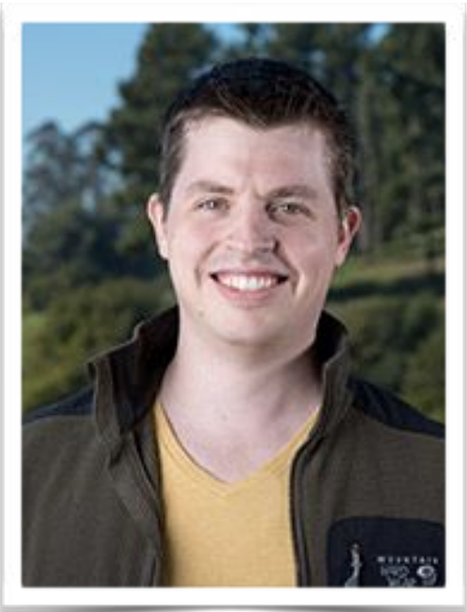
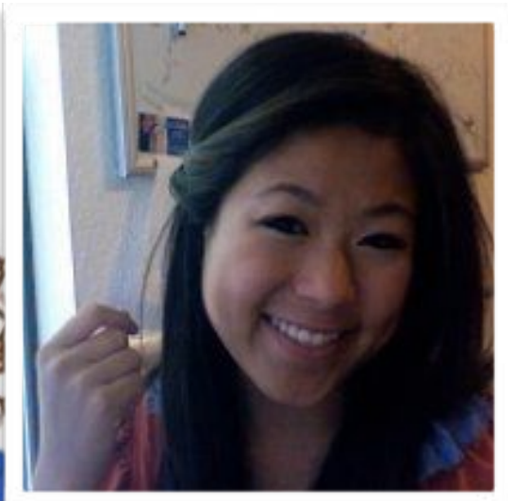
Geometry and Electronic Structure of Metal-Organic Chalcogenide Assemblies (MOChAs)



Nate Hohman



Mary Collins

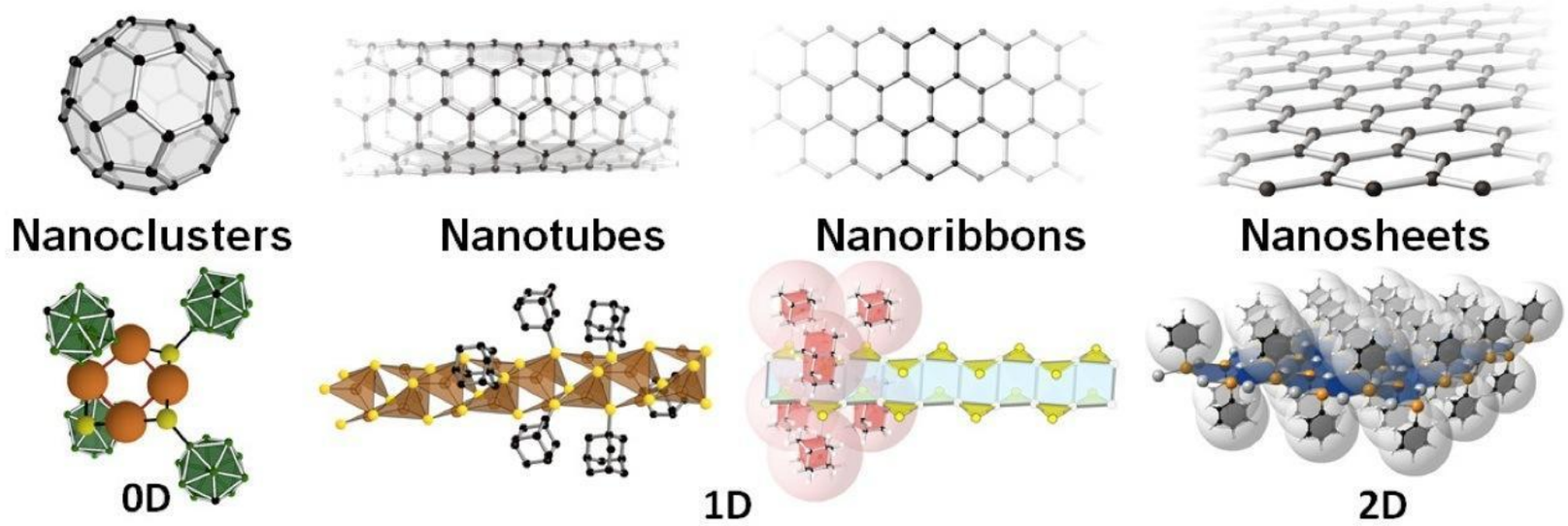
Tess E. Smidt

Neaton Group

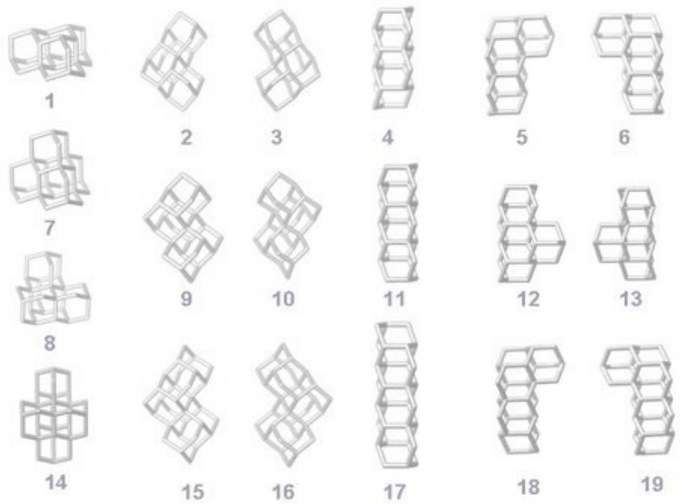
Inorganic Facility Group Meeting | Molecular Foundry | 2016.04.28

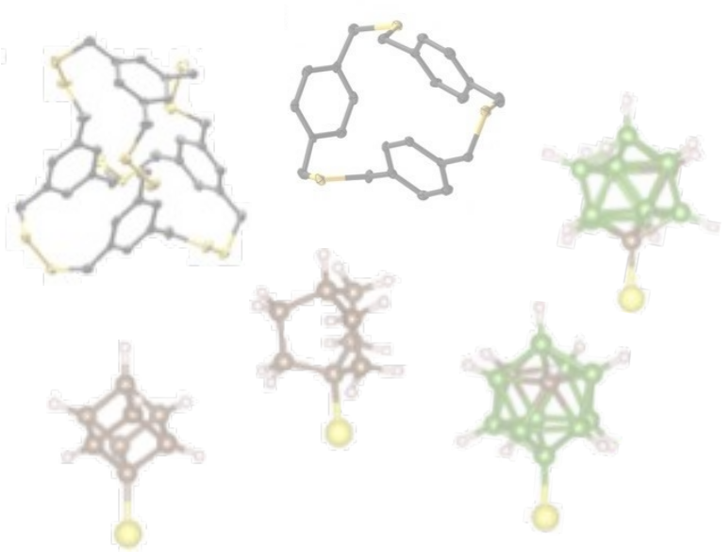
Why MOChAs?

The inorganic structure is continuous, low-dimensional, and <u>dominates electronic structure.</u>

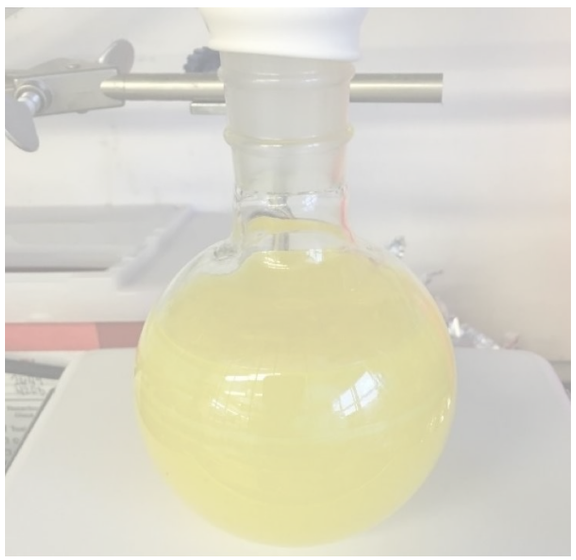


Organic ligands provide scaffolding for inorganic structure. Provides immense tunability.





MOChAs self-assemble and can be synthesized at gram scale or as thin films.



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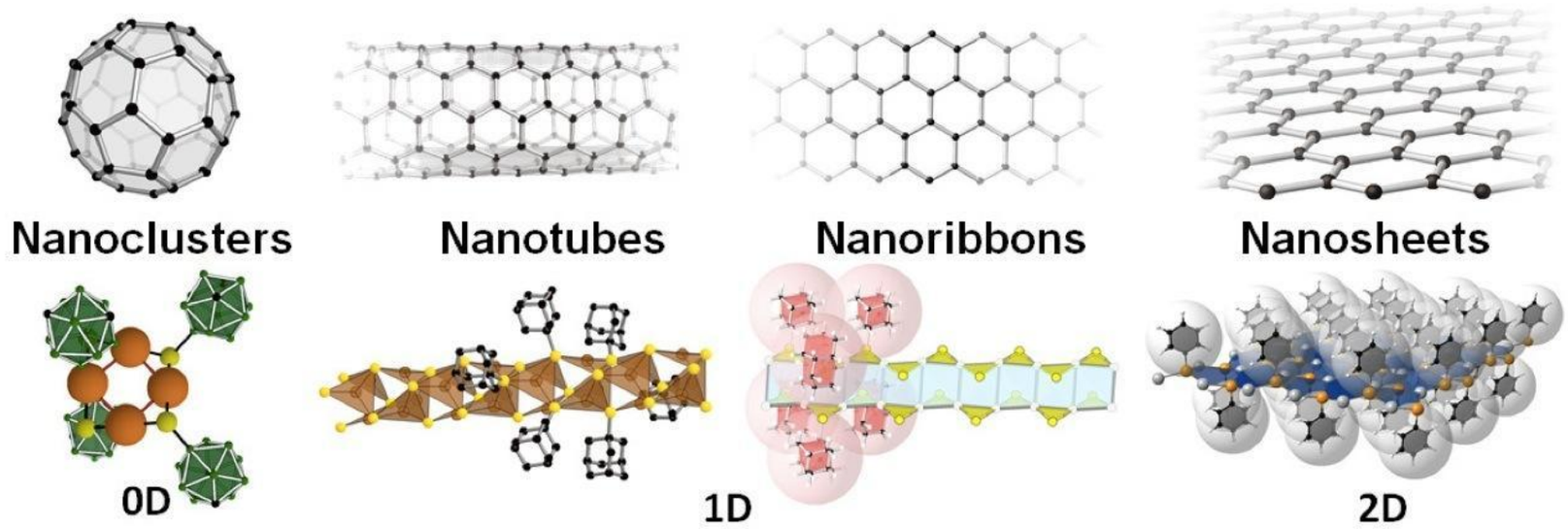

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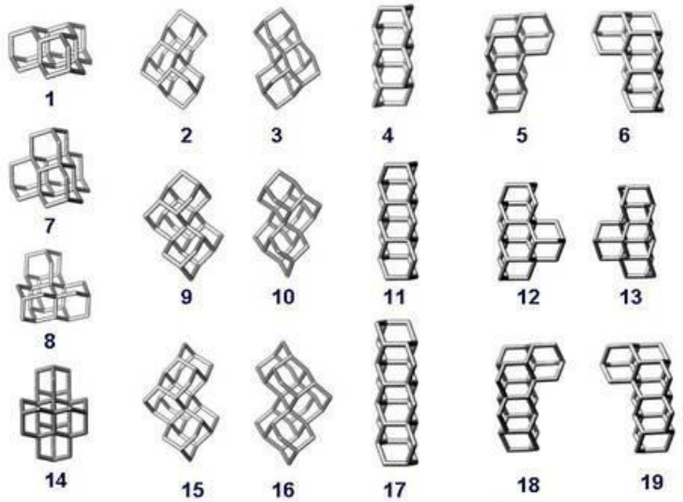

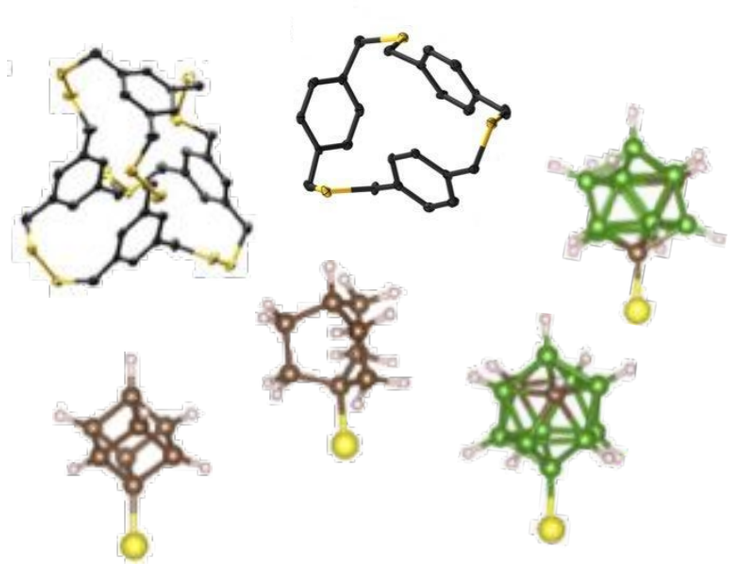

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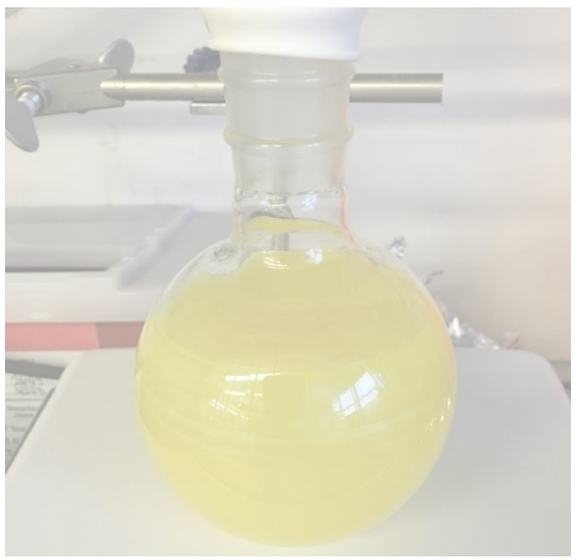

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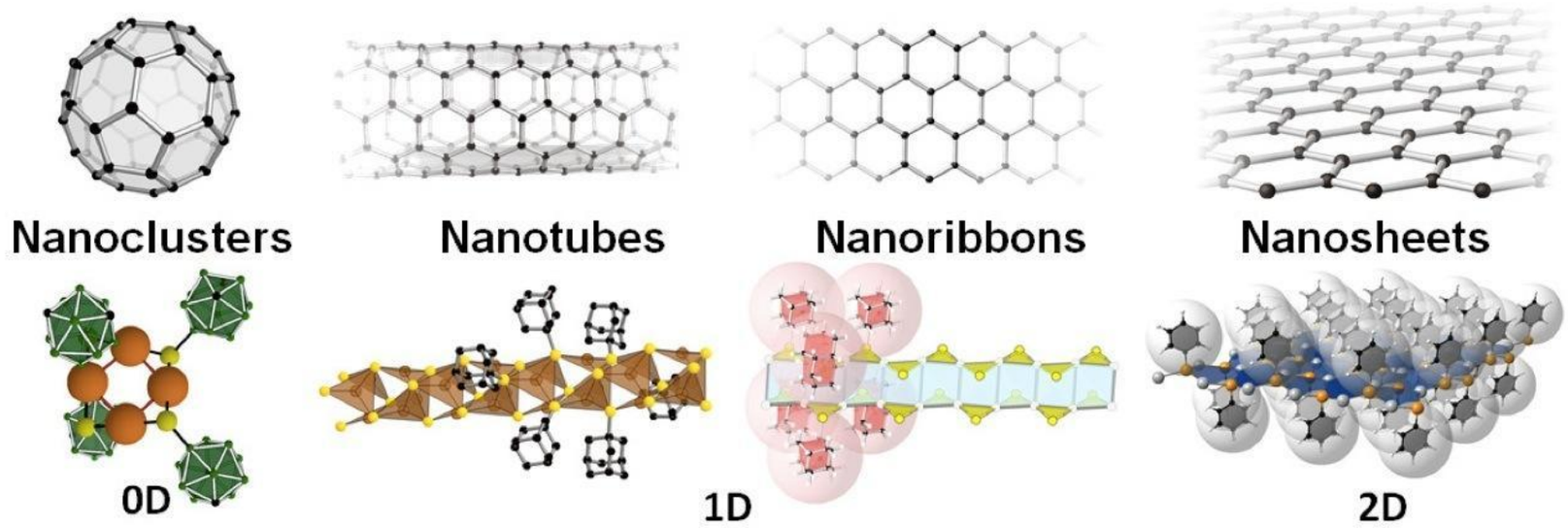

