

Supplementary material

Fast isomerizing methyl iodide azopyridinium salts for molecular switches

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Materials and general instrumentation

All reagents for synthesis were used as received without further purification, except 1,4-benzoquinone that was previously purified by flash column chromatography using CHCl_3 as eluant. Flash chromatography was carried out over silica gel (SDS, 230-240 mesh). Anhydrous THF (Sharlau) was distilled from sodium/benzophenone. DMF (Fluka) was dried by storing it over activated 4Å molecular sieves under inert atmosphere. 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°C 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. ^1H 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. HRMS was performed in a LC/MSD-TOF Agilent Technologies apparatus by means of the electrospray (ESI-MS) technique.

Synthesis of the azocompounds

2-(4-(10-undecenyloxy)phenylazo)pyridine (3). **1** (300 mg) and sodium hydride (90 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 (0.5 cm^3) and a spatula of potassium iodide were added. The reaction mixture was refluxed for 4 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, chloroform and finally a CH_2Cl_2 :AcOEt 9.5:0.5 v/v mixture. **3** was obtained as an orange crystalline solid (Yield = 94 %). **m.p.** (POM): $68\text{-}69^\circ\text{C}$. **IR** (ATR) ν 3067, 3050, 2917, 2849, 1600, 1581, 1536, 1496, 1463, 1411, 1383, 1295, 1236, 1148, 1135, 1114, 1068, 989, 962, 905, 845, 808, 800, 787, 737, 721, 634, 618, 573, 558 cm^{-1} . **UV-vis** (acetone): $\lambda_{\text{max}} = 348\text{ nm}$ ($\epsilon = 20\ 750\ \text{M}^{-1}\ \text{cm}^{-1}$). **^1H NMR** (CDCl_3 , 400 MHz): δ 1.20-1.40 (10H, m), 1.45 (2H, m),

