Photoluminescent lead(II) coordination polymers stabilised by bifunctional organoarsenate ligands
Photoluminescent lead(II) coordination polymers stabilised by bifunctional organoarsonate ligands

Jian-Di Lin\textsuperscript{1,2}, Camelia I Onet\textsuperscript{2} and Wolfgang Schmitt\textsuperscript{2}

\textsuperscript{1} Department of Applied Chemistry, College of Life Sciences, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350002, People’s Republic of China
\textsuperscript{2} School of Chemistry & CRANN, University of Dublin, Trinity College, Dublin 2, Ireland

E-mail: jdlin1981@163.com and schmittw@tcd.ie

Received 31 December 2014, revised 11 February 2015
Accepted for publication 12 February 2015
Published 17 March 2015

Abstract

Four lead(II) coordination polymers were isolated under hydro(solvo)thermal conditions. The applied synthetic methodology takes advantage of the coordination behaviour of a new bifunctional organoarsonate ligand, 4-(1,2,4-triazol-4-yl)phenylarsonic acid (H\textsubscript{2}TPAA) and involves the variation of lead(II) reactants, metal/ligand mole ratios, and solvents. The constitutional composition of the four lead(II) coordination polymers can be formulated as [Pb\textsubscript{2}(TPAA)(HTPAA)(NO\textsubscript{3})]\cdot6H\textsubscript{2}O (1), [Pb\textsubscript{2}(TPAA)(HTPAA)\textsubscript{2}]:DMF\cdot0.5H\textsubscript{2}O (DMF = N,N-Dimethylformamide) (2), [Pb\textsubscript{2}Cl\textsubscript{2}(TPAA)H\textsubscript{2}O] (3), and [Pb\textsubscript{3}Cl(TPAA)(HTPAA)\textsubscript{2}H\textsubscript{2}O]Cl (4). The compounds were characterized by single-crystal and powder x-ray diffraction techniques, thermogravimetric analyses, infra-red spectroscopy, and elemental analyses. Single-crystal x-ray diffraction reveals that 1 and 2 represent two-dimensional (2D) layered structures whilst 3 and 4 form three-dimensional (3D) frameworks. The structures of 1, 2, and 4 contain one-dimensional (1D) [Pb\textsuperscript{II}/AsO\textsubscript{3}] substructures, while 3 is composed of 2D [Pb\textsuperscript{II}/AsO\textsubscript{3}] arrays. Besides their interesting topologies, 1–4 all exhibit photoluminescence properties in the solid state at room temperature.

Keywords: coordination polymers, metal-organic frameworks, lead, photoluminescence, x-ray crystallography

1. Introduction

Over the past decades, the design and synthesis of coordination polymers (CPs) developed into an active research area due to the interesting physicochemical properties and potential applications of the materials in electro-optical devices, in catalysis, sensors, gas storage, or separation materials [1–11]. The hydro(solvo)thermal techniques provide powerful synthetic methodologies for the construction of CPs through the self-assembly of metal ions and designed organic ligands involving elevated temperatures and pressures. However, up until now, it still remains a considerable challenge to achieve controllable preparation conditions to produce crystalline CP materials with desired topological and chemical attributes. The reason for this stems from the complex formation conditions that influence the self-assembly and crystallization process; the applied synthetic approach is influenced simultaneously by numerous parameters, including the structural characteristics of the organic
ligands, the coordination geometry of central metal ions, the metal/ligand molar ratio, available counteranions, the solvent system, the pKₐ value of the solution, temperature, pressure, and reaction time [12–16]. Importantly, the nature of the organic ligand often influences the topology, the stability, the formation, and the crystallization conditions of the resulting hybrid materials.

The coordination chemistry of metal phosphonates has received significant attention over the last decades due to a number of industrial foreseeable applications of the compounds [17, 18]; phosphonates have been used to prepare zero-dimensional molecular species and coordination polymers [19–25]. To date, diverse bi-functional organophosphonic acid ligands containing various functional auxiliary groups (crown ether, amine, hydroxyl, and/or carboxylate, etc) have been used to control the formation and properties of CPs [26–33]. For example, recently a bifunctional aromatic organophosphonic acid ligand that contains a triazole moiety, 4-(1, 2, 4-triazol-4-yl)phenylphosphonic acid (H₂pTZ), has been synthesized and was used to stabilize three two-dimensional (2D) CPs containing Ni(II), Co(II), or Mn(II) metal ions [34, 35]. Up until now, most of the reported extended metal phosphonates display layered structures, while one-dimensional (1D) and porous three-dimensional (3D) networks have rarely been reported [36–40].

