

Supplementary information

for

White-light powered autonomous molecular ratchet drives Pd^{II} capsules out of equilibrium

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S1 General information

Reagents and materials. Commercial solvents and reagents were obtained from the following suppliers and used without further purification unless specified otherwise: abcr, Acros Organics, Alfa Aesar, BLD-Pharm, Merck, Sigma Aldrich, TCI, Thermo Fisher Scientific.

Column chromatography. Column chromatography was carried out using a puriFlash 5.020 (Interchim) flash chromatography machine with PuriFlash 15 μ m Si HP (Interchim) flash cartridges.

NMR spectroscopy. All NMR spectroscopic measurements were carried out using 400 MHz, 500 MHz or 700 MHz spectrometers (Bruker Avance I 400, Bruker Avance I 500, Bruker Avance III HD Prodigy 500, Bruker Avance III HD Ascend 700). ^1H and ^{13}C NMR spectra are referenced to the residual solvent peak for CD_3CN (^1H : 1.94 ppm, ^{13}C : 1.32 ppm), CD_2Cl_2 (^1H : 5.32 ppm, ^{13}C : 53.5 ppm), $\text{DMSO}-d_6$ (^1H : 2.50 ppm, ^{13}C : 39.52 ppm) or $\text{DMF}-d_7$ (^1H : 8.03 ppm, ^{13}C : 163.15 ppm). NMR signals are reported in terms of chemical shift (δ) in ppm, relative integral, multiplicity, coupling constants (in Hz), and assignment, in that order. The following abbreviations for multiplicity are used: s, singlet; d, doublet. Spectra were processed (phase and baseline corrections, integration, peak analysis), evaluated, and plotted using MestReNova 14.2.1 (Mestrelab) and TopSpin 4.1.3 (BrukerBioSpin). All processing operations were manually checked to ensure that the processed spectra accurately represented the raw data.

Mass spectrometry. Mass spectra were acquired using an Orbitrap XL (Thermo Fischer Scientific) and evaluated and plotted using XCalibur 4.2 (Thermo Fischer Scientific).

UV-vis spectroscopy. All UV-vis spectroscopy measurements were carried out using a Cary 60 (Agilent) utilising a flash lamp style spectrometer with a temperature-controlled sample holder.

Elemental analysis. Elemental analysis was carried out using a Vario Micro Cube (Elementar). Approximately 2 mg of the compound were used, and all measurements were carried out in triplicate.

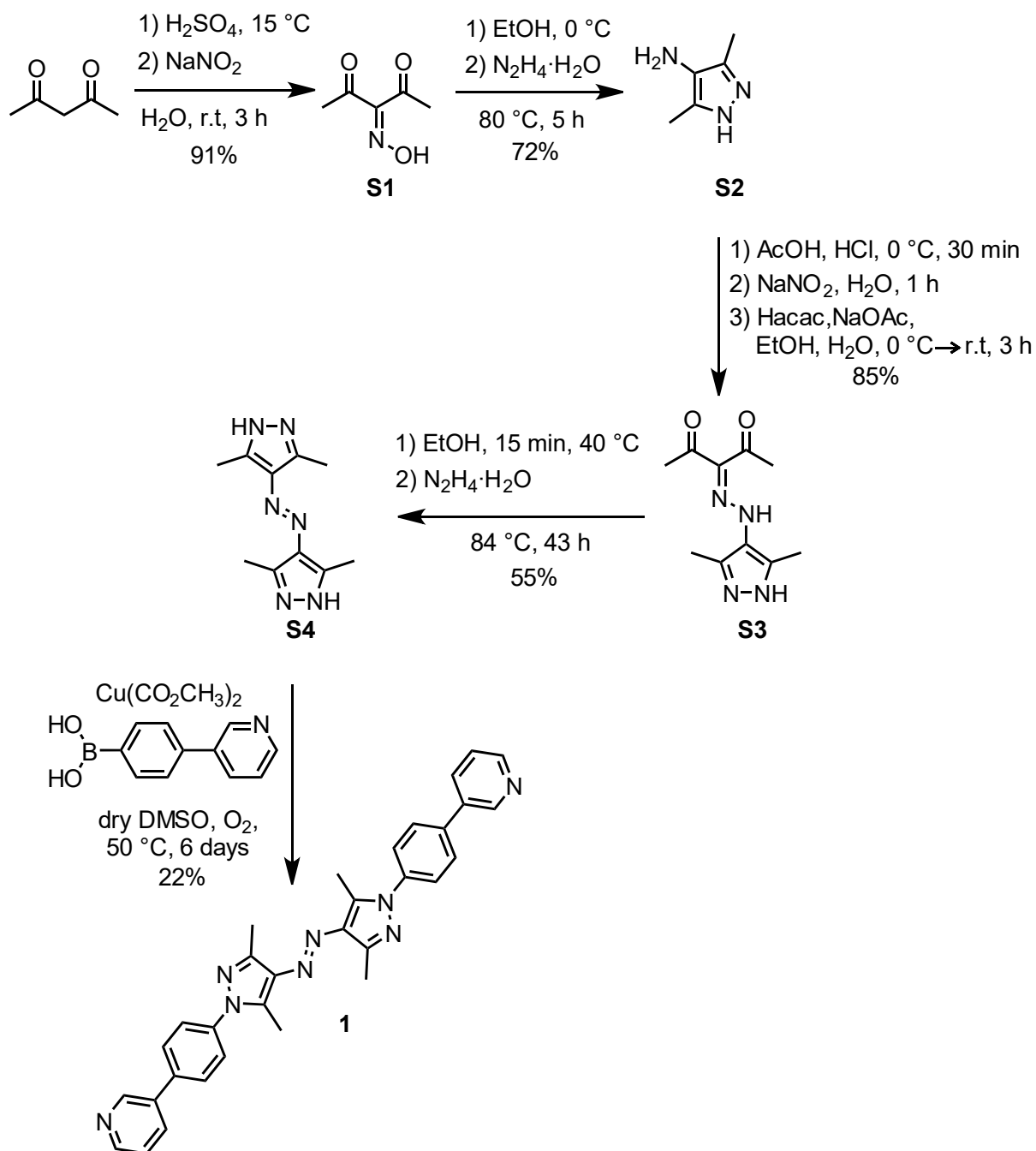
Light sources. All illumination experiments with 500 nm and *in-situ* illumination experiments (NMR and UV-vis) and were carried out using Prizmatrix fibre collimated LEDs (Table S1, for further details see Section S4). Illumination experiments (NMR

and MS) with 365 nm were carried out using a portable, self-built light source incorporating a commercial 365 nm LED chip (Nichia, NCSU275(T)-U365, 1.8 W).

Table S1. Light output of fibre collimated LEDs.

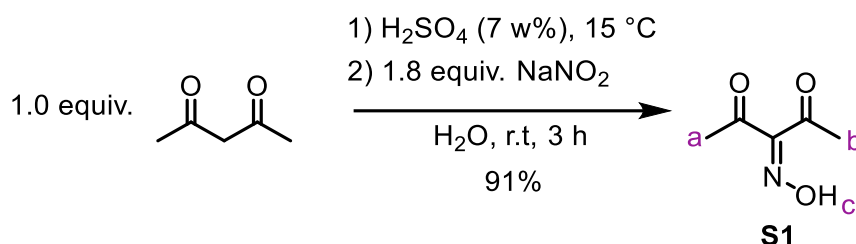
λ [nm]	310	325	365	390	405	430	450	500	white
Output power [mW] (1 m optical fibre)	1	8.6	170	220	260	160	440	165	74

S2 Synthesis



Scheme S1. Synthetic route to azobispyrazole-containing ligand 1.

S2.1 3-(Hydroxyimino)pentane-2,4-dione (**S1**)



3-(Hydroxyimino)pentane-2,4-dione (**S1**) was synthesised after a modified literature procedure.¹

Pentane-2,4-dione (5.0 g, 49.94 mmol, 1.0 equiv.) was dissolved in sulfuric acid (7%, 50 mL) at 15 °C. Subsequently, a solution of NaNO₂ (6.20 g, 89.89 mmol, 1.8 equiv.) in water (30 mL) was added dropwise at 15 °C. After the slightly yellow reaction solution was stirred at room temperature for 3 h, the product was extracted with ethyl acetate (4 × 15 mL) and the combined organic layers dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure on a rotary evaporator and the orange (slushy) solid was washed with cold toluene and later dissolved in methanol. After removing residual solvents under reduced pressure, 3-(hydroxyimino)pentane-2,4-dione (**S1**) was isolated as white crystals with a 91% yield (5.85 g, 45.31 mmol).

C₅H₇NO₃ 129.12 g/mol

R_F value (CH₂Cl₂ / CH₃OH 95:5 (v/v)) = 0.67

¹H NMR (400 MHz, CD₃CN, 293 K) δ_H [ppm] = 2.26 (s, 3H, H-a/b), 2.32 (s, 3H, H-a/b), 10.15 (s, 1H, H-c).

The obtained spectrum matches the literature data.¹

HRMS (ESI⁺): *m/z* (relative intensity) = 152.0320 (100%, [M+Na⁺], calcd 152.0318).

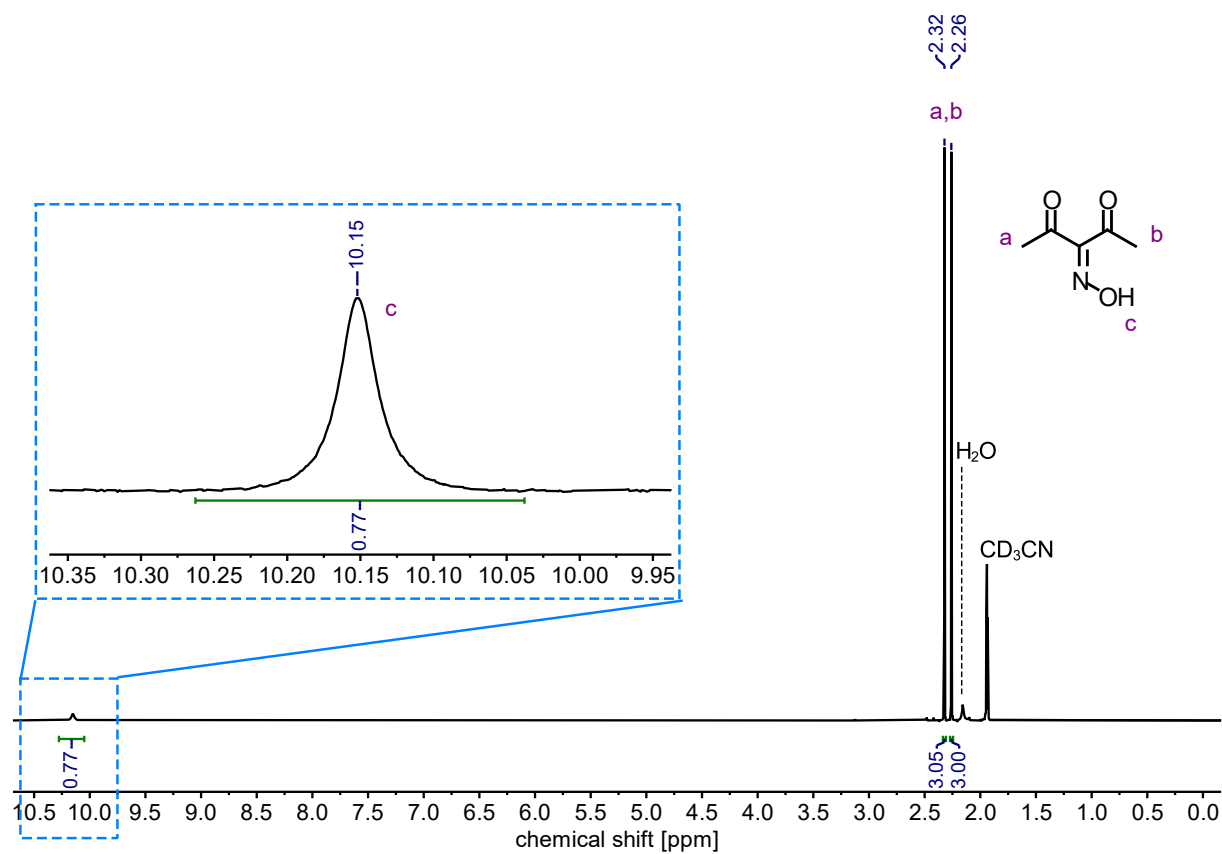
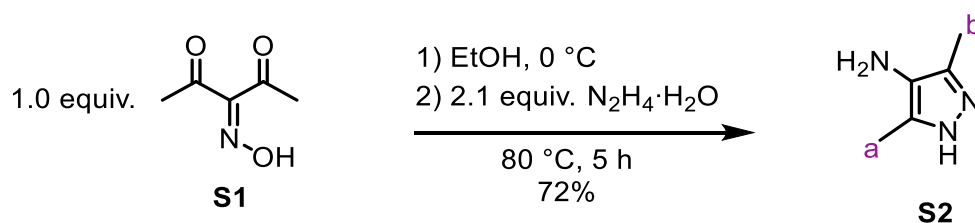


Figure S1. ^1H NMR spectrum (400 MHz, CD_3CN , 298 K) of dione **S1**.

S2.2 3,5-Dimethyl-1*H*-pyrazol-4-amine (**S2**)



3,5-Dimethyl-1*H*-pyrazol-4-amine (**S2**) was synthesised after a modified literature procedure.¹

Hydrazine monohydrate (0.8 mL, 19.52 mmol, 2.10 equiv.) was added dropwise to a solution of dione **S1** (1.0 g, 9.29 mmol, 1.0 equiv.) in ethanol (12 mL) at 0 °C. The resulting turquoise solution was stirred at 80 °C. After 90 min, additional hydrazine monohydrate (0.3 mL, 7.44 mmol, 0.8 equiv.) was added and the turquoise solution was stirred for a further 3.5 h at 80 °C. After allowing the reaction to cool to room temperature, water (20 mL) was added and the aqueous phase was extracted with ethyl acetate (4 × 10 mL). The combined organic layers were washed with water (1 × 10 mL) and dried over Na₂SO₄. The residual solvent was removed under reduced pressure on a rotary evaporator. 3,5-Dimethyl-1*H*-pyrazol-4-amine (**S2**) was obtained as an off-white powder with a yield of 72% (618 mg, 5.56 mmol).

C₅H₉N₃ 111.15 g/mol

R_F value (CH₂Cl₂ / CH₃OH 98:2 (v/v)) = 0.22

¹H NMR (400 MHz, DMSO-*d*₆, 293 K) δ_H [ppm] = 1.99 (s, 6H, H-a/b), 11.37 (s, 1H, NH).

The obtained spectrum matches the literature data.¹

HRMS (ESI⁺): *m/z* (relative intensity) = 112.0870 (100%, [M+H⁺], calcd 112.0869).

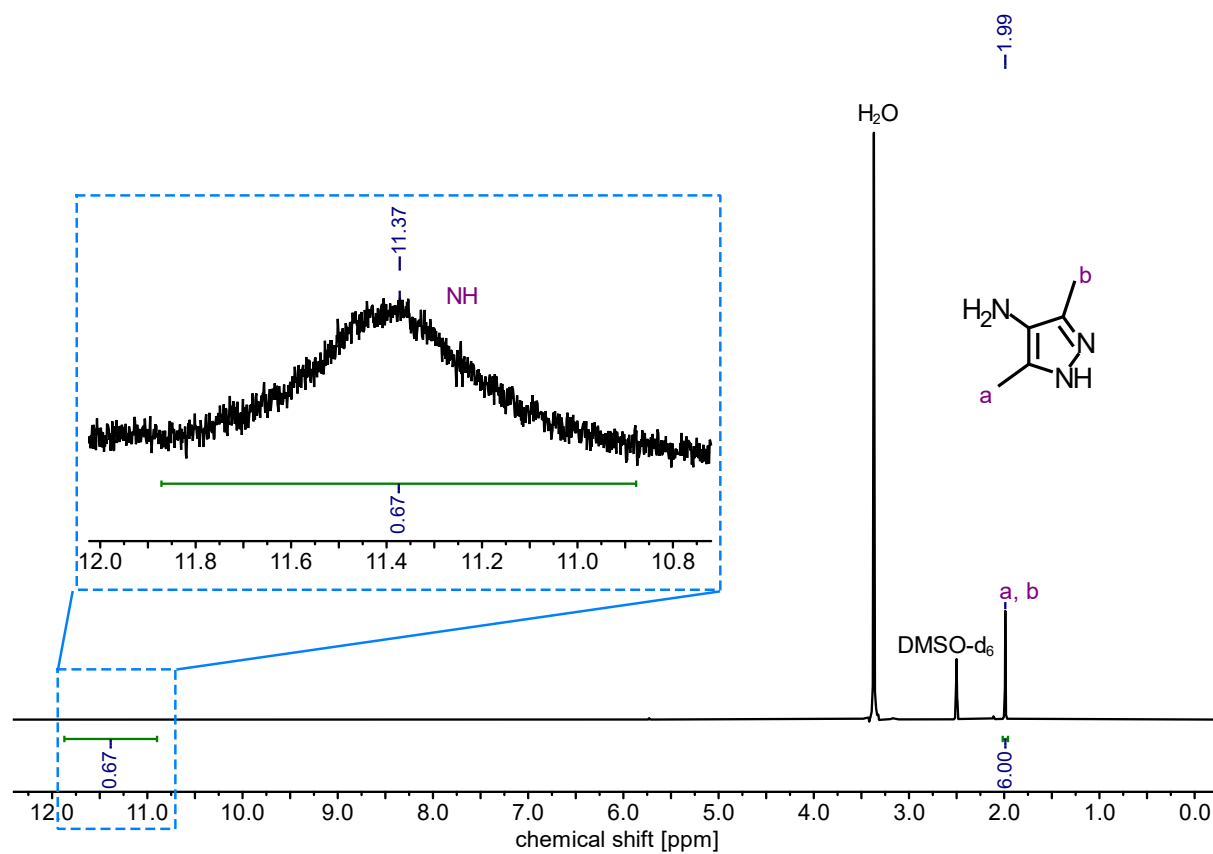
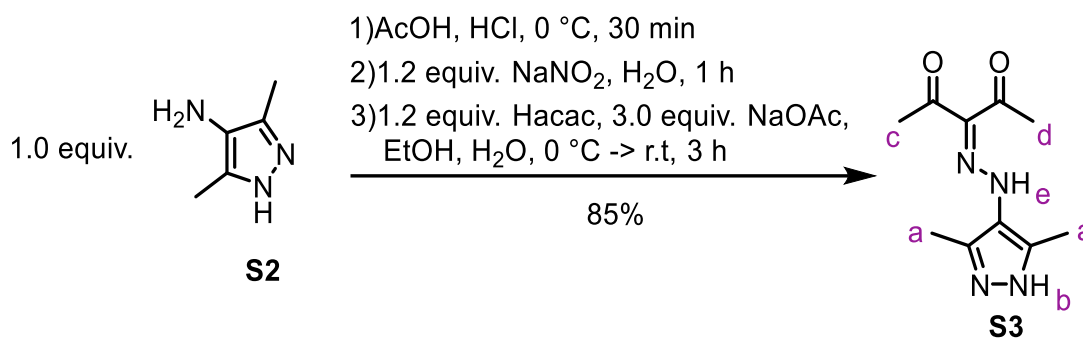


Figure S2. ^1H NMR spectrum (400 MHz, $\text{DMSO}-d_6$, 298 K) of pyrazole **S2**.

S2.3 3-(2-(3,5-Dimethyl-1*H*-pyrazol-4-yl)hydrazineylidene)pentane-2,4-dione (**S3**)



3-(2-(3,5-Dimethyl-1*H*-pyrazol-4-yl)hydrazineylidene)pentane-2,4-dione (**S3**) was synthesised after a modified literature procedure.¹

A suspension of pyrazol amine **S2** (100 mg, 899.70 μmol , 1.0 equiv.) in glacial acetic acid (1.3 mL) and conc. HCl (0.3 mL) was stirred at 4 $^{\circ}\text{C}$ for 30 min. Subsequently, a solution of NaNO_2 (74.5 mg, 1.08 mmol, 1.2 equiv.) in water (1.0 mL) was added dropwise and the resulting clear yellow solution stirred at 4 $^{\circ}\text{C}$ for 1 h. This cold solution of the diazonium salt was added dropwise to a solution of acetylacetone (0.1 mL, 1.0 mmol, 1.2 equiv.) and NaOAc (0.22 g, 2.70 mmol, 3.0 equiv.) in ethanol (2.0 mL) and water (1.0 mL) at 4 $^{\circ}\text{C}$. The resulting solution was warmed to room temperature and stirred for an additional 3 h. The aqueous phase was then extracted with ethyl acetate (4 $\times$ 20 mL). The combined organic layers were washed with water (1 $\times$ 15 mL) and dried over Na_2SO_4 . The residual solvent was removed under reduced pressure on a rotary evaporator and the residue was subjected to column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{EtOAc}$ 100:0 $\rightarrow$ 75:25 (v/v) over 15 column volumes). Dione **S3** was obtained as a yellow powder with an overall yield of 85% (170 mg, 764.91 μmol).

$\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2$ 222.25 g/mol

R_F value (CH_2Cl_2 / CH_3OH , 95:5 (v/v)) = 0.55

^1H NMR (400 MHz, CD_3CN , 293 K) δ_{H} [ppm] = 2.32 (s, 9H, H-a, H-b, and H-d/e), 2.49 (s, 3H, H-d/e), 10.6 (s, 1H, H-c), 15.07 (s, 1H, H-f).

The obtained spectrum matches the literature data.¹

HRMS (ESI⁺): m/z (relative intensity) = 223.1191 (100%, $[\text{M}+\text{H}^+]$, calcd 223.1190).

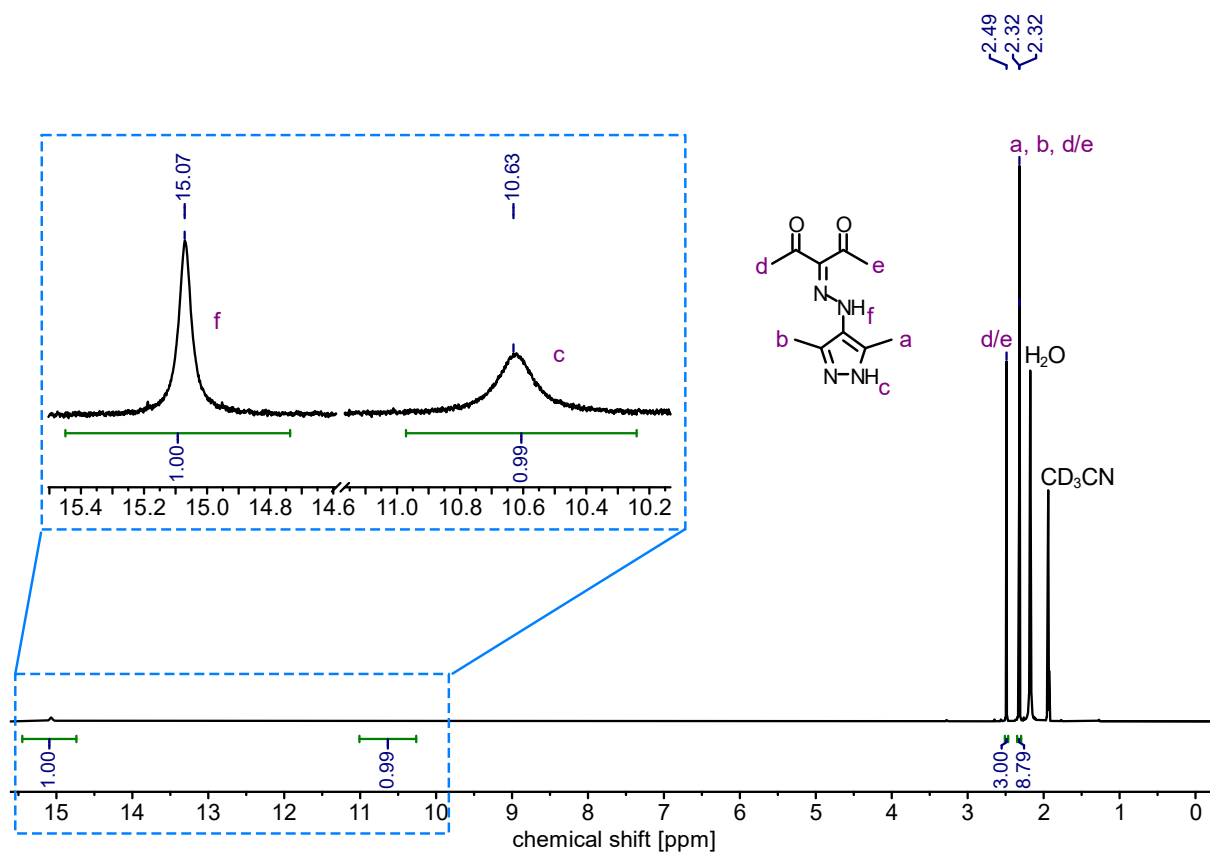
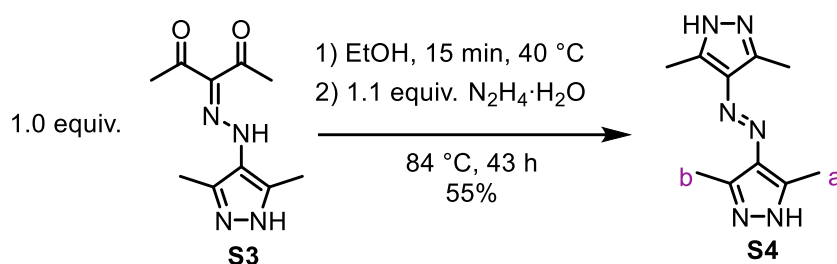


Figure S3. ^1H NMR spectrum (400 MHz, CD_3CN , 298 K) of **S3**.

S2.4 (*E*)-1,2-Bis(3,5-dimethyl-1*H*-pyrazol-4-yl)diazene (**S4**)



(*E*)-1,2-Bis(3,5-dimethyl-1*H*-pyrazol-4-yl)diazene (**S4**) was synthesised after a modified literature procedure.¹

Dione **S3** (3.7 g, 16.6 mmol, 1.0 equiv.) was dissolved in ethanol (150 mL) by stirring the mixture for 15 min at 40 °C. Hydrazine monohydrate (890 μL , 18.3 mmol, 1.1 equiv.) was added and the solution was stirred under reflux (84 °C) for 43 h, during which a colour change from yellow to orange was observed and a yellow precipitate formed. After allowing the reaction mixture to cool down to room temperature, water (150 mL) was added upon which more precipitate formed. The formed precipitate was filtered via gravity filtration and washed with water (20 mL). After allowing the solid to air dry for 5 d, (*E*)-1,2-bis(3,5-dimethyl-1*H*-pyrazol-4-yl)diazene (**S4**) was obtained as a yellow solid in 55% yield (2.0 g, 9.16 mmol).

$\text{C}_{10}\text{H}_{14}\text{N}_6$ 218.26 g/mol

R_F value (CH_2Cl_2 / *i*-PrOH 9:1 (v/v)) = 0.63

^1H NMR (400 MHz, $\text{DMSO}-d_6$, 298 K) δ_{H} [ppm] = 2.34 (s, 3H, H-a/b), 2.40 (s, 3H, H-a/b), 12.53 (s, 1H, NH).

The obtained spectrum matches the literature data.¹

HRMS (ESI⁺): m/z (relative intensity) = 219.1349 (100%, $[\text{M}+\text{H}^+]$, calcd 219.1353).

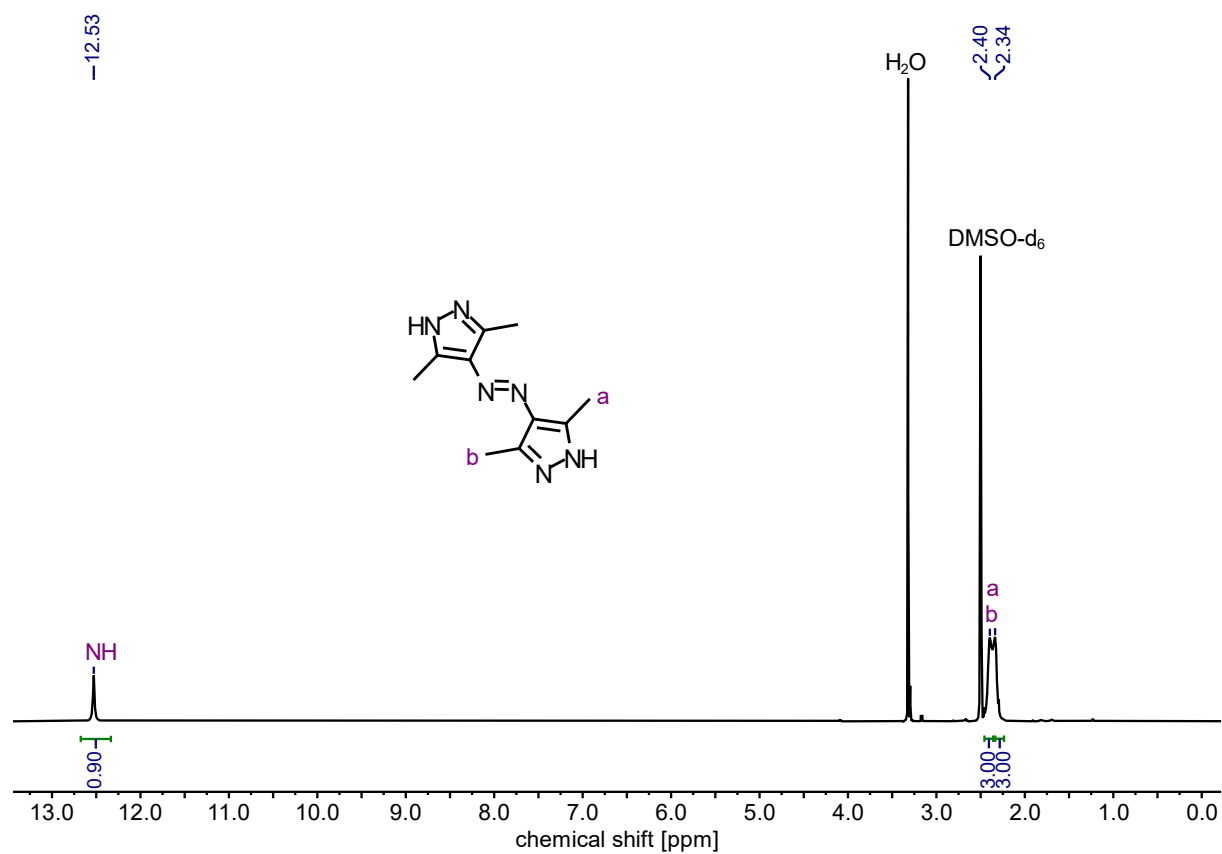
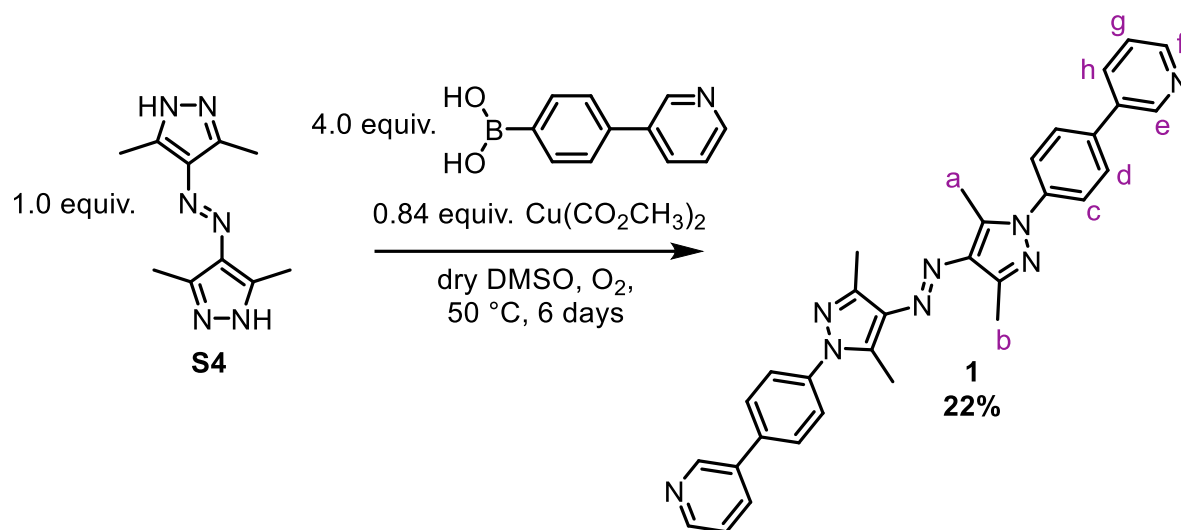


Figure S4. ^1H NMR spectrum (400 MHz, DMSO-d_6 , 298 K) of azobispyrazole photoswitch **S4**.

