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Synthesis of a thiophene-fused isoindigo derivative: a potential building block for organic semiconductors

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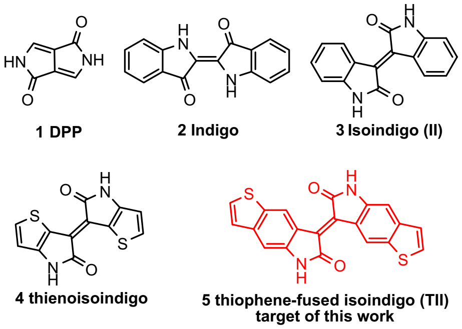
ABSTRACT

Thiophene-fused isoindigo (**TII**) was synthesized from thieno[2,3-*f*]indol-6(7*H*)-one in a one-pot reaction, in which the alkylation, oxidation and condensation were finished in one step. It exhibits better intramolecular charge transfer properties and higher reductive potential compared with isoindigo(II), as evidenced by its optical and electrochemical properties, which shows that it might be used as a building block for *n*-type or ambipolar OFET materials.

Introduction

Nitrogen-containing electron-deficient dyes, such as diketopyrrolopyrrole (DPP),[1–4] indigo,[5–8] and isoindigo(II)[9–13] (as shown in Scheme 1) have attracted an increasing attention as building blocks for organic semiconductors (OSCs) recently. Among them, isoindigo is becoming a popular building block for organic solar cells[14–17] and for organic field effect transistors (OFETs).[10–13] High charge carrier mobility was achieved for conjugated polymers based on isoindigo derivatives. For instance, Pei et al. reported an isoindigo-based conjugated polymer with an exceptionally high hole mobility of 0.79 $cm^2\ V^{-1}\ s^{-1}$,[9] which was later improved to 3.62 $cm^2\ V^{-1}\ s^{-1}$.[12] Bao et al. synthesized a siloxane-terminated isoindigo-based conjugated polymer with a hole mobility as high as 2.48 $cm^2\ V^{-1}\ s^{-1}$.[10]

In many cases, isoindigo was directly used as the building block for oligomers or polymers, and less attention was paid on the manipulation on its core structure. Still, modification on isoindigo core may have dramatic influence on its electric properties. Pei et al. prepared ambipolar polymers based on fluorinated isoindigo,[11] which not only maintained high hole mobility but also increased the electron mobility considerably in OFET devices fabricated in ambient conditions. They also reported chlorinated isoindigo polymers with balanced charge carrier mobility.[18] Ashraf et al. reported the synthesis of a novel thienoisoindigo (Scheme 1, compound **4**) and its copolymer showed ambipolar nature with both hole and electron mobility over 0.1 $cm^2\ V^{-1}\ s^{-1}$.[19]



Scheme 1. N-containing electron-deficient dyes used in organic semiconductors.

There are many factors that influence the charge carrier mobility in polymeric OFETs. Generally speaking, the increase of the effective conjugation length of a conjugated polymer leads to higher intra-chain charge carrier mobility.[20] Good π–π stacking, on the other hand, leads to higher inter-chain mobility.[21] Inter-chain charge carrier mobility is the rate-limiting factor for carrier transportation in polymeric OFETs. One possible way to improve the mobility is to incorporate larger fused aromatic monomers into conjugated polymers, which not only increases the effective conjugation length, but also provides stronger π–π stacking. In fact, many small molecular OFETs based on large fused acenes and heteroacenes were reported to have excellent charge carrier mobility.[21–23] Therefore, we envisioned that using isoindigo fused with

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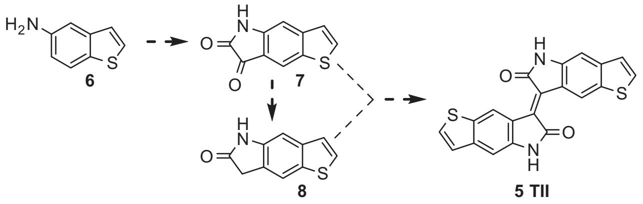


Scheme 2. Proposed synthetic route towards thiophene-fused isoindigo.

aromatic/heteroaromatic rings as a building block in polymers might further improve the carrier mobility of the resulting polymers. Inspired by Ashraf's work, we herein wish to report the synthesis of a novel thiophene-fused isoindigo (**TII**, Scheme 1, compound **5**), and the study on its optical and electrochemical properties. The results show that it might be a promising novel building block for OSCs.

