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Journal Name

ARTICLE

A novel [4+3] interpenetrated net containing 7-fold interlocking *pseudo*-helical chains and exceptional catenane-like motifs

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A novel interpenetrating metal–organic framework, namely $[Zn_3L_2(oba)_3(H_2O)_2]\cdot4H_2O$ (**1**), has been synthesized under hydrothermal conditions. Its structure was determined by single-crystal X-ray diffraction analysis and further characterized by elemental analysis, IR, and thermogravimetric (TG) analysis. In the structure of **1**, the rigid and flexible V-shaped ligands link Zn(II) to form a 3D structure where two types of helices and four types of *pseudo*-helical chains containing three pairs of enantiomers and two pairs of conformational isomers have been characterized. One such 3D framework incorporates six identical networks to form a 7-fold interpenetrated 3D framework. From the topological analysis, the Zn(II) ions act as three- and four-connected nodes, and oba as well as **L** are linkers. The framework of compound **1** can be classified as a new $(6^3)_2(6^5\cdot8)$ topology, which is a novel (3,3,4)-connected [4 + 3] 7-fold interpenetrating net showing 7-fold interlocking *pseudo*-helical chains and an unique catenane-like motif with Hopf links. In addition, the luminescent properties of the compound are discussed.

Introduction

Over the past few years, the design and construction of metal–organic coordination polymers or metal–organic frameworks (MOFs)[1] with novel topologies or intriguing architectures has attracted great attention for their intrinsic aesthetic appeal in addition to their tremendous potential applications as functional materials in gas storage and separation,[2] magnetism,[3] luminescence,[4] nonlinear optics,[5] drug delivery,[6] heterogeneous catalysis,[7] and so on.[8] Many MOFs are particularly fascinating because of the presence of various types of entanglements such as interpenetration, polycatenation, polythreading, and Borromean.[9] Among them, interpenetration is the more abundant and more comprehensively studied subject, which is a term used to describe the mutual intergrowth of two or more networks in a structure where the networks are physically but not chemically linked. As discussed in comprehensive reviews by Robson,[9a] Batten,[9d] Ciani,[9b] Proserpio and their co-workers,[9c] all interpenetrated network structures can be regarded as infinite, ordered polycatenanes or polyrotaxanes. Wells introduced the theme of interpenetrating nets (identical or of two or more kinds) by stating that they "cannot be separated without breaking links''.[9h] As described, polycatenation differs from interpenetration in that the whole catenated array has a higher dimensionality than that of the component motifs and

that each individual motif is catenated only with the surrounding ones and not with all the others.[9b] To date, large numbers of interpenetrated frameworks have been reported.[10] However, there is an unfavorable lack of detailed investigation on multi-fold interpenetrated 3D structures, such as 6-, 7-, 8-, 9- and 10-fold ones, especially for multi-fold interpenetrated structures with [n + m] modes. Based on our survey of literatures, only a few desirable examples showing a three dimensional 4-fold [2 + 2] net,[11] 6-fold [3 + 3] net,[12] 8-fold [4 + 4] nets[13] and 12-fold [6 + 6] networks[14] have been characterized. And in our recent work,[15] a rare nonequivalent [4 + 2] 6-fold interpenetrated **dia** network had been obtained by using a predesigned tetrahedral metal cluster and linear organic ligands. Therefore, the study of this facet is still a challenging issue in coordination chemistry.

Another interest of network which has aroused great interest of chemists is the MOF materials containing helical attributes. Helical structures are widely appeared in, for example, proteins, collagens, quartz, single-walled carbon nanotubes, and many natural or artificial fiber-type derivatives.[16] Multiple helices, which are ubiquitous in nature and are the foundation of genetic codes, are attracting increased attention in coordination chemistry and material chemistry originating from their importance in biological systems, optical devices, and asymmetric catalysis.[17] Driven by the pioneering work of Lehn

and co-workers,[18] some appealing coordination polymers containing multiple helices have been constructed.[19] Up to now, multi-fold interpenetrated 3D structures with [n + m] mode containing multiple helices and catenane-like motifs have not been reported.

An effective and controllable route in building such networks is to employ appropriate bridging ligands that can bind metal ions in different modes and provide a possible way to achieve more new materials with intriguing aesthetic structures and topological features.[20] Keep this in mind, long ligands with bent backbones enter into our sight based on the following considerations: (i) Long ligands, when coordinated with metal ions, have shown the ability to produce unique interpenetrated structures. In a very loose and general sense, it can be said that the longer the ligands in a net the more likely interpenetration occurs.[9a] (ii) Employment of bent bridging ligands could improve the helicity of the polymeric chains, which may thus favor the formation helical structure.[21] (iii) The bent ligands can form loops or rings which are beneficial for the construction of rotaxane- and catenane-like motifs. Recently, we have synthesized the first 2D framework showing 6-fold polyrotaxane interpenetration character with a V-shaped rigid ligand.[22] On the other hand, the strategy of using ancillary ligands has been proven to be interesting and useful for the formation of novel frameworks due to the fact that the coligands tend to adjust themselves to satisfy the needs of the lowest system energy by twisting, rotating, and folding when interacting with inorganic nodes.[23] In order to meet the demand for the interpenetrated nets with helical feature, the flexible V-shaped ancillary ligands will be judicious choice because of their suitable and changeable conformations when they bind to metal ions.[24] As a continuation of our search for new coordination network, in this paper, a compound $[Zn_3L_2(oba)_3(H_2O)_2]\cdot 4H_2O$ (1) is obtained by the reaction of long V-shaped ligand, 4-animo-3,5-bis(4-imidazol-1-ylphenyl)-1,2,4-triazole (L), 4,4'-oxydibenzoic acid (oba) (scheme 1) and Zn cations under hydrothermal conditions. Compound 1 represents a novel [4+3] 7-fold interpenetrated framework containing exceptional 7-fold interlocking *pseudo*-helical chains and catenane-like motifs. In addition, the luminescent properties of the compound are discussed.
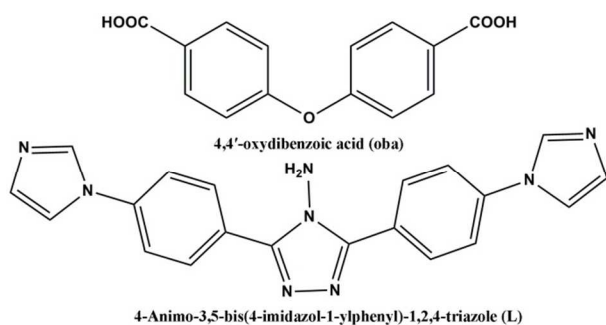
Scheme 1 N-donor L ligand and O-donor carboxylate based coligand.

