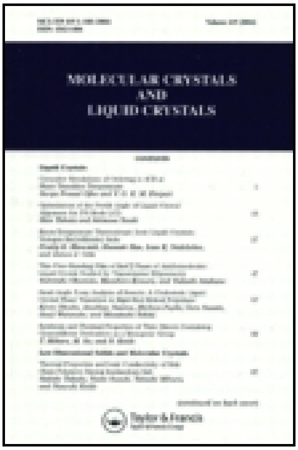

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Characterization of Self-Assembled Dendritic Complex with Pt(II) Ion Using Tapping-Mode Atomic Force Microscopy

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CHARACTERIZATION OF SELF-ASSEMBLED DENDRITIC COMPLEX WITH Pt(II) ION USING TAPPING-MODE ATOMIC FORCE MICROSCOPY

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In this study, the terpyridine-platinum (II) complex on the periphery of the dendritic carbosilane has been prepared from the reaction of Pt(COD)Cl_2 and the 4′-functionalized-(2,2′:6′,2″-terpyridine) on dendrimers. The same self-assembly procedure of the dendrimer was used for two different concentrations. One for the isolated dendrimers, the other for the film. Tapping-mode atomic force microscopy (TM-AFM) has been used to investigate the shape and size of dendrimers individually dispersed on Au (III) substrate, as well as the film of the dendrimer. As a result, the imaged single dendrimer show that dendrimer is dome shaped and its size can be measured by TM-AFM. However, with that of higher concentration, it was difficult to obtain a clear image of the single molecule. In addition, we measured I–V curve using STS, which shows the ohmic contact between -0.22 V and 0.22 V, and beyond that range, the current was increased exponentially.

Keywords: AFM; dendrimer; ion complex; self-assembly; STS

1. INTRODUCTION

Recently, numerous attentions have been devoted to metal-contaning dendrimers such as ruthenium, cobalt and platinum on the periphery due to their potential usage in material science including nano particle, optical

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materials and moleculae electronics. Made *et al.* performed the study on the carbosilane dendrimer, which is based on the organic silicon compound in 1992 [3]. Thereafter, the carbosilane dendrimer has become an important part of new applications of the carrier of the functional. Particularly, Metal complexes of 2,2′:6′,2″ terpyridine (tpy) have been studied as a part of a wide range of new applications, including their usability as building blocks for supramolecular chemistry and molecular electronics [4].

In this study, we synthesized the dendritic carbosilan containing the terphyridine-platinum (II) complex on the periphery. By controlling the concentration of the dendrimer, individually dispersed dendrimers and the film of the dendrimer were obtained. Tapping mode AFM was used to investigate their morphological properties. We attempted to measure the morphologies and electrical properties of a G3-16[tpy-Pt-py] dendrimer, which was formed as one or as a small group of molecules on the Au (III) substrate using the tapping mode AFM for the former and STS for the latter.

2. EXPERIMENTAL

16 terpyridil groups on carbosilane dendritic perphery were synthesised by the use of siloxanetetramer 2,4,6,8-tetramethyl-2,4,6,8-etravinyl-2,4,6,8-tetrasila-1,3,5,7-tetraoxacydo octane, $((CH_2{=}CH)\ MeSiO)_4$ as the core molecule. By the two alternative processes, hydrosilation with $HSiMe_nCl_{3-n}$ and alcoholysis with allylalcohol, the dendrimer carried out up to the fourth generation with 16 Si—Cl bonds on the periphery. The dendrimer, G3-16tpy has 16 groups of 6-hydroxyhexa-1-oxy-4′-[2,2′:6′,2″-terpyridine] on the outermost periphery of the dendrimer.

After the addition of 0.27 g (0.14 mmol) of G3-16tpy dissolved in 25 ml of methanol to 0.22 g (0.58 mmol) of $Pt(COD)Cl_2$ and than refluxed for 2 h. The reaction mixture was changed from brown to yellow by the reflux. And a solution of 6-thiohexa-1-thio-4′-pyridine (0.11 g, 0.49 mmol) in methanol (25 ml) was added to the solution of G3-16[tpy-Pt] (0.40 g, 0.031 mmol) in methanol (25 ml). The reaction mixture was changed from yellow to orange by stirring. The product G3-16[tpy-Pt-py] was obtained as a bright orange needle type solid 0.42 g (0.027 mmol, 88%). The chemical structure of G3-16[tpy-Pt-py] dendrimer is shown in Figure 1.

