Perdeuterated 2,2′-Bipyridine-6,6′-dicarboxylate: An Extremely Efficient Sensitizer for Thulium Luminescence in Solution

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S *Supporting Information*

ABSTRACT: Lanthanoid luminescence has become an important pillar for many modern photonics applications such as bioanalytical research or functional material science. So far, however, thulium despite having one of the most interesting photophysics among the lanthanoids has suffered from extremely low luminescence efficiencies in molecular complexes with organic sensitizer ligands. This has greatly hampered the investigation and application of thulium emission in solution. Here, the discovery of a powerful sensitizer for thulium photo-luminescence is reported. The corresponding thulium complex exhibits emission efficiencies (quantum yield $\Phi >$ 0.12%; lifetime $\tau_{obs} = 4.6$ μs; brightness $\varepsilon\Phi > 30$ M^{-1} cm^{-1}) and can even be detected at low micromolar concentrations in high-phonon solvents like water without the need for laser excitation.

Lanthanoid photoluminescence with its rich photophysics and unique properties (e.g., sharp emission bands and long luminescence lifetimes) is one of the most attractive fields for the development of advanced photonic applications.[1] The population of the emitting lanthanoid states, however, is difficult because direct excitation via the corresponding f–f transitions are Laporte-forbidden and often also spin-forbidden and consequently show only very small molar extinction coefficients (usually $\varepsilon < 3$ M^{-1} cm^{-1}). In molecular lanthanoid complexes, this problem can be overcome either by excitation with powerful light sources such as lasers or by use of the so-called "antenna effect", where organic chromophores in the vicinity of the lanthanoid collect the excitation energy via highly allowed transitions and subsequently transfer the energy to excited metal states. The latter strategy has been especially successful for the realization of molecular lanthanoid luminophores, with the visible emitters europium and terbium reaching quantum yields $\Phi > 50\%$ and brightnesses $\varepsilon\Phi > 10^4$ M^{-1} cm^{-1}.[2] The luminescence from almost all other relevant lanthanoids in solution is also well established albeit with a lesser degree of emission efficiency, especially for those emitting in the near-IR region.[3] One of the very few lanthanoids that still suffer from debilitatingly low-sensitized luminescence in solution is thulium. So far, the use of the very rich photophysics of thulium has been restricted to solid-state materials in low-phonon matrices, where its properties have received tremendous attention for a number of photonic applications such as photovoltaic spectral conversion,[4] optical telecommunication,[5] and light-upconverting materials.[6] In contrast to the vast literature for solid-state thulium

luminescence, only a handful of reports regarding emissive, molecular thulium complexes in solution have been published over the last decades.[7] In this context, we report here the serendipitous identification of a simple, yet extremely powerful sensitizing chelator for thulium luminescence in solution and a rare example of a thulium complex whose emission can easily be detected even in water.

During the course of efforts to develop MRI contrast agents based on bipyridine scaffolds[8] and as part of our continued studies to develop near-IR luminescence probes,[9] we recently revisited the tetradentate ligand 2,2′-bipyridine-6,6′-dicarboxylic acid ($H_2\mathbf{1}$; Scheme 1), which had previously been reported as a

Scheme 1. Synthesis of the Complexes [D_x]-M
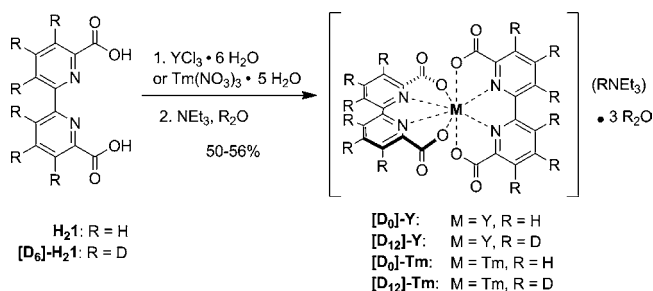
moderately effective sensitizer for terbium and europium luminescence in solution.[10] Because the ligand-centered triplet level of the corresponding gadolinium complex [Gd($\mathbf{1}$)$_2$]-(HNEt$_3$) was given as 20325 cm^{-1},[10] which is far too low for the population of the thulium-centered, emitting $^1G_4$ level at ca. 21350 cm^{-1},[11] we did not expect to observe sizable thulium luminescence.

