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SUPPORTING INFORMATION

Highly Hindered Bithiophene-functionalized Dispiro-oxepine Derivative as Efficient Hole Transporting Material for Perovskite Solar Cells

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General Information

All reagents from commercial sources were used without further purification, unless otherwise noted. All reactions were performed under dry N_2 ambience, unless otherwise noted. All dry reactions were performed with glassware that was flamed under high-vacuum and backfilled with N_2. All extracts were dried over powdered $MgSO_4$ and solvents removed by rotary evaporation under reduced pressure. Flash chromatography was performed using Silicycle UltraPure SilicaFlash P60, 40-63 μm (230-400 mesh). Thin-layer chromatography (TLC) was conducted with Merck KGaA pre-coated TLC Silica gel 60 F_{254} aluminum sheets and visualized with UV. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz), Bruker AvanceIII-400 (400 MHz), Bruker DPX-400 (400 MHz) or Bruker DRX-600 (600 MHz) spectrometer and are reported in ppm using solvent as an internal standard: Chloroform-d at 7.24 ppm and 77.23 ppm for ^1H and ^{13}C, respectively; THF-d_8 at 1.72 and 3.58 ppm for ^1H, and 25.31, 67.21 for ^{13}C, respectively. Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad, ap = apparent; coupling constant(s) in Hz; integration. MS were recorded on Thermo Fisher Q Exactive HF Hybrid Quadrupole-Orbitrap Mass Spectrometer using matrix-assisted laser desorption/ionization (MALDI) technique. UV-Vis spectra were measured with a Hewlett Packard 8453 UV-Vis spectrometer. Cyclic voltammetry (CV) was measured with an Autolab Eco Chemie cyclic voltammeter. Thermogravimetric analysis (TGA) data were collected using TGA 4000 from PerkinElmer. Differential scanning calorimetry (DSC) were recorded on DSC 8000 from PerkinElmer. For the conductivity measurement, solutions of spiro-OMeTAD and DDOF with molar concentrations of 30mM in toluene were prepared and doped with 3 mol% FK-209. The solutions were spin-coated onto OFET substrates (Fraunhofer IPMS) at 4000 rpm for 30 s inside an inert atmosphere glovebox. The conductivity measurement was carried out at room temperature on a 2.5μm channel (by length) using an in-house developed probe station inside an Argon glovebox. The channel width was 10mm and the channel height was 40nm. The data were recorded using a potentiostat from Biologic by taking a hysteresis scan from -10 to 10 V at a scan rate of 2V s^{-1}. The conductivity was calculated from linear fit (Ohm's law).

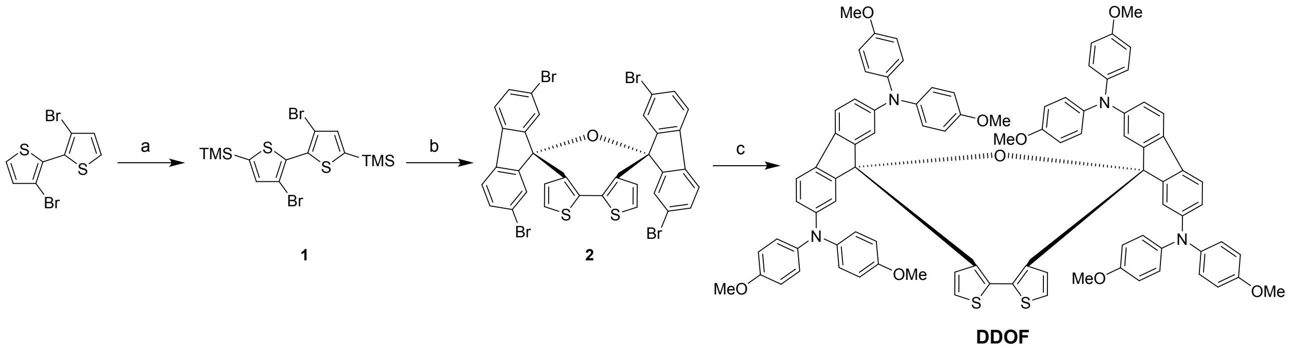
Device fabrication

Chemically etched FTO glass (Nippon Sheet Glass) was sequentially cleaned by sonication in a 2 % Helmanex solution, acetone and ethanol for 30 min each, followed by a 15 min UV-ozone treatment. To form a 30 nm thick TiO_2 blocking layer, diluted titanium diisopropoxide bis(acetylacetonate) (TAA) solution (Sigma-Aldrich) in isopropanol was sprayed at 450 ^{0}C. For the 200 nm mesoporous TiO_2 layer, mesoporous-TiO_2 layers were made by spin-coating a commercially available TiO_2 paste (Dyesol 30NRD). Substrates were baked at 500 ^{o}C for 30 min. Then, Li-doping of mesoporous TiO_2 is treated by spin coating a 0.03 M (0.1 M) solution of Li-TFSI in acetonitrile at 3000 rpm for 10 s followed by another sintering at 500 °C for 20 min before the deposition of the perovskite layer. Mixed-perovskite precursor was prepared by mixing 1.15 m PbI_2, 1.10 m FAI, 0.2 m $PbBr_2$, 0.2 m MABr in a mixed solvent of DMF:DMSO = 4:1 (volume ratio). Perovskite solutions are successively spin-coated in the glovebox as follow: first, 2000 rpm for 10 s with a ramp-up of 200 rpm s^{-1}; second, 6000 rpm for 30 s with a ramp-up of 2000 rpm s^{-1}. trifluorotoluene (110 ml) was dropped on the spinning substrate during the second spin-coating step 20 s before the end of the procedure, then films were annealed at 100 ^{0}C for 90 min. The hole-transporting materials was applied from a 20 mM solution in toluene. *Tert*-butylpyridine (Tbp), Tris(2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine)cobalt(III) (FK209) and Tris(bis(trifluoromethylsulfon-yl)imide) (Li-TFSI) were added as additives. Equimolar amounts of additives were added for hole-transporters: 330 mol% Tbp, 50 mol% Li-TFSI from a 1.8M stock solution in acetonitrile and 3 mol% FK209 from a 0.25M stock solution in acetonitrile. The final HTM solutions were spin-coated onto the perovskite layers at 4000rpm for 30s. The gold electrode of 80 nm weas deposited by thermal evaporation in high vacuum conditions.

