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Syntheses, crystal structures, and fluorescent properties of two d^{10} metal complexes based on 2-(benzoimidazol-yl) methyl)-1*H*-1,2,4-triazole and 1,3,5-benzenetricarboxylate

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Two d^{10} metal complexes, $\{[Zn(Hbtc)(bmt)] \cdot DMF \cdot 5H_2O\}_n$ (**1**) and $\{[Cd(Hbtc)(bmt)] \cdot 0.5DMF \cdot 0.5H_2O\}_n$ (**2**) (H$_3$btc = 1,3,5-benzenetricarboxylic acid, bmt = 2-((benzoimidazol-yl)methyl)-1*H*-1,2,4-triazole), have been synthesized under solvothermal conditions by employing bmt and H$_3$btc. Single-crystal X-ray diffraction shows that Zn(II) ions are connected by bmt with bidentate-bridging coordination and by 1,3,5-benzenetricarboxylate with bis-monodentate coordination leading to the 2D structure of **1**. Complex **2** exhibits a 2D layer structure, in which bmt coordinate tridentate-bridging to Cd(II) and 1,3,5-benzenetricarboxylates coordinate to Cd(II) unidentate/chelating. Photoluminescence and thermogravimetric analyses of the two complexes are investigated.

Keywords: 2-((Benzoimidazol-yl)methyl)-1*H*-1,2,4-triazole; Crystal structure; d^{10}-Metal complexes; Fluorescent property; Thermostability

1. Introduction

Multidentate ligands with imidazole, triazole, tetrazole, benzimidazole, or benzotriazole, such as 1-((benzotriazol-1-yl)methyl)-1-*H*-1,3-imidazole, 1-((benzotriazol-1-yl)methyl)-1-*H*-1,2,4-triazole, 2-((benzoimidazol-yl)methyl)-1*H*-1,3-imidazole, 2-((benzoimidazol-yl)methyl)-1*H*-1,2,4-triazole, and 2-((benzoimidazol-yl)methyl)-1*H*-tetrazole, are versatile in construction of MOFs with specific structures and properties [1–6]. Aromatic polycarboxylic acids, for example, 1,2-benzenedicarboxylic acid, 1,3-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid, 1,2,3-benzenetricarboxylic acid, 1,2,4-benzenetricarboxylic acid, 1,3,5-benzenetricarboxylic acid, and 1,2,4,5-benzenetetracarboxylic acid, have various coordination modes and ability to be hydrogen-bond acceptors and donors in the assembly of supramolecular structures [7–13]. Zn(II) and Cd(II) coordinate to both oxygen-containing and nitrogen-containing ligands. A number of Zn(II) and Cd(II) complexes containing both aromatic carboxylates and *N*-heterocyclic ligands have been reported [2, 14]. To enrich the numbers of complexes with

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N-heterocycles and aromatic acids, in this article, we select multidentate unsymmetrical *N*-heterocycle 2-((benzoimidazol-yl)methyl)-1*H*-1,2,4-triazole (bmt) and 1,3,5-benzenetri-carboxylic acid (H₃btc) as ligands to self-assemble with Zn(II) or Cd(II) and obtain two new 2D complexes {[Zn(Hbtc)(bmt)]·DMF·5H₂O}ₙ (**1**) and {[Cd(Hbtc)(bmt)]·0.5DMF·0.5H₂O}ₙ (**2**). The structures are characterized by single-crystal X-ray diffraction and luminescence and thermogravimetric feathures have also been investigated.

2. Experimental

2.1. *General information and materials*

2-((Benzoimidazol-yl)methyl)-1*H*-1,2,4-triazole was synthesized according to the literature [15]. All other chemicals were commercially available and used as purchased. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets from 400 to 4000 cm⁻¹. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. Solid-state luminescence spectra were recorded with a Fluoro Max-P fluorescence spectrophotometer. TG measurement was performed by heating the sample from 30 to 750 °C (or 850 °C for **2**) at 10 °C min⁻¹ in air on a NETZSCH STA 409 PC/PG differential thermal analyzer.

