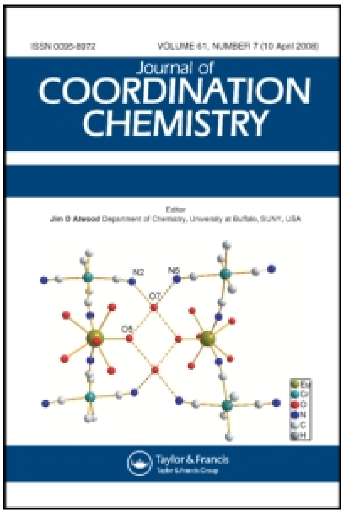


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A new 3-D microporous Ln(III)-Cu(I) framework constructed by pyridine-3,5-dicarboxylate

JiangLong Yi[a]; ZhiYong Fu[a]; Shijun Liao[a]
[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, China

To cite this Article Yi, JiangLong , Fu, ZhiYong and Liao, Shijun(2009) 'A new 3-D microporous Ln(III)-Cu(I) framework constructed by pyridine-3,5-dicarboxylate', Journal of Coordination Chemistry, 62: 14, 2290 — 2298
To link to this Article: DOI: 10.1080/00958970902803358
URL: http://dx.doi.org/10.1080/00958970902803358

Journal of Coordination Chemistry
Vol. 62, No. 14, 20 July 2009, 2290–2298

A new 3-D microporous Ln(III)–Cu(I) framework constructed by pyridine-3,5-dicarboxylate

JIANGLONG YI, ZHIYONG FU* and SHIJUN LIAO

School of Chemistry and Chemical Engineering, South China University of Technology,
Guangzhou 510640, China

(*Received 13 July 2008; in final form 6 November 2008*)

A new 3-D lanthanide-transition metal coordination polymer $[LaCu(PDC)_2H_2O]_n$ (**1**) was hydrothermally synthesized from pyridine-3,5-dicarboxylic acid (H_2PDC) and characterized by single-crystal X-ray diffraction, IR spectroscopy, and thermal gravimetric analysis (TGA). The microporous framework of **1** can be viewed as constructed by planar binuclear $Cu_2(PDC)_4$ building blocks and La(III) chains, a new structural motif in 3d-4f heterometallic coordination polymers. The sample exhibits strong blue emission in the solid state and retains its framework integrity up to ca 380°C.

Keywords: Heterometallic coordination polymer; Pyridine-3,5-dicarboxylate complexes; Microporous frameworks; Fluorescence property; Structure and characterization

1. Introduction

Heterometallic lanthanide-transition metal coordination polymers are of interest for potential applications in magnetism and luminescent materials, and also for their various structural topologies [1]. Many 3d-4f polymeric complexes have been synthesized, but understanding the formation of different structures, which is vital for technological development, is lacking. Usually, it is easy to get homometallic coordination polymers instead of heterometallic complexes because of different coordination behaviors in 3d and 4f metal ions [2]. With lanthanide ions preferring O-donors to N-donors and d-block metal ions coordinating both [3], it is important to select a ligand to meet the distinct coordination requirements of heterometallic ions of 3d-4f networks. The ligands containing both O- and N-donors, such as amino acids [4], iminodiacetate [5, 1g], isonicotinic acid [6], pyrazine-2,6-dicarboxylic acid [1h], pyridine-2,5-dicarboxylate [7a], pyridine-2,4-dicarboxylate [7b] and pyridine-2,6-dicarboxylate [8], have been used to build 3d-4f framework materials. Pyridine-3,5-dicarboxylate (PDC^{2-}) has mostly been used to generate metal organic-frameworks with single d-block [9] or lanthanide ions [10] and the analogous 1,3,5-benzene-tricarboxylate has been used to produce numerous porous metal organic frameworks [11]. However, construction of lanthanide-transition metal coordination polymers with the

---

*Corresponding author. Email: zyfu@scut.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902803358

pyridine-3,5-dicarboxylate are poorly explored. PDC's two carboxylic groups can be easily deprotonated to get a multidentate anion (PDC^{2-}), enabling the ligand to act as a bridge to 3d and 4f metal ions and the rigidity of this dianion reduces the potential for interpenetration [10a]. Herein, we present the first synthesis of a new 3-D 3d-4f heterometallic coordination polymer $[LaCu(PDC)_2H_2O]_n$ (**1**) based on H_2PDC with a porous network structure. The linkage between Cu(I) and La(III) centers generates four kinds of cavities, 12.64×6.38, 8.62×5.40, 5.65×4.85, and 6.56×4.47 Å. The thermogravimetric analysis and X-ray powder diffraction studies indicate that the complex retains its porous structure until 380°C. It has strong luminescence emissions at 460 and 400 nm.

