

Supporting Information

Fastest non-ionic azo dyes and transfer of their thermal isomerisation kinetics into liquid-crystalline materials

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| | |
|---|-----|
| • Materials and general instrumentation..... | S2 |
| • Synthesis of the azo dyes..... | S2 |
| • Preparation of the dye-doped PMMA polymers..... | S6 |
| • Photochromic behaviour of the dye-doped PMMA polymers and thermal isomerisation kinetics..... | S6 |
| • Preparation and analysis of the samples used in the kinetic studies..... | S10 |
| • Kinetic measurements by the nanosecond laser flash-photolysis technique | S10 |
| • Thermal activation parameters in toluene and I52 | S10 |
| • Absorption spectra before and after photoisomerisation | S11 |
| • <i>cis</i> isomer proportion at the photoequilibrium | S12 |

Materials and general instrumentation. 2-Cyanoaniline, 4-cyano-2-nitroaniline, 2-cyano-4-nitroaniline, 2,4-dinitroaniline and *N,N*-dimethylaniline were purchased from Aldrich and used as received. TLC analyses were carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel 60F₂₅₄) and spots were visualised under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (230-240 mesh).

NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ¹H NMR and 75.4 MHz for ¹³C NMR or a Bruker Avance III 400 at an operating frequency of 400 MHz for ¹H NMR and 100.6 MHz for ¹³C NMR using the solvent peak as an internal reference at 25 °C. All chemical shifts are given in ppm using $\delta_{\text{H}} \text{Me}_4\text{Si} = 0$ ppm as a reference and *J* values are given in Hz. Assignments were made by comparison of chemical shifts, peak multiplicities and *J* values and were supported by spin decoupling-double resonance and bidimensional heteronuclear HMBC and HMQC correlation techniques. IR spectra were recorded on a BOMEM MB 104 spectrophotometer using KBr discs. HRMS were recorded in a LC/MSD-TOF Agilent Technologies apparatus by means of the electrospray (ESIMS) technique. All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. UV-visible absorption spectra (200–800 nm) were obtained using a Shimadzu UV/2501PC spectrophotometer or a Varian Cary 500 UV-vis spectrophotometer.

Synthesis of the azo dyes. Bithienylpyrrole **6** was reported by us recently through a Suzuki cross-coupling reaction.¹ Diazotation of 2-cyanoaniline, 2-cyano-4-nitroaniline, 4-cyano-2-nitroaniline and 2,4-dinitroaniline with NaNO₂ in HCl or H₂SO₄ at 0-5 °C afforded the corresponding aryl-diazonium salts **7-10**, which were further reacted with bithienylpyrrole **6** or *N,N*-dimethylaniline **11** in acetonitrile at 0 °C or in a solution of acetic anhydride in ice water to give heteroaryl (**1a-5a**) and aryl azo dyes (**3b** and **4b**) in moderate to good yields (23-66%, see Fig. S1 and S2). All new compounds were completely characterized by ¹H and ¹³C NMR, IR and HRMS, and the data obtained were in full agreement with the proposed formulation.

¹ J. Garcia-Amorós, M. C. R. Castro, P. Coelho, M. M. M. Raposo and D. Velasco, *Chem. Commun.*, **2013**, 49, 11427–11429.

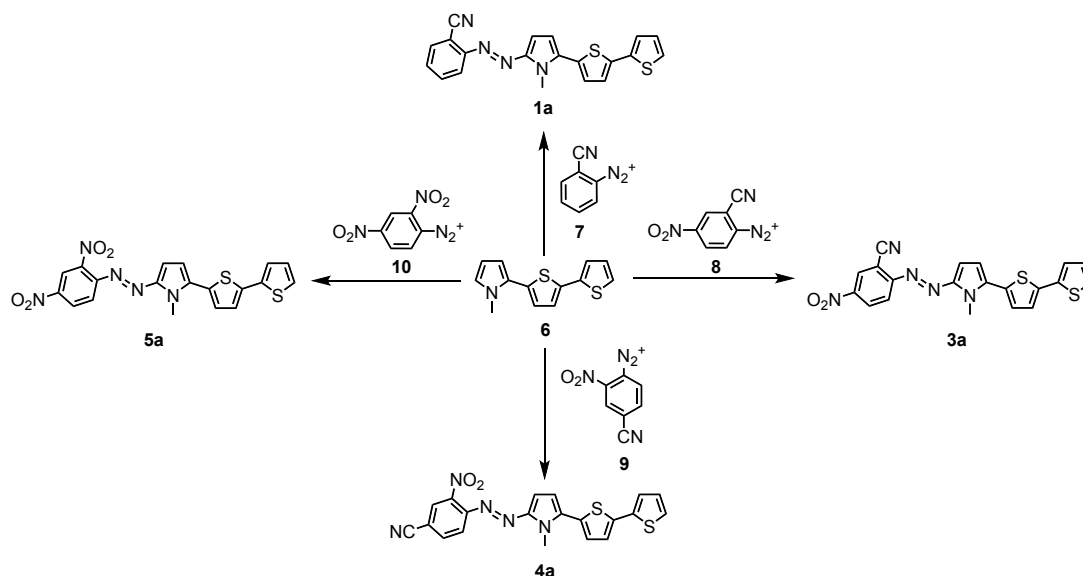


Figure S1. Synthesis of the heterocyclic azo dyes **1a–5a**.

