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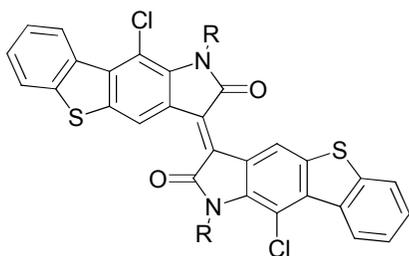
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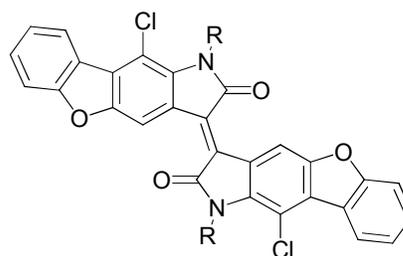
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Graphic Abstract

Extended isoindigo core: synthesis and applications as solution-processable n-OFETs materials in ambient conditions

benzothiophene fused isoindigo (DBTII)

$$\mu_e 0.01 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$$
$$\mu_h 0.00057 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$$



benzofuran fused isoindigo (DBFII)

$$\mu_e 0.07 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$$

COMMUNICATION

Extended isoindigo core: synthesis and applications as solution-processable n-OFETs materials in ambient conditions

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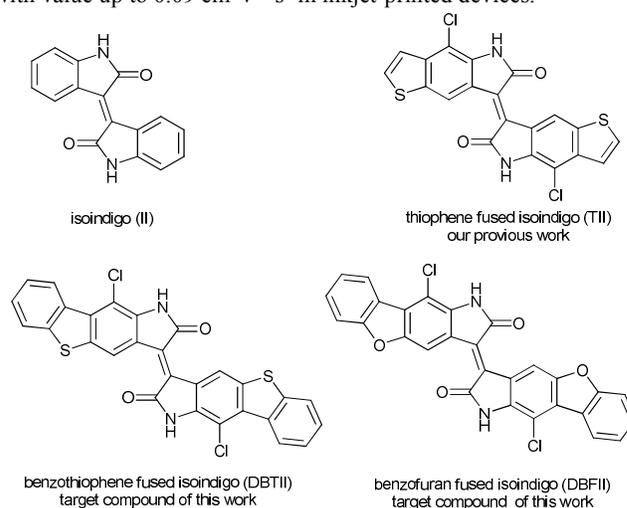
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Two isoindigo derivatives fused with benzothiophene (C20-DBTII) and benzofuran (C20-DBFII) heterocycles have been synthesized. Solution-processed OFETs based on the C20-DBTII showed ambient-stable ambipolar charge transport behaviour. OFETs based on the C20-DBFII show n-channel behaviour with electron mobility up to 0.074 cm² V⁻¹ s⁻¹ in ambient conditions.

Organic semiconductors have received more and more attention as futuristic materials in recent years, and the past decades have seen the rapid development of organic semiconductors including organic field effect transistors (OFETs),¹ organic light-emitting diodes (OLEDs),² and organic photovoltaic cells (OPVCs).³ These materials offer advantages of low-cost and flexible large-area electric circuits. The discovery of novel conjugated pigments boosts the growth in this area. Since two small molecules based on isoindigo core were reported as electron donor materials for solar cells by Reynolds and co-workers in 2010,⁴ more than 100 articles on various aspects have been published involving isoindigo-based materials.⁵ Recently, isoindigo-based materials have received increasing attention for their promising performance in OFETs.⁶ For instance, Pei and co-workers reported a fluorinated isoindigo-based conjugated polymer with a remarkable hole mobility of 3.62 cm² V⁻¹ s⁻¹.⁷ Recently, Kim et al. synthesized a thienoisoindigo-naphthalene polymer with an ultrahigh mobility of 14.4 cm² V⁻¹ s⁻¹.⁸

Although tremendous achievements have been made on polymeric OFET materials containing isoindigo core,⁹ the development of small molecular n-type or ambipolar OFET materials that could be operated in ambient conditions¹⁰ is still an important task, since compared to polymers, small molecules have many advantages: 1) fixed molecular weight, identical structure and physical properties, no batch-to-batch variations,¹¹ 2) easy purification by chromatography, sublimation or recrystallization, 3) diverse fabrication methods of small molecular OFET devices, including high-vacuum deposition, spin-casting and single crystal growth. However, although oligomers based on isoindigo have been tested for OPVs, the use of isoindigo for small molecular OFETs was less studied.¹² It was not until 2014 Yue et al. reported an OFET device based on a dicyanated isoindigo showing electron mobility up to 0.044 cm² V⁻¹ s⁻¹.^{12c} Marder and co-workers also synthesized a a

