Inorg. Chem. **2009**, *48*, 19−21

Inorganic Chemistry
Communication

Linker-Dependent Metal-Sensitized Photoswitching of Dithienylethenes

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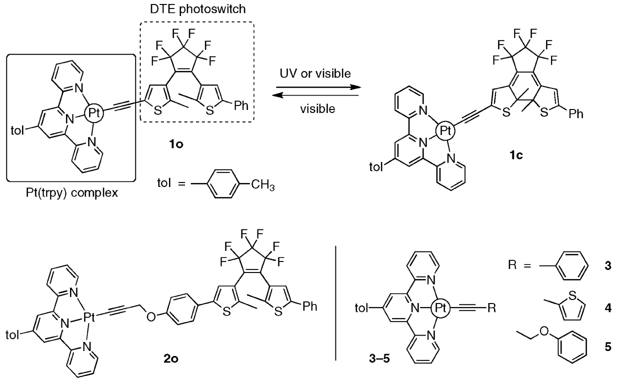
Received August 25, 2008

Intramolecular energy-transfer results in sensitized ring closing of a pendant dithienylethene from a platinum terpyridyl complex only when the two components are connected with a short π-conjugated linker.

Molecular systems that integrate metal-coordination complexes with photoswitchable dithienylethene (DTE) scaffolds represent the next generation of photoresponsive materials[1−4] because they offer numerous new optical and electronic properties by combining those unique to each component. Applications that will benefit from such hybrid systems include optical data storage,[5−10] molecular electronics,[11−13] and catalysis.[14,15] To date, many metals have been incorporated into hybrid photoswitching systems including Ru,[12,13,16−19] Os,[13,18,19] Pt,[3] Re,[2,4,9] Fe,[13] Co,[13] Sn,[10] Zn,[20,21] Mn,[21] Cu,[21,22] and W.[8] One of our specific interests in this area is to control the fate of a platinum(II) terpyridyl complex's excited state and influence how it acts as a photosensitizer for water reduction[23,24] and in the photoinduced oxidation of alkenes.[25] Because the metal complex plays the role of a photosensitizer in both applications, reversibly regulating the lifetime of the metal−ligand's excited state by toggling the DTE component between its two isomers within a hybrid system will provide a means to regulate the catalytic processes on command. This concept is possible assuming the two DTE isomers have unique

Scheme 1



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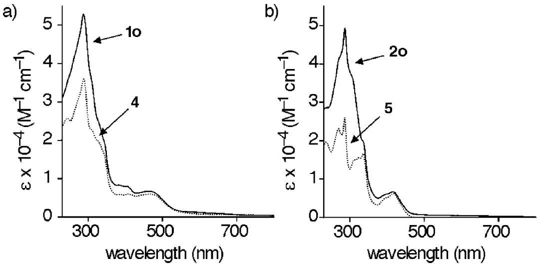

Figure 1. Absorption spectra for CH_3CN solutions (1.5×10^{-5} M) of (a) complexes **1o** (—) and **4** (•••) and (b) complexes **2o** (—) and **5** (•••).

optical and electronic properties, an assumption that is supported by a wide body of published examples.[26,27]

Platinum−DTE complex **1o** was the initial target system to achieve our goals (Scheme 1). The architecture was designed to intimately unite the two components (the platinum terpyridyl [Pt(trpy)] and the photoresponsive DTE) through a shared acetylide linker in order to maximize intramolecular energy transfer[28] and consequently reduce the excited-state lifetime of the metal complex, preventing it from participating in the photocatalytic reduction of water. In this Communication, we describe how complex **1o** undergoes photochemical ring closing when irradiated with light of wavelengths absorbed only by the metal chromophore and not directly by the DTE photoswitch. This phenomenon has been observed for a select few of the previously reported metal−DTE complexes where ring closing occurs by energy transfer from a triplet charge-transfer (^{3}CT) state involving the metal to a localized intraligand (^{3}IL) state on the photoswitch, although only one study has investigated how the linkage affects the rate of energy transfer between the components.[17] Here, we show that a longer, nonconjugated linker (in derivative **2o**, for example) prevents sensitized ring closing, and the photoswitch is only converted into its cyclized isomer when directly irradiated with UV light.

