Molecular Nanostamp Based on One-Dimensional Porphyrin Polymers

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ABSTRACT: Surface design with unique functional molecules by a convenient one-pot treatment is an attractive project for the creation of smart molecular devices. We have employed a silane coupling reaction of porphyrin derivatives that form one-dimensional polymer wires on substrates. Our simple one-pot treatment of a substrate with porphyrin has successfully achieved the construction of nanoscale bamboo shoot structures. The nanoscale bamboo shoots on the substrates were characterized by atomic force microscopy (AFM), UV–vis spectra, and X-ray diffraction (XRD) measurements. The uneven and rigid nanoscale structure has been used as a stamp for constructing bamboo shoot structures of fullerene.

KEYWORDS: polymer wire, porphyrin, uneven surface, molecular orientation, silane coupling reaction
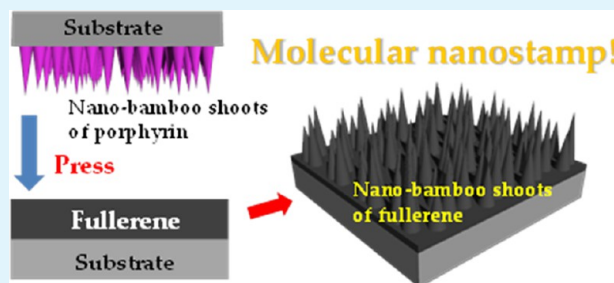
INTRODUCTION

Decoration of electrode surfaces with unique functional materials is an important issue for the creation of outstanding functional molecular devices.[1−7] The spin coating or casting method is known as a simple, convenient technique for electrode modification. In these systems, molecules are physically and randomly fixed on the electrodes; therefore, the migration of electrons randomly occurs in the films.[8−12] Recently, controlling the orientation of assembled molecules on electrodes has become a key project in the fields of chemistry and biology because of directional control and efficiency of electron transfer.[13−19] One of the most important structures of molecules on an electrode surface is an uneven structure. By the contacting of two types of molecules such as donor and acceptor molecules, the effective charge transfer and/or electron hopping occurs between them. For example, Nakamura et al. have reported the intercalated structure (columnar structure) of fullerene and tetrabenzoporphyrin derivatives on an electrode that showed high photocurrent efficiency.[20] However, it has been difficult to prepare an uneven structure of molecules at electrode to date.[21−23]

An effective method of controlling molecular orientation and structure at a substrate is a chemical bond formation between a molecule and the substrate, such as self-assembled monolayers and multilayers.[24] By inducing multiple, rigid spacers onto a functional molecular backbone, orientation of the functional molecules can be easily controlled.[25] Therefore, electrons can be effectively transferred between the redox sites.[13] Much effort has been devoted to preparing well-ordered films.[18] For example, Thompson and Mallouk et al. have reported on the construction of metal–organic hybrid multilayer films on substrates using a bottom-up process.[26,27] The layer-by-layer (LbL) molecular fabrication method is an effective way to obtain uniformly assembled films.[28−32] The advantage of the LbL approach is a precise controlling of the components and thickness of the films.

