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Authors	PARIANI, Giorgio, Quintavalla, Martino, Colella, Letizia, OGGIONI, LUCA, Castagna, Rossella, Ortica, Fausto, Bertarelli, Chiara, BIANCO, ANDREA
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New Insight into the Fatigue Resistance of Photochromic 1,2-Diarylethenes

Giorgio Pariani,[†] Martino Quintavalla,[†] Letizia Colella,^{†,‡} Luca Oggioni,^{†,‡} Rossella Castagna,^{‡,§} Fausto Ortica,^{§,||} Chiara Bertarelli,^{‡,⊥} and Andrea Bianco^{*,†,§}

[†]INAF Osservatorio Astronomico di Brera, via Bianchi 46, 23807 Merate, Italy

[‡]Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano, Piazza L. Da Vinci 32, 20133 Milano, Italy

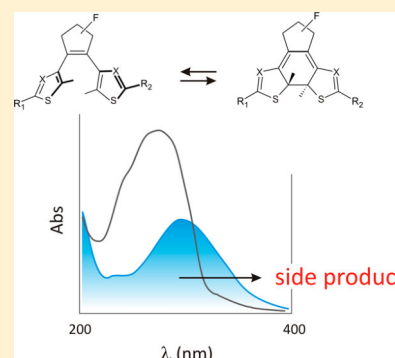
[§]Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, via Elce di Sotto, 06123 Perugia, Italy

^{||}Istituto Nazionale di Fisica Nucleare (INFN), Sezione di Perugia, Via Pascoli, 06123 Perugia, Italy

[⊥]Center for Nanoscience and Technology@PoliMi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy

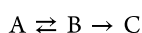
Supporting Information

ABSTRACT: 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 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.



INTRODUCTION

Diarylethenes are one of the most important classes 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 optoelectronic⁴ or optical devices.⁵ When considering their possible technological applications, photofatigue resistance has to be taken into account since a poor resistance leads to a short device lifetime, thus preventing the actual use. Despite that some diarylethene crystals can undergo up to 10⁴ 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 byproducts C



The photochemical mechanisms of degradation in diarylethenes were investigated with both 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 byproducts 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 thienyl⁷ 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 photofatigue resistance has 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, often in the literature, the fatigue behavior of photochromic materials could be overestimated due to a possible contribution of the degraded species to the total absorption in the visible region.^{6,7,13,16} A suitable parameter to describe the fatigue resistance and to distinguish between different degradation mechanisms is the quantum yield of degradation,¹⁷ 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.

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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, i.e., UV wavelength, and on the absorption characteristics of the molecule at this wavelength, besides 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. Note that the six derivatives do not show the presence of any lateral electroactive chemical group that can play a role in the fatigue mechanism and resistance.

1,2-Dithienylethenes (**T-1**, **T-2**, **T-3**) were synthesized following the route published by Hermes et al.¹⁸ (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, again starting from the 1,2-bis(2-methyl-5-chloro-3-thienyl)perfluorocyclopentene (**1**).

The same approach was first 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**.¹⁸ The asymmetric compound **Tz-2** was obtained through two sequential Dixon reactions (Scheme 2). Details are reported in the SI.

All the synthesized diarylethenes were characterized by UV-vis absorption spectroscopy in *n*-hexane (used as received) solutions. Data are reported in Table 1 together with the absorption maxima and absorption coefficients in the visible of the byproducts C. Comparison between the series of 1,2-dithienylethenes (**T**) and 1,2-dithiazolylethenes (**Tz**) shows that the latter 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

