Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information

Water dispersible Eu^{3+}-doped $NaGd(SO_4)_2.H_2O$ nanorods for selective Fe^{3+} sensing applications

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EXPERIMENTAL SECTION

Materials: Gd_2O_3, Eu_2O_3 (99.99%, from Aldrich), ethylene glycol (from Merck), Polyacrylic acid (800 M.W. from Aldrich), H_2SO_4 (98% pure from Merck), NaOH pellet (from Merck) were used for the synthesis. All chemicals were used as received without further purification.

Synthesis: Poly(acrylic acid) coated $NaGd(SO_4)_2$:Eu^{3+} (x%) nanorods [x = 1, 2, 3, 5, 8, 10, 15] were synthesized by mixing gadolinium nitrate, europium nitrate, PAA and sulfuric acid in ethylene glycol medium. Briefly, $Gd(NO_3)_3$ (1.90 mmol, 857.6 mg) and $Eu(NO_3)_3$ (0.10 mmol, 42.81 mg) were added to 5 ml ethylene glycol under magnetic stirring. H_2SO_4 (4 mmol, 2 ml H_2SO_4 / 8 ml EG) was then added as sulphate source, and the solution was stirred vigorously for about 20 min. Sodium hydroxide (NaOH) pellets (150 mg) were directly added to the solution. Once NaOH was completely dissolved, 0.2g PAA was added to the mixture and the stirring was maintained for another 20 min. Subsequently the colloidal solution was transferred to a 30 ml vial used for microwave synthesis (Anton Parr Monowave 300 microwave reactor under temperature control mode). The vial was tightly sealed with Teflon cap and then microwave heated at 120° C for 5 minutes. The final product appeared as precipitate was collected by centrifugation and washed thrice with ethanol, followed by deionized water to remove any unreacted reactants.

XRD measurements: The XRD patterns were collected using the Rigaku-SmartLab diffractometer attached with D/tex ultra detector and Cu K_α source operating at 50 mA and 40 kV. Scan range was set from 10-70° 2θ with a step size of 0.02° with a count time of 2 sec. The samples were well powdered and spread evenly on a quartz slide.

Transmission electron microscopy measurements: TEM images were taken on a UHR-FEG-TEM, JEOL; JEM 2100 F model using a 200 kV electron source. Samples were prepared by placing a drop of aqueous dispersion of the nanorods on a carbon coated copper grid and the grid was dried under air.

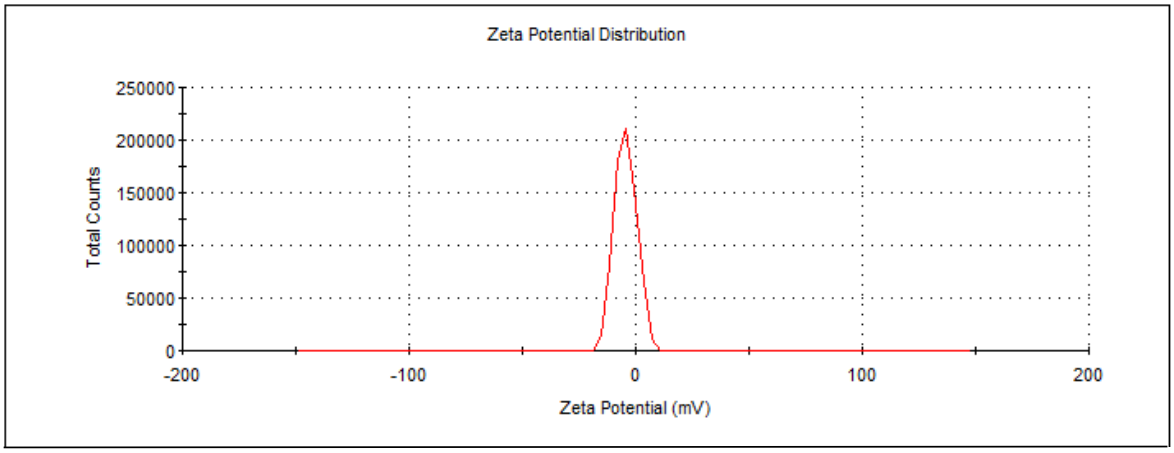
Thermogravimetric analysis: Thermogravimetric analysis was performed using Mettler Toledo TGA 851 instrument under N_2 atmosphere at a heating rate of 10^o min^{-1}.

