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# Transformation of a Luminescent Benzimidazole-Based Yb<sub>3</sub> Cluster into a One-Dimensional Coordination Polymer

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Received October 15, 2009; Revised Manuscript Received November 18, 2009

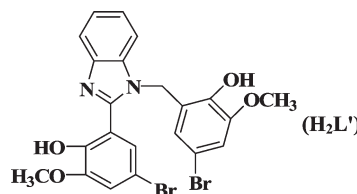
**ABSTRACT:** Reaction of the benzimidazole-based ligand 2-(1H-benzimidazol-2-yl)-4-bromo-6-methoxy-phenol (HL) with LnCl<sub>3</sub>·6H<sub>2</sub>O in a 4:3 mol ratio in refluxing EtOH gave the trinuclear complexes [Ln<sub>3</sub>L<sub>4</sub>Cl<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·Cl·H<sub>2</sub>O·EtOH (**1**) (Ln = Tb (a), Er (b), Yb (c)) in 40–59% yields. Under similar conditions, but with the subsequent addition of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O to the reaction mixture, complex {[Yb<sub>3</sub>L<sub>4</sub>(OAc)<sub>4</sub>]·Cl·EtOH}<sub>n</sub> (**2**) can be isolated in 48% yield. **2** has a one-dimensional coordination structure in the solid state. All complexes display intramolecular  $\pi$ – $\pi$  stacking and hydrogen bonded interactions in the solid state as well as lanthanide ion based luminescence in both solution and the solid.

## Introduction

There is currently considerable interest in metal–organic coordination polymers or framework materials (MOF) from both a structural standpoint and for potential application in, for example, catalysis, molecular recognition, and storage devices.<sup>1</sup> The “node and spacer” methodology has proven to be a very successful strategy for the design of many metal–organic architectures including chain, ladder, grid, brick wall, honeycomb, diamondoid, rutile, and  $\alpha$ -polonium structures.<sup>2</sup> Most of this work has been focused on coordination polymers of d-block transition metals. Coordination polymers based on lanthanides would be of interest for the potential to develop new optical, electrical, and magnetic materials.<sup>3</sup> However, lanthanide ions generally display high and variable coordination numbers and their use as nodes for the construction of coordination polymers is currently of interest.

As part of a general program aimed at the synthesis of multinuclear lanthanide complexes, we recently reported the use of an unusual benzimidazole ligand (H<sub>2</sub>L') which was used to stabilize a range of Ln–Cu heterobimetallic complexes (Scheme 1).<sup>4a</sup> We have also recently reported the construction of several different polynuclear lanthanide framework materials based on 1,4-benzenedicarboxylate and 4-hydroxybenzene sulfonate linker units.<sup>4b–4c</sup> We were therefore interested in the possibility of constructing a coordination polymer from benzimidazole-based lanthanide units and carboxylate linkers. Lanthanide complexes with benzimidazole-based ligands are of interest since they have the potential to exhibit ligand-to-metal energy transfer (LMCT) processes as well as supramolecular architectures based on  $\pi$ – $\pi$  stacking and hydrogen bonded interactions.<sup>5</sup> In this paper, we describe the synthesis, structures, and photophysical properties of Ln<sub>3</sub> clusters stabilized with the simplified benzimidazole ligand HL (Scheme 2). In the case of the Yb<sub>3</sub> complex **1c** we were able to replace the H<sub>2</sub>O and Cl<sup>–</sup> ions with acetate (OAc<sup>–</sup>) by

Scheme 1. The Structure of Benzimidazole Ligand H<sub>2</sub>L'



treatment of the reaction mixture with Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O. The resulting compound has an unusual one-dimensional (1-D) coordination polymeric structure in the solid state in which Yb<sub>3</sub>L<sub>4</sub> clusters are linked by double OAc<sup>–</sup> bridges. We chose Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O for this conversion on the basis that it was reasonably soluble in EtOH. At present we do not know if the reaction is dependent on Zn<sup>2+</sup>, although it seems reasonable to assume that other metal acetates would be capable of producing the same result.

## Experimental Section

**General Methods.** All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. Solvents and starting materials were purchased from Aldrich and used without further purification unless noted. <sup>1</sup>H NMR spectra were recorded on a Varian-500 NMR spectrometer with SiMe<sub>4</sub> as an internal standard, infrared spectra from 4000 to 400 cm<sup>–1</sup> on a Bruker EQUINOX 55 FT-IR, and ESI-MS mass spectra on a Finnigan MAT TSQ 700. Elemental analyses were performed by Atlantic Microlab, Norcross, GA. Melting points were in sealed capillaries under nitrogen and are uncorrected. The solvents used for the photophysical investigations were dried and freshly distilled under nitrogen. Absorption spectra were obtained on a BECKMAN DU 640 spectrophotometer, excitation and visible emission spectra on a QuantaMaster PTI fluorimeter. Near-infrared (NIR) emission spectra were measured with a 1-m SPEX 1704 spectrometer and a liquid-nitrogen cooled Ge detector, using an argon ion laser as the excitation source.

**X-ray Crystallography.** Data were collected on a Nonius Kappa CCD diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 153 K. Absorption corrections were applied using GAUSSIAN. The structures were solved by direct methods and

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Scheme 2. Formation of Lanthanide Complexes 1a–c and 2

