



## Two novel Pb(II)-organic frameworks based on polycarboxylate ligands: Syntheses, structures, and luminescent properties



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### ARTICLE INFO

#### Article history:

Received 3 July 2015

Received in revised form 18 August 2015

Accepted 23 August 2015

Available online 1 September 2015

#### Keywords:

Pb<sup>II</sup>-coordination framework

Organic-acid ligands

Network topology

Fluorescence

### ABSTRACT

Two novel Pb(II) complexes, {[Pb<sub>1.5</sub>(BPTC)]·0.25H<sub>2</sub>O}<sub>n</sub>(1) and {[Pb(ADC)·(H<sub>2</sub>O)]<sub>n</sub>(2), (H<sub>3</sub>BPTC = biphenyl-3,2',5'-tricarboxylate, H<sub>2</sub>ADC = 1,3-Adamantanedicarboxylic acid) were successfully synthesized through varying the different polycarboxylate ligands. The compounds were structurally characterized by elemental analysis, IR and single-crystal X-ray diffraction. Compound 1 exhibits a 3D porous coordination framework, which possesses a new 3-nodal (5,6,8)-connected topology. Compound 2 shows a two-dimensional layer containing a 1D nanotube structure. In addition, compounds 1 and 2 exhibit high thermal stability and fluorescent properties in the solid state at room temperature.

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The current interest in the crystal engineering of coordination polymer frameworks is increasing not only because of their intriguing variety of architectures and topologies but also their fascinating potential applications in functional solid materials, ions exchange, catalysis, and the development of optical, electronic, and magnetic devices [1–4]. A successful strategy in building such networks is to employ appropriate bridging ligands that can bind metal ions in different modes and provide a possible way to achieve more new materials with beautiful architectures and excellent physical properties [5–6]. Among the reported studies, polycarboxylate ligands are widely utilized in the construction of coordination polymers because they can adopt a variety of coordination modes resulting in diverse multidimensional architectures and fascinating topologies, especially interesting properties [7–8]. Among them, the biphenyl polycarboxylate [9–10] and adamantane polycarboxylate ligands [11] can serve as excellent candidates for building complicated coordination frameworks due to their bent backbones and versatile bridging fashions. Up to now, these polycarboxylate ligands have been utilized as a competent building block to successfully construct a series of *d*–*f*-block metal coordination polymers, which exhibit enthralling network structures and the corresponding functionalities. By contrast, *p*-block metal coordination frameworks based on the above polycarboxylate ligands are still comparatively rare [12]. In the report, we introduced the biphenyl-3,2',5'-tricarboxylate and 1,3-Adamantanedicarboxylic acid as the main ligands to react with Pb(II) metal to construct Pb<sup>II</sup>-coordination frameworks (Scheme 1).

