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Molecular Switches

Expanding the Molecular Switches Toolbox: Photoreloadable Dithienylethene Mechanophores

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Abstract: Molecular switches are often thought of as nanoscopic equivalents to the electrical buttons and knobs ubiquitous in everyday life. However, mechanical force is rarely used to reversibly trigger rearrangements at the atomic scale, due to the difficulty in selectively breaking certain bonds, while keeping others intact. Here, we introduce two new mechanophores based on dithienylethene (DTE), which can be toggled between two states by ultraviolet light and sonication. Attaching various lengths of poly(ε-caprolactone) either to the 2,2′ or the 5,5′ positions of the DTE core allowed us to study the kinetics of its mechanochemical cycloreversion. We employed computational methods to understand the root causes of the observed mechano-regiochemical differences. Lastly, we show that our best performing DTE-polymer conjugate can undergo numerous switching cycles by the alternating action of electromagnetic radiation and mechanical force.

Introduction

Photoswitchable molecules have been extensively studied over the last decade due to their unique properties and promising applications in a number of fields. They have been designed to produce color changes for stress-sensing applications,[1] generate reactive functional groups for self-healing[2,3] and catalysis,[4,5] alter electrical conductivity,[6] store and process data,[7,8] sense specific chemicals,[9] as well as to be used in fluorescence microscopy[10] and even in pharmacology.[11] The most commonly used classes of photochromic compounds are azobenzenes,[12,13] spiropyrans,[14] and diarylethenes,[15,16] which all undergo a reversible change in their molecular structure and visible absorption in response to light as an external stimulus. More recently, donor-acceptor Stenhouse adducts (DASA) were shown to exhibit negative photochromism, i.e. going from intensely colored to a clear form[17–19] upon visible light irradiation. Even though dithienylethene (DTE) requires UV light for activation, its derivatives display superior properties such as thermal stability of both isomers, rapid response, and high fatigue resistance.[20–22] Their photochromism is due to UV-induced 6π-electrocyclization that generates intensely colored conjugated species that can be converted back to the colorless ring-open form using visible light.[16,23,24] The pericyclic reaction is thermally 'forbidden', setting DTEs apart from azobenzenes and spiropyrans, whose spontaneous back isomerization is an impediment for their adoption in many practical applications.[12,25,26] Although the DTE scaffold has been extensively studied over the past two decades[25,26] and even used as photo-controllable gate for irreversible polymer chain scission,[27–29] the effects of mechanical force acting directly on this important photoswitchable compound have not been investigated.

The molecular response of synthetic polymeric materials to applied mechanical force was first considered by Staudinger and co-workers in the 1930s when the degradation of natural polymers under ultrasonication was observed.[27] Early work in the field was primarily focused on polymers' response to mechanical stress by simple conformational, bond bending and stretching deformations and ultimately—bond cleavage. However, in recent years, there has been a shift towards harnessing mechanical energy through the use of small molecule 'mechanophores' to imbue polymers with new properties and reactivity.[27,30,31] Examples include color change,[32] turn-on catalytic activity,[33] depolymerization,[26] change of electrical conductivity,[34] chemiluminescence,[35,36] and others.[37,38] In order to convert mechanical to chemical energy most efficiently, the mechanophores must reside near the center of polymer chains, where stress tends to accumulate under elongational flow,[31] typically created by ultrasound in solution. Thus, sonication has been used to test the mechanochemical properties of macromolecules containing spiropyran,[39] Diels–Alder adducts,[40] cyclobutane,[41] cyclopropane.[42] Notably, however, DTEs are absent from

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this list, possibly due to the synthetic challenges of their functionalization. The dithienylethene scaffold has two logical attachment points that could be used to exert pulling force—either at its 2,2′ positions that flank the photoactive σ-bond (highlighted in pink, Figure 1) or on the 'outside' of the molecule at the 5,5′ carbons. Since regiochemical differences have been shown to significantly alter the force required for spiropyran activation,[43] we set to explore both possible mechanophores by incorporating DTE into polycaprolactone (PCL) as shown in Figure 1. We studied the kinetics of their photo-reversible, symmetry-forbidden ring opening and used computational methods to explain the differences in their mechano-regiochemistry.

