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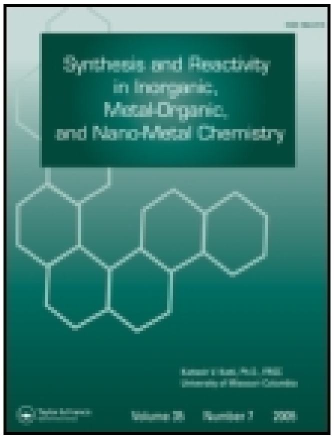

Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
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Syntheses, Crystal Structures, UV-Vis Absorption, and Fluorescent Properties of a Complex: $[btx][Cu_2I_4]$

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Syntheses, Crystal Structures, UV-Vis Absorption, and Fluorescent Properties of a Complex: [btx][Cu_2I_4]

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The self-assembly reaction of organic cation and metal iodides yielded a novel binuclear coordination compound, namely [btx][Cu_2I_4](1) [btx = 1,6-bis(triethylmethylammonium)xylol], which is characterized by X-ray crystallography, IR spectroscopy, fluorescence spectra, and UV-vis absorption spectra. The compound 1 crystallizes in Monoclinic, space group $P2(1)/c$ with a = 8.2246(12), $b = 11.5843(17)$, $c = 15.005(2)$, $\alpha = 90°$, $\beta = 94.218(2)°$, $\gamma = 90°$. In the anion $[Cu_2I_4]^{2-}$, each Cu center is triangularly coordinated by two μ_2-I(2) atoms and one terminal I(1) atom. The organic cationic $[btx]^{2+}$ existed around it through supramolecular interactions.

Keywords binuclear coordination compound, organoammonium cations, photoluminescent properties, self-assembly, UV-vis absorption spectra

INTRODUCTION

The intelligent choice of transition-metal clusters and organoammonium cations (OACs) may yield inorganic-organic supramolecular systems with intriguing structural topologies and desirable properties.[1–5] Self-assembly is one of the most efficient methods for the synthesis of transition metal complexes, and for their wide applications in biological systems, porous materials, catalytic reactions, the nonlinear optical materials, and advanced materials.[6–13] Most significantly, the structural information from the organic template can be imprinted on the final supramolecular frameworks.[14] The term template effect was first used and defined at the beginning of the sixties.[15] This may not only lead to new supramolecular systems with high dimensionality, but also shed light on the cluster coordination complex. Thereby, we chose the organic cation btx·Cl_2 as organic template and organic structural direction agent and inorganic functional building block to assemble a novel binuclear coordination compound [btx][Cu_2I_4](**1**) [btx = 1,6-bis(triethylmethylammonium)xylol]. It is characterized by single-crystal X-ray diffraction, IR spectroscopy, fluorescence spectra, and UV-vis absorption spectra. Moreover, in anion $[Cu_2I_4]^{2-}$, each Cu center is triangularly coordinated by two μ_2-I(2) atoms and one terminal I(1) atom. The organic cationic $[btx]^{2+}$ existed around it through supramolecular interactions.

EXPERIMENTAL

Material and Measurement

All chemicals and solvents are of A.R. grade and used without further purification. The dication btx·Cl_2 is prepared as the chloride salt by direct alkylation of dibenzyl chloride with triethylamine (acetonitrile served as the solvent).[16] Photoluminescent measurement of [btx]Cu_2I_4 and the cation btx·Cl_2 are conducted on a Hitachi F-4500 spectrophotometer (Japan) and the data were collected at room temperature. The UV-vis spectra were measured on a HP-8453 UV-visible spectrophotometer at room temperature. The IR spectrum was recorded on a Shimazu IR435 spectrometer (Japan) as KBr disk (4000–400 cm^{-1}).

Synthesis of the Complex

For [btx][Cu_2I_4] (**1**), a methanol solution of btx·Cl_2 (0.038 g, 0.1 mmol) is added to a stirring colorless solution of CuI (0.019 g, 0.01 mmol) dissolved in 3 mL DMF/H_2O (volume ratio of 4:1) in the presence of excess KI (0.084 g, 0.5 mmol). White precipitation appears and DMF solution is continued to be added until the precipitation disappeared completely. The solution is then filtrated and slowly evaporated in a vial placed in the dark at room temperature. White crystals of [btx][Cu_2I_4] suitable for X-ray analysis are obtained after three days. IR (KBr, cm^{-1}): 3440(s), 2966(s), 2940(m), 1516(s), 1448(s), 1402(s), 1297(s), 1172(s), 1146(s), 1005(s), 813(s), 788(s), 682(s), 628(s), 571(m), 506(s), 454(m).

