**Supplementary Information**

**Perylene diimide-based non-fullerene acceptor as an electron transporting material for inverted perovskite solar cells**

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**Preparation of materials**

CH$_3$NH$_3$I and DMBI were synthesized by following the methods reported in the literatures.$^1$ PbI$_2$ was purchased from Acros organics and dried in vacuum oven at 240 °C for 12 h before use. Poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate) (PEDOT:PSS) (Clevious P VP Al 4083) was purchased from H. C. Stark and passed through a 0.45 μm PVDF syringe filter before spin-coating. diPDI was synthesized through 3 steps by following the method reported in previous literatures.$^2$ TiO$_2$ nanoparticles were synthesized as reported in the literature.$^3$ 0.5 mL of TiCl$_4$ (Sigma-Aldrich, 99.9%) was added slowly to 2 mL of ethanol with stirring and then the whole content was mixed in 10 mL of anhydrous benzyl alcohol (Acros organics, 98+%). After the solution was heated at 80 °C for 6 h, translucent suspension was obtained. 3 mL of the suspension was precipitated in 27 mL of diethyl ether. To isolate TiO$_2$ nanoparticles, the precipitate was centrifuged at 5000 rpm and then re-dispersed in ethanol (6 mg/mL). 14.7 μL of titanium diisopropoxide bis(acetylacetonate) (Sigma-Aldrich, 75 wt% in isopropanol) was added to 1 mL of re-dispersed TiO$_2$
nanoparticle solution. The final solution was diluted 2 times for normal cells and 4 times for inverted cells with ethanol. Methylamine (40% in methanol, TCI), hydroiodic acid (Alfa Aesar, 57% w/w aqueous solution stabilized with 1.5% hypophosphorous acid), N,N’-dimethyl-1,2-phenylenediamine (Sigma-Aldrich), benzaldehyde (Sigma-Aldrich), 3,4,9,10-perylenetetracarboxylic dianhydride (Alfa Aesar), 4-heptylamine (TCI), imidazole (Sigma-Aldrich), zinc acetate (Sigma-Aldrich), and copper powder (Sigma-Aldrich, <100 nm particle size, 99.8%) were purchased and used without further purification.

**Synthesis of N,N’-bis(1-propylbutyl)perylene-3,4:9,10-tetracarboxylic diimide (2)***

A mixture of 1.00 g (2.55 mmol) of 3,4,9,10-perylenetetracarboxylic dianhydride (1), 0.72 g (6.25 mmol) of 4-heptylamine, 5.00 g (73.44 mmol) of imidazole, and 351 mg (1.91 mmol) of zinc acetate was stirred at 160 °C for 2 h. After being cooled to room temperature, the mixture is dissolved in chloroform and purified by column chromatography on silica gel using chloroform as an eluent to yield a red solid of 2 (1286 mg, 86%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.68 (d, 4H), 8.63 (d, 4H), 5.24 (m, 2H), 2.28 (m, 4H), 1.83 (m, 4H), 1.34 (m, 8H), 0.93 (t, 12H).

**Synthesis of 1-bromo-N,N’-bis(1-propylbutyl)perylene-3,4:9,10-tetracarboxylic diimide (3)**

A mixture of 1.00 g (1.70 mmol) of compound 2 and 13.72 g (0.086 mol) of bromine in 50 mL of dichloromethane was stirred at 25 °C for 4 days. The mixture poured into ice-water, and then stirred for 1 h with addition of sodium thiosulfate. The mixture was then extracted 3 times with dichloromethane. After the organic phase was dried over MgSO₄, the solvent was
evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using chloroform as an eluent. The second band yielded an orange solid of 1-bromo-\(N,N^\prime\)-bis(1-propylbutyl)perylene-3,4:9,10-tetracarboxylic diimide 3 (359 mg, 32%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm) 9.8 (m, 1H), 8.93 (s, 1H), 8.6-8.75 (m, 5H), 5.23 (m, 2H), 2.26 (m, 4H), 1.82 (m, 4H), 1.32 (m, 8H), 0.93 (t, 12H).

**Synthesis of diPDI**

A mixture of 260 mg (0.39 mmol) of compound 3 and 248 mg (3.90 mmol) of copper powder in 40 mL of DMSO was stirred at 100 °C for 8 h. After the reaction mixture was cooled to room temperature, the mixture was poured into water, and then extracted with chloroform. After the organic phase was dried over MgSO\(_4\), the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane and hexane mixture (3:1, v:v) as an eluent to yield a deep red solid of diPDI (82 mg, 36%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) (ppm) 8.79 (d, 8H), 8.48 (d, 2H), 8.17 (s, 4H), 5.16 (m, 4H), 2.20 (m, 8H), 1.75 (m, 8H), 1.28 (m, 16H), 0.88 (t, 24H).

