

## ARTICLES

## Synthesis and Photochemical Properties of a Photochromic Iron(II) Complex of Hexaarylbiimidazole

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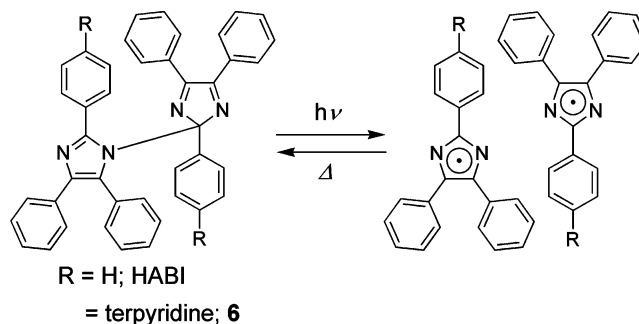
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The photochromic ligand bis(terpyridyl)hexaarylbiimidazole (bistpy-HABI) and the Fe(II) complex of bistpy-HABI with formula  $[\{\text{Fe}(\text{tpy})\}_2 \cdot \text{bistpy-HABI}](\text{PF}_6)_4 \cdot 4\text{H}_2\text{O}$  were synthesized and characterized. Bistpy-HABI is readily cleaved into a pair of terpyridyltriphenylimidazolyl radicals (tpy-TPI $\cdot$ ) on irradiation with UV light. This photochemical reaction is completely reversible, and the light-induced radicals can thermally recombine to form bistpy-HABI in the dark.  $[\{\text{Fe}(\text{tpy})\}_2 \cdot \text{bistpy-HABI}]^{4+}$  is the first example of a transition-metal complex of an HABI derivative and was found to show photochromic reaction in solution. The spin state of the light-induced radical pair in a frozen matrix was investigated by ESR spectroscopy. The triplet state of the light-induced radical pair from  $[\{\text{Fe}(\text{tpy})\}_2 \cdot \text{bistpy-HABI}]^{4+}$ , as well as that from bistpy-HABI, was confirmed to be a ground state or nearly degenerated with a singlet state. Kinetic studies on the radical recombination reaction in solution elucidated the decrease in the activation energy by forming the Fe(II) complex. This is the first observation of a decrease in the activation energy of the radical recombination reaction by the formation of a metal-coordinated radical complex. The syntheses, photochemical properties, and spin states of bistpy-HABI and  $[\{\text{Fe}(\text{tpy})\}_2 \cdot \text{bistpy-HABI}](\text{PF}_6)_4$  are discussed.

## 1. Introduction

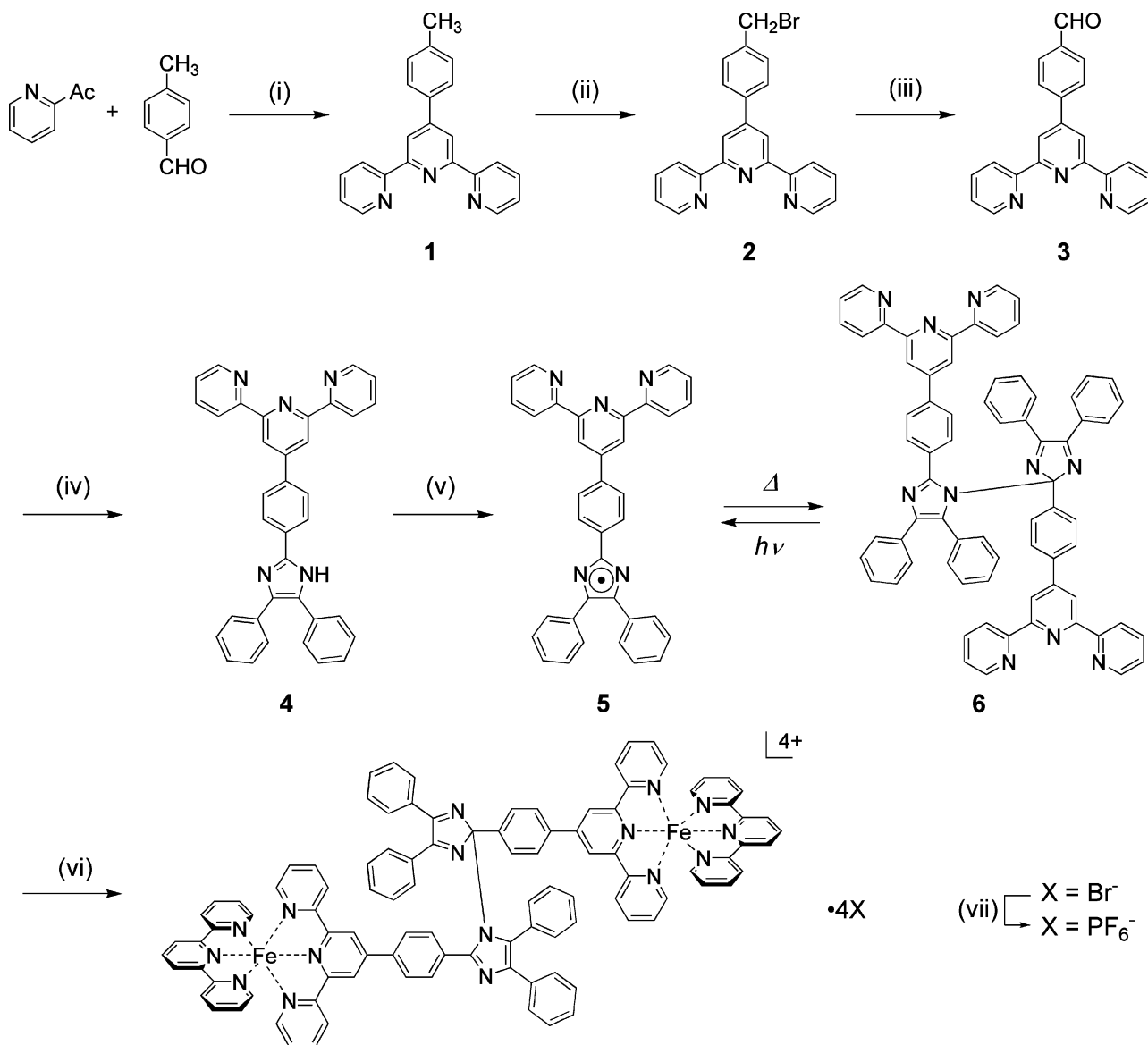
Reversible photocontrolling of the physical properties of a material is a significant technique for the development of advanced photofunctional materials. A large number of photochromic compounds have been investigated in systems bearing various photoresponsive units.<sup>1</sup> Among various photochromic compounds, diarylethenes having heterocyclic five-membered rings as the aryl groups are known to undergo thermally irreversible and fatigue-resistant photochromic reactions.<sup>2</sup> Diarylethenes could change molecular structure and the manner of the  $\pi$ -conjugation pathway even in the solid state by irradiation with light of appropriate wavelengths. Noteworthy studies on the photoswitching of the magnetic interaction were recently reported by Matsuda and Irie.<sup>3</sup> They have investigated the exchange coupling between two nitronyl nitroxide radicals, which are located at both ends of a diarylethene unit. On the other hand, we have been focused on the photochromism of hexaarylbiimidazoles (HABIs), aiming for development in the field of radical chemistry.<sup>4</sup> HABIs are readily cleaved, both thermally and photochemically, into a pair of triphenylimidazolyl radicals (TPI $\cdot$ ) that can recombine to form the imidazole dimer (Scheme 1).<sup>5</sup> There are a number of spectroscopic studies on the photochemical reaction of HABI and its derivatives.<sup>6</sup> While the photochromism of diarylethene is a “closed-ring/open-ring”-type switching, that of HABI is a “closed-shell/open-shell”-type switching which can be regarded as a “diamagnetic/paramagnetic” photoswitching. We have previously reported the

