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Photo-controllable electronic switches based on azopyridine derivatives†

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Stable photo-controllable electronic switches based on new light-sensitive azopyridines are reported herein. Such systems produce notable variations in the cathodic current density on working at low reduction potentials when UV light falls on them. The appropriate design of the azopyridine chromophore allows modulating the response time of the final opto-electronic switch.

Molecular switching materials have attracted much attention in the last few years because of the very rapid development of modern technology. This phenomenon arises from the great usefulness of such materials in data-elaboration, -storage and -communication elements for many devices. Specifically, molecular photo-switches are materials than operate reversibly between two different states just by applying light.[1–3]

Light is a very convenient trigger for switching purposes since it is a cheap and environmentally friendly energy source which can be wireless manipulated both locally and quickly. As a consequence of the molecular variations produced upon illumination of the material, a significant modification of some of its properties is induced. Modifying the conductance of molecules by applying light, that is, opto-electronic switching, is nowadays a very active area of research due to its high impact on nano-electronics.[4–8] Moreover, opto-electronic switches are also of great interest within biology since they are able to mimic photoreceptor cells, which convert the incoming light into electrical impulses that are transmitted to the brain *via* nerve fibers.[9]

Azobenzenes have been widely used for obtaining a great variety of light-controlled materials such as artificial muscles,[10–13] logic gates,[14,15] the photo-control of ion channel blockers and enzymes activity in living organisms,[16,17] among others. Azo-dyes isomerise to their metastable *cis* form upon UV-light irradiation; the initial state is restored by irradiation with visible light or by simply thermal relaxation.

For opto-electronic switching, the design and preparation of new molecules that exhibit both a chromogenic group and an electro-active function is required. In this way, azopyridines are valuable target molecules for this aim since they exhibit completely reversible isomerisation and reduction processes. Indeed, this type of azo derivatives has been already used recently for obtaining fast light-driven optical switches and photo-oscillators.[18,19] However, the ability of the azopyridine chromophore as light-induced electro-switches remains still unexplored. As far as we know, there is only one previous study which deals with the photo-electrochemical properties of azobenzenes.[20]

Here we report on the molecular design and opto-electronic switching of several azopyridine derivatives (Fig. 1). Such compounds induce notable changes in the cathodic current density up to 7 μA cm^{-2} when UV light falls on them with the added benefit that they work at low voltages down to −0.67 V referenced *versus* the Ag/AgCl/KCl (3 M) electrode. The rational molecular design of the azopyridine core allows a proper tuning of the response time of the light-controlled electro-switch which will determine its final applicability.

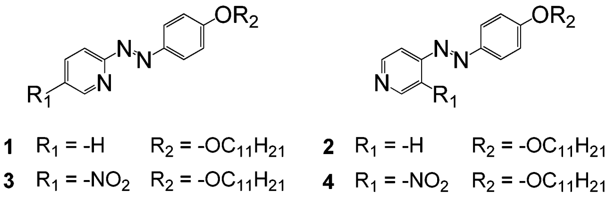

Fig. 1 Chemical structure of azopyridines **1–4**.

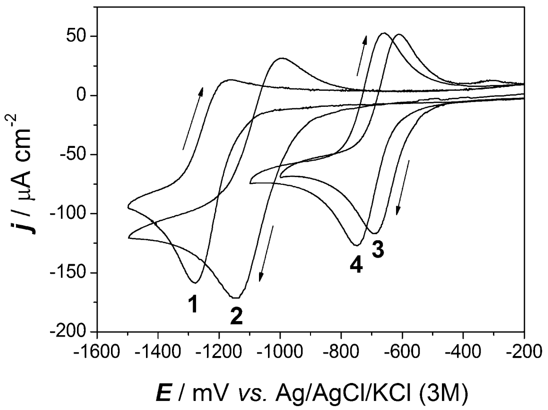

Fig. 2 First reduction process (**O1**/**R1**) for the *trans* isomer of azopyridines **1–4** in anhydrous DMF + 0.1 M TBAP at T = 315 K ([**AZO**] = 1 mM, v = 100 mV s^{-1}).

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The voltammetric study of azopyridines **1–4** allows determining the voltage of operation for each opto-electronic switch, *E*(**O1**/**R1**). All voltammetric experiments were performed in anhydrous DMF + 0.1 M of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte at 315 K (Fig. 2).

Parent *trans*-4-(5-hexenyloxy)azobenzene shows its first reversible reduction (**O1**/**R1**) at −1.42 V (Fig. S1, ESI†) similarly to *trans*-azobenzene (−1.33 V). This result evidences that the introduction of alkoxyl chains in the azobenzene core does not overly disturb the electrochemical behaviour of the azo molecule. The substitution of one of the benzene rings of the azo-dye by a π-deficient pyridine ring produced a clear decrease in the first reduction potential registering values of −1.28 V and −1.14 V for the *ortho*- (**1**) and *para*-substituted (**2**) azopyridines, respectively (Table 1). This first reversible reduction process corresponds to the gain of one electron affording radical anionic species. The reduction potential was notably positively-shifted when the strong electron-withdrawing nitro group was introduced at a conjugated position of the azobenzene core since it provides a more efficient electronic delocalisation of the lone electron. Accordingly, the first reduction process took place at −0.68 V and −0.72 V for the nitro-substituted azopyridines, **3** and **4**, respectively (Table 1). Both **3** and **4** showed lower first reduction potentials than their non-pyridine-containing counterpart, 4-(5-hexenyloxy)-4′-nitroazobenzene (−0.85 V, see Fig. S1 (ESI†)).