S2.5 (*E*)-1,2-Bis(3,5-dimethyl-1-(4-(pyridin-3-yl)phenyl)-1*H*-pyrazol-4-yl)diazene (**1**)



$\text{Cu}(\text{CO}_2\text{CH}_3)_2$ (160 mg, 885 μmol , 0.84 equiv.) was added to a solution of azobispyrazole photoswitch **S4** (230 mg, 1.05 mmol, 1.0 equiv.) and (4-(pyridin-3-yl)phenyl)boronic acid (839 mg, 4.22 mmol, 4.0 equiv.) in dry dimethyl sulfoxide (25 mL). The reaction mixture was equipped with an oxygen balloon and was stirred at 50 °C for 6 d, upon which a green solid precipitated. After allowing the reaction to cool down to ambient temperature, the green solid was filtered via gravity filtration and washed with water. After air drying the solid for 24 h, the green solid was collected and the residue was subjected to column chromatography (silica gel, see **Table S2** for solvent specifications). The solid obtained after column chromatography was further purified by liquid-liquid (dichloromethane/ethyl acetate) diffusion-assisted crystallisation: The solid was dissolved in a minimum amount of dichloromethane (1 mL) and the solution carefully layered with ethyl acetate (2 mL) upon which yellow crystals formed. The mixture was cooled to 4 °C overnight or longer to afford ligand **1** as a yellow crystalline solid in 22% yield (125 mg, 238 μmol).

Table S2. Solvent gradient used to purify ligand **1** via flash column chromatography.

Column volume	EtOAc / NEt_3 (97:3)	CH_2Cl_2	<i>i</i> -PrOH
0	0	100	0
10	50	50	0
14	100	0	0
16	100	0	0
18	80	0	20

$C_{32}H_{28}N_8$ 524.63 g/mol

R_F value (EtOAc / NEt₃, 97:3 (v/v)) = 0.27

Elemental Analysis ($C_{32}H_{28}N_8$):

Calcd (%) C: 73.26 H: 5.38 N: 21.36

Found (%) C: 73.43 H: 5.39 N: 21.25

¹H NMR* (400 MHz, CD₂Cl₂, 298 K) δ_H [ppm] = 1.89 (s, 3H, H-b^z), 2.25 (s, 3H, H-a^z), 2.56 (s, 3H, H-b), 2.69 (s, 3H, H-a), 7.41 (ddd, J = 7.8, 4.8, 0.9, 1H, H-g), 7.52 – 7.59 (m, 2H, H-c^z), 7.63 – 7.69 (m, 2H, H-c), 7.73 – 7.78 (m, 2H, H-d), 7.92 (dd, J = 2.4, 1.6, 1H, H-h^z), 7.96 (ddd, J = 7.9, 2.4, 1.7, 1H, H-h), 8.61 (dd, J = 4.8, 1.6, 1H, H-f), 8.88 (d, J = 1.6, 1H, H-e^z), 8.90 (dd, J = 2.4, 0.9, 1H, H-e).

¹³C NMR (176 MHz, CD₂Cl₂, 298 K) δ_C [ppm] = 11.7 (C-a), 14.6 (C-b), 124.0 (C-g), 125.3 (C-c), 128.2 (C-d), 134.6 (C-h), 135.9 (C-6), 137.4 (C-1), 137.5 (C-5), 138.1 (C-2), 139.8 (C-4), 143.3 (C-3), 148.6 (C-e), 149.3 (C-f).

HRMS (ESI⁺): m/z (relative intensity) = 525.2509 (100%, [M+H⁺], calcd 525.2510).

* Signals with a ^z represent Z-**1**. Not all signals of Z-**1** are visible due to peak overlap with E-**1** (Figure S55). One dimensional ¹H-ROESY spectra enabled the assignment of H-a, H-b, H-a^z, and H-b^z.

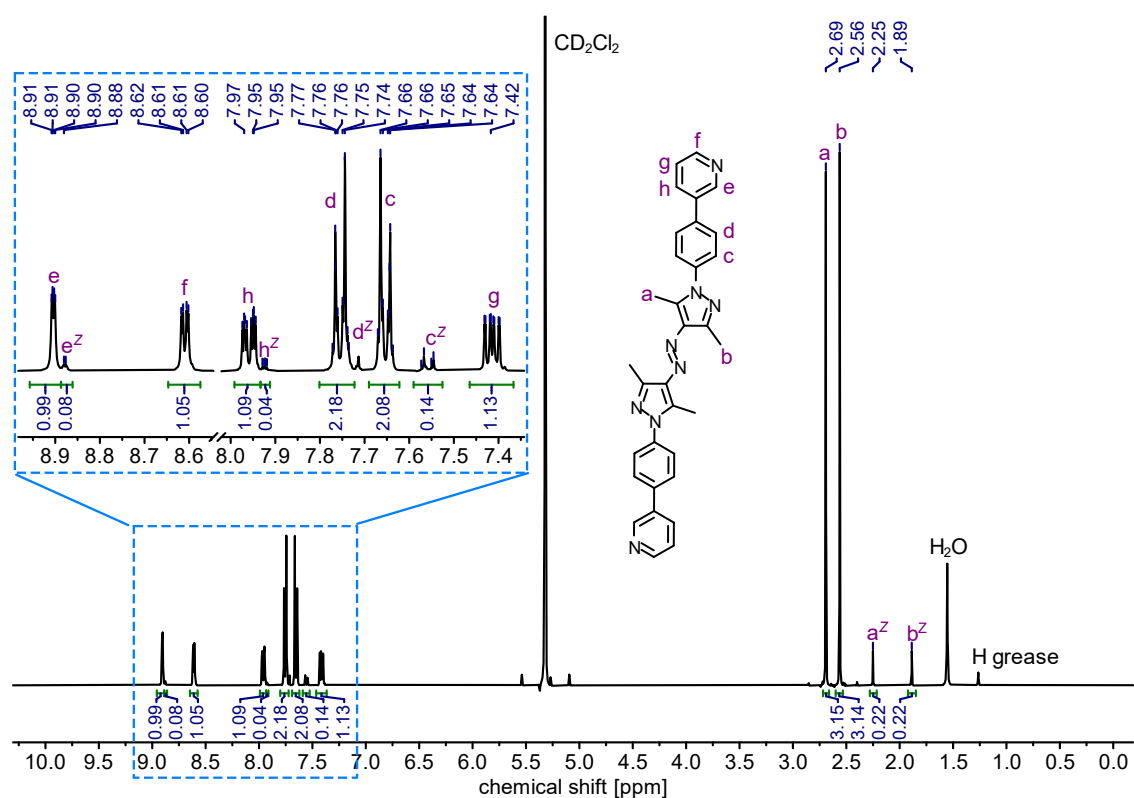


Figure S5. ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of ligand **1**. Signals with a ^{Z} represent Z-1 (92:8, E:Z).

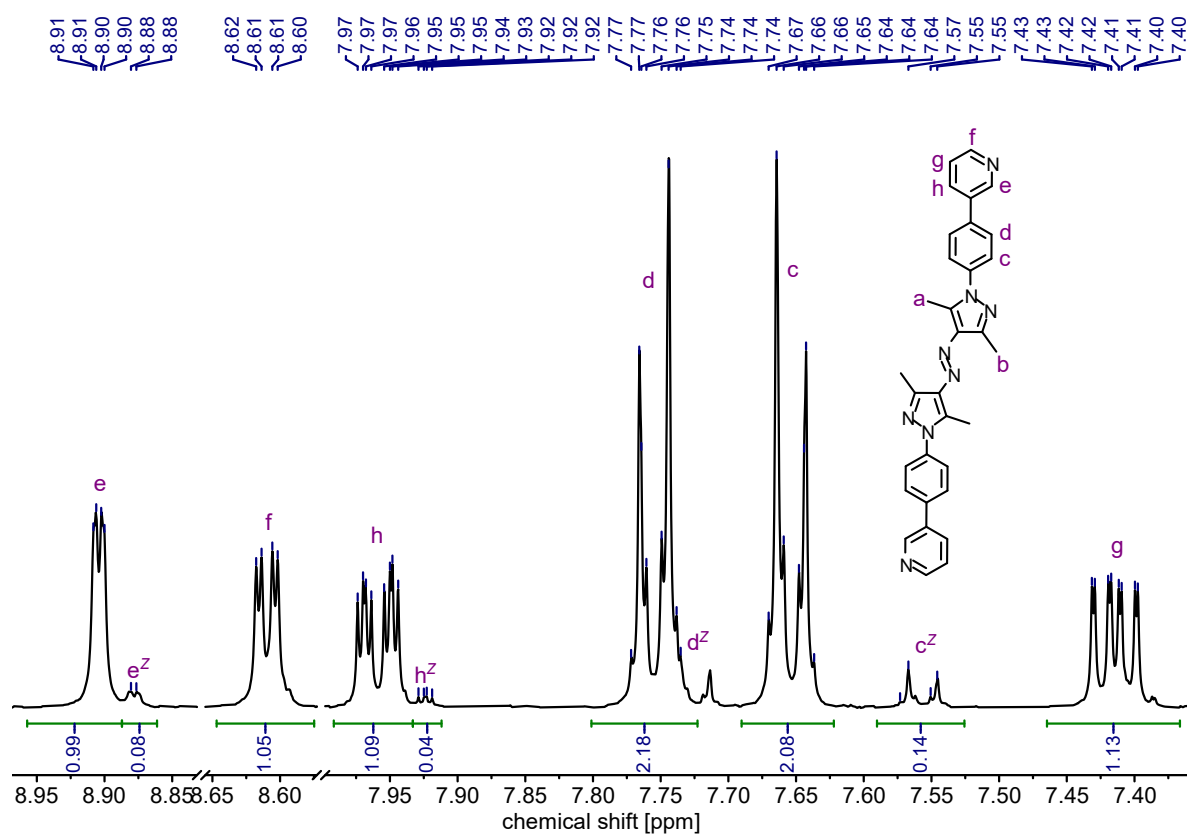


Figure S6. Partial ^1H NMR spectrum (400 MHz, CD_2Cl_2 , 298 K) of ligand **1**. Signals with a ^{Z} represent Z-1 (92:8, E:Z).

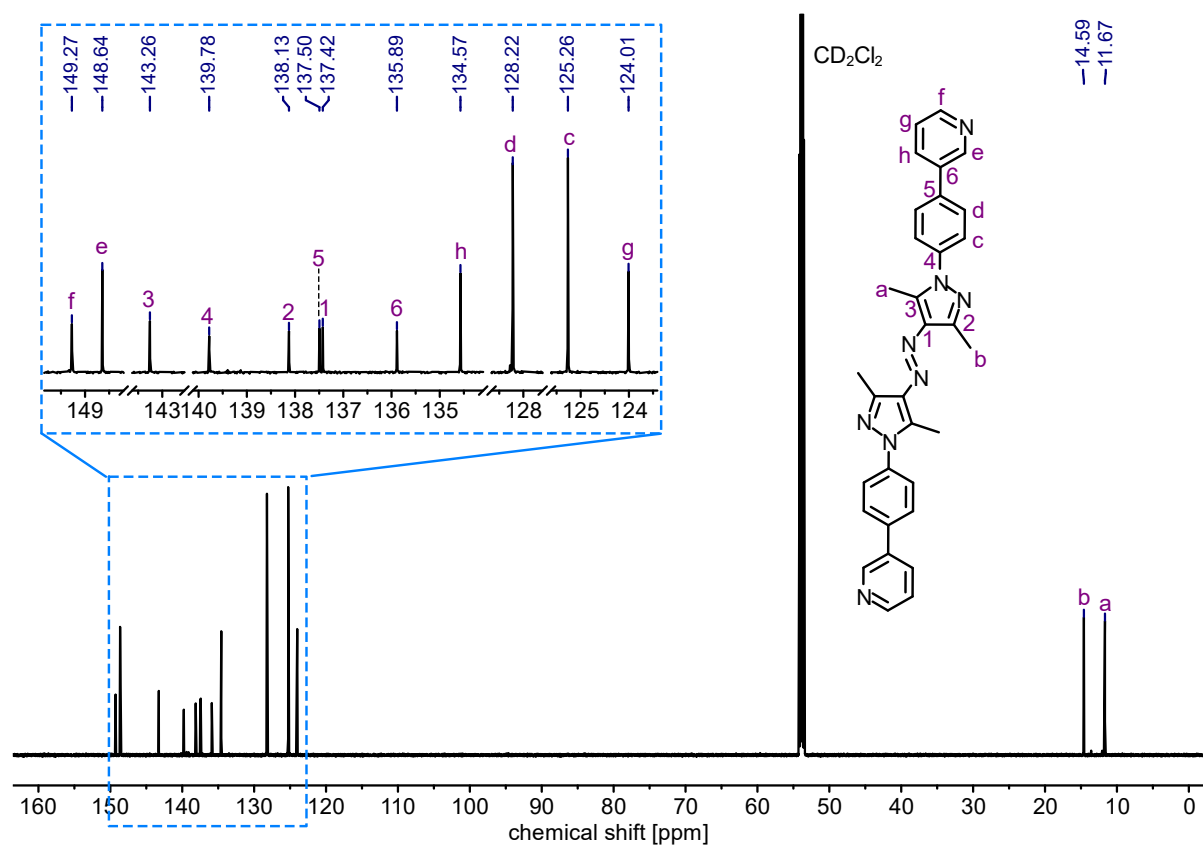


Figure S7. ^{13}C NMR spectrum (176 MHz, CD_2Cl_2 , 298 K) of ligand **1**.

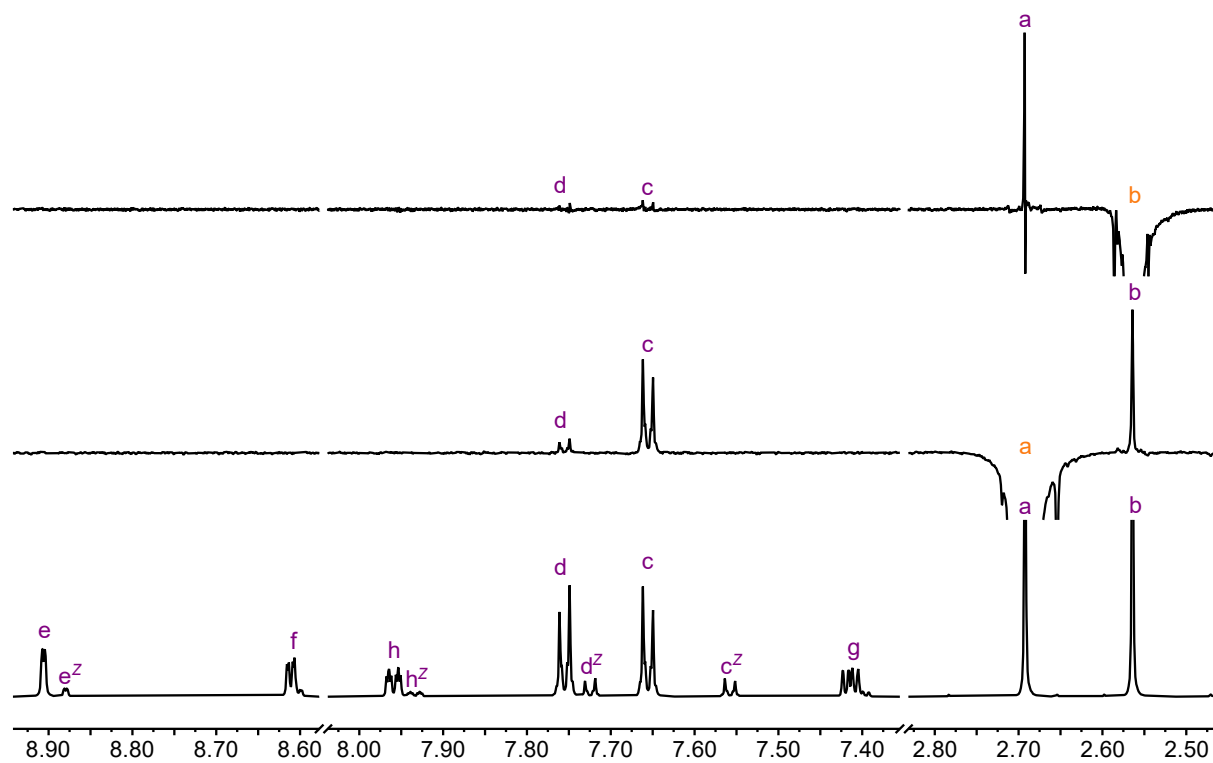


Figure S8. One-dimensional ^1H -ROESY NMR spectra (700 MHz, CD_2Cl_2 , 298 K) of *E*-**1** for signals H-a, and H-b. Signals with a ^Z represent *Z*-**1** (85:15, *E*:*Z*).

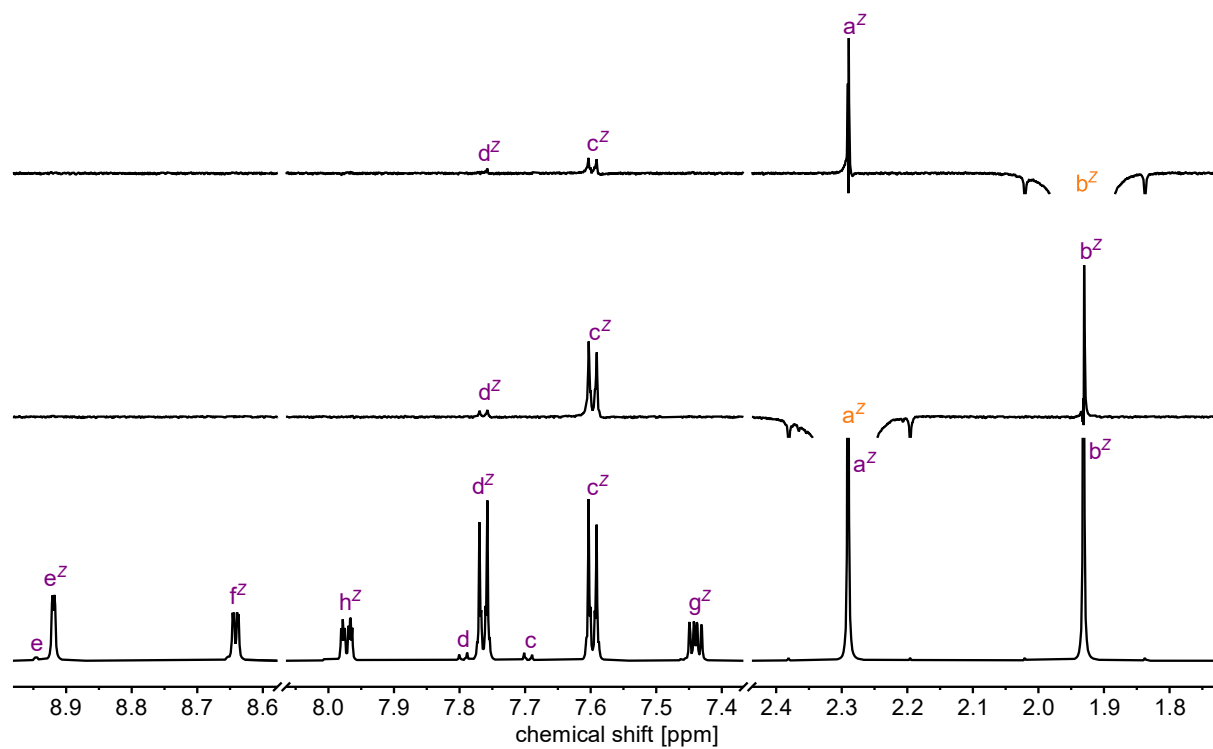


Figure S9. One-dimensional ^1H -ROESY NMR spectra (700 MHz, CD_2Cl_2 , 298 K) of **Z-1** for signals H- a^Z , and H- b^Z . Signals with a^Z represent **Z-1** (5:95, *E:Z*).

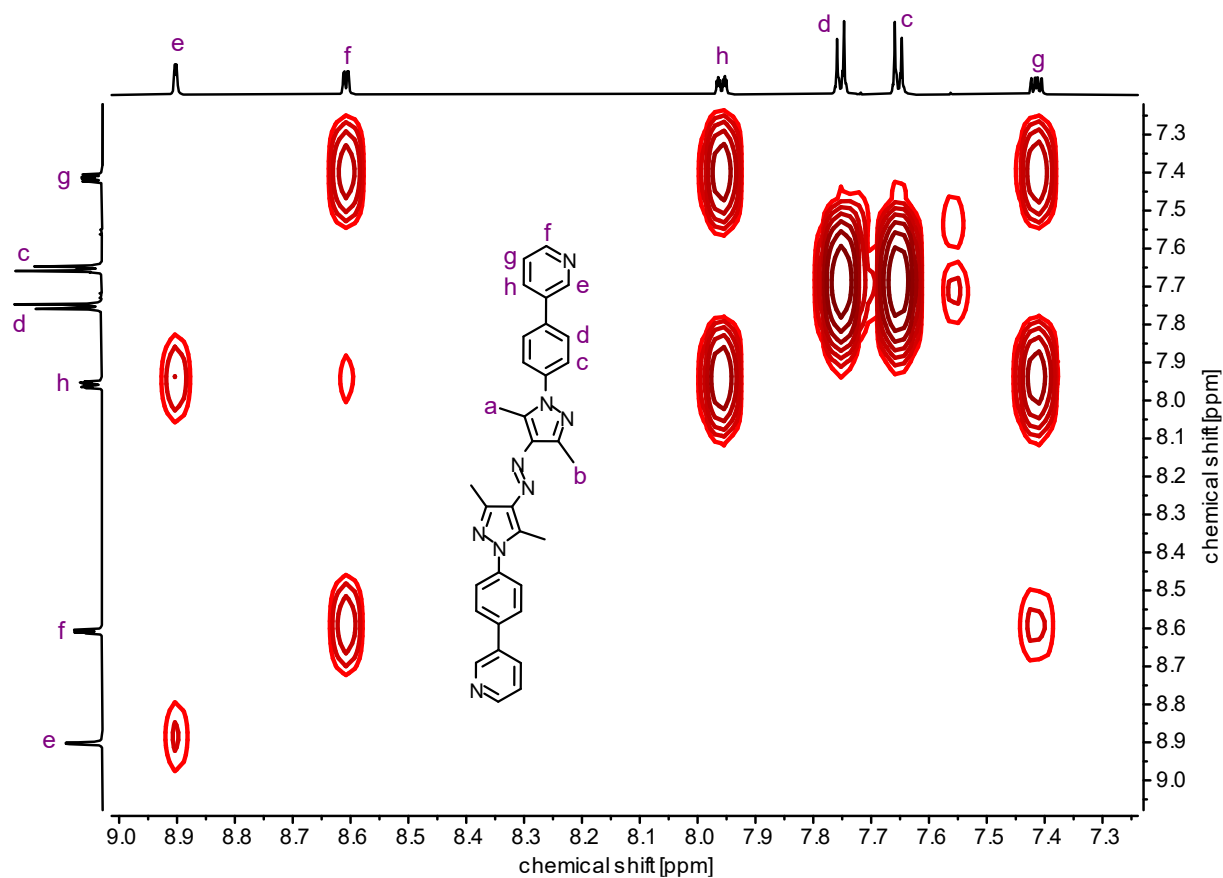


Figure S10. ^1H , ^1H COSY NMR spectrum (700 MHz, CD_2Cl_2 , 298 K) of ligand **1**.

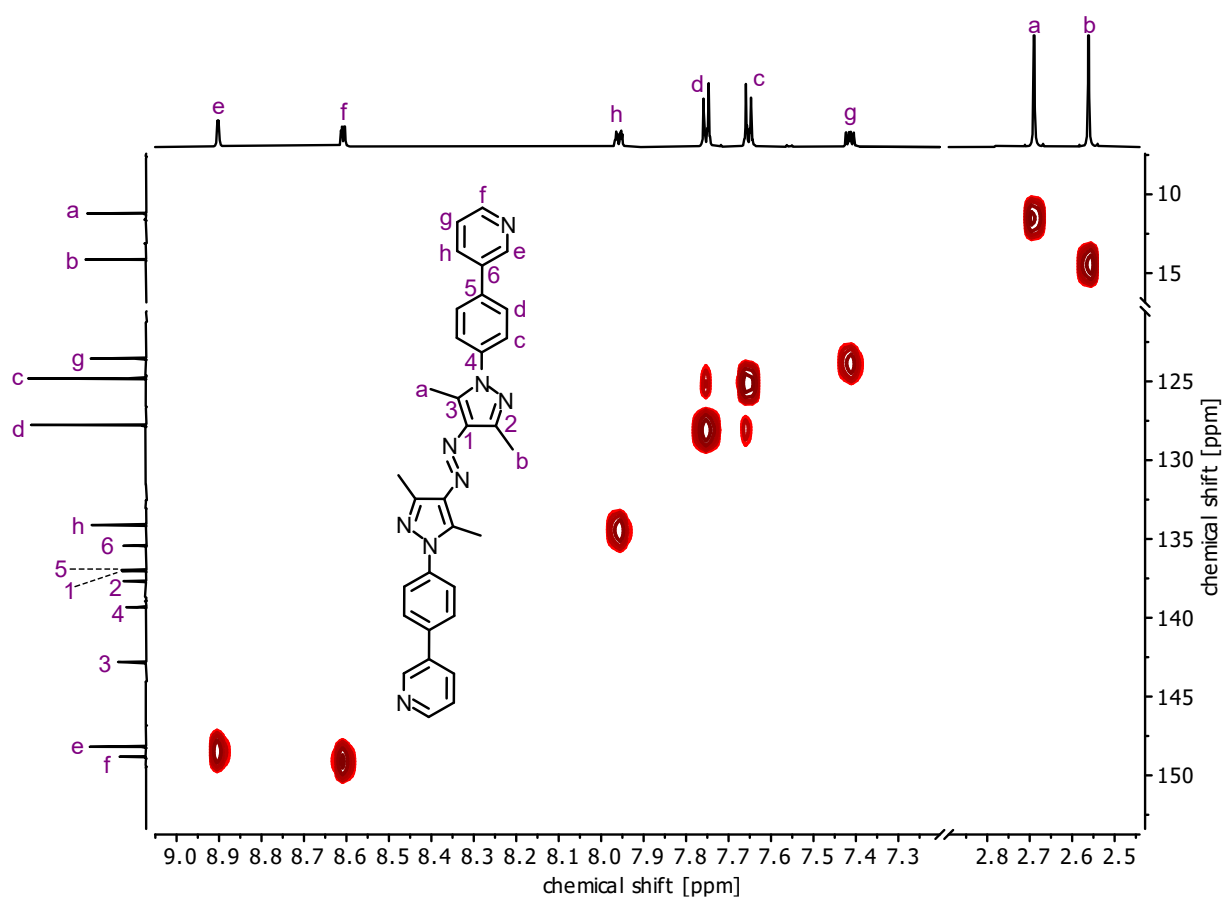


Figure S11. ^1H , ^{13}C HSQC NMR spectrum (700/176 MHz, CD_2Cl_2 , 298 K) of ligand **1**.

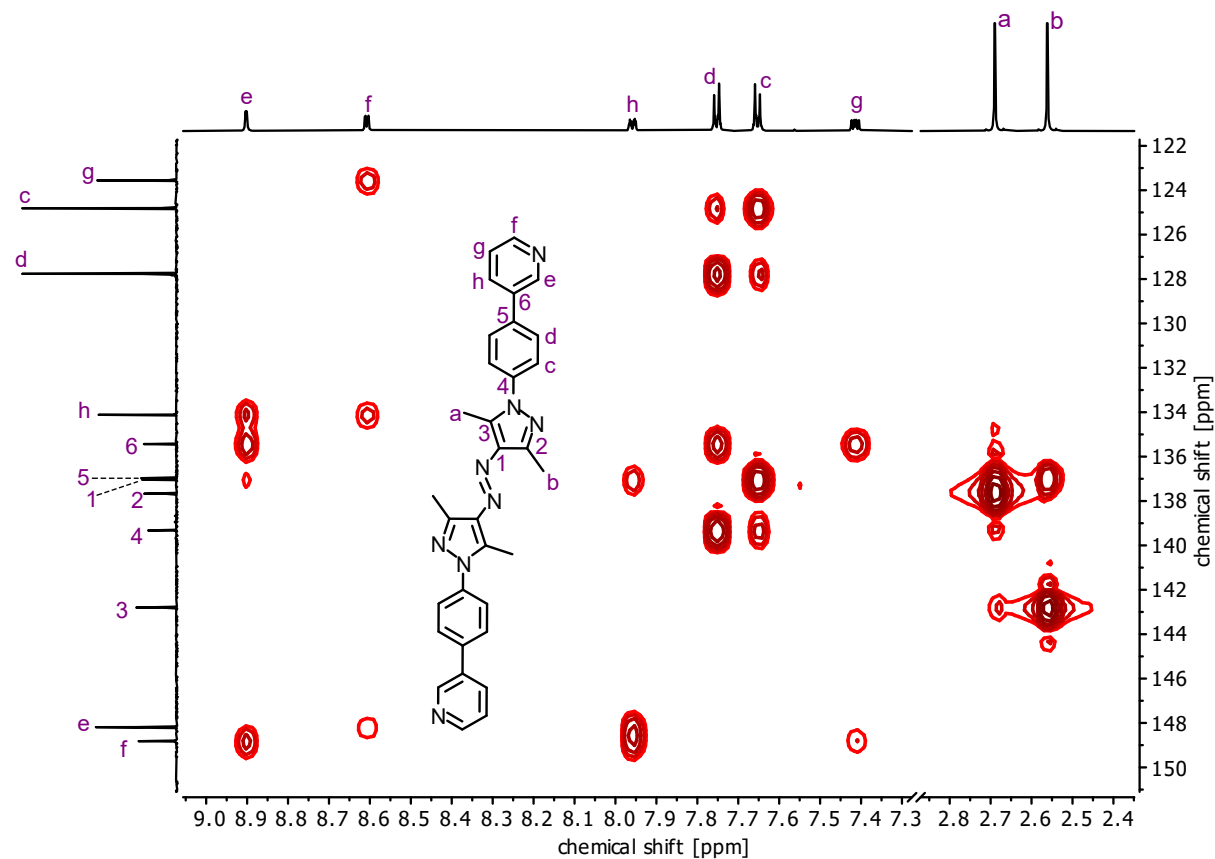
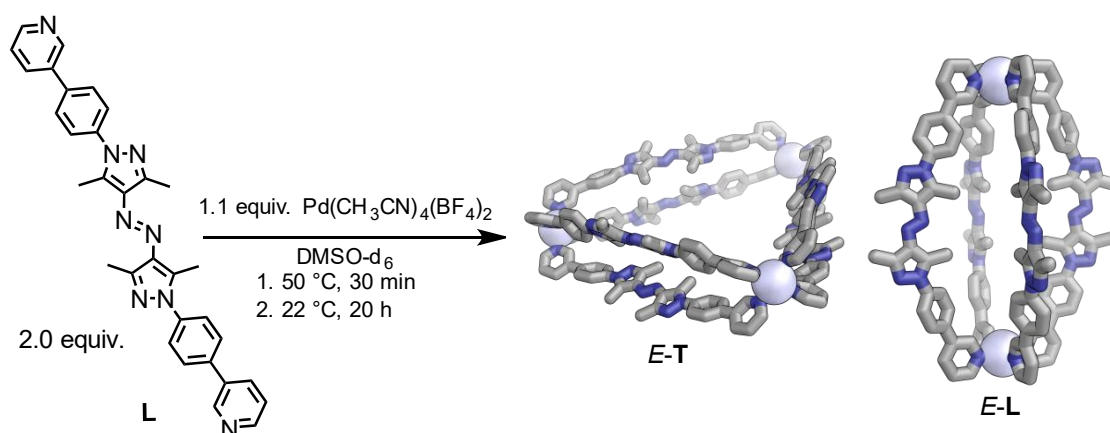


Figure S12. ^1H , ^{13}C HMBC NMR spectrum (700/176 MHz, CD_2Cl_2 , 298 K) of ligand **1**.

S2.6 Self-assembly of the triangle *E-T* / lantern *E-L* mixture



Ligand **1** (2.53 mg, 4.82 μmol , 2.0 equiv.) was suspended in $\text{DMSO-}d_6$ (522 μL) and sonicated for 2 min. A solution of $\text{Pd}(\text{CH}_3\text{CN})_4(\text{BF}_4)_2$ (77 μL , [**1**] = 8.0 mM, 1.18 mg, 2.65 μmol , 1.1 equiv.) in $\text{DMSO-}d_6$ was added and the mixture was stirred at 50 °C for 30 min. The reaction mixture, initially observed as a turbid suspension, became a clear yellow solution after 5 min at 50 °C. The resulting complex solution was then left to equilibrate at 22 °C for a minimum of 6 h (usually overnight, approx. 20 h), resulting in a 78:22 *E-T* / *E-L* mixture.

In some instances, additional minor signals were observed in ^1H NMR (Figure S15). However, no other Pd species (e.g., Pd_4L_8) nor partially self-assembled structures (e.g., Pd_2L_5) were found in the ESI mass spectrum, which led us to tentatively assume that these minor signals correspond to different lantern *E-L* isomers (Figure S24 and Section S8.4). It was possible to reproducibly reduce the signals of these lantern *E-L* isomers by irradiating the sample with 365 nm light for 10 min (forming *Z-L*) and immediately heat it to 85 °C for 6 h. After allowing the mixture to cool to room temperature and equilibrate overnight (approx. 20 h), ^1H NMR revealed a clean 78:22 *E-T* / *E-L* mixture.

