Electronic Supplementary Information (ESI†)

Sensitized luminescence from water-soluble LaF_3:Eu nanocrystals via partially-caped 1,10-phenanthroline: time-gated emission and multiple lifetimes

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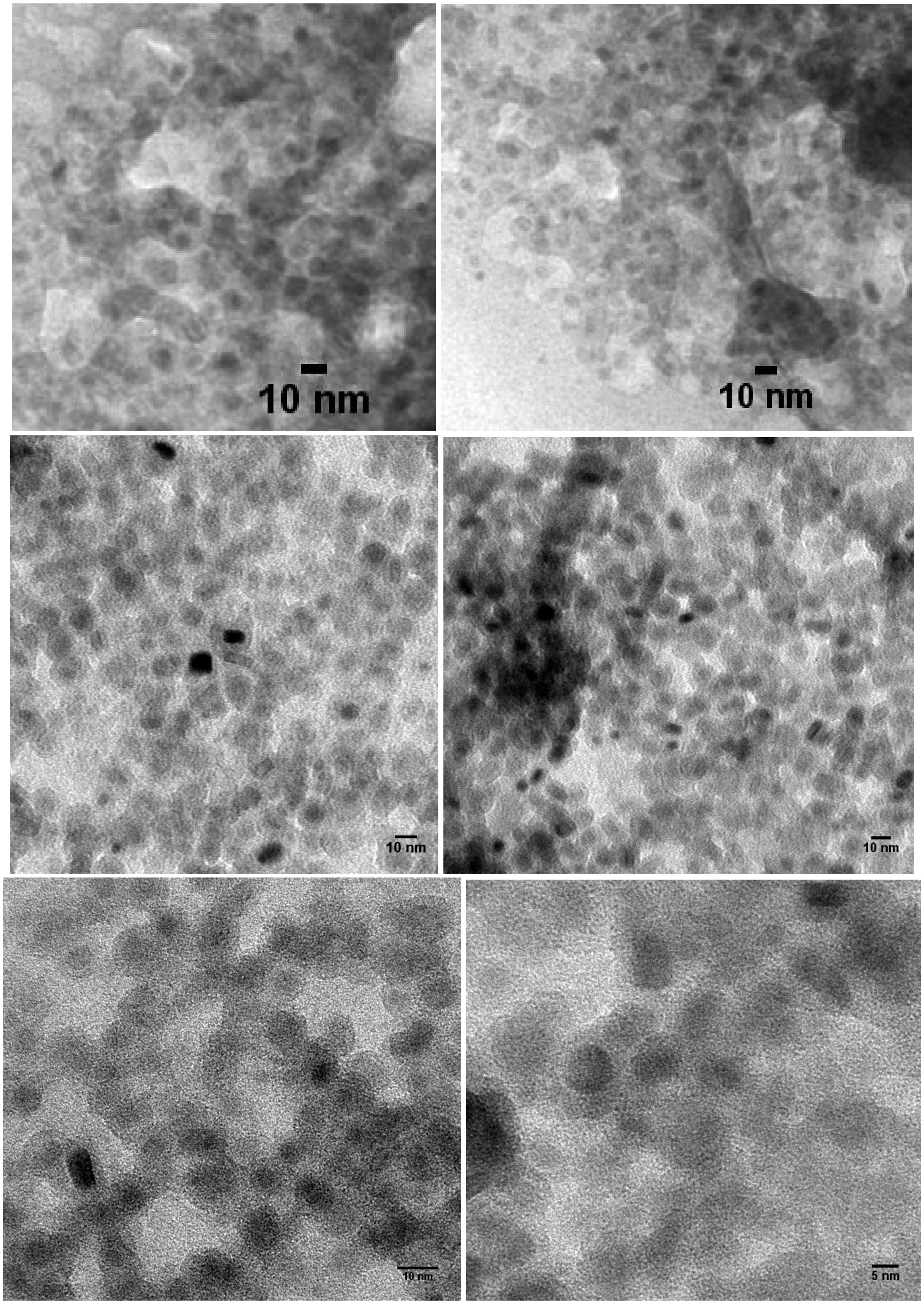

Figure S1. Low-resolution TEM images of citrate-capped LaF_3:Eu(5%) nanocrystals.

