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Strong Circularly Polarized Luminescence from Highly Emissive Terbium Complexes in Aqueous Solution

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Two luminescent terbium(III) complexes have been prepared from chiral ligands containing 2-hydroxyisophthalamide (IAM) antenna chromophores and their non-polarized and circularly-polarized luminescence properties have been studied. These tetradentate ligands, which form 2:1 ligand/Tb^{III} complexes, utilize diaminocyclohexane (cyLI) and diphenylethylenediamine (dpenLI) backbones, which we reasoned would impart conformational rigidity and result in Tb^{III} complexes that display both large luminescence quantum yield (Φ) values and strong circularly polarized luminescence (CPL) activities. Both Tb^{III} complexes are highly emissive, with Φ values of 0.32 (dpenLI-Tb) and 0.60 (cyLI-Tb). Luminescence lifetime measurements in H_2O and D_2O indicate that while cyLI-Tb exists as a single species in solution, dpenLI-Tb exists as two species: a monohydrate complex with one H_2O molecule directly bound to the Tb^{III} ion and a complex with no water molecules in the inner coordination sphere. Both cyLI-Tb and dpenLI-Tb display increased CPL activity compared to previously reported Tb^{III} complexes made with chiral IAM ligands. The CPL measurements also provide additional confirmation of the presence of a single emissive species in solution in the case of cyLI-Tb, and multiple emissive species in the case of dpenLI-Tb.

Introduction

Circularly polarized luminescence (CPL), the emission analog of circular dichroism (CD), combines the sensitivity of luminescence techniques with the specificity of chiroptical spectroscopy.[1–7] The luminescence of lanthanide complexes is especially sensitive to changes in coordination geometry and molecular environment, and as such, CPL-active lanthanide complexes are excellent candidates for luminescent probes that can report on their chiral surroundings.[8] To maximize the sensitivity of a luminescent lanthanide-based chiroptical probe the complex should possess both a large luminescence quantum yield and strong CPL activity. Additionally, solubility and stability of the Ln^{III} complex in aqueous solution is very important for practical applications. Such systems, however, remain elusive; often complexes are optimized in respect to either emission intensity or CPL activity, though not both (see below). A system that combines a large luminescence quantum yield with strong CPL activity in aqueous solution would represent a significant advance in the field of Ln^{III}-based CPL.

We have previously shown that Tb^{III} complexes of 2-hydroxyisophthalamide (IAM)-based ligands are exceptionally bright, displaying some of the highest luminescence quantum yield (Φ) values of Ln^{III} complexes in aqueous solution reported to date ($\Phi \approx 0.60$).[9] While chiral IAM ligands afford CPL-active Tb^{III} complexes that retain the brightness of the parent achiral forms, their CPL activity is relatively modest. CPL activity is commonly reported as the luminescence dissymmetry factor, g_{lum}, defined as $g_{lum} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are the intensities of left- and right-polarized emission respectively. Among chiral Tb^{III}-IAM complexes with large Φ values, $|g_{lum}|$ values ≤ 0.078 are observed.[10,11] As a strategy to increase CPL activity we designed chiral IAM ligands that are more rigid than the previously reported tetrapodal octadenate ligands since CPL activity had been shown to increase with the conformational rigidity of the complex.[12,13] These ligands, cyLI-IAM and dpenLI-IAM (Figure 1), utilize diaminocyclohexane and diphenylethylenediamine backbones respectively. Tetradentate IAM ligands of this type form 2:1 ligand/Ln^{III} (ML_2) complexes,[14] analogous to the previously reported octadentate ligands that form 1:1 ligand/Ln^{III} complexes. Tetradendate ligands offer the advantage of be-

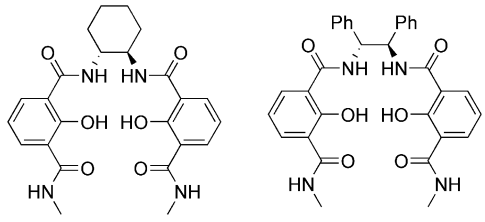

Figure 1. Chemical structures of cyLI- and dpenLI-IAM ligands.

