

## Protonation, Deprotonation, and Protonation: Conjugated Photochemical Reactions of Ferrocenylazophenol

Yi Men, Srinivas R. Korupoju, Masato Kurihara, Jun Mizutani, and Hiroshi Nishihara\*<sup>[a]</sup>

**Abstract:** 4-Ferrocenylazophenol (FAP) and 8-(4-ferrocenylazophenoxy)octanyl-1-bromide (FAOB) have been synthesized and their protonation and photochemical behavior have been investigated. FAP showed reversible protonation and deprotonation behavior in the presence of trifluoroacetic acid and po-

tassium *tert*-butylate, respectively. FAP and FAOB exhibit high photoreactivity, which was induced through excitation

**Keywords:** azo compounds • ferrocenes • isomerization • photochemistry • protonation

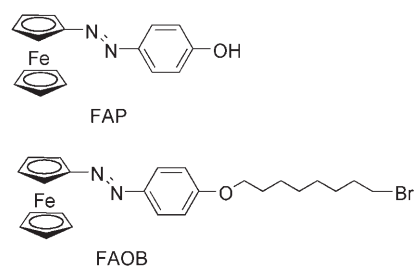
of not only the  $\pi$ - $\pi^*$  band by UV light but also the  $d$ - $\pi^*$  band by green light. The photoreaction of FAP and FAOB in ethanol or acetonitrile with a trace amount of water afforded phenylhydrazonocyclopentadiene (PHP) derivatives, indicating that hydrolysis of the photoexcited species occurs.

### Introduction

Azo compounds have been the subject of numerous spectroscopic and photochemical investigations because of their potential application in photoactive materials.<sup>[1-4]</sup> Compounds of the ferrocene family have been important media for electrochemical investigations due to their high stability and good solubility, and because their reversible electron transfer can be easily controlled.<sup>[5]</sup> The combination of these two molecules should produce a new type of photoresponsive material, in which the energy of the iron *d* orbital in ferrocene lies between the  $\pi$  and  $\pi^*$  levels of azobenzene, and thus the  $d$ - $\pi^*$  interaction should result in a lower energetic transition. In a previous series of studies on azo-conjugated photochromic complexes,<sup>[6-13]</sup> we reported the photoisomerization of azoferrocene, which underwent isomerization to form a *cis* isomer in polar media through excitation of not only a  $\pi$ - $\pi^*$  transition but also a  $d$ - $\pi^*$  transition (metal-to-ligand charge transfer, MLCT).<sup>[10]</sup> But in a subsequent investigation we noticed that the photoreaction was irreversible and complicated, indicating that our initial report was incorrect, and so we published a corrigendum.<sup>[11]</sup> In another study on the ferrocene-azobenzene combined system, we found that 3-ferrocenylazobenzene undergoes reversible *trans*-*cis* photoisomerization through the combination of single green

light irradiation and the ferrocene-ferrocenium redox change.<sup>[12]</sup> The utilization of a low-energy MLCT band for the azobenzene isomerization has also been reported for metalladithiolene complexes.<sup>[8,9]</sup>

In the present study, we carried out a detailed analysis of the photoreaction mechanism of 4-ferrocenylazophenol (FAP) and 8-(4-ferrocenylazophenoxy)octanyl-1-bromide (FAOB). This is because our previous investigation on the



photoreaction mechanism of azoferrocene gave unclear results due to the instability of the reaction product. By using FAP and FAOB we have been able to isolate and characterize the photoreaction products, which are derivatives of phenylhydrazonocyclopentadiene (PHP), indicating an elevated reactivity of the photoexcited form with a proton in solution. We also investigated the protonation of FAP and found it displayed reversible changes of protonation and deprotonation with sensitivity to both base and acid, leading to significant changes in the optical properties accompanied by an intramolecular electron transfer.

