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

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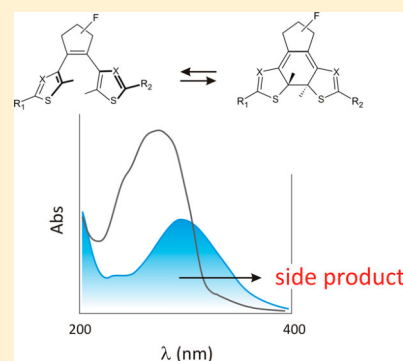
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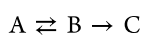
10 **S** Supporting Information

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



23 ■ INTRODUCTION

24 Diarylethenes are one of the most important classes of P-type
25 photochromic compounds due to their thermal stability and
26 fatigue resistance, and they have been proposed over the last
27 two decades for many applications such as switches,¹ optical
28 memories,² photosensors,³ and optoelectronic⁴ or optical
29 devices.⁵ When considering their possible technological
30 applications, photofatigue resistance has to be taken into
31 account since a poor resistance leads to a short device lifetime,
32 thus preventing the actual use. Despite that some diarylethene
33 crystals can undergo up to 10⁴ coloration–decoloration cycles
34 without any significant degradation of their photochromic
35 properties,⁶ it is often observed that loss of performance occurs
36 after a relatively low number of cycles, due to parasitic side
37 reactions.^{7–9} This behavior is described considering that the
38 photochromic reaction from A to B produces one or more
39 undesirable byproducts C



40 The photochemical mechanisms of degradation in diary-
41 lethenes were investigated with both experimental and
42 theoretical studies. It was demonstrated that, without oxygen,
43 degradation leads to a condensed structure, whose absorption
44 spectrum shows characteristic bands both in the UV and in the
45 visible range.⁷ Other byproducts due to oxidation or HF
46 elimination were also observed under prolonged illumination.⁸
47 Moreover, it has been found that degradation occurs starting

48 from the closed ring isomer by UV light absorption through a
49 bicyclohexane intermediate form.^{10,11} In first studies, Irie et al.
50 pointed out the importance of introducing a methyl at the 4-
51 position of the thienyl⁷ and the better fatigue resistance of
52 benzothiophene with respect to thiophene.^{12,13} Recently,
53 Herder et al. suggested that the presence of electron-
54 withdrawing substituents could play a role in the fatigue
55 resistance.¹⁴

56 Despite these studies, no straightforward correlation between
57 the chemical structure and the photofatigue resistance has been
58 found so far, also considering the two energy barriers involved
59 in the process. It follows that, as a matter of fact, there are a few
60 guidelines for the synthesis of new molecules that consider a
61 *priori* fatigue resistance.^{6,7,12,14,15}

62 It is also worth noting that, often in the literature, the fatigue
63 behavior of photochromic materials could be overestimated due
64 to a possible contribution of the degraded species to the total
65 absorption in the visible region.^{6,7,13,16} A suitable parameter to
66 describe the fatigue resistance and to distinguish between
67 different degradation mechanisms is the quantum yield of
68 degradation,¹⁷ but as a matter of fact, this is not sufficient to
69 describe the perceived fatigue behavior, i.e., the survived
70 molecules after a defined number of illumination cycles.

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71 Here, we propose an approach to evaluate the fatigue
72 performance of diarylethenes, which considers the dose of UV
73 photons actually absorbed by the closed form during the ring
74 closure process. For two series of diarylethenes we demonstrate
75 that the perceived fatigue resistance is strongly dependent on
76 the illumination process, i.e., UV wavelength, and on the
77 absorption characteristics of the molecule at this wavelength,
78 besides the quantum yield of the degradation reaction.