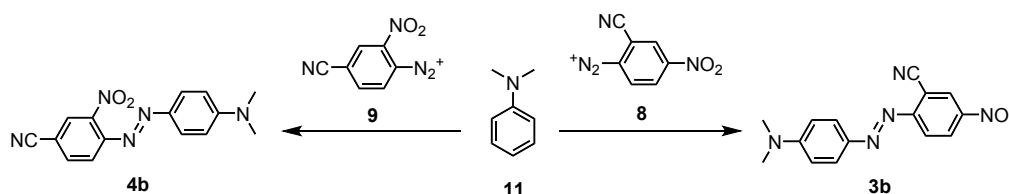


Figure S2. Synthesis of the aryl azo dyes **3b** and **4b**.

General procedure for the preparation of azo dyes 1a, 3a, 3b, 4a and 4b.

Diazotation step. Aril amines (1.0 mmol) were dissolved in HCl 6 N (1 mL) at 0-5 °C. A mixture of NaNO₂ (1.0 mmol) in water (2 mL) was slowly added to the well-stirred mixture of the amine derivative solution at 0-5 °C. The reaction mixture was stirred for 10 min.

Coupling reaction with bithienylpyrrole 6 and *N,N*-dimethylaniline 11. The solution containing the diazonium salt (1.0 mmol) was added dropwise to the solution of bithienylpyrrole 6 or *N,N*-dimethylaniline 11 (0.52 mmol) in acetonitrile (10 mL) and 2-3 drops of acetic acid. The combined solution was maintained at 0 °C for 1-2 h while stirred and then diluted with chloroform (20 mL), washed with water and dried over anhydrous MgSO₄. The solvent was distilled off under reduced pressure and the remaining azo dyes were purified by column chromatography on silica gel using as eluent mixtures of dichloromethane and light petroleum of increasing polarity. Further recrystallization from light petroleum/dichloromethane furnished the pure compounds.

1-(1-Methyl-5-(5-(thiophen-2-yl)thiophen-2-yl)-1H-pyrrol-2-yl)-2-(2-cyanophenyl)-diazene (1a). Dark brown solid (98 mg, 40%). m.p. 134-135 °C. ¹H NMR (DMSO) δ 4.13 (s, 3H, NCH₃), 6.83 (d, 1H, $J=4.4$ Hz, 4'-H), 6.89 (d, 1H, $J=4.4$ Hz, 3'-H), 7.12-7.14 (m, 1H, 4''-H), 7.41 (dd, 1H, $J=3.6$ and $J=1.2$ Hz, 3'''-H), 7.42 (d, 1H, $J=4.0$ Hz, 4''-H), 7.52 (dt, 1H, $J=7.6$ and $J=0.8$ Hz, 4-H), 7.55 (d, 1H, $J=4.0$ Hz, 3''-H), 7.57 (dd, 1H, $J=5.2$ and $J=1.2$ Hz, 5'''-H), 7.77 (dt, 1H, $J=7.0$ and $J=1.2$ Hz, 5-H), 7.89-7.91 (m, 1H, 6-H), 7.93 (dd, 1H, $J=7.6$ and $J=0.8$ Hz, 3-H) ppm. ¹³C NMR (DMSO) δ 31.7, 103.5, 108.6, 113.5, 117.6, 117.9, 124.8, 125.1, 126.2, 128.3, 128.6, 129.2, 130.8, 133.9, 134.1, 134.8, 135.6, 137.6, 147.6, 154.4 ppm. λ_{\max} (Dioxane)/nm 498. IR (liquid film): ν 2225, 1641, 1462, 1329, 1268, 1210, 1171, 1043 cm⁻¹. HMRS: m/z (ESI) for C₂₀H₁₅N₄S₂; calcd 375.0733; found: 375.0725.

1-(1-Methyl-5-(5-(thiophen-2-yl)thiophen-2-yl)-1H-pyrrol-2-yl)-2-(2-cyano-4-nitrophenyl)diazene (3a). Dark brown solid (30 mg, 35%). m.p. 197-199 °C. ¹H NMR (DMSO) δ 4.18 (s, 3H, NCH₃), 7.06 (d, 1H, $J=4.8$ Hz, 4'-H), 7.10 (d, 1H, $J=4.8$ Hz, 3'-H), 7.14-7.16 (m, 1H, 4''-H), 7.48 (dd, 1H, $J=3.2$ and $J=0.8$ Hz, 3'''-H), 7.50 (d, 1H, $J=4$ Hz, 4''-H), 7.62 (dd, 1H, $J=4.8$ and $J=0.8$ Hz, 5'''-H), 7.74 (d, 1H, $J=4$ Hz, 3''-H), 8.06 (d, 1H, $J=8.8$ Hz, 6-H), 8.48 (dd, 1H, $J=8.8$ and $J=2.8$ Hz, 5-H), 8.76 (d, 1H, $J=2.8$ Hz, 3-H) ppm. λ_{\max} (Dioxane)/nm 542 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 6,540). IR (Nujol): ν 2228, 1602, 1575, 1521, 1395, 1244, 1213, 1144, 1120, 1078, 1049 cm⁻¹. HMRS: m/z (ESI) for C₂₀H₁₄N₄O₂S₂; calcd 420.0583; found: 420.0581. Due to the low solubility of the compound it was not possible to record its ¹³C NMR spectrum.

