Photochromic heteroarylethenes with fast thermal isomerization kinetics

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ABSTRACT

Stilbenes (diphenylethenes) are fully examined organic chromophores for very diverse applications. However, these molecules might show poor stability under irradiation because several simultaneous reactions (oxidative photocyclization and dimerization) can take place during the photochemical isomerization of their C=C bond. In this context, heteroarylethenes emerge as powerful counterparts thanks to their improved stability. In addition, the chosen heterocycles and their functionalization allows to fine tune and increase the speed at which the thermal back reaction occurs, broadening the scope of application of the resulting chromophores. Here we report on the thermal *Z*-to-*E* isomerization kinetics of a series of rationally designed heteroarylethenes and how the chemical architecture of the chromophore modulates the speed of the process. Specifically, the metastable *Z* isomers display relaxation times covering a wide time window, from a few hours to hundreds of microseconds. In fact, one of the studied dyes is the fastest photochromic switch based on heteroarylethenes. It should be also noticed that the described heteroarylethenes exhibit great photochemical stability, it being possible to switch them back and forth many times without degradation.

1. Introduction

In recent years there has been a global shift towards the design and use of more sustainable materials that are fueled by cheap, renewable and environmentally-friendly energy sources. In this line, photochromic switches have attracted considerable attention since they are actuated with light, a clean, inexpensive and endless form of energy. Moreover, light offers the possibility to monitor the whole operation in real time in a wireless and remote fashion.

Photochromic switches are molecular or supramolecular entities that swap between two or more distinct states of the system when they are illuminated with light of the appropriate wavelength [1,2]. The initial state and the photogenerated one/s exhibit different chemical structures and display distinct absorption wavelengths or absorbance values. In summary, light triggers a reversible chemical reaction between two or more isomeric forms of the system with different spectroscopic signatures. In particular, stilbenes (diphenylethenes), one of the most studied families of organic chromophores, can exist as two configurational stereoisomers, *E* and *Z*. Illumination of the system promotes the

transformation of the thermodynamically stable *E* form of the chromophore into the metastable *Z* form. The photogenerated *Z* isomer can revert back to the initial state either photochemically or thermally [3,4]. Generally, the thermal back conversion is preferred for applications since it avoids the use of a second light source, reducing the complexity of the final material and preventing undesired photochemical reactions. It should be also noticed that the thermal *Z*-to-*E* isomerization kinetics for stilbenes depends strongly on the precise molecular structure of the chromophore [5]. In this way, subtle rational variations in the chemical constitution of the stilbene chromophore might result in drastic changes in the speed of its thermal back reaction, which determines the ultimate applicability of the system.

Stilbenes have gained in popularity latterly since they enable the modulation of the properties and abilities of a diversity of materials as well as the control of some biological events [6–17]. However, stilbenes have been less exploited than other families of chromophores, for instance azobenzenes, mainly due to possible undesired side reactions (even though they can be extremely useful from a synthetic point of view [18,19]) that can take place during the photoisomerization of the C=C

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double bond. It is well known that stilbenes can experience oxidative photocyclizations to produce phenanthrene derivatives or a [2 + 2] cycloaddition to yield the corresponding dimer with the concomitant formation of a cyclobutane ring [20–25]. In this context, the substitution of the phenyl rings in stilbenes by suitable heterocycles (i.e. heteroarylethenes) can be a valuable strategy not only to preclude these photochemical processes but also to open the door to a new palette of chromophores with attractive photochromic properties.

Literature findings reveal that even though there is a vast number of publications regarding the thermal *Z*-to-*E* isomerization kinetics of stilbenes and azo compounds, and its relationship with the molecular architecture of the chromophore and the environment where it is dissolved [26–32], this information has been scarcely reported for heteroarylethenes [33,34] and, therefore, their photochromic behavior remains still rather unexplored. Thus, this work aims to establish valuable structure-kinetic relationships for a series of heteroaromatic ethenes as a previous step to conceive a future generation of materials based on these organic chromophores. Besides, very fast thermally-isomerizing stilbene derivatives have not been reported yet. So, this work also pursues the development of new heteroarylethenes that can be operated as fast as possible with no sign of fatigue under aerated conditions.

2. Results and discussion

Six heteroaromatic ethene dyes have been selected for the present study (Scheme 1). All heteroarylethenes bear a benzothiazolium salt as a powerful electron withdrawing group (EWG in Scheme 1, compounds **2**–**6**), with the exception of **1** where it has been replaced by a quinolinium cation in order to study the impact of this structural variation on the thermal *Z*-to-*E* isomerization kinetics of the chromophore. Regarding the electron donating group (EDG in Scheme 1), three different scaffolds have been explored: 1-methylpyrrolyl (compounds **1** and **2**), *N,N*-dimethylaminophenyl (compound **3**) and *N,N*-dimethylaminothienyl (compound **6**). In addition, in the case of the *N,N*-dimethylaminophenyl EDG, the removal of the amino functional group (compound **4**) and the extension of the π-system (compound **5**) has been also considered.

