# **Supporting Information**

## Vacancy-Ordered Hybrid Two-Dimensional Bi(III) Iodides with (100)-Oriented Dion-Jacobson Perovskite-related Structures

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### **Experimental Section**

**Powder X-ray Diffraction.** Powder X-ray diffraction data for all three compounds were collected using Rigaku X-ray diffractometer equipped with Cu-K $\alpha$  X-ray source of wavelength 1.54184 Å. The crystals were powdered using a mortar-pestle before mounting on the diffractometer. The experimental patterns were compared with those simulated from the single-crystal X-ray diffraction data by using Le Bail whole powder pattern decomposition method.<sup>S1</sup>

**Thermogravimetric Analysis (TGA).** Thermal stability of all the compounds was examined by thermogravimetric analysis using PerkinElmer TGA 8000 Thermogravimetric Analyzer under continuous flow of N<sub>2</sub> gas at 40 ml/min and a heating rate of 5.0 °C/min. The samples were mounted in ceramic pan.

**X-ray Photoelectron Spectroscopy (XPS).** XPS measurements were carried out using Thermo Scientific K-Alpha X-ray Photoelectron Spectrometer System, equipped with microfocused Al K $\alpha$  X-ray source. The binding energies of all the samples calibrated with reference to adventitious carbon peak at 284.4 eV. We have fitted the XPS spectra to pseudovoigt function to calculate the area under curve. The relative sensitivity factor (RSF), <sup>S2</sup> and the method for calculation of elemental composition were adopted from literature. <sup>S3</sup>

**Absorption Spectra.** Diffused reflectance measurements were carried out on PerkinElmer UV/VIS/NIR lambda-750 Spectrophotometer in the range of 400-800 nm by taking BaSO<sub>4</sub> as reference for 100% reflectance. All the samples were diluted with sample to BaSO<sub>4</sub> ratio of 1:3 and bandgaps were estimated using Kubelka-Munk functions as  $F(\mathbf{r}) = (1-R)^2/2R$ , where *R* is reflectance. Also, we ball-milled the crystals using high-energy ball miller (SPEX 8000M) for 5 minutes and recorded the diffused reflectance spectra.

**Photoluminescence Spectra.** Room temperature PL emission spectra of all three compounds were measured on Edinburgh FLS1000 spectrofluorometer with 455 nm filter to avoid scattering. The excited wavelength of 405 nm, 380 nm and 380 nm were used for  $(H_2DAC)PbI_4$ ,  $(H_2DAC)Bi_{2/3}\square_{1/3}I_4$  and  $(H_2DAP)Bi_{1/2}\square_{1/2}I_3 \cdot (I_3)_{1/2}$ , respectively.

**Excited State Lifetimes.** The lifetimes of all the samples were measured on FLS 1000 spectrofluorometer equipped with TCSPC - pulsed diode laser of 405 nm. Lifetime of  $(H_2DAC)PbI_4$ ,  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$  and  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$  were measured at emission wavelength of 580 nm, 640 nm and 660 nm, respectively. As shown in Figure S15, the decays

were fitted to biexponential equation  $I(t) = A+B_1exp(-t/\tau_1) + B_2exp(-t/\tau_2)$  where  $B_1$  and  $B_2$  are fitting parameters which are listed in Table S6 for all the compounds. We calculated their average lifetimes by  $\tau_{avg} = \frac{B_1\tau_1^2+B_2\tau_2^2}{B\tau_1+B\tau_2}$ , where  $B_1$  and  $B_2$  are fitting parameters. (H<sub>2</sub>DAC)PbI<sub>4</sub> shows the fastest decay with the average lifetimes of 2.58 ns. In the case of (H<sub>2</sub>DAC)Bi<sub>2/3</sub> $\Box_{1/3}$ I<sub>4</sub> and (H<sub>2</sub>DAP)Bi<sub>1/2</sub> $\Box_{1/2}$ I<sub>3</sub>·(I<sub>3</sub>)<sub>1/2</sub>, the lifetimes are longer (5.84 ns and 5.09 ns, respectively) which is plausibly due to vacancy, that can create trap states and contributed to non-radiative recombination of charge carriers.<sup>S4</sup>

