

論文内容の要旨

論文題目 **Photofunctionalization of Molecular Switch Based on Pyrimidine Ring Rotation in Copper Complexes**

(銅錯体のピリミジン環反転に基づく分子スイッチの光機能化)

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Introduction

Metal complexes bearing π -conjugated chelating ligands are valid for both application and novel properties. For example, photophysical properties of metal complexes are of much interest for dye-sensitized solar cell and light-emitting devices. For another example, metal complexes are often found to be redox-active molecule, where two oxidation states can be reversibly switched by electronic stimuli, and they are useful in nanotechnology applications such as in molecular electronics.

Our group has employed copper complex bearing a bidentate ligand that includes a coordinated pyrimidine moiety (Figure 1). The interconversion between pyrimidine ring rotational isomers in copper(I) state is described in Figure 1b, where the notation of inner (*i*-Cu^I) and outer (*o*-Cu^I) isomers indicates the direction of the pyrimidine ring. The steric effects cause a shift of the redox potential as well as photophysics, owing to well-established features of copper complexes. Our group has constructed single molecular systems exhibiting an electrochemical potential response from an artificial molecular rotor with a stimulus-convertible function (Figure 1a). In other words, function of our previous system is based on a collaboration of electrochemistry and rotational bistability.

The aim of studies in my Ph.D course is to develop new functions by photofunctionalization of this molecular system (Figure 1c). I describe herein the new classes of luminescence (Chapter 3) and photo responsibility (Chapter 4).

Detail of Molecular Bistability Based on Pyrimidine Ring Rotation in Copper(I) Complexes (Chapter 2)

The rational molecular design requires a detailed investigation for the equilibrium between $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$. $1\cdot\text{BF}_4$ (1^+ = $[\text{Cu}(\text{Mepypm})(\text{DPEphos})]^+$, Mepypm = 4-methyl-2-(2'-pyridyl)pyrimidine,

DPEphos =

bis[2-(diphenylphosphino)phenyl]ether),

$1\cdot\text{B}(\text{C}_6\text{F}_5)_4$, $2\cdot\text{BF}_4$ (2^+ =

$[\text{Cu}(\text{Mepypm})(\text{dppp})]^+$, dppp = 1,3-bis(diphenylphosphino)propane), and $2\cdot\text{B}(\text{C}_6\text{F}_5)_4$ were newly synthesized and characterized. The rotational bistability of these complexes in common organic solvents was characterized using ^1H NMR analysis at several temperatures (Figure 2b). The interconversion between $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$ is an intramolecular process, as confirmed by ^1H NMR analysis of a mixed solution of $1\cdot\text{BF}_4$ and $[\text{Cu}(\text{bpy})(\text{DPEphos})]\text{BF}_4$ (bpy = 2,2'-bipyridine). The isomer ratio of $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$ was solvent- and counterion-sensitive. X-ray structural analysis revealed that two rotational isomers, $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$, of 2^+ were separately obtained as single crystals (Figure 2a). The reduced contact of the counterion to the complex cation in polar solvent seems to contribute to the relative stability of $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$. The findings are valuable for the design of molecular mechanical units that can be readily tuned via weak electrostatic interactions.

Dual Emission Caused by Ring Rotational Isomerization of a Copper(I) Complex (Chapter 3)

Since $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$ are expected to be different in the emission properties due to well-established relationship between coordination structure and photophysics in copper(I) complexes,^{2,3} dual luminescence caused by ring rotational isomerization can be expected. The complex exhibited characteristic charge transfer absorption and emission bands in solution (Figure 2c). I investigated photophysics of $1\cdot\text{BF}_4$ in acetone ($i\text{-Cu}^{\text{I}}:o\text{-Cu}^{\text{I}}$ = 30:70) using time-resolved emission spectra. I conclude that the photoprocesses of the two isomers, $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$, are

