

## Electronic Supplementary Information (ESI)

### **Achieving Highest Efficiency Using BODIPY Core Decorated with Dithiafulvalene Wings for Small Molecule Based Solution-Processed Organic Solar Cells**

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## S1. Introduction

A summary of recently published BODIPY based small molecule donor is illustrated in **Figure 1** of main manuscript along with their respective PCEs in solar cells. The photovoltaic parameters of the devices made from those molecules are reported in **Table S1**. The previously reported BODIPY core based donor molecules having different structural units with variety of designs, such as D- $\pi$ -D, A-D-A, D- $\pi$ -A- $\pi$ -D and D-A- $\pi$ -A-D, showed absorption in the range of 300-750 nm with two absorption bands at around 300-480 nm and 560-750 nm. In our case, **BODIPY-DTF** with D- $\pi$ -A- $\pi$ -D design template shows a broader absorption profile ranging from 300 to 800 nm with three major peaks at 376, 458 and 627 nm. This will definitely ensure higher light coupling with solar spectrum compared to other BODIPY donors. Higher light absorption efficiency ( $\eta_A$ ) is expected to increase the overall power conversion efficiency ( $\eta$ ) of a solar cell as  $\eta = \eta_A \eta_{ED} \eta_{CT} \eta_{CC}$ .

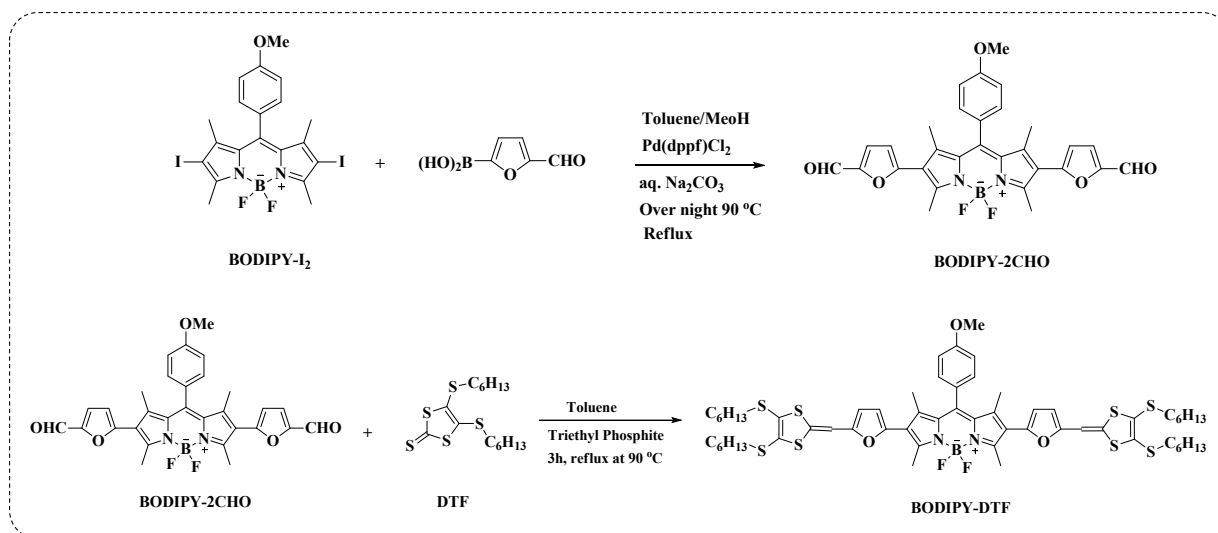
The earlier reported BODIPY based donors, which showed PCEs up to 4.7%, have different electron donating end groups such as carbozyl triphenylamine, benzanulated derivatives and n-hexyls bithiophenes; and variety of  $\pi$ -spacers such as thiophenes, acetylenes. Herein we have associated BODIPY with electron rich dithiafulvalene (DTF) end cap, which has more number of sulphur atoms and  $\pi$ -electrons. A strong  $\pi$ - $\pi$  and S-S interaction is also present in the DTF moiety. It forms a comparatively more stable and efficient charge transfer complex with popular electron acceptors in solar cells.<sup>1,2</sup> The  $\pi$ -spacer furan, which bridges the central BODIPY unit and DTF wing, has good oxidation potential.<sup>3</sup> Attachment of four hexyl chains improves the solubility of the resultant molecule in common organic solvents. This eventually helps in getting smooth film morphology with low roughness, which is beneficial for charge transport and collection. A well balanced hole and electron mobility has also been observed in our thermally annealed solar cell devices prepared from **BODIPY-DTF:PC<sub>71</sub>BM** blends. In summary, a broader absorption spectrum, unique electronic features of DTF unit, smooth morphology of photo-active layer and well-balanced hole and electron mobility altogether drove the molecule towards reaching a high efficiency.

**Table S1.** Photovoltaic parameters of the devices made from the molecules displayed in **Figure 1** as reported in the literature.

