A comprehensive characterization of NaYF$_4$ nanocrystals synthesized in trioctylphosphine oxide has been reported in order to present an effective method of monodisperse, small, hexagonal nanocrystal synthesis in a high boiling organic solvent via a co-thermolysis pathway. We observed the influence of temperature, Na/Y precursors ratio and time of the synthesis on the nanocrystals size, shape and crystal structure. For that purpose, we characterized the structure of as-synthesized nanocrystals by X-ray diffraction and transmission electron microscopy. Moreover, all nanocrystals were doped with Eu$^{3+}$ ions, which were used as an optical crystal field probe. We applied photoluminescence, PL excitation and absorbance spectra to determine the influence of crystal symmetry, surface to volume ratio and ligands on the optical properties of doped Eu$^{3+}$ ions. It was found that trioctylphosphine oxide reduces the free-energy barrier and stimulates the NaYF$_4$ crystallization in the hexagonal phase, even at relatively low temperature. A similar effect was observed when the excess of sodium trifluoroacetate precursors was used. Moreover, the presented nanocrystal evolution within synthesis time confirmed that at suitable conditions NaYF$_4$ crystallized in the hexagonal phase within less than 5 min. Optical spectroscopy investigations confirmed the high quality of small β-NaYF$_4$Eu$^{3+}$ nanocrystals, which are promising candidates for e.g. optical markers in the visible wavelength range.

For application as bio-markers, high quality nanocrystals with a precisely controlled size are required, since NCs smaller than 10 nm undergo efficient body clearance, whereas bigger ones give a stronger optical response and stay in the body for prolonged investigations. Moreover, the preparation of the hexagonal phase of NaYF$_4$ matrix is of paramount importance, as the luminescence comprising excited ion–ion interactions is an order of magnitude less effective in cubic NCs, as compared to hexagonal ones. These interactions are responsible for energy transfer and up-conversion, and enable controlling the optical properties of NCs.

Recently, various groups have carried out a preparation of NaYF$_4$ nanocrystals in cubic (α) and/or hexagonal (β) phase. A simple and efficient one-step protocol was proposed by Yan’s group. They performed co-thermolysis of trifluoroacetate salts in high boiling point organic solvents e.g. oleic acid (OA), oleylamine (OAm) and 1-octadecene (ODE). Lately, Prasad’s group used a co-thermolysis pathway. We observed the influence of radical conditions such as long-time annealing, prolonged...
reaction time and high temperature were reported as required factors.\textsuperscript{18,20,21} Mai et al. proposed that these requirements reflect the free-energy barrier for the $\alpha \rightarrow \beta$ phase transition.\textsuperscript{18} This barrier needs to be overcome and heating at the temperature close to the solvent boiling point is required for that purpose. For example, OM as a capping agent requires a reaction at the reflux temperature (above 330 °C) and still the final product is a mixture of $\beta$-phase NCs with $\alpha$-phase residual.\textsuperscript{13} Similarly, the limitation of a protocol applying oleic acid (OA) and 1-octadecene (ODE), as a ligand and an organic solvent, is their low boiling point.

In our synthesis we proposed to use trioctylphosphine oxide (TOPO) as a solvent, since its boiling point is 409 °C (at 760 mm Hg). This decision arises from our expectation to synthesize NaYF$_4$ nanocrystals in a pure hexagonal phase. Moreover, TOPO, due to its coordinating properties, also acts as a capping agent controlling the growth kinetics and preventing NCs from aggregation.\textsuperscript{22,23} The idea of TOPO application in NaYF$_4$ synthesis was initially proposed by Shan et al. and adapted by Zhuravleva, however it was not developed further.\textsuperscript{24–26} Therefore, the influence of TOPO on the nanocrystals growth, final size and shape has not been investigated yet.

The crystal phase, size and shape control is an important challenge in the synthesis of nanocrystalline materials. Because of that, we performed investigations where the synthesis temperature, Na'/$\text{Y}^{3+}$ precursors ratio and synthesis time were used as parameters of the reaction.

