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Photochromic behavior of a bisthienylethene bearing Cu(I)-1,10-phenanthroline complexes

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ABSTRACT

A novel diarylethene having a 1,10-phenanthroline unit at each end of the molecule has been synthesized. Among the metal ions, it formed a stable complex with Cu(I) ions in acetonitrile. Rational structures of the Cu(I) complexes of the colorless and the photo-generated blue form have been given by PM3 semiempirical molecular orbital calculations to be 2:2 cyclic complexes for both isomers, with the complex of the open form belonging to the C_2 symmetry group while the complex of the closed form belongs to the D_2 symmetry group. Although the ring-closing quantum yield for free diarylethene in acetonitrile was 0.75, that for the complex was 0.026, due to the long distance of the bond-forming carbon atoms in the rigid (open form)$_2$-Cu(I)$_2$ complex.

1. Introduction

Photochromism is a reversible phenomenon of molecular systems induced by light irradiation involving remarkable changes in the absorption spectrum [1,2]. It has attracted much attention because of the wide variety of potential applications to such intelligent systems as photo-driven switches, optical memories, and transportation of materials [3–7]. A combination of metal-ion recognition moieties with photochromic molecules has been reported to afford metal-ion responsive photochromic molecules [8,9]. The most widely adopted functional groups that form metal-ion complexes are crown ethers, and the photochromic chromophores incorporating them are azobenzenes, spiropyrans, and spirooxazines [10–12].

Among photochromic compounds, diarylethenes with heterocyclic groups have been recognized as the most promising candidates for practical applications due to the high thermal stability of both isomers and excellent fatigue resistance. The use of diarylethenes possessing metal-binding groups as the photoswitching unit is interesting since the interaction with metal ions may change their photochromic behavior. Indeed, the complexes composed of diarylethene ligands and metal ions have so far shown the photochemical switching of properties such as changes in the magnetic interaction between two electron spins [13], formation of a 2 + 2 cyclic complex which induced highly diastereoselective photochemical ring closure [14], photochromic electron-transfer switching [15], changes in fluorescence spectra [16], and extension of absorption maximum wavelengths to lower energies [17–19].

In 1996, Munakata and his co-workers reported the synthesis and photochromism of single crystals of coordination-bridged polymers of Cu(I) complexes of diarylethenes possessing a 1,2-dicyanoethene unit for complexation [20]. In recent years, complexes composed of diarylethenes having pyridine or bipyridine groups and various main group or transition metals such as Zn(II), Mn(II), Cu(II), Fe(II), Hg(II), Ru(II), Os(II), Re(I), Cu(I), and Ag(I) have been studied [16,21–27]. However, only a few studies of the photochromic properties of diarylethenes possessing 1,10-phenanthroline ligands have been reported.

There are two ways to incorporate a 1,10-phenantholine ligand into a diarylethene molecule. One has been presented by Matsuda et al. [13] where 1,10-phenanthroline is introduced as a chelating group on C(6) of one of the benzothiophene rings of a bisbenzothienylethene molecule, and the other has been described by Yam et al. [28–30] where the reactive 5,6-double bond of 1,10-phenanthroline was used as the central ethene unit of the diarylethene.

In this paper, we report on the synthesis and properties of a new photocromic diarylethene, 1,2-bis[2-methyl-5-(1,10-phenanthrolin-2-yl)-3-thienyl]hexafluorocyclopentene **1** and its metal complexes. In particular, we have investigated the complex of **1** with Cu(I). Although the properties of the complexes of Cu(I) incorporated in

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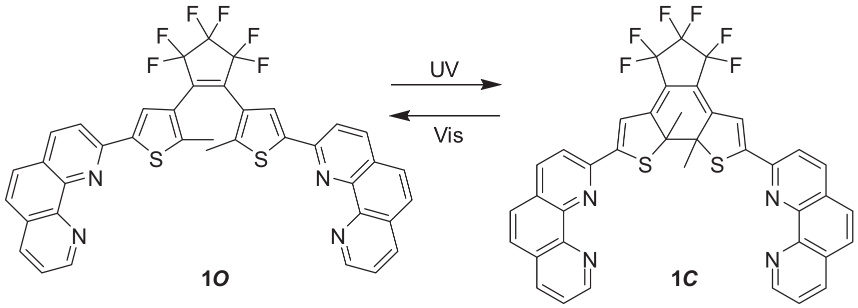


Scheme 1. Photochromism of diarylethene **1** with 1,10-phenanthroline units.

a diarylethene molecule have been reported [14,20,31], to the best of our knowledge, the properties of Cu(I) complexes with 1,10-phenanthroline have not been reported so far. Cu(I)-1,10-phenanthroline complexes have attracted much attention since the late 1970s because of their efficiency as the practical component of chemical sensors, display devices, and solar energy conversion systems [32–38]. Recently the Cu(I)-1,10-phenanthroline complexes have been proposed as the alternatives to Ru(II) polypyridine complexes [39].