Heteroarylethenes functionalized with the benzothiazolium EWG linked to aromatic (phenyl or naphthyl, compounds **3**–**5**) or heteroaromatic (pyrrolyl or thienyl, compounds **2** and **6**) electron donating rings were previously synthesized by us [35] through the condensation of the appropriate aldehyde and 2,3-dimethylbenzo[*d*]thiazol-3-ium iodide. The starting materials were refluxed in ethanol in the presence of piperidine for 6 h. After this time, all compounds precipitated from the

reaction mixture and they were isolated by vacuum filtration to obtain the pure heteroarylethenes **2**–**6** as colored (from orange to dark purple) solids. On the other hand, compound **1**, bearing the quinolinium EWG linked to the 1-methylpyrrolyl EDG, was prepared via the condensation of 1-methyl-1*H*-pyrrole-2-carbaldehyde (**7** in Scheme 2) with 1,4-dimethylquinolin-1-ium iodide (**8** in Scheme 2). In this case, the condensation reaction was carried out in boiling ethanol in the presence of piperidine during 10 h. The corresponding product was isolated by vacuum filtration as a dark orange solid in a yield of 71%. Precursor **8** was also prepared by us in a quantitative yield by alkylating 4-methylquinoline with methyl iodide in acetonitrile at reflux for 14 h (Scheme 2).

The identity of compound **1** was confirmed by ¹H and ¹³C NMR spectroscopy and mass spectrometry. Detailed synthetic protocols and structural data concerning ethene **1** are reported in the Supporting Information.