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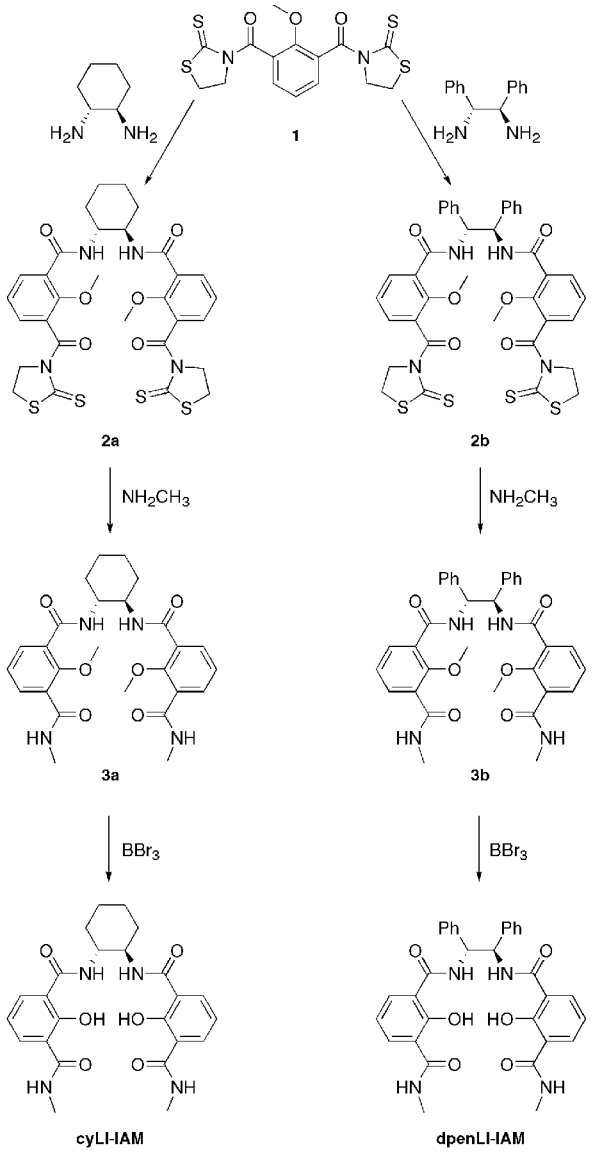
ing more readily synthesized than higher denticity ligands and consequently by utilizing tetradentate ligands we are able to easily investigate how small structural changes in the ligand scaffolds influence the photophysical behavior of the resulting Tb^{III} complexes. Herein we report the syntheses of cyLI- and dpenLI-IAM and their Tb^{III} complexes along with their absorption and luminescence properties in the presence of both circularly-polarized and non-polarized light.

Results and Discussion

CyLI- and dpenLI-IAM were synthesized following the procedure shown in Scheme 1. By starting with the dithiazolide precursor **1**[15] one is able to substitute both ends of the molecule with two distinct amines. Dilute solutions of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine and (1*R*,2*R*)-(+)-1,2-diaminocyclohexane were each added to **1** over 36 h to produce the mono-substituted species, **2a** and **2b**, respectively. These two species were each then combined with methylamine to yield **3a** and **3b**. The methyl-protected ligands were then both deprotected using BBr_3 to yield the final ligands. The Tb^{III} ML_2 complexes (here referred to as cyLI-Tb and dpenLI-Tb) used for the spectroscopic measurements were prepared in situ by combining 1 equiv. of $TbCl_3$ (in 1 M HCl) with 2 equiv. of ligand (in a basic aqueous solution) in 0.1 M Tris buffered H_2O (pH = 7.4). The complexes were characterized using mass spectrometry (ES^-) in addition to the optical techniques that are described in the upcoming sections. The ability to rely on these optical techniques is especially valuable in the study of Tb^{III}-IAM complexes since ^1H NMR spectroscopy is problematic because of signal broadening caused by the paramagnetic Tb^{III} center.[16]