X-Ray Structural Determination

Crystallographic data for the title compound **1** was collected at 293(2) K on a Bruker APEX-II area-detector diffractometer (Germany) equipped with graphite-monochromatized Mo-Ka radiation (λ = 0.71073 Å). Its structure was solved by

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TABLE 1
Crystal data and structure refinement for **1**

Compound	**1**
Formula	$C_{10}H_{19}CuI_2N$
Formula weight	470.60
Crystal system	Monoclinic
Space group	P 2(1)/c
a/Å	8.2246(12)
b/Å	11.5843(17)
c/Å	15.005(2)
α/°	90
β/°	94.218(2)
γ/°	90
Volume/ A^3	1425.7(4)
Z	4
Calculated density, Mgm^{-3}	2.192
μ, mm^{-1}	5.832
F(000)	884
Crystal size, mm	0.31 × 0.10 × 0.08
Temperature/ K	296(2)
Reflections collected	10431
Independent reflections	2638
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2638 / 0 / 130
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	$R1 = 0.0276$, w$R2 = 0.0678$
R indices (all data)	$R1 = 0.0381$, w$R2 = 0.0737$
Largest peak	0.681
Hole(e. Å^{-3})	−0.763

direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical constraints. The structures were refined with full-matrix least-squares techniques on F2 using the SHELXTL-97 program package.[17] Crystal data are summarized in detail in Table 1. Selected bond lengths and bond angles are listed in Table 2.

RESULTS AND DISCUSSION

Synthesis of Discussion

This dinuclear coordination compound was yielded by self-assembly of btx·Cl_2 as organic template and CuI; preparation of the compound was mainly affected by several factors: (a) Solvent: In the formation of the crystal, crystallization rate was not identical because different solvent volatilized at different speed. Polycrystal or microcrystal was easily formed when solvent volatilized fast, but it did not easily form crystals when solvent volatilized too slow. After repeated experiments, the mixed solvent of DMF and methanol was the most appropriate. (b) Temperature: Solvent evaporation method was less affected by temperature because it was carried out at room temperature. While sometimes it might bring some influence on the evaporation of solvent owing to the seasonal temperature difference. (c) Materials ratio: The materials' ratio played a major role in crystallizing of compound **1**. The ratio of CuI and KI could have influence on the growth environment of compound **1**. (d) Crystallization time: The results showed that as long as the ratio of solvents was chosen suitably, the reaction time in a week had not significantly influenced on the shape of crystals.

Crystal Structure

[btx][Cu_2I_4] 1

The structure of compound **1** belongs to monoclinic crystal system with space group *P*2(1)/c. The crystal data and bond length are shown in Tables 1 and 2, respectively. The single-crystal X-ray diffraction analysis revealed that compound **1** consisted of cationic $[btx]^{2+}$ as a structure-directing agent and inorganic anions cluster $[Cu_2I_4]^{2-}$. It belonged to dinuclear compounds. In the inorganic anions cluster $[Cu_2I_4]^{2-}$, the Cu(1) center is three-coordinated in a distorted triangle geometry by two μ_2-I(2) atoms and one terminal I(1) atom. The organic cationic $[btx]^{2+}$ existed around inorganic anions cluster $[Cu_2I_4]^{2-}$ through supramolecular interactions. In the inorganic anions cluster $[Cu_2I_4]^{2-}$, Cu(1)-I(2)-Cu(1)#1- I(2)#1 formed a parallelogram geometry, which was made of Cu(1)-I(2), Cu(1)-I(2)#1, Cu(1)#1-I(2), and Cu(1)#1-I(2)#1 four bonds ranging from 2.5716(7) Å to 2.5947(7) Å. The bond angles I(2)-Cu(1)-I(2)#1 and Cu(1)-I(2)#1-Cu(1)#1 were 119.20(3)° and 60.80(3)°, respectively. Meanwhile, there is also a bond between two Cu atoms to form a metal-metal interaction with the bond length Cu(1)-Cu(1)#1 2.6143(13) Å and the I(1)-Cu(1)-Cu(1)#1 bond angle is 176.16(4)°. It was showed that two terminal I atoms and two metal Cu atoms were essentially in a straight line (Figure 1).

