Electronic Supplementary Information for

**Cyanated isoindigos for n-type and ambipolar organic thin film transistors**

Wan Yue, Tao He, Matthias Stolte, Marcel Gsänger and Frank Würthner*

*Universität Würzburg, Institut für Organische Chemie & Center for Nanosystems Chemistry, Am Hubland, 97074 Würzburg, Germany.

E-mail: wuerthner@chemie.uni-wuerzburg.de; Fax: +49 931 31 84756; Tel: +49 931 31 85340

**Table of Contents**

1. Materials and methods...............................................................S2
2. Synthesis and characterization of new compounds..........................S3
3. X-ray diffraction analysis............................................................S6
4. Cyclic voltammetry.........................................................................S7
5. UV-vis absorption spectra.............................................................S8
6. Device characterization.................................................................S9
7. $^1$H NMR and $^{13}$C NMR spectra of cyanated isoindigos............... S11
8. References....................................................................................S14
1. Materials and methods

The starting compounds, brominated isoindigos 1 and 3, were prepared according to the literature.\textsuperscript{S1} All other reagents and solvents were obtained from commercial suppliers and purified and dried according to standard procedures.\textsuperscript{S2} Column chromatography was performed on silica gel (Merck Silica 60, particle size 0.040-0.063 mm). Solvents for spectroscopic studies were of spectroscopic grade and used as received. The melting points (Mp) of compounds were determined with an Olympus BX-41 polarization microscope equipped with a Linkam THMS 600 hot stage and a temperature controller unit. \(^1\)H and \(^{13}\)C spectra were recorded in CDCl\(_3\) on a Bruker DMX 400 spectrometer. Residual undeuterated solvent was used as internal standard. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Daltronik GmbH (autoflex II) mass spectrometer. Samples were dissolved in chloroform or dichloromethane (0.5 mg/mL), and 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enyldiene]malononitrile (DCTB) was used as matrix, which was also dissolved in chloroform or dichloromethane and mixed with the sample solution in a 1:3 (v/v) ratio. High resolution ESI-TOF mass spectrometry was carried out on a microTOF focus instrument (Bruker Daltronik GmbH). UV-vis measurements were performed in CH\(_2\)Cl\(_2\) in a conventional quartz cell (light pass 10 mm) on a Perkin-Elmer Lambda 950 spectrometer. For cyclic voltammetry, a standard commercial electrochemical analyzer (EC epsilon; BAS Instruments, UK) with a three electrode single-compartment cell was used. Dichloromethane (HPLC grade) was dried over calcium hydride under argon and degassed before using. The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAHFP) was prepared according to the literature,\textsuperscript{S3} and recrystallized from ethanol/water. The measurements were carried out in dichloromethane with ferrocene (Fc) as an internal standard for the calibration of the potential. Ag/AgCl reference electrode was used. A Pt disc and a Pt wire were used as working and auxiliary electrodes, respectively. AFM was performed with a Veeco MultiMode IV instrument in the tapping mode.
2. Synthesis and characterization of new compounds

\(N, N'-(1\text{-octyl})\text{-isoindigo (C8-IID)}\) was synthesized according to the literature.\(^{51}\)

CV (CH\(_2\)Cl\(_2\), 0.1 M TBAHFP, vs Fe/Fe\(^+\)): \(E_{1/2}^{\text{red}} (X/X) = -1.34\) V, \(E_{1/2}^{\text{red}} (X/X^2) = -1.73\) V. UV-vis (CHCl\(_3\)): \(\lambda_{\text{max}}/\text{nm} (\varepsilon / \text{M}^{-1} \text{cm}^{-1}) = 395 \text{ (12300)}, 500 \text{ (3940)}\).

**Compound 2**

Bromo isoindigo 1 (100 mg, 0.18 mmol), copper cyanide (80 mg, 0.45 mmol), 1,1’-bis(diphenylphosphino)ferrocene (20 mg, 0.036 mmol) and bis(dibenzylideneacetone)palladium(0) (10 mg, 0.018 mmol) were mixed in 1,4-dioxane (20 mL) and heated at 140 °C for 3 d under nitrogen. After being cooled down to room temperature, the reaction mixture was diluted with dichloromethane (20 ml), filtered through celite, and the solvent was removed under vacumm. The residue was purified by silica gel column chromatography using dichloromethane as eluent to give 50 mg (55%) compound 2 and 40 mg (40%) of starting compound 1 could be recovered.

