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Four new metal-organic frameworks based on bi-, tetra-, penta-, and hexanuclear clusters derived from 5-(phenyldiazenyl)isophthalic acid: syntheses, structures and properties

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Four new metal-organic frameworks (MOFs), namely [Cu(PDIA)(DMA)]n (JUC-126), [Mn4(PDIA)6(DMF)2]•nDMF•2nH2O (JUC-127), [Zn2y(PDIA)3(μ3-O)2(μ2-O)2(μ3-O)2(OH)4]DMA•12nDMA•6nH2O (JUC-128), [Co3(PDIA)2(HCOO)(μ2-OH)(H2O)(DMA)2]•nDMA•nH2O (JUC-129) (JUC = Jilin University, China), based on a new rigid ligand 5-(phenyldiazenyl)isophthalic acid (H2PDIA) with azobenzene were synthesized under solvothermal conditions. The ligand is connected to different metals to form bi-, tetra-, penta- and hexanuclear cores with distinctive coordination modes to generate different structures. Meanwhile, π-π stacking interactions between arene cores of the ligands also exist to affect the structural assembly process. JUC-126 displays a three-dimensional (3D) NbO topology with the point symbol (6^3•8^2) based on Cu4(COO)4 as secondary building units (SBUs). JUC-127 shows a two-dimensional (2D) sql topology with the point symbol (4^4•6^2) based on Mn4(COO)4 as SBUs. JUC-128 also has a new 3D topology with the point symbol (3^3•4^4•5^6) based on Zn2O(COO)6 and Zn10(μ3-OH)2(COO)9 as SBUs. JUC-129 also exhibits a 2D sql topology with the point symbol (4^4•6^2) based on Co9(μ3-OH)2(COO)10 as SBUs. In addition, JUC-126, JUC-128 and JUC-129 are achiral frameworks. However, JUC-127 shows a chiral framework from an achiral ligand. Furthermore, the luminescent property of JUC-128 and the magnetic properties of JUC-127 and JUC-129 have been studied and discussed.

Introduction

In recent years, metal–organic frameworks (MOFs),1,2 as a new class of organic-inorganic hybrid porous materials, have been attracted a lot of attention due to not only their widely potential applications, but also their rich diversities of architectures.3-18 These materials can be applied potentially in the fields of gas storage, separation,1,6 luminescence,7,9 catalysis,10-12 drug delivery,13,14 magnetism,15,16 etc. Among these researches, design and construction of new MOFs with diverse structures has always been drawn great attention in recently decades. A lot of synthetic parameters affected their structural assembly process, such as metal ions, polymeric clusters, organic ligands, solvent systems, temperature, pH value, etc. It is no doubt that organic ligands play a vital role to tune the structural topology and functionality among of them. Most of the organic ligands have been designed to contain multicarboxylic acid or aromatic N-heterocycles,19,20 because nitrogen and oxygen atoms have strong coordination ability with metals to prepare MOFs. In order to generate richness topologies and interesting structures, a wide range of methods have been developed to synthesize new ligands to achieve this goal. Most works have been reported until now to adopt tune rigidity, length and coordination modes to tentatively control the topology and functionality of the resulting framework.30-37 Yaghi et al. reported elongated organic linkers with the same metal-containing secondary building units (SBUs) to tune the size of pores in isomeric frameworks.38 However, to the best of our knowledge, reports are still rare on the construction of MOFs with a rigid ligand, which contains large aromatic rings without any coordination nodes, not only because the aromatic ring can’t join the work to connect to metals, but also the overcrowded space.39 On the other hand, azobenzene functionalized ligand have been prepared to synthesize dynamic and photo-responsive MOFs.40,41 Evidently, it is a quite interesting and challenging job to synthesize a ligand with azobenzene moiety to prepare MOFs, which maybe show photo-responsive behaviors. From the crystal engineering, it also could be expected to obtain varieties of intriguing molecular architectures or fascinating topological structures.

