Supplementary Information

Polyoxometalate supported complexes as effective electron-transfer mediators in dye-sensitized solar cells

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Experimental Section

Materials

N719, photoanodes, Pt electrodes and hot-melt film (Surlyn) were purchased from Heptachroma (Dalian, China). 3-Methoxypropionitrile, dimethyl formamide (DMF), 4-tert-butylpyridine (TBP), lithium perchlorate and other chemicals were purchased from Aladdin. {$[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2]$ $[Al(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]$ (denoted as POM1-Cu-phen), $[Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)_2\}_2]$ $[Cr(OH)_6Mo_6O_{18}\{Cu(phen)(H_2O)Cl\}_2]$ (denoted as POM2-Cu-phen)} and $[Cu(phen)_2(H_2O)](NO_3)_2$ (denoted as Cu-phen) were prepared by previously published procedures.[1] The valence of Cu in the as prepared POM1/POM2-Cu-phen is II. We obtained the Cu (I) species by reducing the as prepared POM1/POM2-Cu-phen using KSCN as reducer. All the aqueous solutions were prepared with double distilled water. All the chemicals were used as received, without further purification.

Apparatus

Electrochemical experiments were performed on CHI601D electrochemistry station (CH Instruments, Shanghai Chenhua Instrument Corporation, China). The performance

of the DSSCs were measured under 1 sun illumination (AM=1.5). The type of lamp that we used is CHF-XM35-500W.

Preparation of electrolytes based POM1/POM2-Cu-phen redox couples

The electrolyte solutions were prepared by dissolving a certain amount of POM1/POM2-Cu(I)-phen species (10 mg/mL) and POM1/POM2-Cu(II)-phen species (2 mg/mL) in 3-methoxyacetionitrile: DMF (v: v=1: 1) mix solvent. An optimized electrolyte contains 0.3M $LiClO_4$ and 0.5M 4-tert-butylpyridine.

Figure S1 shows the FTIR spectrum of the as prepared solid material POM1/ POM2-Cu(I)-phen and POM1/POM2-Cu(II)-phen. In terms of POM1-Cu(II)-phen, the absorption peaks at 942cm^{-1}， 851 cm^{-1}, 657 cm^{-1}， 580 cm^{-1}， 444 cm^{-1} are ascribed to POM1, [2, 3] these characteristic peaks also appear in the similar position of the spectrum of Cu(I) species. As for POM2-Cu(II)-phen, the absorption peaks at 937cm^{-1}， 848 cm^{-1}, 647 cm^{-1}， 572cm^{-1}， 440 cm^{-1} are ascribed to POM2, there are also appearing characteristic peaks in the similar position of the spectrum of Cu(I) species. The FTIR spectrum indicates that heteropolyanions are still existing in Cu(I) species. The strong absorption peaks at 2100-2300cm^{-1} are ascribed to C≡N in trace amount of reductant. Moreover, TG from 50 ^{o}C up to 600 ^{o}C was performed under nitrogen at the heating rate of 5 °C·min^{-1}. As showed in Fig. S2, no distinct weight loss is observed even heated to 150 ^{o}C, suggesting that the chosen POM has good thermal stability, enough to satisfy the temperature requirement of DSSCs (20-60 ^{o}C).[4,5]

The electrolyte solutions for cyclic voltammetry measurement were prepared by dissolving a certain amount of POM1/POM2-Cu(II)-phen or Cu(II)-phen species (2

mg/mL) in 3-methoxyacetionitrile: DMF (v: v=1: 1) mix solvent which also contained 0.3 M $LiClO_4$ and 0.5 M 4-tert-butylpyridine. Cyclic voltammograms of POM1/POM2-Cu-phen and Cu-phen were carried out by three-electrode method. The working electrode was glassy carbon electrode, the counter electrode was platinum wire electrode and the reference electrode was non-aqueous Ag/ Ag^+ reference electrode.

Fabrication of DSSCs

To fabricate DSSCs, TiO_2 electrode was immersed in N719 dye solution with a concentration of 5×10^{-4} mol/L in dry ethanol for 20 h. The active area of TiO_2 photoanode is 0.16 cm^2 and its thickness is 10-12 μm. The cell was assembled with photoanode and counter electrode separated by electrolyte and sealed with a 25 μm thick hot-melt film (Surlyn) by heating the system at 120 °C. Along with irradiating the DSSCs with the electrolyte under full sun light, the Cu(II) species generate and the proper proportion of the Cu(I) species and Cu(II) species are self generated after 40min of irradiating,[6] the photo-current reach a constant this moment and the fabrication of DSSCs is accomplishment. All the electrochemistry experiments were carried out at laboratory temperature 25 ^oC.

