Electronic Supplementary information

New heterocyclic systems to afford microsecond green-light isomerisable azo dyes and their use as fast molecular photochromic switches

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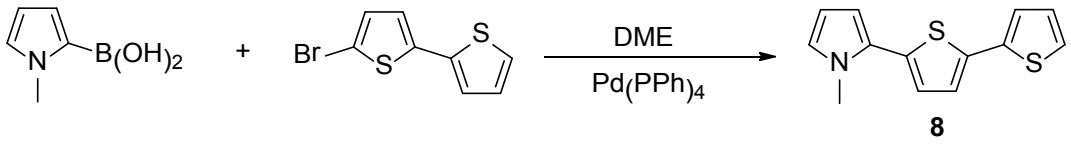
Synthesis of azoderivatives 1-7

Materials: 2-Aminobenzothiazole, 5-aminobenzothiazole, 4-nitroaniline, 2-bromo-2,2´-bithiophene and 1-methyl-1*H*-pyrrole-2-boronic used as precursors for the synthesis of azo dyes **5-7** were purchased from Aldrich and Fluka and used as received. TLC analyses were carried out on 0.25 mm thick precoated silica plates (Merck Fertigplatten Kieselgel $60F_{254}$) and spots were visualised under UV light. Chromatography on silica gel was carried out on Merck Kieselgel (230-240 mesh).

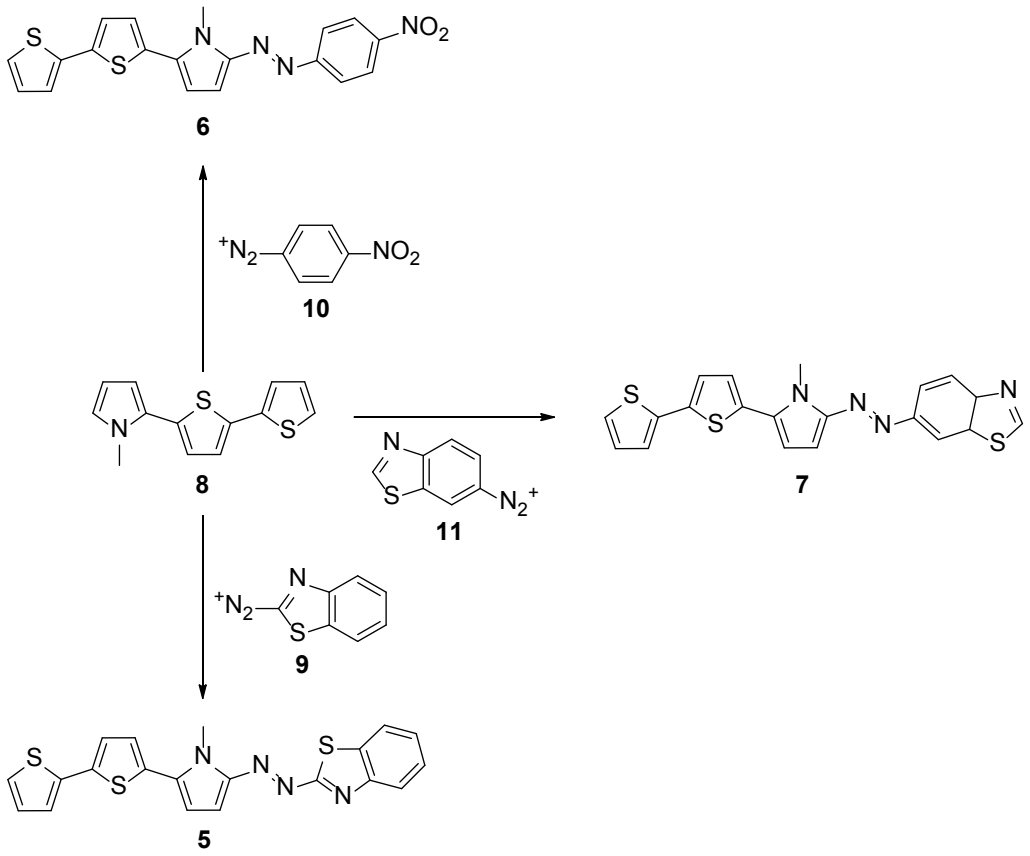
Characterization: NMR spectra were obtained on a Varian Unity Plus Spectrometer at an operating frequency of 300 MHz for ^{1}H NMR and 75.4 MHz for ^{13}C NMR or a Bruker Avance III 400 at an operating frequency of 400 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C NMR using the solvent peak as an internal reference at 25 ºC. All chemical shifts are given in ppm using δ_H Me_4Si = 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). 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 azocompounds: Bithienylpyrrole **8** was synthesized through a Suzuki cross-coupling reaction[4] between the commercially available 1-methyl-1*H*-pyrrol-2-yl-2-boronic acid and 5-bromo-2,2'-bithiophene. (Scheme S1).