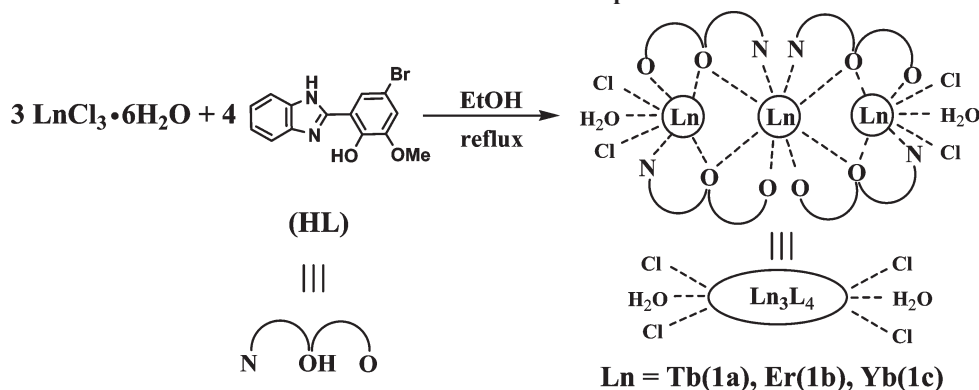


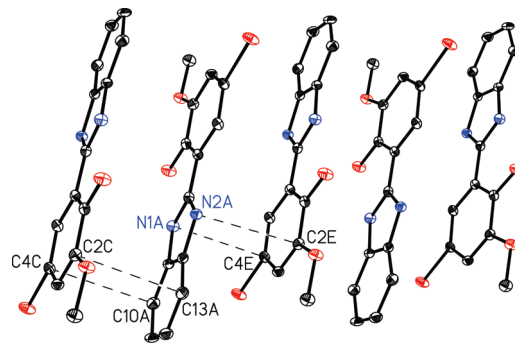
Table 1. Crystal Data and Structure Refinement for the Free Ligand HL, 1a–c and 2

	HL	1a	1b	1c	2
formula	C <sub>14</sub> H <sub>11</sub> BrN <sub>2</sub> O <sub>2</sub>	C <sub>58</sub> H <sub>52</sub> Br <sub>4</sub> Cl <sub>5</sub> N <sub>8</sub> O <sub>12</sub> Tb <sub>3</sub>	C <sub>58</sub> H <sub>52</sub> Br <sub>4</sub> Cl <sub>5</sub> N <sub>8</sub> O <sub>12</sub> Er <sub>3</sub>	C <sub>58</sub> H <sub>52</sub> Br <sub>4</sub> Cl <sub>5</sub> N <sub>8</sub> O <sub>12</sub> Yb <sub>3</sub>	C <sub>64</sub> H <sub>52</sub> Br <sub>4</sub> Cl <sub>5</sub> N <sub>8</sub> O <sub>16</sub> Yb <sub>3</sub>
fw	319.16	2026.68	2051.70	2069.04	2063.35
cryst syst	triclinic	tetragonal	tetragonal	tetragonal	tetragonal
space group	<i>P</i> $\bar{1}$	<i>P4</i> / <i>ncc</i>	<i>P4</i> / <i>ncc</i>	<i>P4</i> / <i>ncc</i>	<i>P4</i> / <i>ncc</i>
<i>a</i> , Å	7.2664(15)	25.992(4)	25.943(4)	25.902(4)	25.912(4)
<i>b</i> , Å	11.972(2)	25.992(4)	25.943(4)	25.902(4)	25.912(4)
<i>c</i> , Å	14.604(3)	23.403(5)	23.312(5)	23.203(5)	22.760(5)
$\alpha$ , deg	75.96(3)	90	90	90	90
$\beta$ , deg	89.72(4)	90	90	90	90
$\gamma$ , deg	86.96(3)	118.08(3)	90	90	90
<i>V</i> , Å <sup>3</sup>	1230.8(4)	15810(4)	15689(4)	15567(4)	15281(4)
<i>Z</i>	4	8	8	8	8
<i>D</i> <sub>calc</sub> , g cm <sup>−3</sup>	1.722	1.698	1.732	1.761	1.794
temp, K	153(1)	153(1)	153(1)	153(1)	153(1)
<i>F</i> (000)	640	7728	7800	7848	7896
$\mu$ , mm <sup>−1</sup>	3.338	4.900	5.442	5.855	5.833
$\theta$ range, deg	2.98–25.00	2.93–25.00	3.14–25.00	3.17–25.00	2.96–25.00
reflns meas	5950	35599	24665	24214	64718
reflns used	4283	6804	6907	6856	6653
params	343	426	426	426	434
<i>R</i> <sup>a</sup> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	<i>R</i> 1 = 0.0378 w <i>R</i> 2 = 0.0894	<i>R</i> 1 = 0.0962 w <i>R</i> 2 = 0.2024	<i>R</i> 1 = 0.0615 w <i>R</i> 2 = 0.1563	<i>R</i> 1 = 0.0563 w <i>R</i> 2 = 0.1461	<i>R</i> 1 = 0.0958 w <i>R</i> 2 = 0.1656
<i>R</i> <sup>a</sup> (all data)	<i>R</i> 1 = 0.0515 w <i>R</i> 2 = 0.0976	<i>R</i> 1 = 0.1879 w <i>R</i> 2 = 0.2334	<i>R</i> 1 = 0.1026 w <i>R</i> 2 = 0.1864	<i>R</i> 1 = 0.0897 w <i>R</i> 2 = 0.1716	<i>R</i> 1 = 0.1578 w <i>R</i> 2 = 0.2484
<i>S</i>	1.072	1.026	1.050	1.077	0.989

$$^a R1 = \sum |F_o| - |F_c| / \sum |F_o|, wR2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{1/2}, w = 1/[\sigma^2(F_o^2) + (mP)^2 + nP], \text{ where } P = (F_o^2 + 2F_c^2)/3.$$

refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.<sup>6</sup> Coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.<sup>7</sup>

