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Metal–organic frameworks (MOFs) constructed from Zn^{II}/Cd^{II}-2,2′-bipyridines and polycarboxylic acids: Synthesis, characterization and microstructural studies[☆]

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ABSTRACT

Metal–organic frameworks with the compositions $[Zn(bpy)(bdc)(H_2O)]_n$ **1**, $[Zn(bpy)(btec)_{1/2}(H_2O)]_n$ **2**, $[Cd(bpy)(bdc)(H_2O)]_n$ **3** and $Cd(bpy)(btec)_{1/2}(H_2O)]_n$ **4** (H_2bdc = 1,4-benzenedicarboxylic acid = terephthalic acid, H_4btec = 1,2,4,5-benzenetetracarboxylic acid and bpy = 2,2′-bipyridine) have been synthesized and characterized using spectroscopic and single-crystal X-ray diffraction techniques. In these complexes, Zn^{II}/Cd^{II}-2,2′-bipyridine units and carboxylate anions exists as nodes and spacers respectively. An infinite 1D zig-zag chain structure is observed for both complexes **1** and **3**, whereas complexes **2** and **4** display a 3D supramolecular architecture. The complexes are found to be photoluminescent, porous and show significant thermal stability.

1. Introduction

Recent years have witnessed rapid progress made in the construction of metal–organic frameworks (MOFs) owing to their intriguing molecular topologies [1–7] and potential applications in porosity [8–10], catalysis [11–15], ion exchange [16], chirality [17–21], luminescence [22–26], non-linear optics (NLO) [27–31], conductivity [32–35], optoelectronics [36,37], magnetism [38–42], spin-transition behavior [43–46], gas storage [47–49] and selective binding of molecules through absorption [13,50]. Most of the current studies in this area involve d^{10} transition metal ions with functional ligands. However, it is still considered a challenge to explore successful synthetic routes for the preparation of MOFs that could be exploited for targeted applications.

In this context, polycarboxylates are widely used in the development of supramolecular networks organized through coordination bonds, hydrogen bonds and π–π stacking interactions. Among these anionic polycarboxylates, 1,4-benzenedicarboxylic (H_2bdc) acid and 1,2,4,5-benzenetetracarboxylic acid (H_4btec) are extensively exploited as ligands in the construction of supramolecular architectures through their self-assembly [51–53].

In recent years, functional coordination polymers caught the attention of researchers owing to their potential applications in technology. Di-anionic dicarboxylate ligands are commonly used as molecular tethers for this work. These ligands can link metal cations into coordination polymer chains, layers or networks, in the process providing the charge balance necessary to avoid the inclusion of porosity-inhibiting smaller anions. The disposition of the donor groups within the dicarboxylate moieties, the coordination geometry preferences at the metal ions and the array of accessible carboxylate binding modes have been shown to act synergistically in the structure directed self-assembly of coordination polymers in solution. On the other hand, auxiliary ligands like 2,2′-bipyridine also impact on the conformations of the flexible carboxylic ligand (*trans*- or *cis*-), and play an important role in the formation of the final structure of the complex [54]. The terminal ligand 2,2′-bpy tends to construct low-dimension structures which can be extended into high-dimensional supramolecular networks through hydrogen bonds and π–π stacking interactions.

Thus, the present article is thought to be of worth as it deals with the synthesis and characterization of the structures obtained on the skeleton of d^{10} divalent metal (Zn^{II},Cd^{II})2,2′-bipyridines together with 1,2-benzenedicarboxylic acid and 1,2,4,5-tetracarboxylic acid. Since such types of metal–organic frameworks show the formation of porous structures [5], micro structural studies have also been carried out on these synthesized complexes.

2. Experimental

2.1. Materials and methods

Reagents of A.R. purity were purchased from standard commercial sources (Sigma–Aldrich, Merck) and were used without further

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purification. Elemental analyses have been carried on a Carbo-Erba elemental analyzer 1108, and IR spectra were recorded as KBr pellets on a Varian 3100 FT-IR spectrometer. TGA measurements were performed on a Perkin Elmer Pyris diamond TG-DTA instrument at a heating rate of 5 °C/min in a nitrogen atmosphere with a flow rate of 200 ml/min in the temperature range 50–800 °C. Photoluminescence (PL) was measured using a Hitachi F-4500 spectrofluorometer. $M(bpy)(NO_3)_2 \cdot H_2O$ ($M = Zn^{II}/Cd^{II}$) were prepared using the procedure as reported by Sen et al. [55] for analogous complexes.

2.2. X-ray crystallographic studies

Suitable X-ray quality crystals of the complexes were grown directly from their corresponding reaction mixtures in DMF/EtOH/H_2O (6:2:0.4 by volume) at room temperature and X-ray crystallographic data were collected by mounting a single-crystal of the sample on a glass fiber. An Oxford diffraction XCALIBUR-S and Bruker SMART CCD area detector diffractometer equipped with an LN-2 low-temperature attachment was used for the determination of cell parameters and intensity data collection. Appropriate empirical absorption corrections using the programs multi-scan were applied. Monochromated Mo Kα radiation (λ = 0.71073 Å) was used for the measurements. The crystal structures were solved by direct methods [56] and refined by full matrix least squares SHELXL-97 [57]. Drawings were carried out using MERCURY [58] and DIAMOND [59], and special computations were carried out with PLATON [60].

2.3. Synthesis of the complexes

The complexes were synthesised by general procedures as reported by Guo et al. [61]. In a typical synthetic procedure, Zn^{II}(2,2′-bipyridyl)$(NO_3)_2 \cdot H_2O$ (0.363 g, 1 mmol) and Cd^{II}(2,2′-bipyridyl)$(NO_3)_2 \cdot H_2O$ (0.410 g, 1 mmol) were added separately to the corresponding solutions of H_2bdc (0.166 g, 1.0 mmol) and H_4btec (0.127 g, 0.5 mmol) dissolved in DMF (6 ml) and ethanol (2 ml) at room temperature, containing an equimolar amount of triethylamine. Few drops of 5N-HNO_3 (pH 4–5) was added until the mixture become clear. The mixture was heated at 120 °C for 6–8 h to give the corresponding complexes in 65–90% yield. The complexes thus isolated were found to be insoluble in water and common organic solvents.

