



Synthesis, structure and fluorescence of novel cadmium(II) and silver(I) complexes with in situ ligand formation of 1-(5-tetrazolyl)-4-(imidazol-1-ylmethyl)benzene

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ABSTRACT

Hydrothermal reactions of cadmium(II) or silver(I) salt, NaN_3 , 4-(imidazol-1-ylmethyl)benzonitrile (IBN) yield three coordination complexes, $[\text{Cd}(\text{L})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**1**), $[\text{Cd}_3(\text{L})_5(\text{OH})]$ (**2**) and $[\text{Ag}_2(\text{L})_2]$ (**3**) where HL = 1-(5-tetrazolyl)-4-(imidazol-1-ylmethyl)benzene. The crystal structure analysis revealed that **1** has 1D hinged-chain structure containing 24-membered ring with a $\text{Cd} \cdots \text{Cd}$ intra-chain distance of 13.18 Å, while **2** is 1D ladder-like chain with Cd_3O core. However, the complex **3** is a 3D 4-connected framework with Schläfli symbol of $(4^2 \cdot 6^3 \cdot 8)(4^3 \cdot 6^2 \cdot 8)$. The L^- ligand was found to show four different coordination modes in **1–3**, as 2-, 3- and 4-connector, respectively. The results indicate that the coordination modes of the ligand and metal centers with different coordination geometry have great influence on the structures of the complexes. In addition, the photoluminescence of the complexes were studied in the solid state at room temperature.

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1. Introduction

In recent years, organic ligands with tetrazole functional group were greatly used in coordination chemistry for construction of metal-organic frameworks (MOFs), not only due to its diverse coordination modes [1–7], but also because of its metal complexes with fancy topologies and potential applications in varied fields such as gas storage, magnetism, pyroelectricity, ferroelectricity, luminescence, second harmonic generation (SHG) effect [8–16]. Sharpless and his coworkers developed a new, safe and convenient method for synthesis of 5-substituted-1H-tetrazoles through 2+3 cycloaddition reaction of organic nitriles and azide salt using Lewis acid as catalyst. A number of MOFs with in situ tetrazolate-containing ligand formation were reported [17–19], for example a new three-dimensional (3D) Cd(II) coordination polymer with 5-methyl-tetrazolate formed in situ from acetonitrile and azide has been obtained recently [19a].

On the other hand, we focus our attention on construction and property of MOFs with imidazole-containing organic ligands and found that such kind of ligands is versatile [20–23]. For example, 1-(1-imidazolyl)-4-(imidazol-1-ylmethyl)benzene (IIMB) was

found to be efficient for construction of MOFs which are usually one-dimensional (1D) chains or two-dimensional (2D) networks since each IIMB only has two coordination sites and one kind of coordination mode [20,21]. There will be more coordination sites and modes if one of the two imidazole groups in IIMB is changed to tetrazole group. Taking into account of this, a new ligand 1-(5-tetrazolyl)-4-(imidazol-1-ylmethyl)benzene (HL) (Scheme 1) was considered. We report herein three novel coordination polymers $[\text{Cd}(\text{L})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ (**1**), $[\text{Cd}_3(\text{L})_5(\text{OH})]$ (**2**) and $[\text{Ag}_2(\text{L})_2]$ (**3**), in which the ligand L^- was generated in situ by 2+3 cycloaddition reaction of the corresponding organic nitriles and azide salt and the Cd(II)/Ag(I) salts acted as the Lewis acid catalyst. The nitrogen atoms of the tetrazole group have good coordination capacities, and thus the HL is a multifunctional ligand with distinct coordination modes as observed in complexes **1–3** (Scheme 2).

2. Experimental section

All commercially available chemicals are of reagent grade and were used as received without further purification. 4-(Imidazol-1-ylmethyl)benzonitrile (IBN) was prepared according to the previously reported method [22,23]. Elemental analysis of C, H and N were taken on a Perkin-Elmer 240C elemental analyzer at

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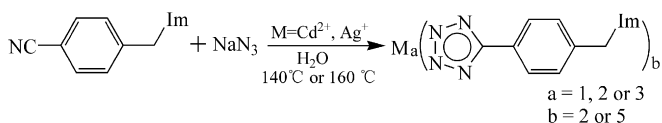
the analysis center of Nanjing University. Infrared (IR) spectra were recorded on a Bruker Vector22 FT-IR spectrophotometer by using KBr pellets. The luminescent spectra for the powdered solid samples were recorded at room temperature on an Aminco Bowman Series 2 spectrofluorometer with a xenon arc lamp as the light source. In the measurements of emission and excitation spectra the pass width is 5 nm. All the measurements were carried out under the same experimental conditions.