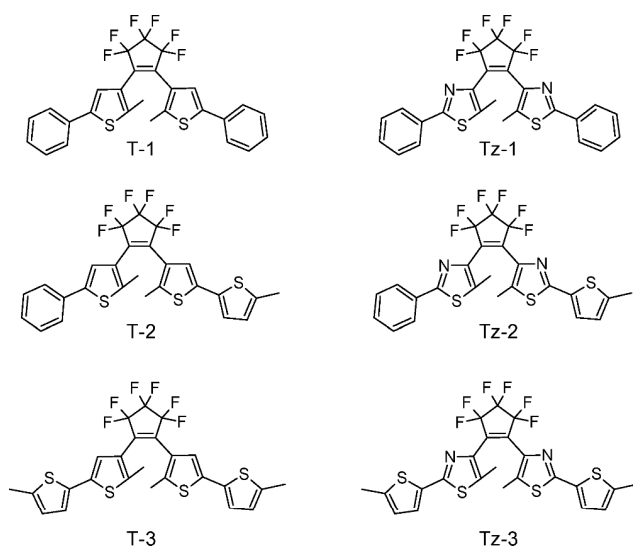
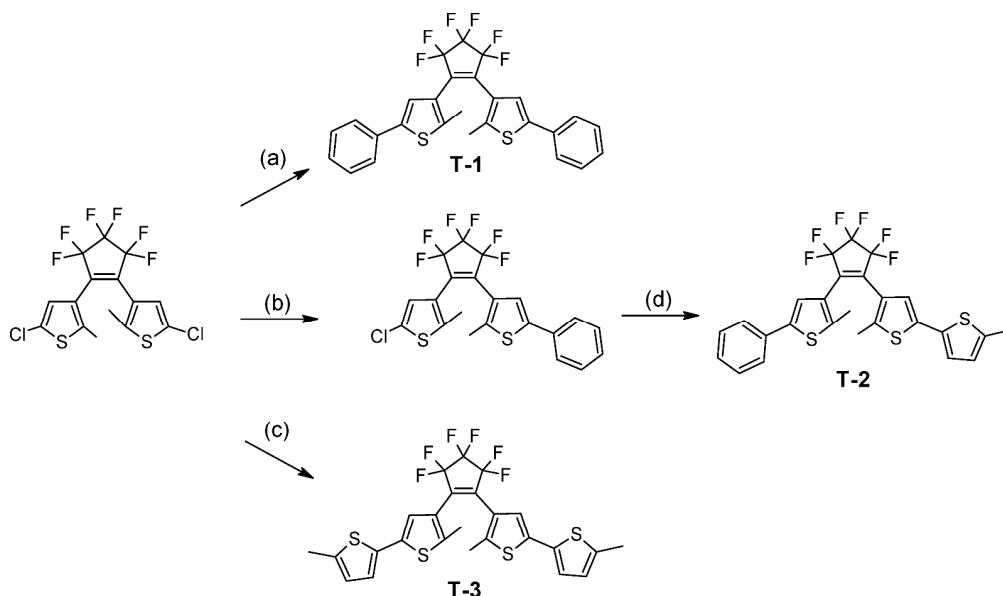
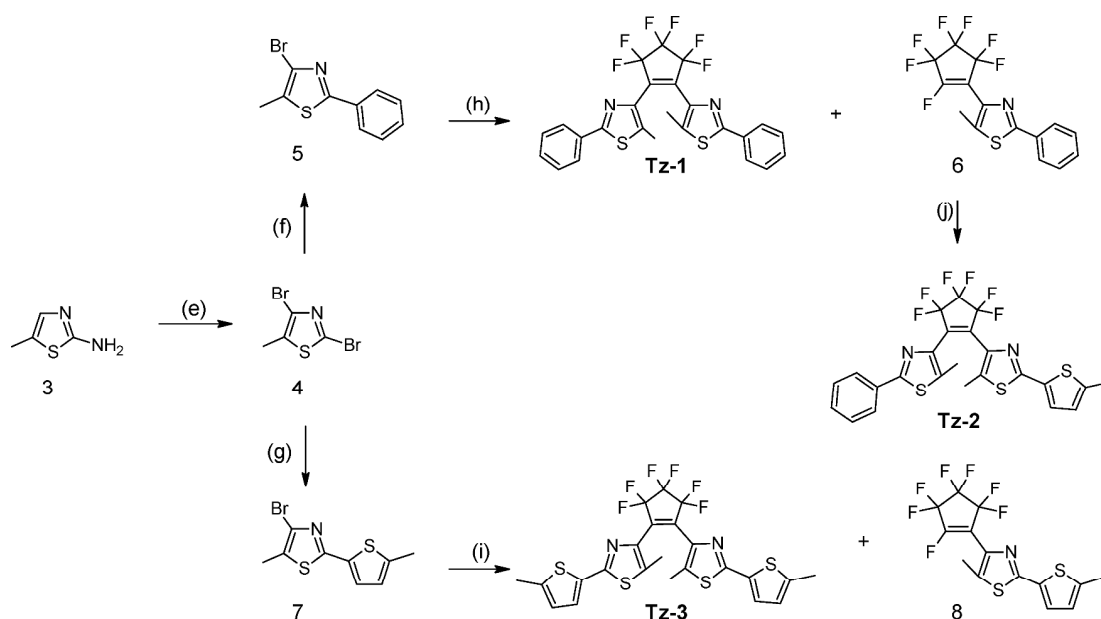


