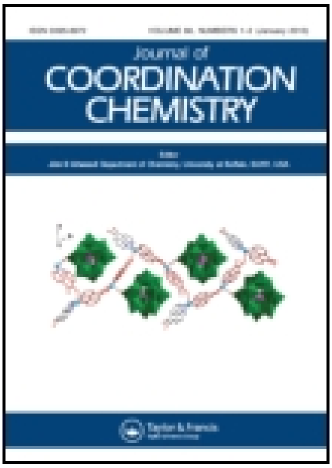

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Synthesis, crystal structure, and characterization of two three-fold interpenetrating Co(II) coordination polymers based on 1,4-benzenedicarboxylic acid and length modulated bisimidazole ligands

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Synthesis, crystal structure, and characterization of two three-fold interpenetrating Co(II) coordination polymers based on 1,4-benzenedicarboxylic acid and length modulated bisimidazole ligands

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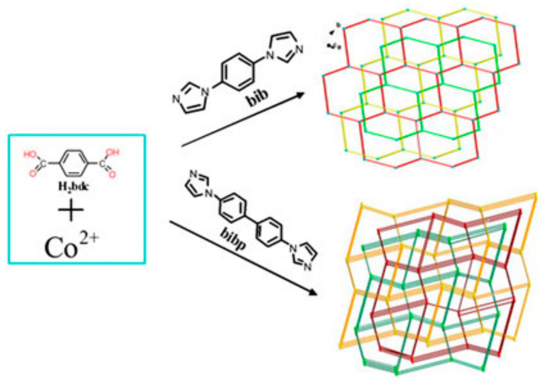

Two Co(II) coordination polymers, $\{[Co(bdc)(bib)(H_2O)]\cdot H_2O\}_n$ (**1**) and $\{[Co(bdc)(bibp)]\}_n$ (**2**), where H_2bdc = 1,4-benzenedicarboxylic acid, bib = 1,4-bis(1-imidazolyl)benzene, and bibp = 4,4′-bis(imidazolyl)biphenyl, have been synthesized by solvothermal methods and characterized by IR spectra, element analyses, thermal analysis, powder X-ray diffraction, and single crystal X-ray diffraction. Complex **1** exhibits a 3-D pillared-layer framework, the ligands of bib and bdc link Co ions to generate a 2-D layer structure, which is further pillared by the bib, giving the final 3-D pillared-layer networks. The void in **1** induces the three-fold interpenetrating structure. Complex **2** features three-fold interpenetrating 3-D architecture, bdc and bibp both adopt a bidentate bridging coordination to link Co ions to afford right- and left-handed helical chains; these helices fuse together and form the 3-D framework.

Keywords: Co(II) coordination polymers; Helical chains; 1,4-Benzenedicarboxylic acid; Bisimidazole ligands

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1. Introduction

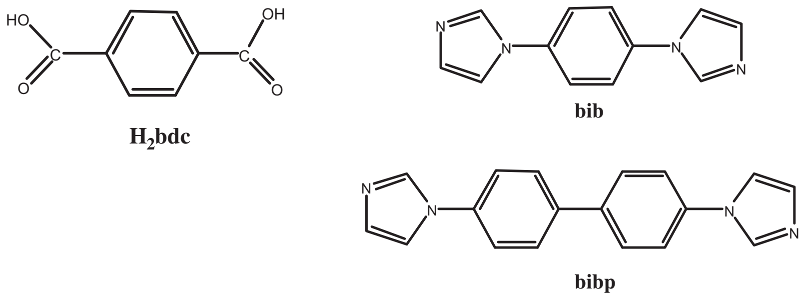
Design and synthesis of porous coordination polymers has attracted attention because of their intriguing structures and promising application as functional materials [1, 2]. To increase the volume and size of pores, ligands with long spacers have been incorporated into the construction of coordination polymers, but often produce interpenetrating frameworks that greatly reduce voids [3–5]. Thus, the goal of predicting and controlling the structure and interpenetration of frameworks is a concern for synthetic chemists. Factors influencing the topology and degree of interpenetration are intricate in self-assembly of coordination polymers, including weak interactions, counterion, length and flexibility of ligands [6–9]. Mixed-ligand coordination polymers are accompanied with even more uncertainty, and it is more difficult to predict and control the structures, but provide good examples to elucidate the effect of ligands on the degree of interpenetration through altering only auxiliary ligands [10–12].

