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# An expedient synthesis of fused heteroacenes bearing a pyrrolo[3,2-*b*]pyrrole core†

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Two linear fused heteroacenes bearing a pyrrolo[3,2-*b*]pyrrole core have been synthesized *via* a novel reductive ring closure methodology in three steps and in good overall yield. Preliminary OFET results showed that dinaphtho[2,3-*b*:2',3'-*f*]pyrrolo[3,2-*b*]pyrrole (DNPP) is a potential candidate for organic electronics.

Linear extended  $\pi$ -conjugated acenes are of great interest for organic electronics applications, such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) and organic photovoltaic cells.<sup>1</sup> One of the most well-known compounds is pentacene (Scheme 1, compound 1), which consists of five-fused benzene rings. It showed a charge carrier mobility benchmark as high as  $5.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>2</sup> It was expected that acenes with longer  $\pi$ -conjugated systems such as hexacene and heptacene would exhibit even better charge carrier mobility. However, those fused acenes, including pentacene, are not air-stable due to their high-lying HOMO energy levels. Furthermore, acenes with the number of fused rings greater than five are also prone to photo-degradation and Diels–Alder reactions. Those fused acenes needed to be protected with bulky protecting groups for better stability.<sup>3</sup>

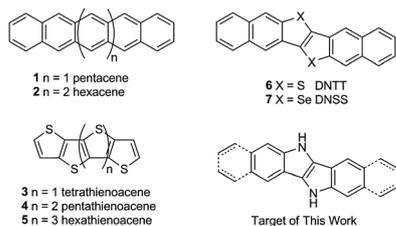
One of the solutions to this problem is to use fused heteroacenes instead of pentacene and its higher homologues. Linear fused

heteroacenes solely based on thiophene rings (up to eight rings) were synthesized.<sup>4</sup> Their potential as OFET materials was widely investigated and summarized in recent reviews.<sup>5</sup> In general, they showed better stability, but mobility was still lower than pentacene. Most recently, heteroacenes bearing a thieno[3,2-*b*]thiophene core and its seleno analogue (Scheme 1, compounds 6 and 7) have received much attention.<sup>6</sup> Those materials exhibited high air-stability and high field-effect mobility, and single crystal transistors of dianthra[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophene even demonstrated a saturation region hole mobility as high as  $12.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>7</sup>

Surprisingly, to the best of our knowledge, there is no report on the synthesis of large heteroacenes (more than four fused rings) bearing a pyrrolo[3,2-*b*]pyrrole core, although their OFET properties were claimed in a few patents.<sup>8</sup> Pyrrolo[3,2-*b*]pyrrole was predicted to be the most efficient electron donor among  $10\pi$ -electron systems,<sup>9</sup> however, it is unstable and very difficult to synthesize.<sup>10</sup> 5,10-Dihydroindolo[3,2-*b*]indole (also known as dibenzopyrrolo[3,2-*b*]pyrrole, DBPP) is the most well-known extended heteroacene bearing a pyrrolo[3,2-*b*]pyrrole core, which was used as a building block for high-spin organic polymers<sup>11</sup> and OLED polymers.<sup>12</sup> Several routes towards DBPP were summarized by Kaszynski and Dougherty and more recently by Samsoniya and Trapaidze, most of them involving the formation of C–N bonds as the key step, and the overall yields were relatively low.<sup>13</sup> The limitation of current synthetic tools hampered the synthesis of more extended fused heteroacenes containing the pyrrolo[3,2-*b*]pyrrole core.

We were interested in the synthesis of linear heteroacenes containing the pyrrolo[3,2-*b*]pyrrole core since: (1) pyrrolo[3,2-*b*]pyrrole is a better electron donor than thieno[3,2-*b*]thiophene, hence might be a better p-type organic semiconductor; (2) a more compact assembly of the molecules might be realized because of the smaller atomic radius of N compared with S; (3) NH– $\pi$  interaction might facilitate bidirectional electronic coupling between the molecules for better charge mobility,<sup>14</sup> and (4) the open valence on the N atom might be utilized to modify the solubility of the molecule for solution-processable OFETs. We here wish to report a novel and expedient way to construct heteroacenes with pyrrolo[3,2-*b*]pyrrole core and the preliminary results of their optical and OFET properties.

