## Supporting Information

# A Metal-Free "Black Dye" for Panchromatic Dye-Sensitized Solar Cells

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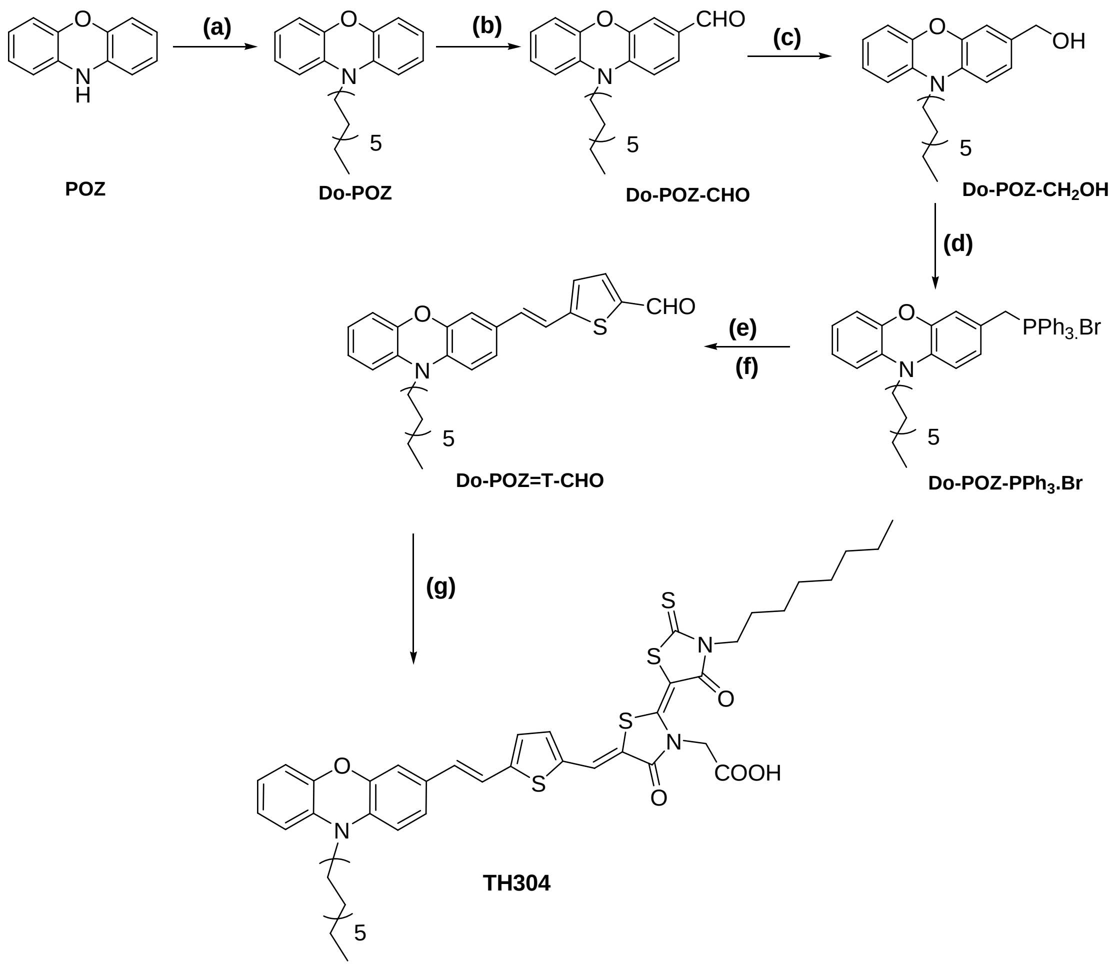
## General

The synthesis routes of the compounds were shown in Scheme S1. Phenoxazine (**POZ**) was commercial available and used as received. 4-Tertbutylpyridine (TBP), lithium iodide (LiI) was purchased from Acros. 3-octyl-5-(3-carboxymethyl-4-oxo-thiazolidin-2-ylidene)rhodanine was presented by Shanghai Green Technology Co, Ltd. All solvents and other chemicals were reagent grade and used without further purification. $^1$H-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. Electrochemistry was measured with BAS100W (USA). 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 of the TH304 dye



(a) Acetone, $CH_3(CH_2CH_2)_5CH_2Br$, NaOH, palmityl trimethyl ammonium bromide, overnight, reflux; (b) $CHCl_3$, $POCl_3$/DMF, overnight, reflux; (c) $CH_2Cl_2/CH_3CH_2OH$, $NaBH_4$, 2h, r.t.; (d) $CHCl_3$, $PPh_3.HBr$, reflux, 2 h; (e) Thiophene-2,5-dicarbaldehyde, DMF, $K_2CO_3$,18-crown-6 ether, r.t., 2 h; (f) THF, $I_2$, reflux, 8 h; (h) AcOH, $AcONH_4$, 3-octyl-5-(3-carboxymethyl-4-oxo-thiazolidin-2-ylidene)rhodanine, reflux, 1 h.

**Scheme S1**. Synthesis routes of **TH304** dye.

## Do-POZ:

To a **POZ (**1.83 g, 10 mmol) solution in 10 ml dry acetone containing palmityl trimethyl ammonium bromide (100 mg) as catalyst, sodium hydroxide (600 mg, 15 mmol ) was added at room temperature and refluxed for 2 h. Then 1-bromododecane (2.98 g, 12 mmol) was added to the refluxing mixture and which was kept refluxing overnight. After removing the solvent, the residue was purified by column chromatography using silica gel and dichloromethane-petroleum ether (1/1; v/v) as the eluent to give **Do-POZ,** colorless liquid (3.00 g, 85.7 %). $^1$H-NMR (400 MHz, Acetone-*d6*): δ (ppm): *δ* 0.88 (3H, t), 1.29-1.47 (18H, m), 1.64-1.68 (2H, m), 3.58 (2H, t), 6.60-6.66 (6H, m), 6.81 (2H, t). TOF MS ES$^+$: Found *m/z* 351.2565. Calc. for $C_{24}H_{33}NO$: 351.2562.

