

3,5-二烷基-1,2,4-三唑衍生物构筑的两个 Cu_4I_4 簇配合物的合成、结构和荧光性质

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摘要: 以 3,5-二甲(丙)基-4-氨基-1,2,4-三唑为配体, 与 CuI 在 $\text{H}_2\text{O}/\text{MeCN}$ 混合溶剂热合成了 2 个构型不同的 Cu_4I_4 超分子化合物 $[\{\text{Cu}_2(\text{aadmtrz})\text{I}_2\} \cdot \text{CH}_3\text{CN}]_n$ (**1**) 和 $[\text{Cu}_2(\text{dptrz})\text{I}]_n$ (**2**) (aadmtrz=4-((1-氨基乙基)-氨基)-3,5-二甲基-1,2,4-三唑, dptrz=3,5-二丙基-1,2,4-三唑), 并进行了元素分析, 红外, X 射线粉末衍射及单晶衍射等表征。2 个配合物中 Cu_4I_4 构型不同, 配合物 **1** 中, Cu_4I_4 簇连成一个 8 环椅式-椅式结构, 通过配体连接成(4,4)二维菱形格子结构; 而配合物 **2** 中, Cu_4I_4 簇呈畸变的立方烷结构, 构成了含有 19.5% 孔隙率三维孔洞聚合物, 其结构可简化为(3,4)-连接的拓扑结构。同时, 在常温下研究了 2 个配合物的固体荧光性质。

关键词: 亚铜碘配合物; 1,2,4-三唑; 晶体结构; 荧光性质

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Syntheses, Crystal Structures and Luminescence Properties of Two Cu_4I_4 Coordination Polymers Based on 3,5-Dialkyl-1,2,4-triazole

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Abstract: Two Cu_4I_4 coordination polymers, $[\{\text{Cu}_2(\text{aadmtrz})\text{I}_2\} \cdot \text{CH}_3\text{CN}]_n$ (**1**) and $[\text{Cu}_2(\text{dptrz})\text{I}]_n$ (**2**) (aadmtrz=4-((1-aminoethylidene)-amino)-3,5-dimethyl-1,2,4-triazole, dptrz=3,5-dipropyl-1,2,4-triazole), have been synthesized by the solvothermal reactions of CuI and 3,5-dialkyl-4-amino-1,2,4-triazole ligands in mixed $\text{H}_2\text{O}/\text{MeCN}$ solution and characterized using elemental analysis, IR, PXRD and single-crystal X-ray diffraction. The structures of the Cu_4I_4 units in the polymers are different. The Cu_4I_4 cluster in complex **1** is an inorganic 8-membered ring with a chair-chair conformation, while the one in complex **2** is a distorted cube. Complex **1** exhibits 2D 4,4-connected rhombic-grid. Complex **2** is a (3,4)-connected framework with 19.5% porosity. In addition, the luminescent properties of the complexes in the solid state were also investigated. CCDC: 1437794, **1**; 1437795, **2**.

Keywords: copper(I) iodide; 1,2,4-triazole; crystal structures; luminescence

Cuprous halide complexes have been of great interest for their various structure, unique topologies^[1-3], as well as attractive properties such as luminescence^[4-5],

pores^[6] and high reactivity in numerous organic and biochemical reactions^[7-8]. $(\text{Cu}_x\text{X}_y)^{x-y}$ ($\text{X}=\text{halide}$)^[9] have richer aggregates of different geometries: Cu_2X_2 ,

