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Introduction

Syntheses, structures, and photoluminescent properties of a series of metal-organic frameworks constructed by 5,5'-bis(1*H*-imidazol-1-yl)-2,2'-bithiophene and various carboxylate ligands[†]

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A series of new metal-organic frameworks (MOFs), namely, $\{[Co(BIBP)(hfipbb)]\}_{n}$ (1), $\{[Co(BIBP)(Hbtc)]\}_{n}$ (2), $\{[Zn(BIBP)(5-OH-bdc)]\}_{n}$ (3), $\{[Cd(BIBP)(bdc)]\}_{n}$ (4), $\{[Zn_{2}(BIBP)_{0.5}(hfipbb)_{2}]-H_{2}O\}_{n}$ (5), $\{[Zn_{4}(BIBP)_{4}(bdc)_{4}]\}_{n}$ (6), $\{[Zn(BIBP)(DL-Ca)] \cdot H_2O\}_n$ (7), $(BIBP = 5,5'-bis(1H-imidazol-1-yl)-2,2'-bithiophene, H_2hfipbb =$ 4,4'-(hexafluoroisopropylidene)bis(benzoic acid), H_3 btc = 1,3,5-benzenetricarboxylic acid, H_2 bdc = isophthalic acid, $5-OH-H_2bdc = 5-hydroxyisophthalic acid, D-H_2ca = D-camphor acid), have been$ hydrothermally synthesized. These compounds were structurally characterized by IR spectroscopy, elemental analysis and X-ray single-crystal diffraction. Compound 1 exhibits a 2D \rightarrow 3D framework with an unusual parallel polycatenation of corrugated 2D (4,4) nets. Compounds 2-4 are structurally similar and display 2D layer structures, in which 2 and 3 extend into 3D supramolecular frameworks through interlayer O-H···O hydrogen-bonding interactions. Compound 5 displays a 3D 2-fold interpenetrating framework with a rare $\{4^4, 6^6\}$ sqp topology, containing an interesting $\cdots LRLR\cdots$ double helical layer structure. Compound 6 is a 2D network with $\{4^4, 6^2\}$ -sql topology and further extends via C-H···O hydrogen bonds into the 3D supramolecular framework. Compound 7 possesses a rare 3D non-interpenetrated cds-type framework with the Schläfli symbol {6⁵·8}. Thermal stabilities for 1–7 and photoluminescence properties of the compounds 3-7 have been examined in the solid state at room temperature. Furthermore, solid-state UV-vis spectroscopy experiments show that compounds 1-7 exhibit optical band gaps which are characteristic for optical semiconductors, with band gaps of 2.41, 2.44, 2.48, 2.46, 2.83, 2.68, and 2.72 eV, respectively.

In recent years, the rational design and synthesis of metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) has been of considerable interest not only owing to their intriguing diverse architectures,¹ but also because of their variety of potential applications in magnetism,² gas storage and separation,³ luminescence,⁴ catalysis,⁵ sensor,⁶ and so forth. However, it is still a challenge to construct predicted structures with desired properties because of the combined influence of metal centers, organic ligands, the ratio of reagents, temperature, reaction solvents, pH value, counterions, and so on.⁷ Therefore, the target MOFs with specific structures and especial functions can be obtained by careful regulation of the synthesis conditions and designation of the organic ligands. It is worth noting that, in comparison with traditional properties of MOFs mentioned previously, this study has received relatively little attention for the photoelectric properties of MOFs.8 So, MOFs possessing photoelectric properties have high theoretical and potential practical value. In our previous work,9 we adopted 5,5'-bis(4-pyridyl)-2,2'-bithiophene (BPBP) which contains a conjugated electrondonating bithiophene group combined with dicarboxylate ligands and successfully obtained six complexes with diverse interesting structures and topologies as well as semiconductor properties. Taking inspiration from previous work, another conjugated electron-donating bithiophene ligand 5,5'-bis(1H-imidazol-1-yl)-2,2'-bithiophene (BIBP) was selected to construct a coordination architecture. Compared with BPBP,

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[†] Electronic supplementary information (ESI) available: Additional figures, FT-IR spectra, TGA curves, UV-vis absorption spectra, patterns of photochemistry, selected bond distances and hydrogen bond parameters for compounds 1–7. CCDC 963191–963197. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce41966e



the prominent characteristic of BIBP ligand is that the nitrogen coordination atoms can adjust their coordination orientation through rotation of C–N single bonds between thiophene and imidazole rings.¹⁰ So the BIBP has a more flexible coordination fashion. Up to now, only one MOFs containing BIBP have been reported.¹¹ But, the mixed-ligand MOFs containing BIBP have not been reported. With the aforementioned consideration, our recent study has been mainly focused on the assemblage BIBP to react with divalent transitional-metal ions in the presence of various carboxylate ligands to get new MOFs with rich structural characteristics and encouraging photoluminescence properties.

