Polymers

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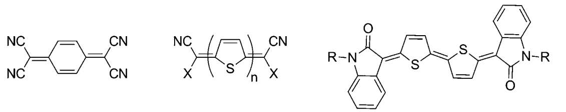
Thiophene-*S*,*S*-dioxidized Indophenine: A Quinoid-Type Building Block with High Electron Affinity for Constructing n-Type Polymer Semiconductors with Narrow Band Gaps

*Yunfeng Deng, Bin Sun, Yinghui He, Jesse Quinn, Chang Guo, and Yuning Li**

Abstract: *Three thiophene-S,S-dioxidized indophenine (IDTO) isomers,* ***3a*** *(E,E,E),* ***3b*** *(Z,E,E), and* ***3c*** *(Z,E,Z), were synthesized by oxidation of an indophenine compound.* ***3b*** *and* ***3c*** *could be converted into the most-stable* ***3a*** *by heating at 110 °C. An IDTO-containing conjugated polymer, PIDTOTT, was prepared using* ***3a*** *as a comonomer through a Stille coupling reaction, and it possesses a narrow band gap and low energy levels. In organic field effect transistors (OFETs), PIDTOTT exhibited unipolar n-type semiconductor characteristics with unexpectedly high electron mobility (up to 0.14 cm^2 V^{-1} s^{-1}), despite its rather disordered chain packing.*

n-Type organic semiconductors are sought after for use in complementary circuits[1–3] and organic solar cells,[4–6] but very few n-type semiconductors, particularly polymers, with high carrier-mobility have been reported when compared to reports of p-type semiconductors. Quinoidal compounds such as TCNQ,[7,8] quinoidal oligothiophenes[9–14] and quinoidal fused thiophenes[15–17] (Figure 1) have been studied as promising n-type electron transport semiconductors and some of them exhibited very high electron mobility[13,15–17] because of their unique features, such as high coplanarity and low energy levels. Hence, incorporation of quinoidal structures into polymers may lead to high-performance n-type polymer semiconductors. Actually, the quinoidal states of conjugated polymers have been extensively studied since the 1980s.[18–20] It was found that a conjugated polymer in its quinoidal form is more electrically conductive than its corresponding aromatic form. However, the majority of quinoidal conjugated polymers have been realized either in the doped state[18] or in the transient state.[21,22] Only a few conjugated polymers with intrinsic quinoidal building blocks have been reported to show p-type (hole carriers) or ambipolar (hole and electron carriers) charge-transport performance.[23–27] n-Type quinoid block-based polymers have not been reported yet.



TCNQ

Quinoidal oligothiophenes
(X = -CN or -C(=O)R; n = 2-4)

Indophenine
(R = H or alkyl)

Figure 1. Structures of several quinoid-type molecules.

Indophenine (R = H in Figure 1), a well-known blue dyestuff consisting of a quinoidal bithiophene,[28] was first prepared by Baeyer in 1879.[29] Recently, an *N*-dodecyl indophenine was reported to show promising electron-transport performance with a mobility of about 10^{-3} cm^2 V^{-1} s^{-1} in OFETs.[30] However, this compound also showed hole-transport performance, thus suggesting that indophenine is not adequately electron-deficient for realizing unipolar electron-transport performance. Furthermore, because of the *E*/*Z* isomerism of the double-bond linkages, there are six geometric isomers in the indophenine compounds. The isolation of a pure indophenine isomer from the product mixture has been unsuccessful.[30,31]

