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Acentric and chiral four-connected metal–organic frameworks based on the racemic binaphthol-like chiral ligand of 4-(1-H(or methyl)-imidaozol-1-yl)benzoic acid[†]

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By modulating the synthetic strategy based on changing substituents on the ligand and solvent used in the synthesis, a series of metal organic frameworks (MOFs) of two chiral binaphthol-like ligands of 4-(1*H*-imidaozol-1-yl)benzoic acid (HIBA) and 4-(1*H*-2-methylimidazol-1-yl)benzoic acid (HMIBA) with various interpenetrating topologies have been synthesized under solvothermal conditions: Zn(IBA)₂ (1), Co(IBA)₂ (2), Cd(IBA)₂·H₂O·1.7DMF (3), Cd(MIBA)₂·H₂O·1.3DMF (4), Co(MIBA)₂·H₂O·1.3DMF (5) and Cd(MIBA)₂·0.5H₂O·1.2DMA (6) (DMF = *N*,*N*dimethylformamide and DMA = *N*,*N'*-dimethylacetamide). X-ray diffraction study reveals that compounds 1 and 2 crystallize in tetragonal crystal system with chiral space groups *P*4₁22 and *P*4₃22, respectively, indicating that they are a pair of structural enantiomers, having a twofold interpenetrating (4,4)-net. Compound 3 crystallizes in orthorhombic crystal system and non-centrosymmetric space group *Pca*2₁, which can be defined as an abnormal fourfold [2 + 2] interpenetrating diamond net. The isostructural compounds 4 and 5 crystallize in tetragonal crystal system and space group *P*42₁2, representing a chiral structure and a normal mode of fourfold interpenetrating diamondoid net. Compound 6 crystallizes in non-centrosymmetric space group *Aba*2 and exhibits a normal mode of fourfold diamondoid interpenetrating net.

Introduction

Metal–organic frameworks (MOFs) are crystalline solids constructed from metal ions and organic ligands, and have attracted much attention from chemists and material scientists owing to their promising applications in magnetism,¹ catalysis,² luminescence and chemical sensing,³ as well as gas adsorption and/or separation.⁴ However, any of these applications has to meet the requirement of material thermal robustness. Since the first porous MOF reported by Robson and others in the early 1990s,⁵ the newly discovered porous materials have developed from the first generation of fragile MOFs to the current third generation of thermally stable ones involving dynamic channels.⁴ This great progress mainly depends on the rational design and reticular synthesis of the MOFs, of which the zeolitic metal– organic frameworks (ZMOFs)⁶ are among the most eye-catching for approaching third generation porous MOFs. Owing to the similar structural features of zeolitic primary building units of TO_4 (T = tetrahedral Si or Al, O–T–O = 109.5°, T–O–T = 145°, in which the T–O bonds could freely rotate), the metal (zinc(II), cobalt(II) and cadmium(II)) imidazolate frameworks not only have adopted the zeolitic topologies, but also have developed several elegant unprecedented zeolite-like structures.⁶⁴ All of these have formed a large family of ZMOFs. Besides the ZMOFs formed by four-coordinated metal ions and imidazole (or substituent imidazole) ligands, the ZMOFs derived from eight-coordinated metal ions and 4,5-imidazoledicarboxylic acid (IDCA)^{6e} have also been realized owing to the four dentate ligands functioning as the linkers of eight-coordinated nodes in four-connected nets. However, due to the rotational inflexibility of the chelate bonds between the ligands and metal atoms, this motif suffers from limited zeolitic topological varieties.

To create novel MOFs having zeolitic structures, another imidazole derivative of 4-(1H-imidaozol-1-yl)benzoic acid (HIBA) may be worthy of consideration. MOFs based on HIBA have scarcely been reported⁷ where the ligand combines with sixcoordinated divalent metal ions in forming four-connected nets. We expect that ZMOFs can also be realized by using HIBA ligand and the divalent metal ions (Scheme 1).

Moreover, the ligand shows a dihedral angle between the imidazolyl and benzoyl rings that affords the ligand with binaphthol-like atropisomeric chirality⁸ (Scheme 2b). Thus, by

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Scheme 1 (a) The coordinate orientation similarity between HIBA and imidazole (b) The schematic illustration of the four-connected nodes based on the six-coordinated metal (M) and the ligand of HIBA (or HMIBA) (only three neighboring M-atoms are selected for clarity).