2.1. Synthesis of $[Cd(L)_2(H_2O)_2] \cdot 3H_2O$ (**1**)

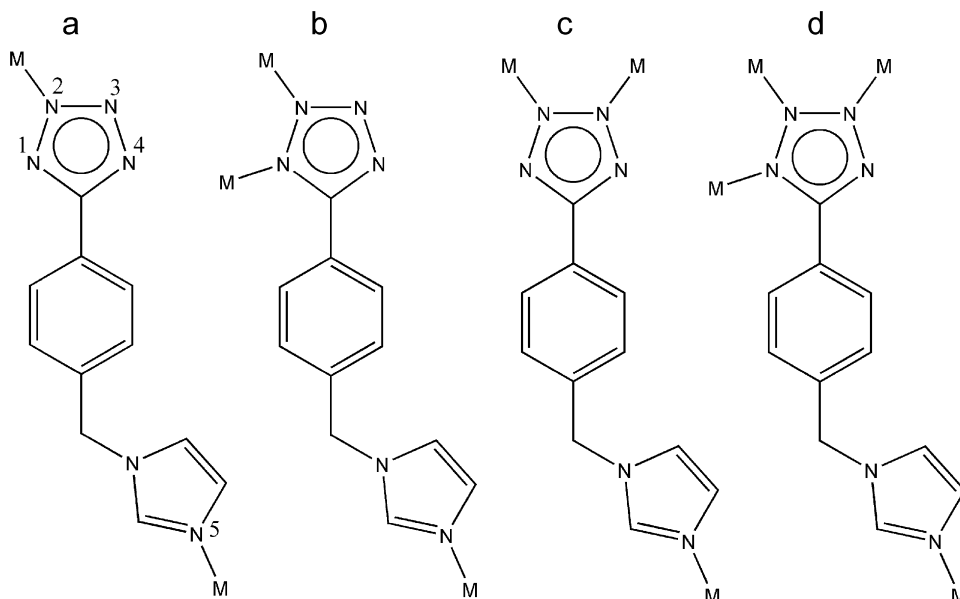
Hydrothermal treatment of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.0419 g, 0.1 mmol), IBN (0.0183 g, 0.1 mmol), NaN_3 (0.0078 g, 0.12 mmol) and water (8 ml) in an autoclave, sealed and placed in oven over three days at 140 °C, yielded colorless platelet crystalline product. The yield of **1** was about 60% based on the amount of IBN consumed. Anal. Calcd. for $C_{22}H_{26}CdN_{12}O_5$ (**1**) (%): C, 40.59; H, 4.03; N, 25.82; Found: C, 40.43; H, 3.89; N, 26.05. IR (KBr, cm^{-1}): 3421(s), 1625(m), 1515(s), 1443(s), 1285(w), 1237(m), 1109(s), 1083(s), 1009(m), 935(m), 821(m), 742(s), 654(w), 527(w), 467(w).

2.2. Synthesis of $[Cd_3(L)_5(OH)]$ (**2**)

The complex **2** was prepared in a manner similar to that for **1** except that $Cd(ClO_4)_2 \cdot 6H_2O$ was replaced by CdI_2 . Colorless block single crystals were separated and washed by water and ethanol for several times with a yield 43% based on the amount of IBN consumed. Anal. Calcd. for $C_{55}H_{54}Cd_3N_{30}O_5$ (**2**) (%): C, 42.55; H, 3.51; N, 27.07; Found: C, 42.35; H, 3.73; N, 27.13. IR (KBr, cm^{-1}): 3384(s), 1660(s), 1613(m), 1517(m), 1429(m), 1397(m), 1234(m), 1109(m), 1086(m), 1010(w), 822(w), 741(s), 653(m), 615(w), 514(w).



Scheme 1. In situ hydrothermal syntheses of complexes.



Scheme 2. Coordination mode of L^- ligand in complexes **1–3**, the numbers in mode (a) refer to the numbering of coordinating nitrogen atoms.

2.3. Synthesis of $[Ag_2(L)_2]$ (**3**)

A mixture of $AgNO_3$ (0.0170 g, 0.1 mmol), IBN (0.0183 g, 0.1 mmol), and NaN_3 (0.0078 g, 0.12 mmol) in H_2O (8 ml) was sealed in a 20 ml Teflon lined stainless steel container and heated at 160 °C for three days. After the sample was cooled to room temperature, light-brown platelet crystals of **3** were collected by filtration and washed by water and ethanol for several times with a yield of 56% based on IBN. Anal. Calcd. for $C_{22}H_{18}Ag_2N_{12}$ (**3**) (%): C, 39.66; H, 2.72; N, 25.23. Found: C, 39.55; H, 2.84; N, 25.43. IR (KBr, cm^{-1}): 3442 (s), 1636 (m), 1518 (m), 1446(s), 1430 (m), 1228 (m), 1109 (m), 1079 (m), 1007 (w), 823 (m), 755 (m), 655 (w), 614 (w).

2.4. X-ray crystal structure determinations

The X-ray diffraction measurements for **1** and **2** were performed on the Bruker Smart Apex CCD diffractometer with graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The diffraction data were integrated by using the SAINT program [24]. Empirical absorption corrections were applied to the data using the SADABS program [25]. The structures were solved by direct methods and refined by full-matrix least-square on F^2 using the SHELXTL program [26]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were generated geometrically. Atoms O3 and O4 in complex **2** disordered into two positions with the site occupancy factors of 0.64(2), 0.36(2) and 0.59(2), 0.41(2), respectively. And atoms C32 and C33 in **2** also split into two positions, and each has a site occupancy of 0.44(8) and 0.56(8). The crystallographic data for **3** were collected using a Rigaku RAXIS-RAPID imaging plate diffractometer at $-73 \text{ }^\circ\text{C}$, with graphite-monochromated $MoK\alpha$ radiation ($\lambda = 0.71075 \text{ \AA}$). The structure was solved by direct methods with SIR92 and expanded using Fourier techniques [27,28]. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2 . The hydrogen atoms were generated geometrically. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation [29]. Details of the crystal parameters, data collection and refinements for **1–3** are summarized in Table 1. Selected bond lengths and angles for

Table 1
Crystallographic data for complexes **1–3**.

	1	2	3
Empirical formula	C ₂₂ H ₂₆ CdN ₁₂ O ₅	C ₅₅ H ₅₄ Cd ₃ N ₃₀ O ₅	C ₂₂ H ₁₈ Ag ₂ N ₁₂
Formula weight	650.95	1552.48	666.22
Temperature (K)	293(2)	293(2)	200
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	C2/c	P-1	Pbca
a (Å)	24.7213(17)	12.2762(13)	8.8049(15)
b (Å)	9.1269(6)	12.6058(13)	12.206(3)
c (Å)	13.8765(10)	22.125(2)	43.845(7)
α (deg)	90	96.347(2)	90
β (deg)	122.2880(10)	90.706(2)	90
γ (deg)	90	113.790(2)	90
V (Å ³)	2646.8(3)	3107.6(6)	4712.2(15)
Z	4	2	8
Dcalc/(g·cm ⁻³)	1.634	1.659	1.878
F(000)	1320	1556	2624
θ range (deg)	1.95–25.00	1.78–25.00	3.00–27.49
Reflections collected	6484	15401	38708
Independent reflections	2328	10738	5402
Goodness-of-fit on F ²	1.098	1.114	1.034
R [I > 2σ(I)] ^a	0.0299	0.0899	0.0417
wR ₂ [I > 2σ(I)] ^b	0.0844	0.1843	0.0731

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2] / [\sum w(F_o)^2]^{1/2}, \text{ where } w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]. P = (F_o^2 + 2F_c^2)/3.$$

compounds **1–3** are listed in Table 2. Further details are provided in the Supporting information in the Appendix A.

