

Supporting Information

**Orthogonal switching
in four-state azobenzene mixed-dimers**

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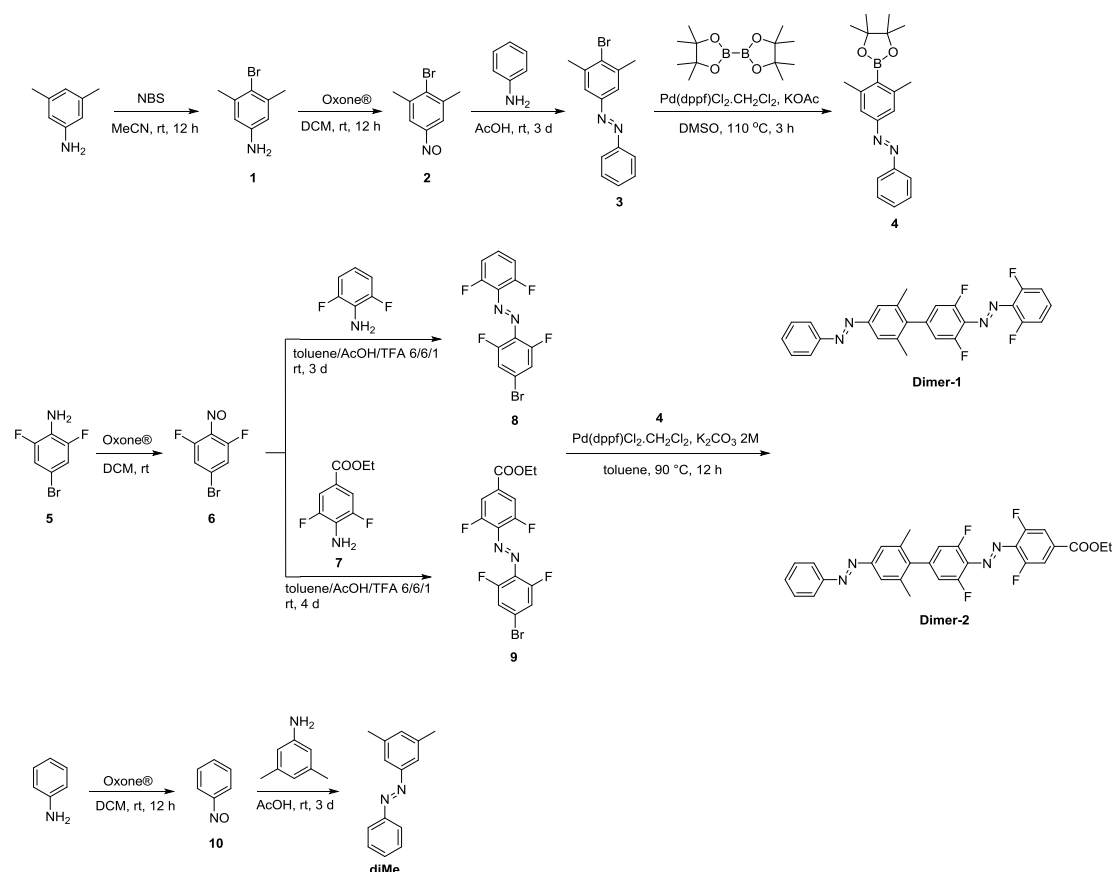
1. General Information

Materials were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel plates (Merck 60F - 254) using UV light for visualization. Silica gel (Merck 60/VWR, particle size 0.040–0.063 mm) was used for column chromatography. NMR spectra were recorded on a Bruker 300 MHz (75 MHz for ^{13}C). Chemical shifts (δ) are reported in ppm from the solvent resonance as the internal standard ($^1\text{H-NMR}$: δ (CDCl_3) = 7.26 ppm, δ (CD_2Cl_2) = 5.32 ppm (THF- d_8) = 1.72, 3.58 ppm and $^{13}\text{C-NMR}$: δ (CDCl_3) = 77.16 ppm, δ (CD_2Cl_2) = 53.84 ppm, (THF- d_8) = 67.21, 25.31 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Ultraperformance liquid chromatography coupled to mass spectrometry detection (UPLC-MS) was performed with a Waters Alliance systems (gradient mixtures of acetonitrile/water) equipped with Acquity UPLC columns. The Waters systems consisted of a Waters Separations Module 2695, a Waters Diode Array detector 996, a LCT Premier XE mass spectrometer, and a Waters Mass Detector ZQ 2000.

2. Synthetic procedures and characterization of products


Standard procedure for oxidation of aniline to nitrosoarene derivatives

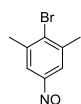
To a solution of aniline derivative (1 equiv) in DCM was added an aqueous solution of Oxone[®] ($\text{KHSO}_5 \cdot \frac{1}{2}\text{KHSO}_4 \cdot \frac{1}{2}\text{K}_2\text{SO}_4$, 2 equiv per amine group), DCM/ H_2O :4/5. The reaction was stirred for 12 h at room temperature. The two phases were separated, the organic phase was washed with distilled water, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The resulting (nitroso) green oils are typically unstable and hence were used without further purification in the subsequent step (Mills reaction).



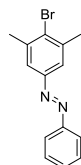
Scheme 1. Synthetic procedures for **Dimer-1**, **Dimer-2** and **diMe**.

The synthesis and characterization of compounds **5**^[1], **7**^[2], **F4**^[1] and **F4-ester**^[2] have been described elsewhere.

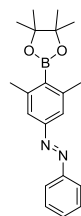
 **4-bromo-3,5-dimethylaniline (1):** To a solution of 3,5-dimethylaniline (3.00 g, 24.79 mmol) in acetonitrile (100 mL) was added *N*-Bromosuccinimide (4.41 g, 24.79 mmol) and the solution was stirred overnight at room temperature. The reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography (petroleum ether/ethyl acetate: 50/1 to 5/1) to give **1** as a white solid (1.64 g, 33%). ¹H NMR (300 MHz, CD₂Cl₂) δ ppm 6.43 (s, 2H), 3.60 (s, 2H), 2.29 (s, 6 H). ¹³C NMR (75 MHz, CD₂Cl₂) δ ppm 146.0, 139.2, 115.8, 115.4, 24.1. HRMS-ESI: *m/z* = 200.0083 (calcd for [M + H]⁺, 200.0075).



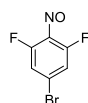
4-bromo-3,5-dimethylnitrosobenzene (2): The standard procedure for the oxidation of aniline to nitrosoarene was used with **1** (500 mg, 2.50 mmol) in DCM (20 mL) and Oxone[®] (3.07 g, 10.00 mmol) in H₂O (25 mL) to give **2** as a deep green liquid that was used as such in the next step.



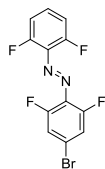
4-bromo-3,5-dimethylazobenzene (3): To a solution of **2** (535 mg) in AcOH (10 mL) was added aniline (186 mg, 2.00 mmol) and the mixture was stirred for 3 days at room temperature. The resulting solution was diluted with water (200 mL), extracted with ethyl acetate, the organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether) to give **3** as a red solid (186 mg, 32%). ¹H NMR (300 MHz, CDCl₃) (*E*-isomer) δ ppm 7.93 (dd, *J* = 8.1, 1.8 Hz, 2H), 7.66 (s, 2H), 7.56-7.48 (m, 3H), 2.53 (s, 6 H). ¹³C NMR (75 MHz, CDCl₃) (*E*-isomer) δ ppm 152.6, 150.8, 139.2, 131.1, 130.5, 129.1, 122.8, 122.2, 24.0. HRMS-ESI: *m/z* = 289.0338 (calcd for [M + H]⁺, 289.0340).



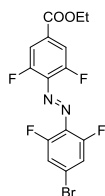
Pinacol boronic(azobenzene)ester (4): A solution of **3** (414 mg, 1.43 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (436 mg, 1.72 mmol), Pd(dppf)Cl₂.CH₂Cl₂ (117 mg, 0.14 mmol), and KOAc (421 mg, 4.30 mmol) in DMSO (15 mL) was stirred for 3 hours at 110 °C. After cooling down, the solution was diluted with water (200 mL), extracted with ethyl acetate, the organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether) to give **4** as a red solid (210 mg, 44%). ¹H NMR (300 MHz, CDCl₃) (*E*-isomer) δ ppm 7.93-7.90 (m, 2H), 7.53-7.51 (m, 3H), 7.49-7.47 (m, 2H), 2.50 (s, 6H), 1.42 (s, 12H). ¹³C NMR (75 MHz, CDCl₃) (*E*-isomer) δ ppm 152.7, 143.0, 130.9, 129.1, 122.8, 120.8, 84.0, 25.0, 22.2. HRMS-ESI: *m/z* = 337.2112 (calcd for [M + H]⁺, 337.2087).



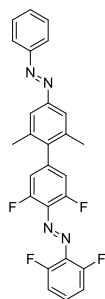
4-bromo-1,6-difluoronitrosobenzene (6): The standard procedure for the oxidation of aniline to nitrosoarene was used with **5** (1.51 g, 7.25 mmol) in DCM (20 mL) and Oxone[®] (8.90 g, 29.00 mmol) in H₂O (25 mL) to give **6** as a deep green liquid that was used as such in the next step.



4-bromo-F₄-azobenzene (8): To a solution of **6** (1.61 g) in toluene/AcOH/TFA (6/6/1) (13 mL) was added 2,6-difluoroaniline (0.75 g, 5.80 mmol) and the solution was stirred for 3 days at room temperature. The resulting solution was diluted with water (200 mL), extracted with ethyl acetate, the organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (CH₂Cl₂/petroleum ether: 1/5) to give **8** as a red solid (1.84 g, 95%). ¹H NMR (300 MHz, CDCl₃) (*E*-isomer) δ ppm 7.44-7.36 (m, 1 H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.06 (t, *J* = 9.1 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) (*E*-isomer) δ ppm 157.3, 153.8, 131.8, 123.9, 116.7, 116.5, 112.8, 112.5. HRMS-ESI: *m/z* = 332.9642 (calcd for [M + H]⁺, 332.9650).