Table 1 Cathodic reduction potentials of the first, *E*(**O1**/**R1**), and second reduction processes, *E*(**O2**/**R2**), for the *trans* isomer of azopyridines **1–4**. Relative, Δ*j*, and absolute, Δj_{max}, current density change at *E*(**O1**/**R1**) upon irradiation with UV-light at $T = 315$ K ([**AZO**] = 1 mM, anhydrous DMF + 0.1 M TBAP, $v = 100$ mV s^{-1})

	E(**O1**/**R1**)/V	*E*(**O2**/**R2**)/V	Δ*j*/%	Δj_{max}/μA cm^{-2}
1	−1.28	−2.09	1.53	2.43
2	−1.14	−1.95	3.97	6.81
3	−0.68	−1.21	4.16	4.86
4	−0.72	−1.39	3.02	3.24

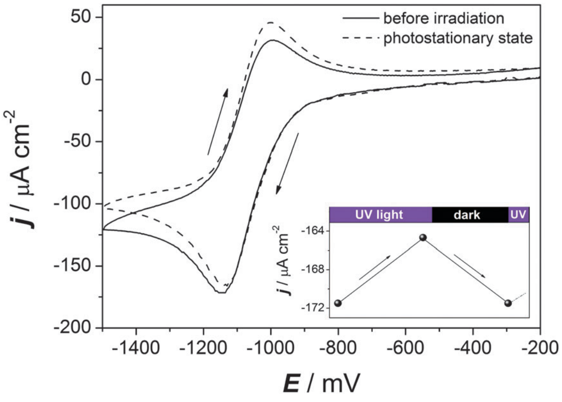

Fig. 3 Photo-voltammetric experiment for azopyridine **2** in anhydrous DMF + 0.1 M TBAP at $T = 315$ K ± 0.1 K ([**AZO**] = 1 mM, $v = 100$ mV s^{-1}). Inset: evolution of the cathodic current density at *E*(**O1**/**R1**) = −1.14 V with the time upon irradiation with UV light ($320 < \lambda < 390$ nm, high pressure mercury lamp 500 W; luminous emittance of the irradiation set-up = 1400 lux) and in the dark isothermally.

Enlarging the reduction scan to more negative potentials, a second irreversible process (**R2**) was detected for azopyridines **1–2** at −2.09 V and −1.95 V, respectively (Table 1 and Fig. S1, ESI†), associated with the gain of a second electron forming the dianionic species. Contrarily, this reduction process was reversible (**O2**/**R2**) for the nitro-substituted azopyridines, **3** and **4**. Furthermore, it took place at a more positive potential, −1.21 V and −1.39 V, respectively. The differential electrochemical behaviour indicates a higher stability of the reduced species formed from the nitro-substituted azo-dyes, **3** and **4**, due to the efficient resonance established between the azo function and the nitro electron-withdrawing group. The scan to positive potentials evidenced that azo compounds **1–4** are stable to oxidation processes.

Photo-voltammetric experiments showed that the isothermal irradiation of the electrochemical bath with UV light at 315 K produced a clear decrease in the cathodic current density (see both Fig. 3 and 4a). This feature can be associated with a lower diffusion coefficient for the *cis* form of the electro-active species.

The dropping of the cathodic current density due to the *trans*-to-*cis* photo-isomerisation of the azo-dye, that is, the absolute efficiency of the opto-electronic switch, Δj_{max}, was quantified by subtracting the cathodic current density value at a constant reduction potential equal to *E*(**O1**/**R1**) before UV-irradiation, j_0, from the one once the photo-stationary state has been reached, j_{irrad} ($\Delta j_{max} = j_{irrad} - j_0$). The relative photo-electronic efficiency, Δ*j*, which is independent of the

