

Growth of poly(pseudorotaxane) on gold using host-stabilized charge-transfer interaction†

Kyungpil Kim, Dongwoo Kim, Jae Wook Lee‡, Young Ho Ko and Kimoon Kim*

National Creative Research Initiative Center for Smart Supramolecules, Department of Chemistry, Division of Molecular and Life Sciences, Pohang University of Science and Technology, San 31 Hyojadong, Pohang 790-784, Republic of Korea. E-mail: kkim@postech.ac.kr; Fax: (+82)54-279-8129

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A novel supramolecular polymer (poly(pseudorotaxane)) in which the repeating units are linked by host-stabilized charge-transfer interaction between the guest molecules is grown on gold and characterized.

Supramolecular polymers in which their monomeric units are linked through noncovalent interactions such as hydrogen bonding, metal-ligand, π - π stacking, charge-transfer (CT), and host-guest interactions have received much attention in recent years.¹ The reversibility of noncovalent interactions in these supramolecular polymers leads to novel properties and behavior that is unique to this class of molecules; most notably, their properties can be altered in a controlled manner. Although studies on the growth of supramolecular polymers on surfaces are important not only for fundamental understanding but also for their applications such as in molecular devices and sensors, such studies are rare.²

Cucurbit[8]uril (CB[8]), a member of the host family cucurbit[*n*]uril,³⁻⁷ containing eight glycoluril units has a cavity comparable to that of γ -cyclodextrin. It exhibits remarkable host-guest properties including the encapsulation of a pair of electron-rich and electron-deficient guest molecules inside the cavity to form a stable 1 : 1 : 1 complex, which is driven by the markedly enhanced charge-transfer (CT) interaction between the guests inside the hydrophobic cavity of CB[8].^{5a} This discovery led us to build novel supramolecular assemblies using CB[8] and a guest molecule containing an electron-rich unit and an electron-deficient unit connected by a suitable linker. Depending on the length and flexibility of the linker between the donor and acceptor, three different types of supramolecular assemblies were obtained; a long and flexible linker favors a 1 : 1 complex by host-stabilized *intramolecular* CT complex formation,^{5b} whereas a short and/or rigid linker leads to a 2 : 2 complex or polymer (or poly(pseudorotaxane))^{7,8} by host-stabilized *intermolecular* CT complex formation.^{5c} Based on these results we have now studied the growth of a novel supramolecular polymer (or poly(pseudorotaxane)) on gold in which the repeating units are noncovalently linked by CT interaction between the guest molecules in a host, which is the subject of this communication.

For the synthesis of a poly(pseudorotaxane) we designed and synthesized the guest molecule **1** containing a 4,4'-bipyridinium unit and a 2-hydroxynaphthalene unit that are connected by a rigid *p*-xylylene linker to prevent the intramolecular CT complex formation inside CB[8]. When 1 equiv of CB[8] was added to **1** in H₂O, the color of the solution changed from yellow to red with a strong absorption band at around 482 nm, indicating formation of a CT complex. NMR spectroscopy using COSY, NOESY and DOSY techniques established that the complex between CB[8] and **1** formed in aqueous solution (2 mM) is a mixture of a 2 : 2 complex and a polymeric (oligomeric) species in a 3 : 2 ratio.⁸ From the hydrodynamic volume of the polymeric species measured by the DOSY technique⁹ the degree of polymerization was estimated to be ~4. The failure to observe species with a higher degree of polymerization in solution is presumably due to their poor solubility.

To grow the poly(pseudorotaxane) on gold, we first anchored the pseudorotaxane **3** comprising CB[8] threaded on **2** which contains a dipyrindiniummethylene unit, a stronger electron-acceptor than a 4,4'-bipyridinium unit, and a thiol terminus on the surface. The immobilized pseudorotaxane functions as a "seed" to initiate the formation of a linear poly(pseudorotaxane) on surface, utilizing the host-stabilized CT interaction as "glue" (Scheme 1). The self-assembled monolayer (SAM) of **3** on gold was prepared by immersing a gold substrate in an aqueous solution of **3** (prepared *in situ* from CB[8] and **2** in water) for 60 h. Using this SAM as a platform, the poly(pseudorotaxane) started to grow upon soaking the substrate in an aqueous solution containing CB[8] and **1**. The growth of the poly(pseudorotaxane) was monitored by reflectance FT-IR spectroscopy. The IR spectra (Fig. 1) show two characteristic CB[8] peaks at 1748 cm⁻¹ and 1470 cm⁻¹ corresponding to C=O and C-N stretching vibrations, respectively. These peaks grow with the increasing dipping time of the substrate in the solution and reach a maximum after a day; a longer immersion did not increase the intensity. The maximum intensity of the C=O peak obtained with 1 mM monomer solution is about 4 times as high as that of the initial SAM, indicating that the poly(pseudorotaxane)

