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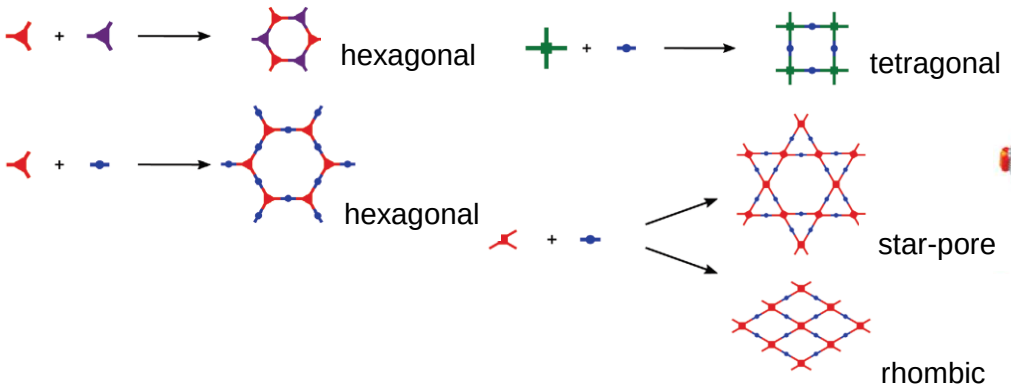
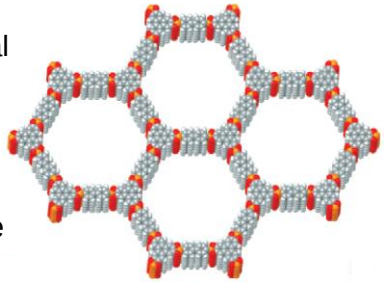
The influence of stacking on properties of layered COFs

Dresden, Wednesday, 01. Sep. 2021

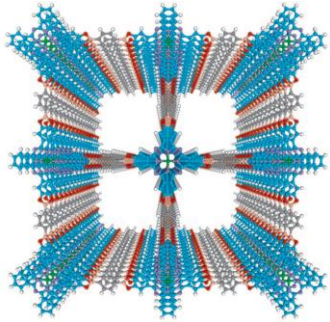
Introduction - LCOFs

- Layered Covalent Organic Frameworks (LCOFs)
  - Build from **organic** linkers and centers
  - Many available **topologies**
  - Variable and tunable structures
- **Properties** of LCOFs **depend on their stacking**





