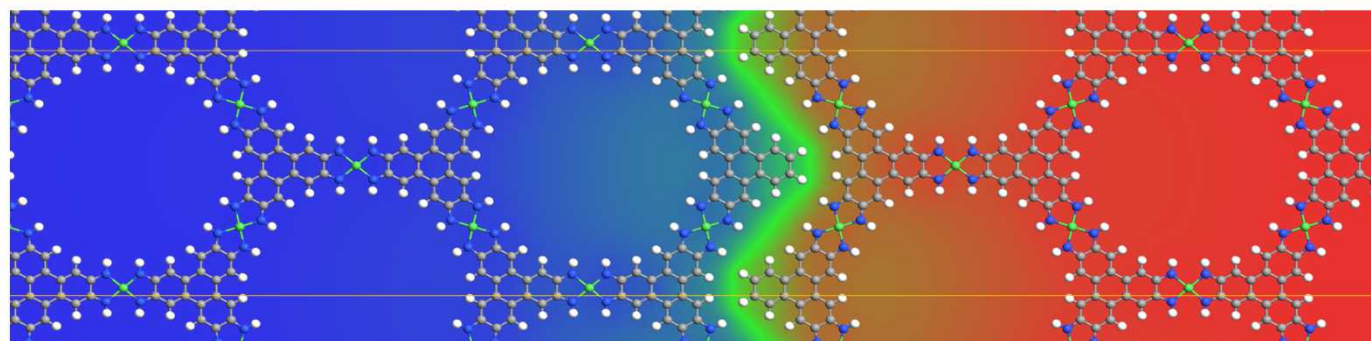
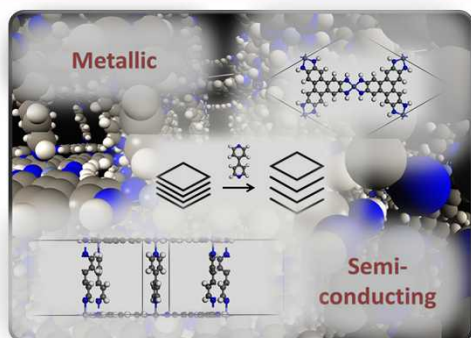


*Exceptional service in the national interest*



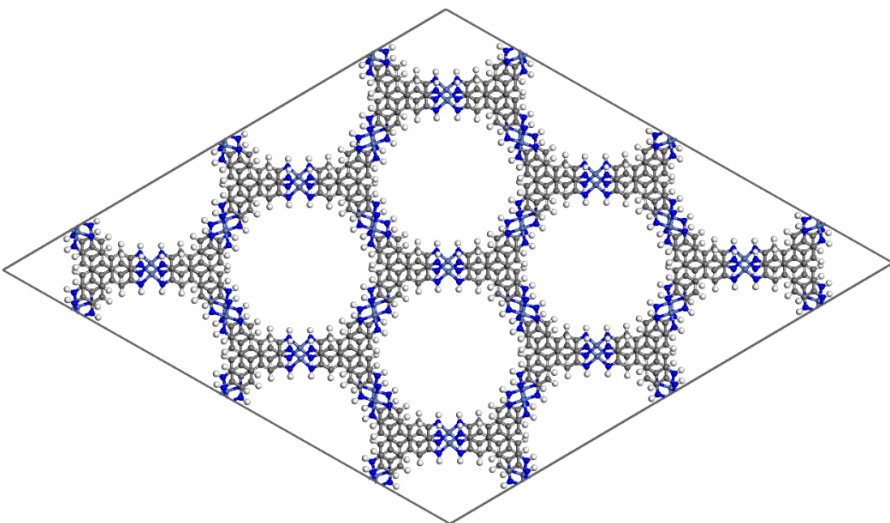
9/12/2016

# Proposed Modification of the Graphene Analogue $\text{Ni}_3(\text{HITP})_2$ to Yield a Semiconducting Material

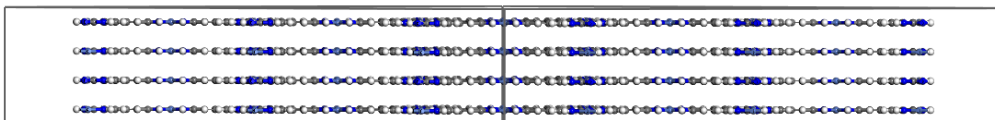
**Michael E. Foster**

Senior Member of the Technical Staff  
Department of Materials Chemistry, 8344

# MOF - Ni<sub>3</sub>(HITP)<sub>2</sub>

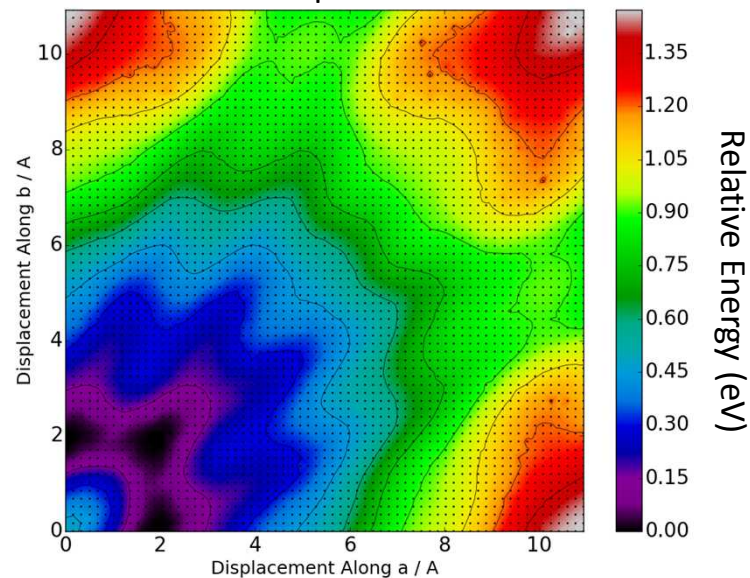


2D Layered Structure



- $\pi$  conjugated 2D layered structure – honeycomb lattice
- HITP = 2,3,6,7,10,11-hexaminothriphenylene
- Space Group – *Cmcm*; layer-layer separation  $\sim 3.3$  Å

