

Supporting Information

Eu (III)-Coordination Polymer Sub-micron Fibers: Material for Selective and Sensitive Detection of Cu²⁺ ions *via* Competition between Photoinduced Electron Transfer and Energy Transfer

Chanchal Hazra,^a Sajjad Ullah,^{a,b} Laís G. Caetano,^a Sidney J. L. Ribeiro^{a*}

^a Institute of Chemistry, São Paulo State University, UNESP, 14800-060, Araraquara, SP, Brazil

^b Institute of Chemical Sciences, University of Peshawar, Peshawar, 25120, KP, Pakistan

KEYWORDS. 3,5-Dinitrosalicylic acid, Guanine, Sub-micron fibers, Photoinduced electron transfer, Energy transfer, Copper (II) ion, Detection.

Preparation of the HEPES buffer solutions at different pH. First, 2.38 g solid HEPES was dissolved in 80 ml milli Q water at room temperature. The pH of the solution was found to be 6.98. To decrease the pH of the solution, 0.1M HCl was added dropwise under vigorous stirring and the pH value reached to 1.03. Now, NaOH micropalates were slowly added to the above solution under vigorous stirring and the particular pH values (i.e. 2.06, 3.05, 4.00, 5.06, 6.04, 7.03, 8.05, 9.08, 10.08, 11.05 and 12.05) were achieved. The total experimental to adjust all certain pH values was followed at room temperature.

Preparation for the stock solutions [10⁻⁶ M concentration] of interference ions. The solution of all interference metal ions was prepared by dissolving CaCl₂.2H₂O, Cd(Ac)₂.4H₂O, CoCl₂.6H₂O, Fe(NO₃)₂.9H₂O, FeCl₂.4H₂O, KNO₃, MnCl₂.4H₂O, NaNO₃, NiCl₂.6H₂O, Pb(NO₃)₂, ZnCl₂, CuSO₄. 5H₂O, AgNO₃, respectively, in water and they were used without any further purification.

Detection of Cu²⁺ ion in tap water samples. The water samples were collected from tap water source. The tap water samples containing different concentrations of Cu²⁺ were prepared by spiking them with standard solutions of Cu²⁺. The Cu²⁺-spiked tap water sample was added to 500 µL 0.1 wt% of Eu-guanine-DNSA suspension and allow the reaction for 10

min. The PL emission intensities at 615 nm were collected under a 355 nm excitation wavelength.

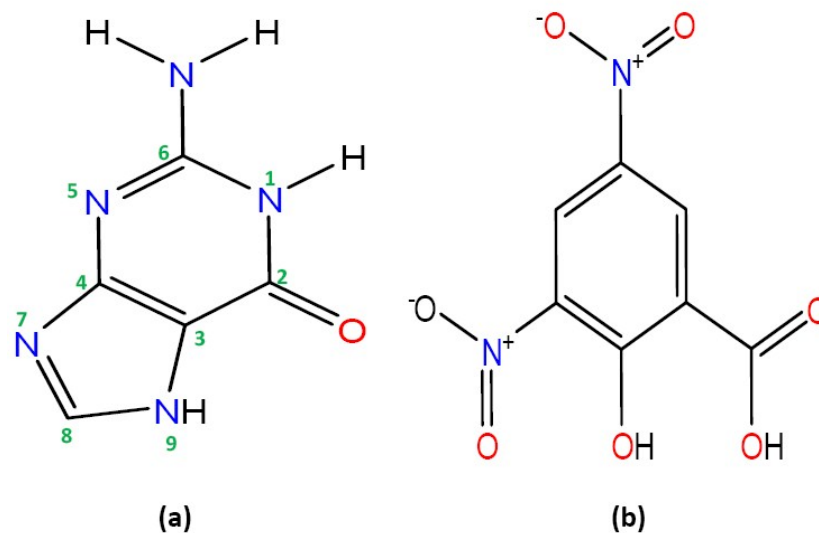


Fig. S1. Chemical structure of (a) Guanine and (b) 2-Hydroxy-3,5-dinitrobenzoic acid (DNSA).

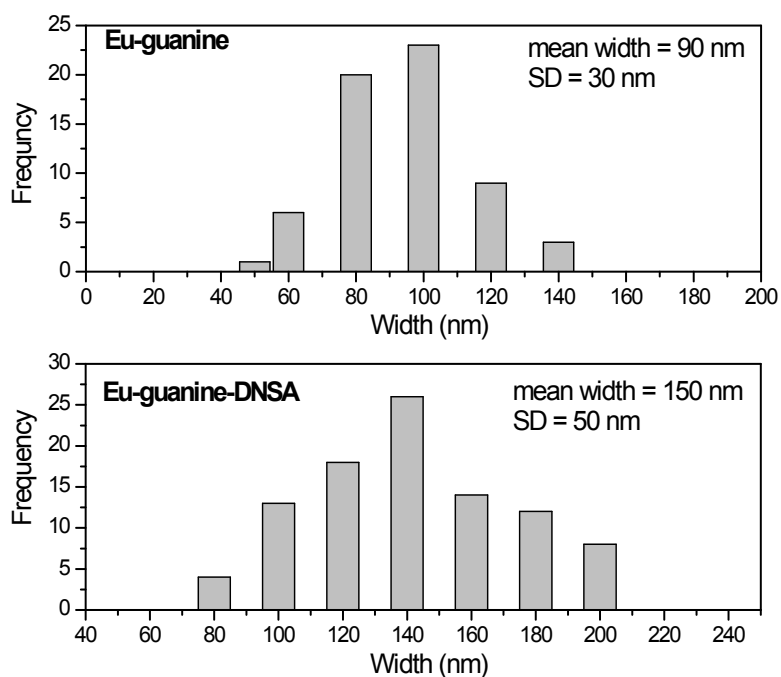


Fig. S2. Width distribution histograms for Eu-guanine (above) and Eu-guanine-DNSA (below) CPMFs.

