

Nano-identification for the Cleavage of Disulfide Bond during the Self-Assembly Processes of Unsymmetric Dialkyl Disulfides on Au(111)

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The formation of striped phases of unsymmetric hexyl octadecyl disulfide ($\text{CH}_3(\text{CH}_2)_5\text{SS}(\text{CH}_2)_{17}\text{CH}_3$, HOD) and 1-hydroxyundecyl octadecyl disulfide ($\text{CH}_3(\text{CH}_2)_{17}\text{SS}(\text{CH}_2)_{11}\text{OH}$, HUOD) on Au(111) and graphite has been investigated by scanning tunneling microscopy (STM) to understand the self-assembly processes of dialkyl disulfides. STM imaging clearly shows the formation of striped phases having corrugation periodicities that are nearly consistent with the molecular length of alkanethiolate moieties formed after the S-S bond cleavage of dialkyl disulfide on a gold surface. On the other hand, self-assembled monolayers (SAMs) of dialkyl disulfides on a graphite surface displayed long-range, well-ordered monolayers with one striped pattern that shows periodicity as a function of molecular length via nondissociative adsorption. From a nonoscopic viewpoint, we have clearly demonstrated that dialkyl disulfide SAMs on gold form via S-S bond cleavage of disulfide.

Key Words : Scanning tunneling microscopy, Self-assembled monolayers, Striped phase, Nano-identification

Introduction

During the past decade, organic self-assembled monolayers (SAMs) prepared from organosulfur compounds on metal surfaces have drawn great interest because of the possibility of various technical applications such as in nanolithography, molecular recognition, corrosion inhibition, and nanoparticles.¹ SAMs derived from alkanethiols and dialkyl disulfides on metal surfaces have been extensively studied because of the formation of highly ordered and densely packed monolayers and their high stability.²⁻⁶ In particular, dialkyl disulfide SAMs on gold have been used for fabrication of nanosensing devices because the molecular sensing efficiency can be enhanced by controlling two alkyl groups attached to disulfide group.⁷ However, there remains a question concerning the adsorption processes of dialkyl disulfide SAMs on gold. For examples, does the S-S bond cleavage of disulfide really occur in the course of the formation of monolayers? Actually, solving this problem is quite important for designing high-efficiency sensing devices. To date, the adsorption issue of disulfide on gold has usually been studied by a variety of macroscopic tools such as X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (EELS), time-of-flight secondary ion mass spectroscopy (TOF-SIMS). On the other hand, although scanning probe microscopy (SPM) is a very powerful tool for obtaining information on the molecular behavior and the surface structures of adsorbates on substrates,⁸⁻¹³ there are very few reports obtained by SPM regarding this matter.¹⁴

The main object of our study is to clearly elucidate the adsorption processes of dialkyl disulfide from the nanoscopic viewpoint using scanning tunneling microscopy (STM). A few earlier studies have attempted to resolve this problem using dialkyl disulfides with atomic force micro-

scopy (AFM); this work was mainly performed on the fully covered monolayers derived from dialkyl disulfides on the gold surface.¹⁴ Contrary to this approach, we have attempted to observe striped phases of dialkyl disulfides formed during the initial growth stage of SAMs based on the following logic. It is well known that the periodicities of striped phases formed on gold depend strongly on the overall length of the molecule used for the preparation of the SAMs.¹⁵⁻¹⁹ From investigations of the patterns and periodicities of striped phases, we can discuss various fundamental aspects of organic molecules on substrates. This is the main concept of this study. To interpret the striped phases of dialkyl disulfides formed on gold more carefully, we have also observed striped phases formed by physisorption on graphite. In our recent studies, we have successfully demonstrated that this approach is very useful to understand the self-assembly processes of organic molecules on a surface^{18,19}

In this study, in order to reveal and confirm the self-assembly processes of dialkyl disulfides on gold clearly, we have monitored the striped phases formed by two kinds of unsymmetric dialkyl disulfides on gold and graphite by STM.

Experimental Section

Materials. As target materials, unsymmetric hexyl octadecyl disulfide ($\text{CH}_3(\text{CH}_2)_5\text{SS}(\text{CH}_2)_{17}\text{CH}_3$, HOD) and 11-hydroxyundecyl octadecyl disulfide ($\text{CH}_3(\text{CH}_2)_{17}\text{SS}(\text{CH}_2)_{11}\text{OH}$, HUOD) were synthesized by modifying previously reported method.²⁰ These two compounds were recrystallized several times from diethyl ether for further purification, and the purity was confirmed by mass spectrometry.

