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trans–cis Photoisomerization of Azobenzene-Conjugated Dithiolato-Bipyridine Platinum(II) Complexes: Extension of Photoresponse to Longer Wavelengths and Photocontrollable Tristability

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Abstract: Azobenzene derivatives modified with dithiolato-bipyridine platinum(II) complexes were synthesized, revealing their highly extended photoresponses to the long wavelength region as well as unique photocontrollable tristability. The absorptions of *trans*-**1** and *trans*-**2** with one azobenzene group on the dithiolene and bipyridine ligands, respectively, cover the range from 300 to 700 nm. These absorptions are ascribed, by means of time-dependent (TD)DFT calculations, to transitions from dithiolene(π) to bipyridine(π*), namely, interligand charge transfer (CT), π–π*, and n–π* transitions of the azobenzene unit, and π–π* transitions of the bipyridine ligand. In addition, only *trans*-**1** shows distinctive electronic bands, assignable to transitions from the dithiolene(π) to azobenzene(π*), defined as intraligand CT. Complex **1** shows photoisomerization behavior opposite to that of azobenzene: *trans*-to-*cis* and *cis*-to-*trans* conversions proceed with 405 and 312 nm irradiation, which correspond to excitation with the intraligand CT, and π–π* bands of the azobenzene and bipyridine units, respectively. In contrast, complex **2** shows photoisomerization similar to that of azobenzene: *trans*-to-*cis* and *cis*-to-*trans* transformations occur with 365 and 405 nm irradiation, respectively. Irradiation at 578 nm, corresponding to excitation of the interligand CT transitions, results in *cis*-to-*trans* conversion of both **1** and **2**, which is the longest wavelength ever reported to effect the photoisomerization of the azobenzene group. The absorption and photochromism of **4**, which has azobenzene groups on both the dithiolato and bipyridine ligands, have characteristics quite similar to those of **1** and **2**, which furnishes **4** with photocontrollable tristability in a single molecule using light at 365, 405, and 578 nm. We also clarified that **1** and **2** have high photoisomerization efficiencies, and good thermal stability of the *cis* forms. Complexes **3** and **5** have almost the identical photoresponse to those of their positional isomers, complexes **2** and **4**.

Keywords: azo compounds · density functional calculations · photochromism · platinum · sulfur

Introduction

Azobenzene[1] exhibits a number of attractive properties, including high quantum yields and conversion ratios for its *cis–trans* photoisomerization, fatigue resistance, ease of chemical modification, and a low free volume for the large structural change. These features have led to its valuable use in the fields of biochemistry,[2] surface chemistry,[3] liquid crystals,[4] polymer materials,[5] and molecular devices,[6] among others. Its utility is limited, however, by the photoresponse below 500 nm, as evidenced in its electronic spectra. Extension of the photoresponse of azobenzene to longer wavelengths gives substantial advantages, in view of further applications such as a development of full-color optical materials[7] and utilization within the body, which requires the use of wavelengths of light that are harmless to tissue[8] and dyes that have enough transparency.[9] Attempts to “red-shift” the photoresponse of azobenzene have so far met

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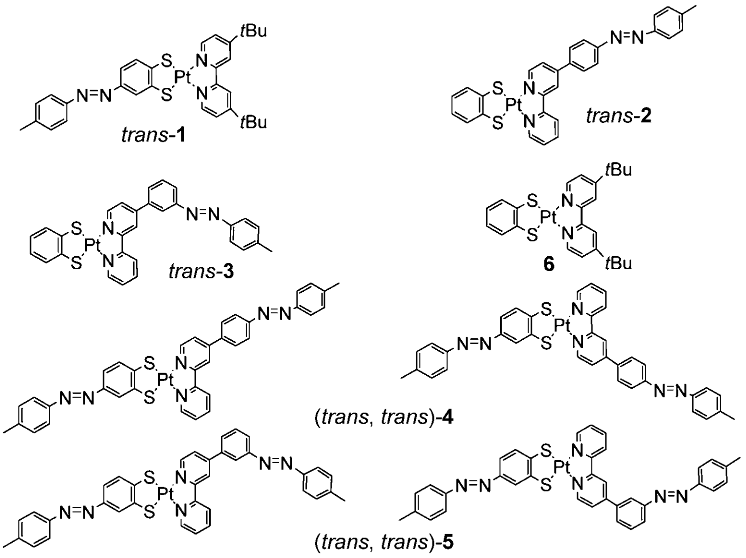
with mixed success. For example, the introduction of pull–push organic substituents affords some redshifting of the absorptions at the cost of a significant decrease of the thermal stability of the *cis* form owing to an increasing contribution of quinoidal structures in the ground state.[10]

We have demonstrated that organic photochromes, such as azobenzene,[11] diethynylethene,[12] and dimethyldihydropyrene,[13] show significant redshifts of their photoisomerization responses by π conjugation with ferrocene, which is a representative organometallic complex, and has good donor ability as a result of its high-lying Fe d orbitals. These redshifts result from the expression of donor–acceptor charge-transfer (CT) transitions from the ferrocene (d) to photochromic (π*) orbitals. In addition, in the case of azobenzene, this modification does not reduce the thermal stability of the *cis* form.[11] However, some of the derivatives in this series suffer from decreases in photoisomerization quantum yields, presumably because of a quenching pathway of energy transfer to a ferrocene-localized low-lying triplet ligand-field (^{3}LF) excited state.[14,15] We note that photochromic properties in a number of metal(organometallics, transition-metal complexes,[15,16] nanoparticles,[17] and surfaces[18])–organic photochromic ensembles, including those composed of azobenzene, are suppressed by electron- or energy-quenching processes.

Against the aforementioned background, we adopted dithiolato M(II) (M = Ni, Pd, Pt) complexes[19] as a new partner for azobenzene. This class of complexes is known to have aromaticity and good donor ability on the basis of its dithiolene five-membered ring.[19] These rings are expected to express CT transitions with a low excitation energy from the dithiolene(π) to the azobenzene(π*) unit, as in ferrocene-containing systems.[11–13] In fact, we investigated azo-conjugated dithiolato-[1,2-bis(diphenylphosphino)ethane]-M(II) complexes, which have lower excitation energies for *trans*-to-*cis* photoisomerization and considerable thermal stability of their *cis* forms.[20] This result further encouraged us to employ dithiolato-bipyridine platinum(II) complexes.[21] The ligand-field splitting of these complexes is large enough to avoid quenching low-lying LF excited states, because of the strong σ-donor ability of the dithiolato ligand, π-acceptor ability of the bipyridine ligand, and the 5d platinum(II) ion. This fact is well reflected in a peculiar low-lying (500–700 nm) interligand CT transition from the dithiolene(π) to bipyridine(π*) unit, which results in a long-lived triplet excited state and phosphorescence from this state at ambient temperature in solution.[21] These characteristic electronic structures and absorptions of dithiolato-bipyridine platinum(II) complexes should provide azobenzene with high efficiency for photoisomerization and further extension of the photoresponse at longer wavelengths.