Before irradiation, the absorption spectrum of **1** (*a* in Fig. 1) in dimethyl sulfoxide (DMSO) shows a main absorption band peaking at 500 nm (λ_{Max} in Table 1), with a molar extinction coefficient of 36 mM⁻¹ cm⁻¹ (ε in Table 1). This major absorption is due to the π-π* transition of the *E* isomer of the heteroarylethene. The irradiation of **1** with continuous green light (λ_{Ex} = 520 nm, Thorlabs collimated laser diode module, 4.5 mW) results in a significant decrease of this absorption, as a result of the photoinduced *E*-to-*Z* isomerization of the C=C bond of the molecule. Irradiation of the sample was pursued until the corresponding photostationary state was reached and no changes in the absorption spectrum were detected (*b* in Fig. 1). The apparent proportion of *Z* isomer present at the photoequilibrium (Y_{app} in Table 1) has been estimated as $Y_{app} = (1 - A_{ph}/A_0) \times 100$, where A_0 and A_{ph} is the absorbance of the solution before irradiation and once the
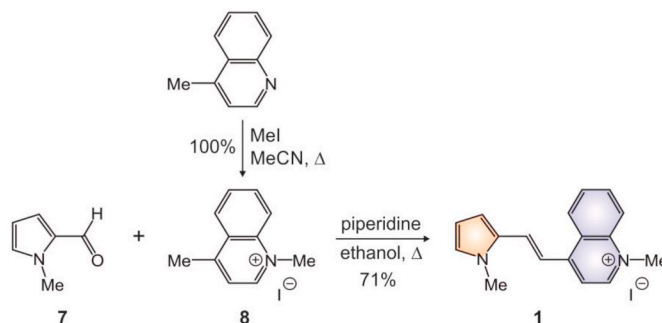
Scheme 2. Synthesis of the precursor **8** and the heteroarylethene **1**.
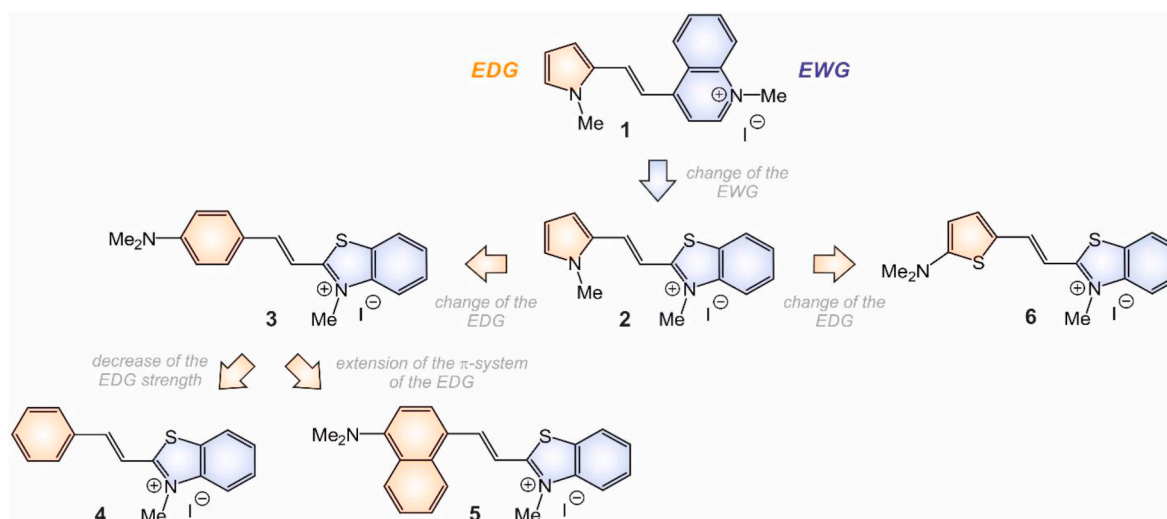
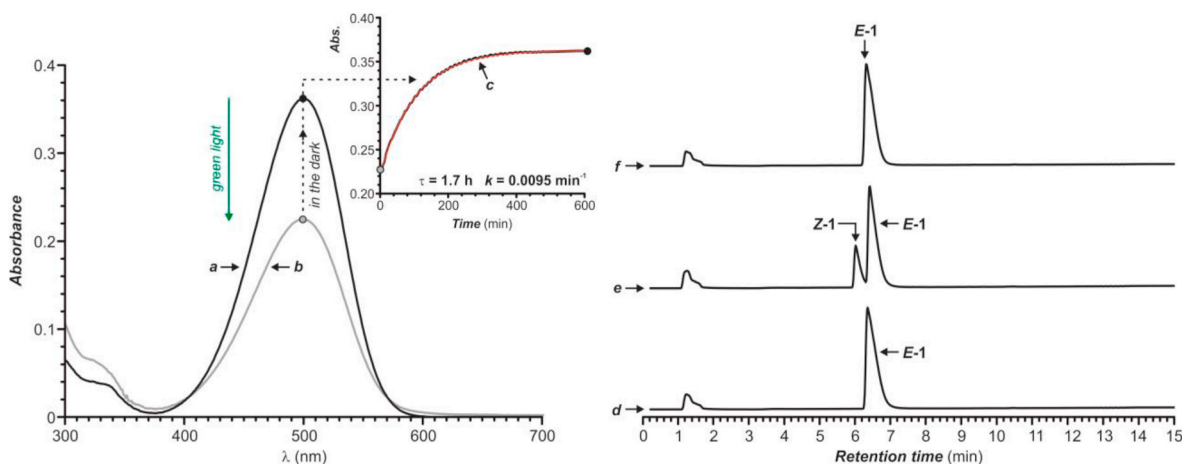**Scheme 1.** Chemical structure of heteroarylethenes **1**–**6**.

Fig. 1. Absorption spectrum of a solution of **1** (10 μM) in DMSO before (*a*) and after (*b*) irradiation with continuous green light (λ_{Ex} = 520 nm, Thorlabs collimated laser diode module, 4.5 mW). Kinetic trace at λ_{Obs} = 500 nm (*c*) for the thermal isomerization of **1** in the dark at 296 K. HPLC chromatogram recorded before (*d*) and after irradiation (*e*) with continuous green light (λ_{Ex} = 520 nm), and after the solution was kept in the dark overnight (*f*).

Table 1
Wavelength of maximum absorption (λ_{Max}), molar extinction coefficient (ε), apparent proportion of Z isomer present at the photoequilibrium (Y_{app}), rate constant (k) and relaxation time (τ) for the thermal Z-to-E isomerization, and oscillation frequency (ν) for heteroaromatic ethenes **1**–**6** in DMSO at 296 K.

Compound	λ_{Max} (nm)	ε (mM^{-1} cm^{-1})	Y_{app} (%)	k (min^{-1})	τ	ν (Hz)
1	500	36	38	0.0095	1.7 h	5.4×10^{-5}
2	470	43	36	0.65	92 s	3.6×10^{-3}
3	523	11	1.1	11.6	5.2 s	6.4×10^{-2}
4	377	22	52	0.56	107 s	3.1×10^{-3}
5	568	14	1.8	500	120 ms	2.8
6	572	20	21	3.1×10^{5}	191 μs	1.7×10^{3}

photostationary state has been achieved, respectively. Specifically, a Y_{app} value of 38% has been determined for compound **1**.

