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ARTICLE TYPE

Packing Arrangements of Copper-seamed C-alkylpyrogallol[4]arene Nanocapsules with Varying Chain Lengths

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The syntheses and single-crystal XRD structures of copper-seamed C-alkylpyrogallol[4]arene (PgC_nCu, n=3, 7, 9) hexamers with different tail lengths are reported. Differences in the packing arrangements as a function of tail length are revealed. The progression in the size of the hexamers in the solid state is in agreement with that in the solution phase.

The self-assembly of molecular capsules and metal-organic frameworks (MOFs) has been an active area of research over the last decade.¹ MOFs have long, extended channels and have been studied for gas storage, separation and sorption properties. Metal cages, in contrast, are enclosed frameworks with finite void volumes that are suitable for encapsulation of various sized guest molecules. The bowl-shaped pyrogallol[4]arene macrocycle is a supramolecular building block that self-assembles into hydrogen-bonded and metal-seamed molecular cages/capsules, as well as into tubular superstructures with extended channels.² Aside from spheres and tubes, these macrocycles self-assemble into ellipsoidal, toroidal, and bilayer type architectures.^{1f, 3} Factors that control the resultant architecture include the reagent ratio (metal cation:macrocycle:base) and solvent system.⁴ For example, the ratio of pyridine:pyridinium nitrate directs the formation of tubular vs. spherical Fe³⁺-seamed pyrogallol[4]arene-based frameworks in solution.⁵

The pyrogallol[4]arene-based nanocapsules that have a spherical topology are of particular interest because of their potential to accommodate guests, such as fluorophores or drugs, within the enclosed space.⁶ Cohen and co-workers have investigated the stability and self-recognition properties of H-bonded pyrogallol[4]arene and resorcin[4]arene hexamers in chloroform using diffusion NMR. The H-bonded pyrogallol[4]arene hexamers are more stable than the resorcin[4]arene hexamers due to the presence of the additional 24 H-bonds in the former. The metal-seamed frameworks were expected to be even more stable in solution than the H-bonded hexamers, but this expectation was not always met.⁷ Cu- and Ni-seamed pyrogallol[4]arene hexamers and dimers have stable scaffolds, whereas the Ga- and Ga/Zn-seamed pyrogallol[4]arene hexamers rearrange from rugby-ball and spherical geometries in the solid state, respectively, to toroids in solution.⁸

The current study compares the packing arrangements of three copper-seamed C-alkylpyrogallol[4]arene hexamers (PgC_nCu) with different tail lengths 'n' (n= 3, 7, 9) (Figure 1). Our interest in these hexamers arises from the fact that although a structural rearrangement is not observed on dissolution or as a function of tail length, a smooth predictable increase in the size of the hexamer is observed as a function of tail length in the solution

phase. In our previous study, the alkyl tails of the PgC₁₁Cu, PgC₁₃Cu and PgC₁₇Cu hexamers were more distinguishable in solution than the tails of hexamers with smaller n values, as evidenced by small-angle neutron scattering (SANS) studies.^{7b, 9} The SANS data for the PgC_nCu hexamers with n ≤ 9 fit best to Schulz spheres, whereas the data for the hexamers with n = 11, 13 fit best to core-shell spheres.⁹ Interestingly, for the longer tail length of C17, the copper hexamer is seen as an ellipsoid in solution, wherein the aggregates of spheres are assembled via interactions between the alkyl tails.⁹ Thus, the solution studies suggest that interactions between the side chains of adjacent nanocapsules are more distinct for longer tail lengths. Even though this effect would be lessened for hexamers with n ≤ 9, the same trend should be observable by studying the interactions of these hexamers using single crystal X-ray diffraction.

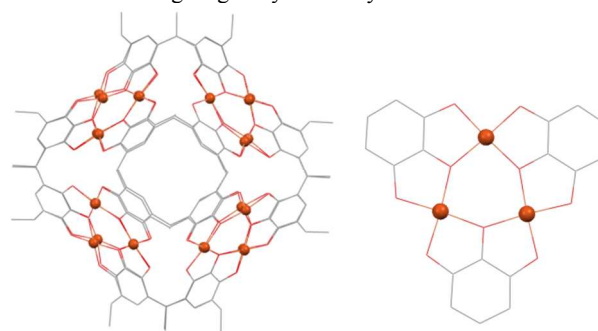


Fig 1. A single copper-seamed C-methylpyrogallol[4]arene hexamer is shown in the figure (left). A zoomed-in view of the triad is shown on right. The hexamer is shown as a wire framework except for metal centers which are shown as orange balls. Hydrogens are removed for clarity.

