

Supporting Information

A pH Responsive Assembly based on Upconversion Nanocrystal and Ultrasmall Nickel Nanoparticles

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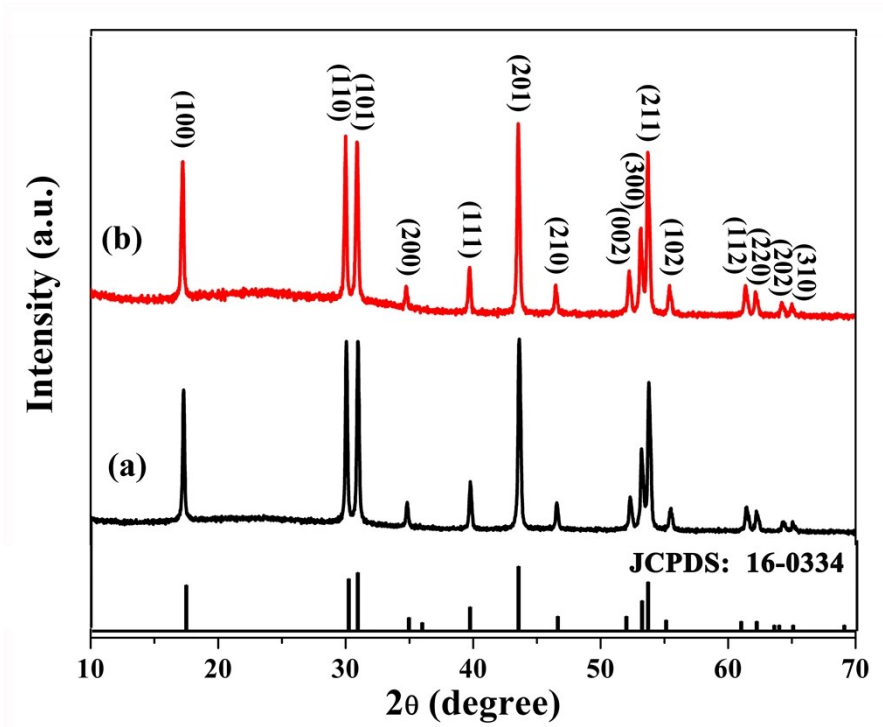


Fig. S1 XRD patterns of (a) NaYF₄:Yb³⁺/Er³⁺ core nanoparticles and (b) NaYF₄:Yb³⁺/Er³⁺@NaYF₄ core@shell nanoparticles.

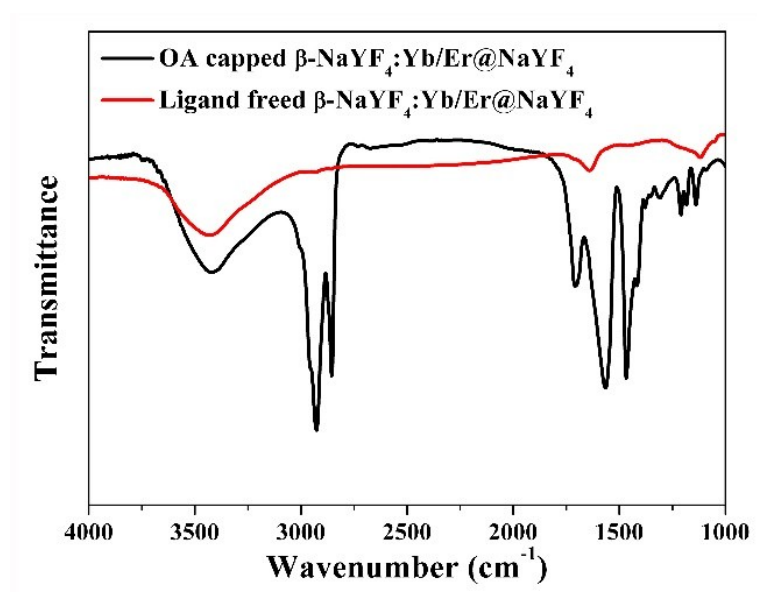


Fig. S2 Corresponding FT-IR spectra of oleic acid-capped (black line) and ligand free (red line) NaYF₄:Yb³⁺/Er³⁺@NaYF₄ core@shell nanoparticles.