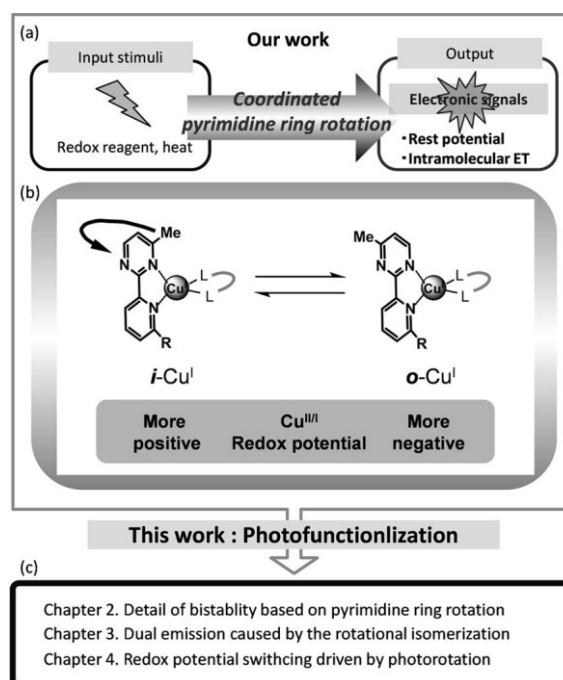


Figure 1. (a) Conceptual diagram showing function of coordinated pyrimidine ring rotation system. (b) Chemical equilibrium between two rotational isomers, $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$. (c) Studies in my Ph.D course.

different in the identity of the excited state. Emission lifetime of $i\text{-Cu}^{\text{I}}$ ($\tau = 40$ ns) is much longer than that of $o\text{-Cu}^{\text{I}}$ ($\tau = 2$ ns) because of inhibition of both steric rearrangement and solvent-coordination quenching in the photoexcited state (Figure 2d). Emission wavelength of $i\text{-Cu}^{\text{I}}$ is blue-shifted from that of $o\text{-Cu}^{\text{I}}$. Heat-sensitivity of emission of $i\text{-Cu}^{\text{I}}$ is larger than that of $o\text{-Cu}^{\text{I}}$ due to difference in photoexcited state properties between isomers. Both $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$ coexist in solution, and emit around room temperature. This finding shows a novel way to handle photophysics of metal complexes bearing π -conjugated chelating ligands.

Repeatable Copper(II)/(I) Redox Potential Switching Driven by Visible Light-Induced Coordinated Ring Rotation (Chapter 4).

As I mentioned above, collaboration of photophysics and rotational bistability enable me to develop a new type of emission. Therefore, combination of photophysics, redox ability, and rotation must provide another new type of function. Since 1-BF_4 and 2-BF_4 did not exhibit reversible redox activities, I designed and prepared a novel copper(I) complex, 3-BF_4 ($3^+ = [\text{Cu}(\text{MepmMepy})(\text{L}_{\text{Mes}})]^+$, $\text{MepmMepy} = 4\text{-methyl-2-(6'-methyl-2'-pyridyl)pyrimidine}$, $\text{L}_{\text{Mes}} = 2,9\text{-dimesityl-1,10-phenanthroline}$). The rotational bistability of 3^+ was characterized in a similar method to 1^+ and 2^+ . Two rotational isomers, $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$, coexist and interconvert in the solution. The rotational interconversion between $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$ is found to be frozen at 203 K and active at 250 K. The two redox reactions, $i\text{-Cu}^{\text{II/I}}$ and $o\text{-Cu}^{\text{II/I}}$, are different in potentials ($\Delta E^{\circ'} = 0.14$ V). The interconversion of oxidized rotational isomers, $i\text{-Cu}^{\text{II}}$ and $o\text{-Cu}^{\text{II}}$, is faster than that of copper(I) state, and $o\text{-Cu}^{\text{II}}$ is thermodynamically more preferred than $i\text{-Cu}^{\text{II}}$. Both $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$ absorb visible light in solution, and the redox potential of the light excited state is sufficiently large to induce photoinduced electron transfer (PET) with a redox mediator, dexamethylferrocenium ion (DMFc^+). Difference in absorption between $i\text{-Cu}^{\text{I}}$ and $o\text{-Cu}^{\text{I}}$ is very small, considering the results of UV-vis spectra upon chemical oxidation at low temperature.