S/n	D:A	$J_{sc}$ (mA·cm <sup>-2</sup> )	$V_{oc}$ (V)	$ff$	PCE (%)	References
1	TAC:PC <sub>61</sub> BM	7.88	0.81	0.31	2.0	RSC Adv., 2015,5, 32283-32289
2	Donor: PC <sub>61</sub> BM	4.4	0.75	0.44	1.3	Chem. Commun., 2009, 1673-1675
3	bDIP:PC <sub>61</sub> BM	8.7	0.81	0.64	4.5	ACS Appl. Mater. Interfaces 2015, 7, 662-669
4	F-TBF:PC <sub>71</sub> BM	8.2	0.98	0.39	3.2	Chem. Commun., 2012, 48, 8913-8915
5	t-2,7-CBC: PC <sub>71</sub> BM	7.5	0.92	0.36	2.5	Chem. Commun., 2012, 48, 8913-8915
6	DIMER:PC <sub>71</sub> BM	11.2	0.74	0.37	3.1	ACS Appl. Mater. Interfaces 2014, 6, 22496-22505
7	H-T-BO:PC <sub>71</sub> BM	6.8	0.67	0.34	1.5	ACS Appl. Mater. Interfaces 2014, 6, 22496-22505
8	Br-T-BO:PC <sub>71</sub> BM	7.6	0.72	0.35	1.9	ACS Appl. Mater. Interfaces 2014, 6, 22496-22505
9	TB2:PC <sub>61</sub> BM	14.3	0.70	0.47	4.7	J. Am. Chem. Soc., 2012, 134 (42), pp 17404-17407

## S2. Synthetic procedure

The synthetic route of the molecule is demonstrated in **Scheme S1**. All materials were purchased directly from commercially available sources and used as it is without any further purification and solvents were made anhydrous. Intermediate molecules were characterized by NMR and mass spectrometry along with the final product and corresponding spectra are shown in **Figure S1-S5**. NMR (<sup>1</sup>H and <sup>13</sup>C) spectra were measured with Avance ACP-400 or, AMX2-500 spectrometers at 400 and 500 MHz, respectively using tetramethylsilane (TMS) as an internal standard. High resolution mass spectra were measured using an instrument from Shimadzu (model LCMS-2010 EV) with ESI probe.



**Scheme S1.** Synthetic routes of **BODIPY-DTF**.

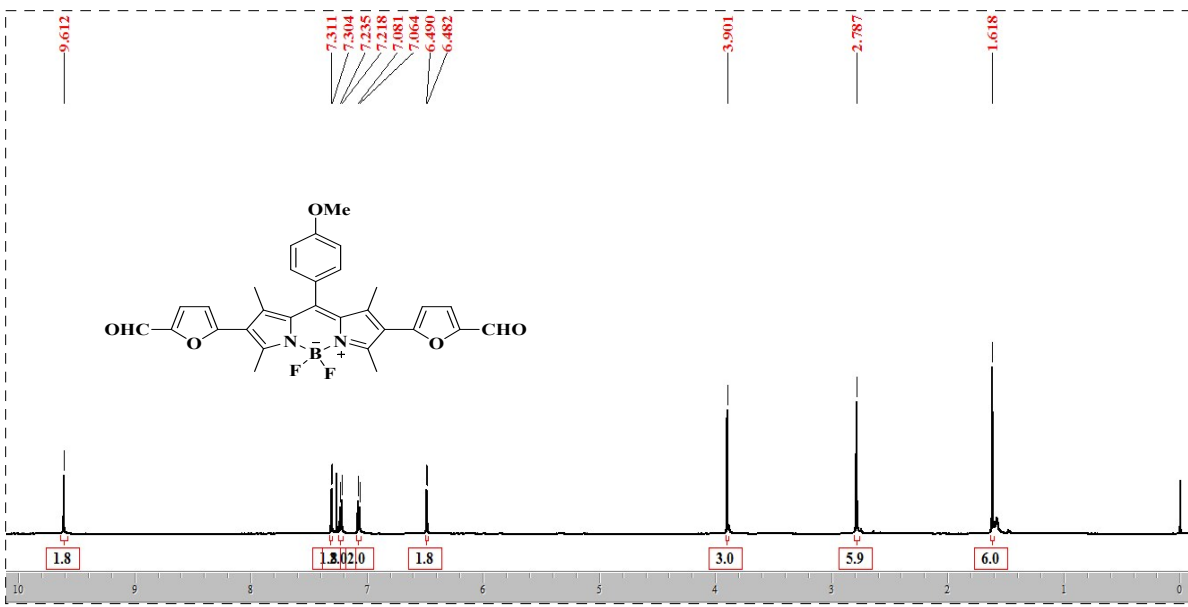
5,5-difluoro-2,8-diiodo-10-(4-methoxyphenyl)-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1.3.2]diazaborinin-4ium-5-uide (**BODIPY-I<sub>2</sub>**) was synthesized according to reported procedures.<sup>4</sup>

5,5-difluoro-2,8-bis(5-formylfuran-2-yl)-10-(4-methoxyphenyl)-1,3,7,9-tetramethyl-5-H-dipyrrolo[1,2-c:2',1'-f][1.3.2]diazaborinin-4ium-5-uide (**BODIPY-2CHO**):

