

Electronic Supplementary Information

Table 1. Spectroelectrochemical data obtained for electro-generated reduced $[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4+}$ species (5 mM in MeCN; 0.1 M Bu_4NClO_4 ; 0.2 M HClO_4 ; 20 °C). The appropriate potential was applied to obtain the (2e⁻, 2H⁺)-, (4e⁻, 4H⁺)-, and (6e⁻, 6H⁺)-reduced anions.^{7b,16,17}

Anion	Absorption Bands, λ , nm	Molar Absorptivity, ϵ , $\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$
$[\text{S}_2\text{Mo}_{18}\text{O}_{60}(\text{OH})_2]^{4+}$	1130	5100
	760	12900
	595	5900
$[\text{S}_2\text{Mo}_{18}\text{O}_{58}(\text{OH})_4]^{4+}$	1030	13700
	695	26700
$[\text{S}_2\text{Mo}_{18}\text{O}_{56}(\text{OH})_6]^{4+}$	995	36200
	795	41900
	670	20600

Figure 1 Photolysis of $[\text{Ru}(\text{bpy})_3]_2[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$ (5×10^{-5} M) in dry DMF at 420 nm.