Experimental section

Materials and instruments

Chemicals were purchased from commercial sources and used without further purification. Powder X-ray diffraction (PXRD) was carried out with an X-ray diffractometer of Rigaku, Rint 2000. The C, H, and N elemental analyses were conducted on a Perkin-Elmer 240C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TG-7 analyzer heated from room temperature to 800 °C at a ramp rate of 5 °C/min under nitrogen. The photoluminescence spectra were measured on a Perkin-Elmer FLS-920 spectrometer. ICP was measured by ICP-9000(N+M) (USA Thermo Jarrell-Ash Corp).

Synthesis of $[Zn_3L_2(oba)_3(H_2O)_2]\cdot 4H_2O$ (1)

The ligand 4-animo-3,5-bis(4-imidazol-1-ylphenyl)-1,2,4-triazole (L) was prepared following the method as described in the literature.[25] A solid mixture of L (37 mg, 0.1 mmol), oba (13 mg, 0.05 mmol), Zn(NO$_3$)$_2$·6H$_2$O (60 mg, 0.2 mmol) was suspended in H$_2$O (8 ml) in a 15ml Teflon-lined stainless steel container. The mixture was heated in an isotherm oven at 150 °C for 72 h resulting in colorless crystals, which were isolated by washing with H$_2$O and ethanol. The sample was dried in air at room temperature overnight. Yield: 57% based on 1 mol of L. Elemental analyses calcd (%) for C$_{82}$H$_{68}$Zn$_3$N$_{16}$O$_{21}$ (1809.63): C, 54.42; H, 3.79; N, 12.38; Found C, 54.37; H, 3.75; N, 12.51. IR (KBr pellet,cm^{-1}): 3363 (m), 3132 (m), 1600 (w), 1563 (w), 1538 (w), 1502 (w), 1379 (w), 1306 (m), 1248 (w), 1159 (m), 1125 (m), 1098(s), 1062 (m), 1010 (s), 963 (m), 878 (m), 841 (m), 782 (m), 737 (m), 695 (m), 650 (m), 516 (s).

X-ray crystallography study

Single-crystal X-ray diffraction data were recorded on a Bruker Apex CCD diffractometer with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71069 Å) at 293 K. Absorption corrections were applied using multi-scan technique. All the structures were solved by Direct Method of SHELXS-97[26] and refined by full-matrix least-squares techniques using the SHELXL-97[27] program within WinGX. Non-hydrogen atoms were refined with anisotropic temperature parameters. A large amount of spatially delocalized electron density in the lattice were found and all these electron density were appointed as free water molecules. However, the very high thermal parameters of most water molecules implied the disorder of some water molecules. In order to get acceptable thermal parameters, the occupancy of some water molecules were fixed to be 0.5 to give total four free water molecules. These water molecules are further estimated by TGA analysis combining with element analysis, and the results agree very well with the one of the single crystal X-ray diffraction analysis. The coordinates of the H atoms on the coordinated and free water were estimated using the Calc-OH program in the WinGX suite and were subsequently fixed

(AFIX 3) with their thermal parameters set to $U_{iso}(H) = 1.2U_{eq}(O)$. For one water molecule (O7W), one hydrogen atom of the two hydrogen atoms has been deleted because of the failure of forming reasonable H-bond network. Because of the ADPs problem, the restraint command 'ISOR' is used to refine O6W. These results have been written into the CIF files. The detailed crystallographic data and structure refinement parameters for **1** are summarized in Table 1. Selected bond lengths and angles for complexes **1** are given in Table S1†.

Table 1 Crystal data and structure refinement parameters for **1**

Compound reference	**1**
Chemical formula	$C_{82}H_{68}N_{16}O_{21}Zn_3$
Formula Mass	1809.63
Crystal system	Orthorhombic
a/Å	17.409(5)
b/Å	18.998(5)
c/Å	24.863(5)
α/°	90
β/°	90
γ/°	90
Unit cell volume/Å³	8223(4)
Temperature/K	298(2)
Space group	$Pna2_1$
No. of formula units per unit cell, Z	4
No. of reflections measured	46325
No. of independent reflections	14534
R_{int}	0.0564
Final R_1 values ($I > 2\sigma(I)$)	0.0522
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1237
Final R_1 values (all data)	0.0822
Final $wR(F^2)$ values (all data)	0.1402
Goodness of fit on F^2	0.988

Results and discussion

Structural descriptions

1 was obtained as colorless block crystals from a reaction of 4-animo-3,5-bis(4-imidazol-1-ylphenyl)-1,2,4-triazole (**L**), 4,4′-oxydibenzoic acid (oba) and $Zn(NO_3)_2 \cdot 6H_2O$ under hydrothermal conditions in moderate yields. The TG curve of **1** demonstrates an initial weight loss of ca. 3.96% between 50 °C

and 114 °C corresponding to the remove of four free water molecules (calculated, 3.97%), and the weight loss of ca. 2.01% between 114 °C and 200 °C corresponding to the remove of two coordinated water molecules (calculated, 1.99%), the decomposition of the whole framework starts at 350 °C (Fig. S1, ESI†). The phase purity of the as-synthesized material is confirmed by the PXRD pattern, which shows great agreement with the simulated one (Fig. S3, ESI†).

