

Supporting Information

Molecular Engineering of Small Molecules Donor Materials Based on Phenoxazine Core Unit for Solution-Processed Organic 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). Elemental Analysis data were obtained with Elemental Analyzer Vario EL III (Germany). 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 8 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 mW·cm⁻² calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.04 cm². The photocurrent-voltage (*J-V*) curves were obtained by the linear sweep voltammetry (LSV) method using an 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).

Mobility measurements of **POZ4:PC71BM** (w:w, 1:1.2) and **POZ6:PC71BM** (w:w, 1:1.0) blend films were carried out with the following diode structures: ITO/PEDOT:PSS/active layer/Al for hole and Ag/active layer/Ag for electron by taking current-voltage curve in the range of 0-8 V. The charge carrier mobilities were calculated using the space-charge limited current (SCLC) model, where the SCLC is described by $J = 9\epsilon_0\epsilon_r\mu V^2/8L^3$, where J is the current density, L is the film thickness of active layer, μ is the hole or electron mobility, ϵ_r is the relative dielectric constant of the transport medium, ϵ_0 is the permittivity of free space (8.85×10^{-12} Fm⁻¹), V is the internal voltage in the device and $V=V_{appl}-V_r-V_{bi}$, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

2. The synthesis of donor materials

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

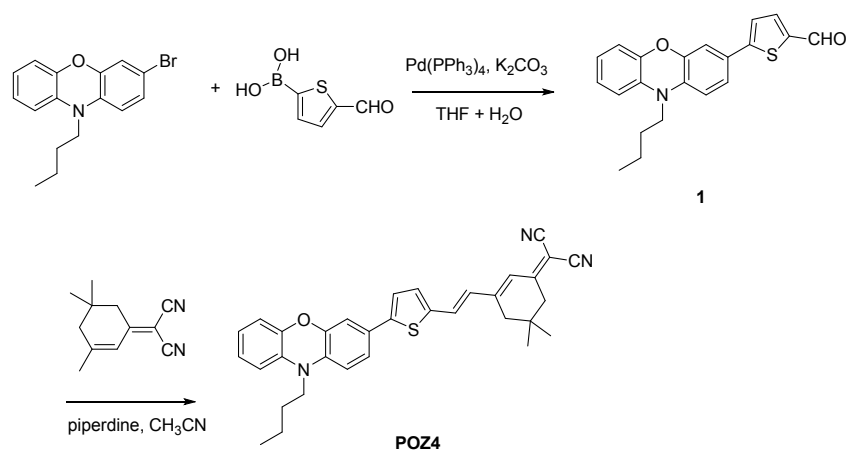


Figure S1 The synthetic route of small molecule donor material **POZ4**

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

Under nitrogen conditions, 3-bromo-10-butyl-10H-phenoxazine (635 mg, 2 mmol), 5-formyl-2-thiopheneboronic acid (375 mg, 2.4 mmol), 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 (496 mg, 64 %). 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* 349.1142, Calc. for C₂₁H₁₉NO₂S 349.1136.

(E)-2-(3-(2-(5-(10-butyl-10H-phenoxazin-3-yl)thiophen-2-yl)vinyl)-5,5-dimethylcyclohex-2-en-1-ylidene)malononitrile (POZ4)

2-(3,5,5-trimethylcyclohex-2-en-1-ylidene)malononitrile (558 mg, 3 mmol) and compound **1** (700 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 **POZ4**. ¹H-NMR (400 MHz, Acetone-*d*₆, ppm) δ_H 7.47 (1 H, d, *J* 15.8), 7.35 (2 H, s), 7.18 (1 H, dd, *J* 8.4, 2.1), 7.02 (1 H, d, *J* 15.7), 6.96 (1 H, d, *J* 2.1), 6.89 – 6.82 (2 H, m), 6.72 (2 H, t, *J* 8.0), 6.69 – 6.64 (2 H, m), 3.69 – 3.62 (2 H, m), 2.66 (2 H, s), 2.59 (2 H, s), 1.73 – 1.63 (2 H, m), 1.51 (2 H, dd, *J* 15.1, 7.4), 1.11 (6 H, s), 1.01 (3 H, t, *J* 7.3). GC/Q-TOF MS: Found *m/z* 517.2182, Calc. for C₃₃H₃₁N₃OS 517.2188. Elem. Anal.: Found C 76.77, H 6.24, N 7.98, S 6.02, Calc. for C 76.56, H 6.04, N 8.12, S 6.19.

