Ligand-dependent luminescence of ultra-small Eu^{3+} -doped NaYF_4 nanoparticles

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Abstract Pure cubic phase ultra-small $\alpha\text{-NaYF}_4$:4 % Eu^{3+} colloidal nanoparticles were synthesized by thermal decomposition reaction using three various capping ligands, i.e., oleic acid, trioctylphosphine oxide, and hexadecylamine. To expose as many Eu^{3+} ions as possible to interactions with the surface-bounded ligands, the nanoparticles were fabricated to have the diameters below 10 nm. The geometrical structure and properties of surface ligands needed for qualitative estimation of their influence on spectroscopic features of the investigated Eu^{3+} doped nanoparticles were obtained from DFT quantum-chemical calculations. Significant changes of luminescence spectra shapes and luminescence lifetime values were observed upon changes in the

local chemical environment. We show that the ratio $R = {}^5D_0 \rightarrow {}^7F_1/{}^5D_0 \rightarrow {}^7F_2$ of the intensities of the forced electric dipole ($J = 2$) and magnetic dipole ($J = 1$) transitions in the synthesized Eu^{3+} doped nanoparticles is highly sensitive to the type of ligand present on the nanoparticle surface. Similarly, 5D_0 luminescence lifetimes are found to be sensitive to the refractive index, and also to the dielectric constant of ligands used during the synthesis to coat nanoparticles surface. We argue that the photophysical and electro-optical properties of colloidal Eu^{3+} doped inorganic nanoparticles show hyper-sensitive response to the chemical surroundings in the close vicinity of the nanoparticle itself. The behavior of both steady-state luminescence and its kinetics demonstrates the potential suitability of the studied nanoparticles for constructing self-referencing optical nano-sensors.

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Introduction

Lanthanide-doped nanoparticles (NPs) are finding increasing interest as they have become an alternative to traditional organic dyes in many biosensing applications (Gnach and Bednarkiewicz 2012). They exhibit not only excellent photostability and narrow spectral emission lines, but also, in the case of co-doped upconverting NPs (UCNPs), efficient conversion of

near infrared photoexcitation into visible emission (Achatz et al. 2011). These features provide a number of advantages including those for micro- or nano-sensors design, and may lead to further improvement of the sensitivity and simplicity of readout methods and devices. For example, UCNPs were recently used to build FRET-based biosensors for indirect quantification of pH (Sun et al. 2009), carbon dioxide (Achatz et al. 2011), ammonia (Mader et al. 2010), mercury (Liu et al. 2011), glucose (Peng et al. 2011), oxygen, and for bioimaging of CN^- ions distribution in living cells (Liu et al. 2011). In all of these sensors, the spectral behavior of lanthanide-doped UCNPs was indirectly modified by organic dyes attached to the NPs surface. The principle of operation of those nanosensors was mostly related to quenching the lanthanides' luminescence through long-range dipole–dipole interactions between donor UCNPs and acceptor molecules, as a response to the occurrence of biochemical reactions (e.g., DNA hybridization, protein conformation changes, etc.). For example, for the UCNPs based pH sensor (Sun et al. 2009), the principle of its operation was spectral filtering of the green UC emission of erbium by phenol red, a well known pH-sensitive dye.

Nevertheless, none of the reported UCNPs based biosensors were related to a direct variation of spectral properties of the lanthanide ion in response to changes in the local surrounding. The absorption coefficients of the trivalent lanthanide ions are rather weak, due to the Laporte selection rule (Hänninen et al. 2011). Simultaneously, their emission is relatively insensitive to the ligand environment of the central metal ion (Lakowicz 2006), and thus little affected by the neighbor environment. The latter is due to shielding of the $4f$ optically active electrons by the filled $5s$ and $5p$ orbitals. However, this is not necessarily true for certain transitions called hypersensitive transitions (HST) or pseudo-quadrupolar (PQP) transitions. They obey selection rules for quadrupolar transitions ($|\Delta J| \leq 2$, $|\Delta L| \leq 2$, $|\Delta S| = 0$), and are more susceptible to changes in the lanthanide ion local symmetry or environment in comparison to other f – f transitions (Hänninen et al. 2011). One of the earliest noticed HSTs was the $^5D_0 \rightarrow ^7F_2$ luminescence transition in Eu^{3+} ion (Sheik Saleem and Srinivasan 1987). It has been proved that the ratio of the intensities of $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions in Eu^{3+} ions (asymmetry ratio, R) can be considered indicative of

