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Exploring Lanthanide Luminescence in Metal-Organic Frameworks: Synthesis, Structure, and Guest-Sensitized Luminescence of a Mixed Europium/Terbium-Adipate Framework and a Terbium-Adipate Framework

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Two lanthanide-organic frameworks were synthesized via hydrothermal methods. Compound **1** ($[(\mathrm{Eu,Tb})(C_6H_8O_4)_3(H_2O)_2]\bullet(C_{10}H_8N_2)$), orthorhombic, *Pbcn*, $a = 21.925(2)$ Å, $b = 7.6493(7)$ Å, $c = 19.6691(15)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$) takes advantage of the similar ionic radii of the lanthanide elements to induce a mixed-lanthanide composition. Compound **2** ($[Tb_2(C_6H_8O_4)_3(H_2O)_2]\bullet(C_{10}H_8N_2)$), orthorhombic, *Pbcn*, $a = 21.866(3)$ Å, $b = 7.6101(10)$ Å, $c = 19.646(3)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 8$) is the terbium-only analogue of compound **1**. Solid-state measurements of their luminescence behavior demonstrate that the neutral guest molecule (4,4′-dipyridyl) residing in the extraframework channels is successful in sensitizing lanthanide ion emission. In compound **1**, columinescence occurs, and both lanthanide ions show emission. Additionally, quantum yield and lifetime measurements support the premise that the Tb^{3+} center is also acting to sensitize the Eu^{3+}, effectively enhancing Eu^{3+} emission.

Introduction

Metal-organic framework (MOF) materials have attracted much attention in recent years due to potential applications in a wide variety of fields, such as catalysis, ion exchange, and molecular separations.[1] One very promising application of these materials is gas storage, and much attention has been focused on exploiting this utility.[2−5] On the other hand, we are investigating lanthanide-containing MOFs with the goal of harnessing the coordination geometry and luminescent properties of these elements. The intention is to explore new applications of MOFs, particularly sensing and molecular recognition. The higher coordination numbers associated with lanthanide ions may allow for more versatile chemistry that utilizes open coordination sites, whereas the sharp and intense luminescent features may be pertinent in sensor development and light-emitting diode applications.[6]

The construction of these framework materials typically consists of the assembly of metal centers through multifunctional organic linker molecules.[7−10] The resulting structures then consist of higher dimensional topologies with or without accessible void space. Coordination of the organic component with the metal centers in these systems is governed not only by the coordination geometry preferences of the metal itself but also by hard/soft acid/base considerations.[11,12] These considerations may be further extended to allow the inclusion of noncoordinated “template” molecules which aid in directing pore formation and overall topology.[13−16]

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We recently reported the synthesis of a praseodymium-adipate framework with neutral 4,4′-dipyridyl molecules residing within the channels.[14] We were successful in synthesizing a europium analogue of this structure and examined the 4,4′-dipyridyl sensitized luminescence of the Eu^{3+} metal centers. We report herein an expansion of these efforts in the synthesis of two isostructural compounds of this adipate, one being a Tb analogue and the other a mixed Eu/Tb solid solution. What is most striking about the mixed-Ln material is the isomorphous substitution of half of the Eu^{3+} sites with Tb^{3+} throughout the single-crystal structure, which allows for not only template-sensitized Eu^{3+} luminescence but also Eu^{3+}-sensitization from the terbium centers as well. This material is the first example of lanthanide sensitized columinescence within a metal-organic framework and, to our knowledge, only the second such occurrence of a mixed-lanthanide framework material.[17]

Lanthanide ion luminescence, due to f−f transitions, is a well-studied and well-understood physical process in solution phase.[18−23] The rare earth elements offer an advantage over other metals in the development of luminescent materials. The spectra exhibit sharp emission features arising from f−f transitions, with negligible environmental influences since the 4f electrons are shielded by filled 5s and 5p orbitals. In addition, these emission characteristics occur in the visible and IR regions of the spectrum, such as green emission for Tb^{3+} or red emission for Eu^{3+}. However, since direct excitation of the lanthanide ion emissive state is not easily accomplished, the emission is often sensitized through a coordinated ligand or antenna.[24,25] The intensity of the luminescent features in these systems can easily be tuned in solution, and effectively enhanced or diminished as seen fit. Rendering such control in the solid state within metal-organic framework materials has yet to be realized as extensively. However, a number of recent studies demonstrate the potential in this area.[13,26−32] Due to the field of potential applications of these solid materials as sensors or in light-emitting diodes technology, the study of this phenomenon in the solid state is extremely important and requires more fundamental research.