In this study, we devised an effective strategy to increase the electron affinity of indophenine by oxidizing the sulfur atoms of the quinoidal bithiophene in indophenine. In contrast to indophenine, the isomers of thiophene-*S*,*S*-dioxidized indophenine (IDTO) could be readily separated. More favorable is that two of the three isomers formed could be conveniently converted into the most-stable isomer by heat treatment. The latter was used as a comonomer for preparing a polymer which exhibits unipolar electron-transport performance (Scheme 1). A mixture of indophenine isomers, **2a**–**f** (R = 4-octadecyldocosan), was prepared from **1** by using procedure similar to that reported in the literature.[31] 3-Chloroperoxybenzoic acid (*m*-CPBA) was used to oxidize the mixture of isomers, **2a**–**f**, thus producing the three IDTO isomers **3a** (*E*,*E*,*E*), **3b** (*Z*,*E*,*E*), and **3c** (*Z*,*E*,*Z*). The mixture of **3a**–**c** was heated in toluene under reflux (110 °C), thus yielding **3a**. Finally, **3a** was used as a comonomer to react with 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene to form the polymer PIDTOTT through a Stille coupling reaction. The number-average molecular weight and polydispersity index of PIDTOTT are 23.5 kDa and 2.15, respectively, as determined by gel-permeation chromatography (GPC) using polystyrene as a standard. Thermogravimetric analysis (TGA) of PIDTOTT showed a two-step decomposition process (see Figure S23 in the Supporting Information) with the first and second onset decomposition temperatures at about 335 and 410 °C, respectively. A weight loss of about 7.5 % in the first step can be ascribed to the loss of SO_2 groups (calcd 7.1 %) because of the relatively weak C–S bonds. A similar phenomenon was observed for other thiophene-*S*,*S*-dioxide-containing polymers.[32] TGA measured in air only showed a slightly lower onset decomposition temperature (ca. 316 °C).

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[*] Dr. Y. Deng, B. Sun, Y. He, J. Quinn, Dr. C. Guo, Prof. Dr. Y. Li
Department of Chemical Engineering and Waterloo Institute for Nanotechnology (WIN), University of Waterloo
200 University Ave West, Waterloo, Ontario, N2L 3G1 (Canada)
E-mail: yuning.li@uwaterloo.ca

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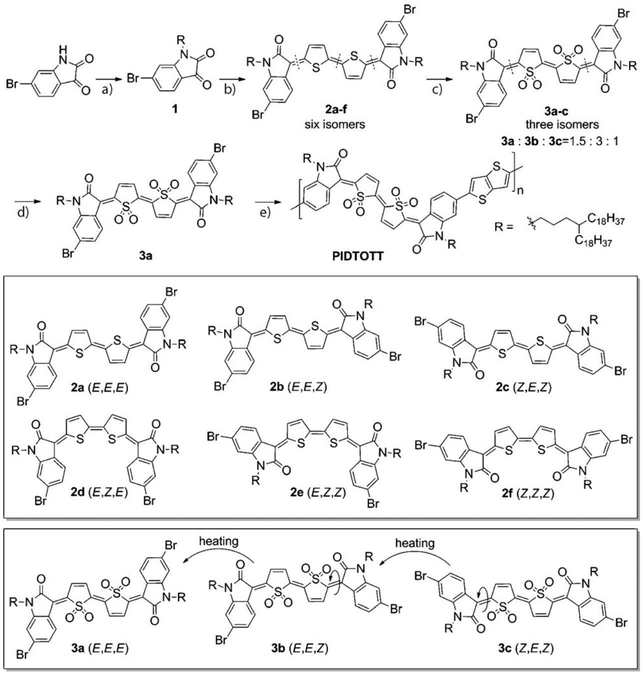

Scheme 1. Synthetic route to IDTO compounds and the IDTO-based polymer PIDTOTT: a) RI, DMF, 80 °C, 84 %; b) thiophene, H_2SO_4, toluene, RT; c) *m*-CPBA, toluene, RT, 10 % for **3a**, 21 % for **3b**, and 7 % for **3c**; d) toluene, reflux; 33 % for 3 steps; e) 2,5-bis(trimethylstannyl)-thieno[3,2-*b*]thiophene, $[Pd_2(dba)_3]/P(o\text{-tolyl})_3$, chlorobenzene, 130 °C, 82 %. dba = dibenzylideneacetone, DMF = *N*,*N*-dimethylformamide, *m*-CPBA = 3-chloroperbenzoic acid.