2.2. *Synthesis of {[Zn(Hbtc)(bmt)]·DMF·5H₂O}ₙ (1)*

ZnCl₂ (0.05 mM), bmt (0.05 mM), H₃btc (0.05 mM), DMF (1 mL), H₂O (2 mL), and CH₃OH (6 mL) were placed in a Teflon-lined stainless steel vessel (25 mL), and the mixture was sealed and heated to 120 °C for 72 h. The reaction system was cooled to room temperature at 10 °C h⁻¹. Colorless prisms of **1**, suitable for X-ray analysis, were obtained. Yield: 39%. Anal. Calcd. for C₂₂H₃₀N₆O₁₂Zn (635.89) (%): C, 41.55; H, 4.76; N, 13.22. Found (%): C, 41.29; H, 4.87; N, 13.03. IR (KBr, cm⁻¹): 3435(m), 3133(m), 2982(m), 1708(s), 1625(s), 1578(s), 1534(m), 1528(m), 1500(m), 1455(m), 1433(m), 1359(s), 1319 (m), 1274(s), 1184(s), 1132(s), 1045(m), 1017(m), 1001(s), 934(w), 904(w), 849(m), 798 (m), 781(w), 755(s), 730(s), 674(s), 649(w), 546(m), 483(w), 455(w), 432(w).

2.3. *Synthesis of {[Cd(Hbtc)(bmt)]·0.5DMF·0.5H₂O}ₙ (2)*

Colorless prism crystals of **2** were obtained similar to **1** except that CdCl₂·2.5H₂O was used instead of ZnCl₂. Yield: 64%. Anal. Calcd for C₂₀.₅H₁₇.₅CdN₅.₅O₇ (565.30) (%): C, 43.56; H, 3.12; N, 13.63. Found (%): C, 43.01; H, 2.93; N, 14.02. IR (KBr, cm⁻¹): 3438(m), 3101 (m), 2929(m), 1708(s), 1663(s), 1615(s), 1560(s), 1495(m), 1426(s), 1374(s), 1317(w), 1299 (w), 1284(m), 1244(w), 1229(s), 1181(s), 1143(s), 1099(s), 1029(s), 984(s), 956(w), 934(w), 878(m), 855(m), 798(s), 757(s), 743(s), 732(s), 673(s), 648(m), 512(m), 480(w), 436(m).

2.4. *Single-crystal structure determination*

A suitable single crystal of **1** or **2** was carefully selected and glued to a thin glass fiber. Crystal structure determination by X-ray diffraction was performed on a Rigaku Saturn

724 CCD area detector with graphite monochromator for the X-ray source (Mo-Kα radiation, $\lambda = 0.710\,73$ Å) operating at 50 kV and 40 mA. The data were collected by ω scan mode at 293(2) K with crystal-to-detector distance of 45 mm. An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by full-matrix least-squares and difference Fourier techniques, based on F^2, using SHELXS-97 [16]. All nonhydrogen atoms were refined anisotropically. Hydrogens bound to carbon and nitrogen were positioned geometrically and refined using a riding model. Hydrogens bound to oxygen were found from difference maps and were included in a fixed position. All hydrogens were included in the final refinement. Crystallographic parameters and structure refinement for the complexes are summarized in table 1. Selected bond lengths and angles of the complexes are listed in table 2. Hydrogen bonds are listed in table 3.

