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Triplet MLCT Photosensitization of the Ring-Closing Reaction of Diarylethenes by Design and Synthesis of a Photochromic Rhenium(I) Complex of a Diarylethene-Containing 1,10-Phenanthroline Ligand

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Abstract: Synthesis of the diarylethene-containing ligand L1 based on Suzuki cross-coupling reaction between thienyl boronic acid and the dibromophenanthroline ligand is reported. On coordination to the rhenium(I) tricarbonyl complex system, the photochromism of L1 could be photosensitized and consequently extended from intraligand excitation at $\lambda \leq 340$ nm in the free ligand to metal-to-ligand charge-transfer (MLCT) excitation at $\lambda \leq 480$ nm in the complex. The photochromic reactions were studied by ^{1}H NMR, UV/Vis, and steady-state emission spectroscopy. Photosensitization was further probed by ultrafast transient absorption and time-resolved emission spectroscopy. The results provided direct evidence that the formation of the closed form by the MLCT-sensitized photochromic process was derived from the ^{3}MLCT excited state. This supports the photosensitization mechanism, which involves an intramolecular energy-transfer process from the ^{3}MLCT to the ^{3}IL(L1) state that initiated the ring-closure reaction. The photophysical and electrochemical properties of the complex were also investigated.

Keywords: luminescence · N ligands · photochemistry · photochromism · rhenium

Introduction

Photochromic compounds are those that are capable of undergoing light-induced reversible transformation between two forms having distinguishable absorption characteristics. They are among the most promising materials for optical data storage, optoelectronics, and molecular switching devices. Diarylethene derivatives, especially those with heterocyclic aryl groups, have recently received much attention, as they have outstanding fatigue resistance and thermally irreversible photochromic behavior.[1] While studies on diarylethenes are mainly confined to the molecular design and synthesis of the organic framework, investigations into the exploitation of these diarylethenes as ligands to form metal complexes are rare and less explored.[2] The combination of diarylethene ligands and metal complex systems is envisaged to give rise to novel properties, such as nondestructive data processing,[2a] electron-transfer switching,[2b] and fluorescence modulation,[2c–f] and may extend the excitation wavelength to lower energies, which are usually less destructive.[2g,h] Recently, we communicated the isolation of a versatile diarylethene-containing 1,10-phenanthroline ligand and its rhenium(I) complex, both of which are capable of photochromic reactivity.[2h] Herein we report the detailed syntheses, characterization, photophysics, and electrochemical properties of this class of photochromic compounds. Insights into the mechanism of their photochromic reactivity were also provided by transient absorption and time-resolved emission studies. Direct evidence for the photosensitization of the cyclization reaction of the diarylethene unit by the ^{3}MLCT excited state of the rhenium(I) diimine chromophore are presented, and a mechanism for the cyclization process that involves the ^{3}IL state of the diarylethene-containing ligand has been demonstrated for the first time.

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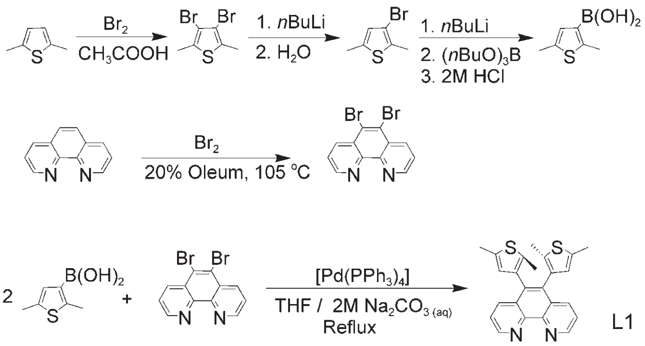
Results and Discussion

Synthesis and characterization: The synthetic route to diarylethene-containing 1,10-phenanthroline ligand L1 is summarized in Scheme 1. Suzuki cross-coupling of 2,5-dimethylthien-3-ylboronic acid with 5,6-dibromo-1,10-phenanthroline in THF gave L1 in moderate yield. Coupling of the second equivalent of boronic acid was inefficient and required long reaction times, probably as a result of the steric bulk of the system. Reaction of L1 with [ReCl(CO)$_5$] in refluxing anhydrous benzene afforded [ReCl(CO)$_3$(L1)] (**1**) as yellow crystals in high yield. The identities of the ligand and the complex were confirmed by satisfactory elemental analyses, ^{1}H NMR and IR spectroscopy, and FAB mass spectrometry. The X-ray crystal structure of L1 has also been determined.[2h] Both L1 and **1** showed two well-resolved sets of ^{1}H NMR signals corresponding to the resonances of parallel (photochromically active) and antiparallel (photochromically inactive) conformers. These two conformations are commonly found in the open forms of diarylethene systems.[1,3] Unlike most other diarylethene systems, in which rapid interconversion of the two forms results in only one set of time-averaged ^{1}H NMR signals,[1,3] the sterically demanding 1,10-phenanthroline ring with protons in the 4- and 7-positions hinders rotation of the thiophene moieties, and thus two sets of signals are observed. At room temperature, interconversion between the two forms is very slow, as reflected by the ratio of the two sets of signals remaining unchanged even on prolonged standing. When the sample was heated to about 65 °C, the conformers started to interconvert, and a ratio of about 1:1 was reached at thermal equilibrium. Complex **1** showed three intense stretches in the carbonyl region (1890–2025 cm^{-1}), which confirm the *fac* arrangement of the tricarbonyl unit in an octahedral environment.[4]



Scheme 1. Synthetic route to the diarylethene-containing 1,10-phenanthroline ligand L1.