Photoluminescence measurements: The photoluminescence spectra were measured on a Horiba Jobin Yvon spectrometer equipped with 150 W Xe lamp. The excitation and emission light were dispersed using Czerny-Turner monochromator with an optical resolution of 1 nm. The emitted photons were detected using a Hamamatsu R928 detector. The output signal was recorded using a computer. The luminescence lifetime measurements were performed with the Horiba Jobin Yvon Fluoromax-4 CP machine equipped with a pulsed Xe source operating at 25 W.

		Mean (mV)	Area (%)	Width (mV)
Zeta Potential (mV): -4.47	Peak 1:	-4.47	100.0	4.69
Zeta Deviation (mV): 4.69	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.867	Peak 3:	0.00	0.0	0.00

Result quality : Good

Eu-doped $NaGd(SO_4)_2$ nanorods



		Mean (mV)	Area (%)	Width (mV)
Zeta Potential (mV): -18.4	Peak 1:	-18.4	100.0	7.35
Zeta Deviation (mV): 7.35	Peak 2:	0.00	0.0	0.00
Conductivity (mS/cm): 0.221	Peak 3:	0.00	0.0	0.00

Result quality : Good

Poly(acrylic acid)

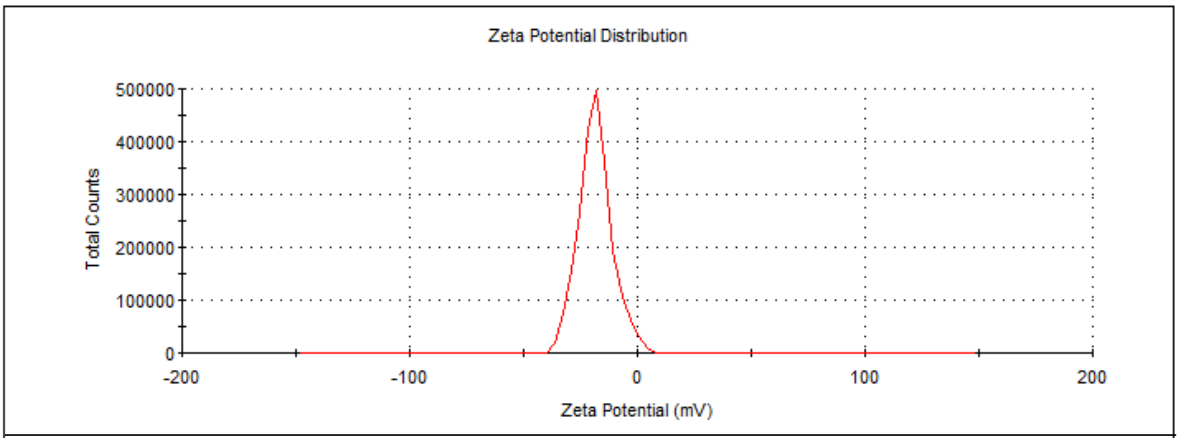


Fig. S1. Zeta potential results for Eu^{3+} -doped $NaGd(SO_4)_2$ nanorods and poly(acrylic acid).