3. Results and discussion

3.1. *IR spectroscopy of 1 and 2*

IR spectra show absorptions at 3435 cm^{-1} for **1** and 3438 cm^{-1} for **2** attribute to stretches of O–H. Absorptions at 3133 cm^{-1} for **1** and 3101 cm^{-1} for **2** originate from stretching vibrations of Ar–H. The absorptions at 2982 cm^{-1} for **1** and 2929 cm^{-1} for **2** come from CH$_2$ stretches. The very strong absorption at 1708 cm^{-1} in both the complexes can be attributed to COOH. Separations (Δ) between v_a (COO) and v_s (COO) are different for unidentate, chelating, and bridging complexes [17]. In **1**, carboxylates exhibit v_a (COO) and v_s (COO) at 1625 and 1433 cm^{-1} ($\Delta = 192$ cm^{-1}). This Δ is comparable to unidentate complexes and the carboxylates of 1,3,5-benzenetricarboxylate can be assigned to unidentate coordination. Different from **1**, coordination of carboxylates of 1,3,5-benzenetricarboxylate in **2** are complicated. Unidentate carboxylates exhibit v_a (COO) and v_s (COO) at 1615 and 1374 cm^{-1} ($\Delta = 241$ cm^{-1}), whereas the chelating carboxylates exhibit v_a (COO) and v_s (COO) at 1495 and 1426 cm^{-1} ($\Delta = 69$ cm^{-1}). So 1,3,5-benzenetricarboxylates coordinate as unidentate and chelating simultaneously in **2**. The stretching frequencies of benzene rings largely overlap those of the carboxylates. The absorption band at 1274 cm^{-1} for **1** and 1284 cm^{-1} for **2** are due to C–N stretches. The absorptions at 798 cm^{-1} for both the complexes can be attributed to stretches of 1,3-substituted benzene rings. The absorptions at 755 for **1** and 757 cm^{-1} for **2** correspond to characteristic stretches of 1,2-substituted benzene rings. The above analyses are confirmed by X-ray diffraction.

3.2. *Crystal structures of {[Zn(Hbtc)(bmt)]·DMF·5H$_2$O}$_n$ (1)*

X-ray crystallographic analysis reveals that **1** crystallizes in the monoclinic space group $P2_1/c$. As shown in figure 1(a), Zn1 is in a distorted tetrahedral environment, coordinated monodentate by two carboxylate oxygens from two distinct Hbtc^{2-} (Zn1-O1 = 2.000(2) Å, Zn1-O4A = 2.002(2) Å) and two nitrogens from two distinct bmt (Zn1-N1 = 2.015(3) Å, Zn1-N5A = 2.018(3) Å). These Zn–O and Zn–N distances are in the normal range of those in other Zn(II) complexes, such as [Zn$_3$(L)(btc)$_2$(H$_2$O)$_2$]·3H$_2$O (L = 1,2,4,5-tetrakis(imidazol-1-ylmethyl)benzene, H$_3$btc = 1,3,5-benzenetricarboxylic acid) and {[Zn(bdic)(bmt)H$_2$O]·0.5H$_2$O}$_n$ (H$_2$bdic = 1,3-benzenedicarboxylic acid, bmt = 1-((benzotriazol-1-yl)methyl)-1-H-1,2,4-triazole) [2, 18]. The bond angles around Zn1 are

Table 1.   Crystal data and structure refinement data of **1** and **2**.

Complex	1	2
Empirical formula	$C_{22}H_{30}N_6O_{12}Zn$	$C_{20.5}H_{17.5}CdN_{5.5}O_7$
Formula weight	635.89	565.30
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	10.159(2)	10.105(2)
b	20.726(4)	13.664(3)
c	13.290(3)	17.180(3)
α	90	90
β	100.47(3)	93.22(3)
γ	90	90
Volume (Å^3)	2751.7(9)	2368.4(8)
Z	4	4
Calculated density (Mg m^{-3})	1.535	1.585
Absorption coefficient (mm^{-1})	0.965	0.973
$F(000)$	1320	1132
θ range for data collection, deg	2.26–25.50	2.37–25.50
h range	$-12 \leqslant h \leqslant 12$	$-12 \leqslant h \leqslant 11$
k range	$-25 \leqslant k \leqslant 22$	$-11 \leqslant k \leqslant 16$
l range	$-15 \leqslant l \leqslant 16$	$-20 \leqslant l \leqslant 20$
Crystal sizes (mm^3)	$0.21 \times 0.18 \times 0.14$	$0.19 \times 0.17 \times 0.11$
Reflections collected/unique	17,365/5091	16,132/4398
R(int)	0.0453	0.0276
Data/restraints/parameters	5091/0/371	4398/5/335
Goodness-of-fit on F^2	1.070	1.107
Final R indices [$I>2\sigma(I)$]	$R_1=0.0530$	$R_1=0.0382$
	$wR_2=0.1242$	$wR_2=0.0975$
R indices (all data)	$R_1=0.0653$	$R_1=0.0419$
	$wR_2=0.1337$	$wR_2=0.1003$
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.632 and -0.344	1.006 and -0.367

Table 2.   Selected bond lengths (Å) and angles (°) for **1** and **2**.