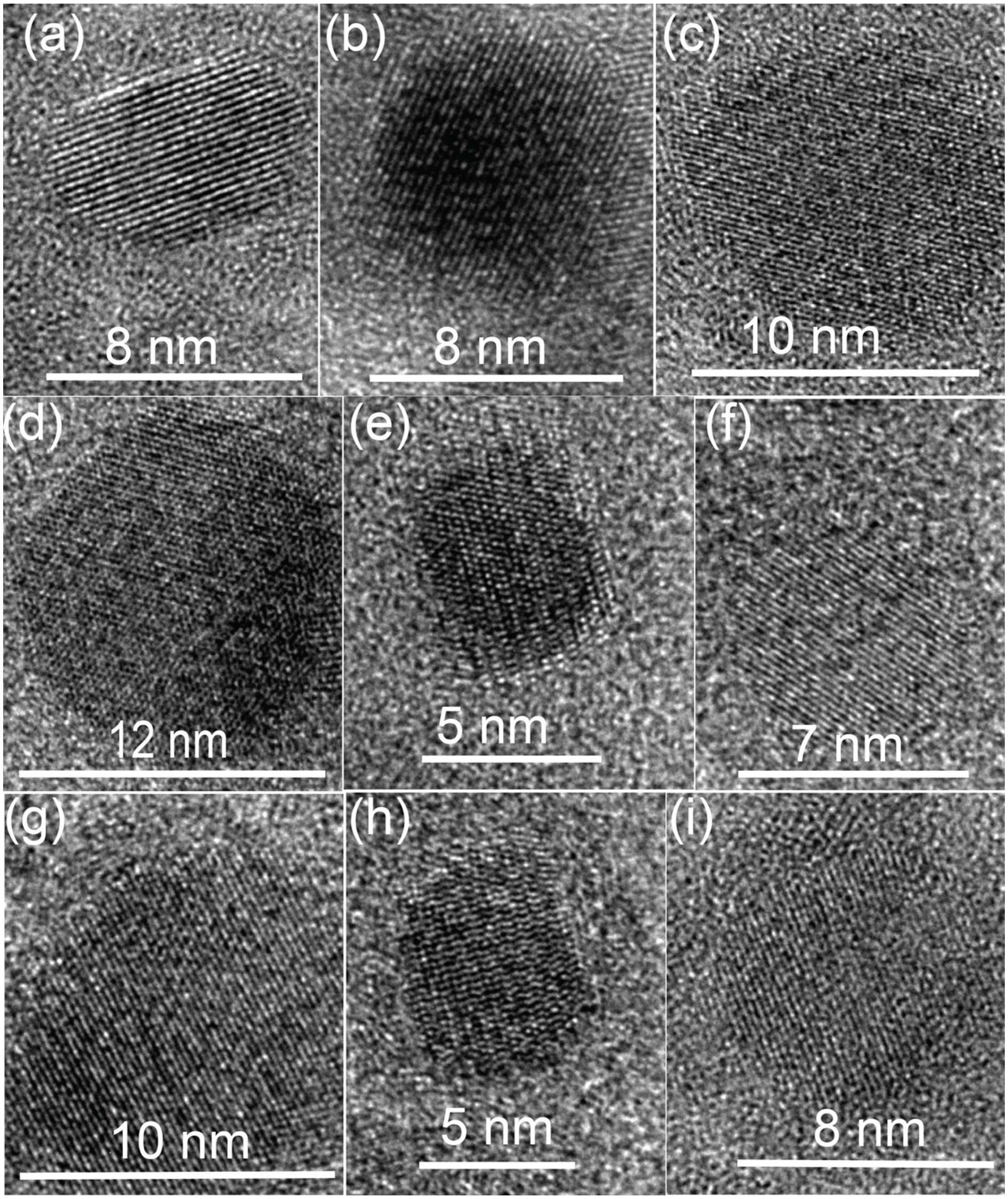

Figure S2. Representative high-resolution TEM images of individual citrate-capped LaF_3:Eu(5%) nanocrystals.

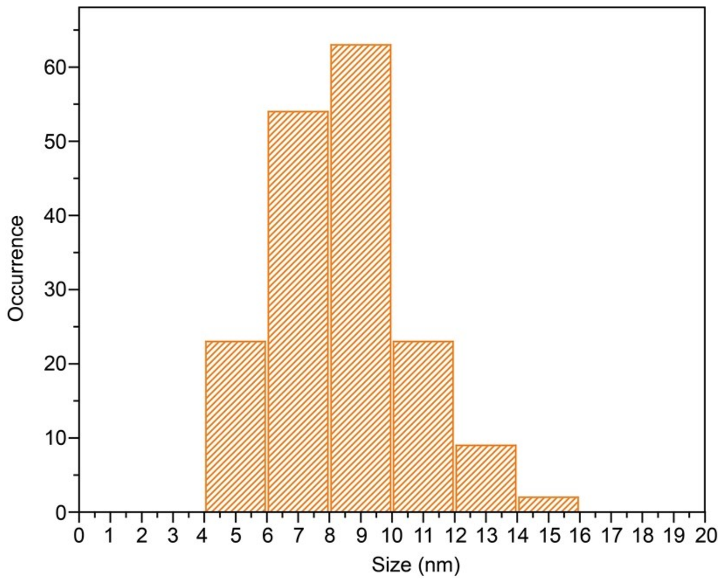

Figure S3. TEM size distribution of citrate-capped LaF_3:Eu(5%) nanocrystals obtained from images of 174 discernible particles.