Here, we successfully synthesize a rigid ligand with azobenzene, 5-(phenyldiazenyl)isophthalic acid (H2PDIA, Scheme 1), which was selected as the organic building block to react with Cu(II), Mn(II), Zn(II) and Co(II) salts to construct...
dive structures. Although the space is overcrowded and without coordination nodes, it also may be used to generate the richness and unpredictability of structures and topologies by π–π stacking between aren cores and assembled with metal cations or polynuclear clusters. Based on this ligand, four MOFs, namely [Cu(PDIA)(DMA)]_n (JUC-126), [Mn_2(PDIA)_2(DMF)_2]_n·nDMF·2nH_2O (JUC-127), [Zn_2(PDIA)]_n(μ_2-O)(μ_2-OH)·DMF·10nDMA·6nH_2O (JUC-128), and [Co_3(PDIA)_2(HCOO)(μ_2-OH)(H_2O)(DMF)]_n·nDMA·nH_2O (JUC-129) (JUC = Jilin University, China), were synthesized under solvothermal conditions, which form different metal clusters as SBUs. Unfortunately, they all do not show photo-responsive behaviors, which is attributed to the structures are closely packed without any space for the tran-cis photoisomerization of azobenzene. However, JUC-126, JUC-127, JUC-128 and JUC-129 display completely different structures, because the distinctive coordination modes of different metals form bin-, tetra-, penta- and hexanuclear cores, and π–π stacking between aren cores of the ligands. JUC-126 displays a 3D NbO topology with the point symbol (6^48^5). JUC-127 shows a 2D sq topology with the point symbol (4^6^6). JUC-128 also has a new 3D topology with the point symbol (3^4^6^5^6), and JUC-129 also exhibits a 2D -type network with the point symbol (4^6^6) just as JUC-127. To our surprise, JUC-127 exhibits a chiral 2D network from an achiral ligand, which is also rare in the early reports. In addition, the luminescent of JUC-127 and the magnetic properties of JUC-127 and JUC-129 have been studied and discussed.

Scheme 1 The ligand of H_2PDIA

Experimental Section

Materials and Methods

All chemical reagents required in this work were purchased from commercial sources without further purification. Powder X-ray diffraction (PXRD) data were obtained on a Rigaku D/MAX2550 diffractometer with Cu-Kα (λ = 1.5418 Å) at 50 kV, 200 mA with a 2θ range of 4-40° at room temperature. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 analyzer. Thermogravimetric analyses (TGA) were carried out on a TGA Q500 thermal analyzer in the range of 30-800 °C under nitrogen atmosphere flow at a heating rate of 10 °C/min for all measurements. Fourier-transform infrared (FT-IR) spectra (using KBr pellets) were obtained by IFS 66V/S Fourier-transform infrared spectrometer in the 4000-400 cm^−1 range. Temperature dependent magnetic susceptibility data were carried out by the use of a Quantum-Design MPMS-XL SQUID magnetometer over the temperature range of 2-300 K under an applied field of 1 kOe. ¹H NMR spectra were recorded on a Bruker AV 400 spectrometer with Me_3Si as the internal standard in deuterated solvents CDCl_3 and DMSO-δ_6 at 298 K. The fluorescence measurements for JUC-128 were recorded on a Fluoromax-4 Spectrofluorometer in the solid state at room temperature.

Synthesis

**Dimethyl 5-(phenyldiazenyl)isophthalate**

A mixture of dimethyl 5-aminoisophthalate (2.1 g, 10 mmol), nitrosobenzene (1.28 g, 12 mmol) and glacial acetic acid (85 mL) in a 250 mL round-bottom flask, which was stirred for 1 day at 40 °C in an oil-bath. After the solution was cooled down, the resulting mixture was slowly added saturated NaHCO_3 solution until no further yellow precipitate formed under stirring. The orange precipitation was filtered and washed with distilled water (3 × 30 mL), then dried in air to afford 1.43 g (48 % based on dimethyl 5-aminoisophthalate). ¹H NMR (300 MHz, CDCl_3), δ (ppm): 8.79 (s, 1H); 8.75 (s, 2H); 7.98 (d, 2H); 7.55 (d, 3H), 4.01 (s, 6H).

