Electronic Supplementary Information

Bent-bis(triazolyl)-based coordination polymers tuned by the dicarboxylate ligands: syntheses, structures and properties

Tien-Wen Tseng,*[a] Tzuoo-Tsair Luo,[a] Kuo-Yang Tseng,[a] Yu-Xian Hong[a] and Guang-Cheng Huang[a]

[a] Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 106, Taiwan.

* To whom correspondence should be addressed (email: f10403@ntut.edu.tw).

Contents

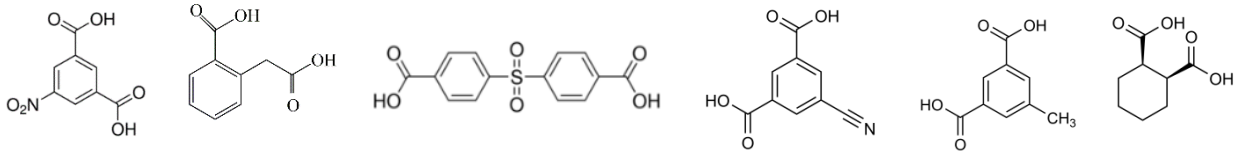

Fig. S1 Comparison of organic species, which were used as the auxiliary ligands: (a) 5-nitrobenzene-1,3-dicarboxylic acid (H_2nbdc, for **1** and **4**), (b) 2-carboxyphenylacetic acid (H_2cpa, for **2**) (c) 4,4′-sulfonyldibenzoic acid (H_2sdb, for **3**), (d) 5-cyano-1,3-benzenedicarboxylic acid (H_2cydc, for **5**), (e) 5-methylbenzene-1,3-dicarboxylic acid (H_2mbdc, for **6**), (f) *cis*-1,2-cyclohexanedicarboxylic acid (H_2chdc, for **7**).

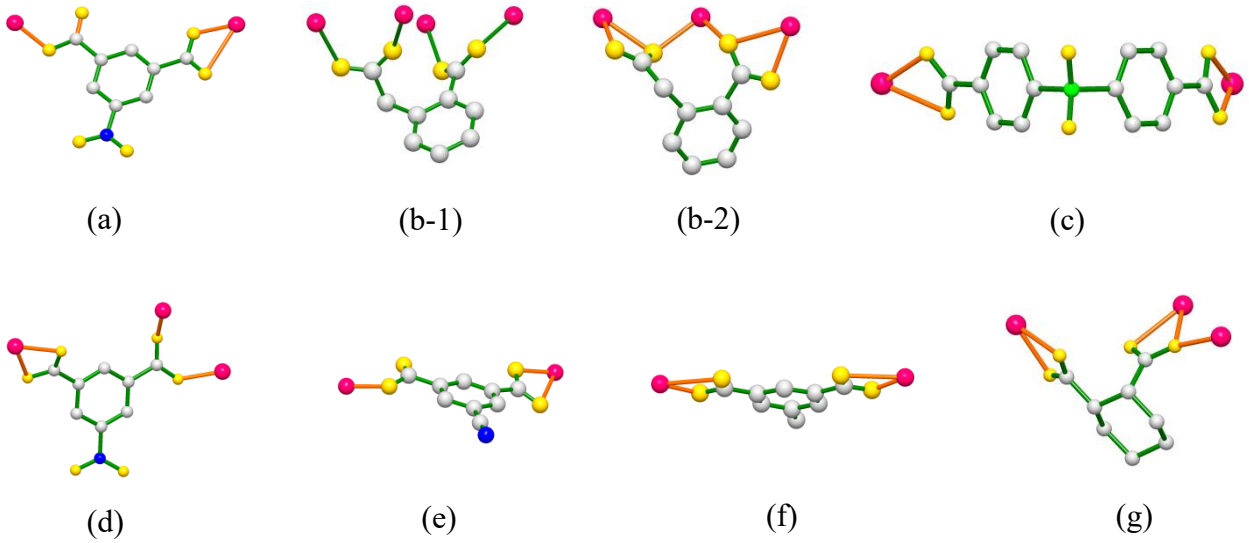

Fig. S2 The coordination modes of di-carboxylate groups in compounds **1**–**7:** (a) the nbdc^{2-} ligand of **1**, (b) the cpa^{2-} ligand of **2** (c) the sdb^{2-} ligand of **3**, (d) the nbdc^{2-} ligand of **4**, (e) the cydc^{2-} ligand of **5**, (e) the mbdc^{2-} ligand of **6**, (f) the chdc^{2-} ligand of **7**.

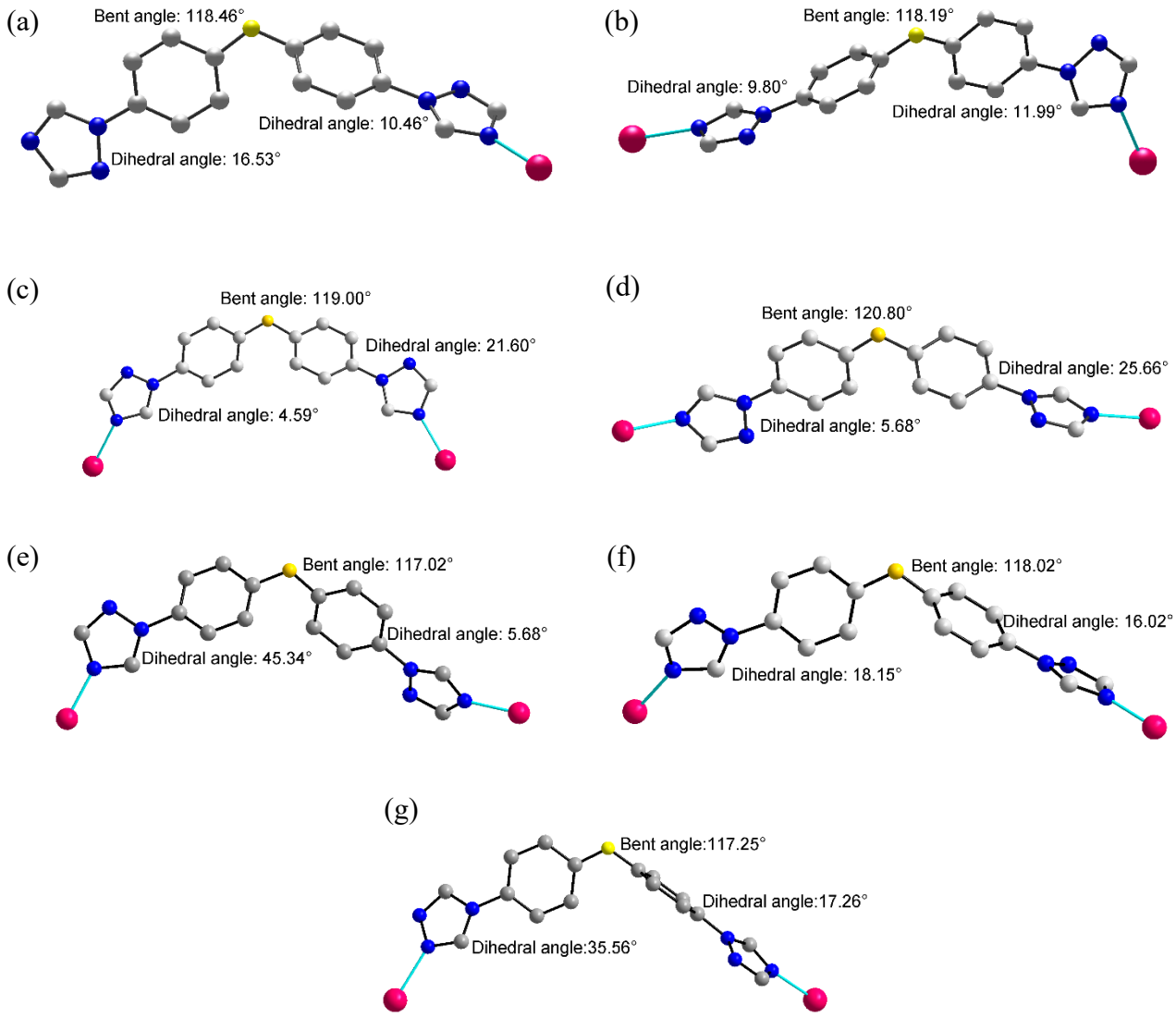

Fig. S3. Comparison of the conformations of the opbt ligands in compound **1**-**7**: (a)-(g).

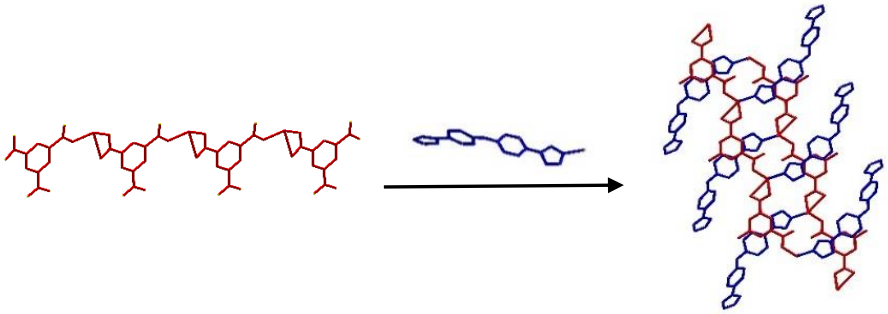

Fig. S4 The 1D nbdc-Zn^{II}-based polymeric chain of **1** was assembled from the opbt ligand and the Zn(II) ions.

