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Supplementary Materials

Rhodamine Derivative-Linked Silica-Coated Upconverting Nanophosphor ($NaYF_4$: Yb^{3+}/Er^{3+}@SiO_2-RBDA) for Ratiometric, Ultrasensitive Chemosensing of Pb^{2+} Ions

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1. Materials and reagents

All chemicals have been used without further purification. $Y(NO_3)_3.6H_2O$ (99.99%), $Yb(NO_3)_3.6H_2O$ (99.99%), $Er(NO_3)_3.6H_2O$ (99.99%), terephthalaldehyde (reagent 99%), (3-aminopropyl)triethoxysilane (APTES 99%), acetic acid (glacial, reagent 99%), and ammonia solution (25%) were purchased from Sigma-Aldrich. Oleic acid (90%, technical grade), 1-octadecene (90%, technical grade), hydrazine hydrate (reagent, 80%), tetraethoxysilane (TEOS 98%), toluene (99.7%), and hydrochloric acid (HCl, analytical reagent 35-38 %) were purchased from Alfa Aesar. Rhodamine B (RhB, 95%) was purchased from Loba Chemie Pvt. Ltd. Ammonium fluoride (NH_4F, 99%), sodium hydroxide (NaOH, 97%), cetyltrimethylammonium bromide (CTAB 99%), cyclohexane (C_6H_{12} 99%), ethanol (C_2H_5OH, analytical reagent 99%), and methanol (CH_3OH, analytical reagent 99%) were purchased from Spectrochem Pvt. Ltd. All of the aqueous solutions were prepared using double-distilled water. Aqueous solutions of Cs^+, Na^+, K^+, Fe^{3+}, Ni^{2+}, Cd^{2+}, Mg^{2+}, As^{2+}, Ca^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Sn^{2+}, Zn^{2+}, and Pb^{2+} were prepared from their corresponding halide salts.

2. Equipment and Characterizations

The synthesized nanophosphors were characterized by field emission scanning electron microscopy (FESEM) using STEM, MERLIN Zeiss-Germany. For that, the suspension of nanophosphors was deposited on a copper TEM-grid coated with carbon film (Ted Pella, USA). To confirm the exact shape and size of the nanophosphors, transmission electron microscopy (TEM) using a TECNAI G2 -30 U TWIN (FEI, Eindhoven, Netherlands) instrument, operated with an accelerated voltage of 300 kV, was utilized. The average hydrodynamic diameter of the nanophosphors was measured by dynamic light scattering (DLS), using a NANO-ZS series MALVERN ZETASIZER instrument. Powder x-ray diffraction measurement was done to analyze the phase composition and crystalline nature of nanophosphors, using a Brukar D8 Discover X-ray spectrometer, which utilizes Cu- Kα radiation (λ= 1.54060 Å) over the 2 theta (2θ) range of 10-80 degrees at the scanning rate of 2.58 degrees/min. FTIR spectra were taken from the range of 4000 to 400 Cm^{-1}, where dried and powdered nanophosphors were mixed with KBr and pressed into a pellet for analysis using a Perkin Elmer RX1 spectrometer. The absorbance and emission/fluorescence spectra were observed by using a Shimadzu UV1601 spectrophotometer (Shimadzu, Kyoto, Japan) and a Cary Eclipse fluorescence spectrometer (Varian, Palo Alto, CA), respectively. An upconversion fluorescence spectrometer (Quanta Master, Model QM-8450-11), attached with an external NIR (980 nm) diode laser, was used to acquire the upconversion luminescence emission spectra.

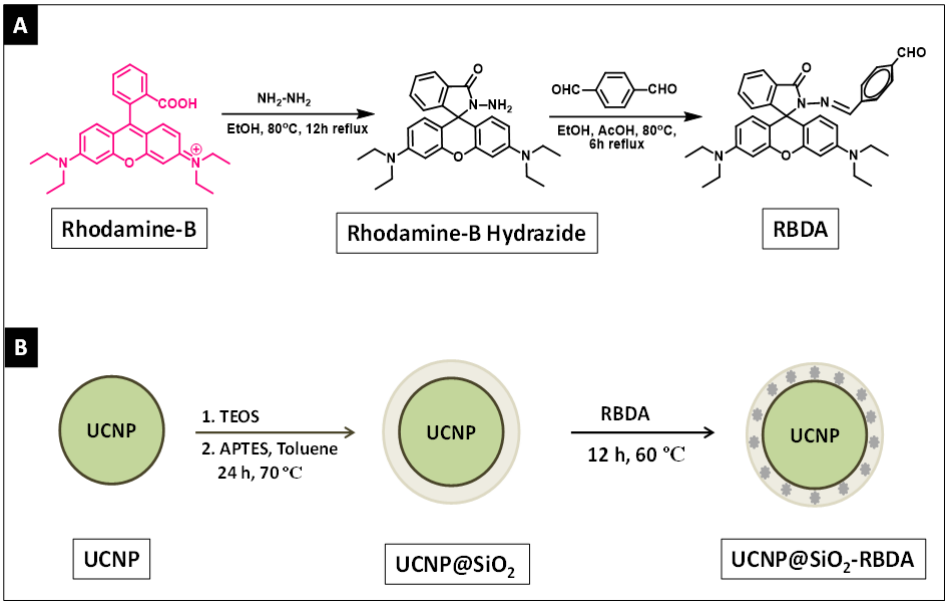

Figure S1. Schematic representation of (**A**) rhodamine–B derivative (RBDA) synthesis, and (**B**) UCNP@SiO_2-RBDA synthesis.