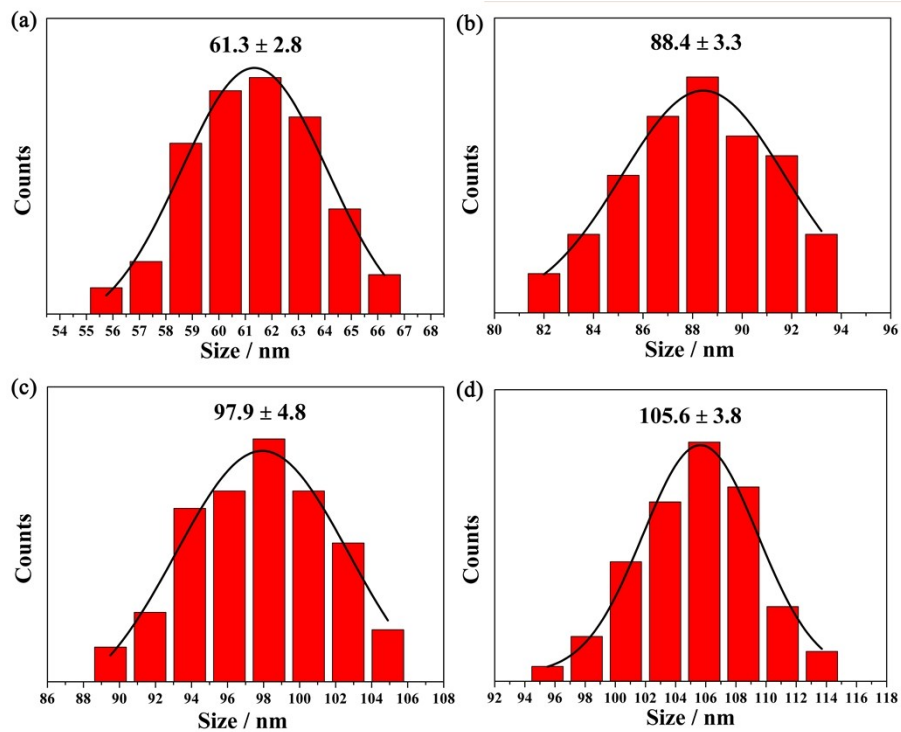


Fig. S3 The size distributions of the prepared particles: (a) $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ core nanoparticles, (b) $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}@\text{NaYF}_4$ core@shell nanoparticles, (c) core@shell@Ni and (d) core@shell@Ni(OH)₂.

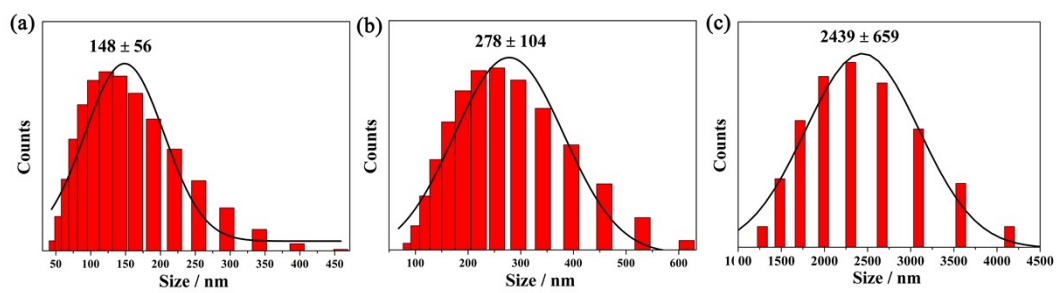


Fig. S4 The dynamic light scattering size distribution of the hydrophilic particles: (a) $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}@\text{NaYF}_4$ core@shell nanoparticles, (b) core@shell@Ni and (c) core@shell@Ni(OH)₂.

