Supporting Information

Amine-Functionalized Lanthanide-Doped $KGdF_4$ Nanocrystals as Potential Optical/Magnetic Multimodal Bioprobes

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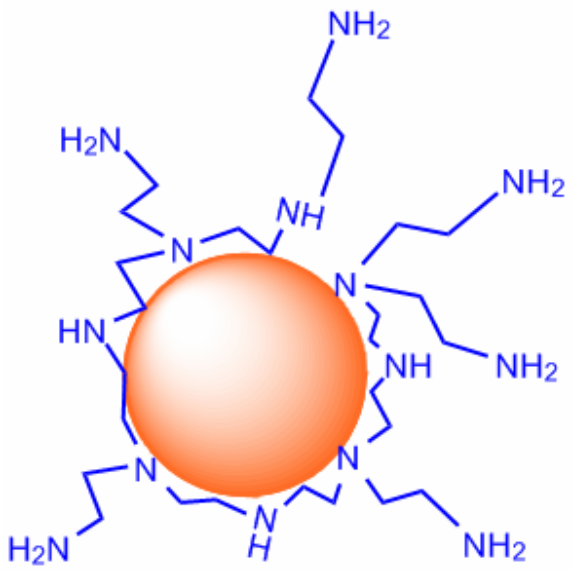

Figure S1. Schematic illustration of PEI-coated $KGdF_4:Ln^{3+}$ NCs. The uncoordinated amino groups of branched PEI extend into the aqueous solution, rendering the NCs water-soluble and functionalized for further linkage of biomolecules through bioconjugate chemistry.[1]

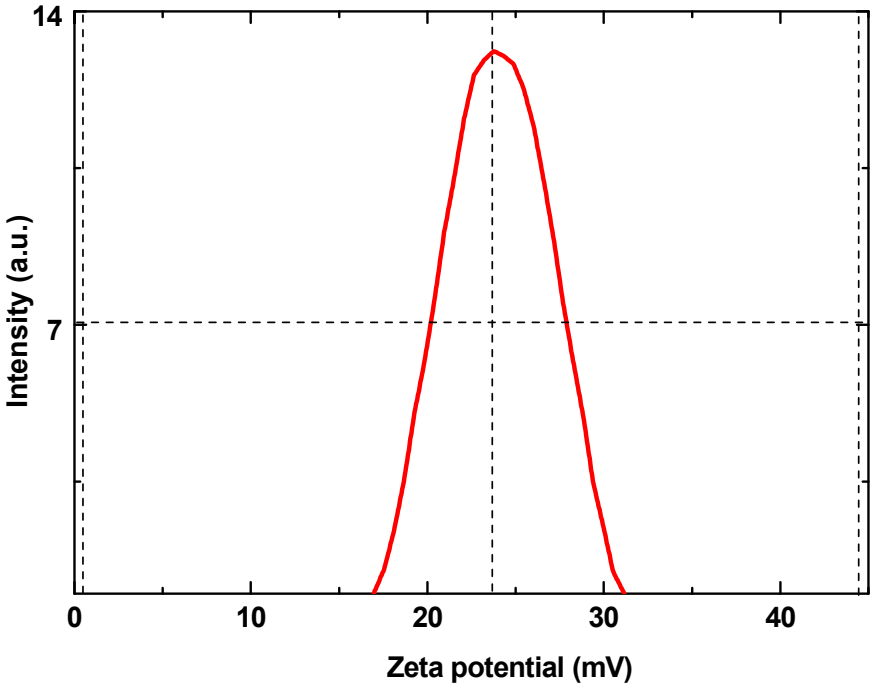

Figure S2. ζ-potential for PEI capped $KGdF_4$ NCs obtained from the dynamic light scattering. The ζ-potential for PEI capped $KGdF_4$ NCs dispersed in aqueous solution (pH = 7.6) was determined to be +23.2 mV.

