## **Supplementary Information for**

Liquid-based cationic ligands engineering in one-dimensional bismuth bromide perovskites: A-site influence on scintillation properties

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Fig. S1. A photograph of (a)  $BMPBiBr_4$  and (b)  $APIBiBr_5$  microcrystals incorporated into the polydimethylsiloxane (PDMS) resin.



Fig. S2. SEM micrograph of (a)  $BMPBiBr_4$  and (b)  $APIBiBr_5$  incorporated with PDMS. The crystal was grinded before the analysis.



Fig. S3. The Rietveld refinement of (a)  $BMPBiBr_4$ , (b)  $BMIBiBr_4$ , (c)  $APIBiBr_5$ , (d)  $APISnBiBr_5$ , and (e)  $APISn_2Br_{10}$  using FullProf software. The resulting parameters are tabulated in Table S1.



**Fig. S4.** (a)–(d) are the XPS core level spectra of C 1s, N 1s, Sn 3d, Br 3d, respectively from APISn<sub>2</sub>Br<sub>10</sub>.

It can be seen that the chemical constituent elements of  $APISn_2Br_{10}$  are clearly observed using XPS spectroscopy measured at room temperature. C 1s core level spectra show four deconvoluted peaks at the binding energy (BE) of 281.4 eV, 284.4 eV, 285.2 eV, and 286 eV attributed to C<sub>aliphatic</sub>, N–C–C, C=C–N, and N=C–N, respectively.<sup>1, 2</sup> Three peaks that appeared in N 1s spectra are correlated to the number of nitrogen atom in API structure. C–NH<sub>2</sub>, quaternary N, and C=N–C are observed at 397.8 eV, 399.1 eV, and 399.9 eV. In Sn 3d spectra, two characteristic peaks, including Sn 3d<sub>5/3</sub> and Sn 3d<sub>3/2</sub>, where each peak consists of Sn<sup>2+</sup> and Sn<sup>4+</sup>. In fact, the precursor of Sn is Sn (IV). The existence of Sn<sup>2+</sup> in both samples reveals that the chemical reduction also takes place during the synthesis procedure.<sup>3</sup> The result is in agreement with previous reported work.<sup>4</sup> The Br 3d shows two deconvoluted peaks correlated with Br  $3d_{5/2}$  and Br  $3d_{3/2}$ . Compared to APIBiBr<sub>10</sub> and APISnBiBr<sub>5</sub>, the observed BE in C 1 spectra is shifted towards lower energy due to the change of resulting geometry, affecting the electron density in the perovskite structure. Meanwhile, BE in N 1s shifts toward higher energy. The highest BE shifting is observed in C–NH<sub>2</sub> since that element directly connects with the terminal Br of [SnBr<sub>6</sub>]<sup>2-</sup>, decreasing the electron density in C–NH<sub>2</sub>.



**Fig. S5.** Left panel, center panel, and right panel are the absorption and photoluminescence profile, time-resolved photoluminescence, and Elliot formalism of samples, including BMPBiBr<sub>4</sub>, BMIBiBr<sub>4</sub>, APIBiBr<sub>5</sub>, APISnBiBr<sub>5</sub>, and APISn<sub>2</sub>Br<sub>10</sub>, respectively.

All prepared bismuth-based hybrid perovskites exhibit similar absorption profile with the variety of intensity. All samples show the sensitivity in UV light and visible light irradiation, with the absorption edge of approximately 430 nm. The variety of absorption intensity is related to the difference of orbital chemistry due to the ionic liquids (IL). Consequently, the band gap of all bismuth-based hybrid perovskite is variety ranging from 3.01 eV to 3.19 eV. The difference of IL arranges the hybridization of Bi 5s–Br 5p and generate the different octahedral tilting.<sup>5</sup> The presence of Sn in bismuth-based hybrid perovskite decreases the octahedral tilting, resulting in wide band gap compared to the pristine bismuth-based hybrid perovskite. This finding is similar to the band gap of tin-based hybrid perovskite has smaller octahedral tilting compared to bismuth-based hybrid perovskite.

