Supporting Information

CO_3^{2-} ion-induced Cu^{2+} ion determination using DPA capped-LaF_3:Eu^{3+} nanocrystals

Venkata N. K. B. Adusumalli[a,b], Stefan Lis[a], and Yong Il Park[b]*

[a]*Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland*

[b]*School of Chemical Engineering, Chonnam National University, Gwangju 61186, Republic of Korea*

Email: blis@amu.edu.pl

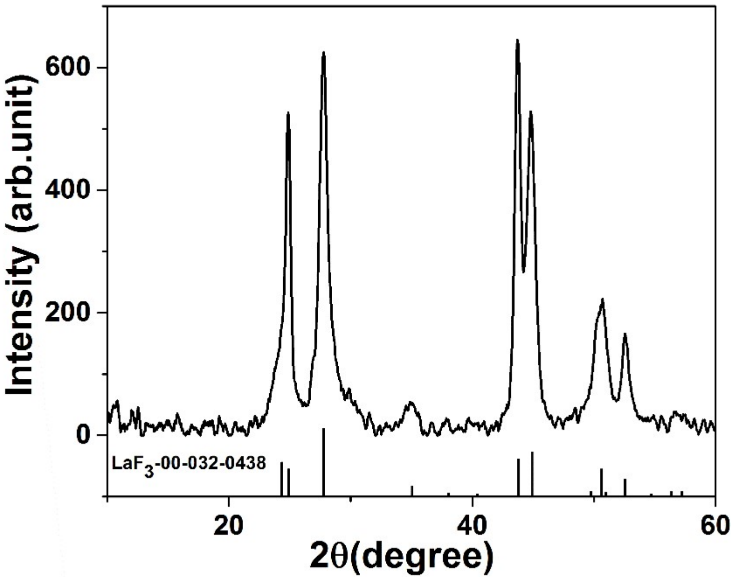

Figure S1. XRD powder pattern of the synthesized DPA-capped LaF_3:Eu^{3+} nanocrystals (NCs), along with a standard reference pattern. The vertical pattern at the bottom is the standard pattern of bulk LaF_3.

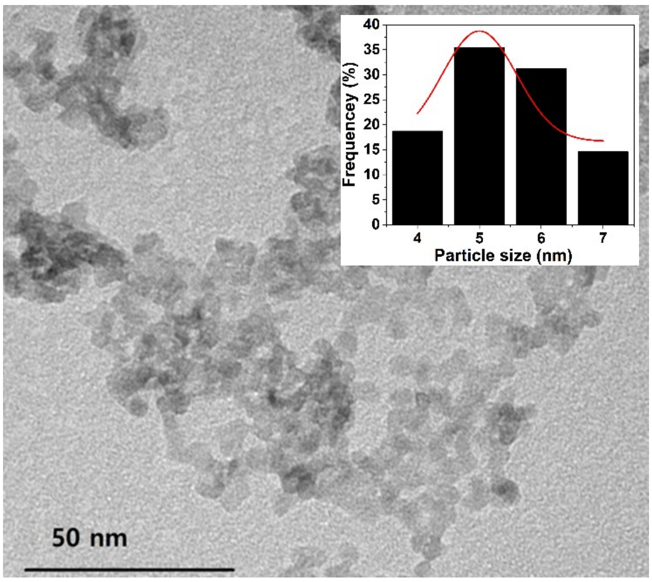

Figure S2. (a) TEM image of the DPA-capped $LaF_3:Eu^{3+}$ NCs. In the inset, the histogram shows the particle size distribution in the sample.

