Upconverted Photosensitization of Tb Visible Emission by NIR Yb Excitation in Discrete Supramolecular Heteropolynuclear Complexes

Nabila Souri,[†,‡] Pingping Tian,[†] Carlos Platas-Iglesias,[§] Ka-Leung Wong,[∥] Aline Nonat,[†] and Loïc J. Charbonnière*,[†] [ID]

[†]Laboratoire d'Ingénierie Moléculaire Appliquée à l'Analyse, Institut Pluridisciplinaire Hubert Curien, IPHC, UMR 7178, CNRS, Université de Strasbourg, ECPM, 25 rue Becquerel, 67087 Strasbourg Cedex, France

[‡]Laboratoire d'électrochimie des Matériaux Moléculaires et des Complexes, LEMMC, Faculté de Technologie, Université de Sétif-1, 19000 Sétif, Algeria

[§]Centro de Investigacións Científicas Avanzadas (CICA) and Departamento de Química Fundamental, Universidade da Coruña Campus da Zapateira-Rúa da Fraga 10, 15008A Coruña, Spain

[∥]Department of Chemistry, Hong Kong Baptist University, Hong Kong SAR

S *Supporting Information*

ABSTRACT: Addition of Tb^{3+} salts to a solution of a (YbL_D) complex in D_2O resulted in the formation of $[(YbL_D)_2Tb_x]$ (x = 1 to 3) complexes that, upon NIR excitation at 980 nm, showed an unprecedented Yb to Tb upconversion sensitization phenomenon resulting in the observation of the typical green emission of Tb.

Photonic upconversion (UC) allows for the conversion of low energy photons, typically in the near-infrared (NIR) region, into photons of higher energy, generally in the visible or NIR regions.[1] This unconventional anti-Stokes process has found many applications such as in lasers,[2] and there is a growing interest to develop fluorescence free bioanalytical assays and theranostic applications.[3] However, UC processes are almost entirely restricted to solid state materials and nanomaterials and only a handle of examples have been reported for discrete molecular systems[4−6] in organic solvents, or very recently in D_2O[7] thanks to the formation of a supramolecular Ln dimer.[8] The development of discrete molecular UC devices would remove the drawbacks associated with the biotoxicity of nanomaterials[9] and might open new perspectives in biological labeling applications. NIR to NIR and NIR to red upconverters would be particularly well adapted for imaging applications,[10] both excitation and emission being suited to the biological window[11] for a better penetration of the exciting/emitting light through biological tissues. Additionally, the lack of spurious fluorescent signals also generates very low background noise and a concomitant improved sensitivity for fluoro-immunoassays.[12,13]

We have recently reported the development of the phosphonated bipyridyl based ligand L (Scheme 1).[14] Considering the very good shielding of the Ln cations by the octadentate ligand and the promising photophysical properties of the (YbL) complex in water and D_2O (Table 1), we also developed the synthesis of L_D, the analogue of L deuterated on all methylenic positions. For the purpose of clarity, the coordination of the complexes inside the cavity of the ligand will be denoted (LnL). In view of the outstanding work of Seitz and co-workers

Scheme 1. Ligand L and Its Partially Deuterated Analogue L_D.
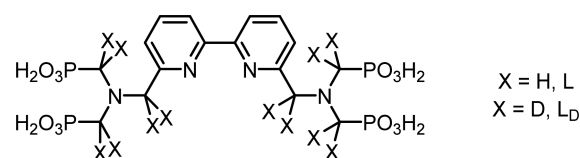
on the luminescence properties of Yb complexes with deuterated ligands,[15] deuteration of the methylene bridge was expected to decrease nonradiative vibrational quenching due to the CH oscillators and to improve the luminescence properties.

Full synthetic details for L_D can be found in the Supporting Information, whereas the mononuclear $[LnL_{(D)}]$ complexes were obtained according to reported protocols.[14] Table 1 summarizes the spectroscopic properties of the isolated mononuclear $(LnL_{(D)})$ complexes.