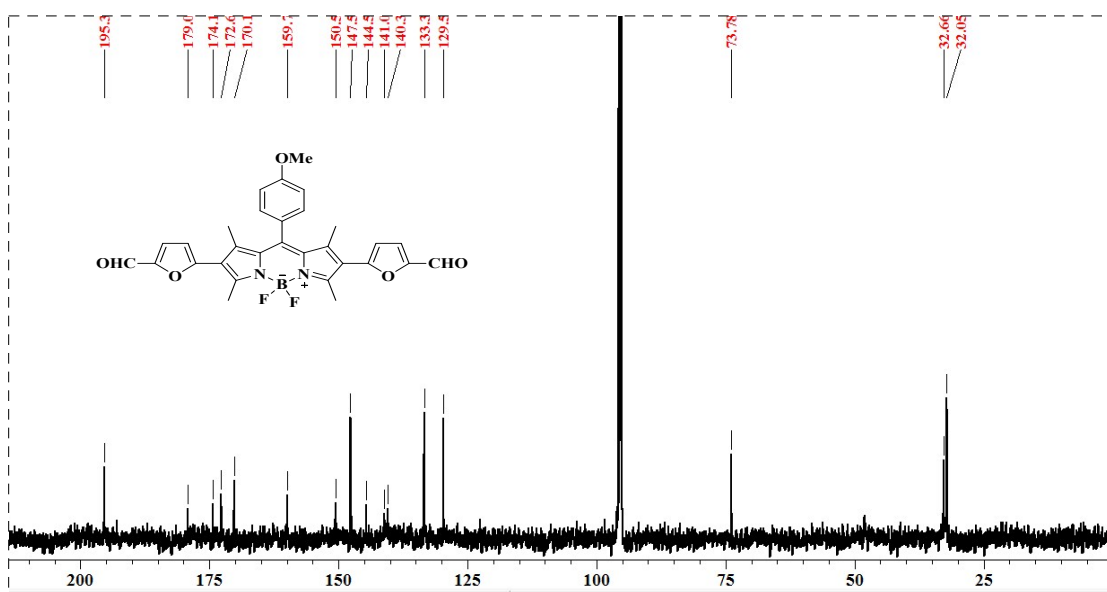
**BODIPY-I<sub>2</sub>** (200 mg, 0.33 mmol), 5-Formyl furan boronic acid (137mg, 0.99 mmol) [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II)]Pd(dppf)Cl<sub>2</sub> (3 mg, 0.033 mmol) and Na<sub>2</sub>CO<sub>3</sub> (210 mg, 2 mmol, 2ml) were taken in a round bottom flask with mixture of toluene (30 mL) and methanol (10 mL) and degassed the reaction mixture about 15 minutes. The reaction carried out at 90 °C for 12h under nitrogen atmosphere. After completion of the reaction, solvent was removed under vacuum and then the residue was dissolved in dichloromethane and washed with water. Organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The filtrate was concentrated under reduced pressure and the crude product was purified by column chromatography (eluent: EtOAc/Hexane 15:85) to furnish **BODIPY-2CHO** (60 mg, 33%) as a black solid. m.p.110 °C. IR (KBr),  $\nu$  (cm<sup>-1</sup>): 3421, 2923, 1673. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.61 (s, 2H), 7.30 (d, *J* = 2.8 Hz, 2H), 7.22 (d, *J* = 6.8 Hz 2H), 7.07(d, *J* = 6.8 Hz, 2H), 6.48 (d, *J* = 3.2Hz, 2H), 3.9 (s, 3H), 2.78 (s, 6H), 1.61(s, 6H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$ = 196.4, 180.20, 175.3, 173.7, 171.28, 163.69, 160.9, 151.6, 148.7, 145.7, 142.11, 141.4, 134.4,

130.7, 74.9, 49.1, 33.7, 33.1 ppm. ESI-MS  $m/z$ : calculated for  $C_{30}H_{25}BF_2N_2O_5$ ,  $[M + H]^+$   $m/z$  542.3377, found 543.00.

**BODIPY-DTF** (2,8-bis(5-((4,5-bis(hexylthio)-1,3-dithiol-2-ylidene)methyl)furan-2-yl)-5,5-difluoro-10-(4-methoxyphenyl)-1,3,7,9-tetramethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide): BODIPY-2CHO (30mg, 0.05mmol), 4,5-bis(hexylthio)-1,3-dithiole-2-thione (DTF, 55mg, 0.16 mmol) were dissolved in toluene (10ml) and refluxed for 40 minutes under nitrogen atmosphere, after that triethylphosphite ( $P(OEt)_3$ ) was added drop wise to reaction mixture through syringe and refluxed 3-4 h. After that reaction mixture was monitored by TLC and reaction mixture was extracted with DCM (Dichloromethane) and washed with brine solution and dried with anhydrous sodium sulphate. Solvent was evaporated under vacuum and the crude was purified by column chromatography on silica gel using petroleum ether: Ethyl acetate (95:5) as an eluent. BODIPY-DTF, green solid. Yield 32 mg (76%). m.p. 148-150 °C. IR (KBr),  $\nu$  ( $cm^{-1}$ ) : 3447, 2955, 2923, 1743, 1607. $^1H$  NMR(500MHz,  $CDCl_3$ )  $\delta$ = 7.23 (d,  $J$  = 10 Hz, 2H), 7.03 (d,  $J$  = 5 Hz, 2H), 6.32 (s 2H), 6.30 (d,  $J$  = 3.5Hz, 2H), 6.17 (d,  $J$  = 3.5Hz, 2H), 3.8 (s, 3H), 2.82-2.78 (m, 8H), 2.76 (s, 6H), 1.66-1.60, (m 8H) 1.54 (s, 6H), 1.43-1.37 (m, 8H) 1.30-1.25 (m, 20H), 0.90-0.80 (m, 12H) ppm.  $^{13}C$  NMR (125MHz,  $CDCl_3$ )  $\delta$  = 178.7, 173.4, 169.3, 1165.2, 160.6, 157.0, 150.2, 149.1, 147.8, 145.4, 145.0, 144.8, 141.5, 133.0, 129.0, 126.0, 120.6, 73.6, 54.4, 54.3, 49.6, 48.0, 46.5, 40.8, 32.3, 31.9, 19.3, 18.3 ppm. HRMS  $m/z$ : calculated for  $C_{60}H_{77}BF_2N_2O_3S_8$   $[M+H]^+$   $m/z$  1179.5928, found 1179.3833.