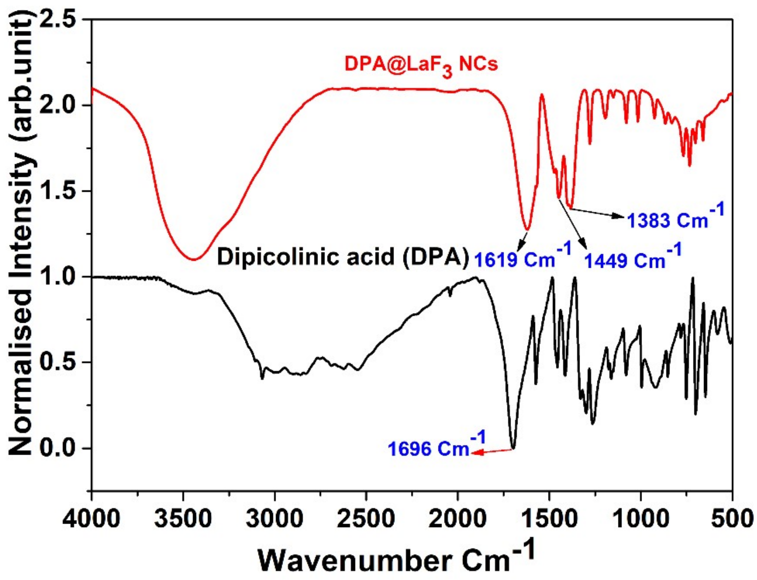

Figure S3. FTIR spectra of pure 2,6-pyridine carboxylic acid (DPA) and DPA-capped $LaF_3:Eu^{3+}$ NCs.

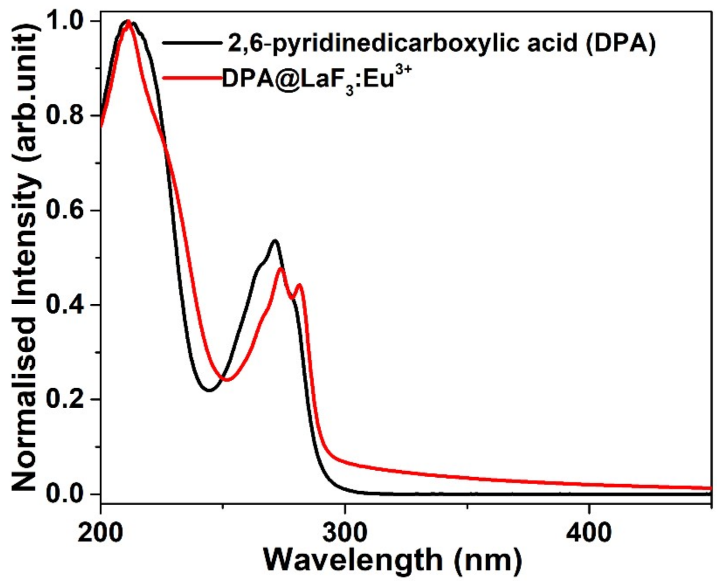

Figure S4. Absorption spectra of pure 2,6-pyridine carboxylic acid (DPA) and DPA-capped LaF_3:Eu^{3+} NCs.

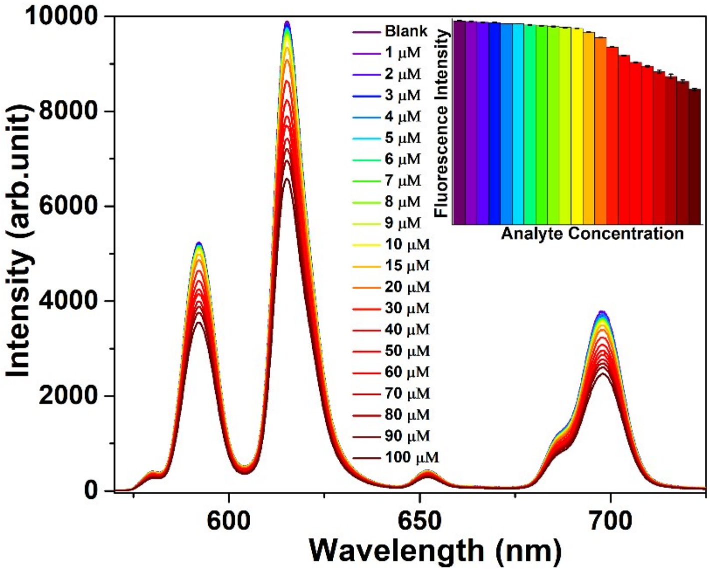

Figure S5. Emission spectra of DPA capped-LaF_3:Eu^{3+} NCs collected with the gradual addition of Cu^{2+} ions only. The inset represents the results of PL quenching in a bar diagram.