Au(111) Substrate and SAM Preparation. Au(111) substrates were prepared by vacuum deposition of approximately 100 nm of gold film onto freshly cleaved mica sheets

prebaked at 320 °C under a pressure of 10^{-7} – 10^{-8} Torr prior to the deposition of the gold. After deposition, the substrates were annealed at 350 °C in a vacuum chamber for 2 h to obtain large, flat, single-crystal terraces. The STM images showed the herringbone reconstruction characteristic of clean Au(111) surfaces on 100–300 nm single-crystal domains. The SAMs were formed by immersing the gold substrates in a freshly prepared 0.25 mM diethyl ether solutions of HOD and HUOD. After the SAM samples were removed from the solutions, the samples were thoroughly rinsed with a large quantity of pure diethyl ether solution to remove weakly adsorbed molecules from the surface. On the other hand, for STM imaging of SAMs formed on graphite, the nearly saturated phenyloctane solutions of HOD and HUOD were prepared. A drop of the solution was applied to the freshly cleaved surface of highly oriented pyrolytic graphite (HOPG). The SAMs on graphite were formed at the liquid/graphite interface.

STM Measurements. All STM images were obtained at room temperature with a Pt/Ir tip using the constant current mode in air. Bias voltages (V_b) between 1.5 and -1.5 V and tunneling currents (I_t) ranging from 0.10 to 0.3 nA were applied between the tips and samples. STM imaging of the HOD and HUOD SAMs physisorbed at the liquid/graphite interface was performed in the same manner as described in previous reports.^{21–23}

Results and Discussion

It has been demonstrated that organic molecules such as R–SH, R–S–R, and R–SS–R (R = alkyl group) physisorbed on graphite are oriented parallel to the surface, which is called as striped phase, and the sulfur atoms in a molecule were observed as brighter molecular spots in STM images due to an enhanced tunneling current compared to alkyl groups.^{21,22,24} On the other hand, such similar striped phases

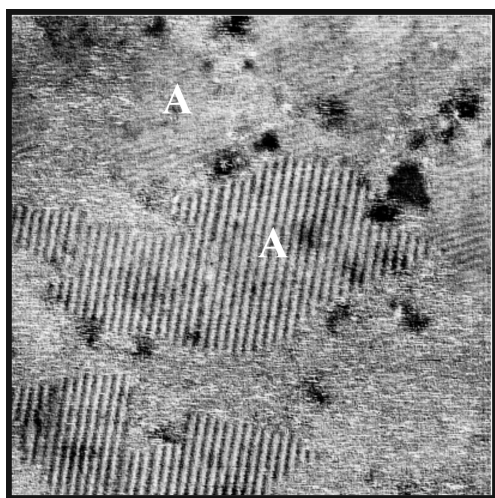


Figure 1. STM image of the striped phase for hexanethiol SAMs on Au(111). Note that molecular axes in the striped phases are oriented parallel to the surface (107 nm \times 107 nm, I_t = 0.17 nA, and V_b = 0.45 V).

(it is often called as β phase) were often observed at the initial SAM growth stage of alkanethiols on a gold surface.^{16,25} For instance, the STM image of Figure 1 exhibits a typical example of striped phases (region A) formed from hexanethiol SAMs on Au(111). Here the bright rows can be assigned to –SS– groups resulting from head-to-head molecular orientation and the dark rows can be assigned to alkyl groups. Based on high brightness of sulfur atoms in STM imaging, the sulfur atoms on gold as well as graphite can be used as “chemical marker group” for monitoring target molecules. However, we should consider that the sulfur atoms on gold can be only observed in striped phase because the alkyl chains in two-dimensional ordered SAMs on gold prevent the direct observation of sulfur atoms chemically attached to gold surfaces. This is a reason for monitoring the striped phases in our study.

To monitor the formation of striped phases on gold, we must investigate the initial process of SAM growth because these phases usually form during the initial self-assembly. In addition, such phases can be observed in SAM samples obtained in extremely dilute solutions containing target molecules. Therefore, to observe striped phases on the gold surface, we used a 0.25 μ M solution and a short dipping time of less than 3 min.

