

Synthesis, structure and optical properties of new organic–inorganic haloplumbates complexes $(C_5H_{10}N_3)PbX_4$ ($X = Br, Cl$), $(C_2H_2N_4)PbBr_3$

Yinyan Li^{a,b}, Cuikun Lin^{a,b}, Guoli Zheng^{a,b}, Jun Lin^{a,*}

^aKey Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, China

^bChina Graduate School of the Chinese Academy of Sciences, Beijing 100049, China

Received 21 May 2006; received in revised form 13 September 2006; accepted 26 September 2006

Available online 29 September 2006

Abstract

Layered organic–inorganic composite materials $(C_5H_{10}N_3)PbX_4$ ($X = Br$ **1**, Cl **2**) containing histaminium dications were grown via a solution-cooling process, and their structure and optical properties were determined. The organic ligand–histaminium introduced into the corner-sharing octahedra of the ‘ PbX_4 -layer’ contains both primary ammonium and imidazolium different from the traditionally primary amine found in this system. As comparison, another analogous amine of 3-amino-1,2,4-triazol was used as ligand to coordinate with $PbBr_2$ in acid solution. A novel complex $(C_2H_2N_4)PbBr_3$ (**3**) was obtained with zigzag $PbBr_2$ chains different from the PbX_4 layer in compound as **1** and **2**. The hybrid $(C_5H_{10}N_3)PbX_4$ show exciton absorption at 339 nm for $X = Cl$ and 419 nm for $X = Br$ with the corresponding emission at 360 and 436 nm, respectively. The different $PbBr_2$ chain structure of compound **3** does not show photoluminescence.

© 2006 Elsevier Inc. All rights reserved.

Keywords: Layer structures; Haloplumbates; Histaminium; Imidazolium

1. Introduction

A family of organic–inorganic composite materials with the general composition $(R-NH_3)_2MX_4$ and $(NH_3-R-NH_3)MX_4$ ($M =$ divalent metal; $X =$ Halogen atoms; $R =$ organic moiety) incorporating interesting physical properties has been widely studied of late [1]. These compounds have often been referred to as “hybrid perovskites”, but are in fact related to the K_2MgF_4 and $TlAlF_4$ structures types [1d–g]. They are composed of monolayers made up of corner sharing metal-halide octahedra of AlF_4 -type [1d,e] alternating with organic ammonium layers.

Recently, much attention has been devoted to the family of the group (IVA) metal organic–inorganic K_2MgF_4 and $TlAlF_4$ structure-type materials, as a result of the strong room temperature photoluminescence and the ease with which the luminescence peak wavelength can be tuned to

virtually any wavelength in the visible spectrum through the appropriate choice of metal atom (Ge, Sn, and Pb), halogen (Cl, Br, and I), or inorganic sheet thickness [2]. These systems can be considered multilayer quantum well structures, with the group (IVA) metal halide sheets acting as wells and the much wider band gap organic layers forming the barrier layers. Strong photoluminescence results from the radiative decay of relative mobile excitons within the inorganic potential wells. The remarkable feature of the exciton state in these systems is the exceptional large binding energy and oscillator strength.

Owing to the confinement of the inorganic layers, the organic cations must satisfy in ionic bond, steric hindrance, as well as hydrogen bond, to fit the coordination environment provided by the inorganic framework. So the organic cations, which can be used to construct this type of structures, are generally restricted to primary ammonium or α , ω -diammonium cations [1a]. Only the analogous formamidinium cation [3] and 2,2'-biimidazolium dication [4] have been used to lead novel hybrid layered structure. Another layered $[(CH_3)_3NCH_2NH_3]SnI_4$

*Corresponding author. Fax: +86 431 569 8041.

E-mail address: jlin@ciac.jl.cn (J. Lin).

with quaternary/primary ammonium dication has been reported with special structure and optical properties [5]. Studies have shown that structure and properties of the organic–inorganic layered structure can be modified by controlling the thickness of the inorganic layer, by making substitutions on either the metal or halogen site, or by selecting different organic cations [6].

Here a new organic ligand histamine, which has imidazolium/primary ammonium dication in acid solution was used to build up the two new composite materials $(C_5H_{10}N_3)PbX_4$ ($X = Br$ **1**; Cl **2**). In this case the inorganic layer is made up of PbX_4 ($X = Br, Cl$) and will henceforth be referred to as the ‘ PbX_4 -layer’. Different from the traditionally primary amine, the histamine, which contains both a usual primary ammonium and a special imidazolium, was introduced in the structure, binding the PbX_4 -layers together. The organic molecule appears to interact strongly with the PbX_4 -layers, drastically distorting them through coupled octahedral rotation. As comparison, another analog 3-amino-1,2,4-triazol which has short primary amine chains was used to coordinate with $PbBr_2$ in acid solution. The zigzag chains structure $(C_2H_2N_4)PbBr_3$ **3** obtained proved that different organic cations influence the inorganic structure greatly. Also the observed strong room temperature photoluminescence of compounds **1** and **2** have not been observed in compound **3**. Like other PbX_4 -layer structures, the new hybrid composites $(C_5H_{10}N_3)PbX_4$ ($X = Br$ **1**; Cl **2**) can also be easily processed into thin films with layered structure by spin coating for potential optoelectronic device application [7].

