

Successful Bifunctional Photoswitching and Electronic Communication of Two Platinum(II) Acetylide Bridged Dithienylethenes

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The addition of molecular switching elements into conjugated polymers would provide a means to modulate the optoelectronic properties these versatile materials offer to molecular electronic,¹ sensing,² and logic³ technologies. Photoresponsive molecular systems based on the dithienylethene (DTE) architecture are particularly suitable choices as “on/off” modulators of conjugation due to their undergoing reversible ring-closing reactions between two isomers, each having markedly different optical and electronic properties.⁴

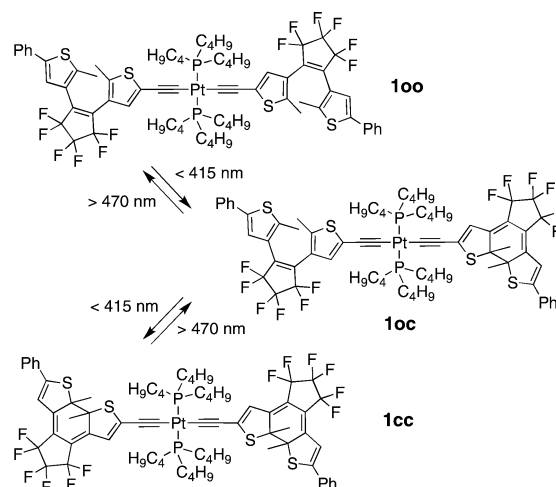
Despite efforts directed toward developing conjugated materials from DTEs,⁵ systems that incorporate multiple chromophores into a single conjugated backbone while retaining the photoswitching behavior of all components have been elusive. The major problem is rapid energy transfer (ET) from the singlet excited state of a ring-open isomer to an adjacent ring-closed DTE that takes precedence over photocyclization. The few examples that have multiple, adjacent DTEs undergoing photoinduced ring-closing tend to have more localized excited states and, therefore, properties similar to those of a single DTE unit.⁶ Therefore, little benefit has been gained from integrating multiple DTEs into a single polymer, and nontraditional approaches to photochromic switching must be exercised to eliminate this paradox.

Here, we demonstrate how metal-sensitized population of the triplet manifold can be used to ring-close more than one DTE via the organic chromophores' triplet state.⁷ This is one of the first systems to show how the interesting optoelectronic properties typical for conjugated oligomers can be reversibly modulated by photoswitching multiple DTEs. Compound **100** (Scheme 1) is used to illustrate this unprecedented approach and is based on the fact that triplet states in Pt-acetylide-based conjugated oligomers are localized on only one conjugated ligand rather than delocalized over the whole oligomer as in the singlet state.⁸ Pt-bis(acetylide) makes an excellent sensitizer in **100** since ligand-localized triplet states can be populated by excitation with visible light to trigger the cyclization of both DTE photoswitches without the ring-open DTE transferring its excited state energy to the adjacent ring-closed DTE in **10c**. Cyclization of the two ring-open isomers produces a fully π -conjugated pathway that extends through the Pt and over the full length of both DTEs.⁹

Compound **100** is prepared by coupling two acetylene-terminated DTE photoswitches to *trans*-Pt(PBu₃)₂Cl₂.¹⁰ The absorption spectrum of **100** in CH₂Cl₂ (Figure 1a) contains a band at 280 nm corresponding to the $\pi \rightarrow \pi^*$ thienyl transitions found in DTE **20** and another at 350 nm assigned to a long-axis $\pi \rightarrow \pi^*$ transition involving both the metal and alkynyl ligands.⁹

Whereas photocyclization of DTE **20** is accomplished by irradiation with light of wavelengths shorter than 340 nm, complex **100** also photocyclizes when it is irradiated at wavelengths as long as 415 nm.¹⁰

