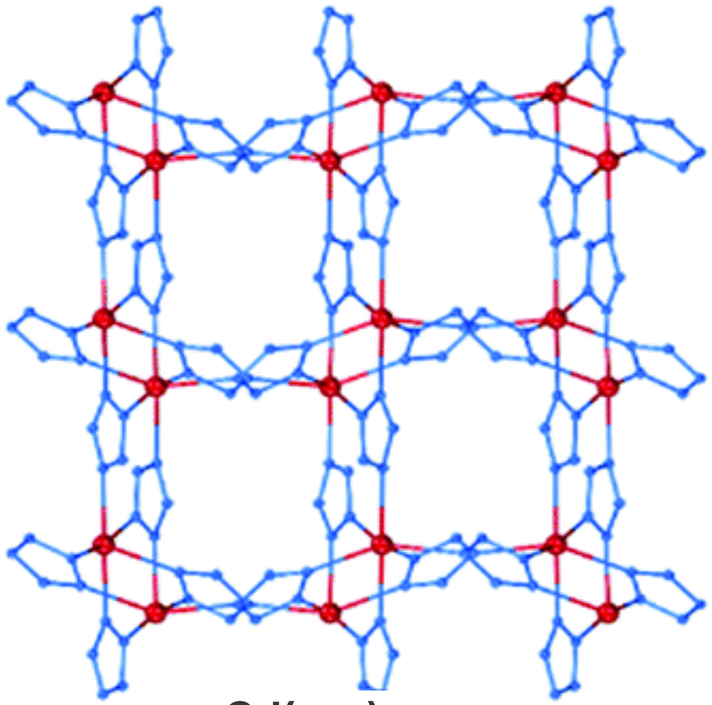
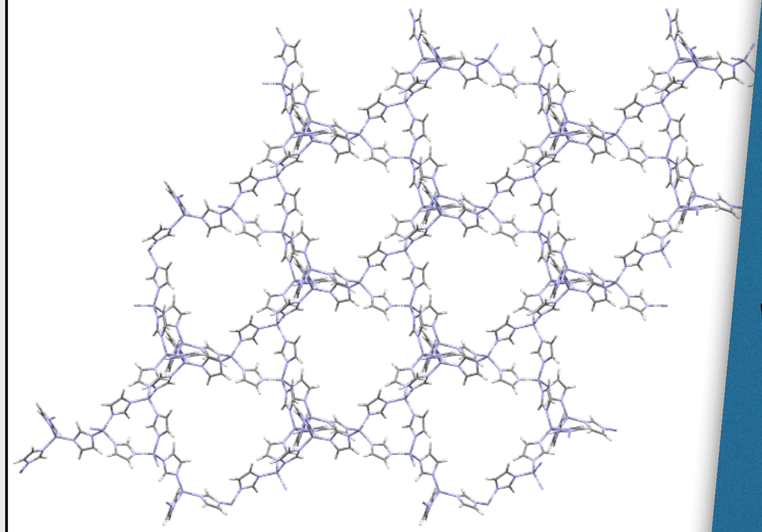
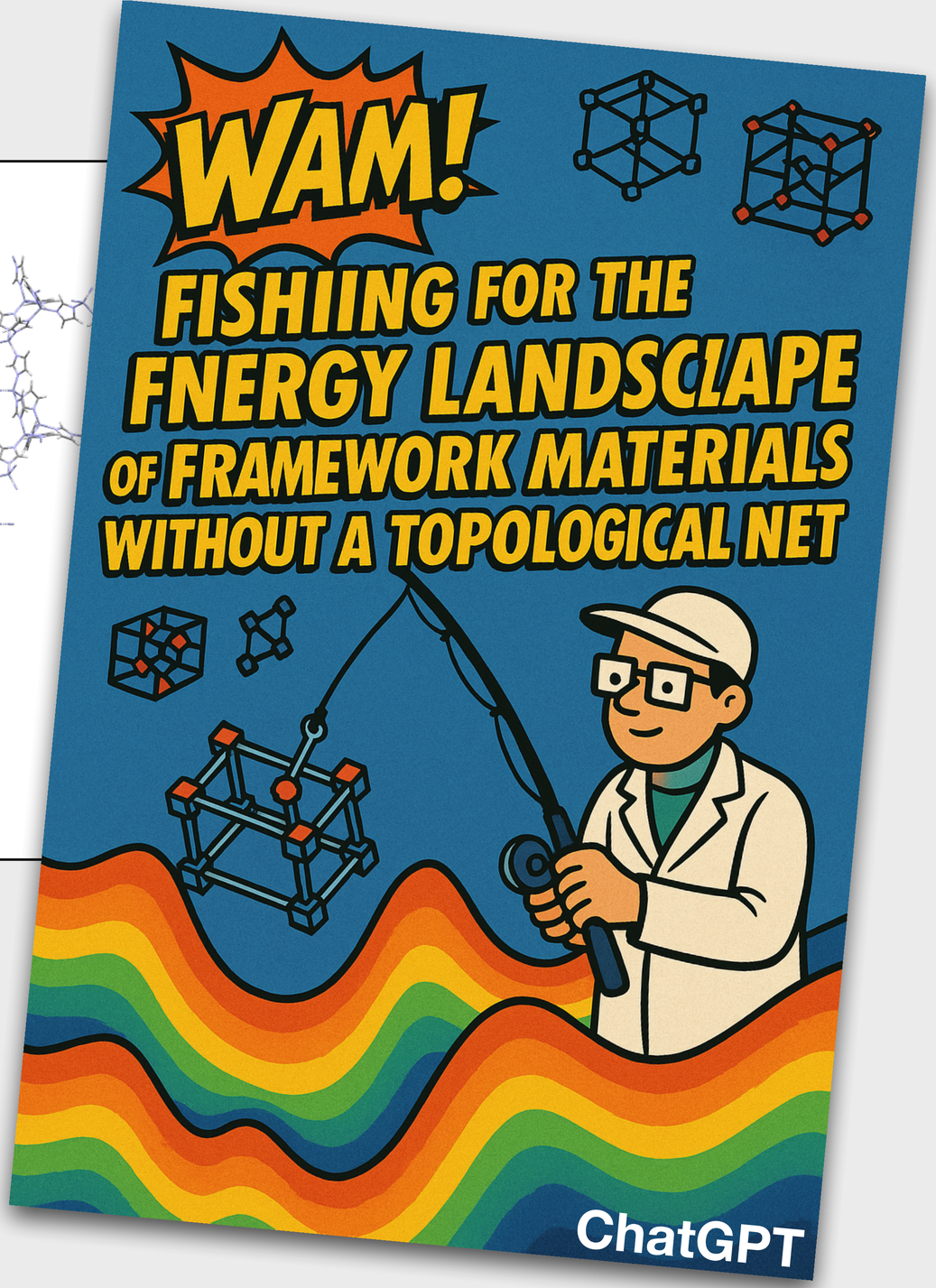


$Cd(pnz)_2$



Zn(Im)



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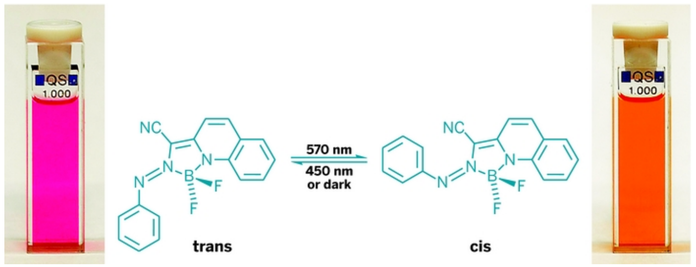
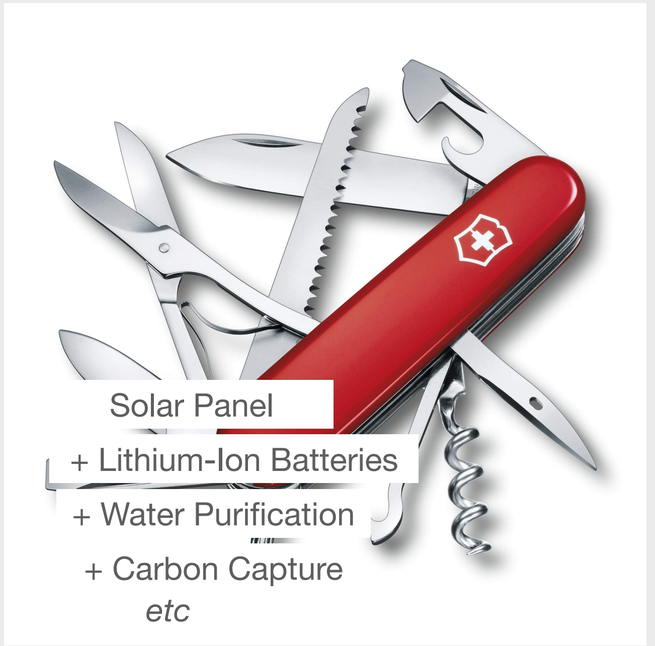
Metal-Organic Frameworks - Uses

The Heidelberg Brevik Carbon Capture facility.[1]



Solid-State Photo Switches



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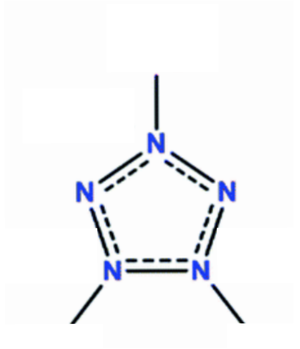
1. By PutTheKettleOn - Own work, CC BY 4.0, https://commons.wikimedia.org/w/index.php?curid=158089453

Metal-Organic Frameworks - Composition

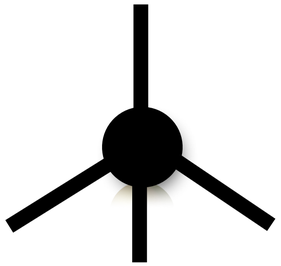
Nodes

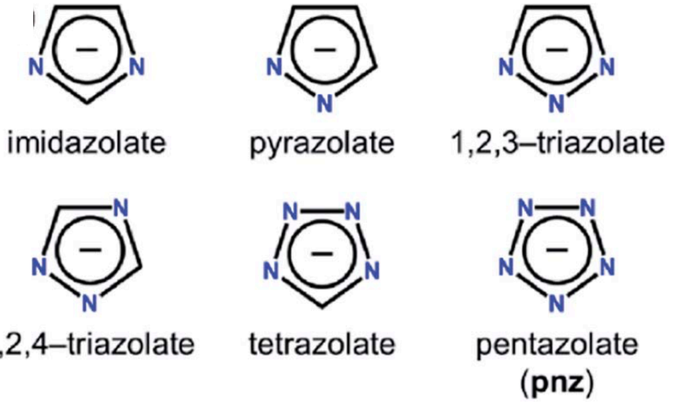
Linkers

Metal - Organic Framework (MOF)

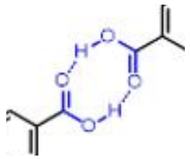


Covalent - Organic Framework (COF)

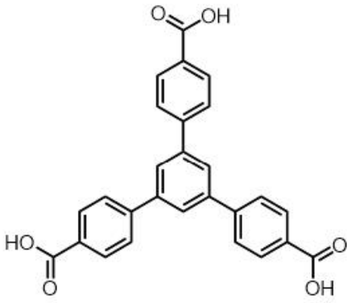




Hydrogen-Bonded Organic Framework (HOF)



etc



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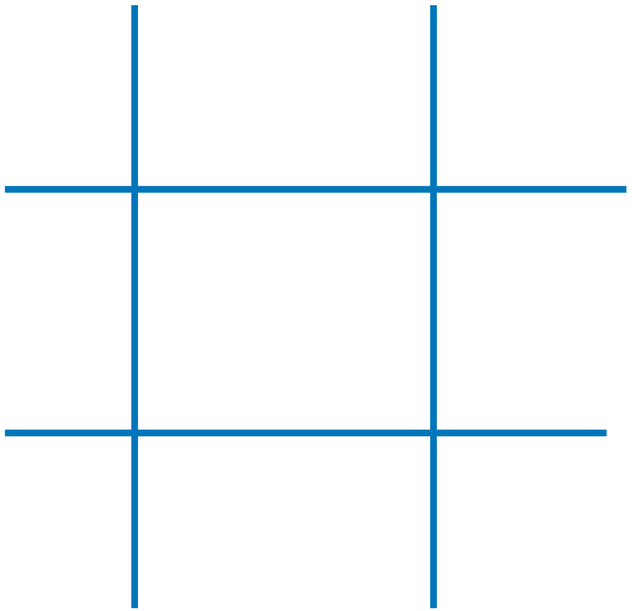
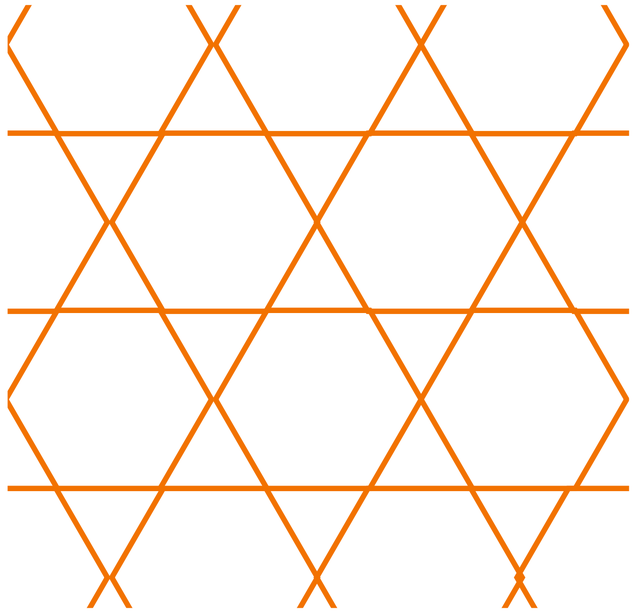
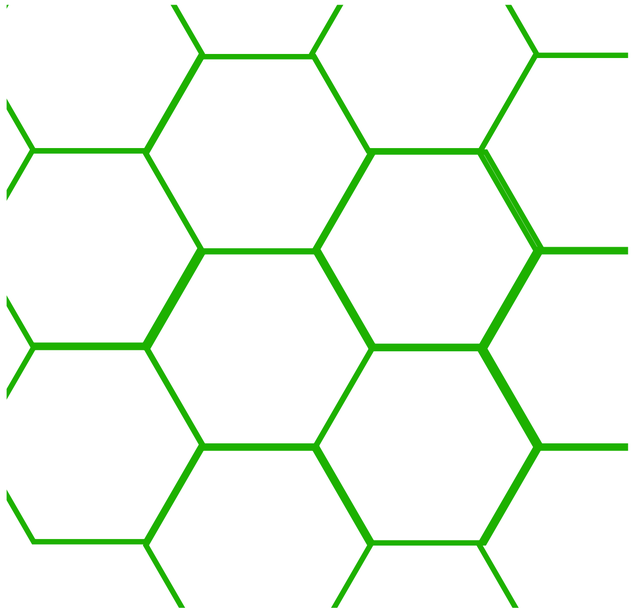
Pick Some Topological Net

