

Efficient two-photon sensitized luminescence of europium (III) complex based on hypersensitive transitions

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Received November 9, 2010; accepted December 7, 2010; posted online April 11, 2011

Red frequency-upconversion fluorescence emission is observed in europium(III) complex with encapsulating polybenzimidazole tripod ligands, pumped with 930- and 1070-nm picosecond laser pulses. The luminescence of transition ${}^5D_0 \rightarrow {}^7F_2$ (612 nm) is induced by two-photon absorption of hypersensitive transitions ${}^7F_0 \rightarrow {}^5D_2$ (465 nm) and ${}^7F_1 \rightarrow {}^5D_1$ (535 nm). Analysis results suggest that the two-photon excitation strength of these hypersensitive transitions is increased dramatically owing to the C_3 symmetry of the coordination field.

OCIS codes: 190.4710, 000.2190, 260.1560, 350.5130.

doi: 10.3788/COL201109.051901.

Lanthanide ions and their coordination complexes have inspired vigorous research activities owing to their unique optical properties, such as high color purity and long lifetimes^[1], giving rise to many potential applications, including biological imaging^[2] and electroluminescent devices. Given that the coordination chemistry of europium(III) shows similarity to that of Ca^{2+} and Fe^{3+} , europium(III) ion is the most commonly used lanthanide ion as luminescent probe in biomolecular systems. Recently, with a combination of the advantages of both lanthanide ions and two-photon scanning microscopy, two-photon sensitized luminescence of lanthanide complexes attracts great attention, which is in favor of less-harmful labeling and deep-penetrating bioimaging applications^[3]. In this new and challenging field, the most popular sensitization mechanism is the “antenna effect”^[4], i.e., two-photon absorption (TPA) of organic ligands and energy transfer to lanthanide ion. However, it is an indirect mode concerning both the synthesis of ligand with large TPA cross section and the energy transfer efficiency from ligand to lanthanide ion. So far, only a few lanthanide complexes have been synthesized to meet the needs^[5].

Although the f-f transitions are allowed with two photons^[6], direct TPA of Eu^{3+} transitions could not efficiently sensitize ${}^5D_0 \rightarrow {}^7F_2$ (612 nm), which is most desirable when the excitation wavelength is shorter than 820 nm. The problem that now requires further research refers to how we can conveniently obtain lanthanide luminescence induced by efficient TPA. “Hypersensitive transition” is a unique property for lanthanide ions^[7,8]. As far as europium(III) ion is concerned, hypersensitive transitions ${}^7F_0 \rightarrow {}^5D_2$ (465 nm) and ${}^7F_1 \rightarrow {}^5D_1$ (535 nm) can efficiently sensitize ${}^5D_0 \rightarrow {}^7F_2$ (612 nm) in Eu^{3+} -doped inorganic crystals^[9]. However, the investigations of sensitization mechanism based on the hypersensitive

transitions in organic coordination environments remain rather rare.

In this letter, we report a novel europium(III) coordination complex $[Eu(L_1)(Antipy)_3(ClO_4)_3]$ consisting of tris(benzimidazol-2-ylmethyl)amine ligand L_1 , secondary ligand Antipy and anion ClO_4^- (Fig. 1). In this 7-coordination europium(III) complex with C_3 symmetry, the hypersensitive transitions ${}^7F_0 \rightarrow {}^5D_2$ and ${}^7F_1 \rightarrow {}^5D_1$ are distinguished. Based on the TPA of ${}^7F_0 \rightarrow {}^5D_2$ and ${}^7F_1 \rightarrow {}^5D_1$ transitions, the bright red emission from ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} is observed. Furthermore, the two-photon excitation strength of hypersensitive transitions ${}^7F_0 \rightarrow {}^5D_2$ and ${}^7F_1 \rightarrow {}^5D_1$ is two orders of magnitude stronger than that of electric dipole transitions.

Figure 1 shows the molecular structure of ligands in $Eu(L_1)(Antipy)_3(ClO_4)_3$ and $Eu(L_2)_2(ClO_4)_3$. In complex $Eu(L_1)(Antipy)_3(ClO_4)_3$, the secondary Antipy ligand is involved in coordination with three O atoms from three different Antipy coordinated directly to the Eu^{3+} ion ($d_{Eu-O} = 0.2208(3)–0.2209(4)$ nm) apart from four N atoms from the ligand

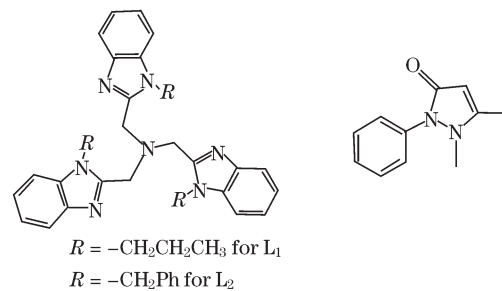


Fig. 1. Molecular structure of ligands L_1 , L_2 (left) and Antipy (right).

