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Preparation of Molecular Assemblies of Porphyrin-Linked Alkanethiol on Gold Surface and Their Redox Properties

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Self-assembled monolayer of porphyrin-linked alkanethiol on gold surface was prepared and the structure was characterized on the basis of X-ray photoelectron spectroscopy (XPS), fluorescence spectra, and cyclic voltammetry (CV). Monolayer with zinc porphyrin chromophore was found to be electroactive in organic solvent.

Self-assembled monolayer of thiols or disulfides on gold has attracted much attention from various points of view.[1-4] Such monolayer seems to be a highly promising approach to efficient utilization of photoinduced charge-separated state of supramolecules, since the monolayer is stable and has favorable vectrial arrangement, compared with planar lipid bilayer membrane,[5,6] and LB films.[7] Until now there exist only a limited number of self-assembled monolayers of alkanethiols bearing porphyrin ring,[8-11] which is frequently employed in model compounds for photosynthetic electron transfer. Further studies on porphyrin-linked alkanethiols on gold are needed for the understanding of redox properties especially in organic solvents, where many data on redox potentials and photophysical properties of porphyrins and related compounds have been accumulated. Comparison of redox behavior of porphyrins in solution and on Au surface will give the physical basis of electron transfer in molecular assemblies. Here we report the preparation of **1a,b** and their redox properties.

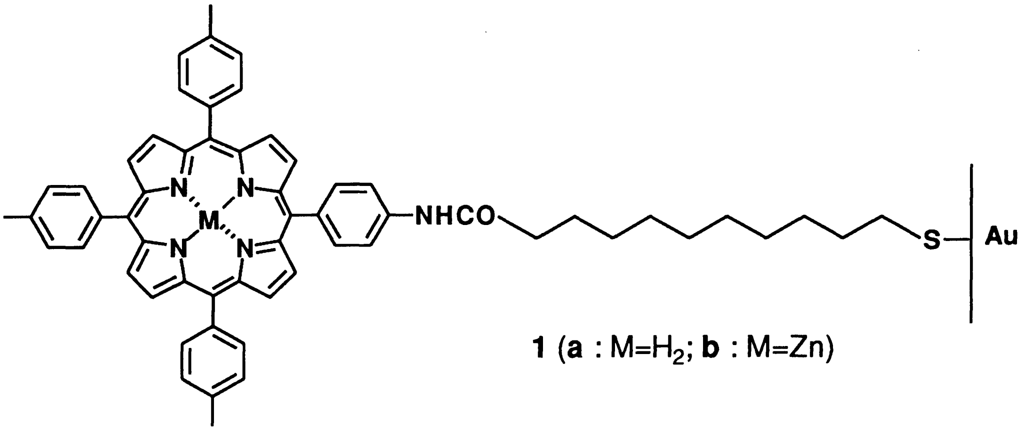
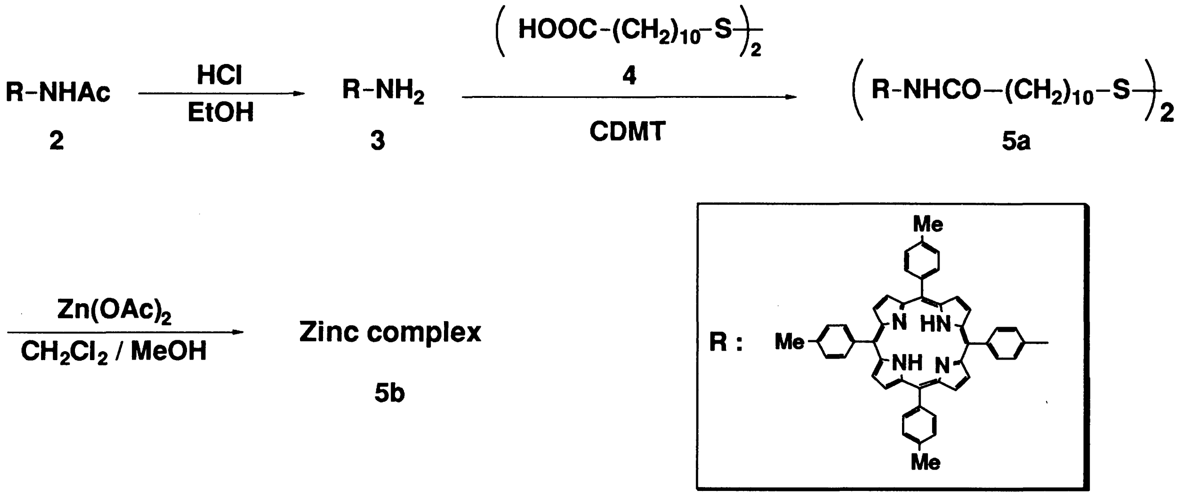


Fig. 1. The structure of porphyrin molecular assembly.