Organoaarsenic acids (R-AsO₃H₂) display geometrical characteristics that closely relate to those of analogous phosphonic acids (R-PO₃H₂); thus metal arsonates are expected to show structural and topological attributes that are similar to those of the metal phosphonates. However, the larger As(V) ionic radius and longer As-O bonds can be expected to result in modified architectures and distinguishing features to the corresponding phosphonate system. Pronounced differences of the pKₐ values may further distinguish the coordination chemistry of arsonates and phosphonates. So far, reports on metal arsonates are rather scarce. Most of the reported metal organoarsonates are hybrid polyoxometalate (POM) clusters based on V, Mo, or W [41–52]. In particular, Zubiesta’s research group has extensively explored the formation of such hybrid POMs [45, 47, 48, 50, 51]. We have reported several capular arsonate-stabilized polyoxovanadates that incorporate substituted R-phenylarsionate and investigated their 3D assembly [53–56]. In such POMs, each arsonate functionality bridges several metal centers and shows a coordination behaviour that is closely comparable to that of the corresponding phosphate-stabilized POMs [33, 53–56]. Synthetic approaches to Sn- and Pd-based organoarsonate complexes have also been explored under hydro(solvo)thermal conditions [57–59]. Recently, Tian et al reported examples of uranyl arsonates that are stabilized by phenylarsionate ligands [60]. To date, arsonate-stabilized metal-organic CPs are significantly less developed and investigated compared to the corresponding phosphonate compounds. The reported CPs predominantly contain s-, d-, and f-block metal ions, while significantly less attention has been paid to the p-block-based metal ions. This is somewhat surprising, as these types of CPs lend themselves to important applications in electroluminescent and photovoltaic conversion devices or fluorescent sensors [61–67]. As a heavy p-block metal ion, lead(II) may provide a potential opportunity to construct novel extended inorganic hybrids with fascinating topologies and interesting optical properties. Its large radius, variable stereochemical activity, and flexible coordination environment make a Pb(II) system to be an interesting candidate to prepare organoarsonate-stabilized network structures. To date, only very few lead arsonates have been reported in the literature [68, 69].

Here we report the synthesis and characterization of 4 lead(II)-organoaarsonate CPs that were obtained under solvothermal reaction conditions using a bifunctional arsionic acid ligand, 4-(1, 2, 4-triazol-4-yl)phenylarsonic acid (H₂TPAA). Our synthetic approach uses different lead(II) reactants that were employed at different metal/ligand mole ratios in solvents of different polarity and resulted in [Pb₂(TPAA)(HTPAA)(NO₃)]·6H₂O (1), [Pb₂(TPAA)HTPAA]·DMF·0.5H₂O (2), [Pb₂Cl₂(TPAA)H₂O] (3), and [Pb₂Cl₂(TPAA)H₂O]Cl (4). Among these four coordination polymers, 1 and 2 represent 2D layered structures whilst 3 and 4 form 3D framework structures. To the best of our knowledge, the reported arsonate coordination polymers mainly adopt 1D chain and 2D layer structures [70–74], whilst 3D dimensional structures are very rare [75, 76]. The structures of 1, 2, and 4 contain 1D {Pb₂AsO₃} structural motifs, while 3 is composed of 2D {Pb₂AsO₃} substructures. The luminescence properties of 1–4 have been investigated in the solid state at room temperature.

2. Experimental section

2.1. Materials and instrumentation

The H₂TPAA ligand was synthesized from N, N-dimethylformamide azine dihydrochloride using a general procedure previously reported by us [77, 78]. All reagents were purchased from Sigma-Aldrich and used as received without further purification. ¹H and ¹³C nuclear magnetic resonance data were recorded on a Bruker DPX 400 spectrometer (400.13 MHz for ¹H, 100.63 MHz for ¹³C). Fourier transform infrared spectroscopy (FTIR) data were collected on a PerkinElmer Spectrum One FTIR Spectrometer. Thermogravimetric analyses (TGAs) were performed in air on a PerkinElmer Pyris 1 TGA from 30–800°C at a heating rate of 10°C/min. Powder x-ray diffraction (XRD) data were recorded on a Siemens D500 x-ray diffractometer at 40 kV, 30 mA with Cu-Kα radiation (λ = 1.54 0.6 Å), with a scan speed of 3°/min and a step size of 0.05° in 2θ at room temperature. The simulated patterns were derived from the Mercury Version 1.4 software (http://www.ccdc.cam.ac.uk/products/mercury/) using the data obtained from the single-crystal x-ray diffraction experiments (cif files). Elemental analyses (C, H, and N) were obtained from the Microanalysis Laboratory, School of Chemistry and Chemical Biology, J-D Lin et al