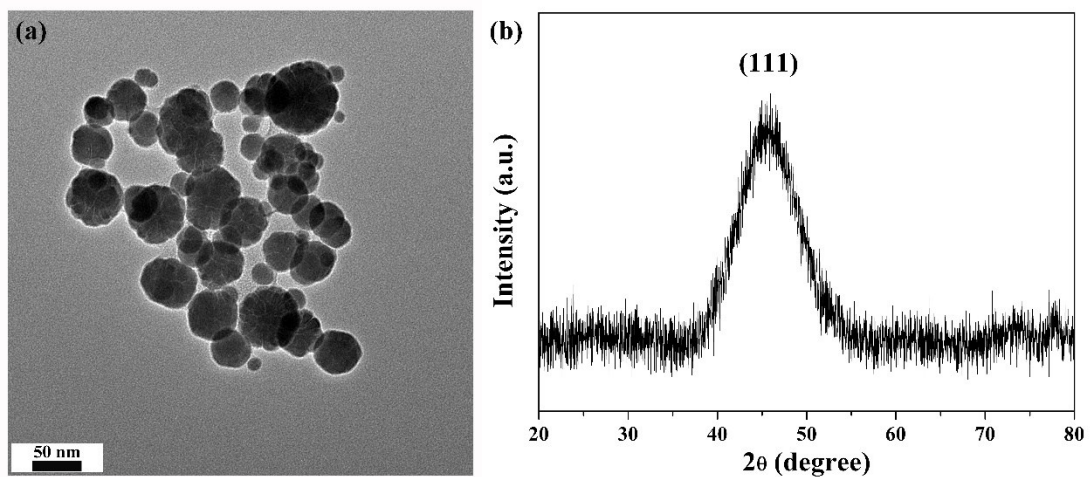


Fig. S5 (a) TEM image and (b) XRD pattern of Ni-B nanoparticles.

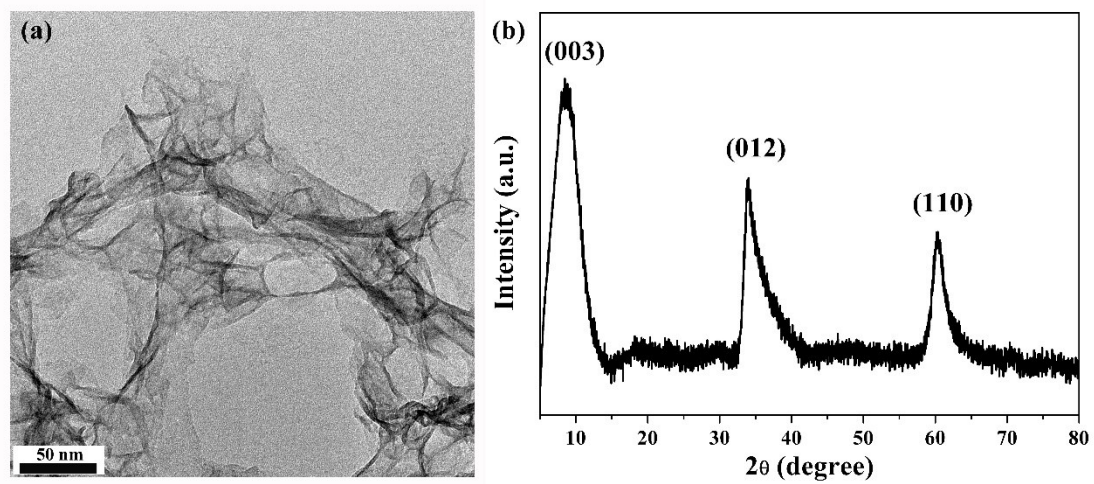


Fig. S6 (a) TEM image and (b) XRD pattern of $\text{Ni}(\text{OH})_2$ nanosheets.