**5-(phenyldiazenyl)isophthalic acid (H_2PDIA)**

Diethyl 5-(phenyldiazenyl)isophthalate (1.49 g, 5 mmol) was added to a 100 flask with THF, ethanol, 20 % NaOH (15 ml-15 ml-15 ml) mixture, which was stirred overnight with reflux. After the organic phase was removed, 1M HCl solution was added to it to get an orange precipitation with pH = 2.0-3.0. After stirring it for 1h, the orange precipitation was filtered and washed with distilled water (3 × 30 mL) to obtain 1.24 g (yield: 92 %). ¹H NMR (300 MHz, DMSO-d_6), δ (ppm): 13.60 (s, 2H); 8.60 (s, 1H); 8.57 (s, 2H); 7.98 (d, 2H); 7.64 (d, 3H). Selected FT-IR data (KBr pellet cm^−1): 2992 (br), 2547 (br), 1612 (s), 1578 (s), 1409 (s), 1108 (s), 796(s), 688 (s), 512 (s).

**Synthesis of [Cu(PDIA)(DMA)]_n (JUC-126)**

A mixture of Cu(NO_3)_2·2.5H_2O (5 mg, 0.022 mmol), H_2PDIA (5 mg, 0.019 mmol), DMA (5 mL), H_2O (0.9 mL) and 0.3 mL of an aqueous HNO_3 solution (2 M) was sealed into a 20 ml capped vessel and sonicated for 2 min at room temperature. The mixture was heated at 85 °C for 4 days and then allowed to cool to room temperature. Blue block crystals of JUC-126 were obtained by filtration, washed with DMA (3 × 5 ml) and dried in air (yield: 52 % based on Cu(NO_3)_2·2.5H_2O). EA (%) Calc. for Cu_2H_7N_3O_5Cu: C, 51.55; H, 4.06; N, 10.02. Found: C, 52.13; H, 4.12; N, 9.98. Selected FT-IR data (KBr pellet cm^−1): 3424 (br), 2929 (br), 2547 (br), 1578 (s), 1409 (s), 1240 (s), 1185 (s), 796(s), 688 (s), 512 (s).

**Synthesis of [Mn_2(PDIA)_2(DMF)]_n·nDMF·2nH_2O (JUC-127)**

A mixture of Mn(NO_3)_2·4H_2O (15 mg, 0.06 mmol), H_2PDIA (5 mg, 0.019 mmol), DMF (5 mL) and H_2O (0.5 ml) was sealed into a 20 ml capped vessel and sonicated for 2 min at room temperature. The mixture was heated at 85 °C for 5 days and collected orange block crystals of JUC-127 by filtration, washed with DMA (3 × 5 ml) and dried in air (yield: 73 % based on Mn(NO_3)_2·4H_2O). EA (%) Calc. for C_77H_75N_50O_35Mn_2: C, 50.24; H, 4.62; N, 11.42. Found: C, 50.11; H, 4.59; N, 11.40. Selected FT-IR data (KBr pellet cm^−1): 3428 (br), 2925 (s), 1654 (s), 1612 (s), 1567 (s), 1440 (s), 1376 (s), 1243 (s), 1110 (s), 925 (s), 786 (s), 715 (s), 684 (s), 518 (s).

**Synthesis of [Zn_2(PDIA)_2(μ_2-O)(μ_2-OH)(H_2O)(DMF)]_n·10nDMA·6nH_2O (JUC-128)**
The procedure was the same as that for JUC-127 except that Mn(NO$_3$)$_2$$\cdot$4H$_2$O, DMF were replaced by Zn(NO$_3$)$_2$$\cdot$6H$_2$O (15 mg, 0.05 mmol) and DMA (yield: 68% based on Zn(NO$_3$)$_2$$\cdot$6H$_2$O). EA (%) Calc. for C$_{316}$H$_{306}$N$_{52}$O$_{102}$Zn$_{23}$: C, 47.68; H, 3.85; N, 9.15; Found: C, 47.21; H, 3.81; N, 9.21. Selected FT-IR data (KBr pellet cm$^{-1}$): 3426 (br), 2921 (s), 1612 (s), 1581 (s), 1476 (s), 925 (s), 779 (s), 715 (s), 690 (s), 524 (s), 480 (s).

