

## Supplementary material

### *Synthesis of the novel azoderivatives 2,4'-OH, 2,4'-OC<sub>6</sub> and 4-OC<sub>6</sub>*

**Synthesis of 2,4'-dihydroxy-5-methylazobenzene (2,4'-OH).** 2-OH-4'-OMe (600 mg, 2.47 mmol) was placed in a round-bottomed flask under nitrogen atmosphere and the system was cooled to -78°C using an external liquid nitrogen bath. Then, a 1M solution of boron tribromide (10 cm<sup>3</sup>, 10.0 mmol), in anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added drop wise. After the addition, the mixture was allowed to reach room temperature and it was stirred under nitrogen atmosphere overnight. Afterwards, the reaction was quenched by careful pouring into ice-water and by addition of diluted sodium hydroxide until basic pH. The mixture was acidified to pH=5-6 by the addition of diluted hydrochloric acid. The product was extracted with ethyl acetate and the combined extracts were dried over anhydrous sodium sulphate, filtered and evaporated under reduced pressure. The crude was purified by column chromatography on silica using a mixture of hexane:ethyl acetate 7:3 (v/v) as eluant to give **2,4'-OH** (481 mg, 86%) as a dark brown solid.  $\nu_{\max}$  (ATR)/cm<sup>-1</sup> 3204 (O-H), 2914 (C-H), 1594 (C=C), 1494 (N=N);  $\delta_{\text{H}}$  (400 MHz; *d*<sub>6</sub>-acetone) 2.35 (3H, s, CH<sub>3</sub>), 5.77 (1H, bs, OH), 6.88 (1H, d, *J* 8.4, <sup>ar</sup>H C-3'), 7.03 (2H, dd, *J* 8.7 and 1.9, <sup>ar</sup>H C-3 and C-5), 7.18 (1H, dd, *J* 8.4 and 2.1, <sup>ar</sup>H C-4'), 7.67 (1H, d, *J* 2.1, <sup>ar</sup>H C-6'), 7.87 (2H, dd, *J* 8.7 and 1.9, <sup>ar</sup>H C-2 and C-6);  $\delta_{\text{C}}$  (100 MHz; CDCl<sub>3</sub>) 21.3 (1C, CH<sub>3</sub>), 118.0 (2C, C-3 and C-5), 119.5 (1C, C-3'), 126.1 (2C, C-2 and C-6), 130.8 (1C, C-1'), 132.7 (1C, C-6'), 135.1 (1C, C-4'), 138.8 (1C, C-5'), 146.2 (1C, C-1), 152.5 (1C, C-2'), 162.7 (1C, C-4); *m/z* (HRMS) 227.0824 (M-H<sup>+</sup>. C<sub>13</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub> requires 228.0899);  $\lambda_{\max}$  (EtOH)/nm 381 ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> 7 433), 422 (3 984).

**Synthesis of 2,4'-di-(5-hexenyloxy)-5-methylazobenzene (2,4'-OC<sub>6</sub>).** 2,4'-OH (493 mg, 2.15 mmol) and NaH (108 mg, 4.51 mmol, 60% dispersion in mineral oil) were dissolved in anhydrous DMF (10 cm<sup>3</sup>) under nitrogen atmosphere. The solution was stirred and heated at 80°C and then 6-bromo-1-hexene (701 mg, 4.30 mmol) was added. The mixture was stirred under reflux for 6 hours. Afterwards, the reaction was cooled to room temperature, diluted with water and the product was extracted with ethyl acetate. The combined extracts were dried over anhydrous sodium sulphate, filtered and evaporated under reduced pressure. The crude was purified by column chromatography