Single crystal X-ray diffraction analysis reveals that **1** crystallizes in the acentric orthorhombic space group $Pna2_1$. There are three crystallographically independent Zn centers, three types of oba ligands and two kinds of **L** ligands according to the coordination modes in the asymmetry unit (Fig. 1). Zn1 coordinates with two oxygen atoms from two oba ligands and two nitrogen atoms from two **L** ligands (Fig. 1a), both Zn2 and Zn3 coordinate with one nitrogen atom from one **L** ligand, and one oxygen atom from one water molecule, two oxygen atoms from two oba ligands, respectively (Fig. 1b, c). It is noteworthy that each oba and **L** ligand in the asymmetry unit demonstrates different conformations (Fig. S4, ESI†). For oba, the two phenyl rings can rotate freely around the central oxygen atom, which will induce the different dihedral angle between the two phenyl rings and the different distance between the two carboxylate group. In compound **1**, three conformers of oba coexist, defined as oba^1, oba^2, oba^3. The dihedral angle between the two phenyl rings and the distance between the two carbon atoms of the carboxylate groups are 82.51° and 10.06 Å for oba^1, 83.07° and 9.80 Å for oba^2, 77.37° and 10.11 Å for oba^3; While, for **L**, partial rotation of the imidazole ring with respect to the phenyl ring around the C-N bond, the phenyl ring with respect to the triazole ring around the C-C bond both can result in different conformations. In compound **1**, two conformers of **L** coexist, defined as L^1, L^2. In L^1, the two dihedral angles between the imidazole ring and the phenyl ring are 12.66° and 19.01°, the distance between the two coordinated nitrogen atoms is 17.52 Å; In L^2, the two dihedral angles between the imidazole ring and the phenyl ring are 20.04° and 35.00°, the distance between the two coordinated nitrogen atoms is 17.31 Å;
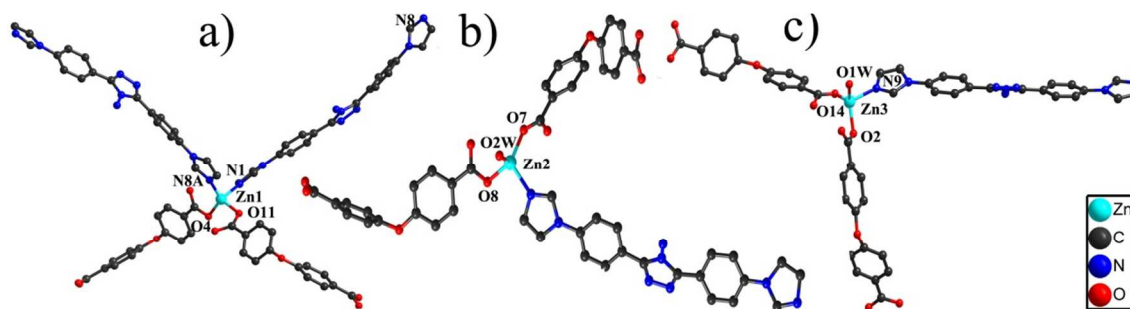

Fig. 1 a), b), c) The coordination environment of Zn1, Zn2, Zn3. symmetry code: A: -0.5-x, 0.5+y, 0.5+z.
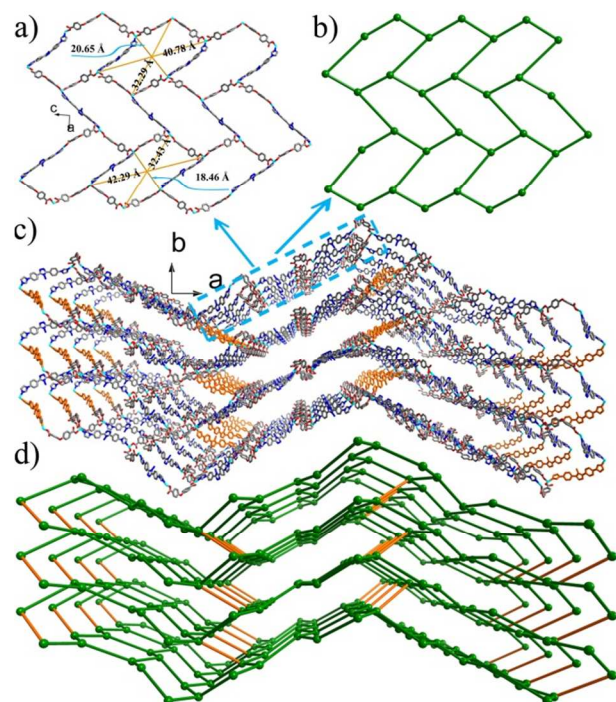
Fig. 2 a), b) The crimpled 2D (6,3) layer; c), d) The single 3D framework where the linkers between two adjacent crimpled 2D (6,3) layers have been highlighted as orange; All the hydrogen atoms and water molecules have been omitted for clarity.