Example in 2D, more options in 3D…







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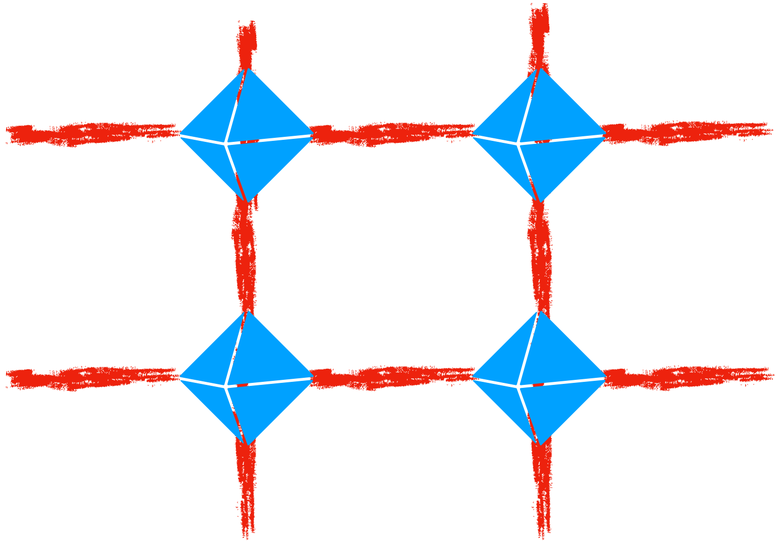
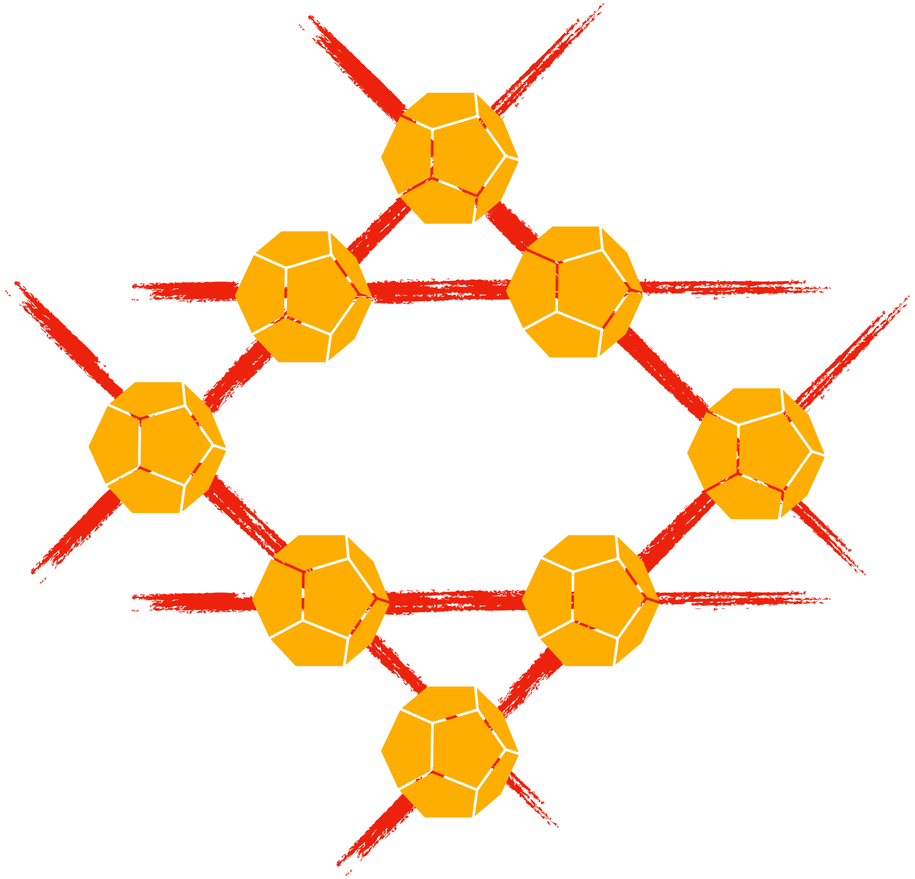
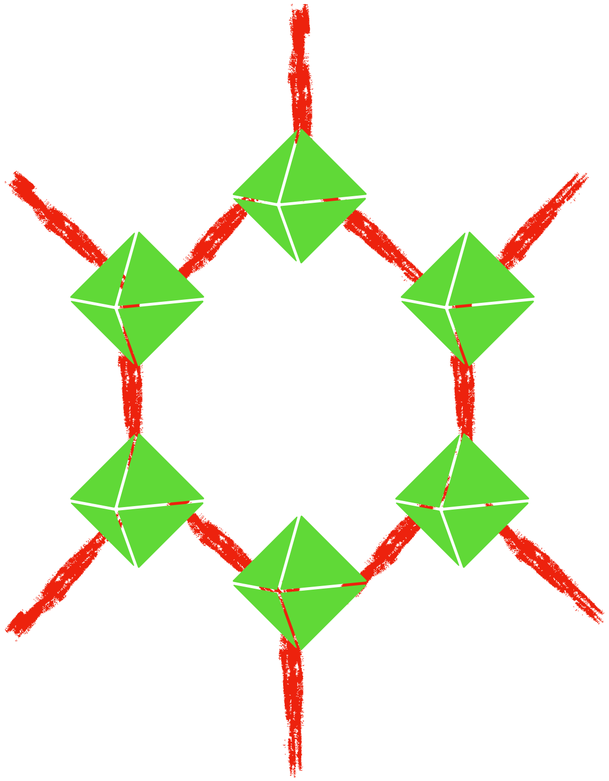
Decorate with Nodes and Linkers







Relax using some flavour of density-functional theory (DFT)

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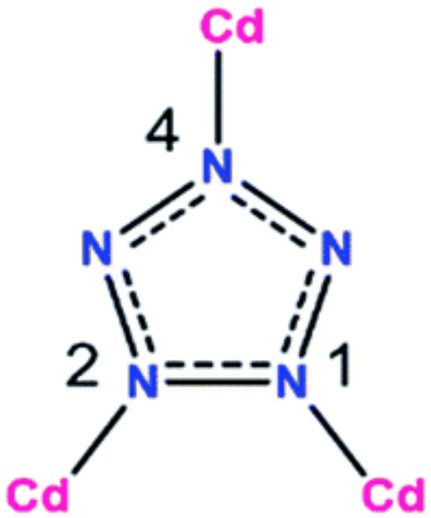
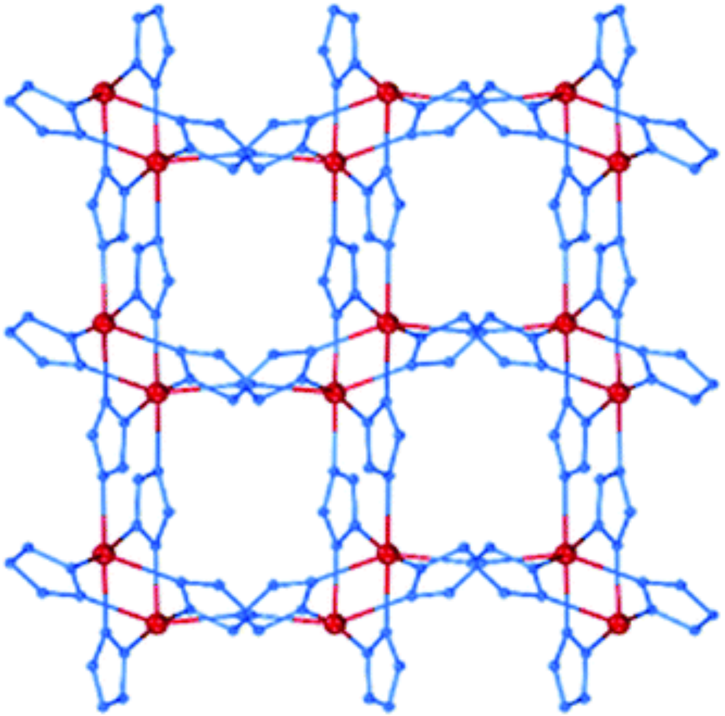
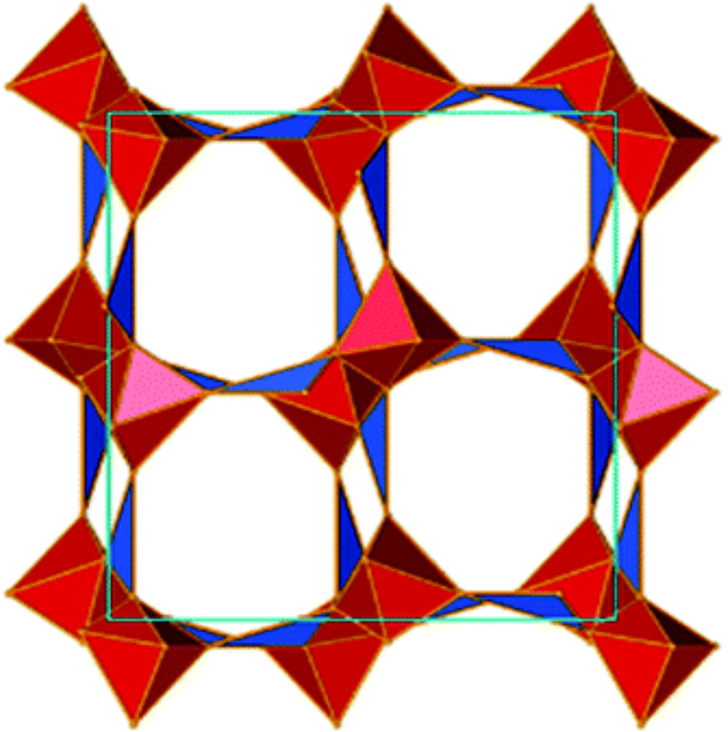
Arhangelskite a New Topology *(arh)* in $Cd(pnz)_2$







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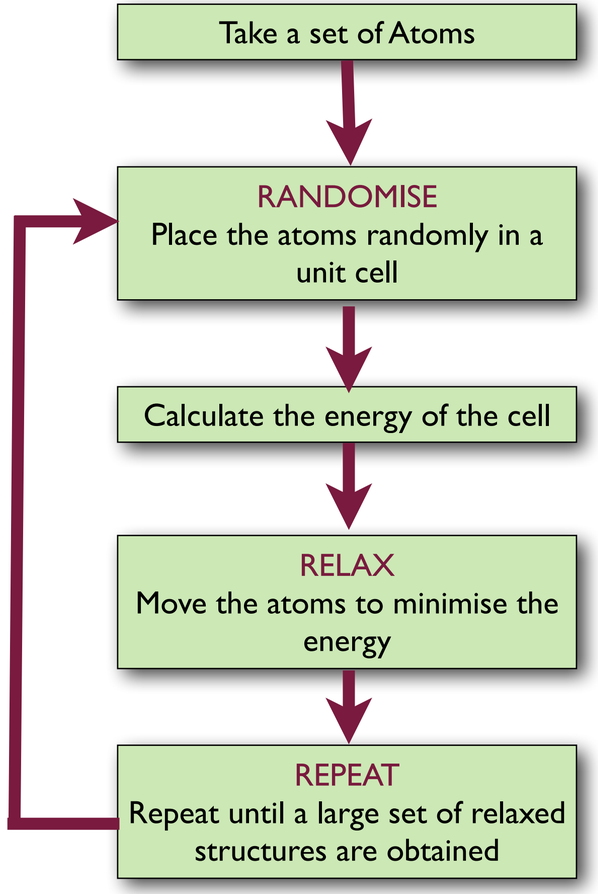
M. Arhangelskis, A.D. Katsenis, **AJM** and T. Friščić, Chem. Sci., **2018**,9, 3367-3375

Ab Initio Random Structure Searching



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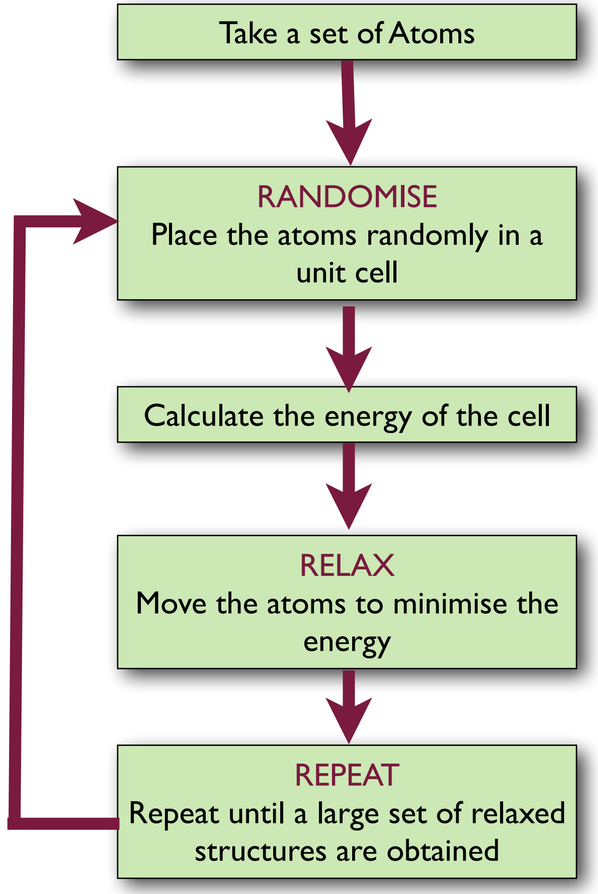
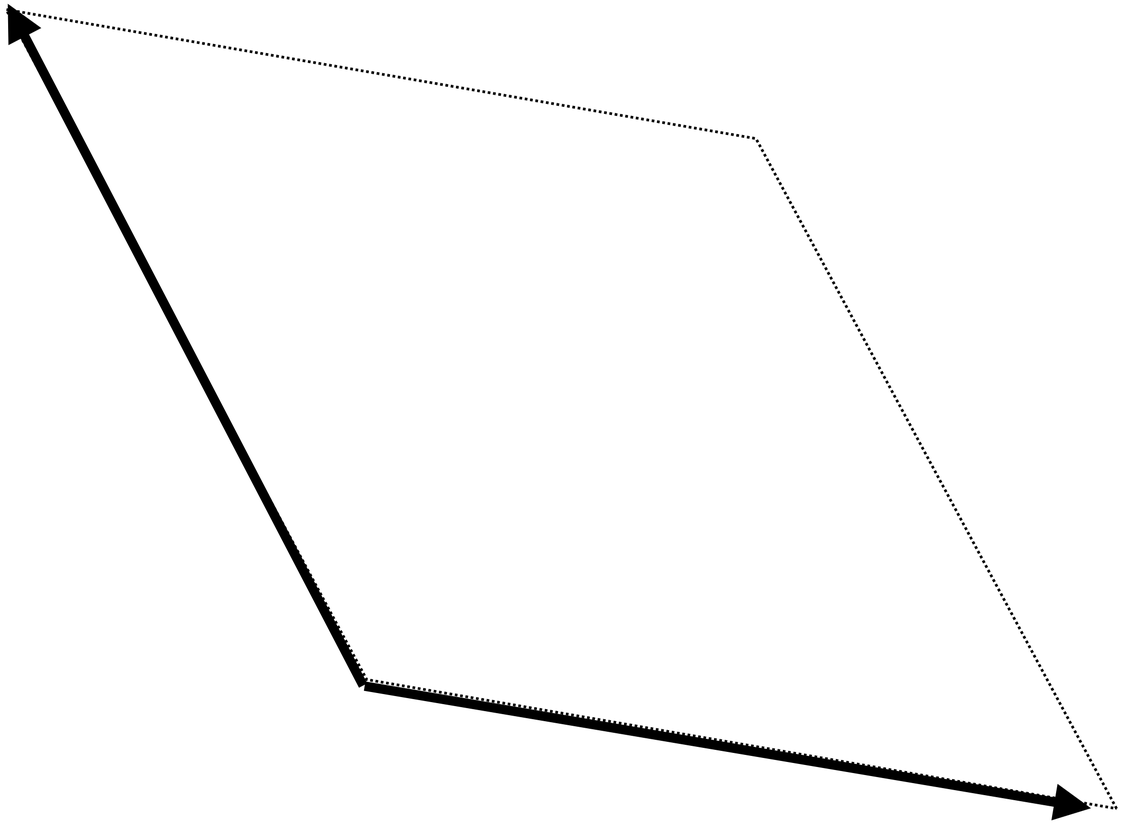
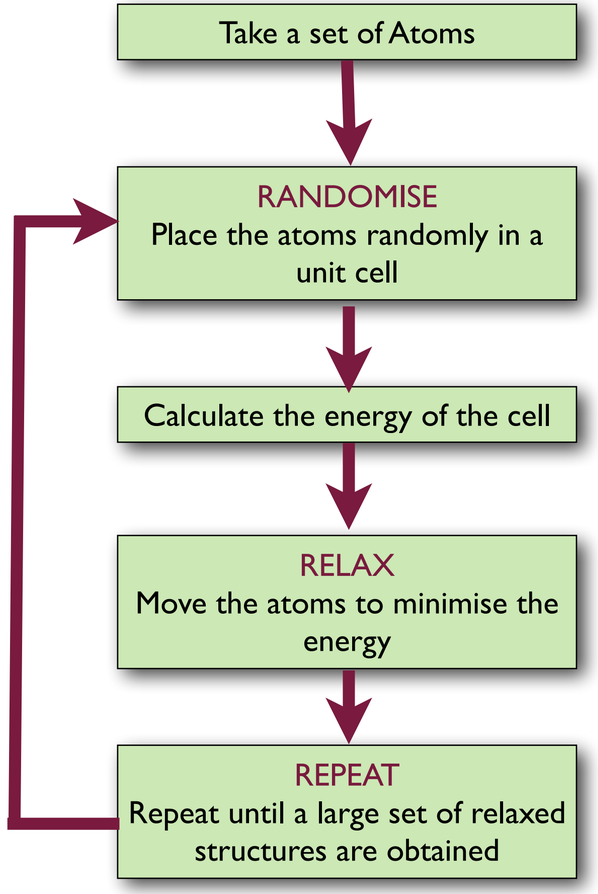
Pickard, C. J.; Needs, R. J. *Nat. Mater.* **2008**, *7*, 775
Pickard, C. J.; Needs, R. J. *J. Phys. Condens. Matter* **2011**, *23*, 053201

