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## COMMUNICATION

## 4,4'-Bithiazole-based tetraarylenes: new photochromes with unique photoreactive patterns<sup>†</sup>

Gildas Gavrel,<sup>*a*</sup> Pei Yu,<sup>\**a*</sup> Anne Léaustic,<sup>*a*</sup> Régis Guillot,<sup>*a*</sup> Rémi Métivier<sup>*b*</sup> and Keitaro Nakatani<sup>*b*</sup>

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Five 4,4'-bithiazole-based tetraarylenes were prepared and their photochromic behavior investigated. With their 1,3,5,7-octatetraene photoreactive backbone, they offer not only more available sites for further functionalizations, but also a novel design principle for the development of a new class of biphotochromes.

Since the first report in the late 1980s, photochromic diarylethenes have attracted widespread attention as versatile light-driven switching elements for the design of various photoresponsive systems.<sup>1</sup> This popularity is mainly due to their generally good photochromic behavior (thermal irreversibility and high photo-resistance) and also to their synthetic flexibility. Based on the pericyclic reaction between 1,3,5-hexatriene open form and 1,3-cyclohexadiene closed form (Scheme 1a), the photochromism of diarylethenes proved to be quite tolerant toward various structural patterns.<sup>2</sup> Indeed, although most of them have a basic structure with two side aryl groups and a cyclic ethene moiety, such as perfluorocyclopentene, cyclopentene, maleic anhydride or maleimide, recent works have also shown that one of the aryl groups can be replaced by substituted olefin groups.3 More interesting is the introduction of variously functionalized ethene moieties, leading to multifunctional diarylethene-based molecular switches.<sup>4-11</sup> In this work, we report on a family of easily accessible photochromes, termed tetraarylenes, that possess a 1,3,5,7-octatetraene core structure with unique photochromic reaction patterns (Scheme 1).



<sup>a</sup> Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR 8182, Université Paris-Sud 11, Bât. 420, 91405 Orsay, France. E-mail: pei.yu@u-psud.fr; Fax: +33 1 69 15 47 54; Tel: +33 1 69 15 61 83

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Two  $6\pi$ -electrocyclizations are now possible within such an octatetraene structure, as shown in Scheme 1b. The central diene moiety  $(C_3-C_6)$  is involved in both electrocyclizations. In the case of symmetrically substituted octatetraene, the two photochromic reactions would result in an identical photoproduct, while two different photoproducts could be expected for dissymmetric octatetraenes. If verified, the latter would constitute a new class of biphotochromes with two mutually exclusive photochromic reactions at the molecular scale, which is different from the conventional biphotochromes where the two photochromic hexatriene backbones are structurally independent from each other.<sup>12</sup> Molecules derived from such a photochromic backbone are interesting not only because they provide more available sites that can be further functionalized to meet specific demand, but they also offer a unique opportunity to investigate parameters controlling the two different and competing electrocyclization pathways in the case of dissymmetric octatetraenes. To illustrate the potential of such photochromic compounds, we have focused our attention on a few 4,4'-di(2-phenyl) thiazole-based symmetric and dissymmetric tetraarylenes.

The choice of 4,4'-di(2-phenyl)dithiazole as the central diene moiety is explained both by the ease of its synthetic access and by the excellent photochromic properties of thiazole-containing diarylethenes either as a side aryl group<sup>1a,13–15</sup> or as a central ethene moiety.<sup>16</sup> Besides thiazole groups, thiophene and oxazole groups are also used as the two side aryl groups in order to assess their impact on the photochromic properties.

As outlined in Scheme 2, **10–50** can be easily prepared in three steps. A double Hantzsch condensation reaction of thiobenzamide with 1,4-dibromo-2,3-butanedione, both commercially available,



Scheme 2 Synthesis of 10–50: (a)  $(COCH_2Br)_2/MeOH/reflux$ ; (b)  $Br_2/MeCN-CHCl_3/reflux$  or NBS-DMF, 70 °C; (c)  $ArB(OR)_{2,}$  Pd(PPh<sub>3</sub>)<sub>4</sub>, CsF/dioxane/reflux.

