Divalent zinc and cadmium coordination polymers of a new flexible tetracarboxylate ligand: syntheses, crystal structures and properties[†]

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A series of seven metal-organic frameworks, namely, $\{[Zn_4(bptc)_2(bpp)_2]\cdot 3.5H_2O\}_n$ (1), $\{[Zn_2(bptc)(bix)] \cdot H_2O\}_n$ (2), $\{[Zn_2(bptc)(bpe)_{1.5}(H_2O)_3] \cdot H_2O\}_n$ (3), $[Zn_2(Hbptc)(\mu_3 - OH)(4, 4'-bpy)]_n$ (4), $[Cd_2(bptc)(bpa)_2(H_2O)]_n$ (5), $[Cd_2(bptc)(bpp)_2(H_2O)_2]_n$ (6), $\{[Cd_4(bptc)_2(bix)_2(H_2O)_2] \cdot 4.5H_2O\}_n$ (7) (bptc = 2, 2', 3, 3'benzophenonetetracarboxylate), have been hydro(solvo)thermally synthesized through the reaction of 2,2',3,3'-benzophenone tetracarboxylic dianhydride (2,2',3,3'-bptda) with divalent zinc and cadmium salts in the presence of ancillary nitrogen ligands (bpa = 1,2-bis(4-pyridyl)ethane, bpe =1,2-bis(4-pyridyl)ethene, bpp = 1,3-bi(4-pyridyl)propane, bix = 1,4-bis(imidazol-1-ylmethyl)benzene, and bpy = 4,4' bipyridine). Due to various coordination modes and conformations of the versatile 2,2',3,3'-bptc ligand and co-ligands, these complexes exhibit structural and dimensional diversity. In compounds 1–5, M–bptc (M = Zn or Cd) ribbons are connected together through bpp, bix, bpe, bpy and bpa, respectively, to form metal-organic sheets, which are then united together to generate 3D supramolecular structures through interlayer hydrogen bonding, $C-H\cdots\pi$, or $\pi\cdots\pi$ interactions. In the structure of 4, the ribbon is formed from interlaced coaxial meso-helical Zn-Hbptc chains, and the meso-helical chains are stabilized by the bpa co-ligand in 5. Compound 6 features a 3D metal-organic framework in which $[Cd_2(bptc)]_n$ meso-helices are bridged by bpp ligands to exhibit a (2,6,2)-connected self-penetrating network with the Schläfli symbol $(12)(4^212^916^4)(4)_2$. Compound 7 also exhibits a 3D metal-organic framework in which $[Cd_2(bptc)]_n$ layers are connected by pillared bix ligands to yield a (4,4,8)-connected network with the Schläfli symbol (4¹⁶6¹²)(4⁴6²)(4⁴6²)₂. Compounds 1 and 7 display intense blue fluorescence emissions at 460 and 465 nm, respectively, and may be suitable as excellent candidates of blue fluorescent materials.

Introduction

The construction of coordination polymers with helical topologies has aroused a great deal of attention^{1,2} owing to the wide appearance of helical structures in, for example, proteins, collagens, quartz, single-walled carbon nanotubes (SWNTs) and many more natural or artificial fiber-type derivatives.³ Its correlative topology is the *meso*-helix which can be described as resulting from helical reversal every half-turn of the helix.⁴ The composite chain is formed by the alternation of helical conformers of opposite chirality instead of molecules of the same chirality in a typical helix. Up to now, knowledge about the *meso*-helical system has remained largely unexplored and only limited examples have been reported.^{4,5}

Carboxylate-based ligands have been successfully employed in the generation of many interesting systems exhibiting multidimensional networks and useful properties.⁶ In the last few years, a new family of multidentate O-donor ligands with a semirigid V-shaped molecular conformation, including 1,1'-biphenyl2,2'3,3'-tetracarboxyl acid, 2,2',3,3'-oxidiphthalic acid, isomeric 2,2',3,3'- and 2,3,3',4'-thiaphthalic dianhydride, as well as 4,4'- (hexafluoroisopropylidene) diphthalic acid, have been used to construct MOFs, leading to interesting structures including helices and interpenetrating networks that have potential applications in the field of separation, absorption, catalysis, and sensing.⁷⁻⁹

In the present study, we constructed a series of coordination polymers of the new ligand 2,2',3,3'-benzophenone tetracarboxylic acid (H₄bptc), which was generated from 2,2',3,3'-bptda (2,2',3,3'benzophenone tetracarboxylic dianhydride)¹⁰ (Scheme 1) under hydro(solvo)thermal conditions. Ligand H₄bptc possesses the following advantageous characteristics. (a) Its four carboxyl groups may be completely or partially deprotonated, allowing it to exhibit a rich variety of coordination modes in generating interesting structural types of higher dimensions. (b) Possessing possible *syn* and *anti* conformations (Scheme 2) and multiple bridging moieties, bptc may be an excellent candidate for the construction of multi-dimensional coordination polymers, especially 2D and



Scheme 1 Structural formula of 2,2',3,3'-bptda (2,2',3,3'-benzophenone tetracarboxylic dianhydride).

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Scheme 2 Syn and anti conformations of 2,2',3,3'-benzophenone tetracarboxylic acid (H₄bptc).

3D metal–organic frameworks. (c) Steric hindrance of the 2and 2'-positioned carboxylate groups and the skew coordination orientation of the carboxylate groups tend to induce the formation of helical segments. (d) Though a few coordination polymers based on its isomer ligand 3,3',4,4'-bptc (3,3',4,4'-benzophenone tetracarboxylic acid)⁴ have been reported, the metal–organic frameworks constructed from 2,2',3,3'-bptc have not been reported to date. Herein we undertake synthetic and structural studies on a series of seven divalent zinc and cadmium complexes of 2,2',3,3'-bptc with co-existing nitrogen heterocyclic ligands: $\{[Zn_4(bptc)_2(bpp)_2]\cdot3.5H_2O\}_n(1), \{[Zn_2(bptc)(bix)]\cdotH_2O\}_n (2),$ $\{[Zn_2(bptc)(bpe)_{1.5}(H_2O)_3]\cdotH_2O\}_n (3), [Zn_2(Hbptc)(\mu_3-OH)(4,4'$ $byy)]_n (4), [Cd_2(bptc)(bpa)_2(H_2O)]_n (5), [Cd_2(bptc)(bpp)_2(H_2O)_2]_n$ $(6), {[Cd_4(bptc)_2(bix)_2(H_2O)_2]\cdot4.5H_2O}_n (7).$

Experimental

Materials and general procedures

Ligand 2,2',3,3'-bptda was prepared according to the literature procedure,¹⁰ and all other starting materials were of analytical grade as obtained from commercial sources without further purification.

