# MATERIALS CHEMISTRY

FRONTIERS

# RESEARCH ARTICLE

Check for updates

Cite this: DOI: 10.1039/d1qm01247a

Received 9th September 2021, Accepted 8th November 2021 DOI: 10.1039/d1qm01247a

rsc.li/frontiers-materials

# Stable two-dimensional lead iodide hybrid materials for light detection and broadband photoluminescence<sup>†</sup>

Mohamed Saber Lassoued, <sup>ab</sup> Yuan-Chao Pang, <sup>ab</sup> Qian-Wen Li, <sup>ab</sup> Xinkai Ding, <sup>b</sup> Bo Jiao, <sup>cd</sup> Hua Dong, <sup>b</sup> <sup>cd</sup> Guijiang Zhou, <sup>b</sup> <sup>a</sup> Shujiang Ding, <sup>b</sup> <sup>a</sup> Zhicheng Zhang, <sup>b</sup> <sup>a</sup> Zhaoxin Wu, <sup>c</sup> <sup>d</sup> Gaoyang Gou, \*<sup>b</sup> Zongyou Yin, <sup>b</sup> <sup>e</sup> Ju Li <sup>b</sup> <sup>e</sup> and Yan-Zhen Zheng <sup>b</sup> \*<sup>ab</sup>

Two-dimensional (2D) organic-inorganic hybrid materials have attracted widespread attention for photodetection. Moreover, such materials with broadband photoluminescence and strong photocurrent response are still rare. Here, we report two new semiconducting 2D organic-inorganic hybrid materials, namely  $\{Pb^{II}_{2}I_{6}[Pb^{II}(TETA)]\}_{n}$  (**1Pb**) and  $\{Pb^{II}_{3}I_{8}[Pb^{II}(TETA)]\}_{n}$  (**2Pb**), where TETA = triethylenetetramine, with broadband yellow-green emission. Both compounds are soluble in DMF and yield high surface coverage films through spin coating. Strikingly, the photocurrent responses of such thin films show *ca.* 600 and 700 nA cm<sup>-2</sup> difference between  $I_{iight}$  and  $I_{dark}$  for **1Pb** and **2Pb**, respectively. To the best of our knowledge, **1Pb** and **2Pb** showed among the highest current obtained in 2D lead iodide hybrid materials under a low voltage (0.7 V). Moreover, **1Pb** and **2Pb** are stable under heat, moisture and light, which may provide realistic applications for light detection.

In recent years, methyl ammonium lead halide materials have become a new path in the photovoltaic field due to their simple manufacturing processes,<sup>1</sup> high absorption coefficient<sup>2,3</sup> and long charge carrier diffusion lengths.<sup>4,5</sup> The interest around these compounds is driven by their fast advancement of the energy conversion efficiency (PCE). Since Miyasaka manufactured the initial device in 2009, its efficiency was 3.8%, and the PCE of organic–inorganic solar cells have been increased to 25.5% in such a short period of time,<sup>6</sup> surpassing the most advanced copper indium gallium diselenide (CIGS) solar cells, and approaching single crystal silicon solar cells.<sup>7</sup> However, under environmental conditions (moisture, oxygen and UV radiation), their stability is still poor and remains a principal drawback for further commercial use.<sup>8–10</sup>

In order to address the long-term stability issue for realworld applications, two-dimensional (2D) hybrid materials have become the best candidates due to their superior stability and wider structural diversity.<sup>11-13</sup> In addition, 2D organic-inorganic hybrid materials also present exciting optical and unique optoelectronic properties, such as widely tunable bandgap energy, extremely large exciton binding energy, layered characteristic and long decay times.<sup>14-18</sup> All these features make those kind of hybrid materials very promising in optoelectronic devices. In particular, 2D lead halide hybrid compounds have been paid extensive attention not only due to their rich structural chemistry (by using different organic cations, a large number of 2D halo-plumbate anions have been investigated such as  $[PbX_4]^{2-}$ ,  $[Pb_3X_9]^{3-}$ ,  $[Pb_5X_{14}]^{4-}$ , and  $[Pb_7X_{18}]^{4-})^{19-23}$  but also because of their interesting stability and photophysical properties. In this context, Dou et al. synthesized stable 2D hybrid perovskite quantum wells (4Tm)<sub>2</sub>PbI<sub>4</sub> and (BTm)<sub>2</sub>PbI<sub>4</sub> using hydrophobic organic semiconducting ligands (4Tm and BTm: thiophene derivatives). Those two compounds showed high stability under harsh conditions (heat and moisture).<sup>24</sup> The employment of larger organic cations with strong  $\pi$ - $\pi$  interactions within a 2D



**View Article Online** 

<sup>&</sup>lt;sup>a</sup> School of Chemistry, Xi'an Key Laboratory of Sustainable Energy and Materials Chemistry, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an 710049, China. E-mail: zheng,yanzhen@xjtu.edu.cn

<sup>&</sup>lt;sup>b</sup> Frontier Institute of Science and Technology (FIST), State Key Laboratory for Mechanical Behavior of Materials, and School of Physics, Xi'an Jiaotong University, Xi'an 710054, China. E-mail: gougaoyang@xjtu.edu.cn

<sup>&</sup>lt;sup>c</sup> Key Laboratory of Photonics Technology for Information, Key Laboratory for Physical Electronics and Devices of the Ministry of Education, Department of Electronic Science and Technology, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China

<sup>&</sup>lt;sup>d</sup> Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan 030006, China

<sup>&</sup>lt;sup>e</sup> Department of Nuclear Science and Engineering, Department of Materials Science and Engineering, Massachu-setts Institute of Technology, Cambridge, MA 02139, USA

<sup>†</sup> Electronic supplementary information (ESI) available. CCDC [2107024, 2107027]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1qm01247a

structure will greatly enhance the stability of these compounds.<sup>25</sup> Moreover, due to the strong van der Waals interactions between the layers, Li et al. showed that 2D Dion Jacobson lead iodide hybrid perovskite (PA)<sub>2</sub>(MA)<sub>3</sub>Pb<sub>4</sub>I<sub>13</sub> and  $(PDA)(MA)_3Pb_4I_{13}$  (PA = propylamine and PDA = 1,3propanediamine) exhibited ultrahigh stability for 4000 h under 40-70% relative humidity and for 168 h damp heat at 85 °C.<sup>26</sup> Other than that, 2D lead halide hybrid compounds were reported to have excellent luminescence properties; for example, Liu et al.27 prepared two 2D organic-inorganic lead bromide hybrid materials (C<sub>7</sub>H<sub>18</sub>N<sub>2</sub>)PbBr<sub>4</sub> and (C<sub>9</sub>H<sub>22</sub>N<sub>2</sub>)PbBr<sub>4</sub>, exhibiting broadband emission with a long-life time emission of  $\simeq 1$  ms; Luo *et al.* also successfully designed a new 2D lead bromide hybrid, ( $\gamma$ -methoxy propyl amine)<sub>2</sub>PbBr<sub>4</sub>, which exhibits bright bluish white light emission with high Color Rendering Index and PLOE of 6.85%;<sup>28</sup> and  $[DMEDA]PbCl_4$  (DMEDA = N,N-dimethylethylenediamine),  $(C_6H_5C_2H_4NH_3)_2PbCl_4$ , [DMPDA]PbCl\_4 (DMPDA = N,N-dimethyl-1,3-diaminopropane), [(CH<sub>3</sub>)<sub>4</sub>N]<sub>4</sub>Pb<sub>3</sub>Cl<sub>10</sub> and (C<sub>4</sub>H<sub>9</sub>NH<sub>3</sub>)2PbCl<sub>4</sub> have also been reported as luminescent materials.<sup>29-32</sup>

On the other hand, despite a few literature reports based on 2D lead halide hybrid photodetectors (particularly for 2D lead iodide hybrids), those works showed very interesting and promising results. For example, a 2D bilayered lead iodide hybrid compound reported by Zhang *et al.* exhibited broadband photoresponsive properties with high photoresponsivity.<sup>33</sup> Another important work reported by Huang *et al.* showed a photodetector with tunable photoresponse by the precise control of the n number of 2D  $(BA)_2(MA)_{n-1}Pb_nI_{3n+1}$  (n = 1, 2, 3) hybrid

materials.<sup>34</sup> Nevertheless, how to realize stable 2D lead iodide hybrid compounds broadband photoluminescence together with strong photo-response is still a huge challenge and very rarely reported.

In light of this discussion, we report two new 2D lead iodide organic-inorganic hybrid materials, namely  $\{Pb^{II}_{2}I_{6}[Pb^{II}(TE-TA)]\}_{n}$  (**1Pb**) and  $\{Pb^{II}_{3}I_{8}[Pb^{II}(TETA)]\}_{n}$  (**2Pb**), which possessed excellent semiconductor properties and broadband yellow-green light emission. In addition to the high solubility and film processable nature, **1Pb** and **2Pb** showed significant stability against moisture, light and temperature, which made **1Pb** and **2Pb** suitable for light detection applications.

**1Pb** and **2Pb** were synthesized through the hydrothermal technique, in which different stoichiometric amounts of  $Pb(NO_3)_2$ , triethylenetetramine (TETA) and KI in a concentrated hydroiodic acid (HI) were added, and the mixture was kept for 24 h at 130 °C for **1Pb**, and at 150 °C for 48 h for **2Pb** (see "Materials and sample preparation" in the ESI† for more details). Structural analyses disclosed that **1Pb** crystallized in a monoclinic system with a centrosymmetric space group of  $P2_1/c$  at 298 K (Table S1, ESI†). The asymmetric unit comprises one organic triethylenetetramine (TETA), three lead( $\pi$ ) ions and six iodine anions (Fig. 1a).

