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Nanowires of indigo and isoindigo-based molecules with thermally removable groups

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ABSTRACT

In this manuscript, indigo and isoindigo-based π -conjugated molecules with thermal removable *tert*butoxycarbonyl (t-Boc) side groups were designed and synthesized. It was noted that the t-Boc side groups can be eliminated in nearly quantitative yields after thermal treatment at 200 °C for 15 min, as confirmed by thermogravimetric analysis and Fourier transform infrared spectroscopy. From the thermal treated solution of isoindigo-based molecule DTIIC8C12 in the co-solvent of 1,2-dichlorobenzene/pyridine with volume ratio of 10/90, one-dimensional nanowires can be formed due to the hydrogen bonding assisted self-assembly. The afforded nanowires exhibited a moderate hole mobility of 1.3×10^{-3} cm² V⁻¹ s⁻¹, as estimated from the organic field effect transistors. These observations illustrated that the utilization of thermal removable side chain functionalized conjugated polymers can be an effective strategy for developing conjugated polymers with impressive charge carrier transport.

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1. Introduction

Over the past decades, much attention has been paid to organic field-effect transistors (OFETs) due to their potential applications in plastic electronics such as memory or storage devices [1–4]. The development of novel conjugated organic semiconductors with high carrier mobility, good ambient stability and low-cost processability has led to significantly improved performances of OFETs. Recently, various pigments such as diketopyrrolopyrrole (DPP) [5-7], indigo [8] and isoindigo [9,10] have been utilized to construct π -conjugated molecules as the semiconductors for OFETs. These molecules exhibited close intermolecular stacking due to their outstanding coplanar architectures. Of particular interests is that these molecules can potentially form NH^{...}O=C hydrogen bonding interaction owing to their unique lactam structure [7].

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In this manuscript, we developed two novel indigo and isoindigo-based π -conjugated molecules consisting of thermally removable *t*-Boc side groups (Chart 1). It was worth mentioning that the thermal cleavage of *t*-Boc groups was conducted in the solutions, which allowed for the hydrogen bonding assisted in-situ self-assembly to form one-dimensional nanowires (Chart 2). Uniform films can be obtained by spin-casting from such nanowires solutions subsequently. Impressively, the obtained nanowires exhibited a hole mobility of 1.3×10^{-3} cm² V⁻¹ s⁻¹, as evaluated by the filed effect transistors. To our knowledge, it is the first work to successfully prepare the isoindigo-based nanowires for OFETs.

It has been well-established that the covalently linked tertbutoxycarbonyl (t-Boc) substituents in the N atoms can impart

semiconducting precursors excellent solubility, and the elimination

of the *t*-Boc unit can give rise to hydrogen bond, which can then

result in completely insoluble products due to the strong molecular

stacking [11–14]. Hydrogen bond can be utilized as the driving

force for self-assembly of molecules in solutions by inducing well-

organized nanostructures [15–18]. By utilizing hydrogen bond as

the driving force, self-assembled π -conjugated small molecules

with highly ordered intermolecular packing motif have been





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Chart 1. Thermal cleavage of t-Boc groups of molecules.



Chart 2. Schematic diagram for the self-assembly of the thermo-cleaved molecules to obtain the one-dimensional nanowires.

2. Results and discussion

2.1. Synthesis of DTIC8C12 and DTIIC8C12

The synthesis routes for molecules DTIC8C12 and DTIIC8C12 are shown in Scheme 1. The iodinization of the commercially available 6-bromoindole (1) by using iodine (1 equivalent) and potassium iodide (1 equivalent) in the presence of sodium hydroxide (1 equivalent) in methanol gave compound 3-iodo-6-bromoindole (2), which was used for the following reaction without purification. By treating compound 2 with silver acetate (2 equivalent) in acetic acid at 90 °C for 3 h, the target compound 6-bromo-3acetoxyindole (3) was afforded. The hydrolysis of 3 in aqueous ethanol containing sodium hydroxide at room temperature gave 6,6'-dibromoindigo (4), which was then reacted with di-tert-butyldicarbonate to give the corresponding t-Boc substituted intermediate compound 8. The intermediate compound 9 was synthesized according to the similar procedure as that of compound 8 by using 6,6'-dibromoisoindigo (7) [23,24] as the starting materials. The following palladium catalyzed Stille cross-coupling reaction of 8 and **9** with tributyl(5'-(2-octyldodecyl)-[2,2'-bithiophen]-5-yl) stannane (10) gave the target conjugated molecules of DTIC8C12 and DTIIC8C12.

