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3,3'-(Ethane-1, 2-diylidene)bis(indolin-2-one) based conjugated polymers for organic thin film transistors

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3,3'-(Ethane-1,2-diylidene)bis(indolin-2-one) (EBI) was used as a new electron-acceptor building block for conjugated polymers. Copolymers of EBI and bithiophene exhibited p-type semiconductor performance with hole mobility up to 0.044 cm^{2}V^{-1}s^{-1} in organic thin film transistors.

Donor-acceptor (D-A) type conjugated polymers have attracted tremendous research interests as active components in organic photovoltaics (OPVs)[1,2a] and organic thin film transistors (OTFTs).[2] Owing to the effect of intramolecular electron transfer from the donor unit to the acceptor unit, D-A polymers generally have relatively small band gaps, making them suitable as active layers in solar cells to harvest a large portion of light in the solar spectrum. On the other hand, the intermolecular D-A interaction could shorten the π-π stacking distance and form well-connected networks in the solid state, resulting in highly efficient charge transport characteristics of many D-A polymers. Some D-A polymers exhibited mobility greater than 1 cm^{2}V^{-1}s-1 in OTFTs.[2-6]

(E)-[3,3'-Biindolinylidene]-2,2'-dione, or isoindigo (IID), the building block of the well-known isoindigo-type dyes and pigments, is composed of two indolin-2-one units bridged by an exocyclic C=C bond (Scheme 1). Small molecules and polymers based on IID were extensively investigated recently and they were found to be very promising semiconductor materials for OTFTs[5] and OPVs.[7] Very recently, we extended the isoindigo structure by incorporating a benzodifuran-dione moiety between two indolin-2-one units. The resulting large fused ring structure, IBDF (Scheme 1), was found to be more coplanar than IID and has lower energy levels. The first polymer of IBDF with thiophene showed stable electron transport performance with mobility of ~10^{-2} cm^{2}V^{-1}s^{-1} in OTFTs.[8] Later, the mobility of IBDF polymers was improved up to 1.74 cm^{2}V^{-1}s^{-1} through optimization of chemical structures and device fabrication,[6b] indicating the great potential of IBDF based polymers for OTFTs. In this study, we report another electron acceptor building block 3,3'-(ethane-1,2-diylidene)bis(indolin-2-one) (EBI),[9] which has two indolin-2-one units linked by an ethane-1,2-diylidene moiety (Scheme 1), for the synthesis of new D-A polymers.

Two EBI-containing monomers, EBI-24 and EBI-26, having bromo groups were readily synthesized according to the route outlined in Scheme 1. A mixture of 6-bromoindoline-2,3-dione, propionic anhydride and pyridine was heated under reflux for 0.5 h to afford compound **1** in a yield of 22.0 %. Subsequently, **1** was heated in an ethanolic solution of potassium hydroxide under reflux for 20 min. Then the potassium derivative was decomposed with hydrochloric acid to give **2** in a yield of 74.7%. **2** was substituted with 2-decyltetradecyl or 4-decylhexadecyl to obtain EBI-24 (44.2% yield) or EBI-26 (49.2% yield), respectively. Stille coupling polymerization between EBI-24 or EBI-26 and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene, followed by purification using Soxhlet extraction, gave **PEBIBT-24** or **PEBIBT-26**, respectively.
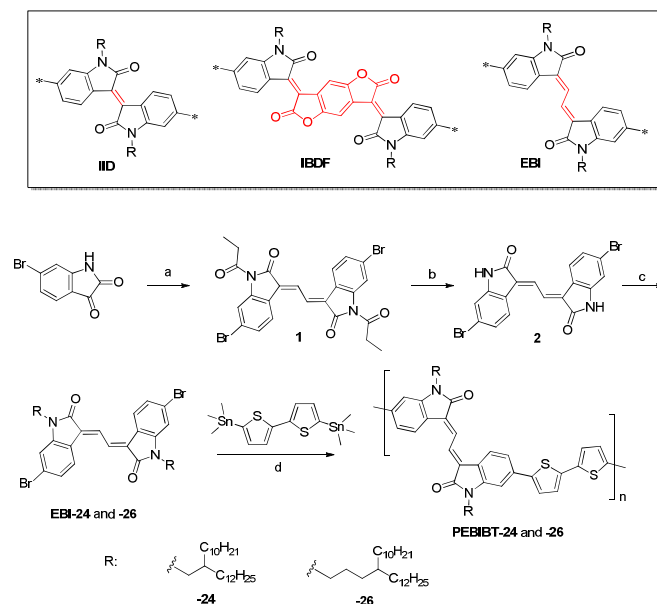
Scheme 1 Top: Structures of IID, IBDF, and EBI building blocks. Bottom: The synthetic route to **PEBIBT** polymers: a) propionic anhydride / pyridine, reflux, 0.5 h, 22.0%; b) KOH-EtOH, reflux, 20 min / aq. HCl, 74.7%; c) K$_2$CO$_3$, DMF, 70 °C, 20 h, for **EBI-24**, 44.2%; for **EBI-26**, 49.2%; d) Pd$_2$(dba)$_3$/P(o-tolyl)$_3$, chlorobenzene, 90 °C, 99.3% for **PEBIBT-24** and 99.4% for **PEBIBT-26**.

