Photon Upconversion in a Molecular Lanthanide Complex in Anhydrous Solution at Room Temperature

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S *Supporting Information*

ABSTRACT: Molecular photon upconversion luminescence was observed from an ion-associated complex of an erbium chelate of 2-thenoyltrifluoroacetone and a near-infrared-emitting cyanine dye in anhydrous solution at room temperature. In the complex erbium was sensitized by the organic antenna dye excited at 808 nm. The result was characteristic erbium emission at 510−565 nm with second-order dependence on the excitation power, suggesting a dye-sensitized energy transfer upconversion mechanism. Compared to inorganic upconverting nanoparticles, the organic molecular dye-sensitized complexes are expected to offer higher molar absorptivity, smaller well-defined size, and simpler addition of functional groups.

KEYWORDS: *chelates, dye-sensitized, lanthanides, luminescence, upconversion*
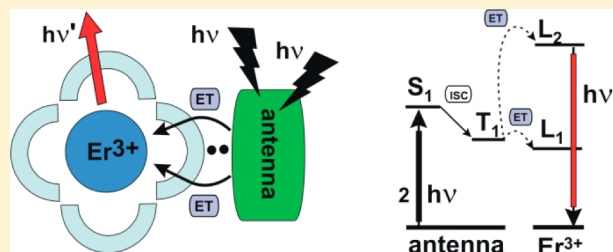
We report for the first time photon upconversion (UC) luminescence from a molecular lanthanide complex measured in anhydrous solution at room temperature. The realized upconverting system was an ion-associated complex of an erbium chelate and organic dye, where the organic dye operates as an efficient light-harvesting antenna of near-infrared excitation. Upon irradiation of the complex at 808 nm, an energy transfer upconversion process between the antenna dye and the erbium ion results in sequential, two-step excitation of the ion. The energy is then released as characteristic erbium emission observed at 510−565 nm with second-order dependence on the excitation power, indicating a dye-sensitized energy transfer upconversion mechanism. Compared to inorganic photon upconverting nanoparticles, the organic molecular dye-sensitized upconverting complexes are expected to offer higher molar absorptivity, smaller well-defined size, and simpler addition of functional groups.

To date, the most efficient photon upconverting compounds are inorganic solid-state materials. They are based on an optically inactive host lattice (e.g., $NaYF_4$) matrix doped with optically active lanthanide ions (such as Yb^{3+}, Er^{3+}, and Tm^{3+}). Anti-Stokes luminescence of these materials has been utilized in a diverse range of applications such as bioimaging,[1,2] biomolecular binding assays,[3,4] solid-state lasers,[5,6] and security and forensic applications,[7,8] and as wavelength converters on solar cells.[9] While the UC efficiency is highest in bulk material, upconverting nanoparticles (UCNP) are more useful in many applications. The UC emission has the characteristic properties of the lanthanide luminescence such as long lifetimes and narrow emission bands. In addition UC luminescence has several unique advantages. The near-infrared (NIR) excitation

is less damaging to organic tissues and offers a deeper penetration depth compared to the ultraviolet and visible excitation used with conventional photoluminescent labels. The possibility of the detection of upconversion emission either at red or even near-infrared wavelengths enables also the measurement of optically challenging physiological samples.[10] Further, the NIR excitation and large anti-Stokes shift result in a total elimination of the autofluorescence and scattered excitation light.[11] However, UCNPs also have some severe drawbacks especially considering their use as molecular labels. Lanthanide-doped crystalline materials suffer from narrow absorption bands and very low molar absorption coefficients of the lanthanide ions ($\varepsilon < 10\ M^{-1}\ cm^{-1}$).[12] Also, the quantum yields of UCNPs are low. Further drawbacks of UCNPs are their large dimension, size and shape distribution, and complex surface chemistry required for water solubility and bioconjugation. The size (ca. 10−100 nm) can result in sterical hindrance and is disadvantageous in applications utilizing Förster resonance energy transfer, which is limited to donor−acceptor distances less than 10 nm.