The E-to-Z isomerization of **1** was also studied by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum of **1**, recorded in DMSO-d_6 before irradiation (*a* in Fig. 2), shows two characteristic doublets centered at 8.15 and 7.91 ppm, with a coupling constant J = 15.6 Hz, corresponding to the two hydrogen atoms linked to each sp^2 carbon of the C=C bond. This profile evidences that the E isomer of the chromophore is the only

species present in solution in the absence of light. Continuous irradiation of the sample for 1 h with green light leads to the appearance of a new set of signals in the NMR spectrum (*b* in Fig. 2; the aliphatic part of the ^{1}H NMR spectrum is shown in Fig. S12 in the Supporting Information), thereby confirming the transformation of **E-1** into its corresponding metastable configurational isomer **Z-1**. Amongst all the photogenerated signals, the most relevant ones are those corresponding to the hydrogen atoms attached to the carbons of the C=C bond. Upon the photochemical transformation two new doublets appear at 7.15 and 6.88 ppm, with a coupling constant of J = 12.4 Hz, which corroborates the formation of the Z form of the chromophore. The analysis of the NMR spectrum after irradiation allows to assess the proportion at which each isomer is present at the photoequilibrium. In the case of **1**, the photostationary mixture contains a 34% of the photogenerated Z form and a 66% of the initial E isomer, in accordance with the data obtained by UV–Vis spectroscopy. The much faster Z-to-E isomerization displayed by ethene derivatives **2**–**6** did not permit this determination with the NMR spectrophotometer currently available.

The absence of additional sets of NMR signals upon irradiation points out that the light-triggered transformation of the E isomer into its Z counterpart is a clean process and that no parallel photochemical reactions occur. This fact can also be confirmed by HPLC-MS. The HPLC chromatogram of a freshly prepared solution of **1** (*d* in Fig. 1) shows a unique peak at a retention time (t_R) of 6.40 min. Continuous irradiation of the solution for 1 h with green light provokes the appearance of a new peak at t_R = 6.00 min (*e* in Fig. 1). The mass spectrum for both peaks reveals that the two species have the same mass-to-charge ratio (m/z =
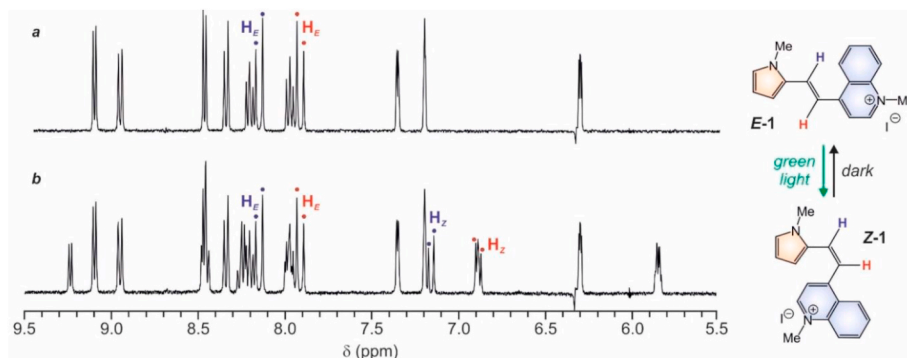

Fig. 2. Aromatic and olefinic region of the ^{1}H NMR spectrum of **1**, recorded in DMSO-d_6, before (*a*) and after (*b*) irradiation with continuous green light (λ_{Ex} = 520 nm, Thorlabs collimated laser diode module, 4.5 mW) for 1 h. The aliphatic region of the ^{1}H NMR spectrum recorded before and after irradiation is shown in the Supporting Information.

249.15; see Fig. S13 in the Supporting Information), which is in perfect agreement with the calculated value for the molecule (249.14 for $C_{17}H_{17}N_2$). This feature corroborates that the *E* and *Z* isomers of the chromophore are the only species involved in the process. After keeping the sample in the dark overnight, a chromatogram identical to the one of the parent solution was registered (*f* in Fig. 1) due to the thermal regeneration of the initial *E* form.

When the illumination is ceased, the thermal *Z*-to-*E* isomerization occurs. The kinetics of the back reaction for ethene derivatives **1–4** was monitored by means of conventional time-resolved UV–Vis spectroscopy. For compounds **5** and **6**, however, flash photolysis was used instead owing to the very short lifetime of the *Z* isomer. In all instances, absorbance at λ_{Obs} increased until the pre-irradiation value was eventually restored. The associated rate constant (*k* in Table 1) and relaxation time (τ in Table 1, $\tau = 1/k$) were determined by fitting a single exponential function to the corresponding absorbance (or ΔA in the flash photolysis measurements) *versus* time trace. It should be also pointed out that a good retention of the isosbestic points was observed during both the photochemical *E*-to-*Z* and thermal *Z*-to-*E* isomerization processes, indicating that the interconversion between the two configurational isomers of the ethene chromophore takes place in the absence of side reactions.