Scheme S1. Synthetic concept for bithienylpyrrole **8**.

Precursor **8** was used as a coupling component together with benzothiazolyl- (**9** and **11**) and aryl- (**10**) diazonium salts in order to prepare bithienylpyrrole azo dyes **5-7** (Scheme S2).



Scheme S2. Synthesis of the heterocyclic azoderivatives **5-7**.

All new compounds were completely characterized by ^{1}H and ^{13}C NMR, IR, MS and HRMS and the data obtained were in full agreement with the proposed formulation.

Synthesis of 1-methyl-2-(5-(thiophen-2-yl)thiophen-2-yl)-1H-pyrrole (8). 2-Bromo-2,2′-bithiophene (1 equiv.) was coupled to 1-methyl-1*H*-pyrrole-2-boronic acid (1.2 equiv) in 1,2-dimethoxyethane (10 cm^3) and a 2M Na_2CO_3 aqueous solution (1 cm^3) using $Pd(PPh_3)_4$ as a

catalyst (3 mol %) at 80 ^{o}C under nitrogen. The reaction was monitored by TLC. After 32 hours, the reaction mixture was cooled down to room temperature. Next, a saturated solution of NaCl was added (20 cm^3) and the product was extracted with chloroform (3×20 cm^3). The organic layer was washed first with water (3×10 cm^3) and, after, with an aqueous NaOH solution (10%, 1×10 cm^3). The combined organic extract was dried over anhydrous $MgSO_4$, filtered, and the solvent was removed. The crude was purified by means of column chromatography using mixtures of chloroform and light petroleum of increasing polarity to afford the coupled product **8** as a dark green oil (126 mg, 85 %). ^{1}H NMR ($CDCl_3$) δ 3.80 (s, 3H, CH_3), 6.27-6.29 (m, 1H, 4-H), 6.47-6.48 (m, 1H, 3-H), 6.78 (m, 1H, 5-H), 7.00 (d, 1H, *J*=3.8 Hz, 4'-H), 7.09 (dd, 1H, *J*=3.6 and *J*=1.2 Hz, 4''-H), 7.21 (d, 1H, *J*=3.8 Hz, 3'-H), 7.25-7.28 (m, 2H, 3''- and 5''-H). ^{13}C NMR ($CDCl_3$) δ 35.2, 107.9, 109.9, 123.3, 123.9, 124.1, 124.3, 124.9, 126.7, 127.7, 133.9, 135.9, 137.2. λ_{max} (Dioxane)/nm 352 (ε/dm^3 mol^{-1} cm^{-1} 17,880). IR ($CHCl_3$): υ 3102, 3071, 2945, 1692, 1503, 1453, 1416, 1318, 1294, 1237, 1200, 1090, 1055 cm^{-1}. MS (EI) *m/z* (%) = 245 ($[M]^+$, 100), 244 (22), 230 (13). HRMS: *m/z* (EI) for $C_{13}H_{11}NS_2$; calcd 245.0333; found: 245.0336.

Procedure for the azo coupling of bithienylpyrrole 8 with the diazonium salt 9 to afford azo dye 5.

Diazotation of 2-aminobenzothiazole. 2-Aminobenzothiazole (1.0 mmol) was dissolved in concentrated H_2SO_4 (1.2 mmol) at 0-5 ºC. A mixture of $NaNO_2$ (1.2 mmol) in water (1 cm^3) was slowly added to the well-stirred mixture of the amine derivative solution at 0-5 ºC.

Coupling reaction with bithienylpyrrole **8.** The previously prepared solution of the diazonium salt **9** (1.0 mmol) was added dropwise to the solution of bithienylpyrrole **8** (1.2 mmol) in acetic anhydride (15 cm^3): ice water (200 cm^3). The combined solution was maintained at 0 ºC for 1 h followed by stirring for 3 h at room temperature. Then, the precipitate was filtered, washed with warm water and *n*-hexane and dried over vacuum.

2-(Benzo[d]thiazol-2-yl)-1-(1-methyl-5-(5-(thiophen-2-yl)thiophen-2-yl)-1H-pyrrol-2-yl)diazene (**5**). Dark purple solid (51 mg, 73 %). m.p. 164-165 ºC. ^{1}H NMR (DMSO-d_6) δ 4.11 (s, 3H, NCH_3), 7.07 (d, 1H, *J*=4.6 Hz, 4'-H), 7.14-7.17 (m, 1H, 4'''-H), 7.18 (d, 1H, *J*=4.6 Hz, 3'-H), 7.41 (dt, 1H, *J*=8.4 and *J*=1.2 Hz, 5-H), 7.47-7.49 (m, 2H, 6- and 3'''-H), 7.51 (d, 1H, *J*=4 Hz, 4''-H), 7.62 (dd, 1H, *J*=4.8 and *J*=0.8 Hz, 5'''-H), 7.73 (d, 1H, *J*=4 Hz, 3''-H), 7.93-7.95 (m, 1H, 4-H), 7.99 (dd, 1H, *J*=7.6 and *J*=0.8 Hz, 7-H). ^{13}C NMR (DMSO-d_6) δ 30.7, 115.9, 122.4, 123.0, 125.2 (2C), 125.4, 126.1 (2C), 126.5, 126.8, 128.7, 130.0, 130.1, 133.0, 135.4, 138.6, 139.3, 152.6, 177.3. λ_{max} (Dioxane)/nm 533 (ε/dm^3 mol^{-1} cm^{-1} 25,950). IR (Nujol): υ 1685, 1552, 1503, 1301, 1250, 1225, 1164, 1125, 1063 cm^{-1}. MS (EI) *m/z* (%) = 406 ($[M]^+$, 35),