In a previous communication, we reported qualitative aspects of the photoisomerization of azobenzene-conjugated dithiolato-bipyridine platinum(II) complexes **1**, **3**, and **5** (Scheme 1).[22] Herein, we report quantitative analyses of the photo and physical properties of complexes **1** and **2** with one azobenzene unit on either the dithiolato or the bipyridine ligand (Scheme 1), for example, estimation of electronic structures with TDDFT calculations to elucidate their peculiar and highly extended photoresponses to longer wavelengths, determination of the photoisomerization quantum yields, and evaluation of the high thermal stability of the *cis* forms. Application of the TDDFT method,[23] as an alternative to the wave-function-based methods such as CASPT2[24] and SACCI,[25] gives us a clear advantage: the active space can be wider, which gives an accurate description of electron correlations and configuration interactions at a less-expensive computational cost. In fact, this method has been widely adopted to low-spin and closed-shell coordination compounds,[11–12,26a–d] including those with Pt^{II} ions,[26e–f] showing fine reproducibility of their electronic spectra and reasonable assignments of their excited states. We also discuss the photochromic responses of the azo-bound complexes synthesized to date (**1**–**5**), especially focusing on photocontrollable tristability in **4** and **5** with two azobenzene groups, one on each ligand (Scheme 1).



Scheme 1. Azobenzene-conjugated dithiolato-bipyridine platinum(II) complexes **1**–**5** and model complex **6**. Two possible geometrical isomers are depicted for (*trans,trans*)-**4** and (*trans,trans*)-**5**.

Results and Discussion

Synthesis, characterization, and structure: All compounds were synthesized from corresponding bipyridineplatinum(II) dichloride[27] and dithiolato dianions. The latter were generated by the deprotonation or deprotection of 1,2-benzenedithiol or 5-(*p*-tolylazo)-1,3-benzodithiole-2-thione[20] with KOH in 2-metoxyethanol, and used without isolation. The azo-bound compounds are apparently labile in the presence of neutral alumina gel, which produces an unidentified yellowish material in the course of column chromatography. Therefore, it is essential to use basic alumina gel (activity II-III).

All compounds were characterized by ^{1}H NMR and ^{1}H–^{1}H COSY spectroscopy, as well as elemental analyses. The *trans* configuration in *trans*-**1** and *trans*-**3** was determined from single-crystal X-ray structure analyses (Figure 1).[22] The complexes (*trans*,*trans*)-**4** and (*trans*,*trans*)-**5** have two possible geometrical isomers (Scheme 1), which could not be isolated by any method. The existence of the two isomers was deduced by ^{1}H NMR spectroscopy. There is a slight splitting (2.3 Hz) of the signals derived from the 5- and 5′-protons of the bipyridine ligand in *trans*-**1** as a result of perturbation by the azobenzene group on the dithiolene ring (Figure S1 in the Supporting Information). This effect is also seen in (*trans*,*trans*)-**4** and (*trans*,*trans*)-**5**, for which signals derived from the 5-proton of the bipyridine ligand are broader than those in *trans*-**2** and *trans*-**3** (Figure S1 in the Supporting Information). However, since the extent of the broadening is slight, and there is no additional difference seen in other measurements, we expect the influence of this different configuration on the photoproperties to be trivial.

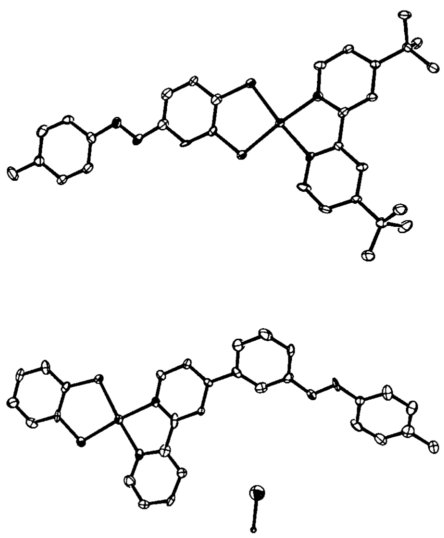


Figure 1. ORTEP drawings for *trans*-**1** (top) and *trans*-**3**$\cdot$0.5 CH_2Cl_2 (bottom) with thermal ellipsoids drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity.

Electronic spectra and TDDFT calculations: Figure 2a shows an overlay of the electronic spectra of *trans*-**1**, *trans*-**2**, and **6**. The spectrum of **6** shows a characteristic absorption in the visible region (band A) with a maximum at 555 nm. We deduce from TDDFT calculations (Figure 3 and Table 1) that this band results from a singlet HOMO–LUMO transition or interligand CT transition from the dithiolene(π) to bipyridine(π*) orbitals, which is consistent with previous reports.[17,26f] In addition, a singlet π–π* band mostly localized on the bipyridine ligand is observed with a maximum at 304 nm (band B, Figures 2a, 3, and Table 1). The TDDFT calculations also indicate the existence of pairs of weaker singlet transitions (Figure S2 and Table S1 in the Supporting Information), some of which are visible at around 350–450 nm (Figure 2a). The heavy-atom effect of the Pt^{II} ion means that the singlet transitions mentioned above might bear slight triplet character.[26f]

