

# Monodisperse Upconverting Nanocrystals by Microwave-Assisted Synthesis

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**ABSTRACT** Upconverting nanocrystals have a tremendous potential for applications in fields such as bioanalysis, medical therapy, or display technologies. However, a prerequisite for many applications is the availability of small, monodisperse, and highly luminescent nanocrystals. Here we show, that a microwave-assisted synthesis approach allows for the synthesis of such monodisperse and luminescent upconverting nanocrystals within 5 min in a closed reaction vessel. Even though the same reactants and solvents as with classical conductive heating reactions were used, microwave-assisted synthesis resulted in differently sized and shaped particles and provided superior reaction control. The nucleation and growth mechanism follows a La Mer scheme and can be controlled extremely accurately. It is expected that the fundamental principles of this synthesis approach can be applied to many other types of nanocrystals as well.

**KEYWORDS:** microwave-assisted synthesis · upconversion, nanocrystals · colloids · La Mer mechanism

Photoluminescence upconversion can be observed when a luminophor is excited with light of lower energy than the light emitted—known as anti-Stokes emission.<sup>1</sup> Recently, rare earth doped, upconverting crystals, especially nanoparticles, have been widely investigated as their unique properties pave the way for many interesting potential applications.

Upconverting nanoparticles require small, uniform sizes and high brilliance in order to be attractive for applications in bioanalytics<sup>2</sup> or medical therapy.<sup>3</sup> Such particles have been synthesized in aqueous media,<sup>4,5</sup> however not as monodisperse as with an “organic” method published by Mai *et al.* in 2006.<sup>6</sup> Nevertheless, only upconverting nanoparticles with relatively large diameters (over 50 nm) have been used for life science applications so far.<sup>2,7,8</sup> In parallel, efforts to increase the luminescence intensity by codoping of nanoparticles with lithium<sup>9</sup> or the preparation of core/shell structures<sup>10</sup> have been successfully undertaken. In this study, we developed a convenient and reproducible microwave-assisted

synthesis method for small, monodisperse, and highly luminescent upconverting nanocrystals that can be performed within 5 min.

Polar reactants with a high microwave extinction coefficient can be excited by direct absorption of microwaves. Thus, the activation energy is essentially decreased as compared with conductive heating and the reaction rate increases accordingly. As a consequence, reactions might be performed at lower temperature and hot-spots or other temperature inhomogeneities can be prevented. Furthermore, reaction parameters such as temperature, time, and pressure can be controlled easily. Microwave-assisted synthesis methods have been primarily used for organic synthesis<sup>11,12</sup> and recently for the preparation of nanoparticles.<sup>13–15</sup> A major advantage of this method for nanoparticle synthesis is that nanocrystal nucleation and growth can be separated very clearly and thus monodisperse nanoparticles can be obtained. Moreover, reactions can be performed very rapidly in a closed system.

Nanocrystal nucleation and growth follows the basic principles of crystallization: a nucleation event precedes the growth of nanocrystals and eventually bulk crystals. This mechanism was studied by Victor La Mer and is therefore frequently referred to as *La Mer-mechanism*.<sup>16</sup> According to the La Mer-mechanism, the reaction can be divided into three phases: first, the concentration of reactant increases gradually and eventually exceeds solubility. Second, the concentration of reactants reaches the critical limit of supersaturation and rapid nucleation occurs. This nucleation burst results in a sudden decrease of reactant concentration. Finally, nuclei grow slowly as the reaction solution depletes in reactants. Since

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growth is usually thermodynamically favored over nucleation, nanoparticles can be grown monodispersely when the second phase can be limited to a short period of time by suitable choice of reactant concentration and temperature.