79 ■ RESULTS AND DISCUSSION

80 We considered 1,2-dithienyloctafluorocyclopentenes (**T**) and
81 1,2-dithiazolyloctafluorocyclopentenes (**Tz**) bearing either a
82 symmetrical or asymmetrical phenyl/methylthienyl at the 5-
83 positions of the aryl rings (Figure 1). In the literature, some

conflicting results are reported on the fatigue resistance of the 84
thiazolyl derivatives,^{14,16} this heterocycle being originally 85
supposed to give diarylethenes excellent fatigue resistance. 86
Note that the six derivatives do not show the presence of any 87
lateral electroactive chemical group that can play a role in the 88
fatigue mechanism and resistance. 89

1,2-Dithienylethenes (**T-1**, **T-2**, **T-3**) were synthesized 90
following the route published by Hermes et al.¹⁸ (Scheme 1). 91 s1
The asymmetric compound **T-2** was not obtained following the 92
one-pot method reported in the paper since the resulting 93
mixture of **T-1**, **T-2**, and **T-3** could not be purified by flash 94
chromatography with any tested eluent. Accordingly, **T-2** was 95
synthesized in a two-step route, again starting from the 1,2- 96
bis(2-methyl-5-chloro-3-thienyl)perfluorocyclopentene (**1**). 97

The same approach was first followed to synthesize the 1,2- 98
dithiazolylethenes (**Tz**), where the 2-chloro-5-methylthiazole 99
was obtained through a Sandmeyer reaction starting from the 100
corresponding amine (**3**). However, the reaction was 101
characterized by a low yield. Therefore, a one-pot Sand- 102
meyer-bromination reaction was performed as a first step to 103
give the 2,4-dibromo-5-methylthiazole (**4**). Suzuki coupling 104
between **4** and the aryl boronate (phenyl boronic acid or 5- 105
methylthiophene-2-boronic acid pinacolester), followed by the 106
Dixon reaction, gave compounds **5** and **7**.¹⁸ The asymmetric 107
compound **Tz-2** was obtained through two sequential Dixon 108
reactions (Scheme 2). Details are reported in the SI. 109 s2

All the synthesized diarylethenes were characterized by UV- 110
vis absorption spectroscopy in *n*-hexane (used as received) 111
solutions. Data are reported in Table 1 together with the 112 t1
absorption maxima and absorption coefficients in the visible of 113
the byproducts C. Comparison between the series of 1,2- 114
dithienylethenes (**T**) and 1,2-dithiazolylethenes (**Tz**) shows that 115
the latter have red-shifted absorption maxima in the open form. 116
This finding can be ascribed to the smaller steric hindrance of 117
nitrogen compared to the CH in the 4-position of thiophene, 118
which leads to a more planar structure (i.e., lower torsional 119