By contrast, the stepwise fabrication method described above is a time-consuming work of obtaining uniform multilayer films. For example, in the LbL fabrication method, several days are needed to obtain 100 nm scale structures on substrates.[32] Fischer et al. recently reported on highly ordered metal–organic frameworks on a substrate using a one-pot reaction.[33] Metal ions and
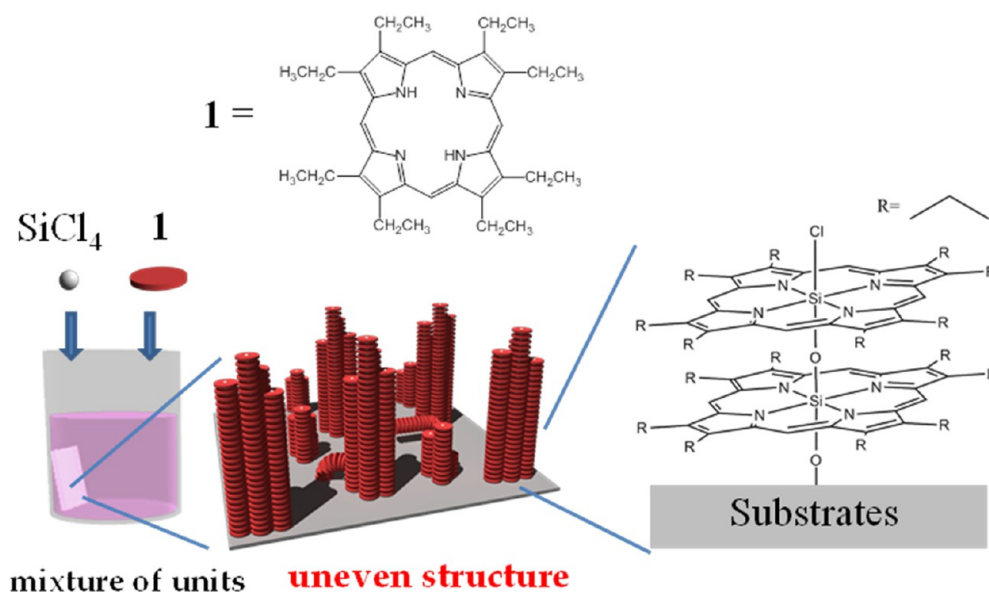
Figure 1. New strategy of preparing an uneven structure by a convenient one-pot treatment based on porphyrin derivatives in the solution process and chemical structures used in this study.
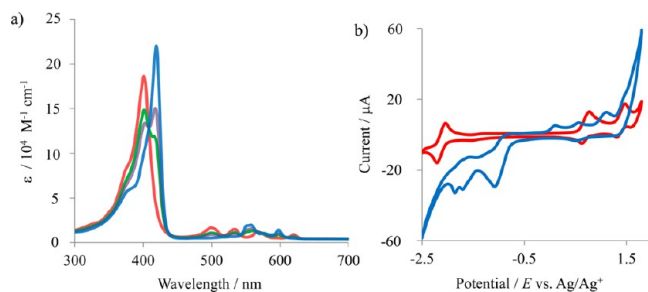

Figure 2. (a) UV−vis absorption spectra of **1** by the addition of $SiCl_4$ (0 red, 0.75 green, 1 purple, and 1.25 equiv blue). (b) Cyclic voltammograms of **1** (red) and **1** containing of $SiCl_4$ (blue) in 0.1 M $TBAPF_6$ at room temperature.
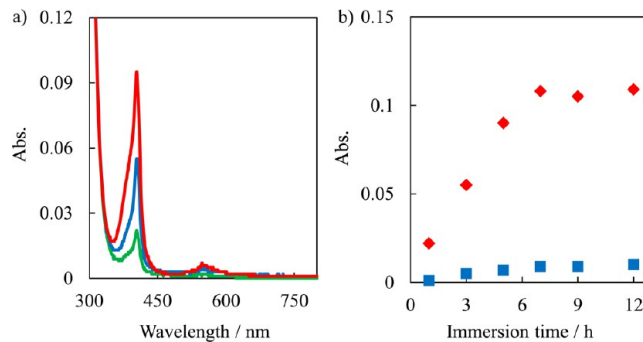

