Synthesis and Self-Assembly of Porphyrin-linked Fullerene on Gold Surface Using S-Au Linkage

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Porphyrin-linked fullerene bearing methylthio group was prepared by 1,3-dipolar cycloadditon of the azomethine ylide, generated *in situ* using N-methylglycine and a formylporphyrin, with C_{60}. Self-assembled monolayer was formed by soaking Au electrode into a solution of the porphyrin-C_{60} dyad. The photocurrent was observed for the photochemical cell in the presence of electron carrier under illumination.

Much information has been accumulated how to prolong the lifetime of charge-separated state in photosynthetic electron transfer (ET) models.[1,2] The next step toward artificial photosynthesis is how to utilize the charge-separated state. Along with this line donor (D) - acceptor (A) linked molecules have so far been arranged unidirectionally by using lipid bilayer membrane,[3,4] LB films,[5] and self-assembled monolayer.[6-9] Among the three techniques the last one where thiolates are assembled on gold surface seems to be most promising from the view points of higher stability and less defects.[10,11] Although a few examples appeared for D - A molecules on modified electrode by using S-Au bond,[12,13] different types of D - A thiolates are needed for the optimization of photocurrent. Here we report the synthesis and photoelectrochemical behavior of **1** - **3** shown in Chart 1. We employed C_{60} as an A in **1** with a hope that C_{60} might facilitate ET to mediator, due to its large size.[14,15]

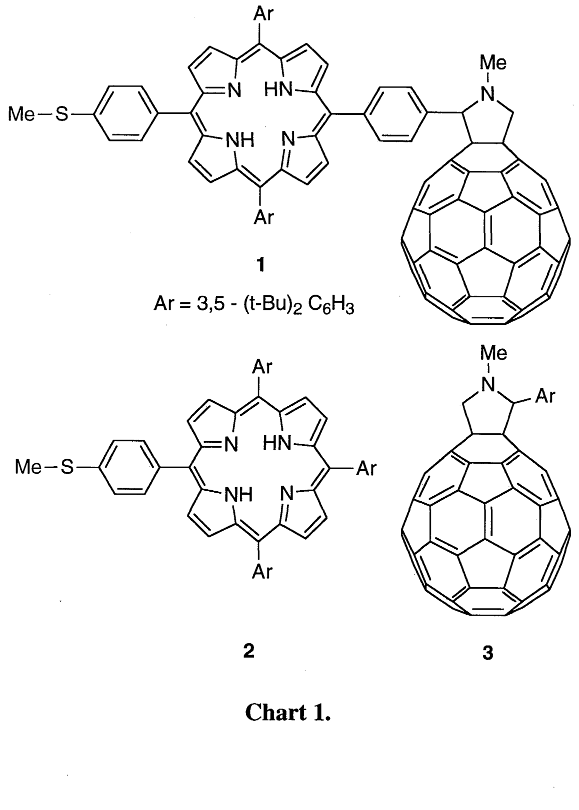
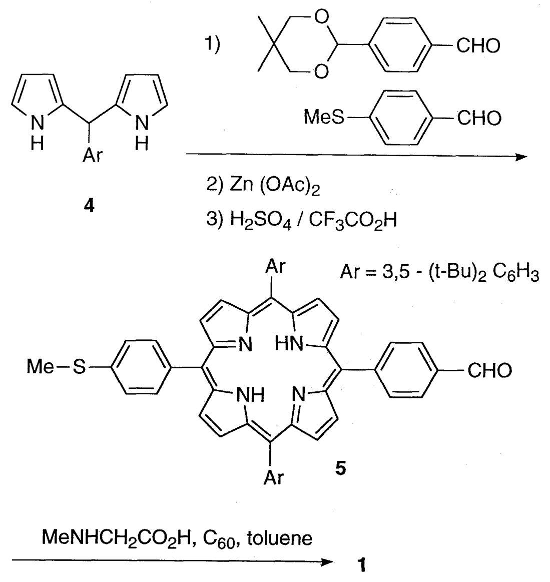


Chart 1.

The synthesis of **1** was carried out as shown in Scheme 1. Pyrrole was converted to dipyrromethane **4** by treatment with 3,5-di(*t*-butyl)benzaldehyde in the presence of trifluoroacetic acid in 55% yield.[16] Acid-catalyzed condensation of **4** with 4-methylthio-benzaldehyde and monoprotected aromatic dialdehyde (1 : 1 ratio) followed by the treatment with $Zn(OAc)_2$ in $CHCl_3$ gave a mixtures of several porphyrins.[17] The desired product was separated by flash column chromatography (Fujisilicia BW300 / C_6H_6) and hydrolyzed to give **5** in 2% yield. Porphyrin-linked C_{60} **1** was obtained by 1,3-dipolar cycloadditon using **5**, N-methylglycine, and C_{60} in toluene in 94% yield.[18] References **2** and **3** were also prepared. All structures of the present new compounds were confirmed by various spectral data including ^{1}H-, ^{13}C-NMR, FT-IR, and FAB mass spectra.[19]



Scheme 1.

Electronic absorption spectrum of **1** in THF was almost a linear combination of those of **2** and **3**, indicating no appreciable interaction between the two chromophores in the ground state. Fluorescence spectrum of **1** was strongly quenched as compared with that of **2** (<1% in THF), showing the rapid quenching of the excited singlet state of the porphyrin by the C_{60}. Redox potentials of **1** (1.24, 0.90, -0.67, -1.06, -1.26 V vs. Ag / AgCl) in CH_2Cl_2 using 0.1 mol dm^{-3} Bu_4NPF_6 as a supporting electrolyte can be explained by the sum of **2** (1.20, 0.87, -1.25 V) and **3** (-0.65, -1.04 V).

