PERKIN 2 COMMUNICATION

Facile construction of an ultra-thin [60]fullerene layer from [60]fullerene–homooxacalix[3]arene complexes on a gold surface

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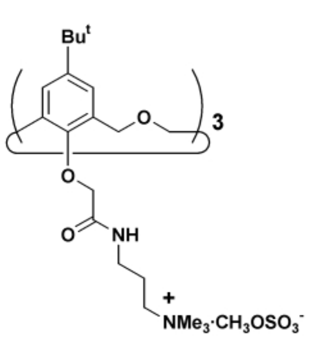
A hexacationic homooxacalix[3]arene–[60]fullerene 2:1 complex can be deposited on an anion-coated gold surface as a monolayer (or at least as a monolayer-like ultra-thin film); as expected, this membrane efficiently shows a redox response in cyclic voltammetry and a photoelectrochemical response under visible light irradiation.

The ready availability of [60]fullerene and its homologues has increasingly invited exploration of their outstanding new physical and chemical properties. In particular, the preparation of fullerene thin films is of interest from both a fundamental and a practical point of view.[1,2] However, the challenge has lain in overcoming the high aggregation tendency of the carbon sphere.[3] One approach is to introduce either thin layer-forming substituents (such as long aliphatic groups)[4] or surface-adsorptive substituents (such as trimethoxysilyl or mercapto groups)[5,6] into fullerenes. In these approaches, however, efficient conjugation inherent to fullerenes must inevitably be cleaved by substitution. An alternative method by which fullerenes are embedded without modification has thus been developed. The most promising approach would be to utilize host molecules.[2] For example, Diederich *et al.*[7] reported that azacrown derivatives bearing long aliphatic groups are useful to prepare mono- and multilayers of [60]fullerene and [70]fullerene at the air–water interface. It was shown by other groups that calixarene derivatives are also useful to prepare monolayers at the air–water interface.[8,9] We have found on the basis of our re-examination, however, that the monolayer formation phenomena of these calixarene–fullerene systems are frequently initial concentration-dependent, not so reversible and therefore, cannot be applied to the formation of Langmuir–Blodgett films on solid substrates.[10] Very recently, we found that a water-soluble homooxacalix[3]arene (**1**) is capable of solubilizing [60]fullerene into water, forming a capsule-like 2:1 calixarene–fullerene complex.[11] This complex possesses six cationic charges. It thus occurred to us that this cationic complex would be adsorbed onto the anionic surface, forming a monolayer or a nanometer-sized thin film. This paper addresses the first example of the construction of such an ultra-thin [60]fullerene layer on a gold surface utilizing host–guest chemistry.

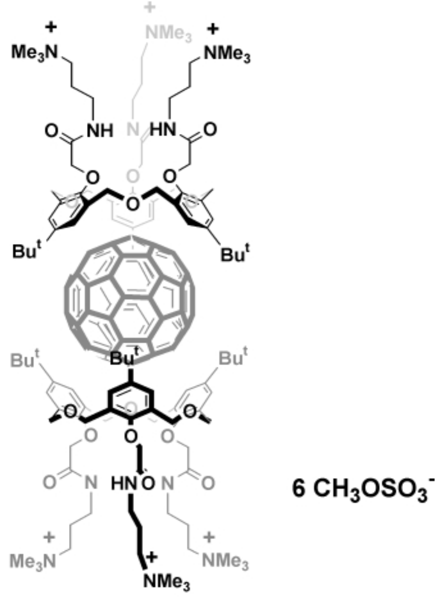
The preparation and solution properties of **1** were reported previously.[11] The adsorption of **1**–[60]fullerene complex from aqueous solution was monitored using a QCM (Quartz Crystal Microbalance: USI system) system.[12] In order to obtain an anionic QCM resonator surface, an AT-cut 9 MHz quartz crystal (USI system), each side of which was coated with a gold electrode, was exposed to ethanol solution containing sodium 2-mercaptoethanesulfonate (1.0 mmol dm^{-3}). After washing with ion-exchange water and drying with a nitrogen stream, the resonator was immersed in an aqueous solution containing **1** (0.50 mmol dm^{-3}) or **1**–[60]fullerene complex (0.25 mmol dm^{-3}). After further similar treatments, the frequency change was estimated.

