Understanding and tuning the electronic structure of covalent organic frameworks

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Covalent organic frameworks (COFs) are crystalline, porous materials composed of light elements connected by strong covalent bonds. Their extended π-conjugation and tunable topologies make them promising for electronic and optoelectronic applications. However, understanding and predicting their electronic structure remains challenging due to the interplay between local building block chemistry and extended topology. This challenge is reinforced by the limited number of experimentally realized COFs and the difficulty of synthesizing well-ordered single crystals, which complicates structural characterization.

I will present two recent studies, in which we applied computational methods to rationalize and tune the electronic properties of COFs.

The first part of the talk will focus on how far the electronic structure of a COF can be understood from its molecular building blocks. While fragment-based approaches are well established for metal-organic frameworks, they are harder to apply to COFs, where covalent bonds form a continuous network and electron delocalization is not easily confined to individual subunits. We developed *deCOFpose*, an automated fragmentation algorithm that identifies chemically meaningful units using a set of graph-based rules. Applied to over 300 experimentally reported COFs, this approach enables large-scale analysis of the relationship between fragment frontier orbital energies and full-framework band gaps. The analysis shows that fragment electronic properties alone do not capture the electronic structure of the periodic COF. Improved correlations emerge when the dataset is restricted to chemically similar subsets, highlighting the combined influence of local chemistry and extended topology.[1]

The second part will address how external perturbations can be used to tune the electronic properties of COFs. Using periodic DFT computations, we studied the effects of hydrostatic pressure and metal intercalation on COF-1, a prototypical two-dimensional framework. Compression up to 10 GPa results in a continuous band gap reduction of approximately 1 eV, which is larger than typically observed in other two-dimensional materials. Metal intercalation induces even more pronounced effects, and, in some cases, a transition to metallic behaviour. These findings demonstrate that pressure and intercalation are effective strategies for tuning the electronic structure while preserving the overall framework connectivity.[2]

Together, these studies illustrate different routes toward a deeper understanding and more systematic control of electronic properties in COFs, relevant to their application in electronic, sensing, and energy-related technologies.

[1] Ernst, M., Fedorov, R., Calzolari, A., Grieser, F. F., Ber, S., Gryn'ova, G. (2025). *Preprint: ChemRxiv (doi: 10.26434/chemrxiv-2025-zbc8x)*

[2] Ernst, M., Hutter, J., Battaglia, S. (2025). *Preprint: ChemRxiv (doi: 10.26434/chemrxiv-2025-4vprm)*