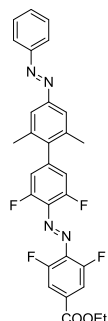
4-bromo-4'-ester-F₄-azobenzene (9): To a solution of **6** (266 mg) in toluene/AcOH/TFA (6/6/1) (10 mL) was added **7** (0.19 g, 0.96 mmol) and the mixture was stirred for 4 days at room temperature. The resulting solution was diluted with water (50 mL), extracted with ethyl acetate, the organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (CH₂Cl₂/petroleum ether: 1/20) to give **9** as a red solid (60 mg, 18%). ¹H NMR (300 MHz, CDCl₃) (*E*-isomer) δ ppm 7.73 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) (*E*-isomer) δ ppm 156.7, 117.0, 116.7, 114.0, 113.7, 62.1, 14.2. HRMS-ESI: *m/z* = 404.9858 (calcd for [M + H]⁺, 404.9862).



Dimer-1: To a solution of **8** (173 mg, 0.52 mmol), **4** (210 mg, 0.62 mmol), and Pd(dppf)Cl₂.CH₂Cl₂ (42 mg, 0.05 mmol) in toluene (5 mL) was added 2M aqueous K₂CO₃ (0.8 mL), and the solution was stirred overnight at 90 °C. After cooling, the solution was diluted with water (100 mL), extracted with ethyl acetate, the organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate: 100/1 to 50/1) to give **Dimer-1** as a red solid (148 mg, 62%). ¹H NMR (300 MHz, CD₂Cl₂) (*E,E*-isomer) δ ppm 7.96-7.92 (m, 2H), 7.71 (s, 2H), 7.59-7.51 (m, 3H), 7.49-7.39 (m, 1H), 7.16-7.09 (m, 2H), 6.97 (d, *J* = 9.3 Hz, 2H), 2.22 (s, 6H). ¹³C NMR (75 MHz, CD₂Cl₂) (*E,E*-isomer) δ ppm

157.5, 152.6, 152.0, 136.9, 131.8, 131.1, 129.1, 122.8, 121.8, 113.7, 113.4, 112.8, 112.6, 20.5.

HRMS-ESI: $m/z = 463.1559$ (calcd for $[M + H]^+$, 463.1546).

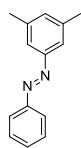


Dimer-2: To a solution of **9** (60 mg, 0.15 mmol), **4** (60 mg, 0.18 mmol), and Pd(dppf)Cl₂.CH₂Cl₂ (11 mg, 0.02 mmol) in toluene (1.5 mL) was added 2M aqueous K₂CO₃ (0.2 mL), and the mixture was stirred for 5 hours at 90 °C. After cooling, the solution was diluted with water (20 mL), extracted with ethyl acetate, the organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/CH₂Cl₂: 20/1) to

give **Dimer-2** as a red solid (46 mg, 59%). ¹H NMR (300 MHz, CDCl₃) (*E,E*-isomer) δ ppm 7.94 (dd, $J = 8.31, 1.56$ Hz, 2H), 7.73 (d, $J = 8.8$ Hz, 2H), 7.70 (s, 2H), 7.57-7.49 (m, 3H), 6.95 (d, $J = 10.6$ Hz, 2H), 4.43 (q, $J = 11.9$ Hz, 2H), 2.21 (s, 6H), 1.44 (t, $J = 7.1$ Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) (*E,E*-isomer) δ ppm 152.6, 152.2, 136.7, 131.1, 129.1, 122.9, 122.0, 114.0, 113.7, 113.5, 62.1, 20.8, 14.2. HRMS-ESI: $m/z = 535.1774$ (calcd for $[M + H]^+$, 535.1757).



nitrosobenzene (10): The standard procedure for the oxidation of aniline to nitrosoarene was used with aniline (1.00 g, 10.70 mmol) in DCM (40 mL) and Oxone[®] (9.90 g, 32.20 mmol) in H₂O (50 mL) to give **10** as a deep green liquid that was used as such in the next step.



3,5-dimethyl-azobenzene (diMe): To a solution of **10** (1.15 g) in AcOH (20 mL) was added 3,5-dimethylaniline (1.00 g, 8.60 mmol) and the solution was stirred for 3 days at room temperature. The resulting solution was diluted with water (200 mL), extracted with ethyl acetate, the organic phase was dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether) to give **diMe** as an orange solid (400 mg, 22%). ¹H NMR (300 MHz, CDCl₃) (*E*-isomer) δ ppm 8.00 (d, $J = 7.9$ Hz, 2H), 7.64 (s, 2H), 7.60-7.49 (m, 3H), 7.17 (s, 1H), 2.47 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) (*E*-isomer) δ ppm 152.9, 152.8, 138.8, 132.8, 130.9, 129.1, 122.9, 120.8, 21.3. HRMS-ESI: $m/z = 211.1222$ (calcd for $[M + H]^+$, 211.1235).

3. Photoisomerization studies

UV/Vis absorption spectra were recorded using quartz cuvettes on a Cary 50 spectrophotometer equipped with a Peltier-thermostated cell holder (temperature accuracy ± 0.1 °C). The solvents used were of spectrophotometric grade. Irradiation experiments were performed using a LOT-Oriel 1000 W medium-pressure Xe/Hg lamp equipped with band-pass filters.

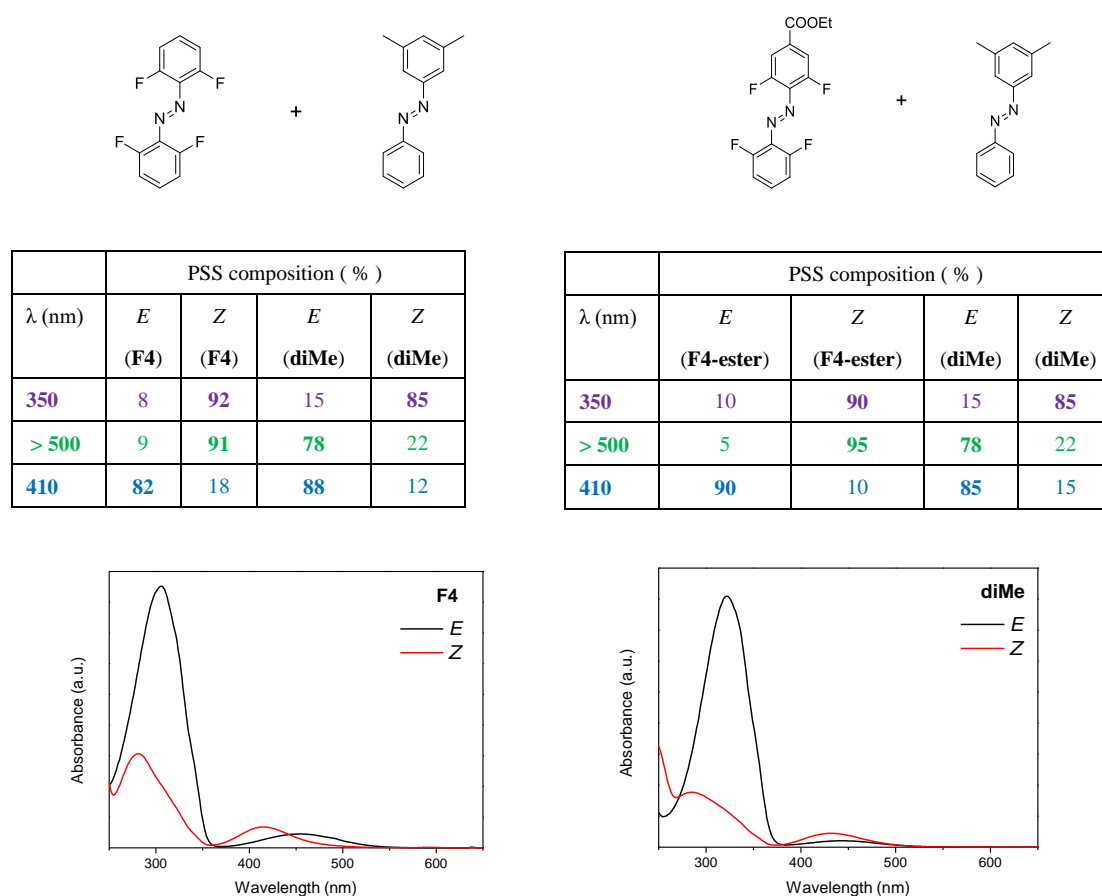


Figure S1. Top: PSS ratios of mixtures of monomers: (**F4** + **diMe**, left) and (**F4-ester** + **diMe**, right) upon irradiation at different wavelengths in MeCN/CHCl₃ (29/1) at 25 °C. PSS compositions were determined by UPLC analysis using integration of the UV signal at either 442 nm (isosbestic point of **F4**) or 271 nm (isosbestic point of **F4-ester** and **diMe**). Bottom: UV/Vis absorbance spectra of **F4** and **diMe** in acetonitrile at 25 °C.

