



# Four novel coordination frameworks with high degree of diamondoid interpenetration containing scarce quadruple-stranded homo-axis helices and quintuple-stranded molecular braids



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## ABSTRACT

Four novel interpenetrated diamondoid (**dia**) networks, namely [Zn(1,4-bdc)(bip)] (**1**), [Mn(bqdc)(bip)] (**2**), [Cd(bqdc)(bip)] (**3**), [Co<sub>4</sub>(bqdc)<sub>4</sub>(bip)<sub>4</sub>] (**4**). (bip = 1,4-bis(4-(imidazole-1-yl)benzyl)piperazine, 1,4-bdc = 1,4-benzenedicarboxylate, bqdc = 2,2'-biquinoline-4,4'-dicarboxylate), have been synthesized by using mixed spacer ligands with significantly different lengths. Their structures were determined by single-crystal X-ray diffraction analyses and further characterized by elemental analyses, IR spectra and TG analyses. Compound **1** is an unusual 8-fold [4+4] interpenetrated **dia** network containing the unique quadruple-stranded braid (i.e. quadruple-stranded homo-axis helices), which is further entangled by another quadruple-stranded braid to produce an unprecedented octuple-stranded braid derived from eight individual **dia** nets. Compounds **2** and **3** are isostructural, while compound **4** is isorecticular to them. They all exhibit 5-fold interpenetrating **dia** networks containing an exceptional quintuple-stranded molecular braid. In addition, the photoluminescence properties of compounds **1** and **3**, and the magnetic property of compound **4** were studied.

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## 1. Introduction

The design and synthesis of entangled metal-organic frameworks (MOFs) have attracted much attention during the past two decades, not only stem from their complicated architectures and various topologies, but also for their intriguing potential applications in many fields as functional materials [1]. As an important subclass of entanglement, interpenetrated frameworks are of great current interest because of their intrinsic aesthetic appeal, and more importantly, due to their potential applications originating from the intertwining nature of the lattices [2]. Diamondoid lattices, which are formed by propagating a tetrahedral nodal point in four directions by coordinating to linear bidentate ligands, are one of the most common types in the interpenetrated coordination networks [3]. So far, a variety of fascinating interpenetrated diamondoid (**dia**) nets with a total degree of interpenetration (hereafter termed *Z*) from 2 to 12 and 25 have been reported [4].

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Nevertheless, the interpenetrated **dia** networks with  $Z \geq 5$  are still rare [5]. Moreover, among the currently known examples of interpenetrated **dia** frameworks with  $Z \geq 5$ —almost all constructed from single ligands [4a,d,6]—only a few elegant examples with mixed spacer ligands have been reported recently [4b,c,7,8]. However, close inspection of these structures reveals that the mixed spacer ligands used in building the **dia** frameworks with high degree of interpenetration usually have similar length. To our knowledge, only five 5-fold, two 8-fold and one 9-fold interpenetrating **dia** networks are constructed from mixed spacer ligands with significantly different lengths [8]. This may be attributed, at least in part, to the fact that two linear ligands with significantly different lengths may lead to highly distorted adamantanoid cages containing four cyclohexane-like windows with different sizes. It is known that **dia** net is self-dual, that is to say, **dia** net can interpenetrate in such a way that it is fully catenated. Therefore, when the cyclohexane-like windows of different sizes coexist in the distorted adamantanoid cages, the degree of interpenetration depends on the smallest cyclohexane-like window. The smaller the cyclohexane-like window is in a **dia** net, the lower degree of interpenetration occurs. Consequently, the use of mixed spacer ligands with significantly different lengths to construct interpenetrated **dia** frameworks with  $Z \geq 5$  is still a

formidable challenge for synthetic chemists, and further research is necessary to enrich and develop this branch.

