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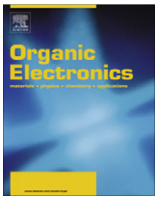

Development of a new diindenopyrazine–benzotriazole copolymer for multifunctional application in organic field-effect transistors, polymer solar cells and light-emitting diodes

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ABSTRACT

A new donor–acceptor (D–A) copolymer (**PIPY–DTBTA)** containing 6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine donor and benzotriazole acceptor was synthesized and characterized for multifunctional applications in organic field-effect transistors (OFETs), polymer solar cells (PSCs) and polymer light-emitting diodes (PLEDs). The polymer exhibits high molecular weights, excellent film-forming ability, a deep HOMO energy level, and good solution processability. Solution-processed thin film OFETs based on this polymer revealed good *p*-type characteristic with a high hole mobility up to 0.0521 $cm^2\ V^{-1}\ s^{-1}$. Bulk-heterojunction PSCs comprising this polymer and $PC_{61}BM$ gave a power conversion efficiency (PCE) of 0.77%. The single-layer PLEDs based on **PIPY–DTBTA** emitted a yellow–red light with a maximum brightness of 385 cd m^{-2} at the turn-on voltage of 6 V.

1. Introduction

In the past decade, conjugated polymers (CPs) have attracted extensive scientific interesting for organic electronic applications, including organic field-effect transistors (OFETs) [1–4], polymer solar cells (PSCs) [2,5–10], polymer light-emitting diodes (PLEDs) [11–13], and electrochromic devices [14,15]. CPs that are applicable to many fields are regarded as multifunctional materials [16–20] offering great potential to lower the cost of active layer production for organic electronics. The attractive properties of CPs are mostly based on the ability to tune the optical and electrical properties with chemical structural modifications, such as controlling of a functional group, conjugation length or the backbone. Tailoring the bandgap of CPs allows variation in absorption in the visible region, the type of charge carriers upon doping, and emission wavelength [21–24]. In recent years, some low bandgap donor–acceptor (D–A) copolymers have been developed and applied in organic electronics [6,9,10]. The exciting power conversion efficiencies (PCEs) over 7% have been achieved for BHJ PSCs [25,26]. OFETs based on D–A copolymers with hole mobilities exceeding 1 $cm^2\ V^{-1}\ s^{-1}$ have also been demonstrated [4,17,27,28], which appear to utilize intermolecular self-assembling properties enhanced by the dipoles along the D–A backbone.

In the previous report, organic small molecules based on 6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine (Diindenopyrazine, **IPY**, Fig. 1) were applied as an efficient deep blue emission with CIE coordinates (0.154, 0.078) and exhibit a high external quantum efficiency of ~4.6% [29]. Yamashita's group used a **IPY** derivative as the channel material in an *n*-type OFET with excellent results (mobility, 0.17 $cm^2\ V^{-1}\ s^{-1}$; on/off ratio, ~10^7) [30]. Therefore, we

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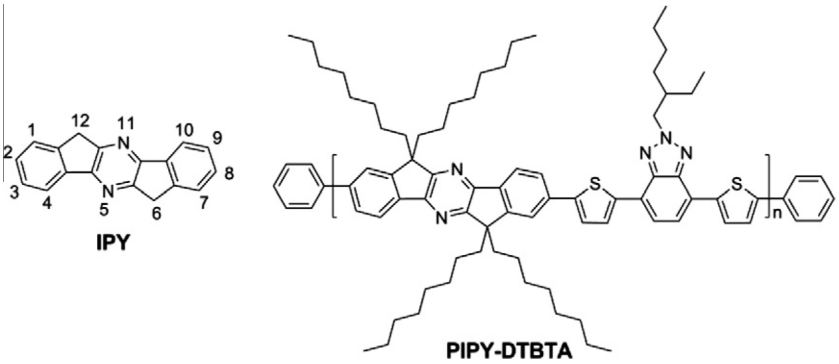

Fig. 1. Molecular structures of diindenopyrazine (**IPY**) and related copolymer **PIPY–DTBTA**.

