Up-Conversion Luminescence in Molecular Cyano-substituted Naphthylsalophen Lanthanide(III) Complexes

Journal:	*ChemComm*
Manuscript ID	CC-COM-12-2020-008128.R1
Article Type:	Communication

COMMUNICATION

New Up-Conversion Luminescence in Molecular Cyano-substituted Naphthylsalophen Lanthanide(III) Complexes

Received 00th January 20xx,
Accepted 00th January 20xx
DOI: 10.1039/x0xx00000x

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A new naphthylsalophen and its 3:2 ligand-to-lanthanide sandwich-type complexes were isolated. When excited at 380 nm, the complexes display the characteristic metal-centred emission for Nd^{III}, Er^{III} and Yb^{III}. Upon 980 nm excitation, in mixed lanthanide and the Er complexes, Er-centred upconversion emission at 543 and 656 nm is observed, with power densities as low as 2.18 W cm^{-2}.

The unique luminescence properties of lanthanide (Ln^{III}) ions make their complexes interesting for a variety of applications.[1-3] These properties include colour purity, due to the core nature of the *f* orbitals involved in the emission process, and long luminescence lifetimes, due to the electronic-dipole forbidden nature of the *f-f* transitions, which enable time-delayed emission spectroscopy with increased signal-to-noise ratio.[4-6] The forbidden nature of these transitions makes sensitization of the emission more efficiently achieved through coordinated ligands in a process called the antenna effect.[4-6]

For low energy sensitization, excitation can be achieved through non-linear optical processes, such as two-photon absorption or cumulative effects of multiple first-order absorption phenomena, namely up-conversion (UC). The latter can occur through either excited-state absorption (ESA) or energy transfer up-conversion (ETU) (Figure 1a).[7] The presence of spin allowed transitions results in a high absorption cross-section, and long-lived intermediate excited states enable the use of inexpensive and low power continuous-wave lasers to access them.[8] In ETU a sensitizer ion absorbs low-energy photons, followed by energy transfer (ET) to the activator ion, which then emits in a characteristic wavelength. Er^{III} and Yb^{III}-doped nanoparticles (NPs) are among the most efficient UC systems.[9-10] The resonance between the excited states of Yb^{III} ($^4F_{5/2}$, ~10,624 cm^{-1}) and Er^{III} ($^4I_{11/2}$, ~10,346 cm^{-1}) improves the ET rates, and thus contributes to high UC emission intensities. While these NPs find wide application in bioimaging,[11-14] as they can be excited in a region of the spectrum where tissues have low absorption,[15-16] controlling their size, low cell penetrability, undesirable accumulation in the body, and stabilizing the crystalline phase that yields the highest UC luminesce intensity, such as the β-phase of $NaYF_4$,[17-18] are challenges for their use *in vivo*.[19-20]

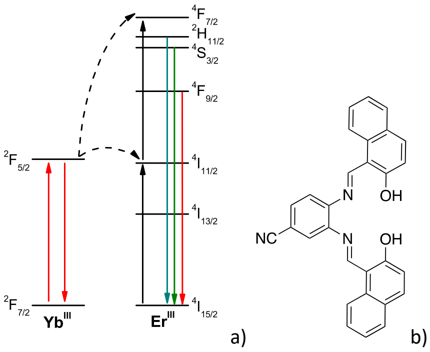

Figure 1. a) Energy level diagram illustrating the up-conversion process through ESA (two black up-arrows on Er^{III}) and ETU (dashed arrows, red up-arrow on Yb^{III} followed by top black up-arrow on Er^{III}). b) Structure of H_2L-CN.

In contrast, in Ln^{III} complexes toxicity and low cell penetrability are not inherent and emission properties do not depend on the crystalline phase. In addition, judiciously designed ligands allow tuning of solubility, biocompatibility, and photophysics of the complexes, among other properties.[21-23]

UC is important in bioimaging and sensing applications and there is substantial interest in small-molecule probes,[24-25] yet examples using Ln^{III} complexes are less common than those of Ln-$NaYF_4$-based NPs. The lattice on the latter is a low-phonon system, which is necessary for good UC efficiency.[26] Piguet and co-workers pioneered the UC luminescence using Ln^{III}

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Financial support of this work is gratefully acknowledged (NSF CHE-1800392 to AdBD and DOE-BES CSGB DE-SC0019177 to AEVG).