Potential Energy Surface of Sheet displacement

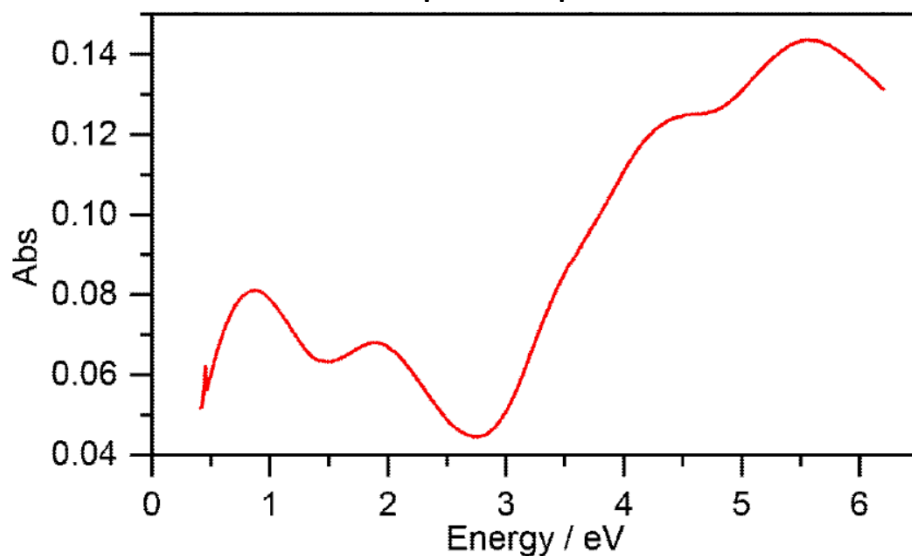


B3LYP/pob-TZVP

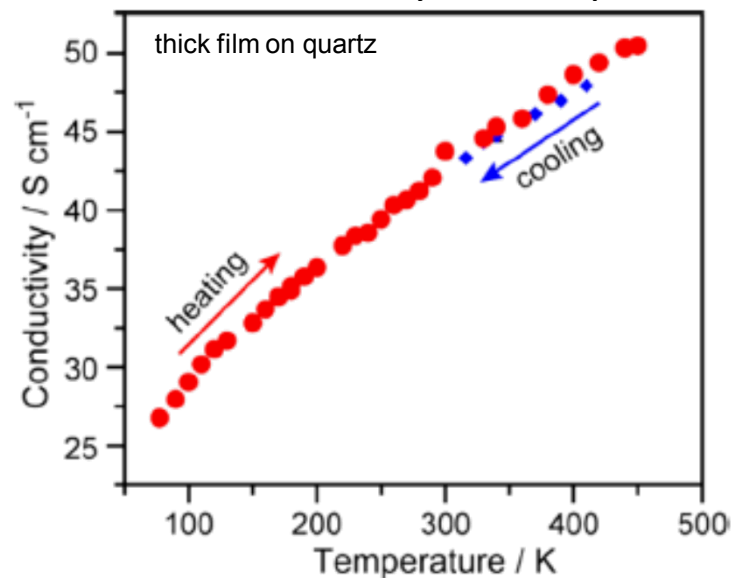
- Optimal sheet displacement  $1/16^{\text{th}}$   $a$  ( $b$  or  $a$  and  $b$ )
- Conductive MOF,  $\sim 40$  S  $\text{cm}^{-1}$
- Semiconducting or metallic?

# Ni<sub>3</sub>(HITP)<sub>2</sub> – Experimental Data

Absorption Spectrum

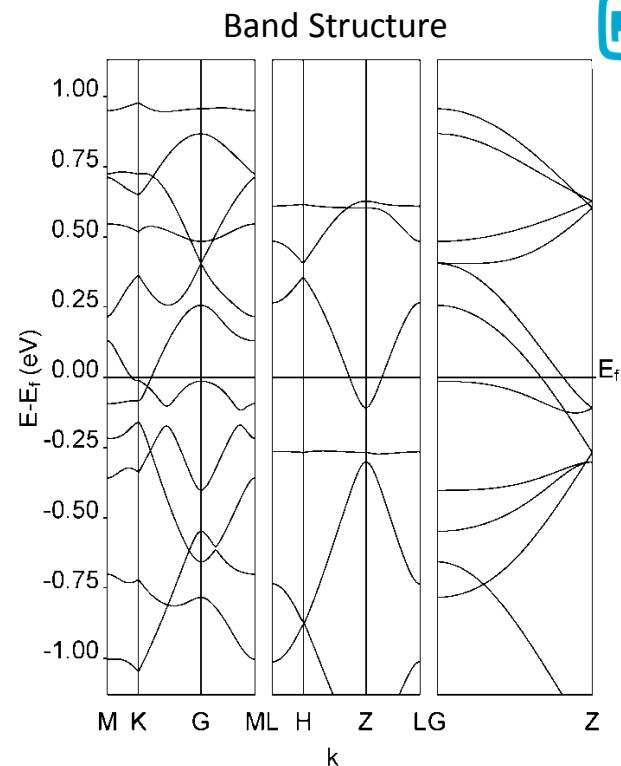
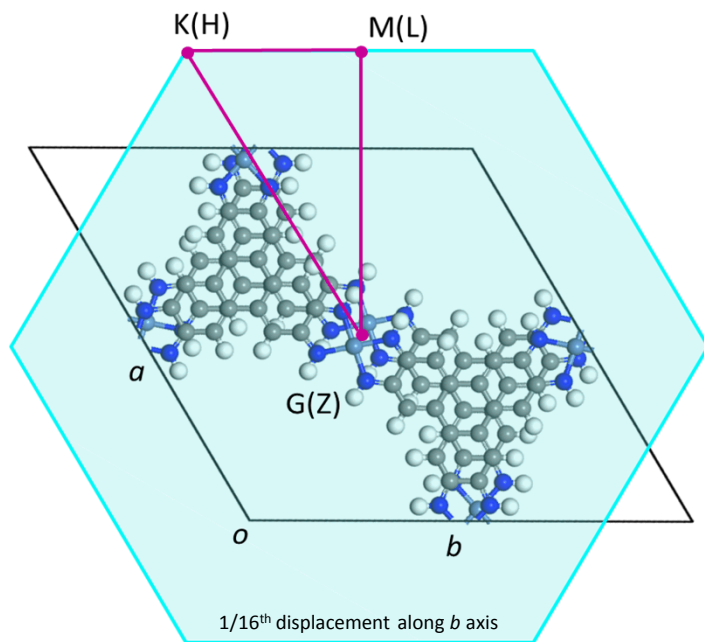


Conductivity vs. Temp.

