Supporting Information for

Perylenothiophene Diimides: Physicochemical Properties and Applications in Organic Semiconducting Devices

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1. Synthesis of mono-halogenated PDIs

\(N,N'-\text{Bis(1-pentylhexyl)-1-bromoperylene-3,4,9,10-tetracarboxydiimide (1a)}\)\(^1\) and \(N,N'-\text{bis(1-pentylhexyl)-2-iodoperylene-3,4,9,10-tetracarboxydiimide (1b)}\)\(^2\) were synthesized from \(N,N'-\text{bis(1-pentylhexyl)-perylene-3,4,9,10-tetracarboxydiimide}\)\(^3\) according to the reported procedures.

![Scheme S1. Synthesis of 1a and 1b.](image)

\(N,N'-\text{Bis(1-pentylhexyl)-1-bromoperylene-3,4,9,10-tetracarboxydiimide (1a)}\)

A mixture of \(N,N'-\text{bis(1-pentylhexyl)-perylene-3,4,9,10-tetracarboxydiimide (3.86 g, 5.52 mmol)}\) and bromine (33.7 g, 212 mmol) in 108 mL of dichloromethane was stirred at rt for 2 days. The mixture was quenched with diluted NaHSO\(_3\) aqueous solution (30 mL) and extracted with dichloromethane (100 mL). Then, the solvent was evaporated and the residue was purified by column chromatography on silica gel eluted with dichloromethane/hexane (1:1, v/v) to give 1a as an orange

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\(\text{1PH} = C_5H_{11}\)
solid (4.60 g, 52%): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.79 (d, $J = 8.0$ Hz, 1H), 8.91 (s, 1H), 8.69–8.67 (m, 3H), 8.59–8.57 (m, 2H), 5.22–5.12 (m, 2H), 2.31–2.21 (m, 4H), 1.94–1.85 (m, 4H), 1.43–1.21 (m, 24H), 0.84 (t, $J = 6.8$ Hz, 6H), 0.83 (t, $J = 6.8$ Hz, 12H); $^{13}$C NMR (100 MHz, CDCl$_3$): 163.9, 163.8, 163.1, 162.8, 139.2, 134.0, 133.7, 133.6, 131.1, 130.61, 130.55, 129.1, 128.9, 128.3, 128.2, 128.1, 127.2, 124.1, 124.0, 123.7, 123.3, 122.9, 122.6, 121.0, 55.1, 54.9, 32.5, 32.4, 31.74, 31.72, 26.63, 26.61, 22.5, 13.9; IR (KBr) $\nu = 1701$, 1661 cm$^{-1}$ (C=O); MP: 198.2–198.7 °C; HRMS (APCI) m/z calcd for C$_{46}$H$_{53}$BrN$_2$O$_4$: [M]$^+$ 777.3267. Found: 777.3263.

$N,N´$-Bis(1-pentylhexyl)-2-iodoperylene-3,4,9,10-tetracarboxydiimide (1b)