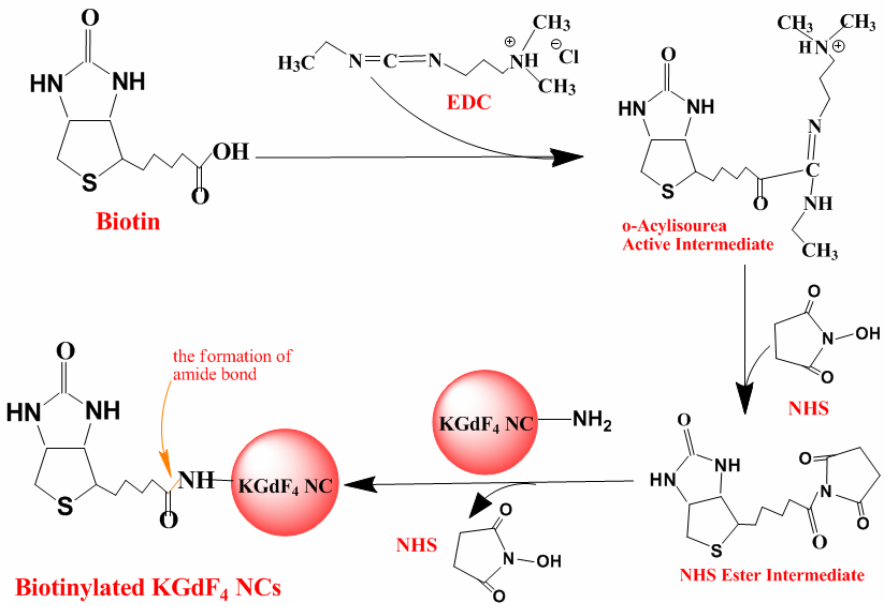

Figure S3. Schematic illustration of the bioconjugation of $KGdF_4$ NC with biotin through a well-established protocol by employing 1-ethyl-3-(3-dimethly-aminopropyl) carboxylate (EDC) and N-hydroxysuccinimide (NHS) as cross-linking reagents. The EDC firstly reacts with the surface carboxyl (-COOH) groups on the biotin to yield an O-acylisourea active intermediate. Then this intermediate reacts with the NHS to generate a more stable active NHS ester intermediate. Finally, this intermediate is attacked by a primary amine (NH_2) group on the $KGdF_4$ NCs, forming a stable amide covalent bond between the biotin and the NCs.