2.2. Syntheses of the complexes

\[ \text{[Pb_2(TPAA)(HTPAA)(NO_3)]·6H_2O} \] (1) Pb(NO_3)_2 (0.1 mmol), H_2TPAA (0.1 mmol), and 5 mL of H_2O were added into a 10 mL reaction vial and sealed. The mixture was heated to 100 °C and kept at this temperature for 1 d. Colourless needle crystals of 1 were obtained and washed with H_2O before drying in air at room temperature (yield: 31 mg, 55% based on Pb(NO_3)_2). Elemental analysis (%): calculated For. C_{16}H_{27}O_{17}N_{10}Pb_{2} (1119.65), C 17.16 H 2.50 N 8.76; Found C 17.23 H 2.50 N 8.71. IR (\nu/cm\(^{-1}\)): 3373 (w), 3111 (w), 1614 (w), 1592 (w), 1415 (w), 1374 (m), 1244 (m), 1218 (s), 1098 (s), 1039 (vw), 1022 (vw), 1003 (m), 963 (vw), 864 (m), 851 (m), 792 (vs), 733 (w), 713 (w).

\[ \text{[Pb_2(TPAA)(HTPAA)(NO_3)]·2H_2O} \] (2) PbBr_2 (0.1 mmol), H_2TPAA (0.15 mmol), and 5 mL DMF (DMF = N, N-Dimethylformamide) were added into a 10 mL reaction vial and sealed. The mixture was heated to 100 °C and kept at this temperature for 4 d. Colourless needle crystals of 2 were obtained and washed with DMF and ethanol before drying in air at room temperature (yield: 45 mg, 69% based on PbBr_2). Elemental analysis (%): calculated For. C_{16}H_{25}N_{7}O_{15}Pb_{2}As_{2} (1119.65), C 17.16 H 2.25 N 8.76; Found C 17.23 H 2.50 N 8.71. IR (\nu/cm\(^{-1}\)): 3373 (w), 3117 (w), 2918 (m), 1664 (s), 1597 (m), 1524 (s), 1413 (vw), 1372 (w), 1327 (w), 1294 (vw), 1245 (s), 1100 (s), 1006 (w), 995 (m), 956 (w), 873 (m), 811 (vs), 727 (m), 708 (m), 670 (vw), 659 (vw).

\[ \text{[Pb_3Cl_2(TPAA)(HTPAA)·6H_2O} \] (3) PbCl_2 (0.2 mmol), H_2TPAA (0.1 mmol), and 5 mL of H_2O were added into a 10 mL reaction vial and sealed. The mixture was heated to 100 °C and kept at this temperature for 1 d. Colourless prism crystals of 3 were obtained and washed with H_2O before drying in air at room temperature (yield: 59 mg, 55% based on PbCl_2). Elemental analysis (%): calculated For. C_{16}H_{25}N_{7}O_{15}Pb_{2}As_{2} (1119.65), C 17.16 H 2.25 N 8.76; Found C 17.23 H 2.50 N 8.71. IR (\nu/cm\(^{-1}\)): 3373 (w), 3111 (w), 1614 (w), 1592 (w), 1415 (w), 1374 (m), 1244 (m), 1218 (s), 1098 (s), 1039 (vw), 1022 (vw), 1003 (m), 963 (vw), 864 (m), 851 (m), 792 (vs), 733 (w), 713 (w).

\[ \text{[Pb_2Cl_2(TPAA)(HTPAA)·2H_2O} \] (4) PbCl_2 (0.2 mmol), H_2TPAA (0.05 mmol), and 5 mL of H_2O were added into a 10 mL reaction vial and sealed. The mixture was heated to 100 °C and kept at this temperature for 1 d. Colourless prism crystals of 4 were obtained and washed with H_2O before drying in air at room temperature (yield: 27 mg, 54% based on PbCl_2). Elemental analysis (%): calculated For. C_{16}H_{25}N_{7}O_{15}Pb_{2}As_{2} (1119.65), C 17.16 H 2.25 N 8.76; Found C 17.23 H 2.50 N 8.71. IR (\nu/cm\(^{-1}\)): 3373 (w), 3111 (w), 1614 (w), 1592 (w), 1518 (s), 1414 (m), 1368 (vw), 1326 (w), 1291 (w), 1262 (vw), 1241 (s), 1196 (vw), 1072 (w), 1086 (m), 1021 (w), 1006 (m), 964 (vw), 859 (s), 835 (m), 816 (s), 782 (vs), 725 (m), 666 (w).

