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Green and Red Three-Photon Upconversion from Polymeric Lanthanide(III) Complexes**

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In the last decade, there has been significant interest in the nonlinear luminescence from organic–lanthanide complexes owing to their potential applications in three-dimensional

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fluorescence imaging, optical data storage, lithographic microfabrication, and laser device fabrication.[1] Multiphoton (e.g. indirect three-photon) processes allow the excitation of fluorophores in a lower energy spectral region—this is useful for optical communications (such as three-dimensional data storage) and is particularly important for imaging and therapy as longer wavelength radiation is less harmful to the body's tissues and cells and allows efficient penetration with less damage.[2] Multiphoton excitation allows molecules that typically absorb in the ultraviolet region to be excited with red or near-infrared light. The photoluminescence processes from organic–lanthanide complexes are usually induced by an organic chromophoric ligand that absorbs light and transfers this excitation energy to the lanthanide ion.[2] A large number of complexes of lanthanide (Ln) ions with organic chromophores have been synthesized and their two-photon upconversion photophysical properties investigated.[3] Complexes of Eu^{III}, Tb^{III}, Dy^{III}, Er^{III}, Nd^{III}, Sm^{III}, and Yb^{III} ions with fluorescent chelators, and complexes of Eu^{III} and Tb^{III} ions with nucleic acids and proteins have been reported.[4]

Until now, only a few multiphoton processes have been observed owing to the limitations of experimental measurements, but with recent advances in technology experimentation has coalesced with theory to allow direct three-photon excitation. Stimulated emission following direct three-photon excitation has only been observed for one organic chromophore,[5] and reports of three-photon upconversion processes from organic–lanthanide complexes are very scarce.[6] Herein, we demonstrate a direct three-photon upconversion process in organic–lanthanide complexes (Ln = Eu, Tb) upon excitation at 845 nm.

The tripodal ligand *N*-[2-(bis{2-[(2-methoxybenzoyl)amino]ethyl}amino)ethyl]-2-methoxybenzamide (**1**)[7] was treated with terbium and europium nitrate salts to give the complexes [Tb(**1**)$(NO_3)_3$] and [Eu(**1**)$(NO_3)_3$]. Single crystals of both complexes were isolated through the slow evaporation of a solution of the respective complex in acetonitrile at room temperature over a few days. The crystal structures of both complexes were determined by X-ray crystallography; the structure of [Tb(**1**)$(NO_3)_3$] is shown in Figure 1. The Ln ion is coordinated by three amide groups from two ligands, which function as bridges to give a one-dimensional covalent (linear polymeric) chain (Figure 2). The distances between the two neighboring Ln^{3+} ions in the homometallic complexes are 9.443 Å for Ln = Tb and 9.465 Å for Ln = Eu along the *c* axis.

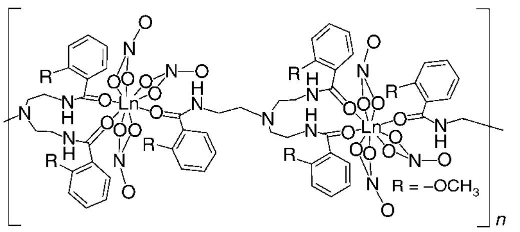

Figure 2. Schematic drawing of the polymeric structure of the complexes [Ln(**1**)$(NO_3)_3$] (Ln = Tb or Eu).

The UV/Vis absorption spectrum of the ligand displays three intense bands at λ ~ 220, 280, and 330 nm (see Figure 3) which are attributed to benzyl π–π* and carbonyl transitions of the benzoate groups of the ligand. Upon complexation of the ligand to the lanthanide ions, the absorption bands undergo small shifts to longer wavelengths.[8,9] The ligand and complexes do not display absorption bands in the spectral range from 400 to 845 nm. However, the blue, green, and red upconversion luminescence emissions from the ligand and the Tb and Eu complexes, respectively, were observed upon excitation at 845 nm (with a Ti:sapphire laser). It can be seen from Figure 3a that at least three photons are required to promote the ligand to the excited state when it is irradiated at 845 nm. Figure 3b shows the nonlinear f→f emission spectra of [Eu(**1**)$(NO_3)_3$] and [Tb(**1**)$(NO_3)_3$] recorded in the solid state upon excitation at 845 nm. The structured emission