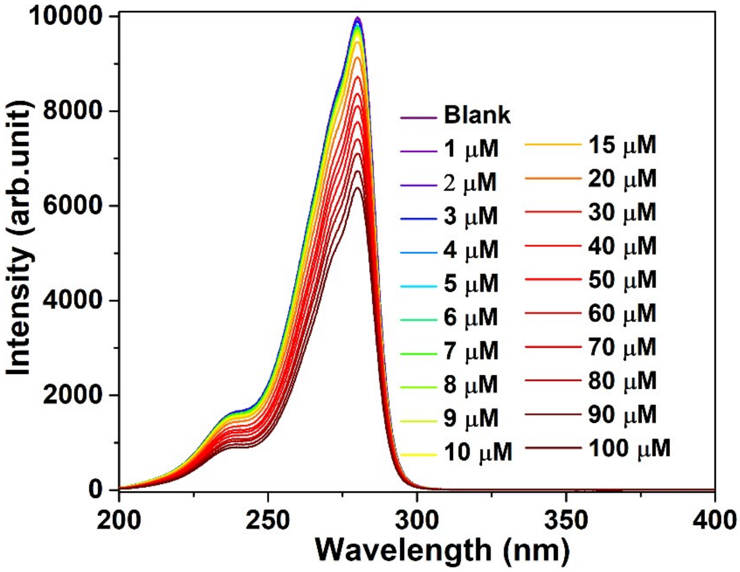

Figure S6. Excitation spectra of DPA capped-LaF_3:Eu^{3+} NCs collected with the gradual addition of Cu^{2+} ions only.

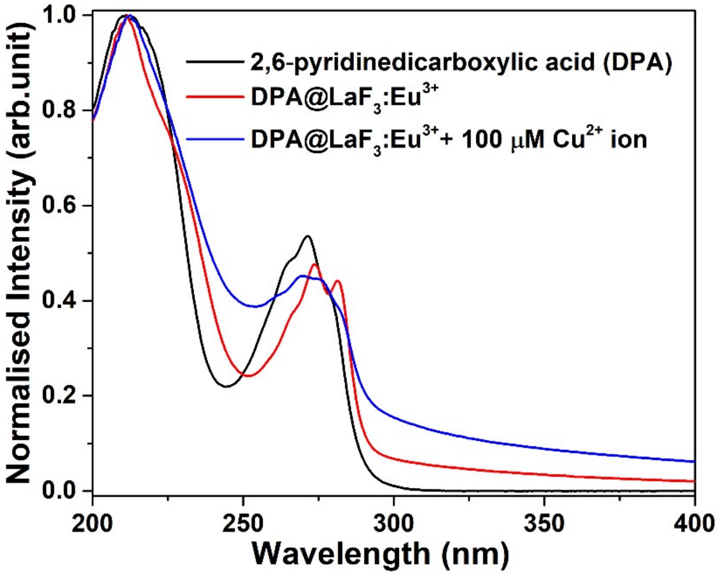

Figure S7. Absorption spectra of pure 2,6-pyridine carboxylic acid (DPA), DPA-LaF_3:Eu^{3+} NCs, and DPA-LaF_3:Eu^{3+} NCs along with 100 μM Cu^{2+} ions.