The heating of a substance by microwave irradiation depends on the ability of the material (solvent or reagent) to absorb microwave radiation and convert it into heat. This is based on two principal mechanisms: dipole rotation and ionic conduction, that is, by reversal of solvent dipoles and the resulting replacement of charged ions of a solute.<sup>11,17</sup> The trifluoroacetate reactants used in this study are polar, have a high microwave extinction coefficient, and undergo thermal decomposition with release of fluoride. Therefore, the microwave-assisted synthesis of  $\text{NaYF}_4$  nanocrystals using these reactants follows a classical La Mer-mechanism. As a result, the reaction can be controlled very conveniently, and the resulting nanocrystals show very good monodispersity and crystallinity.

$\text{NaYF}_4$ , doped with  $\text{Er}^{3+}$  (for NIR to green or red) or  $\text{Tm}^{3+}$  (for NIR to blue or NIR) ions, often combined with  $\text{Yb}^{3+}$  as a sensitizer, is known as a very efficient upconverting material.<sup>18</sup> In our study, we have synthesized cubic  $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+}_{0.2},\text{Er}^{3+}_{0.02}$ ,  $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+}_{0.2},\text{Tm}^{3+}_{0.02}$ , and tetragonal  $\text{Na}_x\text{Li}_y\text{YF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  nanocrystals by microwave irradiation, whereas the emphasis of the study was focused on the feasibility and the characteristics of the microwave-assisted synthesis method. We have demonstrated that highly monodisperse upconverting nanoparticles of different shape can be synthesized using this method.  $\text{NaYF}_4$  nanoparticles synthesized by microwave-assisted synthesis were comparable or even superior as compared with particles prepared by Mai *et al.* whose basic method was used in this work.<sup>6</sup>

## RESULTS AND DISCUSSION

### Microwave-Assisted Synthesis of $\text{NaYF}_4$ -Based Nanoparticles.

Figure 1A) shows the transmission electron micrograph (TEM) of  $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+}_{0.2},\text{Er}^{3+}_{0.02}$  nanocrystals. It was observed that these particles had a hexagonal shape and were highly monodisperse (mean diameter *ca.* 11 nm). Their cubic crystal lattice was confirmed by selected area electron diffraction (SAED, shown in Figure 1C)). The rings of the SAED pattern can be assigned to the (111), (200), (220), (311), (400), and (331) planes of the standard cubic  $\alpha$ - $\text{NaYF}_4$  structure (JCPDS: 6-0342, data not shown here). These nanocrystals self-assembled readily into a regular, hexagonal two-dimensional arrangement over a very large area. Figure 1D) depicts the fast Fourier transform of Figure 1A)