The number average molecular weight (M_n) / polydispersity index (PDI) of **PEBIBT-24** and **PEBIBT-26** are 28.7 kDa / 2.17 and 23.6 kDa / 2.23, respectively, determined by high temperature gel permeation chromatography (HT-GPC) with 1, 2, 4-tricholorobenzene (TCB) as the eluent at 140 °C. The thermal behaviour of these polymers was characterized by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. S9 in ESI). Both polymers showed good thermal stability with 5 % weight loss temperatures ($T_{-5\%}$) at 287 °C and 322 °C, respectively. No phase transition on DSC curves was observed in the range from -20 °C to 320 °C.
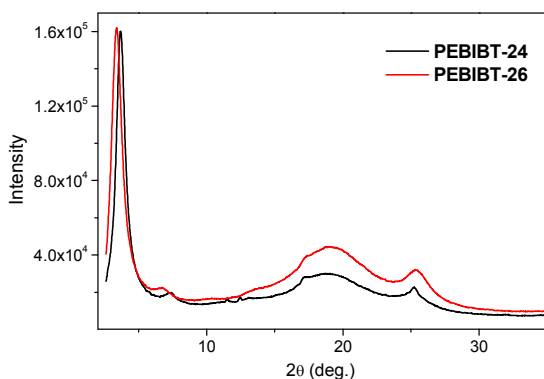

Fig.1 Normalized UV-Vis absorption spectra of polymers **PEBIBT-24** and **PEBIBT-26** in ~10^{-5} M solutions in chloroform and as thin films spin-coated on glass substrates at different annealing temperatures.
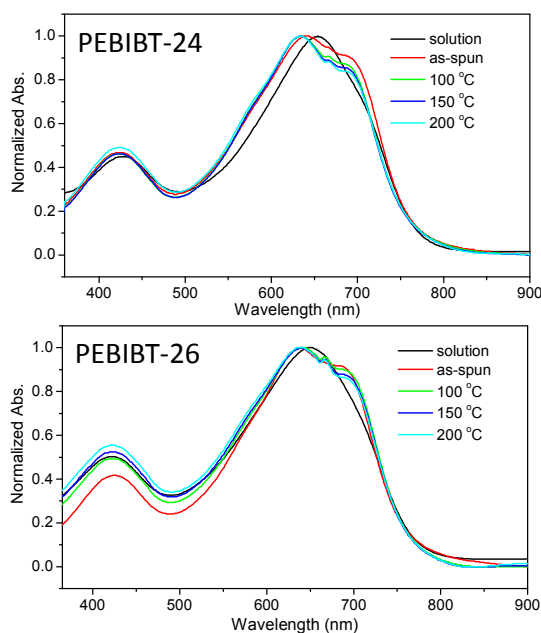

Fig.2 Transmission XRD diagrams of stacked **PEBIBT-24** and **PEBIBT-26** flakes sandwiched between two Mylar substrates measured on a Bruker Smart 6000 CCD 3-circle D8 diffractometer with a Cu RA (Rigaku) X-ray source (λ = 0.15418 nm). .

