# **Supplementary Information**

# Bis(1,1-Bis(2-pyridyl)ethane)copper(I/II) as Efficient Redox Couple for Liquid Dye-sensitized Solar Cells

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# Schematic diagram



Figure S1. A schematic diagram of the DSSCs based on the  $Co(bpy)_3^{2+/3+}$  and  $Cu(bpye)_2^{+/2+}$  redox systems.

# Syntheses and characterization

# 1,1-Bis(2-pyridyl)ethane (bpye)

#### Scheme 1. The procedure of synthesizing 1,1-Bis(2-pyridyl)ethane

The synthesis procedure of 1,1-Bis(2-pyridyl)ethane was modified according to the method of B. Bechlars et al.<sup>1</sup>

2-ethylpyridine (22.6 mL, 198 mmol) was dissolved in 180mL dry THF in a three neck round flask with a reflux condenser and a dropping funnel under N<sub>2</sub> protection. After cooling down to - 78°C (acetone/dry ice), a 2.5 M hexane solution of *n*-butyllithium (75.1 mL, 188 mmol) was added and the reaction mixture turned dark red. After stirring for 60 min, 2-fluoropyridine (8.0 mL, 92.9 mmol) was added via a syringe. Then the ice bath was removed and the mixture was allowed to warm to room temperature, after that the mixture was heated to reflux for 30 min. The reaction solution was allowed to cool down to room temperature before 200 g ice was added. The phases were separated and the aqueous phase was extracted with DCM (60 mL). After filtration, the solvent was removed with a rotavapor. Reactants were removed in a distillation apparatus under reduced pressure (bath temp.: 100 °C) and the remaining red oil (13.85 g; yield: 80.1%) was used without further purification.

<sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.54 (d, *J* = 3.8 Hz, 2H), 7.58 (td, *J* = 7.7, 1.9 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.10 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 2H), 4.46 (q, *J* = 7.2 Hz, 1H), 1.75 (d, *J* = 7.2 Hz, 3H).

# Cu<sup>II</sup>(bpye)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>

 $Cu(ClO_4)_2 + 2 bpye \xrightarrow[EtOH]{} [Cu(bpye)_2](ClO_4)_2 \xrightarrow[H_2O]{} [Cu(bpye)_2](PF_6)_2$ 



The synthesis procedure of  $[Cu^{II}(bpye)_2](PF_6)_2$  was modified according to the method of Spodine E. et al.<sup>2</sup>

1,1-Bis(2-pyridyl)ethane (557 mg, 3.02 mmol) was added to a solution of  $Cu(ClO_4)_2 \cdot 6H_2O$  (520 mg, 1.41 mmol) in 10 mL EtOH and the purple mixture was heated to reflux for 15 min. After allowing the solution to cool down to r.t., it was added to a solution of  $NH_4(PF_6)$  (692 mg, 4.25 mmol) in 10 mL H<sub>2</sub>O. The precipitate was filtrated and dried in vacuum, yielding 633 mg (62.2%) purple product.

<sup>1</sup>H NMR (400 MHz, Acetone- $d_6$ ) no peaks between 17 and -0 ppm. (Cu<sup>II</sup> is paramagnetic). In order to proof that the desired product was obtained, a small fraction was reduced with ascorbic acid and a <sup>1</sup>H NMR spectrum of the reduced species was recorded.

Elemental analysis renders N: 7.777%; C: 40.20%; H: 3.207% (calc. N: 7.76%; C: 39.93%; H: 3.35%).

High-performance liquid chromatography-mass spectrometry (HPLS-MS) spectra were also recorded. The characteristic's peaks of  $[Cu(bpye)_2]^{2+}$  and  $[Cu(bpye)_2(PF_6)]^+$  were found at m/z 215.5642 and 576.0687, (calc. m/z 215.5643 and 576.0933).

Crystals of good quality for a crystallographic analysis could also be isolated, and the corresponding results are given as **Figure 2** in the main article.

### **Procedure for reduction**

 $[Cu(bpye)_2](PF_6)_2$  (100 mg, 0.137 mmol) was dissolved in 5 mL dichloromethane and a few drops of CH<sub>3</sub>CN were added until everything was dissolved. After stirring with an excess of ascorbic acid for 24 h the suspension was filtrated and dried, yielding a yellow solid. After extraction with dichloromethane and evaporation of the solvent 12 mg of yellow powder were obtained (12% yield).