Results and Discussion

Contour length has been shown to be the most crucial factor affecting force transmission and subsequently bond cleavage in macromolecules.[39] While poly(methyl acrylate)[28,29,35,44] is typically used for mechanochemical studies, we chose poly(ε-caprolactone)[41–43] because of its broad range of applications and the synthetic access to **2,2′-diOH** and **5,5′-diOH**. These photochromic di-macroinitiators were prepared through optimized, step-efficient routes from commercially available thiophenes following established procedures,[5,47–49] as summarized in Scheme 1 and described fully in the Supporting Information.[47]

Three different lengths of PCL chains were grown from each photochromic diol by $Sn(Oct)_2$-catalyzed ring opening polymerization (ROP) of ε-caprolactone, affording us six white, powdery polymers with good dispersity, ranging in molecular weights between approximately 20 and 60 kDa (see Figure 2). Additionally, a 38.4 kDa poly(ε-caprolactone) without DTE was synthesized for use in control experiments.

The efficiency of photoconversion to the closed-form DTE (cDTE) for our medium-length polymer-DTE conjugates was estimated spectroscopically using the small molecule analogues **2,2′-diOAc** and **5,5′-diOAc** to be 58 % and 71 % respectively (see Supplementary Info.). This is typical for photochromic systems lacking extensive conjuga-

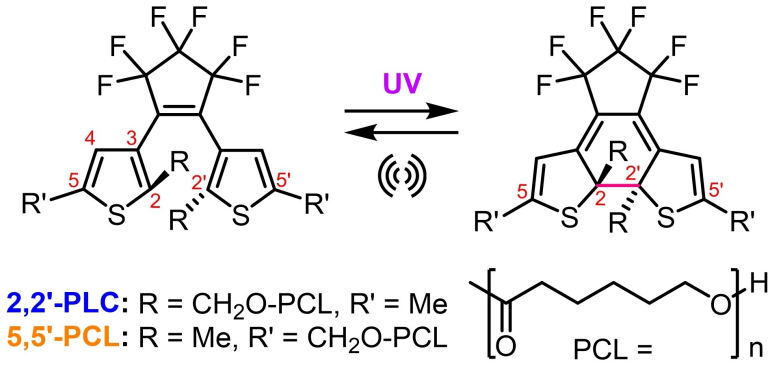
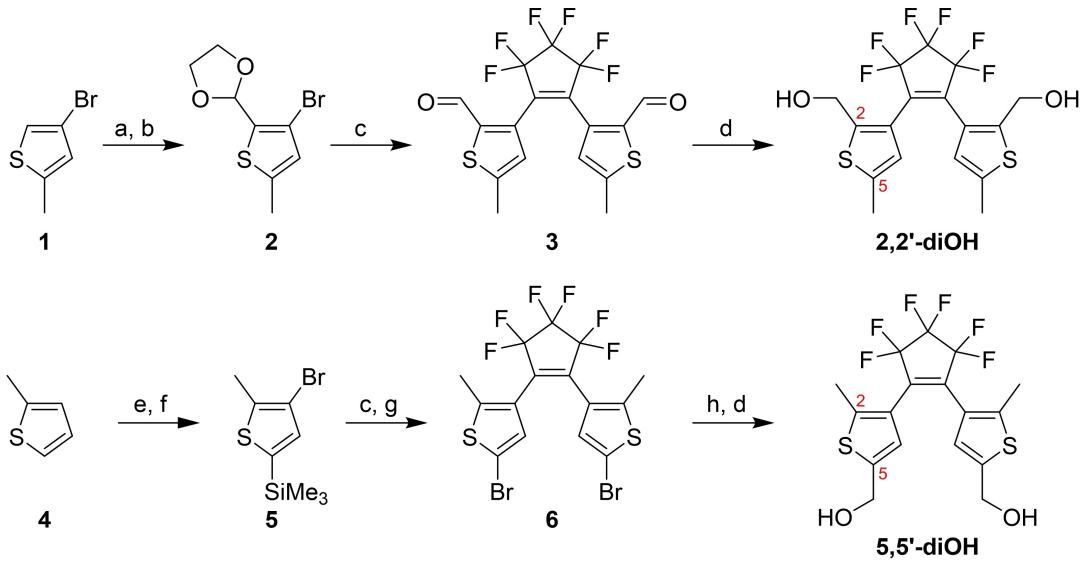