A mixture of [Cp*RhCl$_2$]$_2$ (152 mg, 0.248 mmol) and AgSbF$_6$ (564 mg, 1.63 mmol) in dichloroethane (19 mL) was stirred at room temperature for 20 minutes. Then, $N,N´$-bis(1-pentylhexyl)-perylene-3,4,9,10-tetracarboxydiimide (3.30 g, 4.72 mmol), N-iodosuccinimide (1.385, 5.65 mmol), Cu(OAc)$_2$ (426 mg, 2.34 mmol), and dichloroethane (122 mL) was added and the mixture was stirred at 80 °C for 1 day. After cooling, the solvent was evaporated and the residue was purified by column chromatography on silica gel eluted with dichloromethane/hexane (1:3, v/v) to give 1b as a red solid (1.75 g, 45%): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.12 (s, 1H), 8.69–8.64 (m, 3H), 8.57 (d, $J = 8.0$ Hz, 1H), 8.56 (d, $J = 8.0$ Hz, 1H), 8.52 (d, $J = 8.0$ Hz, 1H), 5.23–5.15 (m, 2H), 2.34–2.19 (m, 4H), 1.69–
1.83 (m, 4H), 1.44–1.23 (m, 24H), 0.86 (t, \(J = 6.8 \text{ Hz}, 6\text{H}\)), 0.85 (t, \(J = 6.8 \text{ Hz}, 6\text{H}\)); \(^{13}\text{C}\) NMR (100 MHz, CDCl\(_3\)): 163.94, 163.86, 162.9, 162.1, 138.2, 137.9, 134.8, 134.2, 133.8, 133.0, 131.8, 131.6, 131.4, 130.9, 129.5, 126.42, 126.35, 124.3, 124.1, 124.0, 123.8, 123.4, 123.2, 123.0, 101.2, 55.6, 55.0, 32.5, 32.4, 31.8, 26.7, 22.5, 13.9; IR (KBr) \(\nu = 1699, 1659 \text{ cm}^{-1} \text{ (C=O)}\); MP: 207.2–208.2 °C; HRMS (APCI) \(m/z\) calcd for C\(_{46}\)H\(_{53}\)IN\(_2\)O\(_4\): [M]+ 825.3128 Found: 825.3130.
2. Fabrication methods of organic devices

Fabrication and characteristics of OFET devices

dPTIa-, dPTIb-, IDT-PTIa–, and IDT-PTIb–based OFET devices were fabricated in a top-contact/bottom-gate (TCBG) configuration on a heavily doped $n^+$-Si (100) wafer with a 200 nm thermally grown SiO$_2$ (capacitance: $C_i = 17.3$ nF cm$^{-2}$). The substrate was treated with octadecyltrichlorosilane (ODTS) as reported previously. The dPTIa- and dPTIb- thin films were fabricated by the spin-coating method (6000 rpm, 30 sec) using chloroform solution (4 g/L) and following thermal annealing (100 °C or 200 °C, 30 min). On the top of the organic thin film, gold films (80 nm) as drain and source electrodes were deposited through a shadow mask. For a typical device, the drain-source channel length ($L$) and width ($W$) are 40 μm and 1.5 mm, respectively. The device characteristics were measured at room temperature under ambient conditions with a Keithley 4200 semiconducting parameter analyzer. Field-effect mobility ($\mu$) was calculated in the saturation regime using the following equation,

$$I_d = C_i \mu (W/2L) (V_g - V_{th})^2$$

where $C_i$ is the capacitance of the SiO$_2$ insulator, and $V_g$ and $V_{th}$ are the gate and threshold voltages, respectively.

Fabrication and characterization of OPV devices

Patterned ITO substrates (purchased from Atsugi Micro) were first pre-cleaned sequentially by
sonicating in a detergent bath, de-ionized water, acetone, and isopropanol at room temperature, and in boiled isopropanol each for 10 min, and then baked at 120 °C for 10 minutes in air. The substrates were then subjected to a UV/ozone treatment at rt for 20 min. ZnO layer was prepared by spin-coating (at 5000 rpm, 30 sec.) a precursor solution prepared from zinc acetate dehydrate (0.27 g) and ethanolamine (0.07 mL) in 2-methoxyethanol (2.5 mL). Then, the substrates were annealed at 170 °C on a hot plate in air. The glass/ITO/ZnO substrate was transferred into a nitrogen-filled glove box (KOREA KIYON, KK-011AS-EXTRA). Active layer (IDT-PTI and PBDB-T) solution (chlorobenzene, 16 mg/ml, donor/acceptor weight ratio is 1:1) was spin-coated at 1200 rpm for 40 s on the substrate. Then, MoO$_x$ (7.5 nm) and Ag anode (100 nm) were deposited in vacuum to complete the solar cell devices. The active area of the cells was 0.16 cm$^2$. $J$-$V$ characteristics of the cells were measured using a Keithley 2400 source-measure unit in nitrogen atmosphere under the 1 sun (AM1.5G) condition using a solar simulator (SAN-EI Electric, XES-40S1). The light intensity was calibrated with a reference PV cell (KONICA MINOLTA AK-100 certified at National Institute of Advanced Industrial Science and Technology, Japan). The EQE of each device was measured with monochromatic light (SM-250F, Bunkoh-Keiki). More than 8 different devices were fabricated to collect the photovoltaic properties. AFM images were obtained on a Nanotechnology, Inc. scanning probe microscope Nanocute system. X-ray studies were carried out using a Rigaku Ultima IV diffractometer with a CuK$\alpha$ source ($\lambda = 1.541$ Å).
3. Absorption and fluorescence spectra of NDI and PDI

