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Synthesis and photophysical characterization of isoindigo building blocks as molecular acceptors for organic photovoltaics



SPECTROCHIMICA

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1. Introduction

Recently, bulk heterojunction organic solar cells (BHJ-OSCs) which use conjugated polymers and fullerene derivatives as donor and acceptor components, respectively, are frequently encountered in solar energy conversion technologies. These types of OSCs give the highly efficient performances with the power conversion efficiency (PCE) of over 10% [1,2]. Even though polymer OSCs exhibit highly efficient solar cell performance, some difficulties of polymers in their synthetic reproducibility, purification of structure, and molecular weight distribution of main structure are major problems to overcome in the field of commercialization for this kind of polymeric donors [3,4]. Small molecule donors for OSC applications with efficient PCE value over 10% [5] have gained as an alternative structure to their polymeric counterparts because of their high purities, well-defined chemical compositions and good solution processabilities [6-8]. Although most OSCs have used fullerene derivatives in the active layers, there have been some undesirable properties for fullerene acceptors including their weak absorption in the vis-NIR regions, limited tunability of their electron affinities, thermal and photochemical instabilities [9,10]. During the last years nonfullerene small molecule organic acceptors have been extensively used and given the much higher PCEs in the range of 11–13% [11–13].

Researchers have designed and developed conjugated small molecules with electron donor-acceptor (D-A) forms in order to obtain highly effective component for OSC devices. It is known that

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ABSTRACT

Five isoindigo-based donor-acceptor-donor (D-A-D) type small molecules have been synthesized in order to investigate their intramolecular charge transfer characteristics. UV-vis absorption of these dyes exhibits a wide absorption band ranging from 300 to 650 nm with two distinct bands, giving the narrow bandgaps between 1.72 and 1.85 eV. Taking into account their HOMO-LUMO energy levels and bandgaps, isoindigo dyes have been used in the active layer of organic solar cell (OSC) devices. When these small molecule semiconductors were used as acceptors with the donor poly(3-hexylthiophene-2,5-diyl (P3HT) polymer in the inverted OSC devices, the highest power conversion efficiency (PCE) was obtained as 0.10% for pyrene-substituted isoindigo derivative. © 2018 Elsevier B.V. All rights reserved.

intramolecular charge transfer (ICT) process between the donor and acceptor side of the molecule reduces the bandgap and lowers the LUMO energy level of the molecule in addition improves charge transport ability of small molecules [14–16]. These are considered some of the main strategies to overcome high efficiency in OSC devices.

Among promising small molecule organic semiconductors, isoindigo dyes get much higher attention because of their outstanding properties such as good electron-accepting capability, quite planar structure, and great availability from natural resources, and easy functionalization by side chain reactions [17,18]. Isoindigo is naturally found in the leaves of *Isatis tinctoria* as a minor isomer of indigo dye [19]. The isoindigo structure is virtually insoluble in common organic solvents due to the intermolecular hydrogen bonding among the lactam rings and due to their strong π - π stacking. Generally, branched alkyl groups can be attached to nitrogen atom of the lactam ring to render them soluble in common organic solvents [17,18]. After the first introduction of isoindigo dyes in OSC applications reported by Reynolds et al. in 2010 [20], researches are mainly focused on the synthesis of conjugated polymer structures of isoindigo derivatives giving high cell efficiencies in the literature [21–27]. In addition, isoindigo-based small molecules have been used in OSC devices giving moderately high cell efficiencies [18,28–33]. Elsawy et al. in 2013 investigated electron-donating effect of different thiophene chains on OSC device performance of isoindigo dye and reported 3.2% cell efficiency for D-A-D type isoindigo dye containing three conjugated thiophene rings. They proved that enhanced ICT in isoindigo dye shifts the absorption to red region of solar spectra [28]. Relatively much lower PCE of isoindigo-based small molecules is generally ascribed to charge transport inefficiencies and morphology

problems [34]. Different electron donor groups were attached to isoindigo-like molecules in order to get better cell efficiency by changing the optoelectronic properties, solution-processabilities, and solid state morphology [34].

In this work, we have synthesized five different isoindigo-based D-A-D type dyes with different donor functional groups including pyrene, indole, benzimidazole, dibenzothiophene, and carbazole donors. Scheme 1 illustrates the molecular structure of the synthesized dyes. Structure-optical property relationship was investigated in different solvents, especially taking into account ICT possibilities. Effect of the different electron donating strengths on photovoltaic performance of inverted BHJ-OSC devices using isoindigo core as acceptor component was compared.