Figure 3. (a) Electronic spectra of a glass substrate after immersion of a mixture of **1** and $SiCl_4$ in $CHCl_3$ (green 1, blue 3, and red 5 h) and (b) plots of peak absorbance at 404 (red) and 547 nm (blue) in the electronic spectra vs immersion periods of time.
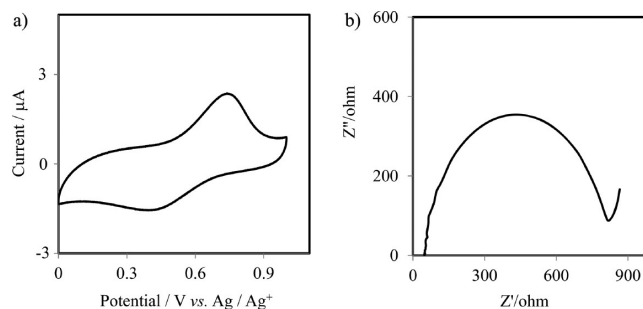

Figure 4. (a) Cyclic voltammogram of the 3-h film on ITO electrode in 0.1 M $TBAPF_6$ and (b) Nyquist plot of the 1-h film on ITO electrode in 0.1 M Na_2SO_4 containing of $K_4[Fe(CN)_6]$ at 0.22 V vs Ag/AgCl.

ligands can be assembled to form frameworks on a substrate in a solution. We have recently focused on a convenient method of constructing substrates that have large surface areas with functional materials. The uneven structure have been used for the creation of high-performance solar cells, thermoelectric conversion elements, and so on.[34,35] In this study we have succeeded in preparing 5−20 nm scale uneven structures composed of a porphyrin derivative using a silane coupling reaction on a substrate conveniently (Figure 1). These structures, namely bamboo shoots structures, were determined by in-plane and out-of-plane XRD measurements, and it was clarified that the periodic network formation occurred on the substrate. This smart connection technique also made it possible to create nanoscale PN heterojunction structures on various substrates conveniently.

■ EXPERIMENTAL SECTION

Materials. Reagents of $SiCl_4$ and 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin were purchased from TCI and Aldrich, respectively. A glass (20 mm × 20 mm) and ITO (indium tin oxide; 10 Ω/cm^2, Furuuchui Kagaku) substrates were washed with 2-propanol, methanol, and then pure water before use. For impedance measurement, $K_2[Fe(CN)_6]$

and Na_2SO_4 were purchased from KANTO Kagaku and TCI, respectively. Fullerene was purchased from Aldrich.

Methods. Impedance measurement was carried out using ALS electrochemical analyzer model 660A in 0.1 M Na_2SO_4 aqueous solution containing $K_2[Fe(CN)_6]$ at 0.22 V. Pulse width was ±0.01 V; frequency

