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Coordination-Synchronized Trans–Cis Photoisomerization of Bipyridylazobenzene Driven by a Cu(II)/Cu(I) Redox Change

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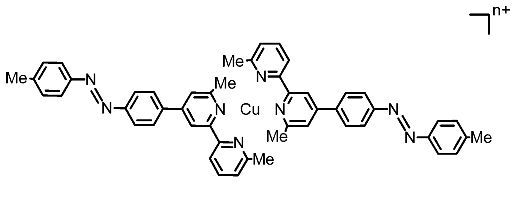
The trans–cis photoisomerization behavior of azobenzene-bipyridine ligand (dmpAB) was synchronized with coordination of the bipyridine moiety to copper. The coordination reaction can be reversibly controlled with reversible redox reaction of copper, to afford $[Cu(dmpAB)_2]^+$ in Cu^I state and free dmpAB in Cu^{II} state. UV irradiations to Cu^I and Cu^{II} samples form trans-rich and cis-rich compositions, respectively. The results enable us to control the trans–cis isomerization reversibly through Cu^{II}/Cu^I redox and a single UV light.

The redox reaction of bis(diimine)copper complexes is accompanied by a unique structural conversion of the favorite geometry from a 4-coordinate square planar or a 5- or 6-coordinate structure of Cu^{II} to a 4-coordinate tetrahedral of Cu^I.[1,2] Recently, several molecular systems have been developed that incorporate a copper complex unit to induce molecular motions by electrochemical signals.[3] If the structural conversion causes a ligand exchange reaction, the physical property of the ligand can be changed, depending on the coordination. Azobenzene, a representative photochromic molecule, has been broadly applied to various functional molecular systems,[4] while its trans−cis structural conversion has been generally considered to be driven only photochemically. We previously reported that the trans−cis isomerization of azobenzene derivatives is seriously affected by coordination to transition metals.[5] In the present study, we constructed a molecularly synchronized system in which the trans−cis isomerization of azobenzene-attached bipyridine was controlled by its binding/release reaction to copper driven by a Cu^{II}/Cu^I redox change. This leads to a new reversible trans−cis isomerization switching with a single light source. Recently, we reported two systems showing reversible photoisomerization controlled by a reversible redox reaction between $[Co(bpy)_3]^{2+}$ and $[Co(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine),[6] or between ferrocene and ferrocenium.[7] Although the present system is the third to present reversible isomerization with a single light source, it is the first example to combine the dynamic motion of the metal complex with that of the azobenzene ligand.



$[Cu(dmpAB)_2]^{n+}$ n = 1, 2

The methyl-substituted ligand dmpAB was prepared using a method similar to that of nonsubstituted pAB.[6,8] A reaction of dmpAB and $[Cu(CH_3CN)_4]BF_4$ yields $[Cu^I(dmpAB)_2]BF_4$, as a deep-red powder.[9] $[Cu^{II}(dmpAB)_2](BF_4)_2$ was prepared

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(8) Characterization data for dmAB follow. Anal. Calcd for $C_{25}H_{22}N_4$: C, 79.34; H, 5.86; N, 14.80. Found: C, 79.14; H, 6.07; N, 14.59. ^1H NMR ($CDCl_3$): δ 8.59 (s, 1H), 8.29 (d, 1H, $J = 7.5$ Hz), 8.04 (d, 2H, $J = 8.5$ Hz), 7.94 (d, 2H, $J = 8.5$ Hz), 7.87 (d, 2H, $J = 8.3$ Hz), 7.74 (t, 1H, $J = 7.7$ Hz), 7.49 (s, 1H), 7.36 (d, 2H, $J = 8.1$ Hz), 7.22 (d, 1H, $J = 7.6$ Hz), 2.70 (s, 3H), 2.65 (s, 3H), 2.45 (s, 3H).