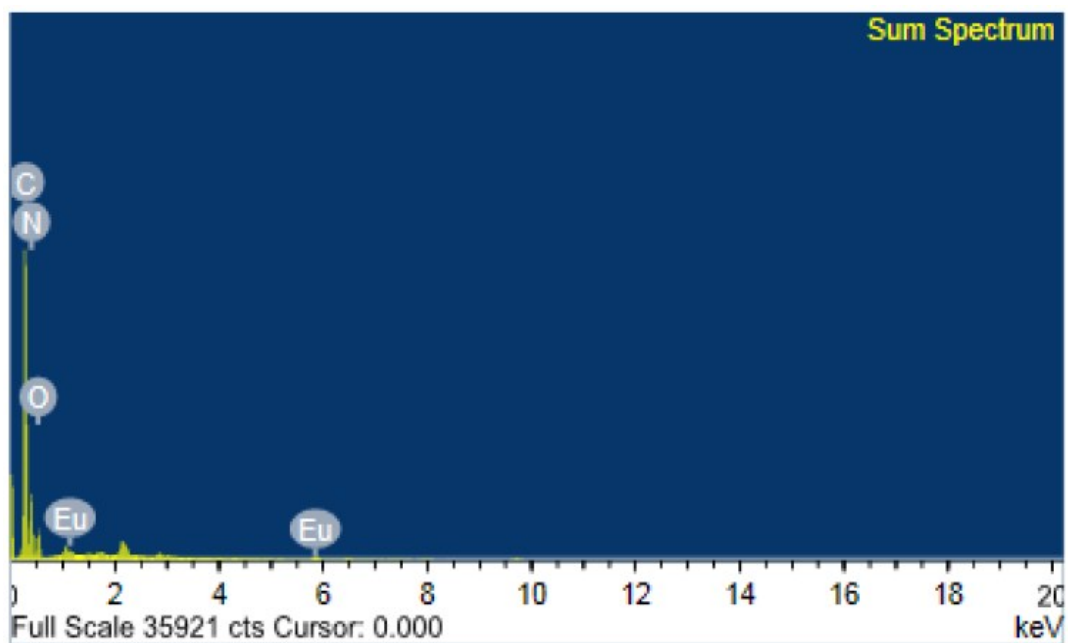


Fig. S3. Energy dispersed spectrum (EDS) of Eu-guanine-DNSA CPMFs.

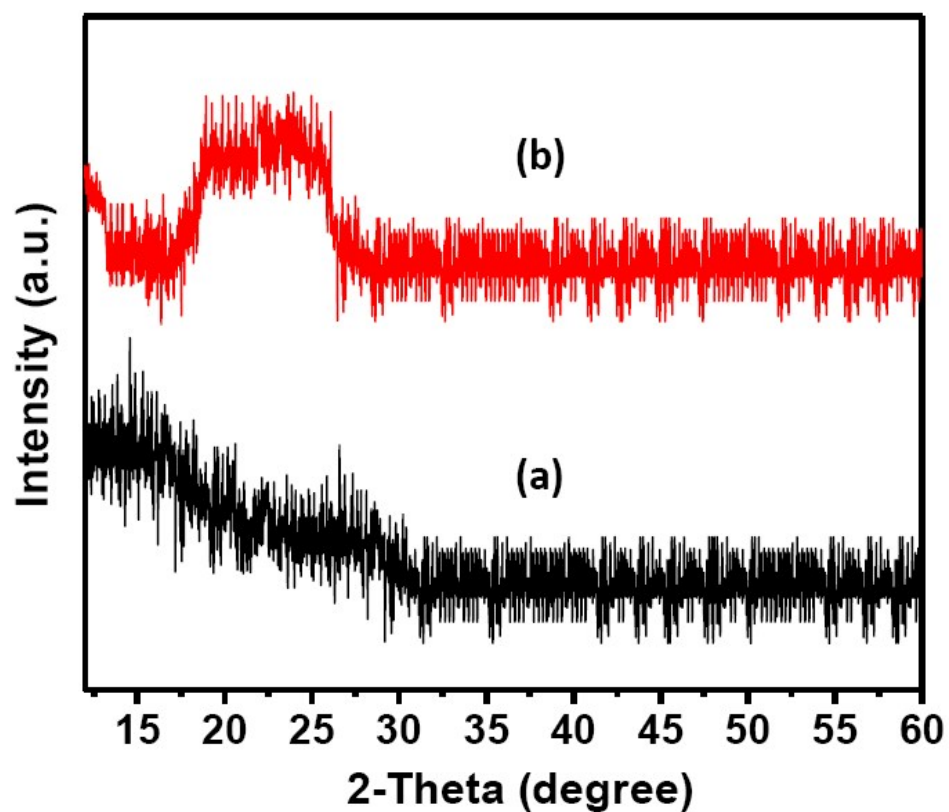


Fig. S4. X-ray diffraction patterns of Eu-guanine (a) and Eu-guanine-DNSA (b) CPMFs.