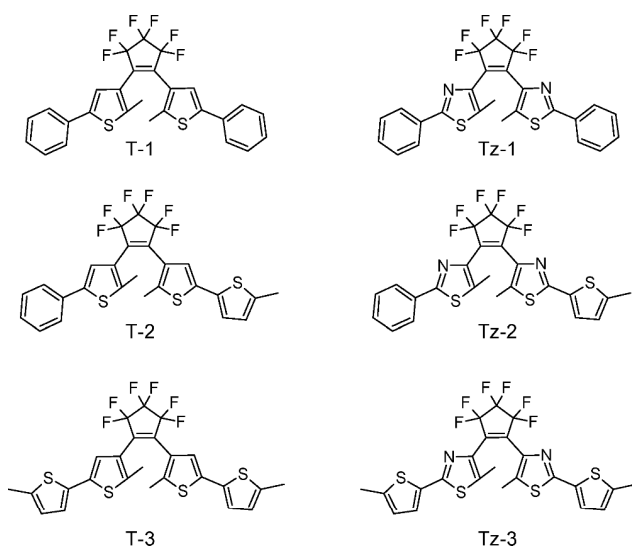
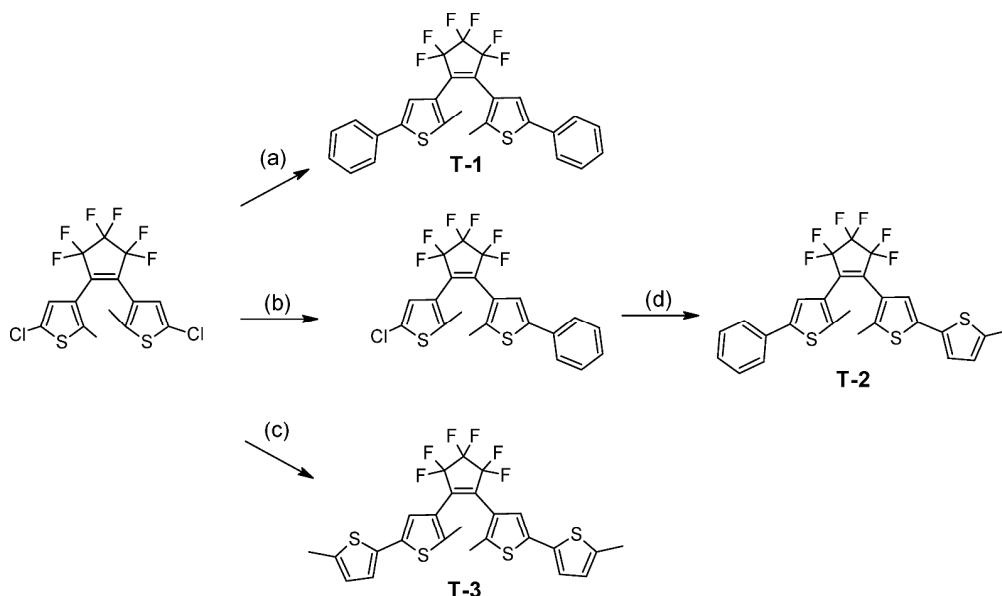
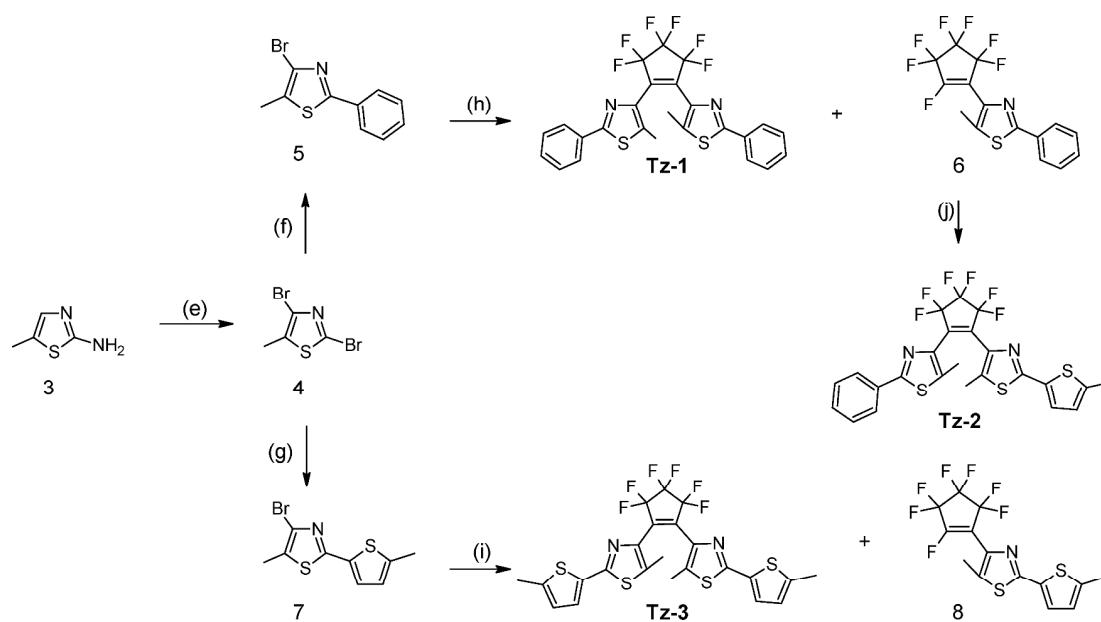


Figure 1. Chemical structure of the diarylethenes herein investigated.