Crystal phase control by a variation in the molar ratio of NaF and LnF$_3$ monomers was described for the first time by Thoma et al., who studied phase diagrams of the NaF–LnF$_3$ systems in a wide temperature range and NaF and LnF$_3$ molar compositions.\textsuperscript{27} Based on that, Mai et al. observed that pure $\alpha$-NaREF$_3$ NCs could be obtained at a low temperature and a low ratio of Na/RE precursors, while $\beta$-NaREF$_3$ required reverse conditions.\textsuperscript{18} Their synthesis was done in a solvent–ligands mixture containing ODE/OA/OAm. Also, Shan and Ju in their experiments observed that a high Na/rare earth precursors ratio accelerates the cubic ($\alpha$) $\rightarrow$ hexagonal ($\beta$) phase transition, and, simultaneously, promotes the growth of smaller $\beta$-NCs (size range of hexagonal prism from 18 to 200 nm).\textsuperscript{24} In this case, the OA and trioctylphosphine (TOP) were used as a solvent and a surface ligand, respectively. Recently, a similar dependence was experimentally proven by Ptacek et al. for NaGdF$_4$ NCs. They have additionally shown that excess F$^-$ ions also promote the growth of NaGdF$_4$ nanocrystals in a hexagonal phase.\textsuperscript{28}

The complex results about temperature effects on the doped NaYF$_4$ nanocrystals synthesis in OA have already been presented by Wang et al.\textsuperscript{15} Excluding the fact that they used LnCl$_3$, NH$_4$F and NaOH as precursors, their product of the reaction at 230 °C yielded mostly polydisperse NaF crystals rather than monodisperse NaYF$_4$ nanoparticles. Moreover, in the synthesis conducted at 300 °C they obtained monodispersed hexagonal particles, however, their average diameter was ~ 20 nm, which is much larger than our NCs.

In order to understand the role of the fundamental parameters on the synthesis, where NaYF$_4$ NCs are prepared using TOPO as solvent and surface ligands, we decided to perform the detailed experiments. At first, the range of synthesis parameters have been evaluated to obtain the efficient synthesis of monodisperse hexagonal NaYF$_4$ NCs with sub-10 nm diameter. The influence of the synthesis temperature, precursors molar ratio and synthesis time on the NCs phase, size and shape was investigated.

Then, the structural properties of NCs are discussed based on XRD and TEM studies. Moreover, we assigned the structural properties of NaYF$_4$ NCs to optical ones. For this purpose, Eu$^{3+}$ ions served as local crystal field probes.\textsuperscript{29} We discussed the resulting optical properties by comparing photoluminescence (PL), PL excitation (PLE) and absorption spectra. The presented results are the first attempt to systematically describe the fluoride nanocrystals growth in TOPO.

### Materials and methods

**Nanocrystals synthesis**

The sodium trifluoroacetate Na(CF$_3$COO) (98%) (NaTFA), europium(III) trifluoroacetate trihydrate Eu(CF$_3$COO)$_3$·3H$_2$O (98%) (EuTFA$_3$), yttrium(III) trifluoroacetate hydrate Y(CF$_3$COO)$_3$·3H$_2$O (99%) (YTFAD) and trioctylphosphine oxide (technical grade, 90%) (TOPO) were purchased from Sigma-Aldrich Ltd. (used as received). The precursors were applied in a modified co-thermolysis method, which was originally proposed by Yan’s group, to synthesize Eu$^{3+}$ doped NaYF$_4$ nanocrystals.\textsuperscript{28} For this, the proposed synthesis with a varying precursors ratio was performed, e.g., a mixture of NaTFA (170.0 mg, 1.250 mmol), YTFAD (203.0 mg, 0.479 mmol) and EuTFA$_3$ (12.5 mg, 0.025 mmol) was dissolved in TOPO (10 g, 26 mmol) in a 100 ml three-neck round-bottom flask. The flask was placed in a heating mantle and heated up to 120 °C under vacuum for 30 min in a standard Schlenk line technique. Then the temperature increased to the desired growth temperature (220–350 °C) within 10 min and the samples were kept at these conditions from 5 to 60 min. The resulting solution was cooled to 70 °C and an excess of dry methanol was added in order to precipitate the nanocrystalline product. NCs solutions were centrifuged with 10,000 rpm for 10 min. Precipitated NCs were easily dispersible in nonpolar solvents, e.g. cyclohexane. The precipitation/dissolution procedure was repeated at least three times in order to dispose any excess of TOPO and unreacted precursors.