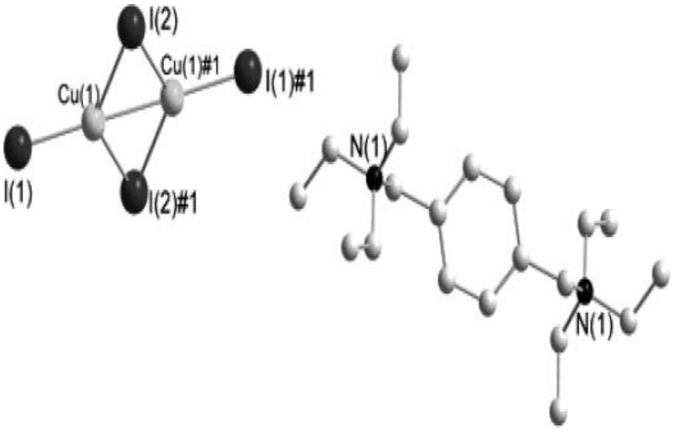

FIG. 1. Structure unit of the compound **1**.

TABLE 2
Selected bond distances (Å) and angles (°) for compound **1**

1			
Cu(1)-I(1)	2.4926 (8)	Cu(1)-I(2)	2.5716 (7)
Cu(1)-I(2)#1	2.5947 (7)	Cu(1)-Cu(1)#1	2.6143 (13)
N(1)-C(1)	1.517 (5)	N(1)-C(3)	1.526 (5)
N(1)-C(5)	1.525 (5)	N(1)-C(7)	1.531 (5)
I(1)-Cu(1)-I(2)	123.12 (3)	I(1)-Cu(1)-I(2)#1	117.63 (3)
I(2)-Cu(1)-I(2)#1	119.20 (3)	I(1)-Cu(1)-Cu(1)#1	176.16 (4)
I(2)-Cu(1)-Cu(1)#1	60.04 (3)	I(2)#1-Cu(1)-Cu(1)#1	59.17 (2)
Cu(1)-I(2)-Cu(1)#1	60.80 (3)	C(1)-N(1)-C(3)	108.5 (3)
C(3)-N(1)-C(7)	111.6 (3)	C(7)-N(1)-C(5)	107.9 (3)
N(1)-C(1)-C(2)	115.5 (4)	C(1)-N(1)-C(7)	109.3 (3)
C(1)-N(1)-C(5)	111.2 (3)	C(7)-N(1)-C(5)	107.9 (3)
C(6)-C(5)-N(1)	115.7 (3)	C(8)-C(9)-H(9)	119.5
C(9)#2-C(10)-H(10)	119.6	N(1)-C(7)-H(7B)	108.4

In the whole structure, the inorganic anions cluster $[Cu_2I_4]^{2-}$ and the organic cationic $[btx]^{2+}$ constituted a 2D planar structure, and both of them mutually filled their gaps through each other. The organic cationic $[btx]^{2+}$ played roles of balance charge and filling agent in this structure (Figure 2).

There were C-H···I and C-H···Cu interactions between I and Cu atoms of each inorganic anions cluster $[Cu_2I_4]^{2-}$ and hydrogen atoms of organic cations $[btx]^{2+}$ (Figure 3). Via these weak interactions and static electricity interactions, each formed unit assembled to form the infinite spatial structure (Figure 4).

Photoluminescent Properties

The fluorescence spectra of the complexes and organic cation in solid state are recorded using a Hitachi F-4500 (fluorescence spectrophotometer) in a 1 cm quartz cell. The excitation and emission bandwidths are set at 5 nm. The spectra of complex and organic cation at room temperature are illustrated in Figure 5. The organic cation emits at 289 nm under excitation at 256 nm. In contrast, compound **1** gives fluorescence center at 463 nm under excitation at 300 nm. Compared with the organic cation a red shift of 174 nm in compound **1** has been observed, which is considered to mainly arise from metal to ligand charge transition (MLCT) inferred in some literature.[18] The results here suggest that compound **1** is a potential candidate for photoactive materials.

