

Photo-controllable tristability of a dithiolato-bipyridine-Pt(II) complex molecule containing two azobenzene moieties†

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A new platinum complex with both an azo-bound dithiolato ligand and an azobenzene-bound bipyridine ligand exhibits tristability reversibly controllable using different energy lights.

The accumulation of multiple photo- and electro-functions in a single molecule has been pursued extensively as a step toward the realization of molecular devices.¹ We have been investigating azo-conjugated metal complexes to create molecules having the functions of both photoisomerizable azobenzene and redox-active transition metal complex moieties. For example, a redox-conjugated reversible isomerization system with a single green light source using ferrocenylazobenzene was created.²

In a series of photochromic complexes of our investigation, azobenzene-conjugated metalladithiolenes with d⁸ transition metals have shown unique photoisomerization behaviour, in which *trans*-to-*cis* isomerization proceeds upon irradiation with longer wavelength, 405 nm purple light.^{3,4a} On the other hand, all of the azobenzene-conjugated transition metal polypyridine complexes reported thus far undergo regular *trans*-to-*cis* photoisomerization upon irradiation of the azobenzene π - π^* band with UV light around 365 nm.⁵

From the viewpoint of function accumulation, we aimed to install two azobenzenes with different photochemical abilities in a single molecule to obtain multi-stability driven only by light sources. As a result, we synthesized a new Pt(II) complex, **3**,⁶ that bears an azobenzene on a dithiolato ligand and another on a bipyridine ligand (Fig. 1). In complex **3**, the Pt(II) center can affect the photochemical behaviour of both azobenzenes on the ligands. Complex **3** is a kind of dithiolato-diimine-Pt(II) complex,⁷ which is known as a photochemically active compound having strong absorption in the visible region assignable to a mixed-metal/ligand-to-ligand charge transfer (MMLL'/CT) band^{7b} and showing phosphorescence from the ³MMLL'/CT state at room temperature.⁷ We have succeeded in utilizing the excitation energy of the MMLL'/CT state towards *cis*-to-*trans* isomerization of both the azobenzenes, thereby extending the photoresponse across the UV region and all of the visible region as well as establishing individual control over the *trans*-to-*cis* photoisomerization of each

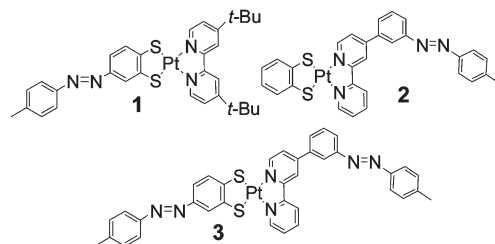


Fig. 1 Azobenzene-conjugated dithiolato-bipyridine-Pt(II) complexes 1–3.

azobenzene. In this communication, we also report on the photoresponses of **1** bearing an azobenzene on the metalladithiolene side, and **2** with one on the bipyridine side (Fig. 1), in order to clarify our explanation of the photoresponse of complex **3**. The mechanism of unique photoisomerization of the azobenzene on the metalladithiolene side was also clarified based on time-dependent density functional theory (TD-DFT) calculations.

Complex **1**† showed four characteristic absorptions I–IV in its electronic spectrum in dichloromethane (Fig. 2(A)(a)). By irradiation with 405 nm purple light corresponding to the energy gap of band II, significant reductions were observed in bands I, II, and III (Fig. 2(A)(b)). This behaviour quite resembles that of the *trans*-to-*cis* photoisomerization of the azobenzene-conjugated metalladithiolenes previously reported, the co-ligand of which was 1,2-bis(diphenylphosphino)ethane.³ This phenomenon was also traced with ¹H-NMR spectroscopy (Fig. S3†), revealing remarkable upfield shifts of the protons located at the azobenzene moiety. The percentage of *cis*-isomer in the photostationary state (PSS) of

