# **Supporting Information**

# A Copper(I) Dye-Sensitized TiO<sub>2</sub>-Based System for Efficient Light Harvesting and Photoconversion of CO<sub>2</sub> into Hydrocarbon Fuel

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#### **Experimental Section**

General information for synthesis and characterization. All reagents and solvents were reagent grade quality. obtained commercially and used without further purification except as noted. 4,4'-dibromo-6,6'-dimethyl-2,2'-bipyridine, 4-aldehydebenzeneboronic acid pinacol ester and  $[Cu(CH_3CN)_4]PF_6$  were prepared according to previously published procedure<sup>1-3</sup>.

<sup>1</sup>H NMR spectra was measured on a Bruker AMX500 MHZ FT NMR spectrometer. Analyses for C, H and N were performed on a Perkin-Elmer 240C element analyzer. The FT-IR spectra was obtained on a on the Nexus 870 FT-IR spectrometer. Absorption spectrum of solution was measured with a Varian Cary 50 UV-Vis spectrophotometer, and absorption spectra of solid sample and film were obtained by using a Shimadzu UV-2550 UV-Visible spectrophotometer. The measurement system for the surface photovoltage spectroscopy (SPS) consisted of a source of monochromatic light, a lock-in amplifier (SR830-DSP) with a light chopper (SR540) and a photovoltaic cell. A 500 W xenon lamp and a grating monochromator (Omni- $\lambda$  500) were combined to provide the monochromatic light. A low chopping frequency of ca. 23 Hz was used to obtain stable and intensive signals. The photovoltaic cell was a sandwich-like structure of ITO-sample-ITO. The transient photovoltage spectra from a Nd:YAG laser (Polaris II, NewWave Research, Inc.) were performed with a Nd:YAG laser (Polaris II, NewWave Research, Inc.) and the signals were registered by a 500 MHz digital phosphor oscilloscope (TDS 5054, Tektronix) with a preamplifier.





# Preparation of 4,4'-di(p-aldehyde)phenyl-6,6'-dimethyl-2,2'-bipyridine.

4,4'-di(p-aldehyde)phenyl-6,6'-dimethyl-2,2'-bipyridine was obtained using a general coupling procedure<sup>4</sup>. 4,4'-dibromo-6,6'-dimethyl-2,2'-bipyridine (1 mmol), 4-aldehydebenzeneboronic acid pinacol ester (3 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%), and K<sub>2</sub>CO<sub>3</sub> (15 mmol) were added to a solution of tetrahydrofuran (50 mL) and water (10 mL). The mixture was stirred at 50 °C under nitrogen for 24 h, its color changed from yellow to dark during reaction. After cooling, water (30 mL) was added, the organic layer was separated and aqueous solution was extracted by ethyl acetate (2 × 30 mL), the organic phases were collected together. After drying over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed under reduced pressure. The pure product was obtained by column chromatography on silica gel (ethyl acetate) to give pale yellow solid.

Yield (71%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): 10.13 (2H, s), 8.57 (2H, s), 8.05 (4H, J = 8.5, d), 7.95 (4H, J = 6.5, d), 7.50 (2H, S), 8.77(4H, s), 2.76 (6H, s).

# Preparation of ligand: 4,4'-di[p-(cyanoacrylic acid)phenyl]-6,6'-dimethyl-2,2' -bipyridine.

4,4'-di[(p-aldehyde)phenyl]-6,6'-dimethyl-2,2'-bipyridine (1 mmol), cyanoacetic acid (2.98 mmol), and piperidine (1 mmol) were added to CHCl<sub>3</sub> (10 mL) solution. The mixture was refluxed overnight; the yellow solid formed in the solution. The precipitate was filtered as product for next use. Yield (57%). <sup>1</sup>H NMR (500 MHz, DMSO): 8.74 (4H, s), 8.55 (4H, s), 8.20 (4H, s), 8.14 (8H, J = 8.5, d), 8.04 (8H, J = 8.5, d), 8.77(4H, s), 2.69 (12H, s).

