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Investigation into Self-Assembled Monolayers of a Polyether Dendron Thiol: Chemisorption, Kinetics, and Patterned Surface

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Different sizes of Fréchet-type dendrons with a thiol group at the focal point were synthesized, well characterized, and used as building blocks for the preparation of self-assembled monolayers (SAMs) on metal surfaces. From the studies of the kinetic process of dendron thiol self-assembling on gold, it is shown that the dendron thiol assembling proceeds with different adsorption rates depending on the assembly time. In contrast to normal alkanethiols forming highly molecular structures on metal surfaces, the SAMs of polyether dendron form patterned surfaces with nanometer-sized features and in long-range order. It is found that the patterned stripes are closely related to the size of the dendron, and the patterned stripes can be improved by thermal annealing.

Introduction

Since Nuzzo and Allara first showed that self-assembled monolayers (SAMs) of alkanethiolates on gold can be prepared by adsorption of di-*n*-alkyl disulfides from dilute solutions,¹ this field has tremendously grown over the past decades.² Their works are significant for the general understanding of the physics and chemistry of complex surfaces and interfaces and play an important role in the success of molecular engineering to produce films with tailored properties. By using the methods of X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), temperature-programmed desorption (TPD), high-resolution electron energy loss spectroscopy (EELS), ellipsometry, etc., Nuzzo et al.^{3,4} carefully studied the chemical and thermal properties of different organic disulfide monolayers on gold surfaces. They also explained the properties of these intriguing chemisorption systems and showed relevant applications for the study of organic model surfaces, interfaces, and their properties. Although many techniques are useful for probing the structure of SAMs, only scanning tunneling microscopy (STM) and related methods can directly reveal the details of the packing of adsorbed molecules on metal surfaces at the molecular level in real space.⁵

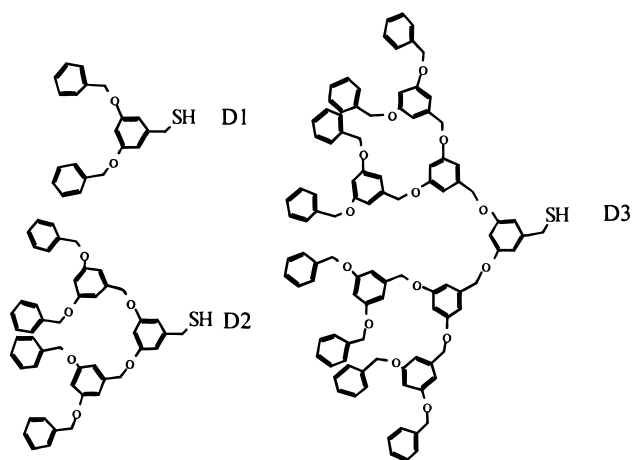
As for the functionalized SAMs, there are also many people who have made and are making contributions in

this field. Using the SAMs as a template, Häussling et al.⁶ studied the molecular recognition of biotin by streptavidin at interfaces, and Küther et al.⁷ realized the templated growth of calcite, vaterite, and aragonite crystals. Moreover, Wang et al.⁸ fabricated a series of azobenzene derivative alkanethiol SAMs on gold and intensively studied the electrochemical behavior of azobenzene chromophores in these films. Combining the self-assembly and photoetching technique, a concept of soft-lithography has been well established by Xia and Whiteside.⁹ The exciting finding leads to the preparation of patterned surfaces in a designed way, which is highly recommended and useful in the development of, e.g., novel optical sensors.

