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Quantification of C−H Quenching in Near-IR Luminescent Ytterbium and Neodymium Cryptates

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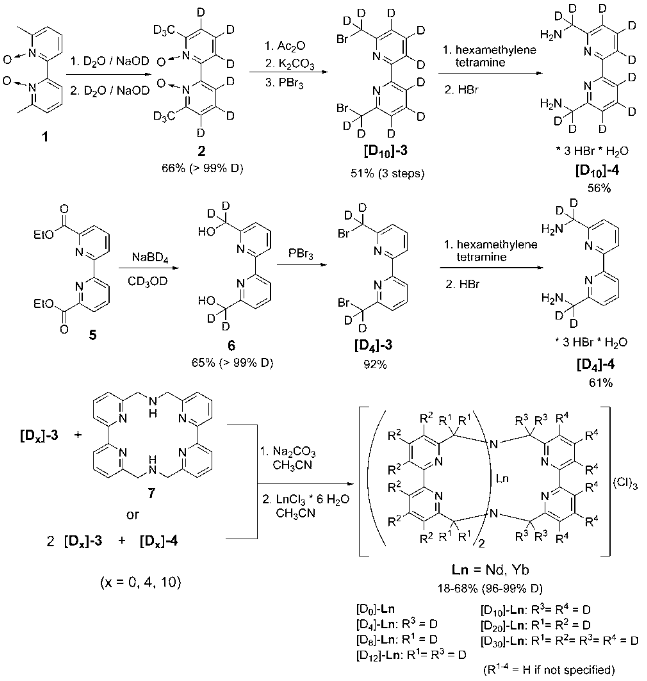
Abstract: Two series of selectively deuterated cryptates with the lanthanoids Yb and Nd have been synthesized, and the luminescence lifetimes for the corresponding near-IR emission bands have been measured. Global fitting of these lifetime data combined with structural analysis allows for the accurate quantification of the contributions of individual C−H oscillators groups in the ligand to the nonradiative deactivation rates of the emissive lanthanoid states.

Scheme 1. Synthesis of the Isotopologic Cryptates[7]



Near-IR luminescent lanthanoids have unique electronic structures which have enabled the development of fascinating optical applications in the recent past, e.g. lanthanoid upconversion materials.[1] Most of the promising systems have been based on extended solid matrices, which provide a good protective environment for lanthanoids. For some applications, however, it is more desirable to use molecular lanthanoid complexes in solution (size, monodispersity, processability, etc.).[2] The fundamental challenge of the latter approach is the exclusion of high-energy X−H oscillators close to the metal center (X = O, N, C, etc.), which efficiently quench lanthanoid excited states. While nonradiative deactivation by O−H and N−H vibrational modes can easily be avoided (e.g., by using solvents like D_2O instead of H_2O or by methylation of N−H groups), the elimination of C−H oscillators is inherently more difficult due to the abundance of this structural motif in organic ligands. Two obvious approaches, deuteration and fluorination, have been used in the past to ameliorate this problem.[3] These solutions, however, are synthetically often challenging and expensive, resulting in a great lack of suitable model systems for the methodical investigation of C−H quenching. As a consequence, this phenomenon and its peculiarities are still ill-understood despite several efforts to quantify these effects.[4]

We report here selectively deuterated Lehn cryptands[5] as an excellent model system to study the effect of C−H quenching. This ligand type is completely devoid of O−H and N−H oscillators and has been shown in the past to sensitize near-IR luminescence from Yb and Nd.[4i,6] Our optimized synthetic procedures required no or only one additional step compared to the nonisotopically labeled route and used either D_2O or $NaBD_4$ as readily available, cheap deuterium sources.[7] Overall deuterium incorporation in the selected positions was greater than 95% in every case. The modular nature of the cryptand synthesis allowed for the facile preparation of seven isotopologic ligands with increasing deuterium content in either the benzylic or the aromatic position. With these ligands, two series of lanthanoid cryptates $[D_x]$-**Ln** (with **Ln** = Yb or Nd) were prepared (Scheme 1).[7] In order to minimize quenching effects in solution, $[D_6]$-DMSO was chosen as solvent for $[D_x]$-**Nd**, whereas D_2O was used for $[D_x]$-**Yb**.[8] Steady-state luminescence spectra showed the typical emission bands in the near-IR region.[7] Luminescence lifetimes were monoexponential in all cases. They showed the expected increase with deuteration level (i.e., the decrease of C−H quenching) and reached $\tau_{obs} = 10.8\ \mu s$ for $[D_{30}]$-**Yb** and $\tau_{obs} = 9.09\ \mu s$ for $[D_{30}]$-**Nd**, the latter being among the longest lifetimes for neodymium complexes in solution reported so far (Table 1).[2b] The dependence of the observed deactivation rates $k_{obs}(y,z)$ for $[D_x]$-**Ln** ($x = 0-20$, **Ln** = Yb, Nd)[9] on the site-specific

