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# Influence of neutral amine ligands on the network assembly of lead(II) 4-sulfobenzoate complexes

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# Abstract

Two new lead(II) 4-sulfobenzoate complexes with amine ligands,  $[Pb(4-sb)(2,2'-bipy)]_n$  (1) and  $\{[Pb(4-sb)(4,4'-bipy)_{1/2}] \cdot (4,4'-bipy)_{1/2}\}_n$  (2) (2,2'-bipy = 2,2'-bipyridine; 4,4'-bipy = 4,4'-bipyridine; 4-sb = 4-sulfobenzoate dianion), were synthesized and characterized by single-crystal X-ray analyses, IR, TG, elemental analyses and fluorescent studies. Complexes 1 and 2, in addition to previously reported  $[Pb(4-sb)(H_2O)_2]_n$  (3) and  $\{[Pb(4-sb)(phen)] \cdot (H_2O)\}_n$  (4) where phen is 1,10-phenanthroline, all contain [Pb(4-sb)] building units, while four [Pb(4-sb)] networks in 1–4 are very different, which is significantly influenced by the neutral ligands. The coordination array of complex 1 is a 2-D network in which each 4-sb acts as a  $\eta_5-\mu_3$  mode while the complex 2 is a 3-D architecture in which each 4-sb performs a  $\eta_5-\mu_6$  mode. Both coordination modes of 4-sb ligands in 1–2 are novel and first reported in this paper.

Keywords: 4-Sulfobenzoate; Lead(II); Coordination polymer; Network assembly

# 1. Introduction

In recent decade, network or framework construction is an interesting issue in the pursuing of functional materials [1-3]. A large number of 1,4-benzenedicarboxylate (bdc) coordination polymers with metal-organic frameworks have been synthesized and these coordination polymers can be potentially used in gas adsorption, chemical sensor, and catalysis [4–14]. The bdc ditopic ligand has two potentially equivalent coordinating carboxylate groups, thus the variable topologies in assembled networks constructed by this ligand are largely limited. The sulfonate group has a very different coordination ability compared to the carboxylate, therefore a ligand with the sulfonate and carboxylate, 4-sulfobenzoate (4-sb), has been chosen for constructing novel diverse networks in our lab [15–17] and other research groups [18,19]. Unexpectedly, only four of the

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4-sb coordination modes in all transition metal complexes were observed in the Cambridge Structural Database (CSD; May 2006 update) [20], as depicted in Scheme 1. Interestingly, our previous exploration exhibited that the Pb<sup>II</sup> salts used in the synthetic chemistry instead of transition metals led to the {[Pb(4-sb)(phen)]·(H<sub>2</sub>O)}<sub>n</sub> and [Pb(4sb)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> complexes [21,22], in which the 4-sb ligands perform interesting coordination modes, therefore, we reasoned that further exploration using different bridging or chelating amine ligands to tune networks may induce more diverse structures. Herein, we report the influence of neutral ligands on the network assembly of lead(II) 4-sulfobenzoate complexes.

# 2. Experimental

#### 2.1. Materials and instruments

All chemicals and solvents used in this work were commercially obtained and were used as received without further purification. Elemental analyses (C, H, and N) were

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Scheme 1. Coordination modes of the 4-sb in all reported transition metal complexes.

carried out on a ThermoFinnigan Flash EA1112. The IR spectra were recorded on a Nicolet Nexus 470 spectrophotometer in the range 400–4000 cm<sup>-1</sup> in KBr pellets. Thermogravimetric analyses (TGA) were performed by a NETZSCH STA 409 in a N<sub>2</sub> atmosphere with a heating rate of 10 °C min<sup>-1</sup> using Al<sub>2</sub>O<sub>3</sub> crucibles. The fluorescence study was carried out on a powder sample at room temperature using a Hitachi 850 spectrometer.

