Supporting Information

NIR absorption D-π-A-π-D structured diketopyrrolopyrrole-dithiafulvalene based small molecule for solution processed organic solar cells

K. Narayanswamy,a,b A. Venkateswararao,a Vinay Gupta,d Suresh Chand,d Surya Prakash Singh a,b,c,*

a Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal road, Tarnaka, Hyderabad-500007, India
b Academy of Scientific and Innovative Research, CSIR-IICT
c Network Institute of Solar Energy, (CSIR-NISE) and Academy of Scientific and Innovative Research (AcSIR), New Delhi, India
d Organic and hybrid solar cells, Physics of Energy Harvesting Division, CSIR-National Physical Laboratory, New Delhi-110012, India.
Email: spsingh@iict.res.in

Materials and methods

All precursor materials were purchased directly from commercial sources and used as such without any further purification and solvents were dried under vacuum by following standard procedure. UV-vis spectrophotometer used to record absorption spectra in dichloromethane (DCM) solution and for TiO₂ film. NMR (¹H and ¹³C) spectra were measured with Avance ACP-300 or AMX2-500 spectrometers at 300 and 500 MHZ respectively, using tetramethylsilane (TMS) as an internal standard. High resolution mass spectra were measured on a Shimadzu LCMS-2010 EV model with ESI probe. Cyclic voltammetry was performed on a CH Instruments with a three electrode system consisting of Ag/AgCl reference electrode, a working electrode and a platinum wire counter-electrode. The redox
potentials of the dyes were measured in DCM containing 0.1 M Bu₄NHClO₄ at a scan rate of 100 mV s⁻¹.

**Fabrication of organic solar cells**

The **DPP-DTF** as well as their blend with PC₇₁BM were dissolved in chlorobenzene and 1,8-diodooctane (97:3 vol/vol). The overall compound concentration was 10 mg ml⁻¹ and the solution was stirred at 60 °C for 12 h under a N₂ atmosphere. ITO glass substrate (Thin Film Devices) was cleaned in water, acetone and isopropyl alcohol for 60 min under sonication. Glasses were then exposed to ultraviolet ozone irradiation for 15 min. Then MoOx (10 nm) was thermal evaporated in a glove box at a chamber pressure of ~ 10⁻⁷ torr. Active layers were spin-coated using the as-prepared solutions at 1500 r.p.m. in a glove box. Finally, Al (100 nm) cathode was thermally evaporated. The fabricated solar cells were encapsulated using an epoxy and a cover glass and kept for 15 min under ultraviolet irradiation. The J-V characteristics of the solar cells were measured by a Keithley 236 source meter unit. The light source was calibrated by using silicon reference cell (NREL) with an AM 1.5 G solar simulator with an intensity of 100 mW/cm². During the testing, an aperture with an area of 10 mm² was used to accurately measure the performance of solar cells. The EQE was measured using a PV measurement, Inc. system after monochromatic power calibration using reference Si-diode.

**Computational details**

The geometry and computed parameters of the **DPP-DTF** were performed with the Gaussian09 program package. Geometry of the **DPP-DTF** was optimized with B3LYP/6-31G (d)² basis set and density functional theory (DFT) calculations performed with BMK³/DGDZVP⁴ basis set and for salvation PCM³ method used with DCM as a solvent. PCM method optimized structure was confirmed by performed frequency analysis and found
no negative peaks. The excitation energies and oscillator strengths for the lowest 10 singlet-singlet transitions at the optimized geometry in the ground state were obtained by TD-DFT calculations using the same basis set.

**Experimental Section**

5',5''-(2,5-bis(2-ethylhexyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrole-1,4-diyl)dil-2,2'-bithiophene-5-carbaldehyde (DPP) was synthesized according to literature procedures. 6

3,6-bis(5',-(4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)methyl)-2,2'-bithiophen-5-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (DPP-DTF). A mixture of DPP (0.25 g, 0.33 mmol) and 4,5-bis(hexylthio)-1,3-dithiole-2-thione (DTF, 0.37 g, 1.0 mmol) dissolved in toluene (15 mL) and refluxed for 1 h under nitrogen atmosphere. Added P(OEt)₃ (2 mL) slowly through syringe and refluxed for 4 h. After that, the reaction mixture was extracted with DCM, washed with brine solution and dried over anhydrous sodium sulfate. Solvents were removed by vacuum and the crude was purified by column chromatography on silica gel using petroleum ether/DCM (2:3) as an eluent. Green solid. Yield 0.36 g (78%). m. p. 165-167 °C; IR (KBr), ν (cm⁻¹) 3447, 2921, 1656, 1550, 1517, 1483, 1419; ¹H NMR (400 MHZ, CDCl₃): δ ppm 8.93 (d, J = 4.1 Hz, 2H), 7.27 (d, J = 4.1 Hz, 2H), 7.24 (d, J = 3.9 Hz, 2H), 6.79 (d, J = 3.9 Hz, 2H), 6.64 (s, 2H), 4.10-4.00 (m, 4H), 2.88 (t, J = 7.2 Hz, 4H), 2.85 (t, J = 7.3 Hz, 4H), 1.94-1.92 (m, 2H), 1.70-1.62 (m, 8H), 1.44-1.25 (m, 40H), 0.94-0.88 (m, 24H); ¹³C NMR (75 MHz, CDCl₃): 161.9, 143.1, 141.9, 139.3, 137.2, 134.7, 133.5, 129.2, 128.0, 126.3, 125.9, 125.2, 124.4, 108.6, 107.7, 77.6, 77.35, 77.1, 46.3, 39.6, 36.7, 36.5, 31.7, 30.7, 30.1, 30.0, 28.9, 28.6, 24.0, 23.5, 22.9, 14.5, 14.4, 10.9; HRMS [M + H]⁺ (m/z): caled for C₇₀H₉₄N₂O₂S₁₂, 1381.4199, found:1381.4182. Anal. Calcd for C₇₀H₉₄N₂O₂S₁₂: C, 60.82; H, 7.00; N, 2.03; S, 27.84. Found: C, 60.82; H, 6.98; N, 2.01; S, 27.82.
Figure S1. $^1$H NMR spectra of DPP-DTF recorded in CDCl$_3$. 
Figure S2. $^{13}$C NMR spectra of DPP-DTF recorded in CDCl$_3$. 
Figure S3. Absorption spectra of DPP-DTF recorded in different solvents.

Figure S4. Simulated absorption spectra of DPP-DTF by BMK/DGDZVP (d) in DCM as phase (PCM method).
**Figure S5.** Cyclic voltammogram of Fc/Fc⁺ recorded in DCM.

**Figure S6.** Cyclic voltammogram of DPP-DTF recorded in DCM.
**Figure S7.** Differential pulse voltammogram of DPP-DTF recorded in DCM.

**Figure S8.** Thermo gravimetric analysis of DPP-DTF measured under nitrogen atmosphere.
Figure S9. HRMS spectra of DPP-DTF.

Table S1. Computational parameters of DPP-DTF by at BMK/dgdzvp level with DCM solvent using PCM method.

<table>
<thead>
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<th>Dye</th>
<th>λ, nm</th>
<th>f</th>
<th>MO transitions</th>
<th>$\mu_g$, D</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>$E_{0-0}$ (eV)</th>
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<td>DPP-DTF</td>
<td>659</td>
<td>2.44</td>
<td>HOMO→LUMO (94%)</td>
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<td>0.45</td>
<td>HOMO-1→LUMO+1 (36%), HOMO→LUMO+2 (44%)</td>
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References


