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Organic Photoelectrochemical Cell Mimicking Photoinduced Multistep Electron Transfer in Photosynthesis: Interfacial Structure and Photoelectrochemical Properties of Self-Assembled Monolayers of Porphyrin-Linked Fullerenes on Gold Electrodes

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Self-assembled monolayers (SAMs) technique has been applied to porphyrin-linked fullerene systems to mimic supramolecular photoinduced charge-separation (CS) events in photosynthesis. Porphyrin-linked C_{60} molecules with a sulfide group were designed to self-assemble on a gold surface using S–Au interaction. The structure of the SAMs formed on gold electrodes was investigated by spectroscopic methods including X-ray photoelectron spectroscopy (XPS), ultraviolet (UV)-visible spectroscopic ellipsometry, UV-visible absorption spectroscopy, and Fourier transform infrared (FTIR) spectroscopy as well as electrochemical studies. These results indicate that the SAMs have loosely packed structure; the porphyrin-C_{60} molecules are tilted and nearly parallel onto the gold surface. Short-circuit photocurrent with a level of sub-μA cm^{-2} was observed for the photoelectrochemical cell in the presence of methylviologen (MV) under illumination with ca. 4 mW cm^{-2}. The maximum intensity of the photocurrent in free-base porphyrin-C_{60} system is five times larger than that in the corresponding free-base porphyrin system, indicating that *C_{60} is an effective mediator in multistep electron transfer (ET) processes*. A possible mechanism for the photocurrent generation is discussed in terms of the photodynamics of porphyrin-linked fullerenes in solution.

Photosynthesis is the most elaborated supramolecular machinery in nature. The fundamental principle for the conversion of light to chemical potential energy in photosynthesis is photoinitiated CS and subsequent multistep electron relay among well-arranged pigments, such as chlorophylls, pheophytins, and quinones, within the reaction center complexes. These nano-structures have been elucidated by X-ray crystal analysis of the reaction centers in bacteria.[1] There have been numerous attempts to construct synthetic molecular arrays which mimics vectorial electron transport across the membrane.[2,3] Although some of them showed a long lifetime with a substantial quantum yield in the resulting charge-separated state, it is still difficult to apply these artificial molecules to light energy conversion systems.

A variety of methodologies for the output of the energy in the charge-separated state have been developed. Donor (D)–acceptor (A) linked molecules, in which intramolecular ET can be controlled, have been prepared so as to arrange the molecules in organized forms such as lipid bilayer membranes, Langmuir–Blodgett (LB) films, and polymers.[4] Unidirectional assembly of the molecules enables us to achieve parallel arrangement of the charge-separated states when photoinduced ET occurs in the donor–acceptor linked molecules. Subsequent vectorial electron flows to the secondary electron acceptor would be produced in macroscopic quantities, leading to eventual generation of the photocurrent or the products. However, conversion efficiencies of light-to-chemical energies in these systems are much lower compared with those of solar cells using semiconductors.

Recently, SAMs have been focussed on as a new method among preparation of organic thin films.[5] Applications include chemical sensing, microlithography, and drug screening. Highly organized monolayers are formed by the spontaneous adsorption of the adsorbates onto surface such as metals, semiconductors, and insulators, in the solutions or vapor phase using covalent interaction. Thus, they make it possible to arrange functional molecules unidirectionally at the molecular level on substrates when substituents which will self-assemble on the substrates are attached to either terminal of the molecules. A variety of examples have been reported to date involving functional molecules such as ferrocenes,[6)] azobenzenes,[7)] fullerenes,[8)] porphyrins,[9)] cyclodextrins,[10)] proteins,[11)] and others.[12)]

Fullerenes have emerged as new and attractive building blocks for acceptors in the last decade.[13—15)] C_{60}, one of the representatives, has a spherical shape as well as large size, moderate electron-accepting abilities (-0.3—-0.5 V vs. SCE), and high stability under severe conditions. A number of donor-linked C_{60} have been synthesized to elucidate the ET chemistry.[2h)] We[16)] and others[17—19)] have shown that C_{60} as an acceptor accelerates photoinduced CS and decelerates charge recombination (CR) in donor-linked fullerenes. It is concluded from our experiments[16f)] that the small reorganization energy (λ) of C_{60} can be ascribed to the peculiar effect of C_{60} in ET.[20)] This resembles the primary photosynthetic CS process from the chlorophyll dimer to the quinone via the pheophytin where λ is small enough to achieve efficient CS; using multistep ET processes with tuning of λ to (i) minimize the expenditure of free energies, $-\Delta G_{CS}$, (ii) accelerate the CS whose position is on the Marcus top region, and (iii) retard the CR whose position is on the Marcus inverted region.[21)] Thus, utilization of C_{60} as an acceptor in intramolecular donor–acceptor systems and their application to SAM are highly promising ways to build up molecular photovoltaic devices which mimic photoinduced initial CS and subsequent multistep ET relay in photosynthetic bacteria and plants (Fig. 1); C_{60} has potentials to facilitate ET processes including acceleration of CS and charge shift (CSH) to ET mediator as well as retardation of CR.[16,20)]

Thus, we designed and synthesized a novel type of donor-linked C_{60}. We chose a porphyrin as a donor because of its well-characterized photophysical properties as a building block in photosynthetic model as well as relatively high-absorbing properties in the visible region. In the molecular design of porphyrin–C_{60} dyads, four *t*-butyl groups were introduced into *meso*-phenyl rings of the porphyrin moiety to increase the solubility in organic solvents, since porphyrins and fullerenes are only slightly soluble in such solvents.[22)] C_{60} is covalently linked to a porphyrin aryl ring with a relatively rigid pyrrolidine spacer which allows the evaluation of ET. It is well established that thiols, disulfides, and sulfides interact strongly with a gold surface.[5)] It is known that porphyrins bearing a thiol group are susceptible to be oxidized by oxygen and/or light.[23)] Furthermore, disulfides with porphyrin–C_{60} linked molecules at both ends would be insoluble because of the aggregation and the low solubility of porphyrins and C_{60}. In contrast, sulfides are relatively stable compared with thiols and disulfides. Therefore, we have chosen a simple methylthio group at one end of a porphyrin ring, while the opposite end has the C_{60} moiety as shown in Fig. 2.

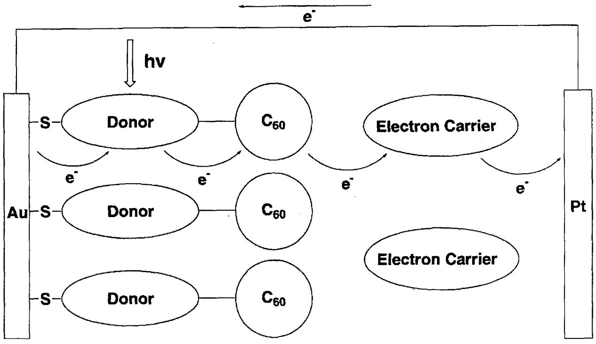
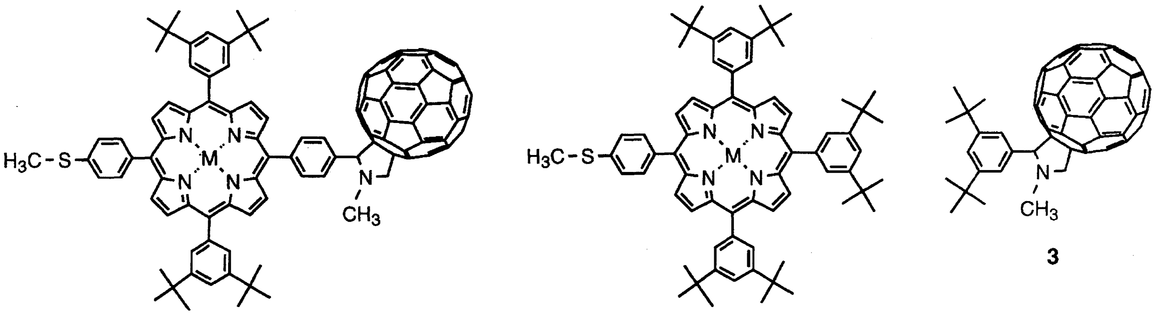


Fig. 1. Schematic representation of photoelectrochemical cell mimicking photosynthetic multistep electron transfer.

Here we report a photoelectrochemical cell with a gold electrode modified by the porphyrin-linked fullerenes using the SAM technique. The porphyrin–fullerene thin films have been characterized by surface analysis including X-ray photoelectron spectroscopy, ellipsometry, Fourier transform infrared spectroscopy, UV-visible absorption spectroscopy, and cyclic voltammetry, whereas the photoelectrochemical measurements have been carried out in two or three electrode systems using the modified Au electrode. ET dynamics of the molecules have been studied in solutions by picosecond fluorescence lifetime measurements and picosecond time-resolved transient absorption spectroscopy, to compare with values on the electrode interface. The relationship between the interfacial structure and the photoelectrochemical properties of the SAMs is also described.

Results

Synthesis and Characterization. Synthesis of compounds **1**—**3** was carried out as shown in Fig. 3. Pyrrole was converted to dipyrromethane (di-2-pyrrolylmethane) **4** by treatment with 3,5-di-*t*-butylbenzaldehyde in the presence



1a: M=H_2; **1b:** M=Zn

2a: M=H_2; **2b:** M=Zn

3

Fig. 2. Structure of compounds **1**—**3**.

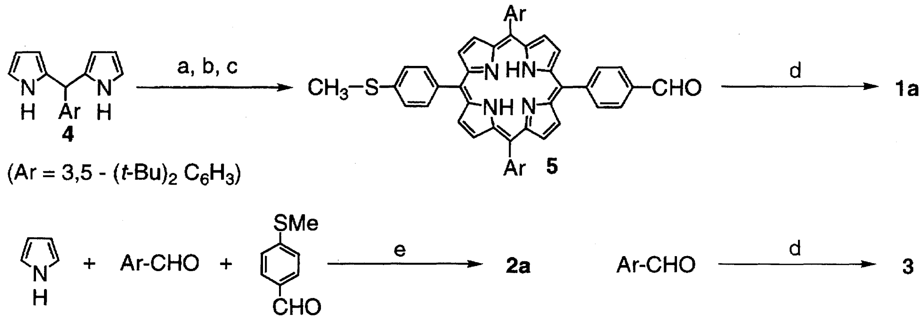


Fig. 3. Synthesis of **1**—**3**. a) 4-(5,5-Dimethyl-1,3-dioxan-2-yl)benzaldehyde, 4-(methythio)benzaldehyde, trichloroacetic acid, acetonitrile, room temperature, overnight; b) $Zn(OAc)_2$, $CHCl_3$, reflux, 2 h; c) Trifluoroacetic acid, acetic acid, sulfuric acid, chloroform, 100 °C, 90 min; d) C_{60}, *N*-methylglycine, toluene, reflux, 6 h; e) $Et_2O{\cdot}BF_3$, chloroform, room temperature, overnight.

of trifluoroacetic acid.[24] Acid-catalyzed condensation of **4** with 4-(methylthio)benzaldehyde and monoprotected aromatic dialdehyde in acetonitrile, followed by treatment with zinc acetate, gave a mixtures of several zinc porphyrins.[25] The desired product was separated by flash column chromatography and then hydrolyzed to give bifunctional porphyrin **5**. Porphyrin-linked fullerene **1a** was obtained by 1,3-dipolar cycloaddition using **5**, *N*-methylglycine and C_{60} in toluene.[26] Porphyrin reference **2a** was synthesized by Lindsey method,[27] while C_{60} reference **3** was prepared by the same method as described for **1a**. Zinc complexes **1b** and **2b** were synthesized from the corresponding free bases **1a** and **2a**, respectively.

