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A Versatile Tripodal Ligand for Sensitizing Lanthanide (Ln^{III}) Ions and Color Tuning

Rodney A. Tigaa ^{1,*}, Raul E. Ortega ², Xinsong Lin ²  and Geoffrey F. Strouse ²
¹ Department of Physical and Environmental Sciences, Concord University, Athens, WV 24712, USA

² Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA; reo15b@my.fsu.edu (R.E.O.); xlin@chem.fsu.edu (X.L.); strouse@chem.fsu.edu (G.F.S.)

* Correspondence: rtigaa@concord.edu

Abstract: Lanthanide (Ln^{III}) ions were successfully chelated and sensitized with a tripodal ligand. The absolute Ln^{III}-centered emission efficiencies were ~3% for both the europium(III) (Eu^{III}) and terbium (Tb^{III}) complexes and up to 54% for the cerium(III) (Ce^{III}) complex. The differences in emission quantum yields for the early lanthanides (Ce^{III}) and the mid lanthanides (Eu^{III} and Tb^{III}) were attributed to their *d-f* and *f-f* nature, respectively. Despite the low quantum yield of the Eu^{III} complex, the combination of the residual ligand fluorescence and the red Eu^{III} emission resulted in a bluish-white material with the Commission Internationale de l'Eclairage (CIE) coordinates (0.258, 0.242). Thus, metal complexes of the ligand could be used in the generation of single-component white-light-emitting materials.

Keywords: lanthanides; luminescence; tripodal; sensitization; cerium; lifetimes; wLEDs; complexes; white light; ligand



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1. Introduction

The unique properties of trivalent lanthanide, Ln^{III}, ions have resulted in their applications in imaging, sensing, and telecommunications [1–5]. The emission spectra of Ln^{III} ions are sharp as the 4*f* orbitals of Ln^{III} ions are shielded from the external environment by the filled 5*s* and 5*p* orbitals [4]. These emission spectra arise from *f-f* transitions; thus, they are parity forbidden by the Laporte rule [4]. Consequently, Ln^{III} ions have long emission lifetimes which makes them ideal probes for imaging of biological tissue, as their long emission lifetimes can be discriminated from the autofluorescence of biological tissue [4]. Another consequence of the parity-forbidden nature of their emission is that Ln^{III} ions have low molar absorptivities ($\epsilon = 1\text{--}10\text{ M}^{-1}\text{cm}^{-1}$); thus, their direct excitation is inefficient [4,6]. Therefore, Ln^{III} ions are often coordinated to organic ligands with well-matched triplet, ³T, excited energy levels that upon excitation can transfer the energy from their excited energy levels (singlet, ¹S, and triplet, ³T) to the excited emissive energy levels of the coordinated Ln^{III} ions [4,7–12]. As a result, extensive research has been devoted to the design and synthesis of organic ligands to sensitize the luminescence of Ln^{III} ions [11,13–16].

However, most efforts are focused on monodentate ligands and often require several synthetic steps that are tedious and reagent consuming. Polybenzimidazole ligands are a less explored class of chelating ligands for sensitizing Ln^{III} ions due to their limited solubility [15,17–25]. This class of ligands provides an opportunity for easy functionalization to yield versatile ligands with improved solubility. Therefore, there remains a need for multifunctional ligands with well-matched ³T excited states for Ln^{III} sensitization that can be synthesized in a few steps and are soluble in a variety of solvents. Efficient sensitization of Ln^{III} ions can be achieved by using ligands with high molar extinction coefficients and significant spectral overlap between the emission of the ligand and the absorption of the Ln^{III} ion [9]. In this work, the efficiency of energy transfer from a triethyl 2,2',2''(2,2',2''nitrilotris(methylene)tris(1*H*-benzimidazole-2,1-diyl)) triethanoate (**BimOEt₃**)

ligand to Ln^{III} ions was investigated using Ln^{III} -complexes of the tripodal ligand. The tripodal **BimOEt₃** ligand was chosen due to its ease of synthesis, high molar extinction coefficient, and high solubility in protic solvents [20,21]. The photophysical properties, along with the emission lifetimes and quantum yields of the three molecular complexes, are discussed.