As we know, dendrimers as a type of regular-branched molecules have attracted extensive scientific interest because of their unusual architecture and many unique properties.¹⁰ These spherical molecules, whose structures

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Chart 1. Chemical Formulas of Dendron Thiols, Generation 1–3

can be precisely controlled at the molecular level, have been hailed as promising nanoscopic building blocks in the fabrication of supramolecular architectures and devices.^{11,12} For the purpose of taking advantage of the specific structures of dendrimers to enrich the area of self-assembled monolayers, recently several specific dendrimers as the building block to fabricate organic thin films have been studied to fabricate organic thin films.¹³ The strategy based on the growth of dendrimers or hyperbranched polymers at the liquid–solid interface provides a new way to fabricate starburst molecules, which can avoid the tedious process used in the usual synthetic procedure. The basic idea is quite simple. The impurities physically adsorbed on the substrate can be easily removed by rinsing with appropriate organic solvents. Usually, dendrimeric systems adsorbed on a surface cannot lead to well-organized closed-packed surfaces.¹⁴ However, recently we find that a type of polyether dendron thiol can form spontaneously ordered stripes on gold substrate.¹⁵ Herein we report a systematic study of self-assembled monolayers of polyether dendron thiols (Chart 1) on metal surfaces. The direct observation of SAMs of a polyether dendron thiol on gold means that STM reveals the formation of interesting nanosize-ordered stripes. It is shown that the width of the pattern depends on the size of the dendrons. Moreover, thermal annealing experiments give the opportunity to increase the molecular order, which means to enlarge the size of ordered regions on a substrate.

Results and Discussion

1. Interaction between a Dendron Thiol and a Substrate. The chemisorption of dendron thiols on a metal surface was characterized by Fourier transform surface-enhanced Raman scattering spectroscopy (FT-SERS). A

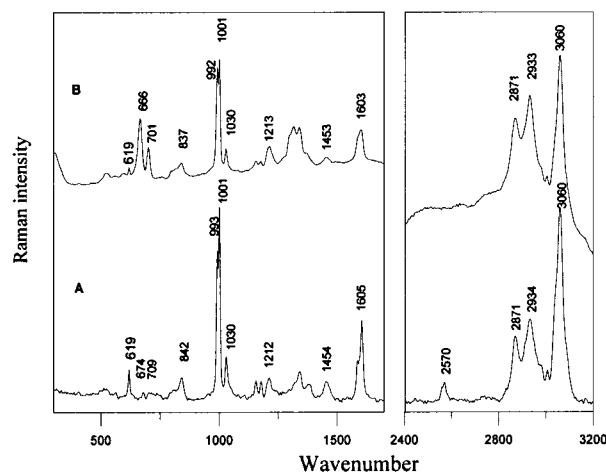


Figure 1. (A) Normal FT-Raman spectrum of dendron thiol. (B) FT-SERS spectrum of dendron thiol adsorbed on a chemical deposited silver film.

silver film was chosen as the substrate because modified silver films provide strongly enhanced effects in SERS. Figure 1A shows the normal FT-Raman spectrum of a pure dendron thiol (D2, a cast film). The bands at 3060, 2934, and 2871 cm^{-1} were assigned to the C–H stretching vibration of the benzene ring and CH_2 , respectively. The peak at 2570 cm^{-1} was due to the stretching vibration of the S–H bond. The bands at 1605, 1030, 1001, and 993 cm^{-1} were assigned to the in-plane ring-breathing mode. The bands at 1454 and 1212 cm^{-1} were assigned to the $-(\text{O})\text{CH}_2$ stretching vibration and CH_2 wagging deformation, respectively. The bands at 842 and 674 cm^{-1} were assigned to the symmetric stretching vibration of C–O–C and the stretching vibrating of the C–S bond, respectively. Figure 1B shows the FT-SERS spectrum of a dendron thiol adsorbed on a chemical deposited silver film. In comparison to the FT-SERS spectrum of a self-assembled monolayer of dendron thiol D2 on a silver film, the normal Raman spectrum of the pure compound depicts some obvious changes. The S–H band in Figure 1A completely disappears in Figure 1B. This leads to the conclusion that there are no free S–H groups in the latter case. The C–S stretching mode at 674 cm^{-1} of the free molecule in Figure 1A has lower-shifted to about 666 cm^{-1} in the adsorbed molecule (see Figure 1B). The shift and enhanced intensity are caused by the electron withdrawal from the C–S band to the S–Ag bond. The benzene ring breathing modes at 1605, 1030, 1001, and 992 cm^{-1} are only slightly affected, indicating that no interaction took place between the ring and the silver substrate. The band at 619 cm^{-1} in Figure 1A was assigned to in-plane benzene ring deformation vibration, and this band cannot be enhanced. From these results we can confirm the cleavage of the S–H bond and the formation of silver dendron thiolate. According to the surface selection rules by Moskovits et al.,¹⁶ the enhanced bands of the benzene ring and the C–S stretch mode suggest that a dendron thiol is chemisorbed almost perpendicularly to the silver surface. The results of compound D1 and D3 are similar to those of D2.

