A Large Trans/cis Conversion Ratio in Redox-Conjugated Single-Light Reversible Isomerization of a Cobalt Complex with *meta*-Bipyridylazobenzene Ligands

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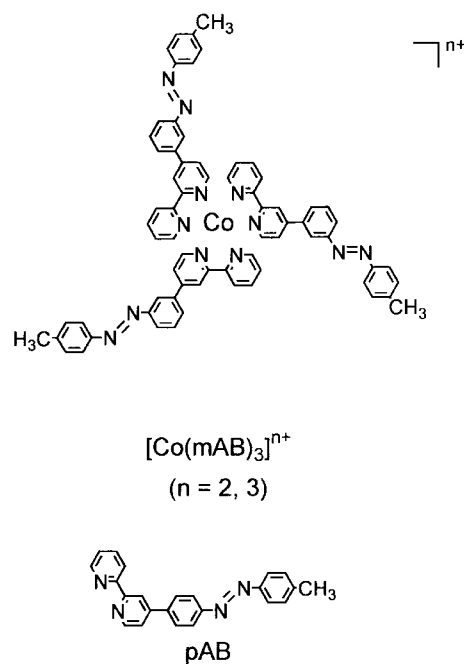
Abstract. Reversible trans-cis isomerization of *meta*-bipyridylazobenzene coordinated to cobalt was achieved by a combination of photoirradiation with a single UV light source and a Co(II)/Co(III) redox reaction. The trans/cis conversion performance was significantly improved in the meta-form compared with the para-form ligated to cobalt.

Key words : Pphotoisomerization, Azobenzene, Cobalt complex, Bipyridine, Redox

Trans/cis photoisomerization of azobenzene, a representative photochromic molecule, has recently attracted much attention since its large conformational conversion between trans and cis isomers suggests its potential availability to broad application. Introduction of azobenzene to various materials, such as surface[1], polymers[2], and liquid crystals[3], portends new photo-switching materials and optical information storage systems. We attempted to construct new optical molecular systems by coupling the photoisomerization of azobenzene with unique electrochemical and photochemical properties of transition metal complexes[4-6]. Recently, we reported that an azo-conjugated Co(bpy)₃ complex, Co(pAB)₃ (see Scheme 1), displays reversible trans-cis isomerization with a Co(III)/Co(II) redox reaction under constant monochromatic UV light irradiation[7]. This system is based on the fact that the coordination of a free azo ligand to a metal atom suppressed the trans-to-cis isomerization with UV light irradiation, and its effect significantly depends on the property of the metal core. Thus, the trans/cis conversion range is not so wide (6-40%) as the cis formation yield remained at 40% at most even in the cis-rich Co(II) state. In this study, we succeeded in enlarging the trans/cis conversion range with the redox reaction in the meta-substituted cobalt complex, Co(mAB)₃ (Scheme 1), by weakening the electronic interaction between bipyridine and azo moieties by altering the substitution position.

The meta-substituted ligand mAB was synthesized in the same manner as the para-substituted ligand pAB[7], starting from 3-aminobenzaldehyde. [Co(II)(mAB)₃](BF₄)₂ and [Co(III)(mAB)₃](BF₄)₃ were obtained[8] from Co(NO₃)·6H₂O in a good yield by the same method as that used for pAB complexes[7]. These complexes are stable under ambient conditions.

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$[Co(mAB)_3]^{n+}$

(n = 2, 3)

pAB

Scheme 1

In a cyclic voltammogram of Co(III)(mAB) in Bu₄NClO₄-MeCN, a reversible Co(III)/(II) wave was observed at -0.11 V vs. ferrocenium/ferrocene, coincident with Co(III)(pAB).