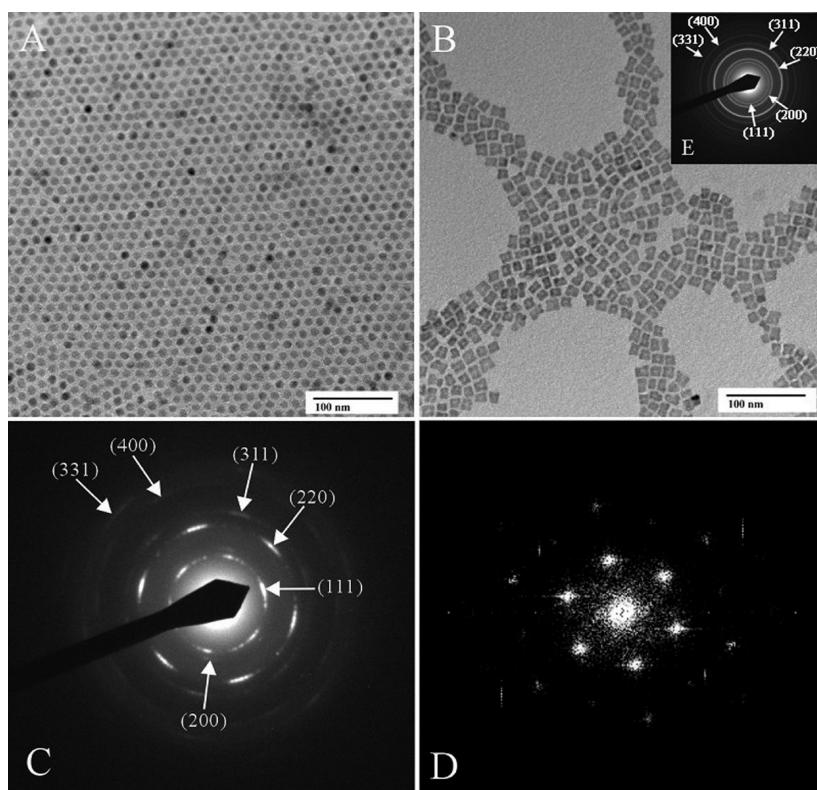


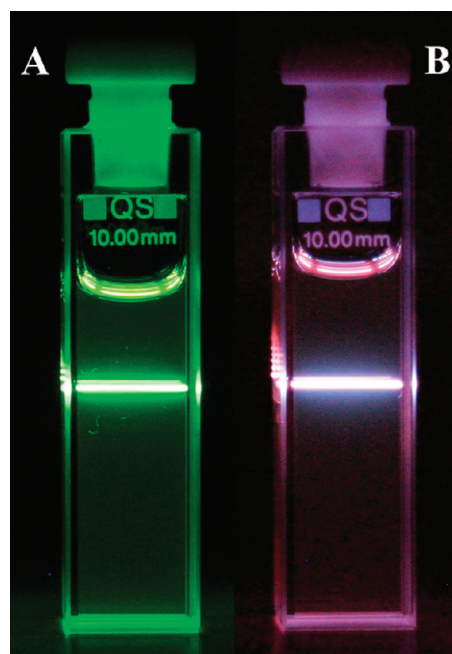
Figure 1. (A,B) TEM images of  $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+}_{0.2},\text{Er}^{3+}_{0.02}$  and  $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+}_{0.2},\text{Tm}^{3+}_{0.02}$  nanocrystals. (C) Selected area electron diffraction pattern (SAED) of  $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+}_{0.2},\text{Er}^{3+}_{0.02}$  nanocrystals. (D) Fast-Fourier transform (FFT) image of picture A. (E) SAED of  $\text{NaY}_{0.78}\text{F}_4:\text{Yb}^{3+}_{0.2},\text{Tm}^{3+}_{0.02}$  nanocrystals.

that confirms the hexagonal assembly of the nanoparticles.

Under the identical synthesis conditions, including concentration, molar ratio, temperature, and reaction time, small and monodisperse nanocrystals, doped with  $\text{Yb}^{3+}$  and  $\text{Tm}^{3+}$  ions, were obtained in a “cubic” morphology with a side length of approximately 10 nm (cf. Figure 1B)). Again, SAED measurements showed that these particles had a single crystalline, cubic crystal lattice (see inset Figure 1E)). Interestingly, different nanocrystal morphologies are formed by replacing the  $\text{Er}^{3+}$  with  $\text{Tm}^{3+}$ . The shape evolution of these nanocrystals seemed to follow a similar mechanism as described previously by Tilley *et al.* for platinum nanocrystals:<sup>19</sup> at first, cuboctahedral nuclei are formed that grow preferentially at their (111) faces. Eventually, these nuclei grow into cubic shape.

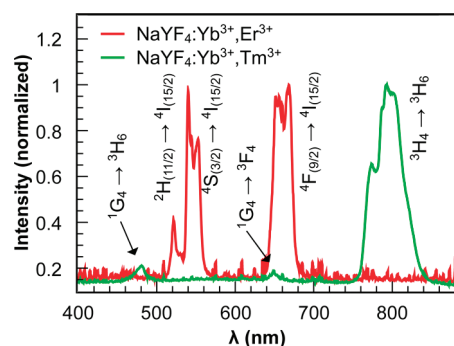
Figure 2 shows the upconversion luminescence of these  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  (A) and  $\text{NaYF}_4:\text{Yb}^{3+},\text{Tm}^{3+}$  (B) nanocrystals dissolved in chloroform under excitation with a 980 nm laser diode (no additional filters were used).

