

Supporting Information

**Adaptable Photochromic Switches with Self-Aggregating
Heterocyclic Azo Dyes**

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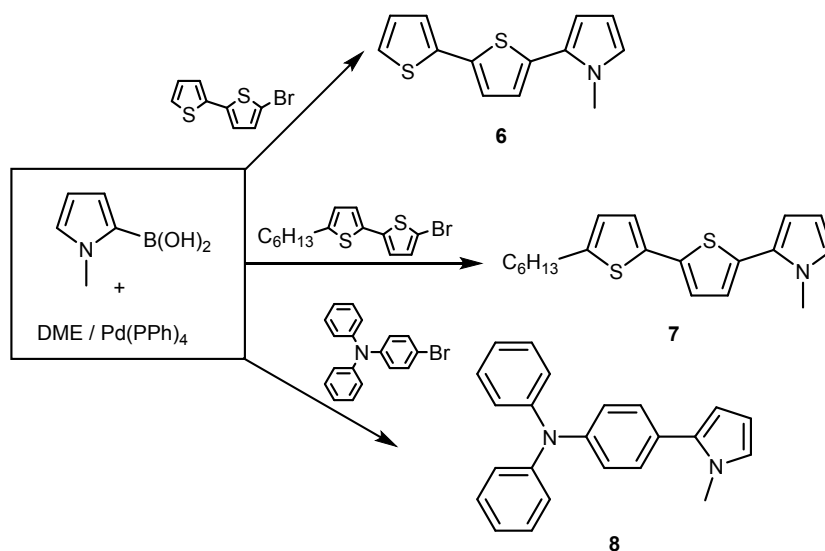
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Synthesis of the heterocyclic azo dyes 1-5 and the pyrrole precursors 6-8.

Materials. 4-Aminobenzaldehyde, 4-aminobenzoic acid, 2-bromo-2,2'-bithiophene, 5-bromo-5'-hexyl-2,2'-bithiophene, 5-bromo-*N,N*-diphenylaniline and 1-methyl-1*H*-pyrrole-2-boronic acid used as precursors for the synthesis of pyrroles **6-8** and azo dyes **1-5** were purchased from Aldrich and Fluka and used as received. TLC analyses were carried out on 0.25 mm thick pre-coated 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).

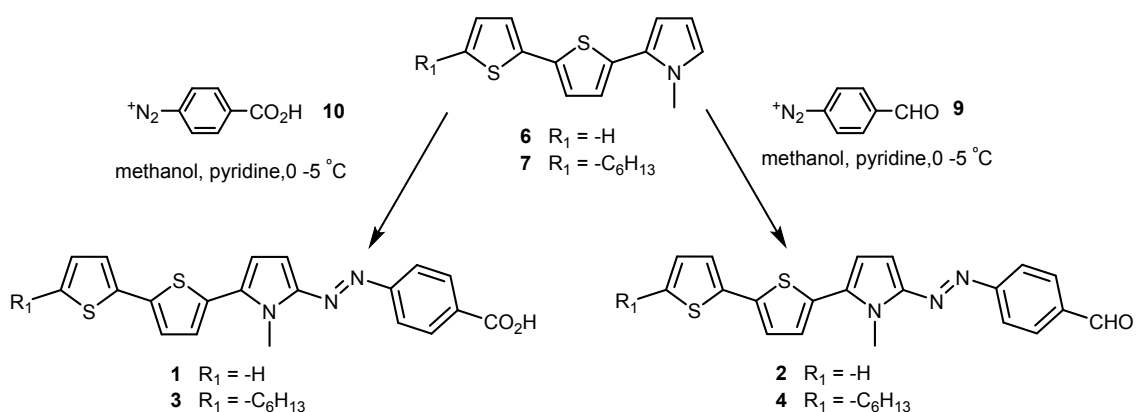
Characterization. NMR spectra were registered on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ¹H NMR and 75.4 MHz for ¹³C NMR or a Bruker Avance III 400 at an operating frequency of 400 MHz for ¹H NMR and 100.6 MHz for ¹³C NMR, using the solvent peak as an internal reference at 25 °C. The NMR spectrometer Bruker Avance III 400 is part of the National NMR Network and was purchased within the framework of the National Program for Scientific Re-equipment, contract REDE/1517/RMN/2005 with funds from POCI 2010 (FEDER) and FCT. 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. Mass spectrometry analyses were performed at the "C.A.C.T.I.-Unidad de Espectrometria de Masas" at the University of Vigo (Spain) and at the *Centres Científics i Tecnològics* of the University of Barcelona (CCiTUB, Spain). High resolution mass spectra (HRMS) were recorded in a LC/MSD-TOF Agilent Technologies apparatus by means of the electrospray ionization technique. All melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. UV-visible absorption spectra (200–800 nm) were registered in a Varian Cary 500 UV-Vis spectrophotometer.