**Structural and optical characterization**

A FEI Tecnai G$^2$ 20 X-TWIN Transmission Electron Microscope was used to obtain TEM images of the nanoparticles. A diluted cyclohexane solution of NCs was dropped on carbon coated copper grids and left to evaporate.

X-Ray powder diffraction patterns were obtained using Bruker D8 AXE diffractometer (Cu-K$_\alpha$). The $\varphi$ nanocrystalline domain sizes were calculated using the Scherrer equation, $D = 0.89 \lambda/(B \cos \theta)$. Here, $D$ is a domain size to be determined, $\lambda$ is the X-ray wavelength, $B$ is width of the diffraction peak of interest, $\theta$ is the angle of the corresponding diffraction peak.

Photon Technology International Inc. systems equipped with a flash xenon lamp and a strob detector (both coupled with monochromators) were used to observe PLE and PL spectra. The absorption spectra were measured on JASCO V-570 spectrophotometer.
Results and discussion

TOPO properties

The uniform and tight coverage of the nanocrystal surface by ligands is a fundamental request in order to obtain highly luminescent nanocrystals stable in colloidal solution for a long time. Alivisatos et al. have already shown that surface coverage by ligands is size dependent for small nanocrystals. They discussed the increase of the percent coverage of ligands on the nanocrystals when the surface curvature increases due to steric hindrance.

The TOPO molecule has a conical shape (Fig. 1b), which makes it difficult to accommodate a close packing film on a flat surface as well as on big nanocrystals with a small surface curvature. On the other hand, the high curvature of small nanocrystals helps in close packing of TOPO ligands. The quantification of this issue can be done assuming that TOPO has a nearly conical shape with 9.9 Å height ($H$), and base radii equal to 5.5 Å. A maximum number of TOPO molecules in a closely packed ligand shell of one NC can be calculated as the surface area of a sphere of radius $r = d/2 + H$ (where $d$ is the nanocrystal diameter and $H$ is TOPO height) divided by the area $s = \pi(55 \text{ Å})^2$.

Fig. 1a shows the calculated number of TOPO and Ln$^{3+}$ ions located at the surface of β-NaLnF$_4$ nanocrystals as a function of the nanocrystal size. For NCs with a diameter smaller than 2.5 nm every Ln$^{3+}$ ion located at the NCs surface can be bound to TOPO. However, the efficiency of the surface coverage by TOPO significantly decreases as the NCs diameter increases. For NCs 8 nm in diameter, only 45% of surface Ln$^{3+}$ ions can be bound to TOPO. For bigger NCs this value decreases further and reaches only ~30% for NCs bigger than 100 nm.

The TOPO has an additional advantage, which is rarely taken into account in the literature. The TOPO molecule has a very small absorption cross section, and its absorption band is in UV (~210 nm) (Fig. S1, ESI†). This is a huge advantage as compared to oleic acid, which has four orders of magnitude more efficient absorption with the first maximum at 280 nm. For this reason, oleic acid is not suitable for NCs doped with e.g. Gd$^{3+}$ ions, which have an absorption band at 272 nm and emission at 310 nm. From the fundamental research point of view, it is much better to have an access to the absorption properties of nanocrystals in a wide spectra range, thus TOPO is a much better choice.

Synthesis temperature effect

We synthesized NaYF$_4$:Eu$^{3+}$ (5%) NCs in a range of temperatures, starting at 350 °C. This temperature is much above the precursors thermal decomposition threshold, which was determined to be around 310 °C, by thermogravimetric (TGA) analysis (Fig. S2, ESI†). The chosen temperature is also higher than the commonly accessible temperature when OA, OAm and ODE are used as solvents and ligands. Then, to determine how the reaction temperature influence the crystal phase and nanocrystal size, we repeated the synthesis procedure at a lower temperature (220, 250, 285 and 320 °C).