Our strategy was initially inspired by a report on the reduction of diazocines, which resulted in substituted tetrahydroindolo[3,2-*b*]indole.<sup>15</sup> We envisioned that if dibenzo[*b,f*][1,5]diazocine **8** could be



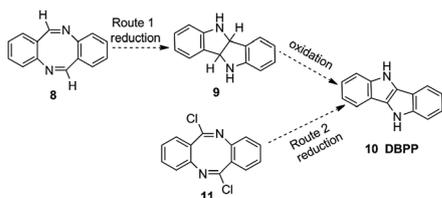
Scheme 1 Representative candidates for OFET.

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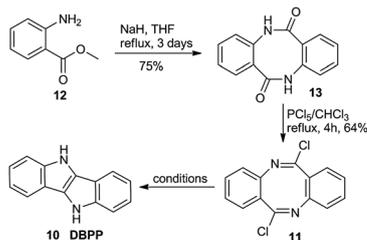
† Electronic supplementary information (ESI) available: Synthesis of DBPP and DNPP, <sup>1</sup>H and <sup>13</sup>C NMR spectra, photophysical and electrochemical data, XRD data, AFM images and FET properties. See DOI: 10.1039/c2cc36689d



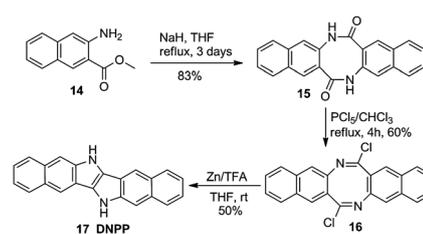
Scheme 2 Design of DBPP synthesis.

obtained, it might be in turn converted into tetrahydroindolo[3,2-*b*]indole **9**, which upon subsequent oxidation would give the desired compound **10** (Scheme 2, route 1). However, the synthesis of compound **8** turned out to be rather difficult: the direct condensation of 2-aminobenzaldehyde was not applicable since it would result in a cyclic trimer or tetramer instead of diazocine,<sup>16</sup> and the newly developed method to synthesize dibenzodiazocine<sup>17</sup> was also not applicable because the corresponding precursor could not be prepared. We then turned our attention to a report on the synthesis of diazocine **8** from 6,12-dichlorodibenzo[*b,f*][1,5]diazocine **11**.<sup>18</sup> We realized that reduction of compound **11** might directly afford DBPP **10**, given that the chlorine atom could act as a good leaving group under reductive conditions (Scheme 2, route 2).

The synthesis of compound **11** is straightforward, as shown in Scheme 3. By treating the commercially available methyl 2-aminobenzoate **12** with sodium hydride under reflux conditions in THF, dibenzo[*b,f*][1,5]diazocine-6,12(5*H*,11*H*)-dione **13** was obtained in satisfactory yield.<sup>19</sup> Compound **13** was then treated with  $\text{PCl}_5$  to afford compound **11** in good yield.<sup>19a</sup> Various conditions were tested to reduce compound **11** into compound **10**, which are summarized in Table 1.  $\text{PtO}_2/\text{H}_2$  was reported to reduce diazocine into the corresponding tetrahydroindolo[3,2-*b*]indole in high yield,<sup>15</sup> but when this condition was directly applied to compound **11**, compound **13** was obtained quantitatively (Table 1, entry 1). The same result was obtained when  $\text{PtO}_2/\text{H}_2$  was removed from the reaction system, indicating that the formation of compound **13** was due to the hydrolysis of **11**. Anhydrous conditions were then applied, however, no reduction occurred.  $\text{SmI}_2$  was effective in reductive coupling of imines,<sup>20</sup> however, although a small



Scheme 3 Synthetic route towards DBPP.



