

Photoswitching of the Magnetic Interaction between a Copper(II) Ion and a Nitroxide Radical by Using a Photochromic Spin Coupler

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Abstract: Photoswitching of an intramolecular spin exchange interaction between a copper(II) ion and a nitroxyl radical by using a metal complex of diarylethene has been studied by means of ESR spectroscopy. As a coordination ligand, a diarylethene with a 1,10-phenanthroline ring and nitronyl nitroxide radical was synthesized. Mixing the diarylethene ligand with [Cu(hfac)₂] (hfac = hexafluoroacetylacetone) in toluene led to a hypochro-

mic shift of the absorption maxima of the closed-ring isomer due to complexation. ESR measurement in toluene at room temperature of the open-ring isomer of the Cu^{II} complex gave a spectrum that is a superposition of the

spectra from the nitroxide radical and Cu^{II}. When the sample was irradiated with 366 nm light, a new peak due to large exchange interaction appeared between those of the nitroxyl radical and Cu^{II}. This ESR measurement revealed that the magnitude of the spin exchange interaction was changed by more than 160-fold by photoirradiation. This is the largest magnetic photoswitching phenomenon recorded in diarylethene systems.

Keywords: diarylethene • EPR spectroscopy • magnetic properties • photochromism • photoswitching

Introduction

Photochromic compounds have attracted considerable attention because of their potential applications in optical memory media and optical switching devices.^[1] Photochromic compounds inherently possess bistability and can be interconverted between two states photochemically. The two states, accessible by irradiation with light of appropriate wavelength, can be regarded as digital signals (0 and 1).^[2] The difference of two states can be read by their spectroscopic and other physical properties. Logic devices may be designed by combination of the multiple switching units and multiple stimuli.

Among several photochromic compounds, diarylethenes with heterocyclic aryl groups are the most promising compounds for these applications, because of their fatigue resistant and thermally irreversible photochromic reactivities.^[3] Diarylethenes have also been proved as excellent photoswitching devices. The open- and closed-ring isomers of the diarylethenes differ from each other not only in their ab-

sorption spectra, but also in various physical and chemical properties, such as absorption and fluorescence spectra,^[4] refractive indices,^[5] oxidation/reduction potentials,^[6] and chiral properties.^[7] The most important difference is that while π -systems of the two aryl rings are separated in the open-ring isomer, the π -conjugation is delocalized throughout the molecule in the closed-ring isomer. On the basis of this idea we are developing materials that exhibit the photoswitching of a magnetic interaction.^[8] When nitroxide radicals were located at both ends of the aryl groups of the diarylethene, the magnetic interaction between nitroxide radicals can be switched more than 150-fold by photoirradiation.^[8g]

Metal complexes of organic radicals are one of the key families of the molecule-based magnetic materials.^[9] The designable crystal structure and predictable magnetic properties are the advantages of this family over other compounds. On the other hand, metal complexes composed of photochromic units are expected to change the properties upon photoirradiation. Although a couple of the metal complexes with diarylethene ligands have recently been reported for the purpose of the photoswitching of physical properties,^[10] there has been no report on the photoswitching of the metal-radical interaction. The introduction of different spin source is important when the extension to the logic devices is considered. In this paper we report on the photoswitching of a magnetic interaction between a copper(II) ion and a nitronyl nitroxide radical.

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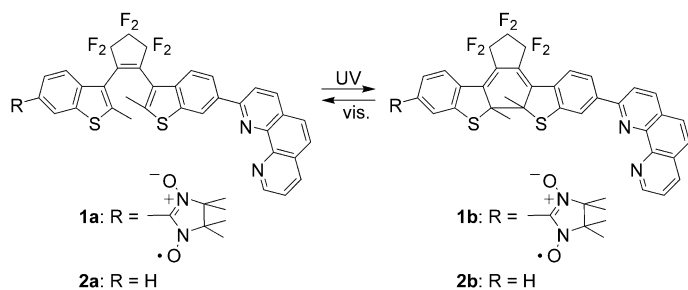
Results and Discussion

Molecular design and synthesis: We have designed and synthesized compound **1a** (Scheme 1). 1,2-Bis(2-methyl-benzothiophen-3-yl) perfluorocyclopentene, which is one of the most robust photochromic units, was chosen for the photochromic core. Nitronyl nitroxide was used as the spin source, because the radical is π -conjugative. 1,10-Phenanthroline was introduced as a chelating group because of the high affinity to the wide range of metal atoms.