As shown in Fig. 1b and c, the topography of **1Pb** can be described as a 2D structure, in which there are two crystallographically independent Pb(II) atoms, which exhibited two different coordination environments:  $[PbI_6]$  octahedra for both Pb1 and Pb2, while  $[PbN_4I_2]$  octahedron for Pb3. Thus, for Pb1



Fig. 1 Asymmetric units of **1Pb** (a) and **2Pb** (d). Crystal structure of the compounds of **1Pb** (b) and **2Pb** (e). Zoom of **1Pb** layer (c) and **2Pb** layer (f). Hydrogen atoms are omitted for clarifications. The colors are used to indicate the following: Lead: dark green, iodine: violet, carbon: black and nitrogen: blue.

and Pb2, each lead atom was connected with six iodine atoms to form PbI<sub>6</sub> octahedra, in that Pb1 and Pb2 were linked together by two bridge I atoms. The Pb-I distances varied between 3.0447 (13) Å and 3.3673 (12) Å, while the  $I_{eq}$ -Pb- $I_{eq}$ ("eq" refers to equatorial) bond angles ranged from 80.41  $(3)^{\circ}$ to 105.96 (3)°, and the  $I_{ax}\mbox{-}Pb\mbox{-}I_{ax}$  ("ax" refers to axial) bond angles varied between 162.51 (3)° and 177.28 (4)°, indicating that the octahedra were distorted. The Pb3 atom was bonded to four N atoms and shared two iodine atoms with [Pb<sub>2</sub>I<sub>6</sub>] units to form [PbN<sub>4</sub>I<sub>2</sub>] octahedron, in which the Pb-I bond lengths varied between 3.5192 (13) Å and 3.662 (16) Å; the Pb-N distance ranged from 2.4470 (15) Å to 2.628 (17) Å and the N-Pb-N angle ranged from 68.6 (6)° to 122.4 (6)° (Table S2, ESI<sup>†</sup>). Hence, a 2D  $\{Pb_{2}^{II}I_{6}[Pb_{7}^{II}(TETA)]\}_{n}$  network was formed by sharing two iodine atoms between the  $[Pb_2I_6]^{2-}$ and [Pb(TETA)]<sup>2+</sup> units.

Using different stoichiometric amounts from 1Pb, yellow crystals of 2Pb were synthesized. Single-crystal X-ray diffraction studies revealed that 2Pb crystallized in a monoclinic system at room temperature with the space group of C2/c. As shown in Fig. 1d, the asymmetric unit of **2Pb** contains four lead( $\pi$ ) ions, eight iodine atoms, and one TETA. Three lead(II) (Pb1, Pb2 and Pb3) ions adopted a geometry of six-coordinated relative regular octahedron (Pb-I: 3.0070 (14) Å-3.3768 (14) Å and I-Pb-I: 85.62  $(3)^{\circ}$ -178.11  $(4)^{\circ}$ ). The Pb-I bond lengths are closer to the sum of the ionic radii of iodide and lead(II) (ri = 2.2 + 1.03 = 3.23 Å) rather than to that of their covalent radii (re = 1.39 + 1.48 = 2.87 Å), proving that these bonds are ionic in nature. However, the Pb4 ion was coordinated with four nitrogen atoms of the bent TETA (Pb-N: 2.505 (15)–2.596 (19) Å), and two iodine atoms to form  $[PbN_4I_2]$ octahedron (Fig. 1e and f). The coordination modes of 2Pb are quite similar to that of 1Pb. However, the difference between 1Pb and 2Pb was that the Pb-I distance and I-Pb-I angle in the 2Pb complex were slightly broader than those in 1Pb, indicating that 2Pb was a bit distorted from 1Pb. As shown with 1Pb, the  $[Pb(TETA)]^{2+}$  units in **2Pb** shared two iodine atoms with  $[Pb_3I_8]^{2-}$ units to connect them into a 2D network.

TETA showed a regular configuration with normal values of C–C and C–N bond lengths varying from 1.41 (3) Å to 1.55 (3) Å, whereas C–C–C, C–N–C and C–C–N angles ranged between 107.7 (19)° and 117.2 (17)° (see Tables S2 and S3, ESI†). Moreover, **1Pb** and **2Pb** exhibited several intermolecular hydrogen bonding interactions between the cationic and  $[Pb_2I_6]^{2-}$  or  $[Pb_3I_8]^{2-}$  anions of the type N–H···I and C–H···I listed in Tables S4 and S5 in ESI.† The XRD powder spectra of **1Pb** and **2Pb** are given in Fig. S1, ESI.† It can be seen that PXRD patterns of these two materials matched perfectly well with the simulated results from the single crystal structure, which indicated the high purity of **1Pb** and **2Pb** powder samples.

To analyse and obtain additional information about intermolecular interactions within the crystal structure of **1Pb** and **2Pb**, molecular Hirshfeld surface (MHS) calculations were performed using the crystal explorer 3.1 program. The blue, red and white areas in the MHS represent the largest, shortest and equal to van der Waals separations, respectively (Fig. S2, ESI<sup>†</sup>). It can be seen from Fig. S3a and c in ESI<sup>†</sup> that 2D finger



Fig. 2 (a, b) Topographical SEM images of the thin film made from **1Pb**. (c) Cross-sectional SEM image of the thin film made from **1Pb**. (d, e) Topographical SEM images of the thin film made from **2Pb**. (f) Cross-sectional SEM image of thin film made from **2Pb**. (g) XRD patterns of the thin film made from **1Pb**. (h) XRD patterns of the thin film made from **2Pb**.

print maps of **1Pb** and **2Pb** provide quantitative contribution of the intermolecular interaction. Two remarkable spikes presented the most abundant interaction of **1Pb** and **2Pb**, which were from  $H \cdots I$  and  $Pb \cdots I$ , consistent with the red area in the MHS. It was very clear that hydrogen bonds played an important role in crystal stabilization. These results are also confirmed by single crystal analysis (Tables S4 and S5, ESI†). Other intercontacts present less to MHS were also calculated, such as  $H \cdots H$  and  $I \cdots I$  (Fig. S3b and d, ESI†).

Significantly, **1Pb** and **2Pb** are highly soluble in dimethylformamide (DMF), and 1 ml DMF can dissolve 0.2 g of each compound (**1Pb** or **2Pb**). Using the one step spin coating technique, we dissolved 20 mg of **1Pb** and **2Pb** single crystals in 1 ml DMF, and then cooled at ambient temperature (More details can be found in the ESI†). Smooth, high coverage, less pin hole films of **1Pb** and **2Pb** readily formed (Fig. 2). **1Pb** and **2Pb** had small grain sizes of 750 nm and 900 nm, respectively ((Fig. 2a and b) and Fig. 2d and e). As shown in Fig. 2c and f, the cross-section images reveal that **1Pb** and **2Pb** have grain thicknesses of 3 µm and 3.1 µm, respectively. XRD patterns of **1Pb** and **2Pb** films match very well with the simulated ones, which indicated their high purity (Fig. 2g and h).

Based on the Kubelka–Munk function,<sup>35</sup> ( $F(R) = \alpha/S = (1 - R)^2/(2R)$ , where *R* is the reflectance,  $\alpha$  is the absorption coefficient, *S* is the scattering coefficient), the diffuse reflectance spectrum was converted to an absorbance spectrum to understand the semiconducting performance of **1Pb** and **2Pb**. As shown in Fig. 3a, the optical band edges of **1Pb** and **2Pb** were determined to be 2.28 eV and 2.02 eV, respectively. These results are consistent with their colors, and are very similar to other lead iodide hybrid compounds.<sup>36,37</sup> Based on the intercepts of the



Fig. 3 (a) Absorption spectra for the powder **1Pb** and **2Pb**. (b) Absorption spectra for thin film **1Pb** and **2Pb**. (c) DFT calculations predicted the band structure for **2Pb** with SOC effect included. (d) Simulated orbital resolved partial density of states (PDOS) for **2Pb**.

curves of  $(F(RN)h\nu)^{1/n}$  (n = 2 or n = 1) *versus* the energy according to the  $\tau_{auc}$  equation, bandgap energies were estimated to be 2.31 eV (indirect) and 2.20 eV (direct) for **1Pb** and **1.86** eV (indirect) and 2.08 eV (direct), respectively, for **2Pb** (Fig. S4, ESI†). These bandgap values could be considered within the range of a typical semiconductor compound and can be used as the absorber for tandem solar cells when these two materials are coupled with silicon.<sup>38</sup> Interestingly, optical absorption spectra were performed on films of **1Pb** and **2Pb**, respectively, and both are similar for those of powder samples (Fig. 3b).

To get an insight into the electronic properties of these two compounds, DFT calculations of 1Pb and 2Pb were performed. After including spin orbital coupling (SOC) effects, GGA-PBE functional predicts that the valence band maximum (VBM) and conduction band minimum (CBM) are both located at the same k points ( $\Gamma$  for **1Pb** and C for **2Pb**), indicating that **1Pb** and **2Pb** are semiconductors with direct bandgaps (Fig. 3c and Fig. S5a, ESI<sup>†</sup>). In addition, the predicted energy bandgaps are 2.12 eV and 1.94 eV for 1Pb and 2Pb, respectively, which are close to experimental results. Without SOC effect, the larger bandgaps of 2.72 eV for 1Pb and 2.24 eV for 2Pb will be predicted (Fig. S5b and S6a, ESI<sup>†</sup>). Based on the partial density of states, we will further analyze the orbital nature for electronic states around VBM and CBM. The top of valence bands was mainly contributed by hybridized I-5p and Pb-6s orbitals, while the bottom of conduction bands had dominant Pb/I-5p orbital characters for both two compounds (Fig. 3d, Fig. S5 (c-f) and S6 (b-d), ESI<sup>†</sup>). These results clearly indicated that optical excitations within 1Pb and 2Pb are mainly determined by the hybridized Pb and I orbitals from the inorganic framework.

