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Incorporating Cobalt Carbonyl Moieties onto Ethynylthiophene-Based Dithienylcyclopentene Switches. 1. Photochemistry

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S Supporting Information

ABSTRACT: The synthesis and characterization of a series of dithienyl perhydro- and perfluorocyclopentene photochromic molecular switches appended with cobalt carbonyl binding 3-ethynylthiophene and phenyl-3-ethynylthiophene substituents are reported. Their photochromic properties, fatigue resistance, and thermal stability were examined to establish the effect of substituents on their performance as molecular photoswitches. The photochemical properties of the dithienylethene core were retained to the greatest extent by the inclusion of phenyl units and a hexafluorocyclopentene ring. The alkyne units of the switches were used to coordinate cobalt carbonyl moieties: i.e., $\text{Co}_2(\text{CO})_6$ and $\text{Co}_2(\text{CO})_4(\text{dppm})$. The cobalt carbonyl moieties were found to reduce the efficiency of cyclization and cycloreversion of the dithienylethene unit. Density functional theory was used to identify the excited states responsible for cyclization.

■ INTRODUCTION

Photochromic switches are of interest because of their ability to convert an optical input into a wide range of output signals.¹ Dithienylcyclopentene-based photochromic switches are an especially important class of thermally stable switches. They undergo large changes in both their electronic and structural properties in the transformation from the acyclic (open) to cyclic (closed) isomers (Scheme 1).^{2,3} UV irradiation of the

Scheme 1. Cyclization and Cycloreversion of Dithienylcyclopentene Switches

nonplanar open isomer results in cyclization of the 1,3,5-hexatriene moiety to the closed cyclohexadiene structure, with pseudo- C_2 symmetry. The photochromic behavior results from the extension of the π conjugation (Scheme 1) in the closed isomer.^{1,3–5} The photoreaction takes place in a conrotatory manner^{3,6} and results in significant changes in their UV/vis absorption, luminescence, Raman, and FT-IR spectra and their electrochemical properties.^{1,7} Irradiation of the closed isomer with visible light ($\lambda_{\text{exc}} > 420$ nm) results in cycloreversion.^{2,3}

The differences in properties between open and closed isomers provides for a wide range of applications in nondestructive optical data recording and storage,^{1,2,4,8–10} molecular wires,^{8,9} molecular switches,^{4,8–10} filters,^{1,2} and polarizers.^{1,2} The photochromic behavior of these dithienylcyclopentene-based switches has been shown to be highly dependent on the substituents attached to the thiophene units and also the nature of the cyclopentene ring (e.g., hexafluoro- and perhydrocyclopentene units, etc.). This tunability allows for the properties of these switches to be modified systematically.^{8,9,11–13} Combining transition-metal-based units with dithienylethenes can change their excited-state reactivity and spectroscopic properties.^{14–23} Metal complexes may also act as photosensitizers for the photochromic process: i.e., inducing the switching process through energy transfer from, for example, the triplet metal to ligand charge transfer (³MLCT) excited states. This can shift the wavelength at which the cyclization can be triggered further into the visible region.^{14,15} The introduction of metal adducts can also improve their absorption characteristics, photo and thermal stability, and quantum efficiencies.^{14–16,22–24}

The dithienylethene structure can exist as either a parallel or an antiparallel conformation in the open form. Only the antiparallel conformer can undergo cyclization.^{2–4,7,25} These two conformers interconvert rapidly; therefore, typically the

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Figure 1. The various complexes investigated in this study. Displayed in the yellow box is a depiction of how the two cobalt atoms bind to the alkyne unit in a bridging fashion.

maximum quantum yield for cyclization is ca. 0.5.² However, the antiparallel form is favored by the incorporation of bulky metal complexes onto the dithienylethene structure, due to steric repulsion between the substituents. Hence, the quantum yield for cyclization is expected to be greater for such complexes.^{14–16,22,23} Introducing metal moieties onto these switches can also have advantages in the development of data storage devices, with nondestructive readout properties.^{2,3,26} Stored information can be lost during light-driven readout processes, as the read photons can themselves alter the state of the photochromic switch. Nondestructive readout processes such as changes in redox properties²⁷ or infrared absorption^{2,10} are possible.