**Synthesis of** [Co$_3$(PDIA)$_2$(HCOO)(µ$_3$-OH)(H$_2$O)(DMA)$_2$]$_n$$\cdot$nDMA$\cdot$nH$_2$O (JUC-129)

The procedure was the same as that for JUC-128 except that Zn(NO$_3$)$_2$$\cdot$6H$_2$O was replaced by Co(NO$_3$)$_2$$\cdot$6H$_2$O (15 mg, 0.05 mmol) and added 0.25 ml HNO$_3$ (2.0 M in DMF). Yield: 42% based on Co(NO$_3$)$_2$$\cdot$6H$_2$O). EA (%) Calc. for C$_{41}$H$_{34}$N$_{12}$O$_{16}$Co$_3$: C, 45.90; H, 4.57; N, 9.14; Found: C, 45.82; H, 4.52; N, 9.13. Selected FT-IR data (KBr pellet cm$^{-1}$): 3355 (br), 2935 (s), 1612 (s), 1581 (s), 1440 (s), 1365 (s), 1103 (s), 1027 (s), 931 (s), 779 (s), 715 (s), 690 (s), 524 (s), 480 (s).

**X-ray structure determination and structure refinement**

Crystallographic data collections for JUC-126, JUC-127, JUC-128 and JUC-129 were collected on Bruker SMART APEX II CCD based diffractometer equipped with graphite monochromatized Mo-Ka radiation (λ = 0.71073 Å) at 298K. The structures were solved by a combination of direct methods and refined anisotropically by a full-matrix least-squares technique based on $F^2$ using SHELXLS-97 program. Some restraints were used to obtain suitable geometry configurations, such as simu, isor, delu, affix, and twin in JUC-127, JUC-128 and JUC-129. Because JUC-127 has lots of disordered solvent molecules, the PLATON/SQUEEZE was applied to remove their diffraction contribution. The H atoms for the µ$_3$-OH in JUC-126 and JUC-129 were located in the overall formula according to the bond length and the charge of the frameworks. The guest molecules of JUC-126 and JUC-128 and JUC-129 can’t be found from X-ray diffraction, which may be owing to their too large disorder. Therefore, it is not needed to use PLATON/SQUEEZE. We can calculate the guest molecules from the TGA and elemental analyses (C, H and N) for JUC-127, JUC-128 and JUC-129. The structure refinement parameters and crystallographic data of JUC-126, JUC-127, JUC-128 and JUC-129 are listed in Table 1, while the selected bond lengths and angles data are reported in Table S1 (Supporting Information).

### Table 1 Crystal data and structure refinements

<table>
<thead>
<tr>
<th>Compound</th>
<th>JUC-126</th>
<th>JUC-127</th>
<th>JUC-128</th>
<th>JUC-129</th>
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<td>Empirical formula</td>
<td>Cu$<em>6$H$</em>{416}$O$<em>{33}$Co$</em>{24}$H$<em>{394}$O$</em>{108}$N$<em>{92}$Zn$</em>{24}$C$<em>{6}$H$</em>{496}$N$<em>{102}$O$</em>{30}$Co$_{2}$</td>
<td>Cu$<em>6$H$</em>{416}$O$<em>{33}$Co$</em>{24}$H$<em>{394}$O$</em>{108}$N$<em>{92}$Zn$</em>{24}$C$<em>{6}$H$</em>{496}$N$<em>{102}$O$</em>{30}$Co$_{2}$</td>
<td>Cu$<em>6$H$</em>{416}$O$<em>{33}$Co$</em>{24}$H$<em>{394}$O$</em>{108}$N$<em>{92}$Zn$</em>{24}$C$<em>{6}$H$</em>{496}$N$<em>{102}$O$</em>{30}$Co$_{2}$</td>
<td>Cu$<em>6$H$</em>{416}$O$<em>{33}$Co$</em>{24}$H$<em>{394}$O$</em>{108}$N$<em>{92}$Zn$</em>{24}$C$<em>{6}$H$</em>{496}$N$<em>{102}$O$</em>{30}$Co$_{2}$</td>
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<tr>
<td>Formula weight</td>
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<td>1840.36</td>
<td>7968.10</td>
<td>1072.66</td>
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<td>Crystal system</td>
<td>Trigonal</td>
<td>Monoclinic</td>
<td>Trigonal</td>
<td>Triclinic</td>
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</table>

