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A photoswitchable bis-azo derivative with a high temporal resolution†

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Jaume Garcia-Amorós,[a] Marta Reig,[a] Alba Cuadrado,[a] Mario Ortega,[a] Santi Nonell[b] and Dolores Velasco*[a]

The novel photoswitchable bis-azo derivative reported herein shows a high temporal resolution of 2 × 10^8 times between the thermal relaxation rates of its two constituting photochromes. Moreover, the slow and fast azo building blocks of this molecular construct can be triggered by using UV and visible light, respectively.

Molecular photoswitches use light, an unlimited, ubiquitous, free, and sustainable source of energy, as a fuel to swap between two or more different states of the molecule with markedly different properties.[1] The photochemical events that occur upon illumination induce structural variations at the molecular scale, which manifest in the modulation of the macroscopic features of the material, for instance, its shape, ability to absorb light, electronic behaviour and fluorescent emission. On this basis, the development of new organic photochromes that respond to light in a desired way has become a demanding challenge in the overall design of photo-responsive smart materials.

Among all organic photochromes, azobenzene and its substituted derivatives are doubtless the most frequently used for light-triggered materials. Azobenzene displays a reversible and clean photoisomerisation process between its *trans* and *cis* isomers. Moreover, the *cis*-to-*trans* conversion also takes place thermally in the dark.[2] In fact, the incorporation of azo dyes into different matrices has led to the preparation of a great variety of photoresponsive all-organic and hybrid materials with unique properties and abilities. Potential applications not only include artificial muscle-like actuators,[3,4] molecular scissors[5] and photo-oscillators,[6,7] but also lie in the biomedical field, *e.g.* as photoswitchable ion-channel blockers,[8] optogenetics[9] and even for restoring visual function to blind mice.[10]

Light-addressable materials integrating multiple azo chromophores on their covalent skeleton are currently of considerable interest since they allow easy access to applications that would, otherwise, be difficult to achieve with individual azo derivatives, including photoactive dendrons for drug delivery,[11] foldamers,[12] and molecular accordions[13] and hinges.[14] However, in these instances, the very same azo compound is used as a repetitive template to create or decorate the basic skeleton of the final material. As a result, the different azo moieties work synergistically, that is, they activate at once upon illumination and recover their initial *trans* form within the same timescale in the dark. Consequently, the final material can only perform one task at a time precluding multifunctionality.

With this in mind, we have engaged in the design of a new bis-azo derivative (**1** in Fig. 1) by combining into the very same molecular entity a 4,4′-dialkoxy-substituted azobenzene (**S1** or ''*slow*'' part in Fig. 1), which requires several hours to undergo its thermal back-reaction, and a 4′-alkoxyazopyridinium salt (**F1** or ''*fast*'' part in Fig. 1), which needs several hundreds of microseconds instead. Such a design principle endows the resulting dye with an unprecedented temporal resolution of more than eight orders of magnitude between the thermal isomerisation rates of its two constituting azo moieties. In addition, and owing

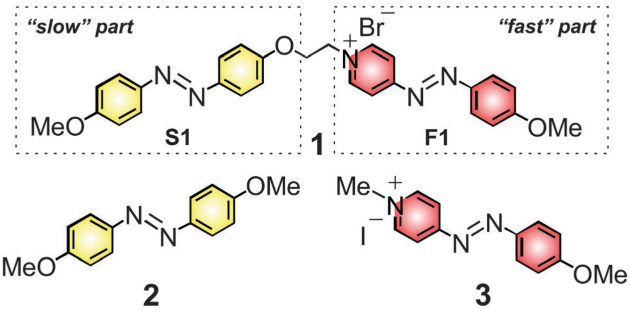

Fig. 1 Chemical structures of azo dyes **1–3**.

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[a] *Grup de Materials Orgànics, Institut de Nanociència i Nanotecnologia (IN^{2}UB), Departament de Química Orgànica, Universitat de Barcelona, Martí i Franquès 1, E-08028, Barcelona, Spain. E-mail: dvelasco@ub.edu; Fax: +34 93 339 78 78; Tel: +34 93 403 92 60*

[b] *Grup d'Enginyeria Molecular, Institut Químic de Sarrià, Universitat Ramón Llull, Via Augusta 390, E-08017, Barcelona, Spain*

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to the different lateral substitution of both azo building blocks, there is a gap of 50 nm between their wavelengths of maximum absorption. This feature enables the activation of the two azo units by using UV and green light, respectively. Thus, the design principle reported herein paves the way to new multifunctional azo dyes for photonic applications where simultaneous switching in two different timescales is required.