### Calculation of Bond length deviation ( $\Delta d$ ) and bond angle variance ( $\sigma^2$ )

Bond length deviation ( $\Delta d$ ) and bond angle variance are calculated from the following equations<sup>S5</sup>:

$$\Delta d = \frac{1}{6} \sum \left[ \frac{d_i - d}{d} \right]^2 \tag{S1}$$

$$\sigma^{2} = \sum_{i=1}^{12} \frac{(\theta_{i} - 90)^{2}}{11} \deg^{2}$$
(S2)

where  $d_i$  is the length of i<sup>th</sup> M-X bond, d is the averaged M-X bond length and  $\theta_i$  is the i<sup>th</sup> X-M-X bond angles

Calculation of valence band maxima (EvBM) and conduction band minimum (ECBM) from valence band XPS spectra. Valence band XPS spectra of all three compounds were measured to estimate  $E_{VBM}$  by linearly extrapolating the lower binding energy region.<sup>S6,S7</sup> UV-Vis absorption spectra for all the three compounds provides their respective optical band gap (E<sub>g</sub>) which could be found from Figure 5a. Now, if we consider Fermi level  $E_F$  at zero and  $E_{VBM}$  levels below  $E_F$  we estimated their respective  $E_{CBM}$  by subtracting their  $E_{VBM}$  values from their optical bandgaps (E<sub>g</sub>).<sup>S8</sup>

**Table S1.** Selected bond lengths and bond angles of  $(H_2DAC)PbL_4$ . Non-bonding N····I distances are also provided.

Bond lengths (Å) Pb1-I1 = $3.1798(5) \& 3.1799(5)$ Pb1-I2 = $3.2394(6) \times 2 \& 3.2112(5) \times 2$ N1I1 = $3.692, 3.594$ N1I2 = $3.727$	Bond angles (°) I1-Pb1-I2 = 93.233(13), 86.766(13), 86.767(13), 86.767(13), 93.233(13), 90.557(13), 89.443(13), 90.557(13) cis I2-Pb1-I2 = 96.323(8), 96.324(9), 83.677(8), 83.676(9) trans I2-Pb1-I2 = $180.0 \times 2$ trans I1-Pb1-I1= $180.0$
	Pb1-I2-Pb1 = 146.407(18)

**Table S2.** Selected bond lengths and bond angles of  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$ . Non-bonding N····I distances are also provided.

Bond lengths (Å)	Bond angles (°)
Bi1-I1 = 3.1522(5)	I5-Bi1-I2 = 94.809(14)
Bi1-I1 = 3.4070(5)	I5-Bi1-I3 = 93.827(15)
Bi1-I2 = 3.0021(5)	I2-Bi1-I3 = 91.270(14)
Bi1-I3 = 3.0158(5)	I5-Bi1-I1 = 91.025(15)
Bi1-I4 = 3.1566(6)	I2-Bi1-I1 = 91.307(15)
Bi1-I5 = 2.9008(6)	I3-Bi1-I1 = 174.298(12)
$N1 \cdots I1 = 3.607(5)$	I5-Bi1-I4 = 93.700(12)
$N1 \cdots I6 = 3.551(6)$	I2-Bi1-I4 =171.417(11)
$N1 \cdots I2 = 3.656(5)$	I3-Bi1-I4 = 87.035(14)
$N2 \cdots I4 = 3.673(5)$	I1-Bi1-I4 = 89.666(15)
$N2 \cdots I6 = 3.517(5)$	I5-Bi1-I1 = 175.470(12)
$N2 \cdots I3 = 3.655(5)$	I2-Bi1-I1 = 87.164(12)
$N3 \cdots I6 = 3.546(5)$	I3-Bi1-I1 = 82.040(13)
$N3\cdots I4 = 3.652(5)$	I1-Bi1-I1 = 93.009(10)
$N3\cdots I1 = 3.607(4)$	I4-Bi1-I1 = 84.269(11)
	Bi1-I1-Bi1=147.928(15)

**Table S3.** Selected bond lengths and bond angles of  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$ . Non-bonding N...I distances are also provided.