2. Results and discussion

2.1. Molecular design and synthesis

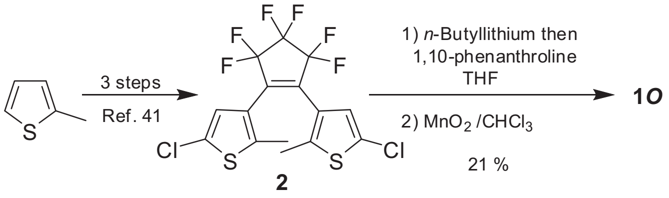
We have designed and synthesized 1,2-bis[2-methyl-5-(1,10-phenanthrolin-2-yl)-3-thienyl]hexafluorocyclopentene having a 1,10-phenanthroline unit as a chelating group at each end of the molecule with elongation of the conjugation when it adopts the closed form (**1*C***) upon photoirradiation of the open form (**1*O***) (Scheme 1). In this structure, if the sulfur atoms on the thiophene rings take part in the coordination, the complex would become more stable. With this structure, we envisage that when a strong coordination occurs, the absorption maximum of the compound might change through electronic communications over the conjugation framework [14]. In addition, if the coordination fixes the conformation of the molecule, then the photoreactivity might be altered whether the metal ions are in the system or not [40]. With this expectation in mind, we started the synthesis of **1*O***.

The synthesis of **1*O*** was carried out according to the synthetic route outlined in Scheme 2. Starting from the known bisthienylhexafluorocyclopentene **2** [41], lithium-halogen exchange followed by addition of 1,10-phenanthroline and oxidation with manganese dioxide [13] afforded **1*O*** with a yield of 21%.

2.2. Photochromic reactions

The photochromic reaction of diarylethene **1*O*** was studied in acetonitrile, chloroform, and dichloromethane. In these solvents, **1*O*** underwent a reversible photochromic reaction by alternative irradiation with 366 and >470 nm light (Figs. 1–4). The color of the solution changed from colorless to blue by UV irradiation, which was attributed to the generation of **1*C***. Upon irradiation of the solution of the UV-photostationary state (PSS) with visible light, absorption due to the closed form decreased in intensity and the blue solution was completely bleached. As clear isosbestic points were observed (e.g. 375 nm in Fig. 3), the conversion occurred only between **1*O*** and **1*C***. The conversion ratio, molar absorption coefficients, and the quantum yields of photoreactions, determined based on the molar absorption coefficient of **1*C*** isolated by flash column chromatography, are shown in Table 1.

The quantum yield of the ring-closing process (0.75) upon 366-nm light irradiation was found to be much larger than that of the ring-opening reaction (0.0066), thus achieving the high conversion ratio to **1*C*** upon UV irradiation was achieved.



Scheme 2. Synthetic route of diarylethene **1*O***.

2.3. Complexation with metal ions

We next examined the complexation ability of the 1,10-phenanthroline moieties of **1**. The degree of interaction of **1** with different metal ions in solution was conveniently examined by observing the absorption maximum wavelength of **1*C*** in the visible region around 630 nm in chloroform or acetonitrile. Assessments of the degree of complexation by comparison of the absorption spectra of **1*O*** in the presence of different metal salts were not informative since the metal ions themselves have absorption bands in the UV region. Thus, the complexation reactions of **1** with metal ions were performed by the addition of an equimolar, two-, or ten-fold amount of metal salts to the solution of **1*O*** in chloroform or acetonitrile, and irradiated with 366-nm light until reaching the PSS. The concentration of **1*O*** was kept constant at 3.52×10^{-5} mol dm^{-3}. When Fe(II), Fe(III), Cu(II), Ni(II), or Zn(II)

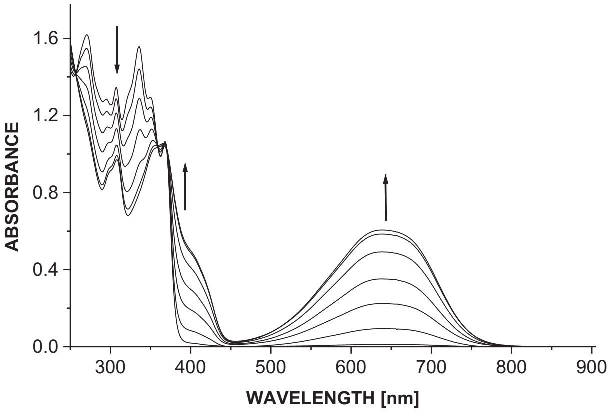


Fig. 1. UV–Vis absorption spectra of 3.52×10^{-5} M **1*O*** in chloroform under different irradiation time by light of 366 nm. Light intensity: 0.30 mW cm^{-2}. 0–240 s.

