A Novel Phenoxazine-Based Hole-Transport Material for Efficient Perovskite Solar Cells

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Measurement

^{1}H NMR spectra were recorded on a VARIAN INOVA 400 MHz spectrometer (USA) using TMS as standard. MS data were obtained with GCT CA156 (UK). The absorption spectra were recorded on HP8453 (USA). Cyclic voltammetry (CV) was performed in acetonitrile with 0.1 M $TBAPF_6$ as the supporting electrolyte, a $Ag^+/AgNO_3$ electrode as the reference electrode, a carbon-glass electrode as the working electrode, a Pt electrode as the counter electrode and ferrocene/ferrocenium (Fc/Fc^+) as an internal reference on electrochemistry workstation (BAS100B, USA). Light source for the photocurrent-voltage (*J*–*V*) measurement is an AM 1.5G solar simulator (Newport 69907, USA). The incident light intensity was 100 mW cm^{-2} calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.16 cm^2. The photocurrent-voltage (*J*–*V*) curves were obtained by the linear sweep voltammetry (LSV) method using a Keithley 2400 source-measure unit. The measurement of the external quantum efficiency (EQE) was performed a Hypermono-light (Newport IQE200, USA). X-ray diffraction (XRD) pattern was obtained using a Rigaku D/MAX 2400 diffractometer with Cu Kα radiation at scan rate of 4^o/min under operation condition of 30 kV and 40 mA. A field-emission scanning electron microscope (Nova NanoSEM 450) was used to investigate cross-sectional morphology of the solid state devices.

For electrochemical impedance spectroscopy study, measurements were carried out using AutoLab Zennium/IM6 under illumination condition and different bias potentials were applied ranging from 0.6 V to 1.0 V and frequencies between 1 MHz and 0.1 Hz.

Hole mobility of **POZ6-2** and Spiro-OMeTAD was measured by using the space-charge-limited current (SCLC) method with the device structure of ITO/MoO_3/**POZ6-2** or **Spiro-OMeTAD**/MoO_3/Ag. For the hole-only devices, SCLC is described as

$$J=\frac{9\varepsilon\varepsilon_0\mu_0 V^2 \exp(0.89\sqrt{V/_{E_0 L}})}{8L^3} \tag{1}$$

where ε is the dielectric constant of the transport material, ε_0 is the permittivity of the vacuum, μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, and L is the thickness of the film.

The synthesis of POZ6-2

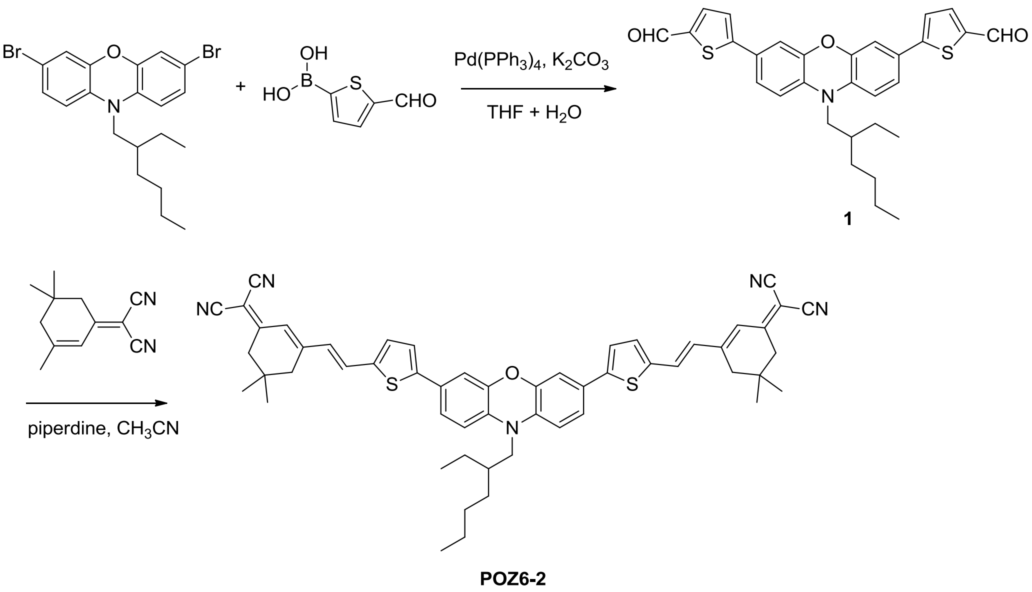

Figure S1 The synthetic routes of HTM **POZ6-2**

5, 5'-(10-(2-ethylhexyl)-10H-phenoxazine-3, 7-diyl)bis(thiophene-2-carbaldehyde) (Compound **1**)

Under nitrogen conditions, 3, 7-dibromo-10-(2-ethylhexyl)-10H-phenoxazine (902 mg, 2 mmol), 5-formyl-2-thiopheneboronic acid (780 mg, 5 mmol), potassium carbonate (4.5 g, 10.0 mmol) and tetrakis(triphenylphosphine)palladium (232 mg, 0.2 mmol) are placed in flask and dissolved in 50 mL of THF/H_2O (4:1; v/v). After the mixtures are bubbled with nitrogen for 0.5 h, the mixtures are then stirred at 80 ℃ for 12 h. After the reaction, 30 mL of water are added and the solution extracted with dichloromethane. The solvent was removed by rotary evaporation and the residue was purified by chromatography (silica gel, dichloromethane: hexane = 2:1) to provide compound **1** as orange solid (767 mg, 74 %). ^1H-NMR (400 MHz, Acetone-d_6, ppm) δ_H 9.88 (2 H, s), 8.01 (2 H, d, *J* 4.0), 7.69 (2 H, d, *J* 4.0), 7.64 – 7.59 (4H, m), 7.12 (2 H, d, *J* 8.4), 3.56 (2 H, d, *J* 7.4), 1.89 (1 H, dd, *J* 12.7, 6.2), 1.53 – 1.22 (8 H, m), 0.94 (3 H, t, *J* 7.5), 0.88 (3 H, d, *J* 7.1). GC/Q-TOF MS: Found m/z 515.1596, Calc. for $C_{30}H_{29}NO_3S_2$ 515.1589.

