

2,3-吡啶二甲酸和 1,4-二咪唑基丁烷构筑的 Cd(II) 配合物的合成、晶体结构及荧光性质

李 可¹ 李书静^{*1} 张小朋² 曲波涛² 郑 玮²

(¹ 周口师范学院化学系, 周口 466000)

(² 南京大学化学化工学院, 配位化学国家重点实验室, 南京微结构国家实验室, 南京 210093)

摘要: 合成了一个配位聚合物 $\{[\text{Cd}(\text{pdc})(\text{bbi})] \cdot 2\text{H}_2\text{O}\}_n$ (H_2pdc =2,3-吡啶二甲酸, bbi =1,4-二咪唑基丁烷), 利用元素分析、红外光谱和 X-射线单晶衍射考察了配合物的结构。配合物中, $\text{Cd}(\text{II})$ 的配位数为 5, 每个 $\text{Cd}(\text{II})$ 与 1 个吡啶二甲酸离子的 1 个羧基氧原子和吡啶氮原子, 另 1 个吡啶二甲酸离子的 1 个羧基氧原子, 以及 2 个 1,4-二咪唑基丁烷的 2 个氮原子配位。吡啶二甲酸离子的配位方式可以表示为 $\mu-(\kappa^3\text{N}, \text{O}^2\text{O}^3)$, $\text{Cd}(\text{II})$ 与之连接形成一维骨架链 $[\text{Cd}(\text{pdc})]_\infty$ 。配体 1,4-二咪唑基丁烷采用了“ Ω ”和“S”两种构型, 它们进一步与中心原子配位形成三维网络结构。配合物为三重穿插的金刚石型网络结构, 拓扑学符号为 6^6 。受光激发, 该配合物在 426 nm 处有一个发射峰。

关键词: 2,3-吡啶二甲酸; 1,4-二咪唑基丁烷; 镉配合物; 晶体结构; 荧光

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Synthesis, Crystal Structure and Luminescence Property of A Cd(II) Coordination Polymer Constructed from 2,3-Pyridine Dicarboxylic Acid and 1,1'-(1,4-Butanediyl)bis(imidazole)

LI Ke¹ LI Shu-Jing^{*1} ZHANG Xiao-Peng² QU Bo-Tao² ZHENG Wei²

(¹Department of Chemistry, Zhoukou Normal University, Zhoukou, Henan 466000, China)

(²State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering,
Nanjing National Laboratory of Microstructures, Nanjing University, Nanjing 210093, China)

Abstract: A coordination polymer, namely $\{[\text{Cd}(\text{pdc})(\text{bbi})] \cdot 2\text{H}_2\text{O}\}_n$ (H_2pdc =2,3-pyridine dicarboxylic acid, bbi =1,1'-(1,4-butanediyl)bis(imidazole)), has been prepared and characterized by elemental analysis, IR spectrum, and single crystal X-ray diffraction. In the complex, each $\text{Cd}(\text{II})$ is five-coordinated by one carboxylate O and one pyridyl N atoms from one pdc anion, one carboxylate O atom from another pdc anion, and two N atoms from two bib ligands. The coordination mode of pdc ligands are described as $\mu-(\kappa^3\text{N}, \text{O}^2\text{O}^3)$, and Cd atoms are bridged by them to form a 1D skeleton chain $[\text{Cd}(\text{pdc})]_\infty$. The bbi ligands show “ Ω ” or “S” shaped conformations, and they further extend the structure into a 3D framework. The complex displays a 3-fold interpenetrating diamond framework with (6^6) topology. Under excitation, it can exhibit an emission peak at 426 nm. CCDC: 943690.

Key words: 2,3-pyridine dicarboxylic acid; 1,1'-(1,4-butanediyl)bis(imidazole); cadmium complex; crystal structure; luminescence

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*通讯联系人。E-mail: zksylk@163.com

The crystal engineering of coordination polymers has received remarkable attention owing to their fascinating architectures and potential applications in many fields such as catalysis^[1], magnetism^[2], proton conductivity^[3], luminescence^[4], hydrogen storage^[5], nonlinear optics^[6]. It is well known that the construction of MOFs are determined by several factors such as the central metals, the organic ligands, the reaction temperature, the solvent system and so on. Among these factors, the organic ligands play a crucial role because they can control and adjust the coordination frameworks and topologies^[7].

