

## Supporting Information

### **NIR absorption D- $\pi$ -A- $\pi$ -D structured diketopyrrolopyrrole-dithiafulvalene based small molecule for solution processed organic solar cells**

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### **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 TiO<sub>2</sub> film. NMR (<sup>1</sup>H and <sup>13</sup>C) 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 Bu<sub>4</sub>NHClO<sub>4</sub> at a scan rate of 100 mV s<sup>-1</sup>.

## **Fabrication of organic solar cells**

The **DPP-DTF** as well as their blend with PC<sub>71</sub>BM were dissolved in chlorobenzene and 1,8-diodooctane (97:3 vol/vol). The overall compound concentration was 10 mg ml<sup>-1</sup> and the solution was stirred at 60 °C for 12 h under a N<sub>2</sub> 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 MoO<sub>x</sub> (10 nm) was thermal evaporated in a glove box at a chamber pressure of ~ 10<sup>-7</sup> 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/cm<sup>2</sup>. During the testing, an aperture with an area of 10 mm<sup>2</sup> 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.<sup>1</sup> Geometry of the **DPP-DTF** was optimized with B3LYP/6-31G (d)<sup>2</sup> basis set and density functional theory (DFT) calculations performed with BMK<sup>3</sup>/DGDZVP<sup>4</sup> basis set and for salvation PCM<sup>5</sup> 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)di-2,2'-bithiophene-5-carbaldehyde (DPP) was synthesized according to literature procedures.<sup>6</sup>

**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(2*H*,5*H*)-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)<sub>3</sub> (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),  $\nu$  (cm<sup>-1</sup>) 3447, 2921, 1656, 1550, 1517, 1483, 1419; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  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); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 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]<sup>+</sup> (*m/z*): calcd. for C<sub>70</sub>H<sub>94</sub>N<sub>2</sub>O<sub>2</sub>S<sub>12</sub>, 1381.4199, found: 1381.4182. Anal. Calcd for C<sub>70</sub>H<sub>94</sub>N<sub>2</sub>O<sub>2</sub>S<sub>12</sub>: 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.