2, 2'-(((1E, 1'E)-(5, 5'-(10-(2-ethylhexyl)-10H-phenoxazine-3, 7-diyl)bis(thiophene-5, 2-diyl))bis(ethene-2, 1-diyl))bis(5, 5-dimethylcyclohex-2-en-3-yl-1-ylidene))dimalononitrile (**POZ6-2**)

2-(3, 5, 5-trimethylcyclohex-2-en-1-ylidene)malononitrile (930 mg, 5 mmol) and compound **1** (1.03 g, 2 mmol) were added into 30 mL CH_3CN and refluxed for 24 h, with piperidine as the catalyst. Then remove the solvent by rotary evaporation and the residue was purified by chromatography (silica gel, dichloromethane: hexane = 1:1) to provide product **POZ6-2**. ^1H-NMR (400 MHz, Acetone-d_6, ppm) δ_H 8.01 (2 H, d, *J* 4.0), 7.69 (2 H, d, *J* 4.0), 7.64 – 7.59 (4 H, m), 7.47 (2 H, d, *J* 15.8), 7.35 (2 H, s), 7.12 (2 H, d, *J* 8.4), 7.02 (2 H, d, *J* 15.7), 3.65 (2 H, t, *J* 7.0), 2.66 (4 H, s), 2.59 (4 H, s), 1.85 – 1.65 (1 H, m), 1.56-1.25 (8 H, m), 1.11 (12 H, s), 0.95 (3 H, t, *J* 7.5), 0.90 (3 H, t, *J* 7.4). GC/Q-TOF MS: Found m/z 851.3684, Calc. for $C_{54}H_{53}N_5OS_2$ 851.3692.

Perovskite Solar Cell Fabrication

1. Preparation of mesoporous TiO_2 film

Perovskite thin film and solar cells were fabricated on FTO-glass substrate with a sheet resistance of 15 Ω sq^{-1}. Fluorine–doped tin oxide coated glass (Pilkington TEC 15) was firstly patterned by etching with Zn powder and 2 M HCl. The etched substrate was then cleaned with surfactant and rinsed with acetone and ethanol and de–ionized water and finally treated under oxygen plasma for 10 min to remove the last traces of organic residues.

A thin layer of compact anatase TiO_2 of roughly 50 nm in thickness was formed through spin–coating of titanium diisopropoxide bis(acetylacetonate) diluted in anhydrous ethanol at a volumetric ratio of 1:20 at 2000 r.p.m. for 60s and consequently heating at 500 ℃ for 30 min. Mesoporous TiO_2 layers were deposited by spin–coating TiO_2 paste (Dyesol 18NR–T) diluted in anhydrous ethanol at ratio of 1:7 by weight at 3000 r.p.m. for 60 s and consequently heating at 500 ℃ for 30 min. The as prepared nanoporous TiO_2 films were then dipped into a 40 mM $TiCl_4$ aqueous solution for 30 min at 70 ℃, dried at ambient atmosphere and then sintered at 500 ℃ for 30min.

2. Device fabrication

The prepared mesoporous TiO_2 films were infiltrated with a solution of PbI_2 in *N, N*-dimethylformamide (460 $mg.mL^{-1}$) by spin coating at 4000 r.p.m. for 30 s and dried at 70 ℃ for 15 min. After cooling to room temperature, dip the resulted TiO_2/PbI_2 film into a solution of CH_3NH_3I in 2-isopropanol (6 $mg.mL^{-1}$) for 60 min. The resulting perovskite film was washed with dry 2-propanol and N_2 flow, and then dried at 70 ℃ for 30 min. The thickness of the perovskite capping layer is about 200 nm. Subsequently, the HTM layer was then spin coated on top of the perovskite film. The pristine **POZ6-2** based HTM layer (20 mg of **POZ6-2** dissolved in 1 mL chlorobenzene) and doped **POZ6-2** based HTM layer (20 mg of **POZ6-2**, 5 μL of 4-tert-butylpyridine (TBP), and 10 μL of a lithium-bis-(trifluoromethanesulfonyl)imide (LiTFSI) solution (28 mg LiTFSI/1 mL acetonitrile) all dissolved in 1 mL chlorobenzene) were deposited by spin coating at 1500 rpm for 30 s. The 2, 2', 7, 7'-tetrakis(*N*, *N*-di(4-methoxyphenyl)amino)-9, 9'-spirobifluorene (Spiro-OMeTAD) HTM layer (80 mg of Spiro-OMeTAD, 28.5 μL of TBP, and 17.5 μL of a LiTFSI solution (520 mg LiTFSI/1 mL acetonitrile) all dissolved in 1 mL chlorobenzene) was deposited by spin coating at 4000 rpm for 30 s. Finally, a layer of 200 nm Ag was deposited sequentially under high vacuum ($<4 \times 10^{-4}$ Pa) by thermal evaporation through a shadow mask to form an active area of ~9 mm^2.