have great interesting on **IPY** containing materials for the following reasons: The **IPY** core possessing rigid and planar structure facilitates the high chemical stability and effective $\pi-\pi$ stacking of molecular in the thin film state [31], which is good for the charge carrier mobility. The alkyl groups can be introduced at the 6- and 12-positions of **IPY** which can easy tuned the solution processability of the polymers. On the other hand, the benzotriazole (BTA) unit can be provide an additional advantage of incorporating soluble alkyl chains onto the acceptor compared with the typical and successful benzothiadizole (BT) unit [32,33]. More important, the synthesis of highly soluble **IPY**-containing copolymers and their applications in organic electronics, especially for PSCs, have not been reported yet.

Expanding on the foregoing points, herein, a new D–A copolymer **PIPY–DTBTA** (Fig. 1) containing **IPY** and BTA units was designed and synthesized for multifunctional organic electronic application. The unique distribution of the alkyl chains allows the polymer backbone to adopt a more planar conformation, which can promote close packing of the polymer chain and increase the hole mobility of the resulting polymers. As a result, we confirmed a high molecular weight, good solubility, film-forming ability, and impressively high mobility for this new **IPY**-based polymer. The preliminary performance of OFETs, PSCs and PLEDs showed that **PIPY–DTBTA** could be use as a promising multifunctional material.

2. Experimental section

2.1. Materials and reagents

5-Bromo-indanone, amylnitrite, 2,1,3-benzothiazole, isopropoxyboronic acid pinacol ester and tetrabutylammonium hexafluorophosphate were purchased from commercial suppliers (Pacific ChemSource and Alfa Aesar) in analytical grade. Toluene was dried and distilled over sodium/benzophenone. DMF, $CHCl_3$, and CH_3CN were dried over by accustomed methods and distilled before using. All other solvents and chemicals used in this work were analytical grade and used without further purification. All chromatographic separations were carried out on silica gel (200–300 mesh).

2.2. Analytical instruments

^1H NMR and ^{13}C NMR spectra were measured with Bruker AVANCE 400 spectrometer. UV–vis spectra were measured on Perkin-Elmer Lamada 25 spectrometer and photoluminescence (PL) spectra were measured on Perkin-Elmer LS-50 luminescence spectrometer. Molecular mass was determined by matrix assisted laser desorption–ionization time-of-flight mass spectrometry (MALDI-TOF MS) using a Bruker Aupoflex-III mass spectrometer. Thermogravimetric analyses (TGA) were performed under nitrogen at a heating rate of 20 °C/min with Netzsch TG 209 analyzer. The average molecular weight and polydispersity index (PDI) of the copolymers were determined using Waters 1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three-electrode cell and an electrochemistry workstation (CHI830B, Chenhua Shanghai). The working electrode was a Pt ring electrode; the auxiliary electrode was a Pt wire, and saturated calomel electrode (SCE) was used as reference electrode. Tetrabutylammonium hexafluorophosphate 0.1 M was used as supporting electrolyte in dry acetonitrile.

2.3. Fabrication and characterization of PSCs

The photovoltaic cells were constructed in the traditional sandwich structure through several steps. The ITO coated glass substrates were cleaned by successive ultrasonic treatment in acetone and isopropyl alcohol, then treated with a nitrogen–oxygen plasma oven for 5 min. Poly(3,4-ethylene dioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS, from Bayer AG) was spin-coated from an aqueous solution on a cleaned indium tin oxide (ITO) glass substrate giving a thickness of about 40 nm as measured by Ambios Technology XP-2 surface profilometer, then it was dried at 150 °C for 15 min. Subsequently, the photoactive layer was prepared by spin-coating the dichlorobenzene solution of polymer:$PC_{61}BM$ (1:2, w/w) with the polymer concentration of 6 mg/mL on the top of the PEDOT:PSS layer and the thickness of the active layers of ca. 80 nm, and then annealed at 150 °C for 5 min in a nitrogen-filled glove box. Finally, the substrates were