Towards rational design of zinc(II) and cadmium(II) sulfonate-arsonates with low dimensional aggregations†

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Hydrothermal reactions of zinc(II) or cadmium(II) salts with *o*-sulfophenylarsonic acid (*o*-HO_3S-C_6H_4-AsO_3H_2, H_3L) afforded two layered compounds, namely, $[Zn_2(L)(OH)(H_2O)]\cdot H_2O$ (**1**) and $[Cd_3(L)_2(H_2O)_3]\cdot H_2O$ (**2**). Introduction of 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and 2,2′:6′,2″-terpyridine (terpy) as auxiliary chelating ligands led to a series of zinc(II) or cadmium(II) sulfonate-arsonates with lower dimensional aggregations, namely, $[Zn(HL)(bipy)_2]_2\cdot 6H_2O$ (**3**), $[Cd(HL)(bipy)]_2$ (**4**), $[Zn(HL)(phen)]_2\cdot 2H_2O$ (**5**), $[Cd(HL)(phen)(H_2O)]_2[Cd(HL)(phen)]_2$ (**6**), $[Cd(HL)(phen)]_2\cdot 2H_2O$ (**7**), $[Zn(HL)(terpy)]_2$ (**8**), $[Cd(HL)(terpy)]_2\cdot 2H_2O$ (**9**), Zn(HL)(bipy) (**10**), $Zn(HL)(bipy)\cdot 2H_2O$ (**11**), and $Zn(HL)(phen)\cdot H_2O$ (**12**). Compound **3** contains two mononuclear cluster units, whereas **4–9** feature five types of dinuclear cluster units in which a pair of Zn^{2+} or Cd^{2+} ions are interconnected by two sulfonate-arsonate ligands (*via* M–O–M, M–O–As–O–M and M–O–S–O–M bridges). Compounds **10** and **11** feature a one-dimensional (1D) chain in which each pair of Zn^{2+} centers are bridged by one arsonate group of a sulfonate-arsonate ligand. In compound **12**, dinuclear clusters and 1D chains coexist. All twelve compounds display very strong fluorescence in the ultraviolet or blue light region.

Introduction

The search for novel inorganic–organic hybrid materials based on metal organophosphonates is of current research interest due to their potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry.[1,2] Most of metal organophosphonates display a layered structure in which the metal centers are bridged by the phosphonate groups, although a variety of zero-dimensional (0D) clusters, one-dimensional (1D) chains, and porous three-dimensional (3D) networks have also been reported.[3–10] Metal organoarsonates are expected to display a similar structural chemistry to that of metal organophosphonates, but the larger ionic radius of As(V) compared to P(V) could lead to some different architectures with different physical properties. So far, reports on metal organoarsonates are still limited.[11–17] A variety of polyoxometalate (POM) clusters of vanadium, molybdenum and tungsten capped by arsonate ligands have been isolated.[11–13] A series of tin cluster compounds with organoarsonate ligands have been prepared by Ma's group by using the solvothermal approach.[16] Under the presence of a second metal linker such as 5-sulfoisophthalic acid monosodium salt (NaH_2SIP) or 1,3,5-benzenetricarboxylic acid (H_3BTC), two 3D and one 1D lead(II) carboxylate-arsonate hybrids of arylarsonate ligand were synthesized by our group.[17] When the N-donor chelating ligands such as phen or bipy were used as the auxiliary ligand, cadmium(II) and manganese(II) arsonates with lower dimensional structures, such as dinuclear clusters or 1D chains, were successfully isolated.[17]

Recently, our increasing attention has been devoted to metal arsonates or phosphonates with isolated polynuclear clusters or 1D chains. Similar to *m*-sulfophenylphosphonic acid,[18] *o*-sulfophenylarsonic acid could adopt a variety of coordination modes under different reaction conditions, and the weak coordination ability and large hindrance effect of the sulfonate group may facilitate the formation of low dimensional compounds such as discrete cluster units, especially when bidentate or tridentate chelating auxiliary ligands such as 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) and 2,2′:6′,2″-terpyridine (terpy) are used. A series of manganese(II) clusters have been synthesized in our laboratory, they exhibit various 0D clusters with interesting magnetic properties.[17] In this paper, we extend our work to zinc(II) and cadmium(II) sulfonate-arsonates in that these metal ions may adopt different coordination geometries from those of Mn^{2+}, furthermore these compounds may display novel luminescent properties. In absence of an auxiliary ligand, hydrothermal reactions of zinc(II) or cadmium(II) salts with *o*-sulfophenylarsonic acid (*o*-HO_3S-C_6H_4-AsO_3H_2, H_3L) led to two layered compounds, namely, $[Zn_2(L)(OH)(H_2O)]\cdot H_2O$ (**1**) and $[Cd_3(L)_2(H_2O)_3]\cdot H_2O$ (**2**). The introduction of the chelating auxiliary ligands (bipy, phen and terpy) led to ten zinc(II) or cadmium(II) sulfo-arsonates, $[Zn(HL)(bipy)_2]_2\cdot 6H_2O$ (**3**), $[Cd(HL)(bipy)]_2$ (**4**), $[Zn(HL)(phen)]_2\cdot 2H_2O$ (**5**), $[Cd(HL)(phen)(H_2O)]_2[Cd(HL)(phen)]_2$ (**6**), $[Cd(HL)(phen)]_2\cdot 2H_2O$ (**7**), $[Zn(HL)(terpy)]_2$ (**8**), $[Cd(HL)(terpy)]_2\cdot 2H_2O$ (**9**), Zn(HL)(bipy)

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(**10**), Zn(HL)(bipy)·2H_2O (**11**), and Zn(HL)(phen)·H_2O (**12**). Their structures feature isolated clusters or/and 1D chains. They also represent the first structurally characterized metal sulfonate-arsonates based on zinc(II) and cadmium(II) metal centers. Herein, we report their syntheses, crystal structures and luminescent property.

Experimental

Materials and instrumentation

The *o*-sulfophenylarsonic acid (*o*-SO_3H-C_6H_4-AsO_3H_2, H_3L) was synthesized according to procedures described previously.[17–19] All of other chemicals were obtained from commercial sources and used without further purification. Elemental analyses for C, H and N elements were performed on a German Elementary Vario EL III instrument. Elemental analyses for the zinc and cadmium elements were carried out on Jobin Yvon Inductively Coupled Plasma OES spectrometer (ICP) Ultima2. The FT-IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer using KBr pellets in the range of 4000–400 cm^{-1}. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 10 °C min^{-1} under a static air atmosphere. X-Ray powder diffraction (XRD) patterns (Cu-Kα) were collected on a XPERT-MPD θ–2θ diffractometer. Photoluminescence analyses were performed on Edinburgh FLS920 fluorescence spectrometer.