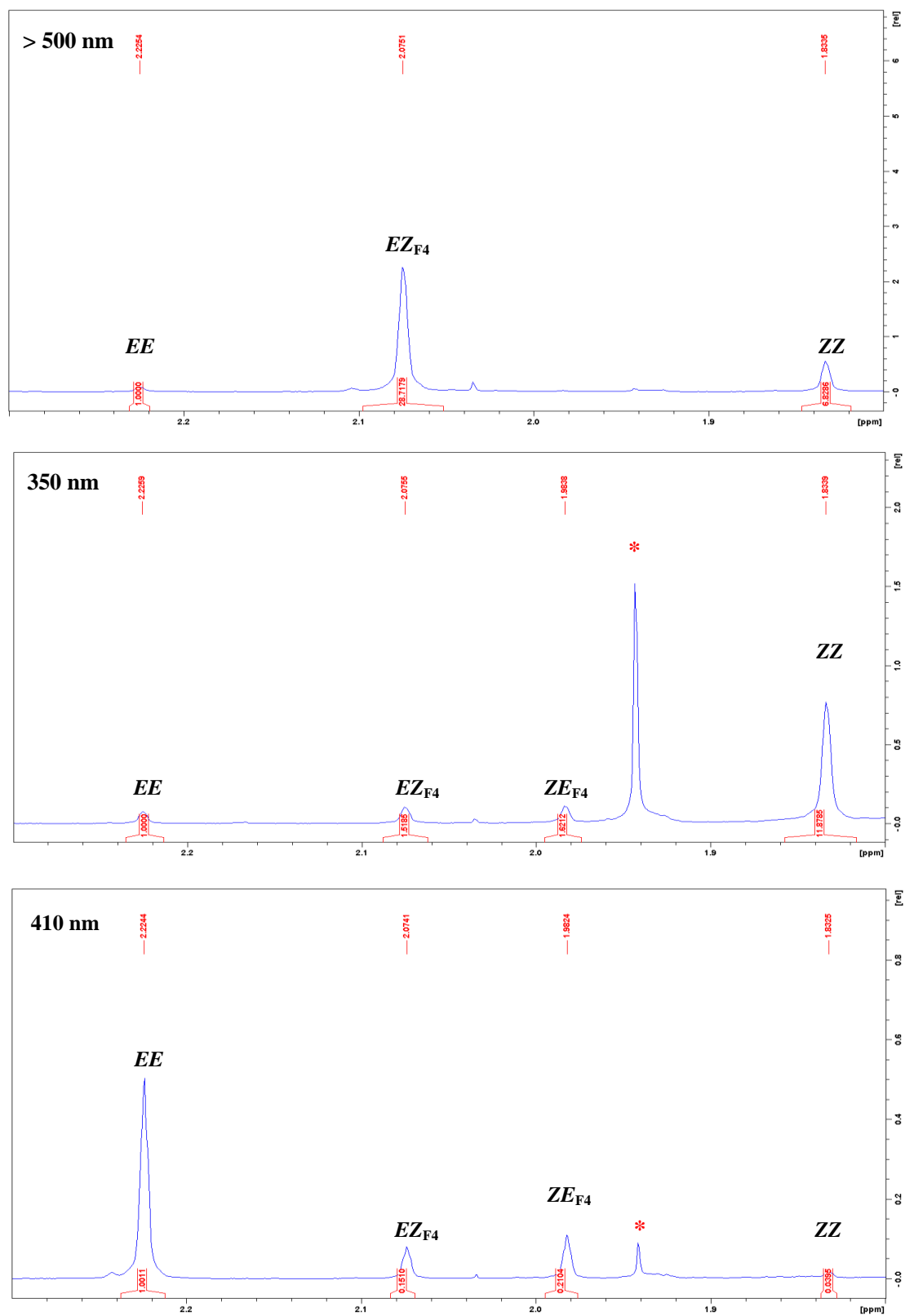


Figure S2. ¹H NMR (aliphatic region, integration of the *ortho*-Me groups) of the PSS mixtures of **Dimer-1** at different wavelengths (*: MeCN). Solutions were irradiated ex-situ in MeCN, evaporated, and dissolved in THF-*d*₈ prior to measurement.

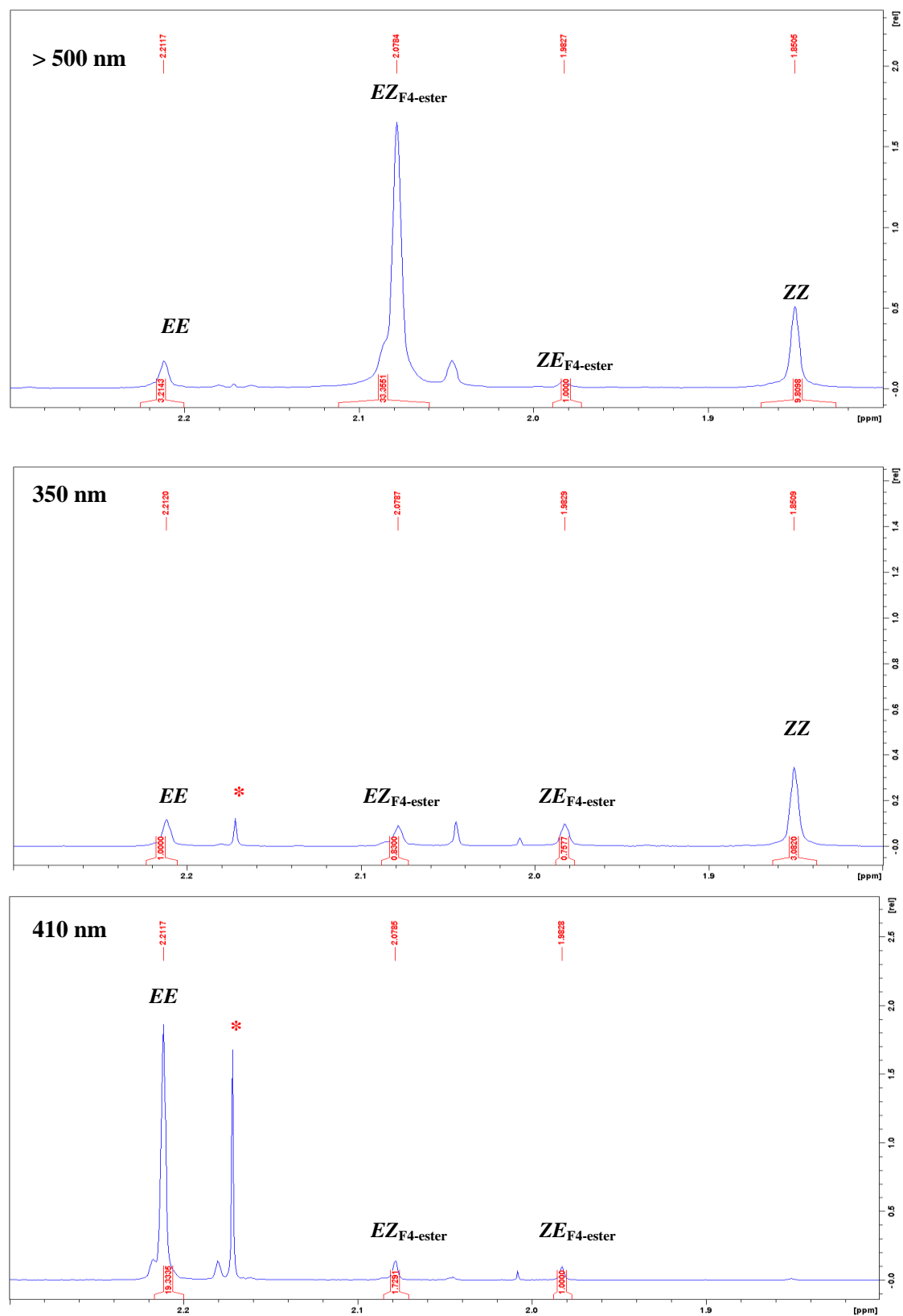


Figure S3. ^1H NMR (aliphatic region, integration of the *ortho*-Me groups) of the PSS mixtures of **Dimer-2** at different wavelengths (*: acetone). Solutions were irradiated ex-situ in MeCN, evaporated, and dissolved in CDCl_3 prior to measurement.

