Network topology and property studies for two binodal self-penetrated coordination polymers[†]

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Two coordination polymers, $[Co^{II}Cu^{I}(m-BDC)(BIPY)_{1.5}(m-NBZ)]_{n}$ (1) and $[Co^{II}_{4}(BPTC)_{2}(BBI)_{4}]_{n}$ (2), (where BIPY = 4,4'-bipyridine, BBI = 1,1'-(1,4-butanediyl)bis(imidazole), *m*-BDC = 1,3benzenedicarboxylate, *m*-HNBZ = *m*-nitrobenzoic acid and H₄BPTC = 3,3',4,4'biphenyltetracarboxylic acid), have been obtained under solvo/hydrothermal conditions, which were characterized by single-crystal X-ray diffraction, XRPD, IR, ICP, TGA, and elemental analysis. Both 1 and 2 feature two unusual binodal self-penetrated architectures: 1 presents a 2-D network with $(4 \cdot 6^{2})_{2}(4^{2} \cdot 6^{2} \cdot 8^{2})$ topology in terms of the rationalization of T-shaped Cu¹ and Co₂ unit as 3- and 4-connected node, respectively; however, compound 2 built up from a flexible long-chain ligand and a polycarboxylate confers a 3-D $(6^{2} \cdot 8^{4})(6^{4} \cdot 8^{2})_{2}$ net based on the definition of square-planar and tetrahedral 4-connected nodes. The magnetic study of 1 was carried out in the temperature range of 5–300 K, showing antiferromagnetic coupling interaction within the dimeric Co₂ unit. In addition, 1 was found to exhibit fluorescence at about 420 nm ($\lambda_{ex} = 330$ nm).

Introduction

Entanglements, such as (poly)catenanes, (poly)rotaxanes and molecular knots, have emerged as a class of supramolecular architectures attracting extensive interest due to their aesthetic attributes and promising functionalities.^{1,2} As reviewed in the CSD database, numerous entangled coordination polymers have been established so far.3 Of those entanglements however, the most frequently encountered are the interpenetrated networks, in which two or more identical nets pass through each other either in parallel or inclined mode. In comparison, the achievement of a self-penetrated superstructure as another typical entangled motif is still a great challenge to synthetic chemists.^{5d} These molecules are composed of a single network where specific rods penetrate the smallest circuits from the same nets. In spite of considerable efforts devoted to self-penetration for the time being, the known examples are confined to a very narrow scope.⁴⁻⁶ Tuning the ongoing self-assembly process would be a primary issue which accounts for the scarcity in self-penetration. It is recognized that the flexibility and adaptability of the applied organic linkers are of particular significance.

Generally, in the entangled systems plenty of free space should be present for the passage of other components.^{3a} Although the existence of voids never guarantees the formation of entanglements, in practice, what we can do now is to select the proper ligands to create large windows in the desired molecule. In terms of the structural characteristics, the incorporation of polycarboxylates with flexible long-chain ligands is believed feasible for generating the entangled nets.^{4f,7} Motivated by this strategy, we prepared the ligand 1,1'-(1,4-butanediyl)bis(imidazole) (BBI), which can selectively adjust the arrangements via rotation and/or bend on the backbone (Scheme 1). As we demonstrated recently in a 3-D self-penetrated net,⁶¹ BBI represents an ideal organic linker that is long and flexible enough for the generation of big windows. In the meantime, the multifunctional ligand 3,3',4,4'biphenyltetracarboxylic acid (H₄BPTC) presents us with the possibility of high-dimensional MOFs as a consequence of the advantages listed below: (i) due to semi-rigidity, the two phenyl rings would be able to twist around the C-C single bond under certain strain; (ii) use of BPTC ligand gives rise to somewhat complicated structures due to diversity in the coordination modes of four carboxyl groups.

In the past several years, the conception of molecular topology was introduced into the field of coordination chemistry, and topological analysis has been proven an excellent tool for the design and investigation of the desired structures. As an extension of our research of entangled structures, we herein report two



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Fig. 1 Local coordination environments of the metal atoms in 1. Hydrogens are omitted for clarity.

binodal self-penetrated coordination polymers: $[Co^{II}Cu^{I}(m-BDC)(BIPY)_{1.5}(m-NBZ)]_{n}$ (1) and $[Co^{II}_{4}(BPTC)_{2}(BBI)_{4}]_{n}$ (2). Compound 1 shows a 2-D $(4 \cdot 6^{2})_{2}(4^{2} \cdot 6^{2} \cdot 8^{2})$ topological net, while 2 features a 3-D network with $(6^{2} \cdot 8^{4})(6^{4} \cdot 8^{2})_{2}$ topology.