Device characterization

The solar cells were measured using a 450 W xenon light source (Oriel). The spectral mismatch between AM1.5G and the simulated illumination was reduced by the use of a Schott K113 Tempax filter (Präzisions Glas & Optik GmbH). The light intensity was calibrated with a Si photodiode equipped with an IR-cutoff filter (KG3, Schott), and it was recorded during each measurement. Current-voltage characteristics of the cells were obtained by applying an external voltage bias while measuring the current response with a digital source meter (Keithley 2400). The voltage scan rate was 10 mV s^{-1} and no device preconditioning, such as light soaking or forward voltage bias applied for long time, was applied before starting the measurement. The starting voltage was determined as the potential at which the cells furnishes 1 mA in forward bias, no equilibration time was used. The cells were masked with a black metal mask (0.16 cm^2) to fix the active area and reduce the influence of the scattered light.

Synthetic methods and procedures



(a) $LiN(Pr\text{-}i)_2$, TMSCl, THF, -78 °C to RT; (b) *n*-BuLi, 2,7-dibromofluorenone, THF, -78 °C to RT; CH_3COOH/HCl, 110 °C; (c) 4,4'-dimethoxydiphenylamine, *t*-BuONa, Pd_2dba_3, XPhos, toluene, 110 °C.

5,5'-Bis(trimethylsilyl)-3,3'-dibromo-2,2'-bithiophene (1). To a solution of commercially available 3,3'-dibromo-2,2'-bithiophene (5 g, 15.4 mmol, 1 equiv) in dry THF (50 mL), lithium diisopropylamide, 2.0M (17 mL, 34 mmol, 2.2 equiv) was added dropwise at -78 °C. After stirring for 1 h, trimethylsilyl chloride (4.3 mL, 34 mmol, 2.2 equiv) was added dropwise at -78 °C. The reaction mixture was then allowed to warm to room temperature and stirred overnight. Water was added to quench the reaction. The resulting mixture was extracted with hexane. This crude residue was purified by flash chromatography with pure hexane. Yield: (6.5 g, 90%). Colorless needles. ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 2H), 0.37 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.81, 137.44, 134.24, 113.37, -0.36. $C_{14}H_{20}Br_2S_2Si_2$ [M^+] exact mass = 465,8912 MS (MALDI-TOF) = 465.880.

2,2",7,7"-tetrabromodispiro[fluorene-9,4'-dithieno[3,2-c:2',3'-e]oxepine-6',9"-fluorene] (2). To a solution of **1** (2 g, 4.3 mmol, 1 equiv) in 50 mL of dry THF at -78 °C under argon atmosphere, *n*-BuLi (2.5 M in hexanes, 3.6 mL, 9 mmol, 2.1 equiv) is dropwise added. After 2 h at the same temperature, 2,7-dibromofluorenone (3.65 g, 10.8 mmol, 2.5 equiv) in THF (50 mL) is added to the mixture dropwise, and the solution was warmed to room temperature and stirred overnight. The mixture was washed with water, extracted with DCM, and the combined organic phases are dried over $MgSO_4$.

The solvent is evaporated and the crude product is precipitated in ethanol to afford a white solid and is used in the next step without further purification.

Obtained solid was dissolved in boiling acetic acid (100 mL), and 1 mL of concentrated hydrochloric acid were added. After refluxing for 2 h, the mixture were washed with water and extracted with DCM, and the combined organic phases are dried over $MgSO_4$. This crude residue was purified by flash chromatography with pure 20 % DCM in hexane. (1.4 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 7.9 Hz, 4H), 7.44 (d, *J* = 8.1 Hz, 4H), 7.18 (d, *J* = 5.1 Hz, 2H), 7.09 (d, *J* = 1.5 Hz, 4H), 6.39 (d, *J* = 5.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 140.8, 137.5, 134.4, 132.4, 129.1, 128.9, 124.8, 122.2, 121.4, 88.1. $C_{34}H_{16}Br_4OS_2$ [M^+] exact mass = 819,7376 MS (MALDI-TOF) = 819.721.

2,2',7,7'-tetrakis-(N,N'-di-4-methoxyphenylamine)dispiro[fluorene-9,4'-dithieno[3,2-c:2',3'-e]oxepine-6',9''-fluorene] (DDOF). In a 50 mL Schlenk-tube, 400 mg of **2** (0.49 mmol, 1 equiv), 560 mg commercially available 4,4′-dimethoxydiphenylamine (2.5 mmol, 5 equiv), and 280 mg *t*-BuONa (2.9 mmol, 6 equiv) were dissolved in 20 mL dry toluene and degassed for 20 min with N_2. After the addition of 70 mg Pd_2dba_3 (0.075 mmol, 15%) and 70 mg Xphos (0.15 mmol, 30%), the reaction was refluxed overnight. The reaction was then diluted with DCM and flashed through a plug of $MgSO_4$ to remove inorganic salts and metallic palladium. This crude residue was purified by flash chromatography with 30% THF in hexane. Isolated compound was dissolved in THF and dropped into MeOH, precipitate was collected by filtration, washed with MeOH and dried. 420 mg (60 % yield) of pale yellow solid was obtained. ^{1}H NMR (400 MHz, THF, 267K) δ 7.28 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 8H), 6.90 (s, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 7.8 Hz, 8H), 6.69 (d, *J* = 5.2 Hz, 2H), 6.65 (s, 16H), 6.56 (d, *J* = 7.8 Hz, 2H), 6.35 (s, 2H), 6.17 (d, *J* = 5.3 Hz, 2H), 3.73 (s, 12H), 3.70 (s, 12H). ^{13}C NMR (100 MHz, THF) δ 155.89, 151.08, 150.15, 148.27, 147.25, 141.77, 141.08, 140.94, 140.92, 133.44, 133.00, 131.40, 129.27, 126.72, 125.53, 122.79, 121.94, 119.77, 118.90, 118.66, 116.72, 114.41, 87.64, 54.58. $C_{90}H_{72}N_4O_9S_2$ [M^+] exact mass = 1416,4741 MS (MALDI-TOF) = 1416.304.

