Supporting Information

Bis[di(4-methoxyphenyl)amino]carbazole-capped Indacenodithiophene as Hole Transport Materials for Highly Efficient Perovskite Solar Cells: the Pronounced Positioning Effect of A Donor Group on the Cell Performance

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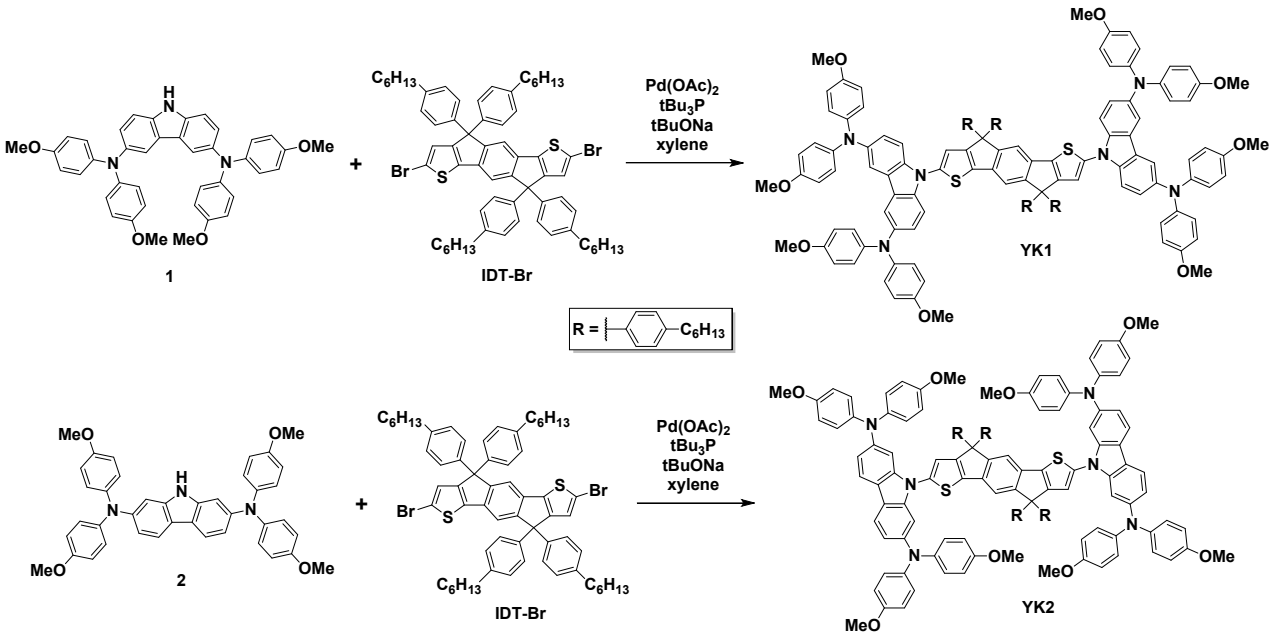
Experimental Section

Materials and Reagents

Materials were all available commercially and used without further purification if not mentioned specially. The key intermediates *N3,N6-bis*(di-4-anisylamino)-9H-carbazole (**1**),[1] *N2,N7-bis*(di-4-anisylamino)-9H-carbazole (**2**)[1] and 2,7-dibromo-4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene[2] (**IDT-Br**) were synthesized according to the previously reported procedure. The synthetic routs of two HTM **YK1** and **YK2** are outlined in Scheme **S1** and the details are depicted. ^{1}H NMR spectra were recorded using a Bruker Ultrashield 400 Plus NMR spectrometer. High-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained with a Bruker Autoflex MALDI-TOF mass spectrometer.