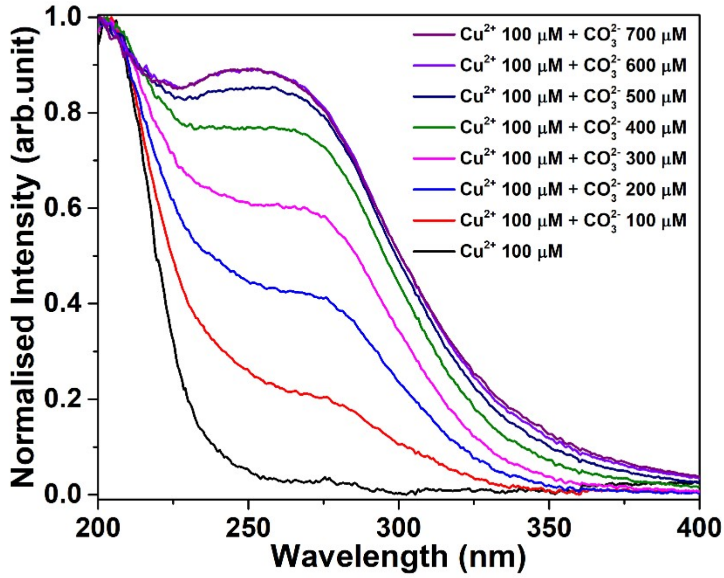

Figure S8. Absorption spectra of Cu^{2+} ions (100 μM) in an aqueous medium with the gradual addition of CO_3^{2-} ions.

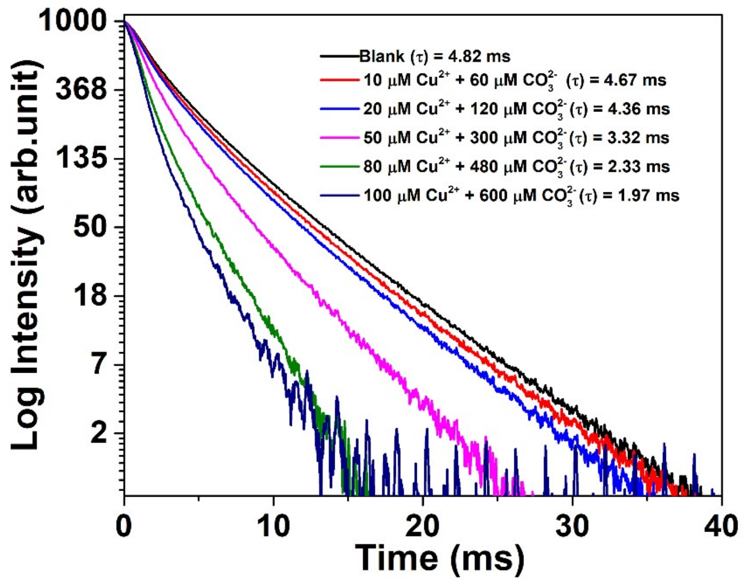

Figure S9. Luminescence decay curves of the DPA-capped $LaF_3:Eu^{3+}$ NCs (1 mg/mL), measured without (blank) and with the addition of the increasing concentration of Cu^{2+} ions along with the optimum concentration of CO_3^{2-} ions (λ_{ex} = 280 nm).

Table S1. Determined luminescence lifetimes of Eu^{3+} and fitting parameters for the DPA-capped $LaF_3:Eu^{3+}$ colloidal NCs, containing different concentrations of Cu^{2+} ions.

Cu^{2+} (µM)	**A_1**	**$\tau_{1\ (ms)}$**	**A_2**	**$\tau_{2\ (ms)}$**	**$\tau_{average\ (ms)}$**	**R^2**
0	59	2.29874	41	6.17906	4.826064	0.99
10	61.7	2.19321	38.3	6.10486	4.670898	0.99
25	62.36	2.0694	37.64	5.72966	4.359391	0.99
50	76.7	1.80296	23.3	5.09478	3.32348	0.99
75	90.97	1.43661	9.03	4.96412	2.337528	0.99
100	95.45	1.28146	4.65	5.36619	1.973567	0.99

Table S2. Comparison of the luminescence quenching constants and the limit of detection (LOD) obtained from this work with other materials for the Cu^{2+} determination.

