Supporting Information

For

_N-alkylation vs. O-alkylation: Influence on the Performance of the Photovoltaic Cells based on a Tetracyclic Lactam Polymer Donor_

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Synthetic procedures

Scheme S1. Synthesis of alkylated DBND.

The synthesis of DBND is followed by our previous work: a) Zn, CF₃COOH, THF, r.t. 1 h, quantitative; b) HCl (conc.), THF, 100 °C, 8 h, 61%; c) K₂CO₃, DMF, bubbling air, r.t., 48 h, quantitative; d) K₂CO₃, DMF, 15-(2-iodoethyl)nonacosane, 110 °C, 36 h, 50% of O-DBND, 33% of H-DBND and 10% of N-DBND.

6,6'-Dibromo-[3, 3'-biindoline]-2, 2'-dione

TFA (4.7 ml, 60 mmol) was added dropwise to a cooled (0 °C) suspension of IID (1 g, 2.39 mmol) and activated Zn dust (940 mg, 14.5 mmol) in THF (125 ml) solution. The mixture was stirred at r.t. for 1 h. Then the mixture was precipitated into a stirring H₂O (500 ml). The white solid obtained were collected on a filter and washed with H₂O and dried under reduced pressure. ¹H-NMR (DMSO-d₆, 600 MHz) δ: 10.51 (s, 2H), 7.09 (d, J = 8.02 Hz, 2H), 6.95 (s, 2H), 6.75 (d, J = 8.02 Hz, 2H), 4.19 (s, 2H).

¹³C-NMR (DMSO-d₆, 150 MHz) δ: 176.33, 145.45, 126.83, 125.72, 124.47, 121.46, 112.71, 45.70.

2, 8-Dibromo-10b, 12-dihydrodibenzo[c, h][2, 6]naphthyridine-5, 11(4bH, 6H)-dione
A suspension of 6,6'-dibromo-[3, 3'-biindoline]-2, 2'-dione (1 g, 2.38 mmol) in conc. HCl (10 ml) and THF (20 ml) was added to a Schlenk tube. The mixture was stirred for 10 h at 100 °C. The mixture was then cooled down to r.t. and the precipitate was collected on a filter and washed with water, ethanol and ethyl acetate to give a white solid which was pure enough to carry out on next step (609 mg, 61%).

\[ \text{1H-NMR (DMSO-d}_6, 600 MHz) \delta: 10.58 \text{ (s, 2H), 7.20-7.16 (m, 4H), 7.06 (s, 2H), 4.23 (s, 2H).} \]

\[ \text{13C-NMR (DMSO-d}_6, 150 MHz) \delta: 168.29, 139.53, 132.29, 125.12, 121.28, 120.13, 118.01. \]

2, 8-Dibromodibenzo[c, h][2, 6]naphthyridine-5, 11(6H, 12H)-dione

To a solution of 2, 8-dibromo-10b, 12-dihydrodibenzo[c, h][2, 6]naphthyridine-5, 11(4bH, 6H)-dione in DMF (0.01 M) was added K$_2$CO$_3$ (4 Eq.). The suspension was stirred for 48 h with air bubbling into the system. The yellow solid (almost quantitative) obtained was filtered and washed with water then THF before drying under reduced pressure, which was to carry out on next step.

Alkylated DBND

To a suspension of K$_2$CO$_3$ (995 mg, 7.2 mmol) in DMF (60 ml) was added DBND (600 mg, 1.44 mmol) and 15-(2-iodoethyl)nonacosane (2.04 g, 3.6 mmol). The mixture was stirred at 110 °C for 36 h before filtration. The filtrate was concentrated under reduced pressure. The obtained crude product was then purified by column chromatography on silica gel eluted with petroleum ether to give a white solid compound O-alkyl-DBND (0.93 g, 50%), white solid N,O-alkyl-DBND (0.61 mg, 33%) and
yellow solid N-alkyl-DBND (0.19 g, 10%). Monomers were then further purified by recrystallization before polymerization.

**O-alkyl-DBND**: $^1$H-NMR (CDCl$_3$, 600 MHz) $\delta$: 9.28 (d, $J$=9.24 Hz, 2H), 8.10 (s, 2H), 7.58 (d, $J$=9.24 Hz, 2H), 4.74 (t, $J$=6.82 Hz, 4H), 1.96 (m, 4H), 1.67 (m, 2H), 1.44-1.18 (m, 104H), 0.87 (m, 12H). $^{13}$C-NMR (CDCl$_3$, 150 MHz) $\delta$: 159.25, 145.57, 129.66, 129.27, 128.14, 123.33, 122.47, 119.40, 66.04, 34.98, 33.86, 32.83, 31.94, 30.12, 29.77, 29.74, 29.72, 29.68, 29.39, 26.77, 22.77, 14.13.