380 (15), 378 (100), 260 (20), 258 (35), 257 (15), 245 (15), 206 (16), 204 (12), 203 (72), 190 (28), 179 (17), 96 (15). HRMS: *m/z* (EI) for $C_{20}H_{14}N_4S_3$; calcd 406.0381; found: 406.0385.

General procedure for the azo coupling of bithienylpyrrole 8 with diazonium salts 10** and **11 to afford azo dyes 6** and **7.

Diazotation of 5-aminobenzothiazole and 4-nitroaniline. Heteroaromatic amines were dissolved in HCl 6 N (1 cm^3) at 0-5 ºC. A mixture of $NaNO_2$ (1.0 mmol) in water (2 cm^3) was slowly added to the well-stirred mixture of the amine derivative solution at 0-5 ºC. The reaction mixture was stirred for 10 min.

Coupling reaction with bithienylpyrrole **8**. The previously prepared diazonium salt solution (1.0 mmol) was added dropwise to the solution of bithienylpyrrole **8** (0.52 mmol) in acetonitrile (10 cm^3) and 2-3 drops of acetic acid. The resulting mixture was maintained at 0 ºC for 1-2 h while stirred and then diluted with chloroform (20 cm^3), washed with water and dried over anhydrous $MgSO_4$. The dried solution was evaporated and the remaining azo dyes were purified by column chromatography using dichloromethane/*n*-hexane as eluent.

1-(1-Methyl-5-(5-(thiophen-2-yl)thiophen-2-yl)-1H-pyrrol-2-yl)-2-(4-nitrophenyl)diazene (**6**). Brown solid (72 mg, 60 %). m.p. 204-206 ºC. ^{1}H NMR (DMSO-d_6) δ 4.15 (s, 3H, NCH_3), 6.86 (d, 1H, *J*=4.6 Hz, 4'-H), 6.95 (d, 1H, *J*=4.6 Hz, 3'-H), 7.12-7.15 (m, 1H, 4'''-H), 7.43 (dd, 1H, *J*=3.6 and *J*=1.2 Hz, 3'''-H), 7.45 (d, 1H, *J*=4 Hz, 4''-H), 7.58-7.59 (m, 2H, 3''- and 5'''-H), 7.96 (d, 2H, *J*=8.8 Hz, 2- and 6-H), 8.34 (d, 2H, *J*=8.8 Hz, 3- and 5-H). ^{13}C NMR (DMSO-d_6) δ 31.6, 113.7, 122 (2C), 124.8, 125.0 (2C), 125.2, 126.3, 128.5, 128.6, 130.8, 135.1, 135.6, 137.8, 146.4, 146.5, 148.1, 157.2. λ_{max} (Dioxane)/nm 507 (ε/dm^3 mol^{-1} cm^{-1} 47,580). IR (Nujol): υ 3108, 2670, 1694, 1603, 1584, 1515, 1313, 1298, 1214, 1206, 1191, 1170, 1139, 1106, 1098, 1083, 1042 cm^{-1}. MS (EI) *m/z* (%) = 394 ([M]$^+$, 62), 365 (16), 364 (73), 257 (12), 246 (10), 245 (31), 244 (65), 217 (10), 203 (100), 190 (10), 179 (42). HRMS: *m/z* (EI) for $C_{19}H_{14}N_4O_2S_2$; calcd 394.0558; found: 394.0575.

