

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231643444>

Two-Dimensional Network Formation in the C₆₀ Malonic Acid Adlayer on Au(111)

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY C · AUGUST 2007

Impact Factor: 4.77 · DOI: 10.1021/jp0739824

CITATIONS

6

READS

16

6 AUTHORS, INCLUDING:



Junji Inukai

University of Yamanashi

100 PUBLICATIONS **1,739** CITATIONS

SEE PROFILE



Osamu Ito

Tohoku University

593 PUBLICATIONS **15,946** CITATIONS

SEE PROFILE



Kingo Itaya

Tohoku University

246 PUBLICATIONS **8,483** CITATIONS

SEE PROFILE

Two-Dimensional Network Formation in the C₆₀ Malonic Acid Adlayer on Au(111)Masashi Matsumoto,[†] Junji Inukai,^{‡,§} Soichiro Yoshimoto,^{†,||} Yoko Takeyama,[‡] Osamu Ito,[‡] and Kingo Itaya^{*,†}

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Sendai 980-8579, Japan, and Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Aoba-ku, Sendai 980-8577, Japan

Received: May 23, 2007; In Final Form: July 23, 2007

The adsorption of fullerene malonic acid (C₆₀ malonic acid) adlayer on a Au(111) was carried out by immersing it in a benzene solution containing C₆₀ malonic acid molecules, and the adlayer was transferred into vacuum. The adlayer structure was determined to be (3.1 × 3.1)R5° by using scanning tunneling microscopy and low-energy electron diffraction. It is suggested that there is a strong interaction through hydrogen bonding between C₆₀ malonic acid molecules.

Introduction

The construction of molecular network architectures with intermolecular hydrogen bonds is of great value, both for construction of nanoarchitectures and for controlling surface properties.^{1–4} In particular, adlayers of terephthalic acid (and its related compounds) formed on highly ordered pyrolytic graphite (HOPG)^{1,2} and single-crystal metal surfaces, such as Pt,⁴ Au,^{5–7} and Cu,^{8–10} have been investigated extensively both in ultrahigh vacuum (UHV) and in solution by using scanning tunneling microscopy (STM). The hydrogen bonds have the advantage of selectivity and directionality, which are important in building nanostructures.

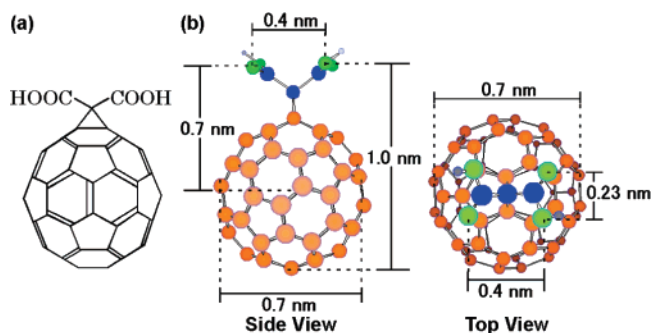
In fullerene derivative adlayers, intermolecular interaction via hydrogen bonding between neighboring molecules is known to play an important role. Therefore, self-organizing structures of fullerene derivatives on flat solid substrates via noncovalent interactions, such as hydrogen bonding, might represent a promising technique to fabricate fullerene-based thin films with precise control and well-defined structures by molecular design.^{11–14} In this respect, C₆₀ functionalized with carboxyl groups is an attractive material, which also has potential to be used for photochemical and electrochemical devices consisting of a fullerene–porphyrin supramolecular assembly.¹⁵

In this letter, we report an adlayer structure of C₆₀ malonic acid consisting of a C₆₀ and a dicarboxylic acid functional group on Au(111) by using STM and low-energy electron diffraction (LEED) in UHV (as shown in Chart 1).