Figure 1. Reversible photo- and mechano-isomerization of **2,2′-PCL** and **5,5′-PCL**.



Scheme 1. Synthesis of **2,2′-diOH** and **5,5′-diOH**: a) LDA, then DMF b) $(CH_2OH)_2$, TsOH; c) ^{n}BuLi, then C_5F_8; d) $NaBH_4$, MeOH; e) NBS, AcOH; f) ^{n}BuLi, then Me_3SiCl; g) NBS, THF; h) ^{n}BuLi, then DMF.

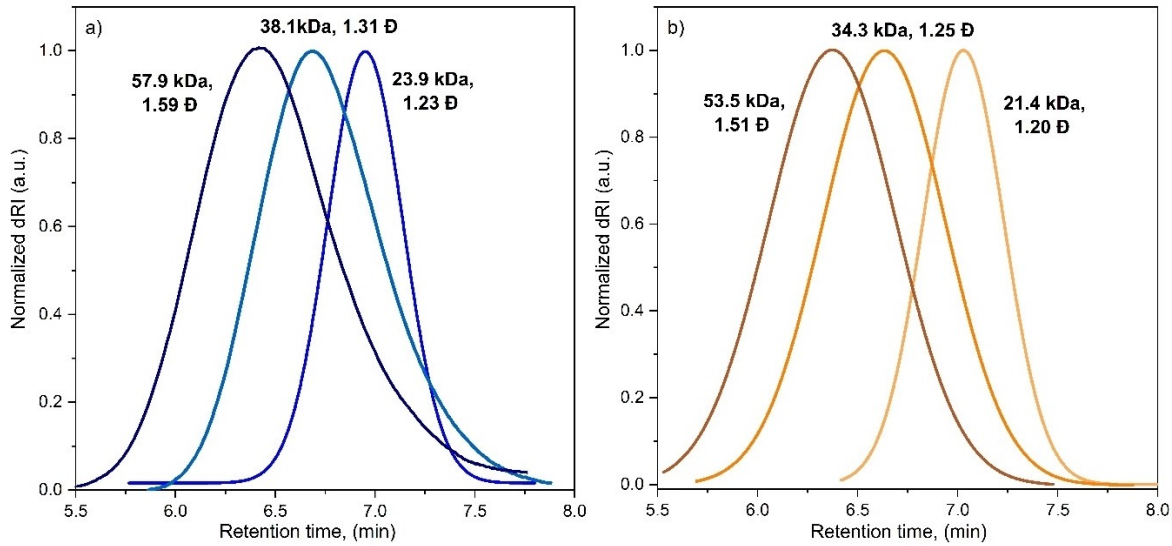


Figure 2. GPC chromatograms of (a) **2,2′-PCL** and (b) **5,5′-PCL** polymers denoted as small ($_{S}$**PCL**), medium ($_{M}$**PCL**), and large ($_{L}$**PCL**) in accordance to their average molecular weight. Respective dispersity (Đ) is shown below the average molecular weight for each curve.

Table 1: Initial first-order rate constants *k* for mechanochemical cDTE opening.