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## Results and Discussion

**Synthesis and structure:** FAP was synthesized by the reaction of *p*-phenyldiazonium chloride<sup>[14]</sup> with lithiated ferrocene, and its bromooctyl ether (FAOB) was prepared by the reaction of FAP with anhydrous potassium carbonate and dibromooctane. They were both characterized by means of NMR spectroscopy, mass spectrometry, and elemental analysis. The combination of the azo group with ferrocene exhibited a distinct color change due to the appearance of an MLCT band around 520 nm, which was an indicator of the reaction. A single crystal of FAP for X-ray crystallography was obtained through recrystallization from dichloromethane/hexane; an ORTEP image of the crystal is displayed in Figure 1. The azo group is in the *trans* form, and the cy-

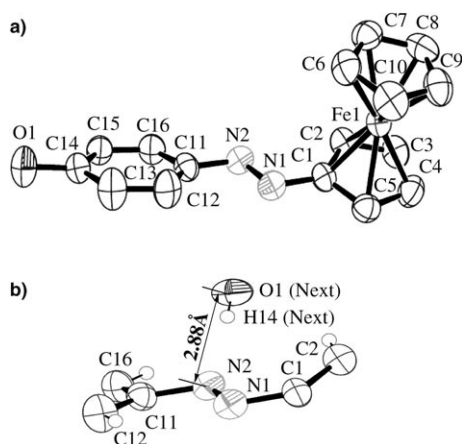


Figure 1. An ORTEP drawing of FAP with 50% probability (a) and the X-ray structure of FAP within 3 Å around the N2 atom (b). Selected bond lengths [Å], bond angles [°], and torsion angles [°] are as follows: Fe1–C1 2.039(3), N1–C1 1.429(4), N1–N2 1.254(4), N2–C11 1.444(4), O1–C14 1.353(4); N1–C1–C2 131.7(3), N1–N2–C11 113.6(3), N1–C1–C5 119.6(3), N2–N1–C1 112.8(3), N2–C11–C12 125.6(3), O1–C14–C15 122.8(3), N2–C11–C16 115.4(3), C1–N1–N2–C11 –179.2(3), N2–N1–C1–C2 7.0(6), N1–N2–C11–C12 14.2(6), N1–C2–C3–C4 –179.6(4), N2–C11–C16–C15 –175.7(4). Hydrogen atoms in b) were added at the positions obtained by calculation.

clopentadienyl (Cp) ring and the phenyl ring are not in the same plane as the azo group, with torsion angles of 7.0 and 14.2 degrees, respectively (Figure 1a). The length of the N=N double bond is between those of azobenzene and azoferrocene,<sup>[15]</sup> that is, it is longer than the former and shorter than the latter. This is related to the groups around the N=N bond:<sup>[16]</sup> two acceptors (Ph) for azobenzene, two donors (Fc) for azoferrocene, and the acceptor–donor (Ph–Fc) combination for FAP. Figure 1b shows the structure of FAP within 3 Å around the N2 atom. The distance between N2 and O1 is 2.88 Å and equals the sum of the length of the O–H bond and the distance between the N2 atom and the H14 atom of a neighboring molecule. This suggests the formation of a hydrogen bond between the N2 and H14 atoms, which probably hinders the three parts—Ph, azo, and Fc—from forming a coplanar structure for  $\pi$  conjugation. More-

over, the formation of a hydrogen bond also plays an important role in the photoreaction of FAP, as noted below.

**Protonation and deprotonation behavior of FAP:** The UV-visible absorption spectrum of *trans*-FAP in acetonitrile shows intense bands at 340 and 520 nm, as displayed in Figure 2, ascribable to the  $\pi$ – $\pi^*$  transition of the azo group

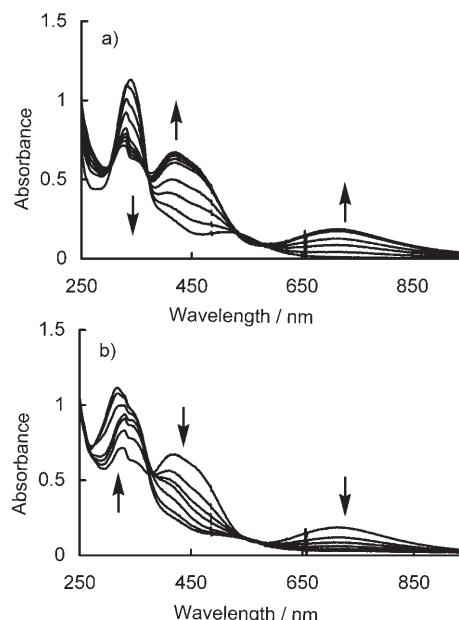
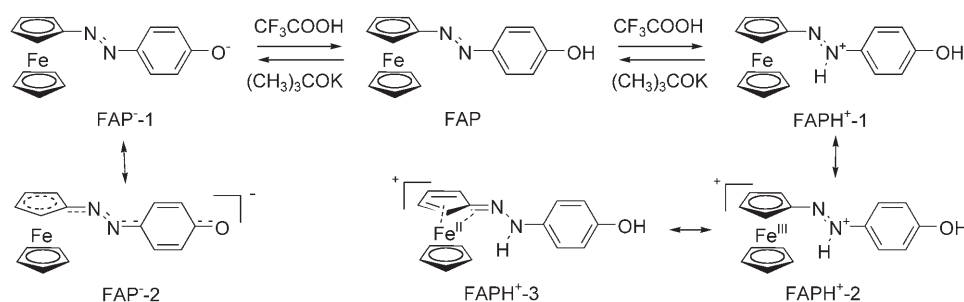