the distortion in the local environment for the Eu^{3+} ions (Boyer et al. 2004). By measuring such a ratio of HST to standard transition intensity, one has access to concentration independent results that can be reliable in complex contexts, such as living cells or sensor microarrays. It has been shown that the radiative lifetime of the 5D_0 metastable excited state of Eu^{3+} ions is sensitive to the changes of refractive index of the surrounding medium (Boyer et al. 2004; Meltzer et al. 1999). Additionally, the Eu^{3+} ions luminescence was successfully used to probe the surface effects, originating from high surface to volume ratio, in nanosized materials (Banski et al. 2013; Chang et al. 2007; Jia et al. 2010). Yan et al. (2003) used combined laser selective excitation spectra and lifetime measurements of Eu^{3+} doped YVO_4 materials to detect the change of site symmetry from the interior to the surface of NPs. Peng et al. (2005) resolved two luminescent centers in $\text{La}_2\text{O}_3\text{S}:\text{Eu}^{3+}$ NPs, through the use of time-resolved and laser selective emission, and one of the optically active centers was attributed to a lower symmetry site occupied by surface Eu^{3+} ions.

Basing on what has been discussed above, we have designed, synthesized, and studied both the steady state and time dependent luminescence response of Eu^{3+} -doped ultra-small NaYF_4 NPs to the ligand type used to stabilize these nanocrystallites in liquid colloids, as well as in powders. The NaYF_4 nanocrystalline host was chosen because of relatively low phonon energy (Wang and Liu 2009) and reported low toxicity (Kumar et al. 2009). Moreover, we have implemented a method to synthesize ultra-small (7–9 nm) NPs uniquely developed for NaYF_4 NPs (Chen et al. 2010). These ultra-small NPs allowed reducing the “core–shell” effect, i.e., studying the impact of ligands and solvents on spectral properties of luminescent nanolabels is hindered within larger nanoparticles, since the luminescence of superficial (shell) lanthanides is dominated by the spectral properties of much more numerous volumetric (core) lanthanide ions. NPs were intentionally fabricated to have the diameters below 10 nm, which was supposed to expose as many Eu^{3+} ions as possible to interactions with the surface bound ligands and the local chemical environment. Properties of ligand molecules were assessed based on quantum-chemical calculations to allow qualitative discussion of the differences between them.

Experimental section

Materials and instrumentation

All chemicals for synthesis of NaYF_4 NPs were purchased from Sigma Aldrich or POCH S.A. (Poland), and used without further purification. X-ray diffraction (XRD) patterns were recorded on a STOE diffractometer with Ge-filtered $\text{CuK}_{\alpha 1}$ radiation. Transmission electron microscopy (TEM) studies were performed using a Philips CM20 SuperTwin microscope at 200 kV with 0.25 nm resolution. Fourier transform infrared (FT-IR) spectra were registered on a Biodra 575C spectrometer with resolution of 2 cm^{-1} for samples in KBr pellets. The emission spectra and luminescence decay curves were obtained under excitation from the second harmonic (394 nm) of a Ti:Sapphire laser (Belarus) pumped by a Nd:YAG LOTIS TII laser (Belarus). The luminescence signals were detected by a Synapse CCD camera (HORIBA JOBIN–YVON). Fluorescence decay curves were recorded with a photomultiplier (HAMAMATSU R928) output fed into a LeCroy Wave Surfer 425 digital oscilloscope.

Calculations

In order to determine geometrical structure of ligands, quantum-chemical calculations have been performed using the Kohn–Sham formulation of the density functional theory (DFT). In particular, geometry optimization followed by the evaluation of force constants was carried out using the B3LYP exchange–correlation functional (Becke 1993) and the 6-31G(d) basis set. Dipole moment and electronic polarizability were determined at equilibrium geometries using the Coulomb–attenuated CAM–B3LYP functional (Yanai et al. 2004). The latter functional has been proved to outperform B3LYP functional as far as polarizabilities of extended conjugated systems are concerned (Jacquemin et al. 2007). Electric-dipole properties were computed using the 6-31+G(d) basis set.

