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#### Note

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# Serendipitous formation of semiconducting semi-NINDIGO indigoid by degradation of diindolopyrrole

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Abstract: We report the serendipitous discovery and synthesis of an indigoid "Semi-Nindigo" (2) via oxidation of a diindolopyrrole (1). Reaction of 2 with  $BF_3Et_2O$  affords the borylated derivate (3). The electronic spectra of 2 and 3 possess intense long wave absorptions near 600 nm and 650 nm. 3 is weakly emissive in the near-infrared. Thin film OFETs fabricated with 1 and 2 both exhibited modest p-type mobilities.

The indigo dye is famous for its distinctive blue color and has been used to dye fabrics and textiles for at least 6000 years.<sup>1</sup> Modern applications of indigoids include redox-active ligands<sup>2</sup>, photodiodes<sup>3</sup>, and more recently as an organic semiconductor (OSC) in organic field effect transistors (OFETs)<sup>4</sup> and in organic photovoltaics (OPVs).<sup>5</sup> Historically, indigo was produced from its natural precursor indican which was extracted from *Indigofera* plants. Today many synthetic routes to the indigo dye exist, most involving the oxidative dimerization of isatin or indolin-3-one.<sup>6</sup> Interest in the properties of indigo led to the development of derivatives and analogues including thioindigo<sup>7</sup>, oxyindigo<sup>8</sup>, and isoindigos<sup>9</sup>. However, such derivatives suffer from poor solubility and limited structural space for tuning their optoelectronic properties. Soluble derivatives with imine substituents like N,N'-diaryldiimines ("Nindigo") can be readily accessed in good yield by refluxing indigo in bromobenzene with an excess of aniline, in the presence of TiCl<sub>4</sub> and DABCO.<sup>10</sup> Nindigo can also be prepared by the dimerization of aryl isocyanides<sup>11, 12</sup> and the reduction of bis-imidoylchlorides of oxalic acid<sup>13</sup>, albeit in poor yields.

Indigo and its derivatives are attractive materials for applications as OSCs. It is a natural dye of a remarkable stability which is believed to be due to strong hydrogen bonding.<sup>14</sup> Interestingly, it was recently shown that an old batch of indanthrone blue (a related dye with similar H-bonding interactions) synthesized in 1932 performed nearly as well in OFETs as a new batch produced in 2010.<sup>15</sup> The parent indigo was first revealed as semiconductor in 2012 by Sariciftci et al.<sup>4</sup> who showed thin film OFETs exhibiting balanced hole/electron mobilities of 10<sup>-2</sup> cm<sup>2</sup>/Vs. OFETs with thioindigo were also studied, however, inferior hole/electron mobilities (~10<sup>-4</sup> cm<sup>2</sup>/ cm<sup>2</sup>/Vs) were achieved. Other derivatives<sup>14, 16-20</sup> achieved mobilities ranging from 10<sup>-4</sup> to 10<sup>-1</sup> cm<sup>2</sup>/Vs. Many indigo and isoindigo-based polymers have also shown semiconducting behavior.<sup>21, 22</sup> However, to the best of our knowledge, no *N*-substituted indigoids have been studied as OSCs thus far. Herein, we report a serendipitous oxidation of a diindole[3,2-b:4,5-b0]pyrrole (1) producing a new indigoid dye "Semi-Nindigo" (2), and its transformation in borylated derivative (3). We also investigate 1 and 2 as OSCs in thin film OFETs.



The dye **2** was discovered serendipitously when a blue compound was formed upon evaporation of  $1^{23, 24}$  in dioxane (**Figure S1**). The effect has not been observed in other solvents, such as THF, DCM, diethyl ether, or acetone. Out of many ethers tested, dioxane was the only unstabilized solvent and we suspect that the observed transformation could be due to the oxidation of **1** with peroxide impurities.<sup>25</sup> To test our hypothesis, we purposefully generated peroxides in dioxane by bubbling air. Indeed, adding **1** to such solvent resulted in immediate deep blue coloration.