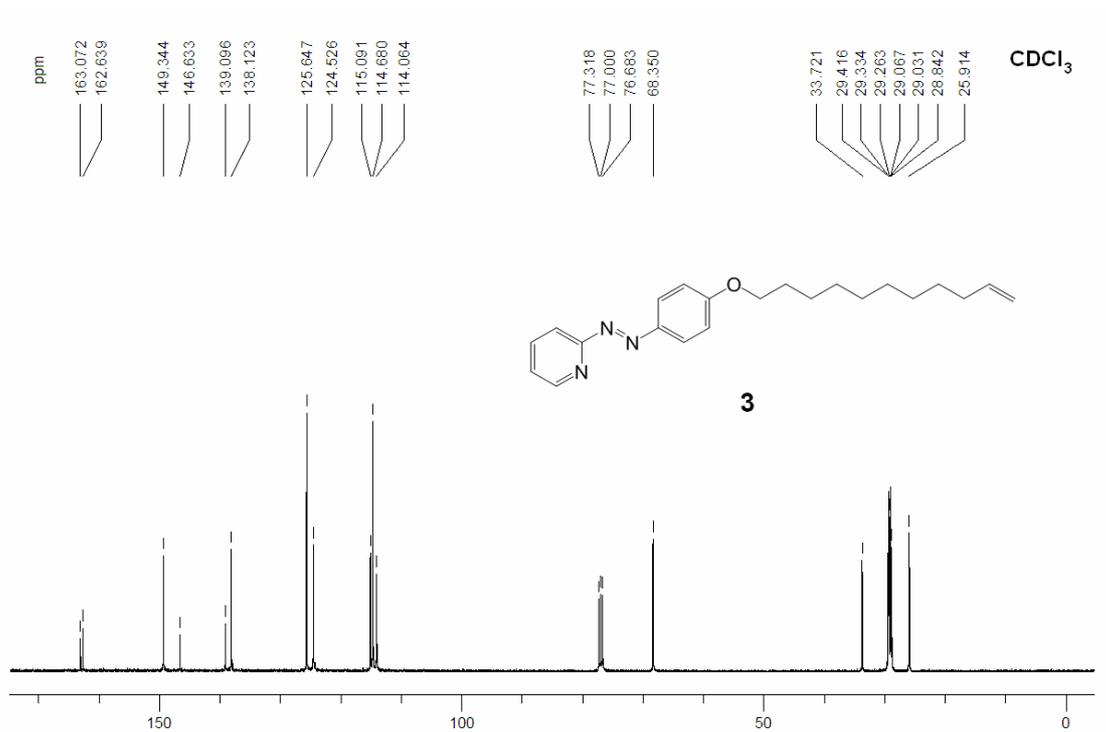
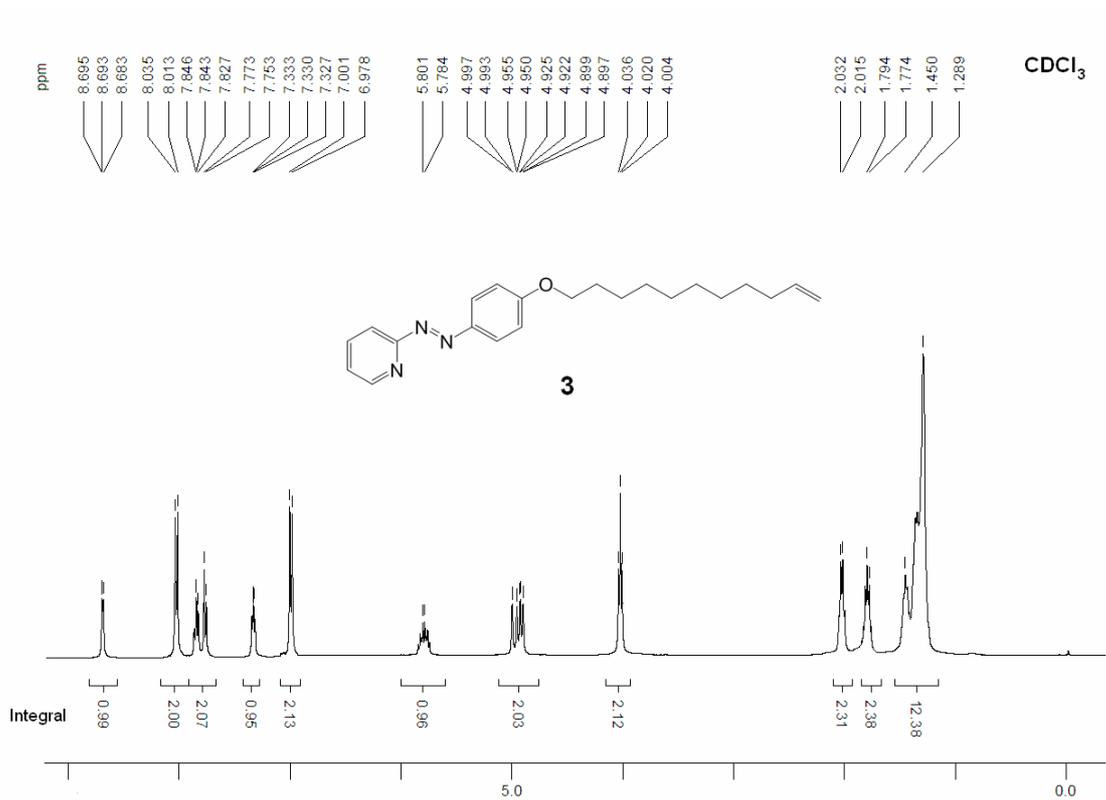
1.78 (2H, m), 2.02 (2H, m) 4.02 (2H, t, $J = 6.5$ Hz), 4.90-5.00 (2H, m), 5.79 (1H, m), 6.99 (2H, d, $J = 9.0$ Hz), 7.33 (1H, m), 7.84 (2H, m), 8.02 (2H, m, $J = 9.0$ Hz), 8.69 (1H, m) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ 25.9, 28.8, 29.0, 29.1, 29.3, 29.3, 29.4, 33.7, 68.3, 114.1, 114.7, 115.1, 124.5, 125.6, 138.1, 139.1, 146.6, 149.3, 162.6, 163.1 ppm. HRMS (ESI-MS): m/z calcd. for $\text{C}_{22}\text{H}_{30}\text{N}_3\text{O}$ [MH^+] 352.2389; found 352.2387 [MH^+].