Complexes **1o** and **2o** and model compounds **3**−**5** are all prepared by the Cu^{I}-catalyzed Hagihara coupling of the appropriate acetylene with [Pt(trpy)Cl]Cl.[29] A CH_3CN solution of complex **1o** exhibits strong absorption in the UV region (λ_{max} = 285 nm; ϵ = 52 800 L•mol^{-1}•cm^{-1}) attributable to a combination of intraligand terpyridyl, thienyl, and acetylide $\pi \rightarrow \pi^*$ transitions (Figure 1). Weaker absorption in the visible region from 400 to 520 nm (λ_{max} = 465 nm; ϵ = 6700 L•mol^{-1}•cm^{-1}) includes overlapping transitions assigned to a mixture of metal-to-ligand charge-transfer (MLCT) and ligand-to-ligand charge-transfer (LLCT) states, with the latter predominating at lower energy.[30,31] The origin of these absorption bands as combinations of MLCT/LLCT states, as opposed to metal-perturbed localized transitions on the DTE component, is confirmed by time-dependent density functional theory (TDDFT) calculations (for details, see the Supporting Information), and by a comparison of the spectrum to that of model compound **4**, which only contains a thiophene ring attached to the acetylide. The absorption spectrum of **4** is virtually identical with that of **1o** (Figure 1a). Further support is provided by the fact that the absorption bands for **1o** demonstrate the negative solvatochromic effect (Figure S1 in the Supporting Information) previously observed for other platinum terpyridines that undergo similar charge-transfer events.[30]

Ring closing of **1o** can be triggered either directly by irradiation with UV light (λ = 302 nm), which is absorbed by the DTE chromophore, or indirectly by selective excitation of the MLCT/LLCT absorption bands (λ_{max} = 465 nm) of the metal complex component with visible light. The latter observation contrasts with the behavior of DTE **6**, which lacks the metal component and requires 365 nm light for ring closing to occur. Cyclization of **1o** to **1c** can be monitored by the appearance of a new low-energy band (λ_{max} = 600 nm) in the UV−vis absorption spectrum (Figure 2a,b) characteristic of the $\pi \rightarrow \pi^*$ transition[32] of the ring-closed DTE isomer. Indirect excitation results in an apparent slower rate of cyclization, although considering the absorbed power from the 302 nm light source is approximately double that from the visible light, this suggests that indirect excitation is potentially as efficient as direct excitation. It is clear that indirect excitation produces a lower amount of **1c** at the photostationary state (Figure 2c). Simultaneously, the MLCT/LLCT absorption band red shifts, overlapping with the low-energy band, largely because of the higher energy of the highest occupied molecular orbital (HOMO) of the ring-closed isomer. The increased HOMO energy is attributed to both a decrease in the Pt contribution to the HOMO in **1c** compared to **1o** (DFT calculated values of 0% and 9% for **1c** and **1o**, respectively) as well as the extended conjugation present in **1c**, resulting in orbital contributions that extend the full length of the acetylide−DTE unit instead of being confined only to the acetylide and proximate thiophene moiety as in **1o** (Figure S2 in the Supporting Information). The observed red shift of the charge-transfer band further supports its assignment as a mixture of MLCT and LLCT states and provides evidence for orbital interaction between LLCT and DTE-localized IL states.

The importance of the nature of the linker connecting the metal and DTE components is obvious when compound **1o** is compared to **2o**, in which a longer, non-π-conjugated linker connects the two chromophores. TDDFT calculations and a comparison of the UV−vis spectrum of **2o** to that of model compound **5** (Figure 1b) suggest that the longer linker eliminates the participation of the thienyl-based molecular orbitals of the DTE chromophore in the MLCT/LLCT transition. Although conventional ring closing of the DTE component in **2o** using UV light (302 nm) occurs, similar cyclization cannot be triggered with broad-band irradiation into the MLCT/LLCT band (λ > 415 nm). Because the lowest ^{3}MLCT/LLCT energy of **2o** is comparable to that of **1o**, there should be sufficient energy to populate the ^{3}IL if

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(32) As discussed later, DFT calculations show that the HOMO in **1c** is delocalized over the full length of the acetylide−DTE.

