Polyoxometalates in dye-sensitized solar cells

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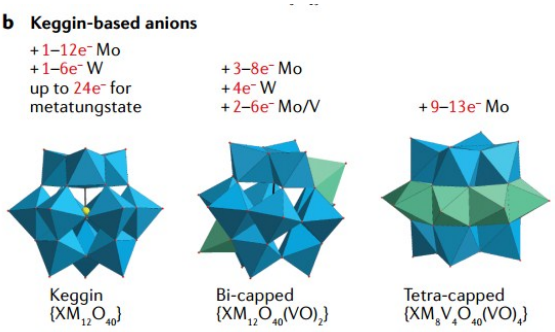

Fig. S1 The number of blue electrons for Keggin-type anions include the classical Keggin anion $\{XM_{12}O_{40}\}$ (X=heteroatom, which is absent from metatungstate; M=Mo, W), as well as bi-capped and tetra-capped pseudo-Keggin anions. Reproduced with permission from ref. S1. Copyright (2018) Macmillan Publishers Limited, part of Springer Nature.

The energy levels measurement approaches of POMs:

The electrochemistry and solid diffuse reflection method

Firstly, the redox potentials of POMs are evaluated by cyclic voltammetry (CV), which was carried out by a three-electrode system comprising a glassy carbon working electrode, a platinum wire CE, and Ag/AgCl reference electrode in the POMs solution with the fixed pH values.[S2] In Fig. S2a, we give the CV of $K_6H_4[\alpha\text{-}SiW_9O_{37}Co_3(H_2O)_3]\cdot 17H_2O$ (SiW_9Co_3) in LiAc/ HAc buffer solution at pH=6.0.[S2] The onset reduction potential was determined as the intersection of the x axis and dashed line, which was determined by finding out the intersection point between two tangents from

the linear portion of the first reduction peak and baseline. Secondly, the solid diffuse reflectance spectroscopy is used to calculate the optical band gap (E_g) of POMs. In Fig. S2b, the optical band gap (E_g) of SiW_9Co_3 could be estimated by its diffuse reflection spectrum.[S2] The plot of Kubelka-Munk function F versus energy E_g is used to evaluate E_g. The vertical coordinates F represents $(1-R)^2/2R$ and R is the reflectance of an fixed thickness layer at a specified wavelength. The horizontal axis represents E_g calculated by the formula $E_g = 1240/\lambda$, which can be decided by the intersection point coming from the energy axis and the line deduced from the linear portion of the absorption edge in the plot of Kubelka-Munk function F. Finally, the HOMO energy levels of POMs can been calculated out by formula E_g= LUMO-HOMO.

The ultraviolet photoelectron spectroscopy and solid diffuse reflection method

The ultraviolet photoelectron spectroscopy (UPS) performed using the **He I** (21.22 eV) excitation line is measured to obtain the HOMO and work function of POMs. A negative bias is applied to the samples during UPS measurements in order to assess the absolute work function value from the secondary electron cutoff of the photoemission spectra. The UPS photoemission spectra of 10 nm films consisting of $H_4SiW_{12}O_{40}$ (SiW_{12}) and $H_5PV_2W_{10}O_{40}$ (PV_2W_{10}) deposited on Al substrates is given in Fig. S3.[S3] The work function (WF) of each sample can be directly obtained by the secondary electron cutoff of the photoemission spectra. Then the ionization energy of each POM was estimated by adding the binding energy of the onset of the band of occupied orbitals, which gives the position of the HOMO with respect to the vacuum level. In the same way, through the previous methods the E_g of POMs has been evaluated. Combined with UPS and solid diffuse reflectance spectrum, the LUMO energy levels of POMs can been calculated out by formula E_g= LUMO-HOMO.[S3]

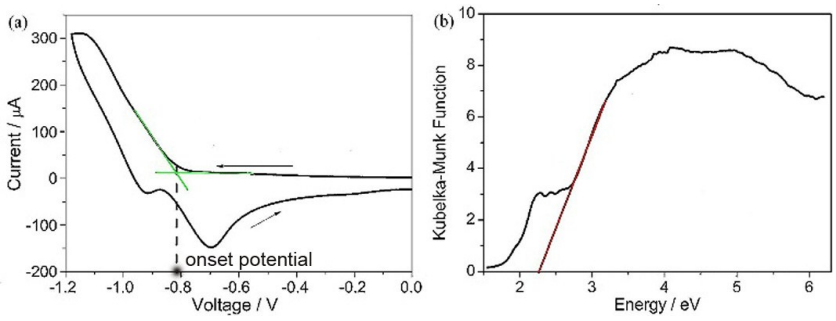

Fig. S2 (a) Cyclic voltammograms of SiW_9Co_3 in LiAc/ HAc buffer solution at pH=6.0; (b) the plot of F against energy Eg for SiW_9Co_3 and the inset are the schematic energy levels of TiO_2 and SiW_9Co_3. Reproduced with permission from ref. S2. Copyright (2015) American Chemical Society.

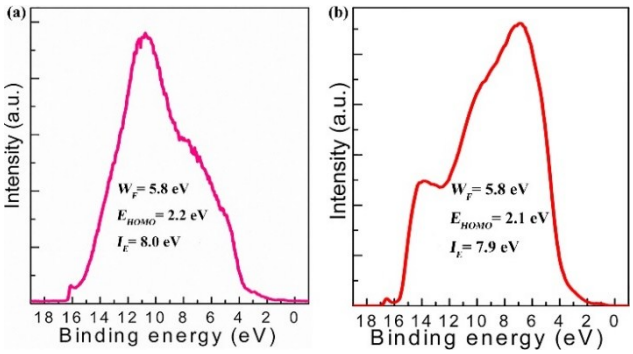

Fig. S3 UPS photoemission spectra of 10 nm films consisting of SiW_{12} (a) and PV_2W_{10} (b). Reproduced with permission from ref. S3. Copyright (2015) American Chemical Society.

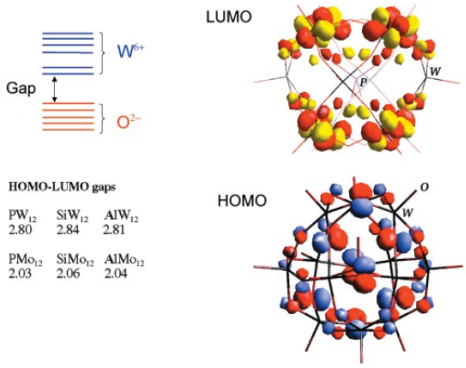

Fig. S4 Schematic orbital diagram, HOMO-LUMO energy gaps (in eV) and 3D representations of one of the two doubly degenerate components of the LUMO and HOMO, the fully oxidized $[PW_{12}O_{40}]^{3-}$ anion. Reproduced with permission from ref. S4. Copyright (2001) American Chemical Society.

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