(N,N-Dimethylphenyl)-4'-(2-cyano-4-nitrophenyl)diazene (3b). Dark violet solid (56 mg, 40%). m.p. 138-140 °C. ¹H NMR (CDCl₃) δ 3.20 (s, 6H, N(CH₃)₂), 6.82 (d, 2H, $J=9.0$ Hz, 2' and 6'-H), 8.01 (d, 2H, $J=9.0$ Hz, 3' and 5'-H), 8.02 (d, 1H, $J=9.2$ Hz, 6-H), 8.41 (dd, 1H, $J=9.2$ and $J=2.6$ Hz, 5-H), 8.60 (d, 1H, $J=2.6$ Hz, 3-H) ppm. ¹³C NMR (CDCl₃) δ 40.7 (2C), 111.6, 112.4 (2C), 115.6, 117.9 (2C), 127.8, 128.2, 129.1, 144.4, 146.3, 154.3, 157.3 ppm. λ_{\max} (Dioxane)/nm 513. IR (liquid film): ν 2227, 1599, 1576, 1521, 1422, 1360, 1333, 1306, 1248, 1203, 1174, 1140, 1115, 1074 cm⁻¹. HMRS: m/z (ESI) for C₁₅H₁₄N₅O₂; calcd 296.1147; found: 296.1144.

1-(1-Methyl-5-(5-(thiophen-2-yl)thiophen-2-yl)-1H-pyrrol-2-yl)-2-(4-cyano-2-nitrophenyl)diazene (4a). Dark brown solid (24 mg, 22%). m.p. 210-211 °C. ¹H NMR (DMSO) δ 4.09 (s, 3H, NCH₃), 6.92 (d, 1H, $J=4.6$ Hz, 4'-H), 6.94 (d, 1H, $J=4.6$ Hz, 3'-H), 7.13-7.15 (m, 1H, 4''-H), 7.45 (dd, 1H, $J=3.6$ and $J=1.2$ Hz, 3'''-H), 7.76 (d, 1H,

$J=4.0$ Hz, 4''-H), 7.60 (dd, 1H, $J=5.2$ and $J=1.2$ Hz, 5'''-H), 7.66 (d, 1H, $J=4.0$ Hz, 3''-H), 8.01 (d, 1H, $J=8.4$ Hz, 6-H), 8.12 (dd, 1H, $J=8.4$ and $J=1.6$ Hz, 5-H), 8.54 (d, 1H, $J=1.6$ Hz, 3-H) ppm. ^{13}C NMR (DMSO) δ 31.7, 105.8, 109.8, 115.1, 117.3, 119.8, 125.1, 125.3, 126.6, 127.9, 128.6, 129.6, 130.2, 135.4, 136.2, 137.7, 138.8, 145.9, 147.5, 148.5 ppm. λ_{max} (Dioxane)/nm 528. IR (liquid film): ν 2924, 2855, 2223, 1626, 1532, 1640 cm^{-1} . HMRS: m/z (ESI-TOF) for $\text{C}_{20}\text{H}_{14}\text{N}_4\text{O}_2\text{S}_2$; calcd 420.0583; found: 420.0577.

(*N,N*-Dimethylphenyl)-4'-(4-cyano-2-nitrophenyl)diazene (4b). Dark red solid (40 mg, 28%). m.p. 193-195 °C. ^1H NMR (DMSO) δ 3.31 (s, 6H, $\text{N}(\text{CH}_3)_2$), 6.88 (d, 2H, $J=9.5$ Hz, 2' and 6'-H), 7.76 (d, 2H, $J=9.5$ Hz, 3' and 5'-H), 7.84 (d, 1H, $J=8.6$ Hz, 6-H), 8.16 (dd, 1H, $J=8.6$ and $J=1.8$ Hz, 5-H), 8.60 (d, 1H, $J=1.8$ Hz, 3-H) ppm. ^{13}C NMR (DMSO) δ 40.9 (2C), 111.6, 112.6 (2C), 116.9, 119.8, 127.2 (2C), 127.8, 135.7, 144.7, 146.9, 147.9, 153.6 ppm. λ_{max} (Dioxane)/nm 480. IR (liquid film): ν 2230, 1598, 1261, 945 cm^{-1} . HMRS: m/z (ESI-TOF) for $\text{C}_{15}\text{H}_{14}\text{N}_5\text{O}_2$; calcd 296.1142; found: 296.1141.

Procedure for the preparation of azo dye 5a.

Diazotation of 2,4-dinitroaniline: 2,4-dinitroaniline (1.0 mmol) was dissolved in concentrated H_2SO_4 (1.2 mmol) at 0-5 °C. A mixture of NaNO_2 (1.2 mmol) in water (1 mL) was slowly added to the well-stirred solution of the amine derivative at 0-5 °C.