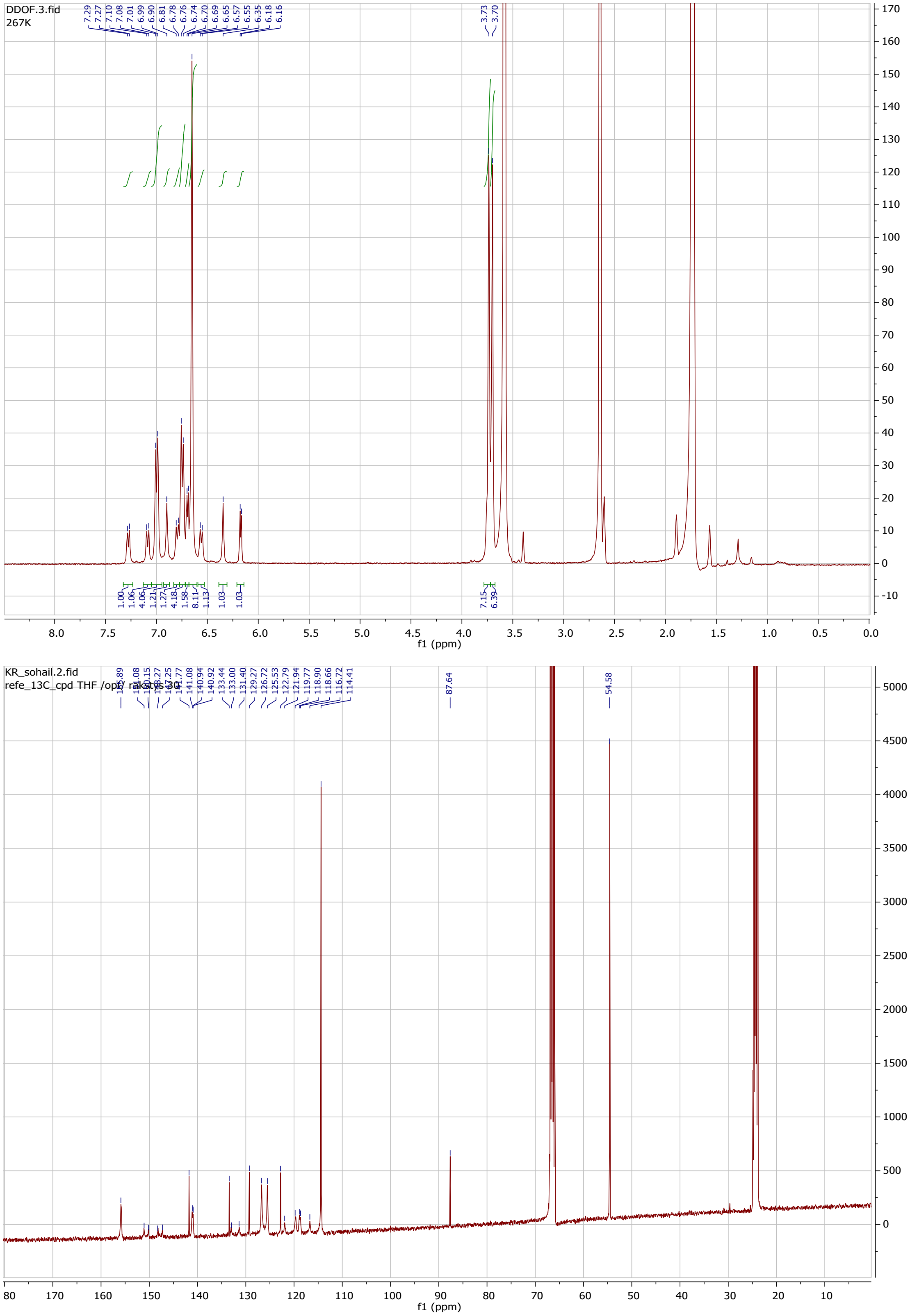


Figure S1. ^{1}H and ^{13}C NMRs of DDOF.