2. Experiment section

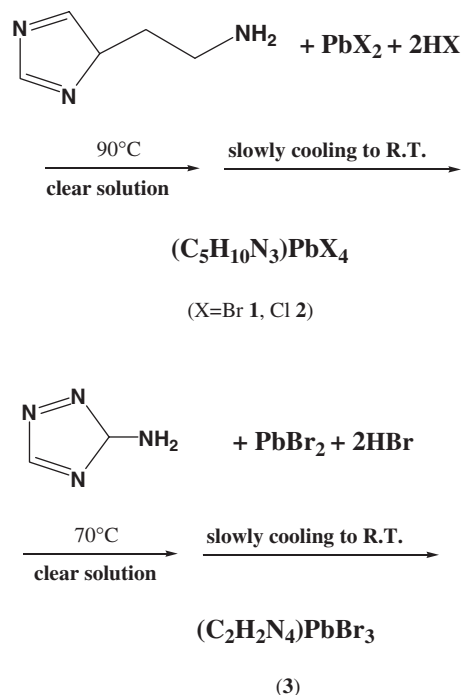
2.1. Materials and synthesis

$PbBr_2$ (99.99%), $PbCl_2$ (99.99%) and 3-amino-1,2,4-triazole were purchased from Aldrich are used without further purification. Histamine (98%), HBr (40%) and HCl (36%) were purchased from Beijing Chemical Industry Co., Ltd. All these materials were used as received. The title compounds were prepared by reacting lead halide and histamine in hydrochloric (or hydrobromic) acid, as shown in Scheme 1.

Compound 1: Equimolar amounts of $PbBr_2$ (0.367 g, 0.1 mmol) and histamine (0.113 g 0.1 mmol) were added to 10 mL hydrobromic acid (40%), and the mixture was heated to 90 °C by refluxing, then slowly cooled to room temperature in N_2 atmosphere and pink crystal of $(C_5H_{10}N_3)PbBr_4$ (**1**) were formed (yielding: 40.3%).

Compound 2: Equimolar amounts of $PbCl_2$ (0.278 g, 0.1 mmol) and histamine (0.113 g, 0.1 mmol) were added to 10 mL hydrochloric acid (36%), and the mixture was heated to 90 °C by refluxing, then slowly cooled to room temperature in N_2 atmosphere, to get compound **2** (yielding: 38.6%).

Compound 3: Same method as that of compound **1** was used and crystals of $(C_2H_2N_4)PbBr_3$ (**3**) were obtained (yielding: 45.5%).



Scheme 1. The growth and formation processes for the compounds $(C_5H_{10}N_3)PbX_4$ ($X = Br$ **1**, Cl **2**) and $(C_2H_2N_4)PbBr_3$.

2.2. Thin film deposition

Thin films of compounds **1** and **2** were prepared by spin coating a DMF solution on quartz substrate. The solution for spin coating was prepared by dissolving 10 mg of recrystallized hybrid of the title compounds in 1.5 mL dried DMF. The film was prepared by flooding the substrate with the solution and spinning cycle with 1 s ramping to 1200 rpm and dwelling 50 s at 1200 rpm. Then the substrate was annealed at 100 °C for 20 min to remove residual solvent.

2.3. Characterization

Diffraction intensities were collected on a Rigaku RAXIS-RAPID image plate diffractometer using the ω -scan technique with $MoK\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). Absorption corrections were applied using the multiscan technique [8a]. The structures were solved by direct methods using SHELXS-97 [8b] and refined by means of full-matrix least-squares techniques using the SHELXL-97 program [8c] as implemented in WINGX [8d]. Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms attached to carbon were generated geometrically. Analytical expressions of neutral-atom scattering factors were employed, with anomalous dispersion corrections incorporated therein [8e]. The excitation and emission spectra were taken on a Hitachi F-4500 spectrofluorimeter equipped with a 150 W xenon lamp as the excitation source. The morphology of the thin film was measured on an atomic force microscope (AFM, Bermad-2000 SPM) with a tapping mode. UV-Vis absorption

spectra were taken on a Hitachi F-4100 spectrofluorimeter. The X-ray diffraction (XRD) of the thin film samples was examined on a Rigaku-Dmax 2500 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 0.15405 \text{ nm}$).