**Results and discussion**

[Cu(PDIA)(DMA)$_n$]$_n$ (JUC-126). The single crystal X-ray diffraction reveals that JUC-126 crystallizes in the trigonal space group R-3. The asymmetric unit of JUC-126 contains one Cu(II), one unique PDIA$^2$ ligand and one terminal coordinated DMA molecule (Fig. S1, Supporting Information). As shown in Fig. 1a, the dinuclear copper paddle-wheel SBU is bound with four carboxylates from four different PDIA$^2$ ligands and two terminal coordinated DMA molecules (Cu-O = 1.951-2.161 Å). As shown in Fig. 1b, each PDIA$^2$ ligand is connected to two Cu$_{2}$O$_{6}$ paddle-wheels, respectively. This result is not needed to use PLATON/SQUEEZE. It can be calculated from the TGA and elemental analyses (C, H and N) for JUC-127, JUC-128 and JUC-129. The structure refinement parameters and crystallographic data of JUC-126, JUC-127, JUC-128 and JUC-129 are listed in Table 1, while the selected bond lengths and angles data are reported in Table S1 (Supporting Information).
bridging chelating mode (O8), where O8 acts as a
terminal coordinated DMF molecules in the asymmetric unit (Fig. 2).

There are four Mn(II), four PDIA ligands and six
terminal coordinated DMF molecules in the asymmetric unit (Fig. S2). As shown in Fig. 2a, the Mn1 (or Mn2) cation is bound with
six oxygen atoms, originating from two chelating (O1, O2, O7, O8) and two bridging carboxylates (O3, O5) of PDIA ligands
(Mn-O = 2.057-2.479 Å). Meanwhile, the Mn3 (or Mn4) cation also exhibits a distorted octahedral geometry with six oxygen
atoms from three bridging carboxylates (O4, O6, O8) of three
different PDIA ligands and six terminal coordinated DMF molecules (O15, O16, O17) (Mn-O = 2.088-2.179 Å). As shown
in Fig. 2a, carboxylate groups of PDIA ligands display three kinds of coordination fashions (modes 1-3). As shown in (Fig.
2b-2d), PDIA ligands show $\mu_4$-$\eta^2$-$\eta^2$ and $\mu_5$-$\eta^2$-$\eta^2$
coordination modes in mode 1, mode 2 and mode 3, respectively.

And the radio of these three coordination modes in JUC-127 is 1: 2 (mode 1: mode 2: mode 3). Each PDIA ligand is connected to
two Mn(II) SBUs to form infinite helical chains and a 2D framework, which is further packed together between arene cores
of two independent PDIA ligands by $\pi-\pi$ stacking interactions (3.521 Å)
to form a 3D supramolecular architecture (Fig. 2f).

Topologically, by considering Mn$_2$(COO)$_4$ SBUs and PDIA
anions as 4-connected nodes and 2-connected linkers, the 2D framework can be symbolized as a sql topology with the point symbol (4^4*6^7) (Fig. 2f).

$[\text{Mn}_4(\text{PDIA})(\text{DMF})]_{10}\cdot 8\text{DMF} \cdot 2n\text{H}_2\text{O}$ (JUC-127). The X-ray
crystallographic study shows that JUC-127 crystallizes in the chiral monoclinic space group $P2_1$ and possesses a 2D framework. There are four Mn(II), four PDIA ligands and six
terminal coordinated DMF molecules in the asymmetric unit (Fig. S2). As shown in Fig. 2a, the Mn1 (or Mn2) cation is bound with
six oxygen atoms, originating from two chelating (O1, O2, O7, O8) and two bridging carboxylates (O3, O5) of PDIA ligands
(Mn-O = 2.057-2.479 Å). Meanwhile, the Mn3 (or Mn4) cation also exhibits a distorted octahedral geometry with six oxygen
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different PDIA ligands and six terminal coordinated DMF molecules (O15, O16, O17) (Mn-O = 2.088-2.179 Å). As shown
in Fig. 2a, carboxylate groups of PDIA ligands display three kinds of coordination fashions (modes 1-3). As shown in (Fig.
2b-2d), PDIA ligands show $\mu_4\eta^2-\eta^2$, $\mu_4\eta^2-\eta^2$ and $\mu_5\eta^2-\eta^2$
coordination modes in mode 1, mode 2 and mode 3, respectively.