Syntheses of metal complexes

{ $[Zn_4(bptc)_2(bpp)_2]$ -3.5H₂O}, (1). A mixture of 2,2',3,3'-bptda (0.0170 g, 0.05 mmol), bpp (0.0198 g, 0.1 mmol), Zn(NO₃)₂·6H₂O (0.0297 g, 0.1 mmol), and NaOH (0.0080 g, 0.2 mmol) in distilled water (7 mL) was placed in a Teflon-lined stainless steel vessel, heated to 120 °C for 3 days, and then cooled to room temperature. Colorless block-like crystals of **1** were obtained in 84% yield based on zinc. Anal. Calc. for C₆₀H₄₇N₄O_{21.5}Zn₄(1429.50): C, 50.40; H, 3.31; N, 3.92%. Found: C, 50.35; H, 3.27; N, 3.95%. IR/cm⁻¹ (KBr): 3447(s), 2937(w), 1622(s), 1554(s), 1392(s), 1268(w), 1018(w), 778(m), 706(m), 670(m).

 $\{[Zn_2(bptc)(bix)]\cdot H_2O\}_n$ (2). The procedure is similar to the synthesis of 1 except that bix (0.0238 g, 0.1 mmol) was used instead of bpp. Yield: 69% based on zinc. Anal. Calc. for $C_{31}H_{22}N_4O_{10}Zn_2$ (741.27): C, 50.23; H, 2.99; N, 7.56%. Found: C, 50.17; H, 2.95; N, 7.51%. IR/cm⁻¹ (KBr): 3045(m), 3108(m), 1684(m), 1617(s), 1560(s), 1399(s), 1379(s), 1242(w), 1115(w), 764(w), 710(w).

 $[Zn_2(bptc)(bpe)_{1.5}(H_2O)_3 \cdot H_2O]_n$ (3). The procedure is similar to the synthesis of 1 except that bpe (0.0182 g, 0.1 mmol) was used instead of bpp. Yield: 82% based on zinc. Anal. Calc. for $C_{35}H_{29}N_3O_{13}Zn_2$ (830.35): C, 50.62; H, 3.52; N, 5.06%. Found:

C, 50.69; H, 3.48; N, 5.01%. IR/cm⁻¹ (KBr): 3431(m), 3160(w), 1666(w), 1614(s), 1580(w), 1453(m), 1365(s), 1268(m), 831(s), 777(m).

 $[Zn_2(Hbptc)(\mu_3-OH)(4,4'-bpy)]_n$ (4). The procedure is similar to the synthesis of 1 except that 4,4'-bpy (0.0192 g, 0.1 mmol) was used instead of bpp. Yield: 92% based on zinc. Anal. Calc. for $C_{27}H_{16}N_2O_{10}Zn_2$ (659.16): C, 49.19; H, 2.45; N, 4.25%. Found: C, 49.10; H, 2.38; N, 4.19%. IR/cm⁻¹ (KBr): 3563(s), 3448(w), 3082(w), 1664(m), 1603(s), 1566(s), 1398(m), 1384(s), 1263(m), 813(m), 639(m).

 $[Cd_2(bptc)(bpa)_2(H_2O)]_n$ (5). The procedure is similar to the synthesis of 1 except that $Cd(NO_3)_2 \cdot 4H_2O$ (0.0308 g, 0.1 mmol) and bpa (0.0184 g, 0.1 mmol) was used instead of $Zn(NO_3)_2 \cdot 6H_2O$ and bpp. Yield: 75% based on cadmium. Anal. Calc. for $C_{41}H_{34}Cd_2N_4O_{11}$ (983.52): C, 50.07; H, 3.48; N, 5.70%. Found: C, 50.13; H,3.39; N, 5.61%. IR/cm⁻¹ (KBr): 3365(s), 1673(m), 1612(w), 1569(s), 1385(s), 1268(s), 1227(m), 1017(s), 767(m), 705(s).

 $[Cd_2(bptc)(bpp)_2(H_2O)_2]_n$ (6). The procedure is similar to the synthesis of 1 except that $Cd(NO_3)_2 \cdot 4H_2O$ (0.0308 g, 0.1 mmol) was used instead of $Zn(NO_3)_2 \cdot 6H_2O$. Yield: 78% based on cadmium. Anal. Calc. for $C_{43}H_{38}Cd_2N_4O_{11}$ (1011.57): C, 51.05; H, 3.79; N, 5.54%. Found: C, 50.98; H, 3.83; N, 5.49%. IR/cm⁻¹ (KBr): 3405(s), 1672(w), 1612(m), 1592(w), 1572(s), 1457(w), 1430(w), 1384(s), 1281(w), 1018(w), 760(w), 703(w).

{[$Cd_4(bptc)_2(bix)_2(H_2O)_2$]·4.5 H_2O }, (7). The procedure is similar to the synthesis of 1 except that $Cd(NO_3)_2$ ·4 H_2O (0.0308 g, 0.1 mmol) and bix (0.0238 g, 0.1 mmol) was used instead of $Zn(NO_3)_2$ ·6 H_2O and bpp. Yield: 83% based on cadmium. Anal. Calc. for $C_{62}H_{33}Cd_4N_8O_{24.50}(1751.72)$; C, 42.51; H, 3.05; N, 6.40%. Found: C, 42.59; H, 2.99; N, 6.33%. IR/cm⁻¹ (KBr): 3423(m), 3113(s), 2938(w), 1684(m), 1557(s), 1454(m), 1385(s), 1266(m), 1083(w), 1016(w), 774(w), 720(m).

