

# Controlled 2D Assembly of Nickel-Seamed Hexameric Pyrogallol[4]arene Nanocapsules

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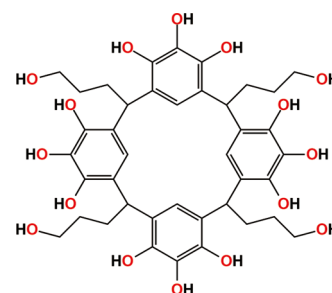
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**S** Supporting Information

**ABSTRACT:** The two-dimensional framework of nickel-seamed hexameric metal–organic nanocapsules has been synthesized by connecting the tailed hydroxyl groups of C-propan-3-ol pyrogallol[4]arene with adjacent hexameric capsules via nickel-hydroxyl coordination. In addition, functionalization of nanocapsules with multiple pyridine molecules at the capsule surface prevents them from assembling into hierarchical structures and leads to the formation of discrete nickel-seamed pyrogallol[4]arene nanocapsules. This work shows that surface functionalization of nanocapsules is an effective and innovative method of controlling the assembly of these nanometric building blocks.

The rational design and construction of hierarchical nanostructures by assembling nano building blocks have emerged as a powerful strategy for preparation of unprecedented functional materials with extensive applications ranging from energy storage,<sup>1–7</sup> sensing,<sup>8,9</sup> to biomedicine.<sup>10,11</sup> As one class of nano building blocks, supramolecular nanocapsules attract interest due to their potential applications in fields such as catalysis,<sup>12</sup> molecular encapsulation,<sup>13,14</sup> and gas adsorption/separation.<sup>15</sup> Extensive studies have been done on the synthesis and applications of supramolecular nanocapsules;<sup>16–19</sup> however, assembling these nanocapsules into more complex hierarchical structures still remains largely unexplored. In our previous studies, we focused on the construction of supramolecular nanocapsules using C-alkylresorcin[4]arenes (R<sub>s</sub>C<sub>n</sub>s) and C-alkylpyrogallol[4]arene (PgC<sub>n</sub>s) and successfully discovered nanocapsules of various sizes and shapes such as hydrogen-bonded and metal-seamed dimeric/hexameric nanocapsules.<sup>17,19–23</sup> The design and preparation of hierarchical nanostructures in a controllable manner is achieved by using these nanocapsules as building blocks,<sup>24–26</sup> and connecting dimeric nanocapsules with bipyridine type linkers into 1D chains of PgC<sub>n</sub>Cu dimers or 2D networks of PgC<sub>n</sub>Zn dimers. However, dimeric nanocapsules only have eight metal ions available for further connection and all the metal ions are in one plane, which limits the use of these building blocks in only 1D and 2D assemblies. In this context, hexameric nanocapsules which can be viewed as an octahedron attract our interest.<sup>17</sup> These nanocapsules have totally eight [M<sub>3</sub>O<sub>3</sub>] trimetallic clusters, each of which located on one of the eight faces of an octahedron. The 24 metal ions and their 3D distribution in an octohedral geometry offer an opportunity for construction

of hierarchical structures with much more variety and complexity, especially on a 3D scale. Considering the overall size and complexity, assembling hexameric nanocapsules into complex hierarchical structures is significantly more challenging. Another strategy for the connection of nanocapsules is the use of pyrogallol[4]arenes with functional alkyl groups such as hydroxyl groups, which can act as both structural components of nanocapsules and as linkers for nanocapsule connection. We previously reported the synthesis of a 2D framework of Cu hexamers by reacting C-propan-3-ol pyrogallol[4]arene (PgC<sub>3</sub>OH, Figure 1) with copper nitrate in a solution of