Figure 2 depicts three possible patterns of striped phases of dialkyl disulfides on a substrate. The striped phase shown in Figure 2a can only be observed in the case of the nondissociative adsorption of these molecules. In this case, a corrugation period corresponding to the overall length of a molecule can be observed in this striped phase. This value was readily measured by STM imaging due to the markedly enhanced contrast of the sulfur atoms relative to that of the methyl groups, as described above.^{23–27} The final molecular features derived from the dissociative adsorption of dialkyl disulfides on gold are identical to those of alkanethiols, as previously reported.³ The R–S moieties produced by the S–S bond cleavage of dialkyl disulfides on gold can give rise to striped phases where the corrugation periods are one-half of the original molecular length due to the head-to-tail orien-

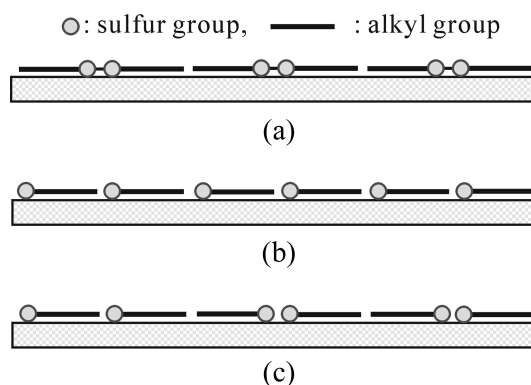


Figure 2. Three possible patterns of striped phases formed during the self-assembly of dialkyl disulfides on a substrate: (a) a striped phase after the nondissociative adsorption of dialkyl disulfides, and (b) and (c) striped phases after the dissociative adsorption of dialkyl disulfides.

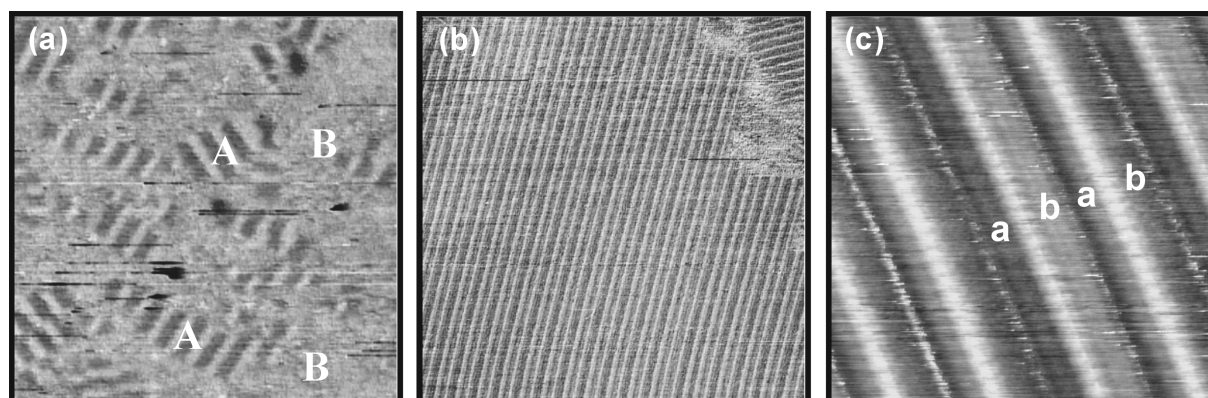


Figure 3. (a) STM image showing the striped phase of hexyl octadecyl disulfide (HOD) SAMs on Au(111) obtained after 5 min deposition in 0.25 μ M diethyl ether solutions of HOD (50 nm \times 50 nm, $I_t = 0.20$ nA, and $V_b = 0.58$ V). (b) and (c) STM images exhibiting the striped phases of HOD physisorbed on graphite ((b) 150 nm \times 150 nm, $I_t = 0.18$ nA, and $V_b = 1.50$ V, (c) 16 nm \times 16 nm, $I_t = 0.15$ nA, and $V_b = 1.45$ V).

tation, as delineated in Figure 2b. Additionally, dissociative adsorption can be observed in the form of a mixed striped phase, as shown in Figure 2c as well as in Figure 2b, resulting in phase-separated domains. Striped phases similar to Figure 2c were reported in SAMs of alkanethiols on graphite surfaces.^{23,26} In the case of alkanethiols on gold, it was often observed that striped phases exhibit corrugation periods with twice the overall length of the molecules because of the head-to-head orientation,^{16,17} as shown in Figure 1.