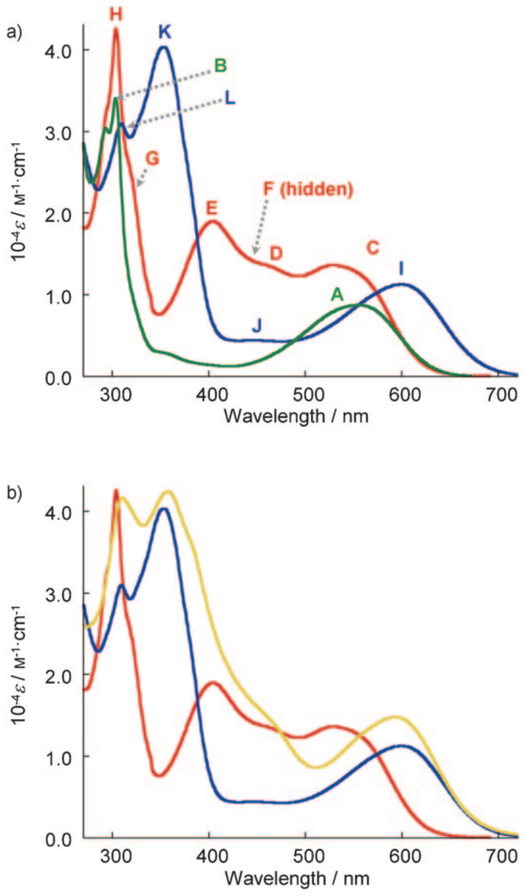


Figure 2. Overlays of the electronic spectra in dichloromethane of: a) *trans*-**1** (——), *trans*-**2** (——), and **6** (——); b) *trans*-**1** (——), *trans*-**2** (——), (*trans*,*trans*)-**4** (——).

The interligand CT transition and π–π* transition of the bipyridine ligand are also observed and assigned by the TDDFT calculations for *trans*-**1** to maxima at 529 and 304 nm, respectively (bands C and H, Figures 2a, 3, and Table 1). The former transition is blueshifted relative to that of **6** because of the electron-withdrawing ability of the azo group and its contribution to the dithiolene(π) (Figure 3 and Table 1). We note that *trans*-**1** shows peculiar electronic bands with maxima at 460 and 404 nm, which cannot be elucidated from a simple overlay of the electronic spectra of azobenzene and **6** (bands D and E, Figure 2a). The TDDFT calculations assign these bands to transitions from the dithiolene(π) to azobenzene(π*), which we define as intraligand CT transitions (Figure 3 and Table 1). The TDDFT calculations also show azobenzene-localized π–π* and n–π* transitions (Figure 3 and Table 1). The former is expected to overlap with the π–π* band of the bipyridine ligand

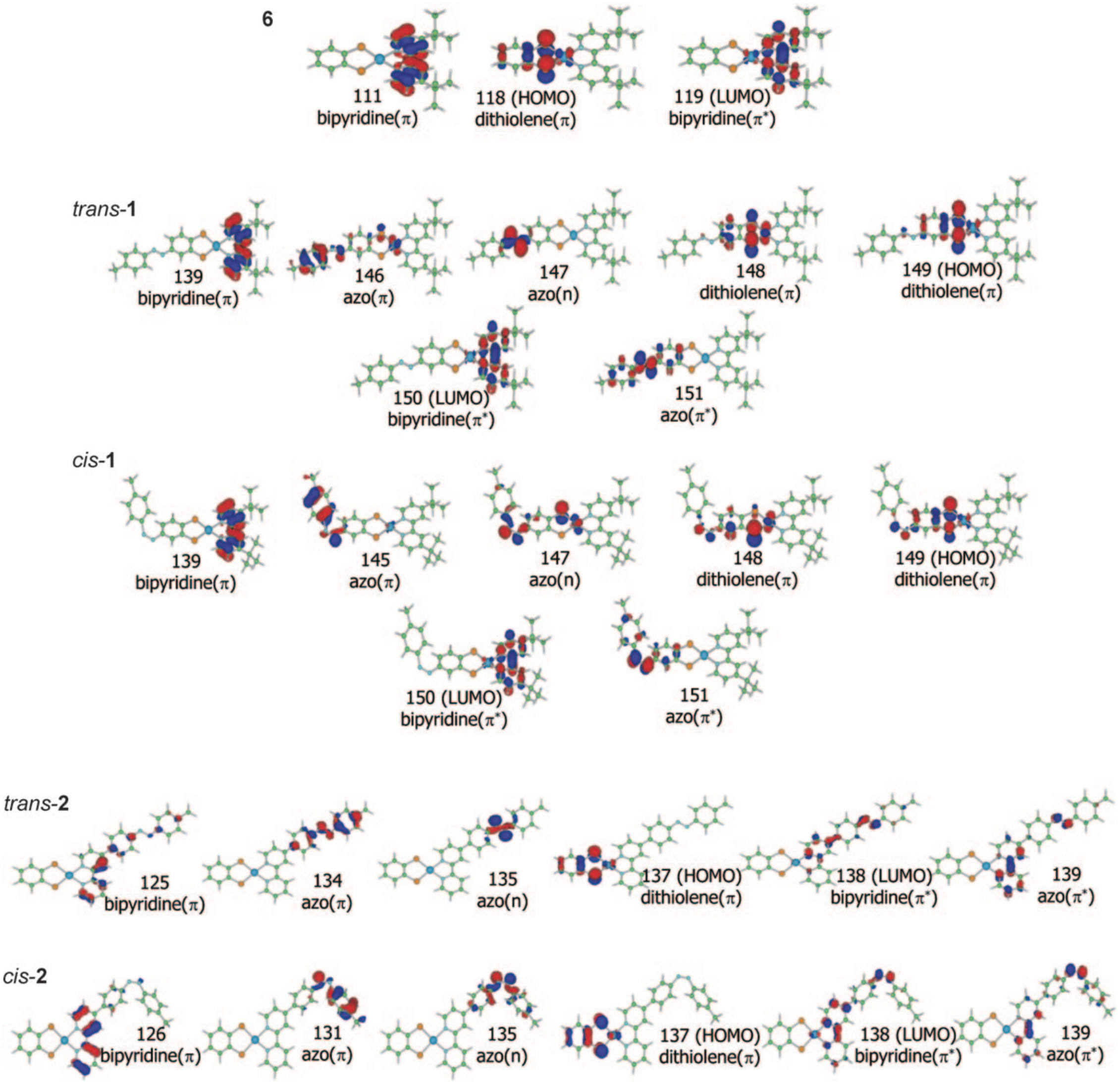


Figure 3. Contour plots of molecular orbitals that play major roles in the significant electronic bands in **6**, *trans*-**1**, *cis*-**1**, *trans*-**2**, and *cis*-**2**.

(band G, Figure 2a), and the latter to be completely hidden by the intense intraligand CT bands (band F, Figure 2a).