The field of metal-organic coordination polymer chemistry has advanced quickly over recent years. Recent reports tend to focus on the functionality of these materials, but much of this is centered on transition-metal containing materials.[1,33−39] This is not unexpected since transition-metal chemistry offers some readily exploitable coordination geometries due to crystal field splitting and as such have been more heavily pursued than the f-elements in MOF systems. Lanthanides, on the other hand, do not display such phenomena and in turn provide an additional challenge in the assembly of topologies of interest. Indeed, it is arguable that the study of lanthanide-containing coordination polymers and metal-organic frameworks, while still in a phase of structural systematics, is now advancing also into material functionality. As such, it is important to harness this unique feature of the luminescent lanthanide ions and direct attention to exploiting this property for potential applications.

Experimental Section

The title compound (**1**) was synthesized via hydrothermal methods in a 23-mL Teflon-lined Parr bomb, in an identical fashion as our previously reported analogous structure.[14] The original metal concentration of 1.5 was halved in this reaction, and as such $Eu(NO_3)_3$, $Tb(NO_3)_3$, adipic acid, 4,4′-dipyridyl, and water were placed into the bomb in a 0.75/0.75/2/2/320 relative molar ratio. The pH of the solution was adjusted to roughly neutral (pH initial = 6.7) with concentrated aqueous ammonium hydroxide. After 3 days of heating at 120 °C and subsequent cooling to room temperature, clear pale yellow thin rodlike crystals were separated from a clear colorless solution of pH in the range of 3.6−4.2 in a 71% yield based on the metals. A powder form of the Eu-only analogue was synthesized in an identical fashion. Efforts to produce single crystals of X-ray diffraction quality were not explored owing to the fact that this is a known structure[14,40] and that powdered samples were sufficient to conduct luminescence studies.

The terbium structure (**2**) was synthesized in a similar fashion as compound **1** (with relative molar $[Tb^{3+}] = 1.5$ as opposed to 0.75.) However, in order to produce a pure phase with crystals suitable for single-crystal X-ray diffraction, it was necessary to increase the molar ratio of the 4,4′-dipyridyl to 2.5. In addition, this reaction was cooled to 35 °C over 5 h at a rate of 0.4 °C per minute. Initial pH of the solution prior to heating was 4.7, and final

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Table 1. Crystal Data and Structure Refinement for Compounds **1** and **2**

	compound **1**	compound **2**
empirical formula	$TbEuC_{28}H_{36}O_{14}N_2$	$TbC_{14}H_{18}O_7N$
formula weight	935.49	471.21
temperature	293(2) K	293(2) K
wavelength	0.71073 Å	0.71073 Å
crystal system	orthorhombic	orthorhombic
space group	*Pbcn*	*Pbcn*
unit cell dimensions	$a = 21.925(2)$ Å $\alpha = 90°$ $b = 7.6493(7)$ Å $\beta = 90°$ $c = 19.6691(15)$ Å $\gamma = 90°$	$a = 21.866(3)$ Å $\alpha = 90°$ $b = 7.6101(10)$ Å $\beta = 90°$ $c = 19.646(3)$ Å $\gamma = 90°$
volume	3298.7(5) Å^3	3269.2(8) Å^3
Z	4	8
density (calculated)	1.884 Mg/m^3	1.915 Mg/m^3
absorption coefficient	4.079 mm^{-1}	4.360 mm^{-1}
F(000)	1758	1840
index ranges	$-29 \Leftarrow h \Leftarrow 30$, $-9 \Leftarrow k \Leftarrow 10$, $-14 \Leftarrow l \Leftarrow 27$	$-30 \Leftarrow h \Leftarrow 30$, $-10 \Leftarrow k \Leftarrow 10$, $-27 \Leftarrow l \Leftarrow 27$
reflections collected	26945	59735
independent reflections	4725 [*R*(int) = 0.1478]	4714 [*R*(int) = 0.1019]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	4342/41/234	4714/ 25/235
goodness-of-fit on F^2	0.765	1.007
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0474$, $wR_2 = 0.0554$	$R_1 = 0.0365$, $wR_2 = 0.0619$
R indices (all data)	$R_1 = 0.1364$, $wR_2 = 0.0715$	$R_1 = 0.0781$, $wR_2 = 0.0722$
largest diff peak and hole	1.304 and −0.998 e.Å^{-3}	0.818 and −0.823 e.Å^{-3}

