Communications

A Photochromic Platinum(II) Bis(alkynyl) Complex Containing a Versatile 5,6-Dithienyl-1,10-phenanthroline

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Summary: A luminescent diarylethene-functionalized platinum(II) diimine bis(alkynyl) complex displays interesting photochromic behavior with successful photosensitization by excitation into the ^{3}MLCT/LLCT excited state of this complex to trigger photocyclization.

The exploration of photochromic materials has aroused a surge of interest in the field of materials science, mainly due to their potential applications in optical data storage and optoelectronic devices. Diarylethenes bearing two thiophene rings are among one of the important classes of photochromic compounds with regard to their thermal irreversibility and high fatigue resistance.[1a] The majority of research work reported has been devoted to their development and investigative studies of their fundamental properties. These results have contributed to our panoramic understanding of the chemistry of diarylethenes.[1b−d] A handful of reports have demonstrated the functionalization of nitrogen ligands, mostly monodentate, through the attachment of diarylethene units as photochromic pendants or bridges.[2] Coordination of these ligands to metal centers such as copper(I),[2a,o] gold(I),[2b,c] manganese(II),[2o] platinum(II),[2d] ruthenium(II),[2e−h] silver(I),[2i] tungsten(I),[2g,k] and zinc(II)[2l,o,p] has been reported. However, functionalization of the photochromic diarylethene moiety as part of the nitrogen ligand framework followed by coordination to metal centers is still an issue in its infancy.[2m,n] We first reported the sensitized photochromism of a rhenium(I) tricarbonyl complex that was ligated with a photochromic 5,6-dithienyl-1,10-phenanthroline (**L**).[3] We envision that by altering the identity of the metal center, the photoluminescence properties of various metal complexes may blend into the interesting photochromic properties of this ligand, resulting in multifunctional materials. Such perturbation brought about by a simple change in the metal center would help to circumvent tedious synthetic procedures required to tune the photochromic behavior of this class of compounds in that a diversity of interesting photochromic properties could be readily realized in a variety of different metal complexes.[4]

Platinum(II) bis(alkynyl) complexes with the general formula [Pt(diimine)(C≡CR)$_2$] were shown to be strongly emissive in fluid solution at room temperature.[5] With our recent interest in the luminescence studies of platinum(II) alkynyls,[6] it is believed that this class of compounds, when furnished with this functionalized ligand, may demonstrate striking photochromic behavior in addition to its rich inherent properties. Herein, we report the syntheses, crystal structures, sensitized photochromic properties, and photoluminescence behavior of a platinum(II)

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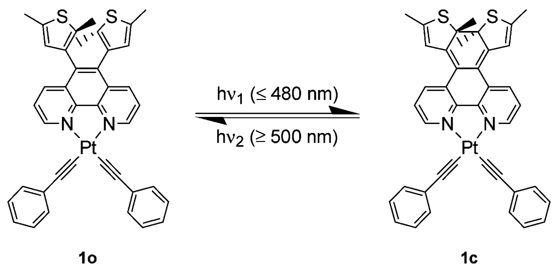
Scheme 1. Photochromism of Complex 1



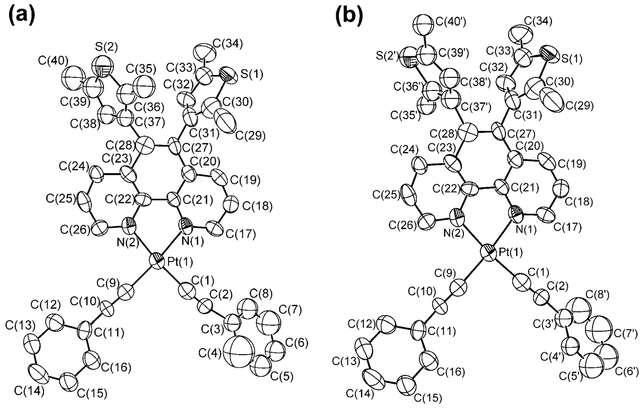


Figure 1. Perspective drawings of **1** as the parallel (a) and antiparallel (b) conformers with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

bis(alkynyl) complex containing the 5,6-dithienyl-1,10-phenanthroline moiety (Scheme 1).

