## **Supplementary Information**

## Low-dimensional hybrid perovskites as high performance anodes for alkali-ion batteries

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Fig. S1 Experimental and simulated powder x-ray diffraction (PXRD) patterns of 1D Bz-Pb-I

hybrid perovskite



Fig. S2 PXRD pattern for 1D Bz-Pb-I, 2D BA<sub>2</sub>PbI<sub>4</sub>, 3D MAPbI<sub>3</sub> hybrid perovskite



Fig. S3 Growth of PbI<sub>6</sub> octahedra in 1D, 2D, 3D hybrid perovskite cases (a) Growth of twin chain of octahedra in one direction for 1D Bz-Pb-I case (b) Growth of octahedra in two directions for 2D BA<sub>2</sub>PbI<sub>4</sub> case (c) Growth of octahedra in all three directions for 3D MAPbI<sub>3</sub>

case



Fig. S4 Areal capacity of 1D, 2D, 3D hybrid perovskites at current density of 100 mA g<sup>-1</sup> for

Li-ion cell



Fig. S5 Rate performance of 1D Bz-Pb-I at different current densities of 50, 100, 250, 500, 1000 mA g<sup>-1</sup> and reversing back to 100 mA g<sup>-1</sup> for Li-ion cell



Fig. S6 Charge Discharge profiles of 2D and 3D hybrid perovskite (a) charge discharge profiles of 2D  $BA_2PbI_4$  at a current density of 100 mA g<sup>-1</sup> (b) charge discharge profiles of 3D MAPbI<sub>3</sub> at a current density of 100 mA g<sup>-1</sup>



Fig. S7 Charge discharge profile of 1D, 2D, 3D hybrid perovskites at a current density of 100 mA g<sup>-1</sup>. First discharge profile of all the three hybrid perovskite cases. In inset 1<sup>st</sup> charging and 2<sup>nd</sup> discharging profiles are illustrated.



Fig. S8 Charge discharge cyclic stability of benzidine and lead iodide for Li-ion half cells at

100 mA g<sup>-1</sup>



Fig. S9 Electrochemical performance of 1D Bz-Pb-I hybrid perovskitefor Na ion half Cell (a)
Cyclic voltammogram of Bz-Pb-I at a scan rate of 0.1 mV s<sup>-1</sup> in a potential window of 0.01 2.5 V and (b) Charge discharge profiles of Bz-Pb-I recorded at a current density of 100 mA

g-1



Fig. S10 Charge discharge cyclic stability of benzidine at a current density of 100 mA g<sup>-1</sup> for

Na-ion battery



Fig. S11 Photograph of opened  $PbI_2$  Na ion half-cell by interrupting the 1<sup>st</sup> charging process



**Fig. S12** X-ray diffraction patterns of Bz-Pb-I electrodes after 1<sup>st</sup> discharge cyclesfor Na ion half-cell. (Cu peaks are from the current collector substrate)



**Fig. S13** FE-SEM images of 1D Bz-Pb-I hybrid perovskite electrodes before and after 1<sup>st</sup> discharge (a)1D Bz-Pb-I hybrid perovskite fresh electrodes (b) 1D Bz-Pb-I hybrid perovskite electrode after 1<sup>st</sup> discharge cycle for Li ion battery case (c) 1D Bz-Pb-I hybrid perovskite electrode after 1<sup>st</sup> discharge cycle for Na ion battery case. Scale bar 10 μm.

Formula	C <sub>6</sub> H <sub>9</sub> I <sub>3</sub> NOPb
FW	699.03 g/mol
Т,К	100
Crystal system, space group	Monoclinic, $P 2_l/c$
<i>a</i> , Å	4.481 (3)
b,Å	13.193(9)
<i>c</i> , Å	22.544(15)
$\beta$ , deg	89.879(13)
$V, Å^3$	1332.7 (16)
Z, Calculated density	4, 3.484
$\mu$ , mm <sup>-1</sup>	19.573
<i>F</i> (000)	1204.0
Crystal size, mm <sup>3</sup>	0.050 x 0.060 x 0.140 mm
R <sub>int</sub>	0.0723
Data/ restraints/parameters	2353 / 72 / 81
Goodness-of-fit on F <sup>2</sup>	1.387
Final <i>R</i> indices [ I>2 sigma(I)] <sup>b</sup>	R1 = 0.0722, wR2 =
	0.1792
Final <i>R</i> indices [ all data]	R1 = 0.0740, wR2 =
	0.1798

**Table S1.** Crystallographic data and structure refinement details

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**Table S2:** Performance of hybrid perovskite materials for Li and Na ion half cell at different stages of cyclic stability.