**Preparation of the Ligand HL.** The new benzimidazole ligand (HL) was synthesized with 5-bromo-2-hydroxy-3-methoxybenzaldehyde (2.31 g, 0.01 mol) and *o*-phenylenediamine (1.08 g, 0.01 mol) in nitrobenzene (30 mL) according to well-established procedures.<sup>8,8b</sup> A solution of 5-bromo-2-hydroxy-3-methoxybenzaldehyde (2.31 g, 0.01 mol) in nitrobenzene (10 mL) was dropwise added to a solution of *o*-phenylenediamine (1.08 g, 0.01 mol) in nitrobenzene (20 mL) over a period of 30 min. The mixture was heated under reflux (12 h). During this time, the color changed from yellow to dark red. The reaction mixture was then allowed to cool to room temperature and volatile materials were removed under vacuum. The residue was treated with EtOH (20 mL), and the mixture was stirred (30 min) and then filtered. The colorless residue (HL) that remained was washed with ethanol (15 mL). Yield 2.39 g, 75%. Anal. Found: C, 52.60; H, 3.34; N, 8.84. Calc. for C<sub>14</sub>H<sub>11</sub>BrN<sub>2</sub>O<sub>2</sub>: C, 52.69; H, 3.47; N, 8.78. FABMS: *m/z* 320 ([M + H]<sup>+</sup>). mp 230–1 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) 3.924 (s, 3H), 7.204 (d, 1H), 7.350–7.381 (m, 2H), 7.628–7.657 (m, 2H), 7.647 (d, 1H). IR (CH<sub>3</sub>CN, cm<sup>−1</sup>): 3348 (br), 1621 (m), 1589 (m), 1525 (m), 1490 (m), 1463 (s), 1444 (m), 1398 (m), 1250 (m), 1052 (w) and 745 (m).



**Figure 1.** Crystal structure and packing of the free ligand HL: C(4c)···C(10a): 3.575 Å, C(2c)···C(13a): 3.387 Å, N(1a)···C(4e): 3.355 Å, N(2a)···C(2e): 3.503 Å. H atoms have been omitted for clarity and thermal ellipsoids are drawn at the 25% probability level.

Colorless single crystals for X-ray crystallography were obtained from an EtOH solution in air at room temperature.

**Synthesis of [Ln<sub>3</sub>L<sub>4</sub>Cl<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·Cl·H<sub>2</sub>O·EtOH (1) (Ln = Tb (a), Er (b), Yb (c)).** A solution of LnCl<sub>3</sub>·6H<sub>2</sub>O (0.03 mmol) in EtOH

**Table 2.** Selected Bond Lengths (Å) and Angles (°) for the Free Ligand HL, **1a–c** and **2**

Free Ligand HL			
Br(1)–C(4)	1.897(4)	N(1)–C(8)	1.315(5)
N(1)–C(9)	1.378(5)	O(1)–C(2)–C(7)	115.3(3)
N(2)–C(8)	1.376(5)	C(5)–C(4)–Br(1)	120.3(3)
N(2)–C(14)	1.389(5)	C(3)–C(4)–Br(1)	117.5(3)
O(1)–C(2)	1.371(4)	O(2)–C(7)–C(2)	118.0(3)
O(1)–C(1)	1.426(5)	O(2)–C(7)–C(6)	122.6(3)
O(2)–C(7)	1.355(4)	N(1)–C(8)–N(2)	112.0(3)
C(8)–N(1)–C(9)	107.0(3)	N(1)–C(8)–C(6)	122.5(3)
C(8)–N(1)–H(1A)	126.5	N(2)–C(8)–C(6)	125.6(3)
C(9)–N(1)–H(1A)	126.5	N(1)–C(9)–C(10)	130.9(3)
C(8)–N(2)–C(14)	106.4(3)	N(1)–C(9)–C(14)	108.6(3)
C(2)–O(1)–C(1)	116.0(3)	C(13)–C(14)–N(2)	132.2(3)
O(1)–C(2)–C(3)	124.4(3)	N(2)–C(14)–C(9)	105.9(3)

<b>1a</b>			
Tb(1)–O(2')	2.260(13)	O(2')–Tb(1)–N(1')	74.1(5)
Tb(1)–O(1W)	2.285(17)	O(2)–Tb(1)–N(1')	134.9(5)
Tb(1)–O(2)	2.334(13)	O(2')–Tb(1)–O(1)	120.3(5)
Tb(1)–N(1')	2.449(17)	O(2)–Tb(1)–O(1)	65.2(5)
Tb(1)–O(1)	2.474(15)	N(1')–Tb(1)–O(1)	159.8(6)
Tb(1)–Cl(1)	2.556(8)	O(2')–Tb(2)–O(2)	70.0(5)
Tb(1)–Cl(2)	2.554(8)	O(2')–Tb(2)–N(1)	137.2(5)
Tb(2)–O(2')	2.256(12)	O(2)–Tb(2)–N(1)	75.1(5)
Tb(2)–O(2)	2.260(13)	O(2')–Tb(2)–O(1')	65.9(5)
Tb(2)–N(1)	2.369(16)	O(2)–Tb(2)–O(1')	112.9(5)
Tb(2)–O(1')	2.529(13)	N(1)–Tb(2)–O(1')	154.1(5)
O(2')–Tb(1)–O(2)	68.7(4)		

