Electronic Supplementary Information for

High-efficiency organic dye-sensitized mesoscopic solar cells with a copper redox shuttle

Yu Bai,[a,b] Qingjiang Yu,[a] Ning Cai,[a,b] Yinghui Wang,[a] Min Zhang[a] and Peng Wang*,[a]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

[b] Graduate School, Chinese Academy of Sciences, Beijing 100039, China

---

* To whom correspondence should be addressed. E-mail: peng.wang@ciac.jl.cn.

Experimental Section

1. Materials

Acetonitrile, *tert*-butanol and chlorobenzene were distilled before use. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), iodine and 4-*tert*-butylpyridine (TBP) were purchased from Fluka. Conductive carbon black was obtained from Shanghai Fuhua Co. Ltd.. $Cu(dmp)_2Cl_2 \cdot H_2O$[S1] and $Cu(dmp)_2Cl \cdot H_2O$,[S2] 1,3-dimethylimidazolium iodide (DMII)[S3] and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI)[S3] were prepared according to the literature methods. The synthesis of C218 has been described in our previous paper.[S4]

2. Synthesis of copper complexes

Synthesis of bis(2,9-dimethyl-1,10-phenanthroline)copper(I) bis(trifluoromethanesulfonyl)imide. To a solution of $[Cu(dmp)_2]Cl \cdot H_2O$ (0.939 g, 1.76 mmol) in 30 mL ethanol was added LiTFSI (0.556 g, 1.94 mmol) in 5 mL water, generating a red solid immediately. The mixture was further stirred for 2 h and the resulting precipitate was collected by filtration, washed thoroughly with water and diethyl ether in turn and dried under vacuum at 55 °C for 5 h to yield red powder (1.240 g, 93%). Anal. Calcd. for $C_{30}H_{24}CuF_6N_5O_4S_2$ ($Cu(dmp)_2TFSI$): C, 47.40; H, 3.18; N, 9.21. Found: C, 47.38; H, 2.92; N, 9.01.

Synthesis of bis(2,9-dimethyl-1,10-phenanthroline)copper(II) bis(trifluoromethanesulfonyl)imide chloride. To a solution of $Cu(dmp)_2Cl_2 \cdot H_2O$ (1.000 g, 1.76 mmol) in 300 mL ethanol and water (*v/v*, 1/2) was added LiTFSI (1.110 g, 3.87 mmol) in 10 mL water, affording a green precipitate immediately. The mixture was further stirred for 2 h and the resulting precipitate was collected by filtration, washed thoroughly with water and diethyl ether and dried under vacuum at 55 °C for 5 h to yield green powder (1.370 g, 98%). Anal. Calcd. for $C_{30}H_{24}ClCuF_6N_5O_4S_2$ ($Cu(dmp)_2TFSI$ chloride): C, 45.29; H, 3.04; N, 8.80. Found: C, 45.07; H, 2.83; N, 8.78.

3. Cell fabrication and photovoltaic characterizations

Conductive carbon black (CCB) paste was prepared by mixing CCB, polyvinylidene fluoride, *N*-methyl-2-pyrrolidone at a mass ratio of 10/9/180. A ~3.6-µm-thick CCB layer was first screen-printed onto a precleaned FTO glass (TEC 15 ohm/sq., Libbey-Owens-Ford Industries, 2.2 mm thick) and then baked at 200 °C for 5 min. Further platinization with a H_2PtCl_6 solution at 400 °C for 5 min produces a CCB positive electrode of DSCs. A bilayer titania film was employed as the negative electrode of DSCs. On a precleaned FTO conducting glass electrode (Nippon Sheet Glass, Solar, 4 mm thick), a 2.5-µm-thick transparent layer consisting of 23-nm-sized titania particles was first screen-printed and further coated by a 4-µm-thick second layer of scattering titania particles (WER2-O, Dyesol). Preparation procedures of the TiO_2 nanocrystals, paste for screen-printing and nanostructured TiO_2 film were reported in a previous paper.[S5] A cycloidal TiO_2 electrode (~0.28 cm^2) was stained by immersing it into a dye solution of 150 µM C218 in a mixed solvent of acetonitrile and *tert*-butanol at a volume ratio of 1/1 for 5 h. After rinsing with chlorobenzene and drying by air flow, the dye-coated titania electrode was assembled with the positive CCB electrode possessing an electrolyte-perfusion hole, which was beforehand produced with a sand-blasting drill. The two electrodes were separated by a 30-µm-thick Bynel (DuPont) hot-melt gasket. The internal space was perfused with a liquid electrolyte with a vacuum back filling system. Ultimately, the hole on the positive electrode was closed hermetically with a Bynel sheet and a thin glass cover by heating. Photovoltaic characterizations were described in our previous publication.[S6]

4. Voltammetric measurements

Square-wave voltammograms of ferrocene were measured on a CHI660C electrochemical workstation. A reference electrode was constructed by dipping a platinum wire into a DSC (copper or iodine) electrolyte-filling glass tube, the bottom end of which was sealed with a ceramic porous frit. A 5-µm-radius platinum ultramicroelectrode was used as working electrode and a platinum wire as counter electrode.