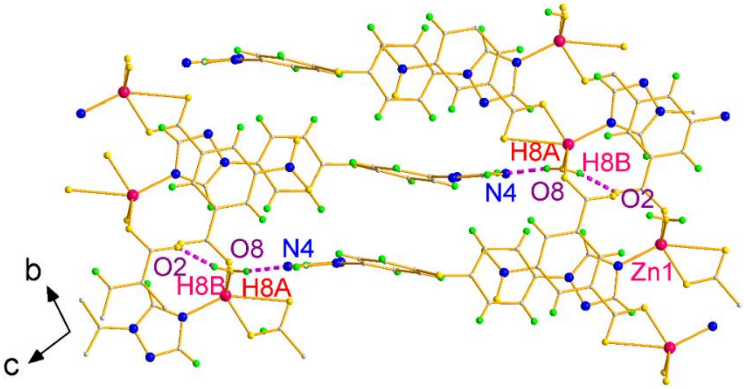

Fig. S5 A view of the coordinated water molecules (O8) of compound **1** that were hydrogen bonded to the nitrogen atoms (N4) of the opbt ligands as well as the carboxylate oxygen atoms (O2) from the $nbdc^{2-}$ ligands.

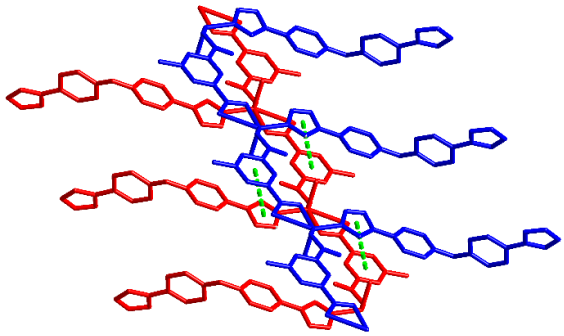

Fig. S6 Two adjacent triazolyl rings of the opbt ligands of compound **1** are regularly packed *via* π–π interactions with 3.950(3) Å (in green dash line).

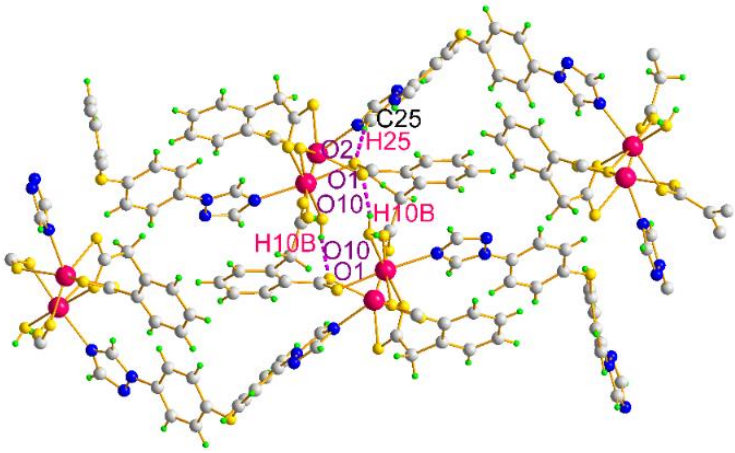

Fig. S7 The hydrogen bonding interactions of compound **2** were observed within framework that arose between the coordinated water molecule (O10) and the carboxylate oxygen atom (O1) of the cpa^{2-} ligand, as well as between the hydrogen atoms (H25) from the opbt ligand and the carboxylate oxygen atom (O2) of the cpa^{2-} ligand.

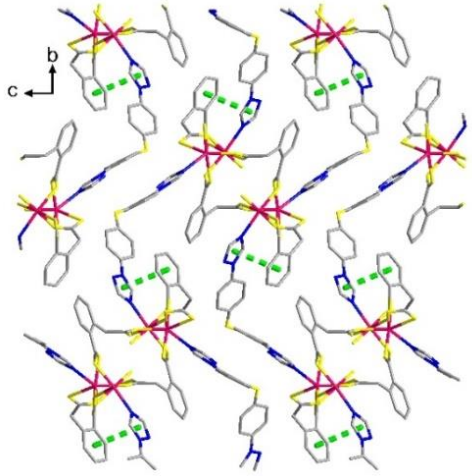

Fig. S8 The triazolyl rings of the opbt ligands and the phenyl rings of the cpa^{2-} auxiliary ligands of **2** were packed together *via* π–π interactions with 3.551(6) Å (in green dash line).

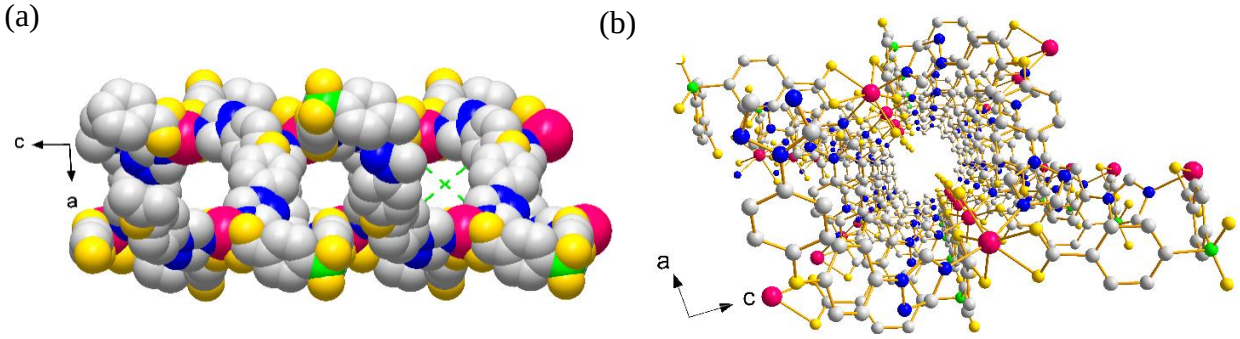

Fig. S9 Structures of **3**: (a) a space-filling diagram of the framework with the pore size of 15.5 × 14.9 $Å^2$, which was excluded by the van der Waals radii of the atoms viewed along the *b*-axis; (b) a 3D packing perspective view along the *b*-axis.

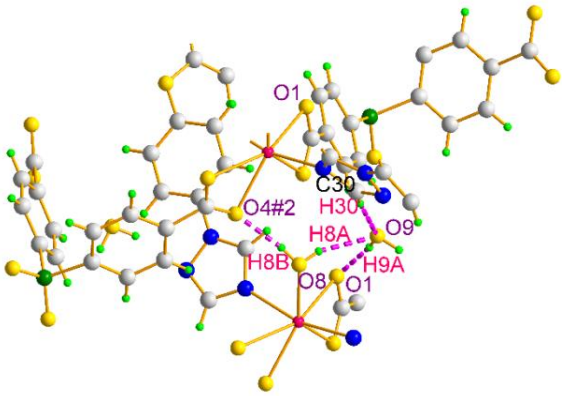

Fig. S10 The hydrogen bonding interactions of compound **3** were observed between the guest water (O9) and the coordinated water molecules (O8), the hydrogen atom (H30) of the opbt ligand, as well as between the hydrogen atoms (H8B) from coordinated water molecules (O8) and the carboxylate oxygen atom (O4#2) of the sdb^{2-} ligand.

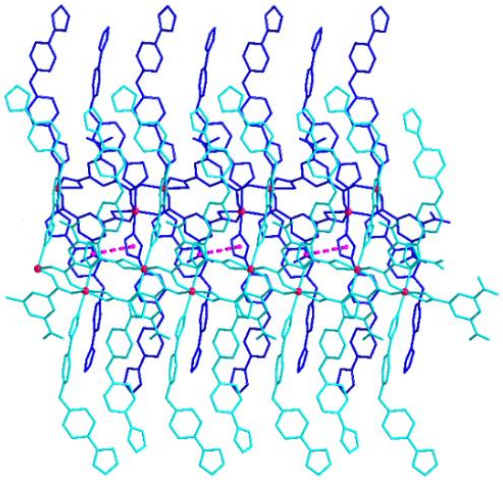

Fig. S11 The triazolyl rings of the opbt ligands in compound **4** were regularly packed with the nbdc^{2-} auxiliary ligand *via* π–π interactions with about 4.344(3) Å (in pink dash line).

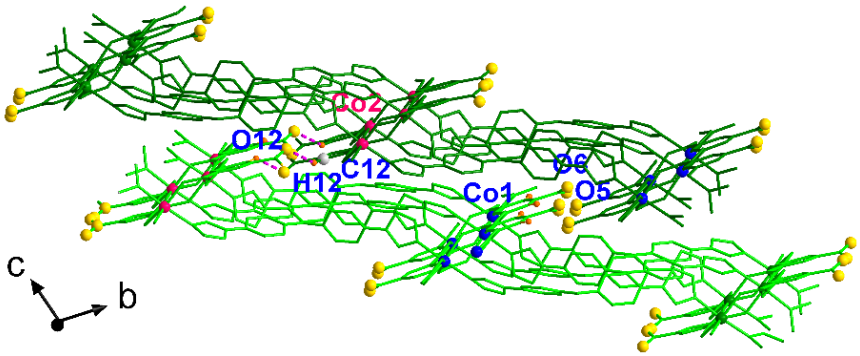

Fig. S12 The hydrogen bonding interactions of **4** were observed among two adjcent layers *via* between the hydrogen atom (H12) of the nbdc^{2-} ligands and the oxygen atom (O12) of the nitro motif from the nbdc^{2-} ligand, which was coordinated to the Co2(II) centres (denoted in red), but that didn't be observed for the case of the Co1(II) centres (denoted in blue)

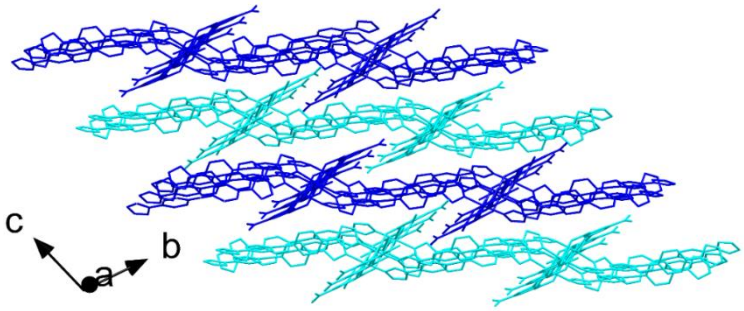

Fig. S13 The 2D layers of **4** were regularly stacked together, resulting into a 3D supramolecular structure.