Electronic absorption and emission properties: The electronic absorption spectrum of L1 in benzene showed an intense band at about 300 nm, with a molar extinction coefficient on the order of 10^4 dm^{3}mol^{-1}cm^{-1}. This is assigned as intraligand (IL) $\pi\rightarrow\pi^*$ transition of the phenanthroline moiety, probably mixed with the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions of the thiophene rings. The electronic absorption spectrum of **1** showed, in addition to the intense IL ($\pi\rightarrow\pi^*$) absorption in the UV region, a moderately intense absorption shoulder with molar extinction coefficients on the order of 10^3 dm^{3}mol^{-1}cm^{-1} at about 400 nm, which is assigned as the metal-to-ligand charge transfer (MLCT) transition [dπ(Re)$\rightarrow\pi^*$(phen)], similar to that found in other rhenium(I) tricarbonyl diimine systems.[5]

On excitation at $\lambda = 300$ nm, the open form of L1 in benzene solution produced luminescence at about 385 nm ($\tau_o <$ 0.1 μs). The close resemblance of the excitation spectrum to the electronic absorption spectrum of L1, together with the small Stokes shift and short excited-state lifetimes, suggests assignment of the emission as fluorescence from states of IL ($\pi\rightarrow\pi^*$) character, most probably derived from the phenanthroline moiety. Attempts to record the weak phosphorescence of the open form of L1 were made by using the back-scattering geometry at 77 K in MeCN. Under these conditions, a vibronic-structured phosphorescence band at about 596 nm, with vibrational progressional spacings of about 1180 cm^{-1}, was observed (see Supporting Information). In contrast, the open form of **1** in benzene solution produced strong luminescence at 595 nm ($\tau_o = 0.26$ μs) on excitation into the MLCT absorption bands at about 400 nm. With reference to previous spectroscopic studies on related rhenium(I) tricarbonyl diimine complexes[5] and the observed low-temperature emission spectrum of L1 in MeCN, this emission band is assigned as phosphorescence derived from states of ^{3}MLCT [dπ(Re)$\rightarrow\pi^*$(phen)] origin with admixture of ^{3}IL character. The close resemblance of the emission energy to the ^{3}MLCT emission maximum of about 600 nm of the related complex [ReCl(CO)$_3$(phen)][5e] and the ^{3}IL phosphorescence of L1 is also supportive of the assignment. The open form of **1** also displayed photoluminescence in the solid state and in EtOH/MeOH (4/1) glass at 77 K. These emissions are also assigned as derived from states of MLCT [dπ(Re)$\rightarrow\pi^*$(phen)] origin, mixed with ^{3}IL character, similar to that reported in the related complex [ReCl(CO)$_3$(Me$_2$phen)].[5k] The blue shift in emission energy in the glass (535 nm) relative to the solution state (595 nm) is attributed to the increased rigidity in the glass, in which the solvent dipoles could not reorient themselves around the complex to stabilize the excited state and thus resulted in an energetically high lying excited state. Such luminescence rigidochromism has also been observed in other related systems.[6] Photophysical data for L1 and **1** are summarized in Table 1.

Photochromic behavior: On UV excitation into the IL absorption band at $\lambda \leq 340$ nm, an intense absorption band and two moderately intense absorption bands at 366, 510, and 540 nm for L1 and 386, 546, and 580 nm for **1** emerged (Figure 1). These new absorption bands were ascribed to absorptions of the closed form, generated by photocyclization of the open form (Scheme 2). The large bathochromic shift of the absorption bands of the closed form with respect to

Table 1. Photophysical data for the open and closed forms of L1 and **1**.

Compound	Absorption λ_{abs}[a] [nm] (ε [$dm^3 mol^{-1} cm^{-1}$])	Medium (T [K])	Emission λ_{em} [nm] (τ_o [μs])
L1 (open form)	300 (8670)	benzene (298)	385 (<0.1)
		solid (298)	–[c]
		solid (77)	–[c]
		glass[b] (77)	–[c]
		MeCN (77)[d]	596
L1 (closed form)	366 (31730), 510 (3950), 540 (3730)	benzene (298)	644 (<0.1)
		glass[b] (77)	577 (5.2)
1 (open form)	338 (4930), 400 (4690)	benzene (298)	595 (0.26)
		solid (298)	558 (<0.1)
		solid (77)	562 (1.9)
		glass[b] (77)	535 (7.2)
1 (closed form)	386 (36670), 546 (5390), 580 (5050)	benzene (298)	626 (<0.1)

[a] In benzene at 298 K. [b] EtOH/MeOH (4/1). [c] Emission not detected. [d] Recorded in backscattering geometry.

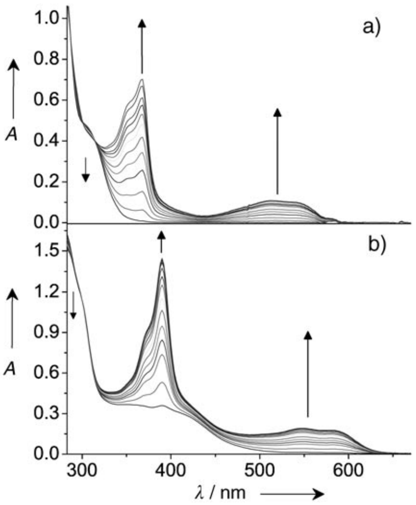
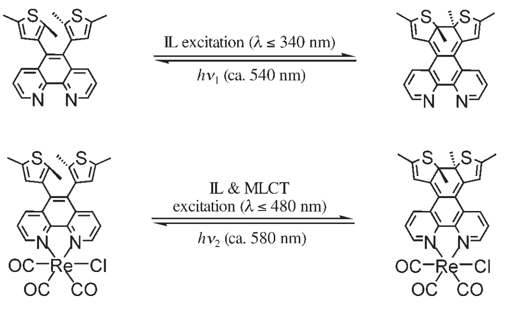


Figure 1. UV/Vis absorption spectral changes of a) L1 (5.52×10^{-5} M) and b) **1** (7.16×10^{-5} M) in benzene solution on excitation at 313 and 440 nm, respectively.