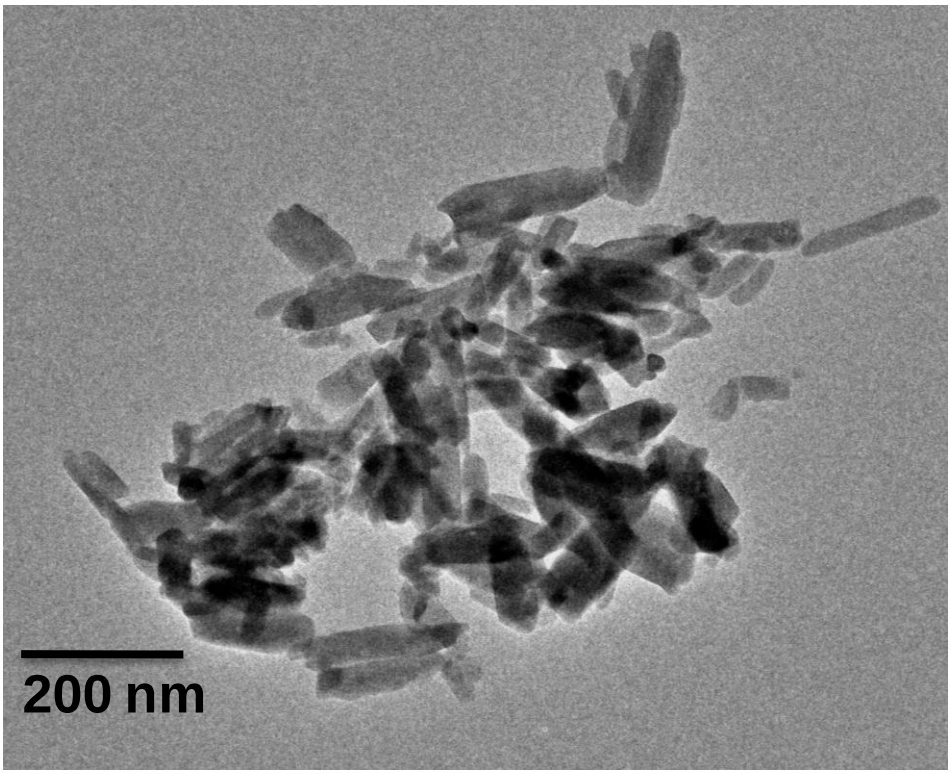


Fig. S2 TEM image of the PAA coated Eu^{3+}-doped $NaGd(SO_4)_2$ nanorods in water after diluting with NH_4OH to increase the pH.

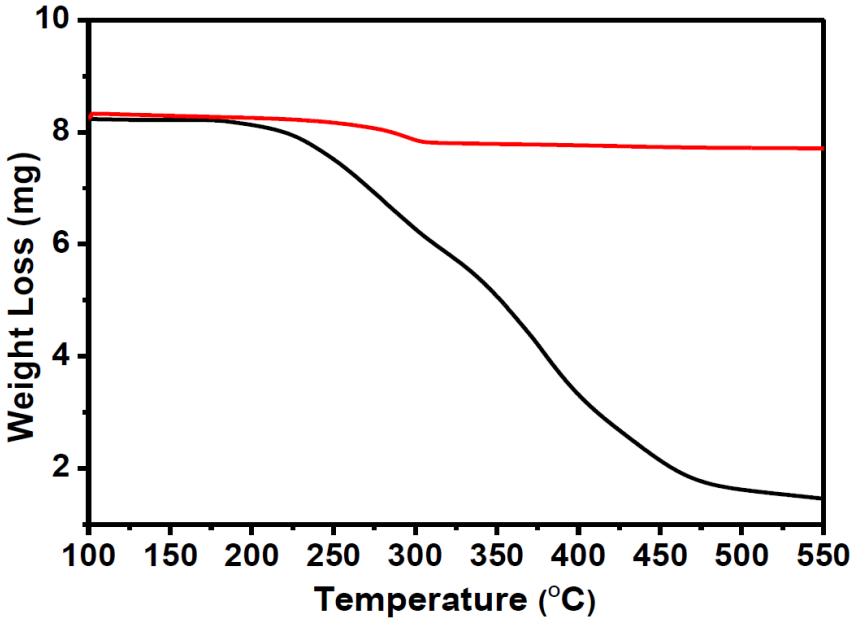


Fig. S3 TGA curves for free PAA (black) and PAA coated Eu^{3+} -doped $NaGd(SO_4)_2$ (red)