Here we report the synthesis of four dithienyl perhydro- and perfluorocyclopentene switches, appended with 3-ethynylthiophene and phenyl-3-ethynylthiophene substituents. The effects of increasing the π conjugation of the system and the effects of the central cyclopentene atoms (i.e., H vs F) on the cyclization/cycloreversion processes were investigated. The thermal stability and fatigue resistance of these switches were evaluated.^{26,28}

A number of metal carbonyl and phosphine based complexes have previously been introduced onto molecular switching units in order to tune their properties.^{14,16,20,22,29} Cobalt carbonyl complexes are photochemically active transition-metal complexes^{30–32} but to date have not been integrated into such switching systems. Incorporating such metal groups onto dithienylethene units should result in changes to the photochemical properties of the switches. Consequently, Co₂(CO)₆ moieties were bound onto the alkynyl units, on both sides of the dithienyl cyclopentene switches. Their effect on the characteristics of these switches provides an additional means

of tuning their properties, hence widening the range of potential applications of dithienylethene switches.^{15,17–19,23} Importantly, cobalt carbonyl complexes have characteristic absorption bands in their IR spectra, which allows for the photochemical processes to be studied through changes in ν_{CO} bands.

Electron-donating bis(diphenylphosphino)methane (dppm) ligands were introduced onto the Co₂(CO)₆-modified switches,^{30,33} generating the corresponding dicobalt tetracarbonyl units (Co₂(CO)₄(dppm)). This was done to increase the photostability of these complexes. The influence of the Co₂(CO)₄(dppm) complexes on the photocyclization reactions of the dithienylcyclopentene switches was also investigated.

RESULTS AND DISCUSSION

Synthesis. Details of the synthesis of all compounds described are provided in the Supporting Information. The synthesis of dichloro and diiodo dithienylcyclopentene precursors has been described previously.^{8,34,35} Compounds **1Ho** and **1Fo** were prepared using a Sonogashira coupling of ethynylthiophene to a diiodo dithienylcyclopentene switch (Figure 1).³⁶ In the case of **2Ho**, 1,4-dibromobenzene was coupled to a dichloro switch via a Suzuki coupling, with subsequent Sonogashira coupling of ethynylthiophene to the bromophenyl group. In the case of **2Fo**, a modified synthetic route was used to improve yields. 1-(3-Thienylethynyl)-4-bromobenzene was appended to both sides of the dichlorodithienyl hexafluorocyclopentene switch using a Suzuki coupling. The corresponding Co₂(CO)₆ complexes (**3Ho**, **3Fo**, **4Ho**, **4Fo**) were synthesized through reaction with Co₂(CO)₈. The 1,2-bis(diphenylphosphino)methane (dppm) ligand was incorporated via a carbonyl ligand substitution, to

form the corresponding $\text{Co}_2(\text{CO})_4(\text{dppm})$ complexes (**5Ho**, **5Fo**, **6Ho**). All compounds were characterized by ^1H , ^{13}C , ^{19}F , and ^{31}P (where applicable) NMR spectroscopy and elemental analysis. The cobalt carbonyl complexes were also characterized by IR spectroscopy. The closed-form $\text{Co}_2(\text{CO})_6$ complexes of **3F** and **4H** were synthesized by reaction of $\text{Co}_2(\text{CO})_8$ with **1Fc** and **2Hc** (prepared by irradiation of either **1Fo** or **2Ho** at 313 nm in THF, respectively), to produce **3Fc** and **4Hc** (where “s” indicates that it is synthesized from **2Hc** and **1Fc**, respectively), in order to compare their photochemistry with that of the corresponding open isomers **3Fo** and **4Ho**.

UV/Vis Absorption Spectroscopy. The UV/vis absorption spectra of **1Ho**, **1Fo**, **2Ho**, and **2Fo** show the expected $\pi-\pi^*$ transitions in the near-UV region with negligible absorbance in the visible region (Table 1). Irradiation at λ_{exc}

Table 1. UV/Vis Absorption Spectroscopic Data for **1H/F** and **2H/F**^a

	λ_{abs} , nm (ϵ , $10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	
	open isomer	closed isomer (PSS _{313 nm})
1H	287 (29.6), 310 (28.3)	266 (sh), 317 (28), 360 (sh), 543 (15) ^c
1F	259 (sh), 306 (43.9), 322 (sh)	262, 351 (27), 376 (sh), 397 (sh), 609 (18)
2H	305 (sh), 343 (69.0)	267 (sh), 329 (51), 382 (sh), 562 (29)
2F	262 (sh), 277 (sh), 333 (76.2)	276 (27), 362 (41), 395 (sh), 614 (23)

^aIn THF. sh denotes a shoulder. ^bMolar absorptivities were determined at the photostationary state. ^cIt should be noted that **1Ho** does not undergo complete conversion to the closed form and the data have been calculated by taking the PSS reached into consideration.

