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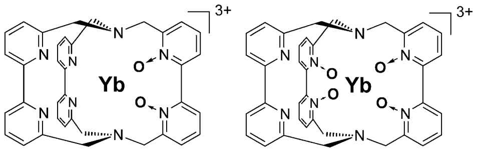
The Radiative Lifetime in Near-IR-Luminescent Ytterbium Cryptates: The Key to Extremely High Quantum Yields[**]

*Christine Doffek and Michael Seitz**

Abstract: *A powerful strategy for the improvement of near-IR lanthanoid luminescence has been successfully employed for the first time, which involves the rational and deliberate shortening of the radiative luminescence lifetimes τ_{rad} in molecular ytterbium complexes. In this context, the bidentate chelating unit 2,2′-bipyridine-N,N′-dioxide has been identified as being responsible for decreasing τ_{rad} substantially in macrobicyclic Yb cryptates. This strategy, when combined with conventional approaches, yields unprecedented absolute near-IR quantum yields of up to 12 %. This extraordinary efficiency represents the highest value measured for any molecular lanthanoid near-IR emitter. The proof-of-concept for the implementation of the new strategy opens up entirely new prospects for the field of lanthanoid luminescence.*

Near-IR luminescence in molecular lanthanoid complexes has long suffered from low absolute quantum yields Φ^{L}_{Yb}, usually well below 1 % and even with the best luminophores only featuring single-digit values.[1] The optimization of emission efficiencies has so far mostly relied on two approaches, either maximizing the energy transfer from the sensitizing moiety to the lanthanoid (e.g. by adjusting the energies of ligand-centered triplet or charge-transfer states) or reducing non-radiative deactivation processes of the lanthanoid-centered emissive states (e.g. by avoiding high-energy oscillators in the vicinity of the lanthanoid).[1] There is, however, a third option which is to make radiative emission more competitive compared to non-radiative deactivation channels by increasing the rate of emission of the corresponding transition while leaving all other processes at approximately the same levels. This path, which is equivalent to decreasing the intrinsic radiative lifetime τ_{rad}, is a rarely trodden one because presently relatively scarce experimental data are available and hence we only have a very crude understanding of how τ_{rad} can be utilized in a systematic and predictable manner.[1a,2] Herein, we show how τ_{rad} can be deliberately and effectively lowered in molecular ytterbium complexes and how this effect can be used to obtain the highest absolute quantum yield for any near-IR emitting molecular lanthanoid complex.

The starting point for our investigations was an earlier finding by Eliseeva et al. that τ_{rad} in the visible emitter europium can be decreased moderately by replacing two inner-sphere water molecules with the bidentate chelator 2,2′-bipyridine-*N*,*N*′-dioxide (bpyO$_2$).[3] Although the effect of the *N*-oxide moieties on τ_{rad} could not rigorously be separated from the effect of the concurrent change in the donor set, we wanted to investigate whether the same phenomenon could be observed in near-IR luminescent lanthanoid complexes and whether we could more clearly isolate the extent and nature of the operative effect on τ_{rad}. Decreasing τ_{rad} for the sake of efficiency gains is not a very pressing need for visible emitters such as europium or terbium because very efficient systems with near-optimum quantum yields have already been developed,[1d] but this effect could greatly benefit near-IR luminophores with their low efficiencies. Therefore, we selected ytterbium as the near-IR emitting lanthanoid of choice owing to its chemical similarity to europium and its great technological importance for photonic applications. For the purpose of our investigation, we designed the new model cryptate **2**-Yb (Figure 1) to be as similar as possible to the known analogue **1**-Yb.[4] The only major change is the replacement of a bipyridine unit with bpyO$_2$ and the expectation was that **2**-Yb should exhibit a decreased value for τ_{rad} as a result of the higher content of bpyO$_2$ units.



1-Yb **2**-Yb

Figure 1. Lanthanoid cryptates **1**-Yb and **2**-Yb used in this study.