Scheme 2. Photochromic reactions of L1 and **1**.

the open form has been attributed to an increase in the extended π delocalization across the condensed thiophene rings (8a,8b-dimethyl-1,8-dithia-*as*-indacene) leading to a reduced HOMO–LUMO energy gap for the π→π* and n→π* transitions. On excitation into the absorption bands of the closed form, absorptions due to the closed form decreased in intensity, indicative of regeneration of the open form as a result of the photochromic backreaction. For the complex, in addition to excitation into the IL absorption band, excitation into the MLCT absorption band at $\lambda \leq 480$ nm also gave rise to these new absorptions, indicative of generation of the closed form with MLCT excitation. This is suggestive of sensitization of the photochromic activity of the diarylethene-containing phenanthroline with the MLCT excited state, which extends the excitation wavelength from the UV region in the free ligand to the visible region in the complex. The photosensitization reaction probably involves intramolecular energy transfer from the ^{3}MLCT to the ^{3}IL state of L1, similar to that reported in our previous studies on spirooxazine-, pyridyl–azo-, and pyridyl–stilbene-containing rhenium(I) complexes,[5i,7] and in a dithienylperfluorocyclopentene-containing bipyridyl ruthenium(II) complex.[2g] Further insights into the photosensitization mechanism were provided by transient absorption spectroscopy and time-resolved emission studies (vide infra). Photochromic interconversion between the open and closed forms was further supported by ^{1}H NMR studies. On excitation at $\lambda =$ 313 nm, the signals due to the open form of the antiparallel configuration decreased due to conversion to the closed form. The concomitant decrease in the signal intensities of the open form of the antiparallel configuration and the increase in the signal intensity of the closed form (Figure 2) is

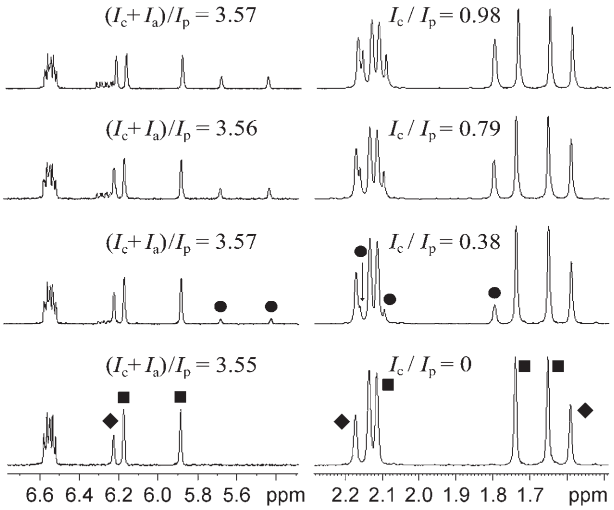


Figure 2. ^{1}H NMR (300 MHz) spectral changes of **1** in C_6D_6 solution at 298 K on irradiation, showing the time course of closed-form formation (from bottom to top). The signals corresponding to the antiparallel (■) and parallel (◆) conformations of the open form and the closed form (●) are labeled. (I_a, I_p, and I_c are the integrals of the methyl protons corresponding to signals of antiparallel and parallel conformations of the open and closed forms, respectively).

indicative of a photochromic reaction originating solely from the antiparallel conformation. This observation is also in agreement with the prediction of the Woodward–Hoffman rule that the photocyclization reaction is active in the conrotatory mode.[8] The photochemical quantum yields of the photochromic reactions in benzene solution, corrected for the active conformer, were determined with excitation at $\lambda = 313$ nm for L1 and 313 and 440 nm for **1** for the forward reaction, and 510 nm for both L1 and **1** for the backward reaction. The quantum yields for the photocyclization of L1 ($\varphi_{313} = 0.33$) and **1** ($\varphi_{313} = 0.55$, $\varphi_{440} = 0.65$) were much higher than those for photocycloreversion (L1, $\varphi_{510} = 0.012$; **1**, $\varphi_{510} = 0.009$; Table 2). Similar findings have also been reported for related diarylperfluorocyclopentene systems.[1,2]

Table 2. Photochemical quantum yields of L1 and **1** in benzene solution at 298 K.