Scheme 2 (a) A schematic illustration of the synthesis of HIBA·HCl and HMIBA·HCl. (b) The binaphthol-like atropisomeric chirality for the ligands of HIBA and HMIBA

a rational synthesis based on this ligand, chiral ZMOFs could be realized that is essentially significant for porous materials.⁹ Therefore, HIBA and 4-(1-methyl-imidazol-1-yl)benzoic acid (HMIBA) were synthesized according to earlier literature¹⁰ (Scheme 2a). And by using the ligands, six MOFs were obtained under solvothermal conditions. Herein, we report the synthesis and characterization of these MOFs.

Experimental

Materials and physical measurements

Solvents and starting materials for synthesis were obtained commercially and used as received without further purification. The IR spectra were recorded from KBr pellets in the range of 4000–400 cm⁻¹ on a FT-IR spectrometer TENSOR 27 (see the ESI, Fig. S1 and S2†). The C, H and N elemental analyses were conducted using a Perkin-Elmer 240C elemental analyzer. The XRD analyses were carried out on a Bruker D8 Advance (see the ESI, Fig. S3†) and the Thermogravimetric Analysis (TGA) was performed under a nitrogen stream with a heating rate of 10 °C min⁻¹ by using a Perkin-Elmer Diamond Thermogravimetric Analyzer (see the ESI, Fig. S4†).

Preparation of binaphthol-like ligands

The synthesis of **HIBA**·**HCl**·**H**₂**O** was performed according to the literature method for preparation of 1,3,5-tri(7-azaindol-1-yl)benzene.¹⁰ A mixture of K₂CO₃ (1.93 g, 0.014 mol), 4-bro-mobenzoic acid (1.00 g, 0.005 mol), imidazole (1.71 g, 0.025 mol),

CuSO₄·5H₂O (0.0025 g, 1.0×10^{-5} mol) were ground sufficiently in an agate mortar. Then, the powdered reactant mixture was transferred into a 30 mL Teflon-lined autoclave, which was sealed and heated at 200 °C for 10 h. After cooling the reaction system to room temperature, the reaction mixture was dissolved in water, and then, filtered off. The filtrate was adjusted with dilute hydrochloric acid for pH 2.0–3.0 and evaporated to dryness in vacuum. This raw product was recrystallized in ethanol and 0.78 g colorless needle crystals of HIBA·HCl·H₂O were obtained (Yield: 62%, based on 4-bromobenzoic acid). IR (cm⁻¹, KBr): 3438 (w), 3266 (m), 1702 (vs), 1608 (m), 1536 (m), 1426 (w), 1386 (m), 1335 (m), 1240 (s), 1106 (m), 1036 (w), 935 (w), 792 (m). Elementary Anal. Calcd for C₁₀H₁₁N₂O₃Cl: C, 49.50; H, 4.57; N, 11.54%. Found: C, 51.06; H, 4.97; N, 11.86%.

HIBA·**HCl**·**H**₂**O** was prepared in a procedure almost the same as above, where the imidazole was replaced by 2.05 g (0.025 mol) 2-methylimidazole. 0.87 g product was obtained (yield: 68% based on 4-bromobenzoic acid). IR (cm⁻¹, KBr): 3356 (m), 3155 (m), 2787 (s), 1703 (vs), 1605 (s), 1515 (m), 1406 (m), 1236 (vs), 916 (w), 856 (m), 756 (m). Elementary Anal. Calcd for $C_{11}H_{13}N_2O_3Cl$: C, 51.47; H, 5.10; N, 10.91%. Found: C, 51.10; H, 5.27; N, 10.56%.