Scheme 1



In both cases, lower energy absorptions (590–630 nm) corresponding to the ring-closed isomers appear (Figure 1a). In the case of **100**, both the long-axis transition at ~ 350 nm and the ring-closed DTEs' $\pi \rightarrow \pi^*$ bands gradually red-shift by 16–20 nm (Figure 1b), resulting from the conversion of the ring-open isomer to a changing mixture of two ring-closed isomers (**10c** and **10cc**). The ring-closing of only one DTE unit (**100** \rightarrow **10c**) can be observed in the early stages of the irradiation, where isosbestic points at 307, 327, and 364 nm exist.¹⁰ These isosbestic points disappear with further irradiation once the more complex equilibrium of isomers is established (**100** \rightleftharpoons **10c** \rightleftharpoons **10cc**). Ring-opening of all compounds is achieved by irradiation with visible light (typically at wavelengths greater than 470 nm).

The sequential ring-closing (**100** \rightarrow **10c** \rightarrow **10cc**) is supported by ¹H and ³¹P NMR spectroscopy, which both show the formation of significant amounts of **10c** prior to **10cc**, ultimately producing a photostationary state (PSS) consisting of 80% **10cc** and 20% **10c**. A plot of the relative concentrations of each component (³¹P NMR) against time is consistent, qualitatively, with consecutive pseudo-first-order kinetics (Figure 1c).¹⁰ The NMR studies also show that the chemical shifts for the phosphorus and the thienyl proton closest to the metal move downfield as **100** is converted to **10c** and then to **10cc**¹⁰ signifying increased donation of electron density from the phosphine to Pt in the case of the ³¹P signals, and decreased electronic shielding from the alkyne due to a withdrawing of electron density by the adjacent ring-closed DTE for the ¹H signals. These effects will become important when explaining the electrochemical properties later in this report.

The 20 nm red shift that appears in the absorption spectra when **100** is converted to the PSS is attributed to increased delocalization of the singlet state over both DTE units in **10cc** relative to **10c**. This is in agreement with other reports that show singlet state delocalization

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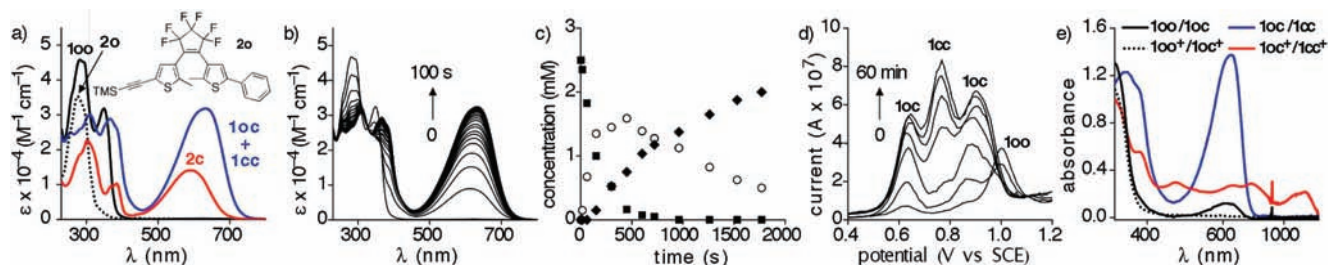


Figure 1. (a) UV-vis absorption spectra of CH_2Cl_2 solutions of **100** and **20**, and the photostationary states generated when solutions of **100** and **20** are irradiated with 365 and 254 nm light, respectively. (b) Changes in the UV-vis absorption spectra of a CH_2Cl_2 solution of **100** (2.3×10^{-5} M) when it is irradiated with 365 nm light. (c) Relative percentages of **100** (■), **10c** (○), and **1cc** (◆) as determined by ^{31}P NMR spectroscopy when a CD_2Cl_2 solution of **100** is irradiated with 365 nm light. (d) Changes in the differential pulse voltammograms of a CH_2Cl_2 solution of **100** as it is irradiated with 365 nm light. (e) vis-NIR absorption spectra of a CH_2Cl_2 solution of **100/10c** (black) and **10c/1cc** (blue) before oxidation and after 1 equiv of oxidant is added to generate **100⁺/10c⁺** (dash) and **10c⁺/1cc⁺** (red).