Herein, we adopted five carboxylate ligands with different rigidity, namely 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (H₂hfipbb),¹² 1,3,5-benzenetricarboxylic acid (H₃btc),¹³ isophthalic acid(H₂bdc),¹⁴ 5-hydroxyisophthalic acid (5-OH-H₂bdc),¹⁵ and D-camphor acid (D-H₂ca)¹⁶ (Scheme 1), as co-ligands to react with the BIBP ligand and different bivalent metal salts. Then, seven new MOFs were obtained under hydrothermal conditions, namely {[Co(BIBP)(hfipbb)]}_n (1), {[Co(BIBP)(Hbtc)]}_n (2), {[Zn(BIBP)(5-OH-bdc)]}_n (3), {[Cd(BIBP)(bdc)]}_n (4), {[Zn₂(BIBP)_{0.5}(hfipbb)₂]·H₂O}_n (5), {[Zn₄(BIBP)₄(bdc)₄]}_n (6), {[Zn(BIBP)(D-ca)]·H₂O}_n (7). Their syntheses, crystal structures, optical band gaps, photoluminescent properties, and thermal stabilities are reported in this article.

Experimental section

Materials and general methods

BIBP ligand was synthesized as reported in the literature,¹¹ and other reagents and solvents were of analytical grade and used without further purification. Elemental analyses for C, H and N were conducted on a Perkin Elmer 240C elemental analyzer. The FT-IR spectra were recorded on a Nicolet Impact 410 spectrometer with KBr pellets in the range of 4000–400 cm⁻¹. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer thermogravimetric analyzer under a nitrogen atmosphere with a heating rate of 10 °C min⁻¹. Solid-state luminescent spectra were recorded with a SHIMADZU VF-320 X-ray fluorescence spectrophotometer at room temperature. UV–vis diffuse reflectance spectra were measured on a Shimadzu UV-3600 double monochromator spectrophotometer

at room temperature using $BaSO_4$ as a standard with 100% reflectance.

Syntheses of the compounds 1-7

Synthesis of {[Co(BIBP)(hfipbb)]]_n (1). A mixture of Co(NO₃)₂·6H₂O (14.6 mg, 0.05 mmol), BIBP (14.9 mg, 0.05 mmol), 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (19.6 mg, 0.05 mmol), DMF (1 mL) and H₂O (5 mL) was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 85 °C for 3 days. Purple block crystals of 7.1 mg (yield of 19% based on Co) were collected. Anal. calcd. for C₃₁H₁₈CoF₆N₄O₄S₂: C, 49.81%; H, 2.43%; N, 7.49%. Found: C, 49.77%; H, 2.48%; N, 7.54%. IR (KBr, cm⁻¹): 3443(w), 1599(s), 1556(vs), 1522(w), 1499(w), 1381(s), 1293(s), 1255(s), 1172(s), 1067(w), 970(w), 851(w), 782(m), 748(m), 459(w).

Synthesis of {[Co(BIBP)(Hbtc)]]_n (2). A mixture of Co(NO₃)₂·6H₂O (14.6 mg, 0.05 mmol), BIBP (14.9 mg, 0.05 mmol), 1,3,5-benzenetricarboxylic acid (10.5 mg, 0.05 mmol), CH₃CN (4.5 mL) and H₂O (1.5 mL) was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 105 °C for 3 days. Purple block crystals of 6.8 mg (yield of 24% based on Co) were collected. Anal. calcd. for C₂₃H₁₄CoN₄O₆S₂: C, 48.85%; H, 2.50%; N, 9.91%. Found: C, 48.81%; H, 2.55%; N, 9.96%. IR (KBr, cm⁻¹): 3441(w), 1722(s), 1622(vs), 1590(m), 1556(s), 1490(w), 1455(m), 1383(s), 1235(m), 1181(m), 1040(m), 935(w), 829(w), 791(w), 649(w).

Synthesis of {[**Zn(BIBP)**(5-**OH-bdc**)]]_{*n*} (3). A mixture of Zn(NO₃)₂·6H₂O (14.9 mg, 0.05 mmol), BIBP (14.9 mg, 0.05 mmol), 5-hydroxyisophthalic acid (10.5 mg, 0.05 mmol), CH₃CN (1.5 mL) and H₂O (4.5 mL) was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 90 °C for 3 days. Yellow block crystals of 6.8 mg (yield of 25% based on Zn) were collected. Anal. calcd. for C₂₂H₁₄N₄O₅S₂Zn: C, 48.58%; H, 2.59%; N, 10.30%. Found: C, 48.52%; H, 2.64%; N, 10.34%. IR (KBr, cm⁻¹): 3450(w), 1621(m), 1573(vs), 1520(w), 1496(w), 1417(s), 1381(s), 1294(w), 1278(w), 1238(w), 1205(w), 1039(w), 983(m), 789(m), 731(w), 502(w).