on silica using a mixture  $\text{CH}_2\text{Cl}_2$ :hexane 1:1 (v/v) as eluant to give **2-OH-4'-OMe** (741 mg, 88%) as a dark orange oil.  $\nu_{\text{max}}$  (NaCl)/ $\text{cm}^{-1}$  3071(=C-H), 2938 and 2867 (C-H), 1600 (C=C), 1471 (N=N);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.63 (4H, m, 2 x  $\text{CH}_2$ ), 1.86 (4H, m, 2 x  $\text{CH}_2$ ), 2.15 (4H, m, 2 x  $\text{CH}_2$ ), 2.33 (3H, s,  $\text{CH}_3$ ), 4.15 and 4.04 (4H, t,  $J$  6.4, 2 x  $\text{CH}_2\text{-O}$ ), 4.93-5.13 (4H, m, 2 x  $\text{CH}_2=\text{CH}$ ), 5.84 (2H, m, 2 x  $\text{CH}_2=\text{CH}$ ), 6.97 (1H, d,  $J$  8.5,  $^{\text{ar}}\text{H C-3}'$ ), 6.99 (2H, dd,  $J$  9.0 and 2.1,  $^{\text{ar}}\text{H C-3}$  and C-5), 7.18 (1H, dd,  $J$  8.5 and 2.1,  $^{\text{ar}}\text{H C-4}'$ ), 7.45 (1H, d,  $J$  2.1,  $^{\text{ar}}\text{H C-6}'$ ), 7.90 (2H, dd,  $J$  9.0 and 2.1,  $^{\text{ar}}\text{H C-2}$  and C-6);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 20.5 (1C,  $\text{CH}_3$ ), 25.2 and 25.4 (2C, 2 x  $\text{CH}_2$ ), 28.6 and 28.8 (2C, 2 x  $\text{CH}_2\text{CH}_2\text{O}$ ), 33.4 (2C, 2 x  $\text{CH}_2=\text{CHCH}_2$ ), 68.0 and 70.0 (2C, 2 x  $\text{CH}_2\text{O}$ ), 114.6 (3C, C-3, C-5 and C-3'), 114.8 and 114.9 (2C,  $\text{CH}_2=\text{CH}$ ), 117.1 (1C, C-6'), 124.7 (2C, C-2 and C-6), 130.4 (1C, C-1'), 132.1 (1C, C-4'), 138.4 and 138.6 (2C,  $\text{CH}_2=\text{CH}$ ), 142.5 (1C, C-5'), 147.4 (1C, C-1), 154.3 (1C, C-2'), 161.4 (1C, C-4);  $m/z$  (HRMS) 393.2537 ( $\text{M}+\text{H}^+$ .  $\text{C}_{25}\text{H}_{32}\text{N}_2\text{O}_2$  requires 392.2464);  $\lambda_{\text{max}}$  (EtOH)/nm 351 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  13 382), 451 (2 245).

**Synthesis of 4-(5-hexenyloxy)azobenzene (4-OC<sub>6</sub>).** **4-OH** (3 g, 15.1 mmol) and triphenylphosphine (4.37 g, 16.7 mmol) were dissolved in anhydrous THF (25  $\text{cm}^3$ ) under nitrogen atmosphere. After 30 minutes, 5-hexen-1-ol (2  $\text{cm}^3$ , 16.7 mmol) and DIPAD (3.3  $\text{cm}^3$ , 16.7 mmol) were added. The reaction was stirred at room temperature overnight. Afterwards, the solvent was removed under reduced pressure and the crude was purified by column chromatography on silica using a mixture  $\text{CH}_2\text{Cl}_2$ :hexane 9:1 (v/v) as eluant to give **4-OC<sub>6</sub>** (4.21 g, 99 %) as an orange solid.  $\nu_{\text{max}}$  (NaCl)/ $\text{cm}^{-1}$  3069 (=C-H), 2939 and 2866 (C-H), 1601 (C=C), 1468 (N=N);  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.59 (2H, m,  $\text{CH}_2$ ), 1.83 (2H, m,  $\text{CH}_2$ ), 2.15 (2H, m,  $\text{CH}_2$ ), 4.02 (2H, t,  $J$  6.5,  $\text{CH}_2\text{-O}$ ), 4.97-5.07 (2H, m,  $\text{CH}_2=\text{CH}$ ), 5.83 (1H, m,  $\text{CH}_2=\text{CH}$ ), 6.98 (2H, dd,  $J$  9.0 and 2.0,  $^{\text{ar}}\text{H C-3}$  and C-5), 7.40-7.50 (3H, m,  $^{\text{ar}}\text{H C-3}'$ , C-4' and C-5'), 7.86-7.88 (2H, m,  $^{\text{ar}}\text{H C-2}'$  and C-6'), 7.91 (2H, dd,  $J$  9.0 and 2.0,  $^{\text{ar}}\text{H C-2}$  and C-6);  $\delta_{\text{C}}$  (100 MHz;  $\text{CDCl}_3$ ) 25.3 (1C,  $\text{CH}_2$ ), 28.6 (1C,  $\text{CH}_2$ ), 33.4 (1C,  $\text{CH}_2=\text{CHCH}_2$ ), 68.1 (1C,  $\text{CH}_2\text{O}$ ), 114.6 (2C, C-3, C-5), 114.8 (1C,  $\text{CH}_2=\text{CH}$ ), 122.5 (2C, C-2' and C-6'), 124.7 (2C, C-2 and C-6), 129.0 (2C, C-3' and C-5'), 130.3 (1C, C-4'), 138.4 (1C,  $\text{CH}_2=\text{CH}$ ), 146.8 (1C, C-1), 152.7 (1C, C-1'), 161.6 (1C, C-4);  $m/z$  (HRMS) 281.1647 ( $\text{M}+\text{H}^+$ .  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}$  requires 280.1576);  $\lambda_{\text{max}}$  (EtOH)/nm 346 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  39 260), 429 (1 681).