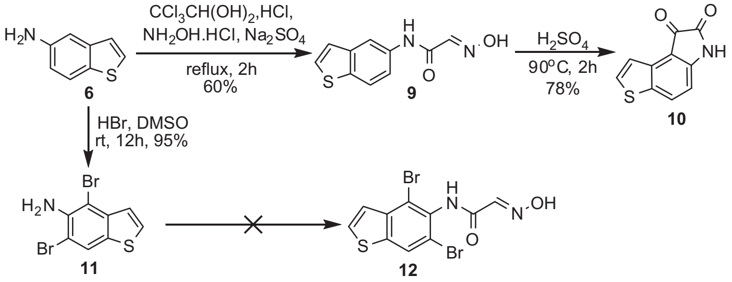
Results and discussion

The original designed synthetic route was quite straight-forward, and shown in Scheme 2. We speculated that thiophene-fused dione **7** could be prepared from benzo[*b*]thiophen-5-amine **6**.[24] It could then be reduced to afford compound **8**. Subsequential condensation between **7** and **8** should give the desired **TII**.

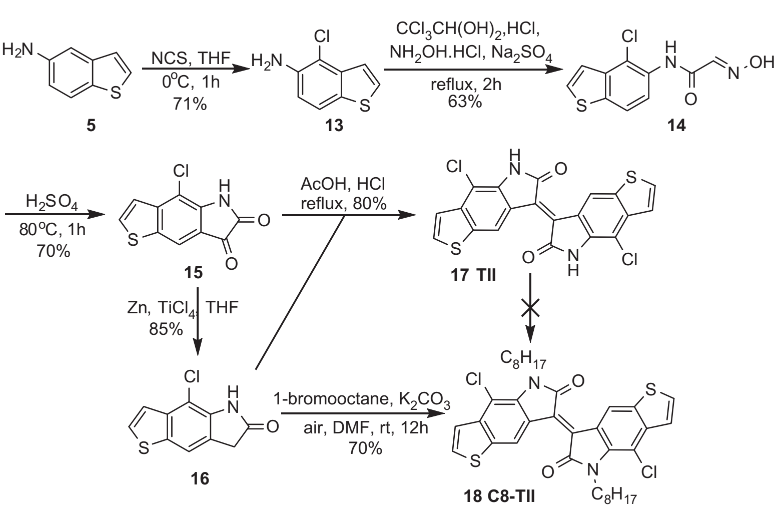
Compound **6** was synthesized from commercially available 2-chloro-5-nitrobenzaldehyde in high yield according to the literature.[25] It was then converted to (*E*)-N-(benzo[*b*]thiophen-5-yl)-2-(hydroxyimino)acetamide (**9**) in 60% yield. However, the rest of route towards the targeted compound became quite tortuous. The Friedel–Crafts cyclization of the corresponding oxime occurred exclusively at 4-position and dione **10** was obtained as the sole product, since 4-position on the benzothiophene is more reactive than 6-position (see Scheme 3).

Although the corresponding isoindigo derivative could be synthesized from compound **10**, the coplanarity of the isoindigo could not be maintained due to the strong steric hindrance around the formed double bond. So 4-position of compound **6** has to be blocked to force the reaction to occur at 6-position. We first tried to introduce bromine to block 4-position of compound **6**. Although NBS failed to brominate compound **6**, double bromination was achieved using HBr as the reagent to afford **11** in 95% yield. Desired mono-brominated derivative could not be obtained even when the amount of HBr was decreased. Since both 4- and 6-position of the benzothiophene ring were blocked, this method could not be applied to synthesize the corresponding dione. Indeed, even the conversion of **11** to the corresponding oxime **12** was impossible due to the strong steric hindrance.

To solve this problem, we turned our attention to chlorine atom, which is smaller than bromine. To our delight, N-chloro-succinimide (NCS) was effective to introduce chlorine atom exclusively at 4-position of **6** to give compound **13** in good yield, as shown in Scheme 4. No chlorination took place at 2-position of **6**, thus left room for further modification (for example, bromination), which will facilitate the incorporation of the final isoindigo derivative into polymers. Treating compound **13** with chloral hydrate and hydroxylamine hydrochloride gave the corresponding oxime **14** and further treatment with conc. sulfuric acid afforded 4-chloro-5*H*-thieno[2,3-*f*]indole-6,7-dione (**15**) in good yield. Subsequently, compound **15** was reduced with zinc and titanium tetrachloride to give 4-chloro-5*H*-thieno[2,3-*f*]indol-6(7*H*)-one (**16**) in 85% yield.