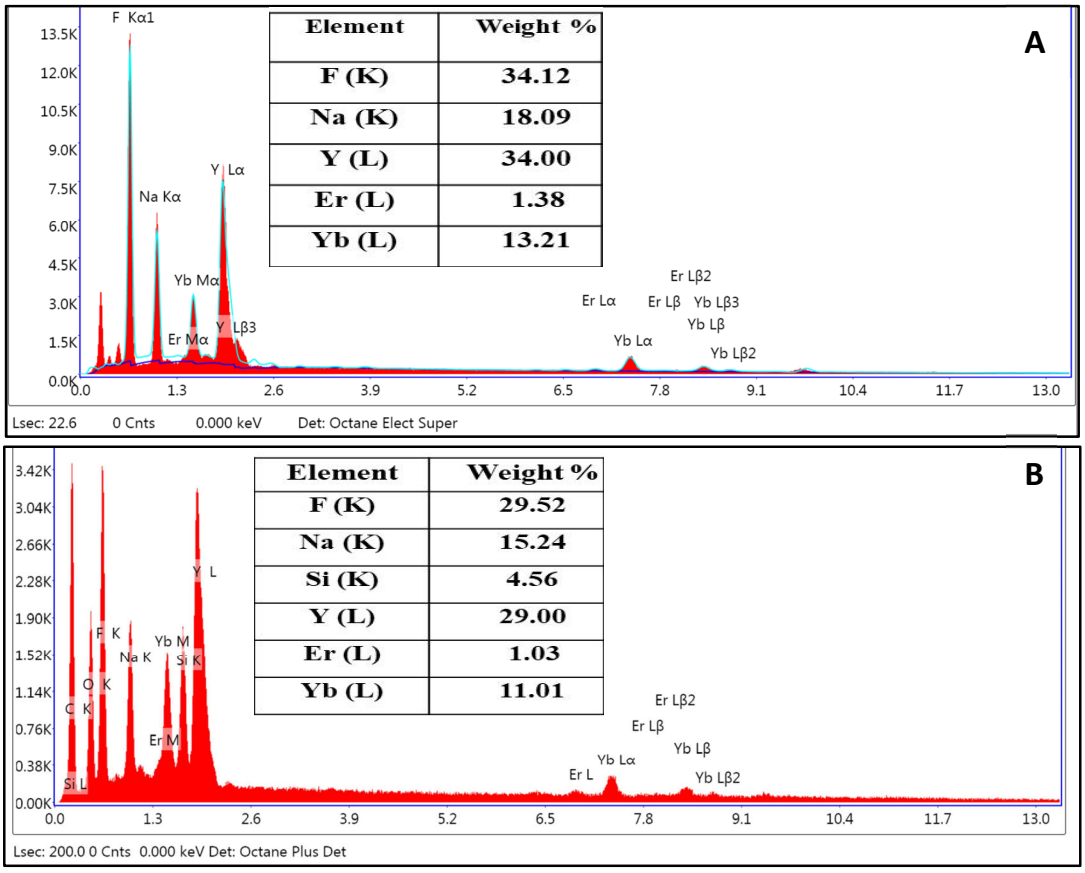

Figure S2. (**A**) EDS spectrum of as-synthesized UCNPs ($NaYF_4$: Yb^{3+}/Er^{3+}) (**B**) UCNP@SiO_2 ($NaYF_4$: Yb^{3+}/Er^{3+}@SiO_2).

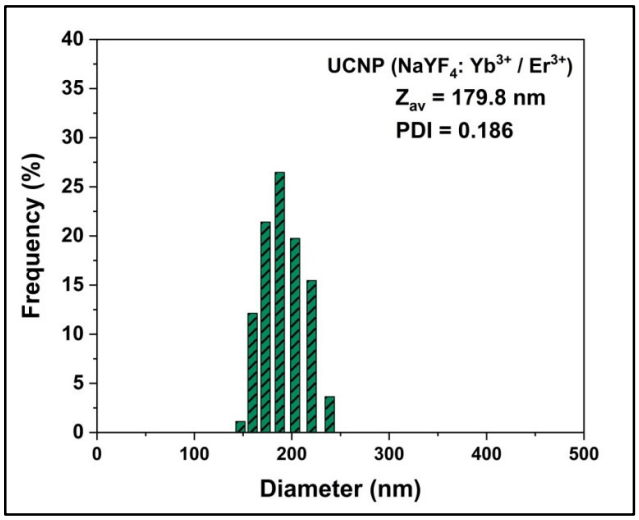

Figure S3. DLS measurement of as-synthesized UCNPs ($NaYF_4$: Yb^{3+}/Er^{3+}) with average size and polydispersity index.