In photoluminescence (PL) profile, BMPBiBr<sub>4</sub> shows the asymmetrical PL spectra with maxima at 490 nm, whereas APIBiBr<sub>5</sub> and BMIBiBr<sub>4</sub> exhibit the symmetrical board PL spectra with maxima at 553 nm and 529 nm, respectively. IL has different nitrogen numbers and affects the PL profile of bismuth-based hybrid perovskite. Additionally, the presence of double bond in API structure leads to the large PL peak shift compared to BMP and BMI. All bismuth-based hybrid perovskite exhibit large Stokes shift due to the strong lattice deformation as a result of trapping process.<sup>6, 7</sup> The time-resolved PL (TRPL) shows that APIBiBr<sub>5</sub> has the fastest decay compared to BMPBiBr<sub>4</sub> and BMPBiBr<sub>4</sub>. The addition of Sn in APIBiBr<sub>5</sub> decreases the decay due to the decrease in octahedral tilting after the substitution of Sn. In line, the decay of tin-based hybrid perovskite is low compared to bismuth-based hybrid perovskite, indicating that tin-based hybrid perovskite.



**Fig. S6.** (a)–(e) and (f)–(j) are the heating profile and thermoluminescence glow curve of perovskite, including BMPBiBr<sub>4</sub> (a, f), BMIBiBr<sub>4</sub> (b, g), APIBiBr<sub>5</sub> (c, h), APISnBiBr<sub>5</sub> (d, i), and APISn<sub>2</sub>Br<sub>10</sub> (e, j).



**Fig. S7.** Radiation hardness of the prepared ILs-based bismuth halide perovskite in the double log-scale.

The effect of the radiation power to the linewidth and intensity of X-ray luminescence was investigated as a function of X-ray tube with high voltage ranging from 15 to 45 kV and a current ranging of 5 and 10 mA. The output dose ( $D_{out}$ , in the unit of  $\mu Sv/h$ ) was calculated following Eq. 1 below.

$$D_{out} = K \times h \times V^2 \times I \times t \times \frac{1}{d^2}$$

where *K* is the constant value (K = 3.265, in the unis of  $(\mu Sv \cdot mm^2)(mA \cdot s \cdot kV^2)^{-1}$ ), *h* is the second-to-hour conversion factor ( $h = 720 h^{-1}$ ), *V* is the peak tube voltage (kV), *I* is the current supply (mA), *t* is the exposure time (5 s), and *d* is the distance (500 mm).

Compound name	BMPBiBr <sub>4</sub>	APIBiBr <sub>5</sub>	APIBiSnBr <sub>5</sub>	APISn <sub>2</sub> Br <sub>10</sub>	BMIBiBr <sub>4</sub>
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	P -1	P -1	P -1	P -1	P -1
$\chi^2$	127	51	9.267	10.9	82.9
Bragg R-factor	3.91	3.85	3.22	3.43	1.23
$R_{\rm f}$ -factor	3.55	6.15	2.04	6.08	0.695
R <sub>p</sub>	51.4	50.1	30.3	46.6	71.8
$R_{wp}$	64.9	53.5	37.5	48.5	85.7
R <sub>e</sub>	5.75	7.49	12.3	14.69	9.42
a/Å	17.196392	15.7941	19.8608	19.8920	17.5097
b/Å	9.145605	27.2069	27.1741	27.1115	8.4839
c/Å	8.004331	7.9536	8.0433	8.0228	9.0017
$\alpha/^{\circ}$	94.596	90	90	90	89.1031
β/°	130.531	94.8090	94.961	94.946	129.8023
$\gamma^{/\circ}$	78.444	90	90	90	85.7322
V/Å <sup>3</sup>	935.2827	3405.7034	4324.7329	4310.6069	1020.9689
2θ range	$5^\circ - 80^\circ$	$5^{\circ} - 80^{\circ}$	$5^\circ - 80^\circ$	$5^\circ - 80^\circ$	$5^\circ - 80^\circ$
GoF index	11	7.1	3	4.6	9.1
N sigma of GoF	834.880	2074.532	368.639	906.996	3403.114

Table S1. Summary of parameters obtained from Rietveld refinement of diffraction patterns.

