

Supporting Information

Gallic acid capped Tb³⁺-doped CaF₂ nanocrystals: An efficient optical probe for the detection of carbonate and bicarbonate ions

Venkata N. K. B. Adusumalli^{#§ a}, Heramba V. S. R. M. Koppiseti^{# a}, Nikita Madhukar^a, Ayan Mondal^a and Venkataramanan Mahalingam^{*a}

a. Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur, Nadia 741246

* mvenkataramanan@yahoo.com

Both authors contributed equally to the work

§ Current affiliation: School of Chemical Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju 61186, South-Korea

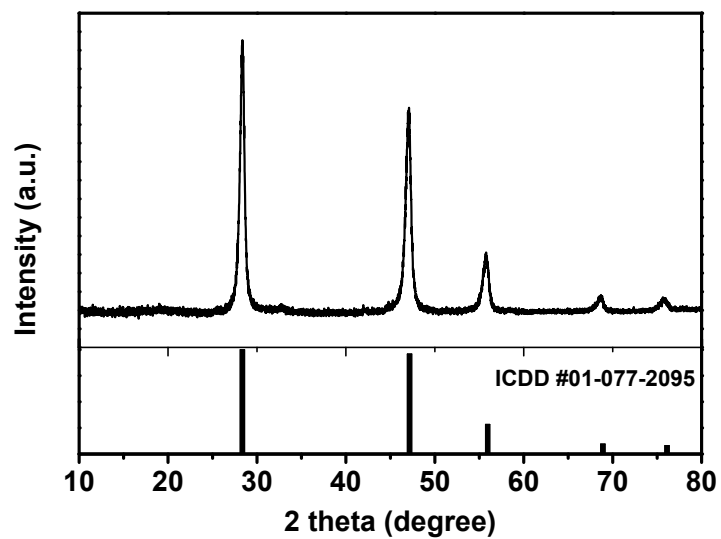


Fig. S1. X-Ray powder diffraction (XRD) pattern of gallic acid (GA)-capped $\text{CaF}_2:\text{Tb}^{3+}$ (2%) nanocrystals (NCs). The vertical lines at the bottom is the standard pattern of bulk CaF_2 .

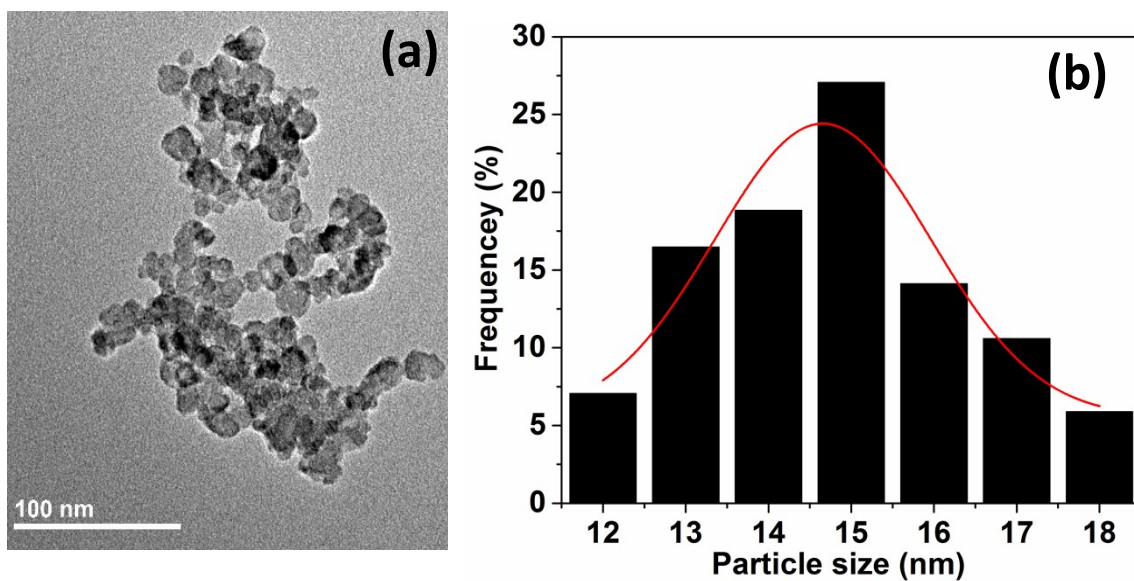


Fig. S2. (a) TEM image of the GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ (2%) NCs. (b) Histogram shows the particle size distribution.