2-(Benzo[d]thiazol-6-yl)-1-(1-methyl-5-(5-(thiophen-2-yl)thiophen-2-yl)-1H-pyrrol-2-yl) diazene (**7**). Brown solid (33 mg, 40 %). m.p. 198-199 ºC ^{1}H NMR (DMSO-d_6) δ 4.16 (s, 3H, NCH_3), 6.73 (d, 1H, *J*=4.5 Hz, 4'-H), 6.80 (d, 1H, *J*=4.5 Hz, 3'-H), 7.11-7.14 (m, 1H, 4'''-H), 7.39-7.40 (m, 1H, 3'''-H), 7.41 (d, 1H, *J*=3.8 Hz, 4''-H), 7.48 (d, 1H, *J*=3.8 Hz, 3''-H), 7.56 (dd, 1H, *J*=5.4 and *J*=0.6 Hz, 5'''-H), 8.0 (dd, 1H, *J*=8.9 and *J*=2.1 Hz, 5-H), 8.2 (d, 1H, *J*=8.9 Hz, 4-H), 8.61 (d, 1H, *J*=2.1 Hz, 7-H). ^{13}C NMR (DMSO-d_6) δ 31.5, 100.7, 112.3, 116.5, 120.1, 123.5, 124.5, 125.0, 126.0, 127.5, 128.5, 131.5, 132.4, 134.9, 135.8, 136.8, 147.4, 150.8, 153.6, 158.0. λ_{max} (Dioxane)/nm 489 (ε/dm^3 mol^{-1} cm^{-1} 45,790). IR (Nujol): υ 2671, 1305, 1168, 1074,

1040, 965 cm^{-1}. MS (EI) *m/z* (%) = 406 ($[M]^+$, 100), 378 (11), 363 (15), 244 (44), 204 (11), 203 (82), 179 (30), 134 (22). HRMS: *m/z* (EI) for $C_{20}H_{14}N_4S_3$; calcd 406.0381; found: 406.0394.

Spectroscopic and kinetic measurements

Time-resolved UV-vis spectroscopy: For measurements in acetone, 20 μM solutions were used. Irradiation experiments were made using a CARY 50 Varian spectrophotometer coupled to a 150W ozone free xenon lamp (6255 Oriel Instruments). The light from the UV–vis lamp was filtered using a water filter (61945 Oriel Instruments) and a long-pass filter (Schott GG 420) at 20 ºC and carried to the spectrophotometer holder, perpendicular to the monitoring beam using a fibre-optic system (77654 Oriel Instruments).

Nanosecond laser flash-photolysis setup: In ethanol, 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 90º 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.

Photo and thermal isomerisation for azo dyes 5-7 in acetone

Compound 5

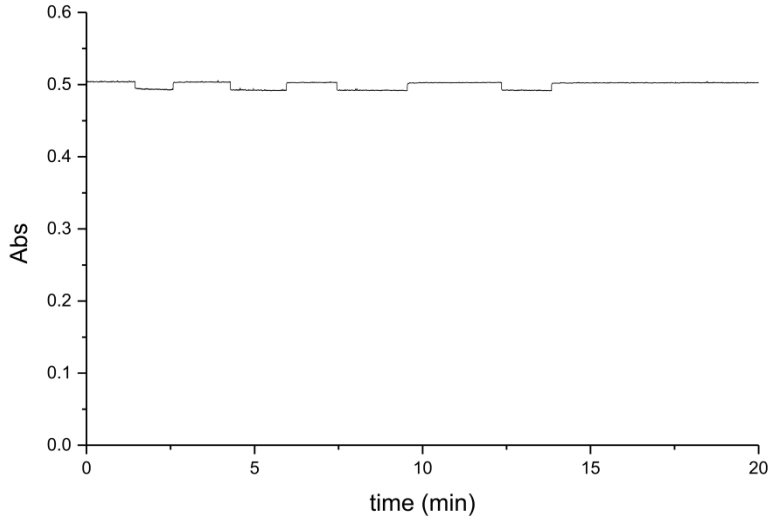


Figure S1. Visible light irradiation / dark cycles for azo compound **5** ([**5**] = 20 μM) in acetone at 298 K.

Compound 6

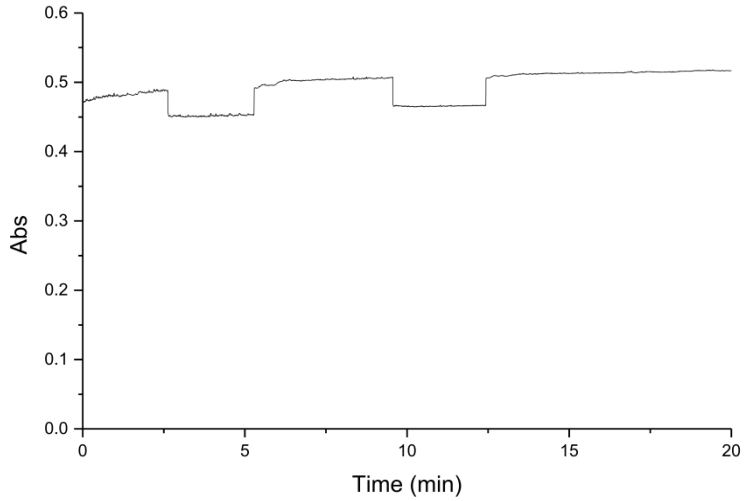


Figure S2. Visible light irradiation / dark cycles for azo compound **6** ([**6**] = 20 μM) in acetone at 298 K.