313 nm resulted in cyclization, as indicated by the appearance of an absorption band in the visible region. For instance, cyclization of the perhydro switches **1Ho** and **2Ho** resulted in a color change from colorless to purple, with the λ_{max} values of the closed species occurring at 543 and 562 nm, respectively. Isosbestic points were maintained throughout the reactions (Figure 2). In the case of the perfluoro derivatives **1Fo** and **2Fo**, a color change from colorless to blue was observed, and the λ_{max} values of the closed isomer products were bathochromically shifted by 66 and 52 nm, respectively, in comparison to the perhydro analogues (**1Hc** and **2Hc**) (Figure 2). This observation can be explained by the electron-withdrawing effect of the fluorine atoms, which reduces the HOMO–LUMO gap.¹³

^1H NMR spectroscopy is especially useful in studying dithienylethene switches.^{7,8} Cyclization results in an upfield shift in the resonance of the hydrogen at the 4-position of the thiophene ring (see Table S1 and Figure S6a–c, Supporting Information). The PSS (photostationary state) at 313 nm can be determined by peak area analysis and was found to be >95% for all switches, except for **1Ho** (<85%). Irradiation of **1Fc**, **2Fc**, and **2Hc** with visible light ($\lambda_{\text{exc}} > 550 \text{ nm}$) resulted in cycloreversion, with a full recovery of the UV/vis absorption spectrum of the open isomer. However, for **1Hc** cycloreversion was incomplete, with a residual visible absorption, even after prolonged irradiation ($\lambda_{\text{exc}} > 550 \text{ nm}$).

The fatigue resistance toward cyclization/cycloreversion of **1H/F** and **2H/F** was measured by UV/vis absorption spectroscopy over five closing/opening cycles, in argon-purged THF. The absorbances at 614 nm for **2F** and at 543 nm for **1H**

Figure 2. UV/vis absorption spectra of (left) **2Ho** upon irradiation at 313 nm over 30 s and (right) **1Hc**, **1Fc**, **2Hc**, and **2Fc** at the PSS_{313 nm} (0.014 mM in THF).

are shown in Figure 3. Overall, the photostability of these switches was found to increase in the order **1H** < **1F** < **2H** < **2F**, with 10%, 4%, 1.5%, and <1% degradation, respectively, after five cycles. These data demonstrate that the presence of the fluorine atoms and/or the presence of the phenyl units improve photochemical fatigue resistance.¹¹ The degradation for **1H**, in particular, is consistent with previous reports for related dithienylethene switches.^{26,37,38} The closed isomers were found to be stable toward thermal cycloreversion, to the open form, for at least 2 h at 80 °C (see Figure S7B, Supporting Information).

Irradiation of **1Ho** at 313 nm resulted in two new resonances at 6.34 and 6.53 ppm in the ^1H NMR spectrum, as shown in Figure 4. The former resonance can be assigned to the closed isomer (**1Hc**) and the latter resonance to a photostable byproduct (**1Hx**, Scheme 2), which has been observed in previous studies.^{26,37,38} The formation of **1Hx** explains the poor fatigue resistance for **1Ho**. Extended irradiation up to 220 min clearly shows a decrease in the signal at 6.34 ppm of **1Hc**, with concomitant growth of the **1Hx** signal at 6.53 ppm. This suggests that the byproduct (**1Hx**) is formed by photolysis of the closed isomer (**1Hc**) as proposed by Patel et al.³⁹

Photochemistry of $\text{Co}_2(\text{CO})_6$ -Modified Switches. Incorporating cobalt complexes onto both alkyne moieties of the open isomers of **1H/F** and **2H/F** resulted in a significant change to their electronic absorption spectra. For **3Ho** and **3Fo**, the absorption bands between 250 and 400 nm were broad and a significant increase in absorption was observed between 259 and 275 nm, assigned to ligand-field “d–d” transitions, with a shoulder present at approximately 327–348 nm, assigned to intraligand transitions.³³ Metal to ligand charge transfer (MLCT) bands were observed at 420–640 nm (Table

Figure 3. Absorbance at (A) 614 nm for **2F** and (B) 543 nm for **1H**, in THF, upon alternating irradiation at 313 and >550 nm.

Figure 4. ¹H NMR spectra of **1Ho**, in acetone-*d*₆: (A) **1Ho** prior to irradiation; (B) after irradiation at 313 nm for 30 min; (C) after irradiation at 313 nm for 220 min.