COF-10

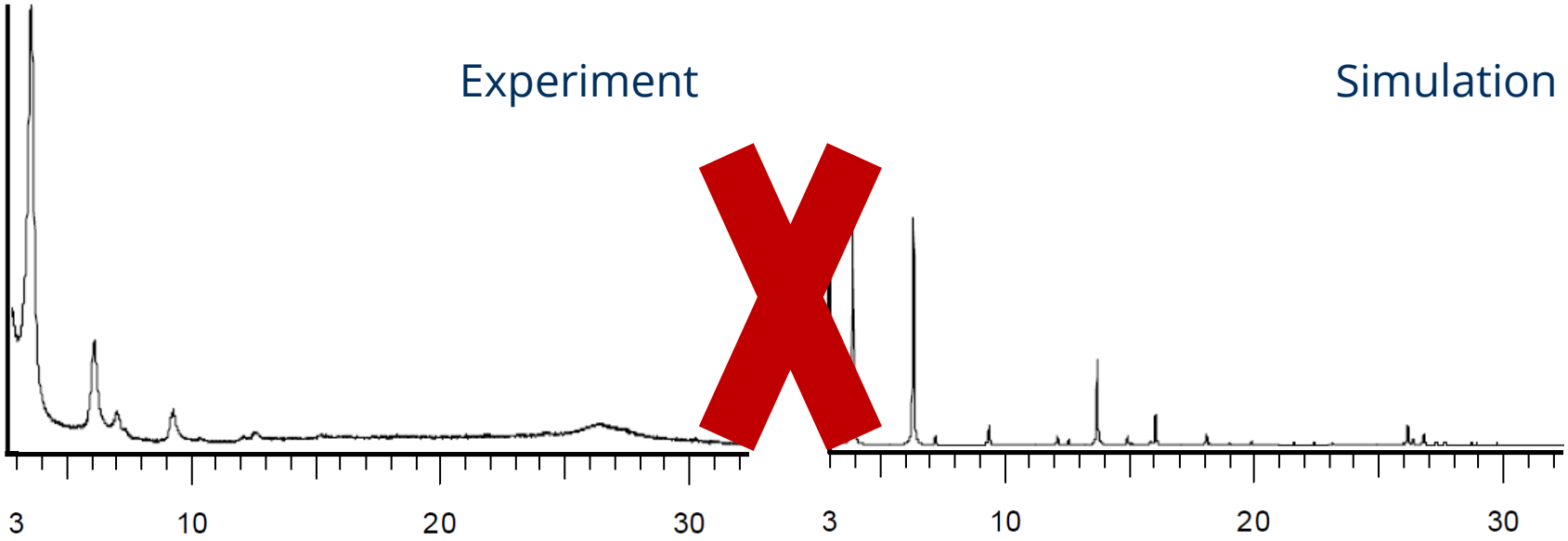


NiPc COF

Lohse, Maria S., and Thomas Bein. *Adv. Funct. Mater.* **2018**, *28*, 1705553
X. Ding, D. Jiang, et al., Angew. Chem., Int. Ed. 2011, 50, 1289
P. Côté, O. M. Yaghi, et al., J. Am. Chem. Soc. 2007, 129, 12914.

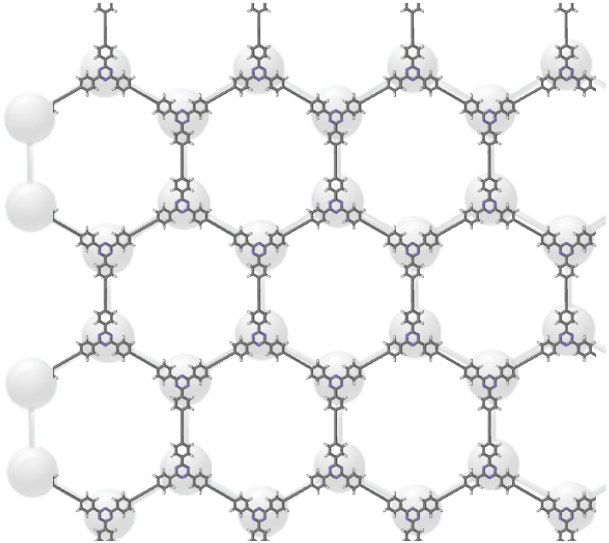
Introduction – PXRD discrepancy

- **A systematic discrepancy** between predicted theoretical and experimental structures of LCOFs.