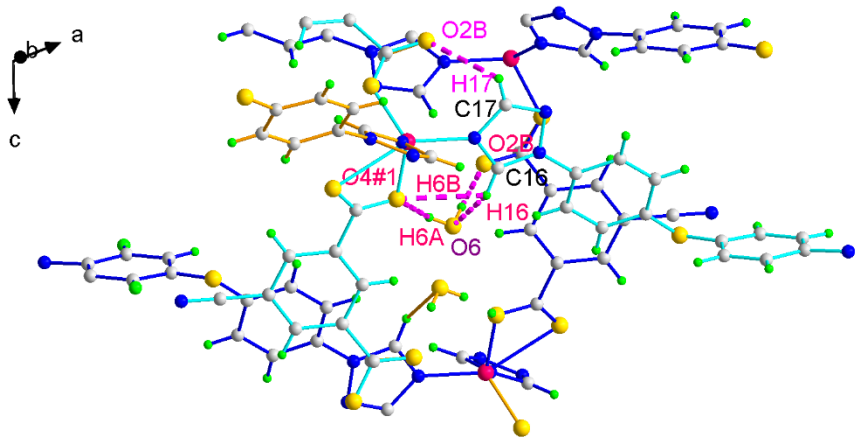

Fig. S14 The guest water molecules of **5** included within framework and hydrogen bonded with the nitrogen atoms of the opbt ligand and the carboxylate motifs of the $cydc^{2-}$ ligands.

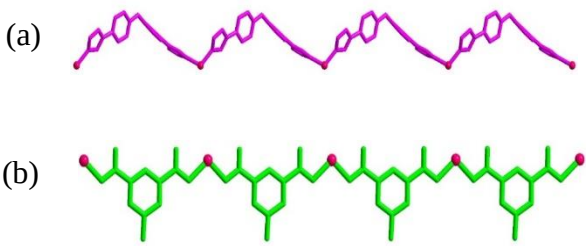

Fig. S15 Structures of **6**: (a) the 1D zigzag chain consists of the Zn^{II}-opbt unit; (b) 1D chain consists of the Zn^{II}-mbdc unit.

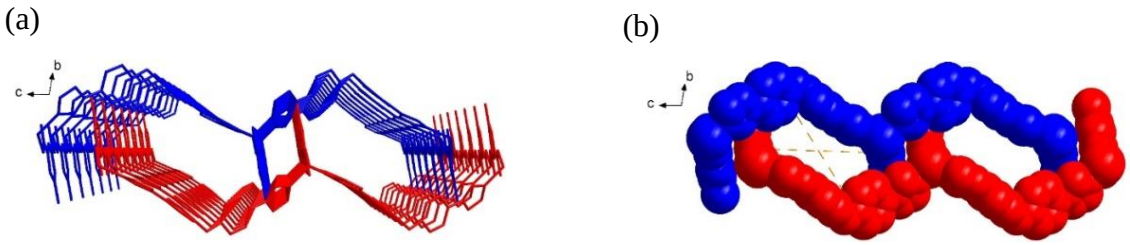

Fig. S16 Structures of compound **6**: (a) shows the 1D open channels viewed along the *a*-axis; (b) the channel with a window size of 7.8 × 7.6 $Å^2$ (excluded by the van der Waals radii of the atoms) in a space-filling mode.

(a) (b)

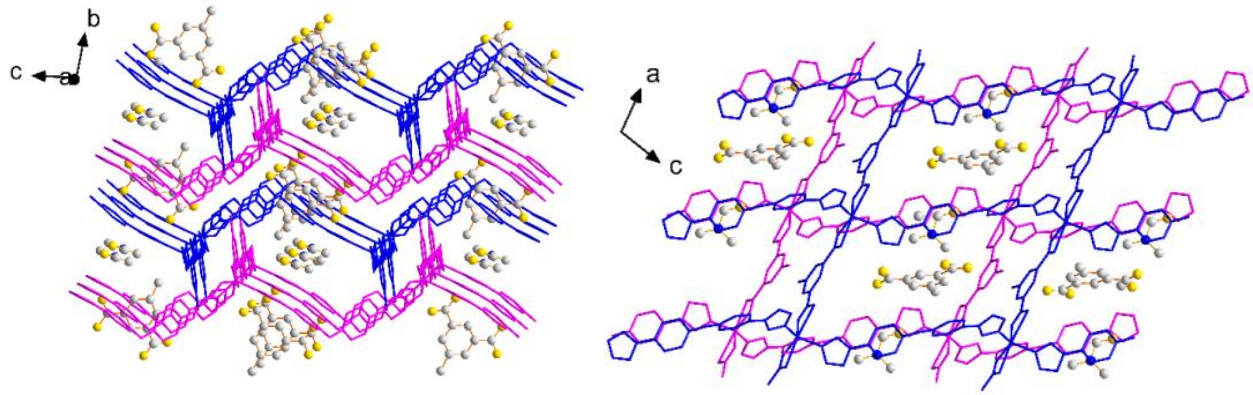

Fig. S17 The disorder guest DMF and H_2mbdc molecules of **6** were included within the networks: (a) viewed along the *a*-axis; (b) viewed along the *b*-axis.

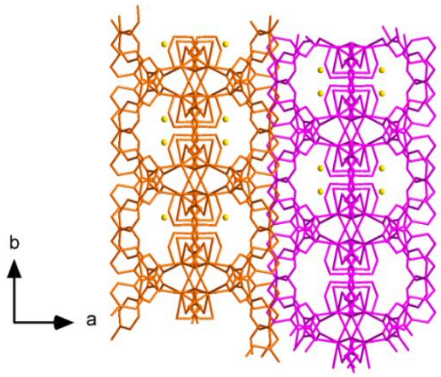

Fig. S18 A 3D supramolecular structure of **7** viewed along the *c*-axis, and the part of the disorder guest water moecules are denoted as yellow sphere.

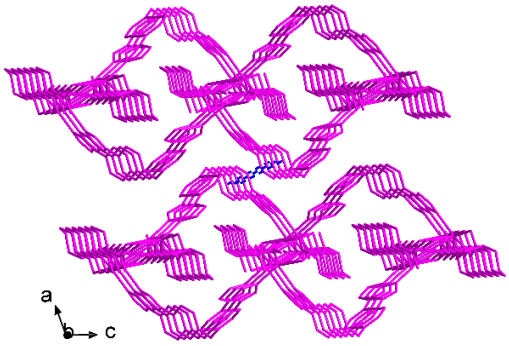

Fig. S19 The adjacent 1D rods of **7** were regularly packed into a 3D supramolecular structure *via* π–π stacking interactions with a distance of 3.760(7) Å (denoted as blue dash lines) between two phenyl rings of the opbt ligands.

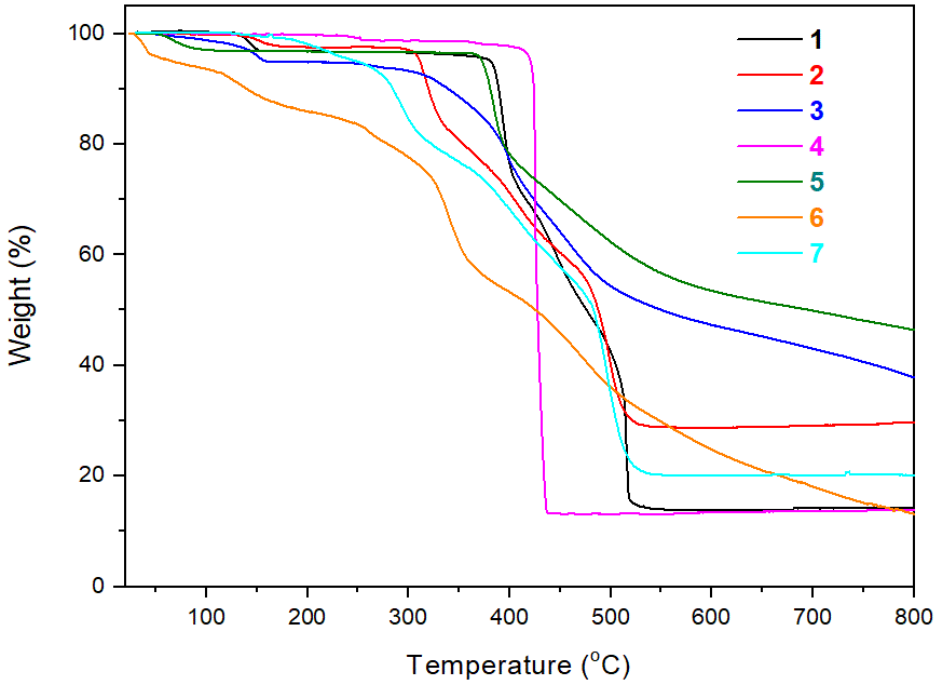

Fig. S20 TGA curves of compounds **1–7**.

