Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

A Resonance Energy Transfer Approach for the Selective Detection of Aromatic Amino Acids

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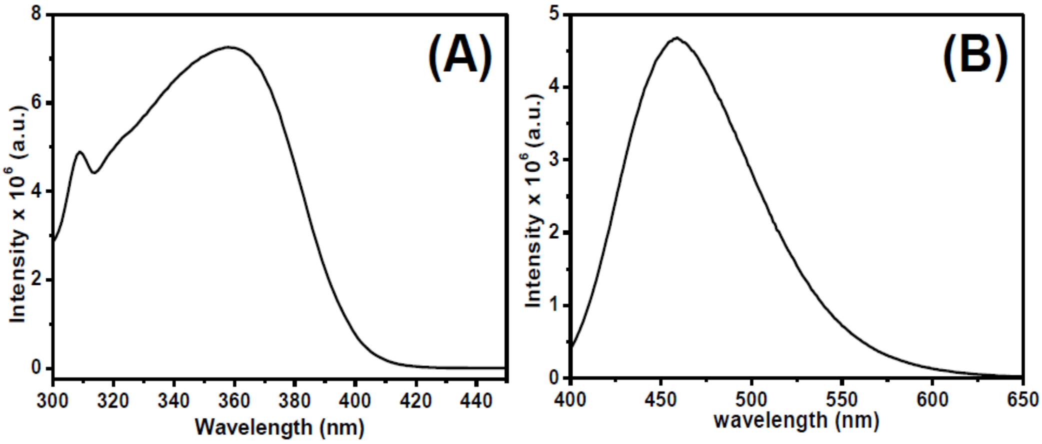

Fig. S1. (A) Absorption (B) Emission spectra of quinine sulphate.

Quantum Yield Calculation

The quantum yield was determined by comparing the luminescence with quinine-sulphate. The quantum yield of Ce^{3+}/Tb^{3+}-doped $CaMoO_4$ nanocrystals was calculated from the following equation-

$Q_{sample} = Q_{ref}\ (A/A_{ref})\ (I_{ref}/I)\ (n^2/n^2_{ref})$ where, Q_{sample} and Q_{ref} are the quantum yield of the nanocrystals and quinine-sulphate respectively, A is the absorbance, I is the integrated area of photoluminescence spectra, and n is the refractive index of the solution. The quantum yield of Quinine sulphate as the reference is 0.546. The quantum yield of molybdate nanocrystals was estimated by comparing the integrated emission spectra of the aqueous solution with that of Quinine sulphate solution. The sample and the reference have the identical optical density at the excitation wavelength. The calculated quantum yield was about 27 % for Ce^{3+}/Tb^{3+}-doped $CaMoO_4$ nanocrystals.