## SCHEME 1. Photochromism of HABI Derivatives



in situ direct observation of a light-induced radical pair (RP) in a crystal of *o*-Cl-HABI by the X-ray diffraction technique and described the first example of measurements of intermolecular exchange coupling for the light-induced RP by ESR spectroscopy.<sup>4d,f</sup> There are two types of RPs, pair A and pair B, differing only in the spatial arrangement of the two lophyl radicals. The temperature dependence of the ESR spectral pattern shows that pair A converts irreversibly into pair B when the temperature is increased. The Curie analyses of the ESR signal intensities show that the triplet state of pair A is the ground state or is nearly degenerate with the singlet state. On the other hand, the triplet state of pair B is thermally populated and the singlet state is the ground state. The exchange coupling between the unpaired electrons in pair B in the crystal was determined as  $-77 \text{ cm}^{-1}$  by assuming thermal equilibrium between the ground singlet state and excited triplet state. The experimental value is in fair agreement with the theoretical value of  $-45 \text{ cm}^{-1}$  evaluated

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SCHEME 2. Synthetic Procedure of the Compounds<sup>a</sup>

<sup>a</sup> Reagents and conditions: (i) KOH,  $\text{NH}_4\text{OH}$ ,  $\text{H}_2\text{O}$ /methanol, room temperature; (ii) NBS, benzene, reflux,  $h\nu$ ; (iii) hexamine, HCl, ethanol, reflux; (iv) benzil,  $\text{CH}_3\text{COONH}_4$ ,  $\text{CH}_3\text{COOH}$ , reflux; (v) KOH,  $\text{K}_3[\text{Fe}(\text{CN})_6]$ (aq)/benzene, room temperature; (vi)  $[\text{Fe}(\text{tpy})\text{Br}]\text{Br}$ ,  $\text{CH}_2\text{Cl}_2$ , methanol,  $0^\circ\text{C}$ ; (vii)  $\text{KPF}_6$ ,  $\text{H}_2\text{O}$ , room temperature.

by the DFT B3LYP/6-31G(d) calculations. Thus, HABI derivatives can be potentially applicable for the construction of a photoresponsive spin coupler.

The application of coordination chemistry is a useful approach for molecular assembly. There has been considerable effort in the construction of molecular magnetic materials by the assembly of organic  $\pi$ -radicals and transition-metal ions.<sup>7</sup> If the complex could be assembled from a photochromic unit which will produce  $\pi$ -radicals by light irradiation, it is potentially possible to control the magnetic properties of the complex by light. Thus, we have come up with the idea that the metal complexes of HABIs should show a unique photoresponse in magnetic properties due to the generation of the light-induced RP. However, there is no literature with regard to the metal complexes of HABIs because of the synthetic difficulty owing to the high reactivities of TPI<sup>•</sup> radicals that prevent themselves from chemical modification. In this paper, we present a new HABI derivative containing terpyridyl groups as the coordination part (**6** in Scheme 2). Prior to the investigation of the photochemical control of exchange coupling between the spins

on metals through the light-induced triplet RP, we did choose a diamagnetic transition metal for the assembly of the metal-coordinated HABI complex to confirm the possibility of the formation of the light-induced triplet RP in the metal complex. The synthesis and photochromic and optical properties of bistpy-HABI and its Fe(II) complex will be described.