The structures of their new compounds were verified by spectroscopic analyses including ^{1}H- and ^{13}C-nuclear magnetic resonance (NMR) spectra and fast atom bombardment (FAB) mass spectra. The ^{1}H NMR spectra of **1** showed marked broadening of signals assignable to the protons of the porphyrin and aryl moieties near the C_{60}, suggesting slow exchange of several conformations involving the rotation around single bonds in the bridge on the NMR time scale. It is well established that Diels–Alder and 1,3-dipolar cycloadditions to C_{60} give the "6,6-closed" structure.[26,28,29] In the ^{13}C NMR spectra of **3** in $C_6D_5CD_3$, there exist two signals for the sp^3 fullerene carbons (69.17 and 77.95 ppm), which are quite close to the reported values for the quarternary carbon at the "6,6-closed" junction of the 1,3-dipolar adduct. Electronic absorption spectra of **1** in THF are almost a linear combination of those of **2** and **3**, indicating no appreciable interaction between the two chromophores in the ground state (Fig. 4). The absorption due to the C_{60} is much weaker and broader compared with that of the porphyrin. Differential pulse voltammograms of **1**—**3** were obtained in CH_2Cl_2 using 0.1 mol dm^{-3} n-Bu_4NPF_6 as a supporting electrolyte. Redox potentials of **1** (**1a**: 1.24 (P^{+2}/P^{+1}), 0.90 (P^{+1}/P), −0.67 (C_{60}/C_{60}^-), −1.06 (C_{60}^-/C_{60}^{2-}), −1.26 V (P/P^-); **1b**: 1.02 (P^{+2}/P^{+1}), 0.67 (P^{+1}/P), −0.66 (C_{60}/C_{60}^-), −1.05 (C_{60}^-/C_{60}^{2-}), −1.43 (P/P^-) V vs. Ag/AgCl, P denotes the porphyrin) can be explained by the sum of **2** (**2a**: 1.20 (P^{+2}/P^{+1}), 0.87 (P^{+1}/P), −1.25 (P/P^-) V; **2b**: 1.05 (P^{+2}/P^{+1}), 0.71 (P^{+1}/P), −1.42 (P/P^-) V) and **3** (−0.65 (C_{60}/C_{60}^-), −1.04 (C_{60}^-/C_{60}^{2-}) V).

Photophysical Properties of Porphyrin- Linked Fullerenes in Solution. Steady-state fluorescence spectra

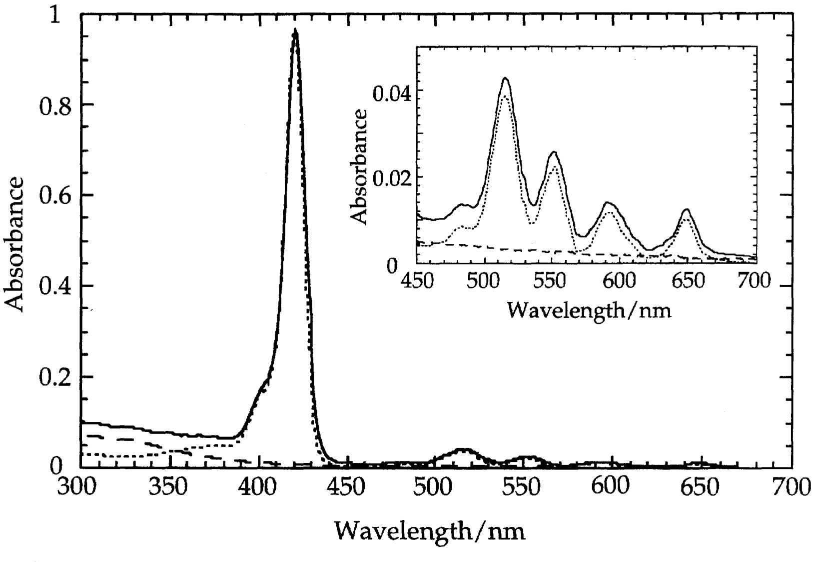


Fig. 4. UV-visible absorption spectra of **1a** (solid line), **2a** (dotted line), and **3** (dashed line) in tetrahydrofuran. All the concentration are 1.81×10^{-6} mol dm^{-3}.

of **1** and **2** were taken in THF, excited at the Soret band under the same concentration. There is no detectable difference in shape or in peak positions (emission maxima, **1a** and **2a**: 654 and 722 nm; **1b** and **2b**: 604 and 657 nm) of the fluorescence spectra in **1** and **2**, while their intensities are quite different. The relative fluorescence quantum yields of **1a** vs. **2a** and **1b** vs. **2b** in THF are less than 0.01, indicating the efficient quenching of the excited singlet state of the porphyrin by the C_{60}. There was no evidence for the emission from the C_{60} moieties (emission maxima, 720 nm in **3**).[16e)]

Transient absorption spectra of **1a** and **1b** were measured in THF by picosecond time-resolved absorption spectroscopy. The typical examples are shown in Fig. 5. In the spectra of **1b** at 20 ps delay of the laser pulse, excited at 590 nm where the porphyrin absorbs mainly, broad bands at around 650 and 900 nm were seen clearly, which can be assigned to zinc porphyrin cation radical (ZnP^+) and C_{60} anion radical ($C_{60}{}^-$), respectively.[16e)] The absorbances at 650 and 900 nm were fitted by a rise with a time constant of 16 ps and a decay with a time constant of 200 ps, whereas that at 460 nm, due to the ZnP^+ and $S_n \leftarrow S_1$ of the porphyrin, was analyzed by a decay with that of 200 ps (Fig. 6). These results clearly show that photoinduced ET from the excited singlet state of the porphyrin to the C_{60} occurs in **1b**, resulting in formation of the charge-separated state (ZnP^+–$C_{60}{}^-$), as we reported previously.[16)] The fluorescence lifetime of **1b** could not be determined because of the weak fluorescence, while the that of **2b** is 1.9 ns ($= 1/k_{\mathrm{ref}}$) in THF. The photoinduced CS takes place with the rate constant of $k_{\mathrm{CS}} = 6.3 \times 10^{10}\ \mathrm{s}^{-1}$ ($= 1/(16 \times 10^{-12})$) from $^1ZnP^*$ to the C_{60}. From the rate constants, yield of the CS from $^1ZnP^*$ ($k_{\mathrm{CS}}/(k_{\mathrm{ref}}+k_{\mathrm{CS}})$) is found to be unity. The rate constant of the CR (k_{CR}) in **1b** is calculated to be $5.0 \times 10^9\ \mathrm{s}^{-1}$ ($= 1/(200 \times 10^{-12})$).

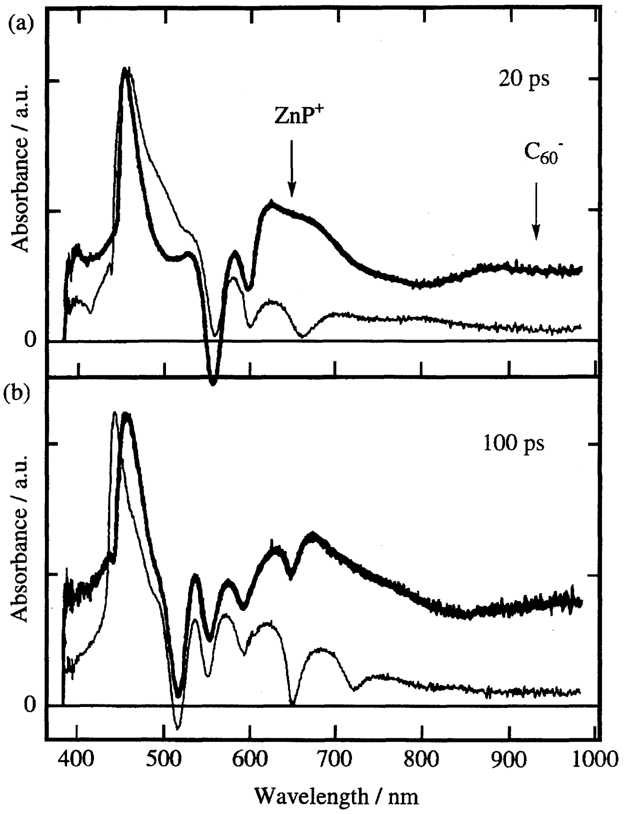


Fig. 5. Picosecond time-resolved transient absorption spectra of (a) **1b** (thick line) and **2b** (thin line) and (b) **1a** (thick line) and **2a** (thin line) in THF. The spectra are normarized at the Soret peak for comparison. The delay times after the excitation of laser pulse at 590 nm are 20 ps and 100 ps, respectively.

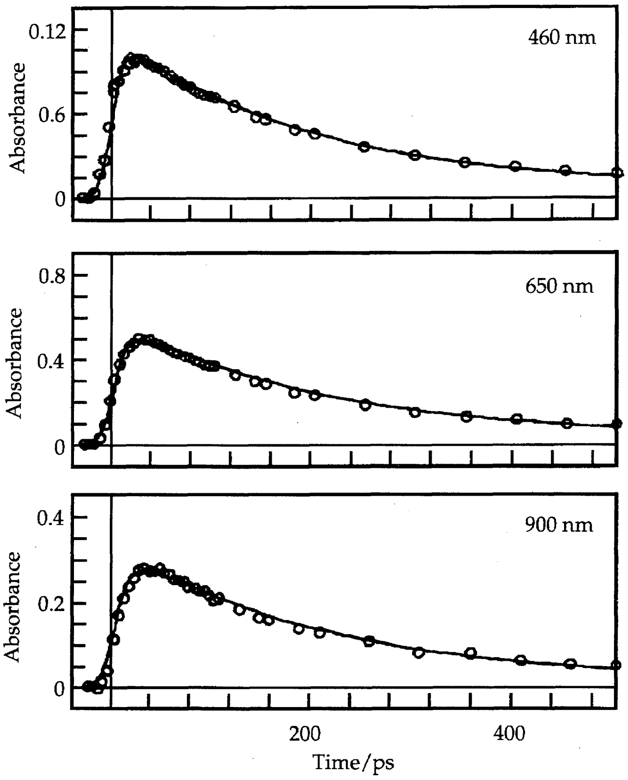


Fig. 6. Time profiles of transient absorbances of **1b** in THF at 460 nm (top), 650 nm (middle), and 900 nm (bottom) excited at 590 nm.

