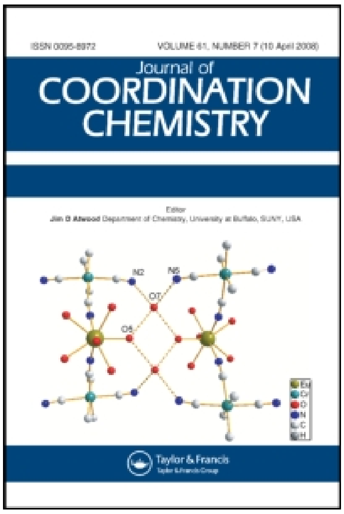

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Hydrothermal synthesis, crystal structure and fluorescence of a 3D organic-inorganic hybrid coordination network [Cu^I(4,4'-bipy)]$_4$[<i>δ</i>-Mo_8O_{26}] exhibiting an interesting polymorphism

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Hydrothermal synthesis, crystal structure and fluorescence of a 3D organic–inorganic hybrid coordination network $[Cu^{I}(4,4'\text{-bipy})]_4[\delta\text{-}Mo_8O_{26}]$ exhibiting an interesting polymorphism

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A new three-dimensional (3D) extended solid $[Cu^{I}(4,4'\text{-bipy})]_4[\delta\text{-}Mo_8O_{26}]$ (**1**) built on $\{Cu(4,4'\text{-bipy})\}^+$ (bipy = bipyridine) and isopolymolybdate anion $[\delta\text{-}Mo_8O_{26}]^{4-}$ has been synthesized and characterized by elemental analysis, IR, TG, X-ray powder diffraction and single-crystal X-ray diffraction analysis. Compound **1** shows six coppers bonded to $[\delta\text{-}Mo_8O_{26}]^{4-}$ to form inorganic planes which are linked by 4,4′-bipy into a 3D network, the first example of $[\delta\text{-}Mo_8O_{26}]^{4-}$ six-connected linkage based on an organic-inorganic coordination polymer. A polymorphism of compound **1** was found which has an identical molecular formula but absolutely different structure. The influence of the synthesis conditions of **1** has been studied. Furthermore, the fluorescence of **1** is reported.

Keywords: Isopolymolybdate; Hydrothermal synthesis; Extended framework; Polymorphism; Fluorescence

1. Introduction

The design and synthesis of metal-organic coordination networks has undergone revolutionary growth since the 1990s, not only because of their intriguing structural diversity, but also because of their potential applications in catalysis, molecular adsorption, photochemistry, and electromagnetism [1]. Polyoxometalates (POMs) are large oxoanions of group VI (and more rarely group V) elements, which have been widely regarded as an important molecular building unit [2]. The current interest in crystal designing of coordination polymer frameworks is developed to integrate POMs into organic-inorganic networks, or POMs covalently linked with metal-organic units to construct the hybrid functional solid-state materials. So far, a variety of polyoxoanion-supported metal materials have been assembled [3]. Typically, they can be divided into three groups: (i) discrete POMs as counter anion or hydrogen bond bonding conventional $OH\cdots N$ and $NH\cdots O$ motifs [4], (ii) POMs as large guest molecules

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reside in metal-organic complicated networks in supramolecular host–guest chemistry [5], (iii) POMs as linkage metal ions or lanthanide complexes to form 1D chain (a), 2D plane (b), or 3D inorganic frame (c) in which organic chains act as linker or decoration [6]. However, structures of type (iii) b and (iii) c are still not explored sufficiently. It remains a challenge to find suitable POMs units and then link them into larger clusters, or to multi-dimensional extended solid framework materials in appropriate ways.