G3-16[tpy-Pt-py] dendrimer was self-assembled onto the flat Au (111) substrate by simply immersing the substrate into a solution diluted with dimetyl sulfoxide $((CH_3)_2SO)$ in two different concentrations, 10 μmol/ml and 100 μmol/ml. After the self-assembly process, the substrate was alternately rinsed with pure dimethyl sulfoxide solution, ethanol and water and then dried in an oven at 40°C.

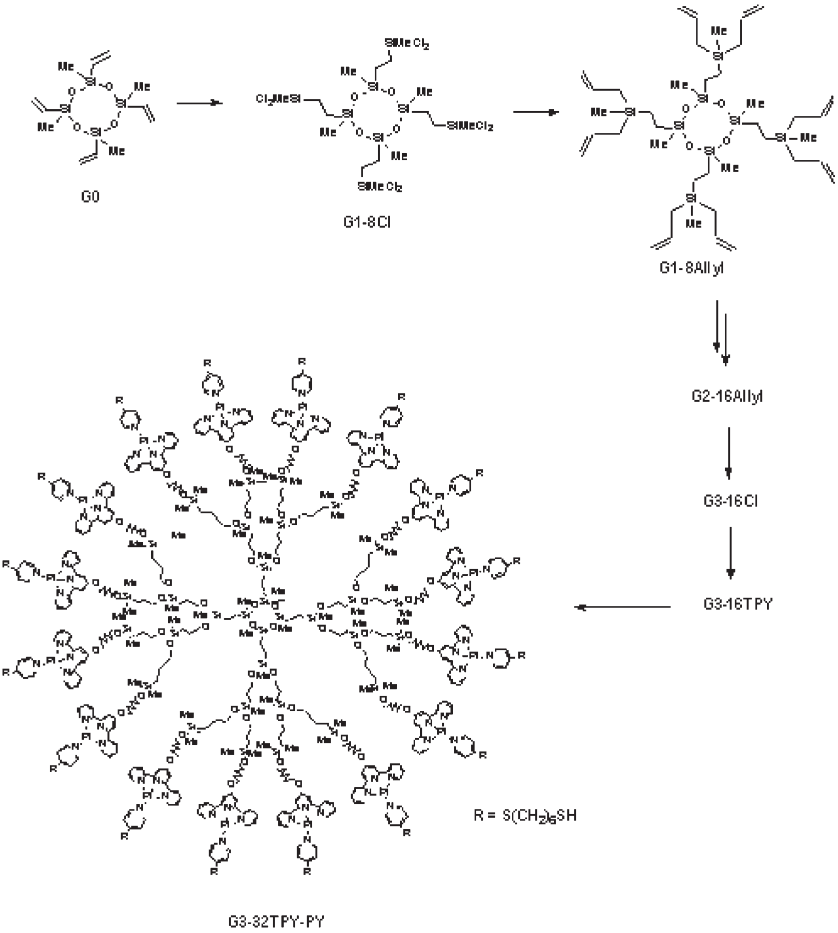


FIGURE 1 The molecular structure of the G3-16[tpy-Pt-py] dendrimer.

To obtain topographical data, the tapping-mode AFM measurement was performed in an atmosphere with a Multimode SPM (Nanoscope III, Digital Instruments, Santa Barbara, CA). In this mode, a 10 μm scanner and cantilever with force constants of 20–100 N/m, and used at a resonance frequency of 200–400 kHz were used. A sharp tip having an apex radius from 5 to 10 nm, was selected for this study. All images were recorded with a slow scan rate, 1 Hz, and a resolution of 512 × 512 pixels per image was chosen. Each sample was examined at least 3 times under the same conditions, and the images were found reproducibly.