The absorption spectra of cyLI-Tb and dpenLI-Tb display broad transitions similar to those previously observed for Tb-IAM complexes in aqueous solution, which are attributed to π-π* transitions in the IAM chromophore (Figure 2, a).[9,17] As with other Tb-IAM complexes, the broad absorption bands of cyLI-Tb and dpenLI-Tb allow for excitation with wavelengths up to ca. 390 nm, which is more favorable for practical biological applications compared to many other high quantum yield Tb^{III} complexes that require more damaging higher energy excitation wavelengths.[18,19] Additionally, both cyLI-Tb and dpenLI-Tb show CD activity as expected (Figure 2, b). The CD spectra show strong Cotton effects[20] for both complexes between 300–380 nm.



Scheme 1. Syntheses of cyLI- and dpenLI-IAM ligands.

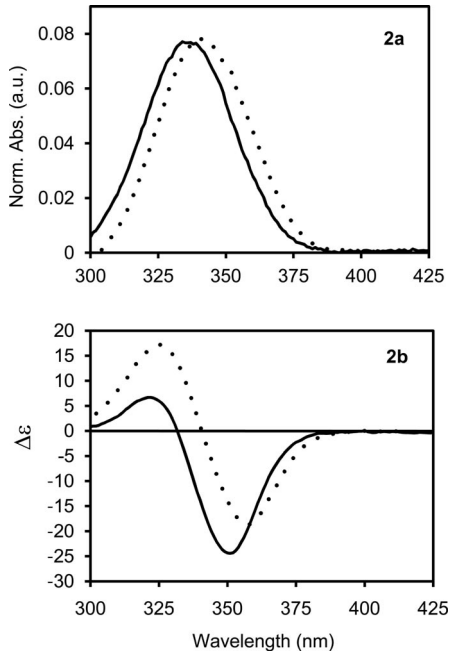


Figure 2. Absorption spectra (**2a**) and CD spectra (**2b**) of cyLI-Tb (solid) and dpenLI-Tb (dashed) in aqueous solution [$C = 10^{-5}$ M, 0.1 M Tris (pH = 7.4)] at 298 K.

To determine the efficiency of Tb^{III} sensitization, the emission behavior of cyLI-Tb and dpenLI-Tb was investigated. A summary of the luminescence quantum yield and lifetime values is given in Table 1. The luminescence spectra display the characteristic bands corresponding to transitions from the $^5D_4$ electronic level to the ^7F_J (J = 0–6) manifold of Tb^{III} (Figure 3). The two complexes show slight differences in the relative intensities and fine structures of the peaks, which points to variation in the coordination environments experienced by the Tb^{III} ions in each complex.[21] This difference in coordination environment is supported by the luminescence quantum yield (Φ) values for the two complexes: cyLI-Tb has a quantum yield of 0.60, while dpenLI-Tb has a quantum yield of 0.32. The cyLI-Tb value is consistent with the high quantum yield values observed for Tb^{III} complexes with octadentate IAM ligands.[9,11,17]

Table 1. Photophysical properties of the Tb^{III} complexes [10^{-5} M (Tris buffer, pH 7.4, λ_{ex} = 340 nm)].

Complex	QY (Φ)	τ (r.t.), ms		q[a]	τ (77 K), ms[b]	
		H_2O	D_2O		H_2O	D_2O
cyLI-Tb	0.60	1.66	1.84	0	1.77	2.05
dpenLI-Tb	0.32	1.51 (84%)	1.68 (88%)	0	1.89 (37%)	2.21 (37%)
		0.550 (16%)	1.68 (12%)	1	1.89 (63%)	2.21 (63%)

[a] Calculated from r.t. values using $q = 5 \times (1/\tau_{H2O} - 1/\tau_{D2O} - 0.06)$.[21] [b] Contained 10% (v/v) glycerol.

