

Magnetic Differentiation of Pyrogallol[4]arene Tubular and Capsular Frameworks

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ABSTRACT: The differences in magnetic properties of metal-based nanometric assemblies are due to distinct contributions from host–guest interactions, structural integrity, and magnetic interactions. To disentangle these contributions, it is necessary to control the self-assembly process that forms these entities. Herein we study the effect of host-to-guest ratios to identify remarkably different structural–magnetic contributions of *C*-methylpyrogallol[4]areneCferrocene/(PgC₁)₂CFc dimers vs (PgC₁)₃CFc nanotubes. At low temperature, a weak anti-ferromagnetic alignment is observed, suggesting a weak dipolar interaction between Fc guest moieties within adjacent dimers or tubes. Also, differences are observed between magnetic atom occupancy as a function of guest (PgC₁CFc tube/dimer) versus magnetic atom occupancy within the framework wall (PgC₃Ni hexamer/dimer). Identification of the role of the framework shape and metal–metal distances in the crystal lattice opens up unparalleled prospects for materials engineering.

Host–guest supramolecular architectures range from zeolite-like helices to molecular tweezers, molecular squares, and molecular capsules.^{1–21} Molecular capsules have been important to the field of supramolecular chemistry for almost two decades.^{22–25} Curved surfaces, such as spherical nanoparticles or molecular capsules, can impart variations in lateral film thickness that could allow alterations in the properties across the layers. A combination of multilayer film deposition with spherical nanoparticles may reveal single-domain, monodispersed, uniform magnetic anisotropy with switching behaviors induced by their spherical architecture.^{26–28} In the interest of investigating such magnetic properties, metal-containing pyrogallol[4]arene-based spherical and tubular architectures are studied here. Our interest in this field stems from the capability of macrocycles to orient in different structural conformations with the same metal centers, thereby providing varied magnetic properties. Compared to uniformly distributed spherical nanoparticles, pyrogallol[4]arenes (PgC_{*n*}'s, where *n* = alkyl chain length) provide uniform spacers between metal centers in a spherical or a tubular nanoassembly that may impart unique magnetic properties. Herein, we present magnetic differences induced by structural modifications by a combined solid-state and magnetic approach.

Molecular capsules based on arenes from the calixarene family, resorcin[4]arenes or PgC_{*n*}'s, can be categorized into

hydrogen-bonded and metal-seamed organic capsules.^{14,15,29–31} Although structurally similar to resorcin[4]arenes, with four additional hydroxyl groups, PgC_{*n*}'s yield more robust nanocapsular architectures. The excess stability may be attributed to the presence of 12 additional H-bonds. Both dimeric and hexameric metal–organic nanocapsules (MONCs) have been constructed from PgC_{*n*}'s and differ with respect to the orientation of the metals around the macrocycles. To date, zinc-, nickel-, copper-, and cobalt-seamed dimeric MONCs and copper-, nickel-, gallium-, and mixed-metal-seamed hexameric MONCs have been observed.^{14,32} Note that the metal:Pg ratio is 4:1 in both dimers and hexamers; however, the product (dimer/hexamer) equilibrium can be shifted as a function of temperature.³² Interestingly, both H-bonded and transition-metal-seamed PgC_{*n*}'s are structurally analogous in the solid and solution phases.³² Gallium-seamed PgC_{*n*} hexamers are architecturally unique in three ways:¹⁵ (a) the Ga:Pg combining ratio is 2:1, (b) they have a rugby-ball shape in the solid state, and (c) they rearrange to a toroid in solution.³³ Similarly to the capsular entities, H-bonded PgC_{*n*}-based tubular nanoassemblies with guests of ferrocene (PgC₁CFc), ethylene glycol (PgC₁Cethylene glycol), and pyrene (PgC₆Cpyrene) have been studied in solution. These H-bonded tubular frameworks rearrange into H-bonded dimers (no guest) in solution.^{34,35}