# 2.1.1. Synthesis of $[Pb(4-sb)(2,2'-bipy)]_n$ (1)

A mixture of Pb(NO<sub>3</sub>)<sub>2</sub> (0.173 g, 0.52 mmol), 4-sulfobenzoic acid monopotassium salt (0.114 g, 0.48 mmol), 2,2'-bipyridine (0.098 g, 0.5 mmol) and H<sub>2</sub>O (15 ml) was placed in a 30-mL stainless-steel reactor with Teflon liner and heated at 150 °C for 24 h. The vessel was then slowly cooled to room temperature, and light yellow block crystals of **1** were collected by filtration. Yield: 62% based on the Pb<sup>II</sup> salt. Anal. Calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>SPb: C, 36.23%; H, 2.14%; N, 4.97%. Found: C, 36.41%; H, 2.25%; N, 4.86%. IR (KBr pellet, cm<sup>-1</sup>): 1590(s), 1536(s), 1496(m), 1478(s), 1437(s), 1389(s), 1323(m), 1255(s), 1172(s), 1150(s), 1110(s), 1004(s), 854(s), 784(s), 768(s), 739(s), 700(m), 642(s), 558(s), 477(s), 417(m).

# 2.1.2. Synthesis of $\{[Pb(4-sb)(4,4'-bipy)_{1/2}] \cdot (4,4'-bipy)_{1/2}\}_n$ (2)

A mixture of Pb(NO<sub>3</sub>)<sub>2</sub> (0.165 g, 0.5 mmol), 4-sulfobenzoic acid monopotassium salt (0.120 g, 0.5 mmol), 4,4'bipyridine (0.098 g, 0.5 mmol) and H<sub>2</sub>O (15 ml) was added in a 30-mL stainless-steel reactor with Teflon liner and heated at 150 °C for 22 h. After cooling naturally, light yellow prism crystals of **2** were collected by filtration. Yield: 47% based on the Pb<sup>II</sup> salt. Anal. Calcd for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>5</sub>SPb: C, 36.23%; H, 2.14%; N, 4.97%. Found: C, 36.17%; H, 2.12%; N, 4.98%. IR (KBr pellet, cm<sup>-1</sup>): 1605(m), 1585(s), 1525(s), 1493(m), 1382(s), 1231(m), 1187(s), 1162(m), 1143(m), 1119(s), 1031(m), 1006(s), 822(w), 797(m), 779(m), 729(m), 641(s), 622(m), 606(w), 569(m), 550(w), 466(m).

These two complexes are insoluble in water and common organic solvents, such as methanol, ethanol, acetone, benzene, chloroform, THF, and N,N'-dimethylformamide.

#### 2.2. X-ray structure determination

Data collection for complexes 1 and 2 were carried out by a Brucker SMART diffractometer equipped with a CCD area detector. The data were integrated by use of the SAINT program, and the intensities were corrected for Lorentz factor polarization and absorption [23]. The two structures were solved by Patterson method and successive Fourier syntheses. Full-matrix least squares refinements on  $F^2$  were carried out using SHELXL-97 package [24]. All hydrogen atoms were placed in calculated positions and refined as riding, with C-H = 0.93 Å and  $U_{iso}(-$ H)= $1.2U_{eq}(C)$ . All the programs used are included in the WinGX Suite with the version of 1.70 [25]. The highest and lowest peaks in the final difference Fourier maps for complexes 1 and 2 are near Pb atoms, indicating meaningless for real atoms. Detail crystal data and structure refinements for 1-2 are listed in Table 1.