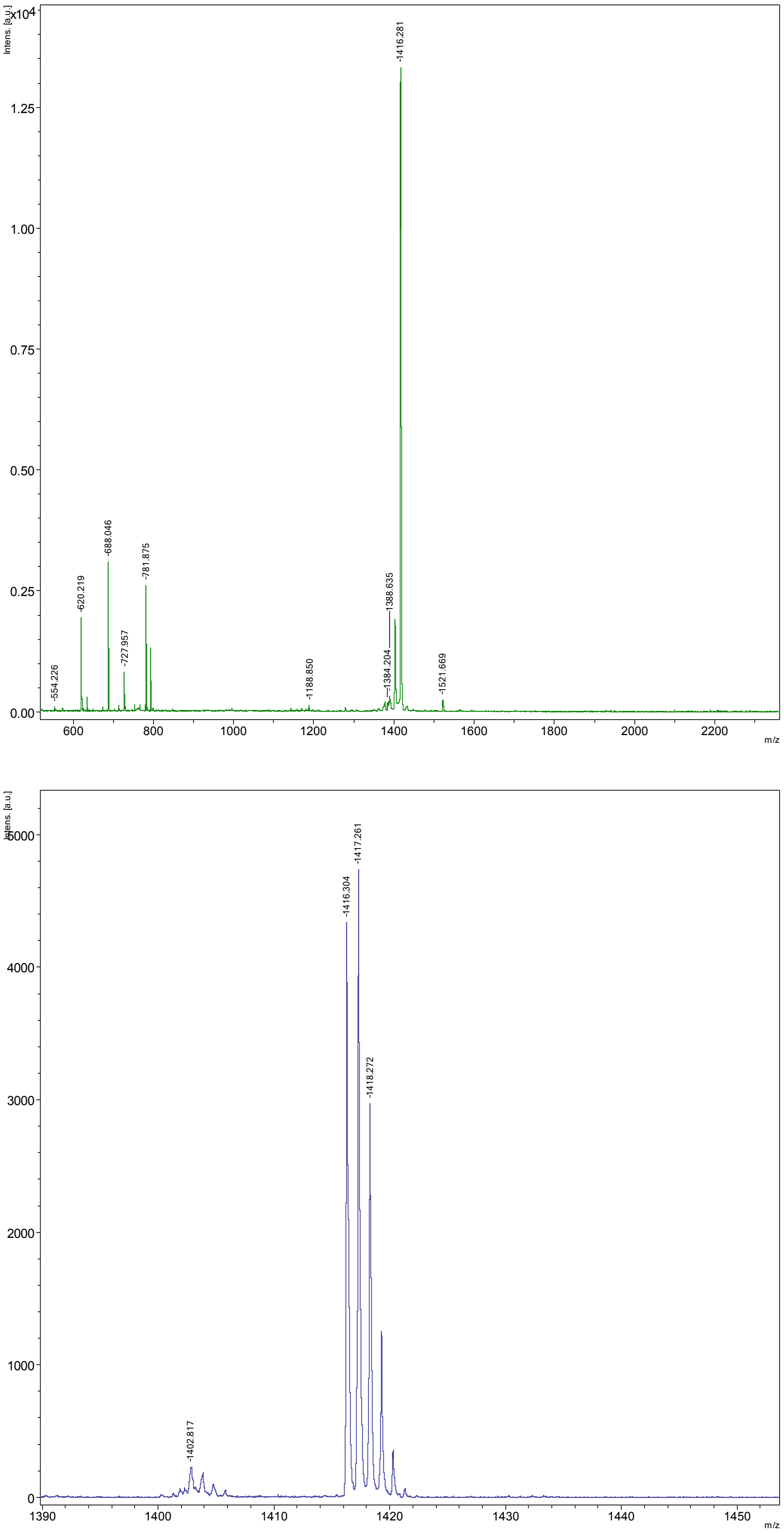


Figure S2. MALDI-TOF-MS spectra in wide and narrow mass ranges of DDOF.

Crystallographic analysis

Intensity data were collected on an Rigaku Supernova, second edition, 2015 diffractometer by using graphite-monochromatized Cu Ka radiation (λ=1.5418 Å) at room temperature [293 K]. A summary of the crystallographic data, the data collection parameters, and the refinement parameters are given in Table S1.

The data reduction was carried out by Crysalis PRO (1). The solution and refinement were performed by SHELX (2). The crystal structure was refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model.

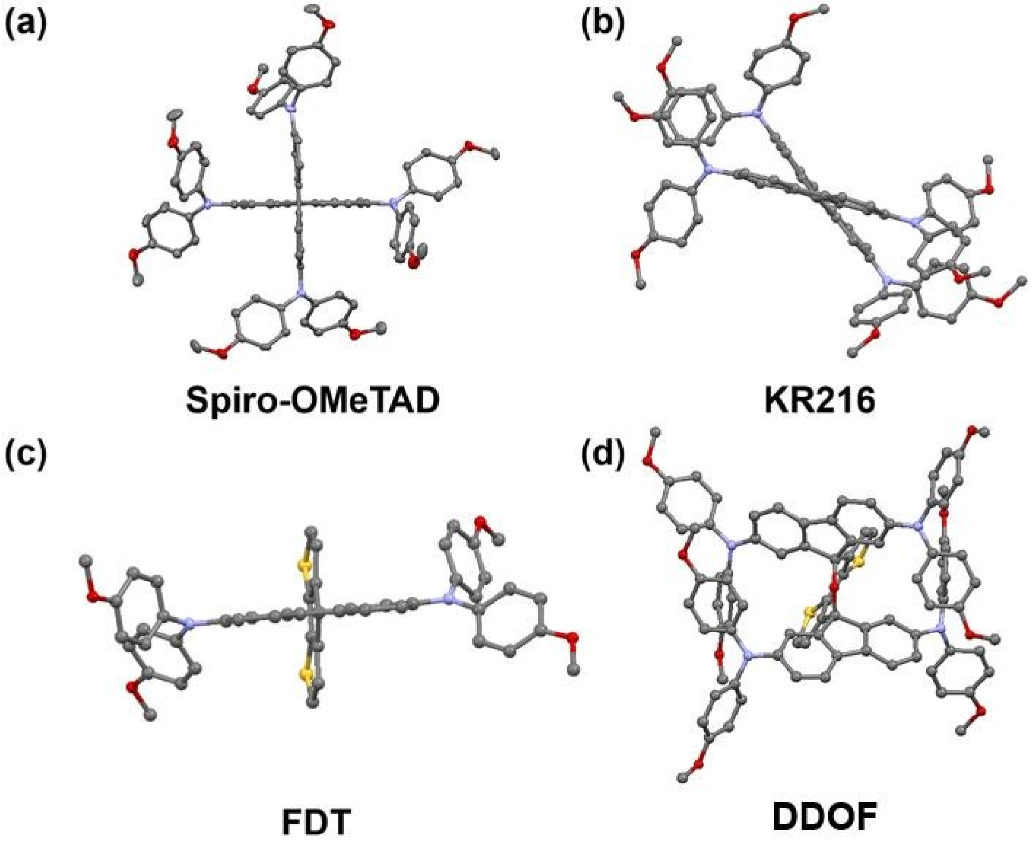


Figure S3. A direct comparison of four different HTM showing different space configuration of 2,7-diphenylamine fluorene