The electronic transitions of *cis*-**1** are also estimated by the TDDFT calculations. A decrease of the intraligand CT bands relative to those of *trans*-**1**, especially the band with higher transition energy, is observed along with a decrease of the π–π* and an increase of the n–π* band of the azobenzene moiety, which is typical of the *trans*-to-*cis* isomerization of azobenzene[1] (Figure 3 and Table 1). Figure S7 in the Supporting Information shows the absorption spectra of *cis*-**1** calculated from the results of photoisomerization experiments described in the following section. The theoretically predicted differences are prominent for all bands except the n–π* band, presumably because of its small change and concealment by the intraligand CT bands. A significant difference in the absorptivity at a certain wavelength can drive the photostationary state (PSS) to either form.

In contrast, no intraligand CT bands are available in *trans*-**2** (Figure 2a). TDDFT calculations were also performed for *trans*-**2** and reveal the existence of an interligand CT (band I), n–π* and π–π* transitions of the azobenzene moiety (bands J and K), and a π–π* transition of the bipyridine ligand (band L) (Figures 2a and 3, and Table 1). The π and π* orbitals of the bipyridine and azobenzene mix by π conjugation (Figure 3). This fact is reflected in the electronic spectrum, for example, in the redshift of the interligand CT band relative to that of **6** (Figure 2a).

TDDFT calculations for *cis*-**2** indicate that the conformational change from *trans* to *cis* affords a significant decrease in the π–π* band and a slight increase in the n–π* band of the azobenzene moiety. These results are also consistent with experimental observations shown in Figure 3, Figure S7 in the Supporting Information, and Table 1. This situation is nearly identical to that for azobenzene.[1]

Table 1. Main singlet excited states of **6**, *trans*-**1**, *cis*-**1**, *trans*-**2**, and *cis*-**2** in dichloromethane calculated by TDDFT.[a]

Band	Assignment	ΔE [eV] (λ [nm])	Oscillator strength	Configuration (CI coefficient)	ΔE [eV] (λ [nm])	Oscillator strength	Configuration (CI coefficient)
		6					
A	interligand CT	2.00 (621)	0.132	118→119 (0.668)			
B	bpy (π–π*)	4.39 (283)	0.195	111→119 (0.512)			
		trans-**1**					*cis*-**1**
C	interligand CT	2.02 (614)	0.224	149→150 (0.674)	1.98 (627)	0.179	149→150 (0.671)
D	intraligand CT	2.56 (485)	0.115	149→151 (0.627)	2.30 (540)	0.108	149→151 (0.476)
E	intraligand CT	2.95 (420)	0.681	148→151 (0.614)	2.69 (461)	0.014	148→151 (0.474)
F	azo (n–π*)	3.01 (412)	<0.001	147→151 (0.697)	3.13 (396)	0.190	147→151 (0.534)
G	azo (π–π*)	3.89 (319)	0.523	146→151 (0.617)	3.99 (311)	0.137	145→151 (0.602)
H	bpy (π–π*)	4.36 (284)	0.128	139→150 (0.486)	4.43 (280)	0.221	139→150 (0.565)
		trans-**2**					*cis*-**2**
I	interligand CT	1.77 (699)	0.196	137→138 (0.660)	1.81 (685)	0.189	137→138 (0.655)
J	azo (n–π*)	3.33 (373)	<0.001	135→139 (0.564)	2.95 (420)	0.069	135→139 (0.513)
K	azo (π–π*)	3.56 (349)	0.447	134→139 (0.630)	4.20 (295)	0.015	131→139 (0.585)
L	bpy (π–π*)	4.15 (299)	0.087	125→138 (0.501)	4.24 (292)	0.084	126→138 (0.469)

[a] Of the mixing states in each electronic transition, the one with the largest configuration interaction (CI) coefficient is described for the sake of clarity. See Figures S2–S6 and Tables S1–S5 in the Supporting Information for the full singlet excited states of each compound.

The electronic spectrum of (*trans*,*trans*)-**4** has characteristics quite similar to those of *trans*-**1** and *trans*-**2** (Figure 2b). These data indicate that there is negligible interaction in the ground state between the two azobenzene groups on the different ligands.

The electronic spectra of meta-substituted *trans*-**3** and (*trans*,*trans*)-**5** are almost the same as those of their positional isomers *trans*-**2** and (*trans*,*trans*)-**4**, respectively, with para substitution except for the blueshifts of some of the absorption bands, ascribable to the weaker π conjugation between the bipyridine and azobenzene groups (Figure S8 in the Supporting Information).

In summary, we find that every compound with azobenzene has absorption bands in the region 300–700 nm, which is also confirmed by a series of TDDFT calculations. This feature of the complexes is expected to lead to photoresponses that are much wider than that of azobenzene.

Photoisomerization behavior: Figure 4a shows the UV/Vis absorption spectra of *trans*-**1** in dichloromethane upon irradiation at 312, 405, and 578 nm. These wavelengths of light chiefly correspond to excitations of the π–π* transitions of the bipyridine and azobenzene moieties, intraligand CT transitions, and an interligand CT transition, respectively. Irradiation at 405 nm shows prominent decreases in the absorption bands and results in minima of the differential spectrum at 301, 318, and 407 nm. This result is consistent with the TDDFT calculations, which indicate that the π–π* transition of the azobenzene moiety and the intraligand CT transition with higher transition energy drastically lose their intensities upon *trans*-to-*cis* isomerization (Table 1).

^{1}H NMR and ^{1}H–^{1}H COSY spectroscopy in [D$_2$]dichloromethane reveals that irradiation at 405 nm results in substantial upfield shifts of signals for the aromatic protons around the azo group (Figures S9 and S10 in the Supporting Information). This change is a characteristic sign of *trans*-to-*cis* photoisomerization of azobenzene as a result of the twist between the two aromatic rings.[28] The proportion of the *cis* isomer in the photostationary state upon irradiation at 405 nm was found from the relative integrals of the methyl group located at the head of the azobenzene to be 45% (Figure S11 in the Supporting Information). In contrast, the UV/Vis spectral changes with light at 312 and 578 nm are much smaller than that with 405 nm (Figure 4a). The proportions of the *cis* isomer in the two PSSs were calculated to be 17 and 14%, respectively, from the UV/Vis spectral changes with the value for the 405 nm irradiation as the standard. Every PSS approaches the same value, irrespective of the starting proportions of the *cis* form. This series of measurements suggest that **1** undergoes reversible *trans–cis* photoisomerization with light at 405 and 312 or 578 nm (Figure 4a). Significant differences in the photochromic behavior between azobenzene and **1** lie in the reversed photoresponses to light at 312 and 405 nm, and the substantial extension of the photoresponse to longer wavelengths, such as light at 578 nm. The former difference is most likely due to the existence of the intraligand CT band with higher excitation energy, which has much larger intensity in the *trans* form than in the *cis* form (Table 1), whereas the latter results from the existence of the interligand CT band. The total photoresponse of **1**, including the three wavelengths mentioned above, is summarized in Table 2 and Figure S12 in the Supporting Information.

