Photoinduced electron transfer at a gold electrode modified with a self-assembled monolayer of fullerene

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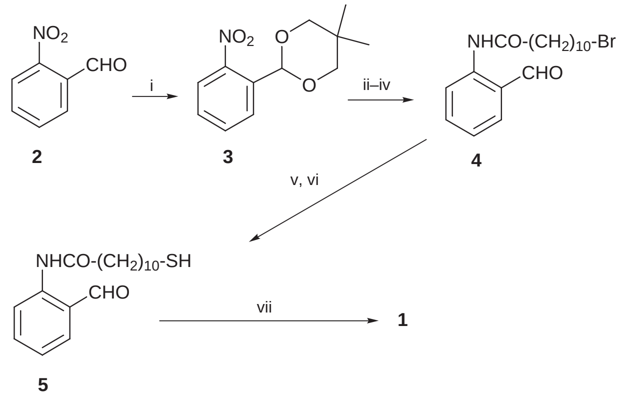
A stable anodic photocurrent was observed in the presence of an electron sacrificer when a gold electrode modified with a self-assembled monolayer of C_{60} was illuminated with monochromic light, indicating the generation of a vectorial electron flow from the electron donor to the gold electrode *via* the excited states of C_{60}.

The unique three-dimensional structure of C_{60} has prompted many researchers to apply it to materials science.[1] In this context, fullerene thin films formed using a variety of methods, including Langmuir–Blodgett (LB) techniques and evaporation, have displayed interesting physical and chemical properties.[2] Self-assembled monolayers (SAMs) are useful for constructing highly ordered, two- and three-dimensional structures on substrates.[3] Several groups have already reported the preparation, electrochemistry and surface properties of C_{60} SAMs.[4–9] However, to the best of our knowledge, there have been no reports of the photoelectrochemical properties of SAMs of fullerenes. Here we report the preparation and photoelectrochemistry of a SAM of C_{60}-tethered alkanethiol **1** on a gold electrode (Fig. 1).

The synthetic route to C_{60}-linked polyalkanethiol **1** is shown in Scheme 1. It is well established that alkanethiols with a polymethylene chain form densely packed monolayers on gold surfaces. It is reported that the presence of an amido group in a chain enhances the stability of monolayers due to intermolecular hydrogen bonding.[10] Thus, it is expected that the attachment of a long alkyl chain to C_{60} with an amide linkage would allow us to produce a well-ordered C_{60} SAM on a gold electrode. Aldehyde **5** was prepared *via* six steps from 2-nitrobenzaldehyde **2**. Compound **1** was synthesized by the condensation of *N*-methylglycine, C_{60} and **5**.[11] The structures of **1** and related compounds were confirmed by spectroscopic methods including ^1H NMR and mass spectra.† Cyclic voltammetry of **1** in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 as electrolyte exhibited reversible waves due to the first and the second reductions of C_{60} (−0.59, −1.00 V *vs.* Ag/AgCl), as shown in Fig. 2.



Scheme 1 *Reagents and conditions*: i, neopentyl glycol, TsOH, 91%; ii, H_2, Pd/C, 72%; iii, 11-bromoundecanoic acid, *N*-methylmorpholine, 2-chloro-4,6-dimethoxy-1,3,5-triazine, 99%; iv, H_2SO_4, TFA, 99%; v, potassium thioacetate, 80%; vi, KOH, 96%; vii, *N*-methylglycine, C_{60}, 13%.

A monolayer of **1** was formed by the spontaneous bonding of **1** onto Au(111)/Cr/Si(100) substrates (hereafter, **1**/Au, where / represents an interface). The bonding was carried out from a 20 μM $CHCl_3$ solution for 20 h to complete the formation. After soaking, the electrode was washed well with $CHCl_3$ and dried with a stream of argon. Cyclic voltammetry of **1**/Au in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 with a sweep rate of 100 mV s^{-1} showed a wave at $E_{1/2} = -0.63$ V (*vs.* Ag/AgCl) and a second smaller wave at $E_{1/2} = -1.07$ V, which correspond to the first and second reduction/oxidation peaks of C_{60}, respectively (Fig. 2). The values of the peak splittings ($\Delta E_{\text{peak}} = 210$ mV) are large, compared with the ideal value in solution, indicating the slow kinetics between the C_{60} and the gold electrode due to structural constraints. Integration of the area under the curve observed for the first reduction due to the C_{60} corresponds to a surface coverage of $\Gamma = 1.4 \times 10^{-10}$ mol cm^{-2} (120 Å^2 molecule^{-1}),‡ which agrees well with the value (1.4×10^{-10} mol cm^{-2}) in similar C_{60} SAM systems.[8,9] The value is somewhat larger than the values of the hexagonal (78 Å^2

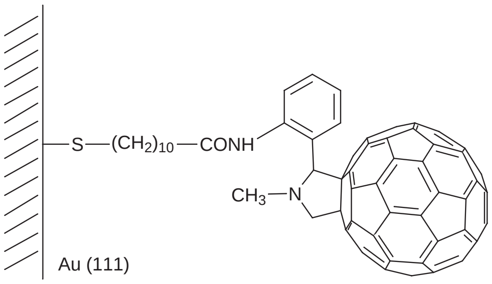


Fig. 1 A self-assembled monolayer of **1**/Au (111).