Experimental Section

The fullerene diethyl malonate, C₆₁(CO₂Et)₂, was first synthesized by the reaction of fullerene with diethyl bromo-

CHART 1: (a) Chemical Structure and (b) Calculated Conformation of a C₆₀ Malonic Acid Obtained from a Semiempirical Molecular Orbital Method



malonate in the presence of base.¹⁶ The C₆₀ malonic acid used in this study was subsequently synthesized by the hydrogenolysis of C₆₁(CO₂Et)₂.¹⁷

The single-crystal bead of Au (3 mm in diameter) was made by the crystallization of a molten ball formed at the end of an Au wire in a hydrogen–oxygen flame.^{18,19} A laser-beam reflection method was employed to determine the orientation of the single-crystal bead to expose the (111) plane, which was then polished with successively finer diamond pastes down to 0.25 μm with an accuracy of 0.1°. Au(111) single-crystal surfaces were prepared by the Clavilier method.²⁰ After annealing in a hydrogen flame and cooling in a stream of hydrogen, the Au(111) single-crystal sample was quickly immersed into ultrapure water (Milli-Q SP-TOC; ≥18.2 MΩ cm) saturated with hydrogen.^{21,22} In this way, the unreconstructed Au(111)–(1 × 1) structure was obtained. The adlayers of C₆₀ malonic acid were prepared by immersing the Au(111) substrate for 10–30 s into a benzene solution saturated with C₆₀ malonic acid. The C₆₀ malonic acid-covered Au(111) surface was then transferred into pure benzene to remove excess C₆₀ malonic acid molecules.

UHV-STM (Omicron Vacuumphysik STM1, Germany) and LEED (Omicron Vacuumphysik, Germany) measurements were

* To whom correspondence should be addressed. Phone/Fax: +81-22-795-5868. E-mail: itaya@atom.che.tohoku.ac.jp.

[†] Graduate School of Engineering, Tohoku University.

[‡] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University.

[§] Clean Energy Research Center, University of Yamanashi.

^{||} National Institute of Advanced Industrial Science and Technology (AIST).

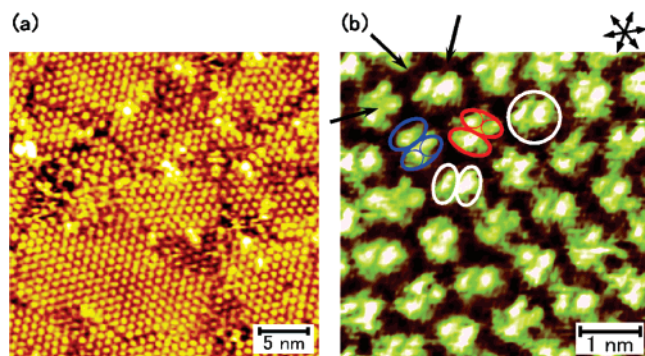


Figure 1. (a) Typical large-scale ($30 \times 30 \text{ nm}^2$) and (b) high-resolution ($4.9 \times 4.9 \text{ nm}^2$) STM images of an ordered C_{60} malonic acid adlayer on Au(111) obtained in UHV. Tip potentials and tunneling currents were 0.59 V and 1.9 nA for (a) and 0.62 V and 1.2 nA for (b), respectively. The set of arrows at the upper right of b indicates $\langle 110 \rangle$ directions of the Au(111) lattice. The longer arrows indicate molecular rows of the adlayer.

carried out in a UHV system consisting of analysis and preparation chambers with a base pressure of 1×10^{-10} Torr.²³ The C_{60} malonic acid-covered Au(111) surfaces obtained as described above were transferred into the chamber filled with ultrapure Ar. This chamber was then evacuated using a sorption pump. It took 2 min to transfer the sample into UHV (1×10^{-10} Torr).²⁴

Spectroscopy-grade benzene (Kanto Chemical Co.) was used as received. Commercial ultrapure Ar (99.999%, Nihonsanso, Japan) was further purified by a Ti getter purifier (Model 2B-20-Q, Centorr). The purified ultrapure Ar contained impurities less than 10^{-5} ppm.²⁴

Results and Discussion

Figure 1a shows a typical large-scale STM image of a C_{60} malonic acid adlayer on Au(111) obtained in UHV after immersing a Au(111) sample in a benzene solution containing the molecules. In the image, acquired in a relatively large area of $30 \times 30 \text{ nm}^2$, atomically flat terraces were almost completely covered with C_{60} malonic acid molecules. Each C_{60} malonic acid molecule is clearly recognized as a round bright spot. The domain size of ordered adlayers of C_{60} malonic acid is small; each domain measures about $10 \times 10 \text{ nm}^2$ on an average. A precise comparison between this STM image and that of the underlying Au(111)–(1×1) lattice revealed that the molecular rows in all domains were rotated at an angle of approximately 5° with respect to the lattice direction of Au(111).