Compound 7

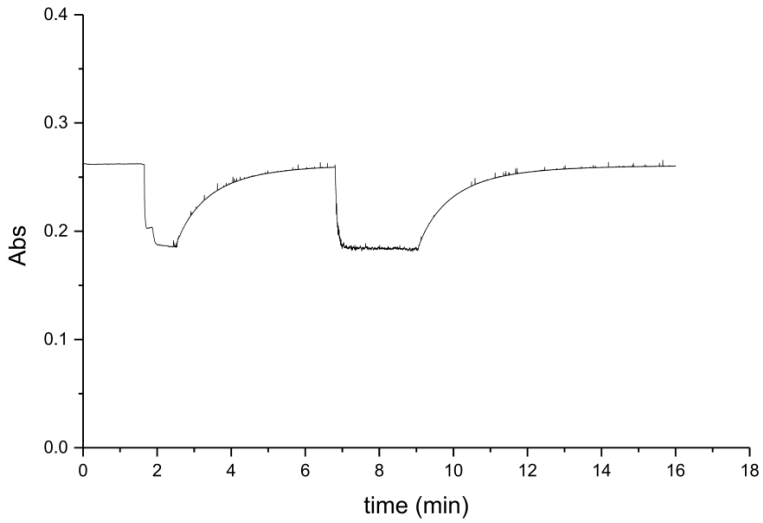


Figure S3. Visible light irradiation / dark cycles for azo compound **7** ([7] = 20 μM) in acetone at 298 K.

Kinetic and thermal activation parameters for the thermal *cis*-to-*trans* isomerisation kinetics for azo dyes 1-7 in ethanol

Compound 1

T / ºC	25	35	45	60
τ / ms	35	19	9.8	3.5

Table S1. Relaxation time for *cis*-**1** in ethanol at different temperatures.

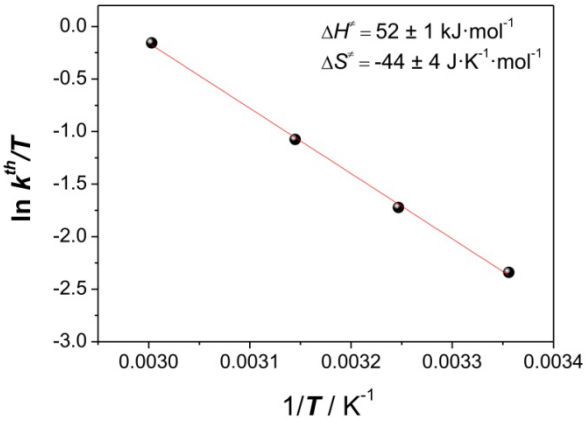


Figure S4. Eyring plot for the thermal back reaction of *cis*-**1**.

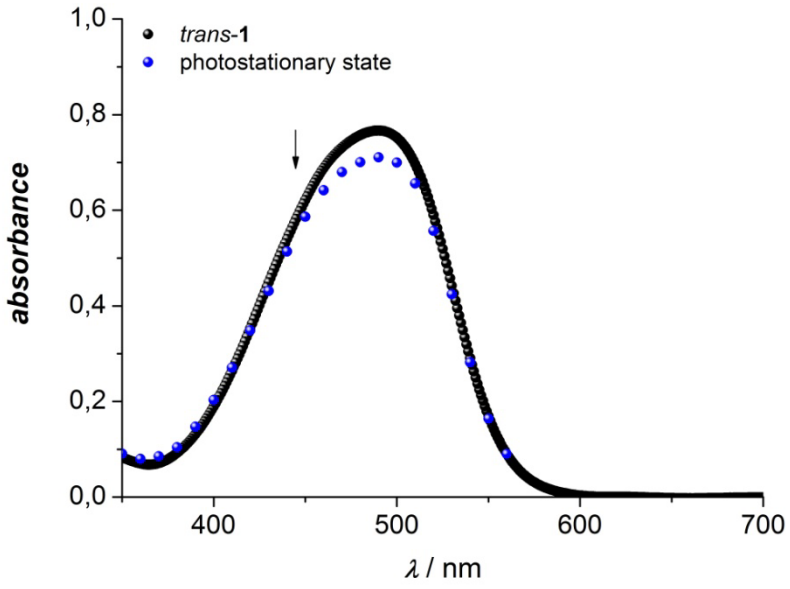


Figure S5. Spectral change for compound **1** after *trans*-to-*cis* photoisomerisation with a green-light laser pulse in ethanol at 298 K (λ_{irrad} = 532 nm, 5 ns pulse width, *ca.* 10 mJ per pulse, [**1**] = 20 μM).

Compound 2

T / °C	25	35	50	65
τ / ms	109	66	32	17

Table S2. Relaxation time for *cis*-**2** in ethanol at different temperatures.