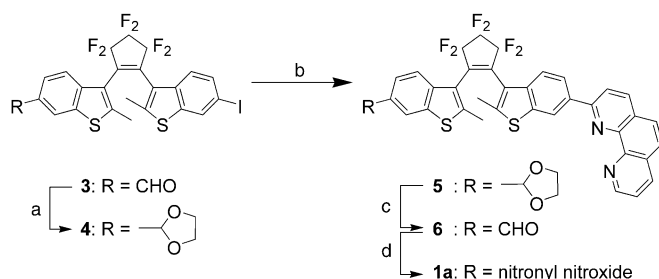
The synthesis was performed according to Scheme 2. The formyl substituent of diarylethene **3** was protected by ethylene glycol to give compound **4**. Compound **5** was synthesized by coupling 1,10-phenanthroline with iodo compound **4**. Compound **5** was deprotected with PPTS, and then coupled with 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate and oxidized to give nitronyl nitroxide **1a**. Compound **2a**, which does not have nitroxyl radical, was also prepared as a reference compound. The characterization of the compounds was performed by ESR and UV-visible spectroscopy and mass spectrometry.

The complexation with copper(II) was performed by the simple addition of an equimolar amount of $[\text{Cu}(\text{hfac})_2]$ (hfac = hexafluoroacetylacetonate) to the ligand **1a** or **2a** in solution, so as to form 1:1 complex $[\text{Cu}(\text{hfac})_2(\mathbf{1a})]$ and $[\text{Cu}(\text{hfac})_2(\mathbf{2a})]$. As described later, this simple procedure was confirmed to be sufficient to give complexes in high yield.

Photochromic properties: A solution of **1a** in toluene underwent a reversible photochromic reaction by alternate irradiation with 366 and 578 nm light (Figure 1a). The color of the solution changed from pale blue to red-purple by UV irradiation.



Scheme 1. Photochromic reactions of **1** and **2**.



Scheme 2. Synthesis of diarylethene ligand **1a**: a) ethylene glycol, *p*-toluenesulfonic acid monohydrate, benzene; b) *n*-BuLi, 1,10-phenanthroline, toluene and then MnO_2 , CH_2Cl_2 ; c) PPTS, acetone; d) 2,3-dimethyl-2,3-bis(hydroxyamino)butane sulfate, methanol and then NaIO_4 , CH_2Cl_2 .

The initial pale blue color originated from the nitronyl nitroxide radical. The conversion from the open- to the closed-ring isomer was 86% in the photostationary state under irradiation with 366 nm light. The absorption maximum of colored isomer **1b** was observed at 569 nm.

The solution of $[\text{Cu}(\text{hfac})_2(\mathbf{1a})]$ also underwent a reversible photochromic reaction (Figure 1b). The conversion from $[\text{Cu}(\text{hfac})_2(\mathbf{1a})]$ to the closed-ring isomer $[\text{Cu}(\text{hfac})_2(\mathbf{1b})]$ was estimated to be 83% in the photostationary state under irradiation with 366 nm light.^[11] The absorption maximum of the colored isomer was observed at 563 nm. The absorption maximum of $[\text{Cu}(\text{hfac})_2(\mathbf{1b})]$ showed a 6 nm hypsochromic shift in comparison with **1b**. Compound **2b** also showed similar hypsochromic shift from 546 nm to 538 nm by the complexation with $[\text{Cu}(\text{hfac})_2]$ (Figure 2). These spectral shifts are attributable to the complexation of the copper(II) ion and 1,10-phenanthroline.

