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

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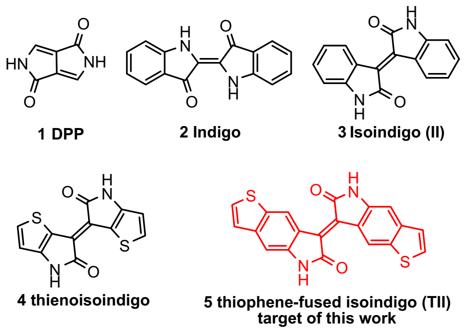
ABSTRACT

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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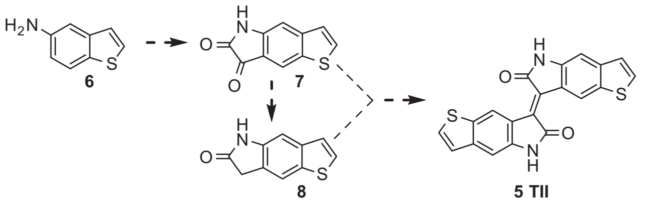


Scheme 2. Proposed synthetic route towards thiophene-fused isoindigo.

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.

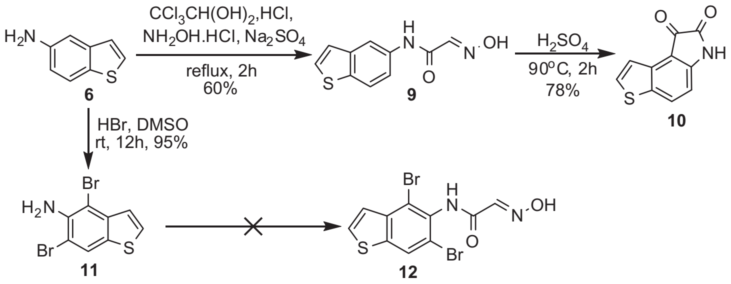
Results and discussion

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**.

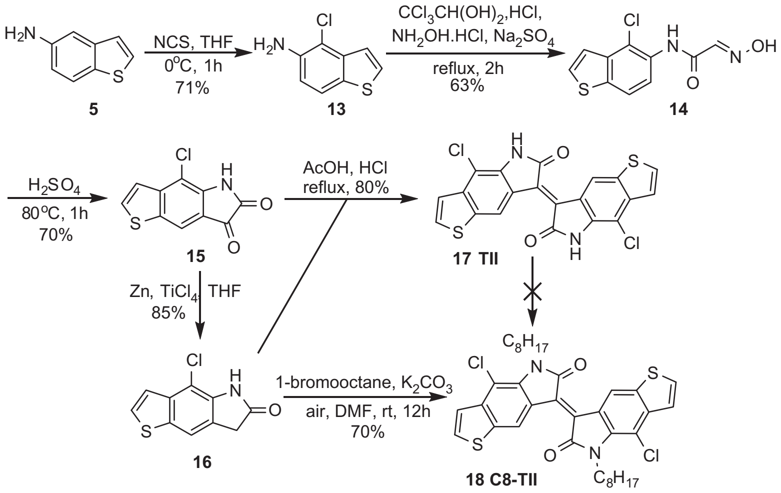
Compound **6** was synthesized from commercially available 2-chloro-5-nitrobenzaldehyde in high yield according to the literature.[25] It was then converted to (*E*)-N-(benzo[*b*]thiophen-5-yl)-2-(hydroxyimino)acetamide (**9**) in 60% yield. However, the rest of route towards the targeted compound became 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.