Figure 1. Chemical structure of the diarylethenes herein investigated.

Scheme 1. Routes for the Synthesis of 1,2-Dithienylethenes (**T**)^a



^aReaction conditions: (a) 2 equiv of phenyl boronic acid, Pd(PPh₃)₄, DME, H₂O, K₂CO₃; (b) 1 equiv of phenyl boronic acid, Pd(PPh₃)₄, DME, H₂O, K₂CO₃; (c) 2 equiv of 5-methylthiophene-2-boronic acid pinacolester, Pd(PPh₃)₄, DME, H₂O, K₂CO₃; (d) 1 equiv of 5-methylthiophene-2-boronic acid pinacolester, Pd(PPh₃)₄, DME, H₂O, K₂CO₃.

Scheme 2. Routes for the Synthesis of 1,2-Dithiazolylenes (Tz)^a

^aReaction conditions: (e) H_3PO_4 , HNO_3 , NaNO_2 , H_2O , CuBr , HBr ; (f) 1 equiv of phenyl boronic acid, $\text{Pd}(\text{PPh}_3)_4$, DME , H_2O , K_2CO_3 ; (g) 1 equiv of 5-methylthiophene-2-boronic acid pinacolester, $\text{Pd}(\text{PPh}_3)_4$, DME , H_2O , K_2CO_3 ; (h), (i) THF , BuLi , -78°C , C_5F_8 ; (j) THF , 7, BuLi , -78°C .

Table 1. Absorption Maxima and Related Absorption Coefficients of the A and B Isomers in Hexane, Forward (Φ_{AB}) Quantum Yield at the Irradiation Wavelength Corresponding to the Isosbestic Point between the Open and the Closed Forms, and Backward (Φ_{BA}) Quantum Yield at the Irradiation Wavelength Corresponding to the Absorption Maximum of the Closed Isomer^a

	λ_{A} (nm)	ϵ_{A} ($\text{M}^{-1} \text{cm}^{-1}$)	λ_{B} (nm)	ϵ_{B} ($\text{M}^{-1} \text{cm}^{-1}$)	Φ_{AB} λ_{exc} (nm)	Φ_{BA} @ λ_{B}	λ_{C} (nm)	ϵ_{C} ($\text{M}^{-1} \text{cm}^{-1}$)
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

^aAbsorption maxima (λ_{C}) and absorption coefficients (ϵ_{C}) of the byproducts C.

120 angle between thiazole and phenyl). At the opposite, the
121 absorption maxima of the closed forms of 1,2-dithiazolylenes
122 are blue-shifted due to the aromaticity of the thiazolyl, which
123 makes less effective the conjugation length.

124 Within the same series, a progressive redshift occurs in both
125 forms by replacing the lateral phenyl with one or two
126 methylthiophenes. Indeed, it is known that thiophene leads
127 to a more effective conjugation, due to both lower inter-ring
128 torsional angles and less aromaticity of thienyl with respect to
129 phenyl. Concerning the quantum yields, they show the typical
130 behavior of diarylethenes, where the forward quantum yield is
131 determined by the dynamic equilibrium between the parallel
132 and antiparallel conformers and the backward quantum yield is
133 2 or 3 orders of magnitude lower.

