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Ferrocene as a Hydrophobic Templating Agent with Pyrogallol[4]arenes

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Crystallization of a methanol solution of *C*-methyl- and *C*-heptylpyrogallol[4]arenes (PgCs) and ferrocene led to the formation of a dimeric inclusion complex wherein ferrocene is encapsulated between two PgC hemispheres seamed together by four water molecules. Small-angle neutron scattering (SANS) was used to determine the structure and stability of this inclusion complex in solution.

Nanoscale materials based on the bowl-shaped members of the calixarene extended family continue to capture the imagination of the scientific community with potential applications in pharmaceuticals,[1–3] catalysis,[4,5] and as molecular magnets.[6,7] One particularly robust, yet less investigated member of this family is the *C*-alkylpyrogallol[4]arene (PgC).[8,9] Recent studies have shown that PgCs self-assemble into a wide range of supramolecular capsules based on both inter- and intramolecular hydrogen bonding,[10] as well as metal ion coordination.[11–14] The guests in such capsules are generally small, polar molecules, but larger entities such as substituted pyrenes may also be housed in tubular[15] structures and hexameric capsules.[16] We now show that ferrocene can be used as a template towards the formation of a capsular motif.

Previous reports of ferrocene/calixarene (or resorcinarene) host–guest complexes cite electrostatic means of encapsulation, wherein oxidation to the ferrocenium cation is necessary for encapsulation.[17] Reports of encapsulating neutral ferrocene do exist, but all of these rely on a customized cavity based on upper rim modification or the addition of large structural elements.[18–20] To our knowledge, neither the complexation of ferrocene nor the ferrocenium cation has been reported with pyrogallol[4]arenes.

A 10^{-2} M solution of 1:1 PgC_1 : ferrocene in a 8:1 mixture of methanol to water was allowed to evaporate under a slow air stream during the course of a week. The orange solution, indicative of free ferrocene, slowly turned green, followed by the growth of blue prismatic crystals **1**. These crystals were analyzed via single crystal XRD and were found to contain dimeric capsular entities of the formula $(PgC_1)_2 \subset Fe(Cp)_2 * [(H_2O)_4\,(MeOH)_4]$. The crystal structure of **1** (Figure 1) shows an orderly hydrogen bonding architecture. The individual dimers are constructed primarily through intermolecular hydrogen bonding, involving the upper-rim hydroxyl groups of each of the two PgC_1s and water molecules as structural components. The iron atom is located on an inversion center, which implies that the asymmetric unit contains one cyclopentadienyl ring and one PgC_1. The smaller volume of the dimeric capsule constrains the ferrocene such that the molecule is crystallographically well ordered. Three of the hydrogens on each cyclopentadienyl ring are positioned toward the hydrophilic periphery of the dimer, while the other two are pointed directly at two aromatic rings in the macrocycle. The C-H···π centroid distances between the cyclopentadienyl hydrogen atoms and the adjacent PgC_1 aromatic rings are 2.68 and 2.77 Å, while

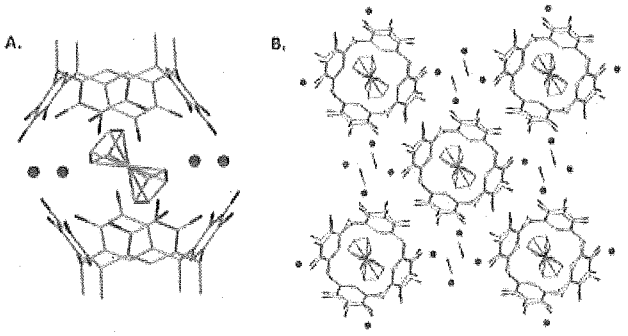

Figure 1. A single ferrocene-containing dimeric capsule **1** (A), and crystal packing of **1** showing full hydrogen bonding network (B)

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the three positioned toward the hydrophilic periphery of the dimer are participating in C–H···O hydrogen bonds with the upper rim of the host PgC_1 molecules. The lengths of the three H···O distances are 2.91 Å, 2.67 Å, and 2.71 Å. The two PgC_1s in the capsule are also slightly offset from one another (Figure 1). This offset arrangement differs from the more symmetrical dimeric structures with quarternary ammonium cations as guests as reported by Rissannen et al., perhaps due to the larger size of the encapsulated ferrocene guest, which does not allow a fully symmetrical capsule due to steric effects.[21]

Due to the similarity in bond lengths between ferrocene and the ferrocenium cation, it was difficult to determine the charge on the guest from the single crystal XRD study. Thus, ^{1}H NMR was used to determine the oxidation state of the encapsulated species. Although the low solubility of **1** led to a poor spectrum, general broadening was seen in the signals, especially those around 4 ppm, showing that this assembly likely consists of the paramagnetic ferrocenium cation. This is surprising, as no oxidizing agents were used during synthesis and no distinct counterions could be found in the crystal structure, although a possible counterion could be the PgC upper rim itself, in a singly deprotonated state. This result does, however, correlate well with the blue color of the crystalline material, which indeed suggests the presence of ferrocenium cation as opposed to neutral ferrocene.