Bis-azo dye **1** was prepared in an overall yield of 25% through a convergent synthetic pathway involving two key precursors (**4** and **5** in Fig. S1, ESI†). 4-(2-Bromoethoxy)-4′-methoxyazobenzene (**4**) was obtained by alkylating 4-hydroxy-4′-methoxyazobenzene with 2-bromoethanol in THF. Methylation of 4-(4′-hydroxyphenylazo)-pyridine with Me_2SO_4 in DMF furnished 4-(4′-methoxyphenylazo)-pyridine (**5**). The nucleophilic substitution between **4** and **5** in MeCN yielded the target bis-azo dye **1**. The characterization of both the spectroscopic and kinetic behaviour of the two azo units of **1** also requires the synthesis of appropriate models. 4,4′-Dimethoxyazobenzene (**2** in Fig. 1) was prepared according to the literature procedure.[15] *N*-Methyl-4-(4′-methoxyphenylazo)-pyridinium iodide (**3** in Fig. 1) was obtained by reacting **5** with MeI in MeCN in a yield of 87%.

Before irradiation, the absorption spectrum of **1** (a in Fig. 2) in ethanol at 25 °C shows two main absorption bands peaking at 370 and 413 nm (λ_{Max} in Table 1) with molar absorption coefficients of 33.0 and 26.9 mM^{-1} cm^{-1}, respectively (ε in Table 1). The former band, which falls within the UV region of the electromagnetic spectrum, arises from the symmetry-allowed π–π* transition of **S1**. Otherwise, the latter one, which extends up to the visible region, can be attributed mainly to the π–π* transition of **F1**. In fact, similar absorption bands peaking at 354 and 403 nm are also present in the absorption spectrum of the corresponding model compounds **2** and **3**, respectively (b and c in Fig. 2). Indeed, the absorption spectrum of **1** resembles the one obtained by adding up those of the two separated model compounds, evidencing that the flexible ethylene spacer keeps both azo dyes close in space but electronically uncoupled.

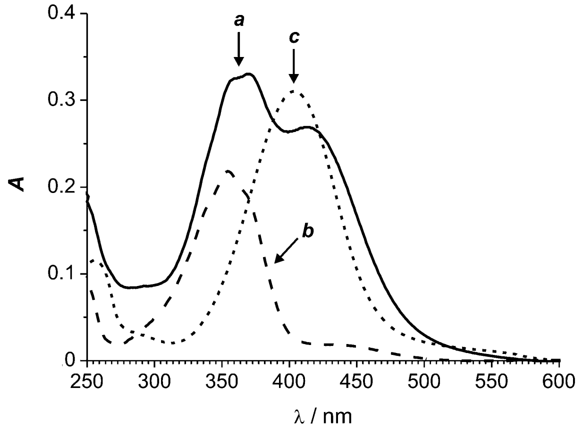

Fig. 2 Absorption spectra of ethanol solutions (10 μM, 25 °C) of the bis-azo dye **1** (a) and its model compounds **2** (b) and **3** (c).

Table 1 Spectroscopic and kinetic data for the *cis*-to-*trans* thermal isomerisation process of azo dyes **1–3** in ethanol

	λ_{Max} (nm)	ε (mM^{-1} cm^{-1})	$\tau_{298\ K}$	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})
1	370, 413	33.0/26.9	15 h 239 μs	91 ± 1 50 ± 1	−31 ± 4 −8 ± 4
2	354	21.8	15 h	92 ± 1	−29 ± 3
3	403	31.0	752 μs	53 ± 1	−9 ± 3

Upon irradiation with UV light (a high pressure Hg lamp, 500 W, λ_{irrad} = 320–390 nm), the steady-state absorption spectrum of an ethanol solution of **1** exhibited a decrease in the intensity of the band peaking at 370 nm, owing to the *trans*-to-*cis* photo-isomerisation of **S1**. Contrarily, the band placed at 413 nm remained unaltered, indicating thereby the short life of *cis*-**F1**. The thermal *cis*-to-*trans* isomerisation kinetics for both photoactive fragments of **1** was studied in ethanol. In all instances, the corresponding relaxation time (τ in Table 1) was determined by fitting a monoexponential function to the corresponding absorbance *vs.* time trace (b and c in Fig. 3). The thermal back-reaction of *cis*-**S1** was monitored by conventional time-resolved UV-vis spectroscopy (a in Fig. 3). *cis*-**S1** exhibited a very slow thermal isomerisation with a relaxation time of 15 h at 25 °C. On the other hand, the thermal relaxation of *cis*-**F1** was analysed by means of the nanosecond laser flash-photolysis technique (c in Fig. 3) prior to activation of **1** with visible light (a Continuum Surelite I-10 Q-switched Nd-YAG laser, 5 ns pulse width, 10 mJ per pulse, λ_{irrad} = 532 nm) registering thereby a relaxation time of only 239 μs. In this way, bis-azo dye **1** exhibits an excellent temporal resolution of 2×10^8 times between the thermal isomerisation rates of its two constituting azo fragments. Model compounds **2** and **3** showed a relaxation time similar to those recorded for **S1** and **F1**, respectively (see Table 1), evidencing, once again, the independent role of the two photoactive platforms of **1**.