**Figure S1.** <sup>1</sup>H NMR spectra of BODIPY-2CHO recorded in CDCl<sub>3</sub>.



**Figure S2.** <sup>13</sup>C NMR spectra of BODIPY-2CHO recorded in CDCl<sub>3</sub>.

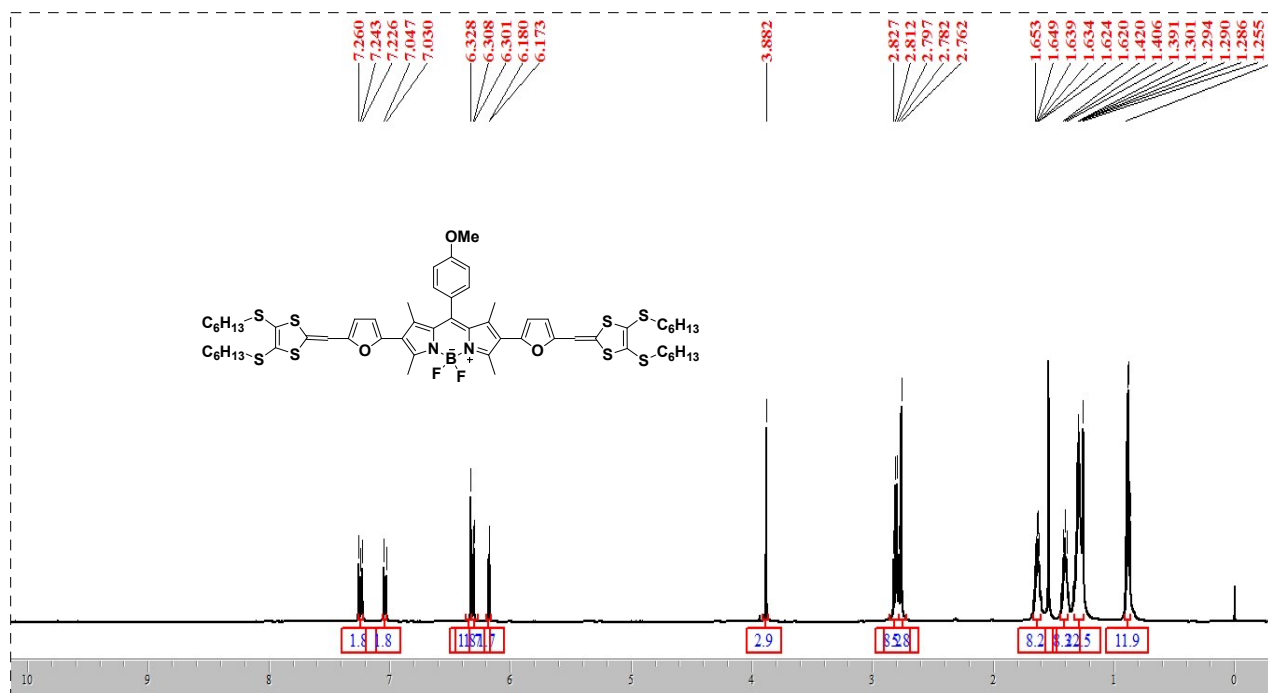


Figure S3. <sup>1</sup>H NMR spectra of BODIPY-DTF recorded in CDCl<sub>3</sub>.

