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Indacenodithiophene and Quinoxaline-Based Conjugated Polymers for Highly Efficient Polymer Solar Cells

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S *Supporting Information*

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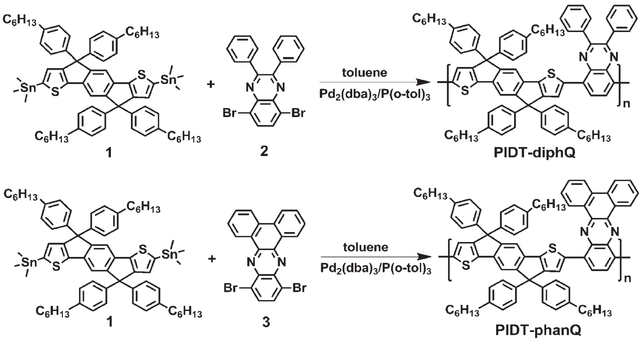
Over the past decade, polymer solar cells (PSCs) based on the bulk heterojunction (BHJ) structure have emerged as a promising sustainable energy source because of their low cost, light weight, and simple fabrication.[1] The BHJ structure is commonly formed by blending a conjugated polymer as donor and an electron-deficient fullerene as acceptor with bicontinuous interpenetrating network. Although much effort has been put into the development of fullerene derivatives,[2] [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$ or $PC_{71}BM$) is still one of the best n-type semiconductors (electron acceptor) in PSCs.[1] Given this fact, most research efforts have focused on the molecular engineering of conjugated polymers to tune their band gap and energy levels.

So far, many low-band-gap conjugated polymers have been designed and synthesized with the aim of improving charge transporting properties, narrowing the band gap to harvest more sunlight and/or deepening the highest occupied molecular orbital (HOMO) energy level so as to increase the open circuit voltage (V_{oc}). However, there are constraints on simultaneously optimizing the latter two cases since decreasing the polymer band gap usually accompanies with increasing HOMO level and/or lowering the lowest unoccupied molecular orbital (LUMO) energy level. This results in lower V_{oc} and/or less efficient exciton dissociation that is governed by the difference in LUMO levels between the polymer and fullerene pair.[3]

Recently, conjugated polymers based on the indacenodithiophene (IDT) unit have exhibited more research interest with promising performance in PSCs,[4] because the IDT unit can enhance the coplanarity of polymer backbone with the reduced energetic disorder of the polymer. For example, Ting and coworkers have reported a PCE of 6.1% from the alternating polymer of IDT and benzothiadiazole (BT) units.[4c] More importantly, the IDT-based polymers show high and stable field-effect hole mobilities. A hole mobility of as high as ~1 $cm^2\ V^{-1}\ s^{-1}$ from the analogous polymer of IDT and BT units has been reported by Zhang et al.[4d]

Quinoxaline has been widely implemented as an electron-deficient comonomer of low-band gap polymers in PSCs. The impressive performance of quinoxaline-based polymers has shown its obvious potential for achieving high performance in PSCs.[5,6] 2,3-Diphenylquinoxaline, which possesses two separated phenyl rings, is one of the commonly investigated quinoxaline derivatives because of its facile synthesis and versatility. Research efforts focusing on tuning the solubility, band gap, and energy levels of 2,3-diphenylquinoxaline-based polymers have resulted in PCEs of ≤6%.[5,6] However, most of these polymers possess large band-gaps (>1.9 eV) and low charge carrier mobilities (~1 × 10^{-5} $cm^2\ V^{-1}\ s^{-1}$).[5] Moreover, two separated phenyl rings on the 2,3-diphenylquinoxaline could induce some steric hindrance to interrupt intermolecular stacking between polymer chains.

