Electronic Supplementary Information

For

Oxidative photoreactivity of mono-transition-metal functionalized lacunary Keggin anions

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1. Instrumentation

UV-Vis spectroscopy: UV-Vis spectroscopy was performed on a Shimadzu UV-2450 spectrophotometer, Varian Cary 50 spectrophotometer or Varian Cary 5G spectrophotometer. All systems were used with standard cuvettes (d = 10.0 mm).

FT-IR spectroscopy: FT-IR spectroscopy was performed on a Shimadzu IRPrestige-21 FTIR spectrophotometer including a Golden Gate ATR unit. Signals are given as wavenumbers in cm^{-1} using the following abbreviations: vs = very strong, s = strong, m = medium, w = weak and b = broad.

Cyclic Voltammetry (CV): CV was performed using an Ivium CompactStat potentiometer using glassy carbon working electrode and platinum wire as counter electrode and pseudo-reference electrode. Ferrocene was used as internal reference. Dry solvent were used with nBu_4NPF_6 as the electrolyte.

Elemental analysis: Elemental analysis was performed on a Euro Vector Euro EA 3000 Elemental Analyzer.

General remarks: All chemicals were purchased from Sigma Aldrich, ABCR or ACROS and were of reagent grade. The chemicals were used without further purification unless stated otherwise. Monolacunary tungstate - based Keggin clusters (α-$[M(H_2O)SiW_{11}O_{39}]^{n-}$ (M = Co^{2+}, Cu^{2+}, Ni^{2+}, Mn^{2+}) were prepared according to a modified literature procedure based on C. M. Tourné, G. F. Tourné, S. A. Malik and T. J. R. Weakley, *J. Inorg. Nucl. Chem.*, 1970, **32**, 3875–3890.

2. Synthetic section

Synthesis of $(n\mathbf{Bu_4N})_6[\alpha\text{-}M(H_2O)SiW_{11}O_{39}]$: 1.0 g (0.31 mmol) $K_8[\alpha\text{-}SiW_{11}O_{39}] \cdot 13H_20$ (1.00 eq.) was dissolved in water and 1.05 molar equivalents the respective transition metal nitrate salt was

added. The mixture was stirred and heated to 55 °C for 1.5 hours. After cooling to room-temperature, 1.09 g (3.38 mmol) of nBu$_4$NBr (1.09 eq.) were added to the reaction mixture. The pH was set to pH = 3 using aqueous HNO_3 (2M). After 20 min. the precipitate was filtered off, washed with water and dried in a desiccator. Compound purity was verified using UV-Vis-spectroscopy, FT-IR-spectroscopy, CHN elemental analysis and ICP-OES.

Photocatalytic measurements: The standard basic blue 41 photooxidation was carried out as follows: a N,N-dimethyl formamide (DMF) solution of the respective cluster (4.0 µM) and basic blue 41 (20.0 µM) was prepared. The homogeneous solution was irradiated with a custom-built LED irradiation setup (standard light source: λ = 390 nm, $P_{nominal}$ = 3 W). BB41 photooxidation was detected spectrometrically by following the decrease of the characteristic absorption signal at λ_{max} = 625 nm. De-aerated experiments were performed by flushing the sample with Ar for 10 min prior to the experiment in a glove box. Hydroxyl radical scavenging experiments were performed by adding ethanol (200 µM) to the solution.

Cyclic Voltammetry: $E_{1/2}$ from cyclic voltammetry of {MW_{11}} in DMF vs. Fc/Fc$^+$, containing 0.1 M (nBu_4N)PF_6. Scan rate = 1000 mV/S. Unless stated otherwise, redox-processes were quasi-reversible.

{MW_{11}}	**$E^{I}_{1/2}$ / V**	**$E^{II}_{1/2}$ / V**	**$E^{III}_{1/2}$ / V**	**$E^{IV}_{1/2}$ / V**
{CoW_{11}}	+0.11	-0.55	-1.43	
{CuW_{11}}	-0.74	-1.42	-1.69	
{MnW_{11}}	-1.39	-2.04		
{NiW_{11}}	-1.45	-2.46		