<sup>&</sup>lt;sup>b</sup> PPSM, ENS Cachan, UMR 8531, 61 av. Président Wilson, 94235 Cachan cedex, France

furnished in high yield 4,4'-di(2-phenyl)thiazole, which was then brominated to give 5,5'-dibromo-4,4'-di(2-phenyl)thiazole. For symmetric **10–40**, the final step was a double Suzuki–Miyaura coupling reaction with the corresponding heteroaryl boronic acid (ester). For the preparation of dissymmetric **50**, stepwise Suzuki–Miyaura coupling reactions proved to be troublesome because of purification and partial debromination problems. Nevertheless, it turned out that simultaneous running of the two Suzuki–Miyaura coupling reactions provided **50** as the major product, which could be readily isolated by chromatography from the two expected symmetric tetraarylenes **20** and **30**. **10–50** are fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS, elemental analyses and single crystal structure determinations for **10**, **20** and **50** (ESI†).

**10–40** display good and qualitatively similar photochromic properties in solution and they all can be switched between their colorless open forms (**10–40**) and colored closed forms (**1c–4c**) by alternate UV and visible light irradiation, as monitored by using electronic absorption and <sup>1</sup>H NMR spectroscopy (for **20–40**, Fig. S2–S4, ESI†). Their main photochromic data are gathered in Table 1, and exemplified by the UV-Vis spectral changes of **10** upon light irradiation (Fig. 1) and discussed below.

The initial solution of **10** is colorless and characterized by an intense absorption at 320 nm. Upon UV irradiation at 320 nm, the solution rapidly turns blue with the appearance of a broad band in the visible region as a result of the ring-closing reaction to produce **1c**. The presence of isosbestic points indicates clean

Table 1 Main photochromic data of symmetric tetraarylenes in MeCN

|    | $\lambda_{max}$<br>(nm) | $\stackrel{\epsilon_{max}}{(M^{-1}\ cm^{-1})}$ | $\Phi_{ m o  ightarrow c} \ (\lambda_{ m irr}/ m nm)$ | $\Phi_{\mathrm{c}  ightarrow \mathrm{o}} \ (\lambda_{\mathrm{irr}}/\mathrm{nm})$ | $t_{1/2}$ | Conversion<br>(%) (320 nm) |
|----|-------------------------|--|---|--|-----------|----------------------------|
| 10 | 321                     | 45000  | 0.55 (334)  | _  |           | 82                         |
| 1c | 612                     | 23 000   | _ ` ´   | 0.03 (657)   | 24 d      |                            |
| 20 | 329                     | 41 000   | 0.67 (334)  | _ ` `  |           | 86                         |
| 2c | 632                     | 14 000   | _ `   | 0.04 (657)   | 16.5 d    |                            |
| 30 | 279                     | 43 000   | 0.59 (313)  |  |           | 90                         |
| 3c | 574                     | 16000  |   | 0.03 (550)   | 91 d      |                            |
| 40 | 299                     | 48 000   | 0.41 (334)  |  |           | 62                         |
| 4c | 634                     | 23 000   |   | 0.03 (550)   | 5.4 h     |                            |



**Fig. 1** Absorption spectra of **10** (red) and its photostationary state (blue) (320 nm) in acetonitrile ( $2.2 \times 10^{-5}$  M) at room temperature.

interconversion between 10 and 1c. The coloration-bleaching cycle can be repeated many times without detectable fatigue, as shown in the inset of Fig. 1. It is interesting to compare these data to those reported for the corresponding triangle terarylene with three phenylthiazolyl groups.<sup>16a</sup> Not surprisingly, the spectral changes are similar, given the almost identical hexatriene structures involved in the two photochromic reactions. However, the thermal stability of 1c, estimated by monitoring the decay of the visible absorption band at various temperatures, is considerably decreased, with a half-life of 24 days at room temperature for 1c as compared to 3.3 years for the terarylene counterpart.<sup>15a</sup> One possible explanation to such a difference could be that the bulky substituent (phenylthiazole) in 1c would induce more strain in its molecular structure, thus decreasing its stability as compared to its terarylene counterpart with a methyl group as a substituent.<sup>15a</sup> A similar effect has been reported and successfully exploited to prepare conventional diarylethenes<sup>17</sup> as well as triangle terarylenes<sup>18</sup> with tunable thermal fading rate of their closed forms.

As can be seen in Table 1, both the absorption spectra of these tetraarylenes and the thermal stability of their closed forms can be significantly tuned by varying the nature of the two side aryl groups. Moreover, they are all characterized by pretty high cyclization quantum yields while those of their cycloreversions are in the usual range for diarylethenes. It is reasonable to think that such tetraarylenes in their open forms are prone to adopt, in order to minimize steric hindrance, the photoactive anti-parallel conformations rather than the photoinactive parallel ones. The fact that **10**, **20** and **50** all possess antiparallel conformations in their molecular structures, as revealed by their single crystal data (Fig. S7–S9, ESI<sup>+</sup>), is also in favor of similar conformations in solution for such tetraarylenes.