Mp = 124 °C. \(^1\text{H} \text{NMR} \text{ (400 MHz, CDCl}_3, \text{ 300 K)}: \delta = 9.32 (d, ^3J = 8.2 \text{ Hz, 1H}), 9.18 (dd, ^3J = 8.1 \text{ Hz, } ^4J = 0.8 \text{ Hz, 1H}), 7.40 (dt, ^3J = 7.7 \text{ Hz, } ^4J =1.2 \text{ Hz, 1H}), 7.34 (dd, ^3J = 8.3 \text{ Hz, } ^4J = 1.5 \text{ Hz, 1H}), 7.06 (dt, ^3J = 8.0 \text{ Hz, } ^4J =1.0 \text{ Hz, 1H}), 7.00 (d, ^4J =1.2 \text{ Hz, 1H}), 6.80 (d, ^3J =7.4 \text{ Hz, 1H}), 3.81-3.74 (m, 4H), 1.72-1.66 (m, 4H), 1.39-1.26 (m, 20H), 0.89-0.85 (m, 6H). \(^{13}\text{C} \text{NMR} \text{ (100 MHz, CDCl}_3, \text{ 300 K)}: \delta = 167.4, 167.2, 145.6, 144.5, 136.9, 133.8, 130.9, 130.8, 130.0, 126.1, 125.5, 122.5, 121.4, 118.8, 114.1, 110.2, 108.2, 40.4, 40.2, 31.76, 31.74, 29.3, 29.23, 29.15, 27.2, 22.6, 14.0. (the signals of aliphatic carbon atoms are overlaped).

MS (MALDI-TOF, neg. mode, CHCl\(_3\)): Calculated for C\(_{33}\)H\(_{41}\)N\(_3\)O\(_2\): 511.36, found: 511.32. HRMS (ESI, pos. mode, acetonitrile): Calculated for C\(_{33}\)H\(_{42}\)N\(_3\)O\(_2\): 512.3199. \([\text{M}+\text{H}]^+\), found: 512.3256.

CV (CH\(_2\)Cl\(_2\), 0.1 M TBAHFP, vs Fe/Fe\(^+\)): \(E_{1/2}^{\text{red}} (X/X) = -1.14\) V, \(E_{1/2}^{\text{red}} (X/X^2) = -1.54\) V. UV-vis (CHCl\(_3\)): \(\lambda_{\text{max}}/\text{nm} (\varepsilon / \text{M}^{-1} \text{cm}^{-1}) = 400 \text{ (14900)}, 504 \text{ (4480)}\).
**Compound 4 and 5**

Dibromo-isoidindigo 3 (200 mg, 0.39 mmol), copper cyanide (350 mg, 1.95 mmol), 1,1’-bis(diphenylphosphino)ferrocene (38 mg, 0.07 mmol) and bis(dibenzylideneacetone)palladium(0) (20 mg, 0.035 mmol) were mixed in 1,4-dioxane (30 mL) and heated at 140 °C for 120 h under nitrogen. After being cooled down to room temperature, the reaction mixture was diluted with dichloromethane (50 ml), filtered through celite, and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using dichloromethane as eluent to give 4 (68 mg, 36%) and 5 (50 mg, 32%) as dark red solids.

**Compound 4:**

Mp = 158 °C. $^1$H NMR (400 MHz, CDCl$_3$, 300 K): δ = 9.31 (dd, $^3$J = 8.3 Hz, $^5$J = 0.4 Hz, 1H), 9.10 (d, $^3$J = 8.6 Hz, 1H), 7.34 (dd, $^3$J = 8.3 Hz, $^4$J = 1.6 Hz, 1H), 7.19 (dd, $^4$J = 1.9 Hz, $^3$J = 8.6 Hz, 1H), 7.00 (d, $^3$J = 1.0 Hz, 1H), 6.94 (d, $^4$J = 1.8 Hz, 1H), 3.86-3.63 (m, 4H), 1.68-1.71 (m, 4H), 1.36-1.27 (m, 20H), 0.89-0.86 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 166.4, 166.2, 145.4, 143.6, 134.5, 130.9, 130.3, 129.2, 127.1, 125.3, 124.4, 124.3, 119.2, 117.7, 113.4, 110.6, 109.3, 39.4, 30.74, 30.73, 28.2, 28.1, 21.59, 21.58. 13.0. (the signals of aliphatic carbon atoms are overlapped).

