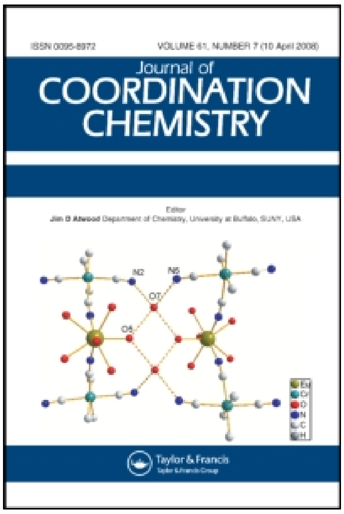

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1-D chain metal-organic polymers bridged by <i>bis</i>-benzimidazole-based ligands: syntheses, structures, and fluorescent properties

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1-D chain metal-organic polymers bridged by *bis*-benzimidazole-based ligands: syntheses, structures, and fluorescent properties

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Self-assembly of a flexible building unit 1,1′-(1,5-pentanediyl)*bis*-1*H*-benzimidazole (pbbm) with different transition metal salts affords two new 1-D chain metal-organic polymers, $[PbI_2(pbbm)]_n$ (**1**) and $\{[HgI_2(pbbm)] \cdot (DMF)_{1/2}\}_n$ (**2**). Polymer **1** features a 1-D double chain architecture in which two neighboring Pb(II) cations are bridged by a pair of I^-′s and the alternate lead atoms are further linked by pbbm; **2** possesses a 1-D zig-zag chain framework. The significant differences of these metal-organic frameworks indicate that metals have remarkable impact on the assembling and structures of the resultant aggregations. The photoluminescent properties of these new materials have also been studied in the solid state at room temperature.

Keywords: Metal-organic polymer; Crystal structure; Center metal; Fluorescence

1. Introduction

Crystal engineering of metal-organic frameworks (MOFs) has been extensively explored for its potential applications as functional materials [1–8]. The most facile approach is appropriate choice of well-designed organic bridging ligands (building blocks) containing modifiable backbones and connectivity, with the metal centers (nodes) with different coordination preferences [9]. Even so, rational control over topologies and optimized properties is a challenge due to labile coordination geometries, versatile coordination modes of organic building blocks, and subtle factors from crystallization conditions such as counteranion, temperature, and the solvent [10–18]. Therefore, more research is indispensable to gain information of the relevant structural types and establish correlation between structures and properties.

In our previous studies, we prepared a series of *bis*-benzimidazole-type bridging ligands, which exhibited ability to join metal ions in a variety of inorganic–organic arrangements ranging from discrete assemblies to infinite molecular networks [19–25]. These structurally varied architectures provide fascinating insight into the design

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of solid-state materials. To further understand coordination of such ligands and explore the structures of diverse metal centers of MOFs, the self-assembly of 1,1′-(1,5-pentanediyl)*bis*-1*H*-benzimidazole (pbbm) [23] with lead and mercury salts are carried out giving $[PbI_2(pbbm)]_n$ (**1**) and $\{[HgI_2(pbbm)]\cdot(DMF)_{1/2}\}_n$ (**2**). Herein, we report the syntheses and crystal structures of the two polymers as well as a discussion of the influence of different metal sites on the product formations and photoluminescent properties.

2. Experimental

2.1. *Materials and measurements*

All chemicals were of A. R. Grade and used without purification. IR data were recorded on a Bruker Tensor 27 spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region. Carbon, hydrogen, and nitrogen analyses were carried out on a FLASH EA 1112 elemental analyzer. Luminescence spectra were measured on powder samples at room temperature using a F-4500 HITACHI fluorescence spectrophotometer. The excitation slit and emission slit were 5 nm and the response time was 2 s. Ligand 1,1′-(1,5-pentanediyl)*bis*-1*H*-benzimidazole (pbbm) was prepared according to the literature [23].

2.2. *Synthesis of $[PbI_2(pbbm)]_n$ (1)*

A methanol solution (5 mL) of pbbm (30.4 mg, 0.1 mmol) was added to aqueous solution (4 mL) of $Pb(NO_3)_2$ (16.5 mg, 0.05 mmol) and KI (16.6 mg, 0.1 mmol) to give a clear solution. Prismatic colorless crystals (57% yield) suitable for X-ray diffraction were obtained 3 weeks later. The crystals are air-stable and soluble in $CHCl_3$, CH_3CN, and DMF. Anal. Calcd for $C_{19}H_{20}I_2N_4Pb$: C, 29.81; H, 2.63; N, 7.32%. Found: C, 29.78; H, 2.66; N, 7.30%. IR (KBr)/cm^{-1}: 3108 m, 2935 m, 1607 w, 1597 s, 1515 s, 1456 s, 1298 m, 755 s.

