

# Heavy main-group iodometallates hybridized by alkali metal via 1,10-Phenanthroline-5,6-dione

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**Abstract.** Alkali metals were introduced into heavy main-group iodometallates to get two new IA/IVA heterometallic frameworks  $[\text{PbI}_3\text{K}(\text{pdon})(\text{H}_2\text{O})_2]_n$  (**1**) and  $\{[\text{Pb}_3\text{I}_9\text{K}_2(\text{pdon})_2(\text{H}_3\text{O})]\cdot\text{H}_2\text{O}\}_n$  (**2**) (pdon=1,10-phenanthroline-5,6-dione), which were obtained as single phases by hydrothermal method at different pH values. Compounds **1** and **2** are three-dimensional heterometallic frameworks constructed from the linkage of pdon ligand between iodometallate chains and potassium oxides/iodide clusters. Specially, these two heterometallic frameworks exhibit broadened absorption bands at 700 and 750 nm compared with those of bulk  $\text{PbI}_2$  and pdon ligand. The band gap of **2** is wider than that of **1**, which is due to the absence of  $\pi \cdots \pi$  interaction in **2**. Their thermal stabilities are also discussed.

**Keywords.** Inorganic/organic hybrid; main group chemistry; iodometallate hybrid; luminescence

## 1. Introduction

Heavy main group halometallate materials have been receiving continuous attention due to their versatile structural diversities and potential applications in many prospective fields such as nonlinear optics,<sup>1,2</sup> luminescence, thermochromisms,<sup>3–5</sup> semiconductors<sup>6</sup> and the newly emerged visible-light sensitizers for photovoltaic cells.<sup>7–10</sup> As a heavy *p*-block metal in Group 14, lead(II)-related iodometallates have attracted special attention because of their interesting optical and electronic properties, which stem from the large radius, flexible coordination environment, and variable stereochemical activity of lead center.<sup>3</sup> The properties of iodoplumbate/organic hybrids originate not only from the inorganic metal halides, but also from the new structural types and the synergistic interactions between metal halides and organic ligands.<sup>11–14</sup> So as to generate novel structures and properties, great effort has been paid to the modification of hybrids. Recently, the strategy of introducing heterometallics was adopted to tune the properties of these materials.<sup>11</sup> Till now, to our knowledge, the following types of second metals were introduced into iodoplumbates: *a.* alkali (Na) or alkali earth (Mg) metal;<sup>15,16</sup> *b.* transition metal complexes with chelating ligands, that is,  $[\text{M}(\text{L})_x]^{n+}$  ( $\text{M} =$

Fe, Co, Ni, Cu, Zn, Ru; L= ethylenediamine, phenanthroline, bipyridine, terpyridine;  $x = 2, 3; n = 2, 3$ ),<sup>17–26</sup> *c.* rare earth metal organic complexes,  $[\text{Ln}(\text{L})_x]^{3+}$  ( $\text{Ln} = \text{Y, Tb, Nd}$ ; L=DMF and/or DMSO;  $x = 7, 8$ ).<sup>27–30</sup> In these systems, most of the second metal exists as counter cations, but the literature on compounds whose second metal is covalently linked to iodoplumbates is still in its infancy.<sup>28,30</sup> In addition, the incorporation of alkali metals is very rare and seems significant, because alkali metal-based materials are important for their promising applications in ion-exchange, nonlinear optics, molecular recognition, etc.<sup>31</sup> The construction of these heterometallic frameworks relies on the choice of proper linkage ligands. 1,10-phenanthroline-5,6-dione (pdon) is a good candidate for the construction of heterometallics-containing neutral frameworks because it incorporates both the orthoquinone and  $\alpha$ -diimine functionalities showing distinct affinities for metal ions.<sup>32,33</sup> In the most of the pdon-containing complexes, the O atom pairs of orthoquinone remain uncoordinated because they cannot compete against the N atoms of the  $\alpha$ -diimine for the metal centers. Only limited complexes with coordinated O atoms using such ligands are reported.<sup>34</sup> In view of the affinity of hard alkali metal ions for O-containing ligands, by using 1,10-phenanthroline-5,6-dione (pdon) ligand, potassium was introduced into iodoplumbate in this work to get two new IA/IVA heterometallic frameworks,  $[\text{PbI}_3\text{K}(\text{pdon})(\text{H}_2\text{O})_2]_n$  (**1**) and  $\{[\text{Pb}_3\text{I}_9\text{K}_2(\text{pdon})_2$

\*For correspondence

$(\text{H}_3\text{O})\cdot\text{H}_2\text{O}]_n$  (**2**). Their band gaps, fluorescence and thermal stabilities are also reported and discussed.