2. Experimental

2.1. *Synthesis and characterization*

Synthesis of **1:** A mixture of La_2O_3 (0.04 g, 0.125 mmol), $Cu(OAc)_2$ (0.05 g, 0.25 mmol), H_2PDC (0.08 g, 0.5 mmol) and 10 mL H_2O was sealed in a 23 mL Teflon-lined bomb at 180°C for 100 h and then cooled to 100°C over a period of 16.7 h; maintained at 100°C for 33.3 h, and finally cooled to room temperature at a rate of $2.4^{\circ}C\,h^{-1}$; yellow-green block crystals were collected by filtration (yield: 53%, based on La_2O_3). Elemental Anal. Calcd (%) for $C_{14}H_8CuLaN_2O_9$: C 30.54, H 1.46, N 5.09; Found: C 30.45, H 1.38, N 5.11.

2.2. *Physical measurements*

Elemental analyses (C, H, and N) were performed on a Vario EL III elemental analyzer. The infrared spectrum (KBr pellets) was recorded on a BRUKE Tensor 27 infrared spectrophotometer from 4000 to $400\,cm^{-1}$. A TA Instrument Q600 SDT thermogravimetric analyzer was used to obtain the TGA curve in N_2 at a rate of $10^{\circ}C\,min^{-1}$. The emission/excitation spectra were recorded on a HITACHI F-4500 fluorescence spectrophotometer. Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-3A X-ray diffractometer with Cu-Kα radiation ($\lambda = 1.5406$ Å) with recording speed $2^{\circ}\,min^{-1}$ over the 2θ range of 5–70° at room temperature.

2.3. *Single-crystal X-ray diffraction*

Suitable crystal of **1** (yellow-green block ($0.18 \times 0.16 \times 0.12\,mm^3$)) was selected and mounted on a glass fiber. The measurements were made on a Bruker-axs Smart APEX-II CCD diffractometer with graphite-monochromated Mo-Kα radiation. Data were collected at 25°C using the ω and φ scans to a maximum θ value of 25.03° and refined by full-matrix least-squares on F^2 with SHELXTL-97. The structure was solved by direct methods of SHELXS-97 [12]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at geometrically idealized positions. Crystallographic data for **1** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

Table 1. Crystallographic summary for **1**.

Chemical formula	$C_{14}H_8CuLaN_2O_9$
Formula weight	550.67
Crystal system	Triclinic
Space group	$P\bar{1}$
Units of cell dimensions (Å, °)	
a	4.9113(10)
b	11.550(2)
c	12.756(3)
α	85.23(3)
β	85.84(3)
γ	83.10(3)
V (Å^3)	714.5(3)
Z	2
$F(000)$	528
Data/restraints/parameters	2461/0/244
Goodness-of-fit on F^2	1.001
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0323$, $wR_2 = 0.0595$
R indices (all data)	$R_1 = 0.0419$, $wR_2 = 0.0623$

Note: $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

La(1)–O(1)	2.439(4)	La(1)–O(2)#3	2.556(3)
La(1)–O(4)#1	2.441(3)	La(1)–O(5)#3	2.649(3)
La(1)–O(7)#2	2.515(4)	La(1)–O(8)#4	2.636(4)
La(1)–O(9)	2.681(3)	La(1)–O(6)	2.521(3)
N(1)–Cu(1)	1.912(4)	Cu(1)–N(2)#6	1.911(4)
Cu(1)–O(3)#5	2.225(3)		
O(1)–La(1)–O(4)#1	86.16(12)	O(4)#1–La(1)–O(6)	76.19(11)
O(6)–La(1)–O(8)#4	73.82(11)	O(8)#4–La(1)–O(5)#3	130.25(11)
O(7)#2–La(1)–O(5)#3	66.43(11)	O(7)#2–La(1)–O(9)	67.69(12)
O(2)#3–La(1)–O(9)	69.14(11)	O(1)–La(1)–O(2)#3	78.34(12)
N(2)#6–Cu(1)–N(1)	151.03(16)	N(2)#6–Cu(1)–(3)#5	102.06(15)
N(1)–Cu(1)–O(3)#5	106.71(15)		

Symmetry transformations used to generate equivalent atoms: #1: $-x, -y, -z$; #2: $-x-1, -y+1, -z-1$; #3: $x-1, y, z$; #4: $-x, -y+1, -z-1$; #5: $-x, -y-1, -z$; #6: $x-1, y-1, z$.

