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## Communication

Achieving high short-circuit current and fill-factor *via* increasing quinoidal character on nonfullerene small molecule acceptorWenxu Liu<sup>1</sup>, Weiping Li<sup>1</sup>, Jiannian Yao, Chuanlang Zhan\*

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## ABSTRACT

Recently, the fused-ring based low band gap (LBG) small molecule acceptors (SMAs) have emerged as efficient nonfullerene acceptors. So far, these LBG SMAs are mainly designed with IC (2-methylene-(3-(1,1-dicyanomethylene)indanone)) or its analogs, the benzo-type electron-accepting (A) units. Compared to benzene, thiophene is less aromatic and thus the thiophene-involving semiconducting molecule has more quinoidal character, which effectively reduces the energy gap between the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO). Herein, we show that replacing the IC units in ITIC with the CT (cyclopenta[c]thiophen-4-one-5-methylene-6-(1,1-dicyanomethylene)), a thiophene-fused A unit, the quinoidal character is enhanced from 0.0353 on ITIC to 0.0349 on ITCT, the CT-ended SMA. The increase in the quinoidal character reduces the optical band gap and enhances the near IR absorptivity. When blended with the wide band gap (WBG) polymer donor, PBDB-T, an average power conversion efficiency of 10.99% is obtained with a short-circuit current-density ( $J_{sc}$ ) of 17.88 mA/cm<sup>2</sup> and a fill-factor ( $FF$ ) of 0.723. For comparisons, the  $J_{sc}$  is of 16.92 mA/cm<sup>2</sup>,  $FF$  is of 0.655 and PCE is of 9.94% obtained from the ITIC:PBDB-T device. This case indicates that the replacement of the benzene ring on the IC unit with a more polarizable five-member ring such as thiophene is an effective way to enhance the absorption of the near IR solar photons towards designing high-performance nonfullerene polymer solar cells.

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Bulk-heterojunction (BHJ) polymer solar cells (PSCs) are being considered as a potential strategy to meet the future demands on the sustainable and green energy sources. They have several features such as semi-transparency, low-cost, and flexibility and have been paid an increasing attention in the past several decades. Fullerene acceptors show absorption in the visible region such as 300–500 nm for the C<sub>60</sub> derivatives and 300–700 nm for the C<sub>70</sub> derivatives. However, they generally show weak absorption in the near infrared (IR) wavelength region and the tuning on the frontier molecular energy levels, absorption, and optical band gap ( $E_g^{opt}$ ) are much more severely restricted than nonfullerene organic acceptors [1–6]. Recent studies have demonstrated that the IDTT (dithieno[2,3d:2',3'd']-s-indaceno[1,2b:5,6b']dithiophene) [7] and IDT (thieno[2,3d:2',3'd']-s-indaceno[1,2b:5,6b']thiophene) [8] based A-D-A (A is the electron-accepting unit and D is the electron-donating unit) type low band gap (LBG) small-molecule

acceptors (SMAs) have strong absorption in the near infrared (IR) region with the absorption onset extending beyond 780 nm, which corresponds to an  $E_g^{opt}$  of <1.6 eV [9–15]. Again, the absorption and  $E_g^{opt}$  can be fine-tuned, for example, through tuning the electron-donating and/or electron-withdrawing ability of the D and A units [16–18], or tuning the molecular coplanarity *via* the aromatic bridge [19]. As one IDT/IDTT based SMA is blended with one WBG polymer donor, the resulting binary BHJ cover a wide range of the solar energy spectrum, PCEs of >11% were reported in single-junction devices [20–28].