The STM image in Figure 3a were observed from SAM samples formed on Au(111) after 5 min deposition in a 0.25 mM diethyl ether solution of HOD. Figure 3a shows striped phases (region A) and disordered phases (region B) formed by HOD molecules. The corrugation period in these striped phases is 2.62 nm, which is nearly consistent with the molecular length of octadecanethiolate molecules adsorbed on a gold surface after the S-S bond cleavage of HOD molecules. However, in this molecular system, we only observed one striped phase formed from octadecanethiolates. It is assumed that the striped phase formed by molecules with a longer alkyl chain (octadecanethiolate) is more energetically stable than that formed by the shorter alkyl chain molecules (hexanethiolate) because both molecule-molecule and molecule-substrate interactions induced by octadecanethiolates would be greater than those induced by hexanethiolates. This suggestion can be strongly supported by the results that hexanethiol SAMs consisting of the shorter alkyl chains can be easily exchanged by octadecanethiol molecules with the longer alkyl chains.²⁷ This exchange phenomena can be driven by a energy gain due to the increase of lateral interactions between the longer alkyl chains. Therefore, it is reasonable to consider that the striped phase formed by octadecanethiolate ($\text{CH}_3(\text{CH}_2)_{17}\text{S}-$) is much easier to observe than that formed by hexanethiolates ($\text{CH}_3(\text{CH}_2)_5\text{S}-$) on gold surface. The pattern and periodicity of the striped phase of HOD molecules on gold are consistent with the model b in Figure 2. As already explained using this model, this result strongly suggests the

dissociative adsorption of disulfides. If there was no bond rupture of the disulfide, such striped phases would not be formed on the gold surface. The disordered phase in region B was often observed in alkanethiol SAMs during phase transitions from a striped phase to a two-dimensional upright phase as surface coverage increased.

To make sure the above results, we have attempted to observe striped patterns of HOD molecules adsorbed on graphite surfaces. The main difference in the self-assembly process of HOD molecules on gold and graphite involves the interactions (*i.e.*, chemisorption or physisorption) between molecules and substrate. Organic molecules physisorbed on a graphite surface usually lie flat on the surface similar to striped phases observed on gold, and mainly follow the striped pattern of model a in Figure 2. The STM image in Figure 3b and c exhibit well-ordered monolayers formed by HOD molecules physisorbed on graphite. The STM image in Figure 3b show the large and long-range ordered single domain having more than about 100 nm size resulting from the maximization of lateral interaction between molecules. High-resolution STM image of Figure 3c reveals that the molecular axis is oriented parallel to the graphite surface and the corrugation period is 4.15 nm, which is nearly consistent with the whole length of HOD molecules. Here, individual molecular spots in the bright rows can be assigned to disulfide groups, as with HUOD. It can also be assigned that the shorter hexanethiolate groups are located in the region a, and the longer octadecanethiolate groups are located in the region b. On the basis of this STM image, HOD SAMs on graphite were formed via alternate adsorption (ab-ab) with one unsymmetric disulfide repeating unit.

In order to confirm these results on gold and graphite more clearly, we examined the self-assembly process of different unsymmetric disulfide molecules, *i.e.*, HUOD. The STM image in Figure 4a clearly exhibits two types of striped-phase domains with phase separation from the HUOD SAM sample on gold after 3 min deposition. The corrugation periodicities of the striped phase in regions A and B are 1.82 and 2.55 nm, which shows good agreement with the length