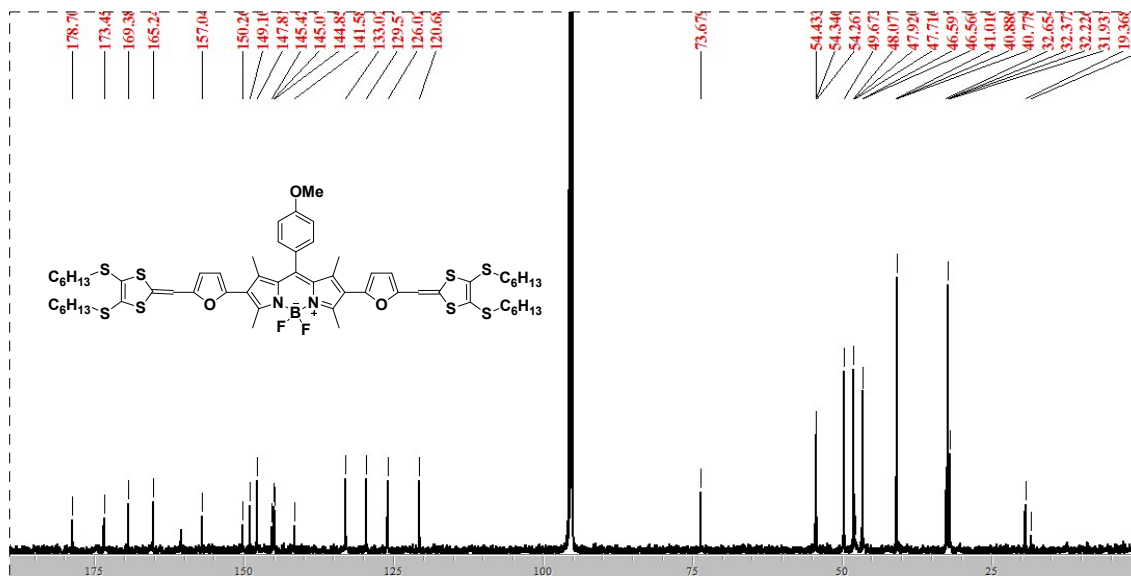
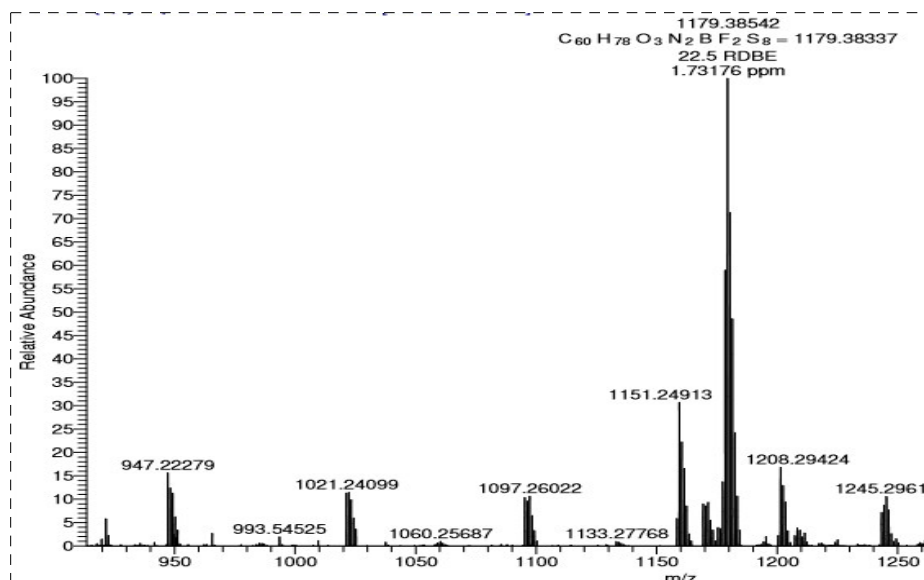


Figure S4. <sup>13</sup>C NMR spectra of BODIPY-DTF recorded in CDCl<sub>3</sub>.

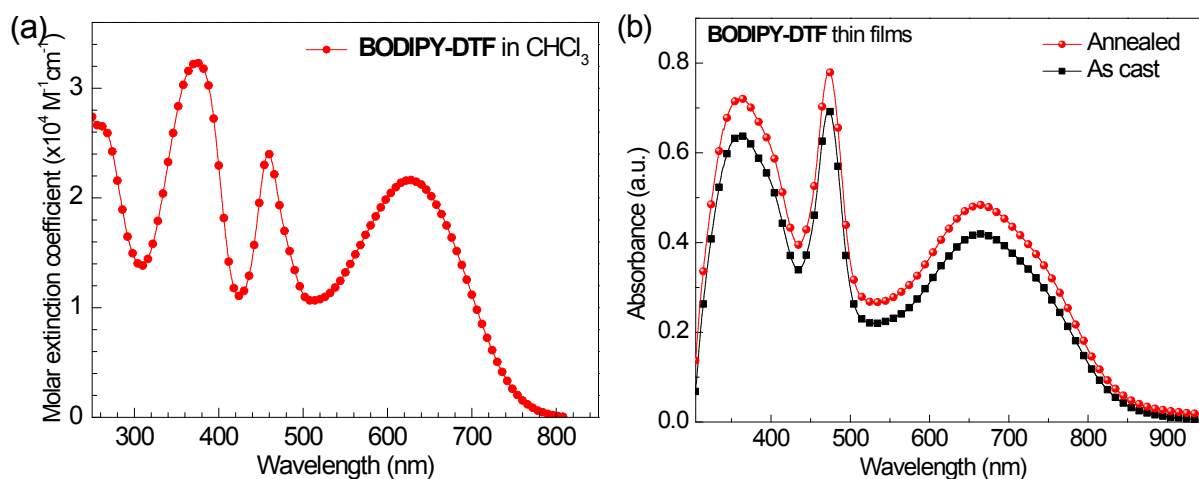




**Figure S5.** HRMS spectra of **BODIPY-DTF**.

### S3. UV-visible absorption spectroscopy

The UV-visible spectrophotometer from Shimadzu (model number UV-1800) was used to record the absorption spectra of **BODIPY-DTF** in chloroform ( $CHCl_3$ ) solution and thin films. **Figure S6a** shows the evolution of the molar extinction co-efficient ( $\epsilon$ ) of **BODIPY-DTF** with wavelength as recorded in  $CHCl_3$ .



**Figure S6.** (a) Molar extinction co-efficient ( $\epsilon$ ) of **BODIPY-DTF** vs. wavelength as recorded in  $CHCl_3$ , (b) effect of thermal annealing on the absorption properties of **BODIPY-DTF** dye.

