New hole-transporting materials for planar perovskite solar cells

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Experimental section

Reagents and chemicals

Starting materials for HTM syntheses were all commercially available and used as received without further purification if not specially mentioned. Tris(dibenzylideneacetone)dipalladium $Pd_2(dba)_3$, tris(1,1-dimethylethyl)phosphine $(t\text{-}Bu)_3P$ and sodium tert-butoxide were purchased from Beijing InnoChem. Science&Technology Co. Ltd. The matrix for MALDI-TOF measurements is α-cyano-4-hydroxycinnamic acid compounds, N3, N6-bis(di-4-anisylamino)-9H-carbazole and 1,3,6,8-tetrabromopyrene were prepared according to reported procedures.[s1-s2] Toluene was refreshly distilled before use.

PbI_2, $PbBr_2$ (99.9985%), 4-*tert*-butylpyridine (TBP) and bis(trifluoromethane) sulfonimide lithium salt (LiTFSI) were purchased from Sigma-Aldrich, N, N-dimethylformamide (DMF), dimethyl sulphoxide (DMSO) and chlorobenzene (CB) were from Alfar Aesar. Methylammonium bromide (MABr), methylammonium iodide (MAI) and formamidinium iodide (FAI) were from Xi'an Polymer Light Technology Corp. *Spiro*-OMeTAD was purchased from Luminescence Technology Corp.. All the chemicals were directly used without further purification. Al_2O_3 nanoparticle (20 nm) for Al_2O_3 layers was from Beijing Jiaanheng Science &

Technology Co., LTD. Laser-patterned FTO glass (Pilkington, thickness of 2.2 mm and sheet resistance of 15 Ω sq^{-1}) was sequentially cleaned with a mild detergent, distilled water and ethanol in an ultrasonic bath. The substrate was treated with ozone for 15 min prior to use.

Syntheses of new HTMs

All reactions were performed in N_2 atmosphere.

dly-1: To a pressure vessel, N3, N6-bis(di-4-anisylamino)-9H-carbazole (621.8 mg, 1.0 mmol), 1,3,6,8-tetrabromopyrene (135.7 mg, 0.2 mmol), sodium tert-butoxide (57.6 mg ,0.6 mmol) and dry toluene (10 mL) were added. The mixture was purged with N_2 for 10 min and then $(t\text{-Bu})_3P$ (24.3 mg, 0.12 mmol) and $Pd_2(dba)_3$ (54 mg, 0.06 mmol) were added. The reaction mixture was heated to reflux for 48 h under N_2. The system was then cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate, 1/2) to afford compound dly-1 as a red solid in 26.5% yield. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 2H), 7.95 (s, 3H), 7.69 (s, 8H), 7.06-6.93 (m, 49H), 6.76 (d, *J* = 9.2 Hz, 32H), 3.76 (s, 48H). MALDI-TOF-MS: m/z 2680.7 for $[M]^+$. HRMS-MALDI-TOF calcd for $C_{176}H_{142}N_{12}O_{16}$: 2679.0661. Found: 2679.0654.

dly-2: To a pressure vessel, N3, N6-bis(di-4-anisylamino)-9H-carbazole (310.5 mg, 0.5 mmol), 1,6-dibromopyrene (72 mg, 0.2 mmol), sodium tert-butoxide (58 mg, 0.6 mmol) and dry toluene (10 mL) were added. The mixture was purged with N_2 for 10 min and then $(t\text{-Bu})_3P$ (24.3 mg, 0.12 mmol) and $Pd_2(dba)_3$ (54 mg, 0.06 mmol) were added. The reaction mixture was heated to reflux for 48 h under N_2. The system was then cooled to room temperature and the solvent was removed under vacuum. The crude product was purified by silica gel chromatography (eluent: petroleum ether/ethyl acetate, 2/1) to afford the dly-2 as a yellow solid in 37.8% yield. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 5.1 Hz, 2H), 8.13 (t, *J* = 6.2 Hz, 4H), 7.85 (t, *J* = 9.3 Hz, 2H), 7.69 (s, 4H), 7.09-7.02 (m, 20H), 6.89 (d, *J* = 8.7 Hz, 4H), 6.79 (d, *J* = 9.0 Hz, 16H), 3.78 (s, 24H). MALDI-TOF-MS: m/z 1441.1 for $[M]^+$. HRMS-