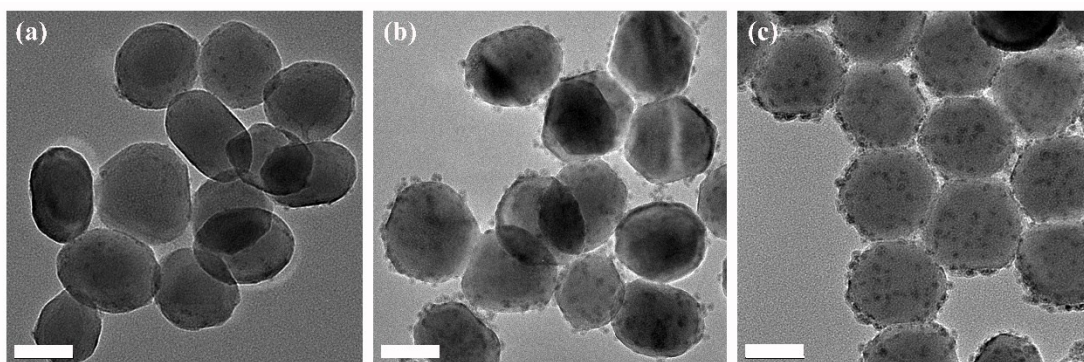


Fig. S7 TEM images of the core@shell@Ni assemblies produced from the molar ratio of Ni nanoparticle to core@shell UCNPs of (a) 0.07:1, (b) 0.14:1 and (c) 0.28:1. Scale bar = 50 nm.

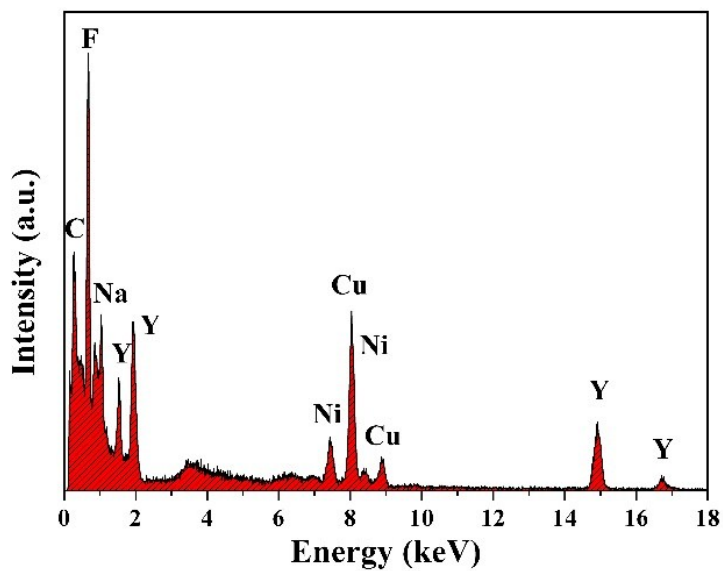


Fig. S8 Energy dispersive X-ray spectroscopy (EDS) spectrum of Ni-modified NaYF₄:Yb³⁺/Er³⁺@NaYF₄ UCNPs, indicating the presence of elemental Na, Y, F and Ni. Note that the strong signal of Cu comes from the copper TEM grid.

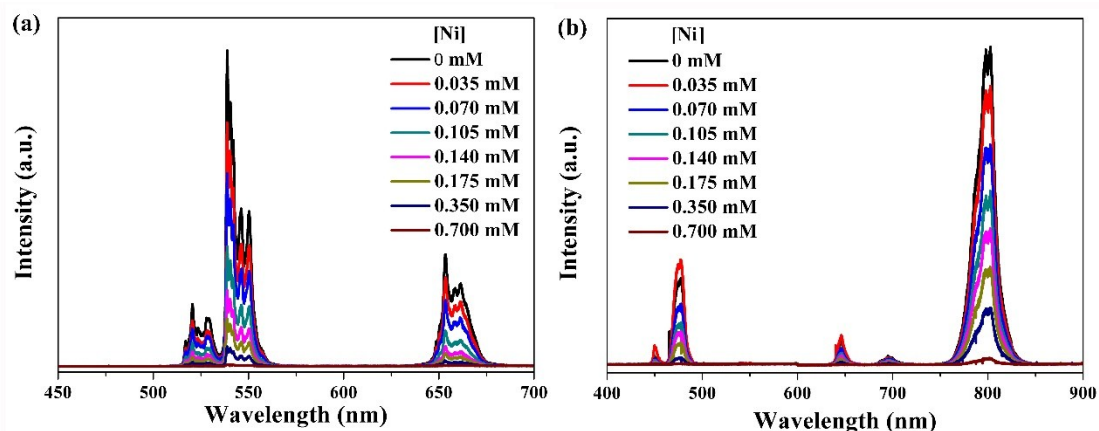


Fig. S9 Upconversion emission spectra of (a) Er^{3+} and (b) Tm^{3+} ions doped $\text{NaYF}_4:\text{Yb}^{3+}@\text{NaYF}_4$ UCNPs modified with Ni nanoparticles at different concentrations. The concentrations of lanthanide ions are fixed at 2.5 mM. All the spectra were characterized in ethanol solution. The power density is 0.3 W mm^{-2} .