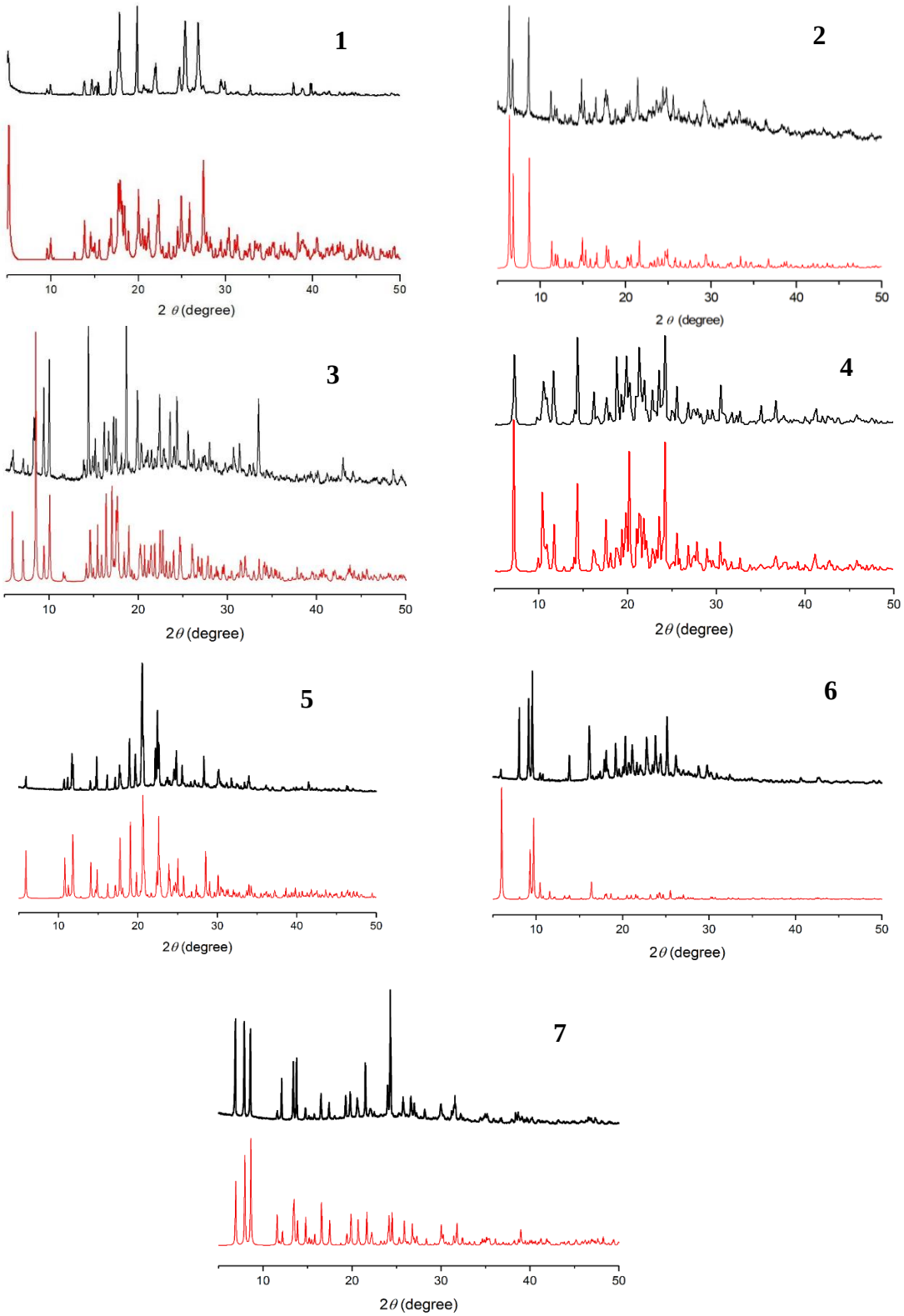

Fig. S21 As-synthesized (black) and simulated (red) powder X-ray diffraction patterns of **1**–**7**.

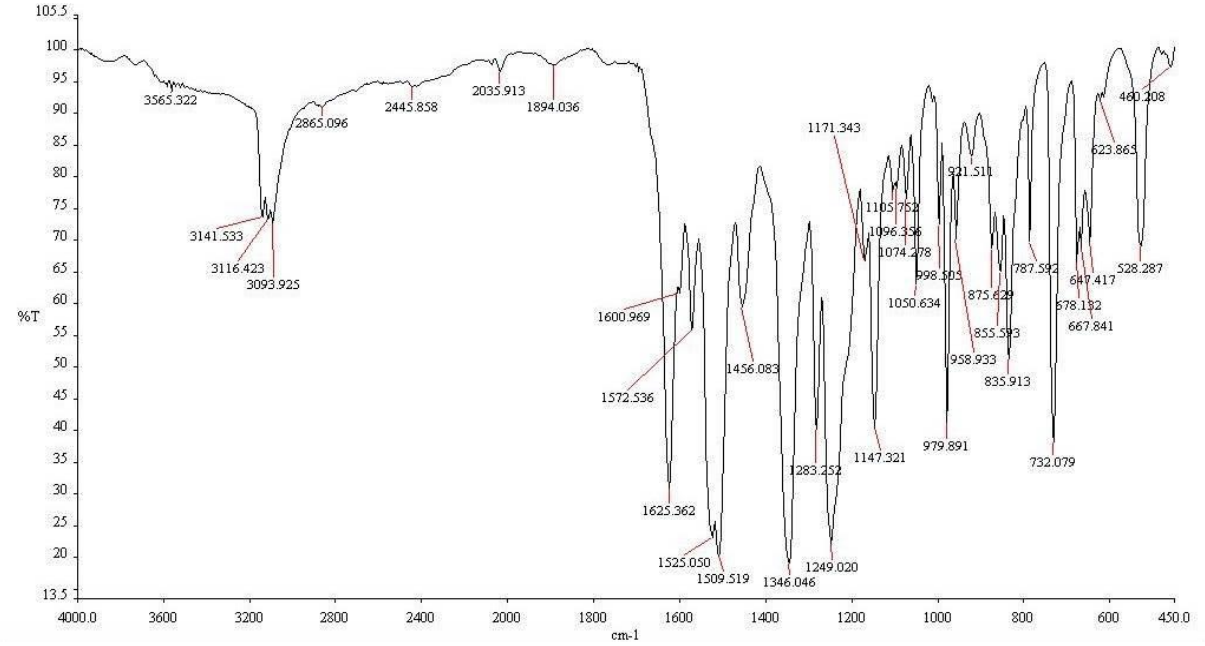

Fig. S22 FT-IR spectrum of compound **1**.

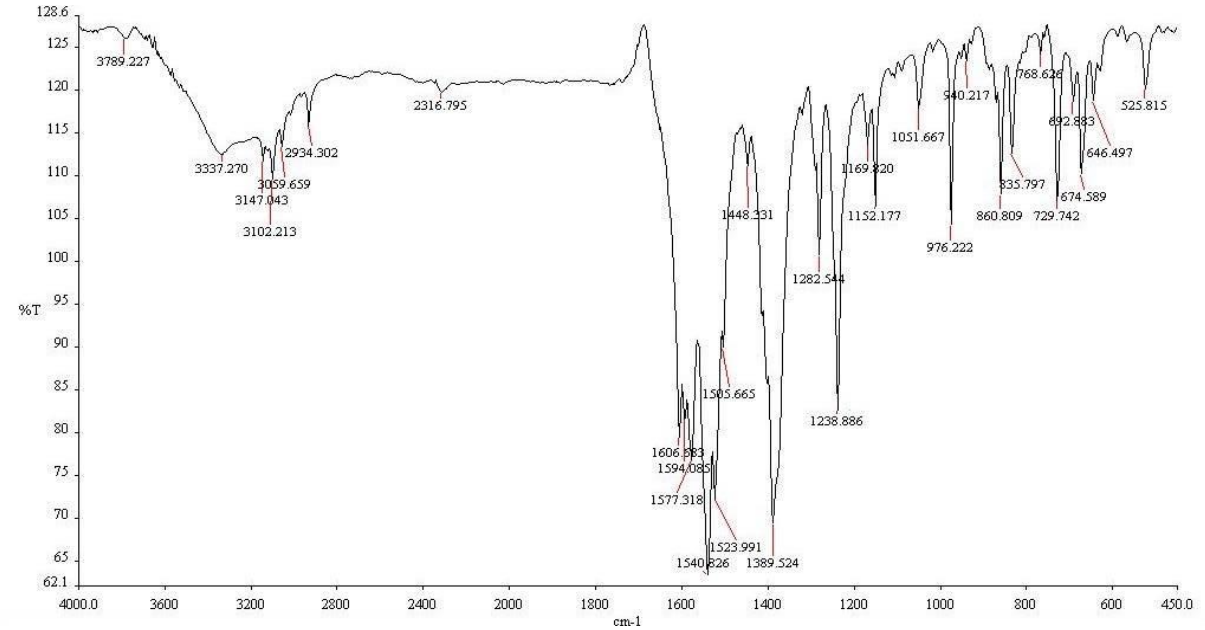

Fig. S23 FT-IR spectrum of compound **2**.

