Poster

NOVEL METHOD TO CONSTRUCT A TWO-DIMENSIONAL MOLECULE-NANOPARTICLE NETWORK BY ORGANOMETALLIC COMPLEX FORMATION

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Reliable formation of metal/molecule/metal junctions is important for investigation of molecular devices. There have been only a few experimental works that showed gate effects with high reproducibility despite considerable efforts to form the junction by fabricating nanometer-scale electrodes. This is due to the low yield of working devices [1]. To avoid the difficulty in the device fabrication, a nanoparticle array interconnected by organic linker molecules [2] can be used because such an array of the metal/molecule/metal junctions spontaneously forms by simply immersing the array into the solution of the linker molecule [2]. We have previously reported that a molecular device consisting of a two-dimensional array of gold nanoparticles interlinked by several dithiol molecules shows different gating behaviour depending on the nature of the molecules used [3]. The fabrication of this device is simple and highly reproducible, but the reliable formation of the junction was limited to the relatively short molecules.

In the present study, we report a novel method to construct a molecule-gold nanoparticle network array by forming organometallic complexes. Prior to the nanoparticle array formation, terpyridine ligands having thiol end group (Fig. 1a) are adsorbed on the surface of gold nanoparticles. Introduction of Fe^{2+} leads to the formation of iron bis(terpyridine) complex (Fig. 1b). As a result, the nanoparticles can be interlinked regardless of the length of the ligand molecules. This method provides more reliable formation of the junctions than that based on double-ended molecules such as dithiols. This is critical for the observation of the gate effect in the three-terminal device.

Thiophene terpyridine (Fig. 1a) was synthesized by coupling of alkyl-substituted terthiophene with 4-chloro-terpyridine under Stille condition. Gold nanoparticles (average diameter, 4.7 ± 1.1 nm) were modified with thiophene terpyridine by mixing nanoparticle and thiophene terpyridine solutions at room temperature for at least 24 h. After removing unreacted thiophene terpyridine molecules, the Au nanoparticle array was formed by Langmuir-Blodgett method and transferred onto the Si/SiO_2 substrate with Au electrode patterns formed in advance. The substrate was subsequently immersed in a $Fe(BF_4)_2$ solution for the complex formation. A densely-packed nanoparticle array was demonstrated by SEM measurements.

Formation of iron bis(terpyridine) complex was confirmed by UV-Vis spectroscopy. UV-Vis spectra of the terpyridine-modified gold nanoparticle array on a quartz substrate were measured before and after the introduction of Fe^{2+}. The difference spectrum between them showed peaks at 330 nm and 480 nm which are attributed to the bis(terpyridine) complex. The observation of red shift of the plasmon absorption peak also supports the molecule-nanoparticle network formation.

Fig. 2 shows two-terminal *I-V* measurements of the gold nanoparticle array before (Fig. 2a) and after (Fig. 2b) the introduction of Fe^{2+}. After the introduction of Fe^{2+}, two-terminal current measurements typically exhibited an about 30-fold increase. Such a large difference in

current is originated from different charge transport mechanisms, *inter*- against *intra*-molecular charge transport before and after the complex formation, respectively.

The three-terminal measurements with applying the gate voltage to the devices (W_g/L_g = 8.8 mm/50 μm; 150 nm thick SiO_2 as a gate insulator) exhibited only negligible gate modulation before the complex formation. On the other hand, p-type gating behavior with transconductance on the order of 0.1 nS was reproducibly observed after the complex formation. These results probably reflect the importance of the intra-molecular charge transport to the gating effect.

Acknowledgement

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References:

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[2] R. P. Andres *et al*., Science, 273 (1996) 1690.
[3] S. Kondo *et al*., 2005 MRS Spring Meeting Abstracts, J17.4 (2005) 274.

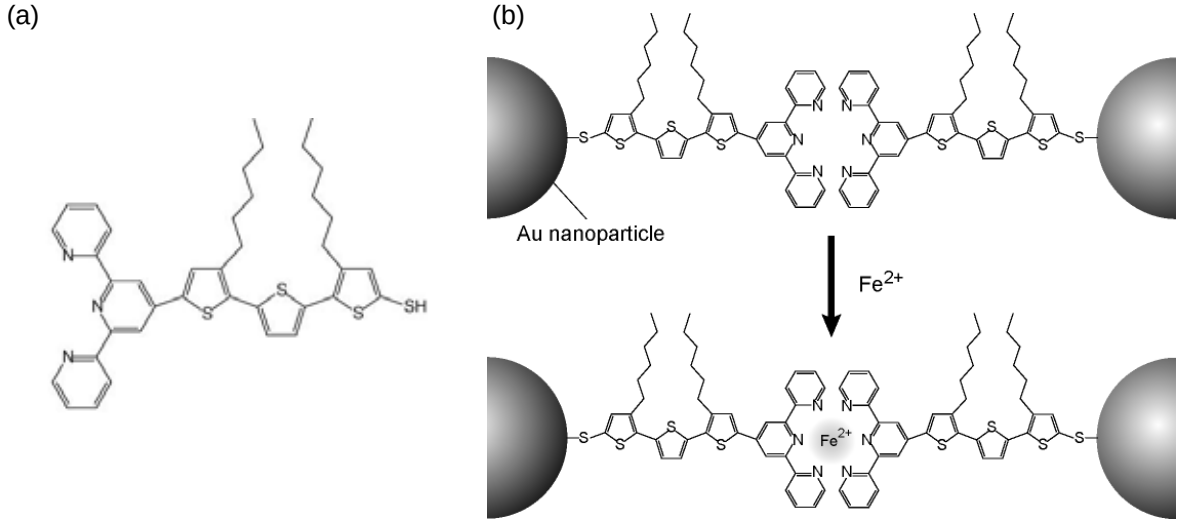

Fig. 1 (a) Thiophene terpyridine molecule, (b) Schematic representing the formation of the complex.

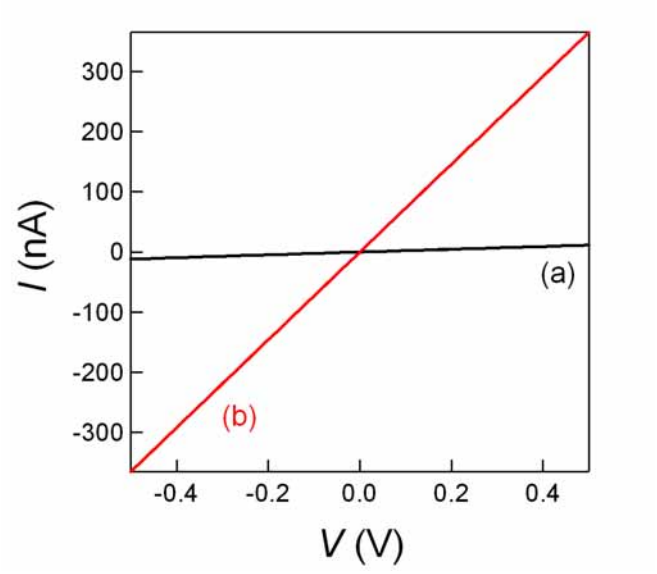

Fig. 2 Two-terminal *I-V* measurements (a) before and (b) after the introduction of Fe^{2+}.