## Electronic Supplementary Information for Phenothiazine-based organic dyes with two anchoring groups on TiO<sub>2</sub> for highly efficient visible light-induced water splitting

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**Experimental General** 

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian 300 MHz spectrometer. High resolution mass spectra of new compounds were obtained using a Jeol JMS 700 spectrometer at Korea Basic Science Institute (Daegu). The UV-visible spectra were recorded using Jasco V630 in  $\gamma$ -butyrolactone. Cyclic voltammetry measurements were carried out using a CH instruments model CHI600 potentiostat. A Conventional three electrode assembly was used under nitrogen to record cyclic voltammograms. The working electrode was an ITO-coated glass electrode. The counter electrode was a platinum wire and Ag/AgNO<sub>3</sub> (Ag/Ag<sup>+</sup>) was used as the reference electrode. The scan rate was 100mV/s. The 0.10 M anhydrous tetrabutylammonium hexafluorophophate (TBAPF<sub>6</sub>) solution in the  $\gamma$ -butyrolactone (GBL) was used as a supporting electrolyte. The 1 mM solutions of each compound were used for measurement.

**Calculation:** All theoretical calculations were carried out using the density functional theory (DFT) approach with a suite in Gaussian 09 programs (M. J. Frisch, *et al., Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, 2009). Geometry optimization for P5 was performed at the B3LYP/6-311+G\*\* level. Then, the frontier molecular orbitals were analyzed.

**Synthesis of P1**: In a 100 mL Schlenk flask, phenothiazine (2.0 g, 0.010 mol) was dissolved in DMF (30 mL). To this solution, NaH (1.2 g, 0.050 mmol) was slowly added. After 30 minutes, 1-bromoethane (0.88 mL, 0.012 mol) was slowly added. Then, the reaction mixture was heated at 70 °C for 3 hours. The product was extracted using hexane and brine solution. The pure 10-ethyl-10H-phenothiazine was isolated by flash column chromatography using hexane as an eluent. In a 100 mL Schlenk flask, POCl<sub>3</sub> (12 mL, 0.12 mol) was added to DMF (30 mL). After stirring the reaction mixture for 30 minutes, 10-ethyl-10H-phenothiazine (2.0 g, 8.8 mmol) was added. The reaction mixture was heated at 60 °C overnight. The crude product was extracted using chloroform. The pure 10-ethyl-10H-phenothiazine-3,7-dicarboxaldehyde was isolated by flash column chromatography using a 3:1 mixture of hexane and ethylacetate as an eluent. In a 20 mL Schlenk flask, 10-ethyl-10H-phenothiazine-3,7-dicarboxaldehyde (0.47 g, 1.6 mmol) was dissolved in THF (7 mL). To this solution, cyanoacetic acid (0.84 g, 0.010 mol) and catalytic amount of piperidine were added. The reaction mixture was heated at 70 °C for 3 hours. The product, 3,3'-(10-ethyl-10H-phenothiazine-3,7-dicyl)bis(2-cyanoacrylic acid) was isolated by column chromatography

using a 1:1 mixture of methylene chloride and methanol. Characterization data for **P1**: <sup>1</sup>H NMR (300 MHz, DMSO-d<sup>6</sup>)  $\delta$  = 8.16 (s, 2H), 7.94 (dd, J = 8.7 Hz, 2H), 7.79 (s, 2H), 7.24 (d, J = 8.7 Hz, 2H), 4.05 (q, J = 6.9 Hz, 2H), 1.33 (t, J = 6.9 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, DMSO-d<sup>6</sup>)  $\delta$  = 164.0, 152.6, 146.0, 131.8, 129.5, 126.9, 121.7, 117.0, 116.3, 100.9, 42.5, 12.5 ppm; HRMS (FAB, [M<sup>+</sup>]) calcd. for C<sub>22</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>S<sub>1</sub>, 417.0738, found: 417.0786.