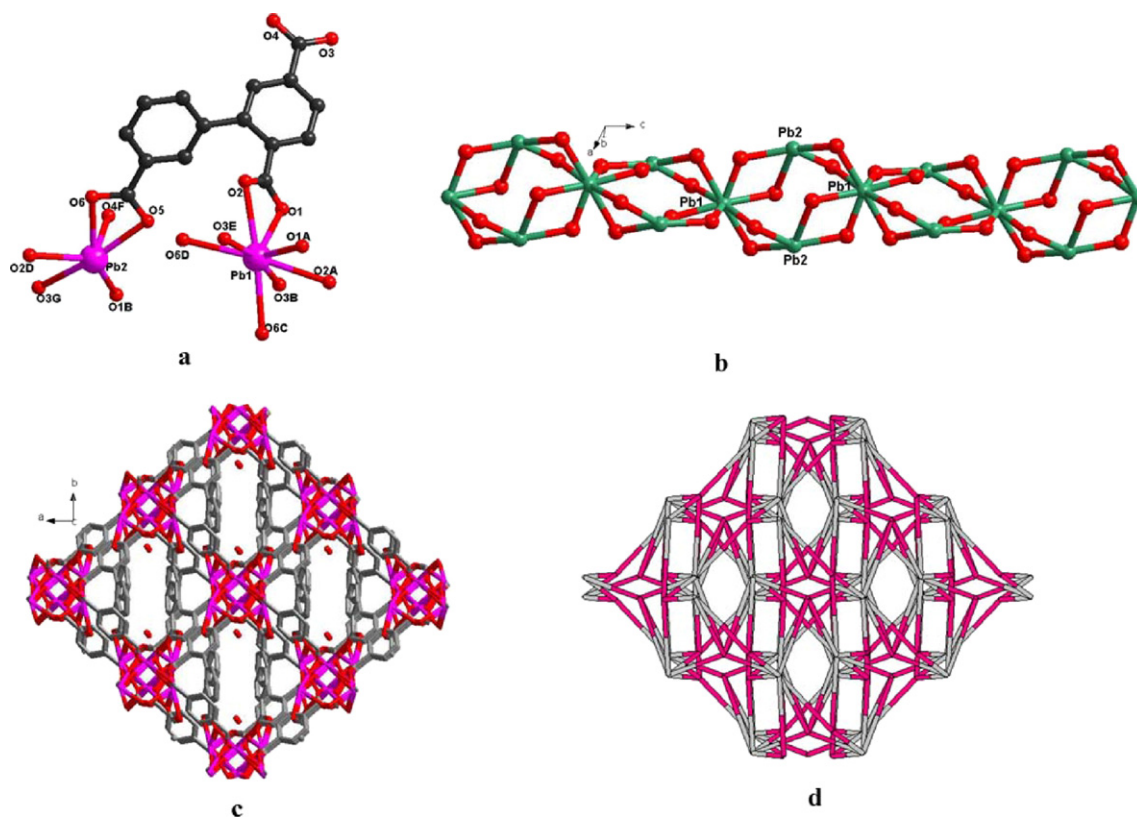
As a heavy *p*-block metal ion, Pb(II) ion, with a lone-pair electron and large ionic radius, can adopt the flexible coordination environment and variable stereochemical activity [13]. Thus, it will provide a good opportunity for the construction of unusual coordination frameworks with suitable organic tectons. Moreover, the reported Pb-crystalline systems not only show structural diversity but also exhibit some important properties of electroluminescence, photovoltaic conversion, and fluorescence [14]. Therefore, it is of great significance to further explore new Pb<sup>II</sup>-coordination polymers and develop their potential applications. In this contribution, two new complexes {[Pb<sub>1.5</sub>(BPTC)]·0.25H<sub>2</sub>O}<sub>n</sub>(1) and {[Pb(ADC)·(H<sub>2</sub>O)]<sub>n</sub>(2), have been successfully isolated and structurally characterized, and exhibit fluorescent properties at room temperature. All crystal structures have been determined by single-crystal X-ray diffraction, and the compounds are also characterized by IR, elemental analysis, and thermal properties.

Hydrothermal reactions of Pb(OAc)<sub>2</sub> with H<sub>3</sub>BPTC in water at 150 °C for three days gave rise to colorless block-shaped crystals of 1, and compound 2 was obtained as colorless prism-shaped blocks by a slow hierarchical diffusion approach [15], which were characterized by elemental analysis, IR, powder X-ray diffraction (Fig. S1) and single-crystal X-ray diffraction [16].

Complex 1 crystallizes in the monoclinic system with space group *C2/c* and its asymmetric unit contains one and a half-occupied Pb<sup>II</sup> ion, one BPTC<sup>3-</sup> ligand. As shown in Fig. 1a, each Pb1 is eight-coordinated and ligated to eight O atoms from six different BPTC<sup>3-</sup> ligands generating a distorted square-antiprism coordination geometry; while Pb2 atom is primarily coordinated by six oxygen atoms from five BPTC<sup>3-</sup> ligands to furnish a distorted pentagonal bipyramidal geometry. Pb1 and Pb2 reveal the holo- and hemi-directed types in 1, respectively.

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**Fig. 1.** (a) View of the coordination environments of  $\text{Pb}^{\text{II}}$  atoms in 1. Symmetry code: A:  $1-x, y, 0.5-z$ ; B:  $0.5+x, 0.5+y, z$ ; C:  $0.5+x, 1.5-y, 0.5+z$ ; D:  $0.5-x, 1.5-y, -z$ ; E:  $0.5-x, 0.5+y, 0.5-z$ ; F:  $-x, 1-y, -z$ ; G:  $x, 1+y, z$ ; (b) the representation of the 1D Pb–O–Pb chain; (c) view of 3D porous framework connected by Pb–O–Pb chain and BPTC ligand; (d) schematic view of the 3D 3-nodal (5,6,8)-connected topology net with the point symbol of  $\{4^{10}, 6^5\}\{4^{18}, 6^{10}\}_2\{4^8, 6^2\}_2$  in 1.