Complex 1

Zn(1)–O(1)	2.000(2)	Zn(1)–O(4)#1	2.002(2)
Zn(1)–N(1)	2.015(3)	Zn(1)–N(5)#2	2.018(3)
O(1)–Zn(1)–O(4)#1	97.75(10)	O(1)–Zn(1)–N(1)	105.21(11)
O(4)#1–Zn(1)–N(1)	104.19(11)	O(1)–Zn(1)–N(5)#2	106.95(11)
O(4)#1–Zn(1)–N(5)#2	110.45(11)	N(1)–Zn(1)–N(5)#2	128.11(11)

Complex 2

Cd(1)–O(1)	2.230(3)	Cd(1)–N(1)	2.284(3)
Cd(1)–N(5)#1	2.354(3)	Cd(1)–O(5)#2	2.362(3)
Cd(1)–O(6)#2	2.447(3)	Cd(1)–N(4)	2.476(3)
O(1)–Cd(1)–N(1)	136.00(11)	O(1)–Cd(1)–N(5)#1	90.82(13)
N(1)–Cd(1)–N(5)#1	92.12(11)	O(1)–Cd(1)–O(5)#2	133.14(10)
N(1)–Cd(1)–O(5)#2	90.59(11)	N(5)#1–Cd(1)–O(5)#2	92.36(11)
O(1)–Cd(1)–O(6)#2	79.48(10)	N(1)–Cd(1)–O(6)#2	144.09(10)
N(5)#1–Cd(1)–O(6)#2	92.68(12)	O(5)#2–Cd(1)–O(6)#2	53.67(10)
O(1)–Cd(1)–N(4)	99.51(12)	N(1)–Cd(1)–N(4)	78.45(11)
N(5)#1–Cd(1)–N(4)	169.27(11)	O(5)#2–Cd(1)–N(4)	82.74(11)
O(6)#2–Cd(1)–N(4)	92.07(11)		

Symmetry transformations used to generate equivalent atoms: For **1**: #1: $x-1$, y, z; #2: x, $-y+3/2$, $z+1/2$. For **2**: #1: $-x$, $y-1/2$, $-z+1/2$; #2: $x-1$, y, z.

Table 3. Hydrogen bonds of **1** and **2**.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	(D–H···A) (°)
Complex 1				
N(2)–H(2)…O(8)	0.86	1.85	2.697(4)	167.1
O(9)–H(9A)…O(2)	0.85	1.91	2.755(4)	179.4
O(9)–H(9B)…O(7)	0.85	2.29	3.058(6)	150.6
O(10)–H(10B)…O(9)	0.85	2.07	2.915(6)	179.0
O(8)–H(8C)…O(10)#3	0.85	1.97	2.818(6)	179.1
O(8)–H(8D)…O(11)#3	0.87	1.92	2.784(6)	179.3
O(11)–H(11A)…O(3)#1	0.85	1.84	2.686(5)	179.3
O(11)–H(11B)…O(7)#1	0.85	2.46	3.154(6)	139.2
O(5)–H(5)…O(7)#5	0.82	1.78	2.601(4)	174.3
O(10)–H(10A)…O(12)#6	0.85	1.86	2.643(6)	153.4
O(12)-H(12A)…O(1)#7	0.85	2.17	3.021(6)	178.5
O(12)-H(12B)…O(4)#8	0.85	2.14	2.972(5)	166.6
Complex 2				
N(2)-H(2B)…O(6)#5	0.86	2.01	2.858(4)	170.9
O(3)-H(3)…O(2)#6	0.82	1.85	2.636(4)	159.3
O(7)-H(1 W)…O(8)#7	0.85	1.76	2.61(2)	173.9
O(7)-H(2 W)…O(6)#5	0.85	2.56	3.40(2)	174.0

Symmetry transformations used to generate equivalent atoms: For **1**: #1: $x-1$, y, z; #3: x, $-y+3/2$, $z-1/2$; #5: $-x+2$, $y+1/2$, $-z+3/2$; #6: $-x+1$, $y+1/2$, $-z+3/2$; #7: $-x+1$, $-y+1$, $-z+2$; #8: $x-1$, $y-1$, z. For **2**: #5: $x-1$, $-y+1/2$, $z+1/2$; #6: x, $-y+1/2$, $z-1/2$; #7: $-x-1$, $-y+1$, $-z+1$.