NO	**Sample**	**Method**	**KSV/Linear range**	**LOD**	**Ref**
1	YVO_4:Eu nanoparticles	Fluorescence	1 to 10 µM	0.57 µM	27
2	UCNPs/TPPS nanokit	Fluorescence	0 to 20 µM	0.21 µM	28
3	Luminol-Tb-GMP Nanoprobe	Fluoriscence	0.02 to 80 µM	4.2 nM	29
4	CDs@Eu-DPA MOFs	Fluorescence	50 nm to 10 µM	26.3 nM	30
5	$Ln(DPA)_3$@POSS-NH_2	Fluorescence	2359.6 M^{-1}	-NA-	31
6	AMP-Tb	Fluorescence	1.5 to 24 µM	300 nM	42

7	PEI-capped UCNPs	Fluorescence	0.1 to 2.0 μM	57.8 nM	43
8	β-$NaYF_4$:Yb,Er,Gd@SiO_2-NH_2 nanorods	Fluorescence	0 to 0.16 mM	2.16 μM	44
9	DPA-LaF_3:Eu^{3+}	Fluorescence	1 to 15 μM	117 nM	This work

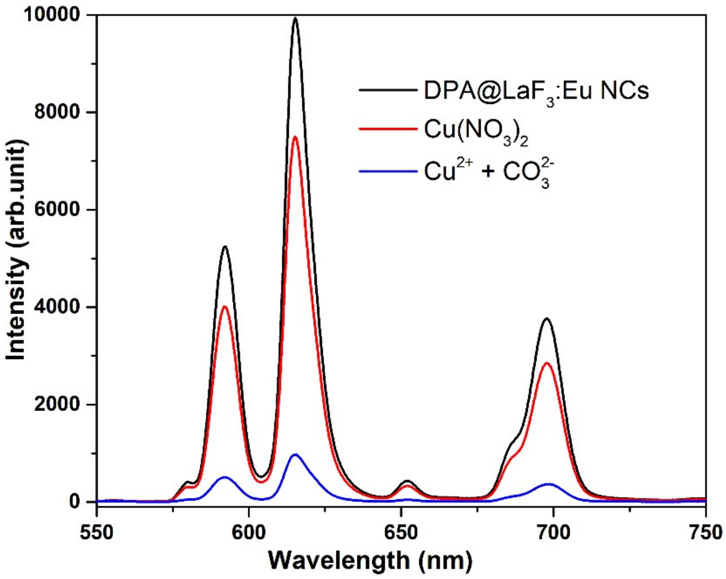

Figure S10. Emission spectra of DPA capped-LaF_3:Eu^{3+} NCs along with the emission spectra after the addition of 100 μM $Cu(NO_3)_2$ and followed by 600 μM CO_3^{2-} ions.