Synthesis of the pyrrole precursors. Pyrroles **6-8** were synthesized through Suzuki cross-coupling reaction between the commercially available 1-methyl-1*H*-pyrrol-2-yl-2-boronic acid and 5-bromo-2,2'-bithiophene, 5-bromo-5'-hexyl-2,2'-bithiophene and 5-bromo-*N,N*-diphenylaniline (Scheme S1).

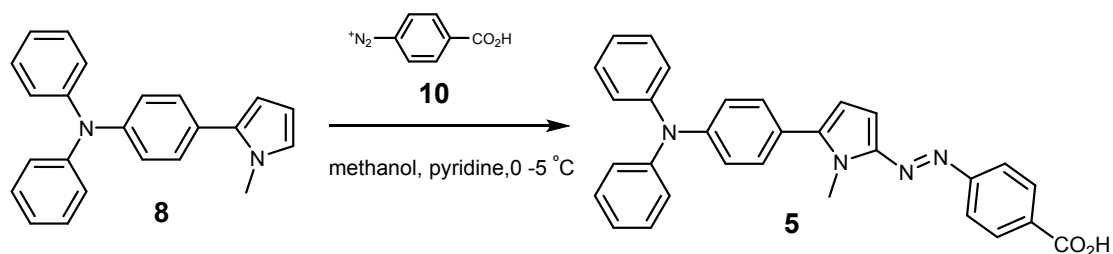


Scheme S1. Synthesis of the pyrrole precursors 6-8.

Pyrrole precursors 6-8 were used as coupling components together with aryl-diazonium salts 9 and 10 in order to prepare the target azo dyes 1-5 (Scheme S2 and S3).



Scheme S2. Synthesis of the *Tph-Tph-Pyr* triad-containing azo derivatives 1-4.



Scheme S3. Synthesis of the pyrrolyldiphenylaniline-based azo derivative 5.

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.

Synthesis of bithienyl-pyrrole 7 and pyrrolyl-diphenylaniline 8 through Suzuki coupling reaction.

5-Bromo-5'-hexyl-2,2'-bithiophene or 4-bromo-*N,N*-diphenylaniline (1 mmol) were coupled with 1-methyl-1*H*-pyrrole-2-boronic acid pinacol ester (1.2 mmol) in a mixture of DME (10 mL), aqueous 2 M Na₂CO₃ (1 mL) and Pd(PPh₃)₄ (3 % mmol) at 80 °C under nitrogen. The reaction was monitored by TLC, which determined the reaction time (24 h). After cooling, the mixture was extracted with dichloromethane (3×20 mL) and a saturated solution of NaCl was added (20 mL), and the phases were separated. The organic phase was washed with water (3×10 mL) and with a solution of NaOH (10 %, 1×10 mL). The organic phase obtained was dried over MgSO₄, filtered, and the solvent was distilled off under reduced pressure to give a crude mixture. The crude products were purified through a silica gel chromatography column using mixtures of dichloromethane and light petroleum of increasing polarity to afford the coupled products **7-8**.