L_1 ($d_{\text{Eu-N}} = 0.2456(3) - 0.2766(6)$ nm). The ClO_4^- counter anions exist in the crystal lattices to balance the charge. For the purpose of studying the influence of symmetry on hypersensitive transitions, another set of europium complexes $\text{Eu}(\text{L}_2)_2(\text{ClO}_4)_3$ are synthesized with pseudo- O_h symmetry.

The ultraviolet-visible (UV-Vis) absorption spectra were recorded using a UV-Vis-NIR (NIR: near infrared) scanning spectrophotometer (Shimadzu, model UV-3101PC). The fluorescent spectra were measured by a fluorescence spectrophotometer (Hitachi, model F-4500).

For the measurement of transient behavior, a Nd:YAG picosecond pulsed laser with a repetition rate of 10 Hz was used as the excitation source, its pulse duration was 40 ps (Fig. 2). The excitation wavelength was tunable from 760 to 1090 nm. An optical multi-channel analyzer was used as the recorder. The ultrafast laser beam passed first through a couple of Nicol prisms that were used as an attenuator to obtain a tunable excitation intensity. The laser beam was focused into the sample by a lens of focal length $f = 5$ cm. The fluorescence was collected by a telescope system at the perpendicular direction of the pump beam. An HA30 filter was inserted before the input slit of optical multi-channel analyzer for cutting off the excitation laser.

The fluorescence spectra of $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ and $\text{Eu}(\text{L}_2)_2(\text{ClO}_4)_3$ were recorded in solid state at room temperature. Figure 3 shows the excitation spectra of $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ and $\text{Eu}(\text{L}_2)_2(\text{ClO}_4)_3$ under the same experimental conditions by monitoring the emission $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Eu^{3+} . In the excitation spectra, the broad excitation bands are assigned to the ligand-centered electronic transitions. In the longer wavelength region of $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ spectrum, direct metal-based f-f transitions are sharp and evident, showing the respective peaks at 465 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_2$), 526 nm ($^7\text{F}_0 \rightarrow ^5\text{D}_1$), and 535 nm ($^7\text{F}_1 \rightarrow ^5\text{D}_1$). Among these transitions, transition strength of $^7\text{F}_0 \rightarrow ^5\text{D}_2$ is the strongest. The $^7\text{F}_0 \rightarrow ^5\text{D}_2$ and $^7\text{F}_1 \rightarrow ^5\text{D}_1$ transitions are considered as the so-called “hypersensitive transitions” with sensitive responses to surrounding environment. However, in comparison, these hypersensitive transitions are too weak to be observed in the excitation spectrum of $\text{Eu}(\text{L}_2)_2(\text{ClO}_4)_3$.

The reason why $^7\text{F}_0 \rightarrow ^5\text{D}_2$ and $^7\text{F}_1 \rightarrow ^5\text{D}_1$ transitions are distinguished in complex $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ but negligible in $\text{Eu}(\text{L}_2)_2(\text{ClO}_4)_3$ is that the intensity of hypersensitive transition depends largely on the

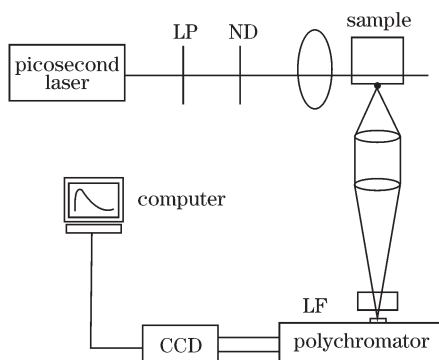


Fig. 2. Schematic diagram of experiment setup. LP: long-pass filter; ND: neutral density; LF: CuSO_4 liquid filter.

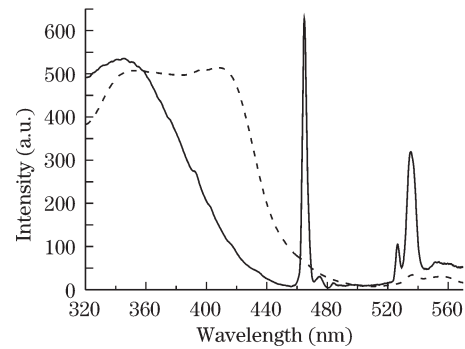


Fig. 3. Excitation spectra of $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ (solid line) and $\text{Eu}(\text{L}_2)_2(\text{ClO}_4)_3$ (dashed line) monitoring the emission $^5\text{D}_1 \rightarrow ^7\text{F}_2$ of Eu^{3+} .

