

# Metal Coordination-Assisted Near-Infrared Photochromic Behavior: A Large Perturbation on Absorption Wavelength Properties of N,N-Donor Ligands Containing Diarylethene Derivatives by Coordination to the Rhenium(I) Metal Center

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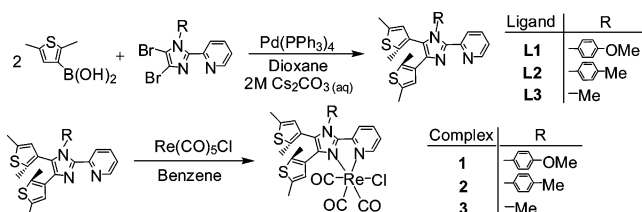
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Photochromic diarylethene materials have drawn much attention in recent years since the first report made by Kellogg et al.<sup>1a</sup> and subsequent extensive studies by Irie and co-workers<sup>1b–d</sup> on the photochromic properties of diarylethene molecules. Their promising fatigue resistance and thermally irreversible properties make them ideal candidates for potential applications in photoswitching molecular devices and optical memory storage. Recently, different attempts have been made to design photochromic compounds that show absorption and reactivity in the near-infrared (NIR) region in order to enhance the semiconductor diode laser susceptibility for applications in optical memory storage.<sup>1c,d,2</sup> One commonly employed approach to achieve NIR absorption is to increase the extent of  $\pi$ -conjugation of the thiophene moiety so as to shift the absorption maxima to longer wavelength.<sup>3</sup> However, the synthesis is usually tedious and non-trivial, and the wavelength shift would eventually reach its convergence limit. Recently, diarylethene derivatives that function as ligands for incorporation into transition metal complexes have been reported by us and others, in which perturbation of the photochromic properties of the diarylethene moiety upon coordination to the metal center has been observed.<sup>4</sup> We believe that, by the judicious design and suitable choice of the ligands and metal centers, the incorporation of diarylethene derivatives as ligands into transition metal complex systems may have an added advantage of extending the wavelength of maximum absorption to the red through an enhancement of the planarity of the  $\pi$ -conjugated system, thus providing an alternative and versatile route toward the design and synthesis of new classes of NIR photochromic materials. Without the need for tedious synthesis, coordination of relatively simple diarylethene molecules into the transition metal complex not only can cause a shift in the absorption and photochromic properties, but also the photochromic behavior can be sensitized through excitation into the relevant excited state of the metal complex chromophore. Herein, we report the syntheses and photosensitized photochromic properties of diarylethene-containing 1-aryl-substituted 2-(2-pyridyl)imidazole ligand derivatives and their rhenium(I) complexes and their NIR photochromic behavior upon rhenium(I) coordination.

4,5-Dithienyl-substituted 2-(2-pyridyl)imidazole ligands **L1**, **L2**, and **L3** were prepared by the Suzuki coupling reaction<sup>5</sup> of 2,5-dimethyl-3-thienyl boronic acid<sup>6</sup> and 1-aryl-4,5-dibromo-2-(2-pyridyl)imidazole using Pd(PPh<sub>3</sub>)<sub>4</sub> as catalyst in a mixture of aqueous Cs<sub>2</sub>CO<sub>3</sub> (2 M) and dioxane under reflux conditions (Scheme 1). Subsequent reactions of the respective ligands **L1**, **L2**, and **L3** with Re(CO)<sub>5</sub>Cl in benzene solution under reflux conditions afforded the target rhenium(I) complexes, [Re(CO)<sub>3</sub>(L)Cl] where

Scheme 1



**L** = **L1** (**1**), **L2** (**2**), and **L3** (**3**). All of the ligands and complexes have been characterized by <sup>1</sup>H NMR, IR, and EI-MS and gave satisfactory elemental analyses. Complex **3** has also been characterized by X-ray crystallography (Figure 1). <sup>1</sup>H NMR spectroscopy of **L1–L3** showed the presence of only one set of <sup>1</sup>H NMR signals for the methyl groups on the thiophene moieties, corresponding to the time-averaged signals for both the antiparallel and parallel configurations,<sup>7</sup> indicating a fast interconversion of the two forms<sup>8</sup> which probably resulted from the lack of steric bulk of the imidazole ring. However, upon coordination to the Re metal complex system, the <sup>1</sup>H NMR signals broadened, probably as a result of a reduction in the interconversion rate between the parallel and antiparallel configurations in the complexes due to the steric hindrance imposed upon coordination to the Re(CO)<sub>3</sub>Cl moiety.