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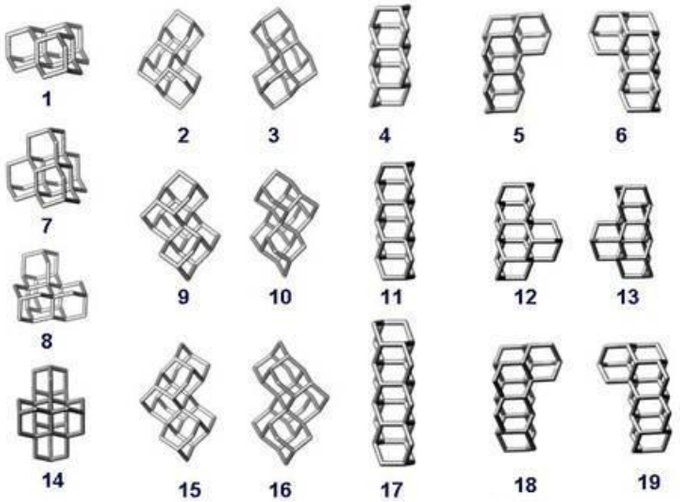

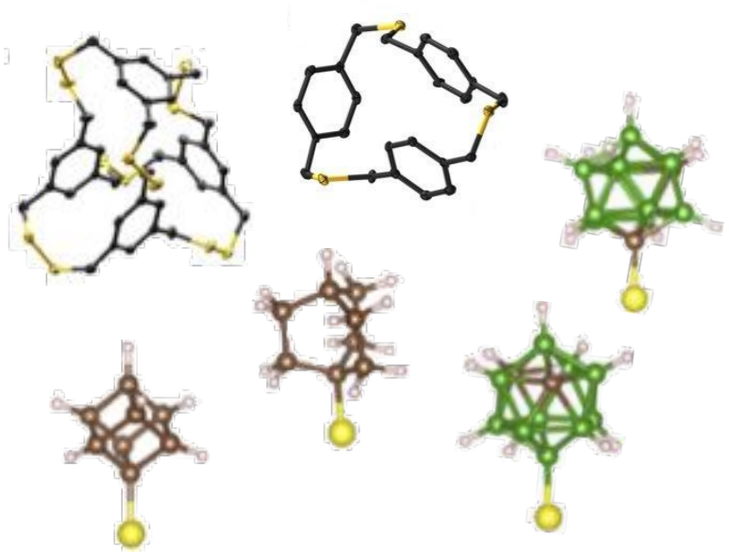

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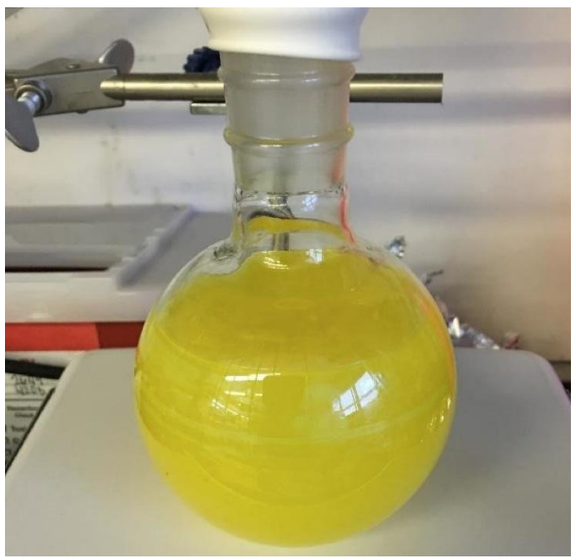
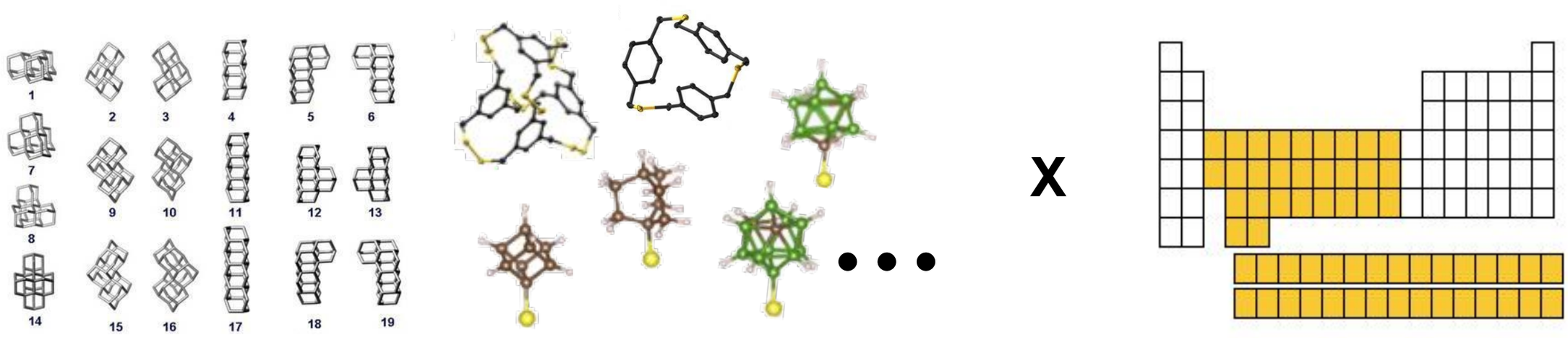


How to design MOChAs?

Given ligand X and transition metal Y? ➜ Combinatorial explosion!

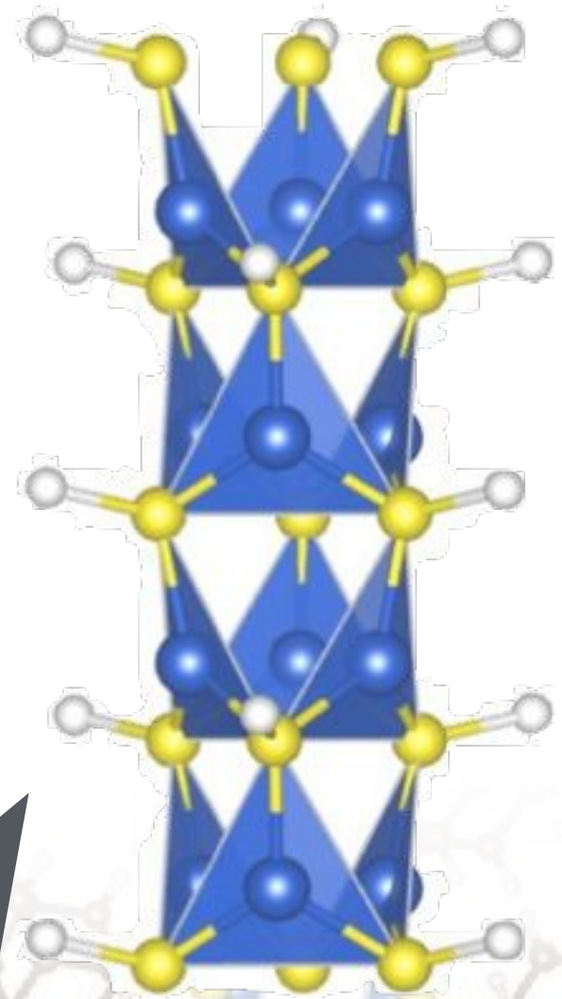


How to design MOChAs?

Simplify problem by first focusing on design of inorganic structure.

Can we explore the low-dimensional inorganic structure independent of bulk?

- How much do VdW bonded subunits interact?
- How much does the ligand impact bands near the Fermi level?



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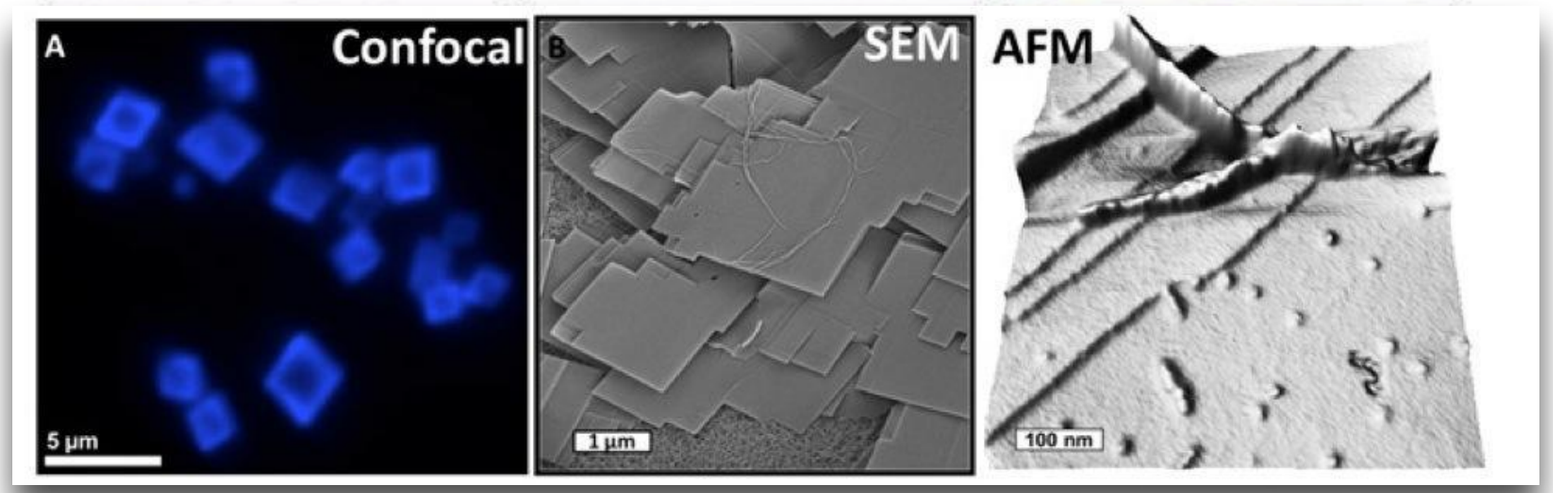
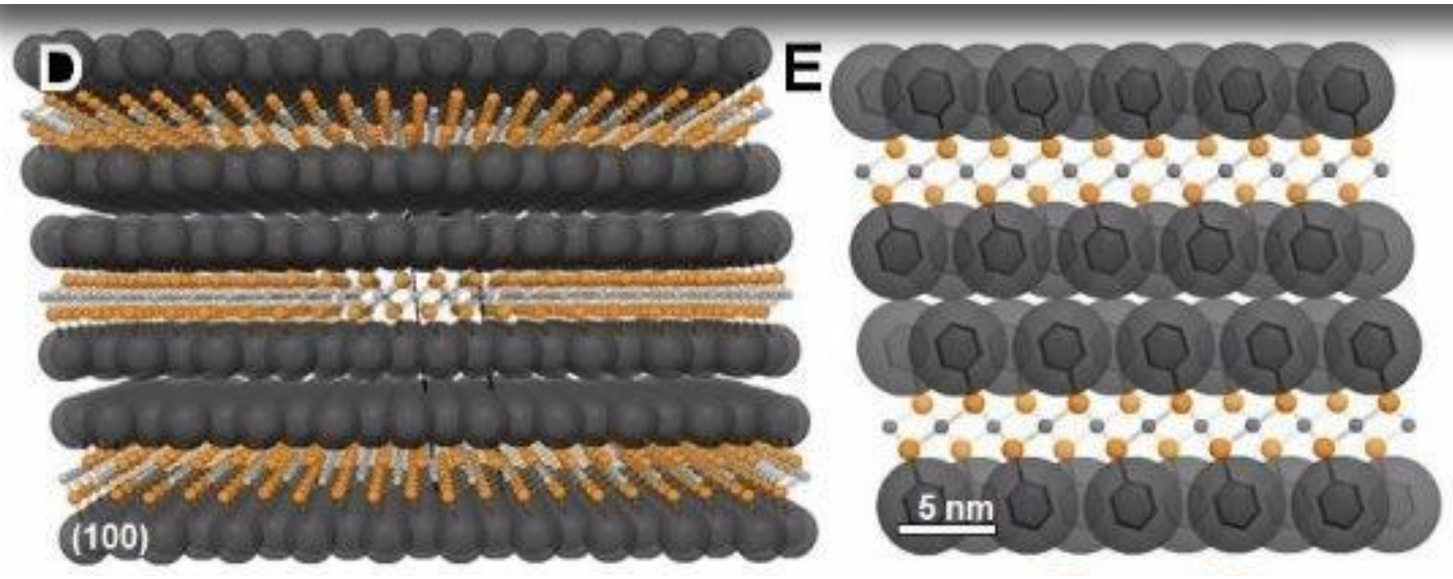
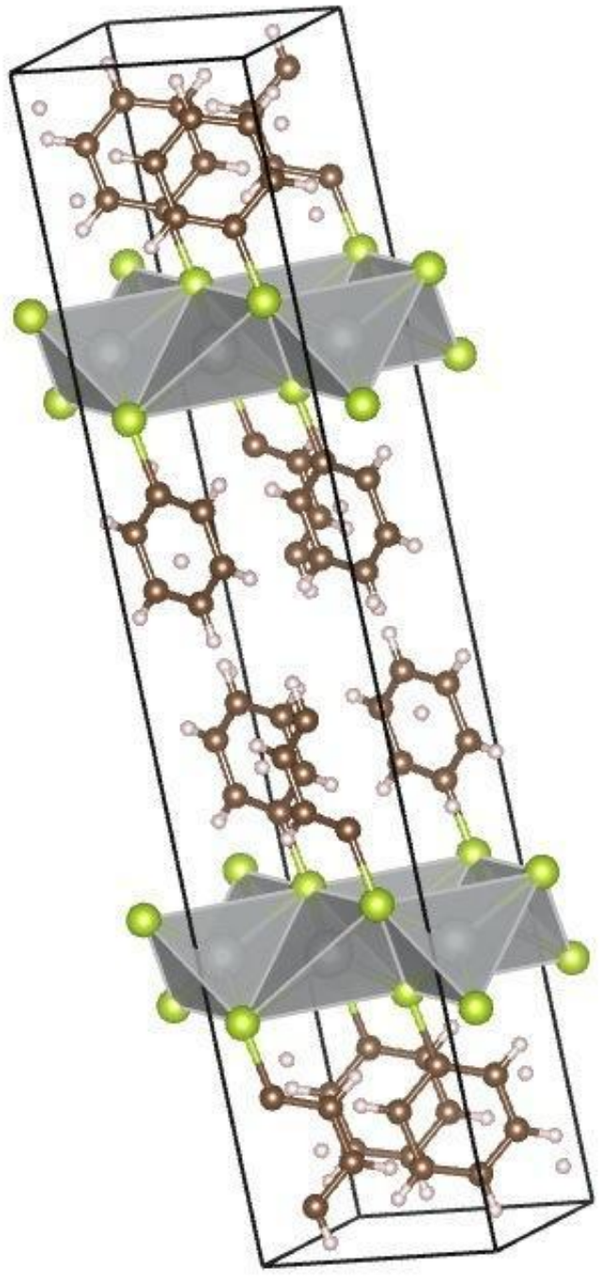
Mithrene (AgSePh)







- Are properties invariant for any number of layers?
- Does this material display 2D quantum confinement?

How to answer? Experiment — hard. Theory — easy(er).
Let's use density functional theory (DFT)!