Fig. 2 shows the XRD spectra of NaYF$_4$ NCs synthesized in the temperature range from 220 to 350 °C. The experimental patterns are compared with ICDD No: 77-2042 and 28-1192 standards, which correspond to a cubic (α) and hexagonal (β) crystal phase, respectively. As we expected, the samples prepared at 350 °C presented a pure hexagonal phase. This is a great advantage of the synthesis procedure, when a single phase is received without any complicated combination of the surface ligands, or specific NCs doping. When the synthesis temperature was decreased, NCs conserved a pure hexagonal phase. This is evident for all synthesized NaYF$_4$ samples.
These results confirm that TOPO reduced the free-energy barrier strengthening the synthesis of NaYF₄ in a thermodynamically stable hexagonal phase.¹⁸

The broadening of diffraction peaks indicates a decrease of NCs size with an increased synthesis temperature. The exact diameter of NaYF₄ NCs was determined based on TEM analysis. Fig. 3 shows the TEM images taken for samples synthesized at 250, 285, 320 and 350 °C. The TEM results are consistent with XRD, as the increase of NCs diameter was determined when the synthesis temperature dropped. For a sample synthesized at 250 °C, beside ~23.4 nm NCs, also very small (~6.2 nm) NCs were distinguished in the TEM image (Fig. 3a). These results suggest that the NCs grown at this temperature requires a longer time to reach a homogenous distribution. More details of the synthesis time dependence will be discussed later in this article. At this point, the dependence of self focusing on the synthesis temperature appears also in other samples, where a standard deviation of the NCs diameter decreases with increasing the synthesis temperature.

The already presented results confirm significant advantages of hexagonal NaYF₄ NCs synthesis with TOPO as a solvent and a surface agent. The small size of as synthesized NCs was obtained without any size sorting. Moreover, TOPO used as a surface ligand promotes fluoride nanocrystal synthesis directly in a thermodynamically stable hexagonal phase.

In a next step the optical properties were examined for every NaYF₄:Eu³⁺ sample and PLE spectra are shown in Fig. 4a. The most efficient excitation band of Eu³⁺ at 394 nm (⁷F₉/⁵I₆ transition) is well resolved. With reduction of the synthesis temperature, the full width at half maximum (FWHM) of this band increases (from 4.1 to 6.3 nm) which reflects the inhomogeneity of the crystal matrix.³⁵ This observation suggests evolution of the crystal field in the vicinity of Eu³⁺ ions and corresponds well with changes in PL spectra, which are presented in Fig. 4b. The observed intensive emission bands are characteristic for Eu³⁺ located in the non-centrosymmetric crystal field.³⁵ The high quality of as synthesized NCs is proven by the range of emission from the upper excited state (⁵Dₓ, ⁷Dₚ), which can be observed due to strongly inhibited non-radiative relaxation, necessary to obtain a high quantum yield of PL.

Fig. 5 summarizes the properties of PL spectra. The open circles represent an electric dipole (ED) to magnetic dipole (MD) integrated PL intensity ratio (⁵D₀–⁷F₂/⁵D₀–⁷F₁ = R₀–₂/₀–₁), which is known as a parameter describing the character of the crystal field.³⁶ R₀–₂/₀–₁ is equal to ~1.28 for NCs prepared at 220 °C and increases to 1.47 for the smallest NCs synthesized at 350 °C. It indicates reduction of the centrosymmetric character of Eu³⁺ ions environment for higher synthesis temperature. We assigned the changes of R₀–₂/₀–₁ values to an increase of the surface to volume ratio (S/V), as it is known that close to the interface a distortion of the crystal field around Eu³⁺ ions can significantly enhance the probability of ED transitions.³⁷,³⁸

The emission from upper excited states was also analyzed. The filled squares in Fig. 5 represent the ratio of integrated PL intensity from upper and first excited state.
excess of Na⁺ cations, which should promote hexagonal crystal phase which is characteristic of all samples prepared in the investigated synthesis temperature range, the emission properties of Eu³⁺ ions vary from sample to sample due to surface and internal crystal matrix oxygen-related defects. These defects are responsible for the crystal matrix distortions (increase of ED transition) and enhanced non-radiative relaxation (decrease of emission from the upper excited states). From the optical investigation of Eu³⁺ doped NaYF₄ NCs we can conclude that despite the conserved hexagonal crystal phase, which is characteristic of all samples prepared in the investigated synthesis temperature range, the emission properties of Eu³⁺ ions quenched by vibronic interactions with ligands and surface phonon modes, which are expected to be different than volume modes. An exception is observed for NCs prepared at the lowest temperature, 220 °C. In this case, despite the big diameter of NCs, the emission from the upper excited state has an unexpected low intensity. It can be explained by considering the defect centers e.g. residual oxygen, which can be present in a matrix crystallized at such low temperature. These defects increase the probability of non-radiative relaxation, reducing the intensity of emission from the upper excited states.