Synthesis of NaYF_4 :4 % Eu^{3+} NPs

Oleic acid capped NaYF_4 :4 % Eu^{3+} NPs (OANPs) were synthesized using the method previously reported by (Chen et al. 2010). Trioctylphosphine

oxide capped NPs (TOPONPs) were synthesized using a previously reported thermolysis method (Shan et al. 2007), with some modifications. For the TOPONPs synthesis aliquots of 1 mmol lanthanide oxides (Y_2O_3 , Eu_2O_3) were mixed and dissolved in ~50 % concentrated trifluoroacetic acid. The transparent solution was evaporated to dryness using a rotary evaporator. The mixture of 15 ml of octadecane (OD) and 20 g TOPO was preheated to form homogeneous solution, and added into the reaction flask together with 1.25 mmol of sodium trifluoroacetate. The solution was then heated to 120 °C under vacuum with magnetic stirring for total oxygen and water removal, during which the flask was purged with dry argon every 5 min. The resulting yellow solution was then heated to 300 °C under inert atmosphere and kept at these conditions for at least 1 h. After the synthesis the solution was cooled to room temperature, precipitated by acetone and then collected by centrifugation. Hexadecylamine capped NPs (HDANPs) were synthesized based on approaches previously proposed for quantum dots (Mntungwa et al. 2011; Nyamen et al. 2011). In an optimized synthesis protocol, fixed amounts of 1.25 mmol lanthanide oxides (Y_2O_3 , Eu_2O_3) were mixed and dissolved in ~50 % concentrated trifluoroacetic acid. The optically transparent solution was evaporated to dryness using a rotary evaporator. The mixture of 15 ml of octadecane and 12 g HDA was preheated, and next added into the reaction flask together with 1.25 mmol of sodium trifluoroacetate. The solution was then heated to 120 °C under vacuum with magnetic stirring for total oxygen and water removal, during which the flask was purged with dry argon every 5 min. The resulting yellow solution was then heated to 300 °C under inert atmosphere and kept at these conditions for at least 1 h. The solution was cooled to room temperature, precipitated by acetone and collected by centrifugation. In OANPs, TOPONPs and HDANPs synthesis protocols the volume ratio of OA:OD, OD:TOPO, OD:HDA was kept at 1:1. Additionally, selection of 4 % Eu^{3+} doping amount allowed to achieve strong luminescence without evident concentration quenching (Kumar et al. 2009). After precipitation, NPs were equally dispersed in four solvents: chloroform, cyclohexane, toluene, and THF. For transferring synthesized NPs to water solutions we performed a ligand removal procedure (Bogdan et al. 2011). To further investigate the influence of the nearest chemical

surroundings on spectroscopic properties of obtained NPs, we have also prepared NPs powders by a simple water evaporation method.

Results and discussion

Figure 1 presents crystallographic and morphological characterization of the synthesized NPs. The diffraction peaks for all the three samples could be indexed to the pure cubic α -NaYF₄ phase (Fig. 1a). The results are in good agreement with the JCPDS no. 77-2042 standard line pattern for α -NaYF₄ matrix. Slight shift

of the diffraction peaks results from the measurement setup geometry, since the 4 % Eu³⁺ dopant should not have any influence on NaYF₄ NPs crystal structure (Podhorodecki et al. 2013). Figure 1b–d shows representative TEM images of OANPs, TOPONPs, and HDANPs, respectively, together with their size distribution histograms obtained from measuring the size of over 300 NPs per sample. The mean size and its standard deviation of OANPs and TOPONPs have been estimated to be $\langle D \rangle \pm \Delta D = 5.8 \pm 1.7$ and 5.1 ± 1.6 nm, respectively. In the case of HDANPs (Fig. 1d) larger NPs and broader size distribution were observed ($\langle D \rangle \pm \Delta D = 9.5 \pm 2.0$ nm). Observation