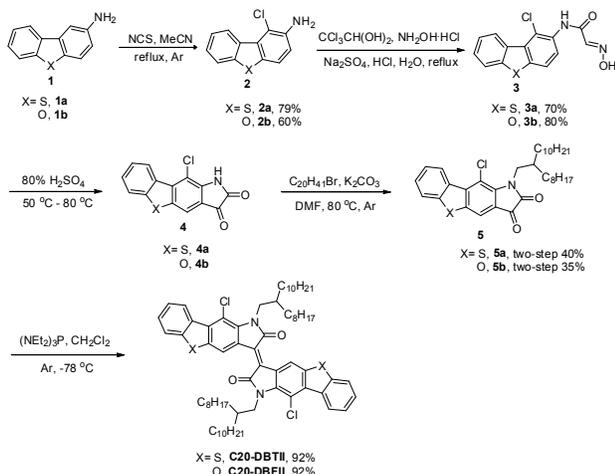
tetracyanated thienoisoindigo which shows good electron mobility with value up to 0.09 cm² V⁻¹ s⁻¹ in inkjet-printed devices.^{12d}



Scheme 1. The manipulation on the isoindigo core.

We are focused on the manipulation of the isoindigo core for better OFETs. Previously, our group synthesized thiophene-fused isoindigo (as shown in Scheme 1) and disclosed its photophysical and electrochemical properties, showing that the intramolecular charge transfer was enhanced.¹³ In this communication, we further extended the conjugated system by fusing isoindigo with benzofuran or benzothiophene moiety, and investigated their OFET performance. Since isoindigo core is electron-deficient and benzothiophene or benzofuran terminal is electron-rich, it forms an intramolecular Donor-Acceptor-Donor (D-A-D) structure, which we speculated will lead to improved performance. Two solution-processable isoindigo derivatives (C20-DBTII and C20-DBFII) were thus synthesized. Both C20-DBTII and C20-DBFII exhibit relatively low-lying LUMO level, which facilitates electron transfer. C20-DBTII shows ambipolar charge transport behavior (0.011 cm² V⁻¹ s⁻¹ for electrons and 5.72 × 10⁻⁴ cm² V⁻¹ s⁻¹ for holes) and C20-DBFII exhibits good electron mobility up to 0.074 cm² V⁻¹ s⁻¹ (as shown in Table 2) in ambient conditions.

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Scheme 2 The synthetic routes towards C20-DBTII and C20-DBFII.

The synthetic route toward both compounds is shown in Scheme 2. Briefly, chlorination at 1-position of commercially available 2-amino-dibenzo[*b,d*]thiophene **1a** afforded compound **2a** in good yield, which is a necessary step to force the subsequent Friedel-Crafts reaction occur at 3-position of the dibenzothiophene core, as reported in our previous work.¹³ Furthermore, since the introduction of chlorine atom to the isoindigo core has been proved to be effective to improve electron transport of conjugated polymers,¹⁴ we anticipate similar effects might be observed on the extended isoindigo core. Treating **2a** with chloral hydrate and hydroxylamine hydrochloric acid afforded **3a** in 70% yield, which cyclized when treated with 80% H₂SO₄ to give the corresponding indole-2,3-dione **4a** as a crude product. The crude product was not purified due to its poor solubility but carried out directly to the next step for alkylation, and the product **5a** was then purified by chromatography. Upon treatment with P(NEt₂)₃, **5a** was converted to C20-DBTII in excellent yield. The overall yield for five steps is 20%. C20-DBFII was synthesized in the same manner with similar overall yield. Both C20-DBTII and C20-DBFII showed good solubility in common organic solvents, such as dichlorobenzene (10 mg mL⁻¹), thus makes them good candidates for solution processable OFETs.