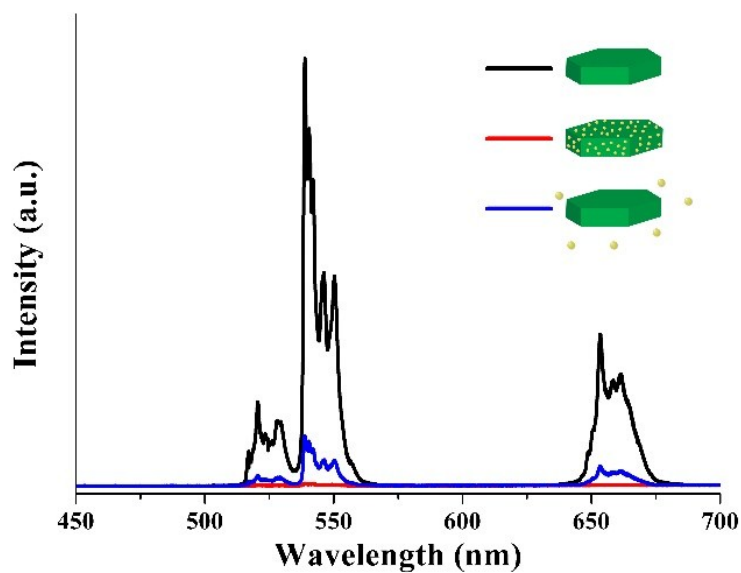


Fig. S10 Upconversion emission spectra taken for NaYF₄:Yb³⁺/Er³⁺@NaYF₄ core@shell UCNPs with different routes of surface modification: no modification, hetero-assembling Ni nanoparticle and core@shell UCNPs and physical mixing of pre - formed Ni-B nanoparticle and the UCNPs. The power density is 0.3 W mm⁻².

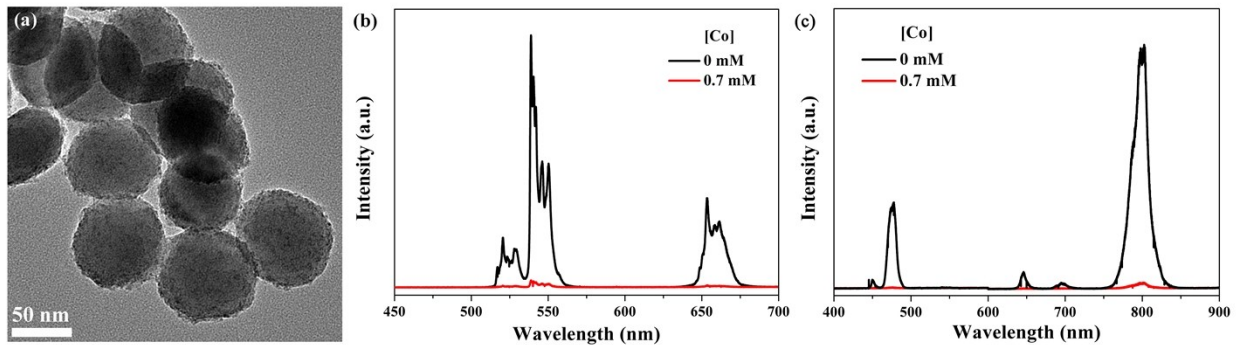


Fig. S11 (a) TEM image of Co-modified core@shell UCNPs, upconversion emission spectra of (b) Er³⁺-doped and (c) Tm³⁺-doped core@shell nanoparticles (black line) and Co nanoparticle-modified core@shell nanoparticles (red lines) with a UCNPs/Co molar ratio of 1:0.28, the concentrations of lanthanide ions are fixed at 2.5 mM. The power density is 0.3 W mm⁻².