3. Results and discussion

3.1. Crystal structure of complex [Cd(L)₂(H₂O)₂]·3H₂O (**1**)

The results of crystallographic analysis revealed that complex **1** crystallizes in monoclinic space group C2/c (Table 1). As shown in Fig. 1a, the Cd(II) atom sits on an inversion center and is coordinated by two tetrazole nitrogen atoms (N12, N12A) and two imidazole nitrogen atoms (N42A, N42B) from four different L⁻ ligands with N–Cd1–N bond angles varying from 87.97(8)° to 180.0° and Cd1–N bond distances of 2.240(2) and 2.402(2) Å (Table 2). Two additional positions of each Cd(II) are occupied by terminal water molecules in a *trans* arrangement with O–Cd1–O bond angle of 180.0° and Cd1–O bond length of 2.369(3) Å (Table 2). Therefore the coordination environment of the Cd(II) atom can be described as a distorted octahedron with an N₄O₂ donor set. On the other hand, each L⁻ ligand links two Cd(II) atoms to form an infinite 1D chain containing 24-membered M₂L₂ rings with a Cd...Cd intra-chain distance of 13.18 Å (Fig. 1b). It is clear that the coordination mode of L⁻ ligand in **1** is η²-(N², N⁵) [Mode (a) in Scheme 2], which is similar to the one observed in reported ligand IIMB [20–21,30]. In crystal packing diagram of complex **1**, the 1D hinged chains pack together via O–H...N, O–H...O and C–H...N hydrogen bonds to generate 3D structure (Fig. 1c), which further consolidate the structure of the complex. The hydrogen bonding data are summarized in Table 3.

3.2. Crystal structure of complex [Cd₃(L)₅(OH)] (**2**)

When CdI₂, a stronger Lewis acid than Cd(ClO₄)₂·6H₂O, was taken into the reaction with IBN and NaN₃, a new coordination polymer **2** with different structure was isolated. It is interesting to find that there are three different Cd(II) atoms in the asymmetric

unit of **2** and the local coordination environment around the Cd(II) centers (Cd1, Cd2, Cd3) is depicted in Fig. 2a with the atom numbering scheme. The three Cd(II) centers are linked together by a capped μ₃-O (O1) of the hydroxyl group with Cd1–O1 = 2.374(7) Å, Cd2–O1 = 2.217(6) Å, and Cd3–O1 = 2.319(6) Å (Table 2) to form a trinuclear Cd₃O core with Cd...Cd distances of 3.814 Å (Cd1...Cd2), 3.760 Å (Cd2...Cd3), and 3.774 Å (Cd1...Cd3), respectively. The Cd1 atom is six coordinated by two nitrogen atoms (N12, N24A) of the imidazole units, three nitrogen atoms (N3A, N8A, N20) of the tetrazole units from five distinct L⁻ ligands and the μ₃-O (O1) of the hydroxyl group. The bond lengths of Cd1–N are in the range of 2.276(9)–2.425(9) Å. The coordination geometry of Cd1 could be described as a slightly distorted octahedral (Scheme S1), with the N–Cd1–N coordination angles varying from 86.0(3)° to 172.4(3)° and the N–Cd1–O ones in the range of 77.3(3)°–177.3(3)° (Scheme S1, Table 2). However, Cd2 is five-coordinated with a slightly distorted trigonal bipyramid coordination geometry by four different L⁻ ligands

Table 2
Selected bond lengths (Å) and bond angles (deg) for complexes **1–3**.