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Cu_3X_3 , Cu_3X_7 , Cu_3X_8 , Cu_4X_4 , Cu_4X_{11} , Cu_4X_9 , Cu_6X_6 ^[10-14], and so on. Neutral cuprous halide clusters show Cu_2X_2 , Cu_4X_4 , and Cu_6X_6 . These aggregates can be linked by organic ligands to form cuprous halide coordination polymers. It has been reported N-donor ligands such as pyrazine, bipyridyl^[11], imidazole, triazole^[13,15], tetrazole^[9], benzotriazole^[16]. To date, a large number of cuprous halide complexes containing triazole ligands have been reported^[17-19]. What we are interested in is that cuprous iodide with 4-aminotriazole shows diversities of Cu(I) coordination geometry and new 4-aminotriazole ligands are self-assembled by the condensation reaction or the reductive deamination^[20]. Herein, we report the syntheses and crystal structures of two Cu_4I_4 aggregates complexes $\{[\text{Cu}_2(\text{aadmtrz})\text{I}_2] \cdot \text{CH}_3\text{CN}\}_n$ (**1**) and $[\text{Cu}_2(\text{dptrz})\text{I}]_n$ (**2**), and illustrate that the length of alkyl side chains of 4-aminotriazole has a certain extent influence on the product formations, structures and topologies. The complexes were characterized by X-ray single crystal analysis and studied by various spectroscopic techniques.

1 Experimental

1.1 Materials and methods

All reagents were purchased commercially and used without further purification. Ligands dmatrz and dptrz were synthesized according to the literature^[21]. Elemental analyses (C, H, and N) were performed on an Elementar Vario EL III analyzer. FTIR spectra were recorded from KBr pellets in the range of 4 000 ~400 cm^{-1} on a Bruker Tensor 27 spectrometer. PXRD data were collected in a Bruker D8 Advance X-ray diffractometer using Cu $K\alpha$ radiation ($\lambda=0.154\ 059\ 8\ \text{nm}$) at 30 kV and 15 mA over the 2θ range of $5^\circ \sim 50^\circ$. The simulated patterns of **1** and **2** were derived from free Mercury Version 2.2 software. Luminescence spectra were recorded on a CARY Eclipse (Varian, USA) fluorescence spectrophotometer at room temperature.

1.2 Synthesis of complex $\{[\text{Cu}_2(\text{aadmtrz})\text{I}_2] \cdot \text{CH}_3\text{CN}\}_n$ (**1**)

A mixture containing CuI (0.10 g, 0.53 mmol), dmatrz (0.056 g, 0.50 mmol), CH_3CN (1 mL) and H_2O

(5 mL) was sealed in a 23 mL of Teflon-lined stainless steel vessel, which was heated at 150 $^\circ\text{C}$ for 4 days, and cooled to room temperature. Light-green block crystals of **1** were obtained, and picked out, washed with $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (1:5, V/V) and dried in air. Yield: 47.5%. Anal. Calcd. for $\text{C}_8\text{H}_{14}\text{Cu}_2\text{I}_2\text{N}_6$ (%): C, 16.71; H, 2.45; N, 14.61. Found(%): C, 16.68; H, 2.51; N, 14.62. IR (cm^{-1}): 3 315 (s), 3 216 (m), 3 004 (w), 2 968 (w), 2 914 (w), 1 622 (s), 1 543 (s), 1 427 (s), 1 373 (m), 1 266 (m), 1 043 (m), 990(m), 891(s), 758(s), 742(m).

1.3 Synthesis of complex $[\text{Cu}_2(\text{dptrz})\text{I}]_n$ (**2**)

The same synthetic procedure as that for **1** was used except that dmatrz was replaced with dptrz (0.084 g, 0.50 mmol), giving pale-green octahedral crystals **2** in 25.8% yield. Anal. Calcd. for $\text{C}_8\text{H}_{14}\text{Cu}_2\text{N}_3\text{I}$ (%): C, 23.65; H, 3.47; N, 10.34, Found(%): C, 23.58; H, 3.44; N, 10.32%. IR (cm^{-1}): 3 318 (s), 3 255 (m), 3 198 (s), 2 970 (s), 2 927 (m), 2 880 (m), 2 052 (s), 1 621 (s), 1 544 (s), 1 460 (m), 1 390 (m), 1 343 (w), 1 293 (w), 1 210 (w), 1 072 (w), 946 (m), 889 (w), 715 (m).

