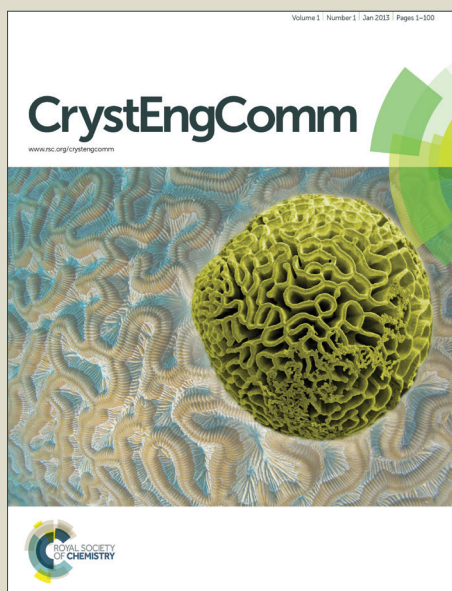


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ARTICLE TYPE

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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Four new metal-organic frameworks (MOFs), namely [Cu(PDIA)(DMA)]_n (**JUC-126**), [Mn₄(PDIA)₄(DMF)₆]_n•nDMF•2nH₂O (**JUC-127**), [Zn₂₃(PDIA)₁₈(μ₄-O)₂(μ₃-OH)₆DMA₆]_n•10nDMA•6nH₂O (**JUC-128**), [Co₃(PDIA)₂(HCOO)(μ₃-OH)(H₂O)(DMA)₂]_n•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 (6⁴•8²) based on Cu₂(COO)₄ as secondary building units (SBUs). **JUC-127** shows a two-dimensional (2D) sql topology with the point symbol (4⁴•6²) based on Mn₂(COO)₄ as SBUs. **JUC-128** also has a new 3D topology with the point symbol (3³•4⁶•5⁶)₂(3⁶•4⁸•5¹⁰•6⁴)₃ based on Zn₄O(COO)₆ and Zn₅(μ₃-OH)₂(COO)₈ as SBUs. **JUC-129** also exhibits a 2D sql topology with the point symbol (4⁴•6²) based on Co₆(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.

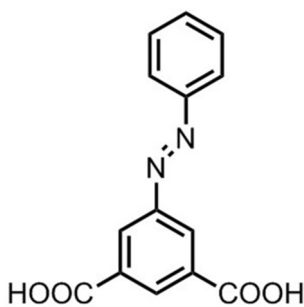
Introduction

In recent years, metal-organic frameworks (MOFs),¹⁻³ 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.⁴⁻¹⁸ These materials can be applied potentially in the fields of gas storage, separation,⁴⁻⁶ luminescence,⁷⁻⁹ catalysis,¹⁰⁻¹² drug delivery,^{13,14} magnetism,¹⁵⁻¹⁸ 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, polynuclear 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,¹⁹⁻²⁹ 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 moieties to prepare MOFs, which maybe show good 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

diverse 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 arene cores and assembled with metal cations or polynuclear clusters. Based on this ligand, four MOFs, namely [Cu(PDIA)(DMA)]_n (**JUC-126**), [Mn₄(PDIA)₄(DMF)₆]_n•nDMF•2nH₂O (**JUC-127**), [Zn₂₃(PDIA)₁₈(μ_4 -O)₂(μ_3 -OH)₆DMA₆]_n•10nDMA•6nH₂O (**JUC-128**), [Co₃(PDIA)₂(HCOO)(μ_3 -OH)(H₂O)(DMA)₂]_n•nDMA•nH₂O (**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 to form bin-, tetra-, penta- and hexanuclear cores, and π - π stacking between arene cores of the ligands. **JUC-126** displays a 3D NbO topology with the point symbol (6⁴•8²). **JUC-127** shows a 2D sql topology with the point symbol (4⁴•6²). **JUC-128** also has a new 3D topology with the point symbol (3³•4⁶•5⁶)₂(3⁶•4⁸•5¹⁰•6⁴)₃ and **JUC-129** also exhibits a 2D -type network with the point symbol (4⁴•6²) 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.^{42, 43} In addition, the luminescent of **JUC-128** and the magnetic properties of **JUC-127** and **JUC-129** have been studied and discussed.



Scheme 1 The ligand of H₂PDIA.

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-K α (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 with 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 air 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 Me₄Si as the internal standard in deuterated solvents CDCl₃ and DMSO-*d*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 NaHCO₃ 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, CDCl₃), 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 (H₂PDIA)

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), 1284 (s), 1108 (s), 920 (s), 769(s), 688 (s), 512 (s).