Coupling reaction with bithienylpyrrole 11: The solution containing the diazonium salt **10** (1.0 mmol) was added dropwise to a solution of bithienylpyrrole **11** (1.2 mmol) in acetic anhydride (15 mL) and iced water (200 mL). The combined solution was maintained at 0 °C while stirring for 3 h. Then, the crude was diluted with chloroform (20 mL), washed with water and dried over anhydrous MgSO_4 . The product was recrystallized from *n*-hexane.

1-(1-Methyl-5-(5-(thiophen-2-yl)thiophen-2-yl)-1H-pyrrol-2-yl)-2-(2,4-dinitrophenyl)-diazene (5a). Black solid (49 mg, 66%). m.p. 175-177 °C. ^1H NMR (DMSO) δ 4.11 (s, 3H, NCH_3), 6.98 (d, 1H, $J=4.8$ Hz, 4'-H), 7.00 (d, 1H, $J=4.6$ Hz, 3'-H), 7.14-7.16 (m, 1H, 4'''-H), 7.47 (dd, 1H, $J=3.6$ and $J=0.8$ Hz, 3'''-H), 7.49 (d, 1H, $J=4$ Hz, 4''-H), 7.61 (dd, 1H, $J=5.2$ and $J=1.2$ Hz, 5'''-H), 7.72 (d, 1H, $J=4$ Hz, 3''-H), 8.05 (d, 1H, $J=8.8$ Hz, 6-H), 8.46 (dd, 1H, $J=8.8$ and $J=2.4$ Hz, 5-H), 8.80 (d, 1H, $J=2.8$ Hz, 3-H) ppm. ^{13}C NMR (DMSO) δ 31.8, 115.7 (2C), 119.5, 119.9, 125.2, 125.4, 126.8, 127.4, 128.7, 129.9, 130.1, 135.4, 138.5, 139.3, 144.9, 145.5, 148.9, 149.8 ppm. λ_{max}

(Acetonitrile)/nm 552 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 22,871). IR (liquid film): ν 3101, 3077, 1592, 1531, 1521 cm^{-1} . HMRS: m/z (ESI) for $\text{C}_{19}\text{H}_{14}\text{N}_5\text{O}_4\text{S}_2$; calcd 440.0487; found: 440.0483.

Preparation of the polymer-doped PMMA polymers. A mixture of poly(methyl methacrylate) (1.0 g) in CH_2Cl_2 (10 mL) was heated at 60 °C with occasional stirring with a glass rod for 10 min after which a transparent and uncoloured solution was obtained. A solution of the corresponding azo dye (1.0 mg) in CH_2Cl_2 (2.0 mL) was then added to the PMMA solution and, after stirring for 2 min., the polymer solution was transferred into a Petri dish and kept at room temperature for 6 days during which the solvent evaporated and a coloured transparent and detachable thin film was formed. The round films, with a diameter of 9 cm, display a mass around 1.0 g with a 0.1% weight percentage of the dye (Fig. S3).



Figure S3. Pictures of the coloured PMMA polymers doped with azo dyes **1a** (left), **3a** (middle) and **4a** (right).

Photochromic behaviour of the polymer-doped PMMA polymers and thermal isomerisation kinetics. All films analysed are intensively coloured with very broad absorption bands (*vide infra*). Upon irradiation with visible light ($\lambda_{\text{irrad}} > 420 \text{ nm}$) for 0.5-1 minute, the *trans* isomer is converted into the corresponding *cis* form with a concomitant slight lowering of the absorption at λ_{Max} . Apparently, both configurational isomers have similar absorption spectra in the visible region of the electromagnetic spectrum. Once the irradiation ceases, the system returns in a few seconds or minutes to the initial state (see Table 1 in the main text of the manuscript for full numerical data), that is, the thermodynamically stable *trans* form of the azo photochrome is recovered. Such process follows a first order kinetics as expected.

