

Photochromic and Luminescence Switching Properties of a Versatile Diarylethene-Containing 1,10-Phenanthroline Ligand and Its Rhenium(I) Complex

Vivian Wing-Wah Yam,* Chi-Chiu Ko, and Nianyong Zhu

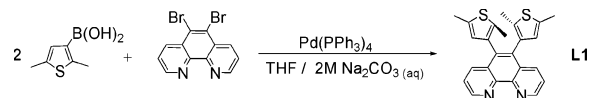
Center for Carbon-Rich Molecular and Nano-Scale Metal-Based Materials Research, Department of Chemistry, and HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong, China

Received April 30, 2004; E-mail: wwyam@hku.hk

Organic diarylethene derivatives have received much attention and have been extensively reported.¹ They have been demonstrated to possess outstanding fatigue resistance and thermally irreversible photochromic behavior.¹ Although a number of these compounds are known, most of the studies are directed toward the molecular design and synthesis of the organic framework of the diarylethenes, while studies on the exploitation of these diarylethenes as ligands to form metal complexes are extremely rare.² The combination of the diarylethene ligands and metal complex systems has shown novel properties. Another possible advantage of incorporating them into metal complexes is the possible extension of the excitation wavelength to lower energies, which are usually less destructive. The metal complex systems, with the various characteristic electronic transitions, may also serve as photosensitizer for the photochromic activity. We recently reported the photosensitization of a photochromic spirooxazine moiety by the triplet metal-to-ligand charge transfer (³MLCT) excited states of rhenium(I).³ We believe that through judicious design, a new series of functionalized diarylethene molecules capable of serving as versatile ligands could be synthesized. This may open up new avenues for the discovery of new classes of interesting ligands and metal-containing photochromic materials, such that through the incorporation of different metal centers, ready tuning of the excitation wavelength and photochromic behavior may result, without the need for difficult and tedious synthesis and preparation of elaborate organic molecular framework. Herein, we report the syntheses, crystal structure, and sensitized photochromic properties of a versatile diarylethene-containing 1,10-phenanthroline ligand (**L1**) and its rhenium(I) complex, [Re(CO)₃(**L1**)Cl] (**1**), which unlike most other studies in which the diarylethene ligands are derived from the attachment of donor atoms or groups as pendants to the bis(thienyl)perfluorocyclopentene core,^{2a-d,g-i} the present design involves the ligand itself directly forming part of the diarylethene framework, which is extremely rare.^{2e,f} The luminescent behaviors of the open-ring and closed-ring isomers are also reported.

L1 is synthesized by Suzuki cross-coupling reaction⁴ of 2,5-dimethyl-3-thienyl boronic acid⁵ and 5,6-dibromo-1,10-phenanthroline⁶ using Pd(PPh₃)₄ catalyst in the mixture of 2 M aqueous Na₂CO₃ and THF under reflux conditions (Scheme 1). Substitution reactions of Re(CO)₅Cl with **L1** in anhydrous benzene under reflux conditions afforded **1**. Both **L1** and **1** show two well-resolved sets of ¹H NMR signals, corresponding to the parallel and antiparallel conformations, commonly found in diarylethene systems.⁷ The two conformations, parallel (photochromic inactive)⁸ and antiparallel (photochromic active),⁸ for most of the diarylethenes would undergo very fast fluxional motion, resulting in only one set of time-averaged ¹H NMR signals even at -90 °C.⁹ It is only for those diarylethenes bearing substituents, which hindered the rotation of the aryl groups, that two sets of NMR signals would be observed.¹⁰ It is likely that

Scheme 1



the sterically demanding nature of the 1,10-phenanthroline ring, in which the protons at the 4- and 7-positions hindered the rotation of the thiophene moieties, would account for the observation of the two sets of signals.

The structure of **L1** has been crystallographically characterized.¹¹ The crystal of **L1** picked for the structure determination adopted a parallel conformation, in which the methyl groups at the 2-position of both thiophene rings were pointing in the same direction. Because of the steric hindrance exhibited by the two thiophene moieties, they tend to orient themselves perpendicular to the plane of the phenanthroline moiety. The interplanar angles between the thiophene rings and 1,10-phenanthroline in the crystal structure of **L1** were determined to be 87.0 and 76.3°, which are essentially orthogonal. As a result, the π -conjugation between the thiophene rings and the phenanthroline moiety is almost negligible in the open form.