**Fabrication of photovoltaic devices**

The configuration of the solar cell device used in this work is glass/ITO/PEDOT:PSS/CH\(_3\)NH\(_3\)PbI\(_3\)/diPDI or diPDI:DMBI/TiO\(_2\)/Al. The ITO-coated glass (10 Ω sq\(^{-1}\), KETI) was cleaned with acetone and isopropanol for 30 min each. After complete drying, the ITO-coated glass was treated with UV-ozone for 15 min. A 40 nm thick PEDOT:PSS was spin-coated on the ITO-coated glass at 3000 rpm for 40 s and then annealed at 150 °C for 30 min in ambient condition. The substrate was transferred into N\(_2\)-filled glove
box and annealed at 120 °C for 10 min. For the CH$_3$NH$_3$PbI$_3$ layer, a 1:1 ratio of CH$_3$NH$_3$I:PbI$_2$ was dissolved in DMSO with concentration of 1.2 M. The precursor solution was spin-coated onto the PEDOT:PSS layer at 3000 rpm for 15 s. The substrate was immediately transferred onto a hot plate and heated at 110 °C for 30 s. For ETL, various ratios of diPDI/DMBI were dissolved in chlorobenzene and then spin-coated onto the CH$_3$NH$_3$PbI$_3$ layer at 3000 rpm for 30 s. TiO$_2$ solution was spin-coated onto the ETL at 3000 rpm for 40 s. Thickness of ETL and TiO$_2$ layer is 52 nm and 10 nm, respectively. Finally, Al (100 nm) cathode was deposited by using thermal evaporator under vacuum (< 10$^{-6}$ Torr) through a shadow mask to give a device area of 0.1 cm$^2$.

**Characterization and measurement**

The absorption spectra were obtained by an UV-Vis spectrophotometer (Lambda 25, Perkin Elmer). UPS measurement was performed using a hemispherical electron energy analyzer (RESOLVE 120, PSP). The base pressure of analysis chamber was maintained under low 10$^{-9}$ Torr. He I ($h\nu = 21.22$ eV) discharge lamp was used as an excitation source with sample bias of −15 and −10 V for secondary electron cutoff and valence band region, respectively. Fermi level was calibrated through Ar$^+$-sputtered clean Au. The electrical conductivity of DMBI-doped diPDI film was measured for the device with planar diode structure. The device for measurement of electrical conductivity was fabricated by spin-coating of DMBI-doped diPDI solution on the top of pre-cleaned glass followed by thermal deposition of Au in a vacuum below 10$^{-7}$ Torr. Au parallel electrode bars with 80 nm thick were separated with a distance of 70 μm. The electrical conductivity was measured by a probe station with a computer-controlled Keithley 4200 source measurement unit. $J$−$V$ curves of photovoltaic
cells were obtained using the Keithley 4200 source measurement unit under AM 1.5G (100 mW cm\(^{-2}\)) simulated by an Oriel solar simulator (Oriel 91160A). The light intensity was calibrated using a NREL-certified photodiode prior to each measurement. The EQE was measured using Polaronix K3100 measurement system (McScience). The light intensity at each wavelength was calibrated with a standard single-crystal Si cell. The photoluminescence spectra were obtained by using a Shimadzu spectrofluorometer (RF-5301PC). PL lifetimes were measured by using 400 nm, second harmonic generated Ti:Sapphire femtosecond laser (MaiTai, Spectra Physics) as excitation source and time-correlated single photon counting module (MPD-PDM Series DET-40 photon counting detector and Pendulum CNT-91 frequency counter) combined with monochromator as detector. The parameter of PL decay were obtained by fitting the spectra with a biexponential decay function, \(I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)\). Average lifetime, \(\tau_{ave}\) were calculated by equation, \(\tau_{ave} = A_1 \tau_2 + A_2 \tau_2\).
**Fig. S1** Synthetic route of diPDI.
**Fig. S2** Photoluminescence spectra of perovskite, perovskite/diPDI, perovskite/DMBI-doped diPDI with various dopant concentrations, and perovskite/PCBM films deposited on quartz glass (excited at 520 nm).
Fig. S3 UV–Vis–NIR absorption spectra of pure perovskite and bilayer perovskite/diPDI with various dopant concentrations.
Fig. S4 Hysteresis curves for devices with (a) pure diPDI, (b) 0.5 wt% DMBI-doped diPDI, (c) 1 wt% DMBI-doped diPDI, (d) 3 wt% DMBI-doped diPDI, and (e) 5 wt% DMBI-doped diPDI.
Fig. S5 $J$–$V$ curves of devices with different ETL.

**Table S1.** Photovoltaic performances of devices with different ETL.

<table>
<thead>
<tr>
<th>ETL</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
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<tr>
<td>diPDI/TiO$_2$</td>
<td>17.2</td>
<td>0.80</td>
<td>0.51</td>
<td>7.1</td>
</tr>
<tr>
<td>diPDI</td>
<td>16.2</td>
<td>0.74</td>
<td>0.48</td>
<td>5.8</td>
</tr>
<tr>
<td>PCBM</td>
<td>17.5</td>
<td>0.84</td>
<td>0.64</td>
<td>9.3</td>
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Table S2. Fitting parameters of PL decays shown in Fig.1b.

<table>
<thead>
<tr>
<th>Quencher</th>
<th>$A_1$</th>
<th>$\tau_1$ (ns)</th>
<th>$A_2$</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_{\text{ave}}^{[a]}$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>0.783</td>
<td>45.964</td>
<td>0.217</td>
<td>12.590</td>
<td>38.722</td>
</tr>
<tr>
<td>diPDI</td>
<td>0.903</td>
<td>1.035</td>
<td>0.097</td>
<td>3.075</td>
<td>1.233</td>
</tr>
<tr>
<td>PCBM</td>
<td>0.776</td>
<td>1.417</td>
<td>0.224</td>
<td>4.939</td>
<td>2.206</td>
</tr>
</tbody>
</table>

Fit function: $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$

$^{[a]} \tau_{\text{ave}} = A_1 \tau_1 + A_2 \tau_2$

References