The photoluminescence properties of **1Pb** and **2Pb** lead iodide hybrid compounds were studied at room temperature using steady state and time-resolved emission spectroscopy. Upon excitation of 450 nm, both compounds exhibited two



Fig. 4 (a) PL emission spectrum at room temperature for **1Pb** and **2Pb**. (b) CIE chromaticity coordinates for **1Pb** and **2Pb**. (c) Time-resolved decay curve for 645 nm emission at room temperature for **1Pb**. (d) Time-resolved decay curve for 645 nm emission at room temperature for **2Pb**.

band emissions, which generally matched very well with the two slopes from the absorption spectra. Indeed, 1Pb and 2Pb display two broadband emissions with the highest bands at 519 nm for 1Pb and 550 nm for 2Pb, and another two weak emissions present in the range of 600-720 nm can be tentatively assigned to lead halide-centered transitions within the inorganic group, as suggested by band structure calculations, and observed recently in other reported iodoplumbate organicinorganic based hybrid materials (Fig. 4a).<sup>39-41</sup> Thus, the broad photoluminescence mainly originated from the inorganic component. We should note that similar emission bands between 1Pb and 2Pb indicate the same radiative recombination route. In addition, the combination of the two emission bands gave rise to the CIE 1931 chromaticity coordinates of (0.39, 0.56) for 1Pb with CCT of 3780 K and of (0.43, 0.53) for 2Pb with CCT of 3825 K. Both compounds exhibited yellow green emission (Fig. 4b). Moreover, the PLQY of 1Pb and 2Pb was measured to be 1% and 1.12%, respectively, which were comparable to those of previous reported 2D hybrid lead materials, such as 0.5% for  $(N-MEDA)PbI_4$  and ~1% for  $(C_6H_5C_2H_4NH_3)_2PbCl_4$ .<sup>42,43</sup>

Using a fitting with a double-exponential function  $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ , the decay life times of **1Pb** and **2Pb** have been calculated (Fig. 4c and d). Interestingly, the average life time for **1Pb** was 16.57 ns and for **2Pb** was 10.57 ns, which were longer than that of other reported 2D lead hybrid compounds (Table S6, ESI<sup>†</sup>). The photoluminescence properties for both compounds are summarized in Table 1.

Table 1         Summary of the photophysical properties of 1Pb and 2Pb							
Compds	$\lambda_{\mathrm{ex}} (\mathrm{nm})$	$\lambda_{\rm em} ({\rm nm})$	CIE	$\tau$ (ns)			
1Pb 2Pb	450 450	518/645 550/645	(0.39, 0.56) (0.43, 0.53)	16.57 10.57			

(a)

(nA/cm<sup>2</sup>) Current -300

(c)

(nA/cm<sup>2</sup>) 300

600

300

-600

900

600

0

j -300

-600

-0.9 -0.6

-0.9

-0.6

Light at 293

Light at 293

Dark at 293 I

-0.3 0.0 0.3 0.6

Voltage (V)

-0.3 0.0 Voltage (V)

0.3 0.6

The photoconductivity of 1Pb and 2Pb was studied using film samples as the active layer under the illumination from a 350 W Xenon lamp irradiation at 0.7 V bias (more details can be found in the ESI<sup>†</sup>). As shown in Fig. 5a and c, both materials exhibited a strong photoresponse in that the photocurrent for **1Pb** enhanced from 20 to 636 nm  $\text{cm}^{-2}$ , and increased for **2Pb** from 42 to 780 nm  $cm^{-2}$ . Those values are higher than that of bismuth halide organic-inorganic materials and comparable to that of lead-based hybrids. However, they were lower than that of 3D MAPbI<sub>3</sub> and those of inorganic systems.<sup>39,40,44-48</sup> To the best of our knowledge, 1Pb and 2Pb had among the highest current obtained in 2D lead iodide hybrid materials under low voltages. We need to mention that the order of photocurrent for these two compounds was well coherent with their optical bandgaps, which signalized that a small bandgap may be better to generate and separate a photoinduced electron/hole.37,49

Fig. 5b and d show that these devices exhibited a broadband, repeatable and periodical switching (on/off) of the light, which means that 1Pb and 2Pb exhibited an obvious photocurrent reproducibility and high stability. Moreover, the photoresponsivity (R) (it is an important figure of merit to represent the sensitivity of the photodetector to the light signal) was calculated to be 7.04  $\mu$ A W<sup>-1</sup> and 8.57  $\mu$ A W<sup>-1</sup> for **1Pb** and **2Pb**, respectively.

Other important parameters of photodetector devices, such as detectivity  $(D^*)$  and external quantum efficiency (EQE), were also determined. A comparative table between 1Pb and 2Pb with other general materials are illustrated in Table S7 in the ESI.† The responsivity, detectivity and external quantum efficiency are obtained using the following equations:

(b)

(d) 1200

900

$$R = \frac{I_{\text{light}} - I_{\text{dark}}}{P_0 S} \tag{1}$$

200

200

Liah

400

Time (s)

400

Time (s)

Liaht Of

800

600



0.9

$$D^* = RS^{\frac{1}{2}} / (2eI_d)^{\frac{1}{2}}$$
(2)

$$EQE = R \times \frac{12408}{\lambda}$$
(3)

where  $I_{\text{light}}$  is the photocurrent,  $I_{\text{dark}}$  is the dark current,  $P_0$  is the intensity of light, S is the area of the device, e is the electronic charge and  $\lambda$  is the wavelength of irradiation.

Moreover, we studied the stability of both 1Pb and 2Pb towards moisture, light and heat. The as-prepared films of 1Pb and 2Pb were stored in the dark at 55% relative humidity for 7 days. The XRD patterns of the film samples of 1Pb and 2Pb remained almost the same as those of the freshly prepared sample (see Fig. S1, ESI<sup>†</sup>) and showed no evidence of peak related to material degradation. However, we noted a decrease in the diffraction peak intensity of 1Pb and 2Pb within 7 days (Fig. S7, ESI<sup>†</sup>). To explore the UV aging effect, we exposed **1Pb** and 2Pb films to UV light for 24 h at room temperature. No obvious change has been observed for the XRD patterns compared to the simulated ones (Fig. S7, ESI<sup>+</sup>). Moreover, to evaluate the thermal stability of 1Pb and 2Pb, thermogravimetric analyses (TGA) were conducted from 30 °C to 600 °C under nitrogen atmosphere (Fig. S8, ESI<sup>†</sup>). It can be seen from the TGA curves that the two compounds are stable up to 225 °C. Hence, 1Pb and 2Pb showed high stability towards moisture, light and heat.

## Conclusions

In summary, two new 2D organic-inorganic hybrid lead iodide using a tetradentate ligand were successfully synthesized and fully characterized. Both compounds exhibited an excellent semiconductor property and showed broadband yellow-green emission. Interestingly, 1Pb and 2Pb showed high stability and exhibited a strong photocurrent response at 0.7 V. In addition, **1Pb** and **2Pb** were processed into high coverage films through the one-spin coating method. Thus, this study showed two new broadband 2D lead iodide hybrid materials with potential for light detection applications.

## Author contributions

M. S. Lassoued, Y.-C. Pang and Q.-W. Li conducted the syntheses, crystallography and photoluminescence. The ab initio calculations were performed by X. Ding, G. Gou and J. Li. The photoresponse measurements were performed by Z. Yin, B. Jiao and H. Dong; G. Zhou, S. Ding, Z. Zhang and Z. Wu drew the pictures and wrote the manuscript; Y.-Z. Zheng supervised the whole project. All authors read and approved the manuscript before submission.

### Conflicts of interest

There are no conflicts to declare.

**Materials Chemistry Frontiers** 

# Acknowledgements

This work was supported by the Natural Science Foundation of China (no. 21971203 and 21773130), the State Key Laboratory for Mechanical Behavior of Materials (20182006), the Key Laboratory Construction Program of Xi'an Municipal Bureau of Science and Technology (201805056ZD7CG40), the China Postdoctoral Science Foundation (2018M631138), the Shaanxi Postdoctoral Science Foundation (2018), the Cyrus Chung Ying Tang Foundation and the Fundamental Research Funds for Central Universities, Key Scientific and Technological Innovation Team of Shaanxi Province (2020TD-001).

# References

- A. Kojima, K. Teshima, Y. Shirai and T. Miyasaka, Organometal halide perovskites as visible-light sensitizers for photovoltaic cells, *J. Am. Chem. Soc.*, 2009, 131, 6050–6051.
- 2 M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, Efficient hybrid solar cells based on mesosuperstructured organometal halide perovskites, *Science*, 2012, **338**, 643–647.
- 3 J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Graetzel, Sequential deposition as a route to high-performance perovskitesensitized solar cells, *Nature*, 2013, **499**, 316–319.
- 4 X. Li, D. Bi, C. Yi, J.-D. Decoppet, J. Luo, S. M. Zakeeruddin, A. Hagfeldt and M. Gratzel, A vacuum flash-assisted solution process for high-efficiency large-area perovskite solar cells, *Science*, 2016, **353**, 58–62.
- 5 W. S. Yang, J. H. Noh, N. J. Jeon, Y. C. Kim, S. Ryu, J. Seo and S. I. Seok, High-performance photovoltaic perovskite layers fabricated through intramolecular exchange, *Science*, 2015, 348, 1234–1237.
- 6 E. L. Unger, E. T. Hoke, C. D. Bailie, W. H. Nguyen, A. R. Bowring, T. Heumueller, M. G. Christoforo and M. D. McGehee, Hysteresis and transient behavior in current-voltage measurements of hybrid-perovskite absorber solar cells, *Energy Environ. Sci.*, 2014, 7, 3690–3698.
- 7 The National Renewable Energy Laboratory (NREL) Best Research-Cell Record Efficiencies, Best Research-Cell Efficiency Chart (nrel.gov).
- 8 L. Martiradonna, Entropy in halide perovskites, *Nat. Mater.*, 2018, **17**, 377–379.
- 9 L. Etgar, The merit of perovskite's dimensionality; can this replace the 3D halide perovskite?, *Energy Environ. Sci.*, 2018, 11, 234–242.
- B. W. Park and S. I. Seok, Intrinsic Instability of Inorganic– Organic Hybrid Halide Perovskite, Materials, *Adv. Mater.*, 2019, 3, 1805337.
- 11 M. S. Lassoued, L.-Y. Bi, Z. Wu, G. Zhou and Y.-Z. Zheng, Piperidine-induced Switching of the direct band gaps of Ag(I)/Bi(III) bimetallic iodide double perovskites, *J. Mater. Chem. C*, 2020, **8**, 5349–5354.
- 12 M. S. Lassoued, L.-Y. Bi, Z. Wu, G. Zhou and Y.-Z. Zheng, Two-dimensional semiconducting Cs(i)/Bi(iii) bimetallic

iodide hybrids for light detection, Mater. Chem. Front., 2021, 5, 973–978.

