# Enhancing Upconversion Luminescence in Lanthanide Nanocrystals by Using Organic Ligands to Inhibit Vibrational Relaxation

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## ABSTRACT

Lanthanide nanocrystals are capable of converting lowenergy photons into high-energy photons via a multiphoton mechanism, which renders them highly promising for applications in bioimaging/detection and photodynamic therapy. However, the practical bioapplication of lanthanide upconversion nanocrystals is hindered by their low upconversion luminescence efficiency and susceptibility to temperature-induced luminescence quenching. Recent studies have demonstrated that the upconversion luminescence intensity can be significantly enhanced through the coordination of small organic molecules, such as picolinic acid (2PA), on the surface of these nanocrystals. Despite this advancement, the underlying physical mechanism of the enhancement induced by organic ligands remains elusive. In this paper, we state our viewpoints on the phenomenon of ligand-induced upconversion enhancement.

**Keywords:** Organic Ligand, Surface Coordination, Lanthanide Nanocrystals, Upconversion Luminescence

## INTRODUCTION

In 2021, Liu et al. [1]. developed a novel surface engineering strategy to enormously amplify the upconversion luminescence of lanthanide nanocrystals (NaGdF<sub>4</sub>:Yb<sup>3+</sup>/Tm<sup>3+</sup>) through the chelating effect of organic small-molecule ligand (e.g., picolinic acid). The observed enhancement was initially rationalized through molecular orbital hybridization theory. According to this hypothesis, the orbital hybridization between coordination-unsaturated surface lanthanide ion and organic ligand eliminates the energy-level mismatch between the  ${}^{2}F_{5/2}$  states of surface and inner Yb<sup>3+</sup> ions (4f<sup>13</sup> configuration), thereby facilitating the resonance energy transfer between surface and inner Yb<sup>3+</sup> ions. Consequently, the multi-photon upconversion process of Yb<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> is substantially enhanced

(Figure 1). However, this explanation appears inconsistent with the observed decrease in the transition probability of  ${}^{2}F_{5/2}$  level of Yb<sup>3+</sup> ions after ligand coupling on the nanocrystal surface (corresponding to the increase in the fluorescence lifetime of Yb<sup>3+</sup> ions at 980 nm).

From the crystal structure perspective, it is well accepted that the breaking translational symmetry in lanthanide fluoride nanocrystal is bound to result in the unsaturated coordination of surface lanthanide ions. Accordingly, upon the chelating of picolinic acid ligands, they will behave as pseudoatoms to support the crystal field for surface lanthanide ions. Thus, it is conceivable that the coordination ligands may affect the surface electronic structures in lanthanide nanocrystals through the perturbation of electrostatic crystal field of ligand to lanthanide inner 4f electronic configuration, or the orbital hybridization of ligand with lanthanide ion. However, in the cases absent of strong spin-orbit coupling caused by the heavy atoms of coordination anions (such as I<sup>-</sup>), the energy levels for the inner 4f electrons of surface Yb<sup>3+</sup> ions are barely affected by the surrounding crystal field due to the shielding effect of outer 5s and 5p electrons. Indeed, no observable difference can be found in the emission peak positions corresponding to Yb<sup>3+</sup> <sup>2</sup>F<sub>5/2</sub>  $\rightarrow$  <sup>2</sup>F<sub>7/2</sub> intra-4f transitions between the nanocrystals before and after surface chelating of picolinic acid ligands. Therefore, we do not expect the orbital hybridization between coordination-unsaturated surface lanthanide ion and organic ligand accounts for the anomalous phenomenon of ligand-induced upconversion enhancement.



**Figure 1.** Left: simulated single-particle 4f energy levels of ytterbium atoms with nine-, six- and eightfold coordination configurations, respectively. 4<sub>femp</sub> and 4<sub>focc</sub> represent the lowest empty and highest occupied 4f orbitals of the ytterbium atom, respectively; ΔE is the energy difference between the 4<sub>femp</sub>-4<sub>focc</sub> gaps of the surface and inner ytterbium atoms. Right: spatial distribution of the partial charge densities of coupling states formed by coordination between Yb<sup>3+</sup> ion and picolinic acid ligand. Cyan, purple, grey, white, red and blue balls denote Yb, F, C, H, O and N atoms, respectively [1].