We compared the presented results with the investigation of NaYF₄:Eu³⁺ synthesized in OA–ODE mixture at 310 °C. In this case NCs crystallized in the hexagonal phase as well, however the average diameter was close to 40 nm, thus much bigger than NCs prepared in TOPO. PL and PLE spectra are shown in Fig. S3 (ESI†).

Precursor ratio effect

Crystal phase control is an important challenge in the synthesis of nanocrystalline materials. Apart from the synthesis temperature, the other possibility for crystal phase control being the variation in the molar ratio of NaF and LnF₃ monomers.

In our experiments we follow the synthesis procedure of NaYF₄ at 285 °C, in which various Na/Y molar ratios were used (1.0, 1.5, 2.0, 2.5). The chosen values of Na/Y precursors ratios cover the range corresponding to stoichiometric NaYF₄ and excess of Na⁺ cations, which should promote hexagonal crystal phase crystallization. The details of sample composition are summarized in Table S1 (ESI†). All NCs were doped with 5% of Eu³⁺ ions to make them suitable for optical investigations.

The XRD spectra presented in Fig. 6 confirm our expectation. The samples prepared with stoichiometric precursors composition crystallized in a pure cubic phase. When the amount of NaTFA precursor in synthesis increased slightly (Na/Y = 1.50, 2.00), the resulting XRD patterns are the composition of α and β phase. Finally, when the sodium precursor was added in a significant excess in relation to YTFA₃, the resulting NaYF₄ NCs exhibited pure hexagonal crystal phase. The conducted XRD spectra examination confirms the ability for NaYF₄ crystal phase management by precursors ratio control.

In Fig. 6 it can also be seen that the broadening of diffraction peaks vary with Na/Y ratio. The NCs diameters were estimated based on the Scherrer equation, and for the cubic NCs, the average size was found to be 7 ± 1 nm. When the Na/Y ratio increased and the hexagonal phase was formed, the diameter of NCs increased to 11 ± 1 nm and ~17 ± 1 nm for Na/Y equals 2.00 and 2.50, respectively. The diameter increase can be explained by an increased amount of precursors in the synthesis solution, when an excess of NaTFA was used, which resulted in a higher precursor to solvent ratio, which influenced the final NCs size.

To better analyze the NCs size and shape, the TEM images were captured for three of the samples prepared with 1.00, 1.50 and 2.50 Na/Y ratio (Fig. 7). It is clearly visible that the obtained NCs are monodispersed and well stabilized by surface ligands. For all the samples no preferable growth direction is observed, and the NC sizes are similar along all axes. From the TEM images the specific shape of NCs can be determined. The NCs prepared with Na/Y = 1.00 ratio obtained a cubic-like shape (Fig. 7a). This is in contrast to NCs prepared with Na/Y = 2.50 which in Fig. 7c clearly exhibits a hexagonal shape. The identified shape of NCs agrees well with the crystal phase determined for these samples.

In Fig. 7 also the NCs diameter distributions are presented. They were calculated from the TEM images of a hundred nanoparticles, and they clearly prove the increase of NCs size with increasing Na/Y precursors ratio. In Fig. 7e, for NCs prepared with Na/Y = 1.50 ratio a double distribution is present. Smaller NCs are the dominant fraction crystallized in a cubic
phase. The less numerous fraction of bigger particles was assigned to the hexagonal phase. It suggests that a cubic to hexagonal phase transition is related to the increase of NCs diameter. Moreover, the smaller size of cubic NCs observed for Na/Y = 1.50 sample, in comparison to Na/Y = 1.00 sample, suggests that in this case the growth of hexagonal NCs is due to dissolution of cubic ones.

The evolution of the crystal phase was evident also in the optical properties of nanocrystals. Fig. 8a shows the PLE spectra, where characteristic peaks of direct Eu\(^{3+}\) excitation are clearly resolved, with the most intensive one at 394 nm (\(^7\)F\(_0\)\(\rightarrow\)\(^5\)L\(_6\)). The ratio of \(^7\)F\(_0\)\(\rightarrow\)\(^5\)D\(_3\) (466 nm) to \(^7\)F\(_0\)\(\rightarrow\)\(^5\)L\(_6\) (395 nm) transition intensities increased ∼2.48 times when Na/Y ratio increased from 1.00 to 2.50. This is a first optical evidence of crystal phase evolution with Na/Y ratio. The broadening of PLE peaks for NCs prepared at a lower Na/Y ratio suggests significant crystal matrix inhomogeneity. Furthermore, for small Na/Y ratio, a wide excitation band at around 300 nm appears in PLE spectra and it can be assigned to oxygen in a crystal lattice. This band has already been observed for small NaYF\(_4\) NCs in cubic phase and was assigned to oxygen impurity, when O\(^{2-}\) ions stabilize cubic NaYF\(_4\) crystal structure.\(^{40}\)