4. Kinetics studies

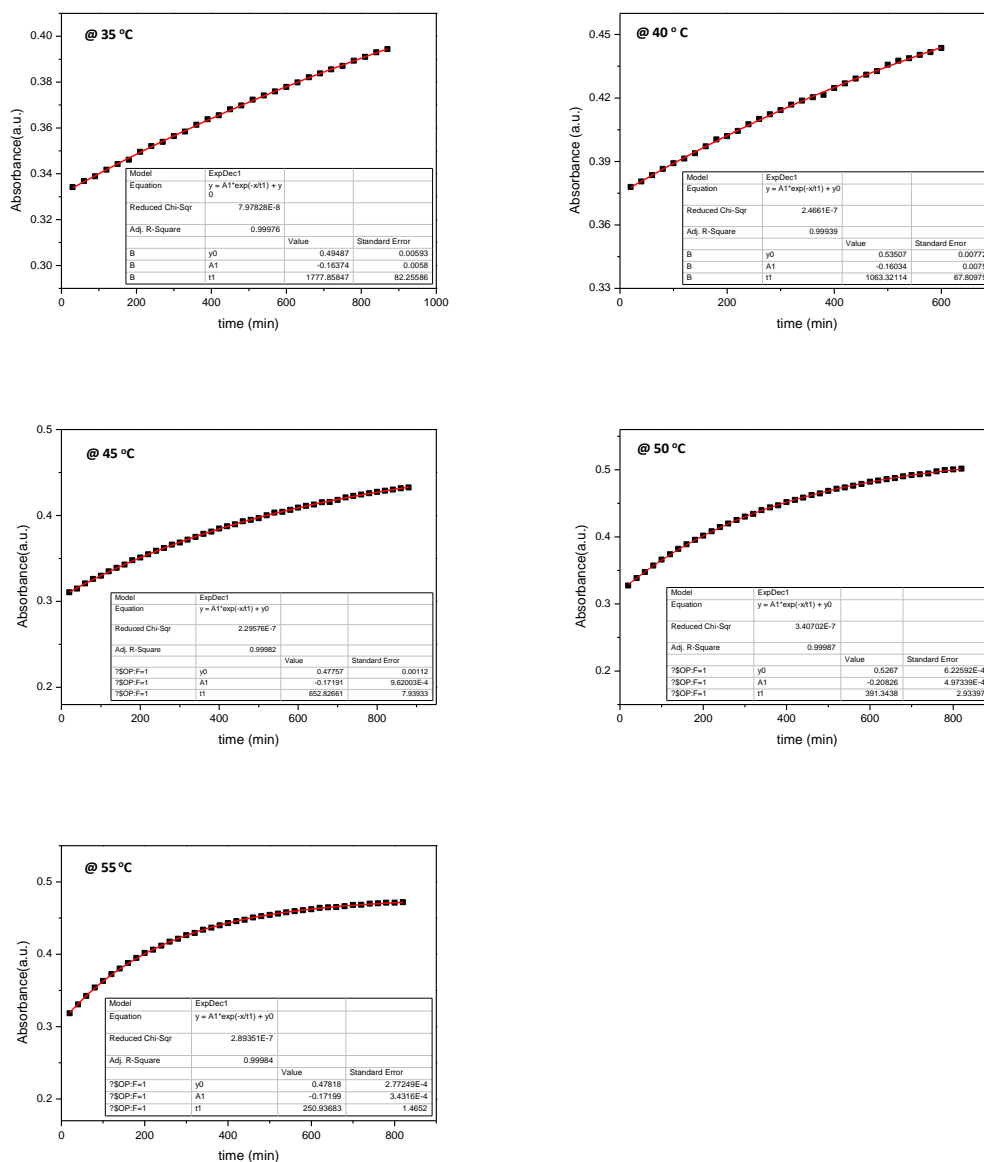


Figure S4. Thermal *Z/E* isomerization in **Dimer-1** (DMSO): plots of absorbance at 335 nm (λ_{\max}) versus time (minutes) at middle-range temperatures (35 °C, 40 °C, 45 °C, 50 °C and 55 °C) fitted with a first-order exponential decay.

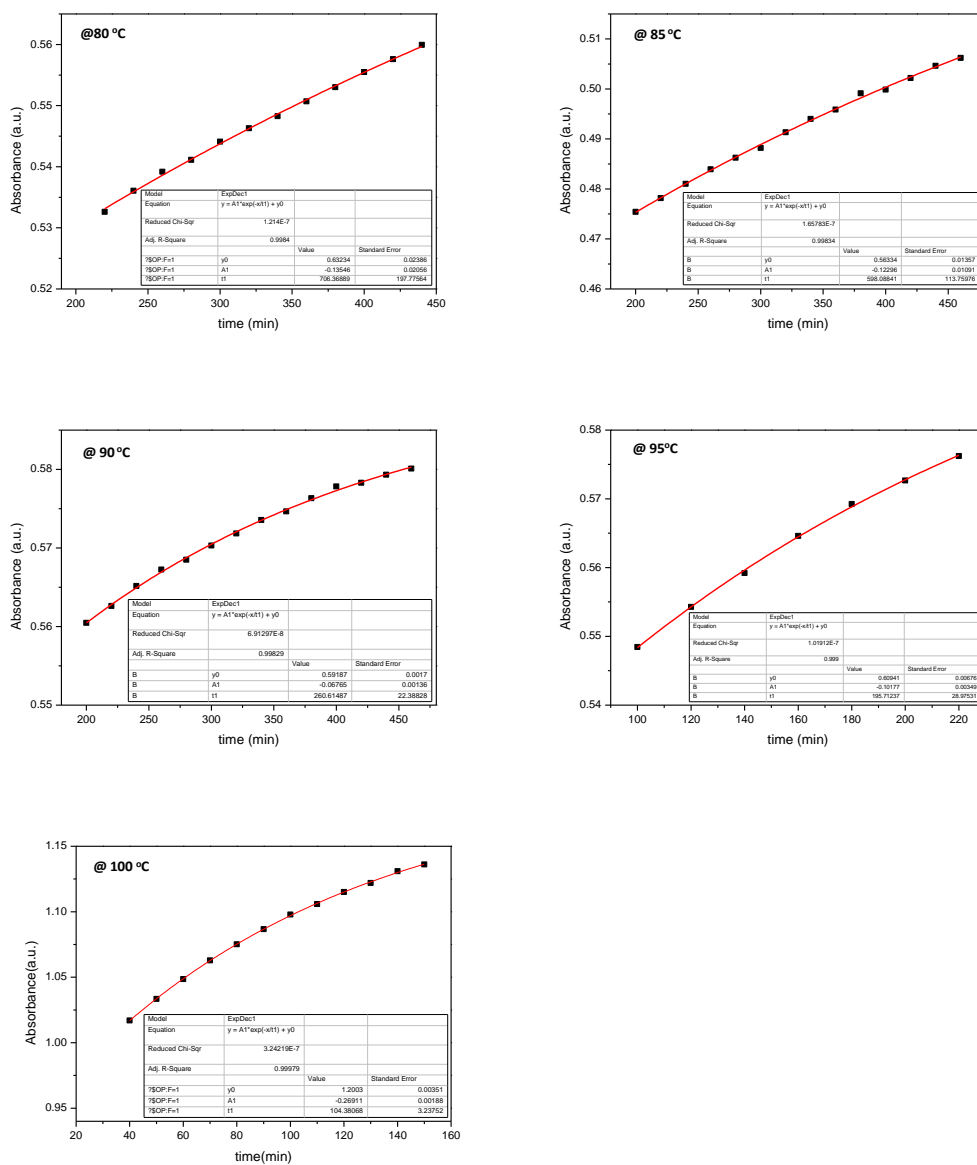
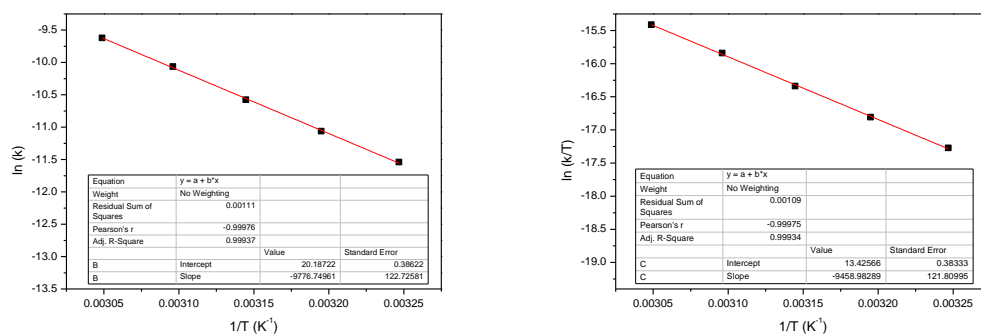
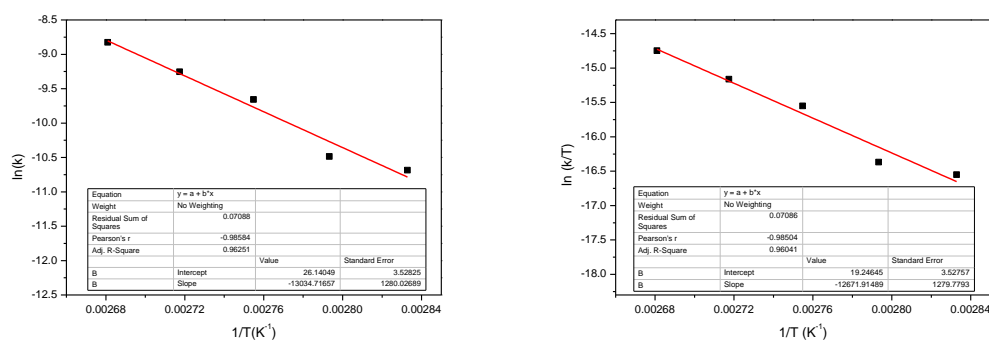


Figure S5. Thermal Z/E isomerization in **Dimer-1** (DMSO): plots of absorbance (after removal of the first data points) at 335 nm (λ_{\max}) versus time (minutes) at higher temperatures (80 °C, 85 °C, 90 °C, 95 °C and 100 °C) fitted with a first-order exponential decay.



k (s ⁻¹)	$\tau_{1/2}$ (h)	A (s ⁻¹)	Ea (kJ.mol ⁻¹)	ΔH^\ddagger (kJ.mol ⁻¹)	ΔS^\ddagger (J.mol ⁻¹)	ΔG^\ddagger (kJ.mol ⁻¹)
3.30×10^{-6}	58	5.8×10^8	81	79	- 86	104

Figure S6. Thermal Z/E isomerization in **Dimer-1** (DMSO) at middle-range temperatures (35 °C, 40 °C, 45 °C, 50 °C and 55 °C): Arrhenius plot (left), Van't Hoff plot (right), and the corresponding kinetic data and thermodynamic parameters (@ 298 K) as calculated using the Arrhenius and Eyring equations.



k (s ⁻¹)	$\tau_{1/2}$ (days)	A (s ⁻¹)	Ea (kJ.mol ⁻¹)	ΔH^\ddagger (kJ.mol ⁻¹)	ΔS^\ddagger (J.mol ⁻¹)	ΔG^\ddagger (kJ.mol ⁻¹)
2.27×10^{-8}	353	2.25×10^{11}	108	105	- 37.5	116

Figure S7. Thermal Z/E isomerization in **Dimer-1** (DMSO) at higher temperatures (80 °C, 85 °C, 90 °C, 95 °C and 100 °C): Arrhenius plot (left), Van't Hoff plot (right), and the corresponding kinetic data and thermodynamic parameters (@ 298 K) as calculated using the Arrhenius and Eyring equations.