Scheme 2. Photostable Byproduct 1Hx Formed upon Extended Irradiation at 313 nm

S2, Supporting Information).³³ For the phenyl-spaced compounds **4Ho** and **4Fo**, the intraligand band was found to be more prominent, indicating that for these compounds the Co₂(CO)₆ units do not perturb the electronic transitions of the dithienylethene unit to any significant extent.

Irradiation of the Co₂(CO)₆-bearing compounds at 313 nm resulted in a color change from yellow-brown to purple in the case of **3Ho** and **4Ho** and to blue in the case of **3Fo** and **4Fo**. In each case, the absorption in the UV region was found to decrease in intensity, and a new absorption band in the visible

Table 2. UV/Vis λ_{max} Absorption Bands and the Time Taken to Reach the PSS (313 and 365 nm) of 1Hc/Fc and 2Hc/Fc and Their Corresponding $\text{Co}_2(\text{CO})_6$ (3Hc/Fc and 4Hc/Fc) and $\text{Co}_2(\text{CO})_4(\text{dppm})$ Complexes (5Hc/Fc and 6Hc)^a

compound	$\text{Co}_2(\text{CO})_6$ compound						$\text{Co}_2(\text{CO})_4(\text{dppm})$ compound			
	313 nm		313 nm		365 nm		313 nm		365 nm	
	λ_{max} (nm)	time (s)	λ_{max} (nm)	time (min)	λ_{max} (nm)	time (min)	λ_{max} (nm)	time (min)	λ_{max} (nm)	time (min)
1Hc	543	50	3Hc	559	8	<i>b</i>	<i>b</i>	5Hc	<i>b</i>	<i>b</i>
1Fc	609	20	3Fc	603	4	<i>b</i>	<i>b</i>	5Fc	<i>b</i>	<i>b</i>
			3Fc _s	661 ^c						
2Hc	562	30	4H	561	8	561	9	6Hc	563	25
			4Hc _s	584 ^c					563	35
2Fc	614	15	4Fc	619	2	619	2.5			

^aIn THF (0.014 mM). ^bCyclization did not occur. ^cThese closed isomers were synthesized directly.

Figure 5. UV/vis absorption spectra of 4Ho (A) and 4Fo (B) in THF (0.014 mM): (black line) before irradiation; (green line) at the photostationary state (PSS) following irradiation at λ_{exc} 313 nm; (blue lines) during irradiation at $\lambda_{\text{exc}} > 550$ nm; (red line) no further changes observed.

Figure 6. UV/vis absorption spectra, recorded in THF: (A) 1Fc (PSS_{313 nm}, green), the corresponding $\text{Co}_2(\text{CO})_6$ complex 3Fc (PSS_{313 nm}, red), and 3Fc_s, prepared by complexation of $\text{Co}_2(\text{CO})_6$ to 1Fc (black); (B) 2Hc (PSS_{313 nm}, green), 4Hc (PSS_{313 nm}, red line), and 4Hc_s, prepared by complexation of $\text{Co}_2(\text{CO})_6$ to 2Hc (black).

region appeared with maintenance of isosbestic points during irradiation. The λ_{max} values in the visible region and the times taken to reach the PSS are summarized in Table 2. These data indicate that cyclization of the dithienyl ethene unit took place for all of the $\text{Co}_2(\text{CO})_6$ complexes.

In comparison to 1Ho/Fo and 2Ho/Fo longer irradiation times were required for the absorbance bands in the visible region of the spectra recorded for the $\text{Co}_2(\text{CO})_6$ complexes (3Ho/Fo and 4Ho/Fo) to reach PSS_{313 nm} (minutes). Furthermore, the maximum absorbances reached in the visible region for the $\text{Co}_2(\text{CO})_6$ complexes were significantly lower than those recorded for the corresponding noncomplexed dithienylethenes at the PSS (Table 2 and Figure 6). These data indicate that the presence of the $\text{Co}_2(\text{CO})_6$ moieties results in a

significant decrease in the percent conversion from the open to the closed isomer, at the PSS, as well as a reduction in the quantum yields for cyclization. For 4Fo, the maximum visible absorbance reached is greater than for the other $\text{Co}_2(\text{CO})_6$ complexes described here and hence more of 4Fc is formed, which is consistent with quantum chemical calculations (vide infra). Furthermore, complexation of the $\text{Co}_2(\text{CO})_6$ moieties results in a shift in the λ_{max} values of the visible absorption bands (Table 2). Cycloreversion was observed upon irradiation at $\lambda_{\text{exc}} > 550$ nm. However, the absorbance bands in the UV region recovered partially (40%) in the case of 3Fo (Figure S9, Supporting Information), and only 8% recovery was observed in the case of 3Ho (Figure S8, Supporting Information), indicating some degradation had occurred. Similarly, in the case

of the phenyl-spaced compound **4Ho**, the original absorption bands at 274 and 341 nm failed to recover significantly, following visible irradiation, and a new band was observed at 311 nm (Figure 5A). On the other hand, the absorption bands in the UV region of **4F** recovered almost completely to their original state (Figure 5B) following visible irradiation.