While attempts to separate the isomers **2a–f** were unsuccessful, the oxidized products, which were later determined to be the IDTO isomers **3a–c**, could be readily isolated by column chromatography. Their ^{1}H NMR spectra are shown in Figure 2 (detailed peak assignments can be found in the legend of Figure S6). We noticed that small amounts of **3a** formed in the **3b** and **3c** samples after the solid samples were stored at 0 °C for a few days, which was confirmed by thin layer chromatography (TLC; see Figure S10), thus indicating that **3a** is more stable than **3b** and **3c**. To accelerate and further confirm this isomerization process, solutions of **3b** and **3c** in deuterated 1,1,2,2-terachloroethane ([D$_2$]TCE) were heated at different temperatures for 15 minutes and monitored by NMR spectroscopy (see Figures S11–S13). After heating at 120 °C, all characteristic peaks that belong to either **3b** or **3c** disappeared and the spectra became identical to that of **3a**. In contrast, the solution of **3a** showed no spectral changes after heating, thus indicating that **3a** is the most stable structure among the three isomers. This observation led to synthesis of **3a** as the sole product by simply heating the mixture of **3a–c** in refluxing toluene for 1 hour.

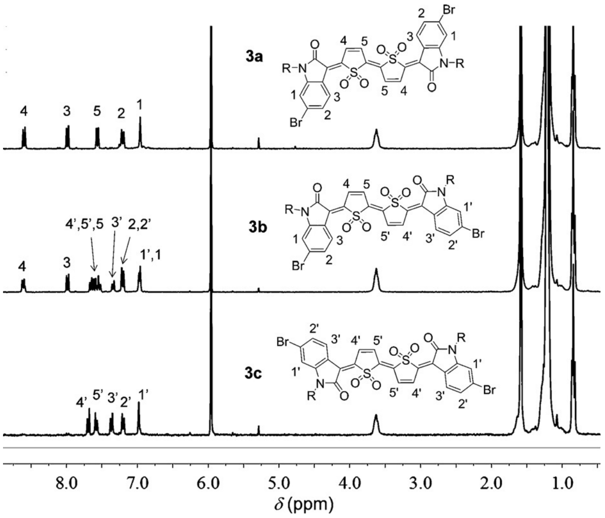

Figure 2. 300 MHz ^{1}H NMR spectra of **3a**, **3b**, and **3c** in [D$_2$]TCE.

Because of the difficulty to grow crystals of **3a** for single-crystal X-ray diffraction (XRD) analysis, another IDTO compound, **3a-C6**(same as **3a** but with R = C_6H_{13}), which has shorter *n*-hexyl alkyl chains for the ease of crystallization, was prepared. **3a-C6** and **3a** have the same backbone skeletons, which was verified by their identical NMR spectra in the aromatic regions (see Figure S14). Based on the single-crystal XRD results the three double-bonds, isatin-thiophene, thiophene-thiophene, and thiophene-isatin, of **3a-C6** are all in the *E* form (Figure 3 a). Therefore, it is reasonable to expect that **3a** has the same backbone geometry (Scheme 1 and Figure 2). As shown in Figure 3 b, **3a-C6** has a completely planar backbone. The two oxygen atoms on each thiophene-*S*,*S*-dioxide lie outside of the backbone plane with an angle of 121.06° between the S−O bond and the plane. The **3a-C6** molecules form a slipped face-to-face π–π stacking pattern with an interplanar distance of 3.76 Å. Figure 3c shows the

