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# **Optical properties and luminescence dynamics of Eu<sup>3+</sup>-doped terbium orthophosphate nanophosphors**

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## Abstract

The development of luminescent inorganic nanocrystals (NCs) doped with rare-earth (RE) ions has attracted increasing interest owing to their distinct optical properties and versatile applications in time-resolved bioassays, multiplex biodetection, DNA hybridization and bioimaging. Hexagonal TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs (10-30 nm) were synthesized via a facile hydrothermal method assisted with oleic acid (OA) surfactants, which exhibit tunable emissions from green to red by varying the concentration of  $Eu^{3+}$ . The  $Tb^{3+}$ -to- $Eu^{3+}$  energy transfer efficiency observed reaches up to 94%. Different from their bulk counterparts, a new interface-state band (316 nm) in addition to the commonly observed spin-forbidden 4f-5d transition band (265 nm) of Tb<sup>3+</sup> was found to be dominant in the excitation spectrum of NCs due presumably to the formation of surface TbPO4/OA complexes, which provides an additional excitation antenna in practical utilization. Two kinds of luminescence sites of Eu<sup>3+</sup> in TbPO<sub>4</sub> NCs, with the site symmetry of  $C_2$  or  $C_1$ , were identified based on the emission spectra at 10 K and room temperature. Furthermore, the photoluminescence (PL) dynamics of  $Tb^{3+}$  ions in pure TbPO<sub>4</sub> NCs have been revealed. Compared to the exponential PL decay in bulk counterparts induced by very fast energy migration, the non-exponential decay from  ${}^{5}D_{4}$  of Tb<sup>3+</sup> in TbPO<sub>4</sub> NCs is mainly attributed to the diffusion-limited energy migration due to more rapid energy transfer from  $Tb^{3+}$  to defects than the energy migration among  $Tb^{3+}$ .

S Online supplementary data available from stacks.iop.org/Nano/22/275701/mmedia

(Some figures in this article are in colour only in the electronic version)

# 1. Introduction

The development of multicolor luminescent bioprobes has been motivated by the demand for simultaneously and precisely detecting the components of complex biomolecule assemblies (e.g. proteins, live cells) and chemical information, such as time-resolved fluorometric immunoassay, multiplex detection, DNA hybridization and bioimaging [1]. To date, the most commonly used luminescent labeling materials are organic dyes and quantum dots (QDs), which might possess intrinsic drawbacks such as photobleaching, broad emission bandwidth, fluorescence intermittency and cytotoxicity [2–6]. As a promising new class of luminescent bioprobes, rareearth (RE) ion-doped inorganic nanocrystals (NCs) show superior properties including narrow emission bandwidths (<10 nm), long luminescence lifetime, high photostability and low toxicity [7–10]. Specifically, RE orthophosphate (REPO<sub>4</sub>) has been regarded as one of the important biolabeling materials because of their outstanding optical properties and

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size similarity to biomolecules via controlled synthesis [11]. The photoluminescence (PL) lifetimes of Tb<sup>3+</sup> and Eu<sup>3+</sup> ions in REPO<sub>4</sub> NCs are in the  $\mu$ s-ms range, which renders their emissions well distinguished from the short-lived background luminescence by utilizing the time-resolved PL (TRPL) detection. Furthermore, efficient energy transfer (ET) from  $Tb^{3+}$  to  $Eu^{3+}$  in REPO<sub>4</sub> NCs may allow the PL color chromaticity to be finely tuned in the visible, which can extend the spectroscopic selectivity of the NCs beyond the range of interferences from biological systems. Previously, efficient ET from Tb<sup>3+</sup> to Eu<sup>3+</sup> have been reported in TbPO<sub>4</sub>:Eu<sup>3+</sup> nanoparticles [12], nanowires [13], inverse opal photonic crystals [14] and other inorganic hosts [15–19]. However, the obtained nanoparticles were too large (>50 nm) and tended to aggregate, which is not suitable for utilizing in biodetection. To the best of our knowledge, there is no report on the synthesis of small-size TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs. The optical properties of Eu<sup>3+</sup> and Tb<sup>3+</sup> in these NCs, such as Tb<sup>3+</sup>-to-Eu<sup>3+</sup> ET, luminescence sites and PL dynamics, are still lacking.

In this work, well-dispersed small NCs of TbPO<sub>4</sub>: $Eu^{3+}$  are synthesized via a simple hydrothermal method assisted with oleic acid (OA) surfactants. Multicolor emissions from green to red are achieved by varying the  $Eu^{3+}$  concentration in TbPO<sub>4</sub>: $Eu^{3+}$  NCs. Moreover, Tb<sup>3+</sup>-to-Eu<sup>3+</sup> ET, luminescence sites and luminescence dynamics of TbPO<sub>4</sub>: $Eu^{3+}$  NCs are investigated in detail.