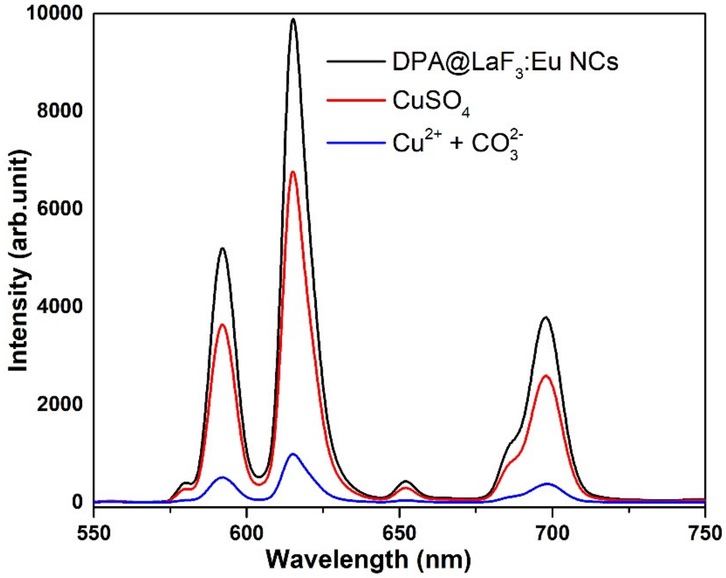

Figure S11. Emission spectra of DPA capped-$LaF_3:Eu^{3+}$ NCs along with the emission spectra after the addition of 100 μM $CuSO_4$ and followed by 600 μM CO_3^{2-} ions.

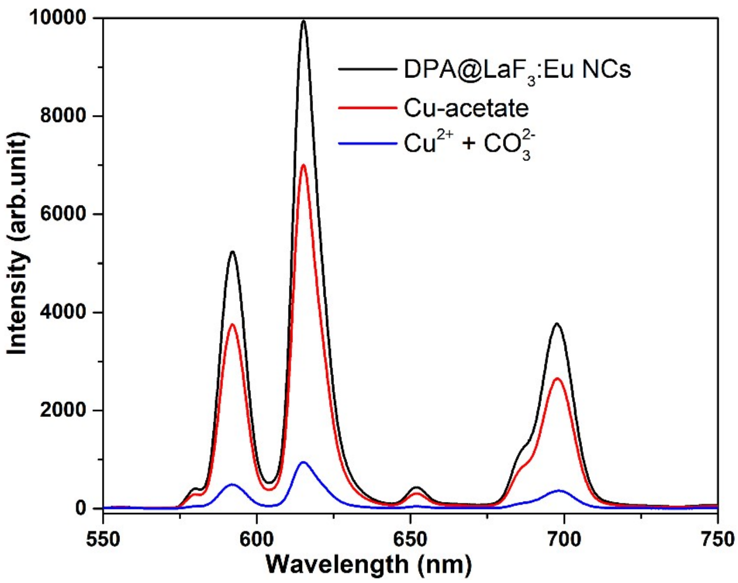

Figure S12. Emission spectra of DPA capped-$LaF_3:Eu^{3+}$ NCs along with the emission spectra after the addition of 100 μM $Cu(CH_3COO)_2$ and followed by 600 μM CO_3^{2-} ions.

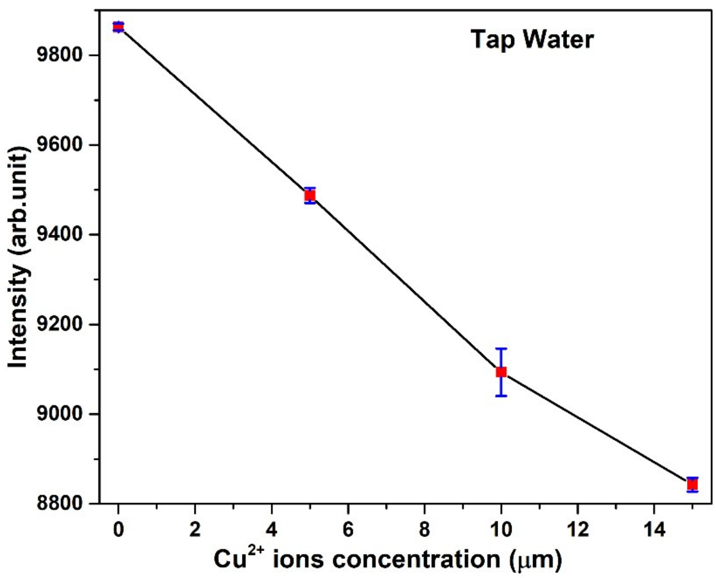

Figure S13. Luminesce quenching plot DPA capped-$LaF_3:Eu^{3+}$ NCs with Cu^{2+} ions along with CO_3^{2-} ions in tap water.