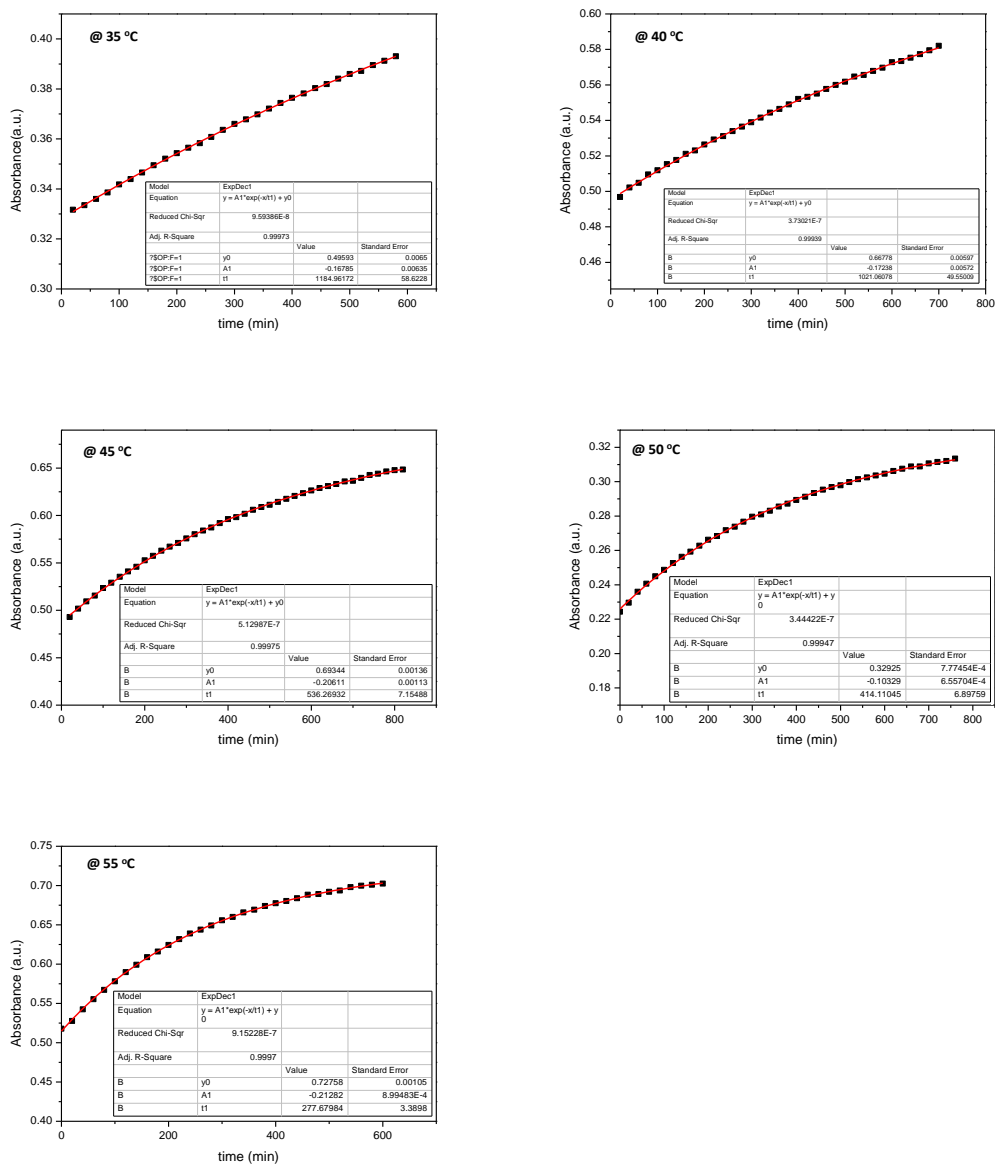


Figure S8. Thermal *Z/E* isomerization in **Dimer-2** (DMSO): plots of absorbance at 337 nm (λ_{\max}) versus time (minutes) at middle-range temperatures (35 °C, 40 °C, 45 °C, 50 °C and 55 °C) fitted with a first-order exponential decay.

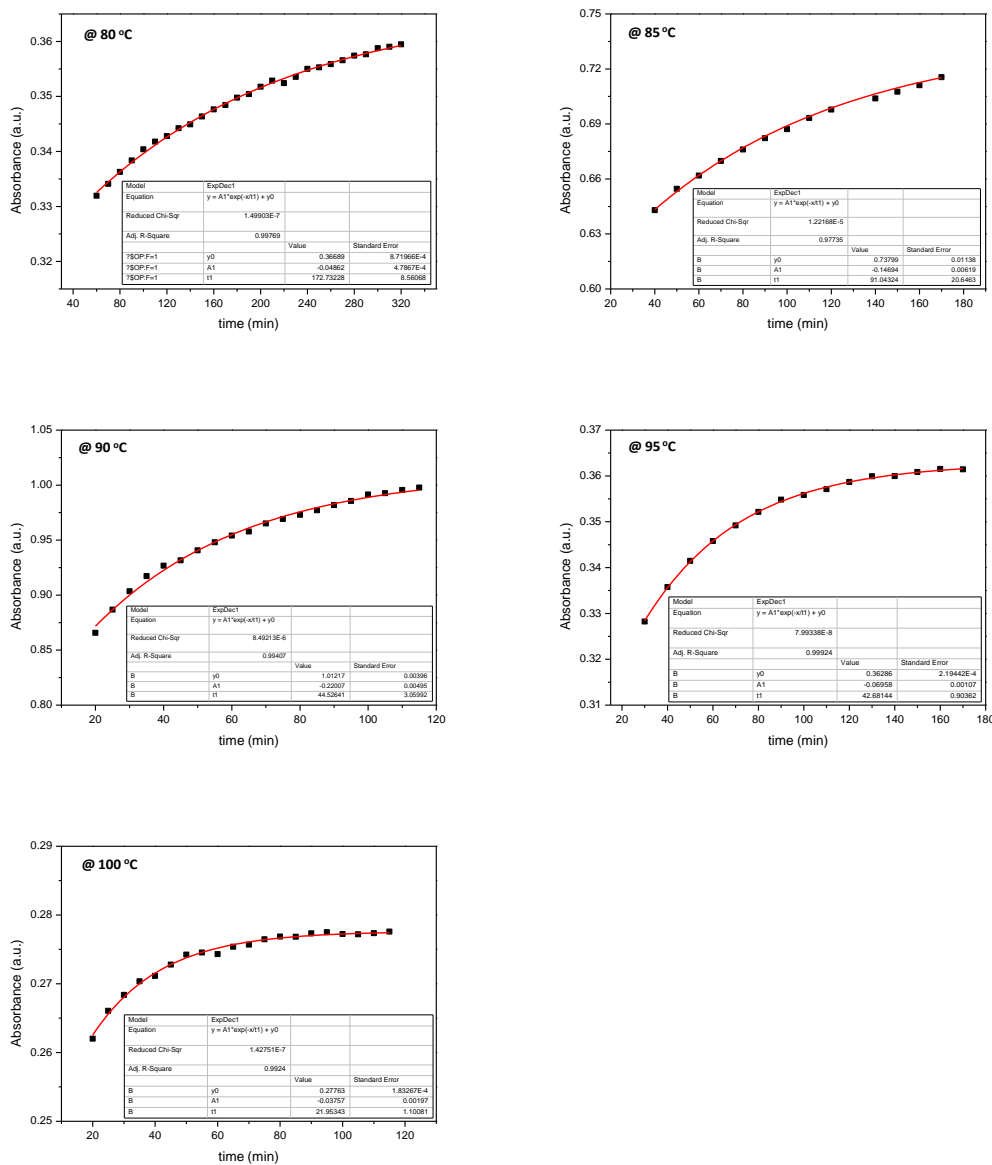
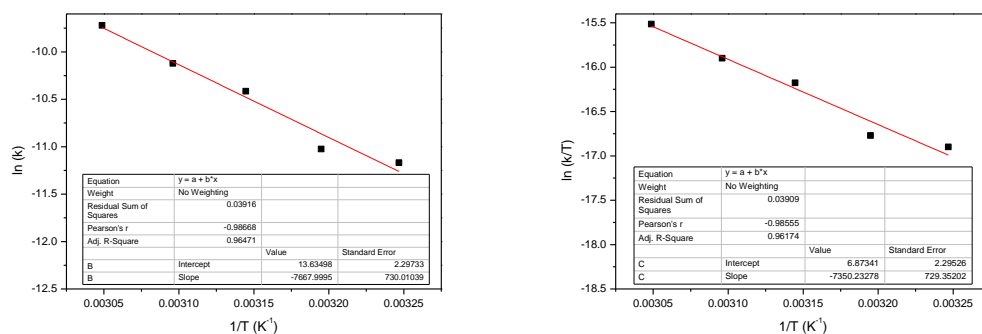
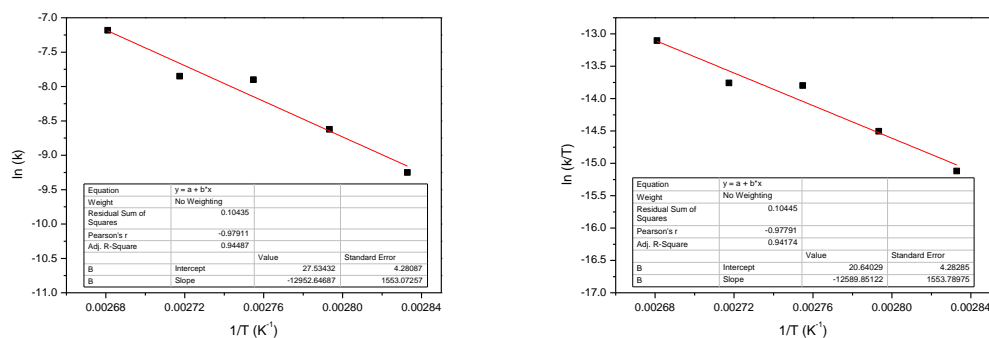