The upconversion luminescence spectra of the  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  and  $\text{NaYF}_4:\text{Yb}^{3+},\text{Tm}^{3+}$  nanocrystals in chloroform were recorded and compared, as shown in Figure 3 (spectra were normalized, based on the peak intensity of each spectrum). The  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  nanocrystals display two distinct emission bands of approxi-

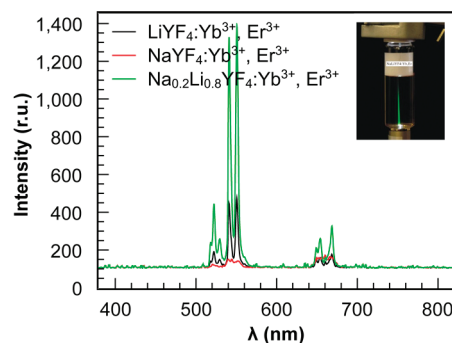


**Figure 2.** Photographs of the upconversion luminescence of the rare-earth codoped NaYF<sub>4</sub> nanocrystals in chloroform, taken by a digital camera without any additional filter, excited with a 980 nm laser diode (Roither Lasertechnik, Vienna, Austria). (A) Luminescence of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> nanocrystals; (B) luminescence of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> nanocrystals.

mately equal intensity in the green (~540 nm) and red (~668 nm) part of the spectrum. These emission bands can be attributed to the 4f–4f transitions of the Er<sup>3+</sup> ions. The green luminescence (510–560 nm) accounts for the <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition; the red emission at 640–680 nm is originated by the <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition. One intense near-infrared (NIR) emission at 760–840 nm and two weak visible emission peaks (~480 and ~648 nm) were observed in the spectrum of the NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> nanocrystals. The NIR emission was caused by the <sup>3</sup>H<sub>4</sub> → <sup>3</sup>H<sub>6</sub> transition, and the weak visible emissions (blue and red) can be attributed to the <sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>6</sub> and <sup>1</sup>G<sub>4</sub> → <sup>3</sup>F<sub>4</sub> transitions, respectively. It should be noted that the infrared emission of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> (~800 nm) is invisible to the human eye.



**Figure 3.** Normalized upconversion luminescence spectra of the upconverting nanocrystals, recorded on a spectrometer (USB2000, OceanOptics, USA), and excited with a 980 nm laser diode (Roither Lasertechnik, Vienna, Austria): (red) NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> nanocrystals; (green) NaYF<sub>4</sub>:Yb<sup>3+</sup>, Tm<sup>3+</sup> nanocrystals.



**Figure 4.** Upconversion spectra of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> (red), LiYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> (black), and Na<sub>0.2</sub>Li<sub>0.8</sub>YF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> (green) nanocrystals in chloroform, excited by a 980 nm laser diode. Inset: upconversion luminescence of Na<sub>0.2</sub>Li<sub>0.8</sub>YF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> nanocrystals at daylight.

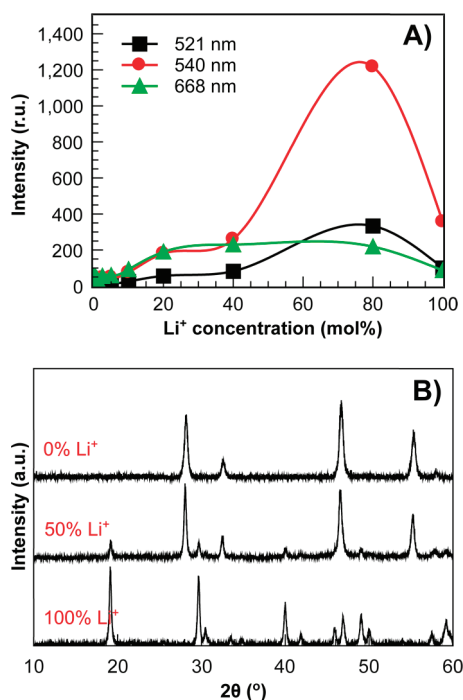
These emission peaks correspond perfectly with the well-known upconversion term schemes for these materials.