PL spectra are shown in Fig. 8b and the characteristic Eu\(^{3+}\) emission peaks are clearly distinguished. Intensive ED transition as well as emissions from the upper excited states (\(^5\)D\(_1,\)\(^5\)D\(_2\)) are characteristic of the hexagonal phase of NaYF\(_4\) NCs. This is the case of samples prepared at 2.5 and 2.0 Na/Y ratio. For samples which were recognized from a XRD study as crystallized in the cubic phase, emission from the upper excited state is suppressed and the peak position of ED transition shifts from 612 to 610 nm. However, ED transition remains the most intensive, which is not the case for bulk \(\alpha\)-NaYF\(_4\) crystals. The shape of the observed PL spectra suggests that cubic NaYF\(_4\) NCs contain a significant number of oxygen-related lattice defects affecting the emission of Eu\(^{3+}\) ions.\(^{40}\)

The emission intensity ratios calculated from PL spectra are summarized in Fig. 9. Decreasing \(^5\)D\(_0\)\(\rightarrow\)\(^7\)F\(_2/\)\(^5\)D\(_0\)\(\rightarrow\)\(^7\)F\(_1\) ratio carries the information about the \(\alpha \rightarrow \beta\) crystal phase transition and increasing NCs diameter when Na/Y ratio increases. Moreover, increase of \(^5\)D\(_1\)\(\rightarrow\)\(^7\)F\(_2/\)\(^5\)D\(_0\)\(\rightarrow\)\(^7\)F\(_1\) provides information on the quality of NCs. For a sample with a high Na/Y ratio, the increase of emission from the upper excited state is strictly related to inhibition of non-radiative relaxation by the multiphonon pathway. The sources of this restriction are the bigger sizes of NCs (smaller fraction of Eu\(^{3+}\) ions on NC surface) and the reduced number of residual oxygen defects for well-crystallized hexagonal NCs. In both cases, the energy of phonons interacting with excited Eu\(^{3+}\) ions is limited.

In this place, it is worth of mentioning that Zeng et al. showed that the F/Ln ratio influences the size and shape of NaLnF\(_4\) NCs as well.\(^{41}\) However, they used other precursors than TFA salts. In our case, the amount of F\(^-\) anion used in the synthesis is strictly combined with Na\(^+\) and Ln\(^{3+}\) precursors. When more NaTFA precursors are used in the applied synthesis method, the Na/Ln but also the F/Ln ratios increase, thus we can not distinguish if an excess of Na\(^+\) or F\(^-\) is principally responsible for the size, shape and crystal phase effects. An additional procedure modification is required to control F\(^-\) amount separately.
Synthesis time

In order to better understand the mechanism of nanocrystals growth and especially the conditions of crystal phase transitions, the series of NaYF₄ NCs was prepared as a function of growth time. These NCs were prepared with precursors ratio Na/Y = 2.50 at temperature 350 °C. The values of these synthesis parameters were chosen based on the previous results in order to obtain pure hexagonal nanocrystals with a diameter of around 11 nm. During the synthesis, 2 ml aliquots of the synthesis solution were sampled at 5, 10, 20 and 30 min after the precursors decomposition.

The as prepared NCs were examined firstly by X-ray diffraction and the patterns are shown in Fig. 10 together with reference diffraction peaks positions. For the sample collected 5 min after the beginning of nucleation, the wide XRD diffraction peaks are visible. The diameter of NCs estimated from the Scherrer equation (the spherical shape of nanoparticles is considered) is less than 4 nm. The peak positions agree fairly well with the hexagonal diffraction standard. It suggests that the NCs crystallized directly in hexagonal rather than in cubic phase. However, the small NCs diameter and the significant broadening of XRD peaks make the identification of the crystal phase difficult.