Synthesis of {[Cd(BIBP)(bdc)]}_n (4). A mixture of Cd(NO₃)₂·4H₂O (15.4 mg, 0.05 mmol), BIBP (14.9 mg, 0.05 mmol), isophthalic acid (10.5 mg, 0.05 mmol), DMF (1.5 mL) and H₂O (4.5 mL) was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 85 °C for 3 days. Yellow block crystals of 8.6 mg (yield of 30% based on Cd) were collected. Anal. calcd. for C₂₂H₁₄CdN₄O₄S₂: C, 45.96%; H, 2.45%; N, 9.75%. Found: C, 45.91%; H, 2.51%; N, 9.79%. IR (KBr, cm⁻¹): 3442(w), 1609(vs), 1557(vs), 1519(s), 1493(m), 1431(w), 1374(vs), 1295(w), 1293(w), 1238(w), 1116(w), 1070(w), 1037(s), 932(m), 817(w), 787(s), 763(s), 643(w).

Synthesis of $\{[Zn_2(BIBP)_{0.5}(hfipbb)_2]\cdot H_2O\}_n$ (5). A mixture of $Zn(NO_3)_2\cdot 6H_2O$ (29.7 mg, 0.1 mmol), BIBP (7.45 mg, 0.025 mmol), 4,4'-(hexafluoroisopropylidene)bis(benzoic acid) (39.2 mg, 0.1 mmol), CH₃CN (3 mL) and H₂O (3 mL) was placed

in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 120 °C for 3 days. Yellow block crystals of 8.6 mg (yield of 16% based on Zn) were collected. Anal. calcd. for $C_{41}H_{23}F_{12}N_2O_9SZn_2$: C, 45.66%; H, 2.15%; N, 2.60%. Found: C, 45.61%; H, 2.19%; N, 2.65%. IR (KBr, cm⁻¹): 3451(w), 1609(s), 1557(s), 1523(w), 1382(s), 1293(w), 1255(w), 1213(m), 1172(s), 1067(w), 945(w), 928(w), 846(w), 726(m), 512(w).

Synthesis of {[$Zn_4(BIBP)_4(bdc)_4$]}_n (6). A mixture of Zn(NO₃)₂·6H₂O (14.9 mg, 0.05 mmol), BIBP (14.9 mg, 0.05 mmol), isophthalic acid (10.5 mg, 0.05 mmol), DMA (3 mL) and H₂O (3 mL) was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 100 °C for 3 days. Yellow needle crystals of 5.8 mg (yield of 22% based on Zn) were collected. Anal. calcd. for C₈₈H₅₄N₁₆O₁₆S₈Zn₄: C, 50.05%; H, 2.67%; N, 10.61%. Found: C, 50.01%; H, 2.73%; N, 10.66%. IR (KBr, cm⁻¹): 3451(w), 1619(vs), 1558(s), 1529(m), 1505(w), 1381(m), 1344(s), 1301(w), 1248(w), 1110(w), 1068(w), 1041(w), 947(w), 788(w), 762(w), 642(w).

Synthesis of {[Zn(BIBP)(pL-ca)]·H₂O}_{*n*} (7). A mixture of Zn(NO₃)₂·6H₂O (14.9 mg, 0.05 mmol), BIBP (14.9 mg, 0.05 mmol), p-camphor acid (10.0 mg, 0.05 mmol), DMF (1.5 mL) and H₂O (4.5 mL) was placed in a Parr Teflon-lined stainless steel vessel (15 mL) under autogenous pressure and heated at 95 °C for 3 days. Yellow block crystals of 3.8 mg (yield of 13% based on Zn) were collected. Anal. calcd. for C₂₄H₂₆N₄O₅S₂Zn: C, 49.70%; H, 4.52%; N, 9.66%. Found: C, 49.66%; H, 4.57%; N, 9.71%. IR (KBr, cm⁻¹): 3444(w), 1597(s), 1536(vs), 1461(m), 1412(s), 1373(m), 1324(w), 1297(w), 1177(w), 1130(w), 1052(w), 1006(w), 810(w), 502(w).

Single crystal structure determination and refinement

Diffraction measurements were performed at room temperature on a Bruker Smart Apex II CCD diffractometer using Mo K α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares procedures based on F^2 using the SHELXTL¹⁷ program. All non-hydrogen atoms were located from the trial structures and then refined anisotropically. The hydrogen atoms were placed at the calculation positions and allowed to ride on the parent atoms. The distribution of peaks in the channels of 5 and 7 were chemically featureless to refine using conventional discrete-atom models. To resolve this issue, the contribution of the electron density by the remaining water molecules in 5 and 7 were removed by the SQUEEZE routine in PLATON.18 The number of solvent molecules were obtained by elemental analyses. A semiempirical absorption correction was applied using the SADABS program.¹⁹ In compound 1, the phenylene and carboxylate groups are disordered over two general positions with the site occupancy of 0.5 for C9-C15/C9'-C15', O3/O3' and O4/O4'. In compound 7, the disordered C atom of camphorate ligand was refined isotropically using C atom split over two sites C20-C21 with a site occupancy of 0.50. The detailed crystallographic data

of 1–7 are listed in Table 1. The selected bond lengths and angles and hydrogen bond parameters are given in Tables S1 and S2 (ESI†). CCDC numbers are 963191–963197 for 1–7, respectively. Topological analyses were performed using the program package TOPOS.²⁰