in Pt-bis(acetylide)s spanning the entire system, including several repeat units in oligomeric and polymeric analogues.¹¹ DFT-calculated orbital plots of **100**, **10c**, and **1cc** suggest that electron density in the HOMO is limited to the metal and its two proximate alkyne thiophene rings in **100** but extends over both DTE thiophenes when ring-closed. In **1cc**, the HOMO is delocalized over the entire molecule with significant orbital density on both DTEs and at the metal.¹⁰

Differential pulse voltammetry of **100** shows a single oxidation wave at 1.00 V (vs SCE) corresponding to oxidation of the ring-open DTE (Figure 1d), less positive than that of **20** due to Pt coordination. When **100** is converted to **10c**, two new waves (0.65, 0.90 V) assigned only to the ring-closed DTE appear, while the remaining ring-open isomer of **10c** is likely oxidized at potentials more positive than the solvent's limit.¹⁰ The fully ring-closed isomer (**1cc**) exhibits a single oxidation wave at 0.76 V. Because the ring-closed DTE isomer is a stronger π -acid than its ring-open counterpart, it accepts more electron density via backbonding from the Pt in **10c** explaining the cathodic shift of the first oxidation potential of **10c** relative to **1cc**. This is supported by DFT calculations, which estimate Pt-C and C≡C bond lengths that indicate greater backbonding to the ring-closed isomer, and by IR data, which show a red shift of the acetylide stretch upon ring-closing.¹⁰ The first reaction (**100** → **10c**) produces a large red shift (~ 24 cm^{-1}) due to π -backbonding and the π -acidity of the adjacent ring-closed DTE in **10c**. In **1cc**, both ring-closed DTEs compete for electron density through a conjugated system that includes the metal center resulting in a smaller red shift (~ 4 cm^{-1}) for the second reaction (**10c** → **1cc**).

Ground state electronic communication in **1cc** is illustrated by comparing the vis-near-IR spectra of each system after it is chemically oxidized with 1 equiv of [(4-Br-C₆H₄)₃N][SbCl₆].¹⁰ Oxidation of a solution containing only **100** and **10c** results in the disappearance of the $\pi \rightarrow \pi^*$ band of **10c** (Figure 1e). The oxidation of a solution of the PSS generates several new bands, notably one in the near-IR region ($\lambda_{\text{max}} = 1301$ nm) assigned as an intervalence charge-transfer (IVCT) transition, the result of electronic coupling between the DTEs in **1cc⁺** to give optically induced exchange of the electron-hole pair.¹² The lack of an analogous low energy band in the spectrum of **10c⁺** indicates that the cation is more localized in this species than in **1cc⁺**. No near-IR absorption bands are observed for any of the species when 2 equiv of oxidant are added.

The IVCT absorption band in **1cc⁺**, the shifts in redox potentials, and the bathochromic shift of the $\pi \rightarrow \pi^*$ transition of **1cc** relative to **10c** support electronic interaction between the two linked DTEs in the ground state and in a delocalized singlet excited state. The generation of **1cc** is significant because the excited state pathway leading to its formation circumvents ET processes that dominate singlet state behavior. Rapid intersystem crossing¹³ likely populates the triplet manifold of DTEs.⁷ Analogous to the localized exciton model¹³ proposed for other Pt-bis(acetylide) oligomers, an energy barrier at

the Pt linkage slows the rate of ET to the lowest energy excited state. Ring-closing must proceed at a faster rate than ET to the remaining closed DTE. Without the metal, the triplet state is inaccessible and delocalization in the singlet state prevents ring-closing of adjacent DTEs.^{5b}

Our system represents a unique approach to photoswitching conjugated oligomers by taking advantage of heavy-metal-induced population of the triplet manifold, from which both DTEs are independently photoactive. The result is a fully conjugated system with electronic communication in the ground state. Analogous DTE-Pt-bis(acetylide) conjugated polymers should enable photomodulation of conductivity.

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Supporting Information Available: Syntheses and characterizations of all chromophores. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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