Fig. 1 shows the layer growth behaviour for deposition of **1** or **1**–[60]fullerene complex. It is seen from Fig. 1 that for **1**, the frequency decreases linearly with the number of adsorption



1

C$_{60}$



1·C$_{60}$ complex

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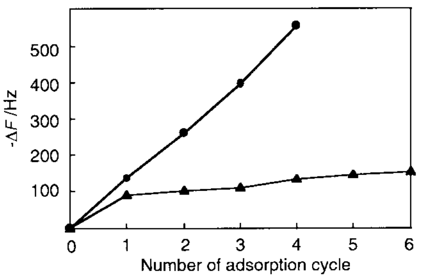

Fig. 1 *In air* frequency decrease in QCM induced by recycle deposition of **1** (●) or **1**–[60]fullerene (▲).

cycles, indicating that the layer grows up infinitely. For **1**–[60]fullerene complex, in contrast, the frequency change is saturated after the 2nd cycle, indicating that the surface once covered by **1**–[60]fullerene complex grows up no longer. The origin of these contrasting behaviours is not clear yet; presumably **1**, which is classified as a flexible calixarene,[11] results in a disordered layer, whereas **1**–[60]fullerene which becomes more rigid because of [60]fullerene inclusion results in a cationic surface which suppresses further adsorption. The QCM resonator surface covered by **1**–[60]fullerene complex was observed by atomic force microscopy and scanning electron microscopy. In both observations, the surface was smooth and very similar to that of the bare gold surface without any cluster-like domain of **1**–[60]fullerene complex.

The thickness of the smooth layer (d) can be estimated from a change in the QCM frequency (ΔF). For this purpose, Kunitake *et al.*[13] used an equation, $d\,(\text{nm}) = -0.016\,\Delta F\,(\text{Hz})$: in their polymeric or protein membrane systems the membrane density was 1.3 ± 0.1 g cm^{-3}. According to the X-ray crystallographic study of a homooxacalix[3]arene–[60]fullerene complex, the density was 1.4 g cm^{-3}.[14] These density data indicate that one may apply the above equation to the present **1**–[60]fullerene complex membrane. As the ΔF after the 2nd cycle was nearly constant (131 ± 27 Hz), the membrane thickness could be computed to be 2.1 nm. The molecular size of **1**–[60]fullerene complex was estimated to be 2.0 nm (long axis) and 1.2 nm (short axis) by a computational method (Discover 98). These results, together with the microscopic observation data, indicate that **1**–[60]fullerene complex is deposited on the QCM resonator surface as a smooth monolayer (or at least as a monolayer-like ultra-thin film) (Fig. 2).

As a preliminary step to exploitation of a light-energy conversion system, we estimated photoresponsive behaviours of a **1**–[60]fullerene complex-deposited gold electrode. Fig. 3 shows a cyclic voltammogram (CV) and a differential pulse voltammogram (DPV) of **1**–[60]fullerene complex in a homogeneous aqueous solution. With a sweep rate of 0.01 V s^{-1} CV exhibited a nearly reversible wave as a result of the first reduction of C_{60} (−0.24 V) and the oxidation of $C_{60}^{\bullet -}$ (−0.12 V).[15] The $C_{60}/C_{60}^{\bullet -}$ redox potential appearing at $E\,(C_{60}/C_{60}^{\bullet -}) = -0.18$ V corresponds to *ca.* 0.25 V positive shift as compared to the $E\,(C_{60}/C_{60}^{\bullet -})$ of C_{60} included in γ-cyclodextrin.[16] This shift is attributed to an increase in the electron-accepting ability of C_{60} arising from inclusion of a cationic homooxacalix[3]arene capsule.[17] On the other hand, the **1**–[60]fullerene complex-deposited electrode gave rise to −0.33 V for the first reduction of C_{60} and 0.24 V for the oxidation of $C_{60}^{\bullet -}$ in CV with a sweep rate of 0.02 V s^{-1} (Fig. 4). The $C_{60}/C_{60}^{\bullet -}$ redox potential on the modified electrode is thus estimated to be $E\,(C_{60}/C_{60}^{\bullet -}) = -0.09$ V. The peak splitting width values in the homogeneous system (0.12 V) and in the modified electrode system (0.47 V) are somewhat larger than the theoretical value. The results imply that the rate of the redox reaction between C_{60} and the gold electrode is so slow as to be comparable with the diffusion rate. The $E\,(C_{60}/C_{60}^{\bullet -})$ in the modified electrode system corresponds to *ca.* 0.2 V positive shift as compared to the $E\,(C_{60}/C_{60}^{\bullet -})$ in the homogeneous solution. The positive shift implies that the electron-accepting ability of [60]fullerene is further intensified in the monolayered assembly. These results clearly support the view that [60]fullerene deposited as the **1** complex in a monolayer-like thin film shows redox activities similar to those of **1**–[60]fullerene complex in homogeneous aqueous solution. From the peak current of the first reduction, the surface coverage by **1**–[60]fullerene complex can be estimated to be 1.7×10^{-10} mol cm^{-2}.[18] This value corresponds to one **1**–[60]fullerene complex per 1.0 nm^2, which agrees well with that obtained from a computational method (1.1 nm^2) or from a π–A isotherm of 7,15,23-tri-*tert*-butyl-25,26,27-tris[(ethoxycarbonyl)methoxy]-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene (1.1 nm^2).[10] The results again support the formation of a monolayer-like ultra-thin film.

