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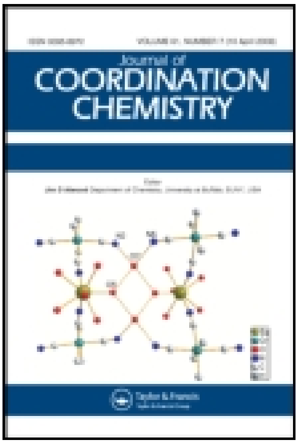

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A new luminescent 3-D metal-organic framework of diamond-like network possessing 8-fold interpenetration

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A new luminescent 3-D metal-organic framework of diamond-like network possessing 8-fold interpenetration

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A new 3-D coordination polymer [Zn(L)$_2$] (**1**) (HL = 4-(pyridin-4-ylmethoxy)benzolic acid) was synthesized under hydrothermal conditions with $Zn(OAc)_2 \cdot 2H_2O$ and HL and characterized by single crystal X-ray diffraction (XRD). Compound **1** displays a 3-D 8-fold interpenetrating structure with diamondoid framework containing large adamantanoid cages. Meanwhile, it exhibits intense fluorescence at 402 nm in the solid state. In addition, powder XRD and thermogravimetric (TG) analysis for **1** are also reported.

Keywords: Coordination polymer; 4-(Pyridin-4-ylmethoxy)benzolic acid; Crystal structure; Luminescent property

1. Introduction

Construction of metal-organic frameworks has aroused attention due to their potential applications in gas storage, nonlinear optics, catalysis and ion-exchange, and fascinating topologies and entanglement motifs [1–4]. As the most common molecular entanglement, there has been a complete analysis of all 3-D interpenetrated metal-organic framework structures contained in the Cambridge structural database (CSD) with a rationalization and classification of the topology of interpenetration [5, 6]. An intriguing variety of topologies and entanglement have been constructed and discussed in several excellent papers [7–9]. Although it is still a challenge to prepare fully predictable interpenetrated structures based on rational design, recent rapid developments in coordination and organic chemistry provide more possibilities for the creative synthesis of desired interpenetrated frameworks [10–13]. Interpenetrated structures have provided a long-standing fascination for chemists. Usually, long (length more than 7 Å) and flexible ligands are needed for the assembly of interpenetrated structures, due to their propensity to form large vacancies in coordination polymers. Large voids may

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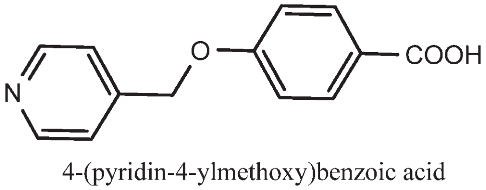

Scheme 1. Structure of 4-(pyridin-4-ylmethoxy)benzolic acid.

result in interpenetrated structures. We have designed a nitrogen-containing asymmetric bridging carboxylic acid, 4-(pyridin-4-ylmethoxy)benzolic acid (HL) [14], which could lead to an intriguing variety of architectures and topologies, due to freely twisting around the $-CH_2-$ group to meet the requirements of coordination geometries of metals, as shown in scheme 1.

The d^{10} (Zn^{II} and Cd^{II}) transition metals are excellent candidates for the formation of polynuclear complexes owing to their high photoluminescent properties and transparency in the UV region [15–17]. Long and flexible HL with Zn^{II} could result in bidentate frameworks with beautiful aesthetics and useful properties. Herein, we report the synthesis and crystal structure of $[Zn(L)_2]$ (**1**), in which L is a linear linker, Zn^{II} is a 4-connected node, and the whole structure of **1** exhibits a 3-D 8-fold interpenetrating diamondoid array typically based on a tetrahedral second building unit (SBU) at a single Zn center.

2. Experimental

All reagents and solvents employed were commercially available and used as received. L was synthesized readily by the procedure reported in "Supplementary material." Elemental analyses (C, H, and N) were performed with a Perkin Elmer 240 C elemental analyzer. PXRD patterns were collected on a Rigaku Dmax 2000 X-ray diffractometer with graphite monochromated Cu-Kα radiation ($\lambda = 1.54$ Å) and 2θ ranging from 5° to 50°. Simulation of the PXRD pattern used the CCDC program Mercury (Mercury: visualization and analysis of crystal structures) [18]. Solidstate luminescence spectra were measured on a Cary Eclipse spectrophotometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature. Thermogravimetric (TG) analysis was performed with a Perkin Elmer TG7 analyzer heated from 40°C to 700°C under nitrogen.