The molecular structures of all monomers and intermediates are confirmed by ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy. Molecular structures of DTIC8C12 and DTIIC8C12

were further confirmed by matrix-assisted laser desorption/ionization time of flight mass spectroscopy (MALDI-TOF). The obtained mass were 1151.52 and 1151.53 for DTIC8C12 and DTIIC8C12, respectively, which were lower than the theoretical molecular weights of 1352.05. This can be understood as the loss of two *tert*-butoxycarbonyl (*t*-Boc) groups during the measurements.

2.2. Thermal properties

Thermal behaviors of these two molecules were evaluated by differential scanning chromatography (DSC) and thermogravimetric analysis (TGA). TGA characteristics illustrate the two-step thermal decomposition procedures of these two molecules. As shown in Fig. 1a, the first decomposition at about 190 °C can be attributed to the elimination of *t*-Boc groups, which yielded two equivalents of isobutene and CO₂ [11,25]. The first weight loss ratio calculated from the TGA properties was 14.4% and 14.7% for DTIC8C12 and DTIIC8C12, respectively, which was nearly identical to the theoretical weight loss value of 14.8% for the cleavage of two *t*-Boc groups from these compounds, indicating the quantitatively thermal cleavage of *t*-Boc side groups. The additional weight loss step occurred at about 380 °C can be ascribed to the decomposition of the molecular backbones, indicating the good thermal stability of the molecular scaffold after the elimination of *t*-Boc groups.



Scheme 1. Synthetic routes for molecules: (i) I₂, KI, NaOH, methanol, room temperature, 3 h; (ii) CH₃COOAg, CH₃COOH, 90 °C, 3 h; (iii) NaOH, ethanol, room temperature, overnight; (iv) CH₃COOH, HCI, reflux; (v) DMAP, di-*tert* butyl dicarbonate, CH₂Cl₂, room temperature 6 h; (vi) tributyl(5'-(2-octyldodecyl)-[2,2'-bithiophen]-5-yl)stannane, Pd₂(dba)₃, P(o-Tol)₃, tetrahydrofuran, 80 °C, 4 h.

We also investigated the thermal properties of these molecules by DSC characterization. The initial heating cycle up to 250 °C was performed to accomplish the thermal cleavage of *t*-Boc groups from molecules and eliminate the thermal history of the molecules (see Figure S1). The trace for the first heating cycle showed the first endothermic peak at 87 °C for DTIC8C12 and 159 °C for DTIIC8C12, which can be attributed to the phase transition caused by the side chains. The second endothermic peaks at 195 °C for both molecules could be attributed to the thermal decomposition of the *t*-Boc groups as demonstrated in TGA characterization. In the second heating cycle (Fig. 1b), the endothermic peaks at 195 °C disappeared, while one can observe the obvious melting point of 197 °C and 213 °C for DTIC8C12 and DTIIC8C12, respectively along with the emergence of apparent crystallization characteristic. By scrutinizing the profiles of DTIC8C12 (Fig. 1b), one can observe weaker endothermic and exothermic peaks in the high temperature region of about 250 °C, which might be attributed to the formation of an additional kind of crystalline structure after thermal elimination of *t*-Boc groups in DTIC8C12. Nonetheless, these observations indicated strong crystallization tendency of these molecules after cleavage of *t*-Boc groups. Detailed thermal properties of these compounds were summarized in Table 1.

2.3. FT-IR spectroscopy

Fourier transform infrared (FT-IR) spectroscopy was utilized to investigate the thermal cleavage of *t*-Boc groups (Fig. 2). The pristine films were spin-coated from the chloroform solutions of



Fig. 1. TGA (a) and DSC (b) characteristics of DTIC8C12 and DTIIC8C12 with heating rate of 10 °C min⁻¹.



Fig. 2. The FT-IR spectra for the pristine films (black curves) and after thermal treatment (red curves) for molecules DTIC8C12 (a) and DTIIC8C12 (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. UV-Vis absorption profiles of DTIC8C12 (a) and DTIIC8C12 (b) in chloroform solution and as films.

DTIC8C12 and DTIIC8C12 with concentration of 10 mg mL⁻¹, which were thermally annealed at 200 °C for 15 min. As shown in Fig. 2, one can clearly observe the characteristic stretching vibration band at 1700 cm⁻¹ of C=O corresponding to the *t*-Boc moiety, which disappeared after thermal annealing the films at 200 °C for 15 min. These observations demonstrated that *t*-Boc groups could be completely removed after thermal treatment.