[Cd(L) ₂ (H ₂ O) ₂]·3H ₂ O (1)			
Cd(1)–N(42)#1	2.240(2)	Cd(1)–O(1)	2.369(3)
Cd(1)–N(12)	2.402(2)		
N(42)#1–Cd(1)–N(42)#2	180.0	N(42)#1–Cd(1)–O(1)	92.47(10)
N(42)#2–Cd(1)–O(1)	87.53(10)	O(1)–Cd(1)–O(1)#3	180.0
N(42)#1–Cd(1)–N(12)	92.03(8)	N(42)#2–Cd(1)–N(12)	87.97(8)
O(1)–Cd(1)–N(12)	86.65(10)	O(1)#3–Cd(1)–N(12)	93.35(10)
N(12)–Cd(1)–N(12)#3	180.0		
[Cd ₃ (L) ₅ (OH)] (2)			
Cd(1)–N(12)#4	2.276(9)	Cd(1)–N(24)#5	2.295(9)
Cd(1)–N(8)	2.320(9)	Cd(1)–N(20)	2.355(9)
Cd(1)–O(1)	2.374(7)	Cd(1)–N(3)	2.425(9)
Cd(2)–O(1)	2.217(6)	Cd(2)–N(30)#6	2.266(9)
Cd(2)–N(26)	2.274(10)	Cd(2)–N(19)	2.354(8)
Cd(2)–N(15)	2.388(8)	Cd(3)–N(18)#4	2.258(9)
Cd(3)–N(6)#7	2.293(9)	Cd(3)–O(1)	2.319(6)
Cd(3)–N(2)	2.340(9)	Cd(3)–N(14)	2.348(8)
Cd(3)–N(9)	2.352(9)		
N(12)#4–Cd(1)–N(24)#5	93.7(3)	N(12)#4–Cd(1)–N(8)	100.2(4)
N(24)#5–Cd(1)–N(8)	165.4(3)	N(12)#4–Cd(1)–N(20)	94.2(3)
N(24)#5–Cd(1)–N(20)	90.6(3)	N(8)–Cd(1)–N(20)	92.6(3)
N(12)#4–Cd(1)–O(1)	177.3(3)	N(24)#5–Cd(1)–O(1)	88.8(3)
N(8)–Cd(1)–O(1)	77.3(3)	N(20)–Cd(1)–O(1)	84.9(3)
N(12)#4–Cd(1)–N(3)	92.8(3)	N(24)#5–Cd(1)–N(3)	86.0(3)
N(8)–Cd(1)–N(3)	89.1(3)	N(20)–Cd(1)–N(3)	172.4(3)
O(1)–Cd(1)–N(3)	88.3(2)	O(1)–Cd(2)–N(30)#6	125.7(3)
O(1)–Cd(2)–N(26)	110.2(3)	N(30)#6–Cd(2)–N(26)	124.0(4)
O(1)–Cd(2)–N(19)	89.1(3)	N(30)#6–Cd(2)–N(19)	91.0(3)
N(26)–Cd(2)–N(19)	93.3(3)	O(1)–Cd(2)–N(15)	89.0(3)
N(30)#6–Cd(2)–N(15)	87.6(3)	N(26)–Cd(2)–N(15)	90.2(3)
N(19)–Cd(2)–N(15)	176.4(3)	N(18)#4–Cd(3)–N(6)#7	95.9(3)
N(18)#4–Cd(3)–O(1)	95.6(3)	N(6)#7–Cd(3)–O(1)	168.3(3)
N(18)#4–Cd(3)–N(2)	90.4(3)	N(6)#7–Cd(3)–N(2)	91.6(3)
N(18)#4–Cd(3)–N(14)	88.3(3)	O(1)–Cd(3)–N(2)	86.2(3)
O(1)–Cd(3)–N(14)	90.1(3)	N(14)–Cd(3)–N(9)	91.1(3)
N(2)–Cd(3)–N(9)	89.7(3)	N(6)#7–Cd(3)–N(14)	92.4(3)
O(1)–Cd(3)–N(9)	77.0(3)	N(6)#7–Cd(3)–N(9)	91.5(3)
N(18)#4–Cd(3)–N(9)	172.6(3)	N(2)–Cd(3)–N(14)	175.9(3)
[Ag ₂ (L) ₂] (3)			
Ag(1)–N(42)#8	2.263(4)	Ag(1)–N(14)#9	2.387(3)
Ag(1)–N(12)	2.328(3)	Ag(1)–N(113)#9	2.316(3)
Ag(2)–N(142)#10	2.297(3)	Ag(2)–N(13)	2.291(3)
Ag(2)–N(112)#9	2.325(3)	Ag(2)–N(114)	2.296(3)
N(42)#8–Ag(1)–N(113)#9	123.35(12)	N(12)–Ag(1)–N(14)#9	120.55(12)
N(113)#9–Ag(1)–N(14)#9	113.31(11)	N(42)#8–Ag(1)–N(12)	102.62(13)
N(42)#8–Ag(1)–N(14)#9	100.08(12)	N(113)#9–Ag(1)–N(12)	98.04(11)
N(114)–Ag(2)–N(112)#9	122.61(12)	N(142)#10–Ag(2)–N(112)#9	97.13(12)
N(13)–Ag(2)–N(114)	110.41(11)	N(114)–Ag(2)–N(142)#10	106.52(12)
N(13)–Ag(2)–N(142)#10	118.61(12)	N(13)–Ag(2)–N(112)#9	101.85(11)

Symmetry transformations used to generate equivalent atoms: #1 x+1/2, y+1/2, z; #2 -x, -y, -z; #3 -x+1/2, -y+1/2, -z; #4 x-1, y, z; #5 -x, -y+1, -z+1; #6 -x+1, -y+1, -z+1; #7 x+1, y, z; #8 -x+1, y-1/2, -z+1/2; #9 -x+3/2, y-1/2, z; #10 -x+2, -y+1, -z+1.

