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Photoswitching of Copper(I) Chromophores with Dithienylethenebased Ligands

Zhen Xu,^[a] Yang Cao,^[a] Brian O. Patrick^[a] and Michael O. Wolf ^[a]*

Abstract: Metal-containing dithienylethenes offers new opportunities for variations in photochromic behavior. We report a series of copper(I) complexes containing dithienylethene-based bidentate phosphine ligands displaying varying photochromic properties. A copper dimer is used as a common precursor, allowing diverse photochromic functionality to be achieved. Calculations show that ring closing of the peripheral dithienyl moiety leads to a slight expansion of the five membered metallacycle. The photochromic properties and photoreaction quantum yields of these complexes are tunable by variation of the ancillary ligands. Photoswitchable catalysis of a hydroboration reaction with one of the copper complexes is demonstrated.

Photochromic diarylethene compounds, first introduced by Irie and co-workers, have been extensively studied over the last few decades due to their excellent thermal stability, fatigue resistance, and distinguishable absorption spectra in open and closed forms.^[1-4] Many potential applications in optoelectronics such as optical recording and data storage, switchable catalysis as well as chemical and biological sensing and imaging are envisioned.^[4-11] In several application areas, the molecular design of photoswitchable diarylethenes has to meet divergent criteria for the quantum yields (QYs) of the photocyclization and photocycloreversion reactions. For example, for super-resolution fluorescence microscopy, the QY of the photocycloreversion reaction must be much lower than that of the photocyclization reaction to ensure sufficient photon collection is possible to construct an image.^[5,6] On the other hand, photochromic compounds for optical data storage should have comparable photocyclization quantum vields for both and photocycloreversion to enable fast read and write times. Systematic tuning of photoreaction quantum yields remains a challenge in this field.

The most widely studied diarylethene building blocks are dithienylperfluorocyclopentenes and dithienylcyclopentenes. In these compounds, the thienyl groups are attached to five or sixmembered rings such as the cyclopentene moiety to prevent unwanted cis-trans isomerization. Most modifications of this basic motif have involved changes to the thienyl units, but now significant efforts have been extended to replace the fivemembered ring systems with various heterocycles.^[10-17] Yam and co-workers in 2004 first reported 1,10-phenanthroline functionalized dithienylethene as a ligand for metal coordinate metals including Ru, Re, Pt, Zn, Au, Pd, Fe and Eu^[9,18-20] to dithienylethene based ligands. In these systems, the

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metals are relatively remote from the dithienylethene group, and therefore only moderately influenced by switching. Thus far, metal centers have not been directly incorporated into the fivemembered ring system. This approach has the advantage that not only can the electronic properties be controlled by light, but light-induced single-to-double bond transformation in the dithienylethene moieties can lead to bond length and angle changes in the metallacycle, and as a result have significant impact on the electronic properties of the metal center (Figure 1).



Figure 1. Examples of metal-containing dithienylethenes^[19] and illustrations of open and closed structures of a prototypical metallacyclic dithienylethene.

Herein, we report the synthesis, characterization and photochromic properties of dithienylethene-containing copper complexes **1-5** (Figure 2), in which four different ancillary ligands are used to attenuate the photophysical properties. The participation of the characteristic metal-to-ligand charge transfer (MLCT) state allows the quantum yields of the photoreactions to be systematically tuned. We chose copper(I) complexes for initial exploration of this approach, due to copper's high earth abundance and the photochemical and photophysical properties of copper(I) complexes which can be applied in organic light-emitting diodes, photoredox catalysis and as CO₂-reduction photosensitizers.^[21-23] Photochromic copper(I) complexes have not been previously reported.

Our approach involves preparation of a key common copper(I) precursor that can be reacted with a range of ancillary ligands, allowing access to a library of copper dithienylethene complexes. Entry to the synthesis of these complexes is provided via the zirconium precursor (**ZrPPh₂-DTE**), prepared from 1,2-bis(2,5-dimethyl-thiophen-3-yl)ethyne (**BDTE**) in a one-pot reaction in 70% yield.^[24] Transmetallation of **ZrPPh₂-DTE** followed by addition of chlorodiphenylphosphine yields the key common copper(I) dimer **6**. Reaction of **6** with various ligands allows the formation of the series of monometallic copper(I)

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complexes **1-4**. Complex **5** was synthesized by adding excess bis[(2-diphenylphosphino)phenyl] ether (**DPEPhos**) to a THF solution of **6** followed by column chromatography. This versatile synthetic pathway gave the desired products in relatively high yields and may also be adapted to prepare other novel dithienyl-containing metal complexes.



