A New Insight into the Fatigue Resistance of Photochromic 1,2-diarylethenes

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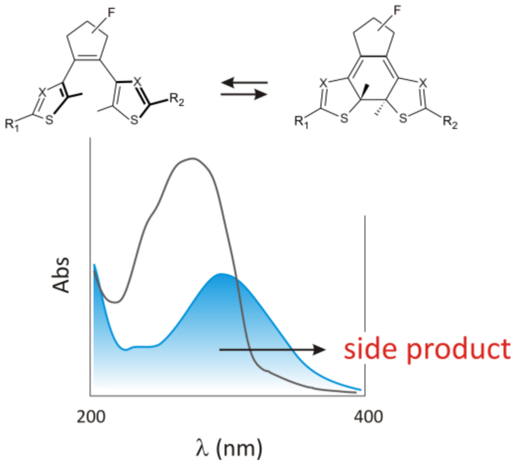
Photochromic diarylethenes represent one of the most important classes of molecular switches, and their fatigue resistance is reported in several papers. Previous studies have demonstrated that the presence of perfluorocyclopentene and methyl in the 4-positions of dithienylethenes improve the switching resistance. However, general guidelines to correlate chemical structure to fatigue resistance have not been found yet. In this work, we provide a different thought in the description of the fatigue resistance of diarylethenes, which is strongly related to the light absorbed by the two isomeric states during photoconversion. For two series of 1,2-diarylethenes, which differ from the aromatic rings without bearing any electroactive substituent, it turns out that their fatigue resistance depends on the dose of light absorbed by the colored form rather than on the specific molecular structure, namely the presence of specific molecular building blocks.

TOC GRAPHICS



KEYWORDS photochromism, diarylethenes, fatigue resistance, UV-vis spectroscopy.

INTRODUCTION

Diarylethenes are one of the most important class of P-type photochromic compounds due to their thermal stability and fatigue resistance, and they have been proposed over the last two decades for many applications such as switches[1], optical memories[2], photosensors[3], and optoelecronic[4] or optical devices[5]. When considering their possible technological applications, photo fatigue resistance has to be taken into account, since a poor resistance leads to a short device lifetime thus preventing the actual use. Despite some diarylethene crystals can undergo up to 10^4 coloration-decoloration cycles without any significant degradation of their photochromic properties[6], it is often observed that loss of performance occurs after a relatively low number of cycles, due to parasitic side reactions[7–9]. This behavior is described considering that the photochromic reaction from A to B produces one or more undesirable by-products C

$$A \rightleftarrows B \rightarrow C$$

The photochemical mechanisms of degradation in diarylethenes were investigated both with experimental and theoretical studies. It was demonstrated that, without oxygen, degradation leads to a condensed structure, whose absorption spectrum shows characteristic bands both in the UV and in the visible range[7]. Other by-products due to oxidation or HF elimination were also observed under prolonged illumination[8]. Moreover, it has been found that degradation occurs starting from the closed ring isomer by UV light absorption through a bicyclohexane intermediate form [10,11]. In first studies, Irie et al. pointed out the importance of introducing a methyl at the 4-position of the thienyl[7] and the better fatigue resistance of benzothiophene with respect to thiophene[12,13]. Recently, Herder et al. suggested that the presence of electron withdrawing substituents could play a role in the fatigue resistance[14].

Despite these studies, no straightforward correlation between the chemical structure and the photo fatigue resistance have been found so far, also considering the two energy barriers involved in the process. It follows that, as a matter of fact, there are a few guidelines for the synthesis of new molecules that consider *a priori* fatigue resistance[6,7,12,14,15].

It is also worth noting that, very often in the literature, the fatigue behavior of photochromic materials is derived from the residual absorption in the visible region (where also the degraded species absorbs, giving a large overestimation of the molecule resistance) CITARE, or from the fraction of degraded molecules after a certain exposure time. This may give very erroneous results as function of the molecular absorption at the exposure wavelength CITARE. A suitable parameter to describe the fatigue resistance and to distinguish between different degradation mechanisms is the quantum yield of degradation CITARE but, as a matter of fact, this is not sufficient to describe the perceived fatigue behavior, i.e. the survived molecules after a defined number of illumination cycles.

Here, we propose an approach to evaluate the fatigue performance of diarylethenes which considers the dose of UV photons actually absorbed by the closed form during the ring closure process. For two series of diarylethenes we demonstrate that the perceived fatigue resistance is strongly dependent on the illumination process and on the absorption characteristics of the molecule, rather than the quantum yield of the degradation reaction.