Description of the crystal structures

{[Co(BIBP)(hfipbb)]}_n (1). Single crystal X-ray analysis reveals that compound 1 is a parallel polycatenated $2D + 2D \rightarrow 3D$ framework based on an undulated 44.62-sql square layer. It crystallizes in the triclinic crystal system, space group $P\bar{1}$. A unique portion of the structure 1 consists of one $Co(\pi)$ cation, two halves of a BIBP ligand and one deprotonated 4,4'-(hexafluoroisopropylidene)bis(benzoic acid). As depicted in Fig. 1a, the Co(II) cation adopts a distorted tetrahedral geometry defined by two oxygen atoms [Co-O = 1.908(7)-1.989(2) Å] from two symmetrical hfipbb ligands and two N atoms [Co-N = 2.036(3)-2.049(3) Å] from two BIBP ligands. The Co-O/N bond lengths are all normal. As shown in Fig. 1b, the BIBP ligands link Co(II) cations to form one infinite 1D zig-zag chain with the Co…Co distance of 16.090 Å and Co-Co-Co angle of 127.78°. Then, the other infinite 1D linear chain with the Co…Co distance of 14.509 Å and Co-Co-Co angle of 180.00° is also generated through the coordination between the carboxylate groups and the $Co(\pi)$ cations. Finally, these two kinds of chains are cross-linked by sharing the $Co(\pi)$ cations into a highly undulating 2D network. In this network, each 54-membered macrocycle is formed by four Co(II) cations, two BIBP ligands, and two hfipbb ligands with a dimension of 26.442 Å × 15.604 Å (diagonal lengths). From a topological viewpoint, the $Co(\pi)$ cations can be considered as 4-connected nodes, and hfipbb and BIBP ligands are considered as linkers; thus, the 2D network can be simplified to a puckered sql network, which contains a window of 14.509 Å \times 16.090 Å (Fig. 1c). Such large windows of the net and high undulation of the single sql sheet allows two nearest neighbouring sheets to penetrate each other in a parallel mode leading to a 3D polycatenated network (Fig. 1d). For interpenetrated 2D networks, the 2D \rightarrow 2D parallel interpenetration or 2D \rightarrow 3D inclined polycatenation are common examples,²¹ but the 2D \rightarrow 3D parallel polycatenation is relatively rare. As far as we know, only a limited number of examples of $2D \rightarrow 3D$ polycatenation structures have been reported in a parallel mode.²²

{[Co(BIBP)(Hbtc)]}_n (2), {[Zn(BIBP)(5-OH-bdc)]}_n (3) and {[Cd(BIBP)(bdc)]}_n (4). The structures of 2–4 are very similar, therefore, only the structure of 2 is described here in detail. The structures of 3 and 4 are shown in Fig. S8 and S9 (ESI†). A single crystal X-ray structural study shows that 2 crystallizes in the triclinic crystal system with $P\bar{1}$ space group. The unique portion of structure 2 consists of one crystallographically independent Co(π) cation, one BIBP ligand and one partial deprotonated Hbtc^{2–} ligand. The two deprotonated carboxylate groups adopt different coordination modes, one carboxylate group takes the bismonodentate coordination mode to