3. Results and discussion

3.1. *Description of crystal structure*

X-ray crystal diffraction analysis reveals that **1** exhibits a 3-D network. The asymmetric unit of **1** (figure 1) contains one La, one Cu, two PDC anions, and one coordinating water. The trigonal-planar coordination geometry of copper indicates that the Cu(II) has been reduced to Cu(I) in the presence of N-containing ligands under hydrothermal conditions [13, 14], proved by calculation of bond valence sum (BVS) values [15]. Each Cu(I) has a T-shaped geometry, coordinated by two nitrogens [Cu1–N1 1.912(4) Å, Cu1–N2F 1.911(4) Å] and one oxygen [Cu1–O3E 2.225(3) Å] from three different PDC^{2-} ligands. The La(III) center has a distorted square antiprism coordination geometry with eight oxygens from seven PDC^{2-} and a coordinating water. La–O bond distances range from 2.439(4) to 2.649(3) Å, similar to literature reports [16].

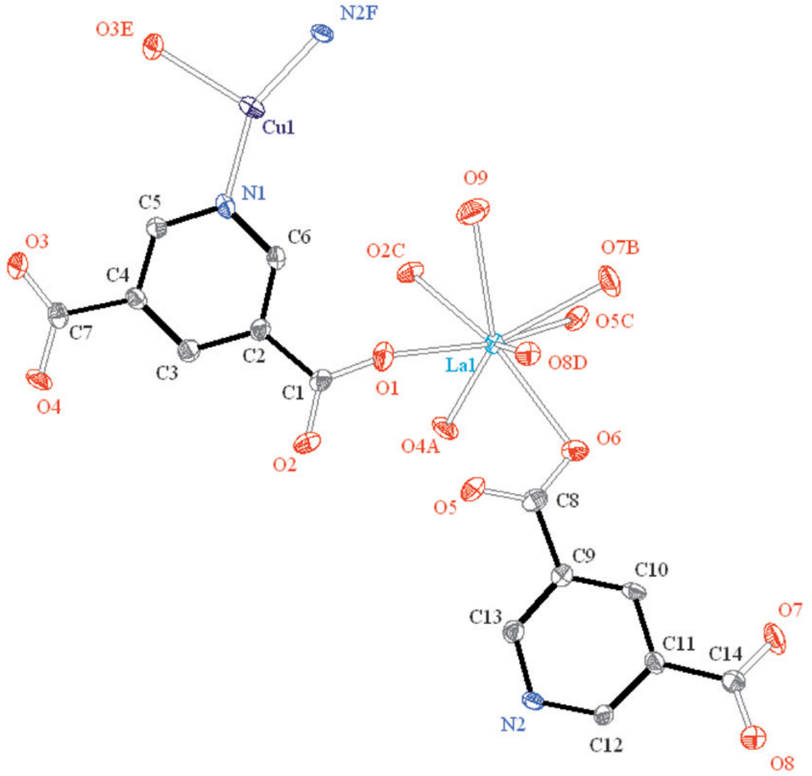
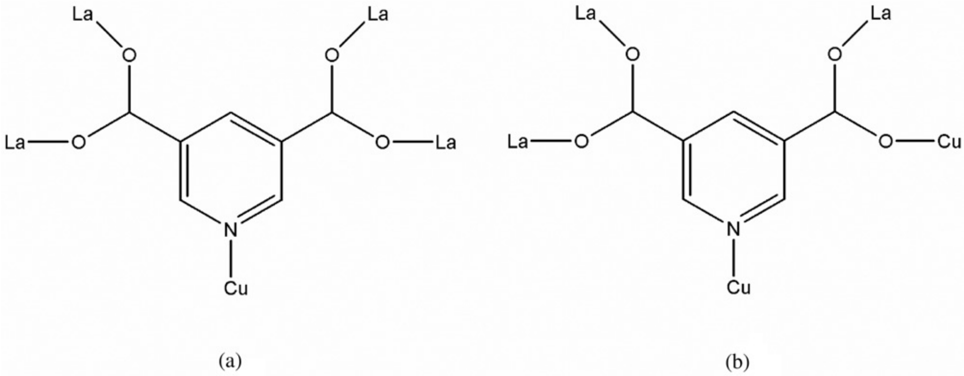


Figure 1. ORTEP view of **1** with 50% thermal ellipsoids; all hydrogen atoms are omitted for clarity. Symmetry codes: A: $-x, -y, -z$; B: $-x-1, -y+1, -z-1$; C: $x-1, y, z$; D: $-x, -y+1, -z-1$; E: $-x, -y-1, -z$; F: $x-1$, $y-1$, z.



