Torsional influences on cross-conjugated thieno[3,4-b]thiophene photochromes

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Abstract

Photoresponsive conjugated polymers are a promising target for modern organic electronics. Numerous photoswitchable repeat units have been included covalently within polymeric structures to enable responsive chromic materials, most commonly through side-chain appendages or through formal conjugation along a π-conjugated backbone. We recently disclosed a new design whereby the photoswitch elements are cross conjugated to a conjugated polymer main chain. In this case, we found that the extent of photoconversion was dictated in part by competitive main chain light absorption which could be suppressed by using a photoswitching motif that carried most of the frontier molecular orbital densities. Here we report the modeling and synthesis of a series of thieno[3,4-b]thiophene (**TT**)-based photochromes with various aromatic flankers imparting varying degrees of steric bulk and π-conjugation in order to elucidate the balancing act between steric and electronic factors to promote photochromism. These model systems provide a better understanding of the behavior of photochromic units within extended oligomeric and polymeric π-conjugated materials.

Introduction

Photochromic molecules exhibit reversible color change triggered by light, and they are common components of many types of modern organic materials[1]. Azobenzenes[2], spirorpyrans[3], furylfulgides[4], and diarylethenes[5] are some of the most thoroughly investigated organic photochromes[6]. The latter class, diarylethenes (DAEs), were pioneered separately by Irie[7] and by Lehn[8] (Figure 1a). DAEs typically feature a central cycloalkene functionalized by two (hetero)aromatic substituents such as thiophenes, although in principle any moiety containing a local 1,3,5-hexatriene can undergo photochromic switching as dictated by orbital control (e.g. Woodward-Hoffman correlations for electrocyclic reactions) An extensive literature [6,9–20] exists on the development and application of molecular DAE photochromes, and more recently, several material-level demonstrations used DAEs to achieve chromic switching as part of solid-state polymer matrices where DAEs can be blended as molecular entities into a host polymer.[21–23] DAEs have also been attached covalently to a polymer via alkyl sidechains (Figure 1b)[24–27] whereby the electronic segregation between the switch and polymer meant that the polymer and molecular DAE switch did not have drastically different absorption profiles, and the polymer did not afford any new conjugation pathways upon electrocyclization.

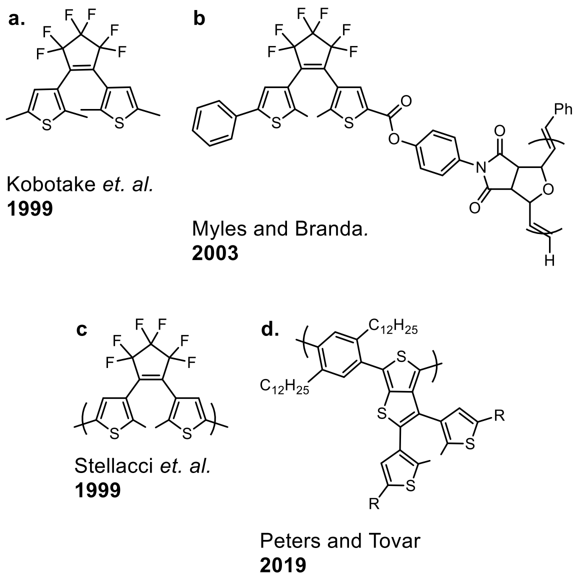


Figure 1. Examples of DAE photoswitches, showing an Irie-type molecular DAE photoswitch (a), a polymer-pendant molecular switch (b), a conjugated polymer whereby the DAEs are embedded within the main chain backbone (c), and a conjugated polymer whereby the DAEs are cross-conjugated to the polymer backbone (d).

Photochromic π-conjugated polymers have also received extensive attention. In addition to the inclusion of photochromes as substituents within non-conjugated polymers derived from vinyl-type monomers (Figure 1b), photoswitchable monomers can also be incorporated directly into the backbones of π-conjugated polymers[12,24,25,27]. Virtually all these fully π-conjugated polymer examples utilize the DAE motif as a π-conjugating bridge such that the DAE electrocyclization directly affects the nature of the conjugation pathway along the polymer backbone (e.g. Figure 1c). However, these main-chain approaches require severe macromolecular reorganization to allow effective switching between open and closed forms of switch units embedded within a larger polymer chain which would be expected to be further impeded in the solid state as a thin-film polymer coating. Furthermore, the electronic properties of the realized conjugated polymers had very localized electronic structures in the open forms due to the negligible conjugation fostered through the thiophene linkages (where the 2,4-thiophene linkage mimics a 1,3 “meta” conjugation pathway in a benzene-based polymer).

