Feasible attachment of dinuclear ruthenium complex to gold electrode surface via new ligand substitution reaction

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ABSTRACT

A general method has been developed for accumulation of a dinuclear ruthenium complex $[Ru_2(dhpta)(\mu-O_2CCH_3)_2]^-$ (H_5dhpta = 1,3-diamino-2-hydroxypropane-N,N,N',N'-tetraacetic acid) on a gold surface. The accumulation using a ligand substitution reaction of bridging acetate in the complex by terminal benzoic acid in a self-assembled monolayer (SAM) with ω-mercaptoalkoxy benzoic acid (HOOC-C_6H_4-O-$(CH_2)_n$-SH) (n = 4, 6, 12) is undergone. The methyl benzoate-containing alkyl disulfides capable to form SAMs on gold electrode have been synthesized utilizing reductive dimerization of the corresponding alkyl thiocyanates with tetraphenylphosphonium tetrathiomolybdate. The methyl benzoate group in the SAM was converted into benzoic acid group by base hydrolysis, which was confirmed by surface-enhanced Raman scattering measurements for silver electrode. After the ligand substitution reactions to accumulate the complex on the gold electrode surface, in the case of n = 6 and n = 12, voltammetric waves for surface confined redox process, which corresponds to $Ru^{III}Ru^{III}/Ru^{III}Ru^{II}$ redox couple are observed, respectively, and these surfaces of gold electrodes are covered with the complex completely. The present ligand substitution reaction should be widely applicable for the accumulation of other complexes and useful for designing of functional electrodes.

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1. Introduction

Molecular monolayers and thin films have been the subject of extensive research [1,2]. Especially, self-assembled monolayer systems (SAM) offer a versatile method for modifying metal surface with molecule-specific thin films. The use of these modified surfaces ranges from fundamental examinations concerning the interfacial electron-transfer kinetics [3,4] to applications such as nanofabrications [5]. Usually, SAMs on gold surface are prepared by use of thiol or disulfide having a particular functional site at the terminal [6,7]. Introduction of such particular functional groups requires special preparation techniques available only for the individual molecule. The difficulties in the preparation of SAMs come from either the reactivity of functional groups toward thiols or the restriction of the formation of well-defined SAMs due to the presence of the bulky functional group on a molecule. To overcome these difficulties alternative methods are developed on the basis of the conversion of the attached molecule in the SAM to the molecule possessing more useful functionality. These methods are attractive for numerous applications such as electrocatalysis and design of models for biological systems [8,9].

Intensive studies have been focused on the non-heme diiron proteins, such as hemerythrin, *R2* subunit of ribonucleotide reductase and methane monooxygenase, which involve dinuclear iron active centres bridged by two carboxylates and an oxo or hydroxo group. The dinuclear iron centres activate the function of the protein by utilizing redox cycles coupled with dioxygen molecule [10–12]. Interest in the parallel chemistry of (μ-oxo, hydroxo, or alkoxo)bis(μ-carboxylato)dinuclear ruthenium complexes are to obtain detailed structual and physical information

of a wide variety of oxidation states ranging from $Ru^{II}Ru^{II}$ to $Ru^{IV}Ru^{IV}$. For the further development of this chemistry, it is desired to utilize their redox properties for biomimetic systems and catalytic organic systems. We have reported the preparation of (μ-alkoxo)bis(μ-carboxylato)dinuclear ruthenium(III, III) complexes [Ru_2(dhpta)(μ-O_2CR)$_2$]$^-$ (H_5dhpta = 1,3-diamino-2-hydroxypropane-*N*,*N*,*N'*,*N'*-tetraacetic acid) (R=CH_3 (**1**), C_6H_5 (**2**), 4-OH-C_6H_4, 4-$NH_2C_6H_4$), and their physical properties tuned by varying the monoatom-bridging group [13–16]. For tuning, compounds [Ru_2(5-CH_3-hxta)(μ-O_2CR)$_2$]$^-$ (H_5hxta = *N*,*N'*-(2-hydroxy-1,3-xylylene)bis[*N*-(carboxymethyl)glycine]; R = CH_3, C_6H_5), [Ru_2(μ-O)(μ-O_2CH_3)$_2$(HBpz$_3$)$_2$] and [Ru_2(μ-OH)(μ-O_2CH_3)$_2$(HBpz$_3$)$_2$]$^+$ (HBpz$_3^-$ = tris(1-pyrazoyl)borate) have been synthesized. Therefore, modification of electrodes with these dinuclear ruthenium complexes by self-assembly method is an interesting subject, which may afford electrochemically useful properties to these electrodes. In addition, the variation of the functional moiety in SAMs provides a screening method to find the functional electrode.

