Design of a linear 6,6' biazulenic π-linker terminated with mercapto junctions

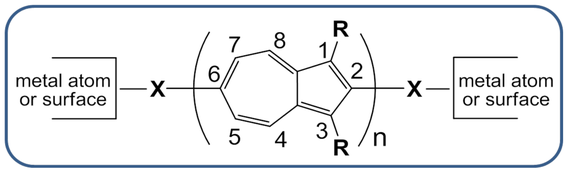
Lauren Feden, Jason C. Applegate, Mikhail V. Barybin*

Department of Chemistry, The University of Kansas

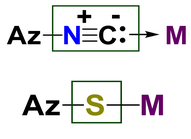
Abstract

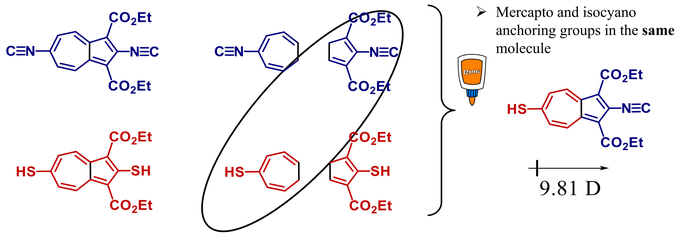
Azulene is a nonbenzenoid isomer of naphthalene, $C_{10}H_8$. Its scaffold is composed of fused 5- and 7-membered sp^2-carbon rings. Linearly terminated azulenic and oligoazulenic molecular linkers have been of increasing theoretical and experimental interest in the design of functional materials for applications in molecular and optoelectronics. We have recently established coordination and surface chemistry of 6,6'-biaazulenic π-linkers linearly terminated with two isocyano (–NC) or an isocyano and a mercapto (-SH) groups at the 2 and 2' positions of the biaazulenyl framework. This poster will introduce the first example of a 2,2'-dimercapto-functionalized 6,6-biazulene derivative. An efficient synthesis, spectroscopic characterization, and electrochemical profile of this novel molecular linker will be discussed in detail. Initial reactivity studies of this 2,2'-dimercapto-6,6'-biazulene bridge toward formation of bimetallic coordination complexes with Au(I) metal centers will be highlighted as well.

Di-isocyano and isocyano/thiolate terminated azulenic π-linkers



Barybin *et al. JACS* **2006**, *128*, 2300





- Mercapto and isocyano anchoring groups in the **same** molecule

Barybin *et al. Chem. Sci.* **2013**, *4*, 4267

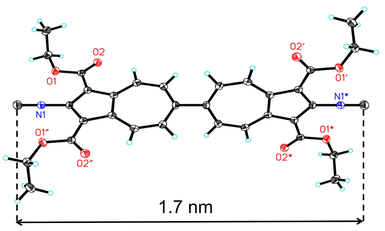
Applegate, J. C. *et al. Chem. Sci.* **2016**, *7*, 1422

2,2'-Diisocyano-1,1',3,3'-tetraethoxycarbonyl-6,6'-biazulene π-linker

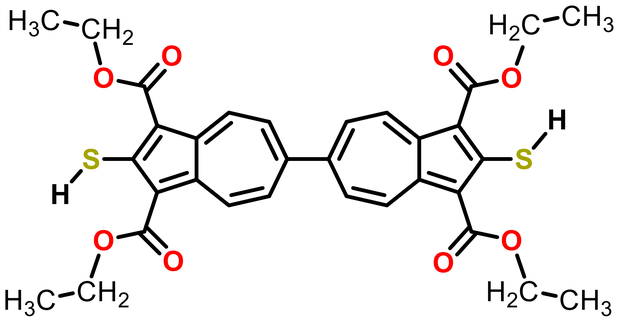
Synthesis, homobimetallic complexation, and monolayer self-assembly on Au(111):
Barybin, M. V. *et al. JACS* **2010,** *132*, 15924