Free energy changes, $-\Delta G_{\mathrm{CS}}$ for CS and $-\Delta G_{\mathrm{CR}}$ for CR, can be calculated as follows:[2,30)]

$$-\Delta G_{\mathrm{CS}} = \Delta E_{0\text{–}0} - E_{\mathrm{ox}} + E_{\mathrm{red}} - \Delta G_{\mathrm{s}} \tag{1}$$

$$-\Delta G_{\mathrm{CR}} = E_{\mathrm{ox}} - E_{\mathrm{red}} + \Delta G_{\mathrm{s}} = \Delta E_{0\text{–}0} - (-\Delta G_{\mathrm{CS}}) \tag{2}$$

$$\Delta G_{\mathrm{s}} = e^2/(4\pi\varepsilon_0)[(1/(2R^+) + 1/(2R^-) - 1/R_{\mathrm{CC}})(1/\varepsilon_{\mathrm{s}}) - (1/(2R^+) + 1/(2R^-))(1/\varepsilon_{\mathrm{r}})] \tag{3}$$

where $\Delta E_{0\text{–}0}$ is the energy of the 0–0 transition between the S_1 and the S_0 states of porphyrin (1.90 eV for **1a** and **2a** and 2.10 eV for **1b** and **2b**), E_{ox} and E_{red} are the half-wave potentials of one-electron oxidation of porphyrins and one-electron reduction of C_{60} in CH_2Cl_2, respectively, R^+ and R^- are radii of D and A, respectively, R_{cc} is center-to-center distance between D and A, and ε_{s} and ε_{r} are static dielectric constants of solvents used and in which the redox potentials were measured, respectively. $R^+ = 5.0$ Å for porphyrin, $R^- = 4.4$ Å for C_{60}, and $R_{\mathrm{cc}} = 12.2$ Å were estimated from CPK models. $\varepsilon_s = 7.4$ in THF and $\varepsilon_r = 8.9$ in CH_2Cl_2 are used for the calculation. The calculated values for $-\Delta G_{CS}$ ($-\Delta G_{CR}$) are 0.34 eV (1.56 eV) in **1a** and 0.78 eV (1.32 eV) in **1b**, showing that the driving forces for CS for **1a** and **1b** are exergonic.

Compared with the spectra of **1b**, the transient spectra of **1a** is broader in all the wavelengths, especially at the longer wavelengths (700—1000 nm) (Fig. 5b). In contrast with **2a**, 450-nm band is red-shifted by ca. 20 nm and no stimulating emission is seen. Considering that free-base porphyrin cation radical (H_2P^+)[31] has no appreciable absorption within the range of 700—1000 nm and C_{60}^- has weak absorption within the range of 900—1000 nm,[2h,16e] the transient absorption of **1a** does not match superposition of those due to H_2P^+ and C_{60}^-. Kinetic analysis of the transient absorbance at 456 and 625 nm yields time constants of 50 ps for the rise and of 700 ps for the decay (Fig. 7). The fluorescence decay curve at 610 nm, when excited at 400 nm, was fitted by two exponential components with time constants of $\tau_1 = 39$ ps (preexponential factor (A) = 0.95) and $\tau_2 = 440$ ps ($A = 0.05$). The time constant of $\tau_1 = 39$ ps roughly agrees with that of 50 ps for rise of the absorbances at 456 and 625 nm obtained by transient absorption spectroscopy. These results suggest that intramolecular exciplex ($H_2P^{\delta+}-C_{60}^{\delta-}$) is produced in **1a**. Based on the fluorescence lifetime of **2a** (9.8 ns = $(1/k_{ref})$ in THF), the exciplex formation occurs with the rate constant of $k_{EX} = 2.6\times10^{10}\ s^{-1}$ ($= 1/(39\times10^{-12})-1/(9.8\times10^{-9})$) from $^1H_2P^*$. From the rate constants, the quantum yield from $^1H_2P^*$ ($k_{EX}/(k_{ref}+k_{EX})$) is found to be unity, whereas the rate constant of the decay (k_{EXR}) is calculated to be 1.4×10^9 s^{-1} ($= 1/(700\times10^{-12})$). Poor solubility of **1** in the other solvents prevented us from detecting satisfactory transient absorption spectra.

Structure of SAM. Monolayers were formed by the spontaneous adsorption of the sulfides onto gold substrates.[12l,32] In all cases adsorption was carried out from CH_2Cl_2 solutions of 1.0×10^{-3} mol dm^{-3} for 4 d to reach the equilibria. The equilibria were confirmed by monitoring time profiles of the adsorbed amount of the molecules on the gold surface using UV-visible absorption spectroscopy. The equilibria are much slower compared with those of typical thiols and disulfides on the gold surface, implying that the binding to the gold surface is much weaker compared with those of thiols and disulfides.

The structure of the monolayers was investigated by XPS, cyclic voltammetry, UV-visible absorption spectroscopy, FTIR, and UV-visible spectroscopic ellipsometry. Figure 8 displays XPS spectra of **1a** as well as methyl phenyl sulfide adsorbed on gold surface (hereafter, **1a**/Au and PhSMe/Au, respectively, where / represents an interface) in the S2p regions. PhSMe/Au showed the $S2p_{3/2}$ (161.9 eV) and $S2p_{1/2}$ (163.1 eV) peaks whose values are in good agreement with the reported values in ethyl phenyl sulfide/Au (162.0 eV ($S2p_{3/2}$); 163.2 eV ($S2p_{1/2}$)).[32h] The values are similar to those (161.8 eV ($S2p_{3/2}$); 163.0 eV ($S2p_{1/2}$)) in benzenethiol/Au and ethanethiol/Au, suggesting the existence of the

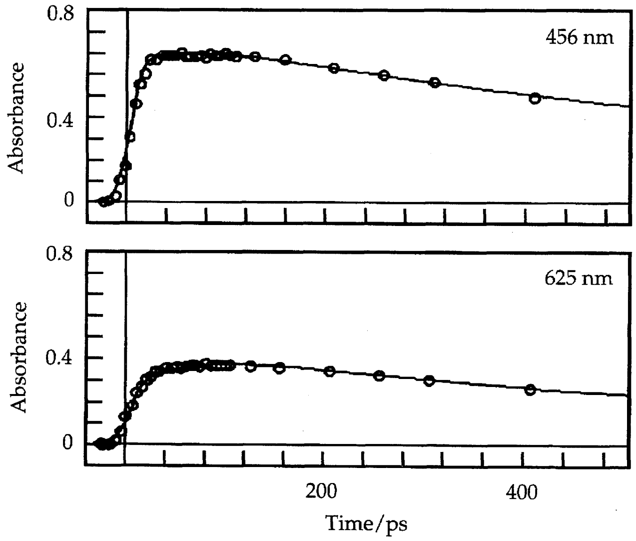


Fig. 7. Time profiles of transient absorbances of **1a** in THF at 456 nm (top) and 625 nm (bottom) excited at 590 nm.

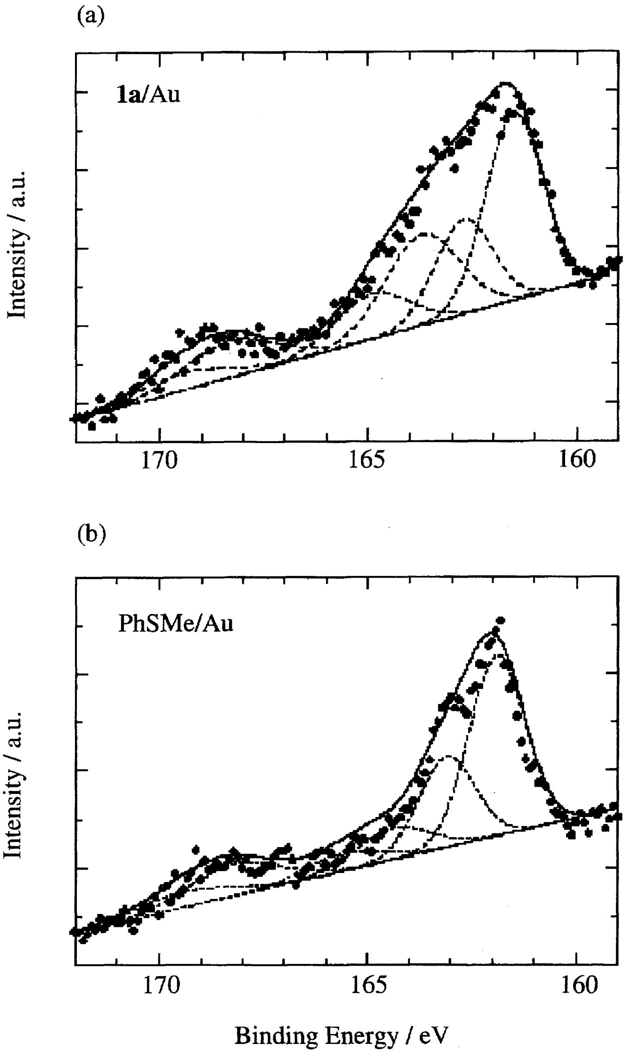


Fig. 8. X-Ray photoelectron S2p spectra of (a) **1a** and (b) methyl phenyl sulfide adsorbed on gold electrodes.

binding state of S–Au linkage (Table 1). The values (161.5 eV ($S2p_{3/2}$); 162.7 eV ($S2p_{1/2}$)) in **1a**/Au are slightly smaller than those in PhSMe/Au. Similar values were observed for **1b**, **2a**, and **2b** as shown in Table 1. These values were somewhat smaller compared with the previously reported values for S–Au bond for alkyl[33)] and aromatic[32h,34)] thiolates. In addition, other peaks due to oxidized sulfur-containing species[33d,34b,35] as well as the non-specific binding state[9c,33a,33c)] were detected at the region of 160—170 eV in all the systems investigated. The peaks around 164 eV are dominant when a sample was prepared by dropping dichloromethane solution of **1a** on Au, confirming the existence of the non-specific binding state under the present condition.

Cyclic voltammograms of bare Au and **1a**/Au in CH_2Cl_2 containing 0.1 mol dm^{-3} n-Bu_4NPF_6 are shown in Fig. 9. Voltammograms of **1a**/Au and **1b**/Au displayed irreversible and ill-defined peaks corresponding to the first oxidation of the porphyrin moiety (**1a**/Au: 800 to 1200 mV; **1b**/Au: 600 to 1000 mV) and the first reduction of the C_{60} moiety (**1a**/Au and **1b**/Au: −500 to −700 mV). No appreciable waves due to the second oxidation of the porphyrin moiety were observed. The peak splittings ($\Delta E_p > 150$ mV) for the first oxidation waves of the porphyrin moiety are large, implying that slow kinetics of the couple. Similar ill-defined peaks due to the first oxidation of the porphyrin were observed for **2a**/Au and **2b**/Au (**2a**/Au: 800 to 1200 mV; **2b**/Au: 600 to 1000 mV), while no discernible waves were seen within the range (0 to −1000 mV). The ill-defined peaks are presumably caused by loosely packed structures in the SAMs.[12d,32d,36)] UV-visible absorption spectra of **1**/Au and **2**/Au showed broad and red-shifted Soret bands compared with those in THF (Fig. 10), while no apparent peaks due to the Q bands were observed. Table 2 summarizes surface coverage of the SAM estimated by the integration of the redox curves as well as the absorbances at the peak maxima of the Soret band on the gold electrode.