Polycaprolactone Size	$k_{2,2'}$/hr^{-1}	$k_{5,5'}$/hr^{-1}
Control (DTE@ $_{M}$PCL)	0.014 ± 0.001	0.013 ± 0.001
Small (DTE-$_{S}$PCL)	0.069 ± 0.005	0.058 ± 0.004
Medium (DTE-$_{M}$PCL)	0.273 ± 0.004	1.140 ± 0.030
Large (DTE-$_{L}$PCL)	0.120 ± 0.002	0.387 ± 0.015

tion. Reaching photostationary state (PSS), where the visible absorbance is at its maximum is quite rapid (120 s for the 2,2′- and 90 s for the 5,5′-DTE as shown in Figures S41 and S43),[29,38,51,52] even with a low-power fluorescent UV bulb that delivers only 2 mW of electromagnetic radiation into the cuvette. We studied the fatigue resistance of these photochromic polymers by subjecting them repeatedly to UV then visible light irradiation without the exclusion of oxygen. The **2,2′-$_{M}$PCL** was able to undergo 19 cycles, while the **5,5′-$_{M}$PCL** fared much better—reversibly switching 28 times (10 and 15 times respectively until half of the absorbance is lost, see S45 and S46). In either case, 100 % ring opening was not observed, due to irreversible isomerization of cDTE, as well as some photodegradation[5] that are to be expected.

We then used sonication to generate shear forces by cavitation bubble collapse and transmit them through the polymer chains of various lengths to the two cDTE mechanophores. Bright red 1,4-dioxane solutions of 2,2′-DTE, and light pink in the case of 5,5′-DTE derivatives, were prepared by irradiation with UV–B light and then subjected to pulsed 20 kHz ultrasound for prolonged periods of time. Figure 3b shows the decrease in normalized visible absorption for **2,2′-$_{M}$PCL** and **5,5′-$_{M}$PCL**, unequivocally proving that the DTE core is mechanochemically active. Absorption spectra of aliquot samples revealed that there was always some cDTE left, so visible light was applied after each ultrasound treatment (Figures 3c and 3d). However, achieving complete conversion back to oDTE was not possible, due to the formation of non-photochromic DTE isomers. Since this was also observed in our purely photochemical reactions, we conclude that it was not a result of the ultrasound-generated force.

There are clearly several stages of sonochemical ring-opening, but given the complexity of the investigated systems arising from polymer dispersity and the coupling mechanism between soft matter and ultrasound energy, only the initial data were fitted to first-order rate equations. The complete set of results from the mechanochemical study can be found in Figures S49–S54, while the reactivity data across our library of DTE-PCL compounds are summarized in Table 1.

The medium polycaprolactone chains ($_{M}$**PCL**) displayed the best reactivity, with attachment at the 5,5′- positions having 4-fold faster ring opening compared to the 2,2′-system. Ultrasonication of the low molecular weight DTE-PCL conjugates, however, induced little color fading with minimal difference between the two DTE cores. Nevertheless, their rate constants were significantly higher than our control samples (**2,2′-diOH** and **5,5′-diOH** mixed with medium-sized polycaprolactone), suggesting that a fraction of the $_{S}$**PCL** polymer chains are long enough to mediate cycloreversion, as well as that the observed discoloration was indeed mechanochemical in origin rather than from potential sonoluminescence or high local temperatures. Moore's research group has shown that the contour length

