

Molecular Switching in the Near Infrared (NIR) to Visible/NIR f-f emission with a Functional-Lanthanide Complexes

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Abstract We report the first observation of three photon induced NIR emission (890–1,400 nm) with NIR excitation (800 nm) from a newly synthesized organic neodymium complex with known molecular structure, suggests the potential use of lanthanide probes for use in three-dimensional imaging and further the study of multi-photon induced emission process in organic-lanthanide complexes.

Keywords Multi-photon absorption · Lanthanide · Terbium · Europium · Neodymium

In recent years, the near infrared (NIR) to visible (VIS) emission by organic compounds and lanthanide complexes have been investigated extensively, due to the possibility of all-solid-state up-conversion lasers operating in VIS spectral domains and the potential applications in areas such as color display, optical data storage, optoelectronics, medical diagnostics, sensor and undersea optical communication [1]. In this process, simultaneous absorption of successive low-energy photons in a single event, through virtual states combine to create a high energy luminescent excitation. So far several multi-photon absorption mechanisms have been established. The potential applications of multi-photon absorption processes shows promise in the photonics and biomedical field and have recently stimulated the scientific community to characterize new molecules with high multi-photon absorption [2–4].

Since then, only a limited class of lanthanide compounds with various organic ligands has been known to have multi-photon induced f-f emission behaviour [5–7], especially with known molecular structures [10]. These complexes act as an antennae for accumulation of energy of more than one longer wavelength radiation and, by energy transfer (singlet/singlet, $S_1 \rightarrow {}^5D_J$ -Tb/Eu; singlet/triplet, $S_1 \rightarrow T_1 \rightarrow {}^5D_J$ -Tb/Eu) from the light-absorbing ligand to the lanthanide emitter to give shorter wavelength emission [5–9].

Near-infrared (NIR) excitation and emission (~700–900 nm) is a prime target of importance because NIR photons will not be absorbed by the cell, even in the blood media, as NIR photons can penetrate deep and thus can be emitted from tissues without causing damage whilst the sharp emission gives clear imaging which is definable from the usual biological auto-fluorescence background [10]. Herein we report, a new type of lanthanide complexes (Ln=Eu, Nd and Tb) which are synthesized with the benzene-

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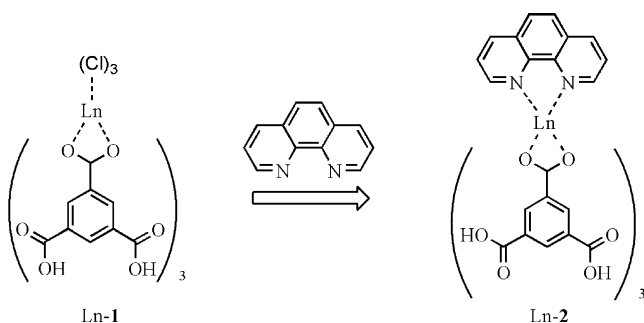


Fig. 1 The synthetic route and molecular structures of lanthanide complexes Ln-1 and Ln-2 (Ln=Eu, Nd and Tb)

1,3,5-tri-carboxylic acid (BTC) and 1,10-phenanthroline (Phen; Fig. 1). The multi-photon induced f-f emission here occurs at the excitation of 800 nm after the binding of the 1,10-phenanthroline to the Ln metal center of [Ln (BTC) Cl₃] (Ln-1).