2.3. X-ray crystallography

The data collections of 1 and 2 were carried out on a Bruker APEX Duo CCD x-ray diffractometer at 100 K using graphite-monochromated Cu-Kα (λ = 1.54 187 Å) and Mo-Kα radiation (λ = 0.71 073 Å), respectively, while those of 3 and 4 were carried out on a Rigaku 724 CCD x-ray diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71 073 Å). The data collection temperatures of 1–4 were 100, 123, 293, and 95 K, respectively. The structures of these four coordination compounds were solved by direct methods using SHELXS-97, integrated using the OLEX2 software [79] and refined with full-matrix least squares on F^2 using the SHELXL-97 program [80]. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms of 1 and 3 were refined on calculated positions. For 2 and 4, the hydrogen atoms belonging to As1O3 groups (H13 and H33 in 1) were repositioned over two sites (C43, O41, C43’, O41’). The site occupancies of C43, O41, C43’, O41’ are all 0.5. Details of x-ray analysis, including the crystal parameters, data collection, and refinement parameters for compounds 1–4 are summarized in table 1. Selected bond lengths, angles, and hydrogen-bond interactions are summarized in tables S1.1–S4.2 (SI). Further details of the crystal structure determination have been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC numbers for 1–4: 999 421–999 424, respectively.

3. Results and discussion

3.1. Syntheses

Compounds 1–4 were reproducibly obtained in moderate yields under hydro(solvo)thermal conditions upon combination of lead salts and H_2TPAA in H_2O or DMF. The products form depending on the nature of the metal salt, the relative metal:ligand mole ratios, or the solvent system. Compound 1 selectively forms when Pb(NO_3)_2 and H_2TPAA are reacted in H_2O. When the nitrate reactant is substituted by PbCl_2, compounds 1 and 2 are obtained, depending on the relative metal:ligand mole ratios. Compound 3 forms when equimolar ratios of PbCl_2 and H_2TPAA are reacted with each other in H_2O. Higher yields can be obtained when a PbCl_2:H_2TPAA mole ratio of 2:1 is used. However, when the relative quantity of PbCl_2 in the reaction system is reduced to a mole ratio of 1:2, phase-pure crystals of compound 4 are obtained. Reactions of PbCl_2 and H_2TPAA at a mole ratio of 1:3 lead to product mixtures of 4 and a white unidentified precipitate. Corresponding hydrothermal reactions of PbX_2 (X = OAc or F) and H_2TPAA in water did not lead to phase-pure products or crystals suitable for single-crystal x-ray diffraction. Compound 2 requires PbBr_2 as a starting material and forms in DMF. Best yields are obtained when the metal salt and the ligand are reacted at 100 °C for 4 d at stoichiometric ratios as...
given by the formula of 2. 1:1 mole ratios or reduced reaction time lead to the co-precipitation of a white unidentified product. If the reactions of PbX2 (X = Cl, OAc, or F) and H2TPAA were carried out in a DMF solvent system, then either a colourless clear solution (for Pb(OAc)2) or microcrystalline solids (for PbF2 or PbCl2) are obtained.

### 3.2. Structural description of the complexes

**[Pb2(TPAA)(HTPAA)(NO3)]·6H2O (1)** Compound 1 crystallizes in the monoclinic space group C2/c. The asymmetric unit consists of two Pb(II) ions, one fully deprotonated TPAA2– ligand, one HTPAA– anion (denoted as LAs11 and LAs21), one NO3 anion, one coordinated water molecule, and five lattice water molecules (the occupancies of O6W and O7W are both 0.5) (SI, figure S1(a)). Both two Pb(II) ions are in hemidirected coordination spheres. The Pb(II) ion is five-coordinate with four arsenate oxygen atoms and one nitrogen atom deriving from five different ligands. The Pb2(II) ion is six-coordinate, whereby three arsenate oxygen atoms originate from three different ligands, two oxygen atoms from a NO3 anion and one water molecule. The Pb–O distances (2.331(5)–2.706(4) Å) are close to those reported for other lead(II) organo arsenates [68, 69]. The long distance of the Pb1–N21+ bond (2.8372 (77) Å) is comparable to some corresponding long Pb–N bonds reported in the literature [81–83]. The As–O distances of the [As11O14] group are 1.684(5), 1.686(5), and 1.687(5) and of [As21–O–] are 1.666 (5), 1.667(5), and 1.735(5) Å. Considering the charge balance of 1, and the fact that the As21–O23 (1.735(5) Å) bond is the longest among these As–O bonds, O23 was assigned as a hydroxyl oxygen atom. According to the research of Shimoni-Livny et al [84], the repulsion effect of the 6s2 lone pair electrons may result in long bonds and weak coordinative binding interactions involving Pb(II) ions. In light of these results, we have used a bond order calculation [85] to further characterize the coordination environment of the Pb(II) center in 1. The valence of Pb1 associated with the four Pb–O bonds is 1.675. Further calculations including the weak Pb1–N21+ interaction increase the valence of Pb1 from 1.675 to 1.864; the valence of Pb2 is 1.907, which is calculated considering all the six Pb–O bonds (the calculated valence contribution of the long Pb–O31 interaction (2.821(49) Å) is 0.1248). LAs11 and LAs21 adopt (κ4η1)κ−κ−κη−κκ3 coordination modes, respectively (figure 1(a)). The two different [AsO3]− functionalities of LAs11 and LAs21 link the Pb(II) ions in 1 into 1D chains that extend in the direction of the crystallographic c-axis (figure 1(b)) and are connected to each other by a LAs21 spacer to form a 2D layer structure (figure 1(c)). Further, parallel aligned 2D layers stack in the direction of the crystallographic b-axis in an ABC fashion to form a 3D supramolecular architecture through hydrogen-bonds involving the H-bond donor/acceptor pairs O2W—H2WA···N22v and O7W—H7WB···N11iv [Symmetry codes: (v) −x+1/2, y= 0, −z+1/2; (vii) −x+1/2, y+1/2, −z+1/2]. Strong hydrogen-bond interactions also occur between the water molecules (SI, figure S1(b)).