- 13 L.-Y. Bi, Y.-Q. Hu, M.-Q. Li, T.-L. Hu, H.-L. Zhang, X.-T. Yin, W.-X. Que, M. S. Lassoued and Y.-Z. Zheng, Twodimensional lead-free iodide-based hybrid double perovskites: crystal growth, thin-film preparation and photocurrent responses, *J. Mater. Chem. A*, 2019, 7, 19662–19667.
- 14 I. C. Smith, E. T. Hoke, D. Solis-Ibarra, M. D. McGehee and H. I. Karunadasa, A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability, *Angew. Chem.*, *Int. Ed.*, 2014, 53(42), 11232–11235.
- 15 D. H. Cao, C. C. Stoumpos, O. K. Farha, J. T. Hupp and M. G. Kanatzidis, 2D Homologous Perovskites as Light-Absorbing Materials for Solar Cell Applications, *J. Am. Chem. Soc.*, 2015, 137(24), 7843–7850.
- H. Tsai, W. Nie, J.-C. Blancon, C. C. Stoumpos, R. Asadpour, B. Harutyunyan, A. J. Neukirch, R. Verduzco, J. J. Crochet, S. Tretiak, L. Pedesseau, J. Even, M. A. Alam, G. Gupta, J. Lou, P. M. Ajayan, M. J. Bedzyk, M. G. Kanatzidis and A. D. Mohite, High efficiency two-dimensional Ruddlesden-Popper perovskite solar cells, *Nature*, 2016, 536(7616), 312-316.
- 17 M. Leng, Z. Chen, Y. Yang, Z. Li, K. Zeng, K. Li, G. Niu, Y. He, Q. Zhou and J. Tang, Lead-Free, Blue Emitting Bismuth Halide Perovskite Quantum Dots, *Angew. Chem.*, *Int. Ed.*, 2016, 55, 15012–15016.
- 18 D. B. Mitzi, Organic–Inorganic Perovskites Containing Trivalent Metal Halide Layers: The Templating Influence of the Organic Cation Layer, *Inorg. Chem.*, 2000, **39**, 6107–6113.
- 19 N. Mercier, S. Poiroux, A. Riou and P. Batail, Unique hydrogen bonding correlating with a reduced band gap and phase transition in the hybrid perovskites (HO(CH<sub>2</sub>)<sub>2</sub>NH<sub>3</sub>)<sub>2</sub>PbX<sub>4</sub> (X = I, Br), *Inorg. Chem.*, 2004, 43, 8361–8366.
- 20 D. G. Billing and A. Lemmerer, Inorganic–organic hybrid materials incorporating primary cyclic ammonium cations: The lead iodide series, *CrystEngComm*, 2007, **9**, 236–244.
- 21 H. Krautscheid and F. Vielsack, Synthese und Kristallstrukturen kettenförmiger und netzartiger Iodoplumbate, Z. Anorg. Allg. Chem., 1997, 623, 259–263.
- 22 H. Krautscheid and F. Vielsack, Discrete and polymeric iodoplumbates with Pb<sub>3</sub>I<sub>10</sub> building blocks:  $[Pb_3I_{10}]^{4-}$ ,  $[Pb_7I_{22}]^{8-}$ ,  $[Pb_{10}I_{28}]^{8-}$ ,  $1 \infty [Pb_3I_{10}]^{4-}$  and  $2 \infty [Pb_7I_{18}]^{4-}$ , *J. Chem. Soc., Dalton Trans.*, 1999, 2731–2735.
- 23 H. Krautscheid, F. Vielsack and N. Klaassen, Polymere Iodoplumbate Synthese und Kristallstrukturen von  $(Pr_3N-C_2H_4-NPr_3)[Pb_6I_{14}(dmf)_2]$  4 DMF,  $(Pr_3N-C_2H_4-NPr_3)[Pb(dmf)_6][Pb_5I_{14}]$  DMF und  $(Me_3N-C_2H_4-NMe_3)_2[Pb_2I_7]I$ , Z. Anorg. Allg. Chem., 1998, **624**, 807–812.
- Y. Gao, E. Shi, S. Deng, S. B. Shiring, J. M. Snaider, C. Liang, B. Yuan, R. Song, S. M. Janke, A. L-Peláez, P. Yoo, M. Zeller, B. W. Boudouris, P. Liao, C. Zhu, V. Blum, Y. Yu, B. M. Savoie, L. Huang and L. Dou, Molecular engineering of organic-inorganic hybrid perovskites quantum wells, *Nat. Chem.*, 2019, **11**, 1151–1157.
- 25 Y. Gao, Z. Wei, S.-N. Hsu, B. W. Boudouris and L. Dou, Twodimensional halide perovskites featuring semiconducting

organic building blocks, Mater. Chem. Front., 2020, 4, 3400-3418.

- 26 S. Ahmad, P. Fu, S. Yu, Q. Yang, X. Liu, X. Wang, X. Wang, X. Guo and C. Li, Dion-Jacobson Phase 2D Layered Perovskites for Solar Cells with Ultrahigh Stability, *Joule*, 2018, 3, 794–806.
- 27 C. Deng, G. Zhou, D. Chen, J. Zhao, Y. Wang and Q. Liu, Broadband Photoluminescence in 2D Organic–Inorganic Hybrid Perovskites: (C<sub>7</sub>H<sub>18</sub>N<sub>2</sub>)PbBr<sub>4</sub> and (C<sub>9</sub>H<sub>22</sub>N<sub>2</sub>)PbBr<sub>4</sub>, *The, J. Phys. Chem. Lett.*, 2020, **11**(8), 2934–2940.
- 28 Y. Li, C. Ji, L. Li, S. Wang, S. Han, Y. Peng, S. Zhang and J. Luo, γ-Methoxy propyl amine)2PbBr4: a novel twodimensional halide hybrid perovskite with efficient bluish white-light emission, *Inorg. Chem. Front.*, 2021, 8, 2119–2124.
- 29 C.-Q. Jing, J. Wang, H.-F. Zhao, W.-X. Chu, Y. Yuan, Z. Wang, M.-F. Han, T. Xu, J.-Q. Zhao and X.-W. Lei, Improving Broadband White-Light Emission Performances of 2D Perovskites by Subtly Regulating Organic Cations, *Chem. – Eur. J.*, 2020, 26, 10307–10313.
- 30 C. Xue, S. Wang, W.-L. Liu and X.-M. Ren, Two-Step Structure Phase Transition, Dielectric Anomalies, and Thermochromic Luminescence Behavior in a Direct Band Gap 2D Corrugated Layer Lead Chloride Hybrid of [(CH<sub>3</sub>)<sub>4</sub>N]<sub>4</sub>Pb<sub>3</sub>Cl<sub>10</sub>, *Chem. Eur. J.*, 2019, 25, 5280–5287.
- 31 C. Ji, S. Wang, L. Li, Z. Sun and M. Hong, The First 2D Hybrid Perovskite Ferroelectric Showing Broadband White-Light Emission with High Color Rendering Index, *Adv. Funct. Mater.*, 2019, 29, 1805038.
- 32 P. Cai, Y. Huang and H. J. Seo, Anti-Stokes Ultraviolet Luminescence and Exciton Detrapping in the Two-Dimensional Perovskite (C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>H<sub>4</sub>NH<sub>3</sub>)<sub>2</sub>PbCl<sub>4</sub>, *J. Phys. Chem. Lett.*, 2019, **10**(14), 4095–4102.
- 33 D. Fu, J. Yuan, S. Wu, Y. Yao, X. Zhang and X.-M. Zhang, A two-dimensional bilayered Dion–Jacobson-type perovskite hybrid with a narrow bandgap for broadband photodetection, *Inorg. Chem. Front.*, 2020, 7, 1394–1399.
- 34 J. Zhou, Y. Chu and J. Huang, Photodetectors Based on Two-Dimensional Layer-Structured Hybrid Lead Iodide Perovskite Semiconductors, ACS Appl. Mater. Interfaces, 2016, 8, 25660–25666.
- 35 J. Tauc, Absorption edge and internal electric fields in amorphous semiconductors, *Mater. Res. Bull.*, 1970, **5**, 721–729.
- 36 C.-Y. Yue, H.-X. Sun, Q.-X. Liu, X.-M. Wang, Z.-S. Yuan, J. Wang, J.-H. Wu, B. Hu and X.-W. Lei, Organic cation directed hybrid lead halides of zero-dimensional to twodimensional structures with tunable photoluminescence properties, *Inorg. Chem. Front.*, 2019, 6, 2709–2717.
- 37 B. Zhang, H.-Y. Sun, J. Li, Y.-R. Xu, Y.-P. Xu, X. Yang and G.-D. Zou, Hybrid iodoplumbates with metal complexes: syntheses, crystal structures, band gaps and photoelectric properties, *Dalton Trans.*, 2020, **49**, 1803–1810.
- 38 R. Sheng, A. W. Ho-Baillie, S. Huang, M. Keevers, X. Hao, L. Jiang, Y. B. Cheng and M. A. Green, Four-Terminal Tandem Solar Cells Using CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> by Spectrum Splitting, *J. Phys. Chem. Lett.*, 2015, 6, 3931–3934.
- 39 T.-t. Zhang, X. Liu, J. Zhou and J.-t. Liu, Two Organic Hybrid Iodoplumbates Directed by a Bifunctional Bis(pyrazinyl) triazole, *Inorg. Chem.*, 2021, **60**, 5362–5366.