Single crystals of Ln-2 (Ln: Eu, Nd and Tb) has been isolated through a solution of Ln-2 in DMF at room temperature over a few days. The crystal structure of Ln-2 was determined by X-ray crystallography and is shown in Figs. 2 and 3. Ln-2 crystallizes in an orthorhombic space group, Pbc_a, it features a two-dimensional coordination network, that consists of an asymmetric unit of [Ln (BTC) (Phen)(DMF)]_n, in which the Ln metal centre is nine-coordinated with six O atoms from three bidentate

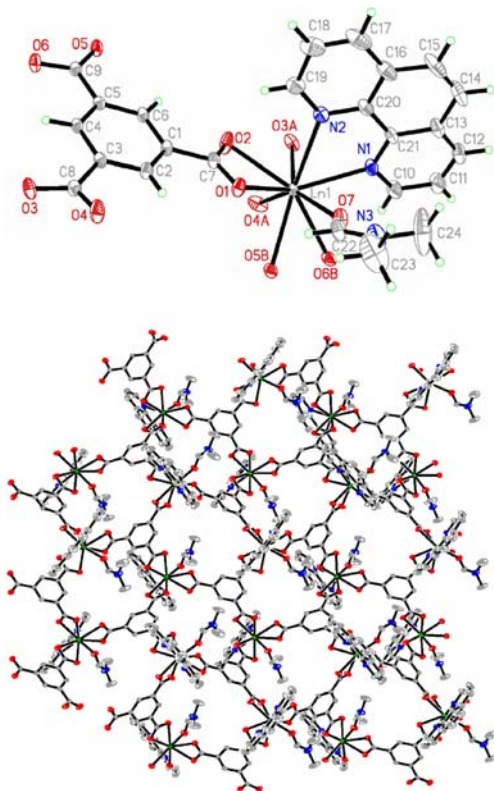


Fig. 2 (Upper) The ORTEP drawings and (Lower) 2-D layer extends on ab plane (viewed down the *c* axis) of Ln-2. (Ln=Eu, Nd and Tb)

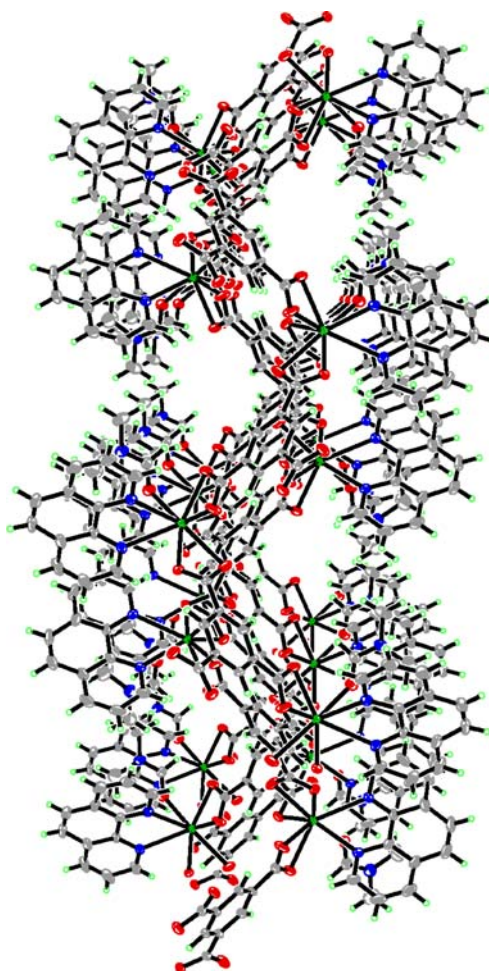


Fig. 3 The packing diagram of Ln-2 which viewed down a axis, with the antennae (1,10-phenanthroline) on a side (Ln=Eu, Nd and Tb)

carboxylate groups of three BTC ligands, and to one bidentate phenanthroline and one O atom from a DMF molecule. This forms a distorted monocapped square antiprism geometry, each Eu connecting to three BTC and each BTC ligand linked to three Eu atom, forming a two-dimensional layer.