(a) (b)

Scheme 1. Coordination modes of the PDC^{2-} in **1**.

Pyridine-3,5-dicarboxylate has two new coordination modes in this lanthanide-transition metal coordination polymer (scheme 1). In the coordination fashion **a**, the ligand has two unidentate carboxylate groups coordinated with four La(III) ions, and the nitrogen binds with Cu(I). The unidentate carboxylate groups in **b** connect with three La(III) ions and one Cu(I). These connections result in an interesting structural motif. The structure of **1** can be viewed as the linkage of planar binuclear $Cu_2(PDC)_4$ building blocks with La(III) chains (figure 2). Connections between the planar units and the LaO_8 cores by sharing PDC ligands generate a 2-D layer. Finally, the La(III) chains extend the structure to a 3-D motif (figure 3). The interlayer distance is about 4.911 Å (based on the Cu···Cu distance from neighboring layer). Four kinds of cavities exist in the framework, constructed by Cu(I) or La(III) centers with PDC^{2-}. The sizes are 12.64×6.38, 8.62×5.40, 5.65×4.85, and 6.56×4.47 Å and these cavities constitute a potential solvent-accessible area of 19.1% of the crystal [17].

3.2. *IR, TGA, XPRD, and luminescent data*

The IR spectrum of **1** shows a broad band centered at 3421 cm^{-1} due to –OH stretch of coordinated water. Lack of the peak at 1700 cm^{-1} for –COOH shows that all carboxyl groups of 3,5-PDC are deprotonated; 1612 and 1551 cm^{-1} are $\nu_{as}(OCO)$ and $\nu_s(OCO)$ stretches.

Thermogravimetric analysis (TGA) was performed on a polycrystalline sample of **1** (12.76 mg) from 22°C to 800°C. The diagram (Supplementary Material) shows an obvious weight loss starting at 180°C suggesting water removal with 3.95% weight loss to 280°C, corresponding to loss of one coordinated water per formula unit (Anal. Calcd 3.27%). Weight loss of 35.34% starts at 380–800°C, attributed to loss of all organic components (Anal. Calcd 37.9%).

The X-ray powder diffraction (XRPD) patterns for the thermal stability studies of **1** show phase purity of the bulk samples by comparison of the observed and simulated XRPD patterns. When **1** is heated at 180°C for 30 min, the XRD pattern shows no phase transition. Being heated to 280°C for 60 min, a coordinating water molecule (per formula unit) evolves from the sample and the XRD pattern has no obvious change, indicating no alteration in the crystal structure topology. Some XRD peaks disappear in the pattern due to local distortions within the structure [18]. After the sample is rehydrated at room temperature, the diffraction peaks are recovered, indicating recovery of the framework structure. Reversibility of the dehydration process has also been confirmed by the FT-IR data (Supplementary Material). The XRD pattern is almost the same as the original one after the sample is heated at 330°C, demonstrating that **1** retains its porous structure integrity at this temperature. Finally, the crystal color changes from yellow to black when the heating temperature reaches 380°C and the XRD pattern indicates that the sample loses crystallinity and the network begins to collapse. These data are consistent with the TG curve.

The solid-state fluorescence spectrum of **1** at room temperature is depicted in figure 4. When excited at 290 nm at room temperature, **1** emits strong blue luminescence with a broad emission maximum centered at ca 460 nm and a strong luminescence with emission maximum at ca 400 nm. The emission band at ca 400 nm may be attributable to intraligand $\pi_L\pi_L{}^*$ transitions (LLCT) [19]. The strong luminescent emission at ca 460 nm is assigned to the ligand-to-metal charge transfer (LMCT) and/or metal-to-ligand charge transfer (MLCT) [19c, 20]. The fluorescence character of **1** shows that it might be a photoactive material.