## 2. Experimental

### 2.1 Reagents and general techniques

All chemicals except pdon were reagent grade and commercially available, which were used without further purification. Elemental analyses were carried out with a Vario EL III element analyzer. IR spectra were recorded on a Nicolet Co. Magna-IR 750 spectrometer with KBr pellet in the  $4000\sim 400\text{ cm}^{-1}$  region. UV-Vis spectra were measured at 293 K on a Perkin-Elmer lambda 900 UV/Vis spectrophotometer equipped with an integrating sphere and  $\text{BaSO}_4$  plates as reference. Luminescence spectra of the crystalline samples were carried out on an Edinburgh FL-FS 920 TCSPC spectrometer. A Perkin-Elmer TGA7 thermogravimetric analyzer was used to obtain thermogravimetry (TG) curves in  $\text{N}_2$  with a flow rate of 20 mL/min and a ramp rate of  $10^\circ\text{C}/\text{min}$  in the temperature range of  $30\sim 800^\circ\text{C}$ .

### 2.2 Synthesis

**2.2a Synthesis of pdon:** 1,10-phenanthroline-5,6-dione (pdon) was synthesized by the oxidation from 1,10-phenanthroline according to the literature method<sup>35</sup> as scheme 1, and the processes of preparation and purification were easily followed from the literature.

**2.2b Synthesis of  $[\text{PbI}_3\text{K}(\text{pdon})(\text{H}_2\text{O})_2]_n$  (**1**):** pdon (0.1050 g, 0.5 mmol) was dissolved in 5 mL DMAC (N,N'-dimethylacetamide) and yellow solution was obtained. In another conical flask,  $\text{Pb}(\text{NO}_3)_2$  (0.3310 g, 1 mmol) and KI (0.4850 g, 3 mmol) were dissolved in 7 mL DMAC and the yellow solution was stirred for 10 min. Afterwards, the former solution was added into the later slowly and the resultant solution was kept stirring for 30 min. The pH of the resultant red solution was adjusted to 7.0 with 10% NaOH/DMAC. Finally, the solution was filtered and the red filtrate liquor was kept at room temperature for evaporation. Black crystals obtained after 3 weeks were washed with absolute

ethanol and ether. Yield: 12.6% (0.11 g, based on Pb).  $\text{C}_{12}\text{H}_{10}\text{I}_3\text{KN}_2\text{O}_4\text{Pb}$  (873.23): calcd. C 16.50, H 1.23, N 3.20%; found C 16.54, H 1.12, N 3.22%. IR (KBr,  $\text{cm}^{-1}$ ): 3436(s), 3066(w), 1693(w), 1574(m), 1427(m), 1300(s), 1019(m), 729(s) 692(s), 729(s), 541(m).

**2.2c Synthesis of  $\{[\text{Pb}_3\text{I}_9\text{K}_2(\text{pdon})_2(\text{H}_3\text{O})]\cdot\text{H}_2\text{O}\}_n$  (**2**):** **2** was synthesized under the same condition as that of **1** except that the final pH was adjusted to 4.0 with 10%  $\text{HNO}_3$ /DMAC. The black crystals (0.2450 g) in 32.1% yield (based on Pb) were obtained after 5 days and washed by ether. Anal. Calc for  $\text{C}_{24}\text{H}_{16}\text{I}_9\text{K}_2\text{N}_4\text{O}_6\text{Pb}_3$  (2298.35): C 12.54, H 0.70 N 2.43%; found C 12.62, H 0.82, N 2.32%. IR (KBr,  $\text{cm}^{-1}$ ): 3469(s), 3052(w), 1691(w), 1570(m), 1421(m), 1300(s), 1116(s), 930(w), 728(w), 633(w), 541(m).