3. Results and discussion

3.1. Crystal structure

Compound **1** belongs to monoclinic crystal system, crystallizing in space group $P2_1/c$. The basic building block of the $(\text{C}_5\text{H}_{11}\text{N}_3)_2\text{PbBr}_4$ structure, as shown in Fig. 1, consists of a well-ordered layer of AlF_4 -type alternating with histaminium dications. The crystal structure of compound **2** is similar to that of the compound **1** which will not be further described here.

The PbBr_4 -sheets of compound **1** consist of distorted corner-sharing PbBr_6 octahedra. Bond lengths of Pb-Br range from 2.9324(9) to 3.0728(9) Å and within the octahedra the bond angles Br-Pb-Br also deviate substantially from 90° , i.e. from $83.06(3)^\circ$ to $102.39(3)^\circ$ (see Fig. 1 and Tables 1, 2). The distortion of the octahedra indicates the stereochemically active lead (II) lone pair electrons as previously reported [3b]. The $\text{Pb-Br}_4\text{-Pb}$ angle is $153.655(41)^\circ$, indicating the corrugation of the PbBr_4 -layers along the b -axis. There is also a rotation of the octahedrons in the b - c plane which is shown in Fig. 1. The much important corrugation and rotation of PbBr_4 -sheets may be attributed to the special structure of the organic dications (Table 3).

The histaminium dications layer interleaves between the neighboring PbBr_4 -layers. It is a special dication which possesses both a usual primary ammonium and an imidazolium. The histaminium dications within compound **1** take forms similar to those observed for the cation of phenethylammonium in $(\text{C}_6\text{H}_5\text{C}_2\text{H}_4\text{NH}_3)_2\text{MCl}_4$ ($M = \text{Pb}, \text{Cu}$) [9]. Between neighboring sheets, hydrogen atoms of

primary ammonium (N1) take terminal halogen configuration hydrogen bond as shown in Fig. 1. Hydrogen atoms of imidazoliums (N2, N3) take weak hydrogen bonds with the two nearest terminal halogens nearby. In these hydrogen bonds, the N-H distances range from 2.4986 to 2.7766 Å and the N-H-Br angles range from 130.106° to 173.495° . Hydrogen bonds between the organic cation and the

Table 1
Crystal data for compounds **1** and **3**

Formula	$(\text{C}_5\text{H}_{11}\text{N}_3)\text{PbBr}_4$	$(\text{C}_2\text{H}_2\text{N}_4)\text{PbBr}_3$
M_w	640.00	529.00
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pna2_1$
a (Å)	10.632(5)	13.308(2)
b (Å)	11.617(5)	8.6033(15)
c (Å)	11.955(5)	8.0841(14)
β ($^\circ$)	110.059(5)	90.00
Volume (Å ³)	1387.0(11)	925.6(3)
Z	4	4
D_c (Mg m^{-3})	3.065	3.796
$F(000)$	1136	928
$R_1/\omega R_2$ [$I > 2\sigma > (I)$]	0.0435/0.1008	0.0505/0.1383

Table 2
Selected bond distances (Å) and bond angles (deg) of compound **1**

Br1 Pb1 2.9324(14)	Br4 Pb1 2.9393(16)
Br1 Pb1 #1 3.0728(15)	Br4 Pb1 #2 3.0412(16)
Br2 Pb1 2.9649(16)	Pb1 Br4 #3 3.0412(16)
Br3 Pb1 3.0158(16)	Pb1 Br1 #4 3.0728(15)
Pb1 Br1 Pb1 #1 174.84(4)	Br2 Pb1 Br1 #4 83.06(3)
Pb1 Br4 Pb1 #2 153.66(5)	Br2 Pb1 Br4 #3 86.77(4)
Br3 Pb1 Br1 #4 99.69(3)	Br4 #3 Pb1 Br1 #4 102.39(3)
Br1 Pb1 Br4 #3 86.06(3)	Br4 Pb1 Br1 #4 83.32(3)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y + \frac{1}{2}, z - \frac{1}{2}$; #2 $-x, y - \frac{1}{2}, -z + \frac{3}{2}$; #3 $-x, y + \frac{1}{2}, -z + \frac{3}{2}$; #4 $x, -y + \frac{1}{2}, z + \frac{1}{2}$.