- 40 Y. He, Y.-R. Huang, Y.-L. Li, H.-H. Li, Z.-R. Chen and R. Jiang, Encapsulating Halometallates into 3-D Lanthanide-Viologen Frameworks: Controllable Emissions, Reversible Thermochromism, Photocurrent Responses, and Electrical Bistability Behaviors, *Inorg. Chem.*, 2019, **58**(20), 13862–13880.
- 41 X.-L. Lin, B. Chen, Y.-R. Huang, K.-Y. Song, P.-K. Zhou, L.-L. Zong, H.-H. Li, Z.-R. Chen and R. Jiang, Achievement of intrinsic white light emission by hybridization-deformable haloplumbates with rigid luminescent naphthalene motifs, *Inorg. Chem. Front.*, 2020, 7, 4477–4487.
- 42 E. R. Dohner, A. Jaffe, L. R. Bradshaw and H. I. Karunadasa, Intrinsic white-light emission from layered hybrid perovskites, *J. Am. Chem. Soc.*, 2014, **136**, 13154–13157.
- 43 C. Ji, S. Wang, L. Li, Z. Sun, M. Hong and J. Luo, The first 2D hybrid perovskite ferroelectric showing broadband whitelight emission with high color rendering index, *Adv. Funct. Mater.*, 2018, **29**, 1805038.
- 44 J. K. Pious, A. Katre, C. Muthu, S. Chakraborty, S. Krishna and C. Vijayakumar, Zero-Dimensional Lead-Free Hybrid Perovskite-like Material with a Quantum-Well Structure, *Chem. Mater.*, 2019, **31**, 1941–1945.
- 45 N. Chen, Y. Gao, Y. Tian, B. Wu, D. Jia and S. Zhao, One-dimensional polymeric iodoplumbate hybrids with lanthanide complex cations: syntheses, crystal structures, and photoelectric and photocatalytic properties, *New J. Chem.*, 2020, **44**, 19166–19173.
- 46 A. Dey, J. Ye, A. De, E. Debroye, S. K. Ha, E. Bladt, A. S. Kshirsagar, Z. Wang, J. Yin, Y. Wang, L. N. Quan, F. Yan, M. Gao, X. Li, J. Shamsi, T. Debnath, M. Cao, M. A. Scheel, S. Kumar, J. A. Steele, M. Gerhard, L. Chouhan, K. Xu, X.-g. Wu, Y. Li, Y. Zhang, A. Dutta, C. Han, I. Vincon, A. L. Rogach, A. Nag, A. Samanta, B. A. Korgel, C.-J. Shih, D. R. Gamelin, D. H. Son, H. Zeng, H. Zhong, H. Sun, H. V. Demir, I. G. Scheblykin, I. M-Seró, J. K. Stolarczyk, J. Z. Zhang, J. Feldmann, J. Hofkens, J. M. Luther, J. P-Prieto, L. Li, L. Manna, M. I. Bodnarchuk, M. V. Kovalenko, M. B. J. Roeffaers, N. Pradhan, O. F. Mohammed, O. M. Bakr, P. Yang, P. M-Buschbaum, P. V. Kamat, Q. Bao, Q. Zhang, R. Krahne, R. E. Galian, S. D. Stranks, S. Bals, V. Biju, W. A. Tisdale, Y. Yan, R. L. Z. Hoye and L. Polavarapu, State of the Art and Prospects for Halide Perovskite Nanocrystals, ACS Nano, 2021, 15, 10775-10981.
- 47 Y. Tang, M. Liang, Bi. Chang, H. Sun, K. Zheng, T. Pulleritsd and Q. Chi, Lead-free double halide perovskite Cs<sub>3</sub>BiBr<sub>6</sub> with well-defined crystal structure and high thermal stability for optoelectronics, *J. Mater. Chem. C*, 2019, 7, 3369–3374.
- 48 Y. Dang, G. Tong, W. Song, Z. Liu, L. Qiu, L. K. Ono and Y. Qi, Interface engineering strategies towards Cs<sub>2</sub>AgBiBr<sub>6</sub> single-crystalline photodetectors with good Ohmic contact behaviours, *J. Mater. Chem. C*, 2020, **8**, 276–284.
- 49 M.-Q. Li, Y.-Q. Hu, L.-Y. Bi, H.-L. Zhang, Y. Wang and Y.-Z. Zheng, Structure Tunable Organic–Inorganic Bismuth Halides for an Enhanced Two-Dimensional Lead-Free Light-Harvesting Material, *Chem. Mater.*, 2017, 29(13), 5463–5467.

# Supporting Information for

# Stable Two-Dimensional Lead Iodide Hybrid Materials for Light Detection and Broadband Photoluminescence

Mohamed Saber Lassoued,<sup>a,b</sup> Yuan-Chao Pang,<sup>a,b</sup> Qian-Wen Li,<sup>a,b</sup> Xinkai Ding, <sup>b</sup> Bo Jiao, <sup>c,d</sup> Hua Dong, <sup>c,d</sup> Guijiang Zhou,<sup>a</sup> Shujiang Ding,<sup>a</sup> Zhicheng Zhang, <sup>a</sup> Zhaoxin Wu,<sup>c,d</sup> Gaoyang Gou,<sup>b,\*</sup> Zongyou Yin,<sup>e</sup> Ju Li <sup>e</sup> and Yan-Zhen Zheng<sup>\*a,b</sup>

- a School of Chemistry, Xi'an Key Laboratory of Sustainable Energy and Materials Chemistry, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiaotong University, Xi'an 710049 China. E-mail: <a href="mailto:zheng.yanzhen@xjtu.edu.cn">zheng.yanzhen@xjtu.edu.cn</a>
- b Frontier Institute of Science and Technology (FIST), State Key Laboratory for Mechanical Behavior of Materials, and School of Physics, Xi'an Jiaotong University, Xi'an 710054, China. E-mail: gougaoyang@xjtu.edu.cn
- c Key Laboratory of Photonics Technology for Information, Key Laboratory for Physical Electronics and Devices of the Ministry of Education, Department of Electronic Science and Technology, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China.
- d Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan 030006, China.
- e Department of Nuclear Science and Engineering, Department of Materials Science and Engineering, Massachu-setts Institute of Technology, Cambridge, MA 02139, United States.

# **Table of Contents**

# **1.Experimental Section**

1.1. General remarks

# 2. Materials and Sample Preparation

- 2.1. Materials
- 2.2. Preparation of 1Pb and 2Pb Single crystals
- 2.3. Fabrication of 1Pb and 2Pb Films

# 3. Characterization methods and Simulation details

- 3.1. Characterization methods
- 3.2. Simulation details

# 4. Supporting Tables and Figures

#### **1. Experimental Section**

#### 1.1. General remarks

Single crystal X-ray diffraction data of **1Pb** and **2Pb** were collected on a Bruker SMART APEX II CCD diffractometer with graphite monochromated Mo-k radiation ( $\lambda$ = 0.71073 Å) by using the  $\theta$ - $\omega$  scan technique at 298 K. PXRD intensities were measured at ambient temperature (298 K) on a Rigaku D/max-IIIA diffractometer (Cu-k $\lambda$ ,  $\lambda$ =1.54056 Å). The crystalline powder samples were prepared by grinding the single-crystals and collected in the 2 $\theta$  range of 5°–50° with a step size of 10°/min. Scanning electron microscopy (SEM) was performed using KYKY-EM3200, 25 KV instrument. Solid-state UV-Vis diffusion reflectance spectra of pressed powder and films samples were measured on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer using BaSO<sub>4</sub> powder as the reflectance reference. All density-functional theory (DFT) calculations were carried out within the Vienna Ab initio Simulation Package (VASP). Room-temperature steady-state emission spectra were collected on powder samples using an Edinburgh FLS980 spectrofluorometer upon 450 nm excitation. The PLQY was achieved by incorporating an integrating sphere into the FLS980 spectrofluorometer. TGA experiments were performed on a TGA-50 (SHIMADZU) thermogravimetric analyzer in temperature range between 30° and 600°.

## 2. Materials and Sample Preparation

#### 2.1. Materials

Chemicals listed were used as purchased and without further purification: (i) Triethylenetetramine (TETA), 97%, sigma Aldrich; (ii) Potassium iodide, 99.995%, sigma Aldrich; (iii) Acetonitrile, 99%, sigma Aldrich; (iv) hydroiodic acid, 57% w/w, sigma Aldrich; (v) Lead (II) nitrate, 99%, sigma Aldrich.

#### 2.2. Preparation of 1Pb and 2Pb Single crystals

Crystals of **1Pb**: A mixture of  $Pb(NO_3)_2$  (0.331 g, 1 mmol), HI (1 mmol), TETA (0.5 mmol), and KI (0.166 g, 1 mmol) were dissolved in 10ml mixed solvent (H<sub>2</sub>O : CH<sub>3</sub>CN = 8 : 2), stirred in the air for 10 minutes before transferred to a 15 mL Teflon-lined auto-clave and heated at 130°C for 24 hrs. The reactants were then cooled to room temperature in a rate of 5°C / h to obtain Luminous yellow needle-like crystals. (Yield: ca. 40% based on Pb). XRD indicates the phase purity (**Figure S1a**).

