Supporting Information

Boosting Electron Transport in Non-Fullerene Acceptors using Non-Chlorinated Solvents
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Experimental Section

Full Name of Materials
O-IDTBR : (5Z,5'Z)-5,5'-(7,7'-(4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole 7,4diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one).

Fabrication of small-molecule non-fullerene acceptor thin-film transistors (TFTs)
The glass substrates were first cleaned by sequential ultrasonication in dilute Extran 300 detergent solution and deionized water for 30 min, respectively. The substrates were then cleaned with acetone and isopropanol using ultrasonication for 10 min each. Then, 35 nm of Au with 5 nm of Al as the sticking layer was thermally evaporated as source-drain electrodes. The substrates with evaporated Au/Al source-drain electrodes were then exposed to UV-ozone treatment for 20 min. To improve the electron injection from the Au electrodes to the organic semiconductors, the UV-treated glass substrates were treated with 0.03 wt% of polyethyleneimine (PEIE) in 2-methoxyethanol by spin-coating at 5000 rpm for 60 s. The substrates were then thermally annealed at 120 °C for 10 min.

Before deposition of the small-molecule non-fullerene acceptor films, o-IDTBR and L8-BO were dissolved in different solvents at a concentration of 10 mg/mL. The solutions were stirred on a hot plate at 80 °C overnight, except for L8-BO dissolved in chloroform, which
was stirred on a hot plate at 50 °C for 1 h. The hot organic semiconductor solutions were then spin cast onto the PEIE-treated glass substrates. For the o-IDTBR, the films were thermally annealed at 120 °C for 5 min. For the L8-BO, the films were thermally annealed at 220 °C for 5 min. After cooling, Cytop (CTL-809M) was spin-coated onto the semiconductor films at 4000 rpm for 90 s. The Cytop film was then thermally annealed at 50 °C for 2 h before the deposition of Al as a gate electrode. All the device fabrication procedures were performed in an N₂-filled glove box. All NFA films for further electrical, electronic, optical, and microstructural characteristic measurements undergo thermal annealing at 120 °C for o-IDTBR and 220 °C for L8-BO.

**Characterization**

**TFT measurements.** The electrical characteristics of the small-molecule NFA TFTs were monitored using a probe station placed in an N₂-filled glove box that was connected to an Agilent B1500A semiconductor parameter analyzer.

**Grazing incident wide angle x-ray spectroscopy (GIWAXs) measurements.** The GIWAXS patterns and in-plane and out-of-plane line-cut profiles were collected from Xenocs Xeuss 3.0 HR Beamline instrument (Xenocs Company, France) equipped with an auxiliary Cu Kα microfocus source and Eiger detector. The working distance is 120 mm, and the grazing incident angle is 0.2 degrees. The in-plan and out-of-plan data were analyzed in XSACT software.

**UV-Visible (UV-Vis) analysis.** UV-Vis analysis was conducted using a Shimadzu UV-2600i spectrophotometer (Shimadzu Corporation, Japan) in the wavelength range of 260–1400 nm.

**Photoelectron spectroscopy in air (PESA) analysis.** PESA analysis was performed using a model AC-2 spectrometer (Riken Keiki Co., Ltd., Japan) in the energy range of 4.80–6.20 eV with a UV intensity of 50 nW and a power number of 0.30.

**Atomic force microscopy (AFM) analysis.** The Bruker Dimension ICON scanning probe microscope was used for topographical information. The measurements were performed using tapping mode with RTESPA-300 probes. AFM raw images were processed using a Gwydion 2.51 software.
Fig. S1. Photograph of o-IDTBR (top) and L8-BO films (bottom) processed from different solvents.

Fig. S2. Photoelectron spectra in air (PESA) intensity of (a) o-IDTBR and (b) L8-BO films processed from different solvents.
Fig. S3. Normalized absorption profiles of (a) o-IDTBR and (b) L8-BO films processed from different solvents.

Fig. S4. Output characteristics of o-IDTBR TFTs processed from (a) chlorobenzene, (b) anisole, (c) mesitylene, (d) toluene, and (e) o-xylene.
Fig. S5. Output characteristics of L8-BO TFTs processed from (a) chloroform, (b) anisole, (c) mesitylene, (d) toluene, and (e) o-xylene.
Fig S6. GIWAXS line cuts of o-IDTBR films cast using different solvents in (a) the in-plane and (b) out-of-plane direction. GIWAXS line cuts of L8-BO films cast using different solvents in (a) the in-plane and (b) out-of-plane direction.
Fig. S7. Atomic force microscopy (AFM) height distribution of (a) o-IDTBR and (b) L8-BO films processed from different solvents with scanning area of 10 µm.

Fig. S8. AFM images of (a) o-IDTBR and (b) L8-BO films processed from different solvents with scanning area of 5 µm.
Fig. S9. Atomic force microscopy (AFM) height distribution of (a) o-IDTBR and (b) L8-BO films processed from different solvents with scanning area of 5 µm.

Fig. S10. AFM images of (a) o-IDTBR and (b) L8-BO films processed from different solvents with scanning area of 20 µm.
Fig. S11. Atomic force microscopy (AFM) height distribution of (a) o-IDTBR and (b) L8-BO films processed from different solvents with scanning area of 20 µm.

Table S1. Summary of parameters in o-IDTBR and L8-BO TFTs cast using different solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>NFA</th>
<th>$\mu_e$ (cm²V⁻¹s⁻¹)</th>
<th>On/off ratio</th>
<th>$V_{th}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anisole</td>
<td>0.35</td>
<td>3.56 x 10⁴</td>
<td>11.5</td>
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<tr>
<td>Chlorobenzene</td>
<td>0.35</td>
<td>7.50 x 10³</td>
<td>7.5</td>
<td></td>
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<tr>
<td>o-IDTBR</td>
<td>Mesitylene</td>
<td>0.32</td>
<td>4.84 x 10⁴</td>
<td>17.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.56</td>
<td>7.59 x 10⁴</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td>0.006</td>
<td>1.94 x 10⁴</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>Anisole</td>
<td>0.05</td>
<td>1.73 x 10⁴</td>
<td>22.9</td>
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<tr>
<td>Chloroform</td>
<td>0.11</td>
<td>2.02 x 10⁴</td>
<td>9.7</td>
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<tr>
<td>L8-BO</td>
<td>Mesitylene</td>
<td>0.08</td>
<td>2.22 x 10⁴</td>
<td>25.5</td>
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<tr>
<td>Toluene</td>
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<td>7.2</td>
<td></td>
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<tr>
<td>o-Xylene</td>
<td>0.10</td>
<td>2.96 x 10⁴</td>
<td>9.3</td>
<td></td>
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