pH was 3.4. All other experimental parameters were unchanged. A yield of 93% was obtained based on terbium.

A single crystal of **1** suitable for X-ray crystallography and representative of the bulk sample was selected. The data were collected at room temperature using a Bruker P4 diffractometer with an APEX CCD detector. The crystal solved readily in the *Pbcn* space group (same space group as the praseodymium and europium analogues[14]) with direct methods and refined using SHELXL-97[41] ($a = 21.925(2)$ Å, $b = 7.6493(7)$ Å, $c = 19.6691(15)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 4$, $R_1 = 0.0474$, $wR_2 = 0.0554$). Powder X-ray diffraction data was collected on the samples using a Scintag XDS 2000 diffractometer (Cu Kα, 3−60°, 0.05° step, 1.0 s/step), and the observed powder pattern was compared to that calculated from the single-crystal data to confirm phase purity. Compositional analysis of **1** was performed using EDAX (Energy Dispersive Analysis by X-ray) on two single crystals, confirming that the Eu and Tb are in a 1:1 ratio throughout the crystal structure.

A single crystal of **2** was selected and mounted for X-ray analysis. Data were collected at room temperature on a Bruker SMART diffractometer equipped with an APEX II CCD detector. The crystal also solved in the *Pbcn* space group using direct methods and refined with SHELXL-97 ($a = 21.866(3)$ Å, $b = 7.6101(10)$ Å, $c = 19.646(3)$ Å, $\alpha = \beta = \gamma = 90°$, $Z = 8$, $R_1 = 0.0365$, $wR_2 = 0.0619$). The calculated powder pattern was compared to the experimental (see previous paragraph for experimental details) and confirmed phase purity. Additional single-crystal X-ray data for **1** and **2** can be found in Table 1.

Photophysical Characterization

Excitation and emission spectra were measured using a Shimadzu RF-5301 PC spectrofluorophotometer with a Xe arc lamp source. Quantum yield and lifetime measurements were performed on a Perkin-Elmer LS 55 with a pulsed Xe lamp, corrected for instrumental response. Absorption and diffuse reflectance spectra were measured on a Perkin-Elmer Lambda 35 spectrometer, equipped with a LabSphere diffuse reflectance accessory utilizing a Spectralon standard for background correction.

Spectra of **1** were taken with 1.5/1.5 nm excitation and emission slit widths and high sensitivity at 615 nm (corresponding to the $^5D_0$ to $^7F_2$ transition of Eu^{3+}) while exciting from 200 to 600 nm or with 3.0/3.0 nm excitation and emission slit widths at low sensitivity, while monitoring the emission from 350 to 700 nm. The spectra were all taken within minutes of each other on pellet-pressed samples of identical mass (0.040 ± 0.002 g) without turning the lamp off to ensure a valid comparison between the emission spectra. For the Tb-only analogue (**2**), the experimental criteria were identical except that the excitation and emission slits widths were set at 1.5/1.5 nm, respectively, as the intensities of the $^5D_4$ to $^7F_5$ and $^7F_6$ transitions were very intense and thus saturated the detector.

