



## Short Communication

# Electrochemical and infrared spectroscopic study of the self-assembled monolayer of a cyano-bridged dimeric triruthenium complex on gold surface



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## ARTICLE INFO

## Article history:

Received 30 May 2013

Received in revised form 14 November 2013

Accepted 8 December 2013

Available online 16 December 2013

## Keywords:

Self-assembled monolayer

Bridged cyanide

Oxo-centered triruthenium complexes

Gold surface

*In situ* infrared spectroscopy

## ABSTRACT

A new cyano-bridged dimeric oxo-centered triruthenium complex  $[\{\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2\}(\mu\text{-CN})\{\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})(\text{L}_{\text{py-SS}})\}]^+$  (py = pyridine,  $\text{L}_{\text{py-SS}} = (\text{C}_5\text{H}_4\text{N-CH}_2\text{NHC(O)(CH}_2)_4\text{CH(CH}_2)_2\text{SS})$ ) (**1**<sup>+</sup>) has been prepared, characterized, and confined on an Au(111) surface to form self-assembled monolayers (SAMs) (**1**/Au). The redox and IR spectroscopic properties observed for the discrete ions are essentially preserved in its SAMs. The molecules of SAMs **1**/Au stand up with the cyano groups tilted to the gold surface. The electronic structures of **1**/Au in different oxidation states have been studied by *in situ* infrared spectroscopy monitoring the stretching modes of the cyano group. The extent of cyano-mediated electronic communications between two triruthenium units in the SAMs has been successfully tuned by simply changing the electrolyte solutions from 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub> to aqueous 0.1 M HClO<sub>4</sub>.

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## 1. Introduction

Self-assembled monolayers (SAMs) on solid surfaces are well-organized thin film nanostructures constructed directly by individual molecules. Those SAMs functionalized by transition-metal complexes are particularly attractive due to their potential applications in many fields such as sensors, optical switches, and other molecule-based electronic devices [1–7].

Our recent studies have focused on developing novel SAM systems using redox-active coordination compounds [8–26], such as dinuclear and trinuclear ruthenium complexes with  $\text{Ru}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2$  [8–10] and  $\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6$  [11–22] cores, respectively, on gold electrode surfaces to study interfacial multi-electron transfer, light-triggered ligand substitution, redox-triggered molecular sensing, and bottom-up preparation of layer-by-layer structures. More recently, we have synthesized some cyano complexes of the oxo-centered triruthenium core  $\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6$ ; *i.e.*  $\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2(\text{CN})$  [27],  $[\{\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2\}(\mu\text{-CN})]^+$  [28], and  $\{\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2\}(\mu\text{-CN})\{\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})(\text{CO})\}$  (py = pyridine) [28]. We have shown that the triruthenium core acts as a poor  $\pi$ -donor (back-donation) as the relevant  $d\pi$  electrons are used for the

$d\pi(\text{Ru})\text{-}p\pi(\text{O})$  conjugation within the core. In the  $\mu\text{-CN}$  dimers, the electronic communication through the cyano bridge between the two triruthenium cores seems to be quite significant.

To characterize any surface effect on the electronic communications, we have now deposited a cyano-bridged dimeric complex of the triruthenium complex on Au electrode surface in the form of SAMs by means of a disulfide-anchor ligand introduced to one end of the cluster, *i.e.*,  $[\{\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2\}(\mu\text{-CN})\{\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})(\text{L}_{\text{py-SS}})\}]^+$  ( $\text{L}_{\text{py-SS}} = (\text{C}_5\text{H}_4\text{N-CH}_2\text{NHC(O)(CH}_2)_4\text{CH(CH}_2)_2\text{SS})$ ) which is represented as **1**<sup>+</sup>. In this paper, we report preparation, redox properties, and *in situ* IR spectroscopy of SAMs of **1**<sup>+</sup> on Au surfaces which are denoted as **1**/Au. The surface modification of cyano-bridged polynuclear compounds on solid surfaces as SAMs is unprecedented and this work addresses cyano-mediated intramolecular communication of the surface deposited “dimer of the trimer” by observing the redox wave splitting and detecting the mixed-valence state with IR spectroscopy.