## 2. Experimental Section

**Materials.** The synthetic route of the compound is shown in Scheme 2. Benzene and dichloromethane were freshly distilled on the appropriate drying reagents prior to use. All other reagents were obtained commercially and were used as supplied. UV-vis absorption spectra were measured on an S-2600 Soma-Kogaku multichannel spectrometer. The NMR and ESR spectra were recorded on JNM-EPC500A (JEOL) and JES-TE200 (JEOL) spectrometers, respectively. The FAB mass spectra were measured with an MS-700 (JEOL) spectrometer by using 3-NBA (3-nitrobenzyl alcohol) as a matrix.

**4'-Tolyl-2,2':2'',6'-terpyridine (1).** 2-Acetylpyridine (12.5 g, 103.75 mmol) and 4-tolualdehyde (6.25 g, 52.5 mmol) were

added to 400 mL of methanol. To the solution were added concentrated  $\text{NH}_4\text{OH}$  (360 mL) and 15% aqueous  $\text{KOH}$  (36 mL), and the resulting solution was stirred for 4 days. The precipitated pale yellow solid was filtrated and frequently washed with water (40 mL  $\times$  15), dried, and purified by silica gel column chromatography in chloroform. The crude material was crystallized from ethanol to give 9.5 g of white needle crystals of a mixture of **1** and 6'-tolyl-2,2':4',2''-terpyridine. These structural isomers cannot be separated by the usual purification method but by the difference in the solubilities of their Fe(II) complexes. A 100 mL portion of an aqueous solution of Mohr salt (5.7 g, 15 mmol) was added to a mixture of **1** and 6'-tolyl-2,2':4',2''-terpyridine (9.5 g) in 250 mL of ethanol and 250 mL of dichloromethane. After 5 min of stirring, dichloromethane was removed from the mixture under reduced pressure. An aqueous solution of  $\text{KPF}_6$  (5.4 g, 15 mmol, in 50 mL of  $\text{H}_2\text{O}$ ) was added to the mixture. The mixture was stirred for 20 min to give a purple precipitate. The purple precipitate was recrystallized three times from toluene and acetonitrile solution to give purple needle crystals of  $(\text{Fe}\cdot\mathbf{1})_2(\text{PF}_6)_2$  (15.9 g). Then the pure  $(\text{Fe}\cdot\mathbf{1})_2(\text{PF}_6)_2$  was dissolved in acetonitrile (200 mL), and 15% aqueous  $\text{KOH}$  (200 mL) was added to the solution. To this solution was added  $\text{H}_2\text{O}_2$  dropwise with stirring, and white precipitates appeared immediately. This precipitate was collected, dissolved in toluene, and then filtered through the Celite filter agent. The filtrate was evaporated in vacuo to give white solids. Recrystallization of the white solid from ethanol gave white needle crystals of **1**, 7.9 g (24 mmol, yield 46%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 8.70\text{--}8.72$  (4H), 8.65 (2H), 7.86 (4H), 7.80 (2H), 7.33 (2H), 7.30 (2H), 2.42 (3H).

**4'-(4-Bromomethylphenyl)-2,2':2'',6'-terpyridine (2)**. **1** (7.9 g, 24 mmol) and *N*-bromosuccinimide (6.5 g, 37 mmol) in benzene (240 mL) were refluxed for 6 h under the irradiation of a room fluorescent lamp. After the mixture was cooled, benzene was removed and the precipitate was extracted with carbon tetrachloride (200 mL). The extract was filtrated and evaporated to dryness. The residue was recrystallized from ethanol to give **2** as white needle crystals (8.1 g, 20 mmol, yield 83%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 8.73$  (4H), 8.67 (2H), 7.88 (4H), 7.54 (2H), 7.35 (2H), 4.58 (2H).

**4-(2,2':2'',6'-Terpyridyl)benzaldehyde (3)**. **2** (8.1 g, 20 mmol) and hexamethylenetetramine (11.3 g, 81 mmol) in 220 mL of ethanol were refluxed with stirring for 6 h. Then the reaction mixture was cooled to room temperature, and 70 mL of  $\text{H}_2\text{O}$  and 70 mL of concentrated  $\text{HCl}$  were added. The solution was refluxed again for 2 h. After cooling, the solvent was neutralized with aqueous  $\text{NaHCO}_3$  and a white precipitate appeared. The precipitate was filtrated and purified by silica gel column chromatography in chloroform and recrystallized from ethanol to give **3** as yellow plate crystals (3.1 g, 9.1 mmol, yield 45%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 500 MHz):  $\delta = 10.12$  (1H), 8.78 (2H), 8.74 (2H), 8.69 (2H), 8.07 (2H), 8.04 (2H), 7.91 (2H), 7.38 (2H).

