Solid Structures of the Stepwise Self-assembled Copillar[5]arene-based Supramolecular Polymers

Yeon Sil Park, Seong Min Hwang, Jaeyeon Shin, and Kyungsoo Paek*

*Department of Chemistry, Soongsil University, Seoul 156-743, Korea. *E-mail: kpaek@ssu.ac.kr*

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Development of supramolecular polymer has attracted much interest because of their interesting properties such as stimuli-responsiveness, recycling, self-healing and degradability, and their consequential applications.[1] The essential feature of this class of polymers is the self-assembly of discrete monomeric subunits via non-covalent interactions or dynamic covalent bonds. Among the many monomeric subunits, pillar[n]arenes[2] have been ideal building blocks for the fabrication of polymeric supramolecules because of their intrinsic characteristics and properties such as facile preparation and flexible modification, π-rich cavities, as well as peculiar guest complexation capability.[3]

In our previous report,[4] we have reported that ureidopyrimidinonyl copillar[5]arene **1**, dicationic **2** or tricationic guest **3** can assemble linear or dendritic supramolecular polymers **P** or **D** in solution, which were assembled through quadruple hydrogen bonds and cation–π interactions. We herein report the solid-state morphologies of their stepwise self-assemblies.

Ureidopyrimidinone-functionalized copillar[5]arene **1** was prepared by reaction of 2-(1-imidazolylcarbonylamino)-6-methyl-4(1H)-pyrimidinone with amino-copillar[5]arene which was synthesized. The repeating guest units, dicationic guest **2** and tricationic guest **3**, have ethynylbenzene moiety and pyridinium salt which are linked together by a flexible C8 alkyl chain, and were synthesized in good yields by a four step process (Figure 1).[4]

Copillar[5]arene **1** with a ureido-4[1H]-pyrimidinone unit forms a stable dimer $\mathbf{1}_2$ ($K_{\text{dimm}} > \sim 10^7\ \text{M}^{-1}$)[5] by quadruple hydrogen bonding in nonpolar conditions, and the dimer $\mathbf{1}_2$ was applied to form a self-assembled supramolecular polymers **P** and **D** through cation–π interactions with dicationic **2** or tricationic guests **3** [K_a of pillar[5]arene-pyridium cation: $7.61 \times 10^2\ \text{M}^{-1}$ in $CDCl_3$-CD_3CN (5:1, v/v)].[4] The dimerization of host **1** and the successive assembly of dimer $\mathbf{1}_2$ with dicationic guest **2** or tricationic guests **3** were observed by ^1H NMR experiments as well as 2D-DOSY NMR experiments through stepwise addition of host and guest (Figure 2).[4]

The combination of copillar[5]arene **1** and dicationic guest **2** could form linear supramolecular polymers **P** - (Figure 2(a)). To visualize the successive formation of each stepwise self-assembly of supramolecular polymer **P** in solid state, atomic force microscopy (AFM) studies were performed (Figure 3). Samples of each stepwise self-assembly confirmed by ^1H NMR experiment were spin-coated onto a Si-wafer surface. The high-resolution AFM images revealed the formation of relatively regular isolated nano-ring structures. According to the stepwise increase from **P1** to **P4**, the diameters of the typical nano-ring gradually increased from 2 μm to 29 μm (**P1** = 2 μm, **P2** = 6 μm, **P3** = 15 μm, **P4** = 29 μm). But, supramolecular polymers **P** maintained its average wall thickness of 2 μm regardless of the stepwise additions.

The ring-shaped morphologies in supramolecular polymer **P** are probably due to the tendency of the end-to-end connection[6] in the solid state of long flexible supramolecular chains. The size increase of nano-rings as the stepwise addition increases might be due to the fact that the linear supramolecular polymer **P** in solution seems to be maintained until the nano-ring formation by solidification.

On the other hand, for one pot addition, the high-resolution AFM image revealed relatively irregular form of nano-structures (see Supporting Information, Figure S13).

