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# Photo- and Protonation-Induced Changes in Structures and Physical Properties of Azo-Conjugated Metal Complex Systems

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**Summary:** Novel photo- and proton-coupled behavior of azo-conjugated metal complexes is described. The trans-to-cis isomerization of azoferrocene proceeds not only by the photoexcitation of the π-π* transition band but also by photoexcitation of the MLCT (d-π* transition) band, by a protonation-deprotonation cycle (proton-coupled isomerization), and by an oxidation-reduction cycle (redox isomerization). A platinum tolylazophenylenedithiolato complex shows reversible trans-to-cis photoisomerization, protochromism, and novel proton-coupled cis-to-trans isomerization.

## Introduction

Intelligent molecules, the structures and properties of which are facilely and reversibly changeable by application of external physical and chemical stimuli, have attracted much recent attention relative to the development of new molecule-based devices. One category of such molecules is comprised of transition metal complexes with π-conjugated spacers; the combination of flexibility of d- and π-orbitals can yield unique optical, magnetic, and electronic properties. We have been studying azo-conjugated metal complexes as examples of such metal complexes.[1-9] In this paper we present novel photo- and proton-coupled isomerization behavior of azoferrocene and azo-conjugated platinaditiolene.

## Azoferrocene

Azoferrocene, **1**, is one of the π-conjugated ferrocene dimers and also one of the simplest analogues of azobenzene, having two redox-active metal complex units.[10] X-ray crystallography of an azoferrocene crystal obtained under ambient conditions

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demonstrated that the azo moiety is in the trans-form, the two cyclopentadienyl rings and the azo moiety are on almost the same plane, and the ferrocenyl moieties are on the opposite side of the plane, leading to that the Fe-Fe distance is 6.80 Å.[1]

The trans-azo bridge acts as a spacer assisting in the electron exchange between ferrocenyl moieties. The cyclic voltammogram of **1** in $Bu_4NClO_4$-benzonitrile exhibits reversible 1e$^-$ oxidation waves at $E^{0'}$ = 0.08 and 0.29 V versus ferrocenium/ferrocene, indicating the formation of a thermodynamically stable mixed-valence cation and the strong electron-withdrawing effect of the azo group.[1]

In addition to the strong π–π* transition of the azo group at 318 nm, strong d-π* transition (MLCT) bands from an Fe(II) d-orbital to a π*-orbital of Cp-N=N-Cp (Cp = $\eta^5$-cyclopentadienyl) appear in the neutral trans-form of trans-**1.** The absorption of the MLCT band at 534 nm diminished, and a new band appeared and increased at 672 nm with the oxidation to $\mathbf{1}^+$. The new band can be identified as a ligand-to-metal charge transfer (LMCT) band associated with an electron transfer from the π-orbital of the azo group to a Fe(III) d-orbital. A more donating solvent afforded the higher IT and LMCT energies of **1** in the mixed-valence states, [1] indicating a hole-transfer mechanism.[11]

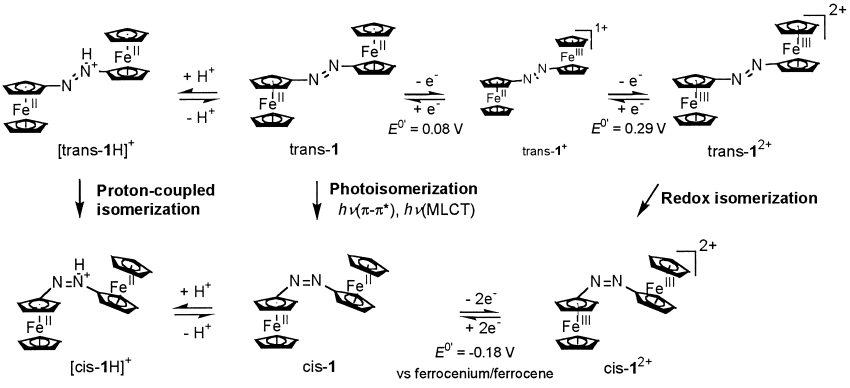
Photo-irradiation of trans-**1** in acetonitrile exposed to UV (365 nm) light from a super high pressure Hg lamp, caused a decrease of the π-π* band and an increase of a new band at 368 nm in intensity, showing isosbestic points.[2] This spectral change indicates the occurrence of trans-to-cis isomerization. The photoisomerization of trans-**1** also proceeded through MLCT with a green (546 nm) light.[4] This is a rare example of isomerization using a low energy band; different from the π-π* transition band. The $\Phi_{t\rightarrow c}$ values at 365- and 546-nm light irradiation are 0.002 and 0.03, respectively.[2] Photoisomerization of trans-**1** was accelerated in polar solvents such as acetonitrile, benzonitrile, and DMSO, and greatly suppressed in less polar solvents such as toluene.