# 3. Results and discussion

Single-crystal X-ray analysis revealed that the coordination array of complex 1 is a 2-D network, in which each

	Tal	ble	1
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Crystal data and details of structural	determination of complexes	1 and 2
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Complex	1	2
Formula	C <sub>17</sub> H <sub>12</sub> PbN <sub>2</sub> O <sub>5</sub> S	C <sub>17</sub> H <sub>12</sub> PbN <sub>2</sub> O <sub>5</sub> S
Mr	563.56	563.56
Crystal color, shape	Light yellow/block	Light yellow/prism
Crystal size/mm	$0.08 \times 0.15 \times 0.15$	$0.11 \times 0.15 \times 0.19$
Space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a/Å	9.6464(7)	10.1711(10)
b/Å	16.4821(12)	28.951(3)
c/Å	10.6570(7)	5.6154(5)
α/°	90	90
β/°	91.307(1)	97.619(2)
γ/°	90	90
$V/Å^3$	1694.0(2)	1638.9(3)
Ζ	4	4
$D/g \text{ cm}^{-3}$	2.210	2.284
T/K	$295\pm2$	$295\pm2$
$\mu/\mathrm{mm}^{-1}$	10.115	10.455
$\theta$ range/°	2.1-26.0	2.0-26.0
Measured reflections	9320	9187
Unique reflections	3321	3211
Observed reflections	3033	2984
<i>F</i> (000)	1064	1064
$R_1$ and $wR_2$ ( $I \ge 2\sigma(I)$ )	0.022, 0.054	0.039, 0.074
$R_1$ and $wR_2$ (all data)	0.025, 0.055	0.043, 0.075
Number of variables	235	235
Goodness of fit (GOF)	1.041	1.212
Largest difference peak and hole/e $\mathring{A}^{-3}$	0.483, -1.710	1.839, -1.739

Table 3

 $Pb^{II}$  center adopts a seven-coordinated geometry completed by two nitrogen donors from one 2,2'-bipyridine, two oxygen atoms from one carboxyl group, and three oxygen atoms from two sulfonate groups, as shown in Fig. 1. Each  $Pb^{II}$  atom is surrounded by three 4-sb ligands (Table 2).

The complex **2**, {[Pb(4-sb)(4,4'-bipy)<sub>1/2</sub>]·(4,4'-bipy)<sub>1/2</sub>}<sub>n</sub>, displays a 3-D network, in which each Pb<sup>II</sup> center is eightcoordinated in a dicapped trigonal prism with a [PbNO<sub>7</sub>] chromophore. The coordination geometry of the Pb<sup>II</sup> atom consists of one nitrogen atom from one 4,4'-bipyridine, three oxygen atoms from three carboxyl groups, and four oxygen atoms from three sulfonate groups (Fig. 3). Each Pb<sup>II</sup> atom is totally surrounded by six 4-sb ligands (Table 3).

Recently, we have reported two Pb<sup>II</sup> complexes containing 4-sb ligands under similar hydrothermal synthetic conditions, {[Pb(4-sb)(H<sub>2</sub>O)<sub>2</sub>]}<sub>n</sub> (3) and {[Pb(4-sb)(phen)]· H<sub>2</sub>O}<sub>n</sub> (4) [21,22]. In contrast to complexes 1 and 2 without water moiety, complexes 3 and 4 contain two and one water molecules, respectively. In these four complexes, there are some similarities and differences in Pb—N and Pb—O bond distances, coordination modes of 4-sb, and assembly of molecular structures.

The Pb–N bond distance in **2** is 2.623(6) Å, which is slightly longer than those in **1**, but all are in the normal range and are corresponding to those in Pb<sup>II</sup>-complexes containing N-donor ligands, such as  $[Pb_2(2-sb)_2(phen)_2]$ ·  $2H_2O$  [26], { $[Pb(4-sb)(phen)] \cdot H_2O$ }<sub>n</sub>, [Pb(3-sb)(phen)(- $H_2O$ )]<sub>n</sub> [27], [Pb(3-sb)(2,2'-bipy)(H\_2O)]<sub>n</sub> [28] and a series of lead(II) 5-sulfosalicylate complexes [29]. The Pb–O(COO<sup>-</sup>) bond distances in **1** and **2** except the Pb1–O1<sup>i</sup> in **2** are similar, and also are corresponding to those in **3**, but slightly different from those in **4**, which is mainly attributed to the different coordination modes of the carboxylate groups. Bond distances of Pb–O(SO<sub>3</sub><sup>-</sup>) in **3** and **4** are similar, but are somewhat different from those