Photocurrent measurements were carried out for **1**–[60]fullerene complex or **1** deposited on the modified Au electrode in 0.1 mol dm^{-3} Na_2SO_4 solution containing 50 mmol dm^{-3} ascorbic acid as an electron sacrificer using a modified Au electrode as the working electrode (1.8 cm^2), a Pt counter electrode,

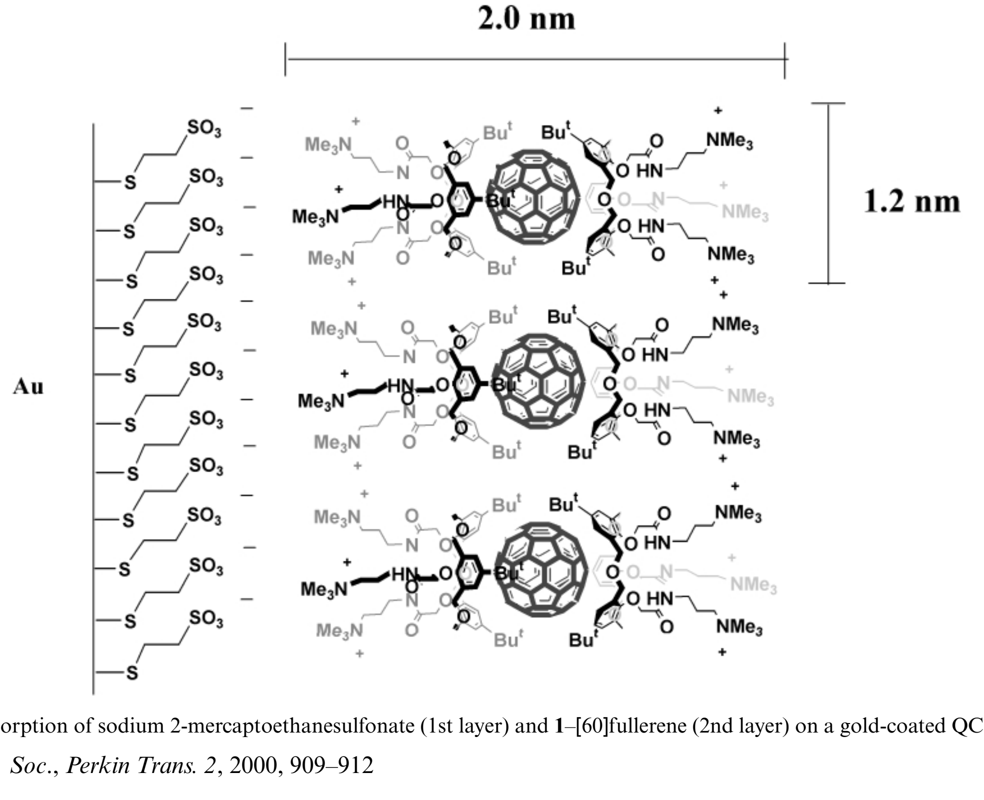

Fig. 2 Adsorption of sodium 2-mercaptoethanesulfonate (1st layer) and **1**–[60]fullerene (2nd layer) on a gold-coated QCM resonator.

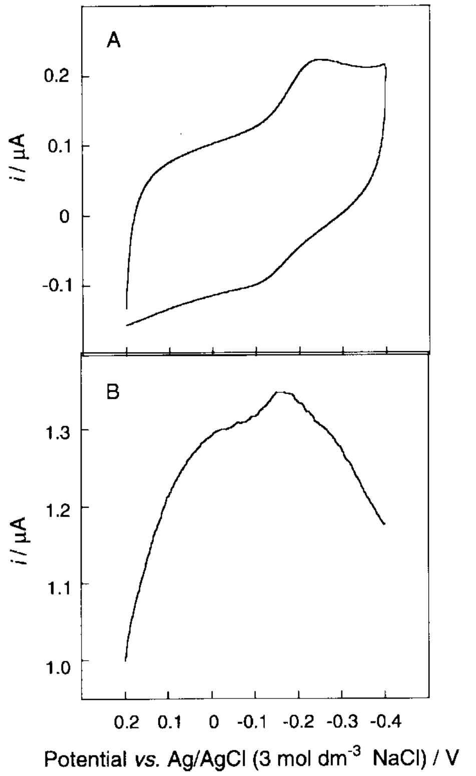

Fig. 3 CV (A) and DPV (B) of **1**–[60]fullerene complex in water: 25 °C, 0.10 mol dm^{-3} Et_4NCl, three-electrode cell with a Au working electrode, a glassy carbon counter electrode and a Ag/AgCl (3 mol dm^{-3} NaCl) reference electrode.

