<div style="text-align:center">論 文 内 容 の 要 旨</div>

論 文 題 目　Construction of novel photoelectric response systems comprising azo-substituted bipyridine copper complexes
（アゾ置換ビピリジン銅錯体を用いる新規光電応答系の構築）

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Introduction

Molecular machines have attracted much attention in nanoscale research, and their development has been accompanied by introduction of new technologies for handling and assembling single molecules. The construction of molecular machines via combination and synchronization of molecular modules with well-characterized responses constitutes an efficient design strategy.

For example, a photoelectric conversion system has previously been developed based on the ligand-exchange reaction between a copper complex containing azobenzene-appended bipyridine ligands and free bipyridines. The ligand exchange was modulated by the reversible photoisomerization of the azobenzene moieties.

The next synthetic goal was to expand the functionalities of this system in novel ways by introducing appropriate substituents to this copper complex system. One purpose of this study is to construct a single molecular machine by introducing the azo-substituted bipyridine complex and bipyridine into a single molecule. The other purpose of this study is to toggle the photoelectric response of the copper complex system using solution pH changes. For these purposes, 4-hydroxyazobenzene-appended bipyridine, oAB-2OH, was synthesized. The hydroxyl groups act as proton sensors.

Construction of a Single Molecular Machine for Photoelectric Conversion
― Synchronization of Isomerization and Ligand Exchange

Construction of a single molecule which undergoes reversible photoelectric conversion was tried. For this purpose, a cyclic ligand, oAB-bpy, was synthesized from oAB-2OH. This cyclic ligand had azobenzene units for photoisomerization and bipyridine units for the coordination site. A cyclic compound, oAB-O13, was synthesized as a model compound.

The photoisomerization behavior of oAB-O13 and oAB-bpy in CD_2Cl_2 was monitored using NMR measurements. Before irradiation, they were in the $trans_2$ form. New signals were observed under 365-nm light irradiation, indicating a $trans$-to-cis isomerization. Both the cis_2 form and the cis-$trans$ form were observed. The isomerization in the reverse direction was observed under 436-nm light irradiation, confirming the reversibility of the isomerization.

Next, the coordination behavior of oAB-O13 to copper was examined. When oAB-O13 and $[Cu(CH_3CN)_4]BF_4$ were mixed in CD_2Cl_2, ^{1}H NMR signals were broadened (Figure 1(a)) because the copper was coordinated by not only bipyridine units but also by polyether chains and was not fixed. Then, oAB-2OH was added and the signals became sharp (Figure 1(b)), indicating stabilization by formation of $[Cu(o$AB-O13$)(o$AB-2OH$)]BF_4$, which had the interligand π-π stacking. This means that oAB-2OH could penetrate the cyclic ligand and coordinated to copper.

Next, synchronization of isomerization and ligand exchange was tried. $[Cu(CH_3CN)_4]BF_4$ was added to the cis form of oAB-bpy and oAB in CD_2Cl_2. ^{1}H NMR signals of $[Cu(o$AB-bpy$)]BF_4$ and oAB were observed (Figure 2(a)). When these were converted to the $trans$ form, the occurrence of penetrating oAB-bpy of oAB was indicated (Figure 2(b)). These results indicate that the construction of a single molecular machine which can convert photo energy into electric energy through synchronization of the photoisomerization and the ligand exchange is feasible.
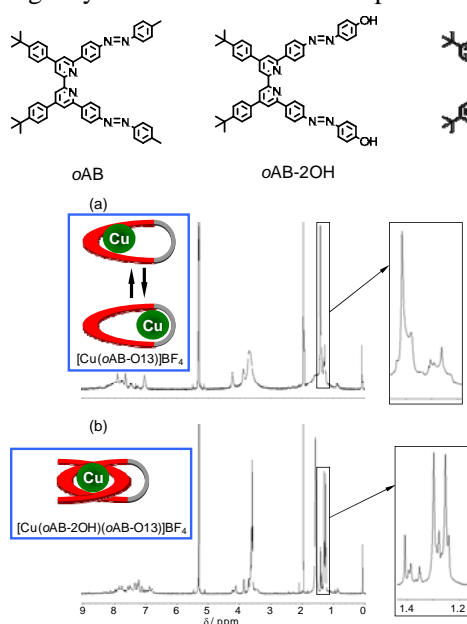