Electronic Supplementary Information (ESI) available: [Crystallographic details, syntheses, spectroscopic and spectrometric characterization]. See DOI: 10.1039/x0xx00000x complexes.[27] Charbonnière and co-workers demonstrated UC luminescence in deuterated water in a dimeric Er^{III} complex, in which this ion is both activator and sensitizer.[28] Hyppännen and co-workers[29] and more recently, Piguet and co-workers demonstrated that mononuclear Er^{III} complexes are capable of showing UC luminescence.[30] Many of the known examples have low UC emission intensity despite deuteration of the ligand, or require a transition metal as sensitizer or use metalorganic frameworks to reduce vibrational quenching; others, due to the long distances between the metal ions, require high excitation laser power densities to increase the ET efficiency.[31-35] Thus, the isolation of efficient Ln^{III}-based UC molecules is a current challenge.[36-37]

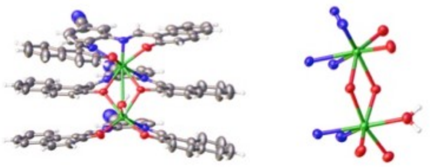

Figure 2. Left. Projection of the front view of [Er_2(L-CN)$_3$(H_2O)]. Right. Coordination environments of Er1(bottom) and Er2 (top). Carbon atoms are shown in grey, nitrogen in blue, oxygen in red, and erbium in green.

Recently, Gorden and co-workers showed that naphthylsalophen ligands form Ln^{III} complexes with a rigid sandwich structure in a 2:3 (Ln^{III}:ligand) stoichiometry.[38] Because the Ln^{III}-Ln^{III} distance in these compounds is in the range 3.768-4.016 Å, well within the range for optimal Förster ET,[7, 39] these structures are good candidates for UC luminescence. Therefore, to increase our knowledge of ligand and complex architectures that enable UC properties in Ln^{III}-based molecular systems, we synthesized mixed Er^{III}, Yb^{III} and pure Er^{III} complexes containing a new naphthylsalophen ligand with the cyano- electron-withdrawing group in the backbone. These compounds indeed display UC luminescence, as described below, adding new examples to a small group of molecular Ln^{III} complexes that exhibit this property.

The protonated cyano-naphthylsalophen H_2L-CN (Figure 1b) is isolated by condensation of 3,4-diaminobenzonitrile with 2-hydroxynaphthaldehyde in EtOH. The Ln^{III} complexes (Gd^{III}, Nd^{III}, Er^{III}, and Yb^{III}) are prepared by addition of the Ln^{III} metal salt, either the chloride or the acetate, in MeOH to the ligand in THF and of triethylamine (TEA) to deprotonate the ligand.

X-ray quality crystals of H_2L-CN indicate that the compound crystalizes in the space group P 21/c (Figure S18) and does not display interactions with solvent molecules of crystallization.

The structure of [Er_2(L-CN)$_3$(H_2O)] (Figures 2 and S19) shows features similar to previously reported Ln^{III} triple decker complexes.[38] The Er2 metal centre is 8-coordinate and the coordination sphere is completed by the ligand, while the Er1 metal centre is seven-coordinate, bound to ligand and one water molecule (Figure 2 right). The distance between metal centres is 3.816 Å, within the Förster ET range.[7, 39]

