Structural chemistry of azulenes

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Azulene is a dark-blue, polar, bicyclic aromatic hydrocarbon (Figure 1) that is a non-benzenoid isomer of naphthalene. In addition to its long-standing medicinal and pharmaceutical relevance, the polar nonbenzenoid aromatic framework of azulene constitutes an attractive building block in the design of redox-addressable, optoelectronic, and conductive materials. This presentation will highlight our recent developments in the chemistry of hybrid metal/azulene platforms featuring isocyanide and thiolate junctions **X** along their molecular axis (Figure 2).

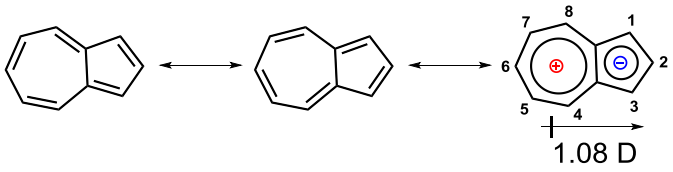

Figure 1. Electronic structure of azulene: resonance forms and origin of a molecular dipole.

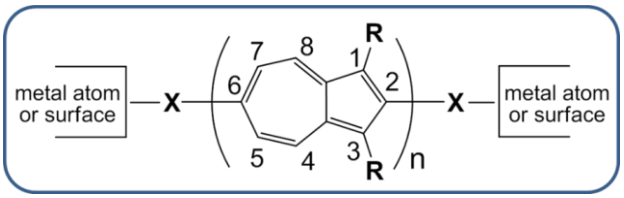

Figure 2. Two ways of functionalization of azulene at 2- and 6- positions that are important for its fixation on a solid support.

Single crystal X-ray structural analysis of a series of novel 2,6-functionalized azulenes will be presented [1,2]. In particular, heterobimetallic ensembles that incorporate the first examples of a conjugated π-bridge equipped with both isocyanide and thiol junction groups in the same molecular linker will be discussed (e.g., Figure 3B).

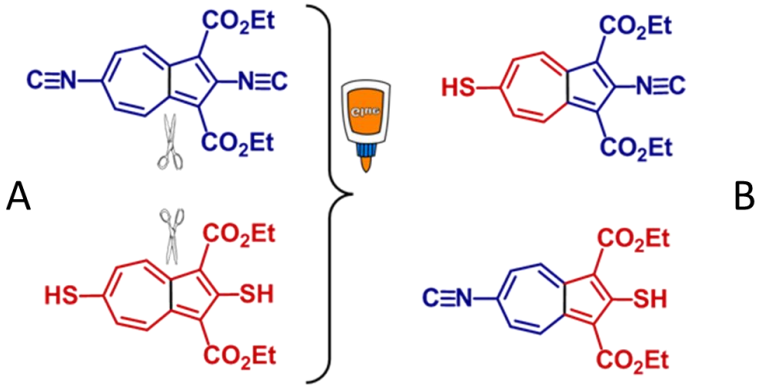

Figure 3. Two different functional groups – isonitrile and thiol – used for chemical modification of azulenes.

[1] Applegate, J.C.; Okeowo, M.K.; Erickson, N.R.; Neal, B.M.; Berrie, C.L.; Gerasimchuk, N.N.; Barybin, M.V. (2016) *Chem. Sci*., **7**, 1422–1429.

[2] Hart, M.D.; Meyers, J.J.; Wood, Z.A.; Nakakita, T.; Applegate, J.C.; Erickson, N.R.; Gerasimchuk, N.N.; Barybin, M.V. (2021). *Molecules,* **26**, 981. https://doi.org/10.3390/molecules26040981

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