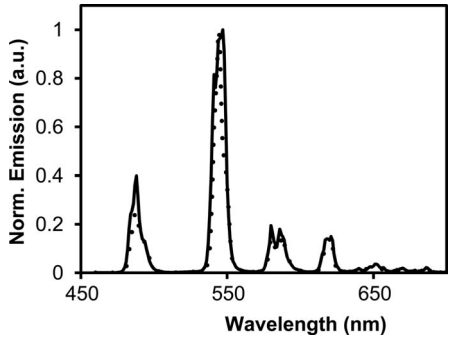


Figure 3. Luminescence spectra of cyLI-Tb (solid) and dpenLI-Tb (dashed) in aqueous solution (0.1 M Tris, pH = 7.4) at 298 K normalized to the intensity of the J = 5 peak.

To further investigate this difference in emission intensity the luminescence lifetimes were measured both in H_2O and D_2O at room temperature (r.t.) and at 77 K (Table 1). Mono-exponential lifetime decays are exhibited by cyLI-Tb, while dpenLI-Tb exhibits bi-exponential decays, indicating that for the former, only one luminescent species is present in solution, while for the latter, two luminescent species are present. The number of bound water molecules (q) was estimated for each of the complexes based on the lifetimes measured at room temperature using the formula developed by Beeby et al.,[22] and q values of zero were obtained for cyLI-Tb and for one of the two dpenLI-Tb species. The other dpenLI-Tb species, however, has approximately one water molecule in the inner coordination sphere, which quenches Tb^{III} emission and contributes to the low luminescence quantum yield observed for dpenLI-Tb. The overall quantum yield for dpenLI-Tb is the weighted sum of the quantum yields of the q = 0 and q = 1 species. Since the latter experiences quenching due to bound water, it has a lower quantum yield than a q = 0 species.

The CPL spectra of cyLI-Tb and dpenLI-Tb are plotted in Figure 4 for the magnetic dipole allowed $^5D_4 \rightarrow {}^7F_5$ transition. The g_{lum} values are summarized in Table 2. The CPL signals provide additional confirmation that stable chiral species are present in solution. Both spectra display several peaks corresponding to crystal-field splitting; the difference in sign, shape and magnitude of the CPL signal are consistent with the fact that the two systems do not exhibit the same crystal field structure in solution. The CPL signal exhibited by cyLI-Tb is similar whether via direct excitation of the Tb^{III} ion (λ_{ex} = 488 nm) or indirect excitation via the ligand absorption bands (λ_{ex} = 341 nm), which indicates that the same species in solution is responsible for the CPL activity detected. Additionally, the g_{lum} values obtained for this complex are the same upon excitation with right-, left-, and plane-polarized light, which is consistent with the presence of only one species in solution;[23] had the solution contained a mixture of diastereomers, the CPL signal would have been dependent on the polarization of the excitation beam.[24] In contrast, the g_{lum} values obtained for dpenLI-Tb are dependent on the polarization of the excitation beam and on whether direct or indirect excitation is used, which indicates that more than one species in solution is responsible for the CPL signal detected. These results support the lifetime data, which indicate the presence of two emitting species in solution that differ in hydration number and therefore also coordination environment.

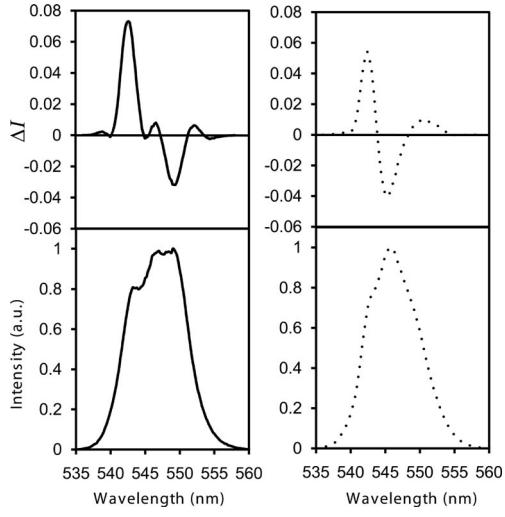


Figure 4. CPL (top) and total luminescence spectra (bottom) for the $^5D_4 \rightarrow {}^7F_5$ transition for cyLI-Tb (solid) and dpenLI-Tb (dashed) in aqueous solution.

