Published as part of a virtual special issue on Structural Chemistry in India: Emerging Themes.



Lanthanide Luminescent Coordination Polymer Constructed from Unsymmetrical Dinuclear Building Blocks Based on 4-((1H-Benzo[d]imidazol-1-yl)methyl)benzoic Acid

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Received November 16, 2010; Revised Manuscript Received December 29, 2010

ABSTRACT: Lanthanide coordination polymers of the general formula $[Ln_2(L)_5(NO_3)(H_2O)_4]_n$ (Ln = Eu (1), Tb (2), Gd (3)) supported by a novel aromatic carboxylate ligand 4-((1H-benzo[d]imidazol-1-yl)methyl)benzoic acid (HL) have been synthesized, characterized, and their photoluminescence behavior is examined. The powder X-ray diffraction patterns of complexes 1–3 showed that 1–3 are isostructural; thus, 1 has been chosen as an example to discuss in detail about the molecular structure by single-crystal X-ray diffraction. Complex 1 is a one-dimensional (1D) helical chain-like coordination polymer consisting of unique unsymmetrical dinuclear lanthanide building blocks. The 1D chains are further linked by the significant intermolecular hydrogen-bonding interactions to form a two-dimensional supramolecular network. The Tb³⁺ complex exhibits bright green luminescence efficiency in the solid state with a quantum yield of 15%. On the other hand, poor luminescence efficiency has been noted for Eu³⁺-benzoate complex.

Introduction

In recent years, the rational design and synthesis of lanthanide organic coordination complexes have attracted great interest for their fascinating architectures and potential applications as functional materials.¹ Notably, because of their unique photophysical properties (characteristic sharp emission, long excited-state luminescence lifetimes up to milliseconds. large Stokes shift > 200 nm), lanthanide-based coordination polymers are excellent candidates for the development of light-emitting diodes and sensors.² However, the f-f transitions that result in light emission from the lanthanides are both spin- and parity-forbidden which, in turn, mandates the use of antenna molecules for indirect excitation of the metal center. This indirect excitation, also known as the antenna effect, takes advantage of the coordinated ligands in the sense that energy transfer from the ligand-centered excited states to the metal center results in lanthanide ion luminescence.³ In 1942, Weissman observed that the use of organic ligands in europium complexes increased the luminescence intensity from the lanthanide ion when such complexes were irradiated with ultraviolet (UV) light.⁴ The β -diketonates and aromatic carboxylic acids are a novel class of ligands emerging as important "antennas" in terms of high harvest emissions because of the effectiveness of the energy transfer from this ligand type to the Ln³⁺ cation.⁵

Lanthanide benzoates coordination complexes with unique photophysical properties and intriguing structural features have been disclosed recently.⁶ The benzoate ligands were selected on the basis of the fact that carboxylate groups interact strongly with the oxophilic lanthanoids and the fact that the delocalized π -electron system provides a strongly absorbing chromophore.⁷ Our own latest work has focused on the potential application of terbium-4-(dibenzylamino)benzoate as luminescent materials with bright green emission in the solid state with a quantum yield of 82%.⁸ In particular, the enhanced emission quantum yield originated from a better match between the pertinant ligand orbitals and terbium ion excited states. Prior results also suggested that derivitization of the benzoic acid analogues with thiophene had a beneficial effect in terms of tuning the triplet state of the antenna.^{7b} The intense fluorescent emissions of homodinuclear lanthanide complexes of 4-cyanobenzoic acid imply that the ligand-to- Ln^{3+} energy transfer is efficient and that coordinated water molecules do not quench the luminescence by nonradiative dissipation of energy.⁹

Given the important potential applications of lanthanide carboxylates and the fascinating properties of benzoate ligands, we were prompted to prepare a new series of lanthanide complexes featuring the 4-((1H-benzo[d]imidazol-1-yl)met-hyl)benzoic acid ligand. In order to modulate the light-harvesting properties of the benzoic acid ligand, herein we have anchored a benzimidazole moiety at the fourth position of the benzoic acid through an alkyl linkage. The molecular structure of the newly designed ligand has been elucidated by single crystal X-ray analysis and utilized for the synthesis of the desired Eu³⁺, Gd³⁺, and Tb³⁺ complexes. One of the new lanthanide benzoate complexes has been structurally

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characterized by single-crystal X-ray diffraction, and the photophysical properties of all the new lanthanide benzoate complexes have been investigated and correlated with the triplet energy levels of the designed ligand.

Experimental Section

Materials and Instruments. The following chemicals were procured commercially and used without further purification: terbium-(III) nitrate hexahydrate 99.9% (Across Organics), europium(III) nitrate hexahydrate, 99.9% (Across Organics); gadolinium(III) nitrate hexahydrate (Treibacher); benzimidazole, 99% (Aldrich); methyl 4-(bromomethyl)benzoate, 99% (Aldrich). All the other chemicals used were of analytical reagent grade.

Elemental analyses were performed with a Perkin-Elmer Series 2 Elemental analyzer 2400. A Perkin-Elmer Spectrum One FT-IR spectrometer using KBr (neat) was used to obtain the IR spectral data and a Bruker 500 MHz NMR spectrometer was used to record the ¹H NMR and ¹³C NMR spectra of the ligands in CD₃OD and dimethyl sulfoxide- d_6 solution. The mass spectra were recorded on a JEOL JSM 600 fast atom bombardment (FAB) high resolution mass spectrometer (FABMS) and the thermogravimetric analyses were performed on a TG/DTA-6200 instrument (SII Nano Technology Inc., Japan). Powder X-ray patterns (XRD) were recorded in the 2θ range of $10-70^{\circ}$ using Cu-K_{α} radiation (Philips X'pert). The absorbances of the ligands were measured in CH₃OH solution on a UV-vis spectrophotometer (Shimadzu, UV-2450) and the photoluminescence (PL) spectra were recorded on a Spex-Fluorolog FL22 spectrofluorimeter equipped with a double grating 0.22 m Spex 1680 monochromator and a 450W Xe lamp as the excitation source operating in the front face mode. The lifetime measurements were carried out at room temperature using a Spex 1040D phosphorimeter. The diffuse reflectance spectra of the new lanthanide complexes and the standard phosphor were recorded on a Shimadzu, UV-2450 UV-vis spectrophotometer using BaSO₄ as a reference. The overall quantum yields ($\Phi_{overall}$) were measured at room temperature using the technique for powdered samples described by Bril et al., 10 along with the following expression:

$$\Phi_{\text{overall}} = \left(\frac{1 - r_{\text{st}}}{1 - r_{\text{x}}}\right) \left(\frac{A_{\text{x}}}{A_{\text{st}}}\right) \Phi_{\text{st}}$$
(1)

where r_x and r_{st} represent the diffuse reflectance of the complexes and of the standard phosphor, respectively (with respect to a fixed wavelength), and Φ_{st} is the quantum yield of the standard phosphor. The terms A_x and A_{st} represent the areas under the complex and the standard emission spectra, respectively. To acquire absolute intensity values, BaSO₄ was used as a reflecting standard. Sodium salicylate (Merck) was employed as the standard phosphor, the emission spectrum of which comprises an intense broad band with a maximum at approximately 425 nm, and a constant Φ_{st} value (60%) for excitation wavelengths between 220 and 380 nm. Three measurements were carried out for each sample, and the reported $\Phi_{overall}$ value corresponds to the arithmetic mean value of the three values. The errors in the quantum yield values associated with this technique were estimated to be $\pm 10\%$.¹⁰

The single-crystal X-ray diffraction data were collected with a Bruker AXS Smart Apex CCD diffractometer at 293 K. The X-ray generator was operated at 50 kV and 35 mA using Mo–K_{α} (λ = 0.71073 Å) radiation. The data were reduced using SAINTPLUS,¹¹ and an empirical absorption correction was applied using the SADABS program.¹² The structure was solved and refined by using SHELXL-97 in the WinGx suit of programs (v.1.63.04a).¹³ All the hydrogen positions were initially located in the difference Fourier maps and for the final refinement, the hydrogen atoms were placed in geometrically ideal positions and refined in the riding mode. Final refinement included the atomic positions of all the atoms, anisotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against $|F^2|$ was carried out by using the WinGx package of programs.¹⁴ Selected crystal data and data collection and refinement parameters are listed in Table 1.

Table 1. Crystallographic and Refinement Data for HL and 1

	HL	1
formula	C ₁₅ H ₁₅ ClN ₂ O ₃	C ₇₉ H ₅₅ Eu ₂ N ₁₁ O ₂₀
fw	306.74	1782.29
cryst sys	monoclinic	triclinic
space group	P21/c	$P\overline{1}$
cryst size (mm ³)	0.37 imes 0.18 imes 0.12	$0.16 \times 0.10 \times 0.08$
temp/K	100(2)	293(2)
$a/(\text{\AA})$	4.9635(4)	12.2234(4)
$b/(\text{\AA})$	15.8250(10)	13.1332(5)
c/(Å)	18.8965(19)	25.6658(6)
α (°)	90	94.762(2)
β (°)	101.544(3)	96.865(2)
γ (°)	90	109.037(3)
$V/Å^3$	1454.2(2)	3834.1(2)
Z	4	2
$D_{\rm calcd}, {\rm g \ cm^{-1}}$	1.401	1.544
$\mu/(Mo,K\alpha) \text{ mm}^{-1}$	0.274	1.696
F(000)	640	1784
$R_1\left[I > 2\sigma(I)\right]$	0.0536	0.0376
$wR_2[I > 2\sigma(I)]$	0.1439	0.0967
R_1 (all data)	0.0573	0.0480
wR_2 (all data)	0.1485	0.0540
GOF	1.044	1.043

Synthesis of 4-((1H-Benzo[d]imidazol-1-yl)methyl)benzoic acid (HL). a. Methyl 4-((1H-Benzo[d]imidazol-1-yl)methyl)benzoate. Potassium carbonate (5.84 g, 42 mmol) and a catalytic amount of KI were added to a solution of benzimidazole (1 g, 9 mmol) in freshly distilled CH₃CN (50 mL). The mixture was then refluxed for 30 min, following which methyl 4-(bromomethyl)benzoate (1.94 g, 8 mmol) was added and the solution was refluxed further at 68 °C for 48 h. The resulting mixture was poured into water and the precipitate was filtered off, washed with water, and dried. The precipitate thus obtained is then purified by column chromatography on silica gel with mixture of ethylacetate and hexane (3:10) as the eluent to get the product as a white solid. Yield, 0.93 g (41%): ¹H NMR (500 MHz, DMSO-*d*₆): δ (ppm) 8.433 (s, 1H), 7.937 - 7.921 (d, 2H, J = 8 Hz), 7.686 - 7.668 (m, 1H), 7.481 - 7.462(m, 1H), 7.412 - 7.395 (d, 2H, J = 8.5 Hz), 7.214 - 7.196 (m, 2H), 5.616 (s, 2H), 3.826 (s, 3H) ¹³C NMR (125 MHz, DMSO-*d*₆): δ (ppm) 165.86, 144.31, 143.47, 142.31,133.55, 129.57, 128.96, 127.51, 122.52, 121.71, 119.52, 110.58, 52.13, 47.20. m/z =267.43 (M + H)⁺. FT-IR (KBr) ν_{max} : 3093, 1710, 1605, 1492, 1421, 1360, 1282, 1182, 1103, 948, 731 cm⁻¹