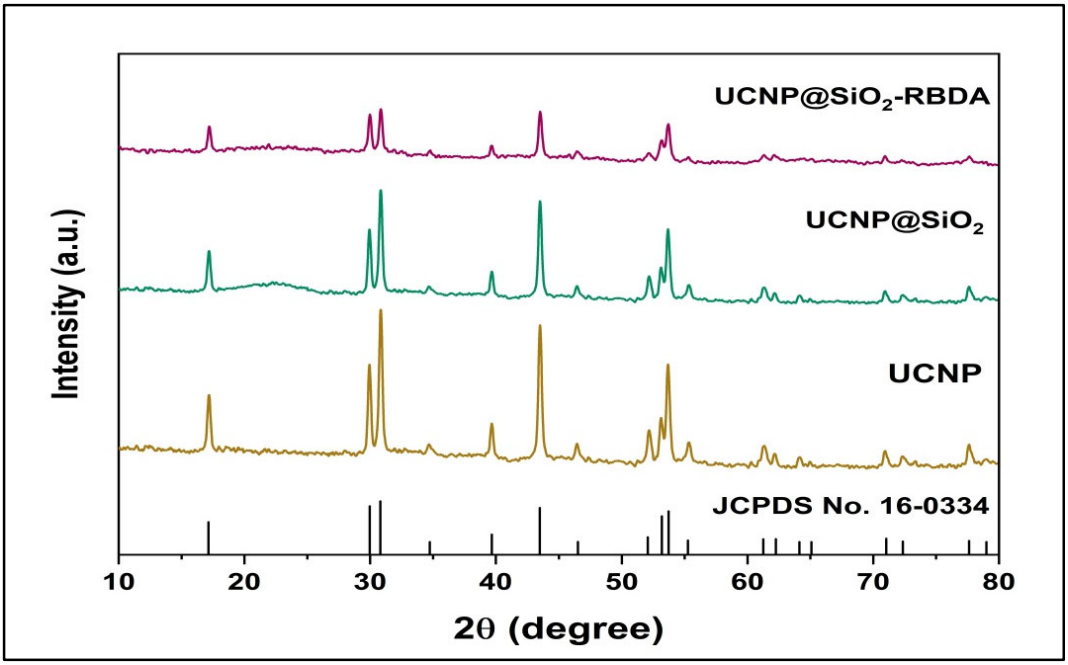

Figure S4. XRD patterns of the UCNP, UCNP@SiO_2, and UCNP@SiO_2-RBDA, along with standard (JCPDS No. 16-0334).

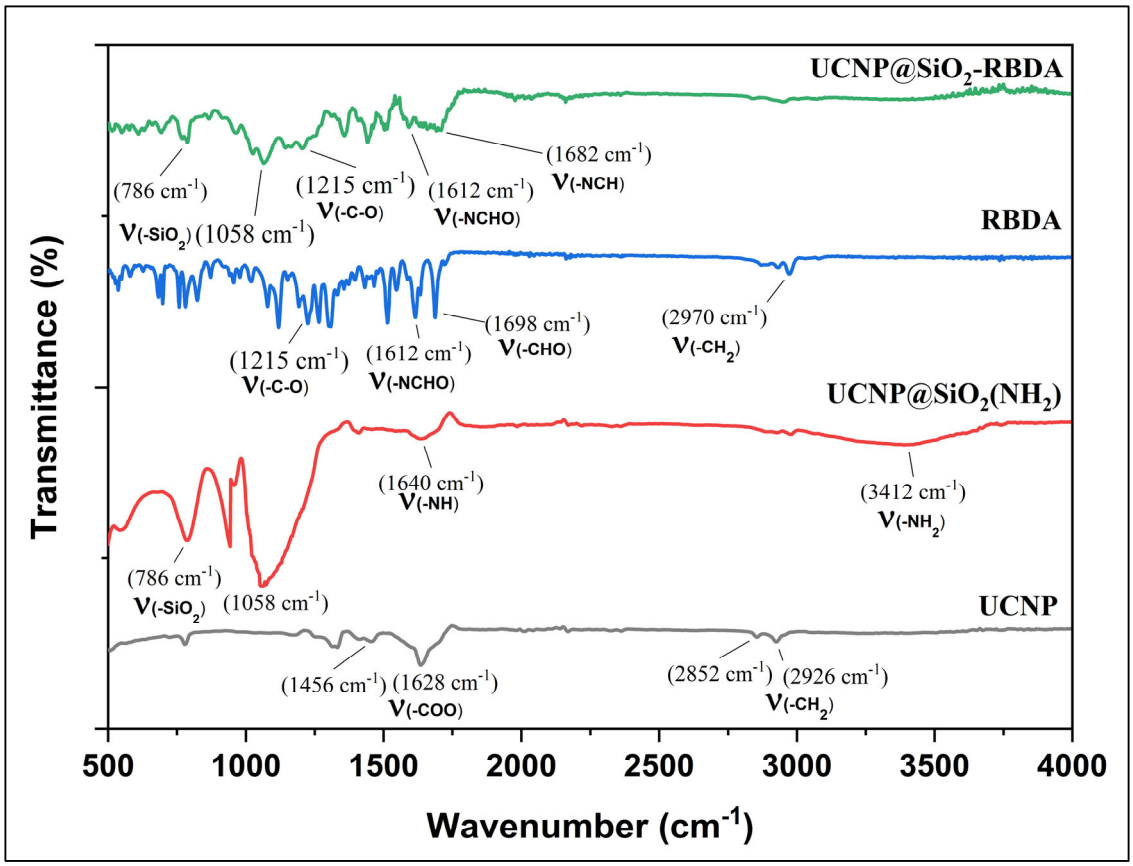

Figure S5. FT-IR of the UCNP, UCNP@SiO2, free RBDA, and UCNP@SiO2-RBDA.