#### S4. Density Functional Theory calculation

In order to visualize the distribution of frontier molecular orbital levels associated with new donor molecule, *ab initio* calculations were performed based on time dependent-density functional theory (TD-DFT) at B1LYP level using 6-311g (d, p) basis set in Gaussian software. **Figure S7** demonstrates the distribution of frontier molecular orbitals of **BODIPY-DTF**. The major allowed transitions in the wavelength range between 450 to 800 nm have been reported in **Table S2**.

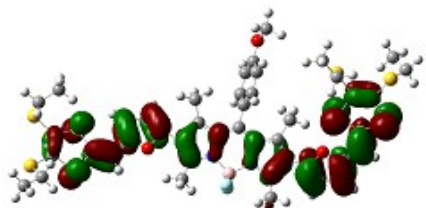
**Table S2.** Major allowed transitions in the range of 450-800 nm of **BODIPY-DTF** calculated at B1LYP/6-311g (d,p) level of theory in DCM solvent.

Excited state	$\lambda$ (nm)	Osc. Strength ( <i>f</i> )	Major contributions
S1	653	0.554	HOMO $\rightarrow$ LUMO (99%)
S2	588	0.0808	HOMO-1 $\rightarrow$ LUMO (99%)
S3	430	0.9987	HOMO-2 $\rightarrow$ LUMO (90%),
S4	400	0.0534	H-5 $\rightarrow$ LUMO (11%), H-4 $\rightarrow$ LUMO (57%), H-3 $\rightarrow$ LUMO (29%)
S5	379	0.2209	H-1 $\rightarrow$ L+1 (11%), H-1 $\rightarrow$ L+2 (10%), HOMO $\rightarrow$ L+1 (41%), HOMO $\rightarrow$ L+2 (13%), HOMO $\rightarrow$ L+4 (10%)
S6	375	0.3838	H-5 $\rightarrow$ LUMO (12%), H-4 $\rightarrow$ LUMO (11%), H-3 $\rightarrow$ LUMO (11%), HOMO $\rightarrow$ L+2 (21%)
S7	371	0.0781	H-1 $\rightarrow$ L+3 (32%), HOMO $\rightarrow$ L+3 (33%)
S8	368	0.1121	HOMO $\rightarrow$ L+2 (12%), HOMO $\rightarrow$ L+4 (22%)
S9	365.5841	0.0225	H-5 $\rightarrow$ LUMO (53%)
S10	364.263	0.1558	H-3 $\rightarrow$ LUMO (31%), HOMO $\rightarrow$ L+4 (12%)

The electron density distributions of the frontier and important molecular orbital are shown along with percentage contribution of groups to each molecular orbital calculated at B1LYP/6-311g (d,p) level of theory in DCM solvent (Figure S7). The plot depicts that the electron densities of HOMO is localized on BODIPY (20%), FURAN (34%), and DTF (47%). The HOMO-1 is distributed on BODIPY (10%), FURAN (32%), DTF (57%) and HOMO-2 is localized on BODIPY (69%), FURAN (4%) and DTF (27%). LUMO is mainly localized on BODIPY (94%), FURAN (4%) and less on DTF (2%) moiety. LUMO+1 is localized on

BODIPY (4%), FURAN (14%) and mostly on DTF (81%). LUMO+2 is localized on BODIPY (9%), FURAN (31%), DTF (60%).

#### HOMO



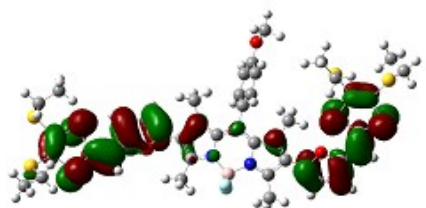
BODIPY (20%), FURAN (34%), DTF (47%)

#### LUMO



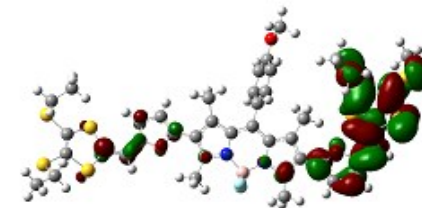
BODIPY (94%), FURAN (4%), DTF (2%)

#### HOMO - 1



BODIPY (10%), FURAN (32%), DTF (57%)

#### LUMO + 1



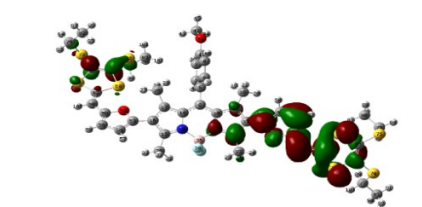
BODIPY (4%), FURAN (14%), DTF (81%)

#### HOMO - 2



BODIPY (69%), FURAN (4%), DTF (27%)

#### LUMO + 2



BODIPY (9%), FURAN (31%), DTF (60%)

**Figure S7.** Distribution of frontier molecular orbitals of **BODIPY-DTF** as estimated by density functional theory calculation at B1LYP/6-311g (d,p) level.