1.4 X-ray crystallography

Single-crystal X-ray diffraction data for complexes **1** and **2** were collected in Beijing Synchrotron Radiation Facility (BSRF) beamline 3W1A which mounted with a MARCCD-165 detector ($\lambda=0.072\ 00\ \text{nm}$) with storage ring working at 2.5 GeV. In the process, the crystals were protected by liquid nitrogen at 100(2) K. Data were collected by the MARCCD and processed using HKL 2000^[22]. Absorption corrections were applied by using the multi-scan program SCALEPACK^[22]. All the structures were solved by the direct methods and refined by the full-matrix least-squares technique using the SHELXL-2014^[23] with all non-hydrogen atoms refined anisotropically. Hydrogen atoms attached to C and N atoms were added theoretically and treated as riding on the concerned atoms. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters. Further crystallographic data and structural refinement details are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

CCDC: 1437794, **1**; 1437795, **2**.

Table 1 Crystallographic data and structure refinement for **1** and **2**

	1	2
Formula	$\text{C}_8\text{H}_{14}\text{Cu}_2\text{I}_2\text{N}_6$	$\text{C}_8\text{H}_{14}\text{Cu}_2\text{N}_3\text{I}$
Formula weight	575.13	406.20
Crystal system	Monoclinic	Tetragonal
Space group	$P2_1/c$	$I4_1/a$
a / nm	0.954 7(1)	1.625 3(2)
b / nm	1.187 3(2)	1.625 3(2)
c / nm	1.494 9(5)	1.907 8(4)
β / ($^\circ$)	111.23(3)	
V / nm^3	1.579 5(7)	5.039 5(1)
Crystal size / mm	0.45× 0.40× 0.40	0.05× 0.04× 0.03
Z	4	16
D_c / ($\text{g}\cdot\text{cm}^{-3}$)	2.419	2.142
μ / mm^{-1}	6.59	5.794
$F(000)$	1 072	3 104
θ range / ($^\circ$)	2.9~26.0	2.51~25.05
Goodness-of-fit on F^2	1.41	1.046
Reflection collected, unique	3 075, 3 067	2 234, 1 940
R_{int}	0.017	0.028 7
R_1, wR_2 [$I > 2\sigma(I)$]	0.019 1, 0.058 6	0.032 9, 0.089 2
R_1, wR_2 (all data)	0.020 9, 0.072 5	0.038 6, 0.092 8
$(\Delta/\sigma)_{\text{max}}$	0.002	0.004
Largest diff peak and hole / ($\text{e}\cdot\text{nm}^{-3}$)	1 180, -1 580	697, -1 880

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$) of complexes **1** and **2**