#### 2. Experimental section

#### 2.1. Nanoparticle synthesis

TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs were synthesized via a modified hydrothermal method according to the procedure reported by Li *et al.* [20]. Typically, NaOH (0.6 g) was dissolved in a solution of OA and ethanol (v/v = 1:1) under vigorous stirring, followed by adding 5 ml Tb(NO<sub>3</sub>)<sub>3</sub> (0.2 M), required amounts of Eu(NO<sub>3</sub>)<sub>3</sub> and 5 ml NaH<sub>2</sub>PO<sub>4</sub> (0.2 M) aqueous solutions drop-wise, which resulted in white precipitates of amorphous TbPO<sub>4</sub>:Eu<sup>3+</sup> immediately. Then, the mixture was added to 15 ml ethanol, transferred into a 50 ml teflon-lined autoclave and heated at 160 °C for 12 h. After being cooled to room temperature (RT) naturally, the precipitates deposited at the bottom of the vessel were collected, washed with deionized water and ethanol for several times, and dried at 60 °C for 12 h in air to yield the final products.

For comparison, the submicron counterparts were synthesized following a similar procedure but without the addition of OA and ethanol: 15 ml Tb(NO<sub>3</sub>)<sub>3</sub> (1.5 M) and required amounts of Eu(NO<sub>3</sub>)<sub>3</sub> were added in 15 ml NaH<sub>2</sub>PO<sub>4</sub> (1.5 M) solution under vigorous stirring. The pH was adjusted to 1 by the addition of HNO<sub>3</sub> and NaOH solutions. Then the mixture was transferred into a 50 ml teflon-lined autoclave and heated at 140 °C for 12 h. The post-synthesis treatment was the same as that of NCs.

#### 2.2. Characterization

X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert Pro powder diffractometer with Cu K $\alpha_1$  radiation ( $\lambda = 0.154$  nm). The sample morphology was characterized Y Ruan et al

by a JEOL-2010 transmission electron microscope (TEM) equipped with an energy dispersive x-ray spectrum (EDS) and a JSM6700F scanning electron microscope (SEM). The Fourier transform infrared (FTIR) spectrum was recorded on a Magna 750 FTIR spectrophotometer in the range of 400-4000 cm<sup>-1</sup>. Luminescence spectra and lifetimes were measured on an Edinburgh Instruments FLS920 spectrofluorimeter equipped with both continuous (450 W) and pulsed xenon lamps. For low temperature measurements, samples were mounted on a closed-cycle cryostat (10-350 K, DE202, Advanced Research Systems). For site-selective spectroscopy, the excitation (or emission) monochromator's slits were set as small as possible to maximize the instrumental resolution. The best wavelength resolution is 0.05 nm. The line intensities and positions of the measured spectra were calibrated according to the FLS920 correction curve and standard mercury lamp. The TRPL spectra were recorded on a Varian Cary Eclipse fluorescence spectrometer by setting the appropriate delay time and gate time. The best wavelength resolution is 1.5 nm. The spectral slit widths for excitation and emission were both set with a resolution of 2.5 nm in measurements.

#### 3. Results and discussion

#### 3.1. Structure and morphology characterization

Figure 1(a) shows the XRD patterns of TbPO<sub>4</sub> NCs doped with different concentrations of  $Eu^{3+}$ , as well as the standard diffraction lines of hexagonal rhabdophane-type terbium orthophosphate (JCPDS no. 20-1244) [21]. The diffraction peaks of all the samples can be well indexed to that of pure hexagonal phase terbium orthophosphate and no traces of other segregated phases or impurities were detected, showing that the hydrothermal method is a feasible way for preparing pure phase RE phosphate products. The relatively broad XRD peaks reveal the small size of TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs.

The morphology and size of TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs were examined by the TEM and high-resolution TEM (HRTEM). It can be seen from figures 1(b) and (c) that  $TbPO_4:Eu^{3+}$ NCs are roughly irregularly spherical with diameters in a range of 10–30 nm. The HRTEM image (figure 1(c)) shows clear lattice fringes with an observed d spacing of 0.58 nm, which is in good agreement with the lattice spacing in the (100) planes of hexagonal TbPO<sub>4</sub>, indicative of the high crystallinity of TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs. The fast Fourier transform (FFT) pattern (figure 1(d)) of the selected NCs in figure 1(c) exhibits regular diffraction spots and can be well indexed as hexagonal TbPO<sub>4</sub> with single-crystalline nature. The statistical analysis (figure 1(e)) reveals that most of TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs have a size in the range of 12–24 nm and the average size of TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs is about 18 nm. The EDS spectrum reveals the presence of Tb, Eu, P and O ions in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs (figure S1, in supporting information available at stacks.iop.org/Nano/22/275701/mmedia). For comparison, the submicron counterparts are composed of bundles of nanorods with 2-3  $\mu$ m in length and 90-100 nm in diameter (figure S2 available at stacks.iop.org/ Nano/22/275701/mmedia). Hereafter, submicron crystals



**Figure 1.** (a) XRD patterns of TbPO<sub>4</sub>:Eu<sup>3+</sup> (*x* at.%, x = 0, 1, 5) NCs; (b) TEM image, (c) HRTEM image, (d) FFT pattern of the selected NC in (c), (e) size distribution, and (f) FTIR spectrum for TbPO<sub>4</sub>:Eu<sup>3+</sup> (5 at.%) NCs.

of TbPO<sub>4</sub>: $Eu^{3+}$  are referred to as bulk counterparts of TbPO<sub>4</sub>: $Eu^{3+}$ .

