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Anomalous Reversal of C−H and C−D Quenching Efficiencies in Luminescent Praseodymium Cryptates

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Supporting Information

ABSTRACT: A series of selectively deuterated praseodymium cryptates has been synthesized. Their luminescence lifetimes in solution range from 150 to 595 ns for the $^1D_2 \rightarrow {}^3F_4$ transition. Global fitting of the nonradiative deactivation rate differences of the isotopologic C−(H/D) oscillators revealed that aromatic C−D overtones anomalously quench the luminescence more than C−H vibrations. This is explained by the dominance of Franck−Condon overlap factors that greatly favor C−D oscillators, which are in almost ideal resonance with the relevant energy gap $^1D_2$−$^1G_4$ of praseodymium.

Near-IR lanthanoid luminescence exhibits a number of favorable characteristics (sharp emission bands, long luminescence lifetimes, etc.) and has attracted considerable attention over the last decades due to a wide array of potential applications.[1] One of the major drawbacks for the use of molecular lanthanoid complexes in solution is the severe sensitivity of lanthanoid excited states toward multiphonon-mediated, nonradiative relaxation processes which are induced by high-frequency vibrational overtones X−H (with X = O, N, C). These detrimental deactivation channels can usually be reduced by replacement of X−H with oscillators of higher reduced mass (e.g., C−D or C−F).[2,3] The heavier analogues require more vibrational quanta in order to bridge a given energy gap between a lanthanoid emissive state and the next lower level, which makes deactivation less favorable. It is therefore commonly believed that, for example, deuteration always increases the luminescence efficiency, albeit to varying extents. This assumption, however, neglects the importance of Franck−Condon overlap (FCO) factors, that is, the resonance of lanthanoid electronic levels and accepting vibrational overtones, which is especially important for near-IR emitting lanthanoids with small energy gaps. These factors could in principle lead to an increase of nonradiative deactivation upon deuteration. There have been very few reports in the past that deuteration of C−H oscillators can also lead to decreased luminescence but the observed differences were too small to be statistically significant and the exact causality could therefore not be established unambiguously.[4] In this report, we can show convincingly for the first time that FCO can indeed be the dominating factor leading to decreased luminescence efficiency in deuterated lanthanoid complexes. In addition, we precisely pinpoint the origin of this effect in a molecular lanthanoid cryptate architecture with different oscillator moieties.

The starting point for our investigation was the choice of a model system which would potentially show sizable FCO between a lanthanoid excited state and a harmonic C−D overtone. Among a number of candidates, praseodymium seemed to be ideal because it has a suitable energy gap of ca. 7000 cm^{-1} between its emissive $^1D_2$ level and the next lower $^1G_4$ state (Figure 1).

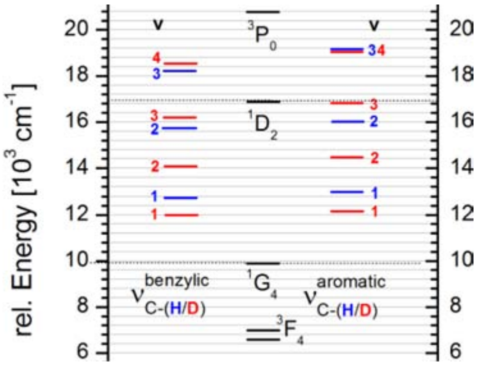

Figure 1. Schematic energy level diagram for Pr(III) and the position of the overtones of C−(H/D) oscillators in a simple harmonic oscillator model relative to the $^1G_4$ level.[5]

This gap should be resonant with the second, harmonic overtone of an aromatic C−D stretching vibration having the energy 6900 cm^{-1} ($\nu_{C-D} \approx 2300$ cm^{-1}). In contrast, the harmonic first overtone of an aromatic C−H oscillator is energetically relatively far away at 6200 cm^{-1} ($\nu_{C-H} \approx 3100$ cm^{-1}), which should considerably reduce efficient FCO (Figure 1, right). This phenomenon should not be observed with aliphatic C−(H/D) oscillators because their marginally lower vibrational wavenumbers are not in resonance with the $^1D_2$ level ($\nu_{C-H} \approx 2900$ cm^{-1} and $\nu_{C-D} \approx 2100$ cm^{-1}) (Figure 1, left).