Quantitative data were measured in the solid state at 20 ± 2 °C. The samples for the solid-state quantum yield determination, based on a previously reported technique,[42] were finely ground with poly(methyl methacrylate) (PMMA) at a $4-7 \times 10^{-3}$ w/w concentration of the sample. The powders were deposited with a thickness of ~2 mm onto the solid-state holder. The solid-state quantum yields were determined against perylene ($\Phi_{ST} = 61\%$ at $\lambda_{exc} = 313$ nm[43]) and sodium salicylate (NaSal $\Phi_{ST} = 53\%$ at $\lambda_{exc} = 340$ nm[44]) in PMMA as described by Bril,[42] with

$$\Phi_x = \frac{1 - R_{ST}}{1 - R_x} \times \frac{I_x}{I_{ST}} \times \Phi_{ST}$$

where Φ is the quantum yield, *R* is the diffuse reflectance, and *I* is the integrated emission spectrum of sample *x* and

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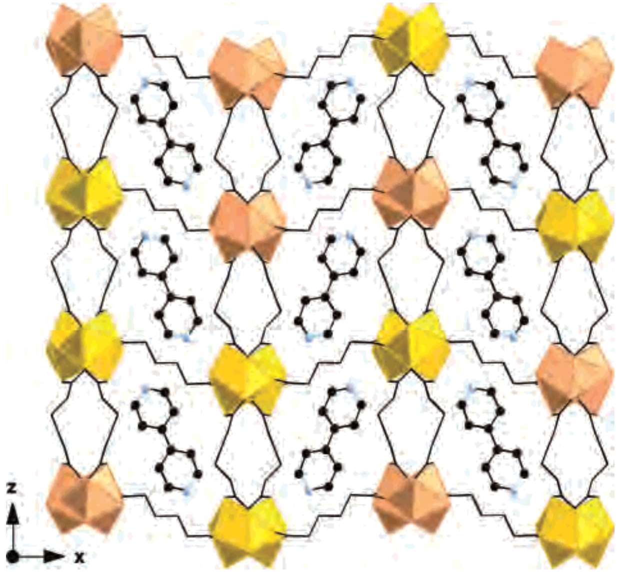

Figure 1. Structure of the title compound viewed down the [010] direction. The arbitrarily colored polyhedra represent TbO_9 and EuO_9 polyhedra, black lines are adipic acid, and the ball-and-stick figure is 4,4′-dipyridyl (blue denotes the nitrogen atoms). This structure is identical for all materials discussed (Eu-only, Tb-only, and mixed Eu/Tb system).

standard ST. *R* for sample x and standard ST were determined with the fluorimeter by scanning the emission monochromator through the excitation range and calibrating with the diffuse reflectance of PMMA. The diffuse reflectance of PMMA was determined to be 54.3% at 313 nm and 59% at 340 nm, with the diffuse reflectance accessory. Samples and standards were ground with PMMA to reduce self-absorbance of emitted light and to avoid refractive index corrections to the quantum yield.[45] Two independently synthesized samples of each system (Eu-only, Tb-only, mixed Eu/Tb) were analyzed for reproducibility. Slit widths were 5 or 10 nm, and the data were collected in phosphorescence mode with zero delay time, at 250 nm/min.

Results and Discussion

The structure (Figure 1) of both compounds **1** and **2** consists of chains of either Eu/TbO_9 or TbO_9 polyhedra edge-shared along the [010] direction. Adipic acid serves to link the Eu/Tb chains in the [100] and [001] directions to create an overall three-dimensional structure. Around each metal center are nine oxygen atoms, seven of which are crystallographically unique. In **1** and **2**, oxygen atoms O1, O2, O5, and O7 are from the adipic acid and coordinate to the metal center in a bridging bidentate motif, whereas O3 and O4 (also from adipic acid) coordinate in a bridging tridentate fashion connecting two metal centers together along the chain direction. Oxygen atom O6 is a bound water molecule. Residing within the channels are neutral 4,4′-dipyridyl molecules. The nitrogen atoms of the pyridyl rings participate in hydrogen bonding with the bound water molecule on the metal center at a donor−acceptor (N−O) distance of 2.778 Å (for **1**) and 2.789 Å (for **2**). The 4,4′-dipyridyl molecule is not planar and has a torsion angle of 27.91° (for **1**) and 28.62° (for **2**). Distance between neighboring 4,4′-dipyridyl molecules down the [010] direction is approximately 7.65 Å (for **1**) and 7.61 Å (for **2**), thus negating the possibility of any $\pi-\pi$ interactions. In both compounds, there is some disorder in one of the adipic chains (C12 and C13 for **1**, and C6 and C7 for **2**; see the Supporting Information). Further description of this structure type in general can be found in our previous contribution.[14]