Figure 1. ^{1}H NMR spectral changes of oAB-O13 (1.0 × 10^{-3} M) and $[Cu(CH_3CN)_4]BF_4$ (1.0 × 10^{-3} M) in CD_2Cl_2 (a) initially and (b) after addition of oAB-2OH (1.0 × 10^{-3} M).
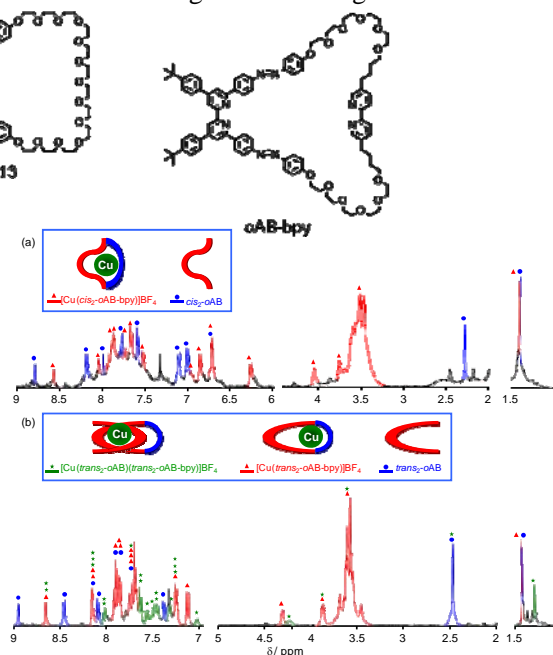
Figure 2. ^{1}H NMR spectral changes of oAB-bpy (4.6 × 10^{-3} M), oAB (4.6 × 10^{-3} M), and $[Cu(CH_3CN)_4]BF_4$ (4.6 × 10^{-3} M) in CD_2Cl_2 (a) in the cis form and (b) in the $trans$ form.

A Hydroxyazobenzene-appended Bipyridine Complex of Copper
─ Acid-base Response and its Application to Photoelectric Response

Acid-base promoted switching of the photoelectric conversion was tried. For this purpose, 4-hydroxyazobenzene-appended bipyridine complex of copper, [Cu(*o*AB-2OH)$_2$]BF$_4$, was synthesized from *o*AB-2OH. The [Cu(*o*AB-2OH)$_2$]BF$_4$ system, shown in Chart 1, contains interligand π–π stacking interactions that stabilize [Cu(*o*AB-2OH)$_2$]BF$_4$. The π-stacking stabilization is lost by the *trans*-to-*cis* isomerization upon UV irradiation, and ligand exchange with bipyridine derivatives is favored. This chemical process modulates the reduction potential of the Cu^{II}/Cu^{I} redox couple. Because the original state can be regenerated by visible light irradiation, this process can be cycled repeatedly. The addition of acid or base respectively lowers or raises the barrier to photoisomerization, modulating the photoelectric response.

The UV-Vis absorption spectrum of [Cu(*o*AB-2OH)$_2$]BF$_4$ in THF showed an intense band at 370 nm (Figure 3), ascribed to the π–π^* transition of the azobenzene moieties. The n–π^* and d–π^* transition (MLCT) bands overlapped in the visible region from 450 nm to 550 nm. The intensity of the π–π^* transition band decreased and the n–π^* transition band increased under 365-nm light irradiation, indicating a *trans*-to-*cis* isomerization. The isomerization in the reverse direction was observed under 436-nm light irradiation (Figure 3(a)). The solution reached a photostationary state by irradiation with 365 nm or 436 nm light for 5 min. It was reversible between these two photostationary states. This confirmed the reversibility of the isomerization. When 0.2 eq. of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was added to this solution, the photoisomerization reaction did not take place (Figure 3(b)). Suppression of the photoresponse was caused by the deprotonation of the hydroxyl group, which accelerated the thermally driven *cis*-to-*trans* isomerization of the azo groups. A small quantity of base was sufficient to suppress the photoisomerization of [Cu(*o*AB-2OH)$_2$]BF$_4$ because the thermally driven *cis*-to-*trans* isomerization of the deprotonated form is much more rapid than the photochemically driven *trans*-to-*cis* isomerization of the protonated form. The photoresponse was recovered, and reversible photoisomerization was observed again after further addition of trifluoroacetic acid (TFA) (Figure 3(c)). In summary, photoisomerization could be toggled using acid or base addition.