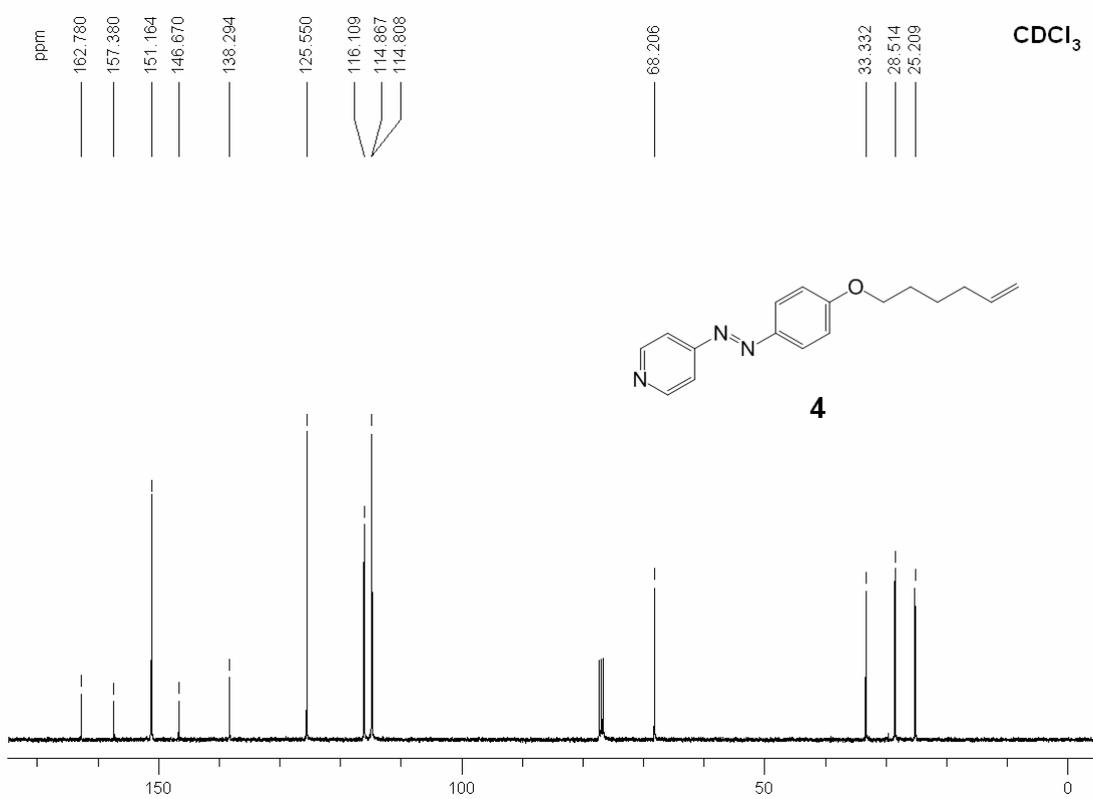
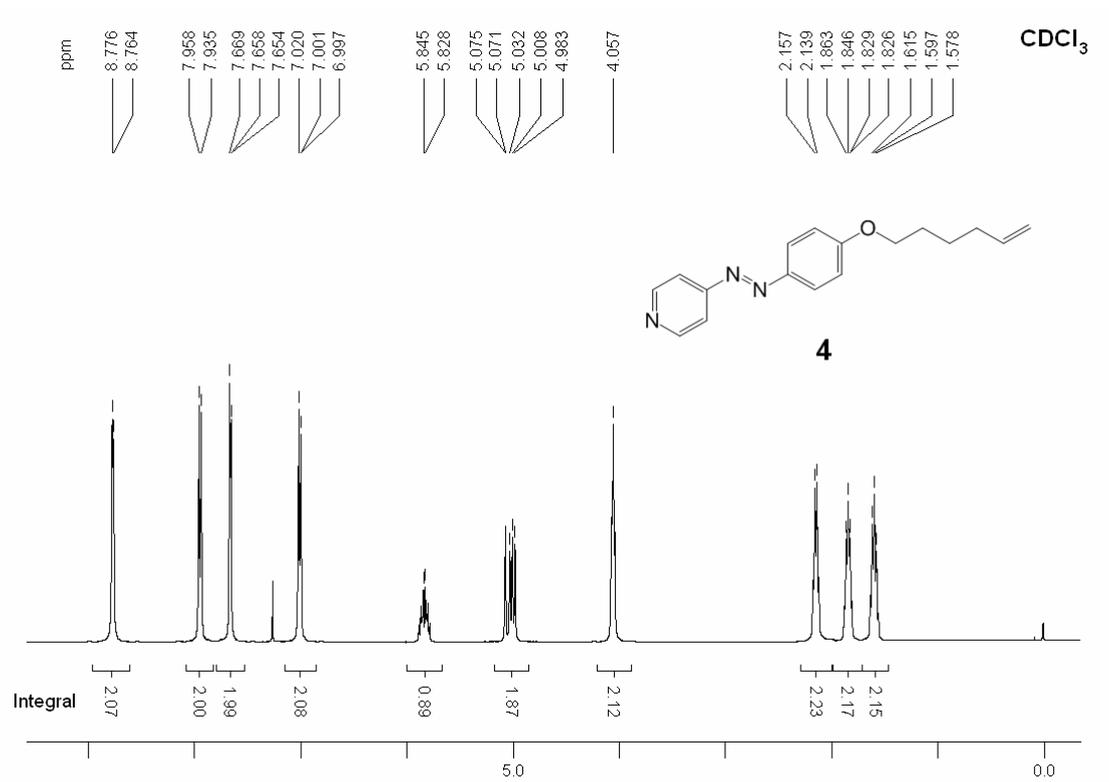
4-(4-(5-hexenyloxy)phenylazo)pyridine (4). PPh_3 (1.37 g) and DIPAD (1.03 cm^3) were dissolved in anhydrous THF (40 cm^3) at 0 °C under nitrogen atmosphere. The solution was stirred at this temperature for 30 min. Next, 5-hexen-1-ol (0.46 cm^3) and a solution of **2** (695 mg) in the minimum amount of anhydrous THF were added. The reaction mixture was stirred at 0 °C for 1 hour and afterwards, refluxed for 3.5 hours. Then, it was cooled down and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography using a CH_2Cl_2 :AcOEt (4:1 v/v) mixture as eluant. **4** was obtained as an orange crystalline solid (Yield = 41 %). **m.p.