Compound	Photochemical quantum yield/φ		
	photocyclization[a]	photocycloreversion	
	φ_{313}	φ_{440}	φ_{510}
L1	0.329	0	0.012
1	0.552	0.648	0.009

[a] Corrected to the ratio of the photochromically active conformation, that is, with respect to the antiparallel configuration

Apart from the UV/Vis absorption changes on conversion to the closed form, the emission maxima of L1 and **1** were also found to shift to the red, from 385 ($\tau_o < 0.1$ μs) to 644 nm ($\tau_o < 0.1$ μs) and 595 ($\tau_o = 0.26$ μs) to 626 nm ($\tau_o < 0.1$ μs), respectively. This red shift is in line with an increase in the extent of π conjugation on photocyclization. Similar emission energy was reported for the closed form of a related diarylethene.[9] The closed forms of L1 and **1** in EtOH/MeOH (4/1) glass at 77 K also showed vibronic-structured emission peaking at 577 nm ($\tau_o = 5.2$ μs) and 620 nm ($\tau_o = 6.4$ μs), respectively, with fairly well-resolved vibronic structures that show vibrational progressional spacings of about 1250 cm^{-1}, typical of ν(C⩦S) stretching modes.[10] The relatively long emission lifetimes in the microsecond range suggest assignment to a phosphorescence origin. Thus, the emission of L1 in its closed form is assigned as being derived from states of IL(π→π*) origin. Furthermore, in view of the close resemblance of the emission energy and vibronic structures of **1** to those of L1 in their closed forms, an emission origin of metal-perturbed IL(π→π*) character is suggested.

Electrochemical studies: The open form of **1** displayed an irreversible oxidation wave at +1.40 V, a quasireversible reduction couple at −1.32 V, and an irreversible reduction wave at −1.79 V versus SCE in acetonitrile containing 0.1 mol dm^{-3} nBu$_4$NPF$_6$ (Figure 3). With reference to previous electrochemical studies on other related rhenium(I) tricarbonyl diimine systems,[5e,11] the first irreversible oxidation was tentatively assigned as the metal-centered oxidation of Re^{I} to Re^{II}, while the first quasireversible reduction couple at −1.33 V was assigned as phenanthroline ligand-centered reduction. The irreversible reduction wave at −1.79 V, which is absent in [ReCl(CO)$_3$(phen)],[5e,11a] was assigned to thiophene-based reduction. The electrochemical changes on conversion of the open form to the closed form were also obtained from the cyclic voltammograms of a mixture of the open and closed forms in their photostationary state. The lack of observable changes in the irreversible oxidation wave at +1.40 V and the quasireversible reduction couple at −1.31 V is suggestive of insignificant perturbation of the π-accepting ability of the phenanthroline moiety on condensation of the thiophene units. A drop in the electrochemical signal of the reduction wave at −1.79 V with concomitant formation of a new reduction wave at less cathodic potential (−1.61 V) was observed on conversion of the open form to the closed form on light excitation, and this confirms the thiophene-based nature of the reduction, as conversion of the thiophene rings in the open form to the condensed thiophene units in 8a,8b-dimethyl-1,8-dithia-*as*-indacene, which has better π conjugation and hence a better π-accepting ability, would cause a shift of the reduction wave to less negative potential. The much smaller perturbation of the phenanthroline-localized reduction than that of the thiophene-based reduction on photochromic ring closure is understandable in view of the indirect involvement and minimal disturbance of the aromaticity of the phenanthroline moiety in the ring-closure process. Similarly, the open form of L1 displayed two irreversible reduction waves at −1.89 and −2.13 V versus SCE in acetonitrile containing 0.1 mol dm^{-3} nBu$_4$NPF$_6$ (Supporting Information). They are assigned to phenanthroline- and thiophene-based reduction, respectively. On conversion to the closed form, a new reduction wave at less cathodic potential (−1.67 V versus SCE), which was assigned to reduction of the condensed thiophene units, was also observed.

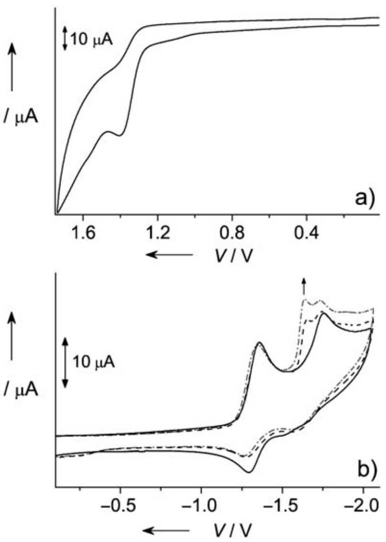


Figure 3. Cyclic voltammograms of a) oxidation of the open form of **1** and b) repetitive reductive scans during the course of the photochromic conversion of **1** from the open form (——) to the closed form in MeCN (0.1 M nBu$_4$NPF$_6$). Scan rate: 100 mV s^{-1}.