Physical measurements. Elemental analysis for C, H and N were performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range from 4000 to 400 cm⁻¹ on a Bruker VECTOR 22 spectrometer. Thermal analysis was performed on a SDT 2960 thermal analyzer from room temperature to 800 °C with a heating rate of 20 °C min⁻¹ under nitrogen flow. Luminescence spectra for the solid samples were recorded on a Hitachi 850 fluorescence spectrophotometer.

X-Ray crystallography. Single-crystal X-ray analyses were conducted on a Bruker SMART APEX CCD diffractometer¹¹ using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) at room temperature using the ω -scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods with SHELXS-97¹² and refined with the full-matrix least-squares technique using the SHELXL-97¹³ program. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms of the coordination water molecules, hydroxide groups and ligands were included in the structure factor calculation at idealized positions by using a riding model and refined isotropically. The hydrogen atoms of the solvent water molecules were located from the difference Fourier maps, then restrained at fixed positions and refined isotropically. Analytical expressions of neutral atom scattering factors were employed, and anomalous

 Table 1
 Crystal data and structure refinement details for 1–7

	1	2	3	4	5	6	7
Formula	$C_{60}H_{47}N_4O_{2150}Zn_4$	$C_{31}H_{22}N_4O_{10}Zn_2$	$C_{35}H_{29}N_3O_{13}Zn_2$	$C_{27}H_{16}N_2O_{10}Zn_2$	$C_{41}H_{34}Cd_2N_4O_{11}$	$C_{43}H_{38}Cd_2N_4O_{11}$	C ₆₂ H ₅₃ Cd ₄ N ₈ O _{24 50}
$M_{\rm r}$	1429.50	741.27	830.35	659.16	983.52	1011.57	1751.72
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\overline{1}$	$P\overline{1}$	$P2_{1}/c$	C2/c	$P\overline{1}$	$P\overline{1}$
a/Å	11.4663(14)	10.9889(7)	10.966(2)	11.0753(7)	21.3161(10)	11.6833(13)	11.659(2)
b/Å	11.4985(14)	11.4124(7)	10.974(2)	8.7427(6)	12.4028(10)	12.4887(14)	11.789(2)
c/Å	12.4691(15)	12.3293(8)	14.562(3)	24.9801(16)	18.6010(10)	16.2276(18)	12.945(3)
$\alpha / ^{\circ}$	93.944(2)	80.8810(10)	84.32(3)	90	90	71.931(2)	70.39(3)
$\beta/^{\circ}$	108.388(2)	84.8950(10)	87.14(3)	97.0080(10)	111.7400(10)	74.323(2)	67.92(3)
$\gamma/^{\circ}$	94.247(2)	68.2990(10)	71.83(3)	90	90	69.001(2)	85.77(3)
$V/Å^3$	1548.4(3)	1417.69(16)	1656.5(5)	2400.7(3)	4567.9(5)	2067.5(4)	1550.5(5)
Ζ	1	2	2	4	4	2	1
$D_{\rm c}/{\rm g~cm^{-3}}$	1.533	1.736	1.665	1.824	1.430	1.625	1.876
F(000)	727	752	848	1328	1968	1016	869
Refins collected	7905	7247	16776	11731	11270	10447	15743
Independent refins	5402	4929	5831	4225	4027	7160	5440
$R_{\rm int}$	0.1042	0.0581	0.0266	0.0913	0.0710	0.0795	0.0342
GOF on F^2	1.058	0.878	1.043	0.896	1.071	0.960	1.167
$R_1^a (I > 2\sigma(I))$	0.0662	0.0431	0.0328	0.0457	0.0290	0.0462	0.0487
$WR_2^a (I > 2\sigma(I))$	0.1652	0.0681	0.0806	0.0872	0.0738	0.1093	0.1400
$\Delta \rho_{\rm max/min}/{\rm e}~{\rm \AA}^{-3}$	1.150/-0.730	0.444/-0.549	0.962/-0.354	0.825/-0.674	0.659/-0.848	1.154/-0.860	0.902/-0.787

dispersion corrections were incorporated. The crystallographic data and selected bond lengths for 1–7 are listed in Table 1 and 2.

Results and discussion

Syntheses

The reaction of 2,2',3,3'-H₄bptc with divalent zinc and cadmium ions under hydro(solvo)thermal conditions usually vielded only white precipitates. Although detailed studies are still required to better understand this phenomenon, we propose that the rate of polymerization of M(II) (M = Zn or Cd) ions with 2,2',3,3'-H₄bptc is too fast to obtain crystalline products. Hydrolysis of 2,2',3,3'-bptda not only reduces the rate of crystallization that may promote crystal growth of the product formed, but may also produce H₃bptc⁻, H₂bptc²⁻, Hbptc³⁻ and bptc⁴⁻ species, which facilitate the construction of high-dimensional metal-organic hybrid compounds. In the "mix-ligand" method for the design of high-dimensional MOFs,14 judicial selection of a co-ligand is important in the construction of the resulting architecture. In our investigation of the coordination chemistry of 2,2',3,3'-bptda, we have selected a series of five nitrogen heterocyclic ligands as ancillaries, namely bpy, bpe, bpa, bpp and bix.

Crystal structures

{[Zn₄(bptc)₂(bpp)₂]·3.5H₂O}_n (1). As shown in Fig. 1a, this compound consists of two types of Zn^{II} cations, one type of bptc⁴⁻ anion, one type of bpp ligand, and uncoordinated water molecules. The coordination mode of μ_5 - η^2 : η^2 : η^2 : η^1 for 2,2',3,3'-bptc⁴⁻ is found in compound 1, in which the anion takes a *trans*-conformation with four carboxylate groups coordinating to five Zn^{II} cations (Scheme 3a). The 2-, 2'- and 3'-COO⁻ groups of the bptc⁴⁻ anion are exobidentate and the 3-COO⁻ group is monodentate. As for bptc⁴⁻, the dihedral angle between two phenyl



Scheme 3 Coordination modes of the bptc⁴⁻ anions in 1 and 2 (a), 4 (c), 5 and 6 (d) and 7 (e), and the Hbptc³⁻ anion in 3 (b). Color code: C gray, O red, H green, Zn turquoise, Cd celatom.

rings is 82.2°, and the four carboxylate groups (2-, 2'-, 3- and 3'-COO⁻) have dihedral angles of 89.2, 76.8, 4.2 and 22.8° with the planes of corresponding linked benzene rings, respectively. The Zn1 center takes a distorted-tetrahedral geometry involving three carboxylate O atoms from two different bptc⁴⁻ anions and one N atom from a bpp ligand. In contrast, Zn2 adopts a distorted square-pyramidal geometry with a Addison trigonality factor $\tau = 0.53$,¹⁶ being surrounded by four carboxylate O atoms from two different bptc⁴⁻ anions and one N atom from a bpp ligand.