In compound **1**, two **L** and four oba coordinated with six Zn(II) ions to form a hexagonal grid. Because the existence of the conformers of the ligands, two different hexagonal grids coexist, and the dimensions of the longest diagonal of the hexagonal grids are 20.65 Å, 32.29 Å, 40.78 Å and 18.46 Å, 32,43 Å, 42.29 Å, respectively (Fig. 2a). Further, these two hexagonal grids act as "brick" to form a crimpled 2D (6,3) layer (Fig. 2b). Then two adjacent crimpled 2D (6,3) layers are connected by ligand **L** to form a 3D framework (Fig. 2c). From a topological viewpoint, it is interesting that this 3D framework can be described as a novel (3,3,4)-connected topology which has not been reported in the literatures (Fig. 2d). Topological analysis was performed by using Topos[28] and Systre[29] programs. The analysis reveals that the 3D framework features a 3-nodal topological structure through assigning Zn(II) ions as nodes, and the **L** ligand and oba ligand as the linkers (Fig. S5, ESI†). According to the determined crystal structure, each Zn1 atom can be defined as a 4-connected node, each Zn2 can be defined as a 3-connected node, Likewise, each Zn3 atom can be defined as a 3-coonected node, too. Thus, the 3D framework represents a (3,3,4)-connected topology. The vertex symbols for the Zn1 node, Zn2 node, Zn3 node are $\{6^5 \cdot 8\}$, $\{6^3\}$ and $\{6^3\}$, respectively, and the molar ratio of the Zn nodes is 1:1:1; thus, the point symbol for this (3,3,4)-connected net is $(6^3)_2(6^5 \cdot 8)$.

Another remarkable feature of this 3D framework is the coexistence of two types of helices and four types of *pseudo*-helical chains[30] which is rare in the coordination polymers and only one example containing peculiar six kinds of helices have

been characterized to date.[19h] And interestingly, the conformation of the ligand plays vital role on the formation of the helices. In compound **1**, the first and the second type of helices are composed of oba[3] and Zn2 with a pitch of 24.863(5) Å along a 2_1 screw axis in the [0 0 1] direction, which have opposite configuration (left-handed, code A^L and right-handed, code A^R) (Fig. 3a, b, S6, ESI†).[19j] As described in the literatures, the V-shape of the ligand is responsible for the formation of helices. However, when different V-shaped ligands are used in the same structure, it is possible to form *pseudo*-helical chains. The first and the second type of *pseudo*-helical chains both running along the [0 0 1] direction with identic pitch of 24.863(5) Å based on the Zn3(Zn1)•••Zn3(Zn1) separation have opposite configuration (left- and right- handed, code B^L and B^R), too (Fig. 3c, d, S6, ESI†). They are generated from oba[1], oba[2] and Zn1, Zn3 where oba[1] and oba[2] are connected by Zn1 and Zn3 alternately. The third and the fourth type of *pseudo*-helical chains both running along the [0 1 0] direction with identic pitch of 18.998(5) Å based on the Zn3(Zn1)•••Zn3(Zn1) separation have opposite configuration (left- and right- handed, code C^L and C^R), which are built from $\mathbf{L}^2$, oba[1] and oba[3] with Zn1 and Zn3 where two $\mathbf{L}^2$ are bridge by Zn1 and oba[1] bridges oba[3] through Zn3 while **L** and oba are bridged by Zn1 (Fig. 3e, f, S7, ESI†). Quite intriguingly, The B^L and B^R type of *pseudo*-helical chains as well as the A^L and A^R type of helices are both constructed by oba ligands and Zn(II) ions in the same direction with the same pitch, while the different conformers of oba bring different structures. From this point of view, we can conclude that the B^L and B^R type of *pseudo*-helical chains as well as the A^L and A^R type of helices are two pairs of enantiomers, and the B^L type of *pseudo*-helical chain and the A^L type of helix as well as the A^R type of *pseudo*-helical chain and the B^R type of helix are two pairs of conformational isomers. To the best of our knowledge, MOFs or coordination polymers show *pseudo*-helical chains of conformational isomers and enantiomers in the same framework has not been reported. The usage of conformation flexible bent ligand is crucial to form *pseudo*-helical chains of conformational isomers, because the conformational isomers of the ligand can transfer their conformation to the whole helical or *pseudo*-helical chain.
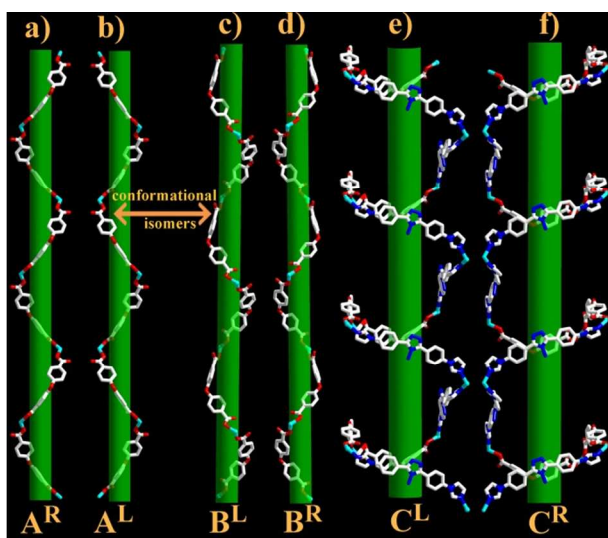
Fig. 3 a), b) The right-handed helical chain (Code A^R) and the left-handed helical chain (code A^L) formed by oba^3 and Zn2; c), d) A pair of enantiomeric *pseudo*-helical chains (code B^L and B^R) formed by oba^1, oba^2 and Zn1, Zn3; e), f) A pair of *pseudo*-helical chains (Code C^L and C^R) as enantiomers formed by L^2, oba^1, oba^3 and Zn1, Zn3; The A^L helical chain and B^L *pseudo*-helical chain as well as A^R helical chain and B^R *pseudo*-helical chain are two pairs of conformational isomers.