The absorption spectra of the complexes are dominated by the strong $\pi \rightarrow \pi^*$ transitions centered on the bipyridyl units, pointing at 310 nm in the complexes (Figure 1). Upon excitation into the maximum of absorption, the emission spectra display the sharp and characteristic emission bands of each Ln ion, with four main emission bands at 485, 545, 580, and 620 nm attributed to the $^5D_4 \rightarrow ^7F_J$ electronic transitions (J = 6 to 3, respectively) for Tb and a broad band with maximum at 980 nm attributed to the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition for Yb.[18] The corresponding excitation spectra (Figure S1) are in perfect agreement with the absorption spectra confirming that the photosensitization originated from an antenna effect with energy transfer from the ligand to the Ln cations. It could be noticed that the deuteration had a very strong influence on both the excited state lifetime and quantum yield of the Yb complex, with a very long 65 μs lifetime for $[YbL_D]$ in D_2O, among the longest reported in the literature for Yb complexes.[15,19]

For all complexes, the luminescence decays could be perfectly fitted with monoexponential functions, pointing to the presence of a single species in solution. Surprisingly, the luminescence

Table 1. Spectroscopic Properties of (TbL), (YbL), and (YbL$_D$) Complexes

	λ_{max} (nm) [ε (M^{-1}·cm^{-1})]	τH$_2$O (μs)	τ_{D_2O} (μs)[a]	ϕ_{H_2O}[b]	ϕ_{D_2O}[b]	q
(TbL)	310 [10700]	890	899	0.33[c]		0
(YbL)	310 [13100]	2.3	35	0.16[d]	1.3[d]	0[e]
(YbL$_D$)	310 [13100][f]	3.3	65	0.2[d]	3.8[d]	0[e]

[a]λ_{exc} = 310 nm, estimated error ±10%. [b]λ_{exc} = 310 nm, estimated error ±15%. [c]Using R6G in water as reference (ϕ = 0.76).[17a] [d]Using cardiogreen in MeOH as reference (ϕ = 0.078).[17b] [e]Calculated according to ref 16. [f]The absorption was assumed to be the same as that of the nondeuterated complex.

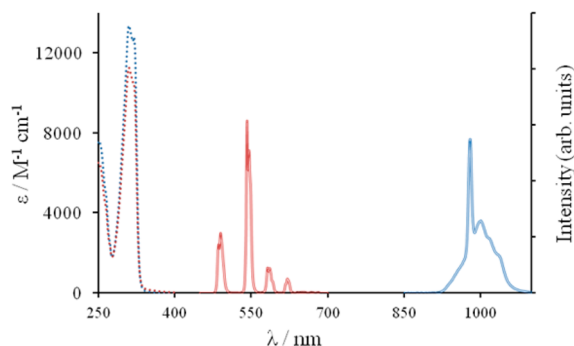**Figure 1.** UV−vis absorption (dotted lines), and emission (λ_{exc} = 310 nm, full lines) spectra for (YbL) (blue) and (TbL) (red) in TRIS/HCl, 0.01 M, pH 7.0.

decay of the Tb complex was rather short (890 μs). This particular behavior was possibly ascribed to a Tb ($^5D_4$) to ligand ($^3\pi\pi^*$) back energy transfer process, as observed in other bipyridyl-based Tb complexes.[20] On the other hand, the luminescence properties of the Yb complexes are quite interesting, particularly regarding the lifetime and quantum yields of (YbL$_D$) in D$_2$O. As previously noticed,[15] the influence of the CH/D oscillators in the proximity of the Yb cation has a modest contribution relative to that of second sphere OH/D ones of the H$_2$O (D$_2$O) solvents. Luminescence lifetimes in D$_2$O and H$_2$O allowed for the calculations of q,[16] the number of water molecules in the first coordination sphere of the cations. For the two complexes, a value of 0 was obtained, confirming the coordination inside the cavity of the octadentate ligand, which perfectly shields the cation from its environment.

