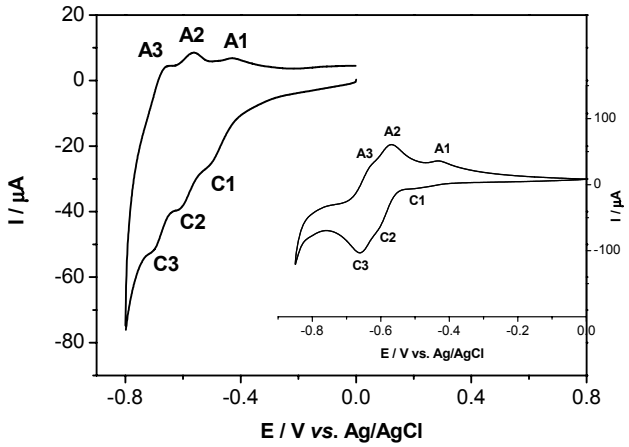

Fig. S1. CV of 2 mM EuGeW using a bare glassy carbon electrode (GCE) as a working electrode (inset) and CV of $(PEI/EuGeW)_3$ thin-film deposited on an ITO-coated glass slides in 0.5 M Na_2SO_4 + H_2SO_4 (pH 2.5) with scan rate of 30 mV s^{-1}.

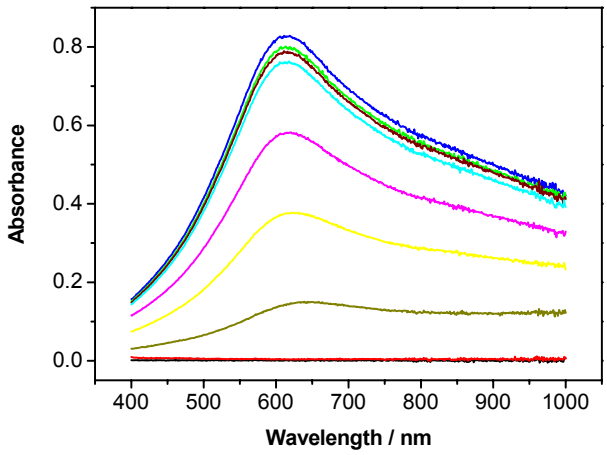

Fig. S2. Time-dependent evolution of the UV-Vis spectra of 0.1 mM EuGeW in 0.5 M Na_2SO_4 + H_2SO_4 (pH 2.5) upon electrochemical reduction at -0.9 V.

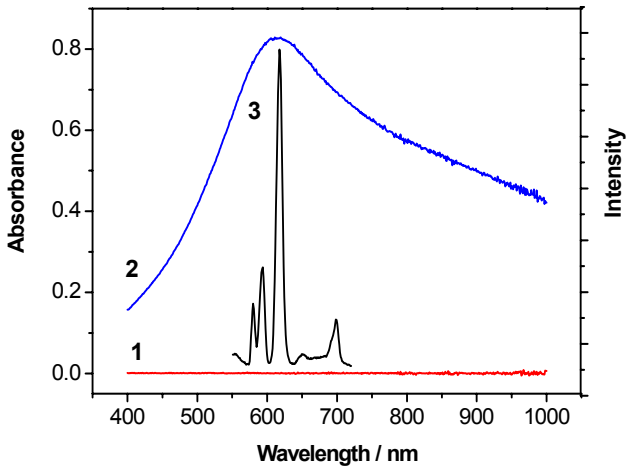

Fig. S3. UV-vis absorption spectra of 0.1 M EuGeW in 0.5 M Na_2SO_4 + H_2SO_4 (pH 2.5) under open circuit (curve 1) and electrochemical reduction at -0.9 V using ITO-coated glass slide as the working electrode as well as luminescence spectrum (λ_{exc} = 254 nm, curve 3).