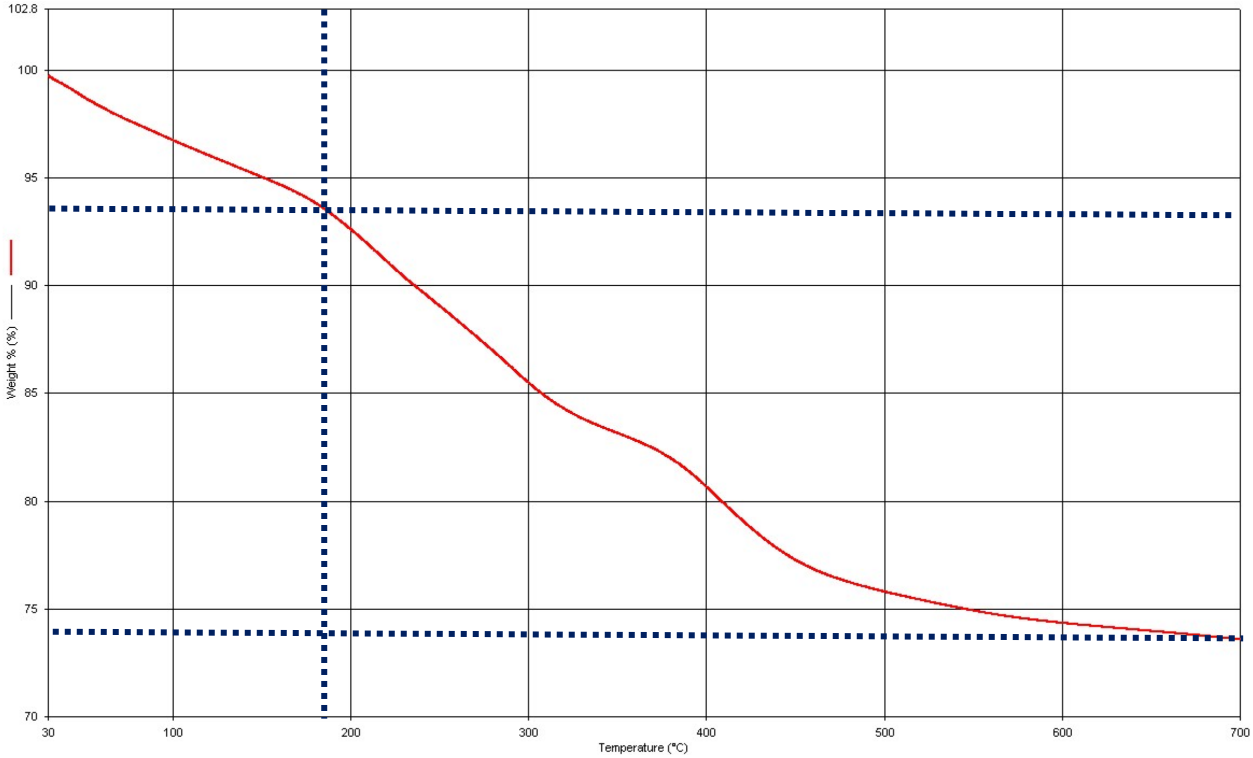

Figure S4. TGA plot of the citrate-capped LaF_3:Eu(5%) NCs.

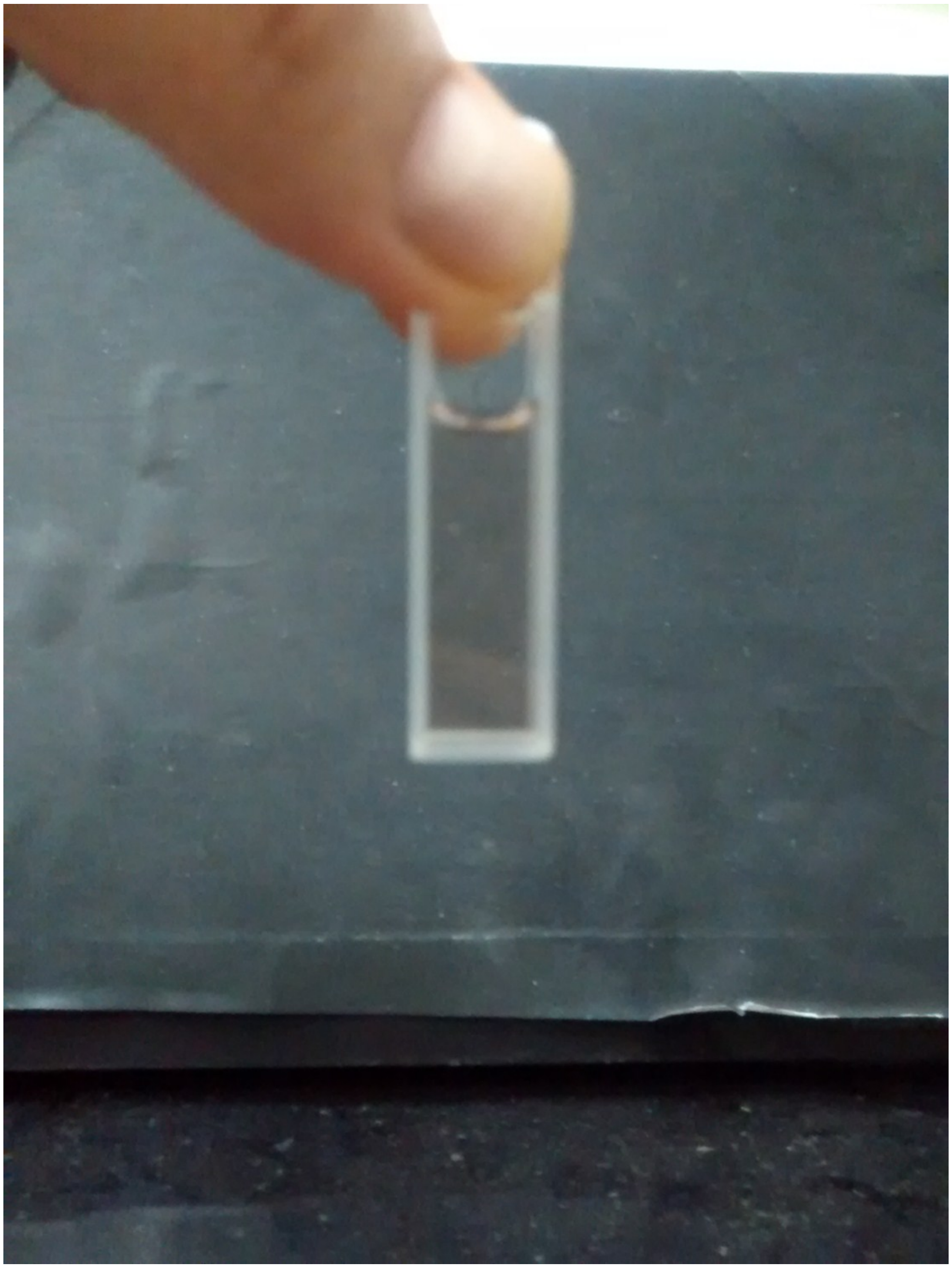

Figure S5**.** Picture of the colloidal solution of citrate/phen-capped LaF_3:Eu(5%) NCs in water. The concentration of the colloidal solution is ~50 mg/mL.