Chemical shifts and coupling constants from the NMR experiments are given in ppm and Hz respectively.

### Tables

<i>Azocompound</i>	<i>Solvent</i>	<i>T / °C</i>	<i>τ / h</i>
<b>4-OC<sub>6</sub></b>	<i>Ethanol</i>	25	70
		50	3.4
		55	1.9
		60	1.2
		65	0.68
	<i>Toluene</i>	25	56
		45	4.8
		60	0.94
		70	0.34
		75	0.21
<b>4-OC<sub>6</sub>-4'-OMe</b>	<i>Ethanol</i>	25	13
		35	4.1
		45	1.3
		55	0.42
		60	0.25
	<i>Toluene</i>	25	15
		35	4.5
		40	2.5
		60	0.29
		65	0.18
<b>4,4'-OC<sub>6</sub></b>	<i>Ethanol</i>	25	12
		35	3.6
		40	2.1
		45	1.1
		55	0.39

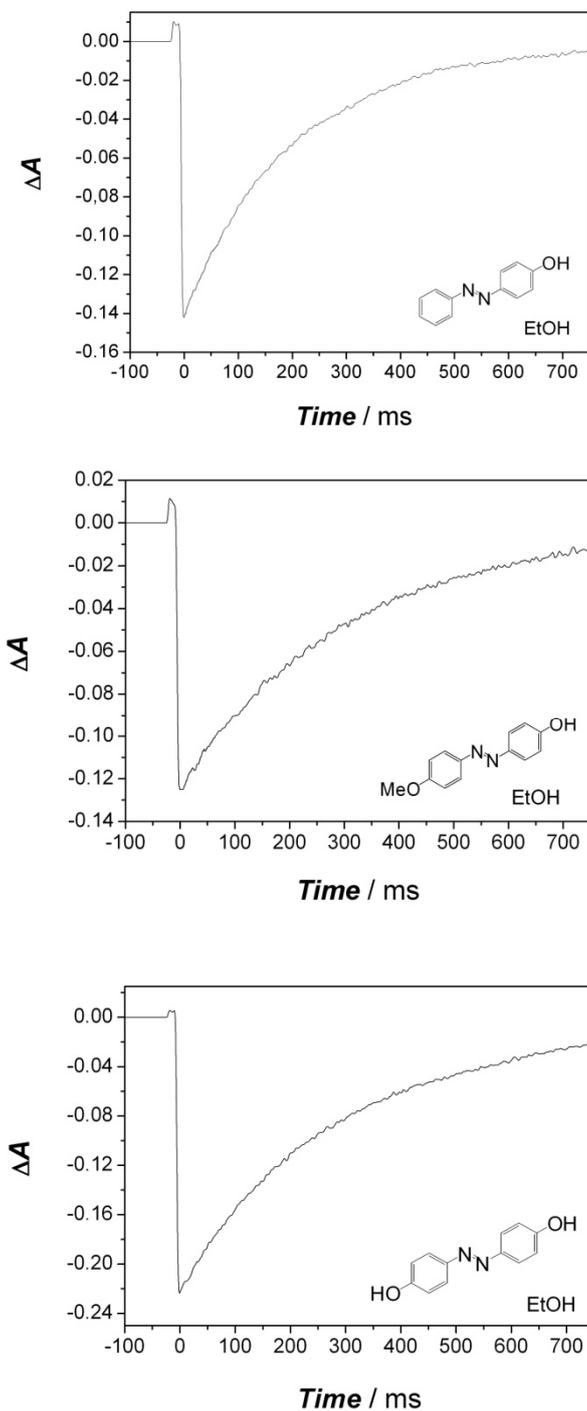
	<i>Toluene</i>	25	14
		35	4.3
		40	2.4
		45	1.3
		55	0.46
<b>2, 4'-OC<sub>6</sub></b>	<i>Ethanol</i>	25	58
		45	5.3
		55	1.8
		65	0.66
		70	0.39
	<i>Toluene</i>	25	65
		40	10
		65	0.69
		70	0.41
		75	0.25
<b>2,4,4'-OMe</b>	<i>Ethanol</i>	25	10
		35	3.1
		55	0.37
		60	0.23
		<i>Toluene</i>	25
		35	5.7
		50	1.1
		55	0.66
		60	0.40

**Table S1.** Relaxation time for the *cis* isomer,  $\tau$ , of the alkoxy-substituted azoderivatives **4-OC<sub>6</sub>**, **4-OC<sub>6</sub>-4'-OMe**, **4,4'-OC<sub>6</sub>**, **2,4'-OC<sub>6</sub>** and **2,4,4'-OMe** at different temperatures. The experimental error associated to temperature and relaxation time was of  $\pm 0.1$  K and less than 10 %, respectively.