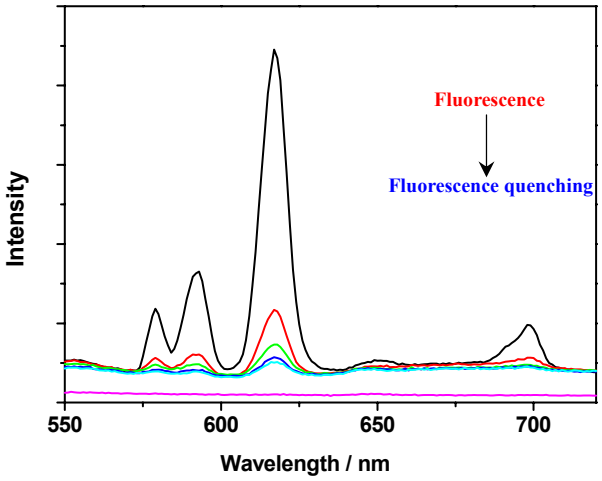

Fig. S4. Luminescent spectra of 0.1 M EuGeW with different electroreduction times at -0.9 V.

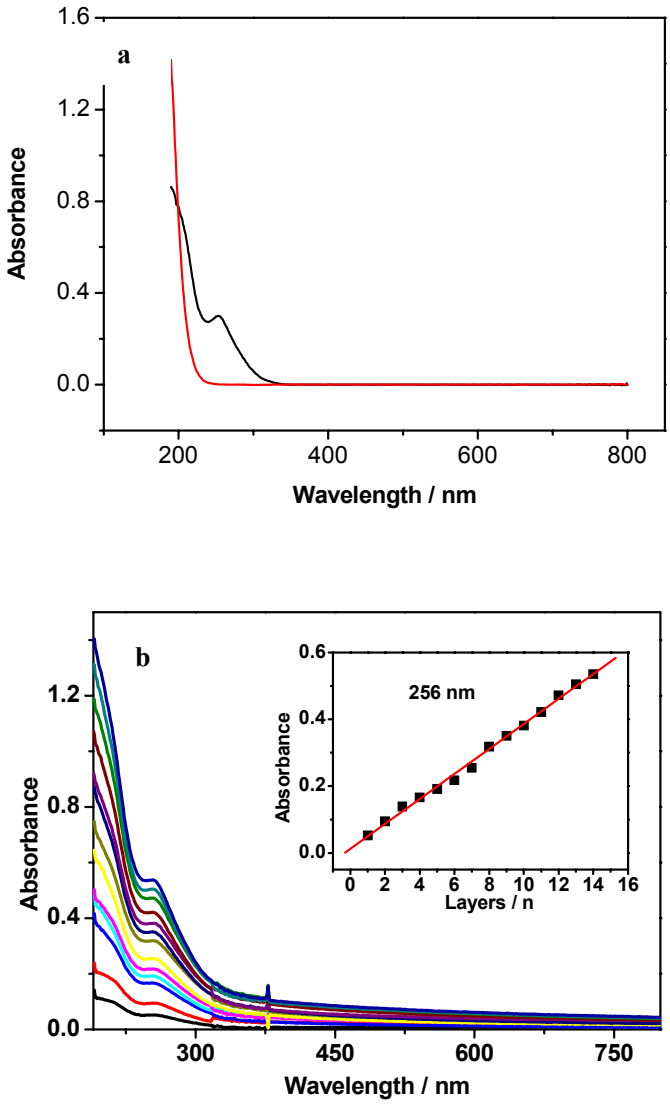

Fig. S5. (a) UV-vis absorption spectra of EuGeW (2.3×10^{-6} M, black curve) and PEI (1.2×10^{-5} M, red curve). (b) UV–vis absorption spectra of a $(PEI/EuGeW)_n$ thin-film fabricated on quartz as a function of the number of layers, n (= 1-14). The inset shows the absorption maxima at 256 nm as a function of n.