To synthesize a substantial quantity of **2**, we explored a variety of oxidizing agents; we found that mCPBA in dioxane at room temperature immediately produced a new deep blue **2** which can be isolated in 65% yield after column chromatography. Based on the similar absorption profile (vide infra) of **2** and indigo, we surmised that **1** was oxidized to an indigoid. We also noted that stronger oxidants (NOBF<sub>4</sub>) transform **1** into isatin. High resolution MS of **2** revealed an addition of one oxygen atom. The IR spectrum (**Figure S2**) of **2** exhibited a stretch at 1682 cm<sup>-1</sup> which we attribute a conjugated C=O group. <sup>1</sup>H NMR analysis of **2** revealed that while **1** and **2** both had 15 protons, the spectrum of **2** contained two non-identical downfield resonances at 10-11 ppm (**Figure S8**), which prompted us to consider an asymmetric structure. Our analysis led us to propose two plausible indigoid structures **2** and **2'** (**Scheme 1**).<sup>26</sup> Based on DFT calculations of the optimized indigoid structures (**Figure S4**), we propose **2** as the oxidation product of **1**. A substituted derivative of **2**, 3'-((2,6-dimethylphenyl)imino)-[2,2'-biindolinylidene]-3-one, has previously been reported by Hicks<sup>27</sup> (prepared from parent indigo) and its IR and NMR spectra are in agreement with those found for **2**. The thermal properties of **2** were investigated by thermal gravimetric analysis (TGA). revealing a decomposition temperature of 265 °C (95% weight loss, **Figure S5**).

The heating of **2** with  $BF_3OEt_2$  produced the mono- $BF_2$  complex **3**. We also considered the possibility of formation of its isomers, oxaazaborepine **3**' and diazaborole **3**'', however we found that the diazaborin **3** with a 6-membered ring was the more stable by 10.4 and 13.7 kcal/mol, respectively (**Figure S4b**).



Scheme 1 Synthesis of 1, 2, and 3 (i) mCPBA in dioxane, 25 °C (ii) BF<sub>3</sub>OEt<sub>2</sub>, NEt<sub>3</sub>, THF

The electronic absorption spectrum of semi-Nindigo **2** (**Figure 1a**) exhibits an intense band at  $\lambda_{max}$  = 597 nm ( $\epsilon = 4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) located between those of indigo ( $\lambda_{max} = 605 \text{ nm}$  in C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>)<sup>6</sup> and Nindigo ( $\lambda_{max} = 585 \text{ nm}$  in CH<sub>2</sub>Cl<sub>2</sub>).<sup>10</sup> The borylated derivative **3** shows a red shifted absorption maxima at  $\lambda_{max} = 669 \text{ nm}$ , which is slightly redshifted compared to Nindigo-BF<sub>2</sub> ( $\lambda_{max} = 649 \text{ nm}$ ). **2** did not exhibit

fluorescence due to the deactivation via proton transfer.<sup>28, 29</sup> Films of **2** prepared by vacuum deposition exhibited broader absorption in the visible region with its absorption maximum red-shifted by ca. 40 nm (**Figure S3**). Literature absorption data for indigo exhibited similar changes in the absorption profile going from solution to thin film, which is attributed to  $\pi$ -interactions in the solid state.<sup>4</sup> Exchanging the NH proton for a BF<sub>2</sub> substituent in **3** leads to emission at  $\lambda_{max} = 695$  nm (**Figure 1a**) corresponding to a Stokes shift of 98 nm, which is similar to that observed in Nindigo-BF<sub>2</sub> (101 nm).