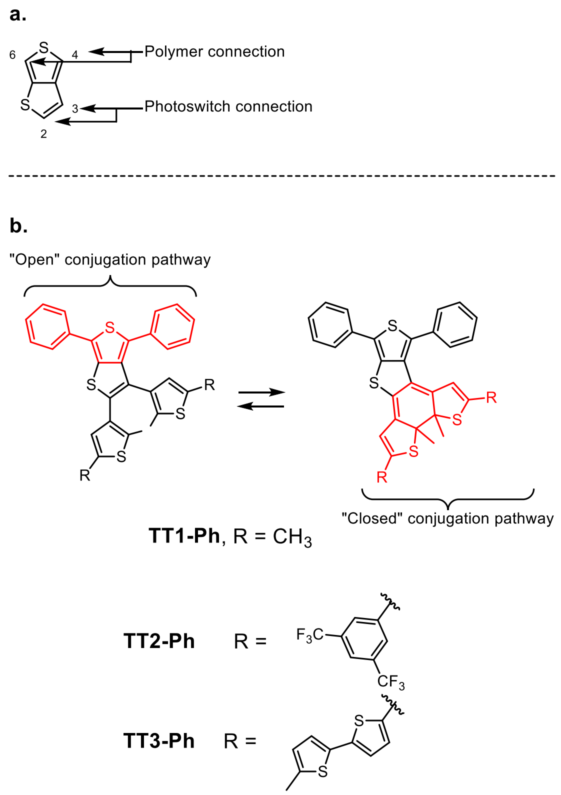


Figure 2. The numbering convention used for the TT core (a) showing connections for polymer extension (4, 6) and for photoswitch installation (2, 3); Our previously reported pendant TT-photochromic switches (b) showing the changes in dominant conjugation pathways in the open (left) and closed (right) forms. Note: TT1-Ph (R = Me) did not exhibit photochromism.

We recently envisioned an alternative design for conjugated photochromic materials whereby a trigger element is *cross-conjugated* with a π-conjugated polymer main chain (Figure 1d). With this design, the expectation was that the main chain polymer electronics could be perturbed in a subtle but distinct and observable manner without requiring excessive macromolecular reorganization. Our first such successful design was realized through the use of a non-canonical DAE photoswitch motif built around a thieno3,4-*b*thiophene (**TT**) core unit (Figure 2).[28] From this 10-π-electron core, one main conjugation pathway could be carved through the 4 and 6 positions of the upper thiophene-like moiety of the **TT** structure while the lower fused thiophene presented a thio enol ether-like "ethene" moiety to which different thiophene-based "aryl" switching arms could be appended at the 2 and 3 positions of the **TT** core (Figure 2a).[28] Upon photocyclization, requiring only the motion of the pendant thiophene trigger units, the polymer main-chain still remains conjugated through the **TT** 4 and 6 positions but now carves through a slightly perturbed 6 π-electron thiophene core. Thus, this polymer presents two conjugated main chains that present different electronic properties depending on the open or closed nature of the local switch units (Figure 2b).

Studies have shown that the photochromism in DAEs can be controlled by external stimuli such as acidification[11] or redox chemistry[17], while others can be influenced by substituent effect[19,28,29]. We showed previously how polymer photochromism depended on a careful balance of directing photoexcitation to the switch elements at the expense of the conjugated main chain, as manifested by inspection of frontier orbitals in the open non-cyclized structures[28]. With simpler switch triggers installed at the 2 and 3 positions of the **TT** scaffold such as dimethyl thiophenes (**TT1**, Figure 2b), π-extension of the conjugated backbone along the **TT** core by way of phenyl substitution at the 4 and 6 positions suppressed photochromism. This was attributed to a competitive absorption of the low-energy diphenyl **TT** backbone at the expense of the higher-energy thiophene-based DAE unit also appended to the **TT** core. As the conjugation within the trigger units was extended to 2-(3,5-bis(trifluoromethyl)phenyl)-5-methylthiophene (**TT2**, Figure 2b) and terthiophene (**TT3**, Figure 2b) trigger units for example, the DAE units had competitive absorption, and photoswitching was observed both within oligomeric and polymeric cross-conjugated **TT2** and **TT3**.

Computational models showed how frontier molecular orbitals (FMOs) were progressively more localized on the switch units as the thiophene components were elongated to di- (**TT2**) and tri-aryl (**TT3**) moieties. While this finding provided a solution to achieve switching in a cross-conjugated polymer, it comes with substantial synthetic cost requiring a much more elaborate switch motif. In the present study, we challenge structural features within the **TT** motif to realize conjugated oligomer photochromism from the tactically much simpler dimethylthiophene switch triggers appended to the **TT** core. We demonstrate how careful tuning of torsional properties of π-extending conjugating groups attached through the 4,6 axis of the **TT** monomer can be used as an additional design element to achieve or suppress photochromism.