Syntheses of $[Zn_2(OH)(L)(H_2O)]\cdot H_2O$ (1) and $[Cd_3(L)_2(H_2O)_3]\cdot H_2O$ (2)

The two compounds were synthesized by similar procedures. A mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.088 g, 0.4 mmol) or $Cd(CH_3COO)_2\cdot 2H_2O$ (0.107 g, 0.4 mmol) and H_3L (0.056 g, 0.2 mmol) in 10 mL of distilled water was put into a Parr Teflon-lined autoclave (23 mL) and heated at 170 °C for 3 d. The initial pH value of solution is 4.0. Colourless-plate crystals of **1** and **2** were collected about 34.0% (0.093 g) and 64.0% (0.129 g) (based on metal), respectively. Their purities were confirmed by X-ray powder diffraction (XRD) (see Fig. S1 of the ESI).† Anal. calcd for **1**: Zn 28.26, C 15.57, H 1.96%. Found: Zn 28.15, C 15.40, H 1.92%. The IR spectra and data for **1** and **2** are shown in Fig. S2 of the ESI.†

Syntheses of 3–12

These compounds were synthesized by a similar procedure. For the synthesis of **3**, a mixture of $Zn(CH_3COO)_2\cdot 2H_2O$ (0.044 g, 0.2 mmol), H_3L (0.056 g, 0.2 mmol) and bipy (0.062 g, 0.4 mmol) in 10 mL of distilled water was put into a Parr Teflon-lined autoclave (23 mL) and heated at 150 °C for **4** d. The initial pH value of solution is close to 3.5. The resultant solution was allowed to evaporate slowly at the room temperature, colourless-prism crystals of **3** were collected about 67% (0.095 g) based on zinc after two weeks. Using a different M/H_3L/bipy molar ratio (1 : 1 : 1 for **10**, 2 : 1 : 1 for **11**), single crystals of **10** and **11** were collected in a yield of about 71% (0.071 g) and 47% (0.051 g) (based on H_3L), respectively. Using phen or terpy ligands instead of bipy, single crystals of **8** and **12** were collected in a *ca.* 76% (0.088 g) and 68% (0.074 g) yield (based on zinc), respectively. When the reacting temperature was increased to 170 °C, colourless-prism crystals of compound **5** were isolated in a yield of about 73% (0.079 g) based on zinc. When $Cd(CH_3COO)_2\cdot 2H_2O$ is used instead of zinc source, single crystals of **4**, **6**, **7** and **9** were isolated in a yield of about 82% (0.090 g), 78% (0.091 g), 57% (0.067 g) and 79% (0.102 g), respectively. Their purities have also been confirmed by XRD powder diffraction (see Fig. S1 of the ESI).† Anal. calcd for **3**: Zn 9.19, C 43.86, H 3.82, N 7.87%. Found: Zn 8.90, C 43.61, H 3.81, N 7.73%. For **4**: Cd, 20.49, C, 35.02; H, 2.39; N, 5.11%. Found: Cd, 20.21, C, 35.21; H, 2.31; N, 5.06%. For **5**: Zn, 12.03, C, 39.76; H, 2.78; N, 5.15%. Found: Zn, 11.91, C, 39.65; H, 2.75; N, 5.11%. For **6**: Cd, 19.32, C, 37.16; H, 2.43; N, 4.82%. Found: Cd, 19.20, C, 37.05; H, 2.51; N, 4.67%. For **7**: Cd, 18.96, C, 36.47; H, 2.89; N, 4.73%. Found: Cd, 18.79, C, 36.49; H, 2.53; N, 4.70%. For **8**: Zn, 11.30, C, 43.58; H, 2.79; N, 7.26%. Found: Zn, 11.03, C, 43.35; H, 2.70; N, 7.01%. For **9**: Cd, 17.46, C, 39.18; H, 2.82; N, 6.53%. Found: Cd, 17.30, C, 39.07; H, 2.80; N, 6.49%. For **10**: Zn, 13.04, C, 38.31; H, 2.61; N, 5.58%. Found: Zn, 12.71, C, 38.20; H, 2.70; N, 5.51%. For **11**: Zn, 12.16, C, 35.74; H, 3.19; N, 5.21%. Found: Zn, 12.10, C, 35.93; H, 3.18; N, 5.18%. For **12**: Zn, 12.03, C, 39.76; H, 2.78; N, 5.15%. Found: Zn, 11.70, C, 39.71; H, 2.76; N, 5.12%. The IR spectra and data for compounds **3–12** are shown in Fig. S2 of the ESI.†

Single-crystal structure determination

Data collections were performed on either a Rigaku Mercury CCD diffractometer (for **1**, **4**, **5**, **7**, **10** and **12**) or a Saturn 70 CCD diffractometer (for **2**, **3**, **6**, **8**, **9** and **11**). Both diffractometers were equipped with a graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data for all twelve compounds were collected by the narrow frame method at 293(2) K. All data sets were corrected for Lorentz and Polarization factors as well as for absorption by a Multi-scan method.[20] The slightly higher R_{int} values for compounds **7** (0.082) and **12** (0.1387) compared with other ones are due to their poorer crystal quality, several data sets were collected but the problem still remained. All of the structures were solved by the direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97.[20] All non-hydrogen atoms were refined with anisotropic thermal parameters. Several atoms (S(2), O(11), O(12), and S(2′), O(11′), and O(12′)) of the sulfonate groups in **2**, are severely disordered over two orientations, hence their occupancy factors were fixed to be 50%. O(5W), O(6W), O(7W) and O(8W) in **3** were reduced to 50% due to their large thermal parameters. All hydrogen atoms were located at geometrically calculated positions and refined with isotropic thermal parameters. The hydrogen atoms for the lattice water molecules (O(5W), O(6W), O(7W) and O(8W)) in **3** are not included in the refinements. Crystallographic data and structural refinements for compounds **1–12** are summarized in Table 1. Important bond lengths are listed in Table S1 of the ESI.†

Results and discussion

Structures of 1 and 2

Compounds **1** and **2** feature two types of layered architectures.