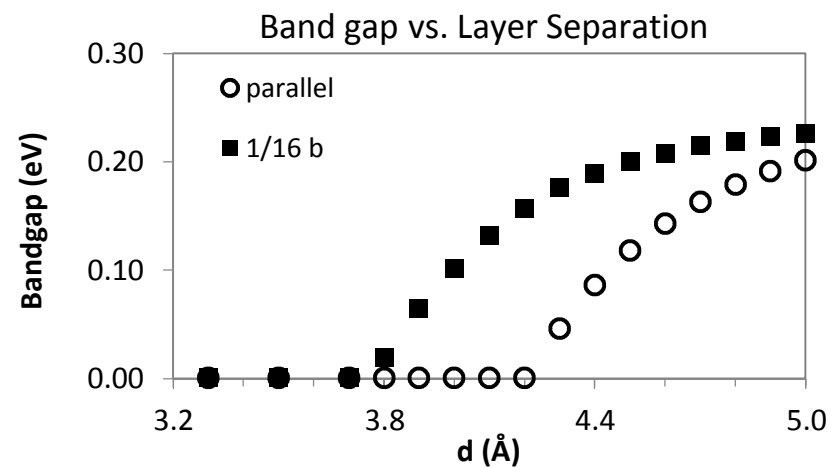


- Experimental evidence seems to suggest that the material is a semiconducting.
- Absorption spectrum – possible optical gap of 0.2 eV
- Conductivity increases with temperature – charge hopping mechanism

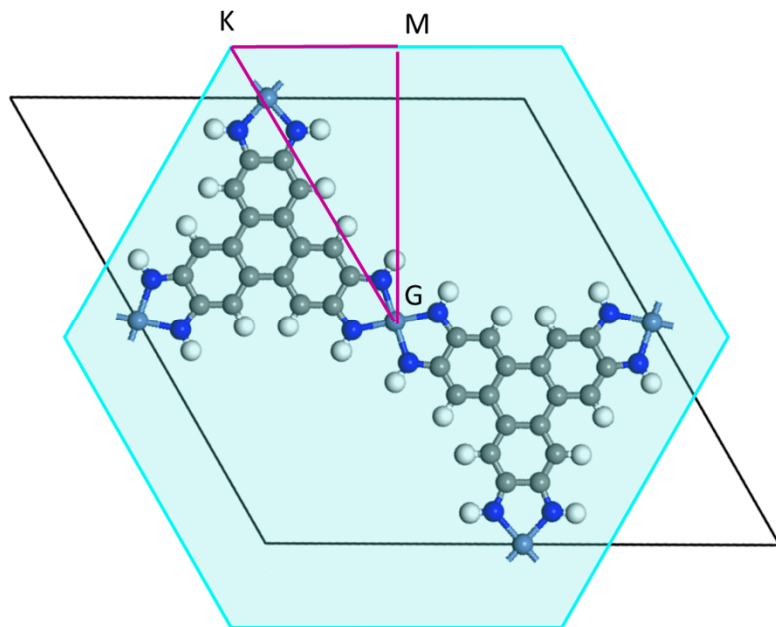
# Ni<sub>3</sub>(HITP)<sub>2</sub> – Bulk



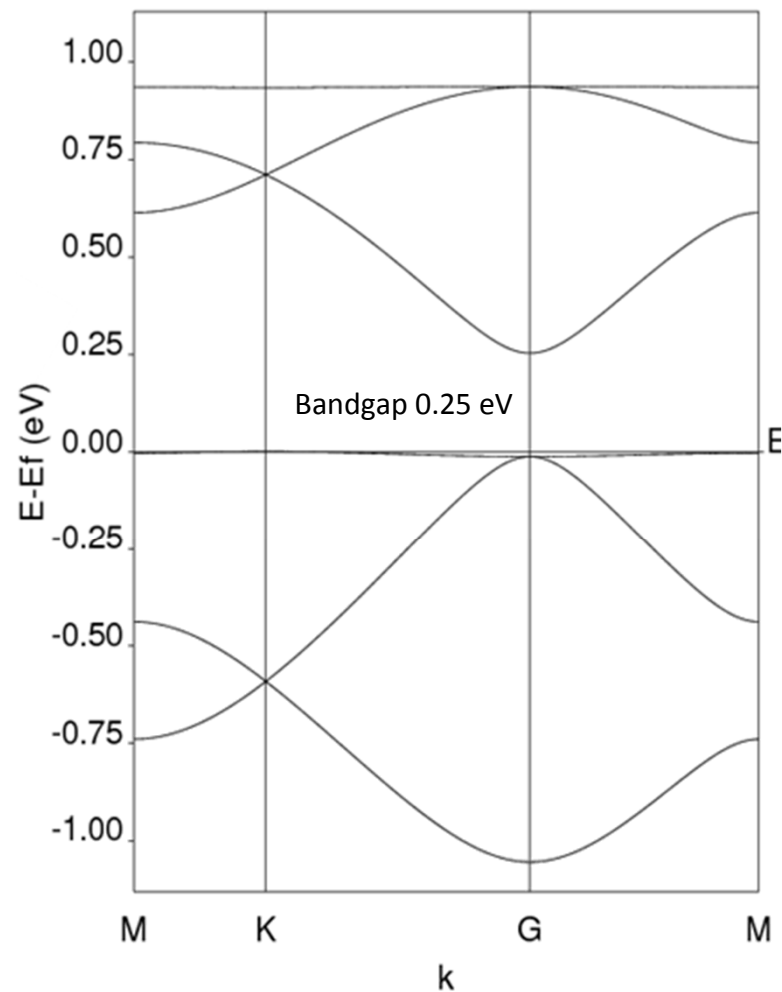
- Bulk NiHITP appears to be metallic; no band gap.
- layers need to be separated by at least 4 Å to obtain a band gap.
- Strategy – Insert pillar linkers (i.e. 4-4'-bipyridine) between the sheets/layers.



