

Short communication

## Two isonicotinate-bridging lanthanide substituted phosphotungstate hybrids

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## ABSTRACT

Two organic–inorganic hybrid isonicotinate-bridging lanthanide substituted phosphotungstates [H<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub>]<sub>8</sub>[Ln(H<sub>2</sub>O)(INA)(α-HPW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>·14H<sub>2</sub>O (Ln = Ho<sup>III</sup> for **1**, Er<sup>III</sup> for **2**) (HINA = isonicotinic acid) have been obtained by reaction of the Na<sub>9</sub>[α-PW<sub>9</sub>O<sub>34</sub>]·16H<sub>2</sub>O precursor, Ln(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, C<sub>2</sub>H<sub>7</sub>N·HCl and HINA in aqueous solution and structurally characterized by elemental analyses, IR spectra, single-crystal X-ray diffraction and thermogravimetric analysis. Isostructural **1** and **2** consist of one inorganic–organic hybrid dimeric {[Ln(H<sub>2</sub>O)(INA)(α-HPW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>8-</sup> core constituted by two symmetrically mono-Ln substituted Keggin subunits [Ln(H<sub>2</sub>O)(INA)(α-HPW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>4-</sup> bridged by two INA<sup>-</sup> ligands in the (η<sup>2</sup>, μ-1,1) fashion. Intriguingly, adjacent hybrid dimeric {[Ln(H<sub>2</sub>O)(INA)(α-HPW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>8-</sup> cores can be extended into a 2-D supramolecular layer via hydrogen bonding interactions. To our knowledge, **1** and **2** represent the first isonicotinate-bridging dimeric mono-lanthanide substituted phosphotungstates. Furthermore, the solid-state fluorescence properties and lifetime decay behaviors of **1** and **2** in visible and near-infrared regions have also been investigated in detail.

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The design and preparation of organic–inorganic hybrid materials is fleetly impelled by the significant interest in their multitudinous structures, various compositions, manifold properties and their extensive applications in a wide range of domains such as, catalysis, ion exchange, gas sorption, electrical conductivity, magnetochemistry and so on [1–2]. In this context, as an excellent class of metal–oxygen clusters, polyoxometalates (POMs) may be versatile inorganic building blocks for the fabrication of multifunctional hybrid materials not only on account of their high negative charges and nucleophilic oxygen-enriched surfaces but also by means of potential applications in catalysis, electrochemistry, photochromism, magnetism, medicine and material science [3–7]. In the POM field, an emerging topic has drawn considerable attention in the design and manufacture of novel carboxylate-based Ln substituted POM materials (LSPOMMs) with unique optical, magnetic and catalytic properties since Dolbecq et al. in 2003 reported two attractive organic–inorganic hybrid LSPOMMs by reaction of the prefabricated ε-Keggin precursor [ε-PMo<sub>12</sub>O<sub>36</sub>(OH)<sub>4</sub>{La(H<sub>2</sub>O)<sub>4</sub>]<sup>5+</sup> and carboxylate ligands [8]. To date, some carboxylate-based LSPOMMs have been synthesized. For instance, in 2003, Kortz reported the first