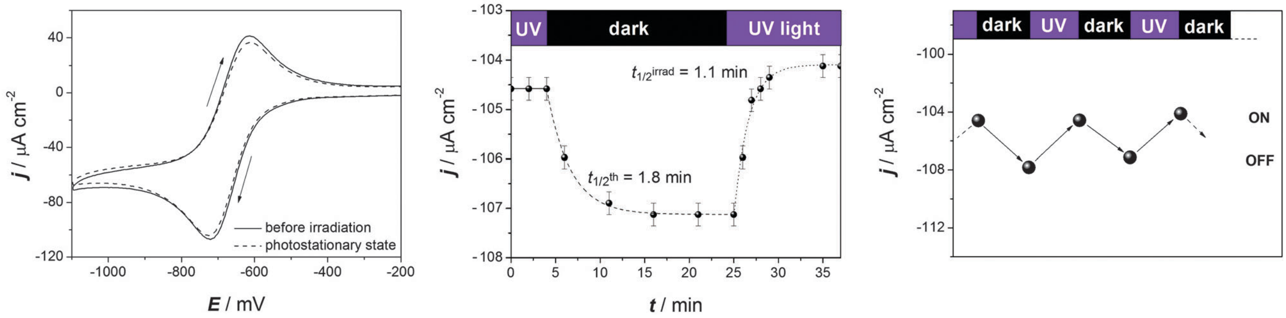

Fig. 4 Photo-voltammetric experiment (a), evolution of the cathodic current density at *E*(**O1**/**R1**) = −0.72 V with the time: increase in the cathodic current density by keeping in the dark a previously UV-irradiated solution (first part of the curve) and decrease in the cathodic current density upon UV-light irradiation of the sample (second part of the curve) (b) and cyclic photo-voltammetric experiment (c) for the nitro-substituted azopyridine **4** in anhydrous DMF + 0.1 M TBAP at $T = 315$ K ([**4**] = 1 mM, $v = 100$ mV s^{-1}, UV irradiation was performed with a high pressure mercury lamp 500 W; luminous emittance of the irradiation set-up = 1400 lux).

scan rate but concentration-dependent,[21] was determined to be $\Delta j = |(j_{\text{irrad}} - j_0)/j_0| \times 100$.

All azopyridines showed notable changes in the cathodic current density upon UV-irradiation thereby showing absolute efficiencies ranging from 2.0 μA cm^{-2} to 5.4 μA cm^{-2}. According to both their absolute and relative efficiency, both azopyridines **2** and **3** were proved as the most appropriate chromophores to be applied in light-driven electronic switches since they exhibited the highest Δj and $\Delta j_{\max}$ values ($\Delta j = 3.97\%$ and $\Delta j = 4.16\%$ and $\Delta j_{\max} = 6.81$ μA cm^{-2} and $\Delta j_{\max} = 4.86$ μA cm^{-2} for **2** and **3**, respectively).

Besides both the absolute and relative efficiency of the opto-electronic switch, the response time is also a crucial parameter to consider in its overall performance and usefulness. Upon turning off the irradiation, the initial value of the cathodic current density was restored in all the cases analysed (Fig. 3 (inset) and Fig. 4b).

Parent azopyridines, **1** and **2**, exhibited slow thermal back reactions needing several hours to recover their stable *trans* form. Hence, the system operates between two very stable states. This feature can be further exploited for the fabrication of light-controlled electronic memories. The return to the initial state was dramatically faster for the nitro-substituted azopyridines, **3** and **4**, due to their push–pull electronic distribution. In this case, the opto-electronic switch shifts in a quick fashion between both states thereby registering relaxation times within a few minutes.

Time-resolved photo-voltammetric experiments were performed with both nitro-substituted azopyridines **3** and **4** in order to determine the characteristic times of the corresponding light-driven electronic system. Fig. 4b shows the evolution of the cathodic current density in a photo-voltammetric experiment carried out with the nitro-substituted azopyridine **4**.

The variation of the cathodic current density in the dark was fitted to eqn (1), whereas the current density change under UV-irradiation was described by eqn (2):

$$j_t - j_0 = \Delta j_{\max} \times \exp(-k^{\text{th}} t) \tag{1}$$

$$j_t - j_0 = \Delta j_{\max} \times [1 - \exp(-k^{\text{irrad}} t)] \tag{2}$$

where k^{th} and k^{irrad} are the rate constants for both processes of the light-controlled electronic switch, respectively.

The half-life to obtain the corresponding photo-stationary state under UV-irradiation, ${t_{1/2}}^{\text{irrad}}$, as well as that for the thermal recovery of the thermodynamically stable *trans* form in the dark, ${t_{1/2}}^{\text{th}}$, were determined to be $t_{1/2} = \ln 2/k$. ${t_{1/2}}^{\text{irrad}}$ was 1.4 min and 1.1 min, while ${t_{1/2}}^{\text{th}}$ was 5.4 min and 1.8 min for azo-dyes **3** and **4**, respectively.

The stability and reversibility of the fast light-driven electronic switches obtained from the nitro-substituted azopyridines **3** and **4** were both tested by subjecting them to some successive UV-light irradiation-dark cycles. No significative fatigue was detected for the light-controlled electronic switches upon cyclic work (see Fig. 4c). Indeed, both photo- and electrochemical properties of the reported opto-electronic switches remained unaltered after more than 20 working cycles.

In summary, azopyridine derivatives are stable photo- and electro-active molecules thereby being valuable materials to be applied further in micro- and nano-light-controllable electronic switches. These molecules induce notable changes in the current density up to 7 μA cm^{-2} when they are irradiated with UV-light. Specially remarkable are those electro-switches based on nitro-substituted azopyridines **3** and **4** which, besides their low voltage of operation (down to −670 mV *versus* the Ag/AgCl/KCl (3 M) electrode), they are able to switch back and forth between both electric states within the minute time scale.

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