Figures 11 and 12 present transmission and reflection absorption FTIR data of **1a**/Au and **2a**/Au that provide insight into the structure of the SAM. The similarities of the band positions on gold surface and in solid state are seen for **1a** and **2a**. Relative intensities of the band around 3300 cm^{-1} and the bands around 2900—3000 cm^{-1} and 1500—1600 cm^{-1} for **1a**/Au are comparable in the two conditions, while those of the band at 3300 cm^{-1} for **2a**/Au are substantially diminished. If one considers the infrared surface selection rule which results from a preferential excitation of vibrational modes with dipoles normal to a highly reflecting metal surface, these data give structural information about the SAM, as discussed later. The thicknesses of the SAMs were measured by UV-visible spectroscopic ellipsometry. The determined thicknesses for **1**/Au and **2**/Au are about 10 Å, indicating the formation of the monolayers, as shown in Table 2.

Photoelectrochemistry. Photoelectrochemical measurements were carried out for **1** and **2** in 0.1 mol dm^{-3} Na_2SO_4 solution containing 5×10^{-3} mol dm^{-3} methylviologen (MV) as an electron carrier using the modified gold electrode as a working electrode, a platinum counter electrode, and a Ag/AgCl reference electrode (hereafter, Au/**1a**, **1b**, **2a**, and **2b**/MV/Pt, where / represents an interface). An increment of cathodic photocurrent with an increase of negative bias to the gold electrode in three electrode systems demonstrated that the direction of the photocurrent takes place from the cathode to the anode through the electrolyte.[9h)] A similar cathodic photoelectrochemical response was observed in the presence of benzylviologen[37)] or oxygen[38)] as an electron carrier instead of MV under the same condition. Figure 13 represents photocurrents produced by on-off illumination of Au/**1** and **2**/MV/Pt cell. The maximum in-

Table 1. XPS Data of **1** and **2** on Gold Surface

SAMs	Band	Binding energy in the S2p region (relative intensites/%)/eV		
		Bounded state	Non-specific binding state	Oxidized state
1a/Au	$S2p_{3/2}$	161.5 (34)	164.1 (21)	168.3(11)
	$S2p_{1/2}$	162.7 (17)	165.3 (11)	169.5 (5)
1a/Au	$S2p_{3/2}$	161.9 (8)	164.1 (51)	168.1 (8)
(Dropping method)[a)]	$S2p_{1/2}$	163.1 (4)	165.3 (26)	169.3 (4)
1b/Au	$S2p_{3/2}$	161.6 (40)	164.1 (11)	168.9 (16)
	$S2p_{1/2}$	162.8 (20)	165.3 (6)	170.1 (7)
2a/Au	$S2p_{3/2}$	161.7 (46)	164.3 (10)	168.4 (10)
	$S2p_{1/2}$	162.9 (23)	165.5 (5)	169.6 (5)
2b/Au	$S2p_{3/2}$	161.6 (50)	164.1 (11)	168.5 (6)
	$S2p_{1/2}$	162.8 (25)	165.3 (5)	169.7 (3)
Methyl phenyl	$S2p_{3/2}$	161.9 (43)	164.4 (10)	168.2 (13)
sulfide/Au	$S2p_{1/2}$	163.1 (22)	165.6 (6)	169.4 (7)
Benzenethiol/Au	$S2p_{3/2}$	161.8 (50)	164.3 (9)	168.3 (7)
	$S2p_{1/2}$	163.0 (25)	165.5 (5)	169.5 (4)
Ethanethiol/Au	$S2p_{3/2}$	161.8 (45)	164.1 (11)	168.7 (11)
	$S2p_{1/2}$	163.0 (22)	165.3 (5)	169.9 (5)

a) Sample was prepared by dropping dichloromethane solution of **1a** on Au.

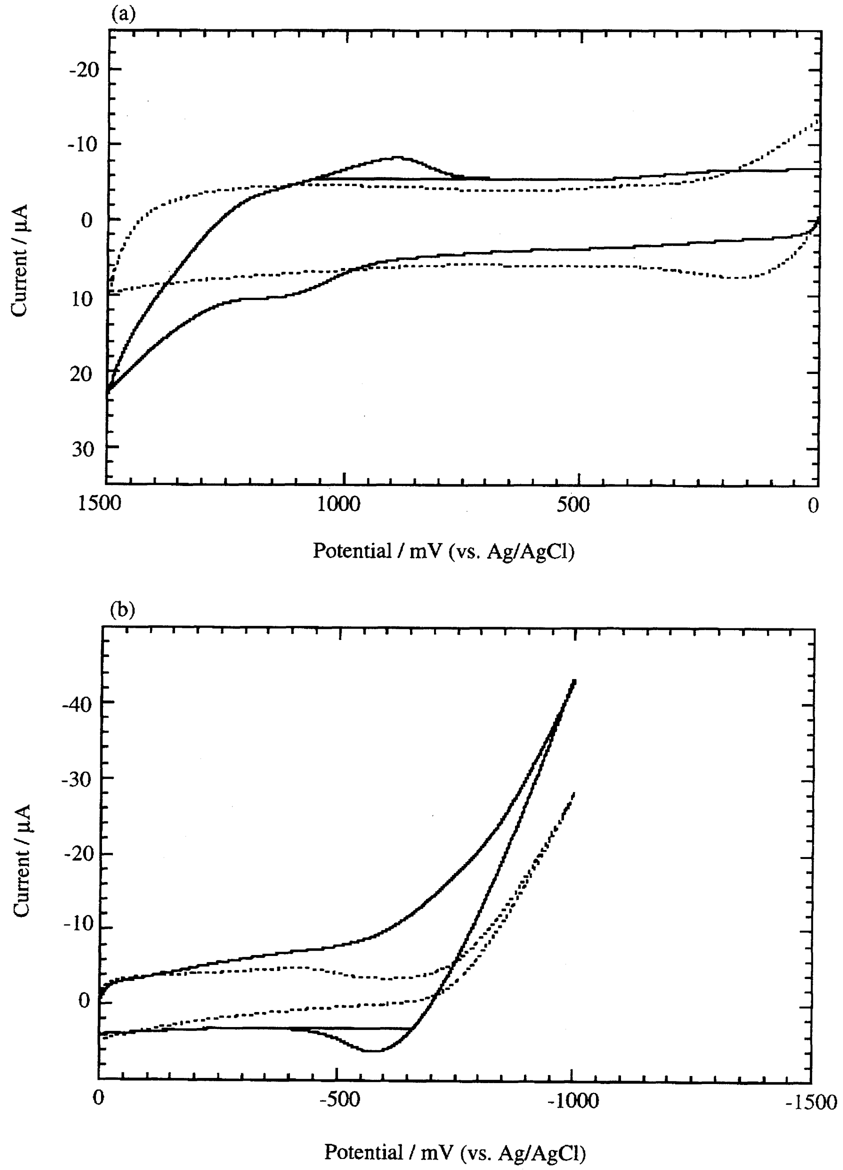


Fig. 9. Cyclic voltammograms of bare electrode (dotted line) and **1a** (solid line) adsorbed on gold electrodes in CH_2Cl_2 solution containing 0.1 mol dm^{-3} n-Bu_4NPF_6. The sweeps are shown in (a) oxidation region and (b) reduction region; sweep rate, 500 mV s^{-1}, electrode area, 0.57 cm^2, initial potential, 0 V.

Table 2. Ellipsometric Thickness, Absorptoion Maximum, and Surface Coverage of SAMs on Gold Surface

SAMs	Thickness[a)]	Surface coverage[b)] Γ	Occupied area[b)]	λ_{max}[c)]	Surface coverage[d)] Γ	Occupied area[d)]
	Å	$\times 10^{-11}$ mol cm^{-2}	$Å^2$ $molecule^{-1}$	(Absorbance) nm	$\times 10^{-11}$ mol cm^{-2}	$Å^2$ $molecule^{-1}$
1a/Au	9.0	1.3[e)]	1300	440 (0.017)	1.6	1000
1b/Au	11.0	2.4[e)]	690	463 (0.053)	3.7	450
2a/Au	11.5	1.5	1100	435 (0.019)	1.8	920
2b/Au	9.0	1.6	1000	440 (0.034)	2.4	690

a) Ellipsometrically determined. b) Estimated by the integration of the cyclic voltammetric curve due to the first oxidation of the porphyrin moiety. c) Peak maxima of the Soret band on gold surface. The spectra were obtained using UV-visible absorption spectroscopy on reflection mode. d) Estimated using the UV-visible absorptoin spectra of **1** and **2** on gold surface, assuming that the molar coefficients at the Soret bands on Au are similar to those in THF. e) The oxidation and reduction charges, due to the first oxidation of the porphyrin and the first reduction of the C_{60}, respectively, were the same within the accuracy of the base line subtraction.

tensity of the short-circuit photocurrent in Au/**1a**/MV/Pt cell (Fig. 13a) is about three times larger than that in Au/**1a**/Pt (Fig. 13b), indicating the involvement of MV for the photocurrent. The relatively large photocurrent in Au/**1a**/Pt may

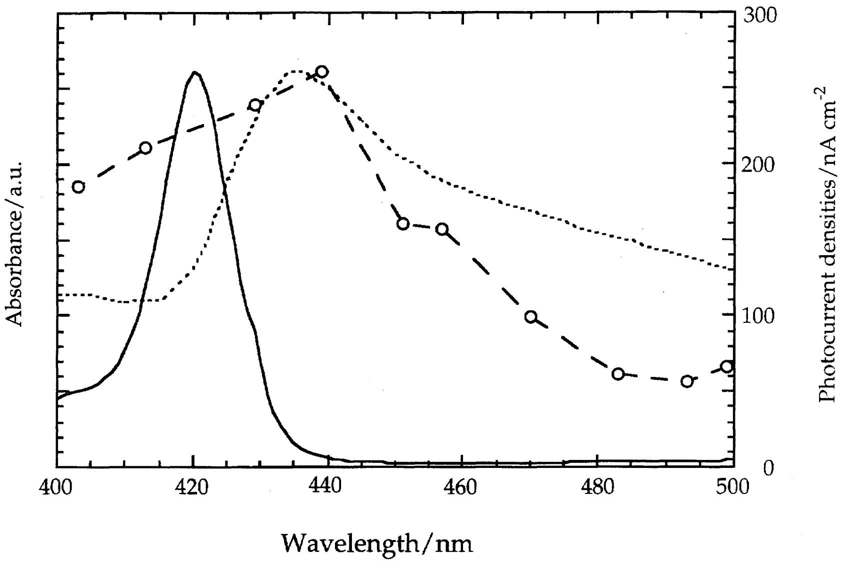


Fig. 10. Action spectrum of Au/**1a**/5 mM MV/Pt cell (circle dashed line), UV-visible spectra of **1a**/Au (dotted line) and of **1a** in THF (solid line). The spectra are normalized at the Soret bands for comparison.