MS (MALDI-TOF, neg. mode, CHCl$_3$): Calculated for C$_{33}$H$_{40}$BrN$_3$O$_2$: 590.696, found: 589.23. HRMS (ESI, pos. mode, acetonitrile): calculated for C$_{33}$H$_{41}$BrN$_3$O$_2$: 590.2382, [M+H]$^+$, found: 590.2376. CV (CH$_2$Cl$_2$, 0.1 M TBAHFP, vs. Fe/Fe$^+$): $E_{1/2}^{\text{red}}$(X/X$^-$) = −1.06 V, $E_{1/2}^{\text{red}}$(X/X$^{2-}$) = −1.45 V. UV-vis (CHCl$_3$): $\lambda_{\text{max}}$/nm (ε / M$^{-1}$ cm$^{-1}$) = 402 (18120), 513 (6220).

**Compound 5:**

Mp = 250 °C. $^1$H NMR (400 MHz, CDCl$_3$, 300 K): δ = 9.33 (dd, $^3$J = 8.2 Hz, $^5$J = 0.3 Hz, 2H), 7.35 (dd, $^3$J = 8.3 Hz, $^4$J = 1.5 Hz, 2H), 7.02 (d, $^4$J = 1.1 Hz, 2H), 3.80-3.76 (m, 4H), 1.72-1.68 (m, 4H), 1.38-1.27 (m, 20H), 0.89-0.86 (m, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 166.8, 145.3, 134.3, 130.9, 126.4, 124.9, 118.4, 115.5, 110.5, 40.5, 31.7, 29.2, 29.1, 27.3, 27.0, 22.6, 14.0.
MS (MALDI-TOF, neg. mode, CHCl₃): Calculated for C₃₄H₄₀N₄O₂: 535.811, found: 536.32. HRMS (ESI, pos.mode, acetonitrile)): Calculated for C₃₃H₄₁BrN₃O₂: 537.3230, [M+H]+, found: 537.3226. (this ia a symemetric molecules and 17 signals are observed for 34 carbon atoms).

CV (CH₂Cl₂, 0.1 M TBAHFP, vs Fc/Fc⁺): $E_{1/2}^{\text{red}}$ (X/X⁻) = −0.92 V, $E_{1/2}^{\text{red}}$ (X/X²⁻) = −1.29 V. UV-vis (CHCl₃): $\lambda_{\text{max}}$/nm (ε / M⁻¹ cm⁻¹) = 372 (20740), 398 (19140), 515 (5590).
3. X-ray analysis

Crystal data for 5 were collected on a Bruker D8Quest Kappa Diffractometer using Cu_Kα-radiation from an Incoatec IμS microsource with Montel multi layered mirror, a Photon100 CMOS detector and Apex2* software at 100 K. The crystal was grown from dichloromethane/methanol at room temperature. The structure was solved using direct methods (SHELXS), expanded with Fourier techniques and refined with SHELXL. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation on geometrically idealized positions. The triclinic unit cell contains 1 molecule on a centre of symmetry.


Crystal data: C_{34}H_{40}N_{4}O_{2}, M = 536.70, thin red plate: 59 x 346 x 749 mm^{3}, triclinic P-1, a: 5.2943(4) Å, b: 9.7777(8) Å, c: 14.7860(12) Å, α: 107.491(2)°, β: 90.824(2)°, γ: 93.038(2)°, cell volume: 728.63(10) Å^{3}, λ: 1.54178 Å, Z = 1, T = 100 K, ρ_{calc} = 1.223 g/mm^{3}, F_{o.o.o.} : 288, μ = 0.602 mm^{-1}, R_{1}: 0.041, R_{w}: 0.116, GooF: S =1.08, 15978 refls (R_{int}: 0.0407), refined: 2707 I>2s(I), 2869 refls total, 182 params, 0 restraints.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centra as supplementary publication no. CCDC-966365. These data can be obtained free of charge from The Cambridge Crystallographic Data Centra via www.ccdc.ac.uk/data.request/cif.
4. Cyclic voltammetry

