Supplemental Material for "Functionality-directed Screening of Pb-free Hybrid Organic-inorganic Perovskites with Desired Intrinsic Photovoltaic Functionalities"

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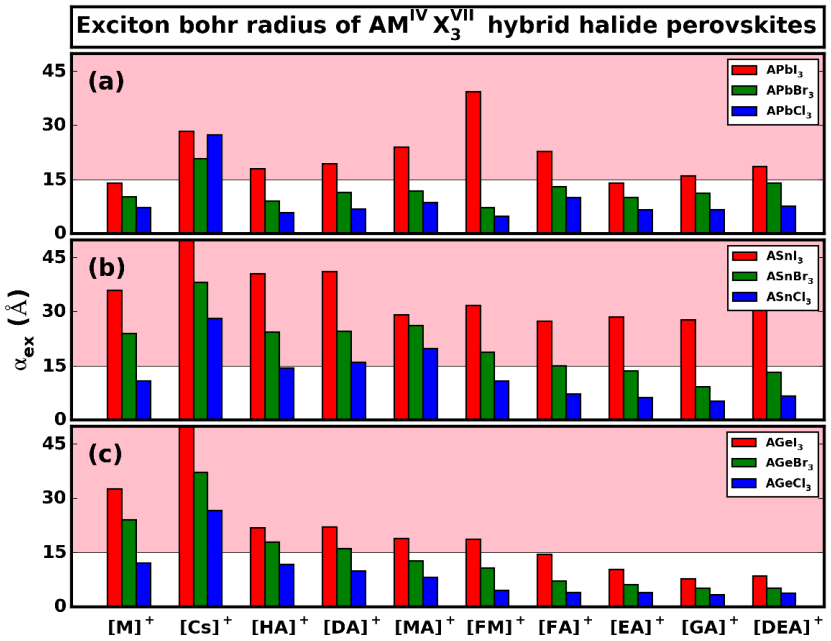

Figure S1: Calculated exciton Bohr radii of (a) Pb, (b) Sn and (c) Ge based $AM^{IV}X_3^{VII}$ perovskites with the hydrogen-like Wannier-Mott model. Shaded areas indicate the criterion applied ($\alpha_{ex} > 1.5$ nm) for the materials screening.