The UV-Vis absorption spectrum of the ligand mAB shows an azo π-π* band at 327 nm, which is blue-shifted compared with that of pAB (342 nm) (Fig. 1). In pAB, the conjugation extension to the bipyridine moiety lowers the π and π* energy gap, and causes a red shift of the π-π* absorption band. The azo π-π* band of Co(III)(mAB) locates at a longer wavelength than that of Co(II)(mAB) (Fig. 1a), which is a similar tendency to that of the pAB complexes(Fig. 1b),
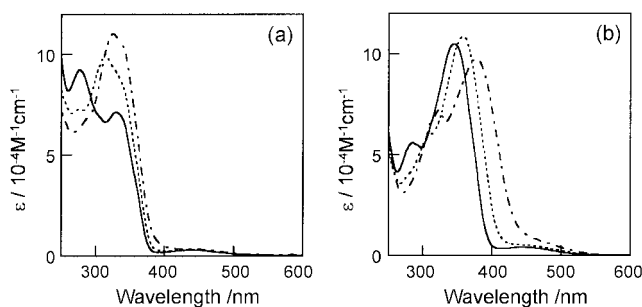
Fig. 1. UV-Vis absorption spectra of azo ligands and cobalt complexes in CH₂Cl₂. The ε values of azo ligands are enlarged three times to normalize with the number of azo moieties in the complexes: (a) mAB (solid line), Co(II)(mAB)₃ (dotted line), and Co(III)(mAB)₃ (dashed line); (b) pAB (solid line), Co(II)(pAB)₃ (dotted line), and Co(III)(pAB)₃ (dashed line).
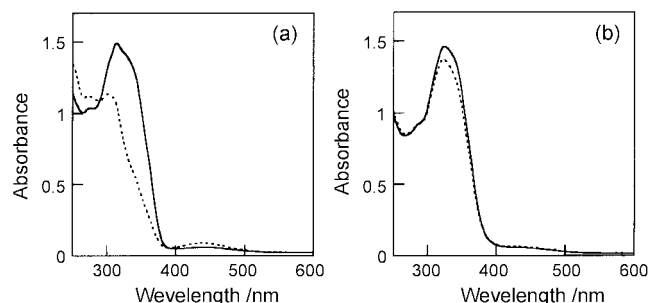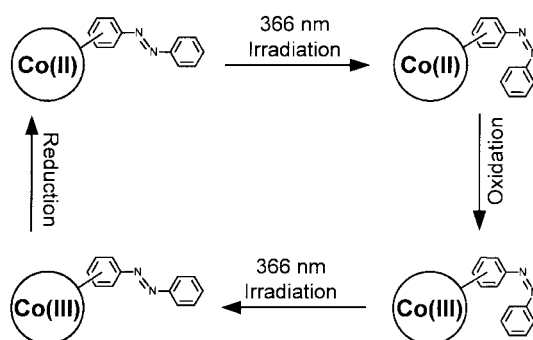

Fig. 2. Absorption spectral changes of (a) Co(II)(mAB)₃ (1.53× 10⁻⁵ mol dm⁻³) and (b) Co(III) (mAB)₃ (1.32× 10⁻⁵ mol dm⁻³) upon irradiation with monochromatic 366 nm light in CH₂Cl₂; at the initial state (all is in the trans form) (solid line) and at the photostationary state (dashed line).

Scheme 2. Redox-controlled reversible trans-cis isomerization.

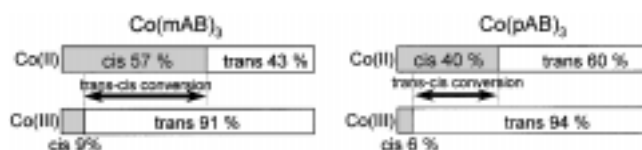**Fig. 3 Trans/cis molar ratio at the photostationary state upon irradiation with monochromatic 366 nm light for the cobalt complexes.**

but the difference in the former is not so large as that in the pAB complexes. This red-shift of the azo π–π* band may be caused by an electron-withdrawing effect of cobalt cation, which can be represented as Co(pAB) > Co(mAB) and Co(III) > Co(II).

Upon irradiation with 366 nm monochromatic light, trans-to-cis photoisomerization proceeded, and the cis molar ratio[9] reached 57% at the photostationary state in Co(II)(mAB). On the other hand, the cis molar ratio remained 9% at most, and also reached the photostationary state in Co(III)(mAB) in response to 366 nm light irradiation (Fig. 2). Because there is a substantial difference between Co(II) and Co(III) in the cis molar ratio at the photostationary state with photoirradiation at the same wavelength, Co(mAB)₃ can undergo reversible trans-cis isomerization accompanied with the Co(III)/Co(II) reversible redox reaction under constant UV irradiation (Scheme 2).