MALDI-TOF calcd for $C_{96}H_{76}N_6O_8$: 1440.5719. Found: 1440.5706. ^{13}C NMR (75 MHz, $CDCl_3$): δ=154.7, 142.6, 141.8, 139.4, 132.1, 131.1, 129.9, 128.7, 128.3, 127.1, 125.8, 124.5, 124.4, 124.0, 123.6, 116.4, 114.5, 110.9, 55.5.

Fabrication of the devices

The perovskite precursor solution was prepared by dissovling 1.32 M PbI_2, 0.12 M $PbBr_2$, 1.08 M FAI, 0.24 M MAI and 0.12 M MABr in DMF/DMSO mixed solvent (v: v= 4: 1). The compact TiO_2 layer was deposited on the FTO glass with a 0.125 M titanium isopropoxide sol-gel precusor solution by spin coating at 3000 rmp, then sintered at 500°C for 1 h. Then, the TiO_2 film was treated with 0.025 M $TiCl_4$ aqueous solution for 30 min, and calcined at 500°C for 1h. 0.1 mg/mL [6,6]-phenyl-C61-butyric acid (PCBA) in CB was firstly spin-coated on the top of TiO_2 compact film.[s3] Then, perovskite films were fabricated by anti-solvent one-step spin-coating method. In details, perovskite precursor solution was spin-coated at 1000 rpm for 10 s and subsequently at 5000 rpm for 30 s, 120 μL CB was poured onto the spinning substrate at 15s in the second spinning step. The half-crystallization perovskite film was heated at 150°C for 10 min and 100°C in vacuum for 30 min. The composition of the HTM solution was 10 mg HTM dissovled in 1 mL CB with 30 μL TBP and 60 μL LiTFSI acetonitrile solution with 150 mg mL^{-1}. About 80 nm-thickness HTM layer was deposited onto the perovskite film at a speed of 2000 rpm and then heated for 5 min at 60°C on a hot plate. For comparison, the same *spiro*-OMeTAD concentration is used. Besides, the PSC with conventional ~180 nm-thickness *spiro*-OMeTAD layer is also fabricated. All the manipulation including the precursor solution preparation, perovskite and HTM spin-coating processes were carried out in the glove box. At last, 80 nm-thickness Au electrode was deposited *via* thermal evaporation under the vacuum of 10^{-7} Torr.