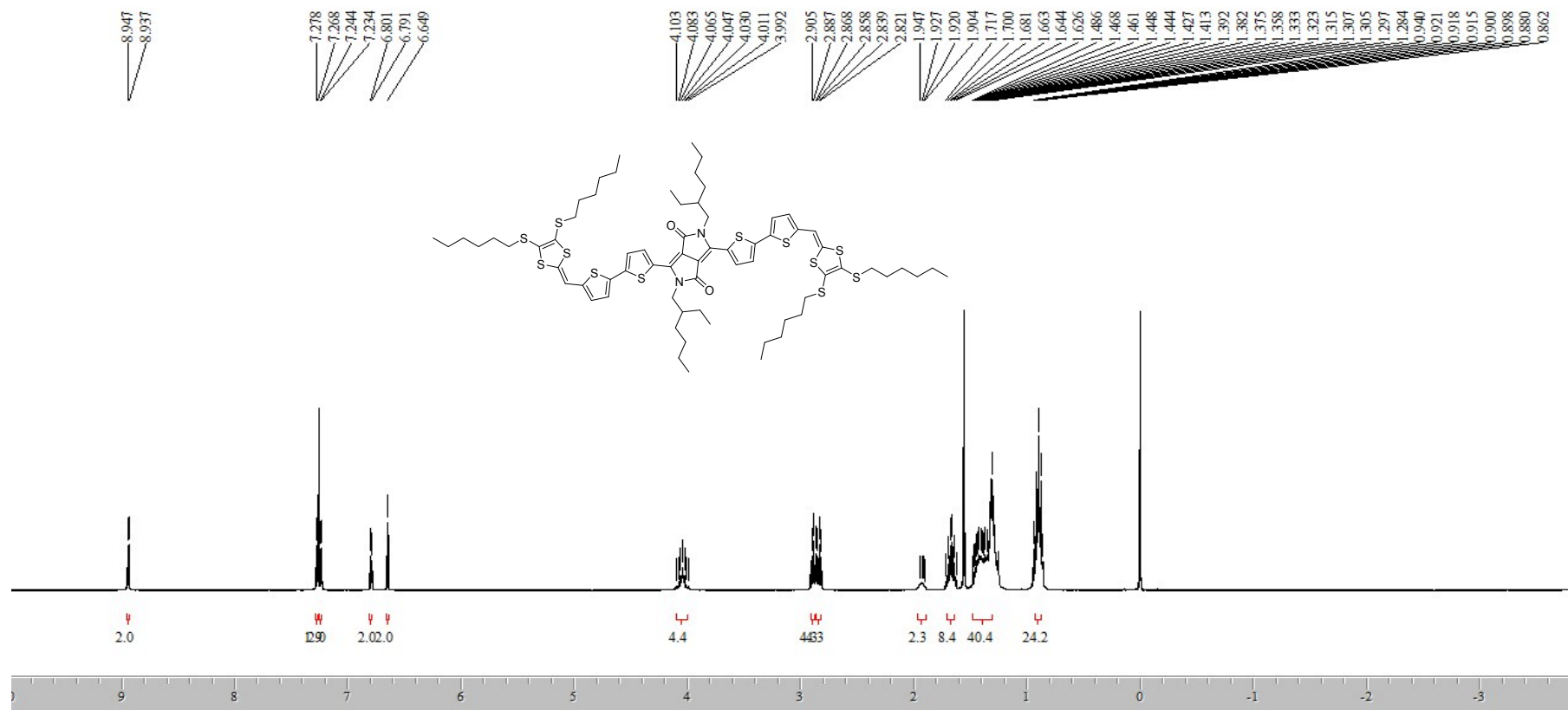
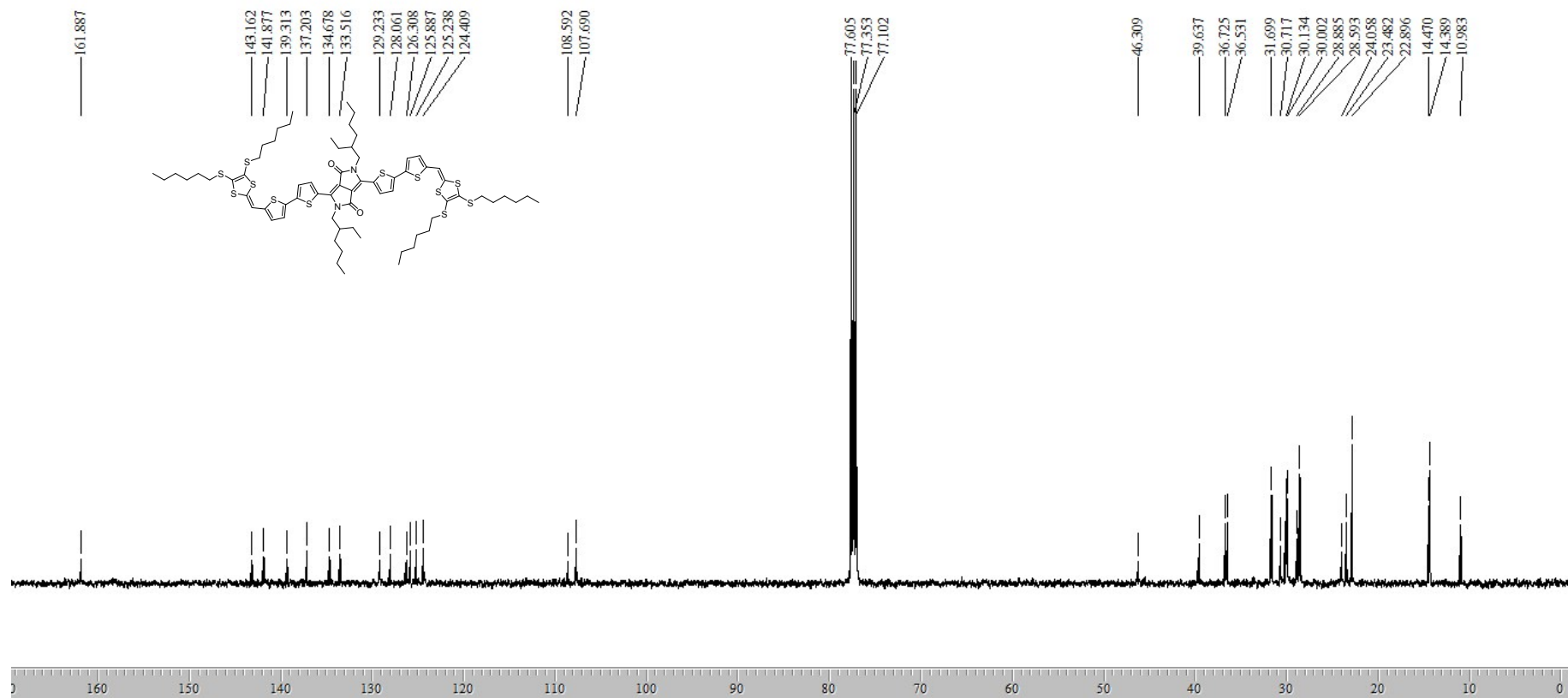


