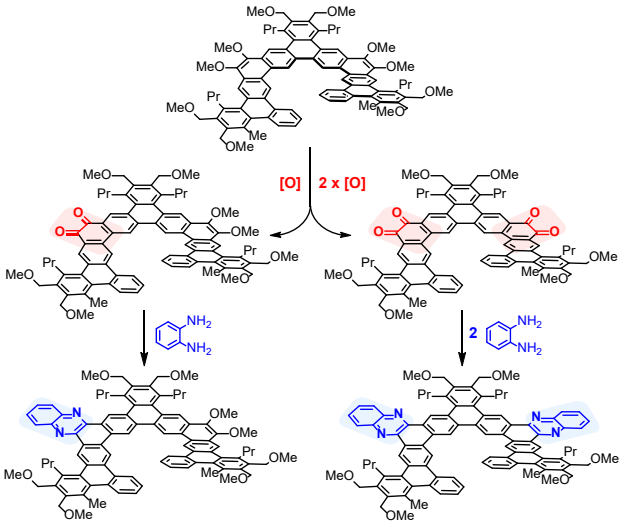
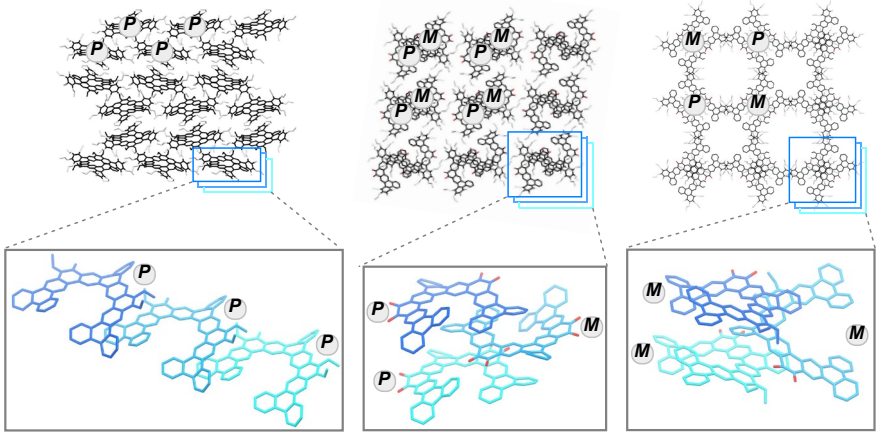
Prof. T. Don Tilley | University of California, Berkeley | NSF grant no. 1708210

Elucidation of Diverse Solid-State Packing in a Family of Electron-Deficient Expanded Helicenes *via* Microcrystal Electron Diffraction

Divergent functionalization of a parent helicene:



Diverse crystal packing elucidated by MicroED:



Samkian, A. E.; Kiel, G. R.; Jones, C. G.; Bergman, H. M.; Oktawiec, J.; Nelson, H. M.; Tilley, T. D. "Elucidation of Diverse Solid-State Packing in a Family of Electron-Deficient Expanded Helicenes via Microcrystal Electron Diffraction" *Angew. Chem. Int. Ed.* **2020**, in press. VIP article. **DOI**: 10.1002/anie.202012213

Project outcome: The Tilley (UCB) and Nelson (UCLA) labs collaborated to synthesize and structurally characterize various polycyclic aromatic hydrocarbons (PAHs) using microelectron diffraction (MicroED). Four new expanded helicenes, incorporating electron-deficient segments that promote intermolecular interactions, were divergently accessed from a parent dimethoxy-substituted helicene. Suitable crystals for single-crystal X-ray diffraction were not available; however, microcrystalline samples were used to obtain high-quality structural data with the newly developed MicroED technique. This data revealed that the PAH functionalities greatly influence packing, with the new compounds featuring homochiral crystals, long-range π-stacking, and nanometer-scale cavities.

Impact and benefits: PAHs and organic materials in general are of intense interest due to their potential for applications in electronic devices. Detailed structural and packing information for such materials is critical to establishing and manipulating key electronic properties. This data has been attainable primarily with single-crystal X-ray crystallography, which limits structural analysis to samples that provide sizable crystals. MicroED promises to offer comparable insight yet allows analysis of nanocrystalline materials, thus greatly increasing the scope of viable samples for structural analysis.

Background and explanation: This work demonstrates selective, oxidative syntheses of expanded helicenes and provides evidence for the potential of MicroED in rapid organic materials characterization. This grant supported two graduate students (coauthors on this paper) and four undergraduates (one coauthor).