2. Results and Discussion

2.1. Synthesis and Characterization of BimOEt₃

The **BimOEt₃** ligand was synthesized following literature reports [20,21,26,27] and the successful synthesis was confirmed by a combination of ^1H and ^{13}C NMR spectroscopy (Figures S1–S3). Investigation of the photophysics of **BimOEt₃** in ethanol via UV–Vis absorption and fluorescence spectroscopy showed three absorption bands (253, 277, and 285 nm) and emission maxima at 322 nm that were attributed to singlet $^1\pi \rightarrow ^1\pi^*$ and $^1\pi^* \rightarrow ^1\pi$ transitions of the benzimidazole groups, respectively (Figure 1) [28]. The emission spectrum of **BimOEt₃** ranges from 300 to 500 nm with a maximum at 322 nm when excited at 280 nm (Figure 1). The measured absolute fluorescence quantum yield, $\phi_{\text{L-Ln}}$, and the lifetime, τ , of **BimOEt₃** (ethanol, 298 K) were $8.1 \pm 2.0\%$ and 1.1 ± 0.1 ns, respectively.

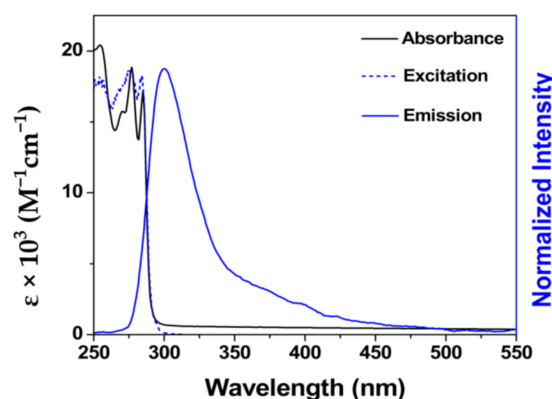


Figure 1. UV–Vis absorption, excitation, and emission spectra of 1.0×10^{-4} M **BimOEt₃** in ethanol at 298 K.

2.2. Photophysical Properties of the Ln^{III} -**BimOEt₃** Complex

Ln^{III} complexes were prepared by mixing 1:2 Ln^{III} -to-**BimOEt₃** stoichiometric amounts in ethanol/acetonitrile solutions due to the tetradentate nature of **BimOEt₃** and the photophysics of the resulting complexes investigated (details in Supporting Information). The coordination of the metal ions was determined through infrared spectroscopy. The infrared spectra showed that the carbonyl $\text{C}=\text{O}$ stretch shifted from 1736 cm^{-1} to 1745 cm^{-1} following complexation of Eu^{III} and Tb^{III} ions by the ligand (Figure 2) [1–4,13,15,19,29,30]. In contrast, the $\text{C}=\text{O}$ stretch of the Ce^{III} complex remained at 1736 cm^{-1} . This was initially surprising and prompted further investigation. Thus, as a proof-of-concept, single crystals of the Ce^{III} complex were grown by slow diffusion in an ethanol/acetonitrile/ether solvent mixture and analyzed via single-crystal X-ray diffraction. The solution to the structure revealed that the Ce^{III} ions were coordinated to the ligand via the central nitrogen and the imidazole nitrogen atoms of **BimOEt₃** (Figure S4). This finding suggested that **BimOEt₃** can selectively bind early (Ce^{III}) and mid (Eu^{III} and Tb^{III}) Ln^{III} ions via its nitrogen and carbonyl groups, respectively. However, further studies by a combination of ^1H and ^{13}C NMR spectral analysis of the metal complexes indicated that the Eu^{III} complex is unstable in solution since the proton resonances of the Eu^{III} complex are not shifted compared to the free ligand (Figures S1–S3). In contrast, the yttrium(III) (Y^{III}) and Ce^{III} complexes were stable in solution as suggested by the shifts in the proton resonances of the central methylene groups. The three absorption transitions of **BimOEt₃** remain at 253, 276, and 284 nm but with subtle changes in their intensities (Figure 1 and S5).