2.3. *Synthesis of $\{[HgI_2(pbbm)]\cdot(DMF)_{1/2}\}_n$ (2)*

A methanol solution (6 mL) of pbbm (30.4 mg, 0.1 mmol) was laid carefully above a DMF solution (4 mL) of HgI_2 (45.4 mg, 0.1 mmol). Colorless crystals (64% yield) suitable for X-ray diffraction were obtained 3 days later. Anal. Calcd for $C_{20.5}H_{23.5}HgI_2N4.5O_{0.5}$: C, 30.96; H, 2.98; N, 7.92%. Found: C, 30.99; H, 2.96; N, 7.90%. IR (KBr)/cm^{-1}: 3112 m, 2944 m, 1509 s, 1297 w, 1251 s, 759 s.

2.4. *X-ray structure analyses*

Data collection was performed on a Rigaku RAXIS-IV image plate area detector using graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation at 291(2) K using the ω-2θ scan technique. The data were corrected for Lorentz and polarization factors and for absorption by using empirical scan data. The structure was solved with the SHELX program [26], and refined by full-matrix least-squares based on F^2, with

Table 1. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Formula	$C_{19}H_{20}I_2N_4Pb$	$C_{20.5}H_{23.5}HgI_2N_{4.5}O_{0.5}$
Formula weight	765.38	795.33
Crystal system	Monoclinic	Monoclinic
Space group	*C2/C*	*P2(1)/n*
Unit cell dimensions (Å, °)		
a	15.243(3)	10.996(2)
b	15.835(3)	14.011(3)
c	9.3480(19)	15.818(3)
α	90	90
β	103.49(3)	95.53(3)
γ	90	90
V (Å^3)	2194.1(8)	2425.6(8)
T (K)	291(2)	291(2)
Z	4	4
μ(Mo-Kα) (cm^{-1})	2.317	2.178
Number of reflections collected [$I > 2\delta(I)$]	3340	6812
Number of independent reflections	1878	4038
Final R^a, R_w	0.0335 0.0695	0.0391 0.0582

$R^a = \Sigma||F_o - F_c||/\Sigma|F_o|$; $R_w^b = [\Sigma(||F_o - F_c||)^2/\Sigma_w|F_o|^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°).

$[PbI_2(pbbm)]_n$ (**1**)					
Bond distances					
Pb–N(1)	2.527(5)	Pb–I	3.3981(10)	Pb–I#2	3.2810(10)
Bond angles					
N(1)–Pb–N(1)#1	82.1(3)	N(1)–Pb–I#2	87.47(13)	N(1)#1–Pb–I#2	88.56(13)
I#2–Pb–I#3	174.73(2)	N(1)–Pb–I#1	166.45(13)	N(1)#1–Pb–I#1	88.94(13)
I#2–Pb–I#1	102.477(19)	I#3–Pb–I#1	80.911(19)	I#1–Pb–I	101.60(3)
$\{[HgI_2(pbbm)]\cdot(DMF)_{1/2}\}_n$ (**2**)					
Bond distances					
Hg(1)–N(1)	2.358(6)	Hg(1)–N(3)#1	2.380(7)	Hg(1)–I(2)	2.6805(11)
Hg(1)–I(1)	2.6819(9)				
Bond angles					
N(1)–Hg(1)–N(3)#1	95.2(2)	N(1)–Hg(1)–I(2)	105.90(17)	N(3)#1–Hg(1)–I(2)	110.53(18)
N(1)–Hg(1)–I(1)	102.68(18)	N(3)#1–Hg(1)–I(1)	100.53(18)	I(2)–Hg(1)–I(1)	135.02(3)

anisotropic thermal parameters for the nonhydrogen atoms. The hydrogen atoms were located theoretically and not refined. Crystal data and structure refinement of **1** and **2** are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Crystal structures of [PbI$_2$(pbbm)]$_n$ (1)*

Single-crystal structural determination reveals that **1** crystallizes in the monoclinic space group *C*2/*C* with a neutral asymmetric unit [PbI$_2$(pbbm)] and assumes an