b. Synthesis of 4-((1H-Benzo[d]imidazol-1-yl)methyl)benzoic Acid. Methyl 4-((1H-benzo[d]imidazol-1-yl)methyl)benzoate (1.5 g, 6 mmol) was refluxed for 24 h with KOH (0.948 g, 17 mmol) in 50 mL of ethanol. The reaction mixture was poured into ice cold water, acidified with dilute HCl, and the precipitate was filtered, washed, dried, and recrystallized from CH₃OH to yield HL·HCl·H₂O. Single crystals of HL suitable for X-ray study were obtained from a methanol solvent after storage for 2 weeks at ambient temperature. Yield, 0.759 g (54%): ¹H NMR (500 MHz, CD₃OD): δ (ppm) 8.348 (s, 1H), 8.007-7.990 (d, 2H, J = 8.5 Hz), 7.718-7.701 (m, 1H), 7.434–7.416 (m, 1H), 7.351–7.335 (d, 2H, J = 8 Hz), 7.298–7.276 (m, 2H), 5.612 (s, 2H). ¹³C NMR (500 MHz, DMSO): δ (ppm) 166.84, 144.23, 143.43, 141.76, 133.51, 130.07, 129.63, 127.26, 122.42, 121.59, 119.44, 110.52, 47.17. $m/z = 253.52 (M + H)^+$. Elemental analysis (%): Calcd for C₁₅H₁₅ClN₂O₃ (306.08): C, 58.73; H, 4.93; N, 9.13 Found: C, 58.61; H, 5.27; N, 9.27. FT-IR (KBr) ν_{max} : 3445, 1686, 1610, 1606, 1665, 1616, 1679, 1294, 1176, 1018, 738 cm⁻¹ 1610, 1496, 1465, 1416, 1379, 1294, 1176, 1018, 738 cm⁻

Syntheses of Lanthanide Complexes. In a typical procedure, an ethanolic solution of $Ln(NO_3)_3 \cdot 6H_2O(0.5 \text{ mmol})$ (Ln = Eu, Tb, or Gd) was added to a solution of the HL (1.5 mmol) in ethanol in the presence of NaOH (1.5 mmol). Precipitation took place immediately, and each reaction mixture was stirred subsequently for 10 h at room temperature. The crude products was filtered, washed with ethanol, and dried. The resulting complexes were then purified by recrystallization from a solvent mixture of dimethylsulfoxide and ethanol. Single crystals of 1 suitable for X-ray study were obtained from DMSO + CH₃CH₂OH solvent mixture after storage for 5 weeks at ambient temperature. However efforts to grow single crystals of complexes 2 and 3 were not fruitful.

Scheme 1. Synthetic Procedure for Ligand HL



 $[{\rm Tb_2(L)_5(NO_3)(H_2O)_4}]_n$ (2). Elemental analysis (%): calcd (found) for C₇₅H₅₇N₁₁O₁₇ Tb₂ (1702.17): C, 52.92 (53.10); H, 3.38 (3.21); N, 9.05 (9.16). FT-IR (KBr) $\nu_{\rm max}$: 3093 (ν (O–H)), 1613 ($\nu_{\rm as}(C=O)$), 1595 ($\nu_{\rm as}(C=O)$), 1414 ($\nu_{\rm s}(C=O)$), 1385 ($\nu_{\rm s}(C=O)$), 1508, 1292, 1211, 1008, 865, 738, 693 cm⁻¹.

 $[{\rm Gd}_2({\rm L})_5({\rm NO}_3)({\rm H}_2{\rm O})_4]_n$ (3). Elemental analysis (%): calcd (found) for C75H55N10O14 Gd2 (1636.81): C, 55.03 (55.45); H, 3.51 (3.69); N, 8.56 (8.83). FT-IR (KBr) $\nu_{\rm max}$: 3330(ν (O–H)), 1644($\nu_{\rm as}$ (C=O)), 1591($\nu_{\rm as}$ (C=O)), 1457 ($\nu_{\rm s}$ (C=O)), 1410 ($\nu_{\rm s}$ (C=O)), 1502, 1292, 1181, 1024, 853, 745, 693 cm^{-1}.

Results and Discussion

Synthesis and Characterization of 4-((1H-benzo[d]imidazol-1-yl)methyl)benzoic Acid and Its Corresponding Lanthanide Complexes. The ligand 4-((1H-benzo[d]imidazol-1-yl)methyl)benzoic acid) was synthesized in 54% yield according to the method described in the Experimental Section (Scheme 1). The new ligand was characterized by single crystal X-ray diffraction, ¹H NMR and ¹³C NMR (Figure S1, Supporting Information), FAB-MS, and elemental analysis. The synthetic procedures for the Ln^{3+} complexes 1-3are described in the Experimental Section. The elemental analyses for these complexes reveal that each Ln³⁺ ion has reacted with the corresponding benzoic acid ligand in a metal-to-ligand mole ratio of 2:5. In order to investigate the coordination modes of the ligand to the Ln^{3+} ions, the FT-IR spectra of complexes 1-3 were compared with those of the free ligand. The FT-IR spectra of the coordinated ligand HL exhibits two intense bands at approximately 1465 and 1686 cm^{-1} , which are attributable to the symmetric $v_{s}(C=O)$ and antisymmetric $v_{as}(C=O)$ vibration modes, respectively. In each case, coordination of the ligand HL to the respective lanthanide ion was confirmed by the absence of the ν (COOH) absorption bands of the ligand at ~1686 cm⁻¹. Moreover, the asymmetric and symmetric stretching vibrational modes of the carboxylate ligand in complexes **1–3** are further split into two peaks [v_s (C=O): 1414, 1385 cm⁻¹; v_{as} (C=O): 1613, 1595 cm⁻¹ in **1**; v_s (C=O): 1411, 1385 cm⁻¹; v_{as} (C=O): 1618, 1585 cm⁻¹ in **2**; v_s (C=O): 1457, 1410 cm⁻¹; v_{as} (C=O): 1644, 1591 cm⁻¹ in **3**]. The difference between the asymmetric and symmetric stretching vibration modes $(\Delta v (C=O) = v_{as} - v_s)$ fall in the ranges 226–233 and $134-185 \text{ cm}^{-1}$, which in turn implies that the carboxylate groups are coordinated to the Ln^{3+} ions in three different ways, namely, via monodentate, chelating and bidentate bridging.¹⁵ Furthermore, the IR spectra of 1-3 also exhibit a broad band around 3200 cm^{-1} , which is characteristic of an O-H stretching vibration and thus indicative of the presence



Figure 1. The asymmetric unit of the hydrochloride of 4-((1H-benzo[d]imidazol-1-yl)methyl) benzoate ligand.