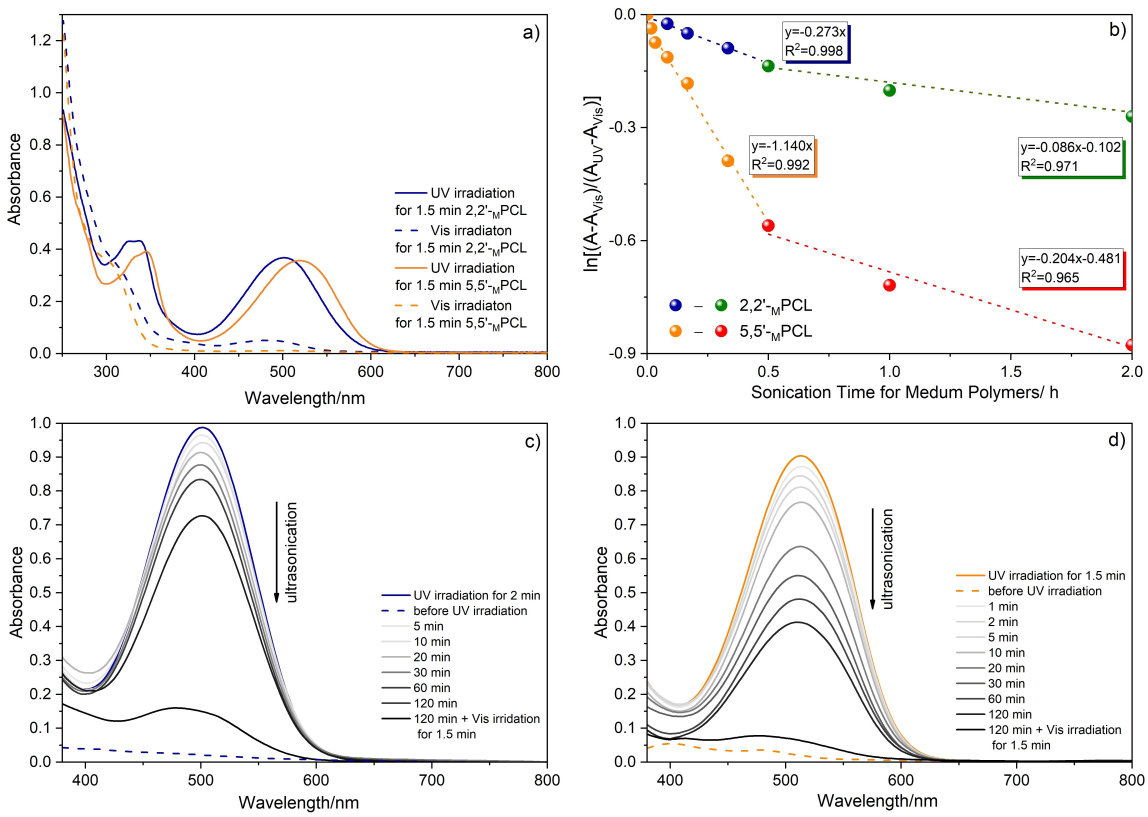


Figure 3. a) UV-Vis Spectra of **2,2′-$_M$PCL** (1.31 wt% in 1,4-dioxane) and **5,5′-$_M$PCL** (1.20 wt % in 1,4-dioxane) after 2 mW irradiation with 311 nm (solid lines) and 115 mW white light (dotted lines) for 1.5 minutes each; b) First-order kinetics of **2,2′-$_M$PCL** and **5,5′-$_M$PCL** cDTE opening measured at λ_{max} of 498 nm and 510 nm respectively; UV-Vis spectra of **2,2′-$_M$PCL** (c) and **5,5′-$_M$PCL** (d) as prepared, after 311 nm UV irradiation, and subsequent ultrasonication.

of a mechanophore-polymer system, rather than its molecular weight, determine the activation kinetics.[39] There is minimal chain length required for ultrasound-induced mechanophore activation, however, and given that a fraction of our small PCL-DTE constructs are mechanochemically active, molecular weights greater than 25 kDa appear to be necessary for proper DTE opening, in line with other mechanophore-polymer systems.[41] The medium-sized polycaprolactones were able to transduce force much better, as indicated by the faster kinetics, which also exposed a significant difference between the two DTE mechano-regioisomers. Contrary to our expectations, the longest PCL-DTE's showed reduced rates of ring-opening—a phenomenon that remains unexplained and warrants further investigation. Nevertheless, the first-order mechanoactivation rate for **5,5′-$_L$PCL** is over 3× higher than for **2,2′-$_L$PCL**, confirming the importance of polymer attachment regiochemistry and pointing towards the existence of a DTE "lever arm" effect.[53]

Unlike previous reports in which the DTE scaffold was used as a light-activated, single-use gate for irreversible polymer chain scission,[28] here we used UV light to quickly restore the DTE mechanophore, making our system photoreloadable. Figure 4 shows the ability of our best performing **5,5′-$_M$PCL** to respond to an unprecedented number of ultrasonication cycles.