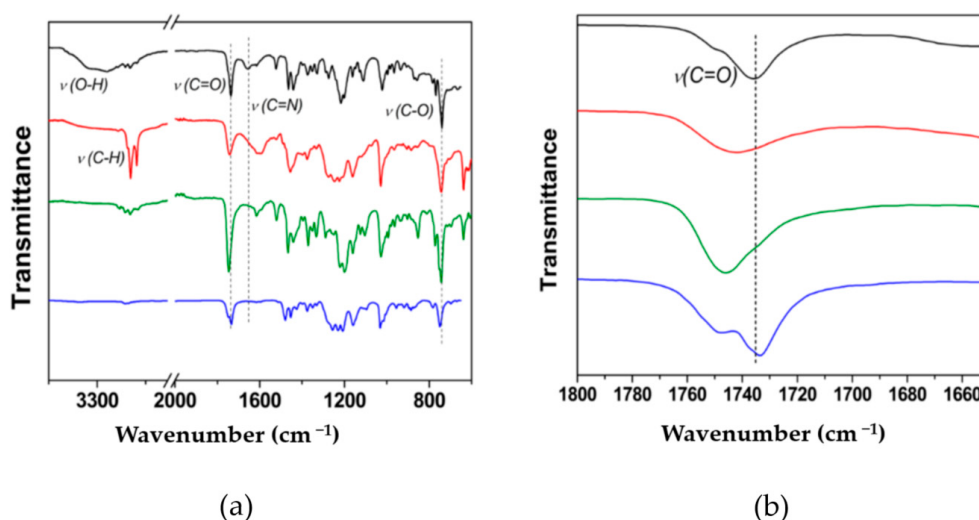


Figure 2. Infrared spectra of BimOEt₃ (black trace), Eu^{III} complex (red trace), Tb^{III} complex (green trace), and Ce^{III} complex (blue trace) with assignment of relevant vibrational frequencies shown in (a) full and (b) selected carbonyl stretching region.

Low-temperature measurements using the analogous Gd^{III}-BimOEt₃ complex indicated that the excited singlet, ¹S, and triplet, ³T, energy levels of BimOEt₃ were 27,800 and 24,500 cm^{−1}, respectively (Table 1 and Figure 6a,b). Thus, the excited ³T energy level of BimOEt₃ is well positioned to transfer energy to the ⁵D₀ and ⁵D₄ emitting levels of Eu^{III} and Tb^{III} ions, respectively [9,31,32]. The excitation of the Eu^{III} and Tb^{III} complexes at 280 nm resulted in typical red ⁵D₀ → ⁷F_J (0–4) and green ⁵D₄ → ⁷F_J (6–3) transitions of Eu^{III} and Tb^{III}, respectively (Figure 3a,b). However, a broad emission band in the range 350–600 nm was observed in both complexes but was more intense in the Eu^{III} complex. This residual ligand emission suggests inefficient energy transfer from the ligand to the metal ions. The measured absolute emission quantum yields for both the Eu^{III} and Tb^{III} complexes were 3% following excitation at 280 nm (Table 1). However, directly exciting the Eu^{III} and Tb^{III} complexes at 394 and 484 nm, respectively, resulted in intrinsic Ln^{III} emission efficiencies of 6% and 4%, respectively. The low efficiencies of the Eu^{III} and Tb^{III} complexes are comparable to values (1–13%) reported for analogous polybenzimidazole-type ligands and are attributed to non-radiative deactivation caused by the rotational freedom via the ester groups of the tripodal ligand [28,33]. Evidence of fluorescence quenching by the ester groups was observed following functionalization of the BimH₃ ligand to BimOEt₃ (Scheme S1). Using the measured excited energy levels of BimOEt₃, the sensitization mechanism of the Ln^{III} ions by the ligand can be described by the Jablonski diagram below (Figure 4).

Table 1. The excited singlet (¹S) and triplet (³T) energy levels, emission quantum yields (φ_{L–Ln}), intrinsic quantum yields (φ_{Ln–Ln}), and lifetimes (τ) of the 1:2 lanthanide (Ln^{III})-to-ligand complexes in air-saturated ethanol at 298 K.

Complex	¹ S (cm ^{−1})	³ T (cm ^{−1})	φ _{L–Ln} (%)	φ _{Ln–Ln} (%)	τ (ms)
BimOEt ₃			7.5 ± 1.7		(1.06 ± 0.06) × 10 ^{−6}
Gd ^{III}	27,800 ± 500	24,500 ± 500	20.0 ± 1.8		(5.38 ± 0.07) × 10 ^{−6}
Eu ^{III}			3.2 ± 0.1	6.0 ± 0.9	0.08 ± 0.01
					0.37 ± 0.02
Tb ^{III}			2.8 ± 0.1	4.4 ± 1.0	0.77 ± 0.01
					2.57 ± 0.02
Ce ^{III}			17.6 ± 3.0	53.6 ± 1.1	(5.50 ± 0.02) × 10 ^{−5}

BimOEt₃ is triethyl 2,2',2''(2,2',2''nitrilotris(methylene)tris(1*H*-benzimidazole-2,1-diyl)) triethanoate.