2.3.1. Synthesis of [Zn(2,2′-bpy)(bdc)(H_2O)] **1**

Using the above procedure, after heating the components together at 120 °C for 6 h then cooling to room temperature, tiny round shaped crystals were obtained after two weeks, which were washed several times with diethylether. Yield: ~77%. *Anal.* Calc. for $C_{18}H_{14}N_2O_5Zn$ (**1**): C, 53.55; H, 3.50; N, 6.94. Found: C, 53.99; H, 3.68; N, 7.52%. IR (KBr, cm^{-1}): 3207 (w), 1590 (vs), 1474 (m), 1439 (s), 1376 (vs), 1313 (s) 1152 (w), 1020 (w), 840 (w), 753 (vs), 658 (m), 549 (m).

2.3.2. Synthesis of [Zn(2,2′-bpy)$(btec)_{1/2}$(H_2O)] **2**

Complex **2** was also synthesized using a similar method as used for the synthesis of complex **1** except that H_4btec was used instead of H_2bdc. After heating at 120 °C for 8 h and then cooling to room temperature colorless block shaped crystals were obtained after 10 days, which were washed with diethylether and dried. Yield: ~93%. *Anal.* Calc. for $C_{15}H_{11}N_2O_5Zn$ (**2**): C, 49.41; H, 3.04; N, 7.68. Found: C, 49.72; H, 3.38; N, 7.79%. IR (KBr, cm^{-1}): 3409 (w), 3071 (m), 1634 (vs), 1580 (s), 1483 (m), 1381 (vs), 1129 (vs), 1020 (s), 817 (m), 763 (vs), 654 (m), 540 (m), 458 (m).

2.3.3. Synthesis of [Cd(2,2′-bpy)(bdc)(H_2O)] **3**

Complex **3** was also synthesized using a similar procedure as used for the synthesis of complex **1** but $Cd(bpy)(NO_3)_2 \cdot H_2O$ was used instead of $Zn(bpy)(NO_3)_2 \cdot H_2O$. Colorless block shaped crystals of **3** were recovered after one week, which were washed several times with methanol followed by diethylether. Yield: ~66%. *Anal.* Calc. for $C_{18}H_{14}N_2O_5Cd$ (**3**): C, 47.97; H, 3.13; N, 6.22. Found: C, 48.22; H, 3.34; N, 5.92%. IR (KBr, cm^{-1}): 3368 (w), 3199 (w), 1571 (vs), 1434 (m), 1380 (vs), 1310 (m) 1153 (s), 1014 (s), 820 (s), 74 (vs), 651 (m), 534 (m).

2.3.4. Synthesis of [Cd(2,2′-bpy)$(btec)_{1/2}$(H_2O)] **4**

Using the above procedure, complex **4** resulted in colorless tiny round shaped crystals after three weeks, which were washed with methanol followed by diethylether. Yield: ~69%. *Anal.* Calc. for

Table 1
Summary of crystallographic data for complexes **1–4**.

Parameters	1	2	3	4
Formula	$C_{18}H_{14}N_2O_5Zn$	$C_{15}H_{11}N_2O_5Zn$	$C_{18}H_{14}N_2O_5Cd$	$C_{15}H_{11}N_2O_5Cd$
M	403.68	364.63	450.73	411.66
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Temperature/K	150(2)	150(2)	133 (2)	298(2)
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$C2/c$
a (Å)	9.0826(11)	7.7085(3)	9.961(2)	18.991(4)
b (Å)	10.1697(12)	8.8712(5)	16.251(3)	7.6220(17)
c (Å)	10.5345(15)	10.7317(6)	11.901(2)	19.921(4)
α (°)	103.392(11)	80.690(5)	90	90
β (°)	113.643(12)	69.966(5)	117.41(1)	95.695(3)
γ (°)	100.673(10)	78.027(4)	90	90
V (Å)^3	823.83(18)	671.17(6)	1710.21	2869.3(11)
Z	2	2	4	8
D_c (Mg m^{-3})	1.627	1.804	1.750	1.906
Reflections collected	7670	6574	16866	14148
Reflections unique	2895	2360	3893	2821
R_{int}	0.0177	0.0280	0.0251	0.0271
Index ranges	$-10 \leqslant h \leqslant 10$	$-9 \leqslant h \leqslant 9$	$-12 \leqslant h \leqslant 12$	$-23 \leqslant h \leqslant 23$
	$-12 \leqslant k \leqslant 12$	$-10 \leqslant k \leqslant 10$	$-21 \leqslant k \leqslant 21$	$-9 \leqslant k \leqslant 9$
	$-12 \leqslant l \leqslant 12$	$-12 \leqslant l \leqslant 12$	$-15 \leqslant l \leqslant 15$	$-24 \leqslant h \leqslant 24$
Refinement method		Full-matrix, least squares on F^2		
wR_2	0.0568	0.0549	0.0689	0.0582
R_1	0.0212	0.0231	0.0283	0.0251
Goodness-of-fit (GoF)	1.059	1.047	0.975	1.058

Table 2
Selected bond lengths (Å) and angles (°) for complexes **1**–**4**.

