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

Youn-Jaung Cho, Hyunjoon Song, Kwangyeol Lee, Kyuwon Kim, Jhyoun Kwak, Sehun Kim and Joon T. Park*

Department of Chemistry and School of Molecular Science (BK21), Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea. E-mail: jtpark@mail.kaist.ac.kr; Fax: +82 42 869 2810; Tel: +82 42 869 2826

Received (in Cambridge, UK) 17th September 2002, Accepted 23rd October 2002

First published as an Advance Article on the web 6th November 2002

Self-assembled monolayers (SAMs) of a μ₃-η²:η¹:η²-C₆₀ trisodium cluster complex Os₃(CO)₈(CN(CH₂)₃Si(OEt)₃)(η₁-η²:η¹:η²-C₆₀)(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. 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 SAMs, 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 C₆₀ by forming π-bonds, and thus the prepared C₆₀ 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 C₆₀-metal cluster complexes with a face-capping μ₃-η²:η¹:η²-C₆₀ bonding mode,5 which exhibit remarkable electrochemical stability and unusual electronic communication between C₆₀ 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 μ₃-η²:η¹:η²-C₆₀ trisodium 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 Os₃(CO)₉(μ₃-η²:η¹:η²-C₆₀)(1)5a with Me₂NO–MeCN and subsequent reaction with 3-(triethoxysilyl)propyl isocyanide in chlorobenzene at 60 °C affords Os₃(CO)₈(CN(CH₂)₃Si(OEt)₃)(μ₃-η²:η¹:η²-C₆₀)(2) in 35% yield. Compound 2 is formulated by the molecular ion isotope multiplets (m/z; highest peak = 1747) in the FAB positive mass spectrum and by spectroscopic and microanalytical data.6 The IR spectrum of 2 shows a similar pattern to that of Os₃(CO)₈(CNCH₃Ph)(μ₃-η²:η¹:η²-C₆₀),26 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 surprisingly reveals three, well-resolved redox waves at −1.08, −1.40, and −1.86 V (E₁/₂) with relative area of 1:1:1:7:1, 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 C₆₀.6 The 2/ITO exhibits an almost ideal

Fig. 1 Cyclic voltammograms of (a) 2 (−−−−) and 2/ITO (−−−−); (b) 1/ITO in CH₂Cl₂ with 0.1 M Bu₄NPF₆ as an electrolyte; scan rate = 0.5 V s⁻¹.
lead to inhomogeneity of surface C₆₀-metall 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 C₆₀ and the resultant perturbation of π-electron delocalization of the C₆₀ moiety.

In conclusion, we have demonstrated that the solution electrochemical behavior of C₆₀ can be directly transferred to a two-dimensional surface structure by immobilizing C₆₀-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 C₆₀-metal cluster SAMs, together with ready modification of the electronic properties of C₆₀ 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.

This work was supported by the National Research Laboratory (NRL) Program of the Korean Ministry of Science & Technology (MOST) and the Korea Science & Engineering Foundation (Project No. 1999-1-122-001-5).

Notes and references

1. Selected data for 2: IR (CH₂Cl₂) ν(NC) 2194(m); ν(CO) 2068(vs), 2037(s), 1983(s), 1956(m), 1920(w) cm⁻¹; 1H NMR (CDCl₃): δ 4.04 (m, 2H), 3.73 (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 C₆₀H₂₂NO₂(Si): C 93.6, H 1.21, N 0.80. Found: C 93.9, H 1.26, N 0.89.

‡ 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 current to the cathodic peak potential (−1.95 V).

|| The surface coverages are calculated using the real surface areas of the electrodes (ITO: 0.36 cm², Au: 0.33 cm²), which are determined by the electrochemical method based on mass transfer and adsorption processes.º

º ½(θ₁,θ₂) = 66° and Γ = 1.5 × 10⁻¹⁰ mol cm⁻² for ITO; ½(θ₁,θ₂) = 45° for 3-(triethoxysilyl)propyl amine-modified ITO.