example of (η<sup>2</sup>, μ-1,1)-acetate-connective mono-substituted Dawson-type phosphotungstate [{La(α<sub>2</sub>-P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>(μ-CH<sub>3</sub>COO)<sub>2</sub>]<sup>16-</sup> [9]. In 2004, Mialane and co-workers synthesized two dimeric Keggin-type silicotungstates {[Ln(α-SiW<sub>11</sub>O<sub>39</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>(μ-CH<sub>3</sub>COO)<sub>2</sub>]<sup>12-</sup> (Ln = Gd<sup>III</sup>, Yb<sup>III</sup>) by utilizing [Yb(SiW<sub>11</sub>O<sub>39</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sup>5-</sup> in potassium acetate buffer, in which two acetate ligands link two Ln centers in the (η<sup>2</sup>, μ-1,1) fashion [10]. Subsequently, they expanded their research work and obtained a tetrameric Yb(III)-substituted Dawson-type polyoxotungstate linked by oxalate ligands {[Yb(P<sub>2</sub>W<sub>17</sub>O<sub>61</sub>)]<sub>4</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>34-</sup> [11]. In 2012, Niu's group also addressed a class of oxalate-bridging rare-earth-substituted Keggin-type phosphotungstates {[Ln(α-PW<sub>11</sub>O<sub>39</sub>)RE(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)]<sup>10-</sup> (RE = Y<sup>III</sup>, Dy<sup>III</sup>, Ho<sup>III</sup>, Er<sup>III</sup>) [12]. Afterwards, they found a series of double-tartaric-bridging mono-lanthanide substituted phosphotungstate hybrids {[Ln(C<sub>4</sub>H<sub>2</sub>O<sub>6</sub>)(α-PW<sub>11</sub>O<sub>39</sub>)<sub>2</sub>]<sup>16-</sup> (Ln = Dy<sup>III</sup>, Er<sup>III</sup>, Yb<sup>III</sup>) [13]. Very recently, our group also prepared two types of unique rectangle versus square oxalate-connective tetra-Ln-containing lacunary Lindqvist isopolytungstates {[Ln<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)(H<sub>2</sub>O)<sub>4</sub>(OH)W<sub>4</sub>O<sub>16</sub>]<sub>2</sub>]<sup>10-</sup> and {[Ln(C<sub>2</sub>O<sub>4</sub>)W<sub>5</sub>O<sub>18</sub>]<sub>4</sub>]<sup>20-</sup> (Ln = Eu<sup>III</sup>, Ho<sup>III</sup>, Er<sup>III</sup>, Tb<sup>III</sup>) [14].

Obviously, the above-mentioned reports on carboxylate-based LSPOMMs are mainly concentrated on the aliphatic acid ligands (such as acetate, oxalate, etc.), however, little investigation has been devoted to LSPOMMs with pyridine carboxylic ligands [15–16]. As we all know, pyridine carboxylic acid ligands have multifunctional coordination sites that can also favor to construct novel polymeric structures. To the best of our knowledge, there is no relevant report on pyridine carboxylic