The variation of the rate constants with temperature allowed for the determination of the associated enthalpies and entropies of activation ($\Delta H^{\neq}$ and $\Delta S^{\neq}$ in Table 1 respectively), using Eyring plots (d and e in Fig. 3). The differential thermal activation parameters registered for the isomerisation process of **S1** and **F1** indicate clearly that these two azo fragments thermally isomerise through different intimate mechanisms. The lower enthalpy of activation (50 *vs.* 91 kJ mol^{-1}, Table 1) and the lesser negative entropy of activation (−8 *vs.* −31 J K^{-1} mol^{-1}, Table 1) measured for the thermal back-reaction of *cis*-**F1** point out to a less energetic and less organized transition state for the process. Such a feature evidences the operation of the rotational mechanism. On the other hand, the thermal isomerisation of *cis*-**S1** proceeds through an inversional pathway, as demonstrated previously for its model compound **2**.[16] In fact, and to the best of our knowledge, bis-azo dye **1** is the first azo compound reported so far where both isomerisation mechanisms coexist in the very same molecule.

As mentioned before, for multifunctionality to be achieved, the target azo dye must not only exhibit a suitable temporal resolution but also enable an orthogonal activation of its constituting photochromes under optical control. In order to

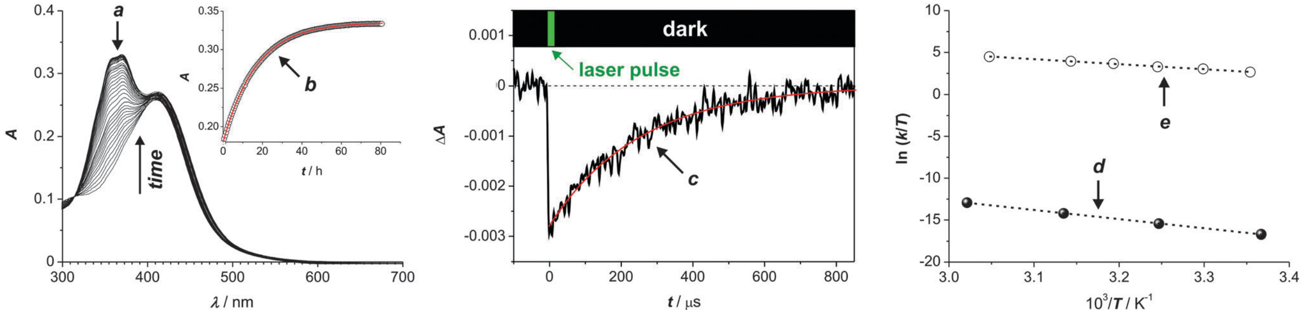

Fig. 3 Changes in the electronic spectrum (a) and first-order kinetic trace at λ_{obs} = 370 nm (b) of a **1** *cis*-to-*trans* thermally isomerising ethanol solution at 25 °C in the dark after its photo-isomerisation with UV light (a high pressure Hg lamp, 500 W, λ_{irrad} = 320–390 nm). Transient absorption change (c) photo-induced by laser pulsed irradiation with green light (an Nd-YAG laser, 5 ns pulse width, 10 mJ per pulse, λ_{irrad} = 532 nm, λ_{obs} = 420 nm) for azo compound **1** in ethanol at 25 °C. Eyring plot for the thermal back-reaction of *cis*-**S1** (d) and *cis*-**F1** (e) in ethanol. In all instances [**1**] = 10 μM.

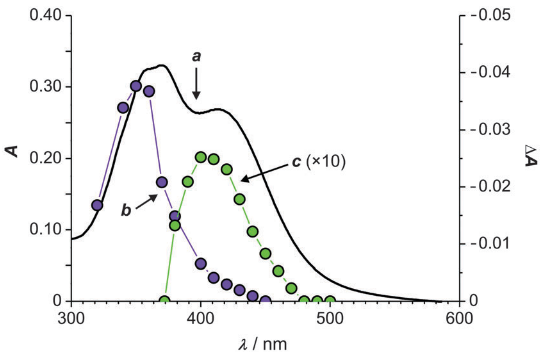

Fig. 4 Absorption spectrum of an ethanol solution (10 μM, 25 °C) of **1** (a) and absorption change after 5 ns of pulsed illumination at 355 nm (b) and 532 nm (c) respectively.

test the latter feature, the transient absorption spectrum of an ethanol solution of **1** at 25 °C was recorded 5 ns after the pulse of a laser operating at 355 nm and 532 nm, respectively (b and c in Fig. 4). Upon irradiation at 355 nm, the system showed response mainly from 320 nm to 400 nm, indicating that the **S1** fragment is activated. On the other hand, after irradiation at 532 nm, the system modified its optical density from 370 nm to 480 nm, owing to the selective activation of the **F1** platform. In the wake of these results, and even though there is some spectral overlap between the main absorption bands of the **S1** and **F1** moieties (see a in Fig. 1), both photochromes can be photoactivated upon suitable illumination.

In summary, the excellent temporal resolution of more than eight orders of magnitude together with the possibility to activate its slow and fast constituting azo photochromes by using UV and green light, respectively, makes this photoactive bis-azo dye a highly valuable chromophore for designing new multifunctional materials for photonic applications where simultaneous switching in two very different timescales might be essential.

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