**2.2d Synthesis summary:** The two compounds were obtained by the reaction of  $\text{Pb}(\text{NO}_3)_2$ , KI and pdon ligand in DMAC under the different pH conditions. In neutral environment, the product is compound **1**, but under acidic condition, compound **2** is preferred. The products were stable in water and air. **1** and **2** were characterized by single-crystal X-ray structural analysis, IR and elemental analysis (for details on crystallographic data, see Supplementary Information). The infrared absorption spectra showed a small shift to higher energy of C=O stretching of the pdon in compounds **1** and **2** compared with that of the free ligand ( $1689\text{ cm}^{-1}$ ).<sup>36</sup>

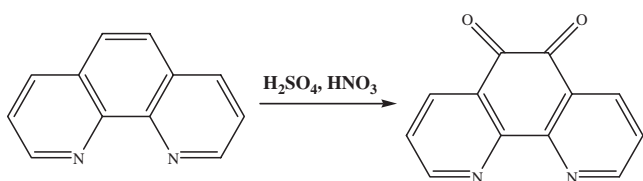
### 2.3 Single Crystal X-ray Diffraction Analyses

The intensity data of compounds **1** and **2** were collected on a Rigaku Weissenberg IP diffractometer using a graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069\text{ \AA}$ ) at 293(2) K. The corrections of  $Lp$  factors and multi-scan absorption corrections were applied. The structures were solved by direct method and refined on  $F^2$  by full-matrix least squares techniques using the SHELXTL-97 program.<sup>37,38</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of C-H were generated geometrically. Selected bond lengths and angles are listed in table 1.

## 3. Results and Discussion

### 3.1 Structural description

Compound **1** crystallizes in the monoclinic system with space group  $P_{21/n}$ , which exhibits a neutral 3-D framework based on the linkage of pdon and iodine ligands. In this IA/IVA heterometallic framework, the



**Scheme 1.** The synthesis of pdon.

**Table 1.** Crystal data and structure refinement for **1** and **2**

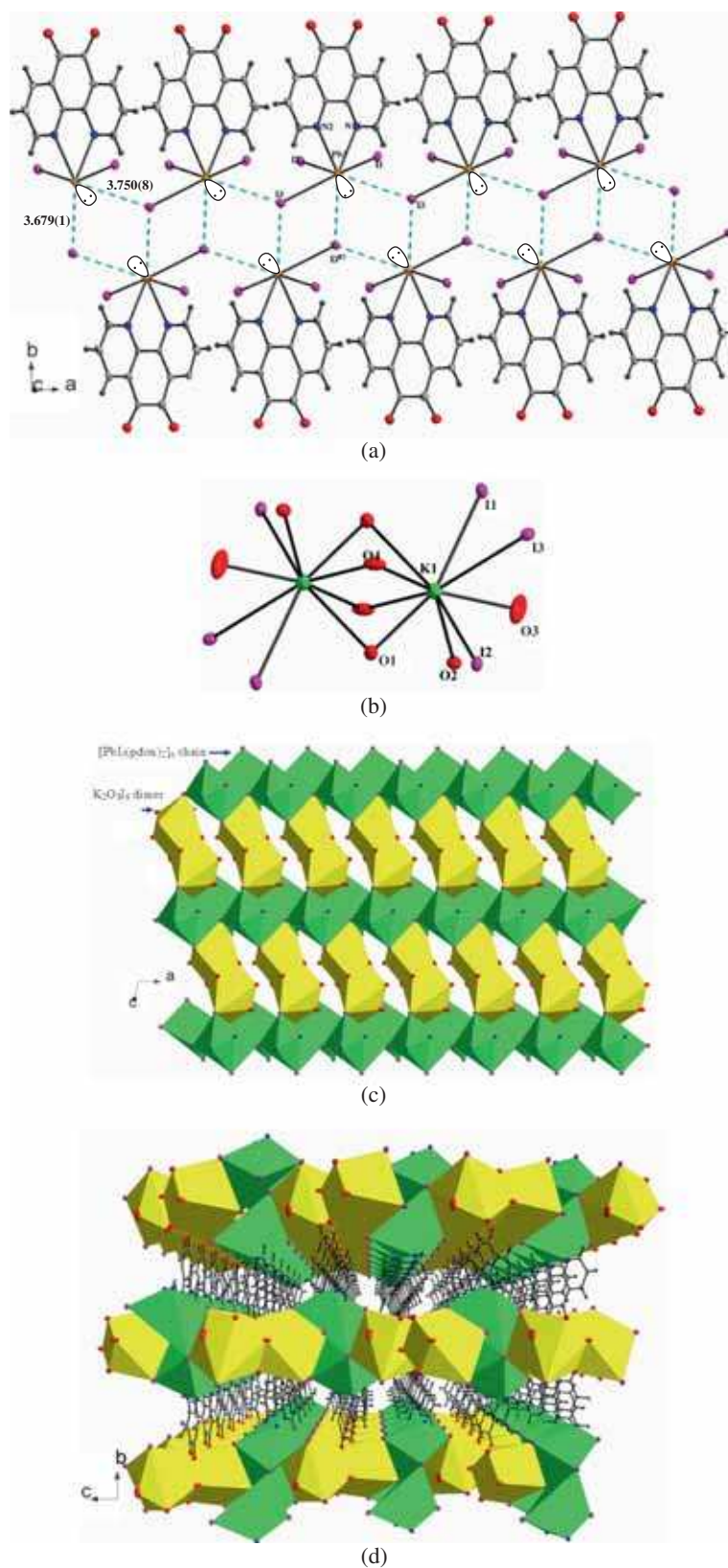
Compound	1	2
Empirical formula	C <sub>12</sub> H <sub>10</sub> I <sub>3</sub> KN <sub>2</sub> O <sub>4</sub> Pb	C <sub>24</sub> H <sub>16</sub> I <sub>9</sub> K <sub>2</sub> N <sub>4</sub> O <sub>6</sub> Pb <sub>3</sub>
Formula mass	873.23	2298.35
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P21/n</i>	<i>Ibam</i>
<i>a</i> [Å]	6.4984(13)	13.160(3)
<i>b</i> [Å]	22.731(5)	27.378(6)
<i>c</i> [Å]	12.914(3)	13.015(3)
$\beta$ (°)	102.48(3)	90.00
<i>V</i> [Å <sup>3</sup> ]	1862.6(6)	4689.3(16)
<i>Z</i>	4	4
<i>D<sub>c</sub></i> [g/cm <sup>3</sup> ]	3.100	3.250
$\mu$ [mm <sup>-1</sup> ]	14.271	16.884
<i>F</i> (000)	1536	3972
Reflections, total	14982	21844
Reflections, independent	4251 ( <i>R</i> <sub>int</sub> = 0.0679)	2805 ( <i>R</i> <sub>int</sub> = 0.0787)
Reflections, observed	4124	2175
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.152	1.061
No. of parameters refined	209	127
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )] <sup>a</sup>	0.0521	0.0503
<i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.1379	0.0883
Residual extremes [e/Å <sup>3</sup> ]	3.554, -2.979	1.362, -1.124

