Electronic structure of a metal-organic super container molecule by single point DFT

Wendi Sapp, Adam Erck, Z. Rick Wang, Dmitri Kilin
University of South Dakota, Vermillion, SD 57069

Metal-organic super container (MOSC) molecules[1] are ideal candidates for photocatalysis due to their construction with transition metal centers and tunable cavity sizes that could house catalytic sites. The basic electronic structure for a model of extremely large size (more than 2,000 ions) is explored by single point calculation using unrestricted density functional theory (DFT), and Perdue Burke Ernzerhof (PBE) in Vienna Ab-initio Simulation Package (VASP) software. The information obtained through these calculations (such as density of states, absorbance spectra, and charge density) will allow for analysis of a MOSC's catalytic ability. Prediction of photo-excitation dynamics is possible through time-dependent theoretical methodology, where non-adiabatic coupling allows to follow charge transfer and recombination in photo-catalytic MOSC materials.[2]

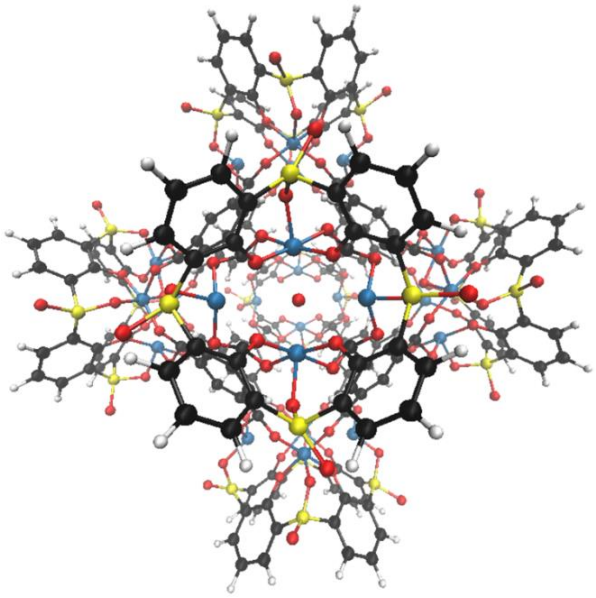

Figure 1. Black (carbon), yellow (sulfur), red (oxygen), blue (cobalt), white (hydrogen).

Electronic characteristics of the nanostructures (MOSCs and their building blocks) in the ground and photoexcited electronic configurations are examined. We explore if the presence of transition metal ions with open shells in such close proximity to one another may result in high spin configurations and show any arrangement into ferromagnetic ordering. Spin-unrestricted computation was applied to evaluate how optical properties could be affected by d-d transitions. The comparison of the density of states and absorbance spectra for the synthetic precursors vs MOSC in indicate that the MOSC is not simply the sum of the parts. Analysis of Kohn-Sham orbitals of interest provides insight into charge transfer mechanisms, which were found to contribute to multiple low-energy charge transfer states to the electronic structure.

This research used resources of the National Energy Research Scientific Computing Center (NERSC), a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231, allocation award 88777, "Computational Modeling of Photo-catalysis and Photo-induced Charge Transfer Dynamics on Surfaces."

1. Dai, F.-R.; Wang, Z., Modular Assembly of Metal-Organic Supercontainers Incorporating Sulfonylcalixarenes. *J. Am. Chem. Soc.* **2012,** *134* (19), 8002-8005.
2. Annapureddy, H. V. R.; Motkuri, R. K.; Nguyen, P. T. M.; Truong, T. B.; Thallapally, P. K.; McGrail, B. P.; Dang, L. X., Computational studies of adsorption in metal organic frameworks and interaction of nanoparticles in condensed phases. *Mol. Simul.* **2014,** *40* (7-9), 571-584.