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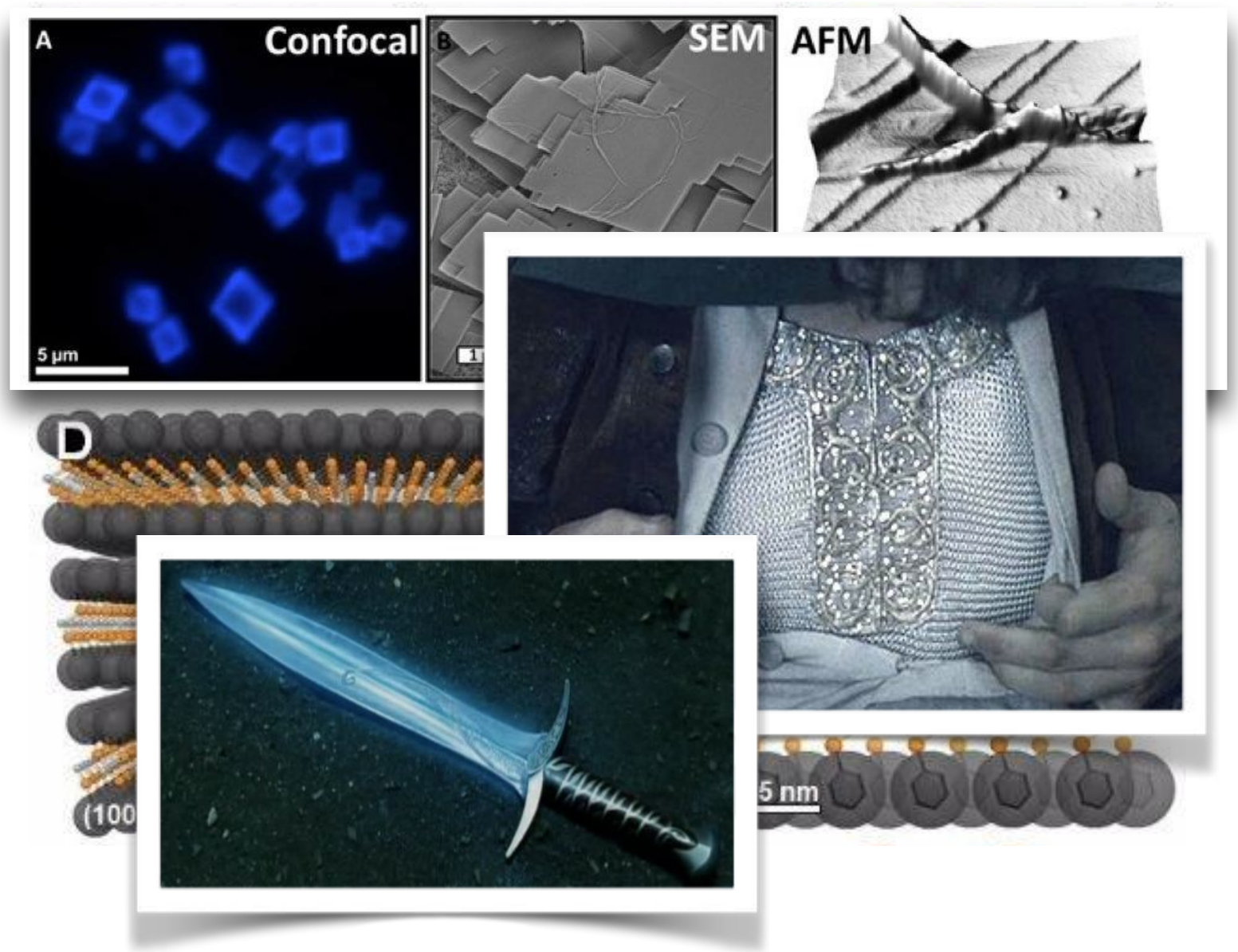

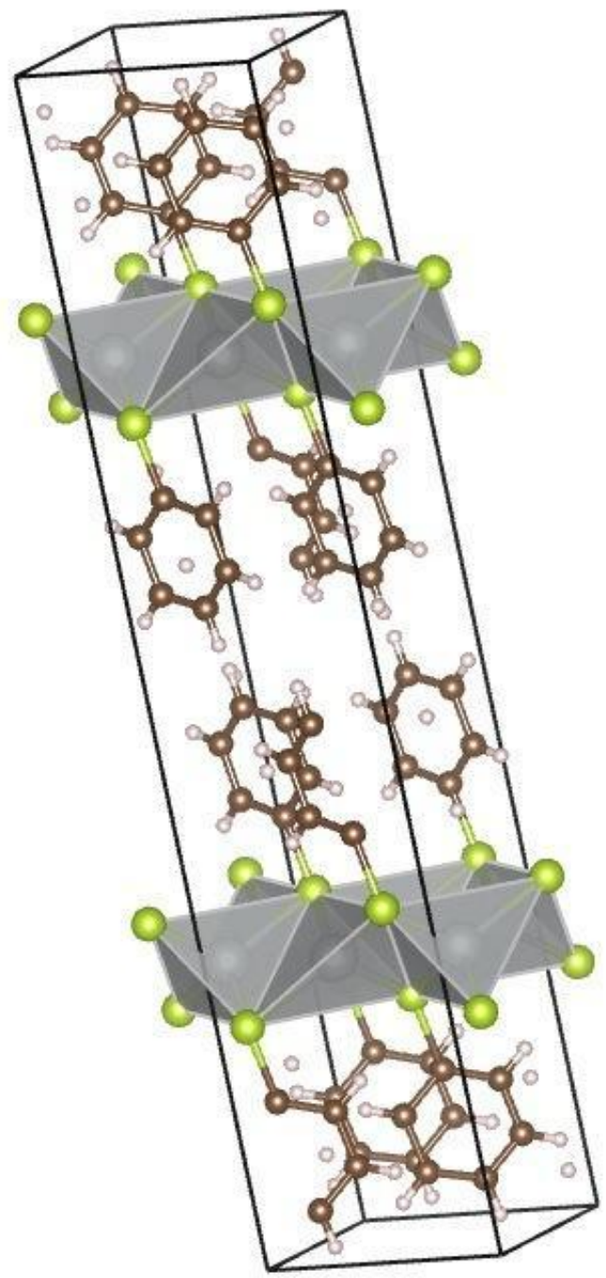

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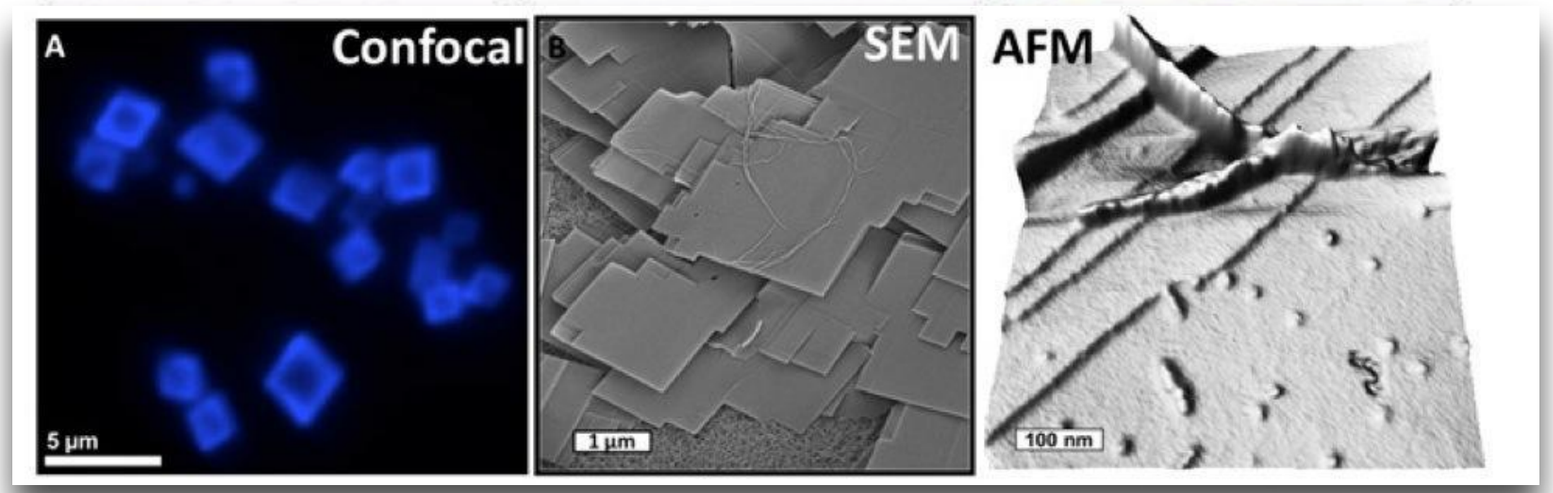

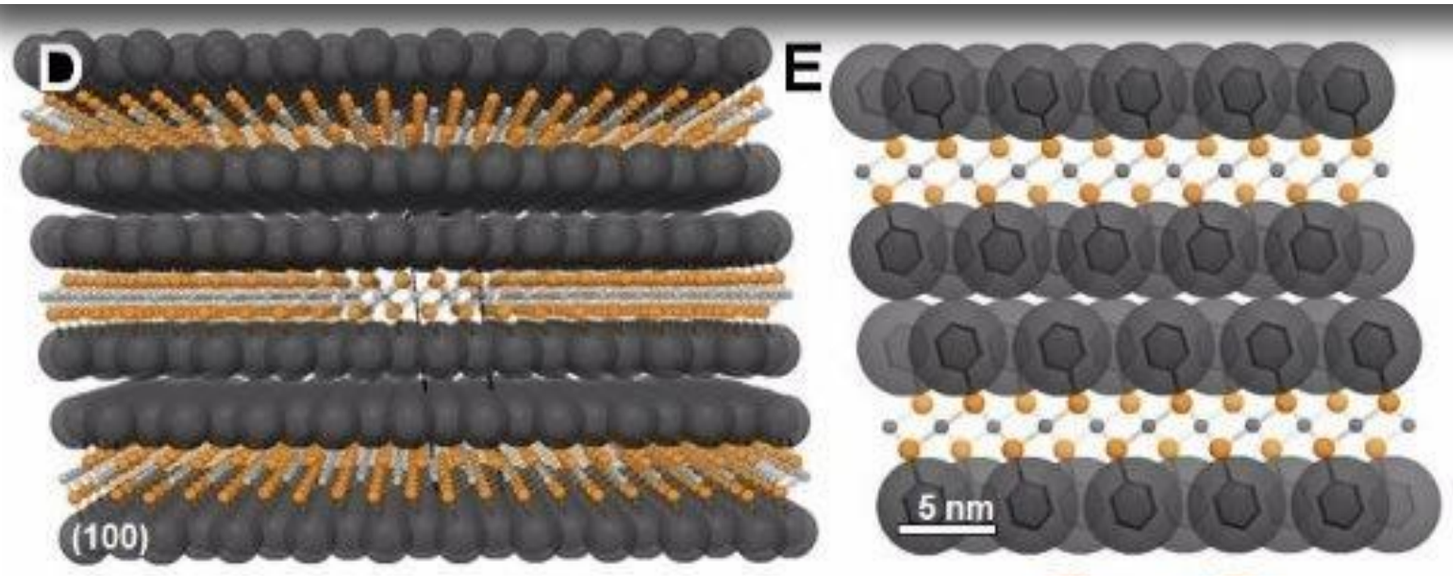

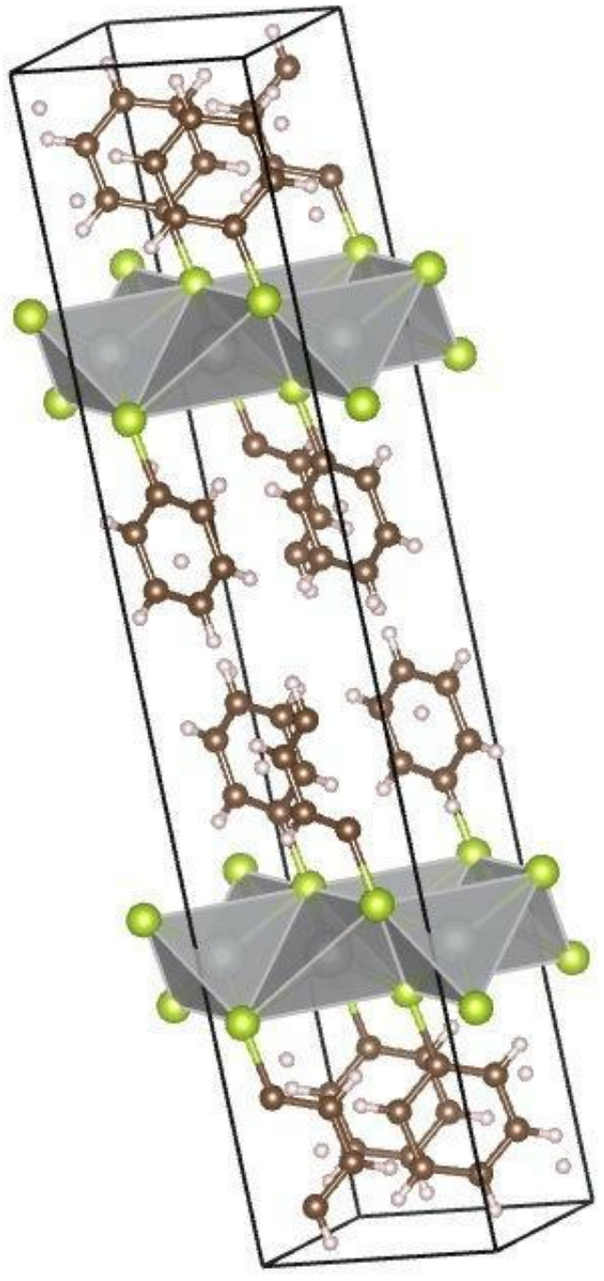

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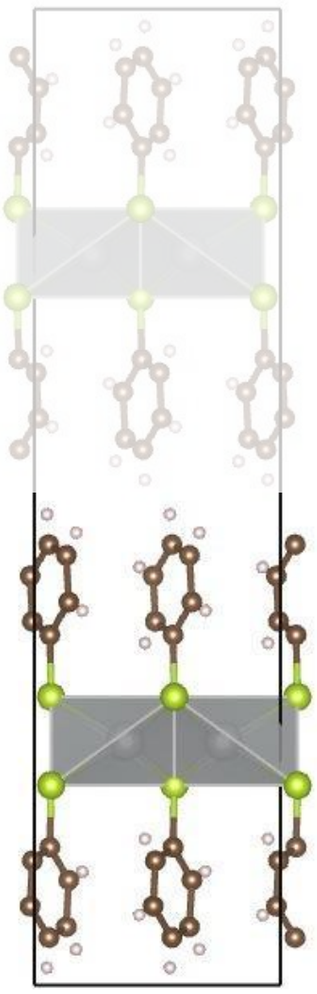
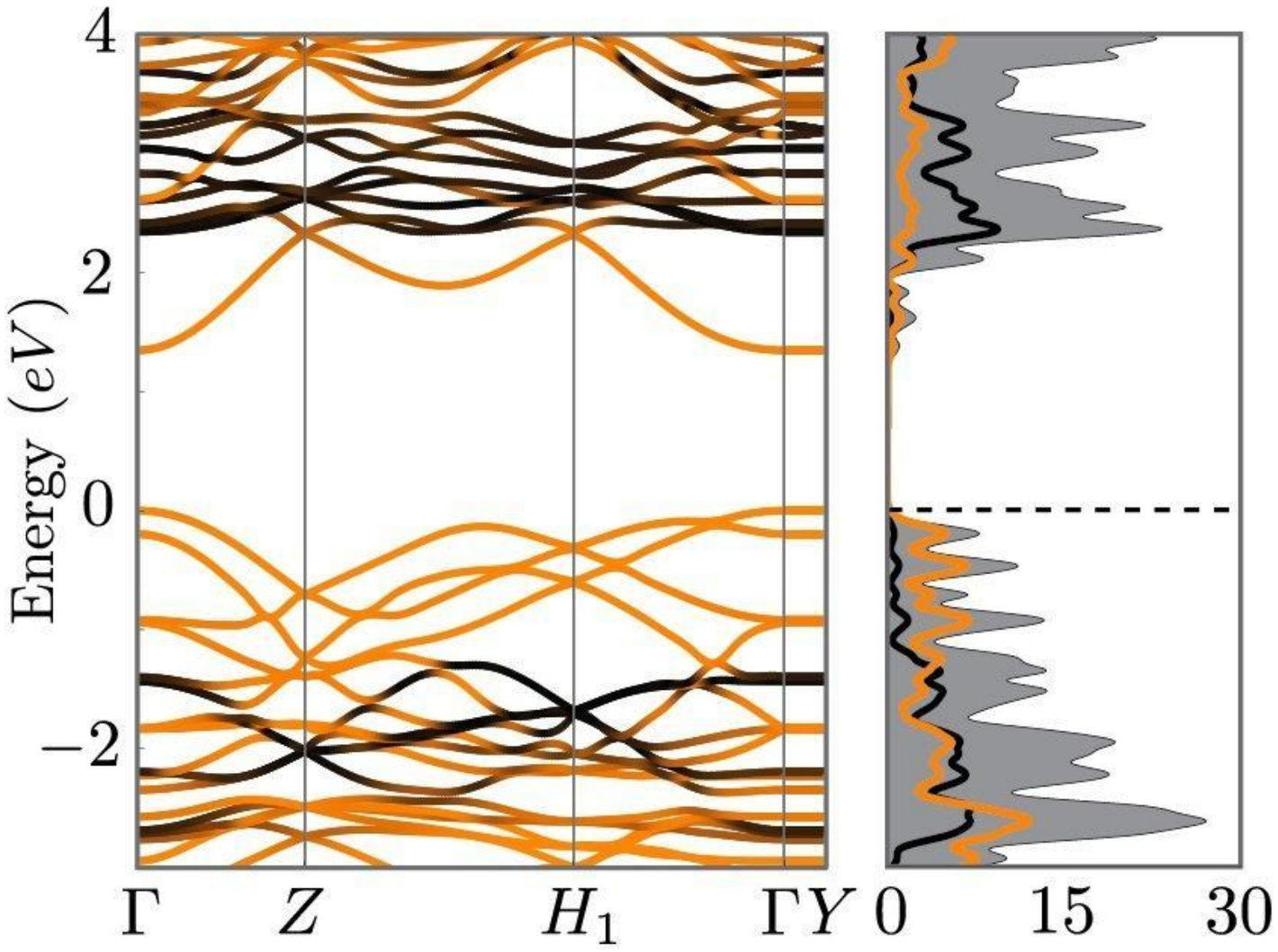
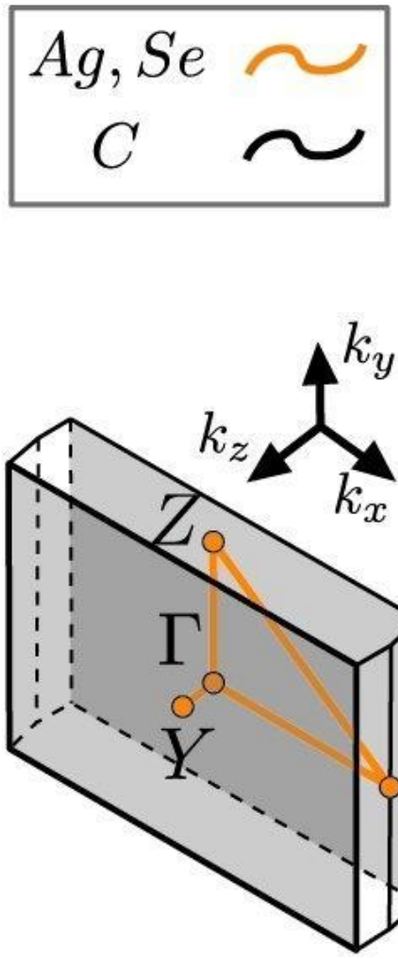
Mithrene — PBE band structure (spaghetti)