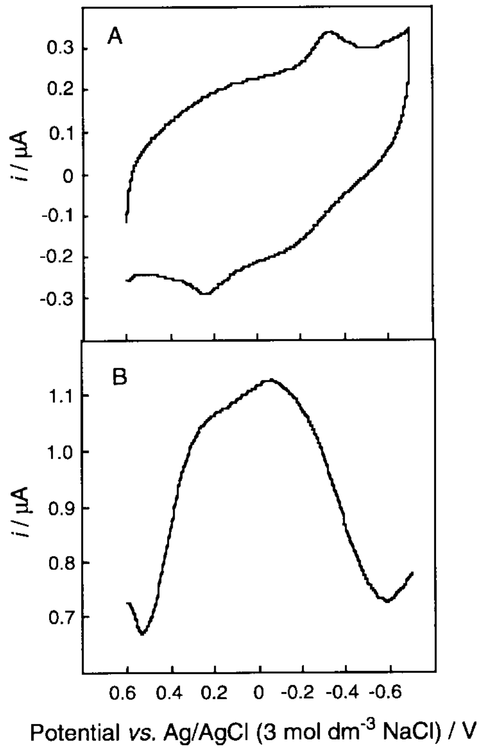

Fig. 4 CV (A) and DPV (B) of **1**–[60]fullerene complex deposited on a modified Au electrode in water: 25 °C, 0.10 mol dm^{-3} Et_4NCl, three-electrode cell with a complex-deposited Au working electrode (0.02 cm^2), a glassy carbon counter electrode and a Ag/AgCl (3.0 mol dm^{-3} NaCl) reference electrode.

and a Ag/AgCl (3 mol dm^{-3} NaCl) reference electrode.[19] When this **1**–[60]fullerene complex-deposited electrode was photo-irradiated ($300 < \lambda < 510$ nm by glass filters) from a 30 cm distance and 0.1 V bias voltage, the appearance of a large photocurrent wave (*ca.* 360 nA cm^{-2}) was observed (Fig. 5). This photoresponsive phenomenon could be repeated many times reversibly. In contrast, the working electrode which deposited only **1** did not show such a photoelectrochemical response at all. Hence, one may propose the mechanism of the present photovoltaic response which is shown in Fig. 6.

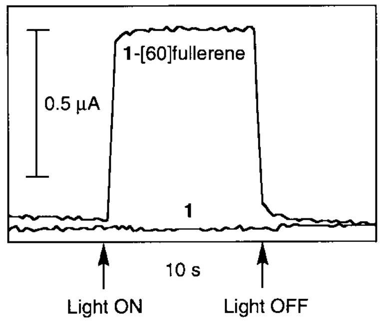

Fig. 5 Photoelectrochemical response of a **1**–[60]fullerene complex-deposited Au/Pt/Ag/AgCl (3.0 mol dm^{-3} NaCl) cell and a **1**–deposited Au/Pt/Ag/AgCl (3.0 mol dm^{-3} NaCl) cell: 25 °C.

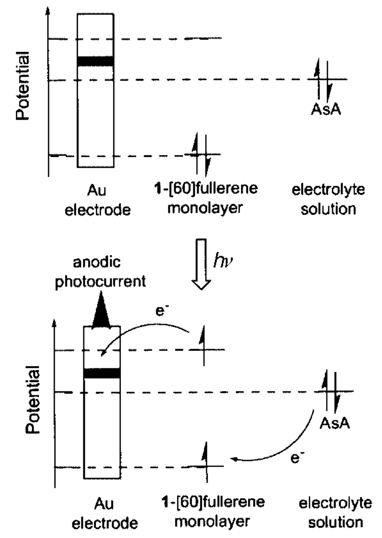

Fig. 6 Schematic representation of the mechanism of **1**–[60]fullerene photovoltaic response in the presence of an electron donor. AsA denotes ascorbic acid used as an electron sacrificer.

In conclusion, the present paper demonstrates that (i) a [60]-fullerene ultra-thin film can be easily prepared by adsorption of hexacationic **1**–[60]fullerene complex onto an anion-covered Au surface and (ii) this ultra-thin film shows a novel photoelectrochemical response to visible light irradiation. Further studies to couple this system with a porphyrin layer and to estimate the quantitative quantum yield are continuing in this laboratory.

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