Electronic Supplementary Information (ESI)

Mixed hole transport material employing a highly planar conjugated molecule for efficient and stable perovskite solar cells

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1. Materials

All starting materials were purchased from commercial suppliers and used without further purification. PbI₂ (99.999%, Alfa Aesar), Spiro-OMeTAD (Woerjiming (Beijing) technical development institute), SnO₂ (tin (IV) oxide, 15% in H₂O colloidal dispersion, Alfa Aesar). Compound **1**, **7** and the end group 2-(3-oxo-2,3dihydroinden-1-ylidene)malononitrile (INCN) were synthesized according to the literature procedures.¹⁻³ The reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. Toluene and THF were distilled from sodium/benzophenone before use.

2. Measurements

The ¹H NMR and ¹³C NMR spectra were obtained via a Bruker ARX400 Spectrometer. Varian 7.0T FTMS was connected to achieve the HRMS data. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry were performed on a Bruker Autoflex III instrument. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA409PC instrument under purified nitrogen gas flow. The heating rate for TGA is 10 °C min⁻¹. UV-vis spectra was obtained with a JASCO V-570 spectrophotometer. Cyclic voltammogram (CV) was employed to evaluate the energy levels with a CHI600E electrochemical workstation (Chenhua Co. Ltd, Shanghai, China) based on a three electrode system, using glassy carbon as the working electrode, Pt wire as the counter electrode, and saturated calomel reference electrode (SCE) as the reference electrode. By the use of versatile calculation formula that assuming the absolute energy level of $FeCp_2^{+/0}$ to be 4.8 eV below vacuum : $E_{HOMO} = -e[E_{OX} + (4.8 - E_{Fc})] (eV); E_{LUMO} = -e[E_{red} + (4.8 - E_{Fc})] (eV), where E_{ox}$ and E_{red} were measured by the use of a standard three-electrode electrochemical cell in acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) at room temperature under nitrogen atmosphere in thin films, and E_{Fc} was 0.398 eV in this work which refers to the half-wave potential of redox couple (Fc/Fc⁺). The optimized geometry structures of DRSBDT-2OT, reorganization energy and images of electrostatic potential surface (ESP) were calculated by using DFT calculations (B3LYP/6-31G*), and the frequency analysis was followed to assure that the optimized structures were stable states. All calculations were carried out using Gaussian 09.

Hole mobility were measured using a diode configuration of glass/ITO/PEDOT: PSS/HTM/MoO₃/Ag by taking current-voltage curves in the range of 0-8 V and fitting the results to a space charge limited form, where the SCLC is described by $J = 9\varepsilon_0\varepsilon_n\mu_h V^2/8L^3$ where J is the current density, L is the film thickness of active layer, μ_h is the hole mobility, ε_r is the relative dielectric constant ($\varepsilon_r = 25$),⁴ ε_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹), V is the internal voltage in the device. The current density-voltage (J-V) curves were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under AM 1.5 G illumination at 100 mW cm⁻² using a xenon-lamp-based solar simulator (SS-F5-3A, Enli Technology Co. Ltd). Simulator irradiance was characterized using a calibrated spectrometer and illumination intensity was set using a certified silicon diode. Scanning electron microscopic (SEM) images were obtained using ZEISS MERLIN Compact. External quantum efficiencies (EQE) were measured using Stanford Re-search Systems SR810 lock-in amplifier. Steady-state Photoluminescence (PL) and time-resolved photoluminescence (TRPL) were measured by Spectrofluorometer FLS1000 with excitation at 475 nm. Electrochemical Impedance Spectra (EIS, ranged from 0.1 Hz to 10⁶ Hz) were measured in the dark by using a ZAHNER Zennium-E electrochemical workstation, made in Germany. TPV and TPC measurements were performed on a Molex 180081-4320 with light intensity about 0.5 sun, Voltage and current dynamics were recorded on a digital oscilloscope (Tektronix MDO4104C), and voltages at open circuit and currents under short circuit conditions were measured over a 1 M Ω and a 50 Ω resistor, respectively.

