Photo- and Proton-Coupled Isomerization of Novel Azo-Conjugated Platinadithiolene Complex

Masayuki Nihei, Masato Kurihara, Jun Mizutani, and Hiroshi Nishihara*
Department of Chemistry, School of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033

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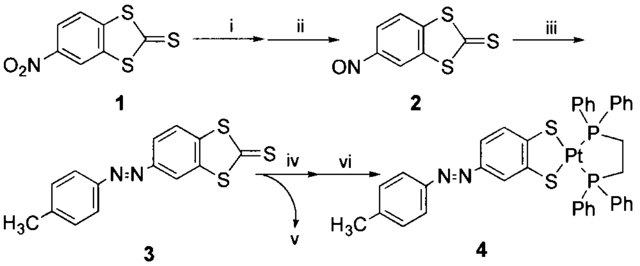
A platinum tolylazophenylenedithiolato complex was synthesized. This new azo-conjugated complex shows reversible trans-to-cis photoisomerization, protochromism, and novel proton-coupled cis-to-trans isomerization.

Azobenzene derivatives undergo reversible trans-to-cis photoisomerization and cis-to-trans thermal isomerization.[1] Combining the azo moiety with functional metal complexes is a tactic for creating intelligent molecular systems, but only a limited number of reports on the photoisomerizable azo-conjugated complexes are available.[2] Metalladithiolenes[3] with aromatic nature exhibit a number of interesting properties including reversible redox activity[4] and various chemical reactivities.[5] Thus, the combination of dithiolene complexes with the azo group can afford photo-responsive multi-functional molecules. In the present study, we synthesized a precursor for a new azo-conjugated benzenedithiolato ligand **3**, as well as its Pt complex **4**, and found reversible photoisomerization and protonation behavior and the protonation catalyzed cis-to-trans isomerization of **4**.

Scheme 1



Reagents: i, Zn, NH_4Cl, $MeOCH_2CH_2OH$; ii, $FeCl_3$•$6H_2O$; iii, *p*-toluidine, CH_3COOH, MeOH; iv, PhLi, THF; v, S=C(Ph)$_2$; vi, dppePtCl$_2$.

The precursor of a tolylazobenzodithiolato ligand **3** was synthesized from 5-nitro-2-thioxo-1,3-benzodithiole **1**[6] by a three-step reaction (Scheme 1). In the first step, **1** was reduced to afford a nitroso compound **2**, [7] by zinc and iron(III) chloride via a hydroxyamino compound as an intermediate. A reaction of **2** and *p*-toluidine afforded **3**[7] in a moderate yield. Tolylazobenzenedithiolato complex **4**[7] was prepared by a reaction of **3** with phenyllithium, which led to a cleavage of the protecting group, followed by an addition of dichloro[1,2-bis(diphenylphosphiono)ethane]platinum(II). The compound **4** was characterized by elemental analysis, ^{1}H NMR, and UV–vis spectroscopy. The low yield of **4**, 8.2% from **3**, appears to have been due to nucleophilic side reactions accompanying the cleavage of the protecting group by phenyllithium.

An ORTEP diagram of the molecular structure of **4** is displayed in Figure 1 with the selected bond lengths, angles and torsion angles in the footnote.[8] The configuration around the Pt center is a typical tetracoordinated square-planar structure. The bond lengths of Pt–S1 and Pt–S2 are 2.310 Å and 2.316 Å, respectively, both of which lie within the usual range of Pt–S distances for Pt dithiolene complexes.[9] The configuration of the azo moiety is trans, but the planarity of the azobenzene moiety[10] is significantly distorted, with the torsion angle of C12–C7–C5–C4 being 55.3°. The bond length of N1–N2 is 1.32(2) Å, which is significantly longer than the usual 1.23–1.24 Å values for azobenzene compounds.[10] These novel features indicate the existence of strong conjugation between the azo and the metalladithiolene moieties.