The chemistry of molybdenum polyoxoanions has been an attractive field due to the stoichiometric and structural complexity. Isopolymolybdate is a large group and represents an important class of beautiful topology. Combining hydrothermal techniques with the structure-directing properties of organic components provides a strategy for isolation of organic-inorganic isopolymolybdates that possess useful optical and mechanical properties. Zubieta *et al.* have described organically templated molybdenum oxides [7], which organic materials exert a significant structural role in controlling the architecture of the inorganic oxide and provide a variety of novel molybdenum oxides $[\{Cu(4,4'\text{-bipy})\}_4Mo_{15}O_{47}]$, $[Cu(4,4'\text{-bipyridylamine})_{0.5}MoO_4]$, $[\{Cu_2(\text{triazolate})_2(H_2O)_2\}Mo_4O_{13}]$, and $[Cu\{1,2\text{-}trans\text{-}(4\text{-pyridyl})\text{ethene}\}MoO_4]$. 4,4′-bipy is a rod-like bifunctional ligand extensively employed as the rigid organic building block for the construction of multi-dimensional networks. Our synthetic strategy is to find appropriate isopolymolybdate pillars via linking Cu(4,4′-bipy) to acquire functional materials.

We report here a hybrid material obtained from the use of 4,4′-bipy ligands, copper, and isopolymolybdate cluster: $[Cu^I(4,4'\text{-bipy})]_4[\delta\text{-}Mo_8O_{26}]$ (**1**), which shows that different types of isopolymolybdate hybrid materials could be effectively assembled on the basis of the pH and the temperature.

2. Experimental

2.1. *General procedures*

All reagents were used as purchased without further purification. Elemental analyses of Mo and Cu were determined by a Leaman inductively coupled plasma (ICP) spectrometer. IR spectrum was obtained on a Nicolet 205 FT/IR spectrometer with KBr pellets in the 400–4000 cm^{-1} region. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^\circ C\,min^{-1}$. Powder X-ray diffraction was performed on a Rigaku D/MAX-3 instrument with Cu-Kα radiation in the range $2\theta = 3\text{–}90^\circ$ at 293 K. Excitation and emission spectra were obtained on a Spex FL-2T2 spectrofluorometer equipped with a 450Wxenon lamp as the excitation source.

2.2. *Synthesis of compound*

Synthesis of $[Cu^I(4,4'\text{-bipy})]_4[\delta\text{-}Mo_8O_{26}]$ (1). A mixture of Na_2MoO_4, $CuAc_2 \cdot 6H_2O$, 4,4′-bipyridine, H_2SO_4 (98%), and H_2O in the molar ratio 3.0 : 1.0 : 1.0 : 0.03 : 450, was sealed in a Teflon-lined stainless autoclave and heated at 180°C for 4 days. Light yellow block crystals of **1** were obtained in ca 70% yield (based on copper). Initial pH, 3.5; final pH, 3.9. Anal. Calcd for $C_{40}H_{32}N_8Cu_4Mo_8O_{26}$ (%): C, 23.29; H, 1.56; N, 5.43;

Table 1. Crystal data and details of the data collection and refinement for **1**.

Empirical formula	$C_{40}H_{32}N_8Cu_4Mo_8O_{26}$
Formula weight	2062.46
Space group	$P21/c$
a (Å)	10.860(2)
b (Å)	11.329(2)
c (Å)	22.092(4)
β (°)	94.18(3)
V (Å^3)	2710.7(9)
Z	2
Temperature (K)	293(2)
Wavelength (Å)	0.71073
d_{calcd} (Mg m^{-3})	2.527
abs coeff. (mm^{-1})	3.409
R_1 $[I > 2\sigma(I)]^a$	0.0342
wR_2 $[I > 2\sigma(I)]$	0.0888
R_1 (all data)	0.0458
Rw (all data)^b	0.0980

$^aR_1 = \Sigma|F_o| - |F_o|/\Sigma|F_o|$. $^bR_w = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega(F_o^2)^2]^{1/2}$.

Cu, 12.32; Mo, 37.21. found: C, 23.17; H, 1.52; N, 5.39; Cu, 12.27; Mo, 37.13. IR (cm^{-1}) for **1**: $\tilde{\nu} = 3740$ (w), 1744 (w), 1700 (w), 1606 (m), 1525 (m), 1411 (m), 1218 (w), 928 (m), 774 (m), 720 (m), 651 (m), 533 (w), 414 (w).