**Synthesis of P2-P5**: For preparation of **P2-P5**, the same procedure was applied using the corresponding alkyl halides. **P2**: <sup>1</sup>H NMR (300 MHz, DMSO-d<sup>6</sup>)  $\delta = 8.16$  (s, 2H) 7.96 (d, J = 8.7 Hz, 2H), 7.81 (s, 2H), 7.27 (d, J = 8.7 Hz, 2H), 4.01 (t, J = 6.9 Hz, 2H), 1.68 (m, 2H), 1.41 (m, 2H), 0.90 (t, J = 6.9 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, DMSO-d<sup>6</sup>)  $\delta = 163.9$ , 150.6, 146.7, 131.2, 129.3, 127.5, 122.6, 117.9, 116.7, 104.4, 47.3, 28.5, 19.6, 14.0 ppm; HRMS (EI<sup>+</sup>) calcd. for C<sub>24</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>S<sub>1</sub>, 445.1096, found, 445.1095.

**P3**: <sup>1</sup>H NMR (300 MHz, DMSO-d<sup>6</sup>)  $\delta$  = 8.17 (s, 2H) 7.96 (d, J = 8.7 Hz, 2H), 7.81 (s, 2H), 7.26 (d, J = 9.0 Hz, 2H), 4.00 (t, J = 6.9 Hz, 2H), 1.69 (m, 2H), 1.39 (m, 2H), 1.30-1.10 (m, 8H), 0.82 (t, J = 6.6 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, DMSO-d<sup>6</sup>)  $\delta$  = 164.0, 152.5, 147.1, 131.7, 129.7, 127.1, 122.6, 117.1, 116.8, 101.3, 47.6, 31.5, 29.0, 28.5, 26.3, 26.2, 22.4, 14.3 ppm .; HRMS (EI<sup>+</sup>) calcd for C<sub>28</sub>H<sub>27</sub>N<sub>3</sub>O<sub>4</sub>S<sub>1</sub>, 501.1722, found, 501.1719.

**P4**: <sup>1</sup>H NMR (300 MHz, DMSO-d<sup>6</sup>) δ = 8.17 (s, 2H), 7.96 (d, J = 9.0 Hz, 2H), 7.81 (s, 2H), 7.26 (d, J = 9.0 Hz, 2H), 4.01 (t, 6.9 Hz, 2H), 1.69 (m, 2H), 1.38 (m, 2H), 1.30-1.15 (m, 16H), 0.83 (t, J = 7.2 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 164.0, 152.2, 147.1, 131.7, 129.6, 127.1, 122.6, 117.1, 116.8, 101.7, 47.6, 31.7, 29.4, 29.2, 29.1, 28.7, 26.2, 26.1, 22.5, 14.3 ppm; HRMS (EI<sup>+</sup>) calcd for C<sub>32</sub>H<sub>35</sub>N<sub>3</sub>O<sub>4</sub>S<sub>1</sub>, 557.2348, found, 557.2352.

**P5**: <sup>1</sup>H NMR (300 MHz, DMSO-d<sup>6</sup>)  $\delta = 8.14$ (s, 2H), 7.94 (dd, J = 8.7, 1.8Hz, 2H), 7.79(d, J = 1.8Hz, 2H), 7.24(d, J = 9.0Hz, 2H), 4.00(t, J = 6.9Hz, 2H), 1.67(q, J = 7.2Hz, 2H), 1.45-1.32 (m, 2H), 1.32-1.09(m, 24H), 0.84(t, J = 6.9Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, DMSO-d<sup>6</sup>)  $\delta = 164.1$ , 150.8, 146.8, 131.3, 129.3, 127.4, 122.7, 117.8, 116.7, 103.9, 47.5, 44.0, 31.7, 29.4, 29.3, 29.2, 29.1, 29.1, 28.8, 26.2, 26.1, 22.6, 22.5, 22.1, 14.4 ppm; HRMS (FAB, [M+H]<sup>+</sup>) calcd for C<sub>36</sub>H<sub>43</sub>N<sub>3</sub>O<sub>4</sub>S<sub>1</sub>+H, 614.3053. found: 614.3053.

