



Linear and propeller-like fluoro-isoindigo based donor–acceptor small molecules for organic solar cells



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ABSTRACT

Two donor–acceptor type fluoro-isoindigo based small molecule semiconductors are synthesized and their optical, electrochemical, thermal, and charge transport properties are investigated. The two molecular chromophores differ by their architecture, linear (**M1**) vs propeller-like (**M2**). Both molecules present a broad absorption in the visible range and a low optical HOMO–LUMO gap (~ 1.6 eV). AFM images of solution-processed thin films show that the trigonal molecule **M2** forms highly oriented fibrils after a few seconds of solvent vapor annealing. The materials are evaluated as electron donor components in bulk heterojunction organic solar cells using PC₆₁BM as the electron acceptor. The devices based on the propeller-like molecule **M2** exhibit a high open-circuit voltage (around 1.0 V) and a power conversion efficiency of 2.23%.

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1. Introduction

Solution-processed bulk heterojunction (BHJ) organic solar cells (OSCs) have great potential as renewable energy sources because of a number of appealing features such as low cost, light weight, aesthetics and facile large-area fabrication on flexible substrates [1–8]. The power conver-

sion efficiency (PCE) of polymer:fullerene BHJ solar cells has improved rapidly over the past few years, from below 1% to over 9% [9–18]. However, some disadvantages related to the polymer nature of the electron donor materials may limit their future practical applications, such as difficult purification, batch-to-batch variations, broad molar mass distributions, and end-group contaminations. Solution-processable small molecule donor materials have a few advantages compared to their polymer counterparts, such as simpler purification, well-defined molecular structures and molar mass, high mobility and high purity with minimal batch-to-batch variations [19,20].

The most critical challenge in developing ideal small molecule donors is to combine appropriate (physicochemical) structural properties such as solubility and miscibility

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(to achieve an optimal blend with the fullerene acceptor in the active layer), well-matching HOMO–LUMO energy levels (to ensure a good charge separation and high open-circuit voltage, V_{oc}), and a high crystallinity (to ensure high hole mobility). Amongst all the strategies used to reach those desired properties, the combination of electron-rich (donor, D) and electron-deficient (acceptor, A) repeating units, forming intramolecular donor–acceptor (D–A) structures, has been very successful for developing low bandgap materials with tuned frontier orbital energy levels [21]. Various D–A type small molecules based on a variety of electron-deficient groups such as squaraine [22], benzotriazole [23], alkyl cyanoacetate [24], diketopyrrolopyrrole [25], benzothiadiazole [26], and isoindigo [27], most often combined with electron-donating oligothiophenes and arylamines, have been reported. To date, the highest PCEs for small molecule:fullerene BHJ OSCs are in the range of 7–10% [28–33].

As a strong electron-deficient molecule, isoindigo has widely been used as a building block for the preparation of D–A conjugated systems for organic electronics [27]. Compared to other electron-poor moieties, isoindigo can be obtained easily from natural sources and the planar π -conjugated symmetrical structure of isoindigo induces high crystallinity [34]. The first isoindigo based conjugated oligomeric D–A chromophore was reported by Reynolds et al. [35]. Since then, a variety of isoindigo based D–A conjugated materials has been successfully incorporated in OSCs, affording relatively high efficiencies [36–38]. This includes both D–A oligomer and copolymer donor materials as well as *n*-type copolymers and dyes for metal-free dye-sensitized solar cells. A PCE of 3.2% for solution-processed organic photovoltaic devices using a linear D–A–D isoindigo based small molecule in combination with PC₇₁BM ([6,6]-phenyl-C₇₁-butyric acid methyl ester) was achieved by Lee et al. [39] still quite far below that of isoindigo based polymer:fullerene devices (with a maximum PCE of 7.3%) [40–44]. Recent developments on isoindigo containing molecular semiconductors mainly focus on linear D–A–D or A–D–A conjugated systems. Nevertheless, ‘propeller-like’ (often designated as ‘star-like’) small molecules have been regarded as promising candidates for photovoltaics due to their 3D electron delocalization [45–50]. Propeller-like molecules with D–A structures allow easy tuning of the HOMO–LUMO energy levels as well as solubility and crystallinity [48,51,52]. Branched structures have also been shown to increase the tendency for the formation of interpenetrating networks when blended with fullerene derivatives [53]. On the other hand, inserting fluorine atoms on isoindigo units has been shown to increase the charge mobility and V_{oc} [42,54]. More generally, fluorination can (potentially) improve all photovoltaic parameters (i.e. open-circuit voltage, short-circuit current density (J_{sc}) and fill factor (FF)) [55,56].

In this paper, we report on the synthesis and characterization of two novel D–A conjugated small molecules based on fluorinated isoindigo that differ in their structure, one being linear and the other one being propeller-like (Scheme 1). The presence of the fluorine atoms on the isoindigo units serves to fine-tune the HOMO–LUMO energy levels. The objective of this study is to investigate how

the molecular architecture of the donor material can affect the organization, the optoelectronic and photovoltaic properties. The thermal, photophysical and electronic properties of both molecules were analyzed by differential scanning calorimetry (DSC), cyclic voltammetry (CV) and UV–Vis absorption spectroscopy, and the experimental results were interpreted with the assistance of density functional theory (DFT) calculations. Finally, the small molecules were combined with PC₆₁BM ([6,6]-phenyl-C₆₁-butyric acid methyl ester) and tested in prototype BHJ OSCs.

2. Experimental section

2.1. Instrumentation and characterization

NMR spectra were recorded on a Bruker AVANCE 250 MHz spectrometer. High resolution electrospray ionization mass spectrometry (ESI-MS) was performed using an LTQ Orbitrap Velos Pro mass spectrometer equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the *m/z* range 220–2000 using a standard solution containing caffeine, MRFA and Ultramark 1621. Optical absorption spectra were taken on a Cary 500 scan UV–Vis spectrometer. DSC measurements were acquired with a TA Instruments Q1000 DSC using standard aluminum pans, an indium standard for calibration, and nitrogen as the purge gas. Melting and crystallization temperatures were determined by taking the peak values of the second heating and cooling scans. Thin film morphologies were characterized by AFM (atomic force microscopy) using a PicoPlus5500 microscope (Agilent Technologies) in tapping mode. The images were realized using silicon cantilevers (Nanosensors, silicon-SPM-sensor, spring constant 10–130 Nm⁻¹, resonance frequency 204–497 kHz) in air and analyzed using Gwyddion data analysis software.

2.2. Materials

N-2-ethylhexyl-substituted 5-fluoro-6'-bromoisindigo **1** was synthesized by a procedure analogous to previous work [57]. (3,4'-Dihexyl-[2,2'-bithiophen]-5-yl)trimethylstannane (**2**) [58] and 1,3,5-tris(2-(5-trimethylstannyl)thienyl)benzene (**5**) were prepared according to reported literature methods [59]. All other chemicals were obtained from Aldrich and used as received. Solvents were distilled over standard drying agents under dry nitrogen.

2.3. Synthesis

2.3.1. Compound **1**

To a suspension of 6-bromooxindole (1.030 g, 4.85 mmol) and 5-fluoroisatin (802 mg, 4.85 mmol) in AcOH (30 mL), a conc. HCl solution (0.2 mL) was added and the mixture was heated at 100 °C for 24 h. The mixture was then allowed to cool down and it was filtered. The solid material was washed with water and ethanol. After drying under vacuum, a mixture of 6,6'-dibromoisindigo,

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