5. Impedance measurements

Electrical impedance experiments were carried out in the dark on an IM6ex electrochemical workstation, with a frequency range from 50 mHz to 100 KHz and a potential modulation of 20 mV. The obtained impedance spectra were fitted with the Z-view software (v2.80, Scribner Associates Inc.) in terms of an appropriate equivalent circuit.

6. Transient absorption/emission measurements

Transient absorption measurements were performed on a LP920 laser flash spectrometer in conjunction with a nanosecond tunable OPOLett 355II laser. Transient absorption spectrum was measured with an Andor iStar ICCD camera. The absorption kinetic traces were detected by a fast PMT and recorded with a TDS 3012C digital oscillograph. Excitation fluences were carefully controlled to guarantee that $\sim 7.2\times10^{13}$ photons cm^{-2} were absorbed by a dye-coated titania film during every laser pulse. The pump wavelength was selected according to a 0.2 optical density of dye-coated titania films, so as to achieve a comparable exciton distribution profile in the titania film permeated with different electrolytes. Time-correlated single photon counting (TCSPC) measurements were carried out on a LifeSpec-II spectrometer equipped with an EPL635 pulsed laser diode and a Hamamatsu H5773-04 PMT.

References

S1 J. R. Hall, N. K. Marchant and R. A. Plowman, *Aust. J. Chem.*, 1963, **16**, 34.

S2 B. R. James and R. J. P. Williams, *J. Am. Chem. Soc.*, 1961*,* **83***,* 2007.

S3 P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasumdaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168.

S4 R. Li, J. Liu, N. Cai, M. Zhang and P. Wang, *J. Phys. Chem. B*, 2010, **114**, 4461.

S5 P. Wang, S. M. Zakeeruddin, P. Comte, R. Charvet, R. Humphry-Baker and M. Grätzel, *J. Phys. Chem. B*, 2003, **107**, 14336.

S6 J. Liu, R. Li, X. Si, D. Zhou, Y. Shi, Y. Wang, X. Jing and P. Wang, *Energy Environ. Sci*., 2010, **3**, 1924.

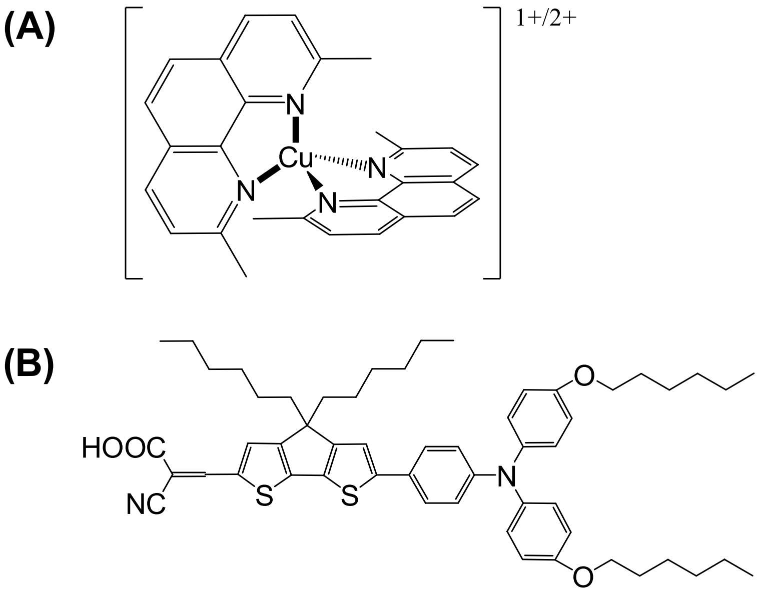

Fig. S1 Molecular structures of (**A**) the copper redox shuttle and (**B**) the C218 dye.

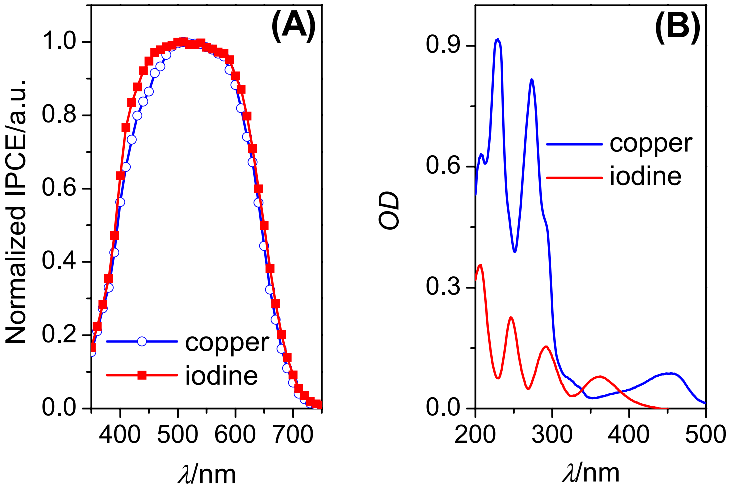

Fig. S2 (**A**) Normalized photocurrent action spectra and (**B**) electronic absorption spectra of the 1600-fold diluted copper and iodine electrolytes with acetonitrile. Optical path: 1.0 mm.