2.1. *Synthesis of [Zn(L)$_2$]*

A mixture of $Zn(OAc)_2 \cdot 2H_2O$ (0.054 g, 0.25 mmol), HL (0.018 g, 0.08 mmol), in H_2O (14 mL) was sealed in a 25 mL Teflon-lined stainless steel container, which was heated at 150°C for 3 days and then cooled to room temperature at a rate of $5°C\,h^{-1}$. Colorless crystals of **1** were collected and washed with distilled water and dried in air to give the product; yield, 67.7% (based on L ligands). Elemental Anal. Calcd (%) for $C_{26}H_{20}N_2O_6Zn$ (521.81): C, 59.84; H, 3.86; N, 5.37. Found: C, 59.85; H, 3.88; N 5.35%.

The simulated and experimental PXRD patterns of **1** are shown in "Supplementary material." The simulated and experimental PXRD patterns are in good agreement with each other, indicating the phase purity of the product. The differences in intensity may be due to preferred orientation of the powder samples.

2.2. *X-ray crystallographic analysis*

Data collection of **1** was performed on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. All absorption corrections were performed by using SADABS. The crystal structure was solved by direct methods and refined with full-matrix least-squares (SHELXTL-97) with atomic coordinates and anisotropic thermal parameters for all nonhydrogen atoms. Hydrogens of aromatic rings were included in the structure factor calculation at idealized positions using a riding model. The detailed crystallographic data and structure refinement parameters for **1** are summarized in table 1. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Description of structure*

Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the orthorhombic space group *Aba*2 and the asymmetric unit of **1** contains half of a Zn^{II} and one L; the Zn^{II} resides on the inversion center in the unit cell. Each Zn^{II} is coordinated by four carboxylate oxygens from two L^- and two nitrogens from two L^- in a distorted tetrahedral coordination geometry, as shown in figure 1. The Zn–O (Zn–O3A 2.417(3) Å, Zn–O4A 2.017(2) Å), and Zn–N (Zn–N7 2.067(3) Å, Zn–N7C 2.067(3) Å) bond distances are in the normal ranges [19–22]. Meanwhile, each Zn^{II} is attached to four L^-, which can be considered as a 4-connected node, each L^- connects to two Zn^{II}, thus, L can be considered as a linear linker. All L^- possess the same coordination mode. The topological analysis of **1** reveals that it is a typically diamondoid framework containing large adamantanoid cages with the topology "Schläfli" symbol (6^6). Figure 2 also exhibits a single cage with four cyclohexane-like windows in chair conformation. The adamantanoid cages are extended significantly in one direction and exhibit maximum dimensions (corresponding to the longest intracage Zn $\cdots$ Zn distances) of $27.08 \times 28.45 \times 33.39$ Å. The void space in an individual framework is so large that eight identical 3-D diamondoid frameworks can interpenetrate to form an intriguing 8-fold interpenetration (figure 3). Interpenetrating diamondoid array structures are often encountered [23, 24], but 8-fold interpenetrating structure with diamondoid framework is still rare [25–29]. This coordination has been observed in several polymeric complexes with a related flexible ligand (e.g., 4,4′-(ethane-1,2-diyl)dibenzoic acid), which results in a 8-fold interpenetrating structure through strong hydrogen bonds [30], but we are not aware of any coordination polymers with a ligand like that found in **1**. Furthermore, adjacent entangled diamondoid frameworks possessing weak π–π interactions [31, 32] occur between pyridine and aromatic rings (parallel stacking with centroid–centroid distances of 3.501 Å and 3.464 Å). Significant π–π and C–H $\cdots$ π

Table 1. Crystal data and structure refinements for **1**.

Complex	**1**
Formula	$C_{26}H_{20}N_2O_6Zn$
Formula weight	521.81
Crystal system	Orthorhombic
Space group	*Aba2*
Unit cell dimensions (Å, °)	
a	13.578(1)
b	21.049(3)
c	8.517(2)
α	90(5)
β	90(5)
γ	90(5)
Volume (Å^3), Z	2434.2(18), 4
Calculated density (Mg m^{-3})	1.424
Absorption coefficient (mm^{-1})	1.053
$F(000)$	1072
Observed reflection/unique	5892/2085
R_{int}	0.0376
Goodness-of-fit on F^2	1.004
$R_1{}^a$, $wR_2{}^b$ $[I > 2\sigma(I)]$	0.0357, 0.0993
R_1, wR_2 (all data)	0.0467, 0.1059