Studies on the photoluminescence of praseodymium complexes in solution are relatively rare and are usually confined to the analysis of steady-state emission spectra.[6] Time-resolved measurements have only been done in a very limited

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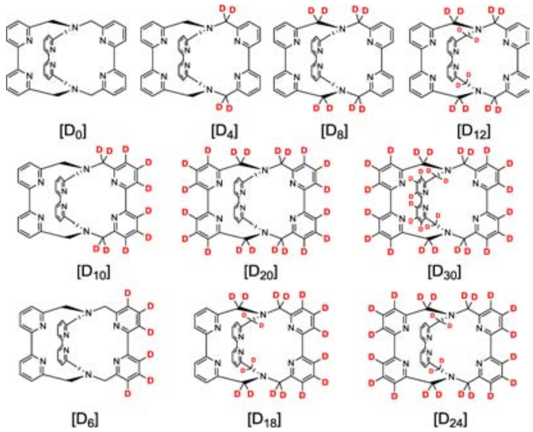
number of instances with typical luminescence lifetimes below τ_{obs} = 100 ns ($^1D_2 \rightarrow {}^3F_4$).[7] We chose a tris(bipyridine)-based cryptand as our ligand system. This class of chelators forms stable rare earth complexes and sensitizes luminescence from a wide variety of lanthanoids efficiently.[8] In addition, we have recently developed very economical synthetic procedures for its deuteration with complete positional control of the isotopic labeling (Chart 1, upper and middle rows).[9] Measurements of differences in deactivation rates upon deuteration (via the corresponding luminescence lifetimes) are usually afflicted with relatively large uncertainties. Hence, the results become statistically much more significant by global fitting of lifetime data for a set of complexes with different but redundantly overlapping isotopic compositions. For this purpose, we have synthesized three additional isotopologic tris(bipyridine) cryptands with new isotopic patterns (Chart 1, lower row: **[D$_6$]**, **[D$_{18}$]**, **[D$_{24}$]**).[10]

Chart 1. Deuterated, Isotopological Tris(bipyridine) Cryptands Used in This Study



The steady-state emission spectra of the corresponding cryptates **[D$_x$]-Pr** in [D$_6$]-DMSO show the typical bands for praseodymium.[10] Luminescence lifetime measurements on the transition $^1D_2 \rightarrow {}^3F_4$ (1025 nm) gave monoexponential decay kinetics in every case in the range from τ_{obs} = 150 to 595 ns (Table 1), the latter being an extraordinarily long lifetime for Pr(III) in solution. In agreement with the premise of our study, we were delighted to find that the species **[D$_{30}$]-Pr** with assumed strongly quenching aromatic C−D oscillators did indeed show a reduced lifetime (τ_{obs} = 528 ns) compared to the corresponding complex **[D$_{12}$]-Pr** with aromatic C−H moieties (τ_{obs} = 595 ns, Figure 2), albeit both values were within the experimental errors (Table 1). A global fitting procedure on the entire data set confirmed that the quenching rate difference (C−H minus C−D) for one pyridine ring Δk_{py} was indeed negative (Table 2: Δk_{py} = −45 ms^{-1}) on a statistically significant level (standard error = 14 ms^{-1}). In contrast to this, the situation for the benzylic oscillators did not show any anomalous behavior, that is, progressive deuteration leads to decreasing deactivation rates (cf. the increasing lifetimes for **[D$_x$]-Pr** with x = 0, 4, 8, 12 in Table 1 or the positive value for Δk_{benzyl} in Table 2). This behavior is also in agreement with our prediction (see Figure 1).

The observed differences in the quenching behavior of benzylic and aromatic C−(H/D) oscillators can only be explained by dramatic differences in FCO factors. The realization that aromatic deuteration leads to an increase in quenching greatly challenges the present paradigm. It greatly underscores the need for a much more detailed understanding of the often neglected FCO factors for different oscillators in near-IR emitting lanthanoid luminophores. The greatly varying differences in FCO for C−(H/D) oscillators has a number of implications:

(a) As a practical matter, deuteration of aromatic C−H oscillators should be avoided for the design of highly luminescent praseodymium complexes.

Table 1. Luminescence Lifetimes τ_{obs} and Excited State Deactivation Rates k_{obs} of the Complexes [D$_x$]-Pr ([D$_6$]-DMSO, $c \approx$ 0.1 mM, λ_{exc} = 337 nm, $^1D_2 \rightarrow {}^3F_4$)[a]

complex	y[b]	z[c]	τ_{obs} [ns][d]	k_{obs} = τ_{obs}^{-1} [10^3 ms^{-1}][d]	calc k_{obs} [10^3 ms^{-1}][e]
[D$_0$]-Pr	0	0	150(10)	6.69(0.45)	6.44
[D$_4$]-Pr	2	0	220(20)	4.57(0.42)	4.86
[D$_6$]-Pr	0	2	157(6)	6.39(0.24)	6.53
[D$_8$]-Pr	4	0	310(17)	3.23(0.17)	3.29
[D$_{10}$]-Pr	2	2	202(6)	4.94(0.15)	4.95
[D$_{12}$]-Pr	6	0	595(13)	1.68(0.04)	1.71
[D$_{18}$]-Pr	6	2	518(18)	1.93(0.07)	1.80
[D$_{20}$]-Pr	4	4	285(5)	3.51(0.06)	3.47
[D$_{24}$]-Pr	6	4	467(35)	2.15(0.16)	1.89
[D$_{30}$]-Pr	6	6	528(18)	1.89(0.06)	1.98

[a] The measured values are averages of three independent experiments. [b] y = number of CD$_2$ groups. [c] z = number of deuterated pyridine rings. [d] Sample standard deviation s (with Bessel correction) in parentheses. [e] Calculated using the parameters obtained from the global fitting procedure (see Table 2).