The open forms of **L1–L3** dissolve in chloroform to give colorless solutions, with an intense absorption band at ca. 320 nm corresponding to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of the 1-aryl-2-(2-pyridyl)imidazole moiety, with mixing of  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of the thiophene moieties. On coordination to the Re complex system, this IL absorption band was shifted slightly to the red at ca. 352 nm. In addition to this intense IL absorption band, an absorption shoulder was observed at ca. 425 nm in the electronic absorption spectra of complexes **1–3**, ascribed to a MLCT [ $d\pi(\text{Re}) \rightarrow \pi^*(\text{L})$ ] transition, with some mixing of a metal-perturbed IL ( $\pi \rightarrow \pi^*$ ) transition. Upon UV excitation at  $\lambda \leq 350$  nm, the ligands showed two additional absorption bands at ca. 410–425 and 576–586 nm. These new absorption bands at longer wavelengths were tentatively assigned as absorptions of the closed forms, resulting from the photocyclization of the open forms upon UV light irradiation. Upon excitation of complexes **1** and **2** at  $\lambda \leq 450$  nm into either the IL or MLCT bands, three absorption bands were generated at ca. 290, 475, and 712 nm and 288, 480, and 713 nm, respectively. These new sets of absorption bands were assigned as metal-perturbed <sup>1</sup>IL transitions of the closed forms of the complexes, with mixing of <sup>1</sup>MLCT transitions in the longest wavelength absorption band. Figure 2a and 2c depict the representative UV–vis absorption spectral changes of **L1** and complex **2** in solution. Such a large shift of the absorption bands of the closed

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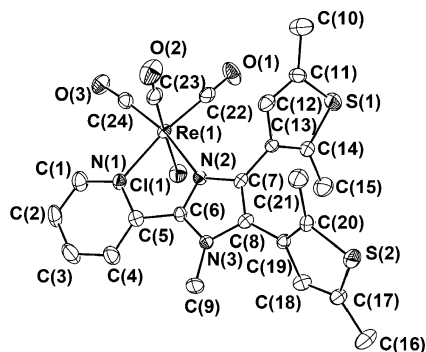


Figure 1. Perspective drawing of complex 3.

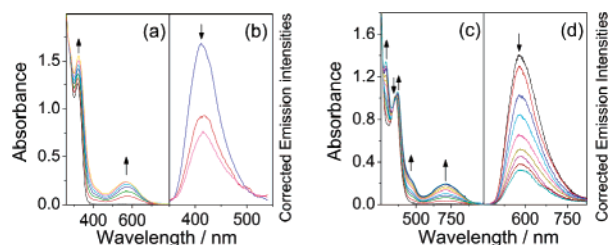


Figure 2. (a) UV-vis absorption and (b) corrected emission spectral changes of **L1** ( $7.16 \times 10^{-5}$  M) in chloroform upon IL excitation at 320 nm at 298 K. (c) UV-vis absorption and (d) corrected emission spectral changes of **2** ( $7.00 \times 10^{-5}$  M) in chloroform upon MLCT excitation at 410 nm at 298 K.

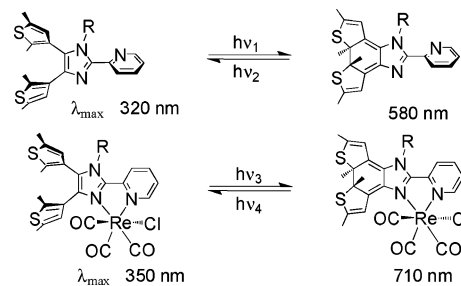
forms of complexes **1** and **2** to the NIR region could be attributed to the planarization of the four heterocyclic rings relative to the open forms. In the open forms of **L1**–**L3**, the pyridyl and imidazolyl rings are twisted with respect to each other and are not coplanar, similar to that of biaryl and biheteroaryl systems. Upon photocyclization, only the imidazole and the two thiophene moieties are locked into a coplanar conformation, leading to a shift of the absorption wavelength to 580 nm in the closed forms. On the contrary, coordination to the rhenium(I) metal center would force the 2,2'-linked pyridyl and imidazolyl rings in complexes **1** and **2** into coplanarity from their twisted conformation, causing an increase in the extent of  $\pi$ -conjugation. Upon photocyclization, the extent of  $\pi$ -conjugation in the closed forms of complexes **1** and **2** would become further enhanced upon photoinduced ring closure and become much greater than that of **L1**–**L3** (Scheme 2), leading to a red shift in the absorption wavelength to the NIR region. In addition, excitation into the MLCT absorption band also triggered photocyclization of the open forms of complexes **1** and **2**. This indicates that the photocyclization can occur via MLCT excited-state photosensitization. Upon excitation into the bands of the closed forms of complexes **1** and **2**, photochromic backward reactions occur (Scheme 2). The quantum yields for the photocyclization reactions at 283 K were determined for complexes **1** and **2** [**1**,  $\phi_{350} = 0.35$ ; **2**,  $\phi_{350} = 0.40$ ], which were found to be much higher than those for the photocycloreversion reactions [**1**,  $\phi_{510} = 0.003$ ; **2**,  $\phi_{510} = 0.004$ ].

