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The first observation of four-electron reduction in [60]fullerene-metal cluster self-assembled monolayers (SAMs)†

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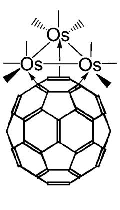
Self-assembled monolayers (SAMs) of a μ_3-η^2:η^2:η^2-C_{60} triosmium cluster complex $Os_3(CO)_8(CN(CH_2)_3Si(OEt)_3)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})$ (2) on ITO or Au surface exhibit ideal, well-defined electrochemical responses and remarkable electrochemical stability being reducible up to tetra-anionic species in their cyclic voltammograms.

Thin films of fullerene-based materials have demonstrated potential usefulness in superconductivity, non-linear optics, and photovoltaic cells.[1] The successful technological application of these thin films relies on rational chemical modification of fullerenes and the development of methodologies to arrange them on a variety of surfaces in molecularly highly ordered fashion. In order to obtain definable, two-dimensional fullerene structure, C_{60} self-assembled monolayers (SAMs) have been prepared by using various linkages such as an amine,[2] azide,[3] and pyrrolidine ring.[4] The usage of surface-tailoring linkages, however, inadvertently disrupts the π-delocalization of C_{60} by forming σ-bonds, and thus the prepared C_{60} SAMs show rather poorly defined electrochemical properties and instability in reduced states, which renders severe limits on technological applications.[2–4] We have reported a number of C_{60}-metal cluster complexes with a face-capping μ_3-η^2:η^2:η^2-C_{60} bonding mode,[5] which exhibit remarkable electrochemical stability and unusual electronic communication between C_{60} and metal cluster units.[6] Furthermore, the electrochemical property of these complexes can be fine-tuned by the nature of the ligands on the metal cluster.[5,6] Herein we report the preparation of robust SAMs of a μ_3-η^2:η^2:η^2-C_{60} triosmium cluster on indium–tin oxide (ITO) or gold (Au) electrode by using an organic linkage 3-(triethoxysilyl)propyl isocyanide, which can bind to both the metal cluster and the electrode surface, and their ideal and well-defined electrochemical responses.

Initial decarbonylation of $Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})$ (**1**)[5a] with Me_3NO–MeCN and subsequent reaction with 3-(triethoxysilyl)propyl isocyanide in chlorobenzene at 60 °C affords $Os_3(CO)_8(CN(CH_2)_3Si(OEt)_3)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})$ (**2**) in 35% yield. Compound **2** is formulated by the molecular ion isotope multiplets (*m*/*z* (highest peak) = 1747) in the FAB$^+$ mass spectrum and by spectroscopic and microanalytical data.‡ The IR spectrum of **2** shows a similar pattern to that of $Os_3(CO)_8(CNCH_2Ph)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})$,[5c] suggesting that the isocyanide ligand in **2** is terminally coordinated at an equatorial site of an Os center.

The cyclic voltammogram (CV) of **2** in deoxygenated dichloromethane exhibits three quasi-reversible redox waves at −1.01, −1.37, and −1.81 V ($E_{1/2}$ *vs.* Fc/Fc$^+$) as shown in Fig. 1a (dotted line). The first and second waves are attributed to successive one-electron reductions, while the third corresponds to overlapped two one-electron processes as similarly observed in $Os_3(CO)_8(PMe_3)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{60})$, due to electronic communication between the C_{60} and metal cluster centers.[6b]



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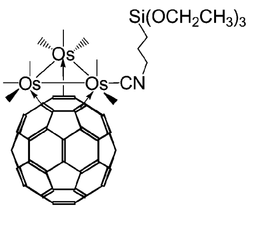

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The SAM of **2** (**2**/ITO) is prepared by immersing an ITO electrode in a 1 mM chlorobenzene solution of **2** at room temperature for 3 days, followed by repeated washing with chlorobenzene and dichloromethane (Scheme 1a). The contact angle θ_{H_2O} = 71° of **2**/ITO is substantially increased from θ_{H_2O} = 34° of bare ITO, consistent with adsorption of hydrophobic **2** on the ITO surface. The observed water contact angle corresponds closely to the values (65–80°) previously reported for C_{60}-terminated SAMs.[2] The X-ray photoelectron spectra of **2**/ITO with C(1s) and Os(4f) lines further confirm the formation of SAM of **2**.