And the radio of these three coordination modes in JUC-127 is 1: 2 (mode 1: mode 2: mode 3). Each PDIA ligand is connected to
two Mn(II) SBUs to form infinite helical chains and a 2D framework, which is further packed together between arene cores
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Topologically, by considering Mn$_2$(COO)$_4$ SBUs and PDIA
anions as 4-connected nodes and 2-connected linkers, the 2D framework can be symbolized as a sql topology with the point symbol (4^4*6^7) (Fig. 2f).
coordinated modes in mode 1 and mode 2, respectively (Fig. 3c, 3d). The tetranuclear Zn4O(COO)8 and pentanuclear Zn5(µ3-OH)3(COO)8 SBUs are further linked with the PDI2 ligands to form a 3D framework (Fig. 2e). From the topologic point of view, the Zn4O(COO)8, SBUs and Zn5(µ3-OH)3(COO)8 SBUs can be regarded as 6-connected node and 8-connected node, respectively. The PDI2 ligands can be simplified for 2-connected linkers. Notably, this topology is with the point symbol (3.4.6.5.3)2(3.4.5.6.4)3, which is unknown in previously reported MOFs.

There are three Co(II), two PDIA2 ligands and crystallizes in the triclinic space group (JUC/129). The tetranuclear Zn4O(COO)8 molecule and one terminal coordinated DMA molecule (Co8O = 2.064-2.132 Å), respectively. Co(II) share the µ3-OH oxygen atoms and oxygen atoms from carboxyl groups each other to form hexanuclear SBUs [Co6(µ3-OH)3(COO)6]4+ (Fig. 4a). As shown in Fig. 2b, 2c, PDIA2 ligands possess two modes in the framework. In mode 1, each PDIA2 ligand links four Co(II) centers through the µ3-π-π' coordination mode, while µ3-π-µ6 coordination mode in mode 2. Each hexanuclear SBU [Co6(µ3-OH)3(COO)6]4+ is linked with eight diverse ligands to form a 2D layer, which is further packed together by π-π stacking interactions between arene cores of two independent PDI2 (3.627 Å) to form a 3D supramolecular architecture (Fig. 4d). To analyze the topology of the structure, PDI2 ligands and hexanuclear SBUs could be simplified as 2-connected and 8-connected node, respectively. The result network could be concerned a 2D network with the point symbol (43.62), which belongs to sq6 topology (Fig. 4e).

![Fig. 3](image1.png) ![Fig. 4](image2.png)

**Fig. 3** (a, b) Coordination environments of Zn(II). Zn4O(COO)8 SBUs and Zn5(µ3-OH)3(COO)8 SBUs viewed as a 6-connected node and 8-connected node, respectively (symmetry code: #1 x+y+1/3, -y+2/3, -z+1/6, #4 -x +y +2, -x +2, z, #5 -y +2, x -y, z); (c, d) two coordination modes in JUC-128 and each PDI2 ligand viewed as a 2-connected node; (e) view of the 3D framework along the c-axis; (The hydrogen atoms are omitted for clarity and C, gray; O, red; N, blue; Zn, green) (f) Simplified network of the 3D coordination framework along the c-axis with the point symbol (3.4.6.5.3)2(3.4.5.6.4)3.