Compound **1** shows a slow thermal isomerization step with a rate constant of 0.0095 min^{-1} at 296 K, which corresponds to a relaxation time of 1.7 h (Table 1). The replacement of the electron withdrawing quinolinium salt of **1** by a benzothiazolium one (compounds **2–6** in Scheme 1) leads to significantly more rapid isomerization kinetics, with thermal relaxation times spanning from a few minutes to some hundreds of microseconds. This result highlights the key role of the benzothiazolium ring as a powerful EWG, thus conferring to the resulting chromophore a fast thermal back reaction even in the absence of an EDG, as it happens in the case of compound **4** (*vide infra*).

The maximum absorption wavelength of compound **2**, which combines the benzothiazolium EWG with the 1-methylpyrrolyl EDG, is hypsochromically shifted by 30 nm with respect to that of compound **1** (λ_{Max} = 470 nm and ε = 43 mM^{-1} cm^{-1} for **2**, Table 1 and *a* in Fig. 3). However, this dye exhibits a much shorter relaxation time of 92 s (*k* = 0.65 min^{-1}, Table 1 and *c* in Fig. 3). It should be mentioned that the registered τ value for *Z*-**2** falls within the same timescale than those reported previously in the literature in different media (from 39 to 620 s depending on the exact solvent used) [35]. The interchange of the 1-methylpyrrole electron donating heterocycle of **2** by a *N*,*N*-dimethylaminophenyl moiety (compound **3**) produces a bathochromic shift of 53 nm (λ_{Max} = 523 nm and ε = 11 mM^{-1} cm^{-1} for 3, Table 1) and a noticeable acceleration of the thermal isomerization reaction. Indeed, *Z*-**3** displays a τ value of only 5.2 s at 296 K (*k* = 11.6 min^{-1}, Table 1 and *a* in Fig. 4).

As it has been widely reported for azo compounds, the combination of electron donating and electron withdrawing scaffolds within the very same molecular construct is essential for rapid thermal isomerization kinetics to be achieved [36–41]. In this regard, compound **4**, which suffers the absence of the NMe$_2$ EDG, shows not only a dramatic hypsochromic shift of its maximum absorption wavelength (λ_{Max} = 377 nm and ε = 22 mM^{-1} cm^{-1}, Table 1) but also a deceleration of its thermal isomerization kinetics (*k* = 0.56 min^{-1} and τ = 107 s, Table 1 and *b* in Fig. 4) in comparison with its dimethylamino-substituted analogue **3** (τ = 5.2 s). Nevertheless, the thermal isomerization of this chromophore is still fast in comparison with that displayed by non-push-pull stilbenes, reinforcing, once again, the key role of the benzothiazolium salt as a powerful electron acceptor. It should be noticed that the relaxation time registered for heteroarylethene **4** is in perfect agreement with those reported previously for this dye in other solvents (111 and 158 s in acetonitrile and water, respectively) [35]. On the other hand, the extension of the π-system of the electron donating unit by fusing a benzene ring along the perpendicular direction to the main axis of the molecule, from *N*,*N*-dimethylaminophenyl to *N*,*N*-dimethylaminonaphtyl, accelerates significantly the thermal back reaction. Indeed, the *Z*-to-*E* isomerization of **5** was analyzed by means of the nanosecond laser flash photolysis technique (λ_{Ex} = 532 nm, Continuum Surelite I-10 Q-switched Nd-YAG laser, 5 ns pulse width, 10 mJ per pulse), due to the very short lifetime of the *Z* form of the chromophore. While the *N*,*N*-dimethylaminophenyl-based ethene **3** shows a relaxation time of 5.2 s, its *N*,*N*-dimethylaminonaphtyl analogue **5** displays a much faster thermal relaxation, with a τ value within the millisecond timescale (*k* = 500 min^{-1} and τ = 120 ms, Table 1 and *c* in Fig. 4). This differential kinetic behavior can be associated with the more red-shifted wavelength of maximum absorption displayed by the latter dye (λ_{Max} = 568 nm and ε = 14 mM^{-1} cm^{-1}, Table 1).