Multicarboxylate ligands have been extensively used as multifunctional organic linkers because of their reliable and rich coordination modes^[8-9]. Pyridine dicarboxylate ligands, including 2,3-, 2,4-, 2,5-, 2,6-, 3,4- and 3,5-pyridine dicarboxylates, have been extensively utilized in the construction of novel frameworks^[10-12]. They can contribute their carboxylate oxygen and pyridyl nitrogen atoms to metal coordination and can also act as both multiple proton donors and acceptors, thus forming interesting network structures. Among the N-donor bridging ligands, bis(imidazole) ligands, as an important family of flexible N-donor ligands, have attracted great interest from chemists. For example, the flexible 1,1'-(1,4-butanediyl)bis(imidazole) ligand can feature *cis*- and *trans*-conformations when coordinating with the central metals. In addition, it can bridge the central metals to form different metal-bbi skeletons by varying the dihedral angles between the two imidazole rings^[13].

In this work, we use the 2,3-pyridine dicarboxylate (pdc) ligand to construct a basic skeleton unit and 1,1'-(1,4-butanediyl)bis(imidazole)(bbi) to extend the framework, thus a novel coordination polymer $[\text{Cd}(\text{pdc})(\text{bbi}) \cdot 2\text{H}_2\text{O}]_n$ was obtained. Its structural features are presented, and its luminescence property is investigated as well.

1 Experimental

1.1 General

The ligand 2,3-pyridine dicarboxylic acid was purchased from Aldrich. Co. 1,1'-(1,4-butanediyl)bis

(imidazole) was synthesized according to the literature method^[14]. All other chemicals were of reagent grade and used without further purification. Elemental analysis for C, H and N were performed on a Perkin-Elmer 240C analyzer. Solid infrared spectra were recorded on a Vector22 Bruker Spectrophotometer with KBr pellets in the 400~4 000 cm^{-1} region. TG and DSC curves were collected on a Perkin-Elmer Pyris 1 TGA analyzer from 28 to 600 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$ under nitrogen atmosphere. The powder XRD pattern was recorded on a Shimadzu XD-3A X-ray diffractometer. Luminescence spectra were recorded in dichloromethane solution on HITACHI F-4600 Fluorescence Spectrophotometer.

1.2 Synthesis

A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.030 8 g, 0.1 mmol), H_2pdc (0.016 7 g, 0.1 mmol), bbi (0.019 0 g, 0.1 mmol), NaOH (0.008 0 g, 0.2 mmol) and water (10 mL) was sealed in a Teflon reactor (15 mL). The mixture was heated at 150 $^{\circ}\text{C}$ for 3 d, then it was gradually cooled to room temperature. The residue was filtered, and colourless crystals were obtained by evaporation of the filtrate in a 21 % yield based on $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. Anal. Calcd. for $\text{C}_{17}\text{H}_{21}\text{N}_5\text{O}_6\text{Cd}(\%)$: C, 40.53; H, 4.20; N, 13.90. Found(%): C, 40.64; H, 4.29; N, 13.81. Selected IR (KBr) / cm^{-1} : 3 447 (m), 3 120 (w), 1 620 (s), 1 575 (s), 1 515 (m), 1 394 (s), 1 375 (s), 1 232 (s), 1 103 (s), 931 (m), 870 (m), 835 (m), 742 (m), 660 (m).

1.3 X-Ray crystallography

The crystal structure of the complex has been solved by X-ray diffraction analysis. Its main crystallographic data are summarized in Table 1. Intensity data was collected on a Bruker SMART CCD diffractometer using monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) at room temperature. The collected frames were processed with the software SAINT^[15]. The structure was solved by the direct method and refined by full-matrix least-squares on F^2 using the program SHELXTL-97^[16]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated position.