Table 2. Summary of CPL data for cyLI-Tb and dpenLI-Tb.

Complex	λ_{ex}	Transition	λ [nm]	g_{lum}
cyLI-Tb	341 nm	$^5D_4 \rightarrow {}^7F_5$	542.0	+0.20
			548.6	–0.063
dpenLI-Tb	343 nm	$^5D_4 \rightarrow {}^7F_5$	542.4	+0.16
			545.4	–0.082
			551.0	+0.043

Conclusions

Tetradentate IAM ligands yield highly luminescent Tb^{III} complexes with large g_{lum} values in aqueous solution at physiologically relevant pH, which may be attributed to the increased rigidity of the ligand frameworks. Varying the chiral amine that serves as the ligand backbone was found to impact solvent access to the Tb^{III} center, which was determined through luminescence lifetime, luminescence quantum yield and CPL measurements. The CyLI-Tb complex is particularly interesting, since it has an extremely high quantum yield, a g_{lum} value over twofold larger than the largest observed for a comparably emissive Tb-IAM complex, and consists of a single emitting species in solution.

Experimental Section

General Methods: All chemicals were obtained from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra, elemental analyses, and mass spectra were obtained at the corresponding analytical facility in the College of Chemistry, University of California, Berkeley.

2a: (2-Methoxy-1,3-phenylene)bis[(2-thioxothiazolidin-3-yl)methanone][15] (**1**) (5.0 g, 12.5 mmol) was dissolved in 10 mL of CH_2Cl_2. A 250 mL solution of (1*R*,2*R*)-(+)-1,2-diaminocyclohexane (0.128 g, 1.1 mmol) in a 95:5 CH_2Cl_2/MeOH solution was cannulated into the solution of **1** over 36 h. The solvents were then removed under vacuum and the reaction mixture was dissolved in CH_2Cl_2 and washed with 1 M NaOH. The product was purified by silica gel chromatography (2% MeOH/98% CH_2Cl_2); yield 0.620 g (84%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.35 (m, 4 H, CH_2), 1.74 (m, 2 H, C*H*H), 2.15 (m, 2 H, C*H*H), 3.35 (m, 4 H, NCH_2CH_2S), 3.76 (s, 6 H, OCH_3), 3.98 (m, 2 H, CH_2CHN), 4.55 (m, 4 H, NCH_2CH_2S), 7.07 (t, *J* = 8 Hz, 2 H, ArH), 7.30 (dd, *J* = 5, 2 Hz, 2 H, ArH), 7.60 (d, *J* = 8 Hz, 2 H, NH), 7.89 (dd, *J* = 8, 2 Hz, 2 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.8, 29.2, 32.6, 53.4, 55.7, 63.1, 124.1, 127.1, 129.1, 132.1, 134.0, 155.7, 165.0, 167.4, 201.3 ppm. MS (FAB+): *m*/*z* = 673 [MH^+].

2b: Compound **1**[15] (7.96 g, 20.0 mmol) was dissolved in 10 mL of CH_2Cl_2. A 250 mL solution of (1*R*,2*R*)-(+)-1,2-diphenylethylenediamine (0.425 g, 2.0 mmol) in a 95:5 CH_2Cl_2/MeOH solution was cannulated into the solution of 1 over 36 h. The solvents were then removed under vacuum and the reaction mixture was dissolved in CH_2Cl_2 and washed with 1 M NaOH. The product was purified by silica gel chromatography (15% EtOAc/85% CH_2Cl_2); yield 0.470 g (30%). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.30 (m, 4 H, NCH_2CH_2S), 3.86 (s, 6 H, OCH_3), 4.52 (m, 4 H, NCH_2CH_2S) 5.50 (m, 2 H, C*H*NH), 6.95 (t, *J* = 8 Hz, 2 H, ArH), 7.16 (m, 10 H, ArH), 7.85 (dd, *J* = 8, 2 Hz, 2 H, ArH), 7.89 (dd, *J* = 8, 2 Hz, 2 H, ArH), 8.80 (q, *J* = 5 Hz, 2 H, N*H*CH_3), 9.21 (m, 2 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 29.7, 53.6, 57.5, 64.2, 118.7, 120.2, 126.9, 128.3, 131.5, 136.6, 142.4, 158.6, 167.2, 175.6, 201.8 ppm. MS (FAB+): *m*/*z* = 771 [MH^+].