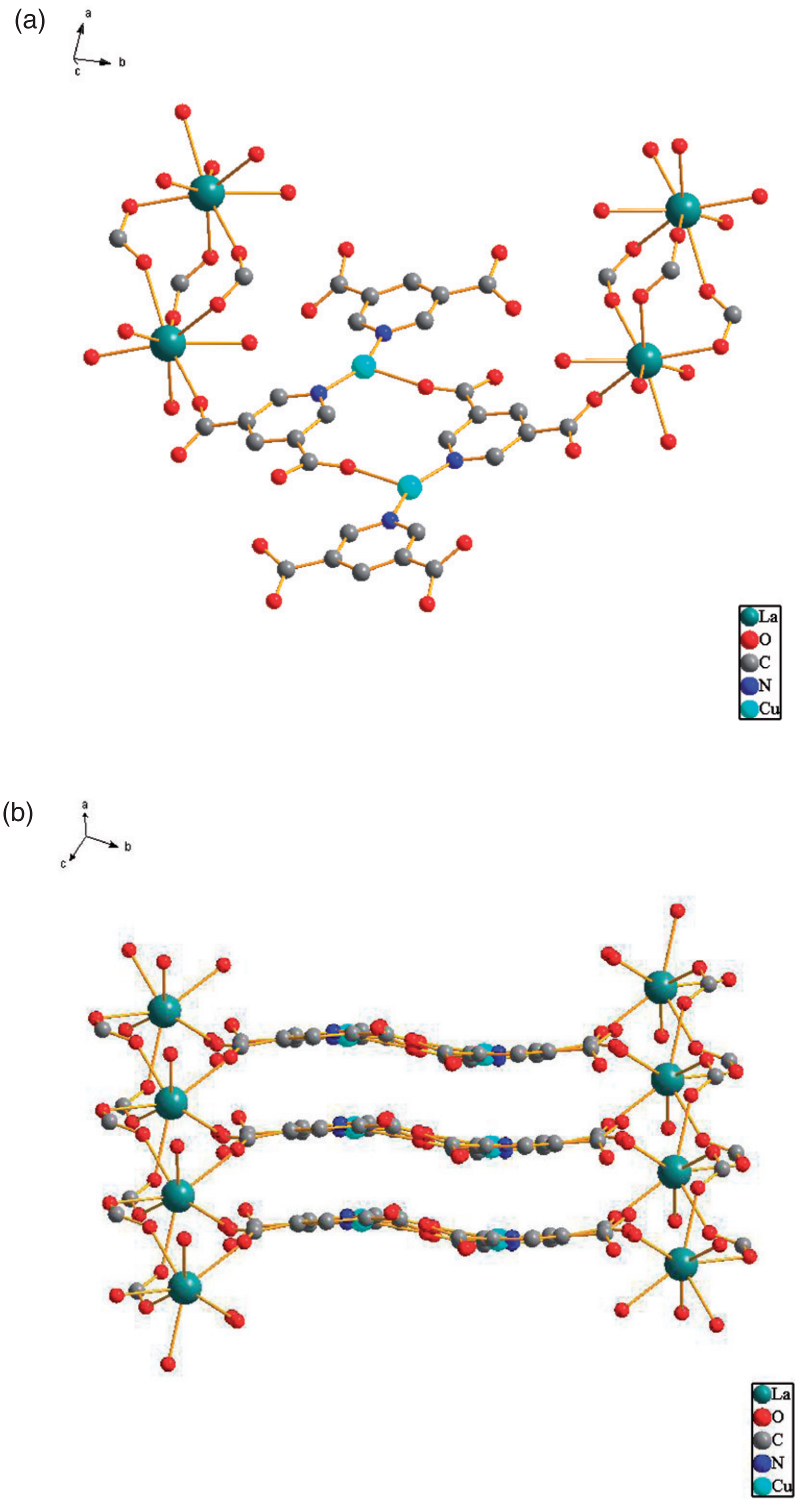


Figure 2. View of the structure unit of **1**.