CCDC: 943690.

Table 1 Crystallographic data for $\{[\text{Cd}(\text{pdc})(\text{bbi})]\cdot 2\text{H}_2\text{O}\}_n$

Empirical formula	$\text{C}_{17}\text{H}_{21}\text{CdN}_3\text{O}_6$	Absorption coefficient / mm^{-1}	1.11
Formula weight	503.79	$F(000)$	2 032
Temperature / K	123(2)	θ range for data collection / $^\circ$	1.84 to 27.53
Wavelength / nm	0.071 073	Index ranges	$-21 \leq h \leq 21, -18 \leq k \leq 19, -15 \leq l \leq 23$
Crystal system	Monoclinic	Reflections collected / unique	18 527 / 4 716 ($R_{\text{int}}=0.070$ 3)
Space group	$I2/a$	Absorption correction	Semi-empirical from equivalents
a / nm	1.666 20(19)	Max. and min. transmission	0.851 2 and 0.746 3
b / nm	1.486 10(17)	Refinement method	Full-matrix least-squares on F^2
c / nm	1.797 77(15)	Data / restraints / parameters	4 716 / 0 / 267
α / $^\circ$	90	Goodness-of-fit on F^2	1.073
β / $^\circ$	113.117(8)	Final R indices [$I > 2\sigma(I)$]	$R_1=0.047$ 1, $wR_2=0.123$ 3
γ / $^\circ$	90	R indices (all data)	$R_1=0.050$ 6, $wR_2=0.124$ 6
Volume / nm^3	4.094 1(7)	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	968 and -666
Z	8		

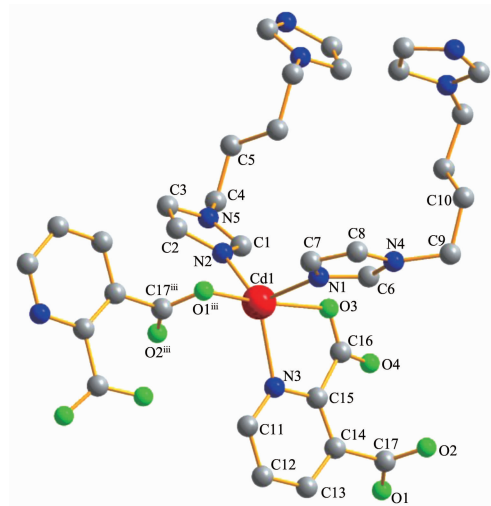
2 Results and discussion

2.1 X-ray structure

X-ray diffraction study reveals that complex $\{[\text{Cd}(\text{pdc})(\text{bbi})]\cdot 2\text{H}_2\text{O}\}_n$ is a 3D supramolecular structure, selected bond lengths and angles are listed in Table 2. As shown in Fig.1, the Cd(II) cation shows a distorted trigonal bipyramidal geometry $\{\text{CdN}_3\text{O}_2\}$, which is surrounded by two carboxylate oxygen atoms from two pdc anions [Cd1-O1ⁱⁱⁱ 0.225 8(2) nm, Cd1-O3 0.236 2(5) nm], two nitrogen atoms from two bbi ligands [Cd1-N1 0.224 7(3) nm, Cd1-N2 0.221 8(3) nm], and one pyridyl nitrogen atom from a pdc anion [Cd1-N3 0.228 8 (3) nm]. The three N atoms occupy the in the triangle plane and the two O atoms are in the axial positions [O1ⁱⁱⁱ-Cd1-O3 169.61(9) $^\circ$].