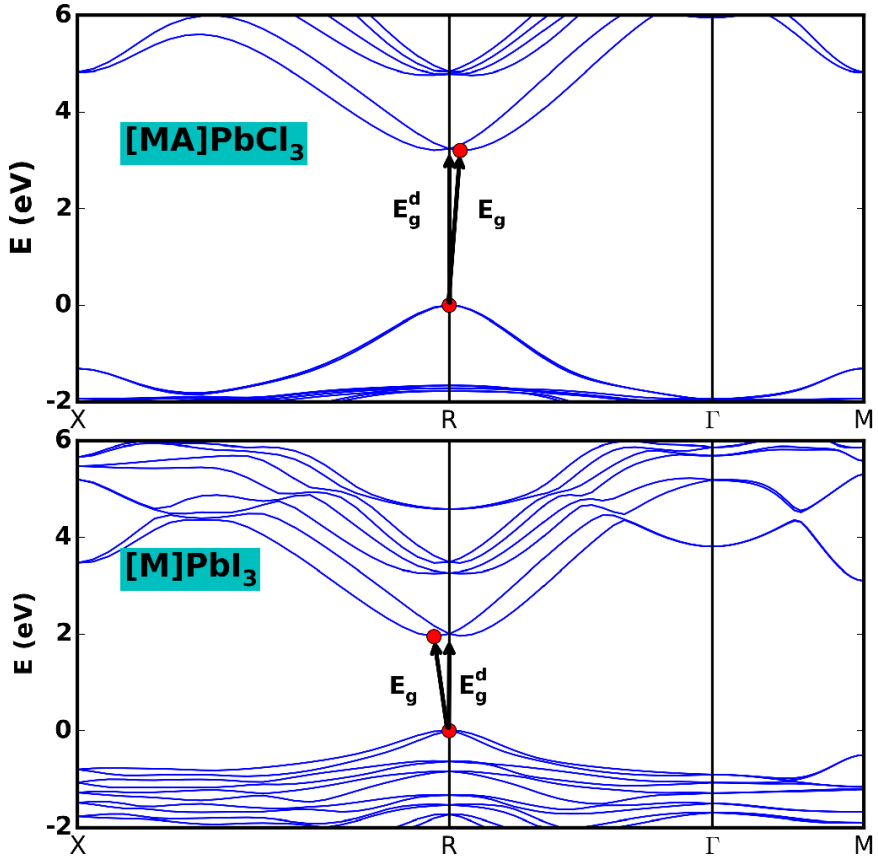

Figure S2: Band structures of the selected $AM^{IV}X_3^{VII}$ perovskites having indirect band gaps. The valence band maximum and conduction band minimum are marked by red circles. The actual band gaps (E_g) and direct band gaps (E_g^d) are indicated.

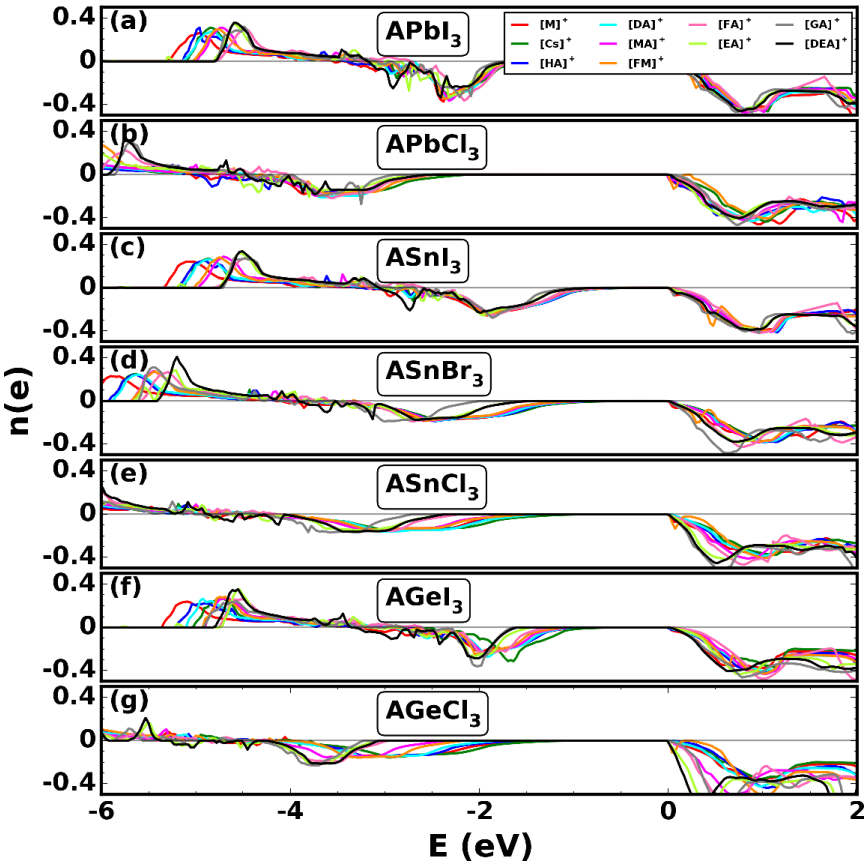

Figure S3: Crystal orbital overlap populations (COOP) of the $AM^{IV}X_3^{VII}$ perovskites. For comparison, the CBM of each material is set to energy zero.