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-Dithiazolylethenes (Tz)^a

^aReaction conditions: (e) H₃PO₄, HNO₃, NaNO₂, H₂O, CuBr, HBr; (f) 1 equiv of phenyl boronic acid, Pd(PPh₃)₄, DME, H₂O, K₂CO₃; (g) 1 equiv of 5-methylthiophene-2-boronic acid pinacolester, Pd(PPh₃)₄, DME, H₂O, K₂CO₃; (h), (i) THF, BuLi, -78°C, C₃F₈; (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 (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

^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-dithiazolylethenes
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

143 color bleaching. The procedure was repeated for a given
144 number of times. Exposure times were determined by
145 monitoring the absorbance of the sample in the visible during
146 the conversion of up to 90% of the PSS during coloration
147 (pseudo-PSS) and 99.9% of conversion after bleaching. The
148 wavelength of the monitoring beam was tuned to match the
149 absorption maximum in the visible region for each investigated
150 molecules. The conversion kinetics was measured also at the
151 end of the cycling, to rule out any significant variation due to
152 the presence of the byproduct. Solution concentrations and
153 characteristic coloration times for the *cycling mode* are reported
154 in the SI. In the *continuous mode*, the transparent solution was
155 exposed to UV light only (311 nm), for a time equivalent to a
156 given number of cycles.

157 Usually, fatigue in diarylethenes is evidenced as the
158 absorbance decrease in the visible region upon UV illumina-
159 tion.^{6,19} Actually, since the parasitic C species may also absorb
160 in the visible, the decrease in absorption due to the decreasing
161 of B is partially compensated by the absorption of C. For a
162 correct description of the fatigue resistance, we considered the
163 fraction of active molecules after a given illumination time as
164 the reference parameter. The fraction of active molecules χ_{act} at
165 the n^{th} cycle can be calculated from the absorption of the 165

166 solution before and after the coloration and bleaching at any
167 illumination cycle, as follows

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

169 where Abs represents the absorbance at the Lambert–Beer
170 regime; superscripts indicate the cycle number (0 is the initial
171 state before any irradiation run); and subscripts 1 and 2 refer to
172 the absorbance after coloration and bleaching of the photo-
173 chromic sample at the monitoring wavelength in the visible
174 region, respectively (the derivation is reported in the SI). This
175 approach allows for eliminating the absorption of the degraded
176 species, which contributes to the total absorption; hence it
177 provides the actual number of active photochromic molecules
178 of the sample. Moreover, this equation is valid either for a
179 partial conversion (pseudo-PSS) or for the achievement of the
180 PSS. Notably, reflectance and baseline errors are also
181 eliminated. The comparison between the present approach
182 and the standard method that considers the total absorption is
183 highlighted in Figure 2. The consistency of our measurement
184 and approach with the data reported in the literature for T-1⁷ is
185 also noticeable.

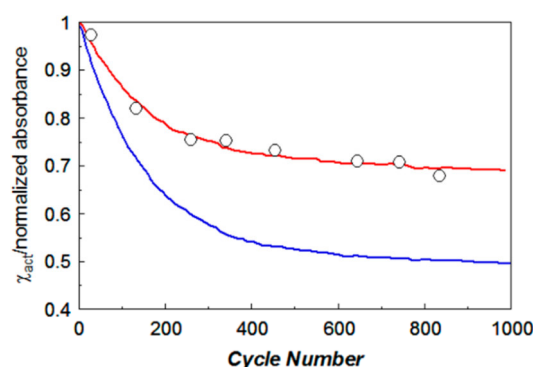


Figure 2. Fraction of active molecules for T-1 as evaluated with the present approach (blue line) and the standard method (red line), which does not disentangle the contribution of the degraded species from the total absorption in the visible. The white circles represent the experimental data reported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

186 The fatigue behavior under *cycling mode* of the two series of
187 molecules here considered is reported in Figure 3, which shows
188 the fraction of active molecules (χ_{act}) as a function of the
189 number of cycles. Measurements were performed both in
190 argon-saturated solutions and in solutions with as-received

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

198 For both the T and Tz classes, replacing phenyls with
199 thiophenes at the 5-position of the aryl rings leads to an
200 increase of fatigue resistance. However, no homogeneous trend
201 is evidenced within the T and the Tz series, which does not
202 allow for a rationalization of the light-induced fatigue related to
203 the specific chemical structure. Moreover, despite that Tz-2 and
204 Tz-3 are more resistant than analogous T derivatives (i.e., T-2
205 and T-3), Tz-1 shows the worst performance. This leads to the
206 hypothesis that thiazole does not unequivocally improve the
207 fatigue resistance of 1,2-diarylethenes.

