

## 以 7H-苯并[c,g]卡唑-4,10-二磺酸为构筑块原位合成具有 晶体学特征的二维层状锶配位聚合物

金杨波 赵红\*

(东南大学化学化工学院, 南京 210096)

**摘要:** 2,2'-二甲酰胺-1,1'-联二萘-5,5-二磺酸( $\text{H}_2\text{DCS}$ )和  $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$  反应生成了一个从未有过的二维层状配位聚合物  $\{\text{Sr}_2[(\text{DCS})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}\}_n$  (**1**) ( $\text{DCS}$ =7H-苯并[c,g]卡唑-4,10-二磺酸阴离子), 其中配体  $\text{DCS}$  是通过原位合成的。另外, **1** 在室温下显示了很强的蓝色荧光(445 nm)。晶体结构分析表明, 化合物 **1** 的晶体属三斜晶系, 空间群为  $P\bar{1}$  ( $a=1.169\,3(2)$  nm,  $b=1.299\,1(3)$  nm,  $c=1.629\,2(3)$  nm,  $\alpha=97.606(4)^\circ$ ,  $\beta=107.691(4)^\circ$ ,  $\gamma=114.536(4)^\circ$ ,  $V=2.047\,2(7)$  nm<sup>3</sup>,  $Z=2$ ,  $M=1\,126.19$ ,  $D_c=1.827$  Mg·m<sup>-3</sup>)。

**关键词:** 锶; 原位合成; 配位聚合物; 水热合成; 荧光

中图分类号: O614.23\*2

文献标识码: A

文章编号: 1001-4861(2007)02-0275-06

## *In Situ* Synthesis a Strontium 2D Layered Coordination Polymer with 7H-dibenzo[c,g]carbazole-4,10-disulfonate as Building Block

JIN Yang-Bo ZHAO Hong\*

(School of Chemistry and Chemical Engineering, Southeast University, Nanjing 210096)

**Abstract:** The reaction of 2,2'-diacetamido-1,1'-binaphthalene-5,5-disulfonic acid ( $\text{H}_2\text{DCS}$ ) with  $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$  yields an unprecedented two-dimensional layered coordination polymer  $\{\text{Sr}_2[(\text{DCS})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}\}_n$  (**1**) ( $\text{DCS}$ =7H-dibenzo [c,g]carbazole-4,10-disulfonate anion) in which **1** contains the *in situ* synthesized ligand  $\text{DCS}$ . Also, **1** displays a strong blue fluorescence emission ( $\lambda_{\text{emax}}=445$  nm) in the solid-state at room temperature. Crystal data for **1**, triclinic,  $P\bar{1}$ ,  $a=1.169\,3(2)$  nm,  $b=1.299\,1(3)$  nm,  $c=1.629\,2(3)$  nm,  $\alpha=97.606(4)^\circ$ ,  $\beta=107.691(4)^\circ$ ,  $\gamma=114.536(4)^\circ$ ,  $V=2.047\,2(7)$  nm<sup>3</sup>,  $Z=2$ ,  $M=1\,126.19$ ,  $D_c=1.827$  Mg·m<sup>-3</sup>. CCDC: 267611.

**Key words:** Sr; *in situ*; coordination polymer; hydrothermal; fluorescence

Recently, novel metal-organic coordination polymers [MOC] generated through *in situ* ligand has received much attention due in part to *in situ* ligand preparation not only providing a powerful synthesis method for organic ligands which are not readily accessible but also representing a potential new direction for novel inorganic-organic hybrid network construction through crystal engineering. Some of *in situ* ligand synthesis involves in the following reactions

under hydrothermal or solvothermal conditions: (a) simple organic ligand hydrolysis, oxidation, dehydration, deamination and dehydrogenation as well as para-sulfonated product in the presence of rare earth ion<sup>[1]</sup>; (b) the metal ion assisted synthesis of tetrazoles through the [2+3] cycloaddition reactions between nitriles with azide in aqueous solution<sup>[2]</sup>; (c) a tetradentate dye molecule, 1,2,4,5-tetra-(4-pyridyl)benzene molecules from the oxidative coupling between two 4,4'-trimethylen-

