

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

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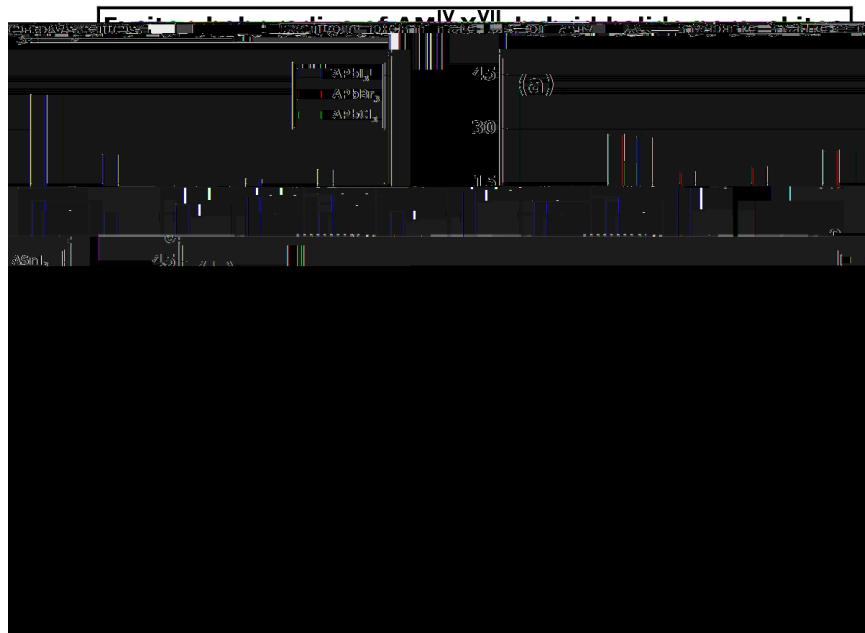
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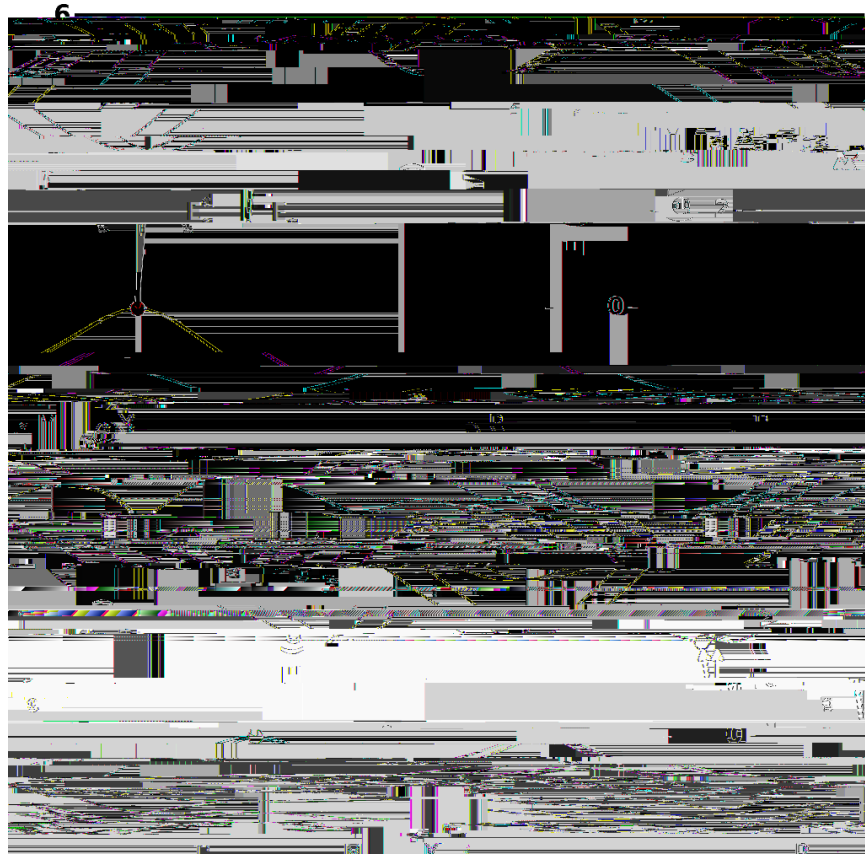


Figure 6 Band structures of the selected  $AM^{IV}X_3^{VII}$  perovskites having indirect band gaps. The valence band maximum and conduction band minimum are marked by red circles. The actual band gaps  $E_g$  and direct band gaps  $E_g^d$ .