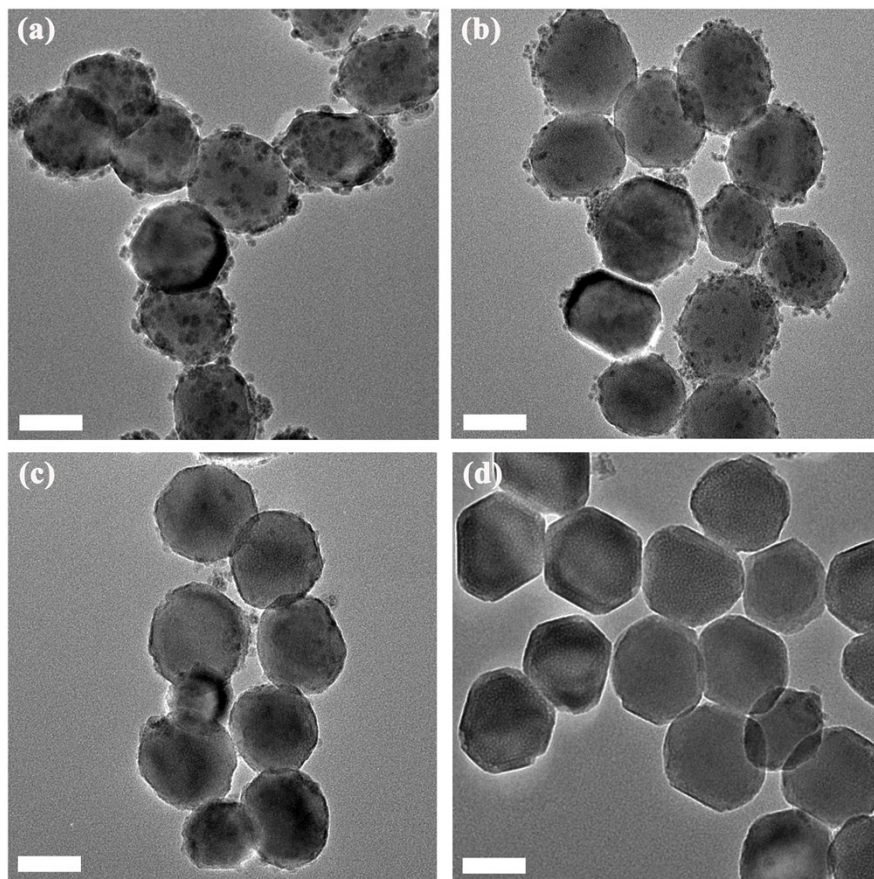


Fig. S12 TEM images of core@shell@Ni nanoparticles responding to pH 5.0 PBS with different reaction times (0, 3, 6 and 9 min). Scale bar = 50 nm.

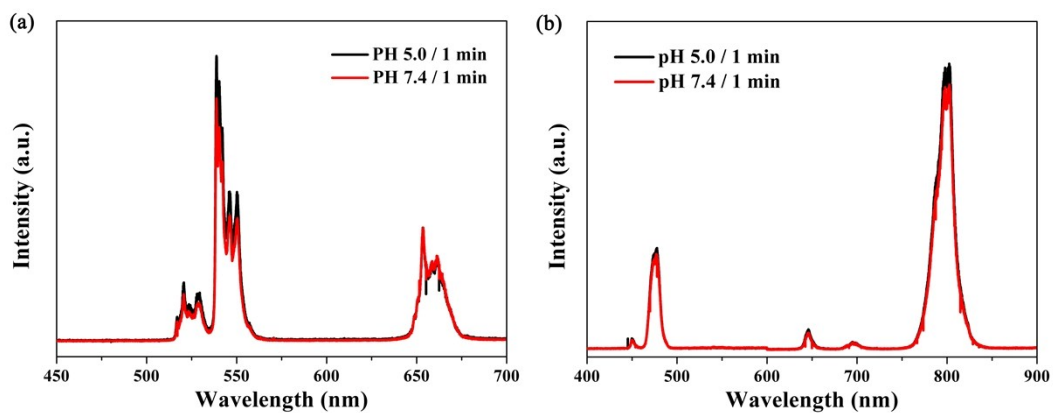


Fig. S13 Upconversion luminescence response of Co-modified (a) $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}@\text{NaYF}_4$ and (b) $\text{NaYF}_4:\text{Yb}^{3+}/\text{Tm}^{3+}@\text{NaYF}_4$ nanoparticles with a UCNPs/Co molar ratio of 1:0.28 (the concentrations of lanthanide ions are fixed at 2.5 mM) against different pH PBS solution at 1 min.