2.4. Optical and electrochemical properties

Fig. 3 showed the UV–Vis absorption spectra of DTIC8C12 and DTIIC8C12 in chloroform solution and as thin films. In chloroform solutions, both DTIC8C12 and DTIIC8C12 exhibited dual characteristic absorption bands, wherein the short wavelength can be attributed to the characteristic absorption of π - π * transition of



Fig. 4. Electrochemical properties of DTIC8C12 (a) and DTIIC8C12 (b), pristine (black curves) and annealed films at 200 °C for 15 min, (red curves). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. The change of dihedral angles of molecules before and after cleavage of t-Boc groups.

molecular backbones, while the long wavelength can be attributed to the intramolecular charge transfer (ICT) effects between electron-donating thiophene unit and electron-withdrawing indigo and isoindigo units [26,27]. In contrast, the absorption profiles as thin films at low-energy band were extended with the appearance of shoulder peaks, indicating that these compounds have strong aggregation tendency in solid state. However, the films are not uniform due to the potential crystallization after thermal treatment, thereby we failed to record reliable absorption profiles of these compounds. The optical band-gap as calculated from the absorption onset in films was 1.64 eV for DTIIC8C12, which was much smaller than that of 2.0 eV for DTIC8C12. All relevant absorption data were summarized in Table 2.

Cyclic voltammetry (CV) measurements were performed to investigate the influence of the elimination of *t*-Boc groups on the frontier molecular orbitals. The measurements were carried out under an inert atmosphere by using tetra-*n*-butylammonium hexafluorophosphate (n-Bu₄NPF₆, 0.1 M in acetonitrile) as the supporting electrolyte with a ITO-coated glass working electrode, a platinum wire counter electrode and a saturated calomel electrode



Fig. 6. Tapping-mode AFM images ($10 \ \mu m \times 10 \ \mu m$) of spin-coated thin films from thermo-cleaved DTIIC8C12 solutions: (a) ODCB/pyridine (100/0); (b) ODCB/pyridine (50/50); (c) ODCB/pyridine (33/67); (d) ODCB/pyridine (0/100).

30.0 10.0 60.0 nm b 20.0 30.0 nm 5.0 10.0 0.0 nm 2.5 10.0 20.0 30.0 10.0 2 ' 5 0 7.9 30.0 10.0 60.0 nm (d) 7 5 20.0 30.0 nm 5.0 10.0 0.0 nm 10.0 2.5 5.0 7.5 10.0 20 0 30 0

Fig. 7. Tapping-mode AFM images of spin-coated DTIIC8C12-based nanowires films with different scanning size, (a) 10 $\mu m \times 10 \mu m$ and (b) 30 $\mu m \times 30 \mu m$ for nanowires selfassembled in solvent of ODCB/pyridine (20/80); (c) 10 $\mu m \times 10 \mu m$ and (d) 30 $\mu m \times 30 \mu m$ for nanowires self-assembled from solvent of ODCB/pyridine (10/90).

(SCE) as reference. The potential of the ferrocene/ferrocenium (Fc/ Fc⁺) redox couple was measured as a standard. It is assumed that the redox potential of Fc/Fc⁺ has an absolute energy level of -4.8 eV to vaccum [28]. Under the same experimental conditions, the onset potential of Fc/Fc⁺ was measured to be 0.32 V with respect to the SCE reference electrode. Therefore, the highest occupied molecular orbital energy levels (E_{HOMO}) and lowest unoccupied molecular orbital energy levels (E_{LUMO}) of the molecules were calculated according to the following equation,

Nws (O/P=10/90)

Nws (O/P=20/80)

film

solution

1.4

1.2

1

0.8

0.6

0.4

0.2

Normalized Absorbance

 $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.48)(\text{eV}); \quad E_{\text{LUMO}} = -e(E_{\text{red}} + 4.48)(\text{eV})$

where the E_{ox} and E_{red} are the onset of the oxidation and redox potential vs. SCE, respectively. The *E*_{HOMO} of the pristine DTIC8C12 and DTIIC8C12 were determined to be -5.51 and -5.33 eV, respectively. After the thermal cleavage of *t*-Boc groups, the *E*_{HOMO} of DTIC8C12 increased to -5.43 eV, which could be attributed to the enhanced molecular coplanarity and elongated conjugation [7,25]. In contrast, the E_{HOMO} of DTIIC8C12 decreased to -5.42 eV, which



films and films of nanowires, (O/P: ODCB/pyridine).



