Supporting Information for

Selective thionation of naphtho[2,3-b]thiophene diimide: Tuning of the optoelectronic properties and packing structure

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1. Optimization of conditions in the reaction of NTI and Lawesson’s reagent

**Table S1.** Reactions of NTI with Lawesson’s reagent.

<table>
<thead>
<tr>
<th>run</th>
<th>solvent</th>
<th>temperature (°C), time (h)</th>
<th>result</th>
<th>remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>toluene</td>
<td>reflux (110 °C), 5h</td>
<td>no reaction</td>
<td>LR(^a): 4.0 eq.</td>
</tr>
<tr>
<td>2</td>
<td>xylene</td>
<td>reflux (110 °C), 5h</td>
<td>NTI-2S: trace</td>
<td>LR(^a): 4.0 eq.</td>
</tr>
<tr>
<td>3</td>
<td>xylene</td>
<td>180 °C, 5h</td>
<td>NTI-2S: 20%</td>
<td>LR(^a): 4.0 eq., Microwave irradiation in a sealed tube</td>
</tr>
<tr>
<td>4</td>
<td>xylene</td>
<td>180 °C, 2h</td>
<td>NTI-2S: 41%</td>
<td>LR(^a): 4.0 eq., Microwave irradiation in a sealed tube</td>
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<tr>
<td>5</td>
<td>o-DCB</td>
<td>180 °C, 2h</td>
<td>NTI-2S: 6%</td>
<td>LR(^a): 4.0 eq.</td>
</tr>
<tr>
<td>6</td>
<td>o-DCB</td>
<td>160 °C, 1h</td>
<td>NTI-2S: 45%</td>
<td>LR(^a): 4.0 eq.</td>
</tr>
<tr>
<td>7</td>
<td>o-DCB</td>
<td>160 °C, 1h</td>
<td>NTI-2S: 59%</td>
<td>LR(^a): 3.0 eq.</td>
</tr>
</tbody>
</table>

\(^a\) LR: Lawesson’s reagent.

2. \(^{13}\)C NMR spectrum of NTI
Figure S1. $^{13}$C NMR spectrum of NTI.

3. Calculated electron density of NDI, NTI and NDTI$^{S1}$

![Diagram showing electron density](image1)

Figure S2. Calculated electron density of NDI, NTI and NDTI (DFT B3LYP 6-31g(d)).

4. Calculated structures of plausible intermediates in the reaction of NTI and Lawesson’s reagent$^{S2}$

![Diagram showing reaction](image2)

Figure S3. Plausible reaction paths of thionation and intermediates: the intermediate A is calculated to be energetically stable compared to the intermediate B by ca. 11 kcal mol$^{-1}$ (DFT B3LYP/6-31G(d)).
5. $^1$H NMR spectra of NTI-2S under different conditions

**Figure S4.** Pristine sample of NTI-2S.

**Figure S5.** $^1$H NMR spectra of NTI-2S under fluorescent light (room light) in air (1h).

**Figure S6.** $^1$H NMR spectra of NTI-2S under fluorescent light (room light) under argon atmosphere (1 day).
6. Preliminary data obtained from solution processed field-effect transistors based on NTI-2S

OFET devices based on NTI-2S were fabricated in a top-contact-bottom-gate (TCBG) configuration on a heavily doped n+-Si (100) wafer with a 200 nm thermally grown SiO₂ ($C_i = 17.3 \text{ nF cm}^{-2}$). The substrate surfaces were treated with octadecyltrichlorosilane (ODTS) as reported previously. Thin films as the active layer were spin-coated from chloroform. On 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.

Characteristics of the OFET devices were measured at room temperature under ambient conditions with a Keithley 4200 semiconducting parameter analyzer. Field-effect mobility ($\mu_{\text{FET}}$) was calculated in the saturation ($V_d = V_g = \pm 60$) of the $I_d$ using the following equation,

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

where $C_i$ is the capacitance of the SiO₂ dielectric layer, and $V_g$ and $V_{\text{th}}$ are the gate and threshold voltages, respectively.

Figure S8. Transfer characteristics of NTI-2S-based transistor: p-channel operation (left) and n-channel operation (right).
7. References