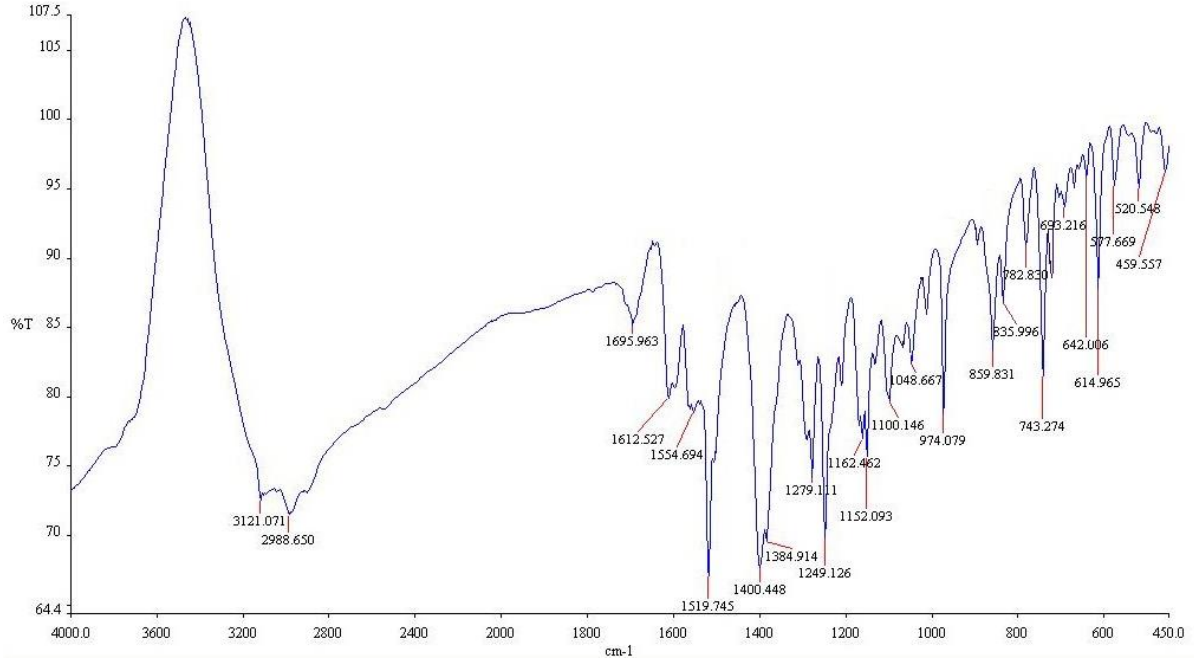

Fig. S24 FT-IR spectrum of compound **3**.

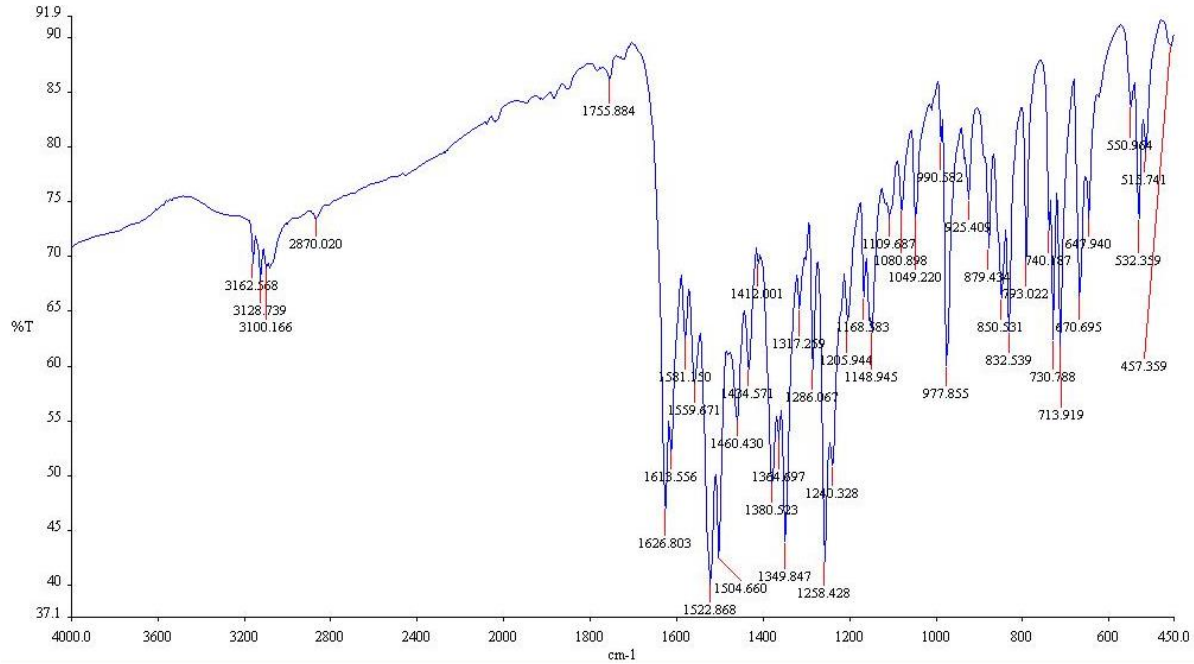

Fig. S25 FT-IR spectrum of compound **4**.

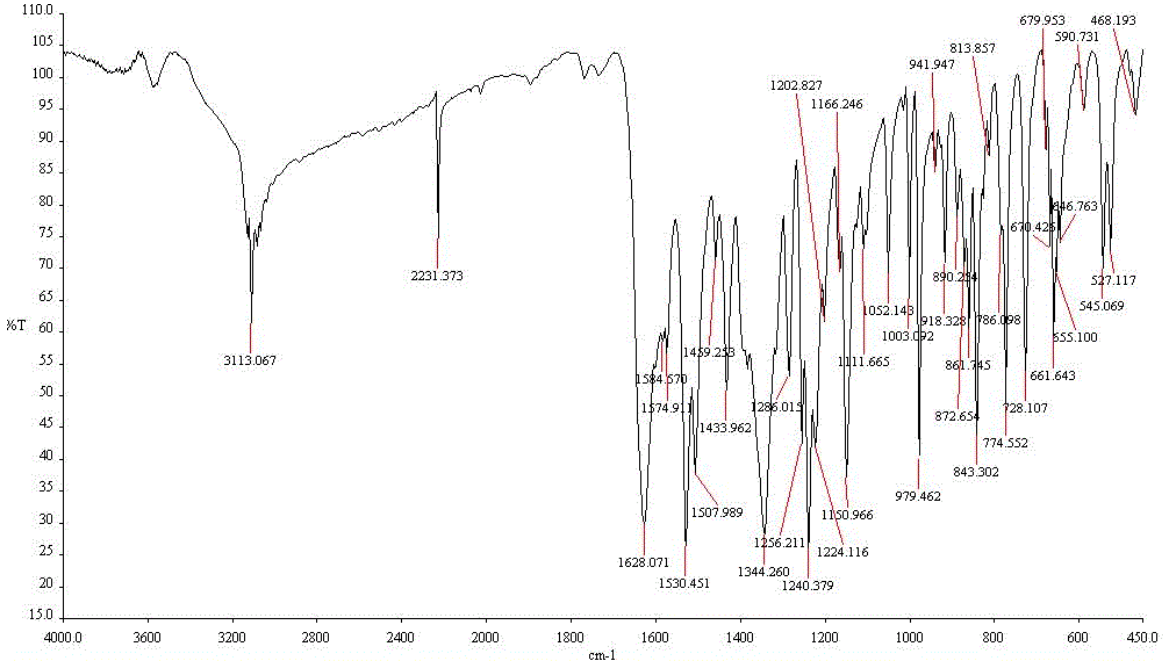

Fig. S26 FT-IR spectrum of compound **5**.

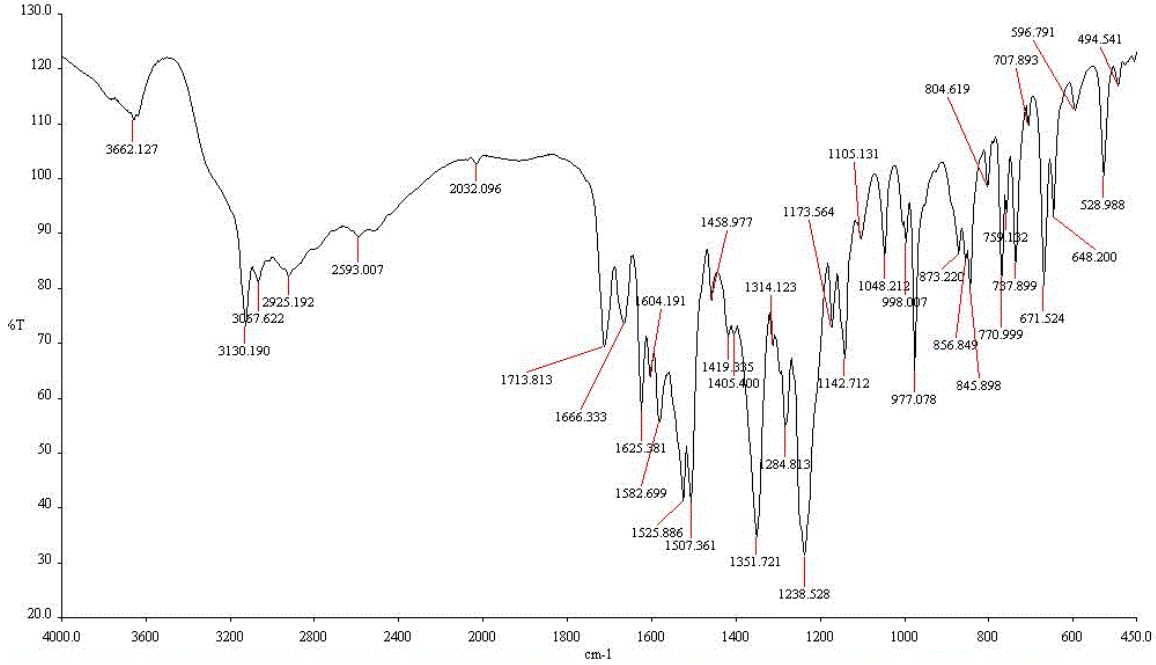

Fig. S27 FT-IR spectrum of compound **6**.