$$^a R_1 = \|F_0\| - \|F_c\| / \|F_0\|, wR_2 = [w(F_0^2 F_c^2)^2 / [w(F_0^2)^2]^{1/2}]$$

crystallographically independent Pb atom is situated in distorted tetragonal pyramid, coordinated with N atoms of the pdon ligands (figure 1a). PbI<sub>3</sub>N<sub>2</sub> tetragonal pyramid is highly distorted with I(1), I(2), I(3) and N(1) located at the bottom of the pyramid and N(2) at the apex, whose distortion can be deduced from its bond distances and angles (table S1, Supplementary Information). The Pb–N distances (2.599(7) and 2.585(7) Å) are in good agreement with other Pb–N (rooting from pyridine) distances.<sup>39</sup> And the Pb–I bond lengths range from 3.1793(11) to 3.2748(11) Å, which are similar to those lengths found in the related Pb(II) complexes.<sup>40,41</sup> The stereochemical activity of the lead-containing complexes could be attributed to their 6s<sup>2</sup> non-bonding lone pair of electrons. In compound **1**, the stereochemical activity of Pb(1) is maximized because the lone pair electron occupies the position of anion and can be regarded as ligand (figure 1a).<sup>42</sup> In addition, the lead atoms have weak axial connections to I(3) atoms (Pb(1)–I(3)<sup>#1</sup>: 3.679(1) Å, Pb(1)–I(3)<sup>#2</sup>: 3.750(8) Å, symmetry code: #1: 1-x, -y, -z, #2: 1+x, y, z), resulting in a 5+2 monocapped octahedral coordination sphere for the lead center (figure 1a). This distance of 3.750(8) Å is the longest Pb–I length observed so far, which is much longer than the other weak Pb–I bonds (3.58(4) Å).<sup>29,30</sup> Adjacent PbN<sub>2</sub>I<sub>5</sub> monocapped octahedra are combined into a 1-D [PbI<sub>3</sub>(pdon)<sub>2</sub>]<sub>n</sub> chain via edge-sharing (defined by