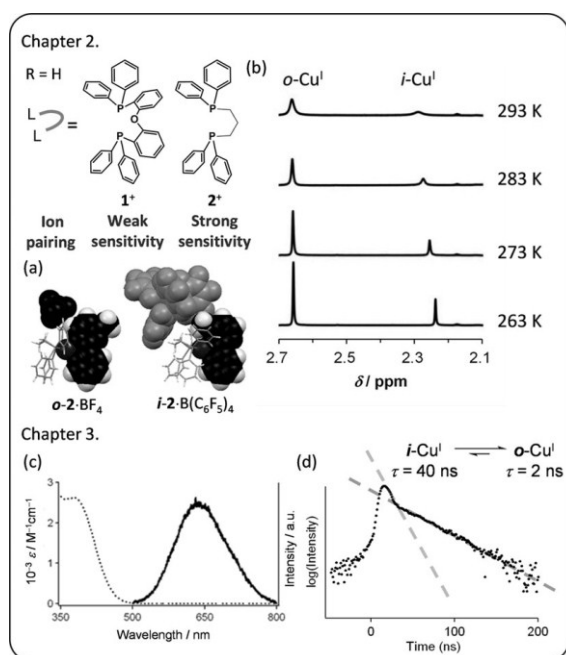


Figure 2. (a) Crystal structures of $o\text{-2-BF}_4 \cdot 0.5\text{MeOH}$ (left) and $i\text{-2-B}(\text{C}_6\text{F}_5)_4$ (right). (b) Aromatic ^1H NMR signal of a Mepypm moiety in 1-BF_4 in acetone- d_6 at several temperatures. (c) UV-vis absorption spectrum (dotted line) and the steady-state emission spectrum using 400 nm excitation (solid line) of 1^+ in acetone at room temperature. (d) Experimental 630 nm emission decay of 1^+ in acetone at room temperature excited at 425 nm.

Two redox waves, one each for the $i\text{-Cu}^{\text{II/I}}$ and $o\text{-Cu}^{\text{II/I}}$ in a ratio of 30:70, were observed in a cyclic voltammogram at 203 K in dichloromethane electrolyte solution in the presence of 4 equiv. DMFc^+ (Figure 3a top). The peak currents of the waves reflect the isomer ratio ($i\text{-Cu}^{\text{I}}:o\text{-Cu}^{\text{I}} = 30:70$). At 60 min, with photoirradiation with visible light ($\lambda > 400 \text{ nm}$) at 203 K, the redox waves gradually converged to a wave corresponding to the $o\text{-Cu}^{\text{II/I}}$ (Figure 3a middle). The ratio of $i\text{-Cu}^{\text{I}}$ to $o\text{-Cu}^{\text{I}}$ in this metastable state is $i\text{-Cu}^{\text{I}}:o\text{-Cu}^{\text{I}} = 12:88$, estimated from a simulated model fit to the cyclic voltammograms. Subsequent heating for 2 min at 250 K recovered the initial voltammogram ($i\text{-Cu}^{\text{I}}:o\text{-Cu}^{\text{I}} = 30:70$) (Figure 3a bottom). Repeatable electrochemical potential switching based on photodriven rotation, $i\text{-Cu}^{\text{I}} \rightarrow o\text{-Cu}^{\text{I}}$ and heatdriven rotation, $o\text{-Cu}^{\text{I}} \rightarrow i\text{-Cu}^{\text{I}}$ was demonstrated. PET processes can take a bypass route in the rotation of the copper(I) complex ($i\text{-Cu}^{\text{I}} + h\nu \rightarrow i\text{-Cu}^{\text{I}*}$, $i\text{-Cu}^{\text{I}*} + \text{DMFc}^+ \rightarrow i\text{-Cu}^{\text{II}} + \text{DMFc}^0$, $i\text{-Cu}^{\text{II}} \rightarrow o\text{-Cu}^{\text{II}}$, $o\text{-Cu}^{\text{II}} + \text{DMFc}^0 \rightarrow o\text{-Cu}^{\text{I}} + \text{DMFc}^+$). The system works not only with a redox mediator but also upon partial oxidation, in which the copper complex itself considerably assists the photo-driven rotation ($i\text{-Cu}^{\text{I}} + h\nu \rightarrow i\text{-Cu}^{\text{I}*}$, $i\text{-Cu}^{\text{I}*} + o\text{-Cu}^{\text{II}} \rightarrow i\text{-Cu}^{\text{II}} + o\text{-Cu}^{\text{I}}$, $i\text{-Cu}^{\text{II}} \rightarrow o\text{-Cu}^{\text{II}}$). Generally, photochromic molecules are accompanied by significant color changes. The photo- and heat-driven rotation system works without a significant color change, which is a representative feature for new type of photoresponsibility.