Table S1. Detailed cell parameters measured at various incident light intensities[a]

electrolyte	P_{in} /mW cm^{-2}	J_{sc} /mA cm^{-2}	V_{oc} /mV	FF	η /%
copper	12.48	1.52	839	0.76	7.7
	23.27	2.80	867	0.75	7.8
	50.09	5.90	901	0.71	7.6
	100	11.29	932	0.66	7.0
iodine	12.48	1.74	646	0.75	6.8
	23.27	3.21	669	0.74	6.8
	50.09	6.91	694	0.71	6.8
	100	13.74	714	0.66	6.5

[a] The spectral mismatch between our light resource and the AM1.5G solar emission spectrum (ASTM G173-03) is ~5%. Lights at various intensities are obtained by attenuating the AM1.5G full sunlight with a set of neutral meshes. Incident power intensity: P_{in}; Short-circuit photocurrent density: J_{sc}; Open-circuit photovoltage: V_{oc}; Fill factor: FF; Total power conversion efficiency: η.

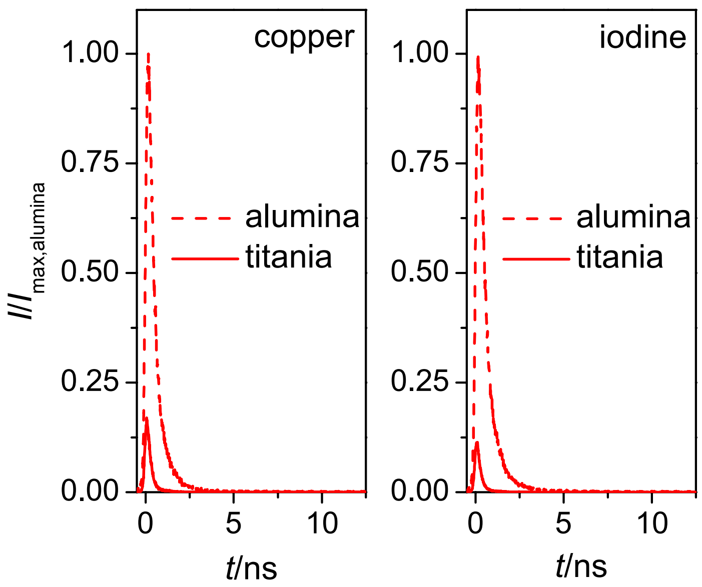

Fig. S3 Time-correlated emission traces of C218-grafted alumina (dashed line) and titania (solid line) films permeated with the copper and iodine electrolytes. Excitation wavelength: 639 nm. The emission intensity (I) was corrected in terms of the film absorbance at 639 nm and further normalized with respect to the emission maximum ($I_{\text{max,alumina}}$) of an alumina sample.

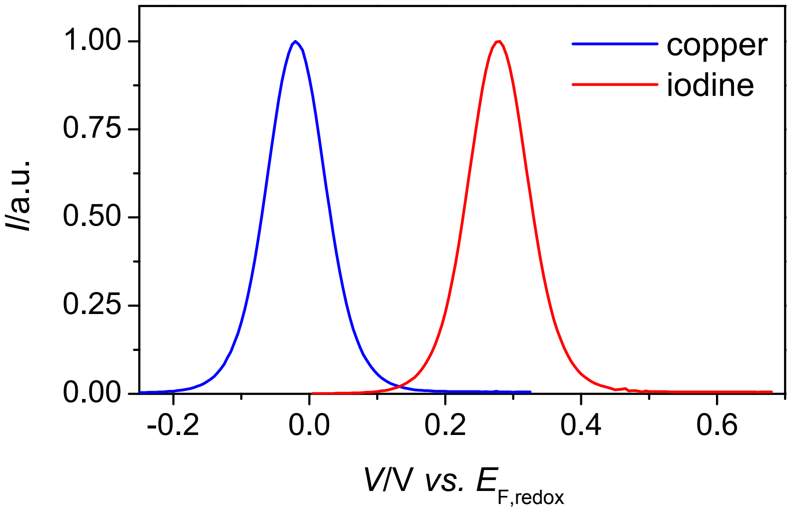

Fig. S4 Square-wave voltammograms of ferrocene in acetonitrile measured with the home-made copper and iodine reference electrodes.