Pyrrole **6** was synthesized using the same synthetic methodology reported previously by us.¹

2-(5'-(5''-Hexylthiophen-2''-yl)thiophen-2'-yl)-1-methyl-1*H*-pyrrole (7). Green oil (83 %). ¹H NMR (acetone-*d*₆, 400 MHz) δ 0.90-0.94 (m, 3H, CH₃), 1.34-1.37 (m, 6H, CH₃(CH₂)₃(CH₂)₂-), 1.70-1.74 (m, 2H, CH₃(CH₂)₃CH₂-CH₂-), 2.83-2.87 (m, 2H, CH₃(CH₂)₄CH₂-), 3.56 (s, 3H, N-CH₃), 6.09-6.10 (m, 1H, 4-H), 6.30-6.32 (m, 1H, 3-H), 6.80-6.83 (m, 2H, 5-H and 4''-H), 7.03 (d, 1H, *J*= 3.6 Hz, 4'-H), 7.08 (d, 1H, *J*= 3.6 Hz, 3''-H), 7.16 (d, 1H, *J*= 3.6 Hz, 3'-H) ppm. ¹³C NMR (acetone-*d*₆, 400 MHz) δ 14.3, 23.2, 29.4, 30.5, 32.2, 32.4, 35.6, 108.6, 110.5, 124.0, 124.3, 125.5, 125.6, 126.1, 127.3, 134.6, 135.3, 136.7, 145.9 ppm. IR (Nujol): ν 1730, 1549, 1517, 1309, 1290, 1263, 1231, 1205, 1155, 1120, 1089, 1054, 1015 cm⁻¹. HMRS: *m/z* (ESI) for C₁₉H₂₃NS₂; calcd 329.1272; found: 329.1279.

4-(1-Methyl-1*H*-pyrrolyl-2-yl)-*N,N*-diphenylaniline (8). Brown oil (96 %). ¹H NMR (DMSO-*d*₆, 400 MHz) δ 3.62 (s, 3H, CH₃), 6.02-6.03 (m, 1H, 4'-H), 6.09-6.10 (m, 1H, 3'-H), 6.78-6.79 (m, 1H, 5'-H), 6.97-7.04 (m, 6 H, 2-, 6-, 2''-, 2'''-, 6''-, 6'''-H), 7.28-7.41 (m, 8 H, 3-, 5-, 3''-, 3'''-, 4''-, 4'''-, 5''-, 5'''-H) ppm. ¹³C NMR (DMSO-*d*₆, 400 MHz) δ 24.9, 107.3, 107.4, 108.1, 108.4, 123.0, 123.1, 123.9, 124.0 (2C), 124.3, 126.5, 127.3, 127.9, 128.5, 128.9, 129.6, 133.1, 145.7, 147.1 ppm. IR (Nujol): ν 2725, 1943, 1699, 1587, 1545, 1488, 1333, 1313, 1277, 1175, 1154, 1111, 1059, 1028 cm⁻¹. HMRS: *m/z* (ESI) for C₂₅H₂₀N₂S₂; calcd 412.1100; found: 412.1150.

Procedure for the azo coupling of pyrrole precursors 6-8 with the diazonium salts 9 and 10 to afford heterocyclic azo dyes 1-5.

Diazotation of 4-aminobenzaldehyde and 4-aminobenzoic acid. Hydrochloric acid (1 mL) was added to a flask with a suspension of 4-aminobenzaldehyde or 4-aminobenzoic acid (1.5 mmol) in water (2.5 mL) at 0-5 °C until the mixture was homogenous. A mixture of NaNO₂ (1.7 mmol) in water (2 mL) was slowly added to the well-stirred mixture of the amine derivative solution. The reaction mixture was stirred for 30 min. at 0-5 °C.