Figure S1. <sup>1</sup>H NMR spectra of DPP-DTF recorded in CDCl<sub>3</sub>.



**Figure S2.** <sup>13</sup>C NMR spectra of DPP-DTF recorded in CDCl<sub>3</sub>.

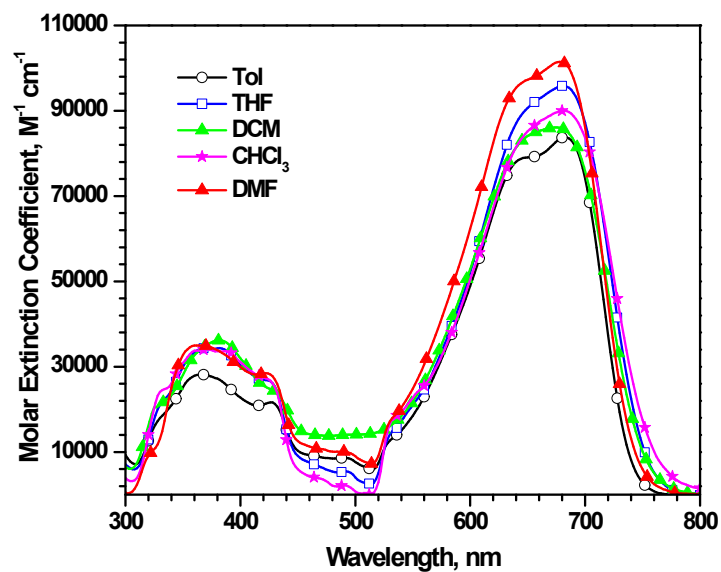


Figure S3. Absorption spectra of **DPP-DTF** recorded in different solvents.