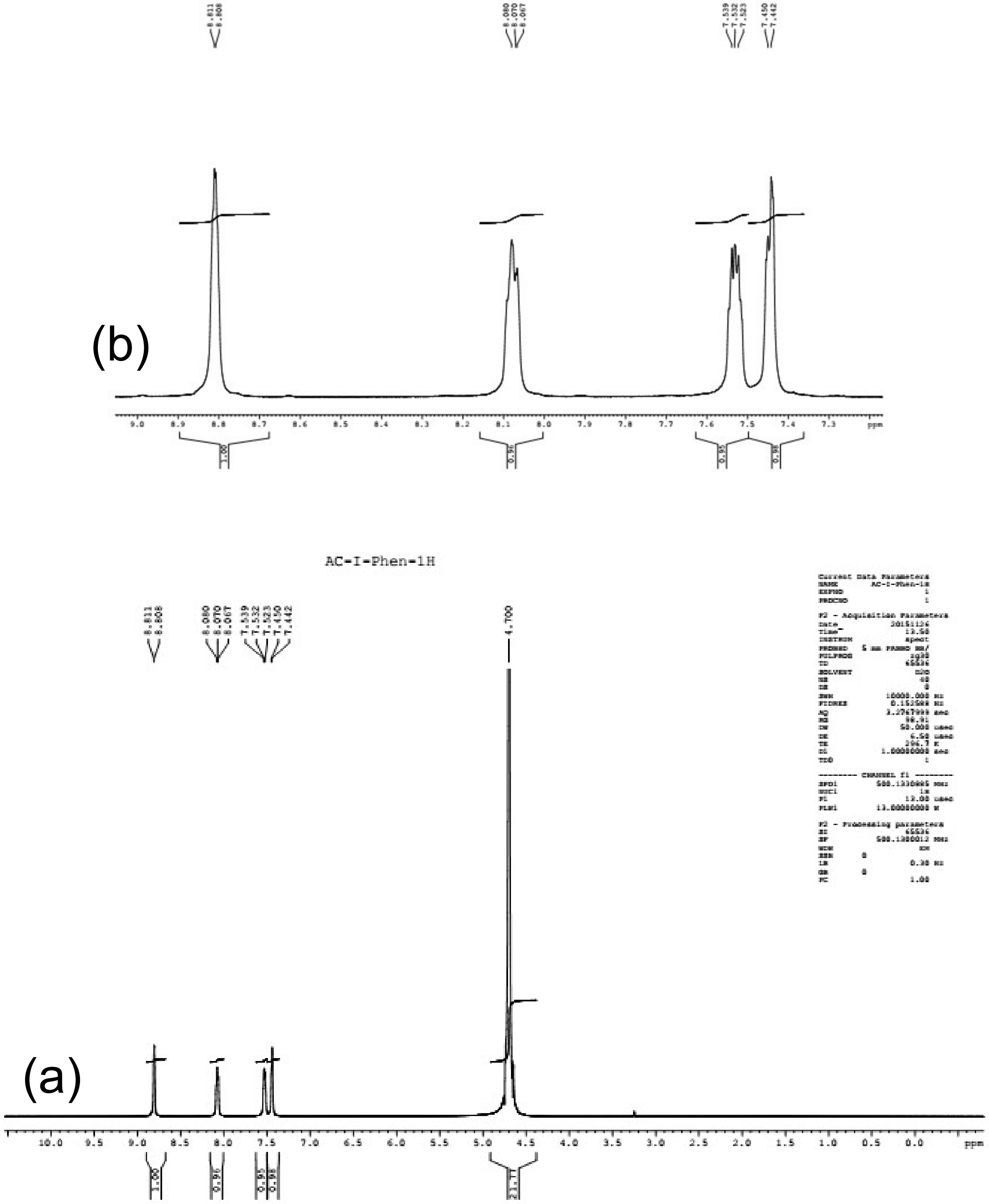

Figure S6. (a) The ^{1}H NMR spectrum of 1,10-phenanthroline dissolved in D_2O. The resonances observed in the aromatic region (between 7.4 and 9.0 ppm) are due to protons of the phen ligand, and the resonance at 4.69 is due to D_2O. (b) The expanded view of the aromatic region showing stark splitting of the proton resonances in D_2O.