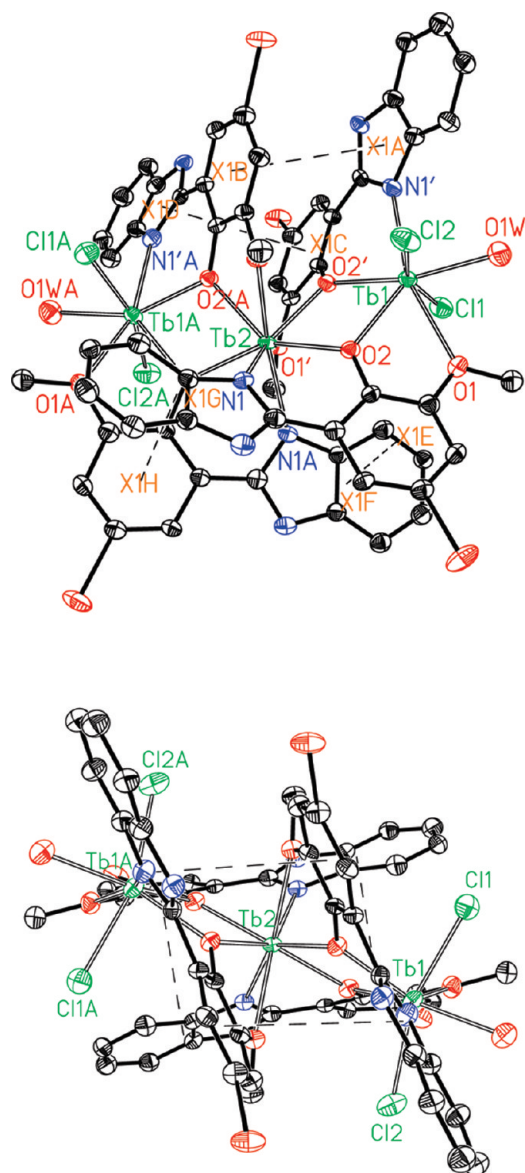
<b>1b</b>			
Er(1)–O(2')	2.235(7)	Er(1)–O(1)	2.455(8)
Er(1)–O(1W)	2.255(9)	Er(1)–Cl(2)	2.549(4)
Er(1)–O(2)	2.315(7)	Er(1)–Cl(1)	2.595(4)
Er(1)–N(1')	2.416(10)	Er(2)–O(2)	2.242(8)
Er(2)–O(2')	2.247(7)	N(1')–Er(1)–O(1)	160.2(3)
Er(2)–N(1)	2.364(9)	O(2)–Er(2)–O(2')	69.6(3)
Er(2)–O(1')	2.510(8)	O(2)–Er(2)–N(1)	75.7(3)
O(2')–Er(1)–O(2)	68.5(2)	O(2')–Er(2)–N(1)	137.7(3)
O(2')–Er(1)–N(1')	74.5(3)	O(2)–Er(2)–O(1')	113.8(3)
O(2)–Er(1)–N(1')	135.0(3)	O(2')–Er(2)–O(1')	66.2(3)
O(2')–Er(1)–O(1)	119.2(3)	N(1)–Er(2)–O(1')	153.7(3)
O(2)–Er(1)–O(1)	64.7(3)		

<b>1c</b>			
Yb(1)–O(2')	2.234(6)	O(2')–Yb(1)–N(1')	74.5(3)
Yb(1)–O(1W)	2.247(7)	O(2)–Yb(1)–N(1')	135.4(3)
Yb(1)–O(2)	2.319(6)	O(2')–Yb(1)–O(1)	119.8(2)
Yb(1)–N(1')	2.397(8)	O(2)–Yb(1)–O(1)	64.7(2)
Yb(1)–O(1)	2.456(7)	N(1')–Yb(1)–O(1)	159.8(3)
Yb(1)–Cl(2)	2.543(3)	O(2)–Yb(2)–O(2')	69.9(2)
Yb(1)–Cl(1)	2.587(3)	O(2)–Yb(2)–N(1)	75.5(2)
Yb(2)–O(2)	2.233(6)	O(2')–Yb(2)–N(1)	137.6(2)
Yb(2)–O(2')	2.243(6)	O(2)–Yb(2)–O(1')	113.4(2)
Yb(2)–N(1)	2.354(7)	O(2')–Yb(2)–O(1')	66.2(2)
Yb(2)–O(1')	2.496(7)	N(1)–Yb(2)–O(1')	153.7(2)
O(2')–Yb(1)–O(2)	68.5(2)		

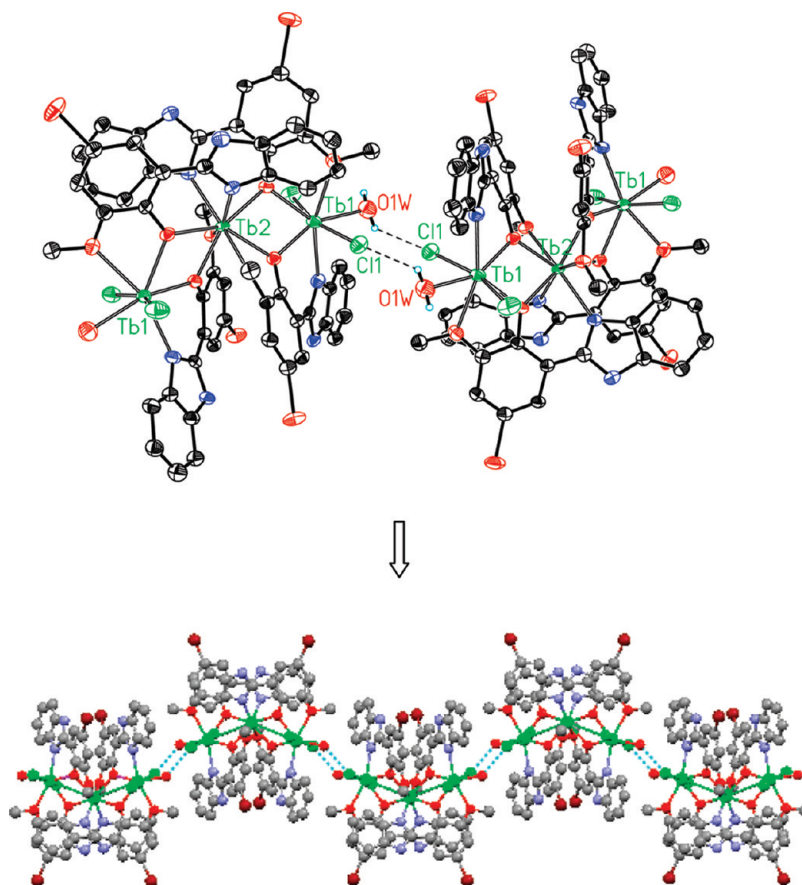
<b>2</b>			
Yb(1)–O(3)	2.207(15)	Yb(2)–O(2')	2.288(13)
Yb(1)–O(2')	2.279(14)	Yb(2)–N(2)	2.371(18)
Yb(1)–N(2')	2.444(15)	Yb(2)–O(1')	2.510(16)
Yb(1)–O(1)	2.444(15)	O(2')–Yb(1)–O(2)	68.2(5)
Yb(1)–O(5)	2.439(18)	O(2')–Yb(1)–N(2')	72.4(6)
Yb(1)–O(2)	2.370(14)	O(2)–Yb(1)–N(2')	133.3(5)
Yb(1)–O(6)	2.40(2)	O(2')–Yb(1)–O(1)	119.0(5)
Yb(2)–O(2)	2.270(14)	O(2)–Yb(1)–O(1)	64.5(5)
N(2')–Yb(1)–O(1)	161.7(5)	O(2)–Yb(2)–O(1')	111.4(5)
O(2)–Yb(2)–O(2')	69.8(5)	O(2')–Yb(2)–O(1')	65.8(6)
O(2)–Yb(2)–N(2)	75.6(5)	N(2)–Yb(2)–O(1')	152.8(6)
O(2')–Yb(2)–N(2)	137.8(6)		