Aromatic polycarboxylic acids such as 1,4-benzenedicarboxylic acid are versatile multidentate ligands to construct fascinating structures [13, 14], and rigid bis(imidazole) ligands such as 1,4-bis(1-imidazolyl)benzene (bib) and 4,4′-bis(imidazolyl)biphenyl (bibp) are good candidates to construct interpenetrating metal-organic frameworks (scheme 1) [9, 12, 15–17]. In this paper, we use 1,4-benzenedicarboxylic acid, 1,4-bis(1-imidazolyl) benzene (bib), and 4,4′-bis(imidazolyl)biphenyl (bibp) as building blocks and solvothermally synthesized two Co(II) coordination polymers with interpenetrating frameworks, $\{[Co(bdc)(bib)(H_2O)]\cdot H_2O\}_n$ (**1**) and $\{[Co(bdc)(bibp)]\}_n$ (**2**). All compounds were characterized by IR, elemental analysis, thermogravimetric analysis, powder X-ray diffraction (PXRD), and X-ray single crystal diffraction analysis.

2. Experimental

2.1. *Materials and methods*

All commercially available chemicals and solvents are of reagent grade and were used as received. Elemental analyses were performed on a Perkin-Elmer 240C Elemental Analyzer. Fourier Transform Infrared spectra were recorded on a Nicolet IR-470 instrument using KBr pellets. Thermogravimetric analyses were carried out on a TA Q600 thermal analyzer



Scheme 1. Schematic drawing of H_2bdc, bib and bibp.

under nitrogen with a heating rate of 10 °C min^{-1}. PXRD measurements were performed on a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation ($\lambda = 0.15405$ nm) in the 2θ range from 5° to 50°.

2.2. *X-ray crystallography*

Data were collected on a SMART CCD 1000 X-ray single-crystal diffractometer with MoKα radiation ($\lambda = 0.71073$ Å) at 293 K. The structures were solved by direct methods using SHELXL97 [18, 19] and all non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculation on F^2. Crystal data and structure refinement are summarized in table 1. Selected bond lengths (Å) and angles (°) are listed in table 2.

Table 1. Crystallographic data and structure refinement parameters for **1** and **2**.

Complex	**1**	**2**
Formula	$C_{20}H_{18}CoN_4O_6$	$C_{26}H_{18}CoN_4O_4$
Formula weight	469.31	509.37
Crystal system	Triclinic	Orthorhombic
Space group	*P-1(2)*	*Pnna*
a (Å)	8.701(3)	13.371(18)
b (Å)	9.587(3)	17.54(2)
c (Å)	12.498(4)	9.432(13)
α (°)	71.329(5)	90
β (°)	89.328(5)	90
γ (°)	79.922(5)	90
Z	2	4
ρ_{Calcd} (g cm^{-3})	1.605	1.530
μ (mm^{-1})	0.932	0.819
F (0 0 0)	482.0	1044
Reflections collected/unique	5995/4486	8936/1839
$R_1{}^{a}$, $wR_2{}^{b}$ ($I > 2\sigma(I)$)	0.0643, 0.1410	0.0535, 0.1344
$R_1{}^{a}$, $wR_2{}^{b}$ (all data)	0.1423, 0.1846	0.0965, 0.1640
GOF (F^2)	0.949	1.072

[a] $R_1 = \sum\left||F_o| - |F_c|\right|/\sum|F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**[a].

