Thomas Sullivan
Dr. Christopher Bejger
UNC Charlotte

Organometallic Frameworks from Isocyanide Ligands and Cubane-type Clusters

Thomas Sullivan[1], Timothy Tsung[1], Jonathan Gillen[1], and Christopher Bejger[1*]
[1]University of North Carolina at Charlotte, Department of Chemistry
[*]e-mail: cbejger@charlotte.edu

Keywords: Metal-Sulfur Clusters, Redox-Active, Conductive, Metal-Organic Frameworks, Coordination Polymers

Abstract:

Metal-organic frameworks (MOFs), or porous coordination polymers, have outstanding potential to serve as catalytic-, energy-carrier-gas-storing-, electrode-, solid-state electrolyte-, and related materials to address the dire need to shift from traditional, environmentally costly forms of energy generation, transfer, and storage to more efficient, cleaner means for a sustainable future, but elucidating and optimizing the redox-conductive nature of these structures is essential before much of their promise can be seen to fruition. Metal-sulfur clusters have garnered significant recent attention for their delocalized electron density and structural tunability which promote their ability to serve as stable building nodes, and to greatly enhance redox-conductivity, in MOFs.[1,2] Described herein is an investigation into the feasibility of using M_4S_4 clusters as preformed nodes in combination with isocyanide ligands as framework linkers. Reported is a strategy of ligand-exchange reactions with clusters of cubane-type core geometry as precursors. Several monotopic aryl isocyanide ligands – e.g., 2,6-dimethylphenyl isocyanide ("CNXyl") and 2,6-diisopropylphenyl isocyanide ("CNDipp"), and several sterically bulky *m*-terphenyl isocyanides ("CNAr$^{\text{dmp2}}$" and "CNAr$^{\text{d}t\text{Bup2}}$" and "CNAr$^{\text{tipp2}}$") – are screened in efforts to maintain the cubane-type geometry. Syntheses of resulting novel discrete clusters, featuring unique core nuclearities, are described. Ongoing efforts to synthetically optimize and characterize crystalline polymers initiated from these discrete clusters and ditopic isocyanide linkers, via modulation with the monotopic analogues of the linkers, and by other variations, are additionally presented. The clusters and a proposed framework – the latter employing 4,4'-diisocyano-3,3',5,5'-tetramethylbiphenyl (BXylDI) as the specific linker – are analyzed via single-crystal and/or powder X-ray diffraction (scXRD/pXRD), and by nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), cyclic voltammetry (CV), and conductivity measurements. Continuing collaborative endeavors to further validate structures and properties of the novel materials by continuous-rotation 3-dimensional electron diffraction (3D-ED) and superconducting quantum interference device (SQUID) magnetometry are also presented.

This work was supported by the National Science Foundation (No. DMR-2045390).

References:

[1] Xie, J.; Wang, L.; Anderson, J.S. "Heavy chalcogenide-transition metal clusters as coordination polymer nodes." *Chem. Sci.*, **11**, 8350 (2020). DOI: 10.1039/d0sc03429k.
[2] Gillen, J.H.; Vuong, M.K.; Paley, D.W.; Bejger, C.M. "Conductive Organometallic Polymers from Soluble Superatom Ions." *ACS Mater. Lett.*, **7(10)**, 3363-3369 (2025). DOI: 10.1021/acsmaterialslett.5c00925.