## 2. Experimental section

## 2.1. Materials

Chemical reagents and solvents were commercially supplied from Wako Chemicals Co., Ltd. or Aldrich, and used without further

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purification unless otherwise stated. Dichloromethane used for electrochemical measurements was distilled over CaH<sub>2</sub> under an argon atmosphere. Milli-Q water (>18 MΩ cm) was used to prepare an aqueous solution of 0.1 M HClO<sub>4</sub>. A gold wire (99.999%, diameter 0.8 mm; Tanaka Precious Metal, Co., Ltd.) was used to prepare the Au(111) electrode. The synthesis and characterizations of complex **[1]**<sup>+</sup> and its precursor  $\{[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2](\mu\text{-CN})\{[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})(\text{CO})]\}$  are described in Supplementary Data.

## 2.2. Electrochemical measurements of complex **[1]**<sup>+</sup>

Cyclic voltammetry and differential-pulse voltammetry of **[1]**<sup>+</sup> dissolved in solutions (1 mM) were carried out at room temperature by using a potentiostat (ALS/CH Instruments, Model 650A) with a glassy carbon working electrode. An electrode Ag|AgCl (saturated KCl) and a Pt mesh were used as the reference and counter electrodes, respectively. Electrochemical measurements were performed under an Ar atmosphere in a CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate (*n*-Bu<sub>4</sub>NPF<sub>6</sub>).

## 2.3. Preparation of Au(111) electrodes and self-assembled monolayers **1/Au** as well as cyclic voltammetry of **1/Au**

The Au(111) disc electrode (diameter, 3.0 mm) was prepared using a gold wire (99.999%, 0.8-mm diameter) as described previously [29,30]. The roughness factor of the Au electrode was 1.12. The SAM-modified Au electrode was prepared as follows. A clean Au(111) electrode was immersed into a CH<sub>2</sub>Cl<sub>2</sub> solution of **[1]**Br (1.0 mM) and kept for 24 h. It was then taken out, rinsed thoroughly with CH<sub>2</sub>Cl<sub>2</sub> and dried in an argon atmosphere. The electrode modified with **[1]**<sup>+</sup> was used as a working electrode for cyclic voltammetry using an aqueous solution of 0.1 M HClO<sub>4</sub> or a 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub> solution as electrolyte solutions. A Pt foil and an Ag|AgCl (saturated KCl) electrode were used as the counter and reference electrodes, respectively. The electrode potential was controlled by a potentiostat (ALS/CH Instruments, Model 650A). The electrolyte solutions were deaerated with Ar gas for 30 min prior to the measurements.

## 2.4. FT-IR study of **1/Au**

All of the FT-IR measurements were performed on a Bio-Rad FTS 60A/896 spectrometer equipped with a liquid nitrogen-cooled MCT detector. IR spectra at a 4-cm<sup>-1</sup> resolution were recorded. All of the IR spectra in this paper are shown in absorbance units, defined as  $A = -\log I/I_0$ , where  $I$  and  $I_0$  represent the reflected IR intensities of the sample state and background state, respectively. The integration times of the IR spectra in different experiments are shown in the figure captions.

Samples used for *ex situ* FT-IR measurements were prepared by adsorbing **[1]**<sup>+</sup> on an Au film evaporated on a Ti-coated glass plate. The resulting samples of SAMs **1/Au** were located on a Harrick grazing angle (*ca.* 70°) reflection accessory and the reflection-absorption spectra in dry air were recorded at room temperature [18].

Samples of **1/Au** used for *in situ* IR measurements were prepared as follows. A thin gold film was chemically deposited on the flat reflecting side of a hemicylindrical Si prism [31]. Prior to the SAM modification, the gold film electrode was electrochemically cleaned and rinsed by Milli-Q water. The gold substrate was then immersed in a CH<sub>2</sub>Cl<sub>2</sub> solution of **[1]**Br (1.0 mM) and kept for 24 h. After taken out, thoroughly rinsed with CH<sub>2</sub>Cl<sub>2</sub> and dried by Ar gas, the gold electrode modified with **[1]**<sup>+</sup> was mounted in a spectroelectrochemical cell for the electrochemical and *in situ* IR

measurements. The spectroelectrochemical cell was fixed on a homemade single-reflection accessory (incident angle of 70°) used for *in situ* IR measurements.