Transient absorption and time-resolved emission studies: Ultrafast spectroscopy has been commonly employed in the study of photosensitization reactions, including those of related rhenium(I) polypyridine systems.[12] Thus, to provide further insights into the photophysical and photochromic behavior of **1** in acetonitrile, transient absorption spectroscopy on the pico- to nanosecond timescale after femtosecond laser excitation at 400 nm was carried out. Transient absorption spectra of **1** in acetonitrile in the wavelength range of 325 to 670 nm recorded at various delay times after photoexcitation are displayed in Figure 4, and the absorption time profiles at selected wavelengths in the insets of Figure 4. Immediately after laser flash excitation, an intense transient absorption feature extending beyond 330 nm evolved, which then underwent fast decay, followed by slower decay to generate a new band at about 386 nm and growth of intensity at about 540 and 580 nm. With reference to previous excited-state absorption studies on [ReCl(CO)$_3$(R-phen)],[5e] which showed that the ^{3}MLCT excited state exhibited two absorption bands peaking at about 300 and 480 nm, the absorption feature extending beyond 330 nm was ascribed to the absorption of the ^{3}MLCT excited state of **1**. Similarly, the initial formation of the absorption features at about 460 nm immediately after laser flash and the subsequent fast decay prior to the growth in intensity on a longer timescale was attributed to the fact that the ^{3}MLCT of **1** also absorbs in this region. Such assignments were further supported by the close agreement of these absorption decays at the early times with the decay of the ^{3}MLCT state in the time-resolved emission measurements under the same conditions (vide infra). The fast decay observed in the early stages was attributed to cooling of the hot ^{3}MLCT excited state to its relaxed state. The evolution of this fast decay was monitored at 460 nm, and a time constant of about 9 ps (see Figure 4a) was determined for cooling of the ^{3}MLCT state. Since the ^{3}MLCT state underwent noticeable vibrational cooling, this implied that the ISC from ^{1}MLCT to ^{3}MLCT occurred very fast and reasonably far away from the equilibrium ^{3}MLCT geometry. Between 50 ps and 6 ns, an absorption feature at around 420 nm increased initially and then decreased in intensity (see Figure 4b and c). The time dependence of this feature was monitored at 420 nm (inset of Figure 4b). A best fit to the time dependence data of Figure 4b with single exponential growth and decay functions gave time constants of 1.8 and 7 ns, respectively. We note that there appeared to be an isosbestic point at 336 nm between 50 ps and 1.5 ns. This suggested that the growth of the 420 nm feature is associated with a process in which the ^{3}MLCT evolves cleanly into another species with a stronger absorption at around 420 nm and a weaker absorption at around 540 nm. We tentatively assigned this new species to the ^{3}IL excited state, and the time constant of 1.8 ns appeared to be associated with internal conversion of the ^{3}MLCT state to the ^{3}IL excited state, or alternatively, it could be visualized as intramolecular energy transfer from the ^{3}MLCT state to the ^{3}IL state. Such internal conversion or intramolecular energy-transfer processes could be substantiated by energetics consideration, since the ^{3}MLCT state of **1** ($\lambda_{em}=595$ nm in benzene) should be of sufficient energy to transfer its energy to the ^{3}IL state of the open form of L1 ($\lambda_{em}=596$ nm in MeCN; Table 1). The slow decay of the 420 nm absorption was found to parallel the growth of the absorption bands at about 386, 540, and 580 nm, which were ascribed to the ring-closing process, since the steady-state absorption of the closed form of **1** also occurred in the same region. This indicated that the ^{3}IL excited state evolved into the characteristic absorption bands associated with formation of the closed form of **1**. We monitored the growth of the strong absorption feature at 386 nm to follow the formation of the closed form of **1**, and a best fit of a single exponential growth function gave a time constant of 7 ns (see Figure 4c and inset). We note that the time constant for decay of the ^{3}IL excited state ($\tau=7$ ns) matches well with the time constant for the growth of the closed form of **1** ($\tau=7$ ns). This, as well as the observation of apparent isosbestic points at about 345 nm and 612 nm, indicates clean interconversion of these two distinct species. This provides direct evidence that the formation of the closed form of **1** by an MLCT-sensitized photochromic process was derived from the ^{3}MLCT excited state via its internal conversion or intramolecular energy transfer to the ^{3}IL state that then underwent ring closure to produce the closed form of **1**. In contrast to photocyclization processes on the picosecond timescale observed in other dithienylperfluorocyclopentenes,[13] in which the reactions originated

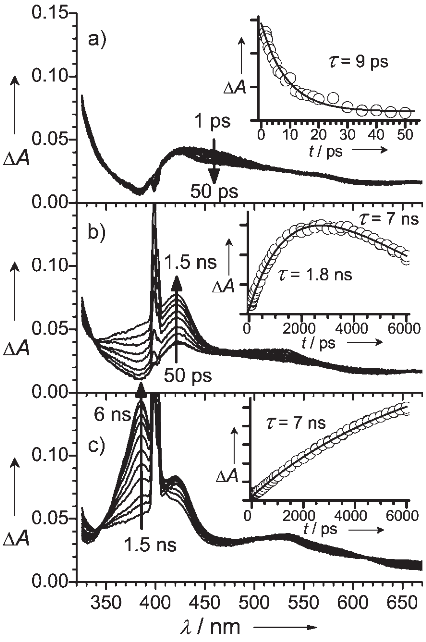


Figure 4. Transient absorption spectra of **1** in MeCN obtained with 400 nm excitation at a series of pump–probe delays: a) 1, 2, 3, 4, 5, 7, 8.5, 14, 30, and 50 ps; b) 50, 100, 250, 400, 600, 800, 1000, 1250, and 1500 ps; c) 1.5, 1.75, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5, and 6 ns. The insets show absorption–time profiles at a) 460 nm, b) 420 nm, and c) 386 nm. The lines are best-fit exponential curves to the data. The sharp features around 400 nm are due to artifacts from the pump pulses.

from the singlet excited states, the relatively slower rate of formation of the closed form on the nanosecond timescale is supportive of the involvement of a triplet excited state. Reaction on a similar timescale has also been reported for a triplet-state photosensitized dithienylperfluorocyclopentene.[2g] Similarly, in contrast to the singlet-state *trans–cis* photoisomerizations, which occur on the picosecond timescale,[14] slower reactions on the nanosecond timescale were also commonly found in triplet-state sensitized photoisomerization processes in azo- and stilbene-containing rhenium(I) complexes.[12]

