

## Phenothiazine Derivatives for Efficient Organic Dye-Sensitized Solar Cells

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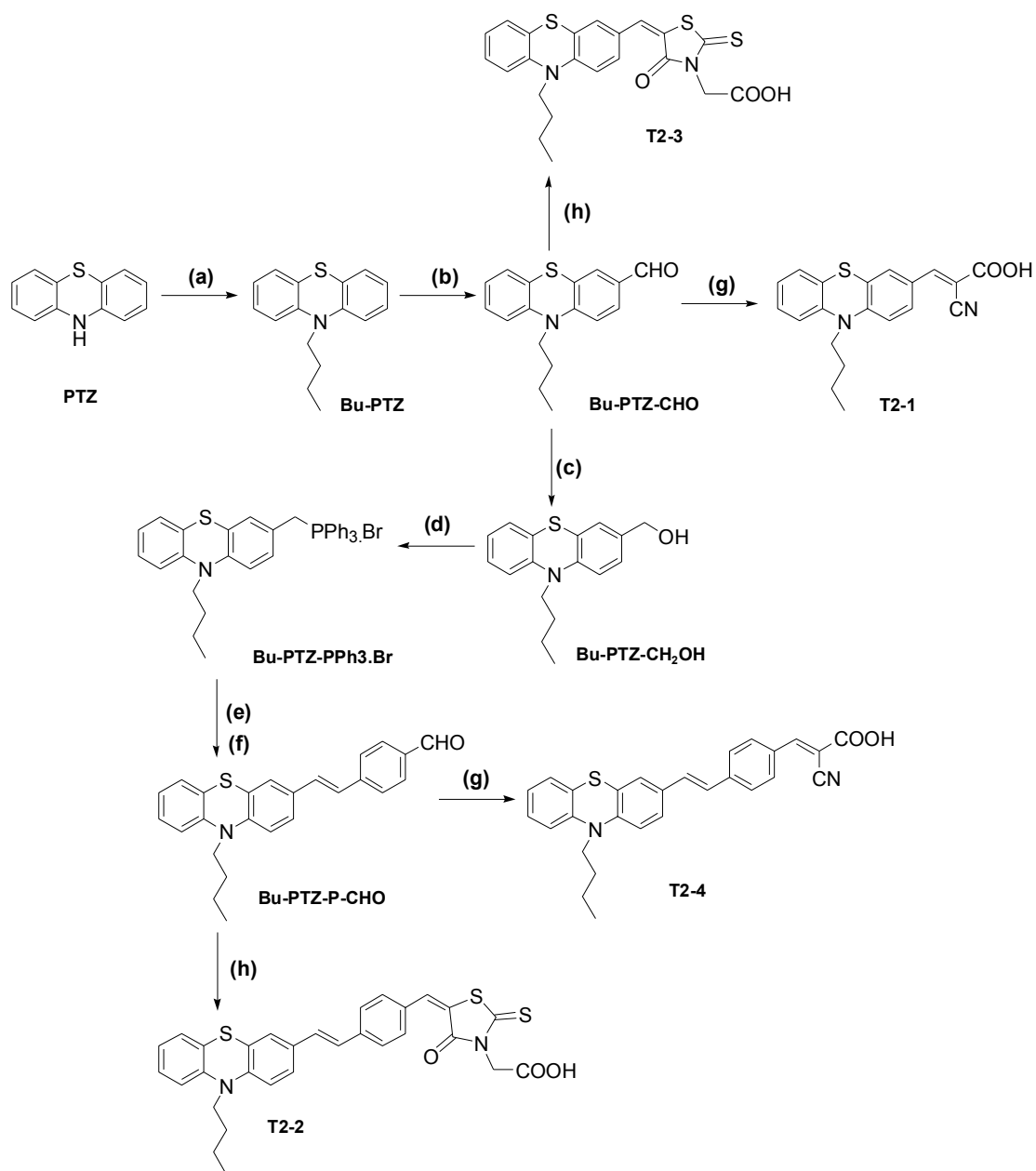
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### General

The synthesis routes of the compounds were shown in Scheme S1. Phenothiazine (PTZ) 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. <sup>1</sup>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).

