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Enhancement of the photochromic switching speed of bithiophene azo dyes

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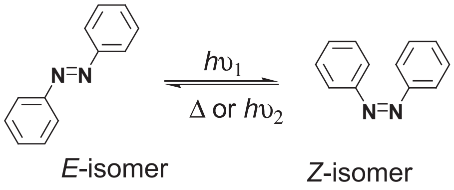
ABSTRACT

A series of heteroaryl substituted bithiophene azo dyes in solution were irradiated with visible light to promote the azo *E–Z* isomerization and then the kinetics of the thermal *Z–E* back reaction was studied. The speed of this process is strongly influenced by the nature of the aromatic ring linked to the N═N function. While thiazole bithiophene azo dyes exhibit high switching speeds between the two isomers, but limited interconversion, for benzothiazole and substituted thiadiazole bithiophene azo dyes the switching between the two photoisomers can be performed in 3 s with a significant conversion of the *trans*-isomer to the thermal unstable *cis*-isomer (19–21%) and therefore a notable variation of the visible spectrum is observed.

Azobenzene exists in two isomeric forms, the *E* (trans) and *Z* (cis), which exhibit different absorption spectra.[1] The more stable *E*-form can be partially converted to the *Z*-form by applying light, and with time, an equilibrium state is established between the populations of trans and cis isomers with a noticeable change in UV–Vis absorption spectra. The *Z*-form is unstable and usually returns thermally to the *E* isomer, following mono-exponential kinetics, although light of a different wavelength can be used to promote this reaction (Scheme 1).

The incorporation of these molecular photoswitches in different matrices, dispersed or covalently linked, led to the preparation of several photoresponsive organic or hybrid advanced materials with a variety of photochromic,[2–6] luminescent,[7–9] non-linear optics,[10–13] polarized light-induced anisotropy,[14–16] and mechanical properties.[17–24] The performance of these materials relies on our ability to control the kinetics of the *E-Z* photoisomerization which can be achieved by the proper choice of the environmental media[3,6] or by the change in the azobenzene structure.[25–28]

Although a large variety of diarylazo compounds are used in the design of optical materials, only a few reports concerning the photoisomerization of heterocyclic azo dyes can be found in the literature.[29,30] In the last years we have synthesized a large variety of heterocyclic azo dyes substituted by electron-donating and electron-withdrawing groups ('push/pull' substitution pattern) that possess solvatochromic, photochromic and nonlinear optical (NLO) properties which are influenced by the electronic nature of the π-conjugated bridge (thienylpyrrole or bithiophene) and by the substitution pattern on the aryl and heteroaryl-diazene moieties (Fig. 1).[31–38]



Scheme 1. Azobenzene photoisomerization.

Earlier, we observed that bithiophene azo dyes exhibit photochromic properties at room temperature, although the speed of the photo and thermal isomerization is quite slow: visible light irradiation of phenyl substituted 2,2′-bithiophene azo dyes, in solution, leads in less than 30 s to a significant decrease of the absorbance at λ_{max} (35–50%) due to the conversion of the *E*-isomer to the *Z*-isomer. When the irradiation ceases the system returns to the initial state following mono-exponential kinetics with a half-life time between 18 and 69 s, depending on the aryl substituents. As a result a noticeable colour intensity change is easily perceivable by a naked eye, due to the switching between the two isomers.[38] In order to increase the speed of this process we decided to substitute the phenyl ring by thiazole, benzothiazole or thiadiazole heterocycles which are known to have a marked influence on the thermal stability of the *Z*-isomer.[33,35]

The thiazolyl-, benzothiazolyl- and dithiazolyl-2,2′-bithiophene azo dyes presented in this study can be divided into four groups

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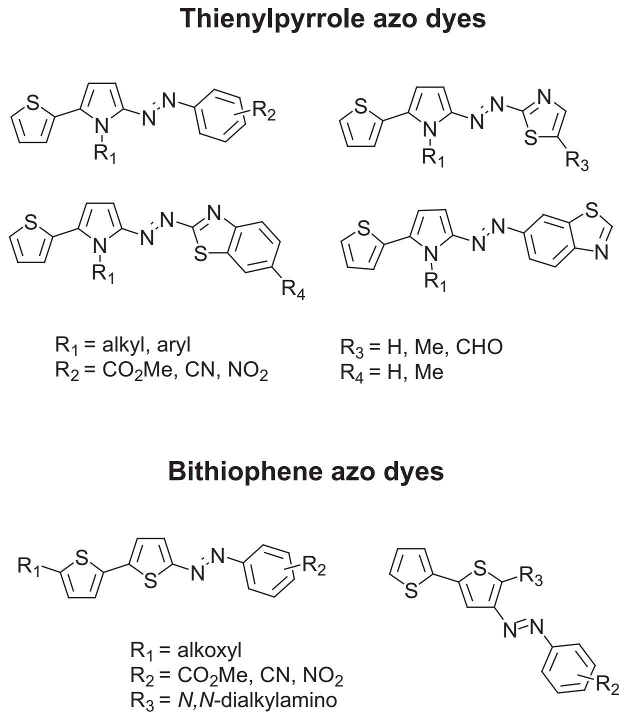

Figure 1. Structure of bithiophene and thienylpyrrole azo dyes bearing aryl-, thiazolyl- and benzothiazolyl-diazene moieties.

