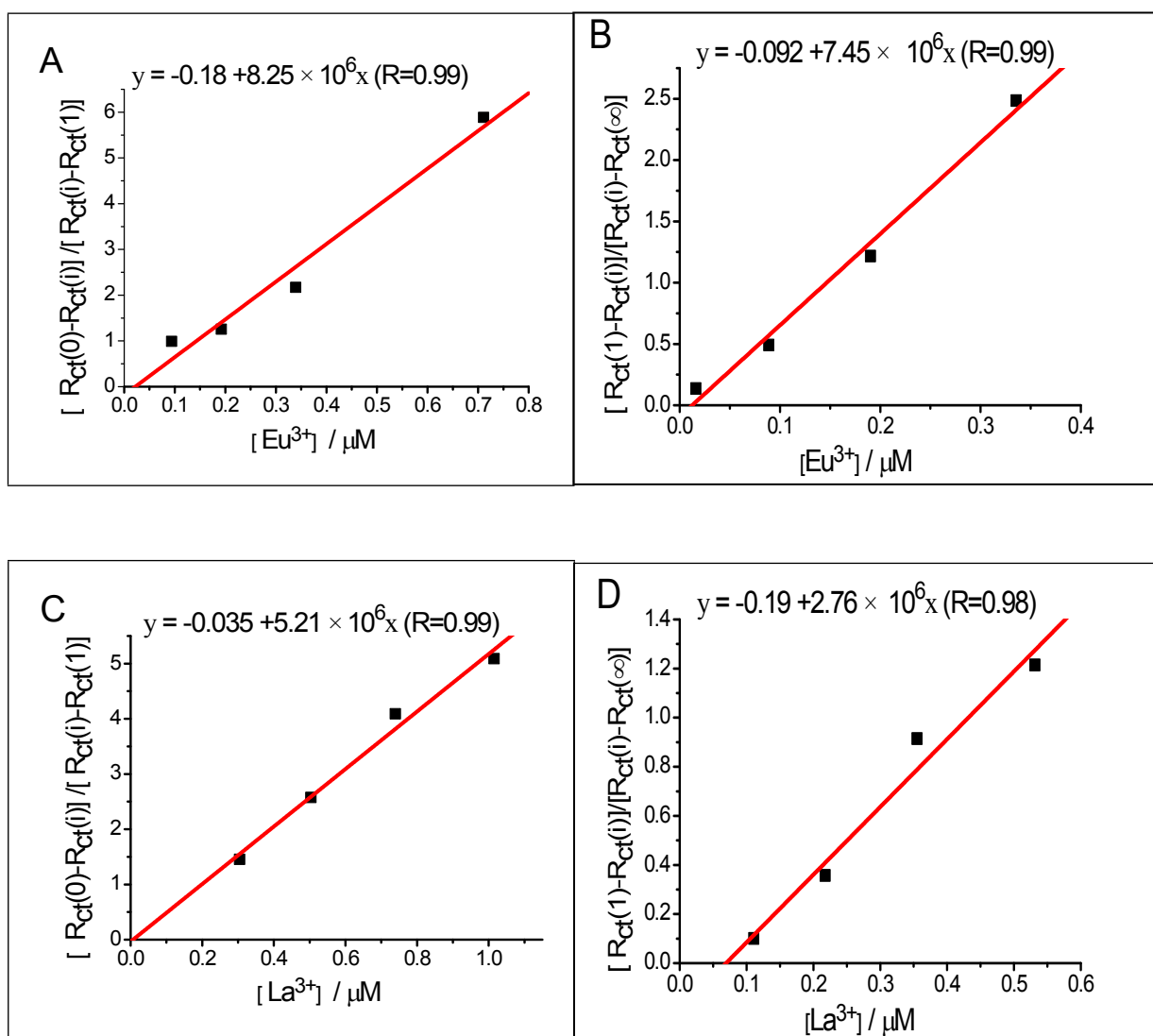
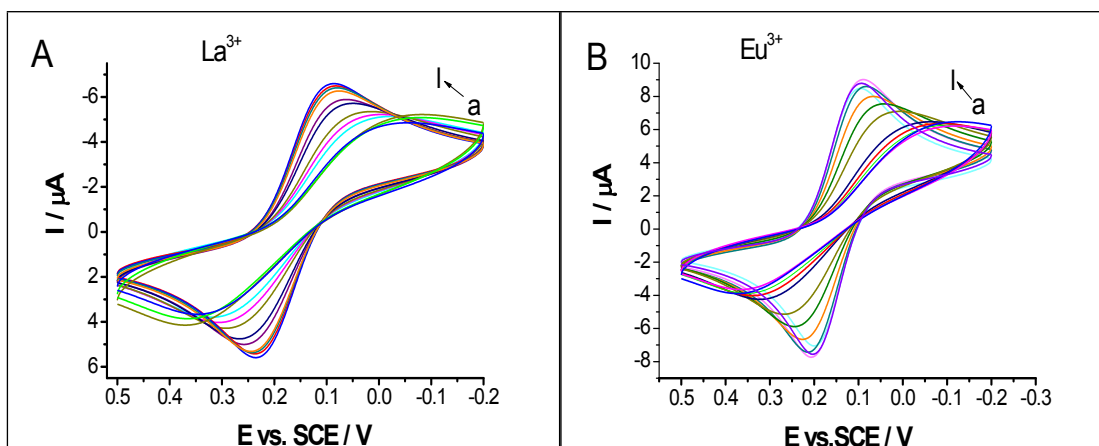