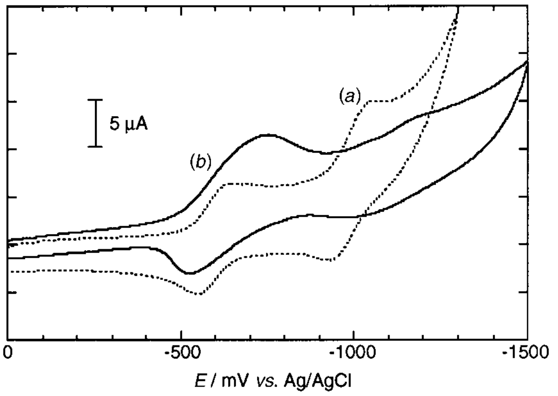


Fig. 2 Cyclic voltammograms of (*a*) **1** in CH_2Cl_2 (dotted line) and (*b*) **1**/Au in CH_2Cl_2: sweep rate 100 mV s^{-1}, electrode area 0.48 cm^2, initial potential 0 V.

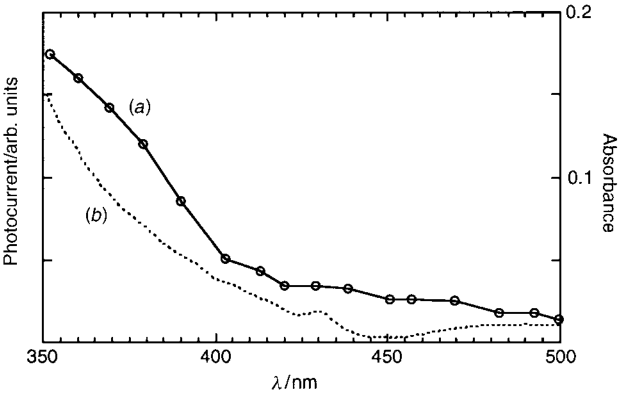


Fig. 3 Action spectrum of (*a*) C_{60} SAM cell and (*b*) absorption spectrum of **1** in $CHCl_3$ (8.88 μM).

molecule^{-1}) or the simple square (98 Å^2 molecule^{-1}) packing in similar C_{60} LB films.[12] This may be related to steric hindrance around the phenyl group on the pyrrolidine ring attached to C_{60}.

Photoelectrochemical measurements were carried out for **1**/Au in an argon-saturated 0.1 M Na_2SO_4 solution containing 50 mM ascorbic acid (AsA) as an electron sacrificer using a modified gold electrode as the working electrode, a platinum counter electrode, and a Ag/AgCl reference electrode (hereafter, Au/**1**/AsA/Pt, where / represents an interface). A stable anodic photocurrent flowed immediately after the gold electrode was irradiated and fell instantly when the illumination was terminated. The photoelectrochemical response was repeated for tens of times without any signs of attenuation when the light was switched on and off. An increment of the anodic photocurrent with an increase of positive bias to the gold electrode (−400 mV to +200 mV) in the system demonstrated that the direction of the photocurrent takes place from the cathode to the anode through the electrolyte. The intensity of the photocurrent for the Au/**1**/AsA/Pt cell is an order of magnitude larger than those of the Au/**1**/Pt cell or the bare Au/AsA/Pt cell, indicating the involvement of AsA and C_{60} for the generation of the photocurrent. The agreement of the action spectrum with the absorption of **1** in $CHCl_3$ from 350–500 nm (Fig. 3) shows that C_{60} is the photoactive species. Under excitation with $\lambda = 403 \pm 6.9$ nm light of 6.6 mW cm^{-2} and 0.1 V bias voltage, we obtained a photocurrent density of 290 nA cm^{-2}. Assuming that the absorption coefficient of **1** on the gold surface is the same as that in $CHCl_3$, absorbance of **1**/Au at 403 nm is calculated to be 7.81×10^{-4}. Given the absorbance for **1**/Au, we can estimate that the quantum yield of the Au/**1**/AsA /Pt cell is 7.5%.§ The value is at least one order of magnitude larger than those in similar photoelectrochemical cells of porphyrin SAMs[13] and comparable to those (1.2–8.2%) in similar C_{60} LB cells.[14] These results indicate that C_{60} is an excellent electron mediator as well as a good electron acceptor.[15] Based on these data together with previous results, we can propose the photocurrent generation mechanism. It is plausible that the excited singlet state (1.11 V *vs.* Ag/AgCl) and/or the triplet state (0.82 V) of the C_{60} are quenched by AsA (−0.19 V).[15] The resulting C_{60} anion radical would give an electron to the gold electrode, resulting in the recovery of the initial state. Overall, electron flow occurs from AsA to the gold electrode *via* C_{60}.

In conclusion, a photoelectrochemical cell with a gold electrode modified with a SAM of C_{60} has been constructed for the first time. The high quantum yield implies that a combination of C_{60} and SAMs is promising for applications in materials science. Our results will provide the basic information for the development of photovoltaic devices and sensors.

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Notes and references

† *Selected data* for **1**: δ_H(270 MHz, $CDCl_3$) 11.84 (br s, 1H), 8.64 (d, *J* 8, 1H), 7.48 (d, *J* 8, 1H), 7.36 (t, *J* 8, 1H), 7.08 (t, *J* 8, 1H), 5.10 (s, 1H), 5.09 (d, *J* 10, 1H), 4.29 (d, *J* 10, 1H), 2.95 (s, 3H), 2.59 (q, *J* 8, 2H), 2.49 (t, *J* 8, 2H), 1.8–0.8 (m, 17H); *m*/*z* (FAB-MS) 1070 (M + H$^+$).

‡ The roughness factor (1.1) was estimated by iodine chemisorption on the Au(111) surface.

§ Absorption spectra for **1**/Au could not be obtained in reflection or transmission mode because of the low absorption coefficient of C_{60} as well as the low value of the surface coverage.

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