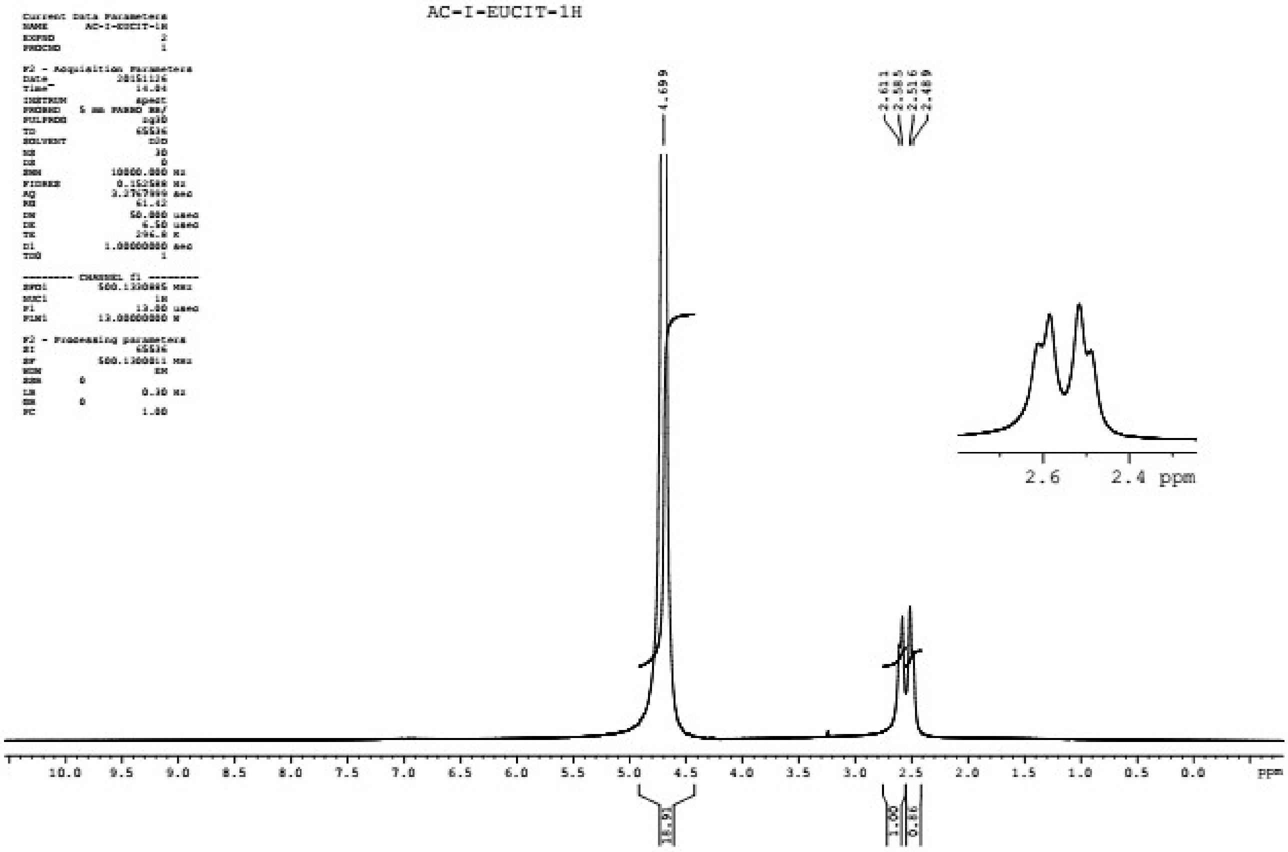

Figure S7. The ^{1}H NMR spectrum of citrate-capped LaF_3:Eu(5%) nanocrystals dispersed in D_2O. The broad doublet between 2.4 and 2.7 is attributed to the proton resenances of citrate ions capped on the surface of LaF_3:Eu nanocrystals (*Langmuir,* 2004, ***20****,* 11763). The resonance at 4.69 is due to D_2O.