To investigate whether this trend is observed in the solid state, we studied the structures of copper-seamed hexamers based on C-heptylpyrogallol[4]arene and C-nonylpyrogallol[4]arene. Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of acetic solutions of PgC₇Cu and PgC₉Cu. Prolonged standing and slow crystallization aided in the formation of brown-coloured single crystals of the two hexamers. The crystals diffracted poorly due to the long alkyl tails; the positions of the framework atoms are clearly defined but the positions of some tail atoms are not. Note that we discuss the crystal structure of both the C7 and C9 hexamers, but we report the crystal structure of only C7, due to the disorder in the tails. However, the overall spherical framework is stable, which allows analysis of the differences in the packing arrangements. Previously reported crystallographic

data for the PgC_3Cu hexamer was used as an additional data point in this comparison.¹⁰

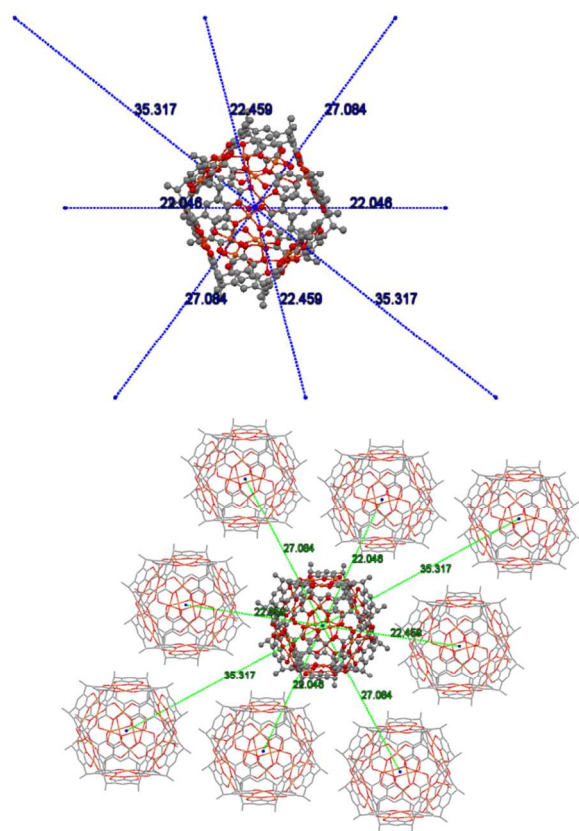


Fig. 2. Packing arrangement of PgC_7Cu hexamer. Blue dots represent hexamer centroids and blue and green lines represent distances between the centroids. H atoms, alkyl tails and solvent molecules have been removed for clarity.

PgC_7Cu and PgC_9Cu crystallize in the triclinic space group P-1. The previously reported PgC_3Cu hexamer crystallizes in the monoclinic space group $\text{C}2/c$.¹¹ The asymmetric unit (ASU) of any given PgC_nCu hexamer consists of a half hexamer composed of one full bowl of PgC_n , two half bowls of PgC_n , 12 Cu centres, and several solvent molecules within and outside the capsules, near the Cu_3O_3 triads. The alkyl tails of these hexamers extend into non-solvated regions, away from the Cu_3O_3 triad faces. The distance between the Cu and pyrogallol oxygen atoms is $\sim 2 \text{ \AA}$, and the distance between outer oxygen atoms of adjacent pyrogallols is $\sim 2.4 \text{ \AA}$, indicating H-bonded interactions between these moieties on the basis of the criteria recommended for supramolecular and biochemical systems.¹¹⁻¹²

The core structure $(\text{PgC}_0)_6\text{Cu}_{24}$ is similar for all of the metal-seamed hexamers studied. However, the packing arrangements and intercapsular distances for the adjacent-, diagonal- and interlayer-positioned hexamers vary at least partially as a function of tail length. The shortest distance between two adjacent PgC_9Cu , PgC_7Cu , and PgC_3Cu hexamers is 22.330, 22.046 and 20.573 \AA , respectively. This distance corresponds to the closest distance between two flat faces of two adjacent hexamers. A smooth decrease in distance with decreasing tail length is not observed because the hexamers are offset rather than directly opposite to each other when $n = 7, 3$.

