

Application of Small Molecule Donor Materials Based on Phenoxazine Core Unit in Bulk Heterojunction Solar Cells

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1. Measurements

¹H 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). Electrochemical redox potentials were obtained by cyclic voltammetry (CV) on electrochemistry workstation (BAS100B, USA). The working electrode was a glass carbon disk electrode; the auxiliary electrode was a Pt wire; and Ag/Ag⁺ was used as the reference electrode. TBAPF₆ was used as supporting electrolyte in CHCl₃. The ferrocenium/ferrocene (Fc/Fc⁺) redox couple was used as an internal potential reference. Atomic force

microscope (AFM) investigation was performed using Bruker MultiMode AFM in "tapping" mode. Light source for the photocurrent-voltage ($J-V$) measurement is an AM 1.5G solar simulator (Newport 69907, USA). The incident light intensity was $100 \text{ mW}\cdot\text{cm}^{-2}$ calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.04 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 incident photon-to-current conversion efficiency (IPCE) was performed a Hypermono-light (Newport IQE200, USA).

2. The synthesis of donor materials

All starting materials were purchased from commercial suppliers and used without further purification.

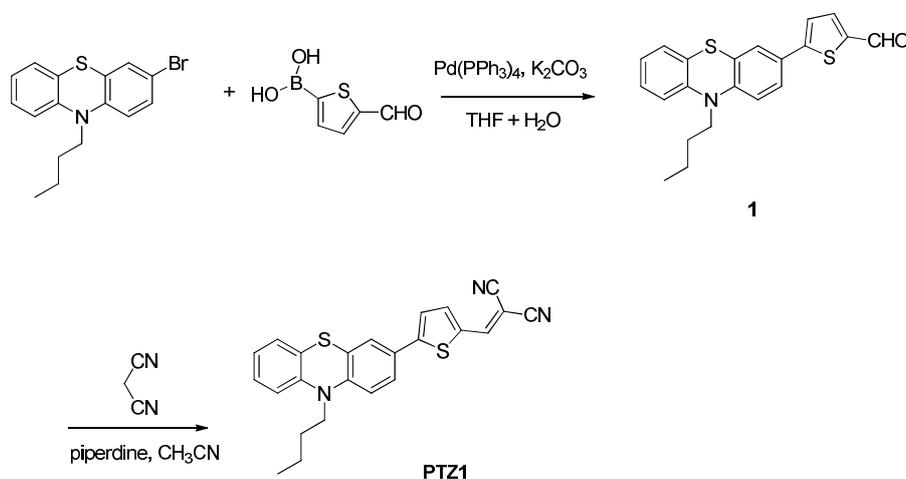


Figure S1 The synthetic route of small molecule donor material **PTZ1**

5-(10-butyl-10H-phenothiazin-3-yl)thiophene-2-carbaldehyde (compound **1**)

Under nitrogen conditions, 3-bromo-10-butyl-10H-phenothiazine (666 mg, 2 mmol), 5-formyl-2-thiopheneboronic acid (375 mg, 2.4mmol), potassium carbonate (2.23 g,

5.0 mmol) and tetrakis(triphenylphosphine)palladium(116 mg, 0.1 mmol) are placed in flask and dissolved in 50 ml of THF/H₂O (4:1; v/v). After the mixtures are bubbled with nitrogen for 0.5 h, the mixtures are then stirred at 80°C for 12 h. After the reaction, 30 mL of water are added and the solution extracted with DCM. The solvent was removed by rotary evaporation and the residue was purified by chromatography (silica gel, dichloromethane: hexane = 1:1) to provide product **1** as orange solid (423 mg, 58 %). ¹H-NMR (400 MHz, Acetone-*d*₆, ppm) δ_H 9.89 (1 H, s), 7.90 (1 H, d, *J* 4.0), 7.51 (1 H, d, *J* 4.0), 7.27 (1 H, dd, *J* 8.4, 2.2), 7.02 (1 H, d, *J* 2.2), 6.91 – 6.85 (1 H, m), 6.78 – 6.70 (2 H, m), 6.70 – 6.64 (2 H, m), 3.69 – 3.61 (2 H, m), 1.68 (2 H, tt, *J* 7.9, 6.6), 1.51 (2 H, dq, *J* 14.6, 7.3), 1.01 (3 H, t, *J* 7.3). GC/Q-TOF MS: Found *m/z* 365.0908, Calc. for C₂₁H₁₉NOS₂ 365.0912.

2-((5-(10-butyl-10H-phenothiazin-3-yl)thiophen-2-yl)methylene)malononitrile (PTZ1)

Malononitrile (200 mg, 3 mmol) and compound **1** (730 mg, 2 mmol) were added into CH₃CN(30 mL) and refluxed for 12 h, with piperidine as the catalyst. Then remove the solvent by rotary evaporation and the residue was purified by chromatography (silica gel, dichloromethane: hexane = 1:2) to provide product **PTZ1**. ¹H-NMR (400 MHz, Acetone-*d*₆, ppm) 8.37 (1 H, s), 7.94 (1 H, d, *J* 4.1), 7.74 – 7.63 (2 H, m), 7.59 (1 H, d, *J* 2.2), 7.27 – 7.19 (1 H, m), 7.14 (3 H, ddd, *J* 27.4, 13.2, 4.6), 7.05 – 6.95 (1 H, m), 4.02 (2 H, t, *J* 7.0), 1.87 – 1.73 (2 H, m), 1.50 (2 H, dd, *J* 15.0, 7.4), 0.94 (3 H, t, *J* 7.4). GC/Q-TOF MS: Found *m/z* 413.1015, Calc. for C₂₄H₁₉N₃S₂ 413.1020.