2.3. *X-ray crystallographic study*

Crystal data for **1** were collected on a Rigaku R-AXIS RAPID IP diffractometer, with Mo-Kα monochromatic radiation ($\lambda = 0.71073$ Å) at 293 K. An empirical absorption correction was applied. The structure was solved by direct methods. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The positions of hydrogen atoms on carbon atoms were calculated theoretically and refined by full-matrix least-squares on F^2 using the SHELXTL crystallographic software packages. Crystal parameters and details of the data collection and structure refinement are listed in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Synthesis*

Our interest is to get new molecular materials by using isopolymolybdate clusters as linkers. Conventionally, isopolymolybdates are isolated from self-assembly processes controlled by oxidation–reduction reactions and/or from condensation-polymerization of Mo^{VI} entities at pH lower than 3 related to $[Mo_2O_7]^{2-}$, $[Mo_5O_{17}]^{4-}$, $[Mo_3O_{10}]^{2-}$, $[Mo_8O_{26}]^{4-}$ [2a]. Under hydrothermal reaction media the reaction might be more complicated. The architecture of the final product is often sensitive to synthesis condition, such as metal ions, ligands, pH and reaction temperature [8b, 8c].

Controlling the pH accurately is a key factor to this system. In the identical reaction conditions, with pH discrepancies of 0.5, yellow $[Cu^I(4,4'\text{-bipy})]_4[\delta\text{-}Mo_8O_{26}]$ (**1**) and red

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

Compound 1					
Cu1–N1	1.896(4)	Cu1–N2	1.907(4)	Cu1–O3	2.650(4)
Cu1–O7	2.574(4)	Cu2–N3	1.905(4)	Cu2–N4	1.877(4)
Cu2–O2	2.672(4)				
N2–Cu1–N1	175.9(2)	N3–Cu2–N4	178.4(2)	O7–Cu1–O3	161.987(12)
N2–Cu1–O7	97.810(13)	N2–Cu1–O3	91.827(13)	N1–Cu1–O7	85.394(13)
N1–Cu1–O3	85.766(12)	N3–Cu2–O2	84.968(12)	N4–Cu2–O2	96.491(12)

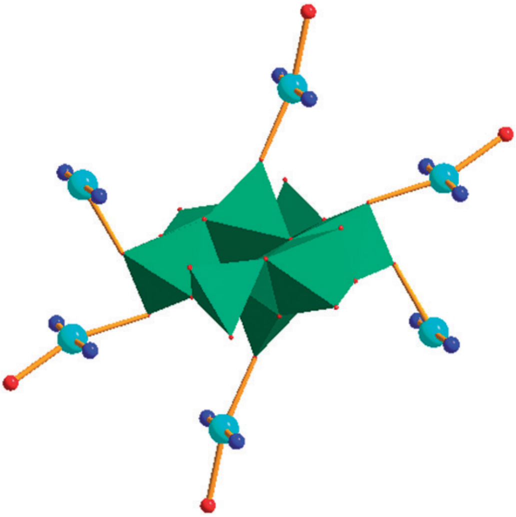

Figure 1. The fundamental building block of **1**, showing the coordination environment around Cu and Mo. (Mo–O polyhedron, green; Cu, turquoise; N, blue; O, red).

$[Cu^I(4,4'\text{-bipy})]_2[Mo_2O_7]$ [8a] can be obtained indicating the assembly is pH-dependent. At the same pH, formation of different isopolymolybdates could be attributed to the reaction temperature; at the higher temperature 180°C **1** is obtained, in which Cu^{II} might be reduced by the 4,4′-bipy ligand to Cu^I, whereas at 120°C blue crystal $[Cu^{II}(4,4'\text{-bipy})(H_2O)][Mo_3O_{10}] \cdot H_2O$ [9] is obtained.

3.2. *Crystal structure of 1*

Single crystal X-ray diffraction indicates that **1** has an interesting 3D structure in which the unit contains a δ-octamolybdate cluster covalently linked to six $\{Cu(4,4'\text{-bipy})\}^+$ coordination cations. To date, seven isomers of octamolybdate clusters, namely the α, β, γ, δ, ε, ξ, and η forms, have been described. There are rare compounds based on δ-Mo_8O_{26}, as previously reported δ form is the $(\alpha-\delta)$ or $(\beta-\delta)$ intermediate structure with poor stability [3a, 7a, 10]. So far only four δ-isomers have been described, $[(RhCp^*)_2(\mu_2\text{-}SCH_3)_3]_4[Mo_8O_{26}] \cdot 2CH_3CN$ [10a], $[\{Cu(4,4'\text{-bipy})\}_4(Mo_8O_{26})]$ [7a], $(H_2tptz)_2[Mo_8O_{26}] \cdot 2H_2O$ [10b] and $[Ni(2,2'\text{-bipy})_3]_2[\delta\text{-}Mo_8O_{26}]$ [10c]. As shown in figure 1, the $[\delta\text{-}Mo_8O_{26}]^{4-}$ anionic unit consists of four $\{MoO_6\}$ octahedra and four