Fig. 9. XRD patterns of initial DTIIC8C12 and nanowires self-assembled in different solvents, (O/P: ODCB/pyridine).



Fig. 10. OFET architecture (a), OFET output (b) and transfer characteristics (c) of DTIIC8C12 nanowires self-assembled in ODCB/pyridine = 10/90.

can be correlated to the decreased electron-withdrawing properties of the isoindigo unit after the elimination of the electrondeficient *t*-Boc groups. The E_{LUMO} of pristine DTIC8C12 and DTIIC8C12 were calculated to be -3.86 eV and -3.70 eV, both of which slightly decreased to -3.92 eV and -3.83 eV, respectively (Fig. 4) (Table 3).

2.5. DFT electronic structure calculation

To get insight into the variation in molecular conformation of molecules after thermal cleavage of *t*-Boc groups of DTIC8C12 and DTIIC8C12, theoretical calculation was carried out by using density functional theory (DFT) at the B3LYP/6-31G(d) basis with the Gaussian 09 package [29]. The calculated torsional angles of molecules before and after the elimination of *t*-Boc groups were shown in Fig. 5, with relevant data summarized in Table 4.

It was realized that after the elimination of *t*-Boc groups, dihedral angles between two thiophene units (φ_1 , φ_5) and dihedral angles between the thiophene units and indigo unit (φ_2 , φ_4) did not show obvious disparity for both DTIC8C12 and DTIIC8C12. However, the dihedral angle between two fused rings of indigo unit (φ_3) for

Table 1

Thermal properties of	molecule	es DTIC8C12 an	d DTIIC8C12
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Molecules	$T_{d}^{1}(^{o}C)$	T_d^2 (°C)	$T_m (^oC)$	Weight loss ^a (%)	Weight loss ^b (%)
DTIC8C12	192	382	194	14.8	14.4
DTIIC8C12	186	385	213	14.8	14.7

 T_{d}^{1} : Temperature of the first decomposition; T_{d}^{2} : temperature of the second decomposition; T_{m} : melting point of molecules after cleavage of *t*-Boc groups.

^a Theoretical weight loss of *t*-Boc side groups.

^b Experimental weight loss of *t*-Boc side groups.

DTIC8C12 significantly decreased from 23.8° to 0.2° after the elimination of *t*-Boc groups. The formation of the nearly quasi-coplanar conformation indicated that the steric hindrance originated from the bulky *t*-Boc side groups can be significantly reduced after elimination. It is worth noting that the improved molecular planarity might be beneficial for the ordered and closed intermolecular stacking, and thereby theoretically leads to the improved charge carrier mobility. For DTIIC8C12, the dihedral angle between two fused rings of isoindigo unit (φ_3) reduced from 18.9° to 10.7°, which is much weaker than that of DTIC8C12. It can be speculated that DTIC8C12 might exhibit much stronger intermolecular aggregation after the elimination of *t*-Boc side groups than that of DTIC8C12.

The calculated HOMO of DTIIC8C12 was delocalized in the molecular backbone, which slightly decreased from -4.97 eV to -5.01 eV after the elimination of *t*-Boc groups. However, the calculated HOMO of DTIC8C12 slightly increased from -5.25 eV to -5.18 eV after the elimination of *t*-Boc groups. This is understandable, since the two indolinone moieties in the single indigo unit were not ideally conjugated, thus the calculated HOMO of DTIC8C12 was not delocalized in molecular backbone due to the steric hindrance effect of *t*-Boc groups. In this respect, the enhanced coplanarity of DTIC8C12 after the elimination of *t*-Boc groups can facilitate the electron delocalization, which in turn led to an increased HOMO. Besides, the calculated LUMOs mainly located in

fable 2	
Photophysical properties of molecules DTIC8C12 and DTIIC8C12.	

Molecules	λ_{max} (nm) Solution	λ_{max} (nm) films	$E_{g}^{opt}\left(eV ight)$
DTIC8C12	365, 496	369, 489	2.00
DTIIC8C12	359, 616	384, 696	1.64

Table 3	
Electrochemical properties of	of DTIC8C12 and DTIIC8C12.

Molecules	Conditions	$E_{ox}(V)$	$E_{red}(V)$	E _{HOMO} (eV)	E _{LUMO} (eV)
DTIC8C12	Pristine	1.03	-0.62	-5.51	-3.86
	Annealed	0.95	-0.56	-5.43	-3.92
DTIIC8C12	Pristine	0.85	-0.78	-5.33	-3.70
	Annealed	0.94	-0.65	-5.42	-3.83

Table 4

.....

