Luminescence

Simultaneous Observation of Green Multiphoton Upconversion and Red and Blue NLO Processes from Polymeric Terbium(III) Complexes**

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Photoexcitation at a certain wavelength in the near-infrared (NIR) region followed by luminescence at a shorter wavelength in the visible domain is called near-infrared-to-visible photon upconversion. This is a rather unusual process as low-energy photons are "converted" into higher energy photons: two or three photons of NIR light are required to generate one photon of visible light.[1] Nonlinear optics (NLO) is another mechanism that can lead to the generation of light at a frequency that is either twice or integral-multiples of the incident light.[2] The phenomena of two- or three-photon upconversion, and second or third harmonic generation (SHG or THG) on organic materials have received considerable attention since fluorescence detection became popular in applications such as photodynamic therapy, optical data storage, and microfabrication.[3]

Multiphoton excitation allows molecules that typically absorb in the UV region to be excited with red or NIR light. The photoluminescence processes from organolanthanide complexes are usually induced by an organic chromophoric ligand that absorbs incident light and transfers its resultant excitation energy to the lanthanide ion.[4] Until now, only a few multiphoton processes in organolanthanide complexes have been observed owing to the limitations of experimental measurements.[5] Although there have been reports on lanthanide complexes that display second harmonic generation, these have been limited and focused only on glassy doped lanthanide materials.[6] In recent years, our group[7] and others[8] have investigated several high-order multiphoton processes from organic ligands and metal complexes. Herein we report, to the best of our knowledge, the first observation of rare multiphoton upconversion emission from a lanthanide complex as well as SHG and THG transmission phenomena, which occur simultaneously from the same excitation source in the IR region at $\lambda \approx 1.26$ and 1.34 μm.

The N-tripodal ligand **L** was treated with terbium nitrate to give the complex $[Tb(\mathbf{L})(NO_3)_3]$ (**1**, see Figure 1), which is thermally stable up to 300 °C, as shown by thermogravimetric analysis (see Supporting Information). Single crystals of **1** were isolated through the slow evaporation of a solution of **1** in THF/MeCN at room temperature over a few days. The crystal structure of **1** was determined by X-ray crystallography and is shown in Figure 2. The coordination geometry of the metal center in **1** can be described as a tricapped trigonal prism, in which each Tb^{3+} ion is coordinated by three carbonyl (amide) groups from three separate but identical tripodal ligands, and doubly coordinated by three nitrate ions. Upon complexation, the tripodal ligand adopts a polymetallic dendritic form, as the branches contain oxygen groups for binding with lanthanide ions. The ensemble of the tripodal ligand and its connectivity with the lanthanide ion, which itself is preorganized as a result of its coordination to three chromophores, forms a metallodendrimer. The metal takes on a "metal as ligand, metal as complex" approach in this dendritic architecture.[8]

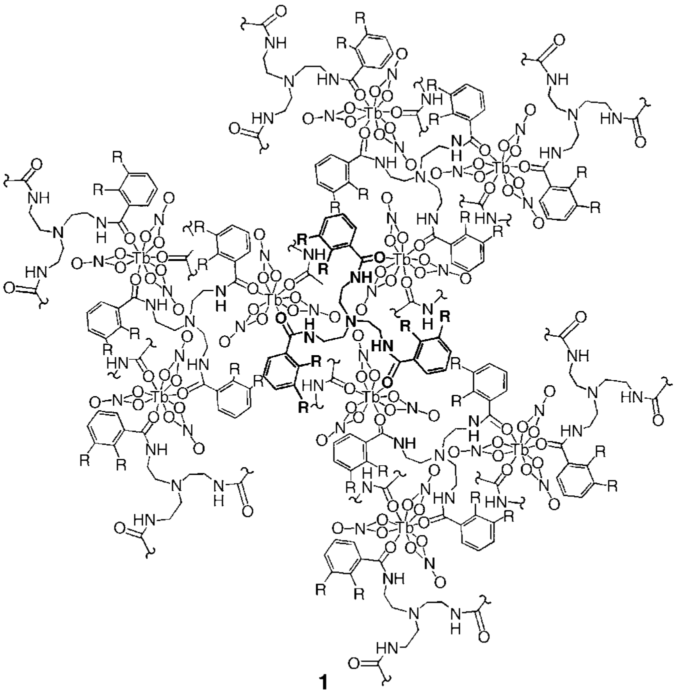

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Figure 1. Polymeric structure of complex **1**. Ligand **L** is highlighted in bold at the center of the structure. $R = OCH_3$.