134 Resistance to irradiation of the compounds was determined
135 in *n*-hexane solutions ($1 \pm 3 \times 10^{-5}$ M) using the apparatus
136 described in the SI. Two different illumination conditions were
137 applied, namely, the *cycling mode* and the *continuous mode*.
138 *Cycling mode* is the usual method employed to determine the
139 fatigue resistance of photochromic compounds, consisting of
140 the subsequent illumination with UV and visible light. The
141 uncolored solutions were exposed to UV light (311 nm) and
142 then exposed to visible light (>500 nm) up to the complete

color bleaching. The procedure was repeated for a given
number of times. Exposure times were determined by
monitoring the absorbance of the sample in the visible during
the conversion of 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 byproduct. Solution concentrations and
characteristic coloration times for the *cycling mode* are reported
in the SI. 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 illumina-
tion.^{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 reference 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

$$\chi_{\text{act}} = \frac{\text{Abs}_1^n - \text{Abs}_2^n}{\text{Abs}_1^0 - \text{Abs}_2^0} \quad (1)$$

where Abs represents the absorbance at the Lambert–Beer regime; superscripts indicate the cycle number (0 is the initial state before any irradiation run); and subscripts 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 SI). 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-1⁷ is also noticeable.

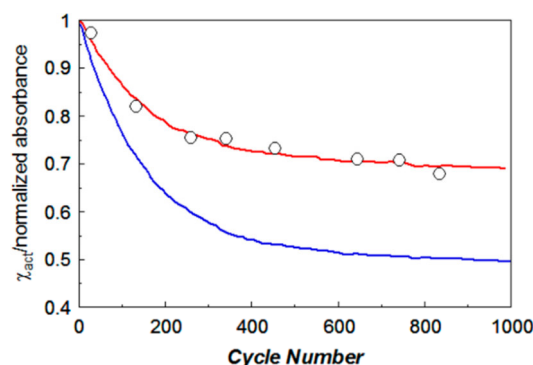


Figure 2. Fraction of active molecules for T-1 as evaluated with the present approach (blue line) and the standard method (red line), which does not disentangle the contribution of the degraded species from the total absorption in the visible. The white circles represent the experimental data reported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

The fatigue behavior 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 both in argon-saturated solutions and in solutions with as-received

solvent, but no significant difference was found up to 100 cycles. This behavior is consistent with the fact that only one major byproduct is formed for short illumination periods, independently of the presence of oxygen,^{8,14} which likely is the condensed derivative observed in similar molecules.⁷ In fact, oxidative or elimination byproducts were found preferentially in aerated solution for prolonged exposures only.⁸

For both the T and Tz classes, replacing phenyls with thiophenes at the 5-position of the aryl rings leads to an increase of 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 that 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 unequivocally improve the fatigue resistance of 1,2-diarylethenes.

The spectra of the degraded byproducts were obtained as difference between the spectra at the initial cycle and after bleaching at the final cycle, and the molar extinction coefficients ϵ_C were also calculated (see SI). Absorption maxima of the byproducts in the visible (see Table 1) are blue-shifted about 30 nm for dithienylethenes (T) and red-shifted less than 10 nm for dithiazolylenes (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 perfluorocyclopentenones.¹⁴ As for the molar extinction coefficient of the byproducts 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 analyzed in the *continuous mode*, and the same equation to retrieve χ_{act} was applied by considering as illumination time an equivalent time at a 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 corresponding number of cycles in the *cycling mode*. The procedure for calculating the equivalent cycle number is reported in the SI, and the results at 80 cycles are reported in Table 2.

A comparison between the *cycling mode* measurements and the *continuous mode* allows us to experimentally determine whether the byproduct 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