Coupling reaction with pyrrole precursors 6-7 or pyrrolyl-diphenylaniline 8 with diazonium salts 9 or 10. The previously prepared solution of the diazonium salt 9 or 10 was added dropwise to the solution of compounds 6, 7 or 8 (1.5 mmol) and pyridine (0.5 mL) in methanol (10 mL) at 0-5 °C. The resulting mixture was stirred for 3 h at 0-5 °C and then concentrated under reduced pressure. The precipitate was filtered, washed with cold water and dried to afford the pure heterocyclic azo derivatives 1-5.

4-((5-[2,2'-Bithiophen]-5-yl)-1-methyl-1H-pyrrol-2-yl)diazenyl)benzoic acid (1). Grey solid (94 %, 45 mg). Mp 159-161. °C ¹H NMR (DMSO-*d*₆) δ 4.13 (s, 3H, CH₃), 6.86 (d, 1H, *J*=4.6 Hz, 4'-H), 6.98 (d, 1H, *J*= 4.6 Hz, 3'-H), 7.13 (dd, 1H, *J*=4.8 and *J*= 3.4 Hz, 4'''-H), 7.43 (dd, 1H, *J*=3.6 and *J*= 1.2 Hz, 3''''-H), 7.45 (d, 1H, *J*=3.8 Hz, 4''-H), 7.58 (d, 1H, *J*=3.8 Hz, 3''-H) 7.59 (dd, 1H, *J*= 4.8 and *J*= 1.2 Hz, 5''''-H), 7.86 (d, 2H, *J*= 6.8, 3- and 5-H), 8.05 (d, 2H, *J*= 6.8, 2- and 6-H) ppm. ¹³C NMR (DMSO-*d*₆) δ 31.2, 103.3, 113.9, 121.2 (2C), 124.9, 125.2, 126.4, 127.2, 128.7, 130.5, 130.6 (2C), 135.0, 135.6, 138.1, 142.0, 147.4, 154.9, 166.9 ppm. λ_{Max} (ethanol)/nm 486 (ε/mM⁻¹ cm⁻¹ 10.2). IR (Nujol): ν 1690, 1603, 1554, 1527, 1503, 1376, 1318, 1287, 1252, 1227, 1194, 1172, 1133, 1076, 1058 cm⁻¹. HMRS: *m/z* (ESI) for C₂₀H₁₆N₃O₂S₂; calcd 394.0684; found: 394.0681.

4-((5-[2,2'-Bithiophen]-5-yl)-1-methyl-1H-pyrrol-2-yl)diazenyl)benzaldehyde (2). Dark brown solid (88 %, 76 mg). Mp 148-150 °C. ¹H NMR (DMSO-*d*₆) δ 4.14 (s, 3H, CH₃), 6.82 (d, 1H, *J*=4.6 Hz, 4'-H), 6.90 (d, 1H, *J*=4.6 Hz, 3'-H), 7.12-7.14 (m, 1H, 4'''-H), 7.41 (dd, 1H, *J*=1.2 and *J*=3.6 Hz, 3''''-H), 7.43 (d, 1H, *J*=4.0 Hz, 4''-H), 7.54 (d, 1H, *J*=4.0 Hz, 3''-H), 7.57 (dd, 1H, *J*=1.2 and *J*=5.2 Hz, 5''''-H) 7.95 (d, 2H, *J*=7.8 Hz, 3- and 5-H), 8.02 (d, 2H, *J*=7.8 Hz, 2- and 6-H), 10.03 (s, 1H, CHO) ppm. ¹³C NMR (DMSO-*d*₆) δ 31.6, 102.6, 113.5, 122.1 (2C), 124.8, 125.2, 126.3, 128.3, 128.7, 130.9 (2C), 131.0, 134.5, 135.7, 135.8, 137.7, 147.9, 156.8, 192.4 ppm. λ_{Max} (ethanol)/nm 471 (ε/mM⁻¹ cm⁻¹ 26.6). IR (Nujol): ν 2725, 1688, 1595, 1554, 1528, 1503, 1326, 1292, 1256, 1229, 1212, 1164, 1135, 1077, 1041 cm⁻¹. HMRS: *m/z* (ESI) for C₂₀H₁₆N₃OS₂; calcd 378.0735; found: 378.0735.

