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Light-controlled real time information transmitting systems based on nanosecond thermally-isomerising amino-azopyridinium salts

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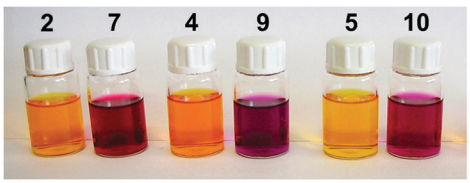
Aminoazopyridines are valuable molecules for stable information transmitting systems as well as for light-controlled optical oscillators. Amino-substituted azopyridinium methyl iodide salts transmit optical information within the time scale of nanoseconds, and moreover, show oscillation frequencies up to 1 MHz at room temperature.

The development of photo-actuators based on materials that reversibly change some of their properties, *e.g.* mechanical, magnetical, electrical, optical, *etc.*, in response to external stimuli is of great interest within materials science. A very attracting possibility comes from light-responsive materials, which allow remote operation without the need for direct contact to the actuator. Specifically, light-driven optical oscillators are photo-active materials that modify their optical properties periodically and extremely fast upon exposure to light of the appropriate wavelength. Oscillating materials have attracted a great deal of attention over the last few years due to their potential application in micropumps and autonomous valves that simulate the heart beating, photo-active polymers that mimic the cilia movement, artificial muscles for robotics, real-time optical information processors, molecular rotary motors, photo-switchable optical reflectors, among others.[1–10]

Azobenzene, a photochromic system, has been widely used for obtaining light-driven actuators since it exhibits a totally clean and reversible photo-isomerisation process between its *trans* and *cis* isomers. Moreover, *cis*-to-*trans* conversion takes place also thermally in the dark. For azobenzene-based ultrafast optical switches to be used in real-time information transmitting systems, it is essential that the return to the thermodynamically stable *trans* form in the dark elapses very quickly, within the sub-microsecond time scale. Push–pull derivatives are promising chromophores for this purpose since they are endowed with a very fast thermal *cis*-to-*trans* isomerisation kinetics at room temperature.

Among all azobenzenes, hydroxy-substituted methyl azopyridinium salts, which combine a strong push–pull configuration with the capability to establish an azo-hydrazone tautomeric equilibrium, have been reported last year as the fastest known thermally-isomerising azo-dyes.[11] These azoderivatives exhibited relaxation times for their thermal back reaction in the microsecond time scale.

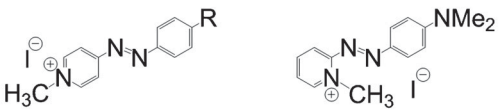
Here we report on the thermal *cis*-to-*trans* isomerisation kinetics of several push–pull amino-substituted azopyridinium methyl iodide salts that exhibit thermal isomerisation kinetics down to the nanosecond time scale at room temperature (Fig. 1). These azoderivatives are able to reach oscillation frequencies of their optical properties up to the MHz scale, which are comparable to the AM radio waves (600 kHz to 1.6 MHz) and the ultrasounds (1–20 MHz), and moreover, they are 10^3-fold higher than the fastest systems reported previously. An additional and noteworthy benefit is their high solubility in water, an environmentally friendly solvent. This is an interesting feature for both biological and medical applications such as photochromic ion channel blockers[12] or the photo-control of neurotransmitters in the central nervous system,[13,14] which both operate in aqueous media.



Non-ionic azopyridine derivatives

1 R = -OH 3 R = -OC_6H_{11} 5
2 R = -NH_2 4 R = -NMe_2

Ionic azopyridine derivatives



6 R = -OH 8 R = -OC_6H_{11} 10
7 R = -NH_2 9 R = -NMe_2

Fig. 1 Chemical structure of azoderivatives **1–10**.

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The kinetics of the thermal *cis*-to-*trans* isomerisation process of the different azoderivatives was studied by means of the nanosecond laser flash-photolysis technique. A population of *cis* isomers was created by pulsed-laser irradiation of the *trans* isomer at 355 or 532 nm employing a Continuum Surelite I-10 Q-switched Nd-YAG laser (5 ns pulse width, *ca.* 10 mJ per pulse). The concomitant absorbance changes were monitored at 90° by a white-light analysing 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. The relaxation time of the *cis* isomers, τ ($\tau = 1/k$), was determined by fitting a monoexponential function to the data. The maximum oscillation frequency of the different azo-dyes, which is a direct measurement of their information transmitting capability, was determined as $\nu_{max} = 1/(3\tau)$.