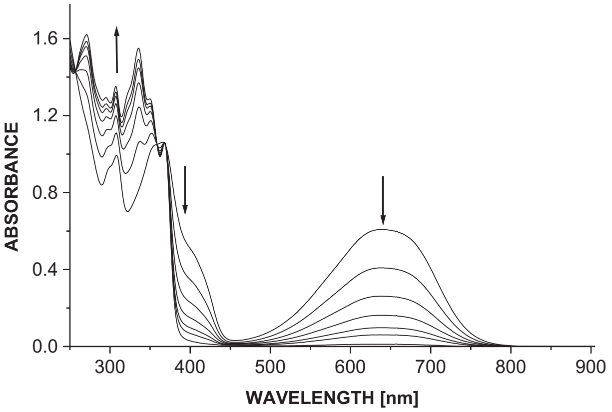


Fig. 2. UV–Vis absorption spectra of 3.52×10^{-5} M **1*O*** in chloroform under different irradiation time by light of >470 nm to the UV-PSS solution. 0–600 s.

were present in the solution together with **1*C***, however, the absorption maximum wavelengths were not greatly affected compared to the value without metal ions (Table 2). This is the evidence that these metal ions do not form a stable complex with **1*C*** in solution, or at least that the electronic state of **1*C*** was not significantly affected by the metal ions. On the other hand, irradiation of **1*O*** in the presence of 1 eq of Cu(I) resulted in the induction of a fairly large bathochromic shift (i.e. 6 nm in chloroform and 13 nm in acetonitrile) of the absorption band in the visible region among the metal ions examined. It is obvious that Cu(I) formed a complex with **1*C***. It should be noted that when the amount of Cu(I) is large, the shift becomes smaller. This indicates that the same amount of **1*C*** and Cu(I) form a complex, which exhibit the bathochromic shift. As the number of 1,10-phenanthroline units in the diarylethene molecule is two and the number of coordinating nitrogen atoms is four, the complex could be an *intra*molecular 1:1 tetrahedral one or a cyclic *inter*molecular 2:2 tetrahedral one. Formation of the cyclic 2:2 structure of a Cu(I) complex with different ligands on the same position of a diarylethene (**3**, Scheme 3) has previously been reported [14].

2.4. Copper (I) complex

Considering the results shown above, we focused our efforts on clarifying the properties and structures of the complex of **1**-Cu(I) since Cu(I) interacts strongly with **1**.

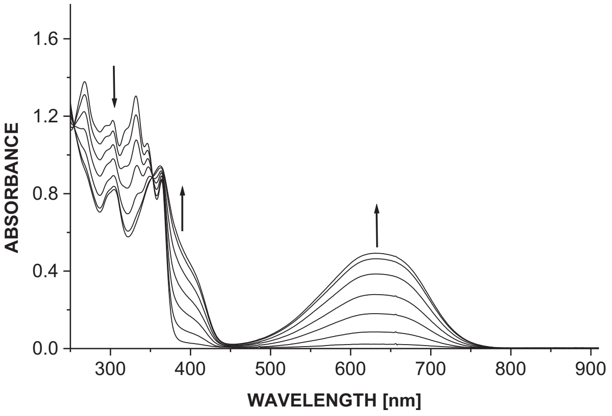


Fig. 3. UV–Vis absorption spectra of 3.52×10^{-5} M **1*O*** in acetonitrile under different irradiation time by light of 366 nm. Light intensity: 0.23 mW cm^{-2}.0–240 s.

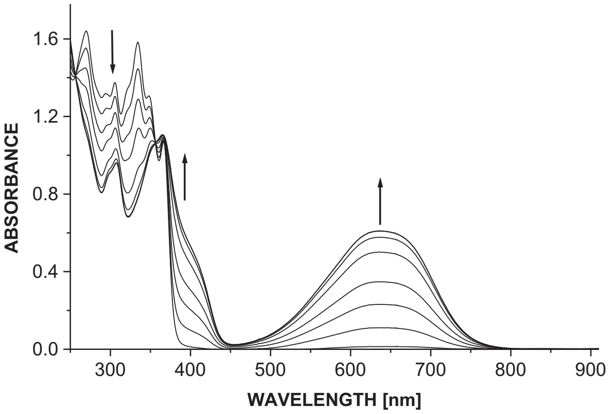


Fig. 4. UV–Vis absorption spectra of 3.52×10^{-5} M **1*O*** in dichloromethane under different irradiation time by light of 366 nm. Light intensity: 0.19 mW cm^{-2}. 0–480 s.