To understand the structural details of the adlayer of C_{60} malonic acid, high-resolution STM images were recorded. Figure 1b shows an STM image in an area of $4.9 \times 4.9 \text{ nm}^2$. In the STM image, spots, as indicated by a large white circle, are regularly arranged. From the cross-sectional profile, the size of one spot was found to be 0.8 nm, in agreement with calculated size of a C_{60} cage (Chart 1b); thus, one spot was assigned to one C_{60} malonic acid molecule. All molecular rows, as indicated by the black arrows in Figure 1b, were rotated at ca. 5° with respect to the lattice direction of Au(111). The average intermolecular spacing along the molecular row directions was found to be 0.89 nm, which corresponds to 3.1 times the Au lattice constant (0.289 nm). The average intermolecular spacing, 0.89 nm, in the molecular row directions of the adlayer structure in the C_{60} malonic acid molecules was shorter by 10% than the spacing of C_{60} on Au(111).^{25–29} The STM image of Figure 1b reveals that each spot that is assigned to one C_{60} malonic acid molecule, consists of two subspots. Some subspots even split

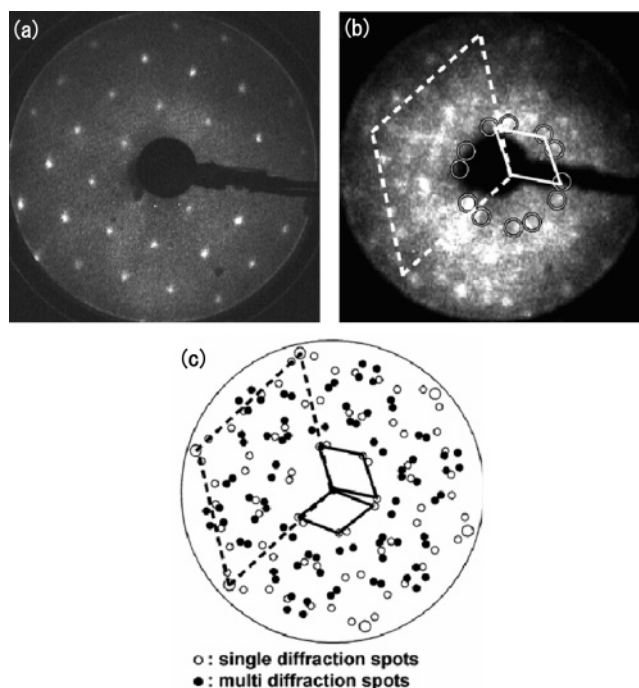


Figure 2. LEED patterns for the ordered adlayer of (a) C_{60} and (b) C_{60} malonic acid on Au(111). The incidental electron energy was (a) 32.7 eV and (b) 40.2 eV. The solid and dashed lines indicate unit cells of the (1×1) substrate lattice and the (3.1×3.1)R 5° adlattice, respectively, in reciprocal space. (c) Simulated LEED pattern. The solid and dashed lines indicate unit cells of the (1×1) substrate lattice and the (3.1×3.1)R 5° adlattice, respectively, in reciprocal space.

into two smaller spots. In Figure 1b, the red, blue, and white ovals indicate the two subspots of C_{60} malonic acid molecules. In blue and red ovals, two smaller spots of a subspot are indicated by the colored smallest ovals. In the high-resolution STM image in Figure 1b, each set of two subspots assigned to the C_{60} malonic acid molecule might be attributed to two $-\text{COOH}$ groups of a C_{60} malonic acid molecule. Consequently, the two smallest spots might be assigned to the two oxygen atoms of a $-\text{COOH}$ group of each C_{60} malonic acid molecule. Such small protrusions in each C_{60} cage were observed in supramolecular assembled adlayers of open-cage C_{60} ^{30,31} and ferrocene-linked C_{60} (C_{60}Fc)³² derivatives formed on the highly ordered zinc octaethylporphyrin (ZnOEP) adlayer on Au(111).^{33,34} The high-resolution STM shown in Figure 1b is very similar to that of a C_{60}Fc array on the ZnOEP-modified Au(111) surface rather than to the open-cage C_{60} derivative on the ZnOEP-modified Au(111) surface.³³ Therefore, we assumed that a C_{60} cage is adsorbed directly on the Au(111) substrate, and two $-\text{COOH}$ groups exist above the C_{60} cage.

