Supporting Information

HAS functionalized $Gd_2O_3:Eu^{3+}$ nanoparticles as MRI contrast agent and potential luminescent probe for detection of Fe^{3+}, Cr^{3+}, Cu^{2+} in water

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Table S1. Specifications of chemicals used.

Name of Chemicals	Purity^a	Source	CAS No.
Gadolinium(III) Nitrate Hexahydrate	99.9 %	Sigma-Aldrich	19598-90-4
Europium(III) Nitrate Hexahydrate	99.9 %	Sigma- Aldrich	10031-53-5
Urea	AR	Rankem	57-13-6
Polyvinylpyrrolidone (PVP)	99.9 %	Sigma-Aldrich	9003-39-8
Human Serum Albumin	97%	Sigma-Aldrich	A9511
Sodium Hydroxide	AR	Rankem	1310-73-2
Ferric Chloride	AR	Rankem	7705-08-0
Ferrous Chloride	AR	Rankem	7758-94-3
Chromium Chloride	AR	Rankem	10025-73-7
Cupric Chloride	AR	Rankem	7447-39-4
Zinc Chloride	AR	Rankem	7646-85-7
Manganese Chloride	AR	Rankem	13446-34-9
Lead Acetate	AR	Rankem	6080-56-4
Nickel Chloride	AR	Rankem	7718-54-9
Cobalt Chloride	AR	Rankem	7646-79-9
Cadmium Chloride	AR	Rankem	10108-64-2
Calcium Chloride	AR	Rankem	10043-52-4
Sodium Chloride	AR	Rankem	7647-14-5
Potassium Chloride	AR	Rankem	7447-40-7
Mercuric Chloride	AR	Rankem	7487-94-7
Magnesium Chloride	99%	Sigma-Aldrich	M9272
Aluminium Chloride	99.99%	Sigma-Aldrich	294713
RPMI-1640 Medium	-	Sigma-Aldrich	R0883
Dulbecco's Modified Eagle's Medium (DMEM)	-	Sigma-Aldrich	D6046

^{a}purity as provided by suppliers
A.R. = Analytical grade

Table S2 Thermodynamic decomposition parameters of $PVP@Gd_2O_3:Eu^{3+}$ NPs calculated from TGA/DTA data.

Thermodynamic Parameters	$PVP@Gd_2O_3:Eu^{3+}$

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E (KJ·mol^{-1})	75.2578
A(min^{-1})	51.5160
ΔS (KJ· mole^{-1}·K)	-0.2181
ΔH (KJ·mol^{-1})	-4.9560
ΔG (KJ·mol^{-1})	127.0019

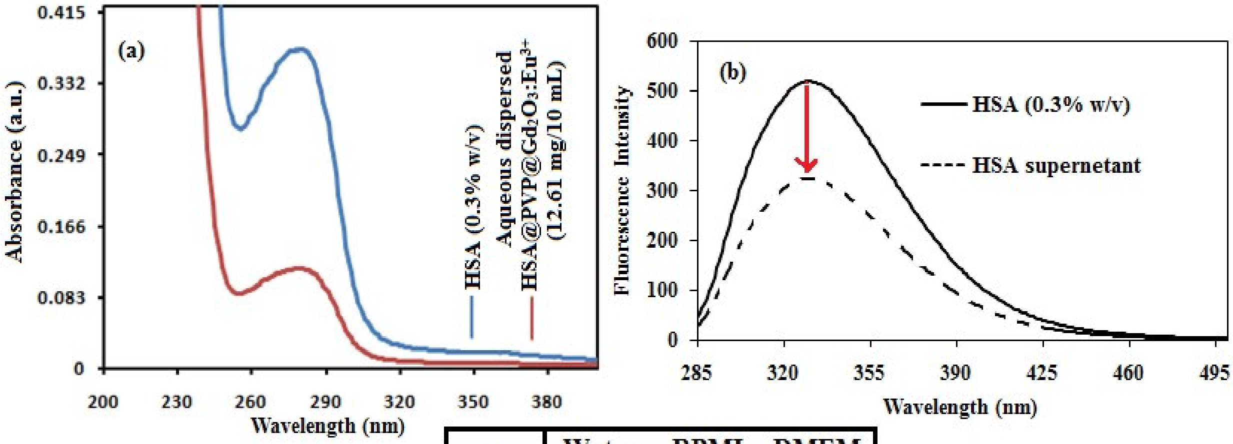
Table S3. Particle size distribution and zeta potential of PVP@Gd_2O_3:Eu^{3+} NPs and HSA@PVP@Gd_2O_3:Eu^{3+} NPs dispersed in different aqueous mediums.

