Redox-Switchable Aromaticity in a Helically Extended Indeno[2,1-c]fluorene

E. Sidler, R. Hein, D. Doellerer, Ben L. Feringa*

University of Groningen, Stratingh Institute for Chemistry,
Nijenborgh 4, Groningen, The Netherlands

*E-mail: e.c.sidler@rug.nl

Antiaromaticity is a fascinating property that has attracted not only significant fundamental interest but is also increasingly relevant in different applications, in particular organic (opto)electronics. However, designing systems in which (anti)aromaticity can be judiciously and reversibly switched ON and OFF remains challenging. Herein, we report a helicene featuring an indenofluorene¹-bridged bisthioxanthylidene² as a novel switch wherein a simultaneous two-electron (electro)chemical redox process allows highly reversible modulation of its (anti)aromatic character. Specifically, the two thioxanthylidene rotors, attached to the initially aromatic indenofluorene scaffold via overcrowded alkenes, adopt an anti-folded structure, which upon oxidation convert to singly bonded, twisted conformations. This is not only associated with significant (chir)optical changes but importantly also results in formation of the fully conjugated, formally antiaromatic as-indacene motif in the helical core of the switch. This process proceeds without the formation of radical cation intermediates and thus enables highly reversible switching of molecular geometry, aromaticity, absorbance and chiral expression under ambient conditions.

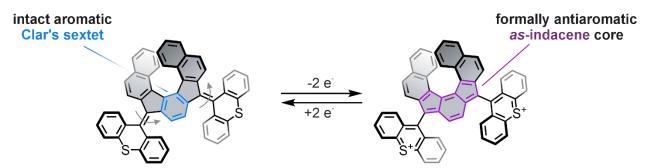


Figure 1: General redox switching scheme of the extended helically chiral indeno[2,1-c]fluorene.

References:

- [1] C. K. Frederickson, B. D. Rose, M. M. Haley, Acc. Chem. Res. 2017, 50, 977–978.
- [2] M. B. S. Wonink, B. P. Corbet, A. A. Kulago, G. B. Boursalian, B. de Bruin, E. Otten, W. R. Browne, B. L. Feringa, J. Am. Chem. Soc. 2021, 143, 18020–18028.