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Synthesis of Tripodal-anchor Units Having Pyridine or Amine Functional Groups and Their Adsorption Behavior on Metal Electrodes

Tomoya Hirose,[1] Yutaka Ie,[1,2] and Yoshio Aso*[1]
[1]*The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047*
[2]*PRESTO-JST, 4-1-8 Honcho, Kawaguchi, Saitama 333-0012*

(Received November 24, 2010; CL-100989; E-mail: aso@sanken.osaka-u.ac.jp)

Synthesis of new tripodal-anchor units composed of a tetraphenylmethane core with pyridine or amine as anchoring functional groups has been successfully accomplished. Cyclic voltammetry measurements of their monolayers on metal electrodes revealed the estimated surface coverage and robust adsorption of three-armed structures on the surface.

Since nanoscale electronic devices based on a single molecule have been proposed as an ultimate miniaturization of electronics, much attention has been focused on the formation of reliable contacts between organic molecules and metal electrodes.[1] It is generally recognized that the contacts between the anchor units of organic molecules and metal electrodes should fulfill the following requirements: (1) appropriate electronic communication for facilitating carrier transportation, (2) kinetically robust binding between them, and (3) inducement to well-ordered molecular orientation.[2] In this context, we have reported the synthesis of tripodal-anchor units composed of a tetraphenylmethane core with three thiol[3] or selenium[4] functional groups and exemplified the practical advantages of the tripodal structure. Quite recently, we have developed a new tripodal anchor having 4-substituted pyridine groups, and the conductance measurement of a single molecule with this anchor and theoretical analysis have suggested the possibility of a new anchoring strategy, for which the direct hybridization of the pyridine π orbital with gold is utilized.[5] This type of contact is expected to form highly conductive molecular junctions.[6,7] Thus, structural investigation fulfilling this strategy is important to accelerate research in single-molecular electronics. With this motivation in mind, we have pursued introduction of 3-substituted pyiridine and *meta*- or *para*-positioned aniline groups into the tetraphenylmethane anchoring core. Note that the amine group has been extensively utilized as an alternative to the most commonly used thiol group,[8–10] and especially, the high conductance of the molecular junction with 1,4-phenylenediamine relative to that of 1,4-benzenedithiol.[10] However, the extension of an amine-based tripodal structure as an anchor unit has never been reported. In this paper, we report the synthesis of our newly designed tripodal anchors and their monolayer formation on gold, silver, copper, and indium tin oxide (ITO) electrodes, because the systematic investigation of adsorption behavior on metal electrodes other than gold has been limited.[11]

To evaluate the adsorption behavior of the tripodal-anchor units on gold electrodes, we have previously utilized phenyl-capped quaterthiophene (**Ph4T**) as a redox-active component linked with the anchor units for cyclic voltammetry (CV) measurements.[5] However, the high oxidation potential of **Ph4T** [0.4 V vs. ferrocene/ferrocenium (Fc/Fc$^+$)] and the low-potential window of silver (0.3 V vs. Fc/Fc$^+$) and copper (0.2 V vs. Fc/Fc$^+$) electrodes disturbed the CV measurements in this study. Thus, we have introduced a ferrocene unit instead of **Ph4T** and incorporated it into tripodal anchors **1**–**4** (Figure 1).

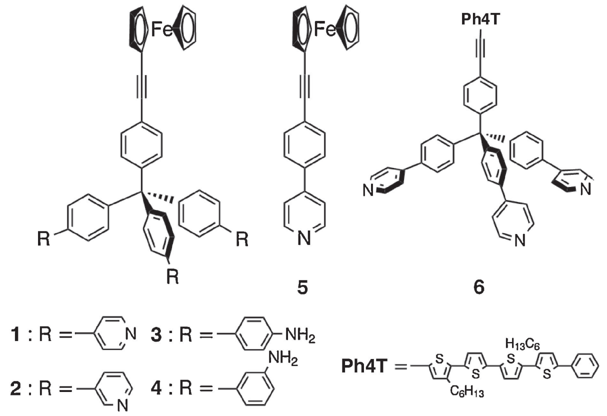
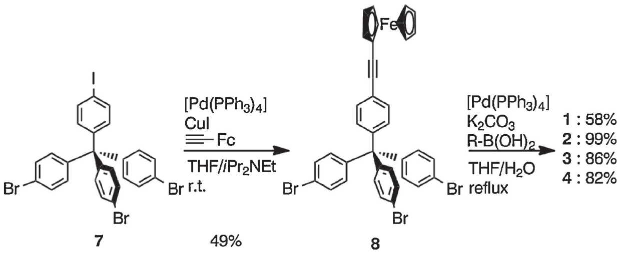


Figure 1. Chemical structures of **1**–**6**.



Scheme 1. Synthesis of **1**–**4**.