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Compound	1	2	3	4	5	9	7
Formula	$\mathrm{C}_{31}\mathrm{H}_{18}\mathrm{CoF}_{6}\mathrm{N}_{4}\mathrm{O}_{4}\mathrm{S}_{2}$	$\mathrm{C}_{23}\mathrm{H}_{14}\mathrm{CoN}_4\mathrm{O}_6\mathrm{S}_2$	$C_{22}H_{14}N_4O_5S_2Zn$	$C_{22}H_{14}CdN_4O_4S_2$	$\mathrm{C}_{41}\mathrm{H}_{21}\mathrm{F}_{12}\mathrm{N}_{2}\mathrm{O}_{8}\mathrm{SZn}_{2}$	$C_{88}H_{56}N_{16}O_{16}S_8Zn_4$	$\mathrm{C}_{24}\mathrm{H}_{24}\mathrm{N}_{4}\mathrm{O}_{4}\mathrm{S}_{2}\mathrm{Zn}$
Formula weight	747.54	565.43	543.86	574.89	1060.40	2111.61	561.96
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	P2/c	$P2_1/c$	$P2_1/c$
a (Å)	10.2077(6)	9.3925(12)	9.4003(6)	9.5686(8)	21.330(3)	17.8224(12)	10.4879(10)
$p\left(\mathbf{\ddot{A}}\right)$	10.5027(6)	10.0156(16)	9.8766(7)	10.3542(8)	8.1009(13)	27.2700(19)	20.6148(19)
c (Å)	14.5086(9)	12.6690(16)	12.0339(8)	11.0911(9)	30.993(3)	18.3256(12)	15.5100(11)
$\alpha \left(\circ \right)$	94.4540(10)	84.282(2)	82.4750(10)	80.1480(10)	06	06	90.00
β (\circ)	98.649(10)	80.105(2)	80.707(10)	83.520(10)	122.460(7)	110.532(10)	121.819(5)
γ (o)	91.2890(10)	71.028(2)	72.3670(10)	72.5150(10)	90	06	90.00
Z	2	2	2	2	4	4	4
$V\left({{ m \AA}^3} ight)$	1532.19(16)	1109.1(3)	1046.79(12)	1030.42(14)	4518.7(11)	8340.8(10)	2849.4(4)
$D_{\rm calcd}$ (g cm ⁻³)	1.620	1.693	1.725	1.853	1.559	1.681	1.310
$\mu \; (\mathrm{Mo} \; \mathrm{K} \alpha) \; (\mathrm{mm}^{-1})$	0.778	1.014	1.419	1.303	1.209	1.418	1.042
F(000)	754	574	552	572	2116	4288	1160
Temperature (K)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
θ min-max (°)	1.42, 27.10	1.63, 27.10	2.17, 27.10	1.87, 27.10	1.13, 27.10	1.22, 27.10	1.83, 27.10
Tot., uniq. data	10228,6723	7239, 4837	6916, 4569	6814, 4506	28076,9981	55045,18395	17968,6271
R(int)	0.0940	0.0176	0.0090	0.0538	0.0508	0.0236	0.0138
Observed data $[I > 2\sigma(I)]$	4735	4344	4134	4092	6588	9343	3850
$N_{ m ref}, N_{ m par}$	6723, 515	4837, 326	4569, 308	4506, 298	9981, 595	18395,1189	6271, 327
$R_1{}^a, \mathrm{w} \dot{R}_2{}^b$ ($I > 2 \sigma(I))$	0.0531, 0.1497	0.0284, 0.0985	0.0256, 0.0817	0.0276, 0.0704	0.0424, 0.1014	0.0468, 0.1054	0.0512, 0.1348
R_1 , wR_2 (all data)	0.0699, 0.1569	0.0318, 0.1007	0.0286, 0.0836	0.0301, 0.0716	0.0704, 0.1091	0.0646, 0.1068	0.0672, 0.1367
S	1.050	1.060	1.028	1.013	1.002	1.000	1.092
Min. and max. resd. dens. (e \AA^{-3})	1.522, -0.679	0.443, -0.364	0.352, -0.278	0.728, -0.617	0.435, -0.382	1.256, -0.630	0.429, -0.445
$^{a} R_{1} = \sum F_{0} - F_{c} \sum F_{0} , ^{b} WR_{2} = \sum_{i=1}^{n}$	$\sum [w(F_{\rm o}{}^2-F_{\rm c}{}^2)^2]/\sum [w(F_{\rm o}{}$	$^{2})^{2}]^{1/2}.$					



Fig. 1 (a) Coordination environment of the Co(II) cation in **1** (30% probability displacement ellipsoids). The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = x, y, -1 + z; #2 = 3 - x, 2 - y, -z; #3 = 2 - x, -y, 1 - z. (b) Left: an infinite 1D zig-zag chain formed by Co(II) cations and BIBP ligands. Middle: an infinite 1D chain generated through the carboxylate groups of hfipbb ligands and the Co(II) cations. Right: undulating 2D network of **1**. (c) View of the single puckered **sql** network of **1**. (d) Schematic representation of the 3D framework of two interpenetrating 2D frameworks with parallel polycatenation structure of **1**.

bridge two Co centers while the other carboxylate group adopts chelating in a bidentate mode. As illustrated in Fig. 2a, the Co(II) center is six-coordinated by four carboxylic oxygen atoms from three symmetrical Hbtc^{2–} ligands at the equatorial positions and two nitrogen atoms from two symmetrical BIBP ligands at the axial position. This gives a slightly distorted $\{CoN_2O_4\}$ octahedral coordination geometry. The Co–N bond lengths are in the range of 2.1187(15) Å–2.1423(15) Å, and the Co–O bond lengths are 2.0303(12)–2.2257(12) Å. As shown in Fig. 2b, pairs of symmetry-related Hbtc^{2–} ligands adopt a bridging mode joining adjacent Co(II) cations to form an infinite 1D double chain, which contains eight-membered and



