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Photo-driven optical oscillators in the kHz range based on push–pull hydroxyazopyridines

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Push–pull azophenols are valuable target molecules for stable photo-driven optical oscillators. Hydroxyazopyridinium methyl iodide salts show oscillation frequencies up to 10 kHz with no signs of fatigue upon continuous work.

Photo-driven oscillators modify dramatically some of their properties, *e.g.* mechanical, optical, *etc.*, quickly and in a periodic fashion upon illumination. Such devices are currently of considerable interest in materials science for their prospective use in, *e.g.*, nanomechanical devices.[1,2]

Azobenzenes are very useful chromophores for designing light-controlled materials because of their reversible photo-isomerisation between their two *trans* and *cis* isomers of different stabilities. Moreover, *cis*-to-*trans* back conversion takes place also thermally in the dark.

Among all azobenzenes, 4-*N*,*N*-dimethylamino-4′-nitro-azobenzene (**DNAB**) is the fastest known azo-dye, with relaxation times for thermal isomerisation ranging from 21 ms to 122 ms in alcoholic solutions.[3–5]

Hydroxyazobenzenes on the other hand show comparable thermal isomerisation kinetics (*e.g.*, 205 ms for **1**, Table 1).[6–8] However, they are still too slow for their use as photo-driven optical oscillators. We hypothesized that the introduction of strong electron-withdrawing groups in the azobenzene core resulting in a push–pull electronic distribution could decrease considerably the thermal *cis*-to-*trans* relaxation time in these azo-dyes and would therefore further increase the oscillation frequency of the optical oscillator. Hence, new substituted azophenols with powerful electron-withdrawing groups were designed for identifying fast photo-driven oscillators.

Table 1 Relaxation time, τ, for the thermal *cis*-to-*trans* isomerisation of the azo-dyes **1–11** in ethanol, effect of 1 eq. phenol added, and maximum oscillation frequencies, ν_{max}, for the corresponding optical oscillators at 298 K

	τ_{EtOH}	ν_{EtOH}/Hz	τ_{phenol}	ν_{phenol}/Hz
1	205 ms	1.63	204 ms	1.63
2	27 ms	12.3	—	—
3	4.6 ms	72.5	—	—
4	399 ms	0.83	—	—
5	50 ms	6.67	—	—
6	49 ms	6.80	11 ms	30.3
7	2.9 ms	115	1.1 ms	303
8	14 ms	23.8	1.4 ms	238
9	1.3 ms	256	644 μs	518
10	33 μs	10 100	—	—
11	150 μs	2220	—	—

Here we report on the synthesis and the thermal *cis*-to-*trans* isomerisation kinetics of several push–pull azophenols, which show relaxation times ranging from 27 ms to 33 μs at room temperature. The very fast relaxation kinetics exhibited by these azo-dyes makes them ideal candidates for applications as light-controlled photo-oscillators. The oscillation frequency of their optical properties spans the range from 10 Hz to 10 kHz, which is comparable to the radio waves (1 Hz to 10^5 Hz) and is also more than 100-fold higher than the hummingbird wingbeat (20–80 Hz). Moreover, the oscillating behaviour of the systems reported herein shows no fatigue over several working cycles. The bistable nature and short excited state lifetime of these azoderivatives are challenging features for their further incorporation as guests in photo-active liquid-crystalline materials[9,10] as well as for obtaining fast photo-controllable polymers and elastomers.[11]

The kinetics of the thermal *cis*-to-*trans* isomerisation process of the different azophenols (Fig. 1)† were studied by means of the laser flash-photolysis technique. *cis*-Azobenzenes were generated by UV-photolysis of the corresponding *trans* isomer using a Q-switched Nd-YAG laser (355 nm, 5 ns pulse-width, 1–10 mJ per pulse) and the recovery of the *trans* isomer was monitored by means of a CW Xe lamp. The relaxation time of the *cis* isomers, τ ($\tau = 1/k$), was determined by fitting a

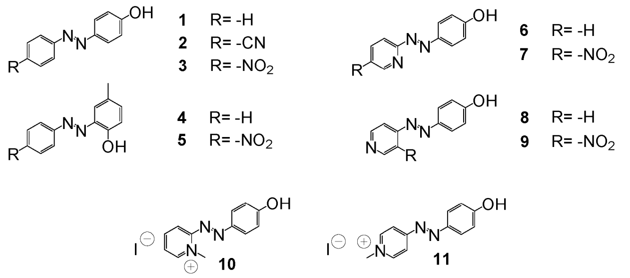

Fig. 1 Chemical structure of azoderivatives **1–11**.