The synthesis of disulfides **5a** and **5b** was carried out as shown in Scheme 1. The coupling reaction of **3**[12] and **4**[13] using 6-chloro-2,4-dimethoxy-1,3,5-triazine(CDMT)[14] and purification by preparative gel permeation chromatography with $CHCl_3$ gave **5a** in 53% yield. Preparation of zinc complex **5b** was carried out by treatment of **5a** with zinc acetate in dichloromethane-methanol. Structures of all new compounds were confirmed mainly by spectroscopic analysis.15) An electrode with smooth gold surface was obtained by vacuum deposition on Pyrex® plate.16)



Scheme 1.

The porphyrin molecules were deposited on the gold surface by soaking the electrode in 0.5mM CH_2Cl_2 solution of **5a** or **5b**. Yielded **1a** and **1b** were washed well with enough amount of CH_2Cl_2 and dried with a stream of N_2.

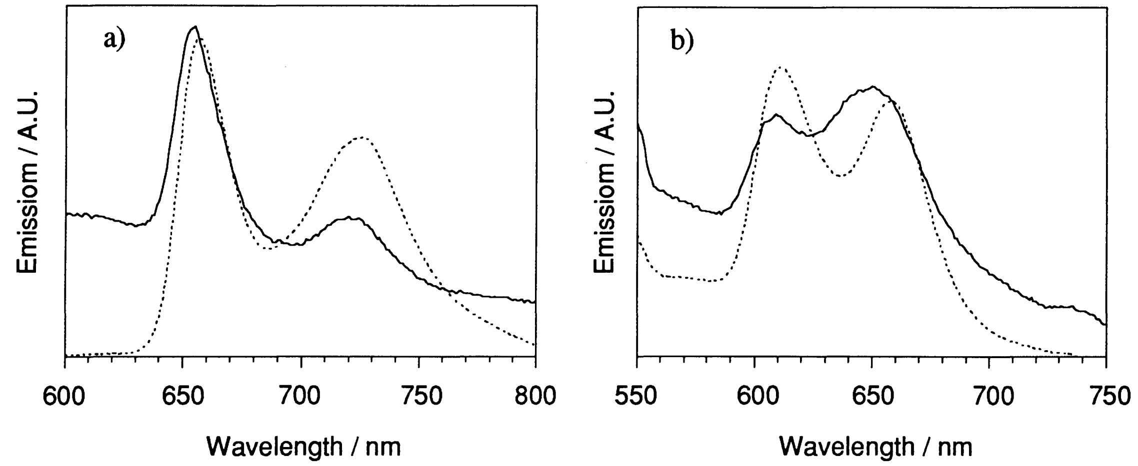


Fig. 2. Fluorescence spectra of **1a**, **1b** and **5a**, **5b** excited at 420 nm.
a) solid line, **1a**; dashed line, **5a** in crystalline state.
b) solid line, **1b**; dashed line, **5b** in crystalline state.

Fluorescence emission spectra of **1a** and **1b** were shown in Fig. 2. The fluorescence maxima of **1a** (655 nm, 720 nm) and **1b** (609 nm, 650 nm) are quite close to those of **5a** and **5b**, respectively, indicating that the porphyrin chromophore is immobilized on the gold electrode surface.

Table 1. Measurement of Binding Energy by XPS / eV[a)]

	C(1s)	O(1s)	N(1s)	$S(2p_{3/2})$
1a	285.0	533.0	400.0	162.1
1b	285.6	533.2	399.7	162.2

a) X-ray radiation source : MgKα (1253.6 eV, 240 W).