The solution photochromic behavior of dissymmetric **50** is qualitatively similar to those of symmetric ones (Fig. S5, ESI<sup>†</sup>). However, two photoproducts can be expected as shown in Scheme 3.

From its absorption spectral changes alone, it is difficult to conclude with the presence of only one closed form ( $5c_1$  or  $5c_2$ ) or both (Scheme 3): despite their structural differences, their absorption bands are expected to overlap in the visible region. However, <sup>1</sup>H NMR monitoring of a UV irradiated solution of **50** elucidates this, by clearly showing the formation of two new photoproducts along with the presence of **50** (Fig. S6, ESI†). By comparing the <sup>1</sup>H NMR spectra with those of two symmetric tetraarylenes **20** and **30** upon UV irradiation, the two new photoproducts are identified unambiguously as the two expected cyclized products **5c**<sub>1</sub> and **5c**<sub>2</sub> (Fig. S6, ESI†). The proportion of **5c**<sub>1</sub> and **5c**<sub>2</sub> varies with irradiation time and reaches 35/65 in the photostationary state (320 nm) with 84% of **50** being converted. The two photochromic reactions are fully reversible as both the initial UV-Vis and <sup>1</sup>H NMR spectra are completely



restored upon irradiation at 600 nm. As it is difficult to isolate pure  $5c_1$  and  $5c_2$  in sufficient amount, the thermal stability of each closed form cannot be easily and precisely evaluated. Nevertheless, monitoring the decay of the broad absorption band in the same way as for 1c-4c allows us to get a rough estimate of their overall thermal stability, with a half-life of 88 days at room temperature for a mixture of  $5c_1$  and  $5c_2$ .

The quantum yield determinations of both cyclization and cycloreversion are also made more complex by the formation of the two closed forms  $(5c_1 \text{ and } 5c_2)$  and their largely overlapped absorption spectra. To overcome these difficulties, analytical amounts of 5c1 and 5c2 were separated by HPLC and (Fig. S1, ESI<sup>+</sup>) their absorption spectra and molar absorption coefficients measured (Fig. S5, ESI<sup>+</sup>). Then, UV-visible absorption spectra of a 50 sample as a function of light irradiation time on a high-rate CCD spectrograph were recorded. Every absorption spectrum of the photochromic mixture at any time was carefully deconvoluted into the sum of its components  $(50, 5c_1, 5c_2)$  by an automatized procedure, yielding their corresponding time-evolution concentration profiles. The numerical fitting of such concentration profiles as a function of time for several UV and visible wavelengths of irradiation, using a 3-components kinetic photochromic scheme, provides the following individual photochromic quantum yields:  $\Phi$  (50  $\rightarrow$  $5c_1 = 0.23 \pm 0.02; \Phi (5o \rightarrow 5c_2) = 0.20 \pm 0.01; \Phi (5c_1 \rightarrow 5o) =$  $0.02 \pm 0.01; \ \Phi \ (5c_2 \rightarrow 5o) = 0.02 \pm 0.01.$  No significant dependence of quantum yields on excitation wavelength (334 and 365 nm for the cyclization, 547 and 657 nm for the cycloreversion) is observed. In contrast, the concentration profile of the three components varies with the light excitation wavelength (Fig. S7, ESI<sup>†</sup>).

Finally, **10** and **50** are also found to display crystalline state photochromism (data not shown), and this is in accordance with their molecular structures since, in addition to their antiparallel conformations, the distance between the two photoreactive carbon atoms involved in each of the two cyclization pathways is much shorter (3.441 and 3.467 Å for **10**, 3.423 and 3.445 Å for **50**) than 4.2 Å, the upper limit for the electrocyclization to take place in the crystalline state.<sup>19</sup>

In conclusion, we have described a new family of easily accessible 4,4'-dithiazole-based tetraarylenes with unique photoreactive patterns, good and tunable photochromic properties. With their octatetraene backbone they offer not only more available sites for further functionalisations but also provide a novel design principle for elaboration of a new class of biphotochromes, of which **50** represents the first example. Synthesis of other dithiazolyl-based tetraarylenes as well as extension of such octatetraene structure to other aryl groups are underway and will be reported in due time.

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## Notes and references

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