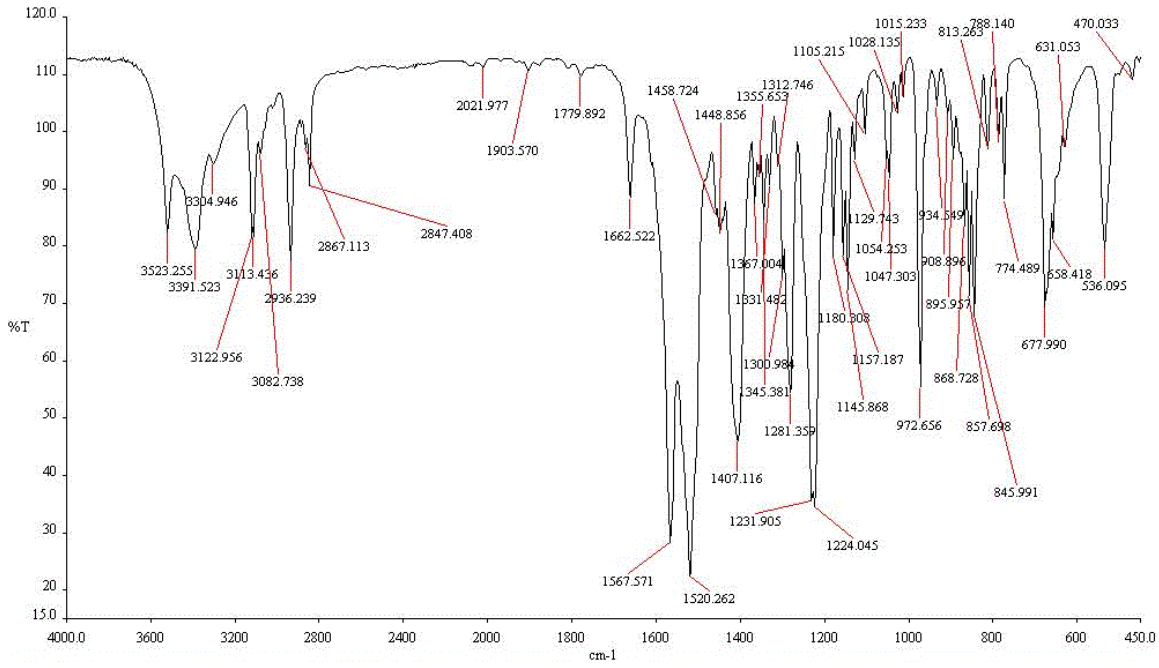

Fig. S28 FT-IR spectrum of compound **7**.

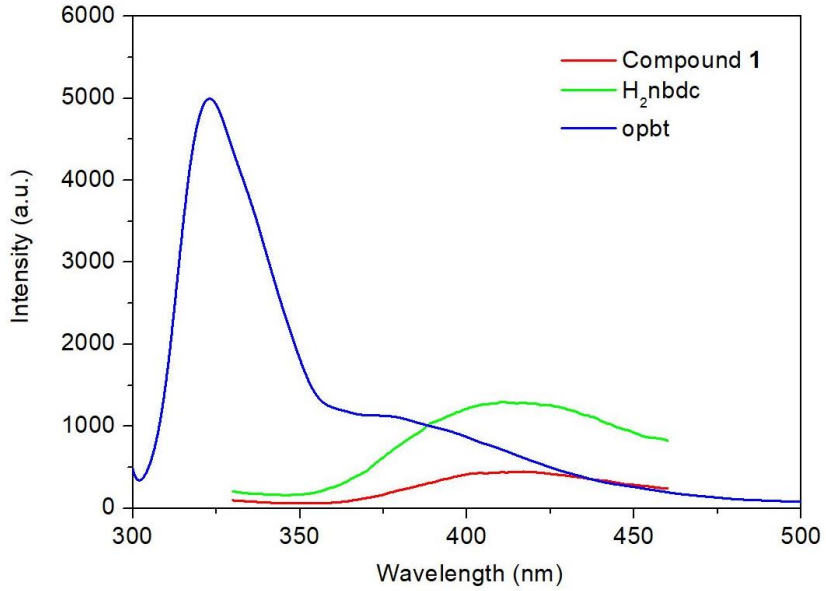

Fig. 29 The solid-state emission spectra of **1** shows the peaks at 417 nm (λ_{ex} = 253 nm), the opbt ligand at 323 nm (λ_{ex} = 290 nm), and 5-nitrobenzene-1,3-dicarboxylic acid (H_2nbdc) at 410 nm (λ_{ex} = 248 nm), respectively.

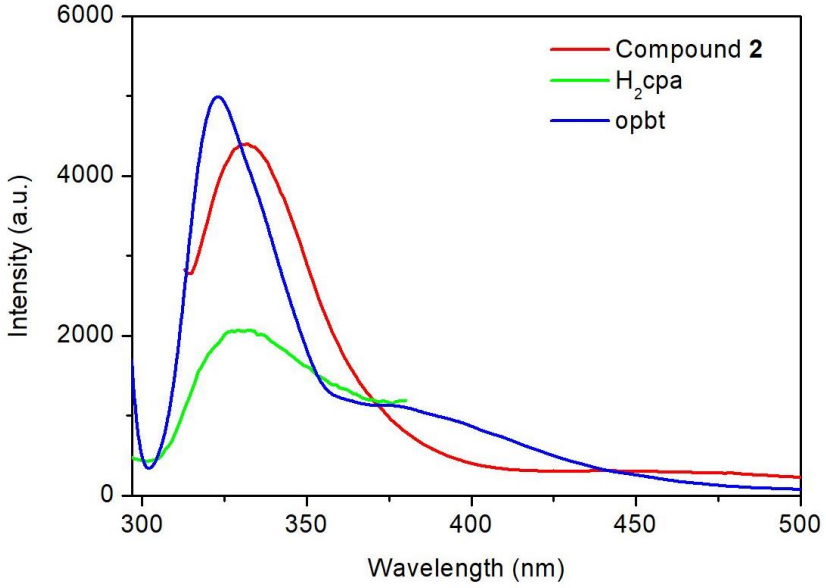

Fig. 30 The solid-state emission spectra of **2** shows the peaks at 330 nm (λ_{ex} = 290 nm), the opbt ligand at 323 nm (λ_{ex} = 290 nm), and 2-carboxyphenylacetic acid (H_2cpa) at 329 nm (λ_{ex} = 246 nm), respectively.

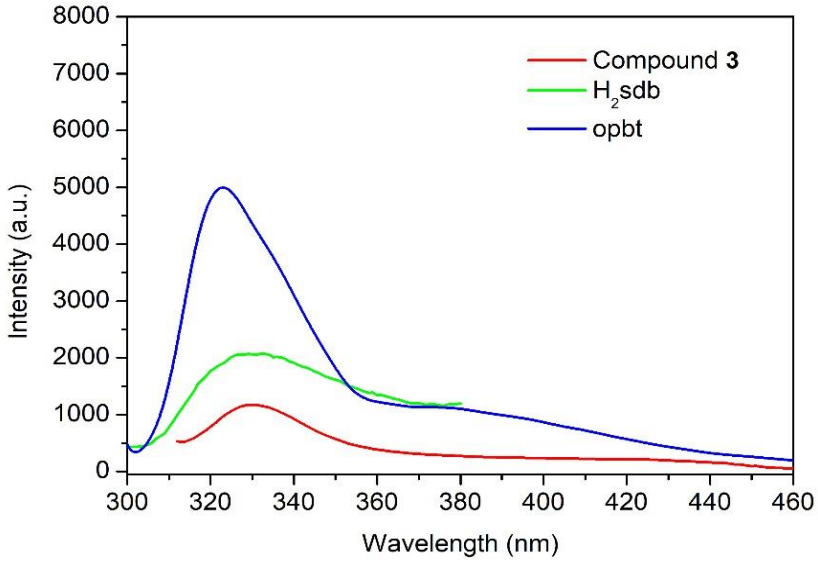

Fig. 31 The solid-state emission spectra of compound **3** shows the peaks at 328 nm (λ_{ex} = 280 nm), opbt ligand at 323 nm (λ_{ex} = 290 nm), and 4,4'-sulfonyldibenzoic acid (H_2sdb) at 332 nm (λ_{ex} = 280 nm), respectively.

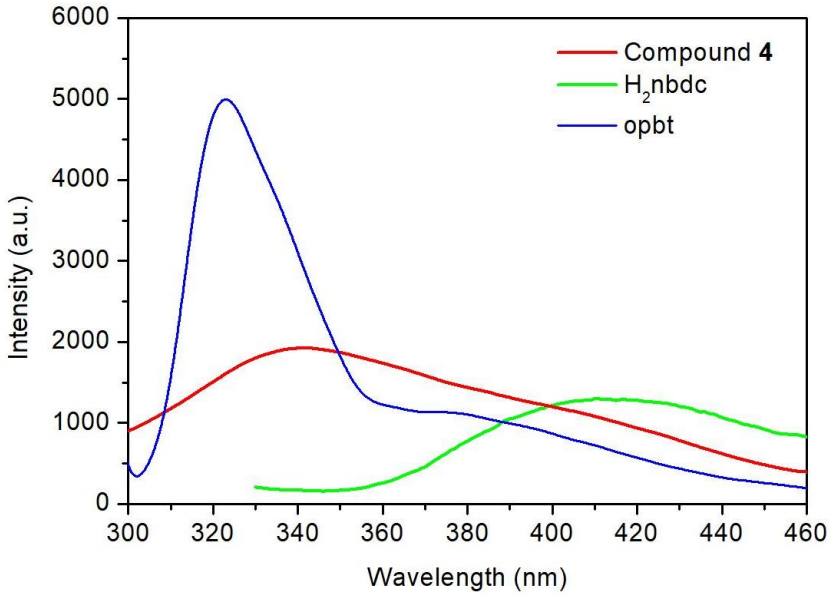

Fig. 32 The solid-state emission spectra of compound **4** shows the peaks at 340 nm (λ_{ex} = 245 nm), opbt ligand at 323 nm (λ_{ex} = 290 nm), and 5-nitrobenzene-1,3-dicarboxylic acid (H_2nbdc) at 410 nm (λ_{ex} = 248 nm), respectively.

