Supporting Information

Phase Selective Synthesis of Quantum cutting Nanophosphors and the Observation of a Spontaneous Room Temperature Phase Transition

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1. Materials and methods

1-Ethyl-3 methyl imidazolium bromide [C₂mim]Br. Modifying a literature procedure, 58 ml of ethyl bromide (0.79 mol, Sigma Aldrich 98%) and 48 ml of N-methyl imidazole (0.607 mol, Sigma Aldrich 99%) were refluxed under Ar atmosphere at 40 °C for 3 hours in a 250 ml round bottom flask.¹ After cooling to room temperature (RT), ethyl acetate (J.T.Baker) was added and the product crashed out of the solution. After filtration the crude product was washed with ethyl acetate and dried under vacuum at 25 °C for 10 hours to give a white solid and checked by ¹H NMR.

1-Ethyl-2, 3 methyl imidazolium bromide [C₂dmim]Br.The same procedure was maintained as above, only 0.607 mol 1, 2 dimethyl imidazole (ABCR, 98%) is used instead of N-methyl imidazole.

1-Butyl-3 methyl imidazolium bromide [C₄mim]Br. Modifying a literature procedure, 39.2 ml distilled 1-bromo butane (Fluka, 96%) was added dropwise to stirring 1-methyl imidazole (24.2 ml) over 30 minutes at 0° C.² Then the flask was covered with aluminum foil and the reaction proceeds at room temperature for 96 hour. The solid product is recrystallized from acetonitrile and dried under vacuum followed by checking with ¹H NMR.

1-Octyl-3 methyl imidazolium bromide ($[C_8mim]Br$),1-decyl-3 methyl imidazolium bromide ($[C_{10}mim]Br$) were purchased from Ioli Tec (Denzlingen, Germany) and tetramethyl ammonium bromide (98%) were purchased from Alfa Aesar and were dried at 80°C under vacuum prior to

use. 1-Ethyl-3-methyl-imidazolium chloride was purchased from Merck KGaA (Dermstadt, Germany) and dried at 80°C under vacuum prior to use.



Scheme S1. ILs used in this study. a) $[C_n mim]Br$: $R^1 = H$, $R^2 = ethyl$, butyl, octyl, decyl; $[C_2 dmim]Br$: $R^1 = CH_3$, $R^2 = ethyl$; b) $[Me_4N]Br$: $R^1 - R^4 = methyl$.

Structural characterization by powder X-Ray diffraction



Figure S1. PXRD pattern of NaGdF₄:Eu³⁺ nanocrystals prepared without IL and 1 hour stirring at room temperature.



Figure S2. (a), PXRD pattern of NaGdF₄:Eu³⁺ nanocrystals prepared with 1 mol% 1-ethyl-di methyl imidazolium bromide. (b), PXRD pattern of NaGdF₄:Eu³⁺ nanocrystals prepared with 1 mol% 1-ethyl-3 methyl imidazolium chloride. Both the cases, reaction mixture were stirred for 1 hour at room temperature.



Figure S3. PXRD pattern of NaGdF₄:Eu³⁺ nanocrystals prepared with 0.1 mol% [C_2 mim]Br IL. The reaction mixture was stirred for 3 hour at 80°C. ("H" and "C" corresponds to hexagonal and cubic phase respectively.)



Figure S4. PXRD pattern of NaGdF₄:Eu³⁺ nanocrystals prepared without IL at room temperature (b), NaGdF₄:Eu³⁺ nanocrystals prepared at 80°C and without IL (c) NaGdF₄:Eu³⁺ nanocrystals prepared at 80°C and with 0.1 mol% [C₂mim]Br. In all the cases, reaction mixture was stirred for 1 hour.