Scheme S1. The synthesis routes of **YK1** and **YK2**

Synthesis of YK1

A two-necked flask containing IDT2Br (532 mg, 0.5 mmol), compound **4** (683 mg, 1.1 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), sodium *tert*-butoxide (414 mg, 3 mmol), tBu$_3$P (6.1 mg, 0.03 mmol) and xylene (10 mL) equipped with a magnetic stirrer, a N_2 purge, and a reflux condenser was heated at 120℃ for 12 h. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography with CH_2Cl_2:petroleum ether (1:1, v:v) as eluent affording the compound as a pale yellow solid. ^{1}H NMR (400 MHz, Benzene-d_6): 7.85 (s, 2 H), 7.81 (d, J = 2.0 Hz, 8 H), 7.44 (d, J = 8.4 Hz, 4 H), 7.39 (s, 2 H), 7.36 (s, 2 H), 7.27 (d, J = 2.0 Hz, 2 H), 7.12 (d, J = 5.6 Hz, 16 H), 7.08 (s, 2 H), 7.02 (d, J = 8.0 Hz, 8H), 6.73 (d, J = 9.2 Hz, 16 H), 3.29 (s, 24 H), 2.44 (t, J = 8.0 Hz, 8 H), 1.47 (m, 8 H), 1.20 (m, 24 H), 0.84 (t, J = 7.2 Hz, 12 H). (MALDI−TOF, m/z) calculated for $C_{144}H_{140}N_60_8S_2$: 2146.0201; found: 2146.0169.

Synthesis of YK2

A two-necked flask containing IDT2Br (532 mg, 0.5 mmol), compound **7** (683 mg, 1.1 mmol), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), sodium *tert*-butoxide (414 mg, 3 mmol), tBu$_3$P (6.1 mg, 0.03 mmol) and xylene (10 mL) equipped with a magnetic stirrer, a N_2 purge, and a reflux condenser was heated at 120℃ for 12 h. The reaction mixture was then poured into water and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography with CH_2Cl_2:petroleum ether (1:1, v:v) as eluent affording the compound as a pale yellow solid. ^{1}H NMR (400 MHz, Benzene-d_6): 7.84 (d, J = 8.4 Hz, 4 H), 7.71 (d, J = 2.0 Hz, 4 H), 7.61 (s, 2 H),

7.21 (m, 28 H), 7.07 (d, J = 8.4 Hz, 8 H), 6.99 (s, 2 H), 6.79 (dd, J_1 = 2.0 Hz, J_2 = 6.8 Hz, 16 H), 3.38 (s, 24 H), 2.68 (t, J = 8.0 Hz, 8 H), 1.73 (m, 8 H), 1.41 (m, 8 H), 1.33 (m, 16 H), 0.95 (t, J = 6.8 Hz, 12 H). (MALDI−TOF, m/z) calculated for $C_{144}H_{140}N_60_8S_2$: 2146.0201; found: 2146.3087. 2146.0201; found: 2146.3087.