Complex **1** exhibits both strong linear and nonlinear luminescence at room temperature and acts as the gain medium. The chromophores and complexes are known to absorb two or more photons ($\lambda_{ex} = 650$ and 800 nm) and be excited to higher energy states with further energy transfer to the terbium center to produce green f–f emission (Figure 3 a).[7] Ligand **L** shows upconversion emission in the blue region ($S_1 \rightarrow S_0$) upon three-photon absorption at $\lambda \approx 800$ nm and four-photon absorption at $\lambda \approx 1.26$ μm (see Supporting

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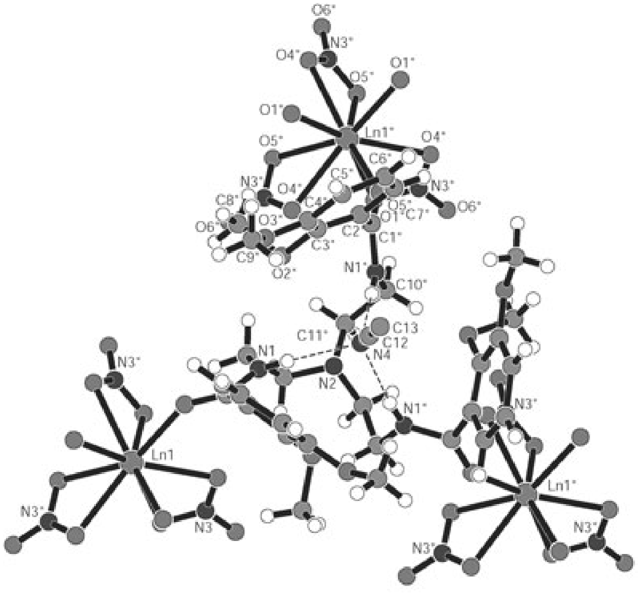

Figure 2. ORTEP drawing of **1** (Ln = Tb) and **2** (Ln = Gd).

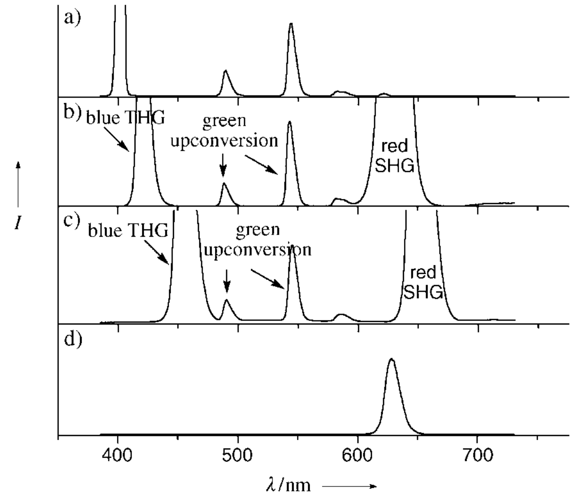

Figure 3. Spectra of the upconversion (λ_{em} = 545 nm, $^5D_4 \rightarrow {}^7F_5$) and NLO emissions produced upon multiphoton absorption in complex **1**: a) Three-photon upconversion (λ_{ex} = 800 nm); b, c) simultaneous green four-photon upconversion and red SHG and blue THG processes upon excitation at $\lambda \approx 1.26$ μm (b) and $\lambda \approx 1.34$ μm (c) with a NIR irradiation source; d) SHG spectrum of urea, which was used as the standard, upon excitation at $\lambda \approx 1.26$ μm with the NIR irradiation source.

Information). Complex **1** exhibits a strong multiphoton absorption when excited by ultrashort laser pulses at $\lambda \approx 1.26$ μm to produce the green structured upconversion emission bands of **1** that arise from the f–f transitions of the $^5D_4 \rightarrow {}^7F_J$ (J = 6–3) states of terbium. This upconversion process occurs simultaneously with two other nonlinear processes, namely SHG and THG, to generate two additional colors, blue and red, under the same excitation process in the NIR region (Figure 3b). Furthermore, by adjusting the wavelength and intensity of the source, the second and third color elements can be continuously tuned around $\lambda \approx 1.34$ μm, while the green upconversion is still detected (Figure 3c). From the observed behavior, the complexes seem to be extremely wavelength-sensitive and provide an effective tunable system. The red SHG effect can be visually observed as it is the more dominant process, however, a suitable filter can be used to cut-off the red SHG emission while the green upconversion and blue THG are still observed.