Scheme 1. Synthesis of Polymers PIDT-diphQ and PIDT-phanQ



If two phenyl rings could be connected by a single bond between the ortho positions, it will significantly increase the planarity of quinoxaline and facilitate both intermolecular packing and charge transport. Moreover, the extended π-conjugation of the fused qunioxaline (named as phenanthrenequnioxaline) will function as a stronger electron-acceptor, leading to lower bandgap in the corresponding polymer. In this communication, we combined IDT and two quinoxaline derivatives to form new polymers (PIDT-diphQ and PIDT-phanQ, Scheme 1). Due to the enhanced planarity of phenanthrenequnioxaline, PIDT-phanQ/$PC_{71}BM$-based BHJ device exhibits an improved PCE of 6.24% compared to the PCE of 5.69% in PIDT-diphQ/$PC_{71}BM$-based device.

The synthetic routes of polymers PIDT-diphQ and PIDT-phanQ are shown in Scheme 1. Compound **1** was synthesized from 2,5-dimethyl-1,4-dibromobenzene *via* several steps with a modified procedure (see the Supporting Information for details).

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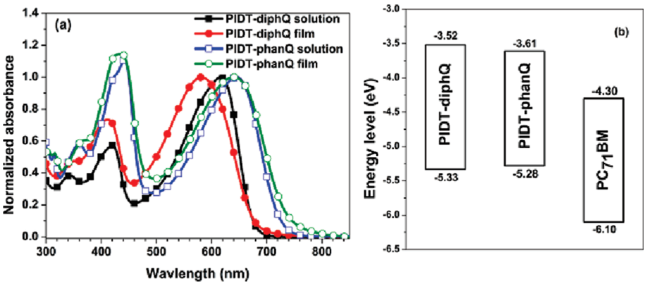

Figure 1. (a) UV−vis spectra of PIDT-diphQ and PIDT-phanQ in chloroform solution and film states. (b) Energy levels diagram of PIDT-diphQ, PIDT-phanQ, and $PC_{71}BM$.

Compounds **2** and **3** were prepared from 3,6-dibromo-1,2-diaminobenzene and benzil and phenanthrenequinone, respectively, in acetic acid solution.[7] The Stille polymerization between compound **1** and **2** or **3** with $Pd_2(dba)_3/P(o\text{-}tol)_3$ catalyst in toluene gave the polymers PIDT-diphQ and PIDT-phanQ. The resulting polymers were purified through Soxhlet extraction using acetone and then hexane for 12 h. Benefiting from the peripheral tetrahexylbenzyl groups in IDT units, both polymers exhibit good solubility in organic solvents, such as THF, chloroform, chlorobenzene, and dichlorobenzene, etc. The GPC measurement with monodisperse polystyrene as standards and THF as the eluent showed that the polymers have the number-average molecular weight (M_n) of 68.2 and 82.4 kg/mol for PIDT-diphQ and PIDT-phanQ with a polydispersity index (PDI) of 2.42 and 2.84, respectively. The results from differential scanning calorimetry (DSC) (heated at 10 °C/min under nitrogen) showed that there is no thermal transition between 20 and 350 °C for both polymers.

The UV−vis spectra of the polymers in chloroform and in the film state are shown in Figure 1a. In chloroform solution, PIDT-diphQ shows an absorption maximum at 617 nm with a weaker peak at 420 nm. The λ_{max} of the solid film of PIDT-diphQ, however, exhibits a blue-shift of 36 to 581 nm (Figure 1a). A similar phenomenon has been reported and is attributed to the decreased conjugation length in solid film due to steric hindrance between the pendent phenyl rings on the IDT and quinoxaline units.[4] This will weaken the interchain packing of polymer in solid state. Interestingly, the absorption of PIDT-phanQ in chloroform gives two peaks at the maximum of 644 and 442 nm, respectively, which shows ∼30 nm red-shift compared with PIDT-diphQ due to the extended conjugation length of the phenanthrenequinoxaline unit on PIDT-phanQ. However, the absorption of PIDT-phanQ thin film is almost identical with that observed in solution (Figure 1a), which showed a 63 nm red-shift compared to PIDT-diphQ. This indicates that the more planar phenanthrenequinoxaline unit not only effectively reduces steric hindrance in the solid state but also promotes stronger chain stacking even in solution. It is well-known that thermal treatment can change the packing of conjugated polymer chains. To understand the chain packing behavior of both polymers, the UV−vis spectra of PIDT-diphQ and PIDT-phanQ films with thermal treatment at 110 °C for 10 min were measured (see Figure S1 in the Supporting Information). It clearly shows that the PIDT-phanQ polymer has stronger polymer chain packing than the PIDT-diphQ. The absorption onsets of PIDT-diphQ and PIDT-phanQ in as-spun film are ∼684 and ∼744 nm, respectively, corresponding to an optical band gap of 1.81 and 1.67 eV. The ∼0.14 eV reduction of polymer band gap is found to be due to the enhanced planarity of using phenanthrenequinoxaline as the comonomer.