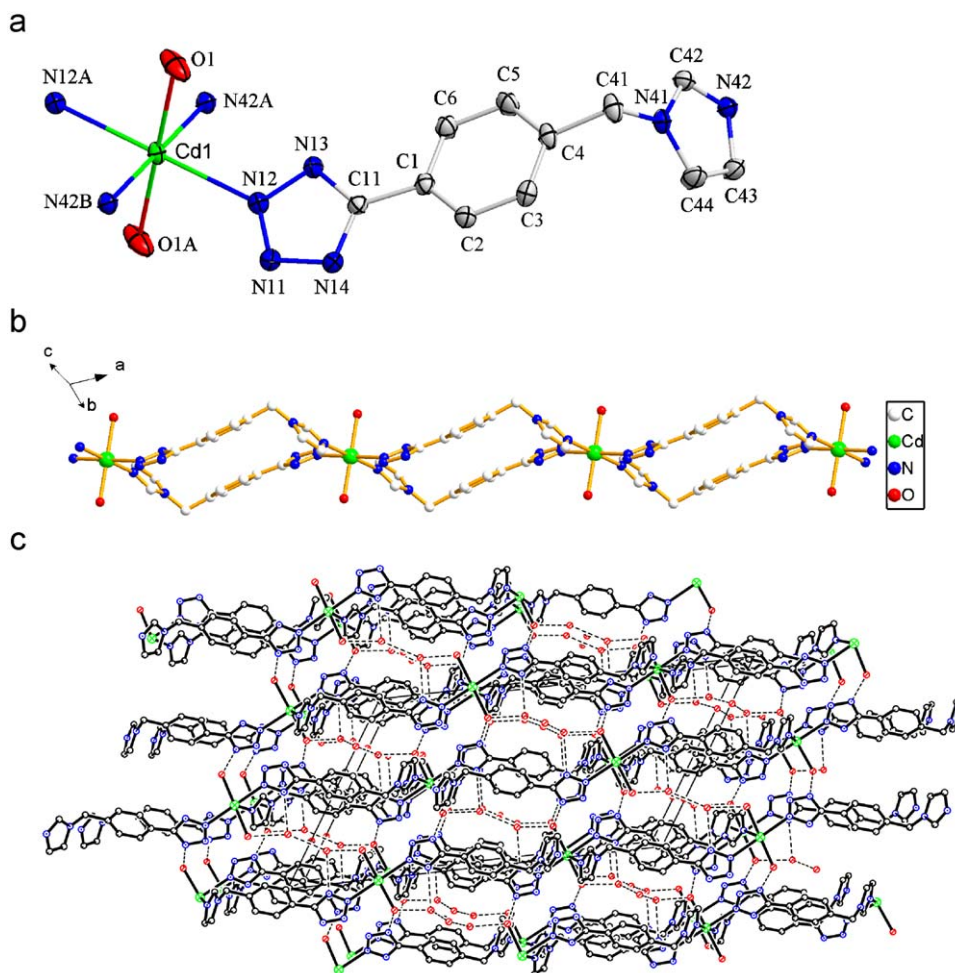


Fig. 1. (a) Coordination environment of center Cd(II) atom in complex **1** with the ellipsoids drawn at the 30% probability level, hydrogen atoms and uncoordinated water molecules were omitted for clarity. (b) Infinite 1D ribbon-like chain of **1** with 24-membered rings. (c) The 3D structure of **1** linked by hydrogen bonds between the adjacent chains.

Table 3
Distance (Å) and angles (deg) of hydrogen bonding for complexes **1–3**^a.

D–H...A	Distance (D...A)(Å)	Angle (D–H–A) (deg)
[Cd(L)₂(H₂O)₂]·3H₂O (1)		
O(1)–H(1A)...O(2)	2.684(6)	164(4)
O(1)–H(1B)...N(14)#1	2.900(4)	172(6)
C(44)–H(9)...N(14)#2	3.264(4)	142
[Cd₃(L)₅(OH)] (2)		
O(1)–H(1A)...O(5)#3	3.185(15)	165
C(9)–H(9A)...N13#3	3.183(15)	142
O(20)–H(20A)...N(4)#4	3.362(15)	143
C(31)–H(31A)...O(5)	3.191(17)	141
C(41)–H(41A)...O(2)#5	3.01(4)	150
C(42)–H(42A)...N(21)#6	3.333(16)	140
[Ag₂(L)₂] (3)		
C(102)–H(10)...N(111)#7	3.363(5)	140
C(142)–H(16)...N(111)#8	3.395(5)	139

^a Symmetry transformation used to generate equivalent atoms: #1 1/2–x, –1/2+y, 1/2–z; #2 –x, y, 1/2–z; #3 –1+x, y, z; #4 1+x, y, z; #5 1–x, 1–y, 1–z; #6 –x, 1–y, 1–z; #7 3/2–x, –1/2+y, z; #8 1/2+x, 3/2–y, 1–z. D: donor; A: acceptor.

using their tetrazole nitrogen atoms (N15, N19, N26A) and imidazole nitrogen atom (N30) with Cd2–N bond distances varying from 2.258(9) to 2.388(8)Å, and the μ_3 -O (O1) of the hydroxyl group (Scheme S1, Table 2). The Cd3 atom is

also six-coordinated by two imidazole nitrogen atoms (N6, N18A) and three tetrazole nitrogen atoms (N2A, N9A, N14) from distinct five L[–] ligands with the bond lengths of Cd3–N ranging from 2.258(9) to 2.352(9) Å (Table 2), and the μ_3 -O (O1) of the hydroxyl group. The coordination geometry of Cd3 atom is a slightly distorted octahedron with N–Cd3–N bond angles in the range of 88.3(3)°–176.4(3)° and N–Cd3–O bond angles varying from 77.0(3)° to 168.3(3)° (Scheme S1, Table 2).

As is shown in Fig. 2b, the Cd₃O core was connected by three L[–] ligands to complete 1D triple-stranded hinged chain with a distance of 6.91 Å between the two adjacent Cd₃O cores. Such 1D triple-stranded chains are further pillared by the L[–] ligands to form a new 1D ladder-like chain (Fig. 2c), with a distance of 11.12 Å between the two adjoining 1D triple-stranded chains. Furthermore, the 1D “ladder-like” chains in complex **2** are linked through O–H...O between the hydroxyl group and water molecule as well as C–H...N and C–H...O hydrogen bonds (Table 3) to form 3D framework as illustrated in Figure S1.

It is noteworthy that in addition to the η^2 –(N², N⁵) coordination mode of L[–] ligand observed in complex **1** [Mode (a) in Scheme 2], the L[–] ligands in compound **2** adopted another two different coordination modes: η^3 (N¹, N², N⁵) [Mode (b) in Scheme 2], η^3 (N², N³, N⁵) [Mode (c) in Scheme 2]. It is clear that the Cd₃O core and three different L[–] ligand coordination modes [Modes (a), (b) and (c)] in compound **2** are completely distinct with those in complex **1**, namely mononuclear Cd(II) unit and one L[–] ligand