[Co6(PDI2)2(HCOO)(µ3-OH)(H2O)6(DMA)4, nDMA•nH2O (JUC-129)](JUC-129). X-ray crystallography confirms that JUC-129 has a 2D framework and crystallizes in the triclinic space group P-1. There are three Co(II), two PDI2 ligands, one HCOO anion, one µ3-µH group, one terminal H2O, two coordinated DMA molecules and one guest DMA molecule in the asymmetric unit (Fig. S4.). The HCOO anion is produced in situ by the hydrolysis of HCOO. The coordination environments of Co(II) are 73, 67, 74, and 65 pm respectively. With the increase of the metal radius, the decrease of corresponding gravity will result in the coordination number reduction. From Table 2, it shows that the ionic radii of Cu2+, Mn2+, Zn2+ and Co2+ have the same charge, theionic radii may be the major factor to affect the structures. The ionic radii of Cu2+, Mn2+, Zn2+ and Co2+ are 73, 67, 74, and 65 pm respectively. With the increase of the metal radius, the decrease of corresponding gravity will result in the coordination number reduction. From Table 2, it shows that the ionic radii of Mn2+ (or Co2+) is less than that of Zn2+ (or Cu2+), but the coordination number of Mn2+ (or Co2+) is more than that of Zn2+ (or Cu2+), which indicates a lower coordination number can generate a high dimension framework. JUC-126 and JUC-
with Cu\(^{2+}\) and Zn\(^{2+}\) respectively obtain 3D frameworks with low coordination number, while JUC-127 and JUC-129 with Mn\(^{2+}\) and Co\(^{2+}\) respectively form 2D structures with high coordination number in the similar synthetic system.

Table 2 The dimensionality and coordination number with different metal centers

<table>
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<tr>
<th>Name</th>
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<th>Ionic radii (pm)</th>
<th>Coordination number</th>
<th>Dimensionality</th>
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<td>JUC-126</td>
<td>Cu(^{2+})</td>
<td>73</td>
<td>5</td>
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<tr>
<td>JUC-127</td>
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<td>JUC-129</td>
<td>Co(^{2+})</td>
<td>65</td>
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</table>

PXRD and thermal analysis

The powder X-ray diffraction (PXRD, Fig. 5) of JUC-126, JUC-127, JUC-128 and JUC-129 were carried out at room temperature. The experimental PXRD are in good agreement with the simulated patterns, which confirmed the phase purity of the bulk crystalline materials. From the thermogravimetric analyses (Fig. S5), JUC-126 shows a slow weight loss of 20.27 % (calculated: 20.80 %) in the range 30–295 °C, corresponds to loss one coordinated DMA molecule. The framework then collapses and decomposes with the increase of temperature. JUC-127 loses six terminal coordinated DMF molecules, one guest DMF molecule and two guest H\(_2\)O molecules, which is about 29.49 % (calculated: 29.76 %) before 300 °C and the framework collapsed at 390 °C. For JUC-128, it is found that there is a weight loss of 18.85 % before 260 °C, which corresponds to the departure of six terminal coordinated DMA molecules, ten guest DMA and six guest H\(_2\)O molecules (calculated: 19.01 %). The desolvated framework can be stable up to 390 °C. The TGA curve of JUC-129 shows the first weight loss of 3.36 % happens in the range 30-105 °C, which is thought to be the release of one free H\(_2\)O molecule and one terminal coordinated H\(_2\)O molecule (calcd: 3.37 %), and the second weight loss of 24.36 % from 200 to 275 °C is ascribed to the loss of one free DMA molecule and two terminal coordinated DMA molecules (calcd: 24.43 %).

Fig. 5 The simulated (black) and as-synthesized (red) PXRD of JUC-126 (a), JUC-127 (b), JUC-128 (c), JUC-129 (d).

Luminescence properties

Luminescent coordination compounds with d\(^{10}\) transition-metal clusters have generally been investigated for luminescent materials. The solid-state luminescence property of JUC-128 was performed collecting both emission and excitation spectra at room temperature. As depicted in Fig. 6, the emission spectrum of the solid compound exhibits a significant fluorescent emission band at 430 nm under an excitation maximum at 374 nm. However, the free ligand H\(_2\)PDIA doesn’t have any luminescence property in solid state. According to previous literatures, the emission of JUC-128 is similar with ZnO oxide nanostructure in MOF structures, which may be mainly attributed to the Zn-O inorganic cluster [Zn\(_n\)(µ\(_3\)-OH)\(_2\)(COO)\(_{8n}\) and Zn\(_5\)O(COO)\(_{24}\)] in the framework.

Magnetic properties

Because of the interesting metal clusters, the temperature-dependent magnetic susceptibility measurements in solid state of JUC-127 and JUC-129 have been carried out in an applied magnetic field of 1 Koe (2-300 K) using a quantum designed SQUID magnetometer.