**Figure S1**: Cyclic voltammograms of reference compound **C8-ID** \(N, N'-(1\text{-octyl})\text{-isoindigo}\) (black), mono cyanated isoindigo 2 (red), mono-bromo-mono-cyanated isoindigo 4 (blue), and dicyanated isoindigo 5 (cyan) measured in dichloromethane (in V vs Fc/Fc\(^+\)) at a scan rate of 0.1 V/s.

**Table S1.** Summary of electrochemical properties and HOMO/ LUMO energies of cyanated isoindigo.

<table>
<thead>
<tr>
<th></th>
<th>(E_{1r}^a)</th>
<th>(E_{2r}^a)</th>
<th>LUMO(^b)</th>
<th>(E_g^c)</th>
<th>HOMO(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8-ID(^e)</td>
<td>-1.34</td>
<td>-1.73</td>
<td>-3.46</td>
<td>1.96</td>
<td>-5.42</td>
</tr>
<tr>
<td>2</td>
<td>-1.14</td>
<td>-1.54</td>
<td>-3.66</td>
<td>1.98</td>
<td>-5.64</td>
</tr>
<tr>
<td>4</td>
<td>-1.06</td>
<td>-1.45</td>
<td>-3.74</td>
<td>2.00</td>
<td>-5.74</td>
</tr>
<tr>
<td>5</td>
<td>-0.92</td>
<td>-1.29</td>
<td>-3.88</td>
<td>1.97</td>
<td>-5.85</td>
</tr>
</tbody>
</table>

\(^a\) Half-wave reductive potential (in V vs Fc/Fc\(^+\)) measured in CH\(_2\)Cl\(_2\) at a scan rate of 0.1 V/s.

\(^b\) Estimated from the first half reductive wave (eV) applying the equation (LUMO = -(4.80 + \(E_{1r}\)).

\(^c\) Band gaps (\(E_g\)) were estimated from the onset of UV-vis spectra of compounds.

\(^d\) Estimated from the LUMO and \(E_g\).

\(^e\) **C8-ID**: \(N, N'-(1\text{-octyl})\text{-isoindigo}\).
5. UV-vis absorption spectra

Figure S2: Absorption spectra of reference C8-IIID (a), and cyanated IID 2 (b), 4 (c), and 5 (d) in chloroform solution (c < 1x10^{-5} M) at room temperature.

Figure S3: UV-vis absorption spectra of the compound 5 in chloroform solution (solid line) and evaporated thin film on the quartz substrate (dotted line) at room temperature.
6. Device characterization

Tetradecylphosphonic acid (TPA) and 12,12,13,13,14,14,15,15,16,16,17,17,18,18,18-pentadecylfluoro-octadecylphosphonic acid (FOPA) modified substrates

Si/SiO₂/AlOₓ substrates were prepared from such Si/SiO₂ wafers by atomic layer deposition of an 8 nm thick layer of AlOₓ. The Si/SiO₂/AlOₓ substrates were coated by isopropanol solutions of TPA and FOPA to obtain densely packed monolayers with a thickness of 1.7 nm and 2.1 nm, respectively. A capacitance per unit area of \( C_i = 32.4 \ \text{nF cm}^{-2} \) was determined for these modified substrates.

Film and transistor fabrication: The films were fabricated by vacuum deposition on the bare and SAM-modified substrates. During deposition the pressure was under 10⁻⁶ mbar, the substrate temperature \( (T_s) \) was set as needed, and the growth rate was adjusted in the range of 0.2–0.6 nm/min by controlling the source temperature. After deposition of a 30 nm thick film, 30 nm gold was thermally evaporated on the film surface through a shadow mask (channel length and width are 100 and 200 μm, respectively) to form bottom gate top contact transistors.