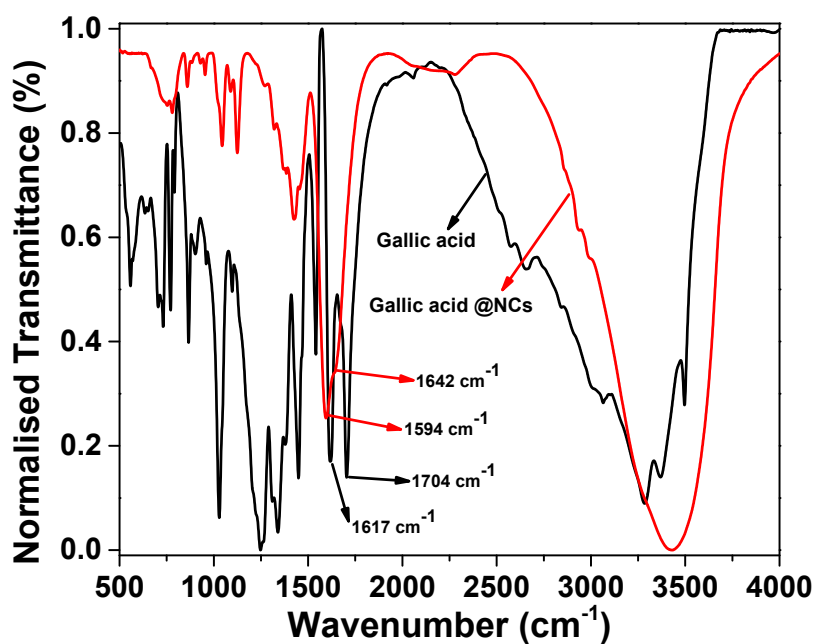


Fig. S3. FTIR spectra of pure gallic acid (GA) and GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ (2%) NCs.

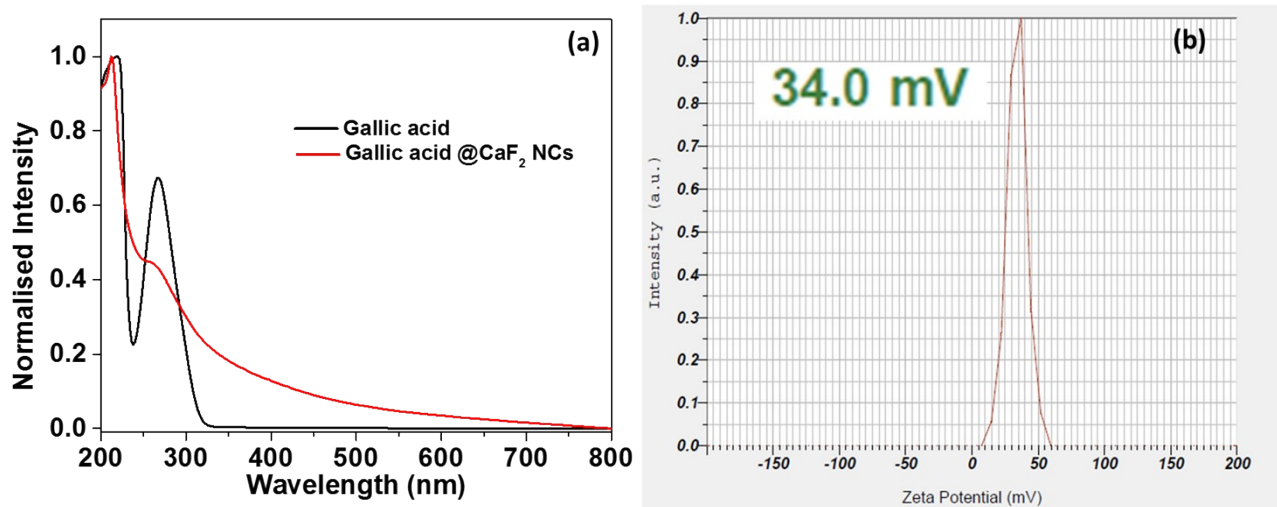


Fig. S4. (a) Absorption spectra of pure gallic acid (GA) and GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ (2%) nanocrystals. (b) Zeta potential of GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ (2%) nanocrystals.