In the cyclic voltammogram of trans-**1** in $Bu_4NClO_4$-benzonitrile after UV light-irradiation, an additional reversible oxidation wave originating from cis-**1** appeared at $E^{0'}$ = -0.18 V versus ferrocenium/ferrocene, and there was no distinct separation of the two 1e$^-$ (i.e., apparently one-step 2e$^-$) waves. This indicates that the mixed-valence state is thermodynamically less stable, due to the fact that the internuclear electronic interaction between the two iron centers, Fe(II) and Fe(III), is significantly weak through the π-conjugated linker of Cp-N=N-Cp in cis-**1**.[2] The loss of the planarity is deduced to be a dominant factor in the weakness of the internuclear electronic interaction in cis-**1**, and in the electrochemical independence of the two iron centers.

Novel protonation- and redox-induced trans-to-cis isomerization of **1** has been also discovered (Scheme 1).[4] In the presence of organic acids, such as $CF_3COOH$ and $CF_3SO_3H$, the azo group of trans-azoferrocene, trans-**1**, was protonated to afford the monoprotonated form, [trans-**1**H]$^+$, which was changed into [cis-**1**H]$^+$ in the dark. The isomerization from [trans-**1**H]$^+$ to [cis-**1**H]$^+$ was accelerated by blue-light irradiation at 436 nm, which corresponds to the intense band of [trans-**1**H]$^+$.

The two-electron oxidized form of trans-**1**, trans-**1**$^{2+}$ was changed into cis-**1**$^{2+}$, accompanied by the red shift of the LMCT band. The chemical oxidation of trans-**1** using an excess amount of 1,1'-dichloroferrocenium hexafluorophosphate resulted in the appearance of a new reversible redox wave at $E^{0'}$ = -0.24 V versus ferrocenium/ferrocene, of which the redox potential is consistent with that of the photo-generated cis-**1**.

Scheme 1.



## Azo-conjugated platinaditiolene

We synthesized a new azo-conjugated benzenedithiolato complex of platinum, **2**, and found reversible photoisomerization and protonation behavior and the protonation catalyzed cis-to-trans isomerization of **2**.[8]

X-ray crystallography of **2** indicates that the configuration around the Pt center is a typical tetra-coordinated square-planar structure, and the configuration of the azo moiety is trans, but the planarity of the azobenzene moiety is significantly distorted, with the torsion angle of 55.3°. The N-N bond length is 1.32(2) Å, which is significantly longer than the usual 1.23-1.24 Å values for azobenzene compounds. These novel features indicate the existence of strong conjugation between the azo and the metalladithiolene moieties.

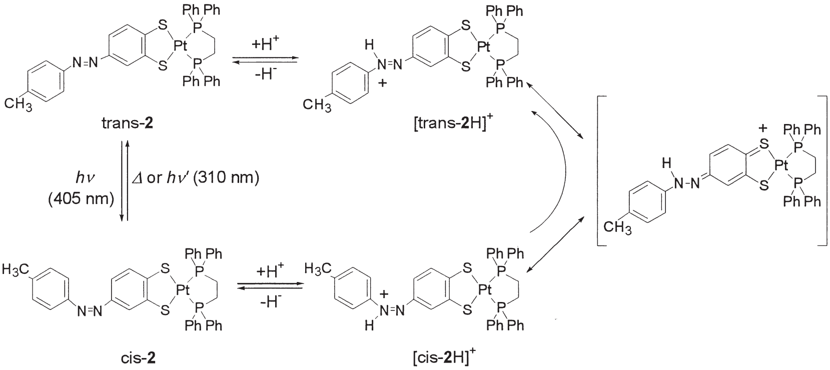
A $\pi-\pi^*$ transition band ascribable to the azo moiety in **2** was observed at 405 nm ($\varepsilon$ = 25600 $\mathrm{mol^{-1}dm^{3}cm^{-1}}$), which is longer wavelength (lower energies) compared with regular azobenzene derivatives. This supports the strong azo-metalladithiolene electronic interaction as indicated in the X-ray structure. The $\pi-\pi^*$ transition band decreased in intensity after photoirradiation, indicating the occurrence of trans-to-cis photoisomerization.