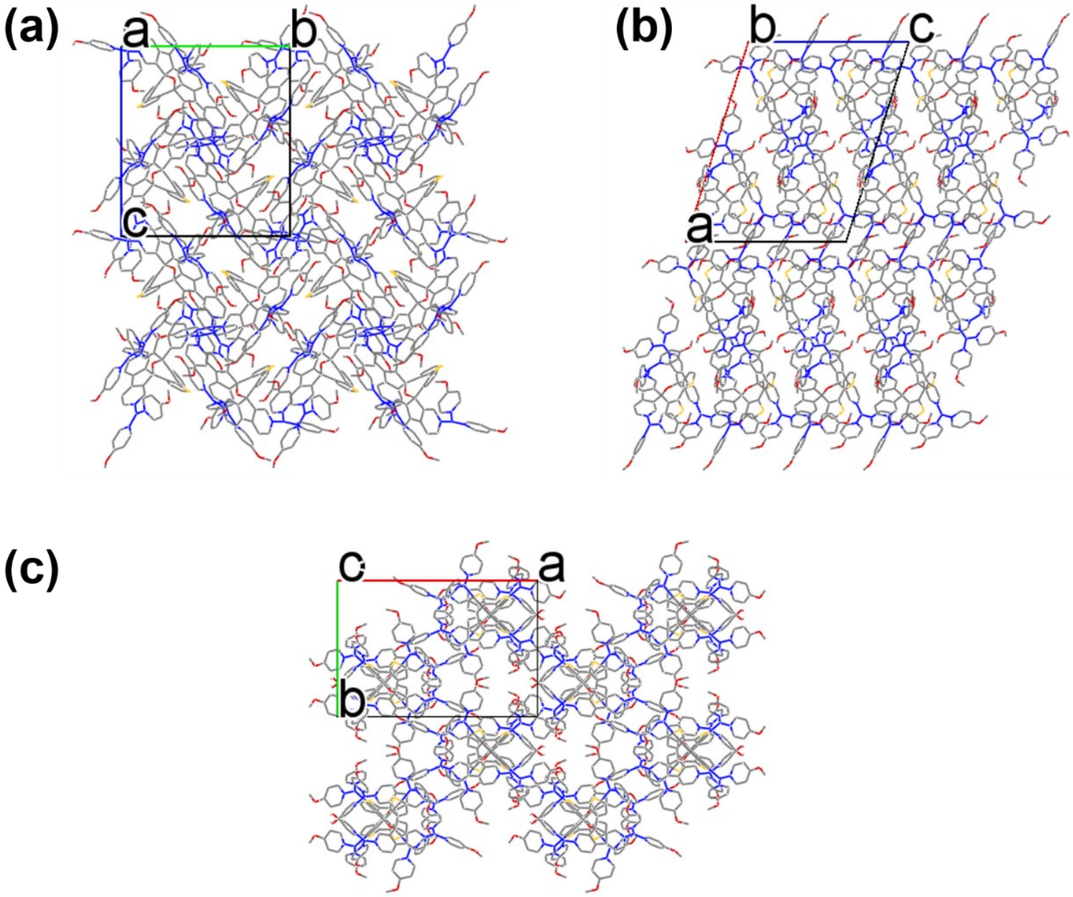


Figure S4. Packing structures of **DDOF**. The blue color indicating the self-assembled region of redox active triphenyl amine.

CCDC-1495258 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic parameters of **DDOF** and spiro-OMeTAD

	DDOF	*spiro-OMeTAD*
Empirical formula	$C_{90}H_{72}N_4O_9S_2$	$C_{81}H_{68}N_4O_8$
Formula weight	1417.71	1225.455
Crystal color, habit	Colorless, needle	Colorless, needle
Crystal system	monoclinic	triclinic
a, Å	25.4756(19)	13.1111(7)
b, Å	16.5543(11)	16.1465(7)
c, Å	19.5340(13)	16.9214(9)
α*, deg*	90	75.200(4)
β*, deg*	107.428(8)	85.670(4)
γ*, deg*	90	75.891(4)
V, Å^3	7859.91(1)	3358.57
ρ *calc, g/cm^3*	1.19792	1.267
Space group	*P 1 21/c 1 (14)*	*P -1*
Z value	4	2
Temperature, K	293 K	140
no. of reflections measured	16089	23601
no. of variables	1090	909
Residuals: R; wR2	0.0891, 0.2758	0.0419, 0.1068

Computation Methods

The geometrical and electronic properties of the compound were performed with the Gaussian 09 program package. The calculation was optimized by means of the B3LYP (Becke three parameters hybrid functional with Lee-Yang-Perdew correlation functional) with the B3LYP/6-31G* atomic basis set. The excitation transitions of **DDOF** were calculated using time-dependent density functional theory (TD-DFT) calculations with B3LYP/6-31g*. Molecular orbitals were visualized using Gaussview.

Geometry optimization

The geometry optimizations for the ground state were performed by density functional theory (DFT) at the B3LYP/6-31G* level. The frontier molecular orbitals of the molecules for the target molecule were calculated with an isovalue of 0.025 obtained by TD-DFT at the B3LYP/6-31G* level. All the DFT calculations were carried out with the Gaussian 09 package 2.