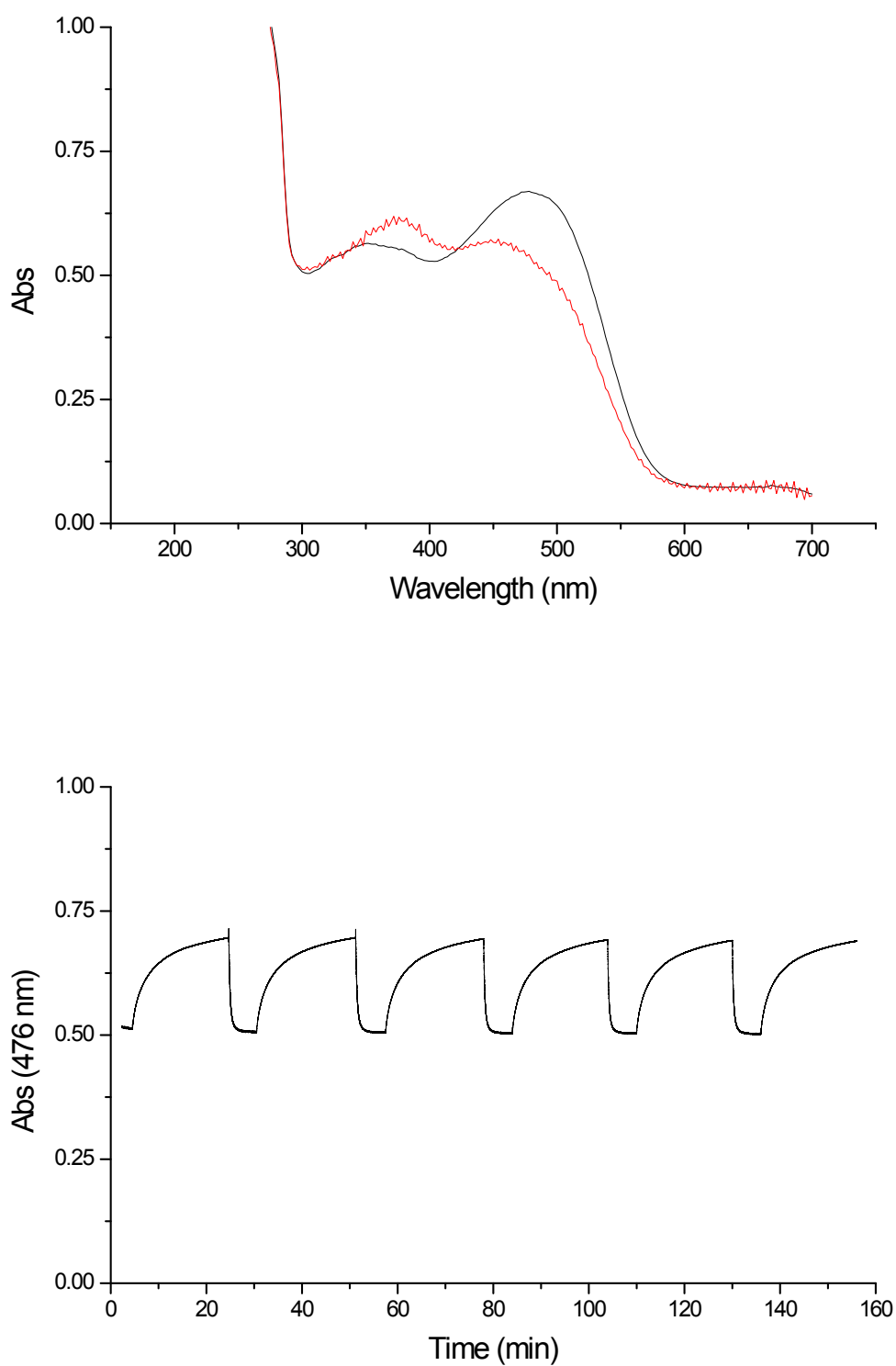


Figure S4. Absorption spectra before and after illumination with visible light ($\lambda_{\text{irrad}} > 420$ nm) and consecutive visible light irradiation / dark cycles ($\lambda_{\text{Obs}} = 476$ nm) of a PMMA film doped with **1a** at 298 K.