**Figure 2.** Crystal structure of **1a**. H atoms have been omitted for clarity and thermal ellipsoids are drawn at the 25% probability level. (a) View showing intramolecular  $\pi$ - $\pi$  stacking interactions: X1A...X1B: 3.958 Å, X1C...X1D: 3.872 Å, X1E...X1F: 3.891 Å, X1G...X1H: 3.891 Å. (b) View showing the crossed ligand configuration.

(5 mL) was added to a solution of HL (0.013 g, 0.04 mmol) in EtOH (5 mL) and the mixture was stirred and heated under reflux (2 h). The reaction mixture was then allowed to cool to room temperature and filtered. Diethylether was allowed to diffuse slowly into the filtrate at room temperature and yellow crystalline **1a–c** was obtained

(1 month). The product was isolated by filtration. For **1a**, Yield 0.008 g (40%). ESI-MS ( $\text{CH}_3\text{CN}$ )  $m/z$ : 1906 ( $[\text{M}-\text{Cl}-2\text{H}_2\text{O}-\text{EtOH}]^+$ ). IR ( $\text{CH}_3\text{CN}$ ,  $\text{cm}^{-1}$ ): 3458 (br), 1620 (s), 1609 (s), 1566 (s), 1525 (m), 1462 (m), 1398 (m), 1202 (m), 1050 (w), 956 (m) and 745 (m). For **1b**, Yield 0.009 g (45%). ESI-MS ( $\text{CH}_3\text{CN}$ )  $m/z$ : 1915 ( $[\text{M}-\text{Cl}-3\text{H}_2\text{O}-\text{EtOH}]^+$ ). mp > 245 °C (dec). IR ( $\text{CH}_3\text{CN}$ ,  $\text{cm}^{-1}$ ): 3500 (br), 1621 (s), 1607 (s), 1567 (m), 1512 (s), 1456 (m), 1410 (m), 1200 (m), 1048 (w), 957 (m) and 742 (m).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  (ppm) –18.953 (3H), –11.520 (1H), –10.687 (2H), –9.907 (1H), 6.692 (2H), 14.402 (2H), 25.387 (2H), 42.151 (3H), 54.313 (1H), 59.711 (1H). For **1c**, Yield 0.012 g (59%). ESI-MS ( $\text{CH}_3\text{CN}$ )  $m/z$ : 1966 ( $[\text{M}-\text{Cl}-\text{H}_2\text{O}-\text{EtOH}]^+$ ). IR ( $\text{CH}_3\text{CN}$ ,  $\text{cm}^{-1}$ ): 3469 (br),





**Figure 3.** View of Cl $\cdots$ H–O hydrogen bonded interactions between the coordinated Cl $^-$  ion and H $_2$ O in **1a**, which result in a 1-D wave-like strand: Cl(1) $\cdots$ O(1w): 2.839 Å.

1620 (s), 1606 (s), 1567 (s), 1515 (s), 1465 (s), 1407 (m), 1201 (m), 1046 (w), 959 (m) and 741 (m).

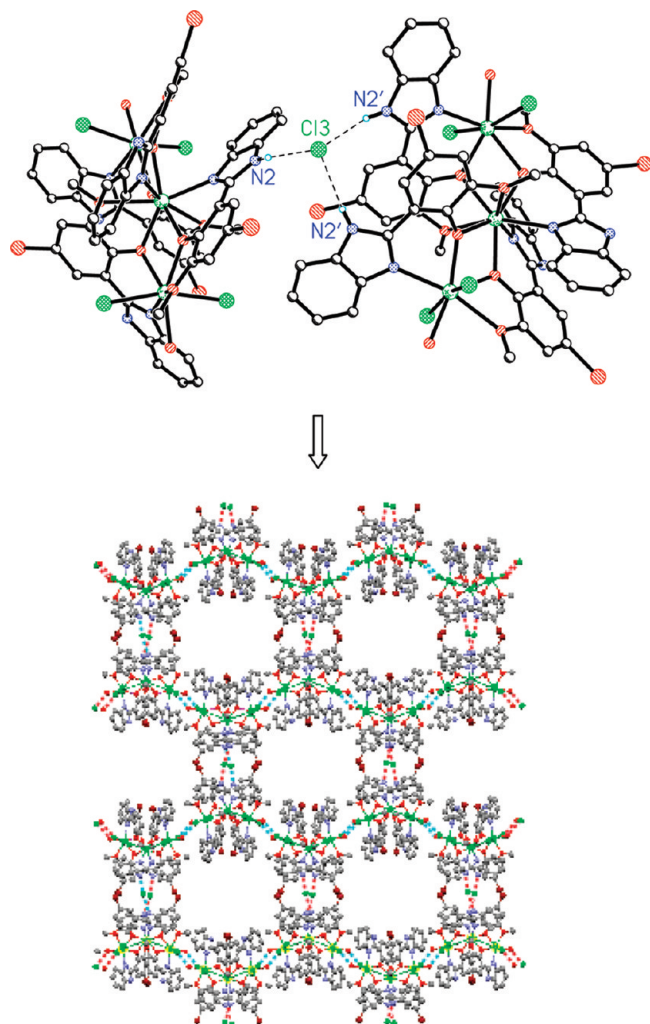
**Synthesis of  $\{[\text{Yb}_3\text{L}_4(\text{OAc})_4]\cdot\text{Cl}\cdot\text{EtOH}\}_n$  (**2**).** A solution of  $\text{YbCl}_3\cdot 6\text{H}_2\text{O}$  (0.012 g, 0.03 mmol) in EtOH (5 mL) was added to a solution of HL (0.013 g, 0.04 mmol) in EtOH (5 mL) and the mixture was stirred and heated under reflux (2 h). The mixture was allowed to cool to room temperature. A solution of  $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$  (0.110 g, 0.50 mmol) in EtOH (5 mL) added and the mixture was heated under reflux (1 h). The mixture was then allowed to cool to room temperature and filtered. Diethylether was allowed to diffuse slowly into the filtrate and pale yellow single crystals of **2** were obtained after two weeks. Yield 0.010 g (48%). ESI-MS ( $\text{CH}_3\text{CN}$ )  $m/z$ : 636 ( $[\text{Yb}_3\text{L}_4(\text{OAc})_2]^{3+}$ ). mp > 272 °C (dec). IR ( $\text{CH}_3\text{CN}$ ,  $\text{cm}^{-1}$ ): 3488 (br), 1626 (s), 1606 (s), 1597 (s), 1560 (s), 1515 (s), 1483 (s), 1465 (s), 1436 (m), 1410 (m), 1202 (m), 1040 (w), 958 (m) and 740 (m).