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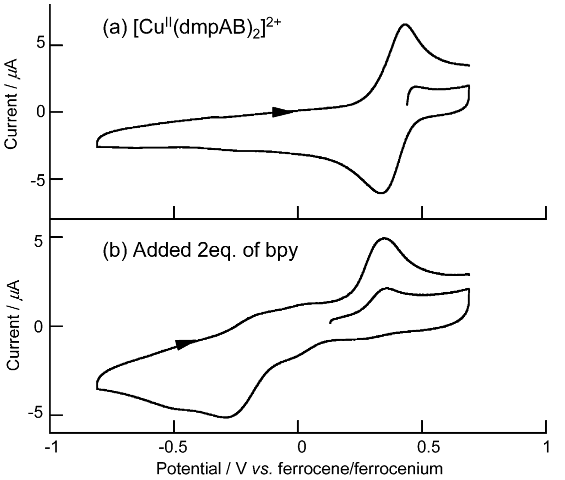


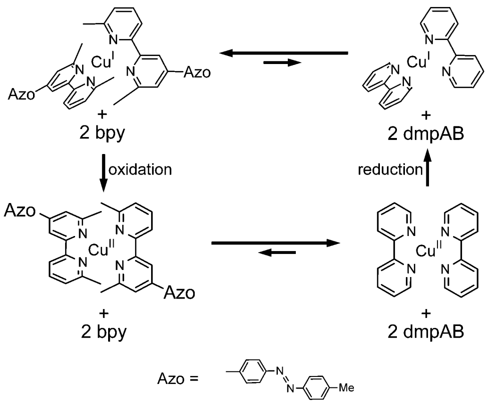
Figure 1. Cyclic voltammograms of [Cu(dmpAB)$_2$](BF$_4$)$_2$ in 0.1 M Bu$_4$NBF$_4$/CH$_2$Cl$_2$ without and with the addition of 2 equiv of bipyridine for (a) and (b), respectively.

from dried Cu(BF$_4$)$_2$ and dmpAB.[10] ^{1}H NMR of the Cu(I) complex and electronic absorption spectra of both complexes have revealed that the azo moiety in these compounds takes the trans form in solution. Irradiation of ligand dmpAB at 365 nm[11] causes effective trans-to-cis isomerization of the azobenzene moiety yielding 94% molar fraction of the cis isomer at a photostationary state (PSS), on the basis of ^{1}H NMR spectra. On the other hand, the cis molar fractions at 365 nm at PSS for [Cu^I(dmpAB)$_2$]$^+$ and [Cu^{II}(dmpAB)$_2$]$^{2+}$ were 18% (from ^{1}H NMR spectra) and 14% (from absorption spectral change[12]), respectively. This implies that the change in the cis ratio at PSS by the redox change is less significant than that for [Co(bpy)$_3$]$^{3+/2+}$.[6]

In a cyclic voltammogram of [Cu^{II}(dmpAB)$_2$]$^{2+}$ (Figure 1a) in dichloromethane, a reversible Cu^{II}/Cu^I redox wave is observed at 0.37 V versus ferrocenium/ferrocene. The redox potential is considerably more positive than that of nonsubstituted [Cu^I(bpy)$_2$]BF$_4$ ($E^{\circ\prime} = -0.12$ V), irrespective of the introduction of electron-donating methyl groups. This positive shift can be attributed to the methyl groups in dmpAB sterically protecting the copper center in the tetrahedral coordination structure, and preventing the formation of a favorable square planar structure in the Cu^{II} state.[13]

Upon addition of 2 equiv of bpy to the solution of [Cu^{II}(dmpAB)$_2$]$^{2+}$, the oxidation wave to Cu^{II} appears at 0.32 V, similar to that without bpy, whereas the reduction wave to Cu^I at ca. 0.3 V disappears and a new wave is observed at -0.30 V in a cyclic voltammogram (Figure 1b).

