

Electronic Coupling in Metalloporphyrin Oligomers

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Research Experiences for Undergraduates

Electron transfer plays an important role in many areas of biology and material science. It functions as both the driving force for photosynthesis as well as the leading edge technology for designing nano-scale transistors. Porphyrins are ubiquitous in biology serving important roles in electron transfer. Our group designs, synthesizes, and probes metalloporphyrin oligomers in order to understand how changes in the metal, porphyrin, and ligands affect the electronic structure of the oligomer.

Undergraduate student Amanda Hickman (HMC) synthesized a variety of cofacial porphyrin dimers. Both ruthenium and osmium porphyrins with different ligands and porphyrins were studied. The oligomers were characterized by ultraviolet, visible, and near infrared spectroscopy as well as nuclear magnetic resonance spectroscopy, and then oxidized to identify the intervalence charge transfer band. This band was used to calculate the coupling (or ability to move charge across the molecule).

Based on empirical studies as well as theoretical work completed by the Cave group (HMC), we determined that the coupling in cofacial dimers depends mostly on the proximity of the porphyrins whereby electron transfer occurs across overlapping orbitals of mainly porphyrin character. No significant changes in coupling were observed by changing the capping ligand.

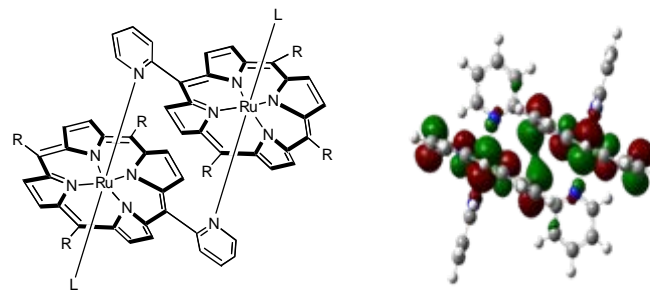


Figure 1. Ruthenium porphyrin cofacial dimer: left) schematic of a generic ruthenium cofacial dimer where L can be CO, pyridine, etc. and R can be phenyl or other aryl substituents, bottom) B3LYP optimized Gaussian 3.0 image of the HOMO-4 (LANL2DZ pseudopotential on Ru and 6-31g on all other centers) which shows overlap between the porphyrin character orbitals conducive to electron transfer (data from A. Kouzelous).