Synthesis of Co(IBA)₂ (1)

A mixture of Co(NO₃)₂·6H₂O (0.0291 g, 0.1 mmol), HIBA·HCl·H₂O (0.0243 g, 0.1 mmol), and DMF (6 mL) was stirred at room-temperature for 10 min and then was placed into a 10 mL Teflon-lined stainless steel container, which was sealed and heated at 200 °C for 12 h. After cooling to room temperature, blue block crystals of **1** were collected (Yield 60%, based on Co). Elementary Anal. Calcd for C₂₀H₁₄N₄O₄Co: C, 55.44; H, 3.26; N, 12.93%. Found: C, 55.61; H, 3.16; N, 12.85%. IR (cm⁻¹, KBr): 3415 (m), 3124 (m), 1612 (vs), 1570 (s), 1523 (s), 1375 (vs), 1240 (m), 1057 (m), 969 (w), 835(m), 787 (m).

Synthesis of Zn(IBA)₂ (2)

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0297 g, 0.1 mmol), HIBA·HCl·H₂O (0.0243 g, 0.1 mmol) and DMF (6 mL) was stirred at room-temperature for 10 min, and then was placed into a 10 mL Teflon-lined autoclave, which was sealed and heated at 70 °C for 11 days. After cooling to room temperature, colorless needle crystals of **2** were collected (Yield 52% based on Zn). Elementary Anal. Calcd for C₂₀H₁₄N₄O₄Zn: C, 54.63; H, 3.21; N, 12.74%. Found: C, 54.46; H, 3.39; N, 12.86%. IR (cm⁻¹, KBr): 3436 (m), 3120 (m), 1619 (s), 1529 (m), 1374 (s), 1123 (m), 1071 (m), 846 (m), 775 (m).

Synthesis of Cd(IBA)₂·H₂O·1.7DMF (3)

A mixture of Cd(NO₃)₂·4H₂O (0.0308 g, 0.1 mmol), HIBA·HCl·H₂O (0.0243 g, 0.1 mmol) and DMF (6 mL) was stirred at room-temperature for 10 min, the mixture was transferred into a 10 mL Teflon-lined autoclave, which was then sealed and heated at 130 °C for 2 days. After cooling to room temperature, colorless block crystals of **3** were isolated by filtration. (Yield 45%, based on Cd). Elementary Anal. Calcd for $C_{22.85}H_{20.65}N_{4.95}O_{6.7}Cd$: C, 46.98; H, 3.57; N, 11.87%. Found: C, 45.68; H, 3.21; N, 11.32%. IR (cm⁻¹, KBr): 3423 (m), 3126 (w), 1664 (m), 1600 (s), 1554 (s), 1525 (s), 1399 (vs), 1303 (m), 1250 (w), 1058 (m), 858 (w), 781 (m), 748 (m), 659 (w).

Synthesis of Cd(MIBA)₂·H₂O·1.3DMF (4)

A mixture of Cd(NO₃)₂·4H₂O (0.0308 g, 0.1 mmol), HMI-BA·HCl·H₂O (0.0509 g, 0.2 mmol) and DMF (6 mL) was stirred at room-temperature for 10 min. Then, the mixture was transferred into a 10 mL Teflon-lined autoclave which was sealed and heated at 130 °C for 2 days. After cooling to room temperature, colorless rod crystals of **4** were isolated by filtration. (Yield 45%, based on Cd). Elementary Anal. Calcd for C_{25.9}H_{27.9}O_{6.1}N_{5.3}Cd: C, 49.96; H, 4.53; N, 11.93%. Found: C, 49.44; H, 4.18; N, 11.45%. IR (cm⁻¹, KBr): 3455 (m), 3126 (w), 3008 (w), 2933 (w), 2858 (w), 1677 (s), 1600 (s), 1548 (s), 1406 (vs), 1303 (m), 1097 (m), 865 (m), 788 (m), 742 (m), 671 (w).

Synthesis of Co(MIBA)₂·H₂O·1.3DMF (5)

Blue rectangle crystals of **5** (Yield 52% based on Co) were obtained by adopting the same procedures for the synthesis of **4**, where $Co(NO_3)_2 \cdot 6H_2O$ (0.0291 g, 0.1 mmol) was used instead of $Cd(NO_3)_2 \cdot 4H_2O$. Elementary Anal. Calcd for $C_{26}H_{29.5}O_{6.3}N_5Co$: C, 54.69; H, 5.22; N, 12.27%. Found: C, 54.31; H, 4.98; N, 11.87%. IR (cm⁻¹, KBr): 3479 (m), 3136 (w), 3080 (w), 2931 (w), 2861 (w), 1674 (s), 1604 (s), 1546 (s), 1417 (vs), 1306 (m), 1094 (w), 862 (m), 790 (m), 740 (m), 678 (w).