Figure 2. UV-visible spectral change of FAP ( $5.6 \times 10^{-5}$  M) in acetonitrile upon the stepwise addition of 0–18  $\mu$ L of  $\text{CF}_3\text{COOH}$  (a), and then upon the stepwise addition of 0–42  $\mu$ L of  $(\text{CH}_3)_3\text{COK}$  ( $1.57 \times 10^{-2}$  M) in ethanol (b).

and the  $d$ – $\pi^*$  transition (MLCT), respectively.<sup>[17]</sup> A purple solution of *trans*-FAP in acetonitrile became yellow with a decrease in intensity of the  $\pi$ – $\pi^*$  band of the azo group at 340 nm and appearance of new bands at 440 and 730 nm upon the addition of  $\text{CF}_3\text{COOH}$  under a nitrogen atmosphere (Figure 2a). An electrospray ionization (ESI) mass spectrum of the product showed a molecular ion peak at 307.1, corresponding to the monoprotonated form of FAP. The facile attack of azo nitrogen by a proton has been observed for azobenzene derivatives with electron-donating moieties, such as metalladithiolene.<sup>[8]</sup> Thus, when  $\text{H}^+$  approaches an FAP molecule, it should attack the electron-rich nitrogen atom next to phenol to form  $\text{FAPH}^+-1$  (Scheme 1), but it should not form any doubly protonated products. A hydrogen bond to the nitrogen atom is formed in the crystal structure of FAP, as noted above. When an electron from ferrocene flows to the nitrogen atom intramolecularly through a delocalized  $\pi$  bond, valence tautomerization between a ferrocenium organic radical species ( $\text{FAPH}^+-2$ ) and a  $\text{Fe}^{\text{II}}$  fulvene complex ( $\text{FAPH}^+-3$ ), which is isoelectronic to the well-known  $\text{CpFe}^+$  arene complexes,<sup>[18]</sup> may occur (Scheme 1). The existence of valence tautomers in the protonated form is suggested by the appearance of low-



Scheme 1. Protonation and deprotonation behavior of FAP.

energy absorption peaks as observed in the azobenzene-bound metalladithiolenes complexes<sup>[8]</sup> and ferrocene–quinone donor–acceptor combined molecules,<sup>[19–22]</sup> that is, electron transfer between the three valence tautomers in Scheme 1 corresponds to the appearance of a broad absorption peak at 730 nm. The strong absorption at 440 nm in FAPH<sup>+</sup> can be assigned to a  $\pi$ – $\pi^*$  transition, because the  $\pi$  electron is significantly delocalized in the state of valence tautomerization. Upon neutralization of FAPH<sup>+</sup> with (CH<sub>3</sub>)<sub>3</sub>COK, the initial absorption spectra were recovered (Figure 2b).

We also studied the deprotonation of FAP. When triethylamine was used as a deprotonation reagent, no change occurred in the UV-visible spectra, indicating weak acidity of the phenol moiety in FAP. When a strong base, (CH<sub>3</sub>)<sub>3</sub>COK, was employed, a UV-visible spectral change occurred (Figure 3a) while the color of the solution changed from purple to reddish orange. The  $\pi$ – $\pi^*$  band of FAP at 340 nm decreased, and a new peak appeared at 440 nm. The electron density in the bridging ligand Cp–N=N–Ph was increased