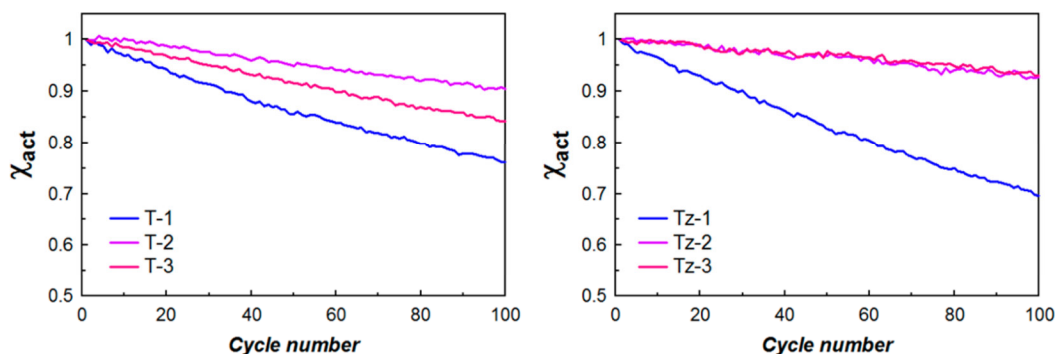


Figure 3. Fraction of active molecules as a function of the cycle number in cycling mode ($\lambda_{\text{UV}} = 311$ nm) for T and Tz.

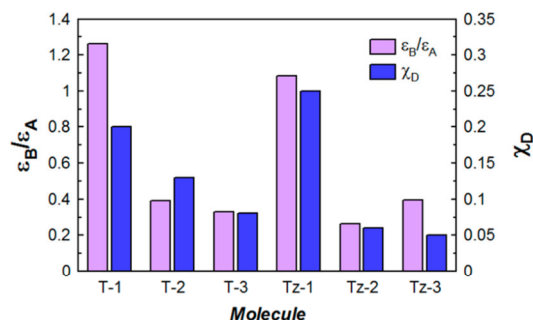
Table 2. Fraction of Active Molecules after 80 Equiv Cycles in the Two Testing Modes

molecule	χ_{act} at 80 equiv 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

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 byproduct 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

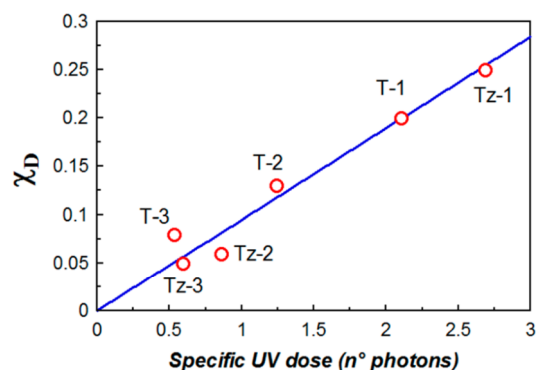
Therefore, considering the central role of the UV light absorption of the B form in the loss of performance of these photochromic switches, we considered the relative absorption cross-section of the two isomeric states at the coloration wavelength (i.e., 311 nm). The ϵ_B/ϵ_A ratio at the illumination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

Interestingly, a correlation between the ratio ϵ_B/ϵ_A and the photofatigue resistance was found. Specifically, if the ratio ϵ_B/ϵ_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 ϵ_B/ϵ_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 the wavelength of the absorption bands in the UV of the open and closed forms (as for molecules T-3 and Tz-3) or to a general lowering of the absorption bands in the UV by the closed form (as for molecule T-2 and Tz-2). In both cases, the ratio is a function of the chemical structure of the specific photochromic derivative.

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 SI for details). For 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 ($\lambda_{\text{UV}} = 311$ nm).

It is worth pointing out that the formation rate of the byproduct 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 conclude 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 (i.e., same bridge) and without electroactive substituents 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 behavior. Since different ϵ_B/ϵ_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 ($\lambda_{\text{UV}} = 370$ nm) to further confirm that the ϵ_B/ϵ_A ratio is a figure of merit to evaluate the fatigue resistance of diarylethenes. In particular, analyzing the UV-vis spectra of all the molecules here investigated, we chose T-3 and Tz-3, showing a ratio ϵ_B/ϵ_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.