收稿日期: 2006-10-10。收修改稿日期: 2006-12-18。

东南大学启动基金资助项目。

\*通讯联系人。E-mail: hongzhaoupr@yahoo.com

第一作者: 金杨波, 男, 24岁, 硕士研究生; 研究方向: 发光化学。

edipyridine<sup>[3]</sup>; (d) Ag<sup>+</sup> ion assisted synthesis of 1,2,3,4-tetrakis(4-pyridyl)-cyclobutane through [2+2] cyclisation reaction between two olefinic molecules<sup>[4]</sup>; (e) the metal ion assisted synthesis of 1,2,4-triazole through the [2+2+1] cycloaddition reaction between two molecule nitriles and ammonia<sup>[5]</sup>; (f) tetrakis(4-pyridyl)cyclobutane generated through a stereo-controlled [2+2] photodimerization in the presence of Zn<sup>2+</sup> ion<sup>[6]</sup>. From the above-mentioned examples it has been realized that metal ion plays an important and key role in the formation of these complicate coordination polymers through its catalytic and coordinating role. Recently during our systematic and continuous investigations on novel metal-organic coordination polymers produced through *in situ* ligand synthesis, it is interesting to find that the MOCP containing carbazoles ligand, in principle can be achieved through above-mentioned method.

As expected, the hydrothermal reaction of 2,2'-diacetamido-1,1'-binaphthalene-5,5'-disulfonic acid with SrCl<sub>2</sub>·2H<sub>2</sub>O yields an unprecedented two-dimensional layers coordination polymer {Sr<sub>2</sub>[(DCS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O·C<sub>2</sub>H<sub>5</sub>OH}<sub>n</sub> (**1**) (DCS = 7H-dibenzo[c,g]carbazole-4,10-disulfonate) in which **1** contains the *in situ* synthesized ligand DCS. To the best of our knowledge, **1** represents the first two-dimensional metal coordination polymer containing disulfonate groups or carbazole group as building blocks produced by *in-situ* synthesis even through there are few reported coordination polymers containing carbazole group as building blocks which were synthesized in direct method<sup>[7]</sup>, and organic solid-state architectures assembled from benzene-1,4-disulfonate, azobenzene-4,4-disulfonate and biphenyl-4,4-disulfonate building blocks<sup>[8]</sup> as well as some alkaline earth metal ions tetra- and disulfonate supramolecular arrays<sup>[9]</sup>. Herein, we report the synthesis, solid-state structure and fluorescent property of **1**.

## 1 Experimental

Synthesis of {Sr<sub>2</sub>[(DCS)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O·C<sub>2</sub>H<sub>5</sub>OH}<sub>n</sub> (**1**): Samples of 2,2'-diacetamido-1,1'-binaphthalene-5,5'-disulfonic acid (1 mmol) and SrCl<sub>2</sub>·2H<sub>2</sub>O (1 mmol)

were placed in a thick-walled Pyrex tube (ca. 20 cm long). After addition of 1 mL of 70% EtOH, the tube was frozen with liquid N<sub>2</sub>, evacuated under vacuum and sealed with a torch. The tube was heated at 105 °C for three days to give brown block crystals (only one phase) in 55% yield based 2,2'-diacetamido-1,1'-binaphthalene-5,5'-disulfonic acid. IR (KBr, cm<sup>-1</sup>): 3 420(ms), 3 398(ms), 1 528(m), 1 377(w), 1 356(w), 1 316(w), 1 202(br,s), 1 160(s), 1 057(s), 971(w), 798(s), 749(m), 719(s), 618(s), 574(m), 548(m), 489(m), 468(m).