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

A mixture of Cu(NO₃)₂•2.5H₂O (5 mg, 0.022 mmol), H₂PDIA (5 mg, 0.019 mmol), DMA (5 mL), H₂O (0.9 mL) and 0.3 mL of an aqueous HNO₃ 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(NO₃)₂•2.5H₂O). EA (%) Calc. for C₁₈ H₁₇ N₃ O₅ Cu: 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 (s), 1656 (s), 1612 (s), 1448 (s), 1384 (s), 1022 (s), 925 (s), 779(s), 723 (s), 684 (s), 532 (s), 480 (s).

Synthesis of [Mn₄(PDIA)₄(DMF)₆]_n•nDMF•2nH₂O (**JUC-127**)

A mixture of Mn(NO₃)₂•4H₂O (15 mg, 0.06 mmol), H₂PDIA (5 mg, 0.019 mmol), DMF (5 mL) and H₂O (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 DMF (3 × 5 mL) and dried in air (yield: 73% based on Mn(NO₃)₂•4H₂O). EA (%) Calc. for C₇₇ H₈₅ N₁₅ O₂₅ Mn₄: 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 [Zn₂₃(PDIA)₁₈(μ_4 -O)₂(μ_3 -OH)₆DMA₆]_n•10nDMA•6nH₂O (**JUC-128**)

The procedure was the same as that for **JUC-127** except that $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, DMF were replaced by $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (15 mg, 0.05 mmol) and DMA (yield: 68% based on $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$). EA (%) Calc. for $\text{C}_{316}\text{H}_{306}\text{N}_{52}\text{O}_{102}\text{Zn}_{23}$: 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 $[\text{Co}_3(\text{PDIA})_2(\text{HCOO})(\mu_3\text{-OH})(\text{H}_2\text{O})(\text{DMA})_2]_n \cdot n\text{DMA} \cdot n\text{H}_2\text{O}$ (JUC-129**)**

The procedure was the same as that for **JUC-128** except that $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was replaced by $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (15 mg, 0.05 mmol) and added 0.25 ml HNO_3 (2.0 M in DMF). Yield: 42% based on $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. EA (%) Calc. for $\text{C}_{41}\text{H}_{49}\text{N}_7\text{O}_{16}\text{Co}_3$: 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), 696 (s), 524 (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-K α radiation ($\lambda = 0.71073 \text{ \AA}$) 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 SHELXS-97 program.⁴⁴ 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.^{45, 46} The H atoms for the $\mu_3\text{-OH}$ in **JUC-128** 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-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

Compound	JUC-126	JUC-127	JUC-128	JUC-129
Empirical formula	$\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_5\text{Cu}$	$\text{C}_{77}\text{H}_{85}\text{N}_{15}\text{O}_{25}\text{Mn}_4$	$\text{C}_{316}\text{H}_{306}\text{N}_{52}\text{O}_{102}\text{Zn}_{23}$	$\text{C}_{41}\text{H}_{49}\text{N}_7\text{O}_{16}\text{Co}_3$
Formula weight	418.89	1840.36	7968.10	1072.66
Crystal system	Trigonal	Monoclinic	Trigonal	Triclinic
Space group	$R\bar{3}$	$P2_1$	$R\bar{3}c$	$P\bar{1}$
a ($\text{\AA}$)	22.004(11)	14.744(7)	26.655(4)	9.862(2)
b ($\text{\AA}$)	22.004(11)	16.525(8)	26.655(4)	13.348(3)
c ($\text{\AA}$)	20.67(2)	19.870(9)	85.130(3)	18.934(4)
α ($^\circ$)	90.00	90.00	90.00	75.217(5)
β ($^\circ$)	90.00	102.968(9)	90.00	81.616(5)
γ ($^\circ$)	120.00	90.00	120.00	88.983(5)
V ($\text{\AA}^3$)	8667(10)	4718(4)	52381(2)	2383.7(9)
Z	18	2	6	2
ρ_{calc} (g/cm^3)	1.445	1.296	1.516	1.494
μ (mm^{-1})	1.167	0.599	1.637	1.107
Nref	4700	13841	14498	11898
F(000)	3869.0	1904.0	24426.0	1106.0
Rint	0.0608	0.1042	0.0518	0.0418
Goodness-of-fit on F^2	1.098	0.858	1.140	1.031
R_1^a, wR_2^b [$I > 2\sigma(I)$]	0.058, 0.125	0.0763, 0.1680	0.0799, 0.2348	0.0572, 0.1377
R_1^a, wR_2^b (all data)	0.0901, 0.1371	0.1555, 0.1910	0.1030, 0.2567	0.1009, 0.1592
Flack	-	0.00(2)	-	-

