

Supporting Information

Tuning of Phenoxazine Chromophores for Efficient Organic Dye-Sensitized Solar Cells

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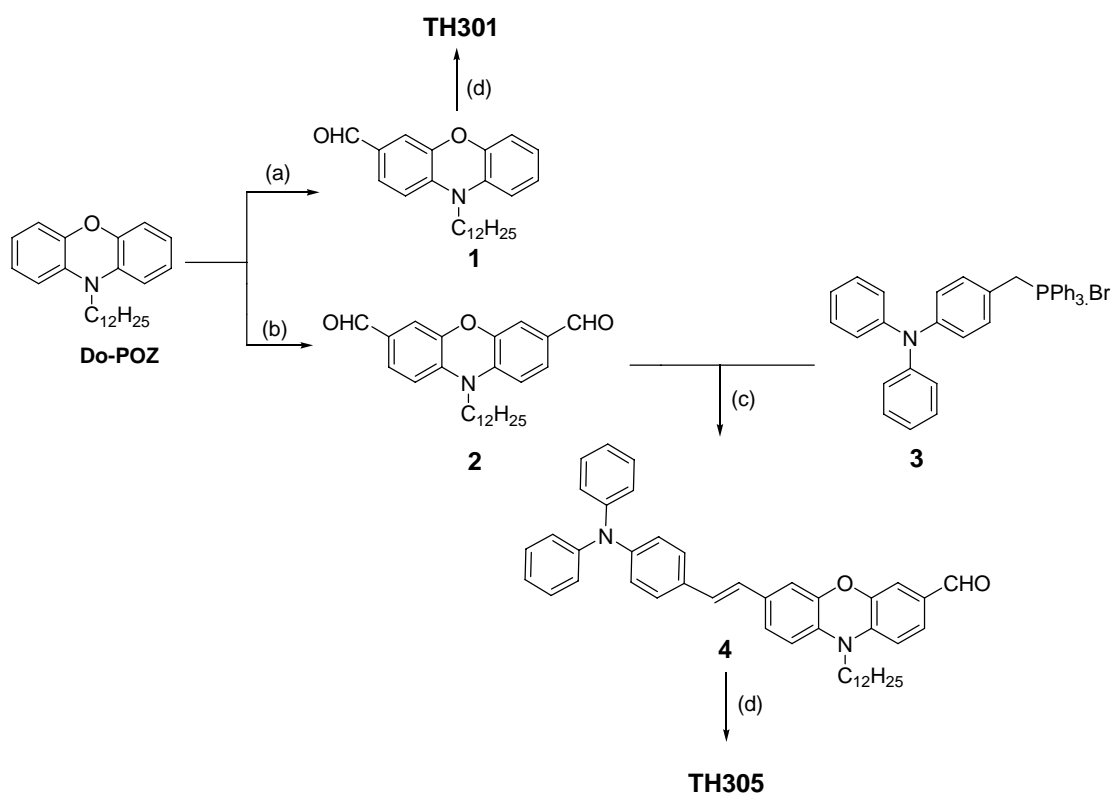
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General

The synthesis routes of the compounds were shown in Scheme S1. Phenoxazine (**POZ**) and triphenylamine (TPA) was commercial available and used as received. 4-Tertbutylpyridine (TBP), lithium iodide (LiI) was purchased from Acros. All solvents and other chemicals were reagent grade and used without further purification. ¹H-NMR spectra were measured with VARIAN INOVA400 MHz (USA) with the chemical shifts against TMS. MS data were measured with GC-Tof MS (UK). Absorption and emission spectra were recorded with HP8453 (USA) and PTI700 (USA), respectively. Electrochemical redox potentials were obtained by cyclic voltammetry (CV) using a three-electrode cell and an electrochemistry workstation (BAS100B, USA). The working electrode was a glass carbon electrode; the auxiliary electrode was a Pt wire and Ag/Ag⁺ was used as reference electrode. Tetrabutylammonium hexafluorophosphate (TBAPF₆) 0.1 M was used as supporting electrolyte in CH₂Cl₂. Ferrocene was added to each sample solution at the end of the experiments and the ferrocenium/ferrocene (Fc/Fc⁺) redox couple was used as an internal potential reference. The photovoltaic performances were obtained with an electrochemistry workstation (LK9805, China) and employed an AM 1.5 solar simulator (16S-002, Solar Light Co. Ltd., USA) as the light source. The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed by a Hypermonolight (SM-25, Jasco Co. Ltd., Japan).

