Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Informataion

Understanding the Role of Spacer Cation in 2D Layered Halide Perovskites to achieve stable perovskite solar cell

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Contents

Figure S1: Optimized geometries of (a) (2-PyrEA)PbI_4, (b) (3-PyrEA)PbI_4, (c) (4-PyrEA)PbI_4

Table S1: The detailed structural parameters of 2D-LHPs.

Table S2: Bond angle and bond lengths of 2D-LHPs.

Figure S2: Structural features of (a) $(BA)_2PbI_4$, (b)$(PEA)_2PbI_4$, (c) (2-PyrEA)PbI_4, (d) (3-PyrEA)PbI_4 and (e) (4-PyrEA)PbI_4

Figure S3: Projected density of states of (2-PyrEA)PbI_4, (3-PyrEA)PbI_4 and (4-PyrEA)PbI_4 using HSE06+SOC method

Figure S4: Calculated band structures of (2-PyrEA)PbI_4, (3-PyrEA)PbI_4 and (4-PyrEA)PbI_4 using PBE+SOC method.

Figure S5: Calculated band structures of $(BA)_2PbI_4$, $(3\text{-APN})_2PbI_4$ and $(PEA)_2PbI_4$ using PBE method.

Figure S6: Optimized geometries of (a) $(3\text{-APN})_2SnI_4$, (b) $(3\text{-APN})_2PbBr_4$, (c) $(3\text{-APN})_2PbCl_4$.

Figure S7: Structural features of (a) $(3\text{-APN})_2SnI_4$, (b) $(3\text{-APN})_2PbBr_4$, (c) $(3\text{-APN})_2PbCl_4$.

Table S3: The calculated band gap values of 2D-LHP based systems using PBE and HSE06+SOC functional and compared with the available experimental values.

Figure S8: Projected density of states of (a) $(3\text{-APN})_2SnI_4$, (b) $(3\text{-APN})_2PbBr_4$, (c) $(3\text{-APN})_2PbCl_4$ using HSE06+SOC method.

Figure S9: Calculated band structures of (a) $(3\text{-APN})_2SnI_4$, (b) $(3\text{-APN})_2PbBr_4$, (c) $(3\text{-APN})_2PbCl_4$ using PBE+SOC method.

Table S4: The calculated effective masses of $(3\text{-APN})_2SnI_4$, $(3\text{-APN})_2PbBr_4$, $(3\text{-APN})_2PbCl_4$.

Figure S10: Calculated absorption spectra of $(2\text{-PyrEA})PbI_4$, $(3\text{-PyrEA})PbI_4$ and $(4\text{-PyrEA})PbI_4$ using PBE+SOC method.

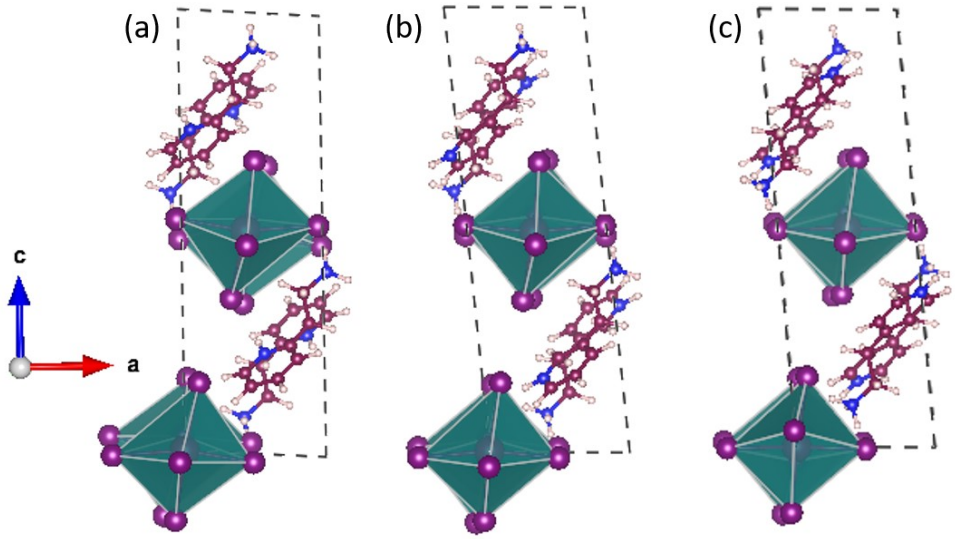


Figure S1: Optimized geometries of (a) (2-PyrEA)PbI_4, (b) (3-PyrEA)PbI_4, (c) (4-PyrEA)PbI_4