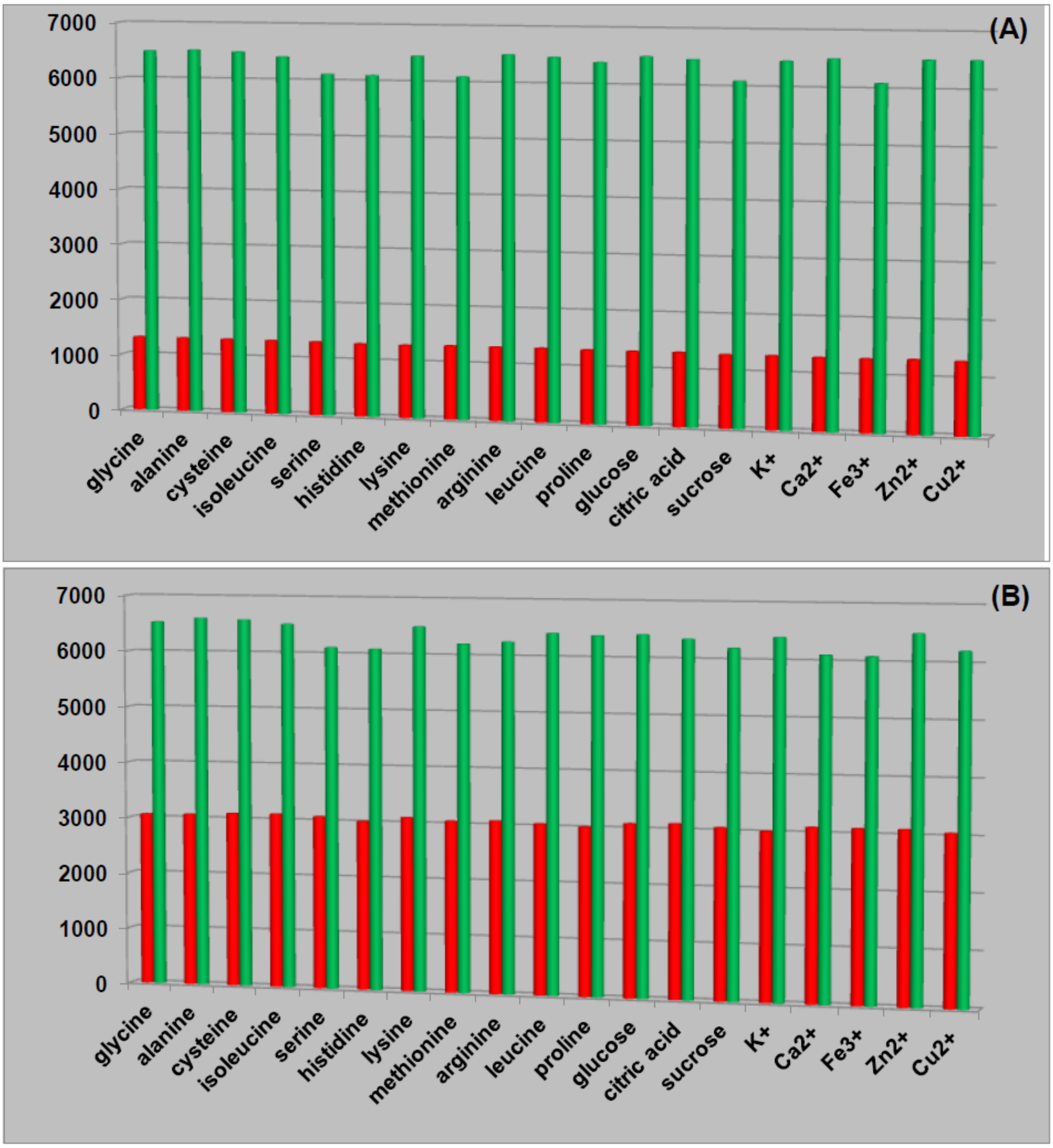

Fig. S2. Interference study of $CaMoO_4$:Ce^{3+}/Tb^{3+} nanocrystals dispersion containing both (A) tyrosine and other analytes (except tryptophan and phenyl alanine) (B) phenyl alanine and other analytes (except tryptophan and tyrosine).

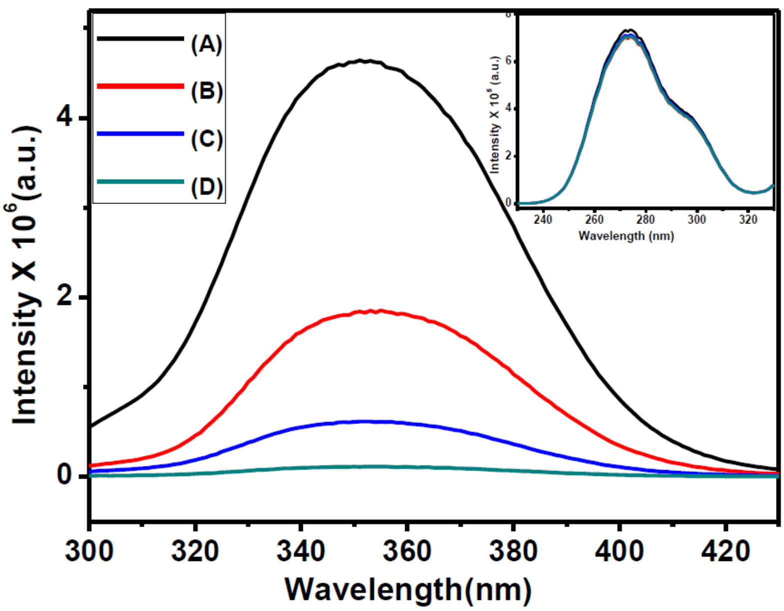

Fig. S3. Emission spectra of Ce^{3+}-doped $CaMoO_4$ nanocrystals in presence of (A) none (B) phenyl alanine (C) tyrosine and (D) tryptophan. The inset shows the excitation spectra of Ce^{3+}-doped $CaMoO_4$ nanocrystals in the presence of AAs.