Compound **6**, which contains the powerful *N*,*N*-dimethylaminothienyl electron donating moiety within its covalent skeleton, absorbs at longer wavelengths than all other chromophores here reported (λ_{Max} = 572 nm and ε = 20 mM^{-1} cm^{-1}, Table 1). Remarkably, this derivative displays a ca. 650 times faster thermal isomerization than its *N*,*N*-dimethylaminophenyl counterpart **3**, with a relaxation time of only 191 μs at 296 K (*k* = 3.1 × 10^5 min^{-1}, Table 1 and *a* in Fig. 5), being, to the best of our knowledge, the fastest photochromic switch based on an heteroarylethene reported in the literature so far and, therefore, the most useful to consider for potential applications.

The repeatability and photostability, in other words, the robustness of derivative **6**, the fastest photochromic switch, was checked by submitting a solution of the dye in DMSO to 1000 pulsed green light (532 nm)–dark cycles. The transient absorption change detected before and after the consecutive operating cycles (*a* and *b* in Fig. 5, respectively) evidences the high robustness exhibited by this particular photoswitch. In fact, after 1000 cycles, neither the absorbance change nor the relaxation time of the system was altered by its continuous work. This feature was also confirmed by the corresponding HPLC chromatogram before and after the operating cycles (*c* and *d* in Fig. 5, respectively). In both instances, the very same profile was observed, i.e. a unique peak at a retention time of 7.49 min, with a *m/z* = 301.13 (Fig. S14), which fits precisely with the mass-to-charge ratio calculated for the molecule (301.08 for $C_{16}H_{17}N_2S_2$). Thus, heteroarylethene **6** can be very rapidly switched back and forth with no sign of photodegradation corroborating, once again, that undesired by-products are not formed upon illumination of the sample.

The very fast thermal isomerization and robustness of ethene **6** opens up the door to its potential application in real time information transmitting materials like, for instance, light-driven photo-oscillators. Light-
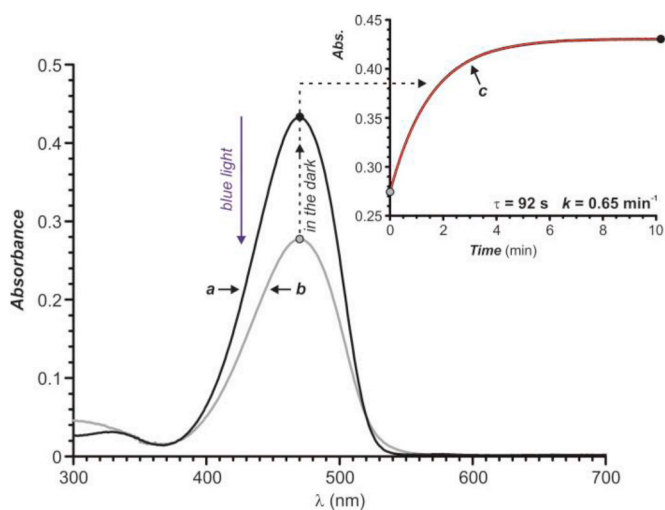