Bond lengths (Å)	Bond angles (°)
$Bi1-I1 = 3.0975(10) \times 2$	I2-Bi1-I2 = 180.0
$Bi1-I2 = 3.0517(8) \times 2$	I2-Bi1-I3 = 90.0
$Bi1-I3 = 3.0529(8) \times 2$	I3-Bi1-I3 = 180.0
$I4\cdots I5 = 2.9169(11)$	I2-Bi1-I1 = 88.09(3) & 91.91(3)
$N1 \cdots I1 = 3.783(10)$	$I3-Bi1-I1 = 90.0 \times 2$
$N1 \cdots I2 = 3.741(11)$	I3-Bi1-I1 = 90.0
$N1 \cdots I4 = 3.887(10)$	I1-Bi1-I1 = 180.0
	I4-I5-I4 = 179.94(8)



**Figure S1.** X-Ray structures of (a)  $(H_2DAC)PbI_4$  (b)  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$ , showing tilted orientation of the  $H_2DAC$  di-cations.



depth of penetration = **0.754** Å

**Figure S2.** Penetration depth of organic diamine cations into the plane passing through the axial iodide anion of inorganic framework of (a) (H<sub>2</sub>DAC)PbI<sub>4</sub>, (b) (H<sub>2</sub>DAC)Bi<sub>2/3</sub> $\Box_{1/3}$ I<sub>4</sub> and (c) (H<sub>2</sub>DAP)Bi<sub>1/2</sub> $\Box_{1/2}$ I<sub>3</sub>·(I<sub>3</sub>)<sub>1/2</sub>. The depth of penetration is the distance between the -NH<sub>3</sub><sup>+</sup> group of spacer and the plane passing through the axial iodine ions.



**Figure S3.** Hirshfeld surfaces of  $[BiI_6]^{3-}$  unit of  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$ , showing intermolecular interactions (a, b) I $\cdots$ I and (c, d) N–H $\cdots$ I.



**Figure S4.** Hirshfeld surfaces of  $[BiI_6]^{3-}$  unit of  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$ , showing intermolecular interactions (a, b) N–H···I and (c, d) I···I.



Figure S5. PXRD patterns of (a)  $(H_2DAC)PbI_4$ , (b)  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$  and (c)  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$ .



Figure S6. XPS survey spectrum of (H<sub>2</sub>DAC)PbI<sub>4</sub>.



Figure S7. XPS survey spectrum of  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$ .



Figure S8. XPS survey spectrum of  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$ .



Figure S9. Core level N(1s) and C(1s) XPS spectra of (H<sub>2</sub>DAC)PbI<sub>4</sub>.



Figure S10. Core level N(1s) and C(1s) XPS spectra of  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$ .



Figure S11. Core level N(1s) and C(1s) XPS spectra of  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$ .

Table S4. Binding energies (eV) obtained from XPS spectra.

Elements	(H <sub>2</sub> DAC)PbI <sub>4</sub>	$(H_2 DAC) Bi_{2/3} \square_{1/3} I_4$	$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$
C 1s	284.4, 285.7	284.4, 285.7	284.4, 285.7
N 1s	401.2	401.2	401.1
I 3d <sub>5/2</sub>	618.5	618.5	618.5
I 3d <sub>3/2</sub>	630.1	630.1	630.0
Pb 4f <sub>7/2</sub>	137.5	-	_
Pb 4f <sub>5/2</sub>	142.5	-	-
Bi 4f <sub>7/2</sub>	-	158.4	158.1
Bi 4f <sub>5/2</sub>	-	163.6	163.3