Table 1. Luminescence Lifetimes τ_{obs} and Excited State Deactivation Rates k_{obs} of the Yb (D_2O, $\lambda_{exc} = 335$ nm, $\lambda_{em} = 980$ nm) and the Nd Complexes ($[D_6]$-DMSO, $\lambda_{exc} = 306$ nm, $\lambda_{em} = 1064$ nm)

Complex	y = no. of CD_2	z = no. of deut. pyridine rings	τ_{obs} [μs][a]	k_{obs} [10^2 ms^{-1}]	calcd k_{obs} [10^2 ms^{-1}][b]
$[D_{12}]$-**Yb**	6	0	9.6	1.0	1.0
$[D_8]$-**Yb**	4	0	8.6	1.2	1.2
$[D_4]$-**Yb**	2	0	7.5	1.3	1.3
$[D_0]$-**Yb**	0	0	6.7	1.5	1.5
$[D_{10}]$-**Yb**	2	2	7.7	1.3	1.3
$[D_{20}]$-**Yb**	4	4	9.2	1.1	1.1
$[D_{30}]$-**Yb**	6	6	11[c]	0.93[c]	−
$[D_{12}]$-**Nd**	6	0	5.4	1.9	2.0
$[D_8]$-**Nd**	4	0	2.5	4.0	3.9
$[D_4]$-**Nd**	2	0	1.7	5.8	5.7
$[D_0]$-**Nd**	0	0	1.3	7.6	7.6
$[D_{10}]$-**Nd**	2	2	1.8	5.5	5.6
$[D_{20}]$-**Nd**	4	4	2.8	3.5	3.5
$[D_{30}]$-**Nd**	6	6	9.1[c]	1.1[c]	−

[a] Estimated error: ±15% for $\tau_{obs} > 3\ \mu s$ and ±20% for $\tau_{obs} < 3\ \mu s$. [b] Calculated using the parameters obtained from the global fitting procedure (see Table 2). [c] Value not used for the global fit in Table 2 (see ref 9).

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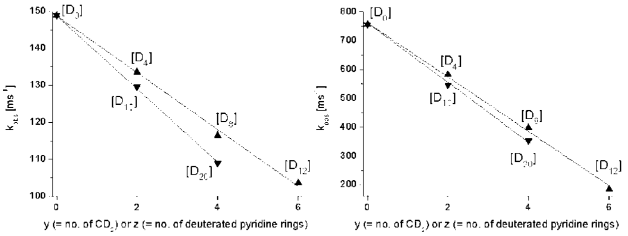

Figure 1. Deactivation rates k_{obs} of the complexes of Yb (left) and Nd (right) for the two series [D_0]-[D_4]-[D_8]-[D_{12}] (▲) and [D_0]-[D_{10}]-[D_{20}] (▼) with the corresponding 2D-projections (solid lines) of the 3D-global fit planes.[7]

Table 2. Quenching Rate Differences Δk for Benzylic and Aromatic C−(H/D) Oscillator Groups in [D_x]-**Yb** and [D_x]-**Nd**[a]

Complex	k_0 [10^2 ms^{-1}][b]	Δk_{benzyl} [ms^{-1}][b]	Δk_{py} [ms^{-1}][b]	R^2
[D_x]-**Yb**	1.5	7.7	2.2	0.997
[D_x]-**Nd**	7.6	94	9.4	0.997

[a] Obtained by global fitting of the lifetime data to the following: $k_{obs} = k_0 - y\Delta k_{benzyl} - z\Delta k_{py}$; with y,z as defined in Table 1, $k_0 = k_{obs}$ ([D_0]-**Ln**); Δk_{benzyl}, Δk_{py} = quenching rate difference for the two/three C−H oscillators of one benzylic methylene group/pyridine ring. [b] Estimated error: ±25%.

deuteration levels (y,z) could successfully be modeled globally with a three-dimensional planar fit function. The 2D-projections thereof show the linear dependence of k_{obs} on y and z in both lanthanoid series (Figure 1).