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

Results and discussion

Structure and topology

[Cu(PDIA)(DMA)]_n (JUC-126**)**. The single crystal X-ray diffraction reveals that **JUC-126** crystallizes in the trigonal space group $R\bar{3}$. The asymmetric unit of **JUC-126** contains one Cu(II), one unique PDIA²⁻ 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 PDIA²⁻ ligands and two terminal coordinated DMA molecules ($\text{Cu-O} = 1.951\text{-}2.161 \text{ \AA}$). As shown in Fig. 1b, each PDIA²⁻ ligand is connected to two $\text{Cu}_2(\text{COO})_4$ SBUs. These copper paddle-wheels are further linked with PDIA²⁻ ligands to form a 3D framework with almost no channels (Fig. 1c). From the topologic point of view, copper paddle-wheel units and PDIA²⁻ ligands can be regarded as 4-connected and 2-connected linkers, respectively. The result network could be concerned as a 3D network with the point symbol $(6^4 \cdot 8^2)$, which belongs to NbO topology (Fig. 1d).

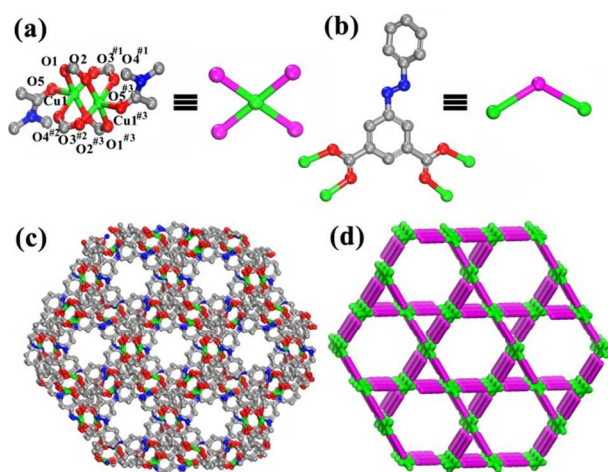


Fig. 1 (a) Coordination environments of Cu(II) and paddle-wheel SBUs viewed as a 4-connected node (symmetry code: #1 $x - y, x, -z + 2$, #2 $-x + y + 1/3, -x + 2/3, z - 1/3$, #3 $-x + 1/3, -y + 2/3, -z + 5/3$); (b) the PDIA²⁻ ligand coordinated to two Cu(II) paddle-wheel SBUs and viewed as a 2-connected linker; (c) the 3D coordination framework along the c-axis; (the hydrogen atoms are omitted for clarity and C, gray; O, red; N, blue; Cu, green) (d) simplified network of the 3D coordination framework along the c-axis with the point symbol (6⁴•8²).

[Mn₄(PDIA)₄(DMF)₆]_n•nDMF•2nH₂O (JUC-127). The X-ray crystallographic study shows that **JUC-127** crystallizes in the chiral monoclinic space group *P*2₁ and possesses a 2D framework. There are four Mn(II), four PDIA²⁻ 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 PDIA²⁻ 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 PDIA²⁻ ligands and three terminal coordinated DMF molecules (O15, O16, O17) (Mn-O = 2.088-2.179 Å). As shown in Fig. 2a, carboxylate groups of PDIA²⁻ ligands display three kinds of coordination modes: the bridging bismonodentate mode (O3, O4, O5, O6), the chelating bidentate mode (O1, O2), and the bridging-chelating mode (O8), where O8 acts as a μ_2 atom. There are three coordination fashions (modes 1-3). As shown in (Fig. 2b-2d), PDIA²⁻ ligands show $\mu_6\text{-}\eta^3\text{:}\eta^3$, $\mu_4\text{-}\eta^2\text{:}\eta^2$ and $\mu_3\text{-}\eta^1\text{:}\eta^2$ coordination modes in mode 1, mode 2 and mode 3, respectively. And the ratio of these three coordination modes in **JUC-127** is 1: 1: 2 (mode 1: mode 2: mode 3). Each PDIA²⁻ ligand is connected to two Mn₂(COO)₄ SBUs to form infinite helical chains and a 2D framework, which is further packed together between arene cores of two independent PDIA²⁻ by π - π stacking interactions (3.521 Å) to form a 3D supramolecular architecture (Fig. 2e). Topologically, by considering Mn₂(COO)₄ SBUs and PDIA²⁻ anions as 4-connected nodes and 2-connected linkers, the 2D framework can be symbolized as a sql topology with the point symbol (4⁴•6²) (Fig. 2f).