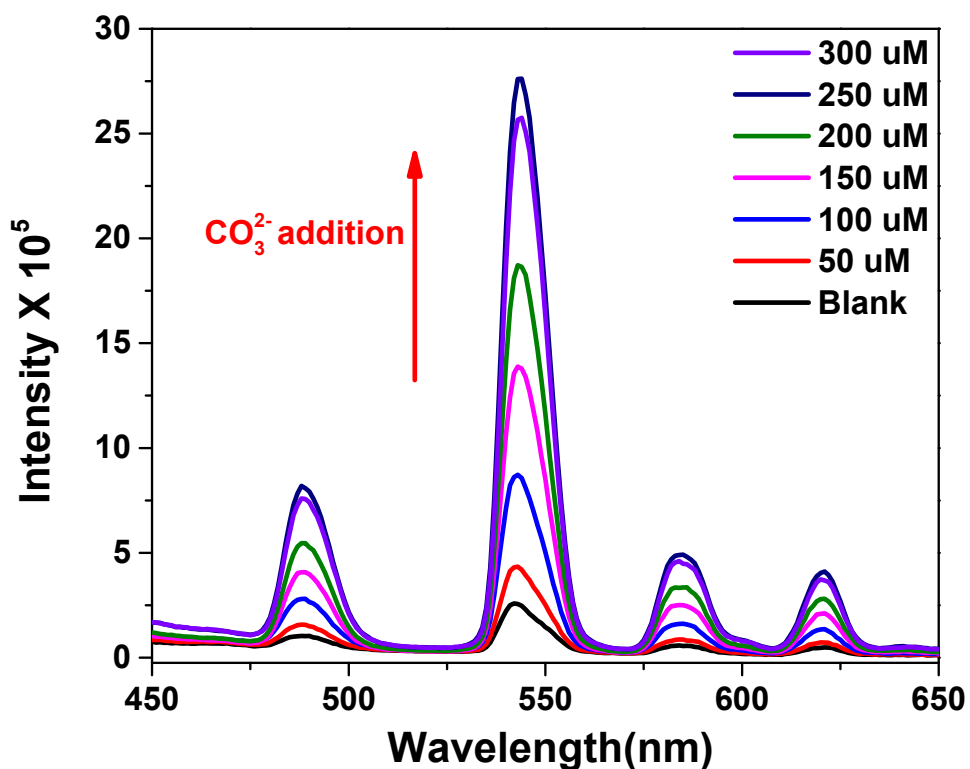


Fig. S5. Photoluminescence spectra of the GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ NCs in D_2O , a ~ 10 -fold enhancement was observed upon addition of Na_2CO_3 .

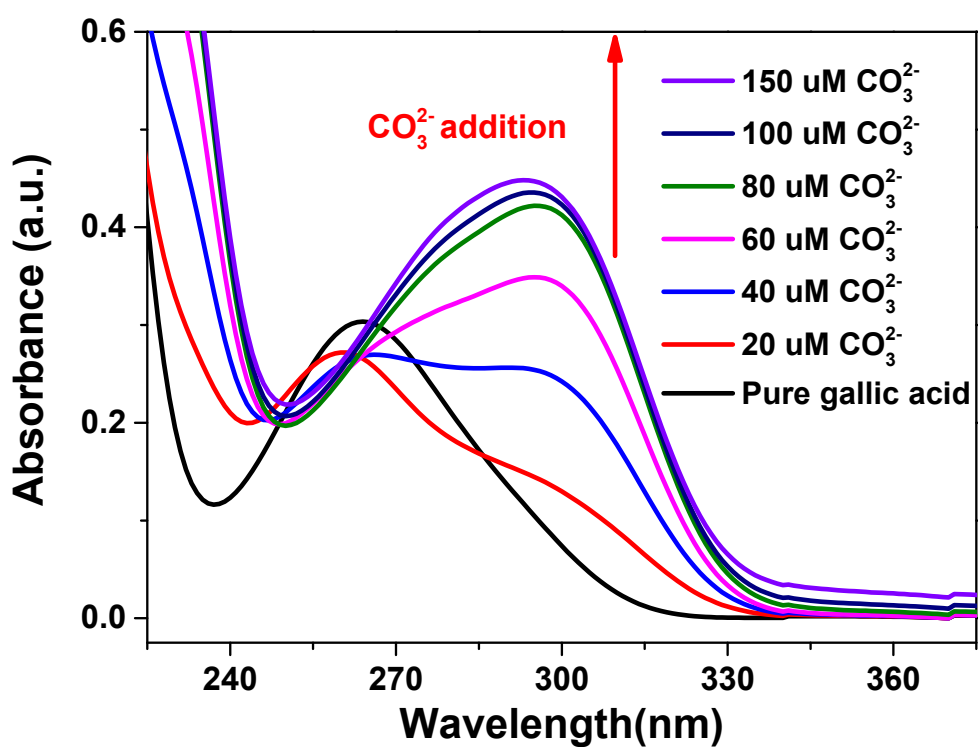


Fig. S6. Absorption spectra of pure gallic acid with the addition of 20 μM , 40 μM , 60 μM , 80 μM , 100 and 150 μM of CO_3^{2-} ion.