Figure 2. Synthetic route to dithienylethene-containing copper(I) complexes 1-5. (a). 2.4 eq. *n*-BuLi, -78°C, THF, 1h; (b). 3 eq. DMAP, RT, 1h; (c). BDTE (1,2-bis(2,5-dimethyl-thiophen-3-yl) ethyne), RT, 1h; (d). 1 eq. PPh₂Cl, RT, 1h; (e). 2 eq. CuCl, 50°C, THF, 1h; (f). 1 eq. PPh₂Cl, 1h; (g). 0.9 eq. DPEphos, RT, THF, 1h; (h). Triphenylphosphine, RT, THF, 1h; (i). 1 eq. 8-(Diphenylphosphino)quinoline, RT, THF, 1h; (j). 1 eq. 1,10- Phenanthroline, RT, THF, 1h; (k). excess DPEphos, RT, THF, 1h; (i). NaBF₄ (aq).

Solid-state structures of all the complexes were obtained, allowing elucidation of the structural differences resulting from the presence of different ancillary ligands. The structures of four of the complexes are shown in Figure 3. In complex 1, the copper center adopts a distorted tetrahedral geometry with a P(3)-Cu-P(4) angle of 103.08(2)° and P(1)-Cu-P(2) angle of 86.93(2)°, illustrating the large bite angle difference between the two phosphine ligands. The Cu-P(3) distance is 2.340(6) Å while the Cu-P(4) distance is 2.351(6) Å, indicating that the steric bulk of the bidentate phosphine ligand distorts the geometry of this complex. The C(13)-C(14) distance is 1.353(3) Å. The two thienyl units are arranged in an antiparallel configuration and the distance between the two reactive carbons is 4.009 Å, indicating that 1 might show photoreactivity in the crystalline phase.^[25] Irradiation of these crystals with a 365 nm hand lamp leads to rapid colour change from yellow to red.

The synthesis of this series of complexes with different ancillary ligands allows us to establish structure-function relationships in copper dithienylethene complexes by combining NMR studies with information obtained from solid state structures. The copper(I) complexes **1-6** were all characterized by ¹H NMR and ³¹P{¹H} NMR spectroscopy and high-resolution mass spectrometry. At room temperature, the ¹H NMR spectra of **2** and **3** are broad, whereas at lower temperature the spectra of both complexes show two well-resolved sets of signals assigned to the structure with the thienyl groups in an antiparallel conformation, an assignment confirmed by NOESY experiments (Figure S22 and S25). At low temperature, the four methyl groups and two thiophene protons are all inequivalent due to the assymetrical ancillary ligand. At room temperature, restricted rotation of the thiophene groups leads to broadening in the spectra. The ¹H NMR spectrum of complex **5** at room temperature contains two sets of signals in a ratio of 3:2, indicating that one of the possible conformers is more stable than the other in this case.



Figure 3. Perspective views of (a) ZrPPh₂-DTE, (b) complex 6, (c) 1 and (d) 4 with partial atomic numbering. Hydrogen atoms have been omitted for clarity.

Irradiation of complexes 1-3 and 5 in solution causes colour changes. These complexes in the open form were dissolved in dichloromethane (DCM) to give either colourless or pale yellow solutions. The solution absorption spectra contain an intense peak at 250 nm with shoulders at ~350 nm (Figure 4(a), Figure S1-3), assigned to π - π * transitions of the thienyl groups, MLCT and ligand-to-ligand charge transfer (LLCT) transitions. Upon UV irradiation at 365 nm using a UV hand lamp, solutions of complexes 1-3 and 5 change color to pale purple or red, indicative of photocyclization. Photophysical and photochromic data are summarized in Table 1. Irradiation of complex 1 to form 1c results in two new absorption peaks with maxima at 360 nm and 535 nm. The low energy peak indicates the formation of a more extended m-conjugated system. The peak at 360 nm is assigned partially to a MLCT transition by TD-DFT calculations, supporting the conclusion that there is perturbation of the electron density at the metal center. On the other hand, complex 4 shows entirely different behaviour. A low energy copper-to-1,10-phenanthroline MLCT transition at 438 nm is observed for this complex (Figure 4(b)). Energy transfer from higher lying π- π^* transitions and the copper-to-phosphine MLCT state to the low-lying MLCT state prevents photoreaction. This demonstrates that ancillary ligand selection enables tunability of the photophysical and photochromic properties of these copper complexes. Even though copper complexes are notorious for COMMUNICATION

exhibiting ligand exchange in solution,^[26] complex **1** shows good reversibility of the photoreaction in DCM solution. As shown in Figure 4(a), even after eight photochromic cycles, complex **1** shows a loss of activity of < 10%.



Figure 4. (a) UV-vis spectral changes for 1 upon UV irradiation. Inset: UV-vis absorbance changes at 527 nm of 1 in DCM solution upon alternate excitation with 313 nm and >500 nm light over eight cycles. (b) UV-vis spectra of 1 and 4.