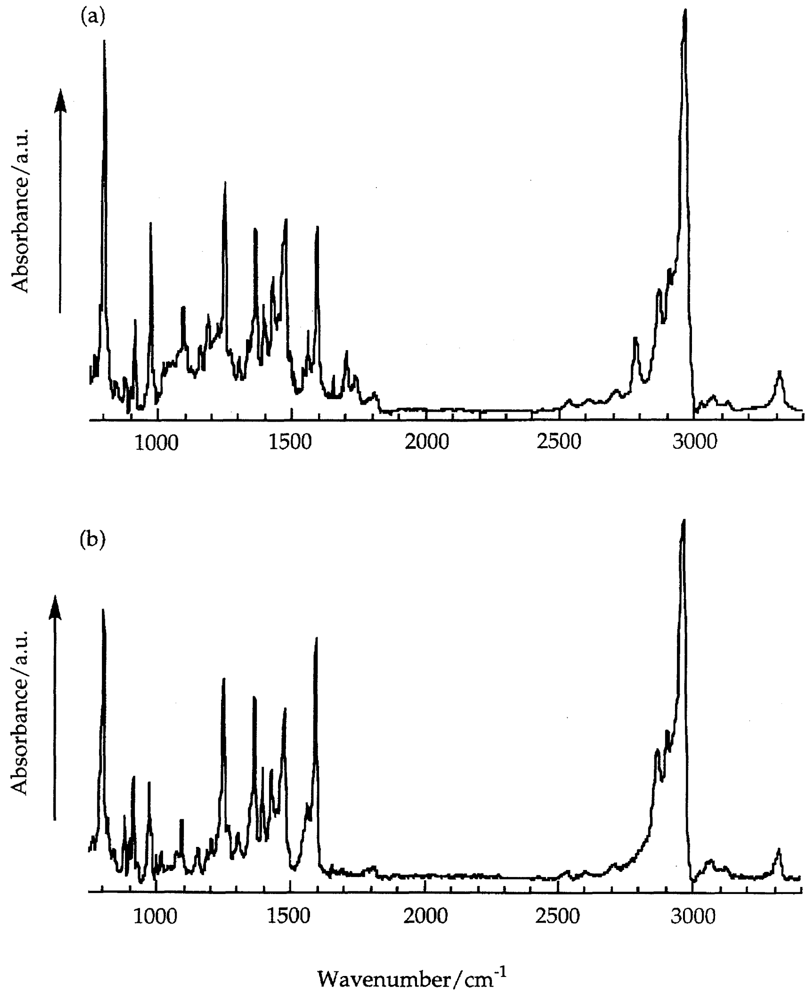


Fig. 11. Transmittance FTIR spectra of (a) **1a**/Au and (b) **2a**/Au.

be due to the small amount of oxygen or impurities dissolved in the solution. The maximum intensity of the photocurrent in Au/**1a**/MV/Pt cell is *larger by a factor of five* compared with that in Au/**2a**/MV/Pt cell, showing the C_{60} moiety contributes greatly to the generation of the large photocurrents (Fig. 13c). Under the excitation with $\lambda = 438.5 \pm 4.9$ nm light

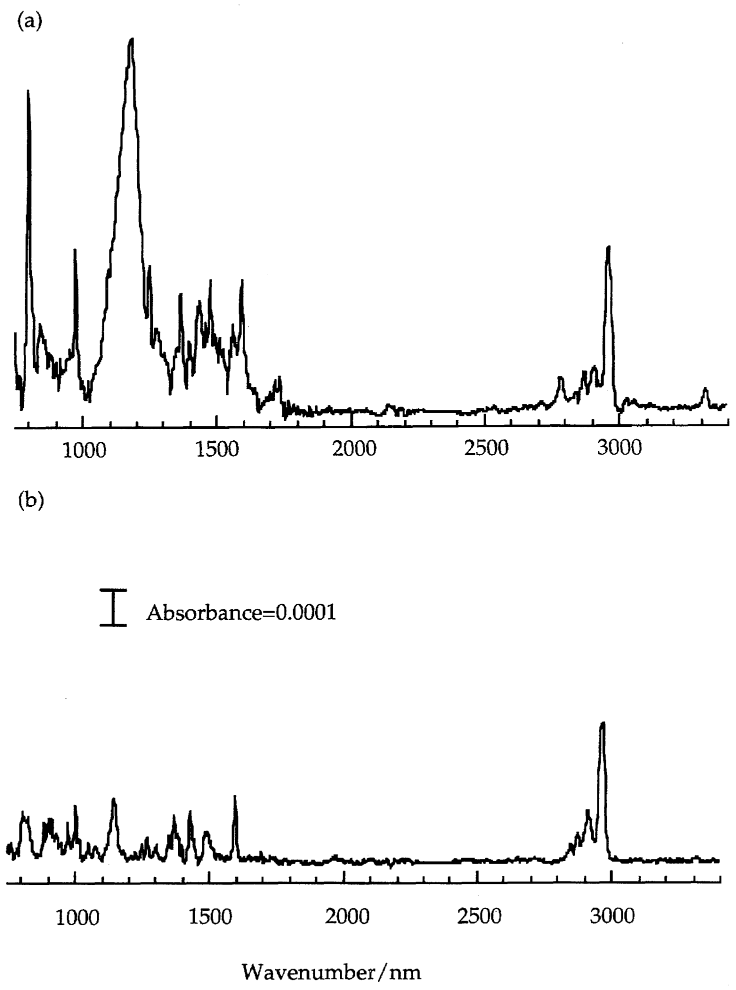


Fig. 12. Reflection absorption FTIR spectra of (a) **1a**/Au and (b) **2a**/Au.

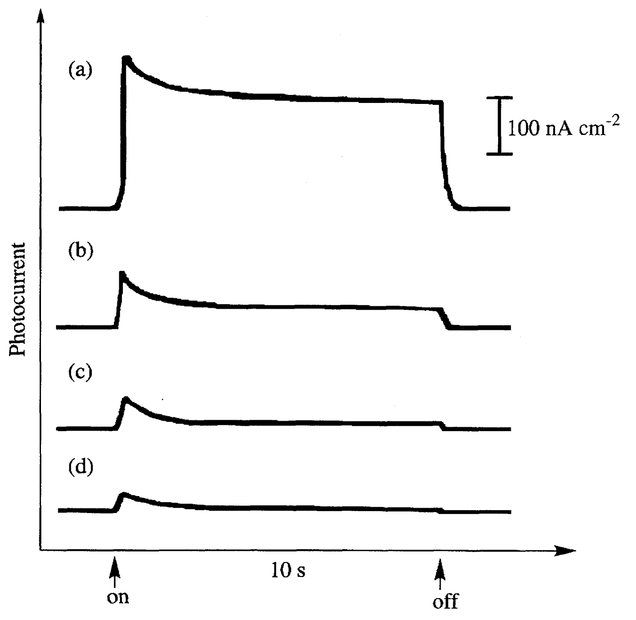


Fig. 13. Short circuit photocurrents of (a) Au/**1a**/5 × 10^{-3} mol dm^{-3} MV/Pt cell, (b) Au/**1a**/Pt cell, (c) Au/**2a**/5 × 10^{-3} mol dm^{-3} MV/Pt cell, and (d) Au/**1b**/5 ×10^{-3} mol dm^{-3} MV/Pt cell irradiated with λ = 438.5 nm light of 4.4 mW cm^{-2} under an argon atmosphere.

of 4.4 mW cm^{-2}, we obtained short circuit current J_{sc} = 260 nA cm^{-2}. However, we could not determine the open circuit voltage (V_{oc}) due to the instability. Given that an optical cross-section of 5.2×10^{8} cm^{2} mol^{-1} at 438.5 nm and surface coverage of $\Gamma = 1.6\times10^{-11}$ mol cm^{-2} for **1a**/Au, we estimate that the quantum yield of Au/**1a**/MV/Pt cell is ca. 0.005. The agreement of the action spectrum with the absorption of **1a**/Au from 400—500 nm (Fig. 10) shows that porphyrin is the photoactive species. The difference of shape between the two spectra may be due to that between the real spectrum on gold surface and actual spectrum obtained on reflection mode as well as to experimental error depending on the intensities of the light and the interference filters. The photocurrents increased linearly with light intensities from 0.01 to 5 mW cm^{-2}. In contrast, the photocurrent was saturated at around 5×10^{-3} mol dm^{-3} MV when adding MV into the solution, implying that the diffusion of the acceptor is a limiting factor for the photocurrent. The SAMs showed a photoelectronic response to switching on and off the light. The photocurrent decreased exponentially, reaching a constant value of approximately half the initial intensity, and this was maintained during irradiation of at least one hour. Similar intensities of the photocurrent were observed in Au/**2a**/MV/Pt cell and Au/**2b**/MV/Pt cell. Maximum intensity of the photocurrent in Au/**1a**/MV/Pt cell is about one order of magnitude larger than those in Au/**1b**/MV/Pt cell (Fig. 13d).

Discussion

Structure of the SAMs. XPS, ellipsometry, and electrochemical studies, as well as UV-visible and FTIR spectroscopy have established the structure of the porphyrin–fullerene thin films. XPS spectra of methyl phenyl sulfide/Au clearly demonstrated the existence of covalent S–Au bonds similar to those in alkanethiols' and arenethiols' SAMs on Au. The binding energies of S2p in **1** and **2** are somewhat smaller than those in typical SAMs on Au. This suggests that the porphyrin moieties give electrons, thereby making it easier to remove electrons from the thiolate, thus causing the sulfur peaks to shift to lower binding energy. There are two other species in the SAM; the non-specific binding state and the sulfur-oxidized states. We can safely conclude from the relative intensities of the S2p peaks that the ratios of the non-specific binding state as well as the sulfur-oxidized states are not dominant. It is known that the sulfur-containing groups such as thiols are susceptible to be oxidized on Au due to the light and/or oxygen.[33d,39] Since all the procedures are carried out at ambient atmosphere under daylight, the sulfide group in **1** and **2** may be oxidized to sulfoxides, sulfones, and sulfonates. However, further detailed studies will be necessary to elucidate the oxidation mechanism as well as the oxidation states.

There exists uncertainty about the structure of the SAMs formed from sulfides on gold. Porter et al. proposed that S–C fission in either of the two S–C bonds results in the formation of the Au–S–C bond like those from thiols and disulfides,[32h] while others have shown that no cleavage of the S–C bonds occurs.[32a—g] We could not confirm these thiolates and/or coordinated sulfides of **1**/Au by using matrix-assisted laser desorption/ionization time of flight (MALDI TOF) mass spectroscopy. We only obtained complicated spectra owing to the fragmentation of the parent peak as well as the low signal-to-noise ratios. Additionally, preliminary linear-sweep voltammetry to distinguish cleavage of the S–Au bonds under alkalic aqueous conditions[40] showed complicated broad redox waves. Therefore, we could not determine the mode of the adsorption or the mechanism at the present, which is consistent with recent studies of sulfide SAMs on Au using two-laser mass spectroscopy.[41]