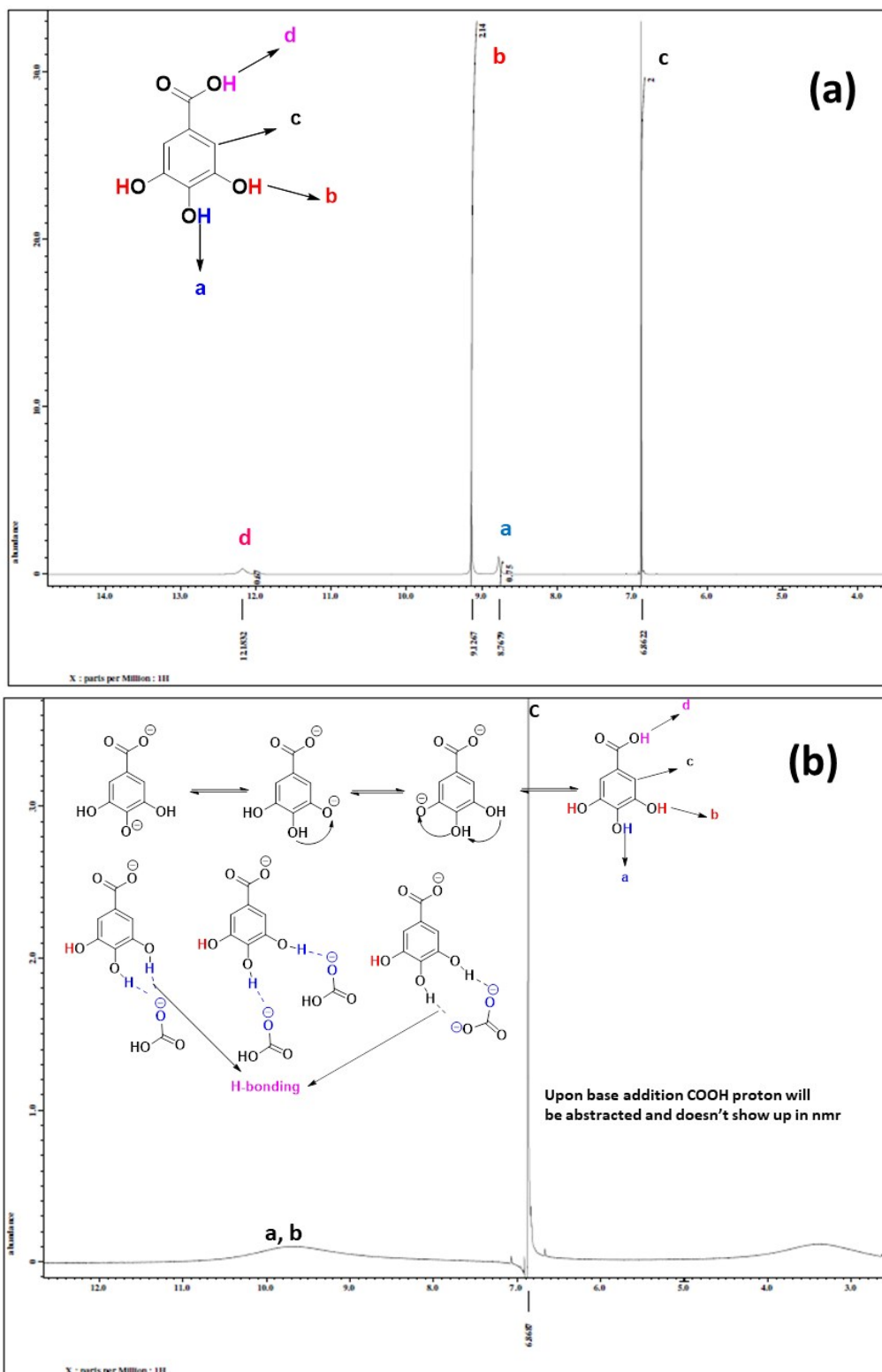


Fig. S7. ^1H NMR spectra of (a) pure gallic acid and (b) gallic acid with CO_3^{2-} ions (D_2O , 400 MHz).

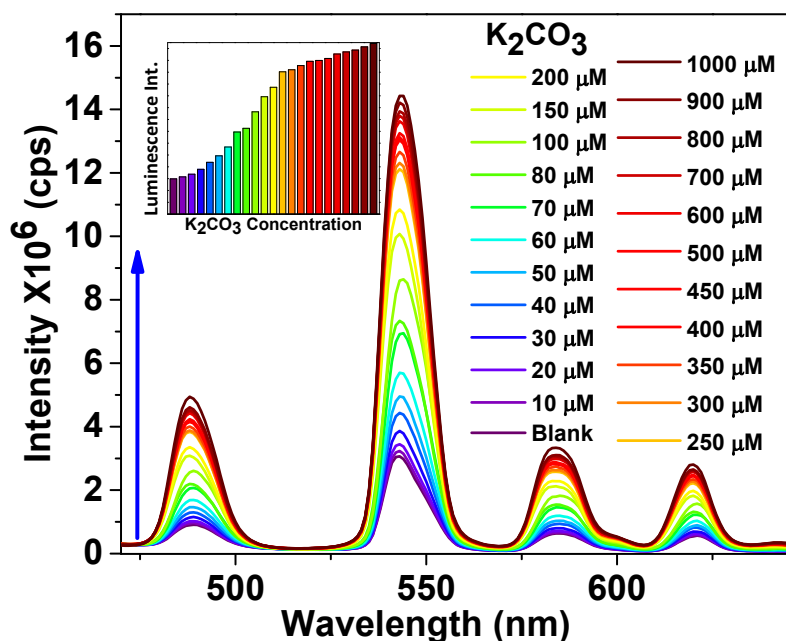


Fig. S8. Photoluminescence spectra of the GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ NCs collected upon gradual addition of K_2CO_3 ions. Inset shows the bar diagram of Tb^{3+} luminescence enhancement pattern with the addition of K_2CO_3 to the NCs dispersion.