3. Device fabrication and characterization

The planner perovskite solar cells were fabricated on ITO substrates. ITO glasses were sequentially cleaned with distilled water, acetone and isopropyl alcohol. The as-cleaned thin layer of SnO₂ colloid precursor was spin-coated onto the ITO surface at 3000 rpm for 30 s in ambient air, and then heated on a hot plate in ambient air at 150 °C for 30 min. After cooling to room temperature, the substrate was treated with UV-ozone for 8 min before spin coating of perovskite solution. The coated substrates were then transferred to a glovebox filled with nitrogen. Typically, PbI2 was dissolved in DMF at a concentration of 1.0 m, followed by stirred at 70 °C for 12 h. Then the PbI₂ solution was deposited by spin coating at 2000 rpm for 30 s, and then annealed at 70 °C for 15 min. After cooling down to room temperature, a solution of FAI:MAI:MACl (weight ratio, 51:9:12; 72 mg mL⁻¹ in total, in isopropanol) was spin-coated on the top of the PbI₂ layer at 3000 rpm for 40 s, followed with thermal annealing at 140 °C for 20 min in air (relative humidity \approx 40%). The doped spiro-OMeTAD/chlorobenzene (80 mg mL⁻¹, 1ml) solution was prepared with the addition of 30 µL 4-tert-butylpyridine and 35 µL Li-TFSI/acetonitrile (260 mg mL⁻¹), and deposited by spin coating at 6000 r.p.m. for 30 s. The dopant-free DRSBDT-2OT/chloroform (18 mg mL⁻¹) was deposited by spin coating at 8000 r.p.m. for 30 s. The mixed HTL solution for DRSBDT-2OT/Spiro-OMeTAD was prepared by mixing the solution of DRSBDT-2OT (10 mg/ml in CB) and Spiro-OMeTAD above mentioned with a v/v of 1:1, and then deposited by spin-coating at 6000 r.p.m for 30 s. Finally, a 15 nm MoO₃ layer and 80 nm Ag layer were deposited by thermal evaporation under a pressure of 1.0 \times 10⁻⁴ Pa. The effective area was 10 mm² defined by mask.

4. Synthesis



Scheme S1. Synthetic routes of DRSBDT-2OT

Synthesis of compound 2: LDA (lithium diisopropylamide) (2.0M, 6.0 mL, 12.0 mmol) was added slowly to the solution of Compound **1** (2.12 g, 10.0 mmol) in 30 mL anhydrous THF under an argon atmosphere. After being stirred for 0.5 h at -80°C, chlorotributyltin (4.03 mL, 15.0 mmol) was added dropwise to the solution, and then being stirred for an hour at -80°C. The reaction was warmed to room temperature and stirred for another 2 hours and then quenched with water and extracted with petroleum ether, the combined organic layer was washed with brine and then dried over Na₂SO₄. After removal of solvent, the crude product was used without any further purification.

Synthesis of compound 3: LDA (lithium diisopropylamide) (2.0M, 30.0 mL, 60.0 mmol) was added slowly to the solution of Compound 1 (8.49 g, 40.0 mmol) in 80 mL anhydrous THF under an argon atmosphere. After being stirred for 0.5 h at -80°C, DMF (9.24 mL, 120.00 mmol) was added dropwise to the solution, and then being stirred for an hour at -80°C. The

reaction was warmed to room temperature and stirred for another 2 hours and then quenched with water and extracted with petroleum ether, the combined organic layer was washed with brine and then dried over Na₂SO₄. After removal of solvent, the crude product was purified by column chromatography on silica gel using hexane/dichloromethane as eluant to afford light yellow oil (7.37 g, 76.6% yield). ¹H NMR (400 MHz, CDCl₃) δ 9.82 (d, *J* = 1.2 Hz, 1H), 7.41 (d, *J* = 1.6 Hz, 1H), 6.77–6.68 (m, 1H), 3.86 (d, *J* = 5.6 Hz, 2H), 1.75–1.67 (m, 1H), 1.51–1.37 (m, 4H), 1.35–1.28 (m, 4H), 0.96–0.88 (m, 6H).