**4'-[4-(4,5-Diphenylimidazol-2-yl)phenyl]-2,2':2'',6'-terpyridine (4, tpy-TPI)**. A mixture of **3** (1.00 g, 2.97 mmol), benzil (630 mg, 3.00 mmol), and ammonium acetate (2.3 g, 30 mmol) in acetic acid (30 mL) was heated at reflux for 10 h. After the mixture was cooled, the solvent was neutralized with concentrated  $\text{NH}_4\text{OH}$ . The precipitate was filtered and washed with  $\text{H}_2\text{O}$ . The residue was purified by silica gel column chromatography in chloroform and recrystallized from methanol to give **4** as pale green flake crystals (1.41 g, 2.68 mmol, yield 87%).  $^1\text{H NMR}$  ( $\text{DMSO}$ , 500 MHz):  $\delta = 12.92$  (1H), 8.80 (2H), 8.71 (4H), 8.32 (2H), 8.10 (2H), 8.07 (2H), 7.59 (2H), 7.55 (2H),

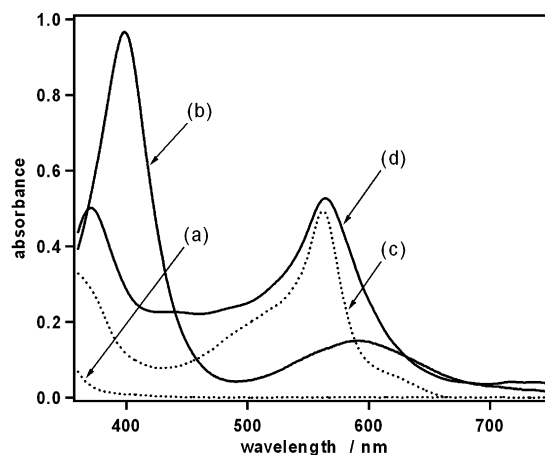
7.47 (2H), 7.41 (1H), 7.34 (2H), 7.26 (1H). FAB-MS:  $m/z$  528 ( $[\text{M} + \text{H}]^+$ ). Anal. Calcd for  $\text{C}_{36}\text{H}_{25}\text{N}_5$ : C, 81.95; H, 4.78; N, 13.27. Found: C, 81.04; H, 4.87; N, 13.02.

**Bistpy-HABI (6)**. All manipulations were carried out with the exclusion of light. A 300 mg sample of **4** (0.56 mmol) and  $\text{K}_3[\text{Fe}(\text{CN})_6]$  (4.0 g, 12 mmol) were added into 15% aqueous  $\text{KOH}$  (50 mL) and benzene (50 mL). **4** was oxidized to tpy-TPI\* (**5**) that readily dimerizes to **6** under dark conditions. The mixture was stirred for 1 day. The benzene layer containing **6** was separated, frequently washed with  $\text{H}_2\text{O}$  (50 mL  $\times$  20), and then dried over  $\text{Na}_2\text{SO}_4$ . The solution was evaporated to give **6** as a pale green amorphous solid (253 mg, 0.24 mmol, yield 86%). FAB-MS:  $m/z$  1053 ( $[\text{M} + \text{H}]^+$ ). Anal. Calcd for  $\text{C}_{72}\text{H}_{48}\text{N}_{10}$ : C, 81.5; H, 4.86; N, 13.6. Found: C, 82.1; H, 4.59; N, 13.3.

**[{Fe(tpy)}<sub>2</sub>·**6**](PF<sub>6</sub>)<sub>4</sub>·4H<sub>2</sub>O**. All manipulations were carried out with the exclusion of light. A mixture of (terpyridine)-bromoiron(II) bromide (48 mg, 0.108 mmol) in methanol (20 mL) and 51.5 mg of **6** (0.0489 mmol) in 20 mL of dichloromethane was stirred for 10 min with ice cooling. After stirring, 20 mL of  $\text{H}_2\text{O}$  was added to the solution. Dichloromethane and methanol were removed from the mixture in vacuo. To the mixture was added  $\text{KPF}_6$  (45.0 mg, 0.244 mmol) in  $\text{H}_2\text{O}$  (20 mL), and the resulting mixture was stirred for 20 min. A purple precipitate appeared and was collected, extracted with dichloromethane, and then dried over  $\text{Na}_2\text{SO}_4$ . The solution was filtrated and evaporated to give **[{Fe(tpy)}<sub>2</sub>·**6**](PF<sub>6</sub>)<sub>4</sub>·4H<sub>2</sub>O as a purple amorphous solid (86 mg, 0.0389 mmol, yield 79%). FAB-MS:  $m/z$  2065 ( $[\text{M} - \text{PF}_6 - 4\text{H}_2\text{O}]^+$ ). Anal. Calcd for  $\text{C}_{102}\text{H}_{78}\text{N}_{16}\text{O}_4\text{F}_{24}\text{P}_4\text{Fe}_2$ : C, 53.65; H, 3.44; N, 9.81. Found: C, 54.15; H, 3.47; N, 9.66.**