Table 2	
Selected bond lengths (Å) and angles (°) for complex 1 $$	

Pb1—O1	2.409(3)	Pb1-O2	2.598(3)
Pb1–O3 <sup>i</sup>	2.794(3)	Pb1-O3 <sup>ii</sup>	2.969(3)
Pb1—O5 <sup>ii</sup>	2.943(3)	Pb1-N1	2.475(3)
Pb1—N2	2.435(3)		
O1-Pb1-O2	52.19(9)	O1–Pb1–O3 <sup>i</sup>	73.65(9)
O1–Pb1–O3 <sup>ii</sup>	139.21(9)	O1–Pb1–O5 <sup>ii</sup>	141.87(8)
O1—Pb1—N1	82.84(9)	O1-Pb1-N2	77.77(9)
O2–Pb1–O3 <sup>i</sup>	104.32(9)	O2–Pb1–O3 <sup>ii</sup>	91.54(8)
O2—Pb1—O5 <sup>ii</sup>	130.94(9)	O2-Pb1-N1	129.06(9)
O2-Pb1-N2	79.88(9)	O3 <sup>i</sup> —Pb1—O3 <sup>ii</sup>	141.69(9)
O3 <sup>i</sup> —Pb1—O5 <sup>ii</sup>	124.49(9)	O3 <sup>i</sup> —Pb1—N1	80.41(9)
O3 <sup>i</sup> —Pb1—N2	138.65(9)	O3 <sup>ii</sup> —Pb1—O5 <sup>ii</sup>	47.56(8)
O3 <sup>ii</sup> —Pb1—N1	116.08(9)	O3 <sup>ii</sup> —Pb1—N2	77.84(9)
O5 <sup>ii</sup> —Pb1—N1	69.75(9)	O5 <sup>ii</sup> —Pb1—N2	67.43(9)
N1—Pb1—N2	66.79(10)		

Symmetry codes, i: -1 + x, y, z; ii: -1 + x, 0.5 - y, 0.5 + z.

	0		
Selected bond 1	engths (A)	and angles (	°) for complex

Pb1—O1	2.548(5)	Pb1-O1 <sup>i</sup>	2.863(5)
Pb1—O2 <sup>ii</sup>	2.428(5)	Pb1-O3 <sup>iii</sup>	2.696(5)
Pb1—O4 <sup>iv</sup>	2.804(5)	Pb1-O4 <sup>v</sup>	2.875(5)
Pb1—O5 <sup>v</sup>	2.669(5)	Pb1-N1	2.623(6)
O1—Pb1—O1 <sup>i</sup>	74.73(13)	O1–Pb1–O2 <sup>ii</sup>	103.61(18)
O1–Pb1–O3 <sup>iii</sup>	88.19(16)	O1–Pb1–O4 <sup>iv</sup>	86.30(16)
O1–Pb1–O4 <sup>v</sup>	147.92(16)	O1-Pb1-O5 <sup>v</sup>	159.60(16)
O1—Pb1—N1 <sup>i</sup>	81.47(19)	O1 <sup>i</sup> —Pb1—O2 <sup>ii</sup>	69.40(17)
O1 <sup>i</sup> —Pb1—O3 <sup>iii</sup>	141.38(16)	O1 <sup>i</sup> —Pb1—O4 <sup>iv</sup>	70.23(15)
O1 <sup>i</sup> —Pb1—O4 <sup>v</sup>	79.39(14)	Ol <sup>i</sup> —Pb1—O5 <sup>v</sup>	125.24(15)
Ol <sup>i</sup> —Pb1—N1	130.33(17)	O2 <sup>ii</sup> —Pb1—O3 <sup>iii</sup>	149.18(18)
O2 <sup>ii</sup> —Pb1—O4 <sup>iv</sup>	133.86(17)	O2 <sup>ii</sup> —Pb1—O4 <sup>v</sup>	84.29(17)
O2 <sup>ii</sup> —Pb1—O5 <sup>v</sup>	82.50(17)	O2 <sup>ii</sup> —Pb1—N1	74.97(19)
O3 <sup>iii</sup> —Pb1—O4 <sup>iv</sup>	74.39(16)	O3 <sup>iii</sup> —Pb1—O4 <sup>v</sup>	100.81(15)
O3 <sup>iii</sup> —Pb1—O5 <sup>v</sup>	77.69(16)	O3 <sup>iii</sup> —Pb1—N1	78.88(18)
O4 <sup>iv</sup> —Pb1—O4 <sup>v</sup>	67.11(12)	O4 <sup>iv</sup> —Pb1—O5 <sup>v</sup>	103.64(15)
O4 <sup>iv</sup> —Pb1—N1	150.88(18)	O4 <sup>v</sup> —Pb1—O5 <sup>v</sup>	51.05(15)
O4 <sup>v</sup> —Pb1—N1	130.34(18)	O5 <sup>v</sup> -Pb1-N1	81.41(18)

