Supplementary Information

Efficient dye-sensitized solar cells with [copper(6,6'-dimethyl-2,2'-bipyridine)$_2$]$^{2+/1+}$ redox shuttle

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1. Synthesis and characterization

The copper(6,6'-dimethyl-2,2'-bipyridine)$_2$BF$_4$ and copper(6,6'-dimethyl-2,2'-bipyridine)$_2$(BF$_4$)$_2$ complexes were synthesized according to previous reports.[1] Other chemicals and reagents were purchased from Sigma-Aldrich or Aladdin Industrial Corporation and used without further purification. Elemental analyses were obtained from a Thermoquest-Flash EA 1112 elemental analyzer. ^{1}HNMR of Cu(dmbp)$_2$BF$_4$ complex were conducted with a Varian INOVA 500 MHz (USA). X-ray single crystal fluorescence spectra were recorded on an ARL9800-230XP spectrometer.

Copper(6,6'-dimethyl-2,2'-bipyridine)$_2$BF$_4$: 6,6'-dimethyl-2,2'-bipyridine (2 equivalents) and CuBF$_4$·4CH$_3$CN (1 equivalent) were dissolved in a mixed solvent of CH_2Cl_2:CH_3OH=3:1 and stirred at room temperature for 2 h. Then, the solvent was removed and the product was recrystallized by acetonitile–diethyl ether mixture and then obtained the red crystalline product Cu(dmbp)$_2$BF$_4$. Anal. Calc. for $C_{24}H_{24}N_4CuBF_4$ (%): C 55.56, H 4.66, N 10.80; found: C 55.25, H 4.59, N 10.78. ^{1}H NMR (500 MHz, CD$_3$CN) δ 8.27 (d, *J* = 8.0 Hz, 1H), 8.03 (t, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 1H), 2.22 (s, 3H).

Copper(6,6'-dimethyl-2,2'-bipyridine)$_2$(BF$_4$)$_2$: Cu(dmbp)$_2$(BF$_4$)$_2$ was synthesised in the same way as Cu(dmbp)$_2$BF$_4$. 6,6'-dimethyl-2,2'-bipyridine (2 equivalents) and Cu(BF$_4$)$_2$·6H$_2$O (1 equivalent) were dissolved in a mixed solvent of CH_2Cl_2:CH_3OH=3:1 and stirred at room temperature for 2 h and then removed the solvent. After the crystallization with acetonitile–diethyl ether mixture, the green crystalline product was obtained. Anal. Calc. for $C_{24}H_{24}N_4CuB_2F_8$ (%): C 47.60, H 3.99, N 9.25; found: C 47.69, H 4.04, N 9.32.

2. Cyclic Voltammetry measurement

Cyclic voltammetry (CV) measurements of Cu(dmbp)$_2$BF$_4$ were recorded on BAS100B electrochemistry workstation (USA) with a three-electrode system using a glassy carbon working electrode, a Pt wire counter electrode and an Ag/Ag$^+$ reference electrode. 0.1 M LiBF$_4$ in acetonitrile was served as the supporting electrolyte and ferrocenium/ferrocene (Fc$^{+/0}$) redox couple (0.63 V versus NHE) was used as a comparison. The reodox potential of Cu(dmbp)$_2$BF$_4$ is 0.34 V versus Fc$^+$/Fc (**Fig. 3 (a)**) affording 0.97 V versus NHE. Cyclic voltammetry (CV) measurements of organic dye **Y123** were recorded by a similar system with that of Cu(dmbp)$_2$BF$_4$ but using dye-sensitized TiO$_2$ film as the working electrode. The calculated redox potential of organic dye **Y123** is 1.08 V versus NHE.

3. UV-Vis absorption spectra measurement

UV–Vis absorption spectrum was measured with spectrophotometer HP8453 (USA).

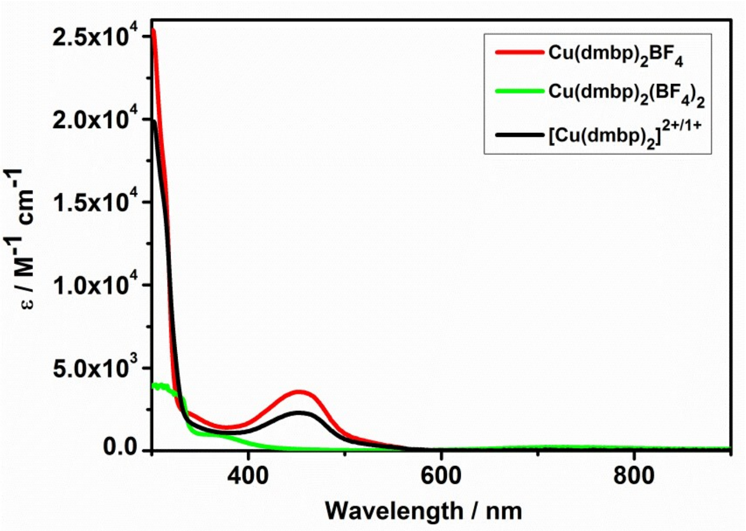

Fig. S1 Absorption spectrum of Cu(dmbp)$_2$ BF$_4$ and Cu(dmbp)$_2$(BF$_4$)$_2$ in CH$_3$CN as well as [Cu(dmbp)$_2$]$^{2+/1+}$ based dilute electrolyte.

