Comparison of computational and experimental approaches to understanding MOSC structural properties and host-guest interaction

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Metal-organic supercontainers (MOSCs) incorporating sulfonylcalix[4]arenes, transition metal ions, and various carboxylate linkers represent a new class of biomimetic container molecules,[1] being a limiting case of infinite periodic metal-organic frameworks (MOFs).[2] Experimentally, these MOSCs were found to selectively bind cationic guests, such as methylene blue dye. The objective of this computational analysis is to further understand the binding selectivity of the MOSCs. The presence of transition metal ions provides a challenge for force field molecular mechanics approaches. Considering the size of these MOSCs approaches the threshold of computational capabilities, we applied a 'divide and conquer' strategy and theoretically investigated the building blocks for these super-containers: tetranuclear complexes (sulfonylcalix[4]arene bound to four cobalt ions furnished by four additional acetate groups), sulfonylcalix[4]arenes, and numerous carboxylate linkers. Density-functional theory with B3LYP exchange-correlation functional and 6-31G(d) and LANL2DZ basis sets (for light elements and transition metals, respectively) in Gaussian software provides spatial electron density distributions for ground state and for Kohn-Sham orbitals. DFT results confirm the binding cavities of the container are negatively charged, accounting for the selectivity. Ongoing theoretical studies examine the building blocks and the MOSC as a whole, including structure, stability and binding energies of the MOSC host with various guest molecules. The adsorption mechanism of guest molecules to the various binding sites of the MOSC will be explored by *ab initio* molecular dynamics.[3] Additional experimental studies will be performed, regarding guest selectivity to optimize the binding of the MOSCs and to expand possible applications of these containers such as drug delivery and biomedical sensing.

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