The cis-to-trans back reaction occurred, allowing for a perfect recovery of the spectra of the trans forms, in response to thermal reaction or photoirradiation at 310 nm. Although the transition corresponding to these UV light energies have not been specified at present, it is intriguing that the cis-to-trans isomerization is promoted by UV light with an energy higher than the $\pi-\pi^*$ transition, since the regular azobenzenes undergo isomerization by irradiating the n-$\pi^*$ band in the visible region. The rate constant of the thermal cis-to-trans isomerization of **2** at 23.3 °C was estimated to be $3.5 \times 10^{-5}\ \mathrm{s^{-1}}$.

The color of trans-**2** in acetonitrile was changed drastically from yellow to deep blue by an addition of $CF_3SO_3H$, showing that the $\pi-\pi^*$ transition band of the azo moiety at 400 nm decreases in intensity, and that a new strong band appeared at 590 nm. The reverse spectral changes were achieved with the addition of potassium *tert*-butoxide. The single protonation was supported by a result of ESI-mass spectroscopic measurement, showing a peak at m/z 852.3 and its isotope pattern of [**2**-H]$^+$. The protonation to the nitrogen atom bound to the tolyl moiety is reasonable in affording the conjugated structure that delocalizes the charge beyond the metalladithiolene moiety. The 590 nm band can be assigned to the metalladithiolene π → azo group π* charge-transfer transition. The metalladithiolene moiety, which is strongly conjugated with the azo group, increases the basicity of the azo group with a resonance stabilization effect to cause the facile protonation behavior.

When a slight amount of acid was added to a solution containing cis-**2** prepared by photoirradiation, cis-**2** transformed into trans-**2** immediately. The rate constant of this isomerization on addition of 0.01 equivalents of $CF_3SO_3H$ was $4.6 \times 10^{-3}$ $s^{-1}$, which is larger than that of the thermal isomerization by two orders of the magnitude. This phenomenon indicates that a protonated cis form, [cis-**2**H]$^+$ instantly produces the trans form [trans-**2**H]$^+$ (Scheme 2). It can be deduced that the N=N bonding is weakened by bonding as a limiting structure. The rotation around the N-N bond is facile, and consequently, thermodynamically favorable trans-**2** is generated (Scheme 2).

Scheme 2.



## Conclusion

The results described above indicate that both the azo-conjugated ferrocene and metalladithiolene systems show trans-cis isomerization behavior responsive to both photon and proton, but the behavior is strongly dependent of the metal complex moieties. These metal complex systems would be useful to develop a multi-mode switching and information storage system in the molecular level.

[1] M. Kurosawa, T. Nankawa, T. Matsuda, K. Kubo, M. Kurihara, H. Nishihara, *Inorg. Chem.* **1999**, *38*, 5113.
[2] M. Kurihara, T. Matsuda, A. Hirooka, T. Yutaka, H. Nishihara, *J. Am. Chem. Soc.* **2000**, *122*, 12373.
[3] H. Nishihara, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 19.
[4] M. Kurihara, T. Matsuda, A. Hirooka, T. Yutaka, H. Nishihara, submitted.
[5] T. Yutaka, M. Kurihara, K. Kubo, H. Nishihara, *Inorg. Chem.* **2000**, *39*, 3438.
[6] T. Yutaka, M. Kurihara, H. Nishihara, *Mol. Cryst. Liq. Cryst.* **2000**, *343*, 193.
[7] T. Yutaka, I. Mori, M. Kurihara, J. Mizutani, K. Kubo, S. Furusho, K. Matsumura, N. Tamai, H. Nishihara, *Inorg. Chem.*, in press.
[8] M. Nihei, M. Kurihara, J. Mizutani, H. Nishihara, *Chem. Lett.*, in press.
[9] S. Kume, M, Kurihara, H. Nishihara, *Chem. Commun.*, in press.
[10] A. N. Nesmeyanov, E. G. Perevalova, T. V. Nikitina, *Dokl. Akad. Nauk SSSR* **1961**, *138*, 118.
[11] C. Creutz, M. D. Newton, N. Sutin, *J. Photochem. Photobiol. A: Chem.* **1994**, *82,* 47.