Both cryptates **1**-Yb and **2**-Yb provide a very similar coordination environment and feature exactly the same three types of donor moieties (tertiary N, bpy, bpyO$_2$ in different ratios), thereby avoiding ambiguities for the interpretation of the changes in τ_{rad} arising from different donor types.[3] The synthetic realization of **2**-Yb was straightforward and involved as the first step the reaction of bis(amine) **3**[5] and benzylic dibromide **4**[4a] in the appropriate ratio (1:2) to give the corresponding sodium cryptate **2**-Na. Remarkably, this macrocyclization does not require elaborate high-dilution conditions to obtain yields that are very high (65 %) for

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[*] Prof. Dr. M. Seitz
Institute of Inorganic Chemistry
University of Tübingen
Auf der Morgenstelle 18, 72076 Tübingen (Germany)
E-mail: michael.seitz@uni-tuebingen.de
M. Sc. C. Doffek, Prof. Dr. M. Seitz
Inorganic Chemistry I, Ruhr-University Bochum
44780 Bochum (Germany)

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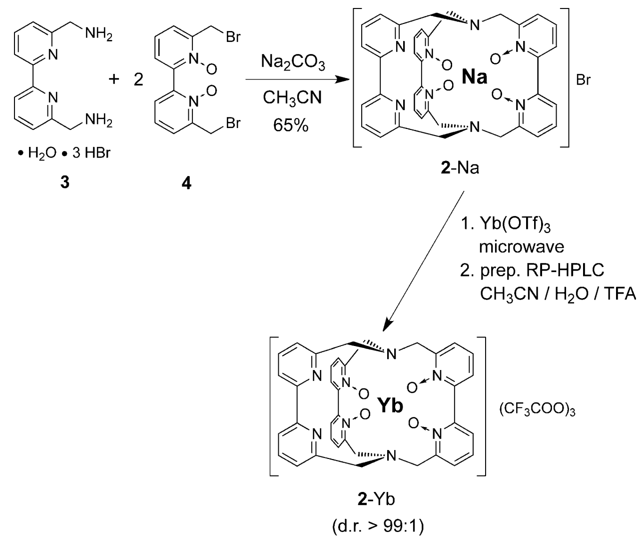

Scheme 1. Synthesis of cryptate **2**-Yb.

a transformation of this kind (Scheme 1). Microwave-assisted metal exchange of ytterbium for sodium and subsequent preparative reversed-phase HPLC purification yielded **2**-Yb as the trifluoroacetate salt.[6] Compound **1**-Yb was prepared as described previously[4c] and subjected to the same HPLC step. In addition to the ytterbium complexes, the lutetium analogues **1**-Lu and **2**-Lu were obtained by the same procedures.[6] The initial structural and photophysical characterization of **2**-Ln revealed that complexation seems to proceed with perfect stereocontrol giving only one detectable C_2-symmetric diastereomer in the ^{1}H NMR spectrum of **2**-Lu (see Figure S2 in the Supporting Information; stereogenic elements: two atropisomeric axes of the bpyO$_2$ units and the overall helicity of the cryptates).[6] In addition, the comparison of the luminescence lifetimes τ_{obs} in CH$_3$OH and CD$_3$OD of the transition $^2F_{5/2}\rightarrow{}^2F_{7/2}$ in **2**-Yb allowed the unambiguous conclusion that this cryptate does not contain any inner-sphere methanol molecules (Table 1. $q_{MeOH}\approx 0$).[7] These findings are in complete analogy to the ones for **1**-Yb[4c] and showed that the two cryptate architectures were indeed very suitable for the purposes of this study. The only major difference that we could find is the significantly higher zero-phonon $T_1\rightarrow S_0$ transition energy $E(T_1)$ in the cryptates **2**-Ln ($E(T_1)\approx 22\,600$ cm^{-1}) compared to the one for **1**-Ln ($E(T_1)\approx 20\,400$ cm^{-1}) as determined through low-temperature emission spectra of the lutetium complexes (Table 1).[6] This phenomenon was not considered a problem for the investigation because the value of $E(T_1)$ is very unlikely to affect τ_{rad} but instead should only have an impact on the energy transfer from the ligand to the lanthanoid.