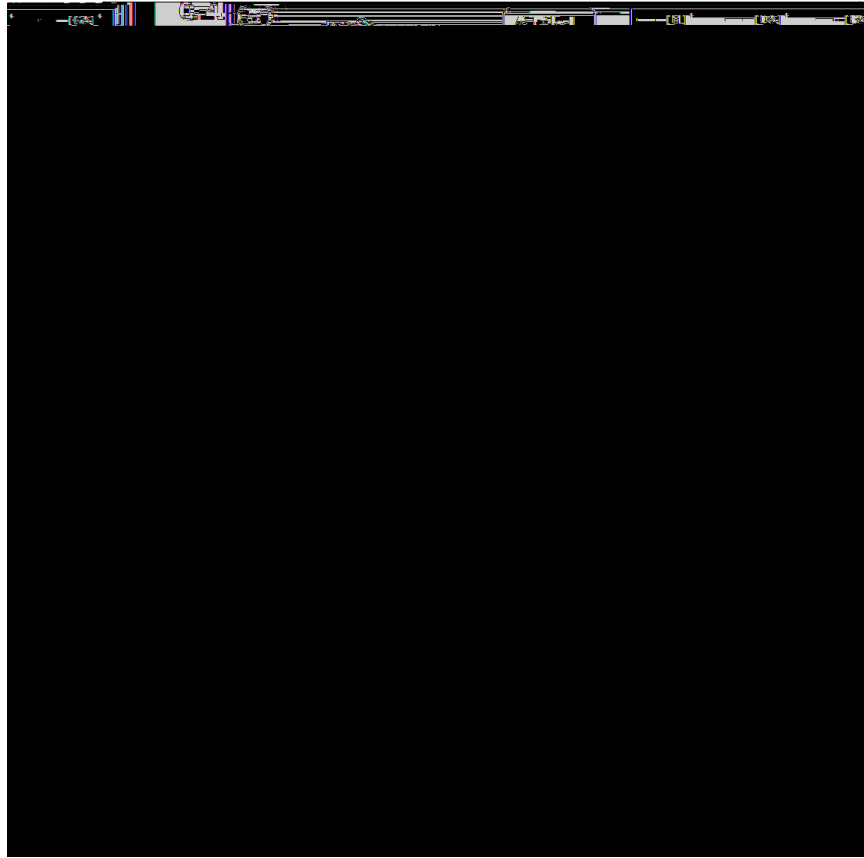
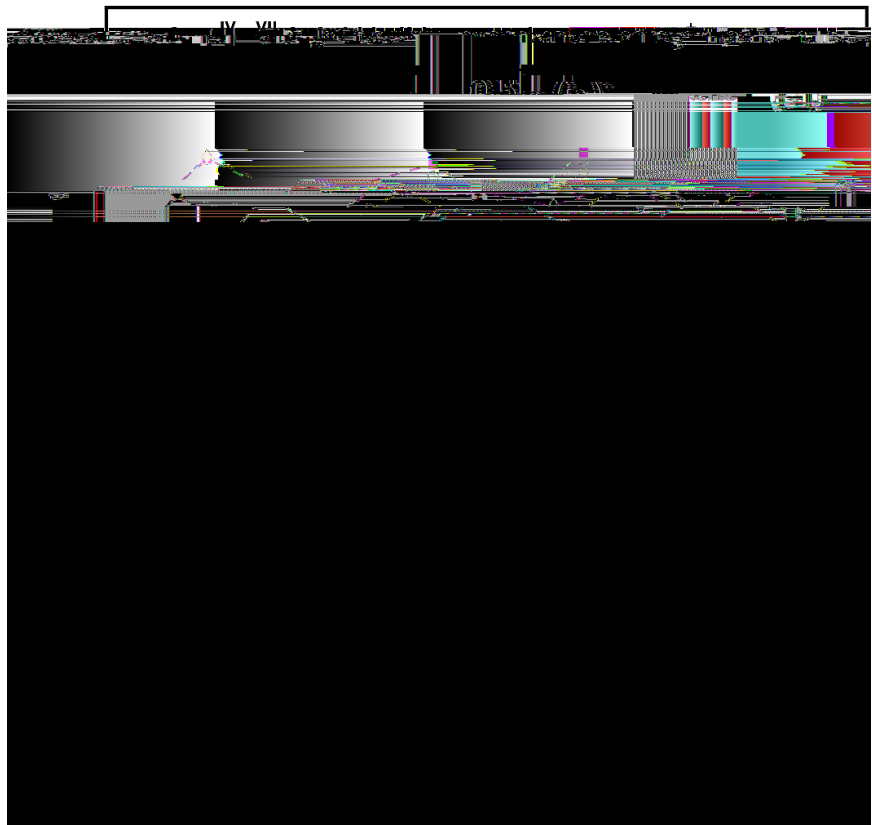