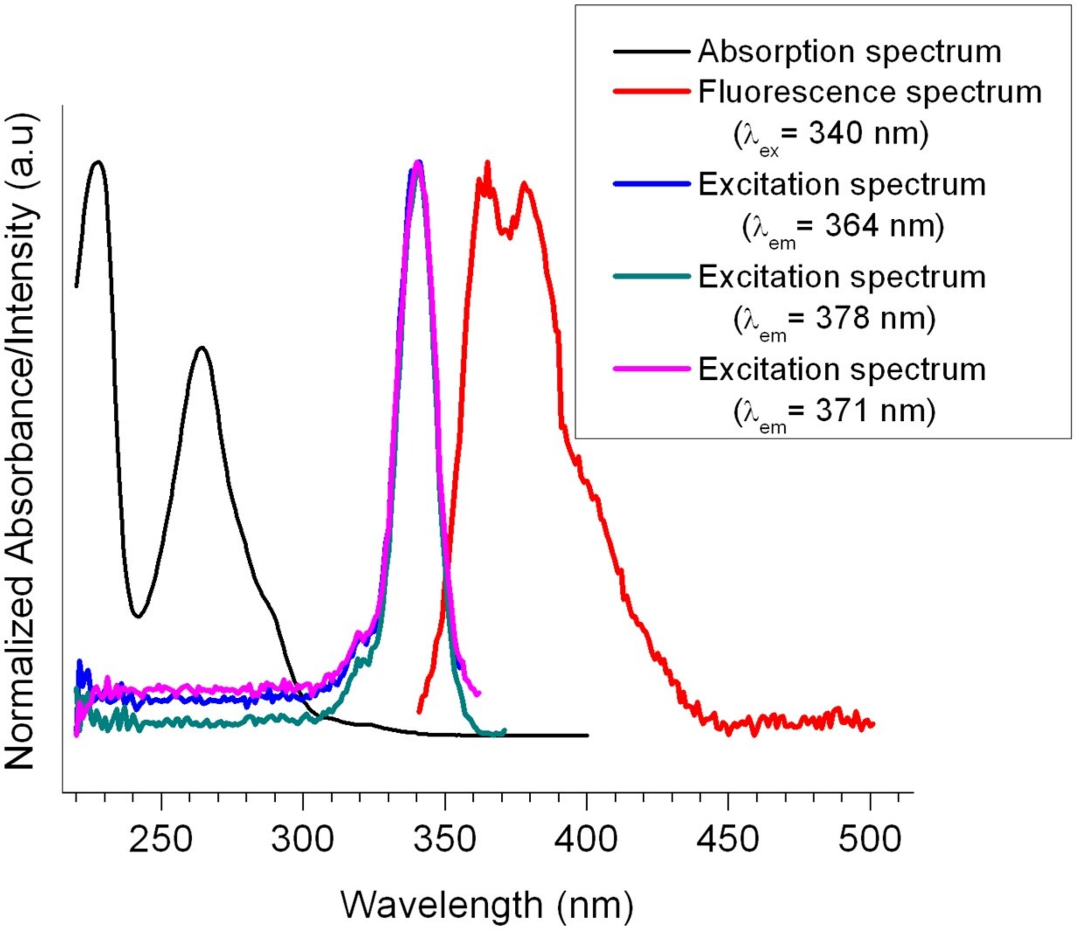

Figure S8. Absorption spectrum (black), fluorescence spectrum (red) and excitation spectra monitored at different fluorescence wavelengths, *i.e.* 364 nm (blue); 371 nm (green); and 378 nm (pink) of 1,10-phenanthroline in water.

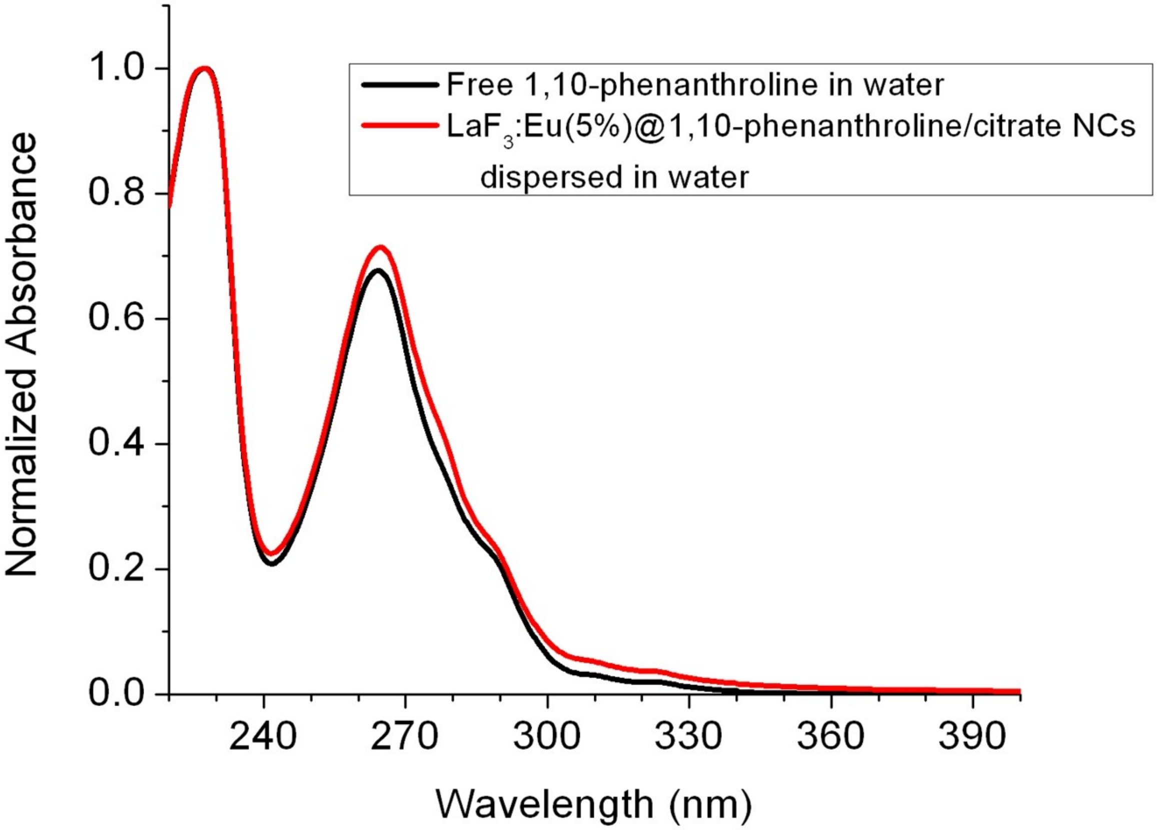

Figure S9. An overlap of the normalized absorption spectra of free 1,10-phenanthroline (black) and citrate/phen-capped LaF$_3$:Eu(5%) NCs (red) in water. There is no significant shift in the absorption bands of phen upon attachment with the NC surface.