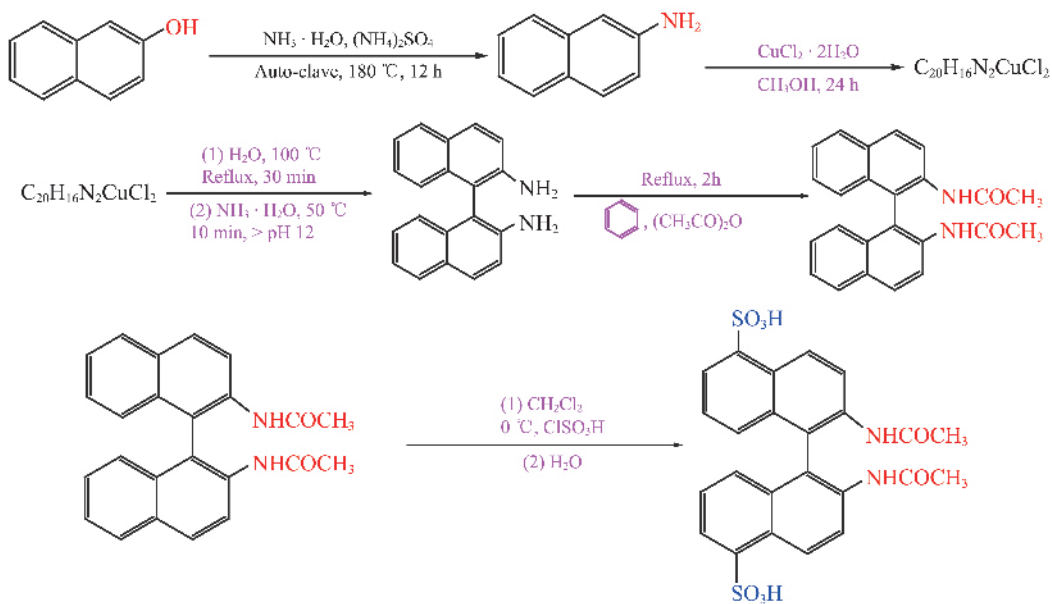
Crystal data for **1**: C<sub>42</sub>H<sub>34</sub>N<sub>2</sub>O<sub>16</sub>S<sub>4</sub>Sr<sub>2</sub>, Triclinic,  $P\bar{1}$ ,  $a=1.169\ 3(2)$  nm,  $b=1.299\ 1(3)$  nm,  $c=1.629\ 2(3)$  nm,  $\alpha=97.606(4)^\circ$ ,  $\beta=107.691(4)^\circ$ ,  $\gamma=114.536(4)^\circ$ ,  $V=2.047\ 2(7)$  nm<sup>3</sup>,  $Z=2$ ,  $M=1\ 126.19$ ,  $D_c=1.827$  Mg·m<sup>-3</sup>, Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073$  nm),  $T=293(2)$  K,  $\mu=2.891$  mm<sup>-1</sup>,  $R_1=0.067\ 3$ ,  $wR_2=0.135\ 2$ , GOF=0.913.

CCDC: 267611.