Fig. 1 shows the absorption spectra of **PEBIBT-24** and **PEBIBT-26** in CHCl$_3$ and in thin films. The wavelength of maximum absorption (λ_{max}) of **PEBIBT-24** in solution is 654 nm, while the λ_{max} slightly blue shifted to 641 nm, accompanied by the appearance of a shoulder at 689 nm, for the as-spun film. Upon annealing, the λ_{max} further blue shifted to 634 nm, while a peak at

666 nm appeared. The more featured absorption profiles are due to the improved chain packing in the annealed films. **PEBIBT-26** showed similar λ_{max} in solution (651 nm) in solution and in the solid state (638 nm for the as-spun film). However, the vibronic splitting patterns are more defined in the annealed **PEBIBT-26** films (the more pronounced peak at 666 nm), indicating that this polymer has slightly more ordered chain packing than **PEBIBT-24**. The optical band gaps of these two polymers calculated from the absorption onset wavelengths of their thin films are ca. 1.6 eV. The λ_{max} and optical band gap values of **PEBIBT-24** and **PEBIBT-26** are similar to those of their analogous copolymers of IID and bithiophene, **PIIDBT-24** and **PIIDBT-24'** (Table S1 in ESI). However, their λ_{max} blue shifted compared with their analogous IBDF copolymer **PIBDFBT-40** (Table S1 in ESI). These results suggest that the conjugation effect of EBI is similar to that of IID, but weaker than the fused IBDF building block.

Cyclic voltammetry (CV) measurements of polymer thin films showed that **PEBIBT-24** and **PEBIBT-26** have the highest occupied molecular orbital / lowest unoccupied molecular orbital (HOMO / LUMO) levels of -5.38 / -3.76 eV and -5.30 / -3.77 eV, respectively. Their HOMO energy levels are higher than those of both their analogous polymers of IID (**PIIDBT-24 / PIIDBT-24'**: E_{HOMO} = -5.70 / -5.52 eV) [5d] and IBDF (**PIBDFBT-40**: E_{HOMO} = −5.72 eV) [6b] (Table S1 in ESI). The LUMO levels of **PEBIBT-24** and **PEBIBT-26** are similar to those of **PIIDBT-24 / PIIDBT-24'** (E_{LUMO} = -3.70 / -3.74 eV), but higher than that of **PIBDFBT-40** (E_{LUMO} = -4.15 eV), indicating that the electron-withdrawing ability of EBI is very close to that of IID, but weaker than that of IBDF.

To gain insight into the molecular ordering of these polymers in thin films, we first performed transmission X-ray diffraction (XRD) measurement on bulk polymer flakes (Fig. 2). The diffraction patterns for both polymers are reminiscent of most of other conjugated polymers that adopt layer-by-layer lamellar ordering.[10] The primary diffraction peaks at 2θ = ~3.66 ° for **PEBIBT-24** and 2θ = ~3.39 ° for **PEBIBT-26** represent the inter-lamellar distances of 2.42 nm and 2.61 nm, respectively. The peaks at 2θ = 25.25° for **PEBIBT-24** and 2θ = 25.36° for **PEBIBT-26** originated from the co-facial π-π stacking distances of ca. 0.35 nm. This π-π distance is very small compared with most other conjugated polymers.[2] It was previously reported that a longer distance of the bifurcation point of the branched alkyl side chains from the polymer backbone could shorten the π-π stacking distance. [5d,11] However, the use of 4-decylhexadecyl in **PEBIBT-26** resulted in no obvious decrease in its π-π stacking distance compared with **PEBIBT-24** having the 2-decyltetradecyl side chains. The broad peak centred at 2θ = ~19° indicates the presence of amorphous regions originating from the disordered branched alkyl side chain segments,[12] which might be in both the amorphous and crystalline phases. We also conducted XRD measurement on spin-coated polymer thin films on dodecyltrichlorosilane (DTS) modified SiO$_2$/Si wafer substrates. However, both polymers showed no diffraction peaks, indicating their very poor crystallinity in thin films (Fig. S10 in ESI). The absence of diffraction peaks for these thin film samples are probably due to the much faster solvent drying during spin-coating, which allowed less time for molecular ordering,[13] compared to the polymer flakes used for the transmission XRD measurement, which were prepared by evaporating solvent at a significantly slower rate (ESI). In addition, the spin-coated thin films are much thinner (~35 nm) than the polymer flakes (~30 μm), resulting in weaker diffraction signals of the former. The surface morphology of **PEBIBT-24** and **PEBIBT-26** thin films spin-coated on DTS-modified SiO$_2$/Si wafer substrates was examined using atomic force microscopy (AFM). Thin films of both polymers are very smooth, having a root mean square (RMS) roughness of less than 1 nm (Fig. S11 in ESI).

