

論文の内容の要旨

論文題目

Study on Single-molecular Rotors, Copper-Pyrimidine Complexes: Electroanalysis and STM Observation of Redox-synchronized Ring Rotation

(銅-ピリミジン錯体単分子ローターの研究: レドックスに連動した環回転の
電気化学解析と STM 観察)

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[Introduction]

The development of a system whereby the molecular motion is controllable at room temperature is one of the ultimate goals in the field of molecular electronics. In particular, when coupled to an electrode surface, molecules undergoing redox-driven motion have the potential of molecular memory device. After decades of studies devoted to seeking new systems, the development of methods to access single molecules at room temperature has now become the most crucial issue to be addressed. In this study, I focused on detecting molecular motion at room temperature at the single-molecule level. To achieve this, I employed a Cu-pyridylpyrimidine complex that changes its redox potential with a small degree of rotational motion and visualized the behavior via the change of electron transportability through the complex by using scanning tunneling microscopy (STM).

[Electrochemical analysis of Cu-pyrimidine complexes immobilized on Au surface]

I synthesized a Cu complex **1** with an asymmetrically substituted pyridylpyrimidine ligand that shows reversible rotational isomerization and immobilized it on a gold electrode (Figure 1a). The two rotational isomers, named as *inner-isomer* (*i-isomer*) and *outer-isomer* (*o-isomer*) according to the direction of a substitution, have different Cu^{II}/Cu^I redox potentials on the Au surface; 0.41 V (vs. Ag⁺/Ag) for *o-isomer* and 0.55 V for *i-isomer* (Figure 1b). During redox reaction, the coordinated pyrimidine ring rotates, which was evidenced by the appearance of two pairs of overlapping redox waves in the cyclic voltammograms at different potential sweep rates. Kinetic analysis on the overlapping waves revealed that the rotation rate on the electrodes surface ($k_{io}^I = 0.06 \text{ s}^{-1}$), was about one-tenth of that in solution ($k_{io}^I = 0.8 \text{ s}^{-1}$). The slowed rotation of the immobilized complexes allowed the observation of individual molecules by STM; the rotation frequency is not too high and not too low against the time scale of STM observation (53 s/frame).

[STM observation of rotational motion]

I could observe individual complex molecules by preparing a mixed self-assembled monolayer (SAM) of **1** and 1-hexanethiol (Figure 2a). The bright spots in the STM image of Figure 2b represent the individual complex molecules inserted at defect sites. The apparent heights of the complex molecules defined as height difference between the complex molecule and hexanethiol varied with time as they switched between the two states; the variation in a particular molecule is displayed in Figure 2d.

Aggregated apparent height data show two Gaussian components (Figure 2c). Least squares fitting of the two components indicates that **1** has two conformations with apparent heights of 0.50 nm and 0.72 nm, which have an area ratio of 7 : 3. This ratio seems consistent with the Cu(I) equilibrium ratio of the *i*- and *o*-isomers (*i* : *o* = 8 : 2). The two components of different heights can be assigned to the two isomers in terms of their electronic structures, where the *o*-isomer is topographically higher than the *i*-isomer.

To confirm further that the blinking images were certainly induced by rotational isomerization, STM images were taken for the mixed SAM of **3** and hexanethiol (Figure 3a). As **3** has no pyrimidine ring, only one electronic state should be observed on the molecule. Aggregated apparent height data of **3**

