Developing Covalent Organic Frameworks for Optoelectronic Applications

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Example Covalent Organic Frameworks
Applications of Covalent Organic Frameworks

Characteristics:
- porous & rigid
- regularly shaped
- predictable
- thermally stable
- low density
- mechanically strong
- unreactive
- customizable
- functionalizable

Hydrogen Storage

Catalysis

Gas separation

Optoelectronics
Simulation details

- \( PE = \text{vdW} + \text{electrostatic} \)
- \( \text{vdW}, \) Buckingham potential
- Electrostatic, coulomb potential with ESP-derived charges
- Rotational degrees of freedom ignored
- Two-layer periodic system
- Multiple-layer effects ignored
- \( PE(x_{\text{trans}}, y_{\text{trans}}, z_{\text{trans}}) \) reduced to \( PE(x_{\text{trans}}, y_{\text{trans}}) \)
Symmetry of Frameworks
## Potential energy surfaces

<table>
<thead>
<tr>
<th>B/C</th>
<th>B</th>
<th>TPB</th>
<th>Ph</th>
<th>BP</th>
<th>Py</th>
<th>DPA</th>
<th>DPB</th>
</tr>
</thead>
<tbody>
<tr>
<td>B/C</td>
<td>A</td>
<td>D/E</td>
<td>C/F</td>
<td>B/C</td>
<td>E/F</td>
<td>D/E</td>
<td>C/F</td>
</tr>
</tbody>
</table>

The figure shows potential energy surfaces for different molecular systems, each represented by a unique color scheme. The legend on the left lists the molecules and their abbreviations:

- BRX
- HHB
- HHTP
- DHC
- Pc

The color maps to the right correspond to the sections of the table, where each color indicates a different energy surface or state transition.

### Color Interpretation:
- **A**: High energy state
- **B**: Medium energy state
- **C**: Low energy state
- **D**: Intermediate energy state
- **E**: Transition state
- **F**: Low energy transition state
Density Functional Theory

- Meta-hybrid GGA M06 functional
  - HF and GGA
  - Used to study pi-orbital stacking calculations
  - 6-31G** basis set
Preferred lateral offset trends

- Offsets greater than 1.6 Å
- Pc and HHTP: no dependence of offset on linker length
- DHC and boroxine: greater dependence of offset on linker length
- Why? Atomic density and highly charged COF components
Stacked structure

• Minimized structure involves stacked sheets with an uncorrelated lateral offset between layers
• Large energy barrier at center restricts layers to offset positions
• Offset dictates disorder of minimal energy structures
• Disorder affects charge transport through layers, diffusion of molecules through pores, etc.
Effect of pore structure on filling

- Three hypothetical but representative COF structures: “eclipsed”, “helical”, and “zig-zag”
- Minimize surface diffusion barriers to increase domain size
- High surface diffusion barriers promote clustering and prevent filling
- Surface modification required
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