Scheme 3. Synthetic exploration of the precursor of thiophene-fused isoindigo.



Scheme 4. Synthetic route of thiophene-fused isoindigo.

With compounds **15** and **16** in hand, the direct condensation was then tested in acetic acid. Thiophene-fused isoindigo **17** was obtained as a red solid in 80% yield, but it is only sparsely soluble. Unfortunately, all the attempts to alkylate compound **17** for better solubility failed, which ended up with either no reaction (K_2CO_3 or KOH in DMF at room temperature or 100 °C) due to its poor solubility in those solvents or decomposition (NaH in THF, reflux). This was disappointing since excellent solubility of the building block is needed to synthesize solution-processable conducting polymers for OFETs. Then alkylation before condensation might be an alternative way to construct soluble thiophene-fused isoindigo. Surprisingly and also delightfully, we found that when treated with excess K_2CO_3 in the presence of 1-bromooctane in DMF at room temperature, compound **16** was directly converted into alkylated thiophene-fused isoindigo (**C8-TII**) in 70% yield in one step. The possible mechanism might involve the alkylation of compound **16**, and the oxidation of the alkylated compound by air under basic conditions to afford the alkylated dione **15a**.[26–29] The alkylated dione then underwent condensation reaction with unoxidized **16a** to give **C8-TII**, as shown in Scheme 5. The aerobic oxidation is the rate-determine step so that compound **15a** generated in situ would be consumed in time to afford the final product.

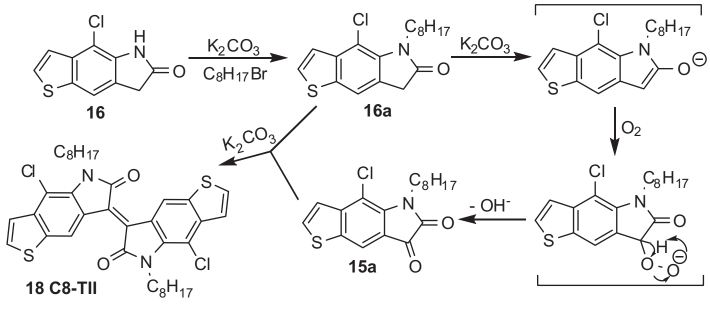
We also noticed that the condition for aerobic oxidation of **16a** could also be applied to the oxidation of its isomer 6*H*-thieno[3,2-*e*]indol-7(8*H*)-one to afford dione **10** in 80% yield (SI). But **10** could not react with the starting material to give the isomer of **18** due to the steric hindrance. However, indolin-2-one could not be converted to indoline-2,3-dione under the same conditions. It seemed that fusing one electron-rich aromatic/heteroaromatic ring to indolin-2-one was crucial for the oxidation to occur.

Similar methodology was also applied to synthesize the benzene-fused isoindigo (**C8-BII**), but with a low yield in the key step (ca. 4%), as shown in Scheme 6. It was presumably due to the instability of compound **23** under basic conditions, since obvious decomposition was observed during the reaction. Other method such as coupling of alkylated **22** using $P(NEt_2)_3$[30] as the coupling agent also end up with low yield (15%).

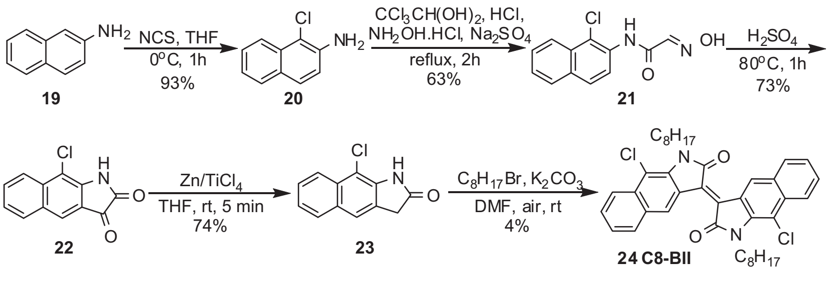
Currently, there are two major methodologies in isoindigo synthesis. One involves the condensation reaction between the corresponding indoline-2,3-dione and indolin-2-one, in which reflux in acetic acid is general needed. The other routes involve dimerization of the dione in one step, using either unpleasant Lawesson's reagent[31] or expensive tris(diethylamino)phosphine[30] as the coupling reagent. Compared to current isoindigo synthesis methodologies, the beauty of this reaction is that the alkylation, oxidation and condensation were completed in one mild step.