For more details on the equilibrium between *E-T* and *E-L*, see Section S3.

$[\text{Pd}_3(\text{C}_{32}\text{H}_{28}\text{N}_8)_6](\text{BF}_4)_6$ 3987.82 g/mol

$[\text{Pd}_2(\text{C}_{32}\text{H}_{28}\text{N}_8)_4](\text{BF}_4)_4$ 2658.54 g/mol

¹H NMR^{†,‡} (500 MHz, DMSO-*d*₆, 298 K) δ_{H} [ppm] = 2.35 (s, 3H, H-b^T), 2.45 (s, 3H, H-b^L), 2.77 (s, 3H, H-a^L)[‡], 7.67z – 7.79 (m, 4H, H-c^T, d^T), 7.82 – 7.98 (m, 6H, H-g^T, g^L, c^L, d^L), 8.44 (s, 1H, H-h^T), 8.46 (s, 1H, H-h^L), 9.36 (d, *J* = 6.6 Hz, 1H, H-f^T), 9.43 (d, *J* = 7.2 Hz, 1H, H-f^L), 9.77 (d, *J* = 2.4 Hz, 1H, H-e^L), 9.87 (s, 1H, H-e^T).

¹³C NMR[§] (176 MHz, DMSO-*d*₆, 298 K) δ_{C} [ppm] = 10.3 (C-a^T), 11.8 (C-a^L), 13.2 (C-b^L), 15.1 (C-b^T), 118.1, 124.6 (C-c^T/d^T), 125.1 (C-g^T/g^L/c^L/d^L), 128.1 (C-g^T/g^L/c^L/d^L), 128.3 (C-c^T/d^T), 136.5, 139.8, 140.3, 140.5, 148.3 (C-e^T), 144.8, 149.2 (C-e^L), 149.7 (C-f^L), 149.9 (C-f^T).

¹⁹F NMR (470 MHz, DMSO-*d*₆, 298 K) δ_{F} [ppm] = -148.24, -148.18.

HRMS (ESI⁺, DMSO-*d*₆/CH₃CN, 298 K): *m/z* (relative intensity) = 542.2474 (15%, [**1**]⁺, calcd 542.2431), 577.7012 (100%, [**T** – 6 BF₄]⁶⁺ and [**L** – 4 BF₄]⁴⁺, calcd 577.6962), 710.6426 (20%, [**T** – 5 BF₄]⁵⁺, calcd 710.6363), 799.2692 (22%, [**L** – 3 BF₄]³⁺, calcd 799.2630), 909.8038 (10%, [**T** – 4 BF₄]⁴⁺, calcd 910.0465), 1242.4077 (8%, [**T** – 3 BF₄]³⁺ and [**L** – 2 BF₄]²⁺, calcd 1242.3966).

[†] The ¹H and ¹³C signals corresponding to *E*-**T** and *E*-**L** are depicted with a T and an L, respectively. One dimensional ¹H-ROESY spectra enabled the assignment of H-a^T, H-b^T, H-a^L, and H-b^L (Figure S19).

[‡] The H-a^T singlet is underneath the DMSO-*d*₆ signal and can only be observed at higher temperatures, see Section S3.4.

[§] Not all ¹³C signals could be assigned unambiguously. C-H couplings for C-e^T, C-e^L, C-f^L, and C-f^T could be observed in the HSQC (Figure S22). However, individual signals could not be observed in the ¹³C NMR (Figure S16).

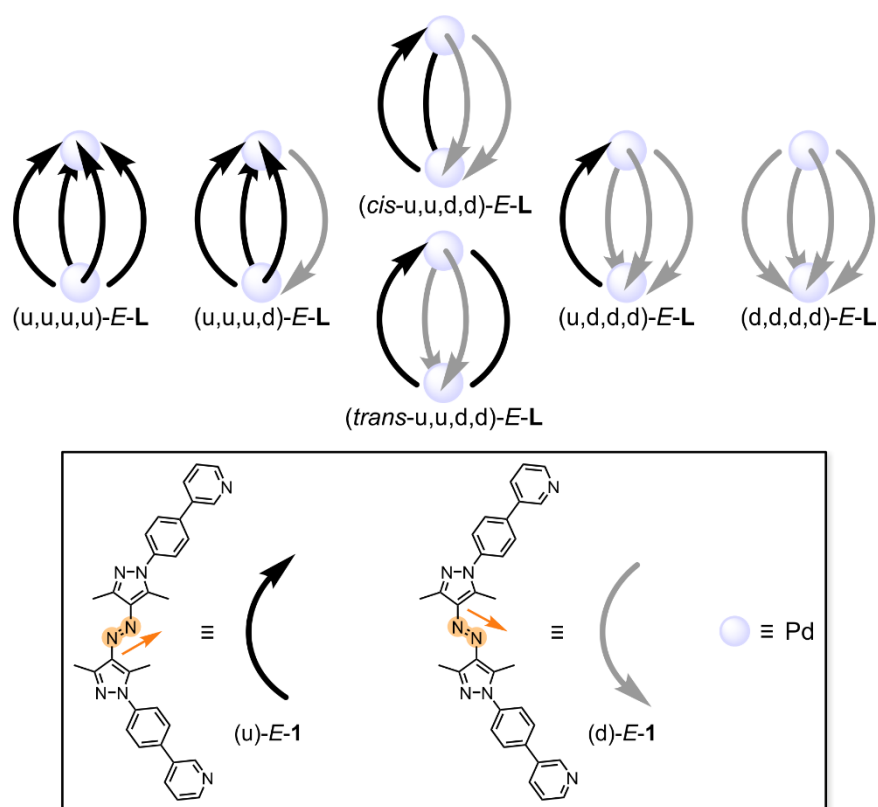


Figure S13. Cartoon representations of the six different possible isomers of *E-L*: $(u,u,u,u)-E-L$ and its enantiomer $(d,d,d,d)-E-L$, $(u,u,u,d)-E-L$ and its enantiomer $(u,d,d,d)-E-L$, $(cis-u,u,d,d)-E-L$, and $(trans-u,u,d,d)-E-L$. Ligand orientations are labelled “up” (u) and “down” (d), respectively, with respect to the orientations of the azo groups: If the $N=N$ double bond of the azo bridge tilts slightly upward and points into the concave side of the ligand (orange arrow), a ligand is assigned the “up” (u) orientation (black curved arrow); if it tilts slightly downward and points into the concave side of the ligand (orange arrow), it is assigned the “down” (d) orientation (grey curved arrow). Computations of these isomers are detailed in Section S8.4. Note that the X-ray crystal structure showed the $(cis-u,u,d,d)-E-L$ isomer (Section S7).

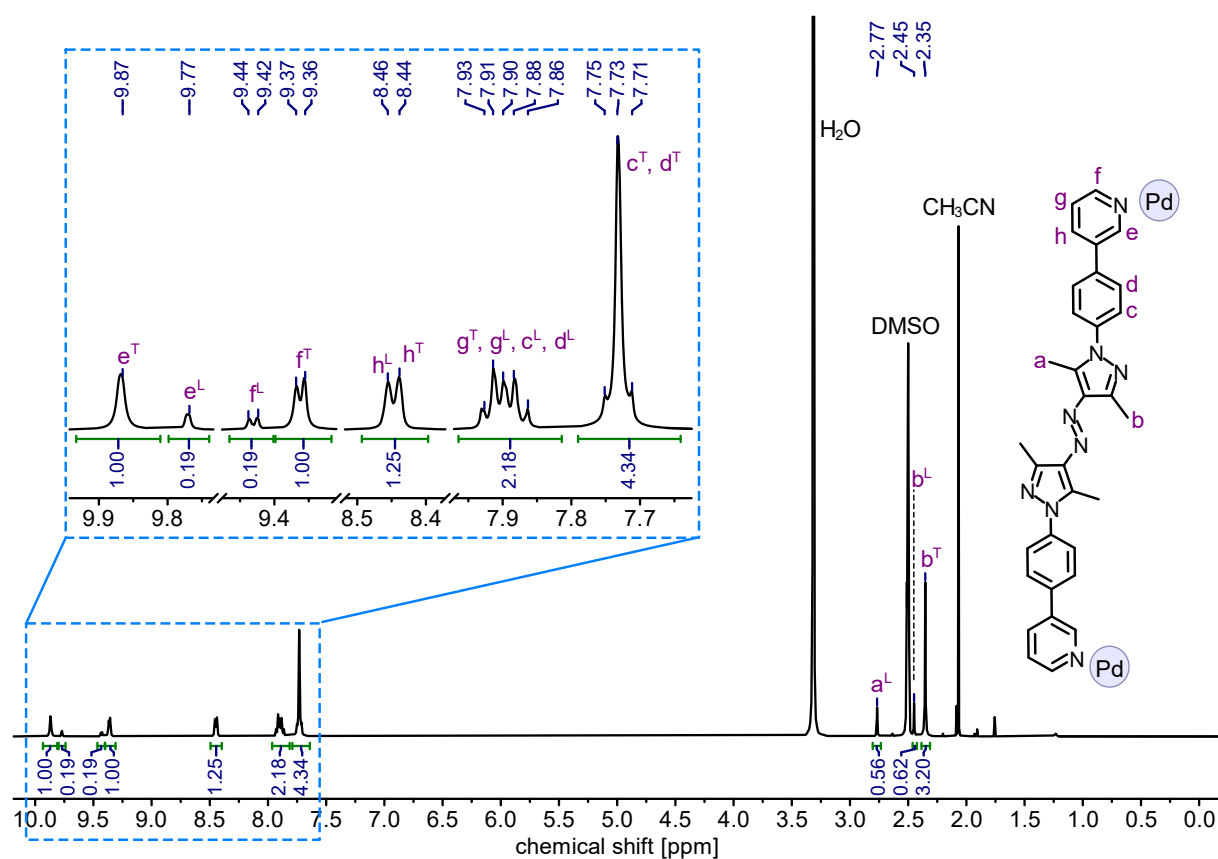


Figure S14. ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$, 298 K) of 78% *E*-T (denoted as T) and 22% *E*-L (denoted as L).

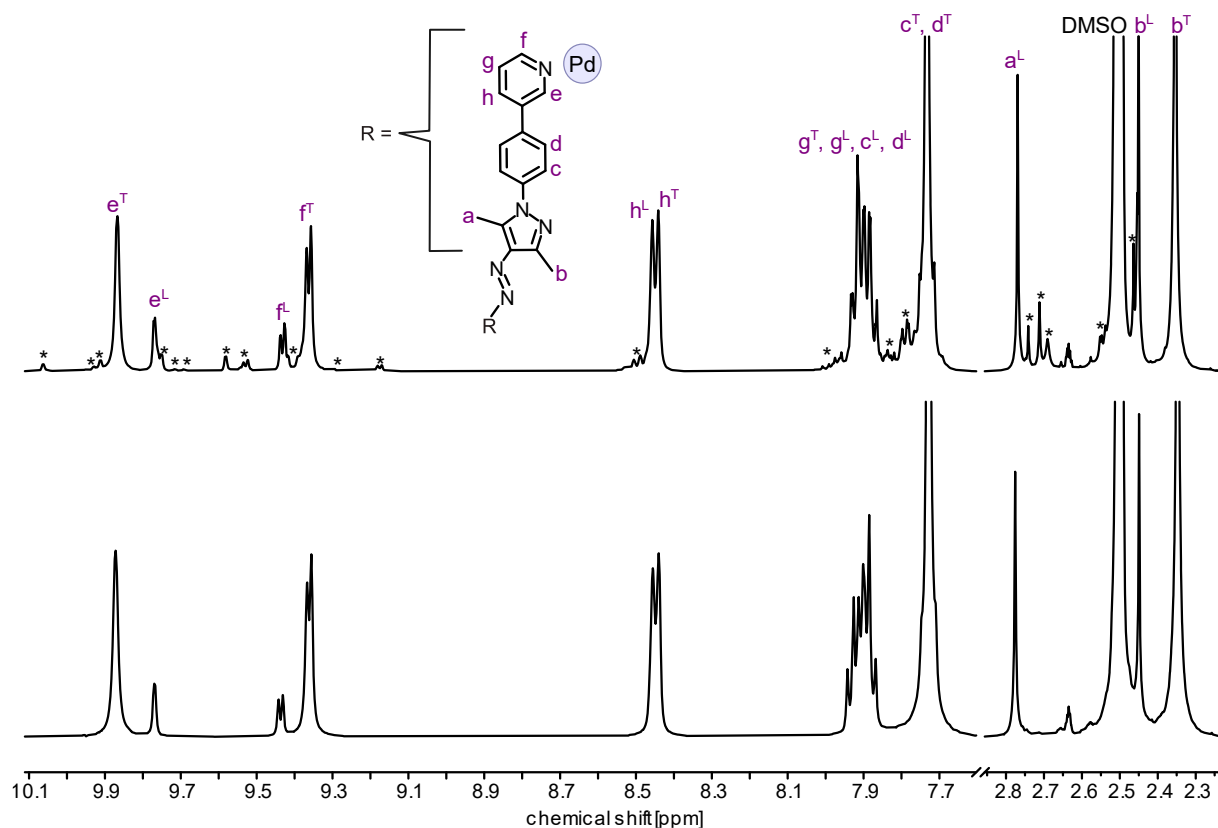


Figure S15. ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$, 298 K) of 78% *E*-T (denoted as T) and 22% *E*-L (denoted as L) before (top) and after (bottom) "clean up". Minor species highlighted with an asterisk.

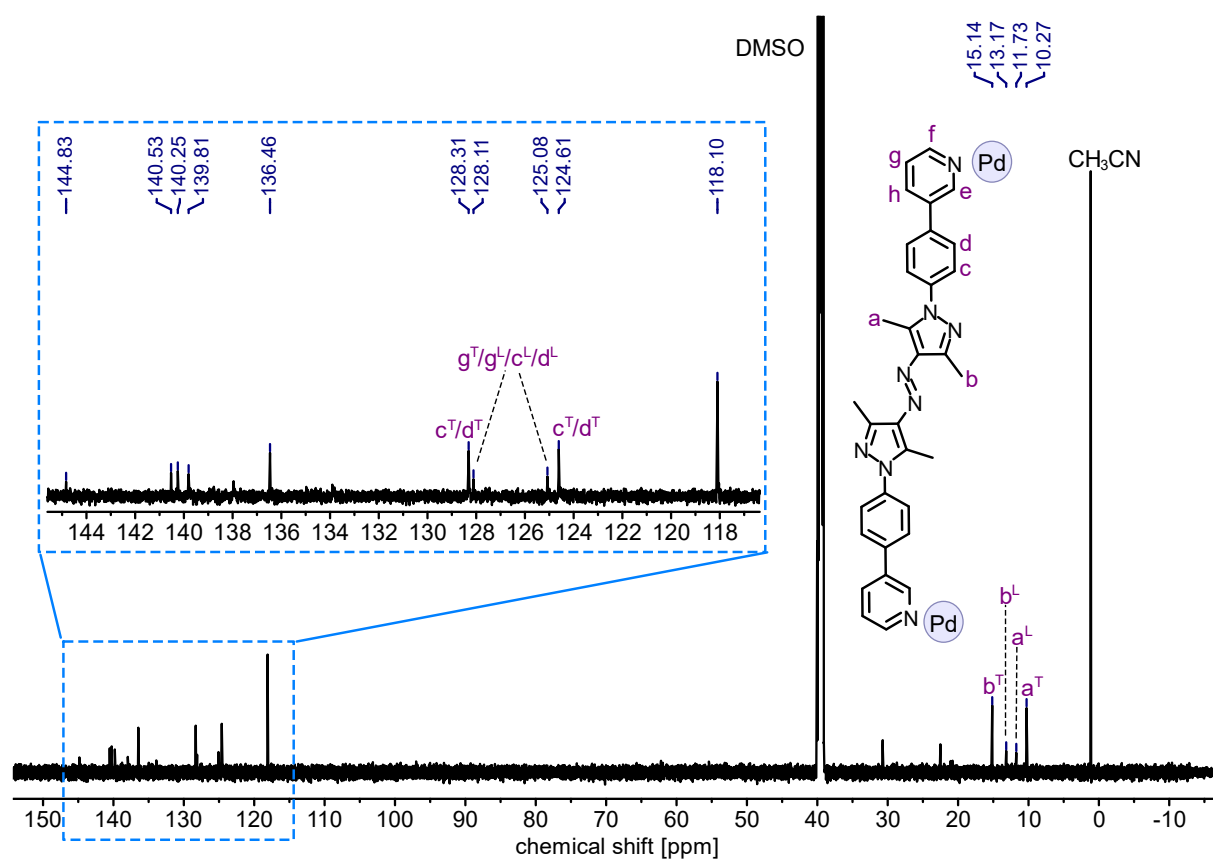


Figure S16. ¹³C NMR spectrum (176 MHz, DMSO-*d*₆, 298 K) of 78% *E*-T (denoted as T) and 22% *E*-L (denoted as L).

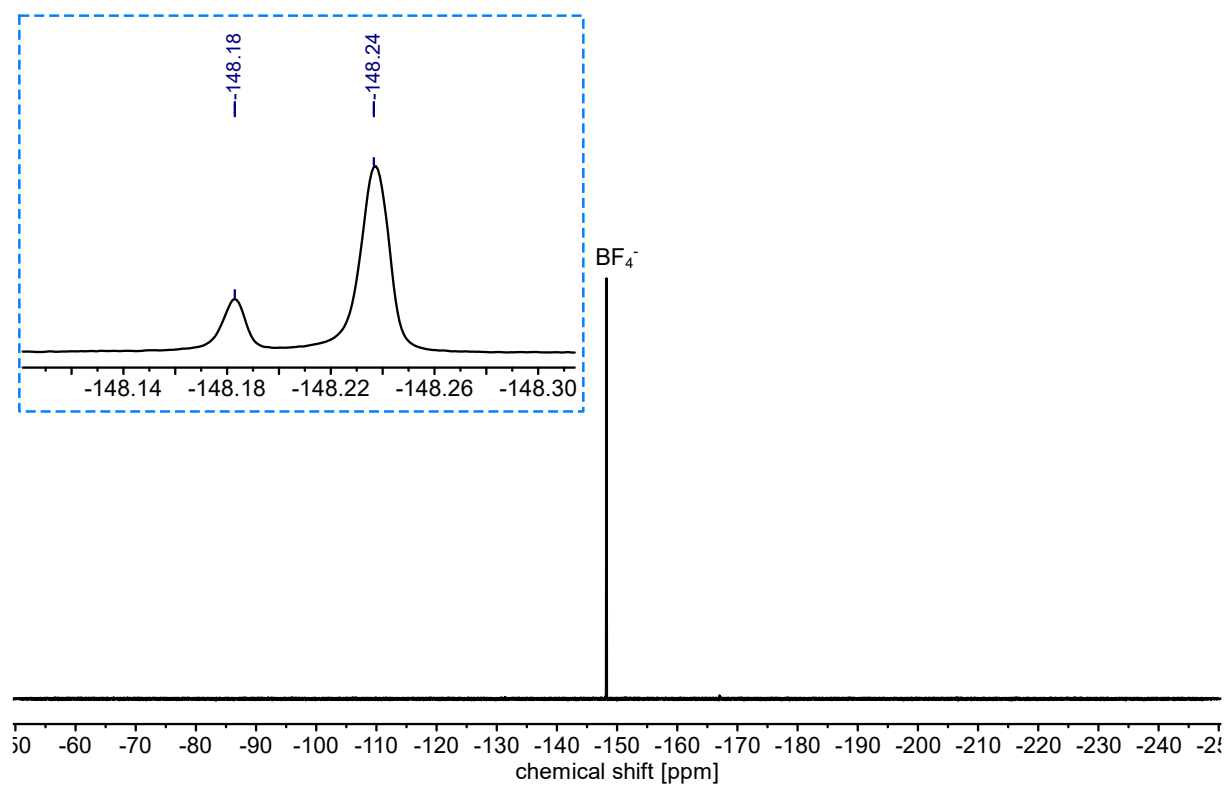


Figure S17. ¹⁹F NMR spectrum (470 MHz, DMSO-*d*₆, 298 K) of 78% *E*-T and 22% *E*-L showing the presence of only one anion environment (the two separate signals arise from the ¹⁰B and ¹¹B isotopomers).

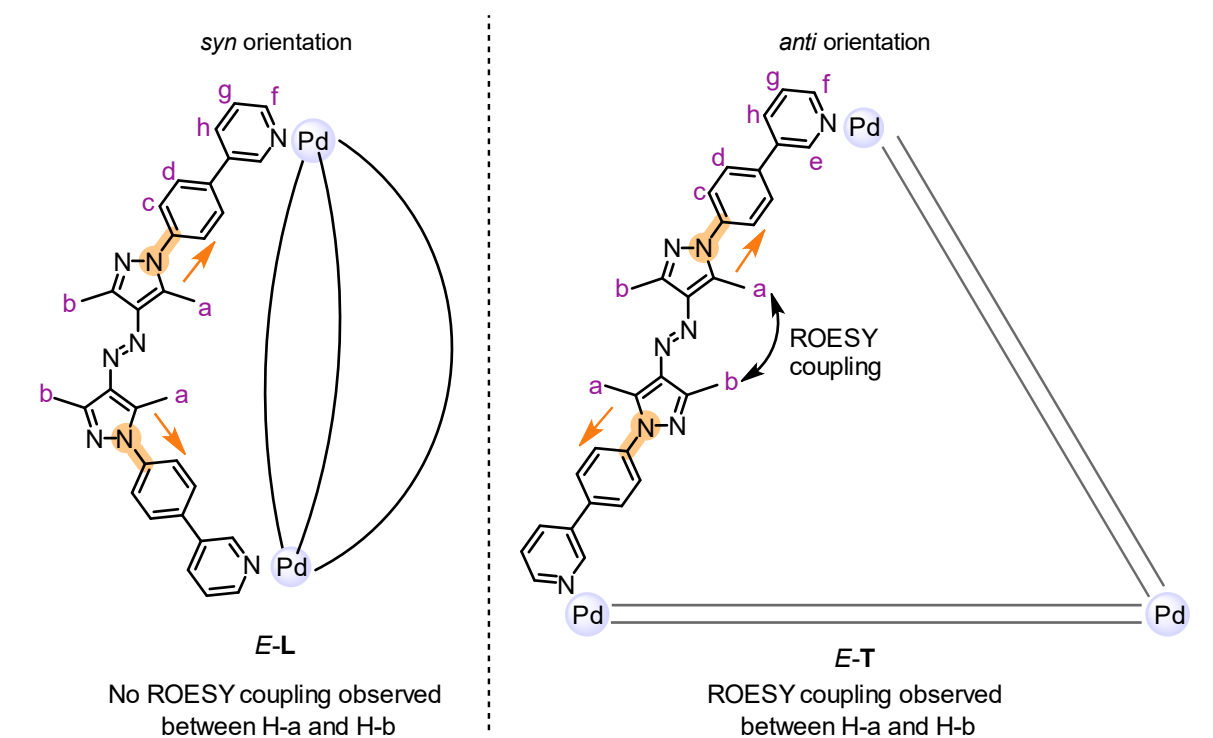


Figure S18. Graphical representation of the *syn* and *anti*-conformers of ligand **1** conformers within *E-L* and *E-T*, respectively. H-a and H-b only show ROESY contacts in the *anti*-conformation present in *E-T*.

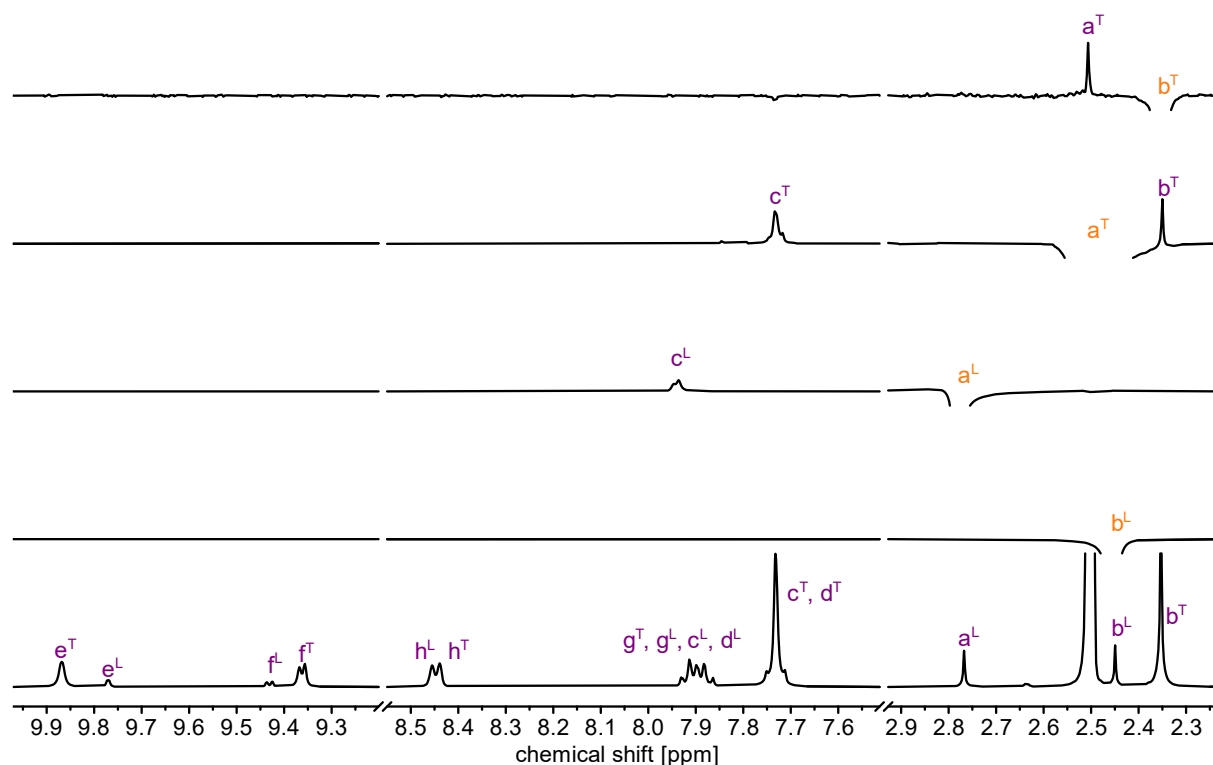


Figure S19. One-dimensional ¹H ROESY NMR spectra (700 MHz, DMSO-*d*₆, 298 K) of 78% *E-T* (denoted with T) and 22% *E-L* (denoted with L) for signals H-a^L, H-b^L, H-a^T, and H-b^T. Clear couplings between H-a^T and H-b^T confirm ligand **1**'s *anti*-conformation within *E-T*. As expected for the *syn*-conformation of ligand **1** in *E-L*, no cross peaks were observed for H-a^L and H-b^L.

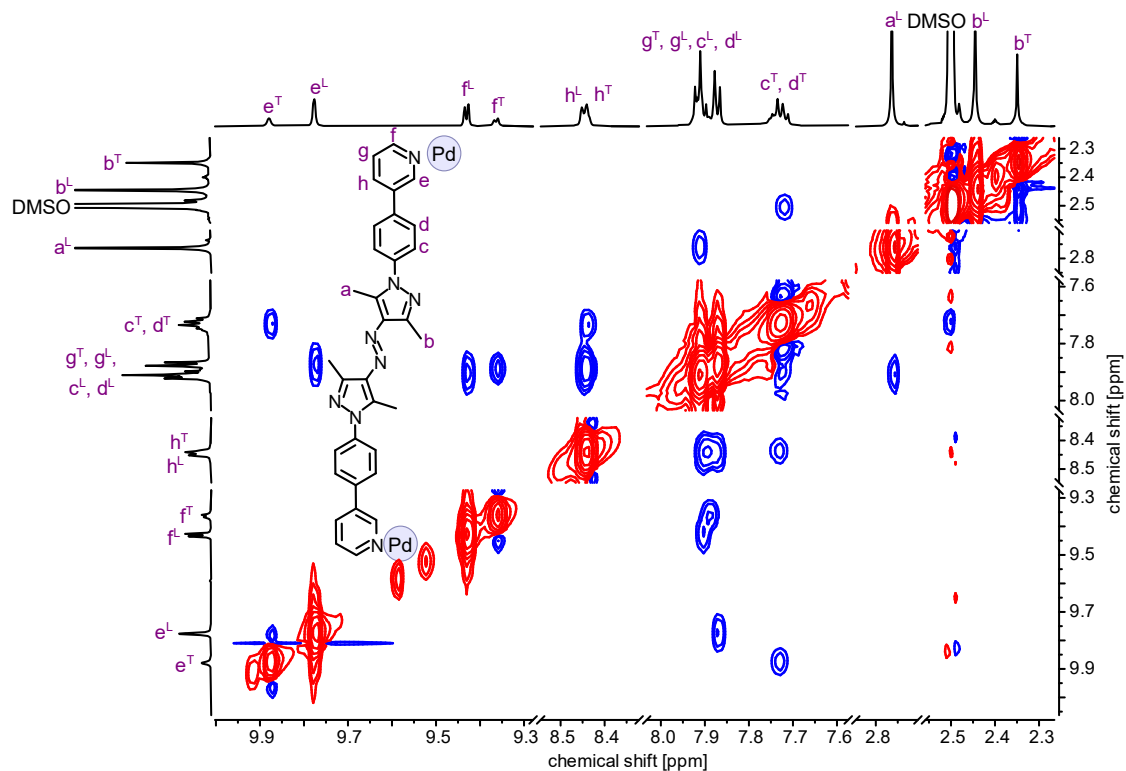


Figure S20. $^1\text{H},^1\text{H}$ ROESY NMR spectrum (700 MHz, $\text{DMSO}-d_6$, 298 K) of 24% *E*-**T** (denoted as T) and 76% *E*-**L** (denoted as L). This mixture enriched with *E*-**L** was obtained by irradiating *Z*-**L** with 500 nm light and measuring the resulting spectrum immediately afterwards. This was necessary to obtain sufficiently intense signals of *E*-**L**, which helped with the proton assignment of *E*-**T** and *E*-**L**. As expected for the *syn*-conformation of ligand **1** in *E*-**L**, no cross peaks were observed for $\text{H}-a^{\text{L}}$ and $\text{H}-b^{\text{L}}$.

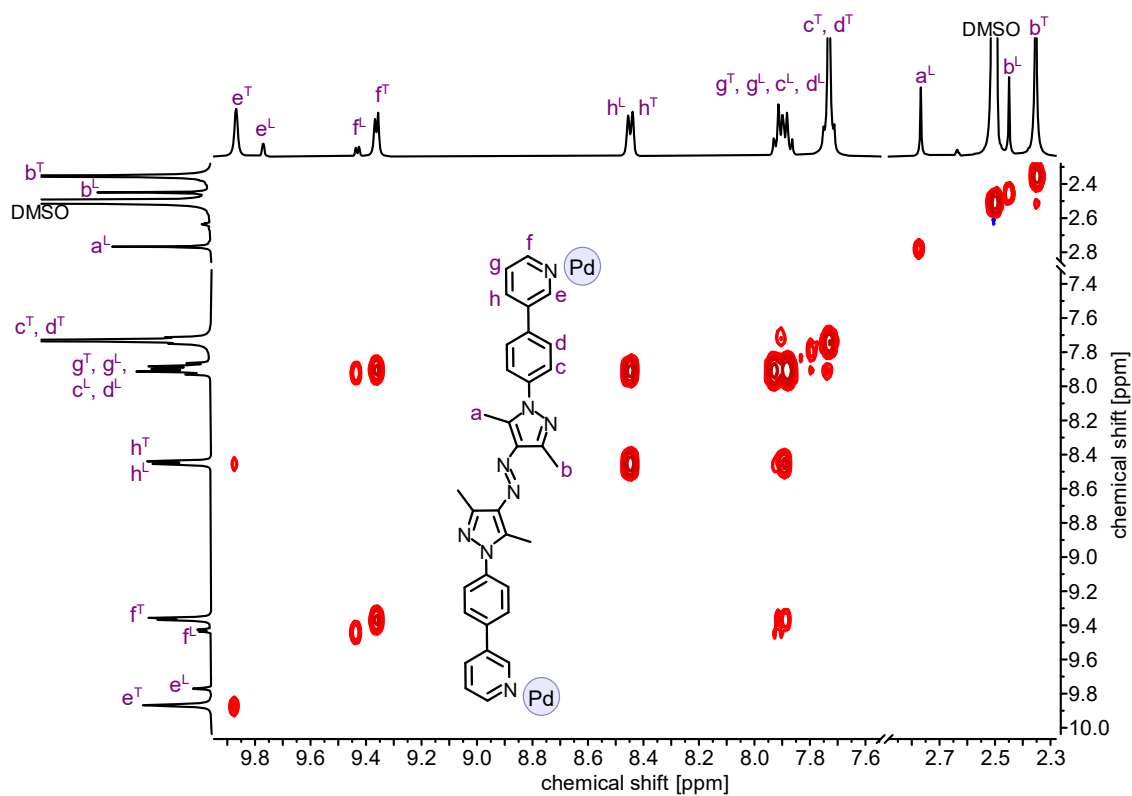


Figure S21. $^1\text{H}, ^1\text{H}$ COSY NMR spectrum (700 MHz, $\text{DMSO}-d_6$, 298 K) of 78% *E-T* (denoted with T) and 22% *E-L* (denoted with L).