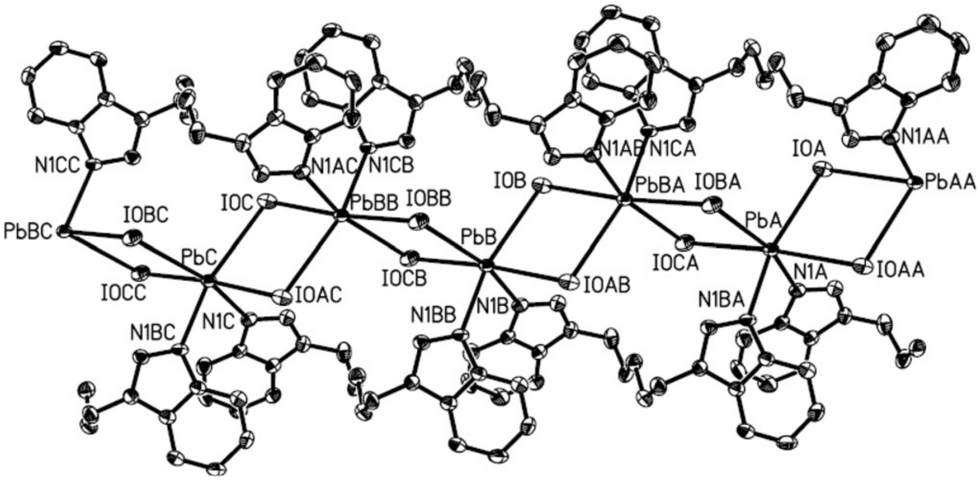

Figure 1. The 1-D double-stranded chain structure of **1**.

infinite 1-D double-stranded chain. As illustrated in figure 1, each Pb(II) is in a slightly distorted octahedral geometry comprised of four iodides and two N donors from different imidazole rings of two individual pbbm ligands. Three iodides (I0AA, I0BA, and I0CA) and one nitrogen (N1A) together with Pb(II) form the equatorial plane (the mean deviation from plane of 0.0714 Å); (I0A and N1BA) occupy the axial positions. The Pb(II)–N bond lengths of 2.527(5) Å are slightly shortened from those observed in related Pb complexes, such as $[Pb(bbbm)_2(NO_3)_2]_n$ (Pb–N 2.588(3) and 2.788(3) Å) (bbbm = 1,1′-(1,4-butanediyl)*bis*-1*H*-benzimidazole) [25] and $[PbL(ClO_4)] \cdot ClO_4$ (Pb–N (from pyrazole) 2.539(10)–2.860(10) Å) (L = 1,4,7-*tris*(pyrazol-l-ylmethyl)-1,4,7-triazacyclononane) [27]. Moreover, all Pb(II)–N bond distances are significantly shorter than those of Pb(II)–I (3.2810(10) and 3.3981(10) Å). The bond angles around Pb(II) ion vary from 80.911(19) to 174.73(2)°. In **1**, all Pb(II) ions and pbbm ligands are equivalent. The dihedral angle between two benzimidazole rings from the same ligand is 41.9°. These ligands twist to meet the requirement of steric exclusion. The torsion angles are −72.4(8)° for both N2–C8–C9–C10 and C10–C9CA–C8CA–N2CA. Counteranion I^- is a bidentate bridging ligand linking Pb atoms in a slightly distorted rhomboid with the average side length of 3.340 Å and inner angles of 80.911° and 99.089°; the nonbonded distance between Pb(II) ions is 5.083 Å. The adjacent dinuclear $Pb(\mu_2\text{-}I)_2Pb$ species are inclined to each other with a dihedral angle of 80.9° and further locked by a single pbbm bridge to form an infinitely 1-D double-stranded chain along the *a*-axis, with Pb···Pb separation through the pbbm bridge of 9.348 Å.

3.2. *Crystal structures of* $\{[HgI_2(pbbm)] \cdot (DMF)_{1/2}\}_n$ *(2)*

Crystallographic analysis provides direct evidence that **2** is different from **1**. Polymer **2** displays a 1-D zig-zag chain (figure 2). The Hg(II) center is tetrahedrally coordinated by two nitrogens from different pbbm ligands and two terminal iodides.