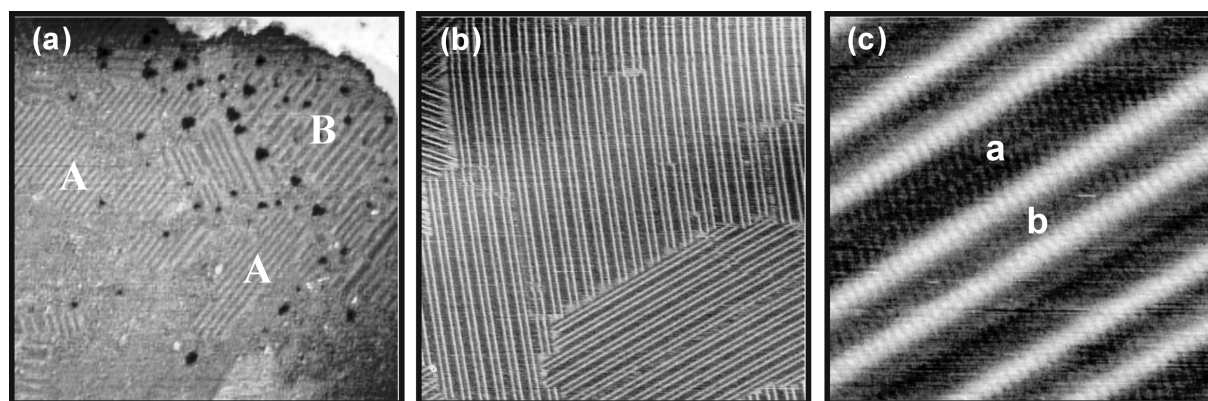


Figure 4. (a) STM image of 11-hydroxyundecyl octadecyl disulfide (HUOD) SAMs on Au(111) obtained after 3 min deposition in 0.25 μM ethanol solutions of HUOD (106 nm \times 106 nm, $I_t = 0.21$ nA, and $V_b = 0.50$ V), (b) and (c) STM images exhibiting the striped phase of HUOD physisorbed on graphite. ((b) 150 nm \times 150 nm, $I_t = 0.12$ nA, and $V_b = 1.5$ V, (c) 15 nm \times 15 nm, $I_t = 0.12$ nA, and $V_b = 1.20$ V).

of $\text{HO}(\text{CH}_2)_{11}\text{S}$ and $\text{CH}_3(\text{CH}_2)_{17}\text{S}$ molecules, respectively. Without the cleavage of disulfide bond, such striped phases with phase separation could not be formed. Moreover, the striped pattern is good consistent with the model b in Figure 2. As already mentioned using this model, this result strongly implies the dissociative adsorption of HUOD molecules.

Again, to confirm our result of S-S bond breaking on Au(111), we have examined molecular arrangements of HUOD molecules physisorbed on graphite. The STM image of a large scan area in Figure 4b shows well-ordered molecular arrangements of HUOD molecules that orient parallel to the graphite surface. The high-resolution STM image in Figure 4c displays individual disulfide groups, as seen in bright rows. The formation of paired bright rows in this image is driven by a hydrogen bond with a hydroxyl group facing another hydroxyl group of adjacent molecules. Here, two longer alkyl groups (octadecanethiolate) are positioned in the large dark area (region a) between two bright rows, and the two shorter hydroxylated alkyl group (11-hydroxyundecanethiolate) are located in the small dark area (region b). From this molecular arrangement, it is clear that the self-assembly process of HUOD molecules physisorbed on graphite is mainly governed by a hydrogen bond without any S-S bond cleavage of the disulfide group, unlike the adsorption process of HUOD molecules on gold. From the investigation of striped phases in HUOD SAMs, we reconfirmed the dissociative adsorption of dialkyl disulfides on gold surfaces from the nanoscopic viewpoint. In fact, our STM results are in accord with previous studies performed by macroscopic techniques.^{3,28,29}

We clearly observed the striped phases resulting from two alkanethiolate molecules formed after S-S bond cleavage of HOD or HUOD molecules on gold. The patterns of striped phases on gold are identical to the model b in Figure 2, implying the S-S bond cleavage of disulfide during the self-assembly. On the other hand, the patterns and periodicities of striped phases for these molecules on graphite are completely different from those observed on gold. The patterns of striped phases on graphite are the same as the

model a in Figure 2, suggesting that SAMs formed via nondissociative adsorption. From the nanoscopic viewpoint, we have successfully elucidated the adsorption processes of dialkyl disulfides during SAM formation on gold and graphite surfaces.

Conclusions

To understand the self-assembly processes of dialkyl disulfides, we monitored the formation of striped phases appeared during self-assembly of hexyl octadecyl disulfide (HOD) and 1-hydroxyundecyl octadecyl disulfide (HUOD) on both gold and graphite surfaces using scanning tunneling microscopy (STM). From the nanoscopic viewpoint, we confirmed that the formation of dialkyl disulfide SAMs on gold proceeds via a dissociative adsorption process without direct adsorption of the disulfide group on the gold surface, as revealed mainly by macroscopic techniques. In this study, we have demonstrated that observation of striped phases with a well-designed model compound will provide new guidelines to examine new fundamental aspects such as surface reactions, interactions and orientations of molecules, as well as the monitoring of target molecules on a surface.