Dihedral angles of molecules before and after thermal cleavage of *t*-Boc groups by DFT calculations.

Molecules	Conditions	Dihedral angles (deg)					
		φ_1	φ2	φ3	φ_4	φ_5	
DTIC8C12	Before cleavage	16.6	23.7	23.8	21.2	15.9	
	After cleavage	16.1	22.3	0.2	23.3	16.9	
DTIIC8C12	Before cleavage	14.9	17.8	18.9	18.3	14.7	
	After cleavage	15.6	20.4	10.7	21.2	15.9	

the electron-deficient indigo and isoindigo moieties. The LUMOs slightly increased from -2.79 eV to -2.76 eV, and from -2.99 eV to -2.80 eV for DTIC8C12 and DTIIC8C12, respectively. The calculated HOMOs and LUMOs were shown in Table S1, which were in good agreement with the observed trends in CV measurements.

2.6. AFM morphology of nanowires

Atomic force microscopy (AFM) was used to investigate the morphology of the self-assembled nanowires. As shown in Fig. 6a, desired nanowires of DTIIC8C12 could be obtained in the solvent of o-dichlorobenzene (ODCB). However, the obtained solution of nanowires was in gel-like state, which cannot be processed to give uniform films by spin-coating method (inset in Fig. 6a). In order to attain homogeneous solution that can be spin-coated to give uniform films for the fabrication of the semiconducting layer for organic field effect transistors, different ratios of pyridine was added to attenuate the intermolecular hydrogen bonding interaction. It was noted that when 50% or 67% of pyridine was added, although the homogeneous solution can be obtained, the nanowires cannot be formed (Fig. 6b, c). It was also noted that the nanowire structures cannot be formed in the pure pyridine solution (Fig. 6d). However, homogeneous solutions along with desired nanowires can be simultaneously obtained by increasing the pyridine ratio to 80% and 90% in the co-solvent systems with ODCB. As shown in Fig. 7, well-defined one-dimensional nanowires with width in the range of 150-200 nm were observed. We noted that the slightly different ratios of pyridine in the co-solvent systems can have pronounced impact in the interpenetrating networks of nanowires. By increasing the volume ratios of pyridine from 80% (Fig. 7a) to 90% (Fig. 7c), more closely entangled nanowires can be observed along with the slightly increased width of nanowires.

Similar strategy was also utilized for the self-assembly of nanowires based on DTIC8C12. However, serious aggregation was observed, which was insensitive to the ratio of pyridine (Figure S2). The fact can be attributed to the exceptionally strong intermolecular stacking tendency owing to the quasi-coplanar conformation after elimination of *t*-Boc side groups, as predicted by DFT calculation. Thus, further investigation about the thermal treatment of DTIC8C12 solutions cannot be accomplished at the current stage. Nonetheless, these observations highlighted that DIC8C12 and DTIIC8C12 exhibit significantly different molecular stacking in solution despite of very similar molecular structures.

2.7. Photophysical properties and XRD of DTIIC8C12-based nanowires

Fig. 8 showed the UV–vis absorption of DTIIC8C12-based nanowires films. It was realized that the absorption profiles of such nanowires films obviously hypsochromic shifted with respect to that of the pristine DTIIC8C12 films, which might be ascribed to the formation of intrinsic *H*-aggregation [15]. Such aggregation would be beneficial for the charge transportation in the nanowires films [30–32]. X-ray diffraction (XRD) was performed to investigate the difference in molecular packing between the pristine DTIIC8C12 film and the self-assembled nanowires film. As shown in Fig. 9, the peak intensity at $2\theta \approx 51.2^{\circ}$ obviously increased in the self-assembled nanowire film that was obtained from ODCB/pyridine co-solvent systems with volume ratio of 20/80 and 10/90. The enhanced peak intensity indicated more ordered and closer intermolecular stacking in the self-assembled nanowires, which can facilitate the charge transporting in the spin-coated films [2,33,34].

