

***Supplementary Information:***

# A New Recognition Concept Using Dye Sensitized Solar Cell Configuration

*Dong-Yi Chen,<sup>a</sup> Kum-Yi Cheng,<sup>b</sup> Mei-Lin Ho,<sup>\*b</sup> I-Che Wu,<sup>a</sup> Min-Wen Chung,<sup>a</sup> Hungshin Fu<sup>a</sup> and*

*Pi-Tai Chou<sup>\*a</sup>*

<sup>a</sup>Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, Email:

chop@ntu.edu.tw

<sup>b</sup>Department of Chemistry, Soochow University, Taipei 111, Taiwan.

*General Information and Materials.* All solvents were distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless stated otherwise. All reactions were monitored by TLC with Macherey-Nagel precoated glass plates, (0.20 mm with fluorescent indicator UV254). Compounds were visualized with UV light at 254 and 365 nm. Flash column chromatography was carried out using silica gel from Merck (230-400 mesh). <sup>1</sup>H NMR spectrum was recorded on a Varian Unity 400 or Bruker Avance 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts ( $\delta$ ) are quoted in parts per million (ppm) against TMS, and coupling constant ( $J$ ) is recorded in Hertz (Hz).

*Synthesis of 13-(4-bromophenyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (3).*

One gram (3.38 mmol) of **2** (Sigma-Aldrich) in 4 mL CH<sub>2</sub>Cl<sub>2</sub> was added into a solution of

tetraethylammonium bromide (5 mg, 0.23 mmol in 0.1 mL MeOH) under inert atmosphere. After being cooled to 0 °C, a mixture of 0.17 mL Br<sub>2</sub> (3.38 mol) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added drop wise and the reaction was allowed to proceed in room temperature overnight to ensure the completion of the reaction. Then water (10 mL) was added to quench the reaction. After 10 minutes of stirring, the product was extracted and dried using diethyl ether and anhydrous magnesium sulfate (MgSO<sub>4</sub>). Filtration, solvent evaporation, and column chromatography were carried out in sequence to yield 0.98 g (78%) of solid crude product. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.64 (m, 16H), 3.72 (m, 4H), 6.51 (d, *J* = 9.6 Hz, 2H), 7.24 (d, *J* = 9.6 Hz, 2H). Anal. Calcd for C<sub>16</sub>H<sub>24</sub>BrNO<sub>4</sub>: C, 51.35; H, 6.46; O, 17.10. Found: C, 51.36; H, 6.50; O, 17.09.

*Synthesis of 5-(4-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)-*

*phenyl)thiophene-2-carbaldehyde (4).*

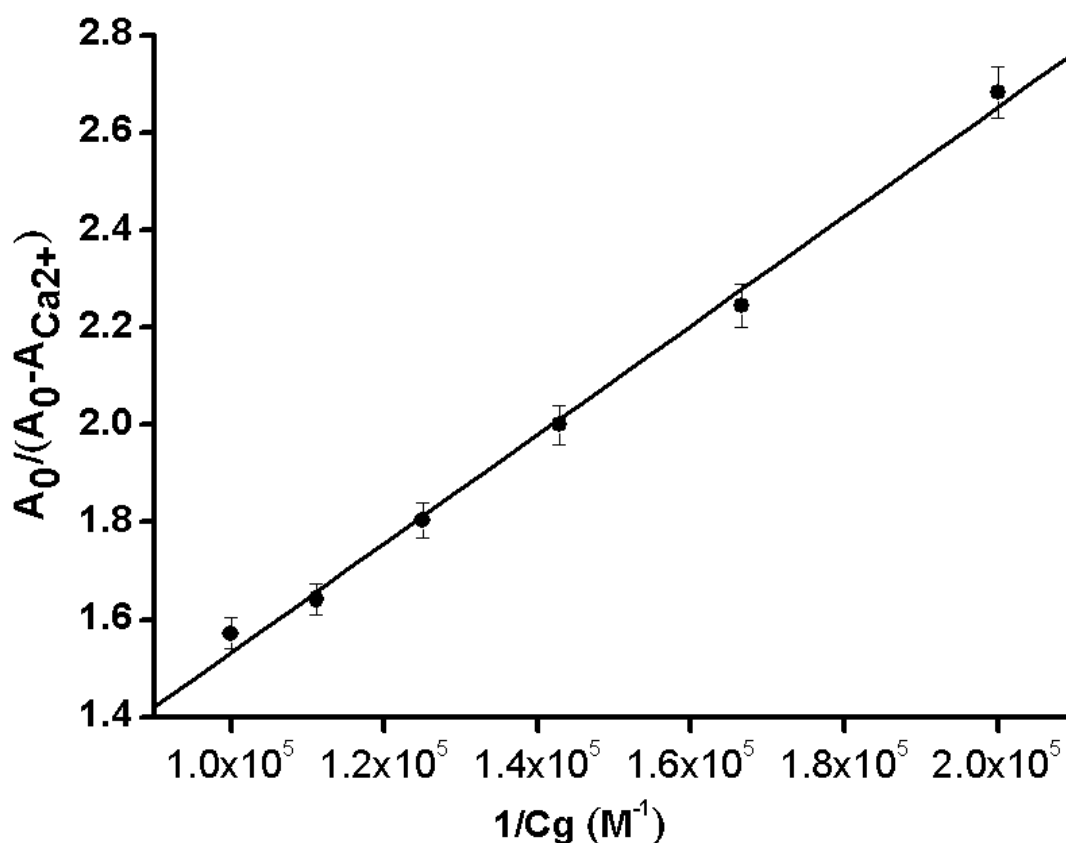
A mixture of **3** (1.1 g, 3.0 mmol), 5-formylthiophen-2-yl-2-boronic acid (493 mg, 3.16 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (173 mg, 0.15 mmol) and 2M Na<sub>2</sub>O<sub>3(aq)</sub> (7 mL) in ethanol (10 mL) and toluene (20 mL) was refluxed overnight under inert atmosphere. After completion of the reaction, the solvent of mixture was removed by rotary evaporation. The resulting residue was washed with ether for three times, and subsequently extracted with water and NaHCO<sub>3(aq)</sub>, then purified using column chromatography on silica gel (hexanes and ethyl acetate). The residue was dried over anhydrous MgSO<sub>4</sub>. After filtration, the solvent was removed by rotary evaporation. The compound was then dried under vacuum to yield 790 mg (65%) of red solid of **4**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.64 (m, 16H), 3.70 (m, 4H), 6.53 (d, *J* = 8.4 Hz, 2H), 7.23 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.67 (m, 2H), 9.79 (s, 1H). Anal. Calcd for C<sub>21</sub>H<sub>27</sub>NO<sub>5</sub>S: C, 62.20; H, 6.71; O, 19.73. Found: C, 62.24; H, 6.69; O, 19.71.