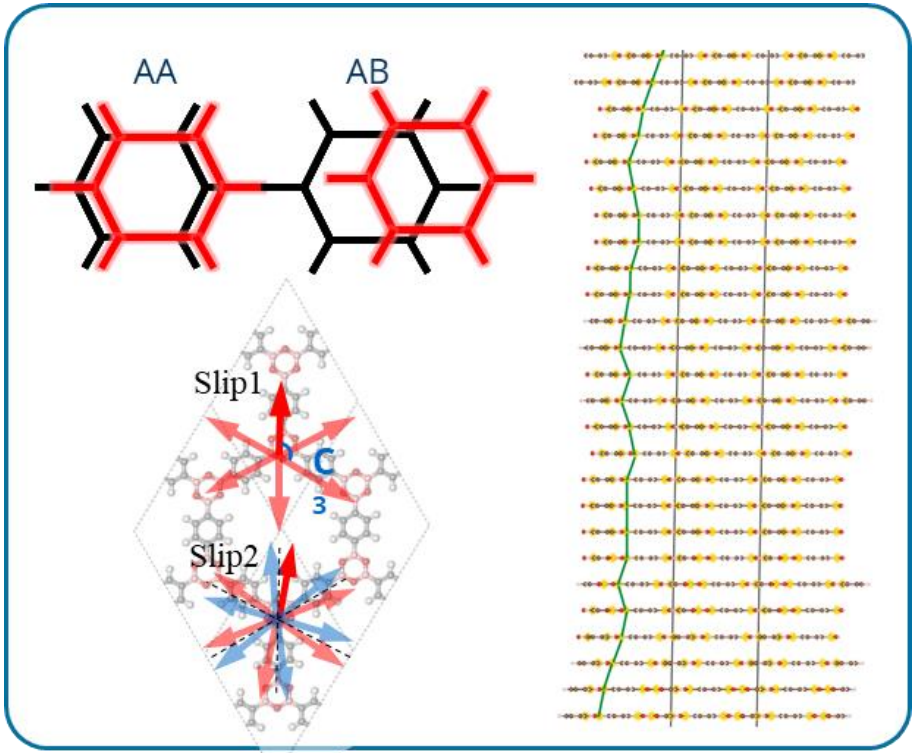


Introduction – disorder along c direction

AA = AA_s



Real structure



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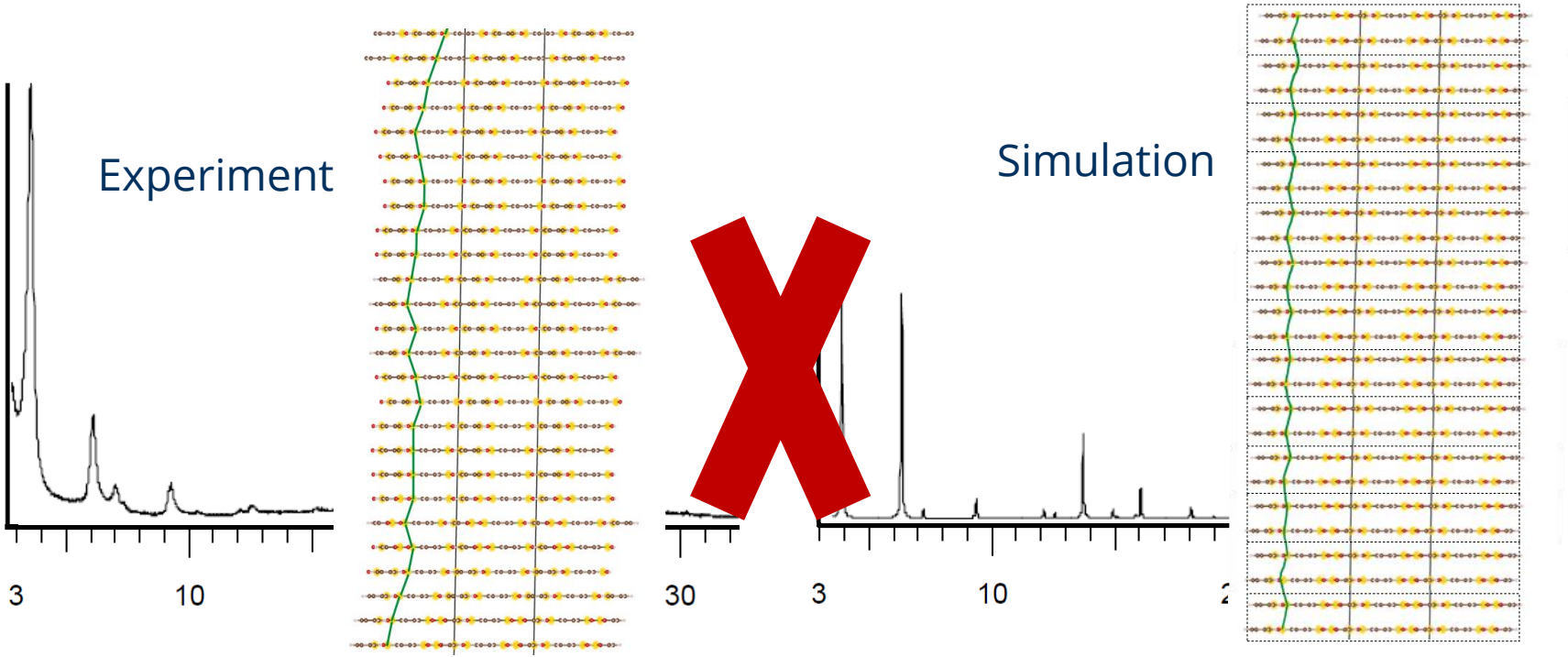
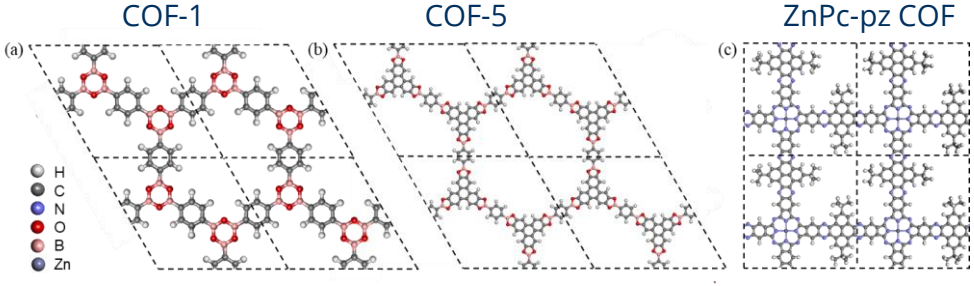