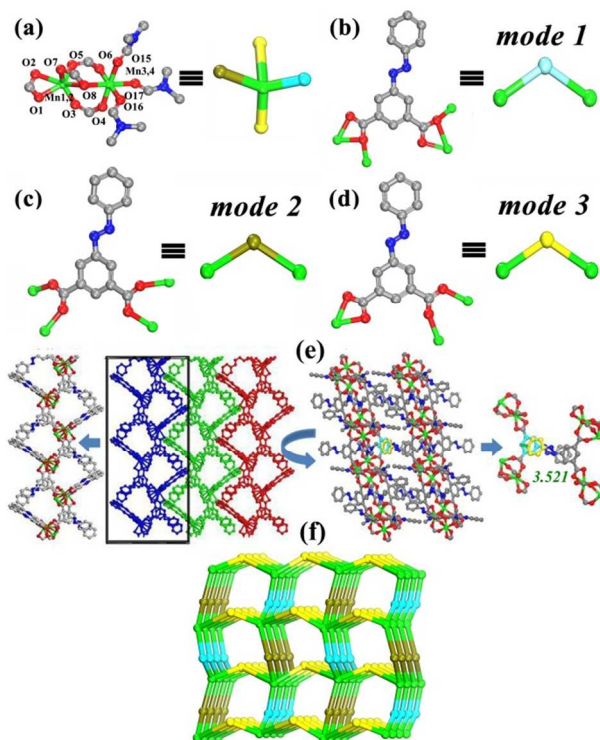


Fig. 2 (a) Coordination environments of Mn(II) and Mn₂(COO)₄ SBUs viewed as a 4-connected node; (b-d) three coordination modes in **JUC-127** and each PDIA²⁻ ligand viewed as a 2-connected linker; (e) view of a single 2D network and 2D networks are packed together to form a 3D supramolecular architecture along the c-axis and b-axis; (The hydrogen atoms are omitted for clarity and C, gray; O, red; N, blue; Mn, green) (f) Simplified network of the 2D coordination framework along the a-axis with the point symbol (4⁴•6²).

[Zn₂₃(TPIA)₁₈(μ_4 -O)₂(μ_3 -OH)₆DMA)₆]_n•10nDMA•6nH₂O (JUC-128). A single-crystal X-ray diffraction analysis reveals that **JUC-128** crystallizes in the trigonal *R*-3c space group and shows a 3D coordination framework. In the asymmetric unit, there is one Zn1, a half Zn2, one third Zn3, one Zn4, one Zn5, three PDIA²⁻ ligands, one third μ_4 -O atom (O14), one μ_3 -OH group (O13) and one terminal coordinated DMA molecule (Fig. S3). It is worth nothing that Zn2 is on a two-fold axis, while Zn3 and μ_4 -O14 are on a three-fold axis. There are two kinds of SBUs in the framework (Fig. 3a, 3b). Zn3 and Zn5 are held together by μ_4 -O (O14) which bind four Zn(II) and form a tetranuclear Zn₄O(COO)₆ SBUs, which is famous in the structures of IRMOFs. On the other hand, five Zn(II) centers (two Zn1, Zn2 and two Zn4) share μ_3 -OH (O13) to generate a pentanuclear Zn₅(μ_3 -OH)₂(COO)₈ SBUs. Zn3 (or Zn5) cation is four coordinated by four oxygen atoms from three bridging bismonodentate ligands and μ_4 -O, respectively, to furnish a tetrahedral geometry (Zn-O = 1.903-1.972 Å). Zn4 cation also shows a distorted tetrahedral geometry with four coordinated oxygen atoms from three ligands and one μ_3 -OH group, respectively, to form a tetrahedral geometry (Zn-O = 1.919-1.994 Å). Zn1 cation is bound with six oxygen atoms from four diverse ligands and one μ_3 -OH group to generate a distorted octahedral geometry. The Zn2 cation also exhibits a octahedral geometry ZnO₆ with two carboxyl groups from two different ligands, two μ_3 -OH groups and two terminal coordinated DMA molecules (Zn-O = 2.067-2.115 Å). It should be noted that PDIA²⁻ ligands exhibit $\mu_4\text{-}\eta^2\text{:}\eta^2$ and $\mu_5\text{-}\eta^2\text{:}\eta^3$

