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Electronic and Defect Properties of $(CH_3NH_3)_2Pb(SCN)_2I_2$ Analogues for Photovoltaic Applications

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Supporting Information

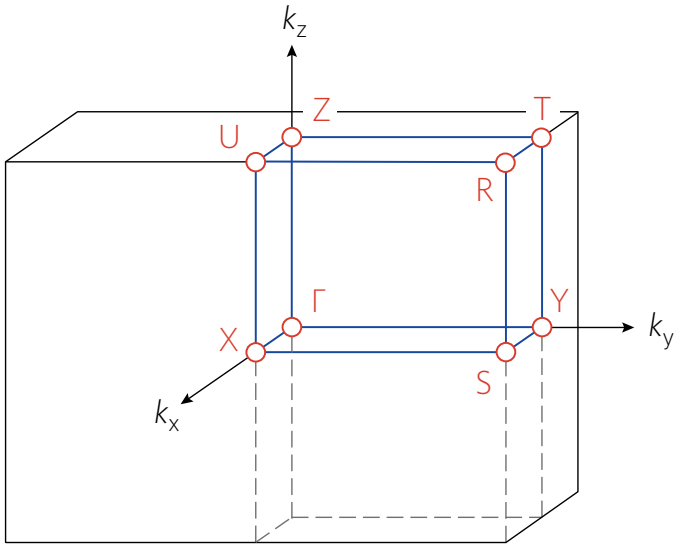

Figure S1: Brillouin zone of the $Pnm2_1$ space group. Coordinates of the high symmetry points used for the band structures and effective masses: $\Gamma = (0, 0, 0)$; $\mathrm{Y} = (\frac{1}{2}, 0, 0)$; $\mathrm{X} = (0, \frac{1}{2}, 0)$; $\mathrm{Z} = (0, 0, \frac{1}{2})$; $\mathrm{U} = (0, \frac{1}{2}, \frac{1}{2})$; $\mathrm{T} = (\frac{1}{2}, 0, \frac{1}{2})$; $\mathrm{S} = (\frac{1}{2}, \frac{1}{2}, 0)$; $\mathrm{R} = (0, \frac{1}{2}, \frac{1}{2})$

Table S1: Relativistic lowering of the indirect ($\Delta_{\mathrm{soc}}E_g^{ind}$) and direct ($\Delta_{\mathrm{soc}}E_g^{dir}$) band gaps of $(CH_3NH_3)_2MPs_2I_2$, where M = Sn, Pb, and Ps = OCN, SCN, SeCN, calculated using HSE06 with and without spin–orbit coupling (SOC))

	Compound	$\Delta_{\mathrm{soc}}E_g^{ind}$ **(eV)**	$\Delta_{\mathrm{soc}}E_g^{dir}$ **(eV)**
Pb	$MA_2Pb(OCN)_2Cl_2$	0.75	0.82
	$MA_2Pb(SCN)_2Cl_2$	0.63	0.65
	$MA_2Pb(SeCN)_2Cl_2$	0.60	0.60
	$MA_2Pb(OCN)_2Br_2$	0.81	0.88
	$MA_2Pb(SeCN)_2Br_2$	0.70	0.73
	$MA_2Pb(OCN)_2I_2$	0.87	0.93
	$MA_2Pb(SCN)_2I_2$	0.77	0.78
	$MA_2Pb(SeCN)_2I_2$	0.73	0.76
Sn	$MA_2Sn(OCN)_2Cl_2$	0.16	0.15
	$MA_2Sn(SCN)_2Cl_2$	0.11	0.12
	$MA_2Sn(SeCN)_2Cl_2$	0.11	0.12
	$MA_2Sn(OCN)_2Br_2$	0.16	0.16
	$MA_2Sn(SCN)_2Br_2$	0.12	0.14
	$MA_2Sn(SeCN)_2Br_2$	0.12	0.14
	$MA_2Sn(OCN)_2I_2$	0.22	0.25
	$MA_2Sn(SCN)_2I_2$	0.20	0.23
	$MA_2Sn(SeCN)_2I_2$	0.20	0.22