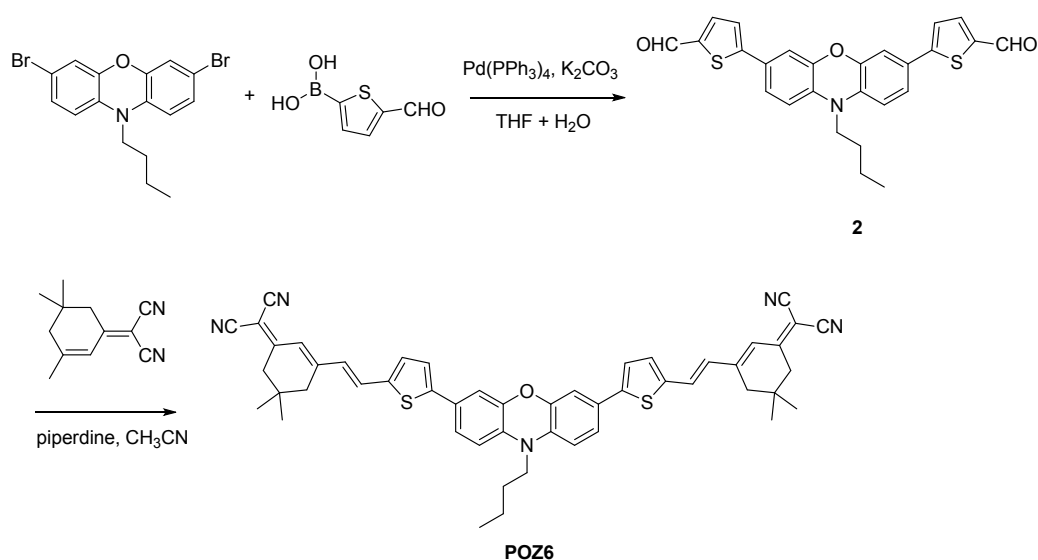


Figure S2 The synthetic route of small molecule donor material **POZ6**

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

(Compound **2**)

Under nitrogen conditions, 3,7-dibromo-10-butyl-10H-phenoxazine (790 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 (596 mg, 65 %). 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* 459.0973, Calc. for C₂₆H₂₁NO₃S₂ 459.0963.

2,2'-(((1E,1'E)-(5,5'-(10-butyl-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-(3,5,5-trimethylcyclohex-2-en-1-ylidene)malononitrile (930 mg, 5 mmol) and compound **2** (918 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 **POZ6**. 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* 795.3061, Calc. for C₅₀H₄₅N₅OS₂ 795.3066. Elem. Anal.: Found C 75.18, H 5.91, N 8.93, S 9.87, Calc. for C 75.44, H 5.70, N 8.80, S 8.06.

3. Solar Cell Fabrication

The devices were fabricated with a conventional structure of glass/ITO/PEDOT-PSS/active layer/BCP/LiF/Al using a solution process. 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 40 nm) of PEDOT-PSS (Clevios PVPAl 4083, filtered at 0.45 μm) was spin-coated at 2000 rpm onto the ITO surface. After being baked at 150°C for 20 min. Subsequently, the active layer (about 100 nm) was spin-coated from donor (10 mg/mL)-acceptor blend *o*-dichlorobenzene solutions with different ratios at 1500 rpm. Finally, a 5 nm BCP, 0.8 nm LiF and 100 nm Al layer were deposited on the active layer under high vacuum (<4 × 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 AM 1.5G irradiation using a solar simulator, calibrated with a standard Si solar cell.