Photoelectron binding energies of **1a** and **1b** measured by XPS were summarized in Table 1. The peaks of C(1s), O(1s), and N(1s) suggest the existence of porphyrin rings in **1a** and **1b**. Furthermore, the $S(2p_{3/2})$ energies, observed for **1a** and **1b** are in good agreement with the reported values (161.9 eV[17)], 161.8 eV[18)]) for thiolate bound to gold. This results clearly indicate that porphyrins are immobilized on gold surface with a S-Au bond.

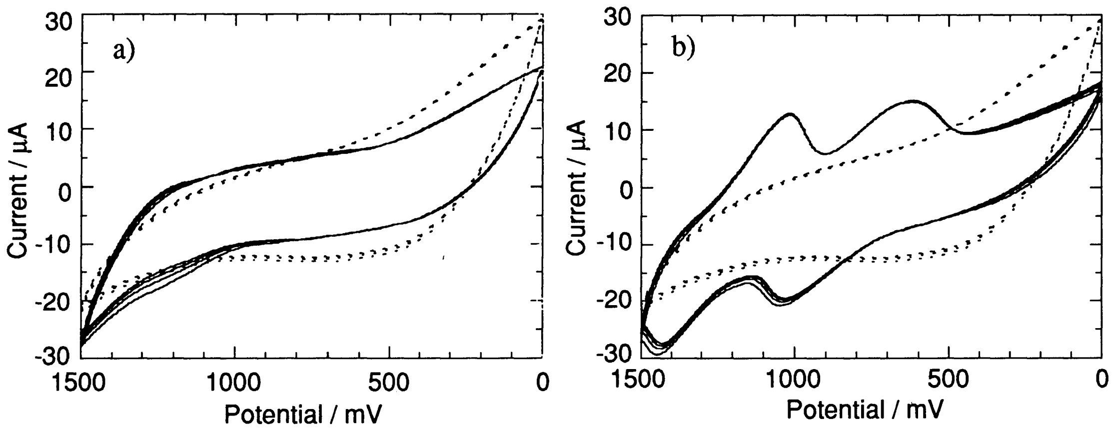


Fig. 3. Cyclic voltamogram (mV vs. Ag / Ag^+) of **1a**, **1b** measured at a Pt electrode in CH_2Cl_2 containing 0.1 mol dm^{-3} Bu_4NPF_6 with a scan rate of 500 mV s^{-1}.
a) solid line, **1a**; dashed line, bare gold. b) solid line, **1b**; dashed line, bare gold.

Figures 3a, b show CV of **1a**, **1b**, and gold surface as a reference. The observed two reversible peaks in **1b** (834 mV, 1225 mV) can be assigned to the oxidation potentials of porphyrin moieties by comparing the values with those for Zn-**2** in CH_2Cl_2 (803 mV, 1124 mV). Large difference in ΔEp value (the difference between the first oxidation and re-reduction peak potentials) was observed between **1b** (423 mV) and Zn-**2** (47 mV). The large difference is ascribable to the lacking of diffusion of the porphyrin rings by covalently bound structure in **1b**. In sharp contrast to **1b**, **1a** showed no redox peak. The reason is not clear at this moment, but it may relate to higher oxidation potential for free base porphyrins than zinc porphyrins.

The redox active properties of porphyrin-linked assemblies on gold in organic solvent were observed for the first time in the present study. This suggest that the self-assembled monolayer of this type can be applied to build up artificial photosynthesis or molecular devices. We are working now on this line.

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15) **5a** : ^{1}H NMR(270 MHz, $CDCl_3$) δ= -2.50 (br. s, 4H), 1.35 (m, 24H), 1.71 (q, 4H, J=7.0 Hz), 1.83 (q, 4H, 7.0 Hz), 2.44 (t, 4H, J=7.0 Hz), 2.66 (s, 18H), 2.69 (t, 4H, J=7.0 Hz), 7.3-8.2 (m, 34H), 8.81 (s, 8H), 8.83 (s, 8H). MS(FAB) 1743 (M^++1).
5b : ^{1}H NMR(270 MHz, $CDCl_3$) δ= 1.26 (m, 24H), 1.50 (m, 8H), 1.68 (t, 4H, J=7.0 Hz), 1.79 (t, 4H, J=7.0 Hz), 2.66 (s, 18H), 7.1-8.1 (m, 34H), 8.86 (s, 8H), 8.92 (dd, 8H, J=8.0 Hz, 4.6 Hz). MS(FAB) 1869 (M^+).
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