The charge transport performance of **PBIBT-24** and **PEBIBT-26** was evaluated in bottom-gate bottom-contact OTFT devices on conductive n[++]-doped silicon wafer with a 300 nm thermally grown SiO_2 layer. The substrate was pre-patterned with gold source and drain pairs and the SiO_2 surface was modified with DTS. The semiconducting layer was deposited by spin-coating a polymer solution (10 mg mL^{-1} in $CHCl_3$) onto the substrate, annealed at 150 °C or 200 °C, and encapsulated with a layer of PMMA (~500 nm) in a glove box filled with nitrogen. The devices were measured in air using an Agilent 4155C I-V source measurement unit. All devices showed p-channel charge transport characteristics (Fig. 3 and Table S2 in ESI). The average (and maximum) mobility values of the polymer films annealed at 150 °C are 0.026 $cm^2V^{-1}s^{-1}$ (0.030 $cm^2V^{-1}s^{-1}$) for **PEBIBT-24** and 0.039 $cm^2V^{-1}s^{-1}$ (0.044 $cm^2V^{-1}s^{-1}$) for **PEBIBT-26**. The higher mobility of **PEBIBT-26** compared with **PEBIBT-24** might be attributed to its slightly more ordered chain packing as evidenced by the UV-Vis data, which was probably brought about by the more distant bifurcation point of the C26 side chains from the polymer backbone.[5d,11] At a higher annealing temperature of 200 °C, the mobility dropped slightly to 0.021 $cm^2V^{-1}s^{-1}$ (0.028 $cm^2V^{-1}s^{-1}$) for **PEBIBT-24** and 0.028 $cm^2V^{-1}s^{-1}$ (0.033 $cm^2V^{-1}s^{-1}$) for **PEBIBT-26**. The mobility values are quite high considering that the polymer thin films had very poor chain ordering based on the XRD data. The performance of polymers based on this new EBI building block is expected to improve further upon optimization of the side chain and screening of the donor co-monomer unit.
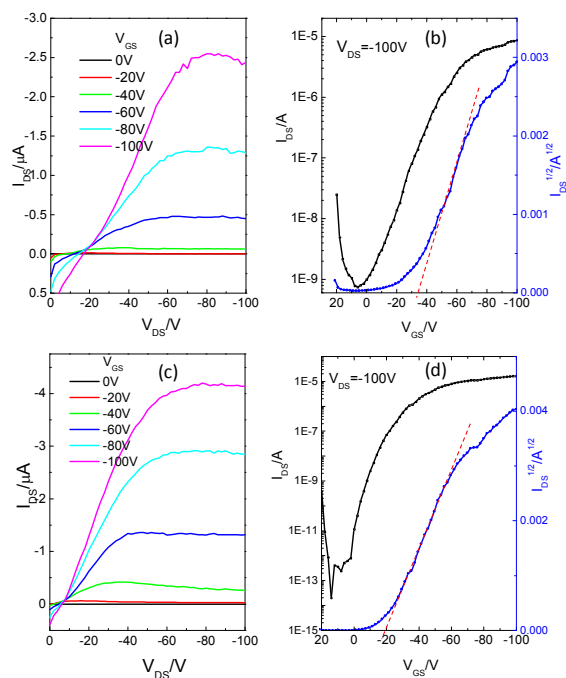

Fig.3 Output and transfer curves of OTFT devices based on a 150 °C-annealed **PEBIBT-24** film (a, b) and a 150 °C-annealed **PEBIBT-26** film (c, d). The hole mobility values calculated in the saturation region are 0.030 $cm^2V^{-1}s^{-1}$ for the **PEBIBT-24** based device (b) and 0.044 $cm^2V^{-1}s^{-1}$ for the **PEBIBT-26** based device (d). Device dimensions: channel length, $L = 30$ μm; channel width, $W = 1000$ μm.

In summary, the electron-accepting building block, EBI, is reported for the first time to synthesize donor-acceptor copolymers, **PEBIBT-24** and **PEBIBT-26**. These polymers showed good solubility and exhibited characteristic p-type semiconductor performance in OTFTs with hole mobility as high as 0.044 $cm^2V^{-1}s^{-1}$[1]. Our preliminary results demonstrated that EBI is potentially a promising electron acceptor building block for polymer semiconductors for OTFTs and OPVs.

Notes and references

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