of coordinated solvent molecules. The presence of coordinated bidentate nitrate in these lanthanide complexes is confirmed by the presence of six fundamental bands at \sim 1292, 1508, 738, 693, 1008, and 865 cm⁻¹, which are assigned to v_1 , v_4 , v_3 , v_5 , v_2 , and v_6 , respectively. The difference between the two highest bands v_4 and v_1 lies in the range $210-216 \text{ cm}^{-1}$, indicating the coordination of nitrate group in a bidentate chelating fashion.¹⁶ It is clear from the thermogravimetric analysis data for 1-3 (Figure S2, Supporting Information) that each complex undergoes a mass loss of approximately 4% (calcd ~4.22%) in the first step (75-126 °C), which corresponds to elimination of the lattice ethanol and water molecules. Subsequent thermal decomposition of 1-3 with the loss of four coordinated water molecules takes place in the temperature region 130-370 °C. A weight loss in the temperature range 400-1000 °C corresponds to the decomposition of one nitrate and five carboxylate ligand molecules. The powder X-ray diffraction patterns of complexes 1-3 depicted in Figure S3 (Supporting Information) are similar, indicating that these complexes are isostructural.

X-ray Crystal Structures. The hydrochloride salt of 4-((1H-benzo[d])midazol-1-yl)methyl)benzoic acid crystallized in the monoclinic space group <math>P21/c. The molecular structure established by X-ray single-crystal of the ligand is displayed in Figure 1. It is apparent from the established structure that the benzimidazole nitrogen N2 is protonated, and this forms a positive charge in the ligand molecule. The charged chloride species present in the crystal lattice acts as the counterion.

The scrutiny of the X-ray crystal structure of the ligand highlights the existence of an intermolecular hydrogen-bonding

interaction between two carboxylate ligand moieties involving O1–H1A and O2 with a distance of O2···H1A = 1.678 Å and angle of 169.24° (Table 3). In addition to the above intermolecular hydrogen-bonding interaction, a CH- π interaction also exists between C8–H8A of the –CH₂ moiety of the carboxylate and the phenyl ring C2–C7 of the neighboring carboxylate ligand. These two van der Waals interactions combine to produce a two-dimensional (2D) molecular array arrangement (Figure 2).

The molecular structure of $[Eu_2(L)_5(NO_3)(H_2O)_4]_n$ $(CH_3CH_2OH)_2 \cdot (H_2O)$ (1) was determined by single-crystal X-ray diffraction (Figure 3). The pertinent data collection parameters and a listing of significant bond distances and bond angles for the metal coordination environments are presented in Tables 1 and 2, respectively.



Figure 2. View of ligand HL showing the intermolecular hydrogenbonding interactions involving O1–H1A and O2 of the carboxylate groups and the CH- π interactions between C8–H8A of –CH₂ moiety and the phenyl ring C2–C7. Symmetry code: -x, -y, -1-z.

Compound 1 crystallizes in the triclinic space group $P\overline{1}$. Each asymmetric unit of compound 1 contains two crystallographically independent Eu³⁺ ions (Eu1 and Eu2), five carboxylate ligands, one nitrate, and four coordinated H₂O molecules. Two uncoordinated ethanol and one water molecules are also present in the crystal lattice. As shown in Figure 3, Eu1 center is eight-coordinated with seven oxygen atoms furnished by four bridging carboxylate ligands, one nitrate and one water molecule, and one nitrogen atom from the benzimidazole moiety of the ligand. The Eu2 is also eightcoordinated and surrounded by eight oxygen atoms form four carboxylate ligands and three oxygen atoms furnished by water molecules.

It is noteworthy to mention that the 4-((1H-benzo-[d]imidazol-1-yl)methyl)benzoic acid ligand adopts only bridging coordination mode around the Eu1 center. On the other hand, carboxylates ligands adopt three different coordination modes around Eu2: bidentate chelating, bridging, and monodentate (Scheme 2).

The longest Eu–O bonds involve the oxygen atoms of the bidentate nitrate group which is coordinated to Eu1 in a chelating mode [Eu1–O13: 2.506 Å], and the shortest such bonds are associated with the bridging carboxylate ligands

Table 2. Selected Bond Lengths (Å) and Angles (°) for 1

		1	
Eu1-Eu1	4.104(4)	Eu2-Eu2	4.869(4)
Eu1-O1	2.363(3)	Eu2-O6	2.338(3)
Eu1-O3	2.363(3)	Eu2-O17	2.369(3)
Eu1-O11	2.386(3)	Eu2-O4	2.477(3)
Eu1-O14	2.332(3)	Eu2-O5	2.517(3)
Eu1-O12	2.480(3)	Eu2-O8	2.359(3)
Eu1-O13	2.506(3)	Eu2-O7	2.448(3)
Eu1-O2	2.461(3)	Eu2-O15	2.462(3)
Eu1-N4	2.559(3)	Eu2-O16	2.420(3)
O1-Eu1-O11	76.81(11)	O6-Eu2-O17	105.22(10)
O1-Eu1-O12	74.57(11)	O6-Eu2-O16	142.44(11)
O12-Eu1-O13	50.94(11)	O8-Eu2-O16	72.75(10)
N4-Eu1-O14	82.31(12)	O16-Eu2-O15	68.76(10)
N4-Eu1-O13	72.66(11)	O17-E2-O15	81.52(10)
O2-Eu1-O11	71.92(10)	O7-Eu2-O15	140.99(10)
O2-Eu1-N4	71.84(12)	O8-Eu2-O7	88.04(10)



Figure 3. Coordination environment of complex 1 with capped stick model and all hydrogen atoms are omitted for clarity. Symmetry code A: -x, -y, 1-z; B: -1 + x, -1 + y, -1 + z; C: 1 - x, 1 - y, 2 - z.

Scheme 2. Different Types of Binding Modes for the Ligand HL Observed in Complex 1





Figure 4. The 1D coordination polymer chain of complex 1 when viewed along the b axis.