### Preparation of Cu(I) complex 1.

4,4'-di[p-(cyanoacrylic acid)phenyl]-6,6'-dimethyl-2,2'-bipyridine (1 mmol), [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (0.5 mmol) were added to a solution of CH<sub>2</sub>Cl<sub>2</sub> (15ml) and CH<sub>3</sub>OH (15 ml), the reaction mixture immediately turn red and then the solution was refluxed under nitrogen for 24h. After cooling, the solvent was removed under reduced pressure. The pure compound was obtain by column chromatography on silica gel (CH<sub>3</sub>OH/CH<sub>3</sub>COOH, v/v = 2:1). The product was dried under vacuum at 100 °C overnight for next. Yield (51%). The well resolved <sup>1</sup>H NMR has been limited by their poor solubility in common organic solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, MeOH, DMSO and so on. <sup>1</sup>H NMR (500 MHz, CF<sub>3</sub>COOD):  $\delta$  8.93 (4H, s), 8.85 (4H, s), 8.59 (4H, s), 8.47 (8H, J = 8.5, d), 8.29 (8H, J = 6.5, d), 3.26 (12H, S). IR (KBr, cm<sup>-1</sup>), 3396, 2217, 1628, 1570, 1544, 1389, 1195, 1015, 834, 788, 724. Anal. Found for CuC<sub>64</sub>N<sub>8</sub>H<sub>32</sub>O<sub>8</sub>PF<sub>6</sub>: C, 61.08; H, 3.62 ; N, 8.92; Calcd for CuC<sub>64</sub>N<sub>8</sub>H<sub>32</sub>O<sub>8</sub>PF<sub>6</sub>: C, 60.93; H, 3.52; N, 8.88.

### **Device Fabrication for DSSCs.**

The TiO<sub>2</sub> paste preparation and device fabrication for sandwich-type DSSCs were carried out according to a previously reported procedure.<sup>5</sup> FTO glass plates were cleaned in a detergent solution using an ultrasonic bath for 15 min, rinsed with water and ethanol. The FTO glass plates were immersed in 40 mM TiCl<sub>4</sub> (aqueous) at 70 °C for 20 min, and washed with deionized water and ethanol. Then, an 80 µm layer of TiO<sub>2</sub> paste was coated onto the FTO. After dried at 125 °C, the electrodes were annealed at 450 °C for 20 min. Another layer of TiO<sub>2</sub> paste was coated onto the films again. After being annealed at 450 °C, the films were immersed in aqueous TiCl<sub>4</sub> at 70 °C again. The films were sintered at 500 °C in an air flow. When cooled to room temperature, the electrodes were soaked into the CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> solution of complex 1 (0.5 mM) for 24 h. The resulting sensitized TiO<sub>2</sub> electrodes were washed with distilled water and dried at room temperature for 30 min. The substrate, film, and counter electrode (a magnetron sputter platinum mirror) constituted a sandwich-like open cell. The electrolyte was composed of 1.0 M BMII, 50 mM LiI, 30 mM I<sub>2</sub>, and 0.5 M tert-butylpyridine in a mixture of acetonitrile and valeronitrile (volume ratio, 85:15). Current density voltage (J-V) curves of the DSSC with an active area of 0.132 cm<sup>2</sup> was measured under AM1.5 (100 mW/cm<sup>2</sup>) illumination, the irradiation source was a 450 W Xenon light source (Keithley 236), and the solar simulator was calibrated by using a reference Si reference cell (Oriel, Model 91150V).

#### Preparation of 1/TiO<sub>2</sub>.

0.25 g P-25 was added into 10 mL of 1 mM CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> solution of complex 1. After sonicated for about 10 min, the mixture was stirred in the dark at 50 °C for about 24 h. Centrifuged and washed with absolute ethanol; the product was dried under vacuum at 100 °C overnight for further CO<sub>2</sub> reaction.