Figure S1. Absorption and fluorescence spectra of N,N′-dioctyl-NDI and N,N′-dioctyl-PDI in chloroform solution. N,N′-dioctyl-NDI did not show clear fluorescence.
4. Plausible mechanism of Na$_2$S-promoted thiophene annulation

Figure S2. Plausible mechanism of Na$_2$S-promoted thiophene annulation on PDI-core from 2a and 2b.
5. Cyclic voltammograms

Figure S3. Cyclic voltammograms of PDI and PTIs (a) and dPTIs and IDT-PTIs(b)

6. Absorption spectra of dPTIs and IDT-PTIs in thin film

Figure S4. Absorption spectra of dPTIs (a) and IDT-PTIs (b) in thin film.
7. Logarithmic absorption spectra of dPTIs and IDT-PTIs

![Absorption Spectra](image)

Figure S5. Logarithmic absorption spectra of dPTIs (a) and IDT-PTIs (b) in chloroform solution.

8. Dihedral angles of $\alpha,\alpha'$-linked thiophenes in the DFT-optimized molecular structures of dPTIs and IDT-PTIs

![Dihedral Angles](image)

Figure S6. Dihedral angles of $\alpha,\alpha'$-linked thiophenes in the DFT-optimized molecular structures of dPTIs (a) and IDT-PTIs (b).
9. DFT-calculated HOMO and LUMO of PTIs

Figure S7. DFT-calculated HOMO and LUMO of PTIs and HOMO/LUMO coefficients at the α-carbon atoms of the fused thiophenes (B3LYP/6-31G*). The coefficients are given as absolute values.
10. AFM images

Figure S8. AFM images (5 μm × 5 μm) of dPTIa- and dPTIb-based OFETs with and without annealing (200 °C).

Figure S9. AFM images (5 μm × 5 μm) of IDT-PTIa:PBDB-T- and IDT-PTIb:PBDB-T-based OFETs with and without annealing (200 °C).
11. Out-of-plane and in-plane XRD patterns of thin-film of π-extended PTIs

Figure S10. Out-of-plane XRD patterns of thin-film of dPTIa and dPTIb (a,b) and in-plane patterns of thin-film of dPTIa and dPTIb (c,d).
Figure S11. Out-of-plane XRD patterns of thin-film of IDT-PTIa and IDT-PTIb (a,b) and in-plane patterns of thin-film of IDT-PTIa and IDT-PTIb (c,d).

Figure S12. Molecular structures of dPTIs (a) and IDT-PTIs (b), and the distances between the edge of alkyl groups.
12. Evaluation of carrier mobilities of IDT-PTIs in the thin films by space-charge-limited current (SCLC) technique

Figure S13. Current density normalized by the cube of the film thickness \( d \) plotted against voltage for the electron-only devices with the thin films of (a) IDT-PTIa and (b) IDT-PTIb (annealed at 200 °C). The device structures of electron-only devices are ITO/ZnO/Active layer/Ca/Ag.

Table S1. Summary of the average slope of \( J-V \) curves for analyzing the Mott-Gurney law, and the averaged electron mobility in SCLC region.