2.4.1. Preparation of Cu(I) complex

The Cu(I) complex was prepared by the addition of a solution of an equimolar amount of **1*O*** in deoxygenated chloroform to the acetonitrile solution of $Cu(CH_3CN)_4PF_6$ under nitrogen in a glove box. The **1*O***-Cu(I) complex was isolated as a solid in high yield by the evaporation of the solvent. Characterization of the **1*O***-Cu(I) complex was performed satisfactorily by ^{1}H NMR, IR, MS, and UV–Vis spectra. In particular, FAB mass spectrum of **1*O***-Cu(I) showed *m/z* 787, which corresponds to (**1*O***-Cu)$^+$ that is $(C_{39}H_{22}N_4S_2F_6Cu)^+$, or multiples of this composition $(C_{39}H_{22}N_4S_2F_6Cu)_n{}^{n+}$.

2.4.2. Job plot

To study the stoichiometry of the complexation between **1** and Cu(I), we employed Job's method as depicted in Figs. 5 and 6. Job plots exhibited a maximum of the difference in absorption at a Cu(I) ratio of 0.5 for both **1*O*** (376 nm) and **1*C*** (363 nm), indicating that the ratio of the components in **1*O***-Cu(I) and **1*C***-Cu(I) is 1:1 in solution. However, it does not mean that one molecule of **1** forms a complex with one Cu(I) atom. It could be 2:2 or more. However, due to the tendency for tetrahedral complex formation of Cu(I), if the formation of intramolecular 1:1 tetrahedral complex is difficult, then 2:2 is the next favored candidate since a similar 2:2 complex has previously been reported [14]. Larger complexes would be less stable from the viewpoint of the entropy term in the Gibbs free energy of the complex. Although we tried to prepare single crystals of **1*O*** and **1*C*** complexes with Cu(I), it was not successful.

2.4.3. Search for stable structures of the complexes by calculations

It is well known that Cu(I) ions form stable tetrahedral complexes with 1,10-phenanthroline while Cu(II) ions prefer complexation with polypyridines [42,43]. Since suitable crystals could not be obtained, in place of X-ray crystallographic analysis of the complexes, we carried out PM3 semiempirical molecular orbital calculations [44] to establish whether intramolecular 1:1 tetrahedral complexation or

Table 1
Spectroscopic data of the colored forms, quantum yields of photoreactions, and the conversion ratio of **1*O*** and [**1*O***-Cu(I)]$^+$ PF_6^- to **1*C*** and [**1*C***-Cu(I)]$^+$ PF_6^- in acetonitrile.

Compounds	λ_{max}/nm (ε_{max}/mol^{-1} dm^3 cm^{-1}) of *C*-form	Quantum yields			***C*/*O*** at PSS (366 nm)
		366 nm		578 nm	
		Φ_{OC}	Φ_{CO}	Φ_{CO}	
1	630 (15,800)	0.75	0.0066	0.0035	99.5/0.5
[**1**-Cu(I)]$^+$ PF_6^-	643 (11,500)	0.026	0.0028	0.0011	92.1/7.9

Table 2
Absorption maximum wavelengths of **1*C*** in the presence of various metal ions (1, 2 or 10 eq).

λ_{max}/nm																			
Solvent	None	Cu(I)X[a]			Cu(II)(acac)$_2$[b]			Fe(III)(acac)$_3$[b]			Fe(II)(acac)$_2$[b]			Ni(II)(acac)$_2$[b]			Zn(II)Y$_2$[c]		
		1	2	10	1	2	10	1	2	10	1	2	10	1	2	10	1	2	10
CHCl$_3$	638	644	646	–[d]	638	641	638	638	638	638	638	638	638	638	638	632	638	634	635
CH$_3$CN	630	**643**[e]	638	638	632	634	634	630	630	630	631	630	630	630	630	624		–[d]	

[a] X: PF$_6$(CH$_3$CN)$_4$.
[b] acac: acetylacetonato.
[c] Y: acetate(H$_2$O).
[d] Metal salts were not fully soluble in solution.
[e] Boldface type number denotes the absorption maximum wavelength with the largest bathochromic shift.

a cyclic intermolecular 2:2 tetrahedral complexation are possible or not as well as which is more stable. As the result, we found that for both **1*O*** and **1*C***, the 2:2 complexes (**1*O***$_2$-Cu(I)$_2$: Fig. 7, and **1*C***$_2$-Cu(I)$_2$: Fig. 8) are stable, while the intramolecular tetrahedral **1*O***-Cu(I) is less stable than the divalent complex in which only one 1,10-phenanthroline participates in the coordination. As for the **1*C***-Cu(I), a stable intramolecular tetrahedral complex cannot be formed due to the rigid framework of the molecule. Therefore, with the aid of a previous report on the formation of 2:2 diarylethene-Cu(I) complex [14], we tentatively concluded that both **1*O*** and **1*C***-form complexes in the manner of 2:2, as shown in Figs. 7 and 8. The heat-of-formation values of the structures obtained by PM3 calculations are shown in Table 3.