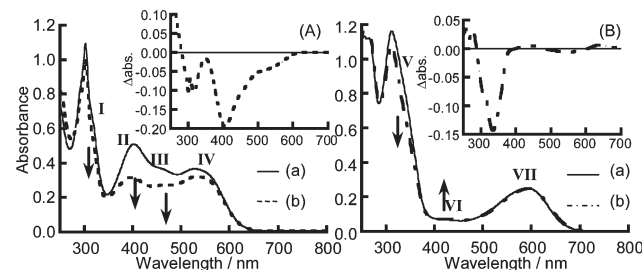


Fig. 2 (A) Electronic spectra of **1** in dichloromethane (a, solid line) and in the PSS upon irradiation with 405 nm light (b, dotted line). The inset shows the difference in the spectra, (b) – (a). (B) Electronic spectra of **2** in dichloromethane (a, solid line) and at the PSS upon irradiation with 365 nm light (b, broken line). The inset shows the difference in the spectra, (b) – (a).

† Electronic supplementary information (ESI) available: ORTEP drawings of complexes **1** (Fig. S1) and **2** (Fig. S2), ¹H-NMR spectra of complexes **1** (Fig. S3), **2** (Fig. S7) and **3** (Fig. S8 and S9) before and after irradiation with monochromatic light, the main transitions in bands I–IV (Fig. S4) and V–VII (Fig. S6) calculated with TD-DFT, emission spectra of complexes **1**–**3** upon excitation of the MMLL'/CT band (Fig. S5), and experimental section. See <http://www.rsc.org/suppdata/cc/b4/b415293j/> *sugimoto@kumamoto-u.ac.jp (Manabu Sugimoto) nishihara@chem.s.u-tokyo.ac.jp (Hiroshi Nishihara)

was estimated to be 45% from the integral ratio of the methyl group at the top of the azobenzene moiety. To clarify the mechanism underlying this unique photoisomerization behaviour, the TD-DFT calculation was carried out (Fig. S4). The result indicates that band II is assignable to a transition from the metalladithiolene(π) to the azobenzene(π^*) level. Therefore the red shift of the *trans*-to-*cis* isomerization wavelength in complex 1 is induced in quite a different way from that of donor/acceptor-substituted azobenzenes.^{4b} Such an MLCT-like transition, which induces *trans*-to-*cis* photoisomerization, is also observed in ferrocenylazobenzenes.²

Table 1 presents in detail the relationship between photoirradiation wavelengths and *cis*-isomer percentages in the PSS of complex 1. Irradiation with 436 nm blue light, corresponding to band III, also afforded a *cis*-conversion to some extent. This phenomenon is elucidated with the MO calculation (Fig. S4†), which describes that a main transition in band III is quite similar to that in band II. It seems possible that band I, assignable to a π - π^* transition of the azobenzene moiety, participates in the *trans*-to-*cis* photoisomerization. However, a high *cis*-isomer percentage was not attained upon irradiation with 312 nm UV light. Excitation of band IV, assignable to an MMLL/CT band with 578 nm yellow light, resulted in *cis*-to-*trans* isomerization. Phosphorescence from the ³MMLL/CT state was thoroughly quenched (Fig. S5b). This is consistent with the consumption of the MMLL/CT excitation energy for the *cis*-to-*trans* conversion. This is the first report that *cis*-to-*trans* isomerization was held by excitation of such the low-lying CT band.

In the electronic spectrum of complex 2† in dichloromethane, three characteristic bands, V–VII, were observed (Fig. 2(B)(a)). Bands V–VII were intuitively assignable to the π - π^* bands of the azobenzene and bipyridine moieties, an n - π^* band of the azobenzene moiety, and an MMLL/CT band, respectively, and the TD-DFT calculation favored this speculation (Fig. S6†). Among the other azobenzene-conjugated bipyridine complexes,⁵ complex 2 showed orthodox photoisomerization behaviour except for upon excitation of the MMLL/CT band. Table 1 presents in detail the relationship between photoirradiation wavelengths and *cis*-isomer percentages in the PSS of complex 2. This complex displayed *trans*-to-*cis* photoisomerization upon irradiation with 365 nm UV light (Fig. 2(B)(b)), and the percentage of *cis*-isomer in the PSS was 23%, estimated by the same method as in the case of complex 1 (Fig. S7†). In contrast, upon irradiation with 436 nm blue light, the PSS was biased in the *trans*-rich direction.