coordination modes in mode 1 and mode 2, respectively (Fig. 3c, 3d). The tetranuclear $\text{Zn}_4\text{O}(\text{COO})_6$ and pentanuclear $\text{Zn}_5(\mu_3\text{-OH})_2(\text{COO})_8$ SBUs are further linked with the PDIA^{2-} ligands to form a 3D framework (Fig. 2e). From the topologic point of view, the $\text{Zn}_4\text{O}(\text{COO})_6$ SBUs and $\text{Zn}_5(\mu_3\text{-OH})_2(\text{COO})_8$ SBUs can be regarded as 6-connected node and 8-connected node, respectively. The PDIA^{2-} ligands can be simplified for 2-connected linkers. Notably, this topology is with the point symbol $(3^3 \cdot 4^6 \cdot 5^6)_2(3^6 \cdot 4^8 \cdot 5^{10} \cdot 6^4)_3$, which is unknown in previously reported MOFs.

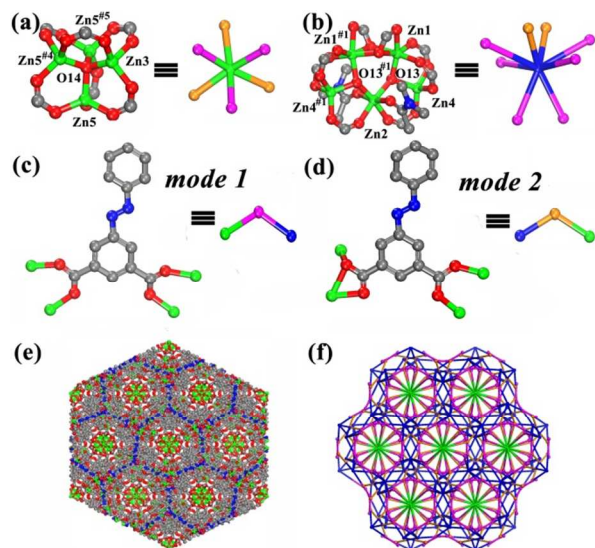


Fig. 3 (a, b) Coordination environments of Zn(II). $\text{Zn}_4\text{O}(\text{COO})_6$ SBUs and $\text{Zn}_5(\mu_3\text{-OH})_2(\text{COO})_8$ SBUs viewed as a 6-connected node and 8-connected node, respectively (symmetry code: #1 $x-y+1/3, -y+2/3, -z+1/6$, #4 $-x+y+2, -x+2, z$, #5 $-y+2, x-y, z$); (c, d) two coordination modes in **JUC-128** and each PDIA^{2-} 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 $(3^3 \cdot 4^6 \cdot 5^6)_2(3^6 \cdot 4^8 \cdot 5^{10} \cdot 6^4)_3$.

[Co₃(PDIA)₂(HCOO)(μ₃-OH)(H₂O)(DMA)₂]_n·nDMA·nH₂O (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 PDIA^{2-} ligands, one HCOO^- anion, one $\mu_3\text{-OH}$ group, one terminal H_2O , 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 DMF molecules under solvothermal conditions.^{47, 48} As shown in Fig. 4a, it shows the coordination environments of Co(II). There are three independent Co(II) in the structure, which adopt the same geometries. The Co1 cation is bound with six oxygen atoms from three carboxyl groups of three diverse ligands, two $\mu_3\text{-OH}$ groups and one HCOO^- anion to form a distorted octahedral geometry (Co-O = 2.047-2.273 Å). The Co2 cation also exhibits a distorted octahedral geometry CoO_6 with six oxygen atoms from four carboxyl groups of four different ligands, one $\mu_3\text{-OH}$ group and one terminal coordinated DMA molecule (Co-O = 2.017-2.142 Å). Meanwhile, the Co3 cation is also form a distorted octahedral geometry CoO_6 , which are three oxygen atoms from three carboxyl groups of three different ligands, others from one HCOO^- anion, one terminal H_2O molecule and one terminal coordinated DMA molecule (Co-O =