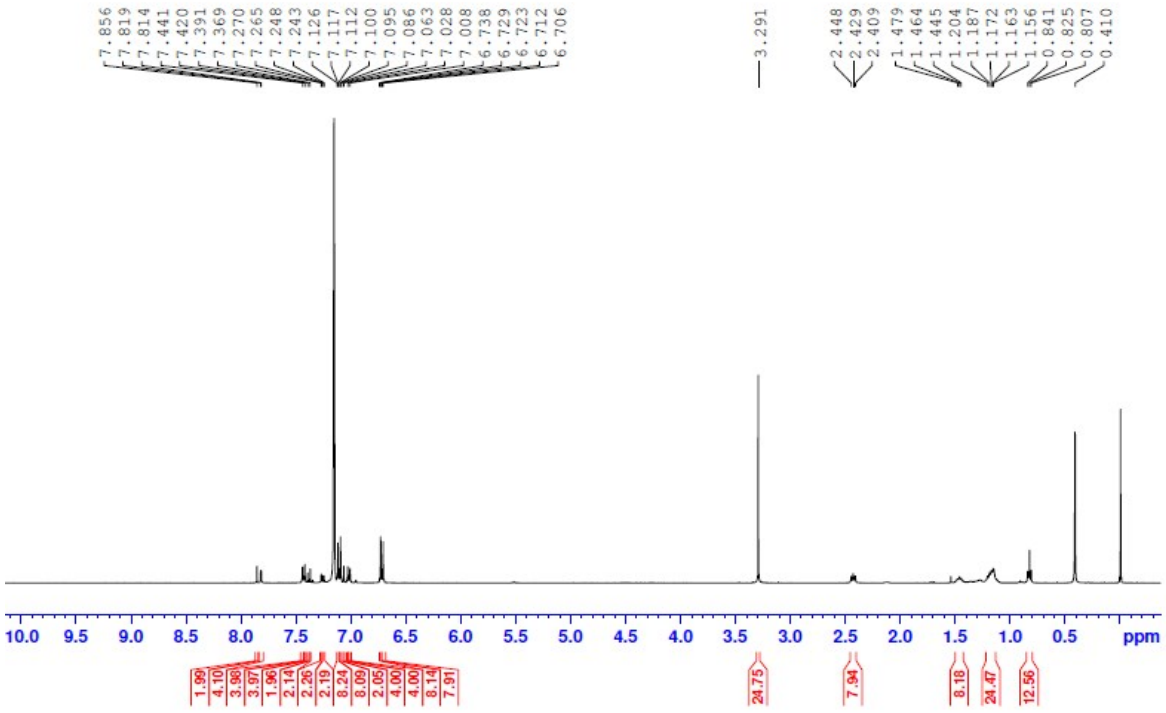


Figure S1. ^{1}H NMR spectra of **YK1**

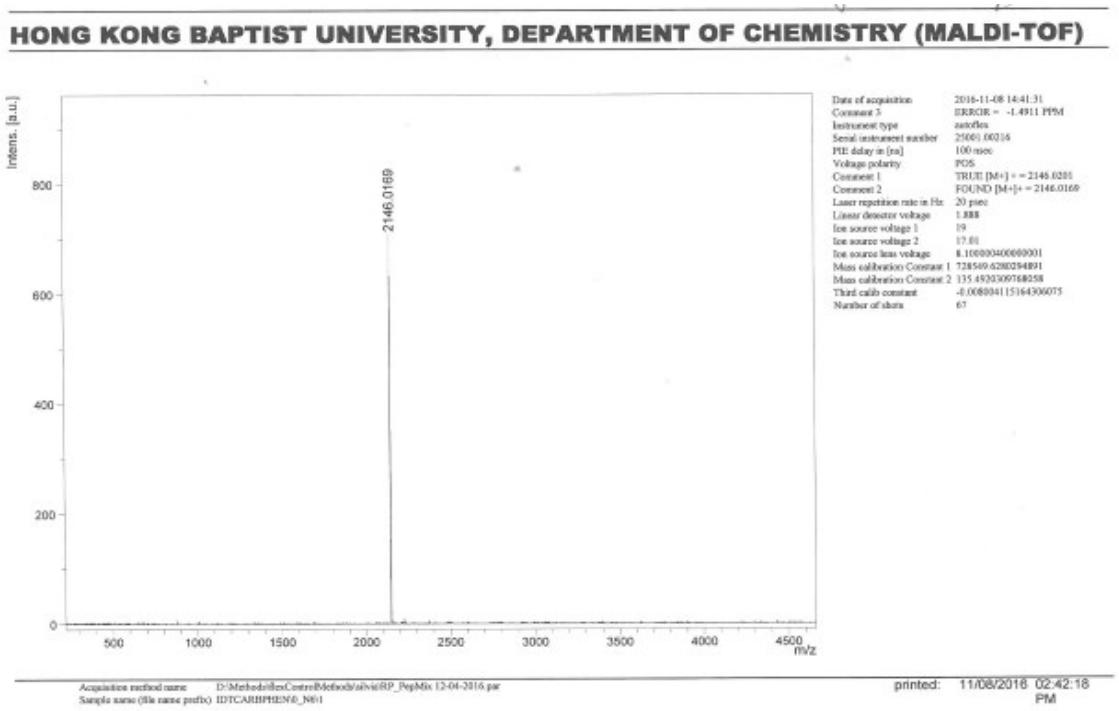


Figure S2. Mass spectrum of **YK1**

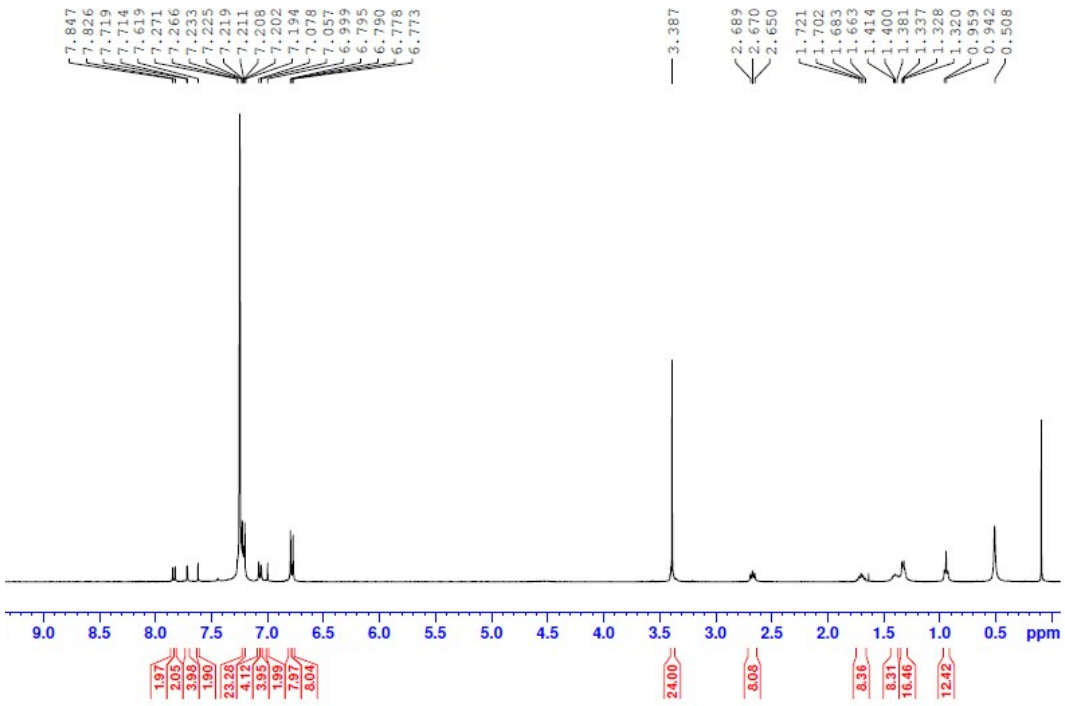


Figure S3. ^{1}H NMR spectra of **YK2**

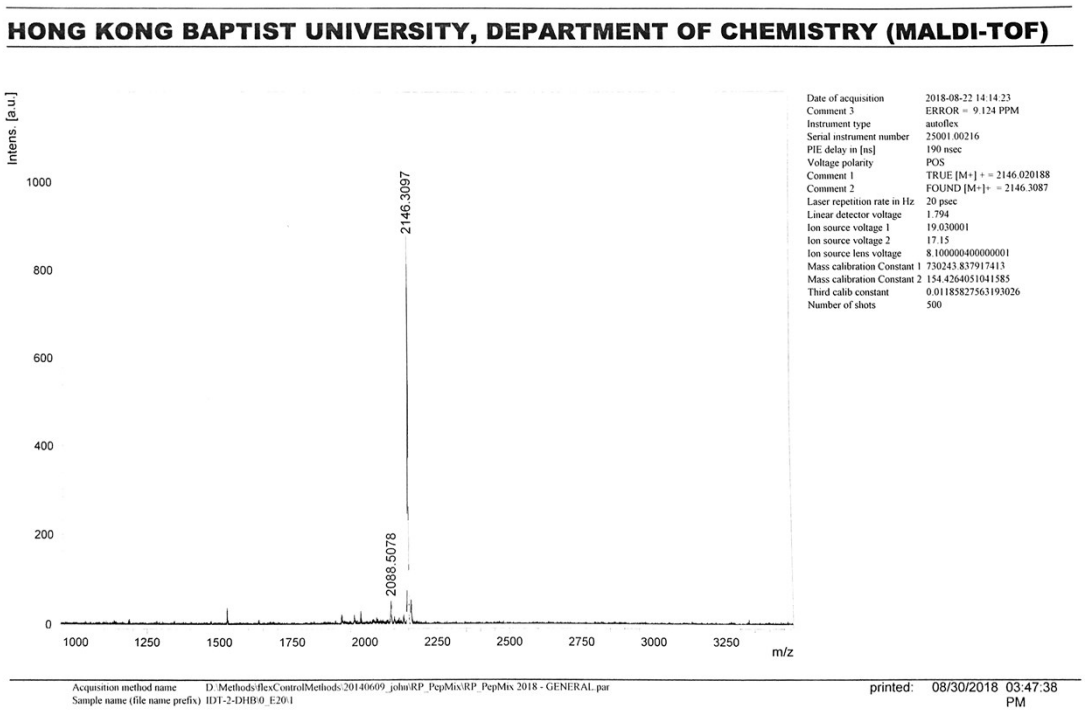


Figure S4. Mass spectrum of **YK2**

Table S1: A summary of the detail performance parameters of the reported highly efficient small-organic molecules HTMs with PCEs >19%.

HTM	Device structure	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)	Ref
FDT	FTO/compactTiO_2/mpTiO_2/[$(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$]/HTM/Au	22.7	1.14	76	20.2	3
X59	FTO/compact-TiO_2/mp-TiO_2/ [$(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$]/HTM/Au	23.4	1.13	73	19.8	4
DDOF	FTO/compact-TiO_2/mp-TiO_2/ $(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$/HTM/Au	22.37	1.10	79	19.4	5