The target complex Pt(**L**)(C≡CPh)$_2$ (**1**) was prepared from Pt(**L**)Cl$_2$, which was prepared according to modification of a literature procedure for Pt(phen)Cl$_2$,[7] under Sonogashira conditions.[8] The ^{1}H NMR spectrum showed two sets of signals corresponding to the two conformers: antiparallel conformer (photochromic active) and parallel conformer (photochromic inactive). This observation agrees with the possible steric hindrance to the free rotation of the two thiophene rings exerted by the protons at the 4- and 7-positions of the phenanthroline ring.[3]

The two conformers were distinguished from each other in terms of the orientations of the thiophene rings. The antiparallel conformer has two thiophene rings in C_2 symmetry, while those of the parallel conformer are in C_s symmetry.[9] The crystal structures of the two conformers of **1** were determined by X-ray crystallography, as depicted in Figure 1. The ratio of the population of parallel to antiparallel conformers in the cocrystal was found to be approximately 2:1, as revealed from the disorder of one of the thiophene rings in **1**. This is the first example of X-ray crystal structures in which both antiparallel and parallel conformers of a single photochromic diarylethene molecule have been resolved. The interplanar angles between the two thiophene rings are 65.9 and 55.3° in the antiparallel and parallel conformers, respectively. The mean Pt−N bond distance of **1** is found to be 2.059(8) Å, which agrees with the trans influence from the σ-bonded alkynyl group in comparison with those from the chlorides in [Pt(phen)Cl$_2$][10] (Pt−N bond distance 2.033(6) Å). The Pt−C(alkynyl) bond distance of **1** is 1.994(1) Å, which is comparable to the close analogues of this class of platinum(II) diimine bis(alkynyl) complexes.[5c] The closest Pt···Pt contact is 4.477 Å, which indicates the absence of any interaction between the metal centers in the crystalline solid state.

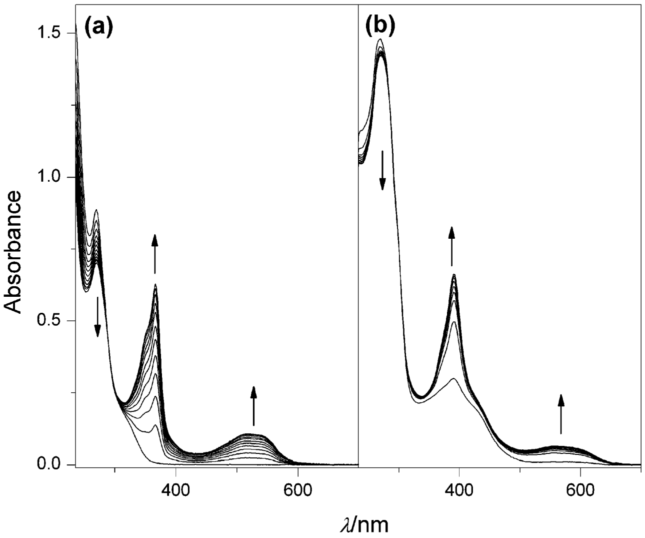


Figure 2. UV−vis absorption spectral changes of (a) **L** in dichloromethane solution (3.78 × 10^{-5} M) upon IL excitation at 313 nm and (b) **1** in dichloromethane solution (2.19 × 10^{-5} M) upon MLCT/LLCT excitation at 420 nm.