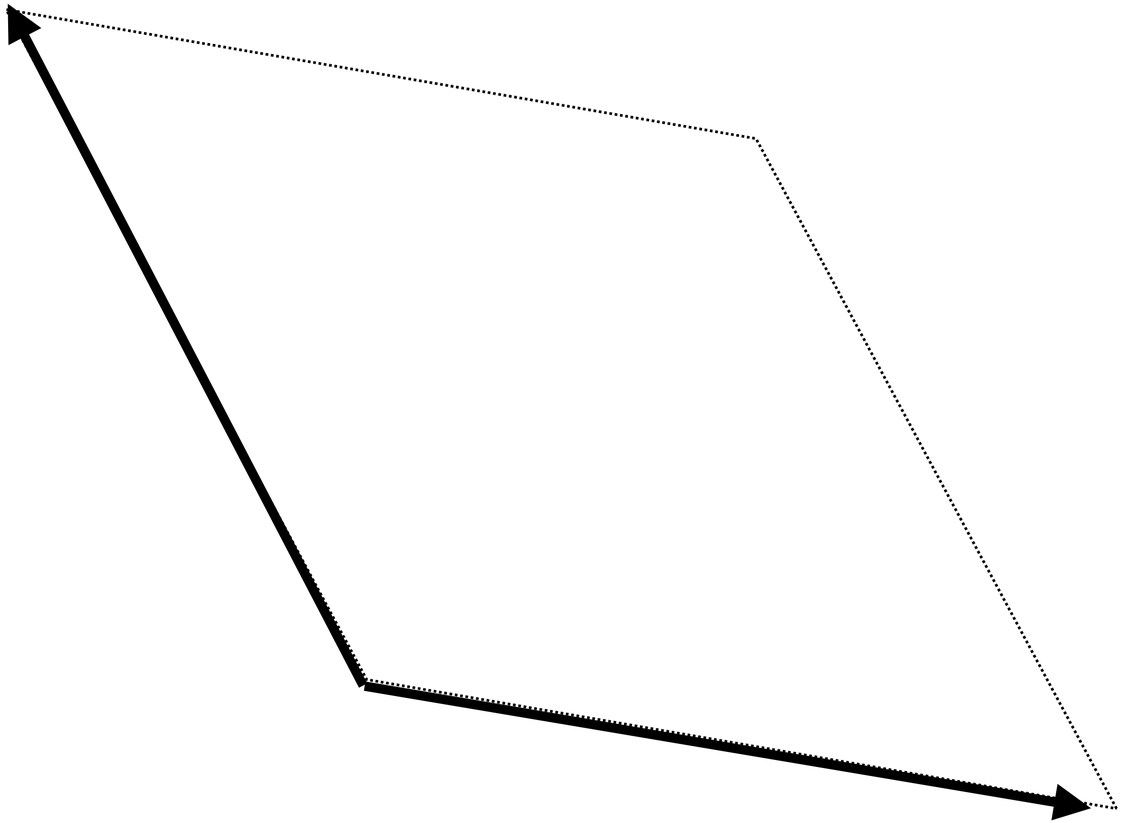
Ab Initio Random Structure Searching (AIRSS)



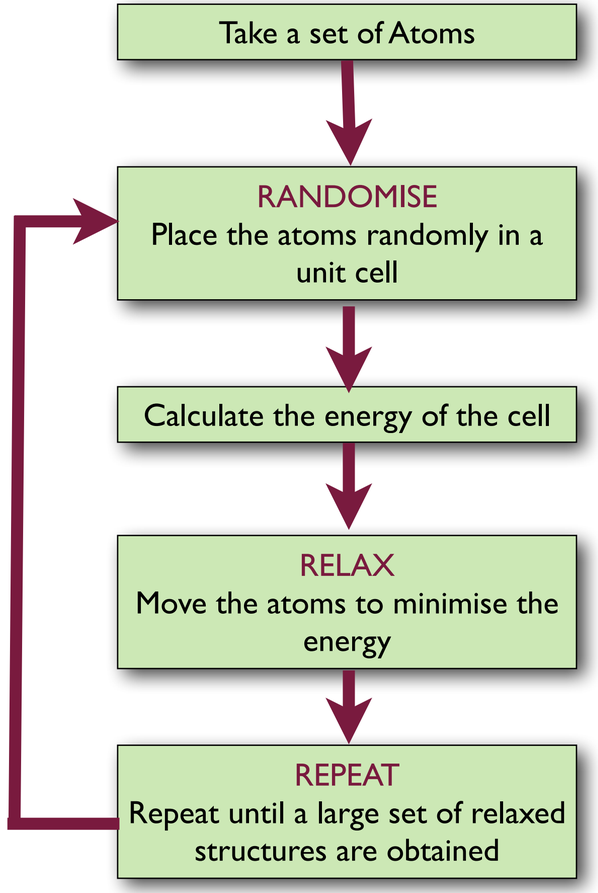


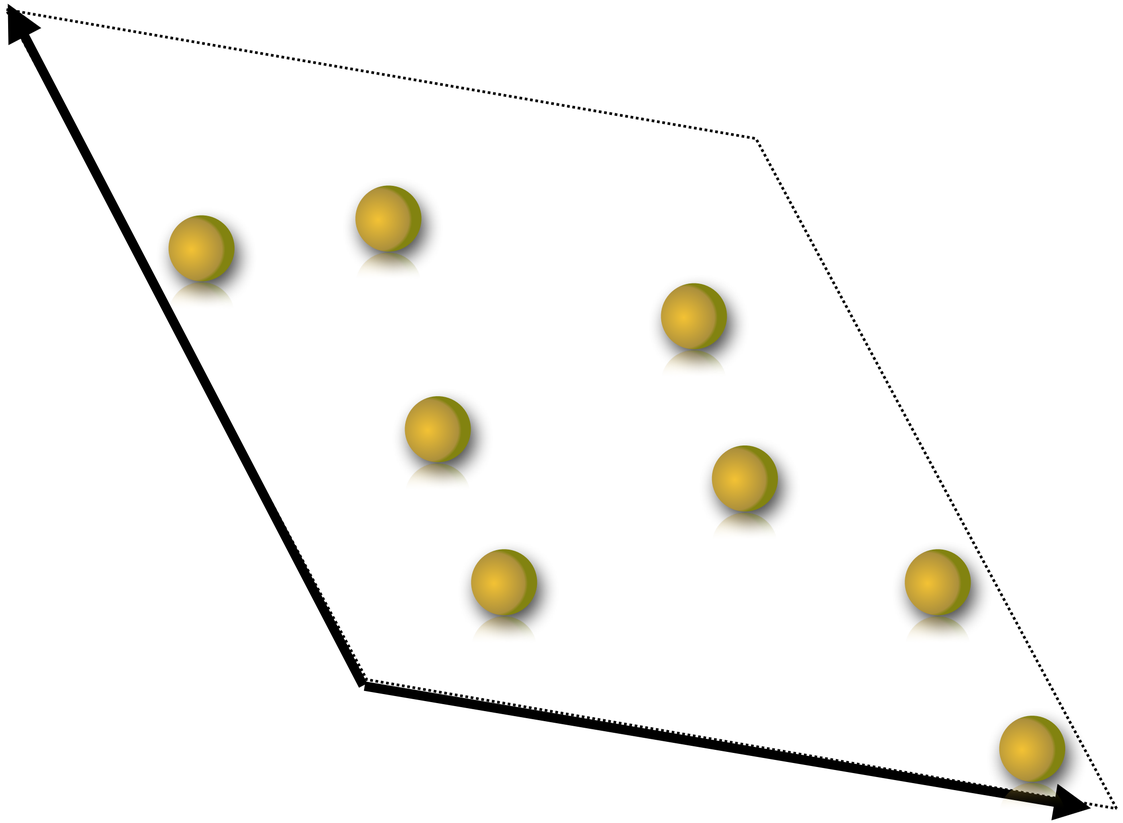
Ab Initio Random Structure Searching (AIRSS)



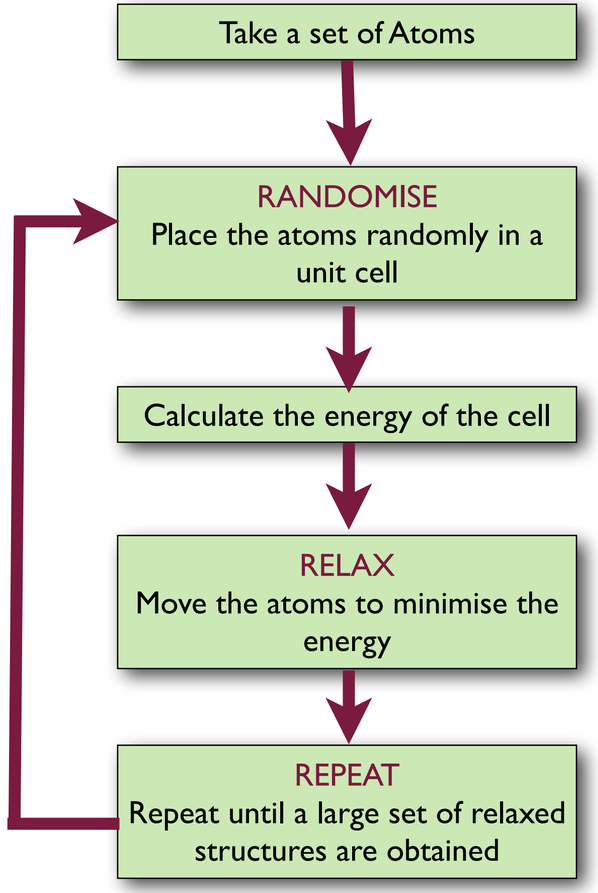


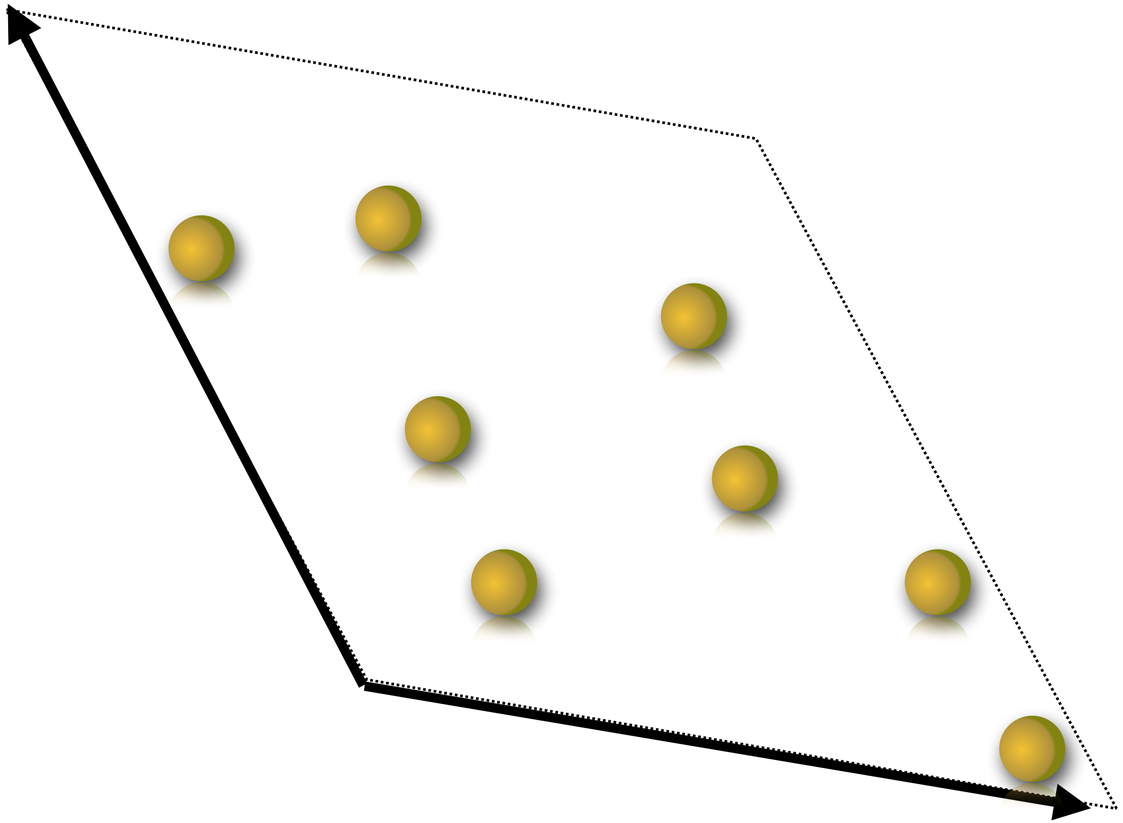
Ab Initio Random Structure Searching (AIRSS)



