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Reversible *trans–cis* photoisomerization of azobenzene-attached bipyridine ligands coordinated to cobalt using a single UV light source and the Co(III)/Co(II) redox change

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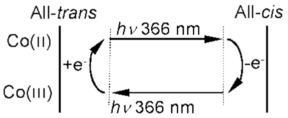
The *trans*/*cis* ratio of the azobenzene-attached bipyridine ligands in a cobalt complex is reversibly altered by a combination of photoirradiation with a single UV light source and the reversible redox change between Co(II) and Co(III).

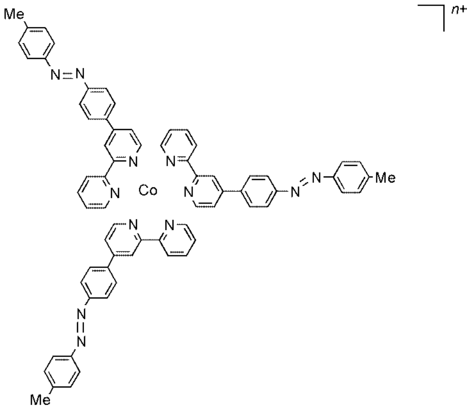
The photoisomerization of organic azobenzenes is a subject of current research interest with regard to information storage and photo-switching molecular devices.[1] Molecular motion induced by isomerization of the azo group can be controlled by a combination of UV- and visible-light irradiation, where the former (π–π* transition) achieves the *trans*-to-*cis* isomerization and the latter (n–π* transition) promotes the reverse isomerization.[2] Thus, use of two different light sources to achieve reversible molecular motion is an essential factor in the development of molecular devices.[3] An exception, which made use of a photochemical–electrochemical hybrid system, has been reported by Fujishima and coworkers.[4] Transition metal-conjugated azo compounds[5,6] can provide new advanced molecular functions utilizing combination of the photoisomerization and redox change of the metal center. In this communication, we report the first example of reversible *trans–cis* isomerization of the azo group achieved through a combination of photoirradiation and a redox cycle between Co(II) and Co(III), that makes possible both forward and backward isomerization in response to irradiation with a single light source (Scheme 1). A novel tris(azobenzene-attached bipyridine)cobalt complex was employed in this system, since both the Co(II) and Co(III) complexes are fairly stable in air under ambient conditions.



Scheme 1

A tolylazophenylbipyridine ligand, azobpy, was synthesized through the coupling of 4-(4″-anilino)-2,2′-bipyridine and 4-nitrosotoluene.[7] The Co(II) complex of azobpy, $[Co^{II}(azobpy)_3](BF_4)_2$, was obtained by reaction of $Co^{II}(NO_3)_2$ with azobpy in dichloromethane at room temperature, followed by exchange of the counter ion with NEt_4BF_4. The oxidation of $[Co^{II}(azobpy)_3]^{2+}$ was carried out with $AgCF_3SO_3$ and $[Co^{III}(azobpy)_3](BF_4)_3$ was precipitated through the addition of an excess amount of NH_4BF_4.† In the ^1H NMR spectrum, two distinct signals of the terminal methyl group and complicated signals of aromatic ring protons were derived from a mixture of *mer*- and *fac*-isomers of $[Co^{III}(azobpy)_3]^{3+}$ with respect to three tolylazophenyl groups.

In a cyclic voltammogram of $[Co^{II}(azobpy)_3](BF_4)_2$, a reversible Co(III)/(II) redox wave and a quasi-reversible Co(II)/(I) redox wave were observed at −0.15 and −1.27 V *vs.* ferrocenium/ferrocene (Fc^+/Fc) in dichloromethane, respectively.



$[Co(azobpy)_3]^{n+}$
($n = 2, 3$)