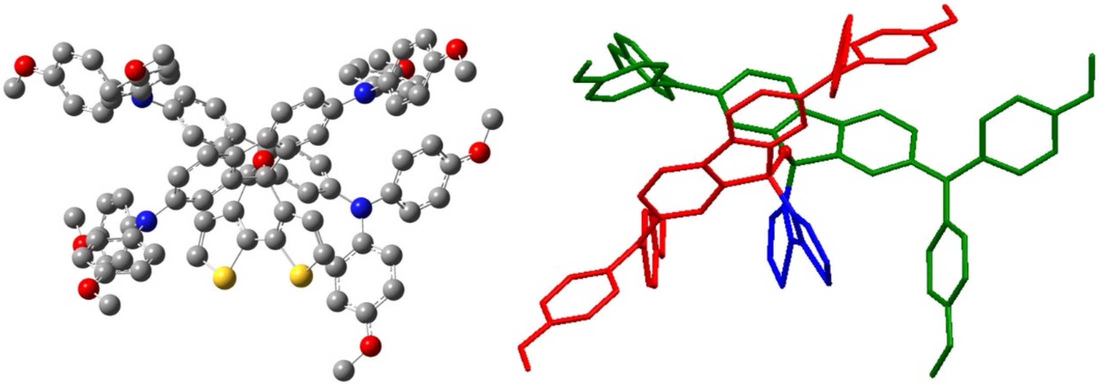


Figure S5. Geometry optimization for the ground state of **DDOF**. Different color highlighted the three conjugated moieties. (Hydrogen atoms are omitted for clarity)

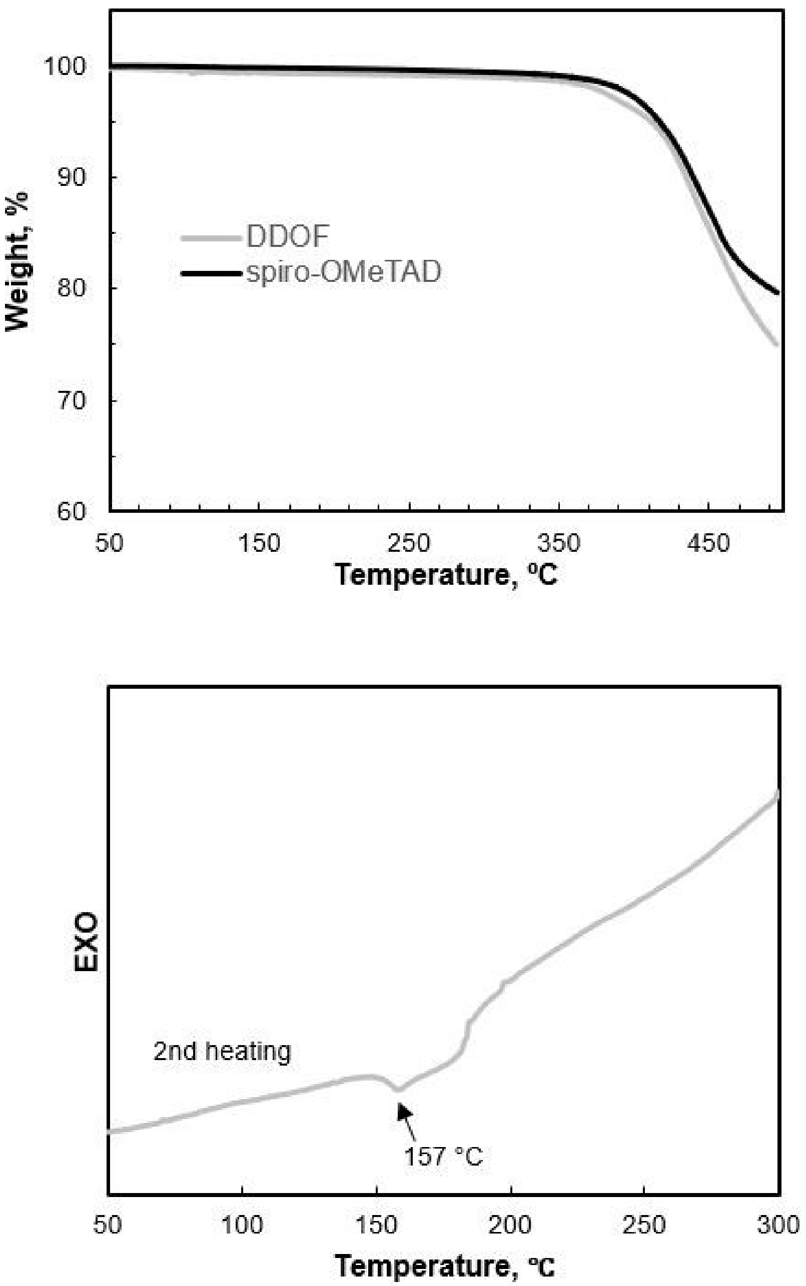


Figure S6. Thermogravimetric analysis (TGA) data of HTMs, heating rate of 10 °Cmin^{-1}, N_2 atmosphere; and DSC second heating curve of DDOF, scan rate 10 °Cmin^{-1}, Ar atmosphere.