Evidence for decomposition of complexes **3Ho**, **3Fo**, and **4Ho** comes from analysis of the UV–vis spectra, as the original absorption bands (assigned to the ligand field “d–d” transitions of the cobalt carbonyl moieties) in the UV region did not recover following the cyclization/cycloreversion process. In an attempt to assess the degradation pathway, complexation of $\text{Co}_2(\text{CO})_6$ to the alkyne units of **1Fc** and **2Hc** (which in turn were prepared by irradiation of **1Fo** and **2Ho**, respectively) was carried out to produce the closed isomers **3Fc_s** and **4Hc_s** (where “s” indicates “synthesized”). It should be noted that the amount of **3Fc_s** and **4Hc_s** prepared was only sufficient for characterization by ^1H NMR and IR spectroscopy (see the Supporting Information for details).

The UV/vis absorption spectra of **3Fc_s** and **4Hc_s** were found to be much broader, and the λ_{max} values were significantly shifted bathochromically, in comparison to those of **3Fc** and **4Hc** (Table 2 and Figure 6). The broadening of the absorption bands for **3Fc_s** and **4Hc_s** could possibly be related to the effect of the MLCT transition due to the presence of the $\text{Co}_2(\text{CO})_6$ moieties and the fact that this broadening is more pronounced for **3Fc_s** due to the fact that the $\text{Co}_2(\text{CO})_6$ units are closer to the switching unit, in comparison to **4Hc_s** (in which phenyl spacers separate the metal carbonyl units from the switch).

From Figure 6, it is clear that the absorptions in the visible region of the spectra for **3Fc** and **4Hc** were found to be more similar to the absorption spectra recorded for their corresponding free ligand switches, **1Fc** and **2Hc**, respectively, than to those for the synthesized closed $\text{Co}_2(\text{CO})_6$ complexes **3Fc_s** and **4Hc_s**, respectively. Furthermore, subsequent cycloreversion ($\lambda_{\text{exc}} > 550$ nm) of **3Fc** and **4Hc** indicated decomposition of the cobalt carbonyl moieties, due to a large decrease in the UV absorbance bands. Thus, overall, these data suggest that irradiation of **3Fo** and **4Ho** at 313 nm may result in loss of the $\text{Co}_2(\text{CO})_6$ units and formation of **1Fc** and **2Hc**, respectively. This hypothesis was further strengthened by the IR steady-state photolysis experiments (as described below), which showed that CO loss occurs during UV irradiation of these cobalt carbonyl switches. A similar conclusion can be reached following the irradiation of **3Ho**, as discussed above. In contrast, for **4Fo**, cyclization was found to be reversible. Thus, it would appear that the $\text{Co}_2(\text{CO})_6$ units are retained in this case. Such a result indicates that the perfluorocyclopentene unit, together with the presence of the phenyl bridging units between the photochromic switch and the $\text{Co}_2(\text{CO})_6$ moieties, improves the photostability of these compounds.

Irradiation at 365 nm was then chosen to induce cyclization in an attempt to reduce the decomposition of the cobalt carbonyl complexes. In the case of **3Ho** and **3Fo**, cyclization was not observed following irradiation at this wavelength. However, decomposition was evident because the absorbance bands in the UV region decreased. It should be noted that cyclization of **1Ho** does not proceed when irradiated at this wavelength either, although **1Fo** does undergo cyclization upon irradiation at 365 nm. Therefore, the presence of the $\text{Co}_2(\text{CO})_6$ units in **3Fo** appears to inhibit cyclization on irradiation at this wavelength. Cyclization was observed for **2Ho**, **2Fo**, **4Ho**, and

4Fo upon irradiation at 365 nm, with spectral changes that are similar to those obtained upon irradiation at 313 nm.