Table S1: Space group and Lattice parameters of 2D-LHPs.

LHP System	Space group	Lattice Parameters					
		a (Å)	b (Å)	c (Å)	α	β	γ
$(BA)_2PbI_4$	Pbca	8.876	8.693	27.601	90°	90°	90°
$(3\text{-APN})_2PbI_4$	Pnma	8.637	9.785	20.346	90°	90°	90°
$(PEA)_2PbI_4$	P1	8.739	8.740	32.995	84.65°	84.66°	89.65°
$(PyrEA)PbI_4$	P 21/c	6.335	12.572	19.801	90°	90°	90.76°
$(2\text{-PyrEA})PbI_4$	P 21/n	6.398	12.522	19.959	90°	93.79°	90°
$(3\text{-PyrEA})PbI_4$	P 21/n	6.356	12.469	20.381	90°	96.06°	90°
$(4\text{-PyrEA})PbI_4$	P 21/n	6.351	12.500	20.200	90°	95.35°	90°
$(3\text{-APN})_2SnI_4$	Pnma	8.724	10.048	21.034	90°	90°	90°
$(3\text{-APN})_2PbBr_4$	Pnma	8.071	9.294	22.588	90°	90°	90°
$(3\text{-APN})_2PbCl_4$	Pnma	7.670	8.878	18.499	90°	90°	90°

Table S2: Bond angle and bond lengths of 2D-LHPs. Where M and X are metal and halides respectively.

	M-X bond lengths in Å						X-M-X angle		
LHP System	1(Eq)	2(Eq)	3(Eq)	4(Eq)	5(Ax)	6(Ax)	1	2	3
$(BA)_2PbI_4$	3.20	3.20	3.21	3.21	3.23	3.23	180.00	179.99	180.00
$(3\text{-}APN)_2PbI_4$	3.35	3.20	3.19	3.34	3.21	3.21	174.40	174.82	170.09
$(PEA)_2PbI_4$	3.19	3.20	3.19	3.18	3.24	3.87	179.50	179.51	179.34
$(PyrEA)PbI_4$	3.20	3.21	3.18	3.18	3.25	3.16	172.72	169.63	167.89
$(2\text{-}PyrEA)PbI_4$	3.17	3.22	3.28	3.17	3.19	3.23	165.43	174.26	175.48
$(3\text{-}PyrEA)PbI_4$	3.18	3.19	3.16	3.22	3.20	3.20	168.35	176.86	175.08
$(4\text{-}PyrEA)PbI_4$	3.16	3.19	3.19	3.22	3.28	3.12	175.99	176.60	173.53
$(3\text{-}APN)_2SnI_4$	3.73	3.59	3.00	2.99	3.21	3.21	177.33	175.82	168.61
$(3\text{-}APN)_2PbBr_4$	3.00	3.03	3.17	3.10	3.06	3.06	179.34	178.86	172.45
$(3\text{-}APN)_2PbCl_4$	3.09	3.02	2.82	2.84	2.83	2.83	171.46	173.30	170.86