## Results and Discussion

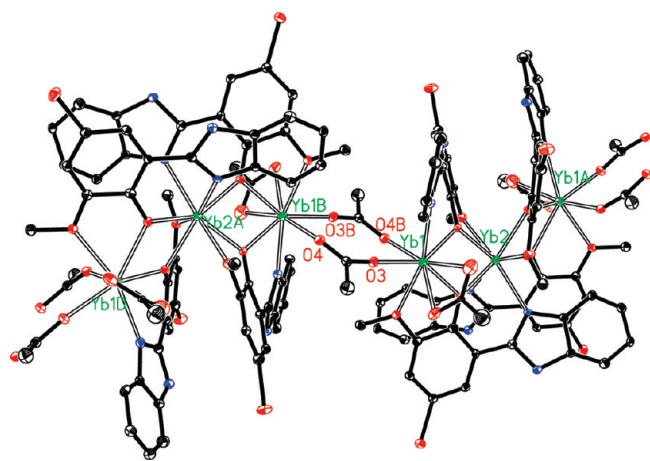
A view of the molecular structure of the free benzimidazole ligand HL along with a view of its packing in the solid state is shown in Figure 1. Details of crystallographic parameters, data collection, and refinements are listed in Table 1, and selected bond lengths and angles are given in Table 2. In the solid state, the molecule packs in an offset head-to-head fashion with the five-membered ring of the imidazole moiety stacked closest to the phenylene ring of its nearest neighbor, resulting in a herringbone effect (Figure 1). As described below this kind of  $\pi$ – $\pi$  stacking interaction is also found in the lanthanide complexes **1a–c** and **2**.

Reactions of the substituted benzimidazole (HL) with  $\text{LnCl}_3\cdot 6\text{H}_2\text{O}$  in a 4:3 molar ratio in refluxing EtOH produce the trinuclear lanthanide complexes **1a–c** in ca. 40–60% yield

(Scheme 2). Single crystals of these complexes suitable for X-ray diffraction studies were obtained by allowing Et $_2$ O to diffuse into the reaction mixture at room temperature. The compounds **1a–c** are isomorphous and crystallize in the tetragonal space group  $P4/ncc$  with eight  $\text{Ln}_3\text{L}_4$  units per unit cell. The view of the X-ray structure of the Tb complex **1a** is shown in Figure 2. Crystallographic details are provided in Table 1, and selected bond lengths and angles are given in Table 2. The structure of **1a** contains of three nonlinear Tb(III) ions (Tb–Tb–Tb angle 141.15°) bound by four deprotonated  $\text{L}^-$  ligands. Interestingly, the  $\text{L}^-$  ligands bind in two distinct ways. Two are arranged so that each pair of phenolic and methoxy O atoms is bound in a chelating fashion to the central Tb(2) ion. The imidazole nitrogen atoms from these groups are then bound to each of the terminal Tb ions. This pair of ligands is arranged so that the aromatic rings are roughly parallel with each other. The distances between rings are 3.958 Å (X1A $\cdots$ X1B) and 3.872 Å (X1C $\cdots$ X1D) (Figure 2a). The other two ligands are coordinated so that the imidazole nitrogen atoms are bound to the central Tb(2) with the O $_2$  binding set of each ligand being coordinated to the two terminal Tb ions. The phenolic oxygen atoms for all four ligands bind to the central Tb and also bridge the outer Tb ions. The latter pair of ligands is also roughly parallel to each other, and the distance between rings is 3.891 Å (Figure 2a). The molecule contains a  $\text{C}_2$  rotation axis which passes through Tb(2), and so the two terminal Tb atoms are crystallographically equal. The unique Tb–Tb distance is 3.737 Å. This ligand configuration results in the central Tb ion having a coordination number of 8. The terminal Tb ions are each

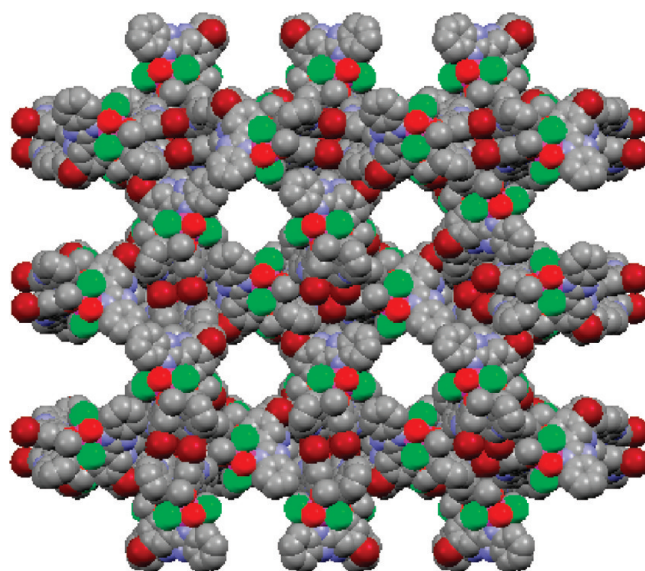


**Figure 4.** View of Cl $\cdots$ H–N hydrogen bonded interactions between uncoordinated Cl $^-$  ions and N–H groups of L $^-$  ligands in **1a**, which result in a 3-D open network viewed along [110]: Cl(3) $\cdots$ N(2): 3.178 Å, Cl(3) $\cdots$ N(2'): 3.111 Å.