**Figure 1**(a) Normalized absorption spectra of **1**, **2**, and **3** and photoluminescent spectrum of **3** ( $\lambda_{ex} = 650$  nm, dashed line) in CH<sub>2</sub>Cl<sub>2</sub>. The arrows show the absorption maxima of (i) Nindigo<sup>10</sup> (ii) Indigo<sup>6</sup> (C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>) (iii) Nindigo-BF<sub>2</sub><sup>30</sup> and (iv) emission of Nindigo-BF<sub>2</sub><sup>30</sup> (b) CV of **1**, **2**, and **3** in DMF.

The redox properties and calculated HOMO/LUMO energies of 1-3 are summarized in Table 1. The cyclic voltammogram (CV) of 1 consists of a single reversible one-electron oxidation wave at -0.01 V vs. Fc/Fc<sup>+</sup> (Figure 1b). The transformation of 1 to 2 is manifested by a +0.32 V shift of the oxidation wave and the emergence of a reversible reduction wave at -0.97 V vs Fc/Fc<sup>+</sup>, corresponding to HOMO and LUMO energies of -5.11 and -3.82 eV, respectively ( $E_e = 1.29 \text{ eV}$ ). The DFT (B3LYP/6-31G(d)) calculated HOMO energy was similar (-4.97 eV), however the LUMO energy was predicted to be significantly higher (-2.57 eV). Borylation of 2 into 3 is manifested by a +0.14 V shift in the oxidation wave (two-electron) and a -0.10 V shift in the reduction wave; in addition, a second one-electron reversible reduction wave appears at -1.56 V. Thus, the replacement of the indole proton with  $BF_2$  is manifested by reversible oxidation and reduction processes, which was also reported for Nindigo-BF2<sup>31</sup>. The calculated HOMO/LUMO energies for **3** were -5.34 and -3.06 eV ( $E_g = 2.28$  eV). Note that going from **2** to **3**, the electrochemical gap shrinks while the optical gap expands. Meanwhile, the large discrepancies between the electrochemically derived and DFT-calculated LUMO energies likely arise from strong solvation (electrostatic stabilization) of the corresponding radical-anion that are not acccounted for in gas phase DFT calculations. The frontier molecular orbitals (FMOs) of the geometry optimized structures of 2 and 3 are uniformly distributed throughout their conjugated cores (Figure S6).

We prepared thin film OFETs of **1** and **2** by vacuum deposition to investigate their charge transport properties. Output and transfer characteristics are displayed in **Figure 2. 1** exhibited modest hole mobility  $\mu_{max} = 10^{-5} \text{ cm}^2/\text{Vs}$ , with an on/off ratio of  $10^4 \cdot 10^5$  and a threshold voltage  $V_{th} = -8 \text{ V} \cdot 10 \text{ V}$ . In contrast, **2** revealed a substantially higher hole mobilies of  $10^{-3} \text{ cm}^2/\text{Vs}$  (on/off ratio of  $10^5$ ,  $V_{th} = -17 \text{ V}$ ). The higher mobility of **2** compared to **1** was unexpected, considering that the transformation from **1** to **2** involves involved desintegration of a fused and planar molecule in a conformationally labile non-planar structure with a highly polar group. However, the low mobility of **1** is readily explained by its packing mode which

exhibits self-complementary H-bonding between the pyrrolic NH groups and the electron deficient core, leading to an edge-to-face arrangement of molecules and poor  $\pi$ -orbital overlap (**Figure 3**). To the best of our knowledge, this the 1<sup>st</sup> OFET with any Nindigo derivatives and exhibits mobilities on the same order as other indigos (10<sup>-2</sup> to 10<sup>-4</sup> cm<sup>2</sup>/Vs). No n-type behavior was observed for either 1 or 2, which was expected based on the high LUMO energy.

Table 1 HOMO/LUMO energies of 1-3 derived from CV and optical measurements and DFT calculations.