The FTIR spectrum verifies the presence of OA molecules on the surface of TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs. For pure oleic acid, the stretching vibration of the C=O group appears at 1711 cm<sup>-1</sup> and this peak is absent in the FTIR spectrum in figure 1(f). Instead, two stretching vibrations of C=O groups appear at 1458 and 1554 cm<sup>-1</sup>, as shown in figure 1(f), which verifies the formation of TbPO<sub>4</sub>:Eu<sup>3+</sup>/OA complexes via chemical bonding of OA to the surface of TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs [22, 23]. Peaks at 2851 and 2920 cm<sup>-1</sup> are assigned to the symmetric and asymmetric methylene (-CH<sub>2</sub>-) stretching vibrations of the OA molecule. Besides, IR peaks at low wavenumbers (540–1050 cm<sup>-1</sup>) were also detected, which are typical of the phosphate group of TbPO<sub>4</sub> [20].

#### 3.2. Emission and excitation spectra

Figure 2(a) shows the emission spectra for TbPO<sub>4</sub>: $Eu^{3+}$  (0– 5 at.%) NCs upon RT excitation at 316 nm, which corresponds to the interface-state band as will be discussed later. The emission spectrum of pure TbPO<sub>4</sub> NCs is dominated by intense green emissions of Tb<sup>3+</sup> centered at 490, 543, 588 and 622 nm, which are ascribed to the <sup>5</sup>D<sub>4</sub>  $\rightarrow$  <sup>7</sup>F<sub>6,5,4,3</sub> transitions of Tb<sup>3+</sup>, respectively. Characteristic <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>0,1,2,3,4</sub> transitions of Eu<sup>3+</sup> centered at 580, 593, 614, 652 and 698 nm were observed in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs, suggesting that the Eu<sup>3+</sup> emission can be achieved via the ET process from Tb<sup>3+</sup> to Eu<sup>3+</sup> ions. The PL intensity of Eu<sup>3+</sup> gradually increases at the expense of the Tb<sup>3+</sup> emission as the Eu<sup>3+</sup> concentration increases from 0 to 5 at.%, which induces a significant emission color change from green to red as revealed by the corresponding CIE chromaticity coordinates (figure 2(b)). It can be seen that such Tb<sup>3+</sup>-to-Eu<sup>3+</sup> ET is rather efficient in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs, and the red emissions of Eu<sup>3+</sup> are predominant when the Eu<sup>3+</sup> concentration reaches 1 at.%.

The TRPL technique can effectively distinguish the emissions of luminescence centers with distinct lifetimes. As will be discussed in section 3.3, the effective lifetime for  ${}^{5}D_{0}$  of Eu<sup>3+</sup> is about one order of magnitude larger than that of Tb<sup>3+</sup> in TbPO<sub>4</sub> NCs. Thus, by setting an appropriate delay time and gate time, the long-lived emissions of Eu<sup>3+</sup>



**Figure 2.** (a) Emission spectra for TbPO<sub>4</sub>:Eu<sup>3+</sup> (*x* at.%, *x* = 0–5) NCs and (b) their corresponding CIE chromaticity coordinates; (c) TRPL spectra for TbPO<sub>4</sub>:Eu<sup>3+</sup> (0.5 at.%) NCs upon RT excitation at 316 nm; (d) excitation spectra for (1) TbPO<sub>4</sub>:Eu (5 at.%) NCs by monitoring <sup>5</sup>D<sub>0</sub>  $\rightarrow$  <sup>7</sup>F<sub>2</sub> (614 nm) of Eu<sup>3+</sup>, (2) pure TbPO4 NCs by monitoring <sup>5</sup>D<sub>4</sub>  $\rightarrow$  <sup>7</sup>F<sub>5</sub> (543 nm) of Tb<sup>3+</sup> and (4) TbPO<sub>4</sub>:Eu (5 at.%) bulk counterparts ( $\lambda_{em} = 614$  nm) at RT, and (3) TbPO<sub>4</sub>:Eu (5 at.%) NCs ( $\lambda_{em} = 614$  nm) at 10 K. The excitation spectrum within 240–335 nm was best fitted and deconvoluted to six Gaussian curves with their peaks centered at 265, 272, 284, 303, 316 and 318 nm, respectively.

can be easily separated from those of short-lived  $Tb^{3+}$  in  $TbPO_4:Eu^{3+}$  NCs. As shown in figure 2(c), at short delay time (0–2 ms), the emission lines of both  $Tb^{3+}$  and  $Eu^{3+}$  ions can be observed simultaneously upon excitation at 316 nm, whereas the emission spectrum was dominated by the long-lived red emission of  $Eu^{3+}$  when the delay time was longer than 2 ms. This TRPL technique, coupled with the color tuning by changing the concentration ratio of  $Eu^{3+}$  to  $Tb^{3+}$  in NCs, may provide remarkably higher detection sensitivity than the conventional steady-state detection in that the short-lived background luminescence is effectively suppressed.