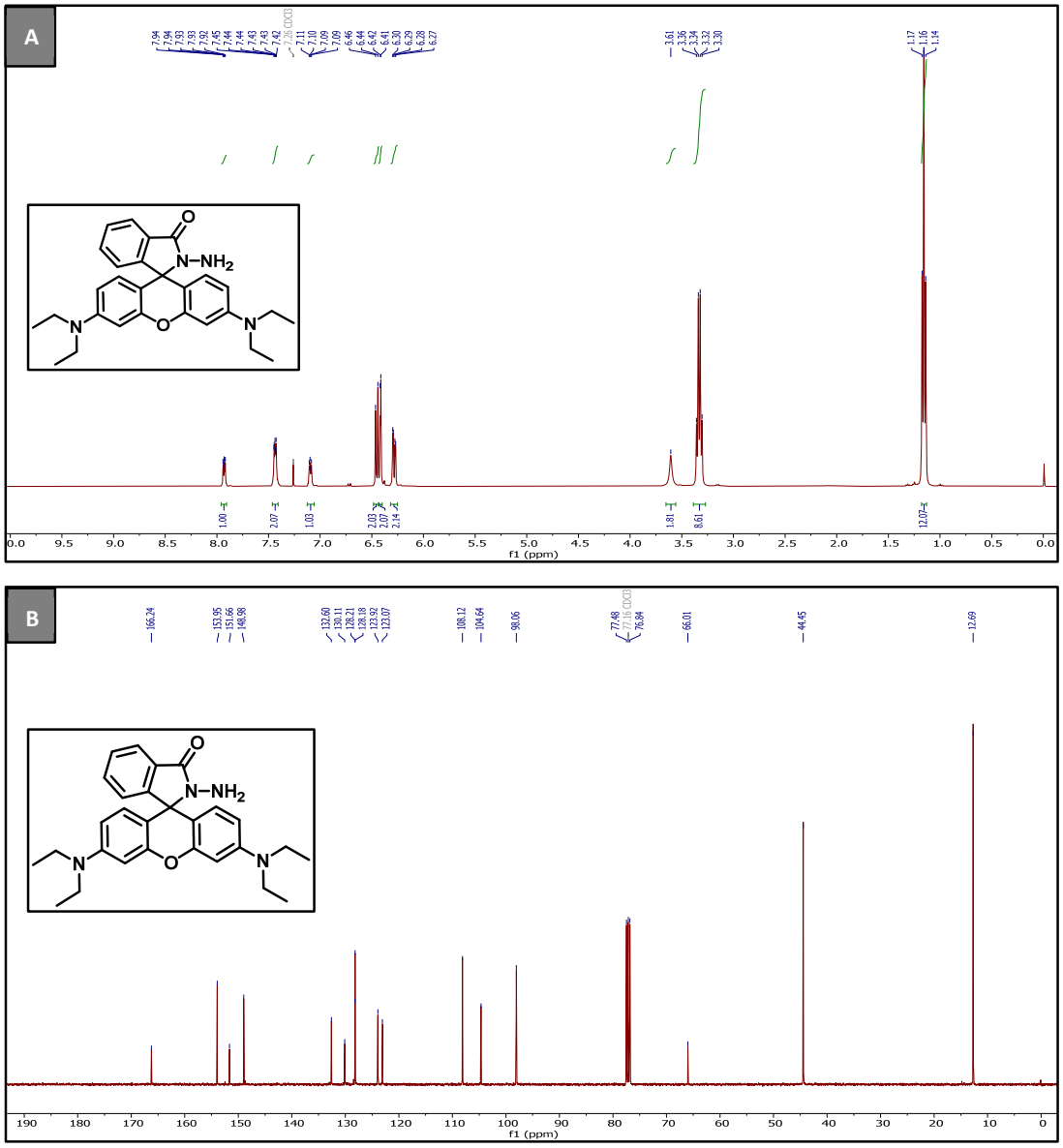

Figure S6. (**A**) [1]H-NMR (CDCl3, 400 MHz) (**B**) [13]C NMR (101 MHz, Chloroform-*d*) spectrum of synthesized Rhodamine B hydrazide.

[1]H NMR (400 MHz, Chloroform-*d*): δ 7.96-7.89 (m, 1H), 7.44 (dt, *J* = 5.7, 1.5 Hz, 2H), 7.13-7.06 (m, 1H), 6.45 (d, *J* = 8.8 Hz, 2H), 6.42 (d, *J* = 2.6 Hz, 2H), 6.28 (dd, *J* = 8.9, 2.6 Hz, 2H), 3.33 (q, *J* = 7.0 Hz, 8H), 1.16 (t, *J* = 7.0 Hz, 12H).

[13]C NMR (101 MHz, $CDCl_3$): δ 166.24, 153.95, 151.66, 148.98, 132.60, 130.11, 128.21, 128.18, 123.92, 123.07, 108.12, 104.64, 98.06, 77.48, 76.84, 66.01, 44.45, 12.69.