UV–VIS absorption spectra of azobpy, $[Co^{II}(azobpy)_3](BF_4)_2$ and $[Co^{III}(azobpy)_3](BF_4)_3$ showed π–π* bands due to the azo group at $\lambda_{max} = 345$ nm ($\varepsilon = 3.5 \times 10^4$ mol^{-1} dm^3 cm^{-1}), 360 (1.1×10^5) and 374 (9.7×10^4), respectively. An increase in the electron-withdrawing effect on the azo group in response to the oxidation of Co(II) to Co(III) resulted in a lower energy of the π–π* band.[8] Upon irradiation to the dichloromethane solution of azobpy with UV light at 366 nm,‡ the π–π* band decreased and the n–π* band of the azo group at 445 nm increased in intensity, showing a typical *trans*-to-*cis* isomerization of the azobenzene moiety [Fig. 1(a)]. The molar ratio of the *cis*-form reached 92% in the photostationary state (PSS). The spectral change of $[Co^{II}(azobpy)_3](BF_4)_2$ in dichloromethane is essentially similar to that of azobpy upon irradiation with the 366 nm light, and 40% of the *trans*-azobenzene moiety was found to be changed into the *cis*-form in PSS [Fig. 1(b)]. The irradiation with 438 nm light reversed the spectral change, indicating a *cis*-to-*trans* isomerization. Intriguingly, almost no decrease in absorbance of the π–π* band of $[Co^{III}(azobpy)_3](BF_4)_3$ was observed under the same 366 nm light irradiation, suggesting that the *cis*-to-*trans* back-reaction of the Co(III) complex is much more effective than that of the Co(II) complex in PSS (*vide infra*).

The difference in the *cis*-form concentrations in PSS between Co(II) and Co(III) described above indicates the possibility of a reversible *trans–cis* conversion with single monochromatic light irradiation by changing the redox state between Co(II) and Co(III). To test this hypothesis, we carried out the following experiments. A dichloromethane solution of the *trans*-form of $[Co^{II}(azobpy)_3](BF_4)_2$ was irradiated with 366 nm light to reach PSS, and the resulting mixture of *trans*- and *cis*-forms was oxidized with a stoichiometric amount of 1,1′-dichloroferrocenium hexafluorophosphate, $[Fe(\eta^5\text{-}C_5H_4Cl)_2]PF_6$ ($E^{0\prime} = 0.19$ V *vs.* Fc^+/Fc).[5] The ratio of the *cis*-form remained constant after the oxidation, the thermal isomerization to the *trans*-form proceeding very slowly in the dark [the recovery of absorbance of the π–π* band was not pronounced in intensity over 30 min

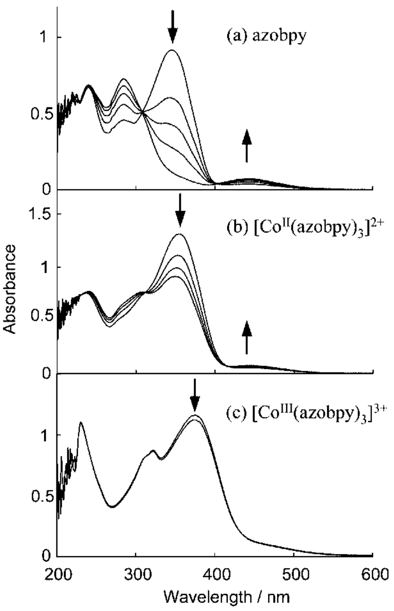


Fig. 1 UV–VIS absorption spectral change of azobpy (2.62×10^{-5} mol dm^{-3}) (a), [Co^{II}(azobpy)](BF$_4$)$_2$ (1.17×10^{-5} mol dm^{-3}) (b), and [Co^{III}(azobpy)](BF$_4$)$_3$ (1.20×10^{-5} mol dm^{-3}) (c), in dichloromethane upon irradiation with 366 nm light.

Fig. 2(b)]. When the oxidized solution was exposed again to 366 nm light, the *cis*-to-*trans* photoisomerization promptly occurred to create the *trans*-rich PSS which is characteristic of the Co(III) state, accompanied by a fast increase in the absorbance of the π–π* band within a few minutes [Fig. 2(a)]. The Co(III) complex in PSS upon irradiation with 366 nm light was re-reduced with a stoichiometric amount of 1,1′-acetylcobaltocene, [Co(η^5-C$_5$H$_4$COMe)$_2$] ($E^{0\prime} = -0.76$ V *vs.* Fc$^+$/Fc)[9] and the exposure to the same 366 nm light resulted in a *trans*-to-*cis* isomerization to reach the different PSS that is characteristic of the Co(II) state. These results suggest that a reversible *trans*–*cis* isomerization can be achieved by a combination of the reversible redox change between Co(II) and Co(III) and irradiation with a single UV light source, which is a novel route differing from the reversible isomerization of general organic azobenzenes with a combination of π–π* and n–π* excitation employing UV and visible light, respectively (Scheme 1).