In the case of gold surfaces, the XPS data show that the binding energy for sulfur atoms ($2\text{P}_{1/2}$) is 163.5 eV in the powder sample and 162.1 eV for the dendron monolayer of D2 on a gold surface. The change of sulfur atom binding energy indicates that chemical bonds have formed between

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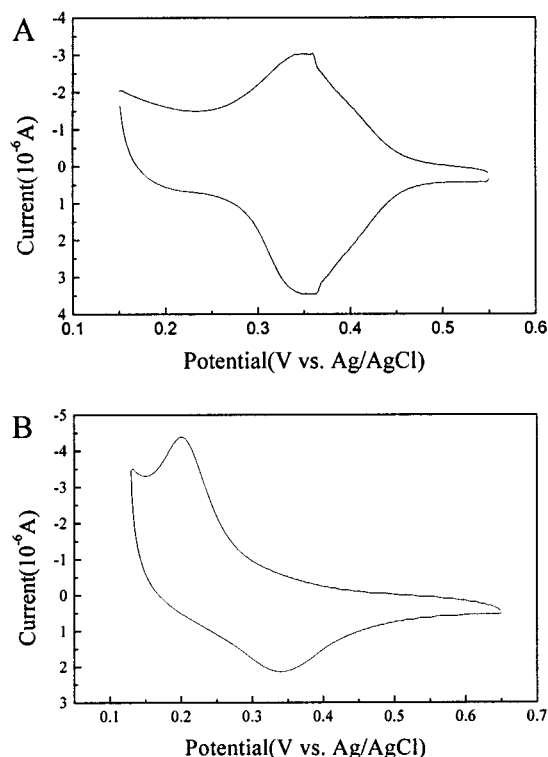


Figure 2. (A) CV of a gold electrode in 0.2 M CuSO_4 /0.1 M H_2SO_4 . (B) CV of a gold electrode modified with dendron thiol D2 in 0.2 M CuSO_4 /0.1 M H_2SO_4 . Scan rate: 100 mV/s. Assembling time: 11 s.

gold and sulfur atoms.³ In addition, compounds D1 and D3 show similar results.

2. Kinetics of Dendron Thiol Self-Assembled on Gold. The process of the assembling kinetics was studied by using the underpotential deposition (UPD) technique.¹⁷ It is found that UPD of copper on a gold surface under a high concentration of the deposited Cu (0.2 M) took place reversibly and was stable at bare and/or SAM modified electrodes. The cyclic voltammograms (CV) without any obvious changes in multicyclic potential excursions indicate that Cu UPD has a high reproducibility and stability. Figure 2A shows a typical CV of a bare Au electrode in a 0.2 M $\text{CuSO}_4 + 0.1$ M H_2SO_4 solution at a scan rate of 100 mV/s. The peaks at 0.358 and 0.361 V correspond to Cu UPD processes occurring on the gold surface. Figure 2B shows the CV of Cu UPD on a Au electrode modified with dendron thiol SAMs (D2). The deposition/stripping peaks of the UPD composition can be easily observed, although there exists an obvious peak to peak separation.¹⁸ The SAMs of a dendron thiol acted as an effective barrier for the deposition of Cu and the stripping of the deposited Cu adlayer.^{18,19} In the self-assembly process of a dendron thiol, the stripping peak exhibits a more clearly defined shape than the deposition peak (Figure 2B), so it can be used for measuring the integrated charge (Q) in the self-assembly process. Based on this Cu UPD method, the self-assembly process of dendron thiols on gold electrodes has been investigated in detail.