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References

1. He, H. X.; Zhang, H.; Li, Q. G.; Zhu, T.; Li, S. F. I.; Liu, J. F. *Langmuir* **2000**, *16*, 3846.
2. Nuzzo, R. G.; Zegarski, B. R.; Dubois, L. H. *J. Am. Chem. Soc.* **1987**, *109*, 733.
3. Kim, D. H.; Noh, J.; Hara, M.; Lee, H. *Bull. Korean Chem. Soc.* **2001**, *22*, 276.
4. Hyun, M.; Rhee, C. K. *Bull. Korean Chem. Soc.* **2001**, *22*, 213.
5. Sung, M.-M.; Kim, Y. *Bull. Korean Chem. Soc.* **2001**, *22*, 748.
6. Char, S.-K. *Bull. Korean Chem. Soc.* **2004**, *25*, 786.
7. Tamada, K.; Akiyama, H.; Wei, T. X.; Kim, S. A. *Langmuir* **2003**, *19*, 2306.
8. Noh, J.; Hara, M. *Langmuir* **2001**, *17*, 7280.
9. Noh, J.; Hara, M. *Langmuir* **2002**, *18*, 1953.

10. Noh, J.; Kato, H. S.; Kawai, M.; Hara, M. *J. Phys. Chem. B* **2002**, *106*, 13268.
 11. Noh, J.; Ito, E.; Nakajima, K.; Kim, J.; Lee, H.; Hara, M. *J. Phys. Chem. B* **2002**, *106*, 7139.
 12. Noh, J.; Ito, E.; Araki, T.; Hara, M. *Surf. Sci.* **2003**, *532/535*, 1116.
 13. Noh, J.; Hara, M. *Langmuir* **2002**, *18*, 9111.
 14. Ishida, T.; Yamamoto, Y.; Mizutani, W.; Motomatsu, M.; Tokumoto, H.; Hokari, H.; Azebara, H.; Fujihira, M. *Langmuir* **1997**, *13*, 3261.
 15. Camillone III, N.; Leung, T. Y. B.; Schwartz, P.; Eisenberger, P.; Scoles, G. *Langmuir* **1996**, *12*, 2737.
 16. Poirier, G. E.; Pylant, E. D. *Science* **1996**, *272*, 1145.
 17. Poirier, G. E. *Langmuir* **1999**, *15*, 1167.
 18. Noh, J.; Hara, M. *Langmuir* **2000**, *16*, 2045.
 19. Noh, J.; Murase, T.; Nakajima, K.; Lee, H.; Hara, M. *J. Phys. Chem. B* **2000**, *104*, 7411.
 20. Takami, T.; Delamarche, E.; Michel, B.; Gerber, Ch. *Langmuir* **1995**, *11*, 3876.
 21. Venkataraman, B.; Breen, J. J.; Flynn, G. W. *J. Phys. Chem.* **1995**, *99*, 6608.
 22. Noh, J.; Lee, D.; Hara, M.; Lee, H.; Sasabe, H.; Knoll, W. *Jpn. J. Appl. Phys., Part I* **1999**, *38*, 3897.
 23. Claypool, C. L.; Faglioni, F.; Gorrdard III, W. A.; Gray, H. B.; Lewis, N. S.; Marcus, R. A. *J. Phys. Chem. B* **1997**, *101*, 5978.
 24. Cyr, D. M.; Venkataraman, B.; Flynn, G. W.; Black, A.; Whitesides, G. M. *J. Phys. Chem.* **1996**, *100*, 13747.
 25. Poirier, G. *Langmuir* **1999**, *15*, 1167.
 26. Gunning, A. P.; Kirby, A. R.; Mallard, X.; Morris, V. J. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2551.
 27. Nishida, N.; Hara, M.; Sasabe, H.; Knoll, W. *Jpn. J. Appl. Phys., Part I* **1997**, *36*, 2370.
 28. Biebuyck, H. A.; Whitesides, G. M. *Langmuir* **1993**, *9*, 1766.
 29. Heister, K.; Allara, D. L.; Bahnck, K.; Frey, S.; Zharnikov, S. M.; Grunze, M. *Langmuir* **1999**, *15*, 5440.
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