Figure 4b shows the UV/Vis spectral changes of *trans*-**2** in dichloromethane upon irradiation at 365, 405, and 578 nm. These wavelengths correspond primarily to excitations of

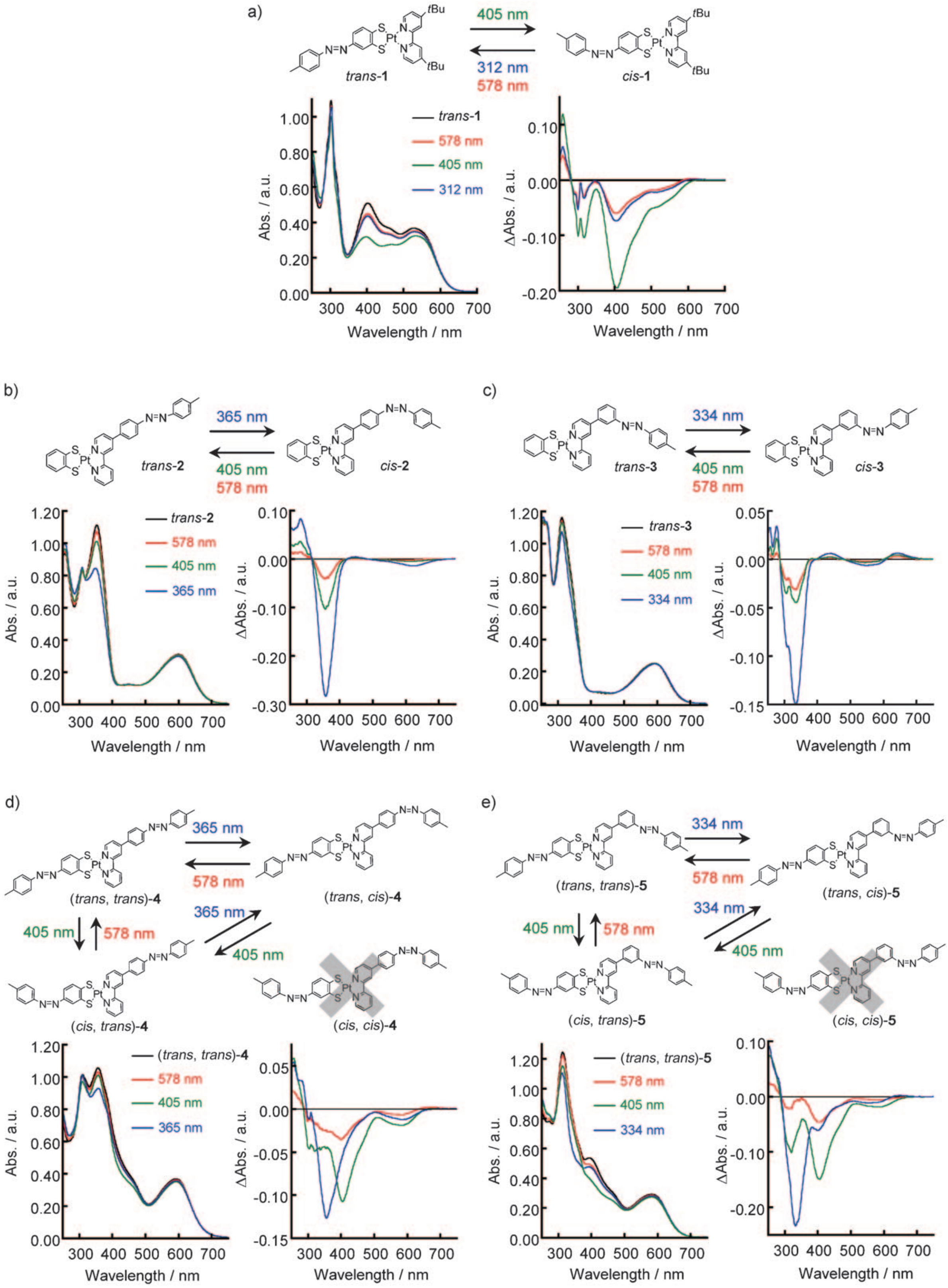


Figure 4. UV/Vis (left) and differential (right) spectral changes before and after irradiation with UV (312, 334, or 365 nm), 405 nm, and 578 nm light for: a) *trans*-**1**; b) *trans*-**2**; c) *trans*-**3**; d) (*trans*,*trans*)-**4**; e) (*trans*,*trans*)-**5**.

Table 2. Relationship between photoirradiation wavelengths and the proportions of *cis* form in the PSSs of **1–5** calculated from ^{1}H NMR spectral changes.

λ [nm]	Proportion of *cis* isomer [%] **1**	**2**	**3**	Dithiolene **4**	Bipyridine **4**	Dithiolene **5**	Bipyridine **5**
312	17[a]	6[a]	16[a]	14[a]	8[a]	21[a]	33[a]
334	20[a]	11[a]	24[a]	13[a]	11[a]	21[a]	50[a]
365	21[a]	33	23	5	21	22	45
405	45	12[a]	7[a]	33	7	44	9
436	37[a]	12[a]	8[a]	29[a]	5[a]	32	10
546	15[a]	5[a]	5[a]	10[a]	4[a]	7	6
578	14[a]	5[a]	5[a]	10	7	8	4

[a] Calculated from UV/Vis spectral changes with the values from the ^{1}H NMR spectra as the standard.

the π–π^* transitions of the azobenzene and bipyridine moieties, n–π^* transition of the azobenzene moiety, and interligand CT transition, respectively. Upon irradiation of *trans*-**2** at 365 nm, the differential spectrum shows a substantial decrease at 357 nm and a faint growth at 449 nm, which can be ascribed, in accordance with the TDDFT calculations, to an increase and decrease, respectively, in the π–π^* and n–π^* transitions of the azobenzene moiety upon *trans*-to-*cis* transformation (Table 1). This photoresponse was also checked with ^{1}H NMR and ^{1}H–^{1}H COSY spectra, which showed substantial upfield shifts of the signals for aromatic protons in proximity to the azo group (Figure S13 and S14 in the Supporting Information), as for those of **1**. The proportion of the *cis* form in the PSS was calculated to be 33 % by using the same method as for **1** with light at 405 nm (Figure S15 in the Supporting Information). The spectral changes afforded by light at 405 and 578 nm are not comparable to that by light at 365 nm (Figure 4b), and the proportions of the *cis* isomer in the two PSSs were determined to be 12 and 5 % by taking the UV/Vis spectral change with light at 365 nm as the standard. The starting proportions of the *cis* isomer again have no effect on the PSSs.