RT excitation spectra of TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs and bulk counterparts were compared by monitoring the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition (614 nm) of  $Eu^{3+}$  (curves 1, 3 and 4 in figure 2(d)). As assigned in curve 1 of figure 2(d), in addition to the  $^7F_0 \rightarrow {}^5L_6, \,\, {}^5D_2$  transitions of Eu^{3+}, abundant excitation peaks ascribed to the characteristic intra-4f transitions from ground state  ${}^{7}F_{6}$  to the excited states of  ${}^{5}L_{10-7}$ ,  ${}^{5}G_{6-2}$ ,  ${}^{5}D_{2-4}$ of Tb<sup>3+</sup> were observed in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs at RT, which provides clear evidence for the presence of the Tb<sup>3+</sup>-to-Eu<sup>3+</sup> ET process. Besides the direct excitation lines of Eu<sup>3+</sup> and Tb<sup>3+</sup> ions, an intense broad band ranging from 250 to 334 nm in the UV region was presented in curve 1 of figure 2(d). A similar broad band was observed in pure TbPO<sub>4</sub> NCs (curve 2 of figure 2(d)). At 10 K, this broad band was split into two excitation bands centered at 265 and 316 nm in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs, respectively, indicating the presence of two excitation centers in the UV region for Eu<sup>3+</sup> in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs (curve 3 of figure 2(d)). These excitation peaks can

be further separated from spectral deconvolution. As can be seen in curves 1-3 of figure 2(d), the excitation spectra within 240-335 nm were best fitted and deconvoluted to six Gaussian curves, with four sharp peaks for the  ${}^{7}F_{6} \rightarrow$  ${}^{5}F_{3}$ ,  ${}^{5}H_{6}$  transitions of Tb<sup>3+</sup> centered at 272, 284, 303 and 318 nm and two broad peaks centered at 265 and 316 nm, respectively. The band centered at 265 nm can be attributed to the spin-forbidden 4f–5d transition of the  $Tb^{3+}$  ions [24], consistent with that observed in bulk counterparts (curve 4 of figure 2(d)). The other band at 316 nm has not been reported in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs before. Such an excitation band at 316 nm may be ascribed to the interface state formed via a carboxylate bonding of OA to the surface of  $TbPO_4$ :Eu<sup>3+</sup> NCs [23, 25], which is consistent with that discussed in the FTIR spectrum. Similar to that in oxide/polymer nanocomposites [26], a broad peak centered at 440 nm corresponding to the interface-state luminescence was observed in the enlarged emission spectrum in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs (figure S3 available at stacks.iop.org/ Nano/22/275701/mmedia). The luminescence intensity of the interface state was negligibly weak compared to that of Tb<sup>3+</sup> and Eu<sup>3+</sup> (figure S3 available at stacks.iop.org/Nano/ 22/275701/mmedia and figure 2(a)), indicating highly efficient ET from the interface state to Eu<sup>3+</sup> and Tb<sup>3+</sup> in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs. In contrast, no such luminescence was observed in bulk counterparts, which further confirms that OA is responsible for the formation of interface state in NCs. Based on the optical properties of TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs we observed at 10–300 K, the ET mechanism from TbPO<sub>4</sub> NCs to Eu<sup>3+</sup> ions is proposed. As schematically depicted in figure 3, an electron-hole pair (carrier) is formed in the interface state of TbPO<sub>4</sub> NCs upon



**Figure 3.** Proposed mechanism describing the ET processes from the interface state and  $Tb^{3+}$  to  $Eu^{3+}$  in  $TbPO_4$ : $Eu^{3+}$  NCs. The dotted, straight and dashed arrows denote multiphonon nonradiative transitions, radiative transitions and ET processes, respectively.

UV excitation at 316 nm. The carrier in the interface state will nonradiatively transfer its energy to the matching energy levels of Tb<sup>3+</sup> such as <sup>5</sup>D<sub>1,0</sub>, followed by nonradiative relaxation to <sup>5</sup>D<sub>4</sub>. The excited <sup>5</sup>D<sub>4</sub> state will nonradiatively transfer its energy to Eu<sup>3+</sup> ions via the transitions of <sup>5</sup>D<sub>4</sub>  $\rightarrow$  <sup>7</sup>F<sub>6</sub> (Tb<sup>3+</sup>) to <sup>7</sup>F<sub>1</sub>  $\rightarrow$  <sup>5</sup>D<sub>2</sub> (Eu<sup>3+</sup>) and <sup>5</sup>D<sub>4</sub>  $\rightarrow$  <sup>7</sup>F<sub>3</sub> (Tb<sup>3+</sup>) to <sup>7</sup>F<sub>0</sub>  $\rightarrow$  <sup>5</sup>D<sub>1</sub> (Eu<sup>3+</sup>), and then characteristic green and red luminescence of Tb<sup>3+</sup> and Eu<sup>3+</sup> is observed. Such an ET mechanism is also applicable for the 4f<sup>7</sup>5d states of Tb<sup>3+</sup> upon excitation at 265 nm.