Table 1 Crystal data and structure refinements for the twelve compounds.[a]

Compound	**1**	**2**	**3**	**4**	**5**	**6**
Formula	$C_6H_9AsO_9SZn_2$	$C_{12}H_{16}As_2Cd_3O_{16}S_2$	$C_{52}H_{54}As_2N_8O_{18}S_2Zn_2$	$C_{32}H_{26}As_2Cd_2N_4O_{12}S_2$	$C_{36}H_{30}As_2N_4O_{14}S_2Zn_2$	$C_{72}H_{56}As_4Cd_4N_8O_{26}S_4$
F_w	462.85	967.41	1423.73	1097.33	1087.34	2326.77
Crystal group	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$C2/c$	$P\bar{1}$
a/Å	12.770(2)	12.5726(8)	10.320(3)	8.191(5)	19.161(6)	8.003(3)
b/Å	8.285(1)	13.0537(7)	14.576(4)	20.66(1)	14.429(4)	11.771(4)
c/Å	11.149(1)	14.029(1)	20.283(6)	21.28(1)	14.001(4)	21.224(9)
α/°	90	90	79.202(7)	90	90	81.526(9)
β/°	95.42(1)	96.830(5)	83.149(6)	94.94(1)	90.449(4)	81.531(9)
γ/°	90	90	88.874(8)	90	90	75.68(1)
V/Å^3	1174.3(3)	2286.0(3)	2976(2)	3588(4)	3871(2)	1903(1)
Z	4	4	2	4	4	1
D_c/g cm^{-3}	2.618	2.811	1.589	2.032	1.866	2.030
μ(Mo-Kα)/mm^{-1}	7.098	5.899	2.057	3.202	3.120	3.026
Goodness-of-fit on F^2	1.023	1.080	1.037	1.155	1.059	0.880
Reflections collected/unique	8697/2688 [$R_{int} = 0.0371$]	17 764/5217 [$R_{int} = 0.0668$]	23 346/13391 [$R_{int} = 0.0445$]	27 302/7822 [$R_{int} = 0.0870$]	14 284/4425 [$R_{int} = 0.0252$]	15 071/8603 [$R_{int} = 0.0887$]
R_1, wR_2 [$I > 2\sigma(I)$]	0.0351, 0.0883	0.0514, 0.1023	0.0668, 0.1751	0.0800, 0.1569	0.0269, 0.0642	0.0645, 0.1334
R_1, wR_2 [all data]	0.0420, 0.0932	0.0727, 0.1122	0.1031, 0.2017	0.1116, 0.1746	0.0300, 0.0660	0.1098, 0.1533

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, w$R_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$.

Compound	**7**	**8**	**9**	**10**	**11**	**12**
Formula	$C_{36}H_{34}As_2Cd_2N_4O_{14}S_2$	$C_{42}H_{32}As_2N_6O_{12}S_2Zn_2$	$C_{42}H_{36}As_2Cd_2N_6O_{14}S_2$	$C_{16}H_{13}AsN_2O_6SZn$	$C_{16}H_{17}AsN_2O_8SZn$	$C_{18}H_{15}AsN_2O_7SZn$
F_w	1185.43	1157.44	1287.53	501.63	537.70	543.67
Crystal group	Triclinic	Triclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$Pna2_1$	$P2_1/c$
a/Å	8.631(7)	8.393(2)	8.430(3)	14.0169(11)	17.880(3)	12.648(6)
b/Å	11.609(7)	9.906(3)	11.210(4)	8.0918(5)	10.4331(17)	8.181(4)
c/Å	11.754(7)	13.577(4)	13.470(5)	15.4783(14)	21.170(4)	37.33(2)
α/°	60.83(3)	88.783(9)	91.350(2)	90	90	90
β/°	73.29(4)	74.243(6)	107.890(5)	93.599(6)	90	94.225(7)
γ/°	75.08(4)	75.784(8)	111.450(4)	90	90	90
V/Å^3	975.3(11)	1051.9(5)	1114.1(6)	1752.1(2)	3949.1(11)	3852(3)
Z	1	1	1	4	8	8
D_c/g cm^{-3}	2.018	1.827	1.919	1.902	1.809	1.875
μ(Mo-Kα)/mm^{-1}	2.956	2.874	2.598	3.433	3.060	3.135
Goodness-of-fit on F^2	0.981	1.033	1.061	1.065	1.044	0.903
Flack factor	—	—	—	—	0.007(6)	—
Reflections collected/unique	7535/4159 [$R_{int} = 0.0820$]	8301/4742 [$R_{int} = 0.0264$]	8199/4825 [$R_{int} = 0.0172$]	13 039/3998 [$R_{int} = 0.0385$]	29 938/8966 [$R_{int} = 0.0369$]	27 305/8644 [$R_{int} = 0.1387$]
R_1, wR_2 [$I > 2\sigma(I)$]	0.0726, 0.1574	0.0389, 0.0801	0.0226, 0.0584	0.0324, 0.0727	0.0330, 0.0586	0.0692, 0.1291
R_1, wR_2 [all data]	0.0896, 0.1712	0.0579, 0.0885	0.0273, 0.0602	0.0399, 0.0766	0.0376, 0.0609	0.1046, 0.1497

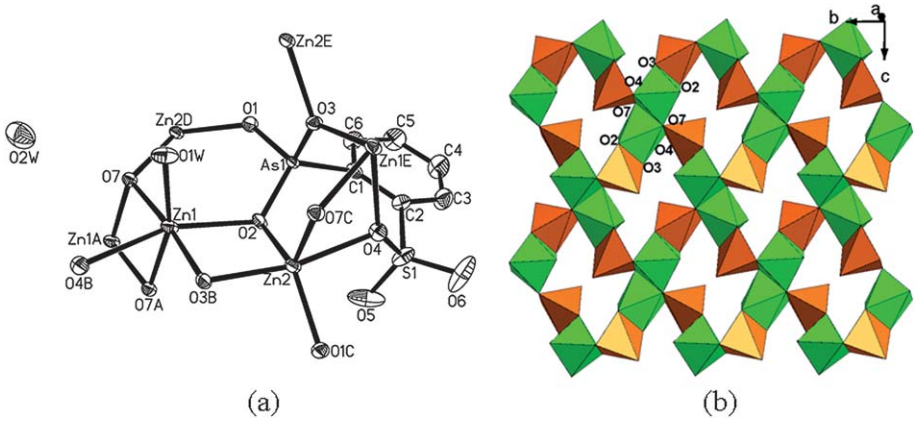


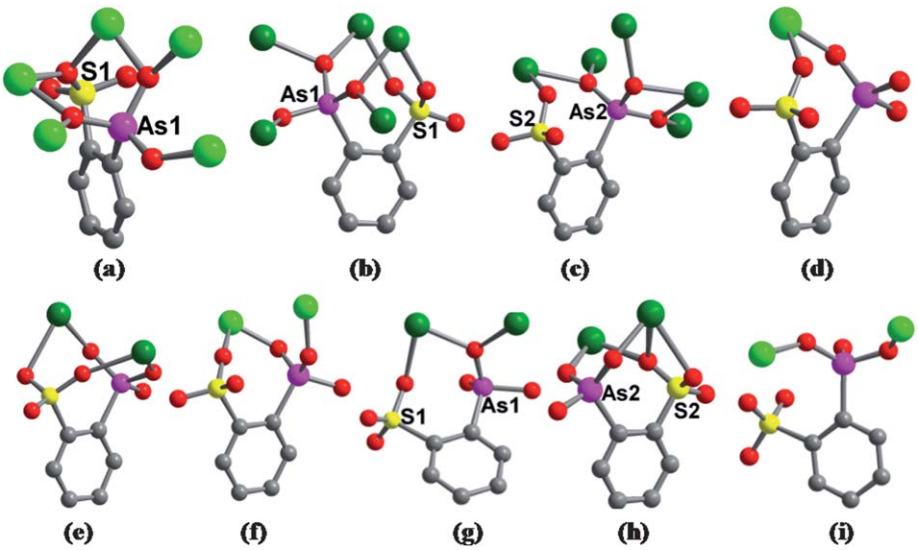
Fig. 1 (a) ORTEP representation of the selected unit in compound **1**. The thermal ellipsoids are drawn at 50% probability level. Symmetry code for the generated atoms: (a) $-x, -y, -z + 1$. (b) $-x, y - 1/2, -z + 1/2$. (c) $x, -y + 1/2, z - 1/2$. (d) $x, -y + 1/2, z + 1/2$. (e) $-x, y + 1/2, -z + 1/2$. (b) A zinc(II) oxide layer in **1**. $Zn(1)O_6$ and $Zn(2)O_5$ polyhedra are shaded in bright green and orange, respectively.