*Synthesis of 3-(5-(4-(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)phenyl)-*

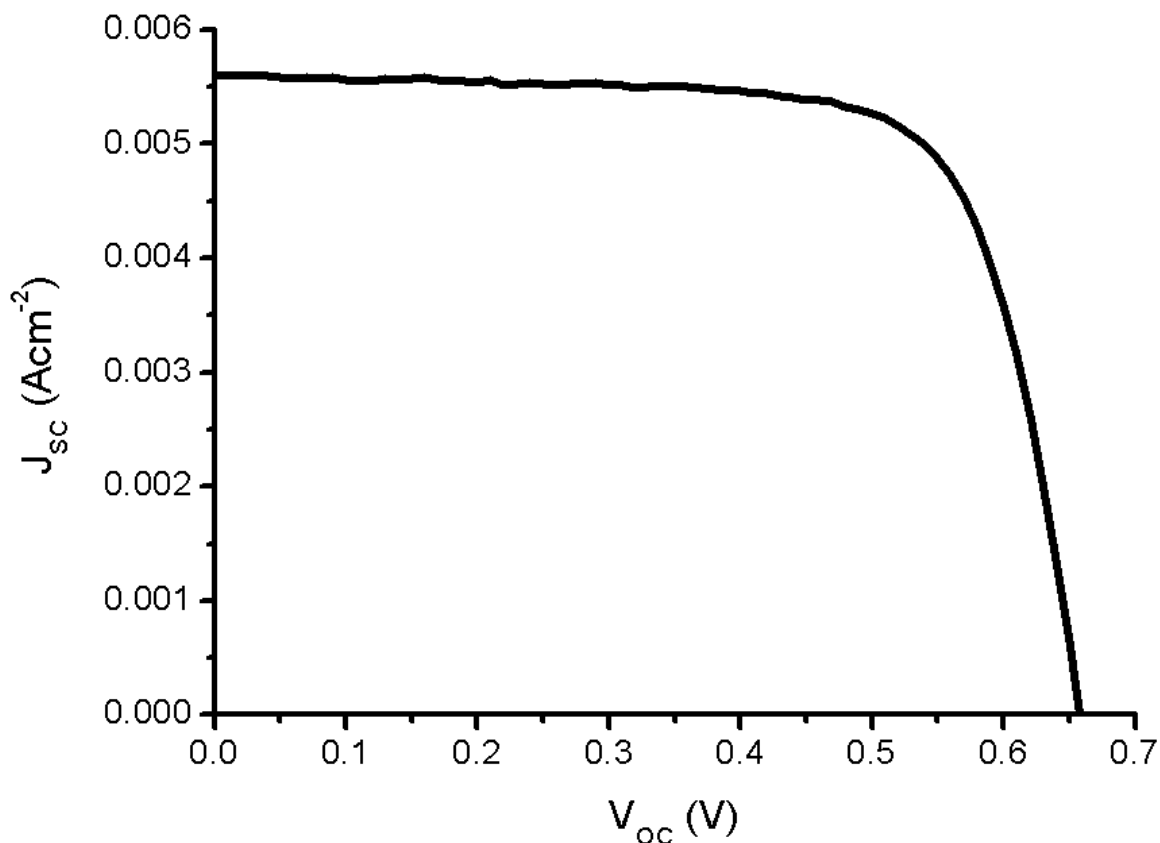
A solution of **4** (423 mg, 1.04 mmol), 2-cyanoacetic acid (133 mg 1.56 mmol), and NH<sub>4</sub>OAc (26 mg, 0.34 mmol) in 10 mL AcOH was stirred at room temperature overnight under inert atmosphere. The solution was poured into water, and the product was extracted by diethyl ether. The diethyl ether solution was then dried by anhydrous magnesium sulfate (MgSO<sub>4</sub>). Filtration, evaporation of the solvent, and column chromatography were carried out in sequence to afford compound **1** as a dark red solid with a yield of 355 mg (75%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 3.63 (m, 16H), 3.77 (m, 4H), 6.76 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 4 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 4 Hz, 2H), 8.28 (s, 1H). Anal. Calcd for C<sub>24</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub>S: C, 61.00; H, 5.97; O, 20.31. Found: C, 61.03; H, 5.99; O, 20.35.