Table 1: Luminescence lifetimes τ_{obs}, radiative luminescence lifetimes τ_{rad}, triplet energies $E(T_1)$, and number of inner-sphere methanol molecules q_{MeOH} for **1**-Yb and **2**-Yb in CD$_3$OD.

Complex	τ_{obs}[a] [μs]	τ_{rad}[b] [ms]	$E(T_1)$[c] [cm^{-1}]	q_{MeOH}[d]
1-Yb	12.3 (n.d.)	1.25	ca. 20 400	(−0.08)[e]
2-Yb	26.1 (7.5)	0.658	ca. 22 600	−0.01

[a] $^2F_{5/2}\rightarrow{}^2F_{7/2}$ (970 nm), values for CH$_3$OH in parentheses; n.d. = not determined. [b] Determined using the Yb-centered absorption bands of **1**-Yb and **2**-Yb in CD$_3$OD according to Ref. [8]. [c] Estimated using the cryptates **1**-Lu and **2**-Lu (see Figure S7). [d] Calculated using the empirical formula $q_{MeOH} = 2.0\ \mu s\ (1/\tau_H - 1/\tau_D - 0.1\ \mu s^{-1})$ from Ref. [7]. [e] See Ref. [4b].

Finally, as the core of our study, we determined the radiative luminescence lifetimes τ_{rad} experimentally for both ytterbium complexes in CD$_3$OD by quantitatively measuring the absorption spectra of the f–f transitions $^2F_{7/2}\rightarrow{}^2F_{5/2}$ in **1**-Yb and **2**-Yb (Figure 2), followed by evaluation of the spectral data using an established equation based on a modified Einstein relation.[6,8]

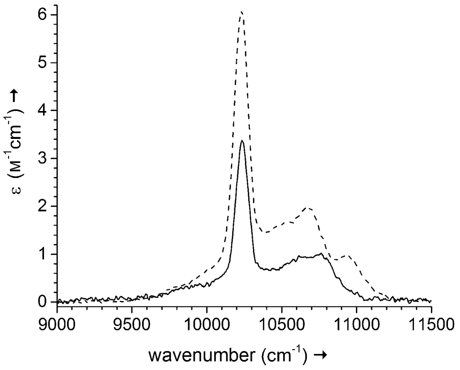

Figure 2. Quantitative absorption spectra of the f–f transitions $^2F_{7/2}\rightarrow{}^2F_{5/2}$ in **1**-Yb (solid line, $c = 2.45$ mM) and **2**-Yb (dashed line, $c = 3.05$ mM) in CD$_3$OD.

In perfect agreement with the premise of our study, τ_{rad} decreases to the surprisingly large extent of almost 50 % from 1.25 ms for **1**-Yb to 0.658 ms for **2**-Yb (Table 1). Both values are in the typical range for molecular ytterbium complexes in solution.[1] As a result of the careful considerations regarding comparability (e.g. donor sets, local symmetry around the metal center, q_{MeOH}, C–H oscillator environments) of our model cryptates **1**-Yb and **2**-Yb, this effect can be attributed with a great degree of confidence, to the exchange of the bpyO$_2$ unit for the bpy moiety. This result shows for the first time that careful design of a new luminophore indeed allows the rational and deliberate manipulation of τ_{rad}, which has previously only been encountered empirically afterwards.