The optical and electrochemical properties of **C8-TII** were studied and compared with that of **C8-BII** and the alkylated isoindigo **C8-II**. Their UV–vis absorption spectra are shown in Figure 1a. All three compounds display broad absorption bands from 230 to 600 nm with similar band edges (Fig. 1a), indicating that they have similar HOMO–LUMO band gap, and fusing a thiophene ring or a benzene ring to the isoindigo core does not lead to a lower band gap. The difference lies in the intensity of the absorption at long wave length. A much more intensed absorption band with the peak around 496 and 478 nm is observed for **C8-TII** and **C8-BII**, respectively, compared to the case of **C8-II** at the same concentration (the insertion in Fig. 1a). This absorption is assigned to the HOMO to LUMO transition of isoindigo derivatives.[32] This band shows an intramolecular charge-transfer character, since HOMO of the isoindigo is much more delocalized throughout the whole molecule, while the LUMO is more localized on the central rings. A strengthened absorption of **C8-TII** and **C8-BII** implies a strengthened intramolecular charge-transfer process[33] that occurs in them. This might be due to the aromatic/heteroaromatic rings fused onto the isoindigo core in **C8-TII** and **C8-BII**.

The electrochemical properties of the three compounds were compared using cyclic voltammetry (CV), as shown in Figure 1b. The energy level of LUMO of the isoindigo derivatives was calculated from the reduction potential onsets, using $\text{LUMO} = 4.44\ \text{eV} + E_{\text{red}}^{\text{onset}}$ equation (referring to ferrocene standard). The optical (UV–vis) and electrochemical properties of **C8-II**, **C8-TII** and **C8-BII** are summarized in Table 1. For each of these isoindigo derivatives two pairs of reduction–oxidation waves were observed.



Scheme 5. Plausible mechanism of the one-pot formation of **C8-TII**.



Scheme 6. Synthetic route of benzene-fused isoindigo.

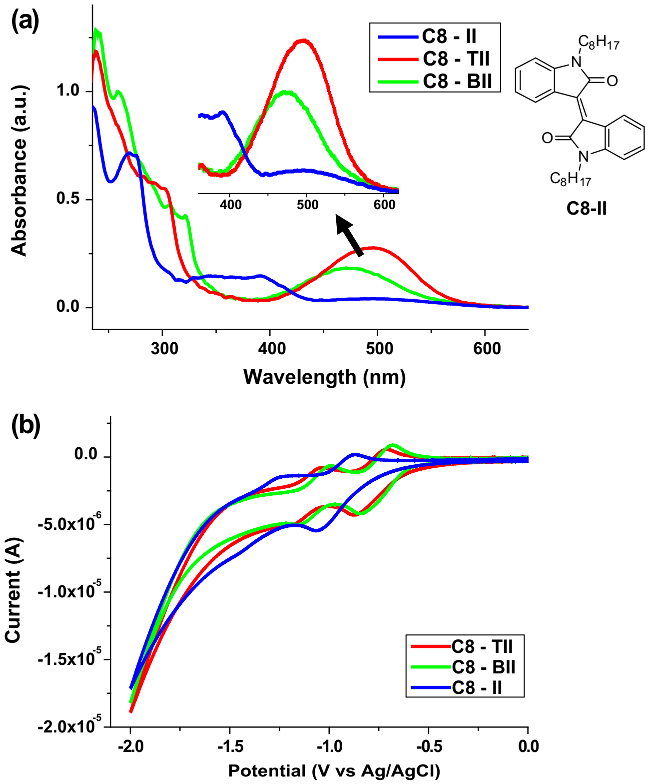


Figure 1. (a) UV–vis absorption spectra of synthesized **C8-II**, **C8-TII** and **C8-BII** in CH_2Cl_2 solution at the same concentration (10^{-5} M); (b) cyclic voltammogram of **C8-II**, **C8-TII** and **C8-BII** in 0.1 M n-Bu_4NPF_6 chloroform solution.