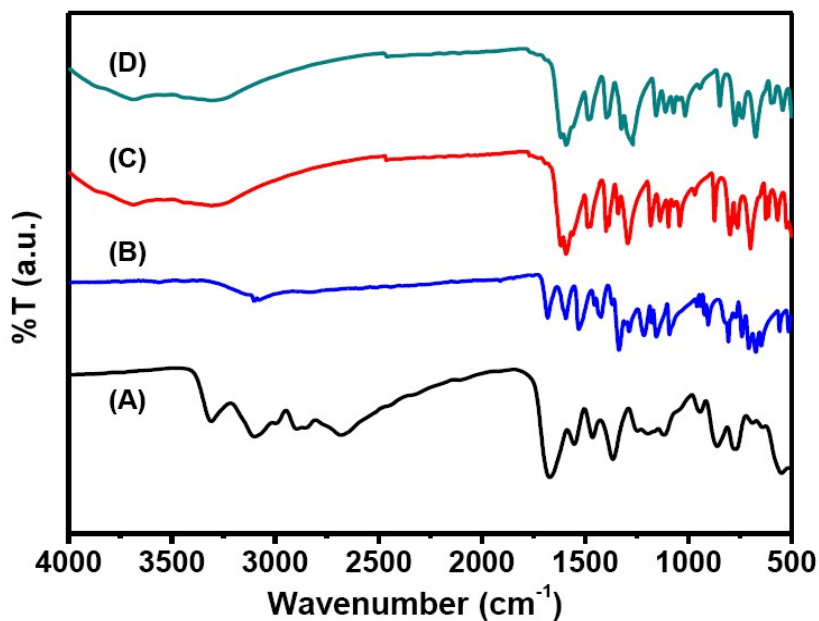


Fig. S5. FTIR spectra of (A) free DNSA molecules (B) free guanine molecules (C) Eu-guanine-DNSA CPMFs (in absence of Cu^{2+}) and (D) Eu-guanine-DNSA CPMFs (in presence of Cu^{2+}).

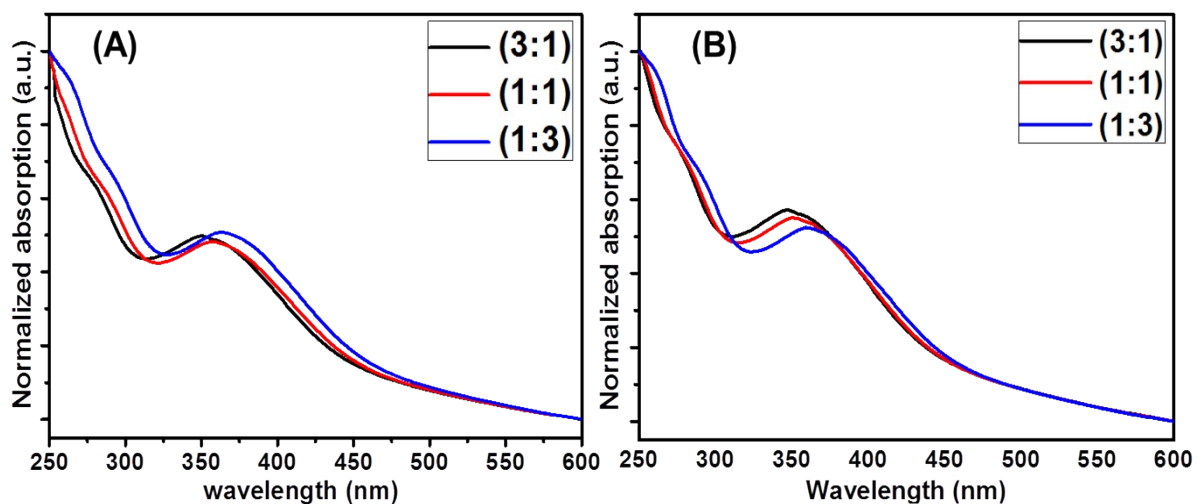


Fig. S6. UV-Visible absorption spectra of isostructural (A) Eu-guanine-DNSA and (B) Gd-guanine-DNSA obtained in $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ solvent mixture of different v/v ratios (3:1, 1:1 and 1:3).

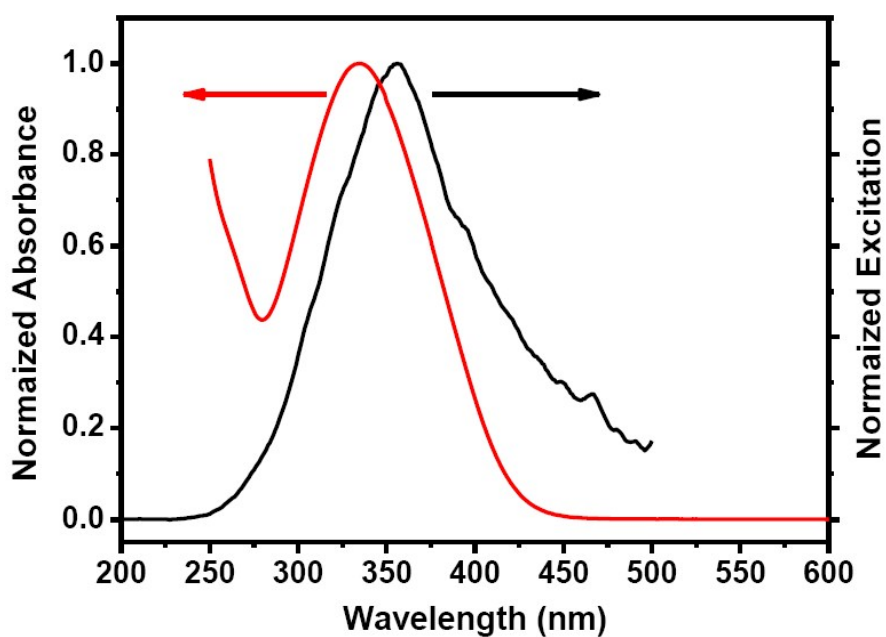


Fig. S7. Normalized absorption spectrum of Eu-DNSA complex (red) and normalized PL excitation spectrum of Eu-guanine-DNSA CPMFs (black). Both spectra are measured in CH₃OH:H₂O (3:1, v/v) mixture.