Carboxylates can act as a ligand for a variety of metal ions. The basicity of alkyl or aryl carboxylate is usually proportional to the coordination ability as a ligand. Benzoate anion has more basic character and stronger coordination ability toward metal ions than acetate. On the basis of these knowledge, we examined (1) a new substitution reaction of two bridging acetates in the complex **1** by two molecules of benzoate at terminal, (2) synthesis of new disulfides having methyl benzoate units, (3) self-assembly of the disulfide on a gold electrode and succeeding hydrolysis of the methyl ester to form free acid, (4) the exchange reaction of bridging carboxylate for the accumulation of electroactive dinuclear ruthenium complex in the SAM and (5) electrochemical characterization using cyclic voltammetry. Preliminary results have already been reported [17].

2. Experimental

2.1. Materials

Acetone was dried over molecular sieves 3 A. Water was purified with a MilliQ purification system. Other purchased reagents were used without further purification. K[Ru_2(dhpta)(μ-O_2CCH$_3$)$_2$]·4H_2O was prepared by the previous method [13].

2.2. Synthesis

2.2.1. Tetraphenylphosphonium tetrathiomolybdate ($(Ph_4P)_2[MoS_4]$)

Tetraphenyl-phosphonium tetrathiomolybdate was obtained by the modification of literature method [18]. An aqueous solution (80 mL) of tetraphenylphosphonium chloride (4.0 g, 10 mmol) was added dropwise to an aqueous solution (300 mL) of ammonium tetrathiomolybdate (1.4 g, 5.4 mmol) under Ar atmosphere. Orange precipitate appeared immediately and the mixture was stirred for an hour at room temperature. The precipitate was filtered off and recrystallized from 5:2 *N*,*N*-dimethylformamide:diethyl ether solution. Red crystals of tetraphenylphosphonium tetrathiomolybdate were obtained. Yield 3.3 g (68%).

2.2.2. 6-(4′-Methoxycarbonylphenoxy)hexyl disulfide (CH_3O_2C-C_6H_4-O-(CH_2)$_6$-S-)$_2$

A methyl 4-hydroxybenzoate (5.0 g, 33 mmol) in acetone solution (80 mL) was added dropwise for 4 h to an acetone solution (400 mL) of excess 1,2-dibromohexane (84 g, 0.34 mmol) and potassium carbonate (30 g, 0.22 mol). The mixture was refluxed for ca. 12 h to complete the consumption of methyl 4-hydroxybenzoate.

After cooling to room temperature, the crystalline material containing 1,6-bis(methoxycarbonylphenoxy)hexane was filtered off and the filtrate was passed through silica-gel. From the first fraction (toluene as an eluent), 6-(4′-methoxycarbonylphenoxy)hexyl bromide was obtained. Yield (4.0 g, 39%).

An ethanol solution (300 mL) of 6-(4′-methoxycarbonylphenoxy)hexyl bromide (500 mg, 1.6 mmol) and potassium thiocyanate (200 mg, 2.1 mmol) was refluxed for 12 h and the mixture was filtered off then the filtrate was passed through silica-gel (toluene as an eluent). To the concentrated first fraction hexane was added to give crystals of 6-(4′-methoxycarbonylphenoxy)hexyl thiocyanate. Yield 760 mg (87%).