Scheme 1



Judging from these potentials, the major species are [Cu^I(dmpAB)$_2$]$^+$ and [Cu^{II}(bpy)$_2$]$^{2+}$ at the Cu^I and Cu^{II} states. This indicates that the facile ligand exchange reaction occurs on the time scale of cyclic voltammetry. This consideration was supported by the UV−vis spectral change of the complex upon addition of bpy. When bpy was added to [Cu^{II}(dmpAB)$_2$]$^{2+}$ solution, a blue shift of the azo $\pi-\pi^*$ band (352 nm) occurred in the UV−vis spectra. When 5 equiv of bpy was added, the shift was saturated at 345 nm, identical to the $\pi-\pi^*$ band location of the free ligand, dmpAB. In [Cu^I(dmpAB)$_2$]$^+$, almost no azo $\pi-\pi^*$ band shift occurs with the addition of bpy. The driving force of this reversible ligand exchange reaction may be the difference in coordination geometry between Cu^I and Cu^{II}; the Cu^I cation prefers the tetrahedral geometry, which the methyl groups in dmpAB stabilize.[2] DmpAB also prevents nucleophilic attacks to the copper center. On the other hand, when Cu^I is oxidized to Cu^{II}, the copper center prefers bpy. This is because the methyl groups in dmpAB cause significant steric hindrance to the coordination of the Cu^{II} cation in the favorite square planar structure (Scheme 1).

Since the redox-controlled coordination reaction of dmpAB is considered to affect an electronic structure of the azo moiety, it enables us to convert photoisomerization behavior through redox reaction. Thus, we investigated photoisomerization behavior of copper complexes in the presence of bpy. When mixed with bpy, absorption changes upon UV irradiation to Cu^I and Cu^{II} complexes exhibited significant difference between these two complexes (Figure 2). From an estimate of these spectra, a trans-rich composition was achieved in a Cu^I sample; on the other hand, a cis-rich composition was formed in the Cu^{II} sample at PSS, despite the same UV light irradiation.

Figure 3 shows the cis molar ratio at PSS (365 nm) versus the amount of bpy added to the solution. In the solution of [Cu^{II}(dmpAB)$_2$]$^{2+}$, the cis molar ratio was increased with the addition of bpy, and saturated when ca. 2 equiv of bpy was added. It is considered that the exchange reaction of the complex with bpy affords free dmpAB, which isomerizes efficiently to the cis isomer. On the other hand, [Cu^I(dmpAB)$_2$]$^+$ shows little increase of the cis form with

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(9) Characterization data for [Cu^I(dmpAB)$_2$]BF$_4$ follow. MALDI-TOF-MS: m/z 819.4 ([M]$^+$). Anal. Calcd for C$_{50}$H$_{44}$BCuF$_4$N$_8$·H$_2$O: C, 64.90; H, 5.01; N, 12.11. Found: C, 64.99; H, 5.12; N, 11.96. ^{1}H NMR (CD$_2$Cl$_2$): δ 8.44 (s, 1H), 8.33 (d, 1H, $J = 8.0$ Hz), 8.11 (d, 2H, $J = 8.5$ Hz), 8.07 (t, 1H, $J = 7.8$ Hz), 7.99 (d, 2H, $J = 8.5$ Hz), 7.89 (d, 2H, $J = 8.2$ Hz), 7.76 (s, 1H), 7.52 (d, 1H, $J = 7.6$ Hz), 7.38 (d, 2H, $J = 8.1$ Hz), 2.46 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H).

(10) Chraracterization data for [Cu^{II}(dmpAB)$_2$](BF$_4$)$_2$ follow. Anal. Calcd for C$_{50}$H$_{44}$B$_2$CuF$_8$N$_8$·H$_2$O: C, 59.34; H, 4.58; N, 11.07. Found: C, 59.76; H, 4.69; N, 10.90.

(11) The photoirradiation experiment was carried out using a 500 W super-high-pressure mercury lamp (USHIO USH-500D) as a light source, and 366 ± 30 nm light was selected with a monochromator (Jasco CT-10).

(12) The cis molar ratio was estimated from the decrease ratio of the azo $\pi-\pi^*$ band of the trans isomer (around 370 nm), because the *cis*-azobenzene moiety is known to show almost no absorption in this region.