The CV of **2**/ITO (Fig. 1a, solid line) in deoxygenated dichloromethane surprisingly reveals three, well-resolved redox waves at −1.08, −1.40, and −1.86 V ($E_{1/2}$) with relative area of 1 : 1 : 1.7,¶ which are very similar to the electrochemical behavior of **2** in solution. The monolayer surface coverage (*Γ*) of **2**/ITO, 1.8×10^{-10} mol cm^{-2},‖ is obtained by current integration of the first reduction peak in CV, which is slightly smaller than ~1.9×10^{-10} mol cm^{-2} for a close packed monolayer of C_{60}.[8] The **2**/ITO exhibits an almost ideal

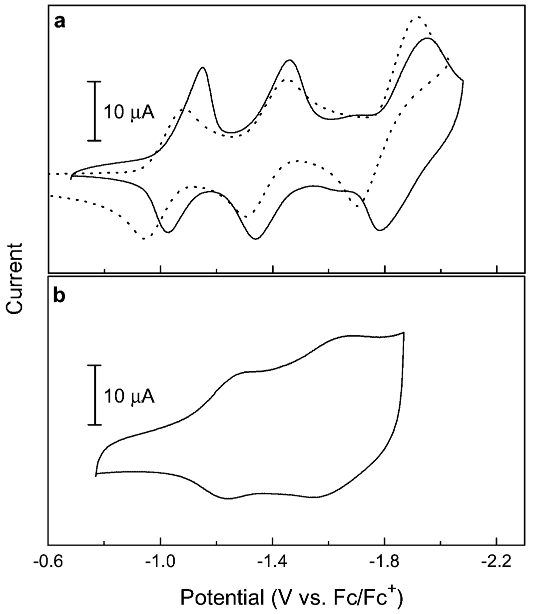

Fig. 1 Cyclic voltammograms of (a) **2** (···) and **2**/ITO (—)§; (b) **1**/ITO in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as an electrolyte; scan rate = 0.5 Vs^{-1}.

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† Electronic supplementary information (ESI) available: CV spectra, half-wave potentials and XPS data. See http://www.rsc.org/suppdata/cc/b2/b209024d/

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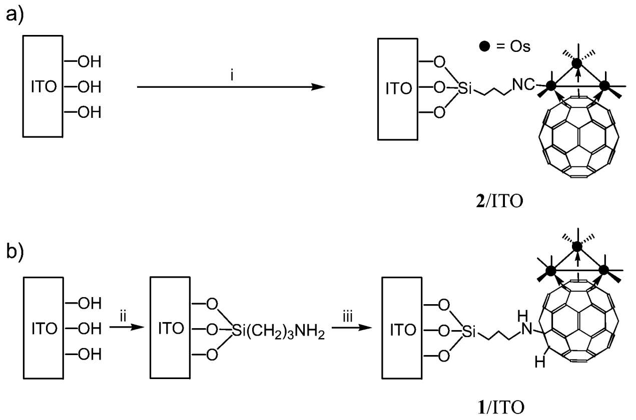

Scheme 1 *Reagents and conditions*: (a) i, **2**, chlorobenzene, RT, 3 days; (b) ii, $(EtO)_3Si(CH_2)_3NH_2$, chlorobenzene, RT, 2 days; iii, **1**, chlorobenzene, RT, 3 days.

electrochemical response due to structural homogeneity of surface C_{60}-metal cluster moieties; the half-width potential (ΔE_{fwhm}) of 103 mV for the first reduction peak at a scan rate of 0.2 V s^{-1} is comparable to the theoretical value of 90.6 mV for the reversible CV.[7] The redox potentials of **2**/ITO are slightly shifted to negative potentials (av. $\Delta E_{1/2} = 0.05$ V) as compared to those of **2** in solution. Much larger negative shifts (0.1–0.2 V)[2,4a,4b] have been observed in other fullerene-based SAMs, in which linkage molecules and C_{60} underwent σ-bond forming reactions. The four-electron reduction of C_{60} in fullerene-based SAMs is unprecedented, which attests the remarkable electrochemical robustness of **2**/ITO. This remarkable reflection of solution redox properties and ideal electrochemical responses in **2**/ITO may be ascribed to the fact that π-delocalization of C_{60} is little perturbed by π-type coordination of C_{60} on the metal cluster and the C_{60} moiety remains intact during SAM formation by confining the C_{60}-metal cluster complex to the electrode surface *via* a linkage to the metal center.