Scheme 4 Synthetic route towards DNPP.

amount of desired compound **10** was obtained, the reaction was sluggish even when large excess of  $\text{SmI}_2$  was used to reduce compound **11** (Table 1, entries 4 and 5). But we were delighted to find that the  $\text{Zn}/\text{AcOH}/\text{H}_2\text{O}/\text{DCM}$  condition<sup>15</sup> was successful in reducing **11** into **10** in 40% yield. When the reaction conditions were further modified using stronger acid (trifluoroacetic acid, TFA), and less Zn reagent (6.0 equiv.) in anhydrous THF, the yield of **10** was increased to 65%, although a longer reaction time was needed (Table 1, entry 7). Doubling the amount of Zn and TFA shortened the reaction time to 8 h and improved the yield to 70%. Further increase of the amount of reducing agent did not lead to further improvement. Overall, DBPP was synthesized in three steps from methyl 2-aminobenzoate **12** in 33% yield, which is superior to the methodologies reported before.<sup>11,13a</sup>

Moreover, this method could be extended to the synthesis of longer linear heteroacenes containing the pyrrolo[3,2-*b*]pyrrole core, as shown in Scheme 4. Starting from methyl 3-amino-2-naphthoate **14** and following the same synthetic route, dinaphtho[2,3-*b*:2',3'-*f*]pyrrolo[3,2-*b*]pyrrole (DNPP, **17**) was obtained as a yellowish solid in an overall 25% yield. It is the N-analogue of dinaphtho[2,3-*b*:2',3'-*f*]thieno[3,2-*b*]thiophene (DNNT).

DNPP is a stable compound and could be stored under ambient conditions without noticeable decomposition in the testing period (for months). It is slightly soluble in DMF or DMSO, hence gives us an opportunity to compare its optical and electrochemical properties with DBPP in solution state, which is summarized in Table 2. The UV-vis spectra of both compounds were recorded and used to estimate their HOMO–LUMO gap ( $E_g$ ) (ESI,† Fig. S1). The band absorption edge is 371 nm for DBPP and 485 nm for DNPP, which corresponds to  $E_g$  of 3.34 eV and 2.56 eV respectively. The large bathochromic shift (> 100 nm) reflects the smaller HOMO–LUMO gap caused by the longer  $\pi$ -conjugation length of DNPP. Compared with DNNT ( $E_g$  of 3.0 eV in solution),<sup>6c</sup> DNPP also exhibits a smaller HOMO–LUMO gap.  $E_{\text{HOMO}}$  of both compounds were estimated using cyclic voltammetry (ESI,† Fig. S2). DBPP showed an irreversible oxidation peak with the peak potential at 0.47 V and an onset around 0.24 V *vs.*

Table 1 Optimization of the reductive ring-closure step toward a pyrrolo[3,2-*b*] pyrrole core

Entry	Conditions	Results
1	$\text{PtO}_2/\text{H}_2$ , AcOH–THF–conc. HCl (1 : 1 : 0.03 vol), rt, 12 h,	<b>13</b> (quant.)
2	$\text{PtO}_2/\text{H}_2$ , anhydr. AcOH–THF (1 : 1, vol), rt, 12 h	N.R.
3	$\text{PtO}_2/\text{H}_2$ , anhydr. AcOH, rt, 12 h	N.R.
4	$\text{SmI}_2$ , 2.0 equiv., THF, rt, 12 h	Conversion ~20%, <5% of <b>10</b>
5	$\text{SmI}_2$ , 10.0 equiv., THF, rt, 12 h	Conversion ~30%, ~8% of <b>10</b>
6	Zn (20.0 equiv.), AcOH–H <sub>2</sub> O–DCM (5 : 1 : 2.5 vol), rt, 0.5 h	40% of <b>10</b>
7	Zn (6.0 equiv.), TFA (12.0 equiv.), THF, rt, 18 h	65% of <b>10</b>
8	Zn (12.0 equiv.), TFA (24.0 equiv.), THF, rt, 8 h	70% of <b>10</b>

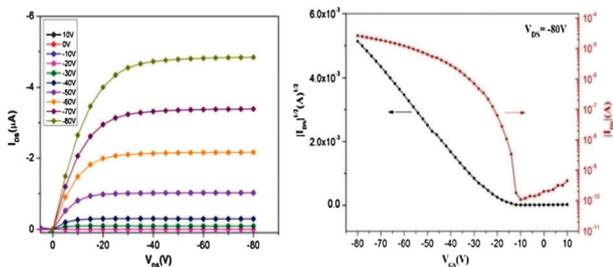
**Table 2** Photophysical properties of DBPP and DNPP