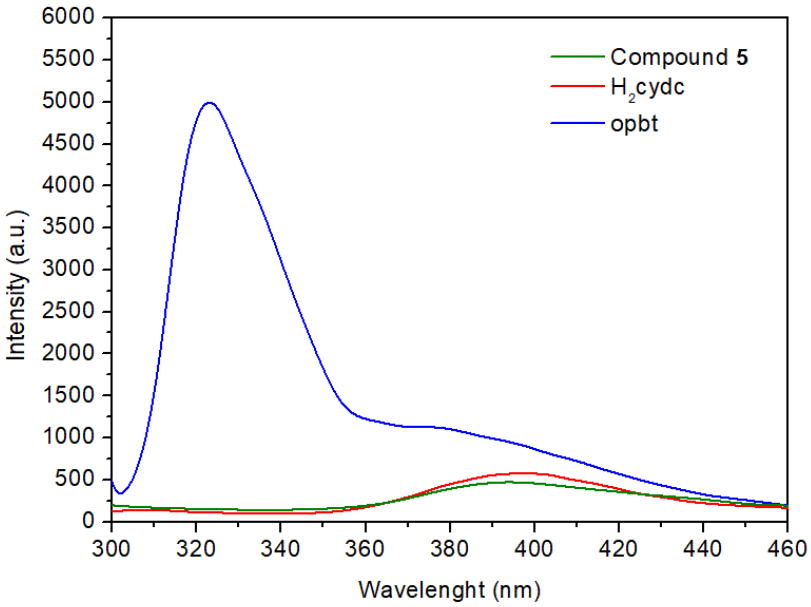

Fig. S33 The solid-state emission spectra of compound **5** shows the peaks at 394 nm (λ_{ex} = 250 nm), opbt ligand at 323 nm (λ_{ex} = 290 nm), and 5-cyano-1,3-benzenedicarboxylic acid (H_2cydc) at 397 nm (λ_{ex} = 250 nm), respectively.

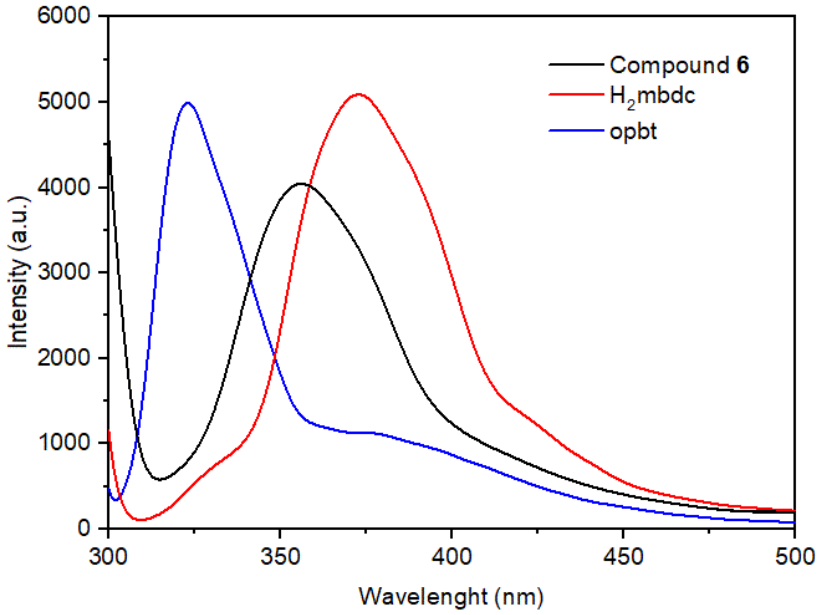

Fig. S34 The solid-state emission spectra of compound **6** shows the peaks at 356 nm (λ_{ex} = 286 nm), opbt ligand at 323 nm (λ_{ex} = 290 nm), and 5-methylbenzene-1,3-dicarboxylic acid (H_2mbdc) at 372 nm (λ_{ex} = 286 nm), respectively.

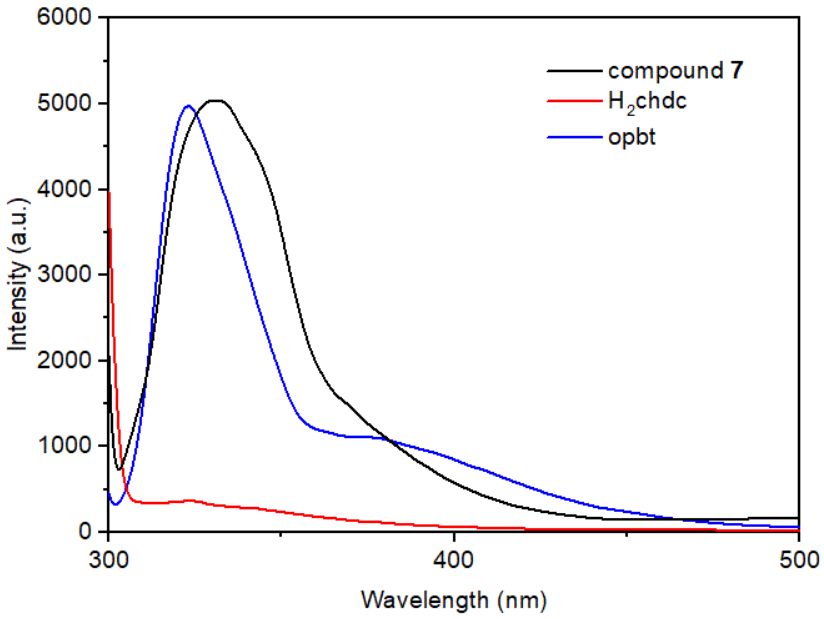

Fig. S35 The solid-state emission spectra of compound **7** shows the peaks at 331 nm (λ_{ex} = 290 nm), opbt ligand at 323 nm (λ_{ex} = 290 nm), and *cis*-1,2-cyclohexanedicarboxylic acid (H_2chdc) at 320 nm (λ_{ex} = 290 nm), respectively.

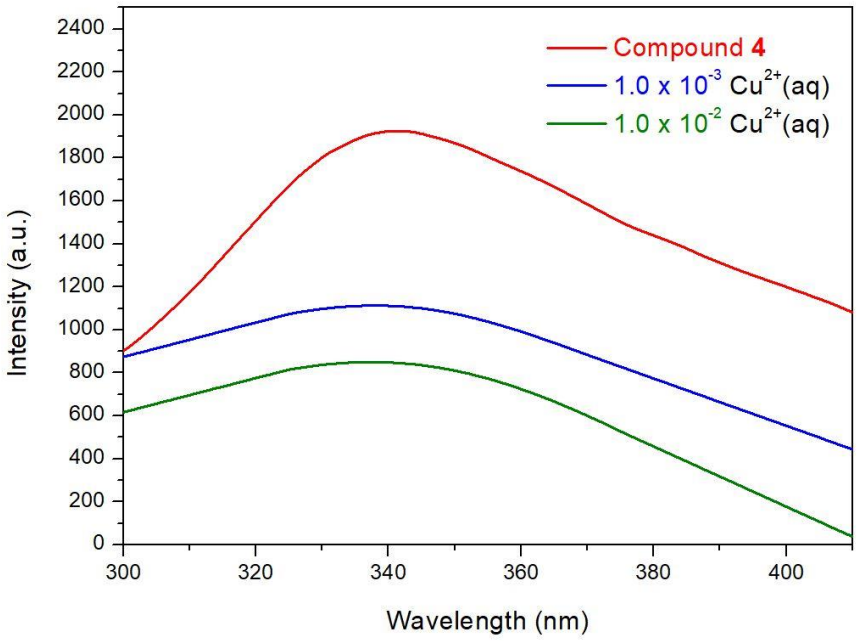

Fig. S36 Luminescence responses in solid state at 340 nm (λ_{ex} = 245 nm) of the compounds **4** and **4***. Two samples of compound **4,** weighting 3.5 mg, were immersed in 10.0 mL of 1.0 x 10^{-3} and 1.0 x 10^{-2} M of $Cu(NO_3)_{2\,(aq)}$, respectively, for one hour at room temperature, upon treatment which were recollected and dried in air for overnight (denoted as **4*)**.

Table S1. The hydrogen bonding distances (Å) and angles (°) of **1**

D—H···A (Å)	**D—H (Å)**	**H···A (Å)**	**D···A (Å)**	**D—H···A (°)**
O8—H8A···N4	0.82(3)	1.88(3)	2.678(3)	165.9(3)
O8—H8B···O2	0.80(2)	1.80(2)	2.648(2)	166.4(3)

Table S2. The hydrogen bonding distances (Å) and angles (°) of **2**

D—H···A (Å)	**D—H (Å)**	**H···A (Å)**	**D···A (Å)**	**D—H···A (°)**
O(10)—H(10B)···O(1)	0.82(2)	1.98(2)	2.781(2)	164.4(2)
C(25)—H(25)···O(2)	0.930(2)	2.318(1)	3.226(2)	165.2(1)

Table S3. The hydrogen bonding distances (Å) and angles (°) of **3**

D—H···A (Å)	**D—H (Å)**	**H···A (Å)**	**D···A (Å)**	**D—H···A (°)**
O(8)—H(8B)···O(4#2)	0.81(4)	1.90(4)	2.701(4)	168.7(4)
O(8)—H(8A)···O(9)	0.81(4)	2.13(4)	2.902(5)	160.3(4)
O(9)—H(9A)···O(1)	0.84(5)	1.94(6)	2.755(5)	162.3(5)
C(30)—H(30)···O(9)	0.930(4)	2.363(4)	3.289(6)	173.4(3)