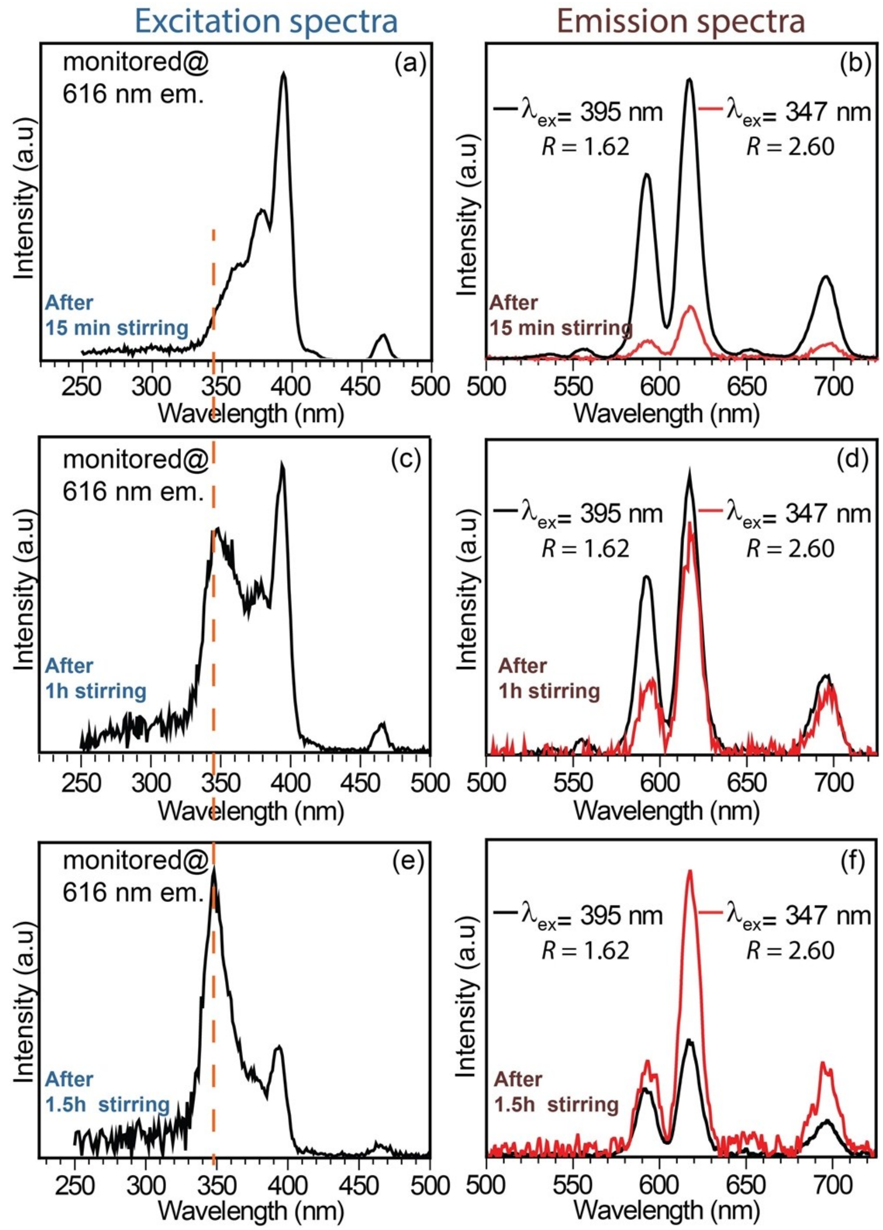

Figure S10. The progress of ligand exchange reaction between 1,10-phenanthroline and citrate capping ligands of LaF_3:Eu(5%) NCs in aqueous medium, monitored over a period of 1.5 hours of continuous stirring at 70 °C. (a,b) Excitation ($\lambda_{em.}$= 616 nm) and emission spectra ($\lambda_{ex.}$= 395 nm and 347 nm) of an aliquot of a reaction mixture of citrate-capped LaF_3:Eu(5%) NCs and phen in water after 15 min stirring, at room temperature, respectively. (c,d)) Excitation ($\lambda_{em.}$= 616 nm) and emission spectra ($\lambda_{ex.}$= 395 nm and 347 nm) of an aliquot of a reaction mixture of citrate-capped LaF_3:Eu(5%) NCs and phen in water after 1 hour stirring, at room temperature, respectively. (e,f) Excitation ($\lambda_{em.}$= 616 nm) and emission spectra ($\lambda_{ex.}$= 395 nm and 347 nm) of an aliquot of a reaction mixture of citrate-capped LaF_3:Eu(5%) NCs and phen in water after 1.5 hour stirring, at room temperature, respectively. The vertical dashed line on the excitation spectra represents evolution of phen-based excitation band with reaction time.

Detailed explanation of Figure S10. The excitation spectrum of the reaction mixture recorded after 15 minutes of stirring (Figure S10a) by monitoring the 616 nm ($^5D_0 \rightarrow {}^7F_2$) emission is slightly different as compared to the excitation spectrum obtained upon direct excitation of the citrate-capped LaF_3:Eu(5%) NCs (see Figure 5a in the main text). In this spectrum, it can be seen that higher energy tail of the $^5D_4, {}^5G_2, {}^5L_6 \leftarrow {}^7F_0$ transitions is extended beyond 350 nm. Upon excitation at 395 and 347 nm wavelengths the mixture displays strikingly different emission profiles (Figure S10b). The emission spectrum obtained upon 395 nm excitation is similar to the one obtained from citrate-capped LaF_3:Eu(5%) NCs dispersed in water (see Figure 5b in the main text), both of which display an R-value of 1.62. However, the emission spectrum obtained upon 347 nm excitation is clearly different and displays a higher R-value of 2.60, which indicates a higher asymmetry around Eu^{3+} dopant sites as well as sensitization of the dopant sites by phen ligands. It is important to note that citrate-capped LaF_3:Eu(5%) NCs in water do not display emission upon 347 nm excitation (see Figure 5b in the main text). The intensity of this emission spectrum is very less as compared to the intensity of spectrum obtained upon 395 nm excitation. From the excitation spectrum it can be observed that$^5L_6 \leftarrow {}^7F_0$ transition (395 nm) is much intense as compared to the intensity observed at 347 nm (Figure S10a). This is unusual of a sensitization process in which the ligand excitation bands as well as Eu^{3+} emission lines are much intense as compared to f-f excitation and emission transitions obtained upon direct excitation. These results suggest that either a very small number of phen ligands are attached on the surface of the NCs in water upon ligand exchange with citrate capping ligands after 15 minutes of stirring, or a very small number of nanoparticles have undergone ligand exchange during this time period in the mixture.