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. Worth noting, T-3 and Tz-3 are two diarylethenes showing high fatigue resistance at 311 nm. Assuming a similar byproduct formation quantum yield as a 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 exposure UV wavelength is negligible. This phenomenon is responsible for

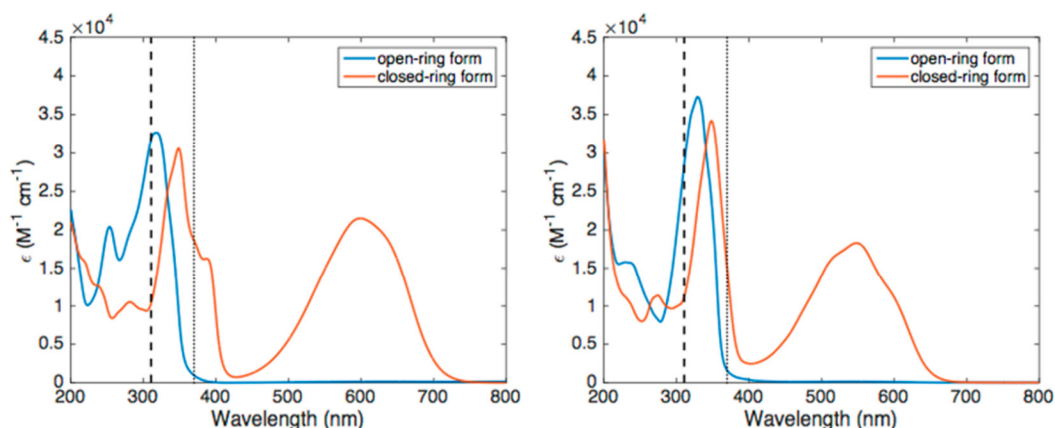


Figure 6. Molar extinction coefficients for the A and B forms of T-3 (left) and Tz-3 (right). Values at 311 and 370 nm are evidenced by dashed and dotted lines, respectively. For both cases, the ratio ϵ_B/ϵ_A remarkably increases going from 311 to 370 nm.

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	
	ϵ_B/ϵ_A	χ_{act} cycling/ continuous mode	ϵ_B/ϵ_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

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b04848.

Details of the material synthesis, mathematical derivation, measurement setup, and fatigue measurement results (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: andrea.bianco@brera.inaf.it. Tel.: +390272320460.

ORCID

Rossella Castagna: 0000-0002-9284-3165

Andrea Bianco: 0000-0002-7691-404X

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Matsuda, K.; Irie, M. Diarylethene as a Photoswitching Unit. *J. Photochem. Photobiol., C* **2004**, *5*, 169–182.
- (2) Irie, M.; Fukaminato, T.; Matsuda, K.; Kobatake, S. Photochromism of Diarylethene Molecules and Crystals: Memories, Switches, and Actuators. *Chem. Rev.* **2014**, *114*, 12174–12277.
- (3) Zhang, J.; Zou, Q.; Tian, H. Photochromic Materials: More than Meets the Eye. *Adv. Mater.* **2013**, *25*, 378–399.
- (4) Tsujioka, T.; Irie, M. Electrical Functions of Photochromic Molecules. *J. Photochem. Photobiol., C* **2010**, *11*, 1–14.
- (5) Bertarelli, C.; Bianco, A.; Castagna, R.; Pariani, G. Photochromism into Optics: Opportunities to Develop Light-Triggered Optical Elements. *J. Photochem. Photobiol., C* **2011**, *12*, 106–125.
- (6) Irie, M. Diarylethenes for Memories and Switches. *Chem. Rev.* **2000**, *100*, 1685–1716.
- (7) Irie, M.; Lifka, T.; Uchida, K.; Kobatake, S.; Shindo, Y. Fatigue Resistant Properties of Photochromic Dithienylethenes: By-Product Formation. *Chem. Commun.* **1999**, 747–750.

the very different perceived fatigue behavior of the same molecule in the same environment.

■ 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 unequivocally ascribed to improved resistance to photodegradation.

We confirmed that the phenomenon of photofatigue in these diarylethenes occurs from the colored form, and we demonstrated that a clear relationship between the fraction of the degraded molecule and the UV dose absorbed by the colored form exists. Consequently, when considering homologous series of diarylethenes, the fatigue resistance strongly depends on the cross section of the open- and closed-ring isomers at the illumination wavelength. The ϵ_B/ϵ_A ratio can be assumed as a figure of merit to determine the fatigue resistance, especially in those molecules that exhibit similar quantum yield of the degradation reaction, as occurs in the systems here studied. In this framework, the presence of an external thienyl ring instead of a phenyl ring increases the fatigue resistance since there is a separation of the UV absorption bands for the open and closed forms, making it possible to find an UV wavelength for which the ratio ϵ_B/ϵ_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 ϵ_B/ϵ_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 photofatigue resistance.