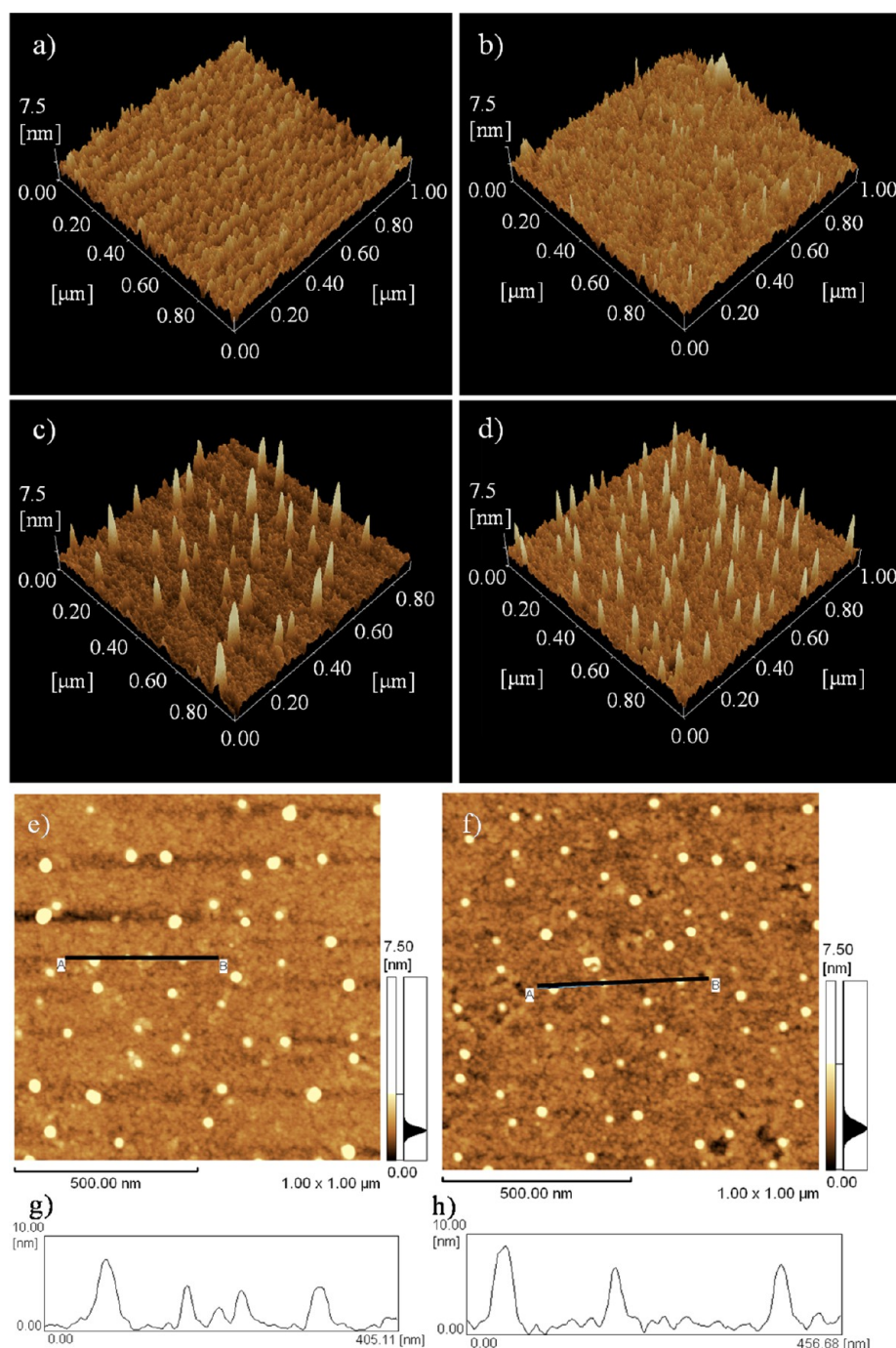**Figure 5.** 3D AFM images of films: (a) **1**, (b) **3**, (c) **5**, and (d) 7-h film. Top-view AFM images of **5** (e) and 7-h film (f), and their topological profiles (g and h), respectively.

was $0.1-10^5$ Hz. Atomic force microscopy (AFM) images were observed using Shimadzu SPM-9600. Cyclic voltammetry (CV) of the films was measured in 0.1 M tetrabuthylammonium hexafluorophosphate (TBAPF$_6$) solution in CH$_2$Cl$_2$. UV–vis absorption spectra were monitored using Shimadzu UV-3150. For stamp experiment, Jasco MP-1 mini press was used and sandwich films were pressed at 100 kg/cm^2 for 10 s. XRD measurement was carried out using RIGAKU Smart lab.

Formation of Nano-Bamboo-Shoots Composed of Porphyrin at Substrates. A small excess amount of SiCl$_4$ was added to a 0.1 mM chloroform solution containing 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphyrin, **1**, at room temperature under the atmosphere. A glass or ITO substrate was immersed in the solution mixture for various periods of time. The plate was thoroughly washed by ultrasonic cleaning for

1 min in order to remove the physically attached molecules, and then, it was dried by a stream of nitrogen gas.

Preparation of Stamped Uneven Surface Films. A glass plate was immersed in a saturated toluene solution of fullerene for 24 h at room temperature. The plate was thoroughly picked up from the solution and, then, dried with a nitrogen gas stream. Two plates (this fullerene film and the plate modified with nano-bamboo-shoots) were put together and pressed at 100 kg/cm^2 for 10 s. The stamped surface morphology was monitored by AFM measurement.