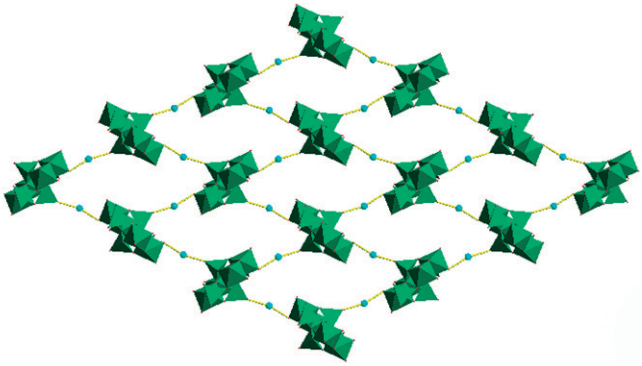

Figure 2. Representation of the two-dimensional plane structure of **1**, the δ-Mo_8O_{26} monomer linked by Cu1 site. (Mo_8O_{26} polyhedron, green; Cu, turquoise).

{MoO_4} tetrahedra. Two pairs of {MoO_6} octahedra and two {MoO_4} tetrahedra construct a Mo_6O_{26} ring, in which every two {MoO_6} octahedra share an edge to give rise to a {Mo_2O_{10}} moiety, and the {MoO_4} tetrahedra are connected with {Mo_2O_{10}} moieties via corner-sharing. The other two {MoO_4} tetrahedra cap the {MoO_6} octahedron by corner sharing. All molybdenum sites exhibit +6 oxidation states, which are confirmed by bond valence sum calculations giving the average value of +5.958. Six copper sites in **1** possess two {MoO_6} octahedra of the Mo_6O_{26} ring and two capping {MoO_4} tetrahedra (see figure 1). All the Cu sites exhibit +1 oxidation state that is also confirmed by bond valence sum calculations and give the average value of +0.931 for the calculated oxidation states of Cu. There exist two kinds of crystallographically independent Cu^I fragments which comprise two distinct environments. One Cu1 is coordinated by two nitrogen atoms (N1 and N2) from two 4,4′-bipy ligands, two terminal oxygen atoms (O3, O7) from two δ-octamolybdate clusters to complete a four-coordinate rhombic plane geometry, similar to the recently reported Cu^I in [Cu_3(pyrazine)($PW_{12}O_{40}$)] by Long *et al.* [11a]. Cu2 in **1** displays a nearly T-shaped trigonal geometry (the bond angle of N3–Cu2–N4 being very close to 180° (178.4(2)°)) which is coordinated by two nitrogen atoms of two 4,4′-bipy ligand and one terminal oxygen atom of a δ-octamolybdate cluster. Complex **1** is the first example of an octamolybdate [δ-Mo_8O_{26}]$^{4-}$ anion as a six-connected linkage based organic-inorganic coordination polymer.

The structure of **1** could be described as δ-octamolybdates bridged by Cu^I to form 2D planes, which are further linked by 4,4′-bipy to form a 3D structure. The [δ-Mo_8O_{26}]$^{4-}$ clusters are linked by Cu1 sites through terminal oxygen atoms to propagate two-dimensional planes parallel to the *bc* plane, resulting in parallelogram grids of 17.07 × 6.44 Å (see figure 2). The adjacent planes are linked by {Cu^I(4,4′-bipy)}$^+$ thus resulting in a three-dimensional network structure (figure 3a). The Cu1 and Cu2 chains all run parallel to the crystallographic *a* axis (figure 3a). The Cu2–O bond distance is 2.672 Å, which can be considered to be a weak long-range interaction between Cu2 and the terminal oxo group of [δ-Mo_8O_{26}]$^{4-}$. So the structure can also be described as 1D {Cu(2)(4,4′-bipy)}$^+$ chains threading into 2D [Cu(1)(δ-Mo_8O_{26})]$^{3-}$ sheets (figure 4). X-ray powder diffraction (XRPD) pattern of compound **1** has been recorded. The computer-simulated pattern obtained using the single crystal X-ray data for **1**