The absorption properties of **L** in benzene solution were previously reported.[3] The open form of **L** (**Lo**) dissolves in dichloromethane to give a colorless solution, with the absorption maxima at ca. 270 nm (ϵ = 23 220 dm^3 mol^{-1} cm^{-1}) and 316 nm (ϵ = 4970 dm^3 mol^{-1} cm^{-1}), ascribed to the intraligand (IL) $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transitions of the phenanthroline backbone with some mixing of the $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transitions of the two thiophene rings. Upon UV irradiation at λ = 313 nm, the colorless solution of **Lo** in dichloromethane becomes red, with emergence of an intense absorption band at ca. 366 nm (ϵ = 19 160 dm^3 mol^{-1} cm^{-1}) and a lower energy band at ca. 518 nm (ϵ = 3100 dm^3 mol^{-1} cm^{-1}), ascribed to the absorptions of the closed form of **L** (**Lc**) via photocyclization of its antiparallel open form (Figure 2a).

The solution of **1** in its open form (**1o**) in dichloromethane appears as a bright yellow solution. It shows an intense absorption band at ca. 268 nm, attributed to the **L**-based and alkynyl-based IL transitions. In addition, it shows a comparatively moderate absorption band at ca. 390 nm, originating from the metal-to-ligand charge transfer (MLCT; dπ(Pt) $\rightarrow \pi^*$(**Lo**)) transition,[5] probably with some mixing of a ligand-to-ligand charge transfer (LLCT; π(C≡C) $\rightarrow \pi^*$(**Lo**)) transition as suggested from DFT calculations by Castellano et al.[11] The values of ϵ of these two bands are on the order of 10^4 dm^3 mol^{-1} cm^{-1}. Upon UV irradiation at λ = 313 nm, an intense absorption band at ca. 390 nm and a broad band at ca. 560 nm emerged as the closed form of **1** (**1c**) was generated. The slight red shift of these bands in **1c** relative to those of **Lc** suggests that they are predominantly metal-perturbed IL $\pi \rightarrow \pi^*$ and n $\rightarrow \pi^*$ transitions of the 8a,8b-dimethyl-1,8-dithia-*as*-indacene moiety. In addition to excitation at 313 nm that triggers photocyclization originated from the IL transitions, excitation into the MLCT/LLCT absorption bands with $\lambda \leq$ 480 nm of

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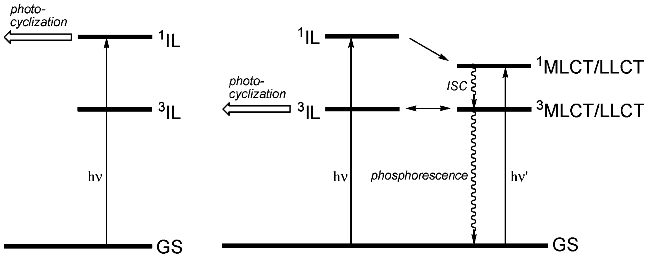
Table 1. Photochemical Quantum Yields of L and 1 in Dichloromethane Solution at 298 K[a]

	photocyclization		photocycloreversion	
	ϕ_{313}	ϕ_{420}	ϕ_{366}	ϕ_{510}
L	0.272		0.029	0.014
1	0.035	0.030		0.012

[a] Values reported are corrected for the ratio of the photochromic active conformation.

Scheme 2. Qualitative Energy State Diagram of Lo and 1o



Lo **1o**

1o also gives rise to photocyclization.[2f,3] Figure 2b shows the absorption spectral changes upon MLCT/LLCT excitation at $\lambda = 420$ nm. The quantum yield for the photocyclization reaction of **1o** when compared to that of **Lo** at $\lambda = 313$ nm was found to be significantly reduced (0.035 vs 0.272) (Table 1). In view of the similar quantum yields (0.035 vs 0.030) obtained upon excitations into the IL and the MLCT/LLCT bands of **1o**, it is likely that an efficient energy transfer from the IL state to the MLCT/LLCT state has occurred upon excitation into the IL band. Once the ^{1}MLCT/LLCT state is populated, intersystem crossing to the ^{3}MLCT/LLCT state would occur that leads to the sensitization of the photochromic reactive ^{3}IL state, which may be very close in energy and in equilibrium with the ^{3}MLCT/LLCT state, going through the same common pathway as the MLCT/LLCT-sensitized photochromic reaction (Scheme 2).[2f,5f] The extension of the excitation wavelengths to the visible region up to $\lambda \leq 480$ nm to trigger the photochromism of **1** favors the use of less destructive visible light sources and is desirable. Upon excitation into the absorption bands of **1c** in the visible regions with $\lambda \geq 500$ nm, the absorbance at 560 nm drops accordingly. This indicates that photocycloreversion has taken place, regenerating the open form of **1**. The quantum yield for the photocycloreversion reaction of **1c** upon excitation at 510 nm is found to be similar to that of **Lc**.