** (POM): 58-59 °C. IR (ATR) ν 3048, 2973, 2938, 2872, 1601, 1581, 1566, 1497, 1471, 1451, 1412, 1404, 1320, 1297, 1253, 1142, 1108, 1037, 1001, 988, 933, 838, 793, 738, 642, 630, 559, 543 cm^{-1} . UV-vis (acetone): $\lambda_{\text{max}} = 354$ nm ($\epsilon = 22\,320$ $\text{M}^{-1} \text{cm}^{-1}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.60 (2H, m), 1.84 (2H, m), 2.15 (2H, m), 4.06 (2H, t, $J = 6.4$ Hz), 5.03 (2H, m), 5.84 (1H, m), 7.01 (2H, d, $J = 9.0$ Hz), 7.66 (2H, d, $J = 6.2$ Hz), 7.95 (2H, d, $J = 9.0$ Hz), 8.77 (2H, d, $J = 6.2$ Hz) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ 25.2, 28.5, 33.3, 68.2, 114.8, 114.9, 116.1, 125.5, 138.3, 146.7, 151.2, 157.4, 162.8 ppm. HRMS (ESI-MS): m/z calcd. for $\text{C}_{17}\text{H}_{20}\text{N}_3\text{O}$ [MH^+] 282.1606; found 282.1601 [MH^+].