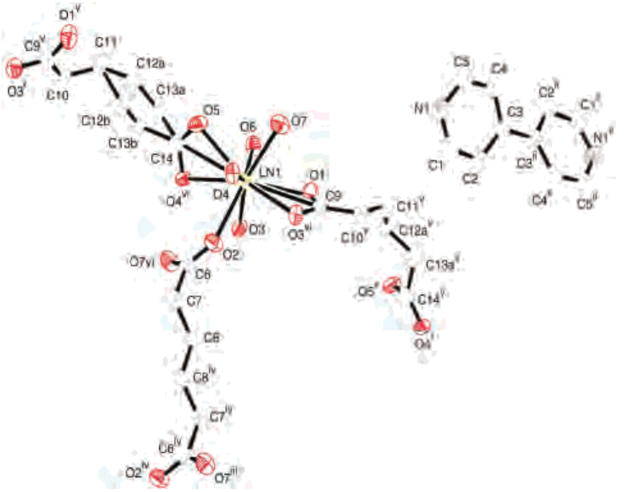

Figure 2. ORTEP drawing of compound **1**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Superscript indicates symmetry transformation: i = $-x+1/2, -y+1/2, z+1/2$; ii = $-x, y, -z+1/2$; iii = $x+1/2, -y+1/2, -z$; iv = $-x, -y, -z$; v = $x, -y, z+1/2$; vi = $-x+1/2, y+1/2, z$.

Qualitative luminescence studies were conducted at room temperature on compounds **1** and **2** and the Eu structure whose synthesis was reported previously. An excitation spectrum of the mixed Eu/Tb system was taken in order to determine the maximum wavelength of excitation of these compounds. There was a maximum excitation in the range of 270−300 nm, so all samples were excited at the median wavelength of 285 nm (see Figures S1 and S2 in the Supporting Information.) In the Eu/Tb system, the emission spectrum shows three major peaks at 545, 595, and 615 nm as seen in Figures 2 and 3 resulting from both Tb and Eu emission. The peaks corresponding to Eu emission (595 and 615 nm) are more intense than in the isostructural Eu-only analogue (Figure 4), and Tb emission at 545 nm is nearly completely quenched. The band with vibrational fine structure centered around 475 nm corresponds to residual fluorescence from the 4,4′-dipyridyl, based on fluorescence spectra taken of pure 4,4′-dipyridyl (obtained in house), showing an almost complete quenching and therefore efficient energy transfer to the metal ions.

The results from this synthesis are 2-fold. First, we have demonstrated that we were successful in synthesizing a mixed-lanthanide analogue of a previously reported Pr-adipate structure and that europium and terbium are equally incorporated into the crystal structure. This is not entirely unexpected since these lanthanides do not vary considerably in their ionic radii.[46] This approach has also been successful with other lanthanide combinations in our laboratory, though not reported herein. By adjusting this approach, modification

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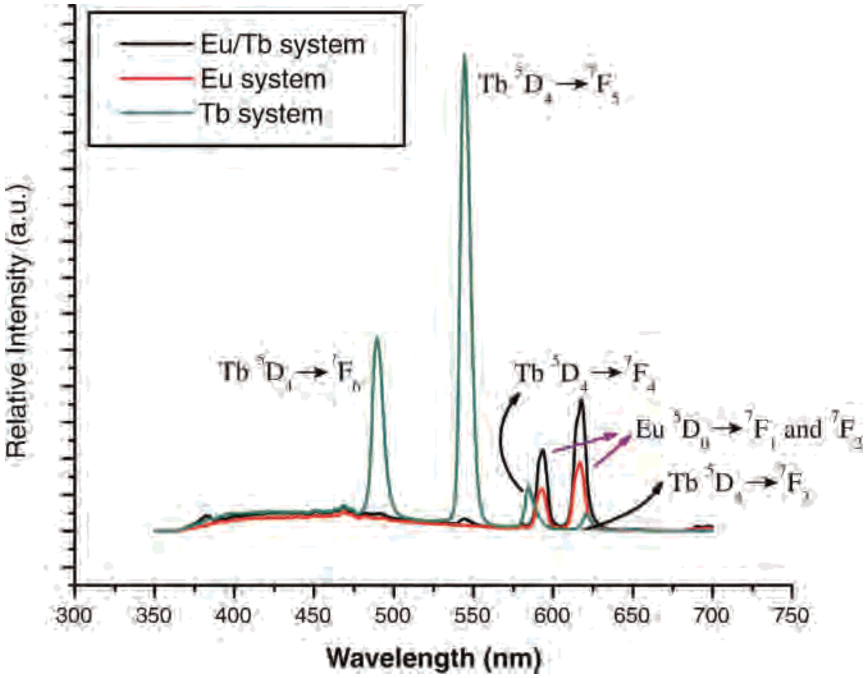