# Ni<sub>3</sub>(HITP)<sub>2</sub> – Monolayer



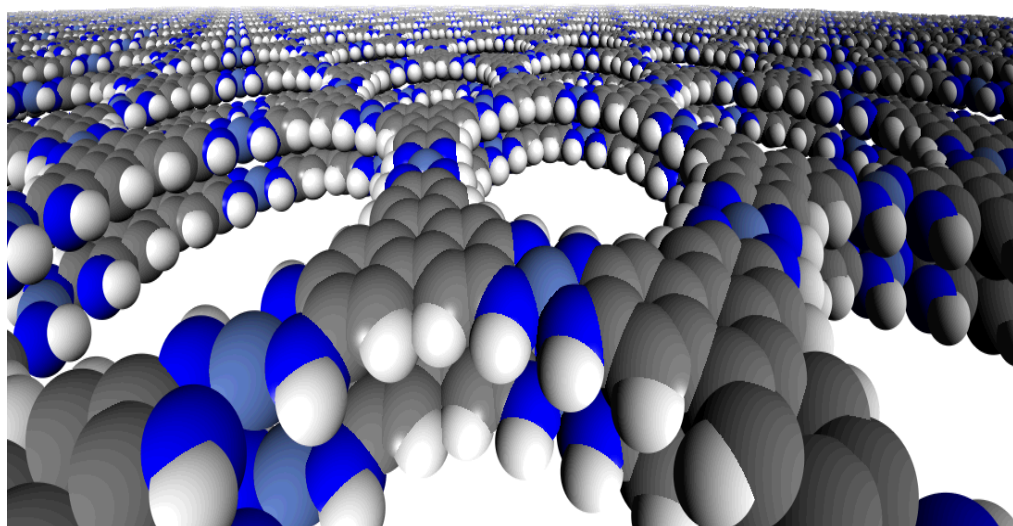
Band Structure



Electron/Hole Effective Mass

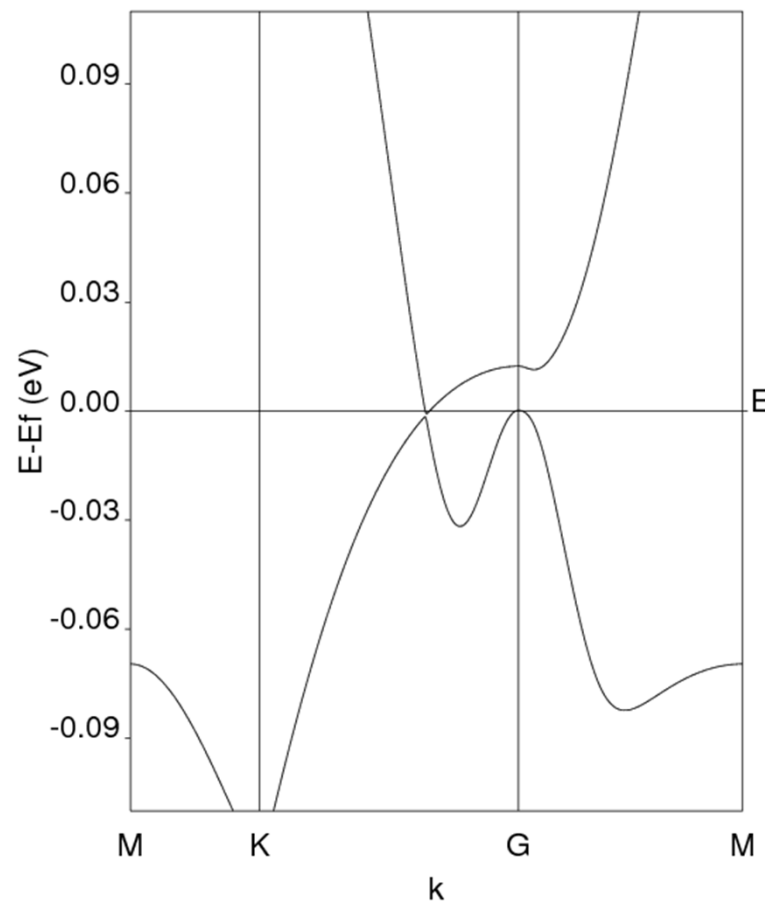
	Ni <sub>3</sub> (HITP) <sub>2</sub>	Si	Ge	GaAs
Light Hole	0.068	0.160	0.044	0.082
Heavy Hole	3.753	0.490	0.280	0.450
Electron	0.073	0.200	0.041	0.067

# Ni<sub>3</sub>(HITP)<sub>2</sub> – Bilayer



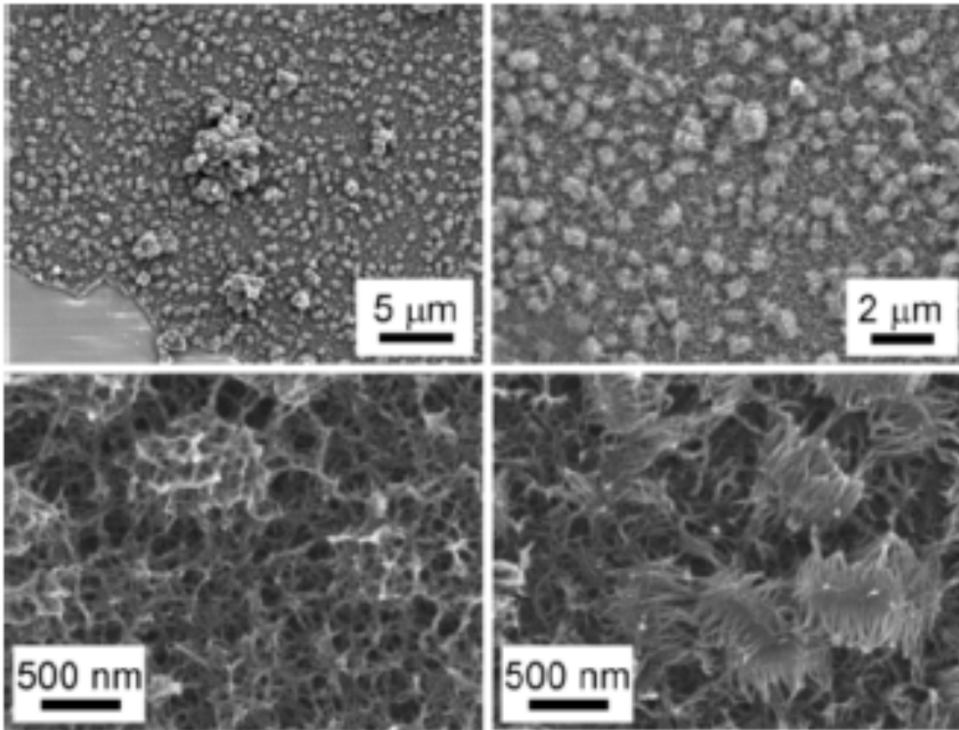
- Bilayer system has no band gap.
- Density of state is zero at the Fermi energy; semi-metal like graphene. This is not the case when the layers are parallel stacked.
- The 2D sheets/layers need to be separate to render the material semiconducting.