Synthesis Routes of Dyes:



Scheme S1. Synthesis of POZ dyes. Reagents and conditions: (a) POCl₃, DMF, CHCl₃, 12h; (b) POCl₃, DMF, CHCl₃, 48 h; (c) (i) DMF, K₂CO₃, 18-crown-6, r.t. 2h. (ii) THF, I₂, 8h; (d) cyanoacetic acid, piperidine, CH₃CN, reflux, 2 h.

Compound **1**: To a solution of **Do-POZ** (1.76g, 5 mmol) and dry DMF (548 mg, 7.5 mmol) in CHCl₃ (15 ml) in an ice water bath, phosphorus oxychloride (2.30 g, 15 mmol) was added slowly below 15 °C. Then the bath was heated to reflux and maintained for 12 h. Dilute sodium hydroxide aqueous solution was added into and extracted by with dichloromethane (10 ml) for 3 times. The organic layer was dried with anhydrous sodium sulfate and then rotary evaporated. The residue was purified by column chromatography using silica gel and dichloromethane as the eluent to give **1**, yellow liquid (1.69g, 88%). ¹H-NMR (400 MHz, Acetone-*d*₆, ppm): δ 0.87 (3H, t),

1.29-1.50 (18H, m), 1.68-1.74 (2H, m), 3.68 (2H, t), 6.68 (1H, dd, $J_1 = 1.6$ Hz, $J_2 = 1.6$ Hz), 6.74-6.89 (4H, m), 7.03 (1H, d, $J = 2.0$ Hz), 7.41 (1H, dd, $J_1 = 2.0$ Hz, $J_2 = 2.0$ Hz), 9.69 (1H, s). HRMS ES⁺ (m/z): calcd. for C₂₅H₃₃NO₂, 379.2511; found, 379.2521.

Compound **2**: To a solution of **Do-POZ** (1.05g, 3 mmol) and dry DMF (1.10 g, 15 mmol) in CHCl₃ (15 ml) in an ice water bath, phosphorus oxychloride (2.3 g, 15 mmol) was added slowly below 15 °C. Then the bath was heated to reflux and maintained for 48 h. Dilute sodium hydroxide aqueous solution was added into and extracted by with dichloromethane (10 ml) for 3 times. The organic layer was dried with anhydrous sodium sulfate and then rotary evaporated. The residue was purified by column chromatography using silica gel and dichloromethane as the eluent to give **2**, yellow liquid (757 mg, 62%). ¹H-NMR (400 MHz, Acetone-*d*₆, ppm): δ 0.87 (3H, t), 1.29-1.54 (18H, m), 1.73-1.77 (2H, m), 3.79 (2H, t), 6.97 (2H, d, $J = 8.0$ Hz), 7.11 (2H, d, $J = 1.6$ Hz), 7.46 (2H, dd, $J_1 = 1.6$ Hz, $J_2 = 1.6$ Hz), 9.75 (2H, s). HRMS ES⁺ (m/z): calcd. for C₂₆H₃₃NO₃, 407.2460; found, 407.2454.

Compound **3** was got according to our early publish [\[ref\]](#)

Compound **4**: To a solution of compound **2** (305 mg, 0.75 mmol), 18-crown-6 ether (10 mg) and anhydrous potassium carbonate (208 mg, 1.5 mmol) in 20 ml DMF, another solution of compound **3** (530 mg, 0.75 mmol) in 20 ml DMF was added slowly with vigorously stirring at room temperature. The reaction was completed within 2 h. The reaction mixture was poured into water and filtered to collect the orange solid (a mixture of *E* and *Z* isomers), which was then dried in *vacuo*. Then the