Nanoparticles		**Diameter (nm)**	**Volume %**	**width**	**Zeta Potential (mv)**
Aqueous dispersed nanoparticles					
PVP@Gd_2O_3:Eu^{3+}		106.40	100.00	78.50	25.39
HSA@PVP@Gd_2O_3:Eu^{3+}		144.90	100.00	78.00	48.22
At varied pH					
PVP@Gd_2O_3:Eu^{3+}	pH 3	11.99	100.00	26.55	61.51
	pH 12	136.50	100.00	97.70	-25.41
HSA@PVP@Gd_2O_3:Eu^{3+}	pH 3	3510.00	21.10	523.00	50.09
		148.40	13.90	2939.00	
		31.70	65.00	18.18	
	pH 12	767.00	4.50	221.40	-31.84
		193.70	95.50	125.30	
with 7 mM NaCl concentration					
PVP@Gd_2O_3:Eu^{3+}		124.80	100.00	173.00	22.12
HSA@PVP@Gd_2O_3:Eu^{3+}		167.40	100.00	100.90	45.97
With 20 mM Surfactant					
PVP@Gd_2O_3:Eu^{3+}	DTAB	6000.00	3.60	637.00	16.20
		162.20	39.00	105.40	
		5.64	57.40	3.69	
	SDS	245.70	26.40	203.80	7.25
		14.98	73.60	3.40	
	Tween 20	1073	1.60	200.00	25.75
		175.90	98.40	112.20	
HSA@PVP@Gd_2O_3:Eu^{3+}	DTAB	193.20	100.00	256.90	11.20
	SDS	182.60	100.00	202.00	28.98
	Tween 20	767.00	4.50	221.40	30.59
		193.70	95.50	125.30	
With DMEM (Biological media)					
PVP@Gd_2O_3:Eu^{3+}	24 h	191.50	100.00	133.20	20.30
	48 h	188.60	100.00	112.20	18.07
PVP@Gd_2O_3:Eu^{3+}-HSA	24 h	145.30	100.00	131.00	65.63
	48 h	143.40	100.00	116.90	58.94
With RPMI (Biological media)					
PVP@Gd_2O_3:Eu^{3+}	24 h	194.40	100.00	155.60	19.31
	48 h	201.10	100.00	138.70	17.67

PVP@Gd_2O_3:Eu^{3+}-HSA	24 h	146.40	100.00	106.90	48.02
	48 h	143.50	100.00	98.10	48.08

Table S4. Stern-Volmer parameters for different metal ions with PVP@Gd_2O_3:Eu^{3+} NPs and HSA@PVP@Gd_2O_3:Eu^{3+} NPs.

Ions	K_Q (M^{-1})	Intercept	R^2	Concentration range (M)
PVP@Gd_2O_3:Eu^{3+}				
Fe^{3+}	16594	0.811	0.994	1.2×10^{-5} to 1.2×10^{-4}
PVP@Gd_2O_3:Eu^{3+} in presence of 3.33 ppm Cu^{2+} and Cr^{3+} ions				
Fe^{3+}	16593	0.799	0.985	1.2×10^{-5} to 1.2×10^{-4}
HSA@PVP@Gd_2O_3:Eu^{3+}				
Fe^{3+}	5155	1.161	0.995	2.7×10^{-6} to 1.1×10^{-4}
HSA@PVP@Gd_2O_3:Eu^{3+} in presence of 0.667 ppm Cu^{2+} and Cr^{3+} ions				
Fe^{3+}	4717	1.194	0.985	2.7×10^{-6} to 1.1×10^{-4}
PVP@Gd_2O_3:Eu^{3+}				
Cr^{3+}	4354	0.828	0.960	3.2×10^{-5} to 2.2×10^{-4}
PVP@Gd_2O_3:Eu^{3+} in presence of 3.33 ppm Fe^{3+} and Cu^{2+} ions				
Cr^{3+}	4434	0.834	0.984	3.2×10^{-5} to 2.2×10^{-4}
HSA@PVP@Gd_2O_3:Eu^{3+}				
Cr^{3+}	1984	1.159	0.979	6.3×10^{-6} to 1.9×10^{-4}
HSA@PVP@Gd_2O_3:Eu^{3+} in presence of 0.667 ppm Fe^{3+} and Cu^{2+} ions				
Cr^{3+}	2138	1.145	0.993	6.3×10^{-6} to 1.9×10^{-4}
HSA@PVP@Gd_2O_3:Eu^{3+}				
Cu^{2+}	1564	1.010	0.991	5.2×10^{-5} to 2.1×10^{-4}
PVP@Gd_2O_3:Eu^{3+} in presence of 3.33 ppm Fe^{3+} and Cr^{3+} ions				
Cu^{2+}	1533	1.009	0.988	5.2×10^{-5} to 2.1×10^{-4}
HSA@PVP@Gd_2O_3:Eu^{3+}				
Cu^{2+}	1011	1.108	0.997	1.0×10^{-5} to 1.6×10^{-4}
HSA@PVP@Gd_2O_3:Eu^{3+} in presence of 0.667 ppm Fe^{3+} and Cr^{3+} ions				
Cu^{2+}	1079	1.103	0.996	1.0×10^{-5} to 1.6×10^{-4}



(c)	Water	RPMI	DMEM
	% HSA leaching		
24 h	1.07	1.00	1.03
48 h	1.16	1.04	1.10

Figure S1. (a) UV-Visible absorbance spectra of aq. HSA and aq. dispersed HSA@PVP@Gd_2O_3:Eu^{3+} NPs (b) fluorescence spectra of HSA supernatant left after PVP@Gd_2O_3:Eu^{3+} NPs surface functionalization with HSA (c) percent HSA leaching in water and cell culture media (RPMI and DMEM).