The magnetic properties of JUC-127 are presented in Fig. 7, the Mn1 (or Mn2) and Mn3 (or Mn4) cations act as a binuclear unit with a Mn•••Mn distance of 3.653 (or 3.537) Å. The variable-temperature magnetic susceptibility measurement of Mn(II) cation has been performed. The observed value of χ\(_M\)T per Mn\(^{2+}\) unit is 4.57 cm\(^3\) K mol\(^{-1}\) at room temperature, which is slightly higher than the value expected for a free Mn(II) cation (4.375 cm\(^3\) K mol\(^{-1}\)). When temperature decreases sharply upon cooling, the χ\(_M\)T value began to decrease gradually until about 50 K and value of 1.06 cm\(^3\) K mol\(^{-1}\) at 2 K. This feature at low temperature could be ascribed to the weak antiferromagnetic interaction between the Mn(II) cation in JUC-127. Moreover, the plot of χ\(_M\)T vs. \(T\) over the temperature range 10-300 K range obeys the Curie-Weiss law [\(\chi = C/(T-\theta)\)] with C = 4.76 cm\(^3\) K mol\(^{-1}\) and θ = -13.61 K. The antiferromagnetic behavior of JUC-127 may originate from the multiple superexchange interactions between the Mn(II) cations in the Mn\(_2\)(COO)\(_4\) cluster by the \(\mu_2\)-η\(^1\)-η\(^1\)-COO\(^-\).
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The magnetic properties of JUC-129 have been performed on the powder sample in the same method. As shown in Fig. 8, the observed value of $\chi_M T$ per Co(II) unit is 3.25 cm$^3$ K mol$^{-1}$ at room temperature, which is higher than a free Co(II) cation (1.875 cm$^3$ K mol$^{-1}$). Upon cooling to 2 K, the $\chi_M T$ value sharply decreases to 0.84 cm$^3$ K mol$^{-1}$, which indicates antiferromagnetic interaction between Co(II) cations in the Co6 SBU. The magnetic data over the temperature range 40-300 K are fitted by the Curie-Weiss law $\chi = C/(T-\theta)$ with $C = 3.70$ cm$^3$ K mol$^{-1}$ and $\theta = -42.37$ K. The antiferromagnetic behavior of JUC-129 may also originate from the multiple superexchange interactions between the Co(II) cations in the [Co6(μ3-OH)2(COO)6]0 cluster by the π-π–OH, $\mu_2$-$\eta^1$-$\eta^1$-COO$^-$ and $\mu_2$-$\eta^1$-$\eta^1$-HCOO$^-$.

Conclusions

In summary, four novel metal-organic frameworks based on a rigid ligand with azobenzene (H2PDIA) and four different metal cations were successfully synthesized. JUC-126 features a 3D Nb6 topology with the point symbol (64848) and JUC-127 shows a 2D sql topology with the point symbol (4464). Meanwhile, JUC-128 exhibits a new 3D topology with the point symbol (344562344510664) and JUC-129 has a 2D sql-type network with the point symbol (4464). Clearly, the diverse coordination fashions of the PDIA$^2$ ligand with different metal cations to form bi-, tetra-, penta- and hexanuclear cores, and the π–π stacking between arene cores have a remarkable effect on molecular architectures and topological structures. It is expected that more extensive researches to explore and develop new kinds of ligands with such large aromatic rings without any coordination nodes to generate the richness and unpredictability of structures and topologies.

Acknowledgements

We are grateful to the financial support from National Basic Research Program of China (973 Program, grant nos.2012CB821703, grant no. 2014CB931804), Major International (Regional), and Joint Research Project of NSFC (grant nos. 21120102034).

Notes and references

Electronic Supplementary Information (ESI) available: a table of selected data in CIF or other electronic format see DOI: 10.1039/b000000x/
Four new metal–organic frameworks (MOFs) were synthesized under solvothermal conditions based on a new rigid ligand 5-(phenyldiazeyl)isophthalic acid (H$_2$PDIA) with azobenzene, which display different structures, fascinating topological structures and achiral/chiral frameworks.