To precisely determine the adlattice, LEED measurements were carried out in UHV. Figure 2a shows a LEED pattern of a C_{60} adlayer formed on Au(111) after transferring the C_{60} -modified Au(111) sample into a vacuum chamber. As reported by several groups, it is well-known that C_{60} forms a ($2\sqrt{3} \times 2\sqrt{3}$)R 30° structure on Au(111) both in UHV^{25–27} and in solution.^{28,29} The real space symmetry of the LEED pattern is consistent with that obtained by STM. In contrast, the LEED pattern for C_{60} malonic acid on Au(111) was quite different from that of C_{60} , as shown in Figure 2b. The incidental electron energy of the LEED pattern shown in Figure 2b was 40.2 eV. The LEED pattern of C_{60} malonic acid on Au(111) appeared as dim spots, indicating that the sizes of ordered domains might be small. However, careful inspection of the patterns performed by changing the acceleration voltage and the irradiation angle

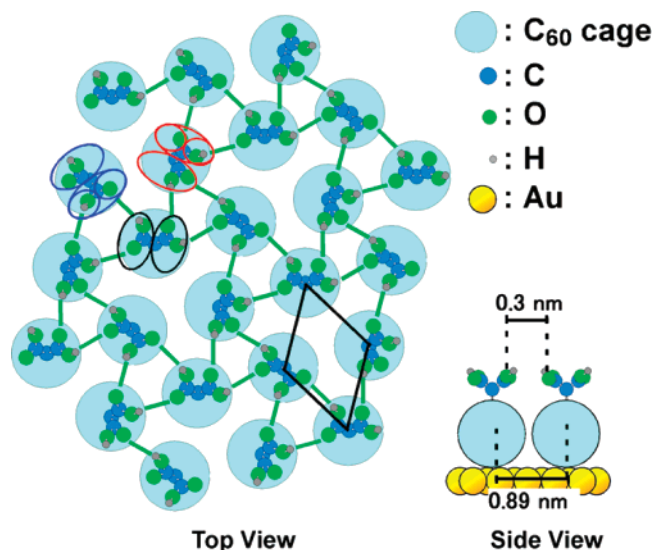


Figure 3. Proposed model of the C_{60} malonic acid adlayer on Au(111)-(1 \times 1) with the (3.1 \times 3.1) $R5^\circ$ symmetry. Unit cell is drawn in black solid lines.

elucidated reciprocal lattice spots of the C_{60} malonic acid with a very-weak intensity. The LEED pattern showed complicated satellite spots. The existence of these satellite spots could be explained by the effect of both single and multiple scattering; thus, this pattern could originate from an incommensurate adlayer structure. The rhombus drawn with dashed white lines in Figure 2b is the reciprocal unit cell of the (1 \times 1) lattice of Au(111), whereas that drawn with solid white lines is the reciprocal unit cell of the C_{60} malonic acid adlayer lattice. Using our homemade program to create reciprocal lattices, we simulated the LEED pattern as shown in Figure 2c based on a (3.1 \times 3.1) $R5^\circ$ incommensurate adlayer. The rhombus indicated by dashed lines is the reciprocal unit cell of the (1 \times 1) lattice, and the two rhombuses by solid lines are of the two domains of the (3.1 \times 3.1) $R5^\circ$ symmetry. Open circles indicate single diffraction spots; whereas filled circles are of multidiffraction spots, which could be observed on incommensurate adlayers. The arrangements of spots in Figure 2b can be explained by the simulated LEED pattern as shown in Figure 2c; thus, the adlayer structure of C_{60} malonic acid on Au(111) in vacuum was assigned as (3.1 \times 3.1) $R5^\circ$ symmetry, which agrees with that determined from STM described above.