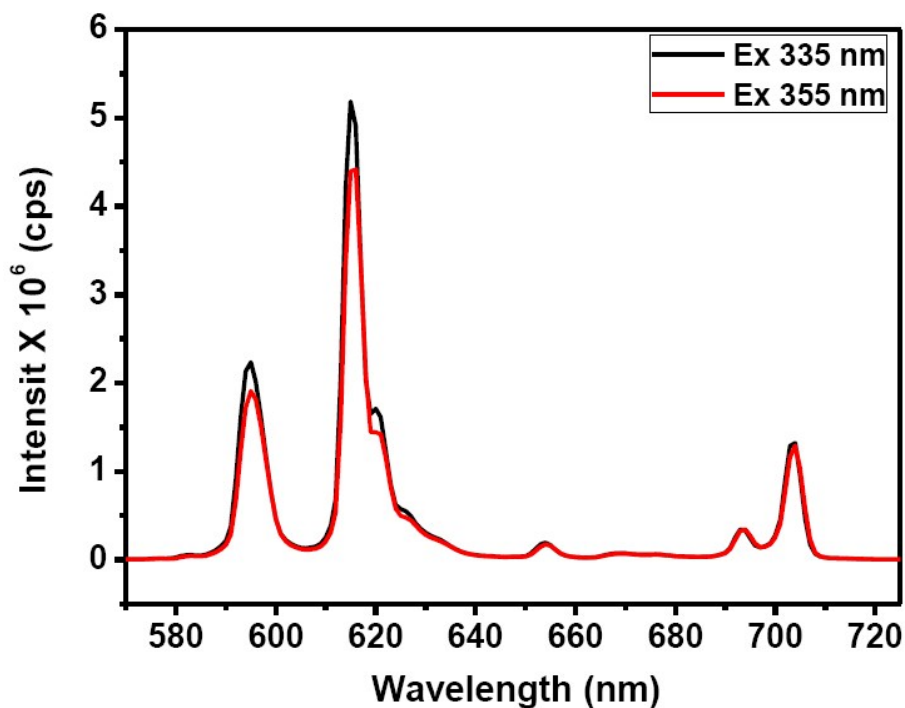


Fig. S8. PL emission spectra of Eu-DNSA complex in CH₃OH:H₂O (3:1, v/v) mixture at both 355 nm and 335 nm excitation.

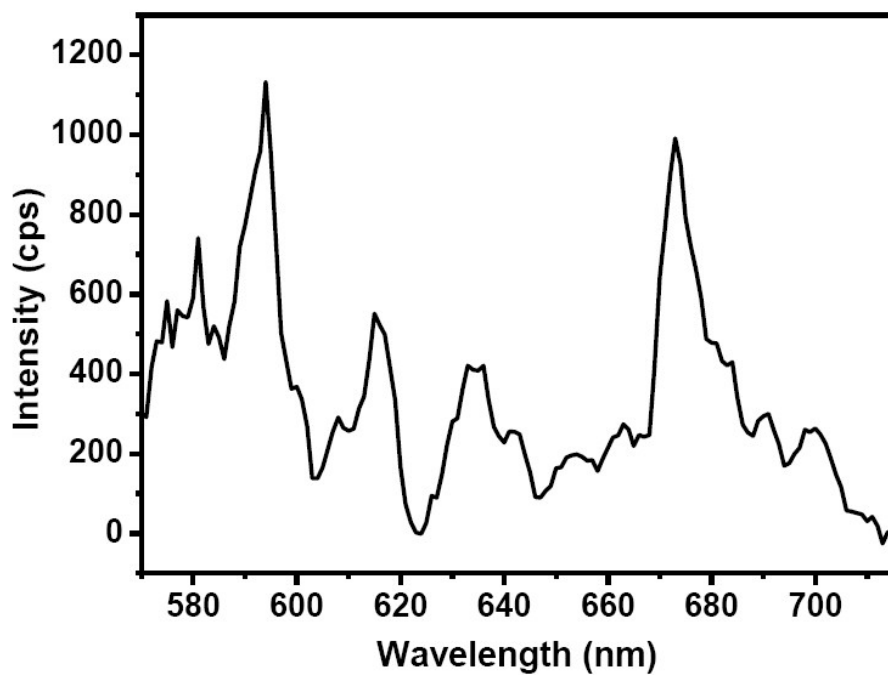


Fig. S9. PL emission of Eu-guanine CPMFs in CH₃OH:H₂O (3:1, v/v) mixture ($\lambda_{\text{ex}} = 355$ nm).

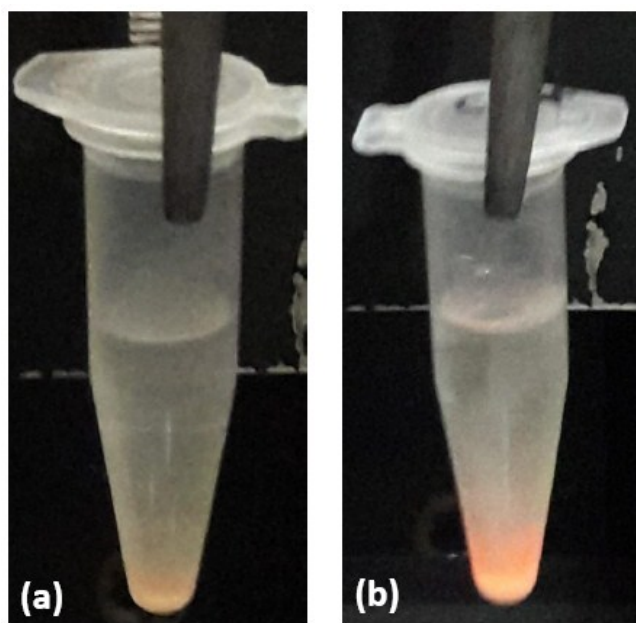


Fig. 10. Digital images (under xenon lamp) showing orange-red emission from the centrifuged sediment of Eu-guanine-DNSA CPMF in absence of Cu²⁺ (weak) (a) and in presence of Cu²⁺ ion (bright) (b).