An acetone-d_6 solution containing [Cu(*o*AB-2OH)$_2$]BF$_4$ and bpy-2COOEt presented ^{1}H NMR signals of [Cu(*o*AB-2OH)$_2$]BF$_4$, *o*AB-2OH, and bpy-2COOEt. The signals from [Cu(bpy-2COOEt)$_2$]BF$_4$ were not observed due to broadening attributed to ligand self-exchange. In contrast, the signals of [Cu(*o*AB-OH)$_2$]BF$_4$ were sharp due to stabilization by interligand π–π stacking. These results indicate the presence of an equilibrium between the copper coordination of *o*AB-2OH and bpy-2COOEt.

Figure 4 shows the cyclic voltammograms of [Cu(*o*AB-2OH)$_2$]BF$_4$. The Cu^{II}/Cu^{I} couple showed a reversible redox wave at 0.31 V *vs*. ferrocenium (Fc$^+$)/ferrocene (Fc), a typical potential for 6,6'-disubstituted bipyridine complexes. The redox potential was not significantly affected by the addition of acid or base (see Figure 4). A cyclic voltammogram of [Cu(bpy-2COOEt)$_2$]BF$_4$ is

also shown in Figure 4. A reversible redox wave for the Cu^{II}/Cu^{I} couple was observed at –0.06 V *vs*. Fc^+/Fc, a typical potential for bipyridine derivative complexes. The large difference between the redox potentials of $[Cu(o\text{AB-2OH})_2]BF_4$ and $[Cu(\text{bpy-2COOEt})_2]BF_4$ can be harnessed to achieve a photoelectric response via the ligand exchange reaction.

The $o\text{AB-2OH}/[Cu^I(\text{bpy-2COOEt})_2]BF_4/[Cu^{II}(\text{bpy-2COOEt})_2](BF_4)_2$ system yielded a reversible rest potential response under alternating photoirradiation at 365 nm (UV) and 436 nm (visible) (Figure 5(a)). The response first exhibited a negative potential shift accompanying the *trans*-to-*cis* isomerization under 365 nm irradiation. This shift was caused by formation of $[Cu^I(\text{bpy-2COOEt})_2]^+$, with a less positive Cu^{II}/Cu^{I} redox potential, through the ligand exchange coupled to photoisomerization. After addition of 0.2 eq. DBU, the rest potential response to irradiation was silenced (Figure 5(b)) due to the suppressed photoisomerization, as noted above. Addition of TFA recovered the reversible rest potential response to UV and visible light (Figure 5(c)), because the barrier to photoisomerization was lowered by protonation. These results indicate that the photoelectric response switched between OFF and ON states by the addition of small amounts of DBU and TFA, respectively. In conclusion, the ON/OFF switching of photoelectric response using acid and base was achieved.
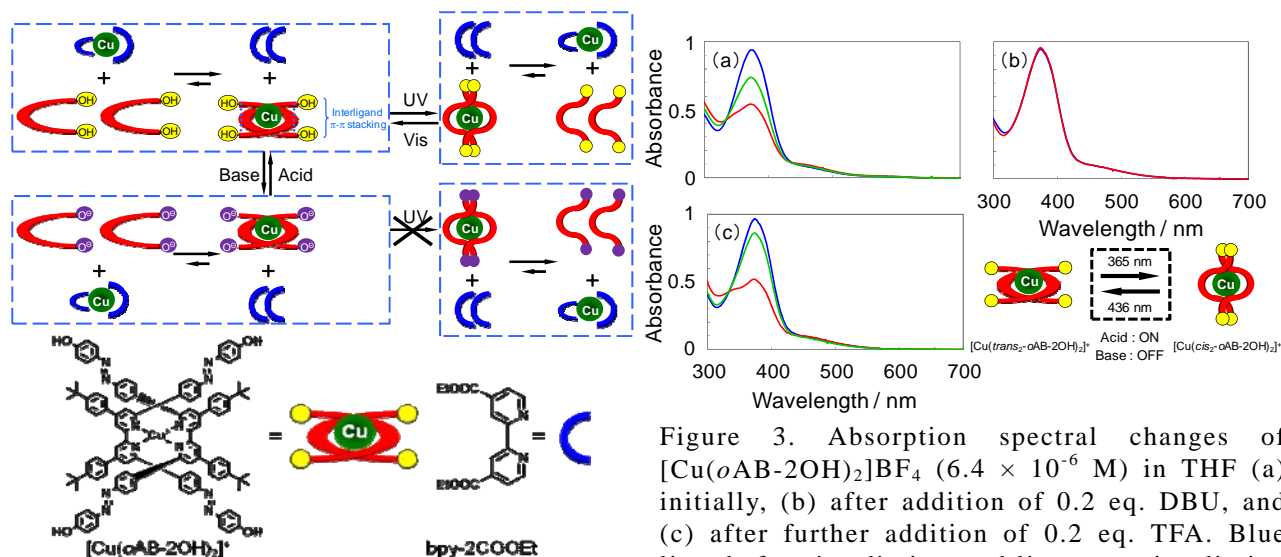