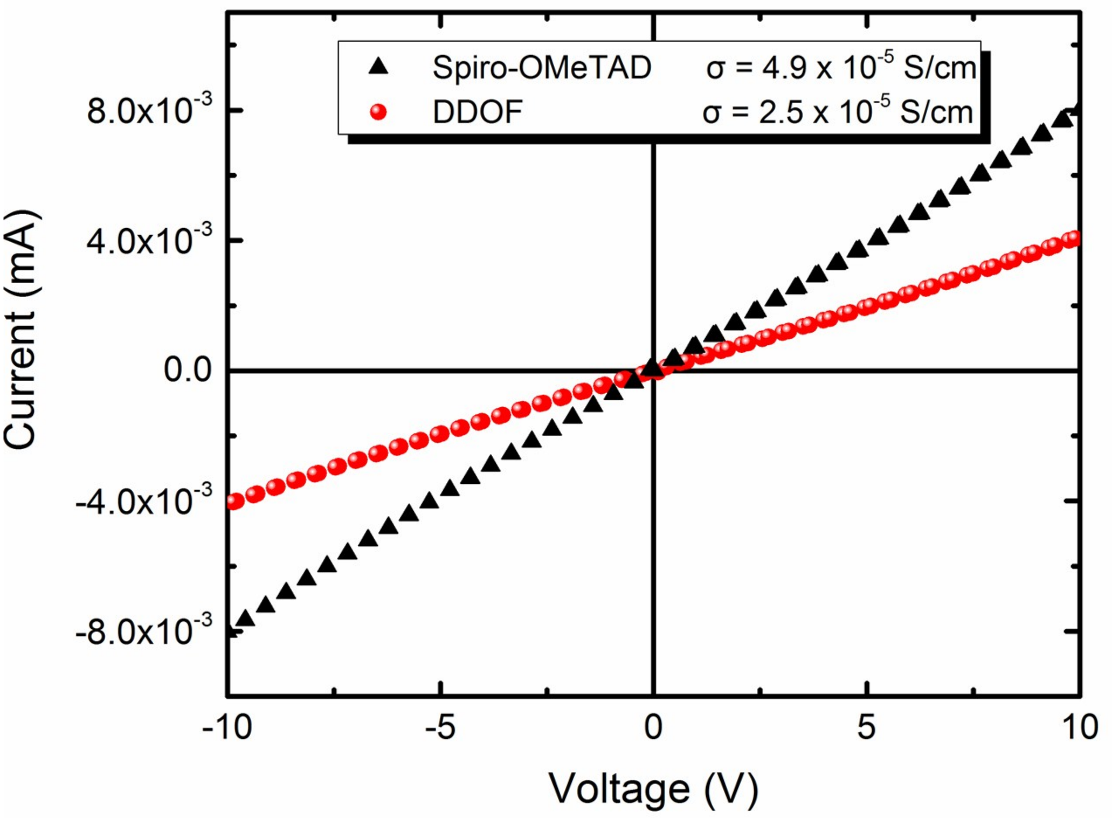


Figure S7. Conductivity measurements on OFET substrates of the HTMs.

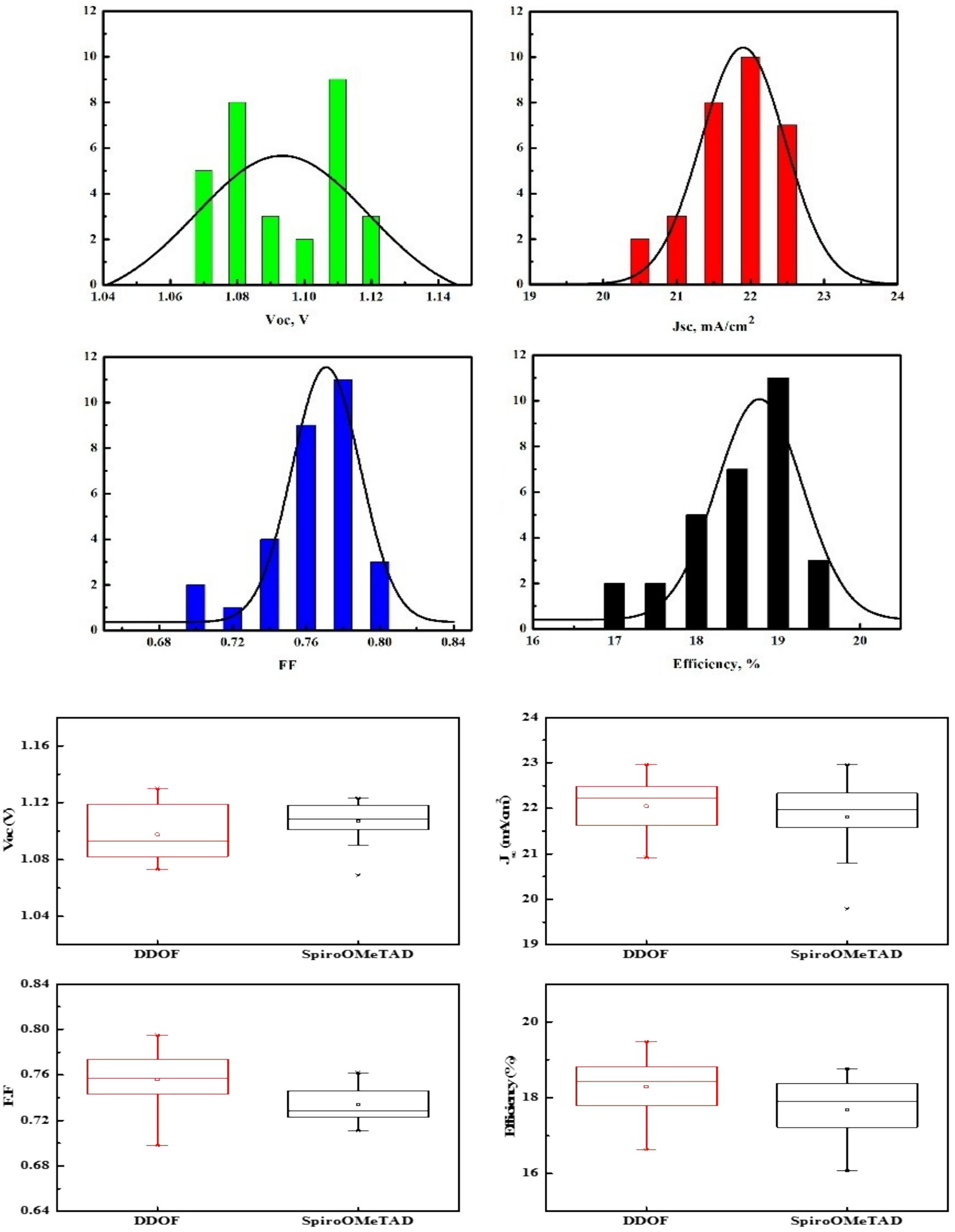
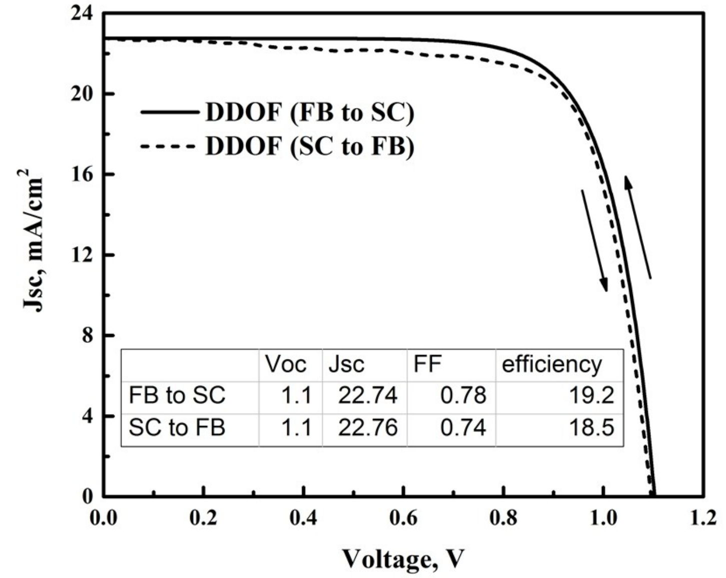