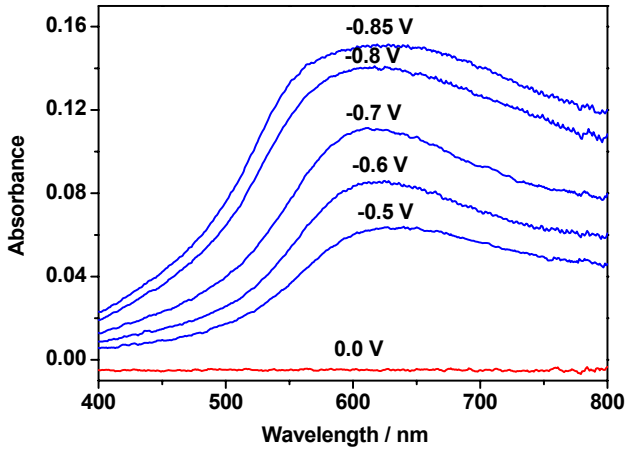

Fig. S6. UV-vis absorption spectra of a $\{PEI/P_2W_{18}\}_7\{PEI/EuGeW\}_{34}$ thin-film on an ITO-coated glass slide in 0.5 M Na_2SO_4 + H_2SO_4 (pH 2.5) under open circuit (red curve) and electrochemical reduction at the different applied potentials for 30s.

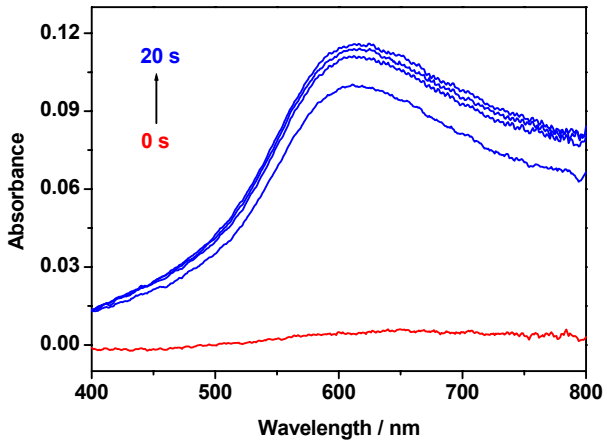

Fig. S7. UV-vis absorption spectra of a $\{PEI/P_2W_{18}\}_7\{PEI/EuGeW\}_{34}$ thin-film on an ITO-coated glass slide in 0.5 M Na_2SO_4 + H_2SO_4 (pH 2.5) as a function of electrochemical reduction time. Red curve: open circuit; blue curves: the applied potential of -0.7 V.

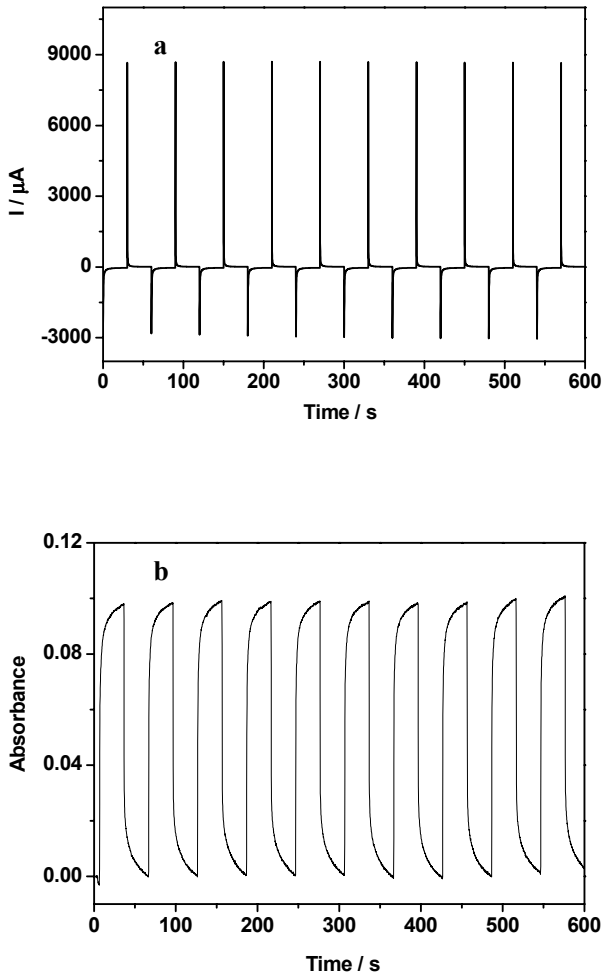

Fig. S8. Potential currents (a) and absorbances (b) at 627 nm of a $\{PEI/P_2W_{18}\}_7\{PEI/EuGeW\}_{34}$ thin-films on an ITO-coated glass slide during subsequent double-potential steps from -0.7 to 0.7 V in 0.5 M Na_2SO_4 + H_2SO_4 (pH 2.5) solution.