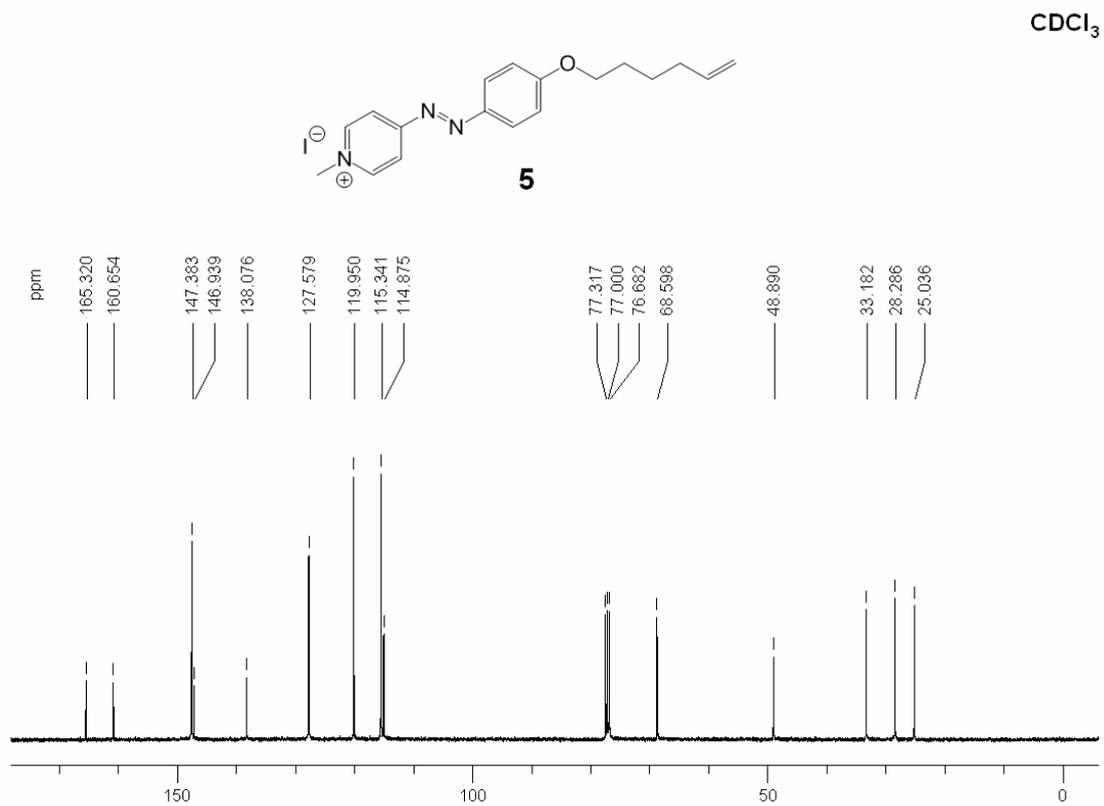
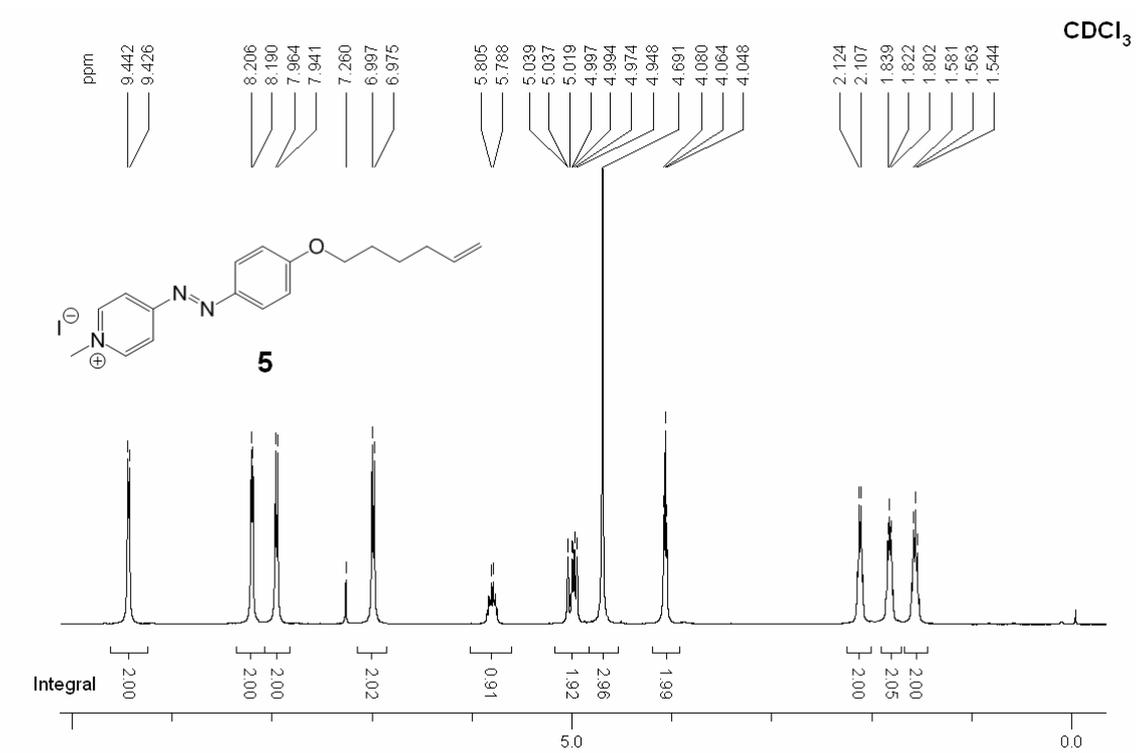
N-methyl-4-(4-(5-hexenyloxy)phenylazo)pyridinium iodide (5). **4** (200 mg) was dissolved in anhydrous THF (10 cm^3) and methyl iodide (1.1 cm^3) was added. The reaction mixture was stirred at reflux for 12 hours. The product was precipitated as a red solid by adding hexane. The solid was isolated by vacuum filtration and dried. **5** was obtained as a red crystalline solid (Yield = 48 %). **m.p.** (POM): 128-129 °C. IR (ATR) ν 3048, 2992, 2945, 2868, 1635, 1599, 1579, 1498, 1471, 1443, 1409, 1325, 1304, 1253, 1138, 1001, 924, 856, 846, 810, 733, 663, 634, 550 cm^{-1} . UV-vis (acetone): $\lambda_{\text{max}} = 403$ nm ($\epsilon = 20\,560$ $\text{M}^{-1} \text{cm}^{-1}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.56 (2H, m), 1.82 (2H, m), 2.11 (2H, m), 4.06 (2H, t, $J = 6.4$ Hz), 4.69 (3H, s), 4.99 (2H, m), 5.79 (1H, m), 6.99