<sup>1</sup>H NMR (400 MHz, Acetone)  $\delta$  8.34 (d, 4H), 8.02 (dd, J = 7.4, 6.9 Hz, 4H), 7.87 – 7.78 (m, 4H), 7.46 – 7.37 (m, 4H), 4.88 (d, 2H), 2.12 (d, 6H).

# Cu<sup>I</sup>(bpye)<sub>2</sub>(PF<sub>6</sub>)

CuCl + 2 bpye  $\longrightarrow$  [Cu(bpye)<sub>2</sub>]Cl  $\xrightarrow{NH_4PF_6}$  [Cu(bpye)<sub>2</sub>](PF<sub>6</sub>)

Scheme 3. The procedures of synthesizing [Cu(bpye)<sub>2</sub>](PF<sub>6</sub>)

bpye (1.07 g, 5.82 mmol) was dissolved in 10 mL ethanol and degassed (N<sub>2</sub>) for 10 min. Afterwards, CuCl (273 mg, 2.76 mmol) was added to the mixture under stirring and it turned green/yellow. Then it was stirred for 2 h under nitrogen atmosphere, before it was added to as solution of  $NH_4PF_6$  (1.41 g, 8.65 mmol) in 25 mL H<sub>2</sub>O. The resulting suspension was filtered, and the product was dried in vacuum for 48 h yielding 1.38 g (87.3%) yellow powder.

<sup>1</sup>H NMR (400 MHz, Acetone)  $\delta$  8.34 (d, 4H), 8.02 (dd, J = 7.4, 6.9 Hz, 4H), 7.87 – 7.78 (m, 4H), 7.46 – 7.37 (m, 4H), 4.88 (d, 2H), 2.12 (d, 6H).

Ultra-performance liquid chromatography coupled with Q-TOF (quadrupole-time-of-flight) mass spectra (UPLC/Q-TOF MS) were used to investigate the composition of the Cu(I) compound. The characteristic peak of  $[Cu(bpye)_2]^+$  was found at m/z 431.1306 (calc. m/z 431.1291), as showed in **Figure S2**.



Figure S2. The Q-TOF mass spectrum of [Cu(bpye)<sub>2</sub>](PF<sub>6</sub>).

Characterization was performed using a Bruker AVANCE 400 MHz NMR spectrometer, an HP 1100, Agilent Co., Ltd., for HPLC-MS, a Q-ToF Micro from Micromass UK, Ltd., for UPLC/Q-TOF MS and a Vario EL III Element Analyzer from Elementar Analysensysteme GmbH for the elemental analyses.

# **Crystal structure determination**

Crystals suitable for a crystallographic analysis of  $[Cu^{\parallel}(bpye)_2](PF_6)_2$  were grown from an acetonitrile solution by slow evaporation. The crystal structure was determined at two different temperatures, 295 and 200 K, and the structures have been deposited at the Figure 2 in the main article. For the crystal structure determination at 295 K, a suitable crystal was selected and mounted on a glass fiber. The diffraction data were collected on a Bruker APEX II CCD diffractometer using Mo K $\alpha$  radiation. The crystals were kept at 295.54 K during the data collection. The crystal structure was determined with the ShelXT<sup>3</sup> structure solution program using direct methods and was refined with the software Olex2<sup>4, 5</sup> employing a Gauss-Newton minimization algorithm. For the low-temperature analysis, crystals were selected and mounted on a cryoloop using low-temperature immersion oil and placed in a N<sub>2</sub> cold stream. Singlecrystal X-ray data were collected on a Bruker APEX II diffractometer (MoKα radiation), equipped with a CCD detector, at 200 K. The data sets were recorded with  $\omega$ - and  $\Box$ -scans, and integrated with the Bruker SAINT<sup>6</sup> software package. The absorption correction (Bruker SADABS<sup>6</sup>) was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements. Solution and refinement of the crystal structures were carried out using SHELXS and SHELX within the Bruker package. Structure solution by direct methods resolved positions of all atoms except hydrogens. The remaining non-hydrogen atoms were located by alternating cycles of least-squares refinements and difference Fourier maps. Hydrogen atoms were placed at calculated positions in both structure determinations. The final refinements were performed with anisotropic thermal parameters for all non-hydrogen atoms. A summary of pertinent information relating to unit cell parameters, data collection, and refinement is provided in the accompanying CIF-files. CCDC-1459030 and CCDC-1457921, respectively,

contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/data\_request/cif</u>.