Results and discussion

Crystal structure of 1

The solvothermal reaction of CoCl₂·6H₂O, CuCl, 1,3-benzenedicarboxylic acid (m-H₂BDC), 4,4'-bipyridine (BIPY), and m-nitrobenzoic acid (m-HNBZ) in the molar ratio of 1:1:1:1.5:1 at 140 °C for 3 days gave rise to light-purple crystals of 1. The structure of this compound contains one Co atom, one Cu atom, one *m*-BDC, one *m*-NBZ, and one and a half BIPY molecules. The structural consistency and phase purity of 1 were confirmed by X-ray powder diffraction (XRPD) analysis (Fig. S1).[†] Bond valence sum (BVS) calculation demonstrates Cu in the +1 oxidation state.8 As shown in Fig. 1, three-coordinate Cu^I with T-shaped geometry is surrounded by two different N_{BIPY} atoms (Cu-N = 1.917(2)-1.920(2) Å) and one O_{m-BDC} atom (Cu-O = 1.917(2)-1.920(2) Å)2.164(2) Å). Such coordination number is always characteristic of Cu^I ion. The coordination environment for Co can be described as a square-pyramid defined by the trigonal parameter $\tau \approx 0,^{9}$ in which four O_{carboxylate} atoms (Co–O = 1.956(2)– 1.976(2) Å) occupy the basal plane, one N_{BIPY} atom (Co–N = 2.150(3) Å) lies in the axial position, and the Co atom is at the center of the square plane. Two crystallographically equivalent Co atoms are connected in pairs by the bridging mono-bidentate m-BDC and terminal m-NBZ to form a paddle-wheel-shaped $[Co_2(CO_2)_4]$ fragment with the Co…Co distance of 2.646(6) Å. Two adjacent Co₂ units and two Cu^I atoms are interlinked via BIPY and *m*-BDC to form ring-shaped SBUs, which are further extended by BIPY into a 2-D network. There are no signals found at about 1700 cm⁻¹ in the IR spectrum, indicating all the



Fig. 2 (a) Schematic representation of the $(4 \cdot 6^2)_2 (4^2 \cdot 6^2 \cdot 8^2)$ topology. Cyan ball: Cu¹ atom as a 3-connected node; Red ball: Co₂ unit as a 4-connected node; (b) local diagram of the self-penetration.

Topological analysis reveals 1 is a (3,4)-connected net with $(4 \cdot 6^2)_2(4^2 \cdot 6^2 \cdot 8^2)$ topology if the Cu¹ and Co₂ units are treated as a 3-connected and 4-connected node, respectively (Fig. 2a). There are one 4-gon and two 6-gons (the smallest circuits) around each Cu¹ atom. Similarly, the shortest rings around each 4-connected node are 4-gon, 6-gon and 8-gon. The ratio of these two nodes is 2:1. The long Schläffi vertical symbol is $4 \cdot 6 \cdot 6$ for the 3-conn node and $4 \cdot 4 \cdot 6 \cdot 6 \cdot 8_2 \cdot 8_2$ for the 4-conn node, giving the net symbol $(4 \cdot 6 \cdot 6)_2(4 \cdot 4 \cdot 6 \cdot 6 \cdot 8_2 \cdot 8_2)$. Although there exist many examples documented as (3,4)-connected nets,^{3,4,11} the majority are involved in boracite, Pt₃O₄ and cubic-C₃N₄.¹² Only one case is observed to be identical to the current topology.¹³ Actually, complex 1 shows a self-penetrated feature, which is evidenced by the passage of the rod through the circuit (Fig. 2b).