Characterization

NMR spectra were recorded on a Bruker Avance 300 or 400 MHz spectrometer in ppm values from residual protons of deuterated solvent. Mass spectra were obtained with a Bruker Daltonics Inc. Apex II FT-ICR or Autoflex III MALDI-TOF mass spectrometer. SEM images were measured by scanning electron microscopy (SEM, Hitachi S4800) under 10 kV at various magnifications. Differential pulsed voltammograms (DPV) of two HTMs were carried out in dichloromethane containing 0.1 M Bu_4NClO_4 as the supporting electrolyte at a scan rate of 100 mV s^{-1}, in which the working electrode was a Pt electrode, the counter electrode was a Pt wire and the reference electrode was Ag/AgCl in saturated aqueous NaCl. The system was calibrated by Fc^+/Fc redox couple. Hole mobility was estimated by using a hole-only device with a configuration of ITO/PEDOT:PSS/HTM/Au, which *J-V* characteristics were carried out in the dark, and hole mobility was estimated by using Mott-Gurney's equation, $J = 9\varepsilon_r\varepsilon_0\mu_h V^2/8L^3$, where ε_r is the relative dielectric constant of the transport medium (for organic materials, $\varepsilon_r = 3$), ε_0 is the permittivity of free space (8.85×10^{-12} C V^{-1} m^{-1}), L is the thickness of the HTM layer, and V is the voltage drop through the device. The HTM thickness for hole mobility is determined by surface profiler (KLA-Tencor). UV-vis absorption spectra of HTM films were carried out on Shimadzu UV-2550 in the wavelength range from 350 to 860 nm. Time-resolved transient photoluminescence (PL) spectra were obtained on PL spectrometer, FLS 900, Edinburgh Instruments, excited with a picosecond pulsed diode laser (EPL-640) with the wavelength of 638.2 nm and measured at 775 nm after excitation. UV-Vis spectra of HTM dichloromethane solutions were recorded on a TU-1810DSPC spectrophotometer at room temperature, with a conventional 1 cm quartz cell. Steady-state PL spectra of the HTM solutions in dichloromethane were recorded using an F-380 spectrofluorimeter of Tianjin Gangdong Sic. & Tech Development Co. Ltd. *J-V* characteristics were measured under AM 1.5 simulated sunlight (100 mW cm^{-2}), Zolix SS150A, which were recorded on a digital source meter (Keithley model 2602). The solar cells were masked with a black aperture to define the active area of 0.1 cm^2, the reverse scanning *J-V* curves (from open circuit to short circuit) are adopted with scanning speed of 30 mV/s. Incident photon-to-current conversion efficiency (IPCE) spectra were measured with our lab-made setup under 0.3~0.9 mW cm^{-2} monochromic light illumination without bias illumination.[s4] Impedance spectra (IS) were performed on a ZAHNER IM6e electrochemical workstation in the dark at the applied bias voltage of 800 mV with a perturbation amplitude of 10 mV in the frequency range from 10^5 to 10^2 Hz. The obtained IS spectra are fitted by

Zview software based on appropriate equivalent circuit. For long term stability testing, the PSCs without encapsulation were stored at about 30 RH% condition in the dark, which *J-V* characteristics were tested every five or six days in 50 days. For thermal stability test, the PSCs without encapsulation were kept at 50°C in the glove box, which *J-V* characteristics were tested every 20 min in 2 hr.

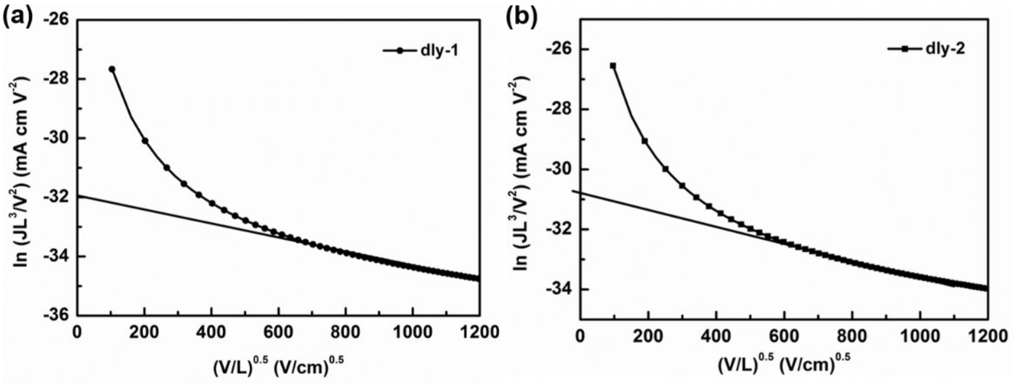

Fig. S1 *J-V* characteristics of hole-only devices based on dly-1, dly-2 and spiro-OMeTAD (optimized) measured in the dark.