In a recent report the low absorbance of lanthanide ions was circumvented by using organic dye molecules as light-harvesting antennas on the surface of UCNPs.[13] The antenna dye provided a wide absorbance spectrum and a high molar absorption coefficient, resulting in a dramatic enhancement (factor of ca. 3300) of the UC luminescence upon dye sensitization. In the core of the inorganic crystalline nanoparticles the lanthanide ions are shielded from the quenching

effect of the environment, while in molecular lanthanide chelates the ions are more vulnerable to quenching by high-frequency oscillators present in the solvent and ligand framework.[14−16] Due to the high probability of nonradiative relaxation, the molecular UC has been considered to be impossible.[17] Despite the issue of quenching, a detectable UC luminescence has been reported for chelates of Er, Tm, and Nd ions in aqueous solutions.[18] This required a very high excitation power as the lanthanide ions were directly excited with two coincident 100 kW laser pulses focused to a spot size of ca. 100 μm. UC in an organic matrix has been obtained in mixed lanthanide polymer systems: $Yb_{1−x}Tb_x(PFBS)_3$ and $Yb_{1−x}Tb_x(PFBS)_3$, where PFBS is perfluorobutanesulfonate.[19] Molecular lanthanide-based upconversion has been reported for a trinuclear chromium−erbium system with d−f−d structure bearing two sensitizing Cr(III) ions in the molecule.[20,21] However, UC luminescence was reported only at very low temperatures in the solid state. Efficient non-lanthanide-based molecular photon upconversion in solution and solid state has been obtained with sensitized triplet−triplet annihilation (TTA).[22] The advantage of the TTA is the low excitation power density requirement, but the need of separate sensitizer and acceptor molecules to obtain TTA in solution will hinder, for example, applications in molecular labeling. Here we present the first evidence of molecular photon upconversion luminescence by an organic antenna-sensitized erbium complex measured in anhydrous solution at room temperature. Our sample was an ion-associated complex of the negatively charged erbium chelate $Er(TTA)_4^-$ (TTA = 2-thenoyltrifluoroacetone) and the organic antenna cation IR-806 (Figure 1).
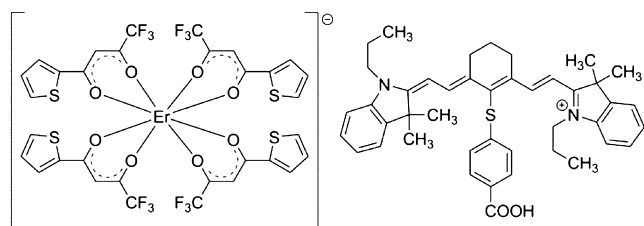

Figure 1. Chemical structure of the ion-associated complex Er(TTA)₄(IR-806).

We chose the ion-associated complex as a molecular platform, because it allowed an easy exchange of the chromophore dye associated with the lanthanide ion without extensive synthesis. The building blocks of the complex were selected based on the performance of the individual parts. The erbium chelate anion $Er(TTA)_4^-$ has been shown to function in an ion-associated complex emitting at 1500 nm,[23] and the chromophore dye IR-806 has successfully been used as an antenna for NaYF₄:Yb,Er nanoparticles.[13] Details of the synthesis and experimental methods are given in the Supporting Information. Normalized absorption and near-infrared fluorescence spectra of the IR-806 dye salt and Er(TTA)₄(IR-806) complex in CDCl₃ are shown in Figure 2. The absorption band of the IR-806 dye salt has a maximum at 808 nm, and the peak wavelength of fluorescence spectra is at 827 nm. In Figure 2 the wavelength of the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ transition of the Er^{3+} ion is shown as a vertical dashed line at 980 nm (10 204 cm^{-1}).[24]

The UC emission spectra of Er(TTA)₄(IR-806) and control samples without the IR-806 or IR-806 alone excited at 808 nm

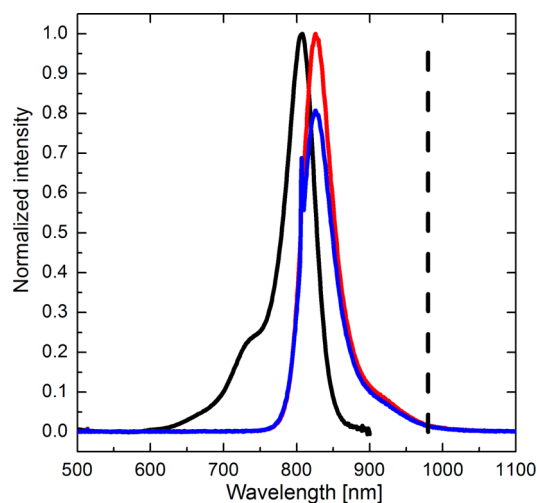**Figure 2.** Normalized absorption and fluorescence emission spectra of the IR-806 dye salt and Er(TTA)₄(IR-806) ion-associated complex in CDCl₃. Fluorescence excited at 808 nm. Normalized IR-806 (100 μM concentration) absorption (black line), normalized IR-806 (1 μM) fluorescence (red), and Er(TTA)₄(IR-806) (1 μM) fluorescence (blue) relative to IR-806 fluorescence. Vertical dashed line presents the wavelength corresponding to the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ absorption transition of the Er^{3+} ion.