On the basis of the STM image and LEED pattern, we propose a structural model of the C_{60} malonic acid adlayer. Figure 3 shows a schematic illustration of the C_{60} malonic acid adlayer derived directly from Figure 1b. The orientations of -COOH groups of C_{60} malonic acid molecules were determined from the positions of the sets of two subspots in Figure 1b. The (3.1 \times 3.1) $R5^\circ$ unit cell is drawn with black solid lines in Figure 3. The sets of red, blue, and white ovals and sets of inner ovals in Figure 3 correspond to those in Figure 1b. Each -COOH group and each oxygen atom are indicated by colored ovals of different sizes. The structural model in Figure 3 illustrates the intermolecular interaction through hydrogen bonding, which exists between two -COOH groups of each adjacent C_{60} malonic acid. The hydrogen bonds were drawn with green solid lines in Figure 3. In this structure, all hydrogen bondings have a length of 0.3 nm, which is within the range of hydrogen bonds (0.27–0.31 nm), corresponding to the length of hydrogen bonds obtained in the trimesic acid (TMA) ordered arrays on HOPG, as reported by Griessl et al.³ The energy for hydrogen bonding is very large, 8–30 $\text{kJ}\cdot\text{mol}^{-1}$; thus, we

believe that C_{60} malonic acid molecules form rigid networks due to hydrogen bonding, the -COOH groups being allowed to be slightly distorted (Figure 3). According to the previous study on trimesic acid by Wandlowski's group, five different packing arrangements of TMA were found on a Au(111) electrode surface in 0.05 M H_2SO_4 .³⁵ For example, several supramolecularly assembled TMA phases were formed by dimerization or trimerization under electrochemical manipulations.^{6,35} On the basis of the packing arrangements of TMA on Au(111) in 0.05 M H_2SO_4 , our proposed model shown in Figure 3 is likely to be consistent with TMA dimerization.³⁵ Note that the (2.56 \times 2.56) $R16^\circ$ structure, which is incommensurate with respect to the substrate, was also found for the hydroquinone (HQ) adlayer on Pt(111), suggesting a strong interaction via hydrogen bonding between adjacent hydroxyl groups in neighboring HQ molecules.^{36,37} This mismatch between the adlayer and substrate lattices might also be present in the C_{60} malonic acid adlayer on Au(111) in vacuum. Therefore, an incommensurate adlayer of C_{60} malonic acid on Au(111) must be formed to maintain the network structure of C_{60} malonic acid molecules.

Conclusions

The C_{60} malonic acid adlayer on Au(111) was characterized in UHV by using STM and LEED, and the adlayer structure was determined to be (3.1 \times 3.1) $R5^\circ$, which was incommensurate with Au(111) lattice. Neighboring C_{60} malonic acid molecules interact strongly through hydrogen bonding between two -COOH groups of neighboring C_{60} malonic acid molecules. The hydrogen bonds can tune the adlayer structure of the fullerene derivative for constructing novel surface architectures.

Acknowledgment. This work was supported partially by Core Research for Evolutional Science and Technology (CREST) organized by the Japan Science and Technology Agency (JST), by a Grant-in-Aid for Young Scientists (B) (no. 16750106/18750132), and the COE project, "Giant Molecules and Complex Systems, 2007" from the Ministry of Education, Culture, Sports, Science and Technology (MEXT). We acknowledge Dr. Y. Okinaka for his assistance in writing this manuscript.

References and Notes

- (1) De Feyter, S.; De Schryver, F. C. *Chem. Soc. Rev.* **2003**, 32, 139.
- (2) De Feyter, S.; De Schryver, F. C. *J. Phys. Chem. B* **2005**, 109, 4290.
- (3) Griessl, S.; Lackinger, M.; Edelwirth, M.; Hietschold, M.; Heckl, W. M. *Single Mol.* **2002**, 3, 25.
- (4) Kim, Y.-G.; Yau, S.-L.; Itaya, K. *Langmuir* **1999**, 15, 7810.
- (5) Ishikawa, Y.; Ohira, A.; Sakata, M.; Hirayama, C.; Kunitake, M. *Chem. Commun.* **2002**, 2652.
- (6) Su, G.-J.; Zhang, H.-M.; Wan, L.-J.; Bai, C.-L.; Wandlowski, Th. *J. Phys. Chem. B* **2004**, 108, 1931.
- (7) Clair, S.; Pons, S.; Brune, H.; Kern, K.; Barth, J. V. *J. Phys. Chem. B* **2004**, 108, 14585.
- (8) Dmitriev, A.; Lin, N.; Weckesser, J.; Barth, J. V.; Kern, K. *J. Phys. Chem. B* **2002**, 106, 6907.
- (9) Stepanow, S.; Lingenfelder, M.; Dmitriev, A.; Spillmann, H.; Delvigne, E.; Lin, N.; Deng, X.; Cai, C.; Barth, J. V.; Kern, K. *Nat. Mater.* **2004**, 3, 229.
- (10) Barth, J. V.; Costantini, G.; Kern, K. *Nature* **2005**, 437, 671, and references therein.
- (11) Lehn, J. M. *Science* **2002**, 295, 2400.
- (12) Lehn, J. M. *Rep. Prog. Phys.* **2004**, 67, 249.
- (13) Bonifazi, D.; Enger, O.; Diederich, F. *Chem. Soc. Rev.* **2007**, 36, 390.
- (14) Diederich, F.; Gomez-Lopez, M. *Chem. Soc. Rev.* **1999**, 28, 263.