2. Influence of post reaction treatment of as-prepared NaGdF₄

To understand the phase stability at higher temperature, both the as prepared hexagonal and cubic (NP1, NP15 of Table 1 respectively and Scheme S2) samples are heated at different temperatures (Figure S5-S6). The hexagonal phase of NP1 prevails upon calcinations at 200°C for 1 hour. Upon heating for an extended time (3-7 hours at 400°C) aside from highly crystalline hexagonal NaGdF₄, the formation of small contributions of orthorhombic GdF₃ (marked by asterix in Figure S5-e) is observed. When the cubic sample prepared at 80°C nucleation temperature (NP15), is heated at higher temperatures, (Figure S6) the cubic phase remains up to 400°C and 3 hour heating time. After 5 hour, a drastic change in phase distribution is observed and mainly hexagonal NaGdF₄ with minor contributions of orthorhombic GdF₃ appear. Thus, if the as prepared hexagonal and cubic material is heated at 400°C for 5 hour, similar material is obtained: hexagonal NaGdF₄ with minor contribution of GdF₃, which undoubtedly proves the thermodynamic stability of hexagonal phase over the cubic (Scheme S2).



Scheme S2. Effect of reaction conditions and sample treatment.



Figure S5. PXRD pattern of NaGdF₄ nanocrystals obtained using 0.1 mol% [C₂mim]Br ionic liquid at room temperature (a) as prepared (b) as prepared sample calcined at 200°C for 1 hour (c) as prepared sample calcined at 400°C for 3 hour, (d) as prepared sample calcined at 400°C for 5 hour and (e) as prepared sample calcined at 400°C for 7 hour. ["H" corresponds to hexagonal phase of NaGdF₄ and * corresponds to orthorhombic phase of GdF₃.]



Figure S6. PXRD pattern of NaGdF₄ nanocrystals obtained using 0.1 mol% [C₂mim]Br ionic liquid at 80°C (a) as prepared (b) as prepared sample calcined at 200°C for 1 hour (c) as prepared sample calcined at 400°C for 5 hour. "H" and "C" corresponds to hexagonal and cubic phase respectively. The peaks marked by asterix are indicating the formation of orthorhombic GdF₃.



Figure S7. PXRD pattern of NaGdF₄ nanocrystals obtained using 1 mol% [C_{10} mim]Br; pattern obtained just after the preparation (below) and after 3 months of its preparation (up). Similar observation is obtained for the samples obtained from [C_8 mim]Br.



Figure S8. PXRD pattern of NaGdF₄:Eu³⁺ nanocrystals prepared with 1.0 mol% [C₂mim]Br IL at room temperature (b) and nanocrystals prepared with 0.1 mol% [C₂mim]Br IL at 80°C (c) . The PXRDs are taken after 3 months of its preparation.



Figure S9. PXRD pattern of NaGdF₄: Eu^{3+} nanocrystals prepared with 1.0 mol% [C₄mim]Br IL at room temperature and calcined at 200°C for 2 hour.

When as prepared cubic NaGdF₄ obtained from [C₄mim]Br was heated at 200°C for 2 hours, hexagonal phase is obtained (Figure S9) which clearly indicates that Ostwald ripening process becomes faster due to heating and activation energy for the phase transformation reached quickly.



Figure S10. Low magnification TEM images of NaGdF₄:Eu³⁺ nanocrystals prepared at room temperature and in presence of (a) 0.1 mol% [C₂mim]Br, (b) 0.5 mol% [C₂mim]Br and (c) 1.0 mol % [C₂mim]Br.



Figure S11. High resolution transmission electron microscope (HRTEM) images of NaGdF₄:Eu³⁺ nanocrystals prepared using 1mol% [C_2 mim]Br IL at room temperature.



Figure S12. Scanning Electron Microscope (SEM) images of (a) NaGdF₄:Eu³⁺ nanocrystals prepared without IL at room temperature, (b) nanocrystal prepared in presence of 0.1 mol% [C₂mim]Br at room temperature, (c) nanocrystal prepared at 80 °C without IL, (d) nanocrystal prepared at 80 °C in presence of 0.1 mol% [C₂mim]Br IL, the reaction time is 30 minutes, (e) & (f) nanocrystal prepared at 80 °C in presence of 0.1 mol% [C₂mim]Br IL, the reaction time is 60 minutes (g) nanocrystal prepared at 80 °C with 0.1 mol% [C₂mim]Br and calcined at 200 °C for 1 hour, (h) nanocrystal prepared at 80 °C with 0.1 mol% [C₂mim]Br and calcined at 400 °C for 3 hours (i) nanocrystal prepared at room temperature with 0.1 mol% [C₂mim]Br calcined at 400 °C for 3 hours.



