## A general strategy for the synthesis of upconversion rare earth fluoride nanocrystals via a novel OA/ionic liquid two-phase system

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## **Supporting Information**

## **Experimental section**

**Materials.** Rare earth oxides  $La_2O_3$  (99.99%),  $Y_2O_3$  (99.99%),  $Gd_2O_3$  (99.99%),  $Yb_2O_3$  (99.99%), and  $Er_2O_3$  (99.99%) were purchased from Aladdin Chemistry Co. Ltd. Sodium oleate , oleic acid (OA), n-octanol were obtained from Sinopharm Chemical Reagent Co. 1–butyl-3-methylimidazolium tetrafluoroborate (BmimBF<sub>4</sub>), which was chosen as the ionic liquid (IL) in this reaction system, was purchased from Shanghai Cheng Jie Chemical Co. Ltd. Deionized water was used throughout. All the chemicals were of analytical grade and were used without further purification.

Synthesis of hydrophobic REF<sub>3</sub> (RE= Y, La, Gd and Yb) nanocrystals in OA phase. RE(oleate)<sub>3</sub> complexes were synthesized according to previously reported methods.<sup>1,2</sup> In a typical procedure, 1 mmoL of RE(oleate)<sub>3</sub> (RE = Y, La, Gd and Yb) was dissolved in certain amount of oleic acid at elevated temperature under vigorous magnetic stirring to form a homogeneous solution. Then the solution was transferred into a 50-mL Teflon-lined autoclave which contains 15 mL of BmimBF<sub>4</sub>. The two phase system was treated at 240°C for 24 hours. The whole system was allowed to cool to room temperature naturally, then the precipitates were found in OA phase and on the interface of the two phase system. The final products were collected by means of centrifugation at a speed of 8500 rpm, washed with cyclohexane and ethanol several times under ultrasonic conditions. Finally, the products are dried at 70°C under vacuum overnight.

Synthesis of cubic-phase oil-dispersible NaREF<sub>4</sub> and NaREF<sub>4</sub>: 20%Yb, 2%Er (RE= Y, Gd and Yb) Nanocrystals in OA phase. The synthetic procedure was the same as that used to synthesize REF<sub>3</sub> (RE= Y, La, Gd and Yb) nanocrystals, except that 1 mmoL sodium oleate and stoichiometric amounts of RE(oleate)<sub>3</sub> (RE = Y, Gd, Yb and Er) was taken as precursors.

**Synthesis of hexagonal-phase water-Soluble NaGdF4: Yb, Er and NaYF4: Yb, Er Nanocrystals in IL phase.** The synthetic procedure was the same as that used to prepare the oil-dispersible NaREF4: 20%Yb, 2%Er, except that 10 mL of n-octanol was added to the two phase system. In contrast, all the precipitates were deposited in the ionic liquid phase.

**Characterization.** The energy-dispersive x-ray (EDX) analysis and the sizes and morphologies of the products were measured by transmission electron microscopy (TEM) using a JEM 2010 microscopy (JEOL, Japan) with an acceleration voltage of 200 kV.

High-resolution TEM (HRTEM) was performed on a JEM 2100F microscopy (JEOL, Japan) with an acceleration voltage of 200 kV.

Powder X-ray diffraction analysis was conducted on a D/max-r C x-ray diffractometer (Rigaku, Japan) with Cu Ka radiation ( $\lambda = 0.154$  nm) at a scanning rate of 6°/min in the 20 range from 10°- 70°.

Fourier transform infrared (FT-IR) spectra were carried out on EQUINOX 55 spectrometer (Bruker, Germany) from samples on KBr pellets.

Upconversion fluorescence spectra were characterized by Fluorolog-3 spectrofluorometer (Jobin Yvon, France) at room temperature.



**Fig. S1** TEM image (a), EDX spectrum (b), SAED pattern (c), and XRD pattern (d) of oil-dispersible LaF<sub>3</sub> nanocrystals in OA phase.



**Fig. S2** TEM image (a), EDX spectrum (b), SAED pattern (c), and XRD pattern (d) of oil-dispersible GdF<sub>3</sub> nanocrystals in OA phase.



Fig. S3 TEM image (a), EDX spectrum (b), SAED pattern (c), and XRD pattern (d) of oil-dispersible  $YbF_3$  nanocrystals in OA phase.