**Table S5**. Fitting parameters to calculate the ratio of iodine to metal by XPS. RSF = Relative sensitivity factor.

Compound	Elements	Peak area	RSF	Peak area /RSF	Ratio
(H <sub>2</sub> DAC)PbI <sub>4</sub>	I 3d <sub>5/2</sub>	851720	6.21	137374.2	Pb:I = 1:4.13
(H <sub>2</sub> DAC)PbI <sub>4</sub>	Pb 4f <sub>7/2</sub>	158230	4.76	33241.6	
(H <sub>2</sub> DAC)Bi <sub>2/3</sub>	I 3d <sub>5/2</sub>	904329	6.21	1,45,624.6	Bi:1 = 1:5.53
(H <sub>2</sub> DAC)Bi <sub>2/3</sub>	Bi 4f <sub>7/2</sub>	137430	5.22	26,327.5	
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	I 3d <sub>5/2</sub>	520320	6.21	83,787.4	Bi:I = 1:7.13
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	Bi 4f <sub>7/2</sub>	61313.3	5.22	11,745.8	



Figure S12. TGA plot of (H<sub>2</sub>DAC)PbI<sub>4</sub>.



Figure S14. TGA plot of  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$ .



Figure S15. Time-resolved photoluminescence (TRPL) spectra of  $(H_2DAC)PbI_{4,}$   $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$  and  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$ .

**Table S6.** Fitting parameters for time resolved photoluminescence spectra.

Compounds	<b>B</b> <sub>1</sub>	<b>B</b> <sub>2</sub>	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_{avg}(ns)$	$\chi^2$
(H <sub>2</sub> DAC) PbI <sub>4</sub>	2310.456	457.166	0.85	4.69	2.85	1.173
$(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$	2127.5	470.4	1.36	8.92	5.84	1.255
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	4166.770	1338.656	2.04	7.65	5.09	1.231



Figure S16. Valence band XPS spectrum of (H<sub>2</sub>DAC)PbI<sub>4</sub>.



Figure S17. Valence band XPS spectrum of  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$ .



Figure S18. Valence band XPS spectrum of  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$ .



**Figure S19.** Optimized structure of (H<sub>2</sub>DAC)PbI<sub>4</sub>. Colour codes for different atoms are Red-Pb, Purple-I, Brown-C, Yellow-H, Blue-N.



**Figure S20.** Optimized structure of  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$ . Colour codes for different atoms are Red-Bi, Purple-I, Brown-C, Yellow-H, Blue-N.



**Figure S21.** Optimized structure of  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$ . Colour codes for different atoms are Red-Bi, Purple-I, Brown-C, Yellow-H, Blue-N.

**Table S7.** Effective mass of electrons and holes as calculated from band structures for all the three compounds in different directions.

Compounds	Directions	me	m <sub>h</sub>
(H <sub>2</sub> DAC)PbI <sub>4</sub>	[0.50, 0.00, 0.00] (Z) -> [0.50, 0.00, 0.50] (D)	-	-0.585
(H2DAC)PbI4	[0,00,0,00,0,00] (E) > [0,00,0,00,0,50] (X)	0.318	-
	[0.00, 0.00, 0.00] (1) -> [0.00, 0.00, 0.30] (1)	0.510	
(H <sub>2</sub> DAC)Bi <sub>2/3</sub>	[0.11, 0.00, 0.50] -> [0.50, 0.00, 0.50]	-	-0.874
$(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$	[0.11, 0.00, 0.50] -> [0.00, 0.00, 0.50] (Y)	-	-0.795
(H <sub>2</sub> DAC)Bi <sub>2/3</sub>	[0.32, 0.00, 0.50] -> [0.50, 0.00, 0.50]	17.021	-
(H <sub>2</sub> DAC)Bi <sub>2/3</sub>	[0.32, 0.00, 0.50] -> [0.00, 0.00, 0.50] (Y)	6.079	-
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	$[0.00, 0.00, 0.00] (\Gamma) \rightarrow [0.00, 0.50, 0.00] (S)$	-	-0.818
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	$[0.00, 0.00, 0.00] (\Gamma) \rightarrow [-0.50, 0.50, 0.00] (Y)$	-	-0.820
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	$[0.00, 0.00, 0.00] (\Gamma) \rightarrow [0.00, 0.50, 0.00] (S)$	-	-0.824
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	$[0.00, 0.00, 0.00] (\Gamma) \rightarrow [0.00, 0.00, 0.50] (Z)$	-	-0.825
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	$[0.00, 0.00, 0.00] (\Gamma) \rightarrow [0.00, 0.00, 0.50] (Z)$		Not defined