Fig. 1 X-ray diffraction patterns of the synthesized NaYF₄ NPs together with the reference JCPDS no. 77-2042 standard line pattern for α -NaYF₄ matrix (a), and TEM images with size distribution histograms for OANPs (b), TOPONPs (c), and HDANPs (d)

of distinct diffraction peaks at XRD spectra, which are well-matched to the JCPDS no. 77-2042 standard line pattern for α -NaYF₄ matrix, led us to conclude that highly crystalline face-centered cubic structure of NaYF₄ was obtained. Additionally, no aggregation of NPs was observed by TEM, which indirectly confirms successful incorporation of capping ligands on the NPs surface. The presence of capping ligands on the NPs surface was further identified by FTIR absorption measurements (for more details see SI Fig. 1S.). The organic ligands present on the NPs surface also allowed their stability in solvents such as: chloroform, cyclohexane, toluene, or tetrahydrofuran.

In order to explain the influence of ligands on the photophysical properties of the NPs, we assumed that it can be related to electrostatic interactions due to the static and induced dipole moment of the surface attached ligand molecules. We evaluated the geometries of the molecules and the relevant properties from quantum-chemical calculations using the Kohn–Sham formulation of the DFT. There are two possible spatial arrangements of OA molecules, but since the *trans* form is more stable we have assumed that the OA molecules attach to NPs surface in this isomeric modification. Table 1 contains the calculated electric dipole moments of the three ligands as well as their linear polarizabilities. We assume that the electric field producing the induced dipole moment in the ligands is parallel to the cartesian z-axis (F_z), thus the

relevant polarizability component is α_{zz} which is presented in Table 1.

Neglecting the effects arising from nuclear motions and assuming the presence of a uniform electric field F_z , the induced dipole moment of a ligand molecule can be calculated as $\mu_z^{\text{ind}} = \alpha_{zz}F_z$. The total electric-dipole moment parallel to the cartesian z-axis will be equal to $\mu_{\text{tot}} = \mu_z + \alpha_{zz}F_z$. In the simplest case, the electric field may result from uncoordinated Eu³⁺ and Y³⁺ ions present on the NPs surface. We also need to take into account that the distribution of dopant ions is not statistical within the NP volume (Dong et al. 2011). For this reason, we have decided to assume equal surface charge density (Q_{surface}) for all types of investigated NPs, and thus roughly even electric field strength F_z , at a fixed distance from the NPs surface, for all three types of investigated NPs. It follows from Table 1 that both the permanent and induced dipole moments, and thus also the highest total electric dipole moment should be the largest in the case of TOPO molecules. We are aware that this calculation uses numerous simplifications, among them neglecting the sterical effects arising from the presence and interaction of neighboring ligand molecules. However, the point is to qualitatively estimate the electrostatic interactions and further exploit those results in the interpretation of the observed changes in luminescence spectra, and kinetic behavior between NPs having different ligands molecules attached to the surfaces.

Table 1 Electric-dipole properties of HDA, OA, and TOPO surface ligands determined at the CAM–B3LYP/6-31+G(d)//B3LYP/6-31G(d) level of theory

	μ_z [D]	$ \mu $ [D]	α_{zz} [a.u.]	$\langle\alpha\rangle$ [a.u.]	Ligand molecules
HDA	−0.1	1.5	253	197
TOPO	5.2	5.2	311	305	
OA (<i>cis</i>)	0.7	0.7	276	220	
OA (<i>trans</i>)	−0.1	1.5	282	221	

The inset in rightmost column shows optimized geometrical structures of the surface ligands. $\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$

In general, the Eu^{3+} doped fluoride NPs exhibit intense luminescence peaks associated with the $^5D_0 \rightarrow ^7F_{1,2,4}$ electronic transitions, under 394 nm laser excitation (Ghosh and Patra 2008b). The $^5D_0 \rightarrow ^7F_{3,5,6}$ are usually observed as well, but are much weaker. According to the appropriate selection

rules, the $0 \leftrightarrow 0$ transitions are forbidden unless the Eu^{3+} ions are located at low symmetry sites. In particular, the intensity of $^5D_0 \rightarrow ^7F_0$ transition, which is of pure electric dipole character, strongly depends on the crystalline matrix. Figure 2 shows normalized (to the $^5D_0 \rightarrow ^7F_1$ transition)