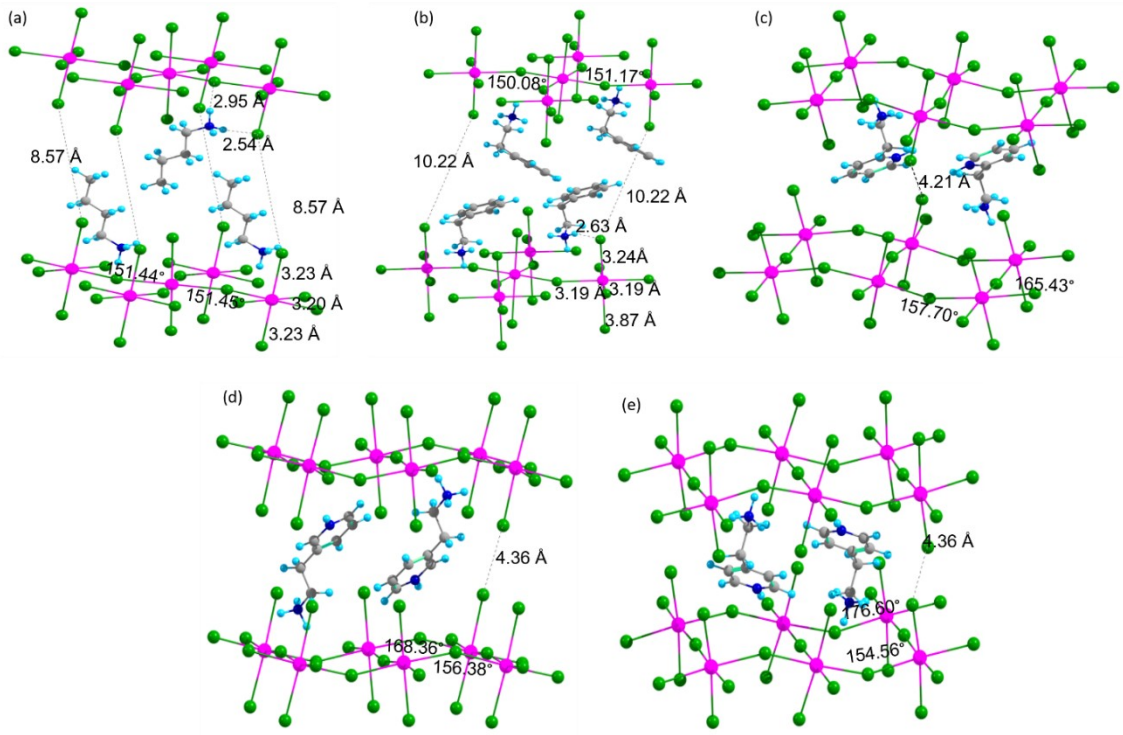


Figure S2: Structural features of (a) $(BA)_2PbI_4$, (b)$(PEA)_2PbI_4$, (c) (2-PyrEA)PbI_4, (d) (3-PyrEA)PbI_4 and (e) (4-PyrEA)PbI_4

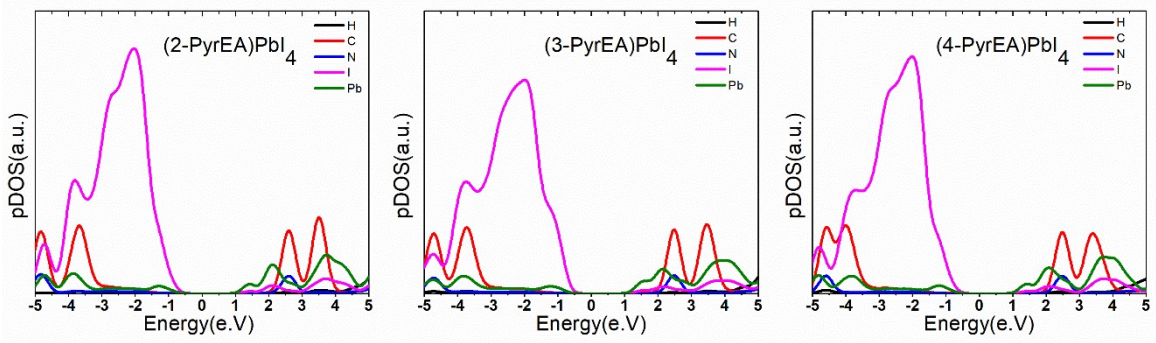


Figure S3: Projected density of states of the 2D-LHP systems using HSE06+SOC level of calculations. Here the Fermi level is set to zero.