[Eu1–O14: 2.332 Å]. At the Eu2 center, the longest Eu–O bonds are associated with the chelating carboxylate groups [Eu2–O5: 2.517 Å] and the shortest bonds are formed by the bridging carboxylate ligand [Eu2-O6 2.338 Å].¹⁷ Interestingly, the two Eu1 centers are interconnected by four carboxylate groups in a bridging mode resulting in the dinuclear paddle-wheel building blocks with Eu1····Eu1 separation of 4.104 Å. In a similar fashion, the two Eu2 centers are also connected by two bridging carboxylate groups to give other types of dinuclear paddle-wheel building blocks with a Eu2····Eu2 separation of 4.869 Å. Finally, these two unsymmetrical dinuclear building blocks are interconnected via one of the carboxylate ligands through nitrogen of the benzimidazole moiety to form an infinite one-dimensional (1D) coordination polymer in a helical arrangement (Figure 4). The scrutiny of the packing diagram of 1 further reveals that these 1D helical chains are connected through an intermolecular hydrogen bonding interaction between bidentate chelating nitrate group and benzimidazole ring of one the ligands, involving C28–H28···O19 (D–A = 3.340 Å, H-A = 2.719 Å and angle 124.93°) and C30-H30···O13 $(D-A = 3.545 \text{ Å}, H-A = 2.719 \text{ Å} and angle 148.46^\circ)$, Table 3). The contact between these helical chains are further strengthened by another intermolecular hydrogen bonding interaction between one of the benzimidazole moieties and a carboxylate group which is coordinated to the metal center in a monodentate mode, involving C39-H39····O9 (D-A = 3.362 Å, H-A = 2.467 Å and angle $161.56^{\circ}, \text{ Table 3}$).¹⁸ The two infinite 1D coordination polymers which extend along

Table 3. Selected Hydrogen-Bond Lengths (\mathring{A}) and Angles (°) for HL and

Complex 1						
compounds	contact type	H · · · ∙ A (Å)	$\begin{array}{c} \mathbf{D}\cdots\mathbf{A} \\ (\mathbf{\mathring{A}}) \end{array}$	$D \cdots H \cdots A$ ^(°)		
HL 1	$\begin{array}{c} O1 - H1A \cdots O2^{i} \\ C28 - H28 \cdots O19^{ii} \\ C30 - H30 \cdots O13^{ii} \\ C39 - H39 \cdots O9^{iii} \end{array}$	1.678 2.719 2.719 2.467	2.673 3.340 3.545 3.362	169.24 124.93 148.46 161.56		

^{*a*} Symmetry codes: (i) -x, -y, -1 - z; (ii) -1 - x, -1 - y, 1 - z; (iii) -1 + x, -1 + y, z.

the directions of both b and c axes combine to form a 2D network arrangement (Figure 5).

Ligand-Centered Electronic States. The UV-vis absorption spectrum of the free ligand and its corresponding Ln² complexes 1–3 recorded in CH₃OH solution ($c = 2 \times 10^{-5}$ M) are shown in Figure 6. The trends in absorption spectra of the complexes are identical to the one observed for the free ligand, indicating that the singlet excited state of the free ligand is not significantly affected by the complexation of the Ln³⁺ ion. However, a small blue shift that is discernible in the absorption maximum of the complexes is attributable to the perturbation induced by the metal coordination. The ligand displays three absorption bands at 233, 274, and 282 nm, which are assigned to singlet-singlet ${}^{1}\pi - \pi^{*}$ absorptions of the aromatic rings. The molar absorption coefficient values for complexes 1-3 at 231 nm of 6.6×10^4 , 7.7×10^4 , and $6.7 \times 10^{4} \,\mathrm{L \, mol^{-1} \, cm^{-1}}$, respectively, are approximately five times higher than that of the ligand $(1.5 \times 10^4 \text{ at } 232 \text{ nm})$, which is consistent with the presence of five carboxylate ligands in each complex. These features point to the ligand being an adequate light-harvesting chromophore for the sensitization of lanthanide luminescence.

In one of the preferred energy migration paths in Ln^{3+} complexes, excitation energy is funnelled to the metal ion through the long-lived ligand-centered triplet state.¹⁹ Thus, for a ligand to be a suitable sensitizer, its triplet state should be situated above the Eu³⁺ (${}^{5}\text{D}_{0} = 17500 \text{ cm}^{-1}$) or Tb³⁺ (${}^{5}\text{D}_{4} = 20500 \text{ cm}^{-1}$) emitting level and the energy gap between them is often correlated with the overall quantum yield; too large a gap leads to inefficient energy transfer, whereas too small a gap results in back-energy transfer.²⁰ In order to understand the energy transfer process in the new Ln³⁺ complexes, it was necessary to determine the singlet and triplet energy levels of the ligand, 4-((1H-benzo[d]imidazol-1-yl)methyl)benzoic acid. The singlet (${}^{1}\pi\pi^{*}$) energy level of



Figure 5. The 2D molecular array formed by the hydrogen bonding involving C39–H39····O9 (D–A = 3.362 Å, H–A = 2.467 Å and angle 161.56°), C28–H28···O19 (D–A = 3.340 Å, H–A = 2.719 Å and angle 124.93°), and C30–H30···O13 (D–A = 3.545 Å, H–A = 2.719 Å and angle 148.46°) when viewed along the *c* axis (some of the ligand atoms were omitted for clarity). Symmetry codes A: -1 - x, -1 - y, 1 - z; B: -1 + x, -1 + y, *z*.



