg/ml) were spin-coated onto the PEDOT:PSS layer (~110 nm) of ITO for 40 s at a speed of 800 rpm in a nitrogen-filled glove box. LiF (0.5 nm) and Al

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