Having established that bpyO$_2$ does seem to have a very positive impact on τ_{rad}, we wanted to use this effect in conjunction with more conventional measures to improve the emission properties to see how far the luminescence efficiency can be pushed by combining different strategies. One of the common approaches for this purpose is the removal of high-energy oscillators such as O–H and C–H stretching modes by deuteration.[9] We have previously used the strategy of perdeuteration to great effect with the cryptand featured in **1**-Ln and in cryptates of a similar nature.[4b,c,10] Consequently, we prepared the perdeuterated cryptate [D$_{30}$]-**2**-Yb[6] and evaluated the luminescence efficiency in comparison to its

Table 2: Luminescence lifetimes τ_{obs}, intrinsic quantum yields Φ_{Yb}^{Yb}, absolute quantum yields Φ_{Yb}^{L}, and sensitization efficiency η_{sens} for [D$_{30}$]-**1**-Yb and [D$_{30}$]-**2**-Yb in CD$_3$OD.

Complex	τ_{obs}[a] [µs]	Φ_{Yb}^{Yb}[b] [%]	Φ_{Yb}^{L}[c] [%]	η_{sens}[d] [%]
[D$_{30}$]-**1**-Yb	91	7.3	5.0	68
[D$_{30}$]-**2**-Yb	172	26	12.0	46

[a] $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (970 nm). [b] $\Phi_{Yb}^{Yb} = \tau_{obs}/\tau_{rad}$ with τ_{rad} values as listed in Table 1. [c] Determined using [Yb(TTA)$_3$phen] as standard (see Ref. [11]) after excitation at 310 nm. [d] $\eta_{sens} = \Phi_{Yb}^{L}/\Phi_{Yb}^{Yb}$.

analogue [D$_{30}$]-**1**-Yb in perdeuterated methanol. [D$_{30}$]-**2**-Yb exhibits extraordinarily long luminescence lifetimes (Table 2, $\tau_{obs} = 172$ µs) which, because of the deliberate decrease in τ_{rad}, results in unprecedentedly large intrinsic quantum yields (Table 2: $\Phi_{Yb}^{Yb} = 26\,\%$). This translates into the highest absolute quantum yield (Table 2: $\Phi_{Yb}^{L} = 12\,\%$) that has been measured for any molecular near-IR luminescent lanthanoid complex in solution and in the solid state.[1] Compared to the cryptate [D$_{30}$]-**1**-Yb, which itself already represents one of the brightest near-IR lanthanoid luminophores in solution up to date,[1] the intentional decrease in τ_{rad} as successfully realized in [D$_{30}$]-**2**-Yb more than doubles the overall luminescence efficiency (Table 2: $\Phi_{Yb}^{L} = 12\,\%$ vs. $\Phi_{Yb}^{L} = 5.0\,\%$) and for the first time double-digit quantum yields Φ_{Yb}^{L} are achieved for such a molecular species.

In summary, our findings represent a conceptual and practical breakthrough for the field of near-IR lanthanoid luminescence. In particular, we could show the following:

a) Our study is the first case where the radiative luminescence lifetime τ_{rad} has been deliberately manipulated to increase the overall near-IR luminescence efficiency in lanthanoid complexes. The generally applicable strategy of lowering τ_{rad} is also highly attractive for all near-IR lanthanoid emitters and needs to be considered in any future work on this matter.

b) The successful implementation of this new strategy has allowed us to realize the most near-IR luminescent molecular lanthanoid complex [D$_{30}$]-**2**-Yb reported, for the first time with double-digit absolute quantum yields in solution.

c) The bpyO$_2$ moiety seems to be largely responsible for the increase in luminescence efficiency and is very likely to be a suitable tool for decreasing τ_{rad} in other complex architectures for ytterbium-based luminophores. The identification of this lead structure for the strategy will be beneficial for ligand design in this and related fields.

With the present results, it is easily conceivable that additional tweaking of the luminophore [D$_{30}$]-**2**-Yb or similar species along well-established routes, for example, by improvements of η_{sens} or embedding the complex into polymeric matrices with high refractive indices, new emissive materials with absolute near-IR quantum yields in excess of 25 % should realistically be within reach for the first time. This highly desirable prospect will enable new possibilities for a wide array of photonic applications.

Keywords: cryptands · deuterium · luminescence · photophysics · ytterbium

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