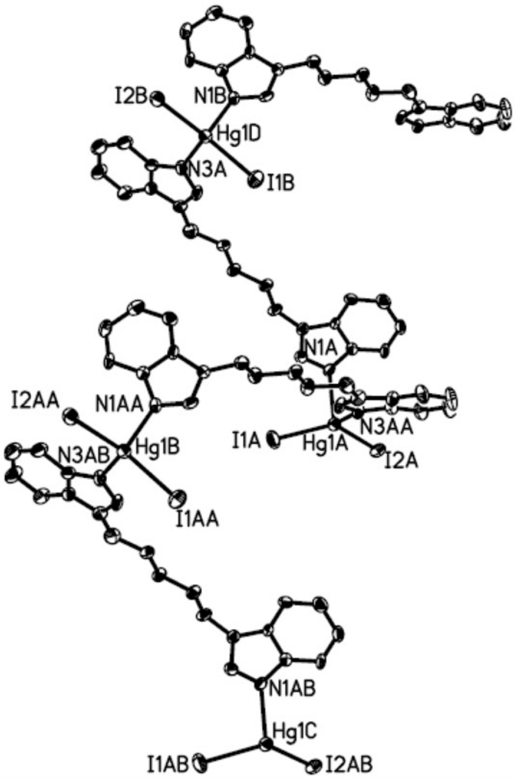

Figure 2. Perspective view of the 1-D zig-zag chain in **2**.

The N–Hg–I bond angles range from 100.53 to 110.53°, the I–Hg–I bond angle is 135.02°, and the N–Hg–N bond angle is only 95.2°. This distortion leads to a significant difference between two Hg–N bond lengths (2.358(6) and 2.380(7) Å). Hg–I bond lengths (2.6805(11) and 2.6819(9) Å) are normal compared to other Hg(II) systems [28]. The deviation from a tetrahedron is caused by the strong preference of Hg(II) for soft donors such as iodide and weak preference for N atoms [29]. The pbbm ligand is twisted with torsion angles of 169.3(7)° and 178.4(6)° for N2–C8–C9–C10 and C10–C11–C12–N4, respectively, and the dihedral angle between two benzimidazole planes is 100.2°, different from those found in **1**. Each *trans*-pbbm binds two Hg(II) ions together into a 1-D zig-zag chain running along *b*. The intrachain Hg $\cdots$ Hg separation is 13.206 Å.

In summary, **1** and **2** contain pbbm and I^-, but have different 1-D chain structures because of differences in coordination geometry with further confirmation by the discrete binuclear structure of $[CdI_2(pbbm)]_2$ [21]. The nature of the metal center plays a dominate role in assembling MOFs. The pbbm exhibits different conformation in the three complexes, namely, the dihedral angles between two benzimidazole planes within a ligand are 41.9° for **1**, 100.2° for **2** and 48.9° for the cadmium complex, and the corresponding torsion angles N2–C8–C9–C10 and C10–C9CA–C8CA–N2CA are −72.4(8)° for **1**, those of N2–C8–C9–C10 and

C10–C11–C12–N3 are 169.3(7)° and 178.4(6)° for **2**, as well as −65.2(5) and −66.6(5)° for the Cd(II)-containing complex. The flexible pbbm ligand can adopt varied conformations when it interacts with metals and control the structure of the final aggregate. Selection of appropriate flexible ligand, central metal, and counteranion is confirmed as important to construct MOFs.

3.3. *Photoluminescent properties of polymers*

Luminescence of MOFs is of interest owing to their higher thermal stability than the pure organic ligand and the ability to affect the emission wavelength and intensity of the organic material by metal coordination [30]. The solid-state photoluminescent behaviors of **1**, and **2** through excitation and emission spectra are depicted in figure 3. Excitation at 245 nm leads to broad fluorescence with emission maxima at 387 nm for free pbbm ligand, 391 nm for **1** and 396 nm for **2**. The similarity between emission spectra of the two polymers and free ligand, excluding emission intensity, implies that luminescence of the polymers is pbbm-based emission. Slight red shifts of 4 and 9 nm in contrast to the free ligands in **1** and **2** are considered to originate from coordination. The significantly weakened intensities of the emission bands for them are attributed to competitive quenching effect of iodide [21, 31]. The explanation for the different emission properties of **1** and **2** is the different metal ions, because photoluminescence is closely associated with the metal ions and ligands coordinated [32].

