Self-assembled Monolayers of Dendron-thiol on Solid Substrate

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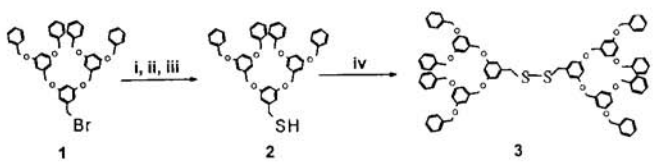
A polyether dendron with a thiol group at the focal point was synthesized and well characterized, and then used for the preparation of self-assembly monolayers (SAMs) on metal surface. The monolayers on metal surface were studied by Fourier transform surface enhanced Raman scattering spectroscopy(FT-SERS) and STM etc.

Recent development in the self-assembly of disulfides and thiols on metal surfaces coincided with the maturation of scanning tunneling microscopy (STM) which have greatly broadened the understanding of the structures of the self-assemblied monolayers (SAMs) on the metal surface.[1,2] Design, synthesis and investigation on different structural small molecules and macromolecules bearing thiol groups have received a great deal attention for their enormous potential in tailoring surface properties for a variety of technologically important application.[3] Recently, a new kind of well-defined regular branched macromolecules called dendrimers have widely attracted scientific attentions.[4] These macromolecules, whose structures could be precisely controlled at molecular level, have been hailed as promising nanoscopic building blocks in the fabrication of supramolecular architectures and devices.[5,6] Here we report on the synthesis, characterization of a dendron thiol, which should be of a flat-cone shaped form with a thiol group at the focal point, and the self-assembling of dendron monolayers on metal surface.

Frechet type dendritic bromide (compound 1, see Scheme 1) was selected as the starting material which was prepared according to the literature.[7] The dendron thiol 2 was prepared according to Scheme 1. Because of the poor solubility of the Frechet type dendritic bromide (compound 1) in ethanol, a mixed solution of THF and ethanol (v:v, 1:1) was used instead of pure ethanol. After compound 1 was reacted with thiourea in ethanol/THF (1:1) solution under reflux in the presence of N_2 atmosphere for 4h, aqueous potassium hydroxide(1M) was added to the mixture and refluxed for 4h, and then acidified with HCl(1M) to produce the dendron thiol which was purified by silica gel column chromatography eluting with dichloromethane in the presence of nitrogen atmosphere.



Scheme 1. Reagents and conditions: i) thiourea, ethanol/THF(1:2), refluxed under N_2 for 8 h; ii) aqueous NaOH, refluxed under N_2 for 4 h; iii) HCl; iv) side reaction caused by oxidation under aerobic condition.

The structure of dendron thiol 2 was characterized by IR, ^{1}H NMR and MALDI-TOF MS (Matrix assisted laser desorption ionization and time of flight mass spectra). Characteristic FTIR data for the dendron thiol (ν_{max}/cm^{-1}) were: Ar-H: 3063, 3030, CH_2: 2925, 2870; SH: 2567; Benzene rings: 1593. While the corresponding ^{1}H NMR data (δ_H, $CDCl_3$)were 7.42-7.31(Ar-H, m); 6.68-6.47(Ar-H, m); 5.03 (exterior $ArCH_2O$-, s); 4.96 (interior $ArCH_2O$-, s); 3.66 ($ArCH_2S$-, d); 1.76 (-SH, t). The molecular weight for the dendron thiol by MALDI-TOF MS is 761.1 dalton, which is attributed to M^++H (Calculated M^++H is 761.9). Because the dendron thiol 2 is easisy oxidized to give the corresponding disulfide, it is stored in the presence of argon.