To summarize the photoresponse described above, we find reversible *cis–trans* photoisomerization in **2** under irradiation at 365 and 405 or 578 nm (Figure 4b). A principal difference in the photochromism between **2** and azobenzene is the extension of the photoresponse to longer wavelengths, owing to the presence of the interligand CT band. Figure S16 in the Supporting Information and Table 2 show the UV/Vis spectral change and the proportion of the *cis* isomer in each PSS upon irradiation with a wide range of UV and visible light.

Figure 4c shows the UV/Vis spectral changes of *trans*-**3** in dichloromethane upon irradiation at 334, 405, and 578 nm. This series of spectral changes is similar to those of its analogue **2** (Figure 4b). ^{1}H NMR and ^{1}H–^{1}H COSY spectroscopy gives spectral changes typical of *trans*-to-*cis* photoisomerization of azobenzene, as in **2** (Figures S17–S19 in the Supporting Information). The maximum proportion of the *cis* isomer (23 %) is attained with light at 334 nm (Figure 4c), as opposed to 365 nm for **2**, which reflects the extent of the π conjugation between the azobenzene and bipyridine moieties. The photoresponse of **3** against various wavelengths of light is summarized in Table 2 and Figure S20 in the Supporting Information. The switching amplitude is larger in **2** than in **3** (Table 2).

Thus, whether azobenzene is bound on the dithiolene ring or bipyridine ligand gives a critical difference in the photochromic behavior. This series of compounds has the longest photoresponsive wavelength reported for azobenzene derivatives. The proportions of the *cis* isomers in the PSSs of **1–3** are smaller than that of azobenzene. This phenomenon is due to the existence of the transitions mostly localized on the dithiolato-bipyridine platinum(II) complexes. The case of **1** upon excitation at 312 nm is a good example, in which the π–π^* band of the bipyridine moiety overlaps that of the azo moiety. The Pt complex based transitions cover the range 300–700 nm, as shown in the electronic spectrum of **6** (Figure 2a), and most of them are expected to retain their intensities upon *trans–cis* conversion. These absorptions decrease in the relative ratio of molar absorptivities between the *trans* and *cis* isomers, $\varepsilon_{trans}/\varepsilon_{cis}$, at any wavelength, which moves the PSS in the *trans*-rich direction. However, at the same time they play essential roles in the reversed photoisomerization behavior in **1**, the significant extension of the photoresponse to longer wavelengths, and the photocontrollable tristability discussed below.

Figure 4d shows the UV/Vis spectral changes of (*trans*, *trans*)-**4** in dichloromethane upon irradiation at 365, 405, and 578 nm. Irradiation at 405 nm gives a similar UV/Vis spectral change to that of **1** (Figure 4a), whereas the response upon irradiation at 365 nm resembles that of **2** (Figure 4b). The same trend is observed in ^{1}H NMR and ^{1}H–^{1}H COSY spectra (Figures S21 and S22 in the Supporting Information for 405 nm irradiation; Figures S21 and S23 for 365 nm irradiation). This series of spectral changes indicates that irradiation at 405 nm mainly induces the *trans*-to-*cis* conversion of the azo group on the dithiolene ring, whereas irradiation at 365 nm chiefly affords conversion of the azo group on the bipyridine ligand (Figure 4d). In contrast, irradiation at 578 nm results in much smaller UV/Vis and NMR spectral changes (Figure 4d and Figure S24 in the Supporting Information) than those at 405 and 365 nm. The percentages of the *cis* states of the individual azobenzene moieties in the PSSs were calculated from the integral ratios of the methyl groups on the two azobenzene groups (Figure S24 in the Supporting Information and Table 2). Complex **4** also shows a photoresponse over a wide range of UV and visible light (Table 2 and Figure S25 in the Supporting Information). There is no wavelength of light that affords high percentages of the *cis* state of both azobenzene groups (Table 2).

The photoresponse of **5** is quite similar to that of **4**, just as **2** and **3** show marked similarities (Figure 4e; Figures S26–S30 in the Supporting Information, and Table 2). The amplitude of the photoswitching behavior is more intense in **5** than in **4**.

Thus, complexes **4** and **5**, which have azobenzenes on both the dithiolato ligand and bipyridine ligand, have photocontrollable tristability in a single molecule with irradiation at 365 or 334, 405, and 578 nm light (Figure 4d and e).

Photoisomerization quantum yield: To explore the photoproperties of the azobenzene group on each ligand further, the quantum yields for *trans*-to-*cis* photoisomerization ($\Phi_{trans\rightarrow cis}$) were determined for **1** and **2** (Table 3), for which relatively large changes in the proportion of the *cis* isomer occur upon photoirradiation (Table 2). The values of $\Phi_{trans\rightarrow cis}$ were calculated from time-dependent UV/Vis spectral changes upon photoirradiation (Figures S31 and S32 in the Supporting Information). Both **1** and **2** show values almost as high as those for azobenzene (0.10 for π–π* excitation, and 0.20 for n–π* excitation in hexane),[29] for any wavelength of light. The ferrocene–azobenzene conjugate 4-ferrocenylazobenzene, which also shows a redshift of the photoisomerization response, has a far lower efficiency ($\Phi_{trans\rightarrow cis}$ = 0.0033 upon excitation with the π–π* band).[11a] This series of facts indicates that the excitation energy is effectively consumed by the photoisomerization phenomena, irrespective of the position of the azobenzene group and irradiation wavelength.

Table 3. Quantum yields for *trans*-to-*cis* photoisomerization ($\Phi_{trans\rightarrow cis}$) for **1** and **2** in dichloromethane at 25 °C.

	λ [nm]	$\Phi_{trans\rightarrow cis}$
1	334	0.071
	405	0.12
	578	0.25
2	365	0.051
	578	0.13

Phosphorescence spectra: Figure 5 shows the emission spectra of *trans*-**1**, *trans*-**2**, and **6** upon excitation into the interligand CT bands at ambient temperature in dichloromethane. As reported by Eisenberg and co-workers,[21] complex **6** shows emission with a wavelength maximum at 703 nm. In contrast, the emissions of *trans*-**1** and *trans*-**2** are strongly quenched. These data are consistent with the efficient photochromic behavior upon excitation of the interligand CT bands in **1** and **2** (Table 3). The complexes *trans*-**3**, (*trans*,*trans*)-**4**, and (*trans*,*trans*)-**5** also show significant quenching of the phosphorescence (Figure S33 in the Supporting Information).