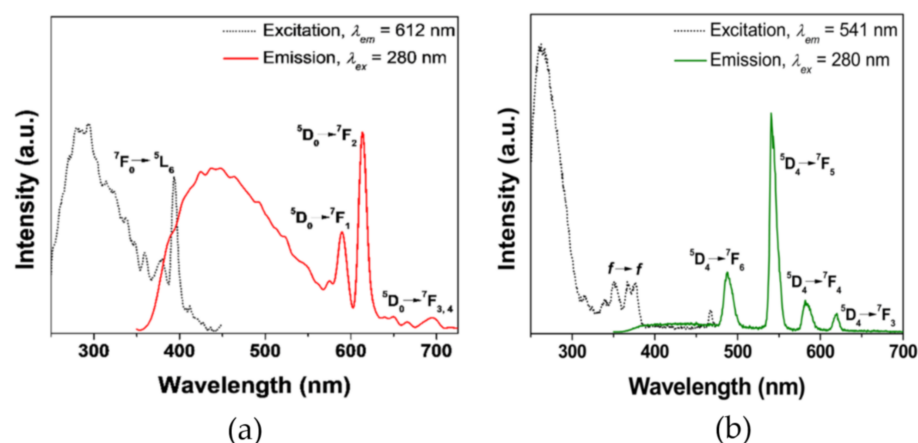


Figure 3. Excitation (dashed traces) and emission (solid traces) of 1.0×10^{-5} M (a) Eu^{III} and (b) Tb^{III} complexes of BimOEt_3 in ethanol at 298 K.

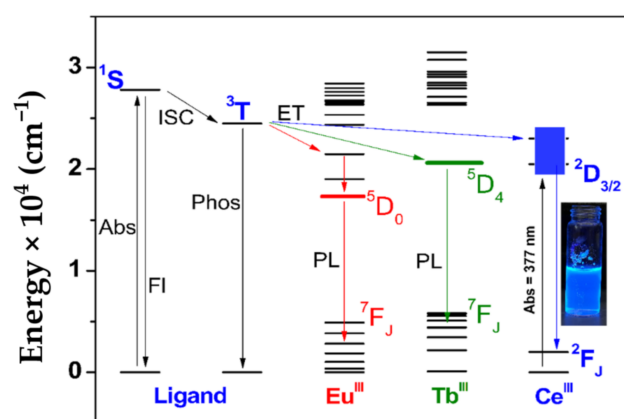


Figure 4. Energy level diagram showing the sensitization mechanism of Eu^{III} , Tb^{III} , and Ce^{III} ions by BimOEt_3 . The nonradiative deactivation pathways are removed for clarity. In the diagram, Abs is absorbance, Fl is fluorescence, PL is photoluminescence, ISC is intersystem crossing, and ET is energy transfer. Energy transfer from the singlet, ^1S , to the excited levels of the Ln^{III} ions is omitted for clarity. The inset shows the intense blue emission of the Ce^{III} complex in ethanol under a handheld 365-nm UV lamp irradiation.

Despite the low emission quantum yields, a bluish-white-emitting material was obtained through a combination of the residual blue ligand fluorescence and weak-red emission of the Eu^{III} complex with the CIE coordinates (0.258, 0.242). This suggests that single-component white-light-emitting devices (wLEDs) could be generated using metal complexes of BimOEt_3 (Figure 5) [10,34–36].

In contrast to the Eu^{III} and Tb^{III} complexes, excitation of the Ce^{III} complex at 280 nm resulted in two broad emission bands that are attributed to the $^1\pi^* \rightarrow ^1\pi$ transitions of the ligand and the $^2\text{D}_{3/2} \rightarrow ^2\text{F}_J$ ($J = 5/2-7/2$) transitions of the Ce^{III} ion (Figure 6a,b). In addition, another transition at 489 nm was observed in the Ce^{III} emission spectrum and can be attributed to ligand perturbation of the Ce^{III} ion [37]. Further analysis of the $^2\text{D}_{3/2} \rightarrow ^2\text{F}_J$ ($J = 5/2-7/2$) transitions of the Ce^{III} emission at 77 K revealed two distinct bands at 434 nm ($23,041 \text{ cm}^{-1}$) and 472 nm ($21,186 \text{ cm}^{-1}$) with a resulting energy gap of $\sim 1900 \text{ cm}^{-1}$, which is in agreement with previous reports (Figure 6b) [19,21,37].