Among the possible 2:2 complexes of **1*O*** and Cu(I) (combination of helical structures of the central hexatriene unit and the helical structures of 1,10-phenanthroline and its adjacent thiophene), the most stable one is depicted in Fig. 7. In this structure, two **1*O*** molecules take photocyclizable antiparallel conformations [4] with the same local C_2 helical chirality. However, although one of the nitrogen atoms on the 1,10-phenanthroline units close to the thiophene ring on both ends of a **1*O*** molecule is located close to the sulfur atom on the thiophene ring, signs of the dihedral angles of S-C-C-N moieties are opposite, so that each **1*O*** molecule is not C_2 symmetric. Thus, two non-symmetric **1*O*** molecules are then nicely oriented to form a C_2-symmetric cyclic 2:2 coordination structure with two sets of tetrahedral complexation with two Cu(I) atoms. Its heat-of-formation value per one complex unit is much lower than that of the intramolecular 1:1 complexes (Table 3).

As for the **1*C***$_2$-Cu(I)$_2$ complex formed from the most stable **1*O***$_2$-Cu(I)$_2$ complex shown in Fig. 8, it belongs to D_2 symmetry with three C_2 axes. Calculations of other possible coordination structures revealed that this form is the most stable. Therefore, we assume that when **1*O*** and Cu(I) salt are mixed in acetonitrile, they form a stable complex, as shown in Fig. 7. Upon photoirradiation, the central hexatriene cyclizes with the low quantum yield due to the remote distance of the ring-closing carbon atoms to form **1*C***. When both **1*O*** in a complex close to become **1*C*** the complex changes form slightly, probably with little activation energy, from C_2 to D_2. The existence of the **1*O***/**1*C***-Cu(I)$_2$ complex during the photoirradiation was equivocal. However, ^{1}H NMR examination during the photoirradiation process did not show any evidence of the presence of other complexes than **1*O***$_2$-Cu(I)$_2$ and **1*C***$_2$-Cu(I)$_2$, though the resolution was low. We have, therefore, concluded that both complexes are in the form of 2:2.

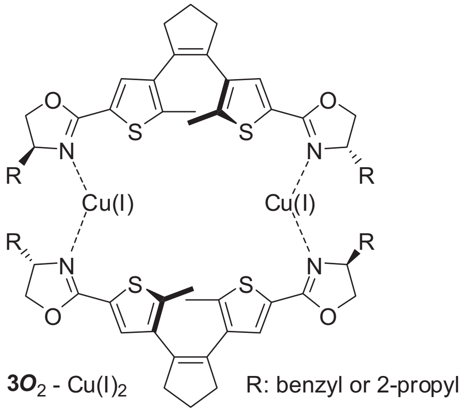
2.4.4. *Spectral properties*

The absorption spectral change of **1*O***-Cu(I) in acetonitrile upon UV irradiation is shown in Fig. 9.

Complexation of **1*O*** with Cu(I) generated a new broad and weak band in the 400–600 nm region which remained unchanged during the photochromic reactions (Fig. 9). This band is assigned to an MLCT band [39]. As we have stated above, a fairly recognizable bathochromic shift was also observed for the absorption band in the visible region of **1*C*** in the presence of Cu(I). This is due to the change in the electronic state of the diarylethene conjugation mode. In most cases, attachment of the electron-donating groups at the termini of the conjugated system of the C-form of diarylethene induces a strong bathochromic shift [45]. Therefore, complexation of 1,10-phenanthroline groups with Cu(I) atoms, which has the tendency to exhibit MLCT, would weaken the electron-withdrawing nature of the 1,10-phenanthroline groups to cause a small bathochromic shift [46,47].

Upon irradiation with visible light, the **1*C***-Cu(I) complex completely reverted to the original **1*O***-Cu(I).

The quantum yields of the photochromic reactions of the complexes are summarized in Table 1. The small cyclization quantum yield of **1*O***-Cu(I) during UV irradiation can be interpreted by the structure of the complex. The distances between the bond-forming carbon atoms in the complex **1*O***$_2$-Cu(I)$_2$ shown in Fig. 7 are 0.478 and 0.477 nm. As the distance of the bond-forming carbon atoms of



Scheme 3. Structure of 2:2 complex of diarylethene **3*O*** and Cu(I) [14].