The coordination mode adopted by the pdc ligand can be classified as $\mu-(\kappa^3\text{N},\text{O}^2:\text{O}^3)$, that is, a 2-position carboxylate O atom and the pyridyl N atom chelate

one Cd atom and a 3-position carboxylate O atom binds to another Cd atom^[17]. The Cd atoms are bridged



Water molecules are omitted for clarity; Symmetry code: ⁱⁱⁱ $-x, y-1/2, -z+1/2$

Fig.1 Coordination environment of the Cd(II) atom in $\{[\text{Cd}(\text{pdc})(\text{bbi})]\cdot 2\text{H}_2\text{O}\}_n$

Table 2 Select bond lengths (nm) and angles ($^\circ$) for $\{[\text{Cd}(\text{pdc})(\text{bbi})]\cdot 2\text{H}_2\text{O}\}_n$

N1-Cd1	0.224 7(3)	O1 ⁱⁱⁱ -Cd1	0.225 8(3)	C16-O4	0.123 1(4)
N2-Cd1	0.221 8(3)	O3-Cd1	0.236 2(2)	C17-O1	0.124 4(4)
N3-Cd1	0.228 8(3)	C16-O3	0.123 1(4)	C17-O2	0.122 4(4)
N2-Cd1-N1	125.96(10)	N1-Cd1-N3	106.20(10)	O1 ⁱⁱⁱ -Cd1-O3	169.61(9)
N2-Cd1-O1 ⁱⁱⁱ	100.47(9)	O1 ⁱⁱⁱ -Cd1-N3	111.77(9)	N3-Cd1-O3	71.81(9)
N1-Cd1-O1 ⁱⁱⁱ	83.86(9)	N2-Cd1-O3	85.17(10)	O3-C16-O4	125.4(3)
N2-Cd1-N3	120.88(9)	N1-Cd1-O3	85.77(9)	O2-C17-O1	122.5(3)

Symmetry code: ⁱⁱⁱ $-x, y-1/2, -z+1/2$.

by pdc ligands to form a 1D skeleton chain $[\text{Cd}(\text{pdc})]_{\infty}$ with $\text{Cd}\cdots\text{Cd}$ separations of 0.841 09(8) nm (Fig.2). The two pdc bonded to the same Cd atom are nearly coplanar with a dihedral angle of 1.686° between the two pyridyl rings.

The bbi ligand serves as a bisconnector to two adjacent Cd atom, and the $[\text{Cd}(\text{pdc})]_{\infty}$ chains are joined together by bbi ligands to generate a typical (6,3) net in the bc plane (Fig.3). This set of bbi ligands adopt “ Ω ” shaped conformations^[18], and the $\text{Cd}\cdots\text{Cd}$ separations across the bbi ligand are 1.143 61(10) nm. The other bbi ligands adopt “S” shaped conformations (with the $\text{Cd}\cdots\text{Cd}$ separations of 1.257 76(16) nm), and they further extend the (6,3) nets into a 3D framework (Fig.3).

To better understand the nature of the intricate framework, a topological approach to simplify the 3D framework can be used. From the topological view, the Cd atoms can be viewed as 4-connected nodes, and pdc anions and bbi ligands can be simplified as linkers. The topological analysis reveals that it is a typically diamond framework containing large adamantanoid cages. Fig.4 shows a single cage delimited by four cyclohexane-like windows in chair conformations. Because of the spacious nature of the single network, it allows two identical diamond networks to interpenetrate it, generating a 3-fold interpenetrating architecture (Fig.5). Analysis of the interpenetrating fashion in it with TOPOS suggests that the 3D network can be seen as a 4-connected