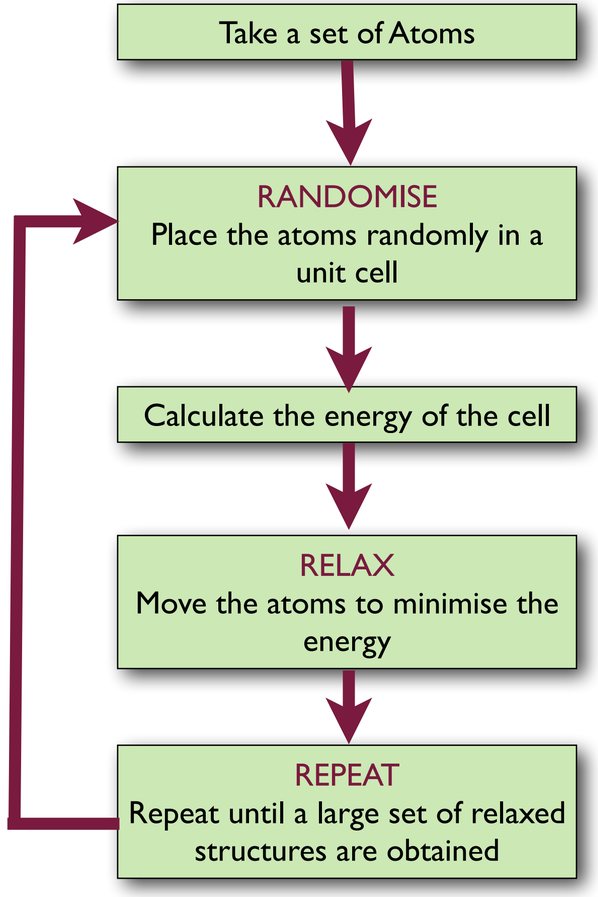


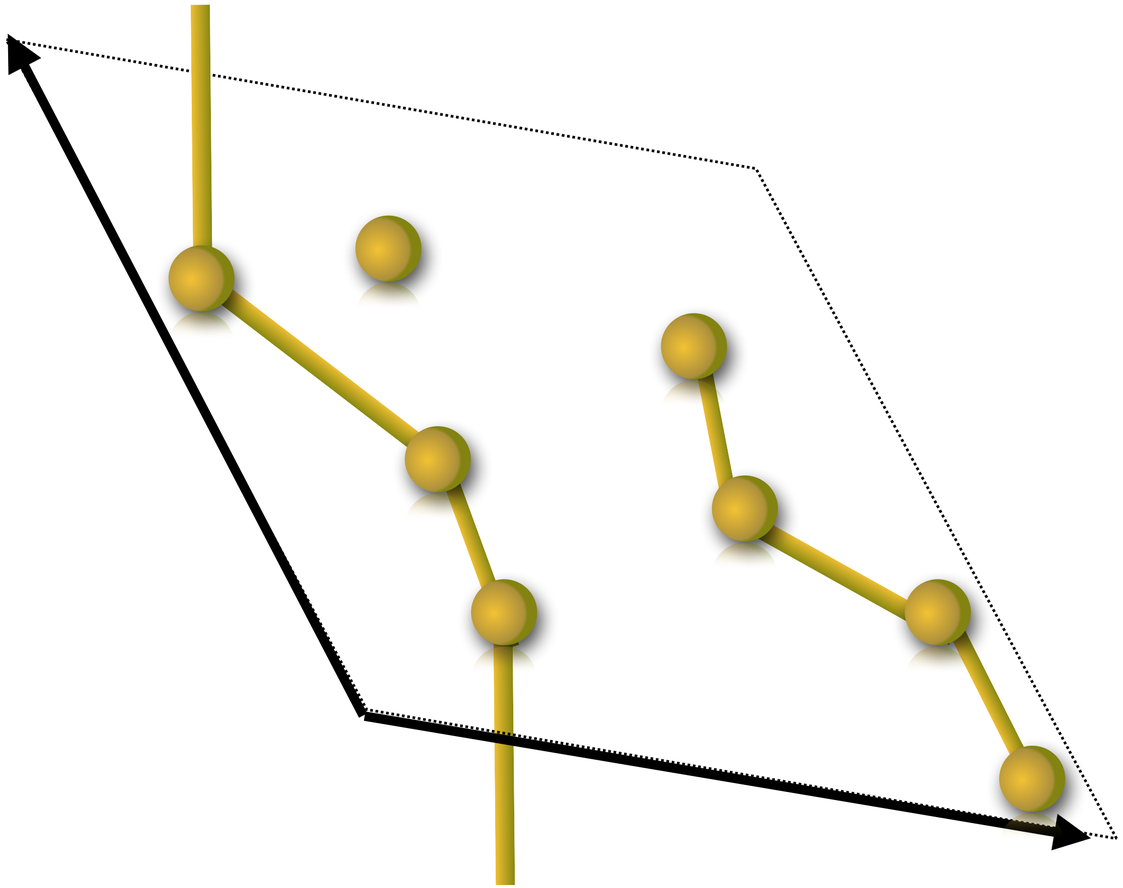
Ab Initio Random Structure Searching (AIRSS)



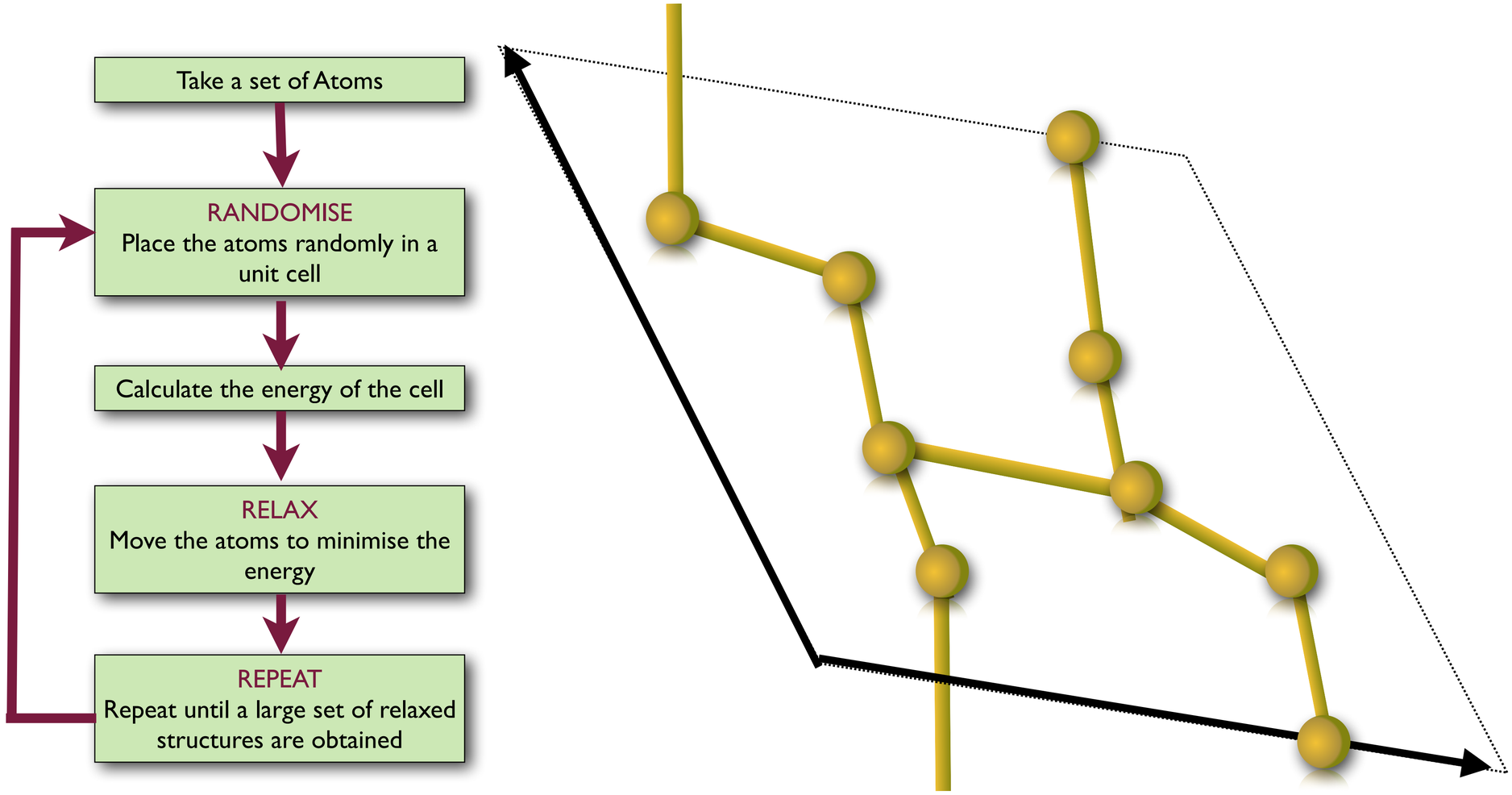


Ab Initio Random Structure Searching (AIRSS)

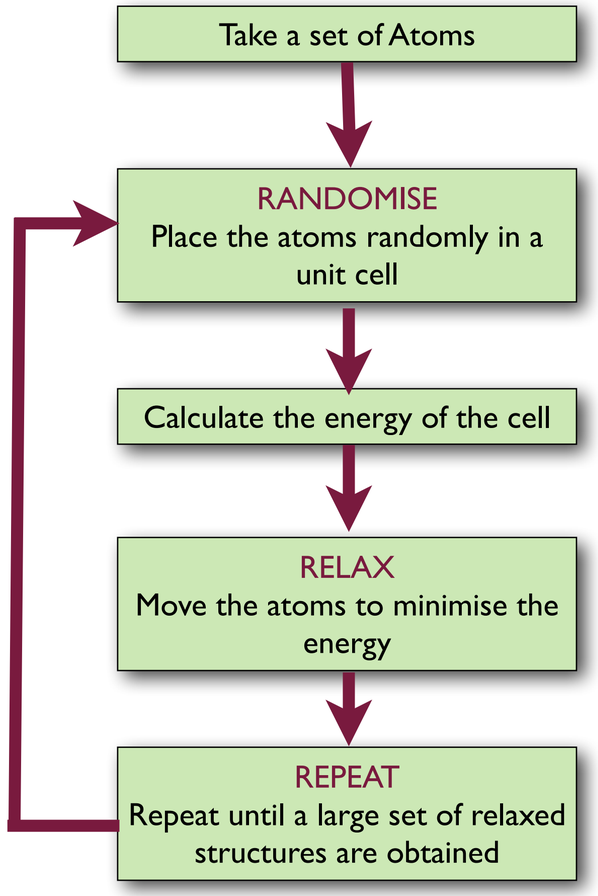


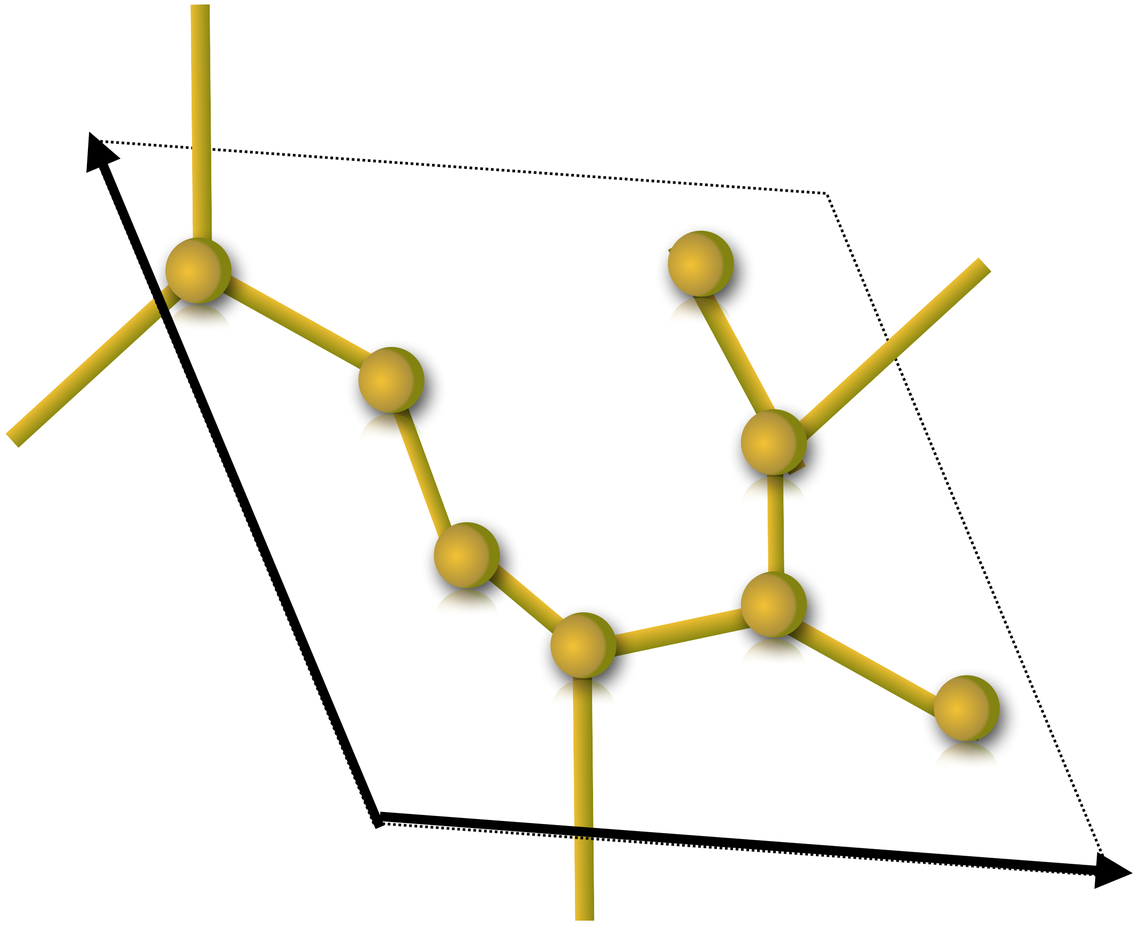


Ab Initio Random Structure Searching (AIRSS)

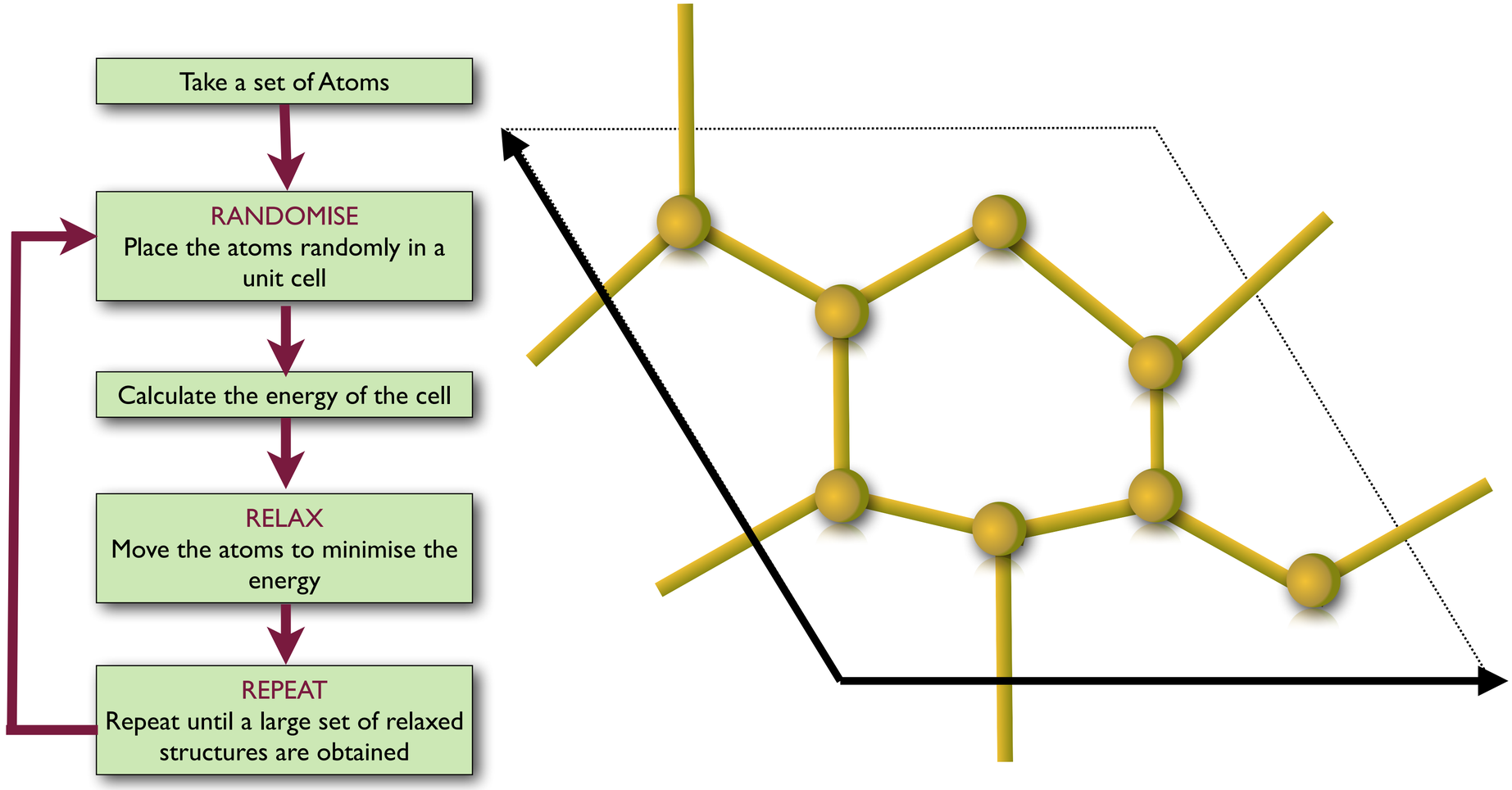


Ab Initio Random Structure Searching (AIRSS)