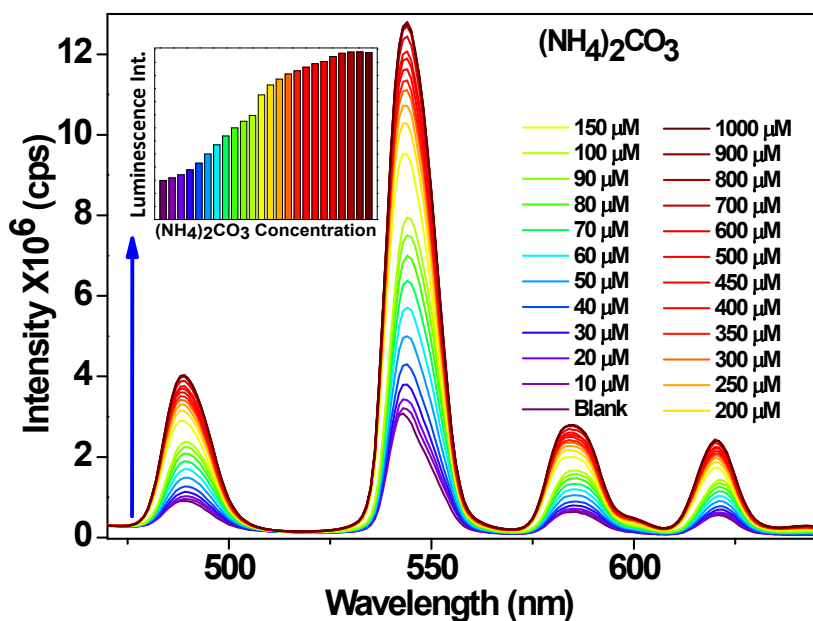


Fig. S9. Photoluminescence spectra of the GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ NCs, collected upon gradual addition of $(\text{NH}_4)_2\text{CO}_3$ ions. Inset shows the bar diagram of Tb^{3+} luminescence enhancement pattern with the addition of $(\text{NH}_4)_2\text{CO}_3$ to the NCs dispersion.

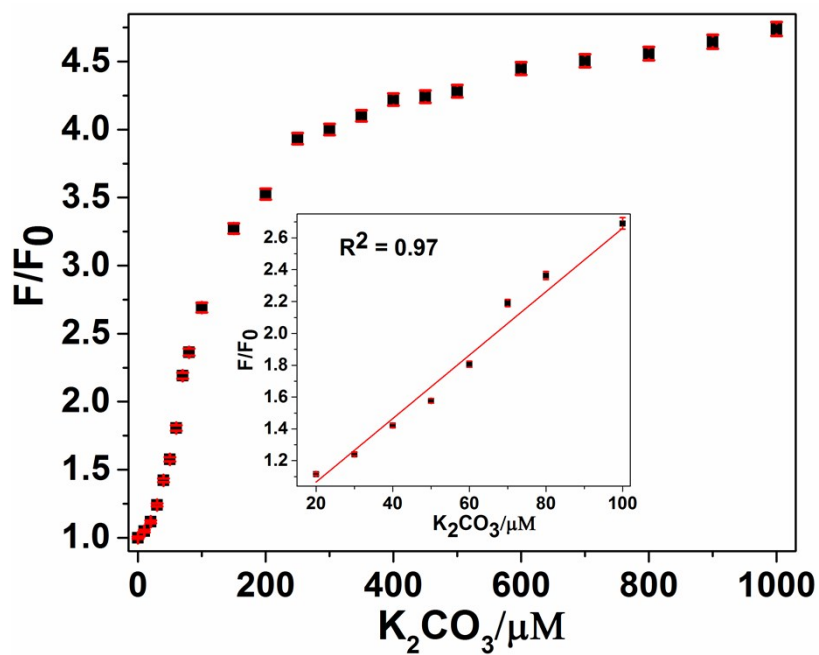


Fig. S10. Stern-Volmer plots of GA-capped $CaF_2:Tb^{3+}$ (2%) NCs with the addition of 1000 μM concentration of K_2CO_3 ions in aqueous medium.

