Electronic supplementary material

Photo-controllable electro-actuators based on azopyridine derivatives

Jaume Garcia-Amorós[1], Elvira Gómez[2], Elisa Vallés[2] and Dolores Velasco[1,]*

[1] Grup de Materials Orgànics, Departament de Química Orgànica, Institut de Nanociència i Nanotecnologia (IN^{2}UB), Universitat de Barcelona, Martí i Franqués 1-11, E-08028, Barcelona, Spain

[2] Electrodep, Departament de Química Física, Institut de Nanociència i Nanotecnologia (IN^{2}UB), Universitat de Barcelona, Martí i Franqués 1-11, E-08028, Barcelona, Spain dvelasco@ub.edu

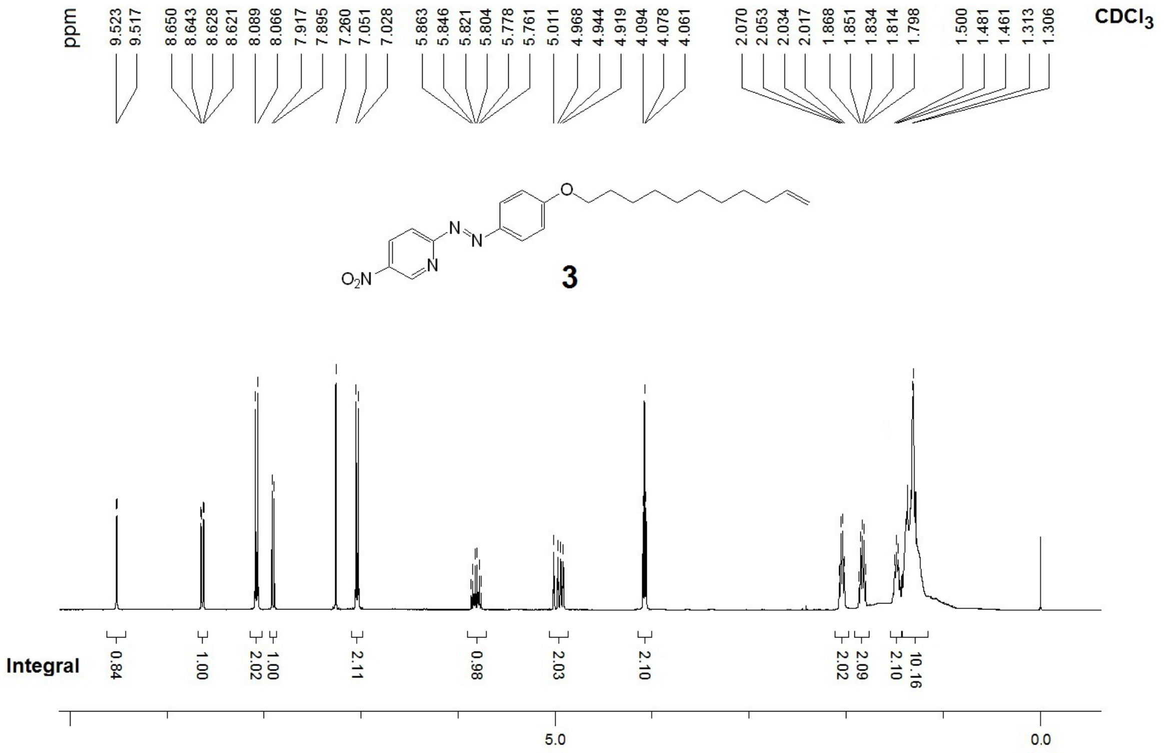
Materials and general instrumentation

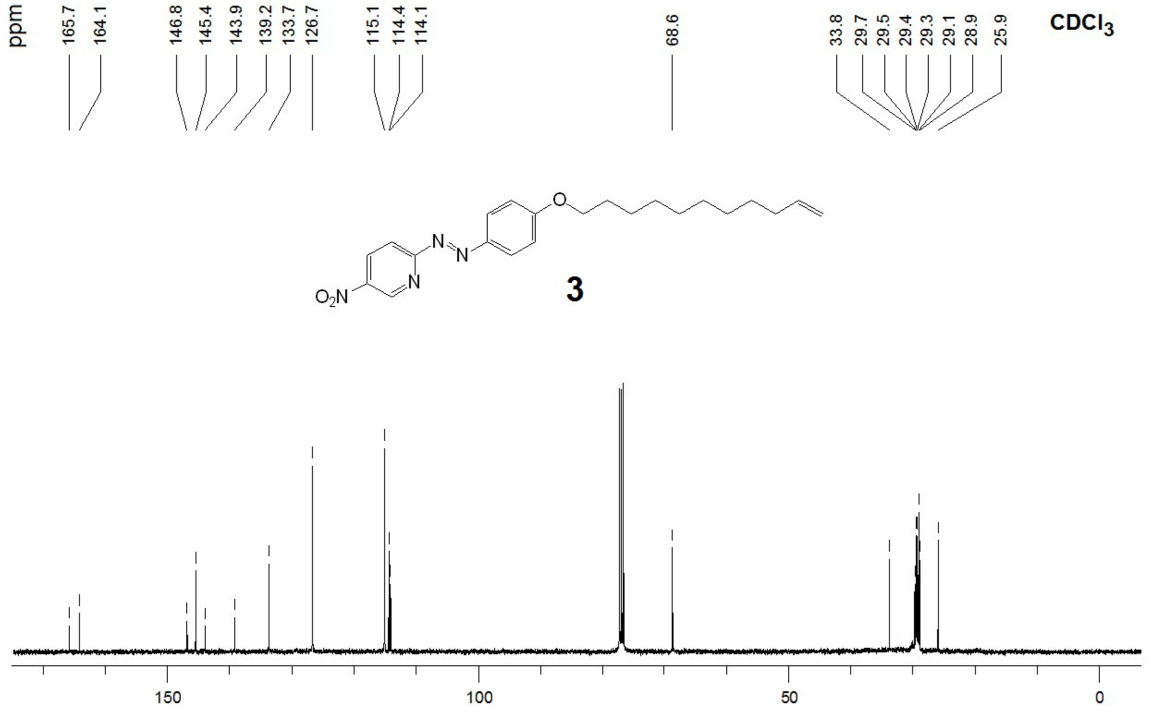
All reagents for synthesis were used as received without further purification. Anhydrous DMF was purchased from Aldrich and it was always stored over activated 4Å molecular sieves under inert atmosphere. Flash chromatography was carried out over silica gel (SDS, 230-240 mesh). Melting points were determined by polarized optical microscopy (POM) using a Nikon Eclipse polarizing microscope equipped with a Linkam THMS 600 hot stage and a Linkam CI 93 programmable temperature controller at a scan rate of 5 ºC·min^{-1}. FT-IR spectra were registered in a Nicolet 6700 FT-IR spectrophotometer from Thermo Scientific. Electronic spectra were recorded in a Varian Cary 500E UV-Vis-NIR spectrophotometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were collected on a Varian Mercury spectrophotometer. NMR spectra have been processed with the MestRec commercially available software. HR-MS was performed in a LC/MSD-TOF Agilent Technologies apparatus by means of the electrospray (ESI-MS) technique.