The asymmetric unit of **1** contains two unique zinc(II) ions, one L^{3-} anions, one hydroxyl anion, an aqua ligand and one lattice water molecule (Fig. 1a). Zn(1) is octahedrally coordinated by two arsonate oxygen atoms, one sulfonate oxygen atom from two L^{3-} anions, two hydroxyl anions and an aqua ligand whereas Zn(2) is five-coordinated with three arsonate oxygen atoms, one sulfonate oxygen atom from three L^{3-} anions as well as a hydroxyl anion in a trigonal bipyramidal geometry. The Zn–O distances (1.964(2)–2.338(2) Å) are comparable to those reported in zinc(II) phosphonates.[7,21]

The L^{3-} anion is heptadentate and bridges with five metal ions *via* one sulfonate and three arsonate oxygen atoms. It forms two Zn–O–S–C–C–As–O seven member chelating rings with two Zn^{2+} ions and also bridges to three other Zn^{2+} ions. Two arsonate oxygen atoms are bidentate whereas the third one is unidentate. One sulfonate oxygen atom is bidentate and the remaining two remain non-coordinated (Scheme 1a).

Neighbouring $Zn(1)O_6$ and $Zn(2)O_5$ polyhedra are interconnected *via* edge-sharing into a zinc(II) oxide layer with eight-member rings (Fig. 1b). A pair of $Zn(1)O_6$ octahedra are edge-sharing (O(7)–O(7)), and $Zn(1)O_6$ and $Zn(2)O_5$ polyhedra are also edge-sharing (O(4)–O(7) and O(2)–O(3)). The arsonate groups are capped on two $Zn(1)O_6$ and three $Zn(2)O_5$ polyhedra. The sulfonate groups and organic groups of the L^{3-} anions are orientated toward the interlayer space (ESI, Fig. S3a).† The interlayer distance is 12.77 Å. These 2D layers are held together *via* weak van der Waals force (ESI, Fig. S3b).†

Compound **2** contains three unique cadmium(II) ions, two L^{3-} anions, three aqua ligands and one lattice water molecule in its asymmetric unit (Fig. 2a). Both Cd(1) and Cd(3) are octahedrally-coordinated with four arsonate oxygen atoms and one sulfonate oxygen atom from three L^{3-} ligands as well as an aqua ligand whereas Cd(2) is octahedrally-coordinated by three arsonate oxygen atoms, one sulfonate oxygen atom from three L^{3-} anions as well as two aqua ligands. The Cd–O distances are in the range of 2.198(5)-2.616(7) Å, which are comparable to those reported in other cadmium(II) phenylarsonates.[17]



Scheme 1 The coordination modes of H_3L ligand in compounds **1** (a), **2** (b, c), **3** (d), **4** and **7** (e), **5** and **9–12** (f), **6** (g, h), and **8** (i).

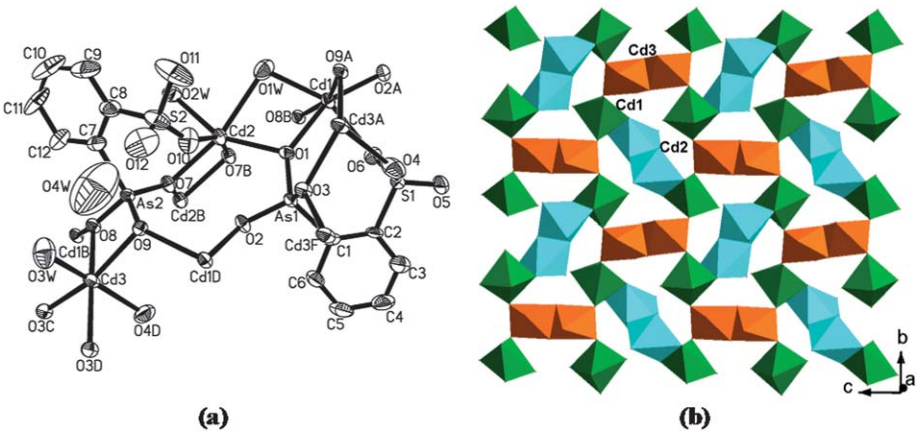


Fig. 2 (a) ORTEP representation of the selected unit in compound **2**. The thermal ellipsoids are drawn at 50% probability level. Symmetry code for the generated atoms: (a) $x, -y + 1/2, z - 1/2$. (b) $-x, -y + 1, -z + 2$. (c) $-x, y + 1/2, -z + 5/2$. (d) $x, -y + 1/2, z + 1/2$. (e) $-x, -y + 1, -z + 3$. (f) $-x, y - 1/2, -z + 5/2$. (b) A cadmium(II) oxide layer in **2**. $Cd(1)O_6$, $Cd(2)O_6$ and $Cd(3)O_6$ distorted octahedra are shaded in green, cyan, and orange, respectively.

Similar to that of compound **1**, the two L^{3-} anions in **2** are also heptadentate and bridge with five metal ions. They adopt two different types of coordination modes (Scheme 1b and 1c). The one containing As(1) and S(1) forms two M–O–S–C–C–As–O seven member chelating rings and also bridges with three other metal ions (Scheme 1b), its main difference from Scheme 1a is that two sulfonate oxygen atoms are unidentate in Scheme 1b whereas one sulfonate oxygen atom is bidentate in Scheme 1a. The arsonate anion containing As(2) and S(2) forms one M–O–S–C–C–As–O seven member chelating ring, one M–O–As–O four member chelating ring and also bridges with three other metal ions (Scheme 1c), the sulfonate group is unidentate whereas all three arsonate oxygen atoms are bidentate.