Fig. S4 TEM image (a), EDX spectrum (b), SAED pattern (c), and XRD pattern (d) of oil-dispersible  $YF_3$  nanocrystals in OA phase.



Fig. S5 TEM image (a), EDX spectrum (b), SAED pattern (c), and XRD pattern (d) of oil-dispersible  $NaGdF_4$  nanocrystals in OA phase.



**Fig. S6** TEM image (a), EDX spectrum (b), SAED pattern (c), and XRD pattern (d) of oil-dispersible NaYbF<sub>4</sub> nanocrystals in OA phase.



**Fig. S7** TEM image (a), EDX spectrum (b), SAED pattern (c), and XRD pattern (d) of oil-dispersible NaYF<sub>4</sub> nanocrystals in OA phase.



**Fig. S8** Scheme showing the mechanism for the synthesis of RE fluoride nanocrystals in the OA/IL two phase reaction system.

In Fig. S8, the synthetic route  $1(a \rightarrow b)$ , marked by the yellow arrow, shows the mechanism for the formation of oil-dispersible RE fluoride nanocrystals in OA phase while the synthetic route  $2(c \rightarrow d)$ , marked by the blue arrow, shows the mechanism for the fabrication of water-soluble NaREF<sub>4</sub> nanocrystals with different crystal phase when n-octanol was added. The schematic diagram is in good agreement with the situation shown in the photographs of the real products (Fig. S13).

In a typical OA/ IL two-phase system, RE(oleate)<sub>3</sub> which was dissolved in oleic acid was taken as precursors. Instead of using highly toxic trifluoroacetate precursors, RE(oleate)3 and oleic acid turned out to be inexpensive, innocuous and environmental friendly.<sup>1,2</sup> 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF<sub>4</sub>) was chosen as ionic liquid in this reaction system. Under high temperature, BmimBF<sub>4</sub> partly hydrolyzes to produce F<sup>-</sup> in the presence of such impurities as ethanol, water, NO<sub>3</sub><sup>-</sup> and so on.<sup>3</sup> As shown in Fig. S8, the oleic acid with RE(oleate)<sub>3</sub> in it constitute the top phase of the OA/ IL two-phase system while BmimBF<sub>4</sub> was the bottom phase. When no n-octanol was added, the OA and BmimBF<sub>4</sub> were immiscible to each other even under high pressure and temperature. Thus, the reaction only took place in the interface area of the two-phase system. The formation of highly uniform and monodisperse RE fluoride nanocrystals in OA phase can be divided into two stages: the first stage is the burst nucleation stage and the second stage is the growing stage of nanocrystals. When the RE fluoride nuclei formed quickly at the interface, due to the strong chelating capacity of oleic acid with RE<sup>3+</sup> ions, the nuclei could enter the OA phase. When the RE fluoride nuclei returned to the interface, they continued to grow. However, the growing process was relatively slow compared to the nucleation process. The quick formation of nuclei as well as the separation of the nucleation and growing stage favors the formation of monodisperse nanoparticles according to the LaMer mechanism.<sup>4</sup> Since the surface of the nanocrystals was covered by an layer of oleic acid, which prevented the particles from aggregating and rendered them hydrophobic, the RE fluoride nanocrystals could be found in OA phase and the interface of the two-phase system. In this reaction, the ionic liquid, BmimBF<sub>4</sub>, function as the fluorine source in the formation of REF<sub>3</sub> and NaREF<sub>4</sub> nanocrystals.

However, due to the complexity of the two-phase system, some complex structures, such as core-shell structure which was evidenced by the relatively low percentage of F atoms and relatively high percentage of O atoms in the EDX spectra, could be formed. Further investigation, including XPS analysis, EELS and single particle EDX line scan, would be carried out to confirm the structure.<sup>5,6</sup>

In the n-octanol induced OA/IL two phase system, when 10 mL of n-octanol was added, n-octanol was dissolved in both OA and IL phase when heated continuously. Therefore, they function as a passageway for the transfer of  $RE^{3+}$  ions from OA-phase to IL-phase. When BF<sub>4</sub><sup>-</sup> partly decomposed and produced F<sup>-</sup> at high temperature, the RE fluoride nuclei began to appear in IL phase and was absorbed by Bmim<sup>+</sup> cations due to coulombic interactions. In this case, the reaction was carried out in IL phase. The role of BmimBF<sub>4</sub> is no longer limited to the fluorine source. However, it also functions as solvent, template and capping agent. Therefore, the IL phase provides a reacting environment which is totally different from that in OA phase. The size and morphologies of products in IL phase have a great disparity with those in OA phase. Generally speaking, they are relatively larger in particle size (Fig. S9), have relative poor dispersity, uniformity and a broader size distribution compared with those in OA phase (Fig. S11). Such disparities can be attributed to the change of reaction environment and the crystal phase transition from cubic to hexagonal, which usually turned out to exist in larger particle size.<sup>7</sup>