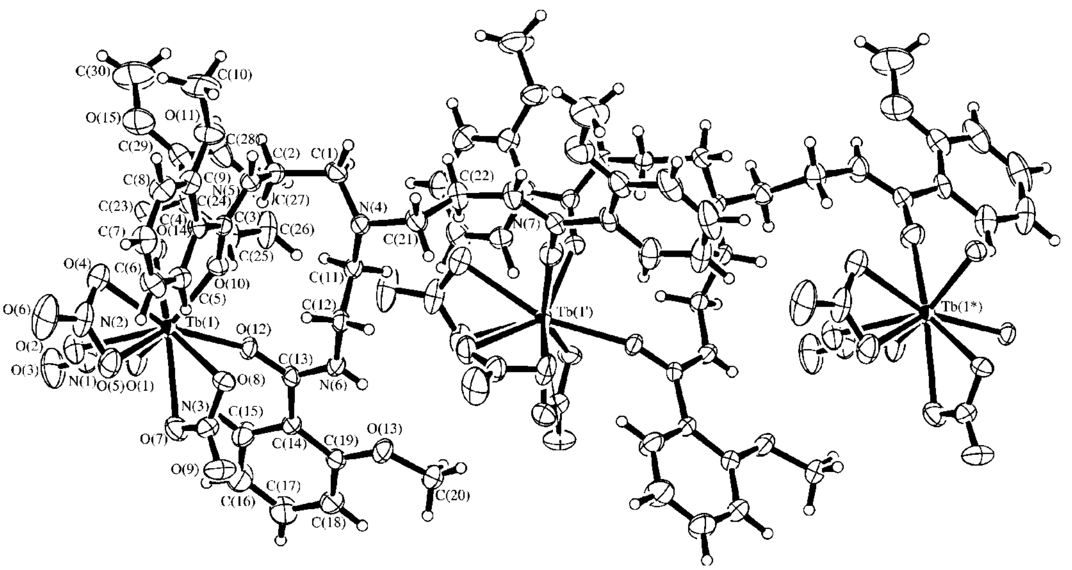

Figure 1. ORTEP drawing of [Tb(**1**)$(NO_3)_3$].

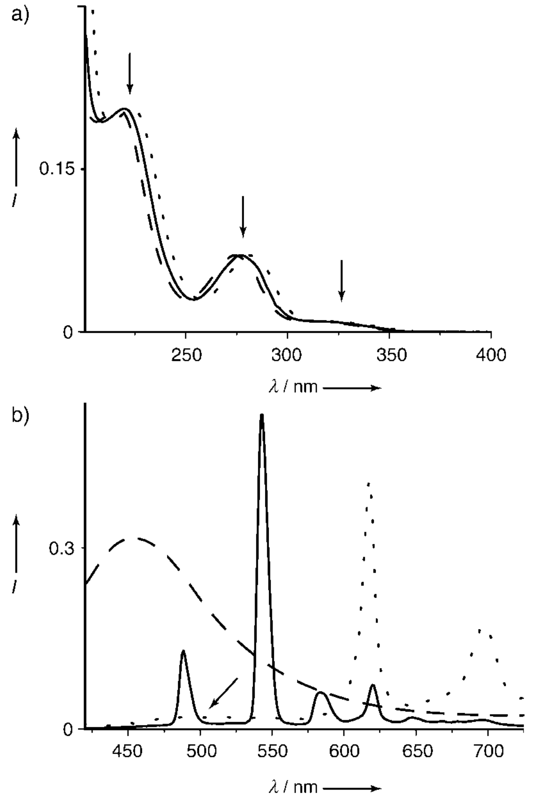

Figure 3. a) UV/Vis absorption spectra of **1**, [Tb(**1**)(NO$_3$)$_3$], and [Eu(**1**)(NO$_3$)$_3$] (1.0×10^{-5} M in MeOH); b) the three-photon-induced upconversion emission of **1**, [Tb(**1**)(NO$_3$)$_3$], and [Eu(**1**)(NO$_3$)$_3$] in the solid state (room temperature, λ_{ex} = 845 nm). – – – = **1**, —— = [Tb(**1**)(NO$_3$)$_3$], ----- = [Eu(**1**)(NO$_3$)$_3$].