# 3.3. Energy transfer from $Tb^{3+}$ to $Eu^{3+}$

The ET from Tb<sup>3+</sup> to Eu<sup>3+</sup> in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs was further investigated by measuring the dependence of the Eu<sup>3+</sup> concentration on the PL decay of Tb<sup>3+</sup>. As shown in figure 4(a), the PL decay rate for <sup>5</sup>D<sub>4</sub>  $\rightarrow$  <sup>7</sup>F<sub>5</sub> (543 nm) drastically increases when the Eu<sup>3+</sup> concentration increases from 0.2 to 5 at.%, indicative of enhanced ET efficiency from Tb<sup>3+</sup> to Eu<sup>3+</sup>. It can be seen in figure 4(a) that the <sup>5</sup>D<sub>4</sub> decays are obviously non-exponential in TbPO<sub>4</sub>:Eu<sup>3+</sup> or pure TbPO<sub>4</sub> NCs, which is due to the competition of multiple ET processes such as energy migration among Tb<sup>3+</sup>, ET from Tb<sup>3+</sup> to neighboring defects, and ET from Tb<sup>3+</sup> to Eu<sup>3+</sup>. The detailed luminescence dynamics of Tb<sup>3+</sup> in pure TbPO<sub>4</sub> NCs will be discussed in section 3.4. Here, the decays of Tb<sup>3+</sup> in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs are analyzed in terms of effective lifetime ( $\tau_{eff}$ ) by [27]

$$\tau_{\rm eff} = \frac{\int_0^\infty I(t) \,\mathrm{d}t}{I_0} \tag{1}$$

where I(t) is the luminescence intensity at time t; and  $I_0$  is the intensity at the initial time. The Tb<sup>3+</sup>-to-Eu<sup>3+</sup> ET efficiency is defined as the ratio of Tb<sup>3+</sup> ions that depopulate by ET to Eu<sup>3+</sup> ions over the total number of Tb<sup>3+</sup> ions excited. Divided by the integrated intensity of the Tb<sup>3+</sup> decay in pure TbPO<sub>4</sub> NCs, the Tb<sup>3+</sup> to Eu<sup>3+</sup> ET efficiency  $\eta_{\text{ET}}$  for TbPO<sub>4</sub>:Eu<sup>3+</sup> (x at.%) NCs



**Figure 4.** (a) PL decays from  ${}^{5}D_{4}$  (543 nm) of Tb<sup>3+</sup> in TbPO<sub>4</sub>:Eu<sup>3+</sup> (*x* at.%, x = 0-5) NCs and the inset shows the PL decays from  ${}^{5}D_{0}$  (614 nm) of Eu<sup>3+</sup>. (b) The determined effective lifetime from  ${}^{5}D_{4}$  of Tb<sup>3+</sup> and Tb<sup>3+</sup>-to-Eu<sup>3+</sup> ET efficiency as a function of the Eu<sup>3+</sup> concentration in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs at RT.

can be approximately estimated by [28]

$$\eta_{\rm ET} = 1 - \frac{\int I_{x\%{\rm Eu}} \, dt}{\int I_{0\%{\rm Eu}} \, dt} = 1 - \frac{\tau}{\tau_0} \tag{2}$$

where  $I_{x\%Eu}$  is the luminescence intensity of Tb<sup>3+</sup> for the sample with the Eu<sup>3+</sup> concentration of x%;  $\tau$  and  $\tau_0$  are the corresponding effective PL lifetimes of Tb3+ ions in TbPO<sub>4</sub>:Eu<sup>3+</sup> and pure TbPO<sub>4</sub> NCs, respectively. The effective lifetime from <sup>5</sup>D<sub>4</sub> of Tb<sup>3+</sup> and Tb<sup>3+</sup>-to-Eu<sup>3+</sup> ET efficiency as a function of the Eu<sup>3+</sup> concentration were calculated and depicted in figure 4(b). The ET efficiency increases rapidly with increasing the  $Eu^{3+}$  concentration from 0 to 1 at.%, which is in accordance with the enhanced red emissions of Eu<sup>3+</sup> observed in the emission spectra. The Tb<sup>3+</sup>-to-Eu<sup>3+</sup> ET efficiency reaches up to 94% in TbPO<sub>4</sub>:Eu<sup>3+</sup> (5 at.%) NCs. The decay curves for  ${}^5D_0 \rightarrow {}^7F_2$  (614 nm) of Eu $^{3+}$  remain essentially unchanged for the dopant concentration of 0.2-5 at.% in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs, showing clearly the absence of concentration quenching for Eu<sup>3+</sup> with a concentration up to 5 at.% (inset of figure 4(a)). The effective PL lifetime for  ${}^{5}D_{0}$  of Eu<sup>3+</sup> is determined to be 1.3 ms at RT in TbPO<sub>4</sub>:Eu<sup>3+</sup> (5 at.%) NCs, which is about one order of magnitude larger than that for  ${}^{5}D_{4}$  of Tb<sup>3+</sup> in pure TbPO<sub>4</sub> NCs (0.12 ms).