1			
Co(1)–O(3)	2.042(3)	Co(1)–N(1)	2.070(5)
Co(1)–N(3)	2.104(4)	Co(1)–O(5)	2.123(4)
Co(1)–O(2)	2.165(3)	Co(1)–O(1)	2.202(4)
O(3)–Co(1)–N(1)	94.67(17)	O(3)–Co(1)–N(3)	90.47(15)
N(1)–Co(1)–N(3)	93.70(18)	O(3)–Co(1)–O(5)	90.69(15)
N(1)–Co(1)–O(5)	94.01(18)	N(1)–Co(1)–O(2)	96.75(17)
N(3)–Co(1)–O(2)	93.29(15)	O(5)–Co(1)–O(2)	84.03(15)
N(3)–Co(1)–O(1)	86.86(16)	O(5)–Co(1)–O(1)	85.35(15)
2			
Co(1)–O(1)#1	2.000(3)	Co(1)–O(1)	2.000(3)
Co(1)–N(1)	2.052(4)	Co(1)–N(1)#1	2.052(4)
O(1)#1–Co(1)–O(1)	94.0(2)	O(1)#1–Co(1)–N(1)	122.33(15)
O(1)–Co(1)–N(1)	112.40(15)	O(1)#1–Co(1)–N(1)#1	112.40(15)
O(1)–Co(1)–N(1)#1	122.33(15)		

[a] Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1/2, -z + 1/2$.

2.3. *Preparation of 1 and 2*

2.3.1. Synthesis of {[Co(bdc)(bib)(H_2O)]·H_2O}$_n$ (1). A mixture of $CoCl_2$ (0.1 mM, 0.0129 g), 1,4-benzenedicarboxylic acid (0.1 mM, 0.0165 g), 1,4-bis(1-imidazolyl)benzene (0.1 mM, 0.0210 g), NaOH (0.2 mM, 0.0800 g), H_2O (10 mL) and DMF (2 mL) was stirred for 1 h in air, then was transferred to, and sealed in, a 25 mL Teflon-lined reactor and heated in an oven to 110 °C for 72 h. After cooling to room temperature, purple block crystals of **1** were collected by filtration, washed with water and DMF several times, and dried in air. Yield: 58% (based on Co). Anal. Calcd for $C_{20}H_{18}CoN_4O_6$: C, 51.18; N, 11.94; H, 3.87. Found: C, 51.23; N, 11.89; H, 3.85. IR (Infrared spectra, KBr pellet, cm^{-1}): 3121(s), 3095 (s), 2794(s), 1690(m), 1600(m), 1532(m), 1424(s), 1376(s), 1317(m), 1135(s), 1060(s), 958 (s), 826(s), 782(s), 734(s), 656(s), 524(s).

2.3.2. Synthesis of {[Co(bdc)(bibp)]}$_n$ (2). Complex **2** was obtained by a similar solvothermal procedure as that for the synthesis of **1** except that 4,4′-bis(imidazolyl)biphenyl (0.1 mM, 0.0286 g) instead of 1,4-bis(1-imidazolyl)benzene was used. After cooling to room temperature, purple block crystals of **2** were collected by filtration, washed with water and DMF several times, and dried in air. Yield: 63% (based on Co). Anal. Calcd for: C, 61.31; N, 3.56; H, 11.00. Found: C, 61.25; N, 3.62; H, 10.95. IR (KBr pellet, cm^{-1}): 3127 (s), 1607(m), 1516(m), 1394(s), 1354(s), 1312(s), 1239(s), 1127(s), 1064(s), 829(s), 756(s), 655(s), 561(s), 524(s).

3. Results and discussion

3.1. *Crystal structures of 1 and 2*

3.1.1. Crystal structure of {[Co(bdc)(bib)(H_2O)]·H_2O}$_n$ (1). X-ray structure determination shows that **1** is a pillared-layer metal-organic framework with three-fold interpenetration, crystallizing in the triclinic space group *P-1*. As shown in figure 1, each Co ion is coordinated by three oxygens of two different bdcs, one water and two nitrogens of two different bibs, resulting in a distorted octahedron. The Co–O and Co–N lengths are 2.041–2.203 and 2.071–2.104 Å, respectively, comparable with those observed in other Co(II) complexes [12, 20, 21]. The bdc ligands adopt two coordination modes, one as monodentate bridging and the other bidentate chelate bridging, alternately linking the Co ions to give a chain-like structure, and adjacent chains are connected by bib ligands generating a 2-D sheet-like structure with a large hexagonal grid (figure 2). The 2-D layer is further pillared by bib linkers to form porous pillared-layer framework with large cavities as shown in figure 3. The large space formed by the single 3-D framework allows incorporation of other identical networks. These nets interpenetrate to form a three-fold interpenetrated 3-D framework, and available void spaces in the single framework are significantly reduced (figure 4).

