

Computational Investigations of Supramolecular Interactions: Anion Binding with Macrocyclic and Cage Receptors

Minwei Che, Sibali Debnath, and Krishnan Raghavachari

Indiana University Bloomington, 800 E Kirkwood Ave, Bloomington, IN 47405, USA

Density functional (DFT) theory including dispersion corrections has been widely used for the investigation of supramolecular interactions involving medium-sized and large molecules. In this work, we present a thorough investigation using DFT methods for the study of supramolecular receptors, viz., macrocycles and cages. In particular, we focus on receptors where the anion binding is via non-conventional C–H hydrogen bond donors. With a series of atomic, molecular, and novel designer anions of different sizes and shapes, we explore the effects of preorganization and complementarity on selective binding of anions with receptors involving different cavity sizes. Additionally, we explore the sterics-modulated recognition by organotrifluoroborate ($R\text{-BF}_3^-$) anions as designer guest molecules for cyanostar macrocycles. Importantly, solvent effects in a variety of nonpolar as well as polar solvent environments are evaluated using the conductor-like polarizable continuum model (CPCM) to calculate the binding affinities of a range of macrocycle-anion and cage-anion complexes. Furthermore, we design a series of cage receptors with tunable chloride affinity by functionalizing a triazolo cage receptor. Finally, we investigate the application of cages as liquid-liquid extractants of aqueous chloride into an organic solvent. This work provides a foundation for the development and application of computational models for anion binding and computer-aided design of anion-receptors.