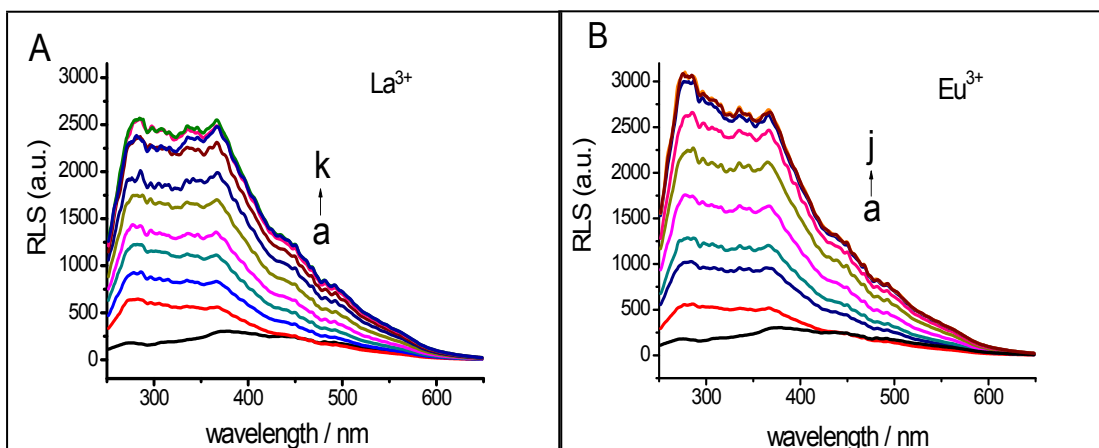
## Supplementary data



**Fig.S1** The linear relationship of  $[R_{ct}(0)-R_{ct}(i)]/[R_{ct}(i)-R_{ct}(1)]$  vs.  $[Eu^{3+}]$ (**A**) and  $[La^{3+}]$ (**C**). The linear relationship of  $[R_{ct}(1)-R_{ct}(i)]/[R_{ct}(i)-R_{ct}(\infty)]$  vs.  $[Eu^{3+}]$  (**B**) and  $[La^{3+}]$ (**D**).