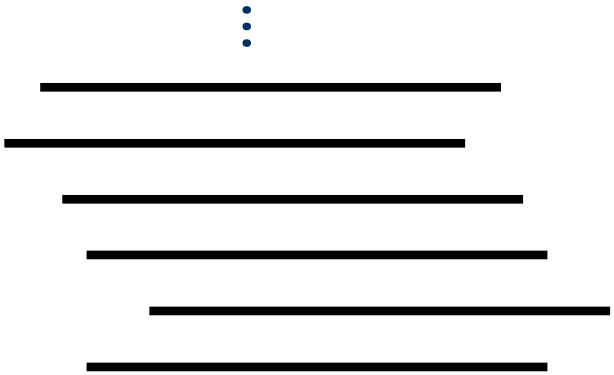
Statistical model

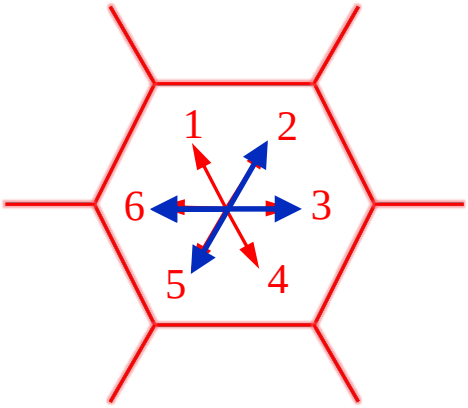
- How the statistical model build:
  - Statistical based on energy

$$\text{Boltzmann}: p = \frac{e^{-\frac{E_i}{kT}}}{\sum e^{-\frac{E_i}{kT}}}$$

- Which structure we studied:
  - COF-1, COF-5, ZnPc-pz COF

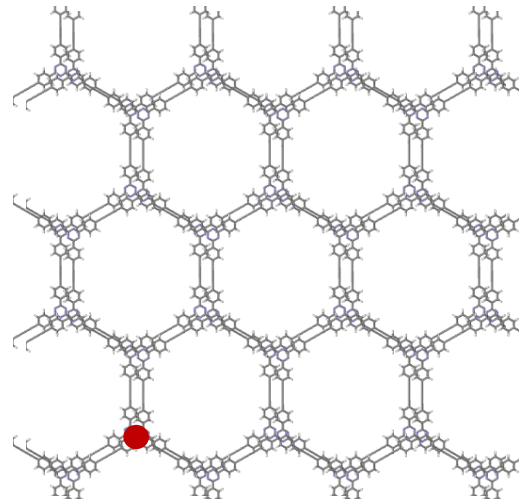




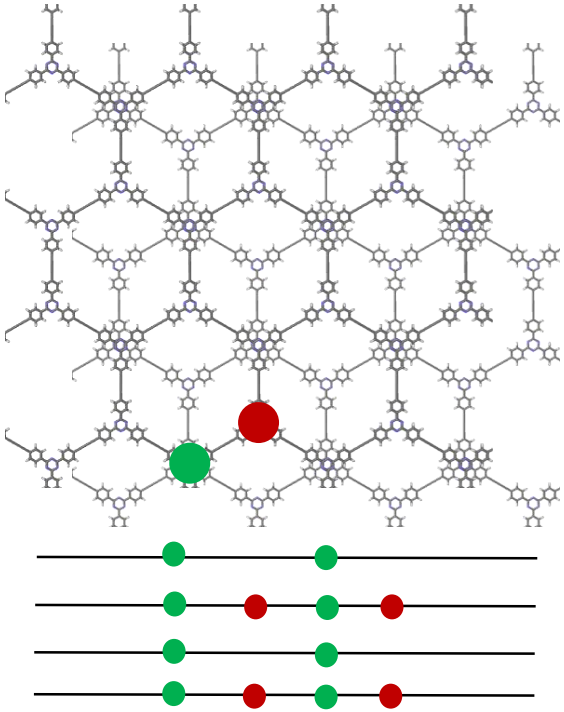


Introduction – stacking modes in hcb lattice

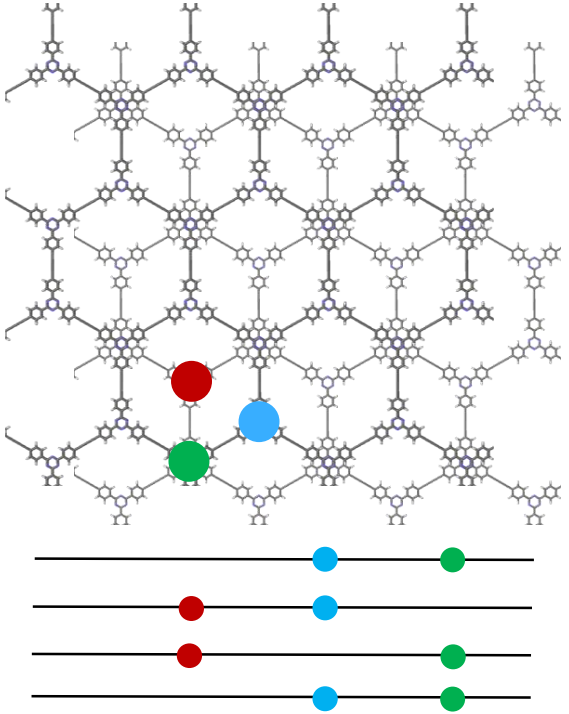
AA (AA_s)