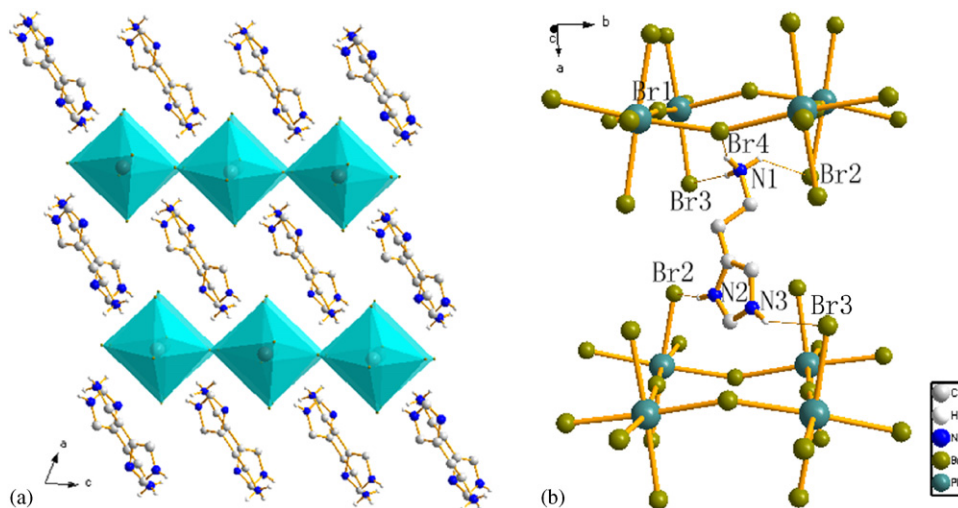


Fig. 1. Crystal structure of compound **1** viewed along b -axis (a) and c -axis (b).

Table 3
Selected bond distances (Å) and bond angles (deg) of compound 3

Pb(1)–Br(3)	2.944(2)	Br(3)–Pb(1)–Br(1)	82.87(6)
Pb(1)–Br(1)	2.969(2)	Br(3)–Pb(1)–Br(2)	79.36(6)
Pb(1)–Br(2)	3.027(2)	Br(1)–Pb(1)–Br(2)	88.63(7)
Pb(1)–Br(2)#1	3.042(2)	Br(3)–Pb(1)–Br(2)#1	84.71(6)
Pb(1)–Br(1)#1	3.098(2)	Br(1)–Pb(1)–Br(2)#1	87.42(6)
Br(2)–Pb(1)#2	3.042(2)	Br(2)–Pb(1)–Br(1)#1	94.18(6)
Br(1)–Pb(1)#2	3.098(2)	Pb(1)–Br(2)–Pb(1)#2	85.37(5)
		Pb(1)–Br(1)–Pb(1)#2	85.38(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y+1, z+\frac{1}{2}$, #2 $-x+1, -y+1, z-\frac{1}{2}$.

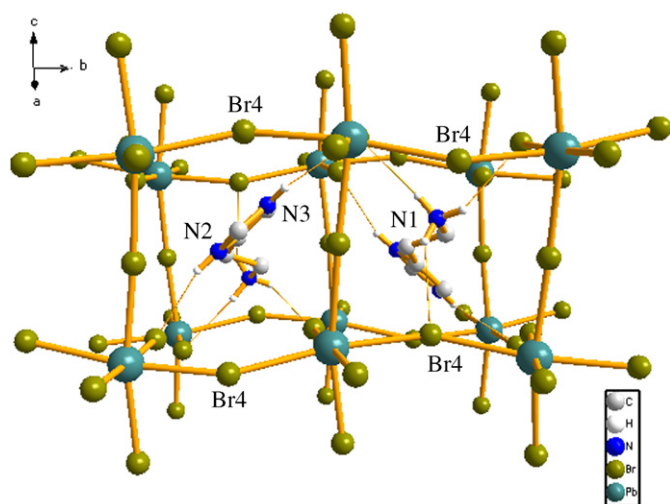


Fig. 2. Crystal structure of compound 1 viewed along a -axis.

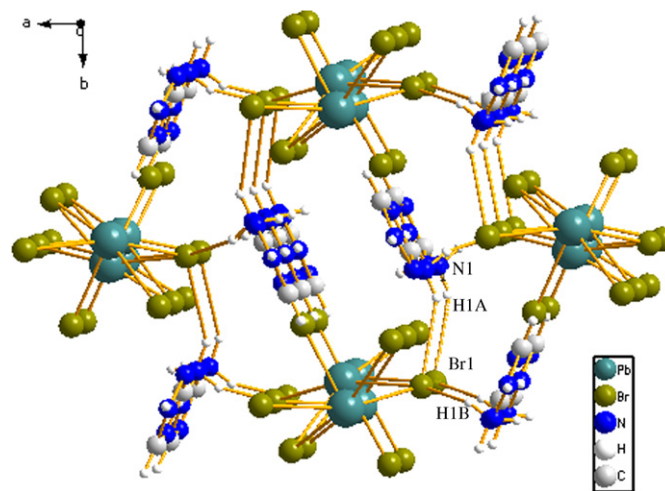


Fig. 3. Crystal structure of compound 3.