### 1 Synthesis of the PTZ dyes:



**Scheme S1.** Synthesis routes of T2-1, T2-2, T2-3 and T2-4.

(a) Acetone, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Br, NaOH, palmityl trimethyl ammonium bromide, overnight, reflux;

(b)  $\text{CHCl}_3$ ,  $\text{POCl}_3/\text{DMF}$ , overnight, reflux; (c)  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CH}_2\text{OH}$ ,  $\text{NaBH}_4$ , 2h, r.t.; (d)  $\text{CHCl}_3$ ,  $\text{PPh}_3\cdot\text{HBr}$ , reflux, 2 h; (e) Terephthalaldehyde,  $\text{DMF}$ ,  $\text{K}_2\text{CO}_3$ , 18-crown-6 ether, r.t., 2 h; (f)  $\text{THF}$ ,  $\text{I}_2$ , reflux, 8 h; (g)  $\text{CH}_3\text{CN}$ , cyanoacetic acid, piperidine, reflux, 2 h; (h)  $\text{AcOH}$ ,  $\text{AcONH}_4$ , rhodanine-3-acetic acid, reflux, 3 h.

### **Bu-PTZ:**

To a **PTZ** (1.99 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-bromobutane (1.64 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 **Bu-PTZ**, colorless viscous liquid (2.00 g, 78.4 %).  $^1\text{H-NMR}$  (400 MHz, Acetone-*d*6):  $\delta$  (ppm): 0.86 (3H, t), 1.40-1.45 (2H, m), 1.69-1.76 (2H, m), 3.90 (2H, t), 6.90 (2H, t), 6.98 (2H, d,  $J = 8.1$  Hz), 7.10 (2H, d,  $J = 7.6$  Hz), 7.15 (2H, t). TOF MS  $\text{ES}^+$ : Found  $m/z$  255.1079. Calc. for  $\text{C}_{16}\text{H}_{17}\text{NS}$ : 255.1082.

### **Bu-PTZ-CHO:**

To a solution of **Bu-PTZ** and dry  $\text{DMF}$  (548 mg, 7.5 mmol) in  $\text{CHCl}_3$  (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 **Bu-PTZ-CHO**, yellow viscous liquid (900 mg, 81.1 %). <sup>1</sup>H-NMR (400 MHz, Acetone-*d*<sub>6</sub>): δ (ppm): 0.87 (3H, t), 1.42-1.48 (2H, m), 1.73-1.80 (2H, m), 4.01 (2H, t), 6.90 (1H, t), 7.07 (1H, d, *J* = 8.0 Hz), 7.13 (2H, m), 7.21 (1H, t), 7.57 (1H, d, *J* = 1.9 Hz), 7.70 (1H, dd, *J*<sub>1</sub> = 1.9 Hz, *J*<sub>2</sub> = 1.9 Hz), 9.79 (1H, s). TOF MS ES: Found *m/z* 283.1024. Calc. for C<sub>17</sub>H<sub>17</sub>NOS: 283.1031.

#### **Bu-PTZ-CH<sub>2</sub>OH:**

To a solution of NaBH<sub>4</sub> (81 mg, 2.1 mmol) in 10 ml dichloromethane and 10 ml ethanol, **Bu-PTZ-CHO** (600 mg, 2.1 mmol) was added rapidly and the bath was stirred at room temperature for 2 h. The solution was extracted with CH<sub>2</sub>Cl<sub>2</sub>-H<sub>2</sub>O. The organic layer was dried with anhydrous sodium sulfate and then rotary evaporated to give **Bu-PTZ-CH<sub>2</sub>OH**, flaxen viscous solid (592 mg, 98.0 %). <sup>1</sup>H-NMR (400 MHz, Acetone-*d*<sub>6</sub>): δ (ppm): 0.87 (3H, t), 1.40-1.45 (2H, m), 1.70-1.74 (2H, m), 3.87-3.91 (2H, t), 4.10 (1H, t), 4.49 (2H, d, *J* = 5.8 Hz), 6.88 (1H, t), 6.93 (1H, d, *J* = 8.3 Hz), 6.97 (1H, d, *J* = 8.2 Hz), 7.18-7.17 (4H, m). TOF MS ES<sup>+</sup>: Found *m/z* 285.1187. Calc. for C<sub>17</sub>H<sub>19</sub>NOS: 285.1187.