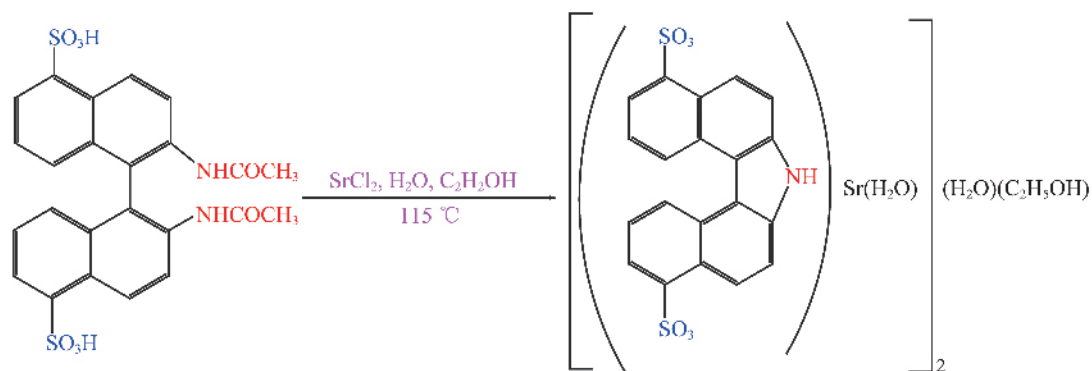
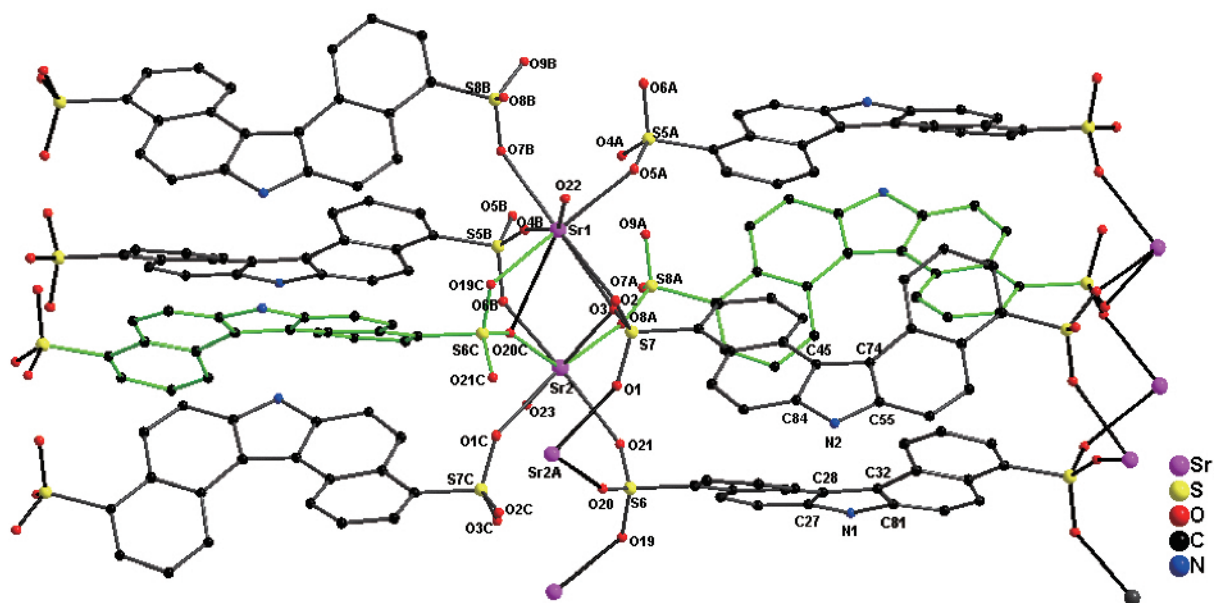
## 2 Results and discussion

Pale yellow block crystals of **1** were obtained by treating 2,2'-diacetamido-1,1'-binaphthalene-5,5'-disulfonic acid (H<sub>2</sub>DBDA) with SrCl<sub>2</sub>·2H<sub>2</sub>O under hydrothermal reaction conditions. DCS was synthesized *in situ* in this case and the Sr<sup>2+</sup> catalytic effect may play an important role in its formation while the H<sub>2</sub>DBDA was prepared from 2-naphthol through four steps as shown in the Scheme 1. In the IR spectrum of **1**, the presence of the sulfonate group was confirmed by two strong peaks at 1 202 and 1 160 cm<sup>-1</sup>, respectively; The absence of a peak at ca. 1 700 cm<sup>-1</sup> that indicated there are no NHC(=O)CH<sub>3</sub> group in DCS and the DCS ligand were synthesized though the intra-molecular cycloaddition reactions between two NHC(=O)CH<sub>3</sub> groups.