1					
Cu(1)-N(1)	0.201 2(3)	Cu(1)-N(4)	0.206 3(3)	Cu(1)-I(1)	0.268 9(0)
Cu(1)-I(2)	0.267 1(1)	Cu(2)-N(2)	0.200 1(3)	Cu(2)-I(1)	0.258 0(1)
Cu(2)-I(2) ⁱ	0.252 3(1)	Cu(1)⋯Cu(2) ⁱ	0.288 4(1)	Cu(2)⋯Cu(1) ⁱ	0.288 4(1)
Cu(2)-I(1)-Cu(1)	81.61(2)	Cu(2) ⁱ -I(2)-Cu(1)	67.41(3)	N(1)-Cu(1)-N(4)	120.04(1)
N(1)-Cu(1)-I(2)	110.45(9)	N(4)-Cu(1)-I(2)	103.08(8)	N(1)-Cu(1)-I(1)	102.81(9)
N(4)-Cu(1)-I(1)	104.16(9)	I(2)-Cu(1)-I(1)	116.90(3)	N(1)-Cu(1)-Cu(2) ⁱ	88.55(9)
N(4)-Cu(1)-Cu(2) ⁱ	149.84(8)	I(2)-Cu(1)-Cu(2) ⁱ	53.84(2)	I(1)-Cu(1)-Cu(2) ⁱ	75.91(3)
N(2)-Cu(2)-I(2) ⁱ	128.18(9)	N(2)-Cu(2)-I(1)	105.90(8)	I(2) ⁱ -Cu(2)-I(1)	122.09(3)
N(2)-Cu(2)-Cu(1) ⁱ	121.26(9)	I(2) ⁱ -Cu(2)-Cu(1) ⁱ	58.75(2)	I(1)-Cu(2)-Cu(1) ⁱ	112.17(2)
2					
Cu(1)-N(1)	0.191 5(4)	Cu(1)-I(1)	0.249 1(1)	Cu(1)⋯Cu(1) ⁱ	0.254 4(1)
Cu(1)-I(1) ⁱⁱ	0.259 9(1)	Cu(1)⋯Cu(1) ⁱⁱⁱ	0.261 1(1)	Cu(1)⋯Cu(1) ⁱⁱ	0.261 1(1)
Cu(1)-I(1) ⁱ	0.273 4(1)	Cu(2)-N(2) ⁱⁱⁱ	0.180 5(4)	Cu(2)-N(3) ^{iv}	0.180 8(4)
Cu(2)-I(1)	0.298 8(1)	I(1)-Cu(1) ⁱⁱⁱ	0.259 9(1)	I(1)-Cu(1) ⁱ	0.273 4(1)
N(1)-Cu(1)-I(1)	119.6(1)	N(1)-Cu(1)-Cu(1) ⁱ	137.22(11)	I(1)-Cu(1)-Cu(1) ⁱ	65.76(3)
N(1)-Cu(1)-I(1) ⁱⁱ	103.8(1)	I(1)-Cu(1)-I(1) ⁱⁱ	115.26(3)	Cu(1) ⁱ -Cu(1)-I(1) ⁱⁱ	111.2(1)
N(1)-Cu(1)-Cu(1) ⁱⁱⁱ	161.81(1)	I(1)-Cu(1)-Cu(1) ⁱⁱⁱ	61.19(2)	Cu(1) ⁱ -Cu(1)-Cu(1) ⁱⁱⁱ	60.83(1)
I(1) ⁱⁱ -Cu(1)-Cu(1) ⁱⁱⁱ	63.32(3)	N(1)-Cu(1)-Cu(1) ⁱⁱ	127.33(14)	I(1)-Cu(1)-Cu(1) ⁱⁱ	112.55(3)

Continued Table 2

N(1)-Cu(1)-I(1) ⁱ	90.8(1)	I(1)-Cu(1)-I(1) ⁱ	116.74(3)	Cu(1) ⁱ -Cu(1)-I(1) ⁱ	56.18(3)
I(1) ⁱⁱ -Cu(1)-I(1) ⁱ	107.43(2)	Cu(1) ⁱⁱⁱ -Cu(1)-I(1) ⁱ	105.09(2)	Cu(1) ⁱⁱⁱ -Cu(1)-I(1) ⁱ	58.13(2)
N(2) ⁱⁱⁱ -Cu(2)-N(3) ^{iv}	163.8(2)	N(2) ⁱⁱⁱ -Cu(2)-I(1)	96.10(15)	N(3) ^{iv} -Cu(2)-I(1)	95.79(15)
Cu(1)-I(1)-Cu(1) ⁱⁱⁱ	61.67(3)	Cu(1)-I(1)-Cu(1) ⁱ	58.06(3)	Cu(1) ⁱⁱⁱ -I(1)-Cu(1) ⁱ	58.55(3)
Cu(1)-I(1)-Cu(2)	75.49(2)	Cu(1) ⁱⁱⁱ -I(1)-Cu(2)	69.93(2)	Cu(1) ⁱ -I(1)-Cu(2)	121.86(2)

Symmetry codes: ⁱ $-x+1, -y, -z+1$; ⁱⁱ $-x+1, y+1/2, -z+1/2$; ⁱⁱⁱ $-x+1, y-1/2, -z+1/2$ for **1**; ⁱ $-x+2, -y+1/2, z$; ⁱⁱ $-y+5/4, x-3/4, -z+9/4$; ⁱⁱⁱ $y+3/4, -x+5/4, -z+9/4$; ^{iv} $-x+2, -y+1, -z+2$ for **2**.