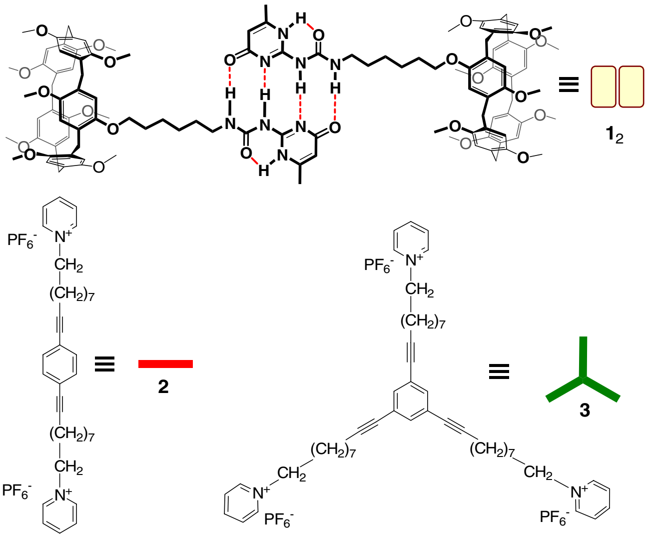

Figure 1. Chemical structures of $\mathbf{1}_2$, dicationic guest **2**, and tricationic guest **3**.

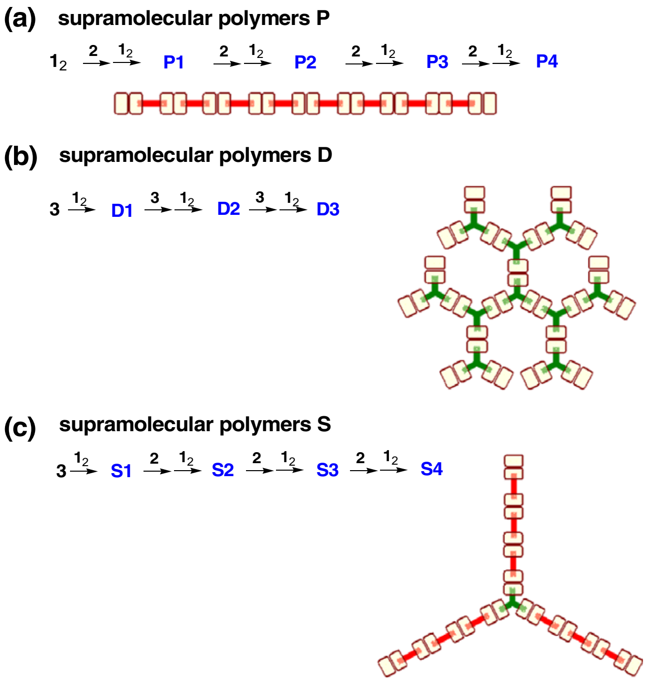

Figure 2. Schematic illustrations of supramolecular polymers (a) **P**, (b) **D**, and (c) **S** by stepwise self-assemblies of monomeric subunit $\mathbf{1}_2$ and **2** or **3**.

Dynamic light scattering (DLS) experiments were also carried out to investigate the size distributions of the supramolecular nanoparticles in each stepwise self-assembly. For supramolecular polymer **P**, the average hydrodynamic radius (D_h) of each stepwise self-assembly appeared **P1** = 6, 160 nm (≈6 μm), **P2** = 10, 276 nm (≈10 μm), **P3** = 16, 057 nm (≈16 μm), and **P4** = 29, 242 nm (≈29 μm), respectively. The measured average diameters of stepwise self-assemblies, especially of **P1** and **P2**, are larger than those of solid-state AFM results, owing to the swelling of the nanoparticles in solution state.