**Do-POZ-CHO:**

To a solution of **Do-POZ (**1.05 g, 3 mmo**l)** and dry DMF (548 mg, 7.5 mmol) in $CHCl_3$ (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 overnight. 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 **Do-POZ-CHO,** light yellow solid (1.00 g, 88.0 %). $^1$H-NMR (400 MHz, Acetone-*d6*): δ (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, d, $J_1$ = 2.0 Hz, $J_2$ = 2.0 Hz), 9.69 (1H, s). TOF MS ES: Found *m/z* 379.2521. Calc. for $C_{25}H_{33}NO_2$: 379.2511.

### Do-POZ-$CH_2OH$:

To a solution of $NaBH_4$ (76 mg, 2 mmol) in 10 ml dichloromethane and 10 ml ethanol, **Do-POZ-CHO (**758 mg, 2 mmol) was added rapidly and the bath was stirred at room temperature for 2 h. The solution was extracted with $CH_2Cl_2$-$H_2O$. The organic layer was dried with anhydrous sodium sulfate and then rotary evaporated to give **Do-POZ-$CH_2OH$,** white solid (750 mg, 98.4 %). TOF MS ES: Found *m/z* 381.2665. Calc. for $C_{25}H_{35}NO_2$: 381.2668.

### Do-POZ-$PPh_3$.Br:

**Do-POZ-$CH_2OH$** (572 mg, 1.5 mmol) and **$PPh_3$.HBr** (581 mg, 1.6 mmol) was dissolved in 20 ml chloroform and refluxed for 2 h, after removing the solvent, the residue was solidified with ether and filtrated to collect the flaxen solid (980 mg, 92.5 %). $^1$H-NMR (400 MHz, Acetone-*d6*): δ (ppm): *δ* 0.86 (3H, t), 1.24-1.39 (18H, m), 1.55-1.60 (2H, m), 3.80 (2H, t), 5.52 (2H, d, *J* = 14.8 Hz), 6.42 (1H, d, *J* = 8.4 Hz), 6.42-6.50 (2H, m), 6.61 (2H, t), 6.69 (1H, d, *J* = 8.4 Hz), 6.79 (1H, t), 7.71-7.76 (6H, m), 7.90 (3H, t), 7.88-8.00 (6H, m). API-ES MS (Positive): Found *m/z* 626.4, Calc. for $[C_{43}H_{49}BrNPO\text{-}Br]^+$: 626.4.

### Do-POZ=T-CHO:

To a 20 ml DMF solution of thiophene-2,5-dicarbaldehyde (140 mg, 1 mmol)**,** 18-crown-6 ether (15 mg) and anhydrous potassium carbonate (276 mg, 2 mmol), the solution of **Do-POZ-PPh3.Br** (706 mg, 1 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 **Do-POZ=T-CHO** (*E*, red solid, 340 mg, yield 69.8%). $^1$H-NMR (DMSO-$d_6$, 400 MHz): δ (ppm): *δ* (ppm): 0.87 (3H, t), 1.28-1.51 (18H, m), 1.67-1.71 (2H, m), 3.64 (2H, t), 6.66-6.73 (4H, m), 6.85 (1H, t), 6.97-7.62 (3H, m), 7.31-7.35 (2H, m), 7.86 (1H, d, *J* = 4.0 Hz), 9.88 (1H, s). TOF MS ES$^+$: Found *m/z* 487.2552. Calc. for $C_{31}H_{37}NO_2S$: 487.2545.

**TH304:**

3-octyl-5-(3-carboxymethyl-4-oxo-thiazolidin-2-ylidene)rhodanine (80 mg, 0.2 mmol) and **Do-POZ=T-CHO** (97 mg, 0.2 mmol) were added into glacial acetic acid (5 ml) and refluxed for 1 h in the presence of ammonium acetate (20 mg). After cooling to room temperature, the precipitate was filtered, washed by distilled water, ethanol, petroleum ether, and purification of flash column chromatography to give **TH304** dye (dark purple solid, 130 mg, 74.7%). $^1$H-NMR (Acetone-$d_6$, 400 MHz): δ (ppm): 0.75

(6H, m), 1.11-2.00 (32 H, m), 3.51 (2H, t), 3.97 (2H, t), 4.81 (2H, s), 6.51-6.60 (4H, m), 6.70 (1H, t), 6.85 (1H, d, *J* = 1.7 Hz), 7.93-6.98 (2H, m), 7.15 (1H, d, *J* = 4.0 Hz), 7.21 (1H, d, *J* = 16.0 Hz), 7.46 (1H, d, *J* = 4.0 Hz), 7.82 (1H, s). TOF MS ES$^+$: Found *m/z* 871.3215. Calc. for $C_{47}H_{57}N_3O_5S_4$: 871.3181.

## DSC Fabrication:

DSC 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, 15Ω/square, Pilkington, USA) by screen printing and then dried for 5 min at 125 °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 scatting layer. The double-layer $TiO_2$ electrodes (area: 6×6 mm) were gradually heated under an air flow at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min, and at 500 °C for 15 min. The sintered film was further treated with 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, then washed with ethanol and water, and annealed at 500 °C for 30 min. After the film was cooled to 40 °C, it was immersed into dye bath and maintained under dark for optimized time (**TH304** for 2 h, **N719** for 24 h). The sensitized $TiO_2$ 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 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.

## The J-V curves of DSC based on TH304 dye without/with CDCA