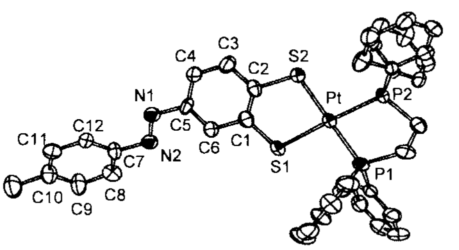


Figure 1. ORTEP plot of **4** with 50% probability ellipsoids. Selected bond lengths [Å], angles[°] and torsion angles[°]: Pt-S1 2.310(10), Pt-S2 2.316(6), Pt-P1 2.259(6), Pt-P2 2.260(9), S1-C1 1.75(5), S2-C2 1.76(2), N1-N2 1.32(2), N1-C5 1.42(2), N2-C7 1.44(2), S1-Pt-S2 88.5(5), S1-Pt-P1 92.4(5), P1-Pt-P2 85.3(5), C4-C5-N1 116.8(17), C5-N1-N2 113.7(15), N1-N2-C7-C12 -27.7(29), C5-N1-N2-C7 174.5(16), N2-N1-C5-C6 -26.6(25).

UV–vis spectra of **4** before and after photoirradiation with a UV light as shown in Figure 2. A π–π* transition band ascribable to the azo moiety can be observed at 405 nm (ε = 25600 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 π–π* transition band decreased in intensity after photoirradiation (Figure 2), 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

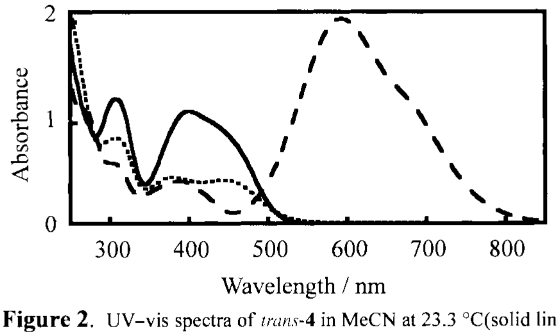


Figure 2. UV–vis spectra of *trans*-**4** in MeCN at 23.3 °C(solid line), after photoirradiation at 405 nm (dotted line), and after addition of 7.5 equivalents of CF_3SO_3H (dashed line).

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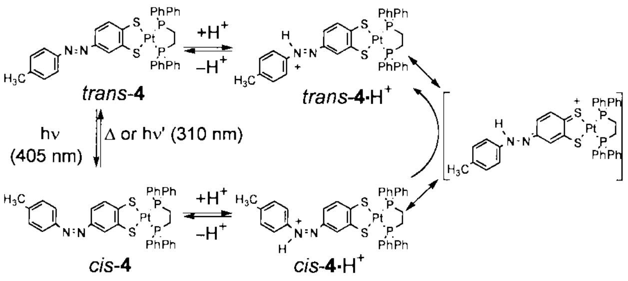
thermal reaction or photoirradiation at 310 nm. Although the transition corresponding to these UV light energies have not been specified at present, it is intriguing that the cis-to-trans isomerization is promoted by UV light with an energy higher than the π–π* transition, since the regular azobenzenes undergo isomerization by irradiating the n–π* band in the visible region.[1] The rate constant of the thermal cis-to-trans isomerization of **4** at 23.3 °C is estimated to be 3.5×10^{-5} s^{-1}.

The color of *trans*-**4** in acetonitrile was changed drastically from yellow to deep blue by an addition of 7.5 equivalents of CF_3SO_3H (Figure 2), showing that the π–π* transition band of the azo moiety at 400 nm decreases in intensity, and that a new strong band appears at 590 nm. The reverse spectral changes were achieved with the addition of potassium *tert*-butoxide. This spectral behavior is similar to that of *N*-heterocycle-substituted metalladithiolenes,[11] indicating that there is protonation of the azo moiety (Scheme 2). The single protonation is supported by a result of ESI-mass spectroscopic measurement, which shows a peak at *m/z* 852.3 and its isotope pattern of **4**·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.