The obtained thiocyanate (180 mg, 0.62 mmol) and (Ph$_4$P)$_2$ [MoS$_4$] (390 mg, 0.43 mmol) were dissolved in acetonitrile (20 mL) and stirred for 14 h at 50 °C. The solution was placed in a refrigerator for 12 h and the resultant precipitate was filtered off and recrystallized from acetonitrile. White powder of 6-(4′-methoxycarbonylpheoxy)hexyl disulfide was obtained. Yield (86 mg, 51%). ^{1}H NMR in CHCl$_3$ (300 MHz): δ 1.3–1.8 (m, 16H), 2.62 (t, 4H), 3.85 (s, 6H), 4.00 (t, 4H), 6.81 (d, 4H), 7.90 (d, 4H). FAB-MS: *m/z* 534 (M$^+$). (Found: C, 63.31; H, 7.22%. $C_{28}H_{38}O_6S_2$ requires C, 62.89; H, 7.16%.)

2.2.3. 4-(4′-Methoxycarbonylphenoxy)butyl disulfide (CH_3O_2C-C_6H_4-O-(CH_2)$_4$-S-)$_2$

This compound was prepared from 1,4-dibromobutane using a procedure similar to that for 6-(4′-methoxycarbonylphenoxy)hexyl disulfide (CH_3O_2C-C_6H_4-O-(CH_2)$_6$-S-)$_2$. From 14 g (67 mmol) of 1,4-dibromobutane and 1.0 g (6.7 mmol) of methyl 4-hydroxybenzoate, 80 mg (0.2 mmol) of 4-(4′-methoxycarbonylpheoxy)butyl disulfide (CH_3O_2C-C_6H_4-O-(CH_2)$_4$-S-)$_2$ was obtained. ^{1}H NMR in CHCl$_3$ (300 MHz): δ 1.8–2.0 (m, 4H), 2.78 (t, 4H), 3.90 (s, 6H), 4.15 (t, 4H), 6.90 (d, 4H), 8.00 (d, 4H). FAB-MS: *m/z* 478 (M$^+$). (Found: C, 59.96; H, 6.28%. $C_{24}H_{30}O_6S_2$ requires C, 60.23; H, 6.32%.)

2.2.4. 12-(4′-Methoxycarbonylphenoxy)dodecyl disulfide (CH_3O_2C-C_6H_4-O-(CH_2)$_{12}$-S-)$_2$

This compound was prepared from 1,12-dibromododecane using a procedure similar to that for 6-(4′-methoxycarbonylphenoxy)hexyl disulfide (CH_3O_2C-C_6H_4-O-(CH_2)$_6$-S-)$_2$. From 19 g (58 mmol) of 1,12-dibromododecane and 1.0 g (6.7 mmol) of methyl 4-hydroxybenzoate, 12 mg (0.02 mmol) of 12-(4′-methoxycarbonylpheoxy)dodecyl disulfide (CH_3O_2C-C_6H_4-O-(CH_2)$_{12}$-S-)$_2$ was obtained. ^{1}H NMR in CHCl$_3$ (300 MHz): δ 1.3–1.8 (m, 40H), 2.68 (t, 4H), 3.88 (s, 6H), 4.00 (t, 4H), 6.89 (d, 4H), 7.97 (d, 4H). FAB-MS: *m/z* = 703 (M$^+$). (Found: C, 68.09; H, 8.79%. $C_{40}H_{62}O_6S_2$ requires C, 68.34; H, 8.89%.)

2.3. Preparation of the dinuclear ruthenium complex-accumulated electrode

As shown in Scheme 1, the polycrystalline gold electrode (effective electrodic area 0.0313 cm^2) was polished with 0.5 mm aluminum slurry and rinsed with pure water and ethanol. The electrode was immersed in ca. 1×10^{-3} M ethanolic solution of the disulfide for 24 h. After rinsing the electrode with ethanol and pure water, the terminal methyl benzoate in the SAM was hydrolyzed in 0.5 M NaOH solution. Then, the electrode was immersed in 10 mM [Ru_2(dhpta)(μ-O_2CCH$_3$)$_2$]$^-$ aqueous solution for 7 days to complete the ligand substitution.

Preparation of electrochemically roughened silver electrode. A silver plate (5 mm × 10 mm × 0.5 mm) was polished with alumina (0.06 mm) slurry and rinsed with pure water. Linear potential sweep oxidation–reduction cycles from −0.20 to +0.20 V versus Ag/AgCl at a scan rate of 10 mV s^{-1} were applied to the mechanically smooth silver electrode in 0.1 M KCl aqueous solution. From