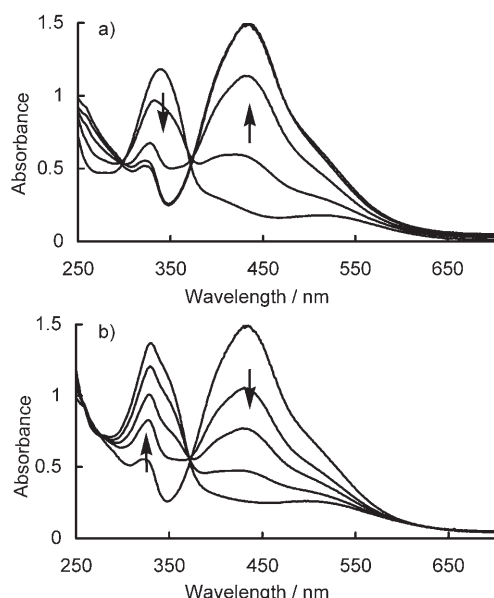


Figure 3. UV-visible spectral change of FAP ( $5.6 \times 10^{-5}$  M) in acetonitrile upon the stepwise addition of 0–28  $\mu$ L of (CH<sub>3</sub>)<sub>3</sub>COK ( $1.57 \times 10^{-2}$  M) in ethanol (a), and then upon the stepwise addition of 15  $\mu$ L of CF<sub>3</sub>COOH (b).

by the addition of (CH<sub>3</sub>)<sub>3</sub>CO<sup>−</sup>, possibly because the proton in the hydroxyl group of FAP was eliminated, and this led to an increase in electron delocalization (Scheme 1). This delocalized  $\pi$ –conjugated bond was energetically higher than that of FAP, resulting in a redshift of the  $\pi$ – $\pi^*$  transition from 340 to 440 nm. On neutralization with CF<sub>3</sub>COOH, the UV-visible spectra were restored to their initial state (Figure 3b).

We also investigated the deprotonation of FAP by using <sup>1</sup>H NMR spectroscopy (Figure 4). Upon addition of

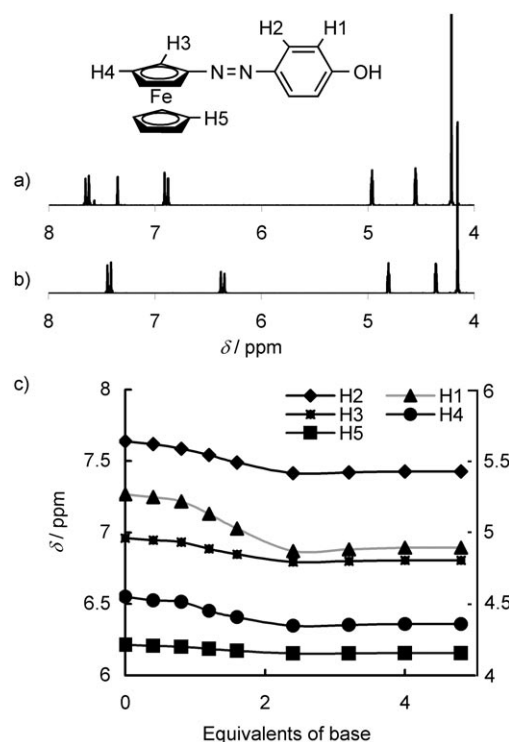


Figure 4. <sup>1</sup>H NMR spectral change of FAP in [D<sub>3</sub>]acetonitrile before (a) and after (b) the addition of (CH<sub>3</sub>)<sub>3</sub>COK in [D<sub>3</sub>]methanol, and the dependence of the shift of proton peaks on base (c) (left scale for H1 and H2, and right scale for H3, H4, and H5).

(CH<sub>3</sub>)<sub>3</sub>COK, all the peaks shifted to a higher field, because the increase of charge density weakened the deshielding effect of electronegative groups. The shift of the H1–H4 signals was affected more than that of the H5 signal, causing a larger shift. This suggests that electron density is dispersed along the whole molecule through the delocalized  $\pi$ –conjugated bond, which is in agreement with the results obtained from UV-visible spectroscopy (Scheme 1).

In summary, FAP showed reversible protonation and deprotonation characteristics in the presence of trifluoroacetic acid or potassium *tert*-butylate, respectively.

**Photoreaction of FAP in wet acetonitrile and in ethanol:**

Upon photoirradiation at 546 nm to excite the MLCT band or at 365 nm to excite the  $\pi$ - $\pi^*$  band of FAP in acetonitrile, the solution turned from purple to yellow, exhibiting decreases in the intensity of the  $\pi$ - $\pi^*$  and d- $\pi^*$  bands and the appearance of a new band at 400 nm, as shown in Figure 5.