3a (Representative Procedure): To a solution of **2a** (0.60 g, 0.89 mmol) in 15 mL of CH_2Cl_2 was added 1.0 mL of methylamine (40% aq. soln.). The reaction mixture was stirred at room temperature for 6 h and was then washed with 1 M NaOH. The resulting off-white residue was applied to a silica column and the product was eluted with 4% MeOH/96% CH_2Cl_2; yield 0.402 g (91%). ^1H NMR (400 MHz, [D_6]DMSO): δ = 1.30 (m, 2 H, C*H*H), 1.44 (m, 2 H, C*H*H), 1.71 (m, 2 H, C*H*H), 1.94 (m, 2 H, C*H*H), 2.76 (d, *J* = 5 Hz, 6 H, $NHCH_3$), 3.70 (s, 6 H, OCH_3), 3.89 (m, 2 H, CH_2CHNH), 7.17 (t, *J* = 8 Hz, 2 H, ArH), 7.53 (m, 4 H, ArH), 8.21 (m, 4 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 24.4, 26.2, 31.7, 52.3, 62.4, 123.4, 130.2, 130.4, 131.0, 131.1, 154.8, 165.4, 166.1 ppm. MS (FAB+): *m*/*z* = 497 [MH^+].

3b: ^1H NMR (400 MHz, [D_6]DMSO): δ = 2.81 (d, *J* = 4 Hz, 6 H, $NHCH_3$), 3.80 (s, 6 H, OCH_3), 5.51 (m, 2 H, C*H*NH), 6.95 (t, *J* = 8 Hz, 2 H, ArH), 7.16 (m, 10 H, ArH), 7.85 (dd, *J* = 8, 2 Hz, 2 H, ArH), 7.89 (dd, *J* = 8, 2 Hz, 2 H, ArH), 8.80 (q, *J* = 5 Hz, 2 H, N*H*CH_3), 9.21 (m, 2 H, NH) ppm. ^{13}C NMR (100 MHz, [D_6]-DMSO): δ = 26.0, 57.5, 64.2, 116.7, 118.1, 120.4, 126.8, 127.3, 127.5, 130.5, 132.4, 138.6, 159.2, 165.6, 168.3 ppm. MS (FAB+): *m*/*z* = 595 [MH^+].

cyLI-IAM (Representative Procedure): A suspension of 3a (0.325 g, 0.66 mmol) in 30 mL of CH_2Cl_2 was cooled to –78 °C and 1.0 mL (10.6 mmol) of BBr_3 was added. The reaction mixture was warmed to room temperature and stirred for 48 h. The volatiles were removed under vacuum and a few milliliters of 1 M HCl were added, causing the product to precipitate out of solution. The product was recrystallized from hot H_2O; yield 0.229 g (74%). ^1H NMR (400 MHz, [D_6]DMSO): δ = 1.31 (m, 2 H, C*H*H), 1.48 (m, 2 H, C*H*H), 1.73 (m, 2 H, C*H*H), 1.98 (m, 2 H, C*H*H), 2.81 (d, *J* = 4 Hz, 6 H, $NHCH_3$), 3.94 (m, 2 H, CH_2CHNH), 6.93 (t, *J* = 8 Hz, 2 H, ArH), 7.91 (t, *J* = 9 Hz, 4 H, ArH), 8.61 (m, 2 H, CH_2CHNH), 8.69 (m, 2 H, N*H*CH_3), 14.71 (s, 2 H, OH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 24.4, 26.1, 31.5, 52.4, 117.9, 118.0, 118.7, 132.2, 132.7, 159.3, 166.6, 167.7 ppm. MS (FAB+): *m*/*z* = 469 [MH^+]. Anal. calcd. (found) for $C_{24}H_{28}N_4O_6 \cdot 0.5H_2O$: C, 60.36 (60.15); H, 6.12 (6.06); N, 11.73 (11.42).

