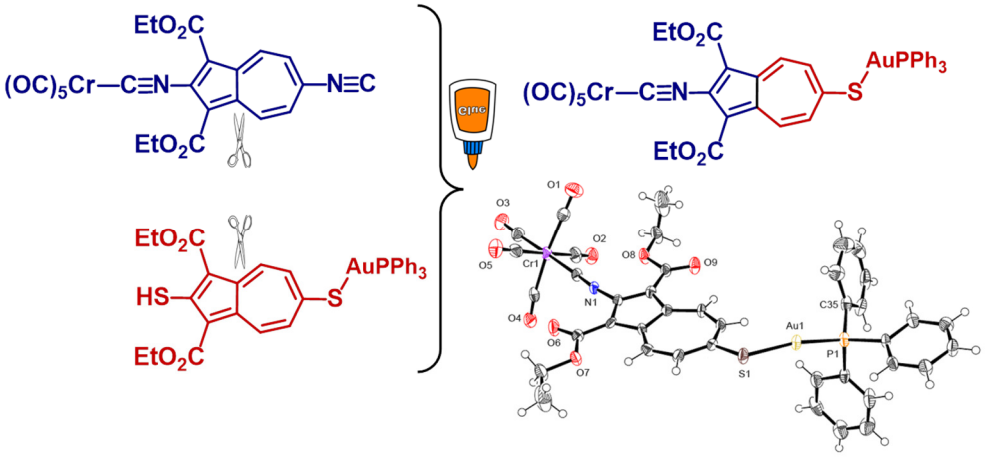
Azulene-based organometallics relevant to molecular and optoelectronics

Substances incorporating the azulenic motif (a nonbenzenoid aromatic framework involving fused 5- and 7-membered carbon rings) have been gaining increasing interest in the design of advanced functional materials for applications in molecular and optoelectronics. Because of its remarkably low aromatic delocalization energy and asymmetric current/voltage characteristics, the azulenic moiety is particularly attractive as a charge transport mediator on the molecular scale and as a critical component in molecular switching systems. In the past few years, the Barybin group has pioneered design of several azulenic linkers and demonstrated their electronic superiority compared to the corresponding benzenoid bridges. In his/her 2017 REU project, the participant will engage in synthetic design of a linear π-linker containing multiple azulenic units connected along their molecular axes. The student will then work on experimental assessment of its electron delocalization capabilities within novel metal-organic frameworks. The single crystal X-ray structure of the first aromatic π-linker featuring mercapto and isocyano junctions within the same molecule is illustrated below. The NSF-REU participant will acquire experience in organic, coordination, and organometallic syntheses (including air-free manipulations) and learn the basics of operation and data interpretation associated with many techniques such as electrochemistry, multinuclear NMR, EPR, FTIR, electronic spectroscopy, X-ray crystallography, and magnetic measurements.



Relevant references

1. Applegate, J. C.; Okeowo, M. K.; Erickson, N. R.; Neal, B. M.; Berrie, C. L.; Gerasimchuk, N. N.; Barybin, M. V. "First π-linker featuring mercapto and isocyano anchoring groups within the same molecule: Synthesis, heterobimetallic complexation and self-assembly on Au(111)," *Chemical Science* **2016**, *7*, 1422-1429.
2. Scheetz, K. J.; Spaeth, A. D.; Vorushilov, A. S.; Powell, D. R.; Day, V. W.; Barybin, M. V. "The 2,6-Dimercaptoazulene motif: Efficient synthesis and completely regioselective metallation of its 6-mercapto terminus," *Chemical Science* **2013**, *4*, 4267-4272.
3. Maher, T. R.; Spaeth, A. D.; Neal, B. M.; Berrie, C. L.; Thompson, W. H.; Day, V. W.; Barybin, M. V. "Linear 6,6'-Biazulenyl Framework Featuring Isocyanide Termini: Synthesis, Structure, Redox Behavior, Complexation, and Self-assembly on Gold(111)," *Journal of the American Chemical Society* **2010,** *132*, 15924-15926.