Upon excitation at $\lambda \geq 300$ nm, **Lo** in dichloromethane solution produced luminescence at 405 nm ($\tau_o < 0.1$ μs). With reference to our previous works,[3] this emission is tentatively assigned as IL ($\pi \rightarrow \pi^*$) fluorescence in origin, most probably derived from the phenanthroline moiety. On the other hand, upon excitation into the MLCT/LLCT band at $\lambda \geq 390$ nm, **1o** in dichloromethane solution displayed luminescence at 580 nm ($\tau_o = 1.6$ μs, $\phi_{em} = 0.18$), in the neighborhood of the emission maximum of the close analogue [Pt(phen)(C≡CPh)$_2$] observed at 561 nm ($\tau_o = 1.9$ μs, $\phi_{em} = 0.42$).[5e] It is therefore assigned as ^{3}MLCT (5d(Pt) $\rightarrow$ π^*(**Lo**))/LLCT (π(C≡C) $\rightarrow$ π^*(**Lo**)) phosphorescence (Figure 3a). The lower luminescence quantum yield of **1o** in compared to the yields of [Pt(diimine)(C≡CR)$_2$] analogues reported in the literature[5e] may be ascribed to the presence of an intramolecular energy transfer pathway from the ^{3}MLCT/LLCT state to the photochromic reactive ^{3}IL state, i.e., the possible quenching by the sensitized photocyclization, rendering the photoluminescence of **1o** from the ^{3}MLCT/LLCT state less efficient (Table 2). The emission spectrum of **1o** in EtOH−MeOH glass (4:1 v/v) at 77 K displayed well-resolved vibronic structures at 512 nm ($\tau_o = 11.0$ μs) with vibrational progressions of around 1250 cm^{-1}, typical of the ring-breathing mode of the phenanthroline ligand. On the basis of the similarity of its band shape to the ^{3}IL ($\pi \rightarrow \pi^*$) emission of [Pt(phen)$_2$]Cl$_2$ in EtOH−MeOH glass (1:3 v/v) at 77 K and the red shift of emission energy relative to [Pt(phen)$_2$]Cl$_2$ ($\lambda_{em} \sim 460$ nm),[12] the emission band of **1o** in 77 K glass is assigned as derived from states of a metal-perturbed ^{3}IL (**Lo**) origin, probably with some mixing of a ^{3}MLCT/LLCT character.