When the samples were kept in the synthesis solution for 10, 20 and 30 min, the diffraction peaks became narrower, which indicates NCs growth. The final NCs diameter is above 11 nm. Simultaneously, the diffraction peaks characteristic of the hexagonal phase of NaYF₄ matrix can be easily distinguished and no contribution of any other crystal phase was observed. These results confirm that in the synthesis approach where TOPO is used as a surface ligand and Na/Y ratio equals 2.5, the NaYF₄ matrix crystallizes almost instantaneously in a hexagonal phase. It is in contradiction to a previously reported synthesis of NaYF₄ NCs in oleic acids and other surfactants, where NCs crystallize in a cubic phase and long annealing time at high temperature is required for completed cubic to hexagonal crystal phase transition.¹⁸

The information about the NCs size and shape was further verified by detailed TEM studies (Fig. 11). The high monodispersity is common for all of the samples as well as the spherical shape indicating a continuous anisotropic growth of NCs during the investigated time range. The distributions of NCs diameters were calculated and are shown in Fig. 11i–l. For a sample grown for 5 min the average diameter of NCs was equal to 4.3 ± 1.2 nm. After another 5 min of the synthesis, the average NCs diameter was calculated to be significantly bigger, 9.9 nm. The increase of NCs size between 5 and 10 min of the synthesis is in good agreement with XRD. For a prolonged synthesis (20 and 30 min), the NCs diameter increases only slightly, up to 11.1 and 11.9 nm, respectively. More important is the fact that the diameter distributions decrease when the synthesis time increases, and are equal to 1.4, 1.1 and 0.9 nm for samples prepared in 10, 20 and 30 min, respectively. The focusing of the NCs size can be attributed to e.g. Ostwald ripening processes. A sample collected after 30 min of synthesis is just in the middle of an Ostwald ripening process, as a second fraction of small NCs can be easily distinguished in Fig. 11l. For samples synthesized in 60 min, which were discussed in the previous paragraphs, the Ostwald ripening process is completed and thus narrow size distributions of NCs diameters are observed (Fig. 3d, h, l). The sampling was not continued for 60 min,
because a significant decrease of the synthesis solution volume was supposed to have an influence on the conditions of NCs growth. This is already visible as an incoherence of the NCs size prepared in a single synthesis and when aliquots were taken, because the final NCs were slightly bigger in a time monitored synthesis ($d = 11.9 \text{ nm vs. } d = 9.3 \text{ nm}$).

Optical spectroscopy methods were used to investigate the evolution of optical properties of NaYF$_4$:Eu$^{3+}$ prepared at various synthesis times as well. For the optical experiments, a similar amount of nanocrystalline samples were dissolved in 1 ml of cyclohexane and the absorption spectra were recorded (Fig. 12). The inset of Fig. 12 shows the magnified spectra in order to visualize the Eu$^{3+}$ related narrow absorption bands. Many characteristic bands related to 4f–4f transition can be recognized, however, due to the small percentage of Eu$^{3+}$ doping, the intensities of these absorption bands are very low. The main contribution to absorption spectra comes from the NCs surface (Fig. 12). The most intensive band in the UV range was identified as related to the surface ligands. The absorption spectrum of pure TOPO is shown as a reference and a good agreement between the absorption of ligands and NCs is obtained for short wavelengths. However, for wavelengths around 270 nm an additional wide absorption band can be distinguished on all spectra. We can relate it to a charge transfer (CT) transition, which is due to interaction of Eu$^{3+}$ ions with O$^{2−}$.

We found that the integrated intensity of CT band decreases with the increase of a synthesis time. Both the increase of the average NCs size as well as the crystalline matrix annealing and reduction of defects number can be responsible for the observed inhibition of O–Eu CT band (Fig. S4, ESI†).

Fig. 13 shows PLE recorded for all samples at Eu$^{3+}$ emission wavelength of 611 nm. Several narrow excitation peaks can be distinguished, e.g. $^7F_0–^5D_1$, $^7F_0–^5D_2$, $^7F_0–^5D_3$, with the most intensive one at 394 nm due to $^7F_0–^5L_6$ transition. The FWHM of excitation peaks getting narrower by 4.75, 3.51, 3.40, 3.36 nm for $^7F_0–^5L_6$ transition at 5, 10, 20 and 30 min, respectively.