■ RESULTS AND DISCCUSSION

Nano-Bamboo-Shoots Composed of Porphyrin at Substrates. Electronic spectra and cyclic voltammograms of **1** and
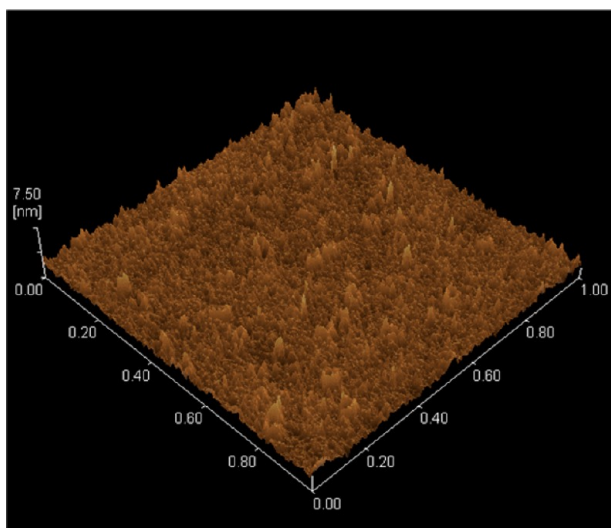
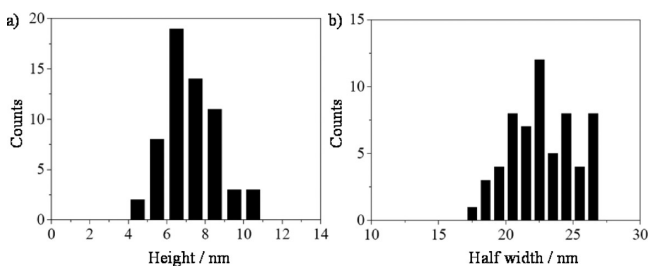**Figure 6.** 3D AFM image of glass plate after the immersion in the solution of **1** without SiCl$_4$.

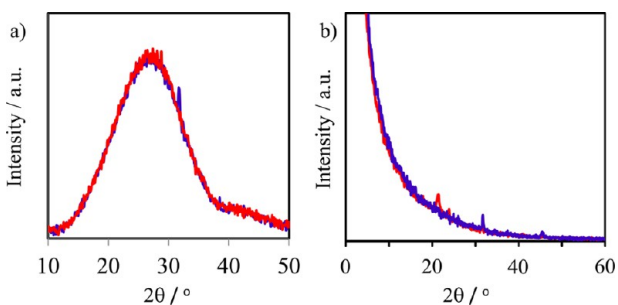**Figure 7.** Height (a) and the half-width (b) distributions of the 7-h film.