The growth of a self-assembled monolayer implies the loss of the active gold surface. Figure 3A shows the

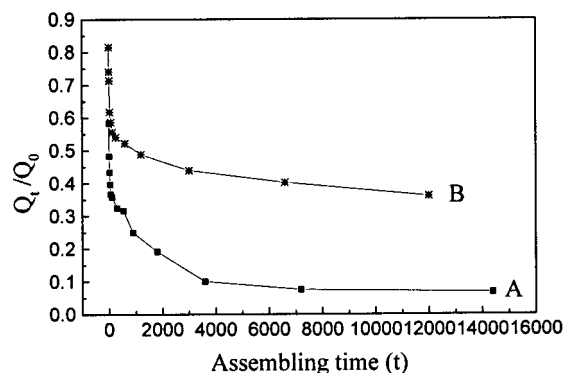


Figure 3. Relationship between Q_t/Q_0 and assembly time of (A) D1 and (B) D2.

decrease of integrated charge (Q) of Cu UPD at different assembly time in a D1 (THF) solution. It is observed that within the first 2 min of the assembling process, the decrease of integrated charge is very rapid and then becomes gradually slower. With increased assembling times, e.g., 10 h, the peak of Cu UPD can hardly be observed. This indicates that the gold surface is almost completely covered with a dendron thiol.

As we know, the ratio of the integrated charge Q_t at a certain assembly time to the Q_0 on a bare gold surface corresponds to the unoccupied fraction of the total surface. Parts A and B of Figure 3 illustrate the relationship between Q_t/Q_0 of D1 and D2 and the assembly time (t). From this figure, we can draw the conclusion that the dendron thiol assembly process proceeds with different adsorption rates: a rapid one at the beginning and then becoming gradually slow. There is nearly no difference between the adsorption rates of D1 and D2, while for self-assembled monolayers of D3 on gold electrodes, no barrier effect during the UPD process is observed. Following previous studies on dendrimers,²⁰ we can conjecture that with increased size of D3, the dendrons are dense on the outside but somewhat hollow on the inside, so copper atoms can be deposited to and stripped from the gold electrode almost freely. The coverages determined by UPD of D1 and D2 are 95% and 65%, respectively. They are smaller compared with linear alkanethiol molecules, which result in almost completely covered surfaces. However, from the STM images discussed later, we can see that SAMs of dendrons lead to effective coverage of gold surfaces. Molecular dynamics (MD) simulations reveal that dendron thiols adopt a cone-shaped conformation comparable with an umbrella. This leads to the conclusion that the top view of a dendron provides a dense structure whereas the sulfur atoms are not able to cover the whole substrate. The adsorption density decreases with the increased size of the dendrons, which means that the coverages determined by the UPD method decrease from D1 to D3 and are always lower than those of linear alkanethiol. Gorman et al.¹⁴ synthesized another type of organothiol dendron and found a porous structure for the adlayers of the first three generations by using capacitance and ferricyanide redox probe experiments. Moreover, they showed that as the number of hyperbranches in dendron increased from one to three the dendron adlayers became initially less and then more permeable.

3. STM Study of Dendron Thiol SAMs. Because of the high sensitivity of STM in the observation of the morphology of the surface, we can use it to study the SAMs