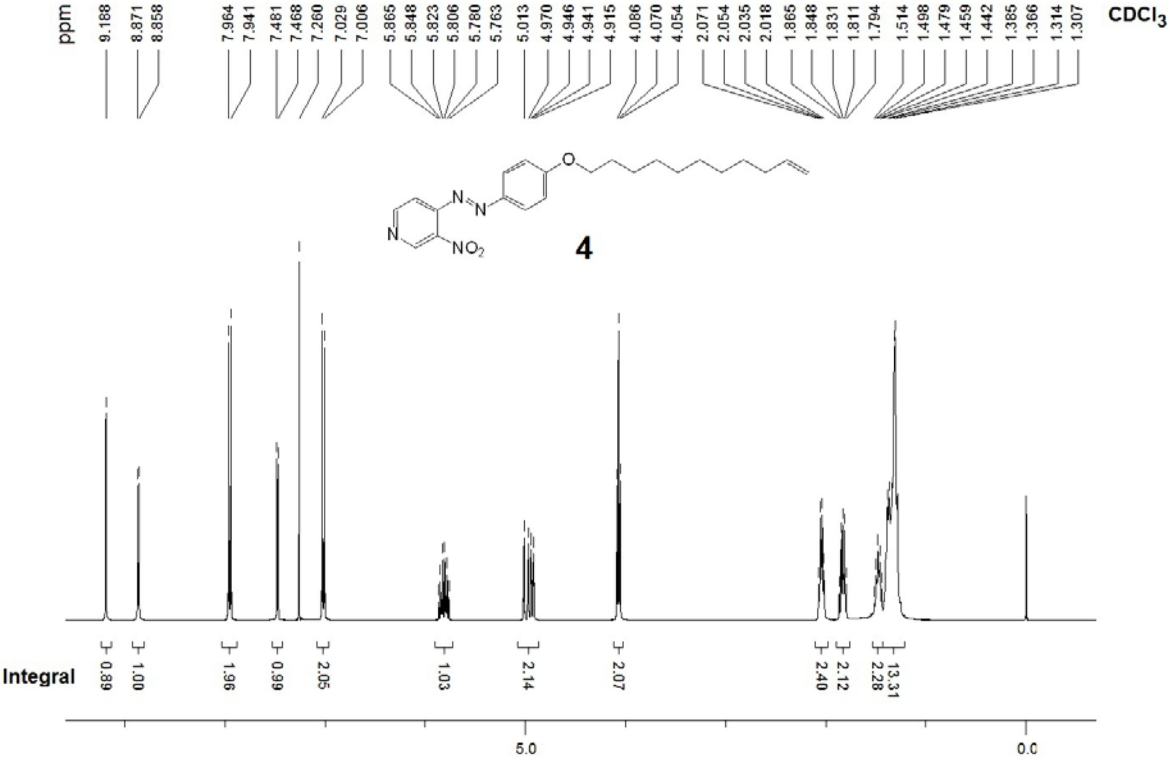
Synthesis of the nitroazopyridines 3 and 4