2. Experimental

2.1. Materials and Reagents

Zinc powder, 2,5-dibromonitrobenzene, diethylmalonate, 6bromoisatin, 2-ethylhexyl bromide, *tetrakis*(triphenylphosphine)palladium (0) (Pd(PPh₃)₄), pyrene-1-boronic acid, 5-formyl-2-thienyl boronic acid, 5-indole boronic acid, dibenzothiophene-2-boronic acid and 9-ethylcarbazole-3-boronic acid were obtained from Sigma Aldrich, and they were used without further purification. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification.

2.2. Analytical Instruments

¹H NMR and ¹³C NMR spectra were recorded using a Bruker 400 MHz spectrometer, with tetramethylsilane (TMS) as the internal reference, chemical shifts were recorded in ppm. FT-IR spectra were recorded on a Perkin Elmer-Spectrum BX spectrophotometer preparing KBr pellets. UV–Vis absorption spectra were recorded on a Perkin Elmer Lambda 950 spectrophotometer. The fluorescence emission and time-resolved fluorescence spectra of Isoi-(IV-VIII) dyes have been measured by using FLS 920 Edinburg instrument. Single photon counting measurements have been taken at the excitation wavelength of 472.4 nm on an apparatus described elsewhere [37]. Fluorescence decays were analyzed globally using exponential tail fit method [38]. Fluorescence decay data were collected at $\lambda_{detection} = 560$ nm for the dyes in toluene solution. The quality of the fits has been judged by the fitting parameters such as $\chi^2 \leq 1.2$ [39].

Cyclic voltammetry (CV) measurements of compounds Isoi-(IV– VIII) dyes in MeCN solution were measured using 100 mM [TBA][PF₆] as the electrolyte in a CH instruments 660B-Electrochemical Workstation at a scan rate of 100 mV/s. Ferrocene was used as the internal standard and its oxidation potential was detected at +0.57 V. A standard three-electrode configuration cell composed of a platinum wire auxiliary electrode, a glassy carbon working electrode, and an Ag/Ag⁺ reference electrode (SCE) was used to measure the oxidation and reduction potentials of the target compounds. The HOMO and LUMO energy levels were calculated from the CV measurements using the given equations below [40]:

$$E_{HOMO} = -e(E_{ox}^{onset} + 4.8); E_{LUMO} = -e(E_{red}^{onset} + 4.8);$$

 $E_{g}^{opt} = {}^{1240}/{}_{\lambda_{obs}^{onset}}; E_{HOMO} = E_{LUMO} - E_{g}^{opt}$

Theoretical calculation was carried out by using density functional theory (DFT) [41] at the B3LYP/6-31G(d) [37] basis with the Gaussian 09 package in order to provide an insight into the disparity in molecular conformation of synthesized small molecules.

2.3. Fabrication and Characterization of OPV Devices

The inverted solar cells were fabricated as follows: ITO/TiO₂/Active layer/MoO₃/Ag common sandwich structure. Scheme 2 shows the schematic illustration of inverted solar cells. The indium tin oxide (ITO) coated glass substrates (sheet resistance = $15 \Omega/sq$) were cleaned in an ultrasonic bath with deionized water, acetone and isopropyl alcohol for 20 min at 50 °C in each step, respectively. Titanium dioxide (TiO₂) solution was synthesized with sol-gel method [42]. Prior to coated, TiO₂ solution was filtered through a 0.45 µm filter. Then, TiO₂ as a cathode buffer layer was coated on the ITO at 1500 rpm for 1 min with spin coating technique. Next, each sample was transferred to a muffle furnace and annealed at 300 °C for 5 min, then 500 °C for 1 h. The photoactive layer was deposited on the TiO₂ layer at 1500 rpm for 1 min as a solution of P3HT and Isoi-(IV-VIII) (1:1 w/w) in chlorobenzene (with concentrations of 20 mg/mL) with spin coater at room temperature in ambient condition. Then, the photoactive layers were thermally annealed at 110 °C for 10 min in glove box. To complete device fabrication, MoO₃/Ag (10 nm/55 nm) top electrodes were deposited by thermal evaporation high vacuum at 2×10^{-6} Torr through a shadow mask with a device area of 0.15 cm². The deposited rate for MoO₃ and Ag were 0.3 and 0.7 Å/s, respectively.



Scheme 1. The synthetic route to Isoi-(IV-VIII) dyes. (i) K₂CO₃, dried DMF, 50 °C, 18 h, Zn(s) H₂SO₄, H₂O, EtOH (1:1:3) [35], (ii) acetic acid, HCl, 26 h, reflux [35], (iii) 2-ethylhexyl bromide, DMF, K₂CO₃, 100 °C [35], (iv) boronic acid derivative, 2 M Na₂CO₃, Pd(PPh₃)₄, EtOH/benzene, 85 °C [36].

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