Each pair of $Cd(3)O_6$ octahedra forms a dimer *via* edge-sharing whereas a pair of $Cd(2)O_6$ octahedra and two $Cd(1)O_6$ octahedra form a linear tetramer *via* also edge-sharing. The tetramer contains a Cd(2) dimer which is further edge-sharing with two $Cd(1)O_6$ octahedra. These tetramers and Cd(3) dimers are further interconnected *via* corner-sharing into a cadmium(II) oxide layer with eight-member rings (Fig. 2b). The arsonate groups are capped on the layer whereas the sulfonate groups are hanging on the 2D layer (ESI, Fig. S4a).† The layer interlayer distance is 12.57 Å, which is very close to that of **1**. The organic groups of the sulfonate-arsonate ligands are orientated toward the interlayer space. The lattice water molecules are also located at the interlayer region. These 2D layers are held together *via* weak van der Waals force (ESI, Fig. S4b).†

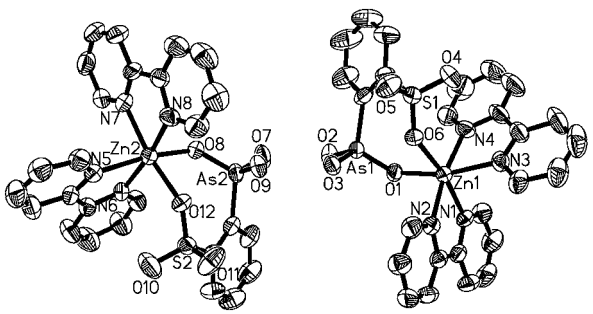


Fig. 3 ORTEP representation of the selected unit in compound **3**. The thermal ellipsoids are drawn at 50% probability level. Free water molecules and the label of all C atoms are omitted for clarity.

Structures of 3–9

By introduction of 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen) and 2,2′:6′,2″-terpyridine (terpy)) as auxiliary chelating ligands, compounds **3–9** were isolated. They display various types of isolated mononuclear and dinuclear cluster units.

Compound **3** contains two similar mononuclear $[Zn(HL)(bipy)_2]$ units. There are two unique zinc(II) ions in its asymmetric unit. Both Zn(1) and Zn(2) ions are octahedrally coordinated by a bidentate chelating HL^{2-} anion as well as two bidentate chelating bipy ligands in *cis*-fashion (Fig. 3). The Zn–O (1.991(4)–2.257(4) Å) and Zn–N (2.135(5)–2.204(5) Å) distances are in the normal ranges.

There are two unique HL^{2-} ligands in **3**. The arsonate groups of both ligands are singly protonated, as indicated by a much-longer As–O bond (As(1)–O(2) 1.730(4) Å; As(2)–O(9) 1.703(4) Å) compared with other As–O bonds (1.659(4)–1.667(4) Å) (ESI, Table S1).† Each of them is bidentate and forms a seven-member chelating ring (Zn–O–As–C–C–S–O) with a Zn^{2+} ion (Scheme 1d).

Compounds **4–9** display five types of dinuclear clusters (Fig. 4). $[Cd(HL)(bipy)]_2$ (**4**) and $[Cd(HL)(phen)]_2 \cdot 2H_2O$ (**7**) feature a similar dinuclear cluster unit in which a pair of Cd^{2+} ions are interconnected by a pair of sulfonate groups and arsonate groups (*via* M–O–S–O–M and M–O–As–O–M bridges) (Fig. 4a and 4e). The $M–(O–S–O)_2–M$ ring and $M–(O–As–O)_2–M$ ring are almost perpendicular to each other. There are two unique Cd(II) ions, two HL^{2-} anions, two bipy ligands in the asymmetric unit of compound **4**. Both Cd^{2+} ions are octahedrally coordinated with two arsonate atoms and two sulfonate atoms from two HL^{2-} anions as well as a bidentate chelating bipy ligand. $[Cd(HL)(phen)]_2 \cdot 2H_2O$ (**7**) contains a similar dinuclear unit to that of **4**, but bipy was replaced by phen. Furthermore, **7** contains two lattice water molecules. The HL^{2-} ligands in compounds **4** and **7** are tetradentate and each forms two Cd–O–As–C–C–S–O seven-member chelating rings by using two arsonate oxygen atoms and two sulfonate oxygen atoms (Fig. 4e).

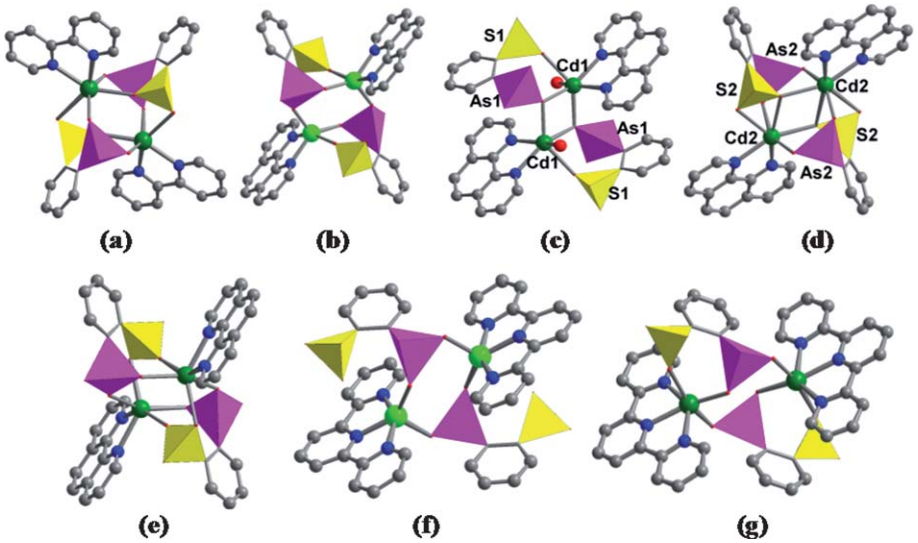


Fig. 4 The dinuclear clusters in **4** (a), **5** (b), **6** (c, d), **7** (e), **8** (f), **9** (g). Zn (or Cd), C and O atoms are represented by green, medium grey and red circles, respectively. The CSO_3, $CAsO_3$ tetrahedra are shaded in yellow and purple, respectively.

The Cd···Cd separations within the dinuclear cadmium(II) cluster in **4** and **7** are 4.197(2) and 4.092(2) Å, respectively.