Synthesis of compound 4: NBS (Bromosuccinimide) (816.3mg, 4.59 mmol) was added slowly to the solution of Compound 3 (1.05g, 4.37 mmol) in 30 mL anhydrous CHCl₃ under an argon atmosphere at ice-bath, After being stirred for 2 h at room temperature, the reaction was quenched with water and extracted with CH₂Cl₂. The organic layer was thoroughly washed with water and then dried over Na₂SO₄. After removal of solvent it was chromatographied on silica gel using hexhane/ CH₂Cl₂ (4:1, v: v) as eluant to afford a yellow oil (1.2 g, 86.7% yield). ¹H NMR (400 MHz, CDCl₃) δ 9.69 (s, 1H), 7.37 (s, 1H), 3.96 (d, *J* = 5.6 Hz, 2H), 1.78–1.66 (m, 1H), 1.55–1.38 (m, 4H), 1.37–1.28 (m, 4H), 0.98-0.86 (m, 6H).

Synthesis of compound 5: $Pd(PPh_3)_4$ (150 mg, 0.13 mmol) was added to a solution compound 4 (2.12 g, 6.67mmol) and crude compound 2 in Toluene (40 mL) under argon protection. After being stirred at 110 °C for 24 h, the reaction mixture was poured into water and extracted with CH_2Cl_2 . The organic layer was washed with water, and then dried over Na_2SO_4 . After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of hexane/dichlo-romethane (3:1) as eluant to afford a yellow oil (1.8 g, 60.0%). ¹H

NMR (400 MHz, CDCl₃) δ 9.75 (s, 1H), 7.46 (s, 1H), 7.08 (d, *J* = 1.6 Hz, 1H), 6.29 (d, *J* = 1.6 Hz, 1H), 4.05 (d, *J* = 5.6 Hz, 2H), 3.84 (d, *J* = 5.6 Hz, 2H), 1.84–1.74 (m, 1H), 1.73–1.67 (m, 1H), 1.67–1.58 (m, 4H), 1.38–1.31 (m, 12H), 0.97–0.87 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 181.9, 157.7, 153.5, 136.1, 132.3, 126.3, 123.5, 117.0, 98.9, 74.3, 72.7, 39.7, 39.4, 30.5, 30.4, 29.1, 28.3, 26.8, 23.8, 23.1, 23.0, 17.4, 14.1, 13.6, 11.2, 11.1.

Synthesis of compound 6: NBS (Bromosuccinimide) (587.4mg, 3.3 mmol) was added slowly to the solution of Compound 5 (1.35g, 3 mmol) in 30 mL anhydrous CHCl₃ under an argon atmosphere at ice-bath, After being stirred for 2 h at room temperature, the reaction was quenched with water and extracted with CH₂Cl₂. The organic layer was thoroughly washed with water and then dried over Na₂SO₄. After removal of solvent it was chromatographied on silica gel using hexhane/ CH₂Cl₂ (4:1, v: v) as eluant to afford a green yellow oil (1.41 g, 89.2% yield). ¹H NMR (400 MHz, CDCl₃) δ 9.76 (s, 1H), 7.45 (s, 1H), 7.02 (s, 1H), 4.06 (d, *J* = 5.2 Hz, 2H), 3.95 (d, *J* = 5.6 Hz, 2H), 1.85–1.77 (m, 1H), 1.76–1.68 (m, 1H), 1.62–1.43 (m, 8H), 1.36 (m, 8H), 0.99–0.92 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) δ 181.8, 154.6, 153.5, 136.2, 132.0, 125.5, 123.4, 113.8, 93.5, 74.7, 74.4, 39.7, 39.6, 30.4, 30.3, 29.1, 29.0, 23.9, 23.7, 23.1, 23.0, 14.1, 11.2, 11.1.

Synthesis of compound 8: n-BuLi (0.7 mL, 1.75 mmol, 2.5 M in hexane) was added slowly to the solution of compound **7** (321.5mg, 0.5 mmol) in 20 mL anhydrous THF under an argon atmosphere at ice-bath, After being stirred at room temperature for 1.5 h. Chlorotributyltin (0.54 mL, 2 mmol) was added dropwise to the solution at ice-bath, and then stirred over night at room temperature. The reaction was quenched with water and then quenched with water and

extracted with petroleum ether, the combined organic layer was washed with brine and then dried over Na₂SO₄. After removal of solvent, the crude product was used without any further purification.