Noteworthy, the solubility of the complexes in D$_2$O allowed for the measurement of the NIR absorption spectrum of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of the (YbL$_D$) complex (Figure 2). Knowing the oscillator strengths for the transition, it was possible to calculate the radiative lifetime τ_{rad} of Yb using the modified Einstein relation:[21]
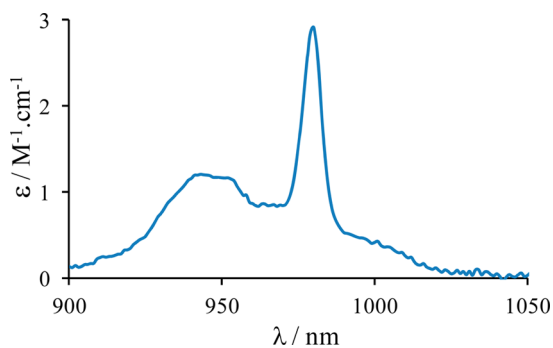

Figure 2. NIR absorption spectra of the $^2F_{5/2} \leftarrow {}^2F_{7/2}$ transition of the (YbL$_D$) complex in D$_2$O (c = 1.07 × 10^{-3} M).

$$\frac{1}{\tau_{rad}} = 2303 \times \frac{8\pi c n^2 \nu_{ul}^2}{N_A} \frac{g_l}{g_u} \int \varepsilon(\nu) d\nu$$

$$\text{with } \nu_{ul} = \frac{\int \nu \times \varepsilon(\nu) d\nu}{\int \varepsilon(\nu) d\nu}$$

in which c is the speed of light in a vacuum (3 × 10^{10} cm·s^{-1}), N_A is Avogadro's constant, n is the refractive index of the medium (1.33 for D$_2$O), ν_{ul} is the barycenter of the transition (in cm^{-1}), g_l and g_u are related to the degeneracies of the lower (l, J_l = 7/2) and upper (u, J_u = 5/2) excited states ($g_i = 2J_i + 1$), and $\varepsilon(\nu)$ is the molar extinction coefficient (in M^{-1}·cm^{-1}) at the wavenumber ν. A value of 1.73 ms was obtained for τ_{rad}. It is to be noticed that this value is prone to a large experimental error.[22] From this value, the Yb centered luminescence quantum yield ϕ_{Yb} can be calculated with

$$\phi_{Yb} = \frac{\tau_{obs}}{\tau_{rad}}$$

Where τ_{obs} is the luminescence lifetime of Yb (65 μs in D$_2$O), leading to a value 0.037 for the Yb centered quantum yield. Considering that the overall luminescence quantum yield obtained by excitation through the ligand (310 nm) was determined to be 0.038 (Table 1), the ligand to Yb energy transfer efficiency is almost quantitative and the nonradiative loss are essentially due to quenching of the Yb excited state.

Considering the excellent spectroscopic properties of the (YbL$_{(D)}$) complexes, the ability of ligand L to form polynuclear complexes of [(LnL)$_2$Ln$_x$] (x = 1 to 3) composition in water,[14] and the high thermodynamic and kinetic stabilities of (LnL) complexes at neutral pH,[14] we were interested in studying the formation of [(YbL$_{(H/D)}$)$_2$Tb$_x$] heteropolynuclear complexes and to check their spectroscopic properties. Starting from a solution of the isolated (YbL) complex in H$_2$O buffered at pH 7.0 with 0.01 M TRIS/HCl, increasing aliquots of TbCl$_3$·6H$_2$O in the same buffer were added. The evolution of the electronic absorption spectra and of the emission spectra (λ_{exc} = 310 nm) were measured during the titration (Figures S2 and S3, respectively). Although the variations in absorption were very weak, those observed in luminescence were very informative, revealing the appearance of the Tb centered emission bands attributed to the $^5D_4 \rightarrow {}^7F_J$ (J = 6 to 3) transitions up to ca. 1.5 equiv of Tb added. Considering the high thermodynamic and kinetic stability of the (LnL) complexes at neutral pD,[14] it is assumed that the coordination of the Yb atom inside the coordination cavity of L$_D$ is kept during the titration. Accordingly, the photosensitization of Tb may arise from a direct through space ligand to metal energy transfer or possibly by other mechanisms involving the (YbL) entities.