Compounds **5** and **9** feature a different dinuclear cluster unit in which the two metal ions are bridged *via* a pair of arsonate groups (M–O–As–O–M bridge) (Fig. 4b and 4g). There is a unique zinc(II) ion, one HL^{2-} ligand, a phen ligand as well as one lattice water molecule in the asymmetric unit of **5**. The Zn^{2+} ion is five-coordinated with two arsonate oxygen atoms, one sulfonate oxygen atom from two HL^{2-} anions, as well as one phen ligand. The dinuclear cluster of **9** can be viewed as the bidentate chelating phen ligand in **5** being replaced by a tridentate chelating terpy, and the Zn^{2+} ion being replaced by a Cd^{2+} ion. Hence the Cd^{2+} ion in **9** becomes octahedrally-coordinated. The HL^{2-} ligands in both **5** and **9** are tridentate, each forms a M–O–S–C–C–As–O seven member chelating ring with a metal ion and also bridges with another metal ion by using another arsonate oxygen atom (Scheme 1f). The Zn···Zn distance within the dinuclear zinc(II) clusters in **5** is 4.240(1) Å and the Cd···Cd separation within the dinuclear cadmium(II) cluster in **9** is 5.417(2) Å.

Compound **6** contains two different dinuclear cluster units, namely, $[Cd(1)(HL)(phen)(H_2O)]_2$ with four-member ring ($Cd(1)_2O_2$) in which a pair of Cd(1) ions are bridged by two arsonate oxygen atoms (*via* Cd–O–Cd bridge) (Fig. 4c), and $[Cd(2)(HL)(phen)]_2$ in which the two metal centers are bridged by a pair of sulfonate oxygen atoms (*via* Cd–O–Cd bridges) as well as a pair of the arsonate groups *via* Cd–O–As–O–Cd bridges (Fig. 4d). In $[Cd(1)(HL)(phen)(H_2O)]_2$, Cd(1) is six-coordinated with two arsonate oxygen atoms, one sulfonate oxygen atom from two HL^{2-} anions, an aqua ligand as well as a bidentate chelating phen ligand. The HL^{2-} anion containing As(1) and S(1) is tridentate, it forms a M–O–S–C–C–As–O seven chelating ring with a Cd^{2+} ion and bridges with another Cd^{2+} ion by using a same arsonate oxygen (Scheme 1g). The Cd(1)···Cd(1) separation within the cluster is 3.609(1) Å. In $[Cd(2)(HL)(phen)]_2$ dinuclear unit, the Cd(2)···Cd(2) separations within the cluster is 4.039(1) Å. Cd(2) is seven-coordinated with two arsonate oxygen atoms, three sulfonate oxygen atom from two HL^{2-} anions as well as a bidentate chelating phen ligand. The HL^{2-} anion containing As(2) and S(2) atoms is pentadentate, it forms two Cd–O–As–C–C–S–O seven-member chelating rings and one Cd–O–S–O four-member chelating ring by using two arsonate oxygen atoms and two sulfonate oxygen atoms. Both arsonate oxygen atoms are unidentate whereas the two coordination sulfonate oxygen atoms are unidentate and bidentate bridging, respectively (Scheme 1h). Two Cd–O bonds are significantly elongated (Cd(2)–O(11) 2.668(6) Å and Cd(2)–O(12) 2.737(6) Å) compared with the remaining Cd–O bonds (2.187(6)–2.469(6) Å). The Cd–N distances are in the range of 2.301(7)–2.364(7) Å.

$[Zn(HL)(terpy)]_2$ (**8**) features a dinuclear cluster unit in which the two zinc(II) centers are bridged by a pair of arsonate groups *via* Zn–O–As–O–Zn bridges (Fig. 4f). Its asymmetric unit contains one unique zinc(II) ion, one unique HL^{2-} ligand and one terpy ligand. The zinc(II) ion is five-coordinated with two arsonate oxygen atoms from two HL^{2-} anions as well as a tridentate chelating terpy ligand in a distorted trigonal bipyramidal geometry. HL^{2-} ligand is bidentate and bridges two zinc(II) ions *via* two arsonate oxygen atoms (Scheme 1i). The sulfonate group of the ligand and the third arsonate oxygen atom remain non-coordinated. There are two intra-cluster hydrogen bonds

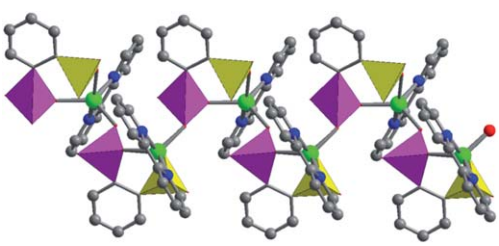


Fig. 5 A 1D metal sulfonate-arsonate chain in **10** or **11**. Zn, C and O atoms are represented by green, medium grey, and red circles, respectively. The CSO_3, $CAsO_3$ tetrahedra are shaded in yellow and purple, respectively.

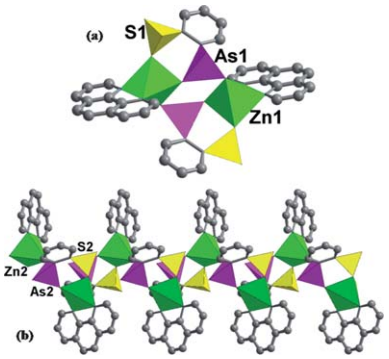


Fig. 6 A dinuclear cluster unit (a) and a 1D metal sulfonate-arsonate chain (b) in compound **12**. The ZnO_5 polyhedra, CSO_3 and $CAsO_3$ tetrahedra are shaded in green, yellow and pink, respectively. C and O atoms are represented by medium grey and red circles, respectively.

between singly protonated arsonate oxygen atom (O(2)) and non-coordinated sulfonate oxygen atom (O(4)). The O(2)–H(2A)···O(4) hydrogen bond distance and angle are 2.720(4) Å and 160.2°, respectively. The Zn···Zn within the dinuclear zinc(II) cluster in **8** is 4.725(1) Å.

The difference of these cluster units in **3–9** lies in the different coordinated modes of the sulfonate-arsonate ligands. In these compounds, the HL^{2-} ligands feature six types of coordinated modes. The arsonate groups bridge with metal ions by its unidentate or bidentate oxygen atoms. In **3–9**, the arsonate group is partially protonated and bridges with fewer metal centers compared with corresponding phosphonate ligands, as in zinc(II) and cadmium(II) *m*-sulfophenylphophonates reported.[18] According to the literature,[22] the pK_a value of the phenylphosphonic acid is 1.86, 7.51 and the pK_a value of the phenylarsonic acid is 3.39, 8.25, which means the second proton of the phenylarsonic acid is much more difficult to be removed than that of the corresponding phosphonic acid.

The isolated mononuclear or dinuclear clusters in **3–9** are further assembled into 3D supramolecular networks *via* aromatic π···π interactions or/and hydrogen bonds if water molecules are present (ESI, Fig. S5, Tables S2 and S3).†

Structures of 10–11

When the reactions were carried out at different Zn/H_3L/bipy molar ratios (1 : 1 : 1 for **10** and 2: 1: 1 for **11**) from 1 : 1 : 2 in **3–9**, compounds **10** and **11** featuring a one-dimensional (1D) chain were isolated (Fig. 5).

