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Isomeric Indacenedibenzothiophenes: Synthesis, Photoelectric Properties and Ambipolar Semiconductivity

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A new strategy via double C-H activation cyclization has been developed for the versatile synthesis of IDBT derivatives with quite different photoelectric properties. Single-crystal field-effect transistors based on IDBT-/-TIPS delivered high and balanced charge carrier mobilities of up to 0.64 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $0.34 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons under ambient conditions.

In organic electronics,¹ ambipolar semiconductors² are essential for complementary metal-oxide semiconductor (CMOS)-like integrated circuits and light-emitting transistors, which should simultaneously possess high HOMO (highest occupied molecular orbital) and deep LUMO (lowest occupied molecular orbital) energy levels to facilitate hole and electron transport. Polyacenes,⁴ especially pentacene derivatives,⁵ are classical *p*-type semiconductors. To date, *N*-heteropentacenes⁶ bearing deep LUMO energy levels have also been developed for electron transport. By contrast, ambipolar polyacenes with high and balanced hole/electron mobilities and, especially, ambient stability are far from being achieved,⁷ which can be ascribed to the dilemma of decreasing LUMO energy levels with electron-withdrawing groups while keeping suitably high HOMO energy levels. With inbuilt five-membered rings,⁸ indenofluorene derivatives⁹ without strong electronwithdrawing substituents have recently been found to exhibit intrinsically low LUMO energy levels and are expected to be excellent candidates as ambipolar semiconductors.¹⁰ However, the ambipolar feature of indenofluorenes is not fully explored, i.e., 10^{-3} cm² V⁻¹ s⁻¹ level in a single-crystal transistor¹¹ and 10^{-1} 6 cm² V⁻¹ s⁻¹ level in thin-film transistors,¹² which can be attributed to the unfavorable solid-state stacking and improper HOMO/LUMO alignment. We think that the indacenedibenzothiophene core $(IDBT, Fig. 1)^{13}$ may possibly

overcome these deficiencies because the extended π conjugation can help induce intermolecular π - π stacking and a suitable HOMO energy level. Depending on the fusing patterns, isomeric indenofluorenes may exhibit unique properties such as small-bandgap absorption^{9c} and biradicaloid^{9f,g} properties, but can only be prepared one at a time. We report herein one-pot construction of two isoelectronic IDBT cores with linear (IDBT-I) and angular (IDBTa) configurations (Fig. 1) by double C-H activation. IDBT-I and IDBT-a show different photoelectric properties. Compared with IDBT-I's, the first two excitation states of IDBT-a-Mes are extremely weak, which results in short-wavelength absorption. However, the electrochemical energy band gap of IDBT-a-Mes is smaller than that of IDBT-I-Mes. By attaching weakly electron-withdrawing triisopropylsilyl (TIPS) groups, IDBT-I-**TIPS** shows significantly decreased electrochemical energy band gap, 1.19 eV (IDBT-I-TIPS) vs 1.60 eV (IDBT-I-Mes), optimal frontier orbital energies of -5.46 eV for HOMO and -4.27 eV for LUMO and ordered intermolecular π - π stacking with a short distance of 3.304 Å, which jointly are beneficial for ambipolar carrier transport. Consequently, single-crystal fieldeffect transistors (FETs) based on IDBT-I-TIPS can operate under ambient conditions and exhibit high and balanced charge carrier mobilities of up to 0.64 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $0.34 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons, which is rare for conjugated polycyclic hydrocarbons.