Nevertheless, we synthesized the complex [D_0]-Tm (Scheme 1), which was unambiguously identified as an anionic 2:1 (ligand/metal) complex in the bulk material (elemental analysis) and in solution {^{1}H NMR in CD$_3$OD and [D_6]-dimethyl sulfoxide (DMSO)}.[12] To our great surprise, the bulk material of [D_0]-Tm showed blue/purple emission so strong that it could even be detected with the naked eye after excitation with a standard laboratory UV lamp. This exceptionally efficient luminescence prompted us to investigate this compound more closely. In addition to [D_0]-Tm, we also synthesized the corresponding isotopologic complex [D_{12}]-Tm (Scheme 1) by perdeuteration of the aromatic ligand scaffold, a commonly used strategy to decrease nonradiative deactivation of lanthanoid

excited states by high-energy C−H oscillators.[13] First, we remeasured the 0-phonon transition energy of low-temperature (77 K) phosphorescence from the excited triplet state of the yttrium complex [D_x]-Y ($x = 0, 12$). In contrast to the previous study,[10] we obtained a much higher value of ca. 23500 cm^{-1} for both isotopologues,[12] which is ideally situated a little more than 2000 cm^{-1} above the emitting $^1G_4$ level (vide infra), preventing thermally activated energy back-transfer onto the ligand and concomitant efficiency losses. Steady-state luminescence spectroscopy on the complexes [D_x]-Tm ($x = 0, 12$) in perdeuterated solvents (CD_3OD and [D_6]-DMSO) showed intense emission bands in the visible and near-IR ranges, the majority of which could expectedly be assigned as originating from the $^1G_4$ level (Figure 1).
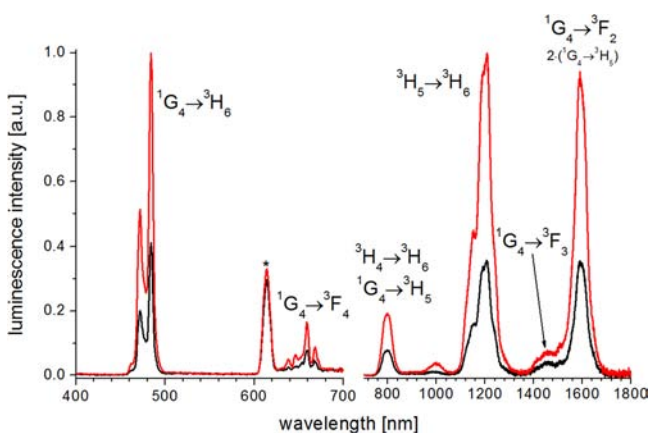

Figure 1. Steady-state emission spectra of [D_0]-Tm (black) and [D_{12}]-Tm (red) in [D_6]-DMSO (left, $\lambda_{exc} = 306$ nm, 4 nm bandwidth, * second-order excitation peak; right, $\lambda_{exc} = 306$ nm, 20 nm bandwidth, emission = long-pass filter RG780).[12]

Time-resolved measurements gave extraordinarily long luminescence lifetimes of up to $\tau = 4.6$ μs in [D_6]-DMSO for transitions from the $^1G_4$ state in [D_{12}]-Tm (Table 1 and Figure

Table 1. Luminescence Data for the Complexes [D_x]-Tm in Solution ($c \approx 10$ μM)[a]

complex	solvent	$\tau(^1G_4)$[b] [μs]	$\tau(^3H_5)$[c] [μs]	$\Phi_{partial}(^1G_4\rightarrow{}^3H_6)$[d,e] [%]
[D_0]-Tm	CD_3OD	1.4		
[D_0]-Tm	[D_6]-DMSO	1.5		
[D_{12}]-Tm	CD_3OD	3.9	1.0	0.08
[D_{12}]-Tm	[D_6]-DMSO	4.6	1.7	0.12

[a]All values are averages of three independent measurements. Estimated uncertainties: $\tau \pm 10\%$; $\Phi \pm 15\%$. [b]Determined for the transition $^1G_4 \rightarrow {}^3H_6$: $\lambda_{exc} = 306$ nm; $\lambda_{em} = 470$ nm. [c]Determined for the transition $^3H_5 \rightarrow {}^3H_6$: $\lambda_{exc} = 320$ nm; $\lambda_{em} = 1200$ nm. [d]Partial quantum yield ($^1G_4 \rightarrow {}^3H_6 \approx 455-505$ nm). [e]$\lambda_{exc} = 316$ nm, determined relative to quinine hemisulfate ($\Phi = 54.6\%$) in 0.5 M sulfuric acid as the standard.[14]

2). No rise time could be observed for these transitions. Compared to the few known literature examples, which usually have lifetimes in the low nanosecond range,[7] the obtained value represents an improvement of two or more orders of magnitude. In addition, a comparison of the lifetimes of [D_0]-Tm and [D_{12}]-Tm allowed the impact of ligand perdeuteration to be evaluated as roughly tripling the efficiency (e.g., Table 1, [D_6]-DMSO; $\tau = 4.6$ μs for [D_{12}]-Tm vs $\tau = 1.5$ μs for [D_0]-Tm). For the
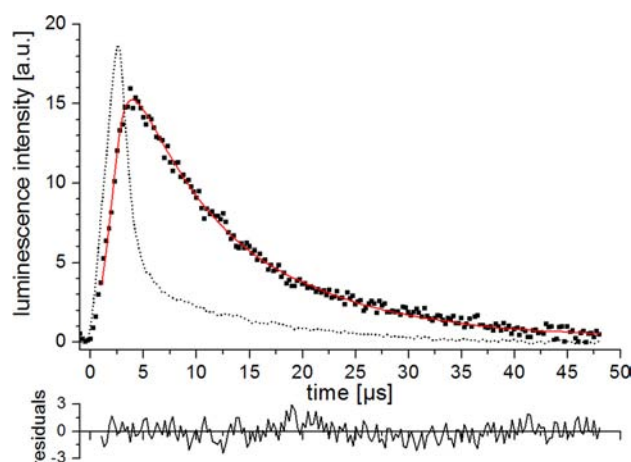
Figure 2. Luminescence decay profile of the transition $^1G_4 \rightarrow {}^3H_6$ (470 nm) in [D_{12}]-Tm ([D_6]-DMSO and $\lambda_{exc} = 306$ nm) with a monoexponential fit (red, $\tau_{obs} = 4.6$ μs) and instrument response (dotted line).