Magnetic switching by photochromism: X-band ESR spectra were measured in toluene ($\sim 10^{-3}\text{M}$) at room temperature. The photochromic ligand **1a** showed a typical five-line ESR spectrum around $g \sim 2.01$ due to nitronyl nitroxide (Figure 3a). A single broad line around $g \sim 2.16$ that originated from hexacoordinated Cu^{II} was observed for compound $[\text{Cu}(\text{hfac})_2(\mathbf{2a})]$ (Figure 3b). Both **1a** and $[\text{Cu}(\text{hfac})_2(\mathbf{2a})]$ did not show any spectral change upon photoirradiation.

The complex of the open-ring isomer $[\text{Cu}(\text{hfac})_2(\mathbf{1a})]$, containing Cu^{II} and radical unit in the molecule, gave a spectrum that is a superposition of the spectra from the nitronyl nitroxide radical and $[\text{Cu}(\text{hfac})_2(\mathbf{2a})]$ (Figure 3c). The spectrum of $[\text{Cu}(\text{hfac})_2(\mathbf{1a})]$ suggested that the intramolecular spin exchange interaction between Cu^{II} and the nitroxyl radical was too small to be detected by ESR measurement. When the solution of $[\text{Cu}(\text{hfac})_2(\mathbf{1a})]$ was irradiated with

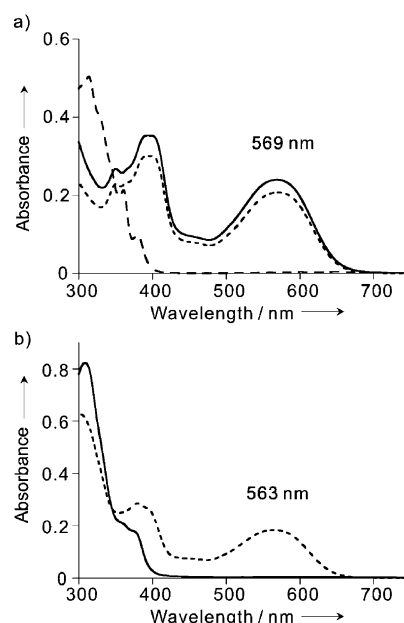


Figure 1. Absorption spectra of **1** in toluene: a) **1a** (dashed line), **1b** (solid line), and in the photostationary state under irradiation with 366 nm light (dotted line); b) $[\text{Cu}(\text{hfac})_2(\mathbf{1a})]$ (solid line) and in the photostationary state under irradiation with 366 nm light (dotted line).

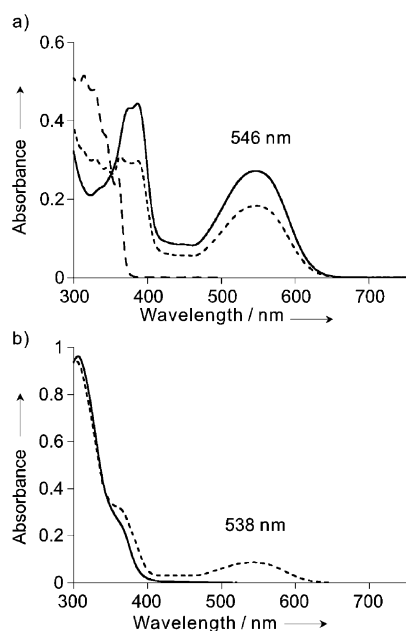


Figure 2. Absorption spectra of **2** in toluene: a) **2a** (dashed line), **2b** (solid line), and in the photostationary state under irradiation with 366 nm light (dotted line); b) $[\text{Cu}(\text{hfac})_2(\mathbf{2a})]$ (solid line) and in the photostationary state under irradiation with 366 nm light (dotted line).