Crystals of **2Pb**: A mixture of Pb(NO<sub>3</sub>)<sub>2</sub> (0.331 g, 1 mmol), HI (2 mmol), TETA (1 mmol), and KI (0.332 g, 2 mmol) were dissolved in 10 ml deionized water, stirred in the air for 10 minutes before transferred to a 15 mL Teflon-lined auto-clave and heated at 150°C for 48 hrs. The reactants were then cooled to room temperature in a rate of 5 °C / h to obtain Luminous yellow rod-like crystals. (Yield: ca. 32% based on Pb). XRD indicates the phase purity (**Figure S1b**).

#### 2.3. Fabrication of 1Pb and 2Pb Films

Indium tin oxide coated glass (ITO) substrates were cleaned thoroughly and sequentially with commercial detergent in soapy water, deionized water, KOH solution, deionized water, and in a sonication bath. The substrates were then treated by UV–ozone treatment for 20 min prior before use. **1Pb** and **2Pb** organic-inorganic hybrid compounds (0.2 g for each compound) were dissolved in 1 mL of dimethylformamide solution (DMF) and were coated onto ITO glass substrate by spin coating method at 1000 rpm for 60 second. To evaporate the residual solvent, the obtained film was followed by annealing on a hot plate at 80 °C for 10 minutes.

#### 3. Characterization methods and Simulation details

#### 3.1. Characterization methods

#### X-ray Crystallographic Study

Single-crystal X-ray diffraction data collections for **1Pb** and **2Pb** were conducted on a Bruker SMART APEX II CCD diffractometer (Mo,  $\lambda = 0.71073$  Å) by using the  $\theta$ - $\omega$  scan technique at 298 K. The structures were solved by direct methods and refined with a full-matrix least-squares technique within the SHELXTL program package and Olex. <sup>[1, 2]</sup> All non-hydrogen atoms were refined anisotropically. The crystallographic details are provided in **Table S1-S5**. The crystallographic data for above compounds can be found in the Supporting Information or can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data\_request/cif. CCDC Numbers: 2107024 (1Pb) and 2107027 (2Pb).

**Optical absorption measurement.** Solid-state UV-Vis diffusion reflectance spectra were measured at room temperature on a SHIMADZU UV-3600 UV-Vis-NIR spectrophotometer using BaSO<sub>4</sub> powder as the reflectance reference. The absorption spectra were calculated from reflectance spectra by the Kubelka-Munk function:  $F(R) = \alpha/S = (1-R)^2/2R$ , where *R*,  $\alpha$ , and *S* are the coefficients for the reflection, the absorption and the scattering, respectively.

**Photo response measurement** During the photocurrent tests, a three-electrode system (a sample coated  $0.5 \times 0.5$  cm ITO glass plate as the working electrode, and Ag/AgCl as the counter and reference electrodes) was used, and Na<sub>2</sub>SO<sub>4</sub> (50 mL, 0.2 mol L<sup>-1</sup>) was utilized as the supporting electrolyte solution. Photoresponse of the photodetector was measured using Keithley 2450 source meter under the illumination from a 350 W Xenon lamp irradiation . The lamp was kept on continuously, and a manual shutter was used to block exposure of the sample to the light. The sample was typically irradiated at intervals of 80 s.

The on/off ratio of the photodetector is calculated using equation 1.

$$\frac{ON}{OFF} = \frac{I_{Light}}{I_{dark}} \quad (1)$$

Where  $I_{\text{light}}$  is the photocurrent (636 nA for **1Pb** and 780 nA for **2Pb** and  $I_{\text{dark}}$  is the dark current (20 nA and 42 nA for **1Pb** and **2Pb** respectively).

The responsivity is obtained using the following equation **2**.

$$R = \frac{I_{light} - I_{dark}}{P_0 S} \quad (2)$$

where  $P_0$  is the intensity of light (0.35 W/cm<sup>2</sup>) and S is the area of the device (0.25 cm<sup>2</sup>). The detectivity (D\*) and the external quantum efficiency (EQE) were calculated using the following equations **3** and **4**.

$$D^{*} = RS^{\frac{1}{2}} / (2eI_{d})^{\frac{1}{2}}$$
(3)  
$$EQE = R^{*} \frac{12408}{\lambda}$$
(4)

Where R is the responsivity , S is the effective area of light irradiation , e is the electronic charge , Id is the dark current,  $\lambda$  is the wavelength of irradiation.

**Stability studies.** Freshly prepared films of **1Pb** and **2Pb** were stored either in the dark to minimize light exposure and the relative humidity was maintained at ~55% humidity for 7 days. Freshly prepared films of **1Pb** and **2Pb** were exposed to UV light for 24 hours at room temperature.

**3.2 Simulation details Computational methods**. The crystallographic data of compound **1Pb** and **2Pb** obtained from Single Crystal XRD tests were used to calculate the electronic band

structures and densities of the states (DOS). All the calculations in this work were carried out using density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) Perdew–Burke–Ernzerhof (PBE) functional was used for electronic structure calculations. <sup>[3,4]</sup> The projector augmented wave (PAW) method was applied to treat the electron–core interactions. <sup>[5]</sup> The cutoff energy for plane waves was set to 550 eV and the Brillouin zone was sampled by a  $5 \times 2 \times 3$  mesh for **1Pb** and a  $4 \times 4 \times 2$  mesh for **2Pb**.

# 4. Supporting Tables and Figures

	1Pb	2Pb
Empirical formula	C <sub>6</sub> H <sub>18</sub> I <sub>6</sub> N <sub>4</sub> Pb <sub>3</sub>	$C_6 H_{18} I_8 N_4 Pb_4$
Formula weight	1529.25	1990.25
Crystal dimensions (mm)	0.11*0.22*0.15	0.13*0.19*0.14
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	C2/c
a/Å	8.8484(8)	24.937(4)
<i>b</i> /Å	19.3860(18)	9.1908(14)
$c/\text{\AA}$	15.5239(11)	26.522(4)
$\alpha/^{\circ}$	90	90
β/°	115.255(4)	94.213(2)
$\gamma/^{\circ}$	90	90
Volume/Å <sup>3</sup>	2408.4(4)	6062.2(16)
Z	4	8
ρ calcg/cm <sup>3</sup>	4.218	4.361
$\mu / mm^{-1}$	28.606	30.299
F(000)	2584.0	6672.0
Index ranges	-11<=h<=11, -25<=k<=25, - 20<=1<=20	-32<=h<=32, -11<=k<=11, - 34<=l<=34
Data Completeness	99.5%	96.6%
Data/restraints/parameters	5536/7/172	6849/2/199
Goodness-of-fit on F2	1.19 w = $1/[\sigma^2(Fo^2) + (0.000P)^2 + 274.2407Ph + 0.000P)^2 + 274.2407Ph + 0.000Ph + 0.00Ph + 0.00Ph + 0.00Ph + 0.00Ph + 0.00Ph + 0.00$	1.025 w = $1/[\sigma^2(Fo^2) + (0.1086P)^2 + (0.$
Weight	2/4.342/P where P = (Fo <sup>2</sup> + 2Fc <sup>2</sup> )/3	49/.420/P where P = (Fo <sup>2</sup> + 2Fc <sup>2</sup> )/3
$R=\sum   Fo-Fc  /\sum  Fo , wR_2$	$R_1 = 0.0435$ , $wR_2 = 0.1225$	R1 = 0.0670, wR2 = 0.192

Table S1 Summary of crystal data and structural refinements of 1Pb and 2Pb

R1 = $\Sigma$ ||F0| - |Fc||/ $\Sigma$ |F0|, wR<sub>2</sub>= [ $\Sigma$ w(Fo<sup>2</sup> -Fc<sup>2</sup>)<sup>2</sup> / $\Sigma$ w(Fo<sup>2</sup>)<sup>2</sup>]<sup>1/2</sup>