The photoreactivity of the $\text{Co}_2(\text{CO})_6$ -based switches was modified by reaction with 1,2-bis(diphenylphosphino)methane (dppm) to form the corresponding tetracarbonyl $\text{Co}_2(\text{CO})_4(\text{dppm})$ complexes **5Ho**, **5Fo**, and **6Ho**. The $\text{Co}_2(\text{CO})_4(\text{dppm})$ analogues were chosen, as the photochemical stability usually increases when a carbonyl ligand is substituted with a phosphine.⁴⁰ In the case of **5Ho** or **5Fo**, cyclization was not observed upon irradiation at 313 or 365 nm, and significant decomposition was observed. Cyclization upon irradiation with UV light was observed for **6Ho**, albeit accompanied by some decomposition of the cobalt carbonyl units.

IR Spectroscopy. IR steady-state photolysis experiments were carried out for the $\text{Co}_2(\text{CO})_6$ and $\text{Co}_2(\text{CO})_4(\text{dppm})$ complexes in order to monitor the effects of UV irradiation on the cobalt carbonyl units. Irradiation of **3Ho**, **4Ho**, **5Ho**, or **6Ho** (in THF), at 313 or 365 nm, resulted in a decrease of the ν_{CO} bands. Although THF is considered to be a good coordinating solvent, no new ν_{CO} bands were observed in the IR spectrum, indicating a complete loss of the cobalt carbonyl units. Irradiation at 313 or 365 nm, in the presence of a trapping agent (PPh_3), resulted in the formation of new complexes formed by the photosubstitution of one or two of the CO ligands with PPh_3 (Table S3, Supporting Information). The resulting photoproducts were assigned according to data reported in the literature,^{31,40–42} although some of the IR absorption bands are masked by other IR bands in that region.

In the case of **3Ho**, irradiation at 365 nm for 10 min resulted in bleaching of the parent bands (2089, 2054, and 2025 cm^{-1}), with the concomitant appearance of four new bands at 2061, 2010, 1960, and 1995 cm^{-1} (Figure S14B, Supporting Information). The metal carbonyl bands at 2061, 2010, and 1995 cm^{-1} are assigned to the pentacarbonyl species (Switch)- $[\text{Co}_2(\text{CO})_5\text{PPh}_3]_2$. The absorption band at 1960 cm^{-1} is tentatively assigned to a tetracarbonyl species, with the remaining bands masked by parent and pentacarbonyl bands. Additional bands at 1973, 1918, and 1885 cm^{-1} were observed when **3Ho** was irradiated at 313 nm for 10 min (Figure S14A, Supporting Information). On the basis of previous studies, these bands suggest the formation of a tricarbonyl and/or dicarbonyl species, following further photoinduced substitution of CO by PPh_3 .⁴² The efficiency of the formation of the photoproducts of **3Ho** was greater at 313 nm than at 365 nm. This observation is in agreement with quantum yields previously reported for CO loss in $\text{Co}_2(\text{CO})_6$ compounds.⁴³ Irradiation of the $\text{Co}_2(\text{CO})_4(\text{dppm})$ bearing **5Ho**, at 365 nm for 10 min (Figure S15B, Supporting Information) resulted in depletion of the parent bands, with new bands appearing at 1989, 1951, and 1915 cm^{-1} , which can tentatively be assigned to the formation of the tricarbonyl species (Switch)- $[\text{Co}_2(\text{CO})_3(\text{dppm})(\text{PPh}_3)]_2$. The same changes were obtained following irradiation at 313 nm (Figure S15A); however, the intensities of the new bands at 1989, 1951, and 1915 cm^{-1} were significantly increased relative to those observed at 365 nm, over the same time scale; thus, it appears that photolysis of the cobalt carbonyl moieties is more efficient at 313 nm. Similar changes were observed in the IR spectrum of $\text{Co}_2(\text{CO})_6$ and $\text{Co}_2(\text{CO})_4(\text{dppm})$ complexes (**4Ho** and **6Ho**, respectively), which incorporate a phenyl spacer, upon irradiation at 365 nm (see Figure S16, Supporting Information) and at 313 nm (Figure 7).

Figure 7. FTIR difference spectra of the $\text{Co}_2(\text{CO})_6$ complex **4Ho** (A) and the $\text{Co}_2(\text{CO})_4(\text{dppm})$ complex **6Ho** (B) in THF, following irradiation at 313 nm for 4 min, in the presence of PPh_3 . Negative bands indicate bleaching of the parent bands, and positive bands indicate formation of the photoproducts, following CO loss.