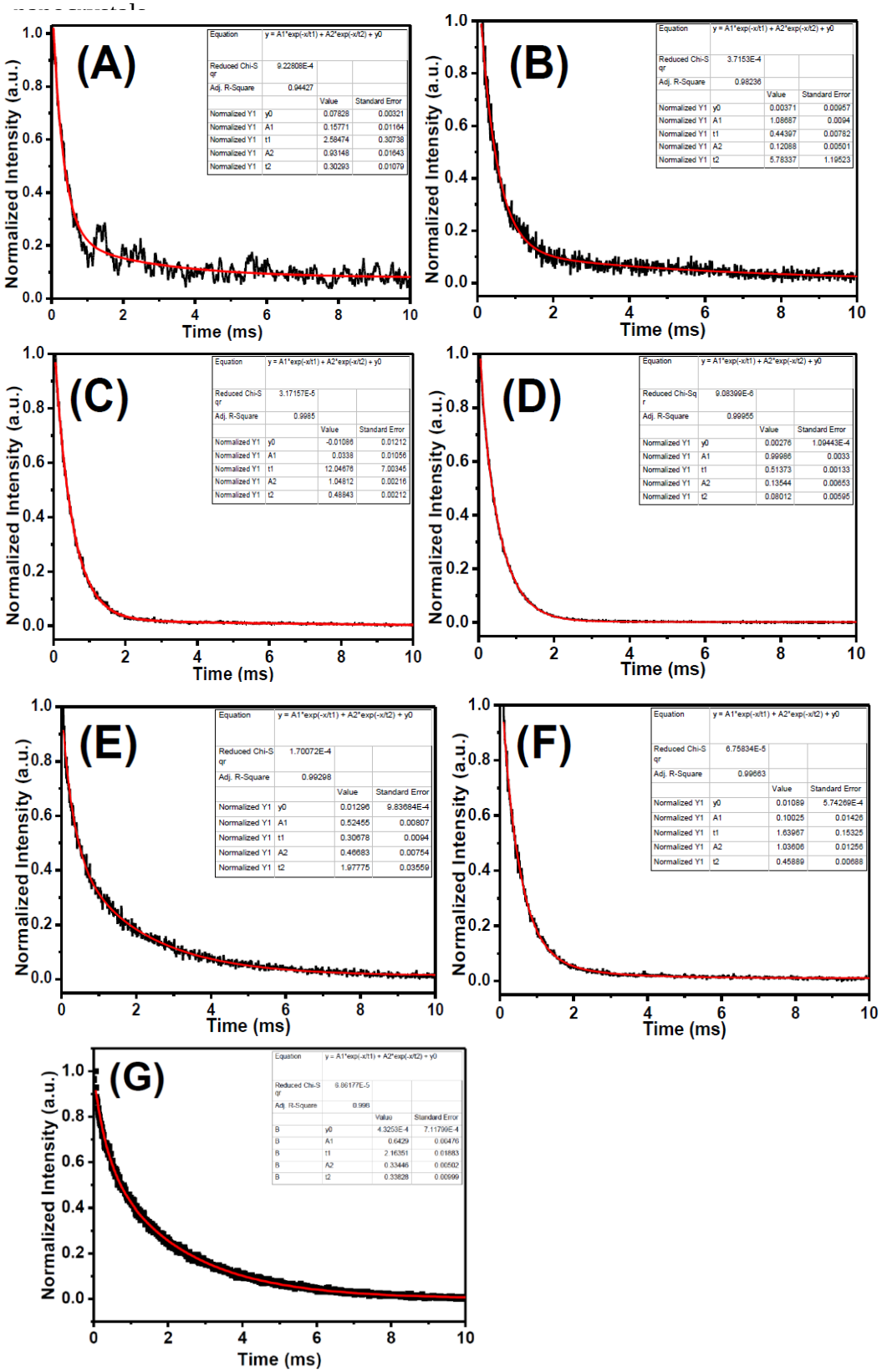


Fig. S4 Photoluminescence decay curve of Eu^{3+} ion in x mol% Eu^{3+} -doped $NaGd(SO_4)_2$ nanocrystals. [x = 1% (A), 2% (B), 3% (C), 5% (D), 10% (E), 15% (F), 8% (G)].