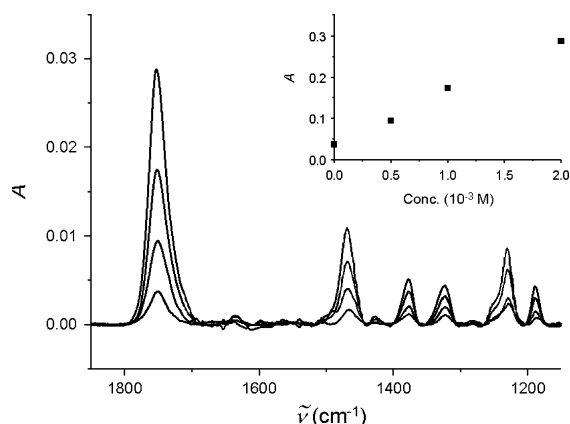
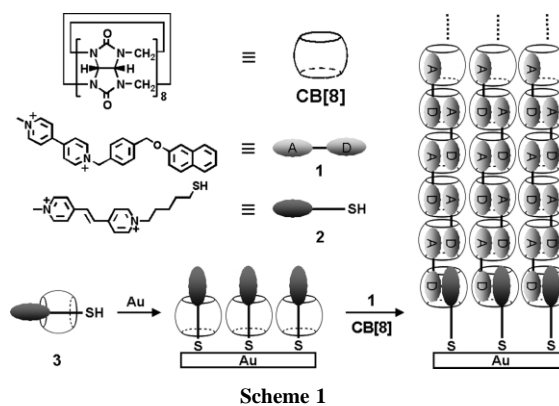


Fig. 1 FT-IR spectra of the poly(pseudorotaxane) grown on gold by dipping in the monomer solutions with different concentrations for a day. Inset: a plot of the absorbance at 1748 cm⁻¹ versus the concentration of the monomer solution.

† Electronic Supplementary Information (ESI) available: experimental details along with Figs. S1–S4. See <http://www.rsc.org/suppdata/cc/b4/b400783b/>

grown on gold has a degree of polymerization of ~ 4 . In addition, the IR data indicate that the degree of polymerization increases with increasing concentration of the monomer solution, which is similar to the typical behavior of supramolecular polymers in solution.^{1b} Therefore, the growth of the poly(pseudorotaxane) on the surface can also be controlled by the concentration of the monomer solution and immersion time. Furthermore, depolymerization occurred when the substrate with a grown polymer was immersed in pure water (see Fig. S2[†]), which confirms that the polymerization at the surface is reversible.

The poly(pseudorotaxane) formation was also monitored *in situ* by the surface plasmon resonance (SPR) technique.¹⁰ The following solutions were flowed over a gold substrate in sequence and the surface was washed with water after each step: (1) 1 mM of **3** (prepared *in situ* from CB[8] and **2** in water), (2) a 1 : 1 mixture CB[8] and **1** (1 mM) in water (325 μ l each injection). Step 2 was repeated several times (water was flowed between each injection). After the final injection, water was flowed for more than 20 min. The resulting SPR sensorgram is shown in Fig. 2. The initial change in the resonance angle, which corresponds to the increase in density to 0.41 ng mm⁻² after step (1) (and subsequent washing), is consistent with the formation of a platform SAM comprising 2.3×10^{-13} mol mm⁻² of the pseudorotaxane **3**. As the solution containing CB[8] and **1** was flowed on the SAM, the resonance angle gradually increased, indicating that the poly(pseudorotaxane) started growing up atop the platform. The SPR signal grows in steps with successive injections, eventually reaching a plateau. After the final washing, the change in the resonance angle corresponds to the increase in density to 1.4 ng mm⁻², which corresponds to about 7.3×10^{-13} mol mm⁻² of monomers (CB[8] + **1**). Assuming that all poly(pseudorotaxane), are grown at the same rate, we conclude that about 3 monomers are noncovalently polymerized on each seed unit **3**. On average, thus, 4 CB[8] molecules (including one CB[8] molecule of the platform SAM) make a stack, which is consistent with the results obtained by IR spectroscopy. No signal increase was observed in the absence of the platform SAM, which means that nonspecific adsorption did not occur on the gold surface.