The similarities as well as differences in the solid- and solution-phase structures of these metal-containing nanoassemblies stir curiosity about their respective magnetic properties. Given the interest in this area, our initial efforts were focused on investigating the overall magnetic behavior of existing nanocapsules. Thus far, among the PgC_{*n*} frameworks, the magnetic properties of PgC₃Ni and PgC₃Co dimers^{36,37} and PgC₃Ni hexamers³⁷ have been studied in the solid state. In these nanocapsules, PgC_{*n*} acts as a ligand for transition metal ions, thereby seaming together the nanocapsular framework. Specifically, eight metal atoms form an equatorial belt of M–O bonds that stitches the two PgC_{*n*} units in the dimer, while eight triads of M₃(μ₃-O)₃(O)₆ units on opposite planes seam the six PgC_{*n*} moieties of the hexameric framework. Among the studied dimers, PgC₃Ni and PgC₃Co are isostructural and reveal paramagnetic behavior. PgC₃Ni hexamers are paramagnetic as well. At lower temperatures, the two dimers and hexamer show weak anti-ferromagnetic alignments that suggest weak dipolar interactions between adjacent metal centers.³⁷

Another interesting PgC_{*n*}-based assembly is one wherein ferrocene is enclosed within PgC_{*n*}, leading to dimers and

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tubes.^{34,38} The PgC_1CFc nanocapsular framework is composed of two PgC_1 units held together with H-bonds that enclose a ferrocene guest (Figure 1).³⁸ On the other hand, the

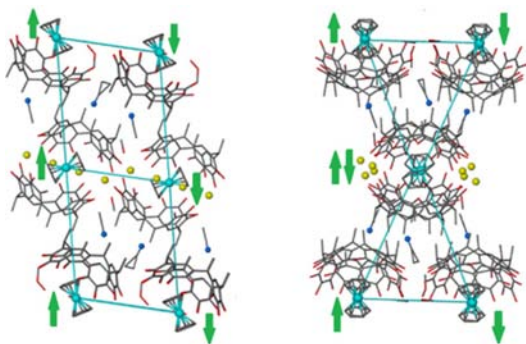


Figure 1. Side views of ferrocene-enclosed dimers showing diagonal and perpendicular distances between iron atoms (turquoise). The green arrows show moment directions.

nanotubular arrangement of PgC_1CFc comprises three alternating units of PgC_1 rotated by 60° relative to one another along the crystallographic C-axis and one ferrocene guest species (Figure 2).³⁴ Note that in both cases ^1H NMR studies

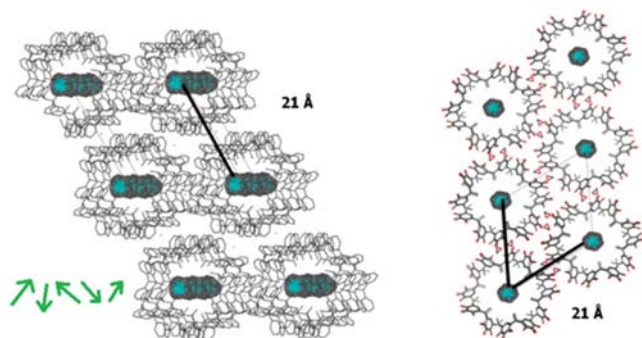


Figure 2. Side view (left) and front view (right) of ferrocene-enclosed tubes. Iron atoms are shown in turquoise. Oxygens have been removed from the side view for clarity. The green arrows show moment directions.

indicate that the ferrocene guest is likely paramagnetic and exists as the Fc^+ cation.^{34,38} The absence of a counterion indicates that the host PgC_1 is singly deprotonated to counterbalance the $1+$ charge of the Fc^+ cation.^{34,38} The host–guest ratios for the spherical and tubular arrangements are 2:1 and 3:1, respectively. We performed solid-state magnetic studies on the dimers and tubes to determine if any differences in magnetism were present. The measurements were made on a superconducting quantum interference device (SQUID) magnetometer. Two types of magnetic measurements were conducted, namely, the hysteresis loops (magnetic moment versus magnetic field) and the M vs T curves (magnetic moment versus temperature). The hysteresis measurements were conducted at 50 and 5 K, and the M vs T measurements were performed at 1.6 kA/m.