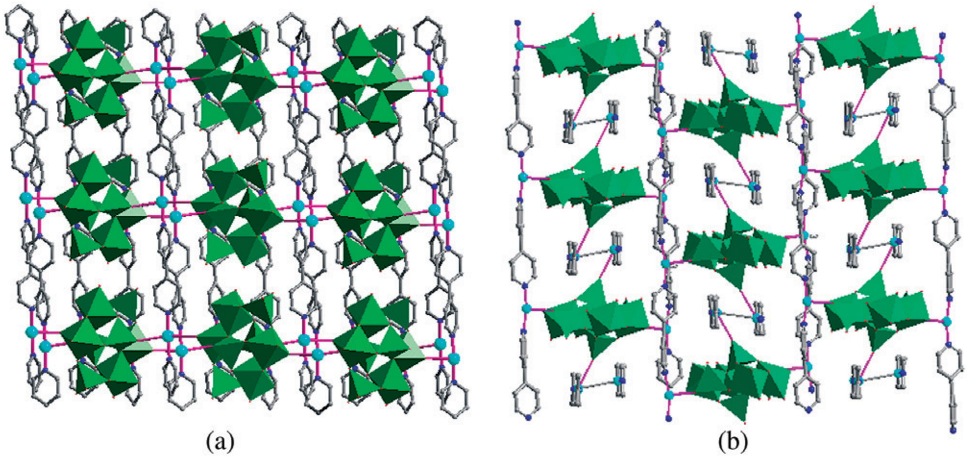

Figure 3. (a) Polyhedral views of the 3D framework of **1** viewing along the *b* axis. (b) The layer structure of the report of Zubieta as viewed perpendicular to the *bc* plane.

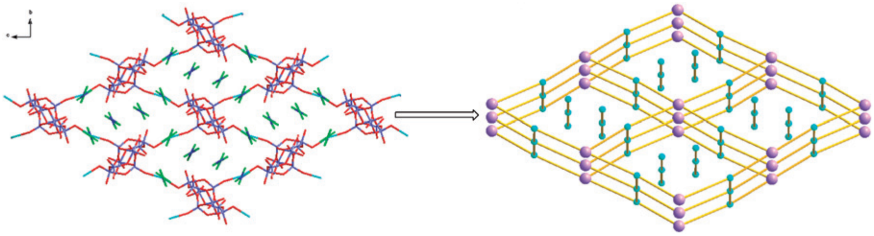

Figure 4. Simplified schematic representation of the 3D network of **1**. The clusters of building units $[\delta\text{-}Mo_8O_{26}]^{4-}$ are replaced by lavender nodes of the net, turquoise nodes represent Cu, brown bonds linking Cu–Cu atoms represent 4,4′-bipy.

match very well with the experimentally observed pattern, confirming the homogeneity and the purity of the bulk sample of **1**.

The molecular formula of **1** is the same as a report of Zubieta [7a], but the structures of the two compounds are absolutely different. In their paper each $[\delta\text{-}Mo_8O_{26}]^{4-}$ cluster bonds four Cu^I and have no shared Cu^I between two $[\delta\text{-}Mo_8O_{26}]^{4-}$ clusters, which form a 2D layer through 4,4′-bipy. As shown in figure 3(b), the $\{Cu(4,4'\text{-bipy})\}^+$ provides the scaffolding as chains of diagonally coordinated Cu^I centers. The chains associated with the Cu(1) site form pairs of parallel, face-to-face rods that run parallel to the crystallographic *a* axis. The Cu(2) chains grow along the crystallographic *b* axis. The $[Mo_8O_{26}]^{4-}$ clusters occupy cavities defined by two adjacent pairs of Cu(1) chains and one Cu(2) strand from each of two adjacent layers. The Cu(1) bilayers and $[Mo_8O_{26}]^{4-}$ subunits are sandwiched between the layers of parallel $\{Cu(2)(4,4'\text{-bipy})\}_n^{n+}$ strands. Adjacent layers are slotted together since alternating Cu(2) strands interact with $[Mo_8O_{26}]^{4-}$ clusters of an adjacent layer. Therefore, both of the two compounds are composed of $[\delta\text{-}Mo_8O_{26}]^{4-}$ clusters and $\{Cu(4,4'\text{-bipy})\}^+$ chains and have identical