Cyclic voltammetry (CV) was used to estimate the energy levels of the polymers. The HOMO levels of PIDT-diphQ and PIDT-phanQ were found to be −5.33 and −5.28 eV, respectively (Figure 1b) The LUMO levels were calculated to be −3.52 and −3.61 eV for PIDT-diphQ and PIDT-phanQ, respectively (Figure 1b). The larger LUMO difference (∼0.10 eV) agrees well with calculations using the Density Functional Theory (DFT) at the B3LYP/6-31G* level,[8] in which it shows that the HOMO wave function is delocalized along the polymer backbone and is minimally affected by the nature of the pendant phenyl rings on the quinoxaline unit, while the LUMO wave function is primarily localized on the qunioxaline moiety (Figure S2).

Moreover, the LUMO delocalization of PIDT-diphQ is mainly limited to the quinoxaline unit while it is extended onto the fused ring system due to the enhanced planarity in PIDT-phanQ. This partially explains the larger LUMO shift, thereby generating a smaller band gap for PIDT-phanQ. It is commonly known that the V_{oc} in PSCs is proportional to the difference between HOMO of polymer donor and LUMO of PCBM electron acceptor (−4.3 eV, Figure 1b).[9] Therefore, the large difference (∼1 eV) between the polymer's HOMO and the PCBM's LUMO indicates the potential of having a large V_{oc} in these PSCs (Figure 1b). In addition, the energy difference (more than 0.6 eV) between the LUMO of polymers and $PC_{71}BM$ is also sufficient for exciton dissociation.[1c]

As the active material for polymer solar cells, charge carrier mobility is one of the important factors dictating device performance. The hole mobilities of both polymers were measured in a field-effect transistor (FET) with a bottom-gate, top-contact device configuration built on an n-doped silicon wafer (see the Supporting Information for details). The hole mobilities of pristine PIDT-diphQ and PIDT-phanQ films determined from the saturation regime were 4.6×10^{-3} and 2.4×10^{-2} $cm^2\ V^{-1}\ s^{-1}$, respectively, with an on−off ratio of 1×10^5 and 1×10^6 (see Figures S3 and S4 in the Supporting Information). After the FET devices were annealed at 110 °C for 10 min under nitrogen, the hole mobilities of annealed PIDT-diphQ and PIDT-phanQ films improved to 1.9×10^{-2} and 2.9×10^{-2} $cm^2\ V^{-1}\ s^{-1}$, respectively with an on−off ratio of $\sim 1 \times 10^6$. The lower FET mobility in the unannealed PIDT-diphQ film is probably due to its weak intermolecular packing, which was improved after thermal treatment to result in a significantly increased mobility. Since PIDT-phanQ film already has quite strong polymer chain packing, thermal annealing has little effect on the mobility improvement. To the best of our knowledge, this is the highest FET hole mobility of quinoxaline-based conjugated polymers, which is very encouraging for using them as efficient polymer donors for polymer solar cells.

Polymer solar cells were fabricated using the same device structure for both polymers (ITO/PEDOT:PSS/PIDT-diphQ or PIDT-phanQ:$PC_{71}BM$ (1:3, w/w)/Ca/Al). The active layers of these devices were spin-coated from *o*-dichlorobenzene (o-DCB) solutions of these polymers. The optimized weight ratio between polymer and $PC_{71}BM$ is 1:3 w/w. $PC_{71}BM$ was selected because of its complementary absorption in the visible region.[10] The devices were measured under the simulated AM 1.5G illumination condition (100 mW cm^{-2}) after the devices were annealed at 110 °C for 10 min. The details of device fabrication processes are provided in the Supporting Information.