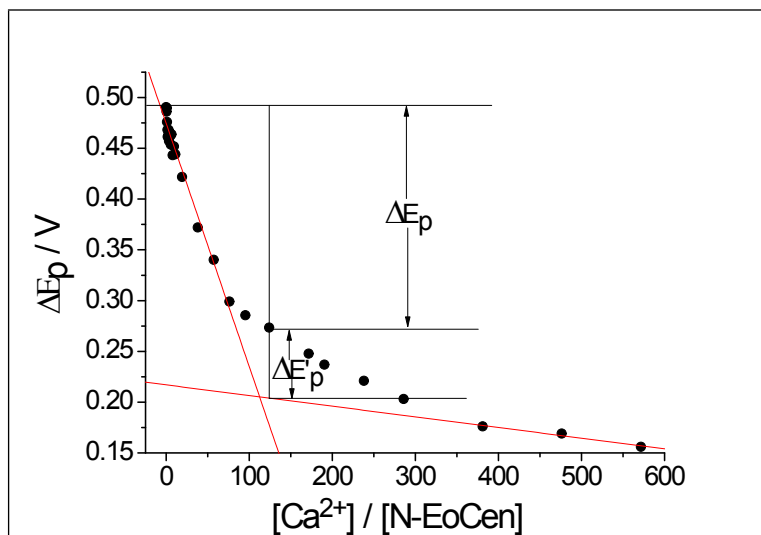


**Fig. S2** Cyclic voltammograms of 1.0 mM  $\text{Fe}(\text{CN})_6^{3-}$  at a N-EoCen coated GC electrode in 0.01 M Hepes, 0.02 M KCl solutions (pH 7.4) containing different concentration of  $\text{La}^{3+}$ (**A**) (from a to l): 0, 1.75, 2.90, 4.58, 5.14, 5.69, 6.24, 6.78, 7.59, 8.38, 9.17, 9.96 $\mu\text{M}$ , and  $\text{Eu}^{3+}$ (**B**) (from a to l): 0, 1.53, 2.14, 3.04, 4.22, 4.81, 5.40, 5.97, 6.55, 7.40, 8.25, 9.91 $\mu\text{M}$ .



**Fig. S3:** **A:** Resonance light scattering spectra for the addition of  $\text{La}^{3+}$  to the solution of N-EoCen in 10 mM Hepes at pH 7.4, 0.02 M KCl at  $[\text{La}^{3+}]/[\text{N-EoCen}] = 0$ (a); 0.32(b); 0.63(c); 0.95(d); 1.26(e); 1.58(f); 1.89 (g); 2.05 (h); 2.37 (i); 2.68 (j); 2.88 (k). **B:** Resonance light scattering spectra for the addition of  $\text{Eu}^{3+}$  to the solution of N-EoCen in 10 mM Hepes at pH 7.4, 0.02 M KCl at  $[\text{Eu}^{3+}]/[\text{N-EoCen}] = 0$ (a); 0.22(b); 0.66(c); 0.88(d); 1.32(e); 1.77(f); 1.98 (g); 2.43 (h); 2.87 (i); 3.09 (j).

### Calculation of average binding constant of $\text{Ca}^{2+}$ to N-EoCen



**Fig. S4** The peak separations ( $\Delta E_p$ ) of the redox reaction as a function of  $[\text{Ca}^{2+}]/[\text{N-EoCen}]$ .

Due to the weak binding ability of  $\text{Ca}^{2+}$  to N-EoCen, the equilibrium concentration of  $\text{Ca}^{2+}$  ( $[\text{Ca}^{2+}]$ ) can be approximate to the total concentrations of  $\text{Ca}^{2+}$  ( $[\text{Ca}^{2+}]_t$ ). So, the average binding constant of  $\text{Ca}^{2+}$  to N-EoCen can be obtained approximately by the following equation:

$$K = \frac{[\text{Ca}^{2+} \text{-N-EoCen}]}{[\text{Ca}^{2+}][\text{N-EoCen}]} \approx \frac{\Delta E_p}{[\text{Ca}^{2+}]_t \cdot \Delta E'_p}$$