### 3. Results and Discussion

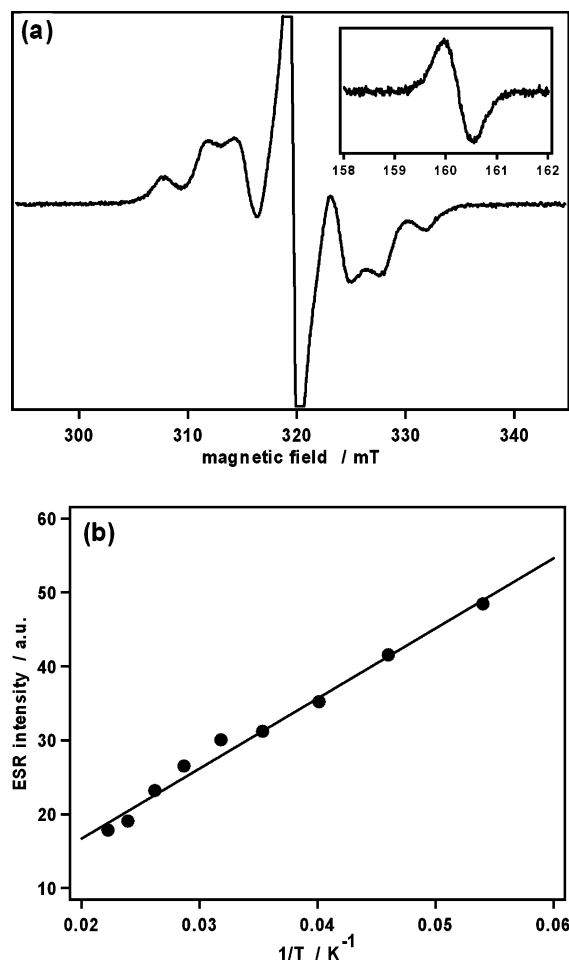
The UV spectrum of **6** in benzene ( $1.5 \times 10^{-5}$  M) is shown in Figure 1a. On irradiation with 360 nm light, the pale yellow solution quickly turned forest green and gave rise to an intense absorption band around 400 nm and a broad absorption band ranging in wavelength from 500 to 700 nm (Figure 1b). The light-induced color change can be attributable to the formation of **5** on the basis of the analogy of the photochromic color change of other HABI derivatives. On standing in the dark, the forest green color gradually faded with a decrease in these light-



**Figure 1.** UV-vis absorption spectra of bistpy-HABI in benzene ( $1.5 \times 10^{-5}$  M) (a) before irradiation and (b) immediately after irradiation and those of **[{Fe(tpy)}<sub>2</sub>·**6**](PF<sub>6</sub>)<sub>4</sub>·4H<sub>2</sub>O in dichloromethane ( $1.5 \times 10^{-5}$  M) (c) before irradiation and (d) immediately after irradiation. Irradiation was carried out with 360 nm light at room temperature. All of the measurements were carried out by using a 10 mm quartz cell.**

induced absorption bands and the spectrum finally reached the original spectrum. Reversibility of this photochromic reaction was also confirmed by repeated measurements of the absorption spectra. In contrast to **6**,  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4$  is colored violet due to the presence of Fe(II) ions. The UV spectrum of  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4$  was measured in dichloromethane ( $1.5 \times 10^{-5}$  M) due to the poor solubility in benzene (Figure 1c). An intense absorption band at 560 nm could be tentatively assigned to the metal-to-ligand charge-transfer (MLCT),  $d-\pi^*$ , transition that is often observed for the N-coordinated octahedral Fe(II) ion in the low-spin state. On irradiation with 360 nm light, the absorbance of the wavelength region between 350 and 680 nm increased due to the photochromic reaction of the HABI moiety (Figure 1d). A weak and broad absorption band appeared around 420 nm after the irradiation, assumed to be the charge-transfer absorption band between Fe(II) ion and the tpy-TPI<sup>•</sup> unit. The light-induced radical complex  $[\text{Fe}(\text{tpy})\cdot\mathbf{5}]^{2+}$  also recombined into  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}]^{4+}$  in a manner similar to that of the free ligand **6**. The kinetics of the recombination processes of light-induced radicals is of interest compared with that of another HABI system; the detailed description will be discussed later.

The photochromic behavior of **6** and  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4$  was also investigated by ESR measurements. A 50  $\mu\text{L}$  sample of a dichloromethane solution ( $1.5 \times 10^{-3}$  M) of **6** in a quartz tube was carefully prepared with exclusion of light, and the sample was irradiated with UV light (300–400 nm) at 18 K. As shown in Figure 2a, the ESR spectrum of the UV-irradiated solution shows a randomly oriented triplet pattern with an overlapping doublet signal derived from a trace of free radicals. The detection of a forbidden weak transition at half-field indicates the presence of a triplet-state species, which can be assigned to the light-induced triplet RP. Only one type of triplet RP could be detected in this molecular system against the case for the light-induced RP in the crystal of *o*-Cl-HABI. The inset depicts the forbidden transition signal corresponding to the  $\Delta M_S = 2$  transition. Lande's *g* value was obtained as 2.0035, and the zero-field splitting (*zfs*) parameter for the triplet RP was estimated as  $|D/hc| = 5.7 \times 10^{-3} \text{ cm}^{-1}$ . Applying the point-dipole approximation, the average distance between the two radical centers of the light-induced RP derived from **6** was estimated as 6.12 Å, which is reasonable by comparison with those of other light-induced RPs estimated for various HABI derivatives.<sup>4</sup> The temperature dependence of the ESR signal intensities of the  $\Delta M_S = 2$  forbidden transition was recorded from 15 to 45 K, and Curie analyses were carried out on the ESR signal intensities as a function of reciprocal temperature as shown in Figure 2b. A linear Curie plot cannot prove absolutely that the observed ESR spectrum belongs to a high-spin ground state but strongly supports that the triplet state of the RP is a ground state or is nearly degenerate with a singlet state. These facts indicate that the photochromic reaction of **6** generates the triplet RP in restricted environments such as a frozen matrix. The diamagnetism of Fe(II) ions in the  $d^6$  low-spin ground state of  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4$  is revealed from the ESR-silent character of the dichloromethane solution ( $1.5 \times 10^{-3}$  M) at room temperature. On irradiation with UV light, a randomly oriented triplet pattern with  $g = 2.0017$  appeared similarly to that of the free ligand **6** as shown in Figure 3a. The forbidden spin-transition signal assignable to the  $\Delta M_S = 2$  transition indicating the presence of a triplet-state species was also observed as shown in the inset of Figure 3a. The average distance between the two radical centers of the light-induced RP from  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4$  calculated from the *zfs* parameter ( $|D/hc| = 5.4 \times 10^{-3} \text{ cm}^{-1}$ ) is 6.23 Å, and the value is slightly longer than that of the free