inorganic sheets have always been taken as an important interaction responsible for the stabilization of the whole structure [10]. The imidazolium group of the organic dication has steric hindrance to hydrogen bond and electrostatically interacts with the inorganic sheets. The four bridging Pb–Br bonds point slightly outward with Br4–Br4–imidazonium distance longer than Br4–Br4 primary ammonium distance (shown in Fig. 2), so as to open up space for accommodating the bulky imidazolium group.

Crystal structure of compound 3 is shown in Fig. 3. With the NH_3^+ directly connecting to the triazole without alkyl between them, compound 3 shows a structure different from that of compound 1. Perhaps due to the steric hindrance of the triazole, PbBr_2 in this structure forms zigzag chains. Lead atoms in compound 3 take square pyramidal geometry, and these square pyramids share near edges to link PbBr_3 -chains. The organic components connecting the inorganic chains through hydrogen bond arrange regularly between them. The Br1 atoms in the inorganic chains take hydrogen bond with two hydrogen atoms (H1A, H1B) of N1 with bond lengths: Br1–H1A 2.831 Å, Br1–H1B 2.778 Å, and bond angles: N1–H1A–Br1 145.832°, N1–H1B–Br1 147.106°.

The inorganic chains of compound 3 is shown in Fig. 4. The near square pyramids share edges to link a zigzag

chain. In these square pyramids the basal bonds are shorter than the axial bonds with Pb–Br bond lengths ranging from 2.944 to 3.098 Å shown in Table 3. The axial bonds along the chain point to alternative direction, which is similar to those previously reported chains in a CuCl_2 complex [10d].

Another imidazolium with longer side chains N-(3-aminopropyl)imidazole has been incorporated into the bromoplumbate. A novel $\langle 110 \rangle$ -oriented organic–inorganic PbBr_4 -layered complex was obtained [11a]. It shows that different side chains of imidazolium bring about different inorganic framework, which indicates that organic ligand can template the inorganic structure to some extent.

3.2. Film morphology

Atomic force microscope (AFM) topology images for spin-coating film of compounds 1 and 2 are shown in Fig. 5. The films show even grain structure with grain size ranging from 100 to 200 nm. The regular films provide the opportunity for the hybrid to potential optoelectronic device application. The films exhibit well-defined ($h00$) ($h = 1, 2, 3, \dots$) diffraction peaks (Fig. 6), indicating that the film is well-crystallized and highly oriented. Comparison

between the two compounds indicates that compound **2** has hybrid structure similar to that of compound **1**.

3.3. Optical properties

Fig. 7 shows the absorption spectra of compound **1** (a) and compound **2** (b). The narrow absorption peaks at 419 nm in compound **1** and at 339 nm in compound **2**, are

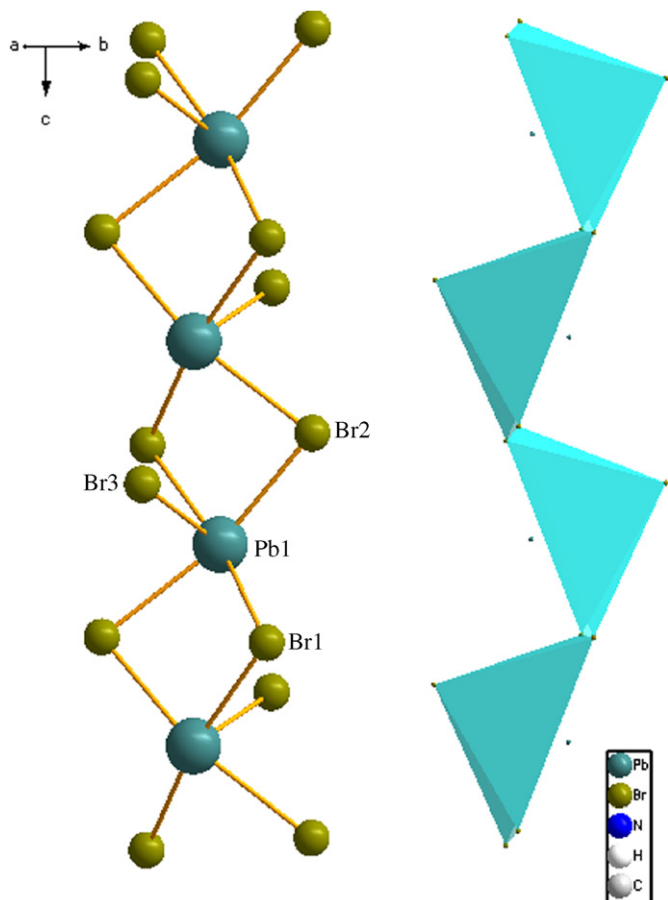


Fig. 4. Chain structure of PbBr_2 of compound **3**.