Fig. 3. Absorption spectrum of a solution of **2** (10 μM) in DMSO before (*a*) and after (*b*) irradiation with continuous blue light (λ_{Ex} = 450 nm, Thorlabs collimated laser diode module, 4.5 mW). Kinetic trace at λ_{Obs} = 470 nm (*c*) for the thermal isomerization of **2** in the dark at 296 K.
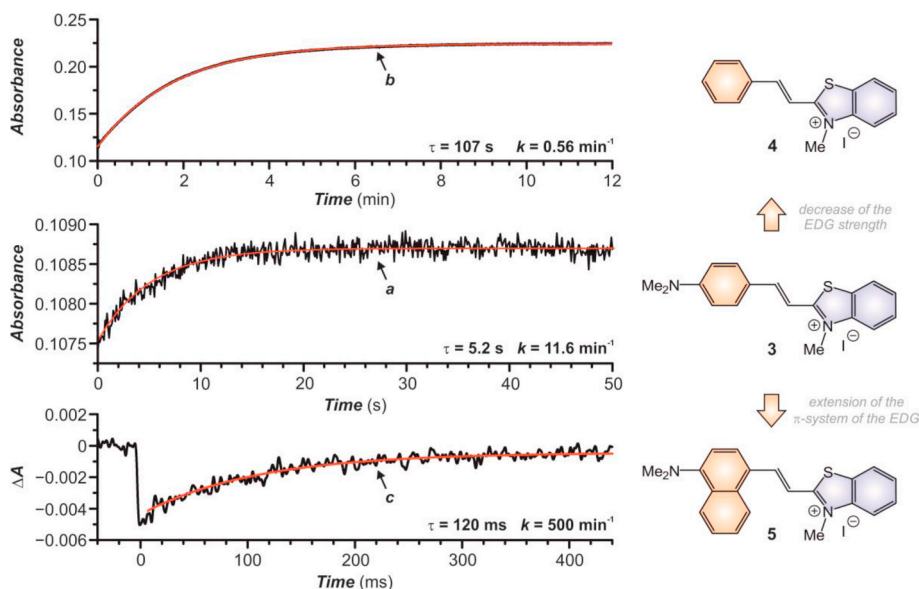
Fig. 4. Kinetic traces for the thermal isomerization of **3** (*a*, λ_{Ex} = 520 nm, Thorlabs collimated laser diode module, 4.5 mW, λ_{Obs} = 523 nm), **4** (*b*, λ_{Ex} = 405 nm, Thorlabs collimated laser diode module, 4.5 mW, λ_{Obs} = 377 nm) and **5** (*c*, λ_{Ex} = 532 nm, Continuum Surelite I-10 Q-switched Nd-YAG laser, 5 ns pulse width, 10 mJ per pulse, λ_{Obs} = 568 nm) in DMSO at 296 K at a concentration of 10 μM.
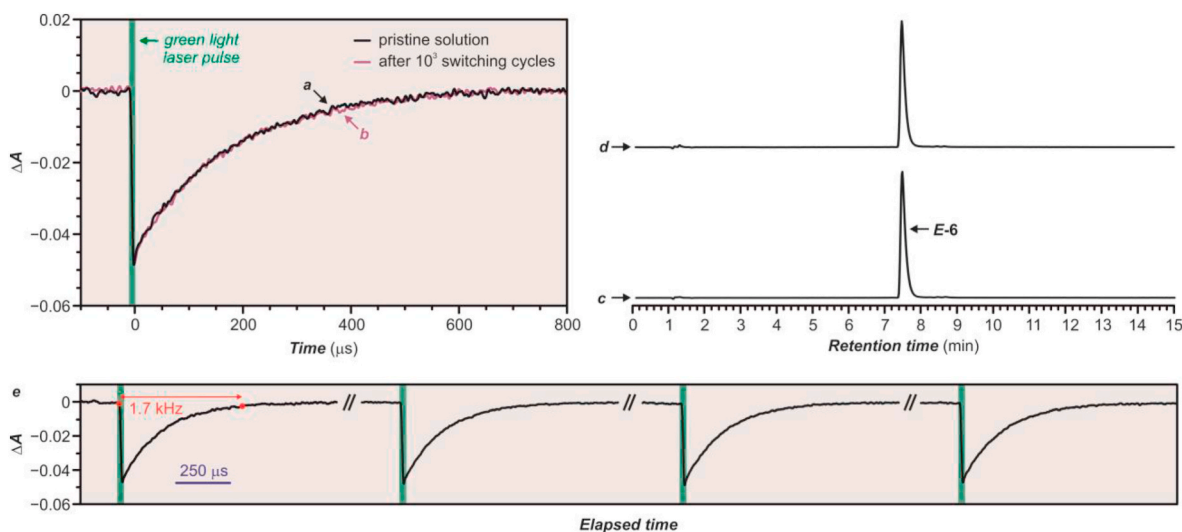

Fig. 5. Transient absorption change generated upon laser pulsed irradiation with green light (λ_{Ex} = 532 nm, Continuum Surelite I-10 Q-switched Nd-YAG laser, 5 ns pulse width, 10 mJ per pulse, λ_{Obs} = 572 nm) of a solution of **6** (10 μM) in DMSO at 296 K before (*a*) and after 1000 consecutive laser pulses (*b*). HPLC chromatogram recorded before (*c*) and after 1000 switching cycles (*d*). Oscillation of the optical density (*e*) at λ_{Obs} = 515 nm generated by laser pulsed irradiation with green light (λ_{Ex} = 532 nm).

driven photo-oscillators are materials that change their optical properties (color or absorbance) quickly and in a periodic fashion upon illumination. The maximum oscillation frequency of a photo-driven oscillator (ν_{Max} in Table 1) is defined as $\nu_{Max} = 1/(3\tau)$ [42]. Accordingly, ethene derivative 6 exhibits a maximum oscillation frequency of ca. 1.7 kHz (*e* in Fig. 5) under ambient conditions, which falls within the range of the radio waves (1 Hz–10^5 Hz). Remarkably, this fast heteroarylethene outperforms the maximum oscillation frequency of the other compounds explored in this work by 3–8 orders of magnitude (see Table 1) being, therefore, the best system for photonic applications in which a very fast switching within the microsecond timescale is required.

