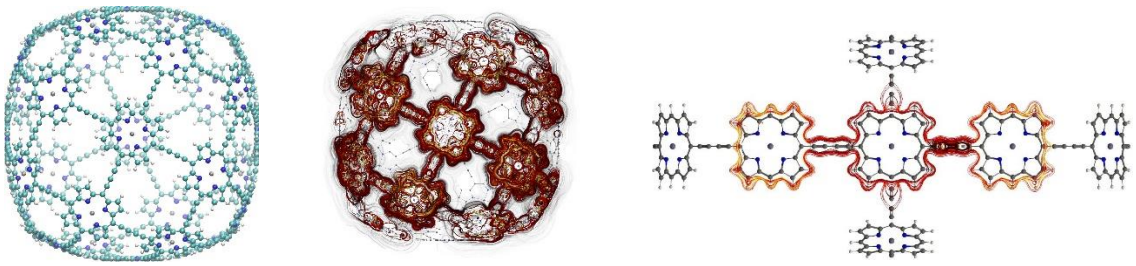
Induced current densities in porphyrin nanostructures

Atif Mahmood, Maria Dimirova, Lukas N. Wirz, Dage Sundholm

Department of Chemistry, Faculty of Science, A.I. Virtasen aukio 1, POB 55, FI-00014 University of Helsinki, Finland

Magnetically induced current densities (MICD) of Zn-porphyrinoid nanostructures have been studied at the density functional theory (DFT) level using the B3LYP functional. Six of the studied Zn-porphyrinoid naostructures consist of two crossing porphyrinoid belts and one is porphyrinoid nanoball belonging to the octahedral (O) point group. The Zn-porphyrin units are connected to each other via butadiyne linkers as in a recently synthesized porphyrinoid cross-belt structure.[1,2] We have also studied a nanotube and a nanocylinder with the neighbors connected via ethyne bridges at their meso carbon atoms.[3,4] A clam-like molecule has porphyrin units connected on one side via butadiyne linkers and on the other side they is fused. The MICDs are calculated using the gauge-including magnetically induced currents (GIMIC) method.[5,6] Current-density pathways and their strengths were determined by numerically integrating the MICD passing through selected planes that cut chemical bonds or molecular rings. The current-density calculations of the cross-belts and the nanoball show that they are globally non-aromatic but locally aromatic sustaining ring currents in the individual porphyrin rings. The ring-current strengths of the individual porphyrin rings are 20% weaker than in Zn porphyrin, whereas oxidation leads to globally aromatic cations sustaining ring currents that are somewhat stronger than for Zn porphyrin. Calculations of the current densities show that there is a paratropic ring current around the nanotube, whereas sealing the ends leads to an almost non-aromatic nanotube. Fusing porphyrinoids as in the fully fused clam-shell molecule results in complicated current-density pathways that differ from the ones usually appearing in porphyrinoids. The neutral fused molecule is antiaromatic, whereas the dication is non-aromatic.



The magnetically induced current density in the nanoball and in a cross-belt porphyrinoid structure.

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