Synthesis of Cd(MIBA)₂·0.5H₂O·1.2DMAC (6)

A mixture of Cd(NO₃)₂·4H₂O (0.0308 g, 0.1 mmol), HIM-BA·HCl·H₂O (0.0509 g, 0.2 mmol) and DMAC (6 mL) was stirred at room-temperature for 10 min, then it was transferred into a 10 mL Teflon-lined autoclave that was sealed and heated at 100 °C for 4 days. After cooling to room temperature, colorless cross-shaped crystals of **6** were isolated by filtration. (Yield 60%, based on Cd). Elemental Anal. Calcd for C_{30.8}H_{37.8}N_{6.2} O_{6.2}Cd: C, 52.36; H, 5.40; N, 12.30%. Found: C, 51.89; H, 4.84; N, 11.94%. IR (cm⁻¹, KBr): 3429 (m), 3114 (w), 3069 (w), 2927 (w), 1602 (s), 1547 (s), 1400 (vs), 1311 (m), 1106 (w), 857 (m), 786 (m), 738 (w), 677 (w).

Single-crystal X-ray crystallography

X-ray single-crystal diffraction data for both of the two free ligands and their coordination polymers 1-6 were collected on a Bruker SMART CCD diffractometer with graphite-monochromatized Mo-Ka radiation (0.71073 Å) at 293(2) K. Data integration and reduction were processed with SAINT¹¹ software. An empirical absorption correction was applied to the collected reflections with SADABS¹² using XPREP.¹³ The structure was solved by the direct method using SHELXTL14 and refined on F^2 by the full matrix least-squares technique using the SHELXL-97 program package. All non-hydrogen atoms were refined with anisotropic thermal parameters. Because guest solvent molecules (DMF or DMA) in the channels of 3-6 were highly disordered, the diffused electron densities resulting from them were removed by the SQUEEZE routine in PLATON¹⁵ and the results were attached to the CIF file. Details of the structural analysis of the two chiral ligands and compounds 1-6 are summarized in Table S1 (see the ESI[†]) and Table 1, respectively. Selected bond lengths and angles are listed in Table S2.[†]

Results and discussion

Syntheses and characterization of the ligands

The ligand of HIBA was synthesized by modulating the literature reported method as illustrated in Scheme 2. In order to obtain the derivatives of HIBA with alkyl substituents on the imidazolyl ring; expecting that the alkyl substituent could function as the template or structure-directing group, we used 2-alkyl (alkyl =methyl, ethyl and propyl) imidazole in place of 2-H-imidazole. However, because of the domain of the S_N2 mechanism in the reaction, a large substituent on the imidazolyl ring serves as an obstacle in hindering the substitution reaction. Therefore, by the present synthetic routine, only ligands of HIBA and HIMBA can be prepared and they were obtained as the salts of HIBA · HCl and HMIBA·HCl. X-ray single-crystal diffraction study on the ligands confirms that they have the binaphthol-like atropisomeric chirality and show dihedral angles of 37° and 50° between the imidazolyl and benzoyl rings, respectively. Despite the ligands being chiral, they were prepared as racemic mixtures in a ratio of R: S = 1:1 (see ESI S5[†]). And the chirality resolution for the ligands was not performed due to racemization of the compounds readily taking place under solvothermal conditions, under which their coordination polymers will then be synthesized.

Syntheses of compounds 1-6

The syntheses of the compounds was carried out under solvothermal conditions, in which the hydrochloric salts of the ligands were used. Thus, the solvent utilized should be DMF and DMA since they can digest the extra acid during the solvothermal reaction. The metal ions employed in the synthesis are divalent six-coordinated transition metal cations because they can incorporate with the ligands to from the neutral four-connected frameworks. So far, only the frameworks of Co(II), Zn(II) and Cd(II) can be obtained and they generate six MOFs, representing four different structural types. X-ray powder diffraction patterns were experimentally obtained on the bulk samples of **1–6** and they are in agreement with those simulated from their X-ray single-crystal data, revealing that the structures of the single crystal **1–6** represent those of the bulk samples.