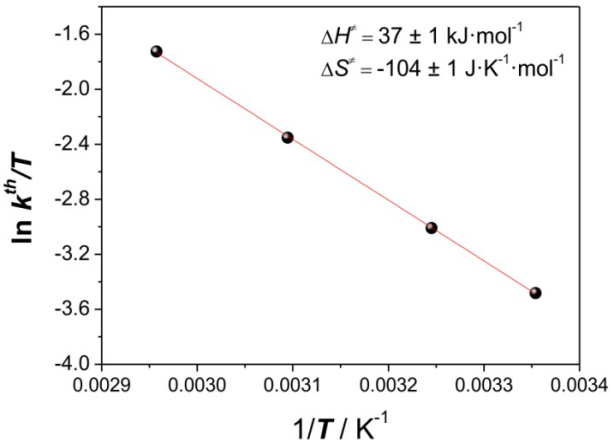


Figure S6. Eyring plot for the thermal back reaction of *cis*-**2**.

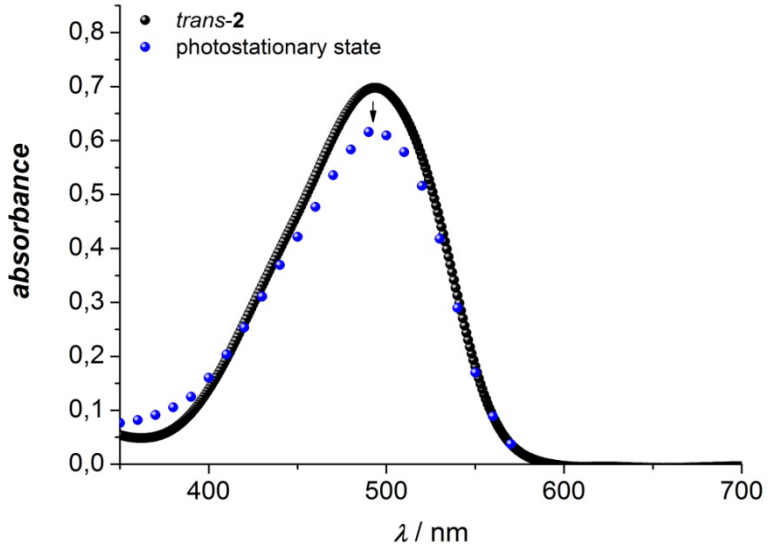


Figure S7. Spectral change for compound **2** after *trans*-to-*cis* photoisomerisation with a green-light laser pulse in ethanol at 298 K (λ_{irrad} = 532 nm, 5 ns pulse width, *ca.* 10 mJ per pulse, [**2**] = 20 μM).

Compound 3

T / °C	25	40	50	65
τ / ms	108	62	44	28

Table S3. Relaxation time for *cis*-**3** in ethanol at different temperatures.

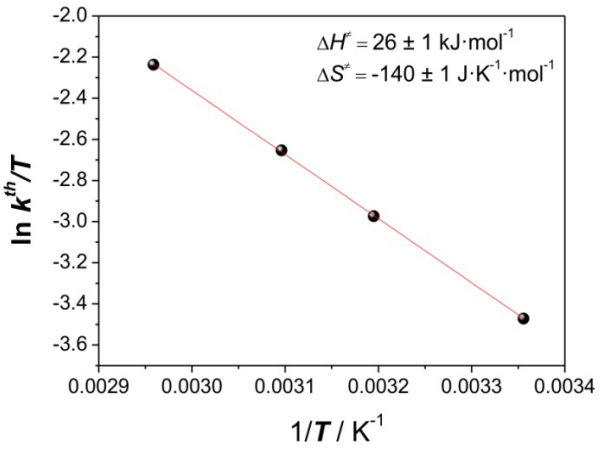


Figure S8. Eyring plot for the thermal back reaction of *cis*-**3**.

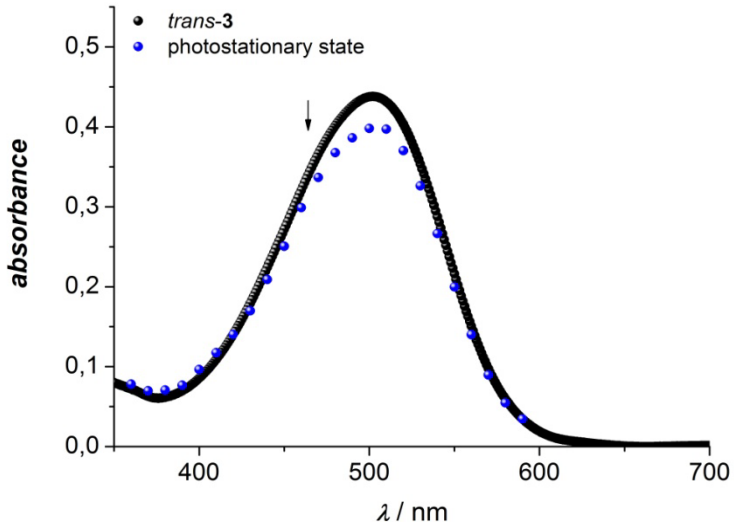


Figure S9. Spectral change for compound **3** after *trans*-to-*cis* photoisomerisation with a green-light laser pulse in ethanol at 298 K (λ_{irrad} = 532 nm, 5 ns pulse width, *ca.* 10 mJ per pulse, [**3**] = 20 μM).