<table>
<thead>
<tr>
<th></th>
<th>IDT-PTIa</th>
<th>IDT-PTIb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>2.29</td>
<td>2.57</td>
</tr>
<tr>
<td>( \mu_e ) / cm² V⁻¹ s⁻¹</td>
<td>( 4.8 \times 10^4 )</td>
<td>( 4.2 \times 10^4 )</td>
</tr>
</tbody>
</table>
13. Out-of-plane and in-plane XRD patterns of thin-film of IDT-PTI:PBDB-T

14. Evaluation of carrier mobilities of blend films with IDT-PTIa:PBDB-T by SCLC technique

Figure S15. Current density normalized by the cube of the film thickness \(d\) plotted against voltage for the electron-only devices with the blend films of (a) IDT-PTIa:PBDB-T and (b) IDT-PTIb:PBDB-T. The device structures of electron-only devices are ITO/ZnO/Active layer/Ca/Ag.

Table S2. Summary of the average slope of \(J-V\) curves for analyzing the Mott-Gurney law, and the averaged electron mobility in SCLC region.

<table>
<thead>
<tr>
<th></th>
<th>IDT-PTIa:PBDB-T</th>
<th>IDT-PTIb:PBDB-T</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slope</td>
<td>2.28</td>
<td>2.62</td>
</tr>
<tr>
<td>(\mu_e) / cm² V⁻¹ s⁻¹</td>
<td>(6.3 \times 10^{-4})</td>
<td>(5.3 \times 10^{-4})</td>
</tr>
</tbody>
</table>
15. Summarized device characteristics

Table S3. Summarized transistor characteristics of dPTI-based OFETs

<table>
<thead>
<tr>
<th>Compound</th>
<th>Anneal / °C</th>
<th>operation</th>
<th>$\mu_{FEt}$ / cm²V⁻¹s⁻¹</th>
<th>$\mu_{FEt}^{max}$ / cm²V⁻¹s⁻¹</th>
<th>$I_{on}/I_{off}$</th>
<th>$V_{th}$ / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>dPTIa</td>
<td></td>
<td>n-channel</td>
<td>0.0092±0.0012</td>
<td>0.0104</td>
<td>-1.9×10⁴</td>
<td>12.3±2.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>p-channel</td>
<td>0.0004±0.0001</td>
<td>0.0005</td>
<td>-44.2±12.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>n-channel</td>
<td>0.0127±0.0041</td>
<td>0.0168</td>
<td>-1.5×10³</td>
<td>10.1±5.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>p-channel</td>
<td>0.0031±0.0009</td>
<td>0.0040</td>
<td>-34.2±12.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>n-channel</td>
<td>0.0892±0.0040</td>
<td>0.0922</td>
<td>-5.0×10²</td>
<td>13.3±3.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>p-channel</td>
<td>0.0198±0.0034</td>
<td>0.0232</td>
<td>-22.5±5.4</td>
<td></td>
</tr>
</tbody>
</table>

| dPTIb     |             | n-channel | 0.0070±0.0014            | 0.0084                      | -1.8×10⁵         | 1.6±2.3       |
|           |             | p-channel | -                        | -                           | -                |               |
|           | 100         | n-channel | 0.0167±0.0023            | 0.0190                      | -9.2×10⁵         | 9.1±4.3       |
|           |             | p-channel | -                        | -                           | -                |               |
|           | 200         | n-channel | 0.0378±0.0053            | 0.0431                      | -7.8×10⁵         | 11.8±6.3      |
|           |             | p-channel | -                        | -                           | -                |               |

Table S4. Summarized properties of IDT-PTIa:PBDB-T– and IDT-PTIb:PBDB-T–based OPVs