RESULTS AND DISCUSSION

We considered 1,2-dithienyloctafluorocyclopentenes (T) and 1,2-dithiazolyloctafluorocyclopentenes (Tz) bearing either a symmetrical or asymmetrical phenyl/methylthienyl at the 5−positions of the aryl rings (figure 1). In the literature, some conflicting results are reported on the fatigue resistance of the thiazolyl derivatives[14,16], this heterocycle being originally supposed to give diarylethenes excellent fatigue resistance.

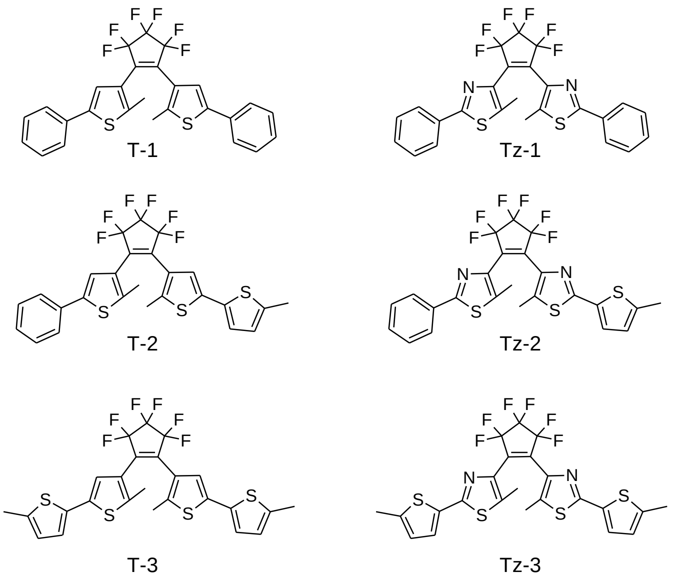
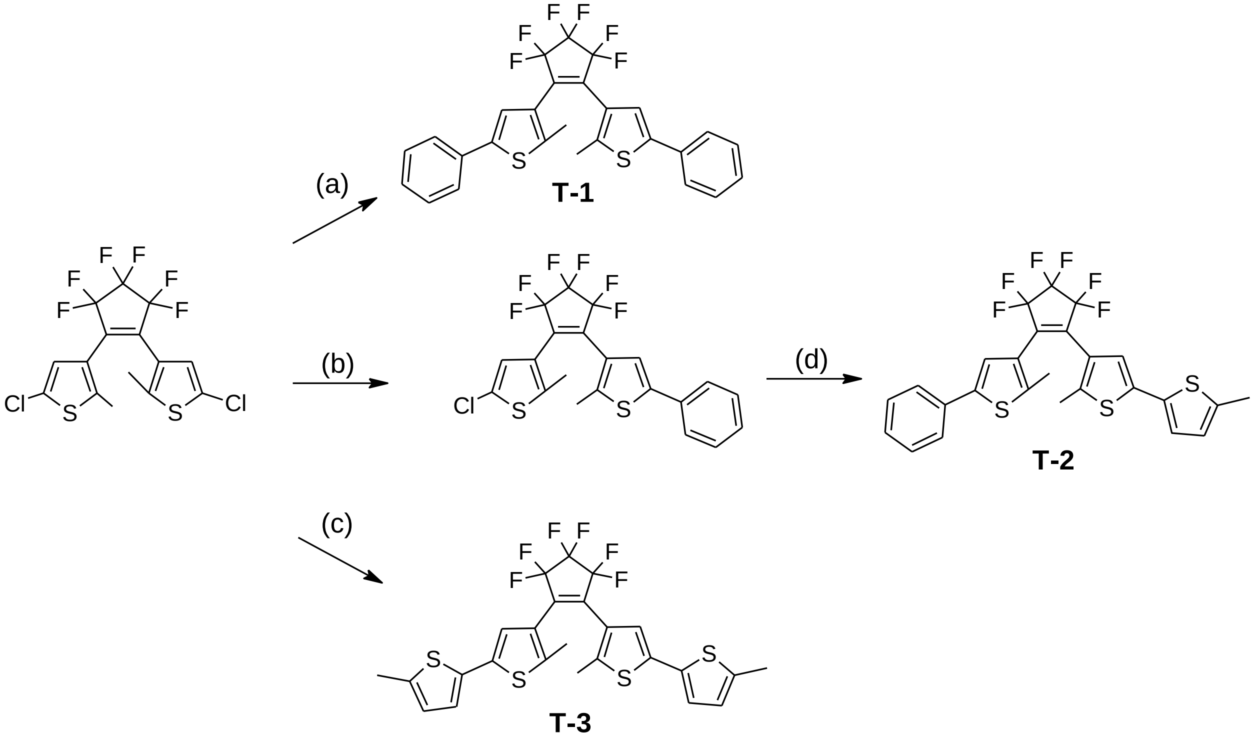