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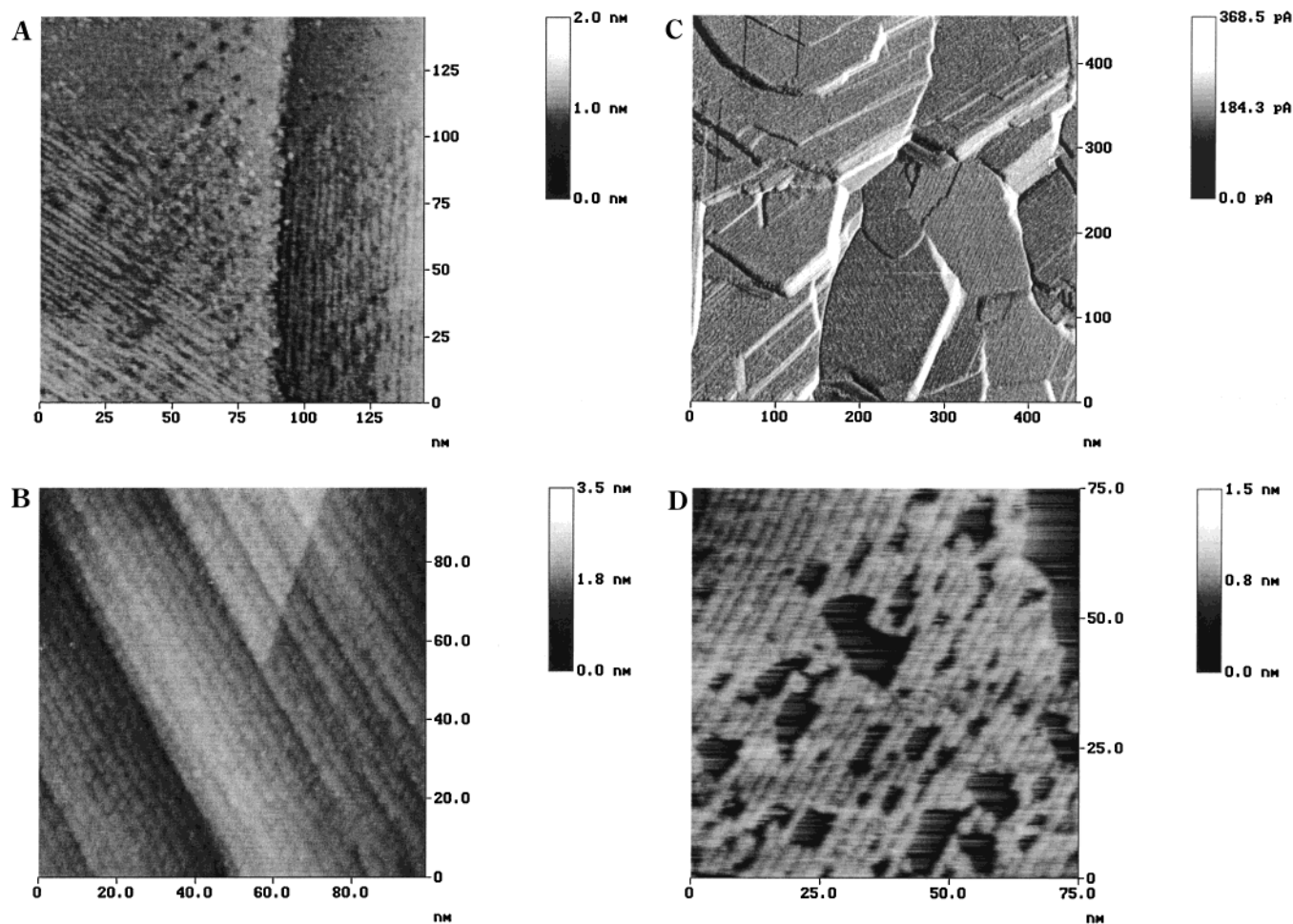


Figure 4. STM images of dendron thiol D2 on a gold surface with partial coverage (A), D2 with full coverage (B), and D2 after annealing with a large scan area (C). After several scans with increased tunneling currents, holes are induced in the initially ordered stripes (D).

of a dendron thiol on gold surfaces. Figure 4A shows the STM image of D2 before annealing. This image depicts ordered stripes which do not cover the whole area. When annealing the sample by 70 °C for about 4 h, we can see the increased size of the order region, with high regularity and in long-range order (see Figure 4B). The width of the stripes is about 3.1 nm, as measured from STM images, e.g., shown in Figure 4B. The mechanism which is responsible for long-range order in the self-assembled monolayer of a dendron thiol on gold substrates is still unclear. Nevertheless, in most cases it is observed that the ordered stripes are parallel to one edge of the gold terrace, which is shown obviously in Figure 4C.

In addition, by an increase of the bias voltage of STM, we can observe that some defects are induced (see Figure 4D), which provides a further proof that the ordered stripes are formed by the dendron thiol and are not caused by artifacts of the gold substrate itself.