Figure 1. Crystal orbital overlap populations (COOP) of the  $AM^{IV}X_3^{VII}$  perovskites. For comparison, the CBM of each material is set to energy zero.





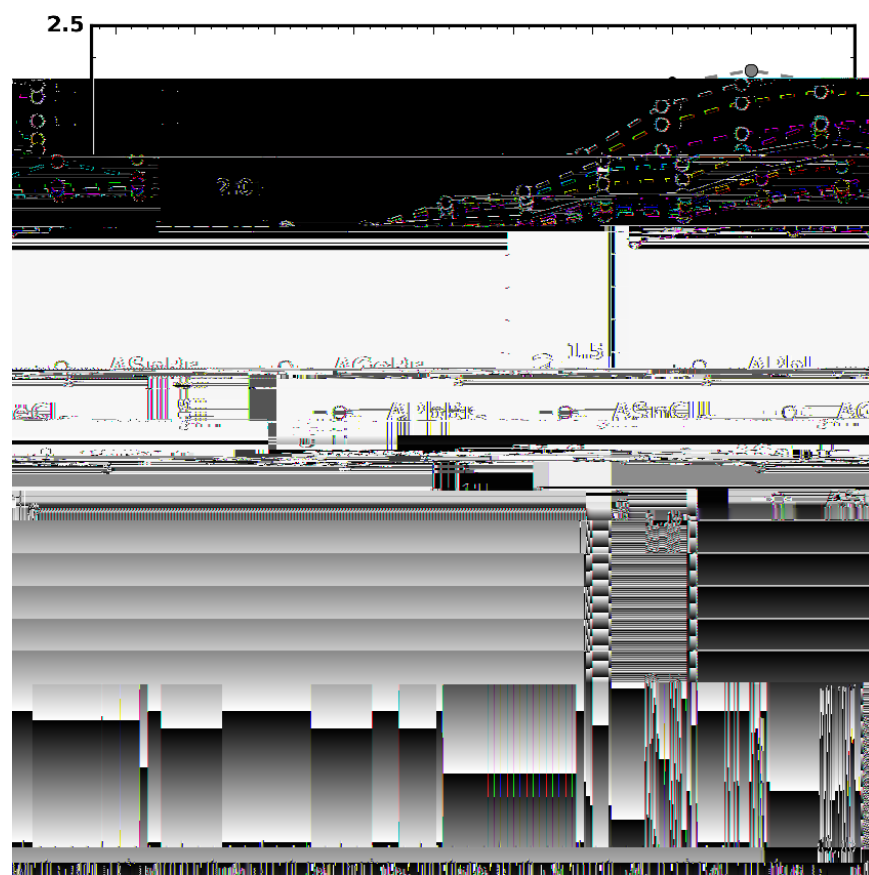


Figure 40 Evaluation of the steric sizes of organic cations within the idealized solid sphere model (see the Experimental section iv)