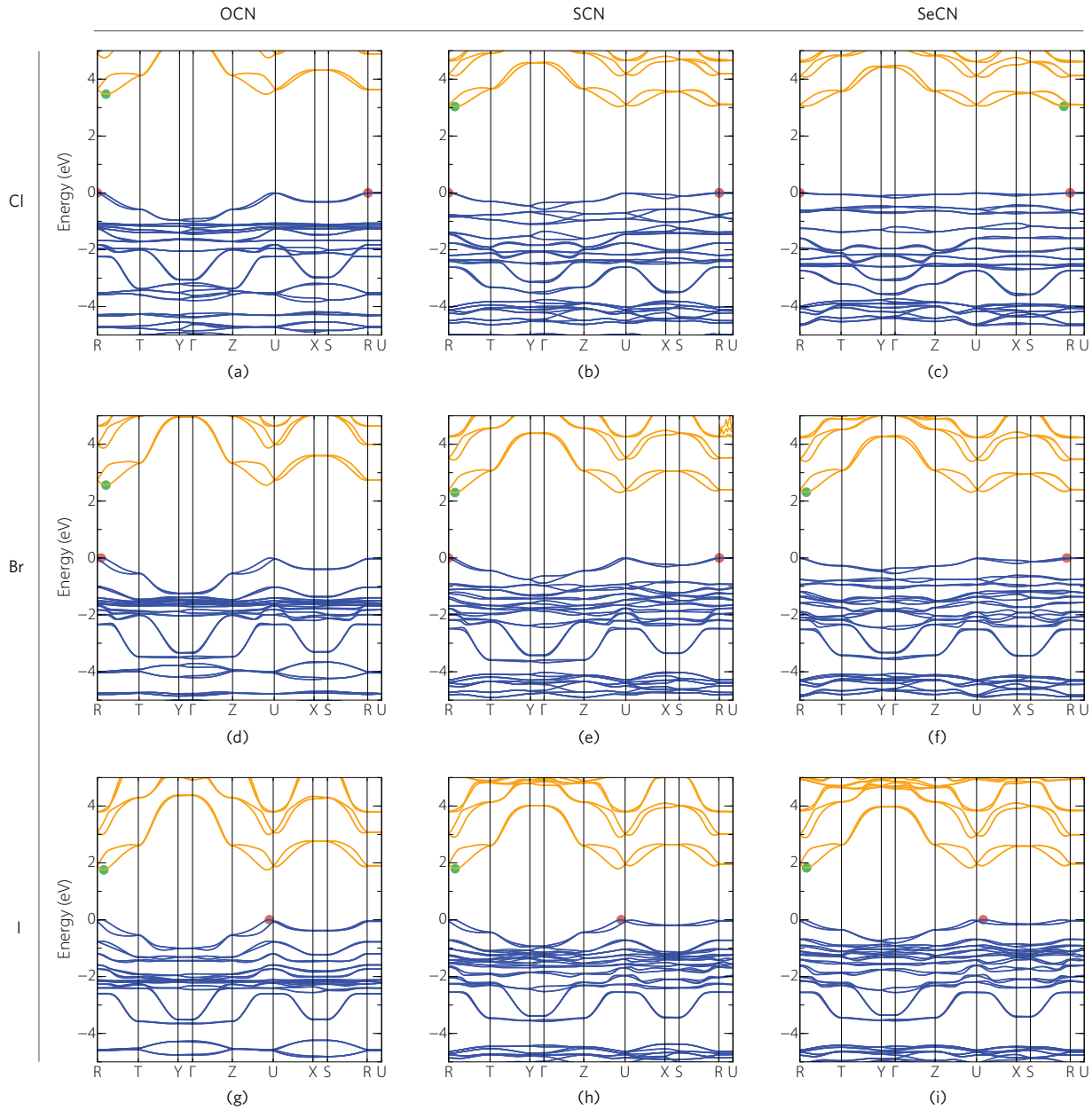

Figure S2: HSE06+SOC calculated band structures of lead-based MAPSI-structured analogues:
a) $(CH_3NH_3)_2Pb(OCN)_2Cl_2$, b) $(CH_3NH_3)_2Pb(SCN)_2Cl_2$,
c) $(CH_3NH_3)_2Pb(SeCN)_2Cl_2$, d) $(CH_3NH_3)_2Pb(OCN)_2Br_2$,
e) $(CH_3NH_3)_2Pb(SCN)_2Br_2$, f) $(CH_3NH_3)_2Pb(SeCN)_2Br_2$,
g) $(CH_3NH_3)_2Pb(OCN)_2I_2$, h) $(CH_3NH_3)_2Pb(SCN)_2I_2$,
i) $(CH_3NH_3)_2Pb(SeCN)_2I_2$.
The valence band maximum is set to 0 eV. Valence and conduction bands indicated by blue and orange lines, respectively. Green and red circles indicate the valence band maximum and conduction band minimum, respectively.