208 The spectra of the degraded byproducts were obtained as
209 difference between the spectra at the initial cycle and after
210 bleaching at the final cycle, and the molar extinction coefficients
211 ϵ_C were also calculated (see SI). Absorption maxima of the
212 byproducts in the visible (see Table 1) are blue-shifted about
213 30 nm for dithienylethenes (T) and red-shifted less than 10 nm
214 for dithiazolylethenes (Tz) with respect to the corresponding
215 closed-ring isomer (Table 1). This is a peculiar feature that has
216 been previously observed on perhydrocyclopentene derivatives
217 but not on perfluorocyclopentenes.¹⁴ As for the molar
218 extinction coefficient of the byproducts in the visible, it is
219 about 0.6–0.8 of the absorption coefficient of the closed form
220 for the different molecules.

221 All the diarylethenes were also analyzed in the *continuous*
222 mode, and the same equation to retrieve χ_{act} was applied by
223 considering as illumination time an equivalent time at a
224 determined numbers of cycles. Therefore, the measurement is
225 expressed as a function of an equivalent cycle number, where
226 the light dose absorbed by the ring-closed isomer in the
227 *continuous mode* corresponds to the dose absorbed during the
228 corresponding number of cycles in the *cycling mode*. The
229 procedure for calculating the equivalent cycle number is
230 reported in the SI, and the results at 80 cycles are reported
231 in Table 2.

232 A comparison between the *cycling mode* measurements and
233 the *continuous mode* allows us to experimentally determine
234 whether the byproduct formation preferentially occurs during
235 the photochromic reaction or from the UV absorption of the
236 closed-ring isomer. If degradation takes place during the
237 photochromic reaction as a parasitic pathway, the fatigue in

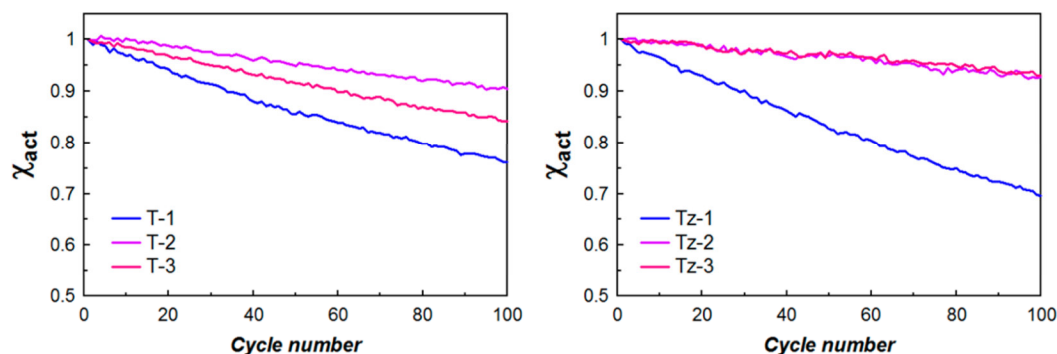


Figure 3. Fraction of active molecules as a function of the cycle number in cycling mode ($\lambda_{\text{UV}} = 311 \text{ nm}$) for T and Tz.