<table>
<thead>
<tr>
<th>Active Materials</th>
<th>Anneal</th>
<th>$J_{SC}$ / mAcm⁻²</th>
<th>$V_{OC}$ / V</th>
<th>FF</th>
<th>PCE / %</th>
<th>PCE$^{max}$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>IDT-PTIa:PBDB-T</td>
<td>-</td>
<td>8.60±0.42</td>
<td>0.83±0.01</td>
<td>0.49±0.02</td>
<td>3.2±0.6</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>12.32±0.46</td>
<td>0.78±0.01</td>
<td>0.48±0.03</td>
<td>4.7±0.4</td>
<td>5.1</td>
</tr>
<tr>
<td>IDT-PTIb:PBDB-T</td>
<td>-</td>
<td>7.57±0.33</td>
<td>0.86±0.01</td>
<td>0.50±0.01</td>
<td>3.3±0.2</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>10.06±0.45</td>
<td>0.82±0.00</td>
<td>0.56±0.02</td>
<td>4.7±0.2</td>
<td>4.9</td>
</tr>
</tbody>
</table>
16. NMR charts

\( N,N'\text{-bis(1-pentylhexyl)-1-bromoperylene-3,4,9,10-tetracarboxydiimide (1a)} \)
$N,N^\prime$-Bis(1-pentylhexyl)-2-iodoperylene-3,4,9,10-tetracarboxydiimide (1b)

\[\text{Chemical Structure Image}\]
$N,N'$-Bis(1-pentylhexyl)-1-(triethylsilyl)ethyl)-perylene-3,4,9,10-tetracarboxydiimide (2a)
$N,N^\prime$-Bis(1-pentylhexyl)-2-(triethysilylethynyl)-perylene-3,4,9,10-tetracarboxydiimide (2b)
$N,N'$-Bis(1-pentylhexyl)-2-(triethylsilyl)-peryleno[2,1-b]thiophene-6,7,12,13-tetracarboxydiimide (TES-PTIa)
$N,N'$-Bis(1-pentylhexyl)-2-(triethylsilyl)-peryleno[1,2-b]thiophene-4,5,10,11-tetracarboxydiimide (TES-PTb)
$N,N^\prime$-Bis(1-pentylhexyl)-peryleno[2,1-$b$]thiophene-6,7,12,13-tetracarboxydiimide (PTIa)
$N,N'$-Bis(1-pentylhexyl)-peryleno[1,2-b]thiophene-4,5,10,11-tetracarboxydiimide (PTIb)
$N,N'$-Bis(1-pentylhexyl)-2-bromoperylene[2,1-b]thiophene-6,7,12,13-tetracarboxydiimide (Br-PTIa)
$N,N'$-Bis(1-pentylhexyl)-2-bromoperyleno[1,2-$b$]thiophene-4,5,10,11-tetracarboxydiimide (Br-PTIb)
[2,2’]Bi[peryleno[2,1-b]thienyl]-N,N’,N’’,N’’’-tetrakis(1-pentylhexyl)-6,6’,7,7’,12,12’,13,13’-tetraimide (dPTIa)
[2,2′]Bi[peryleno[1,2-b]thienyl]-N,N′,N″,N″′-tetrakis(1-pentylhexyl)-4,4′,5,5′,10,10′,11,11′-tetraimide (dPTIb)
$N,N^\prime,N^\prime\prime,N^\prime\prime\prime$-Tetrakis(1-pentylhexyl)-2,7-bis(peryleno[2,1-b]thiophen-2-yl)-4,4,9,9-tetrakis(4-hexylphenyl)-s-indaceno[1,2-b:5,6-b']dithiophene-$6^\prime,6^\prime\prime,7^\prime,7^\prime\prime,12^\prime,12^\prime\prime,13^\prime,13^\prime\prime$-octacarboxytetraimide (IDT-PTIa)
$N,N^\prime,N^\prime\prime,N^\prime\prime\prime$-Tetrakis(1-pentylhexyl)-2,7-bis(peryleno[1,2-$b$]thiophen-2-yl)-4,4,9,9-tetrakis(4-hexylphenyl)-s-indaceno[1,2-$b$:5,6-$b'$]dithiophene-4'-,4''-,5',5'',10',10'',11',11''-

octacarboxytetraimide (IDT-PTIb)
17. References