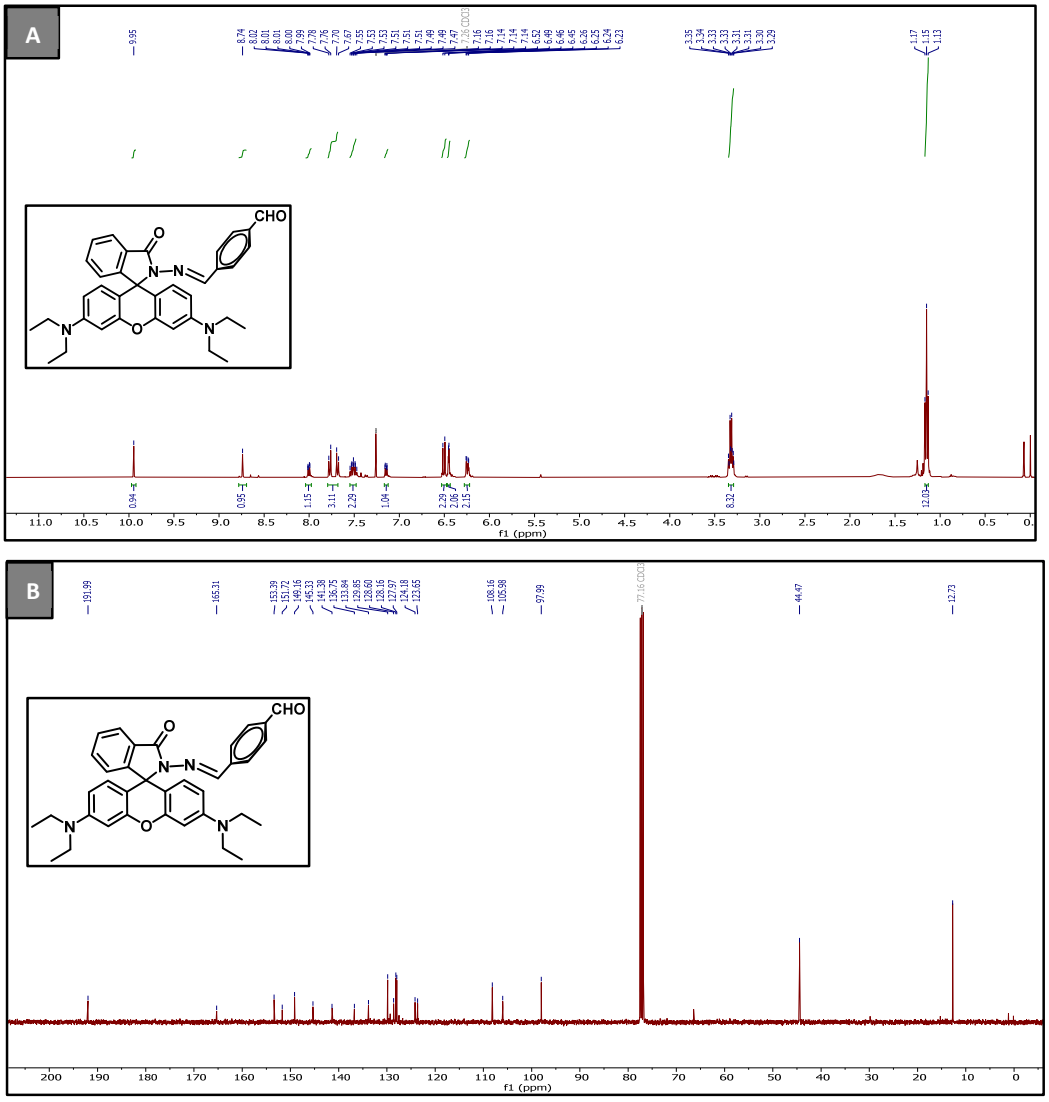

Figure S7. (**A**) ^{1}H-NMR (CDCl3, 400 MHz) (**B**) ^{13}C NMR (101 MHz, Chloroform-*d*) spectrum of synthesized Pb^{2+} sensitive RBDA.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 9.95 (s, 1H), 8.74 (s, 1H), 8.05-7.97 (m, 1H), 7.83-7.65 (m, 3H), 7.57-7.45 (m, 2H), 7.20-7.10 (m, 1H), 6.51 (d, *J* = 8.9 Hz, 2H), 6.45 (d, *J* = 2.6 Hz, 2H), 6.24 (dd, *J* = 8.9, 2.6 Hz, 2H), 3.32 (q, *J* = 7.1 Hz, 8H), 1.15 (t, *J* = 7.0 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 191.99, 165.31, 153.39, 151.72, 149.16, 145.33, 141.38, 136.75, 133.84, 129.85, 128.60, 128.16, 127.97, 124.18, 123.65, 108.16, 105.98, 97.99, 44.47, 12.73.

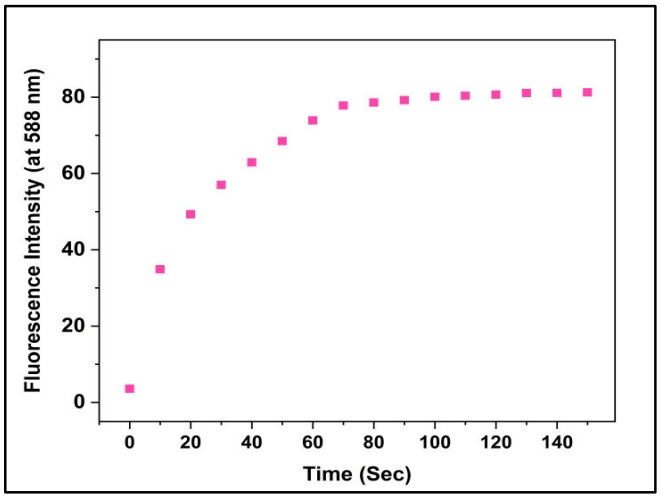

Figure S8. Fluorescence emission intensity of RBDA (at 588 nm) upon addition of Pb^{2+} ions (30 μM) as a function of time.