UV-Vis Absorption Spectra of btx·Cl_2 and 1

The UV-vis absorption spectra of organic cation btx·Cl_2 in methanol solution and compound **1** in DMF solution are shown in Figure 6. The electronic spectra of cation btx·Cl_2 showed strong peak at 220 nm and weak peak at 267 nm. These peaks are probably dominated by the $\pi \rightarrow \pi^*$ transition. However, in

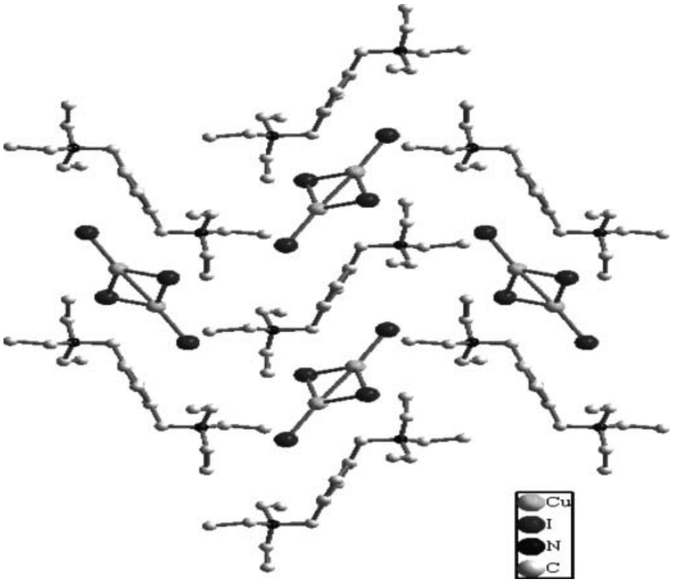

FIG. 2. 2D planar structure of compound **1**.