Excitation into either the IL or MLCT band of the open forms of complexes **1** and **2** in chloroform resulted in light emission with a maximum at 570 nm. This emission can be assigned as  $^3\text{MLCT}$  phosphorescence. Upon prolonged excitation at the isosbestic point ( $\lambda = 352$  nm) of the open forms of complexes **1** and **2**, photocyclization took place, and the emission intensity at ca. 570 nm was found to decrease. Representative emission spectral changes of **L1** and complex **2** are shown in Figure 2b and 2d, respectively.

A metal-containing diarylethene system has been demonstrated to exhibit NIR photochromic behavior, with a large red shift in

absorption maxima upon photocyclization that has been brought about by metal coordination-assisted planarization of the extended  $\pi$ -conjugated system. The present concept of conformational switching via metal coordination may open up new and efficient synthetic strategies for the design of NIR photochromic materials.

#### Scheme 2



**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. The work has been supported by the Research Grants Council of the Hong Kong SAR, PR China (HKU 7050/04P and HKU 7057/06P). P.H.-M.L. acknowledges the receipt of a Postgraduate Studentship administered by The University of Hong Kong.

**Supporting Information Available:** Synthetic procedures, characterization data, details of physical measurements and instrumentation,  $^1\text{H}$  NMR spectra of **L1**–**L3** and complexes **1**–**3**, UV-vis absorption spectral changes of **L2**, **L3**, and complex **1**, absorption spectral changes of complex **2** on alternate excitation at 350 and 610 nm over two cycles, and crystallographic data of complex **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

#### References

- (a) Kellogg, R. M.; Groen, M. B.; Wynberg, H. *J. Org. Chem.* **1967**, *32*, 3093–3100. (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716. (c) Tsujioka, T.; Kume, M.; Irie, M. *Jpn. J. Appl. Phys.* **1996**, *35*, L1532–L1534. (d) Tsujioka, T.; Kume, M.; Irie, M. *Jpn. J. Appl. Phys.* **1996**, *35*, 4353–4560.
- (a) *Photochromism: Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; Vol. 40. (b) *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Main Photochromic Families; Plenum Press: New York and London, 1999; Vol. 1. (c) Yokoyama, Y. *Chem. Rev.* **2000**, *100*, 1717–1740. (d) Tian, H.; Yang, S. *Chem. Soc. Rev.* **2004**, *33*, 85–97.
- (a) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *Chem.-Eur. J.* **1995**, *1*, 275–284. (b) Gilat, S. L.; Kawai, S. H.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1439–1440. (c) Chen, B. Z.; Wang, M. Z.; Wu, Y. Q.; Tian, H. *Chem. Commun.* **2002**, 1060–1061. (d) Tian, H.; Chen, B. Z.; Tu, H.; Müllen, K. *Adv. Mater.* **2002**, *14*, 918–923. (e) Peter, A.; McDonald, R.; Branda, N. R. *Chem. Commun.* **2002**, 2274–2275. (f) Ahmed, S. A. *J. Phys. Org. Chem.* **2002**, *15*, 392–402. (g) Liang, Y.; Dvornikov, A. S.; Rentzepis, P. M. *J. Mater. Chem.* **2003**, *13*, 286–290. (h) Ahmed, S. A. *J. Phys. Org. Chem.* **2006**, *19*, 402–414. (i) Odo, Y.; Matsuda, K.; Irie, M. *Chem.-Eur. J.* **2006**, *12*, 4283–4288.
- (a) Yam, V. W.-W.; Ko, C.-C.; Zhu, N. *J. Am. Chem. Soc.* **2004**, *126*, 12734–12735. (b) Jukes, R. T. F.; Adamo, V.; Hartl, F.; Belsler, P.; De Cola, L. *Inorg. Chem.* **2004**, *43*, 2779–2792. (c) Fernández-Acebes, A.; Lehn, J.-M. *Adv. Mater.* **1998**, *10*, 1519–1522. (d) Takeshita, M.; Irie, M. *Chem. Lett.* **1998**, 1123–1124. (e) Ko, C.-C.; Kwok, W. M.; Yam, V. W.-W.; Phillips, D. L. *Chem.-Eur. J.* **2006**, *12*, 5840–5848.
- (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147–168.
- Shorunov, S. V.; Stoyanovich, F. M.; Krayushkin, M. M. *Russ. Chem. Bull.* **2004**, *53*, 2338–2339.
- Nielsen, L. K.; Deane-Wray, A. PCT Int. Appl. WO 9502046, 1995.
- Nakamura, S.; Irie, M. *J. Org. Chem.* **1988**, *53*, 6136–6138.

JA067425R