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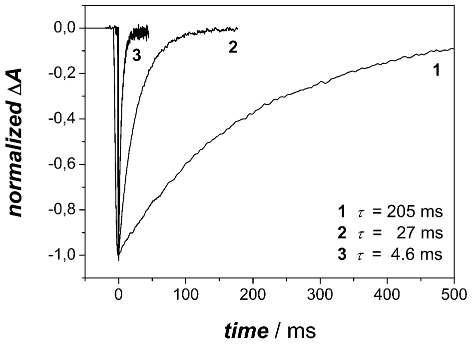

Fig. 2 Transient absorptions generated by UV irradiation (λ = 355 nm) of azo-dyes **1–3** in ethanol at 298 K ([**AZO**] = 20 μM, λ_{obs} = 370 nm).

monoexponential function to the data. The maximum oscillation frequency of the photo-driven oscillator, ν_{max}, is defined as $\nu_{max} = 1/(3\tau)$. Table 1 collects both τ and ν_{max} values for all the photo-driven oscillators studied.

The parent azophenol **1** showed a relaxation time of 205 ms for its thermal isomerisation in ethanol at 298 K. In a first attempt to decrease the relaxation time of the azo-dye, cyano- and nitro- electron-withdrawing groups were introduced at position 4′ of the azophenol (compounds **2** and **3**). The relaxation time of the 4′-cyanoazophenol **2** was 10-fold lower than that of the parent azophenol **1** (27 ms *vs.* 205 ms, Table 1). The relaxation time decreased even further for the 4′-nitroazophenol **3**, as expected, showing a τ value of 4.6 ms (Fig. 2). Thus, on going from the azophenol **1** to its push–pull nitro counterpart **3**, a clear increase of the oscillation frequency from 1.6 to 72.5 Hz was observed.

The placement of the hydroxyl group at position 2 was also considered due to the possible acceleration of the isomerisation kinetics *via* intramolecular hydrogen bonding (compounds **4** and **5**). However, a notable increase of the relaxation time was detected for both azo-dyes, showing τ values of 399 ms and 50 ms in ethanol at 298 K, substantially larger than those of **1** and **3**, respectively.

The results observed for the nitro-substituted compound **3** encouraged us to introduce stronger electron-withdrawing groups at position 4′ of the azophenol core. For this purpose, one of the benzene rings of the azo-dye was substituted by a pyridine ring as hydrogen bonding between ethanol and the pyridine moiety should increase the push–pull electronic distribution of the azo-dye (compounds **6** and **8**). As shown in Table 1, the relaxation time of these two azo compounds was 49 ms and 14 ms in ethanol, respectively, substantially shorter than that of the parent compound **1**, but too large compared to that of **3**. In an attempt to accelerate the thermal isomerisation kinetics phenol was added to the ethanol solution. Phenol forms a stable hydrogen bond with the nitrogen atom of pyridine. Indeed, addition of 1 eq. phenol increased the isomerisation rate of azo-dyes **6** and **8** (Table 1) by a factor of 4.5 and 10, respectively. The differential effect can be associated to the difficulty of the pyridinic nitrogen to establish a hydrogen bond with phenol at position 2 of the azobenzene core due to steric hindrance factors.

In order to increase further the strength of the push–pull electronic distribution as well as the hydrogen-bond acceptor character of the pyridinic nitrogen in the hydroxyazopyridine dye, the introduction of additional nitro groups in the convenient positions was carried out (compounds **7** and **9**). As anticipated, these two azoderivatives showed relaxation times of 2.9 ms and 1.3 ms in ethanol, respectively, which decreased further down to 1.1 ms and 644 μs in the presence of phenol (Table 1). The corresponding oscillation frequencies ranged from 30 Hz to 520 Hz. This demonstrates that the generation of push–pull systems by the establishment of hydrogen bonds between phenol groups and the pyridinic nitrogen, with the subsequent generation of a deficient electron density in the later, is a versatile option towards the generation of fast photo-driven oscillators.

Extending the concept even further, we reasoned that azopyridines with a permanent positively charged nitrogen should increase the kinetics and the stability of the final photo-driven oscillator. For this purpose, methylation of the pyridine nitrogen of azo-dyes **6** and **8** was done to afford the corresponding pyridinium methyl iodide salts **10** and **11**. **10** and **11** presented relaxation times of 33 μs and 150 μs at room temperature in ethanol, respectively (Fig. 3 and Table 1). To the best of our knowledge, these are the fastest thermally isomerising azo-dyes heretofore reported in the literature.

Due to their very fast thermal isomerisation rate, **10** and **11** are the best candidates to be applied as light-controlled optical

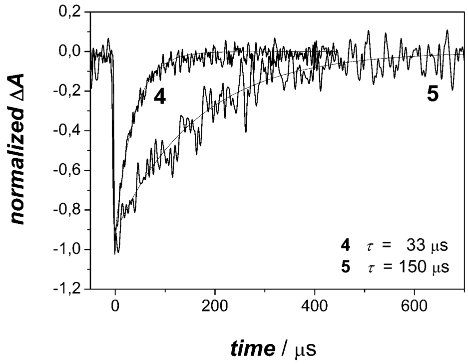

Fig. 3 Transient absorptions generated by UV irradiation (λ = 355 nm) of azo-dyes **10** and **11** in ethanol at 298 K ([**AZO**] = 20 μM, λ_{obs} = 420 nm).