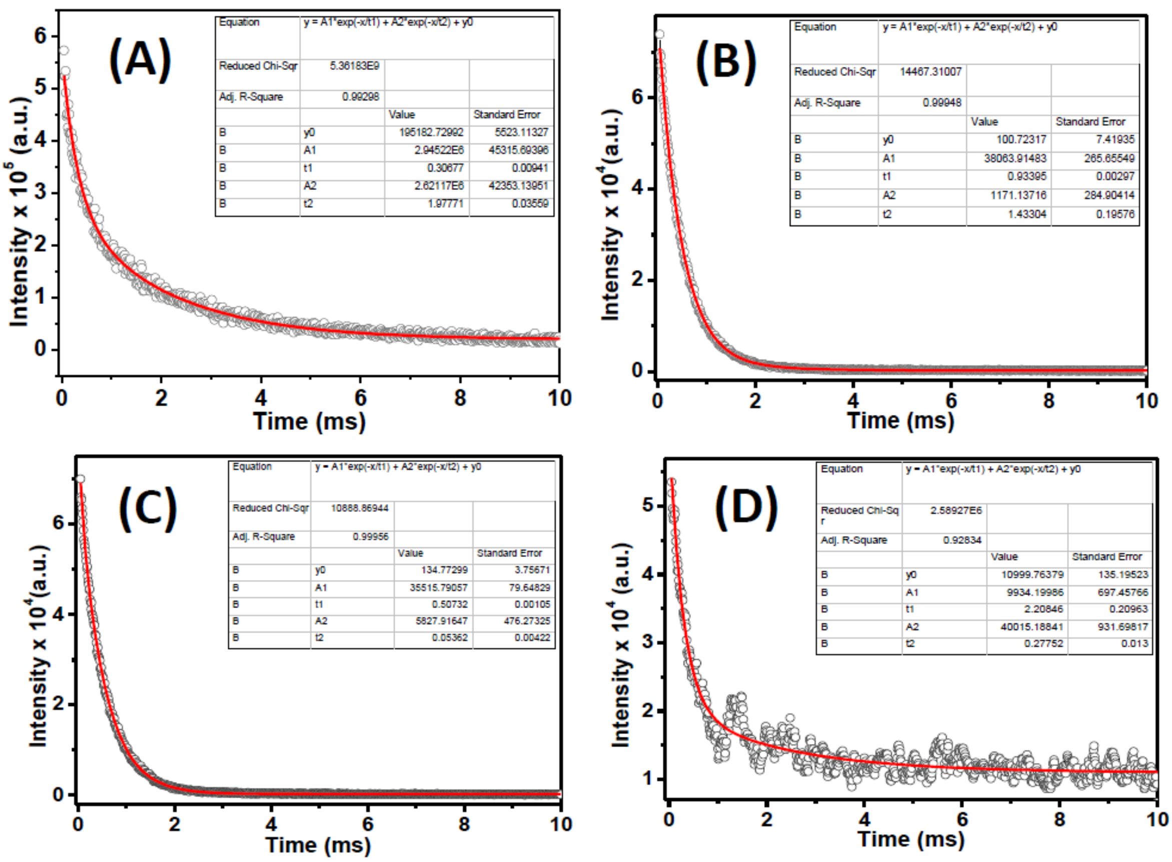

Fig. S4. Decay curves for $CaMoO_4$:Ce^{3+}/Tb^{3+} nanocrystals in the presence of (A) none (B) phenyl alanine (C) tyrosine (D) tryptophan.