Kerr gated time-resolved emission measurements on the open form of the complex in acetonitrile solution were also made. Figure 5 shows the time-resolved emission spectra of **1** in acetonitrile recorded at various delay times after excitation at 300 nm. An intense emission with maximum at about 500 nm predominated at very early times and disappeared in less than 2 ps after excitation. This emission band is assigned as the fluorescence derived from the ^{1}MLCT excited state. At a later time (>2 ps), an emission band at about 550 nm was observed, which showed a gradual wavelength shift to the red, eventually reaching a wavelength maximum at about 590 nm after 40 ps. This emission maximum at 590 nm was similar to that of the ^{3}MLCT emission in the steady-state emission spectrum. The emission at about 550 nm was ascribed to the phosphorescence derived from the vibrationally excited ^{3}MLCT state, which gradually relaxes to the ground ^{3}MLCT excited state, which subsequently emits at about 590 nm. The time-dependence profile of the vibrationally excited ^{3}MLCT emission was monitored at 590 nm and is shown in the inset of Figure 5 as open circles. A best fit of these data with a two-exponential decay function gave time constants of 0.8 and 8 ps. A wavelength of 590 nm was used to fit the late weak emission from the ^{3}MLCT, since it was less influenced by the early intense emission from the ^{1}MLCT state and we found this wavelength more convenient to probe the cooling of the ^{3}MLCT state. The very fast decay of the emission monitored at 590 nm corresponded to ISC from ^{1}MLCT to ^{3}MLCT. Since the time resolution of our Kerr gated emission experiment is about the same as the 0.8 ps time constant, this value should be treated as an upper limit for ISC of ^{1}MLCT to ^{3}MLCT. This timescale is reasonable since ISC of a related $[Ru(bpy)_3]^{2+}$ MLCT system has been shown to occur on a similar timescale.[15] The slower decay of the signal monitored at 590 nm with a time constant of about 8 ps (see Figure 5, inset) correlated with the decay of the signal at 460 nm in the transient absorption spectra that has a time constant of about 9 ps (see Figure 4a). This is consistent with these changes in the time-resolved emission and absorption spectra being due to relaxation of a highly excited ^{3}MLCT state to an equilibrated ^{3}MLCT state.

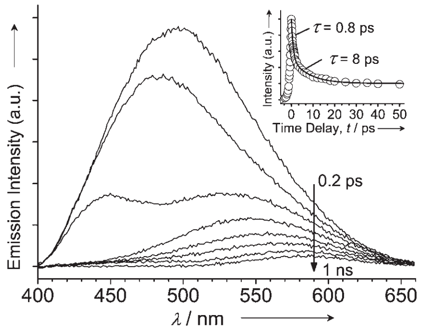


Figure 5. Kerr gated time-resolved emission spectra of **1** in MeCN obtained by 300 nm excitation. The time delays from top to bottom are 0.2, 0.5, 1, 2, 5, 10, 30, and 1000 ps. The inset shows the emission time profile at 590 nm. The line represents the best fit of a two-exponential decay curve to the data.

Our current studies revealed that the ring-closing process of **1** with MLCT excitation proceeds initially with formation of the ^{1}MLCT excited state, which undergoes intersystem crossing to the ^{3}MLCT excited state ($\tau \leq 0.8$ ps). The ^{3}MLCT excited state then undergoes internal conversion or intramolecular energy transfer to produce the ^{3}IL excited state ($\tau =$ 1.8 ns), which subsequently formed the closed form of **1** ($\tau =$ 7 ns). A mechanism for the photochromic reactivity of **1** with MLCT excitation has thus been proposed (Figure 6).

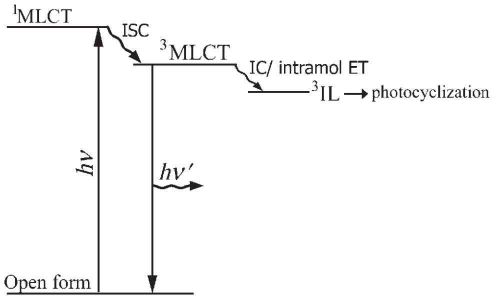


Figure 6. Proposed qualitative energetic scheme for photosensitized photochromism of **1** by MLCT excitation.

Conclusion

The synthesis of diarylethene-containing ligand L1 by Suzuki cross-coupling reaction between thienylboronic acid and the dibromophenanthroline ligand has been reported. On coordination to the chlororhenium(I) tricarbonyl complex system, the photochromism of L1 could be photosensitized and consequently extended from IL excitation at $\lambda \leq$ 340 nm in the free ligand to MLCT excitation at $\lambda \leq 480$ nm in the complex. The photosensitization was studied by ultrafast transient absorption and time-resolved emission spectroscopy. Emission from the ^{1}MLCT state was also observed for the first time in the chlororhenium(I) tricarbonyl phenanthroline system. The results provide direct evidence that formation of the closed form by the MLCT sensitized photochromic process is derived from the ^{3}MLCT excited state. This supports the photosensitization mechanism which involves intramolecular energy transfer from the ^{3}MLCT to the ^{3}IL(L1) state that initiates the ring-closure reaction. The photophysical properties of the complex were also found to change in the photochromic reactions. With our current synthetic strategy, different diarylethene-containing photochromic ligands could be designed, synthesized, and incorporated into various metal complex systems. It is envisaged that, through judicious design of the photochromic ligands, the photophysical properties of the complexes could be readily tuned, the photochromic behavior perturbed, and the source of excitation extended towards the use of lower energy light.