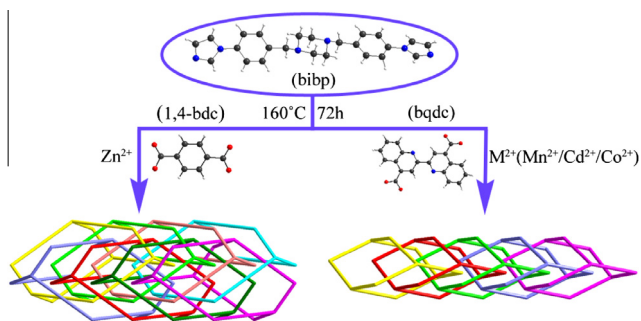
In order to address this challenge, we purposely focused our attention on a new long linear N-donor ligand 1,4-bis(4-(imidazole-1-yl)benzyl)piperazine (bibp, Schemes 1 and 2a), to produce novel coordination polymers with high degree of **dia** interpenetration in the presence of short ditopic carboxylate linkers, based on the following considerations: (i) Usually, long organic ligands will lead to larger voids which may thus favor the formation of interpenetrated networks [4b]. As evidenced by the report of Champness, Schröder, and co-workers [9], lengthening of linear ligands may increase the fold-interpenetrating number of **dia** networks. The bibp ligand (19.5 Å) is much longer than those N-donor ligands (4,4'-bipyridyl, 7.1 Å; 1,2-trans-(4-pyridyl)ethene, 9.4 Å, etc.) used in previously reported interpenetrating **dia** networks [9,10], we thus envision that it should be possible to realize the relatively high degree of **dia** interpenetration by appropriately combining long bibp ligand and short ditopic carboxylate ligands. (ii) The bibp ligand, a novel long linear semi-flexible ligand with imidazole donors at either end, has never been used to construct coordination compounds; therefore, much work is still necessary to understand the coordination chemistry of bibp. Bearing these considerations in mind, we have performed many experiments, and these efforts have led to the isolation of four new interpenetrated **dia** networks with  $Z \geq 5$ , namely [Zn(1,4-bdc)(bibp)] (1), [Mn(bqdc)(bibp)] (2), [Cd(bqdc)(bibp)] (3), [Co<sub>4</sub>(bqdc)<sub>4</sub>(bibp)<sub>4</sub>] (4) (1,4-bdc = 1,4-benzenedicarboxylate, bqdc = 2,2'-biquinoline-4,4'-dicarboxylate, Schemes 1 and 2). Compounds 1–4 have several unusual features: (1) The unusual 8-fold (4+4) interpenetrated **dia** net of 1 contains unique quadruple-stranded intertwined homo-axis helices, which can also be considered as an inextricable quadruple-stranded braid. (2) The octuple-stranded braid constructed from two interwoven quadruple-stranded braids in compound 1 is unprecedented. (3) The 5-fold interpenetrating **dia** networks of 2–4 incorporate exceptional quintuple-stranded molecular braid.

## 2. Experimental

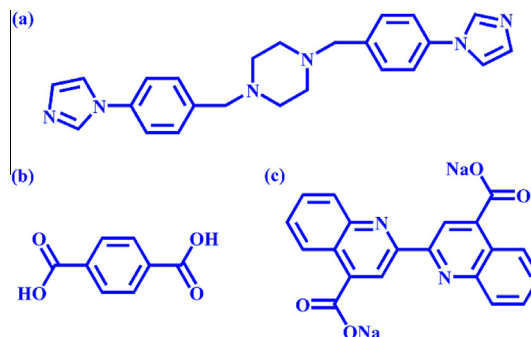
### 2.1. Materials and general methods

All of the available chemicals and solvents were commercially purchased and used as received without further purification.

Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. Zn, Mn, Cd and Co were determined by a tps-7000 Plasma-Spec(I) inductively coupled plasma-atomic emission spectrometer (ICP-AES). IR spectra were recorded in the range 400–4000 cm<sup>-1</sup> on a Bio-Rad FTS-185 FT/IR Spectrophotometer using KBr pellets. TG analyses were performed on a NETZSCH STA 449C instrument in flowing N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup>. XRPD data were recorded on a XD-3 diffractometer using Cu Kα radiation. Excitation and emission spectra were performed on an F-7000 FL fluorescence spectrophotometer



**Scheme 1.** Synthetic conditions for compounds 1–4.



**Scheme 2.** Schematic drawing of (a) bibp, (b) 1,4-H<sub>2</sub>bdc and (c) Na<sub>2</sub>bqdc ligands.

equipped with a 150 W xenon lamp as the excitation source. Variable-temperature magnetic susceptibility data were obtained on a SQUID magnetometer (Quantum Design, MPMS-7) in the temperature range of 2–300 K with an applied field of 1.0 kOe.