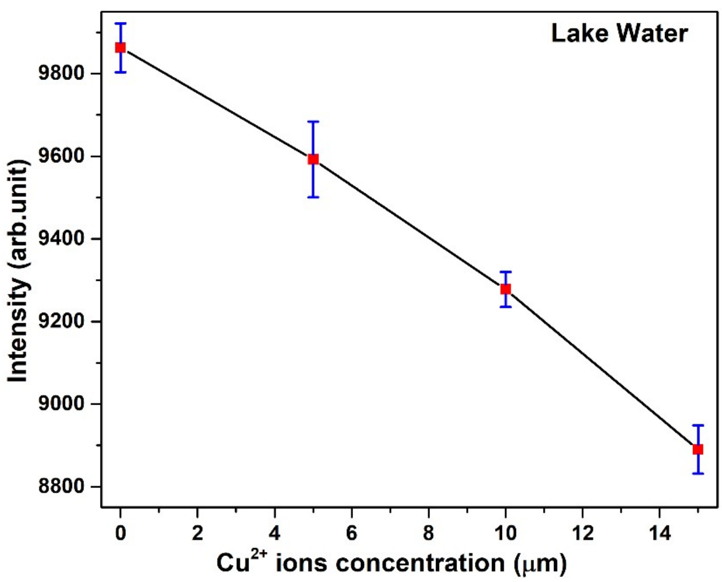

Figure S14. Luminesce quenching plot DPA capped-LaF_3:Eu^{3+} NCs with Cu^{2+} ions along with CO_3^{2-} ions in lake water.

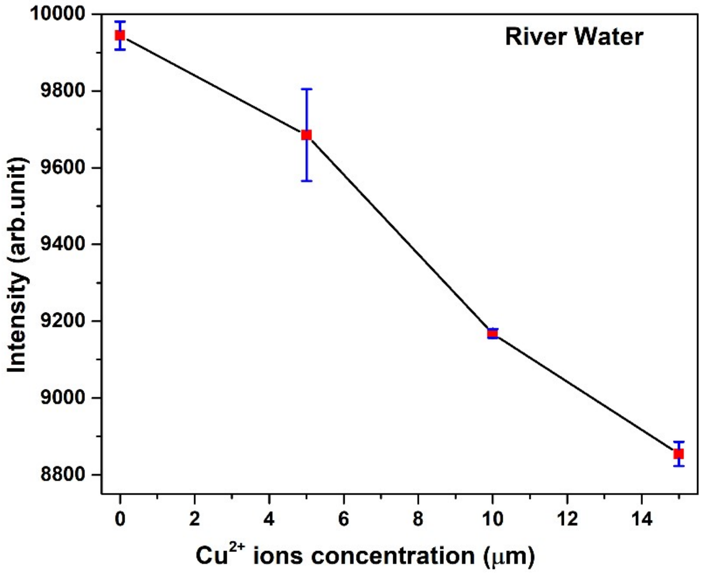

Figure S15. Luminesce quenching plot DPA capped-LaF_3:Eu^{3+} NCs with Cu^{2+} ions along with CO_3^{2-} ions in river water.

Table S3. Results of recovery of the proposed luminescence method for Cu^{2+} ions in tap, lake, and river water.

Analyte	**Sample**	**Added (µM)**	**Found (µM)**	**Recovery (%, n=3)**
Cu^{2+} ion	Tap water	5	4.33, 4.37, 4.33	86.97±0.42
		10	9.02, 9.12, 8.97	90.40±0.76
		15	13.91, 14.07, 13.90	93.06±0.63
	Lake water	5	4.30, 4.33, 4.35	86.59±0.49
		10	8.84, 8.92, 8.84	88.63±0.57
		15	13.84, 14.11, 13.78	92.74±1.50
	River water	5	4.23, 4.21, 4.25	84.66±0.41

		10 15	8.95, 9.06, 8.93 13.89, 14.08, 13.84	89.83±0.68 92.95±0.86