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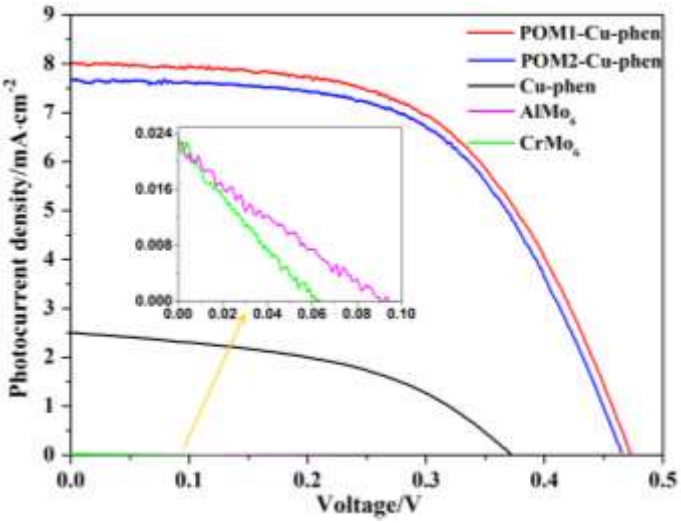

Fig. S1 Photocurrent density-Voltage curves of DSSCs with POM1-Cu-phen, POM2-Cu-phen, Cu-phen redox couples and $AlMo_6$-only, $CrMo_6$-only based electrolytes. The insert shows the amplification of axis.

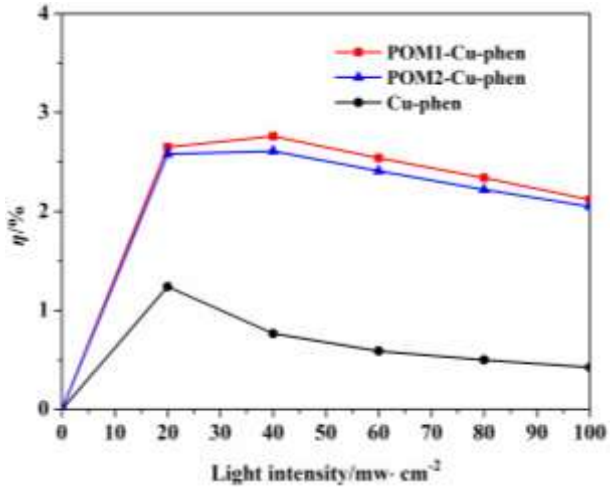

Fig. S2 Relationship between light intensity and energy conversion efficiencies of DSSCs containing POM1-Cu-phen, POM2-Cu-phen and Cu-phen as the redox couples.

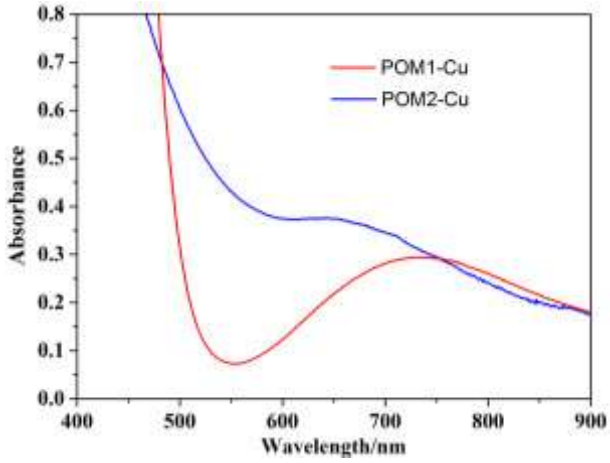

Fig. S3 UV-Visible spectrum of POM1-Cu-phen and POM2-Cu-phen.