2.064-2.132 Å), respectively. Co(II) share the $\mu_3\text{-OH}$ oxygen atoms and oxygen atoms from carboxyl groups each other to form hexanuclear SBUs $[\text{Co}_6(\mu_3\text{-OH})_2(\text{COO})_{10}]$ (Fig. 4a). As shown in Fig. 2b, 2c, PDIA^{2-} ligands possess two modes in the framework. In mode 1, each PDIA^{2-} ligand links four Co(II) centers through the $\mu_4\text{-}\eta^2\text{:}\eta^2$ coordination mode, while $\mu_6\text{-}\eta^3\text{:}\eta^3$ coordination mode in mode 2. Each hexanuclear SBU $[\text{Co}_6(\mu_3\text{-OH})_2(\text{COO})_{10}]$ is linked with eight diverse ligands to form a 2D layer, which is further packed together by $\pi\text{-}\pi$ stacking interactions between arene cores of two independent PDIA^{2-} (3.627 Å) to form a 3D supramolecular architecture (Fig. 4d). To analyze the topology of the structure, PDIA^{2-} 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 $(4^4 \cdot 6^2)$, which belongs to sql topology (Fig. 4e).

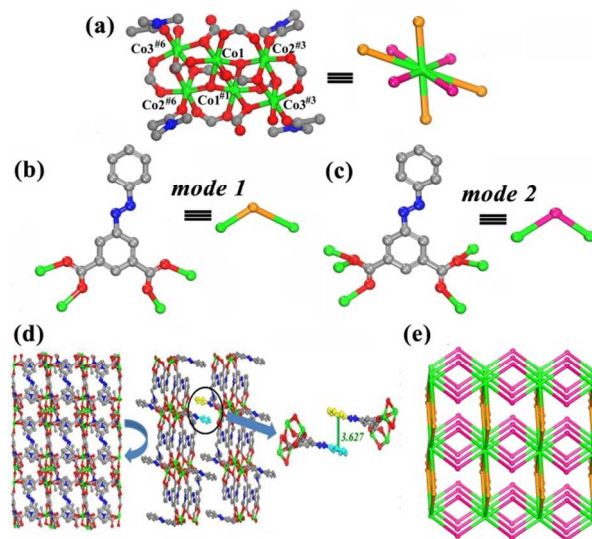


Fig. 4 (a) Coordination environments of Co(II) and $\text{Co}_6(\mu_3\text{-OH})_2(\text{COO})_{10}$ SBUs viewed as a 8-connected node (symmetry code: #1 $-x, -y, -z+1$, #3 $-x, -y+1, -z+1$, #6 $x, -1+y, z$); (b, c) two coordination modes in **JUC-129** and each PDIA^{2-} ligand viewed as a 2-connected node; (d) view of the 2D networks are packed together to form a 3D supramolecular architecture along the c-axis and b-axis; (The hydrogen atoms are omitted for clarity and C, gray; O, red; N, blue; Co, green) (e) Simplified network of the 2D coordination framework along the c-axis with the point symbol $(4^4 \cdot 6^2)$.

The influence of metal ions on the structures

As far as we known, metal ions play a vital role in generating the structures of MOFs, because they have different charges, ionic radii and electron configurations. **JUC-126**, **JUC-127**, **JUC-128** and **JUC-129** are synthesized with the same ligand (H_2PDIA) in similar synthesis conditions, but the structures are very different. Although all the metal ions (Cu^{2+} , Mn^{2+} , Zn^{2+} and Co^{2+}) have the same charge, the ionic radii may be the major factor to affect the structures. The ionic radii of Cu^{2+} , Mn^{2+} , Zn^{2+} and Co^{2+} 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 radius of Mn^{2+} (or Co^{2+}) is less than that of Zn^{2+} (or Cu^{2+}), but the coordination number of Mn^{2+} (or Co^{2+}) is more than that of Zn^{2+} (or Cu^{2+}), which indicates a lower coordination number can generate a high dimension framework. **JUC-126** and **JUC-**

128 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

Name	Central ion	Ionic radii (pm)	Coordination number	Dimensionality
JUC-126	Cu^{2+}	73	5	3D
JUC-127	Mn^{2+}	67	6	2D
JUC-128	Zn^{2+}	74	4, 6	3D
JUC-129	Co^{2+}	65	6	2D

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** losses six terminal coordinated DMF molecules, one guest DMF molecule and two guest H_2O 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_2O 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_2O molecule and one terminal coordinated H_2O 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 %).