cyLI-Tb: [$C_{48}H_{52}N_8O_{12}Tb$]$^-$, MS (ES$^-$): *m*/*z* = 1091.2 [M^-].

dpenLI-IAM: ^1H NMR (400 MHz, [D_6]DMSO): δ = 2.83 (d, *J* = 4 Hz, 6 H, $NHCH_3$), 5.60 (m, 2 H, C*H*NH), 6.97 (t, *J* = 8 Hz, 2 H, ArH), 7.20 (m, 10 H, ArH), 7.88 (dd, *J* = 8, 2 Hz, 2 H, ArH), 7.96 (dd, *J* = 8, 2 Hz, 2 H, ArH), 8.86 (q, *J* = 5 Hz, 2 H, N*H*CH_3), 9.25 (m, 2 H, NH), 14.67 (s, 2 H, OH) ppm. ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 26.1, 57.5, 116.9, 118.2, 119.9, 127.2, 127.6, 128.0, 131.5, 133.4, 139.6, 159.3, 165.8, 168.6 ppm. MS (FAB+): *m*/*z* = 567 [MH^+]. Anal. calcd. (found) for $C_{32}H_{30}N_4O_6 \cdot 0.5H_2O \cdot MeOH$: C, 65.66 (65.46); H, 5.18 (5.35); N, 9.28 (9.48).

dpenLI-Tb: [$C_{64}H_{56}N_8O_{12}Tb$]$^-$, MS (ES$^-$): *m*/*z* = 1287.3 [M^-].

UV/Vis Absorption, Circular Dichroism, Emission, and Circularly Polarized Luminescence Spectra. General Methods: Absorption spectra were recorded on a Cary 300 UV/Vis spectrophotometer using a 1-cm quartz cell. Emission spectra were recorded on a FluoroLog-3 (JobinYvon) fluorimeter using a 1-cm Supracil quartz luminescence cell (room-temperature measurements). The Tb^{III} complexes (10 mM) were prepared in situ in 0.1 M Tris-buffered H_2O (pH 7.4). The complexes were characterized using mass spectrometry (ES$^-$). Quantum yields were determined by the optically dilute method[25] using the following equation:

$Q_x/Q_r = [A_r(\lambda_r)/A_x(\lambda_x)][I(l_r)/I(l_x)][n_x^2/n_r^2][D_x/D_r]$

where A is the absorbance at the excitation wavelength (λ), I is the intensity of the excitation light at the same wavelength, n is the refractive index and D is the integrated intensity. Quinine sulfate in 1.0 N sulfuric acid was used as the reference (Q_r = 0.546).[26] Circularly polarized luminescence and total luminescence spectra were recorded on an instrument according to literature procedures,[23,24,27] operating in a differential photon-counting mode. CPL measurements were performed at 295 K in H_2O (0.1 M Tris, pH = 7.4) with analyte concentrations of 10^{-4} to 10^{-5} M.