#### **Bu-PTZ-PPh<sub>3</sub>.Br:**

**Bu-PTZ-CH<sub>2</sub>OH** (440 mg, 1.5 mmol) and **PPh<sub>3</sub>.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 (900 mg, 95.8 %). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, 400 MHz): δ (ppm): 0.86 (3H, t), 1.33-1.39 (2H, m), 1.58-1.62 (2H, m), 3.80 (2H, t), 5.04 (2H, d, *J* = 15.1 Hz), 6.59 (1H, s), 6.80 (1H, d, *J* = 8.4 Hz), 6.87 (1H, d, *J* = 8.4 Hz), 6.92 (1H, t), 6.99 (1H, d, *J* = 8.1 Hz), 7.07 (1H, d, *J* = 7.5 Hz), 7.18 (1H, t), 7.66-7.77 (12H, m), 7.91 (3H, t). API-ES MS (Positive): Found *m/z* 530.6, Calc. for [C<sub>35</sub>H<sub>33</sub>BrNPS-Br]<sup>+</sup>: 530.6.

### **Bu-PTZ-P-CHO:**

To a solution of terephthalaldehyde (100 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 **Bu-PTZ-PPh<sub>3</sub>Br** (455 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 **Bu-PTZ-P-CHO** (*E*, yellow solid, 140 mg, yield 48.8%). <sup>1</sup>H-NMR (Acetone-d<sub>6</sub>, 400 MHz): δ (ppm): 0.93 (3H, t), 1.45-1.51 (2H, m), 1.75-1.82 (2H, m), 3.97 (2H, t), 6.95 (1H, t), 7.05 (2H, d, *J* = 8.3 Hz), 7.15 (1H, d, *J* = 7.6 Hz), 7.18 (1H, t), 7.25 (1H, d, *J*

= 16.5 Hz), 7.38 (1H, d,  $J = 16.4$  Hz), 7.45-7.48 (2H, m), 7.78 (2H, d,  $J = 8.3$  Hz), 7.90 (2H, d,  $J = 8.3$  Hz), 10.01 (1H, s). TOF MS ES<sup>+</sup>: Found  $m/z$  385.1057. Calc. for C<sub>25</sub>H<sub>23</sub>NOS: 385.1500.

### T2-1 and T2-2:

An acetonitrile solution of **Bu-PTZ-CHO** or **Bu-PTZ-P-CHO** and cyanoacetic acid was refluxed in the presence of piperidine for 2 h. After removing the solvent, the residue was purified by column chromatography using silica gel and dichloromethane-methanol (10/1; v/v) as the eluent to give product.

**T2-1** (yield 81.4 %, dark-red solid), <sup>1</sup>H-NMR (400 MHz, Acetone-*d*<sub>6</sub>):  $\delta$  (ppm): 0.91 (3H, t), 1.42-1.51 (2H, m), 1.75-1.86 (2H, m), 4.02 (2H, t), 6.98 (1H, t), 7.08 (1H, d,  $J = 8.2$  Hz), 7.13 (1H, d,  $J = 7.8$  Hz), 7.16 (1H, d,  $J = 8.4$  Hz), 7.21 (1H, t), 7.85 (1H, d,  $J = 2.0$  Hz), 7.94 (1H, dd,  $J = 2.0$  Hz,  $J = 2.0$  Hz), 8.13 (1H, s). TOF MS ES<sup>+</sup>: Found  $m/z$  350.1085. Calc. for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S: 350.1089.

