# Honeycomb-Kagome Band Structures of Highly Tunable Graphene-Like Covalent Organic Frameworks

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## ABSTRACT

Graphene has transformed the field of materials science since 2004 [1]. Its unique electronic properties encouraged an explosion of research into the electron transport properties of two-dimensional materials. Covalent organic frameworks (COFs) emerged around the same time and were of great interest due to their incredible structural and chemical versatility, as well as permanent porosity and high surface area [2]. As structure determines property, 2D COFs exhibit a range of electron transport behaviors, many of which are present in other 2D materials. One of the most intriguing behaviors is the appearance of topological flat bands and graphene-reminiscent Dirac points at the band edges in $\pi$-conjugated hexagonal 2D COFs resulting from a combined honeycomb-Kagome sub-lattice [3]. It has been demonstrated that these unique band structures can produce topological superconductors, quantum Hall effects, and ferromagnetism [4].

In 2024, the Hoberg and Oliveira groups at the University of Wyoming published a novel synthesis route that used the three-fold Pictet-Spengler reaction to produce a highly $\pi$-conjugated COF from pyranoazacoronene (PAC) nodes [5]. This publication demonstrated the diversity and tunability of PAC COFs with two separate linker molecules (dihydroxyterephthaldehyde and dihydroxynaphthaldehyde) and three functional groups (methoxy, hydroxy, and phenyl rings). The honeycomb-Kagome lattice of these COFs manifests in the band structure (see Figure 1 for an example of a hydrogen functionalized benzene-linked PAC COF), as has been seen in previous works [3].

This study uses extended density functional tight binding to explore the electron transport properties of PAC COFs with 26 functional groups with different electron donating and withdrawing capabilities, combined with six distinct highly-conjugated linkers, two of which are from the original study. The PAC node, molecular precursors for the linkers, and a list of the functional groups are shown in Figure 2. These linkers vary in both conjugation length and conjugation linearity to the node, producing “bent” and “linear” conjugation pathways between pairs of nodes which noticeably impact the band gap. Across the 174 structures, the band gap ranges from 0.4 to 1.9 eV, highlighting the tunability of this series of COFs (the band gap trends across all linkers and functional groups are plotted in Figure 3). The honeycomb-Kagome nature of these band structures is further characterized through spin-orbit coupling calculations and molecular orbital analysis of the molecular precursors.

## ACKNOWLEDGEMENTS

We would like to acknowledge generous support from NSF-DMREF grant #2118592, as well as the University of Wyoming, School of Computing, Graduate Scholars Fellowship. Calculations were performed on the Advanced Research Computing Center, Beartooth and Medicine Bow Computing Environments at the University of Wyoming.

## REFERENCES

[1] K. .S. Novoselov *et al.*, Science **306**, 5751, (2004).
[2] A. P. Côté *et al.*, Science **310** 5696, (2005).
[3] S. Thomas *et al.*, Chem. Mater. **31**, 9, (2019).
[4] Q. Gao *et al.*, Phys. Chem. Chem. Phys. **26**, 3, (2024).
[5] K. Coe-Sessions, A. E. Davies *et al.*, J. Am. Chem. Soc. **146**, 48, (2024).

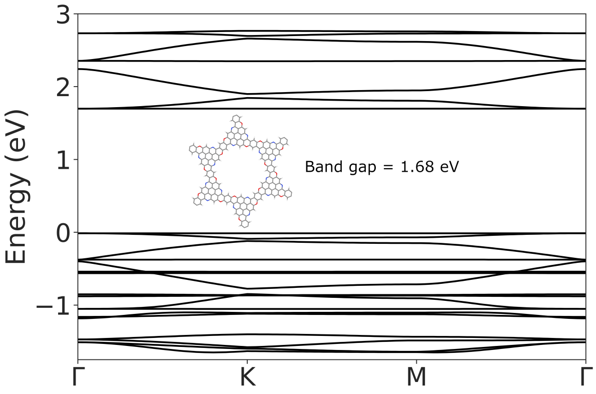

Fig. 1. The hydrogen-functionalized band structure of the benzene-linked PAC COF. The valence and conduction band edges display prominent combined honeycomb-Kagome features, which are present in all of the PACs COFs.

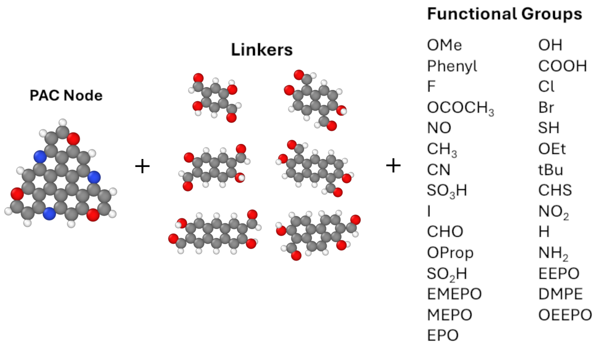

Fig. 2. Molecular precursors showing the generation of PACs COFs, including the PAC node (left column) the selection of six possible conjugated linkers (center column), and 29 functional groups (right column). The functional groups are labeled following the pyCOFBuilder software terminology.

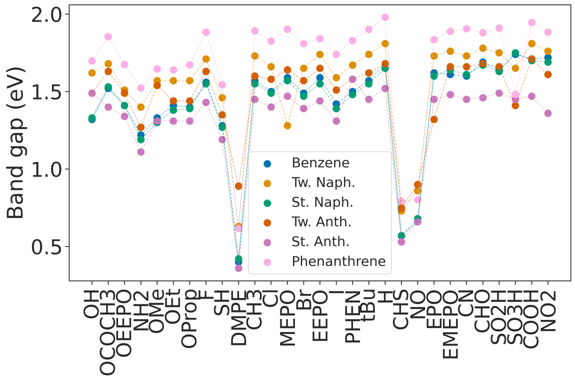

Fig. 3. Band gap trends across all structures with the functional groups labeled in the *x*-axis following the pyCOFBuilder software terminology. Each linker is labeled by a different color, as indicated in the legend.