Formation of Self-Assembled Monolayer of Phenylthiol Carrying Nitronyl Nitroxide on Gold Surface

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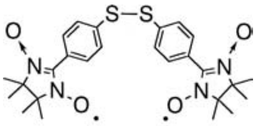
Novel disulfide-derivatized stable π-radical was prepared and it was found to form a dense self-assembled monolayer of π-radical thiols on a gold surface through a reductive cleavage of the S-S bond.

Chemisorption of thiols onto a gold surface has been utilized for organizing organic molecules into a nano-scale two-dimensional structure.[1] If a π-conjugated thiol is used as a chemisorbant, the electronic structure of the gold surface may be modified by the chemisorbed molecule.[2] In this respect, we are interested in constructing a self-assembled monolayer (SAM) of a π-radical thiol on a gold surface because the chemisorbed open-shell molecule may interact with gold atoms electronically at the interface.



DSPN

A novel disulfide derivative (DSPN) carrying a nitronyl nitroxide group (NN) at each of the *para*-positions of phenyl rings was synthesized as a pro-thiol compound to form a SAM of organic radicals.[3] Temperature dependence of the magnetic susceptibility of the polycrystalline sample of DSPN revealed that the intramolecular magnetic interaction between two nitronyl nitroxide moieties was evaluated to $2\,J/k_B = -11.6\,K$ and the Weiss constant $\theta = -2.3\,K$.[4] Judging from the degree of the antiferromagnetic coupling, the two radical units (NN) interact significantly through the π-conjugating disulfide skeleton. The result suggests that the spin-polarization caused by the NN unit is transmitted through the sulfur atom to the electrons of the gold atoms at the surface when the thiol-derivatized phenylnitronyl nitroxide (SPN) is chemisorbed on the gold substrate after the reductive cleavage of DSPN (Figure 1).

A gold thin layer of 50 nm thickness[5] was soaked into an ethanol solution of the disulfide precursor (0.23 mM), and the chemisorbing process of the thiol-derivatized π-radical, SPN, which was generated from a reductive bond fission of DSPN, was traced by the surface-plasmon resonance measurement. Judging from the time dependence of the reflectance at a certain angle (58.1°),[6] the chemisorption of SPN became saturated after 20 min. The chemisorbed sample was not desorbed by washing the surface with organic solvents, such as ethanol, acetonitrile, DMF. The thickness of the chemisorbed layer was determined to be 12 ± 2 Å,[7] from the difference in the angle dependence of the reflectance between the fully chemisorbed surface and the unchemisorbed one (Figure 2), the refractive index of the absorbed layer being estimated to be in a range of 1.5–1.6.[8] The evaluated thickness was in good agreement with the molecular length of 12 Å of SPN, the long molecular axis being perpendicular to the basal plane of the surface. This is strong evidence for the formation of the radical-monolayer on the gold surface.

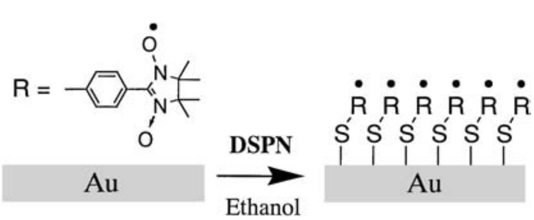


Figure 1. Formation of SAM of thiol-derivatized pheyl nitronyl nitroxide (SPN) on gold surface.

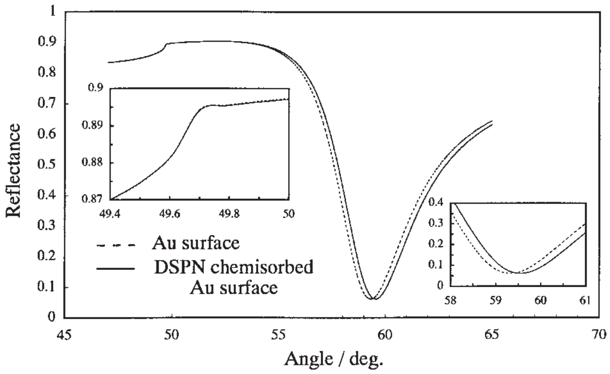


Figure 2. Surface plasmon resonance of thiol-derivatized pheyl nitronyl nitroxide chemisorbed on the gold thin layer placed on a glass prism (solid line). The shift from the dotted line, obtained from the clean gold surface, indicates the formation of the chemisorbed layer. In both cases, the total reflection condition became satisfied from the same angle (49.7°).