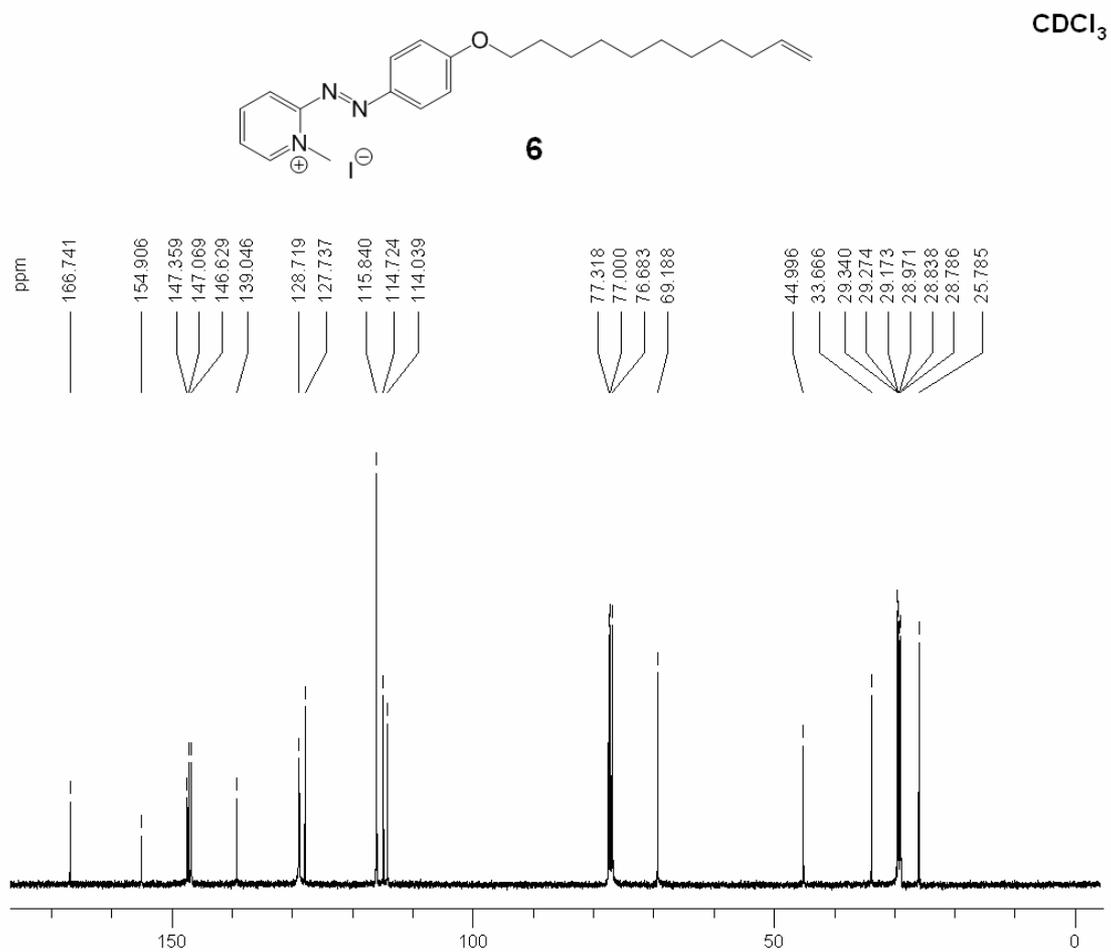
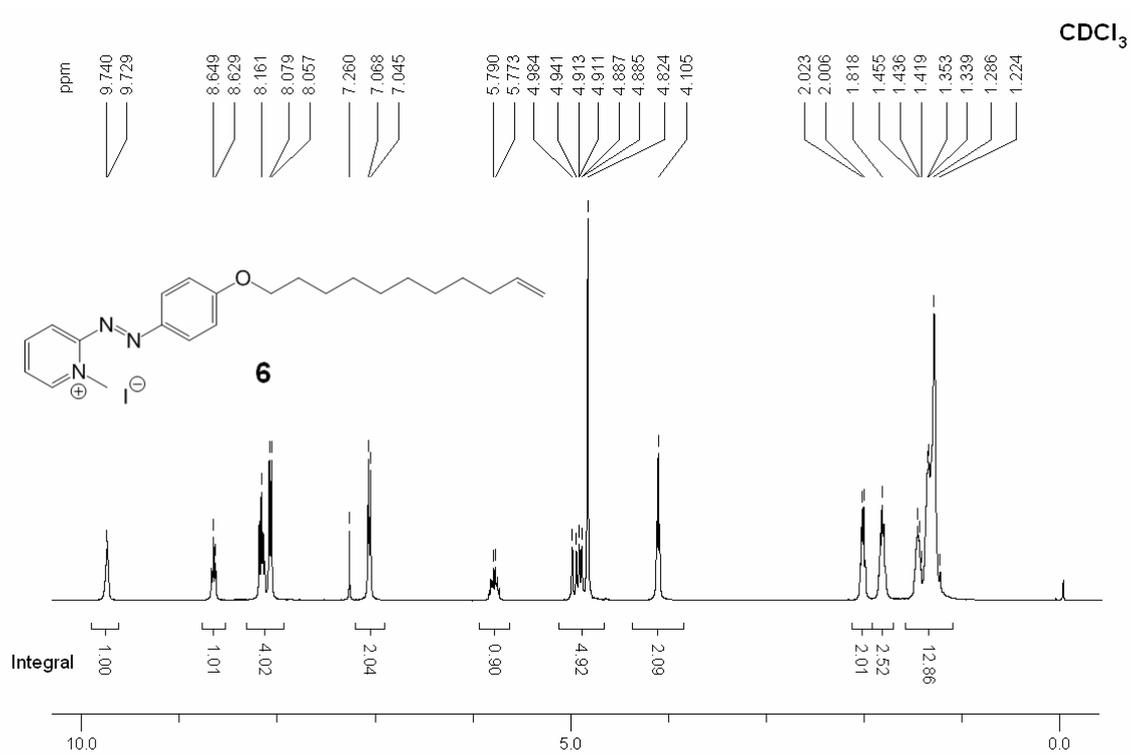
(2H, d, $J = 8.9$ Hz), 7.95 (2H, d, $J = 8.9$ Hz), 8.20 (2H, d, $J = 6.5$ Hz), 9.43 (2H, d, $J = 6.5$ Hz) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ 25.0, 28.3, 33.2, 48.9, 68.6, 114.9, 115.3, 119.9, 127.6, 138.1, 146.9, 147.4, 160.6, 165.3 ppm. HRMS (ESI-MS): m/z calcd. for $\text{C}_{18}\text{H}_{22}\text{N}_3\text{O}^+$ [M^+] 296.1757; found 296.1755.