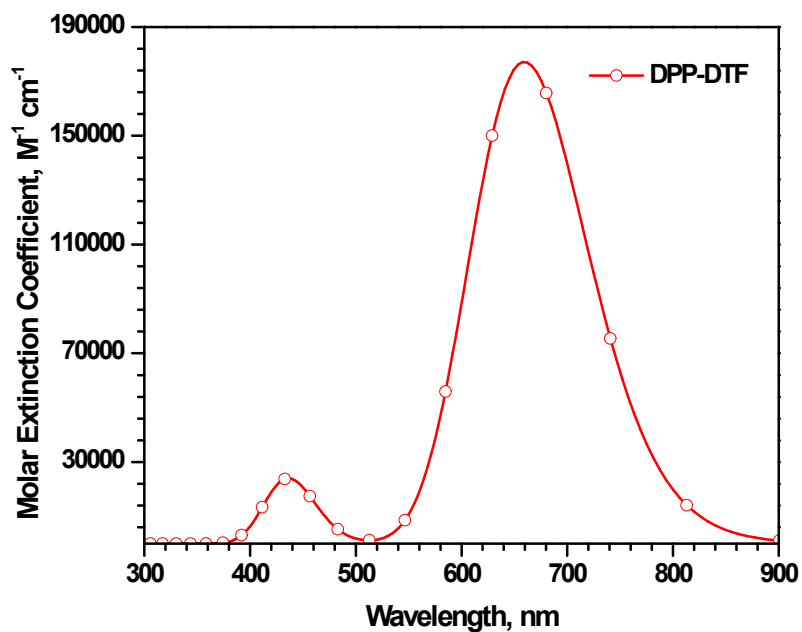


Figure S4. Simulated absorption spectra of **DPP-DTF** by BMK/DGDZVP (d) in DCM as phase (PCM method).

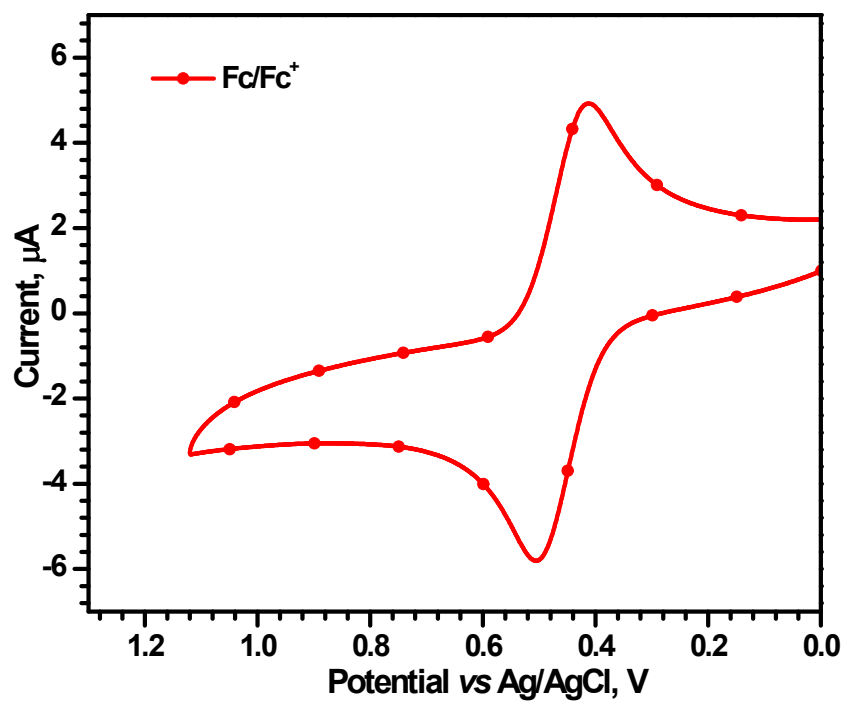


Figure S5. Cyclic voltammogram of  $\text{Fc}/\text{Fc}^+$  recorded in DCM.