2.8. Organic field effect transistor performance

Bottom gate, top contact organic field effect transistors (OFETs) with the architecture of Si/SiO₂/poly(methyl methacrylate) (PMMA)/DTIIC8C12 nanowires/Ag were fabricated to investigate the charge carrier mobility of the self-assembled nanowires films. We initially tried to fabricate the nanowires films on the Si/SiO₂ wafer that was treated with a self-assemble monolaver of octadecvltrichlorosilane (OTS): however, uniform films cannot be formed on the surface of such OTS-treated substrates. Hence, PMMA was used to modify the gate dielectric layer since uniform nanowires can be obtained [35,36]. Semiconducting layer was spin-coated from nanowires ODCB/pyridine (volume ratio of 10/90) solution with concentration of 10 mg mL⁻¹. Herein Ag instead of Au is used as the electrode, since it is more cost-effective and can be easily deposited on the top of the prefabricated semiconducting layer films. We note that Ag electrode is less efficient for hole injection than Au electrode, however, it can effectively reveal the charge carrier mobility of the nanowires films [32,33]. Fig. 10 illustrated the output and transfer characteristics of OFETs based on nanowires self-assembled from solution of ODCB/pyridine (volume ratio of 10/90). The measurement was carried out by sweeping the gate voltage ($V_{\rm G}$) from -50 to 10 V under a source-drain voltage ($V_{\rm D}$) of -50 V. Hole mobility of nanowires self-assembled in ODCB/ pyridine (volume ratio of 10/90) solution was measured to be 1.3×10^{-3} cm² V⁻¹ s⁻¹, with the current on/off ratio of about 10⁵. This result indicated that in-situ self-assembly can be an effective and low-cost method to acquire desired charge carrier mobility for isoindigo-based molecules. To our knowledge, it is the first work to successfully prepare the isoindigo-based nanowires for OFETs. However, we failed characterize the OFET mobility of pristine DTIIC8C12 films and nanowires films in solution of ODCB/pyridine with volume ratio of 20/80, because uniform films cannot formed on the surface of PMMA interlayer.

3. Conclusion

In summary, we developed two novel indigo and isoindigobased π -conjugated molecules DTIC8C12 and DTIIC8C12 consisting of thermal removable *tert*-butoxycarbonyl (*t*-Boc) side groups. It was realized that the solubilizing effect of *t*-Boc side groups can impart the two resultant molecules good solubility in common organic solvents. The *t*-Boc groups can be eliminated from these molecules by thermal treatment in a quantitative yield, as confirmed by the thermal gravimetric analysis and Fourier transform infrared spectroscopy. The molecular coplanarity of the resulted compounds can be significantly enhanced after the elimination of *t*-Boc side groups. DTIIC8C12 can self-assembled into one-dimensional nanowires in solution of ODCB/pyridine with volume ratio of 10/90, which exhibited a hole mobility of 1.3×10^{-3} cm² V⁻¹ s⁻¹ as evaluated by the field effect transistors.

4. Experimental section

4.1. Materials

All reagents and solvents, unless otherwise specified, were obtained from Aldrich and Alfa-Aesar Chemical Co. and were used as received. Solvent of tetrahydrofuran was distilled from sodium/ benzophone. 6,6'-Dibromoisoindigo (7) [23,24] and tributyl(5'-(2octyldodecyl)-[2,2'-bithiophen]-5-yl)stannane (10) [37] were prepared according to the reported procedures. 6,6'-Dibromoindigo (4) was synthesized according to the modified method of the literature [8]. All the related compounds were synthesized as the following procedures as below.

6-Bromo-3-iodoindole (2). To a solution of 6-bromoindole (1) (200 mg, 1.02 mmol) and sodium hydroxide (41 mg, 1.02 mmol) in methanol (10 mL) were added iodine (259 mg, 1.02 mmol) and an aqueous solution (2 mL) of potassium iodide (169 mg, 1.02 mmol). After the mixture was stirred at room temperature for 3 h, water was added. The resulting precipitate was collected by filtration, washed with water, and dried to obtain product 6-bromo-3-iodoindole (2), which was used for the following reaction without purification because of its lability.

3-Acetoxy-6-bromoindole (3). Silver acetate (341 mg, 2.04 mmol) was added to a solution of monomer 2 in acetic acid (8 mL). After stirring for 3 h at 90 °C, the mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was chromatographed on silica gel with dichloromethane as eluent to afford product 3 (yield: 254 mg, 63.0%). ¹H NMR (CDCl₃, 600 MHz): 7.97 (s, 1H), 7.69 (d, 1H), 7.33 (d, 1H), 7.29 (m, 1H), 7.17 (m, 1H), 2.36 (s, 9H); ¹³C NMR (CDCl₃, 600 MHz): 168.65, 131.70, 129.82, 125.78, 121.61, 120.14, 114.64, 113.17, 112.90, 20.93.