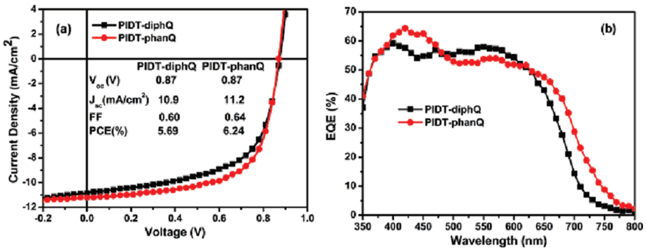

Figure 2. (a) The *J*−*V* curves of PIDT-diphQ:$PC_{71}BM$ and PIDT-phanQ:$PC_{71}BM$ devices under illumination of AM 1.5G, 100 mW/cm^2. (b) EQE spectra of PIDT-diphQ:$PC_{71}BM$ and PIDT-phanQ:$PC_{71}BM$ devices.

The typical current density−voltage curves of PIDT-diphQ and PIDT-phanQ-based devices are shown in Figure 2a.

In the PIDT-diphQ device, it showed a V_{oc} of 0.87 V, a short-circuit current density (J_{sc}) of 10.9 mA cm^{-2}, and a fill factor (FF) of 0.60, resulting a relatively high PCE of 5.69%. Under the same conditions, the PIDT-phanQ device showed an increased PCE of 6.24% with a V_{oc} of 0.87 V, a $J_{sc}$of 11.2 mA cm^{-2}, and a FF of 0.64. It is very encouraging that the device performance of both polymers, especially for the one based on PIDT-phanQ has already shown comparable result with those the state-of-the-art PSCs.[1]

There are several factors that may contribute to the result of getting high PCE in PIDT-phanQ-based device. First of all, the PIDT-phanQ polymer has a relatively low band gap of 1.67 eV and preferred energy levels that are well matched with $PC_{71}BM$.[9] The hole mobilities of polymers/$PC_{71}BM$ blend films measured by using the space-charge-limit-current (SCLC) method also showed high values (1.14×10^{-3} and 2.06×10^{-3} cm^2 V^{-1} s^{-1} for PIDT-diphQ and PIDT-phanQ, respectively). Furthermore, the morphology of the polymer/$PC_{71}BM$ blend films measured by AFM showed very smooth films, indicating homogeneous mixing of polymers and $PC_{71}BM$ (see Figure S4 in the Supporting Information). The combined smooth morphology and high mobility of the blends, therefore, resulted in a high FF (64%). The high V_{oc} value (0.87 V) is related to the deeper HOMO levels of the polymers.

The external quantum efficiency (EQE) spectra of the devices are shown in Figure 3b, and the discussion is provided in the Supporting Information.

In conclusion, two small-band-gap conjugated polymers based on the polymerization of IDT and quinoxaline units have been synthesized. Both polymers show good solubility in common organic solvents because of the peripheral tetrahexylbenzyl side chains of IDT units. Due to the enhanced planarity of phenanthrenequninoxaline unit, the PIDT-phanQ polymer showed higher hole-mobility than PIDT-diphQ. The polymer solar cells fabricated from the blend of polymer and $PC_{71}BM$ exhibit high PCEs of 5.69% and 6.24% for PIDT-diphQ and PIDT-phanQ, respectively. A high V_{oc} of 0.87 V has been achieved for both devices due to deep HOMO levels of the polymers. Further improvements on device performance through device engineering are anticipated. The results indicate that these polymers are promising candidates for the application of polymer solar cells.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Experimental details of synthesis of polymers and device fabrication and characterization, UV−vis spectra of the polymer film and blend film. This material is available free of charge via the Internet at http://pubs.acs.org.

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