Table S1 Absorption properties of Cu(dmbp)$_2$ BF$_4$ and Cu(dmbp)$_2$(BF$_4$)$_2$ in CH$_3$CN as well as [Cu(dmbp)$_2$]$^{2+/1+}$ based dilute electrolyte.

Solution	λ_{max}	ε at λ_{max} ($M^{-1}\cdot cm^{-1}$)
Cu(dmbp)$_2$ BF_4 in CH_3CN	453	3554
Cu(dmbp)$_2$(BF_4)$_2$ in CH_3CN	726	213
[Cu(dmbp)$_2$]$^{2+/1+}$ based electrolyte	452	2281

4. Fabrication of the DSSCs

A compact layer was firstly attached to the cleaned F-doped tin oxide (FTO) conductive glass (Pilkington, 15 Ohm square, 2.2 mm thick) by the treatment with 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min. A 6 × 6 mm^2 transparent layer (5.6 µm or 7.4 µm) was then coated with a diluted TiO_2 paste (60 wt% TiO_2 paste (Dyesol, DSL 18NR-T), 35.6 wt % terpineol and 4.4 wt% ethyl cellulose) by screen printing, followed by a scatting layer (4 µm) with a TiO_2 paste (Heptachroma, TPP200). Next, the electrodes were heated at 500 °C for 60 min, while cooled down treated with 40 mM $TiCl_4$ aqueous solution at 70 °C for 30 min, further by heated at 500 °C for 60 min again. The sintered TiO_2 films were immersed into a 1×10^{-4} M **Y123** (Dyenamo AB., Sweden) dye solution in acetonitrile/tert-butanol mixture (1:1) with 0.5 mM of CDCA at room temperature for 10 h and then were washed with ethanol to get rid of the dyes unattached. Fabrication of the DSSCs was performed by assembling the dye-adsorbed TiO_2 electrodes and platinised counter electrode (Heptachroma) with a Surlyn film (Dupont, 25 µm). Finally, the electrolyte was injected into interlayer through a hole which was then sealed with a Surlyn film.

5. Photocurrent characteristics

The photocurrent density–voltage (*J*–*V*) characteristics of DSSCs were measured with a solar simulator (Newport USA, Oriel Sol3A). A mask of 0.1256 cm^2 was used for keeping work area. The Keithley 2400 Source (Keithley, USA) was served for the acquisition of data. The incident photon-to-current conversion efficiency (IPCE) spectra were recorded with a Hypermono–light (SM–25, Jasco Co. Ltd., Japan).

6. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was measured by an impedance/gain–phase analyzer (PARSTAT 2273, USA) under dark condition with a frequency range from 100 mHz to 1 MHz and a 10 mV of potential modulation. Dark currents of the DSSCs based on I_3^-/I^-, [Co(bpy)$_3$]$^{3+/2+}$ and [Cu(dmbp)$_2$]$^{2+/1+}$

electrolytes were measured by the EIS. Nyquist plots were recorded at the same current of 1.35 mA.

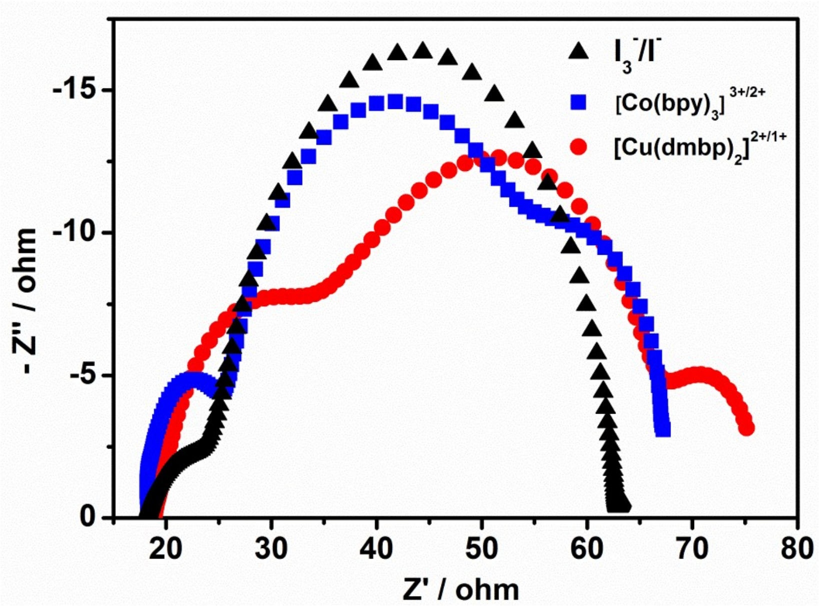

Fig. S2 Nyquist plots of DSSCs based on I_3^-/I^-, $[Co(bpy)_3]^{3+/2+}$ and $[Cu(dmbp)_2]^{2+/1+}$ electrolytes.