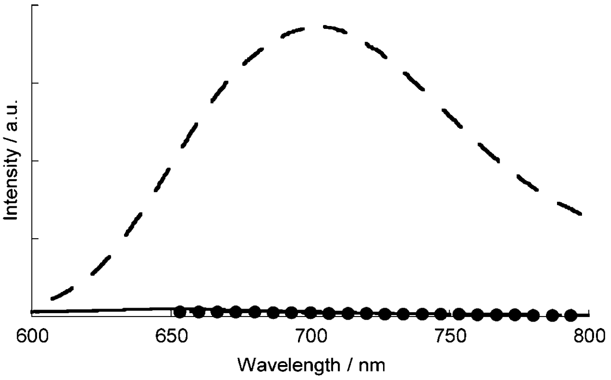


Figure 5. Phosphorescence spectra of *trans*-**1** (——), *trans*-**2** (●), and **6** (– – –) at ambient temperature in dichloromethane under an Ar atmosphere upon excitation of the interligand CT bands (*trans*-**1**: 547 nm, *trans*-**2**: 610 nm, **6**: 566 nm). The optical density of each sample at the excitation wavelength is fixed at 0.05.

Thermal *cis*-to-*trans* isomerization: The thermal stability of the *cis* forms of **1** and **2** was quantified as the first-order rate constants of the *cis*-to-*trans* thermal conversion (k_{th}) according to Equation (1), in which OD_{trans} and $OD(t)$ are the optical densities at a certain wavelength of the *trans* form and of the sample at time *t*, respectively.

$$\ln\{OD_{trans} - OD(t)\} = k_{th}t + \text{const.} \tag{1}$$

The experimental data are shown in Figure S34 in the Supporting Information. The results are tabulated in Table 4 along with those of 4-diethylamino-4′-nitroazobenzene, a representative organic pull–push azobenzene,[10a] and azobenzene.[30] The k_{th} value is actually larger in **1** and **2** than in azobenzene, but much smaller than in the organic pull–push azobenzene. This result indicates that the *cis* forms of both **1** and **2** retain considerable thermal stability, even while exhibiting a significant redshift of the photoresponse limit (Figure 4 and Table 2).

Table 4. First-order rate constants for the *cis*-to-*trans* thermal isomerization in dichloromethane at 25 °C.

Compound	$10^5\,k_{th}$ [s]
4-diethylamino-4′-nitroazobenzene	1.0×10^5[a]
1	25
2	2.3
azobenzene	0.38[b]

[a] Ref. [10], in chloroform. [b] Ref. [30], in *n*-hexane.

Conclusion

We have demonstrated that azobenzene-conjugated dithiolato-bipyridine platinum(II) complexes have intriguing photochromic behavior, including significant extension of the photoisomerization response to longer wavelengths, and photocontrollable tristability.

The complex *trans*-**1**, which has the azobenzene group on the dithiolato ligand, shows unique electronic bands that we attribute to intraligand CT transitions from the dithiolene(π) to azobenzene(π*) on the basis of TDDFT calculations. In contrast, *trans*-**2**, in which the azobenzene group is on the bipyridine ligand, does not have this intraligand CT type of electronic bands. Low-lying interligand CT bands from the dithiolene(π) to bipyridine(π*), characteristic of a class of dithiolato-bipyridine platinum(II) complexes, are commonly observed in both compounds, along with the π–π* and n–π* bands of the azobenzene moiety and bipyridine-localized π–π* band. The electronic spectrum of (*trans*,*trans*)-**4**, which has two azobenzene groups on both ligands, has similar characteristics to those of *trans*-**1** and *trans*-**2**.

Complex **1** shows peculiar photochromic behavior, namely, *trans*-to-*cis* conversion upon irradiation at 405 nm, and *cis*-to-*trans* conversion for irradiation at 312 nm, which is opposite to that of azobenzene. This characteristic photoresponse depends on the intraligand CT transition with higher transition energy, which significantly loses its intensity upon *trans*-to-*cis* isomerization. In contrast, the photochromism of **2** is similar to that of azobenzene, namely, *trans*-to-*cis* transformation with light at 365 nm, and *cis*-to-*trans* conversion for irradiation at 405 nm. Excitation of the interligand CT transitions at 578 nm commonly results in *cis*-to-*trans* isomerization in both **1** and **2**. The photochromism of **4** is almost identical to that of **1** and **2**, resulting in photocontrollable tristability in a single molecule for irradiation at 365, 405, and 578 nm. This series of compounds has the longest photoresponsive wavelength ever reported for azobenzene derivatives.

The absorptions and photoresponses of **3** and **5** are identical to those of their positional isomers **2** and **4**, except for their slight blueshift by the weaker π conjugation between the bipyridine and azobenzene groups.

Both **1** and **2** show photoisomerization efficiencies and thermal stability of the *cis* forms comparable to those of azobenzene alone. Efforts to extend the photoresponse of azobenzene have so far resulted in decreases of these important parameters. Herein we have suggested a new strategy for modification of the photoisomerization behavior of azobenzene, which could expand the field of application of this alluring photochromic material.

Experimental Section

Materials: Compounds *trans*-**1**,[22] *trans*-**3**,[22] (*trans*,*trans*)-**5**,[22] **6**,[22] 5-(*p*-tolylazo)-1,3-benzodithiole-2-thione,[20] and 4-{4″-(4‴-toluazo)phenyl}-2,2′-bipyridine[31] were synthesized according to published procedures. Other chemicals were purchased from Kanto Chemical and Tokyo Chemical Industry, and used as received unless otherwise stated.

[PtCl$_2$(4-{4″-(4‴-toluazo)phenyl}-2,2′-bipyridine)]: K_2PtCl_4 (424 mg, 1.0 mmol) was dissolved in a minimal amount of water. Several drops of concentrated HCl, and 4-{4″-(4‴-toluazo)phenyl}-2,2′-bipyridine (315 mg, 0.90 mmol) were added to the red solution. The suspension was heated at reflux for 1 d. From the resulting brown suspension, brown solid was filtrated off and then washed successively with water, diethyl ether, and hexane to obtain a brown powder of [PtCl$_2$(4-{4″-(4‴-toluazo)phenyl}-2,2′bipyridine)] (505 mg, 91 %). This material was used in the next step without further purification because of low solubility.