3. Materials and methods

3.1. Synthesis

Methyl iodide, 4-methylquinoline and 1-methyl-1*H*-pyrrole-2-carbaldehyde (**7**) were purchased from Aldrich or Acros and used as received. TLC analyses were carried out on 0.25 mm thick pre-coated silica plates (Merck Fertigplatten Kieselgel 60F$_{254}$) and spots were visualised under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (230–240 mesh). NMR spectra were registered on a Varian Unity Plus spectrometer at an operating frequency of 300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR or a Bruker Avance III 400 at an operating frequency of 400 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C NMR, using the solvent peak as an internal reference at 25 °C. All chemical shifts are given in ppm using δ_H Me$_4$Si = 0 ppm as a reference

and *J* values are given in Hz. Assignments were made by comparison of chemical shifts, peak multiplicities and *J* values, and were supported by spin decoupling-double resonance and bidimensional heteronuclear HMBC and HMQC correlation techniques. Mass spectrometry analyses were performed at the "C.A.C.T.I.-*Unidad de Espectrometría de Masas*" at the University of Vigo (Spain). Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected.

3.2. *Monitorization of the E-to-Z and Z-to-E isomerization*

^{1}H NMR spectra performed to monitor the isomerization of the heteroarylethenes were registered with a 400 MHz Varian Mercury spectrometer. HPLC chromatograms were recorded with a Waters 2795 Alliance HT Separations Module equipped with a Waters 2996 photo-diode array detector. The HPLC instrument was coupled to a ZQ micromass 2000 mass spectrometer. The column used was a reverse phase Kromasil C18 (particle size: 5.0 μm, internal diameter: 4.6 mm, length: 100 mm). The mobile phase flowed at 1.0 mL min^{-1}. The mobile phase used was a gradient from CH_3CN and H_2O 95:5 v/v (both containing a 0.1% v/v of formic acid) to pure CH_3CN. This gradient was applied over a period of 15 min. HPLC solutions were prepared using Millipore-MilliQ water and acetonitrile of HPLC-MS grade (VWR-BDH Prolabo).

All solutions used for the spectroscopic monitorization of the isomerization processes were prepared by dissolving the desired amount of the corresponding ethene derivative in DMSO (spectroscopic grade, Acros Organics). A population of *Z* isomer was generated upon irradiation of the sample and its relaxation was followed by time-resolved UV–Vis spectroscopy. For long-lived ethenes, the samples, thermostated in the dark at the desired temperature (± 0.1 K), were irradiated with a Thorlabs collimated laser diode module (4.5 mW) of the appropriate wavelength (λ_{Ex} = 405, 450 or 520 nm). Irradiation was pursued until no further changes could be observed in the electronic spectrum of the sample. Afterwards, the thermal *Z*-to-*E* isomerization was monitored by absorption spectroscopy using a Varian Cary 500E UV–Vis–NIR spectrophotometer. For short-lived samples, the thermal *Z*-to-*E* isomerization process was studied by means of the nanosecond laser flash photolysis technique. In this case, the *Z* isomer of the corresponding heteroarylethene was generated by a Q-switched Nd-YAG laser (λ_{Ex} = 532 nm, 5 ns pulse width, 1–10 mJ per pulse). The concomitant absorbance changes were monitored at 90° by a white-light analyzing beam produced by a Xe lamp (PTI, 75 W) in combination with a dual-grating monochromator (PTI 101) coupled to a Hamamatsu R928 photomultiplier for detection. In all instances, the experiments were realized in 1 cm optical path quartz cells (Hellma).

4. Conclusions

The thermal *Z*-to-*E* isomerization of a series of heteroarylethenes bearing distinct electron donating and electron withdrawing moieties has been explored. These organic chromophores can be triggered by irradiation with continuous or pulsed visible light, depending on their thermal isomerization kinetics. The relaxation time of the chromophores ranges from 1.7 h to 191 μs under ambient conditions. It should be noticed that compound **6**, which combines a *N*,*N*-dimethyl-amino-thienyl ring and a benzothiazolium salt as electron donating and electron withdrawing moieties, respectively, is the fastest photochromic switch based on an heteroarylethene reported so far. In addition, this photoswitch can be operated more than 1000 times without detecting any sign of photodegradation or fatigue, as a main advantage in comparison to the most traditional stilbene derivatives. This feature enables its potential application as a light-triggered optical oscillator, with an operating frequency of 1.7 kHz at room temperature under aerated conditions. Thus, the design schemes presented in this article are an excellent starting point for future investigations regarding the synthesis and kinetic study of fast ethene derivatives that might exhibit a thermal *Z*-to-*E* isomerization kinetics beyond the microsecond temporal domain.

Author contribution statement

Jaume Garcia-Amorós: Investigation, writing-original draft.
M. Cidália R. Castro: Investigation.
M. Manuela M. Raposo: Supervision, writing-original draft, funding acquisition.
Dolores Velasco: Conceptualization, supervision, writing-review, funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2022.111000.

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