$97.75(10)°–128.11(11)°$. In **1**, all Hbtc^{2-} ligands are equivalent and the three carboxylates in each Hbtc^{2-} are coplanar with the phenyl ring (the mean deviation from plane is 0.0471 Å). The internal angles in the benzene ring for the substituted carbons (average value of 119.6°) are slightly smaller than those for nonsubstituted carbons (120.4°). Only two carboxylates of each Hbtc^{2-} coordinate and the third one, which is not deprotonated, remains uncoordinated. For the two coordinated carboxylates, the values for the coordinated carbonyl oxygens are close to the free carbonyl oxygens (C11-O1 = 1.274(4) Å, C11-O2 = 1.233(4) Å, C18-O3 = 1.238(4) Å, C18-O4 = 1.274(4) Å), while the values of C–O bond lengths for uncoordinated carboxylates are different (C19-O5 = 1.316(5) Å, C19-O6 = 1.202(4) Å).

As depicted in figure 1(b), the partially deprotonated 1,3,5-benzenetricarboxylic acid (Hbtc^{2-}), with bis-monodentate coordination, plays a two-connected role in linking two Zn(II) ions to form an infinite 1-D chain parallel to the *a* direction. The Zn…Zn distance separated by Hbtc^{2-} is 10.159 Å. In addition, all bmt ligands in **1** are equivalent and bidentate-bridging (scheme 1, mode I) leading to formation of another infinite 1-D chain parallel to the *c* direction. In each bmt, the benzoimidazole and the triazole rings are planar, respectively (the mean deviations from plane are 0.0141 and 0.0011 Å, respectively). The dihedral angle between the benzoimidazole and triazole rings is 104.4°. The Zn…Zn distance separated by bmt is 8.937 Å. These two linear chains are interconnected to finish the 2D layered framework based on rectangular grids [19–24].

As shown in table 3, there are four kinds of hydrogen bonds between solvent water and solvent water, four kinds of hydrogen bonds between solvent water and carboxylate, two kinds of hydrogen bonds between solvent water and solvent DMF, one kind of hydrogen bond between carboxyl groups and solvent DMF and one kind of hydrogen bond between benzimidazole and solvent water. The 2D layers are further connected by the 12 kinds of hydrogen bonds to generate a 3-D supramolecular framework (figure 1(c)).
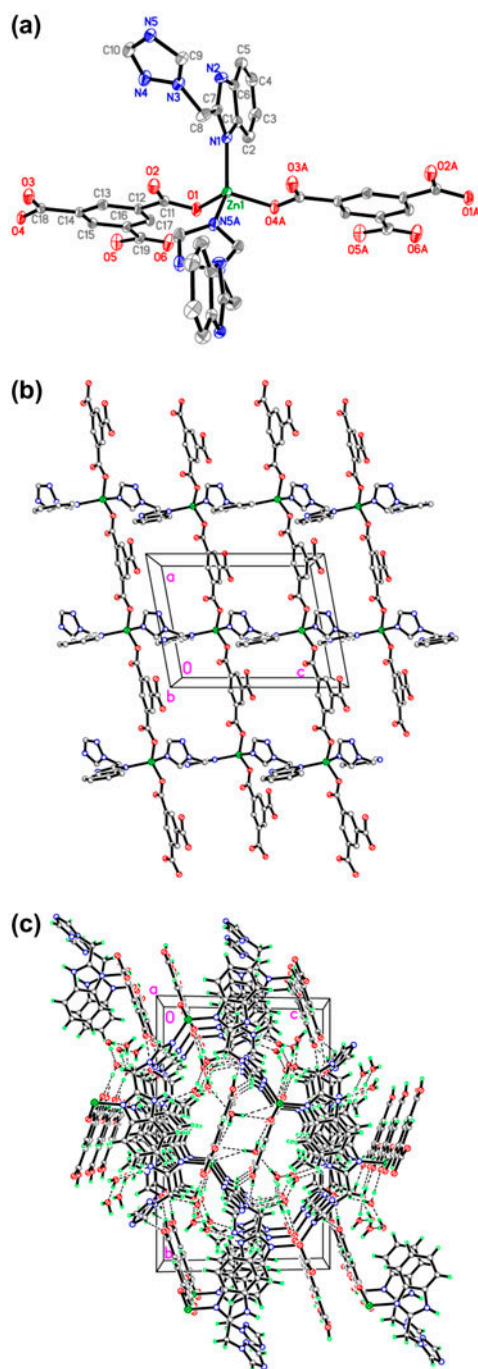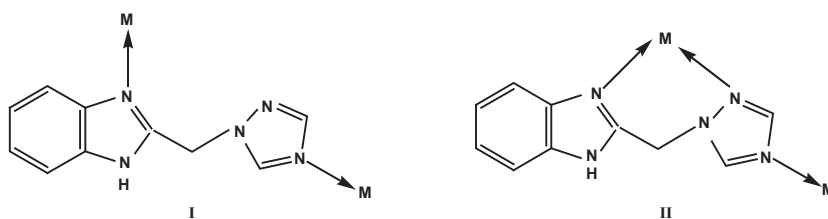
Figure 1.   (a) Coordination environment of Zn(II) in **1** with the atom numbering scheme, hydrogens and solvent water and DMF were omitted for clarity. (b) View of the 2D structure of **1**. (c) View of the 3D structure of **1** formed by hydrogen bonds.