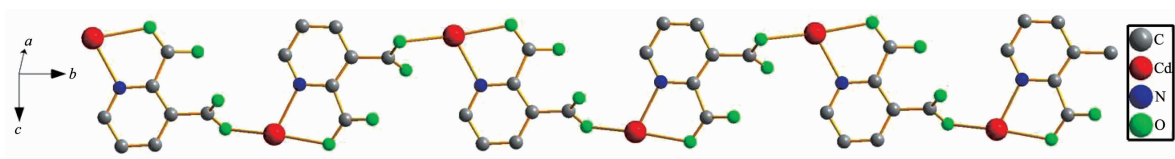


Fig.2 Skeleton chain formed by pdc ligands

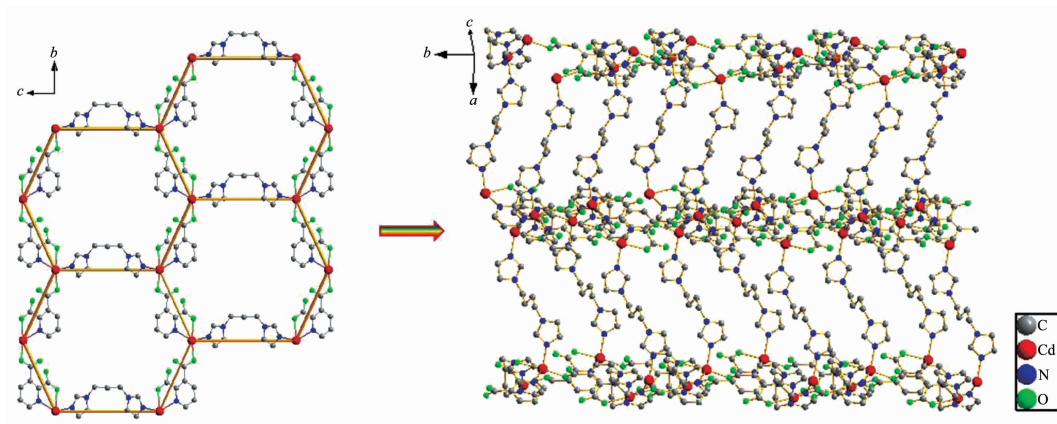


Fig.3 View showing the typical (6, 3) net (left) and 3D framework (right)

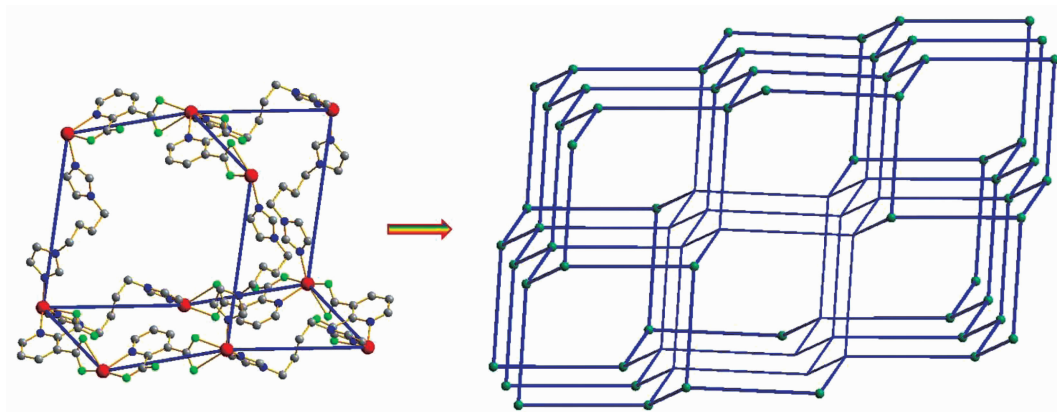


Fig.4 View of the single adamantanoid cages (left) and a schematic view of a single diamond framework (right)

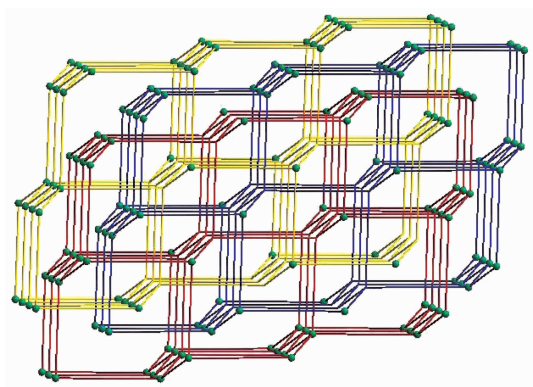


Fig.5 Schematic representation of the 3-fold interpenetrating diamond framework

diamond-like framework with the Schläfli symbol of (6⁶).

