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Electronic Supplementary Information for:

Sensitized Photocurrent Production from Thin Films of Ru (II) Metallopolymer/Dawson Polyoxotungstate Adducts Under Visible Irradiation

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1. Experimental

Materials

Acetonitrile and benzyl alcohol (spectroscopic grade, Sigma-Aldrich) were dried over molecular sieves (3 Å) prior to use. Tetrabutylammonium tetrafluoroborate (Fluka) was used as purchased. $[Ru(bpy)_2(PVP)_{10}](NO_3)_2$ (where bpy is 2,2'-bipyridyl and PVP is poly(4-vinylpyridine)) and $K_6\alpha$-$[P_2W_{18}O_{62}]$ were synthesized as described previously, and their structures are shown in Fig S1 and Fig S2 respectively.[S1, S2] Indium tin oxide (ITO) electrodes were purchased from Delta Technologies Ltd. (Stillwater, MN, USA) and were sonicated in ethanol prior to use.

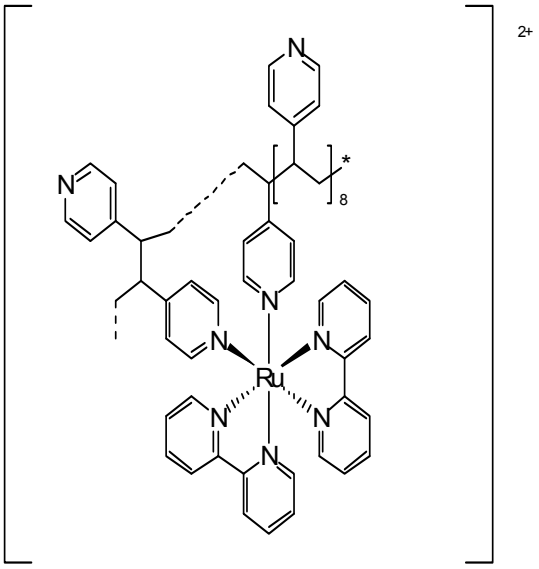

Fig S1: Structure of the $[Ru(bpy)_2(PVP)_{10}]^{2+}$ metallopolymer employed in this study.

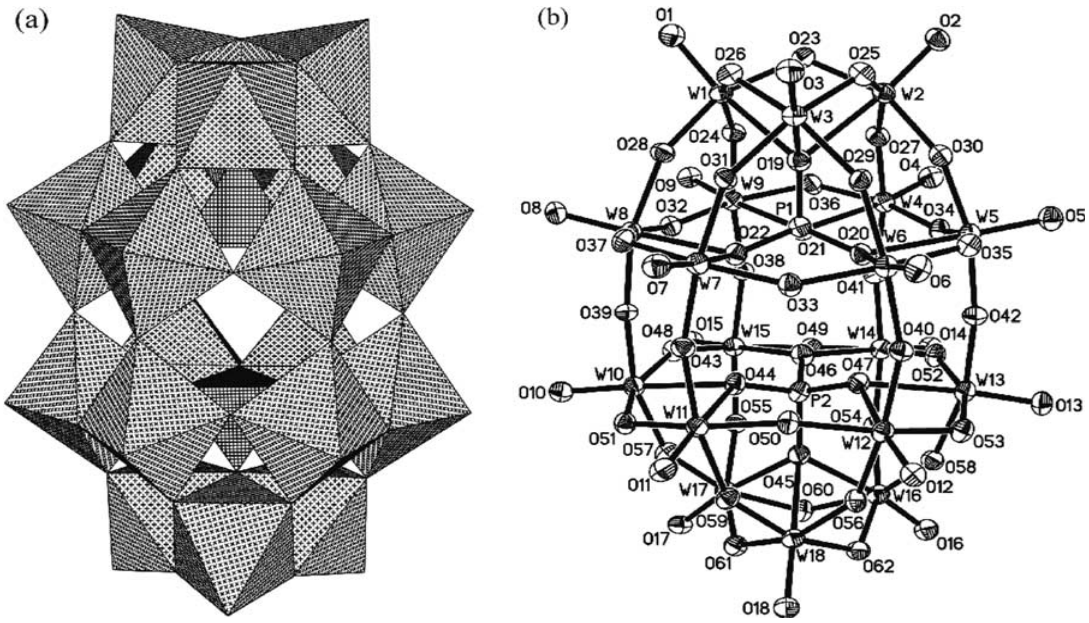

Fig S2 (a): Polyhedral representation of α-$[P_2W_{18}O_{62}]^{6-}$ where each octahedron represents a WO_6 unit and (b) ORTEP diagram of α-$[P_2W_{18}O_{62}]^{6-}$ with thermal ellipsoids at 50% probability.

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Preparation of composite thin films

Thin films of adducts of $[Ru(bpy)_2(PVP)_{10}]^{2+}$ and α-$[P_2W_{18}O_{62}]^{6-}$ were prepared using the layer-by-layer alternate solution (LBL) method.