6,6'-Dibromoindigo (4). To a solution of 3 (53.7 mg, 0.211 mmol) in ethanol (5 mL) was added aqueous 1 M sodium hydroxide (10 mL). After the mixture was stirred at room temperature for 2 h, water was added. The resulting precipitate was collected by filtration, washed with water, and dried to give product as a purple solid. The product was used directly in the next step without purification due to its poor solubility in common solvents.

General procedure for preparing monomer 8 and monomer 9. In a three-necked, oven-dried 100 mL round bottom flask, (1.26 g, 3 mmol) of monomer 1 or monomer 4 was dissolved in 30 mL dichloromethane and the resulting solution was purged with argon for 20 min. Dimethylaminopyridine (DMAP) (37 mg, 0.3 mmol) was added and the reaction mixture was stirred for 30 min under argon at room temperature. Di-*tert*-butyl-dicarbonate (1.44 g, 6.6 mmol) was then added in one portion and the mixture was stirred at room temperature for 24 h. Then the reaction mixture was filtered to obtain a reddish solid, which was further washed with several portions of methanol. The crude product was purified by flash chromatography using dichloromethane as eluent and the solvent was removed in vacuo to give the pure product.

(E)-Di-tert-butyl-6,6'-dibromo-3,3'-dioxo-[2,2'-biindolinylidene]-1,1'-dicarboxylate (8). (yield: 1.44 g, 77.3%). 1H NMR (CDCl3, 600 MHz): 8.25 (s, 1H), 7.62 (d, 1H), 7.36 (d, 1H), 1.61 (s, 9H); 13C NMR (CDCl3, 600 MHz): 182.39, 149.49, 149.41, 131.08, 127.77, 125.01, 121.67, 120.19, 85.25, 28.06.

(E)-Di-tert-butyl-6,6'-dibromo-2,2'-dioxo-[3,3'-biindolinylidene]-1,1'-dicarboxylate (9). (yield: 1.64 g, 88.1%). 1H NMR (CDCl3, 600 MHz): 8.25 (s, 1H), 7.62 (d, 1H), 7.36 (d, 1H), 1.61 (s, 9H); 13C NMR (CDCl3, 600 MHz): 182.39, 149.49, 149.41, 131.08, 127.77, 125.01, 121.67, 120.19, 85.25, 28.06.

General procedure for preparing DTIC8C12 and DTIIC8C12. Monomer 8 or monomer 9 (0.5 g, 0.81 mmol) and monomer 10 (1.42 g, 1.94 mmol) were added into a three-necked, over-dried 100 mL round bottom flask, which was purged with argon for 30 min. Tris(dibenzylideneacetone)dipalladium(0) (9 mg), and tri(o-tolyl)phosphine (18 mg) were then added, after which 30 mL anhydrous THF was added. The mixture solution was heated to 80 °C for 4 h. The reaction solution was allowed to cool down to room temperature and then was poured into 100 mL of water and extracted three times with dichloromethane. The combined organic solution was dried over anhydrous magnesium sulfate. After the solvent was removed under reduced pressure, the raw product was purified with a column chromatography on silica gel using hexane: dichloromethane (1:2) as eluent to obtain final product.

DTIC8C12. (794.7 mg, 72.9%). ¹H NMR (CDCl₃, 600 MHz): 8.29 (s, 1H), 7.76 (d, 1H), 7.42 (d, 2H), 7.12 (d, 1H), 7.07 (d, 1H), 6.70 (d, 1H), 2.75 (d, 2H), 1.67 (s, 9H), 1.31 (s, 1H), 1.31–1.27 (m, 32H), 0.89 (m, 6H); ¹³C NMR (CDCl₃, 600 MHz): 182.14, 149.97, 149.63, 145.11, 141.48, 141.04, 140.07, 134.45, 126.29, 126.12, 124.14, 124.03, 112.88, 84.58, 39.99, 34.64, 33.20, 31.94, 31.93, 29.95, 29.69, 29.63, 29.38, 29.34, 28.19, 26.62, 22.70, 14.13. MS (MALDI-TOF): calcd for $C_{82}H_{114}N_2O_6S_4$ [M]⁺, 1352.05; found, 1151.52.