2.2 X-ray powder diffraction

In order to check the phase purity of this complex, the PXRD pattern was checked at room temperature. As shown in Fig.6, the diffraction peaks of the experimental and simulated patterns match well in key positions, indicating the phase purities of complex. Thus the structure reported is representative of the bulk materials.

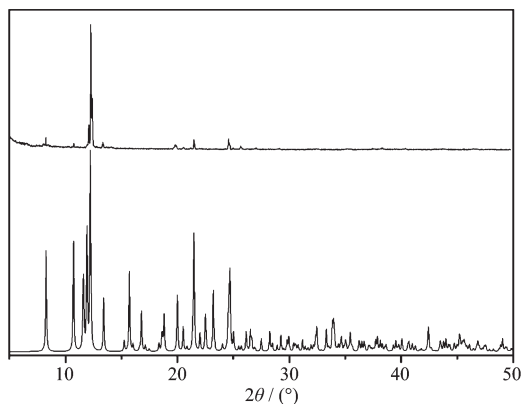


Fig.6 Simulated (bottom) and experimental (top) PXRD patterns of $[\text{Cd}(\text{pdc})(\text{bbi})] \cdot 2\text{H}_2\text{O}$

2.3 Thermal analysis

Because the complex is easy weathering in dry air, the picked samples were dried using filter paper and the thermal test was taken immediately. In the TG curve (Fig.7), the first weight loss, 7.48% (Calcd. 7.15%) in the range of 28~113 °C, is ascribed to the release of the two crystalliferous water molecules in the complex. And the dehydration is connected with two endothermic peaks in the DSC curve. A horizontal

stage corresponding to anhydrous compound is observed in the TG curve, which extends over a temperature range from 113~245 °C. Above 245 °C, the ligands decomposition takes place, and the total weight loss is 63.51% till 600 °C.

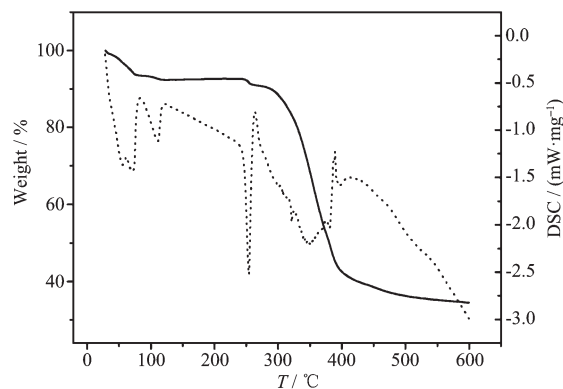


Fig.7 TG and DSC curves of $[\text{Cd}(\text{pdc})(\text{bbi})] \cdot 2\text{H}_2\text{O}$

2.4 Luminescence property

The solid-state photoluminescent spectra of the ligands and complex at room temperature were investigated, as depicted in Fig.8. When excited at 280 nm, the H_2pdc ligand exhibits two weak emission peaks, a broad one at 392 nm and a sharp one at 465 nm^[19]. The spectrum of the free ligand bbi shows one emission peak at 337 nm ($\lambda_{\text{ex}}=252$ nm). These emissions are probably attributable to the $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transitions. The complex exhibits emission band at 426 nm upon excitation at 310 nm and can be attributed to ligand to metal charge transfer (LMCT) transition. The enhancement of the emissions compared with those of the free ligands may be

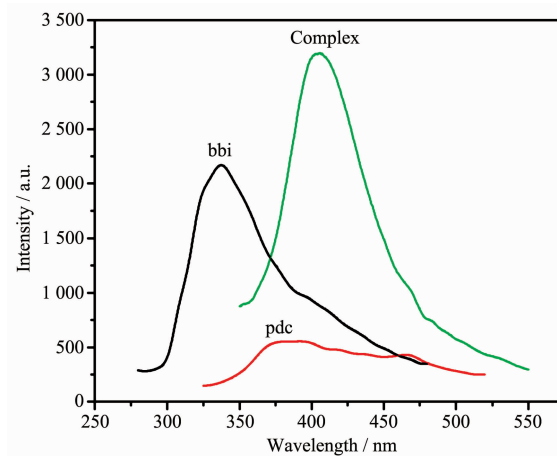


Fig.8 Solid-state emission spectra of the ligands and complex

ascribed to the increase of the ligand conformational rigidity due to their coordination to Cd(II) ions, which might result in a decrease in the non-radiative decay of intra-ligand excited states^[20].