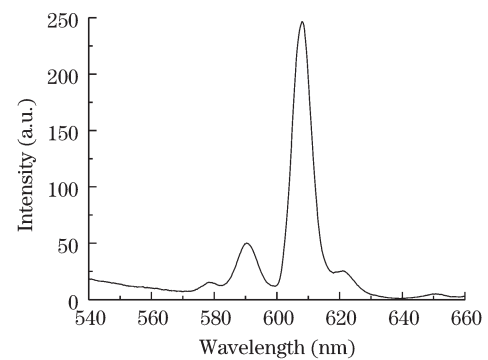


Fig. 4. Emission spectrum of $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ at an excitation wavelength of 465 nm.

environment of lanthanide ion. These transitions are described by the term “pseudo-quadrupole transitions” because they obey the selection rule $|\Delta J| \leq 2$, $|\Delta L| \leq 2$, $|\Delta S| = 0$ ^[10]. Observation of these peaks clearly indicates that Eu^{3+} is in a low symmetry site. The hypersensitive transitions are evidently influenced by Judd-Ofelt intensity parameter Ω_2 , which is determined by the asymmetry of the coordination environment of the lanthanide ion. For $\text{Eu}(\text{L}_2)_2(\text{ClO}_4)_3$, eight N atoms from the ligand L_2 occupy the corners of the slightly distorted cube. In $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$, three O atoms from three different Antipy and four N atoms from the ligand L_1 coordinate directly to the Eu^{3+} ion, the coordination polyhedron can be assigned as a cube short of one corner, $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ has an exact C_3 symmetry imposed by crystallography. Compared with $\text{Eu}(\text{L}_2)_2(\text{ClO}_4)_3$, the increase of the asymmetry leads to the distinguished hypersensitive transitions in $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$.

In the fluorescent emission spectrum of $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ (excitation wavelength $\lambda_{\text{ex}} = 465$ nm), the distinct emission peak of 611 nm corresponds to the transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ of Eu^{3+} (Fig. 4). The relative intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ is more intense than that of $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (590 nm), showing that the Eu^{3+} ion does not lie in a centrosymmetric coordination site. In general, when the Eu^{3+} ion is positioned in a higher-symmetry environment containing inversion center, the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition is predominant; on the other hand, in a lower-symmetry environment without the inversion center, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition becomes stronger. Furthermore, it can be shown from the excitation spectrum

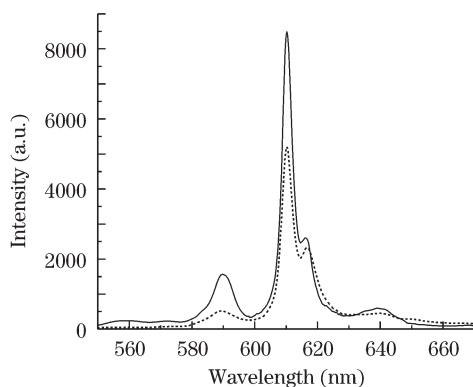


Fig. 5. Fluorescence of $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ at 930-nm (solid line) and 1070-nm (dashed line) ultrashort pulse excitation.

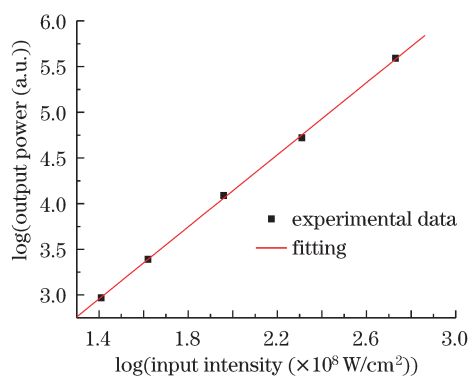


Fig. 6. Fluorescent intensity as a function of the excitation density at 930 nm. The fitting slope is 1.98.

and emission spectrum of $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ that the hypersensitive transitions ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ and ${}^7\text{F}_1 \rightarrow {}^5\text{D}_1$ have high sensitization ability to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$.

Figure 5 shows the emission spectra of $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ irradiated by focused ultrafast laser at 930 and 1070 nm. Strong red light emission is observed clearly by the naked eye on the focused spot when focusing the ultrafast laser on the sample. Figure 6 shows the relationship between fluorescence intensity and excitation density. The excitation-output relationship is an exponential line with exponent of 1.98, which indicates that the up-converted fluorescence is induced by

a three-order nonlinear optical process, i.e., a TPA process. The emission spectrum of $\text{Eu}(\text{L}_1)(\text{Antipy})_3(\text{ClO}_4)_3$ excited by picosecond laser at 1070 nm is similar to that by 930-nm excitation. In the two-photon induced up-conversion spectrum, the emission of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ is more intense than that of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, which is identical to the one-photon emission spectrum. Although 930 and 1070 nm correspond to the wavelength doubling of 465 and 535 nm, respectively, it cannot be concluded that the unconverted emission originates from the TPA of ${}^7\text{F}_0 \rightarrow {}^5\text{D}_2$ and ${}^7\text{F}_1 \rightarrow {}^5\text{D}_1$.

In conclusion, a new kind of europium-organic complex is synthesized. The oscillation strength of hypersensitive transitions depends on the coordination field of europium(III) remarkably, from which very efficient luminescence induced by TPA of hypersensitive transitions is obtained.

This work was supported by the National Natural Science Foundation of China (No. 20903120), the Project of Shandong Provincial Higher Educational Science and Technology Program (No. J10LA10), and the Doctoral Research Foundation of Qufu Normal University.

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