These results show that the microwave-assisted synthesis of NaYF<sub>4</sub>-based nanocrystals results in highly monodisperse nanoparticles under conditions which are significantly superior in terms of convenience and environmental aspects to conventional conductive heating: a typical reaction can be performed within 5 min in a completely closed system. Moreover, the reproducibility and control of nucleation and growth are much better as compared with traditional methods. We have transferred these nanoparticles into aqueous solution by methods published earlier<sup>20–22</sup> and found full compatibility with these procedures.

**Microwave-Assisted Synthesis of Li-Doped Upconverting Nanocrystals.** Zhang *et al.* have reported that doping of a Y<sub>2</sub>O<sub>3</sub> host lattice with Li<sup>+</sup> can be used to tailor the local crystal field and result in an increased lifetime of the intermediate <sup>4</sup>I<sub>11/2</sub> (Er) and <sup>2</sup>F<sub>5/2</sub> (Yb) states.<sup>9</sup> Thus, an increase in the number of optically active sites can be achieved, which results in an enhancement of the upconversion efficiency of the nanocrystals. We tried to introduce Li<sup>+</sup> ions into the NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> nanocrystals' lattice to substitute some sites of the Na<sup>+</sup> ions during nucleation under microwave irradiation to enhance the upconversion efficiency.

Different concentrations of Li<sup>+</sup> ions were introduced to replace the Na<sup>+</sup> ions in the reaction. The upconversion spectra of the resulting nanocrystals were recorded under excitation with a 980 nm laser diode. The concentration of the nanocrystals was held constant by dissolving the same amount of each nanocrystal preparation in a certain volume of chloroform (~50 mg/mL). The upconversion spectra of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup>, Na<sub>x</sub>Li<sub>y</sub>YF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup>, and LiYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> were measured and compared, as shown in Figure 4. It was observed that the LiYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> nanocrystals showed a higher upconversion efficiency than the NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> ones. The emission intensity of LiYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> was about eight times the intensity of NaYF<sub>4</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> at 540 nm,





**Figure 5.** (A) Dependence of upconversion emission at different wavelength of  $\text{NaLiYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  on the concentration of  $\text{Li}^+$  ions, square-line presents the 521 nm peak, round-line presents the 540 nm peak, and triangle-line presents the 668 nm peak. (B) Transition from cubic to tetragonal crystal lattice on increasing concentration of lithium.

and the intensities of the red and green emission bands were approximately equal. The concentration of the  $\text{Li}^+$  ions was gradually increased and reached more than 30 times the intensity of  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  with 20% Na and 80% Li. However, the red emission band displayed a low increase in luminescence intensity (about three times) compared with  $\text{NaYF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  nanocrystals, which suggests that doping with  $\text{Li}^+$  ions mainly affects the green luminescence bands in the  $\text{Yb}^{3+}/\text{Er}^{3+}$  upconversion system. The inset in Figure 4 depicts a photograph of the  $\text{Na}_{0.2}\text{Li}_{0.8}\text{YF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  nanocrystals, taken under daylight conditions, excited with a 980 nm laser diode.

Figure 5A shows the dependence of the  $\text{Li}^+$  ion concentration on the upconversion luminescence intensities at 521, 540, and 668 nm of  $\text{Na}_x\text{Li}_y\text{YF}_4:\text{Yb}^{3+},\text{Er}^{3+}$  nanocrystals. With an increase of the  $\text{Li}^+$  ion concentration ( $\text{Li}^+$  mol%: $\text{Na}^+$  mol %, from 0%:100% to 100%:0%), all peaks of green and red luminescence first increase and then decrease. Below the concentration of 40% lithium, the green and red emissions show a simi-