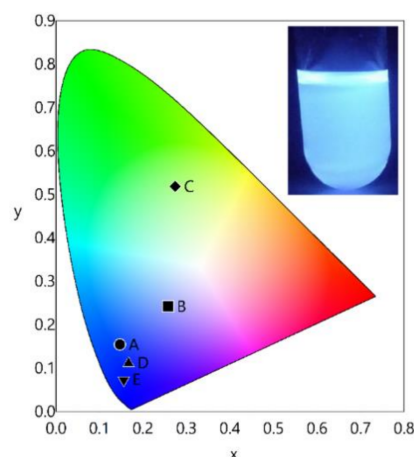


Figure 5. CIE coordinate diagram of (A) BimOEt₃ and its (B) Eu^{III} complex, (C) Tb^{III} complex, (D) Ce^{III} complex at 280 nm excitation, and (E) Ce^{III} complex at 377 nm excitation. The insert shows the intense bluish-white emission of the Eu^{III}-BimOEt₃ complex in ethanol under 365-nm UV irradiation.

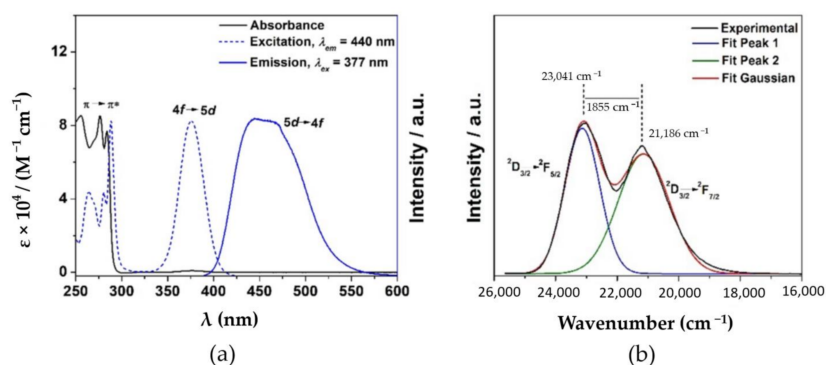


Figure 6. (a) UV-Vis absorption, excitation, and emission spectra of the Ce^{III} complex in ethanol and its (b) fluorescence in 2-methyl-THF at 77 K with excitation at 377 nm.

The emission lifetimes of the Eu^{III} and Tb^{III} complexes were fit to bi-exponential function. The observed lifetimes do not arise from the ligand states by comparison to the Gd^{III} data and, therefore, are assigned as arising from the presence of two Ln^{III} coordination environments in solution (Table 1 and Figure S7a,b). This was assigned to contributions arising from the lack of stability of the Eu^{III} and Tb^{III} complexes in solution.

In contrast, the measured emission lifetime of the Ce^{III} complex was fit to a mono-exponential function following excitation at 280 or 377 nm (Table 1 and Figure S8a,b). In contrast to the Eu^{III} and Tb^{III} emission lifetimes, the Ce^{III} emission lifetime was short lived (55.0 ± 0.2 ns), consistent with a lifetime expected for a parity allowed $5d-4f$ transition (Table 1) [21]. Excitation of the Ce^{III} complex at 280 and 377 nm results in emission quantum yields of $17.6 \pm 2.0\%$ and $53.6 \pm 1.3\%$, respectively. These values are similar to reports by Zheng et al. [21] and Harada et al. [19] for analogous Ce^{III}-polybenzimidazole complexes. Using the measured emission quantum yields, the efficiency of energy transfer, ϕ_{ET} , from BimOEt₃ to Ce^{III} was determined to be 33% using the equation $\phi_{L-Ln} = \phi_{ET} \phi_{Ln-Ln}$, where the subscripts L-Ln and the Ln-Ln denote the overall emission and the $5d-4f$ Ce^{III} emission quantum yields, respectively. These results are in agreement with reports by Harada et al. [19] and Zheng et al. [21].

3. Materials and Methods

3.1. Materials

All the chemicals used were reagent grade and used as received.