AB (AB_s)



ABC (ABC_s)



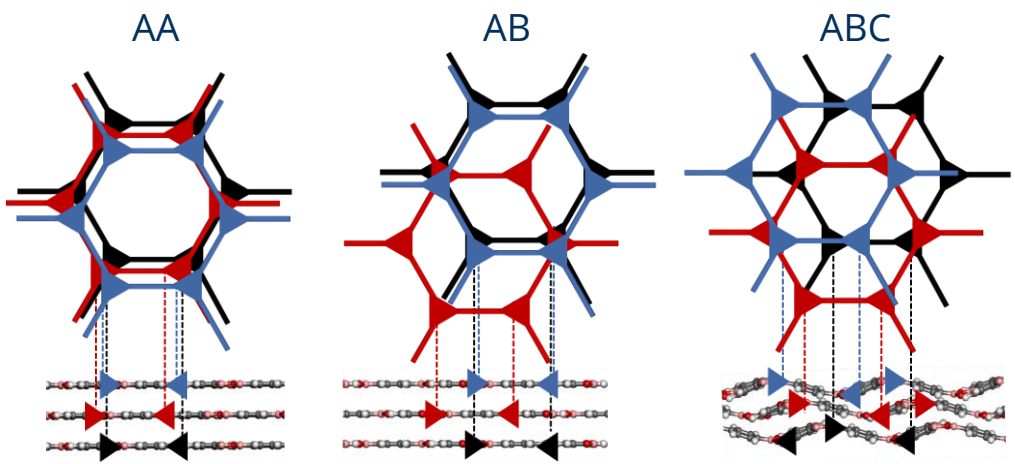
- This shift is present in theoretical structures. Observed experimentally by e.g. Pütz et al.* recently.

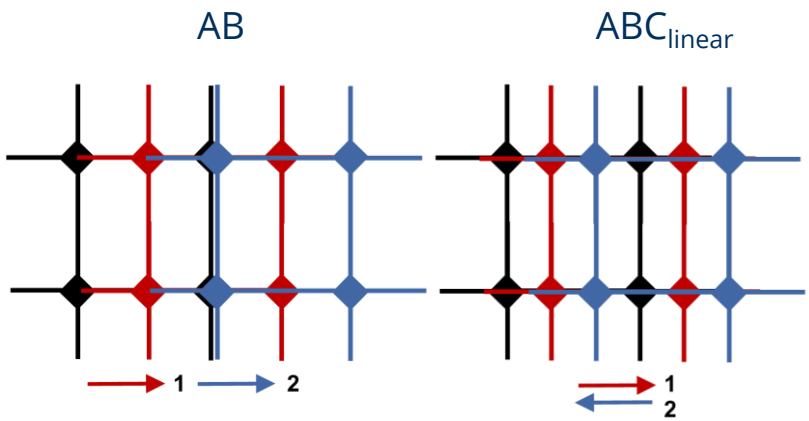
Pütz A. M., Terban M. W., Bette S., et al., Chem. Sci., 2020, 11(47): 12647-12654.

COF stacking modes

Honey-comb	E_{rel}: kJ/mol/BB		Square	E_{rel}: kJ/mol/BB
	COF-1	COF-5		ZnPc-pz COF
AA_{ecl}	35.5	49.1	AA_{slip}	72.4
Aa_{slip}	**5.9**	**0.1**	AB_{diag}	440.2
Ab_{slip}	16.4	98.6	**ABC_{linear}**	**0.0**
ABC_{slip}	**0.0**	**0.0**	ABC_{zigzag}	36.9