The excitation properties vary more significantly for wavelengths shorter than 375 nm. In the wavelength range from 375 to 250 nm, which is limited by the experimental setup, a broad excitation peak appears, and it is more intensive for NCs for which a band at 270 nm was observed in the absorption spectra. The fact that this band takes part in the excitation of Eu$^{3+}$ ions further confirms our suggestion that it is related to CT state absorption.

In the next step, we discuss the PL recorded for all the samples excited resonantly at 394 nm (Fig. 14). Emission bands characteristic for Eu$^{3+}$ ions can be easily distinguished with two most intensive transitions $^5D_0–^7F_1$ and $^5D_0–^7F_2$, at 590 nm and 614 nm, respectively. Moreover, the emission from the upper excited state ($^5D_1$) is also present. The inset in Fig. 14 shows the ratio of ED/MD transition ($^5D_0–^7F_2/^5D_0–^7F_1$), which increases significantly between 5 and 10 min of NCs synthesis. The increase reflects the reduction of the centro-symmetric character of the crystal field in which Eu$^{3+}$ ions are located. Since in XRD we did not determine the crystal phase transition, this change can be assigned to the growth of NCs, where for bigger NCs the strain in the crystalline matrix is reduced as well as the number of Eu$^{3+}$ ions located at the NC surface. These conclusions are in agreement with other observations, e.g. broadening of the emission peaks is significantly smaller for samples grown at
least 10 min, as compared to the ones with 5 min growth. A similar trend was found for the ratio of emission from the lowest and upper excited state (\( ^{5}D_{0} \rightarrow ^{7}F_{1} / ^{5}D_{1} \rightarrow ^{7}F_{2} \)). The lower intensity of emission from the upper excited state confirms that in the case of small NCs, the probability of non-radiative relaxation of excited Eu\(^{3+}\) ions is higher, as compared to bigger NCs with longer annealing time.

**Conclusions**

We have successfully utilized TOPO as a surfactant to prepare NaYF\(_{4}\) NCs with a controlled crystal phase and a small diameter (in the range 5–15 nm).\(^{37}\) TOPO was found to reduce the free-energy barrier for cubic to hexagonal crystal phase transition,\(^{24}\) which enables the synthesis of high quality hexagonal NCs even at a relatively low temperature (from 220 °C). Moreover, the application of TOPO allows to significantly increase the synthesis temperature above 350 °C, to obtain sub-10 nm monodisperse β-NaYF\(_{4}\) nanocrystals.

The several various Na/Y precursors ratios used in the synthesis led to the conclusion that at a stoichiometric precursor composition the NaYF\(_{4}\) NCs crystallize in a cubic phase. The increase of NaTFA precursors assists the cubic to hexagonal crystal phase transition, and for Na/Y = 2.5 NCs in a pure cubic phase transition, the NaYF\(_{4}\) NCs crystallize in a cubic phase. The increase of Na/Y precursors ratio led to the conclusion that at a stoichiometric precursor composition the NaYF\(_{4}\) NCs crystallize in a cubic phase. The increase of NaTFA precursors assists the cubic to hexagonal crystal phase transition, and for Na/Y = 2.5 NCs in a pure cubic phase transition, the NaYF\(_{4}\) NCs crystallize in a cubic phase. The increase of Na/Y precursors ratio led to the conclusion that at a stoichiometric precursor composition the NaYF\(_{4}\) NCs crystallize in a cubic phase. The increase of NaTFA precursors assists the cubic to hexagonal crystal phase transition, and for Na/Y = 2.5 NCs in a pure cubic phase transition, the NaYF\(_{4}\) NCs crystallize in a cubic phase. The increase of Na/Y precursors ratio led to the conclusion that at a stoichiometric precursor composition the NaYF\(_{4}\) NCs crystallize in a cubic phase. The increase of NaTFA precursors assists the cubic to hexagonal crystal phase transition, and for Na/Y = 2.5 NCs in a pure cubic phase transition, the NaYF\(_{4}\) NCs crystallize in a cubic phase. The increase of Na/Y precursors ratio led to the conclusion that at a stoichiometric precursor composition the NaYF\(_{4}\) NCs crystallize in a cubic phase. The increase of NaTFA precursors assists the cubic to hexagonal crystal phase transition, and for Na/Y = 2.5 NCs in a pure cubic phase transition, the NaYF\(_{4}\) NCs crystallize in a cubic phase.