3.1.2. Crystal structure of {[Co(bdc)(bibp)]}$_n$ (2). Crystallographic analysis reveals that **2** crystallizes in the orthorhombic space group *Pnna*. The asymmetric unit of **2** consists of one Co^{2+}, half of a bdc and half of a bibp. As depicted in figure 5, Co1 is four coordinated with two O from two bdc ligands and two N of two different bibp ligands to form a slightly

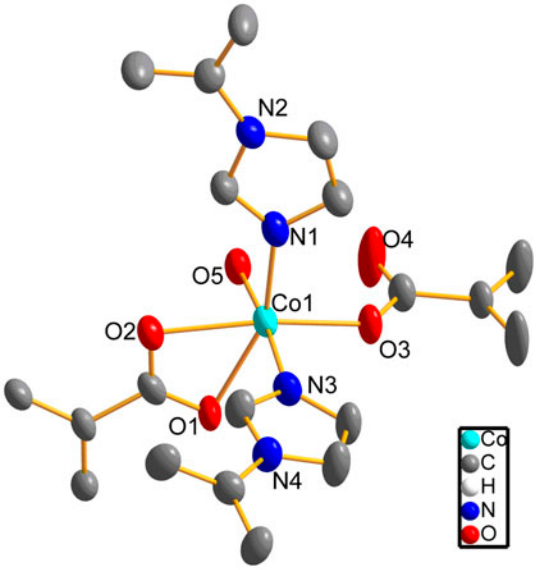


Figure 1. The coordination environment of Co(II) in **1**.

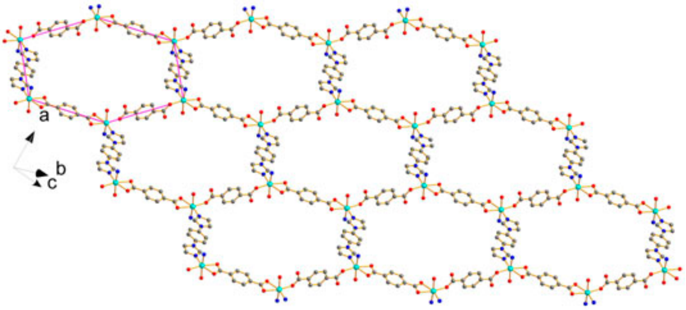


Figure 2. The 2-D network of **1** containing a large hexagonal grid.

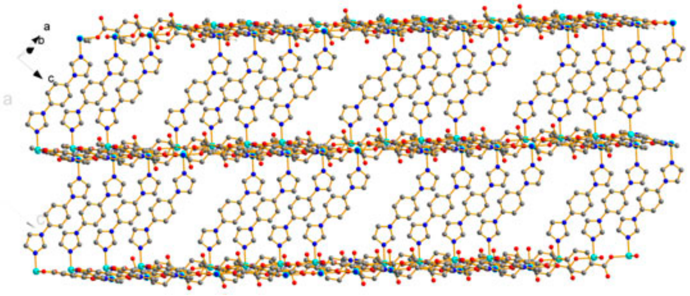


Figure 3. The 3-D pillared-layer structure of **1**.