The asymmetric unit of **10** contains a unique zinc(II) ion, one HL^{2-} anion as well as a bipy ligand whereas that of **11** has two zinc(II) ions, two HL^{2-} anions, two chelating bipy ligands as well as four lattice water molecules. The Zn(II) ions in both **10** and **11** are five-coordinated with two arsonate oxygen atoms, one sulfonate oxygen atom from two HL^{2-} anions as well as one bidentate chelating bipy (or phen) ligand in a trigonal bipyramidal geometry. The coordination modes of the HL^{2-} anions in compounds **10** and **11** are same as those in compounds **5** and **9**, each is tridentate and forms a M–O–S–C–C–As–O seven member chelating ring by using one sulfonate and one arsonate oxygen atoms, and also bridges with another metal ion by using another arsonate oxygen atom (Scheme 1f).

The interconnection of Zn(II) ions in **10** and **11** by bridging and chelating HL^{2-} anions result into a 1D chain (Fig. 5). These chains are further assembled into 3D networks by the aromatic π···π packing interactions for **10**, and additional hydrogen bonds for **11** with four lattice water molecules (ESI, Fig. S5, Tables S2 and S3).† The hydrogen bonds in **11** are formed among the singly protonated arsonate oxygen atoms, non-coordinated arsonate and sulfonate oxygen atom as well as the lattice water molecules. The O···O distances are in the range of 2.583(4)–2.835(4) Å.

Structures of 12

When the reaction temperature was lowered to 150 °C from 170 °C used for the synthesis of compound **7**, compound **12** which contains both dinuclear cluster units and 1D chains was obtained (Fig. 6).

There are two unique zinc(II) ions, two HL^{2-} anions, two phen ligands as well as two lattice water molecules in the asymmetric unit of **12**. Both Zn(II) ions are five-coordinated with two arsonate oxygen atoms, one sulfonate oxygen atom from two HL^{2-} anions as well as one bidentate chelating phen ligand in a square bipyramidal geometry. Their coordinated modes of the HL^{2-} anions are same as those in compounds **5**, **9–11** (Scheme 1f).

A pair of Zn(1) ions are bridged by a pair of HL^{2-} ligands into a $[Zn(1)(HL)(phen)]_2$ dinuclear cluster unit similar to those in compound **5** (Fig. 6a). The interconnection of Zn(2) ions by bridging and chelating HL^{2-} anions resulted into 1D chains similar to those in compounds **10** and **11** (Fig. 6b). These discrete dinuclear clusters are interlinked into 1D supramolecular chain *via* hydrogen bonds among singly protonated oxygen atom (O(2)) and non-coordinated sulfonate oxygen atom (O(6)) (ESI, Fig. S6 and Table S2).† The O···O separation is 2.768(7) Å (symmetry code: $-x + 2, -y + 2, -z$). The 1D chains containing Zn(2) ions are further assembled into a 2D supramolecular layer by the aromatic π···π interactions (ESI, Table S3).† The above two types of building units are further held together by weak van der Waals force (see ESI, Fig. S5).†

Luminescence properties

The solid-state luminescent spectra of the free *o*-sulfophenylarsonic acid (H_3L), auxiliary ligand (bipy, phen and terpy), and compounds **1–12** were investigated at room temperature (Fig. 7). The free *o*-sulfophenylarsonic acid (H_3L) displays a weak fluorescent emission band at λ_{max} = 371, 504 nm under excitation at 310 nm. Upon its complexion with metal ions, **1** and **2** exhibit much stronger fluorescence emission bands at λ_{max} = 332, 498 nm (λ_{ex} = 293 nm) for **1** and λ_{max} = 335, 508 nm (λ_{ex} = 293 nm) for **2**. The enhancement of luminescence may be attributed to the increasing "rigidity" of the ligand when coordinated with the metal center and thus reducing the loss of energy through a radiation-less pathway.[23] These emission bands can be attributed to the ligand-centered fluorescence.[24]

The free bipy ligand displays a strong broad peak at λ_{max} = 546 nm and a very weak peak λ_{max} = 375 nm upon excitation at 340 nm, which can be assigned to π···π* transition. Upon the complexion of both bipy and H_3L ligands with metal ions, compounds **3**, **4**, **10** and **11** each displays a broad band with