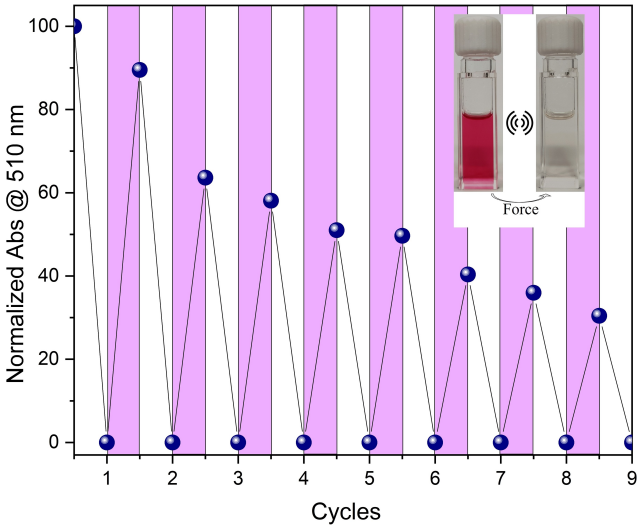


Figure 4. Normalized absorbance at 510 nm of **5,5′-$_M$PCL** (1.20 wt% in 1,4-dioxane) under alternating exposure to sonication (120 min. at 15 °C) and UV irradiation (2 mW at 311 nm for 90 seconds). **Inset**: Appearance of the solution before and after the first cycle.

The alternating force-then-UV treatment could be repeated up to 9 times, but after each cycle the absorbance peak characteristic of cDTE is diminished

(see Figure S54). Gel-permeation chromatography (GPC) of DTE-containing, as well as PCL-only control samples (Figure S39), showed that the polymer breaks into lower molecular weight fragments with prolonged exposure to ultrasound energy. Thus, chain scission events could be contributing to the observed DTE degradation, for example through radical processes. PCL without DTE displays a slightly different GPC peak pattern, which is consistent with a greater variety of fragment sizes produced. This can be attributed to increased random cleavages, compared to polymers containing mechanophore, where degradation could more easily occur at the DTE attachment sites. Nevertheless, the **5,5′-$_M$PCL** material showed surprising resilience given what amounted to 18 hours of sonication, highlighting its ability to absorb relatively large amounts of mechanical energy. The **2,2′-$_M$PCL** mechano-regioisomer showed faster deterioration, which prompted us to use computational methods for insights into the DTE structure under applied force, in order to understand better the properties of our novel systems.

We employed the constrained geometries external force (CoGEF) method[54] to create a potential energy surface (PES) for DTE ring-opening with forces acting along its 2,2′- and 5,5′- axes as shown in Figure 5. Starting with an optimized equilibrium geometry, each intermediate structure was allowed to relax, while keeping only the end-to-end distance constrained to a fixed value along the distortion pathway. All calculations were done using the semi-empirical generalized tight binding method GFN-xTB2[55] within the ORCA computational package.[56] The actual molecular motions may not precisely follow the simulated ones described here, but given the two attachment points, the potential energy surface constructed by incrementally elongating both dimensions, offers a broad overview of the mechanochemical landscape. As long as the displacement remains within the bounds of this PES, the ring-opening process can be captured, enabling predictions of nearly any pathway that could occur during the experiment.

There is a significant energy barrier when the distance between the 2,2′-positions is increased by 1.2 Å or when the 5,5′- attachment points are elongated by 1.4 Å, indicating that the DTE structure transitions from a closed to an open form. In order to explore the two most viable force-induced reaction pathways in greater detail (see orange and blue lines in Figure 5), we then used density functional theory (DFT) at the B3LYP/def2-SVP level of theory.