**[Pb2(TPAA)(HTPAA)2]·4DMF·0.5H2O (2)** Single-crystal x-ray diffraction measurements reveal that compound 2 crystallizes in the triclinic space group P–1. The asymmetric unit of 2 consists of two Pb(II) ions, one fully deprotonated TPAA2– ligand, two HTPAA– anions (denoted as LAs11,
sphere that is completed by four arsonate oxygen atoms and one nitrogen atom that are provided by five different ligands. The Pb–O distances (2.236(2)–2.671(2) Å) are in the expected range. The Pb2–N31 distance (2.676(3) Å) is much shorter than the previously discussed bond in 1. When only the relatively strong Pb–O bonds (Pb–O < 2.88 Å) are taken into account, the valence of Pb1 is 1.828. Further calculation demonstrates that the long Pb1–O31\(^{\text{H}}\) bond has a considerable contribution, increasing the valence to 1.936. The valence of Pb2 calculated from the existing Pb–O bonds and the Pb2–N31 bond is 2.02, which is very close to the assigned oxidation state of Pb(II) ion. The longest As–O bonds in the respective \{AsO\}_3 groups are As11–O13 1.742(3), As21–O23 1.699(2), and As31–O33 1.709(3) Å, so, considering the charge balance of 2, O13 and O33 were assigned as hydroxyl atoms. \(L_{\text{As11}}, L_{\text{As21}}, \text{and } L_{\text{As31}}\) adopt \(xO11-\mu_1, \mu_2 (O21xO22, O22-xO23, O23-xO31) \mu_5\) coordination modes, respectively (figure 2(a)). The three different \{AsO\}_3 functionalities from \(L_{\text{As11}}, L_{\text{As21}}, \text{and } L_{\text{As31}}\) link the Pb(II) ions into 1D chains that extend in the direction of the crystallographic b-axis (figure 2(b)) and which are connected to each other by an \(L_{\text{As31}}\) spacer to form a 2D layer structure (figure 2(c)). There are two distinct, strong intramolecular hydrogen-bond interactions in 2 that occur within the 2D layer between OH functionalities (O13 and O33) of the AsO\(_3\) groups and deprotonated oxygen atoms (O23 and O12) of neighbouring AsO\(_3\) groups. These H-bonds are characterized by O13–H13···O23 and O33–H33···O12\(^{\text{D}}\) distances of 2.649(4) and 2.493(4) Å, respectively [symmetry codes: (vi) \(x, y + 1, z\) (figure S2(b)).

\[
[\text{Pb}_2\text{Cl}_2(\text{TPAA})\text{H}_2\text{O}] \quad (3)
\]