In the case of other sizes of dendron thiols, D1 just forms similar ordered stripes in some regions, and it is influenced slightly by annealing. D3 can also form partially ordered stripes even before annealing. STM data taken from D1 and D3 are similar to those of Figure 4A. The widths of the stripes of D1 and D3 are about 2.3 and 4 nm, respectively.

Conclusion

We demonstrate the formation of self-assembled monolayers of dendron thiols on metal surfaces. The research

in this regard is prospective for dendron-based nanopatterning materials. The pattern formation is completely based on the self-assembly process of dendron thiols on metal surfaces; therefore, the structure sizes of the pattern can reach a very high level, e.g., down to the nanometer scale, which may provide a novel method of forming patterns with structure size of less than 10 nm. Considering the extremely rich structural variation of dendrimers, various tailor-made surfaces would be available for pattern recognition and functional chips. By the design and preparation of other structures of a dendron thiol, we can understand the relationship between the molecular structure and the ordering of these molecules at various interfaces.

Experimental Section

Materials. THF was distilled from sodium before use. Other chemicals were analytical-grade reagents and were used as received. Fréchet-type dendritic bromides were selected as the starting materials, which were prepared according to the literature.²¹

Techniques. ¹H NMR spectra were recorded with CDCl₃ solutions on a Varian 400 (400 MHz) spectrometer using a TMS proton signal as the internal standard. IR spectra were recorded on an ISF-66V spectrometer as thin

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films on KBr plates. XPS was performed on a VG-Escalab Mark spectrometer with an Al K α monochromatized X-ray source, modified gold slide as the substrate. EA (elemental analyses) were obtained on EA 340C. STM images were obtained by using a commercial instrument (Digital Instruments, Multimode II). Tunneling parameters of 750 mV (bias voltage) and 500 pA (current set point) were used for taking images if not indicated.

Preparation of the Gold Surface. Microscopy slides were supplied by the manufacturer. After a thorough cleaning (NOCHROMIX/sulfuric acid), it was precoated with 6 nm of chromium followed by 130 nm of gold, both evaporated at a pressure of 5×10^{-6} mbar from a resistively heated tungsten boat.

Preparation of the Self-Assembled Monolayer on Gold. Gold-coated slides were flame-annealed to make the gold slide of the (111) surface up to even micrometer-size flat areas.^{22,23} After cooling to room temperature, they were dipped into a freshly made THF solution of a polyether dendron thiol (0.325 mM) and kept for 24 h at room temperature. Then the dendron-coated gold slides were rinsed with dry THF and dried under a stream of dry nitrogen before characterization. Samples were annealed at 70 °C for about 4 h in order to increase the size of ordered regions.

Preparation of the SAMs for Raman Spectroscopy. All of the FT-SERS spectra and normal FT-Raman spectra were measured on a Bruker model RFS 100 Fourier Raman spectrometer. A Ge detector operated at liquid-nitrogen temperature was used. The incident laser excitation was 1064 nm from an air-cooled diode pumped Nd:YAG laser source. The spectral resolution was 4.0 cm⁻¹. The outputs were 100 and 30 mW for FT-SERS and normal FT-Raman measurements, respectively. The Raman scattering was measured at an angle of 180°. For the SERS experiment, a fine silver film was prepared by the Xue method.²⁴ Several 10 × 10 × 1 mm glass plates were washed with water and acetone and put into a 10 mL beaker. A total of 5 mL of a 2 M silver ammonia complex and 5 mL of formaldehyde were mixed in the beaker. A few seconds later the color of the solution turned to gray and black. Meanwhile, the silver ions were reduced and deposited on the glass plates to form fine silver films. After the silver films were washed with distilled water, they were dipped in a 0.1 mM dendron thiol solution for 24 h. After withdrawal, the excess liquid was washed away with THF and the samples were then dried in air.

UPD Method for Absorption Kinetics. We use the method of UPD to follow the absorption kinetics. The polycrystal gold electrode (1 mm diameter) was used as a working electrode, which had been polished with 1.0, 0.3, and 0.05 μ m α -Al₂O₃ powder, respectively. Then the Au electrode was electrochemically cleaned by cycling in the range of -0.2 and +1.5 V (vs Ag/AgCl saturated KCl) in 1.0 M H₂SO₄ until a stable voltammogram was obtained. After such potential excursions, the potential was held in the double-layer region to ensure complete reduction of the gold oxide.