respectively, typical absorptions of excitons arising from the 2D PbBr_4^{2-} - and PbCl_4^{2-} -based organic/inorganic layered structures [11]. This reveals a good impact of organic cations on the bonding features of the PbX_4 -layers, which finally influences the physical properties of the inorganic sheets.

Fig. 8 shows the emission spectra of compound **1** (a) and compound **2** (b). Previous work on various organic–inorganic lead (II) and tin (II) compounds has demonstrated strong luminescence in the visible range, arising from an exciton state [1]. The luminescence originates from electronic transitions within the inorganic layer. The sharp peaks at 436 nm in compound **1** and at 360 nm compound **2** are characteristic exciton emissions from inorganic layer of PbBr_4^{2-} and PbCl_4^{2-} , respectively [12]. This type of layered structure can be considered as semiconductors [1a]. Under excitation, an electron (\ominus) is excited from the valence band (VB) to the conduction band (CB), leaving a hole (\oplus) in the VB. The electron (\ominus) and the hole (\oplus) move freely in the

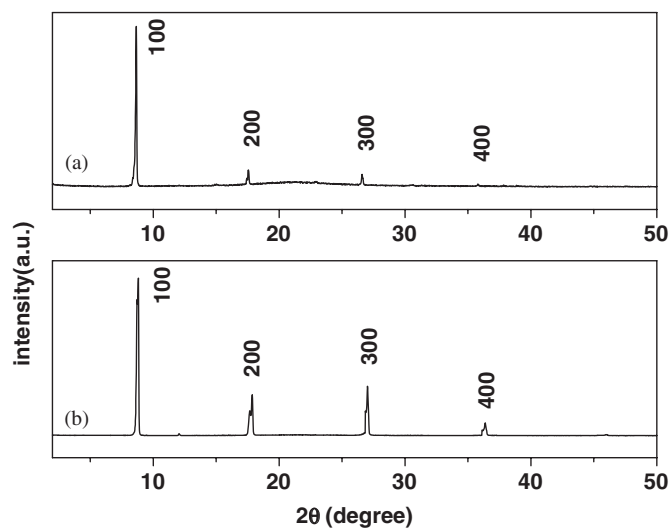


Fig. 6. XRD patterns diffractions for the thin films of compound **1** (a) and compound **2** (b).

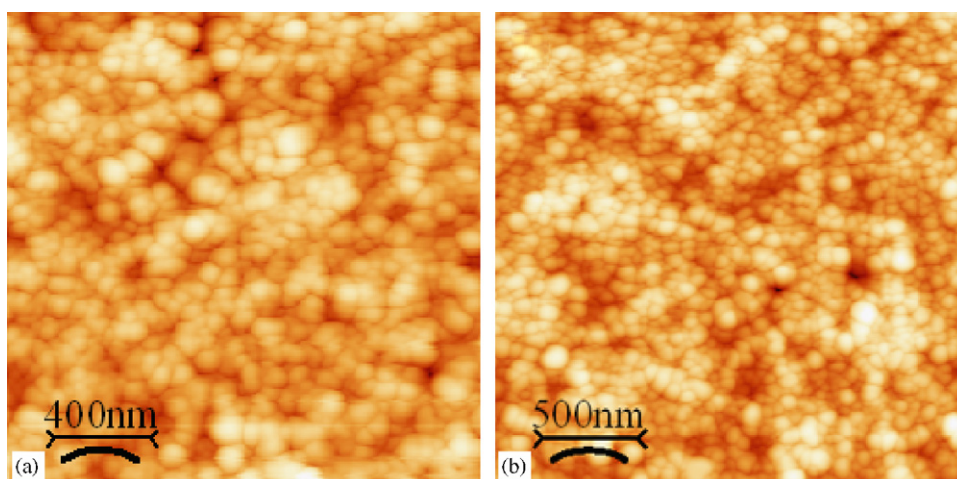


Fig. 5. Atomic force microscope (AFM) topology images for spin-coating films of compound **1** (a) and compound **2** (b).