Deconvolution of the fluorescence and phosphorescence spectra of the Gd^{III} complexes (Figure S14) into the vibrational components yields energies at ~18,400 and ~15,900 cm^{-1} for the excited singlet and triplet levels, respectively (Figures S14(b) and S14(c)). The triplet energy level is suitably located to sensitize the NIR-emitting Ln^{III} (Nd^{III}, Yb^{III} and Er^{III}), as shown in Figure S15. The one-photon solution excitation and emission spectra of Nd^{III}, Yb^{III} and Er^{III} complexes in dichloromethane are shown in Figure S16. The excitation spectra of the complexes are composed of broad bands, consistent with sensitization of Ln^{III} emission through the ligand, as indicated by the overlap of excitation and absorption spectra shown, representatively, for the Yb^{III} complex in Figure S16. The emission spectrum of the Nd^{III} complex shows the expected $^4F_{3/2} \rightarrow {}^4I_J$ (J = 9/2 – 13/2) transitions. For the Yb^{III} complex the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transitions, and for the Er^{III} complex the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions are observed. The quantum yields of sensitized emission (ϕ_L^{Ln}) for the Nd^{III} and Yb^{III} complexes are summarized in Table 1. They are comparable with reported values for other complexes of these ions.[40-42] The emission lifetimes of the Yb^{III} complexes, summarized in Table 1, are comparable as well with values reported for this ion.[41, 43-44] The excited state decay curves were fitted to a bi-exponential, consistent with the presence of ions in two different coordination environments (Figure S17). We attribute the shortest lifetime to the Yb^{III} site with a coordinated solvent molecule, and the longest one to the Yb^{III} bound only to ligand.

We isolated multi-Ln^{III} complexes by adapting the procedure described for the homonuclear complexes. Y^{III} as diluting ion, Yb^{III} and Er^{III}, or Yb^{III} and Er^{III} were added to a solution of the deprotonated ligand in 2:3 (Ln:L) molar ratio. The [($Y_{0.76}Yb_{0.16}Er_{0.08}$)$_2$(L-CN)$_3$($H_2O$)] complex, with metal stoichiometry determined through energy-dispersive X-ray spectroscopy (EDS), can be excited in the solid state by two low energy photons through an UC process.[7] The resulting spectrum (Figure 3) shows Er^{III}-centred transitions in the green ($^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$) and red ($^4I_{9/2} \rightarrow {}^4I_{15/2}$) upon excitation at 980 nm. The quadratic dependence of the emission intensity (I) on the laser power (P) (inset of Figure 3) confirms the 2-photon nature of the process (data in Table S1). UC emission is observed for power densities as low as 2.18 W cm^{-2}, which compares favourably with known efficient systems (29 W cm^{-2}).[28, 30-31, 45]

Emission following UC excitation is also observed for [($Yb_{0.78}Er_{0.22}$)$_2$(L-CN)$_3$(H_2O)] and [Er_2(L-CN)$_3$(H_2O)] (Figure 4, top and bottom traces, respectively) in the solid state. Although there is an increase of the emission intensity for [($Yb_{0.78}Er_{0.22}$)$_2$(L-CN)$_3$(H_2O)] as compared with the trimetallic complex, the concentration of Er^{III} is 4.7-fold higher in the former. In [($Yb_{0.78}Er_{0.22}$)$_2$(L-CN)$_3$(H_2O)] and [Er_2(L-CN)$_3$(H_2O)] UC emission was observed with power densities as low as 2.18 W cm^{-2} and 6.25 W cm^{-2}, respectively. The UC emission intensity of the latter is lower, due to non-radiative cross-relaxation.[46] The complexes did not show upconversion when dissolved in acetonitrile, chloroform and deuterated chloroform.

In conclusion, we isolated three Ln^{III} complexes with a cyano-naphthylsalophen ligand with a 2:3 stoichiometry and sandwich structure. These complexes display efficient one-photon Nd^{III}- and Yb^{III}-centred emission and weak Er^{III}-centred emission.

Complexes containing a mixture of Er^{III} and Yb^{III}, or Er^{III}, Yb^{III} and Y^{III} or just Er^{III} also display Er-centred red and green emission upon excitation with a 980 nm laser at low power densities, indicative of UC, making these systems rare examples of upconverting Ln^{III}-based molecules. This work increases our knowledge of molecular complexes of Ln^{III} ions that can be excited at low energy with a low intensity laser and are thus of potential interest for biological imaging applications.