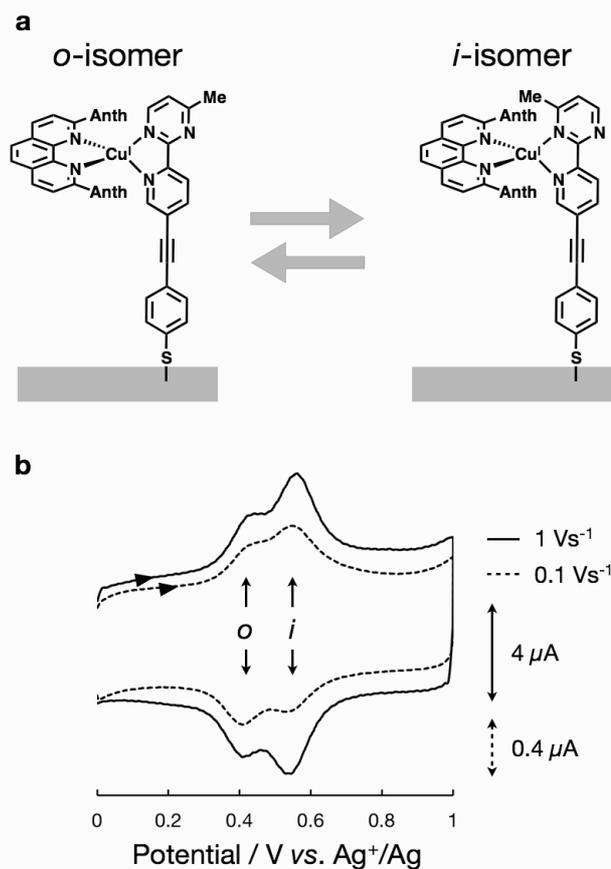


Figure 1. Rotational isomerization. a, The two isomers of **1** (Anth = 9-anthryl). b, Cyclic voltammograms of **1** on an Au electrode at room temperature in 1 M ⁿBu₄NPF₆-CH₂Cl₂. Scan rate: 1 V s⁻¹ (solid line) and 0.1 V s⁻¹ (dotted line).