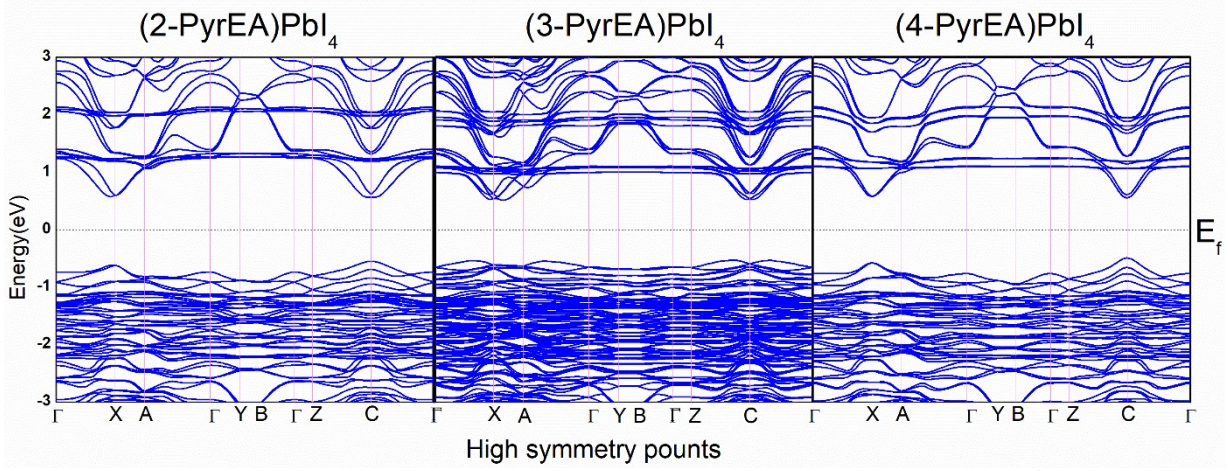


Figure S4: Calculated band structures of the 2D-LHP systems using PBE+SOC method. Here, high symmetry points are Γ = (0, 0, 0), X = (0.5, 0, 0), Y = (0, 0.5, 0), Z = (0, 0, 0.5), A= (0.5, 0.5, 0), B= (0, 0.5, 0.5), C= (0.5, 0, 0.5), and D = (0.5, 0.5, 0.5).