The ligand and complex appeared to have no linear absorption in the spectral range from 400 nm to 1.34 μm. However, the blue and green upconversion luminescence from both the ligand and the lanthanide complex can be seen under excitation at λ = 1.26 and $\approx$1.34 μm when generated by a Ti:sapphire laser. The chromophore absorbs at $\lambda \approx 330$ nm (30303 cm^{-1}),[7] which indicates that the absorption of at least four photons is required for upconversion upon excitation at $\lambda \approx 1.26$ μm (7937 cm^{-1}) and $\approx$1.34 μm (7462 cm^{-1}), whereas for the ligand the accumulation of more than three photons is needed upon excitation at $\lambda \approx 1.34$ μm to reach its lowest emitting state for upconversion emission. The Soga equation[9] is used in auxiliary to verify these SHG, THG, and upconversion processes (Figure 4a–d). The gradients obtained for logarithmic plots of incident power versus intensity are 4.28 (Figure 4b, λ_{ex} = 1.26 μm) and 4.51 (Figure 4c, λ_{ex} = 1.34 μm). These double-logarithmic representations are therefore in good agreement with the multiphoton-upconversion processes, while the slopes in Figure 4b and c for the THG and SHG processes are 3 and 2, respectively, in the region of $\lambda \approx 1.26$ and $\approx$1.34 μm and agree with the theoretical values of photons needed.

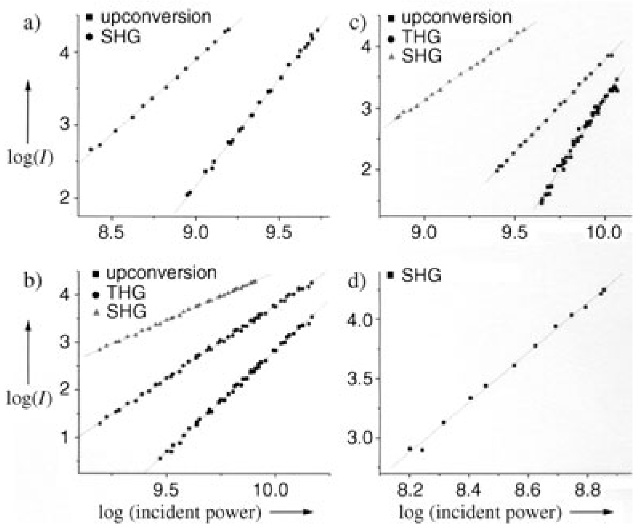

Figure 4. Power dependence of the emission intensities of a) three-photon upconversion (λ_{ex} = 800 nm) and b), c) four-photon upconversion ($^5D_4 \rightarrow {}^7F_5$), SHG, and THG processes in **1** upon excitation at $\lambda \approx 1.26$ μm (b) and $\lambda \approx 1.34$ μm (c); d) spectrum of SHG of urea as standard ($\lambda_{ex} \approx 1.26$ μm).

The suggested energy-transfer diagram for the various multi-NLO processes of the Tb complex **1** is shown in Figure 5. For upconversion: First, the energy provided from either a visible or NIR pulse promotes the ligand from the ground state S_0 to a higher energy excited singlet state S_i after absorption of four photons. Then, the electrons in S_i return to

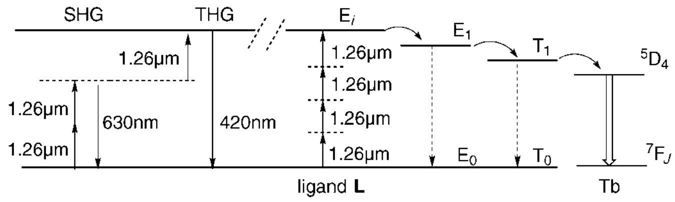

Figure 5. The proposed energy-transfer diagram for the various processes (four-photon upconversion, SHG, THG) in **1**. E_i is a higher energy singlet excited state; E_1 is the radiative lower energy singlet excited state; T_1 is the lowest energy triplet excited state; E_0 and T_0 both refer to the ground state. Linear arrows indicate radiative energy-transfer processes; curly arrows represent nonradiative energy-transfer processes.

the lowest energy excited singlet state S_1 and further, through intersystem crossing, to the lowest energy triplet excited state T_1. This mechanism was further supported by the energies of the S_1 and T_1 states determined for the Gd complex [Gd(**L**)(NO_3)$_3$] (**2**).[4a,10] As a result of the ligand being attached to a heavy-metal ion such as terbium, the rate of intersystem crossing ($S_1 \rightarrow T_1$) is enhanced.[11] Finally, the electrons from the ligand T_1 state transfer their excess energy to Tb^{III} through either nonresonant phonon-assisted energy transfer or resonant energy transfer, which leads to promotion of Tb^{III} to the $^5D_4$ state. Finally, Tb^{III} relaxes to the ground-state ^7F_J configuration and emits its characteristic green luminescence. Meanwhile, the mechanism for the two other NLO processes involves direct accumulation of two or three photons for SHG and THG, respectively, to result in the two other emissions (red and blue) in the visible region (Figure 5).