#### Photocatalytic CO<sub>2</sub> reduction

Photocatalytic CO<sub>2</sub> reduction was conducted in the gas phase over solids under visible-light irradiation using a 300 W Xenon arc lamp with a cut-off filter ( $\lambda > 420$  nm).<sup>6</sup> 0.1 g of solid sample was uniformly placed on a glass reactor with a typical area of 4.2 cm<sup>2</sup>. The volume of the reaction system was about 230 mL. After the setup was fully evacuated to remove any air, high-purity CO<sub>2</sub> gas was introduced into the system at near-ambient pressure. Then, 0.4 mL of deionized water was injected into the reaction chamber. At given irradiation time intervals, a series of gases of a certain volume (ca. 1.0 mL) were taken out via a syringe for analysis with a gas chromatograph (Shimadzu GC-2014) equipped with Porapak-N column. Calibration of the methane gas chromatograph is accomplished by measuring instrument response to a known concentration of methane in argon. For the second run, the setup was fully evacuated again. Then, 0.4 mL of deionized water prior to light irradiation.

**Theoretical Calculation.** The calculation was performed with Gaussian 09 program based on density functional theory, the geometries and energy was optimized by using the B3LYP/LAND2DZ. The calculation was done on the IBM Blade cluster system in the High Performance Computing Center of Nanjing University.

### Reference

(1) Han, W-S.; Han, J-K.; Kim, H-Y.; Choi, M. Jin.; Kang, Y. S.; Pac, C.; Kang, S. O. *Inorg. Chem.* **2011**, *50*, 3271-3280.

(2) Huang, C. S.; Wen, L. P.; Liu, H. B.; Li, Y. L.; Liu, X. F.; Yuan, M. J.; Zhai, L.; Zhu, D. B. Adv. Mater. 2009, 21, 1721-1725.

(3) Kubas, G. J.; Monzyk, B.; Crumbliss, A. L. Inorg. Synth. 2007, 19, 90-91.

(4) Kim, J. J.; Lim, K.; Choi, H. B.; Kang, M. S, Gao, G. H. Inorg. Chem. 2010, 49, 8351-8357.

(5) Wang, P.; Zakeeruddin, S. M.; Comte, P.; Charvet, R.; Humphry-Baker, R.; Grätzel, M. J. Phys. Chem. B 2003, 107, 14336-14341.

(6) (a) Liu, Q.; Zhou, Y.; Kou, J.; Chen, X.; Tian, Z.; Gao, J.; Yan, S. C.; Zou, Z. G. *J. Am. Chem. Soc.* **2010**, *132*, 14385-14387. (b) Yan, S. C.; Ouyang, S. X.; Gao, J.; Yang, M.; Feng, J. Y.; Fan, X. X.; Wan, L. J.; Li, Z. S.; Ye, J. H.; Zhou, Y.; Zou, Z. G. *Angew. Chem. Int. Ed.* **2010**, *49*, 6400-6404.







(b)



**Figure S2.** Comparison of the UV-vis absorption spectra of **1** in methanol solution (ca. 0.01 mM), on P-25 and a thin transparent  $TiO_2$  film (a); Solid-state electronic absorption spectrum of complex **1** at 298 K (b).



Figure S3. FT-IR of complex 1.



Figure S4. Chemical structure of complex 1 optimized by DFT.



Figure S5. HOMO distribution of complex 1 by DFT calculation.



Figure S6. LUMO distribution of complex 1 by DFT calculation.



Figure S7. Absorption spectrum of 1/TiO<sub>2</sub> powder recorded before and after CO<sub>2</sub> photoreduction.



Figure S8. FT-IR of 1/TiO<sub>2</sub> before and after photocatalysis.



Figure S9. Surface photovoltage spectrum of  $TiO_2$  and  $1/TiO_2$ .



 $\begin{array}{c} 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \\ CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \end{array}$ 

