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Acid–Base Responsive Photoelectric Conversion of a Hydroxyazobenzene-appended Bipyridine–Copper Complex System

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We report the synthesis of a new 4-hydroxyazobenzene-appended bipyridine complex of copper, [Cu(*o*AB-2OH)$_2$]BF$_4$, which exhibits a reversible acid–base responsive redox-active photoisomerization reaction. The acid–base modulation of the photoisomerization reaction permits ON/OFF toggling of the photoelectric conversion in devices containing this complex by the addition of small quantities of acid or base in the presence of 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine, bpy-2COOEt.

Molecular machines have attracted much attention in nanoscale research, and their development has been accompanied by the 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.[1] Previously, we developed a photoelectric conversion system 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.[2] The next synthetic goal was to expand the functionalities of this system in novel ways by introducing appropriate substituents to this copper complex system.

The present study aims to toggle the photoelectric response of the copper complex system using solution pH changes. For this purpose, we synthesized a 4-hydroxyazobenzene-appended bipyridine complex of copper, [Cu(*o*AB-2OH)$_2$]BF$_4$, and studied its physical properties in acidic and basic solutions. The reversible acid–base response and the photochromic properties of [Cu(*o*AB-2OH)$_2$]BF$_4$ were characterized, permitting the controllable ON/OFF switching of the photoelectric response through introduction of acids or bases in the presence of 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine (bpy-2COOEt).

The [Cu(*o*AB-2OH)$_2$]BF$_4$ system, shown in Chart 1, contains interligand π–π stacking interactions that stabilize the coordination of azobenzene-containing ligands. The π-stacking stabilization is lost by the *trans*-to-*cis* isomerization of the azobenzene moieties 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, the photoresponse of the Cu^{II}/Cu^{I} redox couple can be cycled repeatedly. The addition of acid or base respectively lowers or raises the barrier to photoisomerization, modulating the photoelectric response.

4-Hydroxyazobenzene-appended bipyridine, *o*AB-2OH, was synthesized from 6,6′-bis(4-aminophenyl)-4,4′-bis(4-*tert*-butylphenyl)-2,2′-bipyridine[3] and 4-nitrophenyl tosyl ether.[4] [Cu(*o*AB-2OH)$_2$]BF$_4$ was synthesized by reaction of *o*AB-2OH and [Cu(CH$_3$CN)$_4$]BF$_4$, and characterized by NMR and elemental analysis.

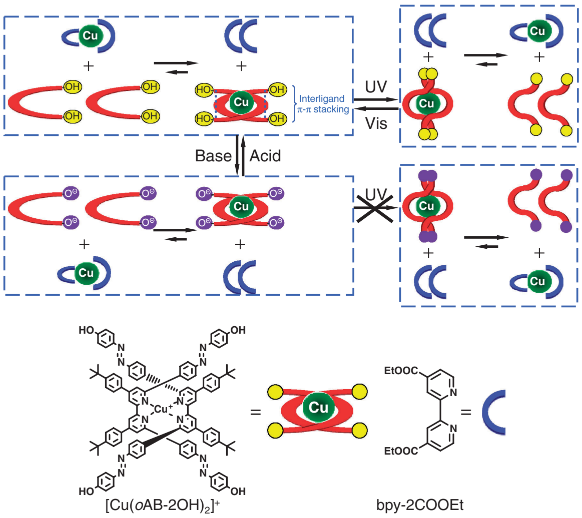

Chart 1. ON/OFF toggling of the photoelectric response.

The UV–vis absorption spectrum of [Cu(*o*AB-2OH)$_2$]BF$_4$ in THF showed an intense band at 370 nm, 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 to 550 nm.[3] When excessive potassium *t*-butoxide was added to this solution, the band at 370 nm decreased and a new band appeared at 480 nm.[3] This indicates the occurrence of deprotonation of hydroxy groups causing further delocalization of π electrons. The original spectrum was recovered by addition of trifluoroacetic acid,[3] confirming the reversibility of deprotonation of [Cu(*o*AB-2OH)$_2$]BF$_4$.

Figure 1 shows UV–vis absorption spectral changes of [Cu(*o*AB-2OH)$_2$]BF$_4$ upon irradiation. 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. The solution reached a photostationary state by irradiation with 365 or 436 nm light for 5 min. It was reversible between these two photostationary states (Figure 1a). When 0.2 equivalents (equiv) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were added to this solution, photoisomerization was not observed (Figure 1b). 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 and the *cis* form hardly existed.[5] The photoresponse was recovered, and reversible photoisomerization was observed again after the addition of TFA (Figure 1c). In

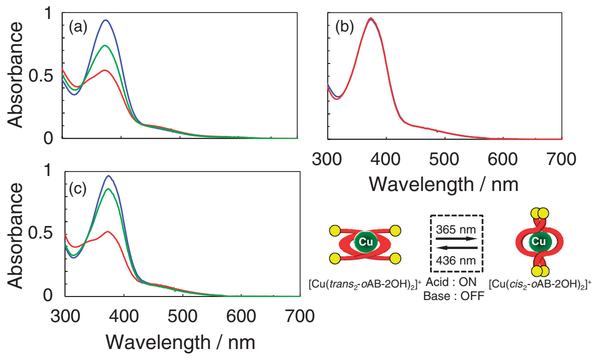

Figure 1. Absorption spectral changes of [Cu(*o*AB-2OH)$_2$]BF$_4$ (6.4×10^{-6} mol dm^{-3}) in THF (a) initially, (b) after addition of 0.2 equiv DBU, and (c) after addition of 0.2 equiv TFA. Blue line: prior to irradiation; red line: irradiation at 365 nm for 5 min; green line: irradiation at 436 nm for 5 min.