Compounds **1** and **2** were deposited separately on the surface of gold electrode[20] by soaking in a solution of **1** or **2** (1.0 x 10^{-3}

mol dm^{-3}) in CH_2Cl_2 for 4 days.[6,8] After soaking the electrode was washed well with CH_2Cl_2 and dried with a stream of N_2. Formation of self-assembled monolayer was confirmed by monitoring reductive wave due to breaking of the S-Au linkage using linear sweep voltammetry in water containing 0.5 mol dm^{-3} KOH[8] and by oxidative wave of the porphyrin chromophore using cyclic voltammetry in CH_2Cl_2 containing 0.1 mol dm^{-3} Bu_4NPF_6.[13] From this oxidative wave, the surface coverage of porphyrin moiety was evaluated to be ~7 x 10^{-12} mol cm^{-2} for **1** - Au.

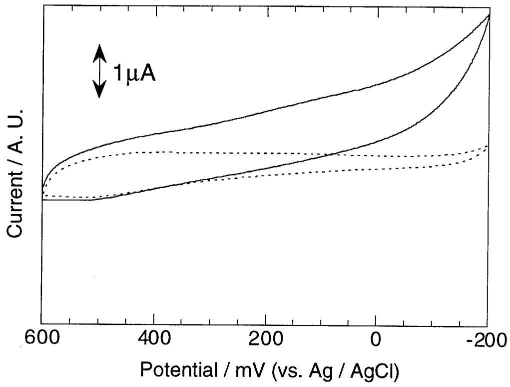


Figure 1. i / V curves for Au / **1** / methylviologen / Pt cell in water under illumination (full line) and dark (dashed line). Ag / AgCl was the reference electrode. Sweep rate, 10mVs^{-1}, [Na_2SO_4] = 0.1 mol dm^{-3}; [methylviologen] = 5 x 10^{-3} mol dm^{-3}.

Electrochemical measurements were carried out using Pyrex cell consisting of modified Au electrode, Ag / AgCl as a reference electrode, and platinum electrode as a counter electrode. The electrode **1** - Au was irradiated with 150W Xenon lamp. The photocurrent-voltage curves were shown in Figure 1. At the negative potentials, the cathodic photocurrents were clearly seen for **1** - Au in the presence of methylviologen.[12] In contrast, no apparent photocurrent was detected for that of **2** - Au. The mechanism for generating photocurrent is not clear at this moment, but it may be produced by electron relay via the excited singlet or triplet states of the porphyrin and the C_{60}.

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19 **1**: ^{1}H-NMR (270 MHz, $CDCl_3$) δ -2.70 (br.s, 2H), 1.53 (s, 36H), 2.71 (s, 3H), 2.86 (s, 3H), 3.36 (d, 1H, J=8.6 Hz), 3.92 (s, 1H), 4.45 (d, 1H, J=8.6 Hz), 7.60 (d, 2H, J=8.6 Hz), 7.78 (br.s, 2H), 7.80-8.20 (m, 10H), 8.70-9.00 ppm (m, 8H). ^{13}C-NMR (67.5 MHz, $CDCl_3$) δ 31.2, 31.6, 32.0, 32.4, 35.1, 67.7, 75.8, 76.2, 78.0, 78.6, 119.3, 119.5, 120.5, 121.5, 121.8, 122.2 123.3, 125.0, 125.6, 129.4, 130.4, 131.6, 133.5, 134.0, 135.0, 135.9, 136.2, 138.1, 138.2, 138.6, 138.7, 139.1, 139.5, 140.5, 140.6, 140.7, 141.0, 141.2, 141.4, 141.5, 141.7, 141.8, 142.4, 142.6, 142.9, 143.1, 143.3, 143.5, 143.7, 143.8, 143.9, 144.1, 144.2, 144.3, 144.8, 145.0, 145.1, 145.2, 145.3, 146.4, 148.8, 151.0, 152.1, 154.8 ppm. MS (FAB) 1662 $(M+1)^+$. UV-Vis (THF) λ max 420, 515, 552, 591, 649 nm. **2**: ^{1}H-NMR (270 MHz, $CDCl_3$) δ -2.69 (br.s. 2H), 1.53 (s, 54H), 2.72 (s, 3H), 7.61 (d, 2H, J=8.3 Hz), 7.79 (t, 2H, J=2.0 Hz), 7.80 (t, 1H, J=1.6 Hz), 8.09 (d, 2H, J=1.6 Hz), 8.10 (d, 4H, J=2.0 Hz), 8.15 (d, 2H, J=8.3 Hz), 8.91-8.86 ppm (m, 8H). MS (FAB) 998 $(M+1)^+$. UV-Vis (THF) λ max 420, 515, 552, 593, 650 nm. **3**: ^{1}H-NMR (270 MHz, C_6D_6 : CS_2=1 : 3) δ 1.25 (s, 18H), 2.76 (s, 3H), 4.13 (d, 1H, J=4.6 Hz), 4.79 (d, 1H, J=4.6 Hz), 4.82 (s, 1H), 7.24 (m, 1H), 7.58 ppm (m, 2H). ^{13}C-NMR (67.5 MHz, C_6D_6) δ 29.9, 31.3, 39.6, 69.8, 70.7, 83.9, 121.5, 128.43, 136.0, 141.6, 141.9, 142.0, 143.0, 144.2, 146.2 ppm. MS (FAB) 1040 $(M+1)^+$.
20 Electrodes with flat gold surface were purchased from SHIBAO. The electrode was prepared by vacuum deposition of gold on Si (100) wafer (SUMITOMO SITX CORP); S. E. Creager, L. A. Hockett, and G. K. Rowe, *Langmuir*, **8**, 854 (1992). It was confirmed by atomic force microscopy that the surface has (111) plane.