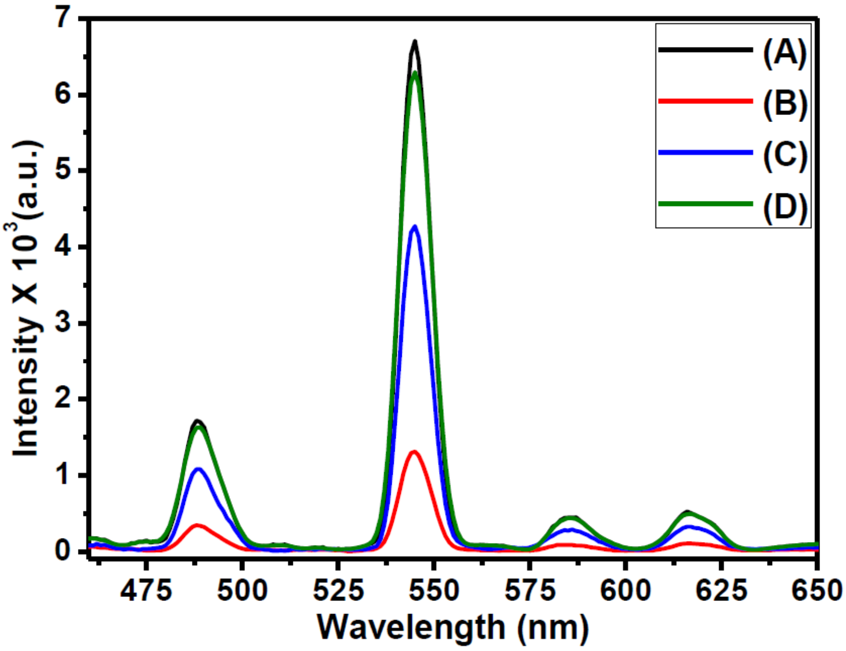

Fig. S5. PL spectra of aromatic amino acid complexed-Ce^{3+}/Tb^{3+} -doped $CaMoO_4$ nanocrystals after the gradual addition of ninhydrin. (A) Luminescence spectra of Ce^{3+}/Tb^{3+} -doped $CaMoO_4$ nanocrystals (B) after addition of 5 X 10^{-8} (M) tyrosine solution (C) after addition of 5 X 10^{-6} (M) and (D) 15 X 10^{-6} (M) ninhydrin.

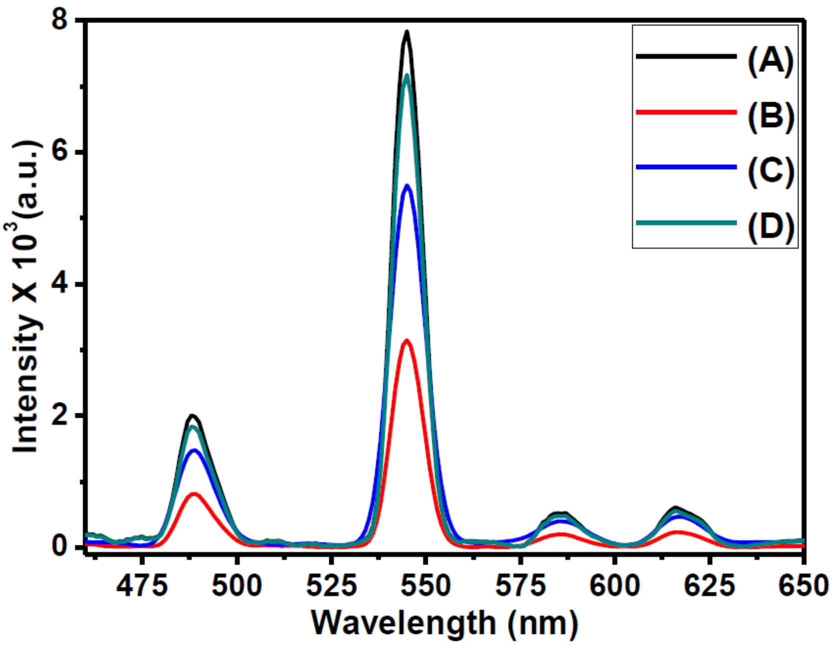

Fig. S6. PL spectra of aromatic amino acid complexed-Ce^{3+}/Tb^{3+} -doped $CaMoO_4$ nanocrystals after the gradual addition of ninhydrin. (A) Luminescence spectra of Ce^{3+}/Tb^{3+} -doped $CaMoO_4$ nanocrystals (B) after addition of 5 X 10^{-8} (M) phenyl alanine solution (C) after addition of 5 X 10^{-6} (M) and (D) 15 X 10^{-6} (M) ninhydrin.