***N*-methyl-2-(4-(10-undecenyloxy)phenylazo)pyridinium iodide (6).** **3** (495 mg) was dissolved in anhydrous THF (20 cm^3) and methyl iodide (3 cm^3) was added. The reaction mixture was refluxed for 1 hour. The product was precipitated as a reddish solid by adding hexane. The solid was isolated by vacuum filtration and dried. **6** was obtained as a red crystalline solid (Yield = 66 %). **m.p.** (POM): 111-112 °C. **IR** (ATR) ν 3061, 3035, 2918, 2848, 1616, 1600, 1577, 1498, 1471, 1438, 1412, 1300, 1251, 1201, 1147, 1127, 1015, 914, 845, 810, 794, 722, 661, 649, 632, 580, 561, 551 cm^{-1} . **UV-vis** (acetone): $\lambda_{\text{max}} = 412$ nm ($\epsilon = 28\,240$ $\text{M}^{-1} \text{cm}^{-1}$). ^1H NMR (CDCl_3 , 400 MHz): δ 1.22-1.42 (10H, m), 1.45 (2H, m), 1.82 (2H, m), 2.01 (2H, m), 4.10 (2H, t, $J = 6.4$ Hz), 4.82 (3H, s), 4.93 (2H, m), 5.78 (1H, m), 7.06 (2H, d, $J = 9.0$ Hz), 8.07 (2H, d, $J = 9.0$ Hz), 8.16 (2H, m), 8.65 (1H, m), 9.74 (1H, m) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ 25.8, 28.8, 28.8, 29.0, 29.2, 29.3, 29.3, 33.7, 45.0, 69.2, 114.0, 114.7, 115.8, 127.7, 128.7, 139.0, 146.6, 147.1, 147.4, 154.9, 166.7 ppm. HRMS (ESI-MS): m/z calcd. for $\text{C}_{23}\text{H}_{32}\text{N}_3\text{O}^+$ [M^+] 366.2540; found 366.2546