In a second step, the same experiment was repeated using the deuterated version of the ligand, so that (YbL$_D$) was titrated by TbCl$_3$·6H$_2$O in D$_2$O (TRIS/DCl 0.01 M at pD 7.0). The

emission spectra in the visible region (450 nm < λ_{em} < 700 nm) were recorded upon excitation into the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ absorption band of Yb at 980 nm with a 2.0 W laser irradiation (Figure 3). In absence of Tb, the visible emission spectrum was devoid of any emission signal.
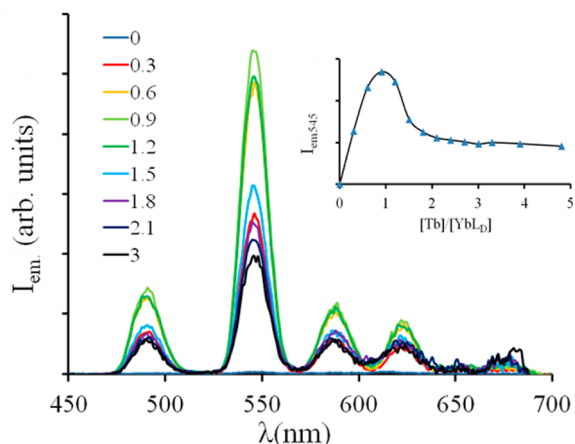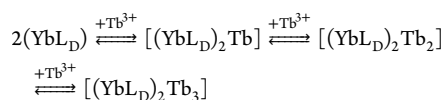

Figure 3. Evolution of the emission spectra (450 nm < λ_{em} < 700 nm) upon titration of a 7.1×10^{-4} M solution of (YbL_D) (D_2O, pD 7.0, TRIS/DCl) by $TbCl_3 \cdot 6H_2O$, with excitation at 980 nm (P = 2.0 W). Inset: Emission intensity of the $^5D_4 \rightarrow {}^7F_5$ emission band of Tb at 485 nm as a function of the Tb/(YbL_D) ratio.

As soon as Tb was added, emission bands appeared at 485, 545, 580, and 620 nm, which could be clearly associated with the characteristic Tb centered emission bands. The intensity of the signal increased up to one equivalent of added Tb and then decreased to reach a plateau after 1.5 equiv of added Tb cations. Although weak with Ln cations, the possibility of photosensitization of the Tb atom by non linear processes[23] was discarded by performing a similar experiment with the (LuL_H) complex[14] in place of the (YbL_D) one, which revealed a total absence of Tb emission upon 980 nm excitation. From these experiments, it appears that the observed emission is the result of an up conversion mechanism in which the Tb emission is arising from a Yb to Tb energy transfer, a phenomenon previously observed in the solid state,[24] but reported here for the first time at the molecular level in solution. To ascertain the UC mechanism, the intensity of the visible emission was integrated as a function of the pump power of the laser. The corresponding Log−Log plot is reported in Figure 4, for mixtures containing 0.3 and 1.0 equiv of Tb in the D_2O solution of (YbL_D). In both cases, the slope of the linear fit is close to two, in perfect agreement with a two photon UC mechanism.

Analysis of the data by nonlinear least-squares methods using the Specfit software[25] revealed, as previously observed for pure Tb and Yb titrations,[14] the presence of three new emitting species and the variations could be accurately fitted to the following model:

$$2(YbL_D) \underset{}{\overset{+Tb^{3+}}{\rightleftarrows}} [(YbL_D)_2Tb] \underset{}{\overset{+Tb^{3+}}{\rightleftarrows}} [(YbL_D)_2Tb_2]$$
$$\underset{}{\overset{+Tb^{3+}}{\rightleftarrows}} [(YbL_D)_2Tb_3]$$

The calculated distributions of the species formed during the titration and the relative UC emission spectra of the heteropolynuclear species are presented in Figures S4 and S5, respectively (Supporting Information).
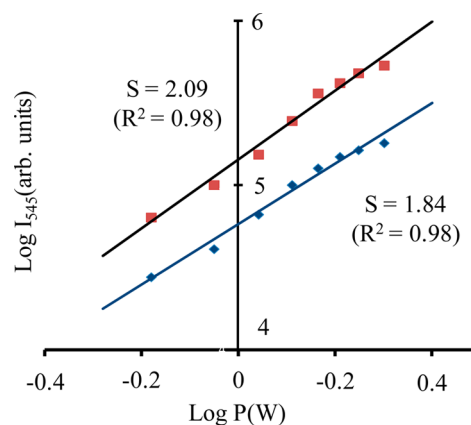

Figure 4. Log−Log plots of the emitted intensity (integrated for the $^5D_4 \rightarrow {}^7F_5$ peak centered at 545 nm) as a function of the incident pump power and slopes of the linear fits for mixtures of 0.3 (blue) and 1.0 (red) equivalents of Tb added to a (YbL_D) solution in D_2O (pD = 7.0, TRIS/DCl).