In addition to the described crystallization scheme, it was conveniently found that HCl added to the solution at a 10^{-2} M concentration greatly hastened the crystallization process, leading to crystallization in days rather than weeks. Interestingly, this modification also had a structural consequence, namely that HCl/Cl^- replaced a single water molecule in the hydrogen bonding network along the capsule's "equator." This modification leads to a slight deviation in hydrogen bond lengths from an average hydroxyl to water distance of around 2.8 in **1** to more than 3.1 Å in the structures containing the structural chlorides, producing a slightly larger opening on one side of the inclusion complex, as compared to that of **1** (Figure 2). In contrast to the previously described dimer **1**, wherein no counterion was apparent, the presence of HCl/Cl^- suggests a possible counterion to ferrocenium in the form of a chloride ion.

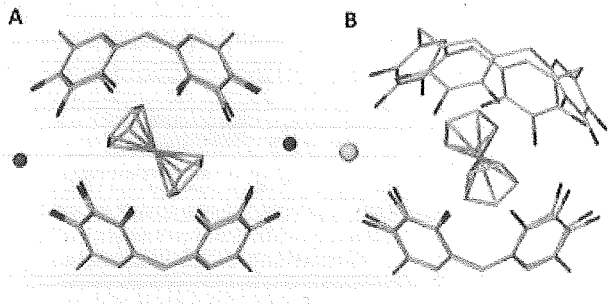

Figure 2. Comparison of cmpd **1** (A) and an analog with a structural chloride (B). Pendant R-groups removed for clarity.

Aside from this minor difference, the resultant PgC_1/ferrocene/HCl complexes are structurally similar to the non-HCl-containing system. Thus, this method was used to quickly determine whether other solvent systems and PgCs could lead to similar assemblies or whether other structural moieties could be realized. With this in mind, both PgC_1 and PgC_7 were used to form host–guest complexes with ferrocene in acetonitrile. This solvent was chosen due to its propensity to form hexameric capsules with PgCs, rather than dimers or bilayers. Both, however, solely formed analogues of **1**. The conservation of the dimeric structural motif in both the long (heptyl) and short (methyl) chain variants of the PgC/Ferrocene inclusion complex shows that this complex is likely preferred over other possible capsular systems such as the previously reported hexameric containers with pyrogallol[4]arenes.[8,9]

In the discussion of a complex supramolecular solid state structure, a question always arises: what does the solid state structure teach about the species present in solution? The answer to this question is typically based on NMR evidence or sheer speculation, the former of which was not viable in this study. Small-angle neutron scattering (SANS), however, is capable of providing geometric insight into the species present in solution, regardless of paramagnetism. SANS measurements were performed on the NG7 30 m SANS instrument at the NIST Center for Neutron Research (NCNR-NIST). Crystals of **1** were dissolved in deuterated methanol and were measured at an optimized concentration of 3% by mass. Scattering from dimeric moiety **1** fit[22] as a polydisperse sphere of mean radius (6.67 ± 0.02) Å with $\sqrt{(x^2/N)} = 1.34$. This radius corresponds rather closely to the experimental radius from our solid state results (6.74 Å, as measured from iron center to the centroid of methyl hydrogen atoms of the PgC_1). Thus, the SANS data provides evidence for at least the short-term stability of dimeric capsule **1** in protic media, a divergence from other hydrogen-bonded PgC-based capsular entities which are typically only stable in aprotic solvents.[23]

In conclusion, ferrocene served as an excellent guest for the study of templation with PgC macrocycles, exclusively producing dimeric nano-architectures in the solid state, regardless of conditions. SANS measurements also showed that this dimeric assembly was stable in methanolic solution, further demonstrating the robust nature of this assembly under typically harsh conditions for PgC-based host–guest systems.

CCDC-837223, 837224, and 837225 contain the supplementary ccrystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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