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A Study on Morphology and Electrical Properties of Dendrimer Complex with Pt Ions

Kyung-Han Jung, Hoon-Kyu Shin, Chungkyun Kim[1] and Young-Soo Kwon

Dong-A University, Interdisciplinary Graduate School of Electrical Engineering
840, Hadan-dong, Saha-gu, Busan 604-714, Korea
Phone: +82-51-200-6949 Fax : +82-51-200-7743 E-mail: khjung@donga.ac.kr
[1] Department of Chemistry, Dong-A University
840, Hadan-dong, Saha-gu, Busan 604-714, Korea

1. Introduction

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, nanoscience etc[1]. The carbosilane dendrimer has become an important part of new applications of the carrier of the functional groups [2].

The new approach including terpyridine on carbosilane dendrimers was an adaptation of metallic components to the dendritic periphery by complexation.

In this study, to investigate the characteristics of the single dendrimer molecular, we attempted to measure morphology and electrical property of the self-assembled dendrimers on Au (111) substrate by tapping mode AFM and STM. The same self-assembly procedure was used for two different concentrations, 10 *μmol/ml* and 100 *μmol/ml*.

The case of lower concentration, we can measure the diameter and the height of the single molecular from the tapping mode AFM image. The imaged single molecules were dome shaped and the average diameter and height were 15.6 nm, 1.2 nm respectively. However, that of higher concentration, it is difficult to obtain obvious image of the single molecule. To add to, we measured I-V curve using STM, on which shows the phenomenon of negative differential resistance (NDR) was observed between 0.14 V and 0.24 V repeatedly.

2. Experimentals

16 terpyridine groups on carbosilane dendritic periphery was synthesized by the use of siloxanetetramer (2,4,6,8-tetramethyl-2,4,6,8-etravinylcyclotrtrasiloxane, $((CH_2{=}CH)\ MeSiO)_4$) as the core molecule, hydrosilation with $HSiMenCl_{3-n}$ and alcoholysis with allylalcohol. By the two alternative processes, hydrosilation and alcoholysis, the dendrimer carried out up to the fourth generation with 16-Cl on the periphery.

Then, G3P-16Cl dendrimer was terminated with 6-hydroxyhexa-1-terpyridine. The final compound, G3-16Tpy has 16-6-hydroxyhexa-1-terpyridine on the outermost periphery of the dendrimer. After the addition of methanol solution of 0.27g (0.14mmol) of G3-16Tpy dissolved in 25 ml to 0.22g (0.58mmol) of Pt (COD) Cl_2 it was refluxed for 2 h.

And a solution of 6-thiohexathiol-1-pyridine (0.11 g, 0.49 mmol) in methanol (25 ml) was added to the solution of G3-16 [Tpy-Pt] (0.40g, 0.031 mmol) in methanol (25 ml). Then, the product G3-16[Tpy-Pt-Py] was obtained (Fig. 1.)

For our study, dendrimers were adsorbed on Au (111) substrate by dipping the substrate into two different concentrations, 10 *μmol/ml* and 100 *μmol/ml*.

Tapping mode AFM and scanning tunneling spectroscopy were used for morphology and electrical properties, respectively.

3. Results and discussion

To obtain topographical data, tapping-mode AFM (Digital Instruments, Nanoscope IIIa) measurements were performed in atmosphere. In this mode, a 10 *μm* scanner was used and cantilevers having force constants of 20-100 N/m used at resonance frequencies of 260-280 kHz. The scan rate was kept at 1 Hz. Images included 512 X 512 data points. Fig. 2 shows the self-assembled dendrimer molecules on Au (111) surface in the two different concentrations, 10 *μmol/ml*(a) and 100 *μmol/ml*(b) respectively.

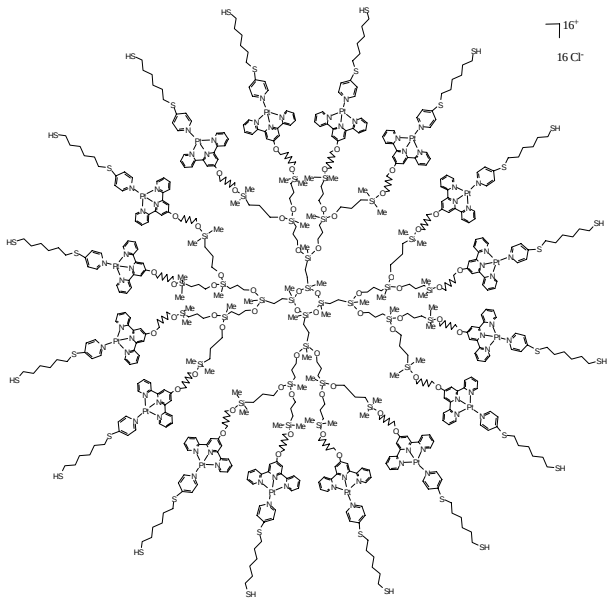

Fig. 1. The molecular structure of G3-16 [Tpy-Pt-Py].

