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Short communication

Syntheses, structures, surface photovoltage and luminescent properties of a novel lead(II) coordination polymer containing anthracene chromophore

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ABSTRACT

A novel 1D lead(II) coordination polymer containing anthracene chromophore through the employment of hydrothermal techniques by using 9-anthracenecarboxylic acid and PbI_2, $[Pb(9\text{-aca})_2(H_2O)_2]$ (**1**) (9-acaH = 9-anthracenecarboxylic acid) has been synthesized and structurally characterized by X-ray single-crystal diffraction as well as by powder X-ray diffraction and elemental analysis. In compound **1**, each PbO_8 polyhedron is linked to each other by oxygen atoms from 9-acaH ligand to form a 1D molecular nanowire with a diameter of 1.22 nm. Surface photovoltage spectroscopy (SPS) and field-induced surface photovoltage (FISPS) of compound **1** indicate that it possesses positive SPV response in the range of 300–800 nm and shows *p*-type semiconductor characteristic. Luminescent properties of compound **1** reveal that the compound exhibit strong luminescence, ascribed to the charge transfer of anthracene chromophore and the semiconductor 1D Pb_2O_2 chain.

Inorganic–organic hybrid materials have been intensively investigated not only due to their unique long-range structure ordering crystalline features, but also owing to their superb light-harvesting and unique electrical properties [1–5]. Inorganic lead (II) ion possesses a large radius, a variable stereochemical activity and a flexible coordination environment, which can provide unique opportunities for the construction of novel inorganic–organic hybrid materials. For example, organolead halid perovskites ($APbX_3$) have recently become one of the most promising light harvesters for mesoscopic solar cells due to the high processability, large optical absorption cross section and excellent thermal stability [6–9]. In the metal-halide-based inorganic–organic hybrid materials, the inorganic component offers rich structural possibilities including discrete cluster, one-dimensional chain, two-dimensional layer, and three-dimensional framework, which is the main structure factor dominating the fascinating physical properties, such as photochromic, thermochromic, luminescence, semiconductivity, nonlinear optical activity, ferroelectricity and so on [10–15].

Recently, multi-functional metal-organic coordination polymers as an inorganic–organic hybrid material, possessing both luminescent and semiconductive properties have attracted considerable attention because of their potential applications in solid-state lighting (SSL) devices [16–18]. The semiconductive properties of materials can be studied by use of the surface photovoltage spectroscopy (SPS), which is a useful tool for surveying the charge change of the solid surface, and it can be used to investigate the photophysics of the excited states and the surface charge behavior of the sample [19–22]. Generally, the multi-functional material is composed of inorganic metal semiconductor frameworks surrounded by organic fluorophores exhibiting excellent photophysical properties. Organic chromophores, such as naphthalene, anthracene or pyrene, show wonderful fluorescence properties [23–25]. Aromatic anthracene and its derivatives are among the most widely studied luminescent materials due to their planar moiety, which is potentially beneficial for a desired long-range face-to-face arrangement *via* π–π interactions in the consequent crystals [26]. Using these chromphores, particularly with anthracene and its derivatives, very few metal — organic coordination polymers have been reported to date [17,27–29]. It is believed that the crystal structures and the optical properties of the resultant organic fluorophores will play an important role in the development of semiconductive luminescent material. In this paper, we synthesized a novel lead(II) coordination polymer using a carboxylate ligand derived from anthracene (Scheme 1) [30]. Furthermore the surface photovoltage, field-induced surface photovoltage and luminescent properties of compound **1** have also been studied.

Single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the monoclinic space group $P2_1/n$ [31]. There are one crystallographically Pb^{2+} ions, two 9-aca anions and two coordinated water

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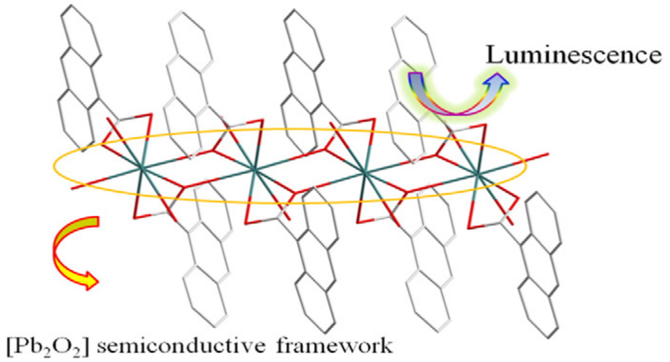

Scheme 1. View of the luminescent and semiconductive 1D $[Pb_2O_2]_n$ chain in the crystals.