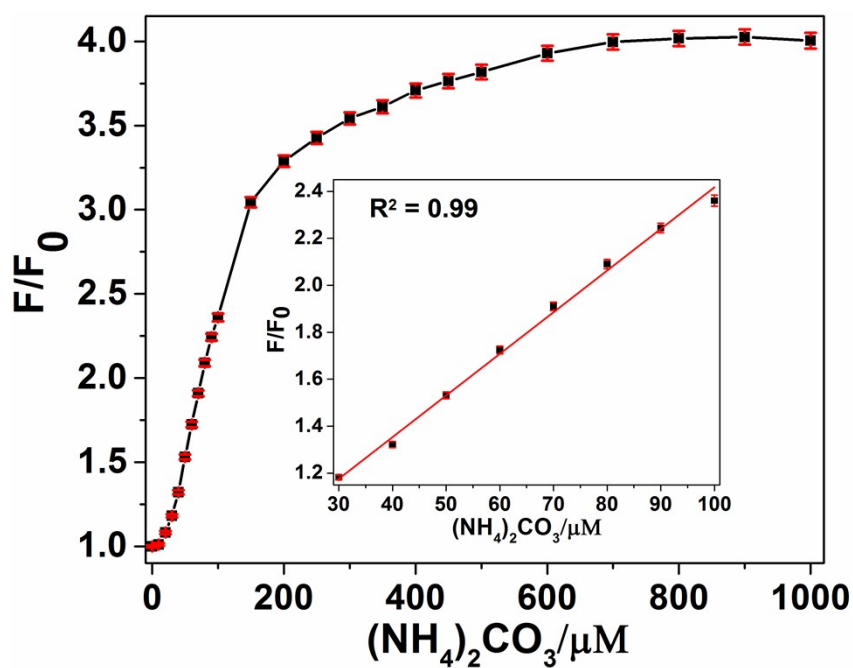


Fig.S11. Stern-Volmer plots of GA-capped $CaF_2:Tb^{3+}$ (2%) NCs with the addition of 1000 μM concentration of $(NH_4)_2CO_3$ ions in aqueous medium.

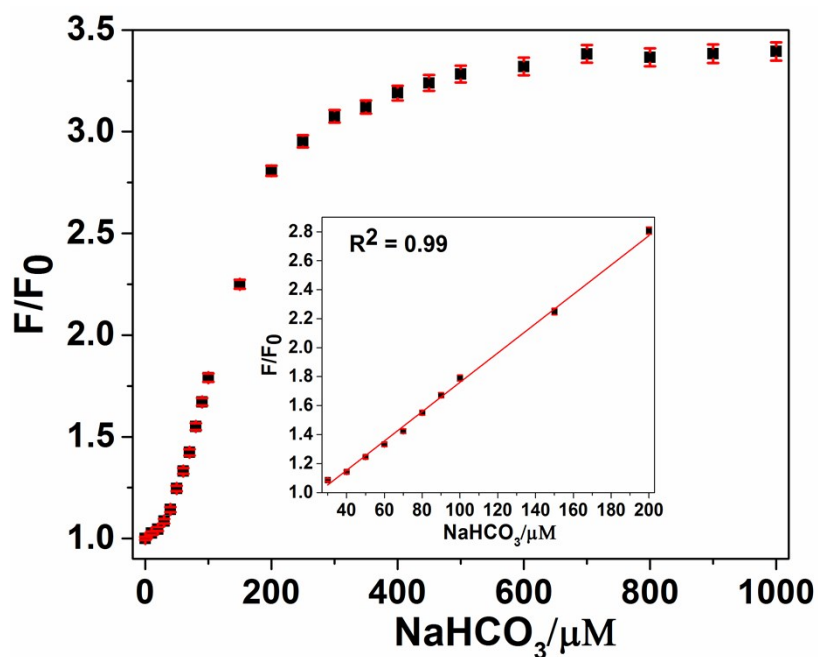


Fig.S12. Stern-Volmer plots of GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ (2%) NCs with the addition of 1000 μM concentration of NaHCO_3 ions in aqueous medium.