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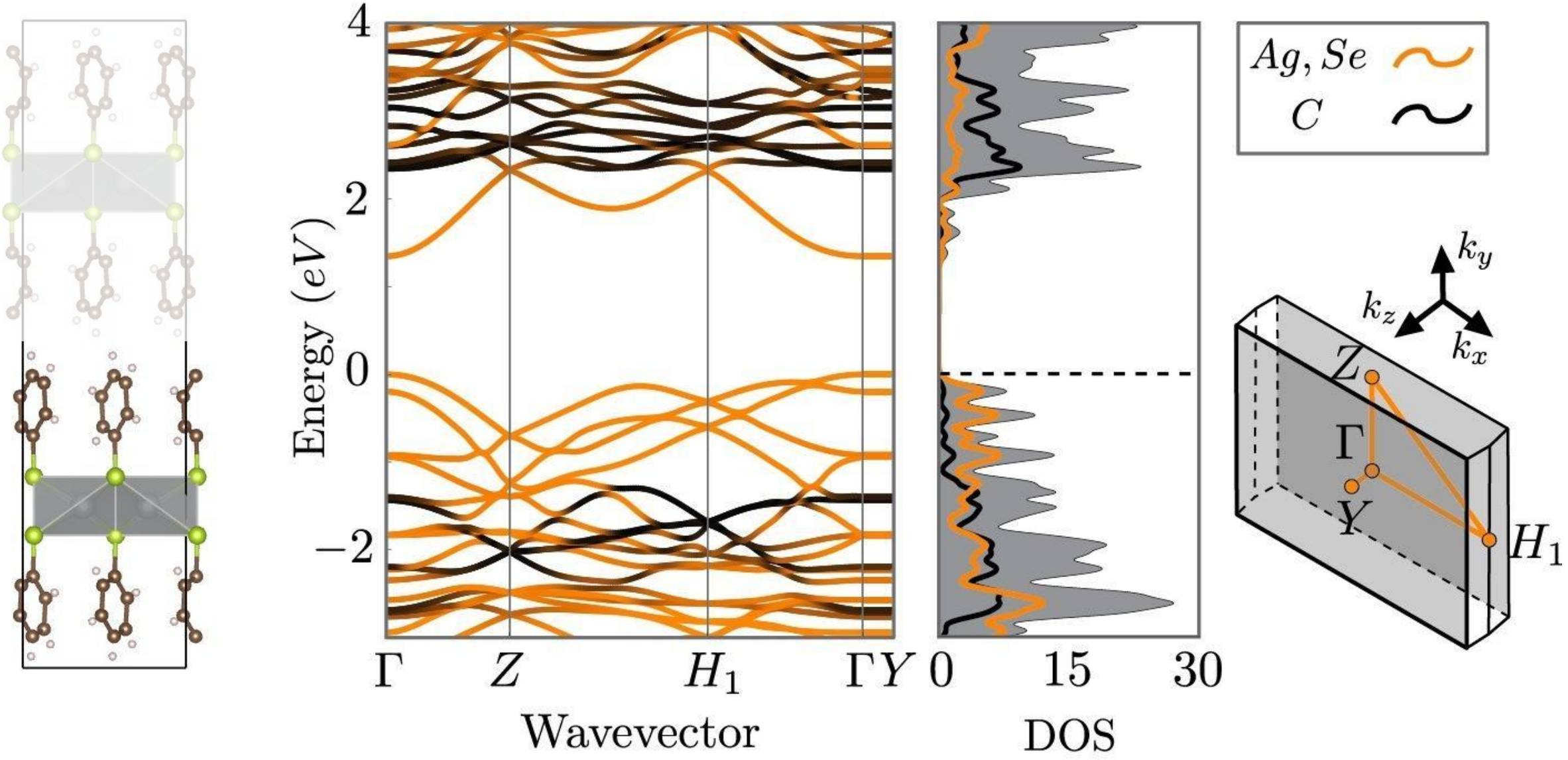

- Direct band gap at Γ.
- Organic bands and inorganic bands are well separated.
- Low mobility between layers.
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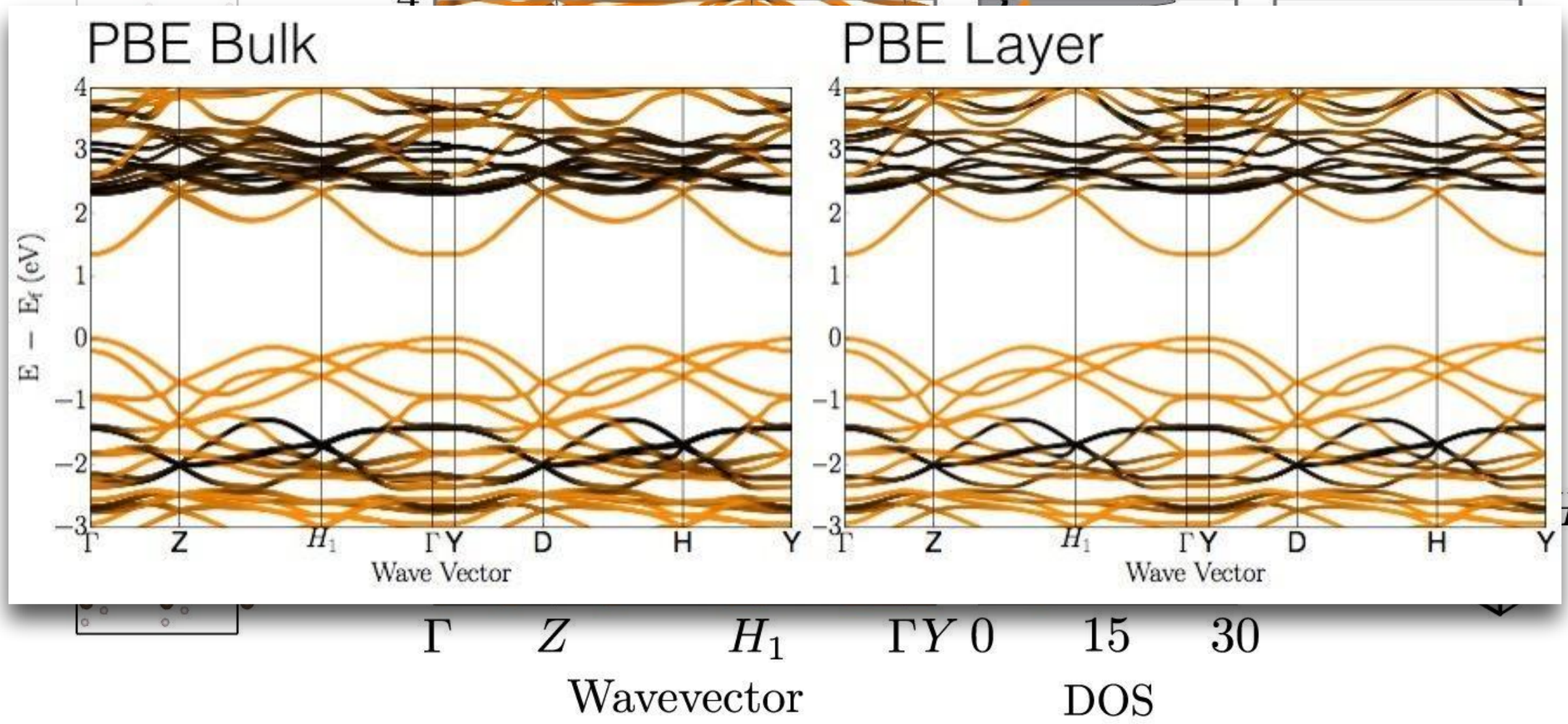

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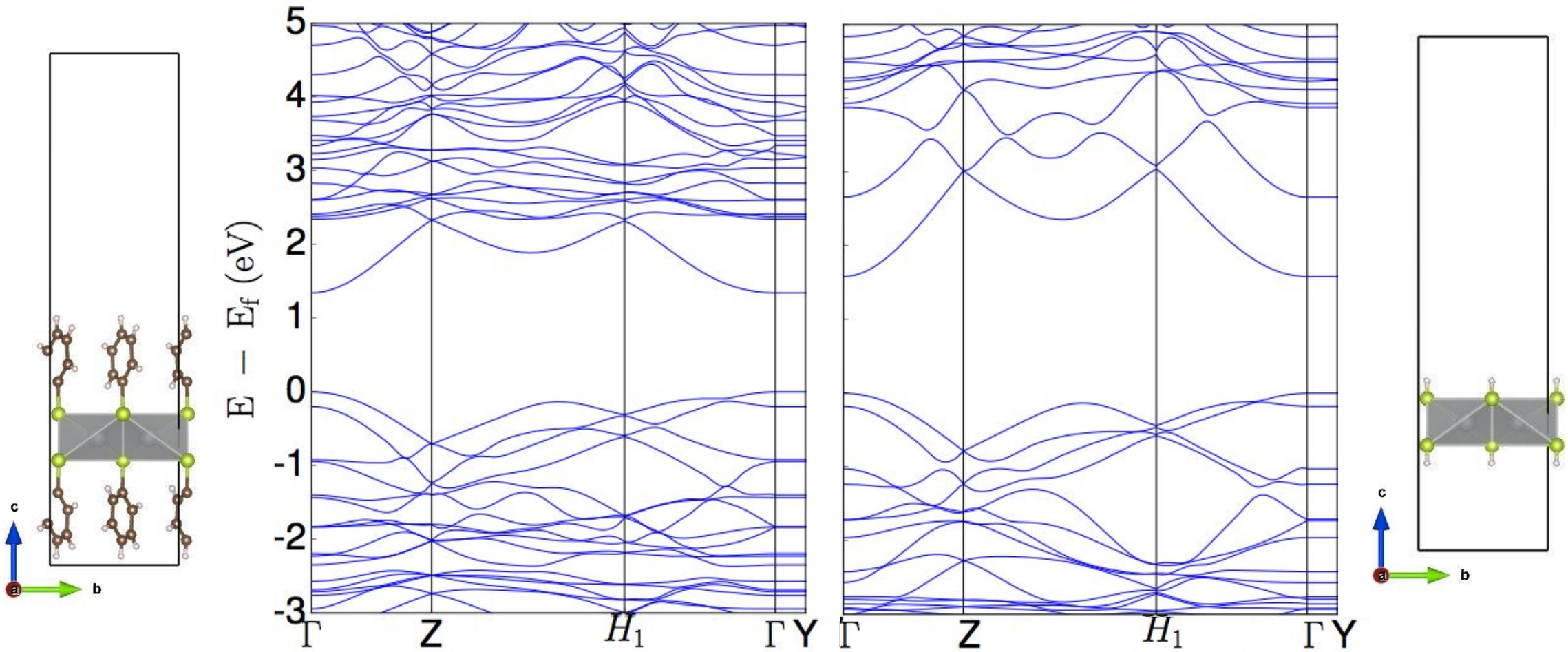
“Ligand agnostic” calculation captures main characteristics of electronic structure.