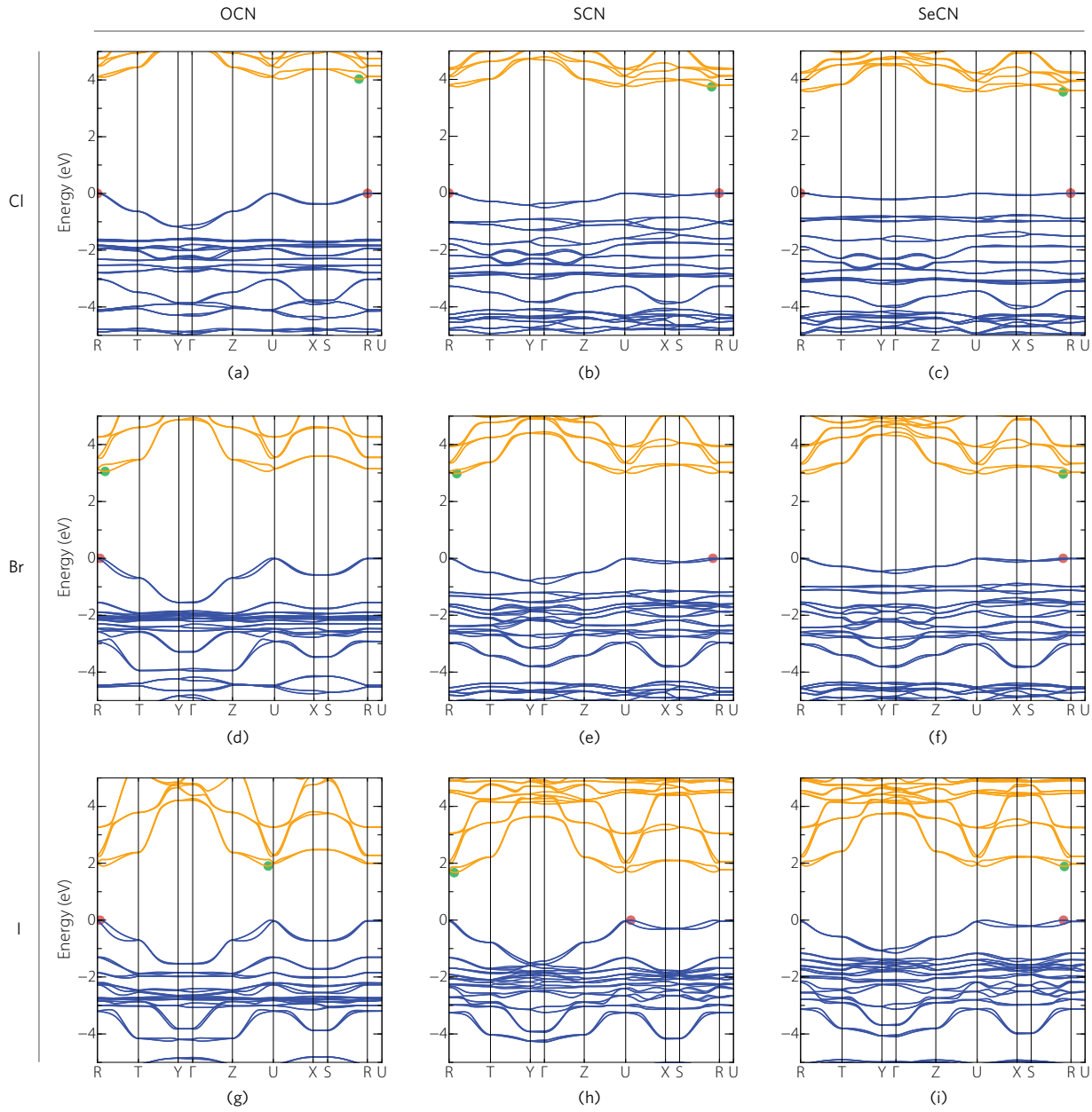

Figure S3: HSE06+SOC calculated band structures of tin-based MAPSI-structured analogues: a) $(CH_3NH_3)_2Sn(OCN)_2Cl_2$, b) $(CH_3NH_3)_2Sn(SCN)_2Cl_2$,
c) $(CH_3NH_3)_2Sn(SeCN)_2Cl_2$, d) $(CH_3NH_3)_2Sn(OCN)_2Br_2$,
e) $(CH_3NH_3)_2Sn(SCN)_2Br_2$, f) $(CH_3NH_3)_2Sn(SeCN)_2Br_2$,
g) $(CH_3NH_3)_2Sn(OCN)_2I_2$, h) $(CH_3NH_3)_2Sn(SCN)_2I_2$,
i) $(CH_3NH_3)_2Sn(SeCN)_2I_2$.
The valence band maximum is set to 0 eV. Valence and conduction bands indicated by blue and orange lines, respectively. Green and red circles indicate the valence band maximum and conduction band minimum, respectively.