The single-crystal structure of complex **1** shows that there are two crystallographically independent Sr atom centers in which each has a different coordination environment (Fig.1a). One Sr center (Sr1) binds to eight oxygen donor atoms, seven of which belong to sulfonate groups from five DCS and the remaining one to one water molecule. Thus, the coordination geometry around the Sr1 atom can be best described as a slightly distorted square antiprism (Fig.1b). The other Sr2 coordinates to six oxygen

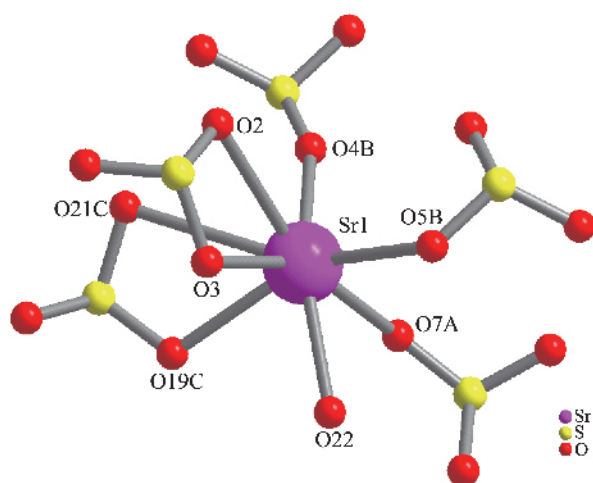


Scheme 1 Synthesis of rac-2,2'-diacetamido-1,1'-binaphthalene-5,5'-disulfonic acid

Scheme 2 Synthesis of  $\{Sr_2[(DCS)_2(H_2O)_2] \cdot H_2O \cdot C_2H_5OH\}_n$  (**1**)Fig.1a Asymmetric unit representation of **1**

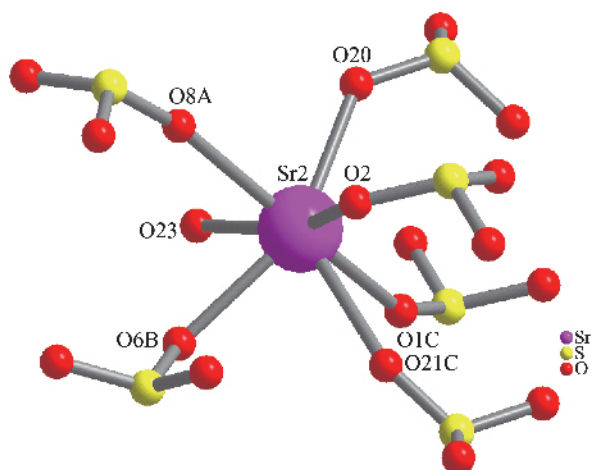
atoms of sulfonate groups from six DCS and remaining one to one water molecule. The coordination geometry around the Sr2 center can be best described as a slightly distorted hexagonal bipyramidal with two O atoms (O(6B), O(20)) in the axial positions and the plane is defined by O(8A), O(23), O(21C), O(1C) and O(2) (Fig.1c). The dihedral angle of two naphthalene planes in the DCS ligand is  $14.7^\circ$ , and there are two crystallographically independent DCS ligands in which one acts as a pentadentate while the other as a hexadentate bridging spacer to link nine different Sr

atoms (Fig.2), resulting in the formation of a 2D layered framework (Fig.3). It is noteworthy that two adjacent layers are not in a staggered arrangement but adopt an AA type arrangement (Fig.4). From Fig.4 it is clearly seen that one ethanol molecule and water molecule are intercalated between two adjacent layers. In addition, the sulfonate groups in DCS ligands display two coordinate modes. One acts as a bidentate bridging spacer while other is a tridentate linking spacer probably due to the steric demand on the metal center.



Organic part (7H-dibenzo[c, g]carbazole) of DCS ligands is omitted for clarity

Fig.1b Local coordination geometry around the Sr1 center in **1** has a slightly distorted square antiprism



Organic part of DCS ligands is omitted for clarity

Fig.1c Local coordination geometry around the Sr2 center in **1** displays a slightly distorted hexagonal bipyramidal