**Figure 5.** Crystal structure of 1-D coordination polymer **2**. H atoms have been omitted for clarity and thermal ellipsoids drawn at the 25% probability level.

bound to two Cl $^-$  groups and a water molecule in addition to the L $^-$  ligands and are seven-coordinate. The pairs of L $^-$  ligands are aligned in a criss-cross fashion with the angles

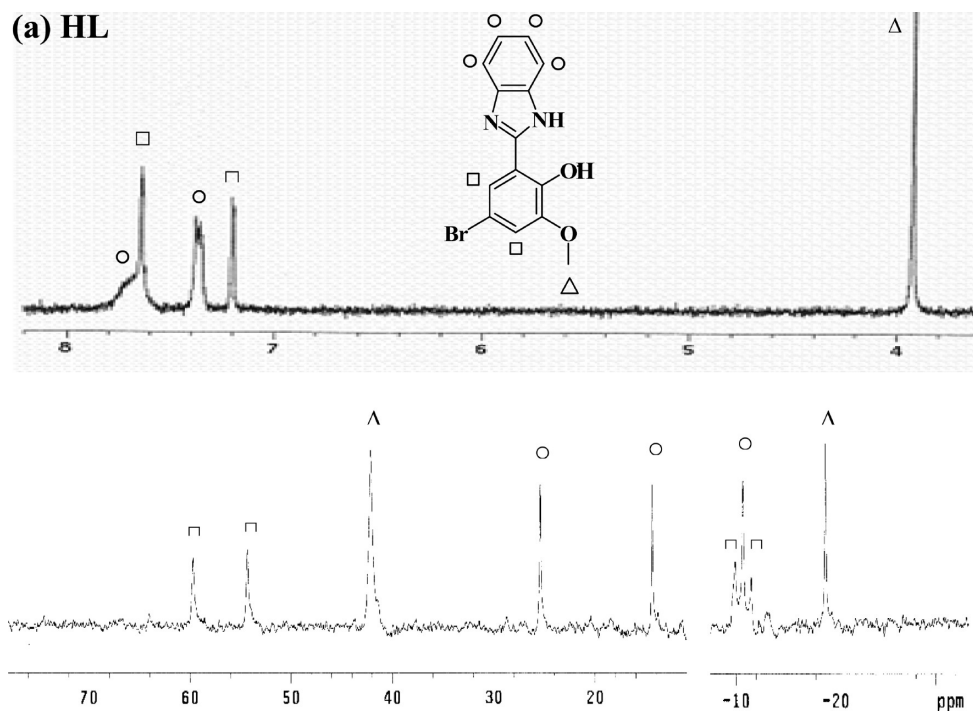


**Figure 6.** Space filling view of **2** along the *c*-axis showing the 3-D network.

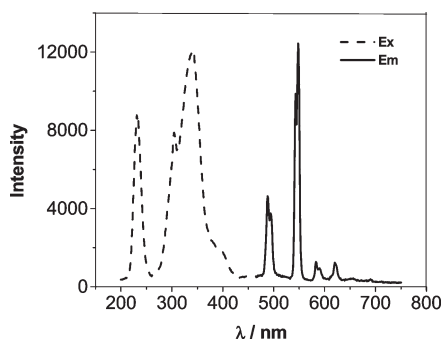
between the least-squares planes of each being 66.8° and 89.5° (Figure 2b). The terminally bound Cl $^-$  and H<sub>2</sub>O groups appear to play a key role in the crystal packing of the Ln<sub>3</sub> clusters since there are close Cl $\cdots$ H–O interactions which link adjacent molecules (Cl $\cdots$ O 2.839 Å, Figure 3) forming 1-D structures. The structures are further connected by Cl $\cdots$ H–N hydrogen bonding between the uncoordinated Cl $^-$  ion and the N–H group of the L ligand (Cl $\cdots$ N 3.178 Å and 3.111 Å). This results in a three-dimensional open network which has extended channels running along the *c*-axis (Figure 4). These channels measure approximately 7 × 7 Å and accommodate guest molecules of H<sub>2</sub>O and EtOH. Hydrogen bonded interactions are present between the entrapped molecules and the surrounding supramolecular framework.

The addition of Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O to the original reaction mixture obtained in the synthesis of **1c** produces the acetate derivative {[Yb<sub>3</sub>L<sub>4</sub>(OAc)<sub>4</sub>]·Cl·EtOH}<sub>*n*</sub> (**2**). The key difference between the structures **1a–c** and **2** is that the coordinated Cl $^-$  and H<sub>2</sub>O units are now replaced with OAc $^-$  groups. The acetates create a zigzag 1-D polymer by forming double (OAc $^-$ ) bridges between Yb<sub>3</sub>L<sub>4</sub> units (Figure 5). Interestingly, **2** crystallizes in the same space group as **1a–c** (*P4<sub>1</sub>nc*) and the 1-D structure exhibit similar crystal packing behavior in the solid state. Thus, **2** also has a Cl $\cdots$ H–N hydrogen bonding interaction between uncoordinated Cl $^-$  and the N–H group of the imidazole ligand (Cl $\cdots$ N 3.215 and 3.305 Å). The resulting 3-D open network structure has extended channels running along the *c*-axis which are again approximately 7 × 7 Å in size and accommodate EtOH molecules (Figure 6). The overall structure of the Yb<sub>3</sub>L<sub>4</sub> core of **2** is similar to that of **1a–c** with the exception that each terminal Yb (III) ion now bears a chelating OAc $^-$  group. This results in the terminal Yb (III) ions having a coordination number of 8. In previous studies of heteropolynuclear Zn<sub>4</sub>Eu<sub>2</sub> cage complex, we discovered that aryl–Br units could engage in short intermolecular Br $\cdots$ O interactions resulting in interesting 3-D frameworks.<sup>9</sup> However, in the complexes described in this paper no such interactions were observed.