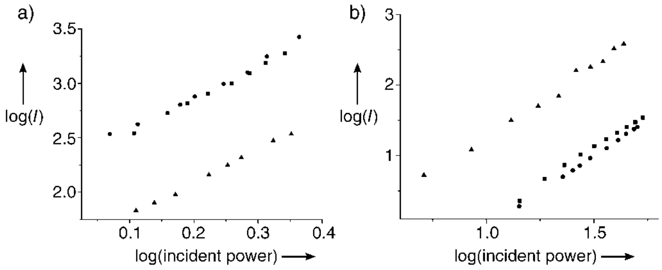

Figure 4. Power dependence of the emission intensities of a) three-photon (λ_{ex} = 845 nm) and b) two-photon (λ_{ex} = 650 nm) upconversion processes of **1** (▲; λ_{em} = 450 nm; $S_1 \rightarrow S_0$), [Tb(**1**)(NO$_3$)$_3$] (■; λ_{em} = 545 nm; $^5D_4 \rightarrow {}^7F_5$), and [Eu(**1**)(NO$_3$)$_3$] (●; λ_{em} = 620 nm; $^5D_0 \rightarrow {}^7F_2$).

bands that arise from transitions of $^5D_4 \rightarrow {}^7F_J$ (J = 6–3) states in [Tb(**1**)(NO$_3$)$_3$] and $^5D_0 \rightarrow {}^7F_J$ (J = 1, 2, 4) states in [Eu(**1**)(NO$_3$)$_3$] are shown. A weak emission from the ligand in [Eu(**1**)(NO$_3$)$_3$] is detected between 400 and 550 nm (as indicated by the arrow in Figure 3b) In a control experiment, the inorganic terbium and europium nitrate salts were also directly excited under the same experimental conditions. Emission through upconversion processes was *not* observed which implies that the three-photon nonlinear energy-transfer emission is induced by the ligand.

Furthermore, two-photon emission was observed when the complexes were excited at 650 nm (with a nanosecond Nd:YAG laser) yet emission was not observed when the sample was excited at 845 nm with the same source (emission was only observed upon excitation at 845 nm with a Ti:sapphire femtosecond laser source). The power output from a femtosecond laser is ten thousand times stronger than that from a nanosecond laser and consequently, the quantum efficiency of the three-photon process is therefore much lower than the two-photon process. To confirm further the nonlinear processes of the ligand and the complexes, the evolution of the intensities of the peaks were plotted as a function of the incident power[10] at 845 and 650 nm (Figures 4a and b, respectively). The results obey the equation derived by Soga and co-workers,[11] whereas the slopes derived from the experimental data for the ligand and the complexes (≈3.0 at λ_{ex}=845 nm; ≈2.0 at λ_{ex}=650 nm) are in good agreement with the upconversion processes; that is, three photons are absorbed at 845 nm.

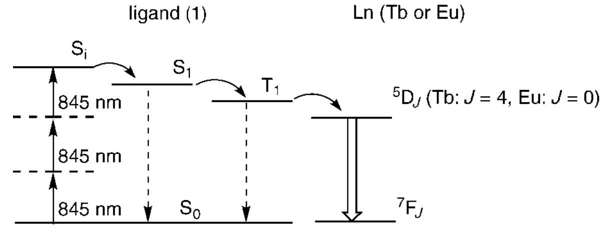

Figure 5. The proposed mechanism for the three-photon excitation and emission process. S_i is a higher energy singlet state; S_1 is the radiative lower singlet state; T_1 is the lowest energy triplet excited state; S_0 refers to the ground state. Linear arrows indicate radiative energy-transfer processes and curly arrows represent nonradiative energy-transfer processes.

The pathway of the three-photon upconversion process for the ligands and complexes is proposed in Figure 5. First, upon excitation with either visible or near-infrared pulses, the ligand absorbs three photons and is excited from the ground singlet state S_0 to a higher energy singlet state S_i. Then, the electrons in S_i relax to the lowest energy singlet state S_1 from where they relax further through intersystem crossing to the lowest triplet excited state T_1.[5,12] A photophysical study of the analogous Gd complex [Gd(**1**)(NO$_3$)$_3$] showed that the transfer of energy from the ligand to the metal takes place from the triplet state of the ligand as opposed to the singlet state (recently, it has been shown that lanthanide luminescence can also be sensitized through energy transfer from the singlet state of an appropriate ligand.[13]) As the ligand is coordinated to a 'heavy' atom (Ln), the ($S_1 \rightarrow T_1$) intersystem-crossing rate is enhanced.[12,13] Finally, energy is transferred from the triplet state of the ligand to Tb^{III} or Eu^{III} through either a nonresonant phonon-assisted or resonant process. This leads to the excitation of Tb^{III} to the $^5D_4$ state and Eu^{III} to the $^5D_0$ state; upon relaxation from these states, they emit their characteristic green and red luminescence, respectively.