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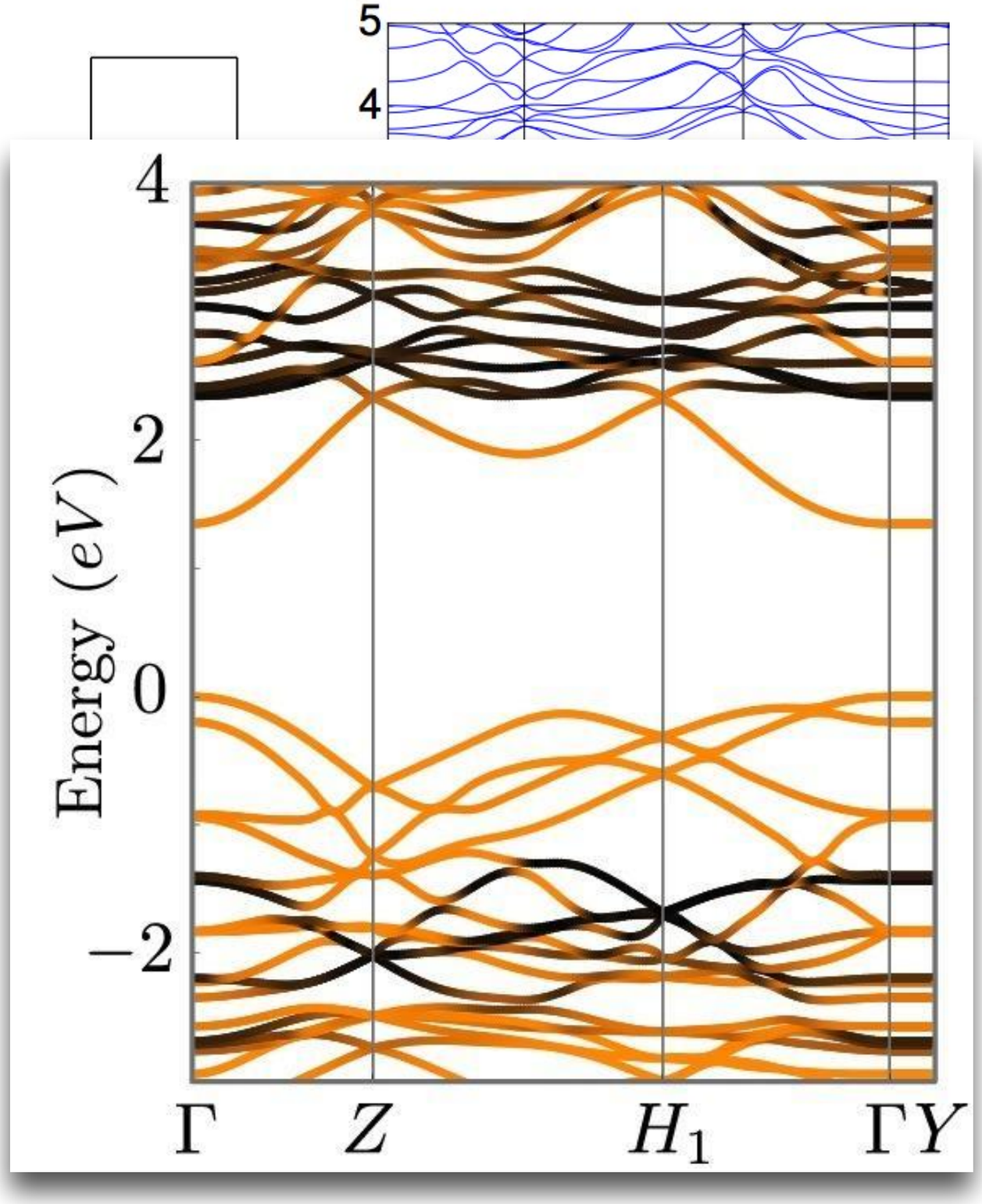
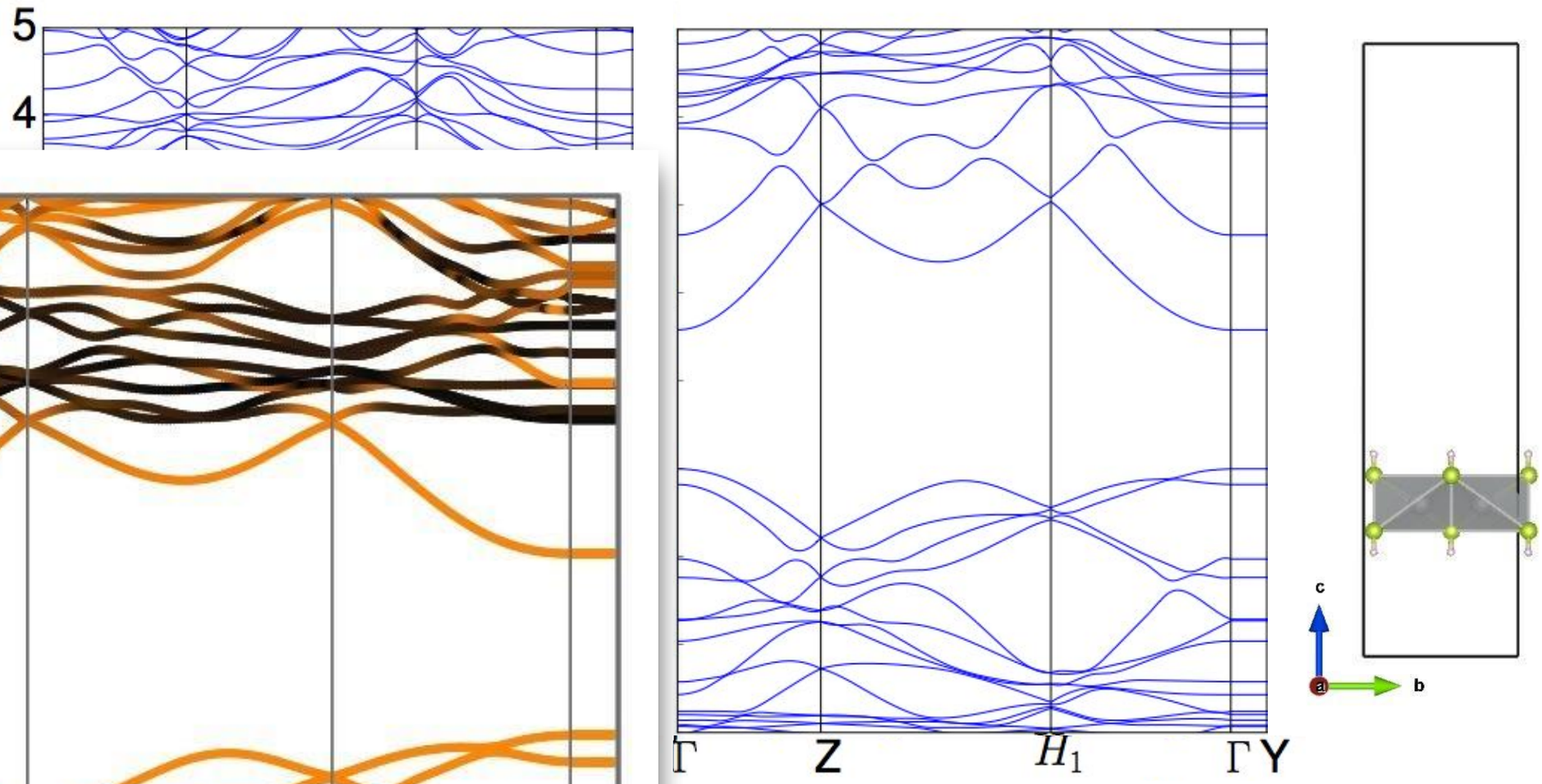
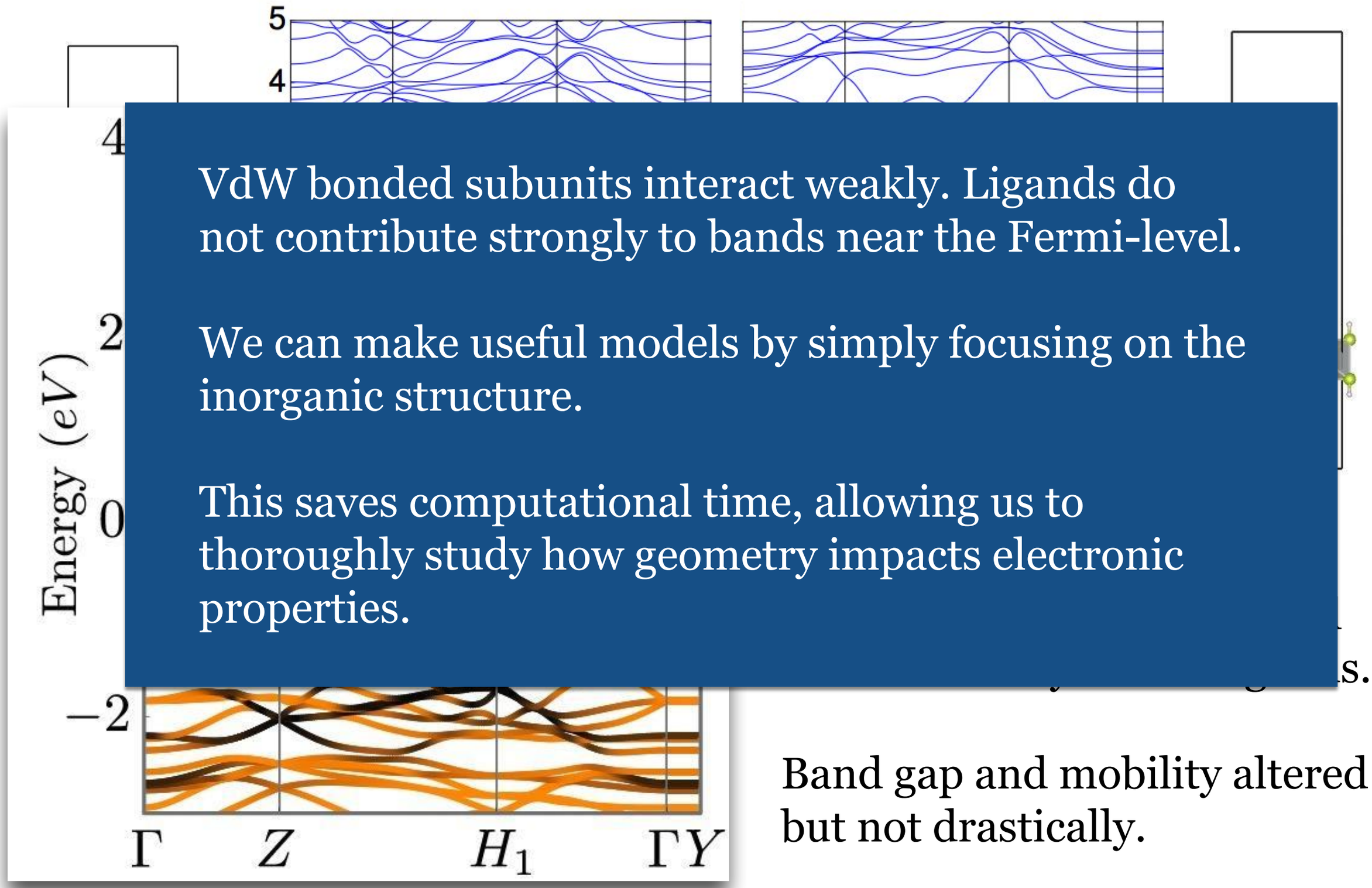




Remaining bands are Ag and Se bands in layer with ligands.

Band gap and mobility altered but not drastically.

“Ligand agnostic” calculation captures main characteristics of electronic structure.



VdW bonded subunits interact weakly. Ligands do not contribute strongly to bands near the Fermi-level.

We can make useful models by simply focusing on the inorganic structure.

This saves computational time, allowing us to thoroughly study how geometry impacts electronic properties.

s.

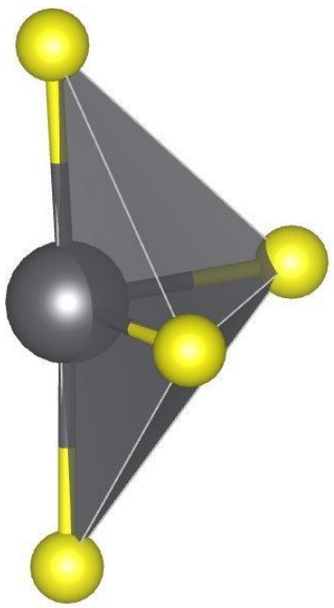
Band gap and mobility altered but not drastically.

GEOMETRY CASE STUDY:

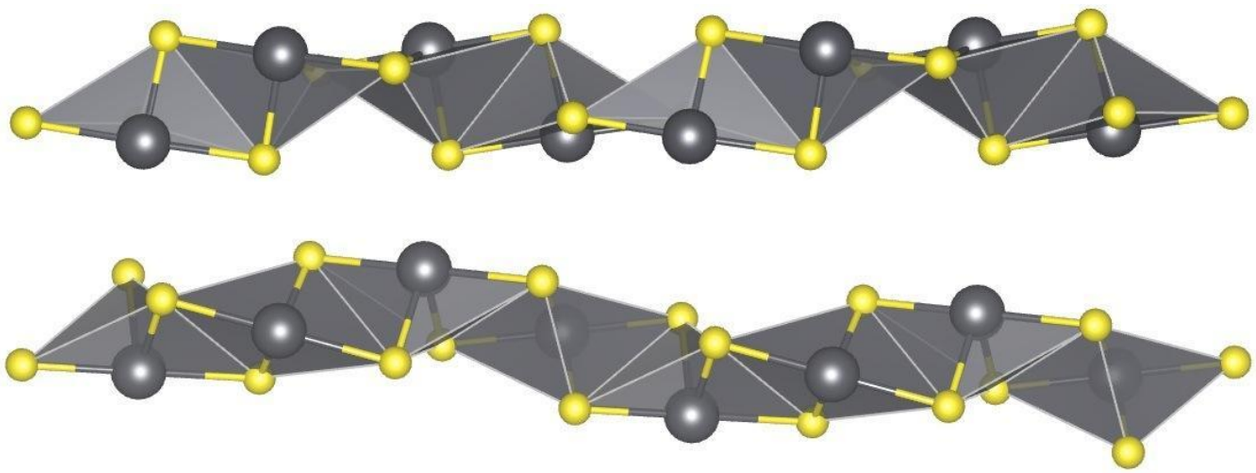
Pb Seesaw chalcogenide chains

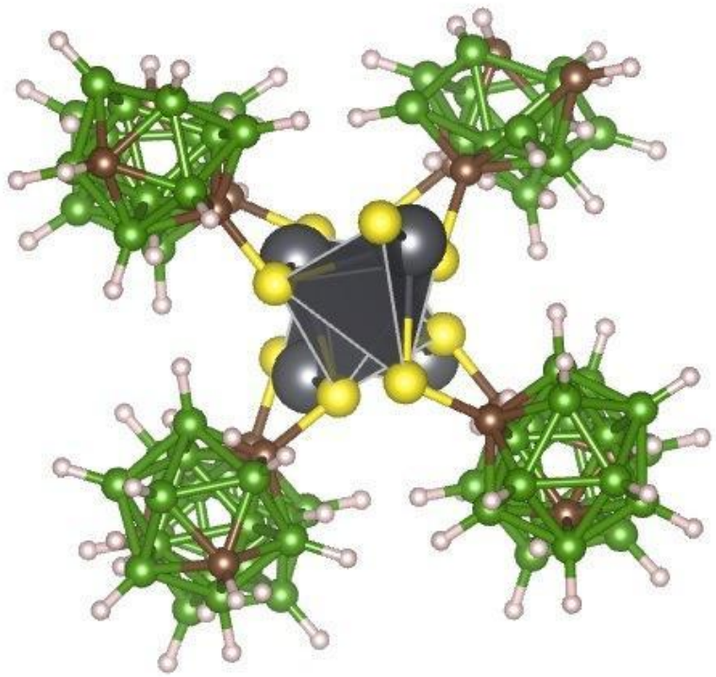
Seesaw units. Pb and S.

C-S bonds. Carboranes coordinating chalcogenide cha



Chiral





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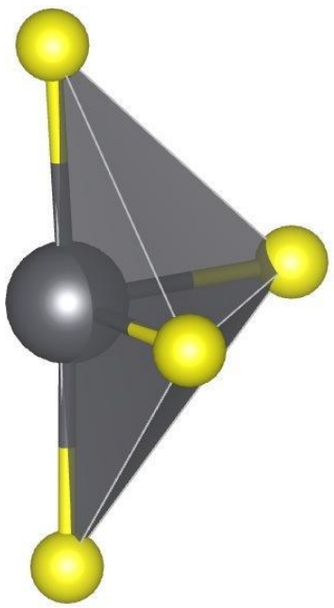