The advantage of our approach can clearly be seen in Figure 1. In contrast to previous reports, we are able to establish the linearity using multiple data points instead of the commonly used but rather error-prone two-point calibrations (perdeuterated vs undeuterated). The rates Δk of the different oscillator groups obtained by the fitting procedures are shown in Table 2.[10]

A meaningful comparison to literature data can be drawn for methylene groups close to Yb (ca. 3.5−4.5 Å). Our value ($\Delta k_{benzyl} = 7.7$ ms^{-1}) is within the range of previous reports (3−13 ms^{-1}).[4j,k] All other deactivation rates are unprecedented. As expected, Δk are always greater for Nd compared to Yb because of the smaller energy gap ($\Delta E_{Nd} \approx 5400$ cm^{-1} vs $\Delta E_{Yb} \approx 10\,250$ cm^{-1}) between the emissive state and the highest receiving state. The quenching ability of C−H groups, in general, is mainly determined by two factors: the distance r_{Ln-H} and the Franck−Condon (FC) overlap between the lanthanoid excited state and the corresponding overtone of a specific C−(H/D) oscillator. With the approximation that within a group of either benzylic or aromatic H-atoms the FC overlap factors are comparable (assumed similar $\nu_{C-(H/D)}$, oscillator strengths, etc.), the quenching ability of a specific C−(H/D) oscillator should solely be influenced by the distance to the lanthanoid center. Therefore, only taking into account the distance dependence ($\Delta k \propto r^{-6}$) using typical r_{Ln-H} obtained from relevant crystal structures,[7] the contributions Δk_i of individual C−(H/D) oscillators can be deconvoluted. Figure 2 shows the calculated estimates for both lanthanoids.[11]

In conclusion, we have developed a cost-effective and practical synthetic route to a series of highly selectively deuterated cryptands. Perdeuteration strongly enhances near-IR luminescence and increases the lifetimes by factors from 1.6 for Yb to a remarkable 6.9 for Nd. With this model system, we have accurately quantified the deactivation rate contributions of individual ligand C−H oscillator groups. These ligands will allow for more detailed investigations into this important phenomenon for Yb and Nd, as well as for other near-IR emitting lanthanoids which are also sensitized by our deuterated cryptands (Pr, Ho, and Er).

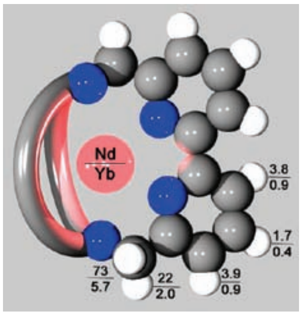

Figure 2. Estimates for the quenching rate differences Δk_i (in ms^{-1}) for individual C−(H/D) oscillators in the Nd (upper value) and Yb complexes (lower value).[11]

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Supporting Information Available: Details for the synthesis and characterization of the compounds, luminescence measurements, deconvolution of k_{obs} values. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) See Supporting Information for details.
(8) The species [D_x]-**Yb** show biexponential luminescence decay in [D_6]-DMSO, presumably due to slow solvent exchange kinetics (see ref 4j). The choice of D_2O for Yb and [D_6]-DMSO for Nd proved to give the cleanest possible monoexponential decay kinetics in both cases.
(9) While all [D_x]-**Ln** for $x = 0-20$ show common behavior, we have indications (triplet level in [D_{30}]-**Gd**, emission band shape of [D_{30}]-**Yb**) that the perdeuterated cryptates are slightly different from the only partially deuterated complexes. For complete comparabiliy, we did not include the complexes [D_{30}]-**Ln** in the fitting procedures.
(10) The quenching rate differences are only lower limits for the actual C−H quenching rates because the vibrational energies of C−D oscillators may also contribute to nonradiative deactivation.
(11) Due to the assumed simplifications (neglect of FC factors, use of average X-ray distances r_{Ln-H}) for the deconvolution procedure, the obtained values for Δk_i can only be approximative estimates.

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