The <sup>1</sup>H NMR spectrum of **1b** supports a structure in solution which is similar to that found in the solid state. The <sup>1</sup>H NMR spectra of the free ligand HL and **1b** at 298 K in

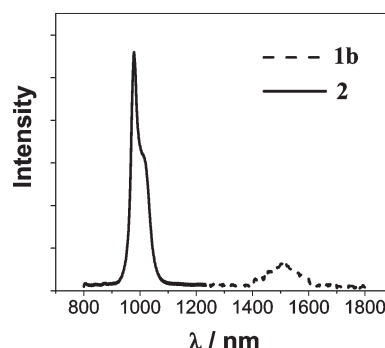


**Figure 7.**  $^1\text{H}$  NMR spectra of the free ligand HL (a) and complex **1b** (b) in  $\text{CD}_3\text{CN}$  at 298 K. In b, the peaks of solvent,  $\text{H}_2\text{O}$  and EtOH, together with the signal at 6.692 ppm of  $\text{L}^-$ , have been omitted for clarity.



**Figure 8.** Excitation and emission spectra of **1a** in  $\text{CH}_3\text{CN}$  ( $5 \times 10^{-6}$  M) at 298 K.

$\text{CD}_3\text{CN}$  are shown in Figure 7. The free ligand shows the presence of five peaks corresponding to nine C–H protons. In the  $^1\text{H}$  NMR spectrum of **1b**, there are 10 reasonably sharp peaks which are assigned to the ligands bound in two different ways as described above. The spectra are unchanged after one month at room temperature indicating that **1b** is thermally stable in solution under these conditions. A detailed analysis of the NMR data (2D-COSY) allows the assignment of these signals. Each  $\text{L}^-$  displays one signal for the three methoxy protons, two signals for the two benzyl protons, and two signals for the four benzimidazole protons. Mass spectroscopic studies (ESI-MS) for **1a–c** support the presence of the  $\text{Ln}_3\text{L}_4$  units in solution (experimental). For **2**, ESI-MS data indicate that the 1-D polymeric structure in the solid state does not persist in solution ( $m/z = 636$ ,  $[\text{Yb}_3\text{L}_4(\text{OAc})_2]^{3+}$ ). The photophysical properties of complexes **1a–c** and **2** have been studied at 298 K both in the solid state and in solution. Upon excitation of the ligand-centered absorption band, all complexes show typical emission spectra of the  $\text{Ln}(\text{III})$  ions. Complex **1a** shows visible emission bands of  $\text{Tb}^{3+}$  ion ( $^5\text{D}_0 \rightarrow ^7\text{F}_j$  transitions,  $j = 1, 2, 3$ , and 4, Figure 8), while **1b** shows the NIR



**Figure 9.** NIR emission spectra of **1b** ( $5 \times 10^{-6}$  M) and **2** ( $2 \times 10^{-6}$  M) in  $\text{CH}_3\text{CN}$  at 298 K.

luminescence of the  $\text{Er}^{3+}$  ion assigned to the  $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$  transition at 1510 nm, and complexes **1c** and **2** show that of the  $\text{Yb}^{3+}$  ion assigned to the  $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$  transition at about 978 nm (Figure 9). A similar luminescence is observed for each lanthanide complex in the solid state. The fluorescence quantum yield ( $\Phi_{\text{em}}$ ) of  $\text{Tb}^{3+}$  complex **1a** in  $\text{CH}_3\text{CN}$  is 0.218,<sup>10</sup> while the NIR luminescence quantum yields of **1b–c** and **2** could not be measured due to instrumental limitations. The relative emission intensities of **1c** and **2** were determined under the same experimental conditions. With the same absorbance value at 275 nm, the relative emission intensity at 978 nm was estimated to be 3.6 for **2:1c** in  $\text{CH}_3\text{CN}$ , indicating that **2** has superior luminescence properties compared to **1c**. The difference in luminescence properties may be because there are no coordinated  $\text{H}_2\text{O}$  molecules in **2** which can efficiently quench lanthanide luminescence.<sup>11</sup>

## Conclusions

A series of luminescent  $\text{Ln}_3$  clusters of formula  $[\text{Ln}_3\text{L}_4\text{Cl}_4(\text{H}_2\text{O})_2] \cdot \text{Cl} \cdot \text{H}_2\text{O} \cdot \text{EtOH}$  (**1**) ( $\text{Ln} = \text{Tb}$  (a),  $\text{Er}$  (b),  $\text{Yb}$  (c))



[Ln<sub>3</sub>L<sub>4</sub>Cl<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]·Cl·H<sub>2</sub>O·EtOH (**1**) (Ln = Tb (a), Er (b), Yb (c)) have been synthesized and characterized (HL = 2-(1H-benzimidazol-2-yl)-4-bromo-6-methoxy-phenol). The Yb<sub>3</sub> cluster **1c** may be converted into a 1-D coordination polymer by treatment with Zn(OAc)<sub>2</sub>·2H<sub>2</sub>O. All complexes display intramolecular  $\pi$ – $\pi$  stacking and hydrogen bonded interactions in the solid state as well as lanthanide ion based luminescence in both solution and the solid.

**Acknowledgment.** We thank Hong Kong Baptist University (FRG/06-07/II-16), the Hong Kong Research Grants Council (HKBU 202407), the Robert A. Welch Foundation (Grant F-816), the Texas Higher Education Coordinating Board (ARP 003658-0010-2006), and the Petroleum Research Fund, administered by the American Chemical Society (47014-AC5) for financial support.

**Supporting Information Available:** X-ray crystallographic data for the free ligand HL and lanthanide complexes **1–4** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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