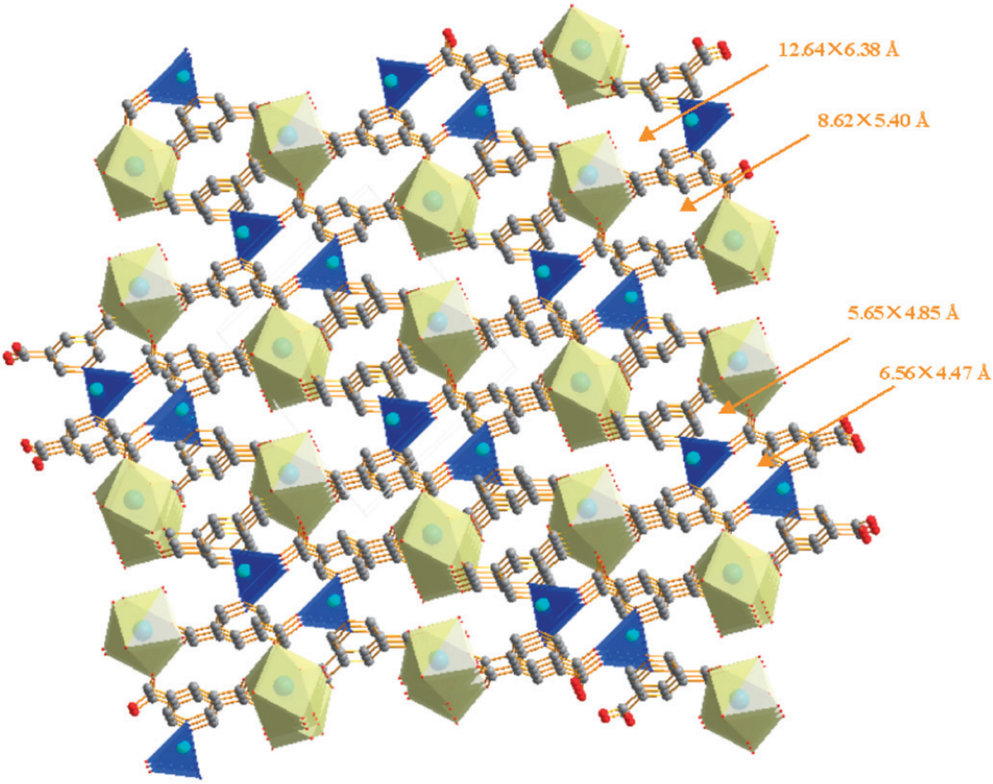


Figure 3. Three-dimensional network structure of **1**; all hydrogens are omitted for clarity.

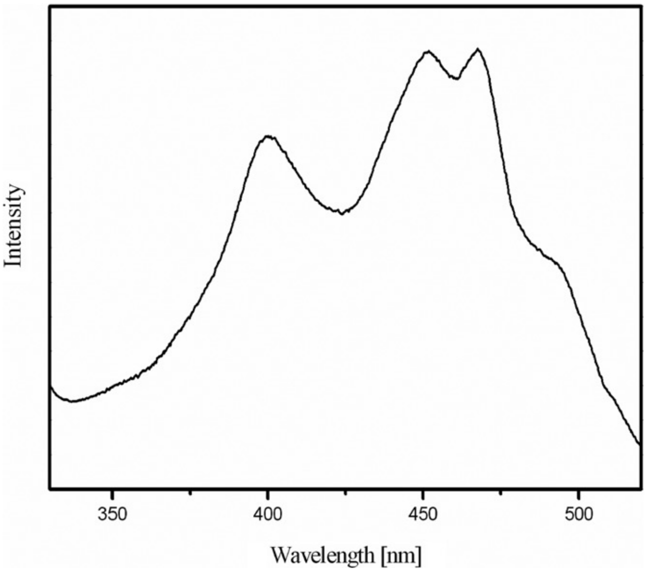


Figure 4. The solid-state fluorescent spectrum of **1**.

4. Conclusions

A new 3-D lanthanide-transition metal coordination polymer $[LaCu(PDC)_2H_2O]_n$ is synthesized and characterized. Its structure contains the 3,5-PDC and the special coordination modes of Cu(I) and Ln(III). The unique 3-D framework structure is built by planar binuclear $Cu_2(PDC)_4$ building blocks and the La^{3+} chain linkers. A non-linear rigid multidentate ligand gives a non-interpenetration network with four kinds of cavities of 12.64 × 6.38, 8.62 × 5.40, 5.65 × 4.85, and 6.56 × 4.47 Å, respectively. TG and XRD data indicate that the complex can retain its porous framework until 380°C with removal of water.

Supplementary material

CCDC-692626 contains the supplementary crystallographic data of **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033.

Acknowledgments

The authors thank the NSFFPC (No. 2003 F006) and the National Science Foundation (20701014) of China, and the SRP program of SCUT for financial support.