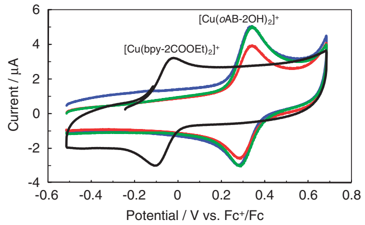

Figure 2. Cyclic voltammograms of [Cu(bpy-2COOEt)$_2$]BF$_4$ (2.4×10^{-4} mol dm^{-3}) in acetone with 0.1 mol dm^{-3} Bu$_4$NClO$_4$ (black line) and [Cu(*o*AB-2OH)$_2$]BF$_4$ (2.8×10^{-4} mol dm^{-3}) in acetone with 0.1 mol dm^{-3} Bu$_4$NClO$_4$. Blue line: prior to addition; red line: after addition of 0.2 equiv DBU; green line: after addition of 0.2 equiv TFA.

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.[3] 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 2 shows the cyclic voltammograms of [Cu(*o*AB-2OH)$_2$]BF$_4$. The Cu$^{\rm II}$/Cu$^{\rm I}$ couple showed a reversible redox wave at 0.31 V vs. ferrocenium (Fc$^+$)/ferrocene (Fc), which is a typical potential for 6,6′-disubstituted bipyridine complexes.[6] The redox potential was not significantly affected by the addition of acid or base (Figure 2). A cyclic voltammogram of [Cu(bpy-2COOEt)$_2$]BF$_4$ is shown in Figure 2. A reversible redox wave for the Cu$^{\rm II}$/Cu$^{\rm I}$ couple was observed at −0.06 V vs. Fc$^+$/Fc, a typical potential for bipyridine derivative complexes.[7] The large difference between the redox potentials of [Cu(*o*AB-2OH)$_2$]BF$_4$ and [Cu(bpy-2COOEt)$_2$]BF$_4$ can be harnessed to achieve a photoelectric response via the ligand exchange reaction.

The [Cu$^{\rm I}$(*o*AB-2OH)$_2$]BF$_4$/bpy-2COOEt/[Cu$^{\rm II}$(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 3a). The response first exhibited a negative potential shift accompanying the *trans*-to-*cis* isomerization under 365 nm irradiation. This shift was caused by

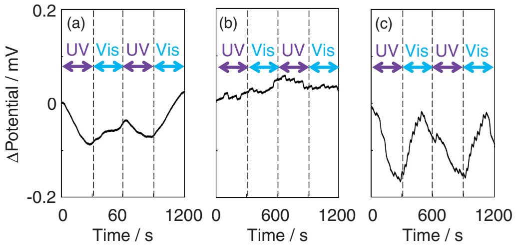

Figure 3. Rest potential changes of [Cu(*o*AB-2OH)$_2$]BF$_4$ (1.0×10^{-5} mol dm^{-3}), bpy-2COOEt (2.0×10^{-5} mol dm^{-3}), and [Cu(bpy-2COOEt)$_2$](BF$_4$)$_2$ (1×10^{-6} mol dm^{-3}) in acetone with 0.1 mol dm^{-3} Bu$_4$NClO$_4$ (a) initially, (b) after addition of 0.2 equiv DBU, and (c) after addition of 0.2 equiv TFA.

formation of [Cu$^{\rm I}$(bpy-2COOEt)$_2$]$^+$, with a less positive Cu$^{\rm II}$/Cu$^{\rm I}$ redox potential, through the ligand exchange coupled to photoisomerization. Upon addition of 0.2 equiv DBU, the rest potential response to irradiation was silenced (Figure 3b) due to the suppression of the ligand exchange caused by the lack of the *cis* form. Addition of TFA recovered the reversible rest potential response to UV and visible light (Figure 3c), because the barrier to photoisomerization was lowered by protonation. The rest potential changes in Figures 3a and 3c were different, caused by the difference of the ratio of the *trans* form to the *cis* form in the photostationary states in Figures 1a and 1c. These results indicate that the photoelectric response switched between OFF and ON states by the addition of small amounts of DBU and TFA, respectively. Further investigation of this response is now ongoing.

In conclusion, [Cu(*o*AB-2OH)$_2$]BF$_4$ undergoes reversible photoisomerization coupled to reversible protonation–deprotonation and redox reactions. The photoisomerization of [Cu(*o*AB-2OH)$_2$]BF$_4$ can be switched ON or OFF by adding small quantities of acid or base, respectively. Facile ligand exchange between [Cu(*o*AB-2OH)$_2$]BF$_4$ and bpy-2COOEt yields [Cu(bpy-2COOEt)$_2$]BF$_4$. A reversible rest potential redox response is obtained under alternating UV and visible photoirradiation of the [Cu$^{\rm I}$(*o*AB-2OH)$_2$]BF$_4$/bpy-2COOEt/[Cu$^{\rm II}$(bpy-2COOEt)$_2$](BF$_4$)$_2$ system. The photoelectric response could be toggled by the addition of acid or base.

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