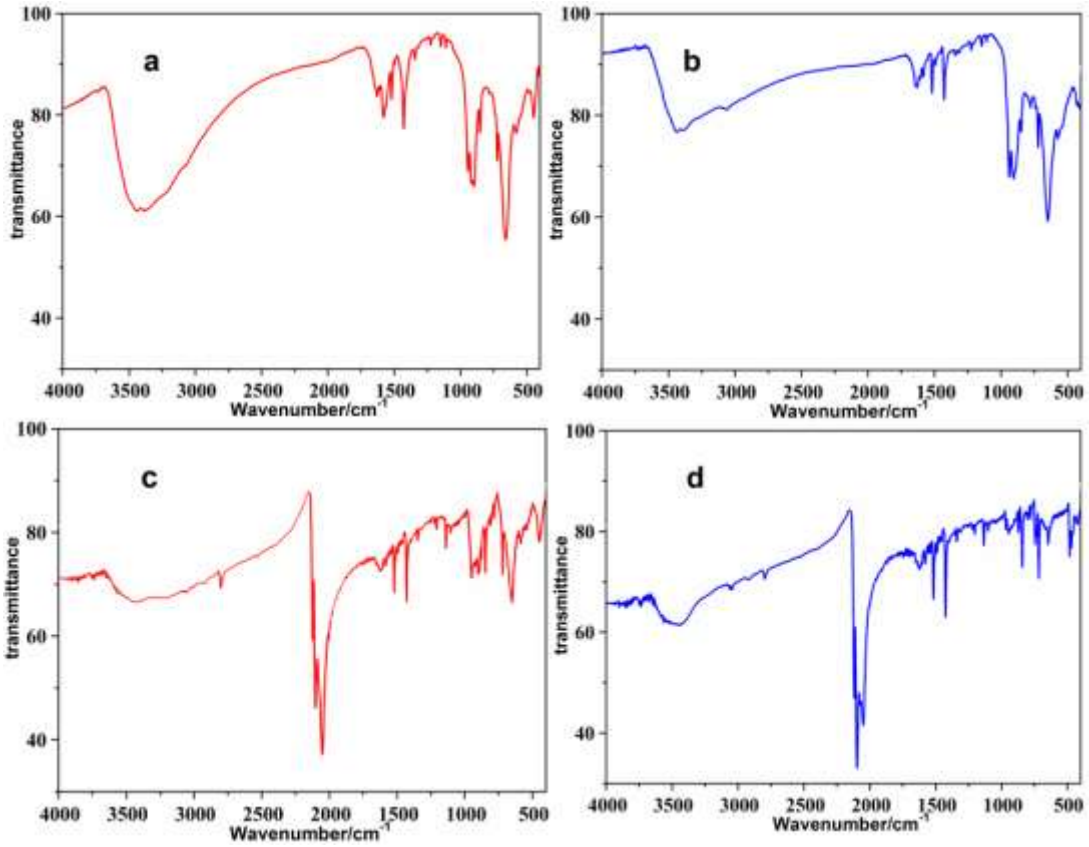

Fig. S4 FTIR spectrum of (a) POM1-Cu(II)-phen, (b) POM1-Cu(II)-phen, (c) POM2-Cu(I)-phen, (d) POM2-Cu(I)-phen.

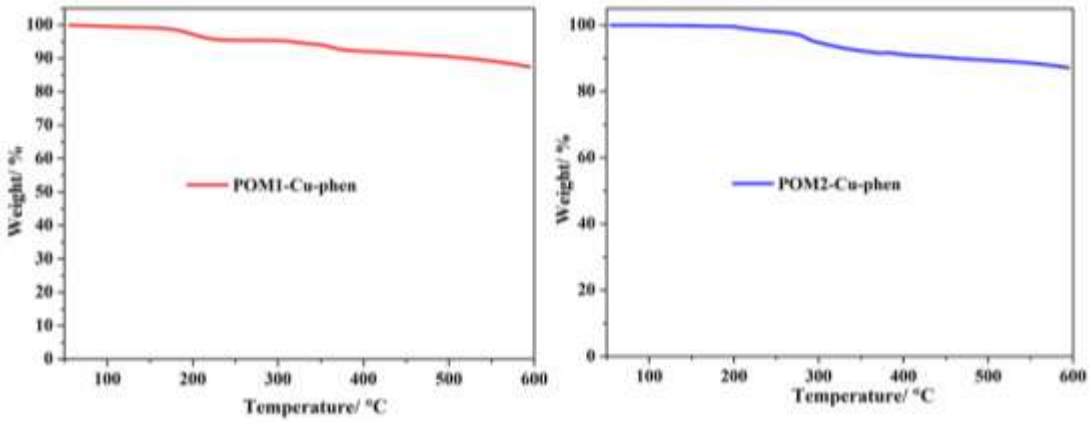

Fig. S5 The TG curve of POM1/POM2-Cu-phen.