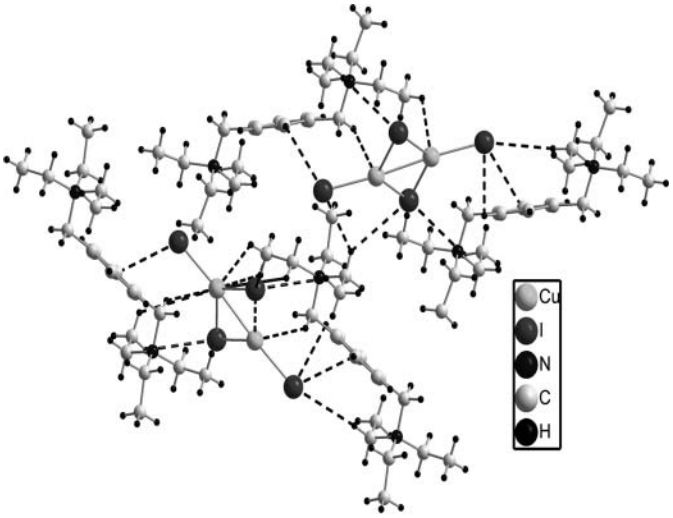

FIG. 3. Interaction diagram of the compound **1.**

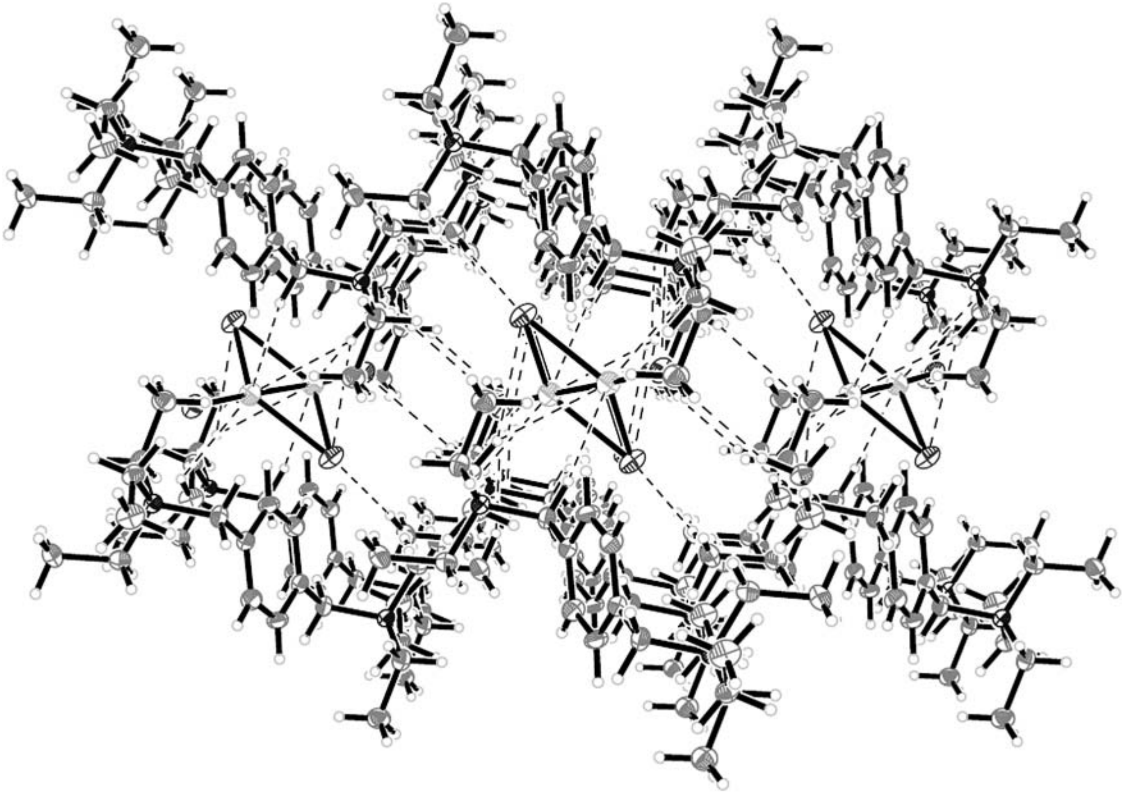

FIG. 4. Packing interaction diagram of the compound **1.**

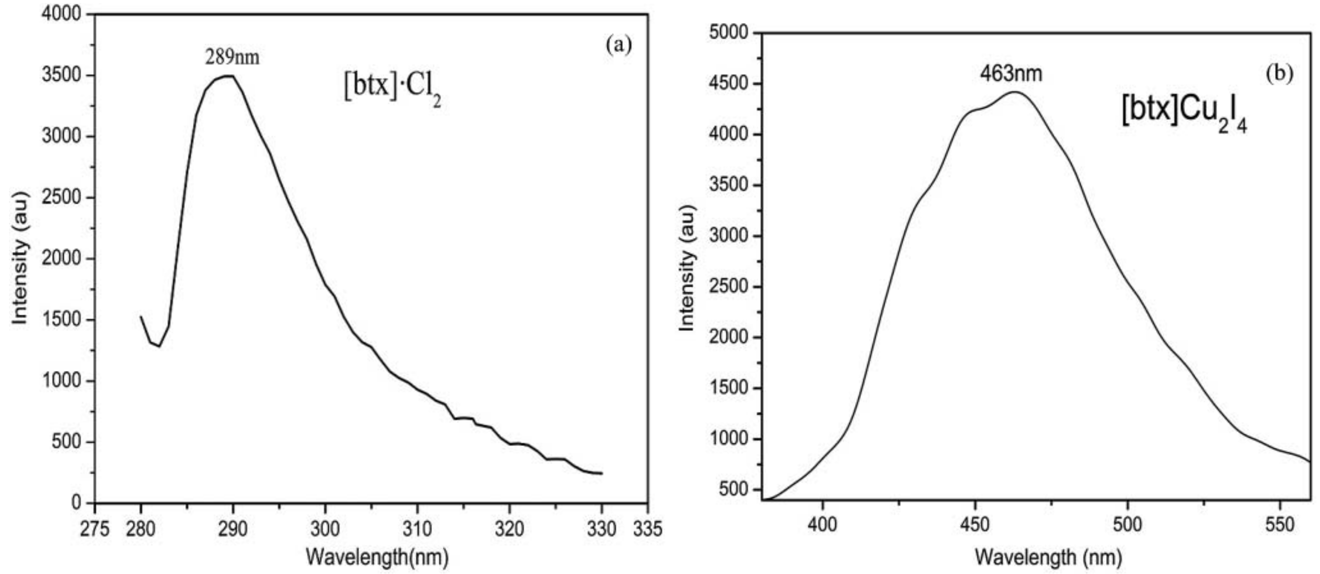

FIG. 5. (a) Photoluminescent spectra of the free cation btx·Cl$_2$ in solid state at room temperature. (b) Photoluminescent spectra of compound **1** in solid state at room temperature.