dry solid was dissolved in 30 ml THF to reflux in the presence of catalysis amount iodine for 8 h. The mixture was added diluted sodium hydroxide aqueous solution to remove iodine, then extracted with dichloromethane. Organic layer was dried with anhydrous sodium sulfate and removed the solvent, and was purified by column chromatography using silica gel and dichloromethane-petroleum ether (1/1; v/v) as the eluent to give yellow solid, yield 64%. $^1\text{H-NMR}$ (400 MHz, Acetone- d_6 , ppm): δ 0.87 (3H, t), 1.28-1.51 (18H, m), 1.69-1.73 (2H, m), 3.70-3.74 (2H, t), 6.78 (1H, d, $J = 8.4$ Hz), 6.85 (1H, d, $J = 8.0$ Hz), 6.96-7.11 (12H, m), 7.31 (4H, t), 7.42 (2H, d, $J = 8.0$ Hz), 7.48 (2H, d, $J = 8.4$ Hz), 9.70 (1H, s). HRMS ES $^+$ (m/z): calcd. for $\text{C}_{45}\text{H}_{48}\text{N}_2\text{O}_2$, 648.3716; found, 648.3721.

An acetonitrile (20 ml) solution of dye precursor (**1** or **4**) (0.5 mmol) and cyanoacetic acid (1 mmol) was refluxed in the presence of piperidine (0.2 ml) for 2 h. After removing the solvent, the residue was purified by column chromatography using silica gel and dichloromethane / methanol (7 / 1; v / v) mixed as the eluent to give the sensitizers (**TH301** and **TH305**).

TH301 (red solid, yield 87%), $^1\text{H-NMR}$ (400 MHz, Acetone- d_6 , ppm): δ 0.86 (3H, t), 1.29-1.53 (18H, m), 1.69-1.77 (2H, m), 3.72 (2H, t), 6.72 (1H, dd, $J_1 = 1.6$ Hz, $J_2 = 1.6$ Hz), 6.76-6.92 (4H, m), 7.51 (1H, d, $J = 2.0$ Hz), 7.56 (1H, dd, $J_1 = 2.0$ Hz, $J_2 = 2.0$ Hz), 8.02 (1H, s). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3 , ppm): δ 168.9, 154.8, 144.9, 139.5, 132.1, 130.1, 124.1, 123.3, 116.3, 116.1, 112.5, 111.0, 95.7, 44.5, 32.1, 29.8, 29.5, 27.0, 25.4, 22.9, 14.3. HRMS ES $^+$ (m/z): calcd. for $\text{C}_{28}\text{H}_{34}\text{N}_2\text{O}_3$, 446.2569; found, 446.2550.

TH305 (dark crystal solid, yield 80%), $^1\text{H-NMR}$ (400 MHz, Acetone- d_6 , ppm): δ 0.74 (3H, t), 1.15-1.38 (18H, m), 1.57-1.60 (2H, m), 3.61 (2H, t), 6.67 (1H, d, $J = 8.4$ Hz), 6.73 (1H, d, $J = 8.4$ Hz), 6.82-7.01 (12H, m), 7.18 (4H, t), 7.35 (2H, d, $J = 8.4$ Hz), 7.42 (2H, d, $J = 8.4$ Hz), 7.90 (1H, s). $^{13}\text{C-NMR}$ (400 MHz, CDCl_3 , ppm): δ 168.3, 154.9, 147.6, 147.2, 144.8, 144.3, 138.3, 132.9, 131.8, 131.4, 129.8, 129.3, 127.3, 127.0, 125.5, 124.5, 124.2, 123.6, 123.0, 122.4, 116.6, 115.9, 112.6, 112.2, 110.8, 96.2, 44.4, 31.9, 29.6, 29.4, 26.9, 25.3, 22.7, 14.1. HRMS ES^+ (m/z): calcd. for $[\text{C}_{48}\text{H}_{49}\text{N}_3\text{O}_3\text{-CO}_2]$, 671.3876; found, 671.3881.