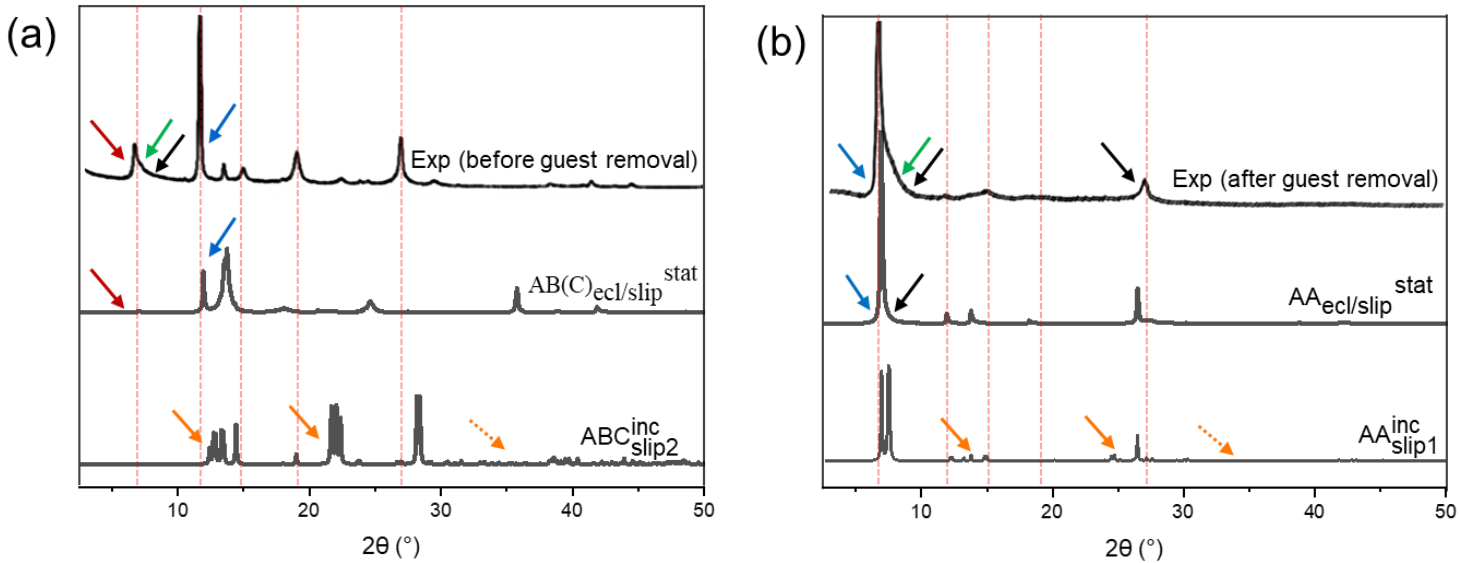
- **ABC can be more stable than AA**
  - Even in materials as COF-1
- Periodic corrugation in ABC stabilizes the structure





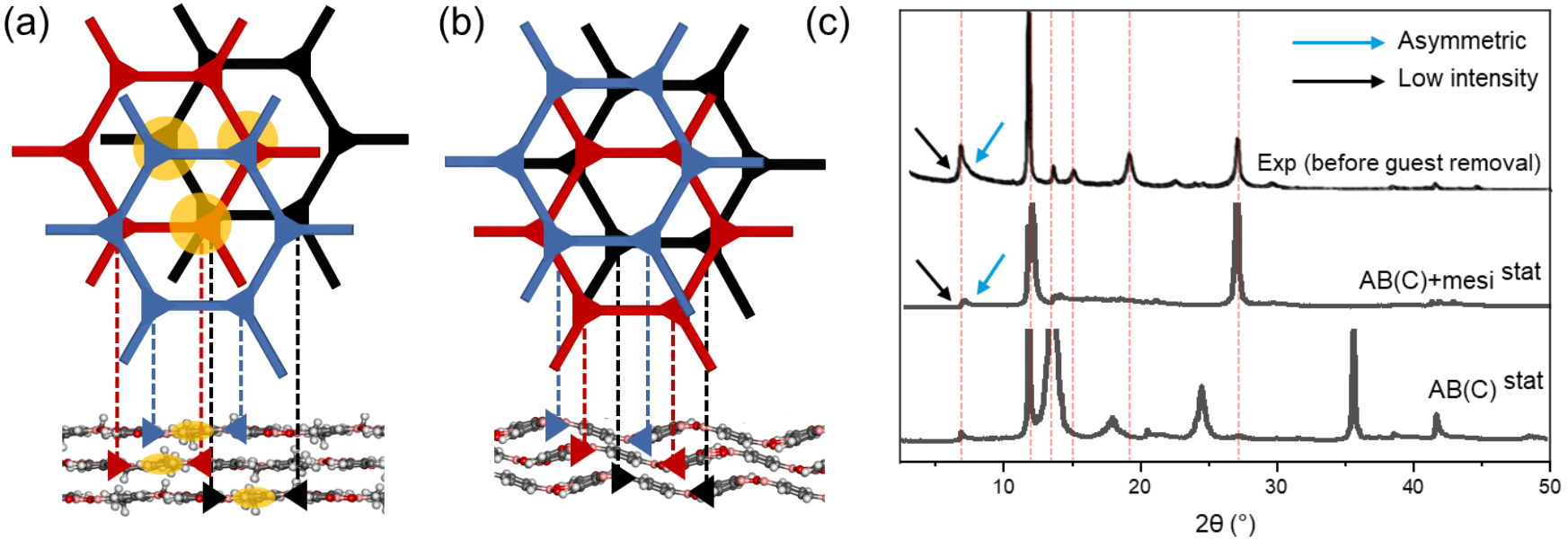
Realistic structure of layered materials
Long range disorder

- COF-1 has totally different stacking behavior before and after guest removal.
- The statistical model improves the PXRD pattern a lot.