366 nm light, a new signal appeared at the position between those of Cu^{II} and the nitroxyl radical (Figure 3d). This signal is due to UV-generated complex $[\text{Cu}(\text{hfac})_2(\mathbf{1b})]$; this spectrum returned to the original one by photoirradiation with 578 nm light. It was previously reported that when the signal at an intermediate position between the signals of Cu^{II} and the nitroxyl radical is observed, the exchange energy is greater than the difference in g values (Δg) of the parent metal and radical.^[12]

Magnetically isolated nitronyl nitroxide radical exhibits its ESR signal at $g=2$ (3260–3360 G region). The signal change in this region is shown in Figure 4. Upon photoirradiation with UV light, the signal from isolated nitronyl nitroxide radical was found to disappear along with photocyclization. The signal decreased to 20% of the original intensity and recovered completely by the photoirradiation with visible light. The conversion from the open- to the closed-ring isomer was estimated at 83% in the photostationary state from UV-visible absorption measurements as described previously. Therefore the signal remaining in the spectrum of the photostationary state is attributable to the remaining open-ring isomers, not from the uncoordinated ligand. The ESR spectral change corresponds to the photochromic structural change. This spectral change was entirely recovered by the photoirradiation with visible light.

The temperature dependence of the magnetic susceptibility of $[\text{Cu}(\text{hfac})_2(\mathbf{1b})]$ was evaluated by monitoring the double integral value of the ESR signal. The double integral value was proportional to the reciprocal of temperature down to 180 K, below which the solution freezes (180 K). In the frozen matrix the signal shape changed due to the restricted motion of the molecule. This suggests that the exchange interaction is much smaller than kT ($\sim 130 \text{ cm}^{-1}$)

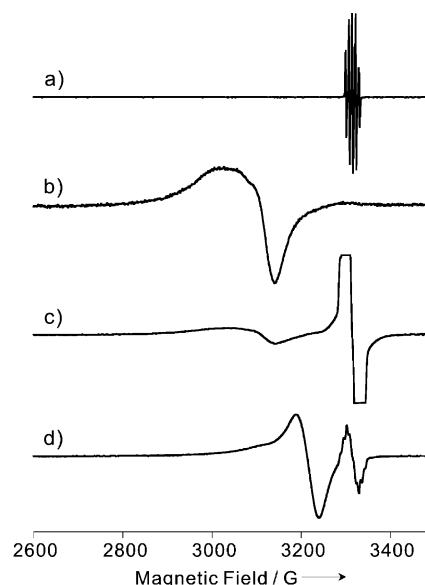


Figure 3. X-band ESR spectra in toluene solution at room temperature (9.33 GHz, 1 mW, 2600–3500 G region): a) spectrum of **1a**; b) spectrum of $[\text{Cu}(\text{hfac})_2(\mathbf{2a})]$; c) spectrum of $[\text{Cu}(\text{hfac})_2(\mathbf{1a})]$; d) spectrum of $[\text{Cu}(\text{hfac})_2(\mathbf{1b})]$ (in the photostationary state under irradiation with 366 nm light). The spectra were obtained with 0.5 G modulation amplitude for a), and with 32 G modulation amplitude for b), c), and d). The same sample was used for measuring spectra c) and d).

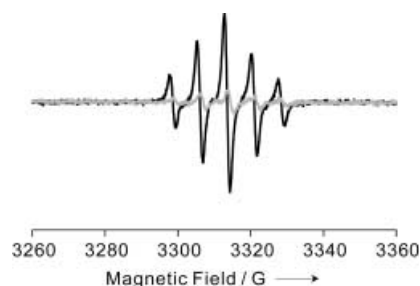


Figure 4. X-band ESR spectra in toluene solution at room temperature (9.33 GHz, 1 mW, 3260–3360 G region, modulation amplitude 0.2 G) of $[\text{Cu}(\text{hfac})_2(\mathbf{1a})]$ (black line) and in the photostationary state under irradiation with 366 nm light (gray line).

The sharp line shape in the nitronyl nitroxide region of $[\text{Cu}(\text{hfac})_2(\mathbf{1a})]$ indicates that the value of spin–spin coupling constant J_{open} must be smaller than the value of its peak-to-peak linewidth of 1.5 G ($\sim 1.4 \times 10^{-4} \text{ cm}^{-1}$). In contrast, the signal of $[\text{Cu}(\text{hfac})_2(\mathbf{1b})]$ that is located in the intermediate position between the parent metal and radical signals indicates that the J_{closed} is greater than $\nu\Delta g/g$ ($\sim 2.3 \times 10^{-2} \text{ cm}^{-1}$). The fairly large difference of exchange interaction between open- and closed-ring isomers was attributed to the substantial difference in π -connectivity. The fully conjugated π -system in the closed-ring isomer made the interaction very large.