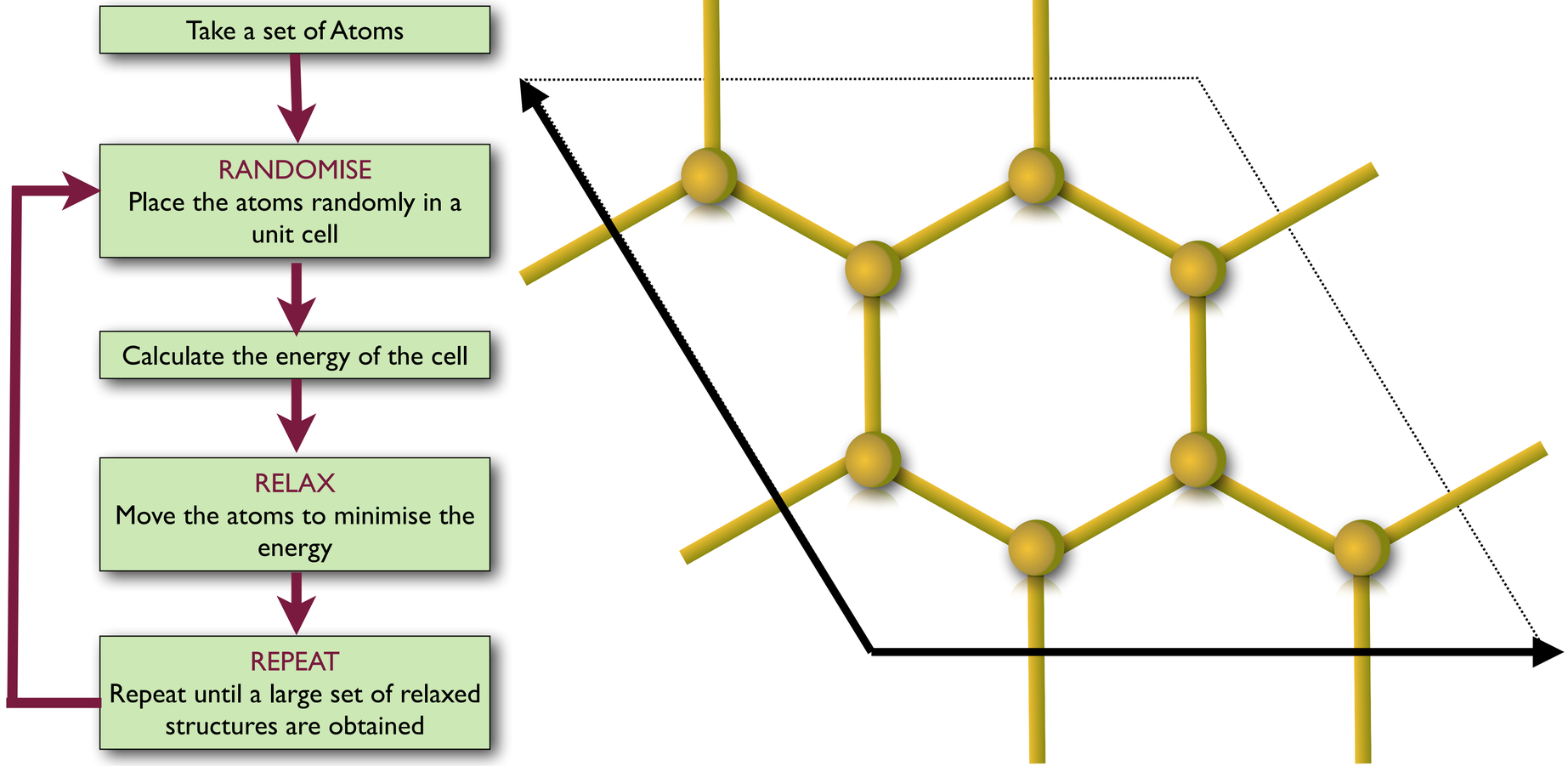




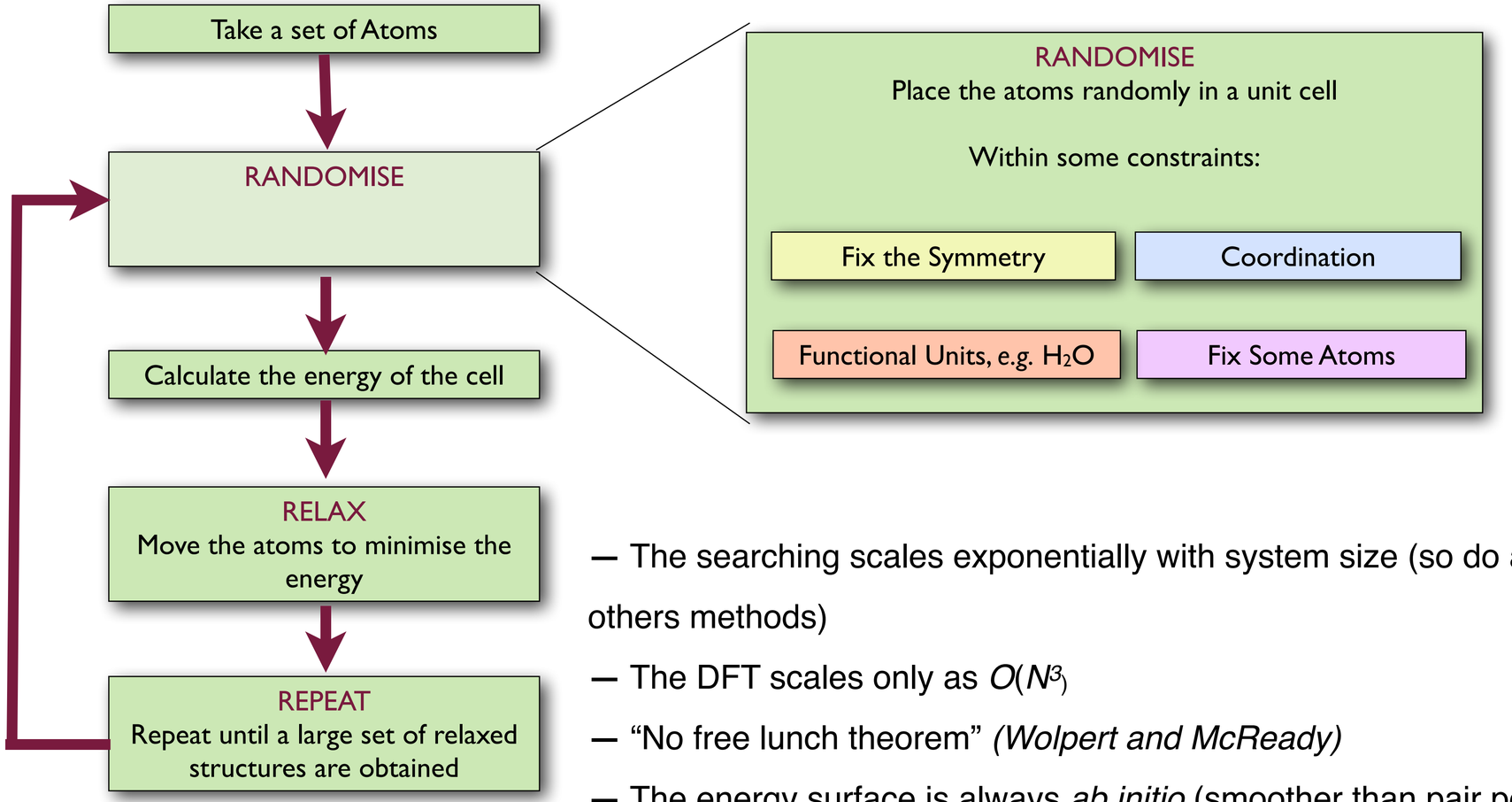
Ab Initio Random Structure Searching (AIRSS)



Ab Initio Random Structure Searching (AIRSS)



Ab Initio Random Structure Searching



— The searching scales exponentially with system size (so do all others methods)

— The DFT scales only as $O(N^3)$

— "No free lunch theorem" *(Wolpert and McReady)*

— The energy surface is always *ab initio* (smoother than pair pots.)

— Chemistry / Experiment / Experience can help you!

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Pickard, C. J.; Needs, R. J. *Nat. Mater.* **2008**, *7*, 775
Pickard, C. J.; Needs, R. J. *J. Phys. Condens. Matter* **2011**, *23*, 053201

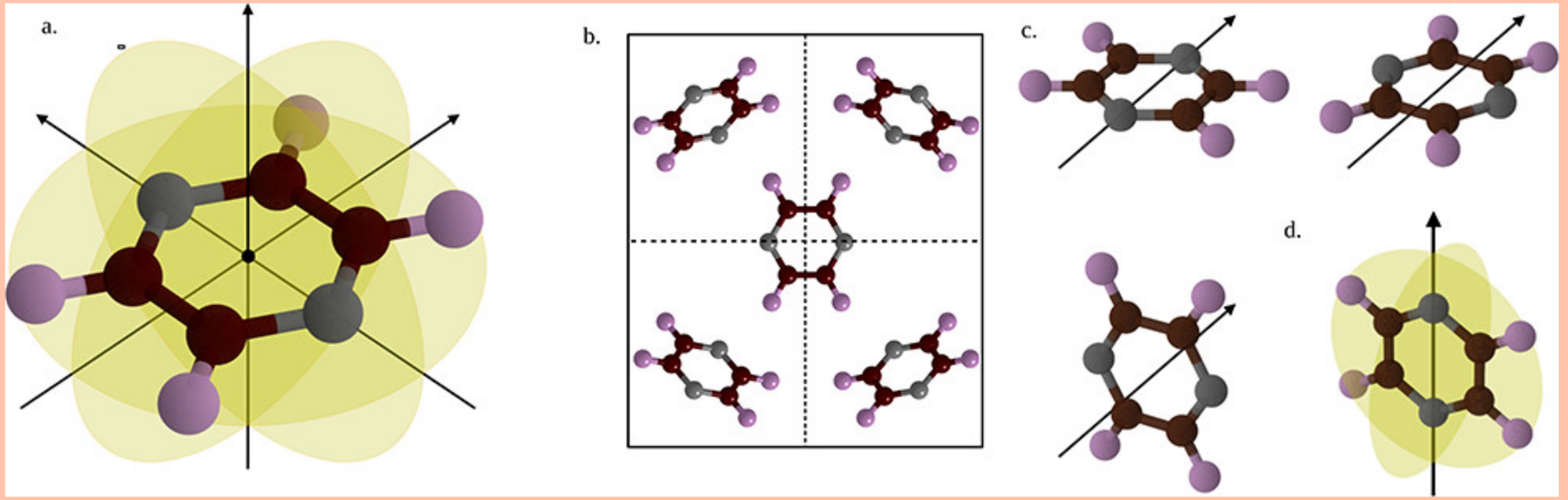
Ab Initio Random Structure Searching - Wycoff-Alignement of Molecules (WAM)

RANDOMISE

Place the atoms randomly in a unit cell

Within some constraints:

- Fix the Symmetry
- Coordination
- Functional Units, e.g. H_2O
- Fix Some Atoms



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Ab Initio Random Structure Searching - Wycoff-Alignement of Molecules (WAM)

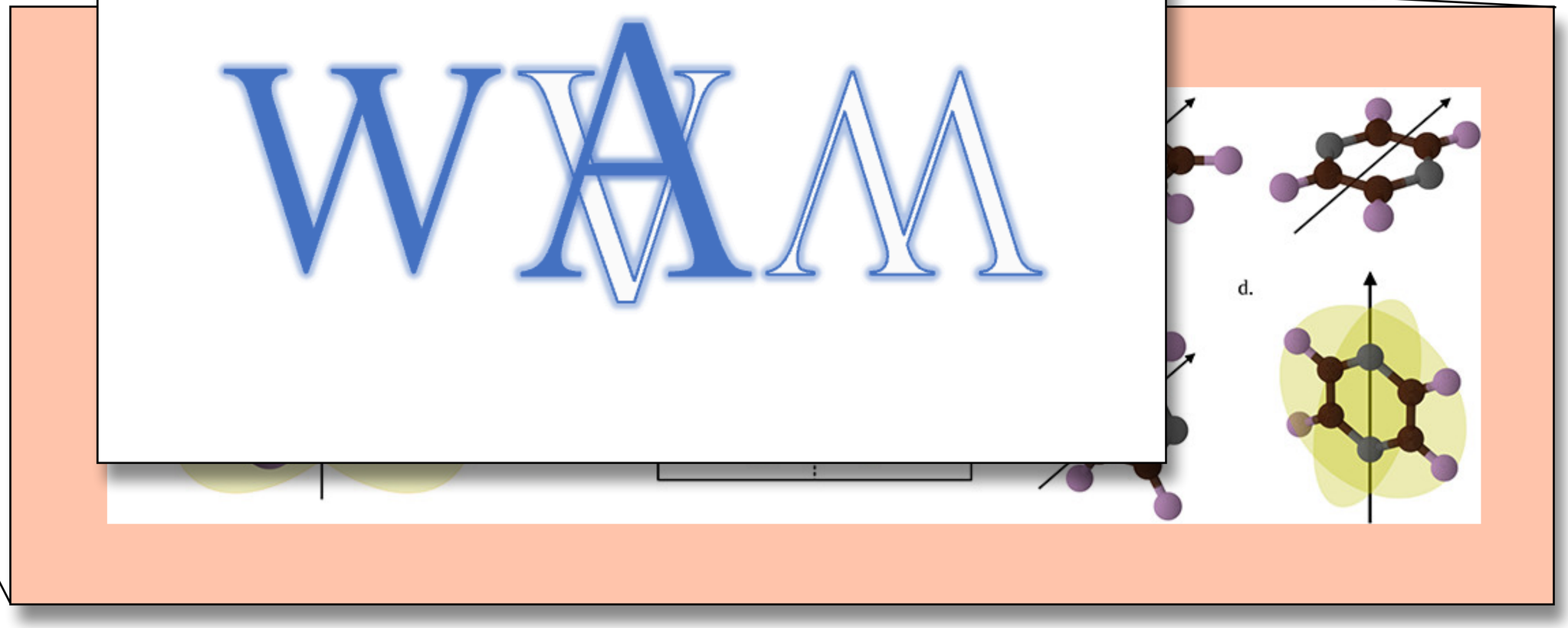
RANDOMISE

Place the atoms randomly in a unit cell

Within some constraints:

- Fix the Symmetry
- Coordination
- Functional Units, e.g. H_2O
- Fix Some Atoms

WAM



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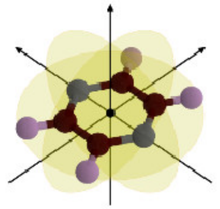
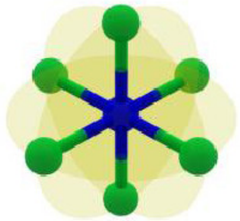
WAM-AIRSS ***SIFSIX-3-Zn Framework of Zinc, Pyrazine, and Hexafluorosilicate***

$$Zn^{2+} + 2pyr + SiF_6^{2-} \rightarrow Zn(pyr)_2SiF_6$$

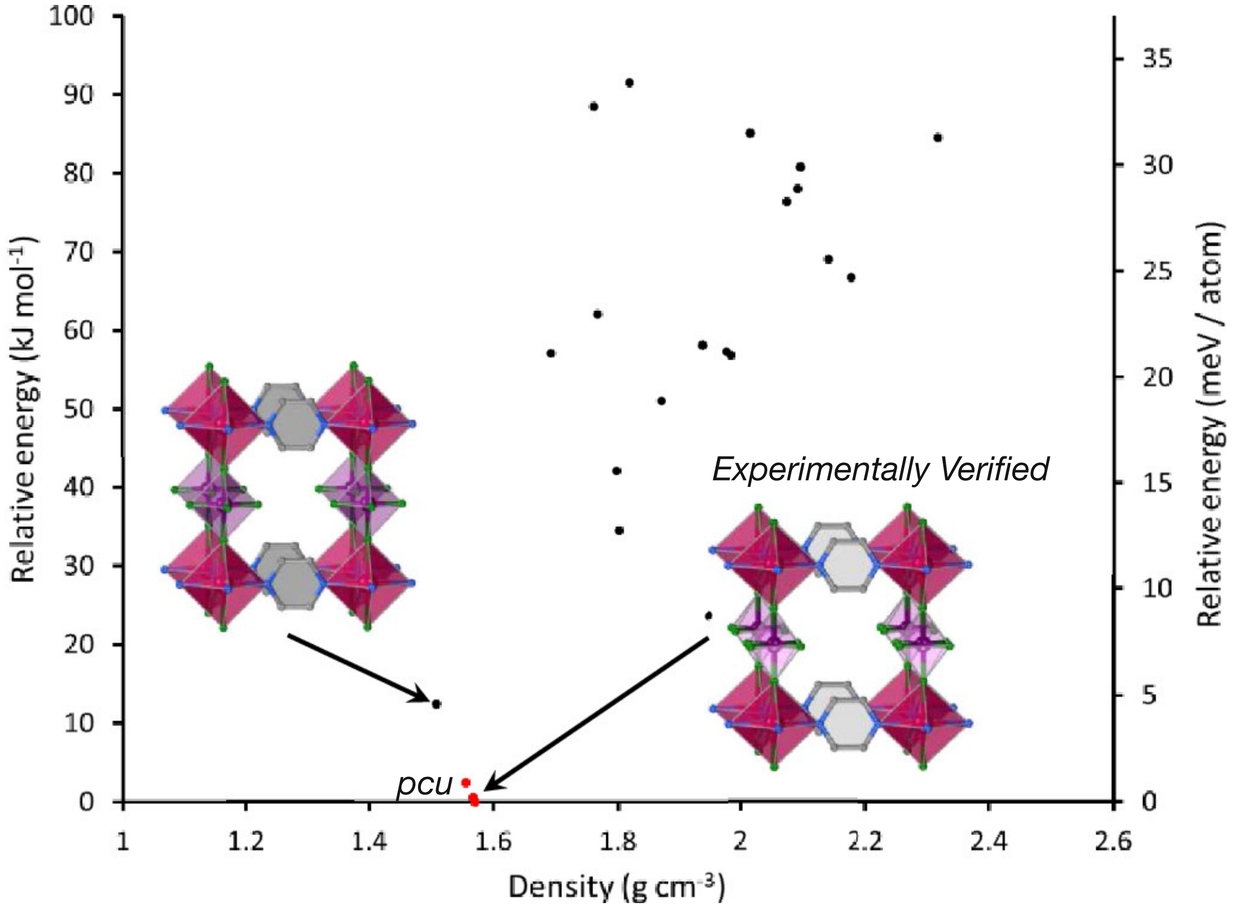


D_{2h}



O_h

pyr and SiF_6 symmetry elements



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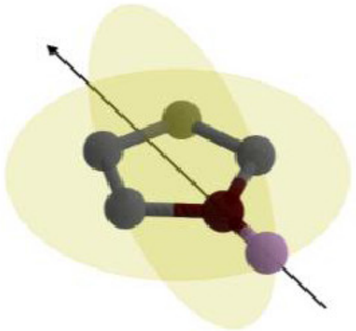
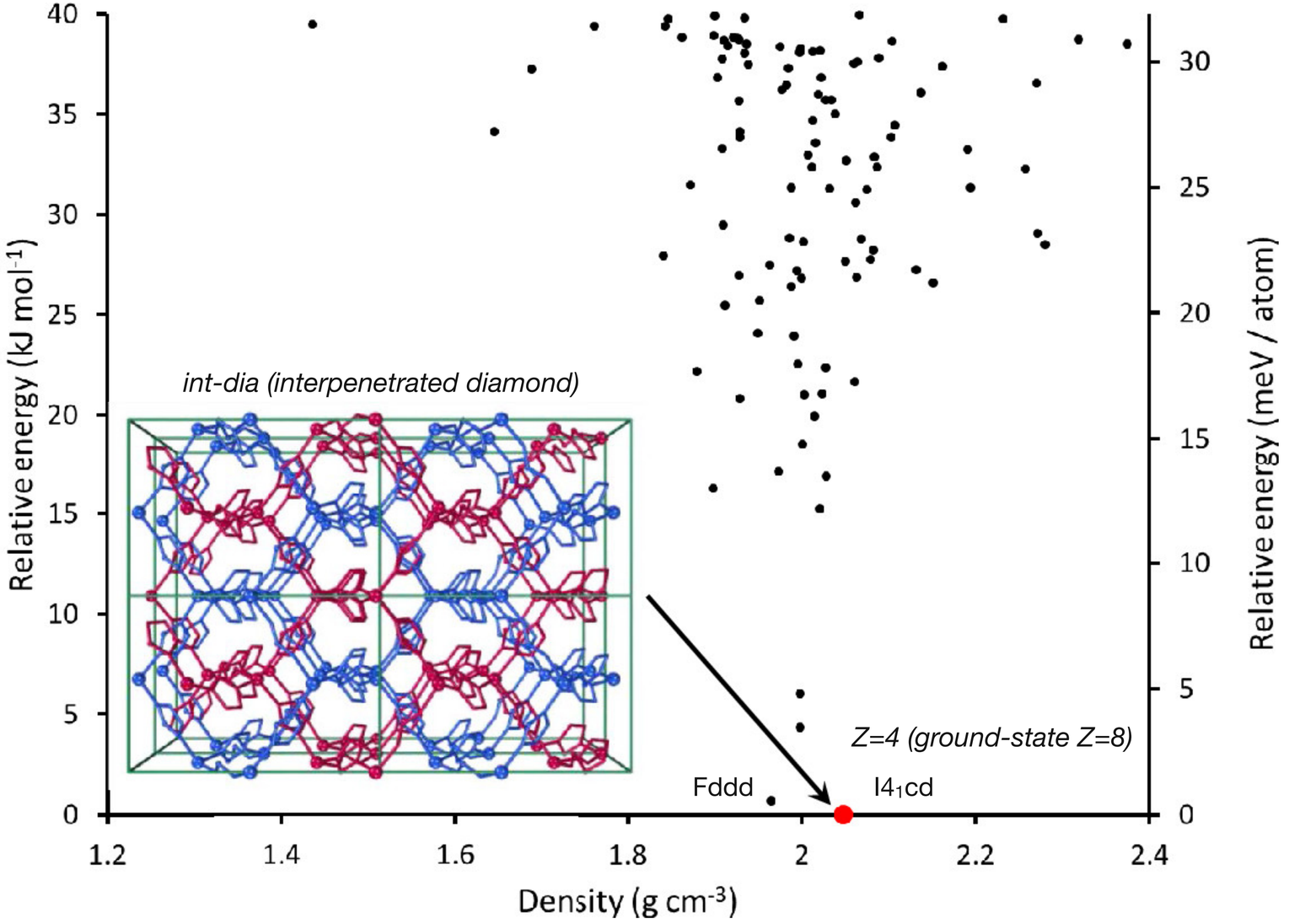
J Darby, M. Arhangelskis, A. D. Katsenis, J. M. Marrett, T. Friscic and **AJM**, Chem. Mater. 2020, 32, 13, 5835–5844

WAM-AIRSS Metal Azolate Frameworks (MAF)s, ***Zinc Tetrazolate,*** **$Zn(ttz)_2$**

$$Zn^{2+} + 2ttz^{-} \rightarrow Zn(ttz)_2$$



ttz symmetry elements



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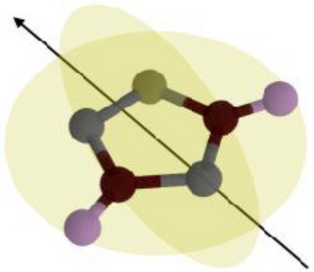
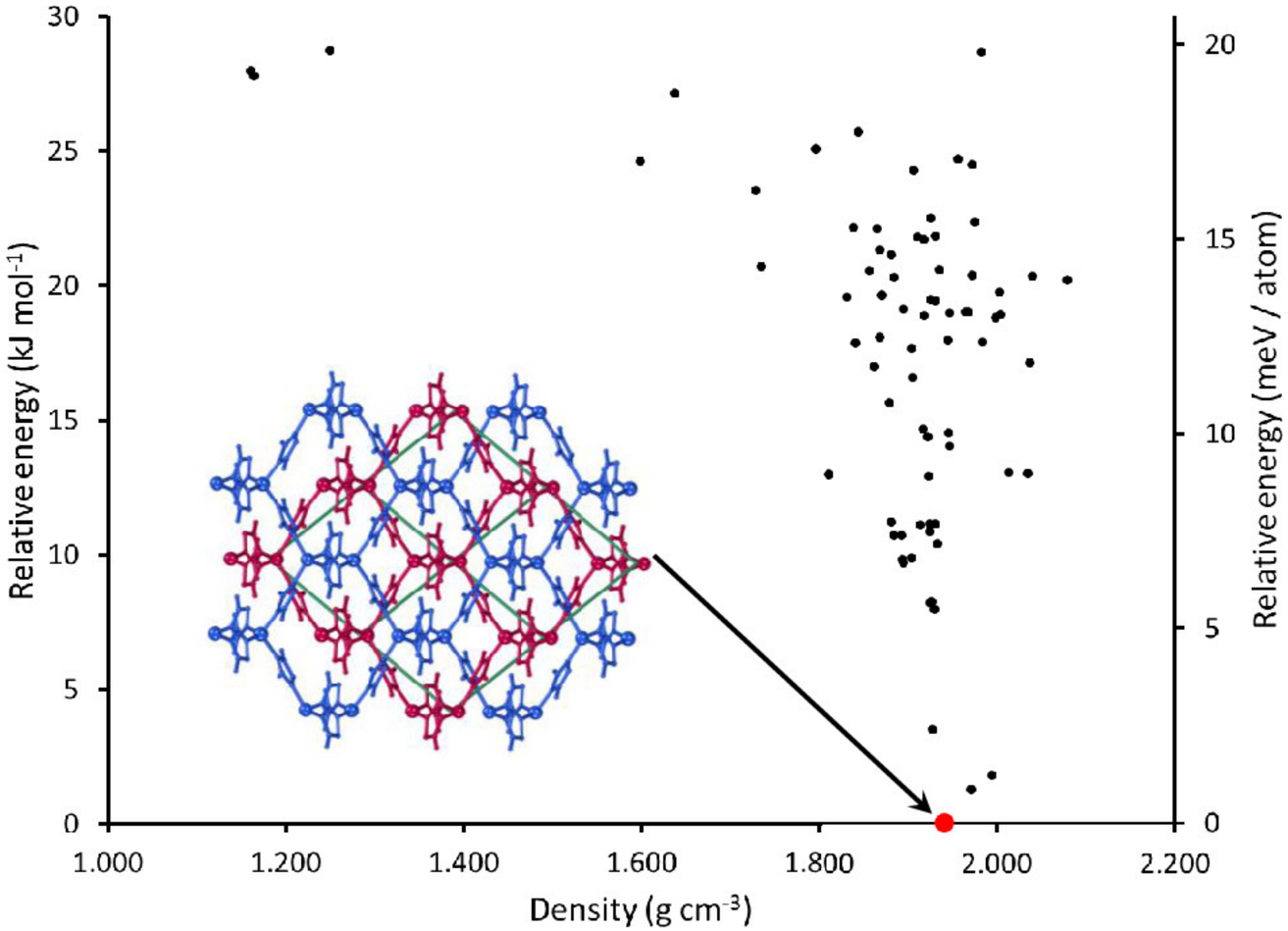
WAM-AIRSS Metal Azolate Frameworks (MAF)s, ***Zn1,2,4-triazolate,*** **Zn(trz)$_2$**

$$Zn^{2+} + 2trz^{-} \rightarrow Zn(trz)_2$$



trz symmetry elements



Zn(trz)$_2$ *trz* protonated?

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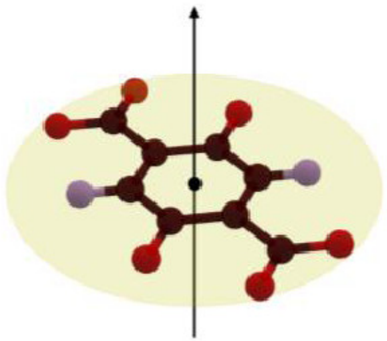
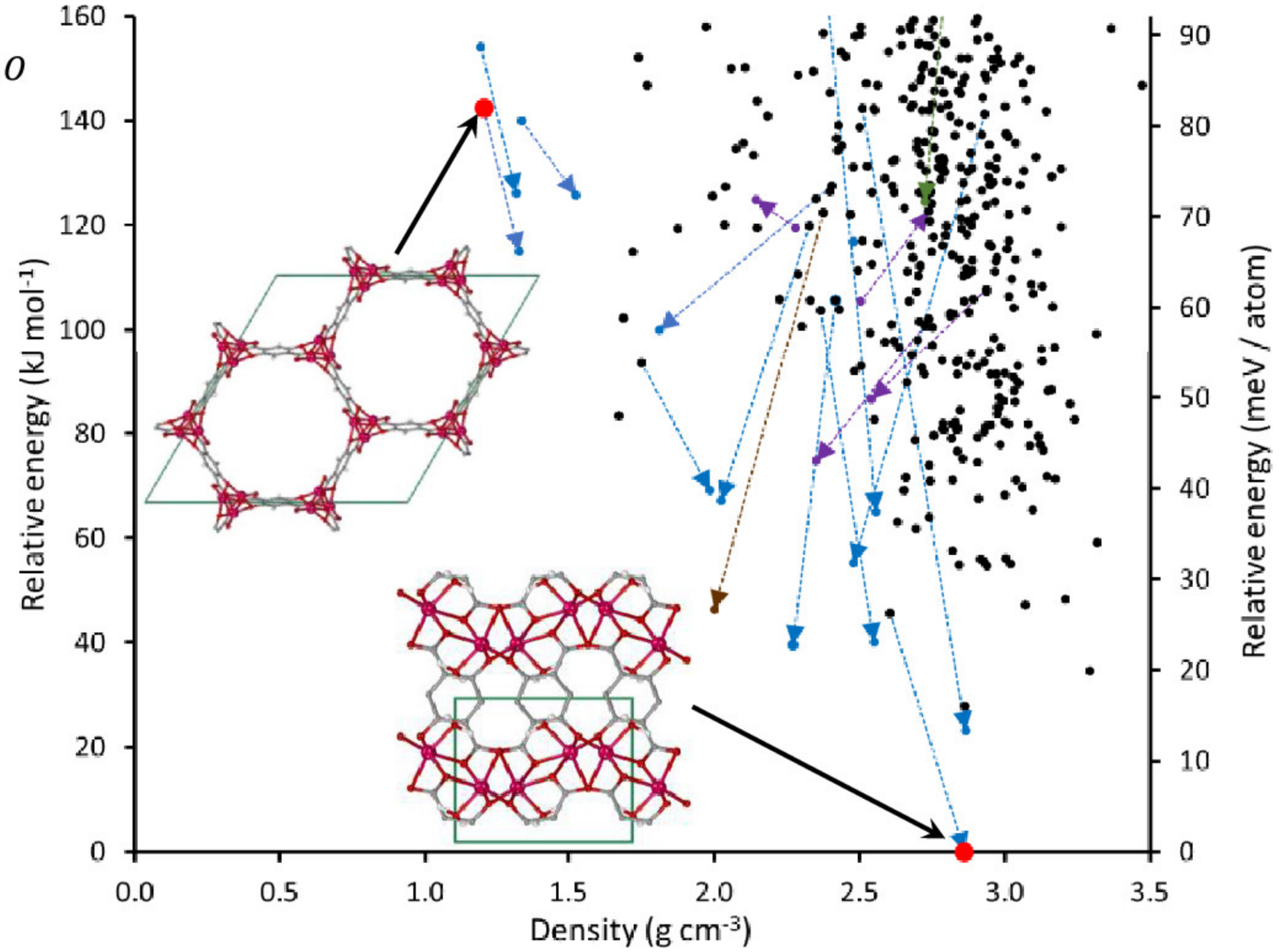
WAM-AIRSS ***MOF-74*** *(*2,4-dihydroxyterephthalate ($DHTA_{4-}$) linkers)