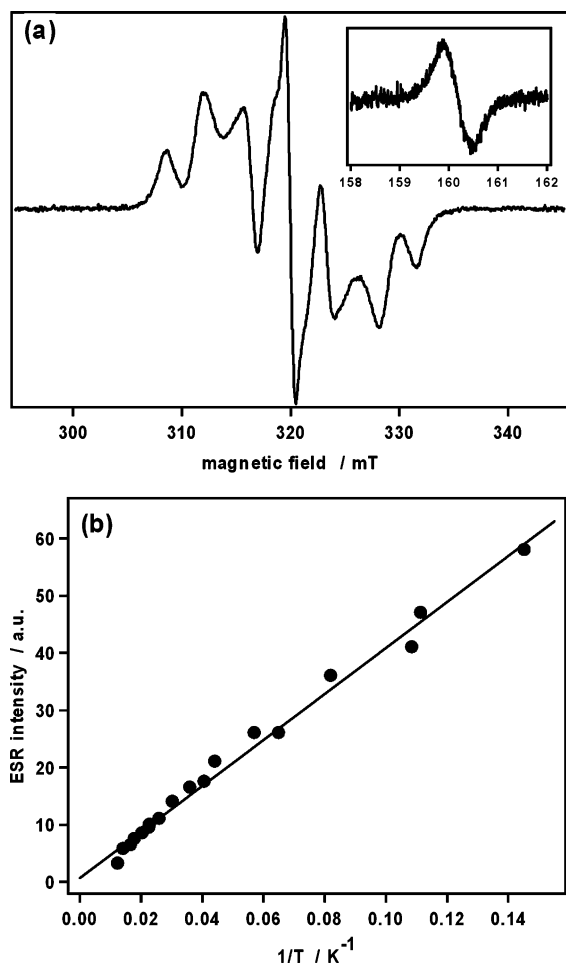


**Figure 2.** (a) ESR spectra of a UV-irradiated dichloromethane solution ( $1.5 \times 10^{-3}$  M) of bistpy-HABI at 18 K. The inset is the detection of a forbidden transition at half-field. (b) Curie plot of the ESR intensity versus reciprocal absolute temperature for the light-induced triplet RP of bistpy-HABI.

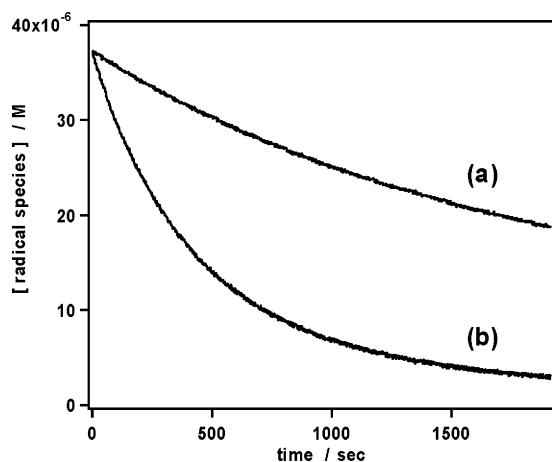
ligand **6**. The difference in the spin-center distance indicates that the spin distribution of tpy-TPI<sup>•</sup> is somewhat affected by the introduction of the transition-metal ion.

The Curie plot of ESR intensities of the light-induced triplet RP derived from  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4$ , as well as that from the free ligand **6**, affords a straight line in the temperature range from 7 to 80 K (Figure 3b). Thus, the triplet state of the light-induced RP from  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4$  is also confirmed to be a ground state or nearly degenerate with a singlet state. The spin state of the light-induced RP of  $[\text{Fe}(\text{tpy})\cdot\mathbf{5}]^{2+}$  is found not to be affected by the perturbation brought about by the introduction of an Fe(II) ion. The presence of magnetic coupling between the light-induced tpy-TPI<sup>•</sup> moieties of metal-coordinated HABIs should be noted for the construction of photoreponsive magnetic materials.