H12	FTO/compact-TiO_2/mp-TiO_2/ $(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$/HTM/Au	24.2	1.15	71	19.8	6
V862	FTO/compact-TiO_2/mp-TiO_2/ $(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$/HTM/Au	22.5	1.14	77	19.9	7
KR321	FTO/compact-TiO_2/mp-TiO_2/ $(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$/HTM/Au	21.70	1.13	78	19.0	8
IDIDF	FTO/compact-TiO_2/mp-TiO_2/ $[FAPbI_3]_{0.92}[MAPbBr_3]_{0.08}$ /HTM/Au	23.55	1.05	77	19.0	9
Z26	FTO/compact-TiO_2/mp-TiO_2/ $(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$/HTM/Au	23.59	1.13	75	20.1	10

X55	FTO/compact-TiO_2/mp-TiO_2/ $(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$/HTM/Au	23.4	1.15	77	20.8	11
X26	FTO/compact-TiO_2/mp-TiO_2/ $(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$/HTM/Au	24.3	1.11	75	20.2	12
SiOMeTPA	ITO/HTL/$MAPbI_3$/PCBM/Al	23.08	1.07	72	19.1	13
Co(II)P/ Co(III)P)	FTO/compact-TiO_2/mp-TiO_2/ $(CsFAMA)Pb(BrI)_3$ /HTM/Au	23.62	1.13	77	20.5	14