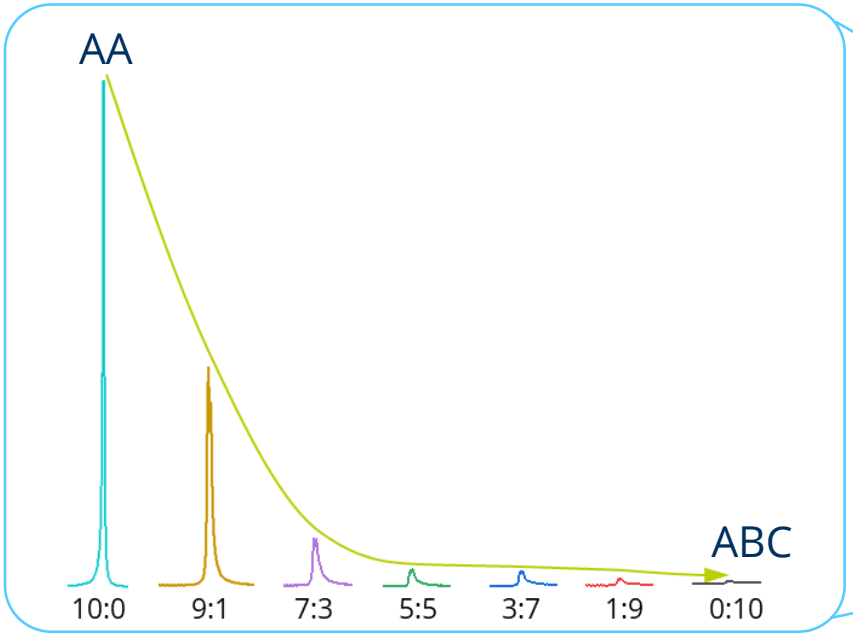
Solvent molecules in ABC

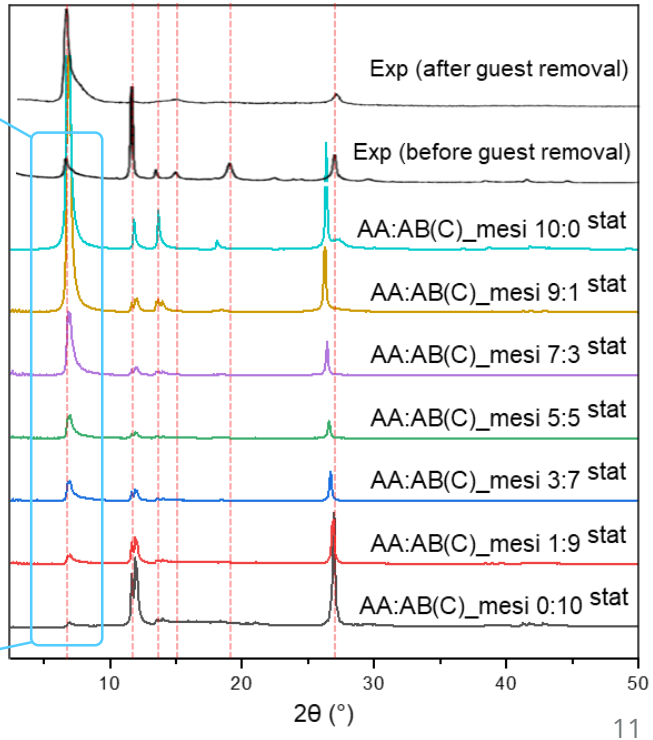
- Mesitylene in COF-1.



Varying probabilities of AA/AB(C)

- During solvent evacuation, structure shifts from ABC to AA in COF-1.
  - They can mix!