Nevertheless, the SMAs are mainly synthesized with the benzo-type electron-accepting units such as 2-methylene-(3-(1,1-dicyanomethylene)indanone) (IC) or its analogs. Compared to benzene, five-ring such as thiophene is less aromatic. One can see that most of organic semiconductors involve thiophene units [29–32]. Studies have indicated that the introduction of the thiophene units can help enhance the quinoidal character and effectively reduce the energy gap between the highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) [33]. As a result, the optical band gap ( $E_g^{opt}$ ) can be reduced. In this

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communication, we use thiophene to replace the benzene ring in the IC unit and synthesized cyclopenta[*c*]thiophen-4-one-5-methylene-6-(1,1-dicyanomethylene) (CT). Further replacing the IC units on the ITIC (3,9-bis(2-methylene-(3-(1,1-dicyanomethylene) indanone))-5,5,11,11-tetrakis(4-*n*-hexylphenyl)-dithieno [2,3-*d*:2',3'-*d'*]-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene) [34] affords ITCT (3,9-bis(5-methylene-4-one-6-(1,1-dicyanomethylene)-cyclopenta[*c*]thiophen)-5,5,11,11-tetrakis(4-*n*-hexylphenyl)-dithieno [2,3-*d*:2',3'-*d'*]-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene, Fig. 1a). A larger quinoidal character on ITCT leads to a smaller  $E^{\text{opt}}_{\text{g}}$  value (1.55 eV for ITCT and 1.59 eV for ITIC) and a larger absorptivity ( $2.0 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  for ITCT and  $1.3 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  for ITIC). When blended with PBDB-T [35], an average PCE of 10.99% is obtained with  $J_{\text{sc}} = 17.88 \text{ mA/cm}^2$ ,  $V_{\text{oc}} = 0.850 \text{ V}$ , and  $FF = 0.723$ .

The quinoidal character in an aromatic  $\pi$ -system can be reflected with the bond-length-alternation (BLA) [36]. The BLA is the length difference between a single bond and the adjacent double/triple bond of that  $\pi$ -system. To estimate the BLA values in the ITCT and ITIC, we performed density functional theory (DFT) calculations at the B3LYP/6-31G (d,p) basis set in vacuum to optimize the molecular conformations, and again, calculate the electronic structures. The BLA value, relative to the aromatic–quinoidal tautomerization (Fig. 1a), decreases from 0.0353 in ITIC to 0.0349 in ITCT, indicating the increase in the quinoidal character by replacing the IC benzene ring with the CT thiophene. In both ITCT and ITIC, the highest occupied molecular orbitals (HOMOs) are localized on the IDTT part and extend to the cyclopenta-5-methylene linkers with small contributions from the 1,1-dicyanomethylene and the ketone units. The lowest unoccupied molecular orbitals (LUMOs) are delocalized over the whole planar conjugated backbone with large contributions from the CT thiophene and the IC benzene (Fig. 1b), respectively. The LUMO level in ITCT shifts down relative to ITIC, and the HOMO levels in both molecules are close to each other (–5.5 eV) because there are no contributions to the HOMOs from the fused-benzene or fused-thiophene. The LUMO–HOMO band gap reduces from 2.12 eV for ITIC to 2.07 eV for ITCT with the increase in the quinoid character.

The CT unit was synthesized by three steps (Fig. 2). The commercial thiophene-3,4-dicarboxylic acid was first converted

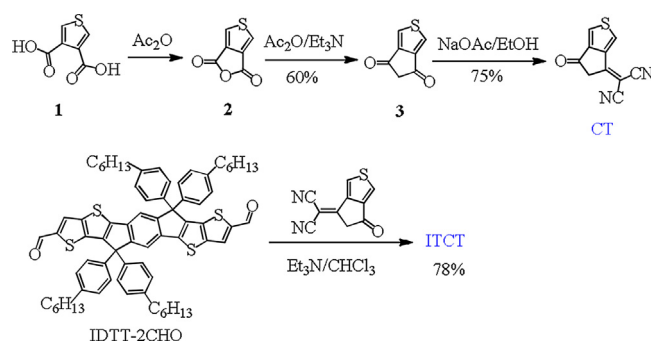


Fig. 2. The synthetic procedures towards CT and ITCT, respectively.

into thieno[3,4-*c*]furan-1,3-dione with acetic anhydride, and the following condensation reaction afforded 5*H*-cyclopenta[*c*]thiophene-4,6-dione (thieno-4,6-dione). The total yield of the two steps was 60%. Reaction between thieno-4,6-dione and malononitrile produced CT in a yield of 75%. Condensation between CT and IDTT-2CHO gave ITCT in a yield of 78%. The details of synthesis are given in Supporting information.