References

[1] (a) D.M.J. Doble, C.H. Benison, A.J. Blake, D. Fenske, M.S. Jackson, R.D. Kay, W.S. Li, M. Schröder. *Angew. Chem. Int. Ed. Engl.*, **38**, 1915 (1999); (b) C.M. Zaleki, E.C. Depperman, J.W. Kampf, M.L. Kirk, V.L. Pecoraro. *Angew. Chem. Int. Ed. Engl.*, **43**, 3912 (2004); (c) J.J. Zhang, T.L. Sheng, S.Q. Xia, G. Leibeling, F. Meyer, S.M. Hu, R.B. Fu, S.C. Xiang, X.T. Wu. *Inorg. Chem.*, **43**, 5472 (2004); (d) P.A. Brayshaw, A.K. Hall, W.T.A. Harrison, J.M. Harrowfield, D. Pearce, T.M. Shand, B.W. Skelton, C.R. Whitaker, A.H. White. *Eur. J. Inorg. Chem.*, 1127 (2005); (e) R. Gheorghe, P. Cucos, M. Andruh, J.P. Costes, B. Donnadieu, S. Shova. *Chem. Eur. J.*, **12**, 187 (2006); (f) K.S. David, S.J.A. Pope, S. Quinn, S. Faulkner, T. Gunnlaugsson. *Inorg. Chem.*, **45**, 10040 (2006); (g) S.C. Manna, S. Konar, E. Zangrando, J. Ribas, N.R. Chaudhuri. *Polyhedron*, **26**, 2507 (2007); (h) F.Q. Wang, X.J. Zheng, Y.H. Wan, C.Y. Sun, Z.M. Wang, K.Z. Wang, L.P. Jin. *Inorg. Chem.*, **46**, 2956 (2007); (i) Q.B. Bo, Z.X. Sun, W. Forsling. *Cryst. Eng. Comm.*, **10**, 232 (2008).

[2] X.W. Wang, X. Li, J.Z. Chen, G. Zheng, H.L. Hong. *Eur. J. Inorg. Chem.*, 98 (2008).

[3] (a) Z. He, C. He, E.Q. Gao, Z.M. Wang, X.F. Yang, C.S. Liao, C.H. Yan. *Inorg. Chem.*, **42**, 2206 (2003); (b) Y.F. Zhou, M.C. Hong, X.T. Wu. *Chem. Commun.*, 135 (2006).

[4] (a) M. Dan, C.N.R. Rao. *Chem. Eur. J.*, **11**, 7102 (2005); (b) J.J. Zhang, S.M. Hu, S.C. Xiang, T.L. Sheng, X.T. Wu, Y.M. Li. *Inorg. Chem.*, **45**, 7173 (2006).

[5] Y.P. Ren, L.S. Long, B.W. Mao, Y.Z. Yuan, R.B. Huang, L.S. Zheng. *Angew. Chem. Int. Ed. Engl.*, **42**, 532 (2003).

[6] (a) M.B. Zhang, J. Zhang, S.T. Zheng, G.Y. Yang. *Angew. Chem. Int. Ed. Engl.*, **44**, 1385 (2005); (b) F. Luo, Y.X. Che, J.M. Zheng. *Cryst. Growth Des.*, **6**, 2432 (2006); (c) X.J. Gu, D.F. Xue. *Inorg. Chem.*, **45**, 9257 (2006); (d) X.J. Gu, D.F. Xue. *Cryst. Growth Des.*, **6**, 2551 (2006); (e) G. Mezei, J.W. Kampf, S. Pan, K.R. Poeppelmeier, B. Watkins, V.L. Pecoraro. *Chem. Commun.*, 1148 (2007).

[7] (a) Y.C. Liang, M.C. Hong, W.P. Su, R. Cao, W.J. Zhang. *Inorg. Chem.*, **40**, 4574 (2001); (b) Y.C. Liang, R. Cao, M.C. Hong, D.F. Sun, Y.J. Zhao, J.B. Weng, R.H. Wang. *Inorg. Chem. Commun.*, 366 (2002).

[8] (a) D.M.L. Goodgame, T.E. Müller, D.J. Williams. *Polyhedron*, **11**, 1513 (1992); (b) B. Zhao, P. Cheng, X.Y. Chen, C. Cheng, W. Shi, D.Z. Liao, S.P. Yan, Z.H. Jiang. *J. Am. Chem. Soc.*, **126**, 3012 (2004).