Crystal structures of Co(IBA)₂ (1) and Zn(IBA)₂ (2)

Both of the compounds 1 and 2 crystallize in tetragonal and have almost the same crystal parameters. Therefore, they are enantiomeric crystals with space groups $P4_122$ and $P4_322$, respectively. In the structures of 1 (or 2), Co(II) (or Zn(II)) ions are four-coordinated, while the carboxyl groups of the ligands are monodentate and they associate with imidazolyl nitrogen atoms in linking the metal cations (Fig. 2a, 2b) into a two-dimensional sheet of (4,4)-network. Two-fold of such networks interpenetrate (Fig. 1c) and are stacked into the individual single crystal. With the Flack factors of 0.04(3) for 1 and 0.01(4) for 2, the two determined single crystals are individually characterized as the pure chiral enantiomers (Fig. 1a and 1b) and their chirality originates from the enantiopure ligands of (*R*)-HIBA and

 Table 1
 Crystallographic data and structure refinement summary for compounds 1–6

Compound	1	2	3	4	5	6
Formula Formula weight	C ₂₀ H ₁₄ N ₄ O ₄ Co 433.28	C ₂₀ H ₁₄ N ₄ O ₄ Zn 439.72	$\begin{array}{c} C_{22.9}H_{20.7}N_{5.0}\ O_{6.7}Cd\\ 584.19\end{array}$	C _{25.9} H ₂₈ N _{5.3} O _{6.1} Cd 622.58	C ₂₆ H _{29.5} N ₅ O _{6.3} Co 570.98	C _{30.8} H _{37.8} N _{6.2} O _{6.2} Cd 706.47
Crystal system	Tetragonal	Tetragonal	Orthorhombic	Tetragonal	Tetragonal	Orthorhombic
Space group	P4 ₁ 22	P4 ₃ 22	$Pca2_1$	P42 ₁ 2	P4212	Aba2
a/Å	8.0814(3)	8.0674(4)	19.0367(16)	18.8725(15)	18.5718(9)	15.573(2)
b/Å	8.0814(3)	8.0674(4)	8.2300(7)	18.8725(15)	18.5718(9)	19.416(3)
c/Å	28.0836(4)	28.0367(6)	18.2963(15)	8.0221(13)	7.7776(8)	19.664(3)
α (°)	90	90	90	90	90	90
β(°)	90	90	90	90	90	90
γ (°)	90	90	90	90	90	90
$V/Å^3$	1834.11 (10)	1824.71(13)	2866.5(4)	2857.2(6)	2682.6(3)	5945.8(15)
Flack	0.04(3)	0.01(4)	0.63(3)	0.36(6)	0.47(3)	0.10(4)
Ζ	4	4	4	4	4	8
$D_c/g \text{ cm}^{-3}$	1.569	1.601	1.458	1.463	1.421	1.406
GOF	0.976	1.007	0.994	1.013	1.074	1.048
RefIns collected/ unique	11555/2343	9881/1771	11412/4623	14296/2503	12408/2128	11183/3653
$R_{\rm int}$	0.0034	0.0699	0.0277	0.1077	0.0503	0.0688
$\frac{R_1^2}{[I > 2\sigma(I)]}$	0.0329/0.0691	0.0435/0.1008	0.0282/0.0686	0.0462/0.0605	0.051/0.128	0.045/0.078

(S)-HIBA, of which compound 1 or 2 consists. It should be noted that the compounds 1 and 2 have been earlier reported by Chen^{7d} and Sun,^{7b} who had occasionally determined the single crystals of 1 and 2 with the space group $P4_322$ and $P4_122$, the enantiomeric crystals of 1 and 2 with the space groups $P4_122$ and $P4_322$, respectively. This result reveals that the racemic form ligands of HIBA (*R*) and HIBA (*S*) can be induced by the metal cations of cobalt(II) (or zinc(II)) into a recognition-driven self-assembly of the enantiopure chiral crystals of (*R*)-1 (with space group $P4_322$) and (*S*)-1 (with space group $P4_122$) (or (*R*)-2 (with space group $P4_322$) and (*S*)-2 (with space group $P4_122$)), respectively. However, these individual enantiopure single crystals are mixed in a ratio of 1 : 1, which are racemic in bulk.