### S5. Cyclic Voltammetry

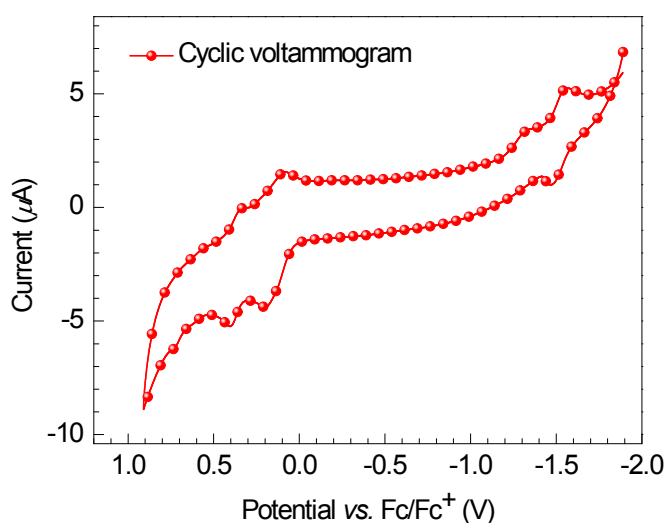
Cyclic voltammetry was performed using an electrochemical analyzer from CH Instruments with a three electrode system consisting of *Ag/AgCl* reference electrode, a working electrode and a platinum wire counter-electrode. The redox potentials of the dyes were measured in chloroform containing 0.1 M tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NHClO}_4$ ) as a supporting electrolyte at a scan rate of  $100 \text{ mV}\cdot\text{s}^{-1}$ . The cyclic voltammogram as illustrated in **Figure S8** shows one reduction and two oxidation peaks, which can be ascribed to the reduction of the

central BODIPY unit and taking an electron out from the DTF and furan units, respectively. The values of frontier molecular orbital energy levels of **BODIPY-DTF** are estimated from the following equations,

$$E_{\text{HOMO}} \text{ (eV)} = - [E_{\text{ox}} - E_{(\text{Fc}/\text{Fc}^+)} + 4.8] \quad (\text{S1})$$

$$E_{\text{LUMO}} \text{ (eV)} = - [E_{\text{red}} - E_{(\text{Fc}/\text{Fc}^+)} + 4.8] \quad (\text{S2})$$

The HOMO and LUMO energy levels of **BODIPY-DTF** are estimated to be -4.93 and -3.28 eV, respectively.



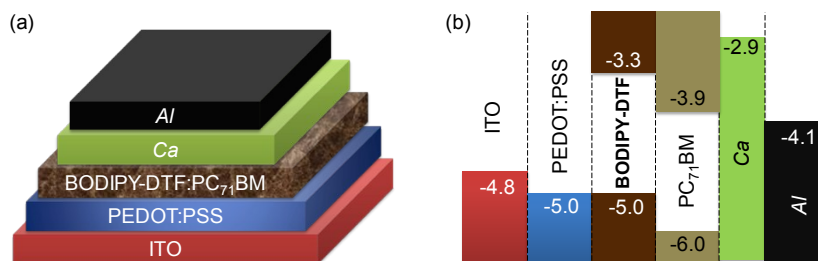
**Figure S8.** Cyclic voltammogram of **BODIPY-DTF** in chloroform containing tetrabutylammonium perchlorate ( $0.1 \text{ mol}\cdot\text{L}^{-1}$ ) measured at a scan rate of  $100 \text{ mV s}^{-1}$ .

## S6. Device fabrication and characterization

### Fabrication of Organic Solar Cells

Commercially available indium tin oxide (ITO) coated glass substrates with sheet resistance about  $20 \Omega\cdot\text{cm}^{-1}$  were used for device fabrication. The substrates were rinsed properly with soap solution and then ultrasonicated in deionized water, acetone and propan-2-ol sequentially for 15 min for each case at an elevated temperature. Substrates were dried overnight inside an oven. Glasses were then exposed to ultraviolet ozone irradiation for 15 min. The **BODIPY-DTF** molecule was tested as electron donor material in a BHJ active layer, following the

standard device structure of ITO/PEDOT:PSS/active layer/*Ca*/*Al* as shown in **Figure S9a**. Firstly, 90 nm thick PEDOT:PSS layer was coated on top of UV treated ITO substrate to form anode. The concentration of the donor in the chloroform was 5 mg/ml with various concentration of the PC<sub>71</sub>BM and the optimum weight ratio of donor and acceptor was found to be 1:3. About 0.5 vol% of 1,8-diiodooctane (DIO) was mixed in the photoactive solution as additive. Active layers were spin-coated using the as-prepared solutions at 1500 rpm in a glove box. The photoactive layer film thickness was measured to be 100 nm. Finally, 4 nm calcium (*Ca*) and 100 nm aluminum (*Al*) cathode was thermally evaporated. The active device area was 10 mm<sup>2</sup> as defined by a shadow mask. The fabricated solar cells were encapsulated using epoxy and cover glasses and cured under ultraviolet irradiation for 15 min. **Figure S9b** schematically illustrates the energy band diagram corresponding to the device.



**Figure S9.** (a) Device structure and (b) energy band diagram of the organic solar cell fabricated to study the photovoltaic performance of newly developed small molecular donor.

### Characterization

The photovoltaic performance on the solar cells were measured at 1 sun illumination, *i.e.*, 1000 W·m<sup>-2</sup> light intensity using a solar simulator from SCIENCETECH (model-SS 150, class-AAA) at room temperature. The light intensity of simulated AM 1.5G irradiance originating from a xenon bulb was calibrated using a National Renewable Energy Laboratory (NREL) certified silicon based reference solar cell before every measurement. A Keithley 2420 source meter was utilized for acquiring current *vs.* voltage data. The topological images of **BODIPY-DTF:PC<sub>71</sub>BM** bulk composite films were captured by atomic force microscopy instrument from Bruker AXS (multimode V, NS V) in the tapping mode and a resonant frequency of 310 kHz was set for AFM tip during scanning.