Fig. 1 Isomeric indacenedibenzothiophenes

The synthetic route toward IDBTs is shown in Scheme 1. The starting material 1 was prepared using a Stille-type crosscoupling reaction between benzo[b]thiophen-3-yltributylstannane and terephthaloyl dichloride in 40% yield after

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recrystallization. Instead of the traditional method, i.e., intramolecular Friedel-Crafts acylation reaction under strong acidic conditions, we selected a more succinct double C-H activation reaction for the synthesis of diketone 2a. After many attempts, we found that the double cyclization of compound 1 can only proceed in pivalic acid (PivOH) because the reaction under the reported conditions in trifluoroacetic acid¹⁴ is quite inefficient, stopping at the monocyclization step. Unexpectedly, angular analogue 2b was also obtained. Both compounds 2a and 2b can hardly be dissolved in any solvent and thus can be used for the next step without further separation. IDBT-I-Mes and IDBT-a-Mes were synthesized from a mixture of 2a and 2b and mesityllithium followed by SnCl₂ reduction as a blue and yellow solid, respectively. With a similar procedure, IDBT-I-TIPS was smoothly synthesized from compound 4a in 20% isolated yield as blue needle crystals after recrystallization.¹⁵ By contrast, IDBT-a-TIPS is highly unstable and cannot be separated.

All three IDBT compounds were fully characterized by conventional methods. IDBT-/-Mes shows the same NMR spectra as those reported, ¹³ with a single peak at δ 6.07 ppm assigned to the two alkenyl hydrogens of the central quinoid ring. By contrast, the corresponding alkenyl hydrogens in IDBT-a-Mes are shifted upfield, δ 5.50 ppm, which indicates the enhanced shielding effect from the two neighboring mesityl groups. By contrast, the alkenyl hydrogens in IDBT-I-TIPS are shifted downfield, δ 6.38 ppm, in the absence of mesityl groups. The downfield-shift tendency from IDBT-a-Mes, IDBT-I-Mes to IDBT-/-TIPS agrees well with the decreased antiaromaticities of the guinoid rings from angular to linear **IDBT** cores, which are -9.60 (IDBT-a-Mes), -12.14 (IDBT-I-Mes) and -11.64 ppm (IDBT-I-TIPS) according to the nucleus-independent chemical shift (NICS) calculations¹⁵ at the B3LYP/TZP level with the Amsterdam Density Functional (ADF) program.¹⁶ The NICS values of five-membered rings in IDBT-a-Mes and IDBT-I-Mes are also guite different, -22.09 and -17.98 ppm, respectively,



Fig. 2 Molecular structure (a, 50% probability ellipsoids) and packing (b) of **IDBT-/-TIPS**. Bond lengths of s-indacene: C1–C2: 1.418 Å, C2–C3: 1.370 Å, C1*i*–C3: 1.445 Å, C1*i*–C12: 1.417 Å; C5–C12: 1.434 Å; C4–C5: 1.396 Å; C3–C4: 1.448 Å.

which indicates the stronger antiaromaticity of the former. **IDBT-I-TIPS** crystals suitable for single-crystal X-ray analysis were grown by slow diffusion of methanol into its dichloromethane solution.¹⁷ **IDBT-I-TIPS** shows a rigid and planar **IDBT** framework (Fig. 2a) with a high C_{2h} symmetry and single/double-bond alternation because of the antiaromaticity. The large **IDBT-I** core and TIPS pendants jointly facilitated onedimensional intermolecular π - π stacking with a short distance of 3.304 Å, which is smaller than that of TIPS-pentacene, 3.349 Å, and a large overlap of the adjacent **IDBT** cores (center-tocenter distance: 8.05 Å), which is very favorable for charge carrier transport (Fig. 2b). By contrast, **IDBT-I-Mes** bearing bulky mesityl groups shows no intermolecular π - π stacking in solid state,¹³ which may be the case for **IDBT-***a***-Mes**, but we did not get its single crystals.