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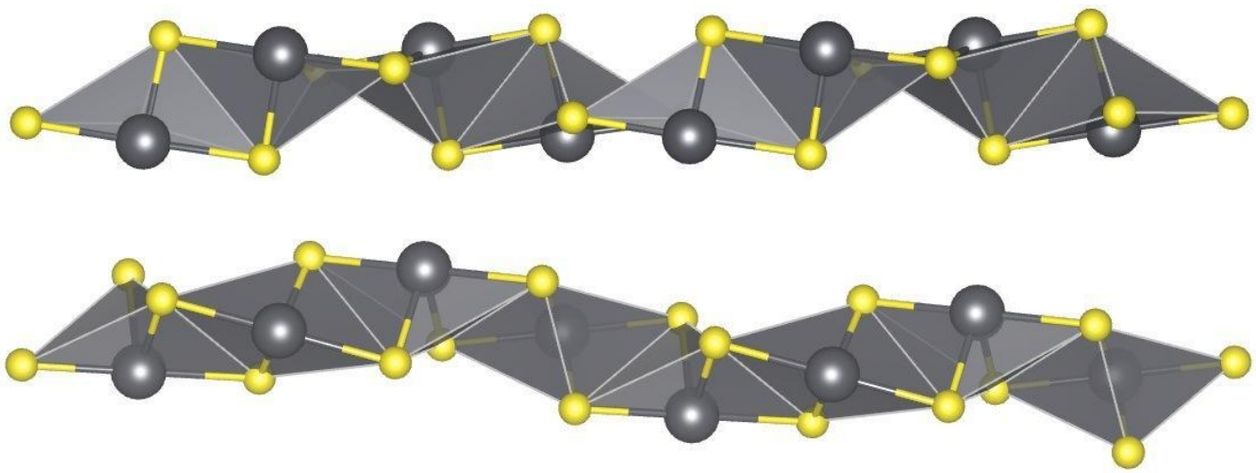
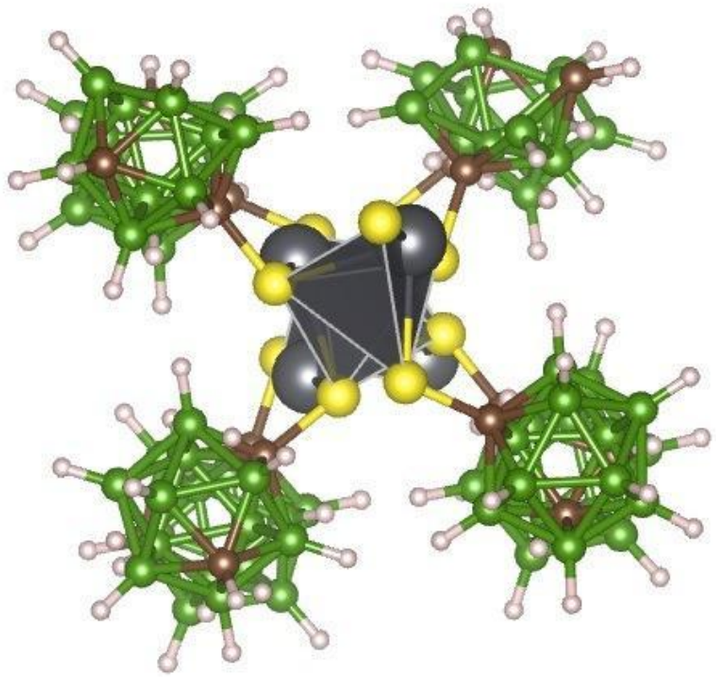
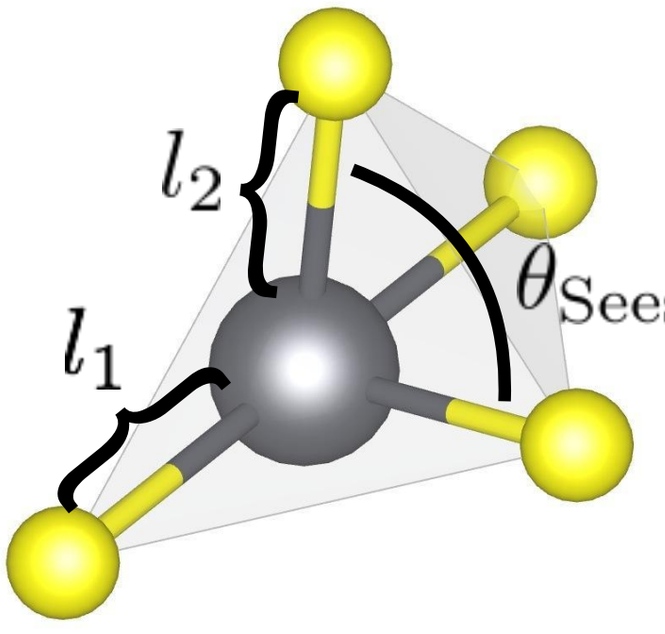
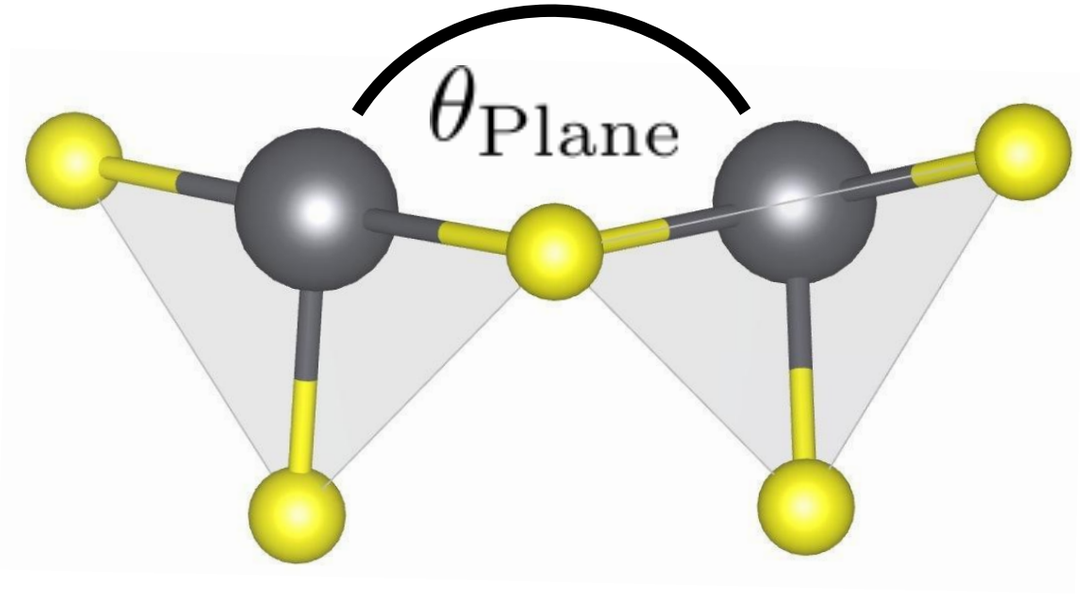




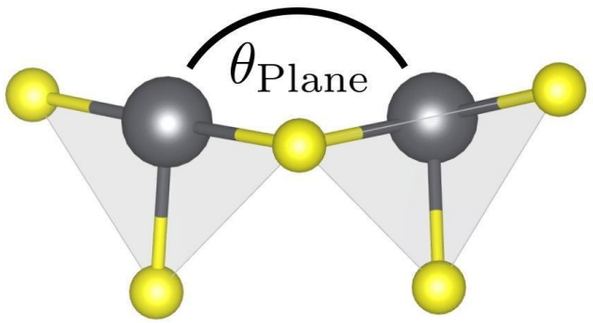
Parameterize structure by two intra-unit parameters and one inter-unit parameter.

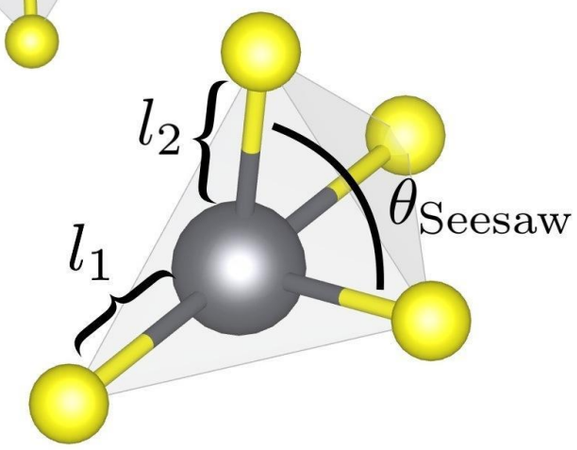


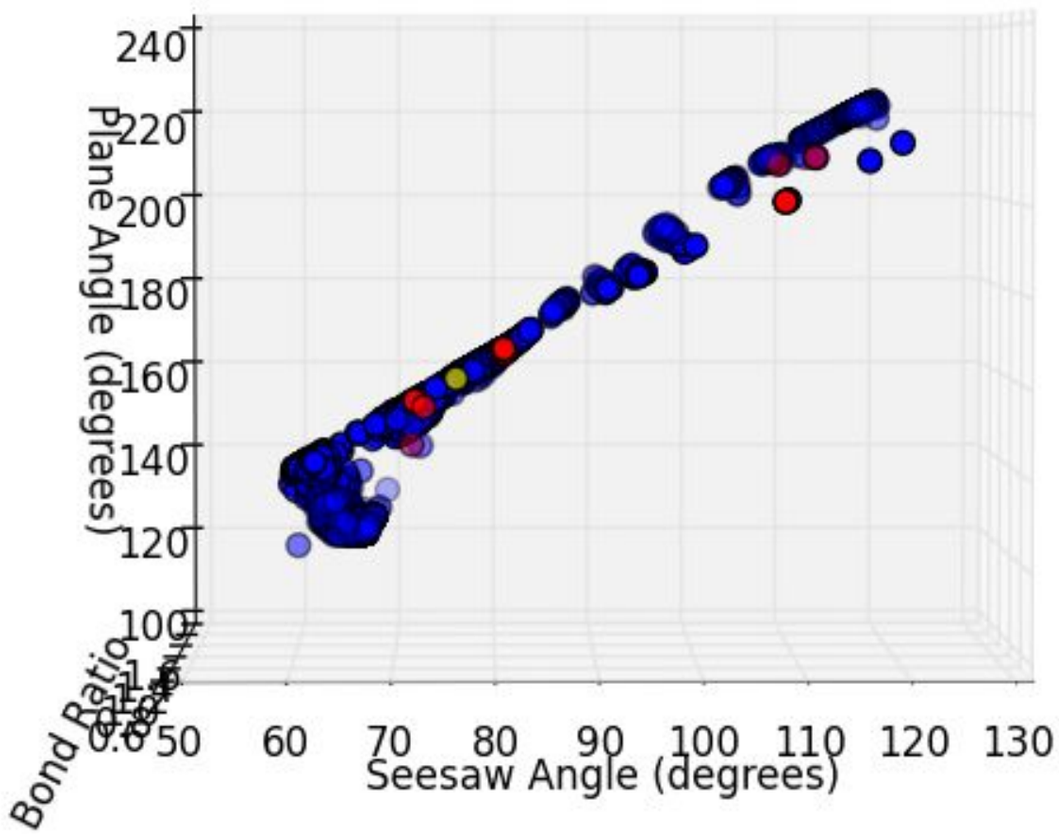
$$\frac{l_2}{l_1} = \text{bond ratio}$$

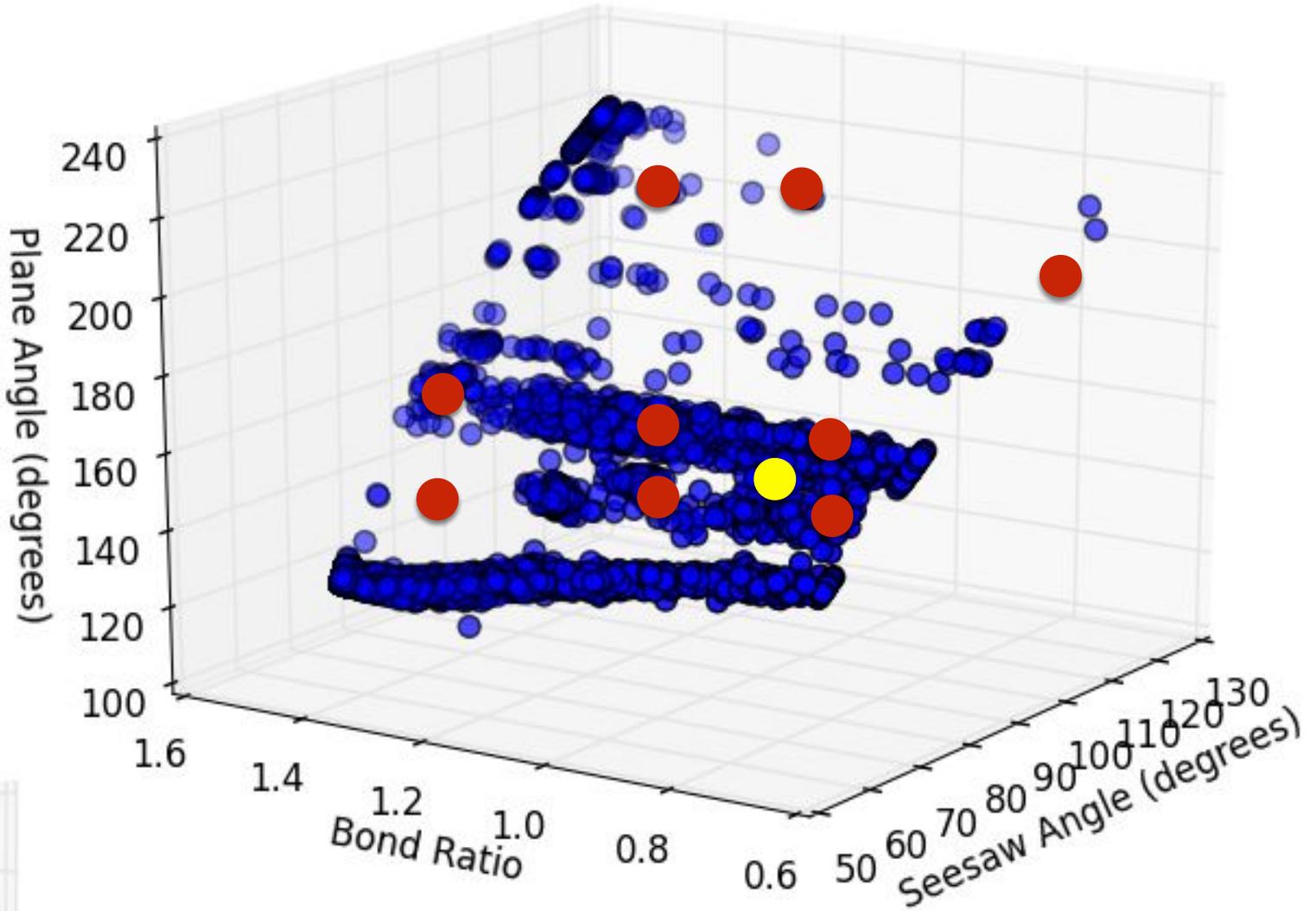


Optimize for periodicity
[ex: 4 tetrahedra / unit cell]