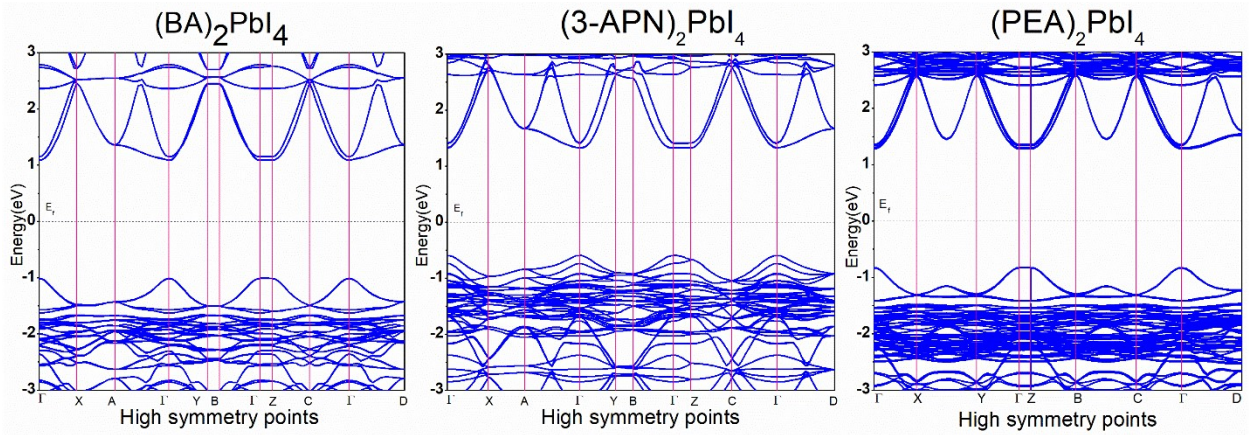


Figure S5: Calculated band structures of the 2D-LHP systems using PBE method. Here, high symmetry points are Γ = (0, 0, 0), X = (0.5, 0, 0), Y = (0, 0.5, 0), Z = (0, 0, 0.5), A= (0.5, 0.5, 0), B= (0, 0.5, 0.5), C= (0.5, 0, 0.5), and D = (0.5, 0.5, 0.5).

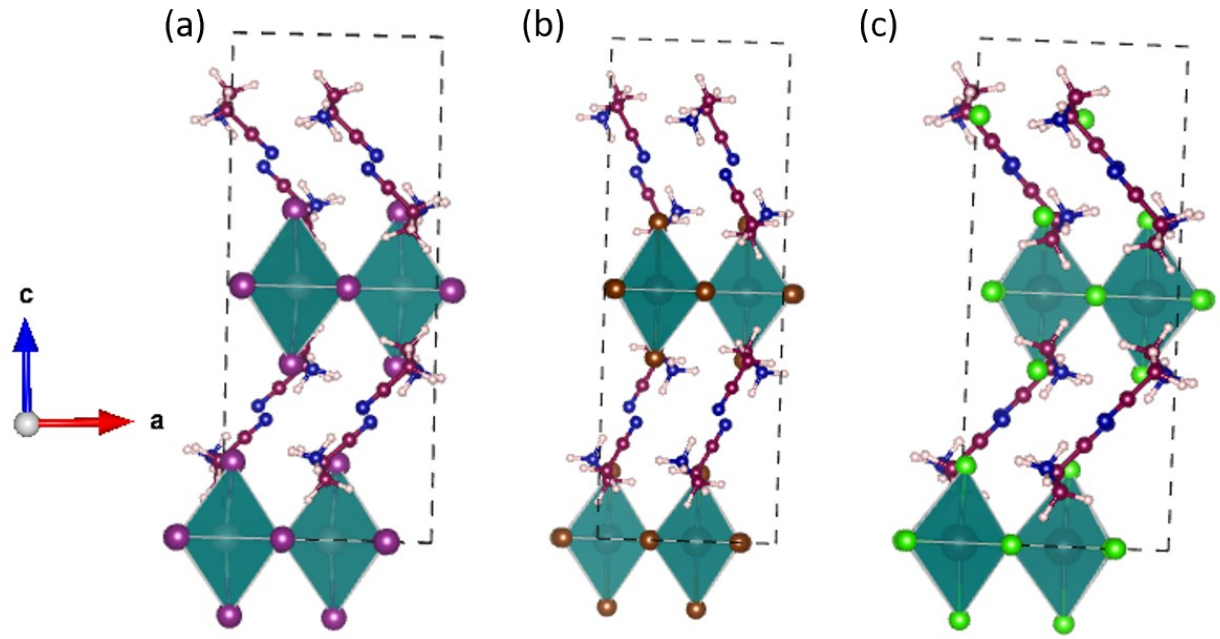


Figure S6: Optimized geometries of (a) $(3\text{-APN})_2SnI_4$, (b) $(3\text{-APN})_2PbBr_4$, (c) $(3\text{-APN})_2PbCl_4$.