Chart 1. ON/OFF toggling of the photoelectric response.

Figure 3. Absorption spectral changes of $[Cu(o\text{AB-2OH})_2]BF_4$ (6.4×10^{-6} M) in THF (a) initially, (b) after addition of 0.2 eq. DBU, and (c) after further addition of 0.2 eq. TFA. Blue line: before irradiation; red line: upon irradiation at 365 nm for 5 min; green line: upon irradiation at 436 nm for 5 min.
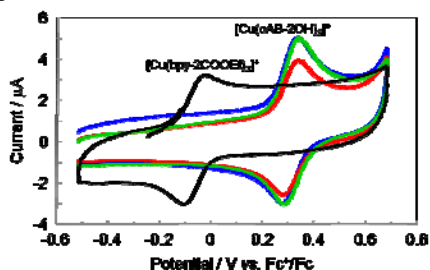

Figure 4. Cyclic voltammograms of $[Cu(\text{bpy-2COOEt})_2]BF_4$ (2.4×10^{-4} M) in acetone with 0.1 M Bu_4NClO_4 (black line) and $[Cu(o\text{AB-2OH})_2]BF_4$ (2.8×10^{-4} M) in acetone with 0.1 M Bu_4NClO_4. Blue line: initially; red line: after addition of 0.2 eq. DBU; green line: after further addition of 0.2 eq. TFA.

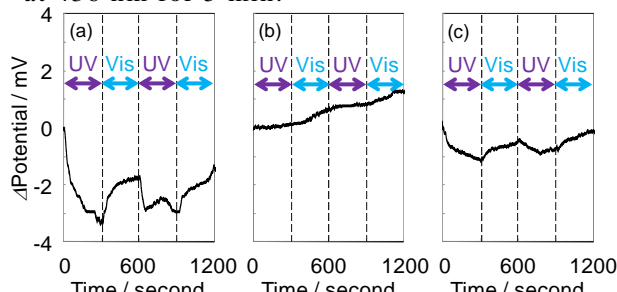Figure 5. Rest potential changes of $o\text{AB-2OH}$ (2.0×10^{-5} M), $[Cu(\text{bpy-2COOEt})_2]BF_4$ (9.0×10^{-6} M), and $[Cu(\text{bpy-2COOEt})_2](BF_4)_2$ (1.0×10^{-6} M) in acetone with 0.1 M Bu_4NClO_4 (a) initially, (b) after addition of 0.2 eq. DBU, and (c) after further addition of 0.2 eq. TFA.