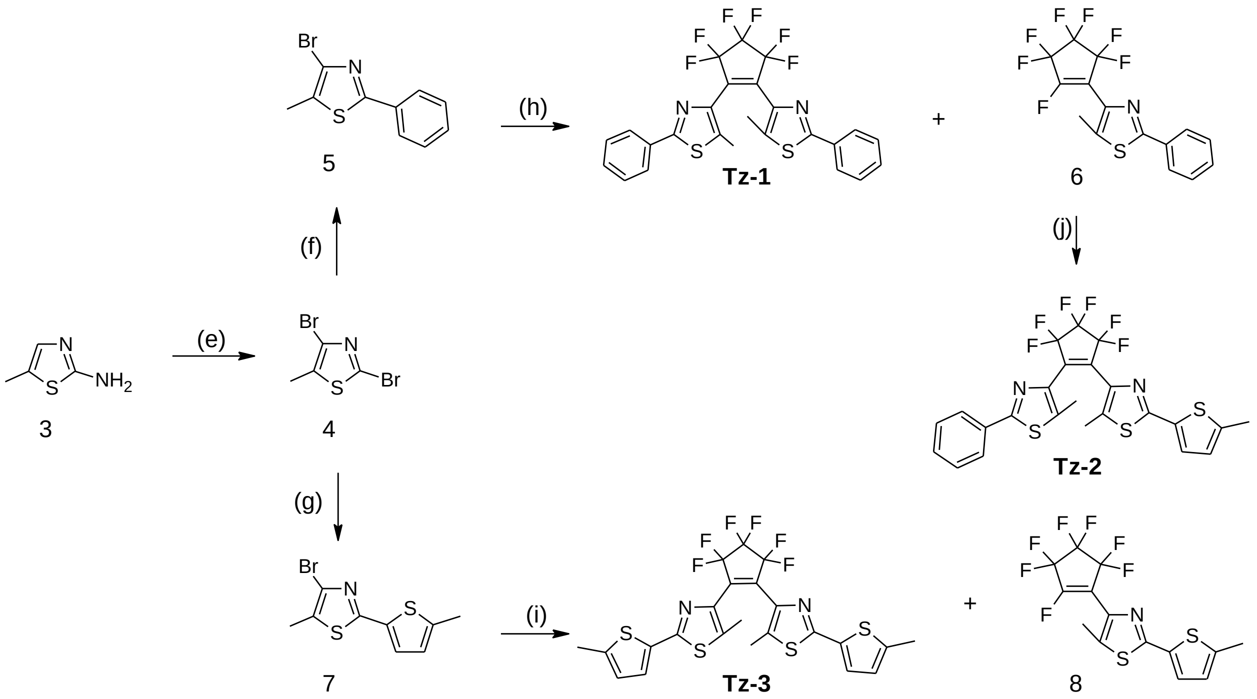
Figure 1. Chemical structure of the diarylethenes herein investigated.

1,2-Dithienylethenes (**T-1**, **T-2**, **T-3**) were synthesized following the route published by Hermes et al.[17] (Scheme 1). The asymmetric compound **T-2** was not obtained following the one-pot method reported in the paper since the resulting mixture of **T-1**, **T-2** and **T-3** could not be purified by flash chromatography with any tested eluent. Accordingly, **T-2** was synthesized in a two-step route starting from the 1,2-bis(2-methyl-5-chloro-3-thienyl)perfluorocyclopentene (**1**).



Scheme 1: Routes for the synthesis of 1,2-dithienylethenes (**T**). Reaction conditions: (a) 2 eq. phenyl boronicacid, $Pd(PPh_3)_4$, DME, H2O, K_2CO_3; (b) 1 eq. phenyl boronicacid, $Pd(PPh_3)_4$, DME, H_2O, K_2CO_3; (c) 2 eq. 5-methylthiophene-2-boronic acid pinacolester, $Pd(PPh_3)_4$, DME, H_2O, K_2CO_3; (d) 1 eq. 5-methylthiophene-2-boronic acid pinacolester, $Pd(PPh_3)_4$, DME, H_2O, K_2CO_3.

The same approach was firstly followed to synthesize the 1,2-dithiazolylethenes (**Tz**), where the 2-chloro-5-methylthiazole was obtained through a Sandmeyer reaction starting from the corresponding amine (**3**). However, the reaction was characterized by a low yield. Therefore, a one pot Sandmeyer-bromination reaction was performed as a first step to give the 2,4-dibromo-5-methylthiazole (**4**). Suzuki coupling between **4** and the aryl boronate (phenyl boronic acid or 5-methylthiophene-2-boronic acid pinacolester), followed by the Dixon reaction gave compounds **5** and **7**. The asymmetric compound **Tz-2** was obtained through two sequential Dixon reactions (Scheme 2). Details are reported in the S.I..