Crystal structure of 2

Pink block-shaped crystal of 2 was hydrothermally synthesized by the reaction of CoCl₂·6H₂O. H₄BPTC and BBI at 160 °C for 60 h. Single-crystal X-ray diffraction reveals that polymer 2 crystallizes in the orthorhombic space group Pccn. As illustrated in Fig. 3, the asymmetric unit contains one crystallographically independent Co ion, one BBI ligand and half a BPTC⁴⁻ anion. The coordination geometry of Co is an elongated squarepyramid CoN_2O_3 where the basal plane comprises three $O_{carboxyl}$ atoms (Co–O = 1.983(2)–2.332(2) Å) from two BPTC ligands and one N_{BBI} atom (Co–N = 2.041(3) Å), and the remaining apical position is occupied by another N_{BBI} donor. In the *ab* plane, a 2-D herringbone-like substructure was formed (Fig. 4a), in which each BPTC ligand ligates four Co atoms, while each Co center is simultaneously connected to six adjacent cobalts via two BPTC ligands. The additional BBI, as pillared modules, extend the 2-D substructures into a 3-D framework. The absence of a peak at 1700 cm⁻¹ or so suggests a coordination of the four carboxyl groups to Co atoms in polymer 2.

The pronounced structural feature is that 2 represents a rare self-penetrated network (Fig. 4b). From the viewpoint of molecular topology, both Co and BPTC anion can be referred to as the 4-connected node. In general, there are two types of nodes



Fig. 3 Local coordination environment for Co^{II} atom in 2. Hydrogens have been omitted for clarity.



Fig. 4 (a) 2-D herringbone-like substructure consisting of organicinorganic composition $[Co_2(bptc)]$; (b) local diagram of the selfpenetration in 2.

to be involved in this category, and the different target nets produced rely on which type is present. For example, the squareplanar node favors the generation of NbO (64.82-a), CdSO4 $(6^5 \cdot 8)$, Ivt $(4^2 \cdot 8^4)$ and quartz dual net $(7^5 \cdot 9)$, whereas the tetrahedral node would typically lead to quartz ($6^4 \cdot 8^2$ -b), diamond (6^6) and SrAl₂ ($4^2 \cdot 6^3 \cdot 8$) nets.^{6b, 14} An exception is PtS ($4^2 \cdot 8^4$) net in which equal numbers of planar and tetrahedral nodes (1:1) are included. In our case, BPTC anion as the square-planar node has a long topological vertex symbol: $6_2 \cdot 6_2 \cdot 8_2 \cdot 8_3 \cdot 8_3$. The Co atom functions as a tetrahedral node with the vertex symbol $6 \cdot 6 \cdot 6 \cdot 8_4 \cdot 8_2$. The ratio of the two nodes is 1:2, obviously being different from the PtS net. Based on the definition of these nodes, polymer **2** exhibits a binodal $(6^2 \cdot 8^4)(6^4 \cdot 8^2)_2$ topological network (Fig. 5) which was calculated via OLEX.¹⁵ The BPTC ligand is surrounded by two 6-gons and four 8-gons. In contrast, there are four 6-gons and two 8-gons around the Co ion. The current framework represents, as far as we know, an unprecedented case of such topology despite a homochiral compound [Zn₂(D-cam)₂-(TPB)]·H₂O having previously been found to have the same Schläfli symbol which does not show an entangled structure.¹⁶

To be noted that the most frequently observed self-penetrated MOFs are classified as 4-, 6-, 8-, (3,5)-, and (3,6)-connected nets,⁴⁻⁶ and the 4-fold connectivity mainly stands for those having a uniform chemical composition, *i.e.* either square-planar or tetrahedral node developed in the targets. Thus, the proposed (3,4)- and (4,4)-connected nets above distinguish themselves in the self-penetrated systems.

Magnetic properties of 1

The variable-temperature dc magnetic susceptibility of 1 has been measured from 5 to 300 K in a 500 Oe applied field. As



Fig. 5 Schematic representation of the $(6^2 \cdot 8^4)(6^4 \cdot 8^2)_2$ topology. Gray ball: BPTC as a planar node; blue ball: Co atom as a tetrahedral node.



