Swivel-Cruciform Thiophene Based Hole-Transporting Material for Efficient Perovskite Solar Cells

Thirumal Krishnamoorthy,[a] Fu Kunwu, [a] Pablo. P. Boix, [a] Hairong Li, [a] Teck Ming Koh, [ab] Wei Lin Leong, [c] Satvasheel Powar,[a] Andrew Grimsdale, [b] Michael Grätzel,[d] Nripan Mathews, [abe] Subodh G. Mhaisalkar. [ab]

Methods

Materials Synthesis

2,2',5,5'-Tetrakis [N,N-di(4-methoxyphenyl)amino]-3,3'-bithiophene (KTM3)
30 ml round bottom flask with compound 2,5-dibromo-3-(2,5-dibromo-3-3thienyl)thiophene (110 mg 0.228 mmol), N,N-bis(4-methoxyphenyl)-4-phenyl boronic acid (400 mg 1.15 mmole) and Pd(PPh3)4 (50 mg) was purged with nitrogen gas for 10 mins. A solution of K2CO3 (2 M) in water and dry Toluene was also purged with nitrogen gas separately and transferred to the round bottom flask. The temperature of the solution is raised to 80 °C and stirred for 48 h. After cooling to room temperature, the mixture was extracted with dichloromethane then the solvent was removed by rotary evaporation. The organic portion was purified by column chromatography (silica gel, dicholotomethane /Hexane =2/1) as eluent to get fluorescence yellow compound as a pure material.

^{1}H NMR (400 MHz, CDCl3) δ (ppm) 3.76 (s, 12H); 3.79 (s, 12H); 6.76-7.36 (br m, 50 H). ^{13}C-NMR (CDCl3, 400 MHz): δ (ppm) 55.46; 55.45; 114.64; 114.73; 120.47; 120.64; 125.27; 126.00; 126.30; 126.54; 126.77; 128.20; 128.53; 129.01; 133.00; 138.15; 140.71; 141.18; 147.53; 148.057; 155.74; 155.93. MALDI-TOF calculated (m/z) for $C_{88}H_{74}N_4O_8S_2$: 1378.49; found: 1374.6. Elemental analysis calculated (%) for $C_{88}H_{74}N_4O_8S_2$: C 76.61; H 5.41; N 4.06; O 9.28; S 4.65 found: C 76.5; H 5.55; N 4.00; S 4.10

Solar cell fabrication
Ultrasonically cleaned, patterned FTO substrates were coated with a thin hole-blocking layer of TiO_2 by aerosol spray pyrolysis at 450°C using 50mM Titanium diisopropoxide bis(acetylacetonate) solution in ethanol as precursor and oxygen as carrier gas. The mesoporous TiO_2 layer was deposited by spin coating the TiO_2 paste (Dyesol, 18NRT) diluted in ethanol (2:7 w/w). After annealing at 125 °C, the films were sintered at 500 °C for 15 min. One molar lead iodide solution was prepared by stirring PbI_2 in DMF solvent at 70 °C. This solution was spin coated on mesoporous TiO_2 film at 5500 rpm and then dried at 70 °C. After cooling to room temperature, the lead iodide films were converted into perovskite films by dipping the films in a solution of methylammonium Iodide in 2-propanol (10 mg/ml). The HTM was then deposited by spin coating the solution at 4000 rpm for 30 seconds. HTM solution was prepared by dissolving 59 millimole of HTM, 196 millimole of TBP, 60 millimole of Li salt, and 7.1 millimole of dopant FK269 in 1 ml of chlorobenzene. Li salt and dopant solution were prepared in acetonitrile and used to make the HTM solution. Finally a gold electrode was deposited by thermal evaporation. The active area of the cell was fixed at 0.2 cm^2.

Characterization
All the measurements were performed in air. UV-Vis absorption spectra were collected with a Shimadzu UV3600 spectrophotometer. Current density-voltage (j-V) plots were measured using solar simulator (San-EI Electrix, XEC-301S, AM 1.5, 100Mw/cm2). The current –voltage data under these conditions was obtained using Keithley model 2612A source meter. The thickness of the photoactive layer was measured by FESEM (JEOL, JSM-7600F) with an accelerating voltage of 5 KeV. Impedance spectroscopy (IS) was measured under a white LED illumination (current matched to the AM 1.5 standard condition) with an Autolab 302 at different DC bias potentials between Jsc and Voc. The applied voltage perturbation had AC amplitude of 20 mV (rms) with a frequency from 1 MHz to 1 Hz. The spectra were fitted using Z-View software. Transient photovoltage dacays (TPV) was measured with a constant bias white LED light which kept an stable open circuit potential in the cell. A small light perturbation (ΔV_{oc} ~20mV) was produced with a square wave generator (Tektronix). The variation of the V_{oc} was recorded with an oscilloscope (Agilent).