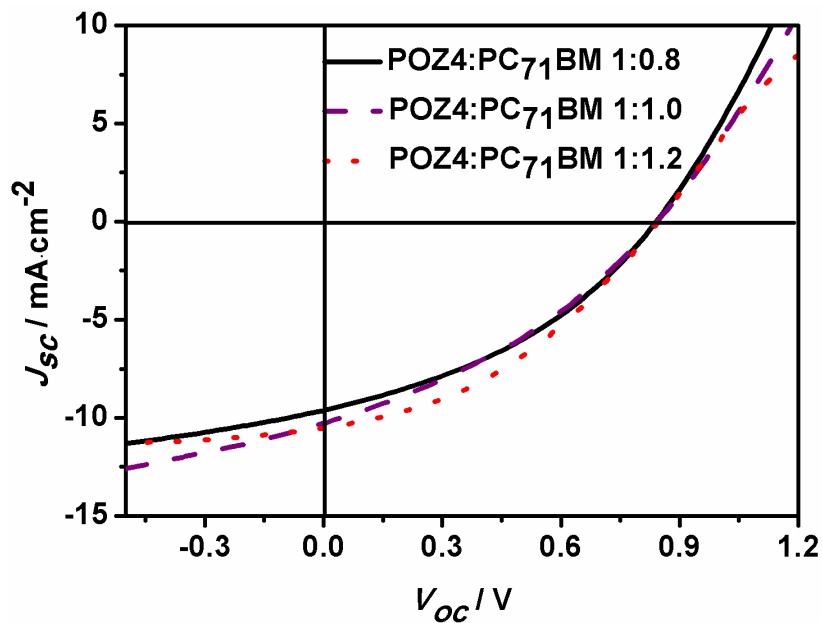


Figure S3. J - V curves of based on **POZ4:PC71BM** with different blend ratios (w:w)

Table S1. Performance parameters for BHJ solar cells based on **POZ4:PC71BM**

POZ4: PC ₇₁ BM (w:w)	$J_{sc} /$ mA·cm ⁻²	V_{oc} / V	$FF / \%$	$\eta / \%$	R at V_{oc} (Ω)
1:0.8	9.6	0.839	37.4	3.01	206
1:1.0	10.2	0.841	35.8	3.07	229
1:1.2	10.5	0.847	40.3	3.58	97.6

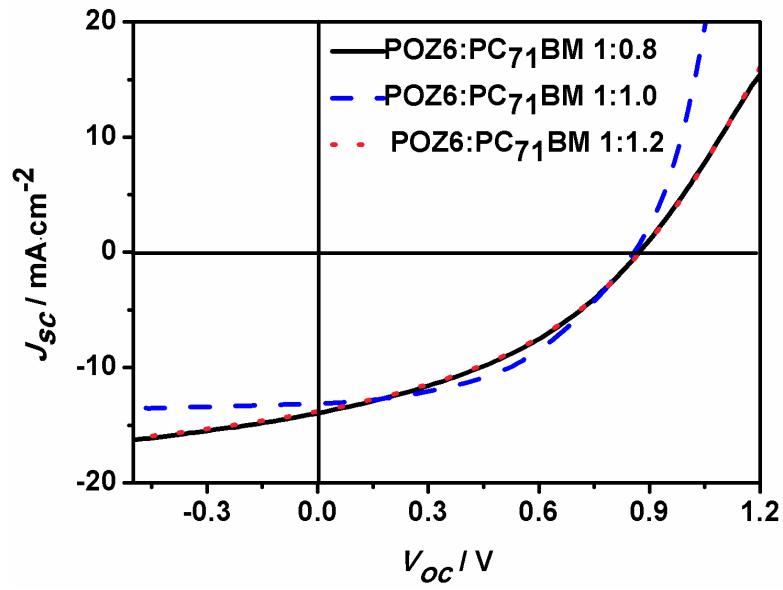


Figure S4. J - V curves of based on **POZ6:PC71BM** with different blend ratios (w:w)

Table S2. Performance parameters for BHJ solar cells based on **POZ6:PC71BM**

POZ6:		$J_{sc} /$ $\text{mA} \cdot \text{cm}^{-2}$	V_{oc} / V	$FF / \%$	$\eta / \%$	R at V_{oc} (Ω)
PC ₇₁ BM (w:w)						
1:0.8		13.9	0.867	43.1	5.19	97.4
1:1.0		13.1	0.862	49.6	5.60	86.2
1:1.2		13.6	0.872	43.4	5.14	92.1