## 3.4. Luminescence sites of $Eu^{3+}$

According to the crystal structure belonging to a space group of  $P3_121$ , Tb<sup>3+</sup> ions are very likely to occupy a lattice site with the highest point-group symmetry of C<sub>2</sub> in hexagonal TbPO<sub>4</sub>, although the precise atomic positions in hexagonal REPO<sub>4</sub> have not been reported yet [21]. The 10 K emission spectra for the  ${}^{5}D_{4} \rightarrow {}^{7}F_{3,4,5,6}$  transitions of  $Tb^{3+}$  in pure  $TbPO_{4}$ NCs and bulk counterparts were measured upon excitation at 265 nm (figure S4a available at stacks.iop.org/Nano/22/ 275701/mmedia). The emission lines are nearly the same in terms of shapes and positions for both samples, suggesting that these emissions lines were originated from the same luminescence site of  $Tb^{3+}$  in hexagonal  $TbPO_4$ . Due to the better crystalline surroundings around Tb<sup>3+</sup>, sharper and wellresolved emission lines were observed in bulk counterparts as compared to that in NCs. Because of the crystal anisotropy, multiple sites are expected for Eu<sup>3+</sup> incorporated in REPO<sub>4</sub> NCs [29, 30]. As shown in curve 1 of figure 5(a), five emission lines peaked at 588.4, 589.8, 591.3, 592.6 and 596.5 nm were observed for the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition of Eu<sup>3+</sup> in TbPO<sub>4</sub>:Eu<sup>3+</sup> (0.2 at.%) NCs upon excitation at 316 nm at 10 K, indicating at least two kinds of luminescence site for Eu<sup>3+</sup> ions in TbPO<sub>4</sub> NCs, because the  ${}^5D_0 \rightarrow {}^7F_1$  transition of Eu $^{3+}$  can only exhibit up to three peaks even at C1 site symmetry. The five line positions are the same as that in TbPO<sub>4</sub>:Eu<sup>3+</sup> (5 at.%) NCs at 10 K or RT (curves 2 and 3 of figure 5(a)). However, the emission lines peaked at 588.4, 589.8 and 591.3 nm (referred to as site I of  $Eu^{3+}$ ) shifted to the red about 15 cm<sup>-1</sup> in TbPO<sub>4</sub> NCs in comparison with that in bulk counterparts (curve 4 of figure 5(a)). Much larger redshifts of these three emission lines (site I) were observed compared to those in TbPO<sub>4</sub>:Eu<sup>3+</sup> nanoparticles with a size of  $\sim 100$  nm [12], suggesting that the local symmetry of  $Eu^{3+}$  at site I varies with the morphology of TbPO<sub>4</sub> NCs. In contrast, the positions for peaks at 592.6 and 596.5 nm (referred to as site II) are not influenced by the sample morphology, which remains unchanged among TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs, bulk counterparts and the sample used in [12]. Note that an additional emission line at 599.5 nm appeared in bulk counterparts and samples in [12] due possibly to better crystalline surroundings, which can be assigned to site II of  $Eu^{3+}$ . As shown in figure 5(a) (curves 1 and 2), compared to  $Eu^{3+}$  at site I, an increase of the relative emission intensity was observed for Eu<sup>3+</sup> at site II in TbPO<sub>4</sub>:Eu<sup>3+</sup> (5 at.%) NCs, which suggests that more Eu<sup>3+</sup> ions occupy the luminescence site II in the high doping sample. Thus, two luminescence sites of Eu<sup>3+</sup>, with three emission lines in the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition for each site, were found in hexagonal TbPO<sub>4</sub>. Moreover, the  $^5D_0 \rightarrow \ ^7F_0$  transition of Eu^{3+}, which is only allowed in the 10 site symmetries of  $C_s$ ,  $C_1$ ,  $C_2$ ,  $C_3$ ,  $C_4$ ,  $C_6$ ,  $C_{2v}$ ,  $C_{3v}$ ,  $C_{4v}$  and  $C_{6v}$  [31], was observed at 579.5 nm in the emission spectra of either TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs or their bulk counterparts. Based on the appearance of  ${}^{5}D_{0} \rightarrow {}^{7}F_{0}$  and three peaks in the  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition, we infer that one of the Eu<sup>3+</sup> sites has low site symmetries of  $C_1$ ,  $C_2$  or  $C_s$  in TbPO<sub>4</sub>. This observation is inconsistent with the crystallographic site symmetry ( $C_2$  or  $C_1$ ) of Tb<sup>3+</sup> in the aforementioned hexagonal TbPO<sub>4</sub>. The observation of two luminescence sites may be due to different