Fig. 2 394 nm excited luminescence spectra (normalized to $^5D_0 \rightarrow ^7F_1$ transition) of OANPs (top row), TOPONPs (middle row), HDANPs (bottom row) in CHCl_3 (left hand column), and

corresponding spectra for NPs after ligand removal and dispersing in water (middle column), as well as for dried NP powders (right hand column)

luminescence spectra of ultra-small Eu^{3+} doped NaYF_4 NPs with different organic ligands present on the surface and dispersed in CHCl_3 (Fig. 2a, d, g), corresponding spectra obtained after ligand removal and dispersing the NPs in water (Fig. 2b, e, h), as well as spectra of powders obtained after drying water dispersion of NPs (Fig. 2c, f, i). Upon 394 nm laser excitation, five peaks at 578, 593, 613, 651, and 700 nm were observed and attributed to the consecutive $^5D_0 \rightarrow ^7F_J$ transitions with $J = 0, 1, 2, 3, 4$, respectively. For NPs powders we have observed significant narrowing of the emission lines. This could indicate the aggregation of NPs, however, there is no change in the symmetry, since the $^5D_0 \rightarrow ^7F_0$ transition is still observed (Georgescu et al. 2005). The emission lines are narrowed only for ligand-free powder samples, indicating that both vibrational modes of ligands and solvents molecules are responsible for broad emission lines as observed for colloidal suspensions of investigated NPs. The Eu^{3+} surface atoms also interact with a high phonon energy environment originating from ligands and solvents molecules, promoting undesirable non-radiative mechanisms that compete with the radiative transfer processes. In order to quantitatively compare the samples, the asymmetry ratio parameter (R) was calculated based on the luminescence spectra. $R = I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ is the ratio of the integrated intensities of the hypersensitive $^5D_0 \rightarrow ^7F_2$ and magnetic-dipole $^5D_0 \rightarrow ^7F_1$ transitions in Eu^{3+} ions. This parameter can be informative about the distortion in the Eu^{3+} ions local surrounding, and thus it is usually higher for the nanocrystalline samples (Boyer et al. 2004) in comparison to their bulk counterparts. For 200 nm size $\alpha\text{-NaYF}_4$ particles, Cao et al. (2011) reported the R parameter to be 0.937. This result is significantly different from the values obtained for nano-glass-ceramics containing Eu^{3+} doped NaYF_4 NPs (Santana-Alonso et al. 2010), where the R parameter was in the range from 1.11 to 1.47, depending on sample treatment during synthesis. Thus, determination of the asymmetry ratio R could potentially allow for optical sensing by monitoring deviations in Eu^{3+} ions local surroundings.

First, we have investigated the influence of four various solvents (chloroform, cyclohexane, toluene, and tetrahydrofuran), in which the NPs were dispersed after synthesis, on the luminescence properties of Eu^{3+} . The changes in either shape of luminescence

Table 2 Asymmetry ratios for NaYF_4 :4 % Eu^{3+} NPs in CHCl_3 with various surface ligands, and the corresponding values for ligand-free NPs in water and NPs powders

Ligand/medium	CHCl_3	H_2O	Air
OA	1.3	0.97	2.2
TOPO	3.0	0.92	2.2
HDA	1.1	0.93	1.9

spectra or R value for the NPs having same surface capping ligands but dissolved in different solvents were negligible (for R values see SI Table 1S.). However, significant differences in those features were found for ligated and non-ligated NPs. Table 2 lists the obtained R parameters for OANPs, TOPO-NPs, HDANPs, corresponding values for ligand-free NPs in water and NPs powders in air.