In the single 3D framework, the big windows formed by the big hexagonal grids provide large enough vacancies to allow the inclusion of another identical 3D motifs (Fig. 4a), and the wavelike (6,3) layers can be organized together in interpenetration or/and catenation mode in the literatures.[9c] Finally, the ligand **L** which connects the adjacent wavelike (6,3) layers is long enough to pass through multiple hexagonal grids, thus creating multi-interpenetration. In consequence of mother nature's *horror vacui*, such a crystal structure with extra-large windows is unstable except by inclusion of suitable guests or by further interpenetration. In order to minimize large void cavities and stabilize the framework, the potential voids formed by a single 3D network show incorporation of another six identical networks, thus giving a 7-fold interpenetrated 3D network. Actually, the seven interpenetrated nets can be categorized into two subsets because of conformation of the single 3D framework. One subset is composed of the three nets (pink, dark yellow, red) (Fig. 4b), another subset is consist of four nets (green, blue, orchid, turquoise) (Fig. 4c), and the nets in the same subset are paralleled. Although the interpenetration in each subset has reduced the voids formed by the single 3D network, there still remain enough spaces to include more single 3D nets. As a result, the two subsets are entangled in a top-to-top fashion which results in the entanglement where the nets from different subsets are interleaved. The whole framework shows an abnormal [4 + 3] mode (Fig. 4d).
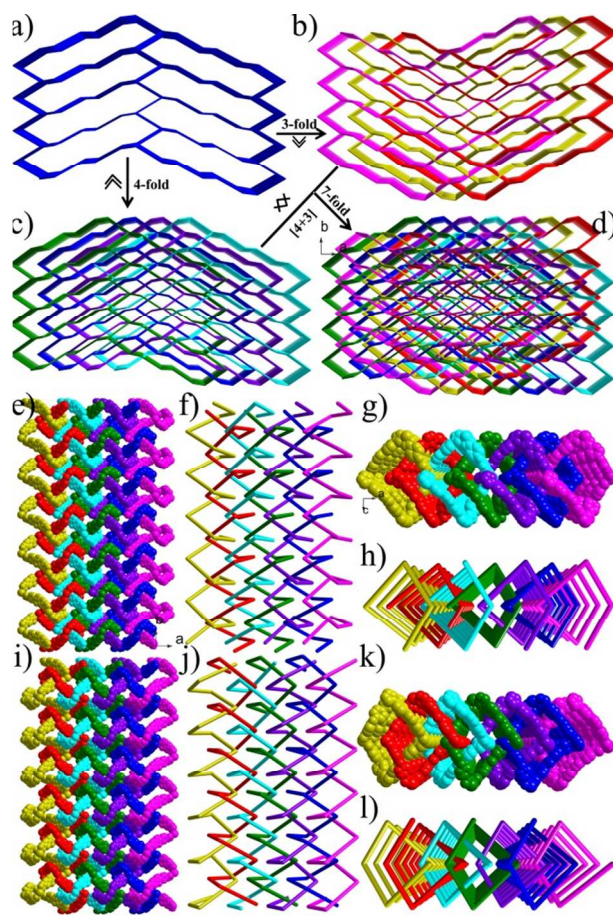

Fig. 4 a) Schematic representation of one single 3D net; b) Three single 3D nets are interpenetrated in parallel mode; c) Four single 3D nets are interpenetrated in parallel mode; d) The abnormal [4+3] 7-fold interpenetration mode; e), f), g), h) Adjacent two C^L-type *pseudo*-helical chains with the same chirality are interlocked to form a novel 7-fold interlocking *pseudo*-helical chains; i), j), k), l) Adjacent two C^R-type *pseudo*-helical chains with the same chirality are interlocked to form a novel 7-fold interlocking *pseudo*-helical chains.

Notably, Closer inspection into the nature of the intricate architecture in **1** reveals that each C^L-type *pseudo*-helical chain of a single net constructed by V-shaped ligand **L** along the [010] direction is also further intertwined with six C^L-type *pseudo*-helical chains from six other nets (all with same chirality) in a similar way to generate a 7-fold interlocking *pseudo*-helical chains (Fig. 4e-h), while each C^R-type *pseudo*-helical chain of a single net is also further interweaved with six C^R-type *pseudo*-helical chains from six other nets (all with same chirality) in a similar way to generate a 7-fold interlocking *pseudo*-helical chains, too (Fig. 4i-l). In our previous work, we have reported a 3D chiral network built from an infinite interlocked array originating from nine-fold interwoven homochiral helices where one central helix is interweaved with other eight same type of helices,[31] and a fivefold interpenetrated network with the presence of the unique racemic motifs originated from nine interwoven helices where one central helix is interweaved with eight equivalent helices appearing in pairs from four other nets, four same handedness and four opposite.[32] Other groups have also reported several similar interwoven helices.[21b, 33] But in

this work, the interwoven *pseudo*-helical chains are different from the ones above. In compound **1**, each *pseudo*-helical chain is interlocked with two adjacent *pseudo*-helical chain from two different 3D single nets in the same direction to form a novel 7-fold interlocking *pseudo*-helical chains. As far as we know, such entangled motifs originating from 7-fold interlocking *pseudo*-helical chains are still not reported in the system of metal–organic complexes.[19g]