As a general approach, the chemical structure of a photochromic diarylethene can be optimized in order to tune the absorption spectra and find an illumination wavelength at which the ratio ϵ_B/ϵ_A is minimized.

- (8) Higashiguchi, K.; Matsuda, K.; Yamada, T.; Kawai, T.; Irie, M. Fatigue Mechanism of Photochromic 1,2-Bis(3-Thienyl)-perfluorocyclopentene. *Chem. Lett.* **2000**, 29, 1358–1359.
- (9) Higashiguchi, K.; Matsuda, K.; Kobatake, S.; Yamada, T.; Kawai, T.; Irie, M. Fatigue Mechanism of Photochromic 1,2-Bis(2,5-Dimethyl-3-Thienyl)perfluorocyclopentene. *Bull. Chem. Soc. Jpn.* **2000**, 73, 2389–2394.
- (10) Celani, P.; Ottani, S.; Olivucci, M.; Bernardi, F.; Robb, M. A. What Happens during the Picosecond Lifetime of 2A1 Cyclohexa-1,3-Diene? A CAS-SCF Study of the Cyclohexadiene/Hexatriene Photochemical Interconversion. *J. Am. Chem. Soc.* **1994**, 116, 10141–10151.
- (11) Patel, P. D.; Mikhailov, I. A.; Belfield, K. D.; Masunov, A. E. Theoretical Study of Photochromic Compounds, Part 2: Thermal Mechanism for Byproduct Formation and Fatigue Resistance of Diarylethenes Used as Data Storage Materials. *Int. J. Quantum Chem.* **2009**, 109, 3711–3722.
- (12) Hanazawa, M.; Sumiya, R.; Horikawa, Y.; Irie, M. Thermally Irreversible Photochromic Systems. Reversible Photocyclization of 1,2-Bis(2-Methyl Benzo[*b*]thiophen-3-yl)perfluorocycloalkene Derivatives. *J. Chem. Soc., Chem. Commun.* **1992**, 206–207.
- (13) Uchida, K.; Nakayama, Y.; Irie, M. Thermally Irreversible Photochromic Systems. Reversible Photocyclization of 1,2-Bis(benzo[*b*]thiophen-3-yl)ethene Derivatives. *Bull. Chem. Soc. Jpn.* **1990**, 63, 1311–1315.
- (14) Herder, M.; Schmidt, B. M.; Grubert, L.; Pätzelt, M.; Schwarz, J.; Hecht, S. Improving the Fatigue Resistance of Diarylethene Switches. *J. Am. Chem. Soc.* **2015**, 137, 2738–2747.
- (15) Jeong, Y.-C.; Park, D. G.; Kim, E.; Ahn, K.-H.; Yang, S. I. Fatigue-Resistant Photochromic Dithienylethenes by Controlling the Oxidation State. *Chem. Commun.* **2006**, 1881–1883.
- (16) Uchida, K.; et al. Thermally Irreversible Photochromic Systems. Reversible Photocyclization of 1,2-Bis(thiazolyl)-perfluorocyclopentenes. *Tetrahedron* **1998**, 54, 6627–6638.
- (17) Jeong, Y.; Yang, I.; Kim, E.; Ahn, K. H. Development of Highly Fluorescent Photochromic Material with High Fatigue Resistance. *Tetrahedron* **2006**, 62, 5855–5861.
- (18) Hermes, S.; Dassa, G.; Toso, G.; Bianco, A.; Bertarelli, C.; Zerbi, G. New Fast Synthesis Route for Symmetric and Asymmetric Phenyl-Substituted Photochromic Dithienylethenes Bearing Functional Groups such as Alcohol, Carboxylic Acids, or Amines. *Tetrahedron Lett.* **2009**, 50, 1614–1617.
- (19) Crano, J. C.; Guglielmetti, R. J. *Organic Photochromic and Thermochromic Compounds*; Plenum Press, 1999.