## Band Structure



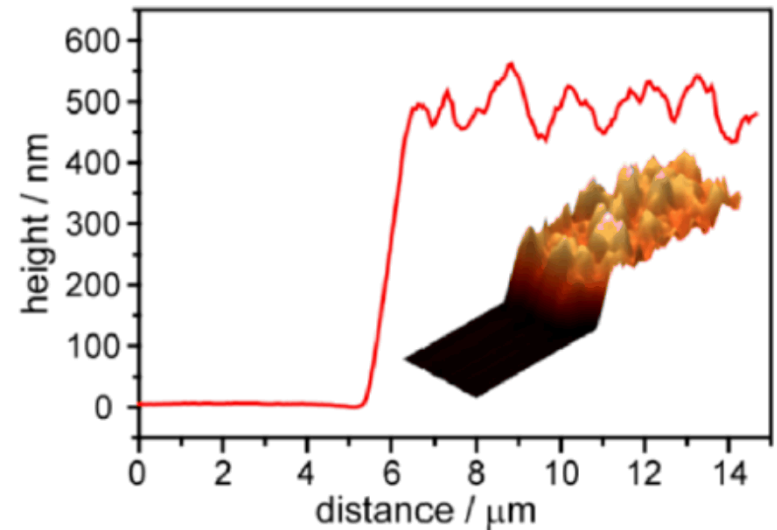
# $\text{Ni}_3(\text{HITP})_2$ – Experimental Thin Films

## SEM micrographs



J. Am. Chem. Soc. 2014, 136, 8859–8862

## AFM

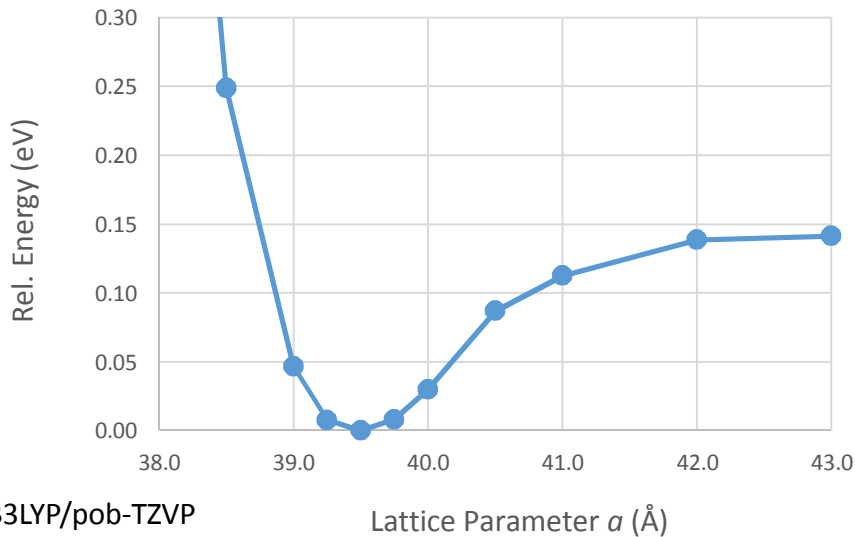
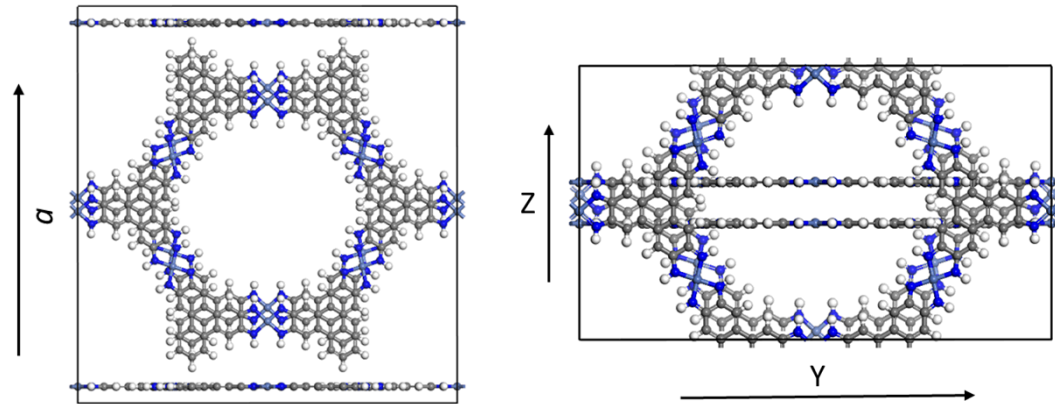
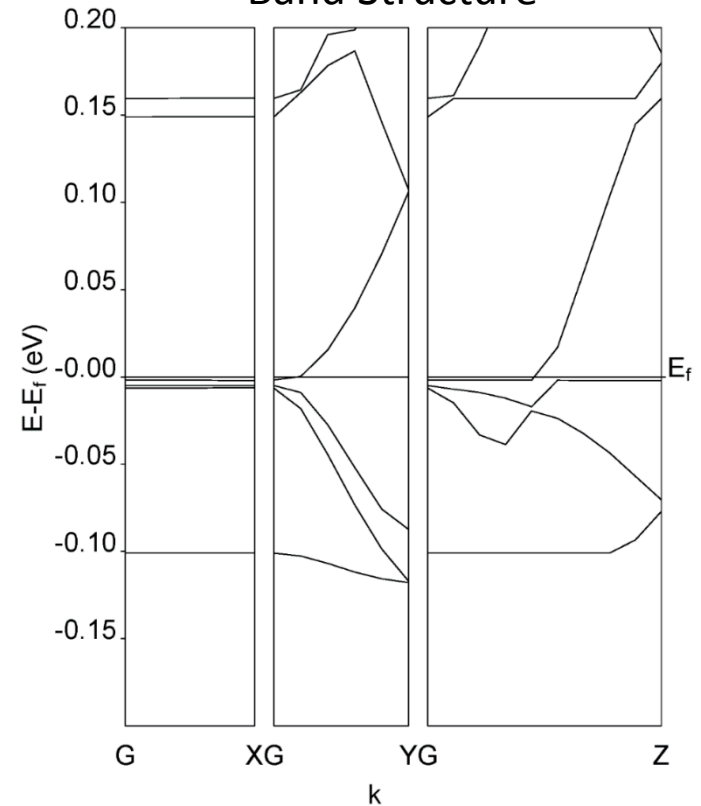


