

Improved Structural Quality of Aromatic Thiol Self-Assembled Monolayers on Au(111) by Microwave Irradiation

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The physical and chemical properties of metal surfaces can be easily tailored by self-assembled monolayers (SAMs), which are formed by spontaneous adsorption of organic thiol compounds with various terminal functional groups and can be utilized for various practical applications in surface and materials sciences.¹⁻⁶ In particular, SAMs formed by aromatic thiols have drawn much interest since they can be applied to the fabrication of versatile electronic devices due to their electrical and optical properties.^{4,5} It was demonstrated that the adsorption configuration of aromatic thiol SAMs significantly affects the molecular electronic properties of devices.^{4,5} Therefore, a number of studies have been conducted to control the structural order and to obtain uniform surfaces for aromatic thiol derived SAMs.⁶⁻¹⁰ For instance, long-range ordered benzenethiol (BT) SAMs were obtained by displacement of pre-covered cyclohexanethiol SAMs of low molecular density with BT molecules.¹⁰

It has been demonstrated that the synthesis of organic compounds and nanomaterials can be considerably promoted using microwave irradiation (MWI) techniques, resulting in increased product yield and purity.^{11,12} Recently, this technique was applied to the preparation of dodecanethiol (DDT) SAMs on polycrystalline gold surfaces, and the authors suggested that the DDT molecules formed closely packed SAMs with a high structural quality after MWI for 120 s.¹³ It seems likely that MWI greatly accelerates the molecular self-assembly of alkanethiols on gold. However, there have been no reports describing the effect of MWI on the formation and structures of aromatic thiol SAMs on Au(111) to date. Therefore, to better understand these issues, we examined aromatic thiol SAMs, constructed from BT and biphenylthiol (BPT) on Au(111) by MWI, using scanning tunneling microscopy (STM) and compared their surface structures to SAMs prepared without MWI.

BT and BPT SAMs were prepared by immersing the Au(111) substrate in a 0.5 mM ethanol solution of the corresponding thiol while irradiating in a microwave oven (700 W, weak intensity mode) for 30 min. We confirmed that microwave irradiation for 30 min raised the solution temperature to approximately 55 °C. Therefore, SAMs were also prepared by dipping the Au(111) substrate in thiol solution without MWI at 55 °C for 30 min or 24 h. To examine the effect of MWI on SAM formation, we directly compared the

surface structures of SAMs prepared with and without MWI. STM measurements were performed using a NanoScope E (Veeco, Santa Barbara, CA, USA) and all STM images were obtained in constant current mode with a tunneling current of 300 pA and a bias voltage of 500 mV.

STM images in Figure 1 clearly show that the ordered domain areas of BT SAMs (Figures 1(b)) prepared by MWI were significantly larger than those prepared without MWI (Figure 1(a)). It has been reported that the adsorption of BT molecules on gold under typical preparation conditions, *i.e.*, 24 h immersion in 1 mM solution at room temperature, led to the formation of disordered SAMs containing many SAM-covered Au adatom islands.^{6-8,14} However, after immersion for 30 min at 55 °C, we observed small ordered domains of BT SAMs with lateral dimensions of less than 10 nm indicated by the white circle in Figure 1(a). Many of the Au adatom islands apparent in the room temperature preparation had completely disappeared with the higher temperature conditions.⁶ These structural changes are attributed to the enhanced diffusion rate of BT molecules and Au adatoms on the top gold layer at a higher solution temperature. However, these preparation conditions still do not lead to fully covered, ordered BT SAMs. On the other hand, our previous work demonstrated that BT molecules could form well-ordered SAMs with a $(2 \times 3 \sqrt{2})R23^\circ$ structure after a longer immersion for 24 h at 50 °C.⁸ This result suggests that BT SAMs with high structural order can be obtained with a longer immersion time and a higher solution temperature. Spacing between the ordered molecular lines in Figure 1(a) was measured to be approximately 1.3 nm. The inset high-

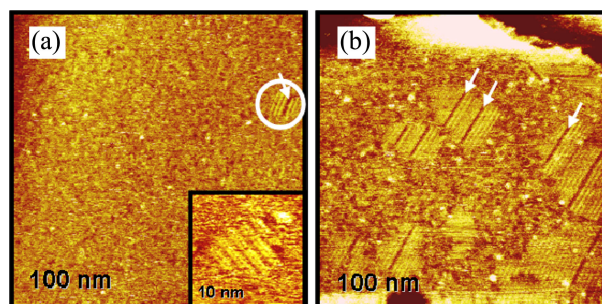


Figure 1. (a) STM image of BT SAMs on Au(111) formed after immersion for 30 min at 55 °C. (b) STM image of BT SAMs on Au(111) formed by microwave irradiation for 30 min.

resolution STM image (10 nm × 10 nm) in Figure 1(a) shows one molecular line (white circle) composed of paired molecular rows, which is quite similar to our previous STM results obtained with a different preparation for BT SAM samples.^{8,10} From these results, we suggest that the molecular packing arrangement of BT SAMs is mainly driven by cofacial interactions between p-conjugated benzene rings.

On the other hand, we found that the structural order of BT SAMs on Au(111) was greatly enhanced using MWI for a short period of time, as shown in Figure 1(b). Although the ordered domains of SAMs prepared without MWI were rarely observed for entire surfaces (Figure 1(a)), BT SAMs prepared by MWI contained ordered domains with more than 30% surface coverage. The size of the ordered domains, in the range of several nanometers to a few tenth nanometers, was much larger than that of SAMs prepared without MWI. Interestingly, a missing molecular line in the ordered domains was observed, designated by white arrows on the STM images in Figure 1. This is the first observation of missing molecular lines in BT SAMs on Au(111), even though similar structural features have often been observed for closely packed alkanethiol SAMs.¹⁵ This result provides strong evidence that BT SAMs grow directionally driven by optimization of *van der Waals* interactions between BT molecules in two adjacent molecular rows.

