Electronic supplementary information

High-performance ternary organic solar cells with photoresponses beyond 1000 nm

Peiyao Xue,a Yiqun Xiao,b Tengfei Li,a Shuixing Dai,a Boyu Jia,a Kuan Liu,a Jiayu Wang,a Xinhui Lu,b Ray P.S. Han,a,* and Xiaowei Zhan,a,*

aDepartment of Materials Science and Engineering, College of Engineering, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Peking University, Beijing, 100871, P. R. China.
bDepartment of Physics, The Chinese University of Hong Kong, New Territories 999077, Hong Kong, P. R. China
Materials

F8IC\textsuperscript{S1} and IDT-2BR\textsuperscript{S2} were synthesized according to reported procedures. PTB7-Th (\(M_w = 124\) kDa, \(M_w/M_n = 1.7\)) was purchased from 1-Materials Inc.; chloroform (99.9%), diphenyl ether (DPE) (99.5%) and 2-methoxyethanol (99.8%) were purchased from J&K Chemical Inc.; zinc acetate dihydrate (99.9%), ethanolamine (99.5%) and MoO\textsubscript{3} were purchased from Sigma-Aldrich Inc.; and all the solvents and chemicals were used without further purification.

Characterization

The ultraviolet-visible (UV-vis) absorption spectra were measured on JASCO V-570 spectrophotometer in thin film (on a quartz substrate). Emission spectra were recorded on Hitachi F-4500 spectrophotometer (for samples with emission wavelength < 900 nm) or FLS980 fluorescence spectrophotometer (Edinburgh Instrument Co., Ltd., for samples with emission wavelength > 900 nm). Electrochemical measurements were carried out under argon in a deoxygenated solution of tetra-butylammonium hexafluorophosphate (0.1 M) in acetonitrile using a potential scan rate of 100 mV s\textsuperscript{-1} with a computer-controlled CHI660C electrochemical workstation, a glassy-carbon working electrode coated with films, a platinum-wire auxiliary electrode and a Ag/AgCl electrode as a reference electrode. The potentials were referenced to a ferrocenium/ferrocene (FeCp\textsubscript{2}\textsuperscript{+/0}) couple using ferrocene as an external standard. The HOMO and LUMO energies are estimated from the onset oxidation (\(E_{ox}\)) and reduction potentials (\(E_{red}\)) versus FeCp\textsubscript{2}\textsuperscript{+/0} (0.45 V vs. Ag/AgCl), respectively, assuming the absolute energy level of FeCp\textsubscript{2}\textsuperscript{+/0} to be 4.8 eV below vacuum.

\[
\text{HOMO} = -e (E_{ox} - 0.45) - 4.8 \text{ (eV)}
\]

\[
\text{LUMO} = -e (E_{red} - 0.45) - 4.8 \text{ (eV)}
\]
The morphology was observed using a Multimode 8 scanning probe microscopy (Bruker Daltonics) in the tapping mode and a JEM-2100 transmission electron microscope (TEM) operated at 200 keV. The grazing incidence wide-angle X-ray scattering (GIWAXS) and the grazing incidence small-angle X-ray scattering (GISAXS) measurements were carried out at BL23A1 of National Synchrotron Radiation Research Center, Hsinchu. The energy of the X-ray source was set to 10 keV (wavelength of 1.24 Å) and the incident angle was 0.15°. Both GIWAXS and GISAXS samples are prepared on silicon substrate by spin coating.