J. Am. Chem. Soc. 2014, 136, 8859–8862

The conductive properties of  $\text{Ni}_3(\text{HITP})_2$  are limited by the microstructure.

# Ni<sub>3</sub>(HITP)<sub>2</sub> – Interface

Band Structure

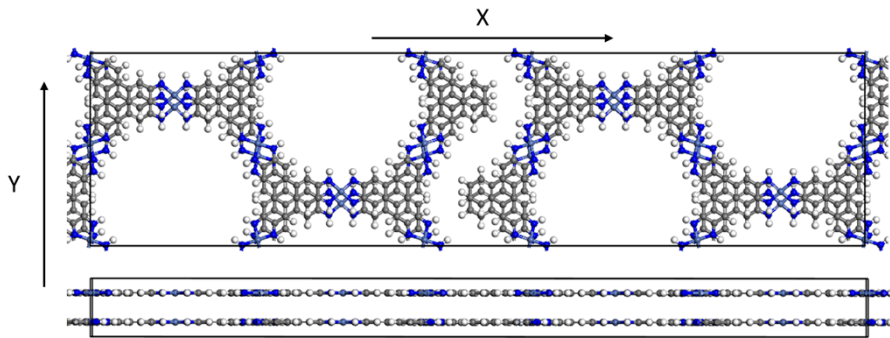


B3LYP/pob-TZVP

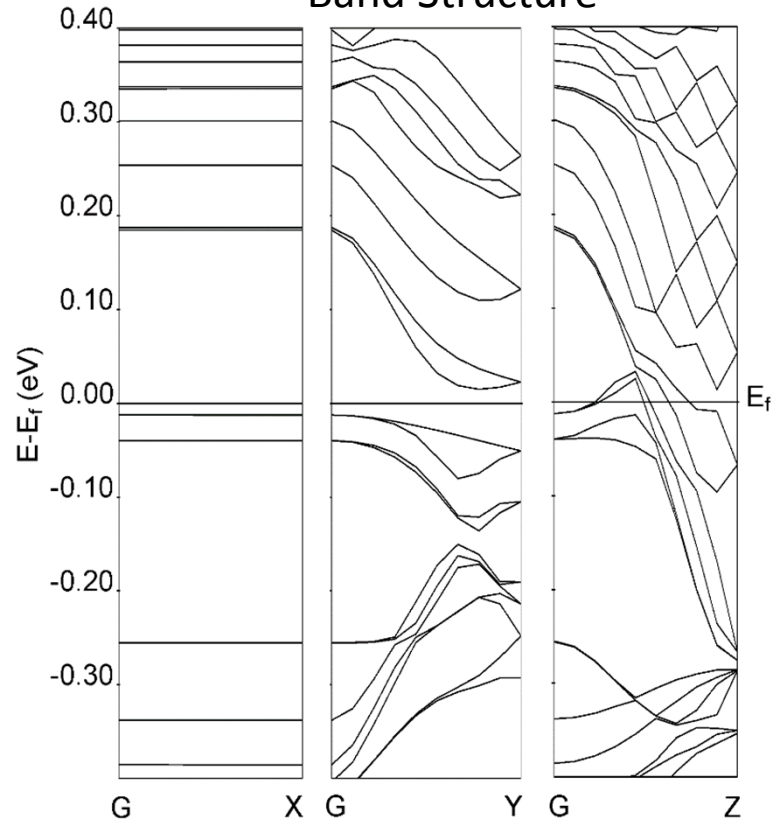
Lattice Parameter  $a$  (Å)

- $\pi$  conjugation is broken at the interface; as a result, there is no band dispersion along that direction.
- Conductivity is governed by charge hopping within the microstructure.

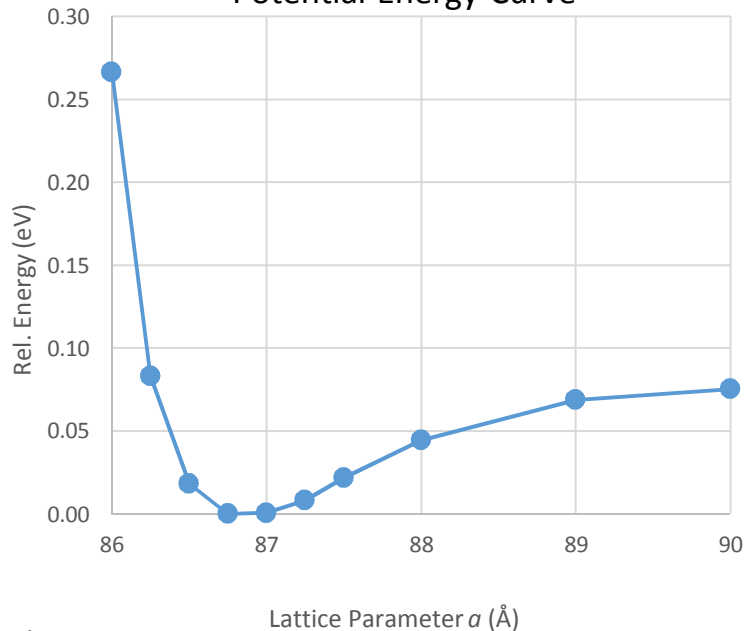
# Ni<sub>3</sub>(HITP)<sub>2</sub> – Interface



