Modification of Material Properties via Non-covalent Interactions in Low Dimensional Organic-Inorganic Halide Perovskites

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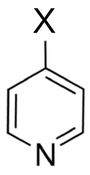
Perovskites: Motivation

Perovskites are a diverse class of materials with important properties for photovoltaics, scintillators, catalysis, etc. Perovskite phases have been explored in recent literature as waste forms for long term storage of radioactive waste from molten salt reactors specifically. Synthesis of new halide perovskite phases can inform these efforts as well as molten salt nuclear reactor chemistry in general. Inorganic perovskites have also shown promise as new scintillating materials for detection of X-rays and gamma rays. Modifying the structure and chemistry of these compounds, perhaps with organic components, could be used to synthesize new scintillating compounds or modify the properties of existing ones.

Synthesis and Characterization

Hydrothermal Synthesis

Materials are mixed with water, sealed in a 23 mL Parr Autoclave, and heated to 150ºC for 48 hours

$HI + TeO_2 +$ 

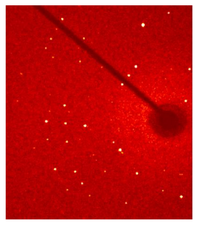
X = H, Cl, Br, I

X-ray beam

$\lambda = 0.7107$ Å

Single Crystal

X-rays scatter from electrons on atoms



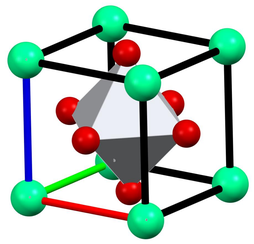
Te is an underexplored perovskite component!

Structural Diversity of Perovskites and Perovskite Derivatives

Ca

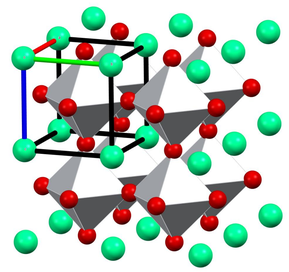
Ti

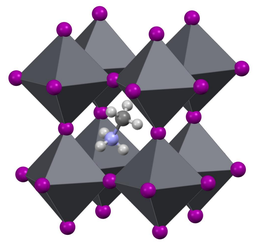
O



Perovskite: $CaTiO_3$

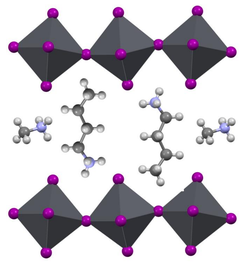
1

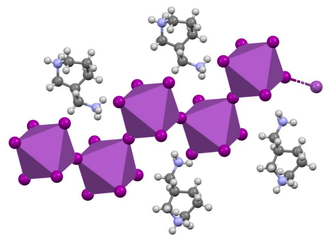




3D Halide Perovskite $(CH_3NH_3)PbI_3$

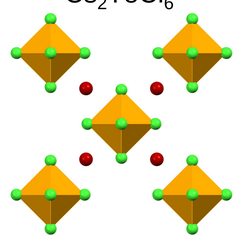
2D Layers $(CH_3(CH_2)_3NH_3)_2(CH_3NH_3)Pb_2I_7$