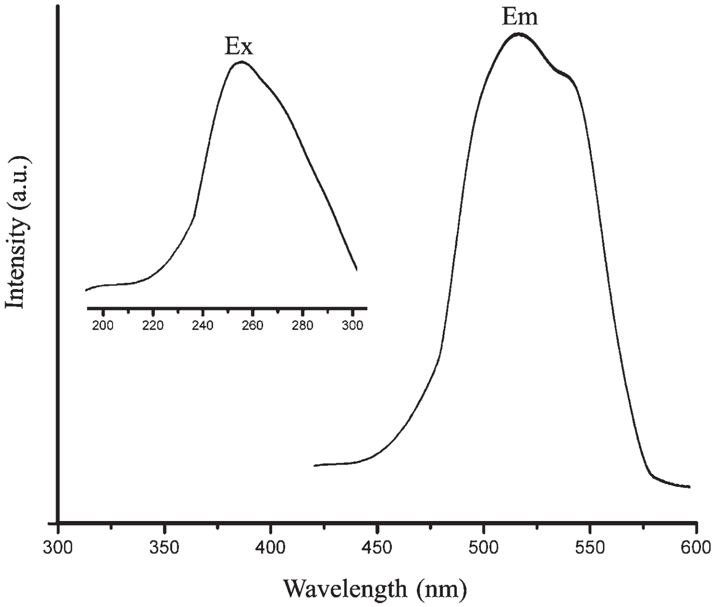

Figure 5. Photoluminescence spectrum of **1** in the solid state at room temperature. Ex = excitation, Em = emission.

molecule formula but absolutely different structures. This polymorphism is unusual in organic–inorganic hybrid materials involving POMs.

3.3. *Thermal gravimetric analysis*

Thermal gravimetry (TG) of **1** was performed on crystalline samples under a nitrogen atmosphere from 20 to 800°C. The thermogravimetric analysis (TGA) results show that this framework exhibits high thermal stability. The TG curve of **1** indicates it is stable up to 400°C. One stage of weight loss (31.02%) is observed in the temperature range 400–490°C, which is in good agreement with the calculated value (30.29%) for the decomposition of 4,4′-bipy.

3.4. *Photoluminescence properties*

Some copper(I) complexes have been found to be photoluminescent with different emitting excited states [12, 13]. Herein, the photoluminescence of **1** containing Cu^I is investigated. The solid-state emission spectrum of **1** at room temperature is depicted in figure 5. Intense emissions occur at 523 nm (figure 5, $\lambda_{ex} = 256$ nm). To understand the nature of the emission band, the luminescence of 4,4′-bipy ligand was analyzed; free 4,4′-bipy displays no photoluminescence from 400 to 800 nm in the solid state at room temperature. Therefore emission of the 4,4′-bipy ligand can be ruled out. The enhancement of photoluminescence may be attributed to 4,4′-bipy change transfer to the Cu^I excited with emission peak maximum at 523 nm, which effectively increases the rigidity of the ligand and reduces the loss of energy [14]. This fact may indicate that the interaction between Cu^I and 4,4′-bipy ligand tightens the whole skeleton. Since **1** is insoluble in water and common solvents such as ethanol, acetone, acetonitrile and benzene, it may be a good candidate for solvent-resistant fluorescent material at room temperature.

4. Conclusion

In conclusion, we have prepared a new 3D organic-inorganic hybrid compound which is constructed from isomolybdate cluster linked by $\{Cu(4,4'\text{-bipy})\}^+$ chains. In this work, we also found an polymorphism of $[Cu^I(4,4'\text{-bipy})]_4[\delta\text{-}Mo_8O_{26}]$, very unusual in organic–inorganic hybrid coordination networks involving POMs. This discovery inspires us to make more efforts in the system of novel materials with functional properties.