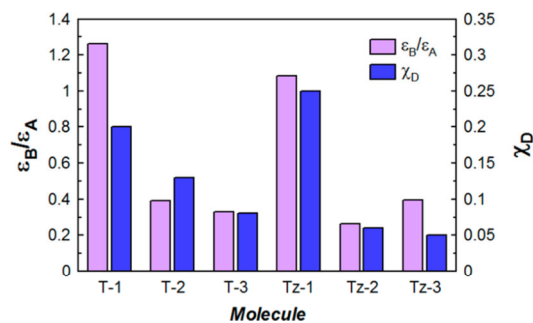
Table 2. Fraction of Active Molecules after 80 Equiv Cycles in the Two Testing Modes

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

238 *cycling mode* will be larger than in *continuous mode* since the
239 system is periodically switched between the A and B forms. On
240 the contrary, if the degradation basically takes place from the B
241 species, the fatigue in *cycling mode* will be less intense.

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

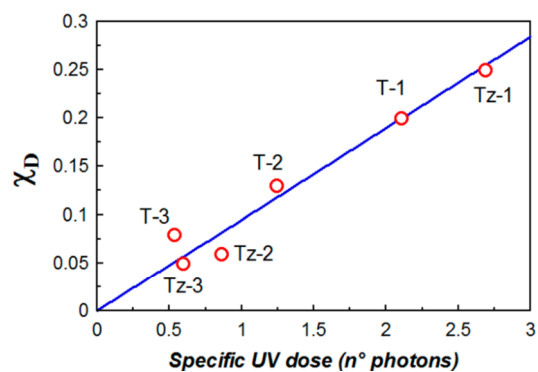
248 Therefore, considering the central role of the UV light
249 absorption of the B form in the loss of performance of these
250 photochromic switches, we considered the relative absorption
251 cross-section of the two isomeric states at the coloration
252 wavelength (i.e., 311 nm). The ϵ_B/ϵ_A ratio at the illumination
253 wavelength (at 311 nm) and the fraction of degraded molecules
254 $\chi_D = 1 - \chi_{\text{act}}$ after 80 cycles in the *cycling mode* are reported in
255 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).

256 Interestingly, a correlation between the ratio ϵ_B/ϵ_A and the
257 photofatigue resistance was found. Specifically, if the ratio ϵ_B/ϵ_A
258 is low, the cross-section of the species in the open form is more
259 relevant, thus the absorption to promote the ring-closing is
260 preferred over the residual absorption of the colored form.
261 Conversely, if the ratio ϵ_B/ϵ_A is large, a consistent amount of
262 the incident light is absorbed by the closed-ring isomer, making
263 degradation more effective. A small value of this ratio can be
264 related to both a separation in the wavelength of the absorption
265 bands in the UV of the open and closed forms (as for molecules
266 T-3 and Tz-3) or to a general lowering of the absorption bands
267 in the UV by the closed form (as for molecule T-2 and Tz-2).
268 In both cases, the ratio is a function of the chemical structure of
269 the specific photochromic derivative.

270 Starting from this new insight, the fraction of degraded
271 species was also related to the specific light dose (number of

photons per molecule) absorbed by the closed-ring isomer in
272 one cycle (the light dose was calculated taking into account the
273 kinetics of conversion during illumination; see SI for details).
274 For the investigated diarylethenes, a linear correlation between
275 the specific UV dose and the fraction of degraded molecules
276 exists (Figure 5).
277 f5

**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).

278 It is worth pointing out that the formation rate of the
279 byproduct is proportional to the number of UV photons
280 absorbed by the closed form times the quantum yield of the
281 side reaction. Since a linear relationship is obtained, we can
282 conclude that the quantum yield of the side reaction is similar
283 for all the derivatives at 311 nm. Similar values of the quantum
284 yield of the side reaction are also reported in the literature
285 when diarylethenes with similar structure (i.e., same bridge)
286 and without electroactive substituents are considered.¹⁴ There-
287 fore, the absorption properties of the investigated molecules at
288 the exposure wavelength are definitely of great importance in
289 the definition of their fatigue behavior. Since different ϵ_B/ϵ_A
290 ratios may be easily found for any compound by changing the
291 illumination wavelength of the fatigue test, we considered to
292 perform measurements at a different wavelength ($\lambda_{\text{UV}} = 370$
293 nm) to further confirm that the ϵ_B/ϵ_A ratio is a figure of merit
294 to evaluate the fatigue resistance of diarylethenes. In particular,
295 analyzing the UV-vis spectra of all the molecules here
296 investigated, we chose T-3 and Tz-3, showing a ratio ϵ_B/ϵ_A
297 lower than one at 311 nm and much larger than one at 370 nm.
298 The absorption spectra in both isomeric states of T-3 and Tz-3
299 f6