In cyclic voltammetry the first cycle for momolayers of **1** and **2** showed irreversible and broad oxidation and/or reduction waves. The further cycles displayed different broad waves. This behavior is in sharp contrast with the other redox active SAMs,[6—12] where reversible waves are seen. This difference suggests that SAMs of **1** and **2** may exist in several structural forms, to give rise to ill-defined and broad waves. The roughness factor on the gold surface was found to be 1.1.[42] Integration of the area under the curve observed for the first oxidation due to the porphyrin moiety corresponds to a surface coverage of $\Gamma = 1—2\times10^{-11}$ mol cm^{-2} for **1** and **2**, as shown in Table 2. These values are slightly smaller than those obtained by UV-vis absorption spectroscopy, and are considerably smaller than those of alkanethiol SAMs with porphyrins as terminal chromophores ($\Gamma = 5—20\times10^{-11}$ mol cm^{-2}).[9] The former result suggests that cyclic voltammetry underestimates the surface coverage because of the ill-defined broad peaks, compared with UV-vis absorption spectroscopy. The latter one implies that monolayers of **1** and **2** on Au are more loosely packed than the ideal SAMs like alkanethiols/Au systems. Assuming that the molecules are densely packed, where they are tilted and parallel onto the Au surface, the occupied areas per a molecule, projected to the gold, are calculated to be ca. 520 Å^2 (26 Å × 20 Å) for **1** and ca. 400 Å^2 (20 Å × 20 Å) for **2**. These values are substantially smaller than those obtained from the electrochemistry as well as those from the UV-visible absorption spectroscopy. Averaged thicknesses of the monolayers in **1** and **2** strongly depend on the orientation of the molecules to the gold surface (9—26 Å) as well as on the surface coverage. On the basis of the facts that averaged values of the thickness (ca. 10 Å), obtained from the ellipsometric measurements, are considerably smaller than the length of the molecules along the long molecular axis (20—26 Å), it is estimated that **1** and **2** occupy 40—60% of surface area on the gold,[43] where the molecules are substantially inclined to the gold surface. These results are in accordance with the facts that SAMs formed from sulfides possess less ordered surface structures compared with those from thiols and disulfides.[32] Aromatic thiols' SAMs on gold have been investigated by many researchers. Simple benzenethiols form poorly defined monolayers on gold electrodes, while oligo-aromatic mercaptans, with a variety of spacers including triple bonds, form densely packed monolayers with the molecules nearly perpendicular to the gold surface, owing to the greater interchain interaction.[34,44,45] On the other hand, Tao et al. also reported that toluene-α-thiols form closely packed and ordered monolayers, implying a preference of the zigzag extension as well as sp^3 hybridization in Au–S–CH$_2$–Ph bond in addition to the intermolecular interaction between the phenyl rings.[46] Seller et al. proposed two chemisorption modes for thiolates on Au(111) surface; sp and sp^3 hybridization with Au–S–C bond angles of 180° and 104°, respectively.[47] The tilted orientation of the molecules implies that sp^3 hybridization is more favorable than sp hybridization. The C$_{60}$ moieties as well as the porphyrin in **1** and **2** would have interaction with the gold surface rather than association using intermolecular interactions, resulting in the formation of loosely packed monolayers where the molecules are nearly parallel onto the gold surface. Lindsay observed a scanning tunneling microscopy (STM) image of *meso*-tetrapenylporphyrin bearing an isothiocyano group on the phenyl ring on Au(111). The completely tilted image on the surface is quite consistent with the results in our system.[9g] These results suggest that the packing structure of large molecules on metal surfaces is greatly affected by a subtle balance between molecule–metal surface and intermolecular interaction derived from size, shape, and atomic compositions of the large molecules as well as interactions of the specific atoms with the surface, such as sulfur atoms with the gold surface.[48)]

We could not assign almost all the peaks in FTIR spectra because **1** and **2** have complex molecular structures. However, some of the features are of interest. The broad peaks at 1100—1200 cm^{-1}, which appeared in reflection absorption spectra but not in the transmission ones, are likely to be due to the presence of surfur-oxidized groups such as sulfoxides, sulfones, and sulfonates in the SAMs. These results are in accordance with the fact that the oxidation product was also seen in the XPS analysis. Considering that sulfur-oxidized species generally display extremely strong IR vibrations in this region, we conclude that the relative ratios of the oxidized states in the SAMs may at least not be dominant.

There is no substantial difference in the relative intensities between the N–H stretching and the C–H or aromatic C–C stretching mode under the two measurements of transmission and reflection absorption FTIR spectra. Reflection absorption FTIR is often employed to give a quantitative basis for the orientation of molecules adsorbed on reflective surfaces. Vibrational bands having transition moments perpendicular to the substrate appear with enhanced intensity in reflection absorption FTIR spectra, while those with parallel transition moments appear with reduced intensity. The N–H stretching can be assigned to the in-plane of the porphyrin ring, while the aliphatic C–H can be assigned mainly to the *t*-butyl group on the *meso*-phenyl groups where they are almost randomly oriented. These results support the conclusion that the molecules are inclined to the gold surface.[49)] It should be noted here that the intensity of the N–H stretching in **2a** is clearly diminished compared with the intensities of the C–H and aromatic C–C ones, as well as that of the N–H stretching in **1a**. This indicates that the porphyrin plane in **1a** is less tilted compared with that in **2a**, presumably due to the bulkiness of the C_{60} moiety within **1a**. In UV-visible spectra of **1**/Au and **2**/Au, broadening as well as the red-shift of the Soret bands were observed compared with those in solutions. Similar red-shifts as well as broadening were reported in the porphyrin–SAMs[9)] as well as in the LB films containing porphyrins.[50)] It may be related to the excitonic coupling among the porphyrins, the aggregation, and/or the differences of microenvironment in the monolayers.

Photocurrent Generation Mechanism. The photocurrent generation in porphyrin–C_{60} SAM systems can be explained by two different electron transport mechanisms: ion pair mechanism for Au/**1b**/MV/Pt cell and exciplex mechanism for Au/**1a**/MV/Pt cell (Fig. 14).

Picosecond time-resolved absorption spectra of **1b** in THF clearly show the charge-separated state. This is in accordance with the previously reported behavior of our zinc porphyrin-C_{60} systems, in which the excitation of the porphyrin and the C_{60} moieties within the molecules leads to the efficient formation of the charge-separated states in polar solvents like THF and DMF.[16)] The efficient CS is consistent with the fact that only a trace amount of the triplet state due to the porphyrin was seen in the transient spectra at 3 ns delay of the laser pulse.[51)] Although the environment around the molecules in solution is likely to be different from that on the gold surface, the charge-separated state may be produced efficiently within **1b**/Au owing to the faster CS rate compared with the rates in the deactivation pathways. The lifetimes may be much longer than those where conventional acceptors like quinones and imides are used instead of C_{60}. However, the lifetimes of the charge-separated state within **1b**/Au are relatively too short to transfer an electron to MV because of the limitation by the diffusion of MV. Since the redox potential for one-electron reduction of MV (−0.59 V Ag/AgCl in ethanol)[52)] is similar to that of the C_{60} moiety, the small driving force for the charge shift would be unfavorable as well. The rather disordered orientation of the donor–acceptor molecules on the electrode would cancel out the charge-separated states partially, resulting in the generation of the poor photocurrent.

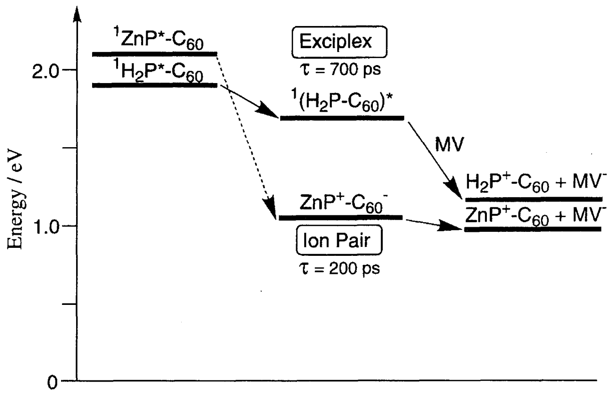


Fig. 14. Energy level diagram of photoelectrochemical cell.

The photocurrent generation mechanism for Au/**1a**/MV/Pt cell is quite different from the above. In transient absorption spectra of **1a** in THF, there exists no evidence for the production of free-base porphyrin cation radical and C_{60} anion radical. No stimulating emission from the excited state of the porphyrin at 650 and 720 nm was observed; this absence means that the excited state is quenched by the C_{60} moiety, followed by immediate formation of the transient species. Fullerenes tend to make an intermolecular complex with electron donors such as amines and aromatics both in the ground and the excited states.[53,54)] Unique interaction between the large planar π system of porphyrin and the spherical π system of C_{60} in **1a** may facilitate the production of a *spacer*-mediated intramolecular exciplex even in an *extended and rigid* conformation.[55)] However, we could not observe distinct exciplex emission at 77 K or at room temperature.[56)] Similar broad and structureless transient absorption is observed in the other free-base porphyrin–C_{60} molecules,[2h,16b)] whereas absorptions due to the ion pair are seen clearly in the corresponding zinc porphyrin–C_{60} molecules.[16)] Considering that the other free-base porphyrin–C_{60} molecules in our system showed the broad transient absorption irrespective of solvent polarity, the excited state may be less polar than typical exciplexes like aromatics–amines systems.[57)] A large degree of delocalization within the three-dimensional framework of porphyrin and C_{60} would produce the less polar excited state in free-base porphyrin–C_{60} systems. The difference of the excited states in **1a** and **1b** may arise from that of the driving forces for photoinduced charge separation; the small driving force results in the formation of the exciplex, while the large one leads to the production of the charge-separated state, as pointed out by some workers.[58,59] Based on the fact that absorbances of **1a** and **1b** on gold electrodes are comparable at the monochromic excitation wavelength (438.5 nm), the longer lifetimes as well as the higher energy level of the intramolecular exciplex in **1a** account for the larger photocurrent in Au/**1a**/MV/Pt cell as compared with that in Au/**1b**/MV/Pt cell. The maximum intensity of the photocurrent in Au/**2a**/MV/Pt cell is one fifth smaller than that in Au/**1a**/MV/Pt cell. The photocurrent in Au/**2a**/MV/Pt cell may be ascribed to intermolecular ET from the excited singlet and/or triplet states of the porphyrin to MV,[60] whereas the intramolecular exciplex in **1a** is an intermediate in Au/**1a**/MV/Pt cell. The low photocurrrent in Au/**2a**, **2b**/MV/Pt cell may be largely caused by the direct deactivation of the excited state of the porphyrin by the Au electrode via energy transfer and/or ET.[9s,61] The maximum intensity of the photocurrent in Au/**1b**/MV/Pt cell is reduced by ca. 50%, compared that in Au/**2b**/MV/Pt cell. As we discussed, the excited singlet state of the zincporphyrin in **2b**/Au is quenched strongly by the gold electrode, whereas that in **1b**/Au is quenched by the C_{60} moiety rather than the gold surface. However, considering the ion pair mechanism for Au/**1b**/MV/Pt cell and the photoinduced intermolecular ET mechanism in Au/**2b**/MV/Pt cell, it is concluded that the charge-separated state in Au/**1b**/MV/Pt cell is less effective for generation of the photocurrent than the excited states of the porphyrin in Au/**2b**/MV/Pt cell. Alternatively, MV is much easier to penetrate into the SAM in Au/**2b**/MV/Pt cell than in Au/**1b**/MV/Pt cell, because **2b** has no C_{60} moiety. Therefore, the photocurrent in the Au/**2b**/MV/Pt cell is larger than that in the Au/**1b**/MV/Pt cell. These results clearly show that the C_{60} moiety is a excellent ET mediator[62] which accelerates the charge shift to MV, quite similar to the photosynthetic multistep ET in the reaction center.