The photocyclization quantum yields (QYs) show some interesting trends. For **1**, the photocyclization QY is 45%, while the photocyclization QY of **3** is only 3%. Photocycloreversion QYs are all below 10%, comparable to those observed in other dithienylethene compounds. By incorporating ligands ranging from an electron-donating bidentate phosphine ligand to an electron-withdrawing phenanthroline ligand, it is possible to establish a relationship between the nature of the ancillary ligands and the photocyclization quantum yield of a copper dithienylethene complex can be predicted by considering the frontier orbital energies of the chosen ancillary ligand, making systematic tuning of the quantum yield of the photocyclization reaction possible.



Table 1. Photophysical and photochromic data for 1-3 and 5.

	Absorption maximum of closed form λ_{abs}/nm $(\epsilon/M^{-1}cm^{-1})^{[a]}$	Conversion at photostationary state ^(a,b)	Photochemical Cyclization ^[b,d]	quantum yields ^[a,c] Cycloreversion ^[e,f]
1	527 (9380)	0.51	0.45	0.05
2	520 (4190)	0.33	0.17	0.05
3	535 (11200)	0.16	0.03	0.05
5	535 (8820)	0.44	0.31	0.09

^a Data obtained in dichloromethane solution at 298 K. ^b Excitation wavelength = 313 nm. ^c ±10%. ^d Data obtained using ferrioxalate actinometry. ^e Excitation wavelength = 530 nm. ^f Data obtained using Aberchrome actinometry.



Figure 5. Frontier molecular orbitals of 1 and 3 in the open (1o and 3o) and closed (1c and 3c) forms, and of 4.

To explore the structural and electronic differences between the open and closed forms, density functional theory (DFT) calculations were utilized (Figure 5). The optimized geometry of complex 1 in DCM shows a significant change in the bond length between C(13) and C(14) from 1.36 Å in the open form to 1.49 Å in the closed form, consistent with the conclusion that photoirradiation can lead to ring expansion in these metallacycles. In the open form of 10, the HOMO is delocalized over the copper d orbitals and a π orbital of the dithienvlethene phosphine ligand while the metal center does not contribute significantly to the LUMO. In the closed form (1c), the HOMO corresponds to a π orbital of the dithienylethene ring system while the LUMO corresponds mainly to a π^* orbital of the ring system. In contrast, both complexes 3 and 4 show a LUMO localized on the quinoline and 1,10-phenanthroline ligands, respectively, consistent with the presence of MLCT transitions from copper to the heterocycles. Photocyclization of 3 can be attributed to excitations from the HOMO to the LUMO+1. Strong MLCT character limits the photoreactivity of 3 and prevents cyclization of 4.

Interest in the development of artificial switchable catalysts is burgeoning since these provide a noninvasive, reversible tool to control reaction rates. Dithienylethene derivatives are good

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candidates for switchable catalysis due to the significantly different electronic structures between open and closed forms and good thermal stability. However, very few examples of switchable catalysts containing this functionality have been developed.^[7-11] We wanted to explore applications of these complexes as photoswitchable catalysts for hydroboration since it has been shown that copper(I) complexes can catalyze this reaction with high regioselectivity and yield under mild conditions.^[27] We used 6 as a precatalyst and generated a reactive copper hydride species in situ by treating it with potassium tert-butoxide and pinacolborane in toluene. Two parallel reactions were conducted, one in the dark while the second was exposed to UV irradiation with a 365 nm UV hand lamp for 20 min. Upon irradiation, the initially orange solution became red. After adding 4-fluorostyrene the reaction was stirred at room temperature in the dark, and the resulting product identified and quantified by gas chromatography-mass spectrometry (GC-MS) as a function of reaction time. The reaction without UV irradiation was faster and had a better overall yield (62%), while the irradiated reaction achieved only a 44% vield (Figure 6). The extended conjugation in the DTE backbone in the closed form decreases electron density at the metal center, thereby reducing the rate of the hydroboration reaction.



Figure 6. Plot of vield versus time for the hydroboration of 4-fluorostyrene with pinacolborane.

In conclusion, this is the first report of direct attachment of a metal center to a photoactive dithienyl backbone, achieved with a key common precursor and easily installed ancillary ligands. This gives access to a series of photochromic copper complexes in which alteration of the energies of the ancillary ligands allows establishment of structure-function relationships and systematic tuning of the photocyclization quantum yield to be established. It also opens the door to further design and synthesis of other novel photochromic metal complexes, which can be achieved by transmetallation with other common metal-based precursors. We have also shown that photochromic copper complexes can be used as photoswitchable catalysts to control the reaction rate of a hydroboration reaction.



Acknowledgements

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Copper(I) centers directly attached to dithienylethene units through phosphine ligands leads to variations in structure and electronic properties, allowing photoreaction quantum yields to be tuned by varying the ancillary ligands. Photoswitchable control of a hydroboration reaction was demonstrated using a photochromic copper complex as catalyst.



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