Scheme 2: Routes for the synthesis of 1,2-dithiazolylethenes (**Tz**). Reaction conditions: (e) H_3PO_4, HNO_3, $NaNO_2$, H_2O, CuBr, HBr; (f) 1 eq. phenyl boronicacid, $Pd(PPh_3)_4$, DME, H_2O, K_2CO_3; (g) 1 eq. 5-methylthiophene-2-boronic acid pinacolester, $Pd(PPh_3)_4$, DME, H_2O, K_2CO_3; (h, i) THF, BuLi, -78°C, C_5F_8; (j) THF, **7**, BuLi, -78°C.

All the synthesized diarylethenes were characterized by UV-vis absorption spectroscopy in non-degassed n-hexane solution. Data are reported in Table 1 together with the absorption maxima and absorption coefficients in the visible of the by-products C. Comparison between the series of 1,2-dithienylethenes (**T**) and 1,2-dithiazolylethens (**Tz**) shows that the latters have red-shifted absorption maxima in the open form. This finding can be ascribed to the smaller steric hindrance of nitrogen compared to the CH in the 4-position of thiophene, which leads to a more planar structure (i.e. lower torsional angle between thiazole and phenyl). At the opposite, the absorption maxima of the closed forms of 1,2-dithiazolylethenes are blue-shifted due to the aromaticity of the thiazolyl, which makes less effective the conjugation length.

Table 1. Absorption maxima and related absorption coefficients of the A and B isomers in hexane, forward (Φ_{AB}) quantum yield at an irradiation wavelength corresponding to an isosbestic point between the open and the closed forms, and backward (Φ_{BA}) quantum yield at an irradiation wavelength corresponding to the maximum absorbance of the closed isomer. Absorption maxima (λ_C) and absorption coefficients (ε_C) of the by-products C. All the parameters have been measured for non-degassed solutions.

	λ_A (nm)	ε_A (M^{-1} cm^{-1})	λ_B (nm)	ε_B (M^{-1} cm^{-1})	Φ_{AB} λ_{exc} (nm)	Φ_{BA} @ λ_B	λ_C (nm)	ε_C (M^{-1} cm^{-1})
T-1	278	34700	580	14900	0.63 305	0.010	545	8700
T-2	282	30800	587	15400	0.65 330	0.015	558	10600
T-3	318	32500	598	19800	0.62 334	0.011	573	11500
Tz-1	301	30600	525	10700	0.58 308	0.006	531	8300
Tz-2	316	23700	534	11800	0.69 335	0.007	544	8500
Tz-3	329	37300	550	19400	0.44 341	0.003	559	12500

Within the same series, a progressive redshift occurs in both forms by replacing the lateral phenyl with one or two methylthiophenes. Indeed, it is known that thiophene leads to a more effective conjugation, due to both lower inter-ring torsional angles and a less-aromaticity of thienyl with respect to phenyl. Concerning the quantum yields, they show the typical behaviour of diarylethenes, where the forward quantum yield is determined by the dynamic equilibrium between the parallel and antiparallel conformers, and the backward quantum yield is two or three order of magnitudes lower.

Resistance to irradiation of the compounds was determined in non-degassed n-hexane solutions ($1 \div 3\ 10^{-5}$ M) using the apparatus described in the S.I.

Two different illumination conditions were applied, namely the *cycling mode* and the *continuous mode*. *Cycling mode* is the usual method employed to determine the fatigue resistance of photochromic compounds, consisting in the subsequent illumination with UV and visible light. The uncoloured solutions were exposed to UV light (311 nm) and then exposed to visible light (>500 nm) up to the complete colour bleaching. The procedure was repeated for a given number of times. Exposure times were determined monitoring the absorbance of the sample in the visible during the conversion up to 90% of the PSS during coloration (pseudo-PSS) and 99.9% of conversion after bleaching. The wavelength of the monitoring beam was tuned to match the absorption maximum in the visible region for each investigated molecules. The conversion kinetics was measured also at the end of the cycling, to rule out any significant variation due to the presence of the by-product. Solution concentrations and characteristic coloration times for the *cycling mode* are reported in the S.I. In the *continuous mode*, the transparent solution was exposed to UV light only (311 nm), for a time equivalent to a given number of cycles.