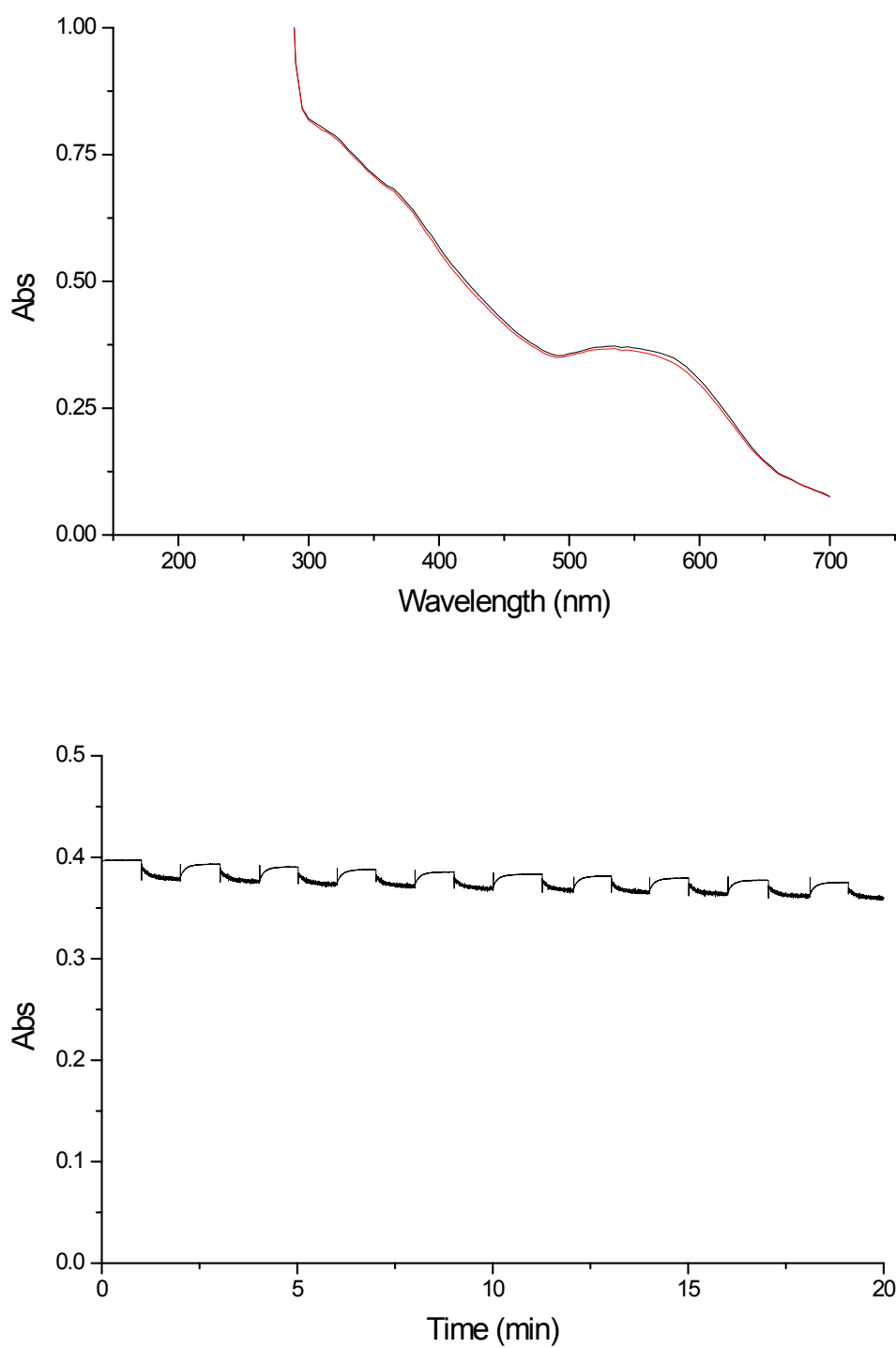


Figure S5. Absorption spectra before and after illumination with visible light ($\lambda_{\text{irrad}} > 420$ nm) and consecutive visible light irradiation / dark cycles ($\lambda_{\text{obs}} = 550$ nm) of a PMMA film doped with **3a** at 298 K.