	Li-ion half cell		Na-ion half cell			
Anode material	1 <sup>st</sup> discharge specific capacity (mAh g <sup>-1</sup> )	Reversible discharge capacity (mAh g <sup>-1</sup> )	50 <sup>th</sup> discharge capacity (mAh g <sup>-1</sup> )	1 <sup>st</sup> discharge specific capacity (mAh g <sup>-1</sup> )	Reversible discharge capacity (mAh g <sup>-1</sup> )	50 <sup>th</sup> discharge capacity (mAh g <sup>-1</sup> )
(1D) C <sub>6</sub> H <sub>9</sub> I <sub>3</sub> NOPb	1580	646	585	961	313	107
(2D) (C <sub>4</sub> H <sub>9</sub> NH <sub>3</sub> ) <sub>2</sub> PbI <sub>4</sub>	1605	508	213	-	-	-
(3D) CH <sub>3</sub> NH <sub>3</sub> PbI <sub>3</sub>	476	202	160	-	-	-

Note S1. Single crystal X-ray diffraction analysis:

For structure determination, a hand-picked crystal was mounted on nylon Cryo loops with Paratone-N oil. Single-crystal data was collected on a Bruker Apex duo Diffractometer with CCD detector with a Mo Kα radiation (0.71073 Å). Data was integrated using Bruker SAINT Software and was corrected for absorption using SADABS. Structure was solved by intrinsic phasing module of the direct methods and refined using the SHELXTL 2014 software suite. All non-hydrogen atoms were located from iterative examination of difference F-maps following which the structure was refined using least-squares method. Thermal parameters for all non-hydrogen atoms were refined anisotropically, if not stated otherwise.Disorder in the (Benzidene) BZ molecules was modeled by constraining the occupancies of disordered corner C-C atoms to be of equal probability respectively, while constraining the sum of the occupancies to unity. Similar rigid-body restraints were also applied to atoms not involved in the disorder to stabilize the refinement. Hydrogen atoms were placed geometrically and placed in a riding model. Details regarding the data quality and a summary of residual values of the refinement are listed in Supplementary Table S1.

## Note S2. Electrochemical measurement for Na ion half cell

Supplementary Fig. S9a shows the cyclic voltammogram of Bz-Pb-I at a scan rate of 0.1 mV s<sup>-1</sup> for Na battery case. Literature depicts that the reactions of Li<sup>+</sup> are analogous to Na<sup>+</sup> for lead based materials, basic charge storage mechanism being alloying-dealloying processes of Pb with Li<sup>+</sup>/Na<sup>+</sup>. In CV the reduction processes represent the alloying reactions of Pb with sodium and oxidation processes represent the corresponding de-alloying reactions. In the first CV cycle the reduction peaks appearing at 2.5, 1.91, 1.6 V can be attributed to the intercalation of Na<sup>+</sup> and reduction of Pb(II) to Pb(0). The peak at 0.9 V represents the SEI formation and below 0.6 V alloying reactions of Pb with sodium (NaPb<sub>3</sub>, NaPb, Na<sub>5</sub>Pb<sub>2</sub>, Na<sub>15</sub>Pb<sub>4</sub>) are likely to happen. The oxidation peaks at 0.28, 0.45, 0.57 V in the first cycle of CV can be ascribed to the de-alloying processes. However the oxidation peaks at 1.86 and 2.0 V start disappearing in the subsequent cycles depicting that the oxidation of Pb(0) to Pb(II) is irreversible, as shown in the case of Li-ion battery. From the CV it is clear that after a few initial cycles the alloying/dealloying processes dominate the charge-discharge performance like in the case of lithium. The charge discharge profiles at constant current density 100 mA g<sup>-1</sup> for Bz-Pb-I are shown in Supplementary Fig. S9b. In the first discharge cycle the plateau above 1.5 V represents the reduction of Pb(II) to Pb(0) and plateau below 1.5 V represents the SEI formation and the multistep Na<sub>x</sub>Pb alloy formation. Though multistep alloy formation processes are not clearly seen in charge discharge profiles it can be clearly seen from the CV measurements. The first charging cycle shows the corresponding de-alloving reactions. However the step around 2 V gradually disappears after few charging discharging cycles reflecting the irreversibility of the Pb(0) to Pb(II) oxidation process. Hence the alloying/dealloying reactions dominate the performance after few initial charging discharging cycles.