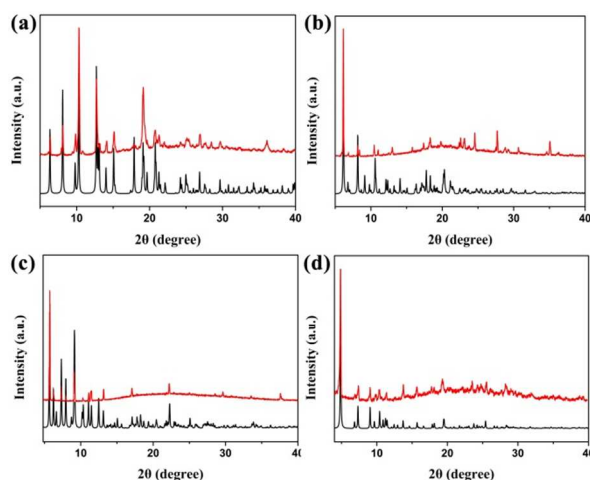


Fig. 5 The simulated (black) and as-synthesized (red) PXRD of **JUC-126** (a), **JUC-127** (b), **JUC-128** (c), **JUC-129** (d).

Luminescence properties

Luminescent coordination compounds with d^{10} transition-metal clusters have generally been investigated for luminescent

materials.^{49, 50} 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 **H₂PDIA** 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 $[\text{Zn}_5(\mu_3\text{-OH})_2(\text{COO})_8]$ and $\text{Zn}_4\text{O}(\text{COO})_6$ in the framework.⁵¹⁻⁵³

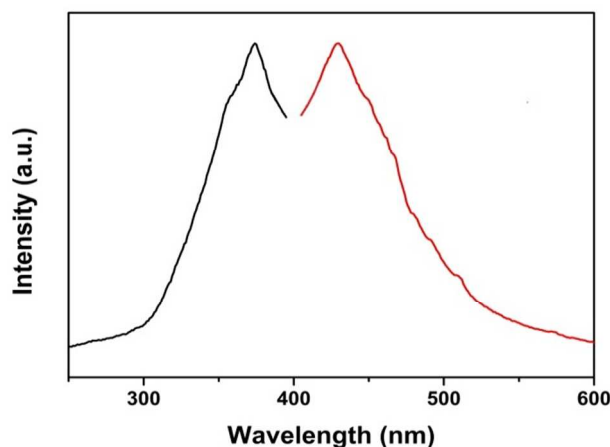


Fig. 6 The excitation (black) and emission (red) spectra of **JUC-128**.

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 $\chi_M T$ per Mn^{2+} unit is $4.57 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature, which is slightly higher than the value expected for a free Mn(II) cation ($4.375 \text{ cm}^3 \text{ K mol}^{-1}$). When temperature decreases sharply upon cooling, the $\chi_M T$ value began to decrease gradually until about 50 K and value of $1.06 \text{ cm}^3 \text{ K mol}^{-1}$ 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^{-1} vs. T over the temperature range 10-300 K range obeys the Curie-Weiss law [$\chi = C/(T-\theta)$] with $C = 4.76 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -13.61 \text{ K}$. The antiferromagnetic behavior of **JUC-127** may originate from the multiple superexchange interactions between the Mn(II) cations in the $\text{Mn}_2(\text{COO})_4$ cluster by the $\mu_2\text{-}\eta^1\text{-}\eta^1\text{-COO}^-$.⁵⁴

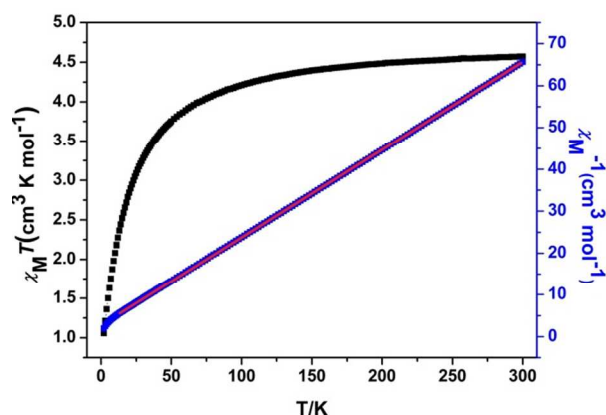


Fig. 7 Temperature dependence of $\chi_M T$ (black) and χ_M (blue) vs. T curve for JUC-127 and the red line indicates the fitting of the Curie-Weiss law.