Compound 1 ^{<i>a</i>}					
Zn(1)–O(3)#1	1.933(5)	Zn(1)–O(2)	1.976(5)	Zn(1)-O(9)#2	1.978(5)
Zn(1)-N(2)	2.011(6)	Zn(2)–O(7)#3	2.000(5)	Zn(2)–O(8)	2.005(5)
Zn(2)-N(1)#4	2.023(7)	Zn(2)–O(1)#3	2.096(5)	Zn(2)–O(6)	2.150(5)
Compound 2^b					
Zn(1) - O(1)	2.006(3)	Zn(1)–O(3)#1	2.008(3)	Zn(1)-N(4)	2.008(4)
Zn(1) - O(6)	2.076(3)	Zn(1)–O(2)#1	2.087(3)	Zn(2)–O(8)#2	1.939(3)
Zn(2)–O(7)	1.959(3)	Zn(2)–O(4)#3	1.984(3)	Zn(2)–N(1)#4	2.006(3)
Compound 3 ^c					
Zn(1) - O(4)	2.061(2)	Zn(1)–O(2 W)	2.071(2)	Zn(1)–O(3 W)	2.098(2)
Zn(1)–O(1 W)	2.132(2)	Zn(1)–O(6)	2.139(2)	Zn(1)-N(3)	2.147(2)
Zn(2) - O(7)	1.9561(2)	Zn(2)–O(8)#1	1.972 (2)	Zn(2)–O(2)#2	1.982(2)
Zn(2)-N(1)	2.040(2)				
Compound 4 ^{<i>d</i>}					
Zn(1)-O(7)#1	2.058(3)	Zn(1)–O(6)#2	2.084(3)	Zn(1)-O(1)	2.127(3)
Zn(1)-N(1)	2.128(4)	Zn(1)–O(10)	2.149(3)	Zn(1)–O(10)#3	2.209(3)
Zn(2)–O(10)	1.915(3)	Zn(2)-O(2)	1.941(3)	Zn(2)–O(8)#2	1.967(4)
Zn(2)–N(2)#4	2.067(4)				
Compound 5 ^e					
Cd(1)-N(1)	2.308(2)	Cd(1)–N(2)	2.320(2)	Cd(1)–O(1 W)	2.362 (2)
Cd(1)–O(1)#1	2.380(2)	Cd(1)–O(3)	2.384 (2)	Cd(1)–O(4)	2.495(2)
Cd(1)–O(2)#1	2.558 (2)				
Compound 6 ^f					
Cd(1)-N(1)	2.333(4)	Cd(1)–N(2)#1	2.339(4)	Cd(1)–O(1 W)	2.384(3)
Cd(1)–O(7)#2	2.388(4)	Cd(1)–O(9)	2.418(4)	Cd(1)–O(6)#2	2.513(4)
Cd(1)–O(8)	2.515(4)	Cd(2)-N(3)	2.304(4)	Cd(2)–N(4)#3	2.348(4)
Cd(2)-O(2 W)	2.377(4)	Cd(2)–O(2)	2.416(4)	Cd(2)–O(4)#4	2.432(4)
Cd(2)-O(1)	2.467(4)	Cd(2)–O(3)#4	2.520(4)		
Compound 7 ^g					
Cd(1) - N(3)	2.202(5)	Cd(1)–O(8)#1	2.246(4)	Cd(1)-N(1)	2.246(5)
Cd(1)–O(7)#2	2.343(4)	Cd(1)-O(2)	2.484(4)	Cd(1)-O(3)	2.590(4)
Cd(2)-O(4)	2.252(4)	Cd(2)–O(1 W)	2.253(4)	Cd(2)–O(2)#3	2.283(4)
Cd(2)–O(5)#4	2.369(5)	Cd(2)–O(6)#4	2.392(5)	Cd(2)–O(1)#3	2.510(5)
Symmetry codes:"#1	-x, -y + 2, -z + 1; #2x, y	y + 1, z; #3 - x, -y + 1, -z + 1;	$#4 x - 1, y - 1, z - 1.^{b} #$	1 - x + 2, -y + 1, -z + 1; #2 - x	+2, -y, -z + 1; #3
x, y - 1, z; #4 x + 1, y,	$, z. ^{c} \# 1 - x + 2, -y, -z; \# 2$	2x, y - 1, z. # #1 - x + 1, -y + 1	, -z + 1; #2 x, y + 1, z; #	3-x+1, -y+2, -z+1; #4x +	1, y - 1, z. * #1 - x
+3/2, -y + 3/2, -z +	$1.^{y} #1 x - 1, y, z; #2 - x - 1$	+1, -y + 1, -z + 1; #3 x, y + 1	, z; #4 - x + 2, -y + 2, -z	x #1 - x, -y + 1, -z; #2 x + 1, y	y, z; #3 - x + 1, -y,
-z; #4 - x, -y, -z.					

In the crystal structure of complex 1, two Zn2 atoms are bridged by symmetry-related bptc⁴⁻ ligands to form a (Zn2-bptc)₂ binuclear cluster, and such units are further connected together by Zn1 atoms to form a ribbon (Fig. 1b). Adjacent ribbons are linked by bpp ligands in *syn*-fashion to form a metal-organic layer with a hole (ca. 9.45 \times 7.24 Å²) (Fig. 1c) in which (H₂O)₈ clusters are present. Two pairs of symmetry-related water molecules O3W and O4W form a planar square, and each O3W is further connected to O1W and O2W through hydrogen bonds to form an octameric water cluster.15 Water O1W is further involved in hydrogenbonding interactions with O4 and O7 from two neighboring carboxylate groups in the covalent framework to stabilize this octameric water cluster. Adjacent layers are further associated through face-to-face $\pi \cdots \pi$ interactions (inter-centroid distance 3.59 Å) between neighboring aromatic rings from two different bptc4- ligands in adjacent layers to yield a 3D supramolecular structure (Fig. S1, ESI[†]).