3.2. General Procedures

The infrared spectra were acquired on a PerkinElmer spectrum 100 FT-IR spectrometer (PerkinElmer, Shelton, CT, USA) in the range 650–4000 cm^{-1} with a 4.0 cm^{-1} resolution and 8 scans per sample. The spectra were corrected for H_2O and CO_2 vibrations before data acquisition. The UV–Vis absorption spectra were acquired using a Cary Varian spectrophotometer operating at a medium scan speed in the range 800–200 nm. The emission spectra were acquired on a Horiba Fluoromax-4 spectrofluorimeter (Horiba Scientific, Piscataway, NJ, USA) equipped with a 150 W CW Ozone free xenon arc lamp, Czerny–Turner monochromators with excitation grating blazed at 330 nm (1200 groove/mm), and emission grating blazed at 500 nm (1200 grooves/mm). All spectra were corrected for the instrument response function and the intensity of the lamp. The emission lifetimes of the samples were acquired by exciting the samples with an Nd:YAG laser that was focused through a variable neutral density filter (Edinburg F-B01 laser mount) and a 2-mm diameter iris (Newport ID-1.0). The emission lifetimes of the Ce^{III} complex were acquired using a TCSPC system equipped with a 370-nm NanoLED.

3.3. Measurement of Ligand Excited States

The excited singlet (^1S) and triplet (^3T) energy levels of **BimOEt₃** (Florida State University, Tallahassee, FL, USA) were determined by measuring the emission spectra of the analogous gadolinium (Gd^{III}) complexes at 77 K [31]. 2-Methyltetrahydrofuran solutions (Alfa Aesar, Tewksbury, MA, USA) of the complexes were excited at 295 nm and the emission spectra collected in the range 300–700 nm. The emission spectra were deconvoluted into their Franck–Condon progression and the highest energy peak acquired at either the zero delay or gated emission taken as the excited ^1S and ^3T energy levels, respectively. The delay time for the fluorescence spectrum was acquired at 0 ms delay while the phosphorescence spectrum was acquired at 0.5 ms delay.

3.4. X-ray Crystallography

The slow-diffusion of a 1:1 ethanol/acetonitrile (Florida State University, Tallahassee, FL, USA) mixture in diethyl ether vapor yielded X-ray-quality single-crystals of **BimOEt₃** after a week. A crystal was mounted on a glass fiber of a Rigaku XtaLAB Synergy-DW dual wavelength X-ray diffractometer ($\text{CuK}\alpha = 1.54184 \text{ \AA}$) at 298 K (Rigaku, Houston, TX, USA). Data reduction was performed using empirical absorption correction based on “multi-scan”. The structures were solved by the intrinsic phasing and least-square refinements using ShelXT and ShelXL (2014/2, Bruker AXS, Madison, WI, USA) of the Olex2 package [38–40]. The best crystal was selected for the data collection; however, the crystal still had quite a few type A and B alerts in the Cifcheck file due to a highly disordered structure caused by unstable solvent (trifluoromethane-sulfonate) in the unit cell.

4. Conclusions

The versatility of a tripodal ligand was demonstrated with successful sensitization of Ln^{III} ions in molecular complexes, leading to an intense blue emission with a quantum yield of 54% for the Ce^{III} complex. However, the measured emission quantum yields of the mid-lanthanide complexes (Eu^{III} and Tb^{III}) were 3%. Despite the low quantum yield of the Eu^{III} complex, the combination of the residual ligand fluorescence and the red Eu^{III} emission resulted in a bluish-white-emitting material with the CIE coordinates (0.258, 0.242). Thus, metal complexes of the ligand could be used in the generation of single-component-white-light-emitting materials. Although with improved solubility in polar solvents, the functionalization with ester groups leads to a rapid quenching of the ligand fluorescence. The coordination nature of the ligand to the metal ions was revealed through a combination of infrared and NMR spectroscopy, as well as single-crystal X-ray diffraction analysis of the metal complexes of **BimOEt₃**. The results serve as a starting point for further studies to better understand the stability of tripodal polybenzimidazole ligands for lanthanide separation/extraction and imaging applications.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2624-8549/3/1/11/s1>, Schemes S1 and S2: synthesis details; Figures S1–S3: NMR spectra; Figure S4: single-crystal X-ray data; Figure S5: UV–Vis absorption spectra; Figure S6: ligand excited singlet and triplet energy levels; Figure S7; Eu^{III} and Tb^{III} emission decay curves; Figure S8: Ce^{III} emission decay curve. Crystallographic data for **BimOEt₃** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 2054591.

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