Results and discussion

This study seeks to probe the extent that torsional constraints of substituents appended to central **TT**-based core units (at the thiophene-like 4 and 6 positions) will influence the efficacy of the photochromism. To do so, we designed, calculated, and synthesized a series of **TT** core molecules that were flanked at these 4 and 6 positions with mesityl groups (Mes), ortho-tolyl (oTol), and phenylethynl (APh) groups. These substituents were chosen intuitively to illustrate the range of the steric influences and π-conjugation on the **TT** core relative to our prior reported diphenyl substituted **TT** core.

Mesityl groups are often used to solubilize or disaggregate large planar molecules by enforcing orthogonal phenyl conformations about the planar periphery of polycyclic aromatic molecule, thus frustrating extended π-stacking [30–33]. We hypothesize that a “Mes-TT-Mes” structure will also promote a conformation that will limit extended π-delocalization and therefore minimize competitive photoexcitation. This should force more frontier molecular orbital density back into the DAE motif which should “reactivate” photochromism in otherwise non-switching **TT** units with dimethylthiophene switching arms. Similarly, aromatic compounds functionalized with o-tolyl groups should have several accessible and dynamically interconverting atropisomers in solution, and, in the crystalline state, the o-tolyl substituents lie perpendicular to the aromatic core on which they are attached.[34] We also expect the o-tolyl-functionalized switches to exhibit a degree of conformational bias that will interrupt polymer conjugation through the main-chain 4 and 6 positions of the **TT** monomer core. In contrast, phenylethynyl substituents tend to adopt coplanar conformations when appended onto π-conjugated structures in order to maximize delocalization[35–37]. Therefore, we envision that phenylethynyl groups on the **TT** switch will similarly encourage a coplanar conformation, providing a greater degree of conjugation through the 4 and 6 positions. We hypothesize that the extended competitive conjugation afforded by the phenylethynyl groups will suppress photocyclization like our prior findings of competitive main chain absorption in 4,6-diphenyl substituted **TT1** monomeric and polymeric systems.

Computational models can help visualize the frontier molecular orbital (FMO) topologies to discern whether a particular chromophore will be photochromic. For the 6π-electrocyclization[38] to proceed within **TT** switches, we showed how FMO density must apparently be concentrated within the local DAE moiety in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). Our previous study and other computational studies showed the FMO density did not need to entirely lie across the DAE motif: molecules even with partial orbital density localized to the DAE portion displayed photochromism[19,28,39]. Because of this defining characteristic for photochromism in these types of molecules, we sought to use computational screening as a predictive tool for further molecular design. We initially evaluated both low-level semi-empirical methods and more demanding density functional theory methods. The spatial distribution of the FMOs were consistent across both approaches, but the FMO energy levels and the topologies for the HOMO-N and LUMO+N energy levels were markedly different. Because our analysis only relies on consideration of the spatial distribution of the FMOs (and not on exact calculation of energy levels) we elected to use semi-empirical methods to compute the FMO topologies in a manner of seconds rather than the hours required for DFT analysis.

Subsequently, we screened a series of candidate **TT** molecules flanked with mesityl (Mes), o-tolyl (oTol) and phenylethynyl (APh) substituents that provided different extents of competitive main chain absorption (Figure 3). We ran our computations using two sets of parameters. One set was based upon geometry optimization to compute the "ideal" conformation as well as the associated MO topologies. The other set "locked" the substituents into certain conformations to further probe the impact of torsional bias, for example by orienting them such that they were completely coplanar (e.g. **TT1-Mes-A** and **TT2-Mes-A** in Figure 3) or perpendicular (e.g. **TT1-Mes-B** and **TT2-Mes-B** in Figure 3) with the **TT** core, illustrating the extremes of accessible conformations. In both sets of computations, the thiophene switching wings were held in an antiparallel conformation necessary to facilitate the electrocyclization[6].