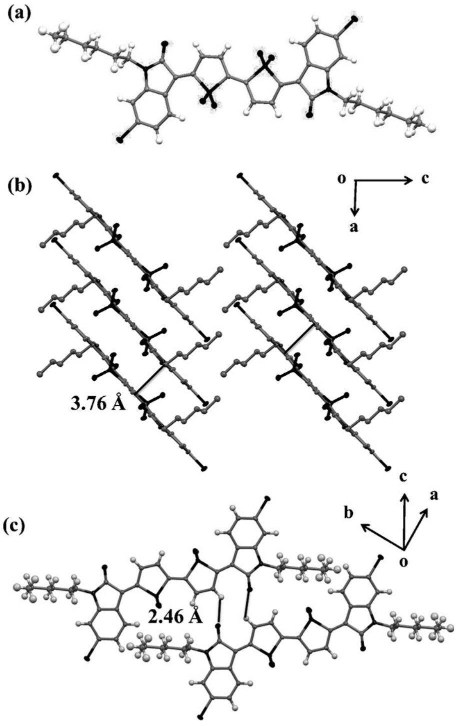

Figure 3. Single-crystal XRD data of **3a-C6**.[43] a) Geometric structure. B) face-to-face π–π stacking. c) C−H⋯O hydrogen bonding between stacks.

close contacts between the H4 protons of the thiophenes and the oxygen atoms of the isatin units, thus suggesting the formation of H···O hydrogen bonds. The H···O distance and the C–H···O angle are measured to be 2.46 Å and 128.5°, respectively.

TLC and NMR data for the samples heated at 100 °C (see Figure S10–S13) indicate that **3b** changed to **3a** directly, while **3c** transformed into **3b** and then into **3a**, without formation of other isomeric products. Consequently, we can deduce that the central double bond between two quinoidal thiophene-*S*,*S*-dioxide units in **3b** and **3c** are also in the *E* form (Scheme 1 and Figure 2), thus indicating that three other possible isomers, having a central double bond in the *Z* form [(*E*,*Z*,*E*), (*E*,*Z*,*Z*), and (*Z*,*Z*,*Z*)], were not produced. The reason for the absence of these IDTO isomers might be because the *E* form of the quinoidal bis(thiophene-*S*,*S*-dioxide) is much more energetically favored over the *Z* form.

The IDTO **3a** (Figure 4b; for **3b** and **3c** see Figures S17 and S18) showed large blue-shifts of the absorption spectra (> 100 nm) compared to that of **2** (Figure 4a) in solution and in the solid state. The optical band gaps (E_g^{opt}) calculated from the film absorption onsets for **2** and **3a** are 1.55 eV and 1.83 eV, respectively. Cyclic voltammetry (CV) measurements showed that the lowest unoccupied molecular orbital (LUMO) energy level of **3a** (as well as **3b** and **3c**) is about −4.08 eV, which is 0.22 eV lower than that of **2** (−3.86 eV; Figures S20 and S21). The highest occupied molecular orbital (HOMO) energy levels for **2** and **3a** were estimated from their E_g^{opt} and LUMO levels to be −5.41 eV and −5.91 eV, respectively. These data support that oxidization of the quinoidal bithiophene unit in **2** could markedly deepen the LUMO and HOMO levels of the resulting **3a**.

The IDTO-based polymer PIDTOTT, prepared from **3a**, absorbs up to 900 nm with a λ_{max} at 710 nm and a vibronic peak at $\lambda = 768$ nm in chloroform (Figure 4c). From solution to film, no obvious shifts in the peak positions were observed, which results from the rather disordered chain packing in the solid state. An E_g^{opt} of 1.42 eV is estimated from the thin-film absorption spectrum. The LUMO and HOMO levels of PIDTOTT were determined by its CV diagram (see Figure S22) to be −3.98 eV and −5.92 eV, respectively. The low-lying energy levels of this polymer again indicate that IDTO is a strong electron-accepting building block. A deep LUMO level is beneficial for electron injection and transport, while a deep HOMO level would build up a large energy barrier to inhibit hole injection, thus potentially enabling unipolar electron-transport performance for this polymer.

