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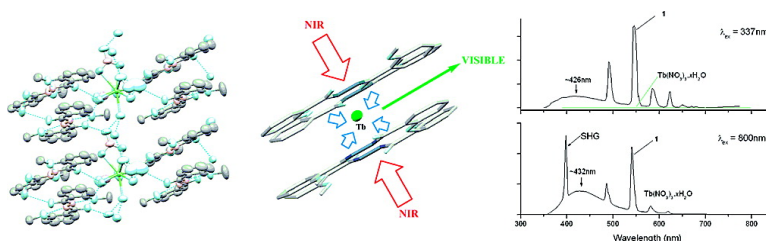
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Terbium Luminescence Sensitized through Three-Photon Excitation in a Self-Assembled Unlinked Antenna

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The organic–terbium hybrid compound designed with the azido molecule **L**, 2-methoxy benzoic acid tris-(2-methoxybenzoyl)hydrazide, exhibits three-photon-excited green emission as well as second-harmonic generation even though the antenna is unlinked from the metal center.

The conversion of low-energy radiation to higher energies has been demonstrated through processes such as nonlinear harmonic generation¹ and upconversion, which comprises mechanisms including multiphoton excitation, excited-state absorption, and energy-transfer cross-relaxation processes.^{2,3} For the first nonlinear processes, there is current interest in second-harmonic generation (SHG) and whether^{4,5} or not⁶ the 4f electrons play a role. For upconversion phenomena, the multiphoton excitation of a coordinated sensitizer and subsequent energy transfer has been shown to lead to visible luminescence from lanthanide ions.^{7,8} Antenna–lanthanide ion energy-transfer processes originate from singlet^{9,10} or triplet states.¹¹ In this paper, we report a novel terbium compound cocrystallized with an azido molecule **L** = 2-methoxy benzoic acid tris-(2-methoxybenzoyl)hydrazide, (C₆H₄(OCH₃)CONH-)₂, which does not function as a ligand, [Tb(NO₃)₃(H₂O)₃]·L₂·H₂O = **1**, and for which multiphoton-induced antenna absorption results in 4f⁶ intraconfigurational emission. Unusually, this antenna–rare earth energy transfer occurs even though the antenna is not directly linked to the metal ion. The compound also exhibits SHG properties.

The motivation for the present work has arisen from some recent studies. He et al. have investigated multiphoton-stimulated green emission from organic dyes,¹² and our group has provided various examples of 4f^N–4f^N luminescence sensitized by the antenna effect following multiphoton absorption of tripodal amide ligands, with simultaneous occurrence of second and third harmonic generation.^{13,14} These phenomena are particularly useful for applications such as two-photon excited fluorescence microscopy, three-dimensional optical data storage, infrared detection, and photodynamic therapy.^{15,16} However, more studies are necessary to understand the design characteristics of the relevant materials and to understand further the mechanisms of the nonlinear processes.

Terbium is an attractive activator ion because it has a wide window in the visible region so that nonradiative processes are of minor importance for the ⁵D₄ luminescent state. From their syntheses, single crystals of both the molecule **L** and **1** were