Parameter -			Sample		
	BMPBiBr <sub>4</sub>	BMIBiBr <sub>4</sub>	APIBiBr <sub>5</sub>	APISnBiBr <sub>5</sub>	APISn <sub>2</sub> Br <sub>10</sub>
Bi–Br (Å)	$2.8286 \pm$	$2.8710 \pm$	$2.9457 \pm$	$3.1094 \pm$	
	0.1031	0.2969	0.1147	0.2976	_
Sn-Br (Å)	_	_	_	$3.0433 \pm$	$2.9002 \pm$
				0.1570	0.1092
Bi–Br–Br (°)	169.9942	156.3230	157.2238	158.3290	_
Bi–Br–Sn (°)	_	_	_	172.7167	_
Sn-Br-Sn (°)	_	_	_	156.2745	159.3690
Br-Br-Br (°)	93.0707	103.502	114.7456	115.3810 <sup>a</sup>	111.2690
				117.0919 <sup>b</sup>	

**Table S2** The Bi–Br bond length, Bi–Br–Bi bond angle, and Br–Br–Br bond angle extracted

 from CIF file using Vesta.

<sup>a</sup> measured between BiBr<sub>6</sub> octahedral; <sup>b</sup> measured between SnBr<sub>6</sub> octahedral

## **Computational details**

DFT calculations were carried out under the Kohn–Sham formulation<sup>8, 9</sup> as implemented in the Vienna Ab–initio Simulation Package (VASP).<sup>10, 11</sup> The Projector Augmented Wave (PAW) method was used to describe the interaction between ion cores and electrons.<sup>12, 13</sup> The electron exchange–correlation was treated by the generalized gradient approximation (GGA) based on the Perdew–Burke–Ernzerhof (PBE) functional.<sup>14</sup> The plane wave basis sets with a cut-off energy of 500 eV were used for all calculations. The Brillouin zone with k-point grid of  $1 \times 3 \times 3$  for BMPBiBr<sub>4</sub> and BMPBiBr<sub>4</sub>,  $1 \times 1 \times 3$  for APIBiBr<sub>5</sub> and APIBiSnBr<sub>5</sub>, and  $5 \times 1 \times 5$  for APISn<sub>2</sub>Br<sub>10</sub> according to the Monkhorst-Pack scheme was used.<sup>15</sup> The zero-damping D3 method was adopted to account for the dispersion correction.<sup>16</sup> During calculations, all atoms were allowed to fully relax. The conjugate gradient method was employed for cell optimizations, and the calculations were considered to converge when the maximum forces on all atoms were less than 0.01 eV/Å.

## References

- 1. A. W. Taylor, S. Men, C. J. Clarke and P. Licence, *RSC Adv.*, 2013, **3**, 9436-9445.
- 2. S. Men, K. R. J. Lovelock and P. Licence, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15244-15255.

- 3. M. M. Byranvand, W. Zuo, R. Imani, M. Pazoki and M. Saliba, *Chemical Science*, 2022, **13**, 6766-6781.
- R. Subagyo, P. Y. D. Maulida, D. Kowal, S. Hartati, R. M. Muslimawati, Y. Zetra, L. J. Diguna, S. Akhlus, M. H. Mahyuddin, L. Zhang, C. S. Tang, C. Diao, A. T. S. Wee, M. D. Birowosuto, Arramel, A. Rusydi and Y. Kusumawati, ACS Appl. Mater. Interfaces, 2023, 15, 54677-54691.
- 5. A. Filippetti, S. Kahmann, C. Caddeo, A. Mattoni, M. Saba, A. Bosin and M. A. Loi, *J. Mater. Chem. A*, 2021, **9**, 11812-11826.
- 6. J. Yin, H. Li, D. Cortecchia, C. Soci and J.-L. Brédas, ACS Energy Letters, 2017, **2**, 417-423.
- 7. A. Mahata, D. Meggiolaro and F. De Angelis, J. Phys. Chem. Lett., 2019, **10**, 1790-1798.
- 8. P. Hohenberg and W. Kohn, *Phys. Rev.*, 1964, **136**, B864-B871.
- 9. W. Kohn and L. J. Sham, *Phys. Rev.*, 1965, **140**, A1133-A1138.
- 10. G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15-50.
- 11. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
- 12. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
- 13. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.
- 14. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- 15. H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188-5192.
- 16. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, **132**, 154104.