The combination of copillar[5]arene **1** and tricationic guest **3** could form dendritic supramolecular polymers **D** - (Figure 2(b)). AFM measurements of each stepwise self-assembly in supramolecular polymer **D** were performed on mica by spin-coating method (Figure 4). It is found that supramolecular polymer **D** formed nano-ring at first, and then aggregated to clods as the stepwise addition proceeds. The average diameter of these aggregates gradually increased from 2 μm to 8 μm. (**D1** = 2 μm, **D2** = 5 μm, and **D3** = 8 μm).

The combination of copillar[5]arene **1**, tricationic guest **3** as core guest, and dicationic guest **2** as expended guest can assemble supramolecular polymers **S** (Figure 2(c)). The morphologies of supramolecular polymers **S** were also investigated by AFM measurement (Figure 5). Interestingly

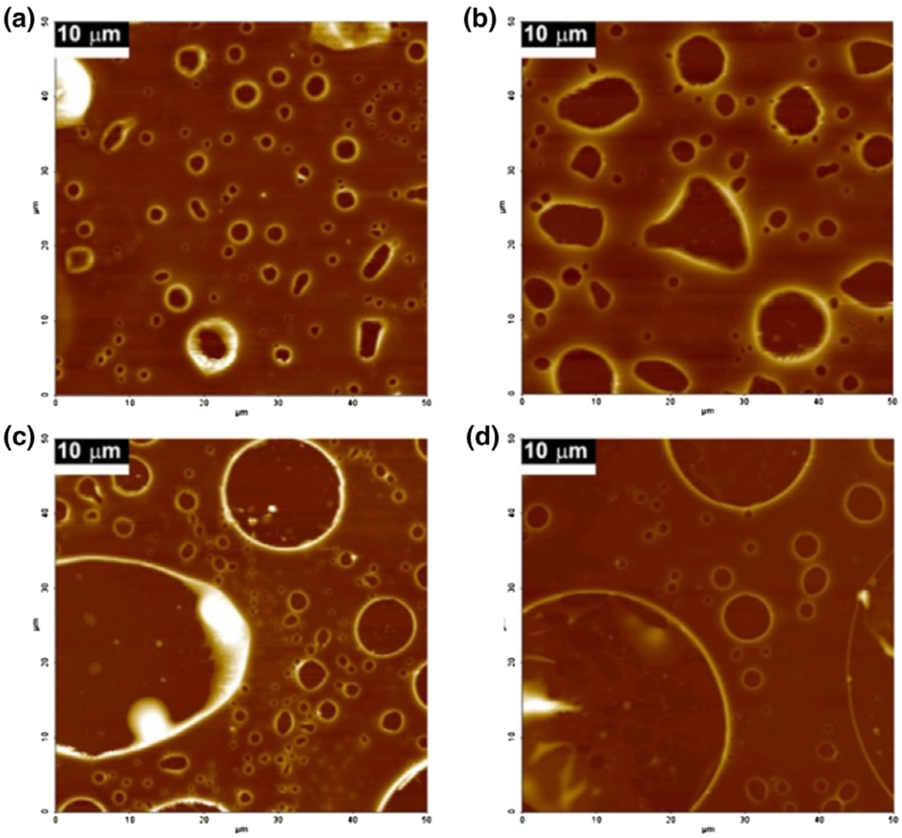

Figure 3. AFM height images of each stepwise self-assembly in supramolecular polymers **P** prepared by spin coating of a chloroform-acetonitrile (5:1, v/v) solution ($c = 1.0 \times 10^{-5}$ M) onto Si-wafer: (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**.