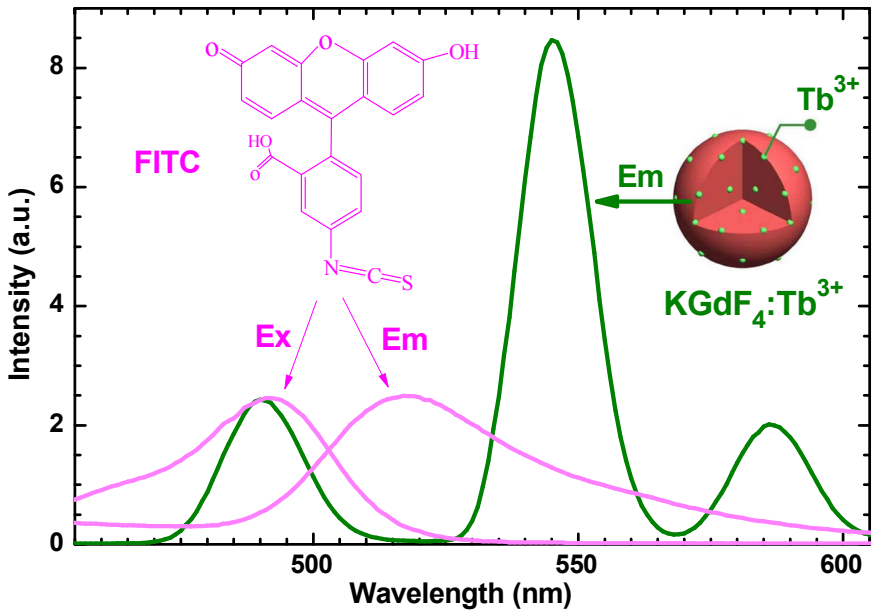

Figure S4. RT emission spectrum of $KGdF_4:Tb^{3+}$ NCs (green); RT excitation and emission spectra (pink) of FITC. The excitation peak of FITC matches well with the emission band of Tb^{3+} centered at 488 nm, and the emission peak of FITC at 518 nm is located within the gap between two emission peaks of Tb^{3+} (488 and 545 nm). Accordingly, FITC and $KGdF_4:Tb^{3+}$ NCs are selected as energy acceptor and energy donor in TR-FRET assays, respectively.

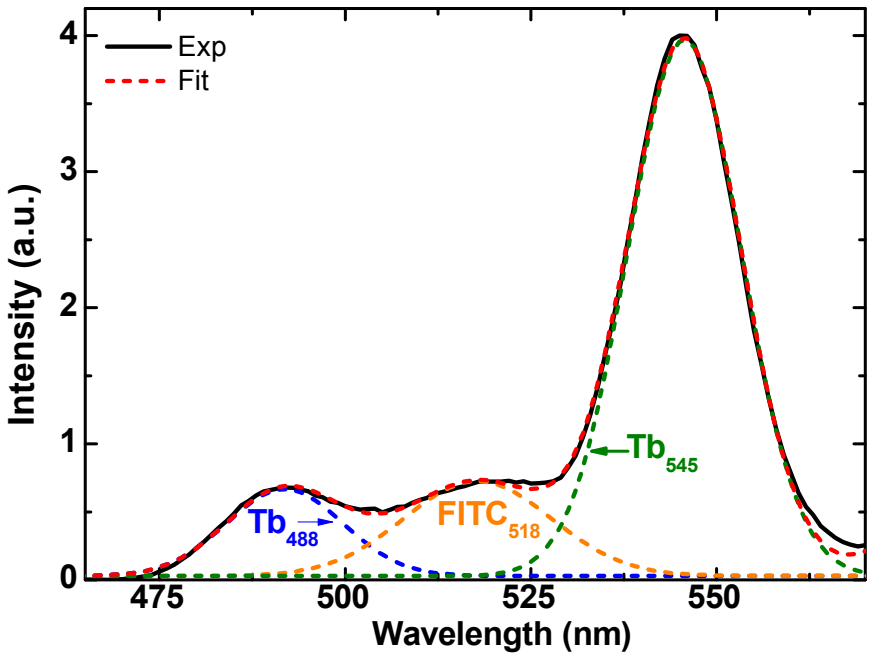

Figure S5. An example showing the determination of the integrated PL intensities of Tb_{488} and $FITC_{518}$ from the deconvolution of the TR-FRET spectrum. The experimentally observed spectrum within 470-570 nm was best fit and deconvoluted to three Gaussian curves with their peaks centered at 488, 518 and 545 nm, respectively.