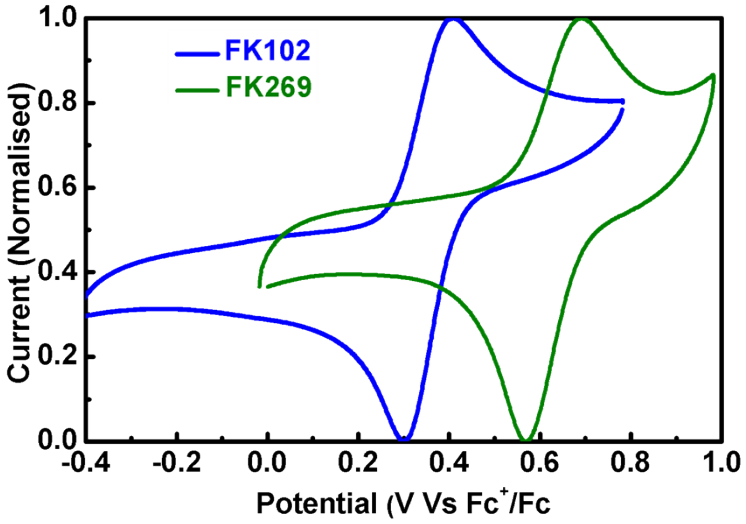

Fig. S1. Cyclic voltammetry of dopant FK102 and FK269

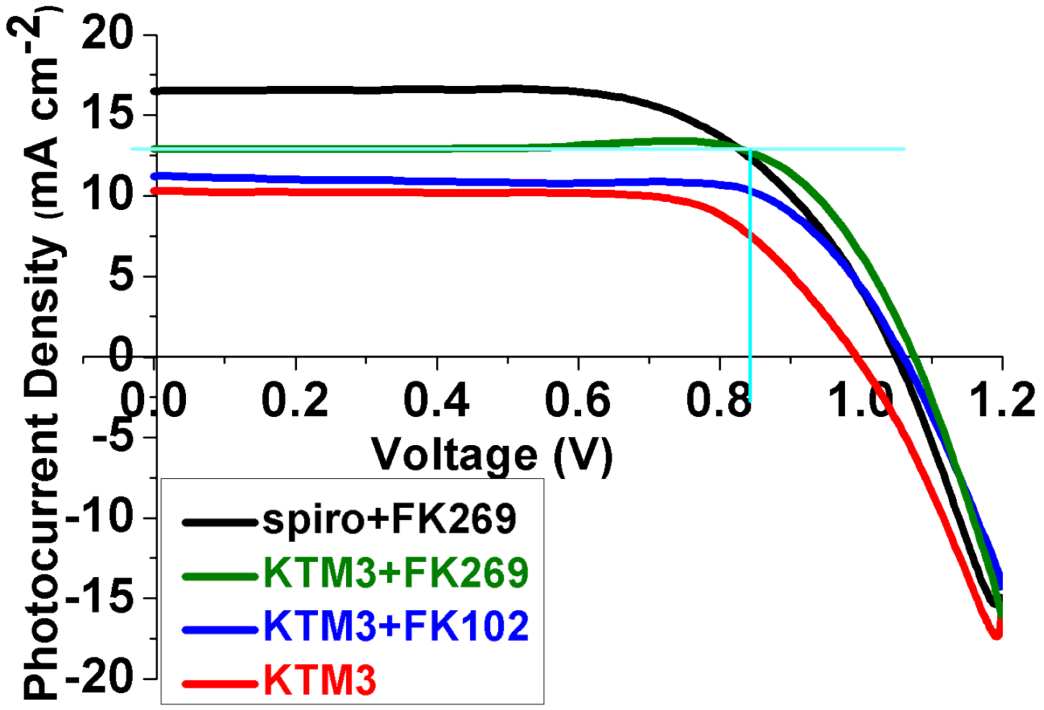

Fig. S2.Manual calculation of FF at Pmax point.