Figure 3. Emission spectra of the terbium, europium, and mixed metal systems. Note the decrease in the Tb $^5D_4$ to $^7F_5$ transition and resulting increase in the Eu transitions.

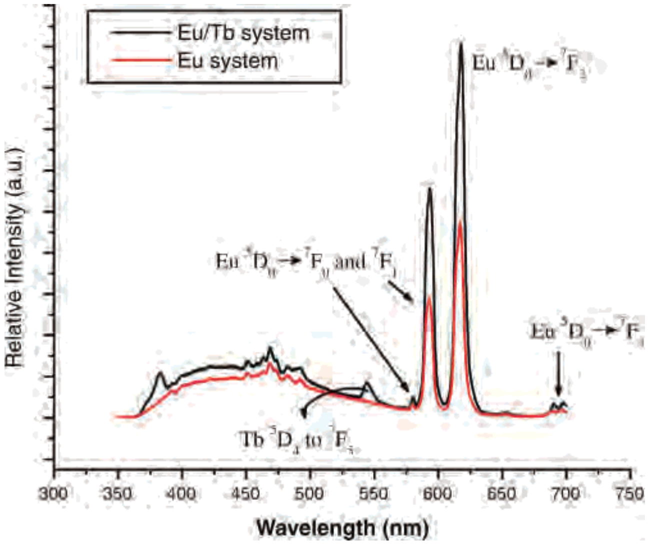

Figure 4. Emission spectra of the europium and mixed metal systems. Here the decreased Tb $^5D_4$ to $^7F_5$ transition is more apparent as well as the increase in the Eu transitions.

of luminescence properties within a variety of lanthanide systems may be feasible as demonstrated below.

Second, here we have evidence that the emission from the europium center is sensitized not only by the uncoordinated 4,4′-dipyridyl but also through the terbium center itself. Since lanthanide ions have low absorption coefficients and thus show inefficient luminescence, a conjugated organic component (such as an aromatic system) is typically coordinated directly to the metal center. Upon excitation of the ligand, intersystem crossing and energy transfer occur, leading to lanthanide ion luminescence. This is often referred to as the 'antenna effect'.[18,24,25,47] We have demonstrated herein that this sensitization pathway can occur through noncoordinated organic moieties in the solid state as well. In mixed-lanthanide systems, a similar pathway occurs through which multiple lanthanide elements may also be excited, yet instead of stimulating emission from each, energy can be transferred from one lanthanide to another, resulting in a preferential enhancement of a single element's luminescence.[48−54] This is also common within mixed-lanthanide-transition-metal systems where lanthanide ion emission is sensitized and in some cases enhanced via the LMCT state.[20,55,56] We believe that such an energy transfer is occurring within the mixed metal ion system presented here. The Tb^{3+} is excited by the 4,4′-dipyridyl as demonstrated by a peak corresponding to the terbium $^5D_4$ to $^7F_5$ transition. However, this transition is hardly detectable, due to an energy transfer to the Eu^{3+} center. In this case, the Tb^{3+} is acting as a bridge between the dipyridyl and Eu^{3+},

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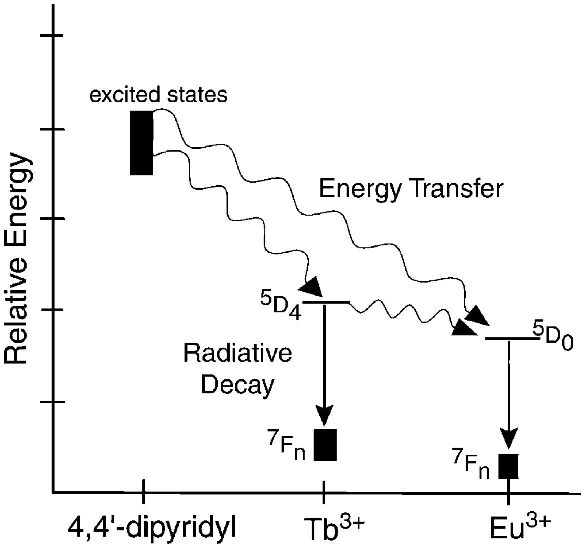
Scheme 1. Energy Transfer Diagram in **1**[a]