Table 1

Optical (UV–vis) properties and electrochemical data of **C8-II**, **C8-TII** and **C8-BII**

	UV–vis λ_{max} (nm)	Eg^{Optical} (eV)	E_{red}^{onset} (eV)	LUMO[a] (eV)	HOMO (eV)
C8-II	497	2.02	−0.8	−3.64	−5.66
C8-TII	496	2.16	−0.63	−3.81	−5.97
C8-BII	478	2.21	−0.62	−3.82	−6.03

[a] Calculated from the reduction onset of CV.

Both redox pairs of **C8-TII** and **C8-BII** are reversible, while only the first pair of **C8-II** is reversible, indicating a better reversibility of the isoindigo derivatives with more fused aromatic/hetero-aromatic rings. Furthermore, the onset potential of reduction of **C8-TII** and **C8-BII** is −0.63 and −0.62 eV respectively, which is higher than that for **C8-II** (−0.8 eV), indicating that the introduction of fused thiophene and benzene ring onto the isoindigo lowers the energy level of the LUMO of isoindigo, making them better candidates for n-type OSCs due to better electron affinity.

Conclusions

In conclusion, novel thiophene-fused isoindigo **C8-TII** was synthesized via a new facile method, and its properties were compared with benzene-fused isoindigo **C8-BII** and the parent isoindigo **C8-II**. Our investigations have shown that the intramolecular charge-transfer process is greatly enhanced and the electrochemical redox reversibility is improved by fusion of one more heteroaromatic/aromatic ring to the isoindigo core, which would be a plus for better OFET materials. Especially, **C8-TII** is a promising building block for n-type or ambipolar OFET materials, due to its excellent electron-affinity, simplicity in synthesis and ease for further modification. The modification of **C8-TII** and its copolymerization study with electron-rich monomers are currently underway in our laboratory.

Experimental section

General

All glassware was thoroughly oven-dried before use. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography plates were visualized by exposure to ultraviolet light and/or immersion in a staining solution (phosphomolybdic acid) followed by heating on a hot plate. Flash chromatography was carried out utilizing silica gel 200–300 mesh. Chemical shifts are given in δ relative to tetramethylsilane (TMS), the coupling constants J are given in Hz. The spectra were recorded in $CDCl_3$ or d_6-DMSO as the solvent at room temperature. Cyclic voltammograms (CV) were carried out in an argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) in anhydrous chloroform, using a three-electrode system (platinum as both the working electrode, and counter electrode, Ag/AgCl as the reference electrode calibrated against ferrocene) at a potential scan rate of 0.1 V s^{-1}.

Typical Procedure for the Synthesis of alkylated thiophene-fused isoindigo C8-TII (18)

To a suspension of 4-chloro-5*H*-thieno[2,3-*f*]indol-6(7*H*)-one (112 mg, 0.50 mmol, 1.0 equiv) and fresh-dried potassium carbonate (0.35 g, 2.5 mmol, 5.0 equiv) in anhydrous DMF (5.0 mL) at 0 °C, 1-bromooctane (190 μL, 1.1 mmol, 2.2 equiv) was injected through a septum under argon. Then adequate amount of dry air was introduced into the system. The mixture was stirred for 12 h at room temperature and then poured into water (50 mL). The organic phase was extracted by CH_2Cl_2, washed with brine and dried over $MgSO_4$. After removal of the solvent under reduced pressure, the deep-red solids were purified by silica chromatography, eluting with (CH_2Cl_2/Petroleum ether = 1:3) to give **C8-TII** (117 mg, 70%). mp 249–250 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 9.74 (s, 2H), 7.66 (d, J = 5.40 Hz, 2H), 7.52 (d, J = 5.40 Hz, 2H), 4.29 (t, 4H), 1.81 (t, 4H), 1.46–1.29 (t, 20H), 0.89 (t, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 168.17, 141.61, 136.66, 134.30, 132.50, 131.65, 123.10, 123.08, 122.70, 108.23, 42.15, 31.81, 29.53, 29.35, 29.24, 26.80, 22.65, 14.11. HRMS (ESI): calcd for $[C_{36}H_{40}Cl_2N_2O_2S_2 + H]^+$: 667.1987, found: 667.1979.

Acknowledgments

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Supplementary data

Supplementary data (experimental details, copies of the ^{1}H NMR and ^{13}C NMR spectra for all key intermediates and final products) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.12.076.

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