Figure S13. Low magnification TEM images of NaGdF₄:Eu³⁺ nanocrystals prepared at RT and in the presence of 1.0 mol% [C_{10} mim]Br, measured after 3 months of preparation.



(b)



Figure S14. The presence of proper elemental components was confirmed by the energy dispersive X-ray analysis (EDXA) and it is seen that concentration of Eu^{3+} in each case nicely matches with the experimental value. Such as both for the hexagonal (a) and cubic (b) Eu^{3+} dopant concentration are very close to the experimental value.[The unassigned peak such as the strong one near 2keV is due to gold which was used to spatter our sample before SEM measurement].

(a)

Optical Characterizations

The excitation spectra of 2 mol% Eu³⁺ doped NaGdF₄ nanocrystals crystallized in the hexagonal and cubic phase using [C₂mim]Br IL at room temperature and 80°C (Figure S15- S16) were measured at room temperature and liquid nitrogen temperature (-196°C, 77 K) respectively. Monitoring the ${}^{5}D_{0}{}^{-7}F_{2}$ electric dipole transition of the Eu³⁺ ion at 615 nm and the ${}^{5}D_{0}{}^{-7}F_{1}$ magnetic dipole transition of the Eu³⁺ ion at 592nm, the narrow transition lines of Gd³⁺, centered at 272 nm (${}^{8}S_{7/2}{}^{-6}I_{J}$) and 310 nm (${}^{8}S_{7/2}{}^{-6}P_{J}$) together with the typical Eu³⁺ transitions can be seen. In the vacuum-UV (VUV) excitation spectrum (Figure S17) the Eu³⁺-F⁻ charge transfer (CT) band below 180 nm becomes apparent but, most importantly, no Eu³⁺-O²⁻ CT band is observed (which would be expected around 230 nm).³ This confirms the absence of oxygen impurities in the sample. The strong band located near 114 nm for hexagonal and 124 nm for cubic originates from the 4f-5d transition of Gd³⁺.



Figure S15. Excitation spectra of hexagonal and cubic NaGdF₄:Eu³⁺ nanocrystals measured at room temperature; (a) prepared with 0.1 mol% [C₂mim]Br at RT, (b) prepared with 0.1 mol%

 $[C_2 mim]$ Br at 80°C, (c) prepared with 0.5 mol% $[C_2 mim]$ Br at RT and (d) prepared with 1 mol% $[C_2 mim]$ Br at RT.



Figure S16. Excitation spectra of hexagonal and cubic NaGdF₄:Eu³⁺ nanocrystals measured at - 196°C; (a) prepared using 0.1 mol% [C₂mim]Br at RT, (b) prepared using 0.1 mol% [C₂mim]Br at 80°C, (c) prepared using 0.5 mol% [C₂mim]Br at RT and (d) prepared using 1 mol% [C₂mim]Br at RT.



Figure S17. Photoluminescence (PL) decays of NaGdF₄: Eu samples obtained by 0.5 mol% [C₂mim]Br and measured at 77K and under 393 nm excitation. The fitted curve is single exponential and average life time value is 11.6ms [$\chi^2 = 0.9998$].



Figure S18. Photoluminescence (PL) decays of NaGdF₄:Eu samples obtained by 0.5 mol% $[C_2mim]Br$ and measured at -196°C (liquid nitrogen temperature) and RT under 393 nm

excitation. The decay curve is monitored at 554 nm and the fitted curve is biexponential and the average life time value is 1.77 and 3.82 ms for RT and -196°C respectively. The average delay time is calculated by $t(\tau) = a_1 \tau_1 + a_2 \tau_2$, where a_1 and a_2 are the contributions of the respective decay component. The χ^2 value is 0.9991 and 0.9998 for S19a and S19b respectively.