[a] Energy is transferred from the excited states of the 4,4′-dipyridyl and is transferred to the excited states of the Tb^{3+} and Eu^{3+} ions. Most of the energy in the $^5D_4$ level of the Tb^{3+} is further transferred to the $^5D_0$ of the Eu^{3+}, effectively enhancing Eu^{3+} emission and diminishing most Tb^{3+} emission.

Table 2. Lifetime Measurements of Compounds **1**, **2**, and Their Eu^{3+}-Only Analogue[a]

sample	Eu^{3+}	Tb^{3+}
Eu-A	732 ± 2.8	
Eu−B	720 ± 4.9	
Tb-A		1375 ± 16.3
Tb−B		1415 ± 16.1
Eu/Tb-A	764 ± 2.7	481 ± 3.2
Eu/Tb−B	771 ± 2.7	564 ± 6.2

[a] Sample letters A and B indicate two independently synthesized samples of each compound. The values are given as microseconds (μs).

facilitating energy transfer to the Eu^{3+} and increasing the efficiency of the transfer, as depicted in Scheme 1.

Quantum yield measurements support the qualitative observations made from the emission spectra and are summarized in the Supporting Information (Table S1). Each quantum yield value is the average of four independent measurements. The Eu^{3+} samples yielded an average quantum yield of approximately 22.5 ± 2.1%, and the Tb^{3+} samples' quantum yield was calculated to be 31.6 ± 7.5%. Within the mixed Eu/Tb system, an average quantum yield of 38.5 ± 2.1% was found, indicating an increase in the quantum yield of the Eu^{3+} by 71%. These results are quite promising and indicate that by careful selection of a second lanthanide center in a controlled molar concentration, lanthanide emission can be enhanced to produce superior quantum yields. Lifetime measurements were also performed and are summarized in Table 2. Samples were excited at 254 nm, and the Eu^{3+} and Tb^{3+} emission were monitored at 615 and 545 nm, respectively. The Eu^{3+} and Tb^{3+} lifetimes indicate a phosphorescent decay pathway from the excited states of the lanthanide, with an average lifetime of 726 μs (range 720−732 μs) and 1395 μs (range 1375−1415 μs), respectively. The lifetime of the Eu^{3+} and Tb^{3+} emission in the mixed system is further indication that an energy transfer from the Tb-center to the Eu-center is indeed occurring, as the lifetime of the Tb^{3+} emission is reduced by roughly one-half (down to 523 μs, range 481−564 μs), whereas the lifetime of the Eu^{3+} emission is hardly affected, with just the slightest of an increase (768 μs, range 764−771 μs). The high range of the Tb^{3+} emission lifetime values in the mixed system is attributed to difficulty in measuring the lifetime due to the weak signal of the $^7F_5$ transition. The investigation of other mixed-lanthanide systems will be the focus of future research, and preliminary results are quite promising.

Conclusion

The luminescence of a mixed europium/terbium material was explored and compared to analogous structures of the single lanthanide ion systems. We have seen not only that the noncoordinated template molecule sensitizes lanthanide emission but also that the Tb metal center acts to sensitize and enhance Eu emission as well. This is evidenced by a significant decrease in terbium emission and a 2-fold increase in europium emission in the Eu/Tb compound. Quantitative data confirm this observation as well. As lanthanide ion luminescence within metal-organic frameworks has not been studied in great detail, this mixed-lanthanide ion system demonstrates the potential for useful applications and is an important advancement in the understanding of the luminescence behavior in these systems.

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Supporting Information Available: X-ray crystallographic data in CIF format, excitation spectrum, and detailed quantum yield values. This material is available free of charge via the Internet at http://pubs.acs.org.

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