Usually, fatigue in diarylethenes is evidenced as the absorbance decrease in the visible region upon UV illumination[6,19]. Actually, since the parasitic C species may also absorb in the visible, the decrease in absorption due to the decreasing of B is partially compensated by the absorption of C. For a correct description of the fatigue resistance, we considered the fraction of active molecules after a given illumination time as the best parameter. The fraction of active molecules χ_{act} at the n^{th} cycle can be calculated from the absorption of the solution before and after the coloration and bleaching at any illumination cycle, as follows:

$$\chi_{act} = \frac{Abs_1^n - Abs_2^n}{Abs_1^0 - Abs_2^0} \quad (1)$$

where Abs represents the absorbance at the Lambert-Beer regime, superscripts indicate the cycle number (0 is the initial state before any irradiation run), subscript 1 and 2 refer to the absorbance after coloration and bleaching of the photochromic sample at the monitoring wavelength in the visible region, respectively (the derivation is reported in the S.I). This approach allows for eliminating the absorption of the degraded species, which contributes to the total absorption, hence it provides the actual number of active photochromic molecules of the sample. Moreover, this equation is valid either for a partial conversion (pseudo-PSS) or for the achievement of the PSS. Notably, reflectance and baseline errors are also eliminated. The comparison between the present approach and the standard method that considers the total absorption is highlighted in figure 2. The consistency of our measurement and approach with the data reported in the literature for **T-1**[7] is also noticeable.

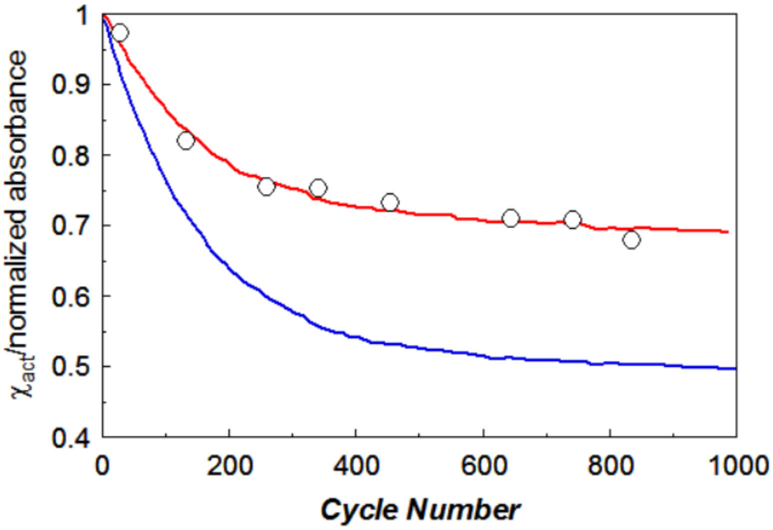


Figure 2. Fraction of active molecules for **T-1** as evaluated with the present approach (blue line) and the standard method (red line), which does not disentangle the contribution of the degraded species from the total absorption in the visible. The white circles represent the experimental data reported by Irie *et al.*[7]

The fatigue behaviour under *cycling mode* of the two series of molecules here considered is reported in Figure 3, which shows the fraction of active molecules (χ_{act}) as a function of the number of cycles. Measurements were performed with both non-degassed and argon saturated solutions, but no significant difference was found up to 100 cycles. This behaviour is consistent with the fact that only one major by-product is formed for short illumination periods, independently of the presence of oxygen[8,14]. Oxidative or elimination by-products were found only for prolonged illuminations[8].

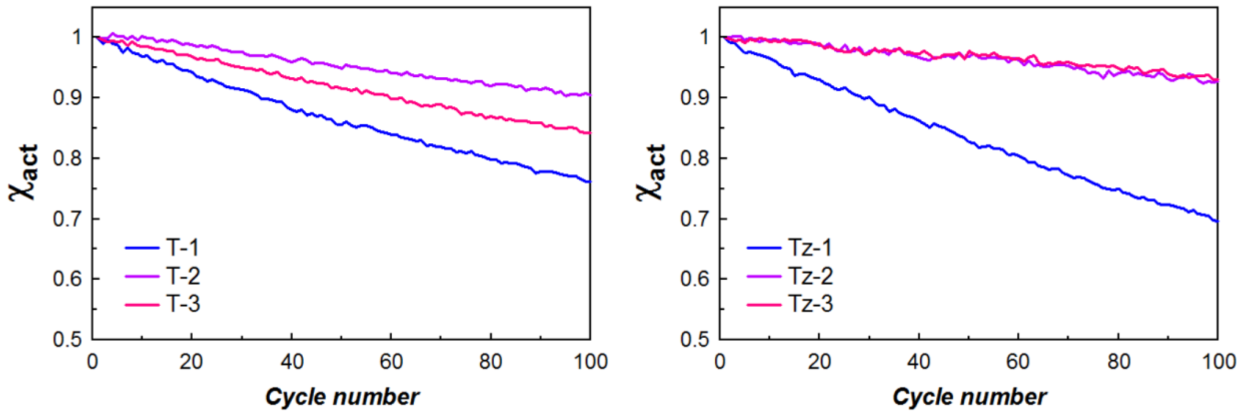


Figure 3. Fraction of active molecules as a function of the cycle number in cycling mode (λ_{UV}=311 nm) for **T** and **Tz**.