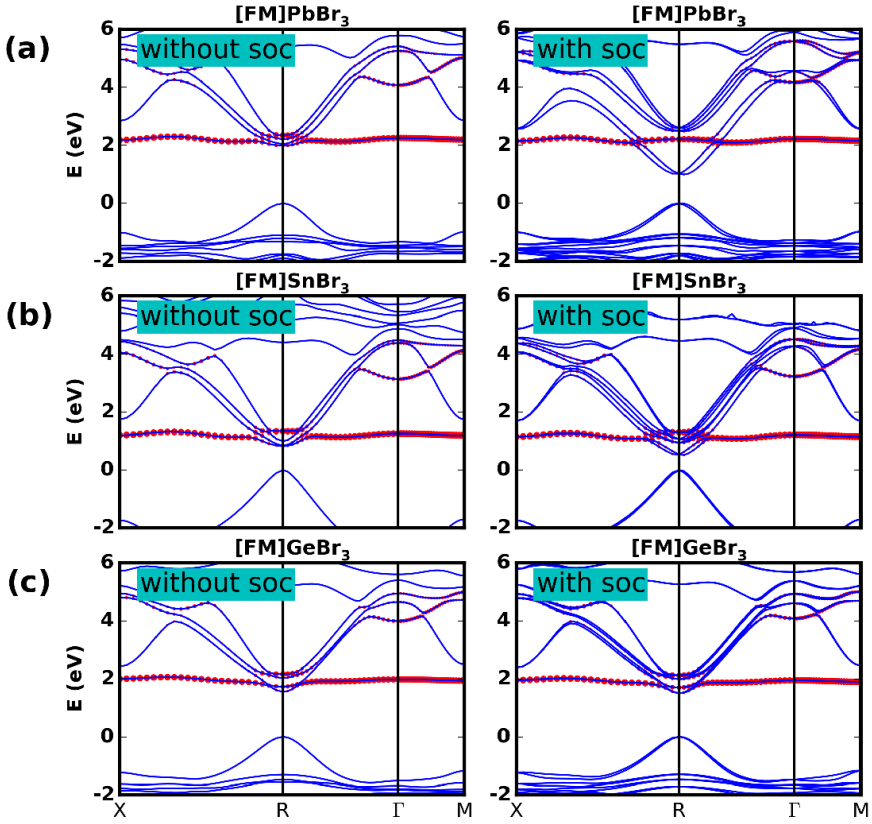

Figure S4: Band structures of (a) [FM]$PbBr_3$, (b) [FM]$SnBr_3$, (c) [FM]$GeBr_3$ calculated without (left panels) and with (right panels) the spin-orbit coupling (SOC) effect. The orbital projections onto the FM molecule are indicated by red circles.