Figure 8. Changes in (A) the UV/vis absorption spectrum of **4Hc**, upon irradiation at >650 nm (0.014 mM in THF), with the absorbance spectrum of **4Ho** overlaid (dashed red line), and (B) the FTIR absorption spectrum of **4Hc**, in THF following irradiation at >650 nm, in the presence of PPh_3 . The parent bands (black line) began to decrease, with new bands forming at lower frequency (blue lines). After 360 min (red line), new bands indicative of the pentacarbonyl species (*) and tetracarbonyl species (#) were present.

Photoinduced Cycloreversion. Photoinduced cycloreversion of the $\text{Co}_2(\text{CO})_6$ complexes **3Fc** and **4Hc** was investigated in order to examine if the presence of the $\text{Co}_2(\text{CO})_6$ moieties has an effect on the cycloreversion process. This study was conducted to investigate the possibility that these systems would open as chemical sinks, thus creating a chemical-locking system, which has been described previously in the literature for an organometallic switching complex.²⁹

Irradiation of **3Fc** and **4Hc** (in THF) at $\lambda >650$ nm resulted in a decrease in absorbance in the visible region, indicating cycloreversion to the open isomer in each case. In the case of **3Fc**, significant changes in the absorbance at 263 nm were not observed (Figure S11, Supporting Information), which is in contrast to the overall decrease in absorbance at 263 nm for **3Fo**, following a cyclization and subsequent cycloreversion process (Figure S9, Supporting Information). This indicates that the $\text{Co}_2(\text{CO})_6$ complexes are significantly more stable on irradiation at longer wavelengths (i.e., >650 nm). However, the efficiency of the opening process for **3Fc** (70 min) and **4Hc** (240 min) was dramatically reduced in comparison to that of **1Fc** (1.5 min) and **2Hc** (6 min), respectively. The UV absorption of **4Hc**, following irradiation with $\lambda >650$ nm, was inconsistent with the open isomer **4Ho**, suggesting photo-decomposition (Figure 8A). The IR spectrum of **4Hc** was monitored upon irradiation at >650 nm in the presence of PPh_3 (Table S3, Supporting Information, and Figure 8B). The parent carbonyl bands at 2089, 2055, and 2025 cm^{-1} decreased in absorbance, and new bands of a pentacarbonyl species at 2111

and 1996 cm^{-1} and of a tetracarbonyl species at 1964 cm^{-1} were produced. Therefore, irradiation of **4Hc** at >650 nm results in cycloreversion to the open isomer and also CO loss from the cobalt carbonyl moieties.

Quantum Chemical Calculations. Quantum chemical calculations were used to explore the photophysics of cyclization⁴⁴ for **1Ho**, **3Ho**, and **4Fo**. **3Ho** was chosen because experiments indicated that extended irradiation at shorter wavelengths (i.e., at 313 nm for 8 min to reach the PSS) was required to achieve cyclization. In contrast, **4Fo** underwent cyclization relatively efficiently even with irradiation at longer wavelengths (365 nm for 2.5 min, to reach the PSS). Thus, these two compounds represent the extremes with respect to photoinduced cyclization for the Co-containing complexes in this study (Table 2). The nonmetalated compound **1Ho** was used to highlight the effects of binding two cobalt centers to the alkynyl functional groups. The internuclear distance between the two carbon atoms involved in the bond formation in the cyclization process (C2 and C2' on the thiophene rings) was reduced in steps of 0.1 Å from the distance in the optimized open structure to a distance less than that in the closed structure. The remaining structural parameters were optimized at each step along the cyclization reaction coordinate. The coordinates obtained at each step on this relaxed potential energy scan were then used in TDDFT calculations to estimate the energies of the lowest 20 singlet excited states.⁴⁵ The resulting plots describe the behavior of these excited states

during the closure. For clarity, only selected results of these calculations are presented in Figure 9.

Figure 9. Behavior of the ground state (GS, black) and selected singlet excited states (S , red) along the cyclization reaction coordinate of (a) compound **3Ho**, (b) compound **4Fo** (only the S_{17} state in **4Fo** exhibits an accelerating profile toward the closed structure (blue)), and (c) compound **1Ho** showing the accelerating profile to cyclization from the lowest energy singlet excited state (S_1).

The lowest energy singlet excited state (S_1) of **1Ho** presents an accelerating energy profile toward the closed compound (Figure 9c). This excited state is populated following absorption of a 313 nm photon. For **3Ho** (Figure 9a), none of the accessible excited states present an accelerating energy profile to the closed structure: i.e., all excited states exhibited a thermal barrier to cyclization. This explains the relative inefficiency of this process under photochemical conditions. In the case of **4Fo**, however, the calculations indicate that the 17th singlet excited state (S_{17}) presents an accelerating energy profile toward cyclization (Figure 9b). The calculated wavelength required to populate this excited state is approximately 360 nm, which explains why exhaustive irradiation into the lowest energy absorption bands (420–640 nm) of **4Fo** failed to induce ring closure.