The hysteresis loops of both the Fc -enclosed dimer and tube at 5 and 50 K demonstrate paramagnetic behavior (Figure 3). To quantify the behavior, the hysteresis loops are fit to quantum mechanical paramagnetic equations with $J = 1/2$ and $g = 2$ (eq 1). For this fit, T is the temperature, H the applied

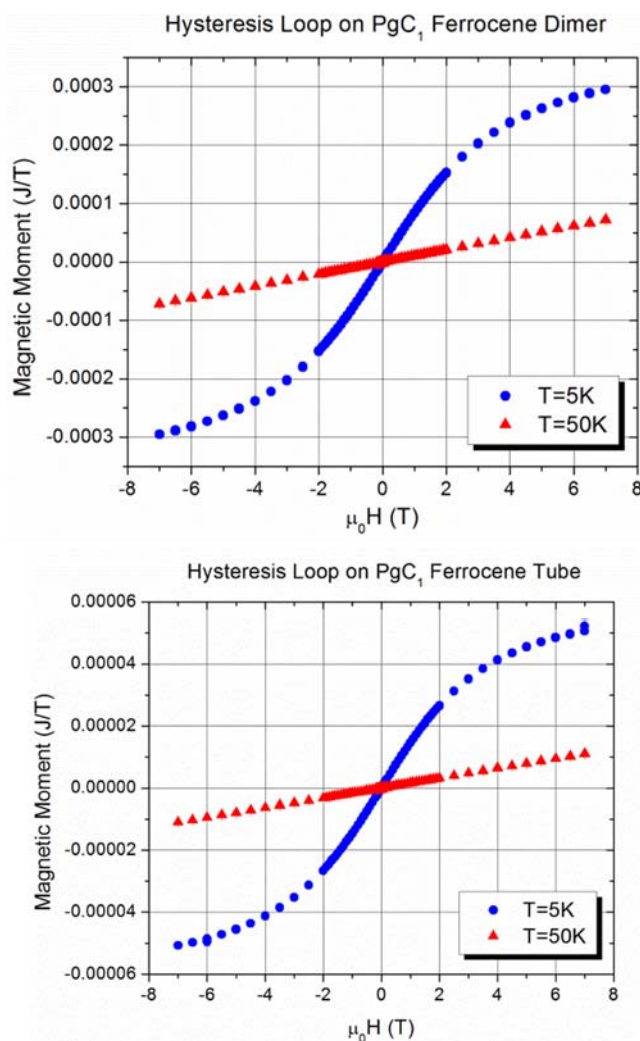


Figure 3. Hysteresis loops of C-methylpyrogallol[4]arene ferrocene-enclosed dimer (top) and tube (bottom). Error bars are included but may be smaller than the symbol.

$$M = Nm \tanh\left(\frac{gmJ\mu_0 H}{k_B T}\right) \quad (1)$$

magnetic field, M the total magnetic moment, N the number of atoms in the sample, m the magnetic moment per atom, k_B Boltzmann's constant, g the spectroscopic splitting factor, and J the spin angular momentum. The fit yields a magnetic moment of $2.35 \pm 0.01 \mu_B$ with 4.1×10^{19} atoms for the PgC_1CFc dimer and $2.16 \pm 0.01 \mu_B$ with 2×10^{18} atoms for the PgC_1CFc tube. This dissimilarity in magnitude of magnetic moments can be attributed to the differences in the architectures of the tube and dimer. Note that the magnetic moments of the earlier-studied PgC_3Ni dimer ($1.65 \mu_B$) and hexamer ($1.68 \mu_B$) are lower than those of the Fc -enclosed tubes and dimers.³⁷

The M vs T measurements at 1.6 kA/m for both the PgC_1CFc dimer and tube yield additional information beyond the paramagnetic behavior. The data were fit to the Curie–Weiss equation to investigate any possible deviation from paramagnetic behavior (eq 2). Here, T_{int} is the interaction temperature, A and C are constants, and γ is the critical exponent, which is set to 1. The deviation from an ideal non-interacting paramagnet takes the form of a non-zero interaction

$$M = \frac{A}{(T - T_{\text{int}})^{\gamma}} + C \quad (2)$$

“temperature”. The Curie–Weiss fits for both dimer and tube showed a slight deviation from paramagnetic behavior at low temperatures (Figure 4). The PgC_1CFc dimer and tube have