Fig. 2 (a) Coordination environment of the Co(II) cation in **2** (30% probability displacement ellipsoids). The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = x, 1 + y, z; #2 = 2 - x, 1 - y, -z; #3 = 1 + x, -1 + y, -1 + z. (b) 1D double chain formed by Co(II) cations and HBTC²⁻ ligands. (c) Polyhedral view of the 2D coordination network of **2**. (d) Packing diagram showing the …AAAA… type offset stacks of 2D sheets in **2**. (e) Schematic representation the 3D supramolecular framework of **2** *via* the hydrogen bonds (green dashed line).

sixteen-membered rings. Then, such chains are further linked by BIBP ligands to form a 2D network (Fig. 2c). If the SBUs $[Co_2(CO_2)_2]$ are considered as 4-connected nodes, and all crystallographically independent ligands are considered as linkers; thus, the 2D network can be simplified to an **sql** net with Schläfli symbol {4⁴·6²}. Furthermore, the adjacent 2D networks are packed parallel in a ···AAAA··· fashion, as depicted in Fig. 2d. It is noted that protonated carboxylate oxygen O3 and coordinated carboxylate oxygen O2 between these adjacent 2D networks could interact with each other and form strong O3–H3A···O2#4 (symmetry code: #4 = 2 - *x*, 1 - *y*, 1 - *z*) hydrogen bonds (Table S2, ESI†), which further link the 2D networks into a 3D supramolecular architecture (Fig. 2e).

 $\{[Zn_2(BIBP)_{0.5}(hfipbb)_2] \cdot H_2O\}_n$ (5). X-ray analysis reveals that compound 5 crystallizes in the monoclinic space group P2/c. As shown in Fig. 3a, the unique portion of structure 5 consists of two crystallographically independent Zn(II) cations, half of a BIBP ligand and two completely deprotonated 4,4'-(hexafluoroisopropylidene)bis(benzoic acids). Both Zn(II)cations are four-coordinated with distorted tetrahedral geometry, but their environments are different. Zn1 is coordinated by three bidentate carboxylate oxygen atoms from three hfipbb ligands and one nitrogen atom from the BIBP ligand, while Zn2 is coordinated by three bidentate carboxylate oxygen atoms from three hfipbb ligands and one monodentate carboxylate oxygen atom from one hfipbb ligand. The Zn-N and Zn-O bond lengths fall in the normal range of 1.988(2) and 1.902(2)-1.953(3) Å, respectively. In compound 5, the left- and right-handed helical chains are formed through the coordination between the hfipbb ligands and the $Zn(\pi)$ cations (Fig. 3d). These adjacent single-handed helical chains are further interconnected into a 2D chiral layer by sharing the $Zn(\pi)$ cations (Fig. 3c). The most interesting is that the two types of chiral layers adopt a rare arrangement²³ by alternate bridging by the BIBP ligands to generate a 3D framework (Fig. 3b) with tubular channels along the *b* axis. Therefore, the amounts of left- and right-helices are equal in compound 5, giving a racemic structure. Topologically, each dinuclear $Zn(\pi)$ unit can be considered as a 5-connected node, so the resulting structure can be regarded as a 5-connected sqp network with point symbol $\{4^4 \cdot 6^6\}$, which is different from the recent publication revealing a rare example of uninodal 5-coordinated net with a point Schläfli symbol $\{4^4 \cdot 6^6\}$ (three-letter notation noz).²⁴ To the best of our knowledge, only a few MOFs with sqp topology especially constructed by mixed organic ligands have been reported.²⁵ Furthermore, open void space within the single 3D framework is minimized by the interpenetration of another identical 3D framework to maintain the stability of the whole structure, which leads directly to the formation of a 2-fold interpenetrated final framework (Fig. 3e). PLATON analysis gives the free void volume ratio of 15.0% in compound 5.

 $\{[Zn_4(BIBP)_4(bdc)_4]\}_n$ (6). Compound 6 crystallizes in the monoclinic crystal system, space group P21/c and exhibits a 2D layer structure. The unique portion of structure 6 consists of four unique $Zn(\pi)$ cations, four BIBP ligands and four



Fig. 3 (a) Coordination environment of the Zn(II) cations in **5**. The hydrogen atoms are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = 1 - x, 1 + y, 1.5 - z; #2 = -x, -1 + y, 1.5 - z; #3 = 1 - x, -2 - y, 2 - z. (b) View of 3D single framework of **5**. (c) A perspective of the left-handed and right-handed layers in **5**. (d) Space-filling diagram of the helical chains in the 2D helical layers. (e) Schematic representation of the 2-fold interpenetrated **sqp** topology of **5**.