Symmetry codes, i: x, 0.5 - y, 0.5 + z; ii: x, y, -1 + z; iii: 1 + x, y, z; iv: 1 + x, 0.5 - y, 0.5 + z; v: 1 + x, y, 1 + z.



Fig. 1. An ORTEP view of complex 1 showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. (Symmetry codes, i: -1 + x, y, z; ii: -1 + x, 0.5 - y, 0.5 + z).



Fig. 2. A view of 2-D network constructed by [Pb(4-sb)] units in complex 1.



Fig. 3. An ORTEP view of complex **2** showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. (Symmetry codes, i: x, 0.5 - y, 0.5 + z; ii: x, y, -1 + z; iii: 1 + x, y, z; iv: 1 + x, 0.5 - y, 0.5 + z; v: 1 + x, y, 1 + z; vi: -x, -y, -z; vii: 1 - x, -y, -z).

in 1 and 2, which is also caused by the different coordination modes of the sulfonate groups.

These four complexes all contain [Pb(4-sb)] units, but the coordination modes of 4-sb ligands are different as shown in Scheme 2, resulting in four different networks. The networks constructed by [Pb(4-sb)] units in complexes 1, 2, and 4 are 2-D (Figs. 2, 4, and 5), but 1-D for complex 3 (Fig. 6). Unlike the monodentate mode or uncoordination of the sulfonate group of the 4-sb in transition metal complexes, it provides two or three coordination sites in lead(II) complexes, which can potentially extend structures into high-dimensional assembly. The coordination mode of the 4-sb in 1 is  $\eta_5-\mu_3$  with the chelating carboxyl and chelating-bridging sulfonate, and  $\eta_7-\mu_6$  in 2,  $\eta_4-\mu_3$  in 3, and  $\eta_5-\mu_4$  in 4. Therefore, three 2-D networks in 1, 2 and 4 have different networks and these diverse networks are significantly influenced by the neutral ligands. It is obvious that the coordination of 2,2'-bipyridine, 1,10-phenanthroline or aqua ligands lead to the modification of basic metal-4-sb networks, which substantially depend upon



Scheme 2. Coordination modes of 4-sb ligands in complexes 1-4.



Fig. 4. A view of 2-D network constructed by [Pb(4-sb)]units in complex 2.

the topology of the donating sites and volume and shape of the terminal ligands.

In these four complexes, the sulfonate groups act as bridging ligands, whereas the carboxyl groups are only associated with the bridging in complexes 2 and 4. Investigating many complexes containing sulfonate groups, we can conclude that the Pb<sup>II</sup> atom is favorably coordinated to sulfonate groups compared with the mono-coordination or non-coordinating behaviors for transition metals in 4-sulfobenzoate complexes.