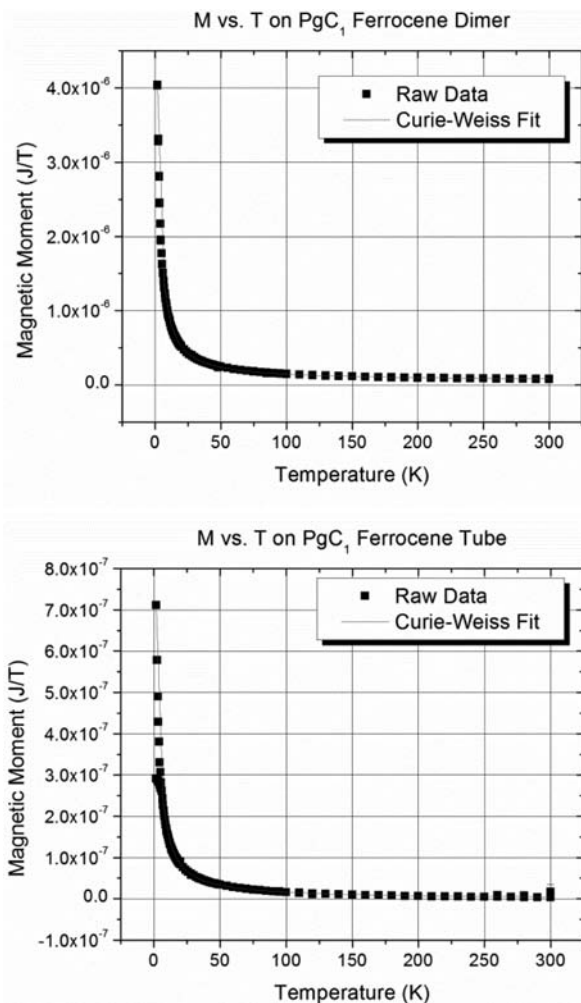


Figure 4. Magnetic moment vs temperature data at $H = 1.6$ kA/m on powder samples of C-methylpyrogallol[4]arene ferrocene-enclosed dimer (top) and tube (bottom). The red line is the fit to the data using eq 2. Error bars are included but may be smaller than the symbol.

interaction temperatures of -0.387 ± 0.001 and -0.474 ± 0.004 K, respectively. The negative interaction temperatures correspond to a weak anti-ferromagnetic alignment of the metal centers at low temperatures. The spacing between the metal centers, 0.65 nm (tube) and 1.2 nm (dimer), indicates a weak dipolar interaction between adjacent iron centers of Fc. The magnitudes of the interaction temperatures are smaller than our earlier reported interaction temperatures for PgC_3Ni hexamers (-2.26 K) and dimers (-1.02 K).³⁷

Although the nickel-seamed frameworks have an interaction temperature that is larger in magnitude, the magnetic moments of the nickel atoms in these frameworks are smaller than those of the iron atoms in the Fc-enclosed frameworks. In an individual nickel-seamed dimeric or hexameric capsular arrangement, the nickel atoms are about 0.4 nm apart; however, the metal centers are bonded through oxygen atoms

(Ni...O...Ni). This separation prevents any direct exchange interaction, so magnetostatic interactions between the metal centers dominate. (It may also reduce the magnetic moment per nickel atom.) In addition, the crystal packing arrangement of PgC_3Ni nanocapsules shows a symmetric arrangement of nanocapsules along the xy and yz planes with equal (nanoscale) distances between the nanocapsules in all directions. This close-packing of the nanocapsular spheres is a dense arrangement of congruent spheres in an infinite, regular arrangement (or lattice) wherein individual hexameric and dimeric nanocapsules are ~ 1.9 and ~ 1.5 nm apart, respectively. Therefore, the metal centers on nearest-neighbor dimers or hexamers are separated by ~ 0.9 and ~ 0.8 nm, respectively; this is twice the distance between the metal centers in a given nanocapsule (0.4 nm), causing the interactions between Ni atoms on a single nanocapsule to dominate.³²