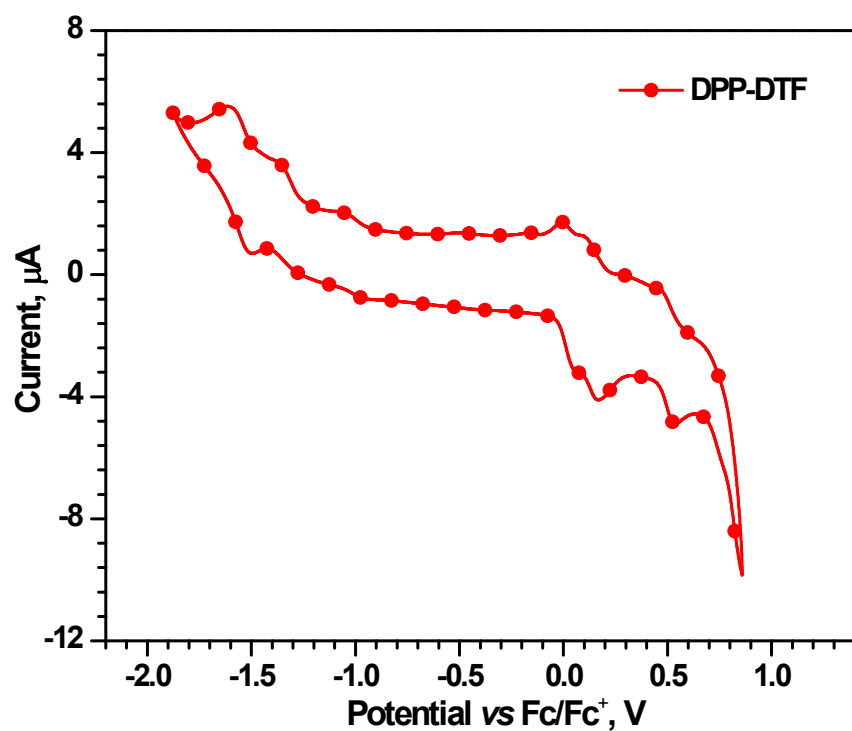


Figure S6. Cyclic voltammogram of  $\text{DPP-DTF}$  recorded in DCM.

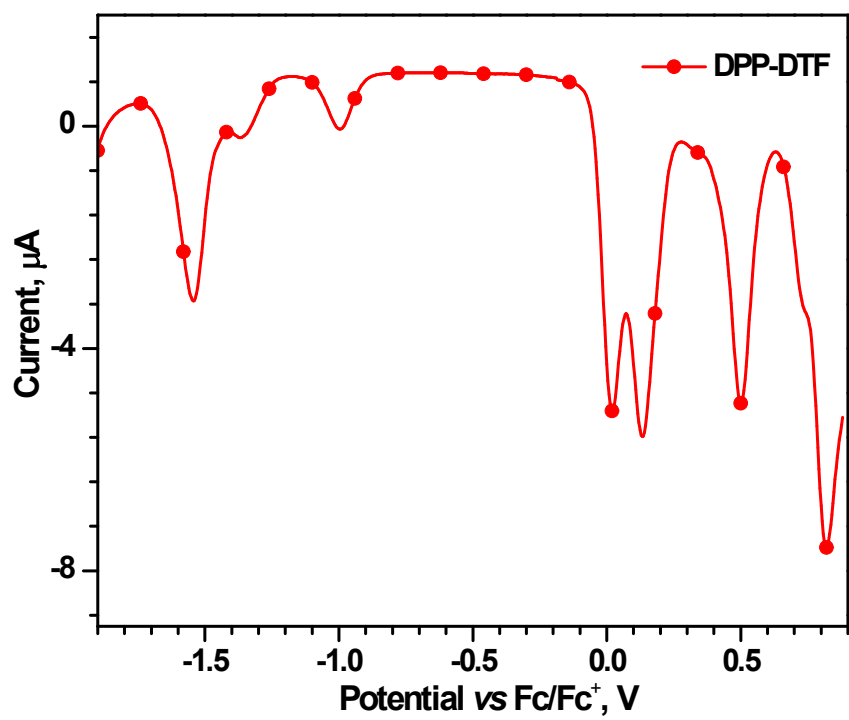


Figure S7. Differential pulse voltammogram of DPP-DTF recorded in DCM.

