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Ferrocene Species Included within a Pyrogallol[4]arene Tube

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Research in host–guest complexes with ferrocene as a guest continues to attract attention. Macrocyclic hosts spanning from curcubiturils[1] and cyclodextrins[2] to resorcinarenes[3] have been used to both encapsulate ferrocene and use as a component in nanometric frameworks. *C*-alkylpyrogallol[4]arenes (PgCs) are bowl-shaped compounds that are commonly used as building blocks in the construction of larger entities, such as capsules[4] and nanotubes.[5] Our work with *C*-methyl and *C*-heptylpyrogallol[4]arene has likewise shown that these compounds can function as hosts for ferrocene.[6] The host–guest complex thus formed is a dimeric capsule with the enclosed and highly ordered ferrocene located between two PgC hemispheres.

In addition to such capsular motifs, the conical shape of the calixarenes,[7] resorcinarenes,[8] and pyrogallolarenes[5] can likewise lead to the formation of tubular solid-state structures. These often incorporate large nonsolvent molecules as part of the tubular framework. An excellent example of a PgC-based tubular framework that accommodates large nonsolvent molecules is the host–guest complex of *C*-hexylpyrogallol[4]arene (PgC_6) with pyrene.[9] In this complex, tetramers of PgC_6 associate with one another through hydrogen bonding, whereas the pyrene molecules intercalate between the *C*-hexyl pendant arms of the PgC. This leads to two distinct regions within the structure: a hydrophilic tube that encloses guest solvents along with a hydrophilic tube that accommodates the pyrene. Herein, we describe a second host–guest complex of C-methylpyrogallol[4]arene (PgC_1) and ferrocene that conforms to a tubular structural motif. In contrast to the capsular motif, a tubular hydrophobic cavity, rather than a capsular cage, is responsible for incarceration of the guest, whereas the hydroxyls of the PgC_1 complexes along with polar solvent molecules form the long-range hydrogen-bonding superstructure.

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Slow changes in concentration of a PgC_1 and ferrocene solution caused by evaporation led to the crystallization of this unique architecture. Methanolic solutions containing various ratios of PgC_1 to ferrocene (with the concentration of ferrocene set at 10^{-3} mol L^{-1}) were allowed to evaporate until crystallization was evident. At a 1:1 PgC_1/ferrocene ratio, crystals of the previously reported dimeric product were the sole product.[6] However, at ferrocene ratios of 6:1 or higher, two different crystal habits formed were found, with green needle-like crystals accompanying the dark blue prisms of the ferrocene dimer. X-ray diffraction analysis of the single crystal showed the dark green needles to be a novel tubular motif **1** featuring ferrocene "beads" in a hydrophobic cylinder of repeating trimers of PgC_1.

The tubular structure **1** (Figure 1) displays a complicated hydrogen-bonding arrangement of PgC_1 complexes. Each tube consists of alternating units of 3 PgC_1 complexes rotated by 60° relative to one another along the crystallographic *C* axis and a single ferrocene guest. The overall structure thus closely resembles a family of resorcinarene-based nanotubes described by Rissannen et al.[8] However, in contrast to both the resorcinarene tubes and our previously reported

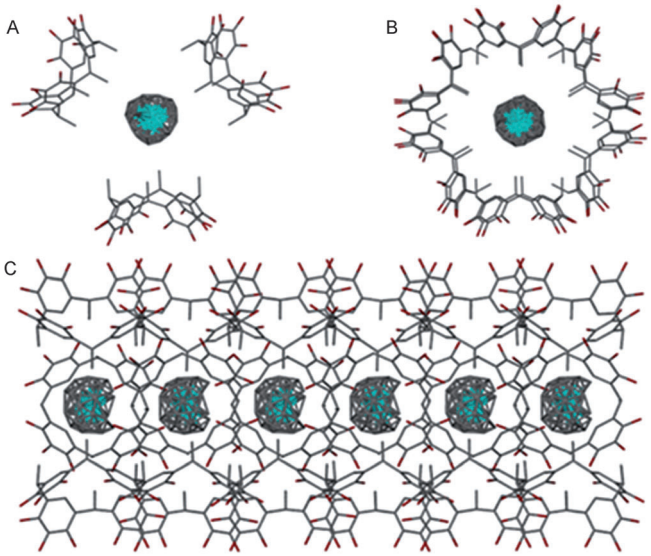

Figure 1. Structure of a single repeating unit of A) 1, B) two overlaid units showing a 60° rotation, and C) a view showing the propagation of the tubular framework. Disorder of encapsulated ferrocene molecules precludes their description as discrete guests (see the Supporting Information for additional images of tubular cavity).