DTHC8C12. (734.5 mg, 67.4%). ¹H NMR (CDCl₃, 600 MHz): 8.92 (d, 1H), 8.03 (s, 1H), 7.35 (d, 2H), 7.08 (d, 1H), 7.03 (d, 1H), 6.66 (d, 1H), 2.73 (d, 2H), 1.73 (s, 9H), 1.63 (s, 1H), 1.30–1.27 (m, 32H), 0.89 (m, 6H); ¹³C NMR (CDCl₃, 600 MHz): 166.24, 148.68, 144.90, 141.79, 141.55, 139.38, 138.07, 134.65, 130.24, 129.55, 126.08, 125.63, 124.09, 123.84, 121.22, 120.53, 110.63, 84.82, 39.99, 34.64, 33.20, 31.94, 31.93, 29.97, 29.69, 29.67, 29.63, 29.38, 29.35, 28.26, 26.61, 22.71, 14.13. MS (MALDI-TOF): calcd for $C_{82}H_{114}N_2O_6S_4$ [M]⁺, 1352.05; found, 1151.53.

5. Measurement and characterization

¹H and ¹³C NMR were characterized with Bruker-300 spectrometer operating at 600 and 75 MHz in deuterated chloroform solution at 298 K. Chemical shifts were recorded as δ values (ppm) with the internal standard of tetramethylsilane (TMS). Mass spectra (MALDI-TOF) were carried out on an instrument of MS Autoflex III Smartbean. Differential scanning calorimetry (DSC) was performed on a Netzsch DSC 204 under nitrogen flow at heating and cooling rates of 10 °C min⁻¹. Thermogravimetric analyses (TGA) were performed on a Netzsch TG 209 under nitrogen at a heating rate of 10 °C min⁻¹. FT-IR spectra were observed on a NEXUS 670 instrument. UV-vis absorption spectra were recorded on a HP 8453 spectrophotometer. Cyclic voltammetry (CV) was performed on a CHI600D electrochemical workstation with a working electrode of ITO-coated glass and a Pt wire counter electrode at a scanning rate of 50 mV s⁻¹ against the reference electrode of saturated calomel electrode (SCE) with a nitrogen saturated anhydrous solution of tetra-n-butylammonium hexafluorophosphate in acetonitrile $(0.1 \text{ mol } L^{-1})$. Atomic force microscopy (AFM) measurements were carried out using a Digital Instrumental DI Multimode Nanoscope III in a taping mode. X-ray diffraction (XRD) measurements were carried out using German Bruker 2 instrument.

5.1. Self-assembly for nanowires

Nanowires (Nws) were attempted to be prepared *via* in-situ selfassembly approaches. To acquire the desired nanowires, 10 mg mL⁻¹ of molecules was dissolved in mixed solvent of ODCB/pyridine (100/0, 50/50, 33/67, 20/80, 10/90, v/v) under vigorous stirring at room temperature overnight. The solution was then heated at 200 °C under stirring for 15 min to complete the elimination of *t*-Boc side groups. After that, the solution was slowly cooled down to room temperature and left for 12 h to allow undisturbed self-assembly of nanowires under the driving force of the intermolecular hydrogen bonding. Considering that N atom in pyridine can also form hydrogen bonding interaction with the NH group in indigo and isoindigo units, different ratio of pyridine was added to regulate the strength of intermolecular hydrogen bonding among the thermo-cleaved molecules, which could thus avoid the serious aggregation in the annealed solutions and realize the assembly of molecules.

6. OFETs fabrication and characterization

To observe the hole mobility of the self-assembled nanowires films, FETs were fabricated in a top contact geometry using silver as source and drain electrode. Highly *n*-doped silicon and thermally grown silicon dioxide (300 nm) were used as the back gate and gate dielectric, respectively. Polymethyl methacrylate (PMMA) was then utilized for surface modification of the gate dielectric layer. The nanowires films (ca. 80 nm) were spin-coated on PMMA treated substrates from self-assembly solutions (10 mg/mL) at 900 rpm. Then silver film (50 nm) was deposited under vacuum as the source and drain electrode. The width to length ratio (W/L) of the FET devices is 100/1. The device characterizations were performed in the atmosphere by using a probe station and a semiconductor parameter analyzer (Agilent 4155C). Then field effect mobility was calculated from the standard equation for saturation region in metal-dioxide-semiconductor field effect transistors: $I_{DS} = (W/2L)$ $\mu C_{\rm i} (V_{\rm G} - V_{\rm T})^2$, where $I_{\rm DS}$ is the drain-source current, μ is the fieldeffect mobility, and C_i is the capacitance per unit area of the dielectric layer ($C_i = 0.8 \times 10^{-8} \text{ nF cm}^{-2}$), V_G is the gate voltage, and $V_{\rm T}$ is the threshold voltage.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.10.003.

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