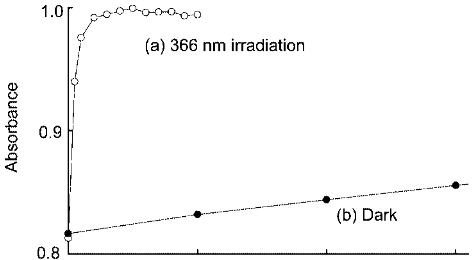


Fig. 2 Change in absorbance at 360 nm with time upon irradiation with 366 nm light (○) and in the dark (●) after a dichloromethane solution of [Co^{II}(azobpy)$_3$](BF$_4$)$_2$ (1.04×10^{-5} mol dm^{-3}) was first irradiated with 366 nm light to reach PSS and then oxidized with [Fe(η^5-C$_5$H$_4$Cl)$_2$]PF$_6$.

The redox-coupled photoisomerization system described above may enable continuous control of total conversion to the *cis*-form of azobenzene moieties in PSS by means of a continuous change in Co(II) to Co(III) complex molar ratio upon irradiation with monochromatic 366 nm light. Solutions consisting of various molar ratios of the Co(III) complex, *x*, were prepared by the addition of *x* equivalents of [Fe(η^5-C$_5$H$_4$Cl)$_2$]PF$_6$ to the solution of [Co^{II}(azobpy)$_3$](BF$_4$)$_3$, which was then irradiated with 366 nm light. After reaching PSS within a few minutes, the Co(II) component was oxidized with

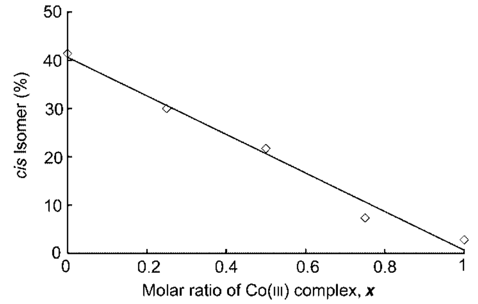


Fig. 3 Correlation between the conversion ratio of the *cis*-form and the molar ratio, *x*, of the Co(III) complex.

$1 - x$ equivalents of [Fe(η^5-C$_5$H$_4$Cl)$_2$]PF$_6$ to estimate the total formation ratio of the *cis*-azobenzene moiety by using the absorbance of the π–π* band normalized as the Co(III) complex (Fig. 3). The contribution of thermal *cis*-to-*trans* isomerization to the *cis* ratio can be neglected, as the process proceeds very slowly compared to the photo-process, as already mentioned. The conversion ratio of the *cis*-form was found to linearly correlate with the ratio *x* within 0–40%. A similar continuous control of the conversion ratio of the *cis*-form for organic azobenzenes can be achieved by tuning the relative intensities of two different monochromatic light sources or by selection of a suitable excitation wavelength closely associated with overlapping of the π–π* and n–π* bands. Compared with these photochemical methods, the combination of the photoisomerization and the redox processes of the metal complex-conjugated azobenzene is a more facile and precise pathway to adjust the *cis* conversion ratio.

In conclusion, reversible *trans*–*cis* isomerization has been achieved by a combination of the reversible redox reaction between Co(II) and Co(III) and single UV-light irradiation. This method should provide a new design for photochemical and electrochemical hybrid molecular devices. We are currently expanding the method developed in the present study to a modified electrode system in which the redox state of Co can be controlled electrochemically.

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Notes and references

† *Characterisation data*: [Co^{II}(azobpy)$_3$](BF$_4$)$_2$; ESI-MS: *m/z* 554.7 ([M − 2BF$_4$]$^{2+}$). Anal. Calc. for C$_{69}$H$_{542}$CoF$_8$N$_{12}$·3.5H$_2$O: C, 61.53; H, 4.56; N, 12.48. Found C, 61.55, H, 4.50; N, 12.34%. [Co^{III}(azobpy)$_3$](BF$_4$)$_3$; ESI-MS: *m/z* 1283 ([M − BF$_4$]$^+$). Anal. Calc. for C$_{69}$H$_{54}$B$_3$CoF$_{12}$N$_{12}$·3H$_2$O: C, 58.17; H, 4.24; N, 11.80. Found C, 58.11, H, 4.27; N, 11.62%.

‡ The light source was a super-high-pressure mercury lamp (500 W, USHIO Electronic. Inc.) and the wavelength was selected with a monochromator (Jasco CT-10).

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