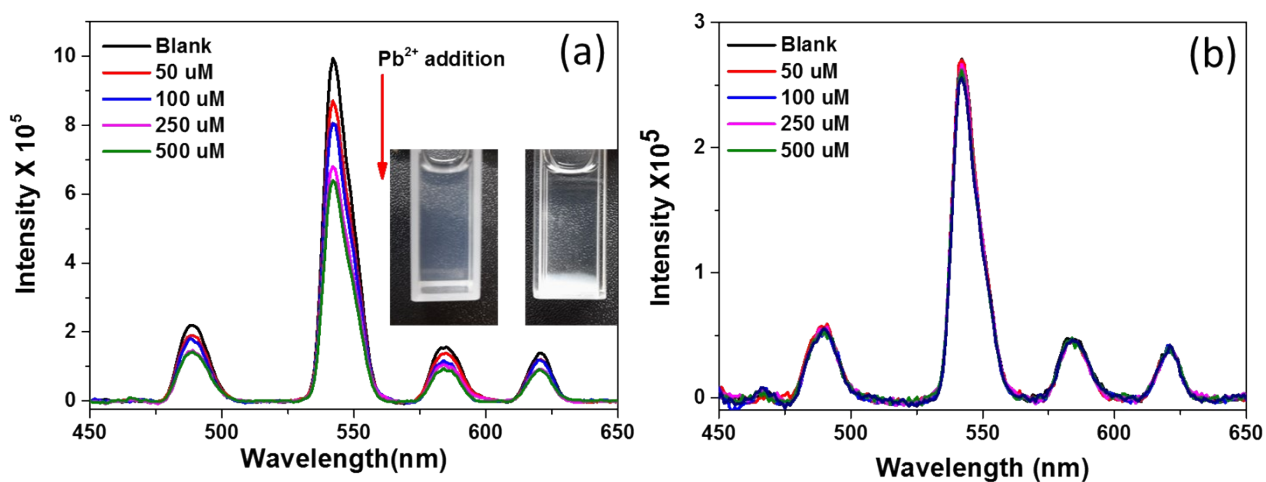


Fig. S13. Photoluminescence spectra of the GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ NCs (a) through gallic acid excitation (inset shows visible residual upon Pb^{2+} ion addition) and (b) through direct excitation (376 nm).

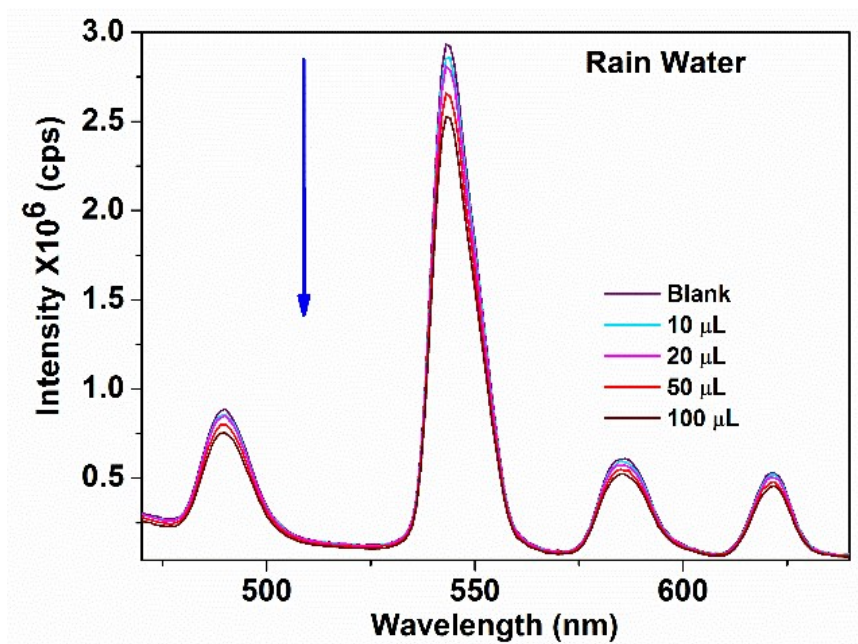


Fig. S14. Photoluminescence spectra of the GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ NCs collected with the addition of different quantity of rain water.

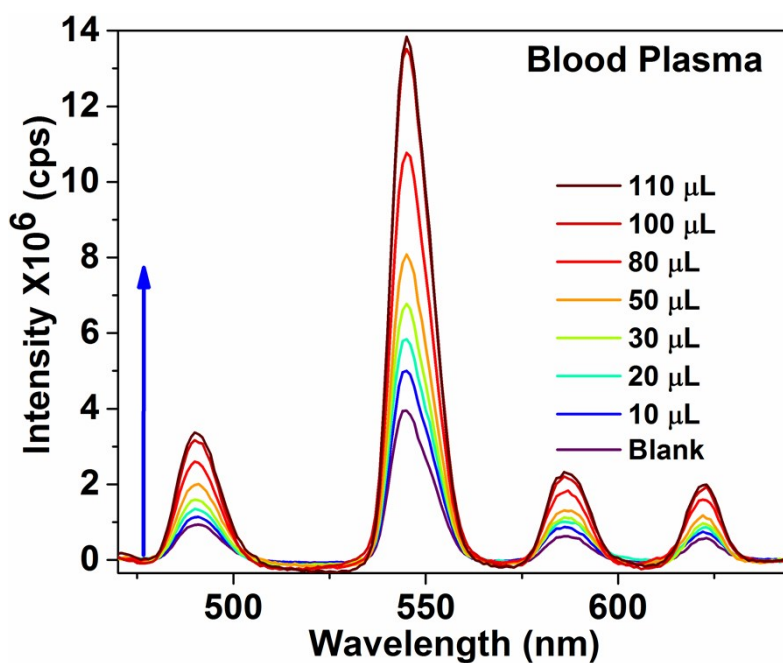


Fig. S15. Photoluminescence spectra of the GA-capped $\text{CaF}_2:\text{Tb}^{3+}$ NCs collected with addition of different quantity of blood plasma.