**Preparation of dye-TiO<sub>2</sub>-Pt composites**: In a 100 mL round-bottomed flask, TiO<sub>2</sub> (2.0 g, Aldrich catalogue No. 637254, size of nanoparticles < 25 nm, anatase) was dispersed in 50 mL methanol. H<sub>2</sub>PtCl<sub>6</sub> (0.50 mL, 8 wt% aqueous solution) was added. The reaction mixture was irradiated by a 200 W Xe lamp (without an optical filter) for 30 minutes. The resultant TiO<sub>2</sub>-Pt composites were retrieved by centrifugation with 3700 rpm rotation rate, washed five times with excess methanol and dried under vacuum. The dyes were dissolved in methanol to prepare 50 mL solution with 0.30 mM concentration of dyes. To this solution, TiO<sub>2</sub>-Pt powder (0.50 g) was added. Under dark conditions, the solution was stirred for 24 hours. The resultant dye-TiO2-Pt composites were retrieved by centrifugation, washed with methanol, and dried under vacuum.

**Photocatalytic tests**: The 10% (v/v) aqueous solution of triethanolamine (TEOA) was prepared and neutralized with HCl and NaOH solution. The 5 mL of this solution was added to tube glassware. Dye-TiO<sub>2</sub>-Pt (16.5 mg) was added and dispersed in tube glassware. After complete sealing with a septum and black insulating tape, the solution was bubbled with  $N_2$  gas for 15 minutes using a needle and a connected bubbler. Using a GC syringe, 1 mL  $N_2$  gas was replaced with 1 mL methane (internal standard). The well sealed-glass ware was stirred and irradiated with a 200 W Xe lamp (with optical filter, the light below 420 nm was cut-off). The temperature of the reaction mixture was maintained at room temperature with a water bath. The amount of generated hydrogen was measured using GC with a TCD detector (Agilent 6890). It should be noted that TCD detector has different detection sensitivities toward methane and hydrogen. The detection sensitivity for methane and hydrogen of the used GC was calibrated by the average value from ten data points obtained using the same amount of methane and hydrogen.

Figure S1. UV/vis spectra of the dyes used in this study (P1-P5).



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Figure S2. Concentration dependent hydrogen evolution of P5-TiO<sub>2</sub>-Pt composites.

**Figure S3.** Comparison of photocatalytic systems based on **P2** and **P5** with 3-(10-butyl-10H-phenothiazin-3-yl)-2-cyanoacrylic acid and 3-(10-hexadecyl-10H-phenothiazin-3-yl)-2-cyanoacrylic acid.



*3-(10-Butyl-10H-phenothiazin-3-yl)-2-cyanoacrylic acid* (A known compound in ref. 11 in text): <sup>1</sup>H NMR (300 MHz, DMSO-d<sup>6</sup>)  $\delta$  = 8.16 (s, 1H), 7.93 (d, J = 8.7 Hz, 1H), 7.82 (s, 1H), 7.26-7.15 (m, 3H), 7.10 (d, J = 8.1 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 3.95 (t, J = 6.9 Hz, 2H), 1.67 (q, J = 7.2 Hz, 2H), 1.41 (q, J = 7.5 Hz, 2H), 0.89 (t, J = 7.5 Hz, 3H) ppm; HRMS (FAB[M+H]<sup>+</sup>) calcd for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub>S<sub>1</sub>, 351.1167, found, 351.1165.

*3-(10-Hexadecyl-10H-phenothiazin-3-yl)-2-cyanoacrylic acid*: <sup>1</sup>H NMR (300 MHz, DMSO-d<sup>6</sup>) δ = 8.15 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.23-7.13 (m, 3H), 7.06 (d, J = 8.1 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 3.92 (t, J = 6.9 Hz, 2H), 1.67 (m, 2H), 1.41-1.12 (m, 26H), 0.83 (t, J = 6.9 Hz, 3H) ppm; <sup>13</sup>C NMR (75 MHz, DMSO-d<sup>6</sup>) δ = 164.0, 152.5, 147.1, 131.7, 129.7, 127.1, 122.6, 117.1, 116.8, 101.3, 47.6, 31.5, 29.0, 28.5, 26.3, 26.2, 22.4, 14.3 ppm; HRMS (FAB[M+H]<sup>+</sup>) calcd for  $C_{32}H_{42}N_2O_2S_1$ , 519.3045, found, 519.3043.







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