As mentioned above, the R value is an indicator of distortion of Eu^{3+} ions by the local environment. Markedly higher R values, as compared to larger nanocrystals or glass-ceramics, e.g., $R = 3.0$ for the TOPONPs dispersed in CHCl_3 , may originate from two reasons. The first one is the ultra-small size of TOPONPs. From all of the synthesized NPs, the TOPONPs were the smallest, and thus had the largest surface to volume ratio. Because, a considerable number of Eu^{3+} ions are exposed to the interaction with the organic ligands there. However, since the OANPs were similarly small but demonstrated only minor change of R from largest HDANPs, we suspect another factor may dominate the spectral changes. The electric field F_z deriving from uncoordinated Eu^{3+} and Y^{3+} ions present on the NPs surface causes polarization of the charge distribution in surface attached ligands. Hence, there may appear a perturbation of the electronic states of the lanthanide ion by the electric field of the ligands (Mason et al. 1975). Since both static and induced electric-dipole moment are the highest for TOPO molecules, their presence on NPs surface would probably cause strongest distortion in the local electric field on the NPs surface, in comparison with other investigated OA and HDA ligand molecules. Thus we assume that, mainly for that reason, the observed R value for TOPONPs was the highest. For the OANPs and HDANPs, the asymmetry ratios were calculated to be 1.1 and 1.3, respectively. These R values correlate with significant differences in electric-dipole moment between the capping molecules. The differences in R values decrease noticeably

after ligands removal from the surface of the NPs, which are then dispersed in water. In this case, the R values vary in the range from 0.92 to 0.97, and the value is the highest for OANPs. These R values represent the interaction of Eu^{3+} ions with mixed host and medium environment, but some ligand residuals on the surface of NPs cannot be excluded as well. Moreover, it must be taken into account that the superficial Eu^{3+} ions exposed to water molecules are efficiently quenched and do not contribute to the NPs emission at all. The R values for powders are symptomatic, since R values appear to correlate with the size of NPs. R is equal to 2.2 for ultra-small ~ 5 nm NPs, whereas, it is equal to 1.9 for HDA originating NPs with average size of ca. 10 nm. One cannot neglect the interaction between NPs in the powders. The grains of NPs definitely touch each other, thus superficial Eu^{3+} ions can be impacted more by structural distortions rather than by different chemical environment.

One may also find some substantial differences in the spectra between the samples after ligand and solvent removal (Fig. 2b, c, respectively) in comparison to original ones (Fig. 2a). The samples after ligand removal and dispersing in water, exhibit slightly more structured emission spectra (OANPs Fig. 2b vs. Fig. 2a), which may originate from more efficient quenching of superficial Eu^{3+} ions by solvent. The ligands are responsible for line broadening and potentially for luminescence quenching to some extent as well. However, since ligands vibration frequencies are not as high as for water molecules ($h\nu_{\text{max}} \sim 2,900 \text{ cm}^{-1}$ vs. $h\nu_{\text{max}} \sim 3,300 \text{ cm}^{-1}$ for oleic acid and water, respectively) the quenching should be more pronounced in ligands-free water colloids than in ligand rich NPs. The quenching of superficial ions is also responsible for the dominance of the luminescence originating from the “core” of NP. This luminescence experiences a higher crystallinity of the NC.

The luminescence kinetics of Eu^{3+} ions embedded in NPs with different capping ligands was also investigated. The luminescence decay of the lanthanide ions provides the information on the degree of quenching from the organic solvents, surface ligands, internal crystal defects, and ions impurities within the NPs. The measured decay curves for ligated NPs exhibited double-exponential behavior, similar to what has been reported in the past for colloidal Eu^{3+} -doped NaYF_4 NPs (Ghosh and Patra 2008a). The decay curves for non-ligated NPs, both water dispersions and

powders, on the other hand, were single exponential (see SI Table 2S for the lifetime values). First, we have investigated the 5D_0 excited state lifetimes values for NPs with the same capping ligands but dispersed in different solvents. Insignificant changes in luminescence lifetimes values for both short (τ_1) and long components (τ_2) (less than 10 %; see SI Table 2S; Figs. 2S, 3S) were found, hence these results are consistent with those of steady-state luminescence. This observation prompted us to perform more detailed investigations of the impact of type of capping ligands on the kinetic behavior of Eu^{3+} ions. This time, significant differences in lifetime values between NPs having different capping ligands were noticed and could be understood by considering the changes produced by the closest surroundings of the NPs. In the first approach, we separately plotted τ_1 (Fig. 4S) and τ_2 (Fig. 5S) as a function of the ligand refractive index, as proposed by (Meltzer et al. 1999) and further by (Boyer et al. 2004), who studied the behavior of Eu^{3+} doped nanocrystalline powder samples mechanically dispersed in different solvents. Surprisingly, we did not manage to correlate our results to the “effective index of refraction” model, since the lifetime values tended to increase with the increasing refractive index of ligand used during the synthesis. However in our case, the investigated systems were more complicated than those studied before. In colloidal solutions, the ligand molecules attached directly to the NPs surface are responsible for homogenous dispersibility of these NPs in organic solvents. In such systems, not only the interaction of surface Eu^{3+} ions with solvent molecules should be taken into account, but also geometrical organization of ligands molecules at the NPs surface as well as interaction of ligands with surface Eu^{3+} ions together with specific interaction between ligands and solvent molecules. In order to understand the relationship between lifetime values and the surrounding environment, in further analysis we included long lifetime component τ_2 together with both the refractive index (n) and the dielectric constant (ϵ) of ligand molecules. Following (Berezin et al. 2008) we plotted the τ_2 values versus ligand orientation polarizability factor Δf (Fig. 3):