The Ln complexes Ln-1 and Ln-2 are found to be luminescent and 1,10-phenanthroline acts as the gain medium in Ln-2 and exhibits much stronger luminescence than Ln-1 at room temperature with the ligand excitation at 355 nm (Fig. 4a) and 337 nm (Fig. 5). However, in the NIR excitation at 800 nm by Ti/Sapphire laser, only Ln-2 exhibits three-photon absorption producing the green (Tb), red (Eu) and NIR (Nd) structured emission bands that arise from the f-f transitions of the Tb: $^5D_4 \rightarrow ^7F_J$ ($J=6-3$), Eu: $^5D_0 \rightarrow ^7F_J$ ($J=6-3$) and Nd: states $^4F_3 \rightarrow ^4I_J$ ($J=13/2-9/2$) states.

A metal-centered NIR luminescence is seen in the Nd-2 powder, especially with the NIR excitation, which is very rare, (Fig. 4b NIR excitation at 800 nm) while the ligand luminescence almost disappears, with only a weak singlet

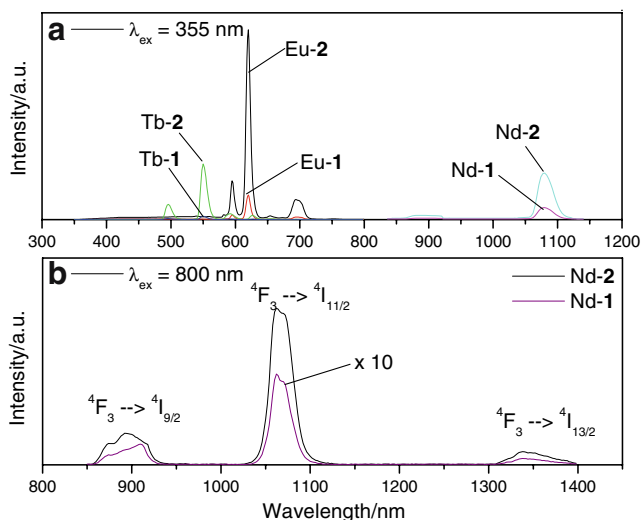


Fig. 4 **a** The enhancement of f-f emission of Ln-2 (Eu, Nd and Tb) with the addition of 1, 10-phenanthroline in Ln-1 at 355 nm and **b** NIR emission spectra of Nd-2 and Nd-1 with NIR excitation at 800 nm

emission. ($S_1 \rightarrow S_0$) At room temperature and upon broad band excitation through the ligand levels, the luminescence spectrum of the Nd-2 complex displays three bands in the spectral ranges 845–947 and 1,000–1,163 and 1,300–1,400 nm with both 355 nm and 800 nm excitation.

The absorption spectra of the Ln-2 chelates clearly demonstrate the antenna effect of the BTC and Phen with, for instance, the component at 355 nm matching the low-energy absorption band of the electronic spectra. (Fig. 6) The ligand and complexes were found to have no linear absorption in the spectral range from 400 nm to 1.00 μ m. Referring to the absorption band [11], the Ln-2 absorbs at ~ 335 nm ($29,851 \text{ cm}^{-1}$) and ~ 350 nm ($28,571 \text{ cm}^{-1}$), indicating that the Ln-2 requires the absorption of three longer wavelength photons to reach the threshold value for the energy transfer to the lanthanide ion. The power dependence experiment [12] (Fig. 7) is used in auxiliary to verify these multi-photon processes. The slopes are 2.84

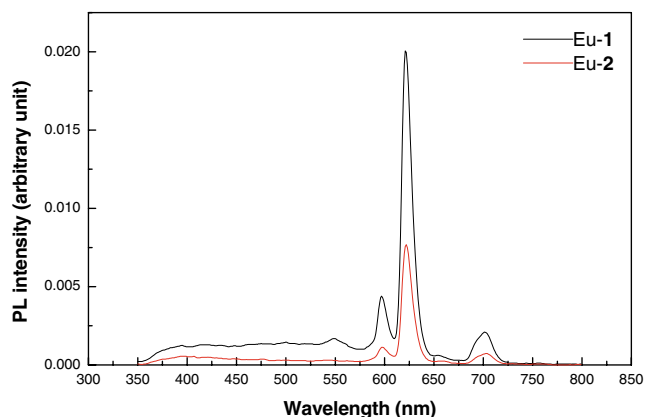


Fig. 5 The linear emission spectra of Eu-1 and Eu-2 ($\lambda_{\text{ex}}=337$ nm)