Compounds	$\lambda_{\text{edge}}$ (nm)	$E_g^c$ (eV)	$E_{\text{onset}}^d$ (V)	$E_{\text{HOMO}}/E_{\text{LUMO}}^e$ (eV)
DBPP	371 <sup>a</sup>	3.34	0.24	-4.72/-1.38
DNPP	485 <sup>b</sup>	2.56	0.02	-4.50/-1.94

<sup>a</sup>  $3 \times 10^{-5}$  mol L<sup>-1</sup> in DMF. <sup>b</sup> Concn. not accurately determined. <sup>c</sup> Determined from UV-vis absorption spectra. <sup>d</sup>  $E_{\text{onset}}^{\text{ox}}$ : onset of oxidation potential. <sup>e</sup>  $E_{\text{HOMO}} = -(E_{\text{onset}}^{\text{ox}} + 4.48)$  eV;  $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$  (eV).

**Table 3** Charge carrier mobilities, on/off ratios and threshold voltages (VT) of OFETs fabricated with DNPP and DBPP

Compounds	Substrate Si/SiO <sub>2</sub>	Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	On/off ratio	V <sub>T</sub> (V)
DBPP	Bare	—	—	—
	OTS	0.0011	$6.6 \times 10^4$	-6.05
DNPP	Bare	0.0024	$3.4 \times 10^4$	-25.7
	OTS	0.014	$4.1 \times 10^5$	-22.5

**Fig. 1** FET output characteristics at various gate voltages and transfer characteristics at  $-80$  V of DNPP.

Ag/AgCl, and the reductive peak at around  $-0.4$  V might be attributed to the reduction of the generated species during the oxidation process. DNPP, on the other hand, showed a semi-reversible oxidation peak at  $0.27$  V with the onset around  $0.02$  V and a reductive peak at around  $0.18$  V. This indicated that DNPP showed better electrochemical reversibility than DBPP.  $E_{\text{HOMO}}$  of DBPP and DNPP was then determined to be  $-4.72$  eV and  $-4.50$  eV, respectively, by their onset of the oxidation potentials.  $E_{\text{LUMO}}$  of both compounds were deduced from their  $E_{\text{HOMO}}$  and  $E_g$ .

Preliminary OFET studies were carried out under ambient conditions using “top-contact bottom-gate”-type devices, with Au as source and drain electrodes and n<sup>+</sup> doped Si as the gate electrode. The Si/SiO<sub>2</sub> surface was either directly used or pretreated with octadecyltrichlorosilane (OTS). Thin films of both DBPP and DNPP were prepared *via* vacuum deposition. The results are summarized in Table 3. DBPP did not show an obvious FET effect on untreated Si, but exhibited a carrier mobility of  $1.1 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and an on/off ratio of  $6.6 \times 10^4$  on the OTS-treated SiO<sub>2</sub>/Si surface. DNPP showed a better FET effect than DBPP both on untreated and OTS-treated SiO<sub>2</sub>/Si surfaces, with the highest carrier mobility of  $1.4 \times 10^{-2}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and on/off ratio of  $4.1 \times 10^5$ . Typical FET output characteristics and transfer characteristics of DNPP are shown in Fig. 1. Thin film XRD analysis indicates that both compounds are crystalline (ESI,† Fig. S4). The mediocre OFET performance might be due to the boundaries between crystal grains in the film, as evidenced by AFM study (ESI,† Fig. S5).

In summary, starting from commercially available materials, two linear fused heteroacenes bearing a pyrrolo[3,2-*b*]pyrrole core, namely DBPP and DNPP, were synthesized *via* a novel reductive ring closure methodology in three steps and in good overall yield. OFET properties of both compounds were studied. Preliminary results showed that DNPP was a better OFET material. The synthesis of other pyrrolo[3,2-*b*]pyrrole-containing heterocycles and the optimization of their OFET properties are currently ongoing in our group.

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