$^aR_1 = \sum||F_o|-|F_c||/\sum|F_o|$; $^bwR_2 = |\sum w(|F_o|^2-|F_c|^2)|/\sum|w(F_o{}^2)^2|^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Complex **1**			
Zn(1)–O(4)	2.018(3)	Zn(1)–N(7)	2.067(3)
Zn(1)–O(3)	2.417(4)	O(4)A–Zn(1)–O(4)B	140.5(2)
O(4)B–Zn(1)–N(7)	110.038(12)	O(4)A–Zn(1)–N(7)	95.68(13)
N(7)–Zn(1)–N(7)	98.4(2)	O(4)B–Zn(1)–O(3)B	57.32(12)
O(4)A–Zn(1)–O(3)	96.16(14)	N(7)–Zn(1)–O(3)B	87.14(15)
N(7)–Zn(1)–O(3)A	152.39(13)	O(3)A–Zn(1)–O(3)B	100.4(2)

Symmetry transformations used to generate equivalent atoms: A, $2.5-x$, $0.5+y$, $-1-z$; B, $-0.5+x$, $1.5-y$, $-1+z$.

(edge-to-face separation 3.525 Å) supramolecular interactions between the aromatic rings contained in this structure stabilize the structure adopted.

A few crystal structures have been observed for systems of low interpenetrated degree. Short ligand (e.g., isonicotinic acid) gives a 2-fold interpenetrating structure [33], while the long ligand provides large adamantanoid cages. Thus, **1** exhibits a 3-D 8-fold interpenetrating framework with "Schläfli" symbols (6^6) and containing large adamantanoid cages based on the diamondoid topology.

3.2. *Thermal properties*

TG analysis of **1** was carried out under N_2 from 40°C to 700°C with a heating rate of 10°C min^{-1} (Supplemental material). The TG curve of **1** shows that the

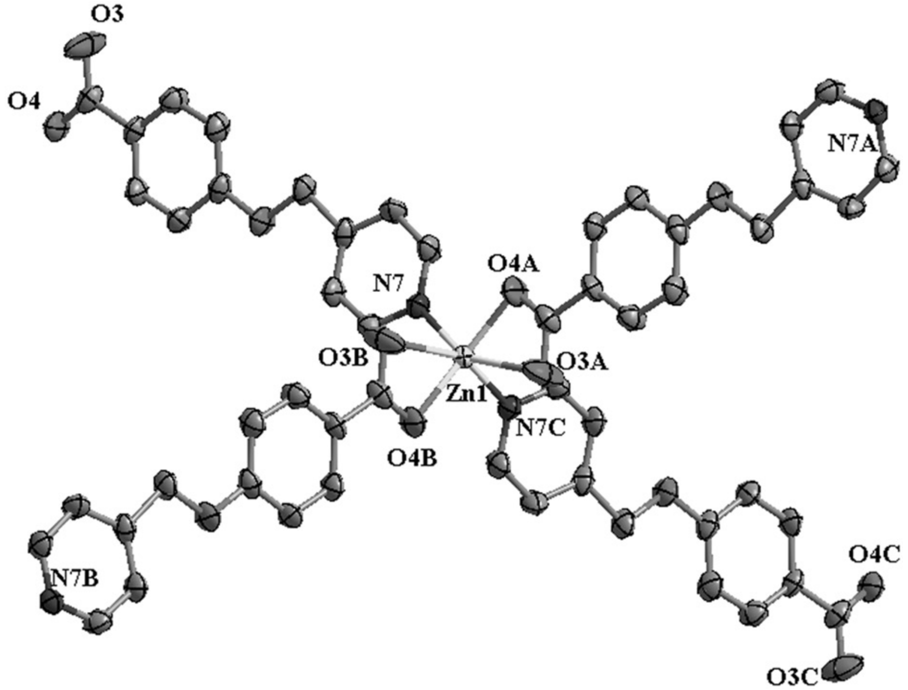

Figure 1. Coordination environment of Zn^{II} in **1** with ellipsoids drawn at the 30% probability level; hydrogens were omitted for clarity. (Symmetry transformations used to generate equivalent atoms: A, $2.5-x$, $0.5+y$, $-1-z$; B, $-0.5+x$, $1.5-y$, $-1+z$; C, $2-x$, $2-y$, z).