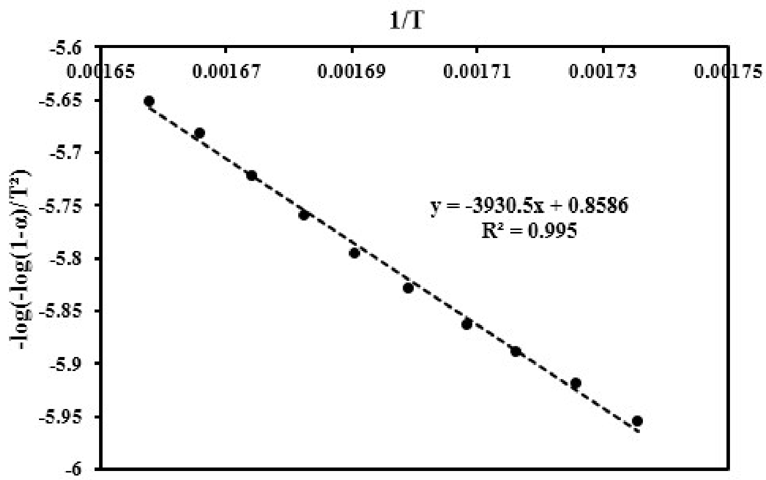


Figure S2 -log(-log(1-α)/T^2) vs 1/T plot for activation energy determination of the PVP@Gd_2O_3:Eu^{3+}.

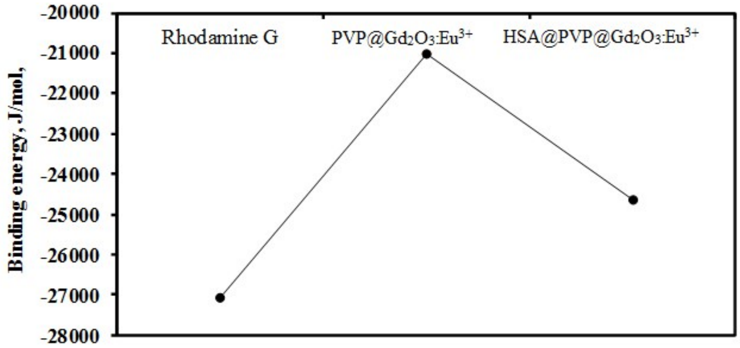
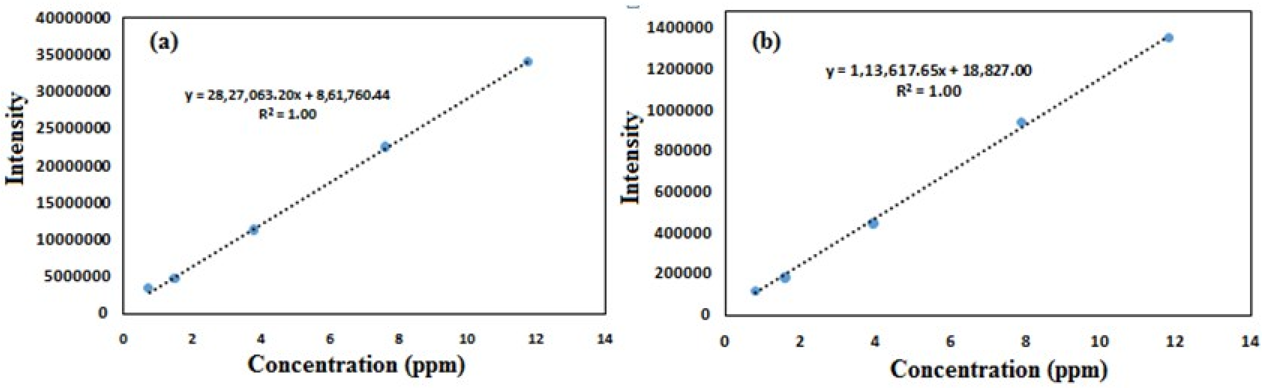


Figure S3 Binding energies of Rhodamine G, PVP@Gd_2O_3:Eu^{3+} and HSA@ PVP@Gd_2O_3:Eu^{3+} calculated with intensities fitted in the Gibbs energy equation.



(c)	PVP@Gd_2O_3:Eu^{3+}	HSA@PVP@Gd_2O_3:Eu^{3+}
	% Gd^{3+} ions leaching	
pH 3	85.28	84.72
pH 5	10.11	10.24
pH 7	0.13	0.17
pH 9	4.13	0.16
	% Eu^{3+} ions leaching	
pH 3	81.58	82.11
pH 5	0.05	0.06
pH 7	0.00	0.00
pH 9	0.02	0.02

Figure S4. ICP-OES calibration plots of: (a) Eu^{3+} and (b) Gd^{3+} ions (c) % leaching of Gd^{3+} and Eu^{3+} ions from NPs when dispersed at different pH as obtained from ICP-OES analysis.