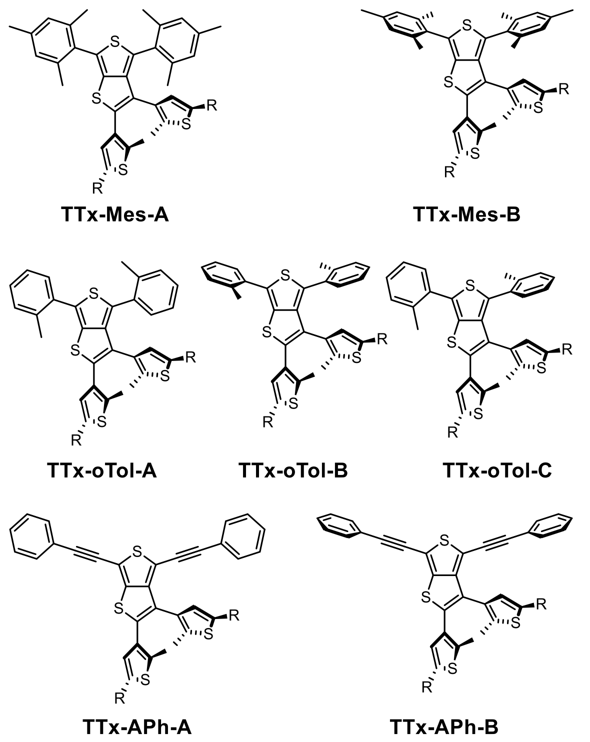


Figure 3. Computational models studied here. **A** corresponds to a zero-degree dihedral along the 4,6 conjugation pathway, while **B** corresponds to 90-degrees and **C** corresponds to one axis at 0 degrees and one axis at 90-degrees. X = 1 (where R = Me); X = 2 (where R = 3,5-bis(trifluoromethyl)phen-1-yl).

As the first case, we will consider Mes-flanked switches (Figure 4). The FMO orbital density for **TT1-Mes-A** (where the Mes groups are forced into coplanarity with the **TT** core) is concentrated away from the DAE moiety, which would suggest that this conformation would lead to deactivated photochromism. The orthogonal Mes conformers present in **TT1-Mes-B** lead to FMO density being localized within the DAE moiety, which would suggest a viable photochromic switch. Considering the perpendicular conformation will be more sterically favorable, we expect mesitylene flankers to reactivate photochromism within **TT1** switches. In contrast, **TT2-Mes** expresses switch-localized MOs regardless of the conformation of the Mes-groups. These MO topologies indicate that these molecules will be photochromic regardless of the conformation, though we expect the perpendicular conformation to be favored. Indeed, the **TT2** monomer was previously shown to display photoswitching both when substituted with π-extending phenyl groups and when placed within a conjugated polymer. Geometry optimization computations showed that both **TT1-Mes** and **TT2-Mes** favor a perpendicular TT/Mes conformation that favor photochromism in both instances (Supplemental, Figure S11).

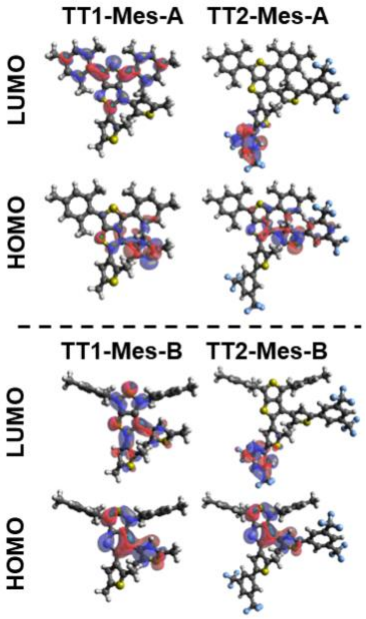


Figure 4. FMO topologies for mesityl-capped switches.

When modeling the o-tolyl-functionalized compounds (Figure 5), we must consider in principle multiple possible conformations due to the presence of two atropoisomeric o-tolyl/TT axes. All permutations of completely coplanar tolyl groups on **TT1-oTol-A** show MO densities localized away from the DAE moiety. If both o-tolyl groups (**TT1-oTol-B**) are rotated out of the plane, the MO density becomes concentrated on both thiophene switching wings, which is indicative of photochromism. We then considered if only one of the o-tolyl groups **(TT1-oTol-C)** are twisted out of planarity, which leads to an intermediate situation wherein MO topologies are partially lying on the DAE moiety, suggesting photochromism is also possible. After considering the expected prevalence of these non-planar atropoisomeric conformations, we would expect that **TT1** systems should be photochromic even with the relatively relaxed torsional constraints when compared to the mesityl cases. In contrast, **TT2-oTol** had MO topologies generally favorable for photochromism in all modeled conformations, where FMO density is concentrated on at least one of the switching arms. This is consistent with our previous report, showing that this 2,3-bis(trifluoromethyl)phenyl)-5-methylthiophene-based DAE unit outcompetes the 4,6 **TT** backbone conjugation[28]. Geometry optimization computations showed a preference for perpendicular TT/oTol conformation for both **TT1-oTol** and **TT2-oTol** (Supplemental, Figure S11).