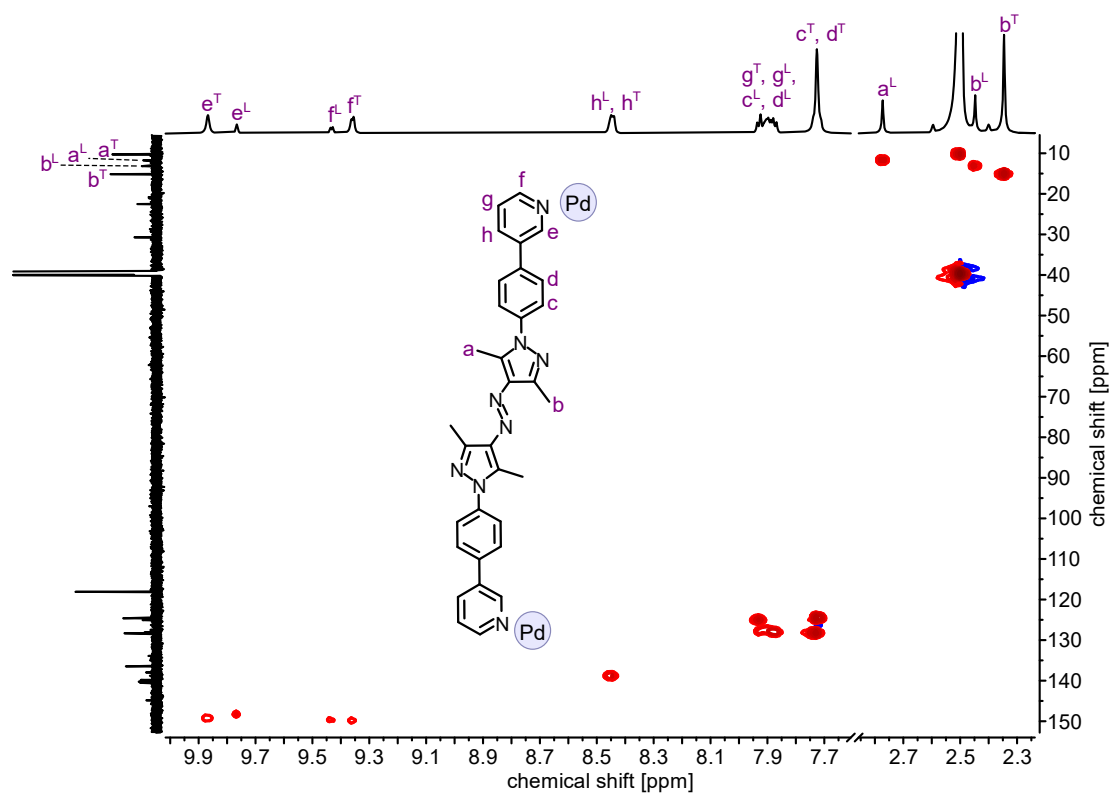


Figure S22. $^1\text{H}, ^{13}\text{C}$ HSQC NMR spectrum (700/176 MHz, $\text{DMSO}-d_6$, 298 K) of 78% *E-T* (denoted with T) and 22% *E-L* (denoted with L).

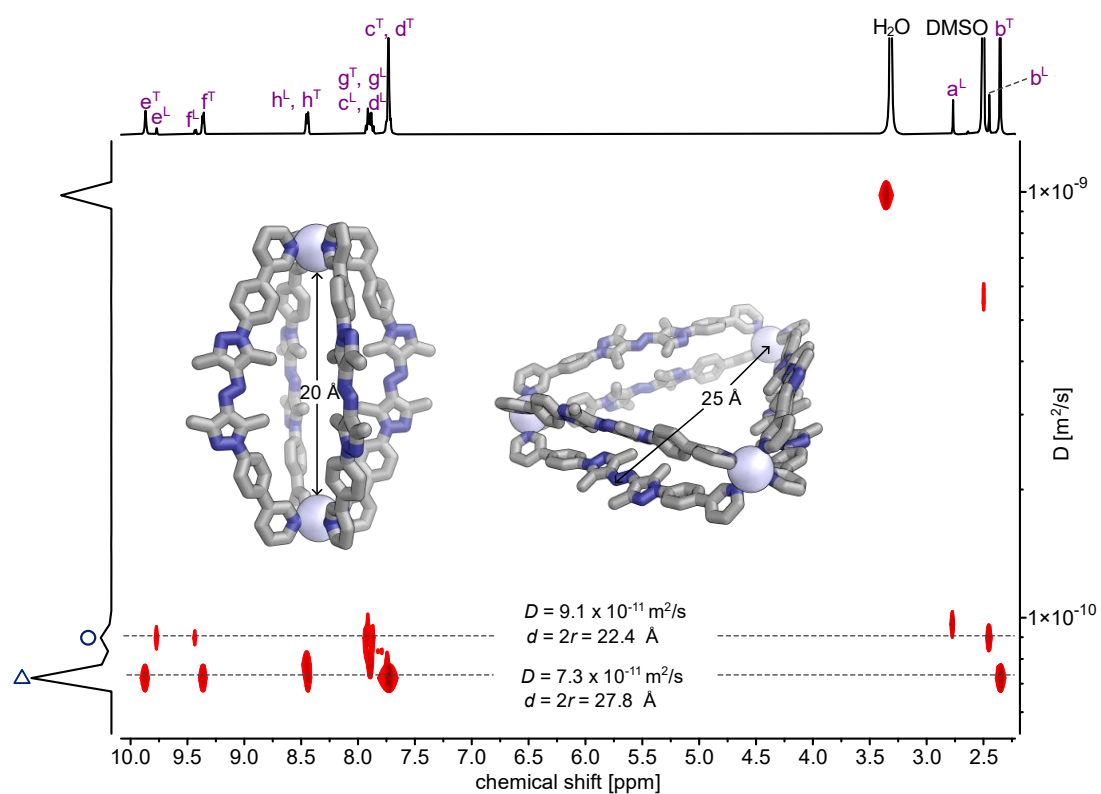


Figure S23. 2D-DOSY NMR spectrum (700 MHz, DMSO- d_6 , 298 K, D20 = 0.35 s) of 78% *E*-T (denoted with T) and 22% *E*-L (denoted with L). Calculated diffusion constants (D) and solvodynamic diameters ($d = 2r$) for each complex are depicted in the spectrum. The crystal structure of *E*-L and the GFN2-xTB structure of *E*-T are shown with their respective distances (Pd – Pd and Pd – N_{azo}) as calculated by Avogadro (Version 1.2.0).²

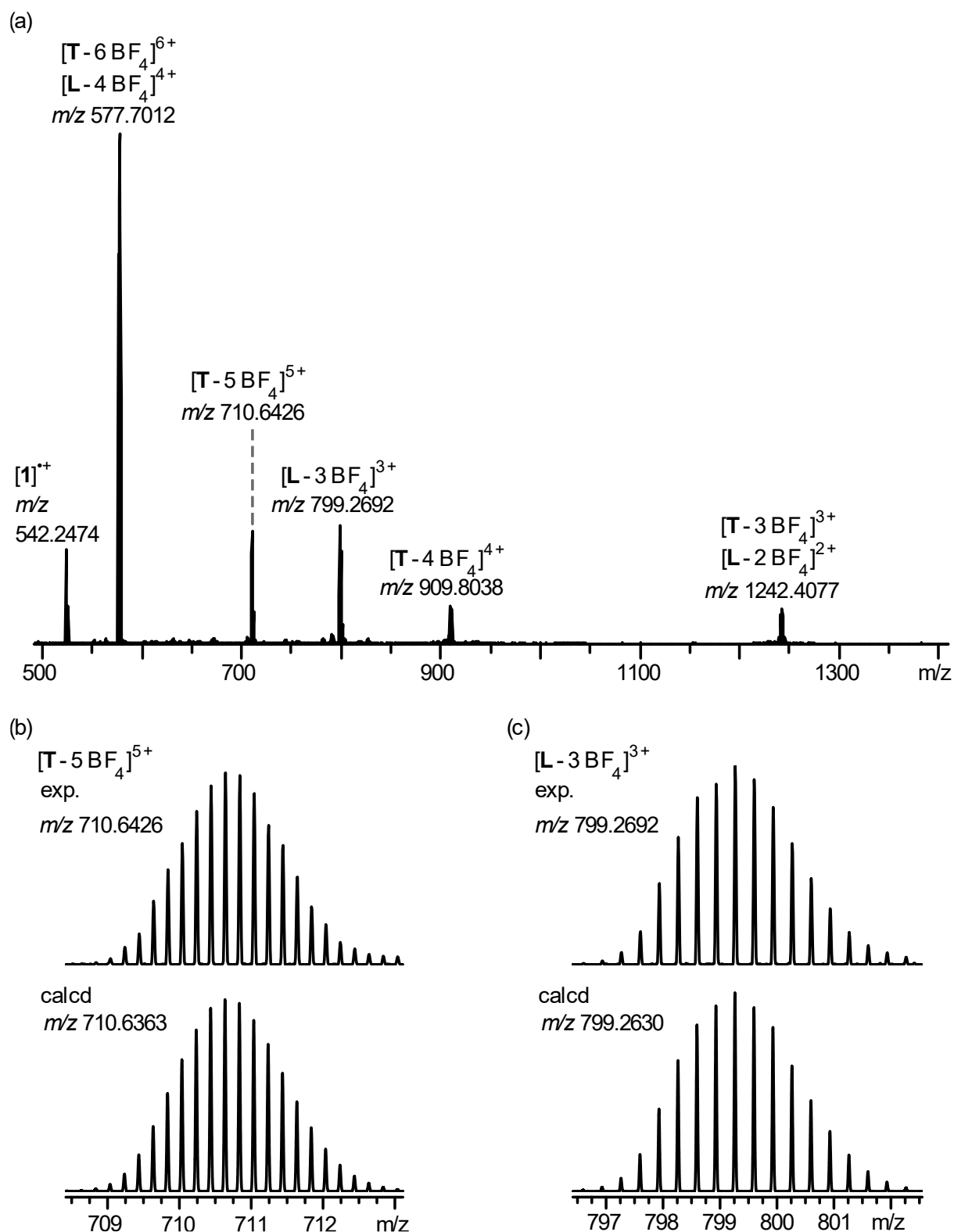
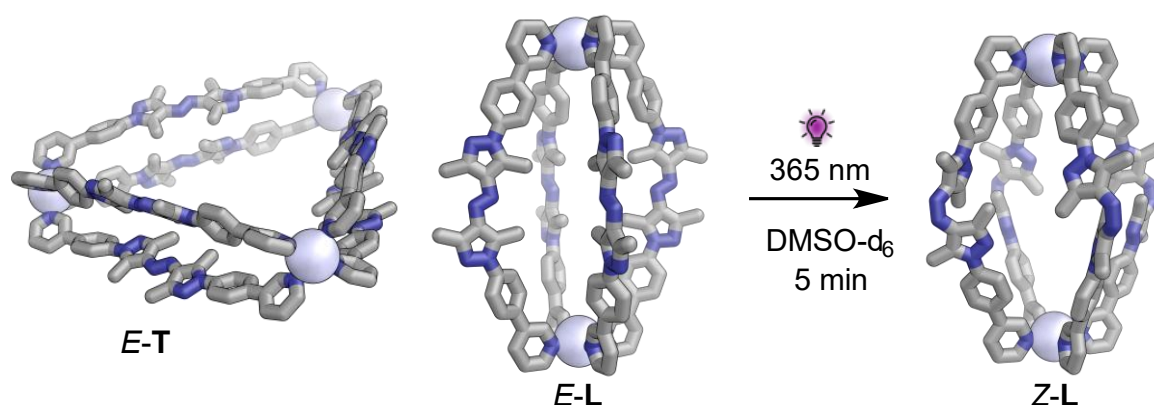


Figure S24. (a) High-resolution ESI⁺ mass spectrum (DMSO/CH₃CN) of *E*-T and *E*-L. Experimental and calculated isotope patterns of (b) $[\text{T}-5\text{BF}_4]^{5+}$ and (c) $[\text{L}-3\text{BF}_4]^{3+}$.

S2.7 Formation of Z-L



The previously prepared 78:22 triangle *E-T* / lantern *E-L* mixture (8.0 mM, 0.6 mL) was irradiated with 365 nm light for 5 min, and complete conversion to *Z-L* was achieved. A slight colour change from yellow to dark yellow/orange was observed upon irradiation. The sample was then kept in an amberised NMR tube wrapped in aluminium foil to avoid any *Z*→*E* isomerisation under ambient light.

Additional minor signals were observed in ¹H NMR (**Figure S27a**). However, no other Pd species (e.g., Pd₄L₈) nor partially self-assembled structures (e.g., Pd₂L₅) were found in the ESI mass spectrum, which led us to tentatively assume that these minor signals correspond to the five other lantern *Z-L* diastereomers, due to *Z-1* being chiral (**Figure S36** and Section S8.3).



¹H NMR** (500 MHz, DMSO-*d*₆, 298 K) δ_H [ppm] = 1.36 (s, 3H, H-b), 2.55 (s, 3H, H-a), 7.81 – 7.86 (m, 2H, H-c), 7.87 – 7.93 (m, 1H, H-g), 7.94 – 7.98 (m, 2H, H-d), 8.54 (d, *J* = 8.1, 1H, H-h), 9.43 (d, *J* = 7.2, 1H, H-f), 9.71 (d, *J* = 1.7, 1H, H-e).

¹³C NMR (176 MHz, DMSO-*d*₆, 298 K) δ_C [ppm] = 10.7 (C-a), 13.7 (C-b), 124.6 (C-c), 127.6 (C-g), 127.9 (C-d), 133.2 (C-5), 135.3 (C-3), 137.6 (C-6), 138.3 (C-1/2), 138.6 (C-h), 139.8 (C-4), 148.4 (C-e), 149.9 (C-f).

¹⁹F NMR (470 MHz, DMSO-*d*₆, 298 K) δ_F [ppm] = -148.24, -148.18

HRMS (ESI⁺, DMSO-*d*₆/CH₃CN, 298 K): *m/z* (relative intensity) = 542.2485 (55%, [**1**]⁺, calcd 542.2431), 577.7024 (100%, [**L** - 4 BF₄]⁴⁺, calcd 577.6962), 799.2709 (20%, [**L** - 3 BF₄]³⁺, calcd 799.2630), 1242.4095 (5%, [**L** - 2 BF₄]²⁺, calcd 1242.3966).

** One dimensional ¹H-ROESY spectra enabled the assignment of H-a and H-b (Figure S30).

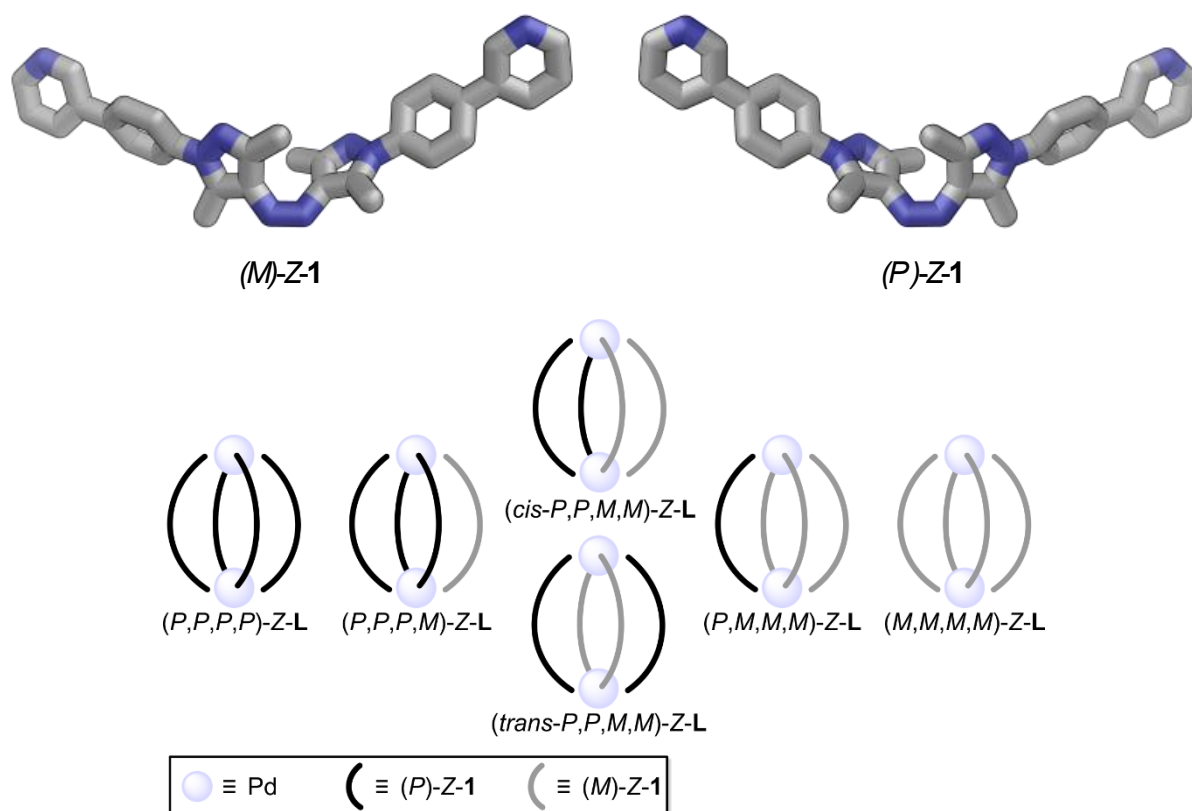


Figure S25. *Top:* Enantiomers of Z-1. *Bottom:* Cartoon representations of the six diastereomers of Z-L: (M,M,M,M)-Z-L and its enantiomer (P,P,P,P)-Z-L, (P,M,M,M)-Z-L and its enantiomer (P,P,P,M)-Z-L, (cis-P,P,M,M)-Z-L, and (trans-P,P,M,M)-Z-L. Computations of these isomers are detailed in Section S8.3.

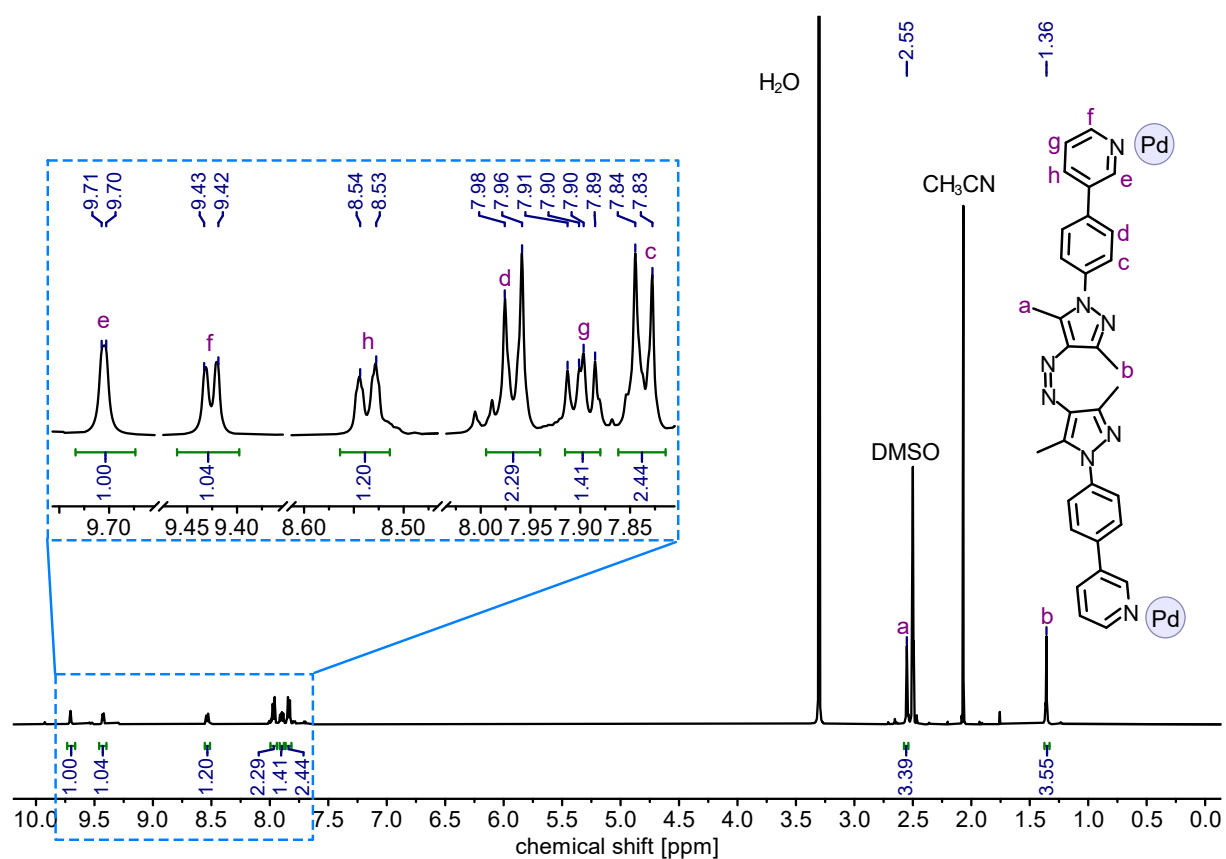


Figure S26. ^1H NMR spectrum (500 MHz, $\text{DMSO}-d_6$, 298 K) of Z-L.

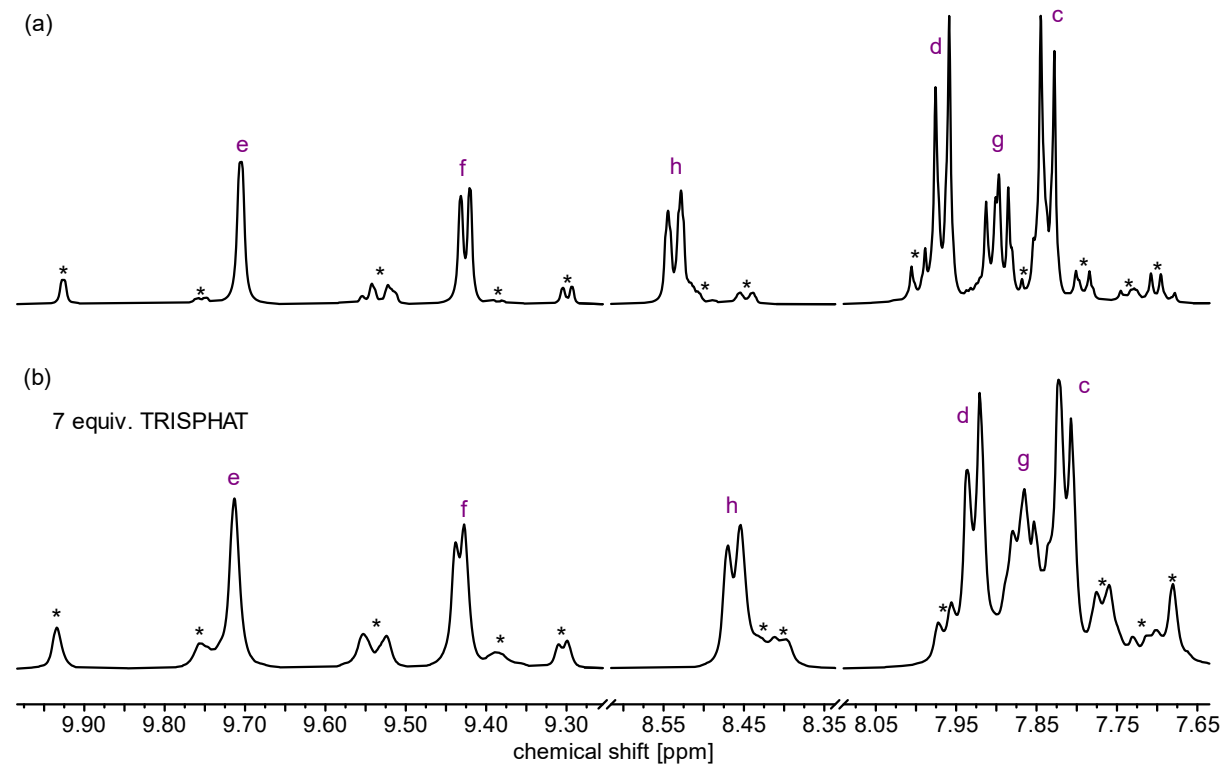


Figure S27. Stacked ^1H NMR spectra (500 MHz, $\text{DMSO}-d_6$, 298 K) of (a) Z-L and (b) Z-L + 7.0 equiv. tetra-*N*-butylammonium Δ -TRISPHAT. Minor species highlighted with an asterisk.

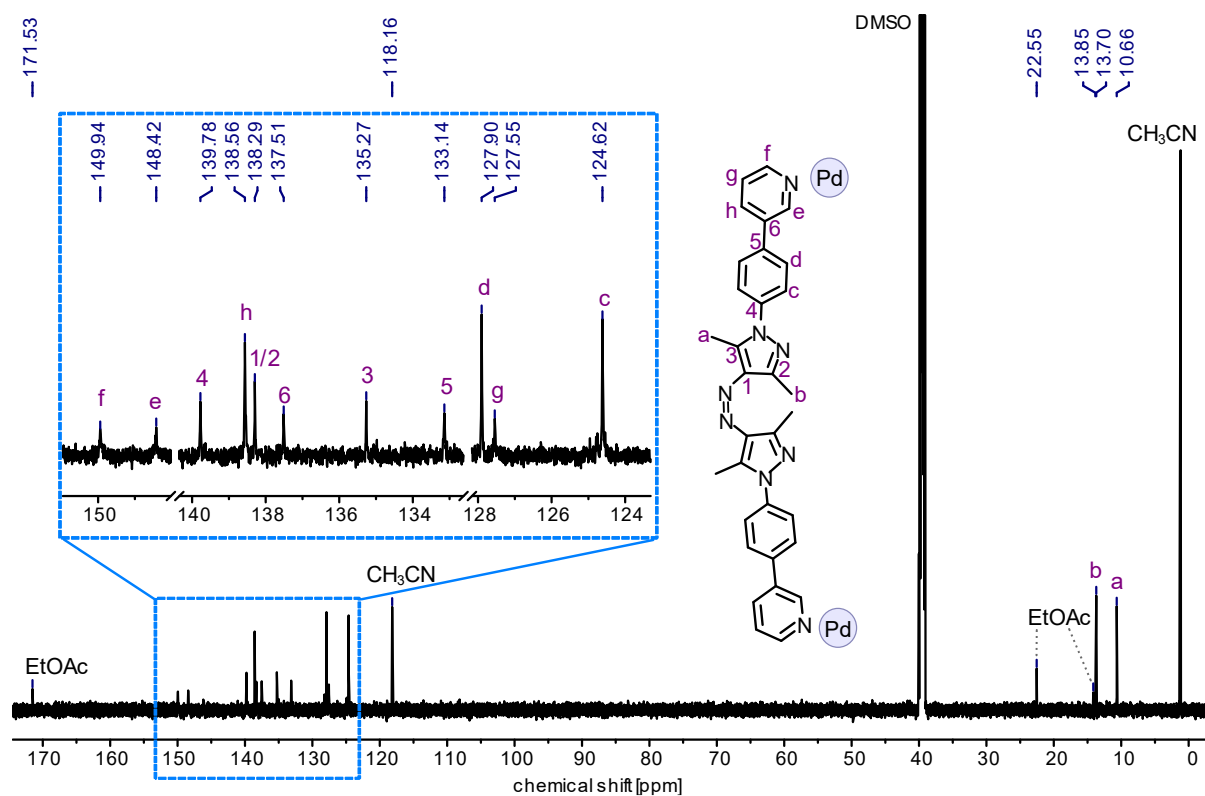


Figure S28. ¹³C NMR spectrum (176 MHz, DMSO-*d*₆, 298 K) of Z-L.

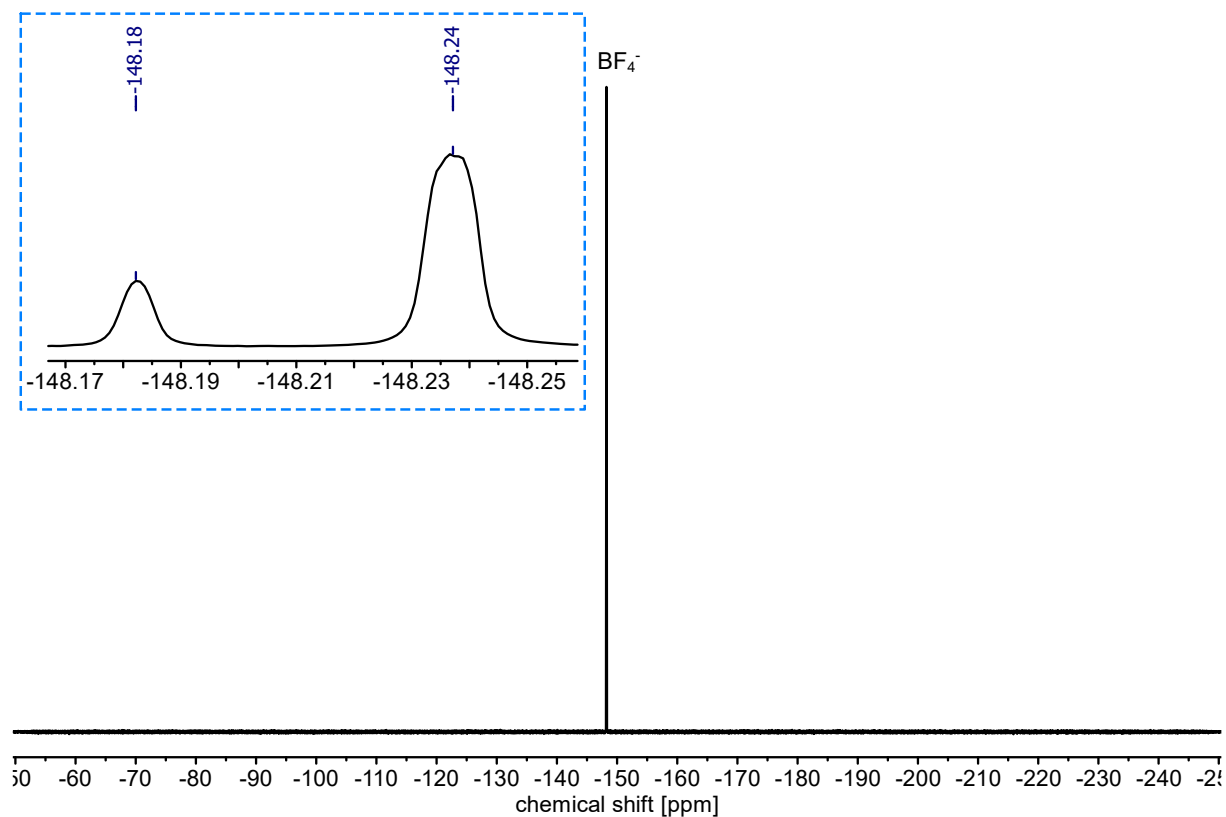


Figure S29. ¹⁹F NMR spectrum (470 MHz, DMSO-*d*₆, 298 K) of Z-L showing the presence of only one anion environment (the two separate signals arise from the ¹⁰B and ¹¹B isotopomers).

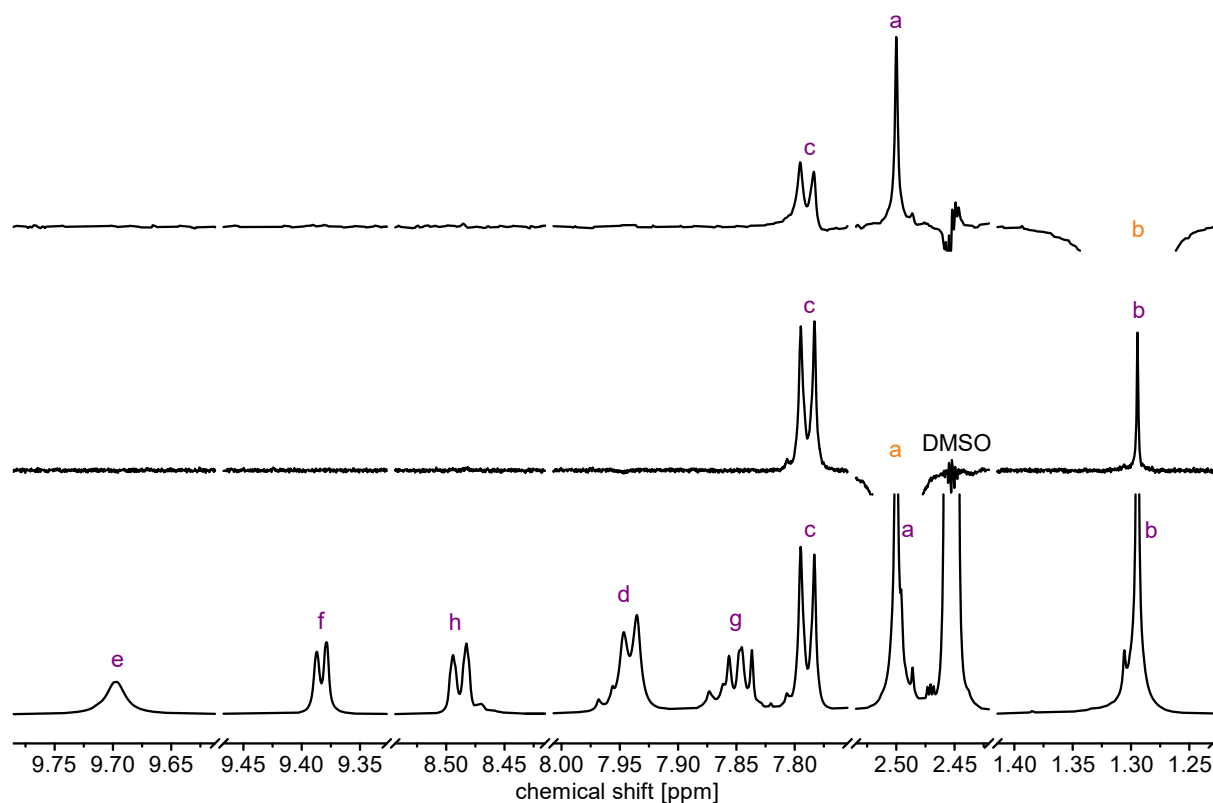


Figure S30. One-dimensional ^1H ROESY NMR spectra (700 MHz, $\text{DMSO}-d_6$, 298 K) of Z-L for signals H-a and H-b showing clear couplings between H-a and H-b, confirming ligand **1**'s Z-configuration within Z-T.