2 Results and discussion

2.1 Syntheses of the complexes

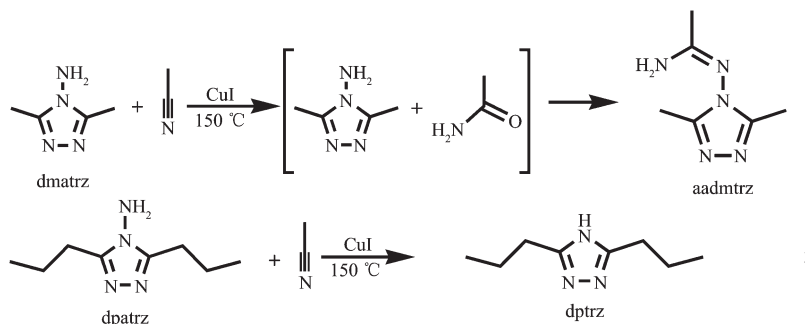
The aadmtrz ligand in complex **1** is *in situ* prepared from the condensation reaction of acetonitrile and 3,5-dimethyl-4-amino-1,2,4-triazole. This condensation reaction is observed between amino compounds and nitrile compounds under solvothermal conditions. The formation mechanism of *in situ* alkylation is suggested as follows: under high temperature and autogenous pressure, the hydrolysis breaks CH_3CN molecules into CH_3CONH_2 ; the nucleophilic substitution reaction of dmatrz and CH_3CONH_2 can generate aadmtrz, which attacks the nitrogen atom of dmatrz to form the 1-aminoethylidene group. The ligand in complex **2**, dptrz, is from the reductive deamination of the 3,5-propyl-4-amino-1,2,4-triazole ligand. The cuprous iodide in both reactions serves not only as the metal catalyst for the other triazole ligands, but also as the source of the cuprous-iodide aggregates.

2.2 Structure description

2.2.1 Structure of $\{[\text{Cu}_2(\text{aadmtrz})\text{I}_2] \cdot \text{CH}_3\text{CN}\}_n$ (**1**)

Complex **1** is a 2D coordination polymer with the monoclinic space group $P2_1/c$, and the asymmetric unit consists of two crystallographically independent cuprous ions, one aadmtrz group, two iodides, one

CH_3CN solvent molecule. As shown in Fig.1a, its monomer is composed of a Cu_4I_4 cluster and two tridentate aadmtrz molecules. The Cu(I) atoms are precisely coplanar, thus forming a parallelogram. Cu(1) shows tetrahedral coordination geometries $[\text{CuN}_2\text{I}_2]$ by two I ions (I(1), I(2)) and two nitrogen atoms (N(1), N(4)) from the different aadmtrz ligands. The distance of Cu(1)-N(1) (0.201 2(3) nm) is longer than that of Cu(1)-N(4) (0.206 3(3) nm), meanwhile the distance of Cu(1)-I(1) (0.268 9(1) nm) is also longer than that of Cu(1)-I(2) (0.267 1(1) nm). Cu(2) is in a slightly distorted $[\text{CuN}_2\text{I}_2]$ triangular planar site with one μ_2 -I(1) and two nitrogen atoms from different aadmtrz groups (N(2)ⁱⁱⁱ, N(3)^{iv}, Symmetry codes: ⁱⁱⁱ $y+1/4, -x+7/4, -z+3/4$; ^{iv} $-x+3/2, -y+3/2, -z+1/2$). The distances of Cu(2)-N (0.180 5(4) and 0.180 8(4) nm) are shorter than those of Cu(1)-N, and the distances of Cu(2)-I (0.257 8(1) and 0.252 2(1) nm) are shorter than that of Cu(1)-I (0.268 9(1) nm). The Cu(1)···Cu(2) interactions (0.288 4(1) nm) are crucial to build the Cu_4I_4 aggregates. The parallelogram Cu_4I_4 unit (Fig.1b) has an inversion center and is formed by four iodine atoms bridges four copper atoms in the μ_2 -bridging modes, generating an 8-membered ring that has the chair-chair conformation of cyclooctane. This chair-chair conformation is similar to those similar