The results from these TDDFT calculations correlate with the UV–vis absorption spectroscopic data, whereby the photochromic behavior of **4Fo** was found to be significantly more reversible than that found for **3Ho**. Optimized

coordinates for **1Ho**, **3Ho**, and **4Fo** are available in the Supporting Information.

CONCLUSIONS

Overall, it can be concluded that the perfluorocyclopentene ring and an extension of the π conjugation of the system improve the performance of such dithienylcyclopentene switches with respect to their cyclization/cycloreversion, fatigue resistance, and thermal stability properties. Incorporating cobalt carbonyl complexes onto the switching units was not found to be advantageous. Their presence reduced the efficiency and reversibility of the photocyclization of the dithienylcyclopentene switches and reduced the stability with regard to the use of such compounds for applications toward optoelectronic properties. In the case of **4Ho**, the changes in UV–vis absorption spectra following irradiation at 313 and 365 nm showed a decrease in the UV region and a new absorbance band in the visible region, the shape and λ_{max} of which were more similar to those of the free ligand, **2Hc**, than to those of **4Hc**, (the synthesized closed isomer of this compound). The IR steady-state photolysis experiments showed that CO loss occurs under these conditions. When **4H** was subsequently irradiated at $\lambda > 550$ nm, to form the initial open isomer, the UV absorbance bands failed to recover significantly, with an obvious change in the absorption at 274 nm (assigned to the “d–d” transitions of the cobalt carbonyl moieties). Thus, these data indicate that irradiation of **4Ho** results in cleavage of the cobalt carbonyl units, and the absorbance band in the visible region of the spectrum is actually a consequence of the cyclization of the free ligand **2H**. A similar conclusion can be made for **3Ho** and **3Fo** on the basis of the results presented here. Incorporating dpmm ligands onto the cobalt carbonyl units was not found to improve the cyclization processes or the stability of these complexes. However, the same conclusion cannot be reached for **4Fo**, which showed improved reversibility in the UV–vis absorption spectrum following the photochromic processes. Therefore, we have demonstrated that the photostability of the cobalt carbonyl moieties can be tuned by varying the substituents on the switching unit: e.g., replacing the hydrogen atoms in the core cyclopentene ring with fluorine atoms and introducing a bridging unit (in this case a phenyl ring) between the switching unit and the cobalt carbonyl moieties. Quantum chemical calculations have explained many of the experimental observations and have identified the singlet excited states responsible for the cyclization process. In the case of **1Ho** the lowest energy singlet excited state presents an accelerating energy profile toward the closed isomer, whereas in the case of the $\text{Co}_2(\text{CO})_6$ -complexed switches population of the 17th singlet excited state of **4Fo** and higher is required to induce cyclization.

EXPERIMENTAL SECTION

Materials and Equipment. Solvents for analytical experiments, deuterated acetone, and triphenylphosphine were of spectroscopic grade and were used as received. UV/vis absorption spectra were recorded on an Agilent 8453 photodiode-array spectrometer. Photochemical experiments were carried out in a 1 cm quartz cell, using a 200 W Hg lamp (Oriel Instruments, Model No. 68911) containing a 313 or 365 nm filter, and a broad-band lamp with a 550 or 650 nm long-pass filter. ^1H NMR spectra were recorded on a Bruker Model AC 400 MHz spectrometer and referenced to the residual solvent signal. FTIR spectra were recorded in a 0.1 mm liquid cell (with NaCl windows) on a Perkin-Elmer “Spectrum GX” FT-IR spectrometer.

The structures of all compounds were optimized in the antiparallel conformation using the Becke three-parameter hybrid functional and the LYP expression for both local and nonlocal correlation terms (B3LYP).^{46–48} The Gaussian 09 (revision B.01)⁴⁹ program suite was used for all calculations running on the computers in the Irish Centre for High End Computing (ICHEC). The 6-31G(d) basis set was used for all calculations.^{50–52}

■ ASSOCIATED CONTENT

■ Supporting Information

Text, tables, and figures giving all synthetic procedures and UV–vis and NMR spectra for the compounds synthesized in this paper and Cartesian coordinates for the calculated structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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