Supporting information

Pentacyclic S,N-heteroacene based electron acceptor with strong near-infrared absorption for efficient organic solar cells

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**Experimental Section**

**Materials:**
Patterned ITO glass with a sheet resistance of 10 Ω sq⁻¹ and PEDOT:PSS was purchased from South China Science & Technology Co., Ltd. and H. C. Stark Company, respectively. PBDB-T-2F, IT-4F, Compound 1, and PFN-Br were provided by Solarmer Materials (Beijing) Inc. 1,8-Diiodooctane (DIO), 1-Chloronaphthalene (CN) and Zirconium Acetylacetonate (ZrAcac) were purchased from Sigma-Aldrich. All materials were commercially available products and used directly without further purification.

**Synthesis:**

*Synthesis of 3,5-dibromo-4-(heptadecan-9-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole-2,6-dicarbaldehyde (compound 2)*

2,6-dibromo-4-(heptadecan-9-yl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (Compound 1) (579mg, 1mmol) was added to the reaction flask with argon gas protection, then add tetrahydrofuran (THF) (16ml) to dissolve. Then cooled with liquid nitrogen and methanol is kept temperature. Lithium dilithium diisopropylamide (LDA) (4.1ml) is added dropwise when the temperature at -78 °C. After rewarming, the reaction was carried out for 1 to 2 hours at room temperature in the dark, and then cooled to -78 °C. N,N-dimethylformamide (DMF) (234mg, 3.2mmol) was added and the mixture was rewarming for 2h. Then the mixture was extracted and dried through anhydrous MgSO₄. The compound 2 was obtained by the separation and purification from silica gel column (567m g, yield 98%)


Compound 2 (631mg, 1mmol) was dissolved in DMF (9mL) and the mixture was added to the reaction flask. Then added ethyl 2-mercaptoacetate (EtOAc) (264mg, 2.2mmol) and K₂CO₃ (690mg, 5mmol) was added in batches at room temperature overnight. The compound 3 was obtained by the separation and purification from silica gel column (303mg, yield 48%)


The compound 3 (674g, 1mmol) and THF were added to a reaction flask, and a solution of LiAlH₄ (158g, 4mmol) in THF at ice-melting state was added thereto, and the mixture was reacted at room temperature for 3.5 h. The compound 4 was obtained by the separation and purification from silica gel column (323mg, yield 48%)


The compound 4 (595mg, 1mmol), Pyridinium chlorochromate (Pcc) (262mg, 1.2mmol) and dichloromethane (DCM) (14.3ml, 25mmol) were mixture and reacted at room temperature for 2 h. and purified using silica gel column. The compound 5 was obtained by the separation and purification from silica gel column (333mg, yield 56%)


Compound 5 (586 mg, 1mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (EG-2F) (230mg, 10mmol) and chloroform (98ml) was added to the reaction. Then the bottle was reacted by adding a few drops of pyridine at 80 °C. The DTP-C17-4F was obtained by the separation and purification from silica gel column (392mg, yield 67%).
$^1$H NMR (400 MHz, CDCl$_3$, Fig. S1) $\delta$ 8.94 (s, 2H), 8.63 – 8.48 (m, 2H), 8.18 (s, 2H), 7.74 (s, 2H), 4.65 (s, 1H), 2.35 (s, 2H), 2.20 (s, 2H), 1.31 (s, 4H), 1.10 (s, 20H), 0.75 (t, $J = 6.6$ Hz, 6H). MS (MALDI-TOF, Fig. S2): m/z 1009.2 (M$^+$$^\ast$). Elemental analysis (Flash EA 1112) for C$_{55}$H$_{43}$F$_4$N$_5$O$_2$S$_4$: C, 65.33; H, 4.26; N, 8.41. Found: C, 65.35; H, 4.19; N, 8.31.

Fig. S1. $^1$H NMR Spectrum of DTP-C$_{17}$-4F.
Fig. S2. MALDI-TOF MS spectrum of obtained material DTP-C_{17}-4F.

**Device Fabrication**

The ITO-coated glass substrates were sequentially pre-cleaned by cleanser essence, water, ultrapure water, acetone, isopropyl alcohol in an ultrasonic bath for 15 min and subsequently dried in an oven at 150 °C for 15 min. PEDOT: PSS aqueous solution filtered through a 0.45 µm filter was spin-coated at 3000 rpm for 30 s on the ITO substrates after 15 min UV-ozone treatment, and then baked at 150 °C for 15 min in air. The thickness of the PEDOT: PSS is around 35 nm. Subsequently, active layer was spin-coated at 3000 rpm for 60 s and then annealing at 100 °C for 10 min in a nitrogen-protected glove box. The thickness of the photoactive layer is about 80 nm. It is remarkable that the PBDB-T-2F:DTP-C_{17}-4F (1:1) chlorobenzene (CB) solution needs to be stirred overnight. The cathode buffer layers of ZrAcac (1 mg mL⁻¹ in ethanol) or PFN-Br (1 mg mL⁻¹ in methanol) were spin-coated on the active layer at 3000 rpm for 30 s. Finally, the 100 nm thick Al cathode was deposited under a pressure of 5×10⁻⁴ Pa in vacuum evaporator. The photoactive area of the device is around 4 mm².