The ESR signal intensities of **5**,  $[\text{Fe}(\text{tpy})\cdot\mathbf{5}]^{2+}$ , and the reference compound DPPH (diphenylpicrylhydrazyl) were recorded in dichloromethane at 293 K to estimate the degree of photodissociation in the photostationary state on irradiation with UV light. By comparing the ESR signal intensity of the sample solutions with that of the dichloromethane solution of DPPH, the degree of photodissociation of **6** was estimated to be 45%. On the other hand, that of  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}]^{4+}$  was ascertained to be only 18% at the photostationary state, indicating the acceleration of the thermal recombination reaction of  $[\text{Fe}(\text{tpy})\cdot\mathbf{5}]^{2+}$  into  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}]^{4+}$ . Indeed, the increase in the decay rate of the metal-coordinated radical species was confirmed by

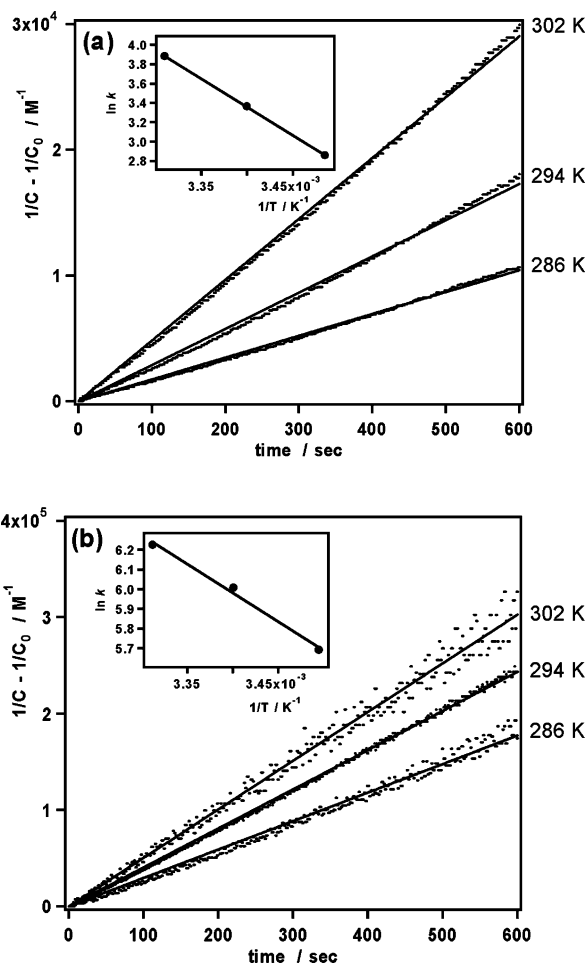


**Figure 3.** (a) ESR spectra of a UV-irradiated dichloromethane solution ( $1.5 \times 10^{-3}$  M) of  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4\cdot 4\text{H}_2\text{O}$  at 15 K. The inset is the detection of a forbidden transition at half-field. (b) Curie plot of the ESR intensity versus reciprocal absolute temperature for the light-induced triplet RP of  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4\cdot 4\text{H}_2\text{O}$ .



**Figure 4.** Decay of the concentration of (a) **5** and (b)  $[\text{Fe}(\text{tpy})\cdot\mathbf{5}]^{2+}$  in dichloromethane kept in the dark at 302 K. The concentration of the radical species was determined from the ESR measurement.

measuring the time course of ESR signal intensities as shown in Figure 4. The decay kinetics of light-induced radical species can be described by second-order kinetics in a manner similar to that of the decay kinetics that were found in other HABI derivatives. Figure 5 shows the second-order plot relating to the radical recombination processes of **5** and  $[\text{Fe}(\text{tpy})\cdot\mathbf{5}]^{2+}$ . The kinetic constants of the recombination processes of the two compounds were determined on the basis of the ESR signal



**Figure 5.** Second-order plot of the decay of (a) **5** and (b)  $[\text{Fe}(\text{tpy})\cdot\mathbf{5}]^{2+}$  in dichloromethane kept in the dark at 286, 294, and 302 K after irradiation. The solid lines are the best fit of the experimental points. The inset is an Arrhenius plot of the second-order rate constants of the dimerization reaction of the radical species.

intensities and were calculated as  $k_5 = 48.4 \text{ L mol}^{-1} \text{ s}^{-1}$  and  $k_{\text{Fe}(\text{tpy})\cdot\mathbf{5}} = 504.6 \text{ L mol}^{-1} \text{ s}^{-1}$  at 302 K. Moreover, the activation energies for the radical recombination reaction were investigated from Arrhenius plots as shown in the inset of Figure 5. The activation energy for the radical recombination reaction of  $[\text{Fe}(\text{tpy})\cdot\mathbf{5}]^{2+}$  ( $E_a = 24.3 \text{ kJ/mol}$ ) is about half that of **5** ( $E_a = 48.6 \text{ kJ/mol}$ ). As far as we know, this is the first observation of a decrease in the activation energy of the radical recombination reaction by the formation of a metal-coordinated radical complex. Though the detailed mechanism cannot be clarified at present, this finding would give significant insight into radical chemistry.

#### 4. Conclusion

In conclusion, we have successfully synthesized the first photochromic radical ligand, **6**, and the Fe(II) complex  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4$ . Both the ligand and the Fe(II) complex exhibited reversible photochromic behavior at room temperature. The triplet states of the light-induced RPs have successfully been detected by ESR spectroscopy in frozen matrixes for **6** and  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4$ . The degree of photodissociation of  $[\{\text{Fe}(\text{tpy})\}_2\cdot\mathbf{6}](\text{PF}_6)_4$  was smaller than that of **6**, because of the rapid recombination process of the Fe(II) complex of tpy-TPI\*. The result reported here would help the progress of a new category of HABI chemistry, namely, the coordination chemistry of the photochromic radical ligand.