Compound ***1***			
Zn(1)–O(4)	2.0240(12)	O(4)–Zn(1)–O(1)	128.65(5)
Zn(1)–O(1)	2.0346(13)	O(1)–Zn(1)–N(2)	128.24(6)
Zn(1)–O(2)	2.0423(12)	O(4)–Zn(1)–N(2)	103.05(5)
Zn(1)–N(2)	2.0946(15)	O(2)–Zn(1)–N(1)	164.17(6)
Zn(1)–N(1)	2.1650(15)	N(2)–Zn(1)–N(1)	76.88(6)
O(1)–H(102)	0.83(3)	O(4)–Zn(1)–N(1)	97.33(5)
O(1)–H(101)	0.91(3)	O(4)–Zn(1)–O(2)	94.87(5)
O(5)–C(15)	1.246(2)	H(102)–O(1)–H(101)	104(2)
Compound ***2***			
Zn(1)–O(2)	1.9843(14)	O(2)–Zn(1)–N(2)	125.10(6)
Zn(1)–O(1)	2.0356(17)	O(1)–Zn(1)–N(2)	134.33(7)
Zn(1)–O(5)#1	2.0580(14)	O(2)–Zn(1)–O(1)	100.04(7)
Zn(1)–N(2)	2.0818(19)	O(5)#1–Zn(1)–N(1)	162.03(6)
Zn(1)–N(1)	2.1649(18)	O(2)–Zn(1)–N(1)	103.70(6)
O(1)–H(101)	0.91(3)	O(2)–Zn(1)–O(5)#1	94.24(6)
O(1)–H(102)	0.76(3)	N(2)–Zn(1)–N(1)	76.85(7)
O(3)–C(11)	1.215(3)	H(101)–O(1)–H(102)	111(3)
Compound ***3***			
Cd(1)–O(1)	2.213(10)	O(3)–Cd(1)–N(1)	88.10(5)
Cd(1)–O(3)	2.395(11)	O(3)–Cd(1)–O(4)	55.18(7)
Cd(1)–O(4)	2.371(13)	O(4)–Cd(1)–N(2)	95.51(7)
Cd(1)–O(5)	2.265(12)	N(1)–Cd(1)–N(2)	71.35(5)
Cd(1)–N(1)	2.314(12)	O(1)–Cd(1)–N(1)	157.63(6)
Cd(1)–N(2)	2.336(13)	O(5)–Cd(1)–N(1)	126.31(6)
O(5)–H(13)	0.943(4)	O(5)–Cd(1)–N(2)	97.41(4)
O(5)–H(14)	0.902(3)	O(1)–Cd(1)–O(4)	106.65(7)
C(11)–O(2)	1.249(4)	H(13)–O(5)–H(14)	112.18(5)
Compound ***4***			
Cd(1)–O(4)	2.2286(18)	O(1)–Cd(1)–N(2)	88.07(9)
Cd(1)–O(2)	2.2753(18)	O(2)–Cd(1)–O(1)	77.03(9)
Cd(1)–O(1)	2.309(2)	O(2)–Cd(1)–O(7)#3	53.18(6)
Cd(1)–N(1)	2.312(2)	O(1)–Cd(1)–N(1)	142.71(9)
Cd(1)–N(2)	2.332(2)	N(1)–Cd(1)–N(2)	70.83(7)
Cd(1)–O(7)#3	2.589(2)	O(4)–Cd(1)–N(2)	157.23(8)
O(1)–H(1A)	0.79(4)	N(2)–Cd(1)–O(7)#3	106.24(7)
O(1)–H(2B)	0.82(5)	O(4)–Cd(1)–O(7)#3	86.34(7)
C(11)–O(5)	1.241(3)	H(1A)–O(1)–H(2B)	108(4)

$C_{15}H_{11}N_2O_5Cd$ (4): C, 43.76; H, 2.69; N, 6.80. Found: C, 44.23; H, 2.61; N, 7.02%. IR (KBr, cm^{-1}): 3405 (w), 3065 (m), 1560 (vs), 1491 (m), 1379 (vs), 1319 (w) 1135 (m), 1014 (s), 869 (s), 769 (vs), 651 (m), 532 (m).

3. Result and discussion

3.1. IR spectra

Major peaks observed between ~1600 and ~1200 cm^{-1} are assigned to υ(bpy) and υ(phenyl) of the benzenecarboxylate ligands. The $\upsilon_{as}(COO^-)$ and $\upsilon_s(COO^-)$ bands are observed at ~1570 and ~1380 cm^{-1} respectively [62]. The peaks lying in the region ~3400 to ~3200 cm^{-1} are assigned to υH_2O(coordinated) whereas ρrH_2O(coordinated) and ρwH_2O(coordinated) appear at ~655 and ~540 cm^{-1} respectively.

3.2. Structural description of the complexes

Crystallographic data and refinement details for the structural analyses of all the complexes are summarized in Table 1. Selected bond lengths and bond angles with their estimated standard deviations are presented in Table 2 while selected parameters for weak interactions are listed in Table 3. Molecular structures (ORTEP diagrams) of the complexes **1**–**4** are shown in Fig. 1.

3.2.1. Complex *1* and *2*

The X-ray single-crystal structure determination reveals that complex **1** exists as a neutral one-dimensional infinite zig-zag coordination chain. Each Zn^{II} center is surrounded by two N donors from the 2,2′-bipyridine ring, two oxygen atoms from two carboxylate groups of two different terephthalic acid molecules together with one water molecule, in a distorted pentacoordinated geometry, as depicted in Fig. 1a. The neighboring Zn^{II} centers are connected by a terephthalate dianionic moiety which acts as a bridge through its benzene ring, as shown in Fig. 2a. The two terephthalate units are almost orthogonal to each other with a dihedral angle of 88.87° and the two Zn^{II} centres are separated at a distance of 11.10 Å. In this structure, the 2,2′-bipyridine molecule acts as a

Table 3
Selected parameters for weak interactions in complexes **1**–**4**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	DHA (°)	Symmetry code
1					
O(1)–H(101) ···O(3)	0.91	1.74	2.6056	158	–
O(1)–H(102)···O(5)	0.83	1.86	2.6895	177	1 − *x*, 1 − *y*, 1 − *z*
C(1)–H(1)···O(5)	0.93	2.54	3.3322	143	1 − *x*, 1 − *y*, 1 − *z*
C(7)–H(7)···O(4)	0.93	2.49	3.3072	146	−*x*, −*y*, −*z*
C(10)–H(10)···O(2)	0.93	2.45	3.0188	119	–
C(18)–H(18)···O(1)	0.93	2.54	3.4108	156	1 − *x*, 1 − *y*, 1 − *z*
2					
O(1)–H(101)···O(2)	0.91	1.75	2.656	176	1 − *x*, 1 − *y*, −*z*
O(1)–H(102)···O(4)	0.76	2.11	2.7422	141	–
O(1)–H(102)···O(4)	0.76	2.59	3.0607	122	−*x*, 1 − *y*, −*z*
C(3)–H(3)···O(3)	0.93	2.55	3.1815	125	1 − *x*, 1 − *y*,1 − *z*
C(7)–H(7)···O(4)	0.93	2.42	3.325	164	−*x*, 1 − *y*, 1 − *z*
C(10)–H(10)···O(5)	0.93	2.52	3.716	118	–
3					
O(5)–H(13)···O(2)	0.94	1.75	2.662	162	–
O(5)–H(14)···O(4)	0.90	1.79	2.688	178	1 − *x*, −*y*, −*z*
C(4)–H(4)···O(3)	0.95	2.35	3.275	165	*x*, 1 − *y*, 1 − *z*
C(7)–H(5)···O(3)	0.95	2.59	3.498	160	−*x*, −*y*, −*z*
C(16)–H(11)···O(3)	0.95	2.49	2.805	131	–
C(14)–H(10)···O(4)	0.95	2.56	2.853	112	*x*, ½ − *y*, ½ + *z*
4					
O(1)–H(1A)· · ·O(5)	0.79	2.07	2.7904	152	½ − *x*, ½ + *y*, ½ − *z*
O(1)–H(2B)···O(2)	0.82	1.89	2.6867	162	½ − *x*, −½ + *y*, ½ − *z*
C(2)–H(2)···O(7)	0.93	2.44	3.3543	166	−*x*, 2 − *y*, −*z*
C(3)–H(3)···O(2)	0.93	2.59	3.5000	165	*x*, 2 − *y*, −½ + z
C(4)–H(4)···O(5)	0.93	2.49	3.3802	162	½ − *x*, 3/2 − *y*, -*z*
C(8)–H(8)···O(7)	0.93	2.58	3.1141	117	½ − *x*, 5/2 − *y*, −*z*

