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The influence of stacking on properties of layered COFs

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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

Introduction – PXRD discrepancy

- A **systematic discrepancy** between predicted theoretical and experimental structures of LCOFs.
Introduction – disorder along c direction

Real structure

AA = AA_s
Introduction – PXRD discrepancy

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

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

  Boltzmann: \( p = \frac{e^{-\frac{E_i}{kT}}}{\Sigma e^{-\frac{E_j}{kT}}} \)

- Which structure we studied:
  - COF-1, COF-5, ZnPc-pz COF
This shift is present in theoretical structures. Observed experimentally by e.g. Pütz et al.* recently.

### COF stacking modes

<table>
<thead>
<tr>
<th>Honeycomb</th>
<th>$E_{\text{rel}}$ (kJ/mol/BB)</th>
<th>Square</th>
<th>$E_{\text{rel}}$ (kJ/mol/BB)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>COF-1</td>
<td>COF-5</td>
<td>ZnPc-pz COF</td>
</tr>
<tr>
<td>$A_{\text{ecl}}$</td>
<td>35.5</td>
<td>49.1</td>
<td>$A_{\text{slip}}$</td>
</tr>
<tr>
<td>$A_{\text{aslip}}$</td>
<td>5.9</td>
<td>0.1</td>
<td>$A_{\text{slip}}$</td>
</tr>
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<td>$A_{\text{aslip}}$</td>
<td>16.4</td>
<td>98.6</td>
<td>$A_{\text{slip}}$</td>
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<tr>
<td>$A_{\text{aslip}}$</td>
<td>0.0</td>
<td>0.0</td>
<td>$A_{\text{slip}}$</td>
</tr>
</tbody>
</table>

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

![Diagram of COF stacking modes](image_url)
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!
Realistic structure of layered materials
Long range disorder

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.
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