Supplementary data

Further details of the crystal structure of **1** may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Email: Crysdata@fiz-karlstruhe.de) on quoting the deposited number 612510.

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References

[1] (a) A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M.A. Withersby, M. Schrcder. *Coord. Chem. Rev.*, **183**, 117 (1999); (b) B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001); (c) O.R. Evans, W. Lin. *Acc. Chem. Res.*, **35**, 511 (2002); (d) X.C. Huang, J.P. Zhang, X.M. Chen. *J. Am. Chem. Soc.*, **126**, 13218 (2004); (e) L. Carlucci, G. Ciani, D.M. Proserpio. *Coord. Chem. Rev.*, **246**, 247 (2003); (f) S. Kitagawa, R. Kitaura, S.I. Noro. *Angew. Chem.*, **116**, 2388 (2004); *Angew. Chem. Int. Ed.*, **43**, 2334 (2004); (g) N.W. Ockwig, O. Delgado-Friederichs, M. O'Keeffee, O.M. Yaghi. *Acc. Chem. Res.*, **38**, 176 (2005).

[2] (a) M.T. Pope. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag, Berlin (1983); (b) M.T. Pope, A. Müller. *Angew. Chem.*, **103**, 56 (1991); *Angew. Chem., Int. Ed.*, **30**, 34 (1991); (c) *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, M.T. Pope, A. Müller (Eds), Kluwer, Dordrecht, The Netherlands (1994); (d) *Chemical Reviews.*, *Polyoxometalates*, C.L. Hill (Ed.), American Chemical Society, Washington, DC (1998); (e) *Polyoxometalate Chemistry: From Topology Via Self-Assembly to Applications*, M.T. Pope, A. Müller (Eds), Kluwer, Dordrecht, The Netherlands (2001);

(f) *Polyoxometalate Chemistry for Nano-Composite Design*, T. Yamase, M.T. Pope (Eds), Kluwer, Dordrecht, The Netherlands (2002); (g) *Polyoxometalate Molecular Scienc*e, J.J. Borrás-Almenar, E. Coronado, A. Müller, M.T. Pope (Eds), Kluwer, Dordrecht, The Netherlands (2004).

[3] (a) P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem.*, **111**, 2798 (1999); *Angew. Chem. Int. Ed.*, **38**, 2638 (1999); (b) A. Müller, S.K. Das, S. Talismanov, S. Roy, E. Beckmann, H. Bcgge, M. Schmidtmann, A. Merca, A. Berkle, L. Allouche, Y. Zhou, L. Zhang. *Angew. Chem.* **115**, 5193 (2003); *Angew. Chem. Int. Ed.*, **42**, 5039 (2003); (c) Y.Y. Niu, H.G. Zheng, H.W. Hou, X.Q. Xin. *Coord. Chem. Rev.*, **248**, 169 (2004); (d) D. Hagrman, P.J. Hagrman, J. Zubieta. *Angew. Chem.*, **111**, 3359 (1999); *Angew. Chem. Int. Ed.*, **38**, 3165 (1999).

[4] H. Kumagai, M. Arishima, S. Kitagawa. *Inorg. Chem.*, **41**, 1989 (2002).

[5] (a) C. Inman, J. Knaust, S. Keller. *Chem. Commun.*, 156 (2002); (b) J. Knaust, C. Inman, S. Keller. *Chem. Commun.*, (2004) 492.

[6] (a) Z.Y. Shi, X.J. Gu, J. Peng, Z.F. Xin. *Euro. J. Inorg. Chem.*, 3811 (2005); (b) M. Clemente-León, E. Coronado, C. Giménez-Saiz, C.J. Gómez-García, E. Martínez-Ferrero, M. Almeida, E.B.J. Lopes. *Chem. Mater.*, **11**, 2176 (2001); (c) E. Coronado, C.J. Gómez-García. *Chem. Rev.*, **98**, 273 (1998); (d) L. Zhang, Y. Wei, C. Wang, H. Guo, P.J. Wang. *J. Solid State Chem.*, **177**, 3433 (2004); (e) S.M. Chen, C.Z. Lu, Y.Q. Yu, Q.Z. Zhang, X. He. *Inorg. Chem. Commun.*, **7**, 1041 (2004); (f) V. Shivaiah, M. Nagaraju, S. K Das. *Inorg. Chem.*, **42**, 6604 (2003); (g) Y. Lu, Y. Xu, E. B Wang, J. Lü, C.W. Hu, L. Xu. *Cryst. Growth Des.*, **5**, 257 (2005); (h) L.M. Zheng, Y. Wang, X. Wang, J.D. Korp, A.J. Jacobson. *Inorg. Chem.*, **40**, 1380 (2001).