Quasi-molecular rectifier:
Chen, Y. *et al. J. Mat. Chem. C.* **2017**, *5*, 2223 ACIE

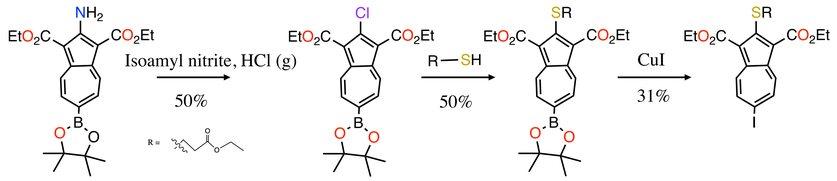
On-chip micro-supercapacitors:
Zhuang, X.; Cánovas, E.; Feng, X. *et al. ACIE* **2017,** *56,* 3920

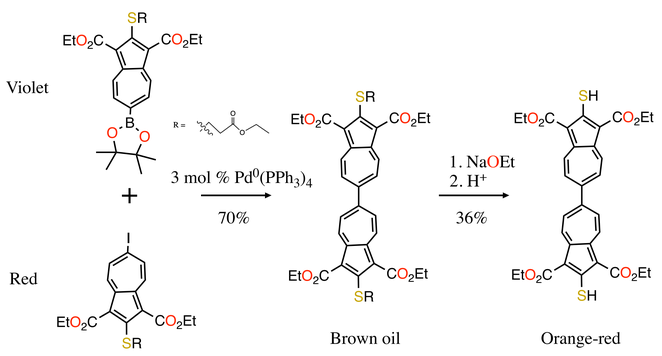


Project Goal

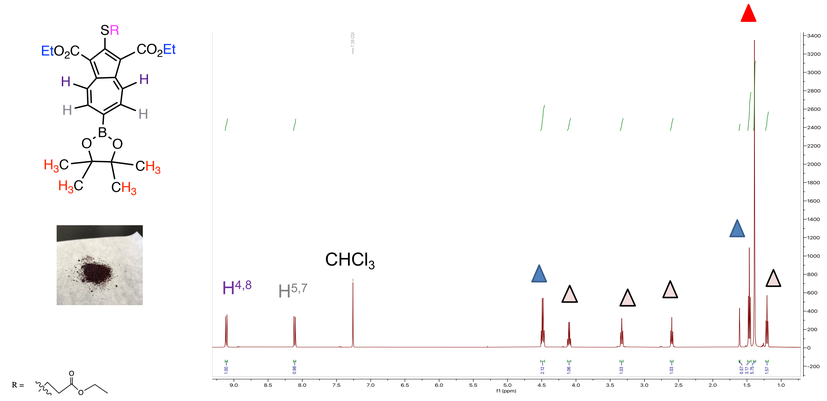


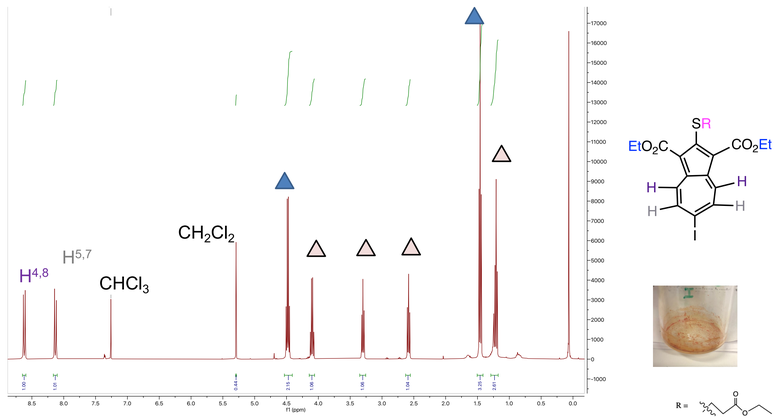
Synthesis of 2,2'-dimercapto-6,6'-biazulene