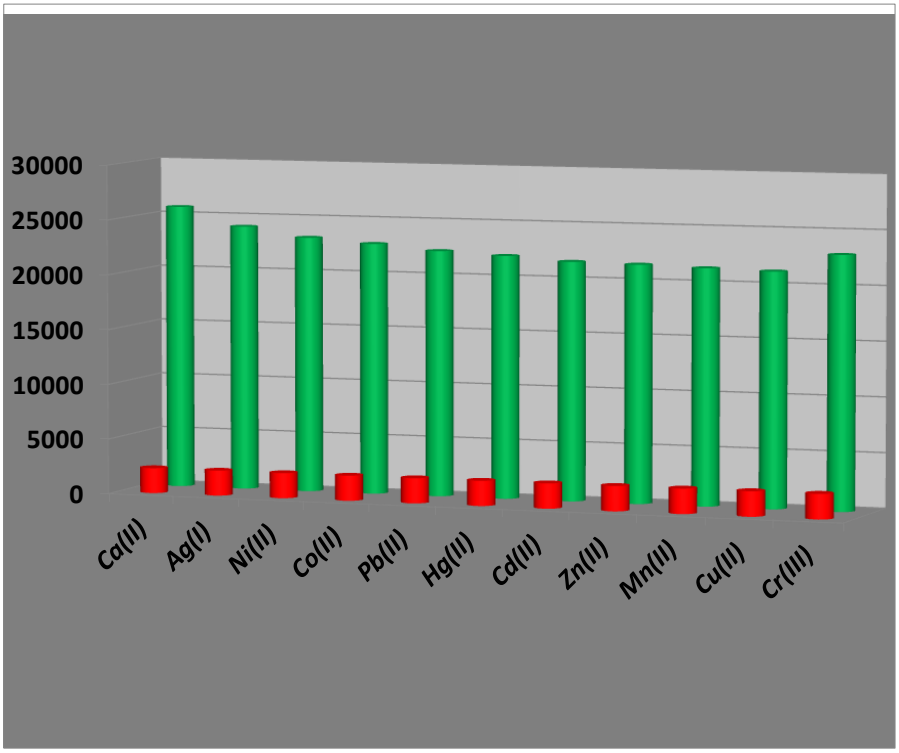


Fig. S5. The bar diagram indicating the selective quenching of Eu^{3+} luminescence intensity for Fe^{3+} adsorption in the presence of various metal ions.

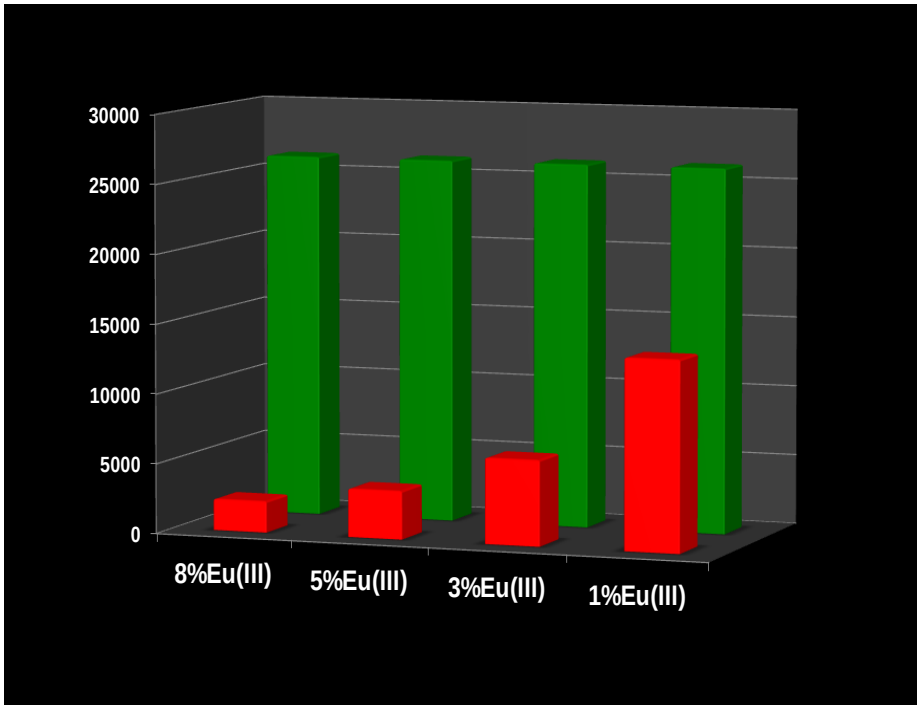


Fig. S6 Plot of normalized Eu^{3+} emission intensity Vs time for 5 and 8 mol% Eu^{3+} -doped $NaGd(SO_4)_2$ nanorods after adding aqueous iron salt solution [10^{-4}(M)] to both.