Table S4. The hydrogen bonding distances (Å) and angles (°) of **4**

D—H···A (Å)	**D—H (Å)**	**H···A (Å)**	**D···A (Å)**	**D—H···A (°)**
C(12)—H(12)···O(12)	0.930(4)	2.491(3)	3.292(4)	144.4(2)

Table S5. The hydrogen bonding distances (Å) and angles (°) of **5**

D—H···A (Å)	**D—H (Å)**	**H···A (Å)**	**D···A (Å)**	**D—H···A (°)**
O(6)—H(6A)···O(4#1)	0.810(2)	2.38(4)	3.043(4)	139.7(3)
O(6)—H(6B)···O(2B)	0.810(2)	2.17(5)	3.968(1)	171.5(2)
C(16)—H(16)···O(4#1)	0.931(4)	2.69(3)	3.126(5)	139.7(3)
C(16)—H(16)···O(2B)	0.931(4)	2.41(4)	3.174(5)	139.1(2)
C(17)—H(17)···O(6)	0.931(4)	2.79(1)	3.138(1)	103.1(3)

Table S6. Selected bond lengths [Å] and angles [°] for **1–7**

1					
Zn(1)−O(1)	1.9476(16)	Zn(1)−O(3)#1	1.9629(16)	O(1)−Zn(1)−N(1)	121.07(7)
Zn(1)−O(8)	2.001(2)	Zn(1)−N(1)	2.028(2)	O(1)−Zn(1)−O(3)#1	124.37(7)
O(8)−Zn(1)−N(1)	99.00(8)	O(1)−Zn(1)−O(8)	103.12(8)	O(3)#1−Zn(1)−O(8)	111.29(8)
O(3)#1−Zn(1)−N(1)	95.48(7)				
2					
Cd(1)−N(1)	2.3059(14)	Cd(1)−O(5)	2.3836(11)	Cd(2)−N(4)#3	2.3209(15)
Cd(1)−O(8)#2	2.2851(13)	Cd(1)−O(6)	2.4575(12)	Cd(2)−O(10)	2.2448(12)
Cd(1)−O(3)#1	2.2379(12)	Cd(2)−O(7)	2.2941(12)	Cd(2)−O(2)	2.2569(12)
Cd(1)−O(1)	2.3663(12)	Cd(2)−O(5)	2.2954(11)	Cd(2)−O(4)#1	2.2764(12)
N(1)−Cd(1)−O(5)	132.15(4)	O(1)−Cd(1)−O(5)	95.75(4)	O(5)−Cd(2)−N(4)#3	85.91(5)
N(1)−Cd(1)−O(6)	79.90(5)	O(3)#1−Cd(1)−O(6)	150.06(4)	O(7)−Cd(2)−N(4)#3	92.85(5)
O(1)−Cd(1)−O(6)	98.27(4)	O(10)−Cd(2)−O(2)	93.52(5)	O(2)−Cd(2)−N(4)#3	174.31(5)
O(5)−Cd(1)−O(6)	54.06(4)	O(10)−Cd(2)−O(5)	177.96(4)	O(10)−Cd(2)−N(4)#3	92.16(5)
3					
Cd(1)−N(1)	2.360(3)	Cd(1)−O(8)	2.322(3)	Cd(1)−O(2)	2.386(3)
Cd(1)−N(4)#1	2.286(3)	Cd(1)−O(4)#2	2.326(3)	Cd(1)−O(3)#2	2.462(3)
Cd(1)−O(1)	2.546(3)	O(8)−Cd(1)−N(1)	85.73(11)	N(4)#1−Cd(1)−N(1)	165.41(12)
O(8)−Cd(1)−O(2)	136.18(11)	O(8)−Cd(1)−O(1)	84.58(10)	N(4)#1−Cd(1)−O(2)	91.44(11)
N(1)−Cd(1)−O(2)	94.75(11)	N(4)#1−Cd(1)−O(4)#2	106.12(11)	N(4)#1−Cd(1)−O(3)#2	106.19(11)
O(2)−Cd(1)−O(3)#2	133.11(10)	O(4)#2−Cd(1)−N(1)	88.06(11)	N(1)−Cd(1)−O(3)#2	78.94(11)
O(8)−Cd(1)−O(4)#2	144.94(10)	O(4)#2−Cd(1)−O(1)	127.29(10)	O(3)#2−Cd(1)−O(1)	155.48(10)
4					
Co(1)−O(1)	2.045(2)	Co(2)−O(9)#5	2.159(2)	O(1)−Co(1)−O(2)#1	104.61(8)
Co(1)−O(2)#1	2.056(2)	Co(2)−O(10)#5	2.212(2)	O(1)−Co(1)−N(9)	95.05(9)
Co(1)−O(3)#2	2.169(2)	Co(1)−N(3)	2.113(3)	O(2)#1−Co(1)−N(9)	90.70(9)
Co(1)−O(4)#2	2.198(2)	Co(1)−N(9)	2.110(2)	O(1)−Co(1)−N(3)	86.35(9)
Co(2)−O(8)#3	2.050(2)	Co(2)−N(6)	2.122(2)	O(2)#1−Co(1)−N(3)	86.47(9)
Co(2)−O(7)	2.048(2)	Co(2)−N(12)#4	2.121(3)	N(9)−Co(1)−N(3)	177.08(10)
O(1)−Co(1)−O(3)#2	158.35(8)	N(9)−Co(1)−O(3)#2	86.69(8)	O(1)−Co(1)−O(4)#2	97.79(8)
O(2)#1−Co(1)−O(3)#2	96.94(8)	N(3)−Co(1)−O(3)#2	92.95(8)	O(2)#1−Co(1)−O(4)#2	156.62(8)
O(7)−Co(2)−N(6)	96.46(9)	O(8)#3−Co(2)−N(12)#4	86.96(9)	O(8)#3−Co(2)−O(9)#5	97.47(8)
O(7)−Co(2)−O(8)#3	105.28(8)	O(8)#3−Co(2)−N(6)	88.77(9)	O(7)−Co(2)−O(9)#5	157.10(8)
O(8)#3−Co(2)−N(12)#4	86.86(9)	N(12)#4−Co(2)−N(6)	175.16(10)	N(12)#4−Co(2)−O(9)#5	91.80(9)
N(6)−Co(2)−O(9)#5	86.50(9)	O(7)−Co(2)−O(10)#5	96.50(8)	O(7)−Co(2)−O(10)#5	157.31(8)
5					
Zn(1)−N(2)	2.027(3)	Zn(1)−O(1A)	1.99(4)	O(4)#1−Zn(1)−N(5)#2	119.28(11)
Zn(1)−O(4)#1	1.999(2)	Zn(1)−N(5)#2	2.015(3)	O(4)#1−Zn(1)−N(2)	95.86(11)
O(1A)−Zn(1)−O(4)#1	121.4(8)	O(1A)−Zn(1)−N(2)	116.1(1)	N(5)#2−Zn(1)−N(2)	104.88(12)
O(1A)−Zn(1)−N(5)#2	99.2(8)				
6					
Zn(1)−N(1)	2.017(4)	Zn(1)−O(1)	1.991(3)	Zn(1)−O(4)#1	1.970(3)
Zn(1)−N(4)#2	2.009(3)	O(1)−Zn(1)−N(1)	112.55(14)	O(4)#1−Zn(1)−N(4)#2	110.58(13)
O(1)−Zn(1)−N(4)#2	110.26(13)	O(4)#1−Zn(1)−N(1)	110.57(14)	N(4)#2−Zn(1)−N(1)	111.80(15)
7					
Cd(1)−N(1)	2.3421(19)	Cd(1)−O(2)	2.3718(15)	Cd(1)−N(4)#3	2.3727(19)
Cd(1)−O(1)	2.4825(15)	Cd(1)−O(4)#2	2.3227(16)	Cd(1)−O(2)#1	2.3132(16)
O(2)#1−Cd(1)−O(4)#2	95.20(6)	O(4)#2−Cd(1)−N(4)#3	100.66(6)	N(1)−Cd(1)−O(1)	76.16(6)
O(2)#1−Cd(1)−N(1)	105.14(6)	N(1)−Cd(1)−N(4)#3	81.53(6)	O(2)−Cd(1)−O(1)	53.66(5)
O(4)#2−Cd(1)−N(1)	159.64(6)	O(2)−Cd(1)−N(4)#3	148.85(6)	N(1)−Cd(1)−O(3)#2	105.66(6)
O(4)#2−Cd(1)−O(2)	102.82(6)	O(2)#1−Cd(1)−O(3)#2	143.57(5)	O(4)#2−Cd(1)−O(1)	91.87(5)
N(1)−Cd(1)−O(2)	83.49(6)	O(4)#2−Cd(1)−O(3)#2	55.65(5)	N(4)#3−Cd(1)−O(3)#2	79.11(6)
O(2)#1−Cd(1)−N(4)#3	86.69(6)	O(2)#1−Cd(1)−O(1)	124.49(5)	N(4)#3−Cd(1)−O(1)	145.34(6)

[a]Symmetry transformations used to generate equivalent atoms, for **1**: #1 x, y – 1, z; for **2**, #1 –x + 2, –y, –z, #2 x + 1, y, z, #3 –x + 7/2, y + 1/2, –z + 1/2; for **3**, #1 –x + 3, y – 1/2, –z + 3/2, #2 x, –y + 1/2, z + 1/2; for **4** #1 –x + 1, –y – 2, –z + 1, #2 x – 1, y, z, #3 –x, –y, –z, #4 x, y + 2, z – 1, #5 x + 1, y, z; for **5** #1 x, –y + 3/2, z – 1/2, #2 x + 1, –y + 1/2, z + 1/2; for **6** #1 x – 1, y, z, #2 x – 1, y, z – 1; for **7** #1 –x + 1, –y + 1, –z + 1, #2 –x + 1, –y + 2, –z + 1, #3 x, –y, z + 1/2.