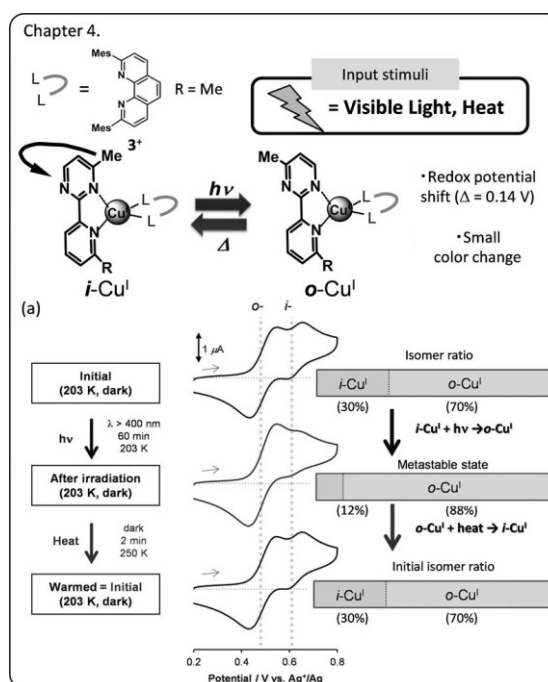


Figure 3. (Top) Conceptual diagram showing the photodriven and heatdriven pyrimidine ring rotational isomerization of 3-BF_4 . (a) Photorotation experiments in the DMFc^+ system with notes about the procedures. Experimental cyclic voltammograms at a scan rate of 50 mV s^{-1} . Investigated DMFc^+ systems comprise 3-BF_4 (0.45 mM) in $0.1 \text{ M Bu}_4\text{NBF}_4\text{-CH}_2\text{Cl}_2$ containing 1.8 mM DMFc-BF_4 at 203 K in the dark. Top: initial state. Middle: after 60 min visible light irradiation ($\lambda > 400 \text{ nm}$) at 203 K . Bottom: after 2 min heating at 250 K in the dark. The reversible changes in the molar ratios of the isomers upon light irradiation and heating are illustrated in the right panels.

The system works not only with a redox mediator but also upon partial oxidation, in which the copper complex itself considerably assists the photo-driven rotation ($i\text{-Cu}^{\text{I}} + h\nu \rightarrow i\text{-Cu}^{\text{I}*}$, $i\text{-Cu}^{\text{I}*} + o\text{-Cu}^{\text{II}} \rightarrow i\text{-Cu}^{\text{II}} + o\text{-Cu}^{\text{I}}$, $i\text{-Cu}^{\text{II}} \rightarrow o\text{-Cu}^{\text{II}}$). Generally, photochromic molecules are accompanied by significant color changes. The photo- and heat-driven rotation system works without a significant color change, which is a representative feature for new type of photoresponsibility.

Conclusion I developed dual emission caused by ring rotational isomerization. This strategy is applicable not only for luminescence itself but also properties in photoexcited state related to photocatalysis and photoelectron conversion. I constructed a PET-induced rotational system which switches redox potential. This finding can provide electronic, magnetic, and other molecular signaling characteristics because of repeatable conversion of external stimuli into redox potential signals.