The band gap and the HOMO-LUMO energy level are important parameters to determine the properties of organic semiconductors. UV-vis spectra of C20-DBTII and C20-DBFII in solution state and in film state are shown in Fig. 1 and Fig S2, ESI† respectively. Both C20-DBTII and C20-DBFII exhibit relatively high and similar absorption coefficient in chloroform ($\epsilon = 3.94 \times 10^4$ and 4.33×10^4 dm³ mol⁻¹ cm⁻¹, respectively). An intense absorption band (compared to that of isoindigo) with the peak at 501 nm and 485 nm was observed for C20-DBTII and C20-DBFII respectively (Figure 1a). Interestingly, an absorption shoulder located around 600 nm was observed for C20-DBFII, which could not be seen for C20-DBTII. The calculated UV-vis spectra (shown in Figure 1b) are in good agreement with the experimental results. The maximum absorption

for both C20-DBTII and C20-DBFII is assigned to energy transition between HOMO-2 and LUMO. The absorption shoulder of C20-DBFII is assigned to its energy transition between HOMO and LUMO. On the other hand, the oscillation strength of HOMO-LUMO transition of C20-DBTII is very weak (located at 613 nm, OS: 0.03, Table. S1 ESI†), indicating that this HOMO-LUMO transition could hardly be detected by UV-vis spectroscopy. This is due to the mismatch of the two orbitals in C20-DBTII. The orbital distribution along the two molecules is clearly shown in Fig. S3, ESI†. The LUMOs of both molecules are similar, in which the orbitals are mainly located the central core. This indicates that the dilactam core contributes most to LUMO. However, the HOMOs of the two species are quite different. The HOMO electron density of C20-DBTII at the central core is quite low, while a rather large density is observed at the same region for the HOMO of C20-DBFII. Therefore, the HOMO-LUMO of C20-DBTII overlap less than that of C20-DBFII, naturally leading to the rather small transition dipole moment between its HOMO and LUMO. In consequence, while the onset of the UV-vis absorption of C20-DBFII represents its HOMO-LUMO gap (1.79 eV), that of C20-DBTII mainly reflects its HOMO-2-LUMO gap (2.20 eV). The HOMO-2-LUMO band gap (2.27 eV) of C20-DBFII could be deduced from its major absorption peak, which is similar to that of C20-DBTII. Overall, the change in UV-vis spectra of the two molecules indicates that the replacement of S atom by O atom leads to an obvious change in the electronic structure in this conjugated system. In thin film state, both the UV-vis spectra of C20-DBTII and C20-DBFII showed an obvious hypsochromic shift (30 nm for C20-DBTII and 19 nm for C20-DBFII, Figure S2, ESI†), suggesting that both molecules might take same molecular stacking mode (H-aggregate) in solid state, due to their similar structure.

LUMO energy level of the two compounds was determined by cyclic voltammetry, as shown in Fig. S4, ESI†.¹⁵ Despite the difference in the structure, both C20-DBTII and C20-DBFII exhibit two pairs of quasi-reversible redox waves, with the similar half-wave reductive potential, indicating that the electron-injection ability was mainly determined by the isoindigo core. The energy level of LUMO of these isoindigo derivatives were calculated using $E_{\text{LUMO}} = -e(E_{1/2}^{0/-} + 4.44)$ eV equation (referring to Ag/AgCl electrode), as shown in Table 1. The $E_{1/2}^{0/-}$ of C20-DBTII and C20-DBFII is -0.72 eV and

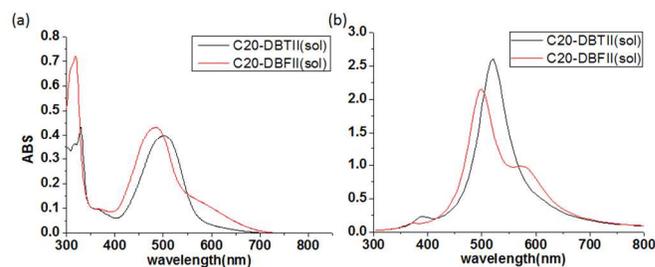
Fig. 1. (a) Normalized UV-vis absorption of 10⁻⁵ mol L⁻¹ C20-DBTII and C20-DBFII in chloroform; (b) Calculated UV-vis absorption of C20-DBTII and C20-DBFII in chloroform (DFT(B3LYP/6-31+G*))

Table 1 UV-vis absorption and electrochemical properties of C20-DBTII and C20-DBFII

Compounds	$\lambda_{\text{max}}^{\text{sol}}$ (nm)	$\lambda_{\text{max}}^{\text{film}}$ (nm)	$E_{1/2}^{0/-}$ (V)	$E_{1/2}^{-7/2-}$ (V)	E_{LUMO} (eV)	E_{HOMO} (eV)	$E_{\text{HOMO-2}}$ (eV)
C20-DBTII	501	471	-0.72	-1.11	-3.72	/	-5.92
C20-DBFII	485	466	-0.71	-1.12	-3.73	-5.52	-6.00