Recently, Uosaki et al. have reported a similar photoelectrochemical cell using a gold electrode modified with porphyrin–ferrocene SAM, where the quantum yield is 0.11.[9p] This is the highest among the organic solar cells mimicking the photosynthesis.[4] They concluded that the ferrocene and the porphyrin moieties are well-arranged on the gold electrode in the order, the ferrocene and the porphyrin, by using long alkyl spacers. Their photocurrent generation mechanism is quite different from our system. The excited singlet or the triplet states of the porphyrin transfer an electron to MV as an electron carrier, followed by the successive hole transfer from the H_2P^+ to the gold electrode via the ferrocene. It seems that the rate-determining step is intermolecular ET for the excited porphyrin to MV. Although the quantum efficiency in their system is much higher than our system, better molecular design to prolong the lifetime of the charge-separated state using fullerenes could improve the efficiency in the present system.

Conclusion

Surface analysis in this study showed that the assembly of large π-aromatics on a metal surface is greatly affected by molecule–metal as well as intermolecular interactions, in addition to specific sulfur–gold interactions. Molecular devices such as photonics generally must include aromatic chromophores as photoresponsive units. Therefore, further information about the relationship between molecular structure and assembly involving the size, shape, and atomic compositions on the interface must be accumulated to design aromatic-containing molecular devices.

We have developed a biomimetic photoelectrochemical cell based on porphyrin–fullerene monolayer films. The relatively large photocurrents were observed in this system, showing the possibility of practical applications as photovoltaic device and/or sensor. Our experiments confirmed that C_{60} can act as an efficient ET mediator in a photosynthetic organic solar cell.

The photoelectrochemical properties are not optimized at the present stage, but it will be much improved by the following considerations about light harvesting and electron relay efficiency. First, the former can be elaborated by an increase in the number of adsorbed molecules on the gold surface. Application of thiols and disulfides with long alkyl chains will increase interchain interaction, and it will be possible to construct a highly ordered structure of SAM where functional molecules are aligned and probably perpendicular to the surface. Besides, design and synthesis of the highly absorbing molecules like antenna complexes in photosynthesis will be required for improving light harvesting properties. Second, well-tailored molecular array systems like triad, tetrad, and pentad molecules containing fullerenes could make a great contribution to the improvement of the multistep electron transfer reactions. Our approach to assemble the large functional molecules in an interface will stimulate many fields, such as chemistry, physics, and biology to develop new principles and concepts in nano-scale science and technology.

Experimental

Melting points were recorded on a Yanagimoto micro-melting apparatus and are not corrected. ^{1}H NMR, ^{13}C NMR, DEPT, and 2D-COSEY spectra were measured on a JEOL EX-270. Fast atom bombardment mass spectra were obtained on a JEOL JMS-DX300. MALDI TOF mass spectra were measured on a Kratos Compact MALDI I (Shimadzu). Microtransmission FTIR spectra were acquired with a Bio-Rad FTS-135/MA-250 at 4 cm^{-1} resolution. The transmission measurements utilized 64—256 scans of the solid materials dispersed on the plate. Reflection absorption FTIR measurements were conducted with a Bio-Rad FTS575C using a liquid nitrogen cooled MCT detector. Reflection spectra of the monolayer films used 2000 scans at 4 cm^{-1} resolution with p-polarized light incident at 75° from the surface normal. UV-visible spectra in solutions were obtained on a Shimadzu UV3000 spectrometer, while those on Au were recorded on a Hitachi U-3500 spectrometer on reflection mode. Fluorescence spectra were measured on a Hitachi 850. Elemental analyses were performed on a Perkin–Elmer Model 240C elemental analyzer.

All solvents and chemicals were of reagent grade; they were purchased commercially and used without further purification, except as noted below. THF was distilled from benzophenone–Na. CH_2Cl_2 for electrochemical studies was distilled from CaH_2 before use. Thin-layer chromatography (TLC) and flash column chromatography were performed with Art. 5554 DC-Alufolien Kiselgel 60 F_{254} (Merck), and Fujisilicia BW300, respectively.

The gold electrode was prepared by a vacuum deposition technique with chromium (50 Å) and gold (2000 Å) in a sequence onto Si (100) wafer (Sumitomo Sitx Corp.). Atomic force microscopy (Seiko Instruments) and X-ray diffraction studies showed that the gold electrode has mainly (111) surface. The gold-coated wafers were cut into slides (ca. 1—3 cm × 1—3 cm), rinsed with dilute hydrochloric acid, millipore water, and ethanol and dried with a stream of argon before being immersed in a solution of sulfides. Monolayers were formed by the spontaneous adsorption of the sulfides onto the gold substrates. In all cases, adsorption was carried out from CH_2Cl_2 solutions of 1.0×10^{-3} mol dm^{-3} for 4 d to reach the equilibrium. After soaking, the electrode was washed well with CH_2Cl_2 and dried with a stream of argon.

XPS was performed on a VG Scientific, Inc. μLab mark III with Mg $K\alpha$ X-ray (1253.6 eV; target voltage: 8 kV; emission current: 16 mA). The ellipsometric data have been obtained using a Rudolph Research S2000 Spectroscopic Ellipsometer. The source is a high pressure Xe arc lamp. The samples have been measured at 70° using 5 mm beam size, from 300 to 800 nm by 10 nm steps (51 points). Readings were taken on the clean gold to establish the bare substrate optical constants and on the modified gold samples. The thicknesses were calculated by using a single film model with an assumed refractive index of 1.50 for the monolayer. We used Newton's Gradient Method for fitting the thickness.

Electrochemical measurements were performed on a Bioanalytical Systems, Inc. CV-50W voltammetric analyzer using a standard three-electrode cell with a modified Au working electrode (0.57 cm^2), platinum wire counter electrode, and Ag/AgCl reference. Photoelectrochemical measurements were performed in a one-compartment columnar Pyrex cell (15 ml) under argon atmosphere. The cell was illuminated with monochromatic excitation through interference filters (MIF-S, Vacuum Optics Corporation of Japan) by 150 W Xenon lamp on the SAM of 0.38 cm^2. Unless otherwise stated, a 0.1 mol dm^{-3} Na_2SO_4 and 5×10^{-3} mol dm^{-3} methylviologen aqueous electrolyte solution (pH 6.0) was used. Short-circuit photocurrents were measured in a two-electrode arrangement, a modified Au working electrode (0.57 cm^2) and platinum plate counter electrode (1.2 cm × 2.5 cm, the distance between the electrodes is 3 cm) by a Keithley 2001 degital multimeter. The light intensity was monitored by an Anritsu ML9002A optical power meter or a Hamamatsu Si photodiode.

THF (Merck Uvasol and Wako ∞Pure) was refluxed in the presence of molecular sieve (Wako 13X) and calcium hydride for 2 h and then distilled before picosecond laser studies. The solution for optical measurements were deoxygenated by purging with nitrogen, and their concentrations were 10^{-6} mol dm^{-3} for the measurements of fluorescence lifetime and 10^{-4} mol dm^{-3} for time-resolved transient absorption spectroscopy.

Fluorescence decay curves were measured by means of a time-correlated single photon counting method using the second harmonic (400—403 nm) of $Ti^{3+}:Al_2O_3$ laser (Spectra-Physics, Tunami, FWHM 60-100 fs) pumped by Ar-ion laser (Spectra-Physics, Beamlock 2060).[63] SALS at the Osaka University Computation Center was used for the nonlinear least-squares analysis of the observed decay curves.

Picosecond transient absorption spectra were measured by means of a picosecond dye laser (FWHM 12 ps) pumped by the second harmonic of a repetitive mode-locked Nd^{3+}:YAG laser (Quantel, Picochrome YG-503 C/PTL-10).[64] The 590-nm output of the dye laser (Rhodamine 6G) was used for excitation.

Syntheses of 1—5. **4:**[24] A solution of 3,5-di-*t*-butylbenzaldehyde[16e] (21.8 g, 0.1 mol) and pyrrole (280 ml, 4 mol) was degassed by bubbling with nitrogen for 10 min; then trifluoroacetic acid (0.8 ml, 10 mmol) was added. The solution was stirred for 60 min at room temperature; no starting aldehyde was observed by TLC analysis after such stirring. The mixture was diluted with $CHCl_3$ (1000 ml), washed with 0.1 M NaOH (1 M = 1 mol dm^{-3}) aqueous solution and water successively and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and then the unreacted pyrrole was removed by vacuum distillation at room temperature. The resulting red oil was dissolved in a minimal amount of the eluant and was purified by flash column chromatography (hexane/ethyl acetate/triethylamine = 80/20/1). The second band was collected and evaporated under reduced pressure. The pale red oil was used immediately without further purification because of the unstableness. Yield 18.41 g (55.1 mmol, 55 %). ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = 7.91$ (br.s, 2H), 7.31 (t, $J = 2$ Hz, 1H), 7.05 (d, $J = 2$ Hz, 2H), 6.69 (m, 2H), 6.16 (q, $J = 3$ Hz, 2H), 5.93 (m, 2H), 5.44 (s, 1H), 1.28 (s, 18H).

5:[25] **4** (18.41 g, 55.1 mmol), 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (6.06 g, 27.6 mmol), and 4-(methylthio)benzaldehyde (3.64 ml, 27.6 mmol) were dissolved in 700 ml of CH_3CN. Trichloroacetic acid (2.70 g, 16.5 mmol) was added, and the mixture was stirred overnight in the dark. A solution of *p*-chloranil (6.79 g, 27.6 mmol) in a minimum amount of THF was added, and the mixture was stirred for an additional 5 h. The solvent was evaporated and the residue was taken up in 500 ml of $CHCl_3$, washed with saturated $NaHCO_3$ aqueous solution and water, successively, and dried over anhydrous Na_2SO_4. To the solution was added 50 ml of saturated solution of zinc acetate in methanol, and the mixture was heated to reflux for 2 h. After cooling, the reaction mixture was washed with water, dried over Na_2SO_4 and evaporated. TLC showed three products (R_f = 0.9, 0.7, and 0.4, benzene) and the second was separated by flash column chromatography. The second fraction was concentrated and dissolved in a mixture of trifluoroacetic acid (5 ml), acetic acid (10 ml), and 5% aqueous sulfuric acid (5 ml). After being heated at 100 °C for 90 min, the mixture was poured into 150 ml of water and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ aqueous solution, dried over anhydrous Na_2SO_4, and evaporated. Flash column chromatography on silica gel with benzene as the eluent and subsequent recrystallization from $CHCl_3$–MeOH gave **5** as black purple solid (71.3 mg, 0.078 mmol, 0.3%). Mp > 300 °C; ^{1}H NMR (270 MHz, $CDCl_3$) $\delta = 10.38$ (s, 1H), 8.92 (d, $J = 5$ Hz, 2H), 8.91 (d, $J = 5$ Hz, 2H), 8.88 (d, $J = 5$ Hz, 2H), 8.77 (d, $J = 5$ Hz, 2H), 8.42 (d, $J = 8$ Hz, 2H), 8.28 (d, $J = 8$ Hz, 2H), 8.15 (d, $J = 8$ Hz, 2H), 8.08 (d, $J = 2$ Hz, 4H), 7.81 (t, $J = 2$ Hz, 2H), 7.63 (d, $J = 8$ Hz, 2H), 2.75 (s, 3H), 1.53 (s, 36H), −2.73 (br.s, 2H); MS (FAB) 915 (M+H$^+$).