Despite the significant differences in fatigue resistance and sonochemistry kinetics between **2,2′-PCL** and **5,5′-PCL**, our calculations revealed that the energy required for mechano-cycloreversion of both isomers is approximately the same at just below 400 kJ/mol, and so are the maximum elongation distances shown in Figure 6a. It is important to note that these values have not been corroborated by physical measurements, so should be used only for comparisons. The thiophenes in cDTE place the 5,5′- attachments further away from the cyclopentyl ring, thus providing greater 'mechanical advantage' around a central pivot point compared to the directly connected 2,2'- positions. Treating the mechanophore as a rigid, type 2 lever would suggest a large difference in the forces needed to overcome the electrostatic attraction of the labile sigma bond, but the computed peak values are 6.99 nN and 7.25 nN respectively (see Figure 6b). The actual forces needed for cDTE ring-opening are most likely lower, because CoGEF neglects thermal fluctuations,[27] but the fact that DFT predicts that they are almost identical excludes a simple 'lever arm' effect. Our calculations show that unlike other mechanosensitive systems, the restoring force of 2,2′-DTE peaks nearly halfway before the ring opening happens. Further stretching the molecule causes electron rehybridization, which weakens the labile sigma bond in the middle. What sets this trajectory

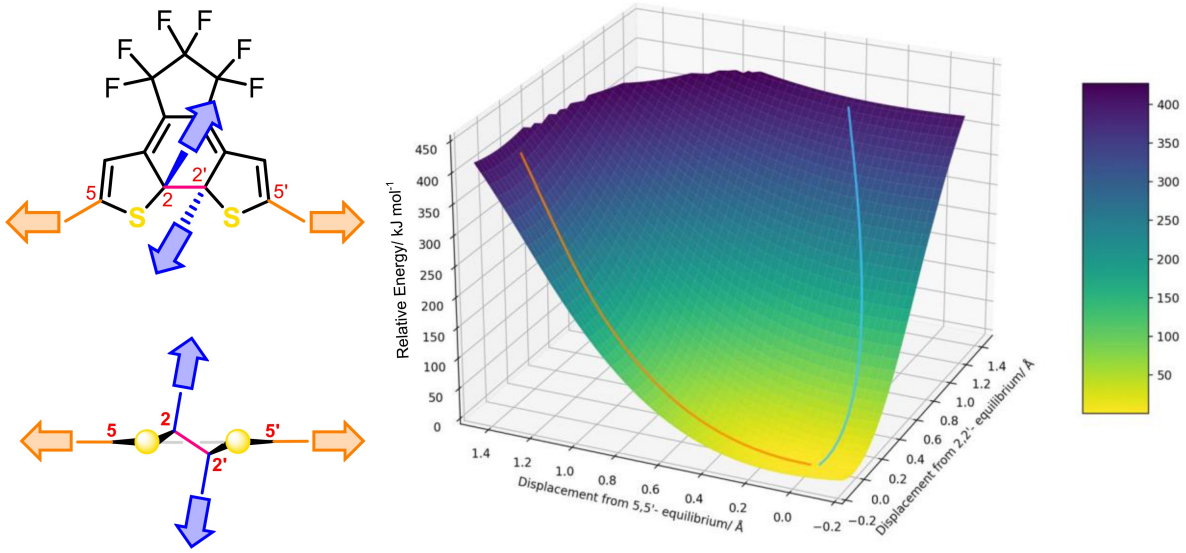


Figure 5. Front and bottom view of DTE and its mechanochemical potential energy surface with lines indicating elongation along its 2,2′- (blue) and 5,5′- (orange) axes.

