## **Supporting Information**



Scheme SI1. Schematic representation of circular conversion process of the Eu-POM solution, reduced Eu-POM solution (blue) and UV-irradiated Eu-POM solution under electrochemical stimulation (blue) and the addition of L ( $L = NO_2^-$ ,  $IO_3^-$  and  $BrO_3^-$ ) (red). The center is combined polyhedral/ball-and-stick representation of Eu-POM, W, blue polyhedra; Eu, black ball; O, red ball.



**Figure SI1**. CVs of 0.5 mM Eu-POM in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH 3) at scan rates of 20, 40, 60, 80, and 100 mV s<sup>-1</sup>. The inset shows the relationship of the scan rates vs. the oxidation peak currents of W (II) and reduction peak currents of W (III').



**Figure SI 2**. CVs of 0.5 mM Eu-POM in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH 3) buffer solution at 20 mV s<sup>-1</sup> in the presence of NO<sub>2</sub><sup>-</sup>. The inset shows the catalytic currents caused by the third cathodic wave of W vs. concentrations of NO<sub>2</sub><sup>-</sup> at various concentrations: 0, 0.2, 0.4, 0.6, 0.8, 1 mM.



**Figure SI 3**. CVs of 0.5 mM Eu-POM in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH 3) buffer solution at 20 mV s<sup>-1</sup> in the presence of IO<sub>3</sub><sup>-</sup>. The inset shows the catalytic currents caused by the second cathodic wave of W vs. concentrations of IO<sub>3</sub><sup>-</sup> at various concentrations: 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7 mM.



**Figure SI 4**. CVs of 0.5 mM Eu-POM in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> (pH 3) buffer solutions at 20 mV s<sup>-1</sup> in the presence of  $BrO_3^-$ . The inset shows the catalytic currents caused by the third cathodic wave of W vs. concentrations of  $BrO_3^-$  at various concentrations: 0, 1, 2, 3, 4, 5 mM.



**Figure SI5**. Fluorescent emission spectra representing the fluorescence recovery of the reduced Eu-POM (0.5 mM) in 0.5 M KAc + HAc solution (pH 4) with  $NO_2^-$  concentrations of 0, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5 mM. The inset shows the plot of the fluorescence intensities at 617 nm in the presence of different concentrations of  $NO_2^-$ .