4-((5'-(5'''-Hexyl-(2'',2''''-bithiophen)-5''-yl)-1'-methyl-1H-pyrrol-2'-yl)diazenyl)benzoic acid (3).

Dark grey solid (91 %). Mp 172-174 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 0.87-0.89 (m, 3H, CH₃), 1.27-1.37 (m, 6H, CH₃(CH₂)₃-), 1.60-1.66 (m, 2H, CH₃(CH₂)₃CH₂-), 2.79 (t, 2H, *J*= 7.6 Hz, CH₃(CH₂)₄CH₂-), 4.10 (s, 3H, CH₃), 6.79 (d, 1H, *J*= 4.8 Hz, 4'-H), 6.82 (d, 1H, *J*= 3.6 Hz, 4''-H), 6.98 (d, 1H, *J*= 4.8 Hz, 3'-H), 7.19 (d, 1H, *J*= 3.6 Hz, 3'''-H), 7.31 (d, 1H, *J*= 4.0 Hz, 4''-H), 7.50 (d, 1H, *J*= 4 Hz, 3''-H) 7.84 (d, 2H, *J*= 8.8 Hz, 3- and 5-H), 8.04 (d, 2H, *J*= 8.8 Hz, 2- and 6-H) ppm. ¹³C NMR (DMSO-*d*₆, 400 MHz) δ 13.4, 21.6, 27.7, 29.1, 30.5, 31.2, 103.3, 113.5, 120.7, 124.1, 124.3, 125.4, 128.4, 130.1, 130.2, 130.3, 132.8, 134.9, 138.4, 145.7, 147.2, 154.7, 166.4 ppm. λ_{Max} (ethanol)/nm 493 (ε/mM⁻¹ cm⁻¹ 22.6). IR (Nujol): ν 1710, 1603, 1556, 1540, 1502, 1377, 1322, 1295, 1261, 1228, 1172, 1158, 1137, 1116, 1088, 1073, 1039, 1000 cm⁻¹. HMRS: *m/z* (ESI) for C₂₆H₂₈N₃O₂S₂; calcd 478.1623; found: 478.1629.

4-((5-(5'-Hexyl-[2,2'-bithiophen]-5-yl)-1-methyl-1H-pyrrol-2-yl)diazenyl)benzaldehyde (4).

Dark brown solid (36 %, 38 mg). Mp 168-170 °C. ¹H NMR (DMSO-*d*₆) δ 0.86 (m, 3H, CH₃), 1.06-1.10 (m, 6H, CH₃(CH₂)₃-), 1.27-1.29 (m, 2H, CH₃(CH₂)₃CH₂-), 2.79 (m, 2H, CH₃(CH₂)₄CH₂-), 4.13 (s, 3H, CH₃), 6.78 (d, 1H, *J*=4.4 Hz, 4'-H), 6.83 (d, 1H, *J*=4.0 Hz, 4''-H), 6.88 (d, 1H, *J*=4.4 Hz, 3'-H), 7.12 (d, 1H, *J*=3.6 Hz, 4''-H), 7.33 (d, 1H, *J*=3.6 Hz, 3''-H), 7.51 (d, 1H, *J*=4.0 Hz, 3'''-H) 7.94 (d, 2H, *J*=6.8 Hz, 3- and 5-H), 8.01 (d, 2H, *J*=6.8 Hz, 2- and 6-H), 10.04 (s, 1H, CHO) ppm. ¹³C NMR (DMSO-*d*₆) δ 13.9, 15.5, 22.0, 28.06, 29.3, 30.9, 31.5, 102.3, 113.1, 122.1 (2 overlapping C), 124.3, 124.4, 125.8, 128.1, 130.5, 130.8 (2C), 133.1, 134.3, 135.7, 137.8, 145.7, 147.9, 156.9, 192.3 ppm. λ_{Max} (ethanol)/nm 476 (ε/mM⁻¹ cm⁻¹ 30.7). IR (Nujol): ν 2726, 1687, 1596, 1560, 1540, 1497, 1294, 1260, 1216, 1135 cm⁻¹. HMRS: *m/z* (ESI) for C₂₆H₂₈N₃OS₂; calcd 462.1674; found: 462.1677.