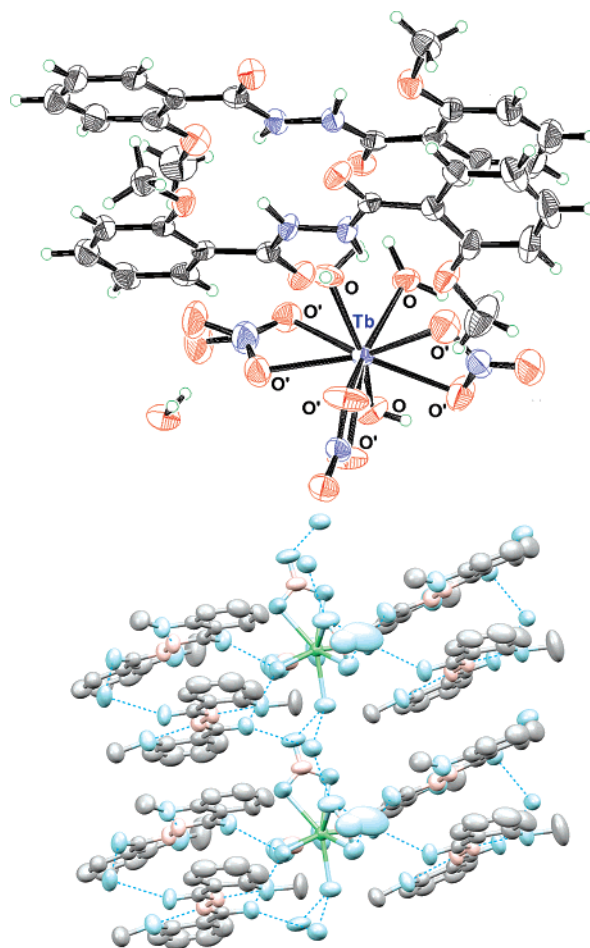


Figure 1. The ORTEP drawing of the Tb³⁺ coordination (O = aqua oxygen; O' = nitrate oxygen) and packing diagram of **1** showing hydrogen bonding.

isolated after a few days so that their structures could be determined by X-ray crystallography, and the coordination geometry and unit cell packing of **1** are shown in Figure 1.¹⁷

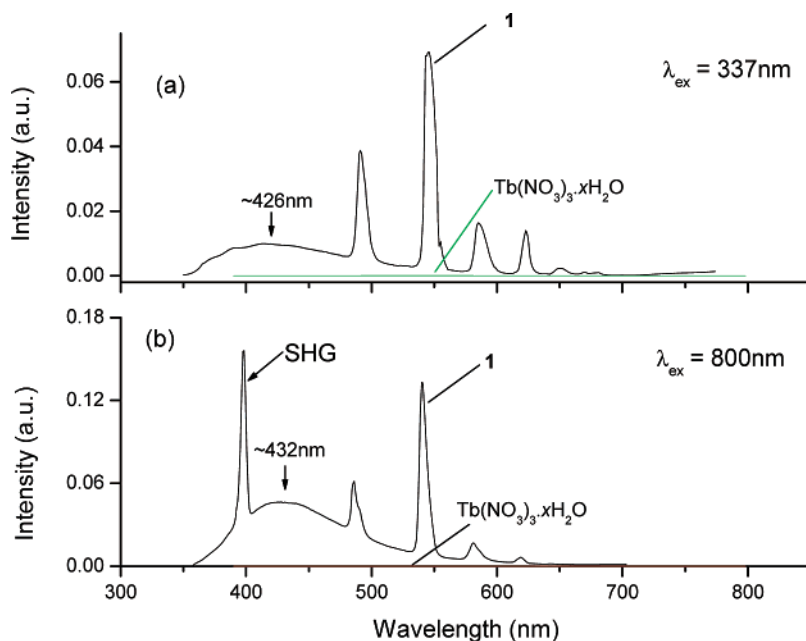


Figure 2. The solid-state linear emission (a) and upconverted emission/SHG (b) spectra of **1** at room temperature. The emission scales for (a) and (b) are arbitrary and not for comparison with each other.

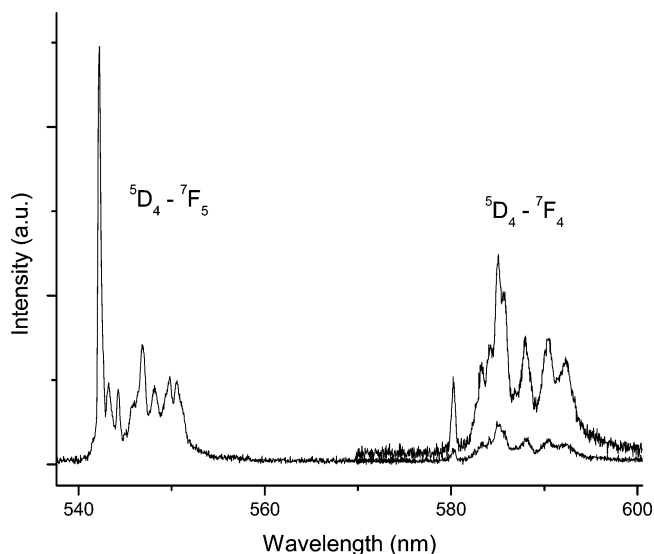


Figure 3. The 488 nm excited 10 K emission spectrum of **1** between 540 and 600 nm. The Tb^{3+} emission transitions from $^5\text{D}_4$ in this region are marked. The scale expansion of the lower-energy group is given.