The photophysical and electrochemical properties of IDBTs were examined in dichloromethane and are summarized in Table 1. The isomeric IDBT-a-Mes and IDBT-I-Mes exhibit disparate absorption spectra with longest absorptions at 472 nm (ϵ : 0.78×10⁴ L mol⁻¹ cm⁻¹) and 618 nm (ϵ : 3.95×10⁴ L mol^{-1} cm⁻¹) in dichloromethane, respectively (Fig. 3a), which can be well explained by the theoretical calculations. According to time-dependent density functional theory (TDDFT) calculations at the B3LYP/TZP level (Fig. 4), we found that the first excitation state of IDBT-/-Mes originated from the HOMO-1 to LUMO transition (604 nm, f: 0.393). By contrast, the first two excitation states of IDBT-a-Mes originating from HOMO to LUMO (1133 nm, f: 0.008) and HOMO-1 to LUMO (611 nm, f: 0.009) transitions are extremely weak and can hardly be distinguished from its absorption spectrum. Only the third excitation state of HOMO-2 to LUMO transition shows reasonable oscillator strength, 470.2 nm (f: 0.36). IDBT-I-TIPS with extended π conjugation exhibits further bathochromic absorption at 682 nm with large absorption coefficient, (ϵ : 7.68×10^4 L mol⁻¹ cm⁻¹), which can be attributed to the HOMO to LUMO transition (708 nm, f: 0.51). Unlike angular-IDBT, the HOMO and HOMO-1 orbitals of linear-IDBTs have very close energy levels with small energy differences of 0.04 eV (IDBT-I-Mes) and 0.11 eV (IDBT-/-TIPS), respectively. The HOMO-1 and HOMO energy alignments of IDBT-I-Mes and IDBT-I-TIPS are reversed with different substitutions, and thus the HOMO-1 of IDBT-/-Mes and the HOMO of IDBT-/-TIPS show the same orbital distribution. The cyclic voltammograms (CVs) of IDBT are shown in Fig. 3b. All IDBT compounds have highly

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Fig. 3 (a) UV–vis absorption spectra and (b) cyclic voltam-mograms of IDBTs in dichloromethane. Inset: a photo of IDBT solutions, IDBT-*a*-Mes (left), IDBT-*I*-Mes (middle) and IDBT-*I*-TIPS (right).



Fig. 4 DFT-calculated orbital energy diagram and pictorial representation of frontier orbitals for IDBTs.

amphoteric ability with at least one reversible or irreversible oxidation and reduction process. **IDBT-a-Mes** can be oxidized and reduced more easily than **IDBT-/-Mes**, 0.30 vs 0.40 V (oxidation) and -1.40 vs -1.61 V (reduction), leading to a smaller electrochemical band gap, 1.42 eV vs 1.60 eV. The apparent inconsistency between electrochemical and optical band gaps can be explained by the different nature of the first excitation state. Compared with **IDBT-/-Mes**, the redox processes of **IDBT-/-TIPS** are negatively shifted by 0.20 V for oxidation and significantly positively shifted by 0.67 V for reduction, which results in appropriate HOMO (-5.46 eV) and LUMO (-4.27 eV) energy levels for ambipolar carrier transport.¹⁸ The HOMO/LUMO energy levels of IDBT-I-Mes are quite close to those reported values.¹³

Taking its optimized frontier orbital energies and compacted π - π stacking into consideration, we selected **IDBT**-I-TIPS to demonstrate the potential of IDBTs as ambipolar semiconductors. IDBT-/-TIPS micronanocrystals were grown using the physical vapor transport (PVT) method, which is better than the solution-growing method because of the absence of solvents. In the optical microscope (Fig. 5a), the micronanocrystals on the modified substrate display as smooth ribbons or sticks several dozens of micrometers in length, which indicates the long range regularity of the array. We prepared a series of micronanocrystal transistors with doped n-type silicon wafer as the gate electrode and octadecyltrichlorosilane-modified SiO₂ as the dielectric layer and selected the transistors with high quality single crystals that are thin enough to ignore the resistance under measuring. To avoid a negative effect from thermal radiation during

Table 1 Photophysical and electrochemical properties of IDBT-a-Mes, IDBT-I-Mes and IDBT-I-TIPS.^o

