Conjugated π-systems and how to describe them

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This talk will discuss the electronic structure of various π-conjugated systems in terms of simple (tight-binding) models. We will explore the relationship between aromaticity, coherence, and electronic structure, using cyclocarbons, annulenes, and porphyrin nanorings as examples.

Cyclo[*n*]carbons (Fig. 1a) are loops of *n* carbon atoms. Recent advances in scanning probe microscopy (SPM) have enabled the on-surface synthesis and characterisation of these unusual molecular carbon allotropes, which have long served as a playground for theoretical approaches [1,2]. We will compare SPM resonance images with high-level ab initio calculations, showing that the electronic structure of cyclocarbons can be captured by a particle-on-a-ring model.

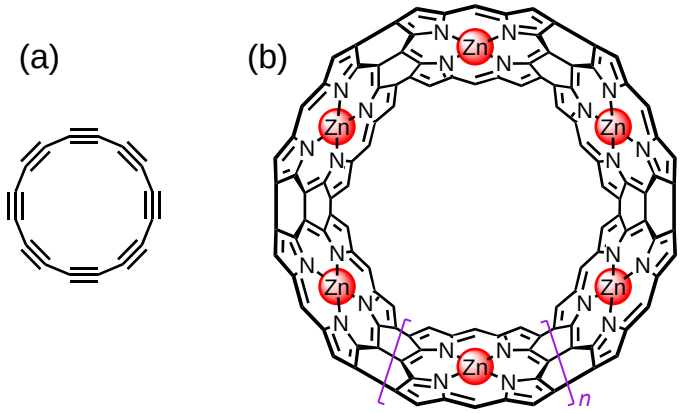

Figure 1. (a) Cyclo[16]carbon. (b) Edge-fused porphyrin nanoring.

Conjugated porphyrin nanostructures (Fig. 1b) display remarkable properties such as quantum interference and length-independent conductance, which make them excellent candidates for molecular electronics [3]. These properties stem from the coherent delocalisation of the wavefunction through the whole molecule, which becomes weaker as the molecule become larger. By analysing the ways in which π-systems can distort, we will estimate the maximum size at which edge-fused porphyrin nanorings (Fig. 1b) can still be expected to exhibit quantum behaviour [4].

References:

[1] I. Rončević, F. J. Leslie, M. Rossmannek, I. Tavernelli, L. Gross, H. L. Anderson, *J. Am. Chem. Soc.* **145** (2023) 26962-26972.

[2] F. Albrecht, I. Rončević, Y. Gao, F. Paschke, A. Baiardi, I. Tavernelli, S. Mishra, H. L. Anderson, L. Gross, *Science* **384** (2024) 677-682.

[3] J.-R. Deng, M. T. González, H. Zhu, E. Leary, *J. Am. Chem. Soc.* **146** (2024) 3651-3659.

[4] M. Vitek, J.-R. Deng, H. L. Anderson, I. Rončević, *ACS Nano* 19 (2024) 1405-1411.