Figure 8. (a) Out-of-plane XRD patterns of 7-h film (blue) and bare glass plate (red) and (b) in-plane XRD pattern of 7-h film (blue) and bare glass plate (red).
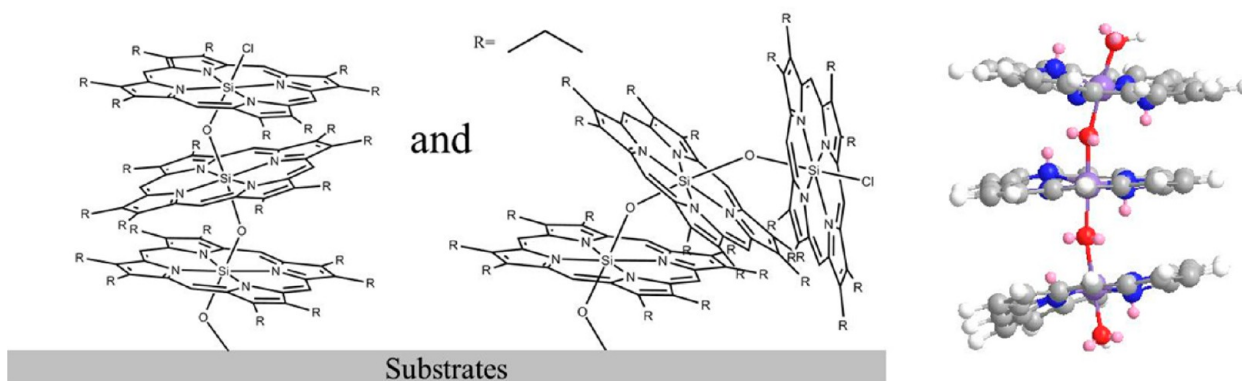
mixtures of **1** and SiCl$_4$ in solutions are shown in Figure 2. The electronic spectrum of **1** gradually changed with the addition of SiCl$_4$ (Figure 2a). The reversible redox waves of **1** were changed to irreversible waves (Figure 2b). The electronic spectra of a glass plate after immersion in a mixed solution of **1** and SiCl$_4$ for 1, 3, and 5 h are shown in Figure 3a (these films are defined as 1, 3, and 5-h films, respectively). Two peaks at 404 and 547 nm were observed in the electronic spectra based on the typical Soret and Q bands of porphyrin derivatives. The number of Q bands was observed as only one peak, which indicates that the Si atom was probably located in the center of the porphyrin core on the substrates. In the present study, SiCl$_4$ reacted with the protons of the porphyrin and then encased the Si-bounded porphyrin, which is similar to the case of Yu.[36] The plots of the peak absorbance vs immersion periods of time are shown in Figure 3b. The absorbance of the films continuously increased with the immersion time. The red shift of Soret and Q bands was not observed, which indicates there is no electronic communication among porphyrins on the substrate. The number of porphyrin derivatives on glass was calculated using absorbance of the films and molar extinction coefficient in solution to be 0.52, 1.3, and 2.2×10^{-10} mol/cm^2 for 1, 3, and 5-h films, respectively.

Electrochemical Behavior of Nano-Bamboo-Shoots. Figure 4a shows CV of the 3-h film on the ITO electrode; the number of molecules was calculated from the anodic area to be 0.70×10^{-10} mol/cm^2. We consider the difference of molecular coverage between glass and ITO is due to the different density of OH group on the substrates. And, the absorbance of porphyrin on substrates depends on not only the molecular orientation[37] but also the aggregation. Therefore, the surface density of porphyrins using absorption spectra might be different from that using CV measurement. Figure 4b shows Nyquist plot of the 1-h film in K$_2$[Fe(CN)$_6$] solution. The resistance of charge transfer was increased in longer immersion time (800 ohms for the 1-h film and 16 500 ohms for the 3-h film), which indicated that the film growth occurred on the electrode.

Morphology of Nano-Bamboo-Shoots. AFM images of 1, 3, 5, and 7-h films are shown in Figure 5a–d. Fine needles appeared on the substrate in a few hours (Figure 5b). In several hours, the numbers of needles and their widths gradually increased (Figures 5c and d). These images also support the continuous wire formation of the porphyrin derivative. The height of the bamboo shoots was ca. 7 nm when the immersion time was 3–7 h, and the polymer was composed of ca. 20–30 porphyrins based on the Si–O–Si length. The topological profiles of the AFM images are shown in Figure 5g and h (2D AFM images are
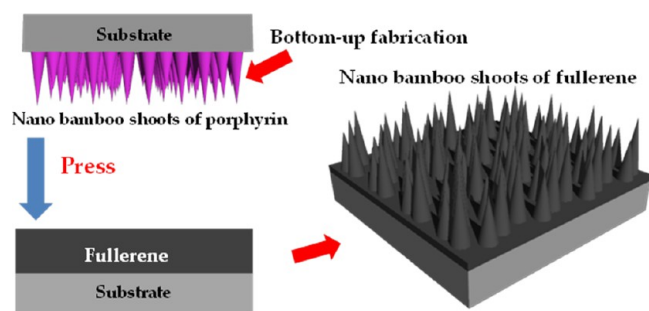

Figure 9. Chemical structures of nanobamboo shoots on a substrate and trimer calculated by MM2.