Figure 5 displays the DFT models calculated for the $[(YbL)_2Tb_x]$ species (x = 1 to 3). They revealed two important

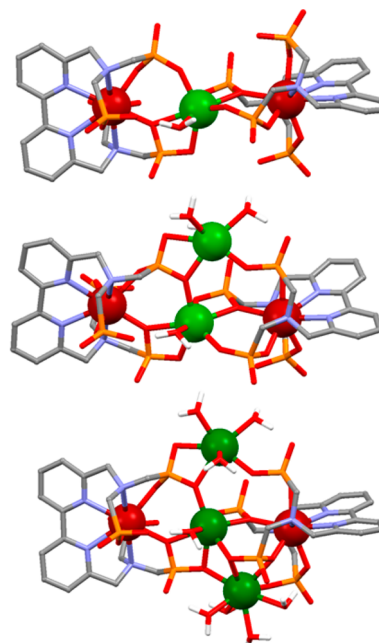**Figure 5.** DFT models of the $[(YbL)_2Tb]$ (top), $[(YbL)_2Tb_2]$ (middle), and $[(YbL)_2Tb_3]$ heteropolynuclear complexes.

points. Whatever the structure, the two Yb atoms are very close to the incoming Tb atoms (dYb-Tb ranged from 3.85 to 4.56 Å in the different structures). This close proximity seems to be a major parameter to allow for the possibility of intermetallic energy transfer in upconversion processes as recently observed in a homodinuclear Er complex in D_2O (d_{Er-Er} = 4.48 Å).[7] A second lesson from DFT is that the income of the second and third Tb atoms in the $[(YbL)_2Tb]$ complex did not perturb much the structure of the complex, explaining the possibility to form these intricate heteropolynuclear structures.

The observation of this unique photosensitization upconversion process is the result of an accumulation of advantageous properties of the system studied here. First, summation of two excited states level of the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition of Yb at 980 nm

is almost perfectly matching the energy level of the $^5D_4 \rightarrow {}^7F_6$ transition of Tb at 485 nm. Then, the excellent luminescence properties of the (YbL$_D$) complex place it as an excellent photosensitizer for upconversion purpose. Of great importance, the Tb^{3+} cations are the less sensitive of the Ln series toward nonradiative deactivation from solvents and its emission could be observed eventhough some water molecules are coordinated to it in the heteronuclear complexes. Finally, the phosphonate functions of the L$_{(D)}$ ligands not only allow a strong coordination of one Ln cation in the cavity, but the formed mononuclear LnL complexes are prone to bind strongly with incoming Ln^{3+} cations through bridging phosphonate interactions. A still unanswered question of this upconversion process is that of its mechanism. Following Güdel's work,[24a] the two main mechanisms are (i) excited state absorption (ESA), in which an Yb atom absorb a first photon and the excited state formed absorb a second one to reach a higher lying excited state which transfers energy to the Tb atom; or (ii) energy transfer upconversion (ETU), in which the excitation of the first Yb atom is followed by absorption of a photon by a second Yb atom, and an energy transfer occurs cooperatively to excite the Tb atom.

Almost 50 years after the first observations of the upconversion phenomenon in the solid state,[1] this unconventional luminescence process is now fully integrated into the luminescence toolbox. Nevertheless, its demonstration at the molecular level is only 6 years old, with the pioneering work of Piguet and co-workers.[4] We postulate that the findings reported here open very interesting perspectives within the field of molecular upconversion, paving the way for the design of new molecular systems, showing upconversion in water.

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b12940.

> Full synthetic details for ligand L$_D$, with ^1H-, ^{13}C-, and ^{31}P NMR spectra and mass spectra, excitation spectra of the complexes and UV−vis absorption, luminescence spectra and speciation diagram for titration of [YbL$_D$] by TbCl$_3$ (PDF)

■ AUTHOR INFORMATION

Corresponding Author
*l.charbonn@unistra.fr

ORCID Ⓞ
Loïc J. Charbonnière: 0000-0003-0328-9842

Author Contributions
N.S. and P.T. contributed equally.

Notes
The authors declare no competing financial interest.

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