3. RESULTS AND DISCUSSION

To get the suitable image of a material with SPM, an appropriate scan-mode must be used for each material. However, in the contact mode, it is known that the tip is in physical contact with the surface during the scanning and can cause physical damage to soft materials. To minimize these problems mentioned above, we selected the tapping mode AFM. In this mode, the cantilever is vibrated so that the tip touches the surface intermittently. This intermittent contact serves to diminish the lateral forces incident on the soft material, reducing the possible damage on the surface or its movement but maintaining resolution [4]. Figure 2(a) and Figure 2(b) show the tapping mode AFM images of the adsorbed dendrimers on the Au (III) surface in the two different concentrations, 10 μmol/ml and 100 μmol/ml respectively. In the case of lower concentration, Figure 2(a), we can observe the dispersed individual dendrimers on the substrate. Most of them are domed shape. However, they are irregular in size. We consider that the variation of these values may arise from differences in the origin of molecular sizes resulting from the synthesis, the differences of geometrical surface or the number of Au-thiol bonds. Some large particles, as marked with arrows, show aggregates of individual dendrimers. We consider that the polarity of dendrimers is responsible for the aggregates. In the higher concentration, Figure 2(b), aggregates of the dendrimer form a film. The sizes of these aggregates were similar with previously mentioned large particles in Figure 2(a). Besides, some isolated dendrimers are seen in Figure 2(b).

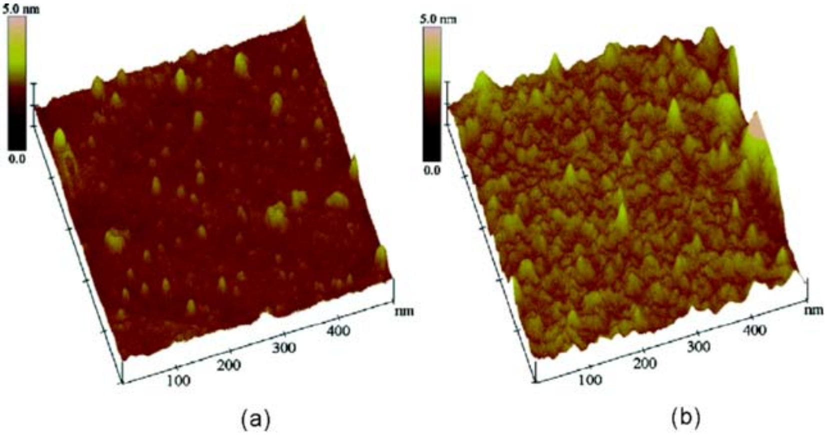
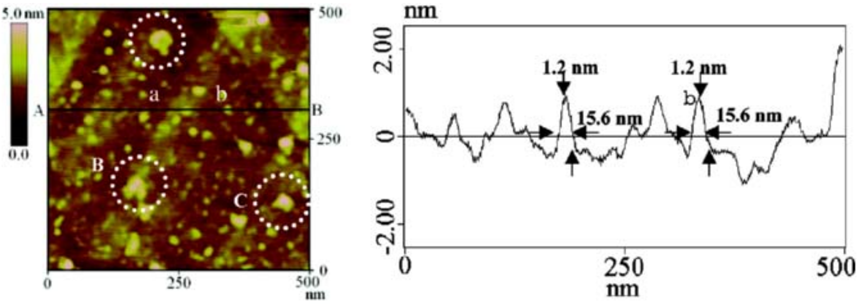


FIGURE 2 Tapping mode AFM images of G3-16[tpy-Pt-py] on the Au (III) substrate at different concentration: (a) 10 μmol/ml, (b) 100 μmol/ml.



(a) (b)

FIGURE 3 (a) Tapping ode AFM images of G3-16[tpy-Pt-Py] dendrimer on Au(III) substrate, concentration; 10 μmol/ml. (b) Cross section of G3-16[tpy-Pt-Py] dendrimer, corresponding to the line AB on left. Two similar size dendrimers, a and b, are on the line.