*Fabrication of DSSC<sup>2</sup> suited for metal ion recognition.* Modification of the hardware of the device suited for metal ion titration is necessary. The TiO<sub>2</sub> photoanode electrode was prepared according to a published procedure.<sup>1</sup> The mixtures of anatase and rutile TiO<sub>2</sub> nanoparticles of 20 nm were dispersed in  $\alpha$ -terpineol with ethyl cellulose as a binder. The TiO<sub>2</sub> thin films of 8  $\mu$ m were prepared by a screen-printing method on a transparent conducting oxide (F-doped SnO<sub>2</sub>, FTO, Tech8). These films were dried at 120°C for 15 min with a dimension of 0.2826 cm<sup>2</sup>. Afterwards, the TiO<sub>2</sub> thin films were sintered at 500°C for 30 min. After sintering, the TiO<sub>2</sub> films were treated with 50 mM of TiCl<sub>4</sub> solution, rinsed with DI water and ethanol, and sintered at 500°C for 30 min. After being cooled to 80°C, the TiO<sub>2</sub> electrode was coated with dyes by dipping it into solution containing **1** ( $3 \times 10^{-4}$  M in CH<sub>3</sub>CN) overnight. The Pt counter electrode was prepared by spin-coating a 0.05M H<sub>2</sub>PtCl<sub>6</sub> in isopropyl alcohol solution on the FTO glass, followed by sintering at 385°C for 15–30 min. These two electrodes were placed into two ends of the home-made cell shown below (also, see TOC). The LiI electrolyte solution (0.10 M in CH<sub>3</sub>CN) was then filled into the cell. The prepared Ca<sup>2+</sup> stock solution was then added gradually into the quartz cell with a micropipet. A typical amount of 10  $\mu$ l was added for each titration to ensure negligible change of the entire volume.

Regarding the concern on stability and the reproducibility of this recognition system, the measurement was performed under dry nitrogen ( $N_2$ ) atmosphere. Light-to-electricity conversion efficiency values were measured using a modified light source, 450 W Xe lamp (Oriel, 6266), an Oriel 81088 Air Mass 1.5 Global Filter and a digital source meter purchased from Keithley Instruments Inc. The incident light intensity was calibrated by using a standard solar cell composed of a crystalline silicon solar cell and an IR cutoff filter (Schott, KG-5), giving the photoresponse range of amorphous silicon solar cell. The applied potential and measured cell current were measured using a Keithley model 2400 digital source meter.



**Figure S1.** The plot of  $A_0/(A_0 - A_{Ca^{2+}})$  against  $1/C_g$  at 455 nm.



**Figure S2.** The I-V curve of organic DSSCs with azacrown dye **1** under conventional fabrication processes. The performance of the device reveals the power conversion efficiency ( $\eta$ ) 2.68%, the short-circuit current density ( $J_{sc}$ ) 5.60 mAcm<sup>-2</sup>, the open-circuit voltage ( $V_{oc}$ ) 0.66V, and the filled factor (FF) 0.72.

#### References:

- 1 P. Wang, S. M. Zakeeruddin, P. Comte,; R. Charvet, R. H. Baker and M. Grätzel, *J. Phys. Chem. B.*, 2003, **107**, 14336.
2. (a) N. Fuke, A. Fukui, R. Komiya, A. Islam, Y. Chiba, M. Yanagida, R. Yamanaka and L. Han, *Chem. Mater.*, 2008, **20**, 4974; (b) Y.-H. Lai, C.-W. Chiu, J.-G. Chen, C.-C. Wang, J.-J. Lin, K.-F. Lin and K.-C. Ho, *Sol. Energy Mater. Sol. Cells*, 2009, **93**, 1860; (c) A. Goetzberger, C. Hebling,

*Sol. Energy Mater. Sol. Cells*, 2000, **62**, 1-6. (c) D. Wang, S. M. Zakeeruddin, P. Comte,; R. Charvet, R. Humphry-Baker and M. Grätzel, *J. Phys. Chem. B.*, 2003, **107**, 14336.