Figure 10. Concept for preparation of uneven surface by stamp method.

shown in Figure 5e and f, respectively). The bamboo shoots were not formed without SiCl$_4$ (Figure 6). This indicates that the SiCl$_4$ is required for growth of the bamboo shoots. The distributions of height and half width of 7-h film are shown in Figure 7. The number of porphyrin on the substrate considering the height and the density observed in AFM supports UV−vis absorbance.

X-ray Analysis of Nano-Bamboo-Shoots. X-ray diffraction analysis was carried out using Rigaku Smart Lab. Figure 8a shows out-of-plane XRD of the 7-h film (blue) and bare glass

(red). The value of 2θ (31.68 deg) indicates that the periodic structure in the film is 0.28 nm. This value was also observed in the in-plane XRD profile (the values were 31.66 (0.28 nm) and 45.38 (0.20 nm) in Figure 8b. This indicates a periodic Si−O−Si network, which is different from the well-known crystal structures of cristobalite and quartz (red line in Figure 8b), exists both perpendicular and parallel to the surface (Figure 9). A chemical structure of trimer of Si-porphyrin (simpler structure than **1**) by using the MM2 calculation is shown in Figure 9. Unfortunately we cannot clarify the exact structure of polyporphyrin wire on the substrate in the present study because the number of peaks was not enough to simulate. However it should be noted that a periodic structure exists in the layers. We considered that SiCl$_4$ reacted with the surface of the hydroxyl groups at the substrate in the initial step, and the porphyrin bearing silyl chloride or silanol attached on the surface. Furthermore, other porphyrin derivatives continuously attached with the porphyrin derivatives (Figure 1). As a result, a needle structure formed on the substrate. Some porphyrin derivatives were assembled near the needle,[38,39] probably because of amphiphilic interaction among porphyrin derivatives, and then formed bamboo shoot structures. The peak observed at 45.38° might be expected to the assembled structures of porphyrin
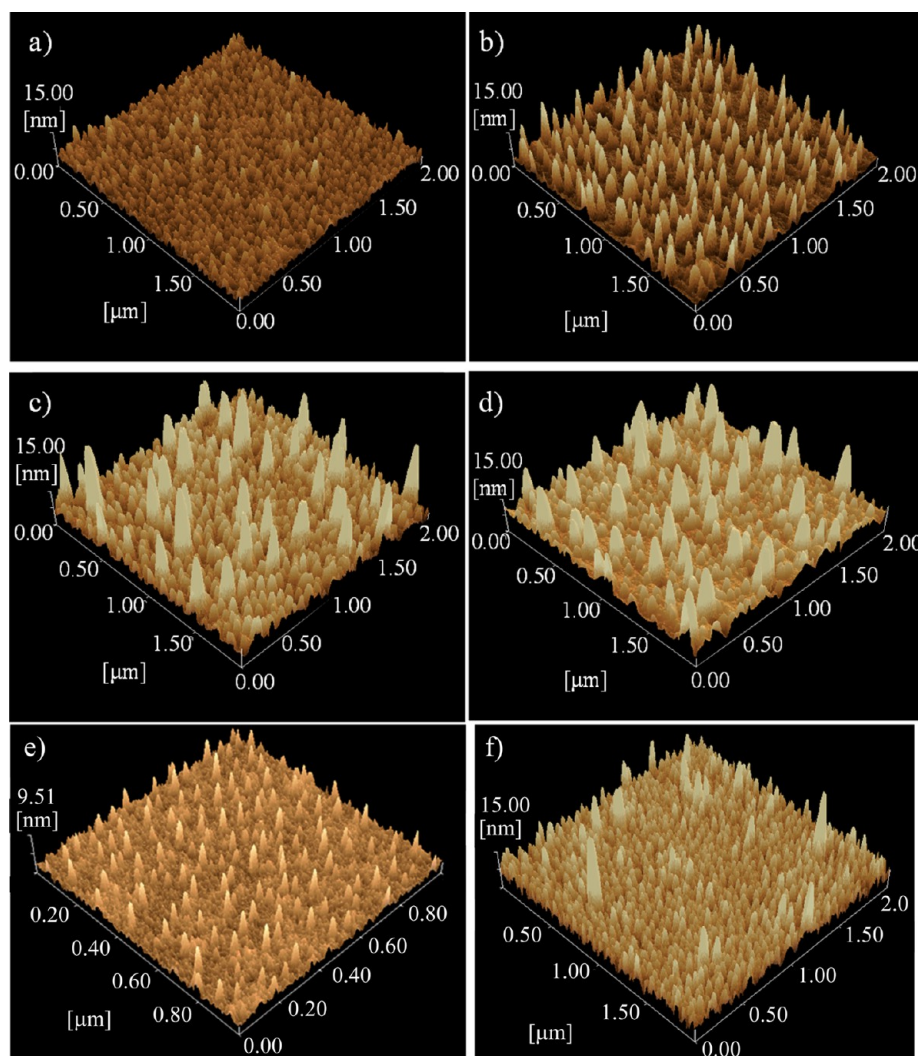