Table 1 The relationship between photoirradiation wavelengths and *cis*-isomer percentages in the PSS of 1–3

λ /nm	Proportion of <i>cis</i> -isomer (%)			
	1	2	Metalladithiolene-3	Bipyridine-3
312	17 ^a	16 ^a	21 ^a	33 ^a
334	20 ^a	24 ^a	21 ^a	50 ^a
365	21 ^a	23 ^b	22 ^b	45 ^b
405	45 ^b	7 ^a	44 ^b	9 ^b
436	37 ^a	8 ^a	32 ^b	10 ^b
546	15 ^a	5 ^a	7 ^b	6 ^b
578	14 ^a	5 ^a	8 ^b	4 ^b

^a Calculated from the UV-vis spectra with the values from the ¹H-NMR spectra as the standard. ^b Calculated from the ¹H-NMR spectra.

Moreover, unlike the other azobenzene-conjugated bipyridine complexes, complex 2 showed *cis*-to-*trans* isomerization by the excitation of the MMLL/CT band with 578 nm yellow light, as complex 1 did. Quenching of phosphorescence from the ³MMLL/CT state was also observed (Fig. S5c†), implying the consumption of the excitation energy for the isomerization of the azobenzene moiety.

In summary, the intrinsic *trans*-to-*cis* photoisomerization behaviour of the azobenzene moieties on the metalladithiolene³ and bipyridine⁵ sides was almost retained in complexes 1 and 2 despite the existence of the low-lying MMLL/CT bands.

Complex 3, bearing an azobenzene on both the metalladithiolene and bipyridine sides, showed a convincing photoresponse. The relationship between photoirradiation wavelengths and *cis*-isomer percentages in the PSS is given in Table 1. By irradiation with 405 nm purple light, complex 3 showed spectral changes similar to those of complex 1 (Fig. 3(A)(b)). In accordance with ¹H-NMR spectroscopy, the *cis*-isomer percentages of the azobenzenes in the PSS were 44% for that on the metalladithiolene side and 9% for that on the bipyridine side (Fig. S8†). On the other hand, on irradiation with 365 nm UV light, complex 3 displayed almost the same changes that complex 2 showed (Fig. 3(B)(b)). ¹H-NMR spectra indicated that the *cis*-isomer percentages in the PSS were 22% on the metalladithiolene side and 45% on the bipyridine side (Fig. S9†).

Furthermore, by excitation of the MMLL/CT band with 578 nm yellow light, both of the azobenzenes almost returned to the *trans*-state (Table 1). The phosphorescence from the ³MMLL/CT state was quenched as it was in complexes 1 and 2 (Fig. S5d†). Thus, the *trans*-to-*cis* photoisomerization behaviour of complex 3 was almost a superposition of those of complexes 1 and 2. As illustrated in Fig. 4, by irradiation with three monochromatic lights in the UV region and across the whole visible region three out of four possible states, the exception being the (*cis*, *cis*)-state, can be reversibly switched.

The photo-controllable tristability of complex 3 found in this study will enlarge the application area of photochromic molecules for molecular devices such as molecular memories.

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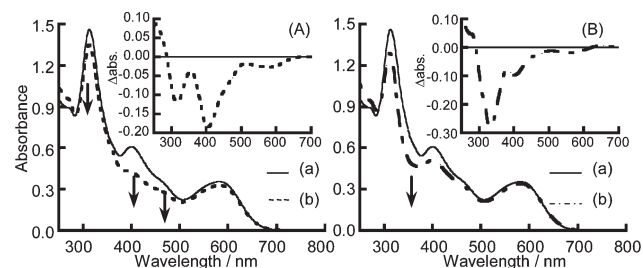


Fig. 3 (A) Electronic spectra of 3 in dichloromethane (a, solid line) and in the PSS upon irradiation with 405 nm light (b, dotted line). The inset shows the difference in the spectra, (b) – (a). (B) Electronic spectra of 3 in dichloromethane (a, solid line) and in the PSS upon irradiation with 365 nm light (b, broken line). The inset shows the difference in the spectra, (b) – (a).