Compound 4

T / ºC	25	35	50	65
τ / ms	1.0	0.66	0.35	0.21

Table S4. Relaxation time for *cis*-**4** in ethanol at different temperatures.

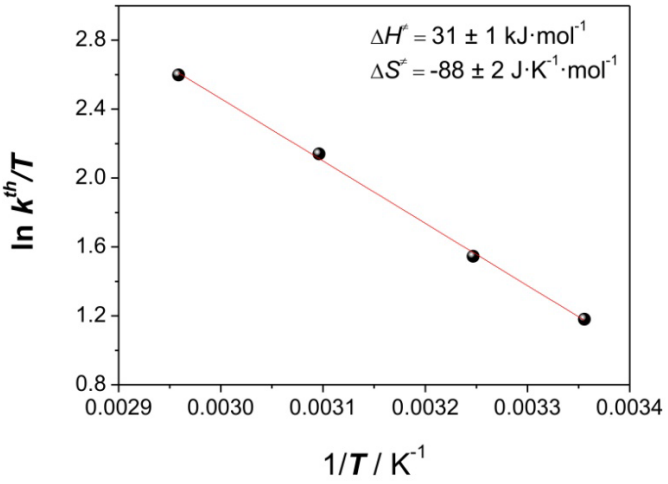


Figure S10. Eyring plot for the thermal back reaction of *cis*-**4**.

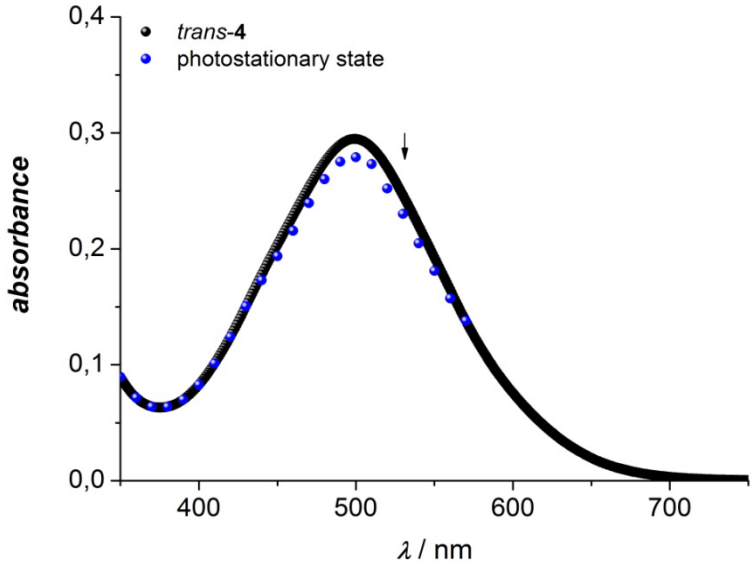


Figure S11. Spectral change for compound **4** after *trans*-to-*cis* photoisomerisation with a green-light laser pulse in ethanol at 298 K (λ_{irrad} = 532 nm, 5 ns pulse width, *ca.* 10 mJ per pulse, [**4**] = 20 μM).

Compound 5

T / ºC	25	40	55	70
τ / μs	69	42	27	18

Table S5. Relaxation time for *cis*-**5** in ethanol at different temperatures.

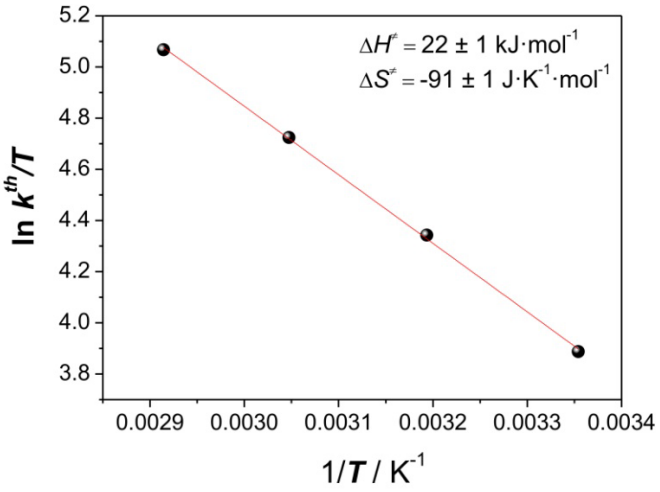


Figure S12. Eyring plot for the thermal back reaction of *cis*-**5**.