$(H_2 DAP) Bi_{1/2} \Box_{1/2} I_3 \cdot (I_3)_{1/2}$	$[-0.50, 0.50, 0.00] (Y) \rightarrow [0.00, 0.00, 0.00] (\Gamma)$	0.807	-
$(H_2 DAP) Bi_{1/2} \Box_{1/2} I_3 \cdot (I_3)_{1/2}$	[-0.50, 0.50, 0.00] (Y) -> [-0.50, 0.50, 0.50] (T)	0.618	-
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	$[-0.50, 0.50, 0.00] (Y) \rightarrow [0.00, 0.00, 0.00] (\Gamma)$	0.701	-
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	[-0.50, 0.50, 0.00] (Y) -> [-0.49, 0.51, 0.00] (X)	Not defined	



**Figure S22.** I-V curves for compound (a)  $(H_2DAC)PbI_4$  (b)  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$  and (c)  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$ . While the linearity of I-V indicates that silver makes an Ohmic contact with the compounds, the increased current in the presence of light shows the positive photo-response of the compounds. Transient photoresponse of compounds (d)  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$  and (e)  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$  without background subtraction which reveals a decreasing background current under the applied electric field irrespective of the illumination.



Figure S23. Transient photocurrents rise and decay for (H<sub>2</sub>DAC)Bi<sub>2/3</sub>□<sub>1/3</sub>I<sub>4</sub>.

**Table S8.** Variations of photocurrent among the five cycles of  $(H_2DAC)PbI_4$  calculated from the I-t curve presented in Figure 9a.

Cycle	Ilight (nA)	Idark(nA)	ΔΙ
1	8.32	2.19	6.13
2	7.54	2.03	5.51
3	7.36	1.89	5.47
4	7.24	1.99	5.25
5	7.10	1.83	5.27

**Table S9.** Variations of photocurrent among the five cycles in  $(H_2DAC)Bi_{2/3}\Box_{1/3}I_4$  calculated from the I-t curve presented in Figure 9b.

Cycle	Ilight (nA)	Idark(nA)	ΔI
1	27	20	7
2	24.98	17.94	7.04
3	22.7	16.7	6
4	20.7	14.5	6.2
5	17.98	13.7	4.28

**Table S10.** Variations of photocurrent among the five cycles of  $(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$  calculated from the I-t curve presented in Figure 9c.

Cycle	Ilight (nA)	Idark(nA)	ΔΙ
1	350	279	71
2	338.8	261.2	77.6
3	310.8	239.6	71.2
4	280	214	66
5	250	200	50

**Table S11.** Device performance for some bismuth-related lead-free low dimensional systems.

Compounds	Photoresponse	Source	Ilight/Idark	$\Delta I =$	Device	Ref.
	type			$I_{light}$ - $I_{dark}$		
Cs <sub>3</sub> Bi <sub>2</sub> Cl <sub>9</sub>	Negative	-	-	-	Crystal	S9
Cs <sub>3</sub> Bi <sub>2</sub> Br <sub>9</sub>	Negative				Crystal	S10
$(TMP)_{1.5}[Bi_2I_7Cl_2]$	Positive	25V, 450W Xe lamp	3.2	0.44uA	Pellet	S11
(H2MPP)2[BiAgI8]	Positive	10V, 350W Xe lamp	4.7	15.06nA	Pellet	S12
$(C_3H_{12}N_2)_2Bi_2I_{10}\cdot 2H_2O$	Positive	1V, 350 μW/cm <sup>2</sup> Xe lamp	2.1	100 nA	Film	S13
$(C_6H_{13}N)_2BiI_5$	Positive	10 V, Xe lamp	2.9	4.9 nA	Film	S14
$(H_2 DAC) Bi_{2/3} \square_{1/3} I_4$	Positive	10 V, 100 mW/cm <sup>2</sup> Xe lamp	1.4	7 nA	Pellet	This work
$(H_2DAP)Bi_{1/2}\Box_{1/2}I_3 \cdot (I_3)_{1/2}$	Positive	10 V, 100 mW/cm <sup>2</sup> Xe lamp	1.3	71 nA	Pellet	This work

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