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## References and Notes

- (1) (a) For recent reviews on photochromism, see, for example: *Photochromism: Memories and Switches*; Irie, M., Ed. *Chem. Rev.* **2000**, *100* (5) (special issue). (b) Nakatsuji, S. *Chem. Soc. Rev.* **2004**, *33*, 348–353.
- (2) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.
- (3) (a) Matsuda, K.; Matsuo, M.; Mizoguti, S.; Higashiguchi, K.; Irie, M. *J. Phys. Chem. B* **2002**, *106*, 11218–11225. (b) Matsuda, K.; Matsuo, M.; Irie, M. *J. Org. Chem.* **2001**, *66*, 8799–8803. (c) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2001**, *123*, 9896–9897. (d) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 8309–8310. (e) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195–7201.
- (4) (a) Nakahara, I.; Kikuchi, A.; Iwahori, F.; Abe, J. *Chem. Phys. Lett.* **2005**, *402*, 107–110. (b) Kikuchi, A.; Iwahori, F.; Abe, J. *J. Am. Chem. Soc.* **2004**, *126*, 6526–6527. (c) Kikuchi, A.; Iyoda, T.; Abe, J. *Chem. Commun.* **2002**, 1484–1485. (d) Abe, J.; Sano, T.; Kawano, M.; Ohashi, Y.; Matsushita, M. M.; Iyoda, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 580–582. (e) Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. *Chem. Lett.* **2000**, 1372–1373. (f) Kawano, M.; Sano, T.; Abe, J.; Ohashi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 8106–8107.
- (5) (a) Hayashi, T.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 565–566. (b) Hayashi, T.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1962**, *35*, 2057–2058. (c) Hayashi, T.; Maeda, K.; Morinaga, M. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1563–1564. (d) Hayashi, T.; Maeda, K.; Takeuchi, M. *Bull. Chem. Soc. Jpn.* **1964**, *37*, 1717–1718. (e) Hayashi, T.; Maeda, K.; Kanaji, T. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 857–858. (f) Hayashi, T.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 685–686. (g) Hayashi, T.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2990. (h) Maeda, K.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 429–438. (i) Maeda, K.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 3509–3514. (j) Shida, T.; Maeda, K.; Hayashi, T. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 652–657.
- (6) (a) White, D. M.; Sonnenberg, J. *J. Am. Chem. Soc.* **1966**, *88*, 3825–3829. (b) Cohen, R. *J. Org. Chem.* **1971**, *36*, 2280–2284. (c) Riem, R. H.; MacLachlan, A.; Coraor, G. R.; Urban, E. J. *J. Org. Chem.* **1971**, *36*, 2272–2275. (d) Cescon, L. A.; Coraor, G. R.; Dessauer, R.; Silversmith, E. F.; Urban, E. J. *J. Org. Chem.* **1971**, *36*, 2262–2267. (e) Tanino, H.; Kondo, T.; Okada, K.; Goto, T. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1474–1480. (f) Goto, T.; Tanino, H.; Kondo, T. *Chem. Lett.* **1980**, 431–434. (g) Lavabre, D.; Levy, G.; Laplante, J. P.; Micheau, J. C. *J. Phys. Chem.* **1988**, *92*, 16–18. (h) Qin, X.-Z.; Liu, A.; Trifunac, A. D.; Krongauz, V. V. *J. Phys. Chem.* **1991**, *95*, 5822–5826. (i) Liu, A.; Trifunac, A. D.; Krongauz, V. V. *J. Phys. Chem.* **1992**, *96*, 207–211. (j) Lin, Y.; Liu, A.; Trifunac, A. D.; Krongauz, V. V. *Chem. Phys. Lett.* **1992**, *198*, 200–206. (k) Morita, H.; Minagawa, S. *J. Photopolym. Sci. Technol.* **1992**, *5*, 551–556. (l) Monroe, B. M.; Weed, G. C. *Chem. Rev.* **1993**, *93*, 435–448. (m) Weidong, Y.; Yongyuan, Y.; Junshen, W.; Cunlin, Z.; Meiwen, Y. *J. Photopolym. Sci. Technol.* **1994**, *7*, 1870–192. (n) Ma, S.; Nebe, W. J. *J. Imaging Sci. Technol.* **1993**, *37*, 498–504. (o) Caspar, J. V.; Khudyakov, I. V.; Turro, N. J.; Weed, G. C. *Macromolecules* **1995**, *28*, 636–641. (p) Oliver, E. W.; Evans, D. H.; Caspar, J. V. *J. Electroanal. Chem.* **1996**, *403*, 153–158. (q) Okada, K.; Imamura, K.; Oda, M.; Kozaki, M.; Morimoto, Y.; Ishino, K.; Tashiro, K. *Chem. Lett.* **1998**, 891–892.
- (7) Miller, J. S.; Drillon, M. *Magnetism: Molecules to Materials II*; Wiley-VCH: Weinheim, Germany, 2001. (b) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993. (c) Kumagai, H.; Inoue, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 1601–1603. (d) Caneschi, A.; Gatteschi, D.; Rey, P. *Prog. Inorg. Chem.* **1991**, *39*, 331–429.