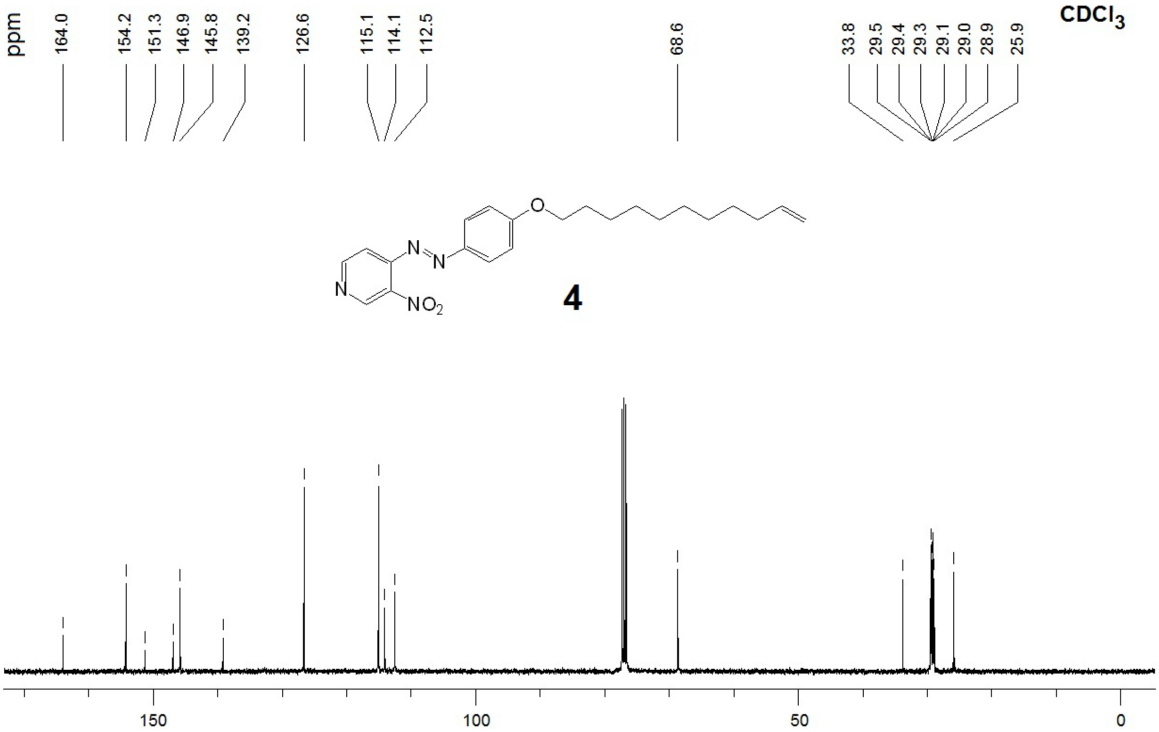
5-nitro-2-(4-(10-undecenyloxy)phenylazo)pyridine (3). 2-(hydroxyphenylazo)-5-nitro pyridine (400 mg) and sodium hydride (98 mg, 60% in mineral oil) were dissolved in anhydrous DMF (20 cm^3). The solution was stirred at room temperature for 30 min. and after 10-bromo-1-undecene (0.91 cm^3) and a spatula of potassium iodide were added. The reaction mixture was heated at 150 ºC for 1.5 hours. Afterwards, the reaction was cooled down and diluted with water. The product was extracted with CH_2Cl_2. The combined organic extracts were dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography using: first, hexane; next, CH_2Cl_2 and finally a mixture of CH_2Cl_2 and AcOEt (9.5:0.5 v/v). **3** was obtained as an orange solid (Yield = 47 %, 309 mg). **m.p.** (POM): 120-121 ºC. **IR** (ATR) *ν* 3064, 2918, 2851, 1595, 1578, 1518, 1497, 1470, 1448, 1415, 1378, 1347, 1299, 1286, 1253, 1192, 1145, 1105, 1007, 918, 845, 769 cm^{-1}. **UV-vis** (EtOH): λ_{max} = 386 nm. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 1.20-1.40 (10H, m), 1.48 (2H, m), 1.83 (2H, m), 2.04 (2H, m), 4.08 (2H, t, J = 6.5 Hz), 4.95 (2H, m), 5.81 (1H, m), 7.04 (2H, d, J = 9.1 Hz), 7.90 (1H, d, J = 8.8 Hz), 8.07 (2H, d, J = 9.1 Hz), 8.63 (1H, dd, J = 8.8 Hz, J = 2.6 Hz), 9.52 (2H, d, J = 2.6 Hz) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 25.9, 28.9, 29.1, 29.3, 29.4, 29.5, 29.7, 33.8, 68.7, 114.1, 114.4, 115.1, 126.7, 133.7, 139.2, 143.9, 145.4, 146.8, 164.1, 165.7 ppm. **HRMS** (ESI-MS): *m*/*z* calcd. for $C_{22}H_{29}N_4O_3$ [M^++H] 397.2234; found 397.2232 [M^++H].

3-nitro-4-(4-(10-undecenyloxy)phenylazo)pyridine (4). 4-(hydroxyphenylazo)-3-nitro pyridine (175 mg) and sodium hydride (43 mg, 60% in mineral oil) were dissolved in anhydrous DMF (20 cm^3). The solution was stirred at room temperature for 30 min. and after 10-bromo-1-undecene (0.40 cm^3) and a spatula of potassium iodide were added. The reaction mixture was heated at 150 ºC for 1 hour. Afterwards, the reaction was cooled down and diluted with water. The product was extracted with CH_2Cl_2. The combined organic extracts were dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography using: first, hexane; next, CH_2Cl_2 and finally a mixture of CH_2Cl_2 and AcOEt (9.5:0.5 v/v). **4** was obtained as an orange solid (Yield = 64 %, 183 mg). **m.p.** (POM): 68-69 ºC. **IR** (ATR) ν 3069, 2917, 2847, 1602, 1577, 1526, 1498, 1463, 1448, 1414, 1394, 1355, 1298, 1257, 1248, 1166, 1132, 1120, 1071, 1033, 993, 909, 839, 829, 804, 768 cm^{-1}. **UV-vis** (EtOH): λ_{max} = 371 nm. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 1.20-1.40 (10H, m), 1.48 (2H, m), 1.83 (2H, m), 2.04 (2H, m), 4.07 (2H, t, *J* = 6.5 Hz), 4.96 (2H, m), 5.82 (1H, m), 7.02 (2H, d, *J* = 9.1 Hz), 7.48 (1H, d, *J* = 5.3 Hz), 7.95 (2H, d, *J* = 9.1 Hz), 8.87 (1H, d, *J* = 5.3 Hz), 9.19 (1H, s) ppm. **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 25.9, 28.9, 29.0, 29.1, 29.3, 29.4, 29.5, 33.8, 68.6, 112.5, 114.1, 115.1, 126.6, 139.2, 145.8, 146.9, 151.3, 154.2, 164.0 ppm. **HRMS** (ESI-MS): *m*/*z* calcd. for $C_{22}H_{29}N_4O_3$ [M^++H] 397.2234; found 397.2239 [M^++H].