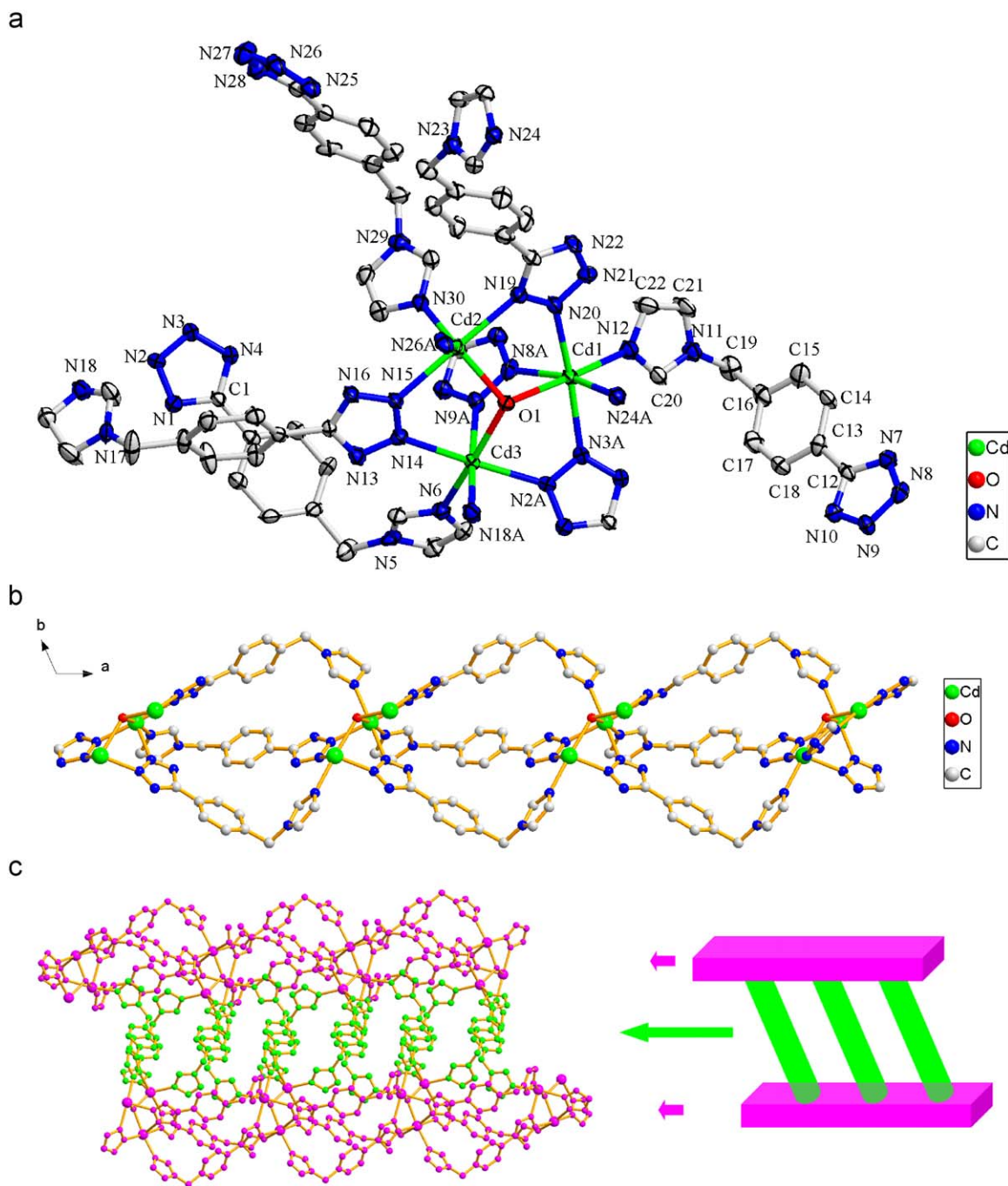


Fig. 2. (a) Coordination environment of center Cd(II) atoms of **2** with the ellipsoids drawn at the 30% probability level, hydrogen atoms were omitted for clarity. (b) The 1D infinite chain with Cd₃O core linked by L ligands. (c) Scheme representation of 1D "ladder-like" chain.

coordination mode. The results imply that the strength of the Lewis acid may have subtle influence on the structure of the complexes.

3.3. Crystal structure of complex [Ag₂(L)₂] (**3**)

The result of the X-ray crystallographic analysis revealed that complex **3** crystallized in the orthorhombic space group of *Pbca*. In the asymmetric unit of **3**, there are two crystallographically different Ag(I) atoms, namely Ag1 and Ag2, and two L⁻ ligands. As illustrated in Fig. 3a, the Ag1 atom is four

coordinated with a slightly distorted tetrahedral coordination geometry by one imidazole nitrogen atom (N42A), and three tetrazole nitrogen atoms (N11, N14A, N114). The Ag1–N bond lengths are in the range of 2.263(4)–2.387(3) Å, and the coordination angles around Ag1 vary from 98.04(11)° to 123.35(12)° (Table 2). Similarly, the Ag2 center is also four coordinated by four nitrogen atoms from four distinct L⁻ ligands in a slightly distorted tetrahedral geometry, one from the imidazole unit and the other three from the tetrazole units. The average coordination angle around Ag2 is 109.5°, and the average Ag2–N bond distance is 2.302 Å. The adjacent Ag(I) atoms are co-bridged by the tetrazole nitrogen atoms