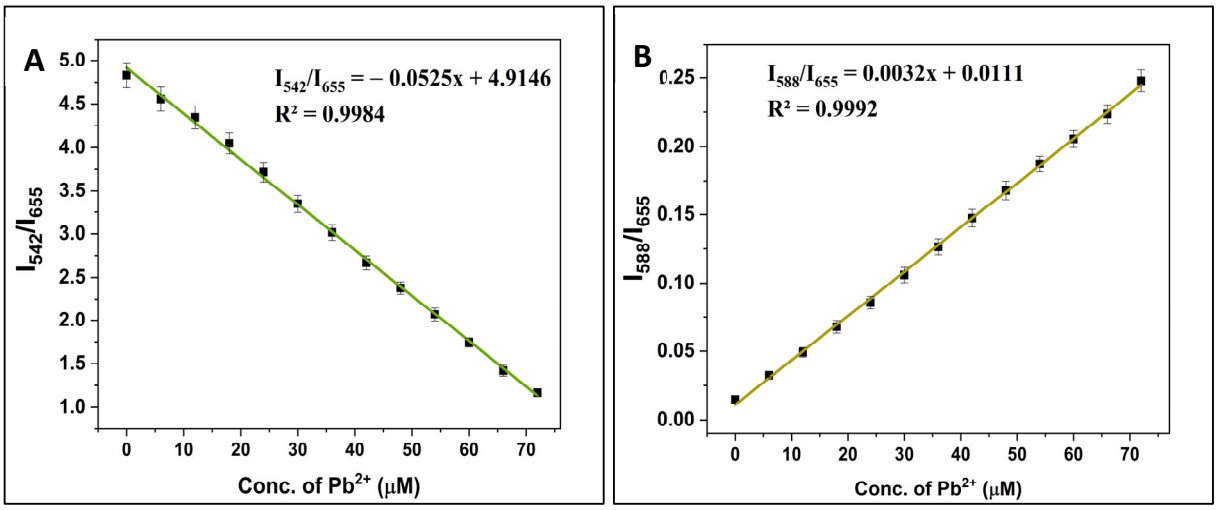

Figure S9. (**A**) The linear calibration plot with the green-to-red emission (GRE) ratios (I_{542}/I_{655}) (**B**) Yellow-to-red (YRE) emission ratios (I_{582}/I_{655}) of UCNP@SiO_2-RBDA in the presence of increasing concentration of Pb^{2+} ions.