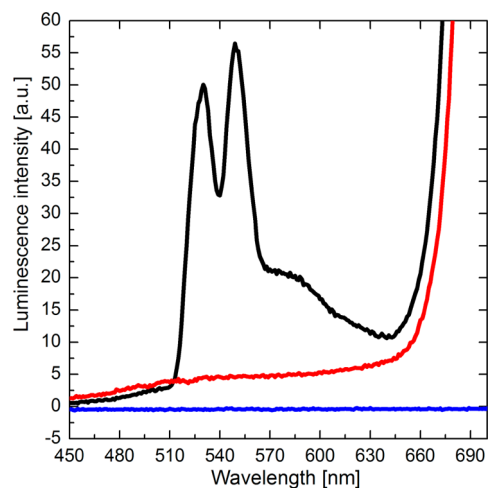are shown in Figure 3. The spectrum of Er(TTA)₄(IR-806) shows emission bands at 510−540 and 540−565 nm, which are

Figure 3. Emission spectra of Er(TTA)₄(IR-806) (black line), Er(TTA)₄K (blue), and IR-806 dye salt (red) dissolved in CDCl₃ (100 μM) excited at 808 nm. Emission slit 10 nm.

characteristic of the Er^{3+} ion and correspond to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^2S_{3/2} \rightarrow {}^4I_{15/2}$ transitions, respectively. Erbium emission bands were not observed when the light-harvesting chromophore was absent (Er(TTA)₄K) or when only IR-806 dye was present. Neither were the bands observed with any of the above-mentioned samples when excited at 968 nm (data not shown). The Er^{3+} transitions as the source of the emission bands are supported first by the wavelength of the emission bands. They overlap reasonably well with green UC emission bands of NaYF₄:Yb,Er nanoparticle material excited at 968 nm (Supporting Information Figure S1). Also the absence of the bands in the spectra of IR-806 indicates the Er^{3+} transitions as the source of these emission bands. The lack of erbium

emission bands in the spectra of the $Er(TTA)_4K$ sample strongly suggests the sensitization of erbium emission through the IR-806 dye. Hence, we conclude that the emission bands observed at 510−565 nm under 808 nm excitation are indeed due to the UC luminescence of Er^{3+} ions sensitized by the IR-806 dye. In addition to the Er^{3+} ion emission bands at 510−540 nm and 540−565 nm the $Er(TTA)_4(IR-806)$ UC emission spectrum has two other features. These are a shoulder at 560−640 nm and a steep rise of the emission intensity starting at 650 nm. These features are discussed in the Supporting Information (Figure S2).

Additional proof of the UC nature of the observed emission bands of $Er(TTA)_4(IR-806)$ under 808 nm excitation was obtained by measuring the UC emission spectra as a function of the excitation power (Supporting Information Figure S3) and plotting the emission intensity at 525 nm as a function of the excitation power (Figure 4). Linear fit of the log−log
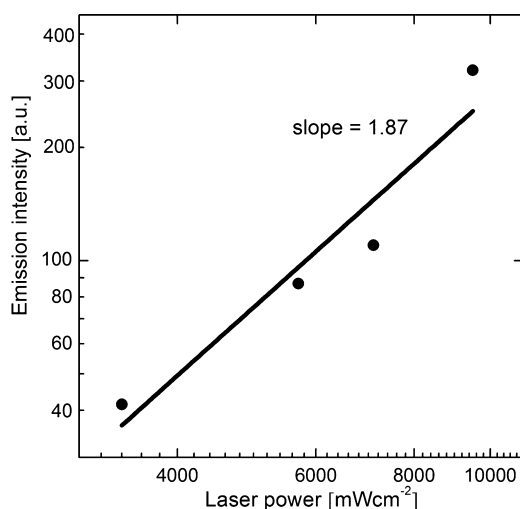