The planarity of carboxylate groups with benzene rings is largely different in 1–4. The dihedral angles between carboxyl and benzene ring are  $4.6(5)^{\circ}$  in 1,  $7.6(5)^{\circ}$  in 2,  $19.6(5)^{\circ}$  in 3, and  $10.2(9)^{\circ}$  in 4. The largest dihedral angle occurs in complex 3, indicating the non-planarity in 3.



Fig. 5. A view of 2-D network constructed by [Pb(4-sb)]units in complex 4.



Fig. 6. A view of 1-D chain constructed by [Pb(4-sb)]units in complex 3.

The co-planarity in 1 is higher than that in 2, but the twisted angle between two rings of the 2,2'-bipyridine  $[6.8(2)^{\circ}]$  is larger than that of the 4,4'-bipyridine in 2, in the latter two pyridine rings are nearly co-planar.

Different networks in 1-4 lead to different Pb...Pb distances separated by 4-sb. The shortest distances between two Pb<sup>II</sup> atoms bridged by the 4-sb in 1 are 9.6464(7) Å, 10.1711(10) Å in 2, 10.6687(8) Å in 3, and 9.8647(5) Å in 4. respectively, clearly indicating the shortest separation distances of Pb...Pb by 4-sb in 1 and 4 are shorter than those in 2 and 3 without neutral chelating ligands. Moreover, the shortest distances of Pb...Pb by sulfonates are 5.4399(3) Å in 1, 4.1552(5) Å in 2, 5.1220(4) Å in 3, and 7.1706(4) Å in 4. The large distance of Pb...Pb in 4 is caused by the anti-bridging coordination mode of the sulfonate. The short distance of Pb...Pb in 2 may indicate the weak Pb...Pb interaction [30,31]. Complex 2 has the second linker, 4,4'-bipyridine, but this linker only serves as dimeric bridge, consisting of a dimeric unit, [Pb<sub>2</sub>(4,4'bipy)(4-sb)2], in which distance of two Pb atoms is 12.3400(11) Å and similar to that in [Pb<sub>2</sub>(2,2'-bipy)<sub>2</sub>(4,4'bipy)(NO<sub>3</sub>)4] [12.3526(5) Å] [32]. The [Pb(4-sb)] 2-D layers in 2 are further extended by dimeric linker of 4,4'-bipyridine into 3-D dimensional architecture without any interpenetration, and the free 4,4'-bipyridine molecules occupy the channel of the 3-D network (Fig. 7).

Compared to several 2-sb or 3-sb lead(II) complexes reported very recently, the 4-sb complexes have some advantages in the network assembly. Each network of two Pb<sup>II</sup>/3-sb complexes,  $[Pb(3-sb)(phen)(H_2O)]_n$  and



Fig. 7. A view of 3-D network of complex **2**. Uncoordinated 4,4'-bipyridine molecules occupy the channels.

 $[Pb(3-sb)(2,2'-bipy)(H_2O)]_n$ , is 1-D, in which each 3-sb ligand acts as a chelating-bridging mode, whereas the molecular structure of the Pb<sup>II</sup>/2-sb complex,  $[Pb(2-sb)(phen)]_2 \cdot 2H_2O$ , is only a dimer. Therefore, 4-sb ligands in lead(II) complexes exhibit abundant coordination modes which are achieved by chelating or bridging neutral amine ligands, resulting in high-dimensional structures.

It is also interesting note that in complex  $1 \pi - \pi$  stacking interactions exist only between 2,2'-bipyridine rings, with the centroid-to-centroid distance of 3.759(2) Å. But in complex  $2 \pi - \pi$  interactions exist not only between coordinated 4,4'-bipyridine and free 4,4'-bipyridine ligands, but also between coordinated 4,4'-bipyridine and 4-sb, and between free 4,4'-bipyridine ligand and 4-sb.