Scheme 1 Syntheses of ligands of **1** and **2**

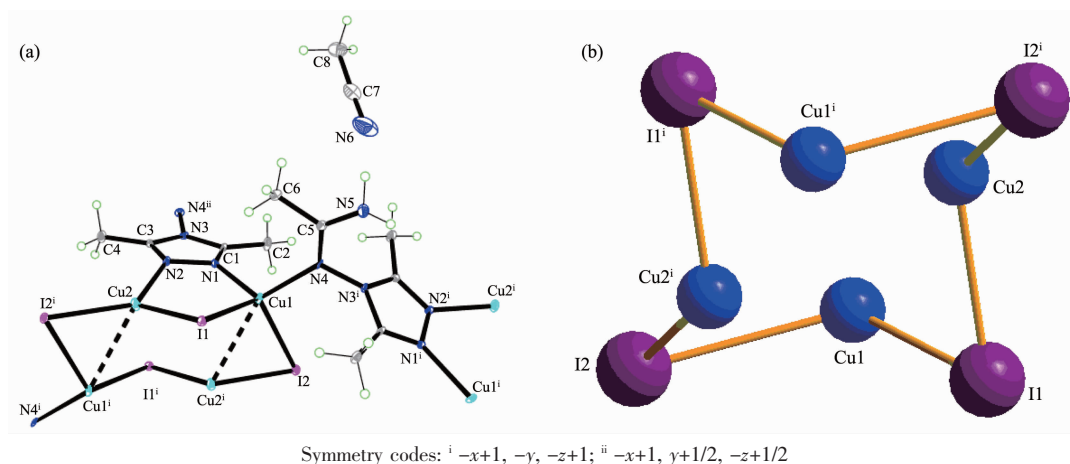


Fig.1 (a) ORTEP drawing of **1** with 30% thermal ellipsoids; (b) Basic building block of Cu_4I_4 cluster

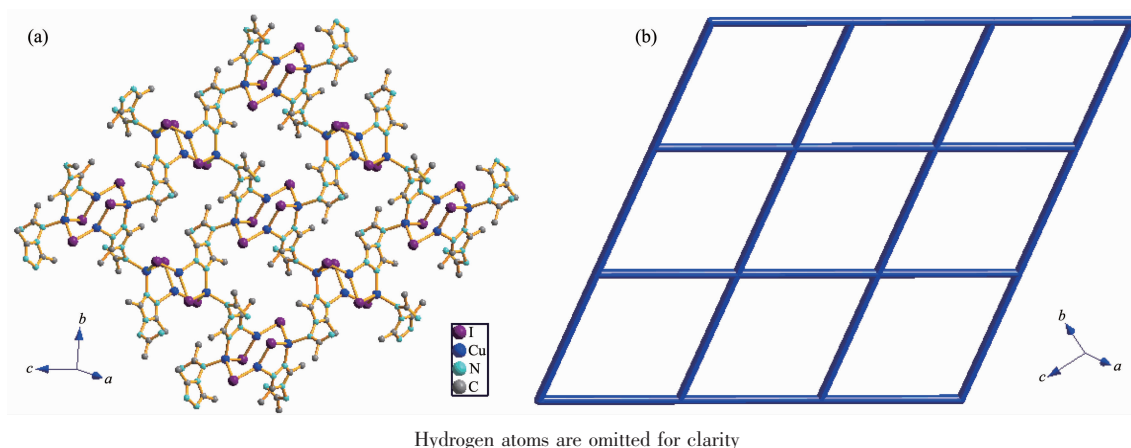


Fig.2 (a) View of the 2D network in **1**; (b) Topological representation of the 4-connected network in **1**

complexes such as $[\text{Cu}_2\text{I}_2(\text{aadtz})]_n$ ^[20].