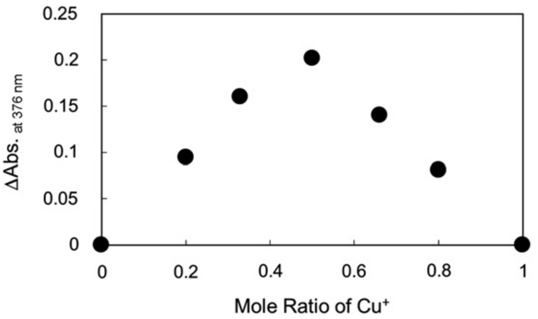


Fig. 5. Job plot of **1*O***-Cu(I) in acetonitrile at 376 nm.

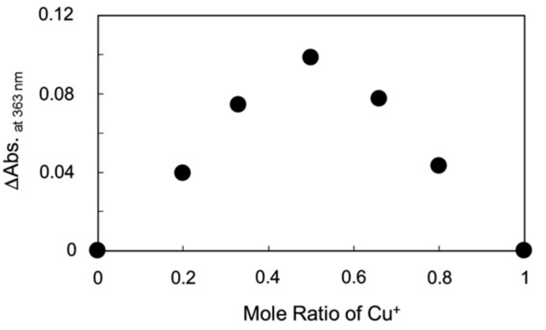


Fig. 6. Job plot of **1*C***-Cu(I) in acetonitrile at 363 nm.

diarylethenes is larger than 0.4 nm in crystals, the molecule cannot cyclize upon photoirradiation [48]. Therefore, the distances of the bond-forming carbon atoms in **1*O***$_2$-Cu(I)$_2$ are too great to induce photocyclization easily even in solution since the **1*O*** molecules are part of rather rigid complexes.

3. Experimental

3.1. General

Chemical reactions were carried out under a dry nitrogen atmosphere. Dry tetrahydrofuran (THF) was purchased from Kanto Chemical Co. Inc. and used as received. All other solvents were also used as received or after appropriate drying procedures. The p.a. grade $Zn(OAc)_2.H_2O$, $Ni(acac)_2$, $Fe(acac)_2$, $Fe(acac)_3$, $Cu(acac)_2$ and $Cu(CH_3CN)_4PF_6$ were purchased from Wako Pure Chemical Industries and were used without further purification. Flash chromatographic separations were carried out on Merck 230–400 mesh silica gel using ethyl acetate and hexane as eluant. Analytical thin-layer chromatography was performed on the pre-coated 0.25-mm thick Merck silica gel TLC plates.

^{1}H NMR Spectra were recorded in deuteriochloroform ($CDCl_3$) or trideuterioacetonitrile (CD_3CN) with a Bruker DRX-300 (300 MHz), a Bruker DRX-500 (500 MHz), a JEOL EX-270 (270 MHz), or a JEOL AL-400 (400 MHz) spectrometers. *J* values are expressed in Hz and quoted chemical shifts are in ppm. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet. Infrared spectra (IR) were recorded on a JASCO FT/IR-4100 FT-IR spectrometer equipped with an attenuated total reflection (ATR) attachment. Low- and high-resolution mass spectra measured either by the electron impact mass spectrometry or FAB mass spectrometry were recorded using a JEOL JMS-AX-600 mass spectrometer. Ultraviolet and visible absorption spectra were recorded on JASCO V-550 and Agilent 8453 UV/Vis spectrophotometers. Melting points were measured using an OLYMPUS BX50 microscope combined with a Mettler Toledo FP82HT hot stage.

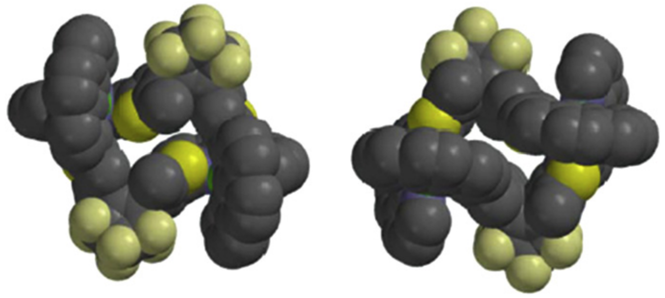


Fig. 7. The most stable structure of the 2:2 complex of **1*O*** and Cu(I) obtained by PM3. Left: Front view. Right: Rear view. Hydrogen atoms are removed for clarity.

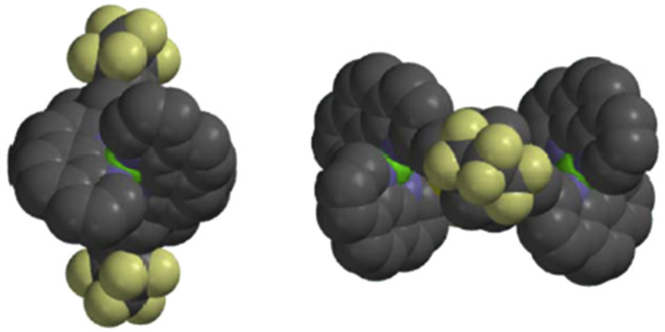


Fig. 8. The most stable structure of the 2:2 complex of **1*C*** and Cu(I) obtained by PM3. Left: Side view. Right: Top view. Hydrogen atoms are removed for clarity.