**Device fabrication and characterization**

All the devices are based on inverted sandwich structure, ITO glass/ZnO/active layer/MoOx/Ag. First, the patterned indium tin oxide (ITO) glass (sheet resistance = 15 Ω □⁻¹) was precleaned in the ultrasonic bath with de-ionized water, acetone and isopropanol. Then, a ZnO layer (ca. 30 nm) was spin-coated at 4000 rpm onto the ITO glass from ZnO precursor solution (prepared by dissolving 0.1 g of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O) and 0.03 mL of ethanolamine (NH₂CH₂CH₂OH) in 1.0 mL of 2-methoxyethanol (CH₃OCH₂CH₂OH)), followed by baking at 200 °C for 30 min. After that, the photoactive layer consisting of PTB7-Th/acceptors mixture solution (10.0 mg mL⁻¹) in chloroform was spin-coated at 1400 rpm onto the ZnO layer (ca. 100 nm, measured by profilometer (Dektak XT)). A MoO₃ layer (ca. 5 nm) and Ag layer (ca. 80 nm) were then evaporated onto the active layer under the vacuum (ca. 10⁻⁵ Pa) to form the anode electrode. The measured area of the active device was 4 mm². The current density-voltage (J-V) curve was measured using a computer-controlled B2912A Precision Source/Measure Unit (Agilent Technologies). An XES-70S1 (SAN-EI Electric Co., Ltd) solar simulator (AAA grade, 70 × 70 mm² photobeam...
size) coupled with AM 1.5G solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW cm\(^{-2}\). A 2 × 2 cm\(^2\) monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. The external quantum efficiency (EQE) spectrum was measured using a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech Co., Ltd.). The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell.

**SCLC measurement**

Hole-only and electron-only devices were fabricated using the architectures ITO glass/PEDOT:PSS/active layer/Au for holes and ITO glass/ZnO/active layer/Ca/Al for electrons. For hole-only devices, the pre-cleaned ITO glass was treated by ultraviolet-ozone chamber (UVO) (Jelight Company, USA) for 15 min. Then PEDOT:PSS (ca. 35 nm) was spin-coated on it, and baked at 150 °C in the drying oven for 15 min. The photoactive layer was spin-coated at 1400 rpm on PEDOT:PSS layer, and Au (ca. 80 nm) was evaporated onto the photoactive layer under vacuum. For electron-only devices, ZnO (ca. 30 nm) was spin-coated onto the ITO glass, then the photoactive layer was spin-coated at 1400 rpm on ZnO. At the end, Ca (ca. 10 nm) and Al (ca. 80 nm) were evaporated under vacuum. The mobility was extracted by fitting the current density-voltage curves using space charge limited current (SCLC). The equation is as follows

\[
J = \frac{9}{8} \mu e_0 \varepsilon \varepsilon_0 V^2 \exp(0.89(V/E_0 L)^{0.5})/L^3
\]

where \(J\) refers to the current density, \(\mu\) is hole or electron mobility, \(\varepsilon_0\) is relative dielectric constant, \(\varepsilon_0\) is dielectric constant of free space, \(V = V_{\text{appl}} - V_{\text{bi}}\), \(E_0\) is characteristic field, \(L\) is the thickness of the active layer. \(L\) was measured by Dektak XT (Bruker).
Table S1 Performance of the OSCs with different IDT-2BR content in acceptors<sup>a</sup>

<table>
<thead>
<tr>
<th>IDT-2BR (%)</th>
<th>DIO (% v/v)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>calc $J_{SC}$ (mA cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.5</td>
<td>0.646</td>
<td>24.6</td>
<td>64.9</td>
<td>10.3</td>
<td>24.2</td>
</tr>
<tr>
<td>10</td>
<td>0.5</td>
<td>(0.645±0.006)</td>
<td>(24.5±0.4)</td>
<td>(63.5±1.8)</td>
<td>(10.1±0.3)</td>
<td>24.2</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>0.702</td>
<td>23.1</td>
<td>66.6</td>
<td>10.8</td>
<td>22.5</td>
</tr>
<tr>
<td>20</td>
<td>0.5</td>
<td>(0.702±0.003)</td>
<td>(22.2±0.8)</td>
<td>(66.6±1.3)</td>
<td>(10.4±0.4)</td>
<td>24.2</td>
</tr>
<tr>
<td>20</td>
<td>1</td>
<td>0.682</td>
<td>24.4</td>
<td>71.4</td>
<td>11.8</td>
<td>23.2</td>
</tr>
<tr>
<td>30</td>
<td>0.5</td>
<td>0.701</td>
<td>23.6</td>
<td>66.1</td>
<td>11.0</td>
<td>22.9</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
<td>(0.731±0.002)</td>
<td>(20.8±0.3)</td>
<td>(47.3±2.3)</td>
<td>(7.20±0.41)</td>
<td>20.8</td>
</tr>
<tr>
<td>100</td>
<td>0.5</td>
<td>1.05</td>
<td>12.9</td>
<td>54.3</td>
<td>7.31</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(1.05±0.006)</td>
<td>(13.0±0.4)</td>
<td>(53.0±1.9)</td>
<td>(7.21±0.09)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>Average values (in parenthesis) obtained from 15 devices.