[7] (a) D. Hagrman, C. Zubieta, D. Rose, J. Zubieta, R. Haushalter. *Angew. Chem.*, **109**, 904 (1997); *Angew. Chem. Int. Ed.*, **36**, 873 (1997); (b) P.J. Zapf, R.C. Haushalter, J. Zubieta. *Chem. Commun.*, 321 (1997); (c) P.J. Zapf, R.P. Hammond, R.C. Haushalter, J. Zubieta. *Chem. Mater.*, **10**, 1366 (1998); (d) D. Hagrman, P.J. Zapf, J. Zubieta. *Chem. Commun.*, (1998) 1283; (e) K.N. Power, T.L. Hennigar, M.J. Zaworotko. *Chem. Commun.*, 595 (1998); (f) D. Hagrman, R.C. Haushalter, J. Zubieta. *Chem. Mater.*, **10**, 361 (1998); (g) D. Hagrman, J. Zubieta. *Chem. Commun.*, 2005 (1998).

[8] (a) C.Z. Lu, C.D. Wu, H.H. Zhuang, J.S. Huang. *Chem. Mater.*, **14**, 2649 (2002); (b) W. Ouellette, M.H. Yu, Charles J. O'Connor, D. Hagrman, J. Zubieta. *Angew. Chem. Int. Ed.*, **45**, 3497 (2006); (c) P.Q. Zheng, Y.P. Ren, L.S. Long, R.B. Huang, L.S. Zheng. *Inorg. Chem.*, **44**, 1190 (2005).

[9] Z.P. Kong, L.H. Weng, D.J. Tan, H.Y. He, B. Zhang, J.L. Kong, B. Yue. *Inorg. Chem.*, **36**, 796 (1997).

[10] (a) R. Xi, B. Wang, K. Isobe, T. Nishioka, K. Toriumi, Y. Ozawa. *Inorg. Chem.*, **33**, 833 (1994); (b) R.S. Rarig Jr, J. Zubieta. *Inorg. Chim. Acta*, **312**, 188 (2001); (c) D.R. Xiao, H.Y. An, E.B. Wang, L. Xu. *J. Mol. Struct.*, **738**, 217 (2005).

[11] (a) Y.P. Ren, X.J. Kong, X.Y. Hu, M. Sun, L.S. Long, R.B. Huang, L.S. Zheng. *Inorg. Chem.*, **45**, 4016 (2006); (b) H.R. Kreusler, A. Förster, J. Fuchs. *Z. Naturforsch.*, **35b**, 242 (1980).

[12] (a) V.W.-W. Yam, K.K.-W. Lo. *Chem. Soc. Rev.*, **28**, 323 (1999); (b) P.C. Ford, E. Cariati, J. Bourassa. *Chem. Rev.*, **99**, 3625 (1999).

[13] (a) R. Li, D. Li, X. Huang, Z. Qi, X. Chen. *Inorg. Chem. Commun.*, **6**, 1017 (2003); (b) M. Henary, J.L. Wootton, S.I. Khan, J.I. Zink. *Inorg. Chem.*, **36**, 796 (1997); (c) H.K. Fun, S.S.S. Raj, R.G. Xiong, J.L. Zuo, Z. Yu, X.L. Zhu, X.Z. You. *J. Chem. Soc., Dalton Trans.*, 1711 (1999).

[14] (a) *Photochemistry and Photophysics of Coordination Compounds*, H. Yersin, A. Vogler (Eds), Springer, Berlin (1987); (b) B. Valeur. *Molecular Fluorescence: Principles and Application*, Wiley-VCH, Weinheim (2002).