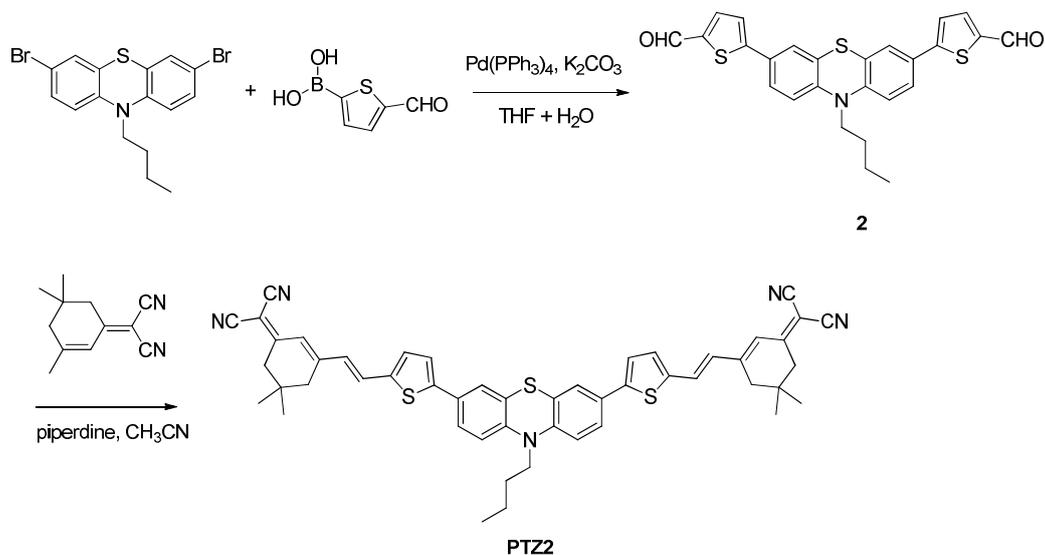


Figure S2 The synthetic route of small molecule donor material **PTZ2**

5,5'-(10-butyl-10H-phenothiazine-3,7-diyl)bis(thiophene-2-carbaldehyde)

(Compound **2**)

Under nitrogen conditions, 3,7-dibromo-10-butyl-10H-phenothiazine (821 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/H₂O (4:1; v/v). After the mixtures are bubbled with nitrogen for 0.5 h, the mixtures are then stirred at 80°C for 12 h. After the reaction, 30 mL of water are added and the solution extracted with DCM. The solvent was removed by rotary evaporation and the residue was purified by chromatography (silica gel, dichloromethane: hexane = 2:1) to provide product **2** as orange solid (589 mg, 62 %). 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), 3.95

(2 H, t, *J* 7.0), 1.75 – 1.65 (2 H, m), 1.43 (2 H, dq, *J* 14.6, 7.4), 0.90 (3 H, t, *J* 7.4).GC/Q-TOF MS: Found *m/z* 475.0736, Calc. for C₂₆H₂₁NO₂S₃475.0734.

2,2'-(((1E,1'E)-(5,5'-(10-butyl-10H-phenothiazine-3,7-diyl)bis(thiophene-5,2-diyl))bis(ethene-2,1-diyl))bis(5,5-dimethylcyclohex-2-en-3-yl-1-ylidene))dimalononitrile (PTZ2)

2-(3,5,5-trimethylcyclohex-2-en-1-ylidene)malononitrile (930 mg, 5mmol) and compound **2** (950 mg, 2 mmol) were added into CH₃CN(30 mL) 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 **PTZ2**. 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), 3.95 (2 H, t, *J* 7.0), 2.66 (4 H, s), 2.59 (4 H, s), 1.75 – 1.65 (2 H, m), 1.43 (2 H, dq, *J* 14.6, 7.4), 1.11 (12 H, s), 0.90 (3 H, t, *J* 7.4).GC/Q-TOF MS: Found *m/z* 811.2813, Calc. for C₅₀H₄₅N₅S₃811.2837.

3. Solar Cell Fabrication

The devices were fabricated with a conventional structure of glass/ITO/ZnO/active layer/MoO₃/Ag using a solution process. The ZnO sol was prepared using a sol-gel procedure by dissolving zinc acetate dihydrate (C₄H₆O₄Zn·2(H₂O), 99.9 %, 2 g) and monoethanolamine (HOCH₂CH₂NH₂, 99 %, 0.28 g) in 2-methoxyethanol (HOCH₂CH₂OCH₃, > 99.8 %, 9.1 ml) under vigorous stirring for 12 h for hydrolysis reaction and aging. The ITO-coated glass substrates

were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 min each. A thin layer (about 30 nm) of ZnO sol was spin-coated at 4000 rpm onto the ITO surface. After being baked at 150°C for 2 h. Subsequently, the active layer (about 100 nm) was spin-coated from donor (10 mg/mL)-acceptor (10 mg/mL) blend *o*-dichlorobenzene solutions at 1400 rpm. Finally, a 5 nm MoO₃ and 50 nm Ag layer were deposited on the active layer under high vacuum ($<4 \times 10^{-4}$ Pa). The effective area of each cell was 4 mm² defined by the mask. The current density–voltage (J – V) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under illumination simulated 100 mW·cm⁻² AM1.5G irradiation using a solar simulator, calibrated with a standard Si solar cell.