Figure S9. Thermal Z/E isomerization in **Dimer-2** (DMSO): plots of absorbance (after removal of the first data points) at 337 nm (λ_{\max}) versus time (minutes) at higher temperatures (80 °C, 85 °C, 90 °C, 95 °C, 100 °C) fitted with a first-order exponential decay.



k (s ⁻¹)	$\tau_{1/2}$ (h)	A (s ⁻¹)	Ea (kJ.mol ⁻¹)	ΔH^\ddagger (kJ.mol ⁻¹)	ΔS^\ddagger (J.mol ⁻¹)	ΔG^\ddagger (kJ.mol ⁻¹)
5.6×10^{-6}	35	8.4×10^5	64	61	- 140	103

Figure S10. Thermal Z/E isomerization in **Dimer-2** (DMSO) at middle-range temperatures (35 °C, 40 °C, 45 °C, 50 °C and 55 °C): Arrhenius plot (left), Van't Hoff plot (right), and the corresponding kinetic data and thermodynamic parameters (@ 298 K) as calculated using the Arrhenius and Eyring equations.



k (s ⁻¹)	$\tau_{1/2}$ (days)	A (s ⁻¹)	Ea (kJ.mol ⁻¹)	ΔH^\ddagger (kJ.mol ⁻¹)	ΔS^\ddagger (J.mol ⁻¹)	ΔG^\ddagger (kJ.mol ⁻¹)
1.1×10^{-7}	73	9.0×10^{11}	108	105	- 26	112

Figure S11. Thermal Z/E isomerization in **Dimer-2** (DMSO) at higher temperatures (80 °C, 85 °C, 90 °C, 95 °C and 100 °C): Arrhenius plot (left), Van't Hoff plot (right), and the corresponding kinetic data and thermodynamic parameters (@ 298 K) as calculated using the Arrhenius and Eyring equations.

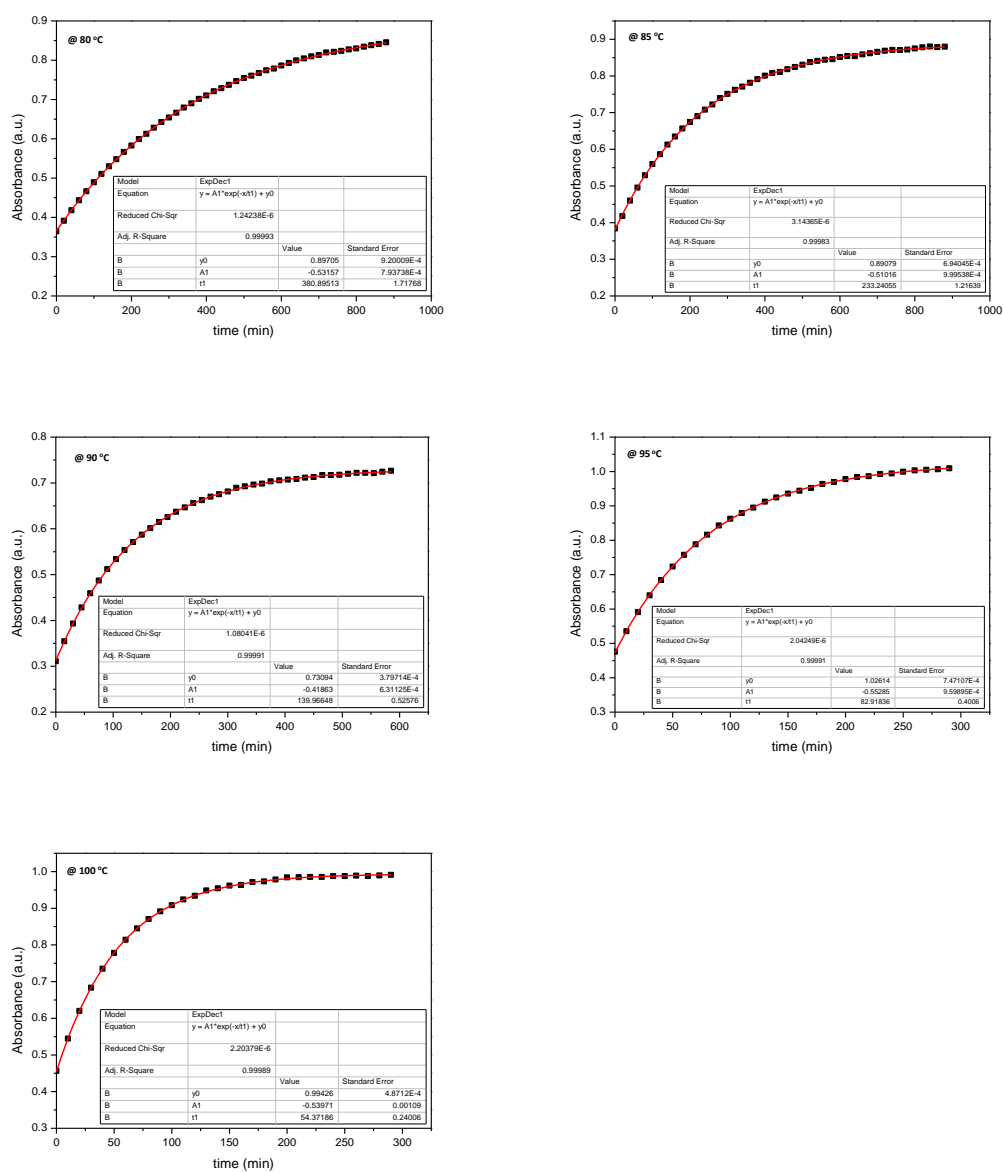
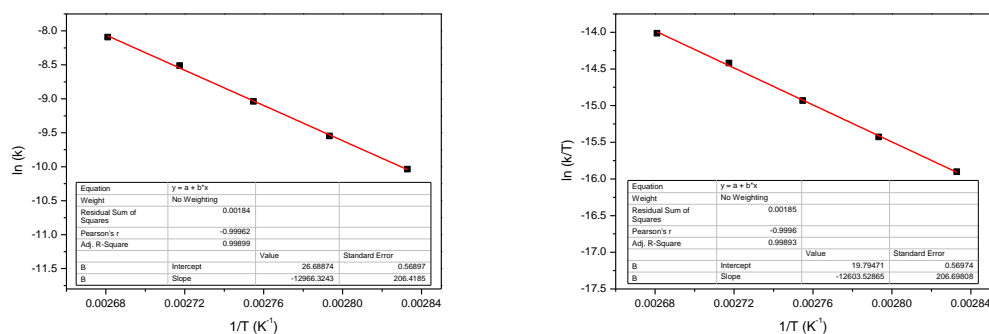


Figure S12. Thermal Z-F4-ester \rightarrow E-F4-ester isomerization in DMSO: plots of absorbance at 305 nm (λ_{\max}) versus time (minutes) at higher temperatures (80 °C, 85 °C, 90 °C, 95 °C, 100 °C) fitted with a first-order exponential decay.



k (s ⁻¹)	$\tau_{1/2}$ (days)	A (s ⁻¹)	Ea (kJ.mol ⁻¹)	ΔH^\ddagger (kJ.mol ⁻¹)	ΔS^\ddagger (J.mol ⁻¹)	ΔG^\ddagger (kJ.mol ⁻¹)
5.0×10^{-8}	160	3.9×10^{11}	108	105	-33	115

Figure S13. Thermal Z-F4-ester \rightarrow E-F4-ester isomerization in DMSO: Arrhenius plot (left), Van't Hoff plot (right), and the corresponding kinetic data and thermodynamic parameters (@ 298 K) as calculated using the Arrhenius and Eyring equations.

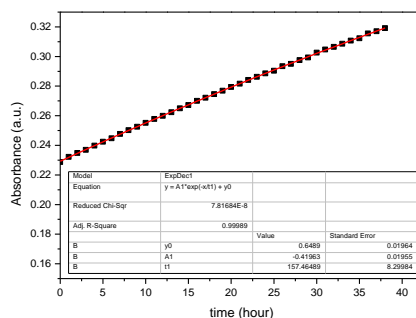


Figure S14. Thermal Z-diMe \rightarrow E-diMe isomerization in DMSO @ 298 K.

5. Electrochemistry

Cyclic voltammetry

Cyclic voltammetry was performed using a PG310 USB (HEKA Elektronik) potentiostat interfaced to a PC with PotMaster v2x43 (HEKA Elektronik) software for data evaluation. A three-electrode configuration contained in a non-divided cell consisting of a Pt disc (d = 1 mm) as working electrode, a platinum plate as counter-electrode, and a saturated calomel electrode (SCE) with an agar-agar-plug in a Luggin capillary with a diaphragm as reference electrode was

used. Measurements were carried out with $1 \cdot 10^{-3}$ M solutions in 0.1 M Bu_4NPF_6 acetonitrile (HPLC-grade, dried over calcium hydride and distilled) using a scan rate of $dE/dt = 1 \text{ V s}^{-1}$. Data are given in reference to the ferrocene redox couple (Fc/Fc^+), which was used as external standard. Cyclic voltammograms of *Z* isomers of azobenzenes were obtained by irradiation of the electrochemical cell using a standard laboratory UV-lamp equipped with a 313 nm or 365 nm UV-tube (Vilber Lourmat, 6W).

Table S1. Cathodic peak potentials of *E*-azobenzene derivatives (HMDE: Hanging Mercury Drop Electrode).

		diMe	F4	F4-ester	Dimer-1	Dimer-2
E_{r1}	Pt	-1.94	-1.63	-1.38	-1.63	-1.35
E_{r2}	Pt		-2.37	-2.06	-1.94	-1.85 ^{*)}
E_{r1}	HMDE	-1.84	-1.60	-1.37	-1.52	
E_{r2}	HMDE	-2.44	-2.32	-1.84	-1.89	

^{*)} Peak contains two 1-electron processes.