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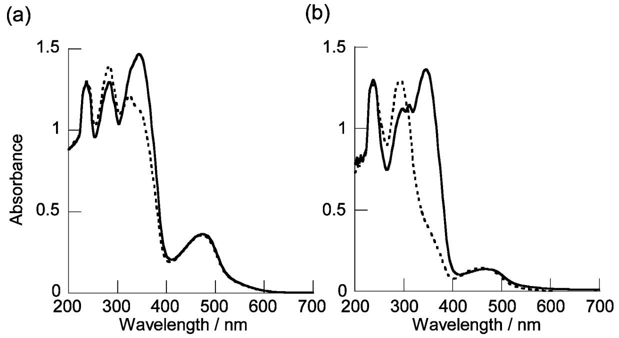


Figure 2. UV−vis absorption spectral changes of $[Cu(dmpAB)_2]BF_4$ (2.0×10^{-5} M) plus bpy (4.0×10^{-5} M) (a) and $[Cu(dmpAB)_2](BF_4)_2$ (2.0×10^{-5} M) plus bpy (4.0×10^{-5} M) (b) upon photoirradiation in dichloromethane. Solid and dotted lines refer to the all-trans form and the trans/cis mixture at PSS at 365 nm, respectively.

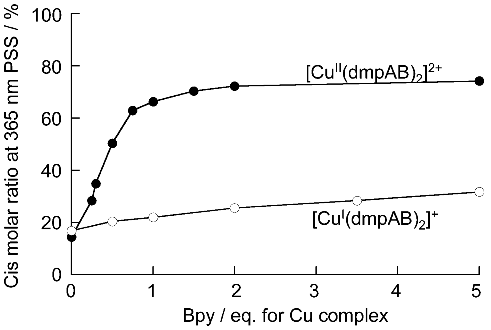
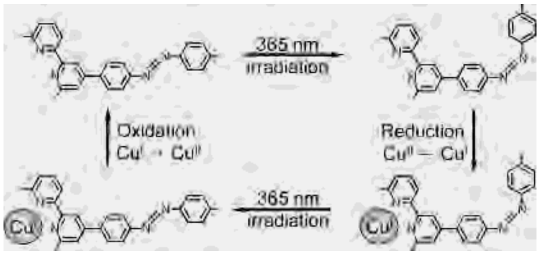


Figure 3. Promotion of the cis molar ratio at 365 nm at PSS accompanied by the addition of bpy in dichloromethane.

the addition of bpy, because bpy cannot outplace dmpAB on copper. Thus, the cis molar ratios at PSS in $[Cu^I(dmpAB)_2]^{2+}$ and $[Cu^{II}(dmpAB)_2]^{2+}$, which were 18% and 14% when they were present solely, converted to 25% and 72%, respectively, when 2 equiv of bpy was added, achieving drastic changes in the isomerization behavior with the oxidation state of copper.

Finally, we tried to convert the oxidation state of Cu^{II} and Cu^I reversibly, and we did observe reversible photoisomerization with a single UV light source. Photoisomerization controlled by a reversible ligand coordination reaction was performed chemically with oxidizing and reducing agents. A mixture of $[Cu^I(dmpAB)_2]^+$ and 2 equiv of bpy in dichloromethane was irradiated with 365 nm light, forming 32% of the cis isomer. Then, the same sample was oxidized to the Cu^{II} state by 1 equiv of $[Fe(\eta^5\text{-}C_5H_4Cl)_2]PF_6$ and reirradiated with the same 365 nm light, further trans−cis isomerization was observed, and the cis ratio reached 70%. Then, the copper was reduced with 1 equiv of $Co(\eta^5\text{-}C_5H_4\text{-}COCH_3)_2$ to the Cu^I state and reirradiated with 365 nm light. The result was inverse cis-to-trans isomerization. These results demonstrate that the isomerization behavior was controllable with a single UV light and the ligand's binding/release reaction, which is reversibly performed with the Cu^{II}/Cu^I redox change (Scheme 2).

Scheme 2



In conclusion, the trans−cis photoisomerization behavior of the azobenzene moiety was synchronized with ligand coordination of the conjugated bpy moiety to copper. The coordination reaction can be reversibly controlled by changing the oxidation state of copper, leading to reversible trans−cis isomerization using a combination of single UV light and redox reaction with a good yield of cis isomer.

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