Public Abstract
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Title:UNDERSTANDING THE SELF-ASSEMBLY PROCESS AND BEHAVIOR OF METAL-SEAMED PYROGALLOL[4]ARENE NANOCAPSULES

Pyrogallol[4]arenes (PgCs) are bowl-shaped compounds that are commonly used as building blocks in the construction of more complex nanomaterials, such as nanocapsules and nanotubes. Nanocapsular materials in particular, are of increasing significance as they may have medicinal applications as targeted drug delivery agents, as “cages” for pharmaceutical entrapment, or as artificial receptors for a wide variety of biomolecules. The building blocks used in the construction of nanomaterials typically interact with one another through weak inter- and intra-molecular forces. Unfortunately, this makes nanomaterials unstable to dissociation into their component parts, which is disadvantageous for any real-world practical application. A prospective way of increasing the stability of these materials, at least in the case of PgCs, is to use transition metal cations as complementary building blocks. Transition metal cations interact with PgCs through stronger coordinate bonds, which leads to the formation of a hybrid metal-organic material that is generally much more stable than one formed through non-covalent bonding. The chemistry involved in this concept, however, has not been studied extensively and is therefore the subject of this text.
Prior work in the Atwood lab has produced three examples of metal-organic nanocapsules (MONCs) based on PgCs. These include two hexameric MONCs (six PgCs) based on Cu2+ and Ga3+ cations, as well as a single example of a dimeric MONC (two PgCs) based on the Zn2+ cation. As it was unknown whether other metal cations could lead to the formation of similar MONCs, PgC complexation experiments were conducted with other cations, notably Ni2+, Co2+ and Mn2+. All of these led to nanocapsular materials, which were identified and studied using single crystal X-ray diffraction (scXRD). Once the foundational studies were complete, syntheses were also performed under varied conditions, specifically with Ni2+ and Cu2+. It was found that certain conditions would lead to hexameric MONCs whereas others would lead to dimeric MONCs. Therefore, these experiments showed that the identity of PgC-based MONCs can effectively be controlled through synthesis. These results, however, were based on scXRD solid-state analysis, which looked only at the crystalline end product. They did not allow for the analysis of MONCs over time or in solution.
To fill in this gap, small angle neutron scattering (SANS) was used to determine the behavior of MONCs in solution and over time. This technique helps to determine the size, shape, and concentration of different analytes in solution. As the two major products from PgC metal coordination (dimer and hexamer) have different radii, the SANS method could clearly differentiate between the two and determine their concentrations in solution. Mirroring the results in the solid-state, this work showed that the formation of the dimer is typically favored at higher temperatures while the formation of the hexamer is favored at lower temperatures. Studies that varied time of measurement as well as the solvent system during synthesis were also performed, and the results were varied depending on other conditional factors. Furthermore, SANS was also used to study Fe3+-PgC complexes. These complexes are difficult if not impossible to crystallize, and therefore cannot be studied in the solid state using scXRD. SANS was used in conjunction with elemental analysis to deduce a structure for these iron-containing materials, showing that they formed a nanotubular assembly.
In addition to understanding the synthesis of MONCs and creating reproducible methods to generate them, another goal was to also use them for other (possibly practical) purposes. To this end, PgC-based MONCs were used as building blocks in metal-organic frameworks (MOFs). MOFs are gas adsorbing agents that are used in research aimed towards the storage of compressed gases such as methane or hydrogen. They

typically consist of metal cations linked together with organic ligands. This forms a porous molecular net that attracts and stores gases. As MONCs can be viewed as cationic clusters, they too can be used as building blocks in MOFs. The ligand 4,4'-bipyridine was used to "link" MONCs together, resulting in one and two dimensional frameworks composed of dimers or hexamers. This work not only produced functional materials that may be useful in future research efforts, but also showed on a more fundamental level that the chemistry and behavior of MONCs can be selectively "tuned" through relatively simple means.
The introduction of radioisotopes into the nanocapsule was another method by which functionality could theoretically be imparted into MONCs. It was envisioned that MONCs could be used as carrier systems for radioisotopes, and thereby function as agents for radiotherapy or medical imaging. Copper hexamers constructed from 64Cu2+ were prepared and studied in a living system. However, these studies were unsuccessful at showing that the copper-seamed MONCs differed in behavior from free 64Cu in vivo, and therefore it is uncertain whether these materials can be used for imaging/therapy. Nevertheless, radiolabeling of hexameric nanocapsules was helpful in understanding the chemistry of these materials. Some of the studies that were conducted include those that gauge the solubility and stability of MONCs, as well as others that explore the conditions required for cationic uptake and exchange.