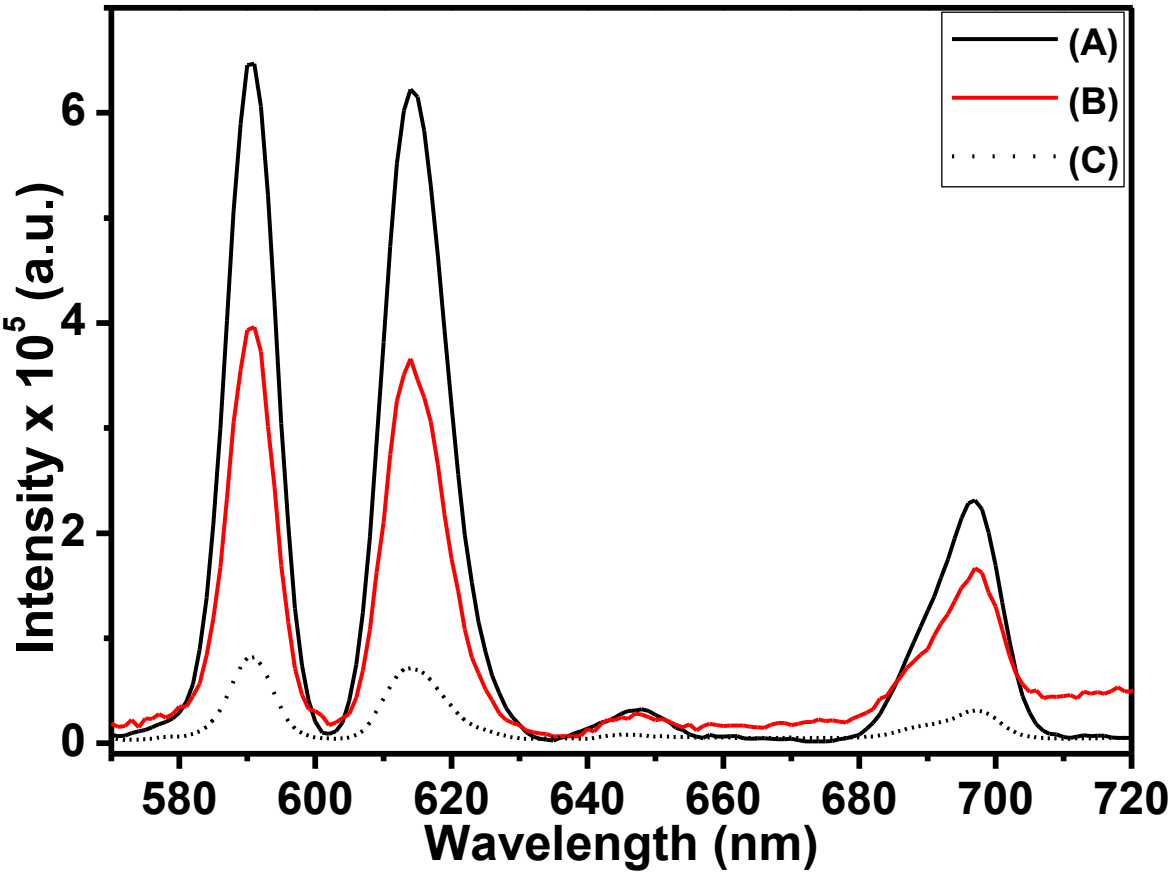


Fig. S7 Emission spectra of (A) Eu-doped $NaGd(SO_4)_2$ nanorods (B) after addition of a mixture containing $6x10^{-4}$ M Fe^{3+} solution and $25\ x10^{-4}$M CH_3COOH (C) addition of $6x10^{-4}$ M Fe^{3+} solution.