The growth of poly(pseudorotaxane) on gold was also studied by atomic force microscopy (AFM). The substrates for the AFM study were prepared by evaporating gold on a Si(100) surface (Fig. 3a). When the SAM of **3** on the substrate was formed by immersing the substrate in a 1 mM aqueous solution of **3** for 60 h, the height of the substrate increased by 2.2 nm on average, which is comparable to the length of **3** when it is fully stretched out (2.1 nm). When the poly(pseudorotaxane) was grown on top of the platform SAM by soaking the substrate in a 1 mM aqueous solution of CB[8] and **1** for a day, large grains whose diameter is approximately 23 nm are observed in the AFM image (Fig. 3b) and the height of the substrate further increased by 3.9 nm on an average. According to a molecular mechanical calculation, the repeating unit of the poly(pseudorotaxane) measures ~ 1.4 nm (see Fig. S4[†]), which suggests that the poly(pseudorotaxane) grown on the gold substrate

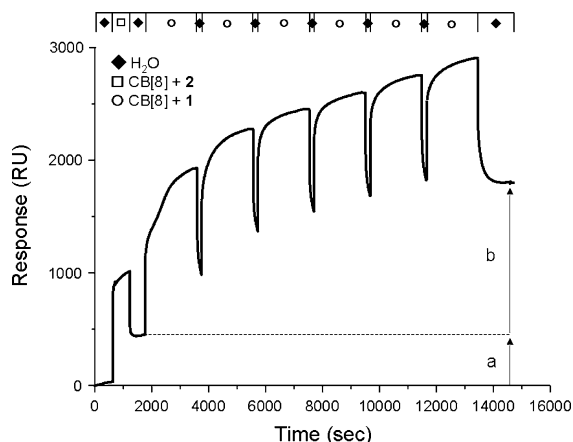


Fig. 2 SPR sensorgram showing a) the formation of SAM of pseudorotaxane **3** and b) the growth of poly(pseudorotaxane) on gold.

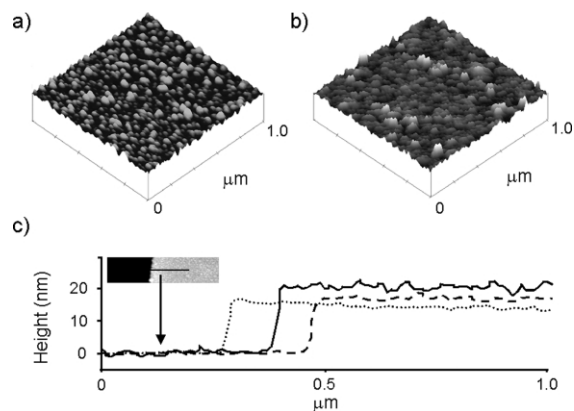


Fig. 3 AFM images of a) bare gold surface and b) the poly(pseudorotaxane) grown on gold by dipping in a 1 mM monomer solution. c) The height profiles near a step edge of gold/Si(100) surface: bare gold (dotted line), SAM of pseudorotaxane **3** on gold (dashed) and the poly(pseudorotaxane) grown on gold (solid).

contains about four “bead” (CB[8]) molecules (including one CB[8] of the platform SAM), which is consistent with the above-mentioned IR and SPR results.

In summary, we present the growth of a novel supramolecular polymer (poly(pseudorotaxane)) on gold in which the repeating units are linked by host-stabilized CT interaction between the guest molecules. Most importantly, the polymerization on the surface can be reversibly controlled. This work contributes not only to the fundamental understanding of its behavior on gold but also to their applications such as in molecular devices and sensors.

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[†] Current address: Department of Chemistry, Dong-A University, Busan 604-714, Republic of Korea.

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