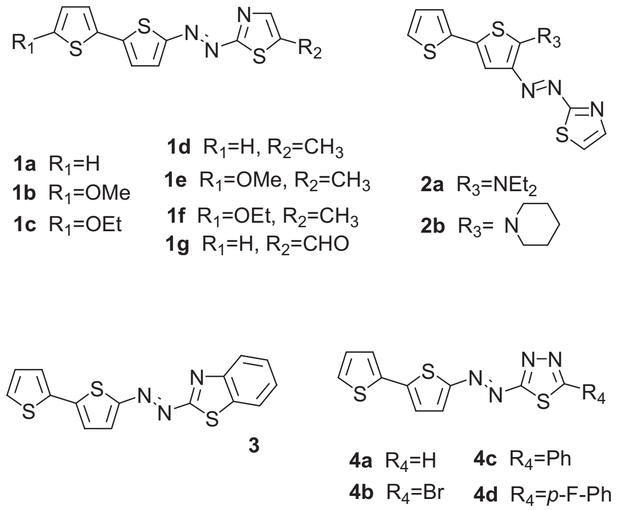

Figure 2. Structure of the bithiophene azo dyes functionalized with thiazole, benzothiazole and thiadiazole heterocycles.

according to the nature of the aromatic ring linked to the azo group and the position of that linkage (Fig. 2).[39,40] Azo bithiophene dyes **1, 3** and **4** possess the azo group linked to the 5 position of the bithiophene while in azo dyes **2** the linkage is at the 4 position; azo bithiophene dyes **1** and **2** are linked to thiazole group whereas azo dyes **3** and **4** are linked to benzothiazole or substituted thiadiazole nuclei, respectively.

The photochromic behaviour of these molecules was studied in 2.0×10^{-5} M acetone solutions by measuring the absorbance of the solution at the maximum wavelength of absorption while irradiating with visible light. The sample solutions (3.5 mL) were placed in a thermostated (20 °C) 10 mm quartz cell (3.5 mL) equipped with magnetic stirring. The visible spectrum was measured using a Cary 50 Varian spectrometer while irradiating with visible light (>420 nm) from a 150 W ozone free xenon lamp (6255 Oriel Instruments, 250–2400 nm range). The light from the UV–vis lamp was filtered using a water filter and a long-pass filter (Schott GG 420) and carried to the spectrophotometer holder, perpendicularly to the monitoring beam, using a fibre-optic system.

In acetone all compounds afforded deeply coloured solutions (orange to red) with molar absorptivities ranging from 1.1×10^4 to 3.3×10^4 M^{-1}cm^{-1}. The maximum absorption band of the stable trans form of unsubstituted thiazole and thiadiazole azo dyes **1a** and **4a** was found at 480 and 477 nm, respectively. A strong bathochromic shift of the maximum wavelength of absorption (33–43 nm) was observed when strong donating substituents (OR or NR_2) were placed in the 5′ or 4 position of the bithiophene ring (compounds **1b–c**,**e–f**, **2a–b**). A lower bathochromic shift (7–25 nm) was measured when methyl, bromine, phenyl or *p*-fluorophenyl were placed at the thiazole or dithiazole rings (compounds **1d**, **4b–d**).

Visible light irradiation of acetone solutions of all azo dyes **1–4** (except **2a**) led to a decrease of the absorption at λ_{max} (2–45%) and, at the same time, an increase in the band located near 400 nm, due to the *E–Z* photoisomerization (Fig. 3). When the light source was removed the absorption increased in few seconds to the initial value. The thermal colouration curves were analysed evaluating the fitting of the experimental data to the mono-exponential equation:

$$A(t) = A_1 e^{-kt} + A_{max}$$

where *A(t)* is the absorbance at λ_{max} at any instant *t*, A_1 a proportional factor, *k* the thermal colouration rate and A_{max} the absorbance in the dark when time approaches infinity. The mono-exponential model was found to accurately fit our data which indicates that the isomerization proceeds via a single pathway. The procedure was repeated several times and the behaviour was fully reproducible indicating that under these experimental conditions no degradation was observed.

For thiazole azo dye **1a** the absorption decrease under visible light was very fast, but short (8%) suggesting a limited transformation of the more stable *E*-isomer into the thermally unstable *Z*-isomer (Fig. 4). The fitting of the colouration/time curve indicates a life-time ($t_{1/2}$) of 0.66 s for the Z-isomer, which means that in 3 s the system returns to the initial state.

A similar behaviour was observed when methoxy and ethoxy groups were introduced on the bithiophene system (compounds **1b** and **1c**) which indicates that these substituents have no effect on the *E–Z* isomerization kinetics. On the other hand the introduction of a methyl group on the thiazole group (compounds **1d** and

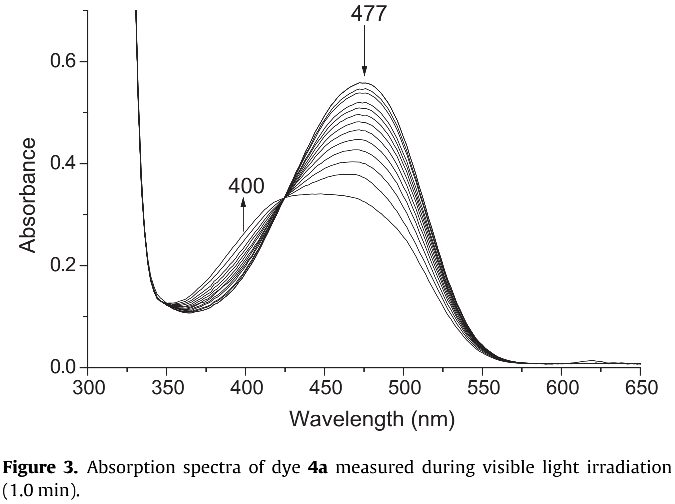

Figure 3. Absorption spectra of dye **4a** measured during visible light irradiation (1.0 min).