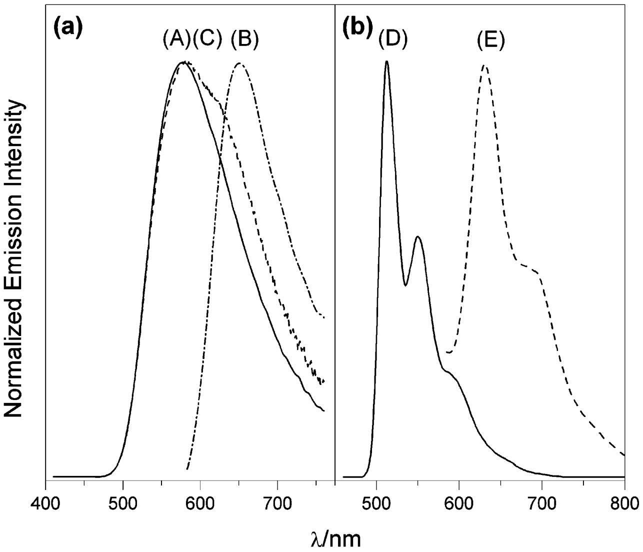


Figure 3. Overlaid normalized corrected emission spectra of (a) the open form **1o** (A) and the closed form **1c** (B) and the species at the photostationary state (C) in dichloromethane solution at 298 K and (b) the open form **1o** (D) and the closed form **1c** (E) in EtOH−MeOH glass (4:1 v/v) at 77 K.

Table 2. Photophysical Properties of Lo, 1o, [Pt(phen)(C≡CPh)$_2$], and [Pt(5,6-dmphen)(C≡CPh)$_2$][a]

	λ_{abs}/nm (ϵ/dm^3 mol^{-1} cm^{-1})[b]	λ_{em}/nm (τ_o/μs)	ϕ_{em}
Lo	270 (23 220), 316 (4970)	405 (<0.1)[c]	0.006[d]
1o	268 (68 000), 390 (11 480)	580 (1.6)[c]	0.18[e]
[Pt(phen)(C≡CPh)$_2$][f]	268 (58 400), 396 (7900)	561 (1.9)	0.42
[Pt(5,6-dmphen)(C≡CPh)$_2$][f]	279 (55 700), 377 (7000), 404 (7900)	554 (2.3)	0.6

[a] 5,6-dmphen = 5,6-dimethyl-1,10-phenanthroline. [b] Absorption maxima measured in dichloromethane solution. [c] Emission maxima measured in degassed dichloromethane solution at room temperature. [d] Data from ref 3a. [e] Values reported are relative to [Ru(bpy)$_3$](PF$_6$)$_2$ in degassed acetonitrile solution ($\phi = 0.062$). [f] Data from ref 5e.

Upon conversion of **Lo** to **Lc** at the photostationary state, the emission maximum was found to show a red shift to 600 nm ($\tau_o < 0.1$ μs) in dichloromethane at 298 K and to 577 nm ($\tau_o = 5.2$ μs)[3a] in EtOH−MeOH glass (4:1 v/v) at 77 K upon excitation at $\lambda \geq 400$ nm. The red shift in emission maximum is probably attributed to the increase in the extent of π conjugation in the closed form. In dichloromethane solution, **1c** emits with a maximum at 650 nm, while in EtOH−MeOH glass (4:1 v/v) at 77 K its emission spectrum exhibits fairly well-resolved vibronic-structured bands at 630 nm. The close resemblance of the emission spectral band shapes of **1c** and those of **Lc** phosphorescence as well as the relatively small red shift of emission energy from **Lc** to **1c** (Figure 3b) in EtOH−MeOH glass (4:1 v/v) at 77 K suggest that the origin of the emission of **1c** is metal-perturbed ^{3}IL in character, probably with some mixing of a ^{3}MLCT/LLCT

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character. The emission lifetimes of **1c** were not obtained, due to the inherently weak emission intensities at 77 K. A similar weakly emissive IL state was reported for the closed form of diarylethenes, in which the distinct emission band was measured to be at 630 nm.[13] We therefore speculate that the IL excited state becomes lower lying in energy in comparison to the MLCT/LLCT state in its closed form, which renders the IL excited state as the predominant emissive state, probably with some mixing of a MLCT/LLCT state into the emission origin; in contrast, the MLCT/LLCT state of **1o** is the predominant emissive state, as it is lower lying than the IL excited state.

To conclude, we have successfully incorporated a photochromic diimine ligand to a platinum(II) center demonstrating ^{3}MLCT/LLCT excited-state photosensitized photochromism while maintaining inherent photoluminescence behavior.

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Supporting Information Available: Text giving details of the characterization of **1** and tables and a CIF file giving full crystallographic descriptions of two conformers of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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