Electronic Supplementary Information

Polycyclic aromatic hydrocarbon with tetraimides as n-type semiconductor

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1. Synthesis and Characterization of the compounds

General: $^1$H NMR and $^{13}$C NMR spectra were recorded in deuterated solvent on a Bruker ADVANCE NMR. $^1$H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard. MALDI-TOF-MS were determined on a Bruker BIFLEXIII Mass spectrometer with trithiophenes as matrix. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified.

Synthesis of compound 3a, and 3b
A mixture of $^1$[1] (0.18mmol), compound 2(0.48mmol), Pd(PPh$_3$)$_4$(0.04mmol), and CuI (0.08mmol) reflux in dry toluene(15ml) under argon for 12h, after cooling to room temperature, the solvent was concentrated in vacuo and purified by silica gel chromatraphy(DCM).

3a: Yield: 73%. $^1$HNMR (400 MHz, CDCl$_3$): 8.75(d, J = 7.6Hz, 2H), 8.66(s, 2H), 8.48(d, J = 7.6 Hz, 2H), 8.01(d, J = 8.0, 2H), 7.64(d, J = 7.6, 2H), 4.21-4.0(m, 4H), 4.04-3.92(m, 4H), 1.99-1.96(m, 2H), 1.58-1.55(m, 4H), 1.44-1.34(m, 15H), 1.25-1.18(m, 21H), 0.99-0.95(t, 6H), 0.93-0.90(t, 6H), 0.84-0.80(t, 6H); $^{13}$CNMR(CDCl$_3$, 100MHz) : 163.92, 163.79, 162.17, 146.69, 145.10, 134.79, 134.29, 131.52, 131.28, 130.42, 129.01, 127.65, 127.07, 126.89, 125.29, 124.63, 123.73, 123.48; MALDI-TOF(m/z): calcd. for C$_{70}$H$_{78}$Br$_2$N$_4$O$_8$: 1263.2, found 1263.3.

3b: Yield: 64%. $^1$HNMR (400 MHz, CDCl$_3$): 8.75 (d, J = 8 Hz, 2H), 8.66(s, 2H), 8.49 (d, J = 8 Hz, 2H), 8.01(d, J = 8 Hz, 2H), 7.63(d, J = 8 Hz, 2H), 4.21(t, 4H), 4.01-3.91(m, 4H), 1.81-1.73(m, 4H), 1.57-1.30(m, 44H), 1.23-0.91(m, 12H); $^{13}$CNMR(100MHz, CDCl$_3$): 163.53, 163.40, 162.18, 162.13, 146.65, 145.12, 134.75, 134.27, 131.43, 131.22, 130.34, 128.97, 127.69, 127.07, 126.89, 125.31, 124.66, 123.73, 123.48. MALDI-TOF (m/z): calcd. for C$_{70}$H$_{78}$Br$_2$N$_4$O$_8$: 1263.2, found 1263.3.
Synthesis of 4a
Bis-(triphenylphosphine)palladium(II)dichloride(11mg, 0.0158mmol) was added to a solution of 3a (100mg, 0.079mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (48mg, 0.316mmol) in dry dimethylacetamide (3mL) under argon. The mixture was heated to 160°C with stirring for 24h, cooled to room temperature, and diluted with methylene chloride. The mixture was washed twice with water, dried over magnesium sulfate and the solvent removed in vacuo. The crude product was purified by column chromatography (silica gel, DCM: hexane=1:2). Yield: 43%. ¹H NMR (400 MHz, CDCl₃): 8.67 (d, J = 7.2Hz, 4H), 7.85 (d, J = 7.2Hz, 4H), 4.15 (s, 4H), 2.97 (s, 4H), 1.97(s, 4H), 1.64-1.47(m, 31H), 1.11-0.67(m, 25H) ; ¹³C NMR (100MHz, CDCl₃): 161.90, 161.56, 141.94, 134.98, 133.67, 130.99, 130.24, 125.15, 123.43, 121.29, 43.04, 42.35, 37.78, 32.00, 30.35, 29.63, 28.29, 28.26, 28.21, 27.72, 23.57, 22.93, 22.81, 14.18, 13.95, 10.10, 10.06; HR-MALDI-TOF(m/z): calcd. for C₇₀H₇₆N₄O₈: 1100.5668; Anal.Calcd for C₇₀H₇₆N₄O₈: C: 76.34%, H: 6.96%, N: 5.09%; Found: C: 75.63%, H: 6.87%, N: 5.26%..

Synthesis of 4b
Bis-(triphenylphosphine)palladium(II)dichloride(11mg, 0.0158mmol) was added to a solution of 3b (100mg, 0.079mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene(48mg, 0.316mmol) in dry dimethylacetamide (3mL) under argon. The mixture was heated to 160°C with stirring for 24h, cooled to room temperature, and diluted with methylene chloride and evaporated. The crude 4a was crystallized in toluene three times. Yield: 35%. ¹H NMR (600 MHz, CD₂Cl₂CD₂Cl₂, 80 °C): 9.05(d, J = 9Hz, 4H), 8.21 (d, J = 9 Hz, 4H), 4.34 (t, 4H), 3.70-3.66(m, 4H), 2.02-1.96(m, 4H), 1.67-1.57(m, 24H), 1.56-1.54(m, 20H), 1.52-1.41(m, 12H); ¹³C NMR (150 MHz, CD₂Cl₂CD₂Cl₂, 80°C) : 162.13, 162.11, 142.86, 135.86, 134.41, 130.54, 126.21, 124.04, 123.91, 122.07, 42.29, 40.28, 31.88, 31.77, 29.45, 29.34, 29.24, 29.17, 28.29, 28.26, 27.52, 27.17, 22.67, 22.56, 14.06, 13.99; HR-MALDI-TOF (m/z): calcd. for C₇₀H₇₆N₄O₈: 1100.5663, found 1100.5641; Anal.Calcd for C₇₀H₇₆N₄O₈: C: 76.34%, H: 6.96%, N: 5.09%; Found: C: 75.86%, H: 6.89%, N: 5.04%.
2. UV and CV spectra of the compounds