$$2Zn^{2+} + DHTA^{4-} \rightarrow Zn_2(DHTA) \cdot xH_2O$$

- $x = 0$
- $x = 2$
- $x = 1$
- $x = 4$
- $x = {}^{2}/_{3}$



DHTA symmetry elements



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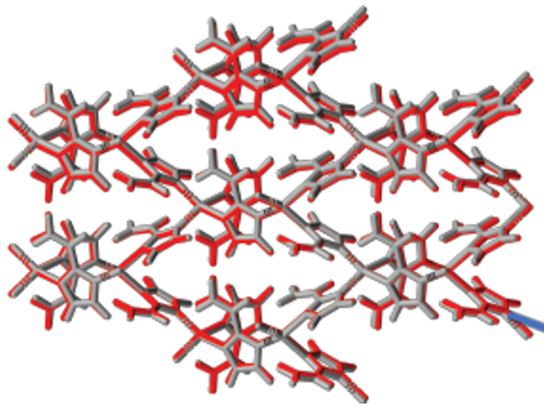
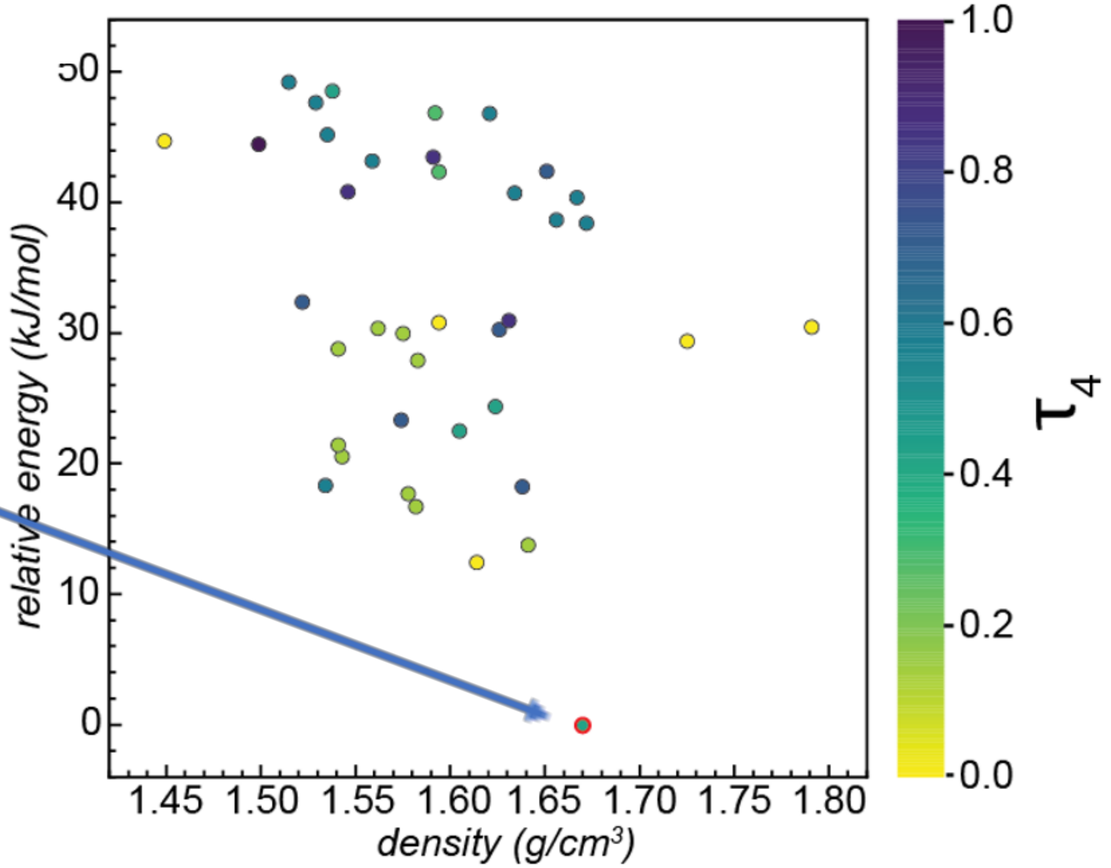
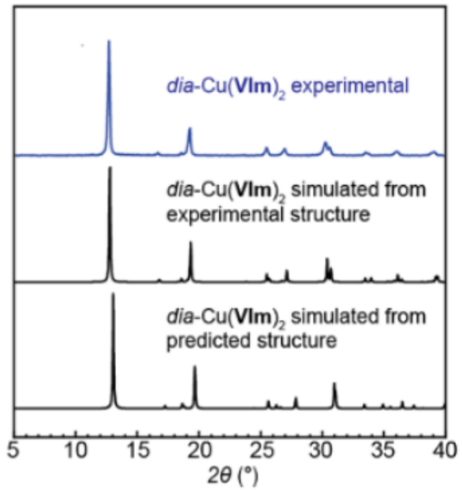
WAM **Cu(VIm)$_2$** (2-vinylimidazol)



dia-Cu(**VIm**)$_2$



Cu coordination geometry index (τ_4), with the value of 0 (yellow) being the perfect square planar geometry and purple being the tetrahedral geometry.



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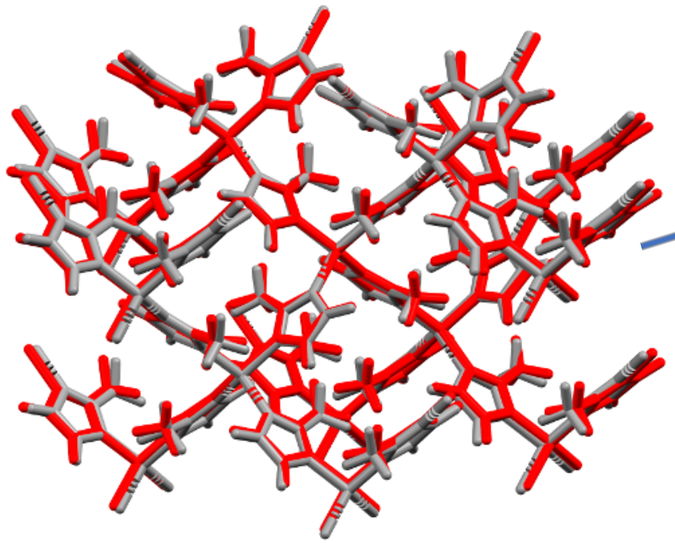
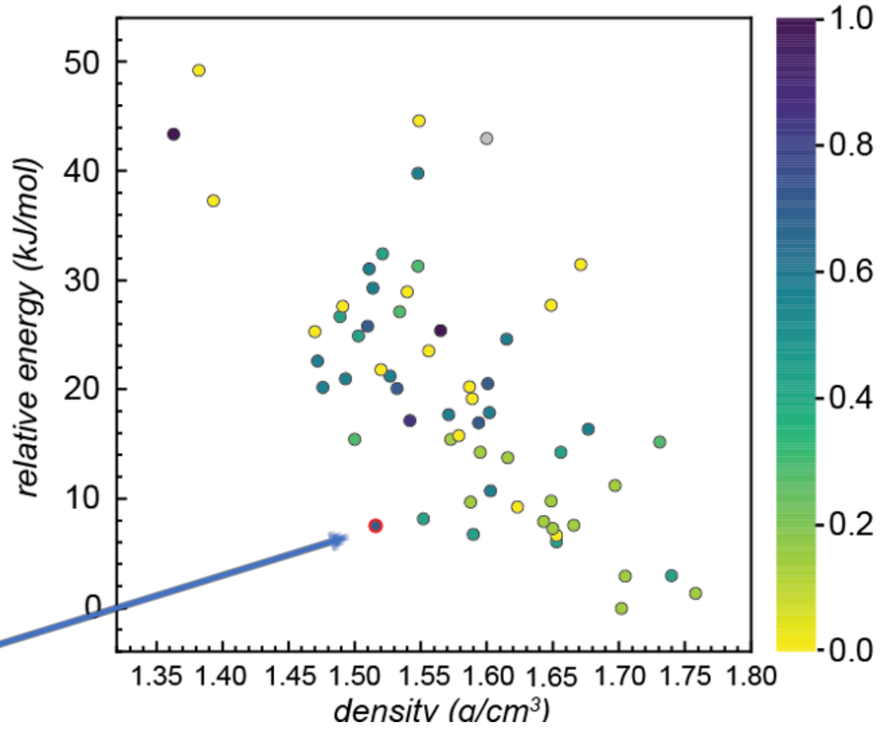
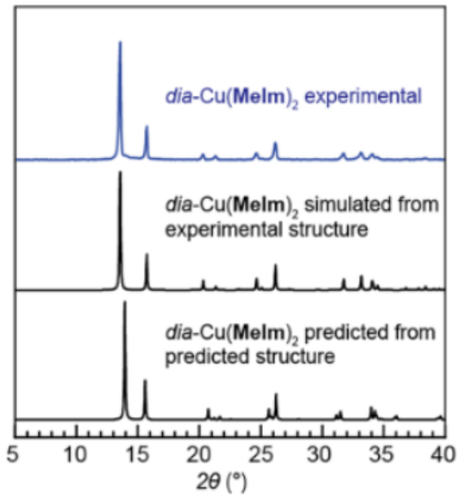
WAM **Cu(MeIm)$_2$** (methyl substituted imidazolate)





Cu coordination geometry index (τ_4), with the value of 0 (yellow) being the perfect square planar geometry and purple being the tetrahedral geometry.



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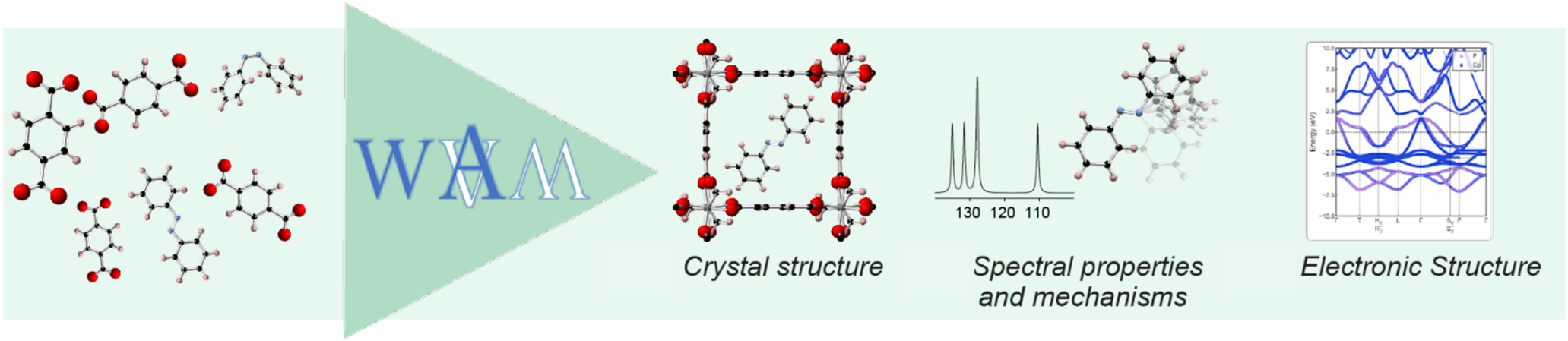
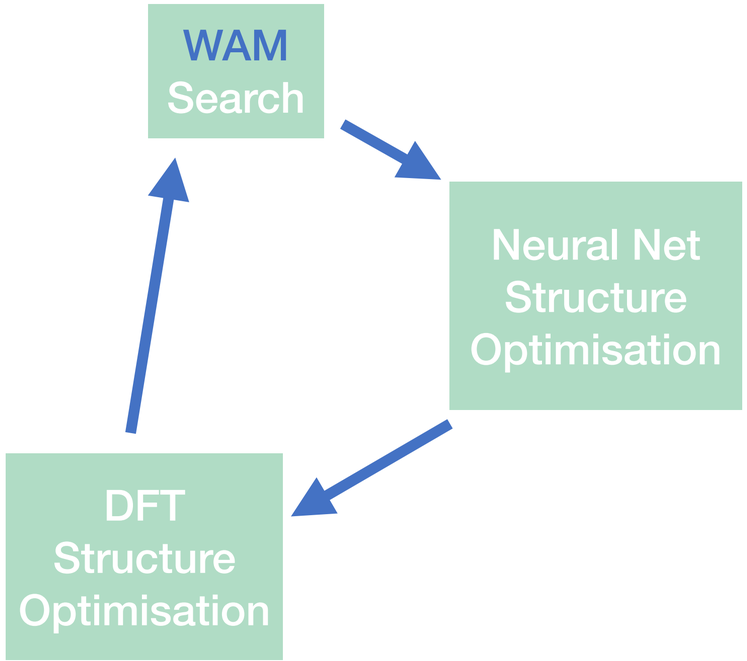
Accelerating WAM





- Highly polymorphic zinc-based zeolitic imidazolate frameworks (ZIF) were chosen to train the potentials
- Deep neural networks-based software SchNetPack was used to train all the potentials
- Data for training was extracted from periodic DFT geometry optimization calculations
- Training including 18873 structures containing 1-4 formula units in the primitive cell; Training set : validation set = 80 : 20
- Trained on 4 v100 GPUs for 72 hours

Schütt, K. T. et al. SchNetPack: A Deep Learning Toolbox For Atomistic Systems. J Chem Theory Comput 15, 448–455 (2019).

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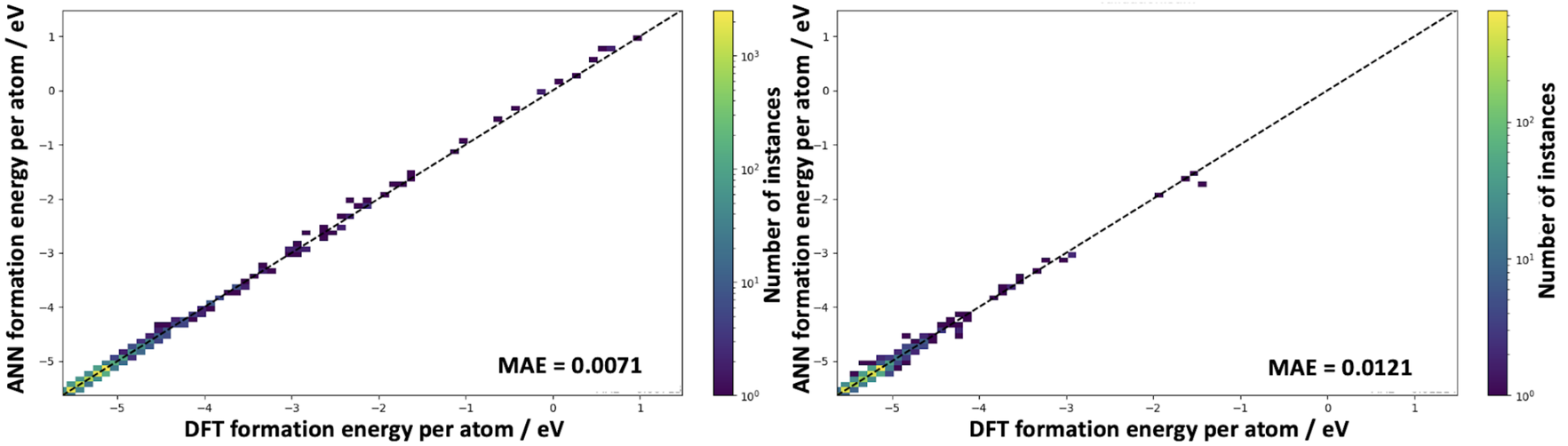
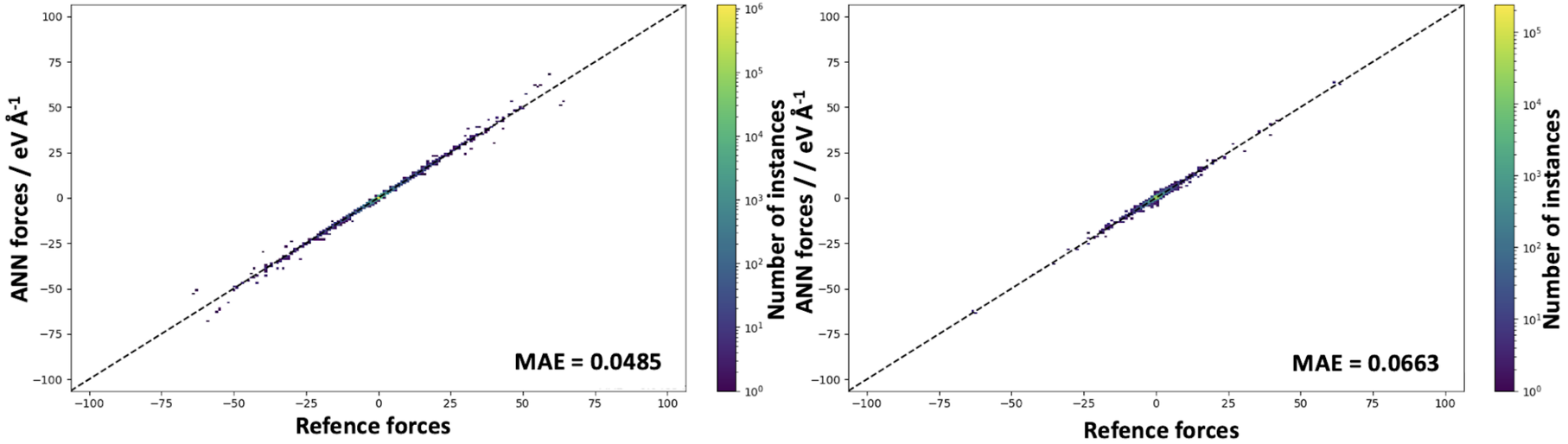
Training set