Scheme 2



When a slight amount of acid is added to a solution containing *cis*-**4** prepared by photoirradiation, *cis*-**4** transforms into *trans*-**4** immediately. The rate constant of this isomerization on addition of 0.01 equivalents of CF_3SO_3H is 4.6×10^{-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*-**4**·H^+ instantly produces the trans form *trans*-**4**·H^+ (Scheme 2). It can be deduced that the N=N bonding is weakened by the protonation to the azo group, and the rupture of the N=N π-bond forms a –NH–N= bonding as a limiting structure. The rotation around the N–N bond is facile, and consequently, thermodynamically favorable *trans*-**4** is generated (Scheme 2).

The results described above indicate that the azo-conjugated metalladithiolene system shows trans-cis isomerization behavior responsive to both photon and proton, which would be useful to develop a multi-mode switching and information storage system in the molecular level.

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7 Selected Data for **2**: Yield 74.2 %, Anal. Calcd for $C_7H_3N_1O_1S_3 \cdot 0.6H_2O$: C,37.52; H, 1.89; N, 6.25%. Found: C, 37.43; H, 1.95; N, 5.99%. ^1H NMR (270 MHz, $CDCl_3$): δ 8.03 (dd, *J* = 11.1, 2.2 Hz 1H, Ph), 7.87 (d, *J* = 2.2 Hz 1H, Ph), 7.73 (d, *J* = 11.1 Hz 1H, Ph). Selected Data for **3**: Yield 43.0 %, Anal. Calcd for $C_{14}H_{10}N_2S_3 \cdot 0.25H_2O$: C,54.78; H, 3.45; N, 9.13%. Found: C, 54.86; H, 3.32; N, 9.19%. ^1H NMR (270 MHz, $CDCl_3$): δ 8.01 (d, *J* = 2.2 Hz 1H, Ph), 7.97 (dd, *J* = 11.5, 2.2 Hz 1H, Ph), 7.84 (d, *J* = 11.1 Hz 2H, Tol), 7.61 (d, *J* = 11.5 Hz 1H, Ph), 7.34 (d, *J* = 11.1 Hz 2H, Tol), 2.46(s, 3H, Me). Selected Data for **4**: Yield 8.2 %, Anal. Calcd for $C_{39}H_{34}N_2P_2S_2Pt \cdot 2H_2O$: C, 54.99 ; H, 4.02 ; N, 3.29 %. Found: C, 54.90; H, 4.08; N, 3.30%. ^1H NMR (270 MHz, $CDCl_3$): δ 8.12 (d, *J* = 3.0 Hz 1H, Ph), 7.92–7.78 (m, 8H, dppe), 7.74 (d, *J* = 11.5 Hz 2H, Tol), 7.50–7.47 (m, 12H, dppe), 7.62 (d, *J* = 11.1 Hz 1H, Ph), 7.43 (dd, *J* = 3.0 Hz, 11.1 Hz 1H, Ph), 7.24 (d, *J* = 11.5 Hz 2H, Tol), 2.51 (d, *J* = 24.8 Hz 4H, dppe), 2.39(s, 3H, Me).

8 Crystal data for **4**: $C_{40}H_{36}N_2P_2S_2PtCl_2$, M_r = 936.80, monoclinic, space group $P2_1/a$, a = 15.4919(11), b = 16.100(3), c = 15.215(2) Å, β = 94.7(7)°, V = 3782.2(9) $Å^3$, Z = 4, $\rho_{\chi alc}$ = 1.645 g cm^{-3}, of 40337 reflections ($2\theta_{max}$ = 55.0°), 8867 were unique. R = 0.063, R_w = 0.089. Crystallographic data (excluding structural factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-155723. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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