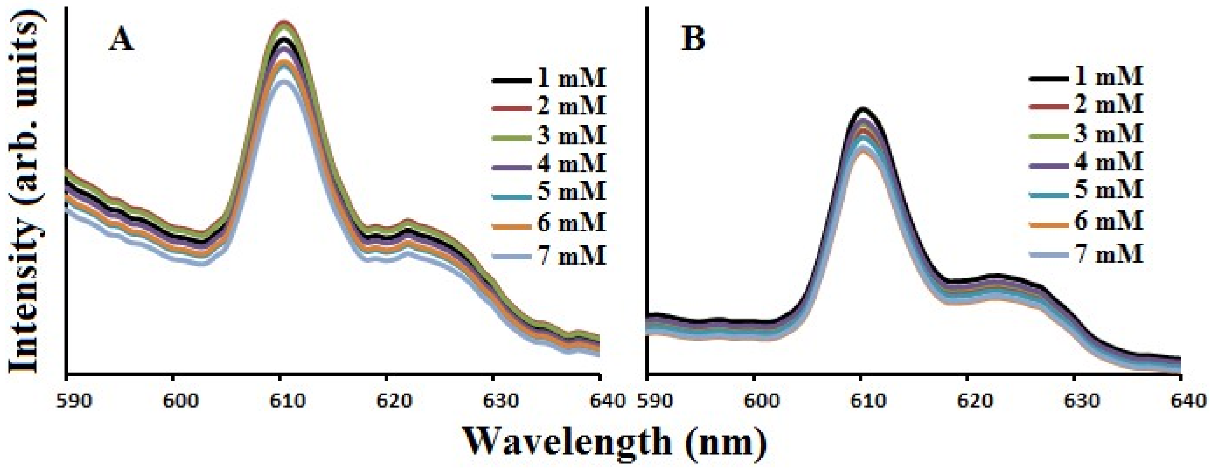


Figure S5. Fluorescence spectra of (A) PVP@Gd_2O_3:Eu^{3+} NPs and (B) HSA@PVP@Gd_2O_3:Eu^{3+} NPs; dispersed in aq. NaCl of different ionic strength.

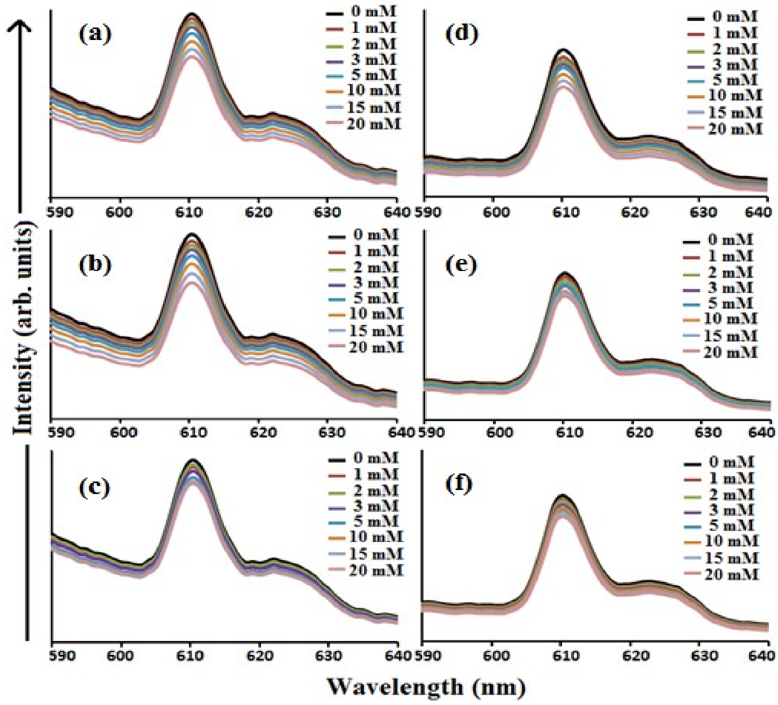


Figure S6. Fluorescence spectra of PVP@Gd_2O_3:Eu^{3+} NPs dispersed in different concentrations of aq. (a) DTAB (b) SDS and (c) Tween 20; and fluorescence spectra of HSA@PVP@Gd_2O_3:Eu^{3+} NPs dispersed in different concentrations of aq. (d) DTAB (e) SDS and (f) TWEEN 20.