**Table S3.** Photovoltaic parameters extracted from light  $J$ - $V$  characteristics of the OSCs fabricated under different conditions. The value of  $J_{sc}$ , calculated by integrating the IPCE curve in the wavelength ( $\lambda$ ) range 300–900 nm using the following expression,  $J_{sc} = \int IPCE(\lambda) d\lambda$ .

D:A	Treatment	$J_{sc}$ (mA·cm <sup>-2</sup> )	$J_{sc}$ (IPCE)	$V_{oc}$ (V)	$FF$	$PCE$ (avg.) (%)
1:1	As cast	11.84	11.77	0.788	0.453	4.2 (3.9)
1:2	As cast	12.13	12.05	0.789	0.497	4.8 (4.5)
1:3	As cast	12.83	12.75	0.786	0.520	5.3 (5.1)
1:4	As cast	12.29	12.18	0.784	0.511	4.9 (4.6)
1:3	Annealed	13.92	13.87	0.787	0.663	7.2 (7.1)
1:4	Annealed	12.79	12.71	0.789	0.584	5.9 (5.6)

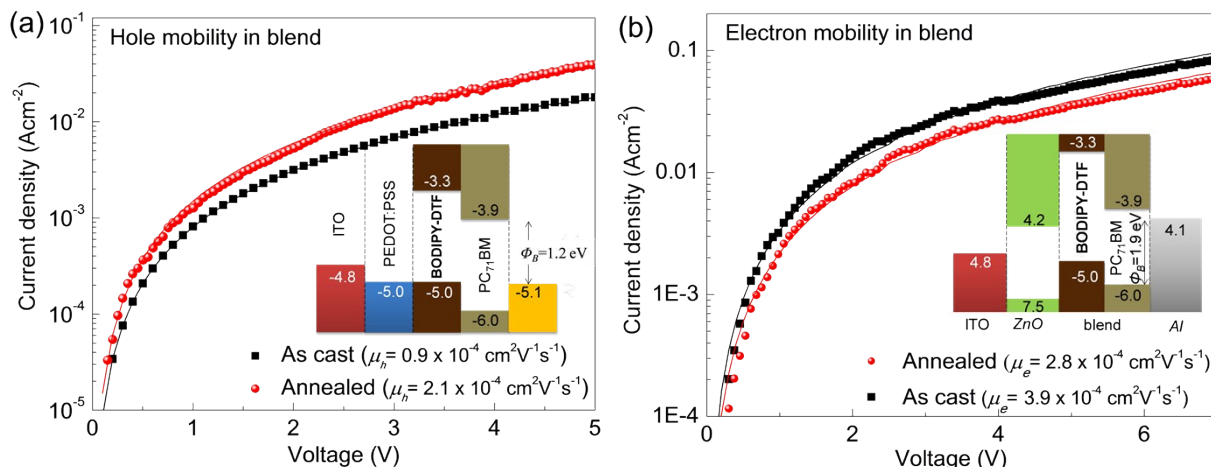
### S7. Charge carrier mobility

To estimate the hole mobility ( $\mu_h$ ) of **BODIPY-DTF** in the blend film, single carrier hole only devices with device structure of ITO/PEDOT:PSS/**BODIPY-DTF**:PC<sub>71</sub>BM/Au were fabricated. Similarly, ITO/ZnO/**BODIPY-DTF**:PC<sub>71</sub>BM/Al based electron-only devices were made to find electron mobility ( $\mu_e$ ) of PC<sub>71</sub>BM in the blend film. The dark  $J$ - $V$  characteristics of ‘as cast’ and thermally ‘annealed’ single carrier devices are shown in **Figure S10**. The experimental data are fitted (continuous line) with Mott–Gurney’s space charge limited current (SCLC) model,

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \quad (S3)$$

where  $\varepsilon_0$  is the free space permittivity,  $\varepsilon_r$  is relative permittivity, and  $d$  is the film thickness. The estimated values of  $\mu_e$  and  $\mu_h$  for both the cases are reported in **Table S4**. The hole mobility of **BODIPY-DTF** in blend is found to be higher in case of thermally annealed films compared to that of as cast film. However, electron mobility of PC<sub>71</sub>BM decreases with thermal annealing probably because of segregation nature of fullerenes. Interestingly, the ratio

of mobilities approaches to unity ( $\mu_e/\mu_h = 1.3$ ) with annealing from 4.3 for as cast films. A well-balanced hole and electron mobility promotes charge transport mechanism in the device and helps in getting higher fill factor, which has been reflected in our device performance.



**Figure S10.** Mott-Gurney's SCLC fitting to calculate (a) hole mobility of **BODIPY-DTF** and (b) electron mobility of PC<sub>71</sub>BM in the 'as cast' and 'annealed' films. **Inset:** energy band diagrams of corresponding single carrier devices.

**Table S4.** Charge transport parameters of **BODIPY-DTF** and PC<sub>71</sub>BM as obtained from single carrier devices.

D:A	Treatment	$\mu_h$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_e$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_e/\mu_h$
1:3	As cast	$0.9 \times 10^{-4}$	$3.9 \times 10^{-4}$	4.3
1:3	Annealed	$2.1 \times 10^{-4}$	$2.8 \times 10^{-4}$	1.3

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