The photophysical properties are intriguing for **1**, but first, the crystal structure merits description since it comprises a cocrystallization of the azido molecule and the terbium salt. Compound **1** crystallizes in the space group $P2_12_12_1$, with Tb^{3+} situated at the C_1 site symmetry. The Tb^{3+} coordination sphere consists of three bidentate nitrate groups and three aqua ligands, providing a total of nine-coordination. The two molecules **L** are linearly aligned in an almost planar sheet, with the terbium nitrate complexes situated between each row of these molecules, hence forming a sort of matrix (Figure 1). There is extensive hydrogen bonding between the aqua ligands on the terbium to the carbonyl oxygen of the azido molecules, with the closest Tb-to-carbonyl oxygen distance being roughly 4.4 Å. However, the X-ray structure shows that there is no direct bonding of the azido molecule to the metal center. The Tb center is 6–9 Å away from the centroid of the π rings in these molecules. The closest π – π interactions between the two overlying azido

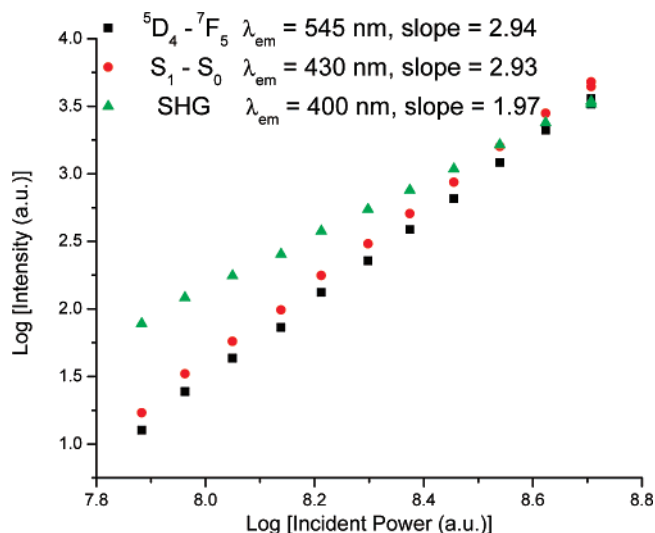


Figure 4. Power dependence of the emission intensities found for **1**: three-photon induced emission (black dots: ligand emission, $\lambda_{\text{em}} = 430 \text{ nm}$; red dots: Tb^{3+} emission, $\lambda_{\text{em}} = 545 \text{ nm}$) and SHG (green dots).

molecules are between 3.6 and 3.9 Å, with the closest identical stacking of the rings being at equivalent distances of 7.9 Å.

The Tb^{3+} ion in **1** emits turquoise emission due to the $^5\text{D}_4 \rightarrow ^7\text{F}_j$ transitions ($J = 6$ and 5 are stronger than $J < 5$) via linear ($\lambda_{\text{ex}} = 337 \text{ nm}$) and multiphoton ($\lambda_{\text{ex}} = 800 \text{ nm}$) excitations, as shown in Figure 2. Compound **1** also shows the usual Tb^{3+} emission under 488 nm excitation at 10 K (Figure 3). Certainly, nonradiative quenching processes by OH vibrations are relatively unimportant for the $^5\text{D}_4$ state because of the large energy gap below it. The fine structure of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition comprises at least 10 peaks (Figure 3), showing that the terminal crystal field levels are nondegenerate, as expected for C_1 site symmetry. In the room-temperature emission spectrum under 337 nm excitation, shown in Figure 2a, the emission from **L** is also observed at $\sim 426 \text{ nm}$, which is similar to the emission of **L** alone.