Fig. 6 Plot of the χ_m and $\chi_m T$ versus T in 1. The red solid line shows the best fit. Inset: graph of χ_m^{-1} .

illustrated in Fig. 6, the $\chi_m T$ value of *ca.* 4.36 cm³ K mol⁻¹ at 300 K is larger than the spin-only value (3.75 cm³ K mol⁻¹) expected for two high-spin Co^{II} ions with $S = {}^{3}/{}_{2}$, indicating the existence of orbital contribution to the magnetic interactions in the Co-containing complex.¹⁷ Upon cooling, the monotonic decrease in $\chi_m T$ until a minimum (1.47 cm³ K mol⁻¹) at 5 K is indicative of dominant antiferromagnetic coupling. The data above 25 K obeys the Curie-Weiss law $\chi_m = C/(T - \theta)$, giving a Curie constant C = 9.53 cm³ K mol⁻¹ and a Weiss constant $\theta = -21.4$ K. To evaluate the exchange coupling interaction, the susceptibility of 1 can be simulated using the binuclear model.¹⁸

$$\chi_{
m m} = rac{Ng^2eta^2}{kT}rac{14+5X^6+X^{10}}{7+5X^6+3X^{10}+X^{12}}+\chi_{
m TIP}$$

where $X = \exp(-J/kT)$, and χ_{TIP} term was added to take into account the temperature-dependent paramagnetic contribution from the sample. The *J* and *g* are obtained by minimizing the error $R = \sum [(\chi_m T)_{\text{exp}} - (\chi_m T)_{\text{calc}}]^2 / \sum [(\chi_m T)_{\text{exp}}]^2$. The best-fit parameters are listed as follows: $J = -1.44 \text{ cm}^{-1}$, g = 2.37, $\chi_{\text{TIP}} = 200 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, and $R = 6.82 \times 10^{-4}$. The negative *J* value indicates a weakly antiferromagnetic exchange coupling within the dimeric Co₂ unit.

Photoluminescence of 1

As we know, Cu¹-containing coordination polymers with d¹⁰ configuration often exhibit fluorescence.¹⁹ Photoluminescence



Fig. 7 Excitation spectrum (...) and emission spectrum (—) of **1** at room temperature.

experiments for 1 were performed at room temperature in the solid state. As shown in Fig. 7, an intense luminescence peak at *ca*. 420 nm was detected from the emission spectrum when it was excited at 330 nm. Free BIPY and *m*-HNBZ ligands do not emit intense luminescence from 400 to 800 nm, and the free m-H₂BDC shows the strongest emission peak at 380 nm or so.²⁰ Thus, this emission can be attributed to the ligand-to-metal charge transfer (LMCT).

TGA of 1 and 2

To evaluate the thermal stability of 1 and 2, thermogravimetric analyses (TGA) were carried out in the temperature range of 25–800 °C. Complex 1 decomposes completely until 322 °C (Fig. S2a).† As shown in Fig. S2b,† complex 2 remains stable up to *ca*. 330 °C and a strong exothermic peak occurs at 413 °C, indicating a complete cleavage of the integrated skeleton.

Experimental

Materials and general procedures

All chemicals were of reagent grade. The BBI ligand was synthesized by the reported procedure.²¹ The IR spectrum was recorded as KBr pellets on a Nicolet Magna-FT-IR 560 spectrometer in the 4000–400 cm⁻¹ region. Elemental analysis for C, H and N was performed on a Perkin-Elmer 240 analyzer. Inductively coupled plasma (ICP) analysis was carried out on a Perkin-Elmer Optima 3300 DV spectrometer. The thermogravimetric analysis (TGA) was investigated on a standard TG-DTA analyzer under nitrogen flow at a heating rate of 5 °C min⁻¹ for all measurements in the temperature range of 25-800 °C. Powder diffraction data were collected with a Rigaku D/max-RC diffractometer using a Cu target ($\lambda = 1.54060$ Å) operated at 50 kV and 180 mA. Fluorescence analysis was carried out on an Edinburgh Instruments analyzer model FL920. The magnetic measurement was performed on the Quantum Design SQUID MPMS XL-7 instruments. The diamagnetism of the sample and sample holder were taken into account.