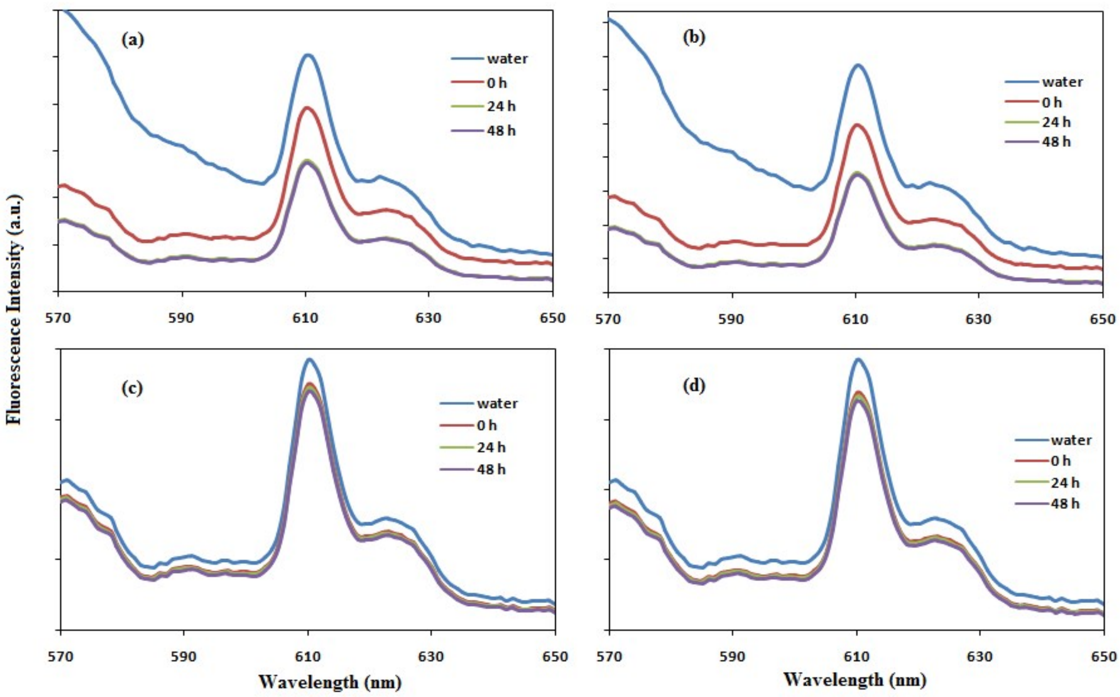


Figure S7. Time dependent fluorescence spectra of PVP@Gd_2O_3:Eu^{3+} NPs dispersed in (a) DMEM (b) RPMI; and HSA@PVP@Gd_2O_3:Eu^{3+} NPs dispersed in (c) DMEM (d) RPMI.

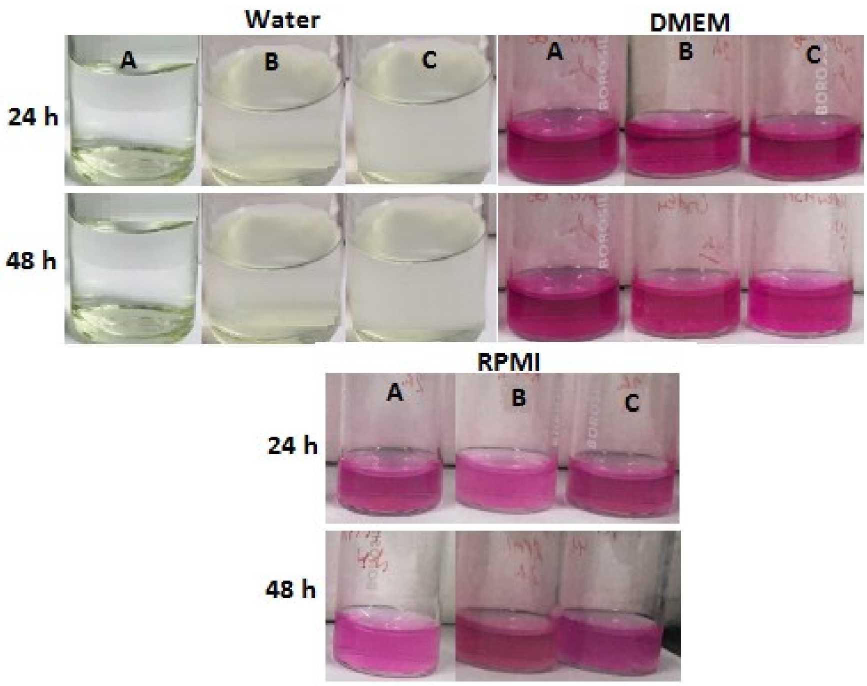


Figure S8. Colloidal stability study: Digital images of (A) blank (B) PVP@Gd_2O_3:Eu^{3+} and (C) HSA@PVP@Gd_2O_3:Eu^{3+} NPs after incubation in different biological media for 48 h.

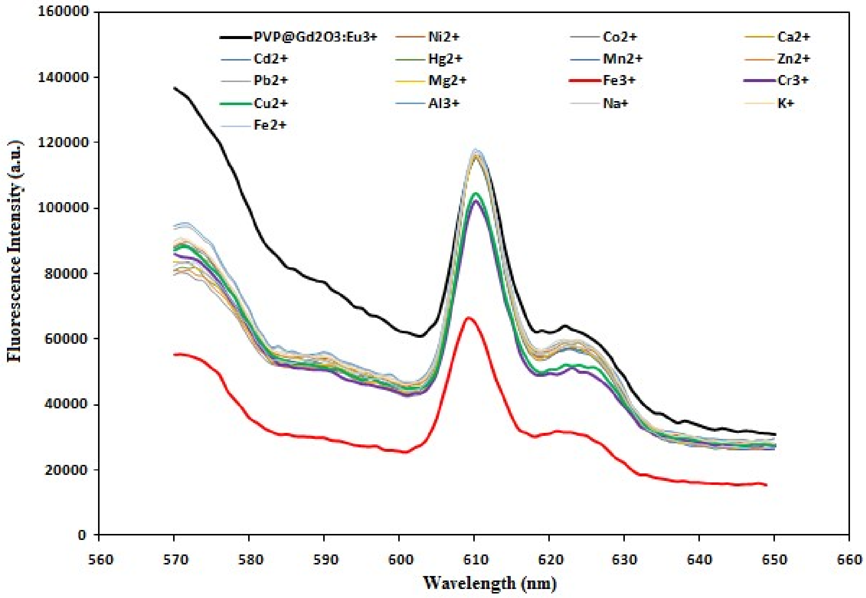


Figure S9. Fluorescence spectra of aq. dispersed PVP@Gd_2O_3:Eu^{3+} NPs in presence of various metal ions of 3.33 ppm concentration.