In addition, the IL layer absorbed on the surface of the nanoparticles make the IL-capped products disperse easily in water due to the hydrophilic properties of Bmim<sup>+</sup> cations. The one-pot synthesis of water-soluble NaREF<sub>4</sub> nanocrystals makes the products facile in surface modification and thus feasible in further biological application. The change in surface capping agents of products in both OA phase and IL phase could be further verified by the FT-IR spectroscopy (Fig. S12).

On the other hand, the crystal phase transition from cubic to hexagonal for NaREF<sub>4</sub> nanocrystals might be ascribed to the change of reaction environment for  $RE^{3+}$  ions. When a certain volume of n-octanol was added, the  $RE^{3+}$  ions transferred to IL phase and surrounded by F<sup>-</sup> of a higher concentration than that in the interface of

the two-phase system. According to previous reports,<sup>8</sup> a higher concentration of  $F^-$  could effectively reduce the energy barrier from cubic to hexagonal and thus favors the formation of hexagonal-phase NaREF<sub>4</sub> nanocrystals.



**Fig. S9** TEM images of (a) NaGdF4: Yb, Er UCNPs in OA phase without n-octanol, (b-d) TEM images of the IL phase products after the adoption of n-octanol:(b) cubic phase NaGdF4: Yb, Er UCNPs, (c) hexagonal phase NaGdF4: Yb, Er UCNPs, (d) a mixture of (b) and (c).

To further illustrate the mechanism of the reaction, we conducted an experiment that OA- NaGdF4 were synthesized firstly and then n-octannol was added.

Firstly, oil-dispersible NaGdF<sub>4</sub>: Yb, Er nanocrystals were synthesized at the interface area of the two-phase system at 240  $^{\circ}$ C after 24 h. Then 10 mL of n-octanol was added to the system, which was heated again to 240  $^{\circ}$ C for another 24 h. After cooling to room temperature naturally, the products were found to be in the IL phase

of the system. The adoption of n-octanol has successfully induced all the products, which were formerly gathering in OA phase and the interface area, to enter the IL phase and the products are turned out to be soluble in water. The corresponding TEM images and XRD patterns are shown as follows.

As disclosed in the TEM images, the particle size of IL phase products was larger than their OA-phase counterparts (Fig. S9a). According to their morphology, the nanoparticles can be divided into two parts, the smaller NPs (Fig. S9b) have a morphology similar to the OA-phase products and the larger ones (Fig. S9c) which resemble the IL-phase products. It might be possible that when n-octanol was added, the OA/ IL two phase system show a certain degree of inter-solubility under high temperature and pressure, the NPs were surrounded by Bmim<sup>+</sup> cations or were coordinated by Bmim<sup>+</sup> due to the strong coordinating properties of imidazole. Therefore, the former hydrophobic particles can be dispersed in water. The reaction was carried out in IL phase. It is speculated that the smaller particles (Fig. S9b) has not yet reacted and their morphology remained the same as their original form in OA phase. On the other hand, the size increase of the large NPs (Fig. S9c) was due to the ripening process of small particles. During that process, the small particles aggregated to form larger ones and the Bmim<sup>+</sup> cations absorbed or coordinated on the surface directed the growing process and finally determined the morphology and size of the particles.



**Fig.S10** (a) XRD pattern of NaGdF<sub>4</sub>: Yb, Er UCNPs in IL phase synthesized when n-octanol was introduced after the synthesis of OA-samples, (b) XRD pattern for products in OA phase synthesized without n-octanol, (c) XRD pattern for samples synthesized when n-octanol was added simultaneously with other regents.

