This journal is © The Royal Society of Chemistry 2005

A pH-insensitive ratiometric chemosensor for citrate using europium luminescence



Department of Chemistry, University of Durham, UK



Fig. 1S. The absorption and luminescence spectrum of EuPheesterPT



Fig. 2S. The luminescence spectra of aqueous **EuPheesterPT** solution $(5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1})$ upon the titration of sodium citrate; excited at 384 nm.



Fig. 3S. The intensity ratio of 616 nm/579 nm of the aqueous **EuPheesterPT** solution $(5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1})$ upon the titration of sodium citrate; excited at 384 nm. The affinity constant is fitted by using equation:

$$[citrate] = \frac{\frac{(F - F_0)}{(F_1 - F_0)} + [Eu]^* (F - F_0)}{K} + [Eu]^* (F - F_0)^{-} [Eu]^* (F - F_0)^{-} (F_1 - F_0)^{-}}{1 - (F - F_0)^{-} (F_1 - F_0)}$$

where [citrate] is the total concentration citrate in the solution; [Eu] is the total concentration of the complex; K is the affinity constant; F is the ratio of 616 nm/579; F_0 is the ratio at the beginning; F_1 is the final ratio. This equation is deduced from

$$K = \frac{[citrateEu]}{[citrate_{f}][Eu_{f}]}$$

where [citrateEu] is the concentration of the citrate-coordinated complex; [citrate_{*f*}] is the concentration of free citrate in the mixture, and $[Eu_f]$ is the concentration of the free complex.



Fig. 4S. The luminescence spectra of **EuPheesterPT** ($5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$) upon the titration of sodium bicarbonate in 0.1 mol·L⁻¹ MOPS buffer; excited at 384 nm. The intensity and spectral forms change little.



Fig. 5S. The luminescence spectra of EuPheesterPT ($5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$) upon the titration of Na₂HPO₄ in 0.1 mol·L⁻¹ MOPS buffer; excited at 384 nm. The intensity decreases as the concentration of phosphate increases.



Fig. 6S. The luminescence spectra of aqueous **EuPheesterPT** solution $(5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1})$ upon the titration of ATP; excited at 384 nm. ADP, AMP, and TMP have the similar behaviors. The intensity decreases as the concentration of phosphate increases, and the spectral forms also change.



Fig. 7S. The luminescence intensity ratio of 616 nm to 579 nm of aqueous **EuPheesterPT** solution $(5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1})$ upon the titration of citrate, phosphate, bicarbonate, lactate, respectively; excited at 384 nm. Here it shows clear that, among these anions, only citrate exhibits good affinity to the complex.



Fig. 8S. The luminescence spectra of aqueous **EuPheesterPT** solution $(5 \times 10^{-6} \text{ mol·L}^{-1})$ at varied pH; the spectrum at pH 3.74 may subject to the decompose of **EuPheesterPT**; excited at 384 nm. The intensity decreases along with the solution from neutral to acidic.



Fig. 9S. The luminescence spectra of aqueous **EuPheesterPT** solution $(5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1})$ at varied pH; excited at 384 nm. The intensity changes very little in this pH range



Fig. 10S. The luminescence intensity ratio of 616 nm to 579 nm of aqueous EuPheesterPT solution $(5 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1})$ at varied pH; excited at 384 nm. The curve of citrate titration is just to show the emission ratio scale of 616 nm to 579 nm upon the titration of citrate, not corresponding to the pH change.