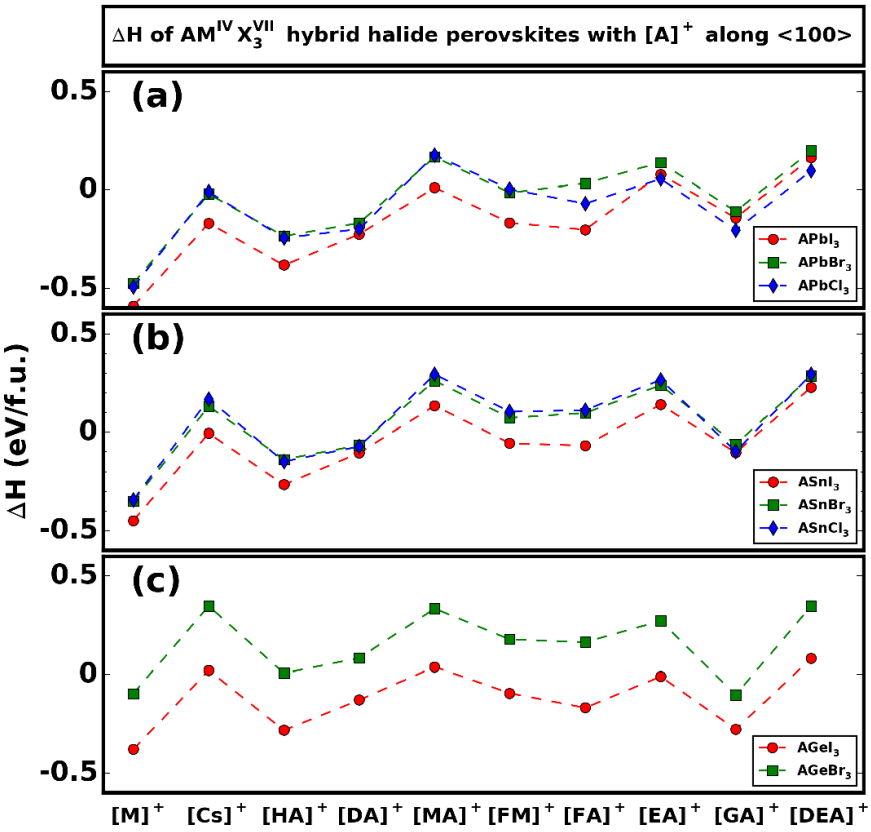

Figure S5: Calculated decomposition enthalpies ΔH of the $AM^{IV}X_3^{VII}$ perovskites with the principal axes of small molecules aligned along the <100> direction, with respect to decomposed products of AX^{VII}+$M^{IV}X_2^{VII}$.

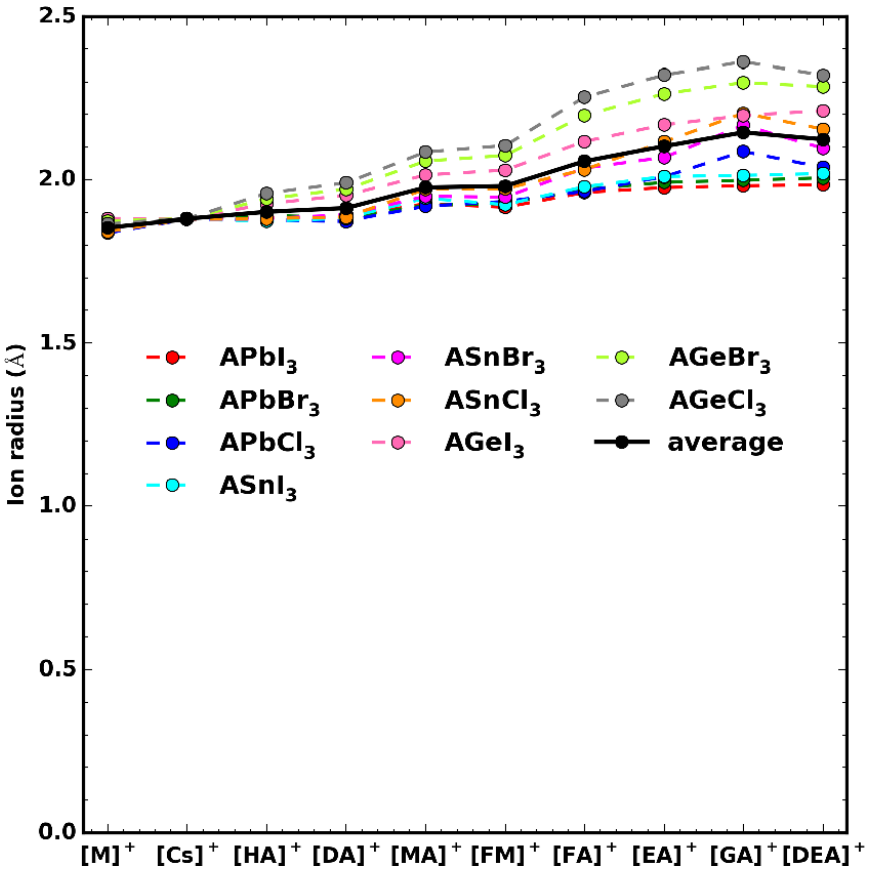

Figure S6: Evaluation of the steric sizes of organic molecular cations within the idealized solid-sphere model [see the Experimental Section (iv)].

Table S1: Calculated decomposition enthalpies (ΔH) of the candidate $AM^{IV}X_3^{VII}$ perovskites with respect to decomposed products of AX^{IV}+$M^{IV}X_2^{VII}$. The compounds passing the screening (with ΔH larger than -0.1 eV/f.u.) are marked by green shading.