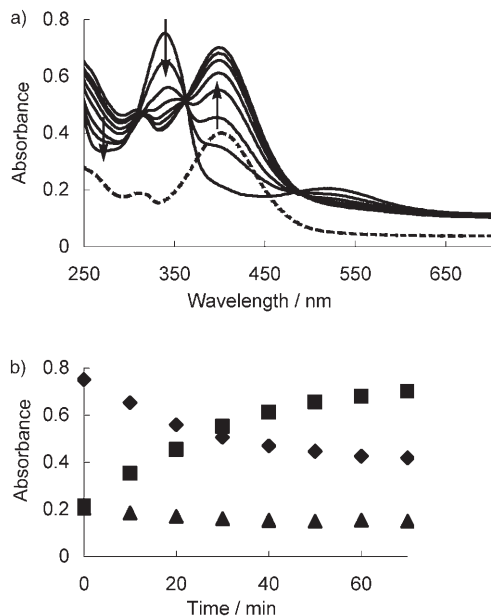


Figure 5. a) UV-visible spectral change of FAP ( $2.6 \times 10^{-5}$  M) in acetonitrile at photoirradiation ( $\lambda_{\max} = 546$  nm) intervals of 10 min (—) and UV-visible spectrum of PHP in acetonitrile (---). b) The plot of the spectral change at 340 (◆), 400 (■), and 520 nm (▲) versus photoirradiation time.

Exactly the same spectral changes were observed when the  $\pi$ - $\pi^*$  transition was excited by irradiation at 365 nm. In ethanol, a photochemical reaction showing similar spectral changes occurred, and the reaction was faster than that in acetonitrile.

From the photoirradiated solution of FAP in chloroform/ethanol, a brownish-yellow photochemical product was isolated by using silica gel column chromatography and was characterized by means of  $^1\text{H}$  NMR spectroscopy (Figure 6a). The integral values of these peaks from the low field in the  $^1\text{H}$  NMR spectrum were estimated to correspond to 1, 2, 3, 1, 1, 1, and 1 hydrogen atoms, with a total corresponding to 10 hydrogen atoms. This number and the spectral pattern indicating the existence of an amine group, a benzene ring, a hydroxyl group, and a cyclopentadiene ring from the low field to the high field strongly suggest the structure of 4-hydroxyphenylhydrazonocyclopentadiene (PHP). This is supported by the results that the peak at 9.5 ppm assignable to amine protons disappeared and the peak at 6.7 ppm assignable to a hydroxyl proton decreased upon the addition of  $\text{D}_2\text{O}$  to the solution of the photoreaction product. ESIMS spectra of the photoreaction product of FAP dehydrogenated with  $(\text{CH}_3)_3\text{COK}$  gave a peak cor-

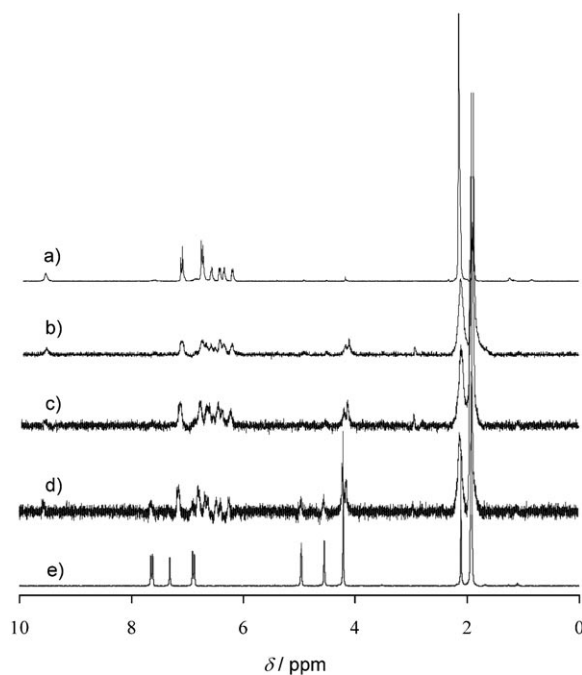
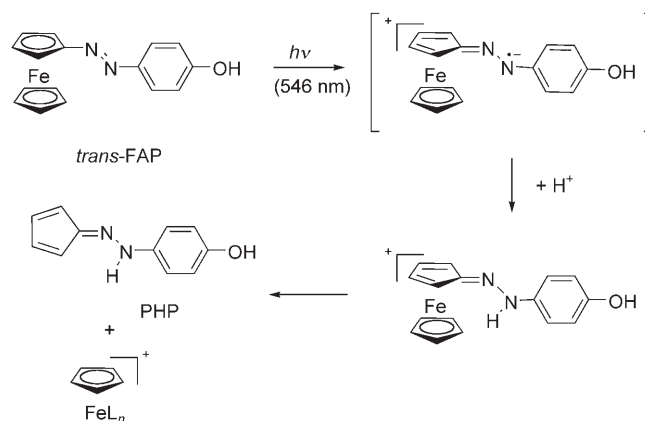