 $\{[Zn_2(bptc)(bix)]\cdot(H_2O)\}_n$ (2). As illustrated in Fig. 2a, the fundamental building unit consists of two crystallographically

independent Zn^{II} centers, one bptc⁴⁻ anion, one bix ligand and one solvent water molecule. As to bptc⁴⁻, the coordination mode of the anion is the same as that in **1**, the dihedral angle between two phenyl rings is 74.4°, and the four carboxylate groups (2-, 2'-, 3- and 3'-COO⁻) have dihedral angles of 71.8, 85.5, 3.96 and 20.9° with the planes of corresponding linked benzene rings, respectively. Zn1 is five-coordinated by four O atoms from four carboxylate groups of two different bptc⁴⁻ ligands and one N atom from a bix ligand to form a square-pyramidal geometry with Addison trigonality factor $\tau = 0.53$,¹⁶ In contrast, the Zn2 center adopts a distorted-tetrahedral geometry: three carboxylate O atoms from two different bptc⁴⁻ anions and one N atom from a bix ligand.

This structure is similar to that of 1, Zn1 and Zn2 atoms are first connected together through 2,2',3,3'-bptc ligands to give a 1D Zn-bptc ribbon (Fig. 2b) and such ribbons are interconnected together by *anti*-bix to generate a 2D sheet (Fig. 2c). Noteworthy of mentioning here is the solvent water molecules play an important role to bridge adjacent sheets to form a 3D supramolecular structure through the formation of $O1W-H\cdots O9$, $O1W-H\cdots O1\#1$,

Table 3 Selected hydrogen-bonding geometries for 1–4 (in Å and $^\circ)$

$D – H \cdots A$	$d(\mathbf{D}\cdots\mathbf{H})$	$d(\mathbf{H}\cdots\mathbf{A})$	$d(\mathbf{D}\cdots\mathbf{A})$	∠DHA
Compound 1 ^{<i>a</i>}				
$O(1 W) - H(1WA) \cdots O(4) #5$	0.85	2.15	2.97(1)	162.8
$O(1 W) - H(1WB) \cdots O(7) \# 6$	0.85	2.36	3.08(1)	142.9
$O(2 W) - H(2WB) \cdots O(3 W) \#7$	0.85	1.99	2.71(3)	142.2
$O(3 W) - H(3WA) \cdots O(4 W)$	0.85	2.20	2.79(3)	126.2
$O(3 W) - H(3WB) \cdots O(1 W) \#6$	0.85	2.29	2.74(2)	112.9
$O(4 \text{ W}) - H(4 \text{WA}) \cdots O(3 \text{ W}) \# 8$	0.85	1.48	2.20(3)	141.4
Compound 2^b				
$O(1 \text{ W}) - H(1 \text{ WA}) \cdots O(9)$	0.86	2.05	2.873(4)	159.5
$O(1 W) - H(1WB) \cdots O(1) #1$	0.85	2.25	3.101(4)	172.5
$C(26) - H(26) \cdots O(1 W) #5$	0.93	2.69	3.475(1)	143.3
$C(29) - H(29) \cdots O(1 W) \# 5$	0.93	2.68	3.542(1)	154.5
Compound 3^{c}				
$O(4 \text{ W}) - H(4 \text{WA}) \cdots O(3) \# 4$	0.85	2.08	2.705(3)	129.9
$O(3 W) - H(3WB) \cdots O(4 W) #5$	0.85	1.85	2.696(3)	175.1
$O(3 W) - H(3WA) \cdots O(9) \# 1$	0.85	1.98	2.798(3)	161.3
$O(2 W) - H(2WB) \cdots O(8)$	0.85	1.88	2.723(3)	173.1
$O(2 W) - H(2WA) \cdots O(3) \# 6$	0.85	1.80	2.646(3)	170.6
$O(1 W) - H(1WB) \cdots O(3) \# 6$	0.85	2.34	2.965(3)	130.5
$O(1 W) - H(1WA) \cdots N(2) #3$	0.85	1.98	2.816(3)	167.9
$C(31)-H(31)\cdots O(4W)$	0.93	2.61	3.348(1)	137.3
Compound 4^d				
O(4)-H(4)O(9)#5	0.82	1.71	2.500(5)	160.4
Symmetry codes: <i>a</i> #5 <i>x</i> + 1, <i>y</i> , <i>z</i> ; #6 - <i>x</i> - 2, - <i>y</i> , - <i>z</i> ; #3 - <i>x</i> + 1, - <i>y</i> + 1, - <i>z</i> + 1; #4 <i>x</i>	+ 1, -y + 1, -z + 1; #7 x, y, z - x-1, y, z; #5 -x + 1, -y + 1, -z;	1; $#8 - x + 1$, $-y + 1$, $-z + 2$. #6 $-x + 2$, $-y + 1$, $-z$. #5 $x - x + 2$	#1 - x + 2, -y + 1, -z + 1, #5 x - 1, y + 1, z.	y, z - 1. ^{<i>c</i>} #1 - <i>x</i> +

C26#6–H····O1W and C29#6–H····O1W inter-layer hydrogen bonds (Table 3),¹⁷ as shown in Fig. S2 (ESI†).

 $\{Zn_2(bptc)(bpe)_{1,5}(H_2O)_3 \cdot H_2O\}_n$ (3). The asymmetric unit of 3 contains two crystallographically non-equivalent Zn^{II} atoms, one bptc4- anion, one and a half bpe ligands, three coordinated and one solvent water molecules (Fig. 3a). The 2,2',3,3'-bptc⁴⁻ anion adopts a trans-conformation with four carboxylate groups to coordinate to four Zn^{II} cations with the μ_4 - η^2 : η^1 : η^1 : η^1 coordination mode as shown in Scheme 3b. The dihedral angle between the two phenyl rings is 73.8°. The four (2-, 2'-, 3- and 3'-COO⁻) carboxylate groups make dihedral angles of 63.7, 62.8, 32.6 and 59.3° with the corresponding linked benzene rings, respectively. The whole ligand exhibits a μ_4 -bridging coordination mode which is shown in Scheme 3b. Zn1 is six-coordinated by two carboxylate O atoms from one bptc⁴⁻ anion, three water molecules and one N atom from a bpe ligand, and it displays distorted octahedral geometry. Zn2 shows a distorted tetrahedral geometry, being surrounded by three carboxylate O atoms from two bptc4- anions and one N atom from one bpe ligand.