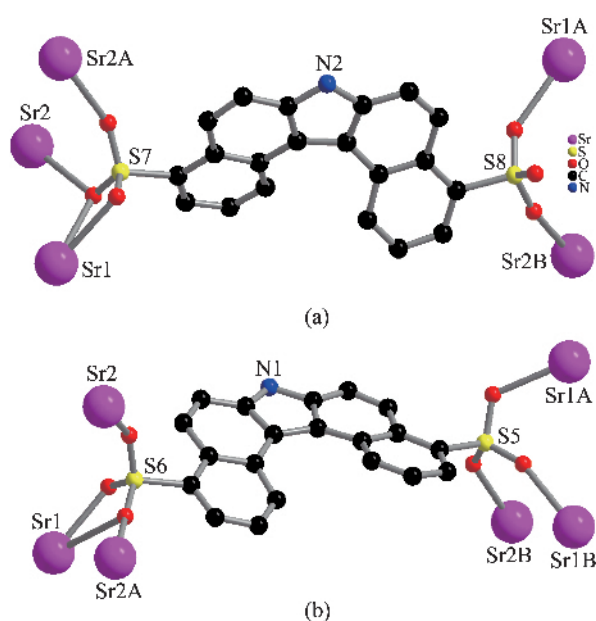


Fig.2 Two crystallographically unique DCS ligands in **1**  
(a) DCS used as a pentadentate linker (b) DCS acting as a hexadentate spacer

If the organic part of ligand DSC is omitted for clarity, the remaining chain can be regarded as a unique molecular ‘ribbon’. Thus, DSC can directly link the ribbon to give rise to a 2D square-like framework. The distance between two adjacent ribbons is about 0.818 1 ~ 0.819 7 nm. Thus, **1**, as we are aware, represents the first example of coordination polymer containing disulfonate and carbazole group as building blocks in strontium chemistry.

Aromatic organic molecules, all organic polymers, and mixed inorganic-organic hybrid coordination polymers have been investigated for fluorescence properties and for potential applications as fluorescence-emitted

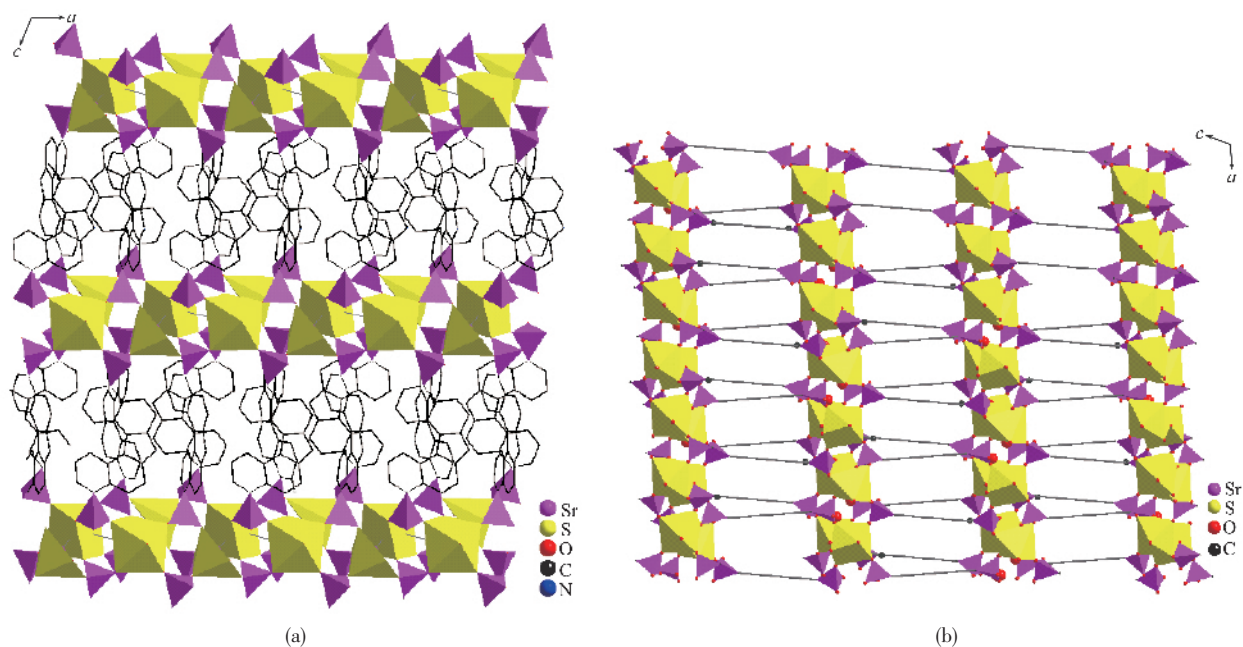


Fig.3 (a) 2D framework representation of **1** (b) Simplified 2D grid network representation of **1** highlighting the Sr1 square antiprism, Sr2 hexagonal bipyramid and S tetrahedron