Figure 6. A  $^1\text{H}$  NMR spectrum of PHP (a), and the  $^1\text{H}$  NMR spectra of FAP upon photoirradiation ( $\lambda_{\max} = 546$  nm) for b) 20, c) 10, d) 5, and e) 0 h in  $\text{CD}_3\text{CN}$ .

responding to the monoanion with a mass number of 185.1, which is in agreement with the molecular mass of 186.2 of PHP. X-ray photoelectron spectroscopy (XPS) measurements showed no peak corresponding to the Fe 2p-orbital binding energy in the spectrum, while peaks of other elements existed, suggesting that the photoproduct did not contain Fe. All of these results indicate that the photoreaction product in ethanol is not the *cis* form of FAP but a hydrolysis product, PHP (Scheme 2). It should be noted that the



Scheme 2. Proposed photochemical reaction mechanism of *trans*-FAP.

UV-visible spectrum of PHP was in agreement with the final spectrum of FAP after photoirradiation (Figure 5) and that the same peaks as for PHP also appeared in the same position in the  $^1\text{H}$  NMR spectrum of the solution of FAP after

photoirradiation (Figure 6). This implies that iron dissociation occurs readily following the photochemical and protonation reactions in acetonitrile (with a trace amount of water) and in ethanol. The quantum yields ( $\Phi$ ) for the reaction of FAP were estimated to be 0.20 and 0.24 in wet acetonitrile and ethanol, respectively, suggesting that the photoinduced reaction has a high level of photoactivity. It should be noted that the photochemical reaction of FAOB in ethanol proceeded in a similar manner to that of FAP, and the isolated photoproduct was characterized as the derivative of PHP, 8-bromooctanylphenolhydrazonocyclopentadiene (BPHP).

Based on the data we collected, we postulated the photo-reaction mechanism shown in Scheme 2. The intermediate formed upon photoirradiation of the *trans* form was possibly an  $\eta^6$ -fulvene complex of  $\text{Fe}^{\text{II}}$  formed by intramolecular electron transfer (see Scheme 2).<sup>[18–22]</sup> If there is a proton source such as ethanol or water in the reaction system,  $\text{H}^+$  attacks first the electron-rich nitrogen atom (*vide supra*), and  $\text{OR}^-$  or solvent molecules coordinate to  $\text{Fe}^{\text{II}}$ , which leads to the complex becoming unstable and quickly decomposing. The  $\text{Fe}^{\text{II}}$  ion probably departed from the unit involving the azo moiety to give solvated cyclopentadienyliron,<sup>[23]</sup> which coprecipitates with other molecules or ions containing  $\text{OH}^-$  and PHP when the solution is concentrated.

## Conclusion

In conclusion, ferrocenylazophenol (FAP) undergoes photo-reactions through excitation of not only the  $\pi-\pi^*$  band but also the  $d-\pi^*$  band, and the reaction is strongly dependent on the existence of protons. The photoreaction gave a hydrolysis product, PHP, in ethanol or in wet acetonitrile. FAP undergoes reversible protonation and deprotonation in the presence of trifluoroacetic acid and potassium *tert*-butylate, respectively.

## Experimental Section

**Materials:** All the solvents and reagents were purchased from Kanto Chemicals and used as received unless otherwise stated. The dichloromethane, acetonitrile, and ethanol used for UV/Vis analyses were of spectroscopy and HPLC grade (Kanto Chemicals).

**Apparatus:** UV/Vis, IR, and  $^1\text{H}$  NMR spectra were recorded with JASCO V-570 and Hewlett Packard 8453 UV/Vis spectrometers, a JASCO FT/IR-62-v spectrometer, and JEOL EX270 and Bruker AM 500 spectrometers, respectively. ESIMS data were recorded with a Micro-mass LCT spectrometer, and samples were prepared by addition of  $1.59 \times 10^{-2} \text{ M}$   $(\text{CH}_3)_3\text{COK}$  in ethanol. FAB mass spectra were recorded with a JEOL JMS-SX102 spectrometer. XPS was carried out with a Rigaku XPS-7000 spectrometer.