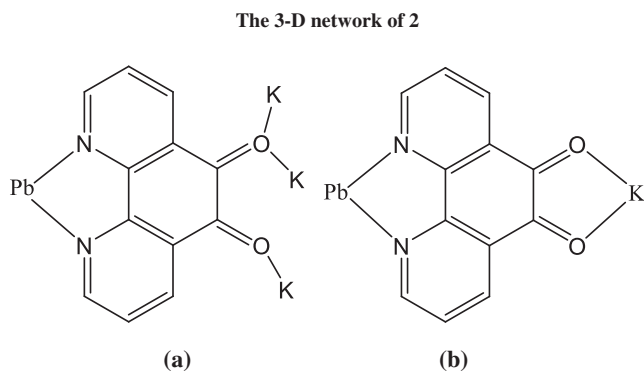
I(3)–I(3)<sup>#1:–x+1, –y, –z</sup>) mode along *a* axis (figure 1a). The potassium ion is in nine-coordinated, highly distorted tricapped trigonal prismatic geometry, where the donors stem from three carbonyl oxygen of pdon ligands, three iodine atoms and three coordinated water molecules. Here, the K–O (pdon) bond distances are in the range of 2.90(4)–3.09(2) Å, and the K–O (water) lengths range between 2.682(48)–2.822(8) Å. Specially, the K–I bonds seem weak with distances of 3.814(2) to 3.997(3) Å, which are much longer than those found in previous works (3.442–3.771 Å).<sup>43,44</sup> A K<sub>2</sub>O<sub>8</sub>I<sub>6</sub> dimer is generated by face-sharing of adjacent KO<sub>6</sub>I<sub>3</sub> tricapped trigonal prisms (figure 1b). And K<sub>2</sub>O<sub>8</sub>I<sub>6</sub> dimers connect with [PbI<sub>3</sub>(pdon)<sub>2</sub>]<sub>n</sub> chain via edge-sharing (defined by I(1)–I(3) and I(2)–I(3)) mode to give a 2-D layer along *ac* plane (figure 1c). And finally, adjacent 2-D layers are linked into a 3-D framework via the bridge mode of pdon ligand (figure 1d, scheme 2a). Besides, strong π ··· π stacking interaction among pdon ligands with centroidal distance of 3.480(5) Å contribute to the structural stabilization.

But compound **2** presents a 3-D framework based on more regular coordinated geometries of Pb and K centers. In compound **2**, two crystallographic independent Pb atoms can be found, both of which are in octahedral coordinated environments. Among them, Pb(1) coordinates to two N atoms from one pdon ligand and four I atoms, resulting in a highly distorted



**Figure 1.** (a) The structure of 1-D  $[\text{PbI}_3(\text{pdon})_2]_n$  chain showing the stereochemical activities of  $6s^2$ ; (b) The structure of  $\text{K}_2\text{O}_8\text{I}_6$  dimer; (c) 2-D layer constructed from  $\text{K}_2\text{O}_8\text{I}_6$  dimers and  $[\text{PbI}_3(\text{pdon})_2]_n$  chains; (d) The 3-D framework based on the pdon ligands.