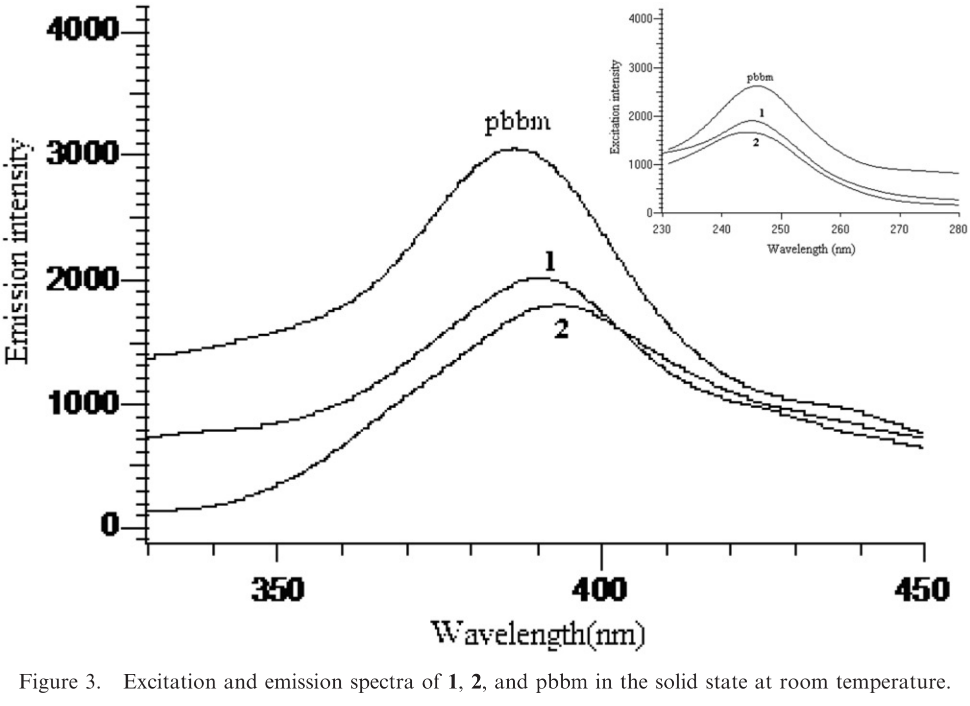

Figure 3. Excitation and emission spectra of **1**, **2**, and pbbm in the solid state at room temperature.

4. Conclusion

The assembly of lead(II) or mercury(II) with the same counteranion I^- and a flexible building unit 1,1′-(1,5-pentanediyl)*bis*-1*H*-benzimidazole (pbbm) results in two different 1-D coordination polymers, $[PbI_2(pbbm)]_n$ (**1**) and $\{[HgI_2(pbbm)]\cdot(DMF)_{1/2}\}_n$ (**2**). Although pbbm links metal centers in exo-bidentate mode, the metals display different coordination geometries; I^- in the two components serve as bridging and terminal ligands. Structural characterizations of organic ligands, metal centers, and counteranions play an important role in the construction of structural frameworks and fluorescence of coordination polymers.

Supplementary material

CCDC-682437 and CCDC-682438 for **1** and **2** contain the supplementary crystallographic data for this article. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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References

[1] O.R. Evans, W.B. Lin. *Acc. Chem. Res.*, **35**, 511 (2002).
[2] K. Kim. *Chem. Soc. Rev.*, **31**, 96 (2002).
[3] G.S. Papaefstathiou, L.R. MacGillivray. *Coord. Chem. Rev.*, **246**, 169 (2003).
[4] S.L. James. *Chem. Soc. Rev.*, **32**, 276 (2003).
[5] S. Kitagawa, R. Kitaura, S. Noro. *Angew. Chem.*, **116**, 2388 (2004); *Angew. Chem. Int. Ed.*, **43**, 2334 (2004).
[6] N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O.M. Yaghi. *Acc. Chem. Res.*, **38**, 176 (2005).
[7] B. Bujoli, S.M. Lane, G. Nonglaton, M. Pipelier, J. Leger, D.R. Talham, C. Tellier. *Chem. Eur. J.*, **11**, 1980 (2005).
[8] K. Biradha, M. Sarkar, L. Rajput. *Chem. Commun.*, **4169** (2006).
[9] (a) M.J. Zaworotko. *Chem. Commun.*, **1** (2001); (b) S.L. Zheng, M.L. Tong, X.M. Chen. *Coord. Chem. Rev.*, **246**, 185 (2003); (c) C. Janiak. *Dalton Trans.*, **2781** (2003); (d) M. Du, C.P. Li, X.J. Zhao. *Cryst. Growth Des.*, **6**, 335 (2006).
[10] X.M. Zhang, M.L. Tong, X.M. Chen. *Angew. Chem.*, **114**, 1071 (2002); *Angew. Chem., Int. Ed.*, **41**, 1029 (2002).
[11] S.R. Halper, S.M. Cohen. *Angew. Chem.*, **116**, 2439 (2004); *Angew. Chem., Int. Ed.*, **43**, 2385 (2004).
[12] N.P. Andrei, G. Marin, K. Suwinska, C.K. Victor, A. Marius, P. Viorica, I.P. Vasile. *J. Mater. Chem.*, **15**, 4234 (2005).
[13] M.L. Tong, B.H. Ye, J.W. Cai, X.M. Chen, S.W. Ng. *Inorg. Chem.*, **37**, 2645 (1998).
[14] M.S. Wang, G.C. Guo, M.L. Fu, L. Xu, L.Z. Cai, J.S. Huang. *Dalton Trans.*, **2899** (2005).