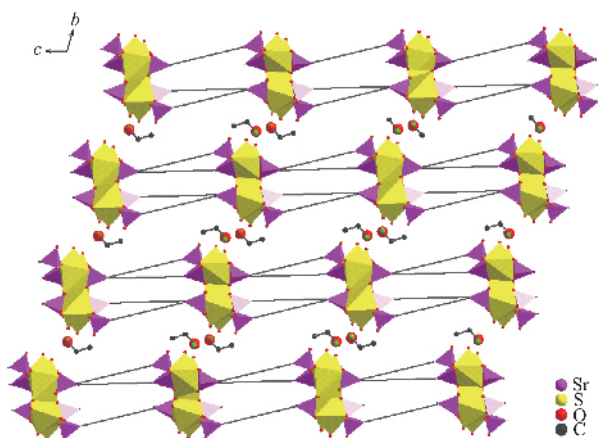


Fig.4 Packing arrangement representation of the two adjacent layers in **1** showing that ethanol molecules and water molecules are intercalated between two adjacent layers

materials<sup>[10]</sup>. Owing to the ability of organic materials to affect wavelength emission, syntheses of inorganic-organic coordination polymers by the judicious choice of organic spacers and metal centers (such as Zn, Cd, Pb, Ca, B etc.) can be an efficient method to obtain new types of luminescent materials<sup>[11]</sup>. Of particular interest is the photoluminescent spectrum of powdered **1**, the solid state fluorescent spectrum of the complexes **1** at

room temperature shows that maximal emission peak occur in 445 nm, (Fig.5). The results suggest that those complexes may be good blue-light-emitted materials. The photoluminescent mechanism may be considered to be ligand-to-ligand transition that is in fairly good agreement with coordination polymers previously reported by our and other groups<sup>[12]</sup>.

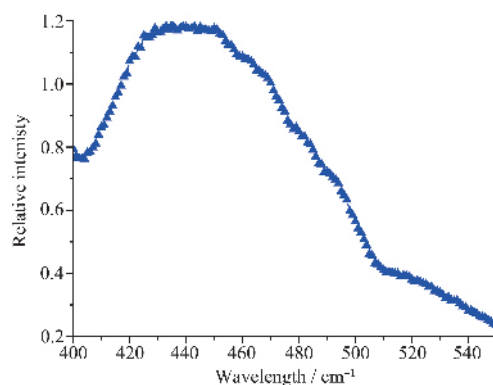


Fig.5 Solid-state fluorescent emission spectrum of powdered **1** at room temperature ( $\lambda_{ex}$ =310 nm)

In conclusion, this one-pot *in situ* ligand synthesis reaction in a supramolecular chemistry system provides a robust strategy for the construction of coordination polymers with promising physical properties.