Independent evidence for the formation of the radical-monolayer on the gold surface was obtained from the IR reflection-absorption spectrum. The observed spectrum resembled well that of the radical precursor as shown in Figure 3. The ESR spectrum of the chemisorbed radical was measured at room temperature to show a sharp line in the $g = 2$ region, indicating that the organic radical was intact during the chemisorption process. The anisotropic g-value and the half line-width of the sample were measured by applying the external field along the perpendicular ($g_{\perp} = 2.0070$, 1.15 mT) or parallel ($g_{//} = 2.0073$, 1.27 mT) direction in respect of the surface. Since

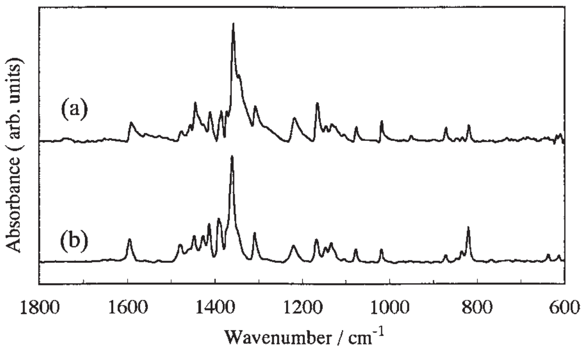


Figure 3. Reflection-absorption spectrum of SPN-chemisorbed gold surface (a), and absorption spectrum of the crystalline sample of DSPN in a KBr pellet (b).

these g-values and the half line-width are close to those of the powdered crystals of DSPN ($g = 2.0071$, 0.90 mT), the spin active species can be safely assigned to DSPN.[9] The anisotropic g values may be originated from the oriented alignment of radicals in a vertical manner on the gold surface, referring the anisotropic g values of the β-phase crystal of *p*-nitrophenyl nitronyl nitroxide ($g_x = 2.0030$, $g_y = 2.0070$, $g_z = 2.0106$).[10]

The oxidation potential of SPN chemisorbed on the gold substrate as an electrode was measured to be +0.89 V (Figure 4).[11] This oxidation peak can be reasonably assigned to the oxidation of the radical moiety because the oxidation potential of the disulfide precursor in acetonitrile solution was +0.95 V. The half width of the oxidation peak measured by differential pulse voltammetry (DPV) was 216 mV and it was much wider than that of the precursor (112 mV) in solution, suggesting the tight-packing of the SAM on the surface.

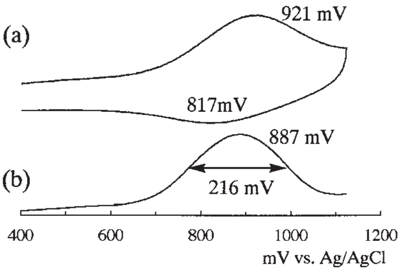


Figure 4. Redox wave of thiol-derivatized pheyl nitronyl nitroxide on gold electrode measured by cyclic voltammetry (a), and redox wave measured by differential pulse voltammetry (b).

Since the shape and the height of the first oxidation wave remained constant during several redox cycles,[12] the quantity of electricity required by the oxidation process was evaluated by the area of the oxidation peak. Then the evaluated value of 1.58×10^{-5} C was converted to the number (9.87×10^{13}) of the oxidized radical molecules. Then the area occupied by the individual radical molecule was estimated to be 42 Å^2 by dividing the area of the electrode of 4.13×10^{15} Å^2 by the number of the oxidized molecules. This value is in good agreement with the calculated area of 42 Å^2 per radical molecule using a close-packing CPK model.