lar slight increase in intensity. The red emission then begins to fade, whereas the green emission shows a dramatic increase and a maximum at a Li concentration of 80%. Again,  $\text{Li}^+$  ions seem to enhance the green upconversion luminescence more effectively than the red. It can be observed that the red emission reached its peak value at a lower  $\text{Li}^+$  ion concentration (about 40%) compared with the green emission. Figure 5B depicts X-ray diffraction patterns of three samples, which show a gradual transition from the cubic to the tetragonal phase on increasing Li concentration (samples with more than 80% lithium content were purely tetragonal). It has been shown previously that this crystallographic transition adds to the increase in luminescence intensity as well.<sup>23</sup> Furthermore, it was found that, with the same low reactants concentration in synthesis, the doping of  $\text{Li}^+$  did not show any effect on the particle size and morphology. However, at high reactant concentrations (such as 20 times the concentration describe above) synthesis, different shapes of nanocrystals were obtained at different doping ratios of  $\text{Li}^+$  (data no shown here).

It has been shown that microwave-assisted synthesis enabled us to prepare and study upconverting nanocrystals of different composition and crystallographic lattice with only minor modification of the synthesis procedure. Again, this synthesis method is much “greener” as compared with conductive heating.

## SUMMARY

In conclusion, we were able to synthesize highly luminescent and monodisperse upconverting  $\text{NaYF}_4$  nanocrystals by irradiation with microwaves for 5 min in a closed vessel. The differently doped nanocrystals were of high quality regarding all relevant properties as compared with upconverting nanoparticles prepared with other methods. Co-doping with lithium ions resulted in a significant increase in upconversion efficiency (more than 30-fold increase in luminescence intensity) and a transition from cubic to tetragonal crystal lattice. The synthesis method introduced in this publication is based on generic principles and might thus be suitable for the “green” synthesis of other nanomaterials. Our method offers a fast, homogeneous, inexpensive, and highly reproducible approach for the synthesis of nanoparticles as compared with methods based on conductive heating.

## METHODS

**Chemicals.** All reactants and solvents were of analytical grade and used without further purification. The trifluoroacetates (TFA) of Yb and Er were prepared according to a literature procedure.<sup>24</sup> Other reagents: sodium trifluoroacetate (Na-TFA, 99%), yttrium trifluoroacetate (Y-TFA, 99.99%), lithium trifluoroacetate (95%), ytterbium(III) oxide (99.99%),

erbium(III) acetate hydrate (99.9%), 1-octadecene (ODE, 95%), and oleic acid (OA, 90%) were purchased from Sigma-Aldrich GmbH (Steinheim, Germany).

**Synthesis of  $\text{NaYF}_4$  Nanocrystals.** Upconverting nanocrystals were prepared using the following procedure: 78.47 mg of Na-TFA, 177.76 mg of Y-TFA, 42.54 mg of Yb-TFA, and 4.22 mg of Er-TFA were dissolved in 6 mL of a 1:1 mixture of OA

and ODE. The reaction mixture was placed in a Schlenk-flask, stirred, and heated to 120 °C. The mixture was repeatedly degassed and purged with nitrogen, until all of the reagents were dissolved in the solvent. The solution was then transferred into the reacting vessel of a Discover LabMate microwave reactor (CEM, USA) and the reaction mixture was heated to 290 °C for 5 min by 300 W of microwave irradiation. The upconversion nanocrystals were collected by addition of excess absolute ethanol and centrifugation when the reaction mixture was cooled to room temperature. The upconversion nanocrystals thus obtained were finally dissolved in chloroform or toluene for further experiments.

**Instruments.** Transmission electron micrographs (TEM) were measured on a JEOL 2000EX instrument at 200 kV. The upconversion spectra were recorded by adapting a 980 nm laser diode (Roithner Lasertechnik, Vienna, Austria) and a home-built couvette holder to a fiber spectrometer (USB2000, OceanOptics, USA). The detector was protected from scattered excitation light by means of a 950 nm low-pass filter (Edmund Optics, Karlsruhe, Germany). The digital photographs of upconversion luminescence of the nanocrystals were taken by a digital camera (Canon 350D, Japan) without adding any filter, excited with a 980 nm laser diode (Roithner Lasertechnik, Vienna, Austria).

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