Conclusion

We have synthesized a photochromic diarylethene that contained both a nitronyl nitroxide radical and a Cu^{II} ion in the

molecule. The complex reversibly changed the ESR spectrum by alternate irradiation with UV (366 nm) and visible (578 nm) light. The exchange interaction difference between open- and closed-ring isomers was estimated from the ESR spectral change to be more than 160-fold. This is the largest magnetic photoswitching observed in diarylethene systems.

Experimental Section

Materials: All reactions were monitored by thin-layer chromatography carried out on 0.2 mm Merck silica gel plates (60F-254). Column chromatography was performed on silica gel (Kanto Chemical, 63–210 mesh). ^1H NMR spectra were recorded on a Varian Gemini 200 instrument. Mass spectra were obtained on JEOL JMS-HX110A, JMS-GCmateII and Shimadzu GCMS-QP5050A mass spectrometers. Melting points were measured by using a laboratory devices MEL-TEMP II, and were uncorrected.

1-(6-Formyl-2-methylbenzothiophen-3-yl)-2-(6-iodo-2-methylbenzothiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (3): A solution of *n*-butyllithium in hexane (1.6 M, 1.2 mL, 1.9 mmol) was added dropwise to a solution of 1,2-bis(6-iodo-2-methyl-benzothiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene^[de] (1.4 g, 1.9 mmol) in anhydrous THF (50 mL) under Ar at -78°C ; the mixture was stirred for 0.5 h at -78°C . Then dimethylformamide (2.0 mL, 26 mmol) was added dropwise. The mixture was stirred for several minutes and allowed to warm to room temperature, and a saturated aqueous solution of NH_4Cl was slowly added. The resultant mixture was then extracted with diethyl ether, and the organic extract was washed with brine and dried (MgSO_4). The solvent was removed. Column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{hexane}=1:3$) afforded compound **3** (0.54 g, 46%) as a colorless amorphous solid. ^1H NMR (200 MHz, CDCl_3): $\delta=2.19$ (s, 2.1H), 2.28 (s, 2.1H), 2.47 (s, 0.9H), 2.54 (s, 0.9H), 7.23–8.23 (m, 6H), 10.00 (s, 0.3H), 10.07 ppm (s, 0.7H); HRMS: *m/z* calcd for $\text{C}_{24}\text{H}_{13}\text{F}_6\text{IO}_2$ [$M^++\text{H}$]: 621.9357; found 621.9352.

1-(6-(2,5-Dioxolanyl)-2-methylbenzothiophen-3-yl)-2-(6-iodo-2-methylbenzothiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (4): A solution of **3** (0.75 g, 1.2 mmol), ethylene glycol (1.4 g, 23 mmol), and *p*-toluenesulfonic acid monohydrate (2 mg, 0.01 mmol) in benzene (100 mL) was refluxed for 15 h with a Dean–Stark condenser. The reaction mixture was poured into aqueous water, extracted with diethyl ether, washed with brine, dried (MgSO_4), and concentrated. Compound **4** (0.79 g, 100%) was obtained as a colorless amorphous solid. ^1H NMR (200 MHz, CDCl_3): $\delta=2.17$ (s, 2.0H), 2.19 (s, 2.0H), 2.46 (s, 1.0H), 2.48 (s, 1.0H), 4.02–4.14 (m, 4H), 5.84 (s, 0.35H), 5.90 (s, 0.65H), 7.26–8.03 ppm (m, 6H); FAB HRMS: calcd for $\text{C}_{26}\text{H}_{18}\text{F}_6\text{IO}_2\text{S}_2$ [$M^++\text{H}$]: 666.9697; found 666.9699.