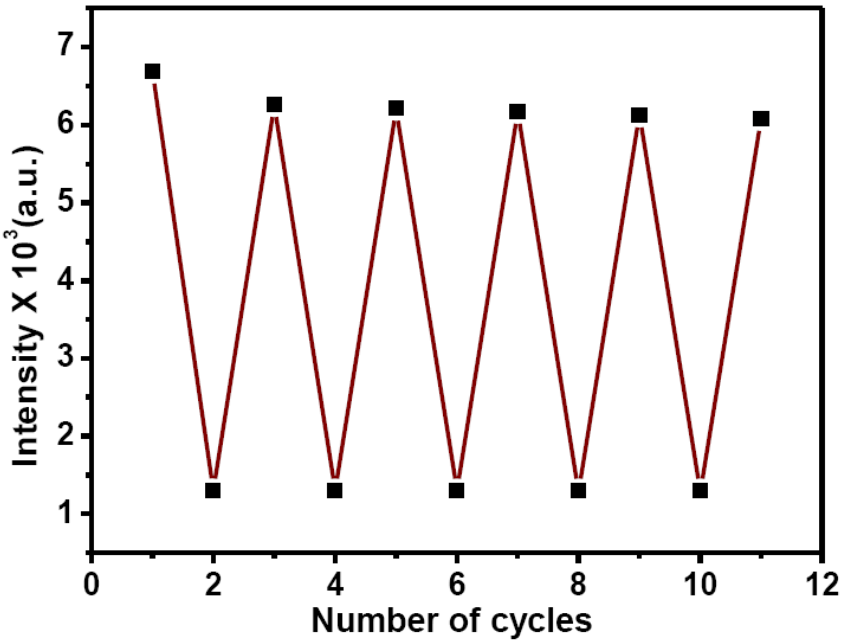

Fig. S7. Regeneration of Ce^{3+}/Tb^{3+} intense luminescence signal after alternate addition of 5 X 10^{-8} (M) tyrosine and 15 X 10^{-6} (M) ninhydrin.

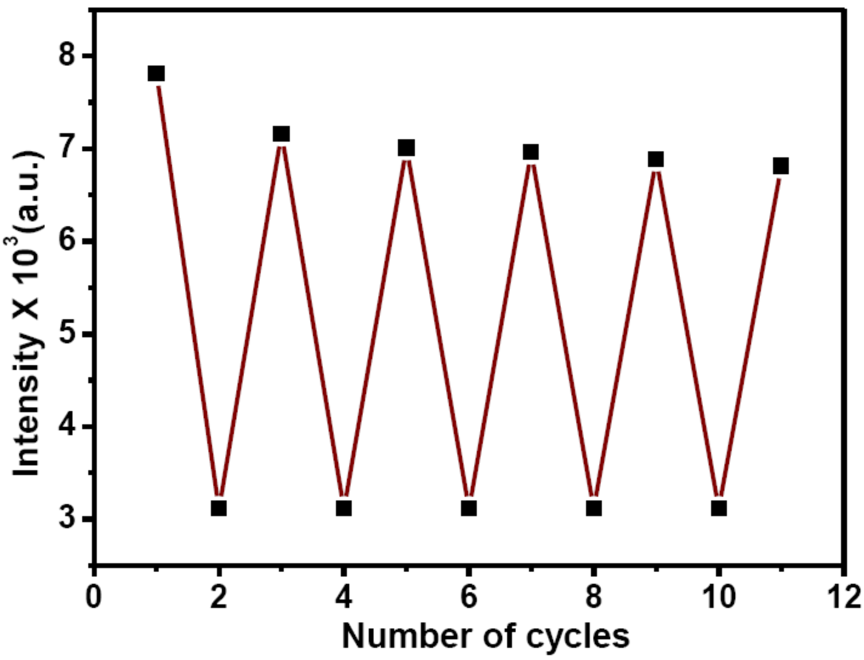

Fig. S8. Regeneration of Ce^{3+}/Tb^{3+} intense luminescence signal after alternate addition of 5 X 10^{-8} (M) phenyl alanine and 15 X 10^{-6} (M) ninhydrin.