Scheme 1. Coordination modes of bmt observed in **1** and **2**.

3.3. *Crystal structures of {[Cd(Hbtc)(bmt)]·0.5DMF·0.5H₂O}ₙ (2)*

Since, the structures of complexes can be influenced by metal centers [25–27], we intro-
duced Cd(II) to the reaction system and a new complex **2** with different structure from **1**
was obtained. As Cd(II) radius is larger than Zn(II), the Cd(II) in **2** is six-coordinate by
two bmt ligands and two Hbtc^{2-} groups. Carefully examining the structure of **2**, we find
that three carboxyl groups of each Hbtc^{2-} exhibit three different conformations. That is,
one carboxylate coordinates to Cd(II) in chelating mode, the second carboxylate coordi-
nates to Cd(II) unidentate and the third, which is not deprotonated, remains uncoordinated.
But in **1**, two carboxylates of each Hbtc^{2-} coordinate to Zn(II) monodentate and the third
is uncoordinated. All bmt ligands in **2** are equivalent and coordinate to Cd(II) tridentate-
bridging (scheme 1, mode II), while in **1**, bmt was bidentate-bridging. Figure 2(a) depicts
the coordination geometry of Cd(II) and table 2 summarizes important bond lengths and
angles. Each Cd(II) is in a distorted octahedral environment with three nitrogens from two
bmt and three oxygens from two Hbtc^{2-}. The equatorial plane is completed by O1, O5A,
O6A, N1, and Cd1 with mean deviations of 0.0263 Å from the plane (Cd1–O1 = 2.230(3)
Å, Cd1–O5A = 2.362(3) Å, Cd1–O6A = 2.447(3) Å, Cd1–N1 = 2.284(3) Å). The apical posi-
tions are occupied by N4 and N5A (Cd1–N4 = 2.476(3) Å, Cd1–N5A = 2.354(3) Å) with
the N4–Cd1–N5A bond angle of 169.27(11). These Cd–N and Cd–O bond lengths are
similar to those in {[Cd(bdic)(bmt)(H₂O)₂]·2H₂O}ₙ, [Cd(bpy)(bdc)(H₂O)]ₙ, and Cd(bpy)
(btec)₁/₂(H₂O)]ₙ   (H₂bdic = 1,3-benzenedicarboxylic   acid,   bmt = 1-((benzotriazol-1-yl)
methyl)-1-H-1,2,4-triazole), bpy = 2,2′-bipyridine, H₂bdc = 1,4-benzenedicarboxylic acid,
H₄btec = 1,2,4,5-benzenetetracarboxylic acid) [2,28]. In **2**, all Hbtc^{2-} are equivalent and
the three carboxylates in each Hbtc^{2-} are coplanar with the phenyl ring (the mean devia-
tion from the plane is 0.0563 Å).