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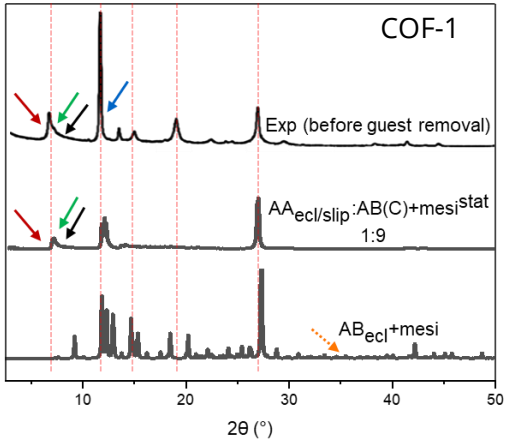
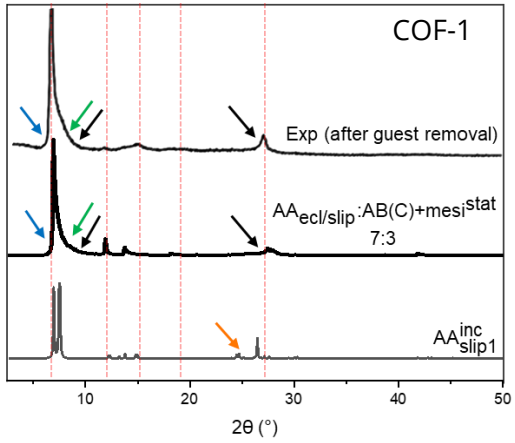
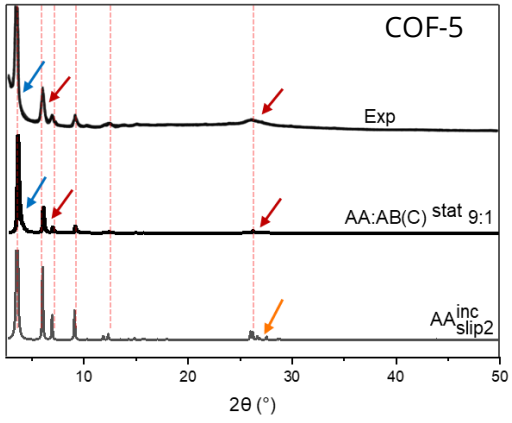
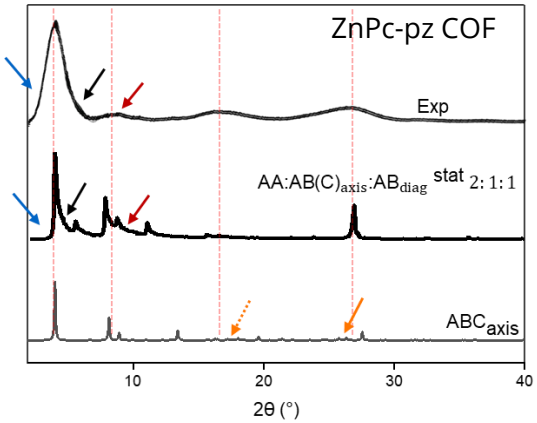








Features in statistical model:
- High intensity
- Low intensity
- Asymmetric
- Broader peak

Features disappeared in statistical model:
- Fine structure
- Small peaks

Summary

COFs are disordered in c direction

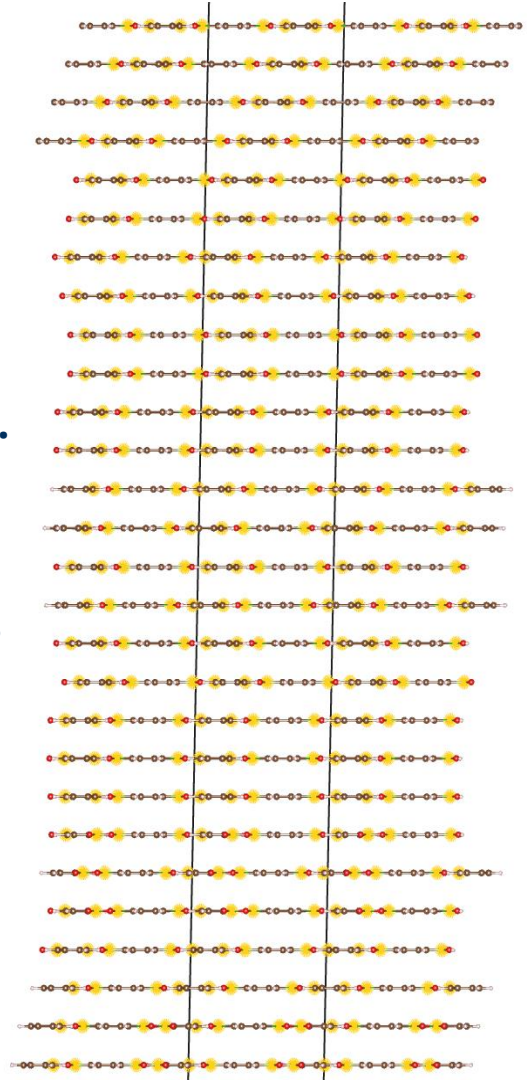
Theoretical structures do **not** have disorder **-> Wrong!**

Statistical model corrects it.

- We **only need standard (bulk) structures and their energies.** Then we just **stack** the layers according to statistics.

Cheap and simple!

- COF structures can be **combinations of more stacking modes**
  - AA+ABC in COF-1.
- The method can be extended to any COFs and MOFs
  - Different characterization - PXRD, TEM, electronics...
  - Can model other types of defects.



Acknowledgements

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