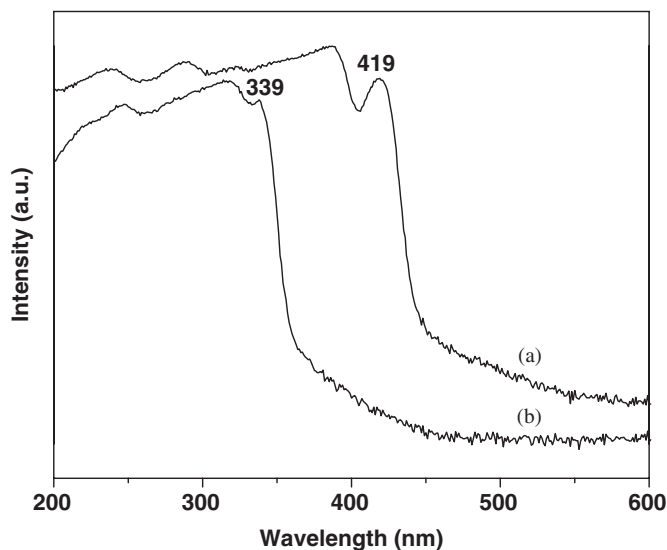


Fig. 7. UV-Vis absorption spectra for compound **1** (a) and compound **2** (b).

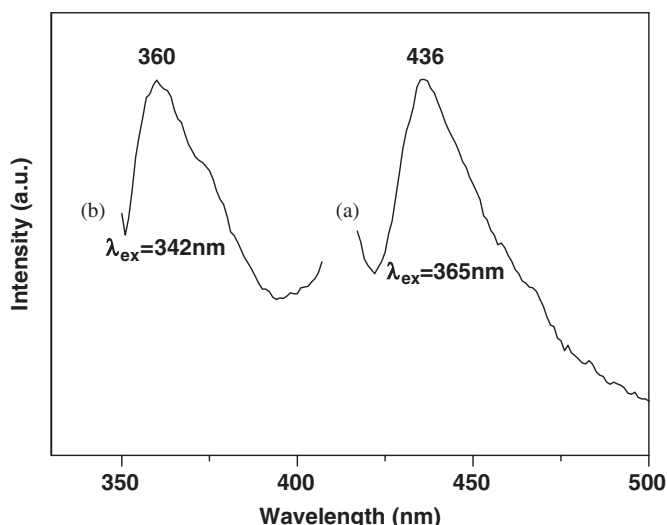


Fig. 8. Room-temperature emission spectra for ground solid state samples of compound **1** (a) and compound **2** (b).

CB and VB, forming an exciton. The recombination of the electron and hole in the exciton yields an emission [11c]. Both dominant features corresponding to the exciton state in the absorption and photoluminescence emission spectra of the two compounds show red shift as the halogen progresses from Cl to Br, which is consistent with previously reported results [1a]. The small Stokes shifts (17 nm for compound **1** and 21 nm for compound **2**) between the adsorption and emission as well as the narrow bandwidth of the peaks are the characteristic of excitons. Measurement of compound **3** has not found photoluminescence of excitons, which indicates that selected organic ligand can both change the structure and the optical properties of the inorganic layers (Figs. 7 and 8).

4. Conclusions

Three novel organic–inorganic complexes ($C_5H_{10}N_3$)Pb X_4 ($X = Br$ **1**, Cl **2**) and ($C_2H_2N_4$)PbBr $_3$ (**3**), which include imidazolium/primary ammonium to template inorganic structures, were obtained. Different ammoniums make different inorganic structures through special hydrogen bonds. Compounds **1** and **2** can be easily processed into thin film with layered structure. A red shift was observed for the absorption and emission from $X = Cl$ to $X = Br$ for ($C_5H_{10}N_3$)Pb X_4 . Continued study of diverse organic amines and metal halides can be expected.

Acknowledgments

This project is financially supported by the foundation of Bairen Jihua of Chinese Academy of Sciences, the MOST of China (no. 2003CB314707) and National Natural Science Foundation of China (50225205, 20431030).