The asymmetric unit of 3 contains two Pb(II) ions, two terminal coordinated chloride anions, one fully deprotonated TPAA\(^{2-}\) ligand (denoted as \(L_{\text{As1}}\)), and one \(\mu_2\) bridging water molecule (figure S3). The compound crystallizes in the orthorhombic space group Pcen. Both two Pb(II) ions are in hemidirected coordination spheres. The Pb1(II) ion is six-coordinate with three arsionate oxygen atoms and one nitrogen atom deriving from three different ligands, one chlorine atom, and the \(\mu_2\)-bridging water molecule. The Pb2(II) ion is five-coordinate, whereby two arsionate oxygen atoms and one nitrogen atom are provided by three different ligands, one chlorine atom, and the \(\mu_2\)-coordinated water molecule, completing the distorted coordination sphere of this ion. The bond length of Pb1–Cl2 is 2.906(9) Å, which may be regarded as a semi-coordination mode. Except for Pb2–Cl1 and Pb2–Cl2, the other Pb–O distances are in the expected range, varying between 2.272(8), 2.783(9) Å. The distances of Pb1–N1\(^{\text{IV}}\) and Pb2–N2\(^{\text{H}}\) are 2.737(10) and 2.851(9) Å, respectively, and those of Pb1–Cl1 and Pb2–Cl2 are 2.685(30) and 2.721(33) Å, respectively. The distance of Pb2–N2\(^{\text{H}}\) is a little longer than the discussed Pb–N bond in 1 (2.837 (8) Å), whilst the Pb–Cl distances are in the expected range. The valence of Pb1 calculated from all the existing bonds (including the Pb2–O4W (2.906(9) Å) bond) is 2.07, which is very close to the assigned oxidation state of +II. If only the relatively strong Pb–O bonds (Pb–O < 2.88 Å) are taken into account, the valence of Pb2 is 1.95.
In 3, the $L_{\text{As1}}$ ligand adopts a ($\kappa$O1, O1-$\kappa$O2-$\kappa$O3, O3-$\kappa$N1-$\kappa$N2)-$\mu_6$ coordination mode (figure 3(a)). The AsO$_3$ functionalities from $L_{\text{As1}}$ link Pb(II) ions into 2D layers that

![Figure 2](image1.png)

![Figure 3](image2.png)

Figure 2. (a) The coordination environment of the Pb(II) ions and the coordination modes of the ligands in 2. Symmetry codes: (i) $x$, $y$, $z$; (ii) $x$, $-y$, $-z$; (iii) $-x$, $-y$, $-z$; (iv) $-x$, $y$, $z$; (v) $x$, $y$, $z$; (vi) $x$, $y$, $z$. (b) Polyhedral representation of the one-dimensional sub-structure in 2 comprising of Pb(II) ions and the three different $\{\text{AsO}_3\}$ functionalities (view in the direction of the crystallographic $b$-axis). (c) Polyhedral representation of the two-dimensional structure in 2 (view in the direction of the crystallographic $b$-axis).

Figure 3. (a) The coordination environment of Pb(II) ions and the coordination mode of the ligand in 3. Symmetry codes: (i) $-x$, $-y$, $-z$; (ii) $-x$, $-y$, $-z$; (iii) $-x$, $y$, $z$; (iv) $-x$, $y$, $z$. (b) Polyhedral representation of two-dimensional layer structure in 3 comprising Pb(II) ions and the $\{\text{AsO}_3\}$ functionalities (view in the direction of the crystallographic $a$-axis). (c) Polyhedral representation of the three-dimensional framework of 3 (view in the direction of the crystallographic $b$-axis).
extend parallel to the $ac$-plane (figure 3(b)) and which are connected to each other by the $L_{A31}$ spacer to form a 3D framework (figure 3(c)). Intramolecular hydrogen-bond interactions occur in 3 between the coordinated water molecule and the $\{AsO_4\}$ group (O3) to give a $O4W$—$H4WB$—$O3^v$ distance of 2.751(10) Å [Symmetry code: (v) $x, y-1, z$].

$[\text{Pb}_3\text{Cl}(\text{TPAA})(\text{HTPAA})_2\text{H}_2\text{O}](\text{Cl})$ (4) There are three Pb (II) ions, two HTPAA$^-$ ligands, one fully deprotonated TPAA$^{2-}$ ligand (denoted as $L_{A21}, L_{A21},$ and $L_{A31}$), one terminal coordinated chloride atom, one terminal coordinating water molecule, and one lattice chloride ion in the asymmetric unit of 4 (figure S4(a)). The compound crystallizes in the triclinic space group $P\bar{1}$. The Pb1(II)–Pb2(II) ions can be considered to adopt hemidirected coordination spheres. However, if the long Pb3–O22 bond (2.888(6) Å) is taken into consideration, the coordination environment of Pb3(II) may be described as holodirected. The Pb1(II) ion is five-coordinate with four arsenate oxygen atoms originating from three different ligands; the remaining binding site is occupied by a chloride ion. The Pb2(II) ion is five-coordinate, whereby four arsenate oxygen atoms and one nitrogen atom are provided by five different ligands. The six-coordinate binding environment of the Pb3(II) ion is composed of four oxygen and one nitrogen atom derived from five different ligands and one coordinated water molecule. The bond lengths of Pb–O range from 2.361(5) to 2.888(6) Å. The bond lengths of Pb2–N21 and Pb3–N31$^v$ are 2.521(7) and 2.737(7) Å, respectively, and that of Pb1–Cl41 is 2.753(2) Å. The valences of Pb1 and Pb2 calculated from all the existing bonds are 1.85 and 1.87, respectively, being smaller than the assigned oxidation state of +II. However, no other weak Pb–O interactions can be found around the Pb1(II) and Pb2(II) centers. If only the relatively strong Pb–O bonds (Pb–O < 2.8 Å) are taken into account, the valence of Pb3 is 1.88. Further calculation shows that the long Pb3–O22 interaction also makes a considerable contribution, increasing the valence to 2.004 for Pb3.