Recently, Wang et al. [2]. performed a combined experimental investigation and theoretical calculation to confirm that the picolinic acid bidentate ligand coupled to the surface Yb<sup>3+</sup> ion of lanthanide nanocrystal can effectively shield the nanocrystal from high-frequency vibration of water molecule. This prevents the vibration-induced non-radiative relaxation process of the  ${}^{2}F_{5/2}$  excited state of Yb<sup>3+</sup> ions, resulting in the enhancement of upconversion luminescence (Figure 2a). Specifically, upon 980-nm laser excitation, the Tm<sup>3+</sup> ion ultraviolet upconversion luminescence (corresponding to the  ${}^{1}D_{2} \rightarrow {}^{3}H_{6}$  transition) was enhanced by approximately 2100 times in the NaGdF<sub>4</sub>:Yb<sup>3+</sup>/

Tm<sup>3+</sup> upconversion nanocrystals (dispersed in ethanol) capped with picolinic acid ligand as compared to nanocrystals without surface ligand (Figure 2b). It is reasonable to infer that the inhibition of vibrational relaxation of Yb<sup>3+</sup> <sup>2</sup>F<sub>5/2</sub> state leads to a decrease in its transition probability, which complies with the experimental observation of an increase in its fluorescence lifetime (Figure 2c). In fact, the inhibition of vibrational relaxation of vibrational relaxation of a be well explained theoretically. The vibrational relaxation rate KVR of the <sup>2</sup>F<sub>5/2</sub> excited state of Yb<sup>3+</sup> ions are assumed to be [3]:

$$K_{\rm VR} = \frac{2\pi}{\hbar} \rho_{\rm NR} \left| \sum_{ja} \frac{\hbar^2}{M_a} \langle \chi_{en}(R) \frac{E_{ja}(R)}{\Delta E(R)} \frac{\partial}{\partial R_j^a} \chi_{e'0}(R) \rangle \right|^2$$
$$E_{ja}(R) = \langle \Phi_e \left| \frac{\partial}{\partial R_j^a} V(r, R) \right| \Phi_{e'} \rangle = \langle \Phi_e \left| Z_a e^2 \sum_{e1} \frac{\left(r_j^{e1} - R_j^a\right)}{r_{e1,a}^3} \right| \Phi_{e'} \rangle$$

Where j refers to x, y, or z,  $\rho_{NR}$  is a density of final state vibrational levels,  $Z_a$  is the nuclear charge of atom a,  $M_a$  is the mass of atom a, V(r, R) describes the interaction between electrons and nuclei,  $\chi_{e'0}(R)$  and  $\chi_{en}(R)$  are vibrational eigenfunctions of initial and final states,  $\Delta E(R)$  is the energy difference between the initial and the final states,  $\Phi_{e'}$  and  $\Phi_e$  are the electronic wave functions of initial and the final states. Apparently, the K<sub>VR</sub> decreases inversely with the sixth power of distance between Yb<sup>3+</sup> ion and water molecule, and scales positively with the gradient of vibrational eigenfunction  $\chi_{e'0}(R)$  (i.e.,  $\frac{\partial}{\partial R_i^3} \chi_{e'0}(R)$ ). It is

noteworthy that the gradient of  $\chi_{e'o}(R)$  denotes the reciprocal of rigidity of picolinic acid that chelate with surface  $Yb^{3+}$  ion. Therefore, upon the surface chelating of picolinic acid ligand, the steric hindrance of ligand enlarges the effective distance between  $Yb^{3+}$  ion and water molecule, and meanwhile the rigid five-membered ring structure formed by the coordination of lanthanide ion with picolinic acid suppresses the phonon interactions between picolinic acid and water molecule, both of which results in the inhibition of vibrational relaxation of  $Yb^{3+}$  ions induced by the high-frequency phonon modes of water molecule.

