Synthesis of tripodal anchor units bearing selenium functional groups and their adsorption behaviour on gold[†]

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Received 7th February 2009, Accepted 6th April 2009 First published as an Advance Article on the web 22nd April 2009 DOI: 10.1039/b906286f

The synthesis of new selenium-functionalized tripodal anchor units composed by a tetraphenylmethane core with three selenocyanate or selenol arms has been successfully accomplished and CV, XPS and UPS measurements of their monolayers on a gold surface were investigated.

Elucidating the nature of electronic communication between metal electrodes and organic molecules via the interface is of great importance for the development of single-molecular devices.^{1,2} Especially, to investigate the electrical conduction behaviour of long π -conjugated systems as "molecular wire",³ critical requirements for a functional group attaching molecules to electrodes include not only the appropriate electronic coupling between them but also the robustness of surface attachment and the control of molecular orientation.² Recently, selenium functional groups have been attracting much attention as a candidate^{4–7} alternative to thiol groups most commonly used to be adsorbed on a gold surface. On the other hand, the application of three-armed anchors to controlled monolayer formation has been widely used,⁸⁻¹² and the practical advantage of the tripodal structure with three mercaptomethyl arms have been exemplified.^{10–12} In this context, the combination of selenium functional groups with the tripodal structure might be an ideal anchoring unit for molecule-metal junctions. However, the realization of this concept has not been accomplished yet owing to the difficulty of synthesis. In this communication, we report on the synthesis of selenium-functionalized tripodal anchor units (1-4, Chart 1) composed by a tetraphenylmethane core with three selenocyanate or selenol arms and their monolayer formation on a gold surface, which have allowed us to investigate the electrochemical properties of the molecular junction and the Se-Au bonding nature.

In contrast to the synthesis of tripodal thiol systems, $^{10-12}$ all attempts to connect the selenocyanate-containing tripodal unit **3**, which was prepared similarly to the corresponding acetylthio derivative, 11a with a phenylquaterthiophene (Ph4T)

unit by transition-metal-catalyzed cross-coupling reactions resulted in failure because of the catalytic poison of the selenium atom. Thus, as shown in Scheme 1, the protected-triol derivative 10 was used as a key intermediate for synthesizing 1. The selenocyanato groups of 1 were converted to acetylseleno groups by reduction with LiBEt₃H followed by treatment with Ac₂O to give 11.¹³ After deprotection of its acetyl groups by using H₂SO₄, obtained 2 was immediately used for monolayer preparation. Compounds **4–6** (Chart 1) were synthesized by similar transformations. The synthetic details and the compound-identification data are described in the ESI.[†]

Monolayers of **1** and **2** on a gold surface were prepared by immersing Au(111)/mica substrates in their CH₂Cl₂ solution $(5.0 \times 10^{-4} \text{ M})$ for 12 h. As shown in Fig. 1, cyclic voltammetry (CV) with the monolayer-modified Au working electrodes in CH₂Cl₂ displayed two successive one-electron redox waves that correspond to the oxidation process of the phenyl-capped quaterthiophene moiety. The integrated anodic charge of the first oxidation peak gave surface coverage of the adsorbed molecules as 1.1×10^{-10} and 1.4×10^{-10} mol cm⁻² for **1** and **2**, respectively, which are almost the same as that of tripodal thiol **7** monolayer (1.4×10^{-10} mol cm⁻²) prepared under the same conditions.

Interestingly, the initially rapidly increased surface coverage for selenocyanate **1** was gradually decreased with increasing immersion time (Fig. 2). In contrast, the surface coverage of selenol **2** reached stable saturation within several minutes. As it has been reported that benzeneselenocyanate can be adsorbed on Au nanoparticle as selenolate with Se–CN bond cleavage,¹⁴ it is assumed that energetically more favourable adsorption of the CN species¹¹ replaces the selenolate species of **1** on Au and causes the gradual decrease of the surface coverage then to reach a steady state. These results apparently indicate the advantage of selenol groups to homogeneous monolayer formation.¹⁵ An electrochemical



Chart 1 Chemical structures of 1–8.

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[†] Electronic supplementary information (ESI) available: Detailed experimental procedures and characterization data of all new compounds, CV charts of selected compounds, and XPS spectra of **3**. See DOI: 10.1039/b906286f



Scheme 1 Reagents and conditions: (a) $Pd(PPh_3)_4$, $Ph4TSnBu_3$, toluene, reflux; (b) (1) nBu_4NF , THF, rt, (2) PPh_3 , CBr_4 , CH_2Cl_2 , rt, (3) KSeCN, THF, rt; (c) LiBEt₃H, Ac₂O, THF, -78 °C.