With regard to optical memory storage, larger trans/cis conversion is favorable. In our reported redox and single light system in Co(pAB), the difference between Co(II) (cis = 40%) and Co(III) (cis< 6%) is 34%. In our new Co(mAB) system, the difference is much improved; to 48% (cis = 57% in Co(II), and cis< 9% in Co(III) (Fig. 3).

It is clear that this enlargement of the difference between Co(II) and Co(III) in meta complexes is based on the modulation of electronic interaction between the cobalt ion and the azo moiety. In both Co(II) and Co(III) mAB complexes, the cis formation efficiency (cis molar ratio/trans molar ratio) with 366 nm light was doubled compared to that of the pAB complexes, and the difference between Co(II) and Co(III) was increased. This is because both Co(II) and Co(III) cations have an effect through π-conjugation to suppress the cis formation of the azo moiety, and the effect can be weakened by meta substitution. There are two possible explanations for the suppression of cis formation by coordination to cobalt; i) the trans-to-cis isomerization efficiency falls as the nature of the π-π* band is transformed during coordination to a cobalt ion, and ii) the cis-to-trans back-isomerization by excitation of the cis isomer at 366 nm occurs in a good yield. The former explanation should be adequate, because there is a relation between the π-π* band position of the trans isomer and the cis molar ratio formed in response to 366 nm irradiation. When the azo π-π* band of the trans isomer is found in longer wavelength, the efficiency of isomerization to the cis isomer drops. To investigate further, the trans-to-cis photoisomerization quantum yields of Co(II) complexes were measured[10] according to the method of Porada et al.[11] In Co(II)(mAB), the quantum yield ($\Phi_{t\rightarrow c} = 0.11$) is almost the same as that of azobenzene[11] ($\Phi_{t\rightarrow c} = 0.10$), but a lower value ($\Phi_{t\rightarrow c} = 0.07$) was obtained in Co(II)(pAB). This result has proved that the coordination to a cobalt ion affects the azo π-π* excitation state through electronic interaction, suppressing the trans-to-cis isomerization efficiency. The effect seems to be more significant in the Co(III) complexes than in the Co(II) complexes. Actually, the azo π-π* absorption band was found in a longer wavelength in the

Co(III) complexes than in the Co(II) complexes, and almost no cis isomer was formed by π-π* excitation in response to 366 nm irradiation in Co(III).

In conclusion, we succeeded in improving the performance of a redox-controlled reversible trans-cis photoisomerization system with a single light source. Construction of an electro-chemical and photochemical hybrid system utilizing azo-complex-modified electrodes is currently under investigation in our group.

Notes and References

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8. Complexes were characterized as follows. $[Co(II)(mAB)_3](BF_4)_2$ Anal. Calcd. for $C_{69}H_{54}B_2CoF_8N_{12}\cdot2H_2O$: C, 62.79; H, 4.43; N, 12.73. Found: C, 62.91; H, 4.77; N 12.82. $[Co(III)(mAB)_3](BF_4)_3$ Anal. Calcd. for $C_{69}H_{54}B_3CoF_{12}N_{12}?2H_2O$: C, 58.92; H, 4.16; N, 11.95. Found: C, 59.18; H, 4.35; N, 11.74.
9. In the Co(II) complexes, the cis molar ratio was calculated according to the method of Porada *et.al.* (ref. 11). In the Co(III) complexes, the cis molar ratio was estimated from the absorbance decrease of the azo π-π* band, which is known to show very weak absorption in the cis isomer around 350 nm.
10. It was difficult to determine an adequate value of the quantum yield for the cis-to trans isomerization because the absorption of the cis isomer was very small at the irradiated wavelength. In the Co(III) complexes, we could not measure the trans-to-cis quantum yield because absorption decrease with the selected irradiation was too small.
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