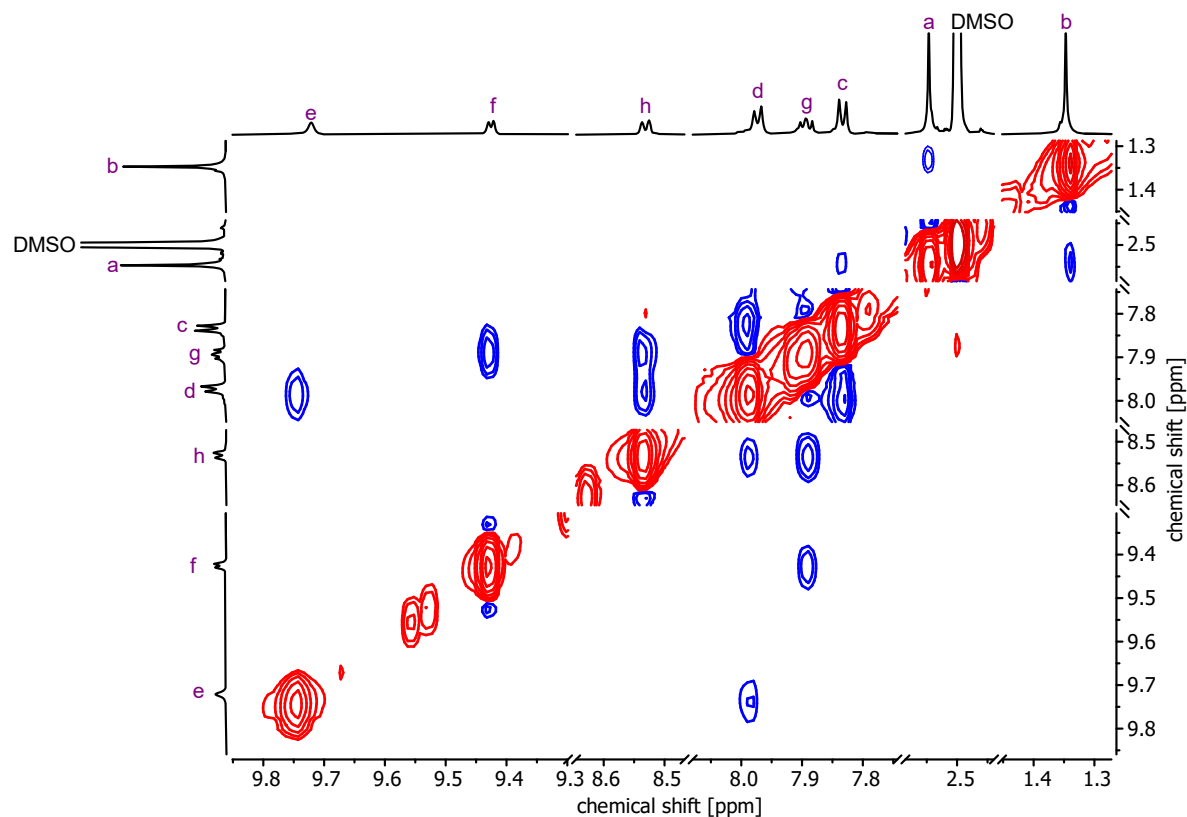


Figure S31. $^1\text{H}, ^1\text{H}$ ROESY NMR spectrum (700 MHz, $\text{DMSO}-d_6$, 298 K) of Z-L showing clear coupling between H-a and H-b, confirming ligand **1**'s Z-configuration within Z-T.

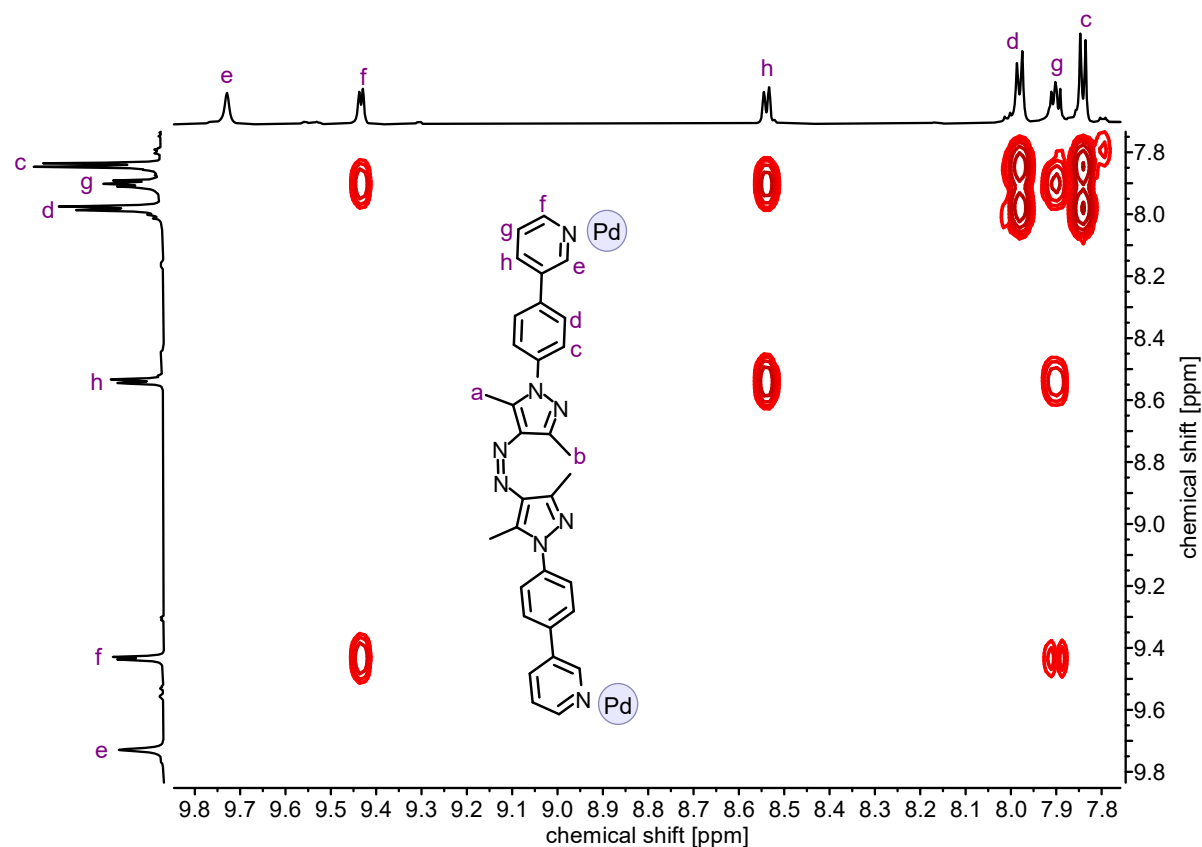


Figure S32. $^1\text{H}, ^1\text{H}$ COSY NMR spectrum (700 MHz, $\text{DMSO}-d_6$, 298 K) of Z-L.

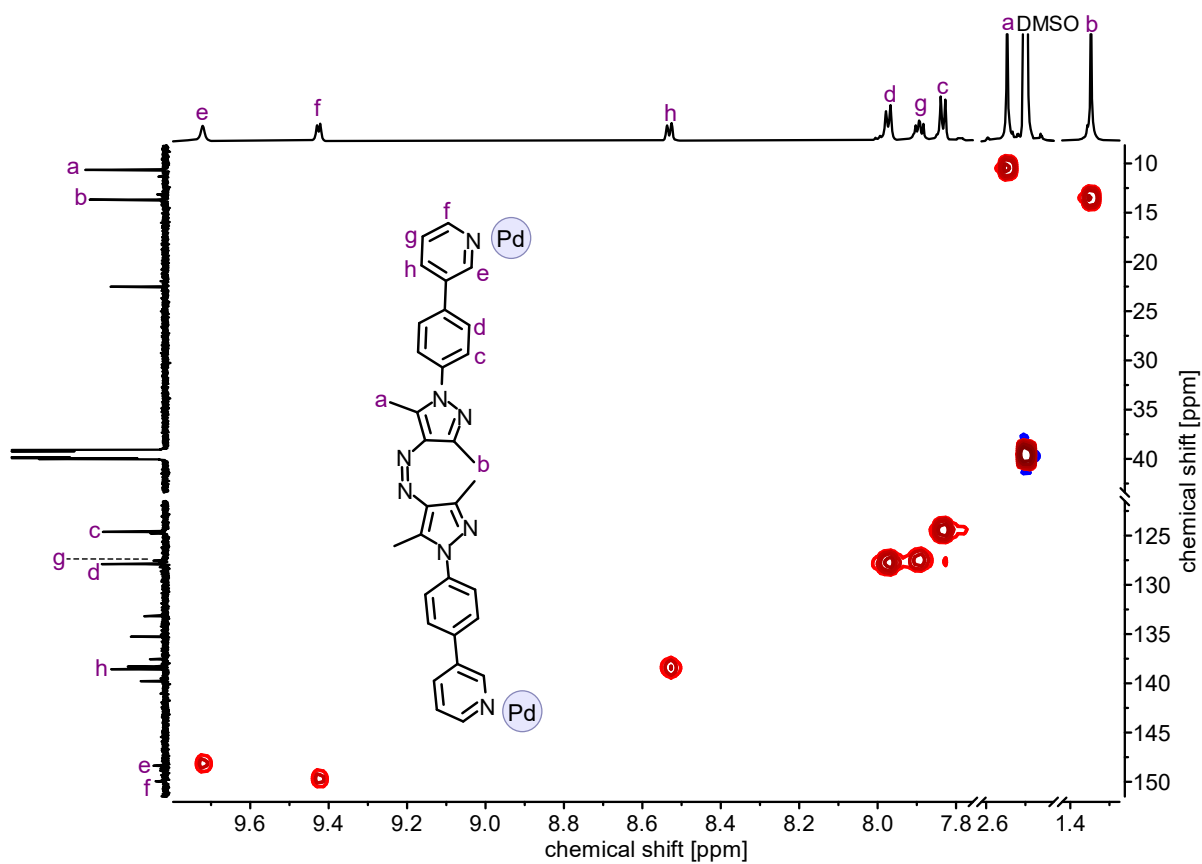


Figure S33. $^1\text{H}, ^{13}\text{C}$ HSQC NMR spectrum (700/176 MHz, $\text{DMSO}-d_6$, 298 K) of Z-L.

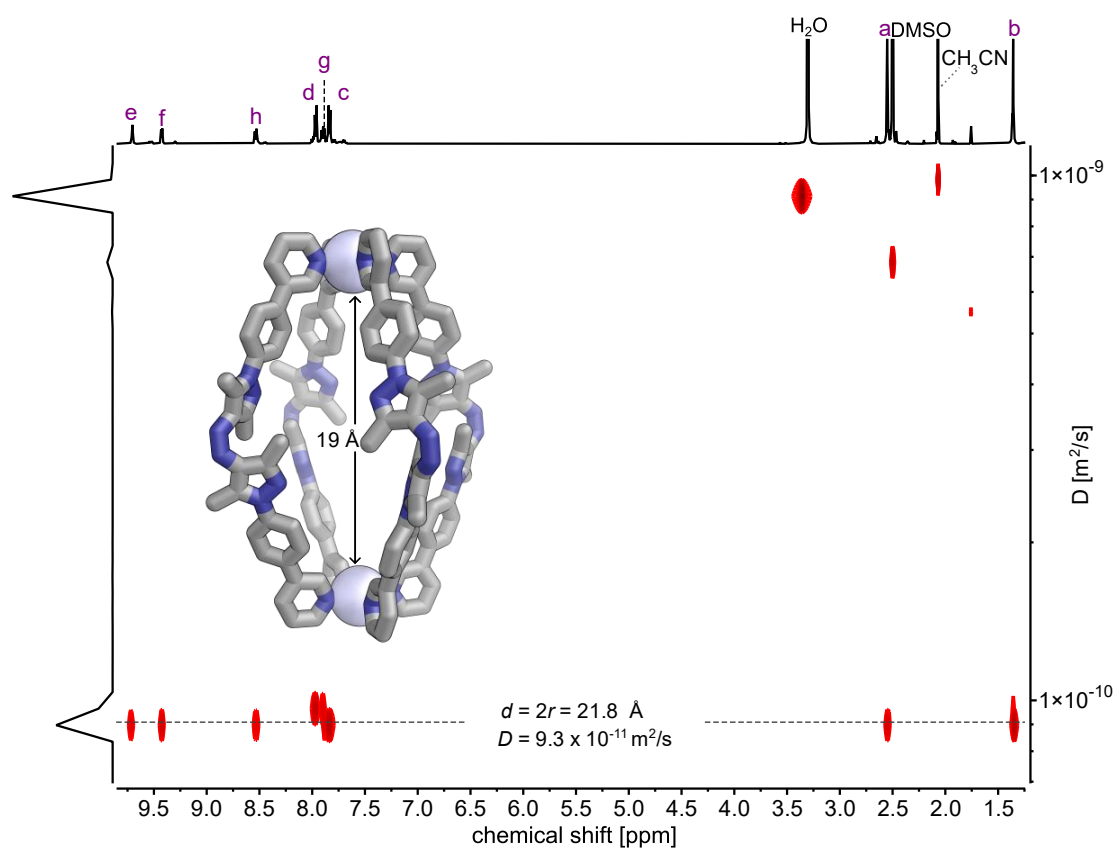


Figure S34. 2D-DOSY NMR spectrum (700 MHz, DMSO- d_6 , 298 K, D20 = 0.35 s) of Z-L. Calculated diffusion constant (D) and solvodynamic diameter ($d = 2r$) are depicted in the spectrum. The GFN2-xTB structure of Z-L is shown with its Pd – Pd distance, calculated using Avogadro (Version 1.2.0).²

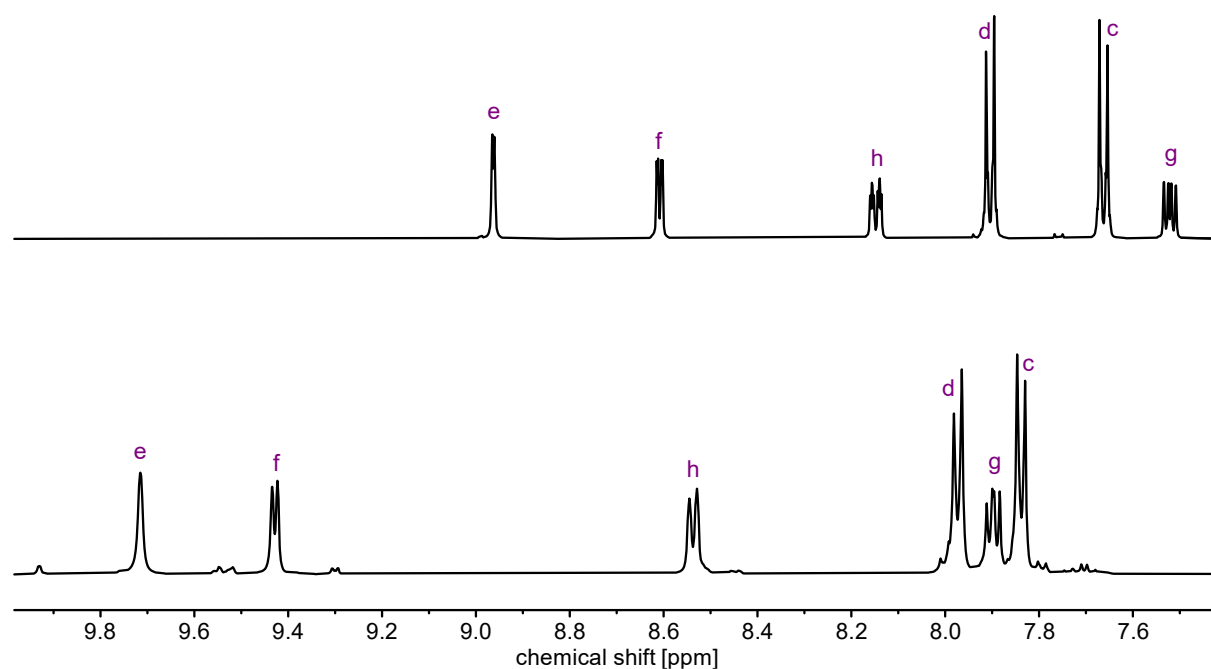


Figure S35. Stacked ^1H NMR spectra (500 MHz, DMSO- d_6 , 298 K) of Z-1 (top) and Z-L (bottom).

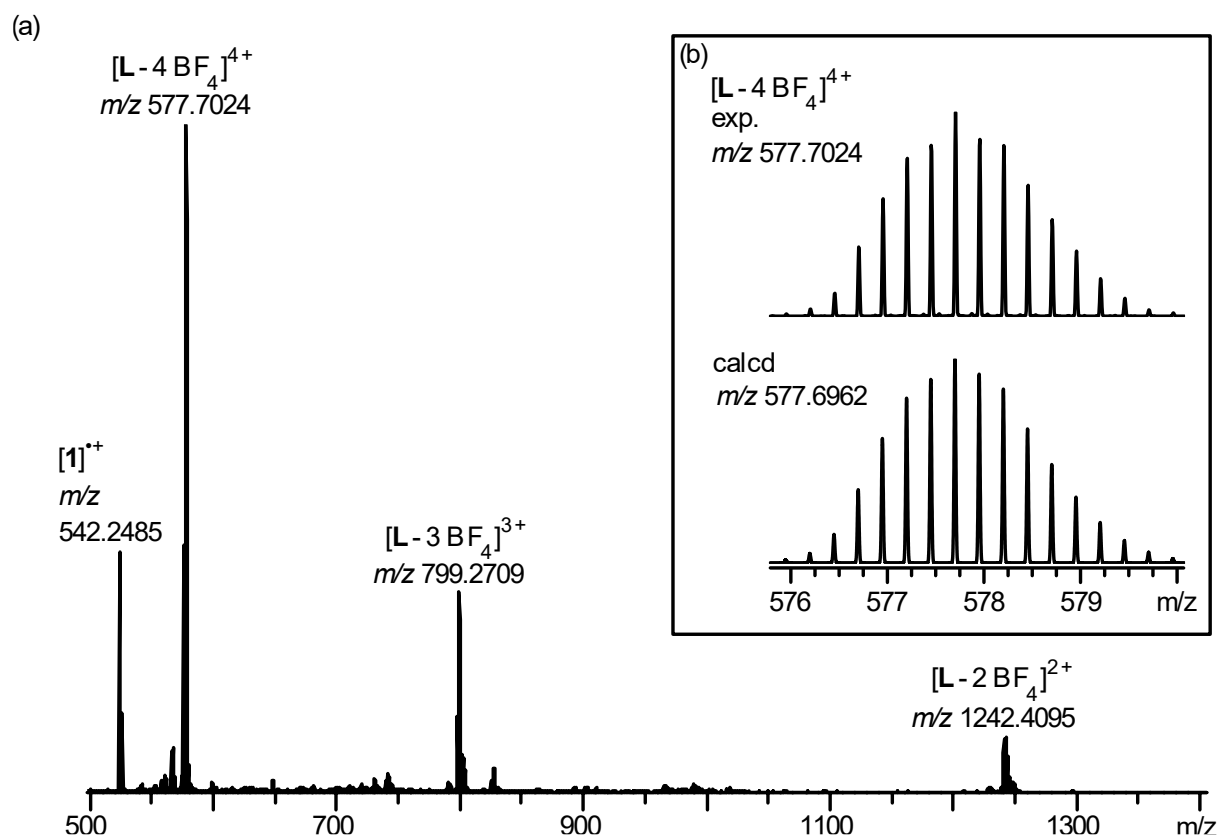


Figure S36. (a) High-resolution ESI⁺ mass spectrum (DMSO/CH₃CN) of Z-L. (b) Experimental and calculated isotope patterns of $[\text{L} - 4 \text{BF}_4]^{4+}$.

S2.8 Lantern scrambling between *E-L* and *Z-L*

To investigate whether assemblies with both ligand *E-1* and *Z-1* within the same lantern structure, namely *Z,E,E,E-L*, *cis-Z,Z,E,E-L*, *trans-Z,Z,E,E-L*, *Z,Z,Z,E-L*, are able to form, as indicated by our computational studies (Section S8.2), lantern scrambling experiments were performed by combining pre-assembled lanterns *E-L* and *Z-L* in ratios of 1:3, 1:1, and 3:1 (*E-L* / *Z-L*). Direct mixing of isomeric ligands was not feasible, because of free ligand **1**'s low solubility in DMSO (the solvent used for cage formation).

Z-L was obtained by irradiating a sample of *E-T* / *E-L* at 365 nm to induce *E*→*Z* isomerisation. As complete thermal relaxation of *Z-L* requires approximately one year (Figure S73), no significant relaxation was expected during the course of the experiment. *E-L* was generated by irradiating a sample of *Z-L* at 500 nm. Due to the equilibration between *E-T* and *E-L* (see Section S3), small amounts of *E-T* were always present in the samples and increased within the course of the experiment.

Each sample was prepared using a freshly irradiated *E-L* solution and mixing it with the *Z-L* solution in 1:3, 1:1, and 3:1 (*E-L* / *Z-L*) ratios. The samples were investigated by ¹H NMR spectroscopy immediately after mixing (2 min / 5 min), and the mixtures were monitored over time (17 min / 20 min, 13 h, 7 d; Figure S37–S39). In all cases, the lantern mixtures gave rise to new sets of signals (highlighted in yellow, orange, and red, respectively, depending on whether they were predominantly found in the 1:3, 1:1 or 3:1 *E-L* / *Z-L* mixtures), which reached their maximum intensity after 13 h. While it was not possible to definitely assign the newly emerged signals to specific lantern structures, namely *Z,E,E,E-L*, *cis-Z,Z,E,E-L*, *trans-Z,Z,E,E-L*, *Z,Z,Z,E-L*, we tentatively assume these signals to arise from the lanterns with mixed ligand configurations, supporting our computational results that formation of such structures should be possible (Section S8.2). After 7 d all mixtures had formed significant amounts of triangle *E-T*, indicating its thermodynamic stability.

Some of the identified signals of lanterns with mixed ligand configurations can also be observed during the thermal relaxation of *Z-L* (Figure S74), further supporting our hypothesis regarding the identity of these signals.

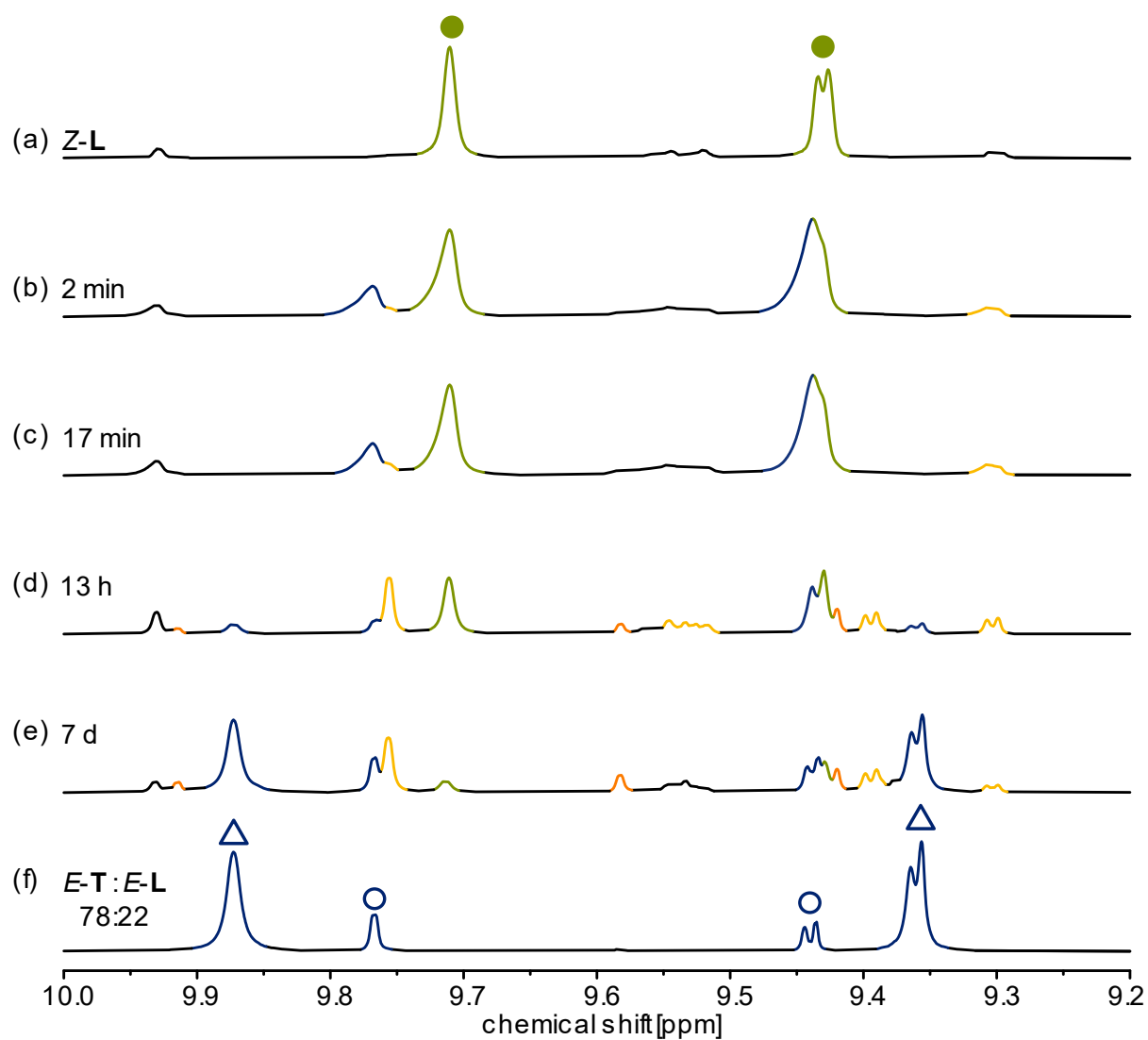


Figure S37. ^1H NMR (700 MHz, $\text{DMSO}-d_6$, 298 K) spectra of the lantern-scrambling experiment with E-L / Z-L (1:3) after (b) 2 min, (c) 17 min, (d) 13 h, and (e) 7 d. For reference: (a) Z-L and (f) E-T / E-L mixture under light exclusion (E-T / E-L, 78:22). E-T is denoted with ▲, E-L is denoted with ○, and Z-L is denoted with ●. Newly emerged signals are tentatively highlighted in yellow, orange, and red, respectively, depending on whether they were predominantly found in the 1:3, 1:1 or 3:1 E-L / Z-L mixtures.

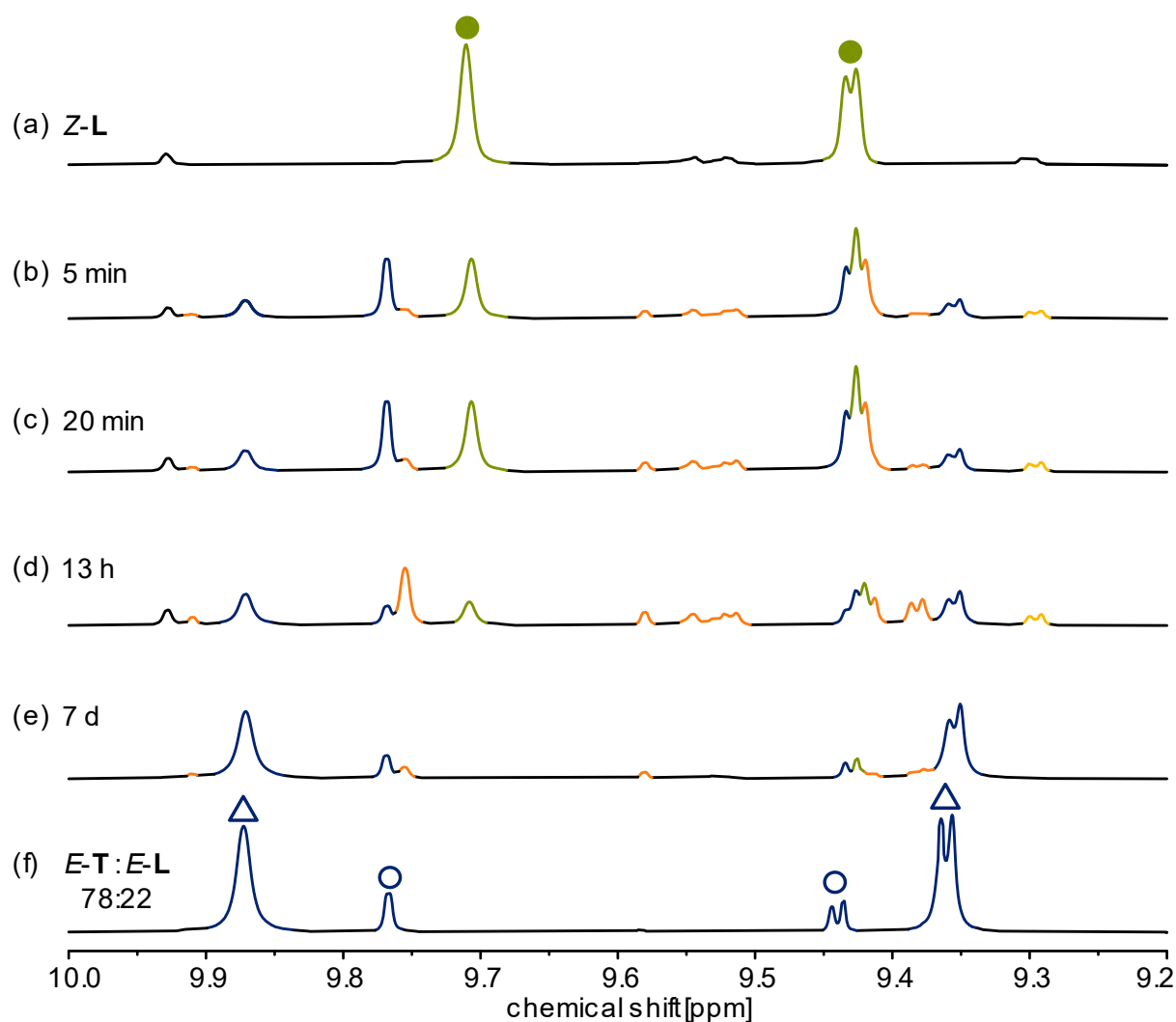


Figure S38. ^1H NMR (700 MHz, $\text{DMSO}-d_6$, 298 K) spectra of the lantern-scrambling experiment with $E-L / Z-L$ (1:1) after (b) 5 min, (c) 20 min, (d) 13 h, and (e) 7 d. For reference: (a) Z-L and (f) $E-T / E-L$ mixture under light exclusion ($E-T / E-L$, 78:22). $E-T$ is denoted with Δ , $E-L$ is denoted with $\circ$, and Z-L is denoted with $\bullet$. Newly emerged signals are tentatively highlighted in yellow, orange, and red, respectively, depending on whether they were predominantly found in the 1:3, 1:1 or 3:1 $E-L / Z-L$ mixtures.

