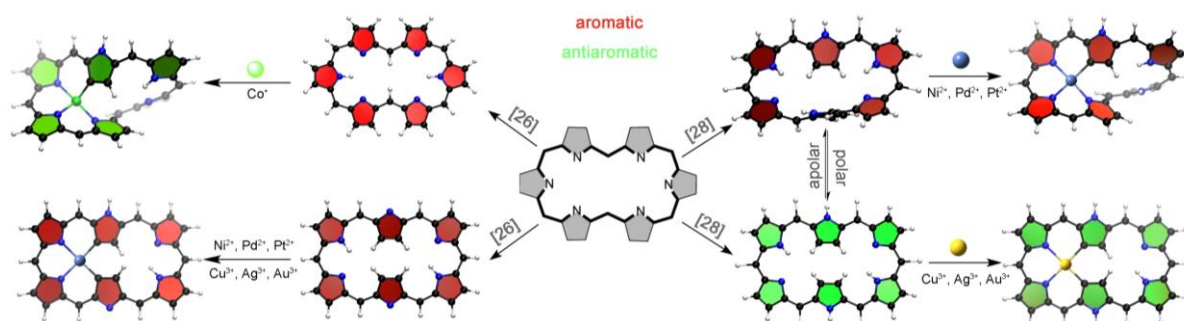


Hückel vs Möbius Aromaticity in Expanded Porphyrins

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The concept of Möbius aromaticity predicts aromatic nature for $[4n]$ annulenes lying on a twisted Möbius strip. Despite numerous synthetic attempts, the first singly twisted Möbius annulene was not prepared until 2003. Recently, expanded porphyrins have emerged as the most promising platform for realizing stable Möbius aromatic molecules aided by metal coordination, solvent or protonation. Besides the Möbius topology, these large macrocycles can adopt a variety of conformations with Hückel and twisted-Hückel topologies encoding different aromaticity and nonlinear properties. In our work, the conformational preferences and aromaticity of several expanded porphyrins, varying in ring sizes and oxidation states, have been elucidated through quantum chemical calculations.¹ We proposed a set of aromaticity descriptors to quantify Hückel and Möbius aromaticity in porphyrinoids based on energetic, structural, magnetic and reactivity criteria. By using these descriptors, the structure-property relationships between the molecular conformation, the number of π -electrons and aromaticity was established and the optimum conditions for viable Möbius expanded porphyrins were determined for penta-, hexa- and heptaphyrins.² Then, the metalation effect on the molecular topology and aromaticity of hexaphyrins was thoroughly investigated.³ Our findings offer a new perspective to rationalize the experimental observations about expanded porphyrins and the proposed guidelines could be useful to design novel structures of expanded porphyrins.



1. Alonso, M.; Geerlings, P.; De Proft, F. *Chem. Eur. J.* **2012**, *18*, 10916; *Chem. Eur. J.* **2013**, *19*, 1617.
2. Alonso, M.; Geerlings, P.; De Proft, F. *Phys. Chem. Chem. Phys.* **2014**, *16*, 14396.
3. Alonso, M.; Balazs, P.; Geerlings, P.; De Proft, F. **2015** *submitted*.