**X-ray crystallographic structure determination:** The single-crystal X-ray diffraction data for compound FAP were collected at room temperature on a Rigaku Mercury CCD imaging plate diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation operating at 50 kV and 40 mA. After Lorentz and polarization corrections, the structure was solved by direct methods (SIR97 program), expanded for the use of Fourier techniques, and was refined by using full-matrix least-squares cycles on  $F^2$ . Selected

crystallographic data and experimental details are as follows: formula =  $\text{C}_{16}\text{H}_{14}\text{FeN}_2\text{O}$ ;  $M_r = 306.15 \text{ g mol}^{-1}$ ; crystal dimensions =  $0.20 \times 0.20 \times 0.20 \text{ mm}$ ; monoclinic;  $a = 10.932(2)$ ,  $b = 9.665(2)$ ,  $c = 12.606(1) \text{ \AA}$ ;  $\beta = 95.153(3)^\circ$ ;  $V = 1326.6(3) \text{ \AA}^3$ ; space group =  $P2_1/a$ ;  $Z = 4$ ;  $\rho_{\text{calcd}} = 1.538 \text{ g cm}^{-3}$ ;  $F_{000} = 636.00$ ;  $R = 0.056$ ,  $wR = 0.137$ .

CCDC-275708 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Photochemical measurements:** Photoisomerization measurements were carried out under a nitrogen atmosphere using a 500 W super-high-pressure mercury lamp USH-500D (USHIO) for the 365 nm light irradiation source and a 500 W Xe short arc lamp 500D-0 (USHIO) for the 546 nm light irradiation source. The light wavelength was selected with a monochromator (JASCO CT-10T). Determination of the photoreaction quantum yields was carried out by using  $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$  as a chemical actinometer.<sup>[12]</sup>

**Synthesis of 4-ferrocenylazophenol (FAP):** FAP was synthesized by using a modified method to prepare 2-bromo-2'-methylazobenzene.<sup>[24]</sup> Under a nitrogen atmosphere, the zinc chloride salt (2.2 g) of *p*-phenyldiazonium chloride<sup>[14]</sup> and dry ether (50 mL) were put into a flask (200 mL) and then cooled to  $-70^\circ\text{C}$  in a dry-ice/acetone bath. A solution of lithiated ferrocene in dry ether<sup>[25]</sup> (prepared from 2 g of ferrocene) was introduced from a dropping funnel into the suspension of the diazonium salt with vigorous stirring, and then the mixture was warmed to room temperature. When it became dark purple, a small amount of dilute hydrochloric acid was added to the solution. The mixture was extracted twice by dichloromethane ( $2 \times 50 \text{ mL}$ ), then washed three times with distilled water, and dried with sodium sulfate. After the solvent was removed, the resulting mixture was purified by using silica gel column chromatography with chloroform/hexane (10:1) to give a dark purple solid (0.50 g, 14%). After recrystallization from dichloromethane/hexane, purple crystals were obtained.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = 7.70$  (d,  $^3J(\text{H,H}) = 8.9 \text{ Hz}$ , 2H; Ph), 6.88 (d,  $^3J(\text{H,H}) = 8.9 \text{ Hz}$ , 2H; Ph), 5.18 (s, 1H; OH), 5.01 (t,  $^3J(\text{H,H}) = 2.0 \text{ Hz}$ , 2H; Cp- $\text{N}_2$ ), 4.51 (t,  $^3J(\text{H,H}) = 2.0 \text{ Hz}$ , 2H; Cp- $\text{N}_2$ ), 4.22 ppm (s, 5H; Cp); FAB MS:  $m/z$  calcd for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$ : 306.15 [ $M^+$ ]; found: 306.20; elemental analysis calcd for  $\text{C}_{11}\text{H}_{14}\text{N}_2\text{O}$ : C 62.77, H 4.61, N 9.15; found: C 62.57, H 4.64, N 8.94.