**N,O-alkyl-DBND**: $^1$H-NMR (CDCl$_3$, 600 MHz) $\delta$: 9.81 (d, $J$=9.29 Hz, 1H), 9.25 (d, $J$=9.29 Hz, 1H), 8.05 (s, 1H), 7.61 (d, $J$=9.04 Hz, 1H), 7.58 (s, 1H), 7.42 (d, $J$=9.04 Hz, 1H), 4.71 (t, $J$=6.71 Hz, 2H), 4.37 (s, 2H), 1.93 (m, 2H), 1.76 (m, 2H), 1.61 (m, 2H), 1.50-1.10 (m, 104H), 0.87 (m, 12H). $^{13}$C-NMR (CDCl$_3$, 150 MHz) $\delta$: 160.16, 158.49, 145.67, 138.68, 130.74, 129.29, 129.26, 128.93, 128.00, 125.29, 124.50, 124.02, 121.11, 121.03, 117.11, 116.14, 66.21, 42.32, 36.32, 35.00, 33.83, 33.61, 32.78, 31.95, 30.64, 30.11, 30.10, 29.76, 29.74, 29.73, 29.69, 29.68, 29.39, 26.79, 26.77, 22.71, 14.13.

**N-alkyl-DBND**: $^1$H-NMR (CDCl$_3$, 600 MHz) $\delta$: 9.80 (d, $J$=9.14 Hz, 2H), 7.56 (s, 2H), 7.45 (d, $J$=9.14 Hz, 2H), 4.36 (s, 4H), 1.74 (m, 4H), 1.58 (m, 2H), 1.50-1.10 (m, 104H), 0.87 (m, 12H). $^{13}$C-NMR (CDCl$_3$, 150 MHz) $\delta$: 159.84, 138.62, 130.91, 126.67, 125.91, 125.19, 119.36, 116.77, 42.48, 36.30, 33.60, 31.95, 30.69, 30.10, 29.74, 29.69, 29.39, 26.78, 22.71, 22.70, 14.14.
Alkylated DBND (0.1 mmol), 5,5'-bis(trimethylstanny1)-2,2'-bithiophene (0.1 mmol), Pd$_2$(dba)$_3$ (1.2 mmol%), P(o-tol)$_3$ (9.6 mmol%) and 2.5 mL of toluene were added to a Schlenk tube. The tube was charged with argon through a freeze-pump-thaw cycle for three times. The mixture was stirred for 72 h at 110 °C. And then the mixture was precipitated into methanol (100 mL). The precipitate was filtered and purified via Soxhlet extraction for 8 hours with methanol, 12 h with hexane, (for P(N-DBND-2T) another 12 h with chloroform are needed) and finally was collected with chloroform (for P(N-DBND-2T) was collected with o-dichlorobenzene). The solution was then concentrated and precipitated into methanol (100 mL). Yield 94% for P(O-DBND-2T), yellow solid, 96% for P(N,O-DBND-2T), yellow solid and 86% for P(N-DBND-2T), red solid.
Figure S1. Gel permeation chromatography (GPC) results of polymers.

Figure S2. The electrochemical cyclic voltammetry measurement of polymer films.
Figure S3. Space-charge-limited current (SCLC) density-voltage curves of hole only devices of polymer blended films (1:2, w/w).

Figure S4. 2D-GIWAXS curves of P(N-DBNB-2T), P(N,O-DBNB-2T) and P(O-DBNB-2T).
Table S1. Optimized geometries of half, $N$ and $O$-DBND-2Ts and the corresponding calculated binding energies $E$ (Kcal/mol), as well as the distances (Å) of two DBND-2T monomer.

<table>
<thead>
<tr>
<th>Geometries</th>
<th>Dipole Moment</th>
<th>IBE (Kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N,O$-DBND-2T</td>
<td>3.05 D</td>
<td>-61.6</td>
</tr>
<tr>
<td>$N$-DBND-2T</td>
<td>1.56 D</td>
<td>-57.2</td>
</tr>
<tr>
<td>$O$-DBND-2T</td>
<td>0.49 D</td>
<td>-30.0</td>
</tr>
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$^1$H and $^{13}$C NMR spectra
IR spectrums