Cd(IBA)₂·H₂O·1.7DMF (3)

Compound 3 crystallizes in orthorhombic system, space group $Pca2_1$. In the crystal, the metal atoms are six-coordinated and the carboxyl groups are bidentate and associated with imidazolyl



Fig. 2 (a) The schematic views of the [2 + 2] interpenetration diamondoid net. (b) A single distorted adamantane cage in **3**, which consists of six (*S*)-IBA⁻ (red), six (*R*)-IBA⁻ (blue) and ten Cd metal ions (pink) (hydrogen atoms have been omitted for clarity). (c) Topological diagram of framework **3**, in which the curved links represent the non-linear ligand of IBA⁻.



Fig. 1 (a) 2D(4, 4)-network for 1 (or 2) with space group $P4_122_2$. (b) 2D(4, 4)-network for 1 (or 2) with space group $P4_322$. (c) Space-filing diagram of the (4,4)-network interpenetration in 1 or 2.

nitrogen atoms in a six-coordinate mode just as that illustrated in Scheme 1b, forming the expected four-connected net. However, it shows an interpenetrating network consisting of four independent equivalent diamondoid nets with the net separation in Cd…Cd distance of 12.390 Å along the *a*-direction and 12.536 Å along the *c*-direction (Fig. 2a), respectively. This fourfold net refers to the "abnormal" interpenetrating diamond-like net¹⁶ which can be described as a [2 + 2] interpenetrating diamondoid net (Fig. 2a, c) that is similar to the eightfold [4 + 4] interpenetrating diamond network.¹⁷ Unlike compounds 1 and 2, compound 3 is achiral because each of its single crystals is constructed by equal proportions of (*R*)-IBA and (*S*)-IBA (Fig. 2).

Cd(MIBA)₂·H₂O·1.3DMF (4) and Co(MIBA)₂·H₂O·1.3DMF (5)

Both of the compounds 4 and 5 crystallize in tetragonal, space group $P42_{1}2$. In the crystals, the metal atoms are also six-coordinated and the carboxyl groups have also the same coordination mode as that illustrated in Scheme 1. With the same four-connected diamond-like net (Fig. 3a), the two compounds characterize not only as the chiral, but also as the isostructural motifs. However, with the Flack parameters of 0.32(10) for 4 and 0.48(5)for 5, the two compounds are almost or totally racemic in the bulk. Topologically, although the compounds of 4 and 5 also exhibit a fourfold interpenetrating diamond-like net (Fig. 3b), they represent a "normal" interpenetration mode¹⁶ (Fig. 3b) that are commonly found in the diamond-like interpenetrating MOFs.

$Cd(MIBA)_2 \cdot 0.5H_2O \cdot 1.2DMA$ (6)

Compound 6 crystallizes in the orthorhombic system, space group *Aba2*. In the structure of 6, the coordination mode of the metals and ligands is the same as that of 3, 4 and 5, while the framework topology is also the fourfold diamond-like interpenetrating net of the "normal" mode (Fig. 4). With the achiral framework, compound 6 contains equal proportions of (*R*)-MIBA and (*S*)-MIBA ligands which are related symmetrically by the mirror-planes in the single crystals.

In review of the MOFs demonstrated above, two 2D layer structures and four 3D frameworks with diamond-like topology based on the HIBA and HMIBA were obtained that were obviously not the expected ZMOFs. With the uninodal net and vertex symbol of $6_26_26_26_26_26_2$, *dia* topology represents the uniform and non-porous frameworks. If a primary building unit has the strong tendency to form the four-connected framework with *dia* topology, this building



Fig. 3 (a) The single adamantane cage in **4** and **5** that consists of enantiopure (R)-MIBA⁻ (or (S)-MIBA⁻) and metal ions. (b) The fourfold interpenetration of diamondoid networks in crystals of **4** and **5**. (c) Topological diagram of framework **4** and **5**, in which the curved links represent the non-linear ligand of IMBA⁻.