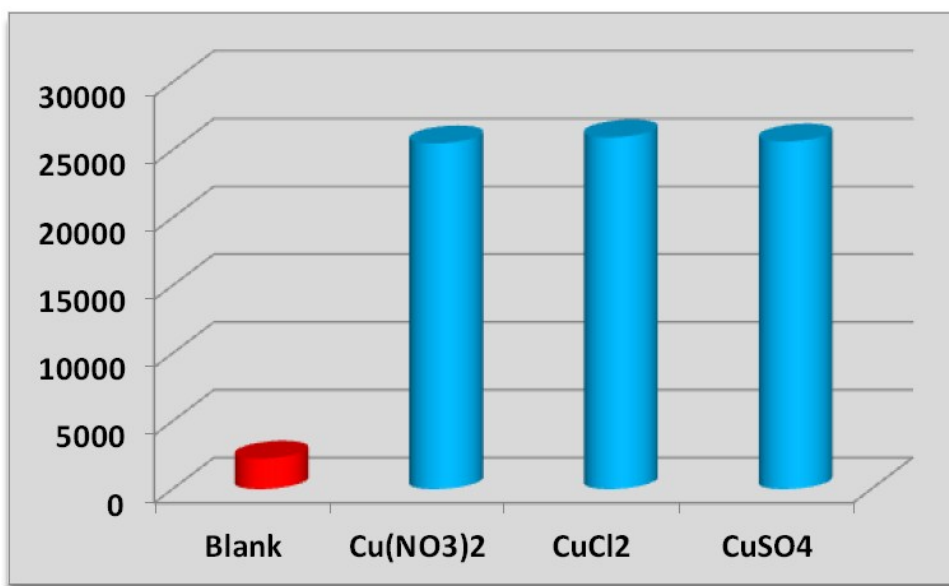


Fig. S11. Bar diagram indicating the absence of any affect by the counter anion of the copper salts on selective detection of Cu²⁺ ions using Eu-guanine-DNSA CPMFs. Blank indicates the PL emission intensity of the Eu-guanine-DNSA CPMFs in the absence of Cu²⁺ ions.

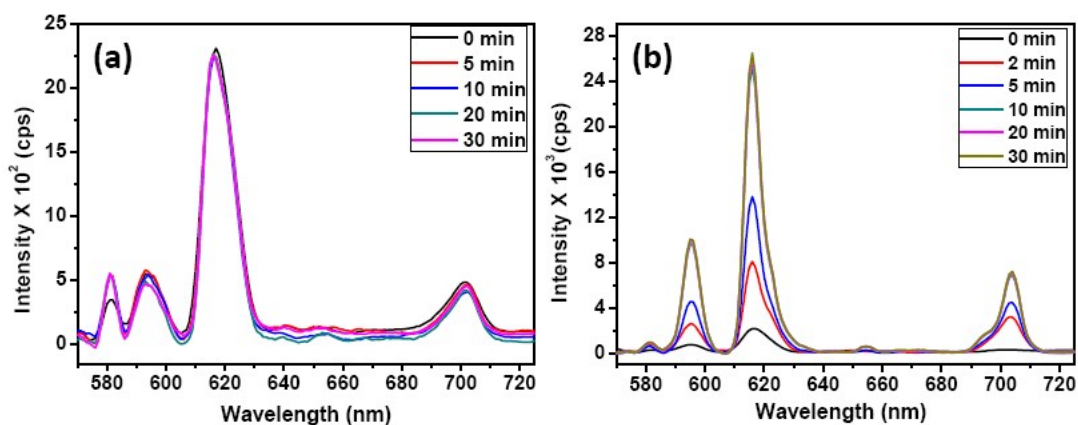


Fig. S12. The change (increase) in the PL emission intensity of Eu-guanine-DNSA CPMFs in absence of Cu²⁺ ion (a) and in presence of Cu²⁺ ion (b) as function of time.

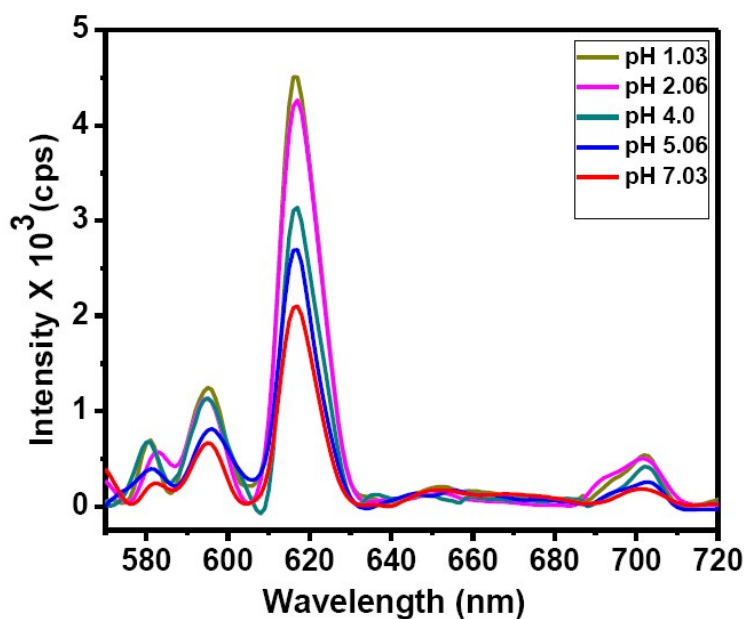


Fig. S13. PL emission spectra of Eu-guanine-DNSA CPMFs with different pH of the solution. All measurements were carried out in CH₃OH:H₂O (3:1, v/v) mixture.