PgC/ferrocene dimeric capsule, the guest is not located within the bowl-shaped cavity of the PgC_1, but rather within the hydrophobic tubular environment spanned by the *C*-methyl pendant arms of the PgC_1 (Figure 1). A disordered methanol molecule instead occupies the space within the bowl. The location of the ferrocene within this environment does not lend well to C–H···π or other interactions with adjacent PgCs. Thus, the Fe center is disordered over two positions, and the cyclopentadiene rings are present as a highly disordered torus of electron density. This indicates a high degree of mobility of the ferrocenes within the tube. The three PgC_1 complexes located in each repeating layer do not participate in hydrogen bonding with one another, but rather with four PgC_1 complexes in adjacent layers, two above and two below (Figure 1a). Each PgC_1 also participates in hydrogen bonding with four other PgC_1 complexes in adjacent tubes. A single-water molecule located outside the cavity also participates in hydrogen bonding with each PgC_1, helping to tie together three adjacent tubes. As an additional note, broadening in the peak corresponding to ferrocene in the ^{1}H NMR spectrum showed that the ferrocene guest was likely paramagnetic and thus present as the ferrocenium cation. The lack of a counterion suggests that a singly deprotonated PgC_1 counterbalances the +1 charge of the ferrocenium ion.

Similar to the previously described ferrocene dimer, small-angle neutron scattering (SANS) was used to study this entity **1** in solution. SANS measurements were performed on NG7 30 m SANS instrument at the National Institute of Standards (NIST) Center for Neutron Research, Gaithersburg, MD.[9] SANS analysis provided structural details in solution that cannot be obtained with conventional techniques. Unlike light scattering techniques or diffusion NMR, SANS technique requires no assumption that dissolved species is spherical in solution.

The tubular assembly **1** was dissolved in [D_4]methanol at a mass fraction of 2% to obtain sufficient scattering statistics with SANS. The sample was then left overnight to ensure saturation without precipitation. Three different sample-to-detector distances, 1.3, 4.5, and 13 m, were used to cover the overall q range of $0.008 < q < 0.54$ Å^{-1}. It is important to note that unlike for capsular entities, scattering measurements for tubular entities were performed at much smaller angles. Scattering data were then analyzed on IgorPro software provided by NIST.[10] To investigate host–guest interaction in solution, we first calculated scattering-length densities (SLDs) of PgC_1 trimers with and without ferrocene guest (Table 1). These SLDs were then held fixed in data analyses, and the measured data were fitted to various cylindrical, spherical, and ellipsoidal models.

Analysis of the data as a polydisperse sphere[11] both with and without ferrocene guest, however, led to a good fit of **1** as spheres of radius 7.01 and 6.6 Å, respectively. A previous investigation revealed the radius of 7 Å for a typical PgC_3 dimer, whereas for a PgC_3 hexamer it is 10 Å.[12] Hence, even though all parameters and their error bars look reasonable for PgC_1 with ferrocene, the size of the sphere reported is equal to that of PgC_3 dimer (see the Supporting Information). On the other hand, the radius of 6.6 Å obtained for PgC_1 without ferrocene guest is similar to that of our previous study of ferrocene-enclosed hydrogen-bonded PgC_1 dimer ($r = 6.7$ Å) in methanol.[6] Thus, Schulz sphere fit for PgC_1 without ferrocene guest represents the best fit and gives a true representation of the PgC_1–ferrocene structure in solution (Figure 2, Table 2).

The structural alteration of solid-state ferrocene-enclosed PgC_1 nanotubes to solution-phase hydrogen-bonded dimer indicates overall higher stability of dimers over tubes in solution. This study is intriguing, because it demonstrates not only the effect of templation towards building molecular hosts with varying architectures, but also unique structural variation

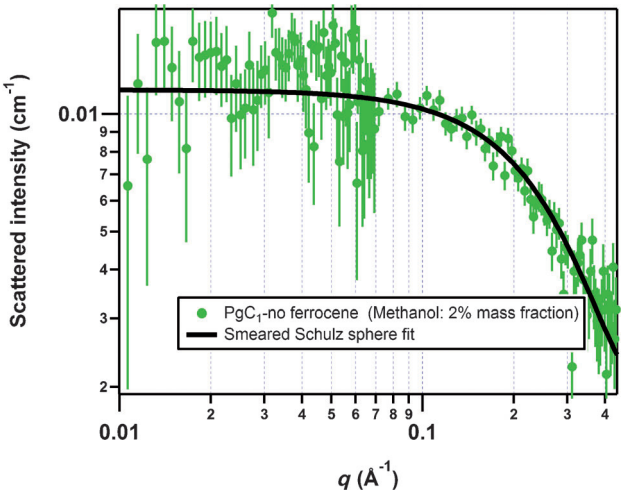

Figure 2. SANS intensity from C-methylpyrogallol[4]arene ferrocene tube at a mass fraction of 2%. The solid line is the model fit with a polydisperse sphere model. The error bars on the SANS-data points represent one standard deviation in the measured intensity.