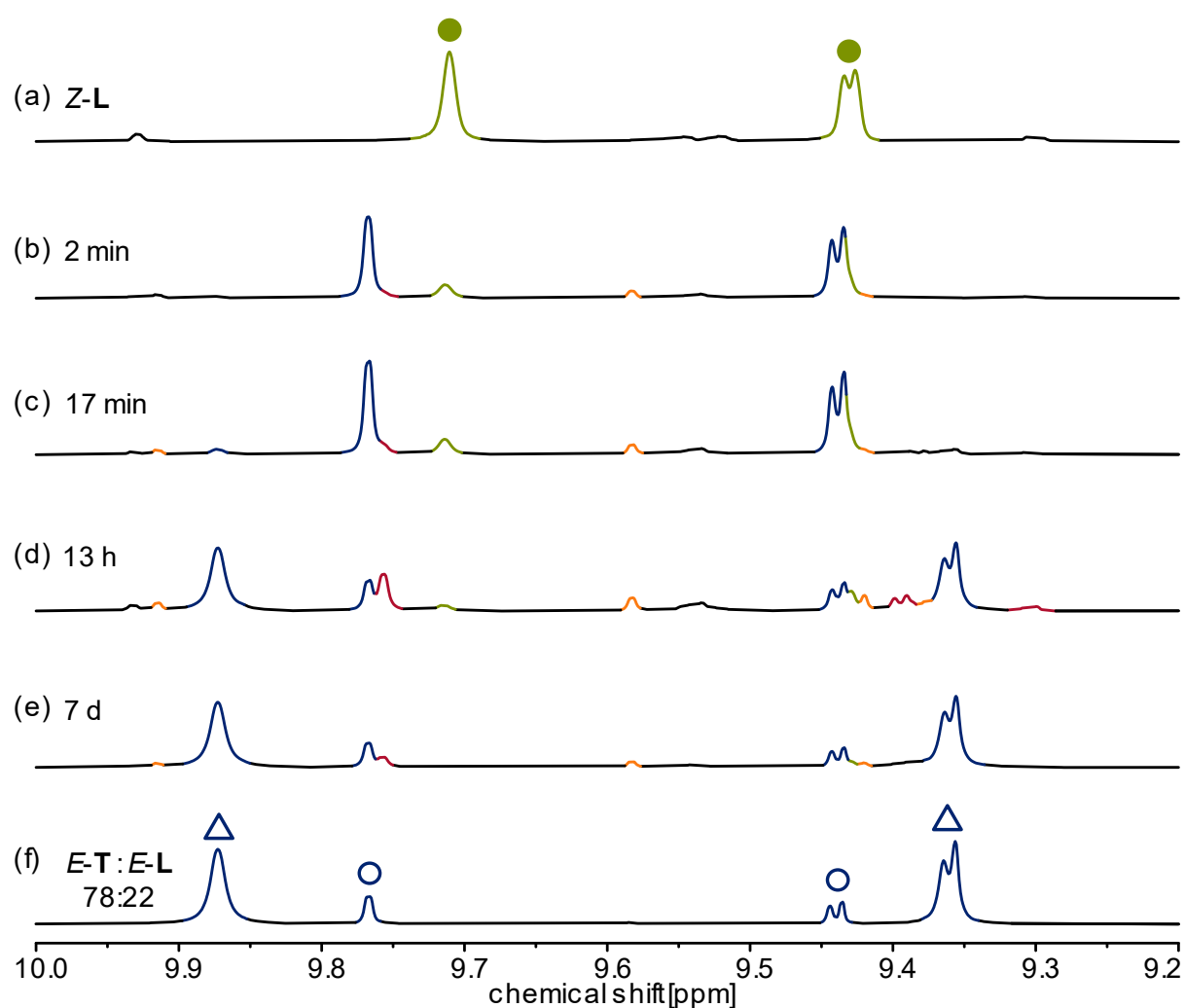


Figure S39. ^1H NMR (700 MHz, $\text{DMSO}-d_6$, 298 K) spectra of the lantern-scrambling experiment with *E*-**L** / *Z*-**L** (1:3) after: (b) 2 min, (c) 17 min, (d) 13 h, and (e) 7 d. For reference: (a) *Z*-**L** and (f) *E*-**T** / *E*-**L** mixture under light exclusion (*E*-**T** / *E*-**L**, 78:22). *E*-**T** is denoted with $\blacktriangle$, *E*-**L** is denoted with $\circ$, and *Z*-**L** is denoted with $\bullet$. Newly emerged signals are tentatively highlighted in yellow, orange, and red, respectively, depending on whether they were predominantly found in the 1:3, 1:1 or 3:1 *E*-**L** / *Z*-**L** mixtures.

S3 Investigation of the triangle *E-T* / lantern *E-L* equilibrium

All samples were prepared according to the experimental procedure outlined in Section S2.6 and were stored in amberised NMR tubes wrapped in aluminium foil in an air-conditioned room at 22 °C to prevent any disruption of the equilibrium caused by either temperature or ambient light.

S3.1 Triangle *E-T* / lantern *E-L* equilibrium

The thermal interconversion between triangle *E-T* and lantern *E-L* was investigated at 298 K and 348 K. For this, an NMR sample containing 78:22 triangle *E-T* / lantern *E-L* mixture was irradiated with 365 nm light for 5 min to obtain *Z-L*. The sample was then immediately irradiated with 500 nm light to obtain a sample that contains almost exclusively *E-L* lantern (Figure S61). The equilibration between triangle *E-T* and lantern *E-L* was followed over time by ^1H NMR spectroscopy (500 MHz, $\text{DMSO-}d_6$, 298 K or 348 K, Figure S41 and Figure S42) and the triangle *E-T* / lantern *E-L* composition plotted over time (Figure S40).

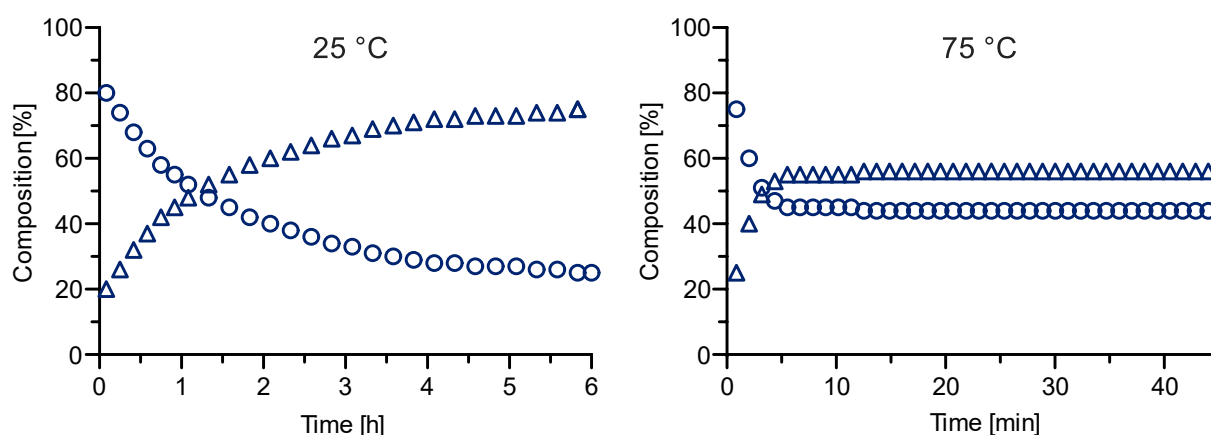


Figure S40. At room temperature, *Z-L* was irradiated with 500 nm for approx. 5 min to induce *Z*→*E* isomerisation. *Left:* A ^1H NMR (500 MHz, $\text{DMSO-}d_6$, 298 K) spectrum was measured every 5 min for 6 h to monitor the equilibrium between *E-T* triangle and *E-L* at 298 K. Between 0 h and 1 h, every second data point was removed for clarity; between 1 h and 6 h, only every third data point was plotted. *Right:* A ^1H NMR (500 MHz, $\text{DMSO-}d_6$, 348 K) spectrum was measured every 70 s for 45 min to monitor the equilibrium between *E-T* and *E-L* at 348 K. *E-T* is denoted with $\blacktriangle$, *E-L* is denoted with $\bigcirc$.

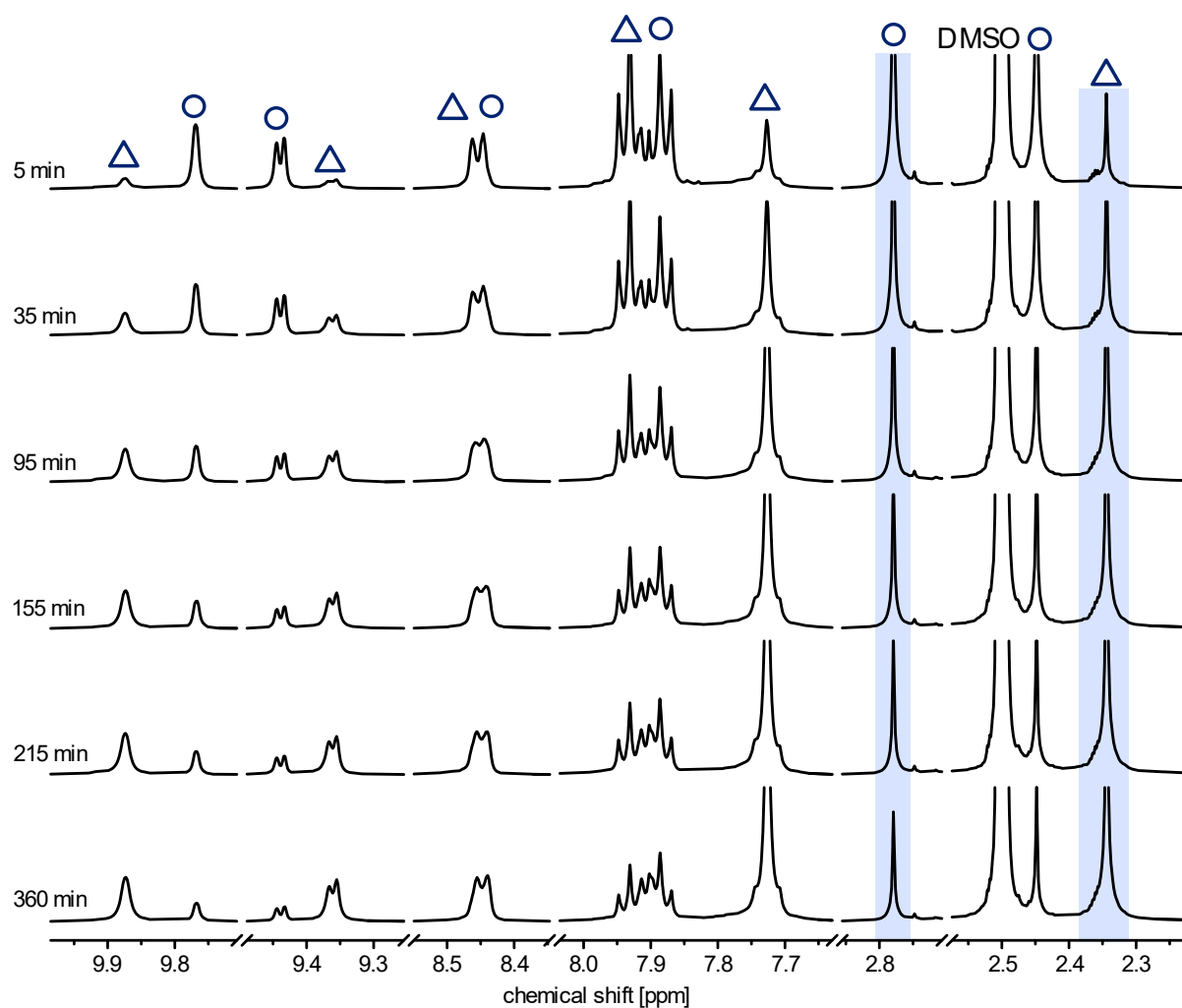


Figure S41. ^1H NMR (500 MHz, $\text{DMSO-}d_6$, 298 K) spectra of the equilibration between *E-T* triangle and *E-L* at 298 K. A ^1H NMR spectrum was measured every 5 min for 6 h. The signals highlighted in blue were chosen to be line-fitted and plotted to display changes in composition between *E-T* and *E-L* (Figure S40). *E-T* is denoted with Δ , *E-L* is denoted with $\circ$.

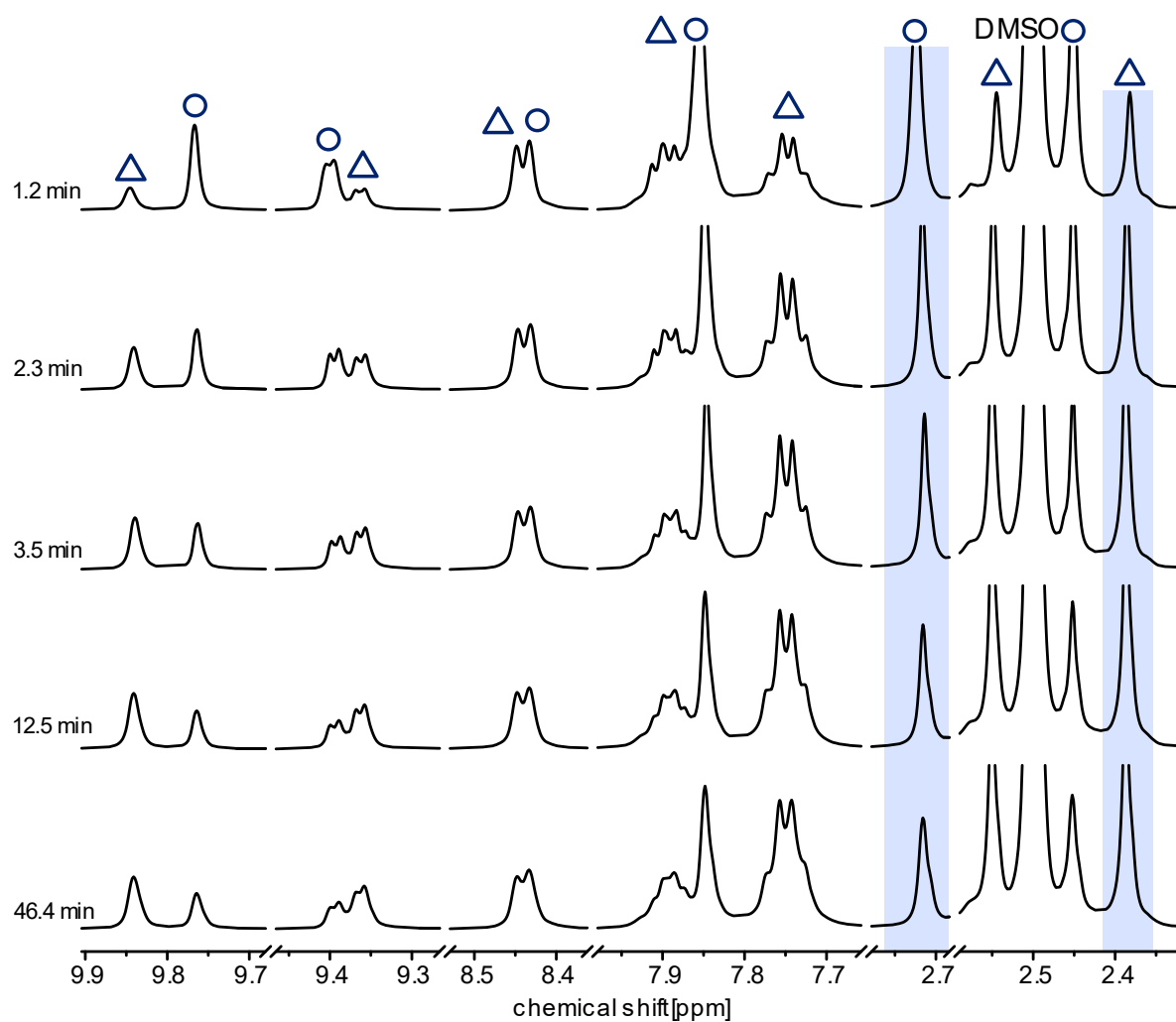


Figure S42. ^1H NMR (500 MHz, $\text{DMSO-}d_6$, 348 K) spectra of the equilibration between *E-T* triangle and *E-L* at 348 K. A ^1H NMR spectrum was measured every 70 s for 45 min. The signals highlighted in blue were chosen to be line-fitted and plotted to display changes in composition between *E-T* and *E-L* (Figure S40). *E-T* is denoted with Δ , *E-L* is denoted with $\circ$.

S3.2 Long-term stability of the triangle *E-T* / lantern *E-L* ratio

To test whether the triangle *E-T* / lantern *E-L* ratio of 78:22 indeed represented the thermodynamic equilibrium of the mixture, ^1H NMR spectra were measured for one month (Figure S43). The spectra show that the ratio of 78:22 between *E-T* and *E-L* is achieved after allowing the complex mixture to equilibrate for a minimum of 6 h (usually overnight) and remains unchanged thereafter.

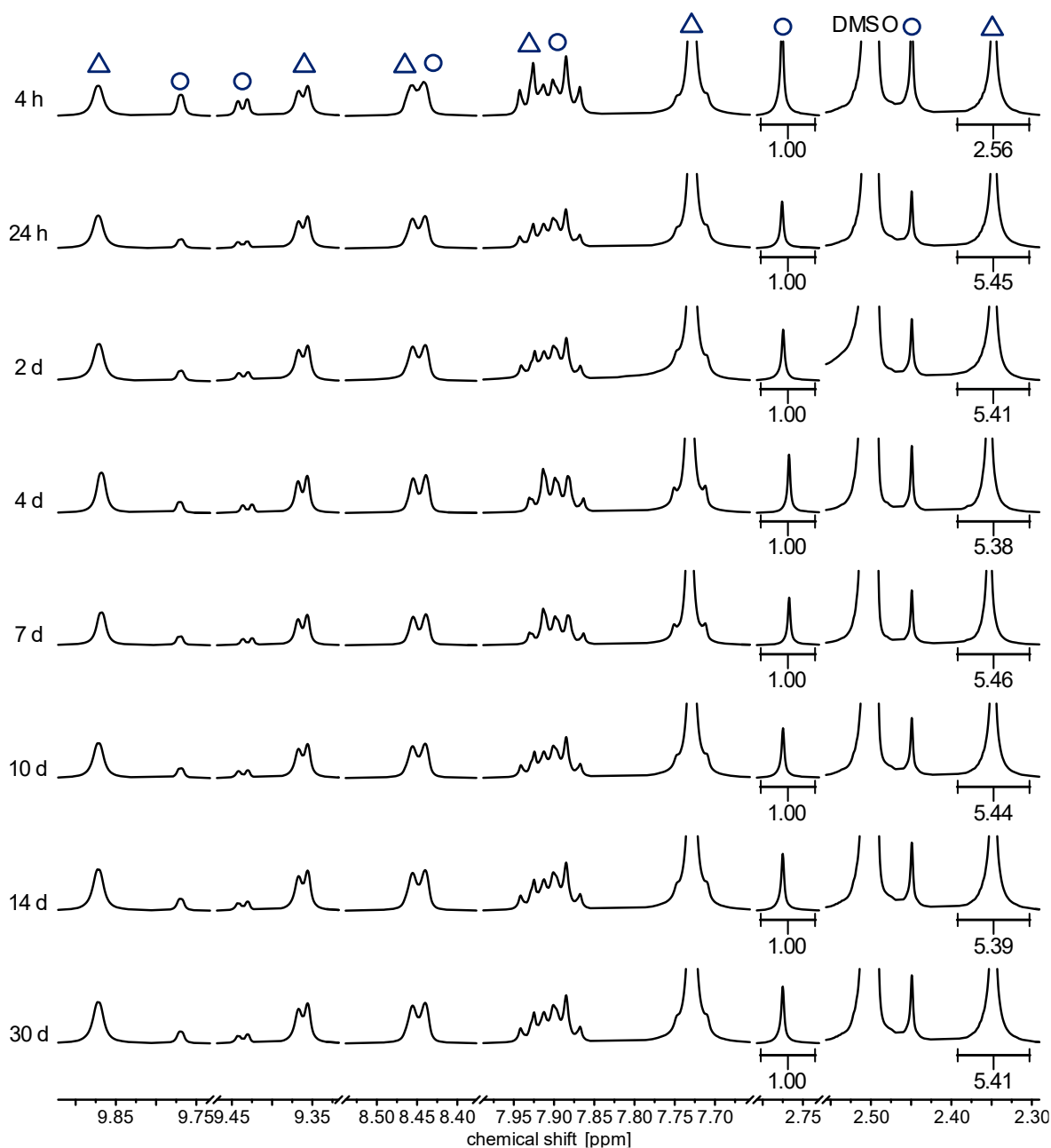


Figure S43. Stacked ^1H NMR (500 MHz, DMSO- d_6 , 298 K) spectra of *E-T* (denoted with Δ) and *E-L* (denoted with $\circ$) over 30 d. Four hours after the reaction turned from turbid to a clear yellow, indicating complex formation, the ratio between *E-T* and *E-L* was 63:37. From day 1 onwards, the ratio between *E-T* and *E-L* remained at 78:22.

S3.3 Concentration dependence

To assess the concentration dependence of the triangle *E-T* / lantern *E-L* equilibrium, a total of 17 samples were prepared with concentrations ranging from 0.2 to 8 mM and a ^1H NMR spectrum was measured from each of them (Figure S44). The signals highlighted in orange were chosen to be line-fitted and plotted against the concentration to illustrate the concentration dependence of the *E-T* / *E-L* equilibrium (Figure S45). This dilution series demonstrated that the complex sample of *E-T* and *E-L* (78:22, respectively) has a critical self-assembly concentration of $csac(\mathbf{1}) \approx 1.75$ mM. Additionally, the ligand concentration should be at least 7 mM to prevent the presence of free ligand in solution and maintain the 78:22 *E-T* / *E-L* ratio.

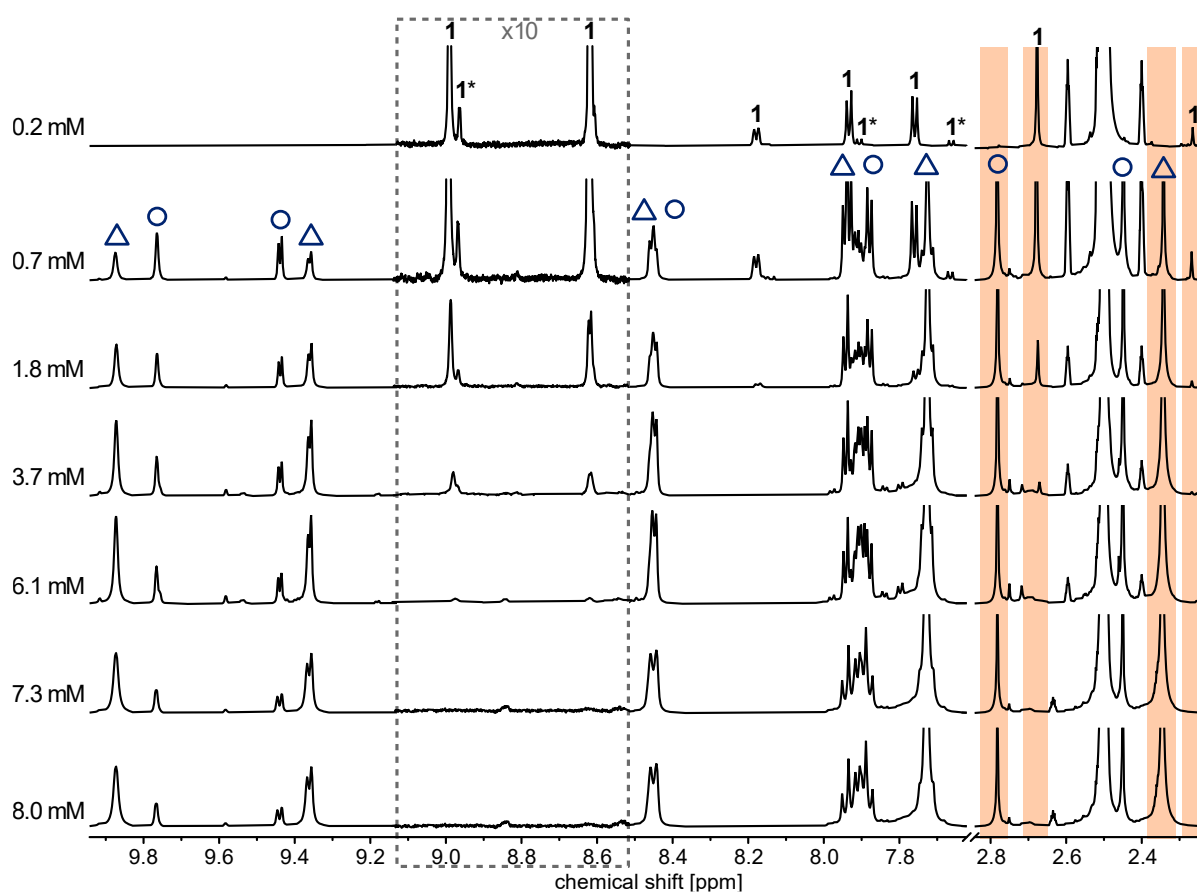


Figure S44. Stacked ^1H NMR (700 MHz, DMSO-d_6 , 298 K) spectra of complexation mixtures at different concentrations. *E-T* is denoted with Δ , *E-L* is denoted with $\circ$, *E-1* is denoted with **1**, and *Z-1* is denoted with **1***. The signals highlighted in orange were chosen to be line-fitted and plotted to display the concentration dependence of *E-T* / *E-L* equilibrium (Figure S45).

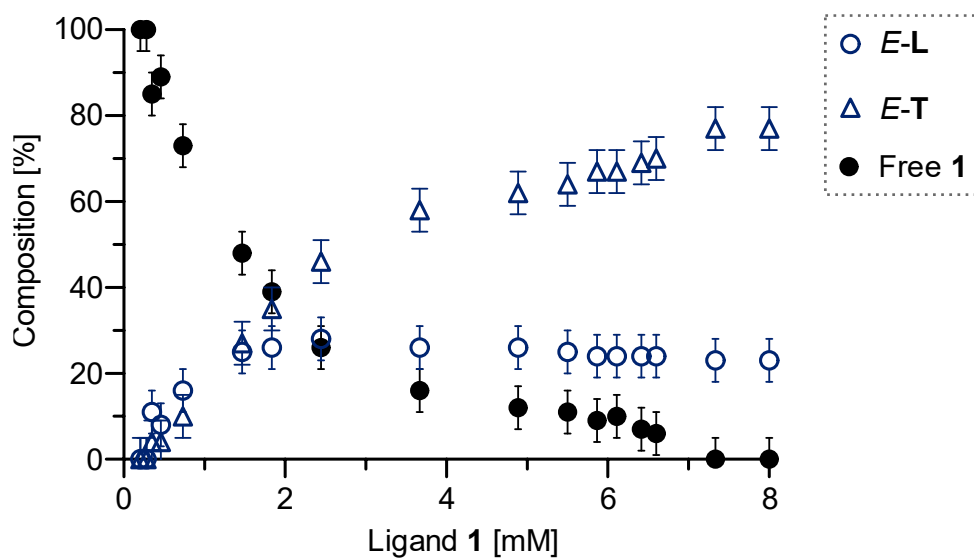


Figure S45. Plot of the percentage of triangle *E-T*, lantern *E-L*, and free ligand **1** as determined by ^1H NMR integration (Figure S44) against the concentration of **1**, showing the concentration dependence of the equilibrium between *E-T* and *E-L*.

S3.4 Temperature dependence

The temperature dependence of the triangle *E-T* / lantern *E-L* equilibrium was investigated using variable temperature ¹H NMR (303 K, 313 K, 323 K, 333 K, 343 K; Figure S46). By integrating the NMR signals corresponding to *E-T* and *E-L*, the equilibrated concentrations for each assembly were calculated based on the initial ligand concentration. Following Eq. S1, $\ln K_{eq}$ was calculated for all temperatures and plotted against T^{-1} (Figure S47). Fitting the data through linear regression and applying the Van't Hoff equation (Eq. S4) allowed for the determination of the thermodynamic parameters ΔH , ΔS , and ΔG (Table S3).



$$K_{eq} = \frac{[E\text{-T}]^2}{[E\text{-L}]^3} \quad (\text{S1})$$

$$\Delta G = \Delta H - T \Delta S \quad (\text{S2})$$

$$\Delta G = -R T \cdot \ln K_{eq} \quad (\text{S3})$$

$$\ln K_{eq} = -\frac{\Delta G_{eq}}{R T} = -\frac{\Delta H_{eq}}{R T} + \frac{\Delta S_{eq}}{R} \quad (\text{S4})$$

Table S3. Thermodynamic data as obtained from Van't Hoff analysis (Figure S46 and Figure S47). K , ΔG and $T \Delta S$ are given for $T = 298 \text{ K}$.

<i>K</i>	ΔG	ΔH	ΔS	$T \Delta S$
[M ⁻¹]	[kJ mol ⁻¹]	[kJ mol ⁻¹]	[J K ⁻¹ mol ⁻¹]	[kJ mol ⁻¹]
76080 ± 36,000	-27.8 ± 13.0	-50.6 ± 7.7	-76.3 ± 23.9	-22.7 ± 7.1

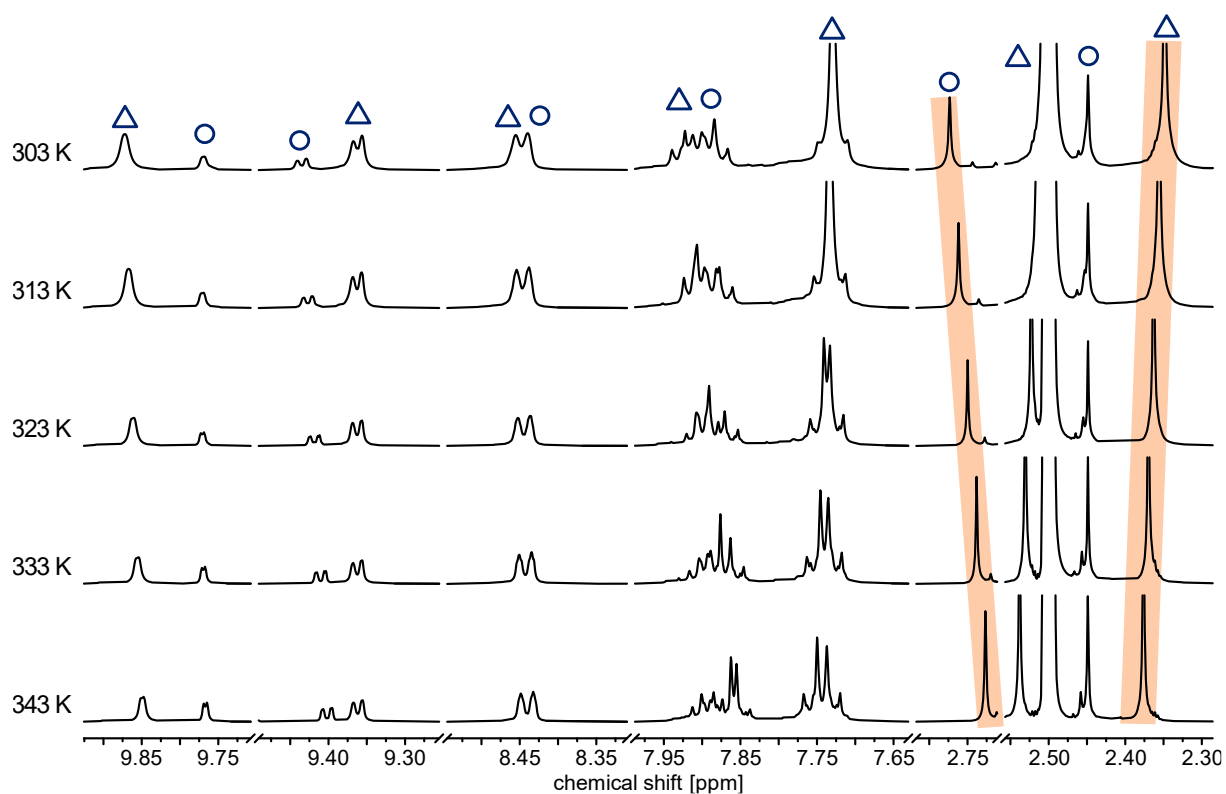


Figure S46. ^1H NMR spectra (500 MHz, $\text{DMSO-}d_6$) of the equilibrium between *E*-T (denoted with Δ) and *E*-L (denoted with $\circ$) at different temperatures (303 K, 313 K, 323 K, 333 K, 343 K). The signals highlighted in orange were integrated to determine the respective concentrations at each temperature for Van't Hoff analysis (Figure S47).

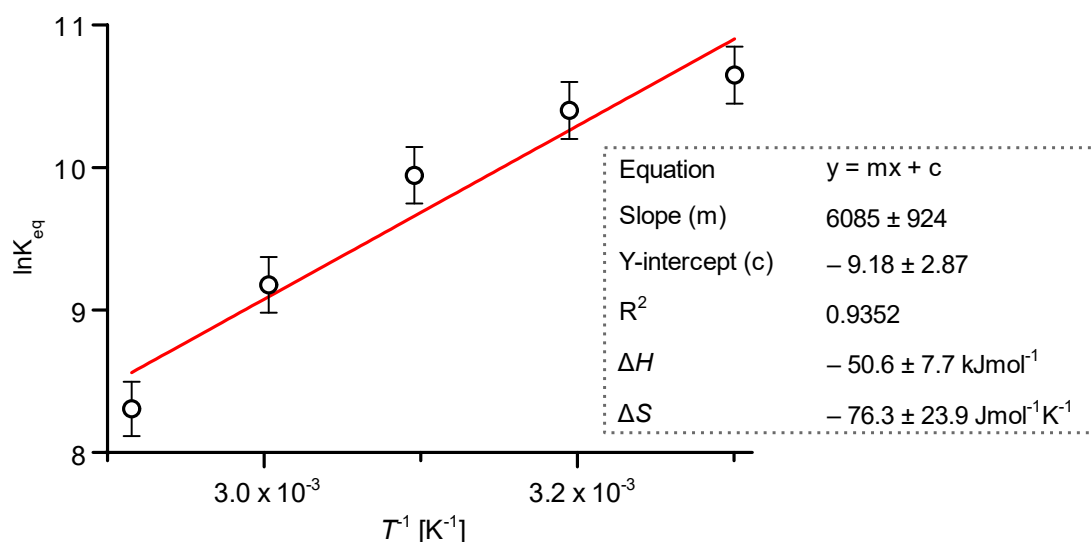


Figure S47. Van't Hoff plot of the equilibrium between *E*-T and *E*-L at different temperatures.