Compared to 24 or 8 metal atoms in a typical hexamer or dimer present in the capsular wall, the PgC_1CFc dimers and tubes have only one iron metal center available as a guest in the cavity. For the PgC_1CFc dimers, the spacing between the iron centers of two adjacent dimers in the xy and yz planes (i.e., the given layer and adjacent layer) is ~ 1.2 and ~ 1.5 nm, respectively. These long-range distances suggest that dipolar interactions dominate. If the moments lie along the y -axis, then the difference in spacing suggests that the magnetic moments are anti-aligned in the xy plane and aligned in the yz plane. Alternatively, the moments can be more random in direction, with dipolar interactions forcing an anti-ferromagnetic alignment where possible. Both configurations would permit magnetic frustration between metal centers (Figure 2) and, more importantly, the weak anti-ferromagnetic interaction present at low temperature.

In contrast, the iron centers are ~ 0.65 nm apart within a PgC_1CFc tube and ~ 2.1 nm apart between adjacent tubes (Figure 1). The longer distance of 2.1 nm between metal centers of adjacent tubes does not allow any direct exchange; however, the relatively smaller spacing of 0.65 nm between the iron atoms along the tubular length could allow for magnetic interaction between metal centers. In particular, the much closer spacing of 0.65 versus 1.2 nm between the metal centers of the PgC_1CFc tube versus dimer, respectively, should allow a much stronger anti-ferromagnetic interaction for the PgC_1CFc tubes. However, the interaction temperature, while larger in magnitude in the tube at -0.474 K, is not significantly larger than that of the dimer (-0.387 K). There are two possibilities for this deviation: (1) the Fc centers are not periodic along the tubular length, or (2) the alignment of the magnetic centers along the tube is multidirectional, resulting in a net reduction in the average interaction temperature. Finally, these crystallographic differences between PgC_1CFc dimers and tubes account for a lower interaction temperature (-0.387 K) for the PgC_1CFc dimer, as explained above, but also for a higher bohr magneton ($2.35 \mu_B$) for PgC_1CFc dimer due to the potential for multidirectional alignment along the length of the tube reducing the average moment in the tube.

A simple comparison of the distances between nickel centers of adjacent nanocapsules with those of iron centers of adjacent PgC_1CFc dimers and tubes suggests that adjacent nanocapsules would have limited effect on their neighbors, and then only through very weak dipolar interactions. This suggestion is supported by the interaction temperatures obtained from the Curie–Weiss fits for the PgC_1CFc tubes and dimers as well as the PgC_3Ni hexamers and dimers. However, the iron center in

Fc proves to be a magnetically stronger guest moiety that overcomes the rapid fall-off in the dipolar interaction and allows the relay of information between guests of adjacent H-bonded PgC_n hosts. The fact that the long-range magnetic interactions between adjacent guests on different hosts is observed exclusively for the PgC_1C_n tube and dimer can be attributed to differences in the coordination environment of the metal centers of the PgC_3Ni hexamer/dimer. The M–M distances for the PgC_3Ni dimer/hexamer obtained from crystallographic evidence suggest that the even number of metal atoms and symmetric triads/equatorial belt of nickel centers in a hexameric or dimeric framework reduces the overall magnetic moment of the nanocapsule.³⁷

Overall, we have studied the magnetic interaction between guest molecules of adjacent tubular and capsular PgC_n -based hosts. Both the PgC_1C_n tube and dimer are paramagnetic in behavior and have weak anti-ferromagnetic alignment at low temperatures. The negative interaction temperature suggests weak dipolar interactions between Fc guest molecules of adjacent nanocapsules. Therefore, the current study allows us to compare the magnetic properties of a PgC_n -based magnetic guest (PgC_1C_n) versus a magnetic wall (PgC_3Ni). This is the first time we have observed measurable magnetic interactions between adjacent nanocapsules and a relay of information between adjacent pyrogallol hosts, due, in part, to the larger moment of the Fc guest. In conclusion, magnetic interaction between metal centers is more pronounced in a magnetic wall versus a guest for a given nanocapsule, whereas a relay of magnetic information between adjacent PgC_n hosts is observed exclusively for PgC_n hosts containing magnetic (Fc) guests. It is likely that combined investigations of solid-state properties and magnetic behavior will prove beneficial in characterizing more species to discern and modify their properties for possible electronic applications.

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Notes

The authors declare no competing financial interest.

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