

Fabrication of a Self-assembled Rotaxane Monolayer Consisting of a Viologen-functionalized Alkanethiol and α -Cyclodextrin Using Potential Sweep Method

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A self-assembled monolayer of a rotaxane (rotaxane-SAM) consisting of *N*-(3,5-dimethoxybenzyl)-*N'*-6-mercaptohexylbipyridinium dibromide and α -cyclodextrin (α -CD) was successfully prepared using a potential sweep method by which unfavorable adsorption of α -CD and viologen dimer can be controlled.

A rotaxane is an interlocked molecule, in which a ring molecule connects to a dumbbell-shaped axis molecule without any covalent bond in-between, i.e., mechanically.¹ Unique properties arisen from its topological structure attract a great deal of interest in the field of nanoscience and nanotechnology. For instant, molecular shuttles based on the rotaxanes where a mobile ring moves back and forth along a linear axis like a shuttle between two recognition sites (stations) in response to external stimuli constitute a class of artificial molecular machines.² Immobilization of a rotaxane onto a substrate is also of considerable interest from the viewpoint of nanoarchitectures fabricated by bottom-up methodology.³

There are three methods to fabricate a rotaxane monolayer: A) stepwise procedure⁴ that contains inclusion of a ring molecule to prepare an axis monolayer, followed by treatment with a bulky stopper for end-capping; B) use of a made-up rotaxane;³ and C) use of a pseudorotaxane,^{5,6} viz., a rotaxane without a bulky stopper at a terminal of an axis molecule. However, both methods A and B may be often unsuitable for immobilization of a rotaxane; in method A, an axis molecule is sterically prevented from its formation of rotaxane structure by adjacent neighbors and in method B, the synthesis of rotaxanes involves many tough steps. In contrast, the use of a pseudorotaxane should be a largely quick and easy method compared to the others. Immobilizations of pseudorotaxanes of cyclodextrins (CDs) with a mercaptoalkylviologen on a Au electrode and a mercaptoalkylferrocene on Au nanospheres have so far been reported by Chen et al.⁵ and Kaifer et al.,⁶ respectively. However, this method often suffers with physical adsorption of excess CD molecules onto electrode surface that interferes with fabrication of a self-assembled monolayer of a rotaxane (rotaxane-SAM). Therefore, we propose here a novel method to prepare the rotaxane-SAM consisting of a mercaptoalkylviologen and α -cyclodextrin (α -CD) using a potential sweep method (PS), by which unfavorable adsorption of α -CD can be controlled. (Figure 1A).⁷

N-(3,5-dimethoxybenzyl)-*N'*-(6-mercaptohexyl)bipyridinium dibromide (**1**) as an axis molecule was synthesized according to the similar manner in the literature.⁸ The compound **1** was obtained as a yellowish orange solid. An electrochemical analyz-

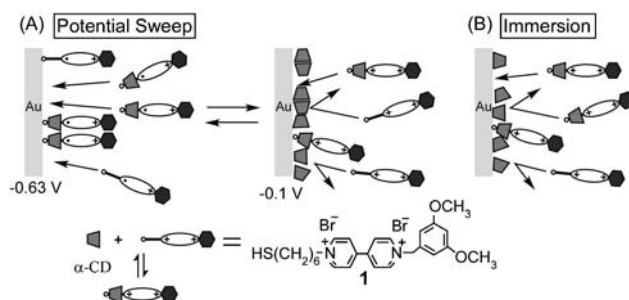


Figure 1. Schematic description of rotaxane-SAM formation processes in the presence of both **1** and α -CD using potential sweep (A) and immersion (B) methods. Potential values are in reference to Ag/AgCl sat'd KCl.

er (BAS-100BW, Bioanalytical Systems) was used for the preparation of an electrode modified from an aqueous solution of **1** containing α -CD (**1**-(α -CD) electrode) and measurements of cyclic voltammogram (CV). The preparation of a **1**-(α -CD) electrode by PS is as follows. A Au disk electrode (0.02 cm²) treated by the oxidation-reduction cycles (ORC) was placed in an electrochemical cell filled with 0.1 mM (**1** M = 1 mol·dm⁻³) aqueous solution of **1** with 0.3 M KBr in the presence of 2 mM α -CD (**1**-(α -CD) solution). A coiled Au wire and an Ag/AgCl sat'd KCl electrodes were used as the counter and reference electrodes, respectively. The Au disk electrode was then subjected to repeated potential cycling at a sweep rate of 50 mV·s⁻¹ between -0.10 to -0.63 V until anodic and cathodic peak currents in the CV reached constant values. The electrode was rinsed well with water before CV measurements in 0.3 M aqueous KBr solution. For comparison, a **1**-(α -CD) electrode was prepared by an immersion method (Im), which is one of the conventional preparation methods for SAMs of alkanethiols: a Au electrode treated by the ORC was immersed in the **1**-(α -CD) solution for 18 h at open circuit condition and then washed with water before CV measurements.

Stoichiometry of a **1**-(α -CD) complex (pseudorotaxane) is most likely 1:1, since one α -CD covers six methylene units⁹ but cannot include the benzyl terminal unit because of the steric hindrance of the two methoxy groups.