Reaction of **2** with $HO(CH_2)_6SH$-treated Au electrode ($\theta_{H_2O} = 20°$) produces SAM of **2** on Au surface (**2**/Au) with $\theta_{H_2O} = 72°$ and $\Gamma = 1.6 \times 10^{-10}$ mol cm^{-2},[¶] which shows essentially identical electrochemical behavior as for **2**/ITO. Imaging of **2**/Au by scanning tunneling microscopy (STM) shows a high coverage of C_{60}-triosmium cluster molecules, which appear as ellipsoidal shapes with a long axis of ~2 nm, on a flat $HO(CH_2)_6SH$-modified Au(111) surface without any discernible over-layer structure as shown in Fig. 2.

The ideal electrochemical response for **2**/ITO is completely lost for **1**/ITO, which is prepared by reaction of **1** and 3-(triethoxysilyl)propyl amine-modified ITO (Scheme 1b).[**] The CV of **1**/ITO shows two broad redox waves at −1.23 and −1.59 V with large cathodic shifts (0.25 V) as previously reported for other C_{60}-based SAMs (Fig. 1b).[2,4a,9] Indiscriminate reactions and multiple additions of the surface amine moieties to various reaction sites of the C_{60} surface of **1** may lead to inhomogeneity of surface C_{60}-metal cluster species, which causes poorly defined electrochemical responses for the resulting SAM. The large negative shift of the reduction waves is also consistent with amine additions to C_{60} and the resultant perturbation of π-electron delocalization of the C_{60} moiety.

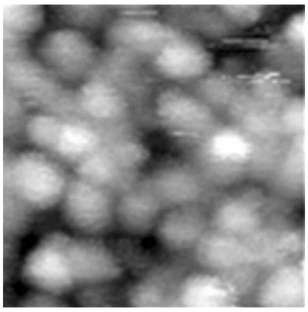

Fig. 2 High-resolution STM image (18 × 18 nm) of **2**/Au(111). The scan parameters for this image were −1.0 V sample bias and 50 pA tunneling current.

In conclusion, we have demonstrated that the solution electrochemical behavior of C_{60} can be directly transferred to a two-dimensional surface structure by immobilizing C_{60}-metal cluster complexes to the electrode surface *via* a linkage to the metal center. The ideal, well-defined electrochemical responses and high stability of the C_{60}-metal cluster SAMs, together with ready modification of the electronic properties of C_{60} by substitution of various ligands on metal centers, promise useful technological applications of fullerene-metal cluster-based SAMs. Efforts are currently underway with these SAMs to manufacture high-performance fullerene-based photovoltaic cells and molecular electronic devices.

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Notes and references

‡ *Selected data for* **2**: IR (CH_2Cl_2) ν(NC) 2194(m); ν(CO) 2068(vs), 2037(s), 2018(s), 1996(m), 1995(w) cm^{-1}; ^1H NMR ($CDCl_3$): δ 4.00 (m, 2H), 3.78 (q, *J* 7, 6H), 1.87 (m, 2H), 1.19 (t, *J* 7, 9H), 0.69 (m, 2H); FAB$^+$ MS, *m/z* 1751 (M$^+$). Anal. Calc. for $C_{78}H_{21}NO_{11}Os_3Si$: C 53.6, H 1.21, N 0.80. Found: C 53.9, H 1.26, N 0.88%.

§ The origin of the small wave between the second and third reduction waves is not clear at the moment.

¶ Integrations for the forward and backward waves are comparable; the integration for the broad third reduction wave was obtained by doubling the integrated charge to the cathodic peak potential (−1.95 V).

‖ The surface coverages are calculated using the real surface areas of the electrodes (ITO: 0.36 cm^2; Au: 0.33 cm^2), which are determined by the electrochemical method based on mass transfer and adsorption processes.[10]

** $\theta_{H_2O} = 66°$ and $\Gamma = 1.5 \times 10^{-10}$ mol cm^{-2} for **1**/ITO; $\theta_{H_2O} = 45°$ for 3-(triethoxysilyl)propyl amine-modified ITO.

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