It can be clearly seen in the XRD pattern that the samples in IL phase are made up of a mixture of cubic phase and hexagonal phase products, which is different from the samples synthesized without n-octanol or synthesized when n-octanol was added simultaneously with other regents. It might be possible that when n-octanol was introduced, the whole reaction took place in IL phase and the concentration of F<sup>-</sup> ions was greatly increased compared with the reaction environment in OA phase or the interface area. Therefore, the cubic-to-hexagonal energy barrier was lowered, which facilitate the fabrication of hexagonal phase structure. It was quite possible that during the ripening process, the crystal phase transition usually accompanied with the aggregation of small particles and the larger particles (Fig. S9c) might be hexagonal structure. On the other hand, owing to the fact that some cubic phase particle has not reacted yet, the final products were a mixture of cubic and hexagonal structures.



**Fig. S11** Histogram showing the size distributions of NaYF4 nanocrystals in OA phase(a) and IL phase(b).

As shown in Fig. S9, the particle size of NaYF<sub>4</sub> nanocrystals were calculated to be  $8.02\pm1.11$  nm (Fig. S9a) for samples in OA phase and  $20.93\pm3.01$  nm (Fig. S9b) for samples in IL phase, estimated by measuring 200 randomly selected particles in their corresponding TEM images. In addition, the histograms of size distributions for both samples fit the Gaussian curve well.



**Fig. S12** FTIR spectra of NaYF<sub>4</sub>: 20%Yb, 2%Er nanocrystals: (a) hydrophobic products capped by oleic acid with no n-octanol added, (b) water-soluble products capped by ionic liquid with 10 mL of n-octanol added.

FT-IR spectroscopy was used to characterize the functional groups present on the surface of the products. In the case of OA capped products (Fig. S10a), the broad band at around 3411 cm<sup>-1</sup> corresponds to the O-H stretching vibration. The peak at 3010 cm<sup>-1</sup>, assigned to the =C-H stretching vibration, can be clearly seen in the spectrum. The transmission band at around 2925 and 2854 cm<sup>-1</sup> can be attributable to the asymmetric ( $v_{as}$ ) and symmetric( $v_{s}$ ) stretching vibrations of C-H in the long alkyl chain. In addition, bands at around 1583 and 1442 cm<sup>-1</sup>, ascribed to the asymmetric ( $v_{as}$ ) and symmetric ( $v_{s}$ ) stretching vibrations of the carboxylic group of oleic acid, are also observed in the spectrum. In the case of IL capped products (Fig. S10b), the peak at 3453 cm<sup>-1</sup> can be associated with O-H stretching vibration. The band at 2927 and 2854 cm<sup>-1</sup> can be related with the methylene (CH<sub>2</sub>) asymmetric ( $v_{as}$ ) and symmetric( $v_{s}$ ) stretching vibrations in the alkyl chain of alkylimidazolium cations. The spectrum also exhibits transmission bands at around 1637, 1569 and 1457 cm<sup>-1</sup>, corresponding to C-N and C-C stretching vibration of the imidazole ring.<sup>9,10</sup> Moreover,

the sharp peak at around 1083 cm<sup>-1</sup> can also be assigned to the C-N stretching vibration mode.<sup>11</sup> So it can be concluded that the products in IL phase are successfully coated by alkylimidazolium cations which render them dispersible in water.



**Fig. S13** (a-g) Photographs of oil-dispersible products in OA phase: (a)  $LaF_3$ , (b) GdF<sub>3</sub>, (c) YbF<sub>3</sub>, (d) YF<sub>3</sub>, (e) NaGdF<sub>4</sub>, (f) NaYbF<sub>4</sub>, (g) NaYF<sub>4</sub>; (h) photographs of water-soluble NaYF<sub>4</sub>: Yb, Er nanocrystals in IL phase.

It can be obviously seen in Fig. S11 (a-g) that nearly all of the products are dispersed in OA phase or on the interface of the two-phase system while the IL phase is clear. However, the situation was just the opposite in Fig. S11 (h), the OA phase was transparent and the products are soluble in IL phase.



Fig. S14 (a-c) Room-temperature upconversion luminescent spectra of products in OA phase: (a) LaF<sub>3</sub>: 20%Yb, 2%Er, (b)  $\alpha$ -NaGdF<sub>4</sub>: 20%Yb, 2%Er, (c)  $\alpha$ -NaYbF<sub>4</sub>: 2%Er; (d) upconversion luminescent spectrum of ( $\alpha$ + $\beta$ )-NaYF<sub>4</sub>: 20%Yb, 2%Er nanocrystal synthesized in IL phase.

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