Bond	Lengths/Å	Bond pair	Angles / °	Bond pair	Angles / °
Pb1—N1	2.447 (15)	N1—Pb1—N3	99.4 (5)	I2—Pb3—I5 <sup>iii</sup>	105.96 (3)
Pb1—N3	2.528 (15)	N1—Pb1—N4	80.0 (6)	I2—Pb3—I6	99.85 (4)
Pb1—N4	2.628 (17)	N1—Pb1—N2	70.0 (7)	Pb2—I3—Pb3 <sup>ii</sup>	94.89 (3)
Pb1—N2	2.548 (17)	N3—Pb1—N4	69.4 (6)	Pb3—I3—Pb2	89.77 (3)
Pb2—I3	3.3028 (12)	N3—Pb1—N2	68.6 (6)	Pb3—I3—Pb3 <sup>ii</sup>	95.22 (3)
Pb2—I1 <sup>i</sup>	3.3314 (13)	N2—Pb1—N4	122.4 (6)	Pb2 <sup>iii</sup> —I1—Pb2 <sup>ii</sup>	92.69 (3)
Pb2—I5	3.1494 (13)	I3—Pb2—I1 <sup>ii</sup>	82.95 (3)	Pb3—I1—Pb2 <sup>iii</sup>	84.08 (3)
Pb2—I4	3.0447 (13)	I3—Pb2—I1i	80.41 (3)	Pb3—I1—Pb2 <sup>ii</sup>	96.79 (3)
Pb2—I6	3.1122 (14)	I1 <sup>i</sup> —Pb2—I1 <sup>ii</sup>	87.31 (3)	Pb2—I5—Pb3 <sup>i</sup>	84.64 (3)
Pb3—I3	3.1099 (12)	I5—Pb2—I3	170.10 (3)	Pb2—I6—Pb3	90.75 (3)
Pb3—I3 <sup>ii</sup>	3.3673 (12)	I5—Pb2—I1 <sup>ii</sup>	87.98 (3)	C5—N1—Pb1	113.7 (15)
Pb3—I1	3.1806 (13)	I5—Pb2—I1 <sup>i</sup>	95.25 (3)	C1—N3—Pb1	113.7 (11)
Pb3—I6	3.2474 (13)	I4—Pb2—I3	98.33 (3)	C6—N2—Pb1	117.3 (17)
Pb3—I2	3.1140 (13)	I4—Pb2—I1 <sup>i</sup>	95.26 (3)	N3—C5—C6	108.9 (14)
N1—C5	1.46 (4)	I4—Pb2—I1 <sup>ii</sup>	177.28 (4)	C6—N2—C2	117.2 (17)
N3—C1	1.50 (2)	I4—Pb2—I5	90.89 (3)	N3—C1—C3	110.7 (15)
N3—C4	1.41 (3)	I4—Pb2—I6	87.10 (4)	N2—C2—C5	113.8 (18)
N4—C3	1.47 (3)	I4—Pb2—I3	88.68 (3)	N4—C3—C1	111.4 (17)
N2—C2	1.48 (3)	I3—Pb3—I3 <sup>ii</sup>	84.78 (3)	N3—C4—C6	112.0 (16)
N2—C6	1.43 (3)	I3—Pb3—I1	93.43 (3)	N1—C5—C2	109.1 (17)
C1—C3	1.513 (10)	I3—Pb3—I5 <sup>iii</sup>	162.51 (3)	N2—C6—C4	109.8 (19)
C2—C5	1.52 (4)	I3—Pb3—I6	89.72 (3)	I1—Pb3—I6	171.44 (4)
C4—C6	1.55 (3)	I3—Pb3—I2	89.72 (3)	I5 <sup>iii</sup> —Pb3—I3 <sup>ii</sup>	80.54 (3)
		I1—Pb3—I3 <sup>ii</sup>	85.14 (3)	I2—Pb3—I1	88.13 (3)
		I1—Pb3—I5 <sup>iii</sup>	94.75 (3)		

Table S2 Summary of selected bond lengths (Å) and bond angles (°) of 1Pb

*Symmetry codes:* (i) x-1, y, z; (ii) -x+2, -y+1, -z+2; (iii) x+1, y, z

Bond	Lengths/Å	Bond pair	Angles / °	Bond pair	Angles / °
Pb1—I1	3.2300 (13)	I1 <sup>i</sup> —Pb1—I1	176.98 (3)	I8—Pb3—I4	92.80 (4)
Pb1—I1 <sup>i</sup>	3.1859 (13)	I1 <sup>i</sup> —Pb1—I2	88.35 (4)	I8—Pb3—I5	101.05 (4)
Pb1—I2	3.2243 (13)	I1 <sup>i</sup> —Pb1—I4	85.74 (3)	I8—Pb3—I7	91.74 (4)
Pb1—I2 <sup>ii</sup>	3.1785 (13)	I1—Pb1—I4	93.81 (3)	N2—Pb4—N1	68.6 (6)
Pb1—I4	3.2743 (14)	$I1^{i}$ —Pb1—I7 <sup>i</sup>	92.40 (3)	N3—Pb4—N2	69.3 (5)
Pb1—I7 <sup>i</sup>	3.2045 (13)	I2 <sup>ii</sup> —Pb1—I1 <sup>i</sup>	88.62 (4)	N3—Pb4—N4	87.3 (6)
Pb2—I2	3.3768 (14)	I2—Pb1—I1	94.65 (4)	N3—Pb4—N1	107.0 (6)
Pb2—I3	3.1318 (13)	I2 <sup>ii</sup> —Pb1—I1	88.38 (4)	N4—Pb4—N2	120.8 (6)
Pb2—I4	3.3690 (14)	I2 <sup>ii</sup> —Pb1—I2	176.96 (3)	N4—Pb4—N1	68.0 (5)
Pb2—I5	3.0784 (14)	I2—Pb1—I4	91.55 (3)	Pb1 <sup>ii</sup> —I1—Pb1	91.51 (3)
Pb2—I6	3.0543 (14)	I2 <sup>ii</sup> —Pb1—I4	87.92 (3)	Pb1 <sup>i</sup> —I2—Pb2	93.10 (3)
Pb3—I3 <sup>iii</sup>	3.2140 (13)	I2 <sup>ii</sup> —Pb1—I7 <sup>i</sup>	91.70 (3)	Pb2—I3—Pb3 <sup>iv</sup>	94.97 (4)
Pb3—I4	3.2598 (14)	I7 <sup>i</sup> —Pb1—I4	178.11 (4)	Pb1—I4—Pb2	89.81 (3)
Pb3—I5	3.2451 (14)	I3—Pb2—I2	85.62 (3)	Pb3—I4—Pb1	90.01 (3)
Pb3—I7	3.2637 (14)	I3—Pb2—I4	167.99 (4)	Pb3—I4—Pb2	86.26 (4)
Pb3—I8	3.0070 (14)	I4—Pb2—I2	87.32 (3)	Pb2—I5—Pb3	91.54 (4)
Pb4—N2	2.588 (15)	I5—Pb2—I2	85.92 (3)	Pb1 <sup>ii</sup> —I7—Pb3	92.65 (3)
Pb4—N3	2.505 (15)	I5—Pb2—I3	98.62 (4)	N1—C2—C3	110.5 (19)
Pb4—N4	2.567 (17)	I5—Pb2—I4	90.55 (4)	N1—C1—C6	109.8 (18)
Pb4—N1	2.596 (19)	I6—Pb2—I2	169.29 (4)	C5—N2—Pb4	112.6 (12)
C2—C3	1.52 (3)	I6—Pb2—I3	88.67 (4)	C6—N2—Pb4	110.9 (13)
C2—N1	1.51 (2)	I6—Pb2—I4	99.77 (4)	C6—N2—C5	111.5 (17)
C1—C6	1.52 (3)	I6—Pb2—I5	85.99 (4)	N2—C5—C4	107.7 (19)
N2—C5	1.50 (3)	I3 <sup>iii</sup> —Pb3—I4	170.46 (4)	C4—N3—Pb4	110.0 (12)
N2—C6	1.47 (3)	I3 <sup>iii</sup> —Pb3—I5	87.99 (4)	N4—C3—C2	110 (2)
C5—C4	1.517 (10)	I3 <sup>iii</sup> —Pb3—I7	88.86 (3)	N2—C6—C1	113.6 (16)
N3—C4	1.466 (10)	I4—Pb3—I7	91.42 (4)	C1—N1—C2	112.9 (17)
C3—N4	1.46 (3)	I5—Pb3—I4	89.64 (3)	C1—N1—Pb4	112.9 (13)
		I5—Pb3—I7	167.10 (4)	C2—N1—Pb4	113.0 (12

Table S3 Summary of selected bond lengths (Å) and bond angles (°) of  $\mathbf{2Pb}$ 

*Symmetry codes:* (i) -x+1/2, y-1/2, -z+1/2; (ii) -x+1/2, y+1/2, -z+1/2; (iii) x, y+1, z; (iv) x, y-1, z

D-H	d(D-H)	d(H···A)	<dha< th=""><th>d(D<sup></sup>A)</th><th>Α</th><th></th></dha<>	d(D <sup></sup> A)	Α	
N1-H1A	0.900	2.919	153.44	3.746	I1	[ x-1, y, z]
N1-H1B	0.900	2.767	159.12	3.622	I6	[-x+1, y-1/2, -z+3/2]
N3-H3	0.910	2.934	153.43	3.770	I5	[-x,-y+1,-z+1]
N4-H4A	0.860	2.422	167.03	3.266	N1	
N2-H2	0.910	3.294	118.48	3.813	I4	

Table S4 Potential hydrogen bonding data of compound 1Pb

Table S5 Potential hydrogen data of compound 2Pb

D-H	d(D-H)	d(H···A)	<dha< th=""><th>d(D…A)</th><th>Α</th><th></th></dha<>	d(D…A)	Α	
C2-H2B	0.970	3.279	125.11	3.918	I2	[ x+1/2, y+1/2, z]
N2-H2	0.980	3.249	154.56	4.155	I8	[ x+1, y-1, z]
N3-H3A	0.890	2.890	163.88	3.753	I1	[ x+1/2, y-1/2, z]
N3-H3B	0.890	3.261	122.67	3.816	I3	[-x+1,-y+1,-z]
N4-H4A	0.890	3.085	123.68	3.654	I3	[-x+1,-y+1,-z]
N4-H4A	0.890	3.167	144.59	3.926	15	[-x+1, -y+2, -z]
N4-H4B	0.890	3.276	119.21	3.791	I3	[ x+1/2, y+1/2, z]
C4-H4C	0.970	3.260	131.11	3.966	I6	[-x+1,-y+1,-z]
C4-H4D	0.970	2.983	172.14	3.946	I2	[ x+1/2, y-1/2, z]
C6-H6A	0.970	3.178	128.22	3.855	I6	[ x+1, y, z]
N1-H1	0.980	3.080	146.99	3.938	I8	[ x+1, y, z]

Compds	λex (nm)	λem (nm)	CIE	τ(ns)	Ref
[H <sub>2</sub> BPP]Pb <sub>2</sub> Br <sub>6</sub>	394	524	(0.38, 0.48)	16.57	[6]
[H <sub>2</sub> BPP]Pb <sub>2</sub> Cl <sub>6</sub>	389	538	(0.33, 0.50)	2.7	[6]
$NPM_2Pb_3Br_{10}$	365	447/538	(0.33, 0.44)	4.21	[7]
(y-MPAPB)	365	399/417/470	(0.22, 0.23)	2.52	[8]
$[(Pb_4Cl_2) (ndc)_4 \cdot A_2]_n$	365	388	(0.25, 0.22)	0.73	[9]
$[(Pb_4Br_2) (ndc)_4 \cdot A_2]_n$	365	393/684	(0.34, 0.29)	0.73	[9]
$[(Pb_4I_2) (ndc)_4 \cdot A_2]_n$	365	390/684	(0.33, 0.28)	0.91	[9]