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 $3.25 \text{ cm}^3 \text{ K mol}^{-1}$ at room temperature, which is higher than a free Co(II) cation ($1.875 \text{ cm}^3 \text{ K mol}^{-1}$). Upon cooling to 2 K, the $\chi_M T$ value sharply decreases to $0.84 \text{ cm}^3 \text{ K mol}^{-1}$, which indicates antiferromagnetic interaction between Co(II) cations in the Co_6 SBU. The magnetic data over the temperature range 40–300 K are fitted by the Curie-Weiss law [$\chi = C/(T-\theta)$] with $C = 3.70 \text{ cm}^3 \text{ K mol}^{-1}$ and $\theta = -42.37 \text{ K}$. The antiferromagnetic behavior of JUC-129 may also originate from the multiple superexchange interactions between the Co(II) cations in the $[\text{Co}_6(\mu_3\text{-OH})_2(\text{COO})_{10}]$ cluster by the $\mu_3\text{-OH}$, $\mu_2\text{-}\eta^1\text{-}\eta^1\text{-COO}^-$ and $\mu_2\text{-}\eta^1\text{-}\eta^1\text{-HCOO}^-$.^{55–56}

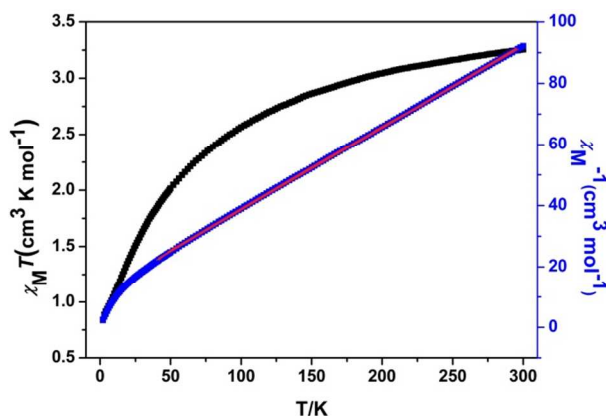


Fig. 8 Temperature dependence of $\chi_M T$ (black) and χ_M (blue) vs. T curve for JUC-129 and the red line indicates the fitting of the Curie-Weiss law.

Conclusions

In summary, four novel metal-organic frameworks based on a rigid ligand with azobenzene (H_2PDIA) and four different metal cations were successfully synthesized. JUC-126 features a 3D NbO topology with the point symbol $(6^4 \cdot 8^2)$ and JUC-127 shows a 2D sql topology with the point symbol $(4^4 \cdot 6^2)$, which is a chiral structure. Meanwhile, JUC-128 exhibits a new 3D topology with the point symbol $(3^3 \cdot 4^6 \cdot 5^6)_2(3^6 \cdot 4^8 \cdot 5^{10} \cdot 6^4)_3$ and JUC-129 has a 2D sql-type network with the point symbol $(4^4 \cdot 6^2)$. Clearly, the diverse coordination fashions of the PDIA^{2-} ligand with different metal cations to form bi-, tetra-, penta- and hexanuclear cores, and the $\pi\text{-}\pi$ 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 more kinds of ligands with such large aromatic rings without any coordination nodes to generate the richness and unpredictability of structures and topologies.

Acknowledgements

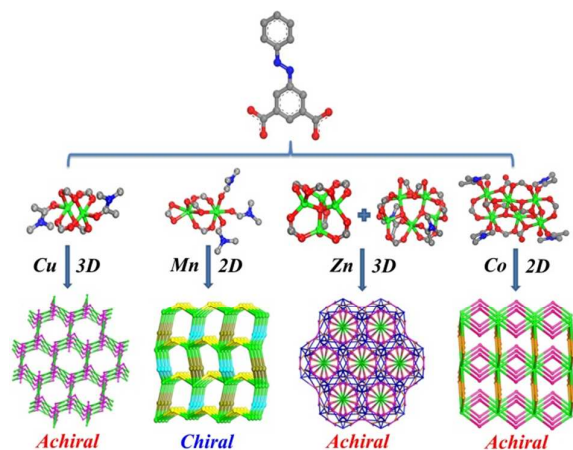
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Notes and references

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- b China Japan Union Hospital, Jilin University, Changchun, 130031, China. E-mail: djs3043@126.com.
- Electronic Supplementary Information (ESI) available: a table of selected bond distances and angles for JUC-126-129, the FT-IR spectra for the H_2PDIA ligand and JUC-126-129, the ^1H NMR spectra of H_2PDIA ligand, and the TGA plot of JUC-126-129. CCDC reference numbers 1021358, 1021359, 1021360 and 1021361. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/
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Entry for the Table of Contents



Four new metal–organic frameworks (MOFs) were synthesized under solvothermal conditions based on a new rigid ligand 5-(phenyldiazenyl)isophthalic acid (H₂PDIA) with azobenzene, which display different structures, fascinating topological structures and achiral/chiral frameworks.