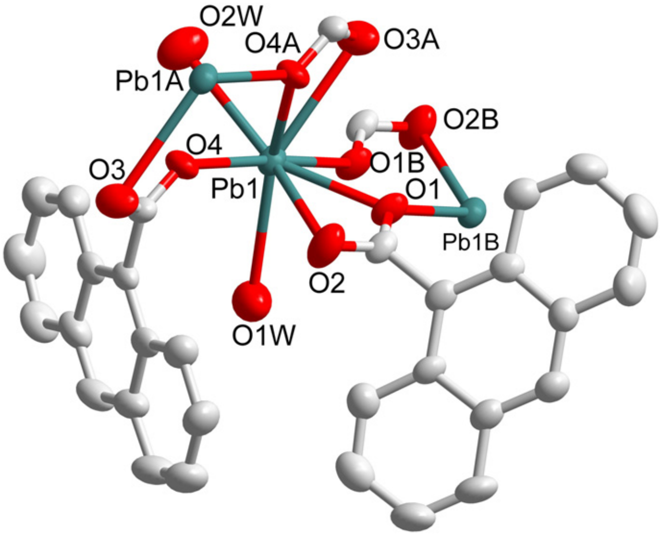

Fig. 1. Asymmetric unit of compound **1** showing the partial atom labeling. All H atoms are omitted for clarity. Selected bond lengths (Å): Pb(1)–O(1), 2.450(3); Pb(1)–O(2), 2.836(3); Pb(1)–O(3 A), 2.838(10); Pb(1)–O(4), 2.624(3); Pb(1)–O(1W), 2.867(11); Pb(1)–O(2W), 2.818(11). Symmetry code: A: –x, −y, −z, B: –x, 1–y, −z.

molecules in the asymmetric unit (Fig. 1). The 9-aca anion acts as a bidentate ligand and exhibits only one coordination mode. The lead ion is eight-coordinated (PbO_8), six oxygens are from four different 9-aca anions and the remaining two oxygens are from the coordinated water molecules. Four of these oxygens (two O1 and two O4) have μ_2 connections, linking two different Pb(1) atoms to form two planar four-membered rings Pb1–O1–Pb1B–O1B and Pb1–O4–Pb1A-O4A. The two four-membered rings link each other to form a 1D Pb_2O_2 chain through a corner-sharing PbO_8 polyhedron along the *b*-axis (Fig. 2), where the angle between the two neighboring planes is 89.41°. The values of the Pb—O bond lengths and O—Pb—O angles are in the range of 2.450(3)–2.867(11) Å and 64.93(12)–174.81(10)°, respectively.

The overall structure of compound **1** can be described as a 1D molecular nanowire with a diameter of 1.22 nm. Interestingly, as shown in Fig. 3, the anthracene-based aromatic ligands between neighboring 1D molecular nanowires interact with each other *via* pi–pi interactions in a zigzag fashion along the crystallographic *b*-axis. Such a structural connection may play an important role in enhancing the long-range charge transport of the 1D space, and improving the semiconductor properties of the coordination polymer.

Powder X-ray diffraction (XRD) has been used to check the phase purity of the bulky samples in the solid state. The powder XRD patterns of the as–synthesized compound **1** with that simulated on the basis of the single–crystal structure are presented in Fig. S1. The diffraction peaks on the patterns correspond well in position, confirming that the product is a pure phase. The differences in reflection intensity are probably due to preferred orientation in the powder samples.

The surface photovoltage technique based on lock-in amplifier, is a well-established contactless and non-destructive technique for semiconductor characterization which depends on analyzing the illumination-induced changes in the surface voltage and can be used to investigate the photophysics of the excited states and the surface charge behavior of the sample [32–34]. It is well documented that the separation of illumination-induced excess charge carriers will lead to a rise in photo-voltage [35]. Therefore, it is noted that the formation of an SPV signal is determined by the transport of excess carriers in a semiconducting material [36]. Compound **1** appears as two positive SPV responses in the range 300–800 nm, which indicates that it possesses *p*-type semiconductor characteristics (Fig. 4) [37]. The SPV response at $\lambda_{max} = 438$ nm is assigned to the $\pi \rightarrow \pi^*$ transition of the ligand and the response at $\lambda_{max} = 465$ nm is attributed to the LMCT (from ligand-to-metal charge transfer) transition, which reveals that a high separation efficiency of photoinduced charge carriers for the compound **1** [38].

Field–induced surface photovoltage spectroscopy (FISPS) can be measured by applying an external electric field to the sample with a transparent electrode. For a *p*-type semiconductor, when a positive electric field is applied on the semiconductor surface, the SPV response increases since the external field is consistent with the built–in field. On the contrary, when a negative electric field is applied, the SPV response is weakened. In contrast to *p*-type semiconductors, the SPV response intensity of *n*–type semiconductors increases as a negative field is applied and reduces as a positive electric field is applied. Fig. 5 shows the FISPS of compound **1** in the range of 300–800 nm when the external electric fields are −0.2, 0, and +0.2 V, respectively. The SPV response intensities of compound **1** enhance when the positive fields increase, while it was weakened when the negative fields increase. The result shows that the positive electric field being beneficial to the separation of photoexcited electron–hole pairs, which results in an increase of response

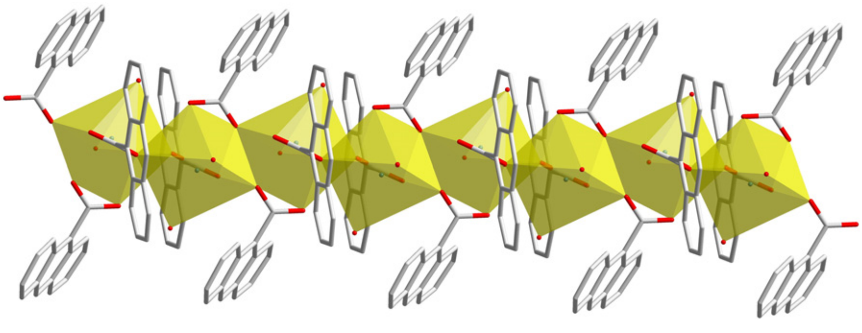

Fig. 2. A polyhedral representation of the 1D molecular nanowires for compound **1** along the *b*-axis.