The results of fatigue tests irradiating at 370 nm in both
300 *cycling* and *continuous modes* at 80 cycles (or equivalent cycles)
301 for T-3 and Tz-3 are shown in Table 3 and compared with data
302 obtained at 311 nm. Despite the lower energy of photons at
303 370 nm than at 311 nm, which would suggest a better material
304 durability, an impressive decrease in fatigue resistance is clearly
305 visible. Worth noting, T-3 and Tz-3 are two diarylethenes
306 showing high fatigue resistance at 311 nm. Assuming a similar
307 byproduct formation quantum yield as a function of the
308 exposure wavelength, the strong difference in the fatigue
309 resistance is ascribed to the very different absorption properties
310 of the B form at the two exposure wavelengths. In fact, when
311 the absorption coefficient of the B form is large, more photons
312 are absorbed by B up to reach the PSS state, increasing the
313 effect of degradation. Accordingly, very low degradation takes
314 place if the absorption of the B form at the exposure UV
315 wavelength is negligible. This phenomenon is responsible for 316

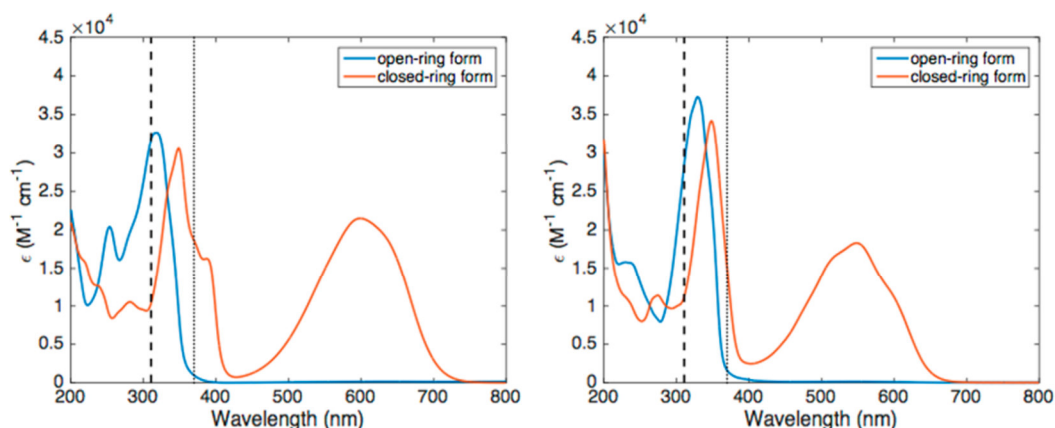


Figure 6. Molar extinction coefficients for the A and B forms of T-3 (left) and Tz-3 (right). Values at 311 and 370 nm are evidenced by dashed and dotted lines, respectively. For both cases, the ratio ϵ_B/ϵ_A remarkably increases going from 311 to 370 nm.

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

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

319 ■ CONCLUSIONS

320 The fatigue resistance of two series of diarylethenes that differ
321 in the nature of the heterocycles linked to the perfluorocyclo-
322 pentene was investigated, and results indicated that thiazole
323 cannot be unequivocally ascribed to improved resistance to
324 photodegradation.

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

341 This finding is of great importance for the practical use of
342 photochromic materials since, given a specific UV illumination
343 source, chromophores can be screened *a priori* on the basis of
344 the ϵ_B/ϵ_A ratio. Alternatively, it allows for the selection of the
345 best UV wavelength to convert a given photochromic molecule
346 to the closed-ring form achieving at the same time the best
347 photofatigue resistance.

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

■ 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)

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Notes

The authors declare no competing financial interest.

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