deprotonated isophthalic acids (Fig. 4a). The four $Zn(\pi)$ cations display two different coordination geometries. As shown in Fig. 4a, Zn1, Zn2, and Zn4 are in a distorted {ZnN₂O₂} tetrahedron derived from two nitrogen atoms of two BIBP ligands and two carboxylate oxygen atoms from two bdc²⁻ ligands, while Zn3 cation adopts a typical five-coordinated {ZnN₂O₃} square-pyramidal geometry with two nitrogen atoms of two BIBP ligands and three carboxylate oxygen atoms from two bdc²⁻ ligands. The Zn-O lengths are in the range of 1.964(3)-2.337(3) Å, while the Zn-N bond lengths are in the range of 2.002(3)-2.089(2) Å, which are in the normal ranges. It is noticed that the four deprotonated isophthalic acids adopt different coordination modes. One adopts bismonodentate mode, while the other three show monodentate modes. The single 2D layer (Fig. 4b) could be simplified to a highly undulated $\{4^4 \cdot 6^2\}$ -sql network. In addition, the adjacent 2D layers are further extended into an intriguing 3D supramolecular framework through weak intermolecular hydrogen bonds C12-H12···O5#3 and C(17)-H(17)···O(3)#4 (symmetry



Fig. 4 (a) Coordination environment of the Zn(n) cation in **6** (30% probability displacement ellipsoids). The hydrogen atoms are omitted for clarity. Symmetry codes: #1 = 1 + x, *y*, *z*; #2 = 1 + x, *y*, 1 + z. (b) Polyhedral view of the 2D coordination network of **6** along the *a* axis. (c) View of 3D supramolecular framework of **6** incorporating hydrogen bonds (purple dashed line).

codes: #3 = 1 - x, 1 - y, -z; #4 = 1 - x, 1/2 + y, 1/2 - z) (Table S2, ESI†) as illustrated in Fig. 4c.

 $\{[Zn(BIBP)(DL-ca)] \cdot H_2O\}_n$ (7). Compound 7 exhibits a rare 3D non-interpenetrated framework with cds topology. Single crystal X-ray analysis reveals that compound 7 crystallizes in the monoclinic crystal system, space group P21/c. The unique portion of the structure consists of one independent $Zn(\pi)$ cation, one deprotonated camphor acid and two halves of a BIBP ligand. It is noted that compound 7 is a racemate, although the chiral ligand of D-H₂Ca was used as starting material. So, the in situ racemisation of the D-H2Ca was caused by the hydrothermal conditions during the synthesis of compound 7.26 As shown in Fig. 5a, the Zn(II) cation is located in a distorted tetrahedral geometry {ZnN2O2}, completed by two N atoms belonging to two BIBP ligands and two O atoms from two DL-ca2- ligands. The Zn-N and Zn-O bond lengths are in the ranges of 2.032(4)-2.041(3) and 1.966(3)–1.980(3) Å. The bond angles around the Zn(II) cation range from 95.18(13)° to 127.40(12)°. In 7, the ca²⁻ ligands bridge the adjacent Zn(II) cations in a monodentate coordination mode to give rise to a 1D infinite chain (Zn(II)-DL-ca²⁻ chain) with Zn…Zn separation of 9.328 Å (Fig. 5b). The 1D zig-zag chain (Zn(II)-BIBP chain) is also formed by the BIBP



Fig. 5 (a) Coordination environment of the Zn(III) cations in 7. The hydrogen atoms are omitted for clarity (30% ellipsoid probability). Symmetry codes: #1 = -1 + x, 1.5 - y, -0.5 + z; #2 = -x, 1 - y, -z; #3 = 1 - x, 2 - y, 1 - z. (b) Left: view of the chain formed by Zn(III) cations and D-ca²⁻ ligands. Middle: view of the zig-zag chain formed by Zn(III) cations and BIBP ligands. Right: view of 3D framework of 7. (c) Schematic view of the **cds** topology of structure 7.

ligands and Zn(II) cations with a Zn···Zn distance of 16.328 Å (Fig. 5b). The combination of 1D chains of Zn(II)–DL-ca^{2–} and Zn(II)–BIBP generates the 3D structure of 7 (Fig. 5b). The desolvated framework shows 16.2% void space to the total crystal volume as calculated by PLATON. A better insight into the nature of this intricate framework is provided by a topology analysis. From the viewpoint of structural topology, the Zn(II) cations can be regarded as 4-connected nodes with all crystallographically independent BIBP ligands and DL-ca^{2–} as linkers; thus, the 3D framework of 7 can be simplified as an uninodal 4-connected network with CdSO₄ (cds) topology (with the Schläfli symbol $\{6^5 \cdot 8\}$), as displayed in Fig. 5c. It is noteworthy that almost all cds-type MOFs are interpenetrated due to the self-duality of the cds net,²⁷ compound 7 is a rare example of a non-interpenetrated cds-type framework.