**Figure 1.** C-Propan-3-ol pyrogallol[4]arene macrocycle.

acetone and water.<sup>17</sup> Due to the hydroxyl groups being exposed to the exterior, one nanocapsule is connected to four other nanocapsules via copper–oxygen(hydroxyl) coordination.<sup>17</sup> The dual function of PgC<sub>3</sub>OH for the construction and connection of nanocapsule frameworks has not been further explored for over a decade. In this report, we present the preparation of a 2D assembly of nickel-seamed hexameric nanocapsules (**I**, [Ni<sub>24</sub>(C<sub>40</sub>H<sub>35</sub>O<sub>16</sub>)<sub>6</sub>(DMF)<sub>2</sub>(H<sub>2</sub>O)<sub>40</sub>]), in which coordination connection is established among the nanocapsules. Furthermore, we show that functionalization of the nanocapsule surface with multiple pyridine ligands blocks the coordination sites and thus prevents this linking and assembly of these nanocapsules, which leads to the formation of discrete nickel-seamed nanocapsules (**II**, [Ni<sub>24</sub>(C<sub>40</sub>H<sub>36</sub>O<sub>16</sub>)<sub>6</sub>(DMF)<sub>4</sub>(H<sub>2</sub>O)<sub>24</sub>(py)<sub>20</sub>]).

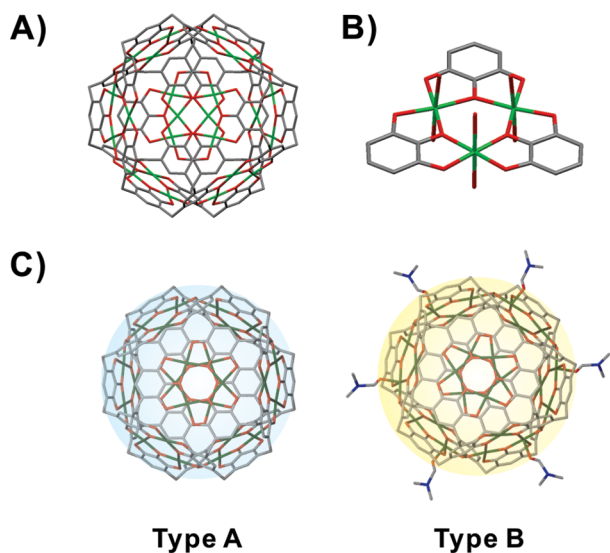
In a typical synthesis of **I**, 0.1 mmol of PgC<sub>3</sub>OH is mixed well with 0.4 mmol of nickel nitrate in DMF/MeCN (1:1) followed by the addition of 0.2 mmol of arginine as a modulator (see Supporting Information for details). Although same crystalline

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products can be prepared without the addition of arginine, the batch with arginine has a better yield and crystal quality. We speculate that the basic nature of arginine would facilitate deprotonation of phenolic/alkyl hydroxyl groups of  $\text{PgC}_3\text{OH}$  and the carboxylic groups would act as ligands and compete with the phenolic/alkyl hydroxyl groups of  $\text{PgC}_3\text{OH}$  for coordination.<sup>27</sup> In this way, the yield and quality of crystalline products are improved. The synthesis utilizes a solvothermal reaction, which produces crystalline materials of high quality and yield in a short time period. After heating the reaction mixture overnight at 100 °C, large green crystals are formed and collected for single crystal X-ray structural analysis.

The crystal structure of **I** shows that the framework is constructed from  $\text{Ni}^{2+}$  seamed pyrogallol[4]arene hexameric nanocapsules. Each nanocapsule consists of six  $\text{PgC}_3\text{OH}$  macrocycles and 24 nickel divalent cations, and the overall geometry corresponds to that of a cuboctahedron, which is similar to the previously reported divalent Cu-, Ni-, or Co-seamed hexameric nanocapsules (Figure 2A).<sup>17,20,23</sup> The