perdeuterated complex [D_{12}]-Tm, partial quantum yields $\Phi_{partial}$ were measured for the visible transition $^1G_4 \rightarrow {}^3H_6$ (Table 1).[15] Because of the presence of moderately quenching O−D oscillators, the partial quantum yield in CD_3OD ($\Phi_{partial} = 0.08\%$) is slightly lower than the one in [D_6]-DMSO ($\Phi_{partial} = 0.12\%$), but both values are already higher than most previously known molecular thulium luminophores in solution, notwithstanding the additional contributions of all other emission bands of [D_{12}]-Tm that could not be quantified. To the best of our knowledge, there is only one molecular thulium complex that shows comparable or better luminescence efficiency (overall $\Phi = 0.82\%$ for visible and near-IR emission in water).[7a]

The sensitization of the thulium center and protection from quenching solvent oscillators in [D_{12}]-Tm are so efficient that visible luminescence can even be detected at low micromolar concentrations in water after excitation with a normal xenon lamp (typically used in standard fluorimeters) without the necessity for specialized laser setups (Figure 3).

It is also worth noting that [D_{12}]-Tm contains a thulium center with a brightness of $\varepsilon\Phi_{partial} > 30$ M^{-1} cm^{-1} ($\varepsilon = 25 \times 10^3$ M^{-1} cm^{-1} at 306 nm[12] and for the emission band $^1G_4 \rightarrow {}^3H_6$

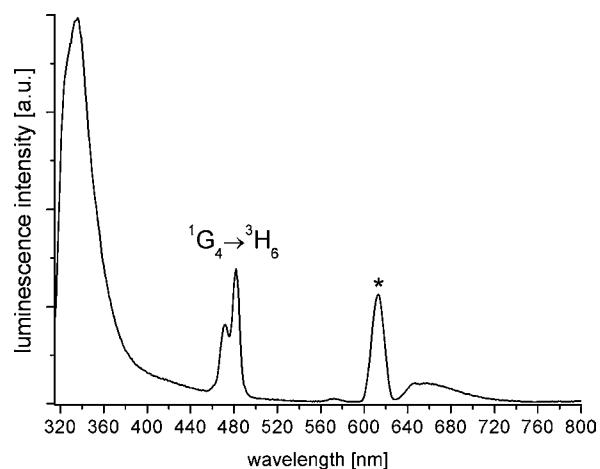**Figure 3.** Steady-state emission spectrum of [D_{12}]-Tm in water ($c \approx 20$ μM) after excitation with a simple 75 W xenon lamp ($\lambda_{exc} = 306$ nm, 6 nm bandwidth, and * second-order excitation peak).

only). This is a higher value per thulium than in all solid-state materials because molar extinction coefficients in these cases do not substantially exceed $\varepsilon \approx 1 \ M^{-1} \ cm^{-1}$ for direct thulium absorption[16] and consequently would have a maximum brightness of $\varepsilon\Phi < 1 \ M^{-1} \ cm^{-1}$ even for hypothetically perfect quantum yields. This fact aptly illustrates the significance and great potential that sensitized thulium luminescence in species like $[\mathbf{D_{12}}]$-**Tm** could have in the future.

In summary, we have identified perdeuterated 2,2′-bipyridine-6,6′-dicarboxylic acid as an extremely efficient sensitizer for molecular thulium luminescence, which has suffered from exceedingly low emission intensities for decades. This new antenna moiety enables the realization of microsecond luminescence lifetimes and of quantum yields greater than 0.12%. In addition, thulium luminescence in $[\mathbf{D_{12}}]$-**Tm** can even be measured in neat water, while most previous systems suffer from the complete disappearance of luminescence in the presence of only trace amounts of water. This discovery will greatly facilitate the investigation and application of thulium's rich photophysics in molecular complexes in solution. This area, which is almost entirely unexplored so far, promises exciting prospects for basic as well as applied research, e.g., with respect to molecular upconversion or optical telecommunication.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthetic procedures and analytical data for $[\mathbf{D_x}]$-**M**, spectroscopic details, and additional photophysical data. 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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