The SAM was formed by immersion of metal substrates into THF solution containing dendron thiol(0.1mM). The adsorption and bonding of dendron thiol on silver film surface was characterized by Fourier transform surface enhanced Raman scattering spectroscopy(FT-SERS). Figure1.A shows the

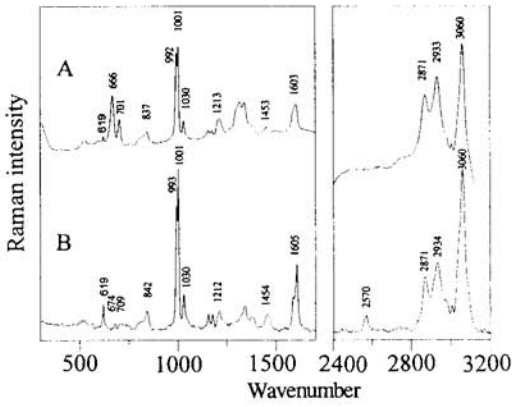


Figure1. A) The normal FT-Raman spectrum of dendron thiol B) The FT-SERS spectrum of dendron thiol adsorbed on chemical deposited silver film.

normal FT-Raman spectrum of pure dendron thiol. The bands at 3060, 2934, 2871cm^{-1} were assigned to the C-H stretching vibration of benzene ring and CH_2 respectivcly. The peak at 2570 cm^{-1} was due to the stretching vibration of the S-H bond. The bands at 1605, 1030, and 1001, 993 cm^{-1} were assigned to the in-plane ring breathing mode. The bands at 1454 and 1212 cm^{-1} were assigned to the -(O)-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 stretching vibrating of the C-S bond. Figure1.B shows the FT-SERS spectrum of dendron thiol adsorbed on chemically deposited silver film (the silver film prepared by Gi Xue method[8]). Compared the FT-SERS spectrum of self-

assembled monolayer of dendron thiol on silver film with its normal Raman spectrum of pure compound, there were some change obviously. The S-H band in Figure1.A disappears in Figure1.B, which suggests that there was no free S-H groups. The C-S stretching mode at 674 cm^{-1} of the free molecule in Figure1.A has lower-shifted to about 666 cm^{-1} in the adsorbed molecule(see Figure1.B). The shifts and enhanced intensity were caused by the electron withdrawal from the C-S band to the S-Ag bond. The benzene ring breathing mode at 1605,1030,1001and 992 cm^{-1} is only slightly affected, indicating that no interaction took place between the ring and silver substrate. From these results we could confirm the cleavage of the S-H bond and formation of silver dendron thiolate. According to the surface selection rules by Moskovits et al.,[9] the enhanced bands of the benzene ring and C-S stretch mode suggested that benzene ring of dendron thiol was chemisorbed almost perpendicularly to the silver surface.

In the case of gold surface, the XPS data showed the binding energies for sulfur atoms is 163.5ev in powder sample, and 162.1ev for the dendron monolayer on gold surface. The change of sulful atom' s binding energy indicates that chemical bonds have formed between gold and sulfur atoms. The dendron monolayer on gold have been carefully studied by STM in our experiments(Figure 2). It could be seen that the SAMs of dendrimer covered the gold surface homogeneously. In high resolution image, ordered regions, especially the ordered stripes can be observed. The width of stripe was about 3.1nm indicating that ordered strips maybe the result of the packing of two flat-cone shaped dendron(see scheme 2). We also

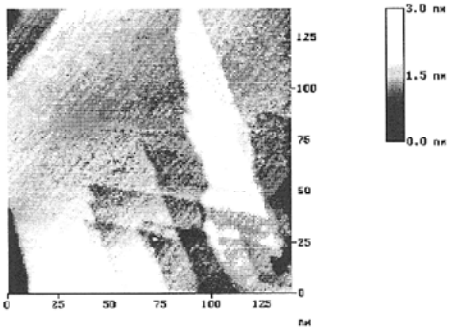
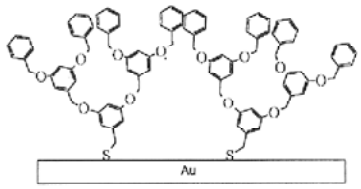


Figure 2. The STM image of a monolayer of dendron thiol 2 on gold surface. Before measurement the sample was annealed by 70 °C for about 4 h. Bias voltage U: 825mV; Tunneling current I: 500pA.

synthesized lower generation dendron thiol and found there also exist some ordered regions, but not as good as the one which we discussed above.



Scheme 2. The self-assembled monolayer of dendron thiol on gold surface.

We herein demonstrated the formation of self-assembled monolayer of dendron thiol on metal surface, and the research in this regard is perspective for dendron based nanopatterning materials and tailor-made surface considering the extremely rich structural variation of dendrimers available.

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