4-((5'-(4''-(Diphenylamino)phenyl)-1'-methyl-1H-pyrrol-2'-yl)diazenyl)benzoic acid (5).

Orange solid (58 %). Mp 217-219 °C. ¹H NMR (DMSO-*d*₆, 400 MHz) δ 3.98 (s, 3H, CH₃), 6.54 (d, 1H, *J*= 4.4 Hz, 4'-H), 6.82 (d, 1H, *J*= 4.4 Hz, 3'-H), 7.03 (d, 2H, *J*= 8.8 Hz, 3''- and 5''-H), 7.09-7.10 (m, 6H, 2'''-, 2''''-, 4'''-, 4''''-, 6'''- and 6''''-H), 7.32-7.37 (m, 4H, 3'''-, 3''''-, 5'''- and 5''''-H), 7.53 (d, 2H, *J*= 8.8 Hz, 2''- and 6''-H), 7.81 (d, 2H, *J*= 8.8 Hz, 3- and 5-H), 8.03 (d, 2H, *J*= 8.8 Hz, 2- and 6-H) ppm. ¹³C NMR (DMSO-*d*₆, 400 MHz) δ 31.6, 101.5, 112.1, 121.4, 121.8, 123.8, 124.3, 124.8, 128.5, 128.9, 129.5, 129.8, 130.5, 140.7, 140.8, 146.7, 147.3, 147.4, 155.8, 167.4 ppm. λ_{Max} (ethanol)/nm 466 (ε/mM⁻¹ cm⁻¹ 20.3). IR (Nujol): ν 1730, 1680, 1591, 1533, 1488, 1316, 1282, 1203, 1172, 1138, 1113, 1043 cm⁻¹. HMRS: *m/z* (ESI) for C₃₀H₂₅N₄O₂; calcd 473.1978; found: 473.1977.

Kinetic studies by nanosecond flash photolysis

Preparation of the samples used in the kinetic studies. Concentrated solutions (330-520 μM) of azo dyes **1-5** in ethanol were used in the kinetic studies. All solutions were prepared by dissolving the desired amount of the corresponding azo dye in ethanol. The solutions were sonicated for 4 hours and kept at room temperature overnight prior their measurement. The different samples were measured in 1 cm optical path quartz cells.

Kinetic measurements by nanosecond laser flash-photolysis. 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. All transient absorptions were analysed at $\lambda_{\text{obs}} = 510$ nm.

Characterization by polarized light optical microscopy (POM), X-ray diffraction (XRD) and dynamic light scattering (DLS).

Dynamic light scattering measurements and optical microscopy observations were performed by the Nanostructured Liquid Characterization Unit, located at the Institute of Advanced Chemistry of Catalonia (IQAC), which belongs to the Spanish National Research Council (CSIC) and it is affiliated to NANBIOSIS ICTS of CIBER-BBN.

Polarized light optical microscopy. The samples were observed by an Olympus BX51TRF-6 microscope equipped with a Olympus DP73 camera under bright field. Observations were performed with either crossed or uncrossed polarizing filters.

Azo dyes **1** and **3** showed the presence of birefringent crystalline microparticles (Fig. S1). These particles were elongated and **1** clearly showed rod-like microparticles. In contrast, micron-sized particles were not observed for dyes **2**, **4** and **5**.