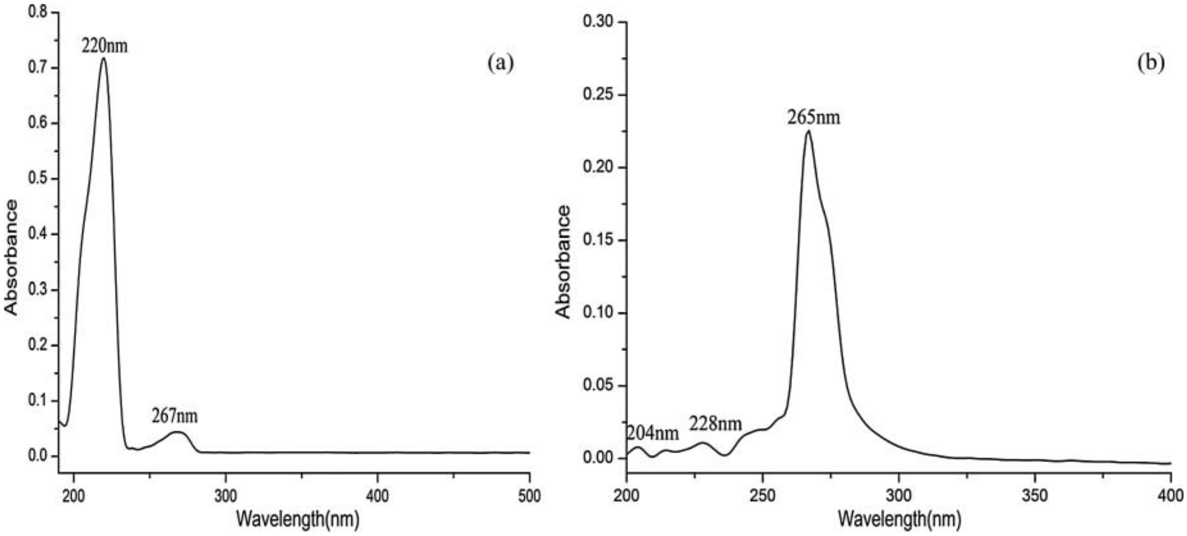

FIG. 6. (a) UV-vis spectrogram for the methanol solution of organic cation btx·Cl_2. (b) UV-vis spectrogram for the DMF solution of compound **1**.

the spectra of compound **1** showed three peaks at 204 nm, 228 nm, and 265 nm, which probably arose from the $\pi \rightarrow \pi^*$ transition. These absorption peaks appeared weak red shift due to the different solvents.

Supplementary Materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 816545 for compound **1**, Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: 44-1223-336-033; email: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