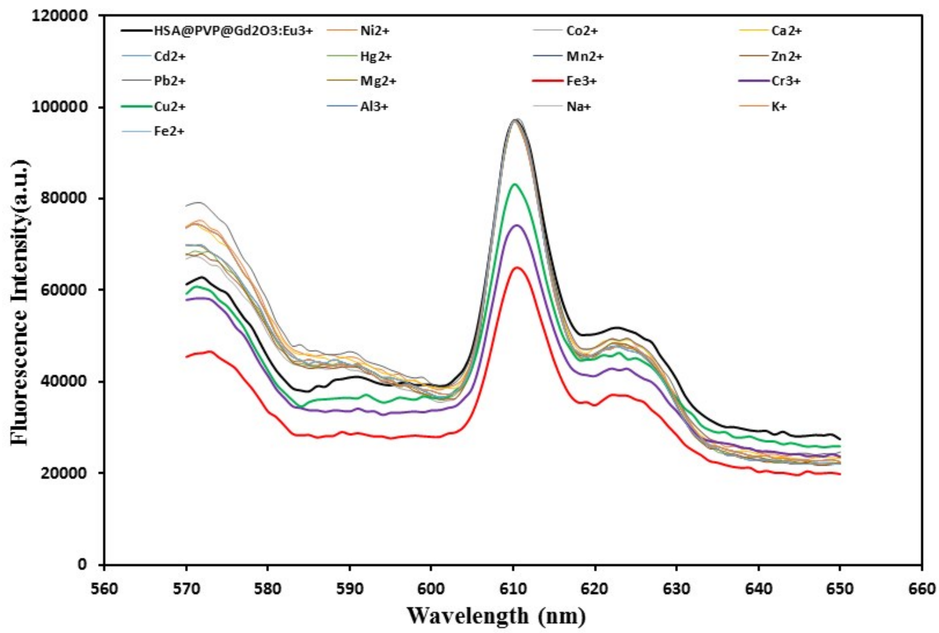


Figure S10. Fluorescence spectra of aq. dispersed HSA@PVP@Gd_2O_3:Eu^{3+} NPs in presence of various metal ions of 3.33 ppm concentration

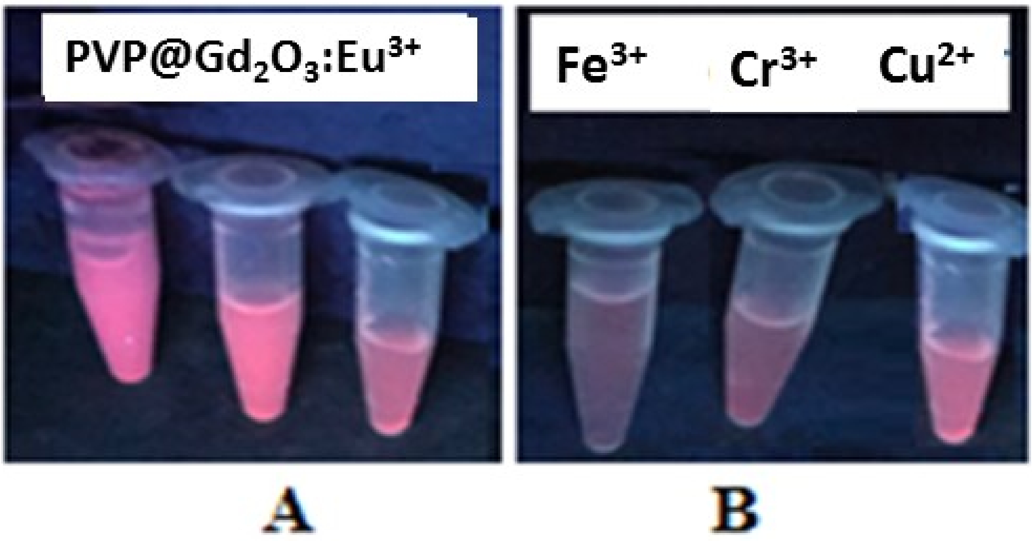


Figure S11. Fluorescence of aqueous dispersed PVP@Gd_2O_3:Eu^{3+} NPs of different concentration (B) fluorescence of aqueous dispersed PVP@Gd_2O_3:Eu^{3+} NPs in presence of metal ions, after being excited by 260 nm UV light.