As shown in figure 2(b), Hbtc^{2-}, with chelating coordination and monodentate coordina-
tion, connects two Cd(II) ions resulting in an infinite 1-D chain parallel to the *α* direction.
The Cd...Cd distance (10.105 Å) separated by Hbtc^{2-} is close to the Zn...Zn distance sep-
arated by Hbtc^{2-} in **1**. All bmt ligands in **2** are equivalent and link Cd(II) ions forming
another infinite 1-D chain parallel to the *b* direction. In each bmt, the benzimidazole and
triazole rings are planar, respectively (the mean deviations from plane are 0.0139 and
0.0011 Å, respectively). The dihedral angle between the benzimidazole and triazole rings is
53.9°. The Cd···Cd distance (6.889 Å) separated by bmt is shorter than the Zn···Zn
distance separated by bmt in **1**. The source of the difference may come from the
tridentate-bridging coordination mode of bmt in **2**. These two kinds of linear chains inter-
connect to finish the 2D layered structure based on rectangular grids.

A rectangular grid is a fairly common secondary building unit. These units can be
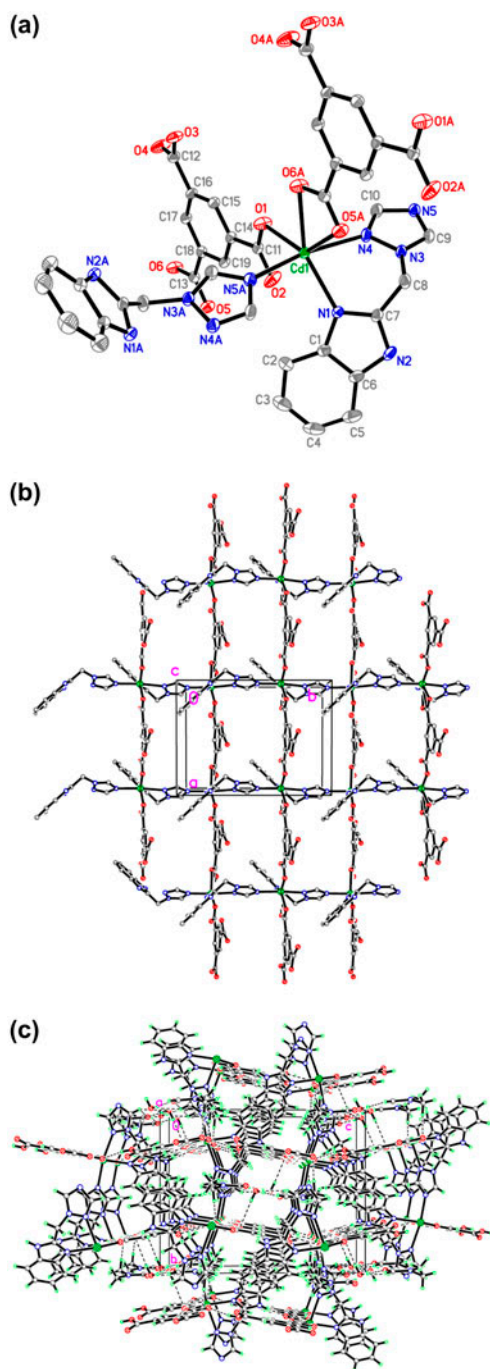connected through metal ions leading to 2D networks, such as **1** and **2**. Change of the

Figure 2. (a) Coordination environment of Cd(II) in **2** with the atom numbering scheme, hydrogens and solvent water and DMF were omitted for clarity. (b) View of the 2D structure of **2**. (c) View of the 3D structure of **2** formed by hydrogen bonds.

ligands can modulate the size of the rectangular grid unit and entrap guest molecules selectively [23, 24, 29]. As shown in table 3, there are four kinds of hydrogen bonds between the carboxy/carboxylate groups, between solvent water and solvent DMF, between solvent water and carboxylate, and between NH of the benzimidazole ring and carboxylate. The 2D layers are further connected by these hydrogen bonds to generate a 3-D supramolecular framework (figure 2(c)).