X-ray diffraction experiments. X-ray diffraction patterns were collected in a Bruker D8 Advance powder diffractometer with monochromatic Cu K α radiation ($\lambda = 1.5405$ Å) operated at 40 kV and 40 mA. The primary parallel X-ray beam was generated by a Göbel mirror and the scattered beam was analyzed by a Sol-X detector. The diffractograms were obtained from 4° to 60° of 2 θ , with a step size of 0.05° and a counting time of 3 s/step.

Dried azo dyes **1** and **3** were studied by XRD. The corresponding X-ray diffraction patterns, shown in Figure S2, clearly indicate that both products are crystalline in the solid state. Indexation of the peaks is complex and it is not within the scope of the present work.

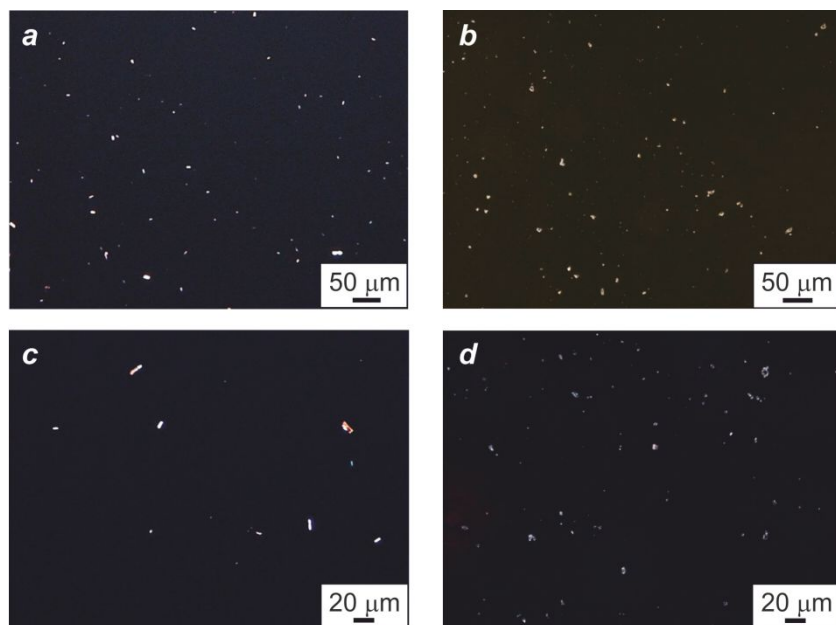


Figure S1. Representative images obtained by polarized optical microscopy for azo dyes **1** (*a* and *c*) and **3** (*b* and *d*) at two different magnifications.