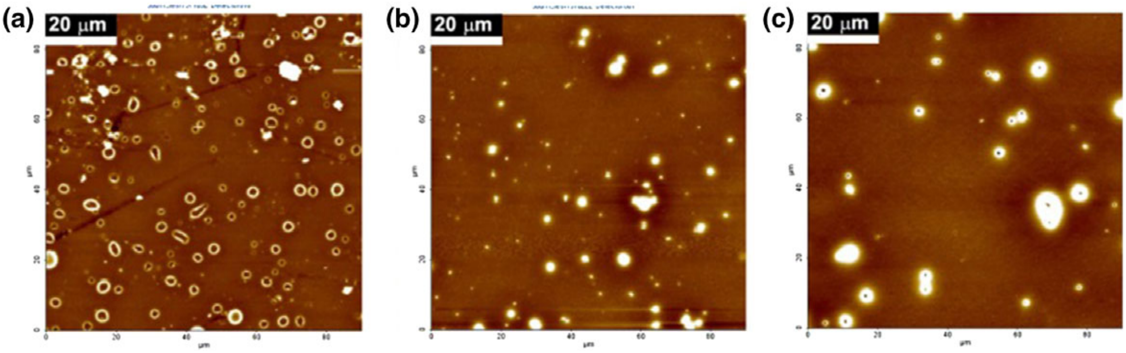

Figure 4. AFM height images of each stepwise self-assembly in supramolecular polymers **D** prepared by spin coating of a chloroform-acetonitrile (5:1, v/v) solution (c = 1.0 × 10^{-5} M) onto mica: (a) **D1**, (b) **D2**, (c) **D3**.

the supramolecular polymers **S** of all the generations self-assembled to nano-rings of the similar diameter (24 – 26 μm) and wall thickness (2 μm). Also branched non-circular structures were surrounded by these nano-rings. It is presumable that the growing polymer **S** was surrounded by a nano-ring formed by supramolecular polymer **P** before completion of its distinct self-assembled final structure, which means the growing polymer **S** acted as a template for the formation of a nano-ring as the solvent evaporated.

In summary, the solid states of self-assemblies of supramolecular polymers **P**, **D**, and **S** by stepwise additions of dimer $\mathbf{1}_2$ and guest **2** or **3** were investigated by AFM and dynamic light scattering experiments. AFM measurements in solid state showed that the linear supramolecular polymers **P** formed nano-ring and its size increased as the stepwise addition increased. Supramolecular polymers **D** which contains dimer $\mathbf{1}_2$ and tricationic guest **3** gave cloddish aggregates due to its dendritic assembling process. Supramolecular polymer **S** which contains dimer $\mathbf{1}_2$, tricationic guest **3** as core guest, and dicationic guest **2** as expended guest could not complete its distinct structure, but surrounded by nano-ring type suprapolymer. The studies for