Band Structure

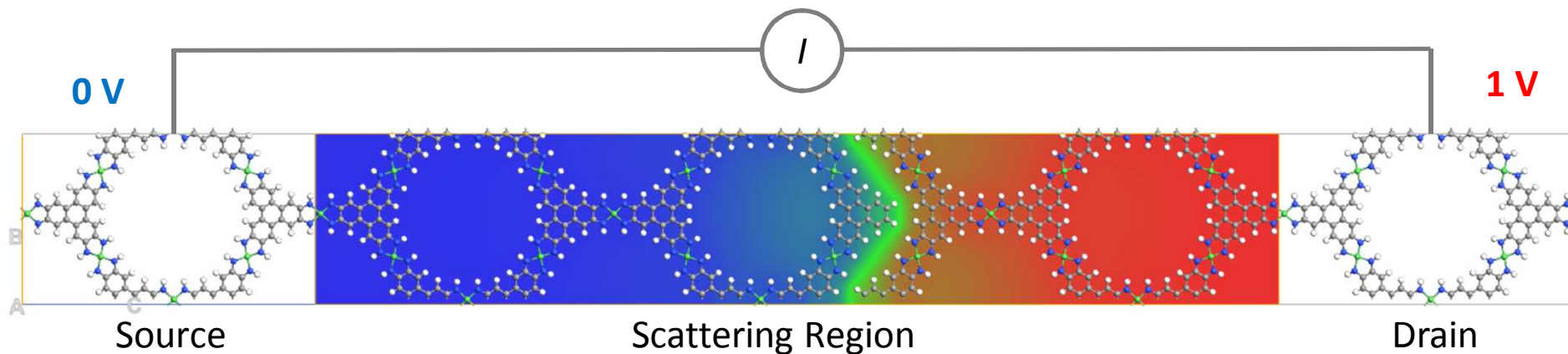


Potential Energy Curve



- $\pi$  conjugation is broken at the interface; as a result, there is no band dispersion along that direction.
- Conductivity is governed by charge hopping within the microstructure.

# Ni<sub>3</sub>(HITP)<sub>2</sub> – Interface



- Non-equilibrium Green's function (NEGF) calculations support charge hopping barrier at the interface.