**T2-2** (yield 85.0 % dark-red solid) <sup>1</sup>H-NMR (Acetone-*d*<sub>6</sub>, 400 MHz):  $\delta$  (ppm): 0.89 (3H, t), 1.42-1.48 (2H, m), 1.74-1.77 (2H, m), 3.95 (2H, t), 6.924 (1H, t), 7.02 (2H, d,  $J = 8.1$  Hz), 7.12 (1H, d,  $J = 7.6$  Hz), 7.16 (1H, t), 7.22 (1H, d,  $J = 16.2$  Hz), 7.38 (1H, d,  $J = 16.1$  Hz), 7.43-7.45 (2H, m), 7.45 (2H, d,  $J = 8.4$  Hz), 8.08 (2H, d,  $J = 8.5$  Hz), 8.27 (1H, s). TOF MS ES<sup>+</sup>: Found  $m/z$  452.1566. Calc. for C<sub>28</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>S: 452.1559.

### T2-3 and T2-4:

**Bu-PTZ-CHO** or **Bu-PTZ-P-CHO** and rhodanine-3-acetic acid were added into

glacial acetic acid and refluxed for 3 h in the presence of ammonium acetate. After cooling to room temperature, the mixture was poured into ice water. The precipitate was filtered, washed by distilled water, dried under vacuum, and purified by column chromatography using silica gel and dichloromethane/methanol (7/1; v/v) as the eluent to give product.

**T2-3** (yield 76.2 %, dark-red solid),  $^1\text{H-NMR}$  (400 MHz, Acetone- $d_6$ ):  $\delta$  (ppm): 0.90 (3H, t), 1.43-1.49 (2H, m), 1.76-1.79 (2H, m), 4.00 (2H, t), 4.84 (2H, s), 6.97 (1H, t), 7.07 (1H, d,  $J = 8.1$  Hz), 7.13 (1H, d,  $J = 7.6$  Hz), 7.17 (1H, d,  $J = 8.0$  Hz), 7.20 (1H, t), 7.85 (1H, d,  $J = 2.0$  Hz), 7.47 (1H, dd,  $J_1 = 2.1$  Hz,  $J_2 = 2.1$  Hz), 7.68 (1H, s). TOF MS ES $^+$ : Found  $m/z$  456.0632. Calc. for  $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_3\text{S}_3$ : 456.0636.

**T2-4** (yield 72.2 %, dark-red solid)  $^1\text{H-NMR}$  (Acetone- $d_6$ , 400 MHz):  $\delta$  (ppm): 0.80 (3H, t), 1.33-1.38 (2H, m), 1.64-1.68 (2H, m), 3.85 (2H, t), 4.77 (2H, s), 6.83 (1H, t), 6.92 (2H, d,  $J = 8.2$  Hz), 7.02 (1H, d,  $J = 7.8$  Hz), 7.08 (1H, t), 7.12 (1H, d,  $J = 16.5$  Hz), 7.24 (1H, d,  $J = 16.4$  Hz), 7.32-7.35 (2H, m), 7.55 (2H, d,  $J = 8.4$  Hz), 7.66 (2H, d,  $J = 8.4$  Hz), 7.70 (1H, s). TOF MS ES $^+$ : Found  $m/z$  558.1109. Calc. for  $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_3$ : 558.1106.

## 2 Fabrication of the Nanocrystalline $\text{TiO}_2$ Solar Cells

Titania paste which was prepared from P25 (Degussa, Germany) following the literature procedure<sup>[1]</sup> and depositing onto the F-doped tin oxide conducting glass (TEC8, sheet resistance of  $8\Omega/\text{square}$ , Pilkington, USA) by doctor-blading. The resulted layer photoelectrode of  $10\ \mu\text{m}$  thickness, was sintered at  $500\ ^\circ\text{C}$  for 30 min in

air. After the film was cooled to 40 °C, it was immersed into a  $2 \times 10^{-4}$  M **PTZ** dye solution in  $\text{CH}_2\text{Cl}_2$  and maintained under dark for 12 h. The electrode was then rinsed with  $\text{CH}_2\text{Cl}_2$  and dried. One drop of electrolyte solution was deposited onto the surface of the electrode and penetrated inside the  $\text{TiO}_2$  film via capillary action. The electrolyte consisted of 0.6 M tetrabutylammonium iodide (TBAI), 0.1 M LiI, 0.05 M  $\text{I}_2$  and 0.5 M 4-tertbutylpyridine (TBP) in dry acetonitrile for **PTZ-dyes** and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M  $\text{I}_2$ , 0.6 M TBP in methoxypropyl nitrile (MPN) for **N3** dye. A platinized counter electrode was then clipped onto the top of the  $\text{TiO}_2$  working electrode to form our test cell.