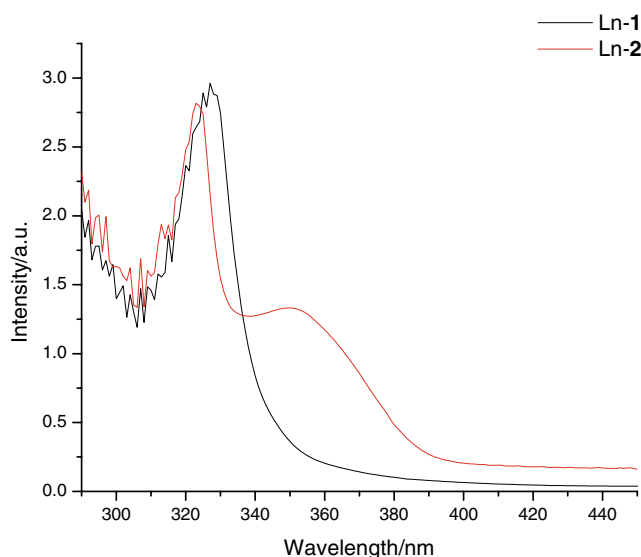


Fig. 6 The absorption spectra of Ln-1 and Ln-2

(Eu-2), 2.89 (Tb-2) and 3.11(Nd-2), $\lambda_{\text{ex}}=800$ nm, hence this double logarithmic representation are in good agreement with the three-photon absorption process.

In summary, we report to, our knowledge the first indirect NIR induced NIR emission from an organic-neodymium complex and demonstrated three-photon absorption induced lanthanide emission from the ligand which can be obtained when it is sensitized with the gain medium 1,10-phenanthroline inside our complexes. These finding can be used in future designs of new materials in human cell studies with the NIR excitation and emission. The novel three photon excitation described herein will allow the development of organic lanthanide complexes for lanthanide probes.

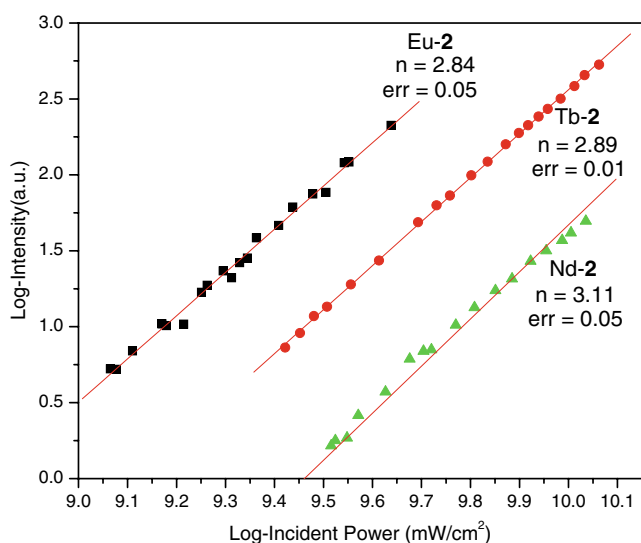


Fig. 7 Power dependence ($\lambda_{\text{ex}}=800$ nm) of three-photon induced f-f emission of the bands at Eu-2: ($\lambda_{\text{em}}=620$ nm, $^5D_0 \rightarrow ^7F_2$), Tb-2: ($\lambda_{\text{em}}=545$ nm, $^5D_4 \rightarrow ^7F_5$) and Nd-2: ($\lambda_{\text{em}}=1064$ nm, $^4F_3 \rightarrow ^4I_{11/2}$)

Experimental details

Synthesis and crystal data

Ln-1: Ln(Cl₃) (~0.06 g, 0.24 mmol) and benzene-1,3,5-tricarboxylic acid (~0.05 g, 0.24 mmol) were dissolved in 10 ml of dimethylform for 24 h. Colourless powders were obtained upon slow evaporation of solvent at room temperature.

