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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 logic[3] 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]

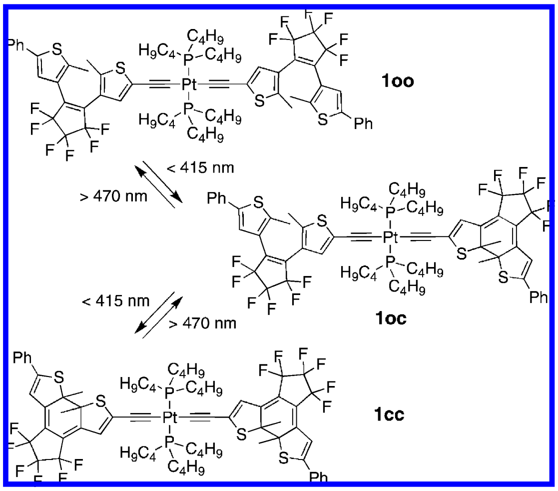
Despite efforts directed toward developing conjugated materials from DTEs,[5] systems that incorporate multiple chromophores into a single conjugated backbone while retaining the photoswitching behavior of all components have been elusive. The major problem is rapid energy transfer (ET) from the singlet 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 states.[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 **1oo** (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 **1oo** 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 **1oc**. 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 **1oo** is prepared by coupling two acetylene-terminated DTE photoswitches to *trans*-Pt(PBu_3)$_2$$Cl_2$.[10] The absorption spectrum of **1oo** in CH_2Cl_2 (Figure 1a) contains a band at 280 nm corresponding to the $\pi \rightarrow \pi^*$ thienyl transitions found in DTE **2o** 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 **2o** is accomplished by irradiation with light of wavelengths shorter than 340 nm, complex **1oo** also photocyclizes when it is irradiated at wavelengths as long as 415 nm.[10] In both cases, lower energy absorptions (590−630 nm) corresponding to the ring-closed isomers appear (Figure 1a). In the case of **1oo**, 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 (**1oc** and **1cc**). The ring-closing of only one DTE unit (**1oo** → **1oc**) 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 (**1oo** ⇆ **1oc** ⇆ **1cc**). Ring-opening of all compounds is achieved by irradiation with visible light (typically at wavelengths greater than 470 nm).

Scheme 1



The sequential ring-closing (**1oo** → **1oc** → **1cc**) is supported by ^1H and ^{31}P NMR spectroscopy, which both show the formation of significant amounts of **1oc** prior to **1cc**, ultimately producing a photostationary state (PSS) consisting of 80% **1cc** and 20% **1oc**. A plot of the relative concentrations of each component (^{31}P 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 **1oo** is converted to **1oc** and then to **1cc**[10] signifying increased donation of electron density from the phosphine to Pt in the case of the ^{31}P 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 **1oo** is converted to the PSS is attributed to increased delocalization of the singlet state over both DTE units in **1cc** relative to **1oc**. This is in agreement with other reports that show singlet state delocalization

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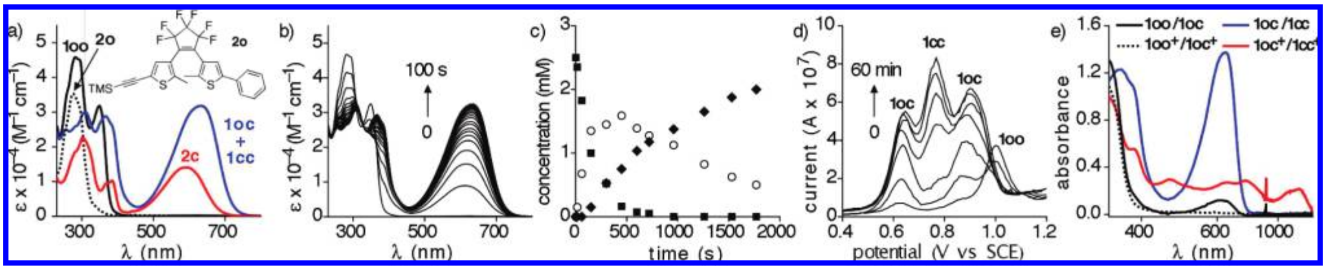

Figure 1. (a) UV−vis absorption spectra of CH_2Cl_2 solutions of **1oo** and **2o**, and the photostationary states generated when solutions of **1oo** and **2o** are irradiated with 365 and 254 nm light, respectively. (b) Changes in the UV−vis absorption spectra of a CH_2Cl_2 solution of **1oo** (2.3×10^{-5} M) when it is irradiated with 365 nm light. (c) Relative percentages of **1oo** (■), **1oc** (○), and **1cc** (◆) as determined by ^{31}P NMR spectroscopy when a CD_2Cl_2 solution of **1oo** is irradiated with 365 nm light. (d) Changes in the differential pulse voltammograms of a CH_2Cl_2 solution of **1oo** as it is irradiated with 365 nm light. (e) vis−NIR absorption spectra of a CH_2Cl_2 solution of **1oo**/**1oc** (black) and **1oc**/**1cc** (blue) before oxidation and after 1 equiv of oxidant is added to generate **1oo**$^{+}$/**1oc**$^{+}$ (dash) and **1oc**$^{+}$/**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 **1oo**, **1oc**, and **1cc** suggest that electron density in the HOMO is limited to the metal and its two proximate alkynyl thiophene rings in **1oo** 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 **1oo** 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 **2o** due to Pt coordination. When **1oo** is converted to **1oc**, two new waves (0.65, 0.90 V) assigned only to the ring-closed DTE appear, while the remaining ring-open isomer of **1oc** 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 **1oc** explaining the cathodic shift of the first oxidation potential of **1oc** 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 (**1oo** → **1oc**) produces a large red shift (~24 cm^{-1}) due to π-backbonding and the π-acidity of the adjacent ring-closed DTE in **1oc**. 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 (**1oc**→**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 $[(4\text{-Br-}C_6H_5)_3N][SbCl_6]$.[10] Oxidation of a solution containing only **1oo** and **1oc** results in the disappearance of the $\pi \rightarrow \pi^*$ band of **1oc** (Figure 1e). The oxidation of a solution of the PSS generates several new bands, notably one in the near-IR region ($\lambda_{max} = 1301$ 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 **1oc**$^{+}$ 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 **1oc** 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 crossing[13] likely populates the triplet manifold of DTEs.[7] Analogous to the localized exciton model[13] 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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