Supplementary Materials

Eu-Doped Citrate-Coated Carbonated Apatite Luminescent Nanoprobes for Drug Delivery

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Figure S1. Standard calibration straight line Doxo on Eu:cit-cAp nanocrystals. Dotted blue line represents the lineal fitting of the experimental data.

Table S1. Kinetics parameters obtained from the lineal fitting of the experimental data.

| Parameter       | Value   |
|-----------------|---------|
| Intercept [ua]  | -0.1 ± 0.3 |
| Slope [mL mg⁻¹] | 24.7 ± 0.6 |

R² = 0.99424
Equation S1:

\[ Q(t) = Q_{\text{max}} \left(1 - e^{-t/\tau}\right) \]  

(Lagergren’s equation)

\( Q \) is the amount of drug adsorbed on the nanoparticle surface and \( \tau \) the time needed to reach approximately a 63% of \( Q_{\text{max}} \).

Figure S2. (a) excitation (dashed line) and emission (solid line) spectra of Eu:cit-cAp nanoparticles suspended in water at 25 °C at several pHs and (b) the effect of the pH on the luminescence emission of these particles; slit-widths \( \text{exc/em} = 10/10 \) nm, \( t_d = 120 \) µs, \( t_g = 5 \) ms, detector voltage 800v.

Figure S3. (a) excitation (dashed line) and emission (solid line) spectra of Eu:cit-cAp nanoparticles loaded with 0.139 mg Doxo/mg Eu:cit-cAp suspended in water at 25 °C at several pHs, and (b) the effect of the pH on the luminescence emission of these particles; slit-widths \( \text{exc/em} = 10/10 \) nm, \( t_d = 120 \) µs, \( t_g = 5 \) ms, detector voltage 800v.
Figure S4. Luminescence decay curve of Eu:3cAp nanoparticles suspended in water at 25 °C at several pHs, λ_{ex/em}=394/618 nm, slit-widths_{ex/em} = 10/10 nm, and detector voltage = 780 V. Circles correspond to experimental data and lines to the fitting equation.
Figure S5. Luminescence decay curve of Eu:cit-cAp nanoparticles loaded with 0.139 mg Doxo/mg Eu:cit-cAp suspended in water at 25 °C at several pHs. $\lambda_{\text{exc/em}} = 394/614$ nm, slit-widths $\text{exc/em} = 10/10$ nm, and detector voltage = 780 V; circles correspond to experimental data and lines to the fitting equation.

| pH   | Equation                           | R.L.I. (a.u.) | S.D.  |
|------|------------------------------------|--------------|-------|
| 5.0  | $\text{R.L.I.} = 4.4307 \cdot e^{-t/0.514} + 0.0808$  | 4.0          | 0.0562|
| 5.5  | $\text{R.L.I.} = 6.7023 \cdot e^{-t/0.530} + 0.0940$  | 5.0          | 0.0751|
| 6.0  | $\text{R.L.I.} = 5.7731 \cdot e^{-t/0.514} + 0.0899$  | 5.5          | 0.0819|
| 6.5  | $\text{R.L.I.} = 4.464 \cdot e^{-t/0.590} + 0.0828$   | 6.0          | 0.0566|
| 7.0  | $\text{R.L.I.} = 2.9332 \cdot e^{-t/0.547} + 0.1005$  | 6.5          | 0.0819|
| 7.4  | $\text{R.L.I.} = 3.3564 \cdot e^{-t/0.325} + 0.0579$  | 7.0          | 0.0407|

S.D. = standard deviation
Figure S6. (a, b) calibration curve of Doxo in water, and (c) determination of the absorbed Doxo on the Eu:ct-cAp nanoparticles versus the equilibrium Doxo concentration.
Figure S7. Luminescence decay curve of Eu:siR/cAp/Doxo nanoparticles with varying concentration of Doxo suspended in HEPES buffer at pH=7.4 and 25°C; \( \lambda_{\text{exc/em}} = 394/614 \text{ nm} \), slit-widths\( \lambda_{\text{exc/em}} = 10/10 \text{ nm} \), and detector voltage = 780 V; circles correspond to experimental data and lines to the fitting equation.
Figure S8. Variation of the apparent quenching constant with the concentration of the quencher.