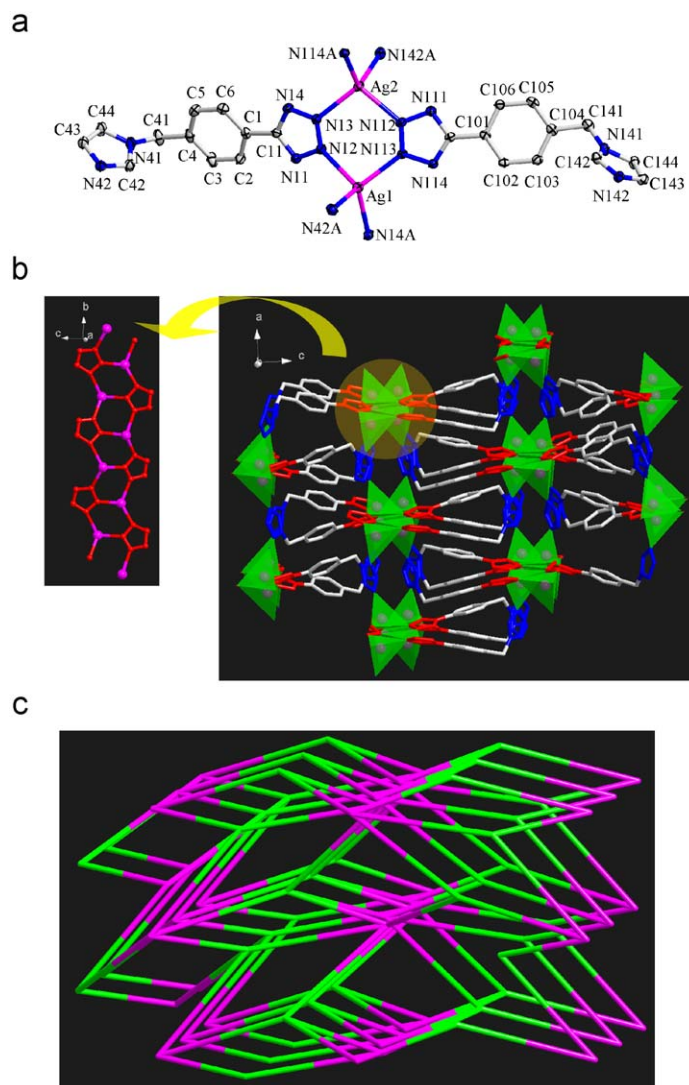


Fig. 3. (a) Coordination environment of center Ag(I) atoms in **3** with the ellipsoids drawn at the 30% probability level, hydrogen atoms were omitted for clarity. (b) Polyhedral representation of the 3D network constructed by tetrazolate-Ag(I) chains and L^- ligands. (c) The scheme representation of the 3D network with its Schläfli symbol $(4^2 \cdot 6^3 \cdot 8)(4^3 \cdot 6^2 \cdot 8)$ (green nodes: Ag(I) atoms; pink nodes: L^- ligands). [For interpretation of the references to color in this figure legend, the reader is referred to the webversion of this article.]

to form an infinite 1D chains, and such Ag-chains are further connected through the imidazole unit to give a 3D supramolecular framework (Fig. 3b). It is noteworthy that another new coordination Mode (d) of L^- was found in compound **3**, which is different from the ones observed in complexes **1** and **2** (Scheme 2). The adjacent three N atoms (N^1 , N^2 , N^3) of the tetrazole unit and the N^5 atom of the imidazole coordinated to the Ag(I) atoms. Therefore, the L^- ligand was found to have four different coordination modes in **1–3**, as 2-, 3- and 4-connector, respectively, as schematically shown in Scheme 2.

To get better insight into the present 3D framework structure, topological analysis was carried out for **3**. Each Ag(I) atom connects four L^- ligands, hence, each Ag(I) can be regarded as a 4-connected node. Each L^- ligand in turn connects four Ag(I) atoms, and thus each L^- can also be treated as 4-connected node. Such connectivity repeats infinitely to give the 3D framework as shown in Fig. 3c. However, the Ag(I) and L^- centered 4-connected nodes are the same and the crystallographic deviations are very small, thus the network is treated as binodal instead of tetranodal. According to the simplification principle using the

TOPOS software [31], the resulting structure of **3** is a 3D network and its Schläfli symbol is $(4^2 \cdot 6^3 \cdot 8)(4^3 \cdot 6^2 \cdot 8)$.

3.4. Photoluminescent property studies

The photoluminescence properties of complexes **1–3** were studied in the solid state at room temperature. The measurements were carried out under the same experiment conditions. As shown in Fig. 4, the emission peaks occur in 452 nm for complex **1** and 461 nm for complex **2** (both excitation at 395 nm), respectively. The maximal emission peaks of **1** and **2** are similarly to that of ligand IIMB (emission maximum at 461 nm upon excitation at 397 nm) [32]. The emissions observed in complexes **1** and **2** are probably ascribed to the π - π^* intra-ligand fluorescence due to their close resemblance of the emission bands [33–35]. No obvious photoluminescence was observed for **3** at room temperature. It is known that silver(I) complex may emit weak photoluminescence at low temperature, and that their luminescence at room temperature is unobservable [36–38].

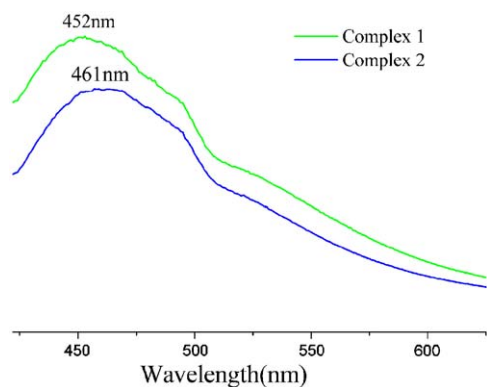


Fig. 4. The emission spectra of complexes **1** and **2** in the solid state at room temperature upon excitation at 395 nm.

4. Conclusions

We successfully synthesized three novel MOFs by Cd(II)/Ag(I) salts reacted with IBN and Na₃ through Sharpless in situ ligand formation. Through introducing tetrazole unit to IIMB, more complicated coordination modes and networks are obtained, which obviously proved that the tetrazole unit are good candidate for construction of MOFs. Blue emissions were observed for Cd(II) complexes **1** and **2** in the solid state at room temperature.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.03.010.