Additionally, they discovered that the lanthanide upconversion nanocrystals capped with picolinic acid ligands exhibited significant upconversion enhancement even at high temperatures (Figure 2d). Notably, during the continuous heating from 303 to 443 K, the humidity impacted the upconversion enhancement because the water coordination under a higher humidity condition reduced the vibrational relaxation inhibition capability of picolinic acid ligand, and intriguingly, the nanocrystals capped with picolinic acid ligands rapidly reached peak luminescence intensity upon laser excitation and maintained stability for the subsequent 5 hours, demonstrating excellent thermal stability (Figures 2de). This is because the five-membered ring chelate structure formed by the coordination of surface lanthanide ion with picolinic acid inhibits the non-radiative dissipation process of excitation energy induced by the thermal field. Nevertheless, if the temperature further exceeds 443 K, the risk of dechelating and even carbonization of picolinic acid ligand will increase sharply.

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Despite these advances, two fundamental questions persist: first, the precise phononic structure of surface lanthanidepicolinic acid chelates and their interaction mechanisms with solvent vibrational modes remain unresolved; second, the design principles for next-generation ligands (such as ligands with larger coordination number and higher chelation strength, more rigidity, and more hydrophobic groups) surpassing picolinic acid's performance in aqueous environments require systematic exploration. Addressing these challenges is paramount for overcoming the intrinsic quantum yield limitations of rare-earth upconversion systems, particularly for advancing their biomedical applications in high-sensitivity bioimaging [4-7], real-time biosensing [8-9], and precise photodynamic therapy.



**Figure 2.** (a) Schematic illustration of upconversion enhancement by an organic surface layer. Left: small nanocrystals typically feature low efficiency due to severe surface quenching through defects (e.g., vacancies) and high-energy oscillators (i.e., -OH). Right: after picolinic acid (2PA) coordination, the organic surface layer can passivate defects and isolates high-energy oscillations, giving rise to high brightness over a wide temperature range [2]. (b) Peak intensities of  $Tm^{3+}$  emissions at different wavelengths and overall integrated intensity for ligand-free, oleic acid (OA)-coated and 2PA-capped NaGdF<sub>4</sub>:Yb<sup>3+</sup>/Tm<sup>3+</sup> (49/1%) colloidal nanocrystals. (c) Luminescence decay curves of Yb<sup>3+</sup>:  $^{2}F_{5/2} \rightarrow ^{2}F_{7/2}$  transition from untreated and solution-annealed NaGdF<sub>4</sub>:Yb<sup>3+</sup>/Tm<sup>3+</sup> (49/1%) nanocrystals after 2PA modification measured in ambient air. (d) Normalized integral intensity of overall emissions (300-900 nm) at 443 K against the 980 nm laser irradiation time in ligand-free and 2PA-capped NaGdF<sub>4</sub>:Yb<sup>3+</sup>/Tm<sup>3+</sup> (49/1%) nanocrystals under different relative humidity conditions. Note that the heating process from 303 to 443 K took around 40 min. (e) Luminescence decay curves of Yb<sup>3+</sup>:  $^{2}F_{5/2}$  Cambria  $^{2}F_{7/2}$  transition in ligand-free (top panel) and 2PA-capped nanocrystals (bottom panel) as a function of temperature measured in dry argon [2]. Among these, UCNP denotes NaGdF<sub>4</sub>:Yb<sup>3+</sup>/Tm<sup>3+</sup> (49/1%) nanocrystals, UCNP@OA, UCNP@2PA and UCNP-Y represent OA-coated, 2PA-capped and solution-annealed NaGdF<sub>4</sub>:Yb<sup>3+</sup>/Tm<sup>3+</sup> (49/1%) colloidal nanocrystals, respectively.

#### **AUTHOR CONTRIBUTIONS**

**Ni Zhang:** Writing-original draft, Methodology, Validation, Investigation, Formal analysis. **Guoqin Ma:** Methodology, Formal analysis. **Jin Xu:** Funding acquisition, Writing-review & editing, Supervision, Conceptualization.

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#### NOTES

Any additional relevant notes should be placed here.

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