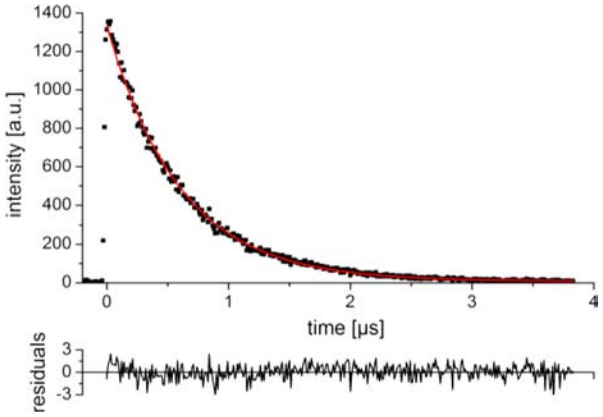


Figure 2. Luminescence decay profile of the transition $^1D_2 \rightarrow {}^3F_4$ (λ_{em} = 1025 nm) in **[D$_{12}$]-Pr** ([D$_6$]-DMSO, λ_{exc} = 337 nm, monoexponential fit in red).

Table 2. Quenching Rate Differences Δk for Benzylic and Aromatic C−(H/D) Oscillator Groups in [D$_x$]-Pr[a]

k_0 [10^3 ms^{-1}][b]	Δk_{benzyl} [ms^{-1}][b]	Δk_{py} [ms^{-1}][b]	R^2
6.44(0.15)	788(26)	−45(14)	0.991

[a] Global fitting of the lifetime data to: $k_{obs} = k_0 - y\,\Delta k_{benzyl} - z\,\Delta k_{py}$; with y,z as defined in Table 1; $k_0 = k_{obs}$ ([D$_0$]-Pr) as an optimized parameter; Δk_{benzyl}, Δk_{py} = quenching rate difference for the two/three C−H oscillators of one benzylic methylene group/pyridine ring (C−H minus C−D); fitting on χ^2 using weighting factors $w_i = 1/s_i^2$ with s_i = sample standard deviation (see Table 1); R^2: coefficient of determination. [b] Standard error in parentheses.

(b) The potentially very strong variation of FCO is not confined to the isotopic substitution with deuterium. In general, every replacement of oscillator moieties for the purpose of influencing nonradiative transitions is in principle subject to the same, potentially equally severe FCO differences. With the possible exception of Yb, which has only one relatively large energy gap ($\Delta E \approx 10\,250$ cm^{-1}), this certainly applies to the great majority of all near-IR emitting lanthanoids (Pr, Nd, Sm, Dy, Ho, Er, Tm: $\Delta E <$ ca. 7800 cm^{-1}).

(c) In addition, the existence of such dramatic differences in FCO has ramifications for the prevalent conceptual understanding of near-IR lanthanoid luminescence. It is a stark reminder that the validity of using the energy gap law[11] in a qualitative way (i.e., only considering the number of required vibrational quanta) is called into question in situations where molecular complexes are present with lanthanoids having small energy gaps.

In summary, we have developed highly emissive praseodymium cryptates with long luminescence lifetimes in solution. We have successfully quantified the influence of different C−H and C−D oscillators on the nonradiative deactivation rates in the praseodymium cryptates **[D$_x$]-Pr** by lifetime measurements. The obtained deactivaton rate differences between isotopologic C−(H/D) oscillators confirm our premise that aromatic C−D moieties anomalously quench praseodymium luminescence more than the corresponding C−H stretching modes. To the best of our knowledge, this is the first statistically significant, experimental proof that Franck−Condon overlap of lanthanoid electronic levels and vibrational overtones of isotopologic C−(H/D) moieties can reverse the "normal" quenching efficiencies of these oscillators. This finding will certainly be very helpful in the future for the principal understanding of near-IR emissive lanthanoid complexes and for the rational design of molecular lanthanoid near-IR luminophores with increased emission efficiencies.

■ ASSOCIATED CONTENT

S Supporting Information

Synthetic procedures for the preparation of **[D$_x$]-Pr**, HPLC traces, details for the spectroscopic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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