	$E_{HOMO}^{CV}(eV)^a$	$E_{LUMO}^{CV}(eV)^a$	$E_g^{CV}(eV)$	$E_{HOMO}^{DFT}$ (eV)	$E_{LUMO}^{DFT}(eV)$	$E_g^{DFT}(eV)$	$E_g^{Opt.}$
1	-4.78	-	-	-4.66	-0.70	3.96	3.31
2	-5.11	-3.82	1.29	-4.96	-2.57	2.00	1.94
3	-5.25	-3.78	1.47	-5.34	-3.06	2.28	1.72

(a) HOMO = -( $E_{ox}$  + 4.8 eV), LUMO = -( $E_{red}$  + 4.8 eV), where  $E_{ox}$  and  $E_{red}$  are oxidation and reduction potentials versus ferrocene, measured at half-maximum.



Figure 2 The output (left) and transfer (right) OFET characteristics of vacuum sublimed thin films of a) 1 and b) 2, (deposition rate  $0.1-0.3 \text{ A}^{\circ}/\text{s}$ , thickness 35 nm).



**Figure 3** Crystal structure of DIP 1 depicting (a) the edge-to-face arrangement of molecules exhibiting short NH... $\pi$  (2.67 Å) and CH... $\pi$  (2.48 Å) contacts and (b) solid state packing showing herringbone packing of  $\pi$ -dimers (interplanar distance 3.36 Å, phenyl groups are hidden for clarity).

In conclusion, we have presented the unusual transformation of a diindolopyrrole **1** into an N-aryl subtituted indigoid **2**, which exhibits a narrow HOMO-LUMO gap along with the emergence of a reversible reduction wave. Reaction of **2** with BF<sub>3</sub> afforded the borylated derivative, which displayed red shifted absorption and NIR emission. Thin film transistors exhibited hole transport with moderate hole mobility of  $10^{-3}$  cm<sup>2</sup>/Vs, which is two orders of magnitude higher than that of the parent compound **1**. To the best of our knowledge, this is the first report of semiconducting behavior in N-substituted indigoids. We believe that the straightforward functionalization of **2** can open up avenues to a new family of highly-functionalized soluble indigoid semiconductors.

# **Experimental Section**

**Materials and methods.** DFT calculations were carried out using the B3LYP functional and the 6-31G(d) basis set in Gaussian 16W. Cyclic voltammetry experiments were carried out at room temperature in a three-electrode cell where a Pt disk (d = 2 mm) was used as the working electrode, a Pt wire as the counter-electrode, and Ag/AgCl as the reference.

**Device Fabrication:** Thin-film FETs were fabricated on pre-patterned bottom-contact bottom-gate configurations (with symmetric Au electrodes as drain and source with different channel lengths of 2.5, 5, 10, and 20 µm). The performance of the resulting OFETs was measured in vacuum and ambient atmosphere using Keithley 4200-SCS semiconductor parameter analyzer. Thin film of both 1 and 2 were grown by vacuum deposition ( $5 \times 10^{-7}$  mbar, deposition rate 0.1–0.3 Å/sec) on octyltrichlorosilane (OTS) surface treated SiO2/Si. SiO<sub>2</sub> was thermally grown (200 nm-thick, C=1.8×10<sup>-8</sup> F/cm<sup>2</sup>) on heavily n-doped (Sb) Si ( $\rho \approx 0.01$  Ohm cm). For OTS functionalization, samples were washed with acetone, 2-propanol, and cleaned in PDC-32G plasma cleaner. The sample was then heated in 5 mM solution of OTS in toluene at 60°C for 40 min. Subsequently, they were rinsed with toluene and dried at 60°C in air for 10 min prior to thin-film deposition.

11-phenyl-6,11-dihydro-5H-pyrrolo[3,2-b:4,5-b']diindole (1) was synthesized. <sup>23</sup>; its NMR spectral data matched that reported in literature.