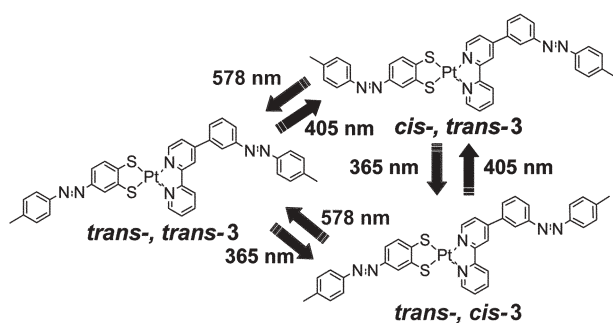


Fig. 4 Photo-controllable tristability of compound 3.

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Notes and references

‡ Crystallographic data. Intensity data were collected at 113(5) K on a RIGAKU Mercury CCD, using monochromated Mo-K α radiation

($\lambda = 0.71073 \text{ \AA}$), **1**: C₃₁H₃₄N₄PtS₂, $M = 721.84$, $P\bar{1}$, $a = 11.230(7) \text{ \AA}$, $b = 11.350(7) \text{ \AA}$, $c = 11.881(8) \text{ \AA}$, $\alpha = 81.96(2)^\circ$, $\beta = 81.53(2)^\circ$, $\gamma = 75.33(2)^\circ$, $V = 1440.7(16) \text{ \AA}^3$, $Z = 2$, $\mu = 5.023 \text{ mm}^{-1}$, unique reflections = 6215 [$R(\text{int}) = 0.040$], $R_1 = 0.054$ [$I > 2.00\sigma(I)$], $wR_2 = 0.179$ [$I > 0.50\sigma(I)$]. CCDC 252380. **2**: C₂₉H₂₂N₄PtS₂·0.5CH₂Cl₂, $M = 728.20$, $C2/c$, $a = 33.57(2) \text{ \AA}$, $b = 7.473(4) \text{ \AA}$, $c = 26.61(1) \text{ \AA}$, $\beta = 127.801(2)^\circ$, $V = 5274.9(47) \text{ \AA}^3$, $Z = 8$, $\mu = 5.586 \text{ mm}^{-1}$, unique reflections = 6008 [$R(\text{int}) = 0.053$], $R_1 = 0.072$ [$I > 2.00\sigma(I)$], $wR_2 = 0.219$ [$I > 0.50\sigma(I)$]. CCDC 252381. In both complexes, large residual electron density peaks lie near the metal centres. See <http://www.rsc.org/suppdata/cc/b4/b415293j/> for crystallographic data in .cif or other electronic format.

- (a) H. Nishihara, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 407; (b) C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 541.
- M. Kurihara, A. Hirooka, S. Kume, M. Sugimoto and H. Nishihara, *J. Am. Chem. Soc.*, 2002, **124**, 8800.
- M. Nihei, M. Kurihara, J. Mizutani and H. Nishihara, *J. Am. Chem. Soc.*, 2003, **125**, 2964.
- (a) P. D. Wildes, J. G. Pacifici, G. Irick, Jr. and D. G. Whitten, *J. Am. Chem. Soc.*, 1971, **93**, 2004; (b) N. R. King, E. A. Whale, F. J. Davis, A. Gilbert and G. R. Mitchell, *J. Mater. Chem.*, 1997, **7**, 625.
- (a) S. Kume, M. Kurihara and H. Nishihara, *Inorg. Chem.*, 2003, **42**, 2194; (b) S. Kume, M. Kurihara and H. Nishihara, *Chem. Commun.*, 2001, 1656.
- Complex **3** has two structural isomers in its (*trans, trans*)-state. We have not succeeded in identifying both of them so far. Their photochemical behaviours, however, are thought to be almost identical to each other.
- (a) W. Paw, S. D. Cummings, M. A. Mansour, W. B. Connick, D. K. Geiger and R. Eisenberg, *Coord. Chem. Rev.*, 1998, **171**, 125; (b) S. D. Cummings and R. Eisenberg, *Inorg. Chem.*, 1995, **34**, 2007.