$$\Delta f = \frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (1)$$

The first term of the equation reflects influence of reorientation of the solvent molecules and redistribution

Fig. 3 Luminescence lifetimes of the 5D_0 excited state of Eu^{3+} ions embedded in NaYF_4 matrix with four different capping surface ligands plotted versus ligand orientation polarizability. The exponential curve was added as the guide for the eye

of the electrons in solvent molecules during the luminescence lifetime, whereas, the second term accounts for reorganization of electrons only (Lakowicz 2006). For calculation of Δf values, the refractive index values n for capping ligands were taken from reagent material safety data sheets (MSDS), and were 1.459, 1.447, 1.4496, and 1.33 for OA, TOPO, HDA, and water, respectively. Dielectric constants were approximated, based on literature data, to be: 2.03 (de Sousa et al. 2009), 2.5 (Jiang et al. 2000), 2.25 (Hoffman and Smyth 1949), and 78.3 for OA, TOPO, HDA, and water, respectively. We found that decreased ligand orientation polarizability factor Δf correlated with the progressive increase of the τ_2 as measured for the 5D_0 excited state of Eu^{3+} ions. The τ_2 value for ligand-free NPs dispersed in water has been taken as the average of measurements for OANPs, TOPONPs, and HDANPs after ligand removal (see SI for the data). This observation supported our hypothesis, that NPs properties are susceptible to both the refractive index n and the dielectric constant ϵ of ligands, which originates from ultra-small size of the synthesized NPs, and exposure of Eu^{3+} ions to the outer environment.

Conclusions

In this article, we have demonstrated the hyper-susceptibility of the steady-state and kinetic optical

properties of colloidal Eu^{3+} doped ultra-small NaYF_4 NPs to the local nano-scale surroundings of the NP. We have engineered and optimized three synthesis protocols for ultra-small Eu^{3+} doped NaYF_4 NPs with different capping ligands attached to the NP surface. We have shown that the ratio of the integrated intensities of the hypersensitive $^5D_0 \rightarrow ^7F_2$ and magnetic-dipole $^5D_0 \rightarrow ^7F_1$ transitions in Eu^{3+} ions as well as 5D_0 luminescence lifetimes are sensitive to the type of ligand present on the NP surface. It is important to underline that not the effective index of refraction, but the orientation polarizability factor of the ligand molecules matters, as was revealed in our experiments. To the best of our knowledge, this is the first report on the hyper-sensitive relation between spectral, temporal, and electro-optical properties of colloidal solution of lanthanide-doped inorganic NPs as a response to the chemical surroundings of the NP itself. Of course, the solvent influence on the emissions in the europium ion-doped fluoride NP needs future investigations to clarify more details of the observed phenomena. Both steady-state and luminescence kinetics showed the suitability of the synthesized NPs for constructing self-referenced, direct optical nano-sensors. The use of lanthanide-doped inorganic nanocrystallites as optical labels offers repeatable and temporally stable measurement conditions, because such materials are not prone to photobleaching. Additionally, due to long living 5D_0 excited

states in Eu^{3+} ions, facile time-resolved signal detection becomes possible under UV excitation. This can be of great importance for biological detection and imaging, since UV radiation readily induces undesired background autofluorescence from cells and tissues.

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