(Z)-2-(3-(phenylamino)-2H-indol-2-ylidene)indolin-3-one (2) mCPBA (40 mg, 0.31 mmol) was added to a solution of **1** (50 mg, 0.16 mmol) in dioxane (5 mL) and the solution was stirred at room temperature for 5 minutes. Dioxane was removed by rotary evaporation and the crude was loaded onto silica and purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>:EtOAc, 10:1). The solvent was removed from the product and the obtained blue solid was suspended in hexanes (5 mL), filtered, and washed with hexanes (2 × 2 mL) yielding a deep blue solid (25 mg, 50%). <sup>1</sup>H NMR (500 MHz, DMSO-d6)  $\delta$  (ppm) 10.76 (1H, s), 10.03 (1H, s), 7.61 (1H, d, J = 8 Hz), 7.48 (t, 2H, 7.5 Hz), 7.43 (t, 1H, 7 Hz), 7.34 (2H, m), 7.30 (1H, t, 7.5 Hz), 7.24 (1H, t, 7.5 Hz), 7.06 (2H, d, 7.5 Hz), 6.89 (1H, t, J = 7.5 Hz), 6.61 (1H, t, J = 7.5 Hz), 6.46 (1H, d, 7.5 Hz). <sup>13</sup>C {<sup>1</sup>H} NMR (500 MHz, DMSO-d6)  $\delta$  (ppm) 113.3, 113.7, 116.8, 119.3, 119.7, 120.0, 120.1, 120.5, 123.5, 124.8, 125.6, 127.2, 129.8, 133.4, 134.8, 150.1, 151.7, 151.9, 161.2, 185.8. HRMS (ESI-ion trap) m/z: [M+H]<sup>+</sup> Calcd for [C<sub>22</sub>H<sub>15</sub>N<sub>3</sub>O + H]<sup>+</sup>: 338.1215; found: 338.1289. FT-IR v (cm<sup>-1</sup>) 3364, 3259, 1684, 1602, 1581

**6,6-difluoro-13-(phenylamino)-5l4,6l4-[1,3,2]diazaborolo[1,5-a:3,4-a']diindol-12(6H)-one** (3) A solution of **2** (40 mg, 0.12 mmol) in toluene (2 mL) and Et<sub>3</sub>N (0.1 mL) was stirred at reflux for 20 minutes. BF<sub>3</sub>Et<sub>2</sub>O (0.27 mL, 2.2 mmol) was added and the reaction was left for another 20 minutes. After cooling to room temperature, the crude was loaded onto silica and purified by column chromatography in hexanes/ethyl acetate (9:1). The solvent was removed by rotary evaporation and the obtained solid was suspended in cold methanol (~5 mL) and filtered yielding a deep green solid (10 mg, 22%). <sup>1</sup>H NMR (500 MHz, DMSO-d6)  $\delta$  (ppm) 11.39 (1H, s), 7.73 (1H, d, J = 7.5 Hz), 7.64-7.58 (4 H, m), 7.47-7.44 (3H, m), 7.35-7.30 (2H, m), 7.13 (1H, t, J = 7.5 Hz), 6.68 (1H, t, J = 7.5 Hz), 6.31 (1H, d, J = 8.5 Hz). <sup>13</sup>C {<sup>1</sup>H} NMR

 $(500 \text{ MHz}, \text{DMSO-d6}) \delta$  (ppm) 114.2, 115.5, 118.1, 120.4, 121.7, 123.4, 125.1, 125.3, 126.9, 129.2, 129.2, 130.2, 135.4, 137.4, 140.7, 150.8, 154.3, 156.8, 187.6. HRMS (APCI-ion trap) m/z Calcd for  $C_{22}H_{14}BF_2N_3O$ : 385.1198, found: 385.1212. FT-IR v (cm<sup>-1</sup>): 3405, 1698, 1649, 1608, 1590, 1543.

# **Supporting Information**

Images illustrating serendipitous discovery of **2**, energy levels diagrams of possible structures for **2** and **3** and molecular orbital surfaces; IR and additional UV-Vis spectra; TGA of **2**; NMR and MS spectra, X-ray crystallographic information for **1**; DFT optimized coordinates.

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