References

- [1] (a) D.B. Mitzi, *Prog. Inorg. Chem.* 48 (1999) 1; (b) L.Q. Fan, L.M. Wu, L. Chen, *Inorg. Chem.* 45 (2006) 3149; (c) Z.L. Xiao, H.Z. Chen, M.M. Shi, G. Wu, R.J. Zhou, Z.S. Yang, M. Wang, B.Z. Tang, *Mater. Sci. Eng. B* 117 (2005) 313; (d) H. Mizoguchi, T. Omata, H. Kawazoe, S. Fujitsu, H. Hosono, N. Ueda, *J. Phys.: Condens. Matter* 8 (1996) 303; (e) K.S. Aleksandrov, *Kristallografiya* 40 (1995) 279; (f) J.M. Garcia-Lastra, J.A. Aramburu, M.T. Barriuso, M. Moreno, *Chem. Phys. Lett.* 385 (2004) 286; (g) M. Arakawa, H. Ebisu, H. Takeuchi, *J. Phys.: Condens. Matter* 14 (2002) 8613.
- [2] (a) T. Ishihara, J. Takahashi, T. Goto, *Phys. Rev. B* 42 (1990) 11099; (b) X. Hong, T. Ishihara, A.V. Nurmikko, *Phys. Rev. B* 45 (1992) 6961.
- [3] (a) D.B. Mitzi, S. Wang, C.A. Field, C.A. Chess, A.M. Guloy, *Science* 267 (1995) 1473; (b) S. Wang, D.B. Mitzi, C.A. Field, A. Guloy, *J. Am. Chem. Soc.* 117 (1995) 5297; (c) D.B. Mitzi, K. Liang, S. Wang, *Inorg. Chem.* 37 (1998) 321.
- [4] Z. Tang, J. Guan, A.M. Guloy, *J. Mater. Chem.* 11 (2001) 479.
- [5] Z. Xu, D.B. Mitzi, D.R. Medeiros, *Inorg. Chem.* 42 (2003) 1400.
- [6] (a) D.B. Mitzi, *Chem. Mater.* 8 (1996) 791; (b) G.A. Mousdis, G.C. Papavassiliou, C.P. Raptopoulou, A. Terzis, *J. Mater. Chem.* 10 (2000) 515.
- [7] (a) K. Liang, D.B. Mitzi, M.T. Prikas, *Chem. Mater.* 10 (1998) 403; (b) D.B. Mitzi, M.T. Prikas, K. Chondroudis, *Chem. Mater.* 11 (1999) 542.
- [8] (a) T. Higashi, Program for Absorption Correction, Rigaku Corporation, Tokyo, Japan, 1995; (b) G.M. Sheldrick, SHELXS-97, a Program for Automatic Solution of Crystal Structure, University of Goettingen, Germany, 1997; (c) G.M. Sheldrick, SHELXL-97, a Program for Crystal Structure Refinement, University of Goettingen, Germany, 1997; (d) L.J. Farrugia, WINGX, a Windows Program for Crystal Structure Analysis, University of Glasgow, Glasgow, UK, 1988; (e) T. Cromer, *International Tables for X-ray Crystallography*, vol. C, Kluwer Academic Publishers, Dordrecht, 1992.
- [9] (a) R.D. Willett, *Acta Crystallogr. C* 46 (1990) 565; (b) D.B. Mitzi, *J. Solid State Chem.* 145 (1999) 694.
- [10] (a) A.L. Gillon, G.R. Lewis, A.G. Orpen, S. Rotter, J. Starbuck, X.M. Wang, Y. Rodríguez-Martín, C. Ruiz-Pérez, *Dalton Trans.* (2000) 3897;

- (b) A. Angeloni, P.C. Crawford, A.G. Orpen, T.J. Podesta, B.J. Shore, *Chem. Eur. J.* 10 (2004) 3783;
- (c) D.B. Mitzi, D.R. Medeiros, P.R.L. Malenfant, *Inorg. Chem.* 41 (2002) 2134;
- (d) K.E. Halvorson, T. Grigereit, R.D. Willett, *Inorg. Chem.* 26 (1987) 1716.
- [11] (a) Y.Y. Li, C.K. Lin, G.L. Zheng, Z.Y. Cheng, H. You, W.D. Wang, J. Lin, *Chem. Mater.* 18 (2006) 3463;
- (b) Z.Y. Cheng, B.X. Gao, M.L. Pang, S.Y. Wang, Y.C. Han, J. Lin, *Chem. Mater.* 15 (2003) 4705;
- (c) Z.Y. Cheng, Z. Wang, R.B. Xing, Y.C. Han, J. Lin, *Chem. Phys. Lett.* 376 (2003) 481;
- (d) G.C. Papavassiliou, I.B. Koutselas, *Synthetic Met.* 71 (1995) 1713;
- (e) N. Mercier, S. Poiroux, A. Riou, P. Batail, *Inorg. Chem.* 43 (2004) 8361.
- [12] (a) M. Braun, W. Tuffentsammer, H. Wachtel, H.C. Wolf, *Chem. Phys. Lett.* 303 (1999) 157;
- (b) G.C. Papavassiliou, G.A. Mousdis, I.B. Koutselas, *Synthetic Met.* 121 (2001) 1339;
- (c) M.D. Segall, P.L.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, *J. Phys.: Condens. Matter* 14 (2002) 2717;
- (d) J.P. Perdew, B.M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.