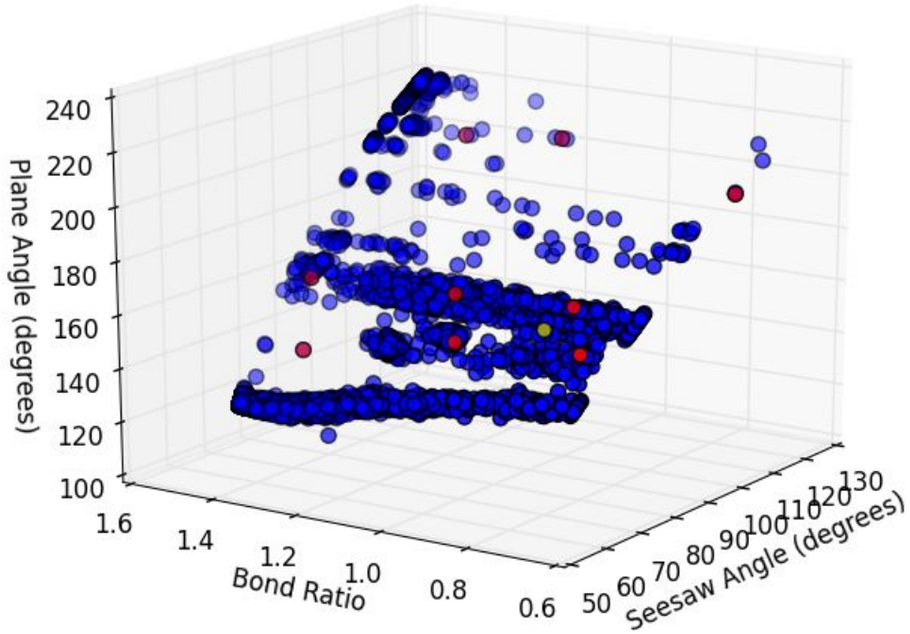




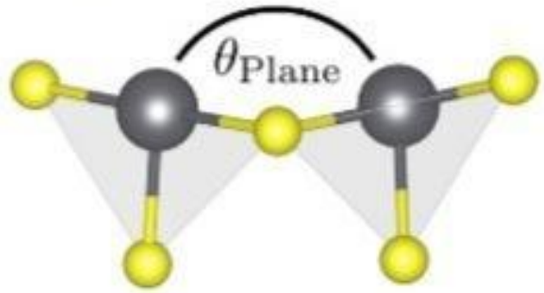
Yellow closest to exp. values

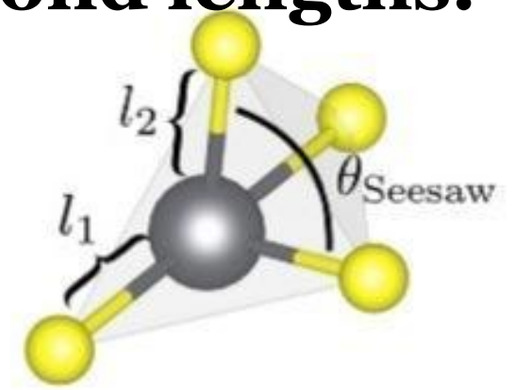
Red structures calculated

Blue other structures periodic with 4 tetrahedra

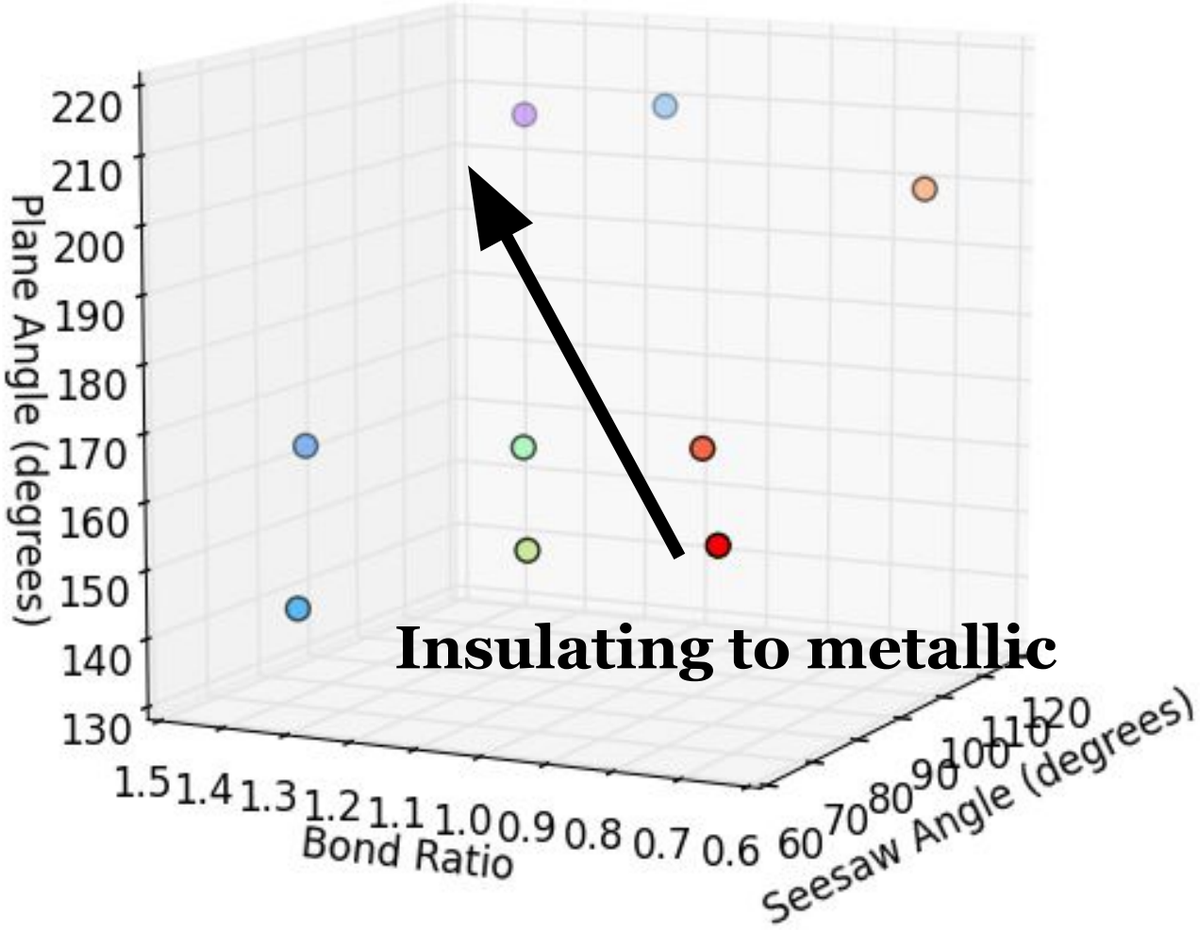


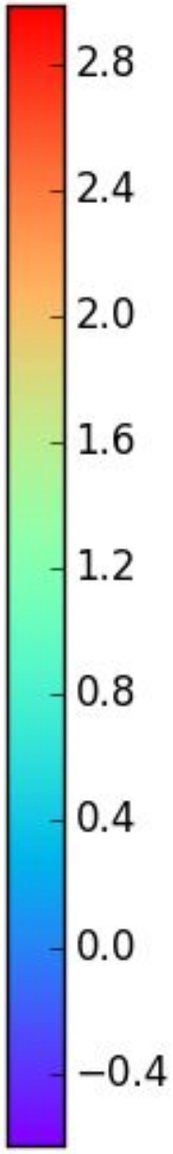
Biggest changes in electronic structure are driven by changes in bond lengths.

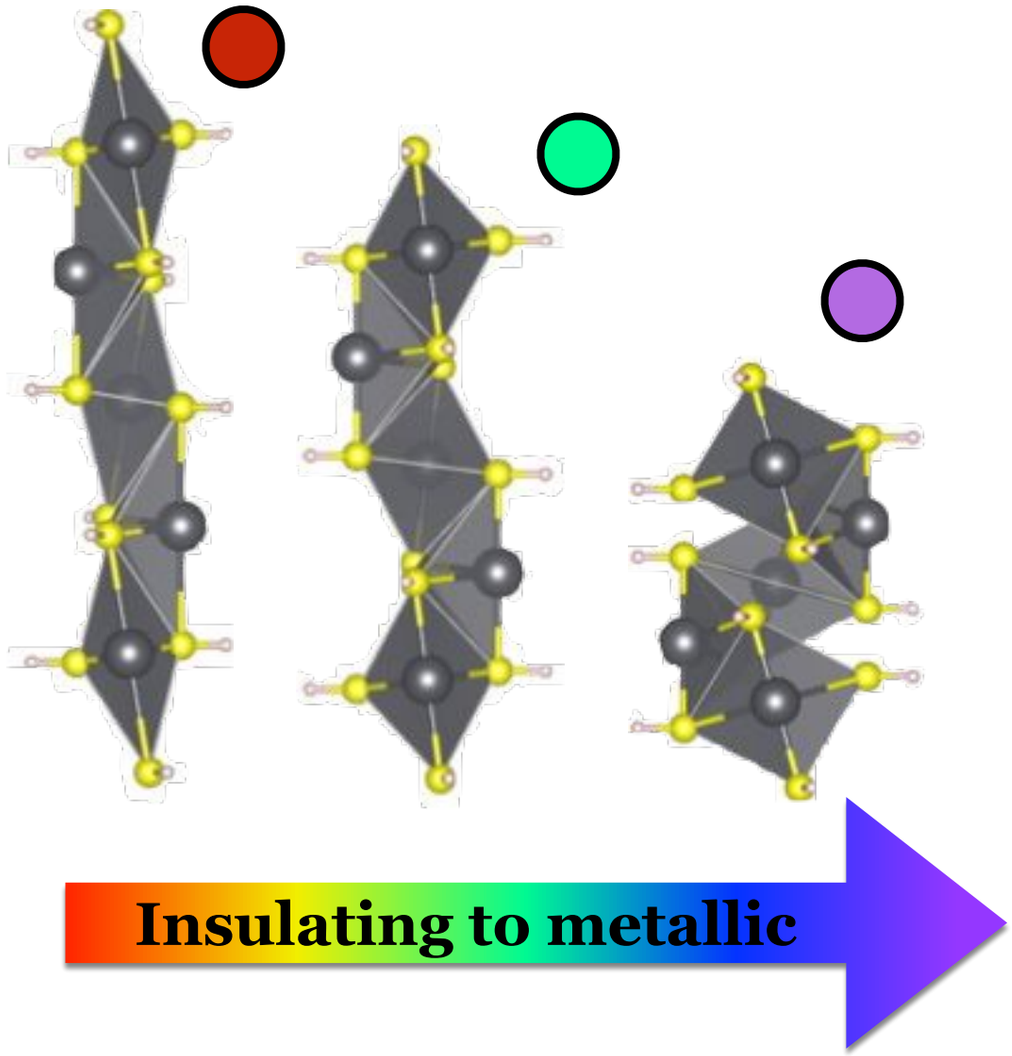




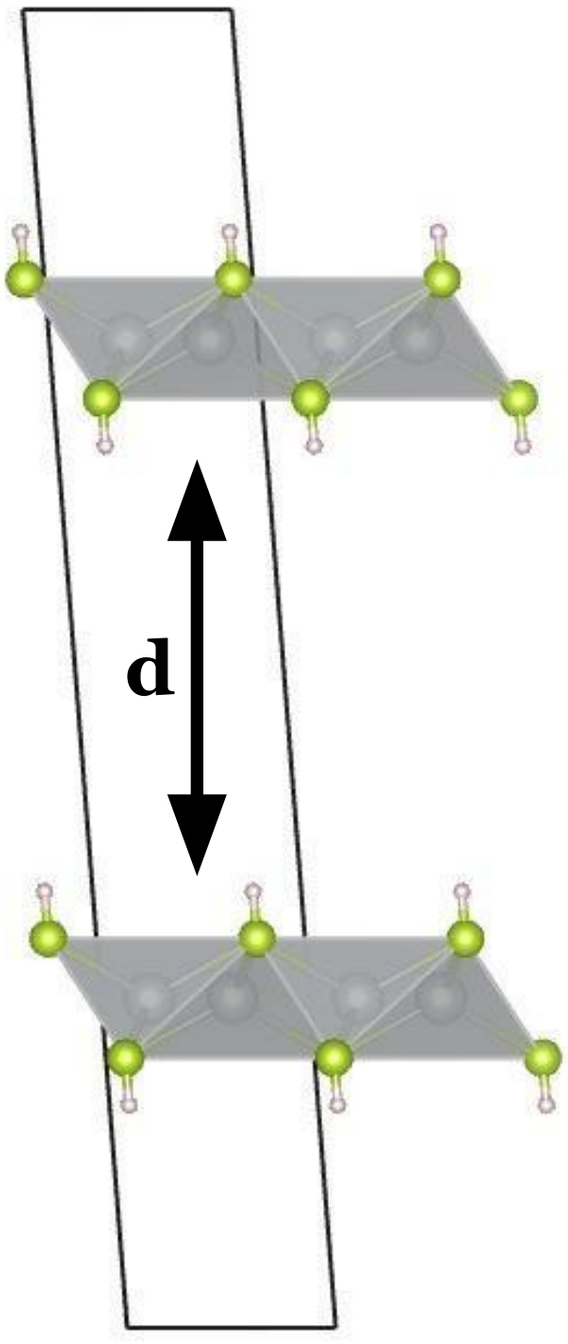
Band Gap (eV) [LDA]







How does screening (GW) affect Mithrene and vary with distance?



DFT+GW calculations are very time consuming.

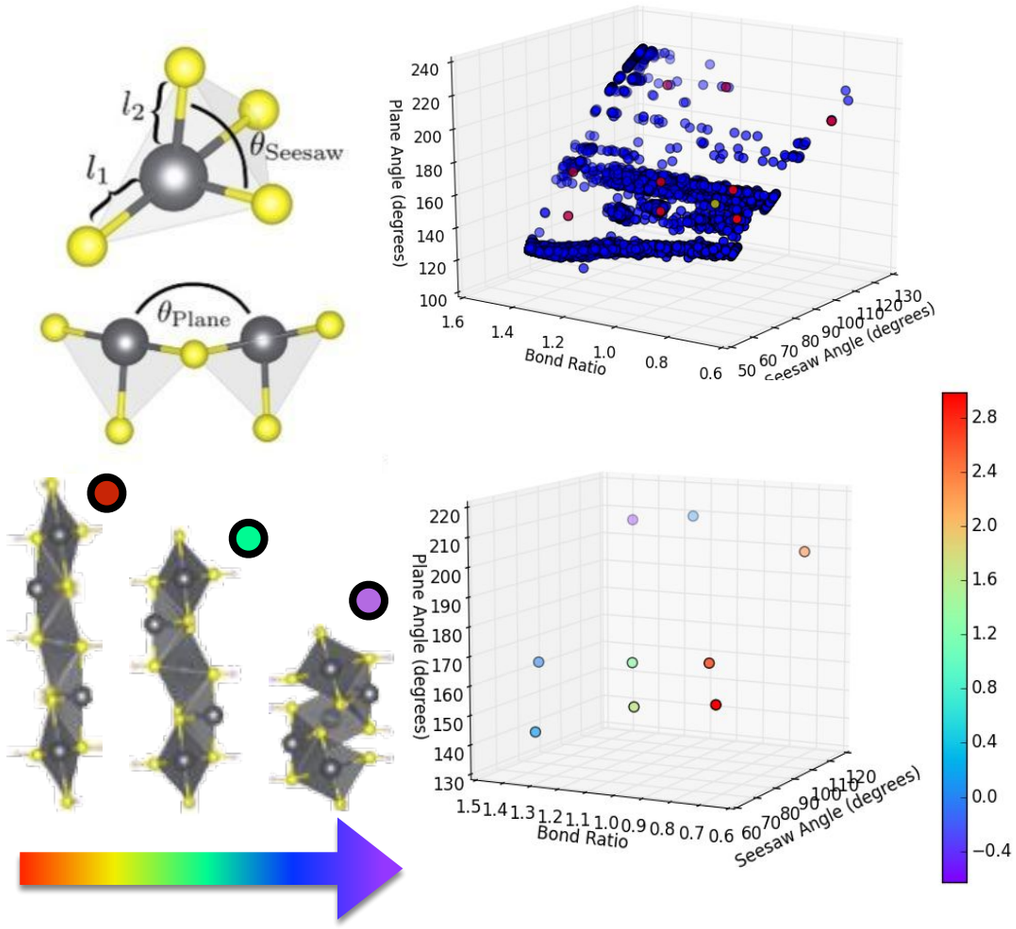
Being able to calculate variation of screening with this toy model is very useful.

Also, able to separate effects of ligands versus inorganic structure.

How to design MOChAs?

Current Strategy:

1. Focus first on inorganic structure.
2. Parameterize unit and connections.
3. Explore deformations and arrangements: geometry and electronics.
4. *Given a configuration, fit for ligands.*
5. *Is the configuration kinetically favored?*

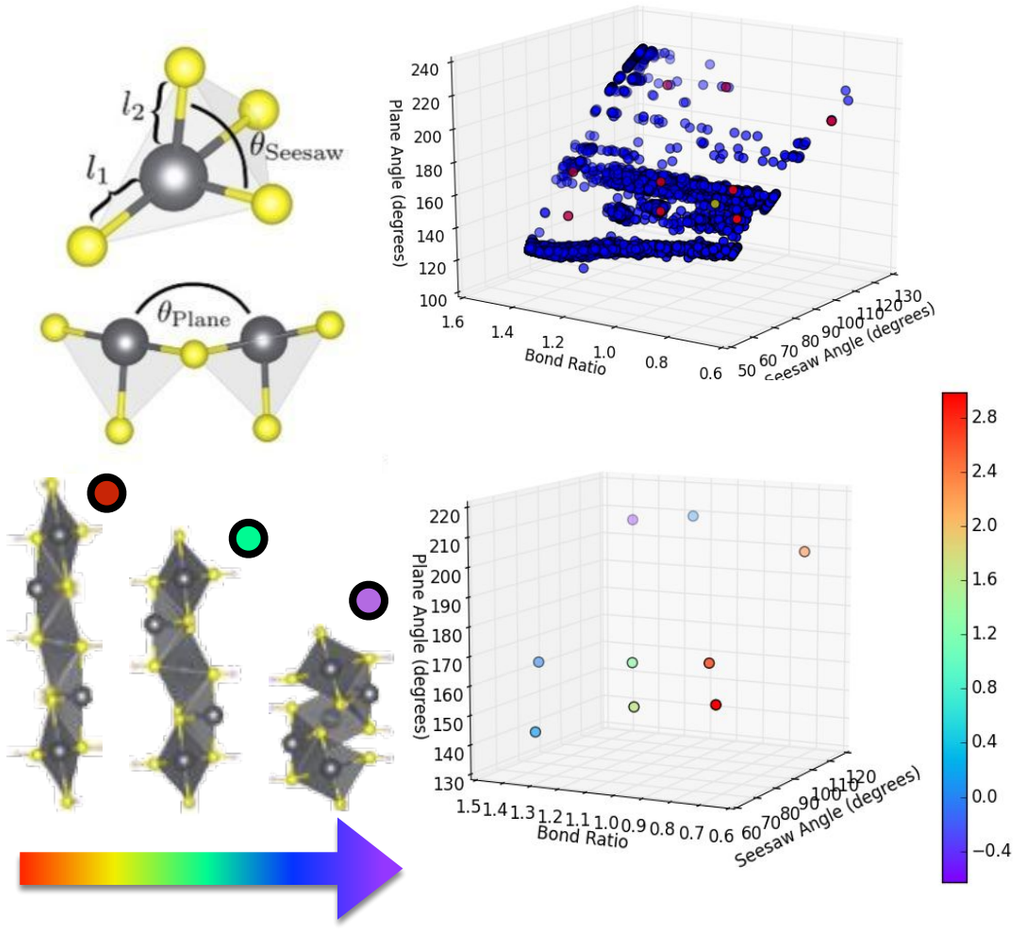


- **Need to generate new inorganic structures to feed into this workflow!**
- **Need to fit for ligand!**
- **Self-assembly oh my!**

How to design MOChAs?

Current Strategy:

1. Focus first on inorganic structure.
2. Parameterize unit and connections.
3. Explore deformations and arrangements: geometry and electronics.
4. *Given a configuration, fit for ligands.*
5. *Is the configuration kinetically favored?*



- **Need to generate new inorganic structures to feed into this workflow!**
- **Need to fit for ligand!**
- **Self-assembly oh my!**

Thanks!

Calling in back up (slides)!