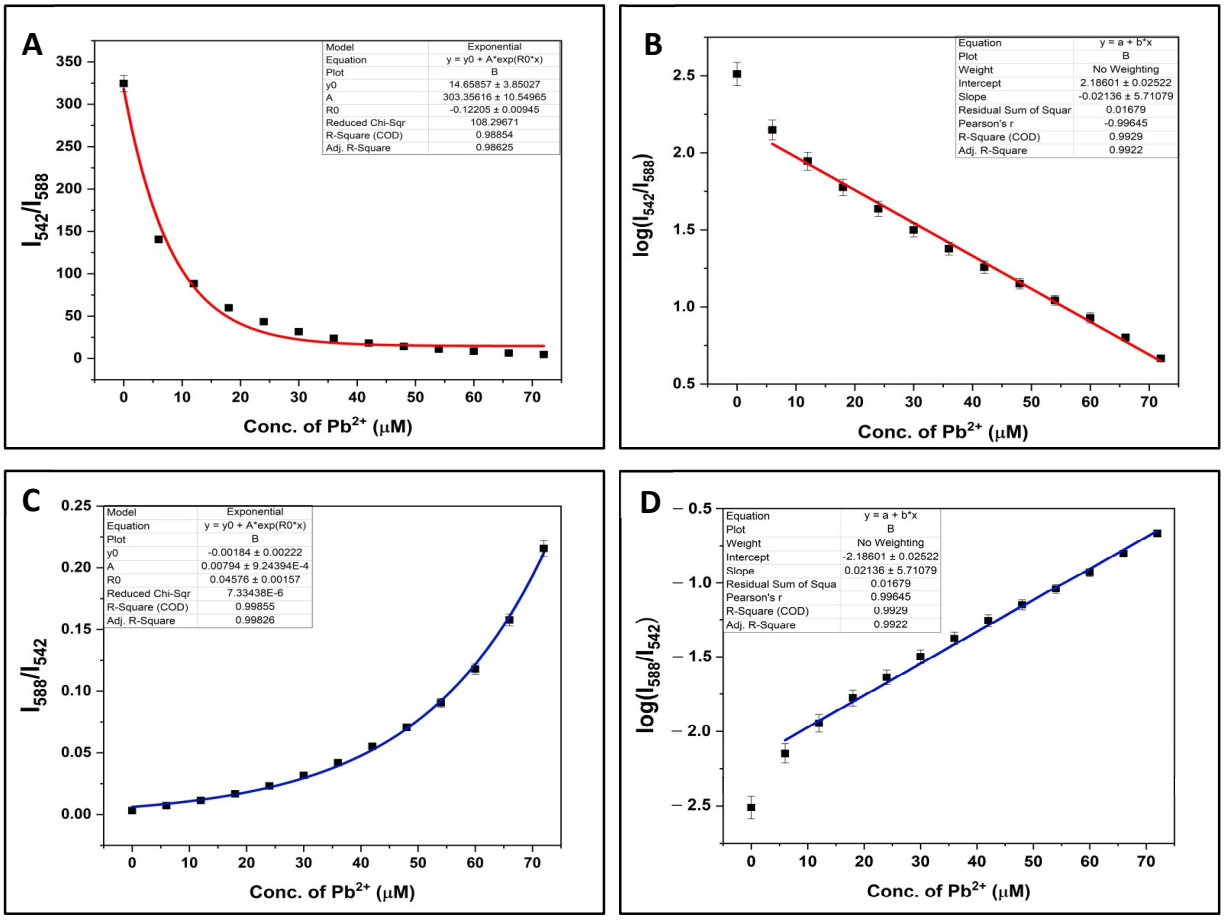

Figure S10. (**A**) The exponential and (**B**) logarithmic calibration curve (I_{542}/I_{588}) with the green to RBDA emission (yellow) ratios of UCNP@SiO_2-RBDA. (**C**) The exponential and (**D**) logarithmic calibration curve with RBDA emission (yellow) ratios to green emission ratio (I_{588}/I_{542}), in the different concentration of Pb^{2+} ions.

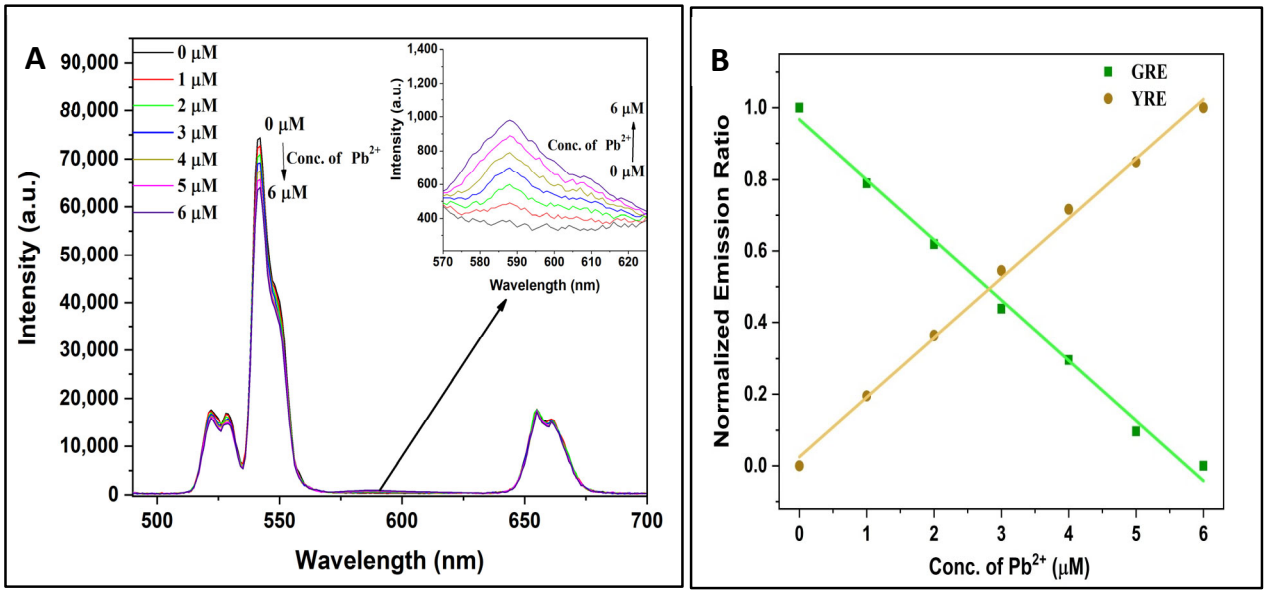

Figure S11. (**A**) Upconversion photoluminescence emission spectra of UCNP@SiO_2-RBDA upon addition of Pb^{2+} ions up to 6 µM. (**B**) Variation in normalized GRE and YRE at the concentration 0-6 µM of Pb^{2+} ions.