In summary, we have demonstrated the indirect, three-photon-induced sensitization of terbium and europium complexes through an upconversion process. Tris(2-methoxybenzamide)triethylamine **1** is a good ligand for the multiphoton nonlinear photoluminescence of the lanthanides and may serve in future designs of new three-photon materials and in the development of organic–lanthanide complexes as biological probes.

Experimental Section

Ligand **1** was prepared according to the literature.[7] $Ln(NO_3)_3 \cdot 6H_2O$ (47 mmol; Ln = Tb or Eu) and **1** (47 mmol) were dissolved in acetonitrile (15 mL) and the mixture was heated at reflux for 24 h. Colorless single crystals of $Ln(\mathbf{1})(NO_3)_3$ were obtained by slow evaporation of the solution. $[Tb(\mathbf{1})(NO_3)_3]$ (65 %); elemental analysis: calcd for $C_{30}H_{38}N_7O_{16}Tb$ (%): C 39.47, H 4.17, N 10.75; found: C 39.46, H 4.18, N 10.74; FAB-MS: m/z: 831 $[M-NO_3-H_2O]^+$, 770 $[M-2NO_3-H_2O]^+$, 708 $[M-3NO_3-H_2O]^+$, 549 $[M-3NO_3-H_2O-Tb]^+$. $[Eu(\mathbf{1})(NO_3)_3]$ (60 %); elemental analysis: calcd for $C_{30}H_{38}N_7O_{16}Eu$ (%): C 40.63, H 4.06, N 11.06; found: C 39.77, H 4.19, N 11.82; FAB-MS: m/z: 825 $[M-NO_3-H_2O]^+$, 763 $[M-2NO_3-H_2O]^+$, 701 $[M-3NO_3-H_2O]^+$, 549 $[M-3NO_3-H_2O-Eu]^+$.

Crystal data for $[Tb(\mathbf{1})(NO_3)_3]$: $C_{30}H_{38}N_7O_{16}Tb$, $M = 911.59$, monoclinic, $P21/c$, $a = 9.922(2)$, $b = 20.738(3)$, $c = 18.849(3)$ Å, $V = 3775.9(11)$ Å^3, $T = 298$ K, $Z = 4$, $\mu(Mo_{K\alpha}) = 1.948$ cm^{-1}, 23674 reflections measured of which 8761 were unique ($R_{int} = 0.048$), 4861 observed reflections [$I > 2\sigma(I)$] were used in all calculations, $R(F) = 0.039$, $R_w = 0.039$. Crystal data for $[Eu(\mathbf{1})(NO_3)_3]$: $C_{30}H_{38}N_7O_{16}Eu$, $M = 904.63$, monoclinic, $P21/c$, $a = 9.987(4)$, $b = 20.783(7)$, $c = 18.893(7)$ Å, $V = 3822.6(25)$ Å^3, $T = 298$ K, $Z = 4$, $\mu(Mo_{K\alpha}) = 1.813$ cm^{-1}, 23452 reflections measured of which 8741 were unique ($R_{int} = 0.034$), 6096 observed reflections [$I > 2\sigma(I)$] were used in all calculations, $R(F) = 0.034$, $R_w = 0.039$. CCDC 237876 ($[Tb(\mathbf{1})(NO_3)_3]$) and 237877 ($[Eu(\mathbf{1})(NO_3)_3]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

UV/Vis absorption spectra (200–1100 nm) were recorded on a HP UV-8453 spectrophotometer. The 845-nm pump excitation sources were generated from the fundamental of a femtosecond mode-locked Ti:Sapphire laser system (output beam ~150-fs duration, 1-kHz repetition rate). The lasers were focused through a 10-cm lens onto the sample and the pumping peak intensity at the sample point was ≈3 to 0.5 GW cm^{-1}. The third harmonics, 325-nm line of a Nd:YAG laser (Quantel Brillant B) was used to pump the OPO (Opotek MagicPrism VIR) system to provide a tunable laser source from 650 nm with a pulse width of ≈4 ns. The emitted light was collected with a backscattering configuration into a 0.5-m spectrograph and detected with a liquid nitrogen-cooled CCD detector.

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