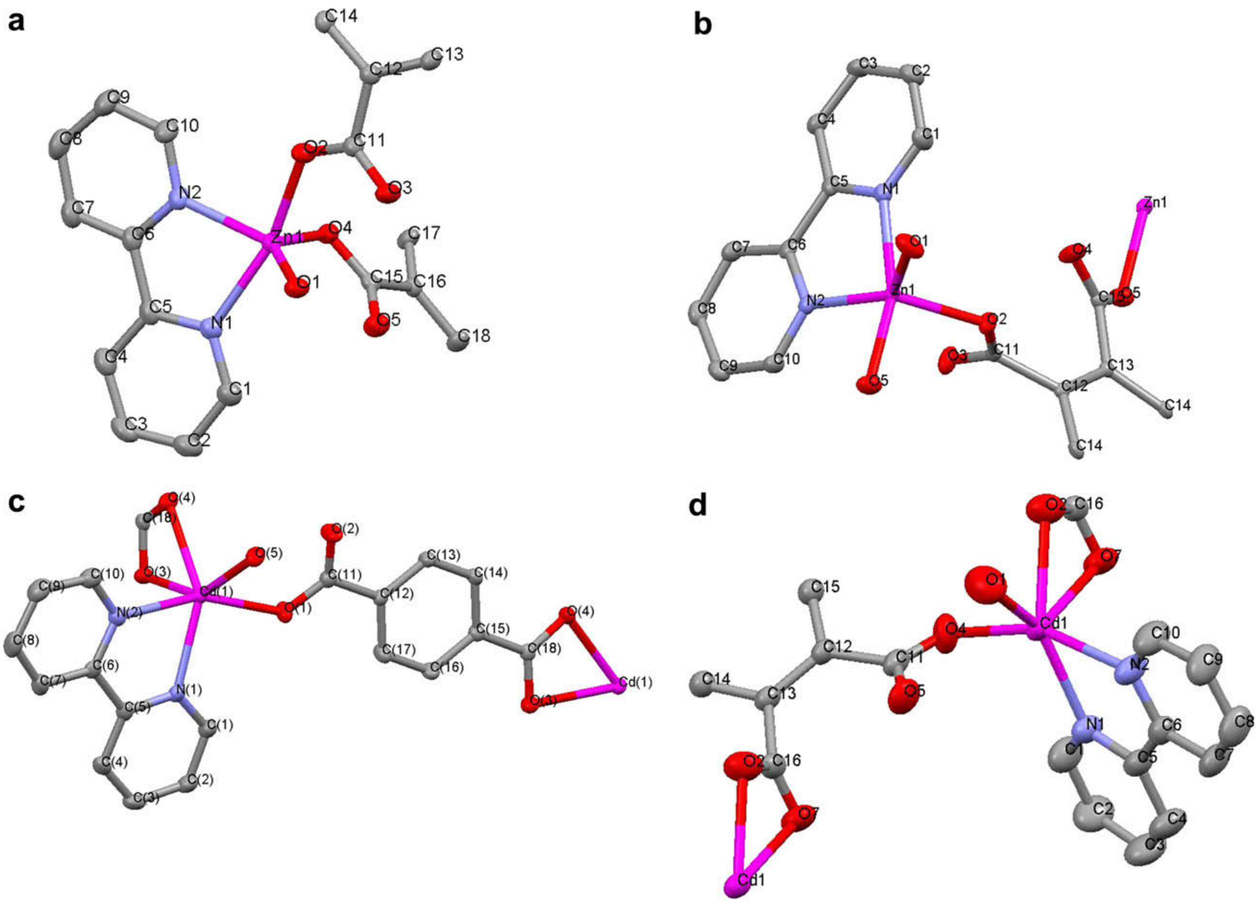


Fig. 1. Molecular structures of complexes **1**(a), **2**(b), **3**(c) and **4**(d).