 $8.0x10^{6} - \frac{1}{6.0x10^{6}} + \frac{1}{6.0x10^{6}}$

Figure 6. UV-visible absorption spectra of HL and Complexes 1-3 in CH₃OH solution (2 × 10⁻⁵ M).

this ligand was estimated by reference to the wavelength of the UV-vis upper absorption edge of the Gd³⁺ complex **3**. The pertinent value was found to be 286 nm (34965 cm⁻¹) in the case of the ligand. The triplet energy level (${}^{3}\pi\pi^{*} = 23980$ cm⁻¹) of this ligand was calculated by reference to the lower wavelength emission edge (417 nm) from the low-temperature phosphorescence spectra of the Gd³⁺ complex of ligand (Figure S4, Supporting Information). According to Reinhoudt's empirical rule, the intersystem crossing process becomes effective when ΔE (${}^{1}\pi\pi^{*}-{}^{3}\pi\pi^{*}$) is at least 5000 cm⁻¹.²¹ The energy gap ΔE (${}^{1}\pi\pi^{*}-{}^{3}\pi\pi^{*}$) for the ligand is 10985 cm⁻¹. With respect to the aim of this work, the energy gap between triplet state and ${}^{5}D_{0}$ state of Eu³⁺ is 6730 cm⁻¹, which is not an ideal situation for the sensitization of Eu³⁺ luminescence. On the other hand, the gap between the triplet state and ${}^{5}D_{4}$ state of Tb³⁺ is 3480 cm⁻¹, which is almost an ideal situation for Tb³⁺ luminescence.

Steady-State Photoluminescence. Under ligand excitation, the Eu³⁺ complex emit characteristic metal-centered luminescence in the solid state, and the corresponding spectrum is

Figure 7. Room-temperature excitation and emission spectra for complex 1 ($\lambda_{ex} = 290$ nm) with emission monitored at approximately 612 nm.

shown in Figure 7. The excitation spectrum displays prominent ligand bands in the UV range and faint f-f transitions at 364 (${}^{5}G_{6} \leftarrow {}^{7}F_{0}$), 380 (${}^{5}H_{4} \leftarrow {}^{7}F_{0}$), 395 (${}^{5}L_{6} \leftarrow {}^{7}F_{0,1}$), and 463 nm (${}^{5}D_{2} \leftarrow {}^{7}F_{0,1}$), thus confirming the sensitization of Eu³⁺ luminescence by the ligand.²² The emission spectrum of the Eu³⁺ complex 1 exhibits characteristic sharp bands of the metal ion in the 590-720 nm spectral range.¹⁸ The intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition (electric dipole) is greater than that of the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition (magnetic dipole), which indicates that the coordination environment of the Eu³⁺ ion is devoid of inversion center.²³ Furthermore, the absence of $\pi - \pi^{*}$ transition of the ligand was evident from the emission spectrum, which is typically diagnostic of the sensitization of the ligand toward the Eu³⁺ ion.

The solid-state excitation and emission spectra of complex **2** recorded at room-temperature are depicted in Figure 8. The excitation spectrum monitored at the characteristic emission of the Tb^{3+} ion in the solid state overlaps with the absorption spectrum in the 230–300 nm region, which indicate that energy transfer from the ligand to the metal



Figure 8. Room-temperature excitation and emission spectra for complex 2 ($\lambda_{ex} = 288$ nm) with emission monitored at approximately 545 nm.



Figure 9. Luminescence decay profiles for complexes 1 and 2 excited at 290 and 288 nm, respectively, and monitored at \sim 612 and 545 nm, respectively.

ion is operative. The excitation spectrum of 2 shows a broad band between 250 and 400 nm, which is attributable to the $\pi - \pi^*$ transition of the aromatic carboxylate ligand. A series of sharp lines that are assignable to transitions between the lanthanide ${}^{7}F_{5}$ and ${}^{5}G_{6}$, ${}^{5}L_{10}$ and ${}^{5}L_{9}$ levels are also observed in the excitation spectrum of complex 2.5d,6b,24 The foregoing transitions are less intense than the absorptions due to the organic ligand and are overlapped by a broad excitation band. In turn, this proves that luminescence sensitization via ligand excitation is considerably more efficient than the direct excitation of the Tb³⁺ absorption level. The roomtemperature emission spectrum of complex 2 exhibits the characteristic emission bands of the Tb³⁺ cation (λ_{ex} 288 nm) centered at 488, 545, 585, and 620 nm which result from deactivation of the ${}^{5}D_{4}$ excited state to the corresponding ${}^{7}F_{J}$ ground state of the Tb³⁺ cation (J = 6, 5, 4, 3). 5d,8,24 Interestingly, no emission bands from the organic ligand were observed, which leads to the conclusion that energy transfer from the ligand to the Tb^{3+} center is efficient.

The luminescence decays measured at both ambient (298 K) and low temperatures (77 K) are single exponential functions for the Ln^{3+} complexes 1-2 (Figure 9 and Figure S5, Supporting Information) and the pertinent values are summarized in Table 4. Collectively, these data imply the

Table 4. Radiative (A_{RAD}) and Nonradiative (A_{NR}) Decay Rates, ${}^{5}D_{0}/{}^{5}D_{4}$ Lifetimes (τ_{obs}), Radiative Lifetime (τ_{RAD}), Intrinsic Quantum Yields (Φ_{Ln}), Energy Transfer Efficiencies (Φ_{sen}), and Overall Quantum Yields ($\Phi_{overall}$) for Complexes 1–2

	compounds		
photophysical parameters	1	2	
$A_{\rm RAD}/{\rm s}^{-1}$	683		
$A_{\rm NR}/{\rm s}^{-1}$	192		
$\tau_{\rm obs}/\mu s$	1141 ± 12	1237 ± 17	
$\tau_{\rm RAD}/\mu s$	1460 ± 12	1324 ± 30	
$\Phi_{Ln}(\%)$	78	93	
$\Phi_{\text{sen}}(\%)$	1.5	16	
$\Phi_{\rm overall}$ (%)	1.22 ± 0.20	14.55 ± 1	

existence of a single chemical environment around the Ln³⁺ ion in each case. Shorter ${}^{5}D_{0}$ lifetime for Eu³⁺ ($\tau_{obs} = 1.14$ ms) noted may be due to the dominant nonradiative decay channels associated with the vibronic coupling because of the presence of solvent molecules in the coordination sphere of the complex 1, as well documented in many of the hydrated Eu³⁺ carboxylate complexes.^{5d,e} On the other hand, longer ⁵D₄ lifetime value ($\tau_{obs} = 1.24$ ms) has been observed for complex 2 even in the presence of solvent molecules in the first coordination sphere, as they are essential vibrational deactivators of the excited states of Ln³⁺ ions. The energy gap between the luminescent state and the ground state manifold is approximately 12000 cm^{-1} for Eu³⁺ and 14800 cm^{-1} for Tb^{3+} . Relatively efficient coupling of the Eu³⁺ excited states occurs to the third vibrational overtone of the proximate OH oscillators ($\nu_{OH} \sim 3300 - 3500 \text{ cm}^{-1}$), and to the fourth harmonic in the case of Tb^{3+} , which is consistent with the less efficient quenching observed for Tb³⁺ where the Franck-Condon overlap factor is less favorable.²⁵