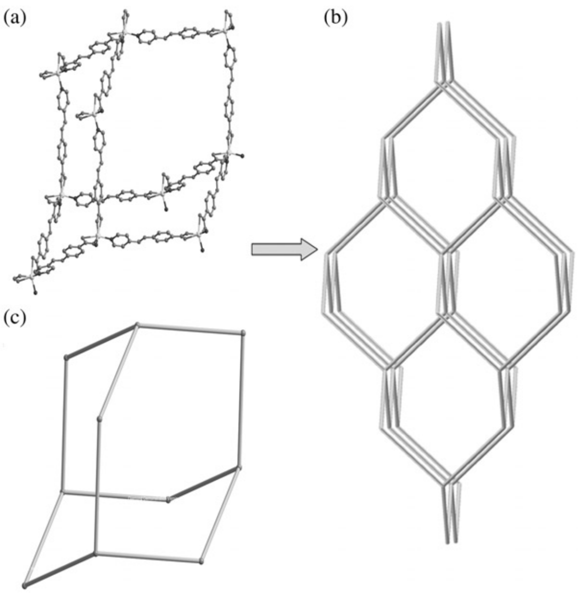

Figure 2. Single adamantanoid cages (left) and a schematic view of a single diamond-like framework (right).

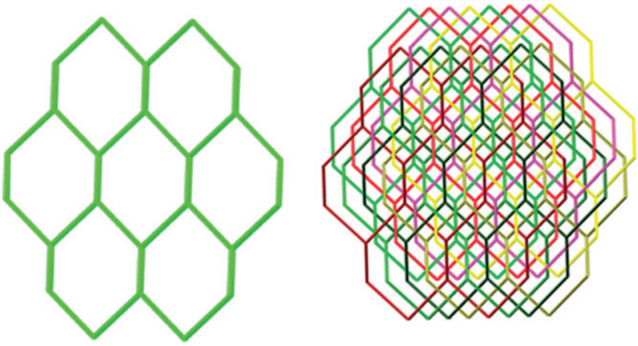

Figure 3. Schematic description of the 8-fold interpenetrating architecture of **1**.

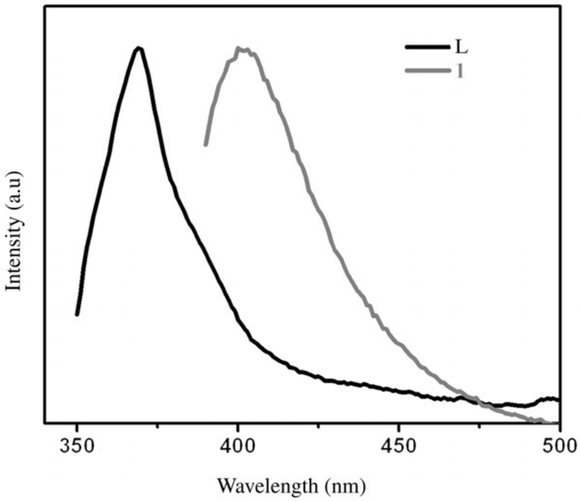

Figure 4. Emission spectra of **1** and HL in the solid state at room temperature.

framework collapsed at 320–500°C, corresponding to release of organic components. The remaining weight of 15.55% corresponds to the percentage (Calcd 15.54%) of Zn and O components, indicating that the final product may be ZnO.

3.3. *Luminescent properties*

The photoluminescent properties of **1** and HL were examined in the solid state at room temperature. As shown in figure 4, the main emission peak of HL is at 370 nm ($\lambda_{ex} = 328$ nm), which can be assigned to $\pi^* \rightarrow n$ and $\pi^* \rightarrow \pi$ transitions of the ligands. Compound **1** shows emission maxima at 402 nm ($\lambda_{ex} = 344$ nm). In comparison with that of the free ligand, the maximum emission wavelength of **1** is slightly red-shifted, probably due to intraligand charge transitions [34, 35].

4. Conclusion

By selecting a flexible ligand, we have hydrothermally synthesized a 3-D 8-fold interpenetrating diamondoid array coordination polymer containing large adamantanoid cages. Compound **1** exhibits intense fluorescence at 402 nm in the solid state and may be a good candidate for fluorescent material.