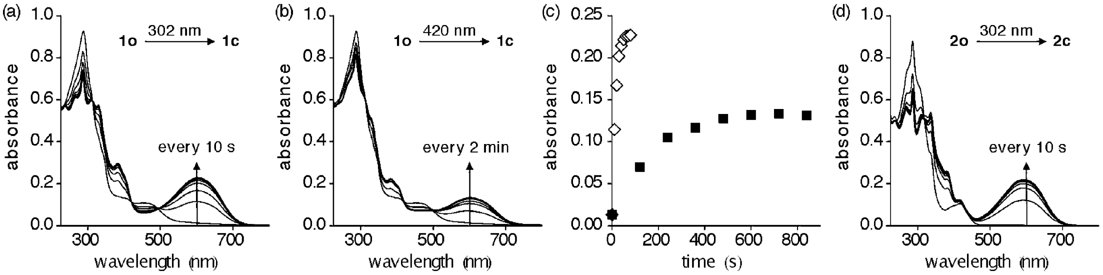
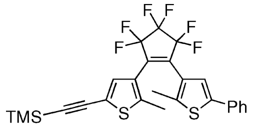


Figure 2. Changes in the absorption spectra when a CH_3CN solution (1.5×10^{-5} M) of (a) **1o** is irradiated with 302 nm light, (b) **1o** is irradiated with >420 nm light, (c) **1o** is irradiated with both types of light, 302 nm (◇) and >420 nm (■), and the absorbance at 600 nm is recorded against time, and (d) **2o** is irradiated with 302 nm light.

energy transfer is possible. The triplet energy of the DTE photoswitch state that leads to ring closing is estimated from DFT calculations to be about 1.9 eV for **1o** and 1.8 eV for **2o**, values that are in good agreement with an experimental value of 1.85 ± 0.16 eV for DTE in a related Ru^{II} complex.[18] DFT calculations of the MLCT/LLCT energies, together with observed absorption spectra of **1o** and **2o**, indicate MLCT/LLCT energies to be ≥ 2.0 eV, in agreement with experimental and DFT-calculated values for related compounds.[33]

Whereas efficient population of the photoactive ^{3}IL state resulting in DTE ring closing dominates the behavior of **1o**, emission from the ^{3}MLCT/LLCT state is an allowed pathway of decay for **2o**. As for **5**, emission is detected at room temperature in CH_2Cl_2 (Figure S3 in the Supporting Information). The wavelength and band shape of the emission are characteristic of platinum terpyridyl ^{3}MLCT-based phosphorescence.[29]



6o

A mixture of **6o** and model complex **3** was studied to examine the importance of a linkage between the two chromophores. Neither intermolecular photosensitized ring closing of **6o** nor quenching of the emission from **3** is observed when **3** is excited in the presence of **6o**. This is the case even at concentrations where, in a separate experiment, quenching of the emission from **3** by the ring-closed form of **6** occurs.[34] This highlights the necessity for the two components to be linked in a particular orientation for energy transfer to occur.

Direct linkage of the DTE to the Pt moiety in **1o** allows for significant orbital overlap between the two components, a key requirement for Dexter energy transfer. The lack of orbital overlap between the Pt and DTE moiety in **2o** compared to **1o** is supported by greatly reduced TDDFT-calculated oscillator strengths for transitions between them (e.g., $f < 0.001$ for **2o** vs $f > 0.1$ for **1o**). Collinear orientation of the orbitals and electronic delocalization through the bridge promote the significant electronic coupling required for energy transfer to occur between adjacent ^{3}MLCT/LLCT and ^{3}IL states. The present study will be useful in designing new linkers for systems intended to utilize metal complexes as sensitizers for triplet energy transfer as well as systems where photoswitchable molecules are used to reversibly modulate the fluorescence from organic chromophores, as has recently been applied to the construction of molecular devices such as logic gates and tranducers.[35−37]

Acknowledgment. This work was supported by an AGENO grant from the Natural Sciences and Engineering Research Council of Canada. N.R.B. was supported by the Canada Research Chairs Program. J.K.N.'s 2007−2008 sabbatical leave at the University of British Columbia was supported by Bowdoin College. M.N.R. was supported by a MEC Fellowship in Sustainability.

Supporting Information Available: Synthesis, experimental and TDDFT details, solvatochromism data, DFT contour plots, and emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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