Fig. 1 Cyclic voltammograms of the monolayers 1 (a) and 2 (b) on Au.



Fig. 2 The changes of the surface coverage of 1, 2, and 5 on Au depending on immersion time.

reductive-desorption experiment of **2** on Au in aqueous KOH showed a clear desorption peak at -1.00 V vs. Ag/AgCl (Fig. S1),† and its integrated cathodic charge was 3.0 times larger than that of the first oxidation peak, suggesting that all the three selenol groups of **2** are bound to Au.

To investigate the bonding characteristics of selenocyanate and selenol groups, we have conducted X-ray photoelectron spectroscopy (XPS) measurements of the monolayers formed from **3** and **4** on Au(111). As shown in Fig. 3a, two photoemission peaks at 160.8 and 166.2 eV were observed for the selenol **4** monolayer, and they can be assigned to Se $3p_{3/2}$ and Se $3p_{1/2}$ peaks, respectively. These values are relatively lower than those found for physisorbed selenium species (162.0 and 167.7 eV) and are consistent with those reported for chemically bound selenium species (160.6 and 166.0 eV).¹⁶ The absence of the peaks associated with the physisorbed species means that



Fig. 3 Normalized Se 3p XPS spectrum of 4 on Au (a) and He I UPS spectra of 4 and 8 on Au along with bare Au (b).

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the three-point chemisorption of **4** occurs on Au. It is noticeable that the XPS spectral features of Se peaks for the selenocyanate **3** monolayer were essentially the same (160.7 and 166.4 eV) as those of **4**, while the former spectrum was accompanied by an N 1s peak at 398.3 eV (Fig. S2).† These results support the assumption that selenocynato groups are dissociatively adsorbed on Au(111) *via* Se–CN bond cleavage to form Se–Au covalent bonds, which is in good agreement with the results obtained from the CV experiments.

To evaluate the electronic states of the anchoring groups on Au(111), ultraviolet photoemission spectroscopy (UPS) measurements for the selenol **4** and thiol 8^{11a} monolayers have been also conducted. The energy scale was referenced to the Fermi level of Au ($E_{\rm F}$). As shown in Fig. 3b, the UPS spectrum of the monolayer **4** has a band at 1.0 eV. This binding energy is smaller by 0.3 eV than that of the monolayer **8**, which indicates that the Se–Au bond has an electronic state more suitable to reducing the barrier for molecular conductance. This result is consistent with the trends reported by Taniguchi *et al.*⁶ⁱ

Finally, monolayers prepared from single-armed 5 and 6 on Au have been compared with those of 1 and 2 by means of CV measurements. The surface coverage of selenocyanate 5 showed progressive desorption with increasing immersion time (Fig. 2) like the monolayer 1, while that of selenol 6 on 12-h immersion was 2.7×10^{-10} mol cm⁻². More importantly as shown in Fig. 4a and d, the electrochemical responses of the tripodal 2 monolayer are stable and remain essentially unchanged after 50 scans within the range of 0-0.55 V, in contrast to rapid fade-out for the single-armed 6 monolayer (Fig. 4b and d). Furthermore, it was also shown that the selenol 2 monolayer is electrochemically more stable when compared with the thiol 7 monolayer (Fig. 4c and d). These results clearly demonstrate the advantage of the selenolfunctionalized three-armed structure as an anchoring group for gold electrodes.



Fig. 4 Cyclic voltammograms of 2/Au (a), 6/Au (b), and 7/Au (c) on consecutive potential scans (1st, 10th, 20th, 30th, 40th, and 50th scans) at 100 mV s⁻¹. (d) The changes of the surface coverage depending on scan number.

In summary, we have successfully synthesized new tripodal anchor units bearing selenium functional groups. CV, XPS, and UPS measurements of their monolayers on gold revealed the effectiveness of the three-armed structure as well as selenol functional groups. Further studies of elucidating the chemisorbed state on a gold surface and measuring the contact resistance of the tripodal selenol anchor for the realization of single-molecular devices are currently in progress and will be reported in due course.

The authors acknowledge Prof. S. Kuwabata and Mr. T. Uematsu at the Graduate School of Engineering, Osaka University, for the helpful discussion of electrochemical measurements. Thanks are given to the MAC, ISIR, for assistance in obtaining elemental analyses. This work was supported by Grants-in-Aids for Scientific Research (no. 17069006, 19022019, and 20027011) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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