# 4. Characterizations

# 4.1. IR spectra

In the IR spectra of complexes 1 and 2 there is no any absorption near  $1700 \text{ cm}^{-1}$ , indicating the absence of the proton on the carboxylate group. The  $v_{as}(COO^{-})$  and  $v_{\rm s}({\rm COO^{-}})$  are at 1590 and 1389 cm<sup>-1</sup> in **1** and at 1585 and  $1382 \text{ cm}^{-1}$  in 2, respectively, indicating the carboxylates are associated with coordination. Bands in the range  $3200-2900 \text{ cm}^{-1}$  for complexes 1 and 2 correspond to the stretching vibrations of C-H group occurring in pyridine-type complexes. Several characteristic peaks of 4,4'bipyridine or 2,2'-bipyridine are overlapping with some peaks of carboxylate or sulfonate, such as peak at 1590  $cm^{-1}$  with shoulder can be verified as the absorptions of  $v_{as}(COO^{-})$  and  $v_{C=N}$ , and in the range 1000–1200 cm<sup>-1</sup> sulfonate and inplane deformations and ring-breathing modes of pyridine occur, but the  $v_{C=C}$  peaks at 1537 cm<sup>-1</sup> in **1** and at 1525 cm<sup>-1</sup> in **2** can be clearly recognized [33]. The peak 622 cm<sup>-1</sup> in **2** may be attributable to the existence of non-coordinated 4,4'-bipyridine molecule [34].



Fig. 8. The fluorescence spectrum of complex 1 in solid state at room temperature.



Fig. 9. The fluorescence spectrum of complex 2 in solid state at room temperature.

#### 4.2. TGA analysis

The thermogravimetric analyses (TGA) have been performed on complexes 1-2 by heating each complex to 800 °C. TGA for 1 showed the loss of one 2.2'-bipvridine in the range 200-326 °C (calculated 27.7%, observed 28.2%), and further weight loss began at 450 °C. TGA for 2 showed that 4,4'-bipyridine was partly lost in the temperature range 140-180 °C, then followed by the further loss of 4,4'-bipyridine ligand in the range 220-340 °C. The sum of weight loss in the range 140–180 °C is 20.9%, corresponding to the removal of 0.75 4.4'-bipyridine molecule (calculated 20.8%). Then complex **2** further lost mass in the temperature range 480-560 °C (observed 16.3%). Totally, the weight loss in the range 140-560 °C is 45.6% and the residue is 54.4%, which corresponds to the residue of  $PbSO_4$  (calculated 53.8%), indicating the TGA process in complex 2 is more complicated.

#### 4.3. Fluorescence property

Two complexes show similar fluorescence emission bands (Figs. 8 and 9) at 405 and 470 nm in the solid state at room temperature. The peak at 405 nm in 1 is maximal whereas the peak of 470 nm is maximal in 2. These emissions may be caused by intraligand and/or ligand-to-metal charge transfer. The intensity of the complex 2 is stronger than that of 1, which is most probably attributed to the formation of dimeric units by 4,4'-bipyridine bridge.

# 5. Conclusion

In summary, two lead(II) 4-sulfobenzoate complexes with amine ligands have been synthesized. These two complexes along with previously reported  $[Pb(4-sb)(H_2O)_2]_n$  (3) and  $\{[Pb(4-sb)(phen)] \cdot (H_2O)\}_n$  (4) show that the assemblies of [Pb(4-sb)] units are significantly influenced by neutral ligands, resulting in different topologies and diverse [Pb(4-sb)] networks. This successful exploration may provide useful information for introducing other neutral ligands to design and construct novel functional frameworks with specific topologies.

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#### Appendix A. Supplementary data

CCDC-626141 and CCDC-626142 for complexes 1 and 2 contain all crystallographic data and these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.03.006.

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