[9] (a) J.C. Yao, W. Huang, H.B. Zhu, J.L. Fang, S.H. Gou. *Polyhedron*, **23**, 1169 (2004); (b) J.F. Eubank, R.D. Walsh, M. Eddaoudi. *Chem. Commun.*, 2095 (2005); (c) P.S. Wang, C.N. Moorefield, M. Panzner, G.R. Newkome. *Cryst. Growth Des.*, **6**, 1563 (2006); (d) X.M. Zhang, Y.Z. Zheng, C.R. Li, W.X. Zhang, X.M. Chen. *Cryst. Growth Des.*, **7**, 980 (2007); (e) Y.H. Zhao, Z.M. Su, Y.M. Fu, K.Z. Shao, P. Li, Y. Wang, X.R. Hao, D.X. Zhu, S.D. Liu. *Polyhedron*, **27**, 583 (2008).

[10] (a) J.H. Jia, X. Lin, A.J. Blake, N.R. Champness, P. Hubberstey, L.M. Shao, G. Walker, C. Wilson, M. Schroder. *Inorg. Chem.*, **45**, 8838 (2006); (b) Q.S. Shi, S. Zhang, Q. Wang, H.W. Ma, G.Q. Yang, W.H. Sun. *J. Mol. Struct.*, **837**, 185 (2007).

[11] (a) O.M. Yaghi, G.M. Li, H.L. Li. *Nature*, **378**, 703 (1995); (b) C. Livage, N. Guillou, J. Marrot, G. Férey. *Chem. Mater.*, **13**, 4387 (2001); (c) N.L. Rosi, J. Kim, M. Eddaoudi, B.L. Chen, M.O. Keefe, O.M. Yaghi. *J. Am. Chem. Soc.*, **127**, 1504 (2005); (d) P. Horcajada, S. Surblé, C. Serre, D.Y. Hong, Y.K. Seo, J.S. Chang, J.M. Grenèche, I. Margiolaki, G. Férey. *Chem. Commun.*, **27**, 2820 (2007).

[12] G.M. Sheldrick. *SHELXTL-97, Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1997).

[13] (a) J.Y. Lu, B.R. Cabrera, R.J. Wang, J. Li. *Inorg. Chem.*, **37**, 4480 (1998); (b) J.Y. Lu, B.R. Cabrera, R.J. Wang, J. Li. *Inorg. Chem.*, **38**, 4608 (1999); (c) S.M.F. Lo, S.S.Y. Chui, L.Y. Shek, Z.Y. Lin, X.X. Zhang, G.H. Wen, I.D. Williams. *J. Am. Chem. Soc.*, **122**, 6293 (2000); (d) J.P. Zhang, S.L. Zheng, X.C. Huang, X.M. Chen. *Angew. Chem. Int. Ed. Engl.*, **43**, 206 (2004).

[14] (a) Y. Shimazaki, H. Yokoyama, O. Yamauchi. *Angew. Chem. Int. Ed. Engl.*, **38**, 2401 (1999); (b) X.M. Zhang, M.L. Tong, X.M. Chen. *Angew. Chem. Int. Ed. Engl.*, **41**, 1029 (2002).

[15] G.P. Shield, P.R. Raithby, F.H. Allen, W.D.S. Motherwell. *Acta Crystallogr., Sect. B*, **56**, 455 (2000).

[16] Y.O. Yang, W. Zhang, Y.H. Feng, G.F. Xu, D.Z. Liao, S.P. Yan. *Inorg. Chem. Commun.*, **10**, 1181 (2007).

[17] A.L. Spek. *PLATON – A Multipurpose Crystallographic Tool* (*Mercury 1.1*), *CCDC 2002*, Utrecht University, Netherlands (2000).

[18] T.M. Reineke, M. Eddaoudi, M. Fehr, D. Kelley, O.M. Yaghi. *J. Am. Chem. Soc.*, **121**, 1651 (1999).

[19] (a) R.G. Xiong, J.L. Zuo, X.Z. You, B.F. Abrahams, Z.P. Bai, C.M. Che, H.K. Fun. *Chem. Commun.*, 2061 (2000); (b) Z.P. Deng, S. Gao, Z.B. Zhu, L.H. Huo. *Z. Anorg. Allg. Chem.*, **634**, 593 (2008); (c) X.W. Wang, X. Li, J.Z. Chen, G. Zheng, H.L. Hong. *Eur. J. Inorg. Chem.*, 98 (2008).

[20] (a) S. Banthia, A. Samanta. *Polyhedron*, **25**, 2269 (2006); (b) M.J. Ren, J. Zhang, P. Zhao, Z. Zhang. *J. Inorg. Organomet. Polym.*, **18**, 284 (2008).