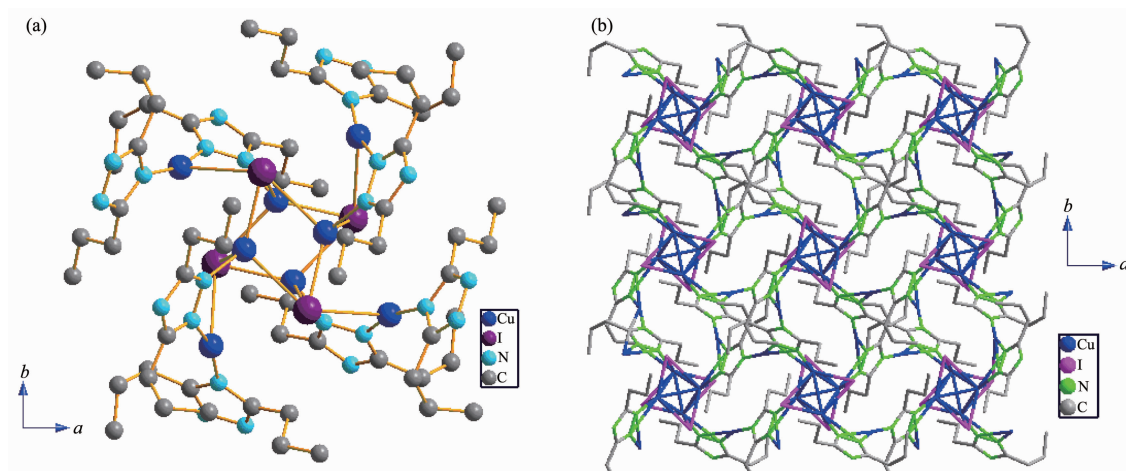
In this complex, each aadmtrz ligand bridges two Cu(I) atoms on the longer side of the Cu parallelogram through N(1) and N(2) nitrogen donors, while 4-substituent N(4) and N(5) atoms link an adjacent Cu_4I_4 unit to form a 2D network (Fig.2a). The overall structure of **1** can thus be simplified as a 2D (4,4) rhombic-grid network with 4-connecting node of the Cu_4I_4 aggregates (Fig.2b). The coplanar sheets of **1** are further built into a 3D supramolecular architecture through the hydrogen bonding interactions (Table 3).

Furthermore, complex **1** is different from previously reported $[\text{Cu}_4\text{I}_4(\text{C}_4\text{H}_8\text{N}_4)]$ ^[15] with the similar reaction, where the ligand 3,5-dimethyl-4-amino-1,2,4-triazole took part in the compound directly. This case is different from 3,5-diethyl-4-amino-1,2,4-triazole compounds^[20], where may attribute to the shorter $-\text{CH}_2$ in the 3,5-position of 1,2,4-triazole.

2.2.2 Structure of $[\text{Cu}_2(\text{dptrz})\text{I}]_n$ (**2**)

Complex **2** shows an interesting 3D porous structure with the tetragonal space group $I4_1/a$. As shown in Fig.3a, the asymmetric unit of complex **2** contains two crystallographically independent Cu(I) ions, one dptrz ligand, one iodide anions. Each Cu(I) or I(1) links three neighboring I(1) or Cu(1) to form a distorted Cu_4I_4 cubane unit (Fig.3b), which is similar to those reported Cu_4I_4 tetramer units^[24-25]. Each Cu(1) is tetrahedrally coordinated $[\text{CuNI}_3]$ by three I ions and a nitrogen from the bridging dptrz ligand. The distances of Cu(1)-I, Cu(1)-N and Cu...Cu are 0.249 1(1)~0.273 4(1), 0.191 4(4) and 0.254 4(1)~0.261 1(1) nm, respectively, which are shorter than those of isostructural complex $[\text{Cu}_2(\text{dtz})\text{I}]$ ^[20], due to the longer $-\text{CH}_2$ group in the ligand of **2**. Furthermore, these values are comparable to those found in other cubane-like $\text{Cu}_4\text{I}_4\text{L}_4$ complexes (L=nitrogen-containing ligand)^[26].