Figure S19. Photoluminescence (PL) decays of NaGdF₄:Eu samples measured at room temperature and under 393 nm excitation; (a) prepared at RT by using 0.1 mol% [C₂mim]Br. The decay curve is fitted bi-exponentially and the average life time is 7.95 ms [$\chi^2 = 0.9994$]; (b) prepared at 80°C by using 0.1 mol% [C₂mim]Br. The decay curve is fitted single exponentially and life time is 9.72 ms [$\chi^2 = 0.9998$]; (c) prepared at RT by using 0.5 mol% [C₂mim]Br. The decay curve is fitted single-exponentially and life time is 11.29 ms [$\chi^2 = 0.998$]; (d) prepared at

RT by using 1.0 mol% [C₂mim]Br. The decay curve is fitted single exponentially and life time is $10.56 \text{ ms}[\chi^2 = 0.9998].$

The average delay time is calculated by $t(\tau) = a_1 \tau_1 + a_2 \tau_2$, where a_1 and a_2 are the contributions of the respective decay component.



Figure S20. Emission spectra of NaGdF₄:Eu³⁺ nanocrystals with different Eu³⁺ dopant concentration (a) 0.5 mol%, (b) 2 mol% and (c) 10 mol% and measured at room temperature and prepared by 0.5 mol% [C₂mim]Br at RT.



Figure S21. Emission spectra of NaGdF₄:Eu³⁺ nanocrystals prepared by [C₈mim]Br and [C₁₀mim]Br. The spectra are taken directly after sample preparation (a & c) and 3 months after (b &d).



Figure S22. Emission spectra of NaGdF₄:Eu³⁺ nanocrystals prepared in the presence of $[C_2mim]Br$ at RT. The spectra are taken immediately after sample preparation and 3 months after.

Judd-Ofelt parameter calculation

Judd-Ofelt (J-O) parameters are calculated to get more insight into the structural changes surrounding the Eu³⁺ ion due to change of crystal phases, morphology etc.⁴⁻⁵ The J-O parameter (Ω_2) gives information on the intensities or nature of the hypersensitive transitions of the Eu³⁺ ion. The experimental intensity parameters (Ω_2) were determined from the emission spectra for Eu³⁺ ion based on the ⁵D₀ \rightarrow ⁷F₂ electric-dipole transition and the ⁵D₀ \rightarrow ⁷F₁ magnetic dipole transitions as the reference and they are estimated according to the equation

$$A = \frac{4e^2\omega^3}{3hc^3} \frac{1}{2J+1} \chi \sum \Omega_2 \langle {}^5D_0 \| U^{(2)} \| {}^7F_2 \rangle^2$$
(1)

Where $A_{0\lambda}$ is the coefficient of spontaneous emission, e is the electronic charge, ω is the angular frequency of the transition, h is Plank's constant, c is the velocity of light, χ is the Lorentz local field correction and is expressed as $\chi = \eta(\eta^{2}+2)^{2}/9$ where η is the refractive index of the sample which is experimentally determined, $\langle {}^{5}D_{0} || U^{(2)} ||^{7}F_{2} \rangle^{2}$ is the squared reduced matrix elements whose value is independent of the chemical environment of the ion and it is 0.0039 for J=2.⁴ Since the magnetic dipole ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition is relatively insensitive to the chemical environment around the Eu³⁺ ion, therefore, it can be considered as a reference for the whole spectrum and the coefficient of spontaneous emission is calculated according to the relation

$$A_{0J} = A_{01} (I_{0J} / I_{01}) (\gamma_{01} / \gamma_{0J})$$
(2)

where γ_{01} and γ_{01} are the energy baricenters of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ and ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions, respectively. A_{01} is the Einstein's coefficient between ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ levels and it is calculated using $A_{01} = \eta^{3}(A_{0-1})_{vac}$; where η is the refractive index of the sample and (A_{0-1}) vac = 14.65 sec⁻¹. J-O parameters (Ω_{2}) for the sodium gadolinium fluoride sample are calculated by the above explained method. The values of J-O parameter (Ω_{2}) are 6.69×10^{-20} cm², 9.88×10^{-20} cm², and 12.29×10^{-20} cm² for 0.1, 0.5 and 1.0 mol% [C₂mim]Br IL, respectively. These points to a less symmetric environment for Eu³⁺ ion with increasing IL concentration. Again the value of J-O parameter is 4.45×10^{-20} cm for as prepared sample obtained by 1 mol% [C₄mim]Br under excitation at 394 nm and room temperature but the value increases with time. Such as sample measured after one month, two months and 3 months of its preparation shows 6.45×10^{-20} cm², 6.97×10^{-20} cm², 9.79×10^{-20} cm² respectively. Higher Ω_{2} value for suggests that Eu³⁺ ion resides at more asymmetric environment than the earlier.