**Scheme 2.** The linkage mode of pdon ligand in **1** (a) and **2** (b).

$\text{PbN}_2\text{I}_4$  octahedron (deduced from the I(2)-Pb(1)-I(1) angle of  $158.49(3)^\circ$  and non-planarity of equatorial plane). But the  $\text{Pb}(2)\text{I}_6$  octahedron is much normal with Pb-I(equator) length of  $3.1759(8)$  Å and Pb-I(axial) distance of  $3.2538(6)$  Å (table S2, Supplementary Information). Besides, one crystallographic independent K atom is in seven-coordinated monocapped octahedral environment with donors derived from two carbonyl oxygen atoms, one oxygen atom of water (the coordinated water is disordered and protonated, only one of them is discussed here) and four iodine atoms. The K-O and K-I distances are comparable to those in compound **1**. Adjacent  $\text{Pb}(2)\text{I}_6$  octahedra are connected into a 1-D  $(\text{PbI}_5)_n^{3n-}$  chain via vertex-sharing mode along *c* axis (figure 2a), which is commonly observed in polymeric iodoplumbate system.<sup>45</sup> In the *b* direction,  $\text{PbN}_2\text{I}_4$  octahedra connect to central  $(\text{PbI}_5)_n^{3n-}$  chain via edge-sharing mode (defined by I(2)-I(3)) (figure 2b). And in the *a* direction,  $\text{KO}_3\text{I}_4$  monocapped octahedron is linked with 1-D  $(\text{PbI}_5)_n^{3n-}$  chain by sharing I(3)-I(4) edge (figure 2b). Consequently, a  $[\text{Pb}_3\text{I}_9\text{K}_2(\text{pdon})_2(\text{H}_3\text{O})]_n^{n-}$  chain is given upon these connections. Three kinds of iodine atoms can be found in this chain: terminal I (I(1)),  $\mu_2$ -I(I(2)),  $\mu_3$ -I(I(3)) and  $\mu_4$ -I(I(4)). Based on the linkage nature pdon ligand (scheme 2b), one  $[\text{Pb}_3\text{I}_9\text{K}_2(\text{pdon})_2(\text{H}_3\text{O})]_n^{n-}$  chain links with adjacent four chains via pdon ligands to result in a 3-D network (figure 2c). The  $\pi \cdots \pi$  stacking interactions can not be found in this network.

### 3.2 Absorption spectra

The room temperature diffuse reflectance UV-Vis spectra of pdon ligand, bulk  $\text{PbI}_2$  and compounds **1** and **2** are presented in figure 3. By comparing the UV-Vis spectra of compounds **1** and **2** with those of pdon and bulk  $\text{PbI}_2$ , we can conclude that among the four peaks at 252, 347, 476 and 522 nm in **1**, the former two (252,

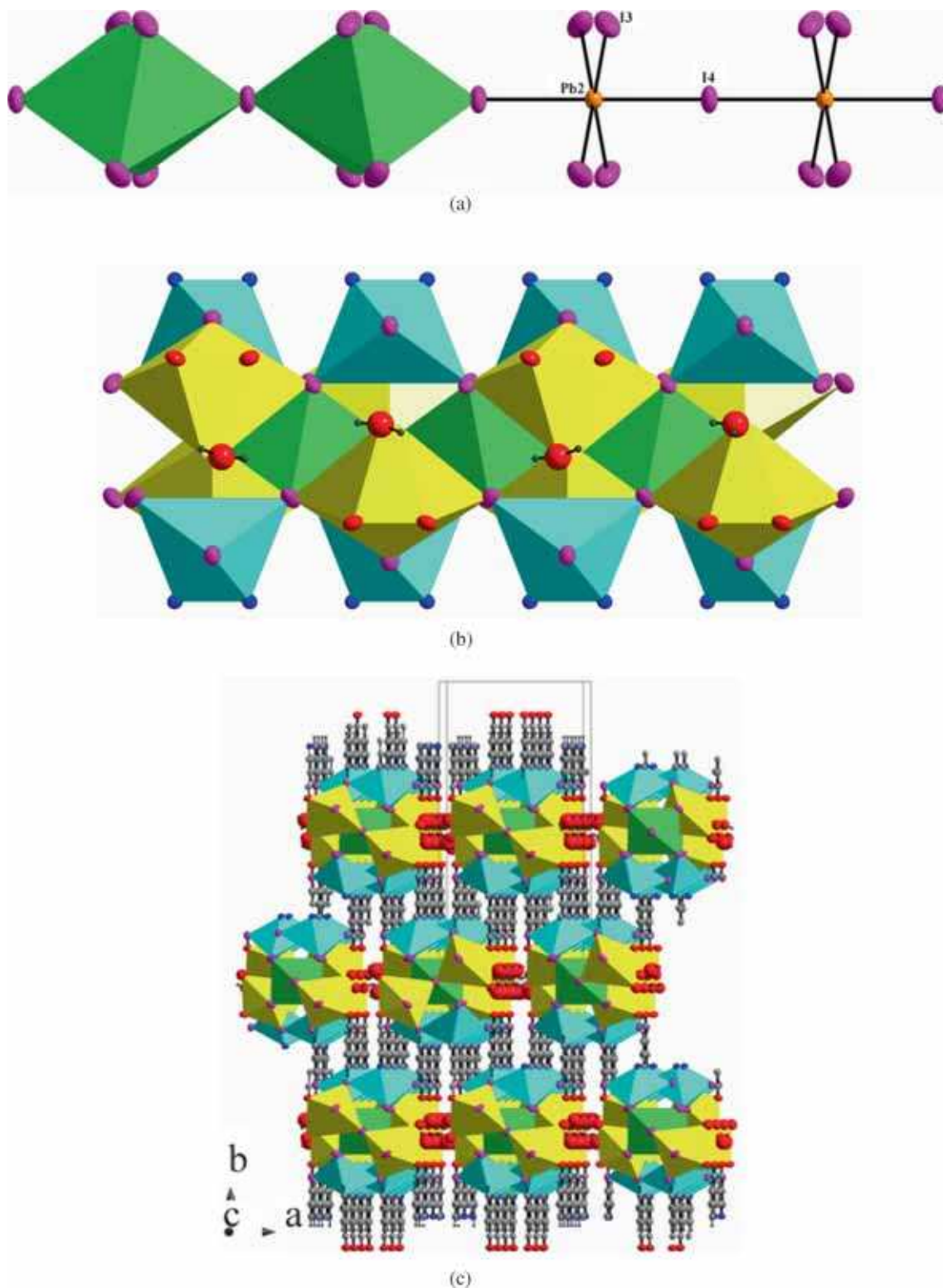
347 nm) can be attributed to the  $n\text{-}\pi^*$  transfer in pdon ligand, and the rest two (476, 522 nm) are the characteristics of the corner, edge-, or face-sharing  $\text{PbI}_6$  octahedra.<sup>36,46,47</sup> Similarly, for **2**, peaks at 248, 384 nm stem from the adsorption of pdon ligand, and the weak peak at 510 nm is associated with the inorganic moiety. It is interesting that these hybrids can inherit and reflect the properties of incorporated organic and inorganic moieties. In addition, judging from the figure 3, going from bulk  $\text{PbI}_2$  to compounds **1** and **2**, the absorption band extends from 550 nm to 700 nm (for **1**) and to 750 nm (for **2**), which might be led by the synergism interaction between heterometallics. The optical absorption spectra of compounds **1** and **2** calculated from the diffuse reflectance data by using the Kubelka-Munk function<sup>48,49</sup> are plotted in figure S1 (Supplementary Information). The absorption edges can be estimated as 1.75 and 2.04 eV, which suggest their potential semiconductor properties. The band gap of compound **2** is larger than that of **1**, which might be led by the absence of  $\pi \cdots \pi$  stacking interaction in **2**. Compared with that of bulk  $\text{PbI}_2$  (2.47–2.49 eV),<sup>50</sup> the band gaps of **1** and **2** are reduced clearly, due to the presence of conjugated systems.