Ln-2: Ln-1 (~0.078 g, 0.1 mol) was dissolved in the methanol (10 ml) with 1,10-phenanthroline (~0.018 g, 0.1 mmol) The mixture was then stirred at room temperature for about 3 h. Colourless crystals were obtained upon slow evaporation of solvent at room temperature.

Crystal data for **Eu-2:** C₂₇H₂₅N₄O₈Eu, *M*=685.47, orthorhombic, Pbc_a (No.61), *a*=15.473(2), *b*=16.662(2), *c*=21.184(3) Å, *V*=5461.7(12) Å³, *T*=293(2) K, *Z*=8, μ(Mo-Kα)=2.353 cm⁻¹, 31,757 reflections measured, 6,209 unique, 4386 observed reflections [*I*>2.0σ(*I*)] were used in all of the calculations. *R*=0.044, *R*_w=0.052. CCDC: 628,646. Anal. Calc. **Eu-2** for C₂₇H₂₅N₄O₈Eu: C, 48.01; H, 2.24, N:8.50%; Found: C, 48.05; H, 2.25, N:8.53%.

Crystal data for **Nd-2:** C₂₇H₂₅N₄O₈Nd, *M*=677.75, orthorhombic, Pbc_a (No.61), *a*=15.573(2), *b*=16.708(2), *c*=21.320(3) Å, *V*=5,547.4(11) Å³, *T*=293(2) K, *Z*=8, μ(Mo-Kα)=1.927 cm⁻¹, 32,420 reflections measured, 6,279 unique, 4,918 observed reflections [*I*>2.0σ(*I*)] were used in all of the calculations. *R*=0.035, *R*_w=0.059. CCDC: 628647. Anal. Calc. **Nd-2** for C₂₇H₂₅N₄O₈Nd: C, 48.57; H, 2.26, N:8.39%; Found: C, 48.58; H, 2.25, N:8.37%.

Crystal data for **Tb-2:** C₂₇H₂₅N₄O₈Tb, *M*=692.43, orthorhombic, Pbc_a (No.61), *a*=15.469(3), *b*=16.664(4), *c*=21.200(5) Å, *V*=5,465(2) Å³, *T*=293(2) K, *Z*=8, μ(Mo-Kα)=2.645 cm⁻¹, 32,148 reflections measured, 6,235 unique, 3,844 observed reflections [*I*>2.0σ(*I*)] were used in all of the calculations. *R*=0.081, *R*_w=0.083. CCDC: 628,645. Anal. Calc. **Tb-2** for C₂₇H₂₅N₄O₈Tb: C, 47.52; H, 2.22, N:8.21%; Found: C, 47.58; H, 2.21, N:8.26%.

Photophysical studies

The UV-visible absorption spectra were recorded by using a HP UV-8453 spectrophotometer to measure the range between 200 and 1,100 nm. The linear luminescence was performed by a Nitrogen laser at 337 nm and Continuum Nd-YAG laser at 355 nm. The three-photon induced emission spectra were recorded using a 800 nm pump source which was from the fundamental of a femtosecond mode-locked Ti/Sapphire laser system (output beam ~150 fs duration and 1 kHz repetition rate.). The lasers were focused to spot size ~50 μm via a *f*=10 cm lens onto the sample. The visible emission was detected by a cooled R636-10 Hamamastu photon-multiplier (PMT) in combina-

tion with a lock-in amplifier system and near infrared emission (NIR) was detected by a liquid nitrogen cooled InSb IR detector (EG&G) with preamplifier and recorded by a lock-in amplifier system [13, 14].

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