Figure S23. VUV excitation spectrum ($\lambda_{em} = 615$ nm for hexagonal and 592nm for cubic) of doped NaGdF₄:Eu³⁺ nanocrystals. The spectrum was taken at the Beamline I (SUPERLUMI) of the HASYLAB synchrotron facility at DESY.



Figure S24. Energy level diagram of Gd³⁺-Eu³⁺ system depicting transitions and energy transfers.⁴

Quantum yield calculation

Quantum yield for the NaGdF₄:Eu³⁺ ion is calculated by the method of Wegh et al.⁶ First the intensity ratio of ${}^{5}D_{0} / {}^{5}D_{1, 2, 3}$ was calculated both for the ${}^{6}G_{J}$ and ${}^{6}P_{J}$ levels excitation. Now from these intensity ratios, the efficiency of the cross relaxation step can be determined according to

$$\frac{P_{CR}}{P_{CR} + P_{DT}} = \frac{R(\frac{{}^{5}D_{0}}{{}^{5}D_{1,2,3}})_{{}^{6}G_{J}} - R(\frac{{}^{5}D_{0}}{{}^{5}D_{1,2,3}})_{{}^{6}P_{J}}}{R(\frac{{}^{5}D_{0}}{{}^{5}D_{1,2,3}})_{{}^{6}P_{J}} + 1}$$

and it is seen that the ratio $P_{CR}/P_{CR}+P_{DT}$ (P_{CR} is the probability of the cross relaxation and P_{DT} is the probability of direct energy transfer from Gd^{3+} to Eu^{3+}) is 0.54; which means that 5.4 of 10 Gd^{3+} ion in the ${}^{6}G_{J}$ excited levels relax through a two step energy transfer to Eu^{3+} , resulting in two visible photons whereas 4.6 of 10 Gd^{3+} ions in the excited ${}^{6}G_{J}$ states transfers all its energy to a high energy levels of Eu^{3+} resulting in the emission of one visible photon. In this way, a visible quantum efficiency of 154% is achieved. Similarly, the quantum yield for the other samples is also measured and their value is given in Table S1 below.

Table S1

Sample name	Nucleati	IL used	Crystal	Quantum
	on temp		phase	efficiency
NaGdF ₄ :Eu(2)	RT	0.1 mol%	Hexagonal	116%
		[C ₂ mim]Br		
NaGdF ₄ :Eu(0.5)	RT	0.5 mol%	Hexagonal	140%
		[C ₂ mim]Br		
NaGdF ₄ :Eu(2)	RT	0.5 mol%	Hexagonal	128%
		[C ₂ mim]Br		
NaGdF ₄ :Eu(10)	RT	0.5 mol%	Hexagonal	114%
		[C ₂ mim]Br		
NaGdF ₄ :Eu(2)	RT	1 mol%	Hexagonal	154%
		[C ₂ mim]Br		
NaGdF ₄ :Eu(2)	RT	1 mol%	Hexagonal	128%
		[C ₂ dmim]Br		
NaGdF ₄ :Eu(2)	RT	1 mol%	Hexagonal	131%

		[C ₄ mim]Br		
NaGdF ₄ :Eu(2)	RT	1 mol%	Hexagonal	134%
		[C ₈ mim]Br		
NaGdF ₄ :Eu(2)	RT	1 mol%	Hexagonal	148%
		[C ₁₀ mim]Br		
NaGdF ₄ :Eu(2)	80°C	0.1 mol%	Cubic	107%
		[C ₂ mim]Br		

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