Compound **3** also exhibits a similar 3D supramolecular structure. The Zn1 and Zn2 atoms are first connected together through 2,2',3,3'-bptc ligands to give a Zn-bptc ribbon which is further stabilized through the formation of hydrogen bonds, as shown in Fig. 3b. The bpe ligands adopt different coordination modes: one bridges two Zn1 atoms from adjacent ribbons to form a sheet; the other has one terminal N atom binding one Zn2 atom while the other N end is fixed by hydrogen bonding with a coordinated water molecule. It is interesting to notice that the bidentate bpe ligand is sandwiched between two monodentate bpe ligands with face-to-face $\pi \cdots \pi$ interactions (inter-centroid distances: 3.92 Å for type A and 3.84 Å for type B) (Fig. 3c). The solvent water molecules are first fixed in one sheet through O4W–H4 \cdots O3#4 and O3W#5–H3 \cdots O4W hydrogen bonds, and further linked with another sheet through weak C31–H31 \cdots O4W hydrogen bonds. Through such hydrogen bonds adjacent sheets are united together to give a 3D supramolecular structure (Fig. S3, ESI†).

 $[Zn_2(Hbptc)(\mu_3-OH)(4,4'-bpy)]_n$ (4). The 2,2',3,3'-Hbptc³⁻ species occurs in compound 4 with an intact 3-COOH group. The whole ligand adopts a trans-conformation with three carboxylate and one carboxyl group attached to five Zn^{II} cations in the μ_5 - η^2 : η^2 : η^1 : η^0 coordination mode (Scheme 3c). As illustrated in Fig. 4a, the Zn1 cation is coordinated by three oxygen atoms from two Hbptc³⁻ anions, two hydroxyl groups, and one nitrogen atom from a bpy ligand in a distorted octahedral geometry. In contrast, Zn2 exhibits slightly distorted tetrahedral coordination geometry, being surrounded by two oxygen atoms from separate Hbptc³⁻ ligands, the hydroxyl group, and one nitrogen atom from a bpy ligand. In 2,2',3,3'-Hbptc³⁻, the dihedral angle between the two aromatic rings is about 83.5°. The carboxylic/carboxylate groups at the 2-, 2'-, 3- and 3'-positions make dihedral angles of 45.4, 64.8, 64.7 and 39.9°, respectively, with the corresponding linked benzene rings.

Two Zn1 atoms and two Zn2 atoms are associated together by two pairs of symmetry-related hydroxyl groups and carboxylic groups (2'-COO⁻) to form a tetranuclear unit, and such units are linked by Hbptc³⁻ ligands to form a chain structure. The most fascinating feature is that such a chain is not the common helix but exhibits a *meso*-helical⁴ structure (Fig. 4b). Actually,



Fig. 1 (a) Metal coordination and atom labeling in complex 1 (thermal ellipsoids at 50% probability level). All hydrogen atoms are omitted for clarity. (b) Metal–organic ribbon along the *b*-axis. (c) Sheet structure with $(H_2O)_8$ cluster in each cavity.

the bptc ligand readily forms helical segments because of the twist of the two phenyl rings and/or the skew coordination orientation of the carboxylate groups. In the crystal structure of **4**, there are two types of ligands with opposite chirality (M and P) due to the reverse twisting direction of the two phenyl rings. More interestingly, such *meso*-helical chains are interlaced together to form a co-axial double *meso*-helical chain (Fig. 4c). To date, a few examples of *meso*-helical coordination polymers have been reported.⁵ However, the interlacing of two *meso*-helical chains presents an unprecedented example among multicarbocyclic acid based coordination polymers. Such double *meso*-helical are connected together by bpy ligands to give a layer structure, which is further stabilized by inter-chain hydrogen bonds (Fig. 4d).

Interestingly, adjacent phenyl rings from different layers are arranged in an almost mutually perpendicular manner, which is ideally situated for the formation of C-H··· π interactions (H11–centroid, 2.85 Å).¹⁸ Adjacent layers are further associated together through such C-H··· π interactions to generate a 3D supramolecular structure (Fig. S4, ESI[†]).



Fig. 2 (a) Metal coordination and atom labeling in complex 2 (ellipsoids at 50% probability). All hydrogen atoms are omitted for clarity.
(b) Metal–organic ribbon structure of 2. (c) Sheet structure for 2. (Connecting bix ligands are marked as purple).

[Cd₂(bptc)(bpa)₂(H₂O)]_{*a***} (5). In this compound, the bptc⁴⁻ anion lies on a crystallographic 2-axis, and there are two independent bpa ligands each occuping an inversion center (Fig. 5a). The dihedral angle between the two bptc⁴⁻ aromatic rings is about 89.2°, and the four COO⁻ groups make dihedral angles of 61.1° (3and 3'-COO⁻) and 46.7° (2- and 2' -COO⁻) with the corresponding linked benzene rings, respectively. The 2,2',3,3'-bptc⁴⁻ ligand acts as a \mu_4-bridge (\mu_4-\eta^1:\eta^1:\eta^1:\eta^1) with all carboxylate groups adopting the bidentate chelating mode (Scheme 3d). The Cd1 atom is seven-coordinated by four carboxylate O atoms from two different bptc⁴⁻ anions, two N atoms from two bpa ligands, and the water molecule.**

The phthalate groups of two bptc⁴⁻ anions link two Cd^{II} cations to form a binuclear cluster, and such clusters are linked together by bptc⁴⁻ to form an infinite Cd-bptc chain (Fig. 5b). This chain is also not a classical enantiomeric helix, but a *meso*-helix because of the alternation of two types of bptc⁴⁻ ligands with opposite chirality (*P* and *M*) around $[Cd_2(CO_2)_2]$ bimetallic units. The bpa ligand with *syn*-conformation (type A) binds two Cd atoms along the chain with its pyridine rings twisted by 75.5° (Fig. 5c) to form a ribbon together with the Cd-bptc *meso*helix. Such ribbons are linked together by the other type of bpa (type B) with *Z*-shaped conformation to form a metal–organic



Fig. 3 (a) Metal coordination and atom labeling in complex 3 (thermal ellipsoids at 50% probability level). All hydrogen atoms are omitted for clarity. (b) Metal–organic ribbon (dotted lines represent H-bonds.) (c) Sheet structure showing $\pi \cdots \pi$ stacking interactions and O–H···O, O–H···N hydrogen bonds.

layer (Fig. 5d). Adjacent layers are further associated together by face-to-face $\pi \cdots \pi$ interactions (inter-centroid distance 3.82 Å) between neighboring bpa ligands (type A and B) to yield a 3D supramolecular structure (Fig. S5, ESI†).