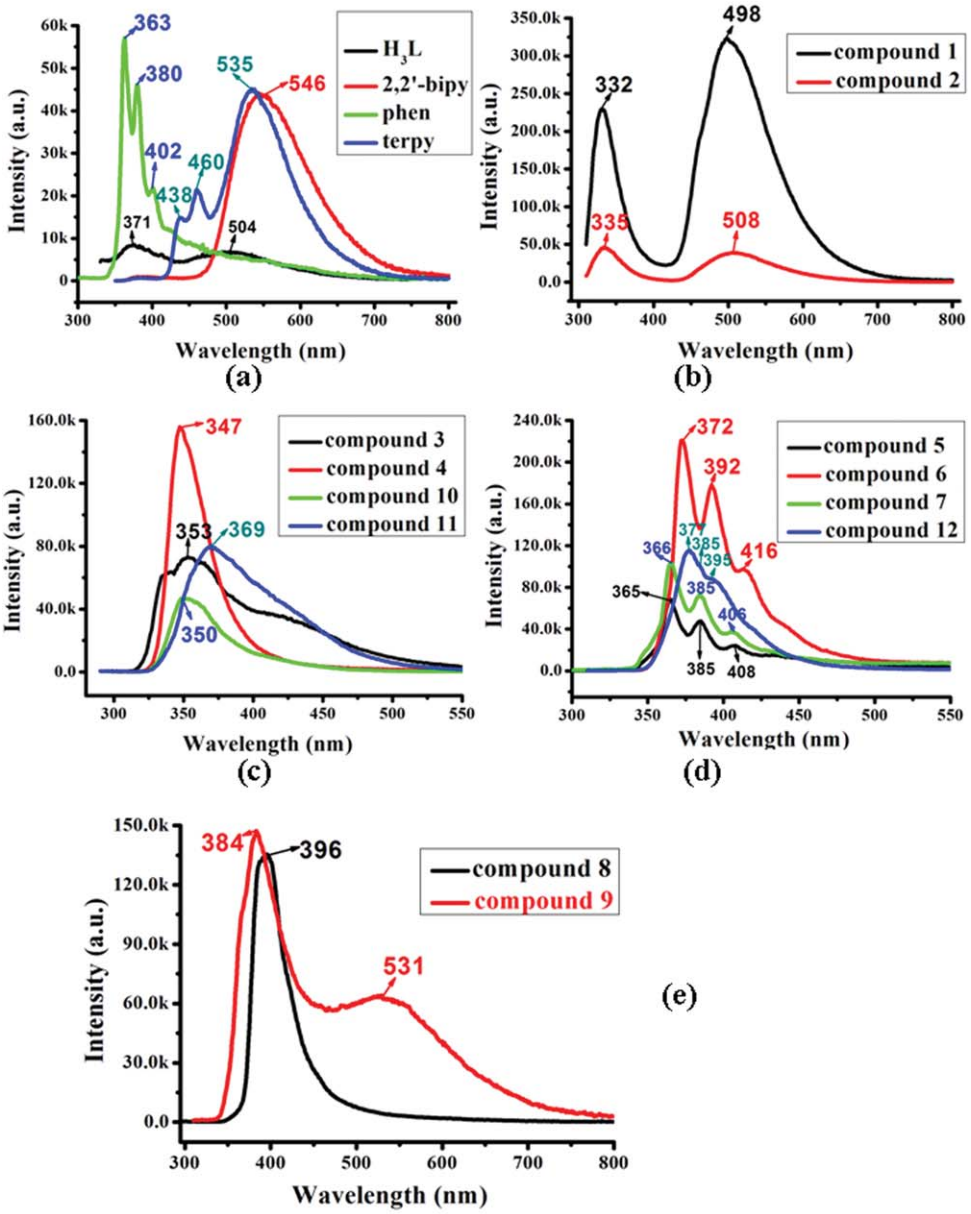


Fig. 7 Solid-state emission spectra of the free arsonate and auxiliary ligands as well as compounds **1–12**.

a shoulder one (Fig. 7). The main emission bands appeared at 353 nm ($\lambda_{ex} = 285$ nm) for **3**, 347 nm ($\lambda_{ex} = 280$ nm) for **4**, 350 nm ($\lambda_{ex} = 290$ nm) for **10**, and 369 nm ($\lambda_{ex} = 290$ nm) for **11**.

The free phen ligand displays two strong sharp emission bands at $\lambda_{max} = 363$, 380 nm with a weak shoulder at 402 nm upon excitation at 275 nm, which can be attributed to the intra-ligand transition. Upon the complexion of both H_3L and phen ligands with metal ions, compounds **5–7** and **12** each exhibits two strong and one weak shoulder bands at $\lambda_{max} = 368$, 385 and 408 nm for **5** ($\lambda_{ex} = 290$ nm), 372, 392 and 416 nm for **6** ($\lambda_{ex} = 280$ nm), 366, 385 and 406 nm for **7** ($\lambda_{ex} = 285$ nm), and 377, 385 and 395 nm for **12** ($\lambda_{ex} = 280$ nm).

The free terpy ligand displays one strong broad emission peak at $\lambda_{max} = 535$ nm and two weak shoulder ones at 438 and 460 nm upon excitation at 325 nm, which can be also attributed to the intraligand transitions. Upon the complexion of both terpy and H_3L ligands with metal ions, compound **9** shows a strong emission band at $\lambda_{max} = 384$ nm and one weak emission band at $\lambda_{max} = 531$ nm upon excitation at 280 nm, whereas compound **8** only exhibits an intense emission band at $\lambda_{max} = 396$ nm upon excitation at 280 nm. All of these emissions bands in compounds **3–12** can be attributed to the intra-ligand transitions.[24]

TGA studies

TGA curves of **1** exhibit three main steps of weight losses (ESI, Fig. S7).† The first step (104–195 °C) corresponds to the release of one aqua ligand and one lattice water molecule. The observed

weight loss (7.68%) is very close to the calculated value (7.78%). The second step (346–406 °C) and the third step overlaps and covers a temperature range of 427–697 °C, during which the hydroxyl anions and the sulfonate-arsonate ligands are decomposed. The total observed weight loss at 697 °C is 46.7%. TGA diagram of **2** reveals two main weight losses. The first step (82–250 °C) corresponds to the release of one lattice water molecule, the observed weight loss (6.7%) is slightly smaller than the calculated value (7.44%). The second step covers a temperature range of 424–714 °C, corresponding to the combustion of L^{3-} anions. The total observed weight loss at 714 °C is 38.92%.

TGA curves of **3**, **5**, **7**, **9**, **11** and **12** are similar and each exhibits two steps of weight losses. The first step corresponds to the loss of lattice water molecules whereas the second one corresponds to the combustion of the organic groups of the arsonate and auxiliary ligands. The total observed weight losses are 78.94% at 751 °C for **3**, 78.85% at 708 °C for **5**, 70% at 705 °C for **7**, 71.1% 681 °C for **9** at, 71.93% at 758 °C for **11**, and 76.89% at 700 °C for **12**.

Compound **6** is stable up to 170 °C, then it displays two steps of weight losses. The first step (170–346 °C) corresponds to the release of an aqua ligand. The observed weight loss of 1.57% is close to the calculated value (1.55%). The second step corresponds to the combustion of the sulfonate-arsonate ligand and phen ligands. The total observed weight loss at 713 °C is 68.77%.

TGA diagrams of compounds **4**, **8** and **10** are similar. They are stable up to 287 °C, 368 °C, 319 °C, respectively, then each exhibits one main step of weight loss, which corresponds to the combustion of the organic groups of both arsonate and auxiliary ligands. The total observed weight losses are 62.57% at 663 °C for **4**, 77.34% at 761 °C for **8**, and 71.89% at 742 °C for **10**.

The final residuals for all compounds were not characterized due to their corrosive reactions with the TGA buckets made of Al_2O_3, however it is expected that they are mainly zinc(II) or cadmium(II) oxide.

Conclusions

In summary, we have successfully reduced layered metal arsonates into various types of isolated clusters or 1D chains by the introduction of various auxiliary ligands. There results provide a few insights into our final goal of the controlled design for the low dimensional materials.

It is found that the different types of clusters isolated depend on many factors such as the coordination mode of the sulfonate-arsonate ligand, the molar ratios of the reactants, the reacting temperature as well as the nature of the auxiliary ligands. Compounds **5** and **6** are obtained instead of compounds **7** and **12** when the reacting temperature is increased to 170 °C from 150 °C. Compound **3** with a Zn/HL/bipy ratio of 1 : 1 : 2 is mononuclear whereas compounds **10** and **11** with a Zn/HL/bipy ratio of 1 : 1 : 1 are one dimensional.

Comparing with the manganese(II) sulfonate-arsonates reported by our group, the similarity is that the two-dimensional structures are obtained with the hydrothermal reaction of metal salts with *o*-sulfophenylarsonic acid ligand; the lower dimensional compounds, such as isolated clusters or 1D chains, were obtained with the introduction of the chelating auxiliary ligands, such as phen, bipy or terpy. The difference among the 2D layers, 1D chains or 0D clusters for manganese(II), zinc(II) and cadmium(II) sulfonate-arsonates lies in the different coordination modes of metal centers and the H_3L ligands. The different transition metal ions with similar radius have not significant impact for formation of novel structures. However, much more systematic studies are needed in order to syntheses materials with a controlled dimensionality and research the effect of different factors in forming the novel structures.

Acknowledgements

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