STM images in Figure 2 show that MWI significantly affected the formation of BPT SAMs, especially the formation of Au adatom islands. BPT SAMs prepared at 55 °C for 30 min had disordered phases containing many SAM-covered Au islands (Figure 2(a)), whereas SAMs prepared by MWI had no Au adatom islands on the surfaces (Figure 2(b)). Note that these islands have usually been observed in SAM formation with various aromatic thiols in which the thiol group was attached directly to the aromatic ring such as for BT, BPT, and substituted benzenethiols.^{8,9,14,16} The observation of Au adatom islands released from the top gold layer during adsorption of aromatic thiols was suggested to result from their low surface mobility.¹⁴ In contrast to BT SAMs, many Au adatom islands emerged from SAM formation of BPT molecules that remained on the surfaces at a higher solution temperature for 30 min, and even after longer immersion for 24 h (data not shown here). Therefore, the migration rate of BPT-covered Au adatom islands could be significantly suppressed by the adsorption of BPT mole-

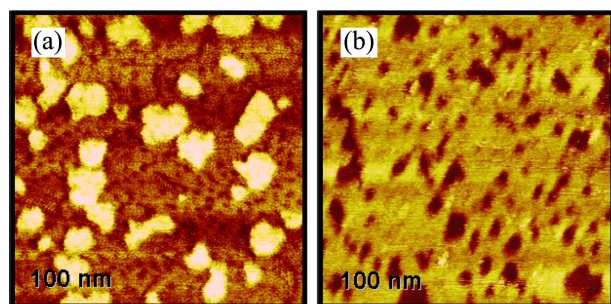


Figure 2. (a) STM image of BPT SAMs on Au(111) formed after immersion for 30 min at 55 °C. (b) STM image of BPT SAMs on Au(111) formed by microwave irradiation for 30 min.

cules, even with a high solution temperature and long immersion time. This affect is mainly due to the larger *van der Waals* interactions both between biphenyl groups and between biphenyl groups and gold surfaces for BPT compared to BT. However, we found that MWI effectively facilitated the removal of Au atom islands during molecular self-assembly of aromatic thiols, resulting in the formation of more uniform SAM surfaces. It was reported that the temperature at metal surface and in near surface region is higher than in bulk solution when MWI was applied.¹⁷ Therefore, we suggest that MWI reduces effectively diffusion barrier of adsorbed molecules and Au atom islands as well as promotes the cleavage of S-H bond during self-assembly of aromatic thiols, resulting in the formation of high-quality SAMs. At present, a systematic study exploring different experimental conditions and different thiol compounds to understand the MWI effect on SAM formation in more detail is underway, and the results of this study will be published separately.

In summary, we have clearly demonstrated that the structural order and surface morphology of BT and BPT SAMs were greatly enhanced by MWI. These results will be very useful for the expeditious fabrication of aromatic thiol SAMs of high structural quality.

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References

- Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzo, R. G.; Whitesides, G. M. *Chem. Rev.* **2005**, *105*, 1103.
- Vericat, C.; Vela, M. E.; Benitez, G.; Carro, P.; Salvarezza, R. C. *Chem. Soc. Rev.* **2010**, *39*, 1805.
- Lee, N.-S.; Kim, D.; Kang, H.; Park, D. K.; Han, S. H.; Noh, J. J. *Phys. Chem. C* **2011**, *115*, 5868.
- Ramachandran, G. K.; Hopson, T. J.; Rawlett, A. M.; Nagahara, L. A.; Primak, A.; Lindsay, S. M. *Science* **2003**, *300*, 1413.
- Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Phys. Chem. A* **1999**, *103*, 7883.
- Dhirani, A. A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 3319.
- Tao, Y.-T.; Wu, C.-C.; Eu, J.-Y.; Lin, W.-L. *Langmuir* **1997**, *13*, 4018.
- Kang, H.; Park, T.; Choi, I.; Lee, Y.; Ito, E.; Hara, M.; Noh, J. *Ultramicroscopy* **2009**, *109*, 1011.
- Kang, H.; Lee, N.-S.; Ito, E.; Hara, M.; Noh, J. *Langmuir* **2010**, *26*, 2983.
- Kang, H.; Lee, H.; Kang, Y.; Hara, M.; Noh, J. *Chem. Commun.* **2008**, 5197.
- Dallinger, D.; Kappe, C. O. *Chem. Rev.* **2007**, *107*, 2563.
- Halodorai, Y.; Zong, T.; Shim, J.-J. *Mater. Chem. Phys.* **2011**, *127*, 385.
- Dai, J.; Cheng, J.; Li, Z.; Shi, Y.; An, N.; Bi, S. *Electrochem. Commun.* **2008**, *10*, 582.
- Yang, G.; Liu, G.-Y. *J. Phys. Chem. B* **2003**, *107*, 8746.
- Noh, J.; Hara, M. *Langmuir* **2001**, *17*, 7280.
- Kang, H.; Shin, D. G.; Han, J. W.; Ito, E.; Hara, M.; Noh, J. J. *Nanosci. Nanotech.* **2012**, *12*, 557.
- Compton, R. G.; Coles, B. A.; Marken, F. *Chem. Commun.* **1998**, 2595.