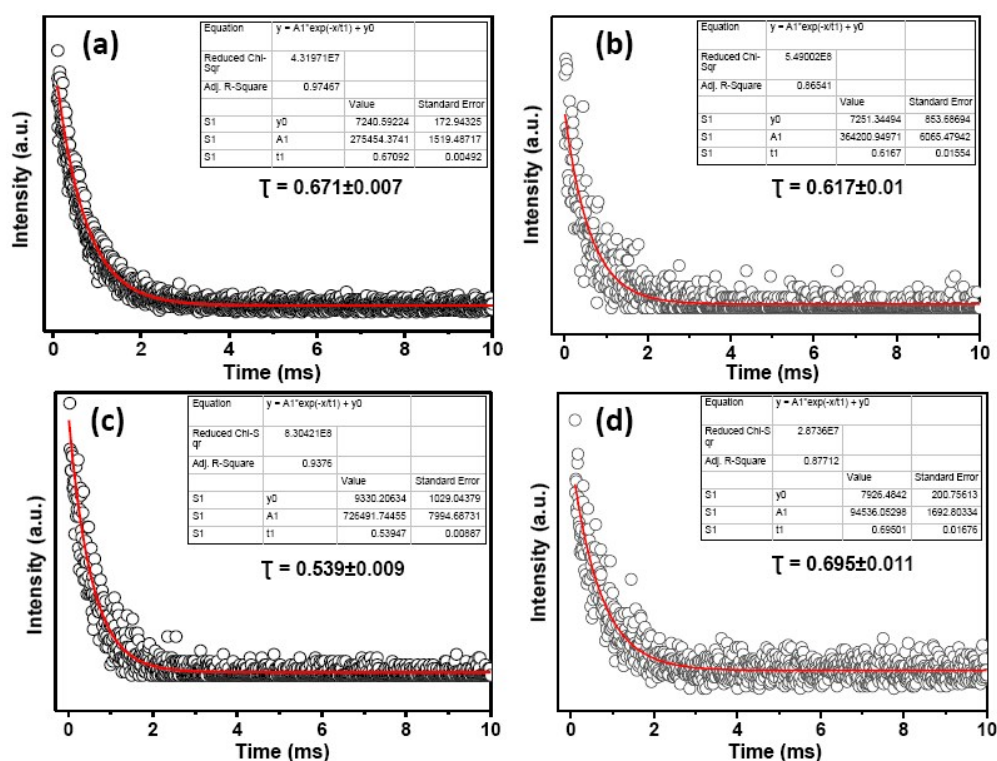


Fig. S14. The PL emission lifetime of (a-c) Eu-guanine-DNSA CPMFs in CH₃OH:H₂O (3:1, v/v) mixture in the absence of Cu²⁺. In the synthesis of CPMFs, the amount of guanine concentration increases from (a) to (c). The PL lifetime of Eu-guanine-DNSA CPMFs in

CH₃OH:H₂O (d) in presence of Cu²⁺ ions (12 μM). (Monitoring wavelength: λ_(ex) = 355 nm and λ_(emi) = 615 nm)

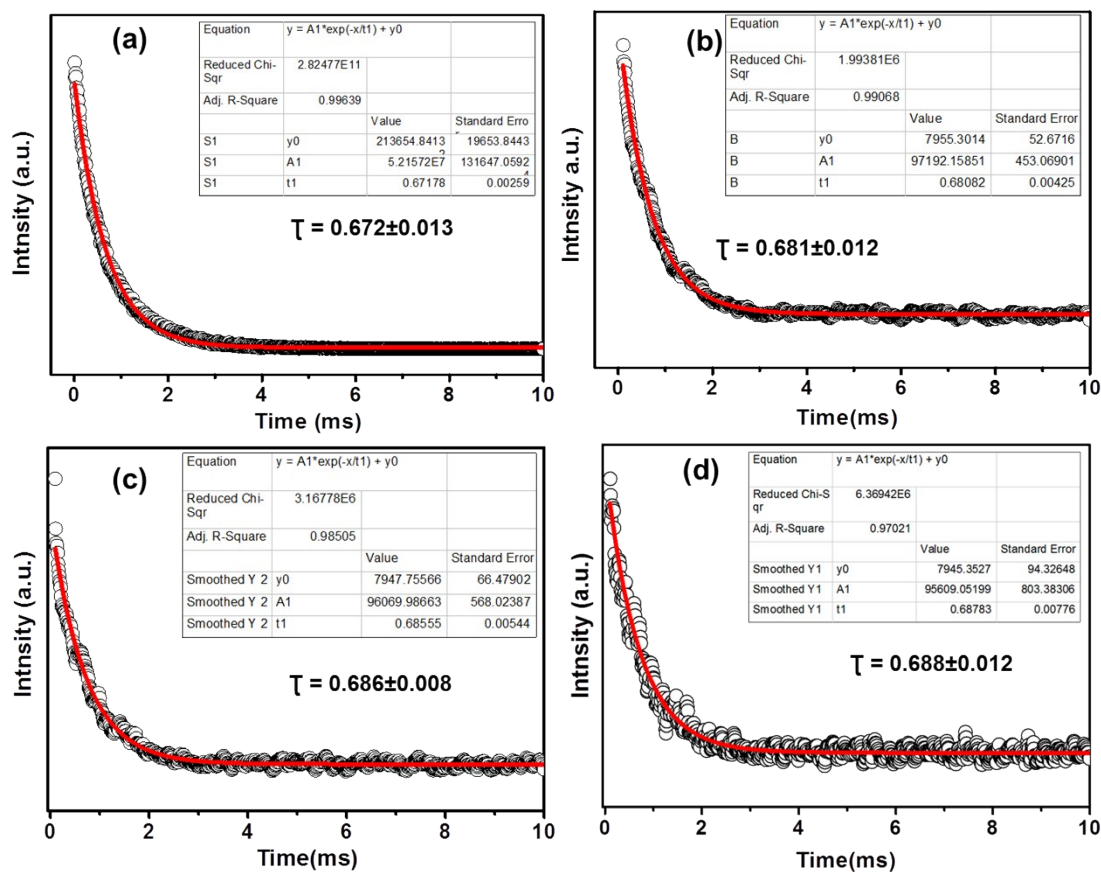


Fig. S15. The PL emission lifetime of Eu-guanine-DNSA CPMFs in CH₃OH:H₂O (3:1, v/v) mixture as function of Cu²⁺ ion concentration. The Cu²⁺ concentration was 2 μM, 5 μM, 7 μM and 10 μM for Fig. a, b, c and d, respectively. (Monitoring wavelength: λ_(ex) = 355 nm and λ_(emi) = 615 nm).