Validation set





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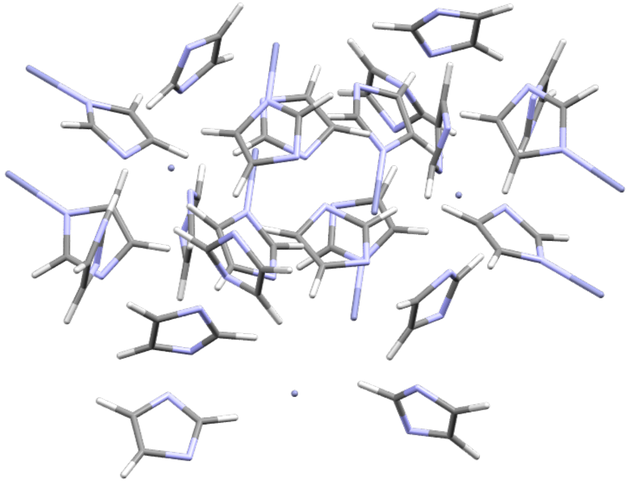
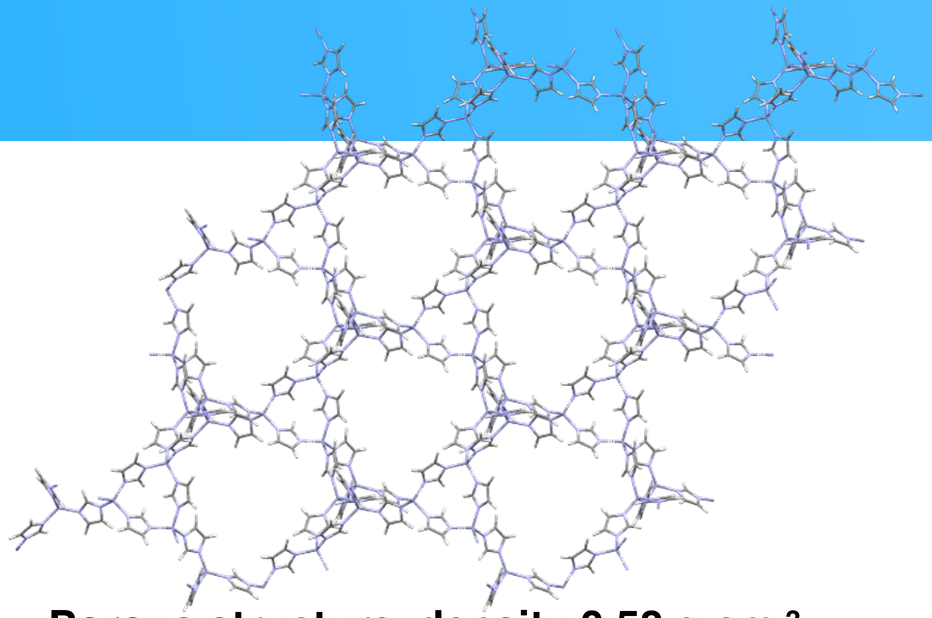
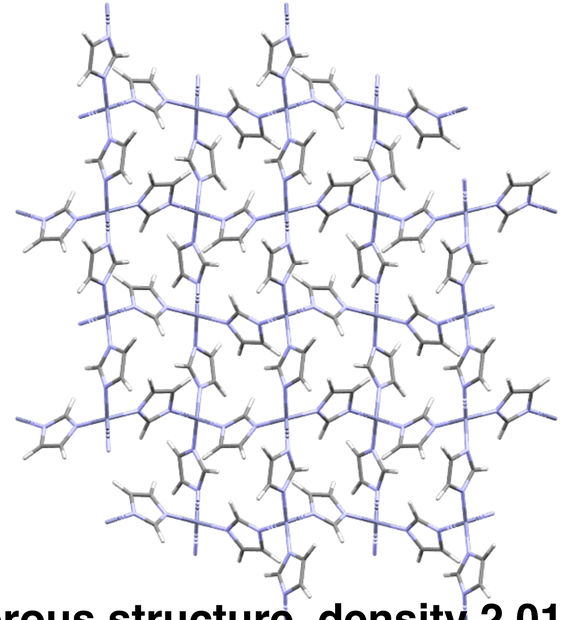


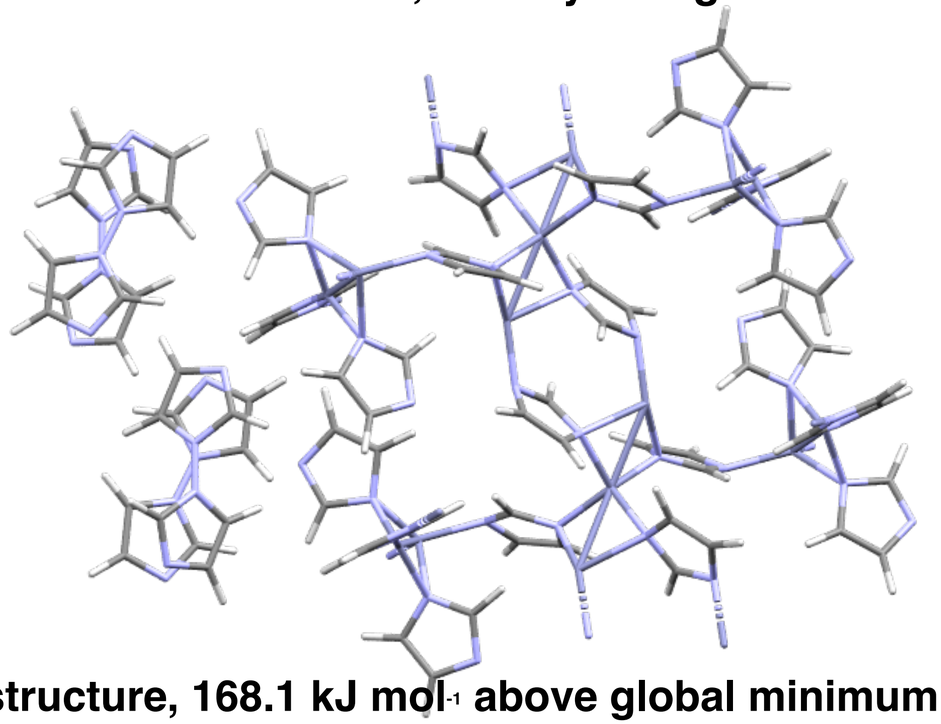
WAM generated input structure



Porous structure, density 0.58 g cm^{-3}



Non-porous structure, density 2.01 g cm^{-3}



“bad” structure, 168.1 kJ mol^{-1} above global minimum

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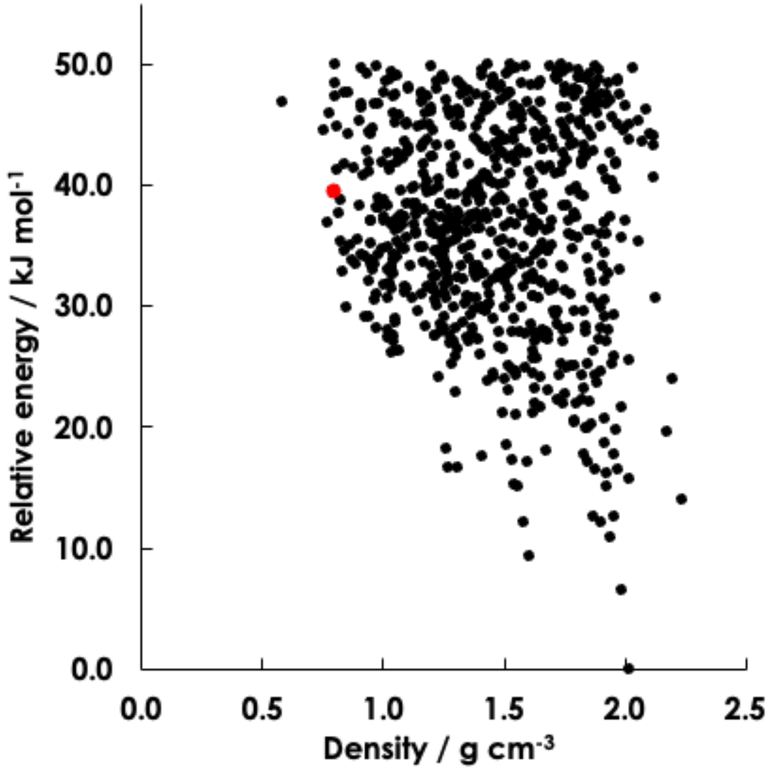
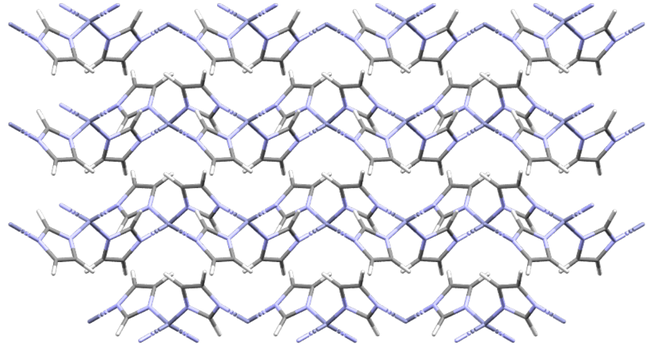
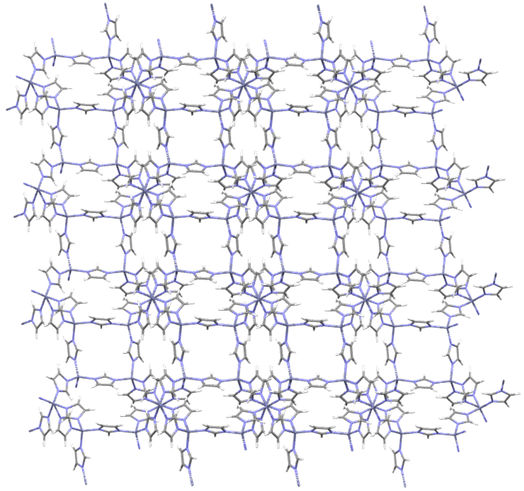
Zn imidazolate, ML Structures @ 6 f.u.



- Global minimum 2D framework; isostructural to mercury analogue



- ML-optimized structure with *SOD* topology matching with Zn 2-methylimidazolate literature



1. Speight, I. R.; Huskić, I.; Arhangelskis, M.; Titi, H. M.; Stein, R. S.; Hanusa, T. P.; Friščić, T., *Chem. – Eur. J.* **2020**, *26* (8), 1811–1818.
2. Karagiaridi, O.; Lalonde, M. B.; Bury, W.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T., *J. Am. Chem. Soc.* **2012**, *134* (45), 18790–18796.

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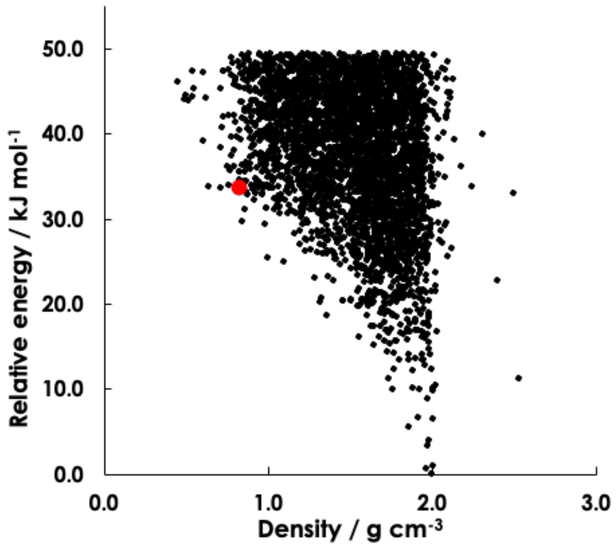
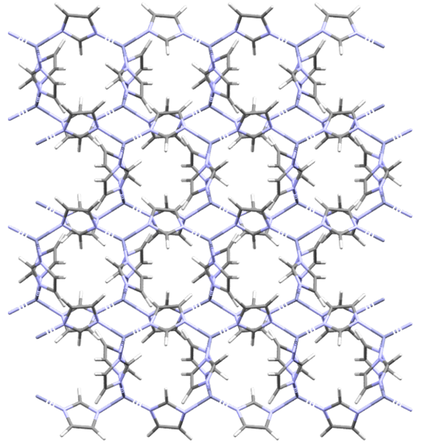
Zn imidazolate, ML Structures @ 8 f.u.

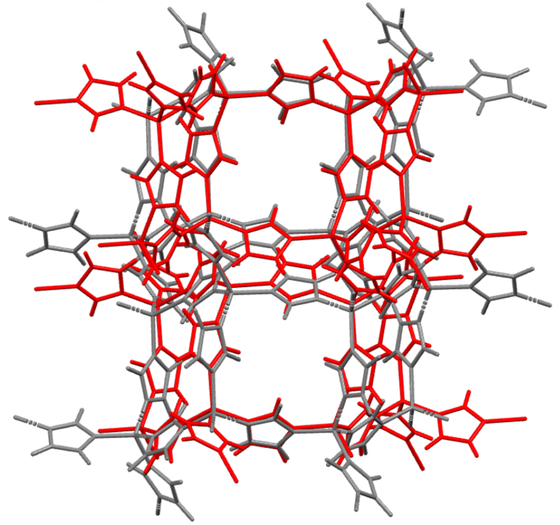


- Global Minimum 3D framework



sql

- Experimental Matching Structure



GIS

(1) Tian, Y. Q.; Zhao, Y. M.; Chen, Z. X.; Zhang, G. N.; Weng, L. H.; Zhao, D. Y., *Chem. - Eur. J.* **2007**, *13* (15), 4146–4154.
(2) Zoubritzky, L.; Coudert, F.-X., *SciPost Chem.* **2022**, *1* (2), 005.

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* ***Ab Initio* Random Structure Searching (AIRSS)** is a powerful too for crystal structure prediction. Provides the philosophy of sensible random structures to reduce the configuration space.

* Adding **WAM** allows us to place fragments without recourse to topologies (but can use crystallography to help if known).

* **Machine Learned** (AI) potentials further accelerated the searches, without too much hassle. (“Polish” the best if you want *ab initio* accuracy.

* Extend to
  * CO_2 / H_2O inclusion
  * COFs, HOFs… *etc*.

J Darby, M. Arhangelskis, A. D. Katsenis, J. M. Marrett, T. Friscic and **AJM**, Chem. Mater. 2020, 32, 13, 5835–5844

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