ΔH (eV)	PbI_3	$PbBr_3$	$PbCl_3$	SnI_3	$SnBr_3$	$SnCl_3$	GeI_3	$GeBr_3$	$GeCl_3$
$[M]^+$	-0.59	-0.48	-0.49	-0.45	-0.35	-0.34	-0.38	-0.10	–
$[Cs]^+$	-0.17	-0.02	-0.01	-0.01	0.13	0.17	0.02	0.35	–
$[HA]^+$	-0.45	-0.26	-0.29	-0.32	-0.23	-0.23	-0.30	-0.03	–
$[DA]^+$	-0.25	-0.19	-0.21	-0.12	-0.09	-0.09	-0.13	0.07	–
$[MA]^+$	-0.02	0.12	0.12	0.10	0.21	0.24	0.03	0.33	–
$[FM]^+$	-0.21	-0.09	-0.11	-0.11	-0.02	-0.01	-0.18	0.08	–
$[FA]^+$	-0.10	-0.01	-0.02	-0.03	0.04	0.08	-0.16	0.10	–
$[EA]^+$	0.09	0.16	0.01	0.16	0.24	0.27	0.01	0.25	–
$[GA]^+$	-0.14	-0.11	-0.24	-0.09	-0.06	0.02	-0.29	-0.07	–
$[DEA]^+$	0.16	0.20	0.10	0.22	0.28	0.30	0.06	0.34	–

Table S2: Calculated decomposition enthalpies (ΔH) of the candidate $AM^{IV}X_3^{VII}$ perovskites (with the principal axes of small molecules aligned along the <100> direction).

ΔH (eV)	PbI_3	$PbBr_3$	$PbCl_3$	SnI_3	$SnBr_3$	$SnCl_3$	GeI_3	$GeBr_3$	$GeCl_3$
$[M]^+$	-0.59	-0.48	-0.49	-0.45	-0.35	-0.34	-0.38	-0.10	–
$[Cs]^+$	-0.17	-0.02	-0.01	-0.01	0.13	0.17	0.02	0.35	–
$[HA]^+$	-0.38	-0.23	-0.24	-0.27	-0.14	-0.15	-0.28	0.01	–
$[DA]^+$	-0.23	-0.17	-0.20	-0.10	-0.07	-0.07	-0.13	0.08	–
$[MA]^+$	0.01	0.17	0.18	0.13	0.26	0.29	0.04	0.33	–
$[FM]^+$	-0.17	-0.01	0.00	-0.06	0.07	0.10	-0.09	0.18	–
$[FA]^+$	-0.20	0.03	-0.07	-0.07	0.10	0.11	-0.17	0.16	–
$[EA]^+$	0.08	0.14	0.06	0.14	0.24	0.27	-0.01	0.27	–
$[GA]^+$	-0.14	-0.11	-0.20	-0.10	-0.06	-0.10	-0.28	-0.10	–
$[DEA]^+$	0.16	0.20	0.10	0.23	0.28	0.29	0.08	0.35	–

Table S3: Calculated direct band gaps (E_g^d) of the candidate $AM^{IV}X_3^{VII}$ perovskites. The green shading indicates the compounds passing the current DM ($E_g^d < 2.5$ eV), as well as the DM in Table S1. The lightblue shading indicates the compounds passing only the current DM.

E_g^d (eV)	PbI_3	$PbBr_3$	$PbCl_3$	SnI_3	$SnBr_3$	$SnCl_3$	GeI_3	$GeBr_3$	$GeCl_3$
$[M]^+$	1.95	2.71	3.39	1.21	1.91	2.68	1.59	2.01	2.54
$[Cs]^+$	1.30	1.98	2.63	0.95	1.53	2.14	1.15	1.64	2.17
$[HA]^+$	1.75	2.74	3.73	1.15	1.87	2.85	1.70	2.26	3.12
$[DA]^+$	1.73	2.55	3.55	1.17	1.91	2.83	1.78	2.47	3.40
$[MA]^+$	1.55	2.43	3.23	1.26	2.00	3.01	1.98	3.01	4.10
$[FM]^+$	1.76	2.65	3.49	1.32	2.16	3.20	2.04	3.08	4.17
$[FA]^+$	1.74	2.60	3.25	1.21	2.54	3.73	2.36	3.79	4.95
$[EA]^+$	1.86	2.67	3.56	1.70	3.13	4.47	2.61	3.99	5.11
$[GA]^+$	1.90	2.70	3.99	1.78	3.77	4.91	3.28	4.13	5.90
$[DEA]^+$	1.81	2.60	3.44	1.62	3.19	4.51	2.82	4.15	5.07