S4 Photoswitching studies

LED irradiation (NMR and MS). This method was previously described by our group.^{3,4} The following description was added here for convenience:

A portable, built-in-house 365 nm LED light source using a commercial LED chip and 3D-printed adapters was employed to irradiate NMR and MS samples. For 500 nm light irradiation, a fibre collimated LED light source was used. Following irradiation, the samples were promptly subjected to measurement to reduce thermal relaxation to a minimum.

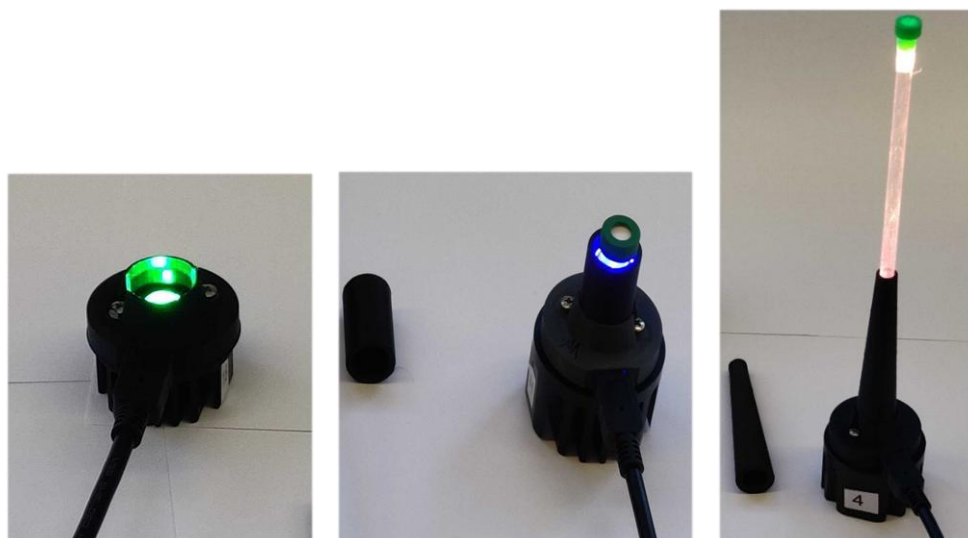


Figure S48. LED illumination setup with USB-powered homemade light sources using commercial LED chips with 3D-printed adapters for 2 mL GC vials and 5 mm NMR tubes.

***In-situ* irradiation (NMR).** This method was adapted from literature^{5,6} and previously described by our group.^{3,4} The following description was added here for convenience:

An NMR sample tube was fitted with an insert tube made of quartz glass, and a quartz glass optical fibre was pushed down into the insert. The end of this fibre was non-terminated, and the exposed surface had been roughened to ensure even and omnidirectional illumination (Figure S49). This construction was lowered into the NMR device using an aluminium rod to avoid damage to the fibre. The other end of the optical fibre was connected to a fibre-collimated LED light source (see Section S1) so the sample could be irradiated inside the spectrometer.



Figure S49. NMR sample with quartz glass insert and optical fibre for *in-situ* illumination during NMR experiments.

***In-situ* irradiation (UV-vis).** This method was previously described by our group.^{3,4} The following description was added here for convenience:

Samples were irradiated perpendicularly to the measurement axis within the UV-vis spectrometer using optical fibres connected to an LED light source (see Section S1). To facilitate the irradiation of the cuvettes perpendicularly to the spectrometer's measurement axis, a hole matching the diameter of the quartz glass fibre was drilled at the centre of the Teflon stopper used to seal the UV-vis cuvettes. This configuration enabled the connection of an optical fibre to the cuvette, allowing the irradiation of the samples from above (Figure S50).



Figure S50. UV-vis *in-situ* illumination setup showing fibre collimated LED-sources connected to the cuvette with open (left) and closed measurement chamber (right).

Determination of the photostationary state (PSS). Photostationary states of the photoswitches were determined using ^1H NMR spectroscopy. For this purpose, two signals corresponding to the same proton were integrated, and the PSS was calculated based on the resulting integral ratios.⁴ To ensure the highest accuracy, well-separated and clearly resolved signals were selected for the analysis, as recommended in the literature.^{7,8}

S4.1 Azobispyrazole photoswitch (**S4**)

To the best of our knowledge, the photoswitching properties of **S4** have not been previously investigated; therefore, we have included their investigation here for convenience.

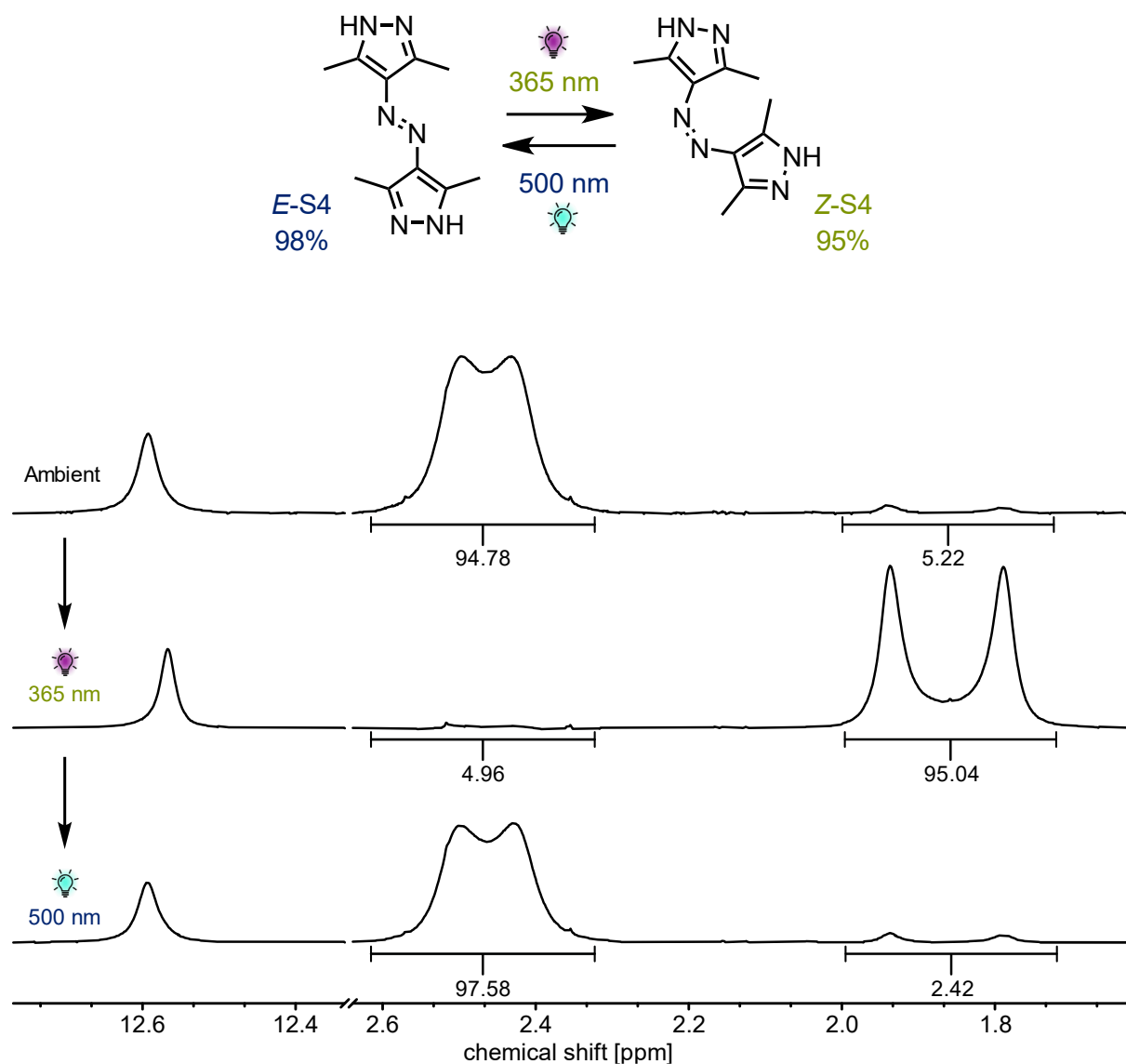


Figure S51. *In-situ* ¹H NMR (700 MHz, DMF-*d*₇, 298 K) of azobispyrazole photoswitch **S4** under ambient light, after irradiation with 365 nm light (1 min, PSS 95% **Z-S4**), and after irradiation with 500 nm light (3 min, PSS 98% **E-S4**).

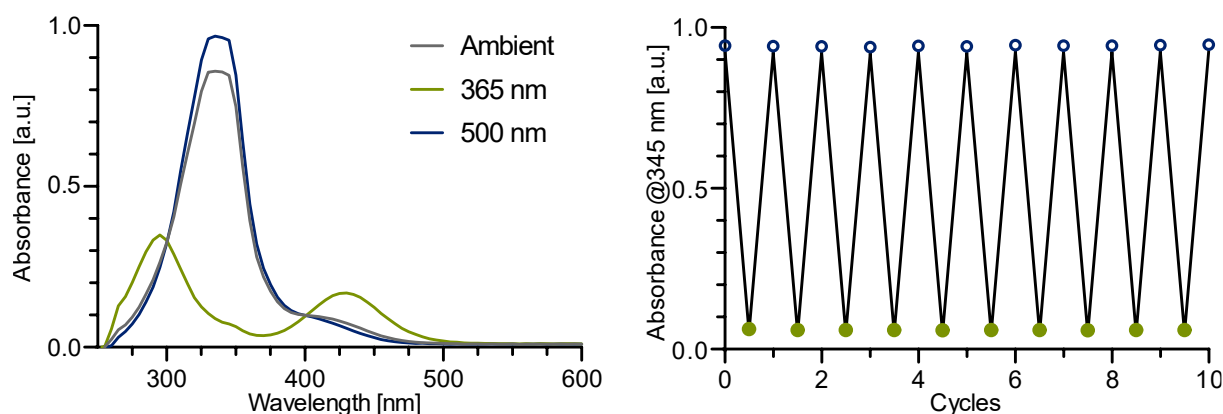


Figure S52. Left: UV-vis spectra of azobispyrazole photoswitch **S4** (69 μM , DMSO, 25 $^{\circ}\text{C}$) under ambient light and after irradiation with 365 and 500 nm for 1 min, respectively. Right: UV-vis switching reversibility experiment of azobispyrazole photoswitch **S4** (69 μM , DMSO, 25 $^{\circ}\text{C}$) showing the absorbance at 345 nm after alternating irradiation with 365 nm (1 min) and 500 nm light (1 min), respectively. No apparent photodegradation was observed over 10 switching cycles.

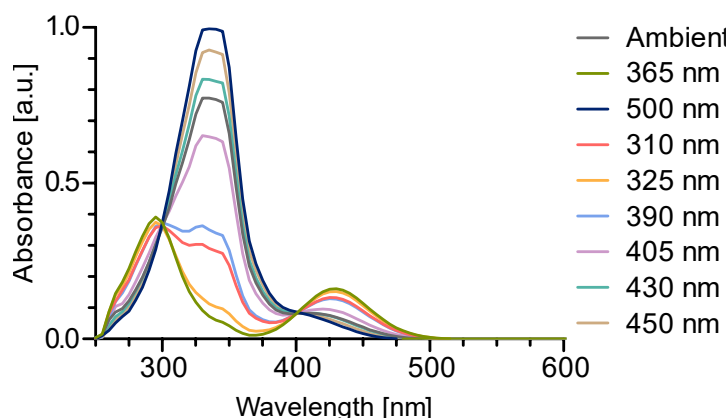


Figure S53. UV-vis spectra of azobispyrazole photoswitch **S4** (69 μM , DMSO, 25 $^{\circ}\text{C}$) before and after irradiation with different wavelengths of light for 1 min each.

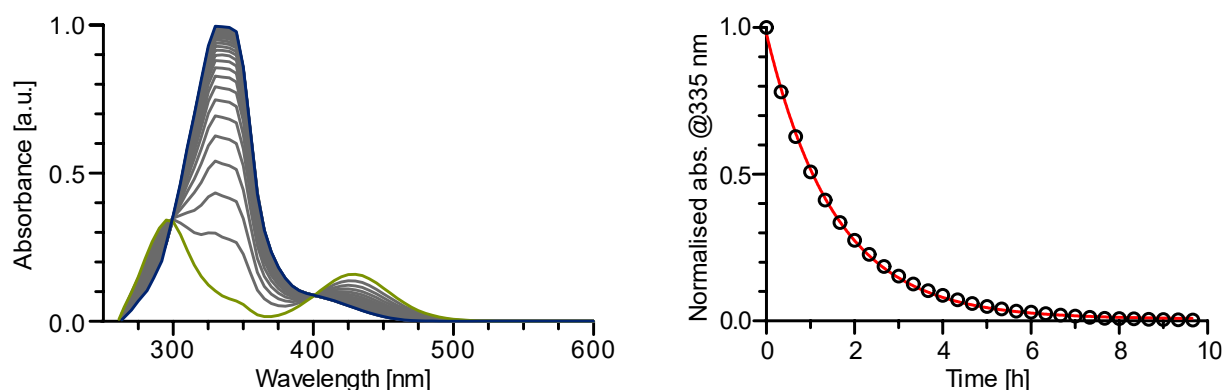


Figure S54. Thermal relaxation of azobispyrazole photoswitch **S4** (69 μM , DMSO, 25 $^{\circ}\text{C}$). Left: UV-vis spectra of azobispyrazole photoswitch **S4** measured every 20 min in the dark after irradiating with 365 nm light. Right: Change in absorption $(A_t - A_{\infty}) \cdot (A_0 - A_{\infty})^{-1}$ plotted over time t following thermal relaxation of azobispyrazole photoswitch **S4** to provide its half-life, $\tau_{1/2} = 69$ min.

S4.2 Ligand (1)

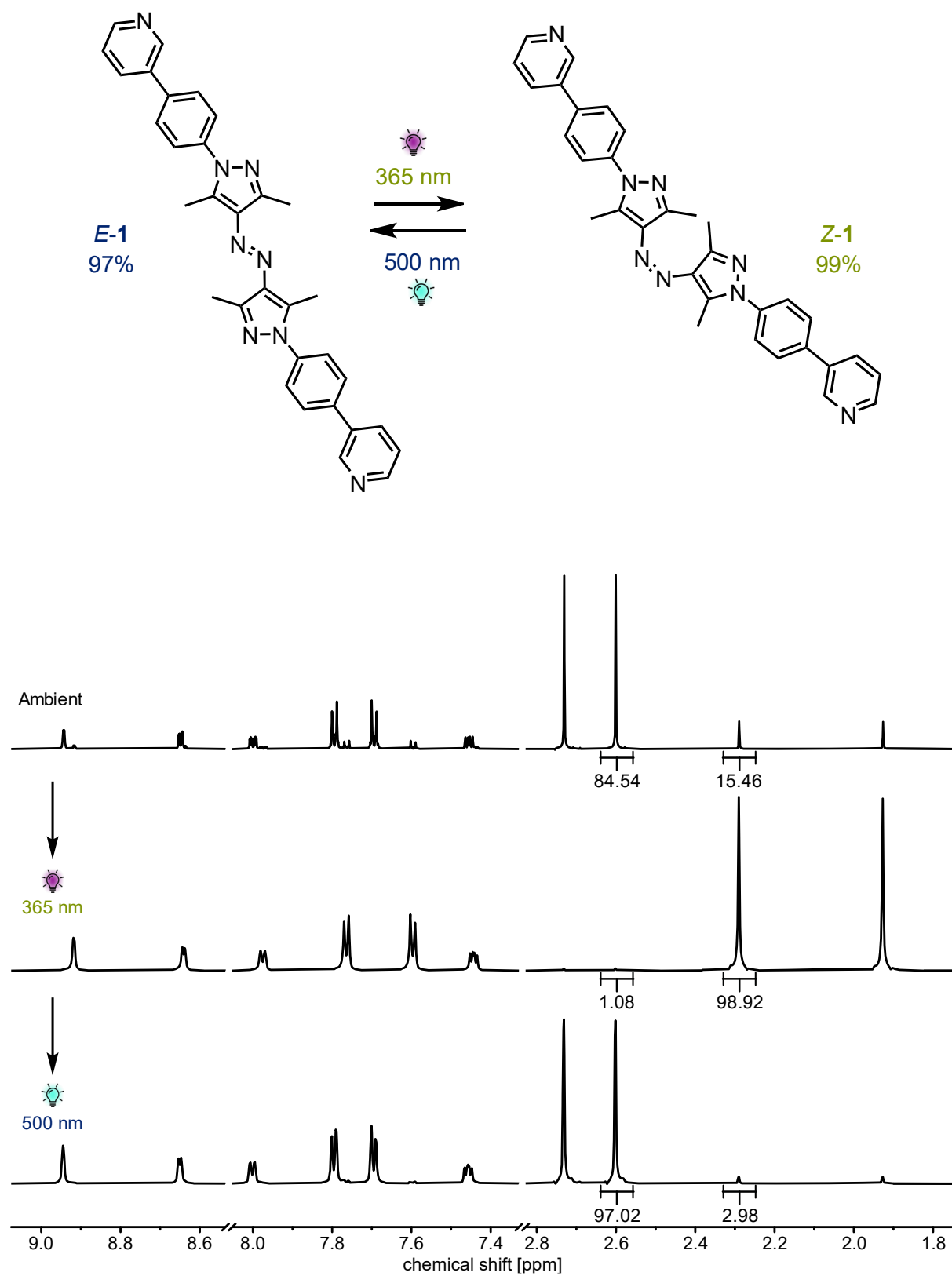


Figure S55. ¹H NMR (700 MHz, CD₂Cl₂, 298 K) spectra of **1** under ambient light, after *in-situ* irradiation with 365 nm light (20 min, PSS 99% *Z*-1), and after *in-situ* irradiation with 500 nm light (10 min, PSS 97% *E*-1).

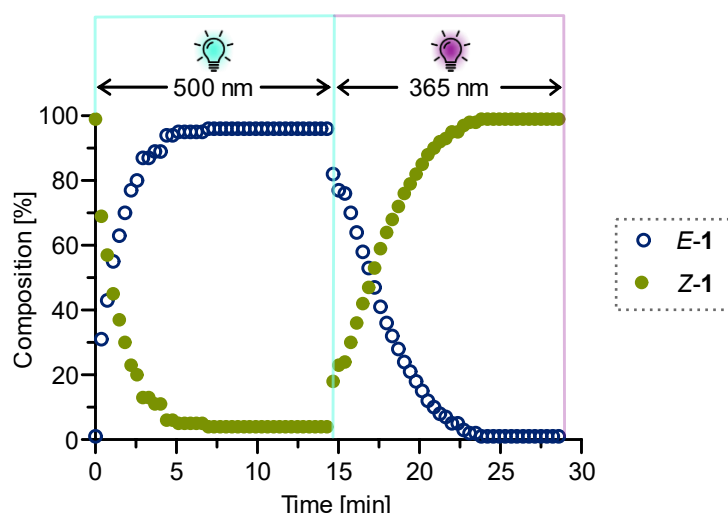


Figure S56. Changes in composition of Z-1/E-1 measured by *in-situ* illumination ^1H NMR (700 MHz, CD_2Cl_2 , 298 K). A sample of Z-1 was irradiated with 500 nm light (LED power reduced to 2%) for approx. 15 min to induce the $Z \rightarrow E$ isomerisation, followed by illumination with 365 nm light (LED power reduced to 2%) for approx. 17 min to switch the ligand back to the Z configuration.

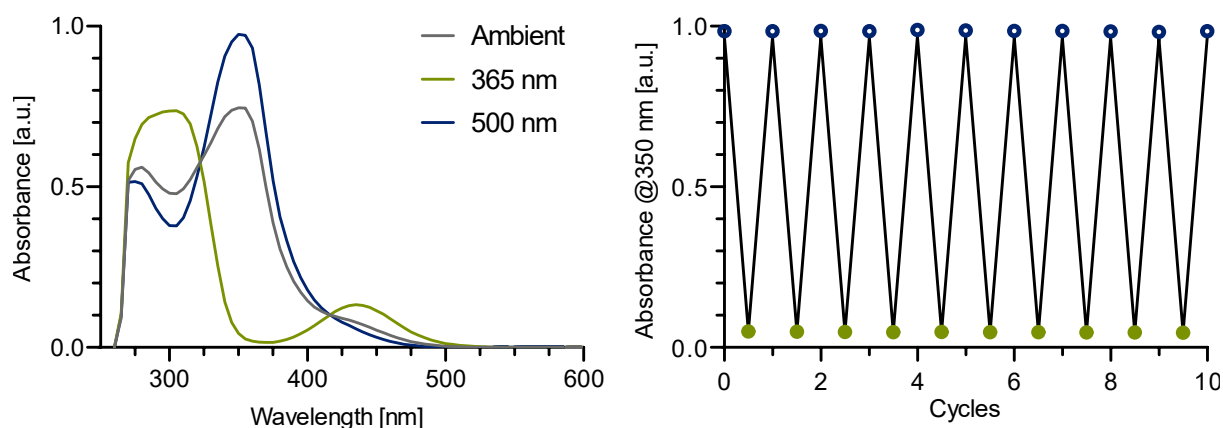


Figure S57. *Left:* UV-vis spectra of ligand **1** (24 μM , DMF, 25 $^\circ\text{C}$) under ambient light and after irradiation with 365 and 500 nm for 1 min, respectively. *Right:* UV-vis switching reversibility experiment of **1** (24 μM , DMF, 25 $^\circ\text{C}$) showing absorbance at 350 nm after alternating light irradiation with 365 nm (1 min) and 500 nm (1 min), respectively. No apparent photodegradation was observed over 10 switching cycles.

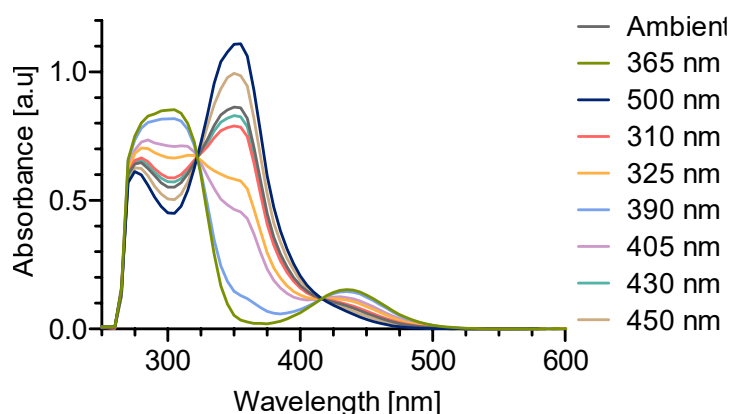


Figure S58. UV-vis spectra of ligand **1** (28 μM , DMF, 25 $^{\circ}\text{C}$) before and after irradiation with different wavelengths of light for 1 min each.

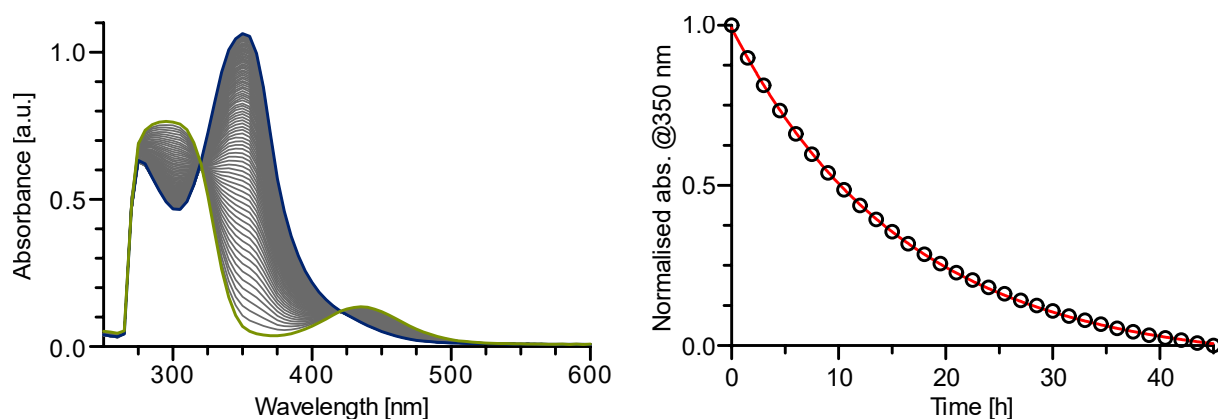


Figure S59. Thermal relaxation of ligand **1** (24 μM , DMF, 60 $^{\circ}\text{C}$). *Left:* UV-vis spectra of **1** measured every 30 min in the dark after irradiating the sample with 365 nm light. *Right:* Change in absorption $(A_t - A_{\infty}) \cdot (A_0 - A_{\infty})^{-1}$ plotted over time t following thermal relaxation of **1** to provide its half-life, $\tau_{1/2} = 10$ h.

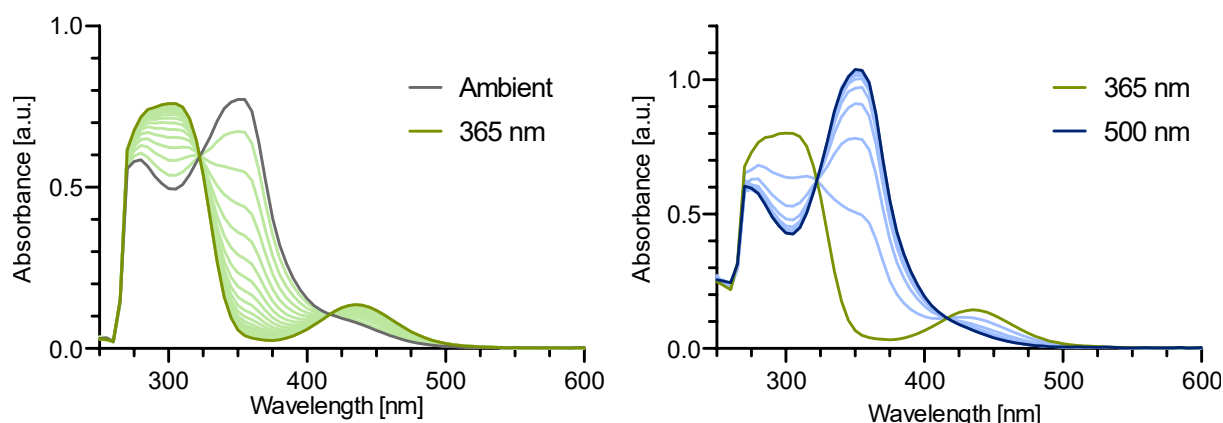


Figure S60. *Left:* UV-vis spectra of **E-1** (24 μM , DMF, 25 $^{\circ}\text{C}$) under constant light irradiation with 365 nm light (2% LED power). A UV-vis spectrum was measured every 3 s for 1 min. Complete $E \rightarrow Z$ conversion was reached after 1 min. The power of the LED was reduced to 2% to observe the transition. *Right:* UV-vis spectra of **Z-1** (24 μM , DMF, 25 $^{\circ}\text{C}$) under constant irradiation with 500 nm light. A UV-vis spectrum was measured every 3 s for 30 s. Complete $Z \rightarrow E$ conversion was reached after 30 s.

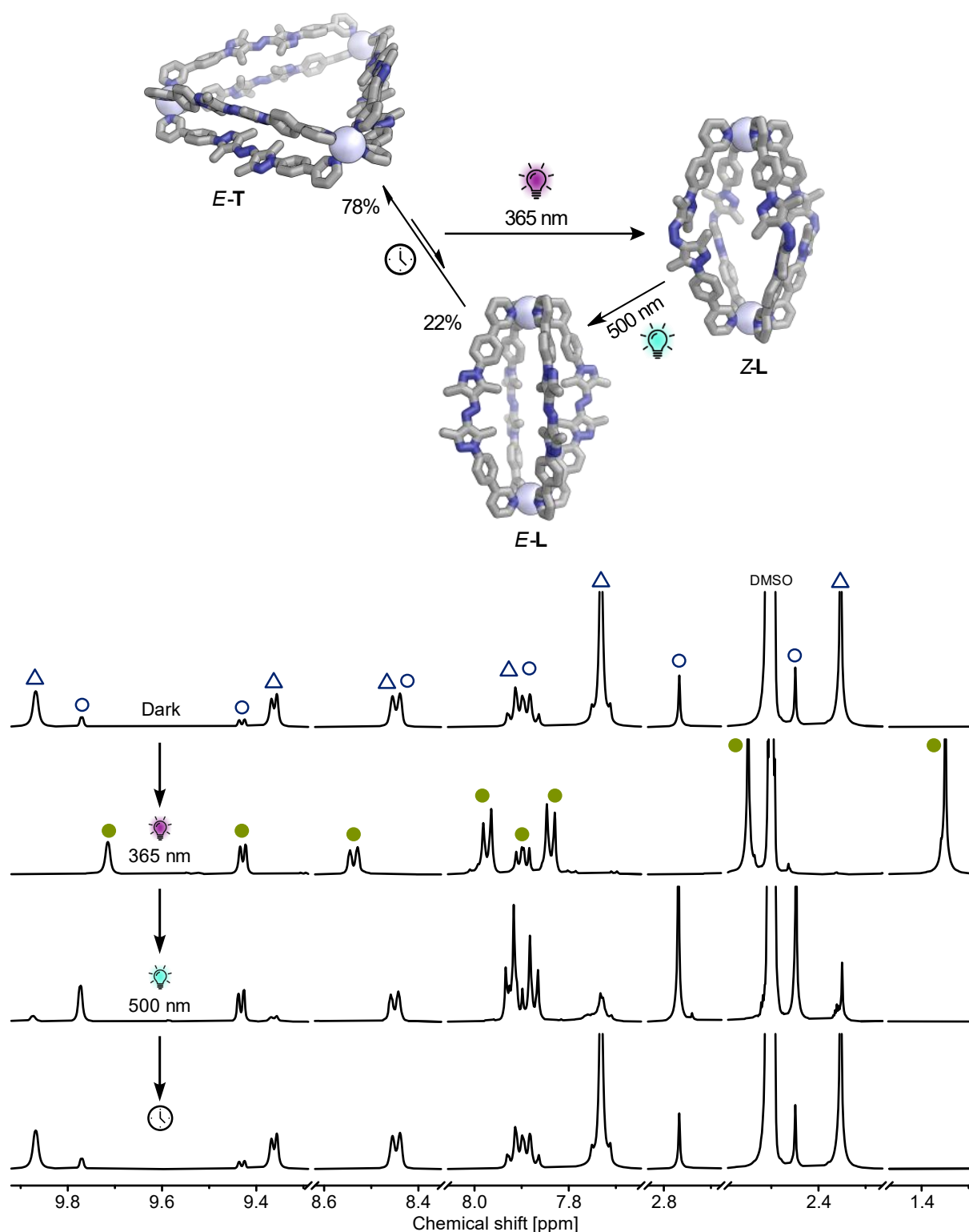
S4.3 Switching between Pd^{II} structures *E*-T, *E*-L, and *Z*-L

Figure S61. ¹H NMR (700 MHz, DMSO-*d*₆, 298 K) under light exclusion (*E*-T: *E*-L, 78:22), after *in-situ* irradiation with 365 nm light (14 min, 10% LED power) (*Z*-L), after *in-situ* irradiation with 500 nm light (6 min, 2% LED power) (*E*-T: *E*-L, 12:88), and after 22 h equilibrating in an amberised NMR tube wrapped in aluminium foil in an air-conditioned room (*E*-T: *E*-L, 78:22). *E*-T is denoted with ▲, *E*-L is denoted with ●, and *Z*-L is denoted with ●.