References

- [1] D. Fiedlere, D.H. Leung, R.G. Bergman, K.N. Raymond, *Acc. Chem. Res.* 38 (2005) 351.
- [2] X. He, C.-Z. Lu, D.-Q. Yuan, *Inorg. Chem.* 45 (2006) 5760.
- [3] P. Lin, W. Clegg, R.W. Harrington, R.A. Henderson, *Dalton. Trans.* (2005) 2388.
- [4] R.-Q. Zou, L. Jiang, H. Senoh, N. Takeichi, Q. Xu, *Chem. Commun.* (2005) 3526.
- [5] Q.S. Lin, J.D. Corbett, *Inorg. Chem.* 47 (2008) 3462.
- [6] X.-W. Wang, J.Z. Chen, J.H. Liu, *Cryst. Growth Des.* 7 (2007) 1227.
- [7] F. Luo, Y.-X. Che, J.-M. Zheng, *Cryst. Growth Des.* 8 (2008) 2006.
- [8] M. Dinca, A. Dailly, Y. Liu, C.M. Brown, D.A. Neumann, J.R. Long, *J. Am. Chem. Soc.* 128 (2006) 16874.
- [9] Q. Ye, Y.-M. Song, G.-X. Wang, K. Chen, D.-W. Fu, P.W.-H. Chan, J.-S. Zhu, S.D. Huang, *J. Am. Chem. Soc.* 128 (2006) 6554.
- [10] A. Rodriguez, A.R. Kivekasb, E. Colacio, *Chem. Commun.* (2005) 5228.
- [11] A.F. Stassen, H. Kooijman, A.L. Spek, L.J. de Jongh, J.G. Haasnoot, J. Reedijk, *Inorg. Chem.* 41 (2002) 6468.
- [12] Q. Ye, Y.-H. Hua, Y.-M. Song, Z.-L. Xue, *Inorg. Chem.* 44 (2005) 3618.
- [13] X.-S. Wang, Y.-Z. Tang, X.-F. Huang, Z.-R. Qu, C.-M. Che, P.W.-H. Chan, R.-G. Xiong, *Inorg. Chem.* 44 (2005) 5278.
- [14] T. Wu, M. Chen, D. Li, *Eur. J. Inorg. Chem.* 45 (2006) 2132.
- [15] C. Jiang, Z.-P. Yu, S.-J. Wang, C. Jiao, J.-M. Li, Z.-Y. Wang, Y. Cui, *Eur. J. Inorg. Chem.* (2004) 3662.
- [16] F. Nouar, J.F. Eubank, T. Bousquet, L. Wojtas, M.J. Zaworotko, M. Eddaoudi, *J. Am. Chem. Soc.* 130 (2008) 1833.
- [17] Z.P. Demko, K.B. Sharpless, *J. Org. Chem.* 66 (2001) 7945.
- [18] [a] Z.P. Demko, K.B. Sharpless, *Org. Lett.* 3 (2001) 4091; [b] Z.P. Demko, K.B. Sharpless, *Angew. Chem. Int. Ed.* 41 (2002) 2110.
- [19] [a] Y.-B. Ding, Y. Cheng, Z.-L. Zhang, J. Zhang, Y.-G. Yin, W.-H. Gao, *Inorg. Chem. Commun.* 12 (2009) 45; [b] H. Zhao, Z.-R. Qu, H.-Y. Ye, R.-G. Xiong, *Chem. Soc. Rev.* 37 (2008) 84.
- [20] H.-F. Zhu, J. Fan, W.-Y. Sun, *Chem. J. Chin. Univ.* 26 (2005) 19.
- [21] H.-F. Zhu, J. Fan, T.-a. Okamura, W.-Y. Sun, N. Ueyama, *Cryst. Growth Des.* 5 (2005) 289.
- [22] S.-Y. Wang, J. Fan, T.-A. Okamura, H.-F. Zhu, X.-M. Ouyang, W.-Y. Sun, N. Ueyama, *Chem. Commun.* (2002) 2520.
- [23] H.-K. Liu, W.-Y. Sun, W.-X. Tang, T. Yamamoto, N. Ueyama, *Inorg. Chem.* 38 (1999) 6313.
- [24] SAINT, Version 6.2, Bruker AXS Inc., Madison, WI, 2001.
- [25] Sheldrick, G.M. SADABS, University of Göttingen, Göttingen, Germany.
- [26] G.M. SHELXTL, Sheldrick, Version 6.10, Bruker Analytical X-ray Systems, Madison, WI, 2001.
- [27] A. Altomare, M.C. Burla, M. Camalli, M. Cascarano, C. Giacovazzo, A. Guagliardi, G. Polidori, SIR92, *J. Appl. Crystallogr.* 27 (1994) 435.
- [28] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M. Smits, M. DIRDIF94: The DIRDIF-94 Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
- [29] teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, 1999.
- [30] H.-F. Zhu, W. Zhao, T.-a. Okamura, J. Fan, W.-Y. Sun, N. Ueyama, *New J. Chem.* 28 (2004) 1010.
- [31] [a] A.T. Balaban, *From Chemical Topology to Three-dimensional Geometry*, Plenum Press, New York, 1997; [b] V.A. Blatov, TOPOS, A Multipurpose Crystallochemical Analysis with the Program Package; Samara State University, Russia, 2004; [c] V.A. Blatov, *IUCr Comput. Comm. Newslett.* 7 (2006) 4 (freely available at <<http://iucrcomputing.ccp14.ac.uk/iucrtop/comm/ccom/newsletters/>> 2006nov).
- [32] H.-F. Zhu, J. Fan, T.-a. Okamura, W.-Y. Sun, N. Ueyama, *Cryst. Growth Des.* 5 (2005) 289.
- [33] G. Wu, X.-F. Wang, T.-a. Okamura, W.-Y. Sun, N. Ueyama, *Inorg. Chem.* 45 (2006) 8523.
- [34] S.-L. Zheng, J.-H. Yang, X.-L. Yu, X.-M. Chen, W.T. Wong, *Inorg. Chem.* 43 (2004) 830.
- [35] L.-Y. Kong, X.-H. Lu, Y.-Q. Huang, H. Kawaguchi, Q. Chu, H.-F. Zhu, W.-Y. Sun, *J. Solid State Chem.* 180 (2007) 331.
- [36] D.H. Pierre, F. Daniel, *Coord. Chem. Rev.* 171 (1998) 351.
- [37] N.S. Fender, F.R. Fronczek, V. John, I.A. Kahwa, G.L. Mcpherson, *Inorg. Chem.* 36 (1997) 5539.
- [38] H.-F. Zhu, L. Li, T.-a. Okamura, W. Zhao, W.-Y. Sun, N. Ueyama, *Bull. Chem. Soc. Jpn.* 76 (2003) 761.