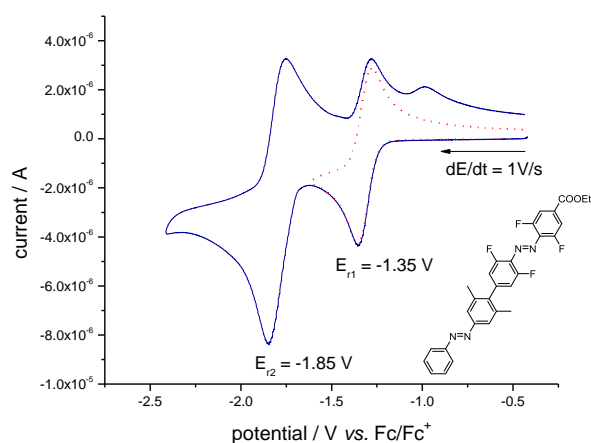


Figure S15. Cyclic voltammogram of **Dimer-2**. The red dashed curve corresponds to the reversible 1-electron process.

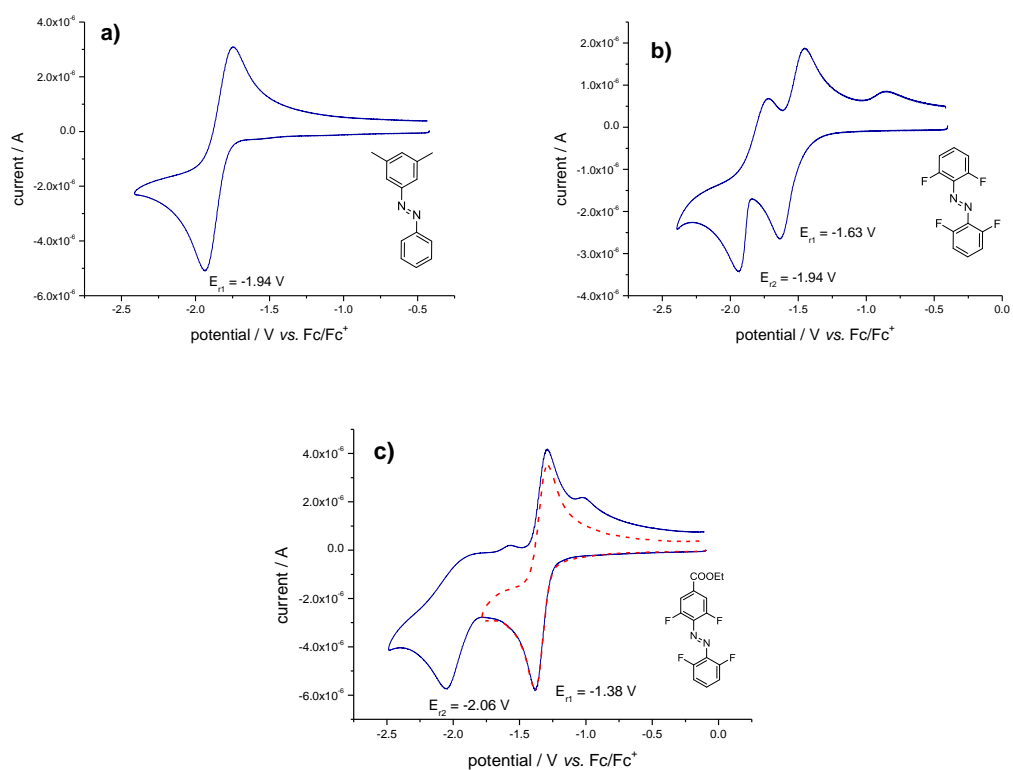


Figure S16. Cyclic voltammograms of a) **diMe**, b) **F4**, and c) **F4-ester**. The red dashed curve corresponds to the reversible 1-electron process.

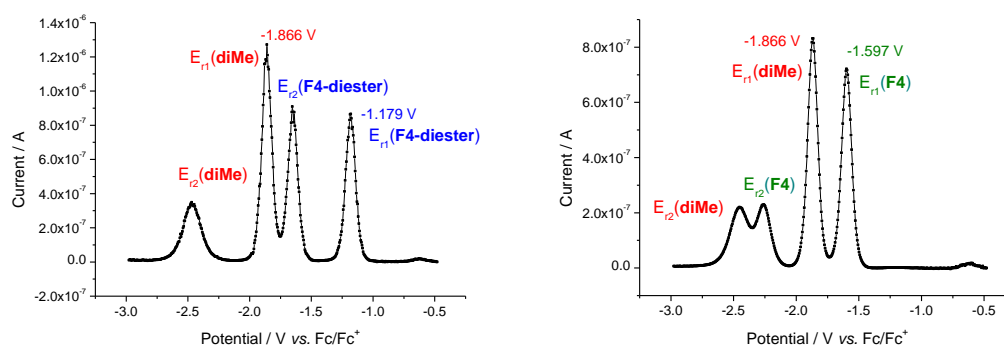


Figure S17. Difference pulse polarograms (using HMDE). Left: mixture of **F4-diester**^[2] and **diMe** ($5 \cdot 10^{-4}$ M in 0.1 M Bu₄NPF₆ acetonitrile); right: mixture of **F4** and **diMe** ($3.75 \cdot 10^{-4}$ M in 0.1 M Bu₄NPF₆ acetonitrile).

Spectroelectrochemistry

Spectroelectrochemistry^[3] was performed using quartz cuvettes with 1 mm or 0.5 mm path length in an Avantes AvaSpec-2048x14 spectrometer combined with an AvaLight-DH-S-BAL light source. The cuvette was equipped with a Pt mesh as working electrode, a Pt wire as counter electrode, and Ag/Ag⁺ (0.01 M AgNO₃ in 0.1 M Bu₄NPF₆ acetonitrile) as reference electrode, connected to an Autolab PGSTAT128N potentiostat from Metrohm GmbH, Germany.

5 · 10⁻⁴ M solutions of the different azobenzene derivatives in 0.1M Bu₄NPF₆ acetonitrile were placed in the cuvette, a scanning rate of 10 mV/s was used while UV/vis-spectra were recorded every 10 mV. As reference the Fc/Fc⁺ redox couple was determined to have an oxidation potential of 0.12 V vs. Ag/Ag⁺ in this configuration.

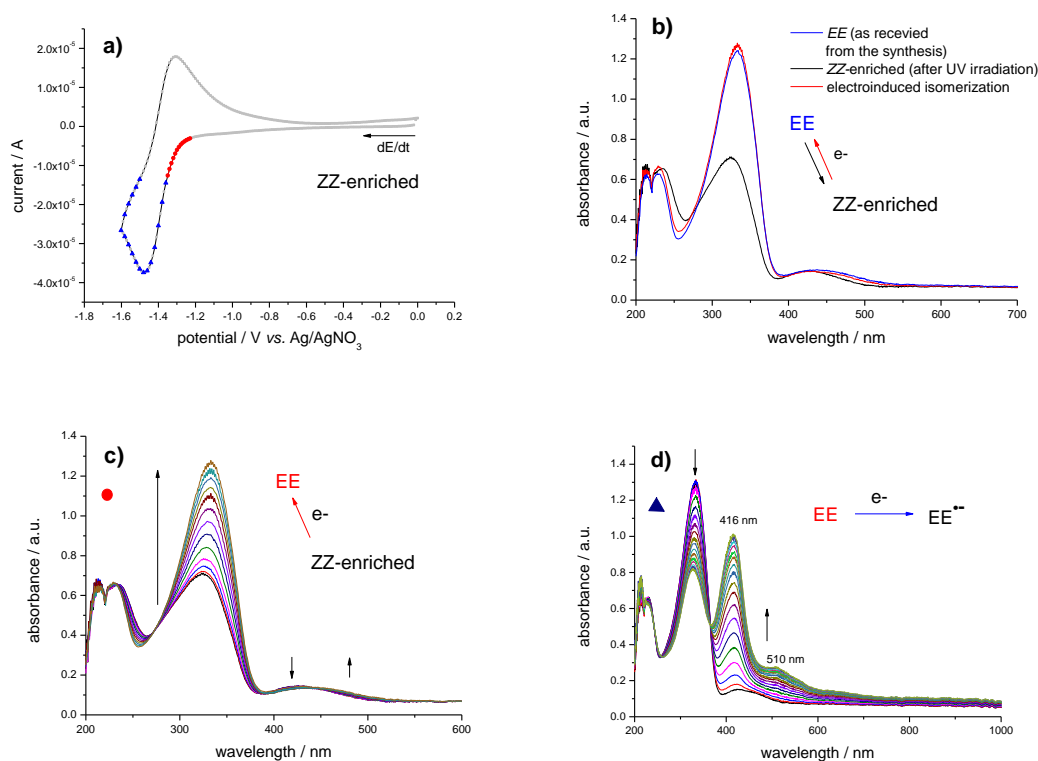


Figure S18. Spectroelectrochemistry of a ZZ-enriched **Dimer-1** solution. a) Cyclic voltammogram. b) UV/Vis spectra, blue: *EE*-isomer, black: *ZZ*-enriched solution, red: after the electrocatalytic isomerization. c) UV/Vis spectroscopic monitoring of the isomerization of the *ZZ*-enriched solution at potential values corresponding to the red dots in a). d) Formation of the radical anion of the resulting *EE*

isomer at potential values corresponding to the blue triangles in a).