L1 in its open form dissolved in benzene to give a colorless solution, with intense absorption bands at ca. 300 nm, which are ascribed to the intraligand (IL) $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the phenanthroline moiety, probably with some mixing of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the thiophene rings. In addition to the intense IL ($\pi \rightarrow \pi^*$) absorptions, in the UV region, **1** in its open form also shows a moderately intense band at ca. 400 nm, with molar extinction coefficient (ϵ) in the order of $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, which is typically observed in rhenium(I) tricarbonyl diimine complex systems,^{3,12} and thus is assigned as a MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{L1})$] transition. Upon UV excitation at $\lambda = 313 \text{ nm}$ of **L1**, an intense absorption band at 366 nm and two moderately intense absorption bands at ca. 510 and 540 nm, with ϵ in the order of 10^4 and $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, respectively, emerged in the absorption spectrum. These new absorption bands were ascribed to absorptions of the closed form, generated by photocyclization of the open form. Similar to the free ligand, three new absorption bands at ca. 390, 546, and 580 nm were formed when **1** was excited at $\lambda = 313 \text{ nm}$. The red shift of the absorption bands of the closed form in **1** (390, 546 and 580 nm) versus that in free ligand **L1** (366, 510 and 540 nm) is attributed to perturbation of the transitions by the metal center in the metal complex. Apart from photocyclization with UV excitation at $\lambda \leq 340 \text{ nm}$, excitation into the MLCT absorption bands of **1** also resulted in the formation of the new bands (Figure 1a). This is indicative of the formation of the closed form with MLCT excitation, probably via the ³MLCT excited state as similar suggestions have also been made in related systems.^{2g,3} As a result, the photochromism could be very much extended from the UV region in the free ligand to the visible region up to a wavelength

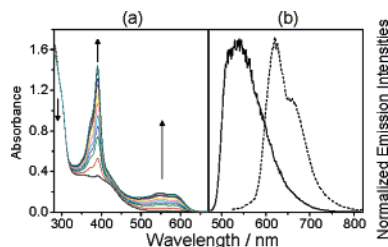
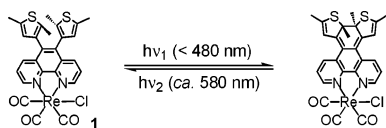


Figure 1. (a) UV-vis absorption spectral changes of **1** in benzene (7.16×10^{-5} M) upon MLCT excitation at 440 nm. (b) Overlaid normalized corrected emission spectra of the open (—) and the closed (---) forms of **1** in EtOH–MeOH glass (4:1 v/v) at 77 K.

Scheme 2



of ca. 480 nm, corresponding to the absorption tail of the MLCT transition, in the complex (Scheme 2). Upon excitation into the absorption bands of the closed form, absorptions due to the closed form decreased in intensities, indicative of the regeneration of the open form as a result of the photochromic backward reaction. The quantum yields corrected for the active conformer for the photocyclization were determined [**L1**, $\phi_{313} = 0.33$; **1**, $\phi_{313} = 0.52$, $\phi_{440} = 0.65$], which were found to be much higher than those for photocycloreversion [**L1**, $\phi_{510} = 0.012$; **1**, $\phi_{510} = 0.009$]. Such trends are typically observed in other related systems.^{1,2}

The closed forms would also undergo slow thermal backward reaction with their half-lives estimated, from the absorption decay, to be 143 ± 0.4 h at 20 °C and 222 ± 0.3 min at 60 °C for **L1** and 78 ± 0.1 h at 20 °C and 80 ± 0.1 min at 60 °C for **1**. It appeared that the half-life for the closed form of **L1** decreases upon coordination to the rhenium metal center in **1**, which may be indicative of a decrease in the stability of the closed form relative to the open form upon coordination to the rhenium(I) system.

Upon excitation at $\lambda \geq 300$ nm, the open form of **L1** in benzene solution produced luminescence at 385 nm [$\tau_o < 0.1$ μ s, $\phi_{em}(\lambda_{ex} 330 \text{ nm}) = 6 \times 10^{-3}$]. This emission is tentatively assigned as IL ($\pi \rightarrow \pi^*$) fluorescence in origin, most probably derived from the phenanthroline moiety. On the contrary, the open form of **1** in benzene solution produced luminescence at 595 nm [$\tau_o = 0.26$ μ s, $\phi_{em}(\lambda_{ex} 470 \text{ nm}) = 2 \times 10^{-2}$] upon excitation into the MLCT absorption band at $\lambda \geq 400$ nm. With reference to previous spectroscopic studies on the related rhenium(I) tricarbonyl phenanthroline complex systems,^{12a} this emission band is assigned as 3 MLCT [$d\pi(\text{Re}) \rightarrow \pi^*(\text{L1})$] phosphorescence. Upon conversion to the closed form in the photostationary state, the emission of both **L1** and **1** changed. These emission changes are reversible even after 10 photochromic cycles. The closed form of **L1** in benzene solution displayed red photoluminescence, with emission maximum at 644 nm [$\tau_o < 0.1$ μ s, $\phi_{em}(\lambda_{ex} 470 \text{ nm}) = 1 \times 10^{-3}$] upon excitation at $\lambda \geq 400$ nm. The red shift in the emission energies of the closed form relative to that of the open form is in line with an increase in the extent of π -conjugation upon photoinduced ring-closing reaction. Besides, the emission spectrum of the closed form of **L1** in EtOH–MeOH (4:1 v/v) glass at 77 K showed fairly well-resolved vibronic structures at 577 nm ($\tau_o = 5.2$ μ s) with vibrational progressional spacings of ca. 1250 cm^{-1} , typical of $\nu(\text{C}=\text{S})$ stretching modes. The relatively long emission lifetime in the microsecond range is suggestive of an assignment of a phosphorescence origin. Thus, the emission is tentatively assigned as IL ($\pi \rightarrow \pi^*$) phosphorescence. Similarly, the closed forms of **1** displayed photoluminescence