Optical absorption properties

The solid-state UV-vis spectra of the free organic ligands and compounds 1–7 are displayed in Fig. S10 (ESI[†]). The absorption peaks at 230, 320 nm (BIBP), 228, 283 nm (H₂hfipbb), 225, 301 nm (H₃btc), 308 nm (5-OH-H₂bdc), 292 nm (H₂bdc),

and 224 nm (D-H₂ca) are shown in Fig. S10a,† which can be ascribed to $\pi \to \pi^*$ and $n \to \pi^*$ transitions of the ligands, respectively. The absorption peaks at 222, 325, 592 nm (compound 1), 219, 328, 521 nm (compound 2), 210, 327 nm (compound 3), 214, 331 nm (compound 4), 215, 338 nm (compound 5), 226, 332 nm (compound 6), and 213, 335 nm (compound 7) are also observed in the respective spectra. In all the spectra, the lower energy bands are assigned as d-d transitions of $Co(\pi)$ cations²⁸ (1 and 2) and ligand-to-metal charge transfer transitions²⁹ of the other five Zn(II) and Cd(II) compounds, and the higher energy bands are considered as intraligand transitions. To investigate the semiconductivity, the diffuse reflectance data is transformed into the Kubelka-Munk function to obtain their band gaps (E_{α}) . As shown in Fig. S10b,† the band gap of BIBP is approximately 2.55 eV, which exhibits a semiconductive nature. The E_{g} values assessed from the steep absorption edge are 2.41 eV for , 2.44 eV for 2, 2.48 eV for 3, 2.46 eV for , 2.83 eV for 5, 2.68 eV for 6, and 2.72 eV for 7. So, these compounds exhibit optical band gaps which are characteristic for optical semiconductors.

Luminescent properties

Luminescent MOFs are of great interest due to their various applications in photochemistry, chemical sensors and lightemitting diodes. Therefore, the solid-state luminescence of free ligands BIBP, H₂hfipbb, H₂bdc, 5-OH-H₂bdc, as well as compounds 3-7 are investigated at room temperature, as depicted in Fig. S1 and Table S3 (ESI⁺). The main emission peaks of the BIBP, H₂hfipbb, H₂bdc, and 5-OH-H₂bdc were observed at 496 nm (λ_{ex} = 354 nm), 325 nm (λ_{ex} = 290 nm), 380 nm (λ_{ex} = 276 nm), and 368 nm (λ_{ex} = 289 nm), which can be assigned to the $\pi^* \rightarrow n$ or $\pi^* \rightarrow \pi$ transitions.³⁰ The emission peaks are observed at 508 nm (λ_{ex} = 394 nm) in 3, 513 nm (λ_{ex} = 397 nm) in 4, 526 nm (λ_{ex} = 392 nm) in 5, 524 nm (λ_{ex} = 393 nm) in 6, and 485 nm (λ_{ex} = 390 nm) in 7. Compounds 3-7 exhibit their emission characters similar to that of the free BIBP ligand. Therefore, the emission bands of the compounds 3-7 can be mainly attributed to the intraligand (BIBP) emissions. Compared to the free BIBP ligand, the emission band of 3, 4, 5 and 6 is 12 nm, 17 nm, 30 nm, and 28 nm, blue-shifted and the emission band of 7 is 11 nm red-shifted, respectively.

Thermal analysis

Thermogravimetric analysis (TGA) was conducted to investigate the thermal stability of compounds 1–7 (Fig. S12, ESI†). Compounds 5 and 7 show a weight loss of 1.58% in 158–202 °C and 2.95% in 162–220 °C assigned to the release of lattice water molecules (calcd. 1.67% for 5 and 3.10% for 7). The remaining frameworks are thermally stable up to 394 and 452 °C, respectively. After that, the organic components start to decompose. Compounds 1–4 and 6 exhibit similar thermal behaviors. They do not contain guest molecules, so there is no obvious weight loss before 392, 360, 371, 364, and 369 °C for 1–4 and 6, respectively. Then the frameworks begin to collapse, accompanying the loss of organic ligands.

Conclusions

In summary, seven new coordination polymers have been successfully synthesized under hydrothermal conditions by the reaction of BIBP and a series of carboxylate ligands together with metal salts. Compound 1 features a fascinating 2D + $2D \rightarrow 3D$ framework with parallel polycatenation of undulated 44.62-sql layers. Compounds 2-4 display 2D layer structures with $\{4^4 \cdot 6^2\}$ -sql topology. Compound 5 exhibits 2-fold interpenetrating 3D frameworks with rare $\{4^4 \cdot 6^6\}$ sqp topology, containing a fascinating ... LRLR... double helical layer structure. Compound 6 is a 2D network with $\{4^4 \cdot 6^2\}$ -sql topology and further extended into a 3D supramolecular framework via C-H···O hydrogen bonds. Compound possesses 7 a rare 3D non-interpenetrated cds-type framework with $\{6^5 \cdot 8\}$ topology. Thermal stabilities for 1-7 and photoluminescence properties of compounds 3-7 have been investigated. Furthermore, the UV-vis absorption spectra and optical energy gaps of 1-7 imply that these compounds are potential wide gap semiconductor materials.

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