Cyclic voltammograms (CVs) were recorded on a 1000B model electrochemical workstation using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/Ag+ electrode as the reference electrode, and ferrocene/ferrocenium as an internal potential marker. 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in dichloromethane was employed as the supporting electrolyte.

![Figure S1. A) UV-vis spectra of 4b in dichloromethane, and B) CV spectra of C₈-NDI and ferrocene in dichloromethane.](image-url)
3. Computational Methodology

MO calculations were carried out with the DFT method at the B3LYP/6-31g(d) level using Gaussian 03 program package. [2]

Figure S2. Calculated HOMO and LUMO of C₈-NDI, and 4a with methyl groups instead of octyl or ethylhexyl (B3LYP/6-31g(d) level).

Figure S3. Optimized structure of 4a with methyl groups instead of ethylhexyl by DFT.
4. OFET Fabrication and Characterization

The micro-/nanocrystals of 4a and 4b were prepared by a facile in-situ drop-coating method, where the compounds were dissolved in the dilute chloroform solution (0.5 mg/ml). The solutions were dropped onto OTS-treated (octadecyltrichlorosilane) SiO₂/Si substrates and the micro-/nanocrystals can be easily obtained with the solutions evaporated. The electrodes were made by an “gold strips” technique according to the literature.[3]

The thin-film FET devices were fabricated in the bottom-gate, top-contact (BGTC) geometry configuration. Thin films were made by spin-coating 10 mg/ml solution of 4a, and 4b in chloroform on OTS-SiO₂/Si and then annealed at 150 or 200 °C for 30 mins in vacuum drying oven. Gold was deposited as source/drain electrodes using the shadow mask.

FET characteristics were obtained at room temperature in air on a Keithley 4200 SCS and Micromanipulator 6150 probe station. The mobility of the devices were calculated in the saturation regime. The equation is listed as follows:

\[ I_{DS} = \frac{W}{2L}C_i\mu(V_{GS} - V_T)^2 \]

where \( W/L \) (~200μm/25μm for thin film FETs) is the channel width/length , \( C_i \) is the insulator capacitance per unit area, and \( V_{GS} \) and \( V_T \) are the gate voltage and threshold voltage, respectively.

The microscope images of all the aligned microcrystal arrays were acquired by an optical microscope (Vision Engineering Co., UK), which was coupled to a CCD camera. Atomic force microscopy (AFM) measurements were carried out with a Nanoscope IIIa instrument (Digital Instruments). X-ray diffraction (XRD) was measured on a D/max2500 with a CuKα source (\( \kappa = 1.541 \) Å). SEM images were obtained with a Hitachi S-4300 microscope (Japan).
**Figure S4.** A) OM image of the thin-film of 4b, B) The transfer and C) Output characteristics of OFET devices based on thin-film of 4b.

**Figure S5.** A) OM image of the thin-film of 4a, B) The transfer and C) Output characteristics of OFET devices based on thin-film of 4a.
Figure S6. A) SEM image of the single-crystalline fiber of 4b with electrodes, B) The transfer and C) Output characteristics of OFET devices based on single-crystalline fibers of 4b (measured under ambient conditions).

Figure S7. A) SEM image of the single-crystalline fiber of 4a with electrodes, B) The transfer and C) Output characteristics of OFET devices based on single-crystalline fibers of 4a (measured under ambient conditions).
Figure S8. A) SEM image and B) AFM of the single-crystalline fiber of 4b, C) XRD of single-crystalline fibers of 4b, D) XRD of single-crystalline fibers of 4a.

Table 1. The carrier mobilities of 4a and 4b fibers.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Atmosphere</th>
<th>Mobility$^{\text{max}}$ /cm$^2$ V$^{-1}$ s$^{-1}$</th>
<th>On/off Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>4b</td>
<td>Air</td>
<td>1.55 (1.28±0.14) $^a$</td>
<td>$10^5$-$10^6$</td>
</tr>
<tr>
<td></td>
<td>Nitrogen</td>
<td>1.75 (1.50±0.15) $^a$</td>
<td>$10^5$-$10^6$</td>
</tr>
<tr>
<td>4a</td>
<td>Air</td>
<td>0.61 (0.46±0.09) $^a$</td>
<td>$10^5$-$10^6$</td>
</tr>
</tbody>
</table>

$^a$Averaged values from 10 FET devices
5. NMR Spectra of the compounds
Figure S9. $^1$H NMR and $^{13}$C NMR of 3b.

Figure S10. $^1$H NMR and $^{13}$C NMR of 3a.
Figure S11. $^1$HNMR and $^{13}$CNMR of 4b.
Figure S12. $^1$HNMR and $^{13}$CNMR of 4a.
6. HR-MALDI-TOF spectra of the compounds

Figure S13. HR-MALDI-TOF spectra of 4b.
Figure S14. HR-MALDI-TOF spectra of 4a.
7. References