1a:[26] C_{60} (94 mg, 0.13 mmol), **5** (60 mg, 0.066 mmol), and *N*-methylglycine (117 mg, 1.3 mmol) in toluene (60 ml) were heated under reflux an nitrogen atmosphere in the dark for 6 h. The reaction mixture was allowed to cool to room temperature and then evaporated to dryness at reduced pressure. Flash column chromatography on silica gel with hexane–benzene (1 : 1) as the eluent and subsequent recrystallization from benzene–MeOH gave **1a** as brown solids (103 mg, 0.062 mmol, 94%). Mp > 300 °C;

^{1}H NMR (270 MHz, CDCl$_3$) δ = 9.00—8.60 (m, 10H), 8.20—7.80 (m, 8H), 7.78 (s, 2H), 7.58 (d, J = 8 Hz, 2H), 4.45 (d, J = 8 Hz, 1H), 3.92 (s, 1H), 3.36 (d, J = 8 Hz, 1H), 2.86 (s, 3H), 2.71 (s, 3H), 1.53 (s, 36H), −2.70 (br.s, 2H); ^{13}C NMR (68 MHz, CDCl$_3$; The symbol $*$ means several superimposed signals.) δ = 154.90, 152.45, 152.00, 151.05, 148.9*, 146.40, 145.30, 145.25, 145.20, 145.10, 145.00, 144.80, 144.30, 144.25, 144.20*, 144.00, 143.90, 143.80, 143.70, 143.50, 143.30, 143.10, 142.80, 142.60, 142.45, 141.80, 141.70, 141.50, 141.40, 141.20, 141.00*, 140.70, 140.60, 140.50, 139.50, 139.10, 138.70, 138.60, 138.20, 138.10*, 136.20, 135.90, 135.00, 134.00, 133.50, 131.60*, 130.40, 129.40, 125.60, 125.00, 123.90, 123.30, 122.20, 121.80, 121.50, 120.50, 119.50, 119.30, 40.16, 35.1, 31.8. Because of the poor solubility and the overlapping with the solvent peaks, some signals in ^{13}C NMR spectrum could not be assigned; MS (FAB) 1662 (M+H$^+$); FTIR (microtransmission, symbols: *s* (strong), *m* (middle), and *w* (weak) corresponding to intensities of the peaks) 3315 (*m*), 3123 (*w*), 3068 (*w*), 3024 (*w*), 2962 (*s*), 2905 (*m*), 2868 (*m*), 2782 (*m*), 1702 (*w*), 1592 (*s*), 1560 (*m*), 1475 (*s*), 1427 (*m*), 1394 (*m*), 1363 (*s*), 1334 (*w*), 1302 (*w*), 1247 (*s*), 1222 (*w*), 1187 (*w*), 1157 (*w*), 1093 (*w*), 1020 (*w*), 973 (*s*), 915 (*w*), 800 (*s*), 730 (*m*) cm^{-1}. Found: C, 89.91; H, 4.30; N, 3.99%. Calcd for C$_{124}$H$_{69}$N$_5$S: C, 89.67; H, 4.19; N, 4.22%. UV-vis $\lambda_{\max}$ (log ε) (THF) 420 (5.73), 515 (4.37), 552 (4.15), 591 (3.88), 649 nm (3.82).

1b: A saturated methanol solution of Zn(OAc)$_2$ (2 ml) was added to a solution of **1a** (13.0 mg, 7.82 μmol) in CHCl$_3$ (20 ml) and refluxed for 30 min. After cooling, the reaction mixture was washed with water twice, dried over anhydrous Na$_2$SO$_4$, and then the solvent was evaporated. Flash column chromatography on silica gel with hexane/benzene (= 1/1) as the eluent and subsequent recrystallization from benzene–MeOH gave **1b** as brown solids (91% yield, 12.3 mg, 7.13 μmol). Mp > 300 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ = 9.20—8.60 (m, 10H), 8.30—7.60 (m, 10H), 7.89 (br.s, 2H), 4.21 (d, J = 8 Hz, 1H), 3.39 (s, 1H), 3.00 (d, J = 8 Hz, 1H), 2.78 (s, 3H), 2.46 (s, 3H), 1.51 (s, 36H); MS (FAB) 1725 (M+H$^+$); FTIR (microtransmission) 3105 (*w*), 3055 (*w*), 2961 (*s*), 2926 (*m*), 2855 (*m*), 2787 (*m*), 1725 (*m*), 1707 (*m*), 1592 (*s*), 1523 (*w*), 1475 (*m*), 1463 (*m*), 1427 (*m*), 1392 (*m*), 1362 (*s*), 1336 (*m*), 1286 (*m*), 1267 (*m*), 1247 (*m*), 1218 (*w*), 1205 (*w*), 1179 (*w*), 1122 (*w*), 1103 (*m*), 1093 (*w*), 1069 (*m*), 1037 (*w*), 998 (*s*), 928 (*w*), 878 (*w*), 823 (*w*), 796 (*s*), 717 (*m*) cm^{-1}. Found: C, 86.71; H, 4.32; N, 3.84%. Calcd for C$_{124}$H$_{67}$N$_5$SZn: C, 86.37; H, 4.00; N, 4.03%. UV-vis $\lambda_{\max}$ (log ε) (THF) 426 (5.86), 557 (4.46), 596 nm (4.12).

2a:[27)] 3,5-Di-*t*-butylbenzaldehyde (6.13 g, 28.1 mmol), 4-(methylthio)benzaldehyde (1.42 g, 9.37 mmol), and pyrrole (2.51 g, 37.5 mmol) were dissolved in dry CHCl$_3$ (900 ml). The mixture was degassed with nitrogen for 30 min. Then Et$_2$O·BF$_3$ (3.2 ml, 6.25 mmol) was added to the solution; this mixture was stirred for 2 h under nitrogen atmosphere. Chloranil (6.92 g) was added to the reaction mixture and this was stirred overnight. The solvent was removed under reduced pressure. Flash column chromatography on silica gel with hexane–benzene (1 : 1) as the eluent and subsequent recrystallization from benzene–CH$_3$CN gave **2a** as black-red solids (120 mg, 0.12 mmol, 1.3%). Mp > 300 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ = 8.91 (s, 4H), 8.90 (d, J = 5 Hz, 2H), 8.87 (d, J = 5 Hz, 2H), 8.15 (d, J = 8 Hz, 2H), 8.10 (d, J = 2 Hz, 4H), 8.09 (d, J = 2 Hz, 2H), 7.80 (t, J = 2 Hz, 1H), 7.79 (t, J = 2 Hz, 2H), 7.61 (d, J = 8 Hz, 2H), 2.72 (s, 3H), 1.53 (s, 54H), −2.69 (br.s, 2H); MS (FAB) 998 (M+H$^+$); FTIR (microtransmission) 3316 (*w*), 3067 (*w*), 2962 (*s*), 2904 (*m*), 2867 (*m*), 1592 (*s*), 1561 (*m*), 1475 (*s*), 1444 (*w*), 1426 (*m*), 1394 (*m*), 1363 (*s*), 1352 (*w*), 1301 (*w*), 1264 (*w*), 1247 (*s*), 1223 (*w*), 1203 (*w*), 1186 (*w*), 1154 (*w*), 1092 (*w*), 1074 (*w*), 1018 (*w*), 1000 (*w*), 980 (*w*), 972 (*s*), 929 (*w*), 914 (*w*), 900 (*w*), 882 (*w*), 843 (*w*), 818 (*w*), 801 (*s*), 765 (*w*), 728 (*m*), 711 (*w*) cm^{-1}. Found: C, 83.21; H, 8.22; N, 5.35%. Calcd for C$_{69}$H$_{80}$N$_4$S: C, 83.09; H, 8.08; N, 5.62%. UV-vis $\lambda_{\max}$ (THF) 420 (5.73), 515 (4.33), 552 (4.10), 593 (3.82), 650 nm (3.74).

2b: This compound was synthesized from **2a** by the same method as that described for **1b**. **2b** as black-red solids from benzene–MeOH (52% yield). Mp > 300 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ = 9.01 (s, 4H), 9.00 (d, J = 5 Hz, 2H), 8.97 (d, J = 5 Hz, 2H), 8.15 (d, J = 8 Hz, 2H), 8.10 (d, J = 2 Hz, 4H), 8.09 (d, J = 2 Hz, 2H), 7.79 (t, J = 2 Hz, 2H), 7.78 (t, J = 2 Hz, 1H), 7.61 (d, J = 8 Hz, 2H), 2.73 (s, 3H), 1.52 (s, 54H); MS (FAB) 1061 (M+H$^+$); FTIR (microtransmission) 3123 (*w*), 3058 (*w*), 2962 (*s*), 2961 (*m*), 2904 (*m*), 2867 (*m*), 1592 (*s*), 1525 (*w*), 1490 (*m*), 1477 (*m*), 1463 (*m*), 1426 (*m*), 1393 (*m*), 1363 (*s*), 1340 (*w*), 1290 (*m*), 1248 (*m*), 1220 (*w*), 1207 (*w*), 1186 (*w*), 1095 (*w*), 1071 (*w*), 1002 (*s*), 948 (*w*), 930 (*w*), 900 (*w*), 883 (*w*), 825 (*w*), 799 (*s*), 718 (*m*) cm^{-1}. Found: C, 83.21; H, 8.22; N, 5.35%. Calcd for C$_{69}$H$_{78}$N$_4$SZn: C, 78.12; H, 7.41; N, 5.28%. UV-vis $\lambda_{\max}$ (log ε) (THF) 426 (5.86), 557 (4.41), 596 nm (4.07).

3: This compound was synthesized from 3,5-di-*t*-butylbenzaldehyde, C$_{60}$, and *N*-methylglycine by the same method as that described for **1a**. **3** as brown solids from benzene–MeOH (47% yield). Mp > 300 °C; ^{1}H NMR (270 MHz, C$_6$D$_5$CD$_3$) δ = 8.3—7.2 (br.s, 2H), 7.43 (t, J = 2 Hz, 1H), 4.75 (s, 1H), 4.51 (d, J = 2 Hz, 1H), 3.87 (d, J = 2 Hz, 1H), 2.64 (s, 3H), 1.30 (s, 18H); ^{13}C NMR (68 MHz, C$_6$D$_5$CD$_3$, The symbol $*$ means several superimposed signals.) δ = 156.75, 154.77, 154.39, 153.56, 147.49, 147.41, 146.83, 146.54, 146.48*, 146.39, 146.32, 146.11, 146.05, 145.86, 145.78*, 145.59, 145.47*, 145.35, 144.99, 144.93, 144.65*, 143.46, 143.29, 142.95, 142.84, 142.80, 142.76, 142.56, 142.51, 142.39, 142.30*, 142.23*, 142.02, 141.90, 141.69, 140.45, 140.31, 139.77, 139.63, 136.89, 136.82, 136.51, 136.27*, 121.82 (*para*-phenyl-C), 84.19 (–$\underline{\mathrm{C}}$H–Ph), 77.95 (C$_{60}$-sp^3), 70.00 (–$\underline{\mathrm{C}}$H$_2$–), 69.17 (C$_{60}$-sp^3), 39.58 (N–$\underline{\mathrm{C}}$H$_3$), 35.03 (–$\underline{\mathrm{C}}$(CH$_3$)$_3$), 31.47 (–C($\underline{\mathrm{C}}$H$_3$)$_3$). Some of the ^{13}C NMR signals could not be assigned because of the overlapping with the solvent peaks.; MS (FAB) 1040 (M+H$^+$).

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