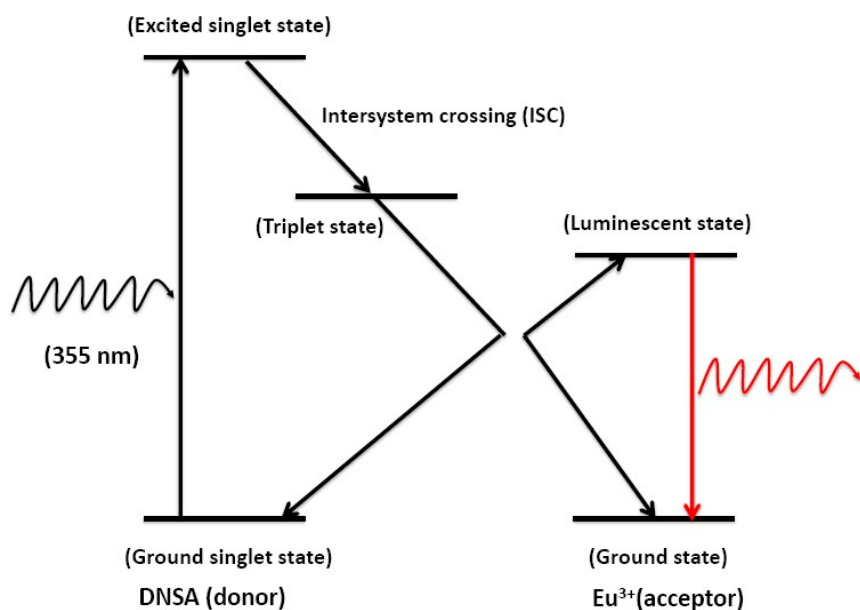


Fig. S16. Intramolecular energy transfer mechanism between DNSA (donor) and Eu³⁺ (acceptor), in presence of Cu²⁺ ion, in Eu-guanine-DNSA CPMFs.

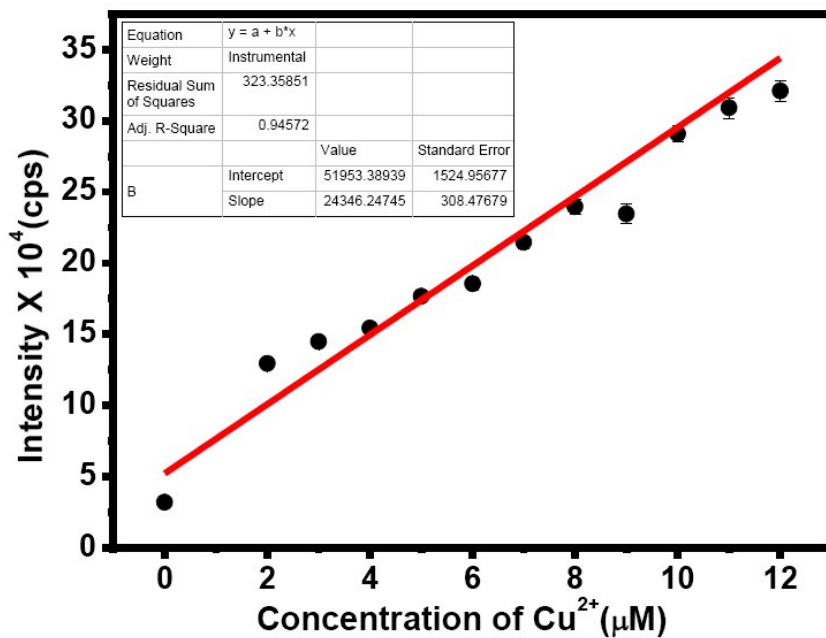


Fig. S17. Calibration curve showing the linear relationship between the integrated luminescence intensity (570–720 nm) of Eu-guanine-DNSA CPMFs (as pristine sample) and Cu²⁺ concentration.

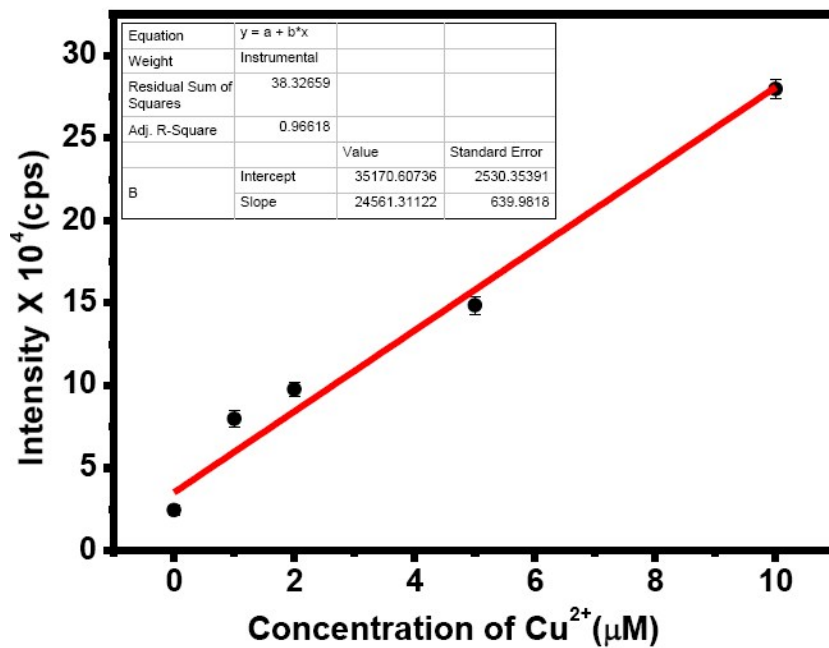


Fig. S18. Calibration curves showing the linear relationship between the integrated luminescence intensity (570–720 nm) of Eu-guanine-DNSA CPMFs (as real or Cu^{2+} spiked tap water samples) and Cu^{2+} concentration.