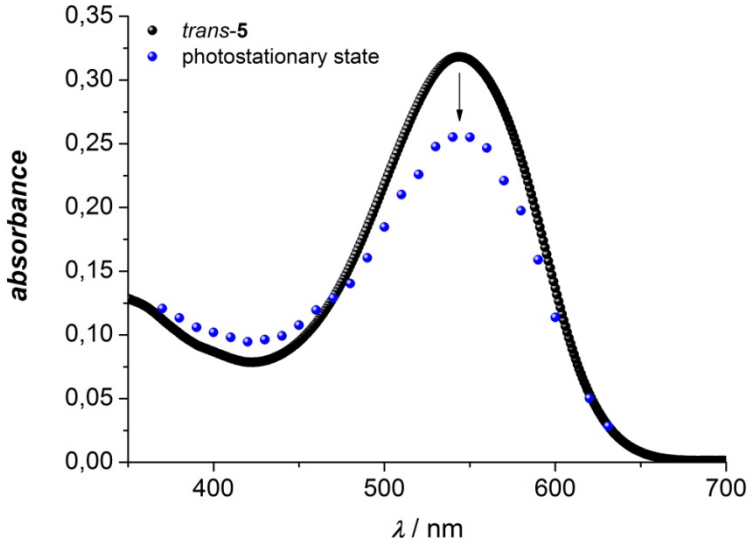


Figure S13. Spectral change for compound **5** after *trans*-to-*cis* photoisomerisation with a green-light laser pulse in ethanol at 298 K (λ_{irrad} = 532 nm, 5 ns pulse width, *ca.* 10 mJ per pulse, [**5**] = 20 μM).

Compound 6

T / ºC	25	40	55	70
τ / ms	1.60	0.99	0.64	0.41

Table S6. Relaxation time for *cis*-**6** in ethanol at different temperatures.

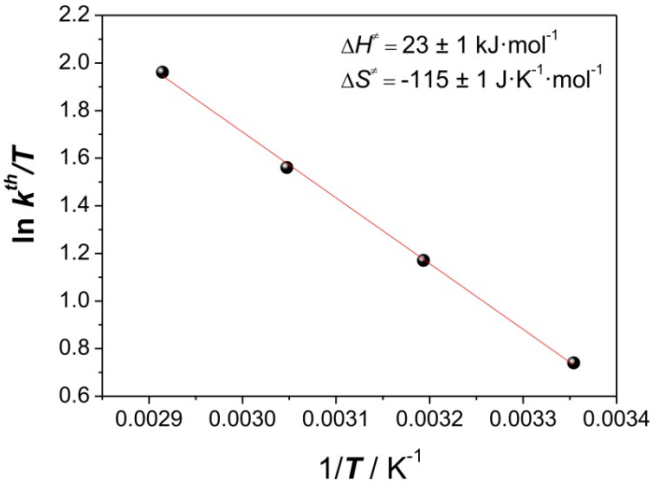


Figure S14. Eyring plot for the thermal back reaction of *cis*-**6**.

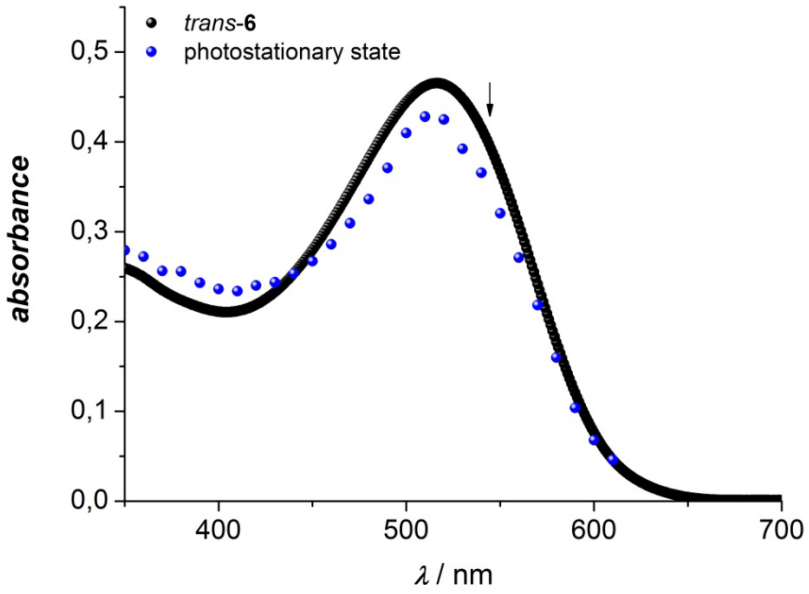


Figure S15. Spectral change for compound **6** after *trans*-to-*cis* photoisomerisation with a green-light laser pulse in ethanol at 298 K (λ_{irrad} = 532 nm, 5 ns pulse width, *ca.* 10 mJ per pulse, [**6**] = 20 μM).