ppm
9.523
9.517
8.650
8.643
8.628
8.621
8.089
8.066
7.917
7.895
7.260
7.051
7.028
5.863
5.846
5.821
5.804
5.778
5.761
5.011
4.968
4.944
4.919
4.094
4.078
4.061
2.070
2.053
2.034
2.017
1.868
1.851
1.834
1.814
1.798
1.500
1.481
1.461
1.313
1.306
CDCl3
O
N
N
O2N
N
3
Integral
0.84
1.00
2.02
1.00
2.11
0.98
2.03
2.10
2.02
2.09
2.10
10.16
5.0
0.0


ppm
165.7
164.1
146.8
145.4
143.9
139.2
133.7
126.7
115.1
114.4
114.1
68.6
33.8
29.7
29.5
29.4
29.3
29.1
28.9
25.9
CDCl3
O
N
N
O2N
N
3
150
100
50
0


ppm
9.188
8.871
8.858
7.964
7.941
7.481
7.468
7.260
7.029
7.006
5.865
5.848
5.823
5.806
5.780
5.763
5.013
4.970
4.946
4.941
4.915
4.086
4.070
4.054
2.071
2.054
2.035
2.018
1.865
1.848
1.831
1.811
1.794
1.514
1.498
1.479
1.459
1.442
1.385
1.366
1.314
1.307
CDCl$_3$
O
N
N
N
NO$_2$
4
Integral
0.89
1.00
1.96
0.99
2.05
1.03
2.14
2.07
2.40
2.12
2.28
13.31
5.0
0.0


ppm
164.0
154.2
151.3
146.9
145.8
139.2
126.6
115.1
114.1
112.5
68.6
33.8
29.5
29.4
29.3
29.1
29.0
28.9
25.9
CDCl$_3$
O
N
N
N
NO$_2$
4
150
100
50
0

Electrochemical and photo-electrochemical measurements

Electrochemical studies were conducted in a microcomputer controlled potentiostat/galvanostat Autolab with PGSTAT30 equipment and GPES software. A cylindrical three-electrode cell was used. The reference electrode was a Metrohm Ag/AgCl/KCl (3M) mounted in a Luggin capillary containing a 0.1 M solution of TBAP in anhydrous DMF. The counter and working electrodes were a platinum spiral and a platinum wire, respectively. The geometrical area of the working cylindrical electrode was estimated to be 0.432 cm^2. All voltammetric curves were recorded under quiescent conditions at a scan rate of 100 $mV\cdot s^{-1}$. All solutions were prepared in anhydrous DMF (Aldrich). Dry DMF was always stored over 4Å molecular sieves under a nitrogen atmosphere. All electrochemical measurements were performed under an argon atmosphere. Tetrabutylammonium perchlorate (TBAP, Aldrich, electrochemical grade) was used as supporting electrolyte. The different peak current intensities in the voltammetric responses were determined by subtracting the current intensity value of the corresponding baseline.