Table 2. Fitting parameters for Schulz sphere model.

Volume fraction (scale)	$0.00363651 \pm 7.35082 \times 10^{-5}$
mean radius [Å]	6.60685 ± 0.00499484
polydisp [sig/avg]	$0.190106 \pm 7.1952 \times 10^{-5}$
SLD sphere [Å^{-2}]	1.93×10^{-6} (held fixed)
SLD solvent [Å^{-2}]	5.8×10^{-5} (held fixed)
bkg [cm^{-1}]	$0.00173012 \pm 9.24176 \times 10^{-6}$
sqrt [χ2/N]	1.24958

Table 1. Calculated SLDs of ferrocene-enclosed C-methylpyrogallol[4]arene assembly.

Sample	Molecular formula	Density [g mL^{-1}]	λ [Å]	SLD [Å^{-2}]
ferrocene	$C_{10}H_{10}Fe$	1.107	6	1.38×10^{-6}
PgC_1 (trimer) + ferrocene	$C_{96}H_{96}O_{36} + C_{10}H_{10}Fe$	1.16	6	1.83×10^{-6}
PgC_1 (trimer) – ferrocene	$C_{96}H_{96}O_{36}$	1.2	6	1.93×10^{-6}

and behavior of hosts in the two phases. In addition, the progression in size observed for pyrogallol[4]arenes dimers is in agreement with solution-phase SANS studies of pyrogallol[4]arene hexamers with varying chain length.[13]

In conclusion, we have described a new inclusion complex of PgC_1 and ferrocene. Unlike the previously reported dimer, the tubular motif **1** is not stable in methanolic solution and dissociates into a dimer. Its formation is thus likely due to a high PgC_1-to-ferrocene ratio coupled with shifting solvent conditions during evaporation. Future research will focus on studying other hydrogen-bonded as well as metal-containing nanotubular frameworks in solution.

Experimental Section

Synthesis of C-methylpyrogallol[4]arene (PgC_1): PgC_1 was prepared in a similar manner to that described in a previous report.[14] Pyrogallol (30.07 g, 99%) was dissolved in ethanol (25 mL). The flask was fitted with a reflux adapter over an oil bath set at 200 °C and was kept under steady nitrogen flow. Through the top of the adapter, acetaldehyde (20 mL, 99.5%) was added along with hydrochloric acid (1 mL, 12.1 mol L^{-1}). The mixture was then heated at reflux for 12 h, during which time the color of the solution changed from colorless to a deep red, accompanied by the precipitation of a white powder. The mixture was then cooled for approximately 30 min following reaction, and precipitate was removed by filtration. The precipitate was washed with additional ethanol and dried in a desiccation oven for 24 h. Proton NMR analysis was used to determine the purity of the resultant powder and showed that both *rccc* (cone) and *rctt* (chair) conformers were present in the solid. To separate the conformers, the powder was mixed into methanol/water 9:1 (100 mL) and heated until boiling. The mixture was then filtered, and the filtrate was evaporated on rotor to a solid and dried along with the undissolved precipitate in a desiccation oven (7.92 g *rccc*; 4.62 g *rctt*; total yield: 35.15%). Proton NMR spectroscopy was used to establish the composition of the resultant powders by peaks at $\delta = 6.695$ (*rccc*) and 6.420 ppm and 5.762 ppm (*rctt*), corresponding to the aryl proton on the two conformers, respectively, in deuterated DMSO.

Synthesis of $(PgC_1)_3(H_2O)_1(MeOH)_1$⊂ferrocene: A stock solution of PgC_1 (10^{-2} mol L^{-1}) was prepared by dissolving PgC_1 powder (0.608 g, rccc) in methanol/water 8:1 (100 mL). Likewise, a stock solution of ferrocene (10^{-1} mol L^{-1}) was prepared by dissolving ferrocene (0.372 g) in carrier solvent (20 mL; benzene, chloroform, ethyl acetate, or acetone). Ferrocene solution (100 μL) was mixed with various volumes of PgC_1 solution, ranging from 1 to 10 mL in scintillation vials. Methanol/water 8:1 was then added to each vial to bring the total volume to 10 mL. The lids on the scintillation vials were partially unscrewed, and crystallization occurred over a period of several weeks. A mixture of crystals often resulted at the higher PgC_1/ferrocene concentrations, and some manual sorting of crystals was necessary for SANS analysis. Some evidence also suggested that use of a lower methanol/water ratio (4:1 or less) can lead to a greater proportion of crystals of the tubular motif.