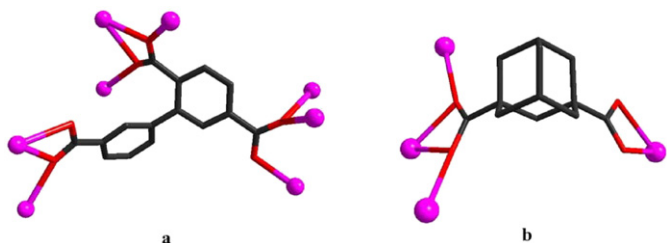
The Pb–O bond lengths vary greatly from 2.328(6) to 2.748(6) Å, which are similar to those observed in the reported Pb-based compounds [17]. And the dihedral angle between the two phenyl rings in compound 1 is 54.41°. Each  $\text{BPTC}^{3-}$  ligand completely deprotonated and bound to seven  $\text{Pb}^{\text{II}}$  atoms with a  $\mu^8-\eta^2:\eta^2:\eta^1:\eta^1:\eta^2$ -bridging coordination mode (Scheme 1a). It is noticed that the  $\mu_2$ -bridged O atoms link neighboring lead(II) ions (Pb1 and Pb2) forming a dimeric lead(II) building block with the Pb1...Pb2 distance of 4.450(5) Å. Further these dimeric lead(II) building blocks are linked to each other to produce a 1D Pb–O–Pb linkage parallel to crystallographic *c* plane (Fig. 1b). Furthermore, these are 1D chains interconnected by flexible tecton of  $\text{BPTC}^{3-}$  ligand to afford a porous 3D framework, which are filled with plenty of lattice water molecule (Fig. 1c). Compared to rigid aromatic ligands, semi-rigid biphenyl ligand possesses more flexibility, because of the free rotation around the C–C bond between the phenyl rings, and therefore may build coordination polymers with more diverse structure [10c].

A topological calculation by using the TOPOS software suggests that such a subnet could be described as a complicated 3D 3-nodal (5,6,8)-connected topology net with the point symbol of  $\{4^{10}, 6^5\}\{4^{18}, 6^{10}\}_2\{4^8, 6^2\}_2$ , in which each Pb1 center acts a 6-connected node, and each

Pb2 atom acts as 8-connected linking, while the  $\text{BPTC}^{3-}$  ligands sever as the 5-connected linkers (Fig. 1d). To the best of our knowledge, the structure of 1 represents a new topology type.

Compound 2 crystallizes in monoclinic space group  $C2/m$  and the asymmetric unit contains one Pb(II), one  $\text{ADC}^{2-}$  ligand and one water coordination molecule. As shown in Fig. 2a, each Pb(II) center is an irregular hepta-coordinated by seven O atoms from four carboxyl groups and one coordinate water molecule, resulting in a distorted hemidirected pentagonal-bipyramidal geometry. This Pb–O bond lengths vary greatly from 2.496(6) to 2.765(13), which are similar to those observed in the reported Pb-based compounds [17]. The crystallographic independent  $\text{H}_2\text{ADC}$  ligands in 2 is completely deprotonated and bound to two  $\text{Pb}^{\text{II}}$  atoms with a  $\mu^4-\eta^2:\eta^2:\eta^1:\eta^1$ -bridging coordination (Scheme 1b). Just owing to such connectivity, these  $\text{Pb}^{\text{II}}$  atoms are bridged by two carboxylate oxygen atoms, forming an infinite 1D rod-shaped Pb–O–Pb chain (Fig. 2b). Furthermore, the carboxylate groups of two  $\text{ADC}^{2-}$  groups are linked by two  $\text{Pb}^{\text{II}}$  atoms to generate a  $[\text{Pb}_2(\text{ADC})_2]$  metalocyclic motif with a Pb...Pb distance of 9.256(2) Å. Interestingly, the Pb–O–Pb chain as a bridging linker connected the  $[\text{Pb}_2(\text{ADC})_2]$  metalocyclic motif along the *b* axis to give rise to a 1D metal-organic nanotube (MONT) (Fig. 2c). According to the report, the terminal ligand as a bridging linker to construct 1D MONT is common in MOFs. However, in 2, the Pb–O–Pb chain as the linker to build the 1D nanotube framework [18,19]. Moreover, these 1D nanotubes are cross-link by each other to give birth to a 2D framework (Fig. 2d).

The differences of polycarboxylate anions lead to the distinction of the resultant structures. In this work, the  $\text{H}_3\text{BPTC}$  that has a rotatable coordination vertex and an asymmetric geometry with three carboxylate groups may be a good candidate for constructing versatile coordination networks with novel topology. On the other hand, the  $\text{H}_2\text{ADC}$  is a V-shaped ligand, and the angle between the coordination sites ca 110°, which can enhance the possibility of formation of a nanotubular



**Scheme 1.** Diverse coordination modes of  $\text{H}_3\text{BPTC}$  in 1 (a) and  $\text{H}_2\text{ADC}$  in 2 (b).

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