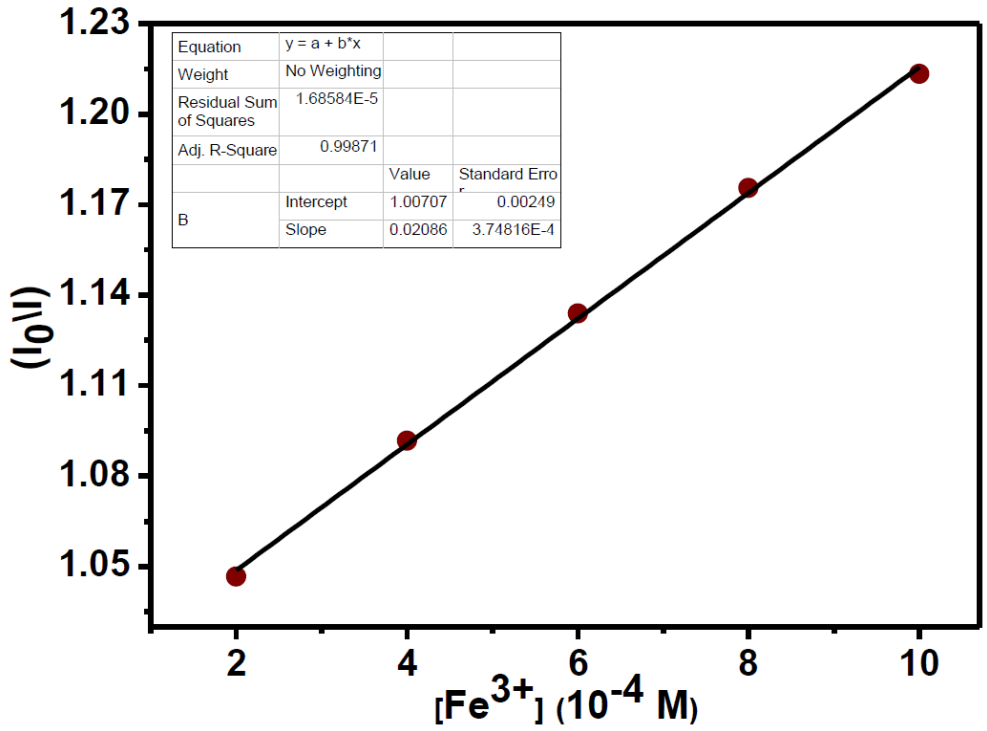


Fig. S8 Stern-Volmer plot of I_0/I Vs Fe^{3+} concentration showing the linear dependence indicating the dynamic nature of the quenching.

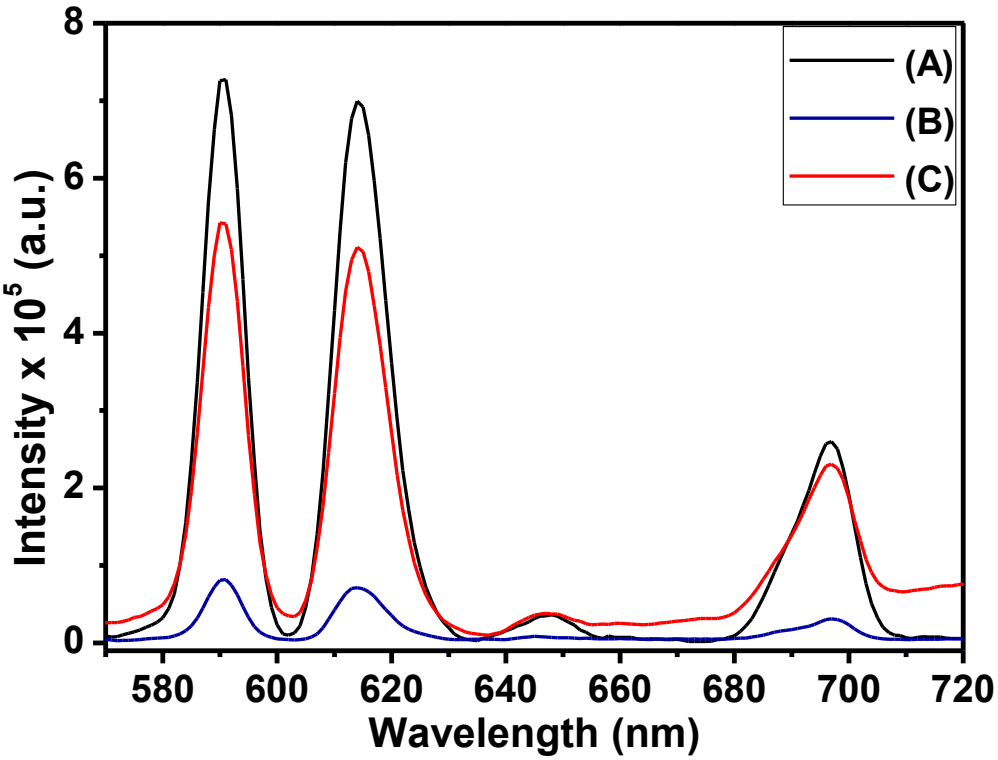


Fig. S9 Photoluminescence of (A) 8 mol% Eu^{3+} -doped $NaGd(SO_4)_2$ nanorods (B) same after addition of $6x10^{-4}$ M Fe^{3+} solution (C) recovery of Eu^{3+} luminescence after addition of 50 $x10^{-4}$M PAA to Fe^{3+}-complexed nanorods.