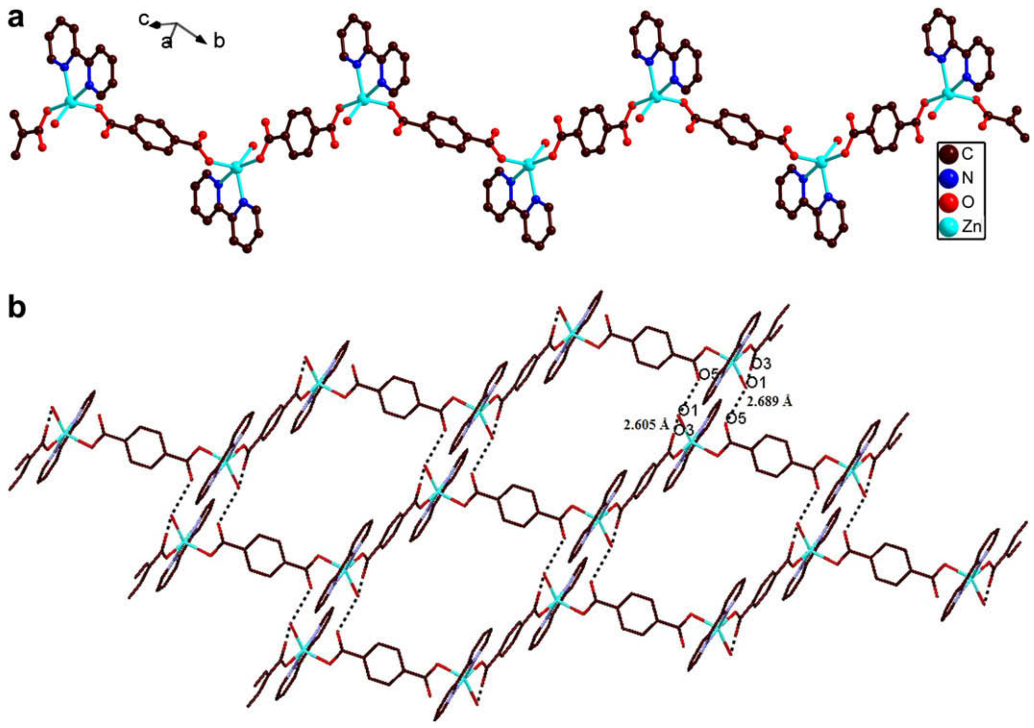
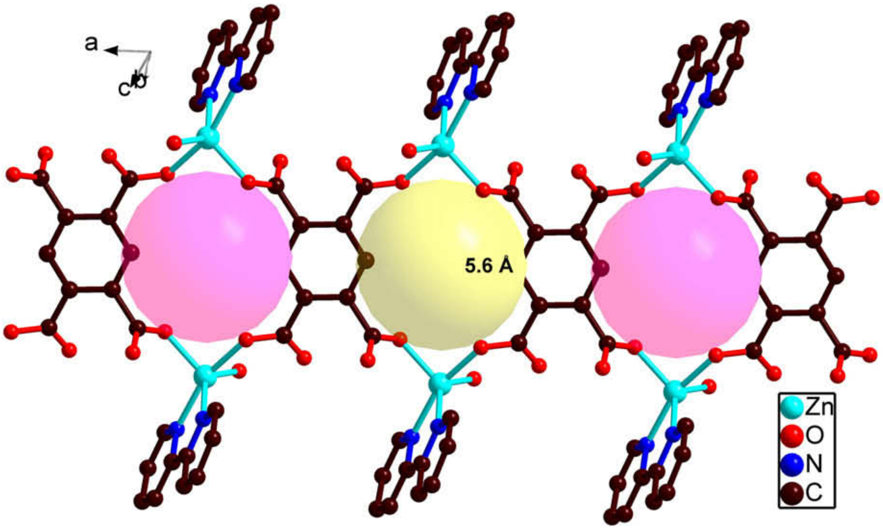


Fig. 2. ID zig-zag chain (a) and supramolecular 2D sheet network of complex **1** containing hydrogen bonds and π–π stacking (b).

peripheral ligand. It prevents the chain growth in a straight forward direction; hence a zigzag chain is formed.

It is very interesting to note that two independent chains are linked through hydrogen bonds formed between coordinated



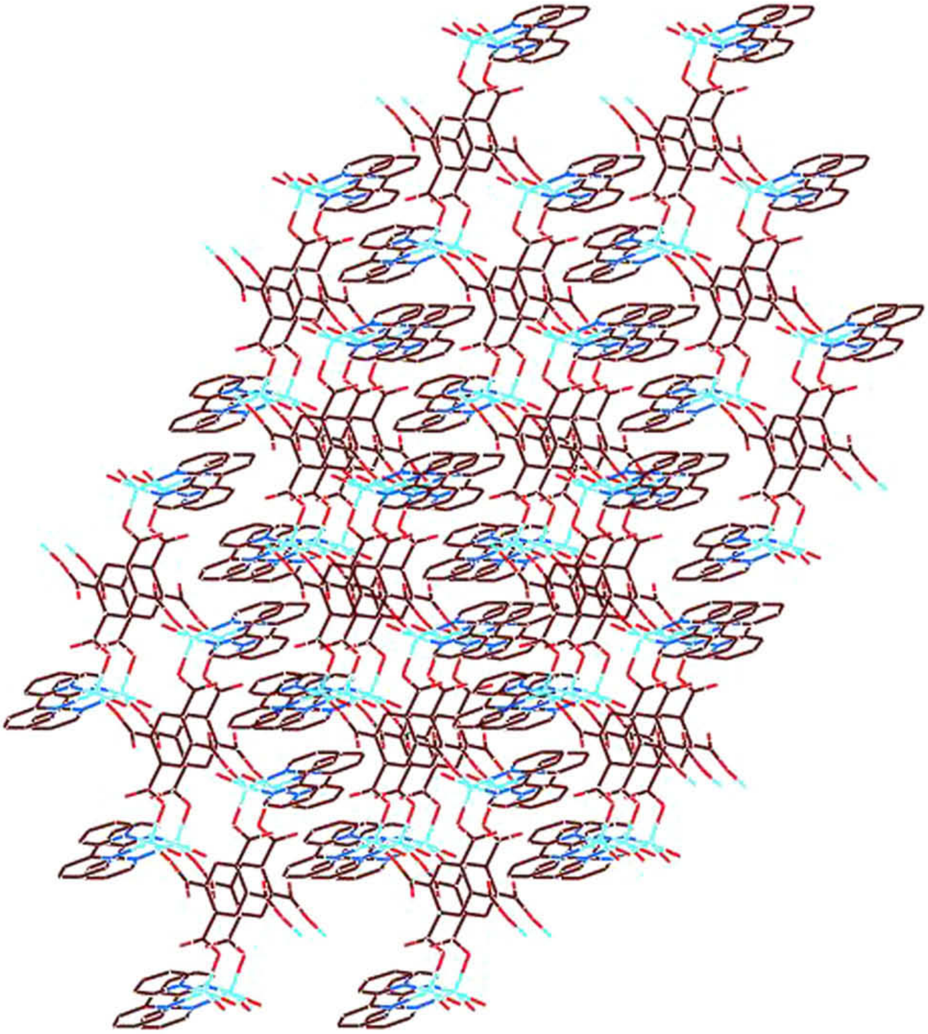


Fig. 3. 1D linear chain with the continuous cavity of diameter ~5.6 Å (a), crystal packing in complex **2** through inter- and intra-molecular H-bonding and π–π stacking (b).

water molecules and the carbonyl oxygen atoms of theterephthalate dianion, in addition to π–π stacking interactions between the 2,2′-bpy rings at a distance of 3.80 Å. It results in the formation of a 2D sheet-like supramolecular structure (Fig. 2c).