Fig. 4 (a) The ball-and-stick (top) and the topological (bottom) diagrams of the normal four-fold interpenetrating diamond-like network of **6**. (b) Toplogical diagram of 3D framework of **6** in which the curved links represent the non-linear ligand of IMBA⁻.

unit must be lacking in, at least, one of the 3 structural features^{6g} owned by the zeolitic primary building unit. We can see in Scheme 1 that the chelating double bonds between the carboxyl groups and the metal atoms have made the four-connected frameworks of M(IBA)₂ and M(MIBA)₂ lose its flexibility of the Si–O bond-like rotation. Although there are also single bonds, such as the C–C (between carboxyl group and benzoic ring) and C–N (between benzoic and imidazolyl rings) bonds, in the ligands of IBA⁻ and MIBA⁻, they do not have the rotational flexibility due to the conjugating effect between the groups. Despite the building unit illustrated in Scheme 1 possessing the Si-like tetrahedral node and Si–O–Si-like angle, however, without the flexibility of the Si–O bond-like rotation, it is still difficult to form the zeolitic structures with the versatility of Si–Si–Iike angles.

Also, in reviewing the MOFs demonstrated above, 50% of the structures (Table 2) are chiral that reveals the use of a racemic chiral ligand being more likely to obtain the chiral structures and chiral recognition of the racemic ligands can be realized by forming enantiopure single crystals of 1 (or 2). However, in order to obtain the homochiral MOFs of the ligands, chiral separation of the ligands is still necessary because these enantiopure single crystals of 1 and 2 are still racemic in the bulk that are optically equal to the racemic twin chiral crystals of 4 and 5, in which chirality is transmitted from the chiral ligands that contain the asymmetric carbon atoms, the binaphthol-like ligands are more rigid and more likely to form the robust MOFs. Therefore, design and synthesis of enantiopure binaphthol-like ligands should be an effective strategy for realizing the robust chiral porous MOFs.

Like the other ZMOF synthesis, the solvent used can function as the structure-directing agent that is especially useful to the ligand with alkyl substituent groups, for example, different structural Cd(MIBA)₂ of **4** and **6** were generated by using DMF and DMA as solvents. But, by using the solvents only one structural Cd(IBA)₂ of **3** was synthesized.

Thermal stabilities of 3-6

In order to examine the thermal stabilities of **3–6**, TGA experiments were performed. The TGA data of compounds **3–6** depicted in Fig. S4† show that each of the compounds has a two-step of *ca.* 19–22% weight-loss before 170 °C, corresponding to the departure of H₂O and DMF molecules. There is no weight-loss or obvious heat change observed in the temperature range of

Table 2 General view and comparison of 2-6

	CoL ₂		CdL ₂		
Ligands L	HIBA	HMIBA	HIBA	HMIBA	HMIBA
Solvent	DMF	DMF	DMF	DMF, DMA	DMA
Single-Crystal	1 and 2	5	3	4	6
Space group	P4122	P42 ₁ 2	$Pca2_1$	P42 ₁ 2	Aba2
Configuration of L	S	S and R	S:R = 1:1	S and R	S:R = 1:1
Absolute configuration	Chiral complex	Twin Crystal	Mesomer	Twin Crystal	Mesomer
Network	(4,4)	Diamond	Diamond	Diamond	Diamond
Degree and mode of	2	4	4	4	4
interpenetration	Normal	Normal	[2 + 2]	Normal	Normal

172-350 °C, indicating that the guest-free frameworks can maintain their framework integrity below 350 °C.

Conclusion

In summary, six MOFs based on the particularly designed binaphthol-like chiral ligands of HIBA and HMIBA have been synthesized under solvothermal conditions. Owing to the structure-directing effect of the substituent on the imidazolyl ring and the solvent used in the synthesis, different interpenetrating diamond-like structures were obtained. However, none of ZMOFtype structures based on the ligands can be synthesized due to the MOFs lack of the Si–O bond-like rotational flexibility. As the binaphthol-like chiral ligands, despite the ligands of HIBA and HMIBA are used as synthesized in the racemic form, 50% of MOFs obtained are chiral that reveals the binaphthol-like ligands being another likely choice for the rational design and synthesis of chiral MOFs with robust structures. Nevertheless, the search for new binaphthol-like ligands in construction of the chiral ZMOFs is still under way.

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