### 2.2. Preparation

#### 2.2.1. Synthesis of bibp

A mixture of anhydrous piperazine (0.1 mol, 8.6 g), 1-bromo-4-(bromomethyl)benzene (0.2 mol, 50.0 g), and K<sub>2</sub>CO<sub>3</sub> (0.2 mol, 27.6 g) in 1000 mL DMF was refluxed for three days and then poured into 5000 mL H<sub>2</sub>O (Scheme S1). The obtained precipitate was crystallized in methanol to give 1,4-bis(4-bromobenzyl)piperazine (79% yield). Elemental Anal. calc. for C<sub>18</sub>H<sub>20</sub>Br<sub>2</sub>N<sub>2</sub>: C, 50.97; H, 4.75; N, 6.60. Found: C, 50.75; H, 4.58; N, 6.41%.

A mixture of 1,4-bis(4-bromobenzyl)piperazine (0.1 mol, 42.4 g), imidazole (0.4 mol, 27.2 g), copper(II) sulfate pentahydrate (4 mmol, 1.0 g), and K<sub>2</sub>CO<sub>3</sub> (0.2 mol, 27.6 g) in 1000 mL DMF was refluxed for 12 h and then poured into 2000 mL H<sub>2</sub>O (Scheme S1). The obtained precipitate was crystallized in methanol to give bibp ligand (65% yield). EI-MS: *m/z* [M–H]<sup>+</sup>, 399.22 (calcd for C<sub>24</sub>H<sub>26</sub>N<sub>6</sub>, 398.22). Elemental Anal. calc. for C<sub>24</sub>H<sub>26</sub>N<sub>6</sub>: C, 72.33; H, 6.58; N, 21.09. Found: 72.08; H, 6.39; N, 20.92%. FT/IR data (cm<sup>-1</sup>): 3424(br), 3101(w), 2968(w), 2949(w), 2811(m), 2764(w), 2660(w), 1630(s), 1605(s), 1523(s), 1488(w), 1458(w), 1397(m), 1349(m), 1301(m), 1284(w), 1265(w), 1247(w), 1110(m), 1059(m), 1012(w), 995(w), 857(w), 835(w), 740(m), 665(m), 539(m).

#### 2.2.2. Synthesis of [Zn(1,4-bdc)(bibp)] (1)

A mixture of Zn(Ac)<sub>2</sub>·2H<sub>2</sub>O (0.088 g, 0.4 mmol), 1,4-H<sub>2</sub>bdc (0.034 g, 0.2 mmol), bibp (0.080 g, 0.2 mmol), Et<sub>3</sub>N (0.25 mL) and distilled water (10 mL) was stirred about 15 min in air, then transferred and sealed in a 17 mL Teflon-lined autoclave, which was heated at 160 °C for 72 h. After slow cooling to room temperature, light yellow block crystals of 1 were filtered off, washed with distilled water, and dried at ambient temperature (yield: 45% based on Zn). Elemental Anal. calc. for C<sub>32</sub>H<sub>30</sub>ZnN<sub>6</sub>O<sub>4</sub>: C, 61.21; H, 4.81; N, 13.38; Zn, 10.41. Found: C, 61.47; H, 4.62; N, 13.21; Zn, 10.63%. FT/IR data (cm<sup>-1</sup>): 3443(br), 3129(w), 3040(w), 2953(w), 2906(m), 2804(m), 2767(m), 2726(m), 2699(m), 1889(w), 1608(s), 1523(s), 1499(m), 1460(m), 1434(m), 1342(s), 1305(s), 1268(m), 1245(m), 1152(m), 1125(s), 1107(m), 1064(s), 1007(m), 964(m), 947(m), 885(w), 849(m), 823(m), 801(m), 764(m), 746(s), 654(m), 621(w), 574(m), 527(m), 500(w), 427(w).

#### 2.2.3. Synthesis of [Mn(bqdc)(bibp)] (2)

A mixture of Mn(Ac)<sub>2</sub>·4H<sub>2</sub>O (0.049 g, 0.2 mmol), Na<sub>2</sub>bqdc (0.039 g, 0.1 mmol), bibp (0.040 g, 0.1 mmol), Et<sub>3</sub>N (0.20 mL) and distilled water (10 mL) was stirred about 15 min in air, then transferred and sealed in a 17 mL Teflon-lined autoclave, which was

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