1-(6-Formyl-2-methylbenzothiophen-3-yl)-2-[6-(1,10-phenanthroline-2-yl)-2-methyl-benzothiophen-3-yl]-3,3,4,4,5,5-hexafluorocyclopentene (6): Compound **4** (0.60 g, 0.90 mmol) was dissolved in dry diethyl ether (20 mL) and cooled to -78°C under Ar. A 1.6 M solution of *n*-butyllithium (0.56 mL, 0.90 mmol) was added dropwise, and the solution stirred for 1 h at -78°C . The solution was then allowed to warm to 0°C and added to a stirred suspension of 1,10-phenanthroline (160 mg, 0.90 mmol) in diethyl ether (10 mL) at -78°C . The dark red solution was held at -78°C for 4 h and allowed to warm to 0°C . The reaction mixture was stirred for 1.5 h at 0°C and carefully quenched with ice water. The organic layer was separated, and the remaining aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were oxidized by stirring with activated MnO_2 (14 g) for 3 h. Then the mixture was dried (MgSO_4) and filtered. The solvent was removed. Column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{MeOH}=98:2$) afforded compound **5** (0.04 g) as a yellow powder. Compound **5** was used for succeeding reactions without further purification. ^1H NMR (200 MHz, CDCl_3): $\delta=2.22$ (s, 4.2H), 2.51 (s, 1.8H), 4.07–4.17 (m, 4H), 5.81 (s, 0.3H), 5.92 (s, 0.7H), 7.27–8.34 (m, 11H), 8.78 (brs, 1H), 9.24 ppm (brs, 1H).

A solution of diarylethene **5** (200 mg, 0.28 mmol) in wet acetone (30 mL) containing pyridinium tosylate (140 mg, 0.56 mmol) was refluxed for 29 h. The mixture was cooled to room temperature and water was added.

The resultant mixture was then extracted with diethyl ether, and the organic extract was washed with brine and dried (MgSO_4). The solvent was removed in vacuo and afforded a pale yellow amorphous solid of diarylethene **6** (190 mg, 6%). ^1H NMR (200 MHz, CDCl_3): $\delta=2.25$ (s, 2.1H), 2.32 (s, 2.1H), 2.53 (s, 0.9H), 2.56 (s, 0.9H), 7.63–8.37 (m, 11H), 8.77 (brs, 1H), 9.23 (brs, 1H), 9.95 (s, 0.3H), 10.08 ppm (s, 0.7H); FAB HRMS: *m/z* calcd for $\text{C}_{36}\text{H}_{21}\text{F}_6\text{N}_2\text{O}_2\text{S}_2$ [$M^++\text{H}$]: 675.1000; found 675.0983.

1-[6-(1-Oxyl-3-oxide-4,4,5,5-tetramethylimidazolin-2-yl)-2-methylbenzothiophen-3-yl]-2-[6-(1,10-phenanthroline-2-yl)-2-methylbenzothiophen-3-yl]-3,3,4,4,5,5-hexafluorocyclopentene (1a): A solution of **6** (190 mg, 0.28 mmol), 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate (180 mg, 0.74 mmol), and potassium carbonate (100 mg, 0.74 mmol) in methanol (10 mL) was heated under reflux for 15 h. The reaction mixture was poured into water, extracted with ethyl acetate, washed with brine, dried over magnesium sulfate, and concentrated to give bishydroxylamine as a yellow oil. Purification was not performed. A solution of sodium periodate (55 mg, 0.26 mmol) in water (5 mL) was added to a solution of bishydroxylamine in dichloromethane (5 mL), and the reaction mixture was stirred for 15 min in the open air. The organic layer was separated, washed with water, dried over magnesium sulfate, and concentrated. Purification was performed by column chromatography (silica gel, AcOEt/MeOH 99:1). Compound **1a** was obtained as a dark blue powder (55 mg, 24%). M.p. $>200^\circ\text{C}$ (decomp); ESR (toluene): 1:2:3:2:1, 5 lines, $g=2.007$, $a_N=7.4$ G; UV/Vis (toluene): open-ring isomer $\lambda_{\text{max}}=313$, 361, 379, 598, 649 nm; closed-ring isomer $\lambda_{\text{max}}=350$, 392, 569 nm; isosbestic point at 349 nm; FAB HRMS: *m/z* calcd for $\text{C}_{42}\text{H}_{32}\text{F}_6\text{N}_4\text{O}_2\text{S}_2$ [$M^++\text{H}$]: 802.1871; found 802.1887.