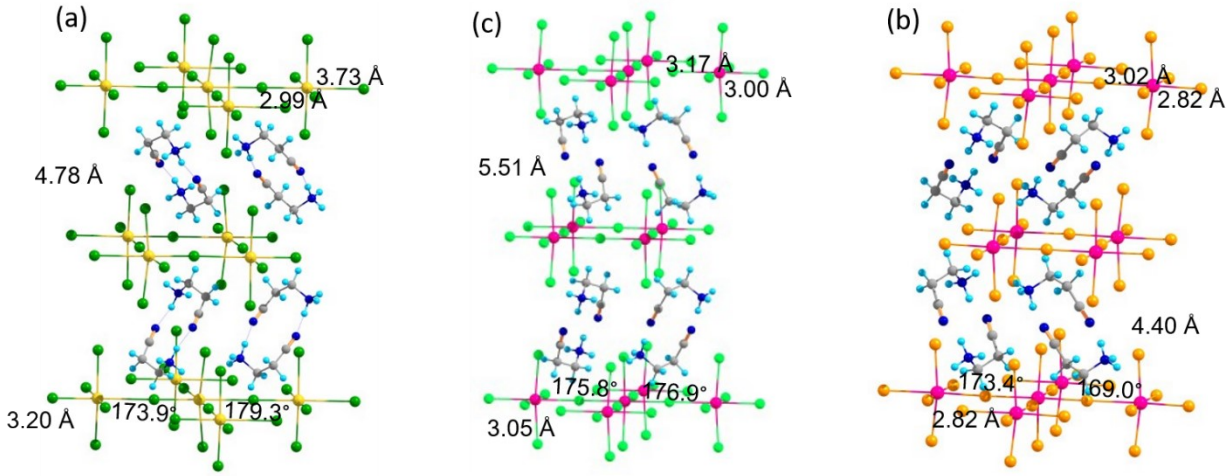
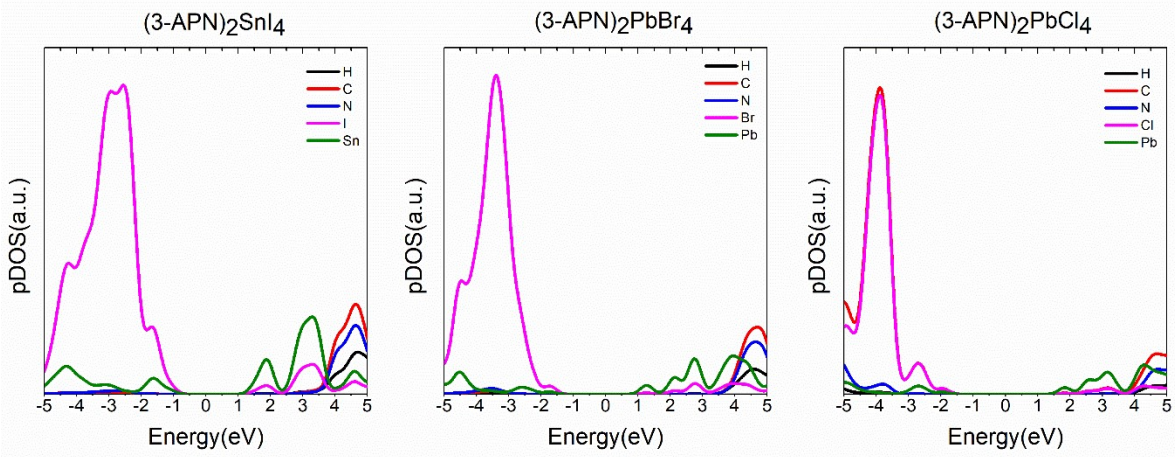


Figure S7: Structural features of (a) $(3\text{-APN})_2SnI_4$, (b $(3\text{-APN})_2PbBr_4$, and (c) $(3\text{-APN})_2PbCl_4$.

Table S3: The calculated band gap values of 2D-LHP based systems using PBE and HSE06+SOC functional and compared with the available experimental values.

Layered Perovskite System	Band gap in eV		
	PBE	**HSE06+SOC**	**Expt.**
$(3\text{-APN})_2SnI_4$	1.73	2.65	-
$(3\text{-APN})_2PbBr_4$	2.37	2.98	-
$(3\text{-APN})_2PbCl_4$	2.83	3.73	-