unit locates on the fourfold inversion axes), respectively (Fig.4a). Each helical chain along the c axis is further linked through Cu(1) of the Cu₄I₄ unit, forming a non-interpenetrating 3D framework (Fig.4b). Topologically, when the Cu₄I₄ SBU are depicted as four-connecting nodes, and dptrz ligands are regarded as three-connecting nodes, complex **2** can be defined as a (3,4)-connected framework, which is similar to the isostructural [Cu₂I(dtz)]_n^[20]. Interesting, PLATON calculations^[27] show that the potential solvent area volume of **2** is estimated to be 0.982 3 nm³, 19.5% of the unit cell volume (5.039 6 nm³), which may hold



Hydrogen atoms are omitted for clarity

Fig.4 (a) Local coordination environment around the Cu_4I_4 cluster in **2**; (b) View of a 3D framework in **2**

10 H_2O molecules. This may indicate that the construction of the cage-like motifs is accomplished by the $-(\text{CH}_2)_n$ spacers of 3,5-dialkyl-1,2,4-triazole.

2.3 PXRD analysis

As shown in Fig.5, the experiment PXRD patterns for **1** and **2** are in agreement with the simulated ones from the single-crystal X-ray data. The result indicates that the growth of crystals of both complexes is well-proportioned and consistent. The structures are representative of the bulk materials.

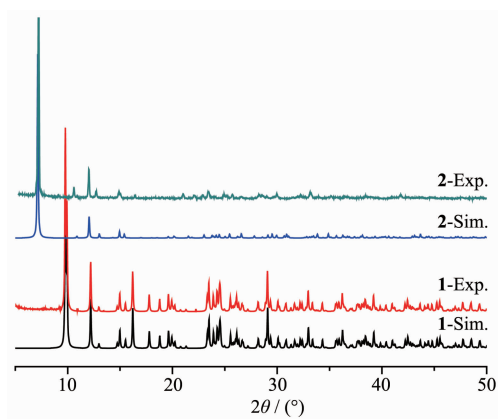


Fig.5 PXRD patterns of complexes **1** and **2**

2.4 Luminescence properties

The emission spectra for **1** and **2** and the ligands dmatrz, dpatrz in the solid state at room temperature are shown in Fig.6. The emission peaks of luminescence of ligands dmatrz, dpatrz are the same at 419 nm. It can be observed that complex **1** and **2** exhibit green emission bands at 498, 493 nm upon excitation at 266, 254 nm, respectively. The emission

spectra for both complexes may be assigned, in character, to iodide(X)-to-ligand charge transfer (XLCT).

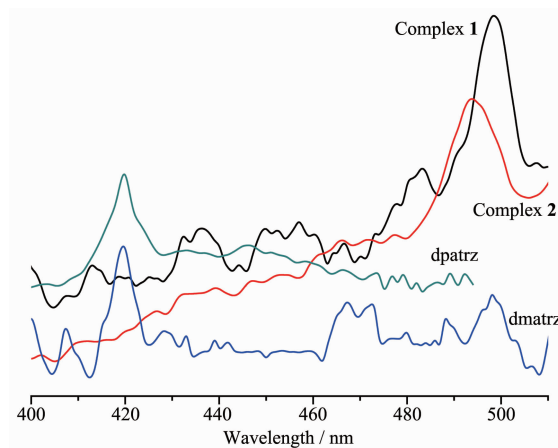


Fig.6 Emission spectra of the ligands dmatrz, dpatrz, and complexes **1~2**

3 Conclusions

In summary, two cuprous halide coordination polymers containing Cu_4I_4 clusters layers as structural motifs have been successfully synthesized, which are further linked by 1,2,4-triazole to form extended 2D 4-connected grid frameworks (**1**) and 3D (3,4)-connected (**2**) frameworks with 19.5% porosity. The Cu_4I_4 cluster in complex **1** is an inorganic 8-membered ring with a chair-chair conformation, while the one in complex **2** is a distorted cubane. The large spacers of alkyl side chains of 4-aminotriazole may accomplished the construction of the cage-like motifs. This provides a method to design the porous metal-organic frameworks

(PMOFs). Both complexes exhibit similar green photoluminescence at room temperature in the solid state.

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Supporting information is available at <http://www.wjhxzb.cn>

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