The overall quantum yield (Φ_{overall}), radiative (A_{RAD}), and nonradiative (A_{NR}) decay rates, intrinsic quantum yields (Φ_{Ln}) , and the energy transfer efficiencies (Φ_{sen}) for complexes 1 and 2 are calculated by the methods described in our earlier publications,^{5b-e,8} and the values are summarized in Table 4. Poor luminescence efficiency noted in complex 1 $(\Phi_{\text{overall}} = 1.22\%)$ may be due to the weak sensitization efficiency of 4-((1H-benzo[d]imidazol-1-yl)methyl)benzoic acid with respect to the Eu³⁺ ion. The latter observation can be explained on the basis of larger energy gap (6730 cm^{-1}) between the triplet state of the ligand and ${}^{5}D_{0}$ level of Eu^{3+} ion. Furthermore, the complex 1 having solvent molecules in the coordination sphere exhibits lower overall quantum yield and lifetime values. This is due to the presence of O-H oscillators in this system, which effectively quenches the luminescence of the Eu³⁺ ion. Relatively higher quantum yield ($\Phi_{overall} = 15\%$) and lifetime values ($\tau_{obs} = 1.24$ ms) have been noticed in Tb^{3+} complex as compared to Eu^{3+} complex. This can be explained on the basis of better energy transfer efficiency of the ligand toward Tb³⁺ ion due to the smaller energy gap between the triplet state and ${}^{5}D_{4}$ level $(3480 \text{ cm}^{-1}).$

Conclusions

A new chromophore ligand 4-((1H-benzo[d]imidazol-1yl)methyl)benzoic acid has been designed and utilized for the construction of a unique 1D lanthanide coordination polymer for the indirect excitation of lanthanide metal center. Single-crystal X-ray diffraction analysis revealed that different coordination modes of the carboxylate ligand with lanthanide atoms could promote the formation of a 1D coordinational polymer, which is constructed from unsymmetrical dinuclear lanthanide building blocks. The coordination polymer possess helical chain structure that is further interlinked to the neighboring coordination polymers based on hydrogen bonding interactions, which results into a 2D architecture. The new benzimidazole anchored benzoate complex of Tb^{3+} exhibits bright green luminescence efficiency in the solid state with a quantum yield of 15%, thus rendering it as promising candidate for use in various photonic applications. By contrast, the poor sensitization observed for the corresponding Eu³⁺ complex is mainly due to the larger energy gap between the ligand triplet state and ⁵D₀ level of Eu³⁺.

Acknowledgment. The authors acknowledge financial support from the Department of Science and Technology (SR/S1/IC-36/2007) and the Council of Scientific and Industrial Research, New Delhi (NWP0010).

Supporting Information Available: X-ray crystallographic data of ligand and complexes 1 in CIF format, ¹H, ¹³C NMR spectra for ligand HL, thermogravimetric data, phosphorescence spectrum of gadolinium complex 3 at 77 K and low temperature luminescence decay profile. This material is available free of charge via the Internet at http://pubs.acs.org.

References

- (a) Bünzli, J.-C. G.; Piguet, C. Chem. Soc. Rev. 2005, 34, 1048– 1077. (b) Eliseeva, S. V.; Bünzli, J.-C. G. Chem. Soc. Rev. 2010, 39, 189–227. (c) Rodrigues, M. O.; da Costa Júnior, N. B.; de Simone, C. A.; Araújo, A. A. S.; Brito-Silva, A. M.; Almeida Paz, F. A.; de Mesquita, M. E.; Júnior, S. A.; Freire, R. O. J. Phys. Chem. B 2008, 112, 4204–4212.
- (2) (a) Kido, J.; Okamoto, Y. *Chem. Rev.* 2002, *102*, 2357–2368.
 (b) Bünzli, J.-C. G. *Chem. Rev.* 2010, *110*, 2729–2755. (c) Liu, D.; Tang, K.; Liu, W.; Su, C.; Yan, X.; Tana, M.; Tang, Y. *Dalton Trans.* 2010, *39*, 9763–9765. (d) Chen, B.; Wang, L.; Xiao, Y.; Fronczek, F. R.; Xue, M.; Cui, Y.; Qian, G. *Angew. Chem., Int. Ed.* 2009, *48*, 500–503.
- (3) (a) Lehn, J. M. Angew. Chem., Int. Ed. 1990, 29, 1304–1319.
 (b) Petoud, S.; Cohen, S. M.; Bünzli, J.-C. G.; Raymond, K. N. J. Am. Chem. Soc. 2003, 125, 13324–13325. (c) Sabbatini, N.; Guardiglia, M.; Lehn, J. M. Coord. Chem. Rev. 1993, 123, 201–228. (d) Piguet, C.; Bünzli, J.-C. G. Chem. Soc. Rev. 1999, 28, 347–358.
- (4) Weissman, S. I. J. Chem. Phys. 1942, 10, 214–217.
- (5) (a) Binnemans, K. Chem. Rev. 2009, 109, 4283–4374. (b) Divya, V.; Biju, S.; Luxmi Varma, R.; Reddy, M. L. P. J. Mater. Chem. 2010, 20, 5220–5227. (c) Biju, S.; Reddy, M. L. P.; Cowley, A. H.; Vasudevan, K. V. Cryst. Growth Des. 2009, 9, 3562–3569. (d) Sivakumar, S.; Reddy, M. L. P.; Cowley, A. H.; Vasudevan, K. V. Dalton Trans 2010, 39, 776–786. (e) Raphael, S.; Biju, S.; Reddy, M. L. P.; Cowley, A. H.; Findlater, M. Inorg. Chem. 2007, 46, 11025–11030.
- (6) (a) Busskamp, H.; Deacon, G. B.; Hilder, M.; Junk, P. C.; Kynast, U. H.; Lee, W. W.; Turner, D. R. *CrystEngComm.* 2007, *9*, 394–411. (b) Raphael, S.; Reddy, M. L. P.; Cowley, A. H.; Findlater, M. *Eur. J. Inorg. Chem.* 2008, 4387–4394. (c) Deacon, G. B.; Hein, S.; Junk,