### 3 Emission spectra of PTZ-dyes

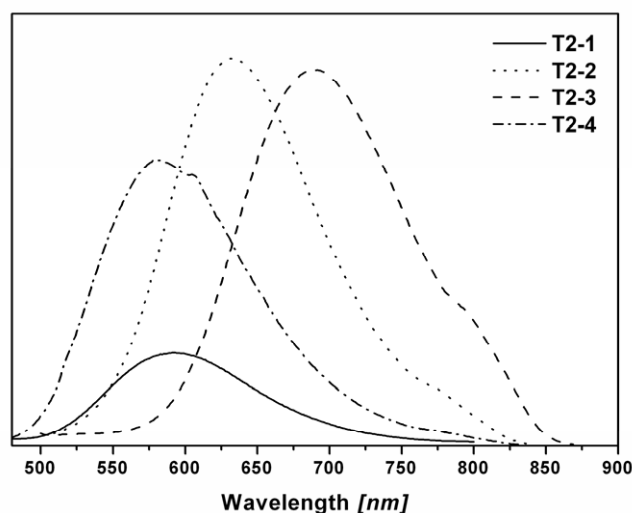


Fig. S1. Emission spectra of **T2-1**, **T2-2**, **T2-3** and **T2-4** in  $\text{CH}_2\text{Cl}_2$  solution ( $2 \times 10^{-5}$  M).

### 4 The solar energy-to-electricity conversion efficiencies of PTZ-dyes and N3 dye with different electrolytes



The photovoltaic properties of DSSCs based on T2-1 and N3 with different electrolytes are shown in Table S1 and  $J-V$  curves of the dyes are shown in Fig. S2. The electrolyte **A** (0.6 M tetrabutylammonium iodide (TBAI), 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.5 M 4-tertbutylpyridine (TBP) in dry acetonitrile) shows good solar energy-to-electricity conversion efficiency ( $\eta$ ) for T2-1 dye and electrolyte **B** (0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII), 0.1 M LiI, 0.05 M I<sub>2</sub>, 0.6 M TBP in methoxypropyl nitrile) gives a prominent  $\eta$  value for N3. The electrolyte with TBAI as additive is suit for DSSCs based PTZ dyes. Some organic dyes also adopt tetrabutylammonium iodide in electrolyte and show high  $\eta$  value in DSSCs.<sup>2</sup>

Table S1. The Photovoltaic performance of DSSCs based on T2-1 and N3 with different electrolytes

Dye	Electrolyte	$J_{sc}$ [mA·cm <sup>-2</sup> ]	$V_{oc}$ [mV]	fill factor [ $ff$ ]	$\eta$ [%]
T2-1	A	10.9	712	0.71	5.5
	B	8.9	660	0.68	4.0
N3	A	11.4	711	0.58	4.7
	B	14.0	695	0.64	6.2

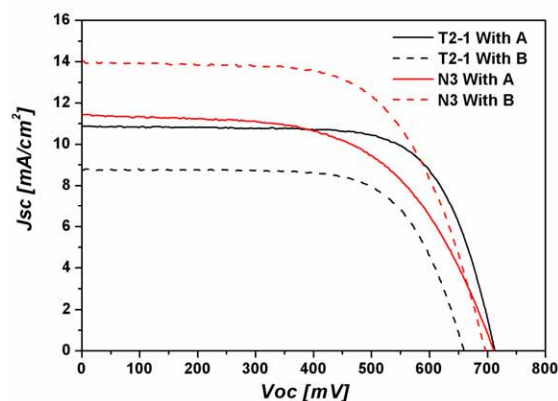


Fig. S2.  $J-V$  curves of DSSCs based on T2-1 and N3 with different electrolytes

## References

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