Preparation and order analysis of the nematic solutions

Nematic solutions of azocompounds **5** and **6** in the nematic mesogens **5CB** and **6CB** were used. The nematic mesogens **5CB** (Alfa Aesar) and **6CB** (Aldrich) were used as supplied. Samples were prepared by mixing the desired amounts of the corresponding mesogen and azo-dye followed by homogenization by magnetic stirring for 10 minutes in the isotropic state.

Monodomain samples were prepared in 10 μm optical path quartz cells. The cell surface was rubbed with a piece of cloth in a single direction, causing the alignment of the mesogens due to their electrostatic interaction with the cell surface. Homogeneity of the samples was checked by local probe microscopy. Polarized optical microscopy (POM) was carried out using a Nikon Eclipse polarizing microscope at room temperature. POM experiments were run by rotation of the analyzer of the microscope with respect to the rubbing direction. On reaching 45° the expected change from darkness to brightness associated to the monodomain was observed. The absence of the characteristic Schlieren texture was also detected by POM. POM microphotographs of a **5-6CB** monodomain nematic solution before irradiation at room temperature is shown in Figure S1.

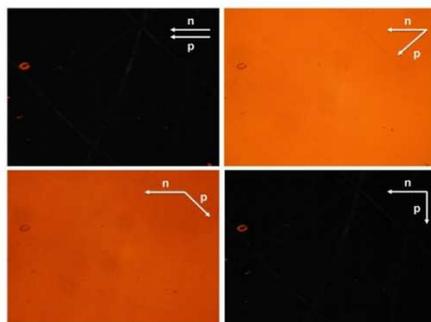


Figure S1. Microphotographs of a **5-6CB** monodomain solution at different angles between the analyzer and the rubbing direction before irradiation at room temperature ($x_{azo} = 0.01$). n and p indicate the director direction and the polarization direction of the analyzer respectively.

Kinetic experiments

A population of *cis*-azobenzenes was generated by UV photolysis and its relaxation was followed by time-resolved UV-Vis spectroscopy. The thermal *cis*-to-*trans* isomerisation process was studied by means of laser flash-photolysis. Thus, the *cis* isomer of the corresponding azoderivative was generated by a Q-switched Nd-YAG laser (355 nm, 5 ns pulse width, 1-10 mJ per pulse) and the time evolution of the sample absorbance was monitored at 90 degrees by a white-light beam produced by a PTI 75 W Xe lamp. The light transmitted by the sample was spectrally resolved using a monochromator and detected with a Hamamatsu R928 photomultiplier, whose output was fed into a digital oscilloscope through a 50 Ohm resistor. The observation wavelength was set at 405 nm for **5** and at 420 nm for **6**. Kinetic analysis of the transients was done with software developed in our laboratory. Samples in isotropic solution were measured in 1 cm optical path quartz cells. Photo-degradation neither *trans*-to-*cis* isomerization promoted by the observation wavelength of the spectrophotometer was detected for all the azocompounds studied. The irradiation of the host liquid-crystal with the laser light did not produce any phase transition related with the possibly heating of the sample.

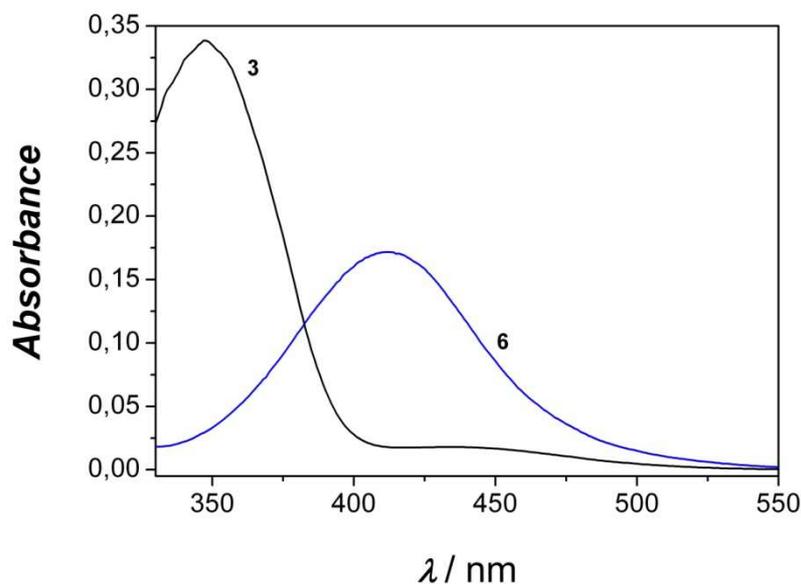


Figure S2. Electronic spectrum of *trans*-**3** and *trans*-**6** in acetone solution at 298 K ([AZO] = 0.01 mM).

<i>Azocompound</i>	<i>Solvent</i>	<i>T / K</i>	<i>τ / ms</i>
5	ethanol	298	0.57
		308	0.28
		318	0.16
		328	0.085
		338	0.049
	acetonitrile	298	4.6
		308	2.1
		318	1.1
		328	0.57
		338	0.30
6	ethanol	298	2.8
		308	1.2
		318	0.61
		328	0.34
		338	0.19
	acetonitrile	298	4.2
		308	2.3
		318	1.1
		328	0.54
		338	0.31

Table S1. Relaxation time, τ , for the thermal *cis-to-trans* isomerization process of azocompounds **5** and **6** in ethanol and acetonitrile at different temperatures ($[AZO] = 0.02$ mM; the observation wavelength was 405 nm for **5** and 420 nm for **6**). The experimental error associated to temperature and relaxation time was of ± 0.1 K and less than 10 %, respectively.