Public Abstract
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Zinc-seamed pyrogallol[4]arene dimeric nanocapsules have been experimentally observed with a variety of exo ligands coordinating to the zinc and a variety of encapsulated guests. In an effort to gain additional insight into the properties of these dimers, electronic structure calculations were carried out on a number of model complexes and capsular assemblies.

Initial calculations focused on simple hydroxide-based and Z-ethene-1,2-diol-based mononuclear zinc model complexes representative of the zinc coordination sphere in the dimers. These calibration studies aided in the choice of an appropriate computational protocol to be implemented on the capsules themselves. The binding dissociation enthalpies of the ligands were evaluated, along with the effect of ligand choice on zinc coordination number. With the success of the Z-ethene-1,2-diol-based model complexes in reproducing the capsular zinc coordination environment, two sets of calculations exploring divergent ligands linking two of these model complexes were performed. The first set of calculations predicted the stability of a metal organic framework (MOF) comprising zinc-seamed pyrogallol[4]arene capsules linked by a 4,4’-bipyridyl ligand and aided in the choice of crystallization solvent in the subsequent synthesis of the MOF. The second set of calculations identified three additional divergent ligands as likely candidates for the construction of MOFs.

To gain further insight as to why pyrogallol forms macrocycles and the remaining trihydroxybenzene-based macrocycles remain unobserved, the proton affinity (PA) of these building blocks was examined. The preferred sites of protonation in the trihydroxybenzenes were compared with those in the mono- and dihydroxybenzenes, as some of the latter hydroxybenzenes are also known to form macrocycles. A key factor with respect to formation of macrocycles appears to be the relative magnitudes of the PAs associated with the ring carbon-linking sites.

To better understand the capsular metric dimensions and encapsulation thermochemistry, studies on the zinc-seamed pyrogallol[4]arene nanocapsules themselves examined the effect of the exo ligands, R group, guest, and calculational level on these properties. In particular, the influence of these factors on the flexibility and robustness of the capsular framework, host-guest interactions, size limitations of a guest, and enhancement in guest basicity upon encapsulation was investigated. The presence of exo ligands has the largest effect on both geometric properties and encapsulation thermochemical values; however, the presence of a guest also has an effect on the capsular dimensions. The enhancement in basicity of an encapsulated guest, although dependent on the nature of the guest, is generally some 50 kJ/mol, a value consistent with those found for other host-guest assemblies. The computational results helped to rationalize the presence of observed guests and the absence of unobserved guests in the dimeric capsules and led to a proposed step in the unknown mechanism of formation of the capsules.