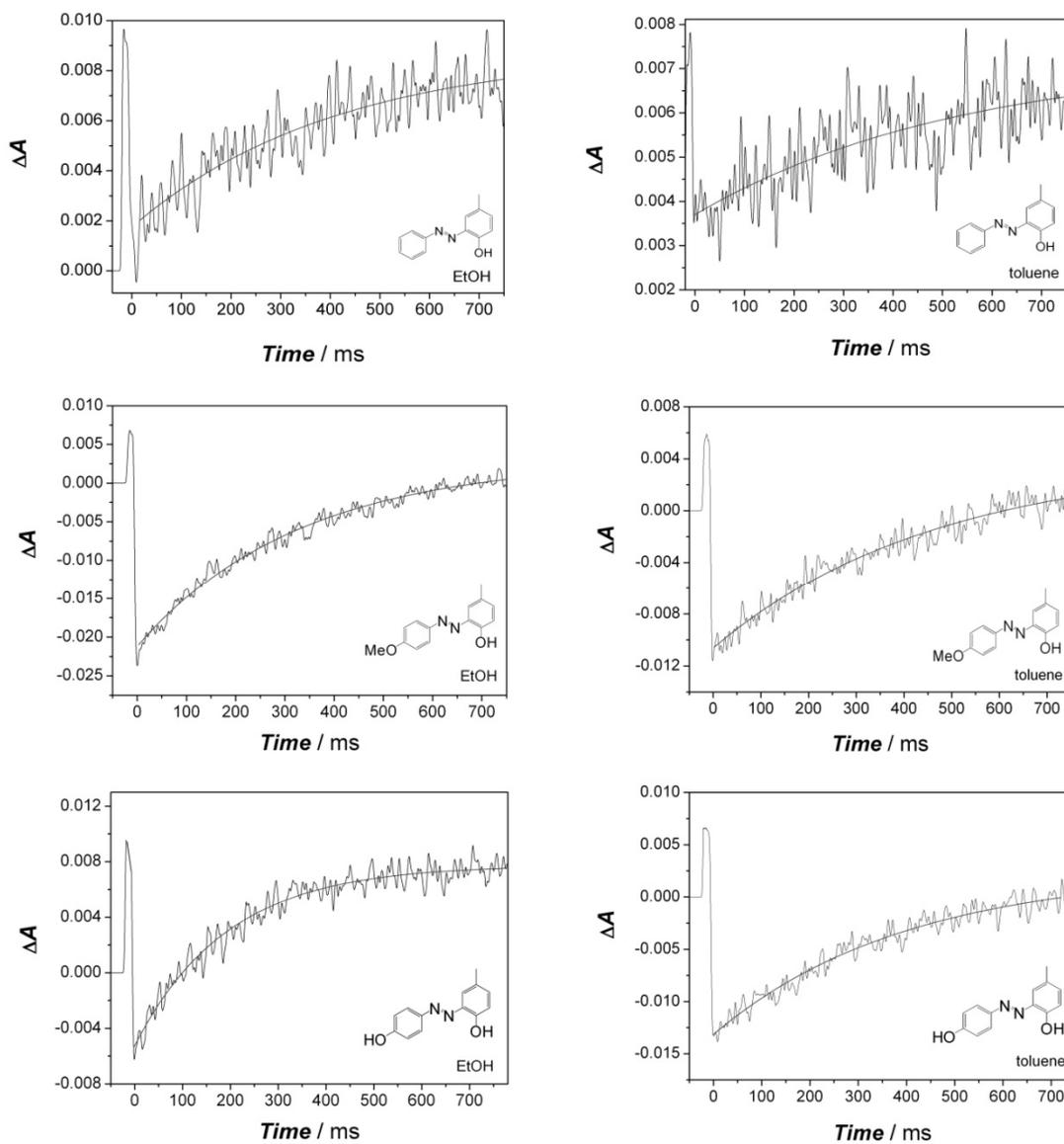
<i>Azocompound</i>	<i>Solvent</i>	<i>T / °C</i>	<i>τ / ms</i>
<b>4-OH</b>	<i>Ethanol</i>	21	265
		30	215
		49	145
		67	102
<b>2-OH</b>	<i>Ethanol</i>	21	398
		30	264
		49	129
		67	72
	<i>Toluene</i>	21	649
		30	485
		49	270
		67	168
<b>2,4,4'-OH</b>	<i>Ethanol</i>	21	6.4
		30	5.1
		49	3.3
		67	2.3
	<i>Toluene</i>	21	31
		49	18
		67	15