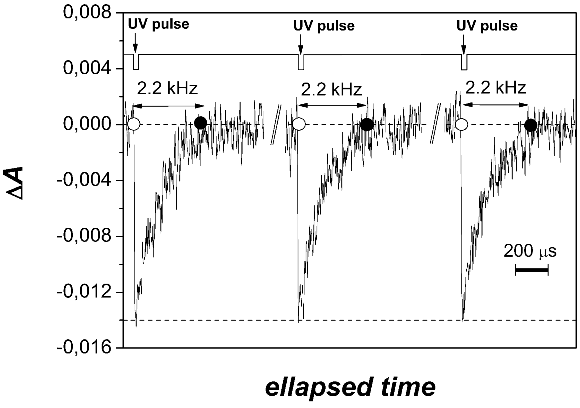

Fig. 4 Oscillation of the optical density of an ethanol solution of azo-dye **11** generated by UV light irradiation (λ = 355 nm, 5 ns pulse-width) at 298 K ([**AZO**] = 20 μm, λ_{obs} = 420 nm).

oscillators. Fig. 4 shows the oscillation of the optical density of azo-dye **11** with time. The oscillation frequencies of azo-dyes **10** and **11** in ethanol solution are of 10 kHz (**10**) and 2.2 kHz (**11**), respectively, at room temperature (Table 1). It can be also seen in Fig. 4 that the optical oscillators reported show no fatigue after several cycles (less than 1% of the signal after 3 pulses with UV-light for all the azo-dyes).

In summary, stable photo-driven optical oscillators based on push–pull azophenols have been reported. The most promising oscillators are those based on hydroxyazopyridinium methyl iodide salts, due to the strong push–pull electronic distribution of the azo-dye which allows a fast thermal isomerisation of the *cis* isomer within the time scale of microseconds. The oscillation frequency of these devices ranges within 2 and 10 kHz at room temperature and they show no fatigue upon continuous work.

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Notes and references

† Azocompounds **1–5** and **8** were prepared by coupling the diazonium salts of aniline, 4-cyanoaniline, 4-nitroaniline or 4-aminopyridine with phenol (**1–3** and **8**) or *p*-cresol (**4** and **5**) in basic media at 0–5 °C.[12,13] Azo-dyes **6**, **7** and **9** were obtained by the reaction between 2-hydrazinopyridine, 2-hydrazino-5-nitropyridine or 4-hydrazino-3-nitropyridine and 1,4-benzoquinone in acidic media.[10,14] 2-Hydrazino-5-nitropyridine and 4-hydrazino-3-nitropyridine were obtained from 2-chloro-5-nitropyridine and 4-chloro-3-nitropyridine, respectively, by means of an S_NAr reaction with $N_2H_4 \cdot H_2O$ in 1,4-dioxane at room temperature overnight.[15] Azoderivatives **10** and **11** were synthesized from **6** and **8**, respectively. First, both azo-dyes were acetylated by using AcCl and Et_3N in dry THF. Next, the methylation of their pyridinic nitrogen was carried out using CH_3I in THF at reflux for 1 h. Finally, the acetyl group was cleaved with a catalytic amount of AcCl in MeOH to afford the methyl iodide azopyridinium salts **10** and **11**.[16] The spectroscopic characterization of the novel azo-dyes **9** and **10** is given below.

9: *^{1}H NMR* (400 MHz, d_6-acetone): 9.23 (1H, s, ^{ar}H), 8.96 (1H, d, ^{ar}H, ^3J = 5.3 Hz), 8.14 (1H, br s, -O*H*), 7.91 (2H, d, ^{ar}H, ^3J = 8.9 Hz), 7.62 (1H, d, ^{ar}H, ^3J = 5.3 Hz), 7.08 (2H, d, ^{ar}H, ^3J = 8.9 Hz) ppm. *HR-MS* ESI, *m*/*z*: Calc. for $C_{11}H_8N_4O_3$: 244.0596; found: 245.0676 (M^+ + H).

10: *^{1}H NMR* (400 MHz, d_6-acetone): 9.07 (1H, m), 8.68 (1H, m), 8.22 (1H, m), 8.12 (1H, m), 8.05 (2H, d, ^{ar}H, ^3J = 9.0 Hz), 7.06 (2H, d, ^{ar}H, ^3J = 9.0 Hz), 4.73 (3H, s, CH_3-N) ppm. *HR-MS* ESI, *m*/*z*: Calc. for $C_{12}H_{12}N_3O^+$: 214.0975; found: 214.0981 (M^+).

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