These results indicate that dendrimer molecules first tend to be adsorbed one by one, then, as the density of the molecule increases, a few molecules form a densely packed globular structures on the surface and the film is finally formed (Fig. 3). From the cross section view, the average diameter and height of dendrimers are measured with 15.6 nm and 1.2 nm respectively. Li *et al*. reported that the molecular volume could be calculated from the following equation [6].

$$V = \frac{1}{6}\ \pi h(h^2 + \frac{3}{4}\ d^2) \tag{1}$$

Here, h is the height and d is the diameter of the molecule. The estimated volume of a single molecule is about 116 nm^3. The volume of particles as marked with A, B and C are calculated at 1951, 2281 and 1800 nm^3 respectively. As a result, we can infer that the numbers of dendrimers composing them are 15.5, 19.6 and 16.8 in order.

The electrical properties of the self-assembled dendrimer molecule were investigated by measuring the current I versus applied voltage V, using STS, which is shown in Figure 4. The measurement was performed over dendrimer molecules on an Au substrate. An ohmic contact behavior was observed when the STM tip was positioned on an Au substrate. This kind of ohmic behavior was observed with good repeatability between dendrimer molecules distributed across the substrate.

From I–V data for cases where the STM tip was positioned over a dendrimer molecule, it was found that the current increases exponentially above 0.22 V regions. The I–V curves are asymmetry and non-linear; i.e., larger currents are observed for forward voltages. The currents follow approximately

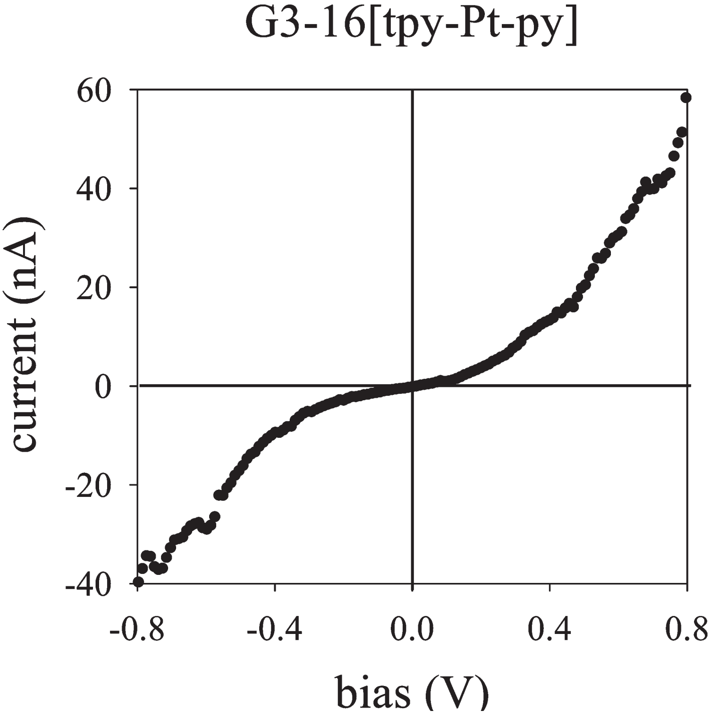


FIGURE 4 A typical I–V characteristic of tip (Pt:Ir)/air gap/molecule/Au substrate.

an exponential trend. This result exhibits moderate rectifying behavior due to the injection of charge carriers from the electrode to the dendrimer. We consider that the asymmetric structure, tip (Pt:Ir)/air gap/molecule/Au substrate, affects that of I-V curve. The calculated conductivity values of the single dendrimer molecule is about 2.13×10^{-6} S/cm.

4. CONCLUSIONS

Dendritic carbosilane with 16 terpyridine-Pt-pyridine groups on the peripary were prepared. We investigate the practical size and shape of a third generation of carbosilane dendrimer adsorbed on the Au (III) substrate with the tapping-mode AFM. The imaged single molecules were dome shaped and the diameter and height were about 15.6 nm and 1.2 nm respectively. From these sizes, we could calculate the volume of the single molecule to be about 116 nm^3. By controlling the concentration of the dendrimer, the film composed of aggregates of the dendrimer can be obtained by using self-assembly process. To add to, we measured the I–V curve using STS, which shows the ohmic contact between $-0.22\,\mathrm{V}$ and $0.22\,\mathrm{V}$, and beyond that range the current was increased exponentially. This result demonstrates moderate rectifying behavior. The calculated conductivity value of the single dendrimer molecule is about 2.13×10^{-6} S/cm.

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