DSCs fabrication: A layer of 13 nm (T/SP, Solaronix, Switzerland) paste (ca. 2 μm) was coated on the F-doped tin oxide conducting glass (TEC15, 15 Ω /square, Pilkington, USA) by screen printing and then dried for 5 min at 125 $^\circ\text{C}$. This procedure was repeated for 6 times (ca. 12 μm) and coated by scatter layer (DHS-SLP1, Heptachroma, China) titania paste (ca. 4 μm) as scattering layer. The double-layer TiO_2 electrodes (area: 6 \times 6 mm) were gradually heated under an air flow at 325 $^\circ\text{C}$ for 5 min, at 375 $^\circ\text{C}$ for 5 min, at 450 $^\circ\text{C}$ for 15 min, and at 500 $^\circ\text{C}$ for 15 min. The sintered film was further treated with 40 mM TiCl_4 aqueous solution at 70 $^\circ\text{C}$ for 30 min, then washed with ethanol and water, and annealed at 500 $^\circ\text{C}$ for 30 min. After the film was cooled to 40 $^\circ\text{C}$, it was immersed into a 2×10^{-4} M CH_2Cl_2 dye bath with saturated chenodeoxycholic acid (CDCA) as coadsorbent for organic dyes and maintained under dark for optimized time (**TH301** and **TH305** for 2 h). The DSCs based on **N719** is sensitized into 3×10^{-4} M ethanol solution for 24 h under dark. The

sensitized TiO₂ electrode was then rinsed with the solvent of dye-bath and dried. The hermetically sealed cells were fabricated by assembling the dye-loaded film as the working electrode and Pt-coated conducting glass as the counter electrode separated with a hot-melt Surlyn 1702 film (25 μm, Dupont). The electrolyte consisting of 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.06M LiI, 0.04 M I₂, and 0.4 M 4-tertbutylpyridine (TBP) in dry acetonitrile (AN) was introduced into the cell via vacuum backfilling by the hole in the back of the counter electrode. Finally, the hole was also sealed using Surlyn 1702 film and cover glass.

Absorption spectra of TH301 and TH305 on TiO₂:

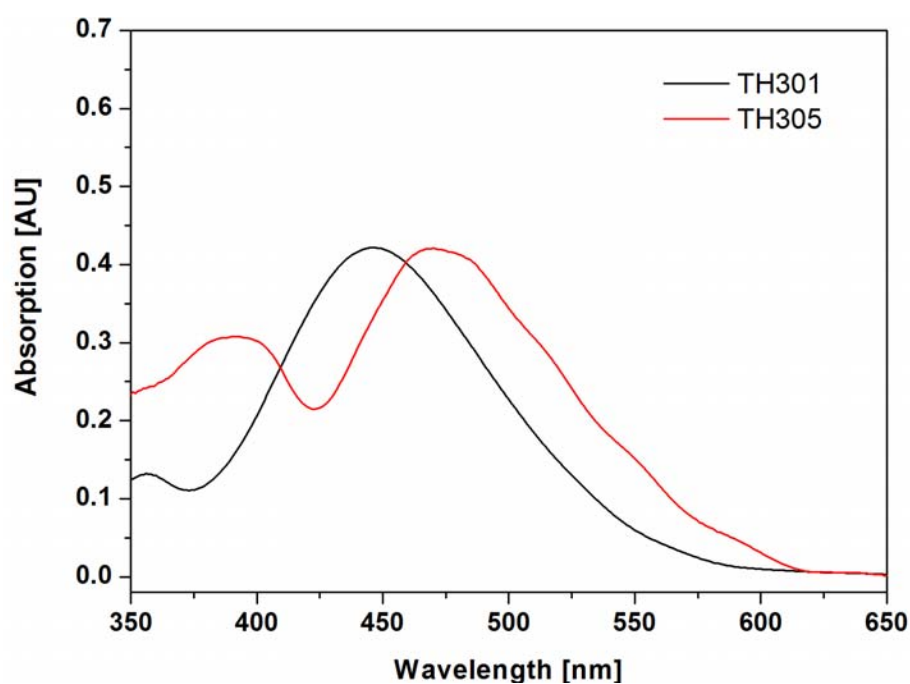


Figure S1. The absorption spectra of TH301 and TH305 on TiO₂

[ref] H. Tian, X. Yang, R. Chen, R. Zhang, A. Hagfeldt, L. Sun, *J. Phys. Chem. C.*, **2008**, *112*,

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