Supplementary material

CCDC 776048 contains the supplementary crystallographic data for this article. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] C.W. Jones, K. Tsuji, M.E. Davis. *Nature*, **52**, 393 (1998).
[2] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 705 (2003).
[3] S.R. Batten, R. Robson. *Angew. Chem., Int. Ed.*, **37**, 1460 (1998).
[4] X.L. Wang, C. Qin, E.B. Wang, L. Xu, Z.M. Su, C.W. Hu. *Angew. Chem., Int. Ed.*, **43**, 5036 (2004).
[5] X.L. Wang, C. Qin, E.B. Wang, Y.G. Li, Z.M. Su, L. Xu, L. Carlucci. *Angew. Chem., Int. Ed.*, **44**, 5824 (2005).
[6] V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio. *CrystEngComm*, **6**, 377 (2004).
[7] L. Carlucci, G. Ciani, D.M. Proserpio. *Angew. Chem., Int. Ed.*, **38**, 3488 (1999).
[8] L. Carlucci, G. Ciani, P. Macchi, D.M. Proserpio. *Chem. Commun.*, 1837 (1998).
[9] I.A. Baburin, V.A. Blatov, L. Carlucci, G. Ciani, D.M. Proserpio. *J. Solid State Chem.*, **178**, 2452 (2005).
[10] L. Brammer. *Chem. Soc. Rev.*, **33**, 476 (2004).
[11] B.J. Holliday, C.A. Mirkin. *Angew. Chem., Int. Ed.*, **40**, 2022 (2001).
[12] M.W. Hosseini. *Acc. Chem. Res.*, **38**, 313 (2005).
[13] G.J. Xu, Y.H. Zhao, K.Z. Shao, G. Yuan, Z.M. Su, L.K. Yan. *Inorg. Chem. Commun.*, **12**, 969 (2009).
[14] G.J. Xu, Y.H. Zhao, K.Z. Shao, Y.Q. Lan, X.L. Wang, Z.M. Su, L.K. Yan. *CrystEngComm*, **11**, 1842 (2009).
[15] E.C. Yang, H.K. Zhao, B. Ding, X.G. Wang, X.J. Zhao. *Cryst. Growth Des.*, **7**, 2009 (2007).
[16] L.Y. Zhang, J.P. Zhang, Y.Y. Lin, X.M. Chen. *Cryst. Growth Des.*, **6**, 1684 (2006).
[17] G.J. Xu, Y.H. Zhao, K.Z. Shao, G.S. Yang, Y.Q. Lan, Z.M. Su, L.K. Yan. *Polyhedron*, **28**, 3155 (2009).

[18] C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Streek. *J. Appl. Cryst*., **39**, 453 (2006).
[19] A.J. Carty, N.J. Taylor. *Inorg. Chem*., **16**, 177 (1977).
[20] J.C. Dai, X.T. Wu, Z.Y. Fu, C.P. Cui, S.M. Hu, W.X. Du, L.M. Wu, H.H. Zhang, R.Q. Sun. *Inorg. Chem*., **41**, 1391 (2002).
[21] R. Wang, M. Hong, J. Luo, R. Cao, J. Weng. *Chem. Commun*., 1018 (2003).
[22] K.Z. Shao, Y.H. Zhao, Y. Xing, Y.Q. Lan, X.L. Wang, Z.M. Su. *Cryst. Growth Des*., **8**, 2986 (2008).
[23] S.R. Batten, A.R. Harris, P. Jensen, K.S. Murray, A. Ziebell. *Dalton Trans*., 3829 (2000).
[24] H.X. Yang, G.L. Li, B. Xua, T.F. Liu, Y.F. Li, R. Cao, S.R. Batten. *Inorg. Chem. Commun*., **12**, 605 (2009).
[25] X.S. Wang, H. Zhao, Z.R. Qu, Q. Ye, J. Zhang, R.G. Xiong, X.Z. You, H.K. Fun. *Inorg. Chem*., **42**, 5786 (2003).
[26] L. Carlucci, G. Ciani, P. Macchi, D.M. Proserpio, S. Rizzato. *Chem. Eur. J*., **5**, 237 (1999).
[27] R.G. Xiong, J.L. Zuo, X.Z. You, B.F. Abrahams, Z.P. Bai, C.M. Che, H.K. Fun. *Chem. Commun*., 2061 (2000).
[28] W. Lin, L. Ma, O.R. Evans. *Chem. Commun*., 2263 (2000).
[29] F. Hohn, I. Pantenburg, U. Ruschewitz. *Chem. Eur. J*., **8**, 4536 (2002).
[30] Q. Yue, X.B. Qian, L. Yan, E.Q. Gao. *Inorg. Chem. Commun*., **11**, 1067 (2008).
[31] C. Janiak. *J. Chem. Soc., Dalton Trans*., 3885 (2000).
[32] E. D'Oria, J.J. Novoa. *CrystEngComm*, **6**, 377 (2004).
[33] Y.P. Wu, D.S. Li, F. Fu, L. Tang, J.J. Wang, X.G. Yang. *J. Coord. Chem*., **62**, 2665 (2009).
[34] L.Y. Zhang, J.P. Zhang, Y.Y. Lin, X.M. Chen. *Cryst. Growth Des*., **6**, 1685 (2006).
[35] Q. Chu, G.X. Liu, Y.Q. Huang, X.F. Wang, W.Y. Sun. *Dalton Trans*., 4302 (2007).