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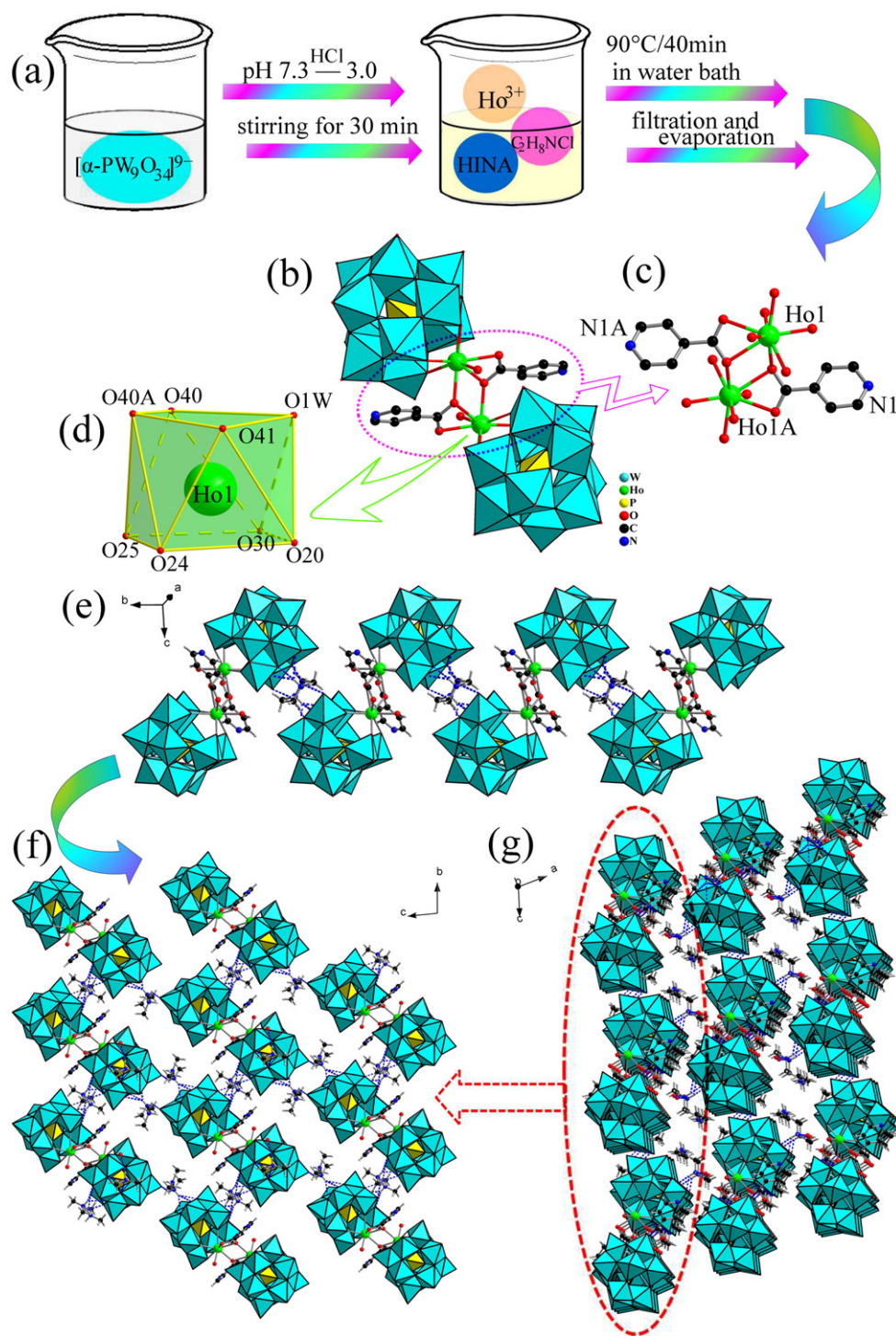
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acid-based Ln-substituted lacunary Keggin-type phosphotungstates, which provides us an excellent opportunity. Based on this background, we selected the precursor  $[\alpha\text{-PW}_9\text{O}_{34}]^{9-}$  to react with Ln ions and HINA in the presence of dimethylamine hydrochloride to prepare pyridine carboxylic acid-based Ln-substituted Keggin-type phosphotungstate hybrids. Fortunately, two organic-inorganic hybrid LSPOMMs with pyridine carboxylic ligands  $[\text{H}_2\text{N}(\text{CH}_2)_2]_8$   $[\text{Ln}(\text{H}_2\text{O})(\text{INA})(\alpha\text{-HPW}_{11}\text{O}_{39})_2] \cdot 14\text{H}_2\text{O}$  (Ln =  $\text{Ho}^{\text{III}}$  for **1**,  $\text{Er}^{\text{III}}$  for **2**) were obtained and structurally characterized, which represent the

first isonicotinate-bridging dimeric POMs constructed from two mono-Ln substituted lacunary Keggin-type phosphotungstate units. Furthermore, the solid-state fluorescence properties and lifetime decay behaviors of **1** and **2** in visible and near-infrared regions have also been intensively investigated.

**1** was synthesized as follows:  $\text{Na}_9[\alpha\text{-PW}_9\text{O}_{34}] \cdot 16\text{H}_2\text{O}$  (1.008 g, 0.370 mmol) was dissolved in 15 mL distilled water under stirring and the pH value of the solution was carefully adjusted from 7.3 to 3.0 by a dilute HCl solution ( $2 \text{ mol} \cdot \text{L}^{-1}$ ). The solution was stirred for 30 min,



**Fig. 1.** (a) The schematic synthetic process of **1**. (b) The view of hybrid dimeric  $\{[\text{Ho}(\text{H}_2\text{O})(\text{INA})(\alpha\text{-HPW}_{11}\text{O}_{39})_2]_2\}^{8-}$  core. (c) The view of the dimeric Ho-INA  $\{[\text{Ho}(\text{H}_2\text{O})(\text{INA})]_2\}^{4+}$  cation. (d) The coordination polyhedron of the  $\text{Ho}^{3+}$  cation. (e) The view of the 1-D zigzag chain. (f) The view of the 2-D supramolecular layer. (g) The packing of **1** along the *b* axis. Symmetry code: A 2-x, 1-y, -z.

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