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[1] a) W. S. Jeon, K. Moon, S. H. Park, H. Chun, Y. H. Ko, J. Y. Lee, E. S. Lee, S. Samal, N. Selvapalam, M. V. Rekharsky, V. Sindelar, D. Sobransingh, Y. Inoue, A. E. Kaifer, K. Kim, *J. Am. Chem. Soc.* **2005**, *127*, 12984–12989; b) L. Yuan, D. H. Macartney, *J. Phys. Chem. B* **2007**, *111*, 6949–6954.
[2] D. Osella, A. Carretta, C. Nervi, M. Ravera, R. Gobetto, *Organometallics* **2000**, *19*, 2791–2797.
[3] a) I. E. Philip, A. E. Kaifer, *J. Am. Chem. Soc.* **2002**, *124*, 12678–12679; b) L. R. MacGillivray, H. A. Spinney, J. L. Reid, J. A. Ripmeester, *Chem. Commun.* **2000**, 517–518.
[4] a) S. J. Dalgarno, J. Antesberger, R. M. McKinlay, J. L. Atwood, *Chem. Eur. J.* **2007**, *13*, 8248–8255; b) A. Ahman, M. Luostarinen, K. Rissanen, M. Nissinen, *New J. Chem.* **2007**, *31*, 169–177; c) O. V. Kulikov, N. P. Rath, D. Zhou, I. A. Carasel, G. W. Gokel, *New J. Chem.* **2009**, *33*, 1563–1569; d) L. Avram, Y. Cohen, *Org. Lett.* **2006**, *8*, 219–222; e) E. S. Barrett, T. J. Dale, J. Rebek, Jr., *J. Am. Chem. Soc.* **2008**, *130*, 2344–2350; f) M. Kvasnica, J. C. Chapin, B. W. Purse, *Angew. Chem.* **2011**, *123*, 2292–2296; *Angew. Chem. Int. Ed.* **2011**, *50*, 2244–2248.
[5] a) S. J. Dalgarno, G. W. V. Cave, J. L. Atwood, *Angew. Chem.* **2006**, *118*, 584–588; *Angew. Chem. Int. Ed.* **2006**, *45*, 570–574; b) O. V. Kulikov, M. M. Daschbach, C. R. Yamnitz, N. Rath, G. W. Gokel, *Chem. Commun.* **2009**, 7497–7499.
[6] A. V. Mossine, H. Kumari, D. A. Fowler, A. K. Maerz, S. R. Kline, C. L. Barnes, J. L. Atwood, *Isr. J. Chem.* **2011**, *51*, 840–842.
[7] S. Kennedy, C. M. Beavers, S. J. Teat, S. J. Dalgarno, *New J. Chem.* **2011**, *35*, 28–31.
[8] H. Mansikkamäki, M. Nissinen, K. Rissanen, *Angew. Chem.* **2004**, *116*, 1263–1266; *Angew. Chem. Int. Ed.* **2004**, *43*, 1243–1246.
[9] C. J. Glinka, J. G. Barker, B. Hammouda, S. Krueger, J. J. Moyer, W. J. Orts, *J. Appl. Crystallogr.* **1998**, *31*, 430–445.
[10] S. R. Kline, *J. Appl. Crystallogr.* **2006**, *39*, 895–900.
[11] a) G. V. Schulz, *Z. Physik. Chem.* **1935**, *B30*, 379–398; b) G. V. Schulz, *Z. Physik. Chem.* **1939**, *B43*, 25–46.
[12] H. Kumari, A. V. Mossine, S. R. Kline, C. L. Dennis, D. A. Fowler, C. L. Barnes, S. J. Teat, C. A. Deakyne, J. L. Atwood, *Angew. Chem. Int. Ed.* **2012**, *51*, 1452.
[13] a) H. Kumari, S. R. Kline, N. J. Schuster, J. L. Atwood, *Chem. Commun.* **2011**, *47*, 12298; b) H. Kumari, S. R. Kline, N. J. Schuster, C. L. Barnes, J. L. Atwood, *J. Am. Chem. Soc.* **2011**, *133*, 18102–18105.
[14] T. Gerkensmeier, W. Iwanek, C. Agena, R. Frohlich, S. Kotila, C. Nather, J. Mattay, *Eur. J. Org. Chem.* **1999**, 2257–2262.

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