Figure 4. Emission intensity at 525 nm vs excitation power dependency of $Er(TTA)_4(IR-806)$ in $CDCl_3$ (100 μM) excited at 808 nm. Linear fit of the log−log transformed data.

transformed data produced a slope of 1.87, which is close to the theoretical value of 2 for a two-photon process.[25] This result supports the hypothesis that the observed emission bands are due to a dye-sensitized two-photon UC process. The energy level diagram of the proposed excitation−emission path is presented in the Supporting Information, Figure S4.

The intensity of the UC emission was lower than obtained with $NaYF_4$:Yb,Er nanoparticles excited at 968 nm. However, we believe that emission intensity can be improved by the design of the molecular structure of the chelate or by optimizing the photophysical properties of the chromophore. In the design of the chelate structure the main concern is to enable efficient energy transfer to the Er^{3+} ion, but at the same time minimize the quenching of the upconverted emission. IR-806 dye's emission at 827 nm is decreased by only about 20% in the $Er(TTA)_4(IR-806)$ complex (Figure 2), indicating an incomplete energy transfer to the Er^{3+} ion. Resonance energy transfer is highly distance dependent, and the efficiency of the resonance energy transfer could be increased by incorporating the antenna chromophore into the ligand structure. A significant part of the energy is probably released through $^4I_{11/2} \rightarrow {}^4I_{15/2}$ (at 980 nm) and $^4I_{13/2} \rightarrow {}^4I_{15/2}$ (at 1500 nm) transitions before the second resonance energy transfer step

raises Er^{3+} to the $^4F_{7/2}$ level. The efficiency of the energy transfer upconversion process can be improved by increasing the number of sensitizers.[21] Hence, incorporation of two chromophore moieties into the complex structure should improve UC efficiency. The assumed critical photophysical properties of the sensitizing chromophore include a triplet level of optimal energy relative to the lanthanide ion energy levels,[26] a low absorbance at the lanthanide ion emission wavelengths, and low photobleaching. In the $Er(TTA)_4(IR-806)$ complex a part of the Er^{3+} excitation energy was lost back to the IR-806 dye (Supporting Information Figure S2) and the IR-806 dye was photobleached ca. 50% in 30 s with the excitation power of 9.5 W cm^{-2} (Supporting Information Figure S5).

The main advantages of antenna-sensitized molecular upconversion compared to the inorganic UCNPs are the substantially higher absorbance, the smaller and uniform size, and simpler addition of functional groups. With UCNPs multiexponential luminescence decays are commonly observed, and hence, the lifetime-based analysis is difficult. Multi-exponential decays are caused by variation in local environment of the dopant ions, which has been explained by surface effects, multiple crystal sites, and differences in local dopant concentrations.[27,28] In organic chelates the site of the lanthanide ion is fixed and single-exponential lifetimes can be expected.

In this study we have demonstrated for the first time an organic antenna-sensitized Er-based molecular photon upconversion luminescence in solution phase at room temperature. The characteristic erbium emission bands at 510−565 nm were observed when ion-associated complex $Er(TTA)_4(IR-806)$ dissolved in deuterated chloroform was excited at 808 nm. The appearance of the emission bands only when the organic antenna dye IR-806 was present in the sample strongly suggests sensitization via the IR-806 dye. The upconversion nature of the emission was confirmed by the second-order dependence between the emission intensity and the excitation power. The efficiency of molecular upconversion is still far below the efficiency of the best inorganic upconverting materials; a rough estimate is that the quantum yield of $Er(TTA)_4(IR-806)$ is below 0.1% at 9.5 W cm^{-2} excitation power. There remains a lot of optimizing to be done before molecular upconversion is feasible in applications. Essential challenges entail improving the resonance energy transfer efficiency, promoting the upconversion process, and protecting the lanthanide ions from quenching. However, our result serves as a first proof of the molecular photon upconversion in solution phase at room temperature and will hopefully arouse interest in the phenomenon.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and measurement details, supporting figures, and details of proposed upconversion mechanism. This material is available free of charge via the Internet at http://pubs.acs.org/photonics.

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Notes

The authors declare no competing financial interest.

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