After 1 hour stirring of the reaction mixture, the intensity of the $^5L_6 \leftarrow {}^7F_0$ transition (395 nm) of the excitation spectrum is almost similar to the intensity of the phen-based excitation band maxima at 347 nm (Figure S10c). Their corresponding emission spectra (Figure S10d) obtained upon excitation at these wavelengths also display almost similar intensity at 616 nm ($^5D_0 \rightarrow {}^7F_2$ transition), but are clearly different emission profiles with R-values of 1.62 (for 395 nm excited emission spectrum) and 2.60 (for 347 nm excited emission spectrum), as observed in the emission spectra obtained after 15 minutes of stirring (Figure S10b). These results clearly suggest that more ligand exchange takes place on the surface of the NCs over this period of time (*i.e.,* 1h).

Further measurements of the excitation and emission spectra at different wavelengths were done after 1.5 hours of continuous stirring (Figure S10e,f). Strikingly, the phen-based excitation band maxima at 347 nm at this time period is more intense as compared to $^5L_6 \leftarrow {}^7F_0$ excitation transition at 395 nm (Figure S10e), and similarly the emission spectrum obtained upon 347 nm excitation is more intense as compared to emission spectrum obtained upon 395 nm excitation (Figure S10f). The emission profiles follow a similar trend as observed above (Figure S10b,d). These excitation and emission spectra (Figure S10e,f) are typical of a sensitization process, and suggest that a signification number phen ligands have been attached on the surface of the NCs upon ligand exchange with citrate ions. Further measurements of the excitation and emission spectra of the aliquots of reaction mixture during 1.5–2 hour continuous stirring at 70 °C, does not further enhance the luminescence intensity of the europium emission, and both emission and excitation spectra are similar to the ones obtained at 1.5 hour stirring. This indicates that ligand exchange does not proceed further and is possibly complete at 1.5 hour after stirring at 70 °C. Considering that despite ligand exchange with phen, these NCs are still dispersed in water is remarkable, and therefore reaction was stopped after 2 hours of stirring.

Synthesis of [Eu(phen)$_2$(NO$_3$)$_3$]. In an attempt to synthesize 1:1 complex of Eu^{3+} with 1,10-phenanthroline (phen), 46.03 mg (0.23 mmol) of phen was dissolved in 10 mL water at 95 °C under stirring. After all the phen dissolved in water, 0.1 gm (0.23 mmol) of Eu(NO$_3$)$_3$·5H$_2$O dissolved in 5 mL of water was added dropwise to the above solution under stirring. The resulting solution was continuously stirred for 2 hours at 95 °C, until final volume of the solution remained just ~7 mL. The solution was cooled and left for slow evaporation of the water. After 30 hours, sharp needle like crystals appeared in the solution, which were filtered out and dried in vacuum. The crystals were further washed with water and dried again. Finally, the crystals were washed with chloroform and stored. Despite 1:1 stoichiometric ratio of europium and phen used in the reaction, the final product has a 1:2 stoichiometric ratio of europium and phen as reported in the literature (*Eur. J. Inorg. Chem.,* **2015**, 4861–4868). *Elemental analysis:* Calcd. for $C_{24}H_{16}N_7O_9Eu\cdot H_2O$: C, 40.24; H, 2.53, N, 13.69 %. Found: C, 40.10; H, 2.51, N, 13.62 %.

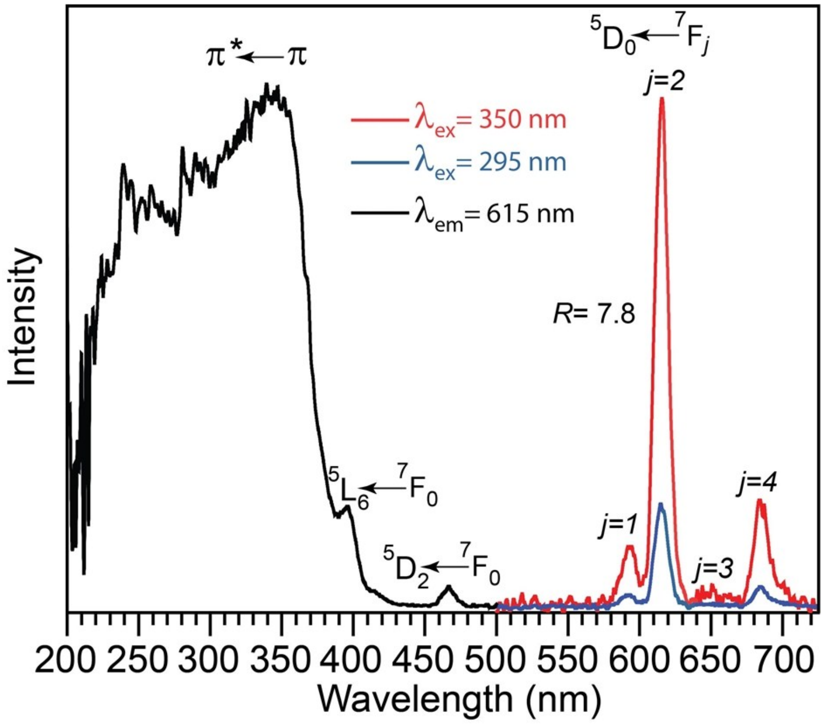

Figure S11. Excitation spectrum (black) and emission spectra (at two different excitation wavelengths) of [Eu(phen)$_2$(NO$_3$)$_3$] complex in solid state. Both emission spectra furnish a similar *R*-value of 7.8.