3.2. Photochromic reactions

All photochromic reactions were carried out in a 10-mm path length quartz cell. Photoisomerization experiments with 366-nm light were performed using 500-W high pressure Hg lamp which was separated by filters (a 5-cm water filter, a 5-cm aqueous solution of $CuSO_4 \cdot 5H_2O$, a UV-35 glass filter, a UV-D35 glass filter, and a UV-D36A glass filter). Photoisomerization experiment with >470 nm was carried out with 500-W Xe lamp using a 5-cm water filter, a Pyrex glass filter, and Y-47 glass filter. Photoisomerization experiments with 578-nm light were carried out with 500-W high pressure Hg lamp using a 5-cm water filter, O-57 glass filter, and a KL-56 interference glass filter. Photoirradiation was performed by continuous stirring of the solution in the cell. Conversion ratios were estimated by the absorption spectra based on that of isolated diarylethene **1*C***. Parker's $K_3Fe(C_2O_4)_3$ chemical actinometer was used for photochromic reactions to determine the intensity of the light source.

3.3. Synthesis

3.3.1. Synthesis of 1,2-bis[2-methyl-5-(1,10-phenanthrolin-2-yl)-3-thienyl]hexafluorocyclopentene (**1*O***)

To a stirred solution of **2** (500 mg, 1.14 mmol, 1.0 eq) in dry ethyl ether (40 mL) was added a hexane solution of *n*-butyllithium (1.6 mol dm^{-3} hexane solution, 2.1 mL, 3.42 mmol, 3.0 eq) at r.t. The resulting solution was stirred for 30 min at r.t. and then was added slowly with cannula to a solution of anhydrous 1,10-phenanthroline (618 mg, 3.43 mmol, 3.0 eq) in dry ethyl ether (100 mL). The mixture was stirred for 1 h at r.t. and the reaction was quenched by adding water, and the resultant mixture was extracted with dichloromethane four times. The combined organic layer was dried over anhydrous sodium sulfate, the drying agent filtered off, and

Table 3
Heat-of-formation values of complexes per **1**-Cu(I) unit obtained by PM3.

Complex	Complexation	Coordination	Symmetry	ΔH_f/kJ mol^1 (per **1**-Cu(I) unit)
1*O*-Cu(I)	1:1	Tetrahedral	C_2	−72.9
1*O*-Cu(I)	1:1	Divalent	C_1	−86.5
1*O*$_2$-Cu(I)$_2$	2:2	Tetrahedral × 2	C_2	**−201.9**[a]
1*O*/1*C*-Cu(I)$_2$	2:2	Tetrahedral × 2	C_1	−152.8
1*C*-Cu(I)	1:1	Tetrahedral	C_1	+328.2
1*C*-Cu(I)	1:1	Divalent	C_1	+277.9
1*C*$_2$-Cu(I)$_2$	2:2	Tetrahedral × 2	D_2	**−115.8**[a]

[a] Bodlface type numbers denote the heat-of-formation values of the most stable conformations for 1*O*-Cu(I) and 1*C*-Cu(I) complexes, respectively.

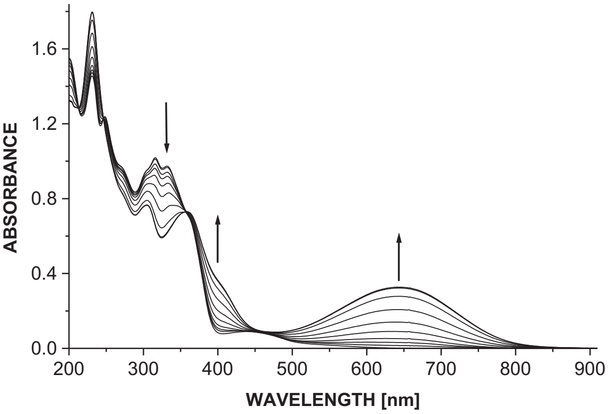


Fig. 9. Absorption spectral changes of 3.04×10^{-5} mol dm^{-3} **1O**-Cu(I) in acetonitrile under different irradiation time by light of 366 nm. (Light intensity: 1.06 mW cm^{-2}) 0–1200 s.

the solvent evaporated. To a stirred solution of the residue in chloroform (10 mL) was added manganese dioxide (1.02 g, 11.7 mmol, 10.2 eq). The mixture was stirred for 2 h at r.t. and then manganese dioxide (reagent grade, 1.02 g, 11.7 mmol, 10.2 eq) was added again. The mixture was stirred overnight, the solid material filtered off, and the solvent evaporated. The residue was purified by column chromatography on silica gel using ethyl acetate as the eluent to give 175 mg (0.241 mmol) of diarylethene **1O** as an amorphous solid in 21% yield.