Figure 2 shows typical CVs of **1** and **1**-(α -CD) electrodes prepared by Im. In the CV of **1**-SAM electrode the redox couple for the viologen moiety was observed at a midpoint potential between anodic and cathodic peaks, $E^{\circ'} = -399$ mV (Figure 2a). The heights of the anodic and cathodic peaks were proportional to the sweep rate in the range from 25 to 225 mV·s⁻¹. This

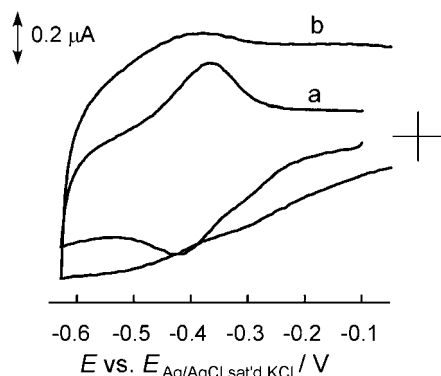


Figure 2. Typical CVs of (a) **1**-SAM and (b) **1**-(α -CD) electrodes in 0.3 M aqueous KBr solution prepared by the immersion method (Im). Sweep rate, $50 \text{ mV} \cdot \text{s}^{-1}$.

reveals that the redox response is due to the surface-confined viologen. The coverage¹⁰ of adsorbed **1** obtained from the peak charge using the real surface area is $1.8 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$ (corresponding to $0.95 \text{ nm}^2 \cdot \text{molecule}^{-1}$) which is almost the same as the reported values for SAMs of viologens.¹⁰ On the other hand, the CV of the **1**-(α -CD) electrode only showed a weak anodic peak at -404 mV (Figure 2b). The coverage¹⁰ of adsorbed rotaxane obtained from the peak charge using the real surface area is $0.67 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$ ($2.5 \text{ nm}^2 \cdot \text{molecule}^{-1}$). This value is obviously lower than predicted amount for the rotaxane-SAM ($1.5 \text{ nm}^2 \cdot \text{molecule}^{-1}$). Most likely, preferentially adsorbed α -CD molecules on the electrode surface are hardly displaced by the pseudorotaxane, preventing the SAM from its formation (Figure 1B).

Figure 3 demonstrates the CVs for the SAMs prepared by PS. The CV for **1**-SAM electrode showed the redox at $E^{\circ'} = -381 \text{ mV}$ and the response of the surface-confined viologen similar to that prepared by Im (Figure 3a). The coverage¹⁰ of adsorbed **1** was $2.2 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$ ($0.75 \text{ nm}^2 \cdot \text{molecule}^{-1}$), indicating that **1** is densely packed on the electrode surface compared to that prepared by Im. It is likely that repeated short time application of negative potentials during the potential cycling facilitates the adsorption of positively charged viologen molecules to the negatively charged electrode surface but, at the same time, inhibits unfavorable adsorption of dimer of reduced **1** (radical cation form), resulting in increase of coverage. Interestingly, the CV for the **1**-(α -CD) electrode showed distinct redox couples for the viologen moiety at $E^{\circ'} = -391 \text{ mV}$ in contrast to that prepared by Im (Figure 3b). The heights of the anodic and cathodic peaks were proportional to the sweep rate in the range from 25 to $225 \text{ mV} \cdot \text{s}^{-1}$, indicative of the response of the surface-confined viologen. The coverage¹⁰ of adsorbed rotaxane was $1.6 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$ ($1.0 \text{ nm}^2 \cdot \text{molecule}^{-1}$). Decrease in the coverage compared to that of **1**-SAM prepared by PS while being still greater value than the prediction for a full coverage of the rotaxane is presumably due to the formation of the rotaxane-SAM with coexistence of uncomplexed **1**. Furthermore, $E^{\circ'}$ and the separation between anodic and cathodic peak potentials (ΔE_p) for the **1**-(α -CD) electrode prepared by PS showed no dependence on the sweep rate, while, for both **1**-SAM electrodes prepared by PS and Im, the $E^{\circ'}$ changed and ΔE_p gradually increased with increasing in the sweep rate. This behavior is in good agreement with that of the rotaxane-

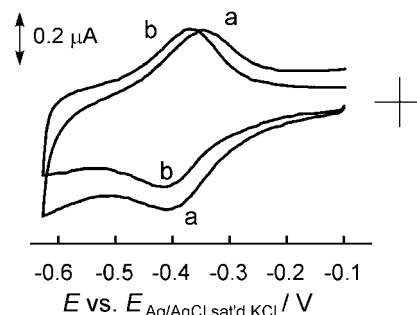


Figure 3. Typical CVs of (a) **1**-SAM and (b) **1**-(α -CD) electrodes in 0.3 M aqueous KBr solution prepared by the potential sweep method (PS). Sweep rate, $50 \text{ mV} \cdot \text{s}^{-1}$.

SAM reported by Chen, et al.⁵ These results suggest that the use of PS make it possible to fabricate the rotaxane-SAM comparable to the adsorption amount of common viologen-SAMs even if excess α -CDs are present in the **1**-(α -CD) solution. This is because α -CDs desorb from the electrode surface at -630 mV ,⁷ allowing the pseudorotaxane to adsorb on the electrode surface (Figure 1A).

In conclusion, we have demonstrated that the rotaxane-SAM consisting of α -CD and a viologen-thiol can be fabricated by controlling the unfavorable adsorption of α -CD and/or viologen dimers. This method is applicable to the fabrication of a SAM containing preferentially adsorbed species. Further optimization of the method and characterization of the rotaxane-SAM and its shuttling behavior are in progress in our laboratory.

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