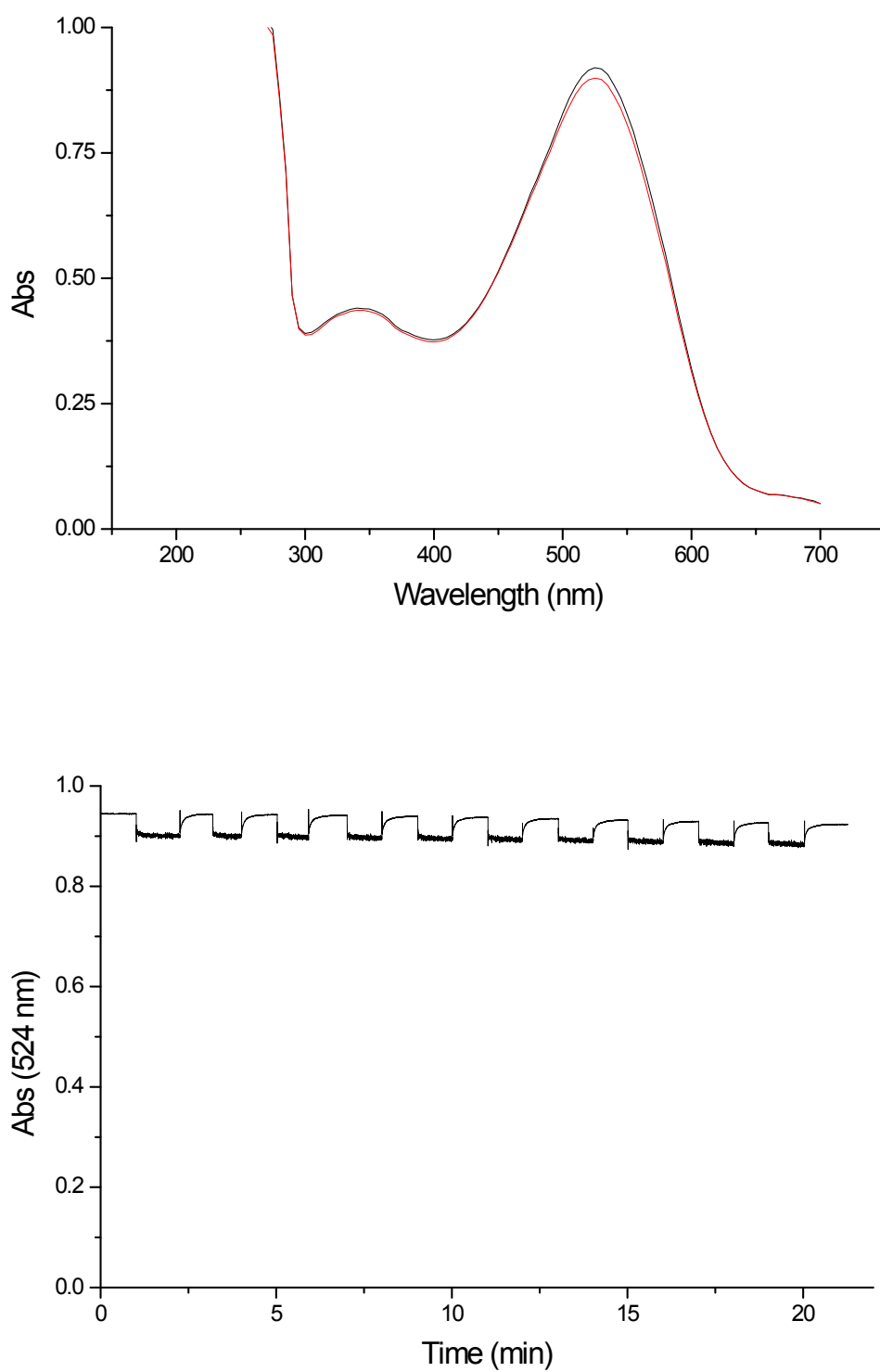


Figure S6. Absorption spectra before and after illumination with visible light ($\lambda_{\text{irrad}} > 420$ nm) and consecutive visible light irradiation / dark cycles ($\lambda_{\text{obs}} = 524$ nm) of a PMMA film doped with **4a** at 298 K.

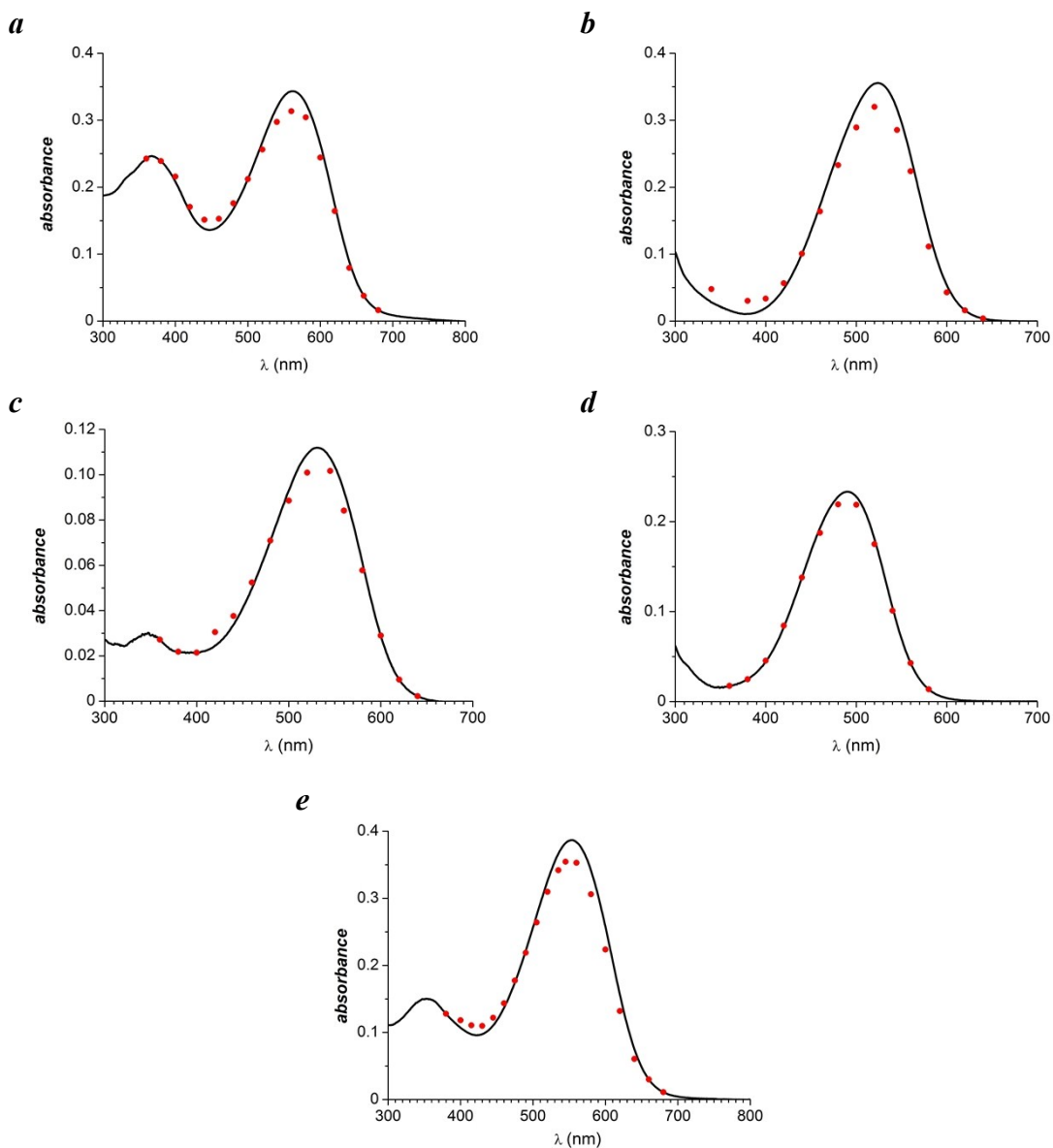
Preparation and analysis of the samples used in the kinetic studies. For the experiments in isotropic solvents, 20 μM solutions of the azo dye in the corresponding solvent were measured in 1 cm optical path quartz cells. For the nematic solutions, the concentration was *ca.* 4 mM and 10 μm quartz cells were used instead. Such samples were prepared by mixing the desired amounts of the mesogen and the corresponding azo dye followed by homogenization by magnetic stirring for 10 minutes in the isotropic state. Monodomain (macroscopically oriented) samples were prepared in 10 μm optical path quartz cells, its surface being rubbed with a piece of cloth in a single direction. Homogeneity of the samples was checked by local probe microscopy. 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 was observed, which together with the absence of any characteristic texture was indicative of a successful macroscopic orientation of the nematic director. Polarized optical microscopy (POM) was performed in a Nikon Eclipse polarizing microscope at room temperature.