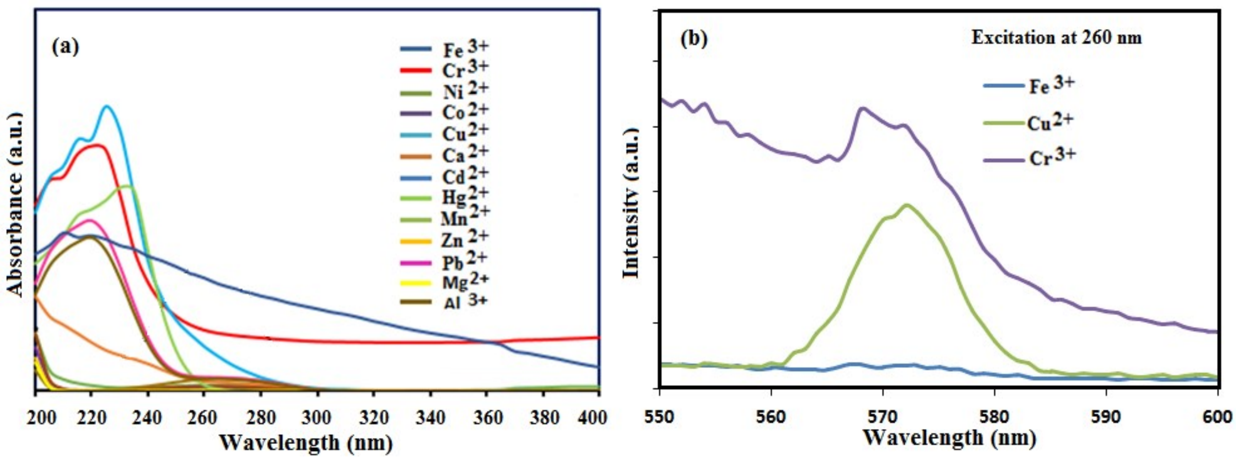


Figure S12 (a) absorbance spectra and (b) Emission spectra of metal ions.

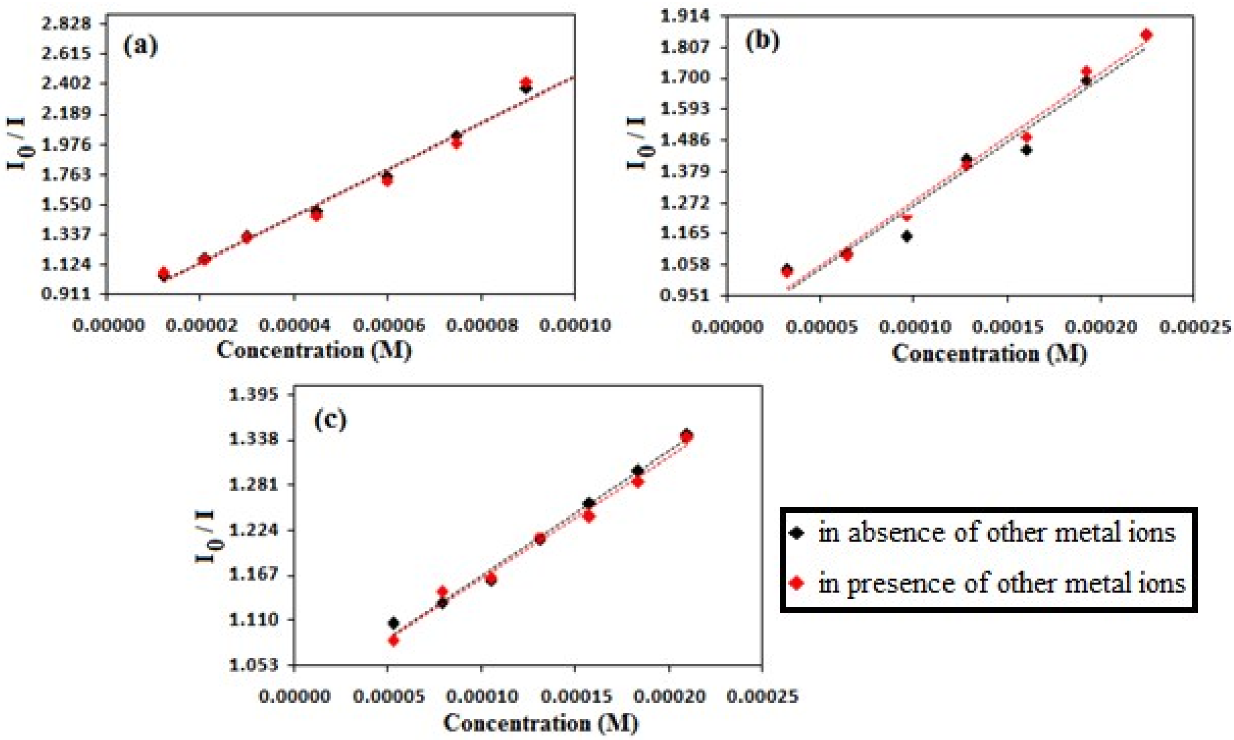


Figure S13. Stern–Volmer plots of aqueous dispersed PVP@Gd_2O_3:Eu^{3+} NPs : (a) I_0/I vs. [Fe^{3+}] in absence and presence of (3.33 ppm Cr^{3+} and Cu^{2+} ions) (b) I_0/I vs. [Cr^{3+}] in absence and presence of (3.33 ppm Fe^{3+} and Cu^{2+} ions) and (c) I_0/I vs. [Cu^{2+}] in absence and presence of (3.33 ppm Fe^{3+} and Cr^{3+} ions).