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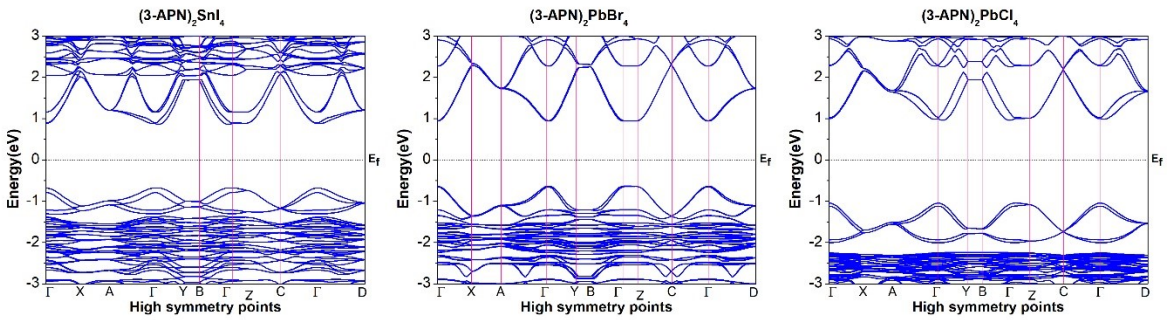
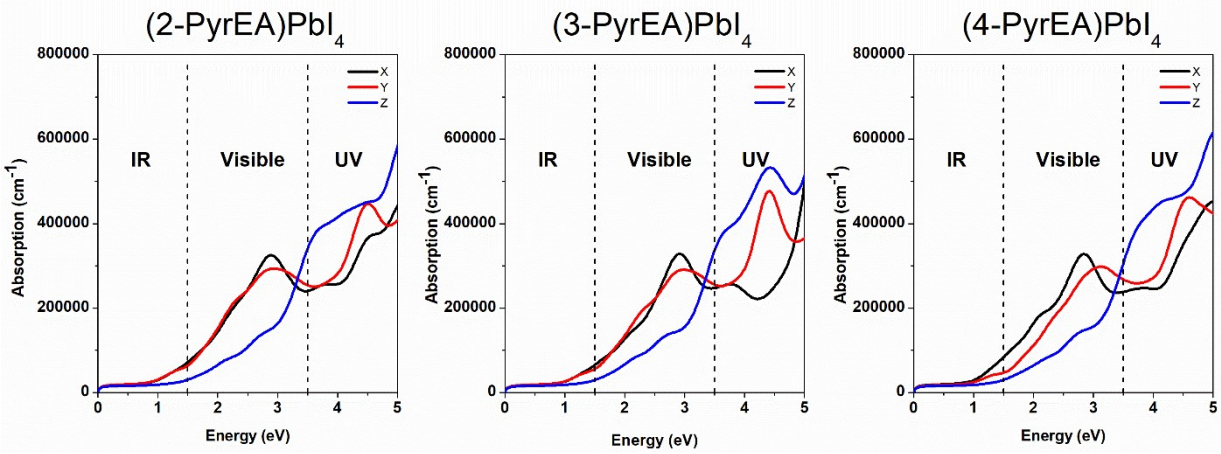


Figure S9: Calculated band structures of the $(3\text{-APN})_2SnI_4$, $(3\text{-APN})_2PbBr_4$, and $(3\text{-APN})_2PbCl_4$ using PBE+SOC method. Here, high symmetry points are Γ = (0, 0, 0), X = (0.5, 0, 0), Y = (0, 0.5, 0), Z = (0, 0, 0.5), A= (0.5, 0.5, 0), B= (0, 0.5, 0.5), C= (0.5, 0, 0.5), and D = (0.5, 0.5, 0.5).

Table S4: Effective mass of $(3\text{-APN})_2SnI_4$, $(3\text{-APN})_2PbBr_4$, and $(3\text{-APN})_2PbCl_4$.

System	Direction	$m_e^*(m_0)$	$m_h^*(m_0)$
$(3\text{-APN})_2SnI_4$	Γ-X	0.22	0.41
	Γ-Y	0.95	3.81
$(3\text{-APN})_2PbBr_4$	Γ-X	0.19	027
	Γ-Y	0.22	0.30
$(3\text{-APN})_2PbCl_4$	Γ-X	0.32	0.38
	Γ-Y	0.31	0.31



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