**Synthesis of 8-(4-ferrocenylazophenoxy)octanyl-1-bromide (FAOB):** FAOB was synthesized by a method similar to that used to prepare 2,6,10-tris[(5-bromopentyl)oxy]-3,7,11-tris(hexyloxy)triphenylene.<sup>[26]</sup> FAP (300 mg) was dissolved in dry ethanol (60 mL), and then anhydrous potassium carbonate (490 mg) and dibromooctane (1.3 g) were added to the mixture. After the reaction mixture had been stirred at reflux for 72 h, the solution was carefully decanted into distilled water (50 mL) and extracted with dichloromethane ( $2 \times 50 \text{ mL}$ ). The organic layer was washed with dilute aqueous hydrochloric acid, and the solvent was evaporated. By using silica gel column chromatography, 8-[4-(ferrocenylazo)phenoxy]octanyl-1-bromide was obtained as a purple solid (408 mg, 84%). The solid was purified by recrystallization from hexane.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.73$  (d,  $^3J(\text{H,H}) = 8.9 \text{ Hz}$ , 2H; Ph), 6.92 (d,  $^3J(\text{H,H}) = 8.9 \text{ Hz}$ , 2H; Ph), 5.00 (t,  $^3J(\text{H,H}) = 2.0 \text{ Hz}$ , 2H; Cp- $\text{N}_2$ ), 4.50 (t,  $^3J(\text{H,H}) = 2.3 \text{ Hz}$ , 2H; Cp- $\text{N}_2$ ), 4.21 (s, 5H; Cp), 4.00 (t,  $^3J(\text{H,H}) = 6.5 \text{ Hz}$ , 2H;  $\text{CH}_2\text{O}$ ), 3.40 (t,  $^3J(\text{H,H}) = 6.9 \text{ Hz}$ , 2H;  $\text{CH}_2\text{Br}$ ), 1.82 (m, 4H;  $\text{CH}_2$ ), 1.3–1.5 ppm (m, 8H;  $\text{CH}_2$ ); FAB MS:  $m/z$  calcd for  $\text{C}_{24}\text{H}_{29}\text{BrFeN}_2\text{O}$ : 496.24 [ $M^+$ ]; found: 496.13; elemental analysis calcd for  $\text{C}_{24}\text{H}_{29}\text{BrFeN}_2\text{O}$ : C 57.97, H 5.88, N 5.63, Br 16.07; found: C 57.89, H 5.78, N 5.74, Br 16.17.

**Isolation of photoreaction products of FAP and FAOB:** A solution of FAP (50 mg) in ethanol/chloroform (100 mL, 1:1) was bubbled with nitrogen for 30 min, then photoirradiated ( $\lambda_{\text{max}} = 546 \text{ nm}$ ) at room temperature until the solution changed from purple to orange. The mixture was concentrated to about 5 mL and then chloroform (100 mL) was added. After alternately concentrating the mixture and adding chloroform three times, the mixture was concentrated to approximately 5 mL and purified by using silica gel column chromatography with dichloromethane/hexane (1:1) as the eluent. The elution of the second band was collected, concentrated to about 5 mL, and then recrystallized to give an orange solid (19 mg, 62%) by adding hexane to the solution.

It should be noted that the photoproduct was unstable in a concentrated solution and could not be obtained directly by evaporating the solvent. The product was characterized as phenolhydrazonecyclopentadiene (PHP), as discussed in the Results and Discussion.  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.58 (s, 1H), 7.16 (d, 2H), 6.80 (d, 2H), 6.67 (m, 1H), 6.43 (m, 1H), 6.32 (m, 2H), 4.60 ppm (s, 1H); ( $\text{CD}_3\text{CN}$ ):  $\delta$  = 9.59 (s, 1H), 7.15 (d,  $J$  = 6.8, 2H), 6.79 (d,  $J$  = 6.8, 3H), 6.59 (m, 1H), 6.46 (m, 1H), 6.39 (m, 1H), 6.23 ppm (m, 1H); ESIMS:  $m/z$  calcd: 185.20 [ $M^+$ –H]; found: 185.12.

By using the same photoirradiation method, we obtained the photoreaction product of FAOB, which was characterized as 8-bromooctanylphenolhydrazonecyclopentadiene (BPHP).  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.60 (s, 1H), 7.14 (d, 2H), 6.86 (m, 2H), 6.67 (m, 1H), 6.42 (m, 1H), 6.33 (m, 1H), 6.30 (m, 1H), 3.92 (t, 2H), 3.40 (t, 2H), 1.86 (m, 2H), 1.75 (m, 2H), 1.43 (m, 4H), 1.34 ppm (m, 4H); GC–MS:  $m/z$  calcd: 377.32 [ $M^+$ ]; found: 378 (double peak).

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