 $[Cd_2(bptc)(bpp)_2(H_2O)_2]_n$ (6). Compound 6 contains two independent Cd^{II} atoms (Cd1 and Cd2) both exhibiting pentagonalbipyramidal coordination geometry (Fig. 6a). Each Cd atom is coordinated by four oxygen atoms of two chelating bidentate carboxylic groups from two different bptc⁴⁻ anions, two nitrogen atoms from different bpp ligands, and a water molecule with bond lengths ranging from 2.304 to 2.520 Å. The coordination mode of the anion is same with that in 5, the dihedral angle between two phenyl rings is 82.7°, and the four (2-, 2'-, 3- and 3'-COO⁻) carboxylate groups make dihedral angles of 60.4, 65.8,



Fig. 4 (a) Metal coordination and atom labeling in complex **4** (thermal ellipsoids at 50% probability level). All hydrogen atoms are omitted for clarity. (b) *meso*-Helix along the *b*-axis: Zn atoms (turquoise), others (purple). (c) Interlace of two *meso*-helical chains: Zn atoms (turquoise). (d) Metal–organic sheet structure in the *ab*-plane; connecting 4,4'-bpy ligands are marked in blue, and dotted lines represent H-bonds.

44.0 and 40.9° with the corresponding linked benzene rings, respectively.

Adjacent Cd atoms are bridged by two different bptc⁴⁻ ligands to form a binuclear cluster, and such clusters are linked by adjacent bptc⁴⁻ ligands to form an infinite $[Cd_2(bptc)]_n$ chain. As expected, this chain also displays an unusual *meso*-helical character (Fig. 6b). The adjacent chains are connected together by one type of bpp ligands (N1–N2) coordinating to Cd1 cations along the *a*-axis to give a sheet structure (Fig. 6c). Based on this arrangement, the neighboring aromatic rings from two different bptc⁴⁻ ligands are oriented parallel to each other with a face-to-face distance of 3.593 Å, which is indicative of $\pi \cdots \pi$ stacking interaction (Fig. 6c). Such sheets are united together by another bpp ligand (N3–N4)



Fig. 5 (a) Metal coordination and atom labeling in complex **5** (thermal ellipsoids at 50% probability level). All hydrogen atoms are omitted for clarity. (b) Cd-bptc *meso*-helical chain. (c) Ball-and-stick representation of the interlacing of unequal coaxial *meso*-helical chains: purple represents bpa. (d) Layer structure of **5**: purple, pink and blue represent bpa, bptc and bridging bpa ligands, respectively.

bridging two Cd2 ions along the *b*-axis to form a robust 3D metal– organic framework (Fig. 6d). A better understanding of this complicated structure can be achieved *via* topological considerations.¹⁹ If the bpp and the bptc^{4–} are considered as individual connecting rods, and the bimetallic $[Cd_2(CO_2)_2]$ unit is regarded as a sixconnected node, the 3D structure of **6** can be simplified as a simple 6-connected lattice. However, this lattice cannot exhibit the real chemical system of the structure. Instead, the bpp and the bptc^{4–} are considered as double-connected nodes²⁰ and the bimetallic unit is regarded as a six-connected node (connecting to two bptc^{4–} and four bpp ligands), then the complex **6** can be classified as



Fig. 6 (a) Metal coordination and atom labeling in complex **6** (thermal ellipsoids at 50% probability level). All hydrogen atoms are omitted for clarity. (b) $[Cd_2(bptc)]_n$ meso-helical chain. (c) Layer structure. (d) 3D Structure view down the *a*-axis: purple coat and turquoise chains represent layer and connecting bpp ligands, respectively. (e) Schematic presentations of a 3D net: bright green, turquoise and pink balls represent binuclear Cd-cluster, bpp and bdta⁴⁻ ligands, respectively. The self-penetrated networks are highlighted in red and blue.



Fig. 7 (a) Metal coordination and atom labeling in complex 7 (thermal ellipsoids at 50% probability level). All hydrogen atoms are omitted for clarity; (b) chain structure; (c) metal–organic layer; (d) 3D structure viewed down the *a*-axis; (e) (4,4,8)-connected network with Schläfli symbol of $(4^{16}6^{12})(4^{4}6^{2})_{2}$ topology: bptc (red), Cd1 cluster (green), Cd2 cluster (turquoise).

a (2,6,2)-connected lattice with a $(12)(4^212^916^4)(4)^2$ Schläfli symbol (Fig. 6e). Moreover compound **6** exhibits another entry of an unusual but growing set of self-penetrated networks: two fourmember rings formed by two six-connected nodes and two doubleconnected nodes which is simplified by bpp perpendicularly penetrating through each other, forming a self-penetrated lattice (Fig. 6e).

[Cd₄(bptc)₂(bix)₂(H₂O)₂·4.5H₂O]_n (7). Both independent Cd^{II} centers adopt a distorted octahedral geometry: Cd1 is coordinated by four O atoms from three bptc⁴⁻ anions and two N atoms from two different bix ligands; Cd2 is surrounded by two chelating carboxylate groups from different bptc⁴⁻ ligands, one carboxylate O atom from the third bptc⁴⁻ ligand, and a water molecule (Fig. 7a). The 2,2',3,3'-bptc⁴⁻ anion adopts a *syn*-conformation with four carboxylate groups linked to six Cd^{II} cations in the μ_6 - η^3 : η^2 : η^2 : η^1 coordination mode, as shown in Scheme 3e. The dihedral angle between the two bptc⁴⁻ aromatic rings is about 67.8°, and the four carboxylate groups (2-, 2'-, 3- and 3'-COO⁻) make dihedral angles of 72.2, 88.0, 39.4 and 10.9° with the corresponding linked benzene rings, respectively.