4-(4-Hydroxyphenylazo)pyridine (**1**) shows a fast relaxation time of 14 ms for its thermal isomerisation in ethanol at 298 K (Table 1). This fact is indicative that its thermal *cis*-to-*trans* isomerisation process in the dark takes place through a rotation around the N–N bond (rotational mechanism). The replacement of the phenol group in compound **1** by an aniline (compound **2**) causes a slight increase of the relaxation time up to 24 ms (Table 1 and Fig. 2a). This differential behaviour between azo-dyes **1** and **2** arises from the fact that although the amino function is a better electron-donating group than the hydroxyl one, azophenols establish the azo-hydrazone tautomeric equilibrium that facilitate the rotation around the N–N bond.[15,16] This was clearly evidenced when azophenol **1** was alkylated to obtain 4-(4-(5-hexenyloxy)phenylazo)pyridine (**3**), which exhibited a slow thermal relaxation kinetics beyond the second time scale since its capability to establish the tautomeric equilibrium was cancelled. This variation in the isomerisation kinetics was not observed for the *N*,*N*-dimethylamino-substituted azocompounds **4** and **5**, with thermal relaxation times of 19 ms and 27 ms in ethanol (Fig. 2b), respectively, comparable with that obtained for its non-alkylated counterpart **2** (24 ms, Table 1). As a whole, all the compounds **1–5** exhibited low oscillation frequencies of their optical properties ranging them from 1 to 54 Hz.

In order to diminish the thermal relaxation time of the azochromophore beyond the millisecond time scale, the pyridinic nitrogen of azo-dyes **1–5** was methylated to obtain their corresponding methyl iodide azopyridinium salts (compounds **6–10**) thereby creating a strong push–pull system.† The alkoxylated azopyridinium **8** exhibited a 1000-fold faster thermal isomerisation process (2.8 ms) in comparison with its non-methylated counterpart **3** ($\tau > 1$ s in ethanol at 298 K). In addition, the hydroxy-substituted azopyridinium salt **6** exhibited a relaxation time of 150 μs, which is 100-fold faster than that registered for the non-ionic hydroxyazopyridine **1** (14 ms, Table 1). The kinetic results arise from the strong electron-withdrawing character of the pyridinium salt, which induces a strong push–pull configuration in the azo-system that facilitates the rotation around the N–N bond of the *cis* isomer to recover the most stable *trans* form.

Extending this concept further, we hypothesized that combining the strong electron-withdrawing character of the pyridinium salt with the high electron-donating behaviour of the amino group which, moreover, is capable to establish an amino-imino tautomeric equilibrium,[17,18] we would obtain very short thermal relaxation times, perhaps under a microsecond. All the amino- and *N*,*N*-dimethylamino-substituted azopyridinium salts **7**, **9** and **10** exhibited very fast thermal relaxation kinetics in ethanol at 298 K ranging from 281 to 368 ns (Table 1 and Fig. 2c and d). The relaxation time of these azoderivatives was up to 10^4-times slower in the non-polar solvent 1,2-dimethoxyethane (DME), thereby registering relaxation times for their thermal isomerisation process ranging from 240 μs to 10 ms. To the best of our knowledge, azo-dyes **7**, **9** and **10** are the fastest thermally-isomerising azo-dyes reported heretofore in the literature.

Table 1 Wavelength of maximum absorption of the *trans* form in ethanol, relaxation time for the thermal *cis*-to-*trans* isomerisation and oscillation frequency for azocompounds **1–10** in different solvents at 298 K

	Non-ionic azopyridines				Ionic azopyridines								
	λ_{EtOH}	τ_{EtOH}	ν_{EtOH}		λ_{EtOH}	τ_{EtOH}	ν_{EtOH}	τ_{water}	ν_{water}	τ_{ACN}	ν_{ACN}	τ_{DME}	ν_{DME}
1	363 nm	14 ms	24 Hz	**6**	413 nm	150 μs	2.2 kHz	—[a]	—[a]	—[a]	—[a]	—[a]	—[a]
2	420 nm	24 ms	14 Hz	**7**	530 nm	281 ns	1.2 MHz	287 ns	1.2 MHz	316 ns	1.1 MHz	248 μs	1.3 kHz
3	358 nm	>1 s	<1 Hz	**8**	415 nm	2.8 ms	120 Hz	7.5 ms	44 Hz	4.2 ms	79 Hz	—[a]	—[a]
4	444 nm	19 ms	53 Hz	**9**	552 nm	329 ns	1.0 MHz	310 ns	1.1 MHz	333 ns	1.0 MHz	1.9 ms	175 Hz
5	433 nm	27 ms	12 Hz	**10**	560 nm	368 ns	0.9 MHz	302 ns	1.1 MHz	305 ns	1.1 MHz	9.7 ms	34 Hz

[a] Not determined.

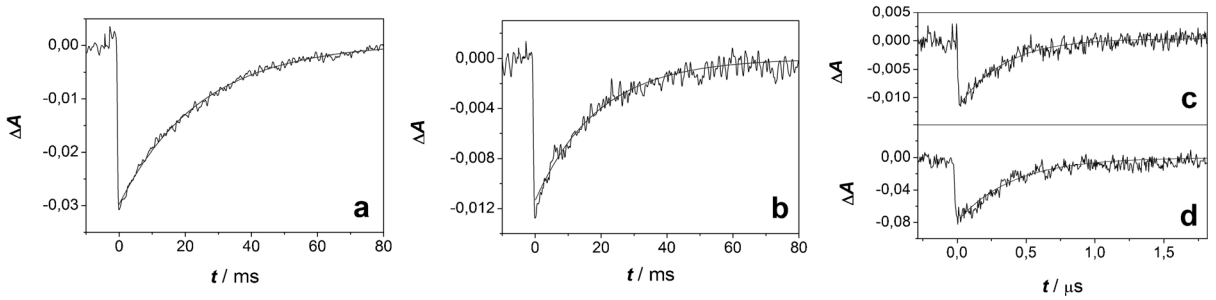

Fig. 2 Transient absorption change photo-induced by laser pulse irradiation ($\lambda_{irradiation}$ = 355 nm for **2** and **4** and 532 nm for **7** and **9**) of azo-dyes **2** (a), **4** (b), **7** (c) and **9** (d) in ethanol at 298 K ([**AZO**] = 20 μM, λ_{obs} = 375 nm for **2** and **4** and 545 nm for **7** and **9**).