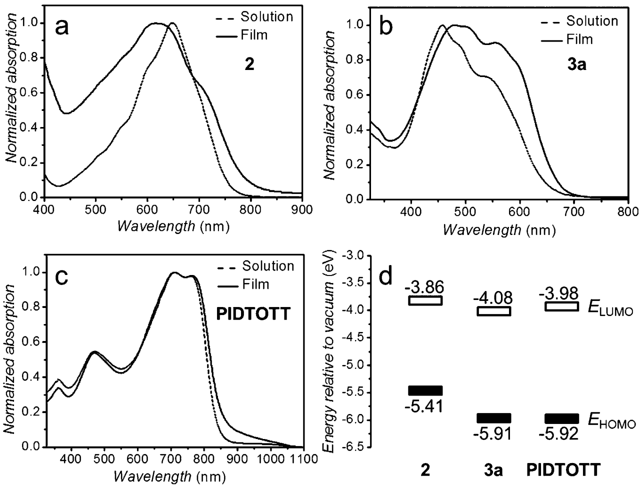

Figure 4. UV/Vis absorption spectra of **2** (containing **2a–f**) (a), **3a** (b), and PIDTOTT (c) in $CHCl_3$ and as a film. d) Energy levels of **2**, **3a**, and PIDTOTT.

Highly ordered chain packing with a close π–π stacking distance is crucial for efficient intermolecular charge hopping. However, the XRD analysis of PIDTOTT thin films indicated that the crystallinity of this polymer is very poor, even after annealing at 200 °C (see Figure S25). The poor chain packing might be due to the presence of the oxygen atoms, connected to sulfur, lying above and under the polymer backbone plane as well as the bulky side chains, thus encumbering close π–π stacking.

Nonetheless, the charge-transport property of PIDTOTT was evaluated in OFET devices with a bottom-gate/bottom-contact (BGBC) configuration using heavily n-doped SiO_2/Si wafer substrates. Surprisingly, this polymer showed very good unipolar n-type semiconductor characteristics with electron mobility as high as 0.14 $cm^2 V^{-1} s^{-1}$, low threshold voltage of 1.8 V, and high on/off ratio of about 10^4 for the 200 °C annealed film (Figure 5). The observed unipolar electron-transport performance for PIDTOTT originates from its low-lying LUMO and HOMO levels as discussed above. The devices showed good air stability when they were annealed and/or measured in air (see Figure S27 and Table S1). Recently, thiophene-*S*,*S*-dioxide-containing (in the aromatic form) oligomers and polymers have been extensively studied because of their interesting optoelectronic properties.[33–41] However, the charge-transport performance of these materials is still poorly understood. One study showed that the mobility of polythiophenes decreases with an increasing amount of thiophene-*S*,*S*-dioxide.[37] A recent study showed that high backbone coplanarity would promote more intramolecular charge delocalization, that is, a highly coplanar polymer, lacking long-range order, could still achieve high mobility, primarily through intramolecular "quasi-one-dimensional" charge transport.[42] We think the high coplanarity of the polymer backbone might improve the intramolecular charge transport, thus leading to the unexpectedly high mobility of the poorly crystalline PIDTOTT.

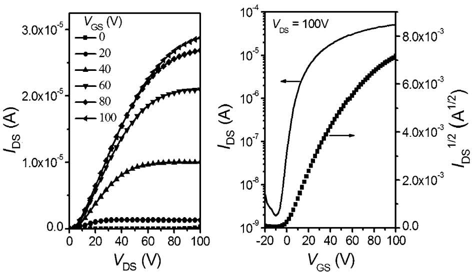

Figure 5. Output (left) and transfer (right) curves of a BGBC OFET device based on PIDTOTT annealed at 200 °C.

In summary, we have synthesized, for the first time, three IDTO isomers, **3a**, **3b** and **3c**, by oxidation of an indophenine compound. **3b** and **3c** can be conveniently converted into the most-stable (*E*,*E*,*E*)-isomer **3a** by mild heat treatment. A donor–acceptor polymer prepared using **3a** as a comonomer possessed a narrow band gap and low LUMO/HOMO levels, and exhibited a high electron mobility of up to 0.14 $cm^2 V^{-1} s^{-1}$ despite its poor chain packing. These results demonstrated that IDTO is a very promising new electron-acceptor building block for constructing high-performance n-type polymer semiconductors.

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Keywords: isomers · molecular electronics · polymers · semiconductors · structure elucidation

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[43] CCDC 1426656 (**3a-C6**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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