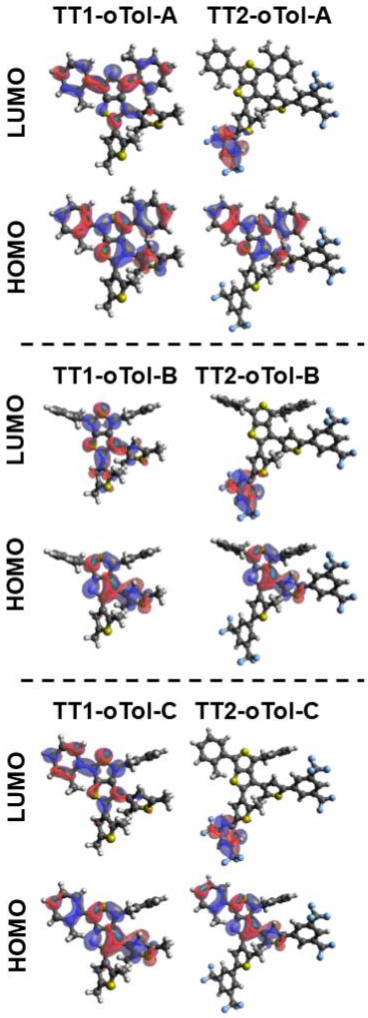


Figure 5. FMO topologies for o-tolyl-capped switches.

These computational insights did not address an open question from our previous report,[28] where we found that TT1-based oligomers (**TT1-Ph**) and polymers with aromatic spacers containing long alkyl chains (**pTT1**) were not photochromic. These alkyl chains imparted solubility and steric bulk to break backbone conjugation. Here we see the less sterically demanding o-tolyl group seems to prefer a conformation which breaks backbone conjugation and restores photochromism. This discrepancy led us to model several **TT1**-containing oligomers with 2,5-dimethylbenzene spacers containing 2-, 3-, 4-, 5-(Figure 6), 6-, 7-, 8-(Supplemental Section) photoswitching units. Geometry optimization showed that the phenyl spacers favor perpendicular conformations for each oligomer model. The 2-unit oligomer shows partial HOMO density lying on one of the two switching motifs, with much of the density lying on the central TT-oTol-TT motif despite these rings lying in a perpendicular conformation. The LUMO density is then localized on the other **TT** switch present in the oligomer. As the oligomers are lengthened, the HOMO and LUMO densities lie on different **TT**-subunits of the oligomers. We see a similar trend observing the HO-1 and LU+1, where MO density are segregated along different regions of the oligomers. Presumably if the HOMO and LUMO lie on two segregate regions of a particular oligomer, the desired cyclization reaction cannot occur in these systems.

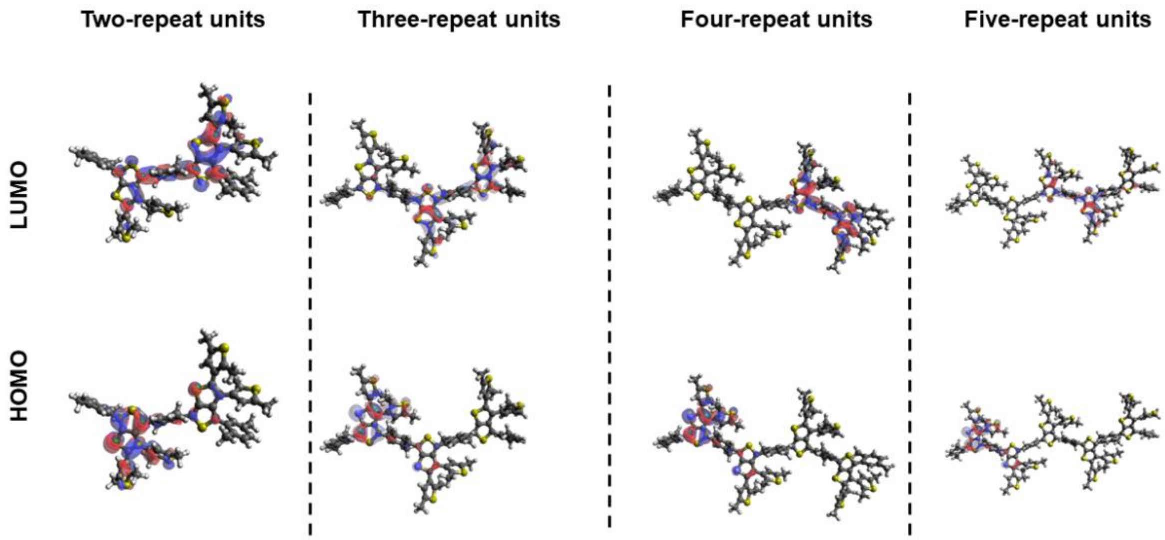


Figure 6 FMO topologies for oligomer models containing TT1.