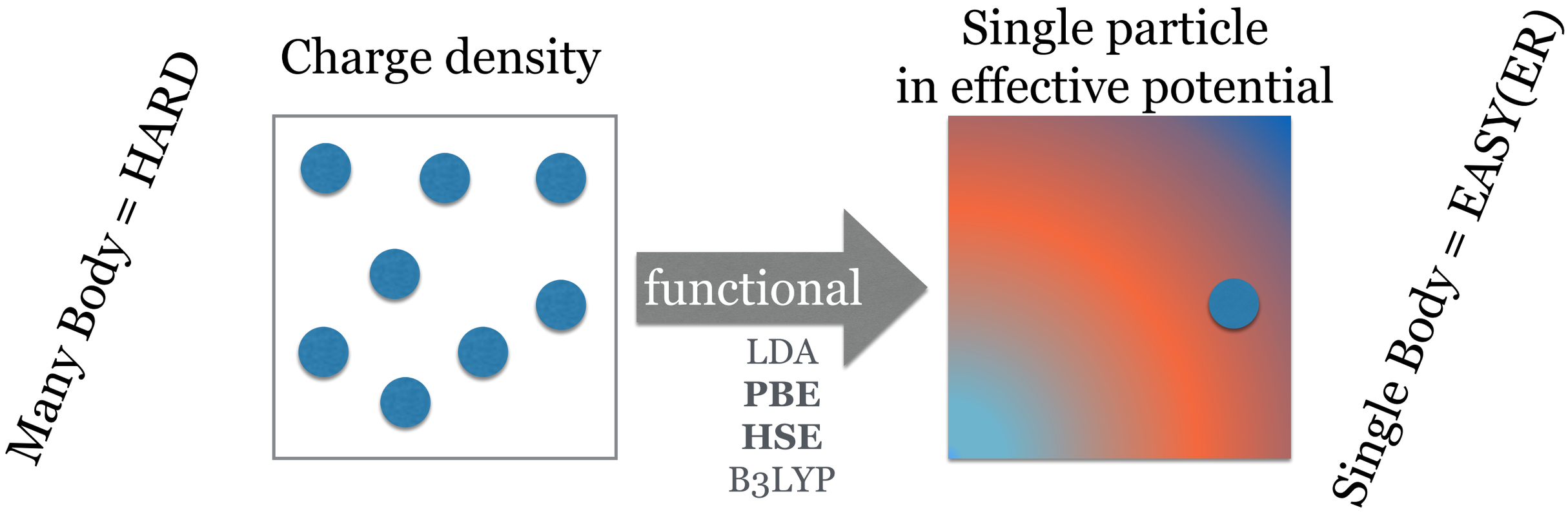
What you should know about density functional theory.

The most widely used method for calculating electronic structure.
Calculates the ground state.

Functional?

A function that takes function(s) as its argument(s).
charge density ➜ functional ➜ single particle wave function

Exact if we knew the “universal functional”.



What you should know about density functional theory.

Alphabet soup!

- LDA (Local Density Approximation) — Fermi gas
- GGA (General Gradient Approximation) — some interactions
- PBE — a type of GGA
- HSE — PBE with "short range" exact exchange (interactions due to electrons being identical particles)
- /GW — used to calculate electron screening
- /BSE — used to calculate quasiparticle production (electron + hole)

The longer your method acronym, the better your calculation!
(Just kidding… almost…)

What you should know about density functional theory.

Computationally tractable for < ~1,000 atoms.
Typically scales $O(n^3)$ where n is number of electrons.

On each person in Jeff's group uses
~3 million CPU hours per year.

Easier to get
Structure
Total formation energy

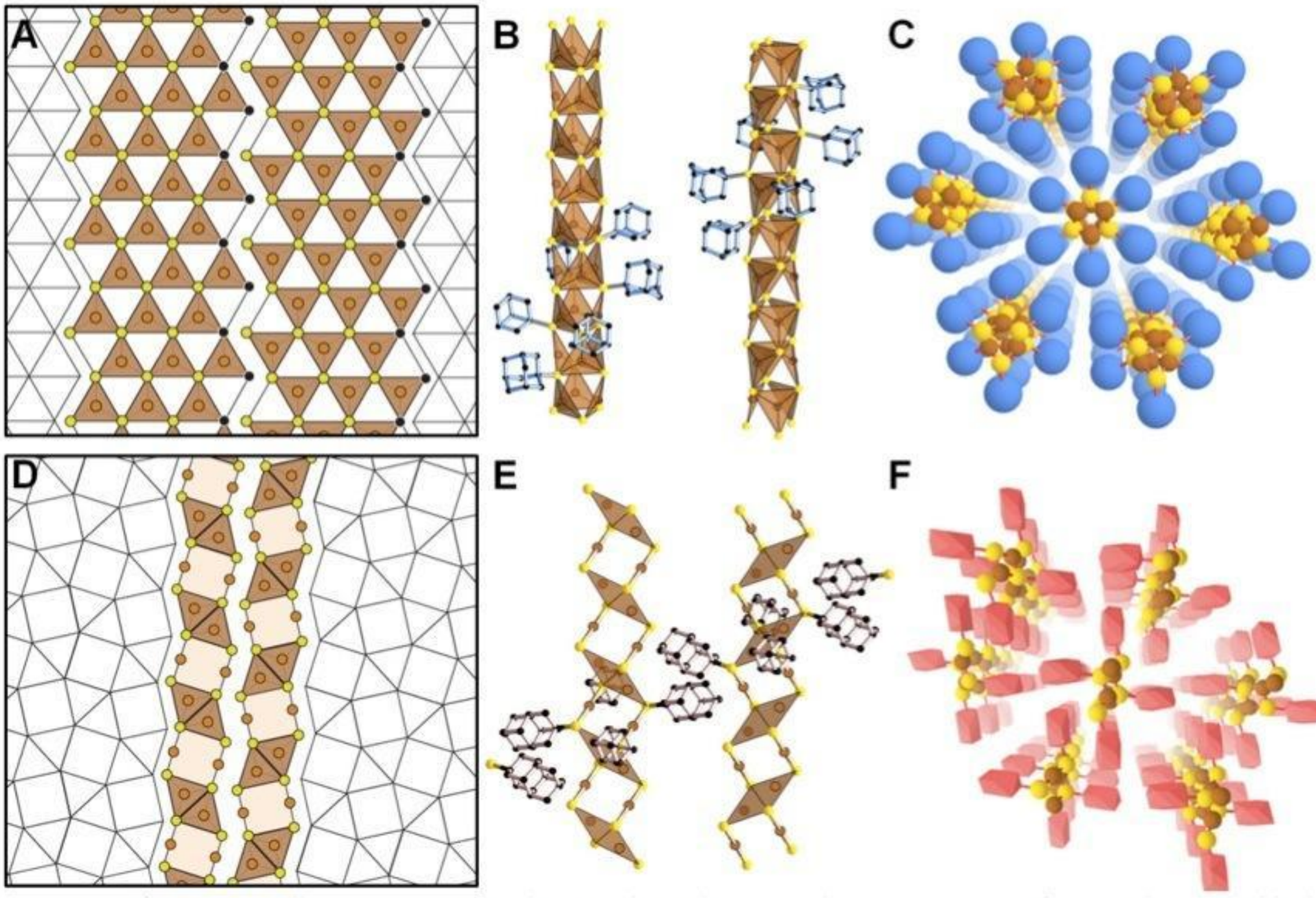
Tricky but possible
Accurate band gaps
Dispersion (VdW, etc.)
Screening
Excited state properties (excitons)

Atoms vs. Theorist

10	
30	
100	
200	
500	
1000	

What are MOChAs?

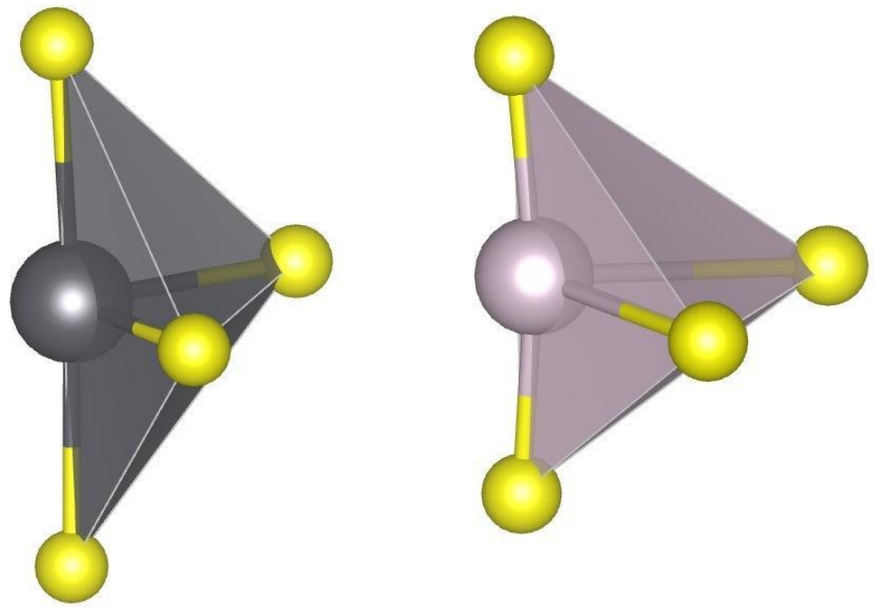
Comprised of regular geometric patterns.



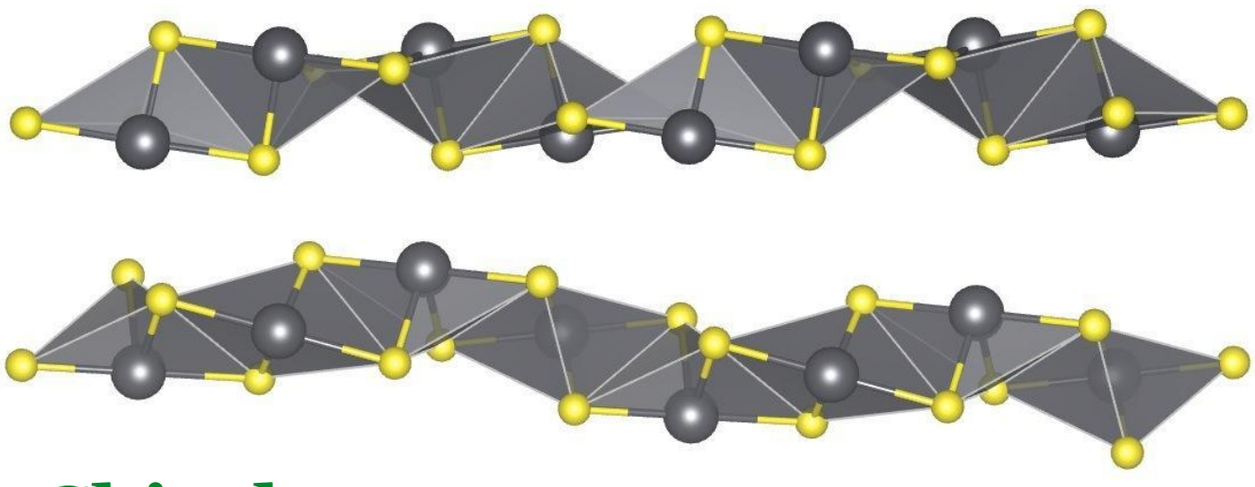
CASE STUDY:

Seesaw chalcogenide chains

Seesaw units. Pb on right Hg on left.

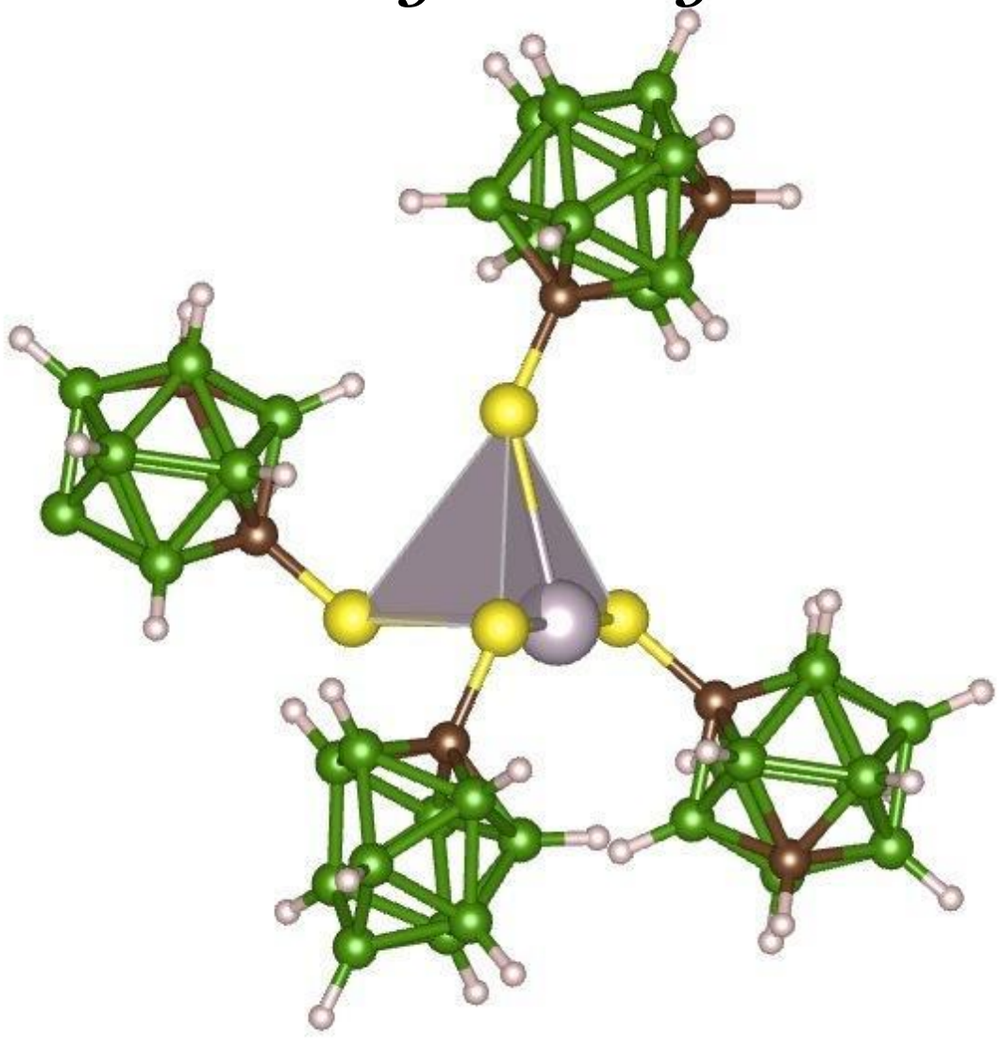


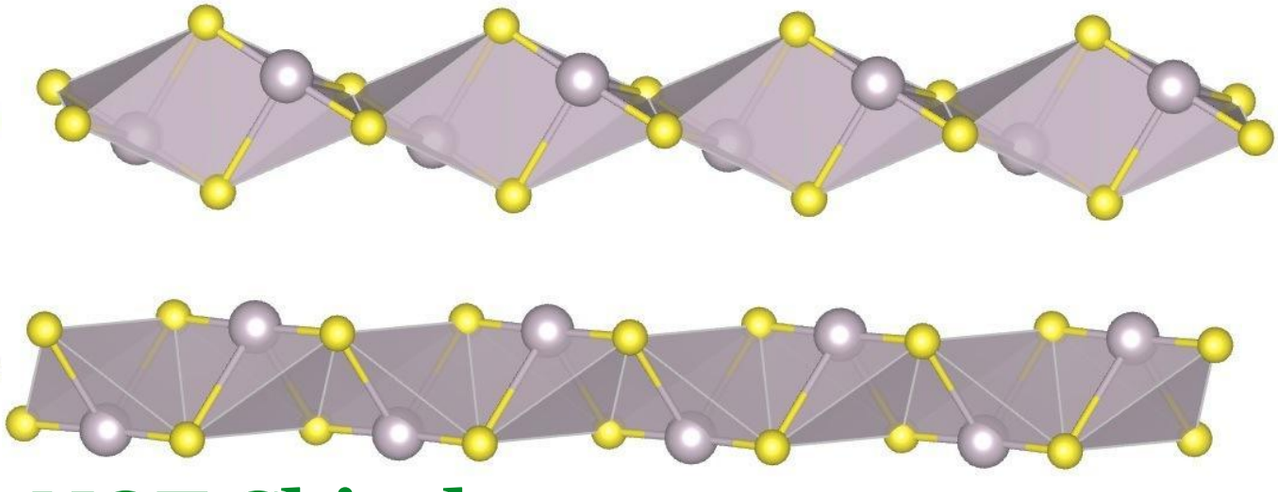
Two different connectivities.



Chiral

C-S bonds. Carboranes coordinating chalcogenide chain.





NOT Chiral

How are the two structures related?