[15] C.N.R. Rao, S. Natarajan, R. Vaidhyanathan. *Angew. Chem.*, **116**, 1490 (2004); *Angew. Chem., Int. Ed.*, **43**, 1466 (2004).

[16] J.P. Zhang, Y.B. Wang, X.C. Huang, Y.Y. Lin, X.M. Chen. *Chem. Eur. J.*, **11**, 552 (2005).

[17] H.P. Jia, W. Li, Z.F. Ju, J. Zhang. *Eur. J. Inorg. Chem.*, **4264** (2006).

[18] J.Y. Lu. *Coord. Chem. Rev.*, **246**, 327 (2003).

[19] B. Xiao, H.W. Hou, Y.T. Fan. *J. Mol. Catal. A: Chem.*, **288**, 42 (2008).

[20] B. Xiao, H.W. Hou, Y.T. Fan. *J. Organomet. Chem.*, **692**, 2014 (2007).

[21] B. Xiao, H.W. Hou, Y.T. Fan, M.S. Tang. *Inorg. Chim. Acta*, **9**, 3019 (2007).

[22] B. Xiao, H.W. Hou, Y.T. Fan, M.S. Tang. *Inorg. Chem. Commun.*, **10**, 376 (2007).

[23] X.R. Meng, B. Xiao, Y.T. Fan, H.W. Hou, G. Li. *Inorg. Chim. Acta*, **357**, 1471 (2004).

[24] B. Xiao, H.Y. Han, X.R. Meng, Y.L. Song, Y.T. Fan, H.W. Hou, Y. Zhu. *Inorg. Chem. Commun.*, **7**, 378 (2004).

[25] X.R. Meng, Y.L. Song, H.W. Hou, Y.T. Fan, G. Li, Y. Zhu. *Inorg. Chem.*, **42**, 1306 (2003).

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

[27] D.V. Massimo, G. Matteo, M. Fabrizio, S. Piero. *J. Chem. Soc., Dalton Trans.*, **1173** (1996).

[28] Y.Y. Niu, H.W. Hou, Y.L. Wei, Y.T. Fan, Y. Zhu, C.X. Du, X.Q. Xin. *Inorg. Chem. Commun.*, **4**, 358 (2001).

[29] Y.Y. Niu, Y.L. Song, H.W. Hou, Y. Zhu. *Inorg. Chim. Acta*, **355**, 151 (2003).

[30] G. Wu, X.F. Wang, T. Okamura, W.Y. Sun, N. Ueyama. *Inorg. Chem.*, **45**, 8523 (2006).

[31] Y.B. Dong, P. Wang, R.Q. Huang, M.D. Smith. *Inorg. Chem.*, **43**, 4727 (2004).

[32] D.M. Ciurtin, N.G. Pschirer, M.D. Smith, U.H.F. Bunz, H.C. zur Loye. *Chem. Mater.*, **13**, 2743 (2001).

[33] P.L. Ng, C.S. Lee, H.L. Kwong, A.S.C. Chan. *Inorg. Chem. Commun.*, **8**, 769 (2005).

[34] J.C. Dai, X.T. Wu, Z.Y. Fu, C.P. Cui, S.M. Wu, W.X. Du, L.M. Wu, H.H. Zhang, Q. Sun. *Inorg. Chem.*, **41**, 1391 (2002).

[35] X.L. Wang, C. Qin, Y.G. Li, N. Hao, C.W. Hu, L. Xu. *Inorg. Chem.*, **43**, 1850 (2004).

[36] S.Q. Zang, Y. Su, Y.Z. Li, Z.P. Ni, Q.J. Meng. *Inorg. Chem.*, **45**, 174 (2006).