Instrumentation and procedures

Cyclic voltammetry was performed in a conventional three electrode cell with a CH Instruments Model 660a electrochemical workstation. Measurements were performed at 25±2 °C and all solutions were deoxygenated with N_2 before measurement. A silver wire was employed as the pseudo-reference, which was calibrated versus the IUPAC recommended ferrocene (Fc/Fc^+) internal reference. The surface coverages were determined by graphical integration of background corrected cyclic voltammograms recorded at a series of slow scan rates, typically less than 10 $mV.s^{-1}$. The films were exhaustively electrolyzed at these slow scan rates as demonstrated by the independence of the measured charge with scan rate. The surface coverages were calculated as an average from three separate electrodes which were prepared in parallel. The photoelectrochemical studies of the $[Ru(bpy)_2(PVP)_{10}]_{4.5}[S_2Mo_{18}O_{62}]$ films were conducted by applying a constant voltage to the modified working electrode which resulted in re-oxidation of the photoreduced polyoxomolybdate centers. The substrate for photocatalytic oxidation was pure benzyl alcohol containing 0.1 M Bu_4NBF_4 as supporting electrolyte. The light source for photochemistry was an Oriel 68811 arc lamp employing a 350 W Xe bulb and a 480 ± 5 nm narrow band filter focused onto the film (1 cm^2), which was kept at a distance of 10 cm from the sample solution. The optical filter was purchased from Spectrogon UK Ltd.

Resonance Raman spectra were collected on a Horiba Jobin Yvon HR800 UV spectrometer. The laser lines were generated by a Coherent Innova 70c tunable Ar-ion laser (457.9, 488, 514.5 nm). A 10x microscope objective was used to focus the laser beam onto a composite thin film self-assembled on an ITO electrode. A 600 lines/mm diffraction grating was employed. The x-axis was calibrated versus the Rayleigh line (0 nm) and the phonon mode from silicon wafer (520 cm^{-1}).

2. Resonance Raman spectroscopy

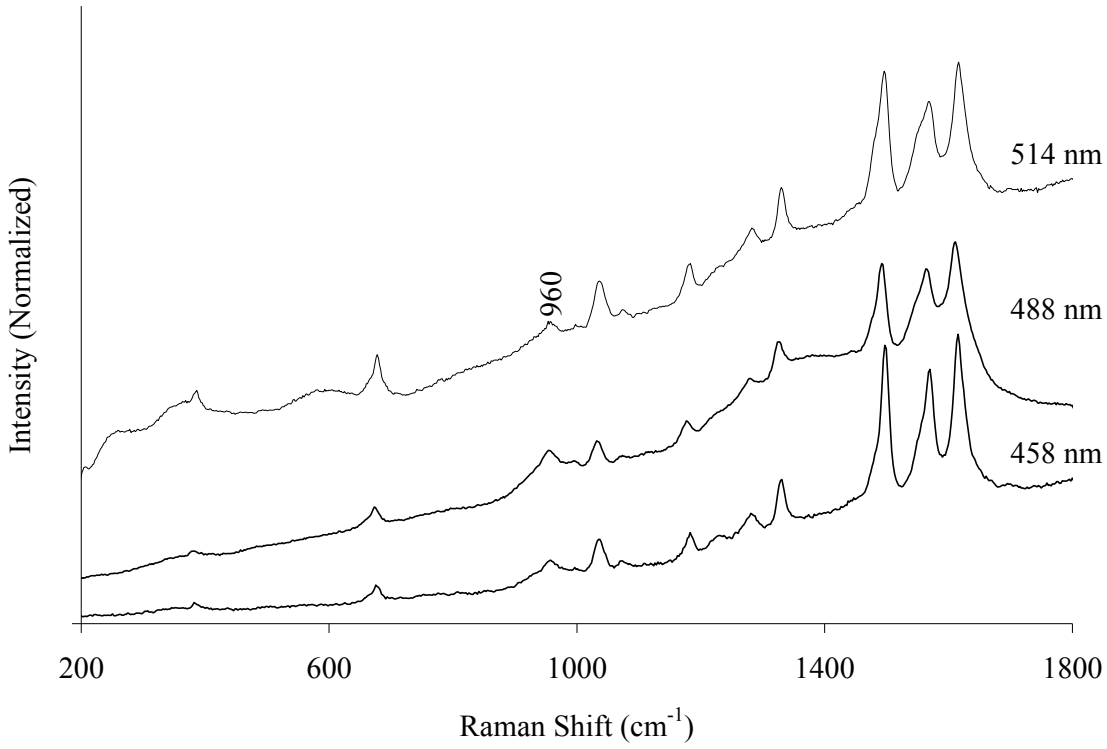

Fig S3: Wavelength-dependant resonance Raman spectra of a thin film of $[Ru(bpy)_2(PVP)_{10}]_{4.5}\alpha$-$[P_2W_{18}O_{62}]$ self-assembled on an ITO electrode.

3. Electrochemistry

Film	Γ (mol.cm^{-2})
$[Ru(bpy)_2(PVP)_{10}]^{2+}$	$(9.83 \pm 3.38) \times 10^{-10}$
α-$[P_2W_{18}O_{62}]^{6-}$	$(1.66 \pm 0.77) \times 10^{-12}$
$[Ru(bpy)_2(PVP)_{10}]_{4.5}[P_2W_{18}O_{62}]$ Ru	$(6.11 \pm 0.32) \times 10^{-10}$
$[Ru(bpy)_2(PVP)_{10}]_{4.5}[P_2W_{18}O_{62}]$ POW	$(1.44 \pm 0.39) \times 10^{-10}$

Table S1: Surface coverage calculated from cyclic voltammetric data (10 mV.s^{-1}) of self-assembled thin films of $[Ru(bpy)_2(PVP)_{10}]^{2+}$, α-$[P_2W_{18}O_{62}]^{6-}$ and $[Ru(bpy)_2(PVP)_{10}]_{4.5}[P_2W_{18}O_{62}]$ on ITO electrodes. Errors calculated from measurements performed on three separate samples of each film.

References:

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[S2] I-M. Mbomekalle, Y. Wei Lu, B. Keita and L. Nadjo, *Inorg. Chem. Commun.*, 2004, **7**, 86 - 90.