^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ/ppm; 2.05 (6H, s), 7.63 (2H, dd, J/Hz = 7.9, 4.3), 7.78 (4H, d, J/Hz = 1.3), 7.80 (2H, s), 8.01 (2H, d, J/Hz = 8.2), 8.24 (2H, dd, J/Hz = 8.1, 1.8), 8.26 (2H, d, J/Hz = 8.6), 9.22 (2H, dd, J/Hz = 4.3, 2.0).

^{1}H NMR (300 MHz, CD_3CN, TMS) δ/ppm; 2.10 (6H, s), 7.70 (2H, dd, J/Hz = 8.1, 4.3), 7.88 (2H, d, J/Hz = 0.8), 7.91 (2H, d, J/Hz = 8.3), 8.15 (2H, d, J/Hz = 8.6), 8.37 (2H, dd, J/Hz = 7.9, 1.9), 8.39 (4H, d, J/Hz = 8.4), 9.09 (2H, dd, J/Hz 4.3, 1.7).

IR (ATR) ν/cm^{-1}; 3043, 3013, 2971, 1587, 1550, 1508, 1489, 1337, 1270, 1190, 1136, 1112, 1054, 844, 739.

LRMS (EI, 70 eV) *m*/*z* (rel intensity): 724 (M$^+$, 33), 709 ((M−CH_3)$^+$, 28).

Mp: 177 °C.

The colored form **1C** was obtained by column chromatography after 366-nm light irradiation to the acetonitrile solution of **1O** in more than 90% yield.

^{1}H NMR (300 MHz, CD_3CN, TMS) δ/ppm; 2.35 (6H, s), 7.31 (2H, s), 7.77 (2H, dd, J/Hz = 8.1, 4.3), 7.98 (4H, d, J/Hz = 3.8), 8.29 (2H, d, J/Hz = 8.3), 8.43 (2H, dd, J/Hz = 8.1, 1.7), 8.47 (2H, d, J/Hz = 8.7), 9.19 (2H, dd, J/Hz = 4.3, 1.7).

3.3.2. *Synthesis of complexes of* **1O** *with Cu(I) ([***1O***-Cu(I)]$^+$ PF_6^-)*

To a stirred solution of $Cu(CH_3CN)_4PF_6$ (16.2 mg, 43.5 μmol, 1.01 eq) in distilled acetonitrile (5 mL) a solution of diarylethene **1O** (31.0 mg, 42.8 μmol, 1.0 eq) in distilled chloroform (5 mL) was added dropwise under nitrogen atmosphere at r.t. The resulting solution was stirred for 30 min at r.t. and the solvent evaporated. After the residue was dissolved in a small amount of acetonitrile, a large amount of chloroform was added to form slightly yellow precipitate. The solid thus formed was separated by filtration and was washed with chloroform to yield 31.3 mg (33.5 μmol, 78%) of the complex [**1O**-Cu(I)]$^+$ PF_6^-.

^{1}H NMR (270 MHz, CD_3CN, TMS) δ/ppm, ca. 2.15 (overlapping with water peak), 7.64–7.74 (4H, m), 8.09–8.16 (4H, m), 8.31 (2H, bs), 8.48 (2H, bs), 8.59 (2H, d, J/Hz = 7.3), 8.70 (2H, d, J/Hz = 8.2).

FAB MS (nitrobenzyl alcohol): 787 $(C_{39}H_{22}N_4S_2F_6Cu)_n^{n+}$.

IR (ATR) ν/cm^{-1}: 3065, 2927, 1559, 1541, 1508, 1265, 1196, 1116, 1055, 982, 838, 734, 556.

Mp: ~350 °C (decomp.).

4. Conclusion

In conclusion, we have synthesized a novel diarylethene **1O** having a 1,10-phenanthroline unit at each end of the molecule, forming a rather stable complex with Cu(I) to show a certain bathochromic shift in the absorption of the colored form. Based on the FAB MS, Job plot, and PM3 molecular orbital calculations, its structure was suggested to be 2:2 cyclic and C_2-symmetric **1O**$_2$-Cu(I)$_2$. This complex underwent photocyclization upon 366-nm light irradiation in acetonitrile with the quantum yield of 0.026, which is much smaller than the value of 0.75 for the metal-free **1O**. This was interpreted to be due to the long distance between the bond-forming carbon atoms even though **1O** takes the antiparallel conformation in the complex. The photochemically generated **1C** molecules also form stable complexes with the Cu(I) ions. The structure was also suggested by calculations to be 2:2 D_2 symmetric. Visible-light irradiation to the colored state gave rise to the complete recovery of the colorless solution of the **1O** complex.

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