As mentioned above, the single 3D framework can be considered as a framework formed by the adjacent wavelike (6,3) nets connected by the ligand **L**. The prominent character of (6,3) layer is the hexagonal grids which can entangle with or connect to each other through polycatenane Hopf links.[9c] In other word, In this compound **1**, the existence of catenane-like motifs is inevitable because of the (6,3) layer and the abnormal [4 + 3] 7-fold interpenetrating mode in addition to the long rigid ligand **L**. In fact, in compound **1**, a novel polycatenane Hopf links is found. Under the [4 + 3] interpenetrated mode, the nets in the same subset are paralleled. Thus each hexagonal grid in the same subset are paralleled, too. However, the arrangement of the hexagonal grids is not in the ideal form which means in the four paralleled hexagonal grids each two paralleled hexagonal grids can be considered as a group and the two groups are parallel staggered. But in the three paralleled hexagonal grids, two paralleled hexagonal grids can be considered as a group, one hexagonal grid is left as a single component (Fig. 5a). As a consequence, the group in the three paralleled hexagonal grids catenates the two groups in the four paralleled hexagonal grids which means two paralleled hexagonal grids in the three paralleled hexagonal grids catenates all the four paralleled hexagonal grids in the four paralleled hexagonal grids, and the left single hexagonal grid in the three paralleled hexagonal grids catenates one group of two paralleled hexagonal grids in the four paralleled hexagonal grids (Fig. 5b). All the hexagonal grids are catenated by Hopf links (Fig. 5c). As far as we know, this kind of catenane-like motif has never been reported in the literatures and may bring a fresh feature into the entangled motifs of polycatenation.[34]
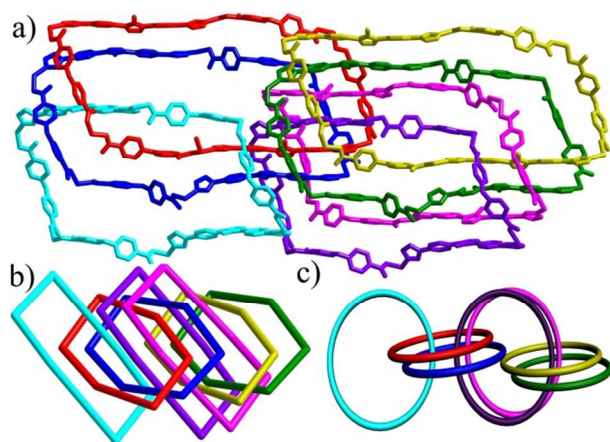

Fig. 5 a) The exceptional catenane-like motifs are catenated through a novel polycatenane Hopf links in **1**; b), c) Schematic representation of the polycatenane characters in **1**.

luminescent properties

Luminescent compounds are of great current interest because of their various applications in chemical sensors, photochemistry and electroluminescent displays.[4, 8b] The luminescent properties of zinc carboxylate compounds have been widely investigated in the field of coordination polymers or MOFs.[35] The solid-state luminescence of **1** was investigated at room temperature. Compound **1** shows an intense emission at 405 nm (λ_{ex} = 330 nm) while one weak emission at 402 nm could be observed for free 4-animo-3,5-bis(4-imidazol-1-ylphenyl)-1,2,4-triazole (**L**), too (Fig. 6, S8, ESI†). In addition, experimental studies have shown that the solid H_2oba ligand is nearly nonfluorescent in the range 400–800 nm at ambient temperature. Therefore, the emission of **1** may be ascribed to the $\pi^* \rightarrow \pi$ transitions of the **L** ligand because the similar peak appears for the free L ligand. In **1**, **L** ligand coordination to the metal center may effectively increase the rigidity and asymmetry of the ligand and reduce the loss of energy by radiationless decay, which is beneficial for the luminescence. These observations indicate that compound **1** may be an excellent candidate for potential photoactive materials.
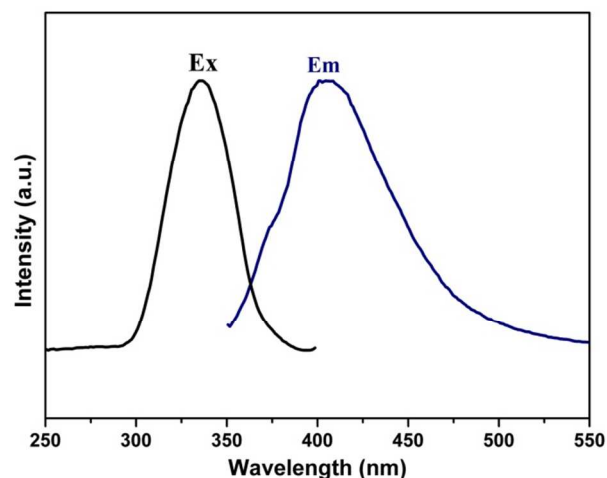

Fig. 6 Photoluminescent spectra of **1** in solid state at room temperature.

Conclusions

In summary, a novel 7-fold interpenetrated metal-organic framework has been successfully synthesized under hydrothermal conditions. In the structure of **1**, the rigid V-shaped ligand **L** and the flexible ligand oba link Zn(II) to form a 3D framework with a new $(6^3)_2(6^5 \cdot 8)$ topology. Another remarkable feature of this 3D framework is the coexistence of two types of helices and four types of *pseudo*-helical chains which contain three pairs of enantiomers and two pairs of conformational isomers. The big windows formed by the

hexagonal grids in the wavelike (6,3) layer as well as the long rigid ligand **L** make the single 3D network incorporation of another six identical networks, thus giving a 7-fold interpenetrated 3D network in an abnormal [4 + 3] mode. Under this interpenetration mode, entangled motifs originating from 7-fold interlocking *pseudo*-helical chains (all with same chirality) are found. Meanwhile, an unique catenane-like motif with Hopf links is reported in the first time. More and more work about construction new types of MOFs with various motifs based on the bent ligands is ongoing.