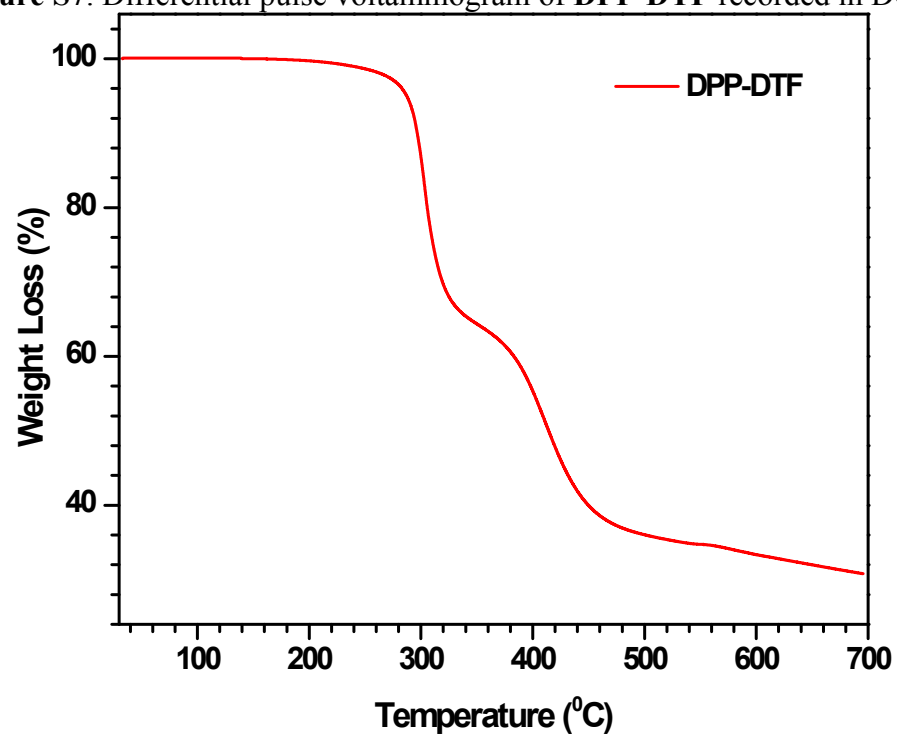
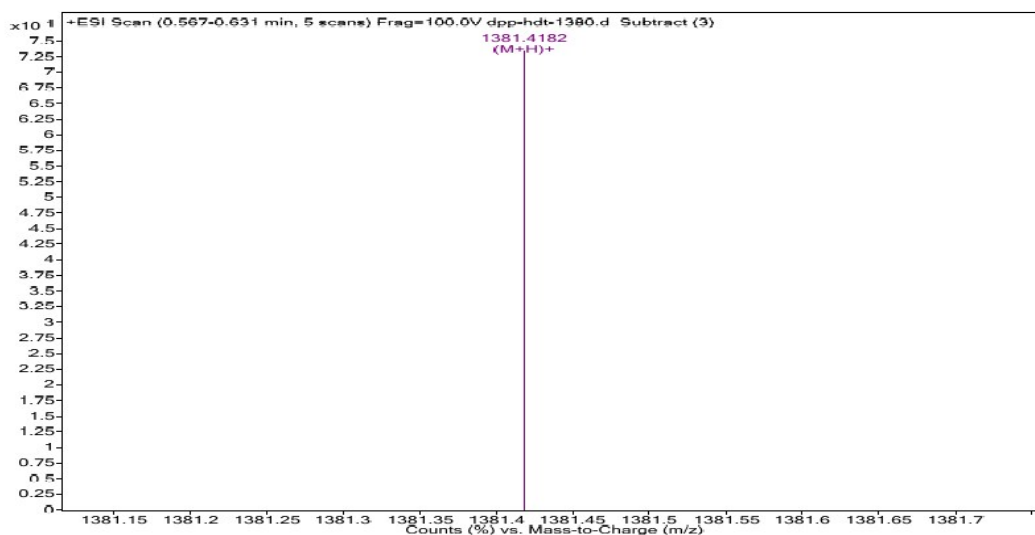


Figure S8. Thermo gravimetric analysis of DPP-DTF measured under nitrogen atmosphere.





**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.

Dye	$\lambda$ , nm	$f$	MO transitions	$\mu_g$ , D	HOMO (eV)	LUMO (eV)	$E_{0-0}$ , (eV)
<b>DPP-DTF</b>	659	2.44	HOMO→LUMO (94%)	0.33	-5.57	-2.66	2.91
	436	0.33	HOMO-2→LUMO (88%), HOMO-1→LUMO+1 (6%)				
	376	0.45	HOMO-1→LUMO+1 (36%), HOMO→LUMO+2 (44%)				

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