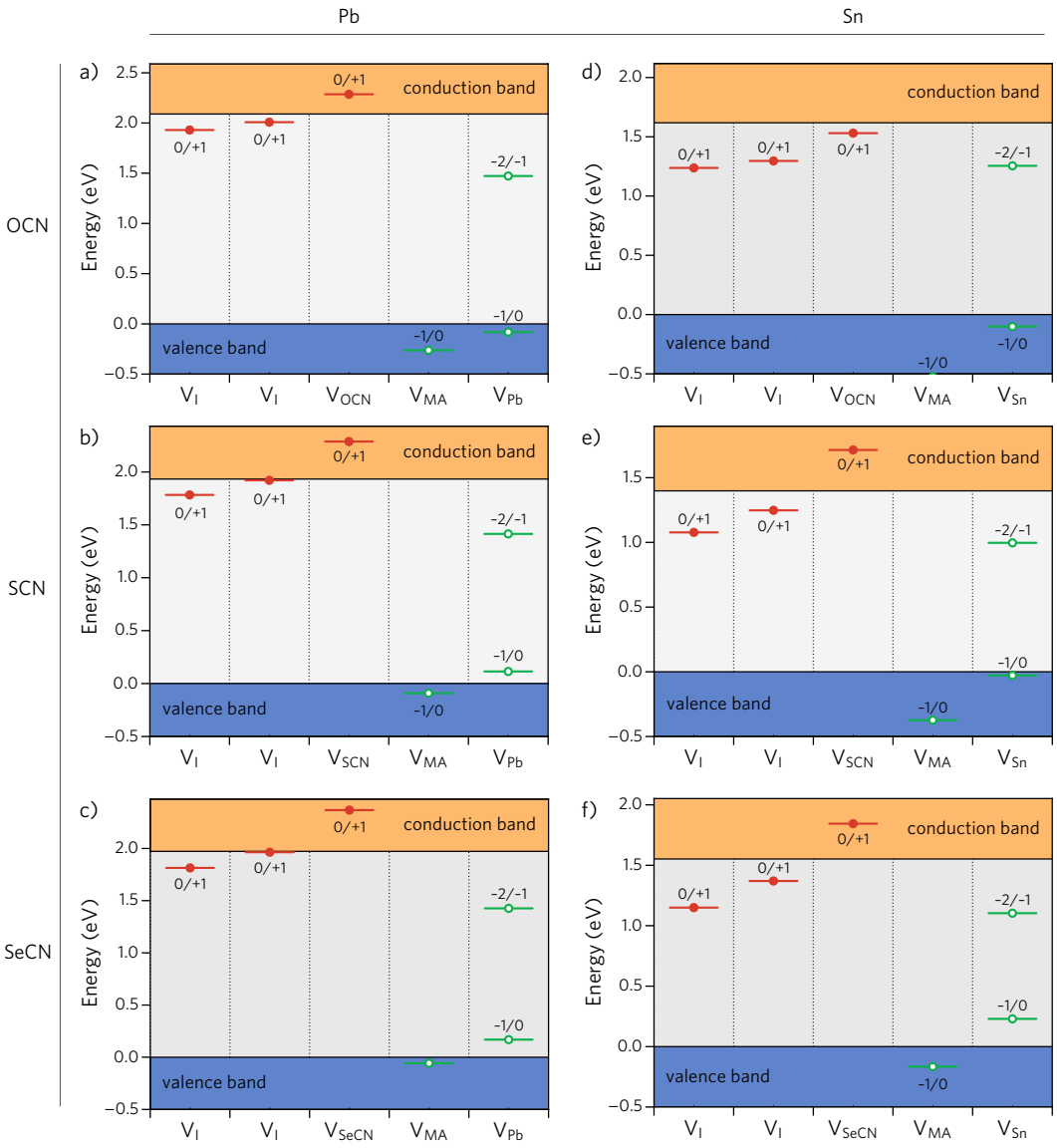

Figure S4: Charge-state transition level diagrams for:
a) $(CH_3NH_3)_2Pb(OCN)_2I_2$, b) $(CH_3NH_3)_2Pb(SCN)_2I_2$,
c) $(CH_3NH_3)_2Pb(SeCN)_2I_2$, d) $(CH_3NH_3)_2Sn(OCN)_2I_2$,
e) $(CH_3NH_3)_2Sn(SCN)_2I_2$, f) $(CH_3NH_3)_2Sn(SeCN)_2I_2$,
The valence band maximum is set to 0 eV. Valence and conduction bands indicated by blue and orange lines, respectively. Green and red circles indicate the valence band maximum and conduction band minimum, respectively. Red bands with filled circles indicate donor defects, green bands with open circles indicate acceptor defects.