Acknowledgements

Notes and references

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1 (a) H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**; (b) H.-C. Zhou, J. R. Long and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 673.

2 (a) M. P. Suh, H. J. Park, T. K. Prasad and D.-W. Lim, *Chem. Rev.*, 2011, **112**, 782; (b) R. B. Getman, Y.-S. Bae, C. E. Wilmer and R. Q. Snurr, *Chem. Rev.*, 2011, **112**, 703; (c) J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2011, **112**, 869; (d) H. Wu, Q. Gong, D. H. Olson and J. Li, *Chem. Rev.*, 2012, **112**, 836; (e) Y. He, W. Zhou, G. Qian and B. Chen, *Chem. Soc. Rev.*, 2014, **43**, 5657.

3 W. Zhang and R.-G. Xiong, *Chem. Rev.*, 2011, **112**, 1163.

4 Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2011, **112**, 1126.

5 C. Wang, T. Zhang and W. Lin, *Chem. Rev.*, 2011, **112**, 1084.

6 P. Horcajada, R. Gref, T. Baati, P. K. Allan, G. Maurin, P. Couvreur, G. Férey, R. E. Morris and C. Serre, *Chem. Rev.*, 2011, **112**, 1232.

7 (a) A. Corma, H. Garcia and F. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606; (b) M. Yoon, R. Srirambalaji and K. Kim, *Chem. Rev.*, 2011, **112**, 1196; (c) J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011.

8 (a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. Van Duyne and J. T. Hupp, *Chem. Rev.*, 2011, **112**, 1105; (b) Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815.

9 (a) S. R. Batten and R. Robson, *Angew. Chem. Int. Ed.*, 1998, **37**, 1460; (b) L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247; (c) L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2003, **5**, 269; (d) S. R. Batten, *CrystEngComm*, 2001, **3**, 67; (e) L. Carlucci, G. Ciani, D. M. Proserpio, T. G. Mitina and V. A. Blatov, *Chem. Rev.*, 2014, **114**, 7557; (f) V. A. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 378; (g) T. Gadzikwa, B.-S. Zeng, J. T. Hupp and S. T. Nguyen, *Chem. Commun.*, 2008, 3672; (h) A. F. Wells, *Three-dimensional nets and polyhedra*, Wiley, New York, 1977; (i) O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705; (j) J. Yang, J.-F. Ma and S. R. Batten, *Chem. Commun.*, 2012, **48**, 7899.

10 (a) H. Wu, J. Yang, Z.-M. Su, S. R. Batten and J.-F. Ma, *J. Am. Chem. Soc.*, 2011, **133**, 11406; (b) S.-Y. Zhang, Z. Zhang and M. J. Zaworotko, *Chem. Commun.*, 2013, **49**, 9700; (c) H.-L. Jiang, T. A. Makal and H.-C. Zhou, *Coord. Chem. Rev.*, 2013, **257**, 2232.

11 H. Y. Lee, J. Park, M. S. Lah and J.-I. Hong, *Crystal Growth & Design*, 2008, **8**, 587.

12 S.-L. Li, K. Tan, Y.-Q. Lan, J.-S. Qin, M.-N. Li, D.-Y. Du and Z.-M. Su, *CrystEngComm*, 2011, **13**, 4945.

13 (a) H. Kim and M. P. Suh, *Inorg. Chem.*, 2005, **44**, 810; (b) Q. Yue, X.-B. Qian, L. Yan and E.-Q. Gao, *Inorg. Chem. Commun.*, 2008, **11**, 1067; (c) J. He, Y.-G. Yin, T. Wu, D. Li and X.-C. Huang, *Chem. Commun.*, 2006, 2845; (d) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *Chemistry – A European Journal*, 2002, **8**, 1519.

14 Y.-F. Hsu, C.-H. Lin, J.-D. Chen and J.-C. Wang, *Crystal Growth & Design*, 2008, **8**, 1094.

15 X.-L. Wang, C. Qin, S.-X. Wu, K.-Z. Shao, Y.-Q. Lan, S. Wang, D.-X. Zhu, Z.-M. Su and E.-B. Wang, *Angew. Chem.*, 2009, **121**, 5395.

16 (a) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; (b) C. Schmuck, *Angew. Chem. Int. Ed.*, 2003, **42**, 2448; (c) D.-R. Xiao, Y.-G. Li, E.-B. Wang, L.-L. Fan, H.-Y. An, Z.-M. Su and L. Xu, *Inorg. Chem.*, 2007, **46**, 4158.

17 (a) M. Albrecht, *Chem. Rev.*, 2001, **101**, 3457; (b) M. Albrecht, *Angew. Chem. Int. Ed.*, 2005, **44**, 6448.