Photo-voltammetric studies were carried out in a homemade irradiation set-up. UV-irradiation ($320 < \lambda < 390$ nm) of the electrochemical bath was carried out *in situ*. The electrochemical cell was covered with a black cloth during the whole experiment to avoid the incidence of ambient light to the system. A 500 W high-pressure Hg lamp (Philips) was used to induce the *trans*-to-*cis* photo-isomerisation of the azo-dye. The incoming light was filtered by using a 0.5 M $Co(NO_3)_2$ aqueous solution in order to remove non-desired light. Irradiation of the electrochemical bath was performed until no change in the corresponding voltammetric curve was detected. The temperature of the electrochemical cell was controlled continuously and kept within 315 ± 0.1 K, in order to avoid possible variations of the diffusion coefficient of the electro-active specie associated to the heating of the sample by the incident UV light.

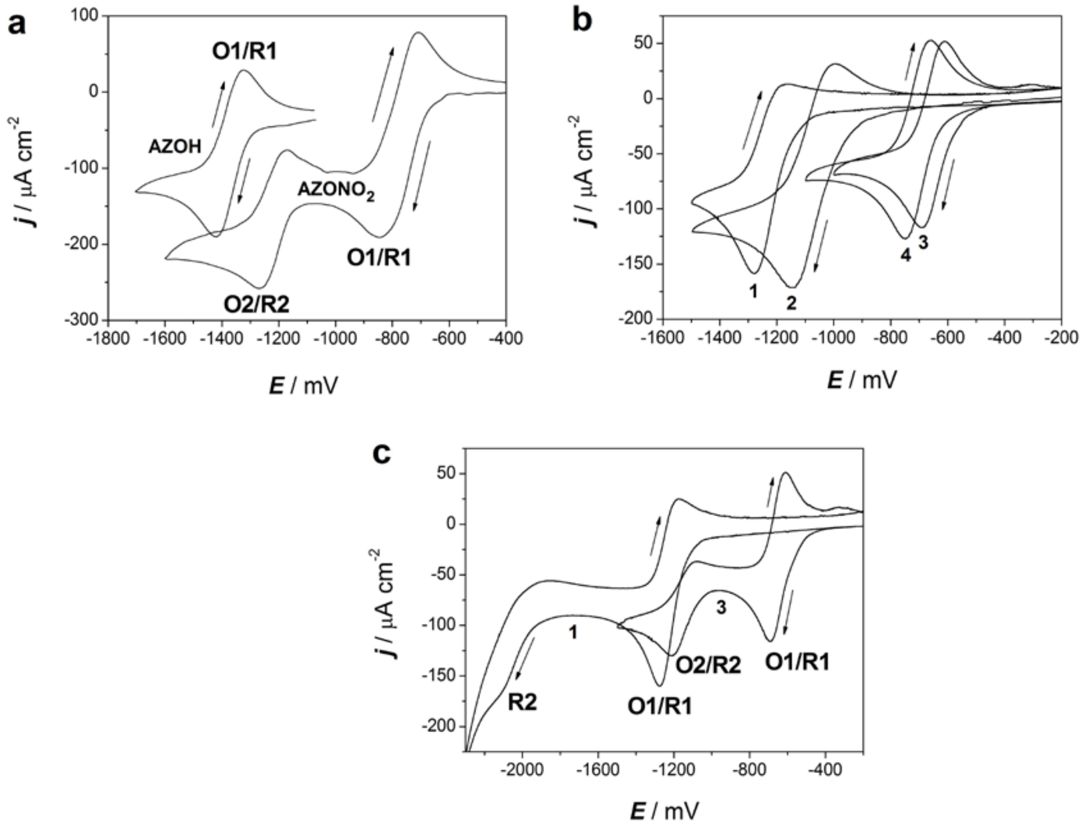


Figure S1. Reduction processes for the standard azoderivatives 4-(5-hexenyloxy)azobenzene (**AZOH**) and 4-(5-hexenyloxy)-4’-nitroazobenzene (**AZONO$_2$**) (a), first reduction process for the *trans* isomer of azopyridines **1**-**4** (b) and reduction processes for azopyridines **1** and **3** (c) in anhydrous DMF + 0.1 M TBAP at 315 K. All potentials are referred to the Ag/AgCl/KCl (3M) electrode. ([**AZO**] = 1 mM, v = 100 mV·s^{-1}).