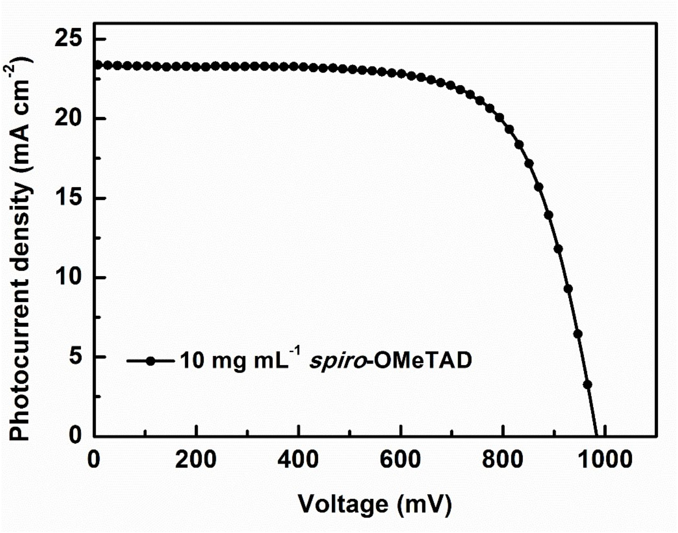

Fig. S2 *J-V* characteristics of PSCs based on *spiro*-OMeTAD with the concentration of 10 mg mL^{-1} and doped with LiTFSI and TBP.

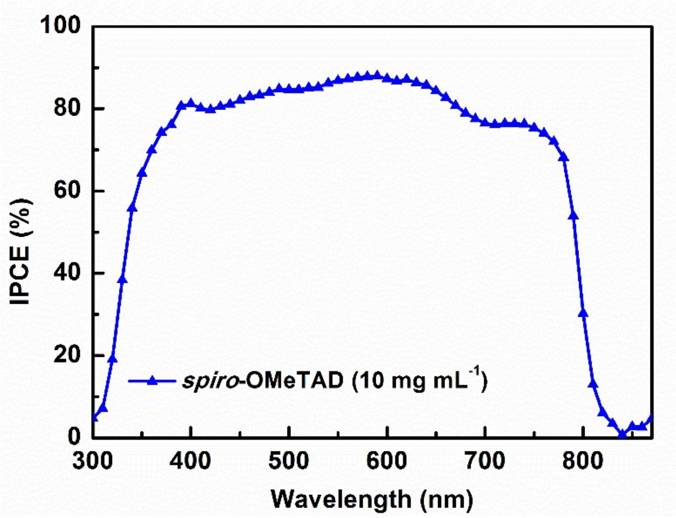

Fig. S3 IPCE spectrum of the PSC with spiro-OMeTAD in different scan directions with 30 mV· s^{-1} scanning speed.

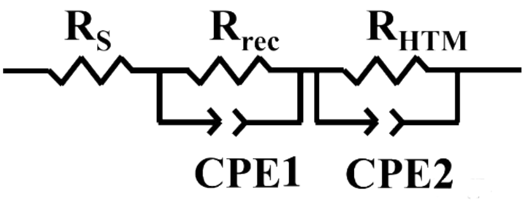

Fig. S4. Equivalent circuit for fitting the Nyquist plot: R_s, series resistance; R_{rec}, recombination resistance at TiO_2/perovskite/HTM interfaces; R_{HTM}: HTM resistance; CPE: constant phase element of electrical double layer.

In general, to the Nyquist plot, high frequency part describes the charge transfer behavior at the Au/HTM interface while the lower frequency part is related to the HTM/perovskite/TiO_2 interfaces, as shown in Fig. S4. In our work, quite similar R_s is obtained, that is, the R_s is 11.93, 11.52 and 11.45 Ω for the PSC with dly-1, dly-2 and *spiro*-OMeTAD (10 mg mL^{-1}), respectively.

Table S1. Detailed I-V parameters of the PSCs based on different HTMs with forward and reverse scanning directions.

		J_{sc}	V_{oc}	*FF*	PCE
dly-1	forward	22.80	932.4	0.595	12.65

	reverse	22.74	955.3	0.780	16.94
dly-2	forward	23.25	955.4	0.572	12.71
	reverse	23.53	971.8	0.791	18.09
spiro-OMeTAD[a]	forward	23.58	932.3	0.461	10.13
	reverse	23.39	980.3	0.698	16
spiro-OMeTAD[b]	forward	23.39	1038.9	0.687	16.69
	reverse	23.38	1070.1	0.777	19.44

[a] The same concentration with dly-1 and dly-2.

[b] Under an optimized condition as the reference.[5]

References

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