Experimental Section

Materials: [ReCl(CO)$_5$] was obtained from Strem Chemicals, Inc. 1,10-Phenanthroline, 20% fuming sulfuric acid, bromine, 2,5-dimethylthiophene, tri-*n*-butyl borate, *n*-butyllithium (1.6 M in hexane) and hydrazine hydrate were obtained from Aldrich Chemical Company and were used as received. 3-Bromo-2,5-dimethylthiophene was prepared according to a reported procedure for 3-bromo-4-deuterio-2,5-dimethylthiophene[16] except water was used in place of deuterium oxide. 5,6-Dibromo-1,10-phenanthroline was synthesized by bromination of 1,10-phenanthroline with bromine in 20% fuming sulfuric acid according to the modification of a procedure reported by Mlochowski et al.[17] Tetrakis(triphenylphosphine)palladium(0) as catalyst for Suzuki cross-coupling was synthesized according to a literature procedure.[18] THF (Lab Scan, AR) was distilled over sodium benzophenone ketyl before use. All other reagents were of analytical grade and were used as received.

Syntheses: All reactions were performed under strictly anaerobic and anhydrous conditions in an inert atmosphere of nitrogen by standard Schlenk techniques.

2,5-Dimethylthien-3-ylboronic acid: *n*-Butyllithium (1.6 M in hexane, 9.7 mL, 15.6 mmol) was slowly added to a stirred solution of anhydrous 3-bromo-2,5-dimethylthiophene (2.7 g, 14.1 mmol) in anhydrous THF (40 mL) at −78 °C, and the reaction mixture was then stirred at this temperature for 90 min. A solution of tri-*n*-butyl borate (3.85 mL, 14.2 mmol) in THF (10 mL) was then added over 15 min. After stirring for 5 h, aqueous HCl (2 M) solution was added and the mixture was stirred at room temperature for 10 h. This was followed by extraction with diethyl ether and the combined extracts were then washed with copious water. The product was then obtained by extracting the ethereal layer with aqueous sodium hydroxide solution (2 M, 20 mL), followed by acidification with HCl (12 M) to commence the precipitation of 2,5-dimethylthien-3-yl boronic acid as an analytically pure white powder. Yield: 1.9 g, 7.8 mmol, 87%. ^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C, TMS): $\delta = 2.33$ (s, 3H; 5-CH$_3$), 2.50 (s, 3H; 2-CH$_3$), 6.85 (s, 1H; thienyl 4-H), 7.72 ppm (brs, 2H; B(OH)$_2$).

5,6-Bis(2,5-dimethylthien-3-yl)-1,10-phenanthroline (L1): The ligand was synthesized by the bis-coupling reaction of 2,5-dimethylthien-3-yl boronic acid with 5,6-dibromo-1,10-phenanthroline according to standard Suzuki coupling procedure in a heterogeneous mixture of water and THF. Aqueous sodium carbonate solution (2 M, 40 mL, 80 mmol) was added to a solution of 5,6-dibromo-1,10-phenanthroline (600 mg, 1.78 mmol), 2,5-dimethylthien-3-yl boronic acid (692 mg, 4.44 mmol), and tetrakis(triphenylphosphine)palladium(0) (200 mg, 0.17 mmol) in THF (50 mL). The resulting heterogeneous mixture was vigorously stirred and heated under reflux, and the course of reaction monitored by TLC. It was then extracted with diethyl ether (3 × 50 mL), and the combined extracts were dried over anhydrous magnesium sulfate. After filtration and removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (70–230 mesh) with chloroform as eluent. Further purification was achieved by recrystallization from chloroform/ethanol. Yield: 312 mg, 0.78 mmol, 44%. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS): $\delta = 1.79$ (s, 3H; 5-CH$_3$ of antiparallel conformation), 1.95 (s, 3H; 5-CH$_3$ of parallel conformation), 2.12 (s, 3H; 2-CH$_3$ of antiparallel conformation), 2.15 (s, 3H; 2-CH$_3$ of parallel conformation), 6.28 (s, 1H; thienyl 4-H of parallel conformation), 6.29 (s, 1H; thienyl 4-H of antiparallel conformation), 6.98 (m, 2H; phenanthrolyl 3,8-H), 7.89 (m, 2H; phenanthrolyl 4,7-H), 9.11 ppm (m, 2H; phenanthrolyl 2,9-H); positive-ion EI-MS: *m/z* (%): 400 (100) [M^+], 385 (12) [$M^+ - CH_3$], 370 (6) [$M^+ - 2CH_3$]; elemental analysis calcd (%) for $C_{24}H_{20}N_2S_2 \cdot 0.5H_2O$ (409.6): C 70.38, H 5.17, N 6.84; found: C 70.57, H 4.96, N 6.71.

[ReCl(CO)$_3$(L1)] (1): The complex was prepared by modification of a literature method for related Re(I) diimine complexes.[19] [ReCl(CO)$_5$] (100 mg, 0.27 mmol) and L1 (113 mg, 0.28 mmol) were suspended in benzene (25 mL). The suspension was heated to reflux for 10 h under nitrogen, during which the starting materials dissolved gradually to give a yellow solution. After removing the solvent under reduced pressure, the residue was purified by column chromatography with chloroform as eluent. Yellow crystals of **1** were obtained by slow diffusion of *n*-hexane into a dichloromethane solution of **1**. Yield: 155 mg, 0.22 mmol, 82%. ^{1}H NMR (400 MHz, C$_6$D$_6$, 25 °C, TMS): $\delta = 1.59$ (s, 6H; 5-CH$_3$ of parallel conformation), 1.66 (s, 3H; 5-CH$_3$ of antiparallel conformation), 1.74 (s, 3H; 5-CH$_3$ of antiparallel conformation), 2.12 (s, 3H; 2-CH$_3$ of antiparallel conformation), 2.14 (s, 3H; 2-CH$_3$ of antiparallel conformation), 2.17 (s, 6H; 2-CH$_3$ of parallel conformation), 5.89 (s, 1H; thienyl 4-H of antiparallel conformation), 6.17 (s, 1H; thienyl 4-H of antiparallel conformation), 6.23 (s, 2H; thienyl 4-H of parallel conformation), 6.47 (m, 4H; phenanthrolyl 3,8-H), 7.60 (m, 4H, phenanthrolyl 4,7-H), 8.79 ppm (m, 4H; phenanthrolyl 2,9-H); positive-ion FAB-MS: *m/z* (%): 706 (60) [M^+], 678 (16) [$M^+ - $CO], 671 (100) [$M^+ - $Cl], 650 (14) [$M^+ - 2$CO], 622 (14) [$M^+ - 3$CO]; IR (KBr disk): $\tilde{\nu} = 1890, 1912, 2025$ cm^{-1} (C≡O); elemental analyses calcd (%) for $C_{27}H_{20}ClN_2O_3ReS_2$ (706.2): C 45.91, H 2.83, N 3.96; found: C 45.86, H 2.41, N 3.94.