Crystal packing analysis of complex **1** shows the formation of independent intra-chain (O–H···O) as well as inter-chain (O–H···O) hydrogen bonds (Table 3). The intra-chain hydrogen bond is formed between the O–H group of the coordinated water molecule and an uncoordinated carboxylate oxygen at a D···A distance of 2.6056 Å and an O–H–O angle of 158°. However, in the formation of the inter-chain O–H···O hydrogen bonds, the O–H group of the coordinated water molecule of one chain is linked through the uncoordinated oxygen atoms of the terephthalate dianion of the adjacent chain at a D···A distance of 2.6895 Å and an O–H–O angle of 177°. The KPI for this complex, found to be 71.8%, indicates compact packing in its crystal lattice.

The molecular structure of the Zn^{II} complex with benzenetetracarboxylic acid (H_4btec), **2**, is depicted in Fig. 1b. This complex is also pentacoordinated, but the two carboxylate oxygen atoms (O2 and O5) come from two different carboxylate groups, acting in a monodentate fashion, together with one oxygen atom (O1W) of the coordinating water molecule and in addition to two nitrogen atoms (N1 and N2) from the 2,2′-bipyridine ring. As shown in Table 2, one Zn–O (carboxylate) distance, Zn(1)–O(2) 1.9843(14) Å, is found to be shorter than the Zn–O (carboxylate) distance Zn(1)–O(2) = 2.0423(12) Å as found in complex **1**. Other distances in this complex are comparable with the bond distances observed in complex **1**.

It is quite interesting to observe from Fig. 3a, that each carboxylate group is acting as a linker between four Zn(bpy) units, out of these four units, two units are common in the formation of a 16-membered macrocyclic ring of diameter ~5.6 Å. This 16-membered macrocyclic ring extends along the molecular axis in a linear fashion and provides a chain structure. The distance between two Zn^{II} centres across the cavity is found to be 8.144 Å, whereas adjacent Zn^{II} centres are separated by a distance of 7.709 Å (Fig. 3b).

Weak force studies reveal that six hydrogen bonds are formed in the molecular packing of complex **2**. Three hydrogen bonds are conventional hydrogen bonds whereas the remaining three

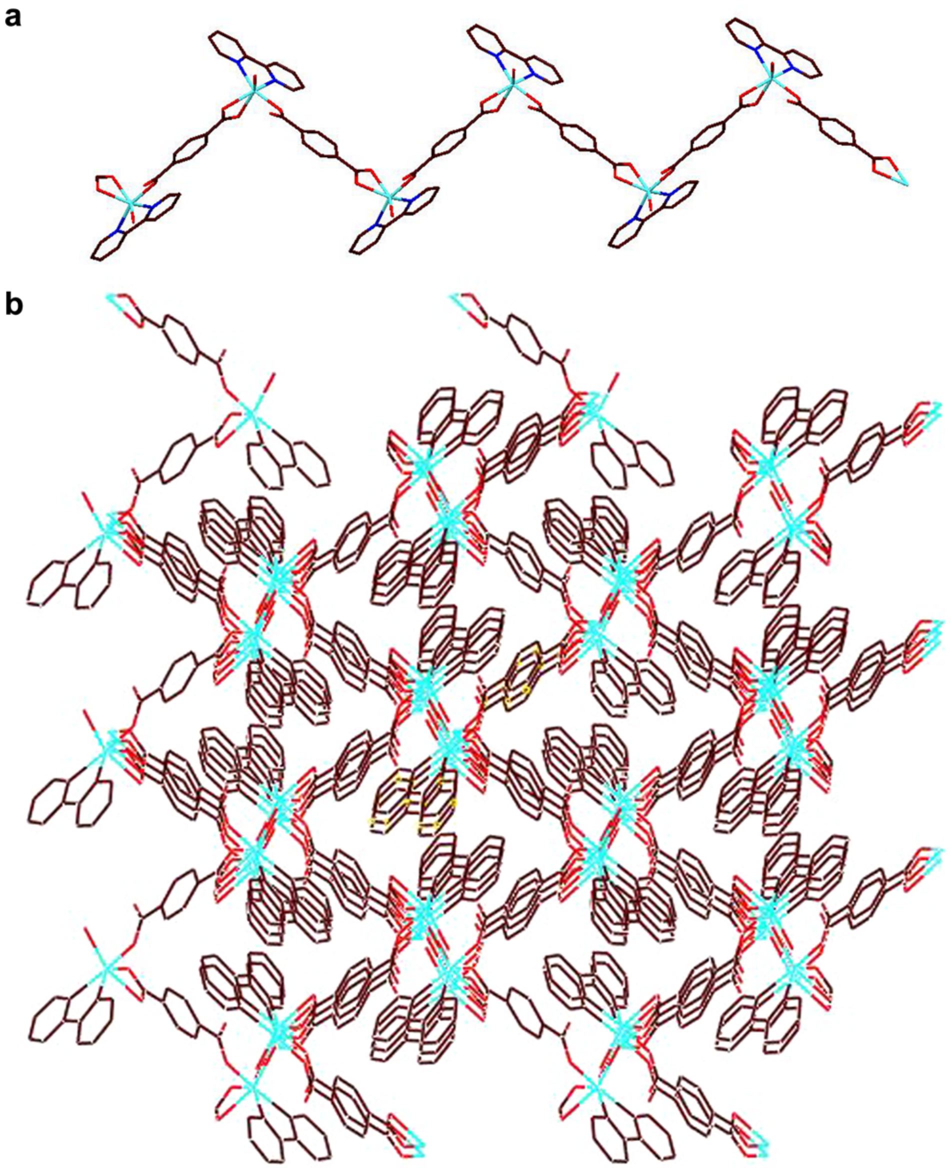


Fig. 4. 1D zig-zag chain (a), view of the crystal packing along the *a*-axis, the packing is stabilized through π–π stacking between bipyridyl rings and H-bonding in complex **3**.

bonds are non-conventional hydrogen bonds. The non-conventional hydrogen bonds involve C–H units as donor groups, whereas the acceptors are oxygen atoms in each case (Table 3). This complex has a Kitagorodskii Packing Index (KPI) of 76.6%, indicating a compact packing with no solvent accessible voids. In complex **1** the KPI value is found to be 71.8%. Thus the Zn(bpy)-benzenetetracarboxylate complex **2** possess more compact packing as compared to the Zn(bpy)-dicarboxylate complex **1**.