REFERENCES

1. Xu, Q.F.; Chen, J.X.; Zhang, W.; H.; Ren, Z.G.; Li, L.X.; Zhang, Y.; Lang, J.P. Construction of [(η^5-C_5Me_5)WS_3Cu_3]-based supramolecular compounds from preformed incomplete cubane-like clusters [PPh_4][(η^5-C_5Me_5)$WS_3(CuX)_3$] (X = CN, Br). *Inorg. Chem.* **2006**, *45*, 4055–4064.
2. Dessapt, R.; Kervern, D.; Bujoli-Doeuff, M.; Deniard, P.; Evain, M.; Jobic, S. Hybrid organic-inorganic molybdate material design? *Inorg. Chem.* **2010**, *49*, 11309–11316.
3. Zhang, Z.H.; Gu, Z.M.; Liu, X.C.; Zhao, F.K.; Yue, J.M.; Wang, L.F.; Niu, Y.Y. Self-assembly, crystal structure and fluorescent property of a coordination polymer [(Cu_4I_6)(BPE)]$_n$. *Synth. React. Inorg. Met.-Org. Chem.* **2009**, *39*, 633–636.
4. Li, Z.H.; Du, S.W.; Wu, X.T. Assembly of molecular squares and helical chain polymers of Mo(W)/Cu/S clusters using thiolato ligands as linkers. *Polyhedron* **2005**, *24*, 2988–2993.
5. Yue, J.M.; Wang, W.J.; Fu, W.Z.; Han, X.N.; Zhang, Z.H.; Wang, L.F.; Niu, Y.Y. Syntheses, crystal structures and fluorescent properties of two cation-induced complexes: [(CdI_4)(BPHX)] and [(Ag_2I_4)(BPHX)]. *Synth. React. Inorg. Met.-Org. Chem.* **2011**, *41*, 1–7.
6. Xu, H.W.; Wu, J.G.; Chen, Z.N. Self-assembly and crystal structures of two heteronuclear complexes with [$Ag_2(\mu$-dppm$)_2(MeCN)_2$]$(SbF_6)_2$ and [Bu_4N]$_2$[$M(mnt)_3$] (M = Mo, W) as components. *Transition Met Chem.* **2008**, *33*, 17–21.
7. Liang, K.; Zheng, H.G.; Song, Y.L.; Li, Y.Z.; Xin, X.Q. Novel cluster coordination polymers based on tetranuclear nest-shaped [WOS_3Cu_3] heterothiometallitic secondary building units and 4,4'-bipyridine ligand. *Cryst. Growth & Des.* **2007**, *7*, 373–376.
8. Lang, J.P.; Xu, Q.F.; Zhang, W.H.; Li, H.X.; Ren, Z.G.; Chen, J.X.; Zhang, Y. Mo(W)/Cu/S cluster-based supramolecular arrays assembled from preformed clusters [Et_4N]$_4$[$WS_4Cu_4I_6$] and [(n-Bu$)_4$N]$_2$[$MoOS_3Cu_3\times_3$] (X = I, SCN) with flexible ditopic ligands. *Inorg. Chem.* **2006**, *45*, 10487–10496.
9. Huang, K.X.; Song, Y.L.; Pan, Z.R.; Li, Y.Z.; Zheng, H.G. Porous nonlinear-optical material based on a twin-nest-shaped heterothiometallic cluster: $\{[NH_4][W_2O_2S_6Cu_6I_3(4,4'\text{-bipy})_4]\cdot 5H_2O\}_n$. *Inorg. Chem.* **2007**, *46*, 6233–6235.
10. Zhang, Q.F.; Niu, Y.Y.; Leung, W.H.; Song, Y.L.; Williams, I.D.; Xiu, X.Q. Synthesis of a 2D polymeric cluster $\{[NEt_4][Mo_2O_2S_6Cu_6I_3\text{-}(4,4'\text{-bipy})_5]\cdot MeOH\cdot H_2O\}_n$ with a significant improvement of optical limiting effect. *Chem. Commun.* **2001**, 1126–1127.
11. Liang, K.; Zheng, Z.G.; Song, Y.L.; Lappert, M.F.; Li, Y.Z.; Xin, Q.Q.; Huang, Z.X.; Chen, J.T.; Lu, S.F. Self-assembly of interpenetrating coordinationn nets formed from interpenetrating cationic and anionic three-dimensional diamondoid cluster coordination polymers. *Angew. Chem. Int. Ed.* **2004**, *43*, 5776–5779.
12. Dou, J.M.; Zhang, D.P.; Li, D.C.; Wang, D.Q. Two type skeleton hetero-bimetallic trinuclear Cu–Mo–S clusters containing closo carborane diphosphine ligand 1,2-bis(diphenylphosphino)-1,2-dicarba-closo-dodecaborane. *Inorg. Chem. Commun.* **2006**, *9*, 1099–1102.
13. Sadr, M.H.; Sardroodi, J.J.; Zare, D.; Brooks, N.; Clegg, R.W.; Song, Y.L. Nonlinear optical properties and crystal structure determination of a pentanuclear copper(I) cluster $(NEt_4)_2[MoS_4(CuBp)_4]$ (Bp = H_2B(pyrazolyl$)_2$). *Polyhedron* **2006**, *25*, 3285–3288.
14. Hagrman, P.J.; Hagrman, D.; Zubieta, J. Organic-inorganic hybrid materials: From "simple" coordination polymers to organodiamine-templated molybdenum oxides. *Angew. Chem. Int. Ed.* **1999**, *38*, 2638–2684.
15. Hoss, R.; Vogtle, F. Template syntheses. *Angew. Chem. Int. Ed. Engl* **1994**, *33*, 375–384.
16. Wang, M.L.; Hsieh, Y.M. Kinetic study of dichlorocyclopropanation of 4-vinyl-1-cyclohexene by a novel multisite phase transfer catalyst. *J. Mol. Catal. A: Chem.* **2004**, *210*, 59–68.
17. Sheldrick, G. M. SHELXS-97. Program for X-ray Crystal Structure Solution; Göttingen University: Germany, **1997**.
18. Tao, J.; Tong, M.L. Blue pH to luminescent zinc coordination polymers with supertetranuclear cores. *Chem Comm.* **2000**, 2043–2044.