Table 2 OFET performance of C20-DBTII and C20-DBFII thin films under ambient

compounds	$\mu_e(\text{cm}^2\text{V}^{-1}\text{s}^{-1})$	V_T (V)	$I_{\text{on}}/I_{\text{off}}$	$\mu_h(\text{cm}^2\text{V}^{-1}\text{s}^{-1})$	V_T (V)	$I_{\text{on}}/I_{\text{off}}$
C20-DBTII	0.011	47	1.8×10^2	5.72×10^{-4}	-53	2.5×10^2
C20-DBFII	0.074	40	1.5×10^4		N.A.	

-0.71 eV, which corresponds to E_{LUMO} at -3.72 eV and -3.73 eV respectively. The HOMO energy level (E_{HOMO}) of C20-DBFII is -5.52 eV, deduced from the equation $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g}}^{\text{opt}}$. The HOMO-2 energy level ($E_{\text{HOMO-2}}$) of C20-DBTII and C20-DBFII can also be estimated using the similar equation $E_{\text{HOMO-2}} = E_{\text{LUMO}} - E_{\text{g-2}}^{\text{opt}}$, which is -5.92 eV and -6.00 eV respectively.

In order to evaluate the performance of the electronic devices of C20-DBTII and C20-DBFII, two top-gate/bottom-contact organic thin-film transistors were fabricated with a SiO_2/Si substrates and Au source/drain electrodes (Fig. S5, ESI[†]). The thin films were spin-coated onto SiO_2/Si substrates using C20-DBTII and C20-DBFII dissolved in dichlorobenzene (DCB) solution (10 mg/mL) in a nitrogen-filled glovebox. A CYTOP solution was spin-coated on the top of the semiconducting layer and cross-linked at 100 °C for 1 h as the dielectric layer. Then, an aluminium layer was thermally evaporated as the gate electrode. The device performance was investigated in ambient conditions (Fig. 2 and Fig. S6, ESI[†]) and the results were summarized in Table 2. OFETs based on C20-DBTII show ambipolar charge transport behaviour. The electron mobility is up to $0.011 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, with a threshold voltage of 47V. The hole mobility is up to $5.72 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, with a threshold voltage of -53V. On the other hand, OFETs based on C20-DBFII show only n-channel charge transport behaviour, with electron mobility up to $0.074 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, with the threshold voltage value of 40V. It is worthwhile to mention that C20-DBTII and C20-DBFII decomposed at 356°C and 348°C respectively, showing their excellent thermal stability (TGA trace, as shown in Figure S1, ESI[†]).

DBFII could not be detected. Although according to the calculated results, C20-DBTII and C20-DBFII should have similar HOMO/LUMO energy level thus should show similar charge transport behaviour, there might be some other reasons to explain why DBFII does not exhibit p-type character. One possible reason is that O atom is more electronegative than S atom, while S atom is easier to be polarized since it is larger in size than O atom. Overall, the removal of an electron from C20-DBTII is easier than from C20-DBFII.

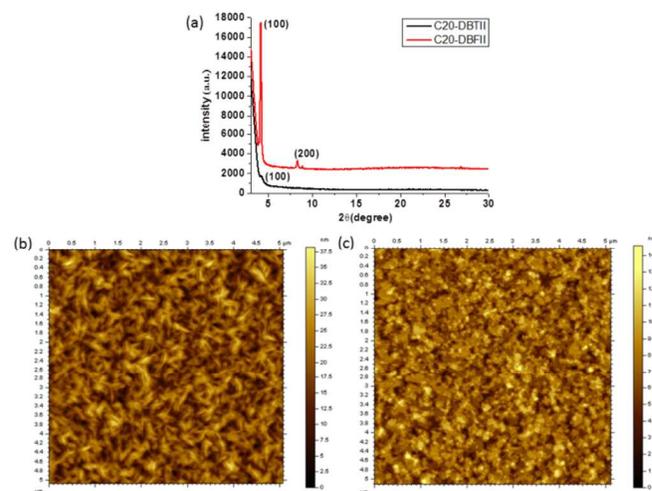


Fig.3 (a) Out-of-plane X-ray diffraction (XRD) patterns of C20-DBTII and C20-DBFII thin films; (b) AFM height images ($5 \times 5 \mu\text{m}^2$) of C20-DBTII thin films; (c) AFM height images ($5 \times 5 \mu\text{m}^2$) of C20-DBFII thin films; Thin films were spin-coated onto SiO_2/Si substrates from DCB solutions (10 mg/mL).