Both inter and intra molecular hydrogen bonds, in addition to π–π stacking interactions, provide a 3D supramolecular architecture (Fig. 3b) in complex **2**.

3.2.2. Complex *3* and *4*

Complex **3** is a Cd^{II} analogue of complex **1**. It also possesses an infinite zig-zag one-dimensional chain structure, but each Cd^{II} ion is hexa-coordinated in a highly distorted octahedral geometry (Fig. 4a). The formation of a seven coordinated CdN_2O_5 core has been reported [63] for a complex of Cd^{II} with the terephthalate dianion, but it contains 1,10-phenanthroline as one of the components instead of 2,2′-bipyridine as used in the present complex.

In the present complex **3**, the CdN_2O_4 coordinated core consists of two nitrogen atoms (N1 and N2) from 2,2′-bpy, one oxygen atom [O(5)] from a water molecule together with one oxygen atom (O1) from one terephthalate dianion and other two oxygen donors atoms [O(3) and O(4)] from another terephthalate unit which lies nearly orthogonal to the first terephthalate unit (dihedral angle: 80.16 °). It is interesting to note that each terephthalate unit serves as a bridging ligand between two cadmium atoms, forming a one-dimensional zig-zag polymeric chain (Fig. 4a). However, the bridging terephthalate dianion linked to two Cd^{II} ion, acts as monodentate at one coordination end and bidentate to another coordination end. Thus, one bridging terephthalate unit overall acts as a tridentate ligand and links two Cd^{II} ions at a distance of 11.341 Å. This distance is a little larger than the distance of 11.10 Å observed between the two Zn^{II} ions in complex **1**. This difference may be explained by the larger size and higher coordination mode of the Cd^{II} ion as compared to the Zn^{II} ion.

The cell packing analysis, as depicted in Fig. 4b, shows that both coordinated planes, as well as the bridging ligand plane, are more tilted from the crystallographic plane as compared to that

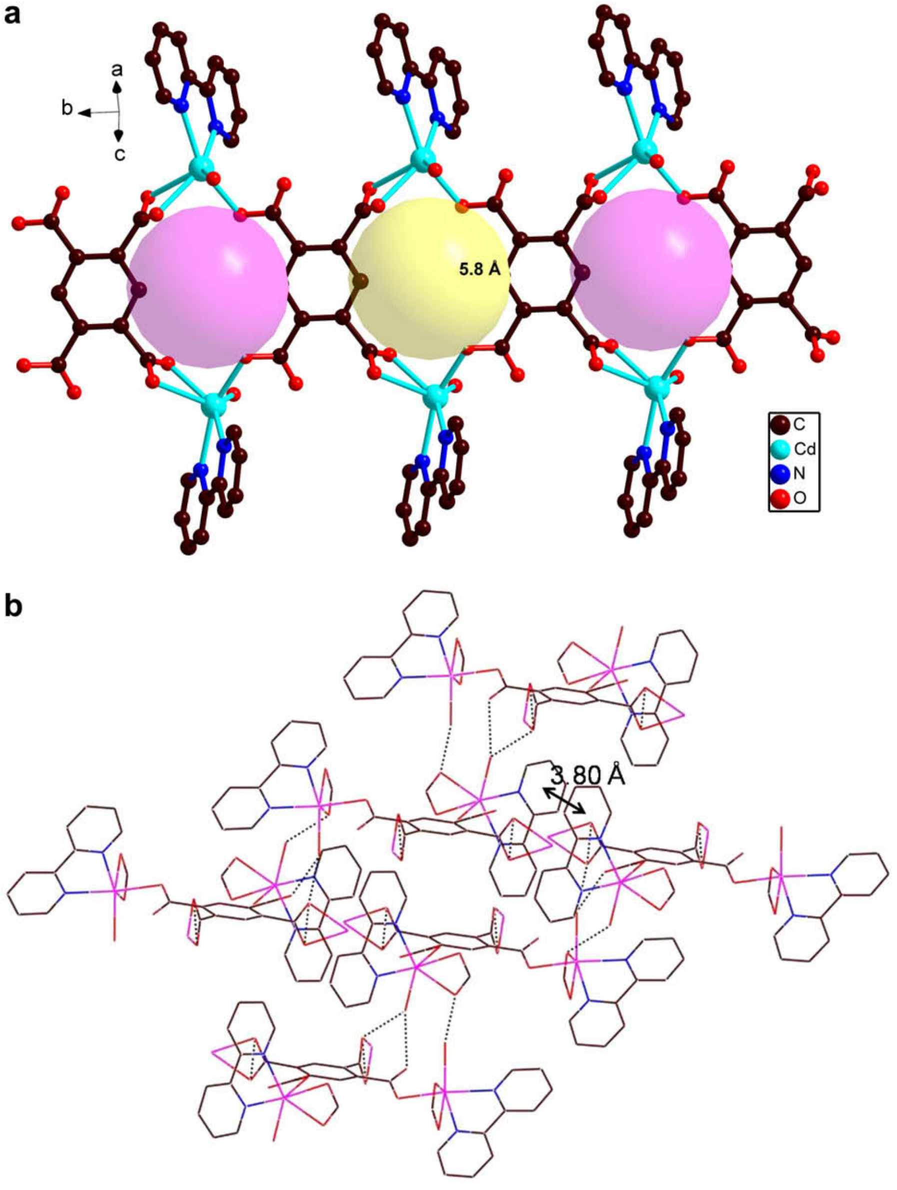


Fig. 5. 1D linear chain containing the continuous cavity of diameter of ~5.8 Å (a), packing of molecules in the crystal lattice; H-bonding and π–π stacking in complex **4**.

observed in the analogous Zn^{II} complex **1**. This may be understood due to the different modes of coordination (monodentate and bidentate) of the same ligand.

The crystal packing of complex **3** consists of two conventional and four non-conventional hydrogen bonds. In all cases, oxygen atoms acts as the acceptor atoms. The intra-molecular hydrogen bonding is formed between O(5)–H(13) and O(2) at a H···A distance of 1.75 Å with an O–H–O angle of 162°, whereas inter-molecular hydrogen bonding between O(5)–H(14) is formed at a H···A distance of 1.79 Å with an O–H–O angle of 178°. It indicates that two structural units are attached closely through hydrogen bonding. Out of the four non-conventional hydrogen bonds, two intra-molecular hydrogen bonds are formed at H···A distances of 2.35 (C4–H4···O3) and 2.59 Å (C7–H5···O3), whereas inter-molecular non-conventional hydrogen bonds are formed at the larger distances of 2.49 and 2.56 Å.