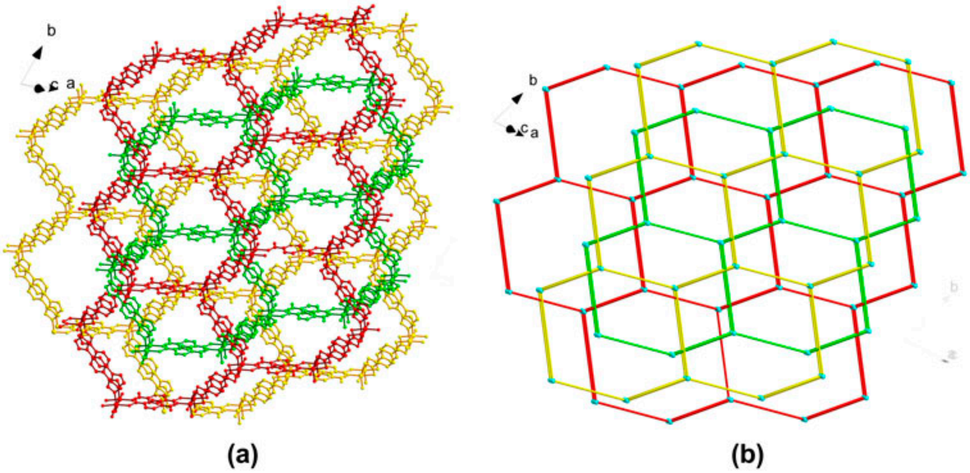


Figure 4. (a) The three-fold interpenetrating structure of **1**. (b) Schematic illustration of the three-fold interpenetrating structure of **1**.

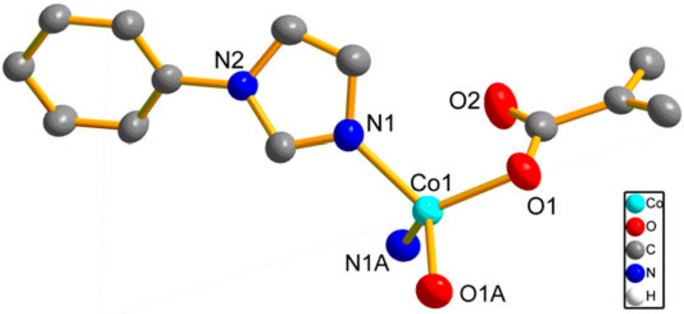


Figure 5. The coordination environment of Co(II) in **2**.

distorted tetrahedral geometry. The Co–O and Co–N bond lengths are 2.000(3) and 2.052 (4) Å, respectively, similar to those observed in tetrahedral Co(II) complexes [22]. The bdc and bibp both adopt bidentate bridging coordination, linking Co(II) ions to generate alternating (Co-bdc-Co-bdc-Co-bibp-Co-bibp-Co) single stranded right- or left-handed helical chains (see figure 6). Within these helices, the pitch of each chain is 9.432 Å, and the screw axes of each helix are parallel to the *c* axis. Adjacent helical chains of the same handedness are further interconnected by bibp, while the two types of helical chains, one left-handed and the other right-handed, are fused by sharing bdc ligands to generate a 3-D framework with 1-D rhombus-shaped chiral channels along the *c* axis (figure 6). All Co ions reside on a center of symmetry and the two types of helical chains with different chiralities are arranged in the same way, leading to a non-chiral structure for **2**. Some previously reported metal-organic frameworks containing helical chains are non-chiral as they contain the same

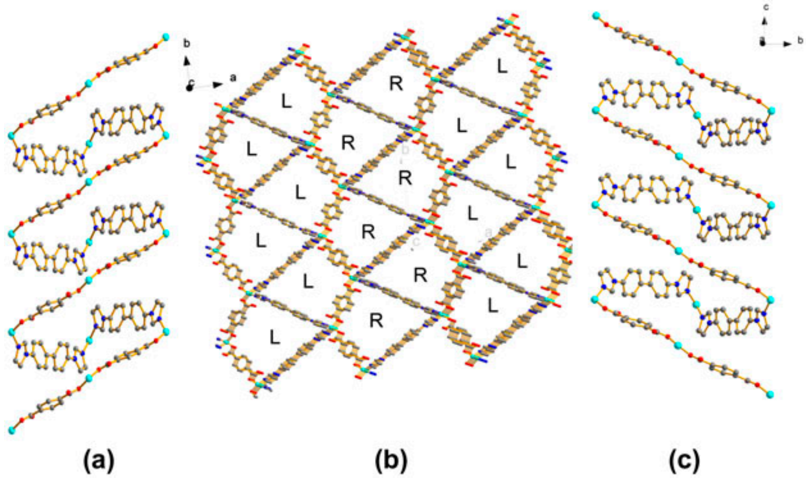


Figure 6. (a) and (c) right- and left- handed helical chains constructed by Co^{2+}, bdc and bibp. (b) The 3-D framework of **2** viewed along the *c*-axis, showing two types of helical channels (L: left-handed helical channel; R: right-handed helical channel).

number of right- and left-handed chains [23–26]. There are large enough cavities in **2** to allow inclusion of other 3-D frameworks, leading to three-fold interpenetrating 3-D architecture (figure 7).