SCZF-5	FTO/compact-TiO_2/mp-TiO_2/ $MAPbI_3$/HTM/MoO_3/Ag	24.40	1.11	74	20.1	15
G2	FTO/compact-TiO_2/mp-TiO_2/ $(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$/HTM/Au	23.52	1.13	76	20.2	16
OMeTATPyr	FTO/compact-TiO_2/mp-TiO_2/ $Cs_{0.05}FA_{0.81}MA_{0.14}PbI_{2.55}Br_{0.45}$/HTM/Au	23.3	1.10	81	20.6	17
EDOT-Amide-TPA	FTO/compact-TiO_2/mp-TiO_2/ $MAPbI_3$ /HTM/Au	22.7	1.16	77	20.3	18
YK1	FTO/compact-TiO_2/mp-TiO_2/ $(FAPbI_3)_{0.85}$ $(MAPbBr_3)_{0.15}$/HTM/Au	23.55	1.11	77	20.13	This work

Mobility Measurements

Hole mobility was measured by using the SCLC method, which can be described by the following equation

$$J = \frac{9}{8}\mu\varepsilon_0\varepsilon_r\frac{V^2}{d^3}$$

where J is the current density, μ is the hole mobility, ε_o is the vacuum permittivity (8.85×10^{-12} F/m), ε_r is the dielectric constant of the material (normally taken to approach 3 for OSs), V is the applied bias, and d is the film thickness.