For both the **T** and **Tz** classes, replacing phenyls with thiophenes at the 5–position of the aryl rings leads to a better fatigue resistance. This is an indication that a that larger spectral separation between the open and closed isomers could increase the fatigue resistance. However, no homogeneous trend is evidenced within the **T** and the **Tz** series, which does not allow for a rationalization of the light-induced fatigue related to the specific chemical structure. Moreover, despite **Tz-2** and **Tz-3** are more resistant than analogous **T** derivatives (i.e. **T-2** and **T-3**), **Tz-1** shows the worst performance. This leads to the hypothesis that thiazole does not univocally improve the fatigue resistance of 1,2-diarylethenes.

The spectrum of the degraded by-product was obtained as difference between the spectra at the initial cycle and after bleaching at the final cycle, and the molar extinction coefficient ε_C was also calculated (see S.I). Absorption maxima of the by-products in the visible (see table 1) are blue-shifted of about 30 nm for dithienylethenes (**T**) and red-shifted of less than 10 nm for dithiazolylethenes (**Tz**) with respect to the corresponding closed-ring isomer (Table 1). This is a peculiar feature that has been previously observed on perhydrocyclopentene derivatives but not on perfluorocyclopenetenes[14]. As for the molar extinction coefficient of the by-products in the visible, it is about 0.6 – 0.8 of the absorption coefficient of the closed form for the different molecules.

All the diarylethenes were also analysed in the *continuous mode*, and the same equation to retrieve χ_{act} was applied by considering as illumination time an equivalent time at determined numbers of cycles. Therefore, the measurement is expressed as a function of an equivalent cycle number, where the light dose absorbed by the ring-closed isomer in the *continuous mode* corresponds to the dose absorbed during the same number of cycles in the *cycling mode*. The procedure for calculating the equivalent cycle number is reported in the S.I. and the results at 80 cycles are reported in table 2.

Table 2. Fraction of active molecules after 80 equivalent cycles in the two testing modes.

Molecule	χ_{act} at 80 equivalent cycles	
	Cycling mode	Continuous mode
T-1	0.80	0.79
T-2	0.87	0.87
T-3	0.92	0.94
Tz-1	0.75	0.80
Tz-2	0.97	0.96
Tz-3	0.95	0.97

A comparison between the *cycling mode* measurements and the *continuous mode* allows to experimentally determine whether the by-product formation preferentially occurs during the photochromic reaction or from the UV absorption of the closed-ring isomer. If degradation takes place during the photochromic reaction as a parasitic pathway, the fatigue in *cycling mode* will be larger than in *continuous mode*, since the system is periodically switched between the A and B forms. On the contrary, if the degradation basically takes place from the B species, the fatigue in *cycling mode* will be less intense.

In the present case, values obtained in the *continuous mode* did not show any significant difference, leading to the conclusion that the same chemical species is formed as a by-product for the two test modes, through the absorption of UV photons by the closed-ring isomer. This is actually consistent with the evidence already reported in the literature[8].

Therefore, considering the central role of the UV light absorption of the B form in the loss of performance of these photochromic switches, we considered the relative absorption cross-section of the two isomeric states at the coloration wavelength (i.e. 311 nm). The $\varepsilon_B/\varepsilon_A$ ratio at the illumination wavelength (at 311 nm) and the fraction of degraded molecules $\chi_D = 1- \chi_{act}$ after 80 cycles in the *cycling mode* are reported in figure 4.

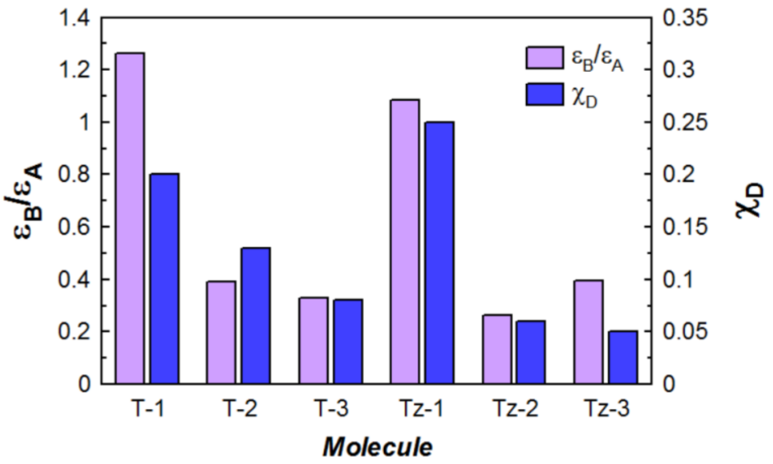


Figure 4. Ratios between the extinction coefficients of the B and A forms ($\varepsilon_B/\varepsilon_A$) at 311 nm and the fraction of degraded molecules (χ_D) at 80 cycles in *cycling mode* (λ_{UV}=311 nm).