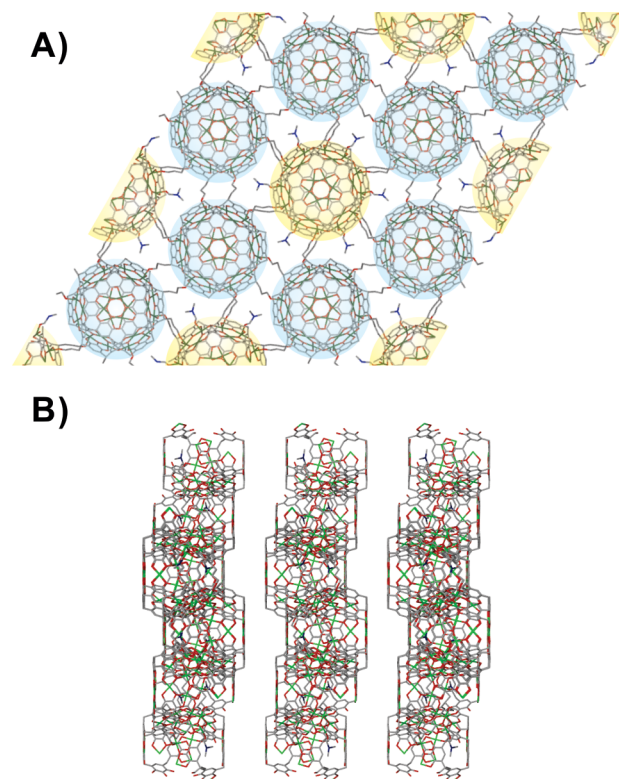


**Figure 2.** (A) Side view of nickel-seamed hexameric pyrogallol[4]arene nanocapsules along the direction of [001]. (B) Coordination environment of nickel atoms. (C) Two types of nickel nanocapsules as building blocks (Type A in blue and Type B in yellow). Color codes: nickel (green), carbon (gray), oxygen (red), and nitrogen (blue). Hydrogen atoms, axial water ligands, and hydroxyl alkyl tails were removed for clarity.

nanocapsule is held together by eight  $[\text{Ni}_3\text{O}_3]$  trimetallic clusters (Figure 2B) with Ni–O distances ranging from 1.976 to 2.056 Å; O–Ni–O angles, 99.48–100.30°; and Ni–O–Ni angles, 139.08–139.82°. All nickel centers employ an octahedral ligand field. The equatorial positions are all coordinated with oxygen atoms from the upper rim of a pyrogallol[4]arene. Within the structure, there are two types of individual nanocapsules (Figure 2C). For Type A nanocapsules, all axial ligands are water molecules, while, for Type B, the 24 axial positions are occupied by six DMF and 18 water molecules outward and 24 water molecules inward. In order to counterbalance the charges of nickel cations, 48 phenolic groups are deprotonated to form nickel–hydroxyl bonds, and the remaining 24 upper-rim hydroxyl groups still hold the assembly together through strong O–H $\cdots$ O<sup>−</sup> type hydrogen bonding as evidenced by the short distance between oxygen

atoms (2.437–2.480 Å). This leads to totally 96 metal–oxygen coordination bonds and 24 intramolecular hydrogen bonding interactions, which endows the nanocapsules with high stability in both solid and solution states.<sup>28</sup> Furthermore, strong hydrogen bonding interactions are also found between the axial metal-coordinated water molecules of two neighboring  $[\text{Ni}_3\text{O}_3]$  units considering the O $\cdots$ O distance (2.516–2.638 Å).

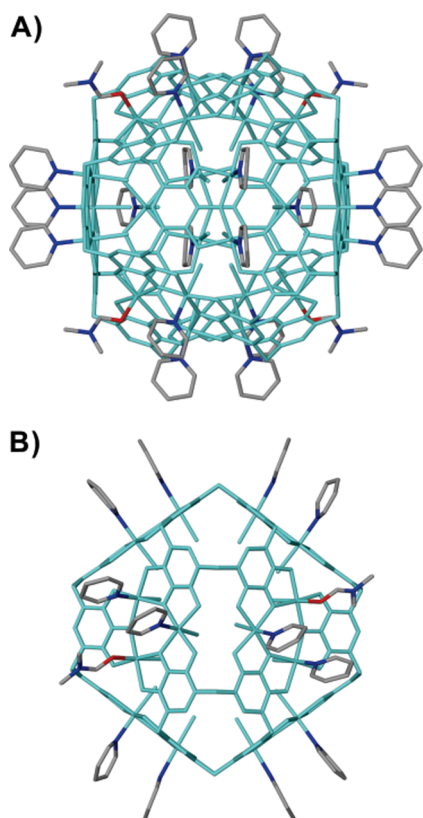
An extended view of **I** along the direction of [001] shows that each nanocapsule is connected with six nanocapsules via nickel-hydroxyl coordination (Figure 3). Within each pair of