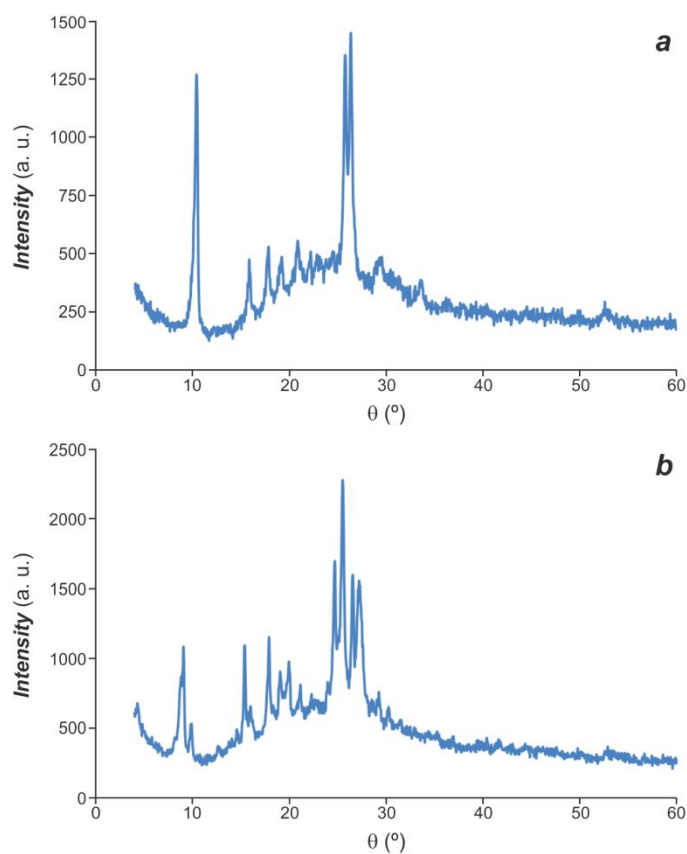


Figure S2. X-ray diffraction (XRD) pattern of a dry powder of azo dyes **1** (*a*) and **3** (*b*).

Dynamic light scattering. A Photon Correlation Spectrometer (PCS) 3D from LS Instruments was used for dynamic light scattering measurements. Multiple scattering was suppressed thanks to 3D-cross correlation technology (down to 5% of transmission for sub-micrometer sample thickness). The instrument is equipped with a He-Ne laser (632.8 nm). Measurements of at least 50 s were recorded at an angle of 90°. The hydrodynamic radius (R_h) of the particles is related with the diffusion coefficient, which is obtained from the autocorrelation function by manual exponential fitting of the first cumulant parameter.² The measurement temperature, 25 °C, was maintained with a decaline bath, which matches the refractive index of glass and therefore, it does not interfere with measurements.

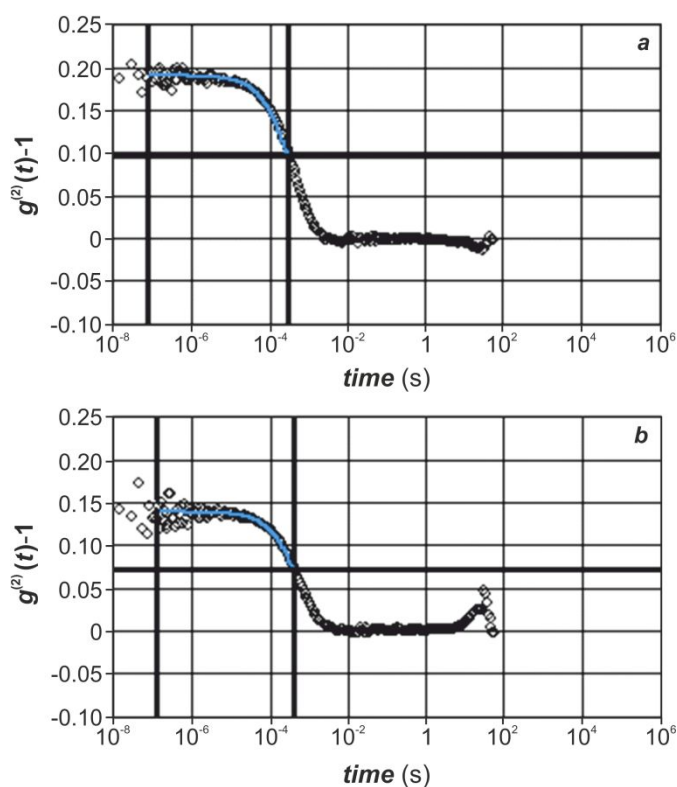


Figure S3. Second order autocorrelation functions of **2** (**a**) and **5** (**b**) in ethanol at 0.52 and 0.34 mM, respectively, obtained by dynamic light scattering.

References

- [1] Garcia-Amorós, J.; Castro, M. C. R.; Raposo, M. M. M.; Velasco, D. New heterocyclic systems to afford microsecond green-light isomerisable azo dyes and their use as fast molecular photochromic switches. *Chem. Commun.* **2013**, *49*, 11427–11429.
- [2] Brown, W. *Dynamic light scattering: the method and some applications*, Oxford University Press, New York, 1993.