Interestingly, a correlation between the ratio $\varepsilon_B/\varepsilon_A$ and the photo fatigue resistance was found. Specifically, if the ratio $\varepsilon_B/\varepsilon_A$ is low, the cross-section of the species in the open form is more relevant, thus the absorption to promote the ring-closing is preferred over the residual absorption of the colored form. Conversely, if the ratio $\varepsilon_B/\varepsilon_A$ is large, a consistent amount of the incident light is absorbed by the closed-ring isomer, making degradation more effective. A small value of this ratio can be related to both a separation in wavelength of the absorption bands in the UV of the open and closed forms (molecules **T-3** and **Tz-3**) or to a general lowering of the absorption bands in the UV by the closed form (molecule **T-2** and **Tz-2**).

Starting from this new insight, the fraction of degraded species was also related to the specific light dose (number of photons per molecule) absorbed by the closed-ring isomer in one cycle (the light dose was calculated taking into account the kinetics of conversion during illumination, see S.I. for details). For all the investigated diarylethenes, a linear correlation between the specific UV dose and the fraction of degraded molecules exists (Figure 5).

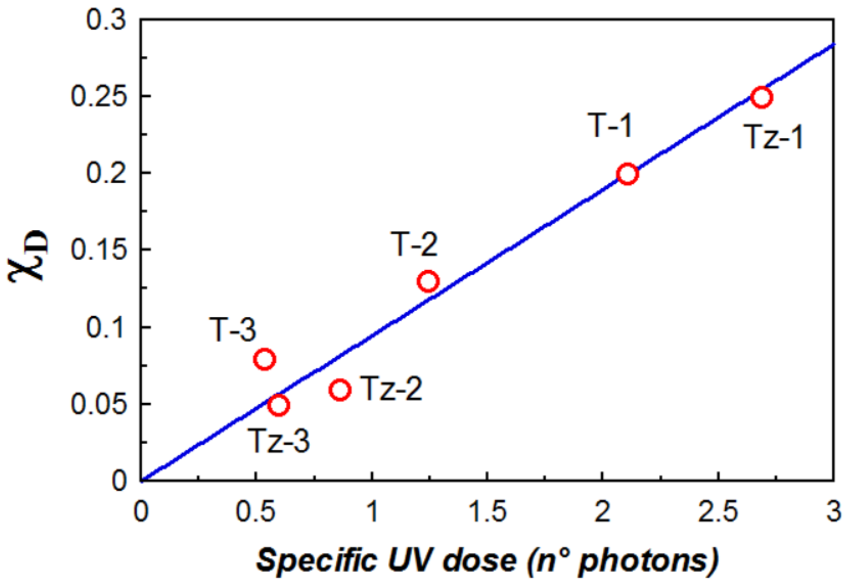


Figure 5. Fraction of degraded molecules χ_D versus the specific dose absorbed by the closed-ring isomer after 80 cycles (λ_{UV}= 311 nm).

It is worth pointing out that the rate of formation of the by-product is proportional to the number of UV photons absorbed by the closed form times the quantum yield of the side reaction. Since a linear relationship is obtained we can considered that the quantum yield of the side reaction is similar for all the derivatives at 311 nm. Similar values of the quantum yield of the side reaction are also reported in the literature when diarylethenes with similar structure are considered[14]. Therefore, the absorption properties of the investigated molecules at the exposure wavelength are definitely of great importance in the definition of their fatigue behaviour. Since different $\varepsilon_B/\varepsilon_A$ ratios may be easily found for any compound by changing the illumination wavelength of the fatigue test, we considered to perform measurements at a different wavelength (λ_{UV}=370 nm) to further confirm that the $\varepsilon_B/\varepsilon_A$ ratio is a figure of merit to evaluate the fatigue resistance of diarylethenes. In particular, analysing the UV-vis spectra of all the molecules here investigated, we chose **T-3** and **Tz-3**, showing a ratio $\varepsilon_B/\varepsilon_A$ lower than one at 311 nm and much larger than one at 370 nm. The absorption spectra in both isomeric states of **T-3** and **Tz-3** are shown in figure 6.