## References:

- [1] (a) Qu Z R, Zhao H, Wang Y P, et al. *Chem. Eur. J.*, **2004**, **10** (1):54~60  
(b) Xiong R G, Zhang J, Chen Z F, et al. *J. Chem. Soc., Dalton Trans.*, **2001**, (6):780~782  
(c) Xiong R G, Wilson S R, Lin W B. *J. Chem. Soc., Dalton Trans.*, **1998**, (24):4089~4090  
(d) Xiong R G, Zuo J L, You X Z, et al. *Organometallics*, **2000**, **19** (20):4183~4186
- [2] (a) Xiong R G, Xue X, Zhao H, et al. *Angew. Chem. Int. Ed.*, **2002**, **41** (20):3800~3803  
(b) Xue X, Wang X S, Wang L Z, et al. *Inorg. Chem.*, **2002**, **41** (25):6544~6546  
(c) Xue X, Abrahams B F, Xiong R G, You X Z. *Aust. J. Chem.*, **2002**, **55** (8):495~497  
(d) WANG Li-Zhong(王立中), WANG Xi-Shen(王锡森), LI Yong-Hua(李咏华), et al. *Wuji Huaxue Xuebao(Chin. J. Inorg. Chem.)*, **2002**, **18** (12):1191~1194  
(e) Wang L Z, Qu Z R, Zhao H, et al. *Inorg. Chem.*, **2003**, **42** (13):3969~3971  
(f) Qu Z R, Zhao H, Wang X S, et al. *Inorg. Chem.*, **2003**, **42** (24):7710~7712  
(g) Zhao H, Ye Q, Wu Q, et al. *Z. Anorg. Allg. Chem.*, **2004**, **630** (10):1367~1370
- [3] Zheng N F, Bu X H, Feng P Y. *J. Am. Chem. Soc.*, **2002**, **124** (33):9688~9689
- [4] Blake A J, Champness N R, Chung S S M, Li W S, Schroder M. *Chem. Commun.*, **1997**, (17):1675~1676
- [5] (a) Zhang J P, Zheng S L, Huang X C, Chen X M. *Angew. Chem. Int. Ed.*, **2004**, **43** (2):206~209  
(b) Mao X J, Gao E Q, Zheng H, et al. *Inorganic Chemistry Communications*, **2004**, **7** (3):353~355
- [6] Papaefstathiou G S, Zhong Z M, Geng L, MacGillivray L R. *J. Am. Chem. Soc.*, **2004**, **126** (30):9158~9159
- [7] (a) Zhang X J, Wu J Y, Zhang M L, et al. *Transition Met. Chem.*, **2003**, **28** (6):707~711  
(b) Muller-Buschbaum K, Quitmann C C. *Z. Anorg. Allg. Chem.*, **2003**, **629** (9):1610~1616  
(c) Bock H, Arad C, Nather C, Havlas Z. *Helv. Chim. Acta*, **1997**, **80** (2):606~620
- [8] (a) Russell V A, Evans C C, Li W, Ward M D. *Science*, **1997**, **276** (5312):575~579  
(b) Swift J A, Pivovar A M, Reynolds A M, Ward M D. *J. Am. Chem. Soc.*, **1998**, **120** (24):5887~5894  
(c) Evans C C, Sukarto L, Ward M D. *J. Am. Chem. Soc.*, **1999**, **121** (2):320~325  
(d) Deacon G B, Gitlits A, Meyer G, et al. *Rare Earths' 98, Proc. Int. Conf.*, 1998, **1999**:315~317, 465  
(e) Deacon G B, Gitlits A, Zelesny G, et al. *Z. Anorg. Allg. Chem.*, **1999**, **625** (5):764~772
- [9] (a) Hoffart D J, Cote A P, Shimizu G K H. *Inorg. Chem.*, **2003**, **42** (26):8603~8605  
(b) Cote A P, Shimizu G K H. *Chem. Commun.*, **2001**, (3):251~252  
(c) Cote A P, Shimizu G K H. *Chem. Eur. J.*, **2003**, **9**:5361~5372  
(d) Cai J, Chen C H, Liao C Z, et al. *Acta Cryst. Sect. B Struct. Sci.*, **2001**, **57**:520~530.
- [10] Bunz U H F. *Chem. Rev.*, **2000**, **100** (4):1605~1644
- [11] Ciurtin D M, Pschirer N G, Smith M D, et al. *Mater. Chem.*, **2001**, **13**:2743~
- [12] (a) Xiong R G, Zuo J L, You X Z, et al. *Chem. Commun.*, **2000**, (20):2061~2062  
(b) Fun H K, Raj S S S, Xiong R G, et al. *J. Chem. Soc., Dalton Trans.*, **1999**, (12):1915~1916  
(c) Zhang J, Lin W B, Chen Z F, et al. *J. Chem. Soc., Dalton Trans.*, **2001**, (12):1806~1808