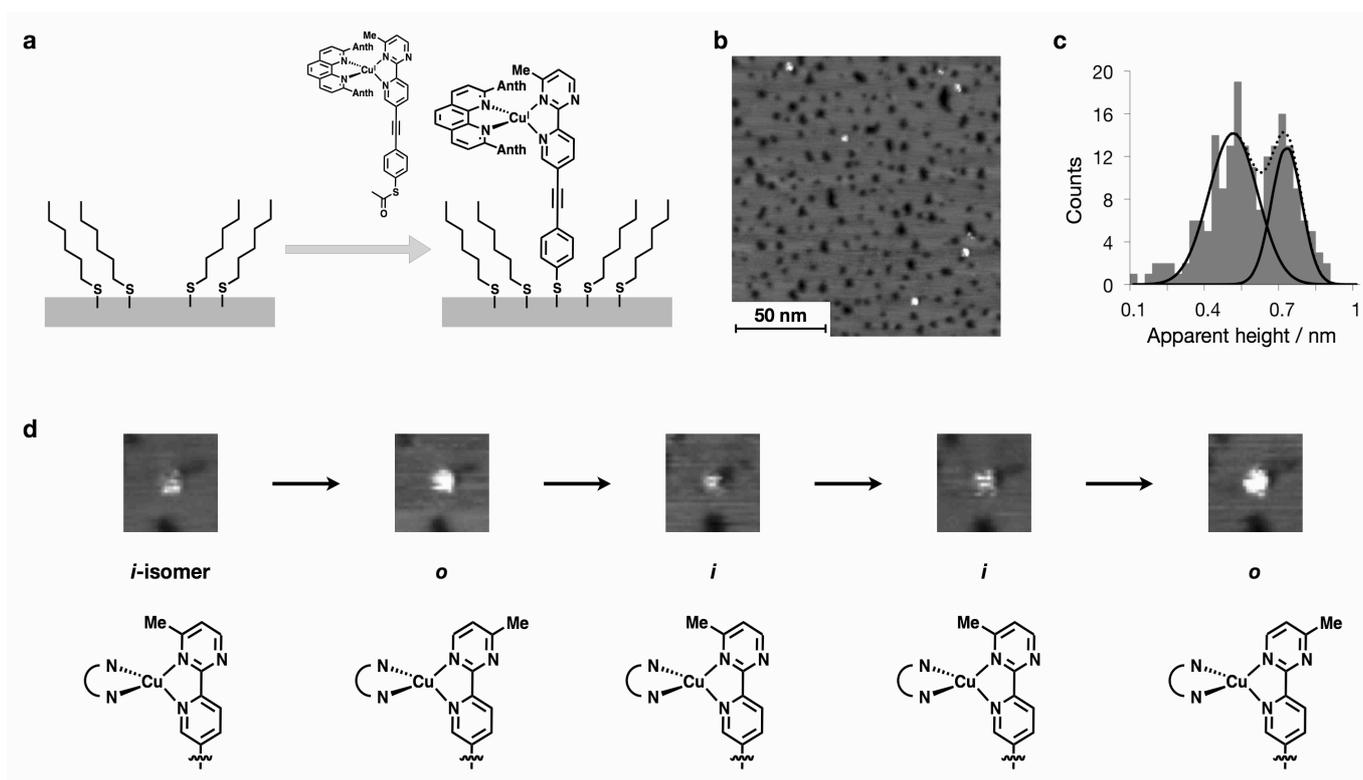


Figure 2. Rotation of individual molecules. a, The preparation of the mixed SAM of **1** and hexanethiol used during STM. b, STM topographic image of the mixed SAM of **1** and hexanethiol (150 nm × 150 nm). $V_s = 1.1$ V, $I_t = 0.1$ nA. c, Apparent height counts aggregated over 60 frames of **1**. d, Topographic changes and corresponding isomer structures.

was fitted with one Gaussian component with an apparent height of 1.0 nm by the least square method (Figure 3c), which firmly supports our conclusion that the rotational isomerization of **1** could be visualized as the conductivity changes.

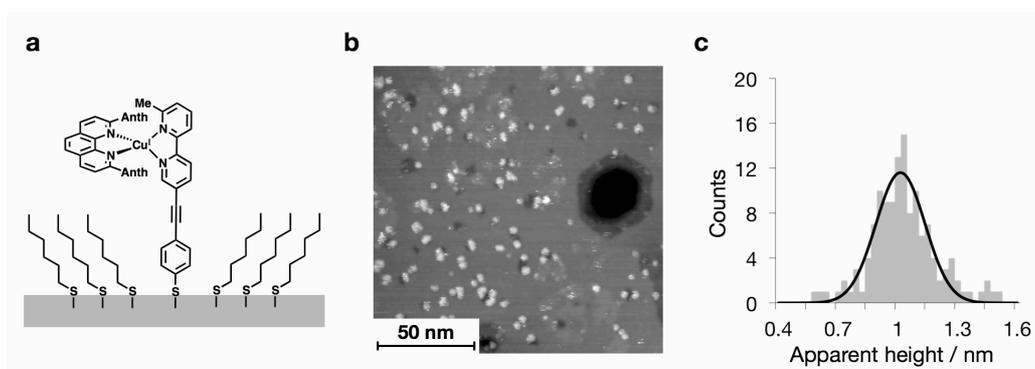


Figure 3. STM observation of **3**. a, The mixed SAM of **3** and hexanethiol. b, STM topographic image of the mixed SAM of **3** and hexanethiol (150 nm × 150 nm). $V_s = 1.1$ V, $I_t = 0.1$ nA. c, Apparent height counts of **3**.

[Two-step rotation of a twin rotor]

I synthesized a copper complex with bipyrimidine ligand for the further increase of the potential changes. Complex **4**, a twin rotor comprising of 4,4'-dimethyl-2,2'-bipyrimidine, has three isomers derived from two rotational steps (Figure 4a). Variable-temperature ^1H NMR in acetone- d_6 revealed that the three isomers coexist.