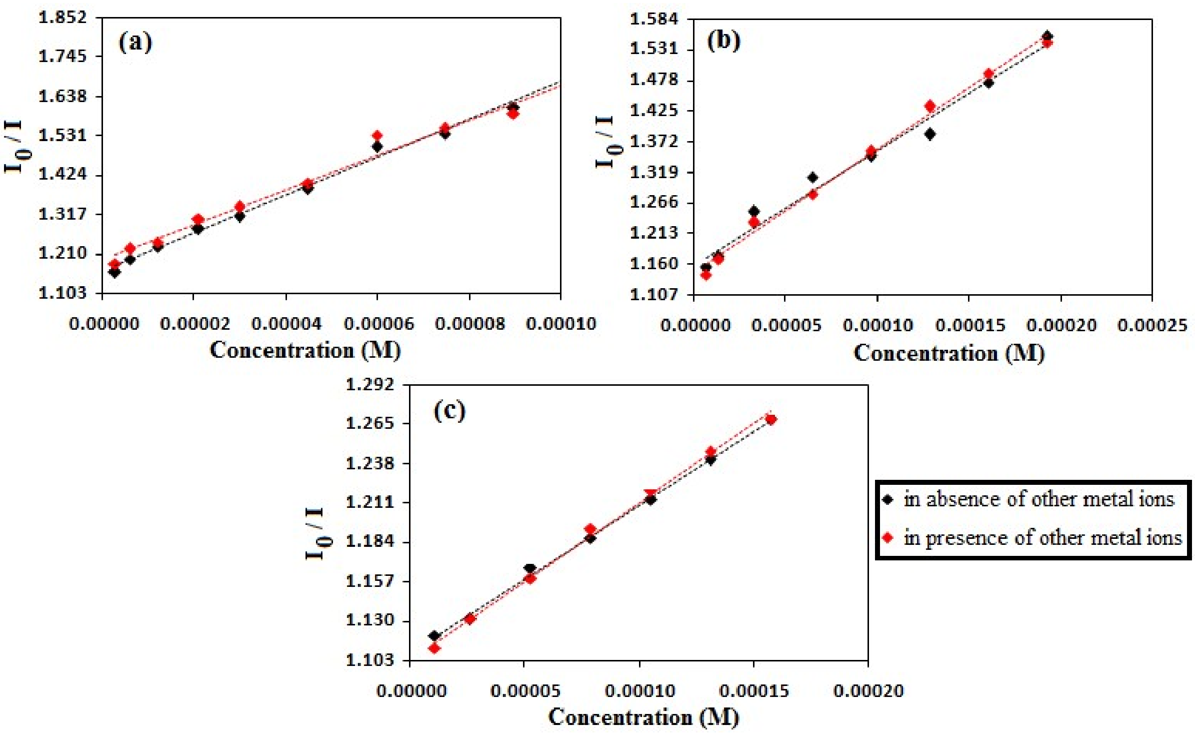
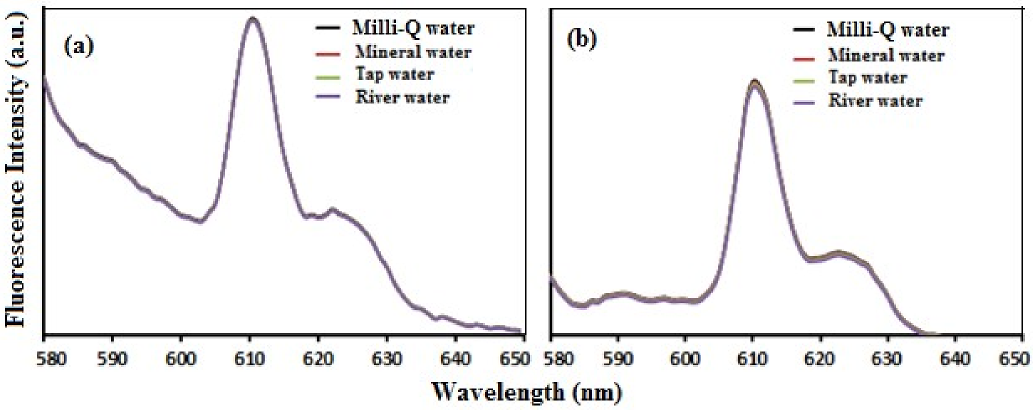


Figure S14. Stern–Volmer plots of aqueous dispersed HSA@PVP@Gd_2O_3:Eu^{3+} NPs: (a) I_0/I vs. [Fe^{3+}] in absence and presence of (0.667 ppm Cr^{3+} and Cu^{2+} ions) (b) I_0/I vs. [Cr^{3+}] in absence and presence of (0.667 ppm Fe^{3+} and Cu^{2+} ions) and (c) I_0/I vs. [Cu^{2+}] in absence and presence of (0.667 ppm Fe^{3+} and Cr^{3+} ions).



(c)	Elements (mg/L)		
	Cr^{3+}	Fe^{3+}	Cu^{2+}
Mineral water	0.113	0.131	0.101
Tap water	0.115	0.071	0.082
Sabarmati river water	0.108	0.065	0.083

Figure S15. Fluorescence of (a) PVP@Gd_2O_3:Eu^{3+} NPs (b) HSA@PVP@Gd_2O_3:Eu^{3+} NPs dispersed in different real water samples (c) ICP-OES analysis of real water samples.