**Table S2.** Relaxation time for the *cis* isomer,  $\tau$ , of the hydroxy-substituted azoderivatives **4-OH**, **2-OH** and **2,4,4'-OH** at different temperatures. The experimental error associated to temperature and relaxation time was of  $\pm 0.1$  K and less than 10 %, respectively.

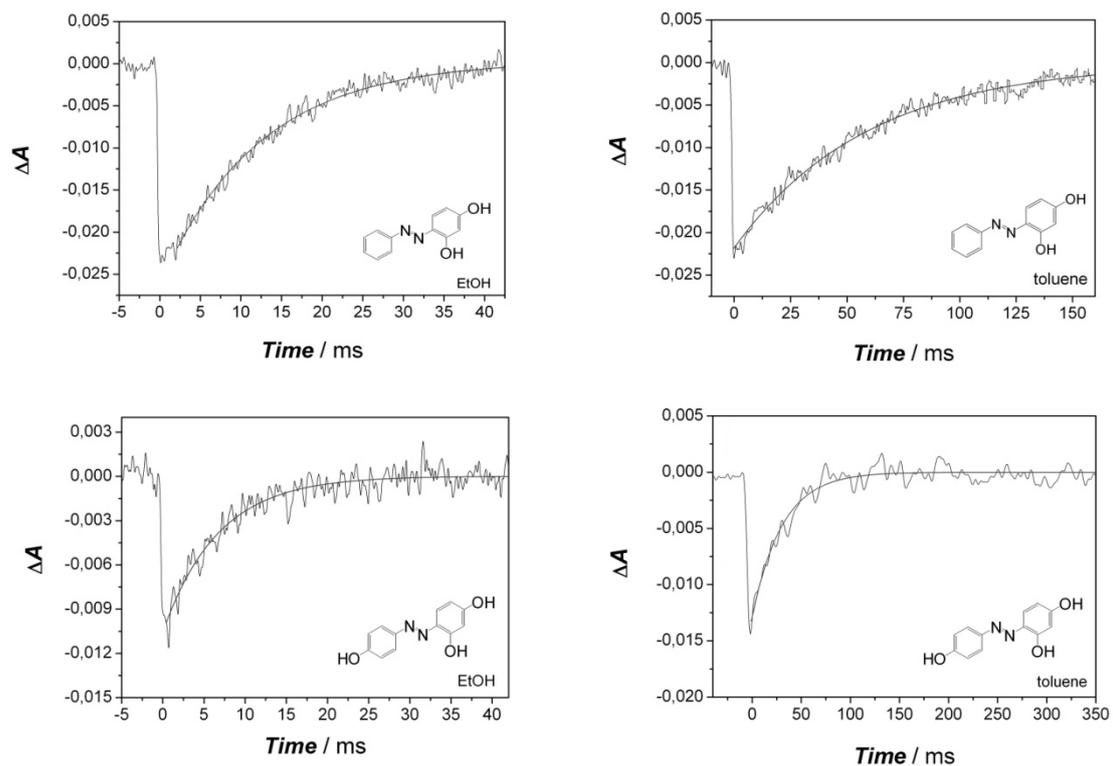
## Figures



**Figure S1.** Transients generated by irradiation with UV-light ( $\lambda=355$  nm) for azobenzenes **4-OH**, **4-OH-4'-OMe** and **4,4'-OH** in ethanol ( $[AZO]=2 \times 10^{-5}$  M) at 298 K.



**Figure S2.** Transients generated by irradiation with UV-light ( $\lambda=355$  nm) for azobenzenes **2-OH**, **2-OH-4'-OMe** and **2,4'-OH** in ethanol and toluene ( $[AZO]=2\times 10^{-5}$  M) at 298 K.



**Figure S3.** Transients generated by irradiation with UV-light ( $\lambda=355$  nm) for azobenzenes **2,4-OH** and **2,4,4'-OH** in ethanol and toluene ( $[AZO]=2 \times 10^{-5}$  M) at 298 K.