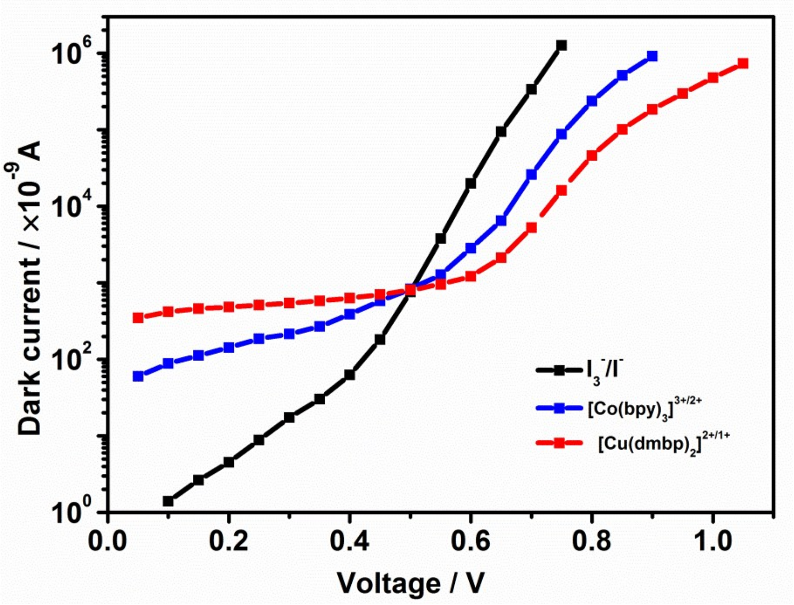

Fig. S3 Dark currents of the DSSCs based on I_3^-/I^-, $[Co(bpy)_3]^{3+/2+}$ and $[Cu(dmbp)_2]^{2+/1+}$ electrolytes were measured by the EIS.

7. Transient absorption measurements

The transient absorption kinetics were measured with the similar cells but replaced the Pt-FTO in DSSCs with FTO glass. The measurements were recorded by a laser flash photolysis spectrometer (Edinburgh

Instrument, LP920) in combination with a probe xenon light (Edinburgh Instrument, Xe920). The transient absorption decays were measured at 700 nm with the laser pulse excited at 532 nm. The energy of excitation laser pulse was kept below 10 mJ in order to avoid simultaneous excitation of neighborhood dye molecules.

8. Stability Test

The crystals of Cu(I) and Cu(II) were stable in the dry air. Stability tests were performed with $[Cu(dmbp)_2]^{2+/1+}$ based device for 15 days. It exhibits a relative stability with a drop about 10% in PCE mainly because of the evaporation of AN under dark condition. While a distinct drop in PCE with light exposure occurs which can be ascribed to a light-induced ligand exchange.

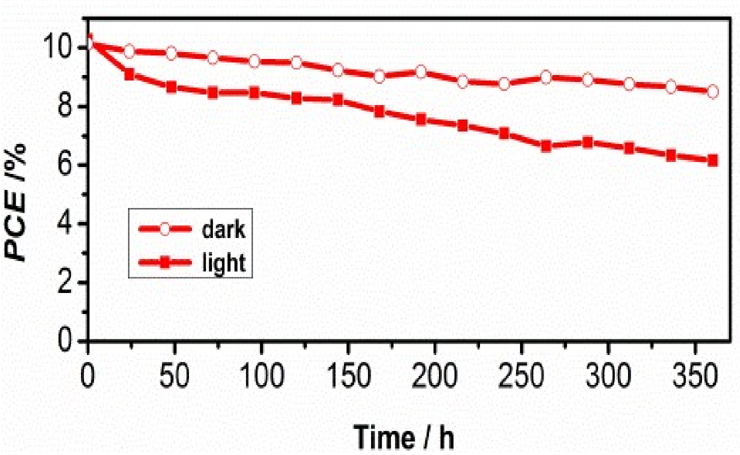

Fig. 4 The stability of DSSCs based on $[Cu(dmbp)_2]^{2+/1+}$ system.

References:

1. R. M. Williams, L. D. Cola, F. Hartl, J.-J. Lagref, J.-M. Planeix, A. D. Cian and M. W. Hosseini, *Coordin. Chem. Rev.*, 2002, **230**, 253.