Most helical chains in metal organic frameworks are constructed by flexible ligands or angled semi-rigid ligands, which may assume different conformations to coordinate with metal ions and more easily form helical chains [27–33]. In **2**, the right- and left-handed helical chains are formed by long rigid ligands and aromatic carboxylic acid, which is rarely reported [34]. Many helical complexes have been obtained in a single ligand synthesis system, although some helical chains in mixed ligand coordination compound are reported, which are also formed by a single main ligand or auxiliary ligand and may be pulled apart from the metal-organic framework without destroying the structure [29, 35–37]. Like **2**, both

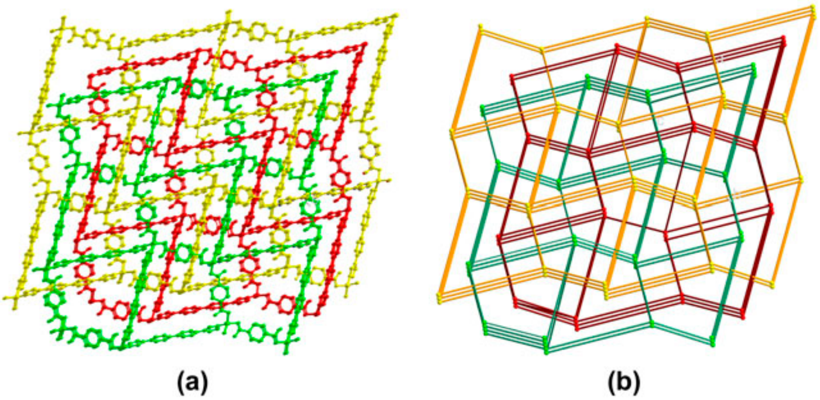


Figure 7. (a) The three-fold interpenetrating structure of **2**. (b) Schematic illustration of the three-fold interpenetrating structure of **2**.

the main ligand and auxiliary ligand involved in the construction of a helical chain are very rare [38].

3.2. *Infrared spectra*

In IR spectra of **1** and **2**, ν_{as}(–COO) is at 1600 (**1**) and 1607 cm^{-1} (**2**) together with ν_s(–COO) at 1376 (**1**) and 1354 cm^{-1} (**2**). Bands of –C=N are observed at 1532 cm^{-1} for **1** and 1516 cm^{-1} for **2**, and the –C–N stretches are observed at 1317 and 1312 cm^{-1} for **1** and **2**, respectively.

3.3. *PXRD and thermal analysis*

To check the phase purity of samples, PXRD at room temperature was carried out. As shown in figures S1 and S2 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.895822), PXRD patterns of the synthesized sample are in agreement with that simulated from the corresponding X-ray single-crystal data, indicating the homogeneous nature and phase purity of the final products.

Thermal behaviors of **1** and **2** were studied by thermogravimetric analysis under N_2 from 26 to 800 °C. As shown in figure S3, **1** is stable to 60 °C, its thermogravimetric curve exhibits two main weight losses, the first of 7.65% agrees with the loss of lattice and coordination water (7.68%), the second with 44.63% from 210 to 500 °C indicates the release of bib (Calcd: 44.79%) and the collapse of the framework. Complex **2** is stable to 420 °C, then it exhibits a weight loss of 57.65% between 420 and 504 °C, which corresponds to the loss of bibp (Calcd: 56.21%).

4. Conclusion

Using bdc and two rigid bisimidazole ligands, bib and bibp, reacted with Co(II) salts under solvothermal conditions, we have prepared two Co coordination polymers, $\{[Co(bdc)(bib)(H_2O)]\cdot H_2O\}_n$ (**1**) and $\{[Co(bdc)(bibp)]\}_n$ (**2**), showing a 3-D layer pillared framework and 3-D network with helical chains, respectively. The channels in both complexes are large enough to induce three-fold interpenetration. The structural difference is ascribed to different auxiliary ligands used in the assembly processes, and it is found that the degree of interpenetration was not only influenced by the length of ligands.

Supplementary material

Supplementary material has been deposited with the Cambridge Crystallographic Data Center (No. 900520 for **1**, 928530 for **2**; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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