Table 1: Calculated decomposition enthalpies  $H$  of the candidate  $AM^{IV}X_3^{VII}$





Table 1: 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  $E_g^d < E_{DM}$ , as well as the DM in Table 1. The light blue shading indicates the compounds passing only the current DM.

$E_g^d$ (eV)	PbI <sub>3</sub>	PbBr <sub>3</sub>	PbC <sub>3</sub>	nI <sub>3</sub>	nBr <sub>3</sub>	nC <sub>3</sub>	GeI <sub>3</sub>	GeBr <sub>3</sub>	GeC <sub>3</sub>
[M <sup>+</sup> ]	/	/	/	/	/	/	/	/	/



Table 4: 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  $E_B < 1$  eV, as well as the DMs in Tables 1, 2, and 4. The light blue shading indicates the compounds passing on by the current DM.

$E_B$ (eV)	PbI <sub>3</sub>	PbBr <sub>3</sub>	PbC <sub>3</sub>	nI <sub>3</sub>	nBr <sub>3</sub>	nC <sub>3</sub>	GeI <sub>3</sub>	GeBr <sub>3</sub>	GeC <sub>3</sub>
M <sup>+</sup>	0.4	1.0	0.4	0.9	0.9	1.4	0.9	0.9	1.1
Cs <sup>+</sup>	0.9	0.0	0.4	0.0	0.0	0.0	1.4	0.4	0.4
HA <sup>+</sup>	0.9	0.9	0.9	0.9	0.4	1.9	0.0	0.0	1.4
DA <sup>+</sup>	0.9	1.4	0.4	0.0	0.9	0.9	0.4	1.4	0.9
MA <sup>+</sup>	0.4	0.9	0.0	0.0	0.9	0.9	0.0	0.9	0.4
FM <sup>+</sup>	0.0	0.9	0.4	0.9	0.0	0.4	0.9	0.4	0.4
FA <sup>+</sup>	0.0	0.9	1.9	0.9	1.9	0.4	0.4	0.9	0.0
EA <sup>+</sup>	0.9	1.9	0.0	0.0	1.1	0.0	1.4	0.0	0.0
GA <sup>+</sup>	0.0	0.0	0.4	0.0	0.0	0.9	0.0	0.9	0.0
DEA <sup>+</sup>	0.9	1.1	0.9	0.4	1.9	0.0	0.9	0.4	0.0

ab e  $\epsilon_0$  Ca cu ated exciton Bohr radii  $\alpha$

Table 1. Calculated various DMs for the  $AM^{IV}X_3^{VII}$  perovskites containing pseudo halogen anions,  $AM^{IV}BF_4$  and  $AM^{IV}CN_3$  with A = Cs<sup>+</sup>, MA<sup>+</sup>, FA<sup>+</sup> and M<sup>IV</sup> = Pb<sup>2+</sup>, Sn<sup>2+</sup>

Materials	H	$E_g^d$	$\epsilon_e^*$	$\epsilon_h^*$	$E_{Be}$	$\alpha_{ex}$
Compounds based on $BF_4^-$						
CsPb $BF_4$	1	1	1 $\epsilon_0$	1 4		1 4
CsSn $BF_4$			1 $\epsilon_0$	1 4		1 4
MAPb $BF_4$	1	3 4	$\epsilon_0$ 3		1	
MA <sub>n</sub> $BF_4$		3 1	4 $\epsilon_0$	3	3	$\epsilon_0$
Compounds based on $CN^-$						
CsPb $CN_3$	3 1					