Figure 11. AFM images of (a) fullerene modified film, (b−d) fullerene film after stamping with the porphyrin uneven plate, and (e and f) porphyrin uneven plate used as stamps for b and c−d, respectively.

chains. However the interaction was so weak that the peak shift in electronic spectrum was not observed.

Preparation of Uneven Surfaces Using a Nano-Bamboo-Shoot Stamp. Our next target is the formation of a nanoscale uneven structure using this porphyrin bamboo shoot plate as a molecular stamp (Figure 10).[40] The AFM images of the fullerene film before and after stamping, and the stamps with bamboo shoots are shown in Figure 11. The simple domain structure of the fullerene was observed; there was no large uneven structure in the film (Figure 11a). After the bamboo shoot film was put on the uniform fullerene film, the two plates were pressed for 10 s. The AFM image of the fullerene plate after the stamp is shown in Figure 11b (AFM image of the stamp is shown in Figure 11e). Many bamboo shoots at heights of 10−20 nm could be observed. Figure 11c also shows an AFM image of fullerene film after the stamp (AFM image of the stamp is shown in Figure 11f). The density of the bamboo shoots of fullerene can be controlled by that of porphyrin's bamboo shoots. After the washing of the porphyrin stamp with toluene in order to remove physically adsorbed fullerene, the porphyrin stamp was pressed onto another fullerene film. The AFM was similarly observed to the previous one (see Figure 11d) indicating the repeatability of the porphyrin stamp. This stamp with porphyrin bamboo shoots can be useful for soft materials and not for hard surfaces such as gold electrode.

Conclusion. We have for the first time prepared a nano-bamboo-shoot structure on a substrate using a simple and convenient solution process via a continuous silane coupling reaction. The height and density of the bamboo shoots on substrates can be controlled by changing the immersion conditions. The structure of the bamboo shoots is determined by an X-ray diffraction pattern, and the Si−O−Si networks of the porphyrin form perpendicular and parallel to the substrate. Furthermore, the rigid bamboo shoots composed of a porphyrin derivative can be used as a stamp for preparing nanoscale uneven structures conveniently.[41−44] These convenient and reproducible methods for preparing uneven structures will be useful to create not only high-performance organic solar cells but also thermoelectric conversion elements.

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Notes

The authors declare no competing financial interest.

ABBREVIATIONS

AFM, atomic force microscope
CV, cyclic voltammetry
ITO, indium tin oxide
LbL, layer-by-layer
XRD, X-ray diffraction

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