1D Chain $(3AMP)BiI_5$

0D Halide Perovskite Cs_2TeCl_6



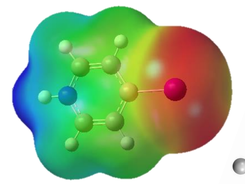
Reduction In Dimensionality

Low Band Gap, Low Stability

High Band Gap, Higher Stability

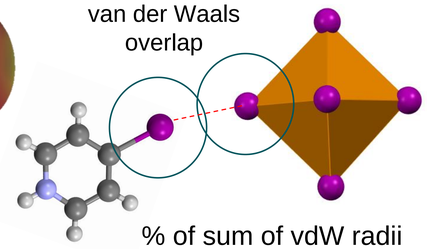
Non-covalent Interactions

Halogen bonding



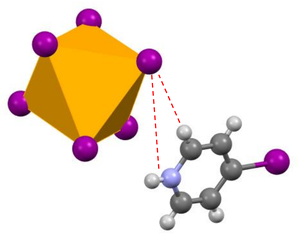
Polarization of Halogen

van der Waals overlap

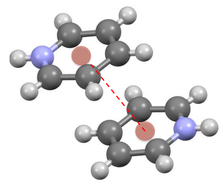


% of sum of vdW radii

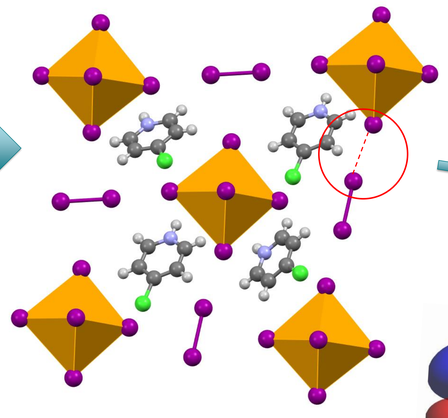
Hydrogen Bonding



π-π Stacking



Crystallographic and Computational Metrics for Te

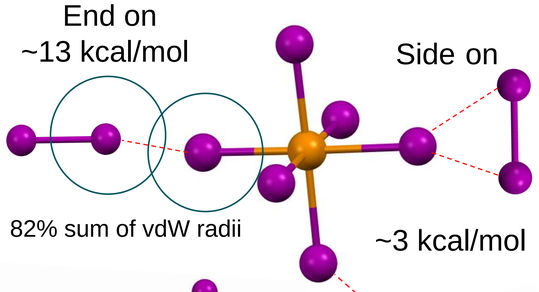


Zero-Dimensional Halide Perovskite Derivative $(ClPy)_2TeI_6 \cdot I_2$

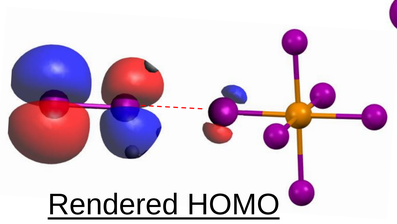
Analysis *via* Natural Bond Orbital and Second Order Perturbation Theory

End on ~13 kcal/mol

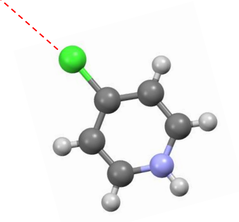
Side on ~3 kcal/mol



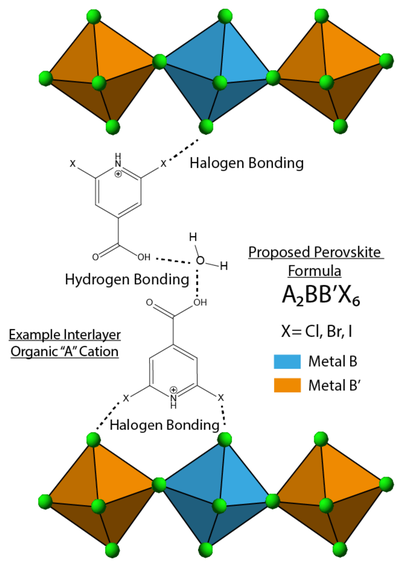
82% sum of vdW radii



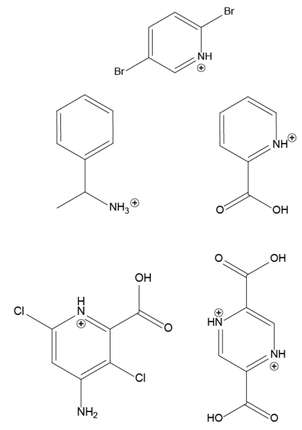
Rendered HOMO



Proposed Research Directions



More Proposed Interlayer "A" Site Cations



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