3.4. *Luminescent properties*

A large number of d^{10} transition metal complexes exhibit interesting luminescent properties [30–34], so the luminescence of **1** and **2** are investigated in the solid state at room temperature. As shown in figure 3, **1** displays an emission band at 394 nm when excited at 346 nm, while **2** gives an emission band at 444 nm ($\lambda_{ex} = 387$ nm). To understand the nature of the emission bands, the luminescent properties of bmt and H_3btc are also measured in the solid state. Free bmt shows an emission band located at 378 nm ($\lambda_{ex} = 336$ nm) and H_3btc molecules give emission bands at 389 nm ($\lambda_{ex} = 347$ nm). In comparison with the band for uncoordinated bmt and H_3btc, the emission spectra for **1** and **2** have bathochromic shift, which may be ascribed to coordination of these organic ligands [18]. The emissions of **1** and **2** likely originate from the intraligand $\pi \rightarrow \pi^*$ transitions of neutral bmt [35–37] and $n \rightarrow \pi^*$ transitions within H_3btc [38–41]. The *N*-donors and *O*-donors contribute to the fluorescent emissions of the two complexes simultaneously [35].

3.5. *Thermogravimetric analysis*

Thermogravimetric analyses of **1** and **2** are performed by heating the complexes from 30 to 750 °C (or 850 °C for **2**) in air. The TG data of **1** (Supplemenatry material) indicate mass loss from 49 to 238 °C is due to dehydration of the crystallized water and free DMF (Obsd 25.92%, Calcd 25.66%). Mass loss from 308 to 641 °C corresponds to decomposition of 1,3,5-benzenetricarboxylate and 2-((benzoimidazol-yl)methyl)-1*H*-1,2,4-triazole.
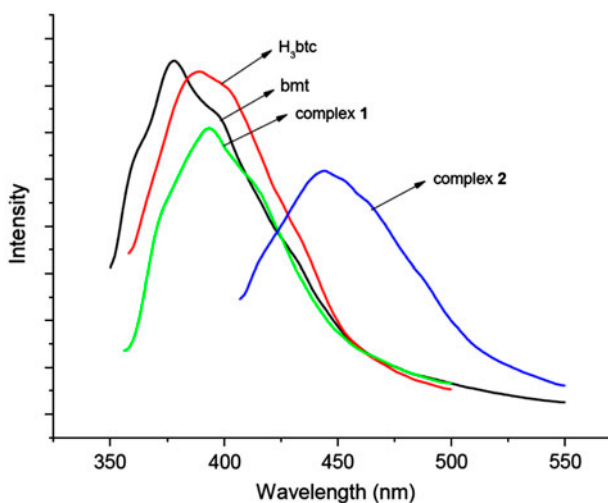

Figure 3.   Solid-state emission spectra of uncoordinated bmt and H_3btc, **1** and **2** at room temperature.

Finally a plateau is observed from 641 to 750 °C. The residue is 13.03%, which should be ZnO (Calcd 12.80%). The TG data of **2** show that the first weight loss of 7.86% between 58 and 215 °C corresponds to release of uncoordinated water and DMF (Calcd 8.06%). Then **2** loses weight from 254 to 725 °C corresponding to decomposition of 1,3,5-benzene-tricarboxylate and 2-((benzoimidazol-yl)methyl)-1H-1,2,4-triazole. Finally a plateau is observed from 725 to 850 °C. The residue is 22.1%, which should be CdO (Calcd 22.7%). These results are in agreement with the crystal structures.

4. Conclusion

Two d^{10} transition metal complexes, $\{[Zn(Hbtc)(bmt)]\cdot DMF\cdot 5H_2O\}_n$ (**1**) and $\{[Cd(Hbtc)(bmt)]\cdot 0.5DMF\cdot 0.5H_2O\}_n$ (**2**), have been obtained through reactions of $ZnCl_2$ or $CdCl_2\cdot 2.5H_2O$ with 2-((benzoimidazol-yl)methyl)-1H-1,2,4-triazole ligand (bmt) in the presence of 1,3,5-benzenetricarboxylic acid (H_3btc). Both complexes exhibit 2D structure but bmt and 1,3,5-benzenetricarboxylate show different coordination modes. The change of metal influences coordination of bmt ligands and 1,3,5-benzenetricarboxylate groups, affecting the detailed architectures of the complexes.

Supplementary material

Crystallographic data reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication. CCDC numbers are 885336 and 885337. This data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336 033).

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