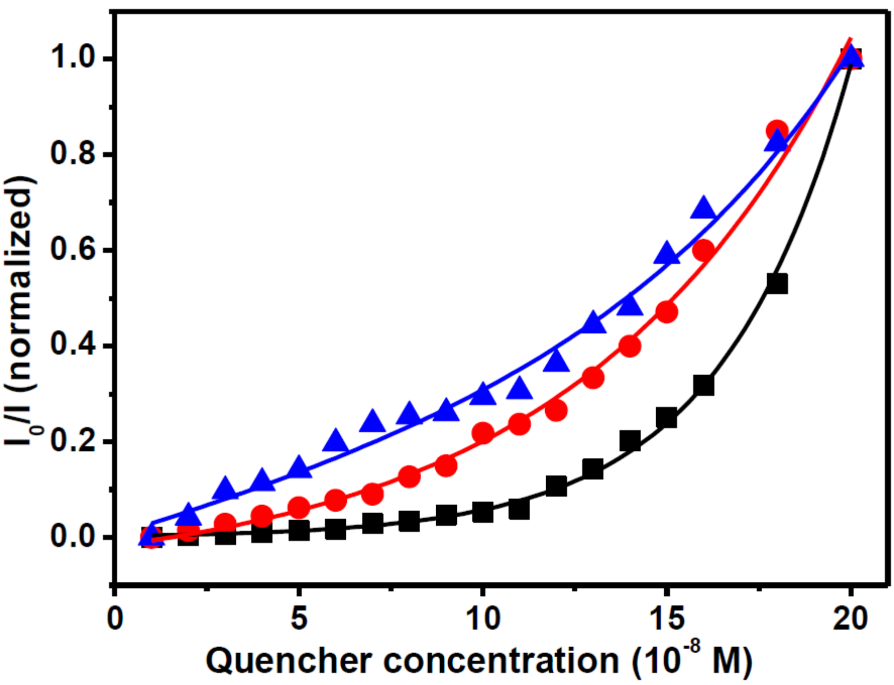

Fig. S9. Stern-Volmer plot of Ce^{3+}/Tb^{3+}-doped $CaMoO_4$ nanocrystals in the presence of tryptophan (black), tyrosine (red) and phenyl alanine (blue).

Table S1. Dynamic and static quenching constants of Ce^{3+}/Tb^{3+}-doped $CaMoO_4$ nanocrystals in the presence of tryptophan, tyrosine and phenyl alanine.

System	**Dynamic Quenching Constant (K_{sv})**	**Static Quenching Constant (K_{sv})**
$CaMoO_4:Ce^{3+}/Tb^{3+}$ + tyrosine	2.6 X 10^5 (M^{-1})	9.42 X 10^5 (M^{-1})
$CaMoO_4:Ce^{3+}/Tb^{3+}$ + phenyl alanine	3.37 X 10^5 (M^{-1})	7.98 X 10^5 (M^{-1})

Table S2 Comparison of linear range and LOD of amino acids obtained from lanthanide luminescence method (present work) with that reported for other analytical methods.

Methods	**Linear range**	**Limit of detection (LOD)**	**References**
Upconversion (LRET)	0-10 eq.	28.5μM	ACS Appl. Mater. Interfaces, 2014, 6, 11190−11197.
Colorimetric	1.5 X 10^{-7} to 3.0 X 10^{-5} (M)	7.5 X 10^{-8} (M)	Chinese Chem. Lett., 2014, 25, 995-1000.
Fluorometric (via ligand exchange)	1 X 10^{-7} to 5 X 10^{-4} (M)	4.5 X 10^{-6} (M)	Nanotechnology, 2008, 19, 205501 (8pp)
Fluorometric	0.5 to 10 μM	0.5 μM	Nanotechnology, 2008, 19, 465503-7.
Lanthanide luminescence (LRET)	1 X 10^{-10} to 5 X 10^{-8} (M)	2.09 X 10^{-8} (M) (tryptophan), 2.72 X 10^{-7} (M) (tyrosine), 9 X 10^{-6} (M) (phenylalanine)	Present work