The synthesis of these compounds is shown in Scheme 1. The palladium-catalyzed Sonogashira coupling of tris(*p*-bromophenyl)-*p*-iodophenylmethane (**7**) with ethynylferrocene under ambient conditions gave **8** in 49% yield with the bromo substituent intact. Compound **8** was then reacted with the corresponding boronic acids by use of Suzuki coupling reactions to give desired target compounds **1**–**4**. Reference compound **5** was also synthesized in a similar manner. These compounds are soluble in common organic solvents and characterized by NMR spectroscopy, mass spectrometry, and elemental analysis.[12]

Monolayers of compounds **1** and **5** were prepared by immersing Au/mica substrates in their CH_2Cl_2 solutions (5.0×10^{-4} M) for 12 h. As shown in Figure 2a, CV with a modified-gold-working electrode of **1** in CH_2Cl_2 showed a reversible redox couple corresponding to the oxidation of the ferrocene moiety. From the integration of the anodic charge, the surface coverage (Γ) of the adsorbed molecule **1** was estimated to be 6.3×10^{-11} mol cm^{-2}. This value is comparable to that of **6** (7.1×10^{-11} mol cm^{-2}),[5] indicating that these compounds can be adsorbed on gold electrodes in the same manner, irrespective of the attached groups. It is important to note that these values are larger than the maximum surface coverage estimated from a lying orientation

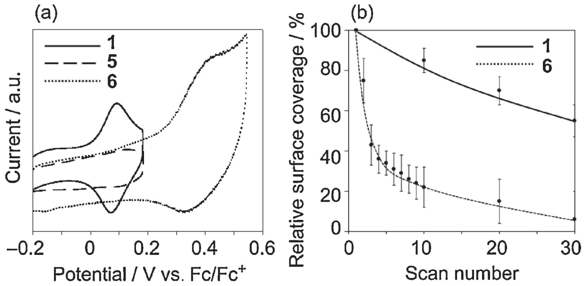


Figure 2. (a) CVs of the monolayers **1**, **5**, and **6**. (b) The changes of the surface coverages depending on scan number.

Table 1. Estimated surface coverages (Γ/mol cm^{-2}) of **1**–**4**

Comp	Electrode			
	Au[a]	Ag[a]	ITO[a]	Cu
1	6.3×10^{-11} (56)	6.5×10^{-11} (86)	2.7×10^{-11} (89)	n.d.[b]
2	7.2×10^{-11} (77)	8.1×10^{-11} (80)	3.3×10^{-11} (58)	n.d.[b]
3	1.5×10^{-10} (42)	1.7×10^{-10} (82)	3.8×10^{-11} (66)	n.d.[b]
4	1.9×10^{-10} (58)	1.2×10^{-10} (92)	6.4×10^{-11} (88)	n.d.[b]

[a] Numbers in parenthesis indicate the percentage of remaining monolayers after 30 continuous scans. [b] Not detected.

(3.7×10^{-11} mol cm^{-2}), confirming the standing orientation on the substrate. On the other hand, a gold electrode treated with one-leg compound **5** did not show an oxidation wave (Figure 2a). This provides evidence that the multiplier effect of the pyridyl tripodal structure in **6** is reproduced by the present ferrocene-linked system **1**. The electrochemical responses of the monolayer of **1** remained at 56% relative to the initial charge after 30 scans within the range of $-0.2 - +0.2$ V (Figure 2b). This value is much larger than that of **6** (28%)[5] after 10 scans under biased voltage of up to +0.55 V. These results indicate that the stability of adsorption is largely dependent on the biased conditions.

To understand the influence of position and variation of the anchor groups on adsorption behavior, monolayer, of **2**, **3**, and **4** on gold were investigated. The preparation of monolayers and their CV measurements were conducted by the same methods written above. Their CVs are shown in Figure S1,[12] and the estimated surface coverages are summarized in Table 1. The surface coverages of amine-based compounds **3** and **4** were more than twice as much as those of pyridine-based compounds **1** and **2** and are comparable to a maximum surface coverage estimated from the molecular sizes. It has been calculated by Venkataraman and coauthors that the bonding between amine and gold results from the delocalization of the lone pair of amine nitrogen to surface gold with sufficient angular flexibility.[8b] In addition to this, taking account of the higher basicity of aniline than that of pyridine, the observed increase of the surface coverages might be attributed to the contribution of the lone pair of the amino group rather than the π orbital hybridization. On the other hand, the position of the anchor groups little influences the surface coverage irrespective of the anchor functional groups. This is in contrast with Tour's proposal for a thiol anchoring group that *meta*-positioned molecules adopt proper orientation for assembly compared to *para*-positioned molecules.[11] This unexpected result might indicate the possibility of high single-molecular conductance for π-conjugated systems having *para*-positioned-amine anchors because it has been proposed that the aromatic stabilization of dicationic species in diaminoacenes is important to electron transport.[8c]

Finally, we compared the adsorption properties of compounds **1**–**4** to gold, silver, copper, and ITO electrodes, and the CVs of their modified electrodes are shown in Figures S2–S4.[12] As summarized in Table 1, these compounds can form monolayers not only on gold but also on silver and ITO. Interestingly, the surface coverages on silver and ITO showed a similar trend to that on gold. Furthermore, these monolayers remained at 42–95% after 30 scans of continuous biases between −0.2 and +0.2 V.[13] This suggests the effectiveness of a combination between tripodal-anchor units and metal electrodes with robust junction.

In summary, we have synthesized tripodal-structured compounds bearing pyridine and amine as anchoring functional groups and investigated the surface coverages of these compounds on the basis of the CV measurements of their monolayers. From this work, we have succeeded in broadening the repertories of tripodal compounds as well as the combination with metal electrodes. It should be mentioned that the most important point in this study is exemplifying the possibility of adsorption (not quantitative evaluation) and the robustness of adsorbed molecules on metal electrodes, which will open the way for the realization of *single*-molecular electronics. Theoretical calculations for analysis of transport mechanism as well as single-molecular conductivity measurements of π-conjugated systems having tripodal anchors will be reported in due course.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

13 Without bias scans, any decrease of the surface coverages was not observed under the same conditions.