P. C.; Jüstel, T.; Lee., W; Turner, D. R. *CrystEngComm* **2007**, *9*, 1110–1123.

- (7) (a) de Bettencourt-Dias, A.; Viswanathan, S. *Dalton Trans.* 2006, 34, 4093–4103. (b) Viswanathan., S.; de Bettencourt-Dias, A. *Inorg. Chem.* 2006, 45, 10138–10146.
- (8) Ramya, A. R.; Reddy, M. L. P.; Cowley, A. H.; Vasudevan, K. V. Inorg. Chem. 2010, 49, 2407–2415.
- (9) Li, Y.; Zheng, F. K.; Liu, X.; Zou, W. Q.; Guo, G. C.; Lu, C. Z.; Huang, J. S. *Inorg. Chem.* **2006**, *45*, 6308–6316.
- (10) Bril, A; De Jager-Veenis, A. W. J. Electrochem. Soc. 1976, 123, 396–398.
- (11) SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL; Bruker AXS Inc.: Madison, WI, 2004.
- (12) Sheldrick, G. M. Siemens Area Correction Absorption Correction Program; University of Göttingen: Göttingen, Germany, 1994.
- (13) Sheldrick, G. M. SHELXL-97 Program for Crystal Structure Solution and Refinement; University of Göttingen: Göttingen, Germany, 1997.
- (14) Farrugia, J. L. J. App. Crystallogr. 1999, 32, 837-838.
- (15) (a) Deacon, G. B.; Phillips, R. J. Coord. Chem. Rev. 1980, 33, 227–250. (b) Teotonio, E. E. S.; Brito, H. F.; Felinto, M. C. F. C.; Thompson, L. C.; Young, V. G.; Malta, O. L. J. Mol. Struct. 2005, 751, 85–94.
- (16) Gudasi, K. B.; Shenoy, R. V.; Vadavi, R. S.; Patil, M. S.; Patil, S. A.; Hanchinal, R. R.; Desai, S. A.; Lohithaswa, H. *Bioinorg Chem Appl.* **2006**, 2006, 1–8.
- (17) (a) Ye, J.; Zhang, J.; Ning, G.; Tian, G.; Chen, Y.; Wang, Y. Cryst. Growth Des 2008, 8, 3098–3106. (b) Liu, M.-S.; Yu, Q.-Y.; Cai, Y.-P.; Su, C.-Y.; Lin, X.-M.; Zhou, X.-X.; Cai, J.-W. . Cryst. Growth. Des. 2008, 8, 4083–4091.
- (18) (a) Chen, J.-Q.; Cai, Y.-P.; Fang, H.-C.; Zhou, Z.-Y.; Zhan, X.-L.; Zhao, G.; Zhang, Z. Cryst. Growth Des. 2009, 9, 1605–1613. (b) Cai, Y.-P.; Zhang, H.-X.; Xu, A.-W.; Su, C.-Y.; Chen, C.-L.; Liu, H.-Q.; Zhang, L.; Kang, B.-S. J. Chem. Soc., Dalton Trans. 2001, 16, 2429– 2434.
- (19) (a) Shavaleev, N. M.; Eliseeva, S. V.; Scopelliti, R.; Bünzli, J.-C. G. *Inorg. Chem.* 2010, 49, 3927–3936. (b) Shavaleev, N. M.; Eliseeva, S. V.; Scopelliti, R.; Bünzli, J.-C. G. *Chem.*—*Eur. J.* 2009, 15, 10790– 10802.
- (20) Latva, M.; Takalo, H.; Mukkala, V. M.; Matachescu, C.; Rodriguez-Ubis, J. C.; Kanakare, J. J. Lumin. 1997, 75, 149–169.
- (21) Steemers, F. J.; Verboom, W.; Reinhoudt, D. N.; Vander Tol, E. B.; Verhoeven, J. W. J. Am. Chem. Soc. 1995, 117, 9408–9414.
- (22) (a) Biju, S.; Ambili Raj, D. B.; Reddy, M. L. P.; Kariuki, B. M. *Inorg. Chem.* **2006**, *45*, 10651–10660. (b) Zucchi, G.; Olivier, M.; Pierre, T.; Gumy, F.; Bünzli, J.-C. G.; Michel, E. *Chem.—Eur. J.* **2009**, *15*, 9686–9696. (c) Pavithran, R.; Reddy, M. L. P.; Junior, S. A.; Freire, R. O.; Rocha, G. B.; Lima, P. P. *Eur. J. Inorg. Chem.* **2005**, *20*, 4129–4137.
- (23) (a) Ambili Raj, D. B.; Francis, B.; Reddy, M. L. P.; Butorac, R. R.; Lynch, V. M.; Cowley, A. H. *Inorg. Chem.* **2010**, *49*, 9055–9063.
 (b) Francis, B.; Ambili Raj, D. B.; Reddy, M. L. P. *Dalton Trans.* **2010**, *39*, 8084–8092.
- (24) Biju, S.; Reddy, M. L. P.; Cowley, A. H.; Vasudevan, K. V. J. Mater. Chem. 2009, 19, 5179–5187.
- (25) (a) Dossing, A. Eur. J. Inorg. Chem. 2005, 8, 1425–1434. (b) Beeby, A.; Clarkson, I. M.; Dickins, R. S.; Faulkner, S.; Parker, D.; Royle, L.; de Sousa, A. S.; Williams, J. A. G.; Woods, M. J. Chem. Soc. Perkin Trans. 2 1999, 3, 493–503.