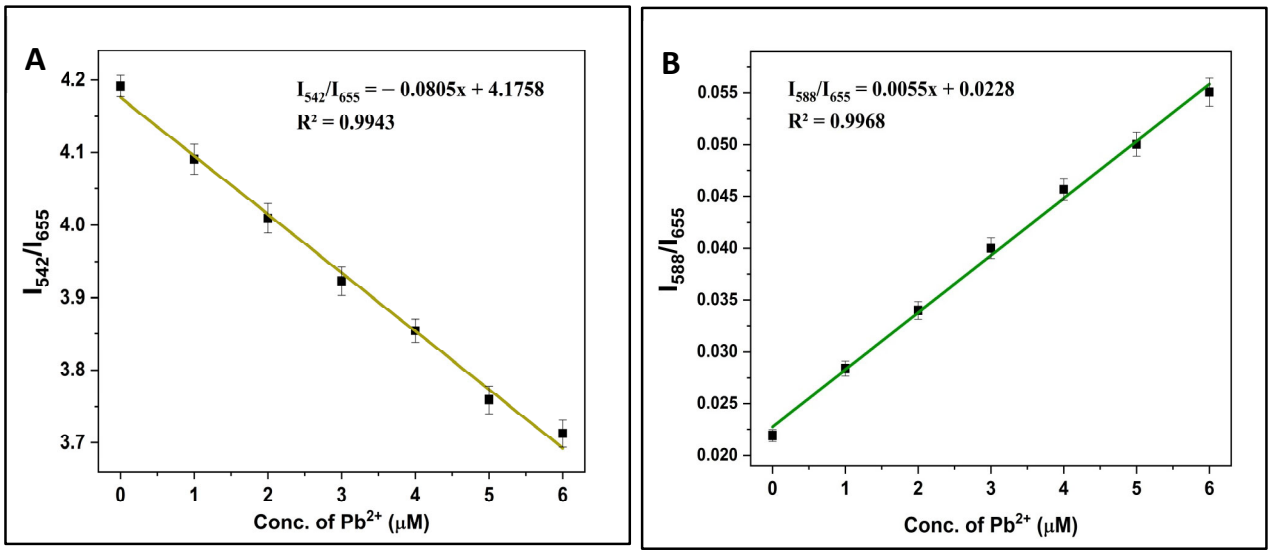

Figure S12. The linear calibration plot of UCNP@SiO_2-RBDA in the presence of Pb^{2+} ions in the range of 0-6 µM (**A**) Green-to-red emission (GRE) ratios (I_{542}/I_{655}) (**B**) Yellow-to-red (YRE) emission ratios (I_{588}/I_{655}).

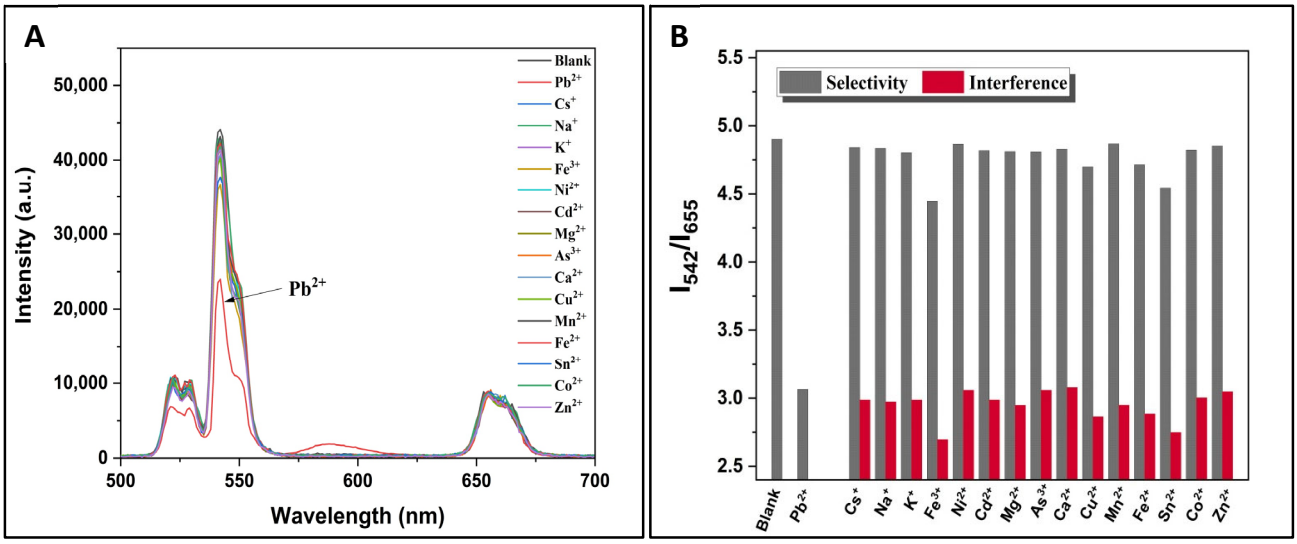

Figure 13. (**A**) Emission spectra of UCNP@SiO_2-RBDA in the presence of different metal ions, including Pb^{2+} ions. (**B**) Selectivity (gray bar) and interference test (red bar). The selectivity data were obtained using different metal ions, including Pb^{2+}. The interference tests were performed by the addition of 30 μM Pb^{2+} with the coexistence of an excess of interfering ions.

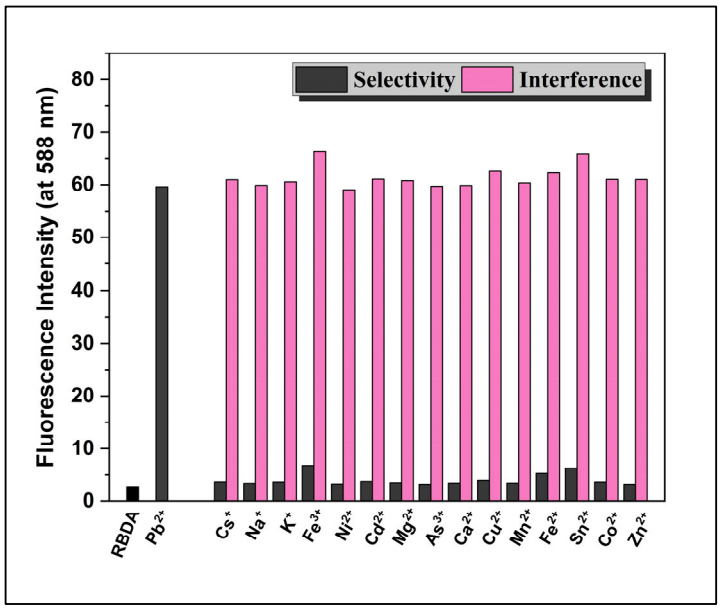

Figure S14. Selectivity (black bar) and interference test (pink bar) of RBDA towards different metal ions. The selectivity results were obtained using different ions, and the anti-interference tests were carried out by adding 15 μM of Pb^{2+} ions while an excess of interfering ions was present.