Table S6 Photophysical properties of reported haloplumbate-based hybrids

 $[H_2BPP]: 1,3-bis(4-pyridyl)-propane / NPM: N-propyl-morpholine / \gamma-MPAPB: \gamma-methoxy propyl amine) 2PbBr4/ ndc: naphthalene dicarboxylate; A: (CH_3)_3NH^+ and (CH_3)_2NH_2 + (CH_3)_3NH^+ and (CH_3)_3NH^+ and$ 

Table S7 Comparaison of photodetectors performances for 1Pb and 2Pb with others reported systems

Compounds	D	Voltage (V)	I <sub>light</sub> (nA)	R (µA/W)	D (Jones)	EQE (%)	Ref
1Pb	2D	0.7	636	7.04	6.4*10 <sup>6</sup>	2.39	This work
2Pb	2D	0.7	780	8.457	7.7*10 <sup>6</sup>	2.87	This work
PDBI	0D	1	194	1.14	1.9*10 <sup>6</sup>	0.4	[10]
${(Pb_4Cl_2)(ndc)_4 \cdot [(CH_3)_3NH]_2}_n$	1D	-	380	-	-	-	[9]
$\{[Pb(cbpy)_2](I_3)_4 \cdot I_2\}_n$	2D	0.5	2600	-	-	-	[11]
MAPbI <sub>3</sub>	3D	3	-	3.49*10 <sup>6</sup>	-	1.19*10 <sup>3</sup>	[12]
(C <sub>4</sub> H <sub>9</sub> NH <sub>3</sub> ) <sub>2</sub> PbBr <sub>4</sub>	2D	0.5	-	2.1*108	-	-	[12]
$(I-BA)_2(MA)_2Pb_3I_{10}$	2D	30	1000	12.78	-	-	[13]
Boron	2D	0	-	91.7	1.6*10 <sup>8</sup>	-	[14]
Cs <sub>3</sub> BiBr <sub>6</sub>	0D	6	-	25	6*10 <sup>8</sup>	0.008	[15]
Cs <sub>2</sub> AgBiBr <sub>6</sub>	3D	5	_	900	109	-	[16]

 $\label{eq:pdb1} PDBI: (1,3-propanediammonium)_2Bi_2I_{10}\cdot 2H_2O \ / \ ndc: \ naphthalene \ dicarboxylate \ / \ cbpy: 1-(3-carboxybenzyl)-4,4'-bipyridinium \ / \ MA: \ methylammonium \ / \ BA: \ butylammonium.$ 





Figure S1. (a) Powder XRD patterns of 1Pb. (b) Powder XRD patterns of 2Pb.



# 1Pb

2Pb

Figure S2. Hirshfeld surfaces mapped with dnorm 1Pb (a) and (b) 2Pb (color coding: white, distance d equals VDW distance; blue, d exceeds VDW distance, red, d, smaller than VDW distance).



Figure S3. Two-dimensional finger print plots of 1Pb (a) and 2Pb (c). The population of close contact of 1Pb (b) and 2Pb (d) in crystal stacking.



Figure S4. The Tauc Plot for a direct band gap (a) and for indirect band gap (b) semiconductor of 1Pb and 2Pb.



**Figure S5.** (a) Band structure of **1Pb** with SOC. (b) Band structure of **1Pb** without SOC. (c-f) Partial density of states (PDOS) of compound **1Pb** (inorganic part, organic part, Pb-s, Pb-p, and I-s, I-p).



Figure S6. (a) Band structure of 2Pb without SOC. (b-d) Partial density of states (PDOS) of compound 2Pb (organic part, Pb-s, Pb-p, Pb-d and I-s, I-p).



**Figure S7**. XRD patterns of **1Pb** (a) and **2Pb** (b) thin films after storage in ambient temperature for 7 days (relative humidity of 55%) and after exposing to light for 24 hours.



Figure S8. TGA curves of 1Pb and 2Pb

#### References

- [1] G. M. Sheldrick, Acta Crystallogr. A., 2008, 64, 112-122.
- [2] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K, Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341.
- [3] G. Kresse and J. Furthmüller, Phys. Rev. B: Condens. Matter Mater. Phys., 1996, 54, 11169–11186.
- [4] G. Kresse and J. Furthmüller, Comput. Mater. Sci., 1996, 6, 15–50.
- [5] G. Kresse and D. Joubert, Phys. Rev. B: Condens. Matter Mater. Phys., 1999, 59, 1758– 1775.
- [6] X-Y. Sun, M. Yue, Y-X. Jiang, C-H. Zhao, Y-Y. Liao, X-W. Lei, and C-Y. Yue, Combining Dual-Light Emissions to Achieve Efficient Broadband Yellowish-Green Luminescence in One-Dimensional Hybrid Lead Halides, *Inorg. Chem.* 2021, 60, 1491–1498.
- [7] C-Q. Jing, J-Z. Li, T. Xu, K. Jiang, X-J. Zhao, Y-F. Wu, N-T. Xue, Z-H. Jing and X-W. Lei, Organic cations directed 1D [Pb<sub>3</sub>Br<sub>10</sub>] 4–chains: syntheses, crystal structures, and photoluminescence properties, *CrystEngComm*, 2021, 23, 292-298.
- [8] Y. Li, C. Ji, L. Li, S. Wang, S. Han, Y. Peng, S. Zhang and J. Luo, (γ-Methoxy propyl amine)<sub>2</sub>PbBr<sub>4</sub>: a novel two-dimensional halide hybrid perovskite with efficient bluish white-light emission, *Inorg. Chem. Front*, **2021**, *8*, 2119-2124.
- [9] X-L. Lin, B. Chen, Y-R. Huang, K-Y. Song, P-K. Zhou, L-L. Zong, H-H. Li, Z-R. Chen and R. Jiang, Achievement of intrinsic white light emission by hybridization-deformable haloplumbates with rigid luminescent naphthalene motifs, *Inorg. Chem. Front*, 2020, 7, 4477-4487.
- [10] J. K. Pious, A. Katre, C. Muthu, S. Chakraborty, S. Krishna, and C. Vijayakumar, Zero-Dimensional Lead-Free Hybrid Perovskite-like Material with a Quantum-Well Structure, *Chem. Mater.*, 2019, 31, 1941–1945.
- [11] L-M. Zhao, W-T. Zhang, K-Y. Song, Q-Q. Wu, Y. Li, H-H. Li and Z-R. Chen, Leadcarboxylate/polyiodide hybrids constructed from halogen bonding and asymmetric

viologen: structures, visible-light-driven photocatalytic properties and enhanced photocurrent responses, *CrystEngComm.*, **2018**, *20*, 2245-2252.

- [12] A. Dey, J. Ye, A. De, E. Debroye, S. K. Ha, E. Bladt, A. S. Kshirsagar, Z. Wang, J. Yin, Y. Wang, L. N.Quan, F. Yan, M. Gao, X. Li, J. Shamsi, T. Debnath, M. Cao, M. A. Scheel, S. Kumar, J. A. Steele, M. Gerhard, L. Chouhan, K. Xu, X-g. Wu, Y. Li, Y. Zhang, A. Dutta, C. Han, I. Vincon, A. L. Rogach, A. Nag, A. Samanta, B. A. Korgel, C-J. Shih, D. R. Gamelin, D. H. Son, H. Zeng, H. Zhong, H. Sun, H. V. Demir, I. G. Scheblykin, I. M-Seró, J. K. Stolarczyk, J. Z. Zhang, J. Feldmann, J. Hofkens, J. M. Luther, J. P-Prieto, L. Li, L. Manna, M. I. Bodnarchuk, M. V. Kovalenko, M. B. J. Roeffaers, N. Pradhan, O.F. Mohammed, O. M. Bakr, P. Yang, P. M-Buschbaum, P V. Kamat, Q. Bao, Q. Zhang, R. Krahne, R. E. Galian, S. D. Stranks, S. Bals, V. Biju, W. A. Tisdale, Y. Yan, R. L. Z. Hoye, and L. Polavarapu, State of the Art and Prospects for Halide Perovskite Nanocrystals., *ACS Nano.*, 2021, *15*, 10775–10981.
- [13] X. Tian, Y. Zhang, R. Zheng, D. Wei, and J. Liu, Two-dimensional organic-inorganic hybrid Ruddlesden–Popper perovskite materials: preparation, enhanced stability, and applications in photodetection, *Sustainable Energy Fuels.*, 2020, *4*, 2087-2113.
- [14] D. Ma, R. Wang, J. Zhao, Q. Chen, L. Wu, D. Li, L. Su, X. Jiang, Z. Luo, Y. Ge, J. Li, Y. Zhang and H. Zhang, A self-powered photodetector based on two-dimensional boron nanosheets, *Nanoscale.*, 2020, *12*, 5313-5323.
- [15]Y. Tang, M. Liang, Bi. Chang, H. Sun, K. Zheng, T. Pulleritsd and Q. Chi, Leadfree double halide perovskite Cs<sub>3</sub>BiBr<sub>6</sub> with well-defined crystal structure and high thermal stability for optoelectronics, *J. Mater. Chem. C*, **2019**, *7*, 3369-3374.
- [16] Y. Dang, G. Tong, W. Song, Z. Liu, L. Qiu, L. K. Ono and Y. Qi, Interface engineering strategies towards Cs<sub>2</sub>AgBiBr<sub>6</sub> single-crystalline photodetectors with good Ohmic contact behaviours, *J. Mater. Chem. C.*, **2020**, *8*, 276-284.