Since nitronyl nitroxide derivatives bear geminal dimethyl groups for kinetic stabilization of the radical center, the presence of such bulky groups might disturb the formation of the SAM of nitronyl nitroxides. However, it was not the current case but SPN was found to form a dense SAM. This may be due to the quadrupolar interaction among the highly polarized N-O groups as shown in Figure 5.

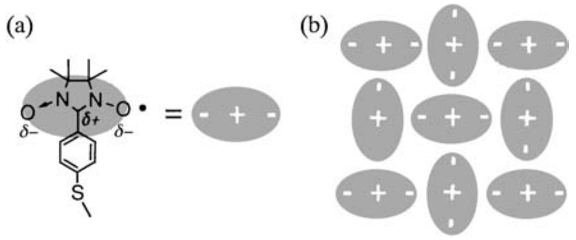


Figure 5. Polarized structure of NN moiety of SPN (a), and herringbone-type packing pattern resulted from the quadrupolar interaction between SPNs (b).

In summary, the novel π-conjugated disulfide, DSPN, was synthesized and it was introduced onto a gold surface. Formation of the self-assembled monolayer of the radical thiol on the gold surface was confirmed by the surface plasmon resonance, IR reflectance-absorption spectra, ESR spectra, and the electro-chemical measurement. The electronic structure of the SAM of the π-radical thiol on the gold surface is intriguing from the aspect of magnetic and conductive properties.

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References and Notes

1 For a recent overview, see: A. Ulman, *Chem. Rev.*, **96**, 1533 (1996).

2 T. A. Tanzer, P. W. Bohn, I. V. Roshchin, L. H. Greene, and J. F. Klem., *Appl. Phys. Lett.*, **75**, 2794 (1999).

3 Preparation of p-NN derivatized phenyl disulfide will be published: G. Harada, T. Gin, H. Sakurai, A. Izuoka, and T. Sugawara, *to be published.*

4 Temperature dependence of the magnetic susceptibility of the DSPN polycrystals was well reproduced by the following equation (a ST model): $\chi = \{C/(T-\theta)\}\{3\exp(-2J/k_BT)\}/\{1+3\exp(-2J/k_BT)\}$.

5 A gold thin layer was formed by the vacuum evaporation method on a prism made of high-refractivity glass ($n = 1.70$).

6 This is the angle around which the difference in the reflectance becomes largest.

7 The evaluation method of the thickness of the chemisorbed layer by the surface plasmon resonance measurement is described elsewhere: L. Haubling, W. Knoll, H. Rinsdorf, F.-J. Schmitt, and J. Yang, *Makromol. Chem., Macromol. Symp.*, **46**, 145 (1991); T. Wink, J. de Beer, W. E. Hennink, A. Built, and W. P. van Bennekom, *Anal. Chem.*, **701**, 801 (1999).

8 Generally, refractive indeces of small aromatics are in the range of 1.5–1.6 (e.g. the refractive index of phenylthiol is 1.58).

9 The g-value of DSPN in benzene solution was obtained as 2.0065 with the hyperfine structure parameter of $a_N = 0.372$ mT (4 N).

10 P. Turek, *Mol. Cryst. Liq. Cryst.*, **233**, 191 (1993).

11 The electrochemical properties of DSPN and SPN-chemisorbed gold surface were measured in an acetonitrile solution containing 0.1 M of $n\text{-Bu}_4\text{N}{\bullet}\text{ClO}_4$ using Ag/AgCl and Pt electrodes as refernce and counter electrodes, respectively. A Pt electrode was also used as a working electrode for the measurement of the redox potential of DSPN in solution. The refernce electrode was corrected with the redox potential of ferrocene/ferricinium (+0.67 V) measured under the same condition.

12 The irriversible redox waves in Figure 4 is presumably caused by restricted motions of the chemisorbed molecules and counter ions in the SAM upon the redox behavior, because the redox potential and the half width of the redox waves in DPV are much influenced by the occupancy of SPN.