Table S4: Calculated electron (m_e^*, the upper value) and hole (m_h^*, the lower value) effective masses of the candidate $AM^{IV}X_3^{VII}$ perovskites. The green shading indicates the compounds passing the current DM ($m_e^* < 0.5\ m_0$ and $m_h^* < 0.5\ m_0$), as well as the DMs in Tables S1 and S3. The lightblue shading indicates the compounds passing only the current DM.

m_e^* / m_h^*	PbI_3	$PbBr_3$	$PbCl_3$	SnI_3	$SnBr_3$	$SnCl_3$	GeI_3	$GeBr_3$	$GeCl_3$
$[M]^+$	0.49	0.70	0.92	0.59	0.70	0.73	0.35	0.52	0.57
	0.37	0.36	0.38	0.18	0.20	0.16	0.24	0.10	0.13
$[Cs]^+$	0.18	0.23	0.38	0.24	0.32	0.38	0.19	0.26	0.33
	0.22	0.21	0.21	0.17	0.15	0.10	0.21	0.18	0.19
$[HA]^+$	0.46	0.65	0.85	0.43	0.55	0.63	0.33	0.38	0.41
	0.33	0.46	0.59	0.19	0.22	0.25	0.29	0.17	0.24
$[DA]^+$	0.47	0.67	0.97	0.42	0.53	0.62	0.32	0.37	0.47
	0.31	0.36	0.47	0.19	0.21	0.23	0.27	0.21	0.31
$[MA]^+$	0.42	0.70	0.88	0.27	0.50	0.58	0.38	0.51	0.70
	0.18	0.28	0.31	0.18	0.19	0.17	0.28	0.31	0.37
$[FM]^+$	0.54	1.12	8.81	0.56	0.66	4.50	0.40	0.57	7.83
	0.25	0.36	0.42	0.19	0.21	0.22	0.30	0.34	0.43
$[FA]^+$	0.44	0.68	0.54	0.33	0.73	0.75	0.38	0.57	0.78
	0.23	0.35	0.29	0.25	0.31	0.44	0.37	0.51	0.73
$[EA]^+$	0.46	0.60	0.80	0.38	0.57	0.82	0.40	0.58	0.88
	0.28	0.34	0.41	0.14	0.30	0.50	0.42	0.61	0.81
$[GA]^+$	0.39	0.61	0.68	0.32	0.85	0.91	0.51	0.55	0.77
	0.37	0.35	0.51	0.21	0.39	0.54	0.64	0.80	0.95
$[DEA]^+$	0.26	0.40	0.66	0.30	0.48	0.61	0.41	0.56	0.57
	0.33	0.32	0.36	0.20	0.29	0.46	0.55	0.73	0.82

Table S5: Calculated exciton binding energies (E_B) of the candidate $AM^{IV}X_3^{VII}$ perovskites. The green shading indicates the compounds passing the current DM ($E_B < 100$ meV), as well as the DMs in Tables S1, S3 and S4. The lightblue shading indicates the compounds passing only the current DM.