Synthesis of compound 9 (DRSBDT-2OT-CHO): Pd(PPh₃)₄ (28.9 mg, 0.025 mmol) was added to a solution compound 6 (530 mg, 1.0mmol) and crude compound 8 in Toluene (40 mL) under argon protection. After being stirred at 110 °C for 24 h, the reaction mixture was poured into water and extracted with CH₂Cl₂. The organic layer was washed with water, and then dried over Na₂SO₄. After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of hexane/ ethyl acetate (10:1) as an eluent to afford a red oil (300 mg, 39.0%).¹H NMR(400MHz, CDCl₃), δ(ppm): ¹H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 2H), 7.78 (s, 2H), 7.47 (s, 2H), 7.37 (d, J = 3.6 Hz, 2H), 7.24–7.17 (m, 4H), 4.15-4.02 (m, 8H), 2.97 (d, J = 6.4 Hz, 4H), 1.88-1.80 (m, 2H), 1.80-1.73 (m, 3H), 1.71-1.61 (m, 2H), 1.80-1.73 (m, 2H), 1.80-(m, 6H), 1.58–1.44 (m, 20H), 1.37–1.27 (m, 24H), 1.03–0.98 (m, 6H), 0.96–0.88 (m, 30H). ¹³C NMR (101 MHz, CDCl₃) δ 181.7, 154.5, 153.9, 142.3, 138.5, 137.3, 136.7, 136.3, 135.9, 132.3, 130.9, 128.3, 125.9, 123.2, 122.1, 118.1, 116.0, 114.2, 74.5, 74.0, 43.7, 39.8, 39.3, 32.2, 30.6, 30.5, 29.1, 29.1, 28.8, 25.4, 24.0, 23.9, 23.1, 23.0, 14.12, 11.4, 11.3, 10.8. (MALDI-TOF): calc for C₈₄H₁₁₄O₆S₁₀ [M⁺], 1538.582; found: 1538.505.

Synthesis of DRSBDT-2OT: piperidine (0.3 mL) was added to the solution of **compound 9** (130 mg, 0.084 mmol) and **INCN** (98 mg, 0.51 mmol) were dissolved in 30 mL anhydrous CHCl₃ under an argon atmosphere at room temperature. After being stirred for 24 h at 65 °C. The mixture was poured into methanol and filtered, and the residue purified by column

chromatography using CHCl₃ as an eluent to afford compound DRSBDT-2OT as a black solid (120 mg, 75.6%). ¹H NMR (400 MHz, CDCl₃) δ 7.78 (s, 2H), 7.63 (s, 2H), 7.34 (d, *J* = 3.6 Hz, 2H), 7.14 (d, *J* = 3.6 Hz, 2H), 6.99 (s, 2H), 6.93 (s, 2H), 4.18–4.07 (m, 4H), 4.08–3.94 (m, 8H), 2.92 (d, *J* = 6.4 Hz, 4H), 1.82–1.70 (m, 4H), 1.66–1.55 (m, 6H), 1.50–1.39 (m, 20H), 1.34–1.23 (m, 30H), 0.98–0.90 (m, 12H), 0.89–0.80 (m, 24H). ¹³C NMR (101 MHz, CDCl₃) δ 165.5, 165.2, 154.7, 142.1, 138.3, 137.4, 136.4, 135.8, 132.0, 131.0, 130.3, 128.4, 127.9, 125.4, 125.4, 122.4, 121.7, 117.9, 116.7, 113.5, 113.00, 112.5, 112.3, 75.0, 74.1, 55.2, 43.7, 40.4, 39.9, 39.8, 39.3, 32.3, 30.4, 29.7, 29.3, 29.1, 28.8, 25.5, 24.0, 23.8, 23.2, 23.1, 23.0, 14.2, 14.2, 14.1, 11.5, 11.4, 10.8. (MALDI-TOF): calc for C₁₀₀H₁₂₄N₆O₆S₁₂ [M⁺], 1889.626; found: 1889.293.

5. Supporting Figures



Figure S1. The optimized geometries of DRSBDT-2OT.



Figure S2. TGA plots of DRSBDT-2OT with a heating rate of 10 °C min⁻¹ under N_2 atmosphere.



Figure S3. (a) Normalized UV-vis absorption spectra of DRSBDT-2OT in CF solutions and films. (b) The extinction coefficient of the DRSBDT-2OT in CF solution. (c) Cyclic voltammograms of DRSBDT-2OT and Spiro-OMeTAD are measured in the film using the ferrocene/ferrocenium redox couple (Fc/Fc⁺) as the reference with a scanning rate of 50 mV s^{-1} .