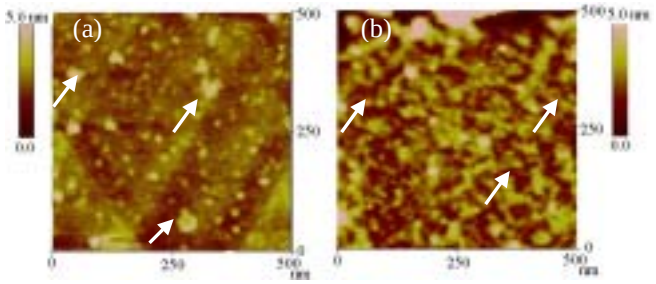

Fig. 2. Tapping mode AFM images of G3-16[Tpy-Pt-Py] dendrimer on Au (111) substrate at different concentrations: (a) 10 *μmol/ml*, (b) 100 *μmol/ml*, scan size : 500 X 500 nm^2.

The case of lower concentration, we can observe the isolated dendrimer molecules, which were dome shaped uniformly and distributed randomly

From the sectional analysis (not shown), it was found that the average diameter and height of the dendrimers are 15.6 and 1.2 nm respectively. The variation of these values may arise from differences of origin molecular size resulting from the synthesis, number of Au-thiol bonds, or geometrical surface. Some large particles indicated by arrows (Fig. 2a) represent that a few dendrimer molecules are assembled on the same site. We suppose that polarity of molecules adjacent works on these assemblies.

In contrast, that of the higher concentration shows randomly deposited globular structures of different sizes (Fig. 2b). The sizes of these particles were similar with previously mentioned large particles in Fig. 2a. Besides, the isolated molecules that have shown in Fig. 2b (also indicated by arrows) were the similar sizes with molecules in Fig. 2a. These results indicate that dendrimer molecules first tend to isolate, then, as increasing the density of molecules a few molecules form a densely packed globular structure on the surface in order to maintain lower surface tension.

I-V measurement was performed using scanning tunneling microscopy (STS) at room temperature.

During measurement, STM-tip was positioned over a dendrimer molecule and the bias voltage between tip and sample was applied in the range –1 ~ 1 V. We discard the range in which the current overflow (Fig. 3.).

The I-V characteristics show the symmetry. NDR (negative differential resistance) phenomenon was observed with good repeatability in the range of 0.14 ~ 0.24 V. To explain this NDR, we proposed “double barrier junction model” by Gorman et al. [3]. That is, the thiol-braches between Au substrate and the molecule and air gap between the molecule and the tip are composed of double barrier junction.

First, upon positive bias of the Au substrate, the molecular states are shifted to a lesser degree than that of the Au substrate. As the system approaches a resonance between the tip and terpyridine-platinum-pyridine in the molecule, tunneling current increase (0.14 ~ 0.16 V) and

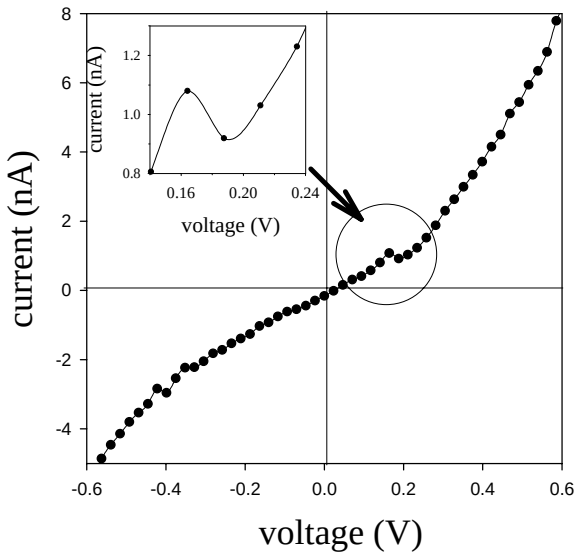

Fig. 3. I-V characteristic of G3-16[Tpy-Pt-Py] at 299 K.

moving out of resonance, the current decreases (0.16 ~ 0.18 V). Finally, the current increase after the potential is large enough to allow thermionic emission (over 0. 18V).

And we consider that the tunnel barrier heights and position of the tip on the molecule influence the position of NDR, which should be varied. NDR phenomenon is not understudied completely, so further complementary studies are needed.

4. Conclusions

The case of lower concentration, we can measure the diameter and the height of the single molecular using the tapping mode AFM image. The imaged single molecules were dome shaped and the average diameter and height were about 15.6 nm, 1.2 nm respectively. To add to, we measured I-V curve using STM, in which NDR phenomenon was observed with good repeatability between 0.14 V and 0.24 V.

Acknowledgements

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