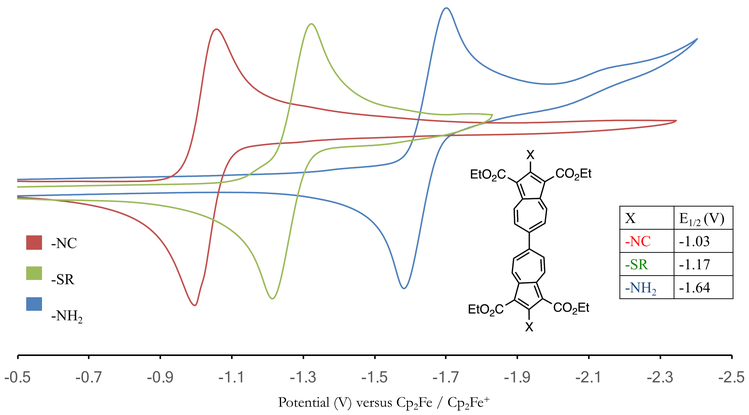


^{1}H NMR spectra of the partners for Suzuki-Miyaura cross-coupling



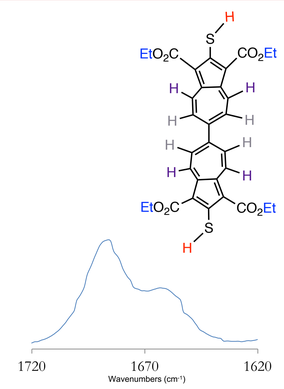


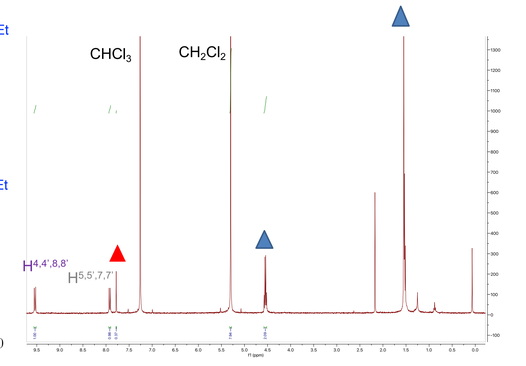
Cyclic voltammetry in CH_2Cl_2 / $^nBu_4N^+PF_6^-$ at 25 °C



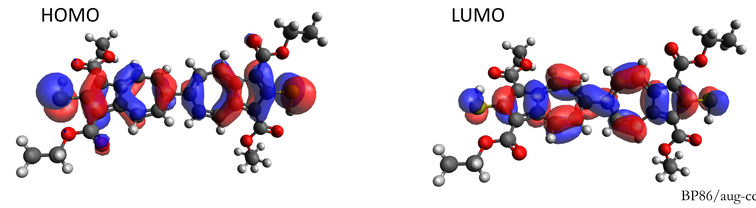
X	$E_{1/2}$ (V)
-NC	-1.03
-SR	-1.17
$-NH_2$	-1.64

De-protection of the S-termini (^{1}H NMR and FTIR characterization)





DFT-calculated orbital density plots for the frontier molecular orbitals



Conclusions

- Synthesis of the hitherto unknown 6,6'- biazulenic linker featuring mercapto-termini at both ends has been accomplished by the installation of the protected mercapto termini prior to the suzuki-miyaura coupling of the monoazulenic components.
- Similar to other 2,2'-functionalized 6,6'-biazulenes, the new linker exhibits reversible 2-e$^-$ redox behavior.
- Future work will involve anchoring of the 2.2'-dimercapto-6,6'-biazulene linker to electron-rich metal atoms and/or surfaces to probe electron delocalization across the biazulenic bridge.

Acknowledgements

BARYBIN GROUP
UNIVERSITY OF KANSAS

KU DEPARTMENT OF CHEMISTRY
College of Liberal Arts & Sciences

CHE-1808120
MSN Program

CHE-1560279
NSF REU – Chemistry
KU Site