# Cyclic voltammetry (CV) measurements

Cyclic voltammetry measurements have been performed on an Ivium technologie Vertex with IviumSoft 2.561 under Argon gas protection. The electrolyte was freshly prepared from acetonitrile and tetrabutylammonium hexafluorophosphate (TBA(PF<sub>6</sub>), 0.1 M). Plane glassy carbon (diameter 3 mm) was used as working electrode, Pt wire as counter electrode and Ag/AgNO<sub>3</sub> as reference electrode (0.1 M). The data were calculated to *NHE* (normal hydrogen electrode) with a reference of Fc/Fc<sup>+</sup>(0.63 *vs. NHE*<sup>7</sup>).

# Device fabrication, measurements and stability

#### **PEDOT** counter electrodes preparation

Predrilled TEC7 fluorine-doped tin oxide (FTO) glass was cleaned (in the order of detergent water solution, and ethanol) using an ultrasonic bath. Solution for electropolymerization was prepared as previous reported.<sup>8</sup> Aqueous solution of 0.1 M Sodium Dodecyl sulfate (SDS) and 0.01 M 3,4-ethylenedioxythiophene (EDOT) was prepared through sonicating for 1.5 hour. Electro-oxidative polymerization was performed by Autolab potential station with a GPES 4.9 electrochemical interface (Eco Chemie). A 4 × 4 cm cleaned predrilled FTO was used as working electrode and same size cleaned FTO was used as counter (and reference) electrode. Preparation was performed under in galvanostatic mode with 3.2 mA current for 170 seconds. The blue colored films were washed with immersing in deionized water for 1 min.

## **Device fabrication**

Fluorine-doped tin oxide (FTO) glass substrates (Pilkington, TEC15) were cleaned with the same procedure of cleaning FTO substrates for the counter electrodes. Then the substrate was treated, with 40 mM aqueous TiCl<sub>4</sub> solution at 70 °C for 30 min to make a thin blocking layer. A layer of 5  $\mu$ m thick 18 nm size mesoporous TiO<sub>2</sub> with a diluted commercial paste (dilute the "DSL 18NR-T, Dyesol" paste by 60 wt % paste + 36 wt % terpineol + 4 wt % ethyl cellulose) and a layer of 5  $\mu$ m thick 150-250 nm size TiO<sub>2</sub> (WER2-O, Dyesol) were screenprinted on to the pre-treated FTO glass surface. The double-layer TiO<sub>2</sub> electrodes (area: 5×5 mm) were heated in air at 480 °C for 30 min, and heated to 450 °C for 15 min. The films were then immersed into a 2 × 10<sup>-4</sup> M dye 3-(6-(4-(bis(2',4'-dibutoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)-4,4-dihexyl-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)-2-cyanoacrylic acid (LEG4) solution in ethanol and maintained in the dark for 18 h. The resulting sensitized TiO<sub>2</sub> electrodes were then rinsed with ethanol and dried. Hermetically sealed cells were fabricated by assembling the dye-loaded film

as the working electrode and a PEDOT counter electrode separated with a hot-melt Surlyn 1702 film (25  $\mu$ m, Dupont). Then the electrolyte was filled in by vacuum, and sealed the back hole with another hot-melt film.

#### Photovoltaic characterization

Current density-voltage (*J-V*) characteristics were recorded by a Keithley 2400 source/meter, and simulated AM 1.5 G sunlight was provided by a Newport solar simulator (model 91160), which was calibrated using a certified reference solar cell (Fraunhofer ISE) to an intensity of 1000 W·m<sup>-2</sup>. A 5×5 mm mask, which is the exact size of active solar cell area, was applied on top of the solar cell.

#### Comparison between PEDOT and platinized FTO as counter electrode

As can be noted in the I-V curves in Figure S3 below, DSSCs based on a platinized FTO counter electrode exhibit significantly larger overall series resistance than those based on PEDOT (*cf.* Figure 4 in the main article).



**Figure S3.** The *J-V* curve of a device based on the copper-complex redox couple and a platinized FTO counter electrode.

## References

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