3 Conclusion

In summary, a 3D coordination polymer $\{[\text{Cd}(\text{pdc})(\text{bbi})] \cdot 2\text{H}_2\text{O}\}_n$ has been obtained. In the complex, the center cadmium atom is five-coordinated in a trigonal bipyramidal geometry. The pdc ligands adopt $\mu-(\kappa^3\text{N}, \text{O}^2:\text{O}^3)$ coordination mode, and the bbi ligands show “ Ω ” or “S” shaped conformations. From the topological view, the 3D network can be seen as a 4-connected diamond-like framework with the Schläfli symbol of (6^6) . In the solid state, the complex exhibits medium-strong fluorescent emission ($\lambda_{\text{em}}=426\text{ nm}$) at room temperature. These results are expected to provide new important information for understanding supramolecular assemblies.

References:

- [1] Qu H, Qiu L, Leng X K, et al. *Inorg. Chem. Commun.*, **2011**, **14**:1347-1351
- [2] Zhang W L, Liu Y Y, Ma J F, et al. *Polyhedron*, **2008**, **27**: 3351-3358
- [3] Sadakiyo M, Hisashi Ō, Akihito S, et al. *J. Am. Chem. Soc.*, **2012**, **134**:5472-5475
- [4] TAO Wu(陶武), LIU Jie-Min(刘杰民), ZHENG Yan-Jun(郑延军), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2011**, **27**(12):2419-2424
- [5] Rowsell J L C, Yaghi O M. *Angew. Chem. Int. Ed.*, **2005**, **44**: 4670-4679
- [6] Wen L L, Zhou L, Zhang B G, et al. *J. Mater. Chem.*, **2012**, **22**:22603-22609
- [7] Yang Y Q, Yang J, Kan W Q, et al. *Eur. J. Inorg. Chem.*, **2013**, 280-292
- [8] Wen L L, Lu Z D, Ren X M, et al. *Cryst. Growth Des.*, **2009**, **9**, 227-238
- [9] WANG Zhuo(王卓), BAI Feng-Ying(白凤英), XING Yong-Heng(邢永恒), et al. *Chinese J. Inorg. Chem.* (无机化学学报), **2010**, **26**(4):713-716
- [10] Lü Y Y, Qi Y, Sun L X, et al. *Eur. J. Inorg. Chem.*, **2010**, 5592-5596
- [11] Shit S, Chakraborty J, Sen S, et al. *J. Mol. Struct.*, **2008**, **891**:19-24
- [12] Feng X, Zhao J S, Wang L Y, et al. *Inorg. Chem. Commun.*, **2009**, **12**:388-391
- [13] Li X J, Cao R, Bi W H, et al. *Cryst. Growth Des.*, **2005**, **5**: 1651-1656
- [14] Yang J, Ma J F, Liu Y Y, et al. *Eur. J. Inorg. Chem.*, **2005**, 2174-2180
- [15] SAINT, *Area Detector Control and Integration Software*, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, **1996**.
- [16] Sheldrick G M. *SHELXTL-97, Program for Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.
- [17] Wang G H, Li Z G, Jia H Q, et al. *CrystEngComm*, **2009**, **11**:292-297
- [18] Zhang W L, Liu Y Y, Ma J F, et al. *Cryst. Growth Des.*, **2008**, **8**:1250-1256
- [19] Semerci F, Yesilel O Z, Keskin S, et al. *CrystEngComm*, **2013**, **15**:1244-1256
- [20] Lin J G, Zang S Q, Tian Z F, et al. *CrystEngComm*, **2007**, **9**: 915-921