Complex **4** also possesses a distorted octahedral coordination geometry with a CdN_2O_4 coordination core around the Cd^{II} ion. In the construction of this structure, btec acts as hexadentate ligand, bis (bidentate + monodentate). However, again in a recently reported Cd^{II} complex containing 1,10-phenanthroline as a terminal ligand, btec acted in a tetrakis(bidentate) fashion [63]. Thus, the presence of the 2,2′-bipyridine ring as a terminal ligand alters the mode of coordination of the btec ligand. Additionally, one btec ligand links four Cd^{II} ions in the present complex **4** whereas the same btec ligand linked six Cd^{II} ions in the earlier reported complex [63]. Thus, the effect of the terminal ligand on the coordinating mode of the tetradentate ligand is quite evident.

The unit cell packing mode of complex **4**, depicted in Fig. 5a, again shows the formation of a 16-membered ring, but a little change in the ring size is observed (5.8 Å diameter in complex **4** as compared to 5.6 Å in complex **2**). Six hydrogen bonds (two conventional and four non-conventional) are found in the weak force studies of complex **4**.

3.3. Photoluminescent properties

The photoluminescent properties of complexes **1–4** are examined at room temperature and the corresponding spectral features are shown in Fig. 6. Upon excitation at $\lambda ex = 340$ nm, complex **1** emits at 365 nm with a shoulder at 430 nm, while in complex **2** the corresponding peaks are red shifted and appear at 370 and 435(sh) nm. Since solid-state emissions from the free 2,2′-bpy group are also observed in a similar region at $\lambda em = 360$ and 385 nm due to the π–π^* transition, the strong emissions arising from complexes **1** and **2** are assigned to intra-ligand fluorescence of the coordinated 2,2′-bpy ligand. However, weak emissions from complexes **1** and **2** observed at 430 (sh) and 435 (sh) nm respectively are considered to arise from a charge-transfer transition, consistent with earlier reports [64–66]. Additionally, multiple emissions arising at 400, 462(sh) and 520(sh) nm for complex **3**, and 401, 465(sh) and 523(sh) nm for complex **4** are assigned to a combination of strong π–π^* transitions of the coordinated 2,2′-bpy ligand along with weak π–π^* transition from both bdc and btec ligands.

3.4. Thermogravimetric (TG) analysis

Thermogravimetric analyses (TGA) performed on crystalline samples under a nitrogen atmosphere are depicted in S1. In complex **1**, a weight loss of 4.40% at 100–220 °C is assigned to the loss of coordinated water molecules (calculated per formula unit weight loss = 4.45%). This loss is further followed by a second weight loss of 38.60% in the temperature range 241–270 °C, corresponding to the loss of the terminal 2,2′-bpy group. The final decomposition starts at 280 °C and continues up to 800 °C, at which only 45% residue remains, which may be due to carbon residues as well as metal oxides. Complex **2** shows a weight loss (47.9%) only after 230 °C, corresponding to the removal of the coordinated water molecule together with the 2,2′-bpy ligand (calculated 47.71%) from the structural framework. At 800 °C complex **2** also shows 41.25% residue remains. Multiple steps of weight loss occur upon heating complexes **3** and **4**.

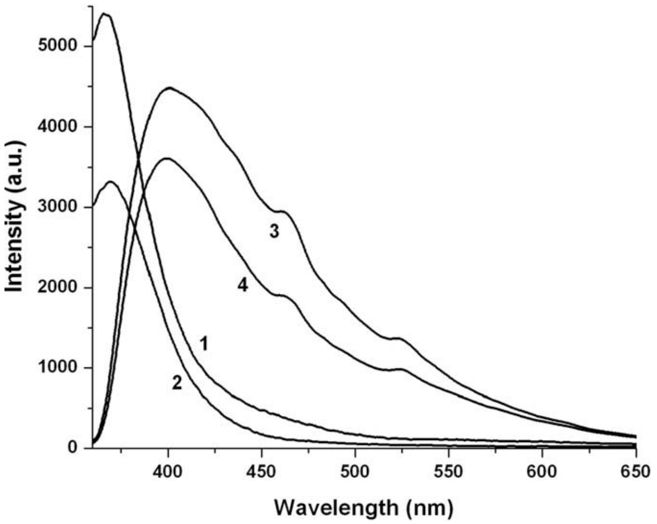


Fig. 6. Photoluminescence spectra of complexes **1–4** in the solid-state at room temperature.

3.5. Microstructural studies

Since such structural frameworks of complexes are constructed from hetero components, the formation of porosity in their bulk structure may be looked upon. Therefore, their SEM images were recorded. The SEM images of the complexes show the formation of micro-sized grains varying from 10–30 μm in complex **1** to 15–70 μm in complex **2**. In between these grains, pores can be seen which are dispersed throughout the structure (marked as ‘P’) (S2). The SEM micrograph of complex **3** shows the presence of parallelepipeds crystals with an average size of $25 \times 5 \times 4\ \mu m^3$ whereas in complex **4**, the grain size varies in the 15–30 μm range.

4. Conclusion

In summary, the reactions of Zn^{II}/Cd^{II}-2,2′-bipyridine with di and tetra carboxylates under mild conditions (pH 4–5) provide a series of photoluminescent polymeric complexes with diverse architectures from zig-zag chains (complexes **1** and **3**) to straight chains (complexes **2** and **4**). The weak forces of inter-molecular and intra-molecular hydrogen bonding interactions together with π–π aromatic stacking interactions provide a two-dimensional layer for complex **1**, whereas for complexes **2**, **3** and **4**, three-dimensional supramolecular networks result as a secondary structure. The complexes with the tetracarboxylate ligand provide a 16-membered metallomacrocyclic cavity of diameter 5.6 Å in **2** and 5.8 Å in **4**. Additionally, the presence of 2,2′-bipyridine rings is found to alter the coordination behavior of the carboxylates.

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Appendix A. Supplementary data

CCDC 646994, 650284, 685998 and 696004 contain the supplementary crystallographic data for **1–4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.11.059.

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