Three redox couples observed in cyclic voltammograms were assigned at three isomers (Figure 5). The ratio of isomers varied with scan rate, indicating the interconversion between the isomers. The

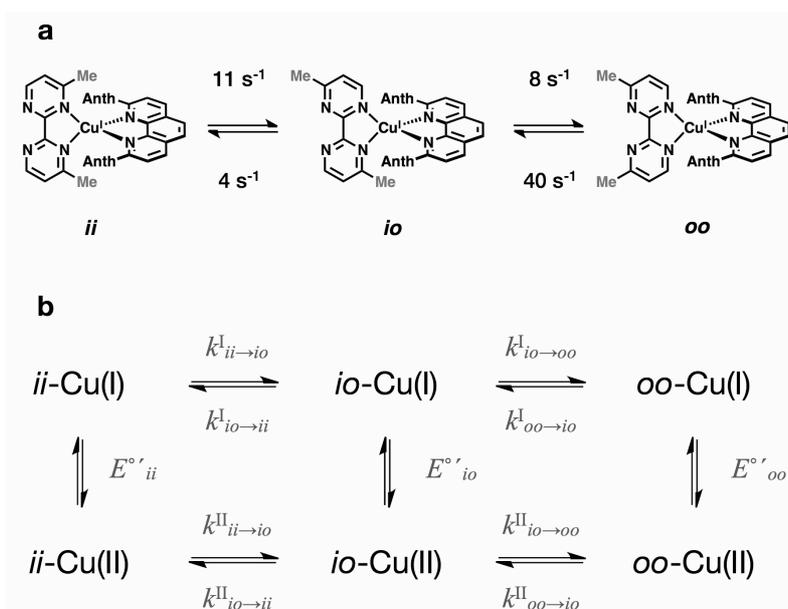


Figure 4. Rotational isomerization. (a) The three rotational isomers of 4^+ and rotational rate constants (s^{-1}). Anth = 9-anthryl. (b) Schematic of the isomerization in the Cu(I) and Cu(II) states.

and $E^o'_{ii} - E^o'_{io} = 0.13$ V. Rotation rate constants estimated by simulative analysis revealed that first ring rotates faster than second, suggesting the correlation between the two rotational steps (Figure 4b).

[Conclusion]

I could visualize changes in the electronic structures of individual copper complexes induced by reversible rotational isomerization. Even a small degree of molecular motion influences the electronic structure of the copper complex to allow clear observation of the two isomers. The tristability was achieved by increasing the number of rotors. This study would open up the possibility to achieve the meaningful single molecular device working under ambient conditions.

overlapping redox waves were analyzed by simulative method, which gave the redox potentials of three isomers: $E^o'_{oo} = 0.28$ V, $E^o'_{io} = 0.48$ V, and $E^o'_{ii} = 0.61$ V vs Ag^+/Ag . This result showed the redox potential difference of 0.33 V for the isomerization from *oo*-isomer to *ii*-isomer. Considering the redox potential change of 0.14 V for **1**, a single rotor, the redox potential shift accompanied with rotation was successfully doubled by simply increasing the number of rotors. More interestingly, the clear difference was found in the redox potential shifts of each rotational step: $E^o'_{io} - E^o'_{oo} = 0.20$ V

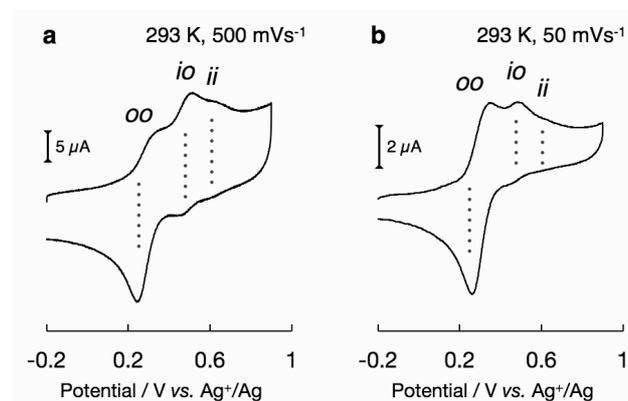


Figure 5. Cyclic voltammograms of 4^+ in 0.1 M nBu_4NPF_6 -acetone at 293 K. Scan rate: 500 mVs^{-1} (a), 50 mVs^{-1} (b).