Under excitation at 800 nm, compound **1** shows a strong green emission from f–f transitions (Figure 2b). At first

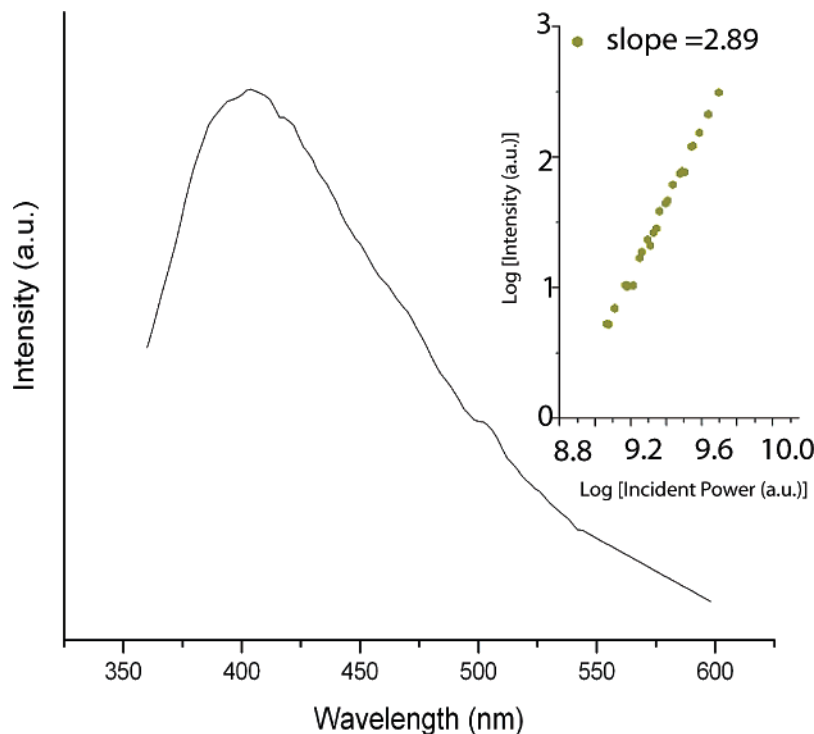


Figure 5. Emission spectrum and power dependence of **L** under 800 nm excitation.

consideration, it could be due to directly excited Tb^{3+} emission, and such transitions of Tb^{3+} in centrosymmetric environments have been thoroughly investigated by Denning and co-workers.¹⁸ The two-photon $f-f$ transitions are parity-allowed processes which occur by parity-allowed virtual transitions (to f^2d electronic states) involving the initial and final f electronic states. However, as shown for the typical inorganic system $\text{Tb}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ in Figure 2b, the two-photon cross sections are very small because the observed emission is extremely weak. Actually, the distinction between two-photon absorption by Tb^{3+} or a multiphoton absorption by the organic moiety is also clear because two-photon absorption bands of Tb^{3+} are sharp, but they are broad for the azido molecule absorption. Note that for Ti:sapphire femtosecond laser excitation at 800 nm (12500 cm^{-1}), a two-photon process cannot populate the ligand singlet state (lifetime at 300 K: $2.48 \pm 0.07 \text{ ns}$), which from the absorption spectrum of **L**, is located at $<315 \text{ nm}$ ($>31750 \text{ cm}^{-1}$). A three-photon process is parity-forbidden for intraconfigurational $f-f$ transitions but is possible for ligand excitation. In fact, the pump power– Tb^{3+} emission intensity plot indicates a three-photon process (Figure 4). This may be unexpected because the azido molecule does not participate in the coordination geometry in **1**. Thus, it is the three-photon absorption of **L** (with the mechanism involving the sums over two other virtual singlet states in addition to S_0 and S_1) that induces $f-f$ luminescence from the lanthanide ion. The mechanism of energy transfer from the antenna to Tb^{3+} is from a single (and not twin¹⁹) donor since simultaneous blue ligand emission is observed. Our previous studies have encountered multiphoton absorption via the ligand antenna effect with subsequent energy transfer to the metal center.^{13,14} This also occurs in **1**, although the antenna is unattached (Figure 2b).

The lifetime of the Tb^{3+} emission in **1** was the same ($3.78 \pm 0.04 \text{ ms}$) as that when measured from linear or multiphoton excitation. The room-temperature excitation spectrum of the Tb^{3+} emission of **1** shows a broad feature between 400 and 250 nm, for which the lower-energy part is assigned to the triplet state of **L**.

The 800 nm excited emission spectra of **1** also exhibits a strong band at 400 nm due to SHG, and the emission intensity–power dependence on a log scale is linear with a slope of 2 (Figure 4). It is interesting that the ligand **L** alone gives $S_1 \rightarrow S_0$ emission under three-photon excitation at 800 nm, as demonstrated by the power dependence (Figure 5). However, **L** does not exhibit SHG, as expected for a centrosymmetric material.