Table S1.A Comparison of luminescence constants and limit of detection (LOD) values obtained from present work with that reported for other materials.

| No | Sample | Method | KSV/Linear range | LOD | Ref. |
|----|--------------------------------------------------|--------------------------|-----------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| 1 | Azino bis-Schiff base ligand | fluorescent-colorimetric | -NA- | 96 nM | 6 |
| 2 | Meso-aryl calix[4]pyrrole derivative | Fluorescence | $1.0 \times 10^7 \text{ M}^{-1}$ | 4 nM | 17 |
| 3 | SERS probe | optophysiology | 1.00 to 35.0 μM | 0.16 μM | 24 |
| 4 | TPEMO | Fluorescence | -NA- | 71.6 nM | 28 |
| 5 | Eu/Pt-MOFs | Fluorescence | 0 to 500 μM | 0.021 μM | 41 |
| 6 | 2-(arylidenehydrazinyl) pyridines | Optical sensor | $0.77 \times 10^4 \text{ M}^{-2}$ | 0.11 mM | 45 |
| 7 | 7,8-dihydroxy-3-(3-chlorophenyl) coumarin (DHMC) | Fluorescence | $9.49 \times 10^4 \text{ M}^{-1}$ | 1.03 μM | 46 |
| 8 | GA- capped $\text{CaF}_2:\text{Tb}^{3+}$ NCs | Fluorescence | 10 to 1000 μM | 0.99 μM (Na_2CO_3) 1.3 μM (K_2CO_3) 1.23 μM ($(\text{NH}_4)_2\text{CO}_3$) 2.15 μM (NaHCO_3) | This work |

Table S2 : geographic locations and other details on the collected tap water, pond water and river water samples.

| Sample | pH | Geographic coordinate | Sample collected date |
|------------------------------------|-----------|------------------------------|------------------------------|
| Sample-1 (IISER-Tap water) | 8.03 | 22°57'50.3"N 88°31'34.3"E | 14-7-2020 |
| Sample-2 (IISER- Pond water) | 8.4 | 22°57'46.6"N 88°31'33.5"E | 14-7-2020 |
| Sample-3 (MN-Saha pond water) | 8.72 | 22°57'15.7"N 88°31'14.6"E | 14-7-2020 |
| Sample-4 (Mohanpur pond water) | 8.49 | 22°56'40.6"N 88°31'44.3"E | 14-7-2020 |
| Sample-5 (BCKV pond water) | 8.93 | 22°56'53.0"N 88°31'54.8"E | 14-7-2020 |
| Sample-6 (Lichi pond water) | 8.71 | 22°56'18.5"N 88°30'46.9"E | 14-7-2020 |
| Sample-7 (Kancharapara pond water) | 8.87 | 22°57'00.6"N 88°27'33.3"E | 15-7-2020 |
| Sample-8 (Bara-Jaguli pond water) | 8.79 | 22°56'53.1"N 88°32'35.5"E | 14-7-2020 |
| Sample-9 (Kolkata municipal water) | 7.96 | 22°31'23.6"N 88°21'05.4"E | 17-7-2020 |
| Sample-10 (Nico-park water) | 7.88 | 22°34'15.0"N 88°25'16.4"E | 6-8-2020 |
| Sample-11 (Hoogli river water) | 8.08 | 22°51'49.5"N 88°22'29.6"E | 20-7-2020 |

Table S3: Luminescence enhancement of GA-capped CaF₂:Tb³⁺ NCs with addition of specific amount of tap water, pond water and river water samples.

| Sample | Amount of sample water added | No. of Folds in Luminescence enhancement to blank emission |
|------------------------------------|-------------------------------------|-------------------------------------------------------------------|
| Sample-1 (IISER-Tap water) | 200 μ L | 3.1 |
| Sample-2 (IISER- Pond water) | 300 μ L | 3.25 |
| Sample-3 (MN-Saha pond water) | 300 μ L | 3.05 |
| Sample-4 (Mohanpur pond water) | 150 μ L | 2.74 |
| Sample-5 (BCKV pond water) | 200 μ L | 2.90 |
| Sample-6 (Lichi pond water) | 250 μ L | 2.51 |
| Sample-7 (Kancharapara pond water) | 300 μ L | 3.29 |
| Sample-8 (Bara-Jaguli pond water) | 200 μ L | 2.90 |
| Sample-9 (Kolkata municipal water) | 500 μ L | 2.96 |
| Sample-10 (Nico-park water) | 400 μ L | 2.95 |
| Sample-11 (Hoogli river water) | 200 μ L | 3.02 |