Figure S8. Statistical distribution of 30 perovskite solar cells performance with DDOF. The distribution curves are fitted by Gaussian function (top). Statistical distribution of 30 perovskite solar cells performance with DDOF and Spiro-OMeTAD (down).



	Voc	Jsc	FF	efficiency
FB to SC	1.1	22.74	0.78	19.2
SC to FB	1.1	22.76	0.74	18.5

Figure S9. Current (J)-voltage (V) curves of the solar cell with DDOF collected under AM1.5 simulated sun light. The curves were recorded scanning at 0.01 V s^{-1} from forward bias (FB) to short circuit condition (SC) and the other way round.

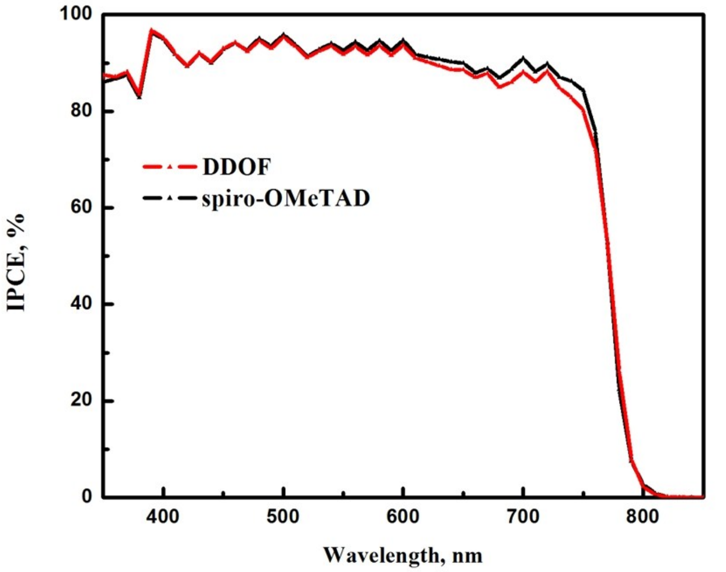


Figure S10. IPCE spectra as a function of the wavelength of monochromatic light

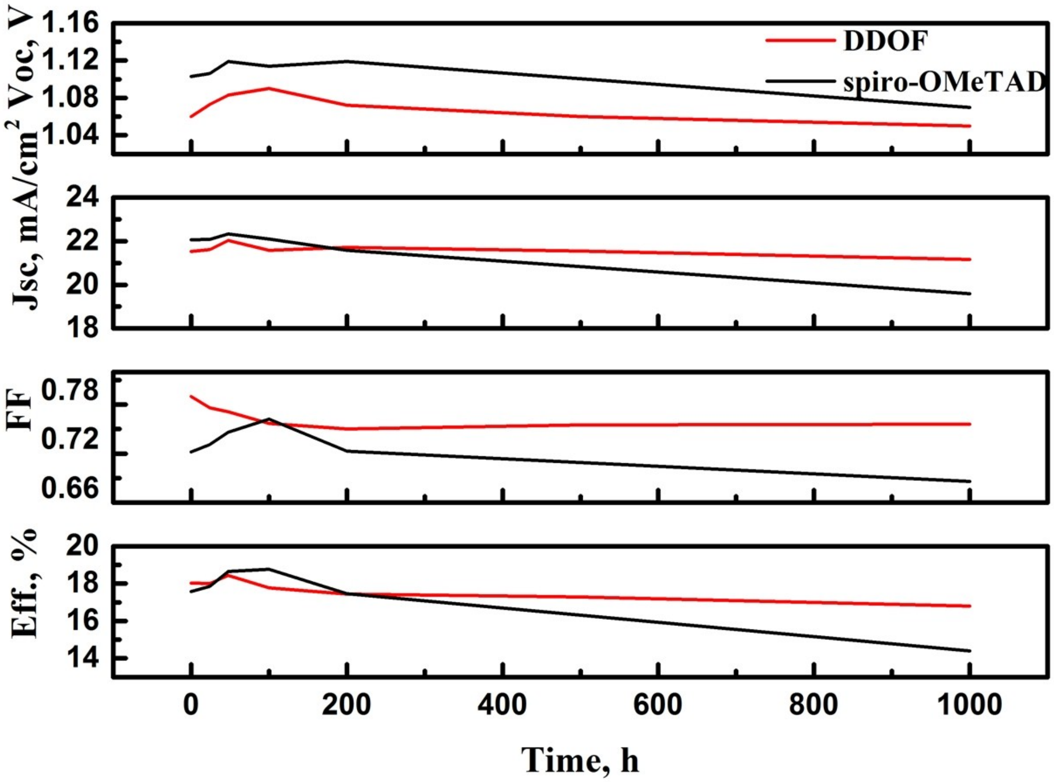


Figure S11. V_{OC}, J_{SC}, FF and PCE of devices with spiro-OMeTAD and DDOF as HTMs versus time. Stability tests were carried out keeping devices at a relative humidity of 10% without any encapsulation for 1000 h. The cells with **DDOF** maintained around 95% of their initial PCE, while the PCE of devices with spiro-OMeTAD dropped by 20% under identical conditions.