1-(2-Methylbenzothiophen-3-yl)-2-[6-(1,10-phenanthroline-2-yl)-2-methylbenzothiophen-3-yl]-3,3,4,4,5,5-hexafluorocyclopentene (2a): 1,2-Bis(6-iodo-2-methyl-benzothiophen-3-yl)-3,3,4,4,5,5-hexafluorocyclopentene (0.50 g, 0.69 mmol) was dissolved in dry diethyl ether (25 mL) and cooled to -78°C under Ar. A 1.6 M solution of *n*-butyllithium (0.90 mL, 1.4 mmol) was added dropwise, and the reaction mixture was allowed to warm to 0°C for 1 h. The solution was added to a stirred suspension of 1,10-phenanthroline (0.31 g, 1.7 mmol) in diethyl ether (25 mL) at 0°C . The resulting dark red solution was stirred for 3 h and allowed to warm to room temperature. The reaction mixture was carefully quenched with ice water. The organic layer was separated, and the remaining aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were oxidized by stirring with activated MnO_2 (6.0 g) for 3 h. Then the mixture was dried (MgSO_4) and filtered. The solvent was removed. Column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{MeOH}=95:5$) afforded compound **2a** (0.14 g, 31%) as a white powder. M.p. 226–227 $^\circ\text{C}$; ^1H NMR (200 MHz, CDCl_3): $\delta=2.23$ (s, 4.0H), 2.51 (s, 1.0H), 2.52 (s, 1.0H), 7.14–8.37 (m, 12H), 8.75 (brs, 0.7H), 8.78 (brs, 0.3H), 9.24 (brs, 0.7H), 9.27 ppm (brs, 0.3H); MS: *m/z*: 646 [M^+], 631 [$M-\text{CH}_3$] $^+$, 617 [$M-2\text{CH}_3$] $^+$; UV/Vis (toluene): open-ring isomer $\lambda_{\text{max}}=314$, 328, 343, 361 nm; closed-ring isomer $\lambda_{\text{max}}=374$ (sh), 386, 546 nm; isosbestic point at 352 nm; elemental analysis calcd (%) for $\text{C}_{35}\text{H}_{20}\text{F}_6\text{N}_2\text{S}_2$: C 65.01; H 3.12; N 4.33; found: C 64.95; H 3.06; N 4.34.

[Cu(hfac) $_2$ (1a)]: Solutions of **1a** (4.4 mg, 5.5 mmol) in toluene (10 mL) and $[\text{Cu}(\text{hfac})_2]$ (1.3 mg, 2.7 mmol) in CH_2Cl_2 (5 mL) were prepared separately. Equivalent volumes of them were mixed and stirred several minutes, dried in vacuo, and then redissolved in appropriate volume of toluene for the measurement.

[Cu(hfac) $_2$ (2a)]: Solutions of **2a** (2.2 mg, 3.4 mmol) in CH_2Cl_2 (5 mL) and $[\text{Cu}(\text{hfac})_2]$ (1.6 mg, 3.3 mmol) in CH_2Cl_2 (5 mL) were prepared separately. Equivalent volumes of them were mixed and stirred several seconds, dried in vacuo, and then redissolved in appropriate volume of toluene for measurement.

Photochemical measurement: Absorption spectra were measured on a spectrophotometer (Hitachi U-3500). Photoirradiation was carried out by using an USHIO 500 W super high-pressure mercury lamp. Mercury lines of 366 nm and 578 nm were isolated by passing the light through combinations of band-pass filter (UV-D33S) or sharp-cut filter (Y-52) and monochromator (Ritsu MC-20 L).

ESR spectroscopy: A Bruker ESP300E spectrometer was used to obtain X-band ESR Spectra. The sample was dissolved in toluene and degassed with Ar bubbling for 10 min.

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