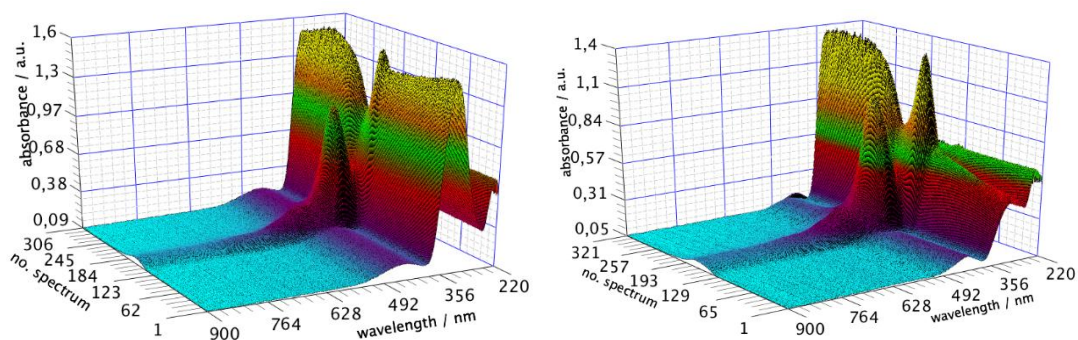


Figure S19. 3D spectro-electrochemical plots (x, wavelength; y, time (as the number of recorded spectra, from 1 to ca. 300); z, absorbance) of **Dimer-1**. Left: starting from the *EE*-isomer, right: starting from the *ZZ*-enriched isomer, following the cycle 0 V \rightarrow -1.6 V \rightarrow 0 V.

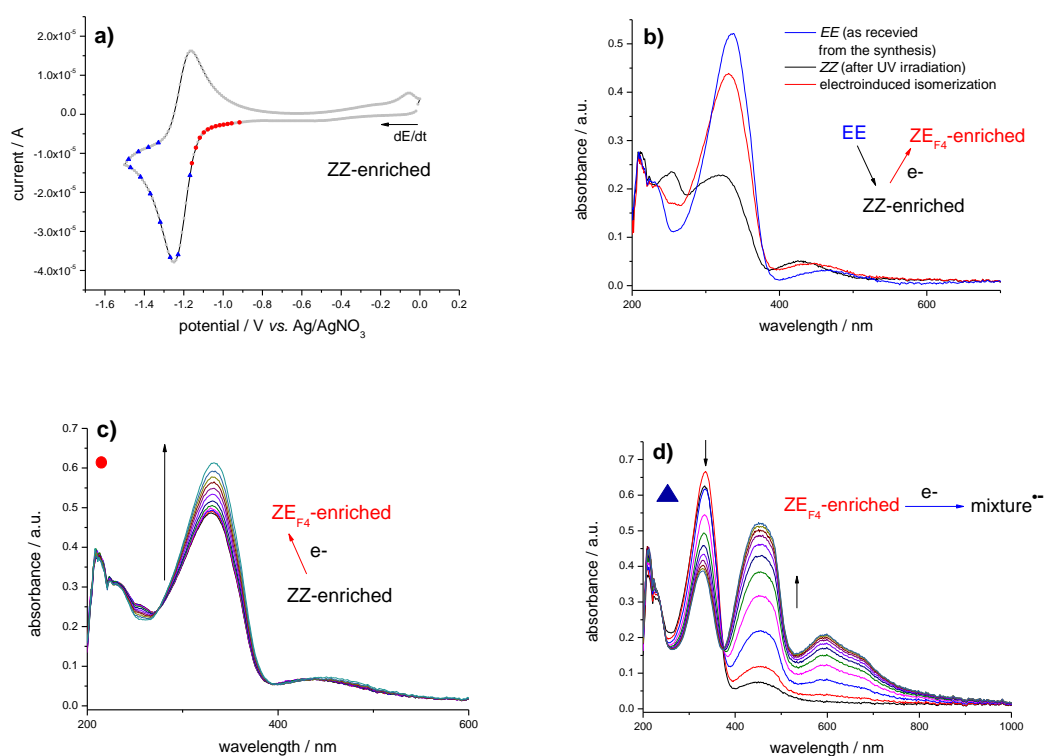


Figure S20. Spectroelectrochemistry of *ZZ*-enriched **Dimer-2**. a) Cyclic voltammogram. b) UV/Vis spectra, blue: *EE*-isomer, black: *ZZ*-enriched solution, red: after the electrocatalytic isomerization. c) UV/Vis spectroscopic monitoring of the isomerization of the *ZZ*-enriched solution at potential values corresponding to the red dots in a). d) Formation of the radical anions of the resulting ZE_{F_4} -enriched solution at potential values corresponding to the blue triangles in a).

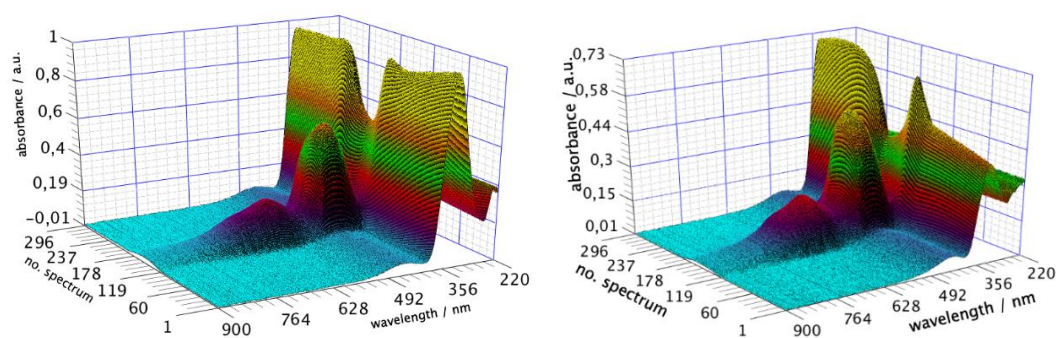


Figure S21. 3D spectro-electrochemical plots (x, wavelength; y, time (as the number of recorded spectra, from 1 to ca. 300) ; z, absorbance) of **Dimer-2**. Left: starting from the *EE*-isomer, right: starting from the *ZZ*-isomer, following the cycle 0 V \rightarrow -1.5 V \rightarrow 0 V.

Cathodically initiated Z \rightarrow E isomerization

A 0.015 mM solution in 0.1 M Bu₄NPF₆ acetonitrile (40 mL) was prepared for each sample (**Dimer-1**, **Dimer-2**, mixtures of **diMe/F4** and **diMe/F4-ester**). The solutions were filled into the cathode compartment of a double H-cell, purged with argon, and irradiated with a laboratory UV-lamp (365 nm) to enrich the solutions with *Z*-isomers. A Pt-mesh was used as the cathode. The anode chamber contains the electrolyte, the electrode is a Pt-mesh as well. As a reference electrode, a standard calomel electrode was placed in the third electrode chamber. Coulometry was performed potentiostatically (Bipotentiostat PG 287 HEKA Electronics, Lambrecht Pfalz, Germany) at a working potential (E_{r0}) below the maximum peak potential. The composition was followed by UPLC analysis, see Figure S21 (note that the % do not reflect the exact composition of the solutions, as no isosbestic point can be used for integrating the peaks in the case of such mixtures containing four isomers).

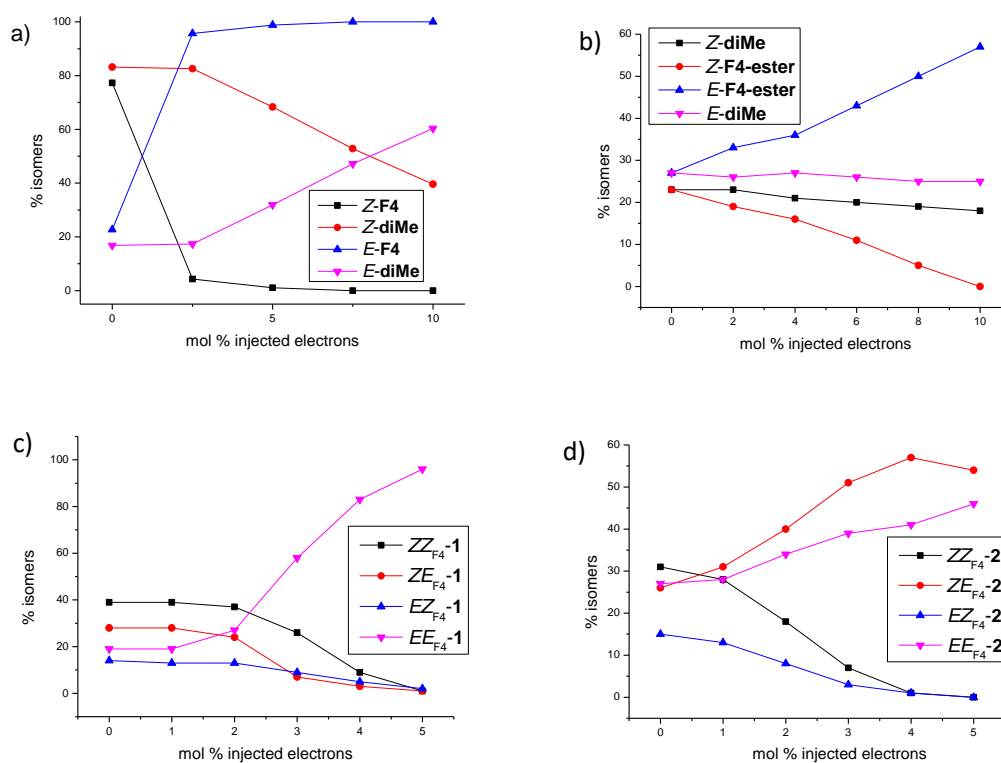


Figure S22. Changes of the isomer ratios during the cathodically initiated $Z \rightarrow E$ isomerization at E_{r0} .

a) mixture of **diMe/F4**, b) mixture of **diMe/F4-ester**, c) **Dimer-1**, d) **Dimer-2**.

[1] D. Bléger *et al.*, *J. Am. Chem. Soc.* **2012**, *134*, 20597-20600.

[2] C. Knie *et al.*, *Chem. Eur. J.* **2014**, *20*, 16492-16501.

[3] A. Goulet-Hanssens *et al.*, *J. Am. Chem. Soc.* **2017**, *139*, 335-341.