- (15) Imahori, H.; Liu, J.-C.; Hosomizu, K.; Sato, T.; Mori, Y.; Hotta, H.; Matano, Y.; Araki, Y.; Ito, O.; Maruyama, N.; Fujita, S. *Chem. Commun.* **2004**, 2066.
- (16) Bingel, C. *Chem. Ber.* **1993**, 126, 1957.
- (17) Lamparth, I.; Hirsch, A. *J. Chem. Soc., Chem. Commun.* **1994**, 1727.
- (18) Honbo, H.; Sugawara, S.; Itaya, K. *Anal. Chem.* **1990**, 62, 2424.
- (19) Itaya, K. *Prog. Surf. Sci.* **1998**, 58, 121.
- (20) Clavilier, J.; Faure, R.; Guinet, G.; Durand, R. *J. Electroanal. Chem.* **1980**, 107, 205.
- (21) Yoshimoto, S.; Narita, R.; Itaya, K. *Chem. Lett.* **2002**, 356.
- (22) Yoshimoto, S.; Narita, R.; Wakisaka, M.; Itaya, K. *J. Electroanal. Chem.* **2002**, 532, 331.
- (23) Yamada, T.; Batina, N.; Itaya, K. *J. Phys. Chem.* **1995**, 99, 8817.
- (24) Wakisaka, M.; Sugimasa, M.; Inukai, J.; Itaya, K. *J. Electrochem. Soc.* **2003**, 150, E81.
- (25) Altman, E. I.; Colton, R. *J. Surf. Sci.* **1992**, 279, 49.
- (26) Altman, E. I.; Colton, R. *J. Surf. Sci.* **1993**, 295, 13.
- (27) Altman, E. I.; Colton, R. *J. Phys. Rev. B* **1993**, 48, 18244.
- (28) Yoshimoto, S.; Narita, R.; Tsutsumi, E.; Matsumoto, M.; Itaya, K.; Ito, O.; Fujiwara, K.; Murata, Y.; Komatsu, K. *Langmuir* **2002**, 18, 8518.
- (29) Yoshimoto, S.; Tsutsumi, E.; Narita, R.; Murata, Y.; Murata, M.; Fujiwara, K.; Komatsu, K.; Ito, O.; Itaya, K. *J. Am. Chem. Soc.* **2007**, 129, 4366.
- (30) Yoshimoto, S.; Tsutsumi, E.; Honda, Y.; Murata, Y.; Murata, M.; Komatsu, K.; Ito, O.; Itaya, K. *Angew. Chem., Int. Ed.* **2004**, 43, 3044.
- (31) Yoshimoto, S.; Honda, Y.; Murata, Y.; Murata, M.; Komatsu, K.; Ito, O.; Itaya, K. *J. Phys. Chem. B* **2005**, 109, 8547.
- (32) Yoshimoto, S.; Saito, A.; Tsutsumi, E.; D'Souza, F.; Ito, O.; Itaya, K. *Langmuir* **2004**, 20, 11046.
- (33) Yoshimoto, S. *Bull. Chem. Soc. Jpn.* **2006**, 79, 1167.
- (34) Yoshimoto, S.; Itaya, K. *J. Porphyrins Phthalocyanines* **2007**, 11, 313.
- (35) Li, Z.; Han, B.; Wan, L.-J.; Wandlowski, Th. *Langmuir* **2005**, 21, 6915.
- (36) Inukai, J.; Wakisaka, M.; Yamagishi, M.; Itaya, K. *Langmuir* **2004**, 20, 7507.
- (37) Inukai, J.; Wakisaka, M.; Yamagishi, M.; Itaya, K. *J. Electrochem. Soc.* **2005**, 152, E35.