E_B (meV)	PbI_3	$PbBr_3$	$PbCl_3$	SnI_3	$SnBr_3$	$SnCl_3$	GeI_3	$GeBr_3$	$GeCl_3$
$[M]^+$	94.25	165.80	274.85	23.92	49.79	143.66	29.05	49.39	117.68
$[Cs]^+$	43.89	75.87	68.84	13.73	26.75	48.69	14.29	26.40	47.42
$[HA]^+$	73.51	187.52	347.17	20.93	48.35	109.24	46.83	75.02	146.80
$[DA]^+$	67.51	144.02	287.43	20.75	48.01	96.39	48.14	87.14	183.32
$[MA]^+$	52.34	135.85	223.67	30.05	45.93	83.12	61.63	127.55	247.88
$[FM]^+$	33.00	230.12	412.57	28.93	67.96	158.42	64.59	152.64	460.45
$[FA]^+$	56.75	125.80	192.72	38.09	101.64	282.48	94.22	274.09	607.20
$[EA]^+$	109.75	191.90	357.38	36.26	115.80	337.07	144.62	338.33	632.50
$[GA]^+$	83.06	153.76	313.45	38.22	200.53	432.95	202.35	419.56	772.06
$[DEA]^+$	69.89	116.20	315.05	30.94	123.16	322.60	188.67	408.48	653.61

Table S6: Calculated exciton Bohr radii (α_{ex}) of the candidate $AM^{IV}X_3^{VII}$ perovskites. The green shading indicates the compounds passing the current DM ($\alpha_{ex} > 1.5$ nm), as well as the DMs in Tables S1, S3 and S4. The lightblue shading indicates the compounds passing only the current DM.

α_{ex} (nm)	PbI_3	$PbBr_3$	$PbCl_3$	SnI_3	$SnBr_3$	$SnCl_3$	GeI_3	$GeBr_3$	$GeCl_3$
$[M]^+$	1.40	1.01	0.73	3.60	2.40	1.09	3.26	2.41	1.20
$[Cs]^+$	2.83	2.07	2.74	5.56	3.82	2.82	5.19	3.72	2.66
$[HA]^+$	1.79	0.91	0.58	4.06	2.43	1.44	2.18	1.79	1.18
$[DA]^+$	1.93	1.14	0.68	4.12	2.47	1.60	2.21	1.61	0.98
$[MA]^+$	2.40	1.19	0.86	2.91	2.62	1.99	1.89	1.26	0.82
$[FM]^+$	3.94	0.72	0.47	3.17	1.88	1.08	1.86	1.08	0.44
$[FA]^+$	2.29	1.30	1.00	2.74	1.50	0.72	1.45	0.70	0.39
$[EA]^+$	1.40	1.00	0.66	2.85	1.36	0.62	1.04	0.60	0.39
$[GA]^+$	1.61	1.12	0.67	2.78	0.92	0.52	0.77	0.50	0.32
$[DEA]^+$	1.87	1.41	0.75	3.21	1.33	0.67	0.84	0.51	0.37

Table S7: Calculated various DMs for the $AM^{IV}X_3^{VII}$ perovskites containing pseudo-halogen anions, $AM^{IV}[BF_4]_3$ and $AM^{IV}[SCN]_3$ with A=Cs^+, MA^+, FA^+ and M^{IV}=Pb^{2+}, Sn^{2+}.

Materials	ΔH	E_g^d	m_e^*	m_h^*	E_B (eV)	α_{ex} (nm)
	Compounds based on $[BF_4]^-$					
$CsPb[BF_4]_3$	0.31	8.71	1.60	1.43	2.70	0.14
$CsSn[BF_4]_3$	0.32	8.70	1.63	1.45	2.58	0.14
$MAPb[BF_4]_3$	0.71	9.43	6.97	7.70	12.07	0.03
MASn[BF4]3	0.53	9.15	4.86	2.93	5.89	0.06
	Compounds based on $[SCN]^-$					
$CsPb[SCN]_3$	0.39	4.42	1.82	1.12	0.79	0.26
$CsSn[SCN]_3$	0.34	4.97	1.86	1.12	0.71	0.28
$MAPb[SCN]_3$	-0.33	4.46	2.38	1.20	0.93	0.23
$MASn[SCN]_3$	-0.17	4.75	2.59	1.01	0.72	0.27
$FAPb[SCN]_3$	-0.47	4.61	1.74	1.24	0.81	0.26
$FASn[SCN]_3$	-0.38	4.68	2.31	1.02	0.69	0.28