either in solution at 298 K or in EtOH–MeOH glass (4:1 v/v) at 77 K. The emission spectrum of the closed form of **1** in EtOH–MeOH (4:1 v/v) at 77 K (Figure 1b) also displayed fairly well-resolved vibronic structures, similar to that found in the emission spectrum of the closed form of **L1**, at 620 nm ($\tau_o = 6.4$ μ s). The different emission band structure and the shorter emission lifetime of the closed form of complex **1** compared to its open form in solution may be suggestive of a different emission origin. In view of the close resemblance of the emission energies and the vibronic structures of **1** to that of **L1** in their closed forms, an emission origin of metal-perturbed IL character is suggested in **1**. It is likely that in the closed form of **1**, the IL excited state became lower-lying in energy than that of the MLCT excited state, rendering the IL excited state the predominant emissive state, although one could not completely exclude the possibility of some mixing of a MLCT state into the emission origin. On the contrary, in the open form of **1**, the MLCT state is lower-lying than the IL state and becomes the predominant emissive state.

Extension of this work toward the incorporation of this ligand into other transition metal complex systems is now in progress.

Acknowledgment. V.W.-W.Y. acknowledges support from the University Development Fund of The University of Hong Kong and the HKU Foundation for Educational Development and Research Limited, and C.-C.K. acknowledges the receipt of a Croucher Scholarship and a University Postdoctoral Fellowship. The work has been supported by the Research Grants Council of the Hong Kong SAR, China (HKU 7120/02P).

Supporting Information Available: Characterization of **L1** and **1**, crystallographic data and perspective drawing of **L1**, and emission spectra of **1** after 10 photochromic cycles (CIF, PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716. (b) Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85–97.
- (2) (a) Murguly, E.; Norsten, T. B.; Branda, N. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1752–1755. (b) Frayssé, S.; Coudret, C.; Launay, J. P. *Eur. J. Inorg. Chem.* **2000**, 1581–1590. (c) Fernández-Acebes, A.; Lehn, J. M. *Adv. Mater.* **1998**, *10*, 1519–1522. (d) Fernández-Acebes, A.; Lehn, J. M. *Chem.–Eur. J.* **1999**, *5*, 3285–3292. (e) Chen, B. Z.; Wang, M. Z.; Wu, Y. Q.; Tian, H. *Chem. Commun.* **2002**, 1060–1061. (f) Tian, H.; Chen, B. Z.; Tu, H.; Müllen, K. *Adv. Mater.* **2002**, *14*, 918–923. (g) Jukes, R. T. F.; Adamo, V.; Hartl, F.; Belser, P.; De Cola, L. *Inorg. Chem.* **2004**, *43*, 2779–2792. (h) Matsuda, K.; Takayama, K.; Irie, M. *Chem. Commun.* **2001**, 363–364. (i) Konaka, H.; Wu, L. P.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y. *Inorg. Chem.* **2003**, *42*, 1928–1934.
- (3) (a) Yam, V. W. W.; Ko, C. C.; Wu, L. X.; Wong, K. M. C.; Cheng, K. K. *Organometallics* **2000**, *19*, 1820–1822. (b) Ko, C. C.; Wu, L. X.; Wong, K. M. C.; Zhu, N. Y.; Yam, V. W. W. *Chem.–Eur. J.* **2004**, *10*, 766–776.
- (4) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147–168.
- (5) Nielsen, L. K.; Deane-Wray, A. PCT Int. Appl. **1995**, WO 9502046.
- (6) Mlochowski, J. *J. Roc. Chem.* **1974**, *48*, 2145–2155.
- (7) Nakamura, S.; Irie, M. *J. Org. Chem.* **1988**, *53*, 6136–6138.
- (8) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 2045–2048.
- (9) Gilat, S. L.; Kawai, S. H.; Lehn, J. M. *Chem.–Eur. J.* **1995**, *1*, 275–293.
- (10) (a) Uchida, K.; Nakayama, Y.; Irie, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1311–1315. (b) Irie, M.; Miyatake, O.; Uchida, K. *J. Am. Chem. Soc.* **1992**, *114*, 8716–8717. (c) Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305–8309.
- (11) The crystallographic data and perspective drawing of **L1** can be obtained in the Supporting Information.
- (12) (a) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, 2401–2415. (b) Wrighton, M.; Morse, D. L. *J. Am. Chem. Soc.* **1974**, *96*, 998–1003.

JA047446Q