The PgC_7Cu hexamer crystallizes in the same space group (P-1) as that of PgC_9Cu and packs with a centroid-to-centroid distance of 22.05 \AA between adjacent hexamers (Figure 2). The oppositely and diagonally positioned hexamers are 27.08 and 35.32 \AA apart. Note that the distances between adjacent hexamers are shorter for PgC_7Cu than for PgC_9Cu , whereas the progression is reversed with respect to the diagonal distances. The latter trend is due to the larger offset in triad faces for PgC_7Cu vs. PgC_9Cu . The PgC_3Cu hexamer has a longer adjacent distance of 24.5 \AA (translation along the c-axis) and shorter diagonal distances of 20.5, 22.4 and 21.5 \AA between hexamers (Figure 4).¹⁰

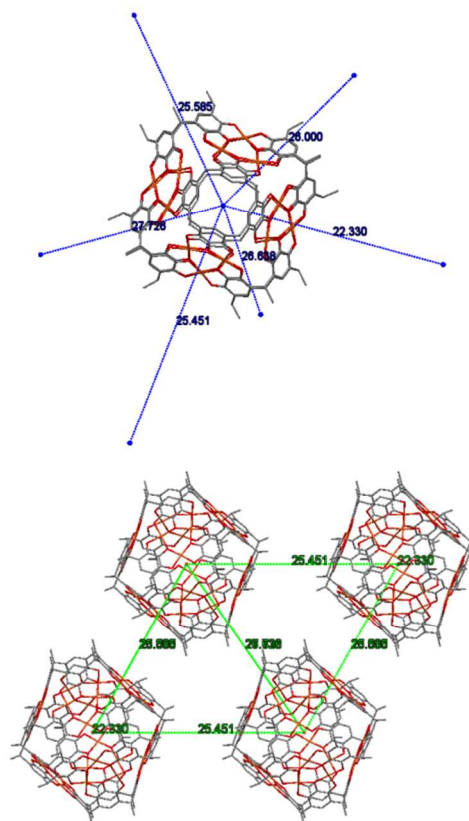


Fig. 3. Packing arrangement of PgC_9Cu hexamer. Blue dots represent hexamer centroids and blue and green lines represent distances between the centroids. H atoms, alkyl tails and solvent molecules have been removed for clarity.

Figure 3 shows the packing arrangement of PgC_9Cu along the a-axis. Considering the centroid of the hexamer positioned at the origin of the a-axis, the centroid-to-centroid distances between adjacent hexamers along the b- and c-axes are 25.45 and 25.59 \AA , respectively (translation along the unit cell axis). The centroid-to-centroid distances of diagonally aligned hexamers in adjacent layers and along the same plane/layer are 26.64 and 27.73 \AA , respectively.

Some of the tails of all the hexamers are ordered, whereas the tails close to the Cu_3O_3 planes are disordered. This disorder is due to the presence of solvent molecules, either as Cu^{2+} ligands or independent molecules, close to the copper centres. Some of these molecules have a site occupancy factor of less than one, which leads to several possible packing arrangements for the C-alkyl tails. The radius of a PgC_nCu hexamer in the solid state, as measured from the centroid of the hexamer interior to the last carbon of the longest alkyl chain,

matches closely with that in solution. That is, the estimated radius (Å) of 11.1 for PgC_3Cu , 16.6 for PgC_6Cu and 18.6 for PgC_9Cu in the solid state is close to that of 10.2 for PgC_3Cu , 14.9 for PgC_6Cu and 17.6 for PgC_9Cu in solution.^{7b} This similarity suggests that the PgC_nCu hexamers are monodisperse in solution and that the solid-state structures are mirrored in solution.