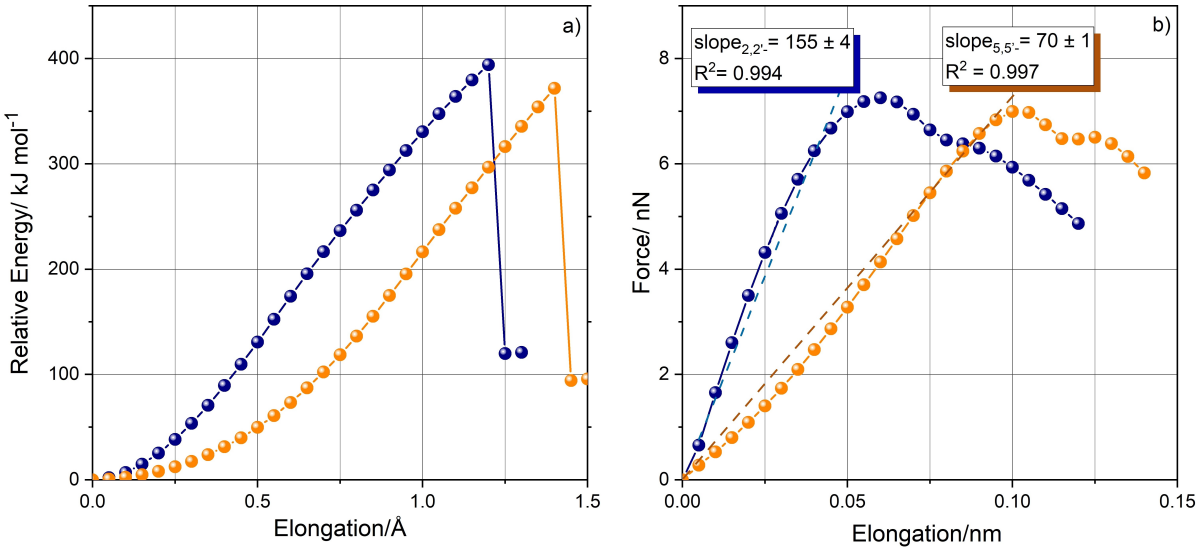


Figure 6. Calculated relative energies of DTE under gradual elongation along its 2,2′- (blue) and 5,5′- (orange) axes (a), and the corresponding forces involved (b).

apart from the 5,5′-DTE is the initial slope, i.e. its Hooke's law 'spring constant'. In essence, the DTE molecule is more than twice stiffer when pulled apart from the inside than from the outside (155 N/m vs. 70 N/m respectively). As a result, the solvodynamic shear forces during sonication can be resisted and transmitted to the rest of the polymer better when applied at the 2,2′- positions, leading to slower ring opening. In addition, PCL polymer bonds could be broken irreversibly during the steeper gradient climb, causing radical-induced mechanophore degradation and thus lower fatigue resistance, which is consistent with our experimental results.

Conclusion

Dithienylethene possesses excellent photochromic properties, which have made it the molecular switch of choice for many applications. Our studies on PCL-functionalized DTEs reveal that it is also a well-behaved mechanophore. Owing to the synthetic ease of preparing the **2,2′-diOH** and **5,5′-diOH** initiators, DTE can be easily incorporated into other polymeric matrices. Similar to dithiomaleimide,[46] spiropyran,[39] and others,[31,41,58] approximately 25 kDa of polycaprolactone attached to the 2,2′- or the 5,5′- positions can transmit sufficient force to facilitate thermally-forbidden ring opening. There is distinct mechano-regiochemistry that we observed between the two isomers, which can be explained by marked differences in the elasticity of DTE depending on the axis of elongation, as predicted by DFT calculations. However, the estimated peak forces of 7 nN to accomplish the retro-6π-electrocyclization greatly surpass reported values for other pericyclic reactions,[13,28,29,34,42,58] so we are currently developing novel soft materials, which will allow us to make direct measurements using single molecule force spectroscopy. Crucially, with our unique DTE-polymer systems, photochemical and mechanical reactions can now be sequentially performed, opening up more venues for exploration, including the development of mechano-photo-reloadable catalytic systems.

Author Contributions

S.P. and M.S. conceived the idea and designed the experiments. M.S. and D.M. synthesized and made measurements on the presented molecules. B.Z. and L.U. conducted the theoretical studies. M.S. and S.P. analyzed the data and wrote the manuscript. All authors discussed the results and agreed on the final interpretations.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: mechanophore · dithienylethene · photoswitchable · CoGEF calculations · lever-arm effect

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