Physical measurements and instrumentation: Electronic absorption spectra were recorded on a Hewlett-Packard 8452 A diode-array spectrophotometer. Steady-state emission and excitation spectra at room temperature and 77 K were recorded on a Spex Fluorolog-2 Model F 111 fluorescence spectrophotometer equipped with a Hamamatsu R928 photomultiplier tube detector. The 77 K low-temperature phosphorescence spectrum of the open form of L1 was obtained with 309 nm excitation by a single-shot 5-ns laser pulse. By employing a single laser pulse to obtain the spectrum, one can avoid emission from any closed form that may be produced from any previous laser pulse. The emission was collected in back-scattering geometry to increase the collection efficiency. The emission was detected by a liquid-nitrogen-cooled CCD spectrometer. Excited-state lifetimes of solution samples were measured by using a conventional laser system. The excitation source was the 355 nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence decay traces were recorded on a Tektronix Model TDS 620A digital oscilloscope and the lifetime τ was determined by single exponential fitting of the luminescence decay traces with the model $I(t) = I_o \exp(-t/\tau)$, where $I(t)$ and I_o are the luminescence intensity at time $= t$ and time $= 0$, respectively. Solution samples for measurements of luminescence lifetime were degassed with at least four freeze–pump–thaw cycles. ^{1}H NMR spectra were recorded on a Bruker DPX-400 (400 MHz) FT NMR spectrometer. Chemical shifts (δ, ppm) were reported relative to tetramethylsilane. All positive-ion FAB and EI mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the newly synthesized compounds were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry in the Chinese Academy of Sciences in Beijing.

The transient absorption measurements were performed with a Ti:Sapphire regenerative amplified source operated at 1 mJ/pulse, 150 fs, 1 kHz, and 800 nm that has been described in detail elsewhere.[20] The pump pulses were obtained at 400 nm by frequency doubling of the regenerative amplifier fundamental, providing 2 μJ after attenuation. A white-light continuum, used for the probe, was generated by focusing 1–2 μJ of the 800 nm light onto a rotating CaF$_2$ crystal plate. The white light continuum was separated into two beams by a fused-silica Al beam splitter. One beam, used as the probe, crossed the pump in the sample (1 mm thickness), and the other, which passed through an unpumped spot in the sample, was used as reference to monitor the intensity and spectral characteristics of the white light. The probe and reference beams were collimated and then focused into the sample. The beams were then focused into a monochromator and detected separately in different stripes by a CCD. The signals from the CCD were downloaded to a PC and analyzed by comparing the spectrum with the pump beam blocked and without the pump beam being blocked to obtain the absorbance difference spectrum. The reference spectrum permits correction for variation over time of the white-light fluctuations. The pump and probe spot sizes at the sample were about 200 and 100 μm, respectively. The instrument response function was about 200 fs.

For the Kerr gated time-resolved emission measurements, the 300 nm excitation pulses were generated by mixing of the 800 nm pulses and the 480 nm output from a home-built OPA system pumped by the 400 nm laser pulses.[20] The excitation pulses (about 1 μJ) were focused (about 100 μm) into a 0.5 mm thick jet stream of sample placed at one focus of an elliptical mirror. The emission from the sample was collected by the elliptical mirror and passed through a film polarizer, and then focused into the Kerr medium (a 2 mm UV cell containing CS_2) placed at the other focus point of the ellipse. The Kerr medium was placed between a pair of crossed polarizers with extinction ratio of about 10^4. The 800 nm gating beam was polarized at 45° and focused into the Kerr medium with adjusted intensity to create, in effect, a half-waveplate that rotated the polarization of the light from the sample and allowed it to be transmitted through a Glan Taylor polarizer for the duration of the induced anisotropy created by the femtosecond gating pulse. The emission that passed through the second polarizer was focused into a monochromator and detected by a liquid-nitrogen-cooled CCD detector. All the time-resolved emission spectra were obtained by subtracting the negative time delay signal from the positive time delay signal. The instrument response function was about 1 ps.

Both time-resolved measurements were performed at the magic-angle configuration to eliminate the effect of sample reorientation. The various time delays following the excitation pulse were achieved by employing a computer-controlled optical delay line. Complex **1** with a concentration of about 1.5 mM was circulated for the measurements. To keep the closed form of **1** at a very low concentration in the overall sample solution, an unfocused 527 nm laser beam constantly irradiated the glass sample reservoir to convert the closed form of **1** back to the open form of **1**.

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