Finally, we consider phenylethynyl substituents to evaluate what the complete absence of a steric influence would have on photoswitch ability that is due to an inherent preference to increase π-conjugation along the **TT** backbone. All conformations for both **TT1-APh** and **TT2-APh** (with both planar and orthogonal phenyl groups with respect to the **TT** core) indicate photochromic deactivation (Figure 7): the extended π-conjugation afforded by the alkynyl groups siphons FMO density away from the DAE motif and towards the local dialkynyl **TT** chromophore. Geometry optimization indicated that both **TT1-APh** and **TT2-APh** would favor the coplanar conformations (Supplemental, Figure S11). These models suggest that these switching motifs do not have enough effective π-conjugation to overcome that of the phenylethynyl capped **TT** unit. Based on these findings, we expect these molecules would not display photoswitching behavior.

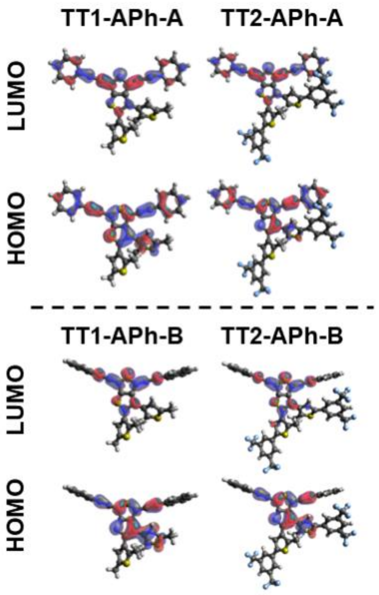
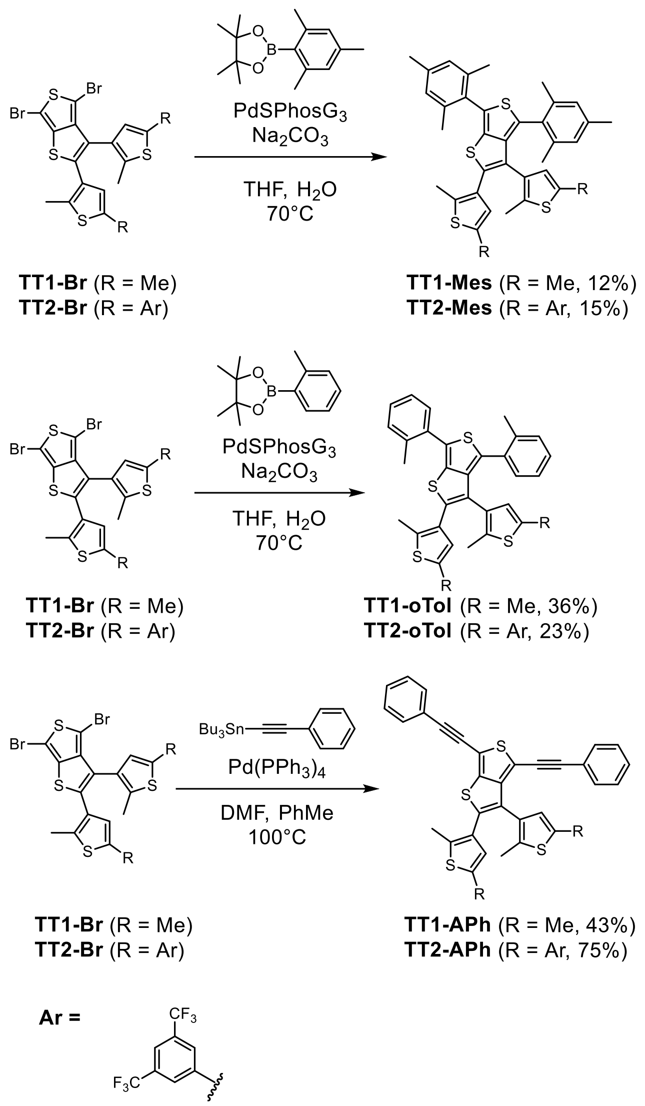


Figure 7 FMO topologies of phenylethynyl capped switches

TT1-Br and **TT2-Br** were synthesized according to our prior report[28] with the intention to use standard palladium-catalyzed cross-couplings to install the requisite **TT** flanking groups at the 4 and 6 positions (Scheme 1). After some preliminary trial reactions using standard catalytic systems, it became clear that the functionalization of sterically congested mesityl and o-tolyl substituents would require more forceful conditions. For example, the mesityl-flanked compounds required freshly made Pd-Sphos-GIII[40] with up to a seven-fold excess of the transmetallating reagent, with **TT1-Mes** obtained in 12% yield and **TT2-Mes** obtained in 15% yield. The o-tolyl flanked compounds were synthesized using the same Suzuki-Miyaura conditions as the Mes-capped switches, affording **TT1-oTol** in 36% yield and **TT2-oTol** in 23% yield. Stille conditions[41] were used for the phenylethynyl substituted TT cores because they afforded better and cleaner yields of the desired products compared to standard Sonogashira conditions[42], leading to **TT1-APh** in 43% yield and **TT2-APh** in 75% yield.