Kinetic measurements by the nanosecond laser flash-photolysis technique. A population of *cis* isomers was created by pulsed-laser irradiation of the *trans* isomer at 532 nm employing a Continuum Surelite I-10 Q-switched Nd-YAG laser (5 ns pulse width, *ca.* 10 mJ per pulse). The concomitant absorbance changes were monitored at 90° by a white-light analysing beam produced by a Xe lamp (PTI, 75 W) in combination with a dual-grating monochromator (PTI 101) coupled to a Hamamatsu R928 photomultiplier for detection.² All transient absorptions were analysed at $\lambda_{\text{obs}} = 500$ nm.

Thermal activation parameters in toluene and I52.

| | | ΔH^\ddagger kJ mol ⁻¹ | ΔS^\ddagger J K ⁻¹ mol ⁻¹ |
|------------|-----------|--|--|
| Toluene | 3b | 39±1 | -73±2 |
| (isotropic | 4b | 49±1 | -41±2 |
|) | 5a | 39±1 | -60±3 |
| I52 | 3a | 20±1 | -151±1 |
| (nematic) | 3b | 28±1 | -83±1 |

² N. Rubio, A. Jiménez-Banzo, T. Torres and S. Nonell, *J. Photochem. Photobiol. A*, 2007, **185**, 214–219.

Table S1. Thermal activation parameters for selected azo dyes in toluene and LC **I52**.**Figure S7.** Spectral change for compounds **3a** (**a**), **3b** (**b**), **4a** (**c**), **4b** (**d**) and **5a** (**e**) upon *trans*-to-*cis* photoisomerisation with a green-light laser pulse in ethanol at 298 K ($\lambda_{\text{irrad}} = 532$ nm, 5 ns pulse width, *ca.* 10 mJ per pulse, [AZO] = 10–20 μM).

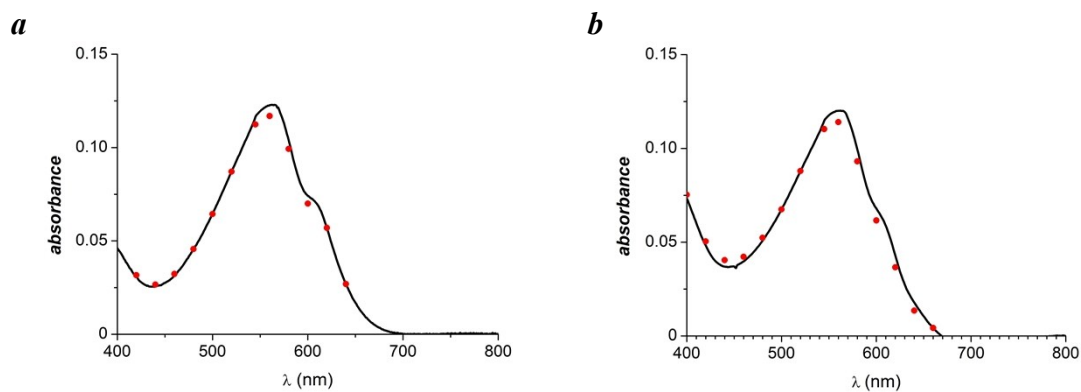


Figure S8. Spectral change for compounds **3a** (*a*) and **5a** (*b*) upon *trans*-to-*cis* photoisomerisation with a green-light laser pulse in the nematic mesogen **I52** at 298 K ($\lambda_{\text{irrad}} = 532$ nm, 5 ns pulse width, *ca.* 10 mJ per pulse, $[\text{AZO}] = 4$ mM).

| Compound | Y_{app} ethanol (%) | Y_{app} I52 (%) |
|-----------|------------------------------|---------------------------------|
| 3a | 8.6 | 4.6 |
| 3b | 9.7 | - |
| 4a | 8.0 | - |
| 4b | 5.4 | - |
| 5a | 8 | 4.8 |

Table S2. Proportion of the *cis* isomer at the photoequilibrium ($Y_{\text{app}} = (1 - A_{\text{ph}}/A_0) \times 100$) for azo dyes **3a**, **3b**, **4a**, **4b** and **5a** in ethanol and the nematic mesogen **I52** at 298 K.