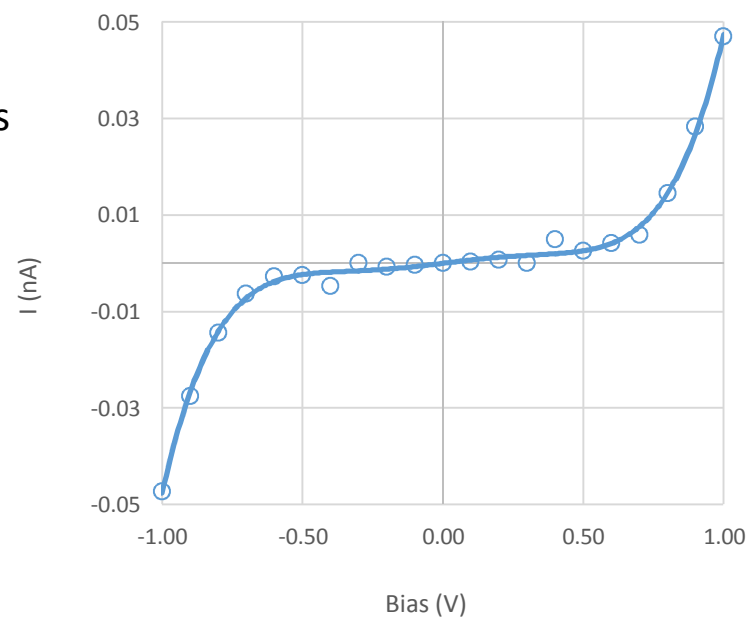
## Calculation Details

Geometry: 1 layer

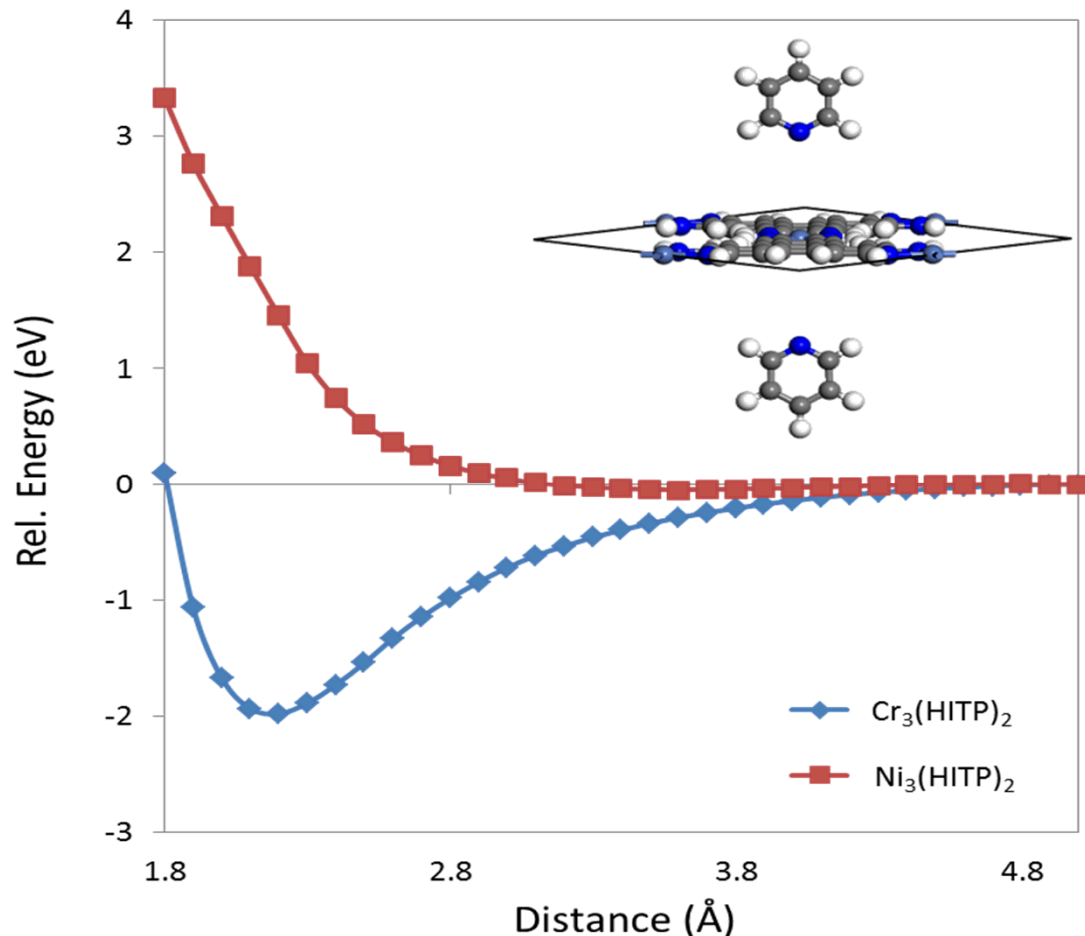
Functional: GGA-PBE

Basis: DoubleZetaPolarized

Atoms in Scattering Region: 520

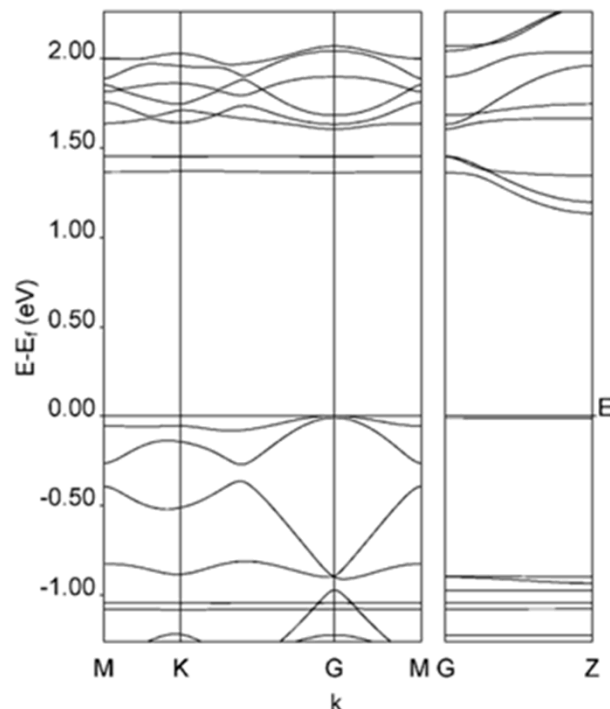
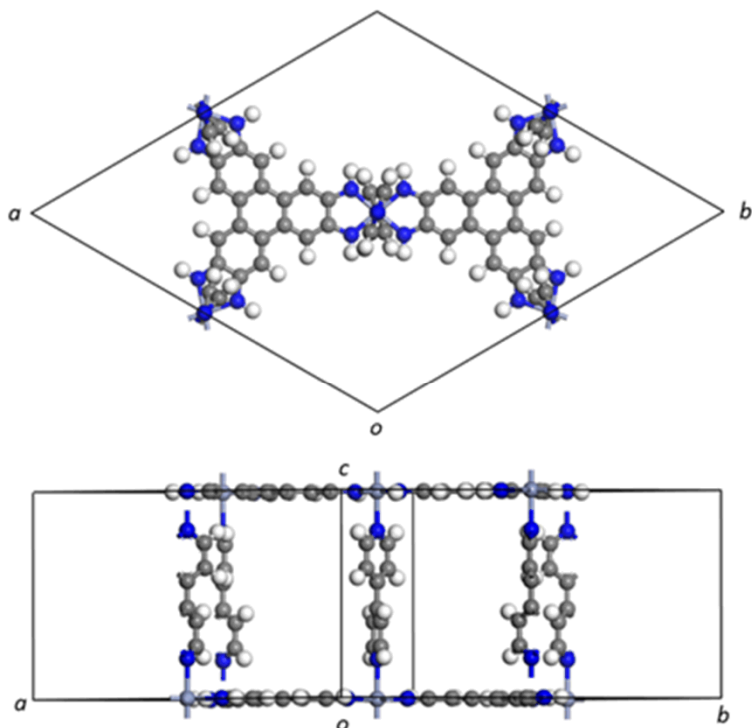


# Adding a Pillar Linker



- Use a “pillar” linker to separate the 2D layers.
- Issue –  $\text{Ni}_3(\text{HITP})_2$  does NOT want to accept a pillar linker and become octahedral ( $d_{z^2}$  orbital is full).
- Fix - change the coordinating metal to chromium.
- It is energetically favorable for  $\text{Cr}_3(\text{HITP})_2$  to go octahedral.

# Electronic Transformation: $\text{Cr}_3(\text{HITP})_2$



1.1 eV  
(~1100 nm)

### Electron/Hole Effective Mass

Light Hole	0.268
Heavy Hole	0.269
Electron	1.048

- Bulk  $\text{Cr}_3(\text{HITP})_2$ , with 4,4'-bipyridine pillar linker, is predicted to have a bandgap of 1.1 eV.
- Note – bulk  $\text{Cr}_3(\text{HITP})_2$ , with NO pillar linker, is predicted to have no appreciable band gap.
- The effective mass is greater than the Ni version; however, the predicted values are comparable to traditional semiconductors (e.g. silicon - light hole: 0.16; electron: 0.20).

# Thank You

## Collaborators

Mark Allendorf  
Alex Talin  
Catalin Spataru  
Karl Sohlberg (Drexel University)

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