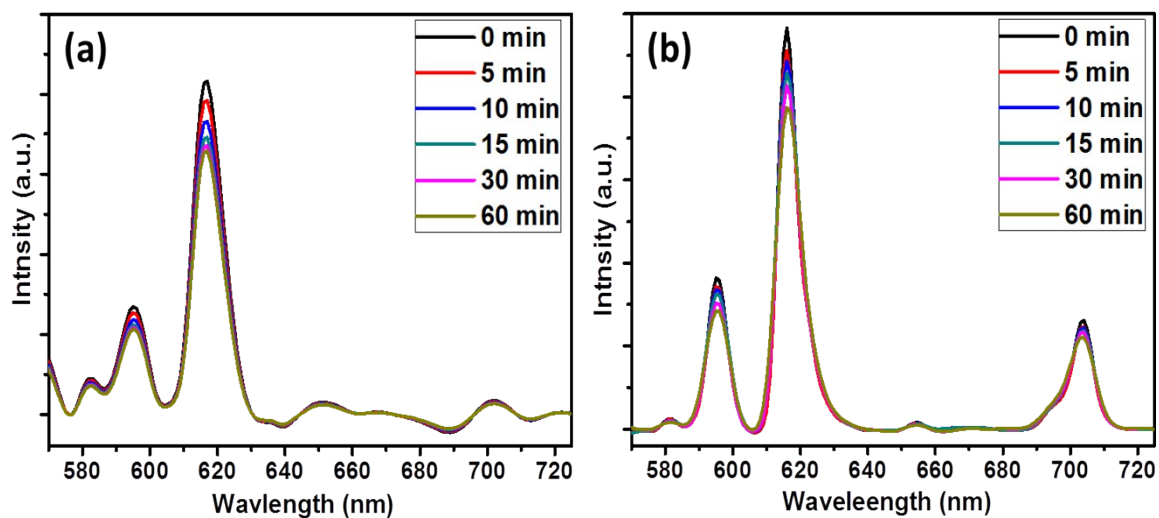


Fig. S19 PL emission spectra of Eu-guanine-DNSA CPMFs in the (a) absence and (b) presence of Cu^{2+} ion upon exposure to UV irradiation (355 nm) for different time intervals.

Table S1. Comparison of different methods for Cu²⁺ detection.

Methods	Linear range	LOD	References
Förster Resonance energy transfer (FRET)	10 ⁻⁶ –10 ⁻⁵ (M)	10 ⁻⁶ (M)	Chem. Commun., 2012, 48, 4860-4862.
Energy transfer using upconverting nanoparticles	0-500 μM	4.6 ppb	Nanoscale, 2012, 4, 6065-6071.
Aggregation induced fluorescence quenching	1-10 μM	0.48 μM	Chem. Eur. J. 2014, 20, 3311-3316.
Fluorescence spectroscopy using fabricated carbon dots	0.833-833 μM	0.3 μM	ACS Appl. Mater. Interfaces, 2015, 7 27262-27270.
Eu ³⁺ luminescence using Eu-guanine-3,-dntrosalicylic acid coordination polymer sub-micron fibers	2-12 μM	1.42 μM	Present work

Table S2. The asymmetric ratio, $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$, values for Eu-guanine-DNSA (as pristine sample) CPMFs for different concentrations Cu^{2+} ions.

Cu²⁺ concentration (μM)	0	2	3	4	5	6	7	8	9	10	11	12
I (⁵D₀→⁷F₁)	659 7.6 34	1855 7.07	2208 7.45	2451 9.61	2826 9.35	3120 6	3525 5.63	3992 2.71	4390 9.04	5807 4.67	5794 1.34	6731 0.63
I (⁵D₀→⁷F₂)	223 57. 81	6720 0.62	7882 2.53	8417 4.72	9630 7.67	1070 98.9	1218 39.8	1401 55	1476 90.2	1716 47.2	1831 37.6	2007 33.5
Asymmetric ratio	3.3 9	3.62	3.57	3.43	3.41	3.43	3.46	3.51	3.36	2.96	3.16	2.98

Table S3. Asymmetric ratio, $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$, values for Eu-guanine-DNSA (as real sample) CPMFs for different concentrations Cu^{2+} ion.

Cu²⁺ concentration (μM)	0	1	2	5	10
I (⁵D₀→⁷F₁)	6236.441	11653.39	16567.91	26197.05	49381.85
I (⁵D₀→⁷F₂)	21179.07	42852.58	57273.94	89925.63	172137.8
Asymmetric ratio	3.396018	3.677265	3.45692	3.432663	3.485853

Table S4. % recovery and RSD values for determination of Cu²⁺ in tap water sample.

Samples	Added tap water	Concentration of Cu²⁺ added (μM)	Concentration of Cu²⁺ found (μM)	RSD (% , 3 measurements)	% Recovery
1	100 μL	1	1.207	2.64	120.7
2	"	2	2.178	3.00	108.90
3	"	5	4.683	9.77	93.66
4	"	10	9.34	7.33	93.40