In conclusion, another possible alternative to metal-center sensitization has been provided, which opens up the potential for further studies of probes and imaging linkers, particularly in biosystems where the metal center has previously been linked to both an antenna and a target. Previously proposed mechanisms for antenna–lanthanide ion energy transfer have involved the ligand triplet¹³ or singlet¹⁰ states. In the present case, the ligand $S_1 \rightarrow S_0$ emission overlaps the $\text{Tb}^{3+} {}^5\text{D}_4$ energy level. Therefore, following excitation from S_0 to S_1 , the energy-transfer pathway in **1** most likely corresponds to $S_1 \rightarrow {}^5\text{D}_4$. The major distinction with previous studies is that the antenna is unlinked in the present case. Clearly, at such relatively large separations, the antenna–metal energy transfer in **1** does not occur through exchange interactions or higher multipole interactions but more likely by a dipole–dipole process.

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- (17) The 2-methoxy benzoic acid *N'*-(2-methoxybenzoyl)hydrazide (**L**) was obtained from malonic acid (19.4 mg, 0.147 mmol), which was dissolved in 40 ml of dichloromethane with sodium hydroxide (2 equiv) in 10 ml of water. Then 2-methoxybenzyl chloride (125 mg, 0.734 mmol) was added dropwise to the mixture in an ice bath. The mixture was then stirred at room temperature for 1 h. After the reaction was complete, the solution was neutralized, extracted, and evaporated to leave the crude product, which was then purified by column chromatography on silica gel. Colorless crystals were obtained upon the slow evaporation of solvent at room temperature. The ligand **L** (2-methoxy benzoic acid *N'*-(2-methoxybenzoyl)hydrazide) was isolated as an off-white powder (16mg, 0.053 mmol, 73%), which was recrystallized. Analysis of **L**. ¹H NMR (400 MHz, MeOD): δ 7.96–7.95 (1 H, d, J = 7.84 Hz), 6.98–6.96 (1 H, d, J = 8.4 Hz), 7.65–7.63 (1H, d, J = 7.6 Hz), 3.85(2H, s). ¹³C NMR (400 MHz, MeOD): δ 169.1 (C), 165.4 (C), 130.2 (C), 128.3 (2 \times CH), 114.7 (2 \times CH), 56.0 (CH₃). ESI–MS: m/z 301.3 [M+H]⁺. Crystal data for **L**: C₁₆H₁₆N₂O₄, M = 300.31, orthorhombic, *Pbca*, a = 13.825(2), b = 7.1620(10), c = 15.098(2) Å, V = 1494.7(4) Å³, T = 298 K, Z = 4, μ (Mo K α) = 0.97 cm⁻¹, 9380 reflections measured, 1705 unique, 998 observed reflections [$I > 2.0\sigma(I)$] were used in all of the calculations. R = 0.0400, R_w = 0.0440. Tb(NO₃)₃·6H₂O (47 mmol) and **L** (90 mmol) were dissolved in methanol (15 ml). Single crystals of **1** were obtained by slow evaporation (yield 78%). Anal. Found for **1**: C, 37.49; H, 3.94; N, 9.58. Calcd. for C₃₂H₄₀N₇O_{21.5}Tb: C, 37.47; H, 3.93; N, 9.56. FAB–MS: m/z 1642. Crystal data for **1**: C₃₂H₄₀N₇O_{21.5}Tb, M = 1017.63, orthorhombic, *P2₁2₁2₁* (#19), a = 7.9118(9), b = 21.464(3), c = 24.667(3) Å, V = 4188.9(8) Å³, T = 298 K, Z = 4, μ (Mo K α) = 17.74 cm⁻¹, 26020 reflections measured, 5364 unique, 4655 observed reflections [$I > 2.0\sigma(I)$] were used in all of the calculations. R = 0.031, R_w = 0.031. Crystallographic information is available as CCDC 618011 (**L**) and 617835 (**1**) from the Cambridge Crystallographic Data Centre (CCDC). These data may be obtained free of charge from the CCDC via the web link www.ccdc.cam.ac.uk/data_request/cif.
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