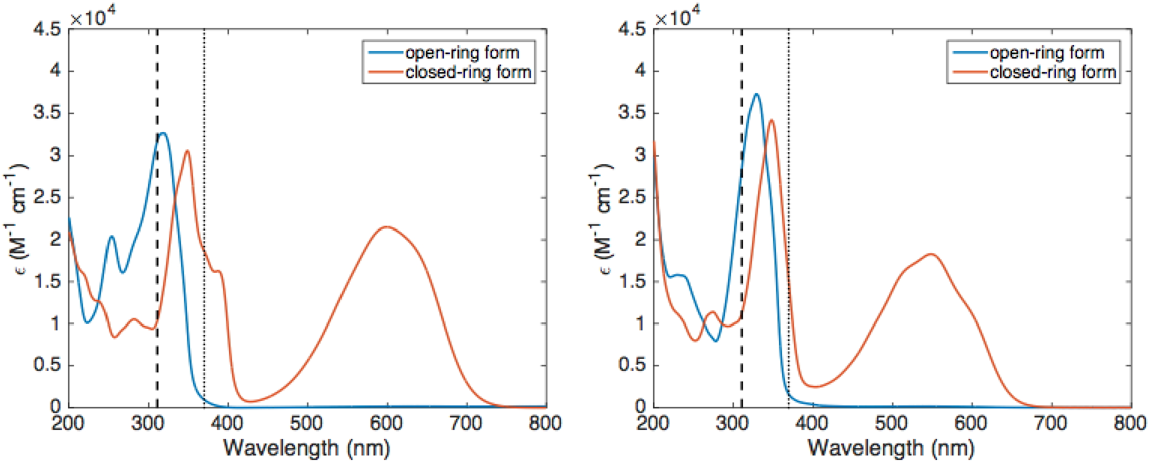


Figure 6. Molar extinction coefficients for the A and B forms of **T-3** (left) and **Tz-3** (right). Values at 311 and 370 nm are evidenced by dashed and dotted lines, respectively. For both cases, the ratio $\varepsilon_B/\varepsilon_A$ remarkably increases going from 311 to 370 nm.

The results of fatigue tests irradiating at 370 nm in both *cycling* and *continuous modes* at 80 cycles (or equivalent cycles) for **T-3** and **Tz-3** are shown in table 3, and compared with data obtained at 311 nm. Despite the lower energy of photons at 370 nm than at 311 nm, which would suggest a better material durability, an impressive decrease in fatigue resistance is clearly visible, meaning that the absolute amount of by-product formed after a specific irradiation time is much larger at 370 nm than at 311 nm. Worth noting, **T-3** and **Tz-3** are two diarylethenes showing high fatigue resistance at 311 nm. Supposing a constant by-product formation quantum yield as function of the exposure wavelength, the strong difference in the fatigue resistance is ascribed to the very different absorption properties of the B form at the two exposure wavelengths. In fact, when the absorption coefficient of the B form is large, more photons are absorbed by B up to reach the PSS state, increasing the effect of degradation. Accordingly, very low degradation takes place if the absorption of the B form at the absorption wavelength is negligible.

Table 3. Fraction of active molecules χ_{act} after 80 cycles for molecules **T-3** and **Tz-3** at different exposure wavelengths.

Molecule	311 nm		370 nm	
	$\varepsilon_B/\varepsilon_A$	χ_{act} *cycling/continuous mode*	$\varepsilon_B/\varepsilon_A$	χ_{act} *cycling/continuous mode*
T-3	0.330	0.92/0.94	23.6	0.50/0.52
Tz-3	0.395	0.95/0.97	9.3	0.65/0.72

CONCLUSIONS

The fatigue resistance of two series of diarylethenes that differ in the nature of the heterocycles linked to the perfluorocyclopentene was investigated, and results indicated that thiazole cannot be univocally ascribed to improve resistance to photo-degradation.

We confirmed that the phenomenon of photo fatigue in these diarylethenes occurs from the colored form and we demonstrated that a clear relationship between the fraction of degraded molecule and the UV dose absorbed by the colored form exists. Consequently, the fatigue resistance depends on the cross section of the open- and closed-ring isomers at the illumination wavelength, rather than on their specific chemical structure. At least for the species herein considered, $\varepsilon_B/\varepsilon_A$ ratio can be assumed as a figure of merit to determine fatigue resistance, especially when molecules exhibit similar quantum yield of the degradation reaction. In this framework, the presence of an external thienyl instead of a phenyl increases the fatigue resistance, since there is a separation of the absorption bands in the visible for the open and closed form, and it is possible to find an UV wavelength for which the $\varepsilon_B/\varepsilon_A$ is small.

This finding is of great importance for the practical use of photochromic materials since, given a specific UV illumination source, chromophores can be screened *a priori* on the basis of the $\varepsilon_B/\varepsilon_A$ ratio. Alternatively, it allows for the selection of the best UV wavelength to convert a given photochromic molecule to the closed-ring form achieving at the same time the best photo fatigue resistance.

ASSOCIATED CONTENT

Supporting Information. Details of the material synthesis, mathematical derivation, measurement setup, and measurement results are reported in the Supporting Information.

ACKNOWLEDGMENT

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