Two Cd1 cations are bridged by two bidentate 3-COO⁻ groups from symmetry-related bptc⁴⁻ ligands to form a centrosymmetric $[Cd1_2(CO_2)_2]$ unit, and adjacent units are linked by μ_2 -O and μ_2 -COO⁻ bridges to a pair of Cd2 centers to form an infinite

chain (Fig. 7b). Adjacent chains are interconnected to each other by bptc⁴⁻ ligands to form a metal–organic sheet (Fig. 7c). Such sheets are stabilized by $\pi \cdots \pi$ interactions between phenyl rings of neighboring ligands (inter-centroid distance 3.65 Å). The bix ligand exhibits an S-shaped conformation and connects the 2D sheets to generate a 3D structure (Fig. 7d). If the bptc⁴⁻ ligand is considered as a four-connected node (connecting to two Cd1 cations and two Cd2 cations), the bimetallic unit [Cd1₂(CO₂)₂] as an eight-connected node (connecting four bptc⁴⁻ and four bix), a pair of Cd2 bridges as a four-connected node (connecting four bptc⁴⁻ anions), the structure of 7 can be described as a (4,4,8)connected network with a Schläfli symbol of (4¹⁶6¹²)(4⁴6²)(4⁴6²)₂ topology (Fig. 7e).

Formation of meso-helix.

In compounds **4–6**, the coordination mode of the bptc^{4–} ligands leads to the formation of helical segments with chirality because of the twist of the two phenyl rings and the skew coordination orientation of the carboxylate groups, and two types of ligands with opposite chirality (M and P) could be formed due to the reverse twisting direction of the two phenyl rings. To form centrosymmetric structures, *meso*-helices are formed by the alternation of helical conformers with opposite chirality instead of molecules of the same chirality in the typical helix. In summary, the bptc ligand shows different coordination modes in these complexes, exerting an important influence on the final architectures, which demonstrated that bptc could be a potential candidate for constructing novel coordination polymers.

Thermogravimetric analysis.

Thermogravimetric analysis (TG) was performed on complexes 1-7 to study the thermal stability of these polymers. TG curves for complexes 1-7 are shown in Fig. S6 (ESI[†]). For complex 1, a gradual weight loss between 20 and 100 °C is attributed to the release of uncoordinated water molecules (observed, 4.65%; calculated, 4.41%). Decomposition of the anhydrous residue was observed at 400 °C. For compound 2, weight loss corresponding to the release of water molecules occurred from 110 to 155 °C (observed, 2.51%; calculated, 2.43%), and then the host framework started to decompose beyond 380 °C. For compound 3, a weight loss of 8.44% indicated that both the solvated and coordinated water molecules (calculated, 8.67%) were lost in the range of 60-170 °C. A gradual weight loss from 180 °C corresponded to removal of the organic components. In the case of compound 4, no obvious weight loss was observed until the temperature reached 345 °C, indicating that this metal-organic framework material has high thermal stability. As for compound 5, weight loss of coordinated water molecules took place in the range of 50-150 °C (observed, 1.90%; calculated, 1.83%), and the anhydrous component began to decompose at 285 °C. The TG curve of 6 showed that this complex lost its coordination water molecules between 148 and 180 °C (observed, 3.31%; calculated, 3.56%). Rapid weight loss was observed from 286 °C, which indicated collapse of the whole structure. For 7, the weight loss of 4.32% in the range of 35-130 °C is attributable to the uncoordinated water molecules (calculated, 4.62%), whereas the loss of coordinated water occurred above 175 °C. The anhydrous component of compound 7 began to decompose at 285 °C.

Photoluminescent properties

As complexes 1-7 are hybrid inorganic-organic coordination polymers with d¹⁰ metal centers,²¹ their emission spectra in the solid state were investigated at room temperature. As shown in Fig. 8, excitation at 352 nm leads to intense blue fluorescent emission bands at 460 nm for 1 and 465 nm for 7 while weaker fluorescence emissions occur at 474 nm for 2, 397 nm for 3, 473 nm for 4 and 396 nm for 5, respectively. Compound 6 gives two peaks at 459 and 490 nm with a weak shoulder appearing at 432 nm when irradiated at 352 nm. The emissions of 1-7 can probably be assigned to the intra-ligand $(\pi - \pi^*)$ fluorescent emission because similar emissions are observed at 396 nm for the free bptda ligand. Compared to the weak emission peak for free bptda ligand, the emissions of 1 and 7 with the enhancement of luminescence may be attributed to ligand chelation at the metal center, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay.²² Bathochromic shifts of emission occurring in 1, 2, 4, 6 and 7 are possibly assigned to different coordination environments around the metal ions, since photoluminescence behavior is closely associated with the metal center and the ligands coordinated around it.²³ Compounds 1 and 7 may be suitable as excellent



Fig. 8 Fluorescent emission spectra of complexes 1–7 and free ligand.

candidates for the exploration of blue-fluorescent materials, since they are highly thermally stable and insoluble in common solvents.

Conclusions

In this paper, we have presented the results of our investigation on a series of seven MOFs exhibiting various types of architectures constructed from deprotonated forms of the new aromatic tetracarboxylic acid ligand H₄bptc, which adopt syn and anti conformations and a variety of modes in coordination to divalent zinc and cadmium metal centers. The complexes were crystallized with nitrogen heterocycles as co-ligands, and the bptc4- anion is found in all except compound 3, which alone contains the Hbptc³⁻ anion. The most notable structural feature is that two types of bptc⁴⁻ ligands with opposite chirality (M and P) are arranged in an alternating manner to form a meso-helix, as found in 4, 5 and 6, which deserve further investigation for the construction of MOFs with meso-helix systems. Compounds 6 and 7 possess novel 3D metal-organic networks with different interesting topologies. Subsequent work will focus on the construction of new coordination polymers by reacting the present ligand and its positional isomer 2,3,3',4'-bptc with a wide range of metal salts.

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