### 3.3 Luminescence spectra

The luminescence properties of compounds **1** and **2** were studied in the solid state at room temperature, which are depicted in figure 4. Both compounds exhibit generally the same emissions in visible region in the range of 450–720 nm upon excitation at 300 nm. In detail, five emission peaks occurred at 475, 566, 615, 649 and 701 nm, among which the peak at 615 nm is the strongest. The emission band related to phenanthroline molecule has been found at about 440 nm,<sup>51</sup> so the emission at 475 nm can be attributed to the  $\pi\text{-}\pi^*$  intraligand transition of pdon ligand. And the rest four emissions can be assigned to the contribution of lead/potassium iodides.<sup>52</sup>

### 3.4 Thermal analysis

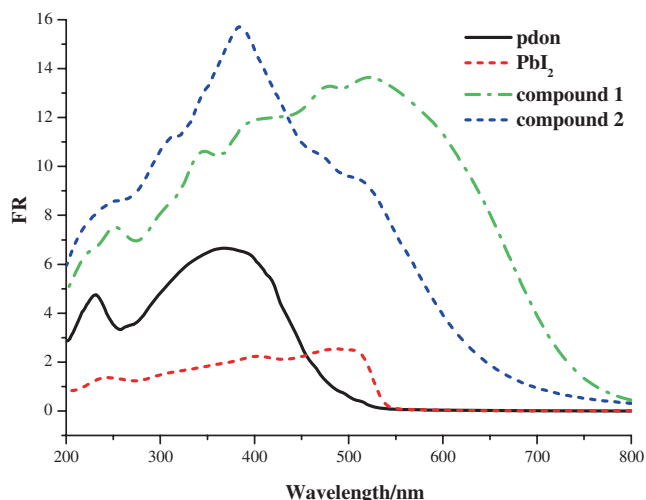
The thermogravimetric analyses (TGA) were performed in order to verify the thermal stability of complexes (figure S2). For compound **1**, three stages of weight loss were observed. The first occurred at 90–145°C (weight loss: 7.66%) which is due to the loss of coordinated water molecules in the lattice (theoretical value: 7.78%). In the second stage occurring among 240–350°C, K was oxidised into  $\text{K}_2\text{O}$ , whose O stems from the carbonyl of pdon ligand, so the weight loss