In 4, $L_{A311}, L_{A211},$ and $L_{A31}$ adopt $\{\kappa\text{O}11-\kappa\text{O}12\}-\mu_2,$ $\{\kappa\text{O}21, \kappa\text{O}22-\kappa\text{O}23-\kappa\text{N}21\}-\mu_4,$ and $\{\kappa\text{O}31, \kappa\text{O}31-\kappa\text{O}32, \kappa\text{O}32-\kappa\text{O}33-\kappa\text{N}31\}-\mu_6$ coordination modes, respectively (figure 4(a)). The three different $\{AsO_4\}$ functionalities from $L_{A311}, L_{A211},$ and $L_{A31}$ link the Pb(II) ions into 1D chains that extend in the direction of the crystallographic $b$-axis (figure 4(b)), and which are connected to each other by the $L_{A31}$ spacer to form a 2D layer structure (figure 4(c)). These 2D layers are further linked by the $L_{A31}$ spacer to form a 3D framework.

The lattice chloride anions are located in the channels of the 3D framework (figure 4(d)). From the topological point of view, the resulting Pb6 clusters (two Pb1, two Pb2, and two Pb3, denoted as S) can be viewed as nodes. Connectors between adjacent S nodes are provided by $L_{A211}$ and $L_{A31}$ (17.480(4) and 13.708(3) Å) and through innode linkages within the 1D chain (7.2305(14) Å (see SI, figures S4(b) and (c))). Consequently, the 3D framework of 4 can be abstracted as a six-connected network with the Schlafli and vertex symbols being $\{4^2\}_6$ and $4\{4\}_4\{4\}_4\{4\}_4\{4\}_4\{4\}_4\{4\}_4$, respectively. This topology is consistent with a pecu-type network, according to the Reticular Chemistry Structure Resource (RCSR) notation (figure 4(e)).

There are two distinct, strong intramolecular hydrogen-bond interactions in 4 within the 3D framework: one type of interaction occurs between OH functionalities (O23) of the $\{As210\}$ groups and deprotonated oxygen atoms (O33) of neighbouring $\{As310\}$ groups; the other type of interaction prevails between the coordinated water (O51W) and the neighbouring N11 atom. These H-bonds are characterized by O23–H23–O33$^{vi}$ and O51W–H51A–N11$^{vi}$ distances of 2.527(8) and 2.880(10) Å, respectively [symmetry codes: (iii) $x, -y, z+1$; (vi) $x-1, y, z+1$].

3.3. X-ray powder, FTIR spectral, and thermogravimetric analyses

The phase-purity of the here presented compounds was confirmed by PXRD. The 2 theta values of the major reflections of the experimentally recorded PXRD patterns of the bulk solids of 1–4 match well to those of the simulated patterns, which were calculated from respective single-crystal data (SI, figures S5(a)–(d)). The FTIR spectra of the four compounds show typical As–C stretching vibration bands at 1098 cm$^{-1}$ for 1, 1100 cm$^{-1}$ for 2, 1097 cm$^{-1}$ for 3, and 1099 cm$^{-1}$ for 4. The vibrations associated with the $\{AsO_4\}$ moiety are very strong and occur at 864 and 851 cm$^{-1}$ for 1, 873 cm$^{-1}$ for 2, 859 and 835 cm$^{-1}$ for 3, and 864 and 844 cm$^{-1}$ for 4 (SI, figures S6(a)–(d)) [76]. The thermal stability of 1–4 was examined by TGA in an air atmosphere between 30–800 °C (SI, figure S7). The TGA curve of 1 reveals the removal of constitutional lattice water molecules and the coordinated water molecule in a range between 30–320 °C. 2 loses its lattice water and DMF molecules between 30–280 °C. After 280 °C, the framework of 2 undergoes oxidative degradation. The coordinated water molecule of 3 is lost between 30–110 °C, after which the framework architecture of 3 decomposes gradually due to the oxidation of the organic ligand. The coordinated water molecule of 4 is lost between 30–245 °C. The remaining structure of 4 is stable up to ~305 °C, after which the framework collapses due to the combustion of the organoarsonate ligands.