Jsc	Voc	Jmax	Vmax	FF
13.0	1.08	13.0	0.84	77.8

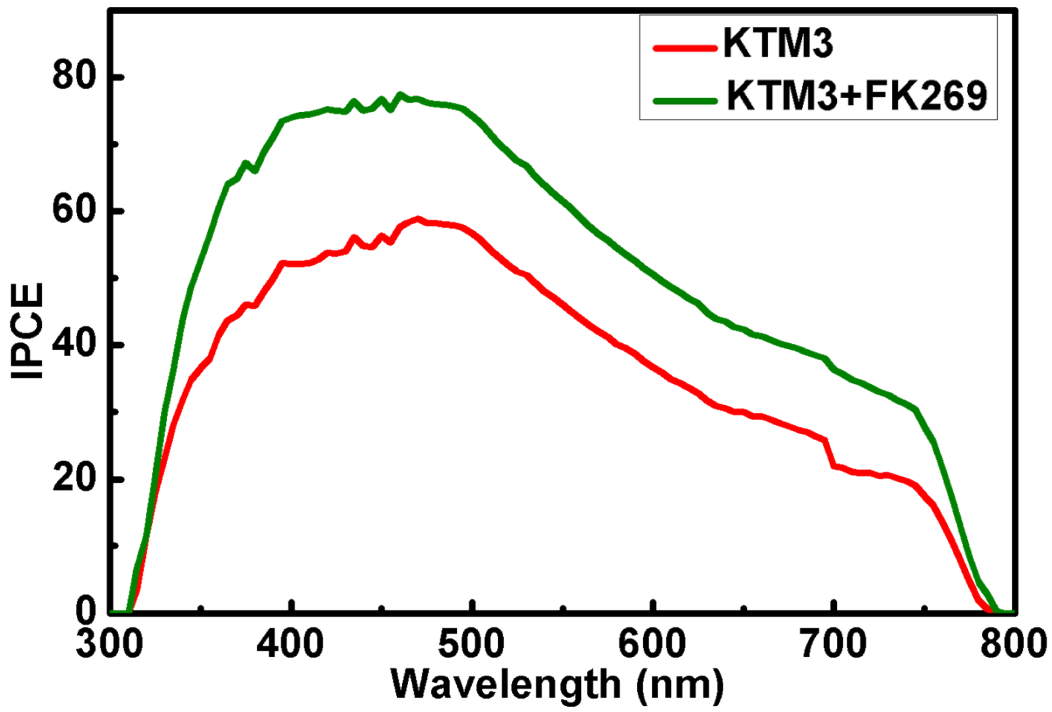

Fig. S3. IPCE spectrum of KTM3 and doped KTM3 with FK269

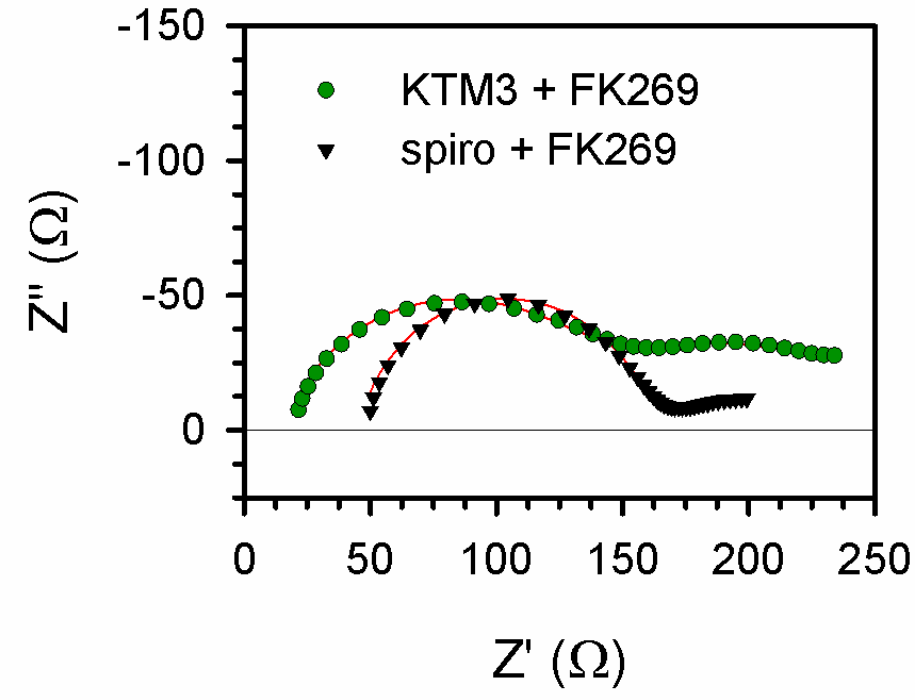

Fig. S4. Example of impedance spectra recorded at 900 mV under white LED. The straight lines correspond to the equivalent circuit fitting. The highest frequency arc corresponds to the hole transport effects.