Acknowledgments

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[1] H. G. Brittain, in: *Lanthanide Probes in Life, Chemical and Earth Sciences: Theory and Practice*, 3rd ed. (Eds.: J.-C. G. Bünzli, G. R. Choppin), Elsevier, Amsterdam, **1989**.
[2] F. S. Richardson, J. P. Riehl, *Chem. Rev.* **1977**, *77*, 772–792.
[3] J. P. Riehl, F. S. Richardson, *Chem. Rev.* **1986**, *86*, 1–16.
[4] J. P. Riehl, F. S. Richardson, *Methods Enzymol.* **1993**, *226*, 539–553.
[5] H. G. Brittain, *Appl. Spectrosc. Rev.* **2007**, *35*, 175–201.
[6] H. P. J. M. Dekkers, in: *Circular Dichroism* (Eds.: N. Berova, K. Nakanishi, R. W. Woody), Wiley-VCH, Weinheim, **2000**.
[7] J. P. Riehl, G. Muller, in: *Handbook on the Physics and Chemistry of Rare Earths*, vol. 43 (Eds.: K. A. Gschneider, J.-C. G. Bünzli, V. K. Pecharsky), North-Holland Publishing Company, Amsterdam, **2005**, p. 289.
[8] G. Muller, *Dalton Trans.* **2009**, 9692–9707.
[9] S. Petoud, S. M. Cohen, J.-C. Bünzli, K. Raymond, *J. Am. Chem. Soc.* **2003**, *125*, 13324–13325.
[10] S. Petoud, G. Muller, E. G. Moore, J. Xu, J. Sokolnicki, J. P. Riehl, U. N. Le, S. M. Cohen, K. N. Raymond, *J. Am. Chem. Soc.* **2007**, *129*, 77–83.
[11] M. Seitz, E. G. Moore, A. J. Ingram, G. Muller, K. N. Raymond, *J. Am. Chem. Soc.* **2007**, *129*, 15468–15470.
[12] R. S. Dickins, J. A. K. Howard, C. W. Lehmann, J. M. Moloney, D. Parker, R. D. Peacock, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 521–523.
[13] J. L. Lunkley, D. Shirotani, K. Yamanari, S. Kaizaki, G. Muller, *J. Am. Chem. Soc.* **2008**, *130*, 13814–13815.
[14] A. P. S. Samuel, J. Xu, K. N. Raymond, *Inorg. Chem.* **2009**, *48*, 687–698.
[15] S. M. Cohen, B. O'Sullivan, K. N. Raymond, *Inorg. Chem.* **2000**, *39*, 4339–4346.
[16] Attempts to characterize IAM-Tb^{III} complexes using ^1H NMR spectroscopy yielded spectra with no distinct resonances that could be assigned unambiguously to IAM protons and thus these results were uninformative.
[17] A. P. S. Samuel, E. G. Moore, M. Melchior, J. Xu, K. N. Raymond, *Inorg. Chem.* **2007**, *46*, 7535–7544.
[18] H. Takalo, V.-M. Mukkala, L. Meriö, J.-C. Rodríguez-Ubis, R. Seadno, O. Juanes, E. Brunet, *Helv. Chim. Acta* **1997**, *80*, 372–387.
[19] M. Xiao, P. R. Selvin, *J. Am. Chem. Soc.* **2001**, *123*, 7067–7073.
[20] G. Snatzke, in: *Circular Dichroism*, 2nd ed. (Eds.: N. Berova, K. Nakanishi, R. W. Woody), Wiley-VCH, New York, **2000**.
[21] J.-C. G. Bünzli, in: *Lanthanide Probes in Life, Chemical and Earth Sciences: Theory and Practice* (Eds.: J.-C. G. Bünzli, G. R. Choppin), Elsevier, Amsterdam, **1989**.
[22] A. Beeby, I. M. Clarkson, R. S. Dickins, S. Faulkner, D. Parker, L. Royle, A. S. d. Sousa, J. A. G. Williams, M. Woods, *J. Chem. Soc. Perkin Trans. 2* **1999**, 493–503.
[23] K. Do, F. C. Muller, G. Muller, *J. Phys. Chem. A* **2008**, *112*, 6789–6793.
[24] M. Seitz, D. King, A. J. Ingram, E. G. Moore, G. Muller, K. N. Raymond, *Inorg. Chem.* **2009**, *48*, 8469–8479.
[25] G. A. Crosby, J. N. Demas, *J. Phys. Chem.* **1971**, *75*, 991–1024.
[26] S. R. Meech, D. Philips, *J. Photochem.* **1983**, *23*, 193–217.
[27] S. D. Bonsall, M. Houcheime, D. A. Straus, G. Muller, *Chem. Commun.* **2007**, *35*, 3673–6378.

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