The electrochemical experiments were performed in a single-compartment cell at room temperature (25 °C). A

platinum wire was used as the counter electrode and an Ag/AgCl (saturated KCl) electrode as the reference electrode. The cyclic voltammetric measurements were performed with a CHI 660 system. All solutions were thoroughly deaerated with high pure nitrogen.

The clean gold electrode was rinsed with distilled water and then immersed in a 0.2 M CuSO₄ solution with 0.1 M H₂SO₄ for 5 min to measure the value of Q_0 . Monolayers were conventionally prepared by a self-assembly technique. The cleaned gold electrode was rinsed with distilled water and then was immersed in a 50–60 μ M dendron thiol/THF solution for different times. Then, the electrode was completely rinsed with THF and distilled water to remove the physically adsorbed composite. Finally, the self-assembled electrode was transferred into an electrochemical cell with a 0.2 M CuSO₄/0.1 M H₂SO₄ solution for the UPD process.

Preparation and Characterization of a Dendron Thiol. Different sizes of Fréchet-type dendritic bromides are selected as the starting material. Dendron thiols D1–D3 (as shown in Chart 1) are prepared by thiourea substitution of corresponding dendritic bromides. Because of the poor solubility of the Fréchet-type dendritic bromide in ethanol, a mixed solution of THF and ethanol (1:1, v/v) was used instead of pure ethanol. After the compound of dendritic bromide is reacted with thiourea in an ethanol/THF (1:1) solution under reflux in the presence of a N₂ atmosphere for 4 h, aqueous potassium hydroxide (1 M) is added to the mixture and refluxed for 4 h. Then it acidified with HCl (1 M) to produce the dendron thiol, which is purified by silica gel column chromatography eluting with dichloromethane in the presence of a nitrogen atmosphere.

The structures of dendron thiols D1–D3 are characterized by IR, ¹H NMR, and EA. For the compound D1: FTIR ($\nu_{\max}/\text{cm}^{-1}$) 3063, 3031 (Ar–H), 2925, 2869 (CH₂), 2566 (SH), 1595 (benzene rings); ¹H NMR (d_H, CDCl₃) 7.41–7.33 (Ar–H, m), 6.58–6.45 (Ar–H, m), 5.02 (ArCH₂O–, s), 4.99 (ArCH₂O–, s), 3.87 (ArCH₂S–, d), 1.78 (–SH, t). EA (%). Calcd: C, 75.00; H, 5.95. Found: C, 75.02; H, 5.60. For the compound D2: FTIR ($\nu_{\max}/\text{cm}^{-1}$) 3063, 3030 (Ar–H), 2925, 2870 (CH₂), 2567 (SH), 1593 (benzene rings); ¹H NMR (d_H, CDCl₃) 7.42–7.31 (Ar–H, m), 6.68–6.47 (Ar–H, m), 5.03 (ArCH₂O–, s), 4.96 (ArCH₂O–, s), 3.66 (ArCH₂S–, d), 1.76 (–SH, t). EA (%). Calcd: C, 77.37; H, 5.79. Found: C, 77.20; H, 5.80. For the compound D3: FTIR ($\nu_{\max}/\text{cm}^{-1}$): 3062, 3030 (Ar–H), 2927, 2869 (CH₂), 2575 (SH), 1594 (benzene rings); ¹H NMR (d_H, CDCl₃) 7.33–7.26 (Ar–H, m), 6.59–6.42 (Ar–H, m), 4.92–4.89 (ArCH₂O–, m), 4.80 (ArCH₂O–, s), 3.51 (ArCH₂S–, d), 1.28 (–SH, t); EA (%). Calcd: C, 78.4; H, 5.7. Found: C, 78.1; H, 5.9.

Because the dendron thiols are easily oxidized to give the corresponding disulfides, they are stored in the presence of argon.

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