Cpd.	λ_{max}^{abs}	$E_{\rm red}^{1/2c}$	$E_{\rm ox}^{1/2c}$	ELUMO ^ε	E _{HOMO} ε
	(nm)	(∨)	(V)	(eV)	(eV)
IDBT-a-Mes	472	-1.31	0.30	-3.88	-5.30
	(3.89) ^b	$(-1.40)^{d}$			
IDBT-/-Mes	618	-1.61^{d}	0.40	-3.79	-5.38
	(4.60) ^b				
IDBT-/-TIPS	682	-0.90	0.50	-4.27	-5.46
	$(4.89)^{b}$	(-0.94) ^d			

^{*a*} Measured in dichloromethane. ^{*b*} Logarithmic values of absorption coefficients (L mol⁻¹ cm⁻¹). c CV on a carbon electrode with *n*-Bu₄NClO₄ in dichloromethane (0.1 M, vs Fc⁺/Fc). ^{*d*} The potential of the peak cathodic current. ^{*e*} The LUMO/HOMO energy levels were determined from ELUMO/HOMO = $-(5.10 + E_{red/ox}^{onset})$.¹⁸



Fig. 5 (a) The micronanocrystal images of optical microscope and (b) FET device model for the measurements of **IDBT-I-TIPS**. (c) TEM image of micronanocrystal from PVT method with its matching to the SAED pattern. (d) XRD pattern of micronano-crystals. (e) and (f) *I–V* transfer characteristics for hole and electron mobilities of the representative **IDBT-I-TIPS**-based single-crystal FET devices.

thermal gold (Au) deposition, Au foils were pasted directly onto the micronanocrystals as the source and drain electrodes, which has been proved to be an efficient and convenient method. The FET devices were fabricated along the growing direction of micronanocrystals, and the method of FET measurements is shown in Fig. 5b.¹⁹ Because of the LUMO energy level below -4.0 eV,²⁰ all of the FET measurements can be performed under ambient conditions without any protection. The transmission electron microscope (TEM) patterns with the corresponding selected area electron diffraction (SAED) of the single-crystal micronanocrystals are seen as neat and smooth patterns in Fig. 5c, which suggests that the carrier transporting direction in the a-b plane is parallel to the substrate, while the X-ray diffraction (XRD) image in Fig. 5d exhibits sharp and pure peaks, which indicates that the d spacing is 10.95 Å between the adjacent layers. The transistors exhibit a balanced ambipolar property with hole mobilities of up to 0.64 cm² V^{-1} s⁻¹ (average value: 0.23 cm² V^{-1} s^{-1} from 15 devices) and electron mobility up to 0.34 cm² V⁻¹ s⁻¹ (average value: 0.15 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from 14 devices). Typical transfer characteristics are shown in Fig. 5e and 5f.

In summary, we have developed a new strategy, i.e., double C–H activation cyclization, for the versatile synthesis of **IDBT** derivatives, including isomeric **IDBT-***a* and **IDBT-***I*, which we believe can be expanded for the preparation of various indenofluorene analogues. Isomeric **IDBT**-*I* and **IDBT**-*a* have



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quite different photoelectric properties. Angular IDBT-a-Mes shows shorter-wavelength absorption than linear IDBT-/-Mes but with a narrower electrochemical energy band gap, the origin of which has been elucidated by theoretical investigations. Compared with IDBT-a-Mes and IDBT-I-Mes, IDBT-/-TIPS shows the most optimized HOMO/LUMO energy levels of -5.46 eV for HOMO and -4.27 eV for LUMO and ordered intermolecular π - π stacking with a short distance of 3.304 Å. Indeed, single-crystal FETs based on IDBT-I-TIPS delivered high and balanced charge carrier mobilities of up to 0.64 cm² V⁻¹ s⁻¹ for holes and 0.34 cm² V⁻¹ s⁻¹ for electrons under ambient conditions. Following the successful array of the *p*-type TIPS-pentacene and *n*-type *N*-heteropentacenes, nominally antiaromatic IDBT derivatives should function as very promising candidates in the field of ambipolar carrier transport and be worthy of intensive study.

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Notes and references

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