Scheme 1 Synthesis mesityl-, o-tolyl-, and phenylethynyl capped photochromic switches

Stock solutions were made of each structure in acetonitrile, and each solution was diluted to 40 µM for spectral analysis. Changes, resulting from irradiation of each sample with a UV light source (254 nm), were apparent to the naked eye (Figure 8 insets). Consistent with our computational models, we found that **TT1-Mes** was photochromic as apparent from the transition from a colorless solution of the open ring isomer (ORI) to a light pink color in the solution of the closed ring isomer (CRI) form. Unsurprisingly, **TT2-Mes** was also photochromic, exhibiting a colorless-to-blue change in color when progressing from the ORI to the CRI. We then observed that **TT1-oTol** was weakly photochromic and exhibited a pink CRI while **TT2-oTol** exhibited a blue CRI upon switching. Finally, consistent with computations, **TT1-APh** and **TT2-APh** did not exhibit photochromism, and solutions of these switches remained yellow before and after irradiation at 254 nm.

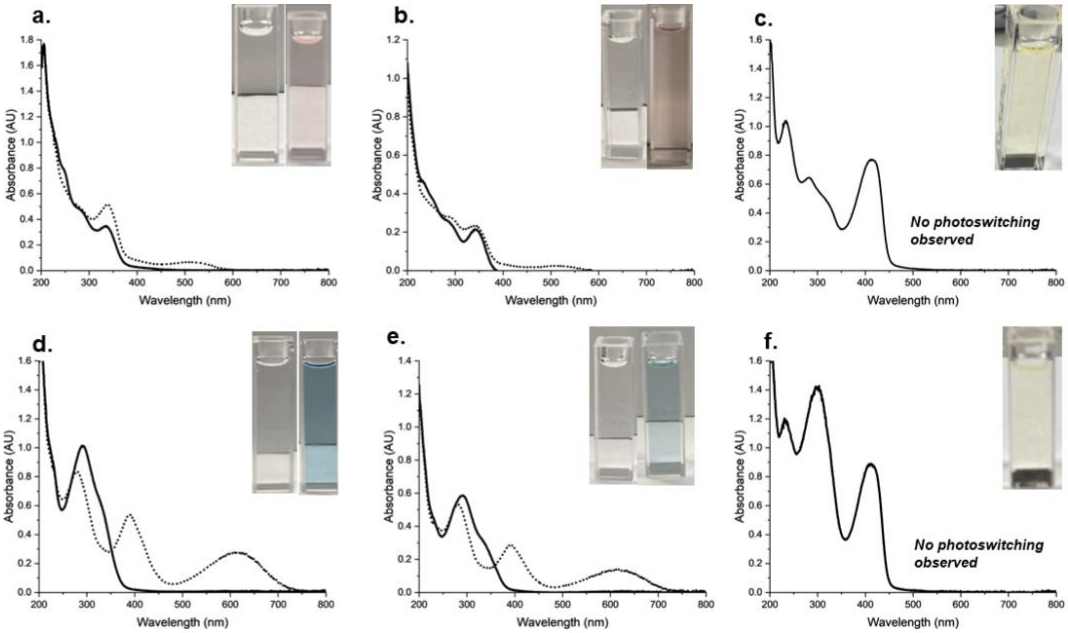


Figure 8 a.) TT1-Mes; b.) TT1-oTol; c.) TT1-APh; d.) TT2-Mes; e.) TT2-oTol; f.) TT2-APh; All samples measured at 40μM in MeCN concentrations under ambient light (——) and after irradiation with a 254 nm UV lamp for ~2 min (- - - -).

UV-vis spectra provided more specific explication of electronic changes accompanying the photocyclization events. Within the TT1 family, the CRI of **TT1-Mes** showed a more pronounced new absorption feature at 506 nm, although the low energy feature in the ORI at 336 nm similarly persisted in the irradiated CRI sample, albeit at a slightly higher intensity. The ORI of **TT1-oTol** showed the lowest energy feature centered at 341 nm. Upon photocyclization, the CRI form exhibited a similar feature at 341 nm accompanied by a weaker broad peak centered at 510 nm. These observations suggest that the CRI and ORI coincidentally absorb at the same energy, and the extent of photocyclization being driven forward is minimal. In contrast, **TT1-APh** presented the same absorption profile before and after exposure to a UV light source (254 nm) and no color change, indicating not only that the photochromic reaction did not proceed, but also that no other photoinduced transformations or degradations occurred.