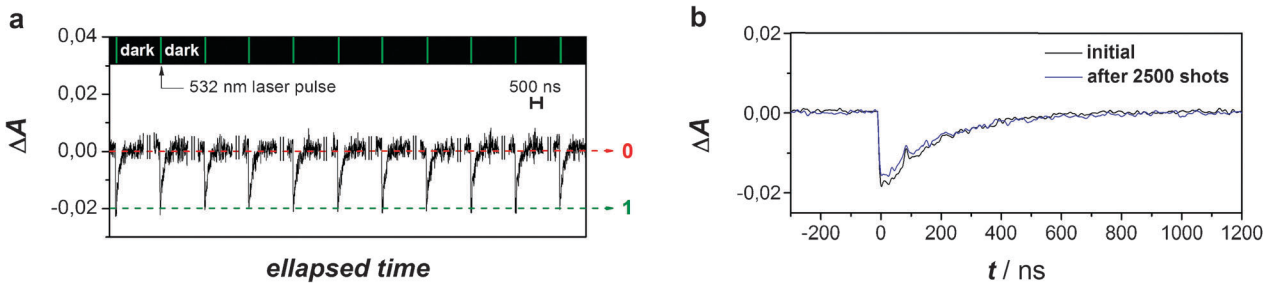

Fig. 3 Oscillation of the optical density generated by green light irradiation ($\lambda_{irradiation}$ = 532 nm) (a) and photostability after 2500 laser pulses (b) of an ethanol solution of azo-dye **10** at 298 K ([**AZO**] = 20 μM, λ_{obs} = 545 nm).

Taking into account the very fast thermal isomerisation kinetics exhibited by the amino-substituted azopyridinium salts **7**, **9** and **10**, they are the best candidates thus far for light-driven real time information processing and optical oscillating systems. Fig. 3(a) shows the oscillation of the optical density of azo-dye **10** in ethanol solution at room temperature with the time. The maximum oscillation frequency in the optical properties for azocompounds **7**, **9** and **10** ranges from 0.9 MHz to 1.2 MHz at 298 K (Table 1).

Both the repeatability and photostability of our prototypes were checked by submitting them to several pulsed green light (532 nm)–dark cycles. Fig. 3(b) evidences the high photostability exhibited by the amino-substituted azopyridinium salt **10** in ethanol solution at 298 K thereby observing that after 2500 cycles neither the absorbance change nor the relaxation time of the molecular oscillator was altered by the continuous work of the system. A similar behavior was registered for azo-dyes **7**, **9** and **10** in the different solvents analyzed.

In summary, the bistable nature, short excited life time (down to 281 ns at 298 K) and high photostability of the aminoazopyridinium salts reported herein make them ideal photo-active molecules for real time information transmitting systems and optical oscillators. In fact, the information transmission capability of these azopyridinium salts elapse 10^5-fold faster than that by means of the neuronal synapses (0.5 ms to 10 ms). The oscillation frequency of the systems reported herein is around 1 MHz at room temperature and they show no fatigue upon continuous work. On the other hand, their high solubility in aqueous media makes them valuable chromophores for photo-controlled biological and medical applications.

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Notes and references

† Synthesis of 4-[(4-aminophenyl)azo]-1-methylpyridinium iodide (**7**): **2** (150 mg) was dissolved in anhydrous CH_2Cl_2 (10 cm^3) under an inert atmosphere, and then, CH_3I (3 cm^3) was added. The solution was stirred at room temperature for 2 hours. After, the product was precipitated by adding hexanes, isolated by vacuum filtration and dried. **7** was obtained as a reddish crystalline solid (160 mg, 63%). ^{1}H NMR (400 MHz, d_6-acetone) δ: 9.05 (2H, d, ^{ar}H, J = 7.1 Hz), 8.24 (2H, d, ^{ar}H, J = 7.1 Hz), 7.93 (2H, d, ^{ar}H, J = 9.0 Hz), 6.93 (2H, d, ^{ar}H, J = 9.0 Hz), 4.58 (3H, s, CH_3) ppm. FT-IR (ATR) ν: 3343 and 3272 (N–H st), 3170 (=C–H st), 1600 (C=C st), 1474 (N=N st) cm^{-1}. HR-MS (ESI-MS): m/z Calcd. for $C_{12}H_{13}N_4^+$ [M^+] 213.1135; found 213.1140.

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