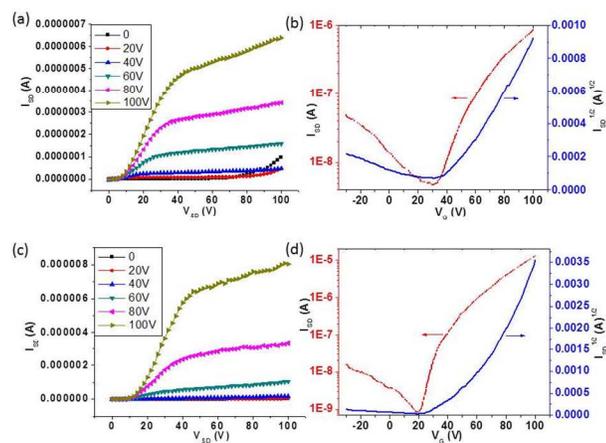


Fig.2(a) output characteristics and (b) transfer characteristics of C20-DBTII OFET devices; (c) output characteristics and (d) transfer characteristics of C20-DBFII OFET devices; Output characteristics at n-channel operation and transfer characteristics at electron-enhancement operation; Device dimensions ratio of channel width to channel length = 20; All devices are measured in ambient conditions.

The device test results indicate that both molecules are good n-type semiconductors (C20-DBTII is better), but not good p-type semiconductors: the hole mobility of C20-DBTII is twenty times smaller than its electron mobility, and the hole mobility of C20-

As to their n-type OFET performance, C20-DBFII showed better electron mobility and smaller threshold voltage than C20-DBTII. We reasoned that the difference in the OFET performance of the two molecules might be due to their different crystallinity and morphologies. The crystallinity and molecular orientations of thin films were then investigated by X-ray diffraction (XRD) analysis. The out of plane XRD patterns of the thin films of C20-DBTII and C20-DBFII are shown in Fig. 3. C20-DBFII shows sharp and intense peaks, but C20-DBTII shows weak peaks, indicating the better crystallinity of C20-DBFII film. The d -spacing of both molecules were calculated from the out-of-plane XRD patterns and Bragg equation. C20-DBTII and C20-DBFII films exhibited primary diffraction peaks at 2θ of 4.28° and 4.13° , corresponding to $d(100)$ -spacing of 20.65 and 21.37 Å, respectively. The $d(100)$ -spacing of C20-DBTII and C20-DBFII are a little bit longer than the theoretically calculated molecular lengths (C20-DBTII, molecular length ~ 19.94 Å; C20-DBFII, molecular length ~ 19.45 Å), suggesting a vertical alignment of molecular configuration on the substrate surface. C20-DBFII also showed a diffraction peak at 2θ of 8.28° , which is assigned to (200) diffraction, with $d(200)$ -spacing of 10.67 Å. Clearly, C20-DBFII shows stronger d -spacing signal, indicating a better layer-by-layer packed lamellar structure, which accounts for better electron mobility of C20-DBFII than C20-DBTII.

Besides crystallinity, the semiconductor film morphology is another decisive factor that affects charge transport properties. The morphologies of the as-grown C20-DBTII and C20-DBFII films for OFET study were investigated using atomic force microscopy (AFM), and the results are shown in Figure 3. AFM height images showed that both films formed densely packed nanofibrillar network with relatively smooth surface roughness. However, although C20-DBTII films exhibited larger fibrillar aggregates (RMS ~ 5.04 nm) than C20-DBFII (RMS ~ 1.71 nm), they also showed more obvious grain boundaries than C20-DBFII. Larger boundaries are deleterious to the charge transport, which explains why the electron mobility of C20-DBTII film is almost seven times smaller than that of C20-DBFII film.

Conclusions

Two isoindigo derivatives fused with benzothiophene and benzofuran heterocycles (C20-DBTII and C20-DBFII) have been synthesized and characterized. Solution-processed OFETs based on these two molecules exhibited stable performance in ambient conditions due to their low-lying LUMO level. C20-DBTII showed ambipolar charge transport behaviour while C20-DBFII showed n-channel behaviour with electron mobility up to $0.074 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in ambient conditions. This is the first example using fused isoindigo small molecules for OFET applications, indicating the potential applications of isoindigo derivatives not only in polymeric system, but also in small molecular system for organic semiconductors.

Notes and references

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