Film and transistor characterization: The transistor current voltage characteristics were measured under ambient condition using Agilent 4155C semiconductor parametric analyzer (Agilent Technologies, Inc., Santa Clara, CA) keeping the devices at 298 K. The n-channel transfer curves on bare Si/SiO₂ and TPA-modified substrates were measured at \( V_{DS} = 50 \ \text{V} \) and \( V_{GS} = -10 \ \text{V} \) to 50 V. On FOPA-modified substrate, the p-channel transfer curves characterization were measured at \( V_{DS} = -50 \ \text{V} \) and \( V_{GS} = 10 \ \text{V} \) to –50 V and the n-channel transfer curves were measured at \( V_{DS} = 50 \ \text{V} \) and \( V_{GS} = -10 \ \text{V} \) to 50 V, unless otherwise noted.
Figure S4: The transfer curve of 5 ($T_s = 80 \, ^\circ\text{C}$) on ($V_{DS} = -40 \, \text{V}$) FOPA-modified substrate.

Table S2. Mobility ($\mu$), threshold voltage ($V_T$) and current on/off ratio ($I_{on}/I_{off}$) of transistors of 5 were prepared at different substrate temperatures ($T_s$) on TPA-modified substrate.

<table>
<thead>
<tr>
<th>$T_s$ / °C</th>
<th>$\mu$ / cm$^2$ V$^{-1}$ s$^{-1}$</th>
<th>$I_{on/off}$</th>
<th>$V_T$ / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.002(e)</td>
<td>$10^4$</td>
<td>37</td>
</tr>
<tr>
<td>60</td>
<td>0.02(e)</td>
<td>$10^5$</td>
<td>16</td>
</tr>
<tr>
<td>80</td>
<td>0.044(e)</td>
<td>$10^6$</td>
<td>8</td>
</tr>
<tr>
<td>95</td>
<td>0.047(e)</td>
<td>$10^6$</td>
<td>7</td>
</tr>
</tbody>
</table>

Table S3. Mobility ($\mu$), threshold voltage ($V_T$) and current on/off ratio ($I_{on}/I_{off}$) of transistors of 5 were prepared at different substrate temperatures ($T_s$) on FOPA-modified substrate.

<table>
<thead>
<tr>
<th>$T_s$ / °C</th>
<th>$\mu$ / cm$^2$ V$^{-1}$ s$^{-1}$</th>
<th>$I_{on/off}$</th>
<th>$V_T$ / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.03(e)</td>
<td>$10^5$</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>0.005 (h)</td>
<td>$10^5$</td>
<td>-20</td>
</tr>
<tr>
<td>50</td>
<td>0.018 (e)</td>
<td>$10^5$</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>0.01 (h)</td>
<td>$10^5$</td>
<td>-18</td>
</tr>
<tr>
<td>65</td>
<td>0.044 (e)</td>
<td>$10^6$</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>0.02 (h)</td>
<td>$10^6$</td>
<td>-16</td>
</tr>
<tr>
<td>80</td>
<td>0.11 (e)</td>
<td>$10^5$</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>0.045 (h)</td>
<td>$10^6$</td>
<td>-20</td>
</tr>
<tr>
<td>95</td>
<td>0.035 (e)</td>
<td>$10^6$</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>0.0047(h)</td>
<td>$10^6$</td>
<td>4</td>
</tr>
</tbody>
</table>
7. $^1$H NMR and $^{13}$C NMR of spectra of cyanated isoindigos

**Figure S5:** $^1$H NMR spectrum of mono cyanated isoindigo 2 (CDCl₃, 400 MHz, 300 K)

**Figure S6:** $^{13}$C NMR spectrum of mono cyanated isoindigo 2 (CDCl₃, 100 MHz, 300 K)
**Figure S7:** $^1$H NMR spectrum of mono bromo mono cyanated isoindigo 4 (CDCl$_3$, 400 MHz, 300 K)

**Figure S8:** $^{13}$C NMR spectrum of mono bromo mono cyanated isoindigo 4 (CDCl$_3$, 100 MHz, 300 K)
**Figure S9:** $^1$H NMR spectrum of dicyanated 5 (CDCl$_3$, 400 MHz, 300 K)

**Figure S10:** $^{13}$C NMR spectrum of dicyanated isoindigo 5 (CDCl$_3$, 100 MHz, 300 K)
8. References