The detailed device fabrication follows: Indium Tin Oxide (ITO) coated glass substrates (Pilkington TEC15) were patterned by etching with zinc powder and 2 M hydrochloric acid. The substrates were carefully cleaned in ultrasonic baths of detergents, deionized water, acetone and ethanol successively. The remaining organic residues were removed with 10 min by airbrush. A 40 nm thick PEDOT: PSS layer was spin-coated onto the substrates, which were then annealed at

120 °C for 30 min in air. The substrates were then transferred into a glovebox for further fabrication steps. The HTMs were dissolved in anhydrous chlorobenzene. Here the concentration of YK1/YK2 is 40 mg mL^{-1} in chlorobenzene with addition of 8 µL Li-TFSI (520 mg Li-TFSI in 1 mL acetonitrile), 14 µL tert-butylpyridine (*t*BP) and 1 µL FK209 solution (2 M FK209 in acetonitrile). This HTMs solution was spin-coated at 4000 rpm to yield films. The thicknesses of the films are measured by using a Dektak 6M profilometer. 80 nm of gold was then evaporated onto the active layer under high vacuum (less than 10^{-6} mbar). *J-V* characteristics of the devices have been measured with a Keithley 2400 Source-Measure unit, interfaced with a computer. Device characterization was carried out in air.

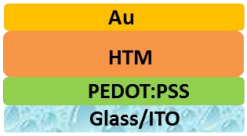


Figure S5. Schematic illustratuion of the mobility device.

Fabrication of $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite solar cells

The fluorine-doped SnO_2 (FTO, 15 Ω-square) substrates were etched with zinc powder and HCl acid (concentration 4 M) to form the desired electrode pattern. The substrates were cleaned in an ultrasonic bath for half an hour in the following order: deionized water, acetone and ethanol. A compact layer of TiO_2, intended to block the recombination current at the FTO support, was prepared on cleaned FTO substrate by spray pyrolysis of solution (0.2M titanium isopropoxide and 2M acetylacetone in isoproponal). Afterwards, a layer of mesoporous TiO_2 particles were spin-coated on the FTO glass with a thickness of 200 nm. The perovskite films were deposited from a precursor solution containing FAI (1 M), PbI_2 (1.1 M), MABr (0.2 M) and $PbBr_2$ (0.2 M)

in anhydrous DMF: DMSO=4:1 (v/v). The perovskite solution was spin-coated in a two-step program; first at 1000rpm for 10 s and then at 4000 rpm for 30 s. During the second step, 100 uL of chlorobenzene were poured on the spinning substrate 15s prior to the end of the program. The substrates were then annealed at 100 ℃ for 1 h in a nitrogen filled glove box. Then, the YK1, YK2 and Spiro-OMeTAD/chlorobenzene solution were spin-coated at 4000 rpm for 30 s. For Spiro-OMeTAD HTMs, Spiro-OMeTAD in chlorobenzene solution (80 mg mL^{-1}) was employed with the additives containing 17.5 μL Li-TFSI/acetonitrile (520 mg mL^{-1}), 28.8 μL TBP and 2 μL FK209 solution (2 M FK209 in acetonitrile). For YK HTMs, YK1/YK2 in chlorobenzene solution (40 mg mL^{-1}) were prepared by mixing the additives containing 8 μL Li-TFSI/acetonitrile (520 mg mL^{-1}), 14 μL TBP and 1 μL FK209 solution (2 M FK209 in acetonitrile). As a last step 80 nm of gold top electrode were thermally evaporated under high vacuum. Current-voltage characteristics were measured under 100 mW/cm^2 (AM 1.5G illumination) using a Newport solar simulator (model 91160) and a Keithley 2400 source/meter. A certified reference solar cell (Fraunhofer ISE) was used to calibrate the light source for an intensity of 100 mW/cm^2. Incident photon-to-current conversion efficiency (IPCE) spectra were recorded using a computer-controlled setup consisting of a Xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectra Products CM110), and a potentiostat (LabJack U6 DAQ board), calibrated by a certified reference solar cell (Fraunhofer ISE). Electron lifetime measurements were performed using a white LED (Luxeon Star 1W) as the light source. The photocurrent decay was determined by monitoring photocurrent transients by applying a small square-wave modulation to the base light intensity. The voltage scan rate was 10mV s^{-1} and no device preconditioning was applied before starting the measurement, such as light soaking or

forward voltage bias applied for long time. The cells were masked with a black metal mask limiting the active area to 0.09 cm^2 and reducing the influence of the scattered light.

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