**Figure 3.** (A) Extended view of 2D assemblies of nickel-seamed hexameric nanocapsules along the direction of [001]. (B) Extended view of 2D assemblies along the direction of [100]. Color codes: nickel (green), carbon (gray), and oxygen (red). Hydrogen atoms, axial water molecules, and hydroxyl alkyl tails not involved in metal–ligand coordination to adjacent capsules were removed for clarity.

nanocapsules, one capsule provides a hydroxyl tail and a metal coordination site for another. Therefore, every nanocapsule is linked with six adjacent nanocapsules via 12 hydroxyl alkyl chains (Figure 3A), which stabilize the 2D framework. The framework employs the hexagonal packing pattern with one Type B nanocapsule surrounded by six Type A nanocapsules and one Type A nanocapsule surrounded by three of each type (overall Type A: Type B = 2:1). The extended view along the [100] direction shows the layered structure of these 2D assemblies (Figure 3B). Within each layer, these nanocapsules also hold a wave-like packing pattern (Figure 3B).

To test the effect on the formation of nickel nanocapsules using other modulators, pyridine was introduced in similar reaction conditions as **I**. Surprisingly, discrete nickel hexameric nanocapsules (**II**) were synthesized in the presence of pyridine. These nanocapsules have similar hexameric structures as in **I** (Figure 4A and 4B). The prominent difference is that the discrete nanocapsules have 20 pyridine and four DMF



**Figure 4.** (A) Side view of pyridine/DMF ligated nickel-seamed hexameric pyrogallol[4]arene nanocapsules along the direction of [001]. (B) Side view of pyridine/DMF ligated nickel-seamed hexameric pyrogallol[4]arene nanocapsules along the direction of [010]. In order to highlight the pyridine and DMF ligands on nanocapsule surface, the nanocapsule structure was shown in light blue. Hydrogen atoms, axial water ligands, and hydroxyl alkyl tails were removed for clarity. Color codes for pyridine and DMF molecules: carbon (gray), oxygen (red), and nitrogen (blue).

molecules coordinated exterior to the nanocapsule at the axial positions. Compared with alkyl hydroxyl groups, pyridine molecules have stronger binding affinity to nickel atoms. Therefore, functionalization of the nanocapsule surface with pyridine ligands can prevent further assembly of nanocapsules into hierarchical structures by competing with metal–hydroxyl coordination. This demonstrates that surface functionalization of nanocapsules is an effective method of controlling the assembly of such nanomeric entities. The extended views of I along the directions [100] and [001] show that these nanocapsules are separated from each other (Figure S1). All the hydroxyl alkyl chains are exposed to the exterior, which allows for possible postsynthetic functionalization.

In summary, we have shown the preparation of a 2D assembly of nickel-seamed  $\text{PgC}_3\text{OH}$  hexameric nanocapsules. Interestingly, by using pyridine as functional ligands at the nanocapsule surface, the nanocapsules remain as discrete entities rather than in a 2D framework arrangement. This study demonstrates that the use of  $\text{PgC}_3\text{OH}$  as both a nanocapsule component and bridging linker is an effective strategy for the rational design and synthesis of nanocapsule frameworks. Future effort can be extended to the design and preparation of 3D frameworks of nanocapsules. In addition, surface functionalization of the nanocapsules can be utilized as

a method of controlling the assembly of these nanocapsules into complex hierarchical structures.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b00037.

Full details for sample preparation and characterization results (PDF)

Crystallographic data; CCDC 1521975 and 1521976 contain the supplementary crystallographic data for this paper, provided free of charge by The Cambridge Crystallographic Data Centre (CIF, CIF)

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### Notes

The authors declare no competing financial interest.

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