Within the **TT2** family, the ORI of **TT2-Mes** displayed a peak absorption at 289 nm. The corresponding CRI for **TT2-Mes** exhibited features at 279 nm along with new low-energy features at 391 nm and 620 nm. Notably, the CRI lacked the pronounced shoulder at ca. 350 nm that is present in the ORI. The changes upon irradiation for **TT2-oTol** were comparable: the ORI presented a profile with a low energy absorption at 290 nm with a shoulder at ca. 337 nm while the CRI showed much more noticeable lower-energy features at 391 nm and 612 nm along with a higher energy peak shifted to 271 nm. The more intense absorption features that evolve in the o-tolyl-substituted (**TT2-oTol**) upon irradiation (compared to **TT1**) suggest more efficient photoconversions from the **TT2-oTol** ORI to the CRI. Finally, **TT2-APh** was not photochromic as apparent in the similar absorption profiles before and after exposure to 254 nm light. Like **TT1-APh,** these features indicated the compound is neither photochromic nor undergoing other photoinduced transformations. The competition between main chain arylene ethynylene conjugation and DAE switch conjugation again shows the importance of localized DAE FMO density to achieve successful photoswitching, even in systems with longer and more conjugated switch arms.

Conclusions

We show here how controlling the torsional angle between the TT-core and the substituents at the 4- and 6-positions can influence photochromism depending on proper π-extending substituent choice. For example, mesityl groups attached to the 4 and 6 positions of the **TT** photoswitch do not serve to extend competitive conjugation due to the inherent torsional bias, and thus encourage a successful photoswitch in a manner consistent with our computations. When the impact of this bulky group is mitigated through inclusion of a less demanding o-tolyl unit, the extent of the photochromism is reduced for the **TT1** switch family but not entirely suppressed. While computations showed **TT1-oTol** could be photochromic, it must be noted that **TT1-oTol** departs from what we previously found for **pTT1** in our previous study[28]. Our computations show, that despite breaking backbone conjugation, other conjugation pathways are present deactivating photochromism. Similarly, a lack of steric congestion leading to increasing conjugation along the 4,6 positions of the **TT** core deactivates photochromism. Even for photoswitch motifs with extended conjugation and electron withdrawing groups (**TT2**) which would otherwise be photochromic, the competitive conjugation in the APh systems led to photochromic deactivation. Because both coplanar orthogonal conformations were computationally shown to deactivate photochromism, the switching motif would need have much more effective π-conjugation to overcome the competitive backbone absorption. These compounds are models to better understand the balance between steric and electronic effects in pendant photochromic switches. Our oligomer models seem to suggest that even sterically bulky groups may not be enough to reactivate photochromism in less π-extended switching motifs once incorporated into extended polymeric systems as other pathways for deactivation arise. These insights will be important for the continued development of photochromic switches and polymers, especially in cases where colorless (non-absorbing in the visible region) conjugated polymers may be desired as precursors to more vibrantly colored materials.

Experimental Section

See the Supporting Information

Computational Methods

See Supporting Information

Associated Content

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information

Supporting Information

The Supporting Information is available at DOI: ###

General information, synthesis, ^{1}H-NMR and ^{13}C-NMR, Cartesian coordinates, and molecular orbital images of all reported compounds

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Notes

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Torsional influences on cross-conjugated thieno[3,4-b]thiophene photochromes

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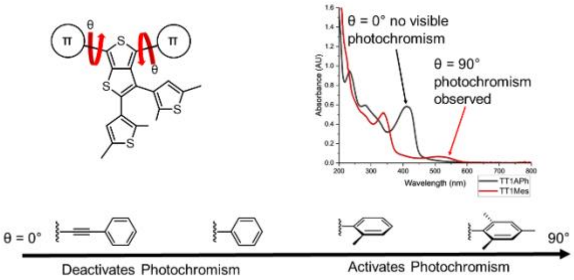

Thieno[3,4-b]thiophene-based diarylethene photochromes present an opportunity to engineer orthogonal conjugation pathways through photoswitchable conjugated polymers. We previously showed the importance of balancing main-chain polymer conjugation with that of the pendant photochrome arms. Herein we examine structural challenges to this conjugation, using computational tools to predict photochromism based on conformational considerations. We found that steric biases along the polymer backbone led to differing degrees of frontier molecular orbital localization which subsequently influenced the extent of observed photochromism.