18 V. Berl, I. Huc, R. G. Khoury, M. J. Krische and J.-M. Lehn, *Nature*, 2000, **407**, 720.

19 (a) X.-J. Luan, Y.-Y. Wang, D.-S. Li, P. Liu, H.-M. Hu, Q.-Z. Shi and S.-M. Peng, *Angew. Chem. Int. Ed.*, 2005, **44**, 3864; (b) Y.-Q. Sun, J. Zhang, Y.-M. Chen and G.-Y. Yang, *Angew. Chem. Int. Ed.*, 2005, **44**, 5814; (c) C.-D. Wu and W. Lin, *Angew. Chem. Int. Ed.*, 2005, **44**, 1958; (d) X.-R. Hao, X.-L. Wang, C. Qin, Z.-M. Su, E.-B. Wang, Y.-Q. Lan and K.-Z. Shao, *Chem. Commun.*, 2007, 4620; (e) S.-N. Wang, H. Xing, Y.-Z. Li, J. Bai, M. Scheer, Y. Pan and X.-Z. You, *Chem. Commun.*, 2007, 2293; (f) S. Zang, Y. Su, C. Duan, Y. Li, H. Zhu and Q. Meng, *Chem. Commun.*, 2006, 4997; (g) J. He, H. Chen, D. Xiao, D. Sun, G. Zhang, S. Yan, G. Xin, R. Yuan and E. Wang, *CrystEngComm*, 2011, **13**, 4841; (h) M.-D. Zhang, C.-M. Di, L. Qin, Q.-X. Yang, Y.-Z. Li, Z.-J. Guo and H.-G. Zheng, *CrystEngComm*, 2013, **15**, 227; (i) L. Han, H. Valle and X. Bu, *Inorg. Chem.*, 2007, **46**, 1511; (j) F. Luo, J. Zou, Y. Ning, Y. Wang, X.-F. Feng, G.-l. Yan, F.-s. Wei, W.-w. Luo, W.-y. Xu and G.-l. Huang, *CrystEngComm*, 2011, **13**, 421.

20 W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle Iii, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev.*, 2014, **43**, 5561.

21 (a) O.-S. Jung, Y. J. Kim, Y.-A. Lee, J. K. Park and H. K. Chae, *J. Am. Chem. Soc.*, 2000, **122**, 9921; (b) Y. Cui, S. J. Lee and W. Lin, *J. Am. Chem. Soc.*, 2003, **125**, 6014; (c) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.

22 B.-Q. Song, X.-L. Wang, G.-S. Yang, H.-N. Wang, J. Liang, K.-Z. Shao and Z.-M. Su, *CrystEngComm*, 2014, **16**, 6882.

23 (a) S.-S. Chen, Z.-S. Bai, J. Fan, G.-C. Lv, Z. Su, M.-S. Chen and W.-Y. Sun, *CrystEngComm*, 2010, **12**, 3091; (b) X. Wang, J. Luan, H. Lin, C. Xu, G. Liu, J. Zhang and A. Tian, *CrystEngComm*, 2013, **15**, 9995; (c) R. Singh and P. K. Bharadwaj, *Crystal Growth & Design*, 2013, **13**, 3722; (d) B.-Q. Song, X.-L. Wang, J. Liang, Y.-T. Zhang, K.-Z. Shao and Z.-M. Su, *CrystEngComm*, 2014, **16**, 9163.

24 Z.-J. Lin, J. Lu, M. Hong and R. Cao, *Chem. Soc. Rev.*, 2014, **43**, 5867.

25 A. Aijaz, P. Lama and P. K. Bharadwaj, *Inorg. Chem.*, 2010, **49**, 5883.

26 G. M. Sheldrick, *SHELXS-97: Program for X-ray crystal structure solution;*, University of Göttingen: Göttingen, Germany, 1997.

27 G. M. Sheldrick, *SHELXL-97: Program for X-ray Crystal Structure Refinement;* , University of Göttingen: Göttingen, Germany, 1997.

28 V. A. Blatov, A. P. Shevchenko and V. N. Serenzhkin, *Acta Crystallographica Section A*, 1995, **51**, 909.

29 O. Delgado-Friedrichs and M. O'Keeffe, *Acta Crystallographica Section A*, 2003, **59**, 351.

30 (a) C.-Y. Su, X.-P. Yang, B.-S. Kang, K.-B. Yu, Y.-X. Tong and T. C.-W. Mak, *Bull. Chem. Soc. Jpn.*, 1999, **72**, 2217; (b) W.-X. Ni, M. Li, X.-P. Zhou, Z. Li, X.-C. Huang and D. Li, *Chem. Commun.*, 2007, 3479; (c) Z.-X. Li, X. Chu, G.-H. Cui, Y. Liu, L. Li and G.-L. Xue, *CrystEngComm*, 2011, **13**, 1984.

31 X.-L. Wang, C. Qin, E.-B. Wang, L. Xu, Z.-M. Su and C.-W. Hu, *Angew. Chem.*, 2004, **116**, 5146.

32 X.-L. Wang, C. Qin, E.-B. Wang, Y.-G. Li and Z.-M. Su, *Chem. Commun.*, 2005, 5450.

33 G.-Q. Kong, S. Ou, C. Zou and C.-D. Wu, *J. Am. Chem. Soc.*, 2012, **134**, 19851.

34 (a) Y. Pei, R. Pal, C. Liu, Y. Gao, Z. Zhang and X. C. Zeng, *J. Am. Chem. Soc.*, 2012, **134**, 3015; (b) J.-Q. Liu, Y.-Y. Wang, L.-F. Ma, G.-L. Wen, Q.-Z. Shi, S. R. Batten and D. M. Proserpio, *CrystEngComm*, 2008, **10**, 1123; (c) F. B. L. Cougnon, N. A. Jenkins, G. D. Pantoş and J. K. M. Sanders, *Angew. Chem.*, 2012, **124**, 1472; (d) L. Fang, C. Wang, A. C. Fahrenbach, A. Trabolsi, Y. Y. Botros and J. F. Stoddart, *Angew. Chem. Int. Ed.*, 2011, **50**, 1805.

35 S. L. Zheng and X. M. Chen, *Aust. J. Chem.*, 2004, **57**, 703.