We previously reported crystallographic details for a ligand that is similar to **L** but differs in its mode of coordination to Tb to consequently give rise to a different center of symmetry. Only green multiphoton upconversion was observed in that particular system (see Supporting Information). Therefore, the geometry and symmetry of the complex, as controlled by the configuration of coordination of the chromophore to Tb, together with the exceptional properties of the chromophore bring about this unique multiphoton process.

In summary, we have reported tunable second and third harmonic generation with simultaneous indirect multiphoton-upconversion-sensitized luminescence processes in a terbium complex. This phenomenon occurs when the Tb^{III} center has an appropriate symmetry center and is sensitized with a suitable organic ligand. Complex **1** appears to be a very good system for multiple-photon nonlinear photoluminescence and may be useful in future designs of new multiphoton materials. The novel simultaneous multiphoton processes described here may allow the further development of organolanthanide complexes as probe molecules.

Experimental Section

N-[2-(bis{2-[(2,3-dimethoxybenzoyl)amino]ethyl}-amino)ethyl]-2,3-dimethoxybenzamide (**L**) was prepared according to a reported method.[12]

1: Tb(NO_3)$_3$·6H_2O (47 mmol) and **L** (141 mmol) were dissolved in methanol (15 mL), and the mixture was allowed to heat at reflux for 24 h to give complex **1** (62 %). Single crystals of **1** were obtained by slow evaporation of a solution of **1** in THF/MeCN. Elemental analysis: calcd for $C_{33}H_{42}N_7O_{18}Tb$: C 40.28, H 4.27, N 9.97; found: C 40.29, H 4.26, N 9.96; FAB-MS: m/z: 797 $[M-3NO_3]^+$, 645 $[M-3NO_3-Tb]^+$. Crystal data for **1**·MeCN: $C_{35}H_{45}N_8O_{18}Tb$, $M=1024.71$, trigonal, $P3c1$, $a=10.877(1)$, $c=21.360(2)$ Å, $V=2188.5(3)$ Å^3, $T=298$ K, $Z=2$, $\mu(Mo_{K\alpha})=16.94$ cm^{-1}, 13728 reflections measured, 1960 unique, 1468 observed reflections $[I>1.5\sigma(I)]$ were used in all of the calculations, $R=0.0977$, $R_w=0.0822$. Although the crystal data were not of high quality, the crystal structure is essentially isomorphous with the Gd complex **2** and other complexes of **L** with the middle members of the lanthanide series.

2: Gd(NO_3)$_3$·6H_2O (47 mmol) and **L** (141 mmol) were dissolved in methanol (15 mL), and the mixture was heated at reflux for 24 h to give **2** (66 %). Single crystals of **2** were obtained by slow evaporation of a solution of **2** in THF/MeCN. Elemental analysis: calcd for $C_{35}H_{45}N_7O_{18}Gd$: C 41.06, H 4.40, N 9.57; found: C 41.08, H 4.41, N 9.58; FAB-MS: m/z: 792 $[M-3NO_3]^+$, 643 $[M-3NO_3-Gd]^+$. Crystal data for **2**·MeCN: $C_{35}H_{45}N_7O_{18}Gd$, $M=1023.03$, trigonal, $P3c1$, $a=10.885(1)$, $c=21.403(2)$ Å, $V=2196.1(3)$ Å^3, $T=298$ K, $Z=2$, $\mu(Mo_{K\alpha})=15.95$ cm^{-1}, 13901 reflections measured, 1497 unique, 1468 observed reflections with $[I>2\sigma(I)]$ were used in all of the calculations, $R=0.0963$, $R_w=0.0871$. CCDC 258846 (**1**) and 258847 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The 800-nm pump source was generated from the fundamental of a femtosecond mode-locked Ti:Sapphire laser system (output beam: ≈150-fs duration and 1-kHz repetition rate). The 1.26–1.34 µm pump wavelengths were generated from a homebuilt optical parametric amplifier, which was pumped by the SHG of the 800-nm femtosecond pulses.[13] The lasers were focused to a spot size of ca. 50 µm by means of a lens ($f=10$ cm) onto the sample. The emitting light was collected with a backscattering configuration into a 0.5-m spectrograph and detected by a liquid-nitrogen-cooled CCD detector.

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