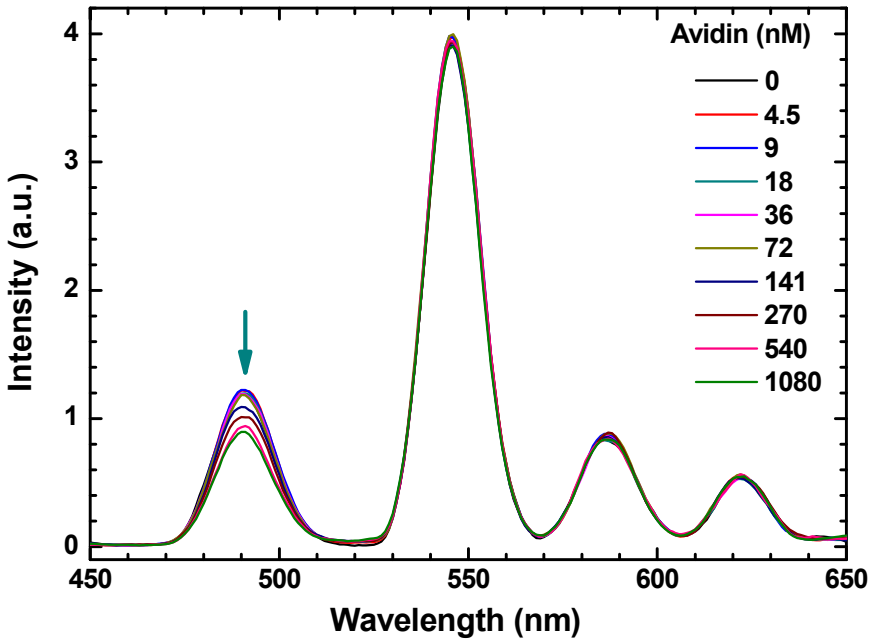

Figure S6. TR-FRET spectra for the control experiments by employing the as-prepared NCs instead of the biotinylated NCs as bioprobes under otherwise identical conditions, where no binding and hence no FRET occurs. The spectra were measured at different concentration of FITC-labeled avidin as indicated (nM) and normalized to unity at the maximum emission peak at 545 nm. Each data point represents average of quintuplicate measurements.

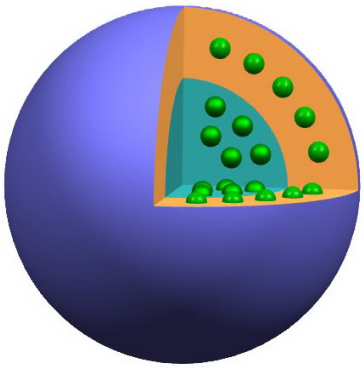

Figure S7. Schematic illustration of $KGdF_4$ NCs in longitudinal relaxation measurement. To quantitatively estimate the longitudinal relaxivity per $KGdF_4$ NC, we assume that only Gd^{3+} ions residing within a spherical shell (< 5 nm) of each $KGdF_4$ NC (diameter of 25 nm) contribute to the observed relaxivity, based on the fact that the close-to-surface Gd^{3+} ions in NCs play a dominant role in changing the relaxation of the water proton.[2] The number of Gd^{3+} ions N_{Gd} in the surface shell of one $KGdF_4$ NC can be calculated by the following equation to be 6.82×10^4, and the longitudinal relaxivity per $KGdF_4$ NC r_{NC} was then calculated to be 3.99×10^5 $S^{-1} \cdot mM^{-1}$.

$$N_{Gd} = \frac{4}{3} \times \pi \times (r_0^{\ 3} - r_{core}^{\ 3}) \times 2/a^3$$

$$r_{NC} = r_1 \times N_{Gd}$$

where r_0 is the radius of $KGdF_4$ NC, which is 12.5 nm; r_{core} is the inner radius of $KGdF_4$ NC, which is 7.5 nm; the space group of cubic $KGdF_4$ is *Fm*3*m* with unit cell a = 5.73 Å,[3] and every unit cell contains two $KGdF_4$ molecules.

References

(1) Yi, G. S.; Peng, Y. F.; Gao, Z. Q. *Chem Mater* **2011**, *23*, 2729.

(2) Park, Y. II.; Kim, J. H.; Lee, K. T.; Jeon, K.-S.; Na, H. B.; Yu, J. H.; Kim, H. M.; Lee, N.; Choi, S. H.; Baik, S.-II.; Kim, H.; Park, S. P.; Park, B.-J.; Kim, Y. W.; Lee, S. H.; Yoon, S.-Y.; Song, I. C.; Moon, W. K.; Suh, Y. D.; Hyeon, T. *Adv Mater* **2009**, *21*, 4467.

(3) Wong, H.-T.; Vetrone, F.; Naccache, R.; Chan, H. L. W.; Hao, J.; Capobianco, J. A. *J. Mater. Chem.* **2011**, *21*, 16589.