Relative to ITIC, the maximum molar extinction coefficient ( $\epsilon_{\text{max}}$ ) of ITCT increases ( $1.3 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$  vs.  $2.0 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), the absorption bands in solution and in film both red-shift (Fig. S1a, 3a and Table S1 in Supporting information), and

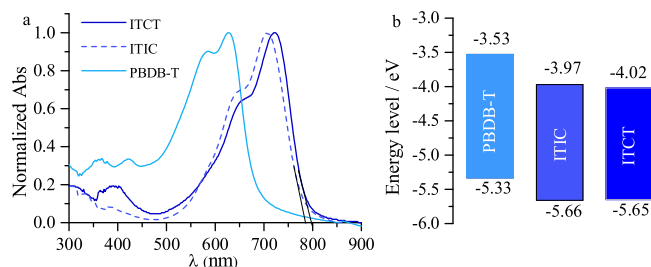


Fig. 3. Film absorption spectra (a) and energy levels diagram (b) of PBDB-T, ITIC, and ITCT.

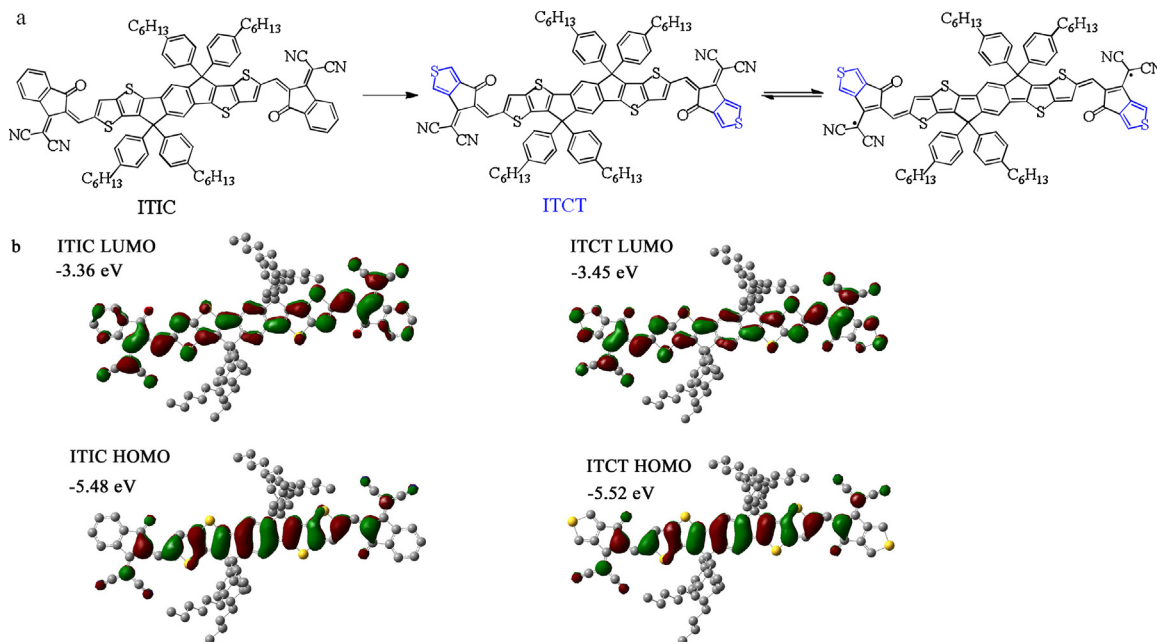


Fig. 1. (a) Molecular structures of ITIC and ITCT with the aromatic–quinoidal tautomerization on the ITCT molecule depicted. (b) LUMO and HOMO levels and MOs distributions on ITIC and ITCT, calculated with DFT calculations.

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