**Device Characterization**

The current density–voltage (J–V) curves of organic solar cells were measured in a nitrogen-filled glove-box using a computer controlled Keithley 2400 Source Measure Unit (SMU) under simulated AM1.5G illumination at 100 mW/cm² by a xenon-lamp-based solar simulator (AAA grade, SAN-EI
ELECTRIC Co., Ltd) at the temperature of $25 \pm 1^\circ C$. The EQE was obtained under ambient conditions at room temperature using a Systems model QE-DLI lock-in amplifier coupled with a QE-M110 monochromatic and 75 W xenon lamp (Enli Technology Co., Ltd.), and the light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

**Instrumentation**

A Lambda 950 UV-Vis NIR spectrophotometer was used to obtain the optical absorption spectrum of active layer materials. The surface morphologies of the solid thin films were analyzed by an Agilent 5500 atomic force microscope (AFM) operated in the tapping mode under ambient atmosphere at room temperature. C–V measurements were carried out on a Zahner Zennium electrochemical workstation, with glassy carbon, Pt wire, and Ag/Ag+ (Ag wires dipped in 0.01 M AgNO3 in acetonitrile) anhydrous electrode as the working electrode, the counter electrode, and the reference electrode, respectively. The thickness of the active layer was measured by Dektak XT surface profometer (Bruker). The molecular weight were evaluated by high temperature Gel permeation chromatography (GPC) at 140°C using 1, 2, 4-trichlorobenzene (TCB) as the eluent and polystyrene was used as a standard. The stability of devices were obtained under continuous LED illumination in ambient environment using a Multi-channel thin film photovoltaic attenuation test system (PVLT-6001M-16A), and its LED illumination spectral range from 410 nm to 690 nm.

**Space charge-limited current (SCLC)**

The structure of electron-only devices is ITO/Al/active layer/Al and the structure of hole-only devices is ITO/PEDOT: PSS/active layer/Au. The fabrication conditions of the active layer films are same with those for the solar cells. The charge mobilities are generally described by the Mott-Gurney equation:[1-3]

$$ J = \frac{9}{8} \varepsilon \varepsilon_0 \mu V^2 \frac{L^3}{L} $$

where $J$ is the current density, $\varepsilon_0$ is the permittivity of free space ($8.85 \times 10^{-14}$ F/cm), $\varepsilon_r$ is the dielectric constant of used materials, $\mu$ is the charge mobility, $V$ is the applied voltage and $L$ is the active layer thickness. The $\varepsilon_r$ parameter is assumed to be 3, which is a typical value for organic materials. In organic materials, charge mobility is usually field dependent and can be described by the disorder formalism, typically varying with electric field, $E=V/L$, according to the equation:

$$ \mu = \mu_0 \exp[0.89 \sqrt{\frac{V}{L}}] $$

Where $\mu_0$ is the charge mobility at zero electric field and $\gamma$ is a constant. Then, the Mott-Gurney equation can be described by:

$$ J = \frac{9}{8} \varepsilon \varepsilon_0 \mu_0 V^2 \frac{L^3}{L} \exp[0.89 \sqrt{\frac{V}{L}}] $$

In this case, The charge mobilities were estimated using the following equation:[4-6]
\[
\ln \left( \frac{JL^3}{V^2} \right) = 0.89 \gamma \sqrt{\frac{V}{L}} + \ln \left( \frac{9}{8} \varepsilon \varepsilon_0 \mu_0 \right)
\]  

(4)

**Fig. S3.** Normalized absorption spectra of PBDB-T-2F, DTP-C₁₇-4F and ITIC solid thin films.

**Fig. S4.** EQE curves of OSCs based on PBDT-T-2F:DTP-C₁₇-4F with different thickness and different additives.
Fig. S5. Photovoltaic parameters ($V_{OC}$, FF, $J_{SC}$, PCE) of the devices with seven kinds of conditions. 12 devices were investigated for the error bars.

Fig. S6. SCLC plots of PBDT-T-2F: DTP-C$_{17}$-4F based blending film of (a) hole-only ITO/PEDOT:PSS/active layer/Au devices and (b) electron-only ITO/Al/active layer/MoO$_3$/Al devices.

Table S1. The mobility data of organic solar cells based on PBDB-T-2F:DTP-C$_{17}$-4F blend films with and without additives.

<table>
<thead>
<tr>
<th>condition</th>
<th>$\mu_h$ (cm$^2$/V·s)</th>
<th>$\mu_e$ (cm$^2$/V·s)</th>
<th>$\mu_e/\mu_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>w/o additive</td>
<td>2.34×10$^{-4}$</td>
<td>3.48×10$^{-3}$</td>
<td>14.87</td>
</tr>
<tr>
<td>0.5 % DIO</td>
<td>9.51×10$^{-5}$</td>
<td>2.11×10$^{-3}$</td>
<td>22.71</td>
</tr>
<tr>
<td>1 % CN</td>
<td>3.17×10$^{-5}$</td>
<td>2.86×10$^{-4}$</td>
<td>9.02</td>
</tr>
</tbody>
</table>
Fig. S7. Variation of $V_{OC}$, FF, $J_{SC}$ and PCE of the highest performing device under continuous LED (spectral range from 410 nm to 690 nm, 100 mW/cm$^2$) illumination in ambient environment.

References