3.4. Luminescence properties of 1–4

Hybrid coordination compounds containing Pb(II) ions may have interesting photochemical and photophysical properties [61–67, 86]. However, in comparison to many transition metal or lanthanide systems, the photoluminescence properties of lead(II)-organic frameworks are less explored. To further characterize 1–4, their photoluminescence properties were investigated in the solid state at room temperature. As illustrated in figure 5, emission bands at 461 and 486 nm ($\lambda_{ex} = 380$ nm) for 1, 438 nm ($\lambda_{ex} = 380$ nm) for 2, 458, 478, and 531 nm ($\lambda_{ex} = 380$ nm) for 3 and 458 and 550 nm ($\lambda_{ex} = 370$ nm) for 4 are observed. For H$_2$TPAA, an emission band maximum centered at 456 nm is apparent upon photoexcitation at 373 nm (SI, figure S8). The emission bands at 461 nm of 1, 438 nm of 2, 458 nm of 3, and 458 nm of 4 may
Figure 4. (a) The coordination environment of the Pb(II) ions and the coordination modes of the ligands in 4. Symmetry codes: (i) \(x-1, y, z\); (ii) \(-x, -y, -z\); (iii) \(-x, -y, -z+1\); (iv) \(-x, -y+1, -z+1\); (v) \(x+1, y, z\). (b) Polyhedral representation of the one-dimensional sub-structure in 4 involving Pb(II) ions and the three different \{AsO\_3\} functionalities (view in the direction of the crystallographic \(b\)-axis). (c) Polyhedral representation of the two-dimensional layer sub-structure in 4 in which LAs\_2 moieties link between the adjacent one-dimensional subunits (view in the direction of the crystallographic \(b\)-axis). (d) Polyhedral representation of the three-dimensional framework structure in 4 in which LAs\_3 moieties pillar between the adjacent two-dimensional layers (view in the direction of the crystallographic \(a\)-axis). (e) The NaCl-type network representing the topology of the 3D framework in 4.
be due to the $\pi \rightarrow \pi^*$ transition, as an approximate emission peak (456 nm) also appears in the spectra of the H$_2$TPAA ligand. The emission bands at 486 nm of 1 and 478 nm of 3 can be attributed to ligand-to-metal charge transfer (LMCT) transitions involving delocalized $\pi$ bonds of the aromatic arsenic group and the $p$ orbitals of Pb(II) centers. The low-energy emissions with large stokes shift, characteristic for the bands at 531 nm for 4, can be assigned to metal-centered transitions involving $s$ and $p$ orbitals, as proposed by Vogler [87, 88].

4. Conclusions
In summary, four lead(II) coordination polymers with distinctively different structural motifs were successfully isolated using hydro(solvo)thermal preparative conditions. The applied preparative approach utilized different lead reactants that were reacted with various metal/ligand molar ratios with a bifunctional organoarsonate ligand in H$_2$O or DMF. These applied reaction parameters, including the counterions, played a crucial role of the topology and composition of the resulting Pb(II) coordination polymers. The results demonstrate that the coordination modes of the H$_2$TPAA ligand are highly flexible, adopting $\mu_1$, $\mu_2$, $\mu_3$-, $\mu_4$-, $\mu_5$-, and $\mu_6$- bridging modes. 1 and 2 represent 2D layered structures, whilst 3 and 4 form 3D frameworks. The structures of 1, 2, and 4 contain 1D [Pb-AsO$_3$] sub-structural units, while the framework of 3 is characterized by 2D [Pb-AsO$_3$] sub-structural motifs. Compounds 1–4 all exhibit photoluminescence properties in the solid state at room temperature. The arsonic acid functionalities in the examined compounds have a high propensity to be partially protonated under the applied reaction conditions. Among these four lead(II) coordination polymers, only 3 is stabilized by fully deprotonated arsonate functionalities. This reaction behaviour and the consequent lower tendency to bridge metal centers than corresponding phosphate ligands can be interpreted in light of their pK$_a$ values. According to the literature, the pK$_a$ values of phenylphosphonic acid are 1.86 and 7.51 [89], and the pK$_a$ values of phenylarsonic acid are 3.8 and 8.5 [90], suggesting that the 2nd deprotonation event occurs more readily for phosphonic acids than that for the arsonic acids. Despite the fact that arsonate anions can also adopt a variety of potential coordination modes, their ability as complexing agents has not yet been fully explored. Consequently, new synthetic methodologies are required to explore to further fully understand the coordination chemistry of organoarsonates.

Acknowledgments
We gratefully acknowledge the Science Foundation Ireland (SFI) for financial support. Financial support from Irish Research Council (IRC) (postdoctoral fellowship for J-DL) is gratefully acknowledged.

References