**Figure 5.** (a) Emission spectra for (1) TbPO<sub>4</sub>:Eu<sup>3+</sup> (0.2 at.%) NCs at 10 K ( $\lambda_{ex} = 316$  nm), (2) TbPO<sub>4</sub>:Eu<sup>3+</sup> (5 at.%) NCs at 10 K ( $\lambda_{ex} = 316$  nm), (3) TbPO<sub>4</sub>:Eu<sup>3+</sup> (5 at.%) NCs ( $\lambda_{ex} = 316$  nm) at RT and (4) bulk counterparts ( $\lambda_{ex} = 265$  nm) at RT. (b) PL decays from <sup>5</sup>D<sub>0</sub> (614 nm) of Eu<sup>3+</sup> in TbPO<sub>4</sub>:Eu<sup>3+</sup> (0.2 at.%) NCs at 10 K and RT ( $\lambda_{ex} = 316$  nm), respectively. The corresponding lines are multiple-exponential fitting results.

crystal fields experienced by  $Eu^{3+}$  at near-surface and inner lattice sites of TbPO<sub>4</sub>: $Eu^{3+}$  NCs.

As shown in figure 5(b), PL decays for the  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition of Eu<sup>3+</sup> in TbPO<sub>4</sub> NCs deviate significantly from the exponential function upon excitation to the interface state at 10 K or RT, which may involve the decays of Eu<sup>3+</sup> at both sites I and II due to the overlap in their emission spectra. By fitting with biexponential functions, the PL lifetimes for  ${}^{5}D_{0}$  of  $Eu^{3+}$  in TbPO<sub>4</sub> NCs were determined to be 2.81 (87.3%), 1.12 ms (12.7%) and 2.78 (52.5%), 0.87 (47.5%) ms at 10 K and RT, respectively. It seems that the long lifetime decay is insensitive to temperature, whereas the short lifetime components at RT is smaller than at 10 K. The rise time of 0.23 and 0.14 ms can be derived for the Eu<sup>3+</sup> decay at 10 K and RT, respectively, by fitting the initial stage in the decay curve. Since no emission from upper levels such as  ${}^{5}D_{1,2}$  of Eu<sup>3+</sup> was observed at 10 K and RT, the appearance of such a rise time may imply relatively slow nonradiative ET from  ${}^{5}D_{4}$  of  $Tb^{3+}$  to  ${}^{5}D_{1,2}$  of  $Eu^{3+}$ , followed by fast nonradiative relaxation to  ${}^{5}D_{0}$  of Eu $^{3+}$ .

# 3.5. Luminescence dynamics of $Tb^{3+}$ in $TbPO_4$

The decay behaviors of Tb<sup>3+</sup> ions in the concentrated systems such as TbPO<sub>4</sub> are mainly influenced by two categories of ET processes: energy migration among Tb<sup>3+</sup> ions and ET from  $Tb^{3+}$  to the near-trapping defects [32, 33]. As shown in figure S4b, upon excitation at 265 nm, a much faster PL decay for  ${}^{5}D_{4}$  of Tb<sup>3+</sup> was observed at 300 K than at 10 K in TbPO<sub>4</sub> bulk counterparts, revealing that the energies in the <sup>5</sup>D<sub>4</sub> state might be quenched by the near-trapping states such as defects. Furthermore, the decay curves show single-exponential characteristics at 10 or 300 K, rather than the predicted non-exponential forms for the typical donoracceptor ET process [34], verifying that energy migration among  $Tb^{3+}$  ions cannot be neglected in  $TbPO_4$  samples. According to the hopping model [32], a much more rapid energy migration exists among the Tb<sup>3+</sup> ions as compared to ET from Tb<sup>3+</sup> to defects, thus making all Tb<sup>3+</sup> sites equivalent for the decays in TbPO<sub>4</sub> bulk counterparts. By fitting with a single-exponential function, the PL lifetime for  ${}^{5}D_{4}$  of Tb<sup>3+</sup> in TbPO<sub>4</sub> bulk counterparts was determined to be 1.31 and 0.98 ms at 10 K and RT, respectively. Different from their bulk counterparts, the decay curves for <sup>5</sup>D<sub>4</sub> of Tb<sup>3+</sup> in TbPO<sub>4</sub> NCs deviated from the single exponential upon excitation at 316 nm at 10-300 K (figure 6(a)), indicating that ET from  $Tb^{3+}$  to defects is faster than or at least comparable to the energy migration among Tb<sup>3+</sup>, and thus all Tb<sup>3+</sup> ions will no longer be equivalent in TbPO4 NCs. Such a phenomenon is understandable as more defects often exist in nanoparticles than in bulk. For this case, the diffusion-limited energy migration model is valid [33]:

$$I(t) = I_0 \exp\left(-\frac{t}{\tau_0}\right) \exp\left\{-\frac{4}{3}\pi^{3/2} N_a(Ct)^{1/2} \\ \times \left(\frac{1+10.87x+15.50x^2}{1+8.743x}\right)^{3/4}\right\}$$
(3)

where  $\tau_0$  is the radiative decay time of donors,  $N_a$  is the number of acceptors, C is the interaction parameter for donor-acceptor interaction,  $x = DC^{-1/3}t^{2/3}$  and D is the diffusion constant for ET among  $Tb^{3+}$  ions. By utilizing equation (3) and fitting the decays at various temperatures, the radiative lifetime of  $Tb^{3+}$  in pure  $TbPO_4$  NCs were determined to be 1.82 ms, which is about four times that reported previously [12]. The very good agreement between the observed and the fitted decay curves at all temperatures indicates the success of the diffusionlimited energy migration model for Tb<sup>3+</sup> in pure TbPO<sub>4</sub> NCs (figure 6(a)). The temperature dependence of the donoracceptor interaction parameter C was extracted from fitting the decays of Tb<sup>3+</sup> in TbPO<sub>4</sub> NCs at 10–300 K, assuming that  $N_a = 1 \times 10^{16}$  cm<sup>-3</sup>. As shown in figure 6(b), C is very sensitive to temperature, which suggests that phononassisted nonradiative ET processes are a dominant nonradiative relaxation mechanism. The C(T) is proportional to  $T^n$  (n = $1.1 \pm 0.1$ ), indicating that the ET mechanism from Tb<sup>3+</sup> to defects may be ascribed to direct one-phonon-assisted ET processes, according to the theory of diagonal phonon-assisted ET processes systematically formulated by Holstein et al [35]. As depicted in the inset of figure 6(b), the ratio of C to



**Figure 6.** (a) PL decays from  ${}^{5}D_{4}$  (543 nm) of Tb<sup>3+</sup> in pure TbPO<sub>4</sub> NCs at 10–300 K ( $\lambda_{ex} = 316$  nm) and (b) the temperature dependence of interaction parameter *C* and (inset) *C/D* values, assuming that  $N_{a} = 1 \times 10^{16}$  cm<sup>-3</sup>.

*D* increases gradually with elevated temperature from 10 to 300 K, showing a relatively large ET rate from  $Tb^{3+}$  to defects at high temperature compared to the energy migration among  $Tb^{3+}$  ions. As a result, the PL intensity from  ${}^{5}D_{4}$  decreased and the PL decay deviated drastically from the single-exponential function at high temperature.

### 4. Conclusions

In summary, well-dispersed hexagonal TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs have been synthesized via a simple hydrothermal method assisted with OA surfactants. By varying the concentration of Eu<sup>3+</sup> in TbPO<sub>4</sub> NCs, the chromaticity coordinates can be finely tuned from green to red with Tb<sup>3+</sup> and Eu<sup>3+</sup> emissions. Efficient Tb<sup>3+</sup>-to-Eu<sup>3+</sup> ET has been demonstrated and the highest ET efficiency can reach a value of 94% in TbPO<sub>4</sub>:Eu<sup>3+</sup> NCs. Distinct from their bulk counterparts, a new interface-state band (316 nm) in addition to the commonly observed spinforbidden 4f–5d transition band (265 nm) of Tb<sup>3+</sup> was found dominant in the excitation spectrum of NCs, which is due presumably to the formation of surface TbPO<sub>4</sub>/OA complexes. Two kinds of luminescence sites of Eu<sup>3+</sup> in TbPO<sub>4</sub> NCs, with the site symmetry of C<sub>2</sub> or C<sub>1</sub>, were identified based on the emission spectra at 10 K and room temperature. Furthermore, the luminescence dynamics for  ${}^{5}D_{4}$  of Tb<sup>3+</sup> ions in TbPO<sub>4</sub> NCs has been revealed at temperatures of 10–300 K. Compared to the exponential decay in bulk counterparts induced by very fast energy migration, the non-exponential decay from  ${}^{5}D_{4}$  of Tb<sup>3+</sup> has been observed in NCs, which is mainly attributed to the diffusion-limited energy migration due to more rapid energy transfer from Tb<sup>3+</sup> to defects than the energy migration among Tb<sup>3+</sup> ions. The radiative lifetime of  ${}^{5}D_{4}$  is determined to be 1.82 ms in TbPO<sub>4</sub> NCs, which is significantly larger than that in bulk counterparts (1.31 ms). Small-size TbPO<sub>4</sub>:Ln<sup>3+</sup> NCs featuring superior optical performance and long PL lifetime are highly promising for potential applications such as time-resolved biodetection and bioimaging.

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