***trans*-2**: Under a nitrogen atmosphere, KOH (141 mg, 2.5 mmol) was dissolved in hot 2-metoxyethanol (60 mL). The solution was cooled to ambient temperature, and 1,2-benzenedithiol (130 mg, 0.91 mmol) was added. The solution turned pale blue. [PtCl$_2$(4-{4″-(4‴-toluazo)phenyl}-2,2′-bipyridine)] (400 mg, 0.65 mmol) was then added to the solution. The mixture became a deep green suspension. After 1 d of stirring at ambient temperature, the solvent was removed in vacuo. The black residue was extracted with dichloromethane, washed with water and brine, and then desiccated with Na_2SO_4. Dichloromethane was removed under reduced pressure, and then the black-green residue was purified by basic alumina (activity II-III) column chromatography with dichloromethane as an eluent. *trans*-**2**•0.25 CH_2Cl_2 was obtained as black-purple microcrystal by recrystallization from dichloromethane and acetonitrile (134 mg, 30 %). ^{1}H NMR (500 MHz, [D$_2$]dichloromethane): $\delta = 9.35$–9.33 (m, 2 H), 8.32 (d, $J = 1.7$ Hz, 1 H), 8.23 (d, $J = 7.8$ Hz, 1 H), 8.18 (ddd, $J = 7.8$, 7.8, 1.3 Hz, 1 H), 8.10 (d, $J = 8.6$ Hz, 2 H), 7.96 (d, $J = 8.6$ Hz, 2 H), 7.89 (d, $J = 8.3$ Hz, 2 H), 7.81 (dd, $J = 6.0$, 2.1 Hz, 1 H), 7.59 (ddd, $J = 7.3$, 5.8, 1.4 Hz, 1 H), 7.38–7.35 (m, 4 H), 6.78 (dd, $J = 6.0$, 3.1 Hz, 2 H), 2.46 ppm (s, Me); elemental analysis (%) calcd for $C_{29}H_{22}N_4PtS_2 \cdot 0.25CH_2Cl_2$: C 49.69, H 3.21, N 7.93; found: C 49.77, H 3.26, N, 7.77.

(*trans*,*trans*)-4: Under a nitrogen atmosphere, KOH (303 mg, 5.4 mmol) in 2-metoxyethanol (100 mL) was added to an orange solution of 5-(*p*-tolylazo)-1,3-benzodithiole-2-thione (327 mg, 1.1 mmol); the mixture was then heated at reflux for 1.5 h with shielding from light. The mixture turned into a reddish black suspension. After cooling the suspension to ambient temperature, [PtCl$_2$(4-{4″-(4‴-toluazo)phenyl}-2,2′-bipyridine)] (492 mg, 0.80 mmol) was added, and the mixture was stirred for 1 d. The solvent was evaporated in vacuo, and the reddish black residue was purified with basic alumina (activity II–III) column chromatography with dichloromethane as the eluent. Recrystallization from dichloromethane and acetonitrile gave a reddish black powder of (*trans*,*trans*)-**4** (192 mg, 30 %). ^{1}H NMR (500 MHz, [D$_2$]dichloromethane): $\delta = 9.40$–9.25 (m, 2 H), 8.32 (d, $J = 1.2$ Hz, 1 H), 8.24 (d, $J = 8.0$ Hz, 1 H), 8.20 (ddd, $J = 7.8$, 7.8, 1.3 Hz, 1 H), 8.10 (d, $J = 8.6$ Hz, 2 H), 7.96 (d, $J = 8.3$ Hz, 2 H), 7.90–7.88 (m, 3 H), 7.84 (dd, $J = 5.6$, 2.0 Hz, 1 H), 7.79 (d, $J = 8.3$ Hz, 2 H), 7.64–7.60 (m, 1 H), 7.46 (dd, $J = 8.3$, 1.7 Hz, 1 H), 7.42 (dd, $J = 8.3$, 1.7 Hz, 1 H), 7.38 (d, $J = 8.1$ Hz, 2 H), 7.31 (d, $J = 8.3$ Hz, 2 H), 2.46 (s, Me), 2.42 ppm (s, Me); elemental analysis (%) calcd for $C_{36}H_{28}N_6PtS_2$: C 53.79, H 3.51, N 10.45; found: C 53.56, H 3.66, N 10.22.

Photoirradiation: In an Ar glove box, all the samples were dissolved in distilled dichloromethane or ampuled [D$_2$]dichloromethane, and tightly sealed in quartz cells or NMR tubes. Since the isomerization behavior of the azobenzene moiety on the dithiolene side is extremely sensitive to protic impurities, the distilled solvents were further deacidified with calcium hydride prior to use. An Hg high-pressure lamp (Ushio Inc.) was used as a photon source, and the desired bright lines were selected with a monochromator (CT-10T, JASCO Inc.). Photon fluxes were measured with a Q8230 and Q82311 semiconductor photon counter set by ADVANTEST for $\lambda >= 390$ nm and with a chemical actinometer, [Fe(C_2O_4)$_3$],[32] for $\lambda <= 390$ nm. Numerical treatment was performed to determine the photoisomerization quantum yields.[33] The solution samples of the *trans* forms were stored in darkness for 1 d before the measurements so as to convert *cis* forms that may be produced by stray light in the course of the preparation into the *trans* forms. The solution samples of *trans*-**1** and *trans*-**2** were irradiated at 405 nm and 365 nm, respectively, before measuring the time-course plots for the determination of k_{th} to maximize the proportions of the *cis* isomers.

Apparatus: UV/Vis spectra were measured with Jasco V-570 and Hewlett-Packard 8453 UV/Vis spectrometers, IR spectra with a Jasco FT/IR-620v spectrometer, ^{1}H NMR and ^{1}H–^{1}H COSY spectra with a Bruker DRX 500 (500 MHz) spectrometer, and fluorescence spectra with a Hitachi F-4500 spectrofluorimeter.

DFT and TDDFT calculations: In DFT calculations, the three-parameterized Becke–Lee–Yang–Parr (B3LYP) hybrid exchange-correlation functional was employed.[34] The geometries of the complexes were optimized by the DFT(B3LYP) method including the solvent effect with the polarized continuum model (PCM). For comparisons with the electronic spectra observed in dichloromethane, the solvent effect was considered with the PCM. As basis sets, Lanl2DZ (Hay–Wadt ECP)[35] was adopted for Pt, and 6–31G was chosen for other atoms.

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