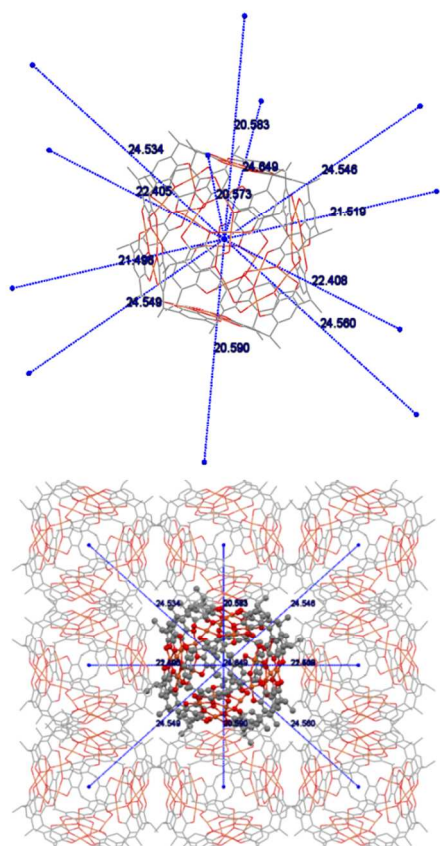


Fig. 4. Packing arrangement of PgC_3Cu hexamer.¹⁰ Blue dots represent hexamer centroids and blue and green lines represent distances between the centroids. H atoms, alkyl tails and solvent molecules have been removed for clarity.

Conclusions

In summary, we discuss the packing arrangements of copper-seamed pyrogallol[4]arene hexamers (PgC_3Cu , PgC_7Cu , PgC_9Cu) as a function of tail length. The closest distance of ~ 20.5 Å is observed between adjacent PgC_3Cu hexamers across the faces of the Cu_3O_3 triads. A progression in closest contact distance is observed from PgC_3Cu to PgC_9Cu in the solid state; however, this effect is not observed when the triad faces are offset (C7). In addition, the progression in radius of PgC_nCu hexamers across extended chains is observed in both the solid and solution phases.

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Notes and references

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Crystal data for PgC_7Cu : $\text{C}_{384}\text{H}_{432}\text{O}_{12}\text{Cu}_{24}\cdot 14(\text{C}_3\text{H}_6\text{O})\cdot 10(\text{CH}_4\text{O})$, $M = 8857.73$, red plate, $0.05 \times 0.25 \times 0.45$ mm³, triclinic, space group $P-1$, $a =$

$22.0457(7)$, $b = 22.4594(7)$, $c = 23.5621(8)$ Å, $\alpha = 65.687(2)^\circ$, $\beta = 82.024(2)^\circ$, $\gamma = 74.965(2)^\circ$, $V = 10261.0(6)$ Å³, $Z = 1$ Bruker Apex II CCD Diffractometer with Incoatec microfocus tube, $\lambda = 1.54178$ Å, $T = 100(2)$ K, $2\theta_{\text{max}} = 65.1^\circ$, 111222 reflections collected, 31348 unique ($R_{\text{int}} = 0.0344$). Final $\text{Goof} = 1.016$, $R1 = 0.0903$, $wR2 = 0.2783$, R indices based on 25697 reflections with $I > 2\sigma(I)$ (refinement on F^2). CCDC No: 973458

Crystal data for PgC_9Cu : $\text{C}_{384}\text{H}_{479}\text{O}_{103.50}\text{Cu}_{24}$, $M = 8620.49$, red plate, $0.05 \times 0.25 \times 0.45$ mm³, triclinic, space group $P-1$, $a = 22.3303(3)$, $b = 25.4510(4)$, $c = 25.5851(4)$ Å, $\alpha = 114.188(2)^\circ$, $\beta = 114.686(2)^\circ$, $\gamma = 94.065(2)^\circ$, $V = 11527.0(3)$ Å³, $Z = 1$ Bruker Apex II CCD Diffractometer, $\lambda = 0.71073$ Å, $T = 173(2)$ K, $2\theta_{\text{max}} = 23.3^\circ$, 96688 reflections collected, 33084 unique ($R_{\text{int}} = 0.0698$). Final $\text{Goof} = 1.230$, $R1 = 0.0998$, $wR2 = 0.3617$, R indices based on 17838 reflections with $I > 2\sigma(I)$ (refinement on F^2).

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Graphical Abstract**Packing Arrangements of Copper-seamed C-alkylpyrogallol[4]arene Nanocapsules with Varying Chain Lengths**

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The synthesis and structural elucidation of copper-seamed C-alkylpyrogallol[4]arenes hexamers with different tail lengths ($n=3,7,9$) reveal differences in packing-arrangements.