**Figure 2.** (a) Structure of central 1-D chain  $(\text{PbI}_5)_n^{3n-}$  via vertex-sharing mode; (b) The formation of  $[\text{Pb}_3\text{I}_9\text{K}_2(\text{pdon})_2(\text{H}_2\text{O})]_n^{n-}$  chain via the connection of central  $(\text{PbI}_5)_n^{3n-}$  chain with  $\text{PbN}_2\text{I}_4$  octahedra and  $\text{KO}_3\text{I}_4$  monocapped octahedron (green: central chain; cyan:  $\text{PbN}_2\text{I}_4$  octahedra; yellow:  $\text{KO}_3\text{I}_4$  polyhedra); (c) The 3-D network of **2**.

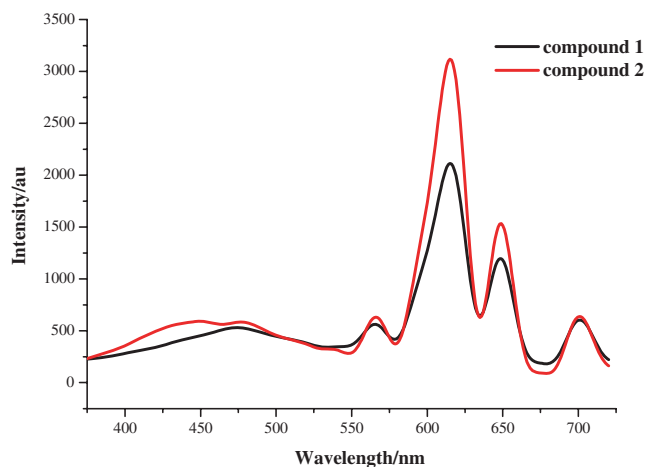
of 21.04% can be assigned to the loss of pdon fragment (two oxygen atoms were combined into  $\text{K}_2\text{O}$ , theoretical value: 20.40%). The third stage happened in

the temperature of 450–640°C (weight loss: 51.14%) corresponds to sublimed  $\text{I}_2$ . For compound **2**, similar weight loss processes can be observed. The first stage



**Figure 3.** Optical adsorption spectra of pdon,  $\text{PbI}_2$ , **1** and **2**.

takes place in the range 40–80°C with weight loss of 1.34% due to the loss of adsorbed water on crystal surfaces. Secondly, the 2.79% weight loss in the temperature range of 90–200°C was due to the dissociation of coordinated and isolated water molecules in the lattice (theoretical value: 3.00%). Afterwards, pdon fragment dissociated with weight loss of 13.87% from 280–520°C (theoretical value: 15.50%). Finally, the skeleton collapsed from 520–800°C accompanied by sublimed  $\text{I}_2$  with weight loss 51.21% (theoretical value: 49.69%). The residual weight of 19.9% (for **1**) and 30.79% (for **2**) can be assigned to  $\text{K}_2\text{O}$  and  $\text{PbO}$ . Clearly, the thermal stability of compound **2** is better than that of **1**. In summary, the presence of versatile weak Pb-I or K-I bonds lead to lower stability in compound **1**.



**Figure 4.** Room temperature solid-state luminescence spectrum of **1** ( $\lambda_{\text{ex}} = 300\text{nm}$ ).

## 4. Conclusions

In conclusion, alkali metals were introduced for the first time into heavy main-group iodometallates to get two new IA/IVA heterometallic frameworks, which were obtained by hydrothermal method under different pH conditions. The two compounds were three-dimensional heterometallic frameworks constructed from the linkage of pdon ligand between iodometallate chains and potassium oxide/iodide clusters. Interestingly, the heterometallic frameworks exhibit broadened absorption bands compared to those of bulk  $\text{PbI}_2$  and pdon ligand. The structure-property correlations of the two compounds were studied.

## Supplementary Information

Supplementary data associated with this article (optical band gaps and TGA curves) can be found in the online version available at [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci). Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-704836 (**1**), 696106 (**2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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