The spectroelectrochemical cell was of a three-electrode design. The working electrode was the gold film electrode modified with **[1]**<sup>+</sup>. A Pt foil and an Ag|AgCl (saturated KCl) electrode were used as the counter and the reference electrodes, respectively. A solution of CH<sub>2</sub>Cl<sub>2</sub> with *n*-Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) or an aqueous solution of 0.1 M HClO<sub>4</sub> was used as the electrolyte solutions, which were deaerated with Ar gas for 30 min prior to the measurements. The *in situ* IR spectra were recorded simultaneously while the potential, controlled by a potentiostat (model 263 A, EG&G PARC), was applied on the electrode of SAMs **1/Au**.

The redox processes of the SAMs were monitored by means of *in situ* IR measurements with the Kretschmann attenuated total reflection (ATR) configuration [32–34]. The use of an ATR configuration for IR measurement facilitates the *in situ* monitoring of the electrode process owing to the high surface selectivity and sensitivity, and also to free mass transport [32–34].

## 3. Results and discussion

### 3.1. Synthesis

The synthetic routes to dimeric triruthenium cyano complexes  $\{[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2](\mu\text{-CN})\{[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})(\text{CO})]\}$  and  $\{[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2](\mu\text{-CN})\{[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})(\text{L}_{\text{py-SS}})]\}$  (**[1]**<sup>+</sup>) are given in Scheme S1 (Supplementary Data). Facile ligand substitution for the solvent molecule of  $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})(\text{CO})(\text{H}_2\text{O})]$  [35] was applied for the preparation. Complex  $\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2(\text{CN})$  was used to react with slightly excess amount (ratio 1:1.1) of  $[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})(\text{CO})(\text{H}_2\text{O})]$  in a mixed solvent of CH<sub>3</sub>OH/CH<sub>2</sub>Cl<sub>2</sub> to obtain  $\{[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2](\mu\text{-CN})\{[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})(\text{CO})]\}$ . To facilitate the confinement of the cyanide complex onto the gold surface, the disulfide ligand L<sub>py-SS</sub> was introduced to the cyanide complex. The disulfide-containing complex **[1]**<sup>+</sup> was then prepared from the precursor complex  $\{[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})_2](\mu\text{-CN})\{[\text{Ru}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{py})(\text{CO})]\}$ . On oxidation of the CO-coordinated Ru from Ru(II) to Ru(III) [14,18–20,36], the Ru–CO bond was destabilized and the CO ligand was substituted by a solvent molecule or Br<sup>-</sup>. The incoming ligand was then replaced by the disulfide ligand L<sub>py-SS</sub> to give **[1]**<sup>+</sup>. The products were purified by the column chromatography.

The positive-ion electrospray ionization mass spectra (ESI-MS) for the cyanide complexes showed prominent signals corresponding to their expected molecular ion peaks. The infrared spectra showed the characteristic bands were located at around 2130 cm<sup>-1</sup> for the cyano ligands. The  $\nu_{\text{as}}(\text{COO}^-)$  was located at *ca.* 1550 cm<sup>-1</sup>, while the  $\nu_{\text{s}}(\text{COO}^-)$  at 1420 cm<sup>-1</sup> [23,37]. Both cyanide complexes were also well characterized by <sup>1</sup>H NMR, elemental analysis, and electronic absorption spectroscopy (see Supplementary Data).

Three methods have been used to prepare the Au(111) surface. The gold substrates used for electrochemical measurements, the *ex situ* IR measurements, and *in situ* IR measurements were prepared by the single crystal growth of a gold wire, the evaporation of Au, and the chemical deposit of Au, respectively. SAMs **1/Au** were prepared by immersing the Au(111) substrate into the solution of **[1]**Br (1.0 mM) in CH<sub>2</sub>Cl<sub>2</sub> for 24 h. After rinsing with CH<sub>2</sub>Cl<sub>2</sub> and dried under an Ar stream, the gold substrates modified with SAMs were used as working electrodes in the electrochemical measurements. The electrolyte solutions were aqueous 0.1 M HClO<sub>4</sub> or 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub>.

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