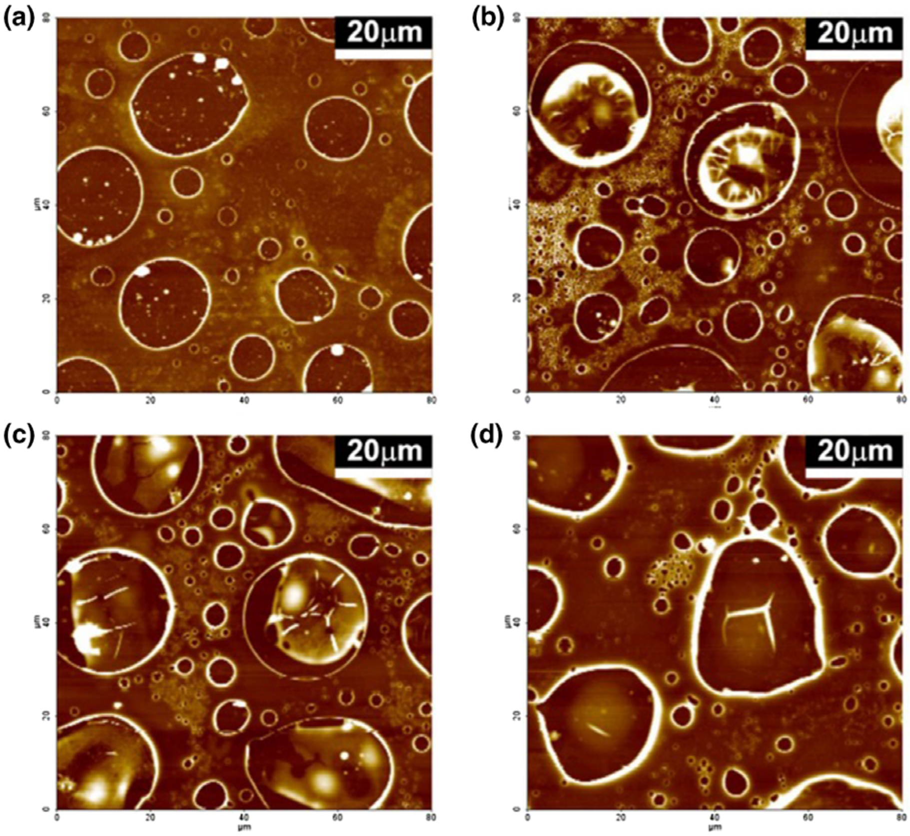

Figure 5. AFM height images of each stepwise self-assembly in supramolecular polymers **S** prepared by spin coating of a chloroform-acetonitrile (5:1, v/v) solution (c = 1.0 × 10^{-5} M) onto Si-wafer: (a) **S1**, (b) **S2**, (c) **S3**, (d) **S4**.

structures of supramolecular polymer in solution and its solid states will accelerate their applications.

Experimental

Synthesis of Copillar[5]arene 1. A suspension of aminocopillar[5]arene **7** (1.00 g, 1.20 mmol) and 2-(1-imidazolylcarbonylamino)-6-methyl-4(1H)-pyrimidinone **8** (0.27 g, 5.04 mmol) in $CHCl_3$ (60 mL) was stirred for 16 h at 60°C under argon atmosphere. After cooling to room temperature, the solvent was concentrated under reduced pressure. The precipitates were obtained by addition of CH_3OH (30 mL) to the residue. The precipitates were collected by filtration and washed with acetone. The crude product was recrystallized from CH_2Cl_2/CH_3OH (8:2) to give a white solid (1.01 g, 85%): ^1H NMR (400 MHz, $CDCl_3$) of $\mathbf{1}_2$ δ 13.11 (s, 1H), 11.87, (s, 1H), 10.26 (br t, 1H), 6.79–6.75 (m, 10H), 5.81 (s, 1H), 3.83 (t, J = 6.4 Hz, 2H), 3.78–3.76 (m, 10H), 3.70–3.65 (m, 27H), 3.30 (q, J = 6.4 Hz, 2H), 2.21 (s, 3H), 1.80 (m, 2H), 1.68 (m, 2H), 1.58 (m, 2H), 1.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) of $\mathbf{1}_2$ δ 173.1, 156.6, 154.6, 150.8, 150.74, 150.68, 150.6, 150.1, 148.2, 128.4, 128.33, 128.30, 128.27, 128.2, 128.14, 128.1, 125.5, 114.9, 114.2, 114.1, 113.9, 106.6, 68.5, 55.9, 55.8, 55.7, 40.0, 30.3, 29.8, 29.7, 29.6, 29.5, 29.4, 27.0, 26.2, 25.6, 18.9; HRMS (MALDI-TOF; $[M + H]^+$) calcd for $C_{56}H_{67}N_4O_{12}^+$: 987.4750, found 987.4765.

Atomic Force Microscopy. The AFM images were obtained using a XE-BiO (Park systems, Santa Clara, CA, USA). AFM thin film samples of each stepwise self-assembly confirmed by ^1H NMR experiment were prepared by spin coating of a chloroform-acetonitrile (5:1, v/v) solution ($c = 1.0 \times 10^{-5}$ M) onto cleaned Si-wafer or freshly cleaved mica.

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Supporting Information. Additional supporting information is available in the online version of this article.

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