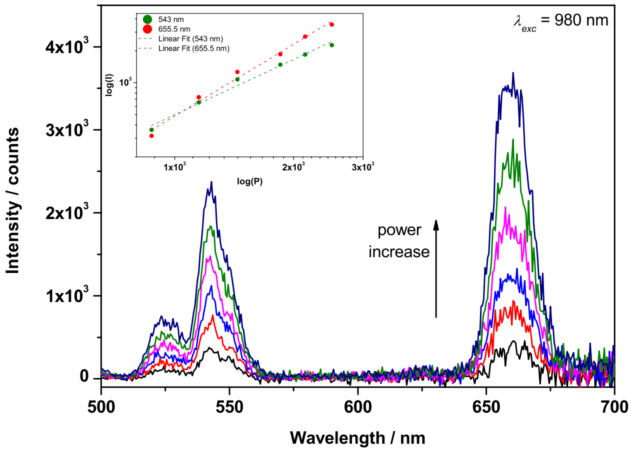

Figure 3. Two-photon UC emission spectra of [(Y$_{0.76}$Yb$_{0.16}$Er$_{0.08}$)$_2$(L-CN)$_3$(H$_2$O)] in the solid state using variable laser power. Inset shows plot of the log of the emission intensity *I* at 543 nm (green dots) or 655.5 nm (red dots) as a function of the log of the laser power *P*. λ_{exc} = 980 nm, *P* = 0.873 – 2.500 W.

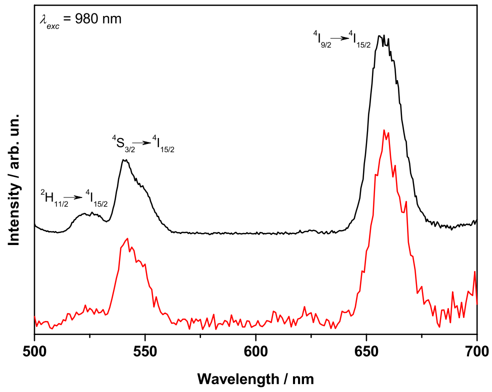

Figure 4. Two-photon UC emission spectra of (a) [(Yb$_{0.78}$Er$_{0.22}$)$_2$(L-CN)$_3$(H$_2$O)] (black upper trace) and [Er$_2$(L-CN)$_3$(H$_2$O)] (red bottom trace) in the solid state. λ_{exc} = 980 nm, *P* = 2.5 W.

Table 1. Singlet ^1S and triplet ^3T state energies of the ligands, excited state lifetime τ, and quantum yield Φ_L^{Ln} of sensitized efficiency for the Nd^{III}, Yb^{III} and Er^{III} complexes. λ_{exc} = 380 nm and [complex] = 1×10^{-4} M.

Complexes	Solvent	1S[a] [cm^{-1}]	^{3}T[a] [cm^{-1}]	τ[b] [μs]	Φ_L^{Ln} [%]
[Nd$_2$(L-CN)$_3$(H$_2$O)]	CH$_2$Cl$_2$	18,420±70	15,910±50	[c]	0.0054±0.0009
[Yb$_2$(L-CN)$_3$(H$_2$O)]				1.230±0.027 (81.1) 6.801±0.197 (18.9)	0.154±0.013
[Er$_2$(L-CN)$_3$(H$_2$O)]				[c]	[c]

[a]Determined at 77 K, using the analogous Gd complexes.[47] [b] The values in parenthesis indicate the percent contribution of each lifetime. [c] Too weak to be quantified.

Author Contributions

JHSKM performed the one- and two-photon characterization of the complexes, EAH synthesized ligand and metal complexes and performed solution characterization, EEH initially synthesized the ligand, GWR contributed to synthesis and solution characterization, JDG did X-ray crystallographic characterization. Experimental work and manuscript preparation were supervised by AEVG and AdBD.

Conflicts of interest

There are no conflicts to declare.

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