Synthesis of $[Co^{II}Cu^{I}(m-BDC)(BIPY)_{1.5}(m-NBZ)]_{n}$ (1)

A mixture of CoCl₂·6H₂O (0.12 g, 0.5 mmol), CuCl (0.05 g, 0.5 mmol), *m*-H₂BDC (0.09 g, 0.5 mmol), BIPY (0.15 g, 0.75 mmol) and *m*-HNBZ (0.09 g, 0.5 mmol) was dissolved in 6 mL of CH₃CN. The pH value was then adjusted to 6 with 2 M KOH. Consequently, the resulting solution was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel, which was heated at 140 °C for 3 days. After the reactor was slowly cooled to room temperature at a rate of 5 °C h⁻¹, light-purple block crystals were filtered off, washed with water, and dried in air. Yield: 64%. ICP analysis of compound 1 gave the contents of Co and Cu as 8.62 and 9.22 wt%, respectively (Calcd: Co, 8.58; Cu, 9.25 wt%), indicating a Co:Cu ratio of 1:1. Elem. Anal. Calcd for 1: C, 52.45; H, 2.93; N, 8.16. Found: C, 52.43; H, 2.99; N, 8.20. IR (KBr, cm⁻¹): v = 1615 (s), 1508 (m), 1465 (m), 1376 (s), 750 (s), 719 (m).

Synthesis of $[Co^{II}_4(BPTC)_2(BBI)_4]_n$ (2)

A mixture of $CoCl_2 \cdot 6H_2O$ (0.12 g, 0.5 mmol), H_4BPTC (0.08 g, 0.25 mmol) and BBI (0.10 g, 0.5 mmol) in a molar ratio 2:1:2 was

	1	2
Formula	C ₃₀ H ₂₀ CoCuN ₄ O ₈	C ₇₂ H ₆₈ Co ₄ N ₁₆ O ₁₆
Fw	686.97	1649.14
T/K	293(2)	298(2)
Crystal system	triclinic	orthorhombic
Space group	<i>P</i> -1	Pccn
a/Å	10.6979(8)	20.584(4)
b/Å	10.8874(8)	11.949(2)
c/Å	14.7652(16)	15.098(3)
αI°	91.6510(10)	
βl°	93.5430(10)	
$\gamma/^{\circ}$	118.5640(10)	
$V/Å^3$	1504.2(2)	3713.5(12)
Ζ	2	2
$d_{\rm calc}/{\rm mg}~{\rm m}^{-3}$	1.517	1.475
μ/mm^{-1}	1.314	0.956
Θ range/°	2.13-25.03	3.19-27.48
R _{int}	0.0127	0.0454
Completeness	98.7%	99.8%
GOF	1.044	1.058
R_1	0.0366	0.0492
wR_2	0.1055	0.1318
Residual peak/e Å ⁻³	0.950, -0.561	1.140, -0.568

dissolved in 6 mL of distilled water. The pH value was then adjusted to 6.5 with 2 M KOH. Consequently, the resulting solution was transferred and sealed in a 25 mL Teflon-lined stainless steel vessel, which was heated at 160 °C for 60 h. After the reactor was slowly cooled to room temperature at a rate of 5 °C h⁻¹, pink block-shaped crystals were filtered off, washed with distilled water, and dried in air. Yield: 34% based on Co. Elem. Anal. Calcd for **2**: C 52.44, H 4.16, N 13.59. Found: C 52.41, H 4.18, N 13.63. IR (KBr, cm⁻¹): $\nu = 1609$ (vs), 1554 (s), 1457 (m), 1385 (s), 793 (s), 737 (m), 712 (m).

X-Ray crystallographic measurements

Crystal data and experimental details are summarized in Table 1. Single crystal analysis was performed on a Bruker SMART 1000 CCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) by the ω -2 θ scan technique. All data were collected for absorption by the semiempirical method using the SADABS program. The program SAINT²² was applied for integration of the diffraction profiles. Data analyses were carried out with the program XPREP. The structures were solved with the direct method using SHELXS-97 followed by structure refinement on F^2 with the program SHELXL-97.²³ All non-hydrogen atoms were refined anisotropically. Aromatic hydrogen atoms were assigned to calculated positions with isotropic thermal parameters. The CCDC reference numbers are 630068 (1) and 642458 (2).

Conclusions

In conclusion, a couple of self-penetrated coordination polymers have been constructed *via* a hydrothermal reaction and they both fall into the binodal topological networks. The 2-D framework of **1** shows a (3,4)-connected $(4 \cdot 6^2)_2(4^2 \cdot 6^2 \cdot 8^2)$ topology; however, polymer **2** features a 3-D $(6^2 \cdot 8^4)(6^4 \cdot 8^2)_2$ net which contains square-planar and tetrahedral nodes. More importantly, this study demonstrates the utilisation of flexible long-chain ligand BBI for entangled structures, and also the related investigations are now in progress to explore the desirable materials.

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