Table S2 Hole mobilities and electron mobilities of blend films.

<table>
<thead>
<tr>
<th>active layer</th>
<th>$\mu_h$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_e$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\mu_h/\mu_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTB7-Th/F8IC</td>
<td>$4.5 \times 10^{-4}$</td>
<td>$8.4 \times 10^{-5}$</td>
<td>5.4</td>
</tr>
<tr>
<td>PTB7-Th/IDT-2BR</td>
<td>$1.3 \times 10^{-5}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>1.3</td>
</tr>
<tr>
<td>PTB7-Th/F8IC/IDT-2BR</td>
<td>$1.1 \times 10^{-3}$</td>
<td>$6.4 \times 10^{-4}$</td>
<td>1.7</td>
</tr>
</tbody>
</table>
**Fig. S1** Absorption spectra of PTB7-Th/IDT-2BR (blue), PTB7-Th/F8IC (red) and PTB7-Th/F8IC/IDT-2BR films (black).

**Fig. S2** Cyclic voltammograms of IDT-2BR, F8IC and PTB7-Th films in CH$_3$CN/0.1 M [But$_4$N][PF$_6$] at 100 mV s$^{-1}$, the horizontal scale refers to an Ag/AgCl electrode.
Fig. S3 (a) Normalized photoluminescence spectrum of IDT-2BR thin film and UV-vis absorption spectra of F8IC and IDT-2BR thin films. (b) Photoluminescence spectra of pure F8IC film and F8IC/IDT-2BR blend film. (c) Photoluminescence spectra of PTB7-Th, PTB7-Th/F8IC, PTB7-Th/IDT-2BR and PTB7-Th/F8IC/IDT-2BR films.
**Fig. S4** (a) $J-V$ characteristics and (b) EQE spectra of the OSCs with different IDT-2BR content.

**Fig. S5** (a) $V_{OC}$, (b) $J_{SC}$, (c) FF, and (d) PCE as a function of IDT-2BR weight ratio in acceptors.
Fig. S6 Stability curves of PTB7-Th/F8IC and PTB7-Th/F8IC/IDT-2BR devices under air conditions (a) and continuous heating at 80 °C in nitrogen atmosphere (b).

Fig. S7 $J-V$ characteristics in the dark for hole-only (a) and electron-only (b) devices measured by SCLC method based on PTB7-Th/F8IC, PTB7-Th/IDT-2BR and PTB7-Th/F8IC/IDT-2BR blends.
Fig. S8 AFM height images (2 μm × 2 μm) of (a) PTB7-Th/F8IC; (b) PTB7-Th/IDT-2BR; (c) PTB7-Th/F8IC/IDT-2BR blend films; phase images (2 μm × 2 μm) of (d) PTB7-Th/F8IC; (e) PTB7-Th/IDT-2BR; (f) PTB7-Th/F8IC/IDT-2BR blend films.

Fig. S9 TEM images of (a) PTB7-Th/F8IC; (b) PTB7-Th/IDT-2BR; (c) PTB7-Th/F8IC/IDT-2BR blend films.
Fig. S10 (a) 2D GIWAXS patterns of the pure acceptors and (b) the corresponding intensity profile along the out-of-plane (solid lines) and in-plane (dashed lines) directions.

Fig. S11 (a) 2D GISAXS patterns of the blends. (b) 2D GISAXS patterns of the pure acceptors and (c) the corresponding intensity profile along the in-plane directions.

References