Figure S4. The steady-state PL spectra and of perovskite, perovskite/spiro-OMeTAD, perovskite/DRSBDT-2OT, and perovskite/mixed HTMs.



Figure S5. FTIR spectra of the powder of perovskite, DRSBDT-2OT, and perovskite with DRSBDT-2OT HTM.



Figure S6. The *J*–V curves of the devices based on spiro-OMeTAD (a), dopant-free DRSBDT-2OT (b), and mixed HTM (c) under different scan directions.



Figure S7. Stabilized PCE measurement of the best device for spiro-OMeTAD, dopant-free

DRSBDT-2OT and mixed HTM.



Figure S8. Histogram of PCEs measured for 30 cells using spiro-OMeTAD, DRSBDT-2OT, and mixed HTM as HTM.



Figure S9. Photovoltaic parameters of PSCs with different optimization using spiro-OMeTAD, dopant-free DRSBDT-2OT, and mixed HTM as HTM. Histograms of a) PCE, b) V_{OC} , c) J_{SC} , and d) FF of corresponding devices.



Figure S10. (a) $J^{0.5}$ –V plots for the spiro-OMeTAD, dopant-free DRSBDT-2OT, and mixed HTM based devices in the SCLC region. (b) log(J) - log(V) plots of the devices in the SCLC region with slop of 2.0. The solid lines are fits of the data points.



Figure S11. AFM morphology of a) perovskite covered with doped spiro-OMeTAD, b) perovskite covered with undoped DRSBDT-2OT, and c) perovskite covered with mixed-HTM.



Figure S12. Evolution of the normalized V_{OC} (a), FF (b) and J_{SC} (c) measured from the unencapsulated devices which were stored in ambient air with a relative humidity (RH) of $35\pm5\%$, respectively.

Figure S13. Evolution of the normalized V_{OC} (a), FF (b) and J_{SC} (c) measured from the unencapsulated devices which were exposed to continuous light soaking (100 mW cm⁻²) in N₂, respectively.

Figure S14. Normalized PCEs measured from the unencapsulated devices stored in N_2 at 70 °C

Figure S15. ¹H NMR of DRSBDT-2OT in deuterated chloroform

Figure S16. ¹³C NMR of DRSBDT-2OT in deuterated chloroform

Figure S17. MADLI-TOF mass spectrometry of DRSBDT-20T

 Table S1. Summary of the optical electrochemical and photoelectrical properties for

 DRSBDT-2OT.

HTMs	$\lambda_{max}[nm]$	$\lambda_{max} \left[nm ight]$	$\lambda_{onset}[nm]$	E_g^{opt}	НОМО	LUMO	μ_h
	solution.	film	film	[eV]	[eV]	[eV]	cm ² V ⁻¹ s ⁻¹
DRSBDT-20T	675	736	811	1.53	-5.09	-3.76	1.70×10 ⁻⁴
Spiro- OMeTAD	-	-	-	-	-4.83	-2.0	2.13×10 ⁻⁵

Table S2. The obtained carrier lifetimes of perovskite films based on Spiro-OMeTAD,DRSBDT-2OT and mixed HTM as HTLs.

Sample	Lifetime
Control	142.63 ns
Spiro-OMeTAD	0.63 ns
DRSBDT-20T	0.97 ns
mixed HTM	0.56 ns

Sample	$R_{ct}(\Omega)$	$R_{rec}(\Omega)$
spiro-OMeTAD	323.21	151.33
DRSBDT-20T	523.28	139.22
mixed HTM	258.92	265.24

Table S3. The obtained charge transport resistance (R_{ct}), charge recombination resistance (R_{rec}) of perovskite solar cells based on Spiro-OMeTAD, DRSBDT-2OT and mixed HTM as HTLs.

Table S4. Device performance parameters of the device with differet HTMs under different scan directions (corresponding to Figure S4).

Sample		$V_{OC}(V)$	FF (%)	Jsc (mA cm ⁻²)	PCE (%)
Spiro-OMeTAD	o-OMeTAD Reverse		79.63	22.14	19.04
	Forward	1.05	67.57	22.11	15.74
DRSBDT-2OT	Reverse	1.092	68.81	22.84	17.13
	Forward	1.089	68.74	22.85	17.11
mixed HTM	Reverse	1.10	81.85	23.67	21.31
	Forward	1.09	76.33	23.92	19.89

Reference

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