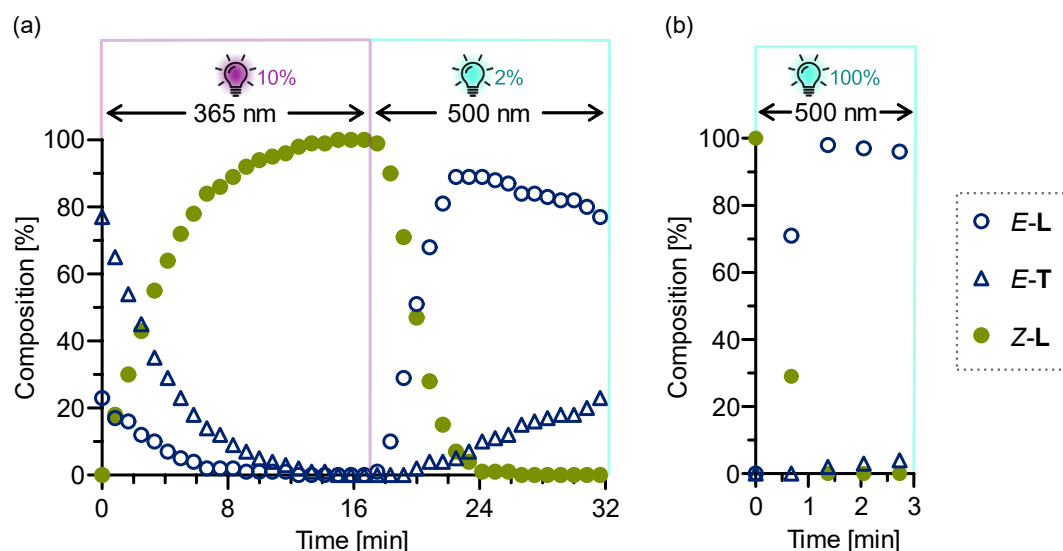


Figure S62. Changes in composition between *E*-T, *E*-L, and *Z*-L measured by *in-situ* illumination ^1H NMR (700 MHz, $\text{DMSO}-d_6$, 298 K) spectroscopy. (a) A sample of *E*-T / *E*-L (78:22, respectively) was irradiated with 365 nm light (LED power reduced to 10%) for approx. 17 min to induce *E*→*Z* isomerisation, followed by illumination with 500 nm light (LED power reduced to 2%) for approx. 16 min to induce *Z*→*E* isomerisation. The respective spectra are depicted in Figures S63 and S64, respectively. (b) A sample of *Z*-L was irradiated with 500 nm light (LED power 100%) for less than 3 min.

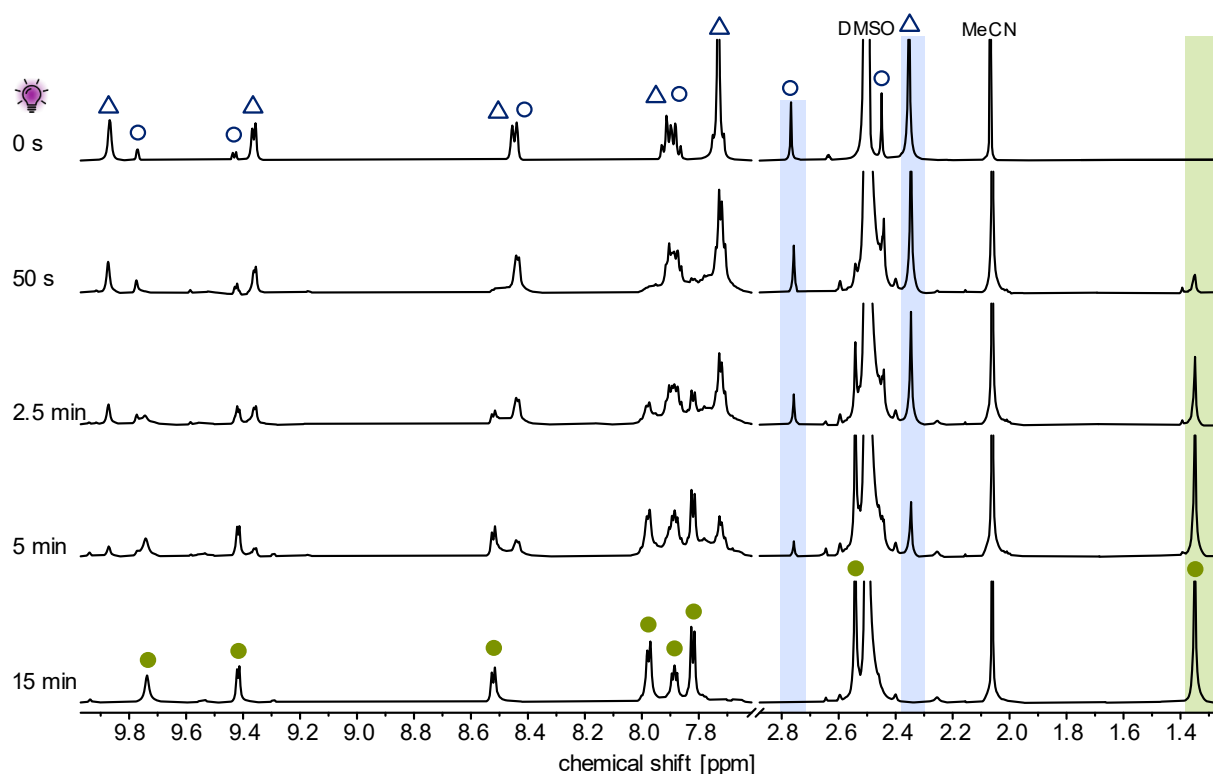


Figure S63. ^1H NMR (700 MHz, $\text{DMSO}-d_6$, 298 K) spectral changes during *in-situ* illumination with 365 nm light (10% LED power). The signals highlighted in blue and green were chosen to be line-fitted and plotted to display changes in composition between *E*-T, *E*-L, and *Z*-L (Figure S62). *E*-T is denoted with Δ , *E*-L is denoted with $\circ$, and *Z*-L is denoted with $\bullet$.

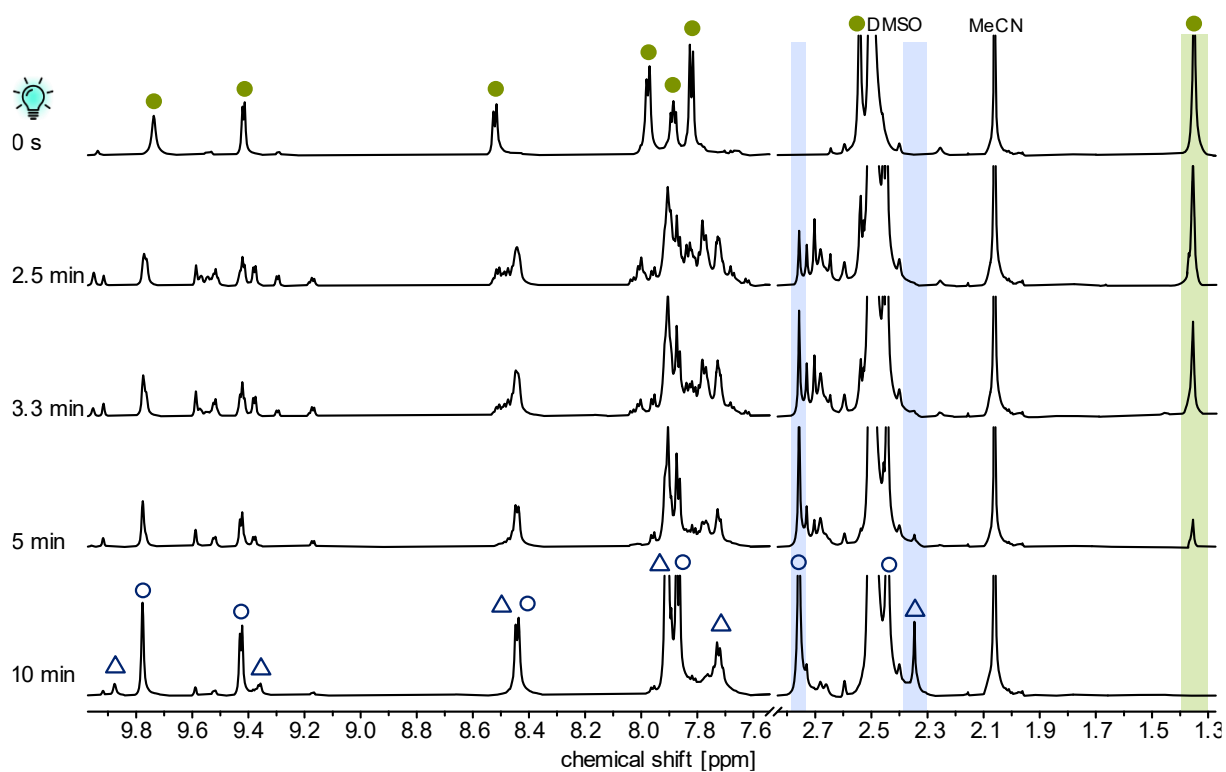


Figure S64. ^1H NMR (700 MHz, $\text{DMSO}-d_6$, 298 K) spectral changes during *in-situ* illumination with 500 nm light (2% LED power). The signals highlighted in blue and green were chosen to be line-fitted and plotted to display changes in composition between triangle *E-T*, *E-L*, and *Z-L* (Figure S62). *E-T* is denoted with Δ , *E-L* is denoted with $\circ$, and *Z-L* is denoted with $\bullet$.

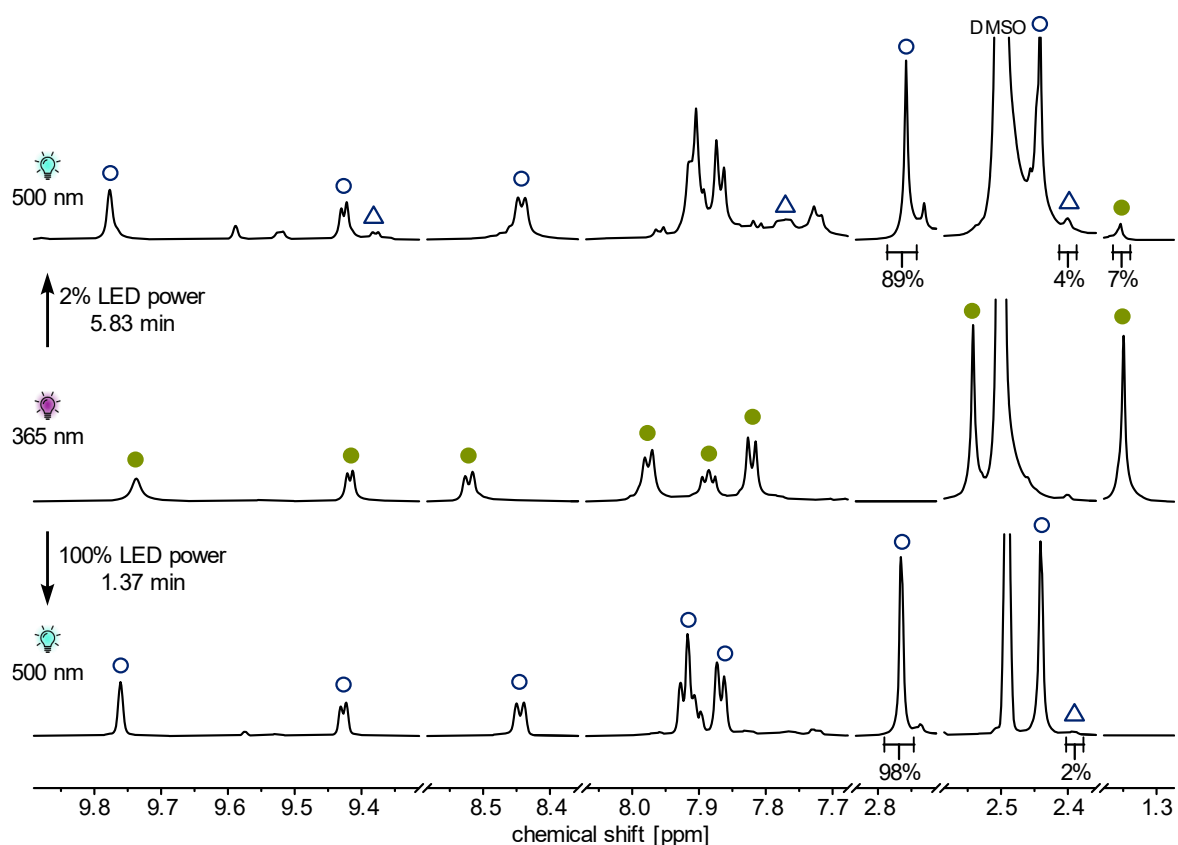


Figure S65. ^1H NMR (700 MHz, $\text{DMSO}-d_6$, 298 K) spectra of Z-L prior (middle) and after *in-situ* irradiation with 500 nm light with two different LED powers (2% LED power and 100% LED power, top and bottom, respectively). *Top:* When exposing Z-L to 500 nm light with a reduced 2% LED power, the maximum amount of E-L observed was 89% after 5.83 min of irradiation. *Bottom:* When exposing Z-L to 500 nm light with 100% LED power, the maximum amount of E-L observed was 98% after 1.37 min of irradiation. The spectra with the highest % of E-L were chosen to be displayed here, demonstrating the changes in composition when using different LED light powers. E-T is denoted with Δ , E-L is denoted with $\circ$, and Z-L is denoted with $\bullet$.

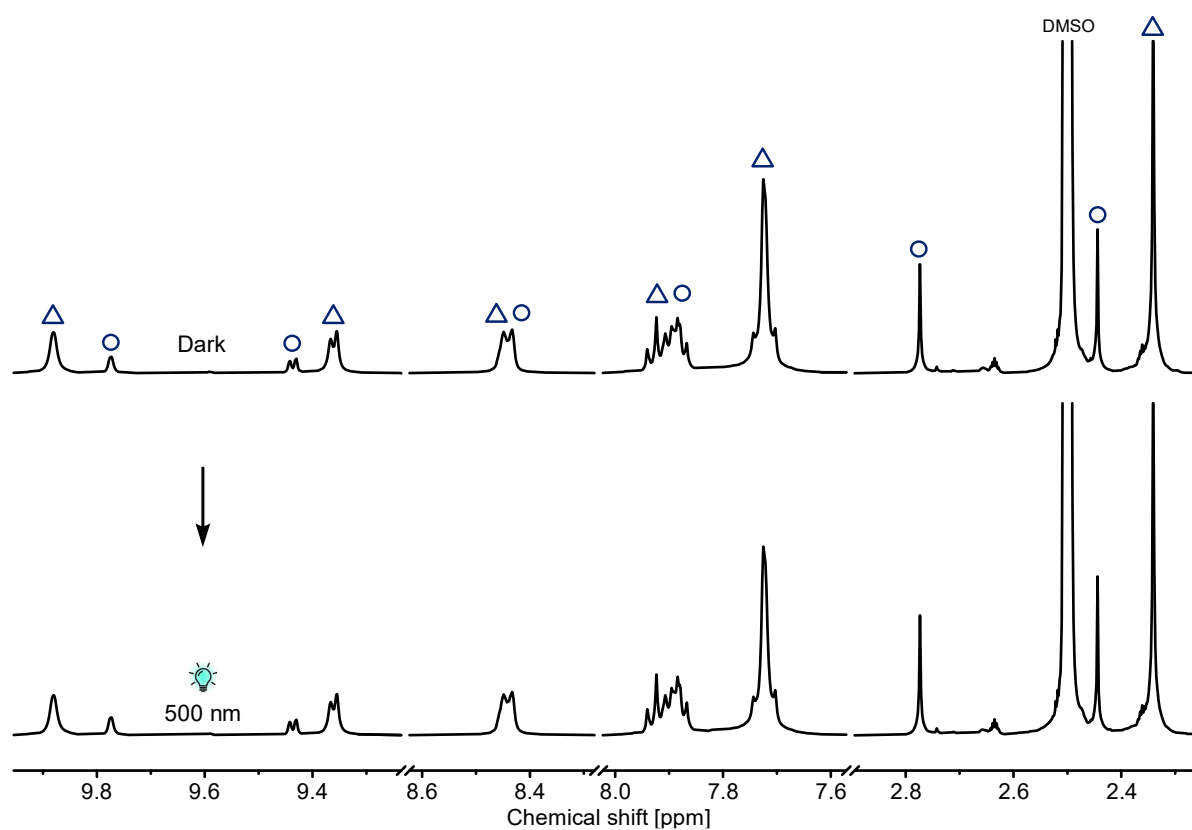


Figure S66. ^1H NMR (700 MHz, $\text{DMSO-}d_6$, 298 K) spectra under light exclusion (*E-T* / *E-L* 78:22; top) and after irradiation with 500 nm light (5 min; *E-T* / *E-L* 78:22; bottom). No change in cage composition was observed after irradiation with 500 nm light. *E-T* is denoted with Δ , *E-L* is denoted with $\circ$.

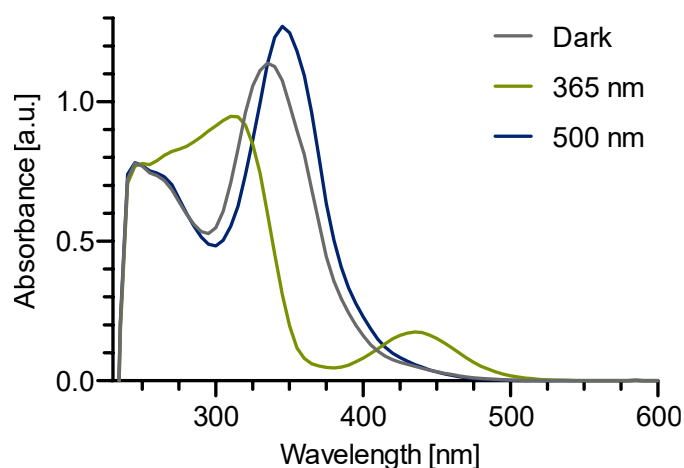


Figure S67. UV-vis (18 mM, DMSO, 298 K) spectra of *E-T* / *E-L* mixture under light exclusion and after light irradiation with 365 nm (i.e. *Z-L*) and 500 nm (i.e. *E-L*) for 1 min, respectively.

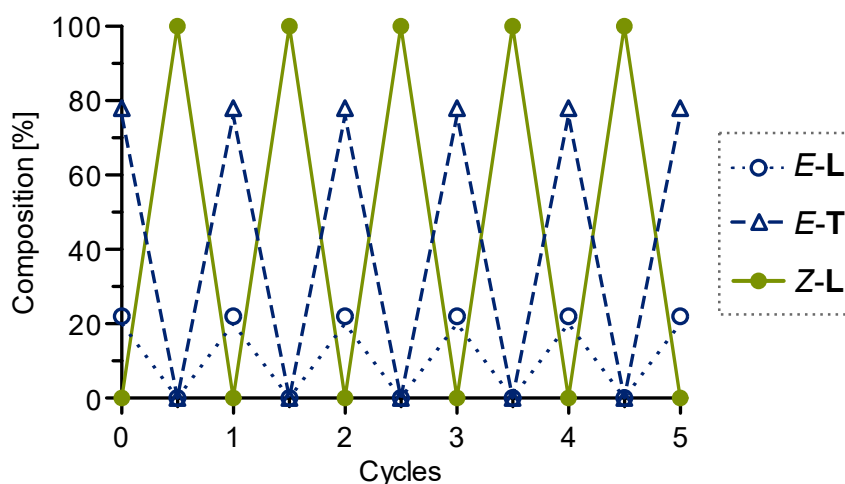


Figure S68. Investigation of switching reversibility by ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 298 K) of *E-T*, *E-L*, and *Z-L*. A 78:22 *E-T* / *E-L* mixture was subjected to alternating light irradiation with 365 nm (5 min) and 500 nm (5 min), respectively. After irradiation with 500 nm light, the sample was left equilibrating for 22 h in an amberised NMR tube wrapped in aluminium foil in an air-conditioned room (22 °C) to allow for equilibration to the 78:22 *E-T* / *E-L* ratio. No apparent photodegradation was observed after five switching cycles.

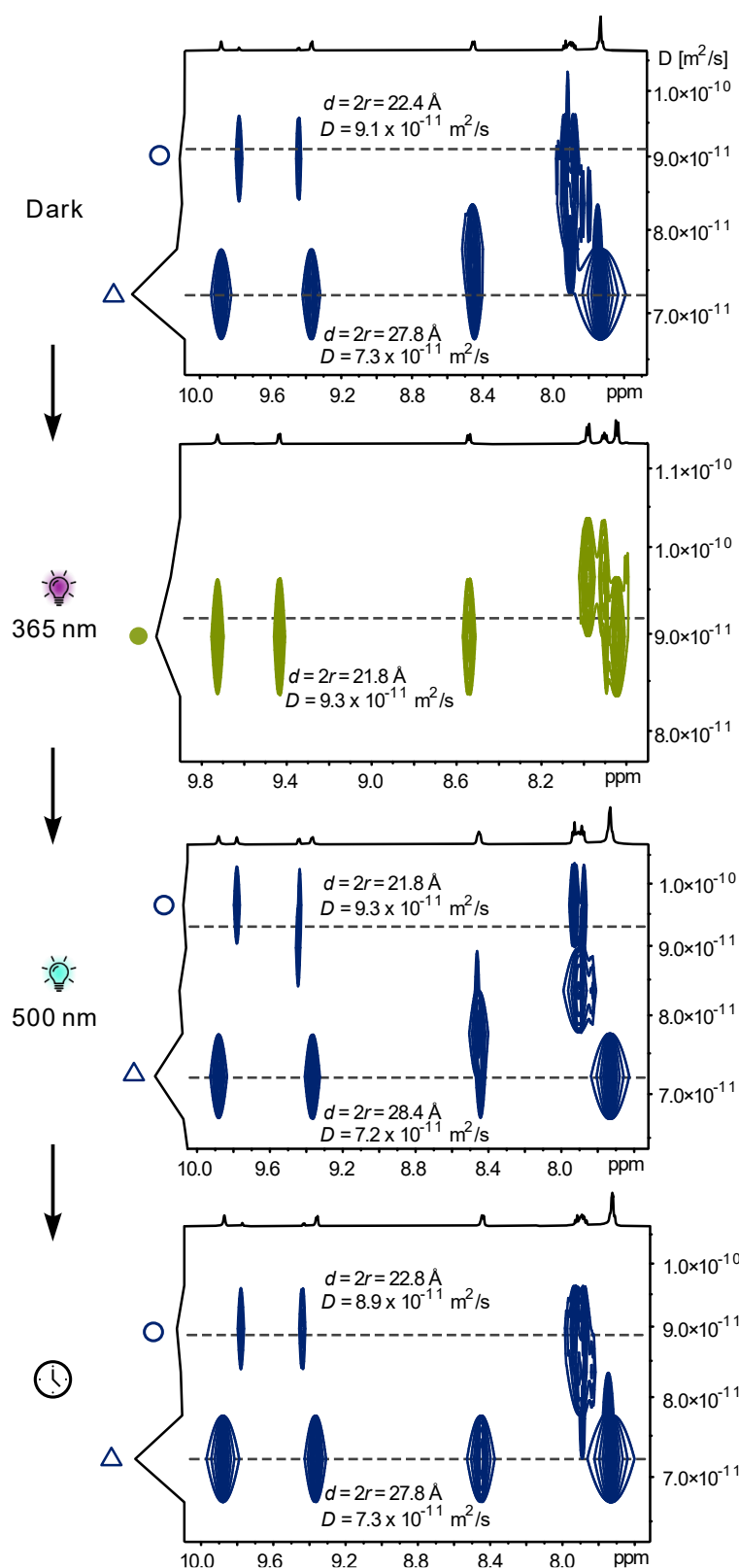


Figure S69. 2D-DOSY NMR (700 MHz, DMSO- d_6 , 298 K, D20 = 0.35 s) spectra under light exclusion (*E*-*T* / *E*-*L* 78:22), after irradiation with 365 nm light (5 min) (*Z*-*L*), after irradiation with 500 nm light (5 min) (*E*-*T* / *E*-*L* 63:37), and after 22 h equilibrating in an amberised NMR tube wrapped in aluminium foil in an air-conditioned room (22 °C; *E*-*T* / *E*-*L* 78:22; top to bottom). *E*-*T* is denoted with Δ , *E*-*L* is denoted with $\circ$, and *Z*-*L* is denoted with $\bullet$. Calculated diffusion constants (D) and solvodynamic diameters ($d = 2r$) for each complex are depicted in the respective spectra.

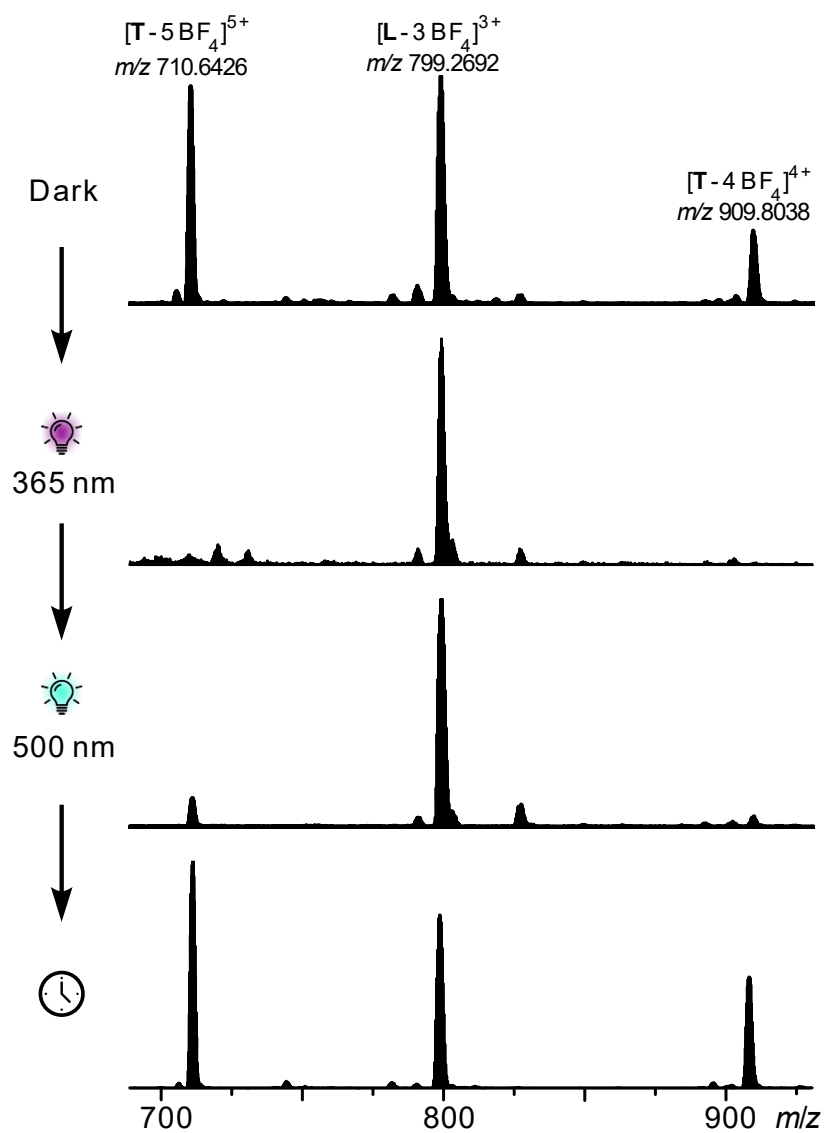


Figure S70. High-resolution ESI⁺ mass spectra (DMSO/CH₃CN) of an *E-T* / *E-L* mixture under light exclusion, after irradiation with 365 nm light (5 min; i.e. *Z-L*), after irradiation with 500 nm light (5 min), and after 21 h equilibrating at 22 °C (top to bottom).

S5 Kinetic studies

S5.1 Thermal relaxation of Z-L

To investigate the thermal stability of lantern Z-L, an NMR sample containing *E-T* / *E-L* mixture in a ratio of 78:22 was irradiated with 365 nm for 5 min to obtain lantern Z-L. ^1H NMR spectra were immediately measured over a period of 2 h at 75 °C (Figure S72) and the change in % of Z-L was plotted over time t (Figure S71). Non-linear curve fitting provided a half-life at 75 °C of $t_{1/2} = 21$ min.

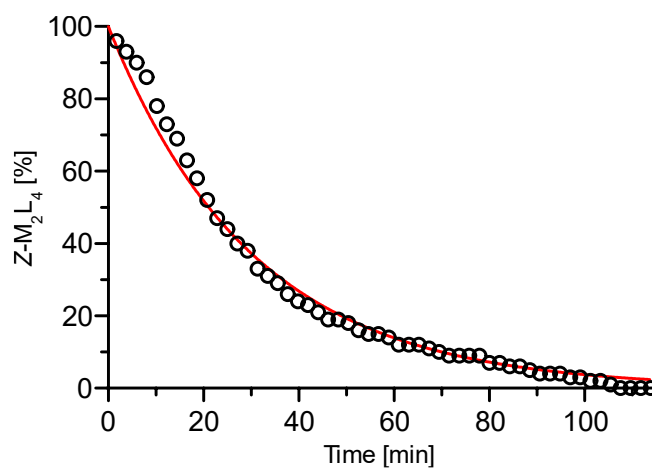


Figure S71. Thermal relaxation of Z-L (7.5 mM) investigated by ^1H NMR (500 MHz, $\text{DMSO-}d_6$, 348 K). Change in % of Z-L plotted over time t following thermal relaxation provides its half-life at 75 °C of $t_{1/2} = 21$ min.

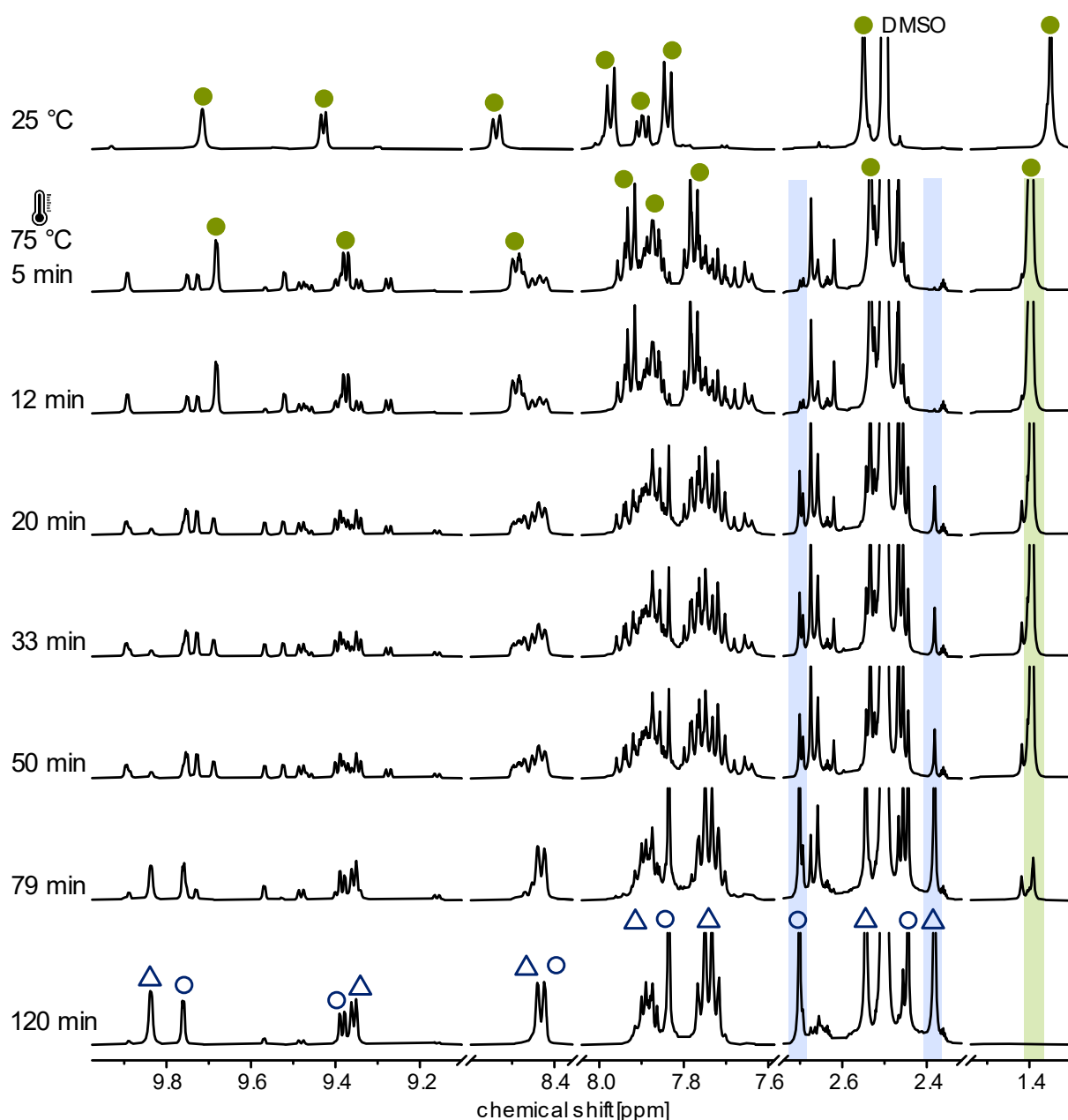


Figure S72. At the top ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 298 K) spectrum of Z-L measured at 25 °C. The thermal relaxation of Z-L to E-T and E-L was then followed by ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 348 K) at 75 °C under light exclusion over a period of 120 min. The signals highlighted in blue and green were chosen to be line-fitted and plotted to display changes in composition between triangle E-T, E-L, and Z-L (Figure S71). E-T is denoted with Δ , E-L is denoted with $\circ$, and Z-L is denoted with $\bullet$. The signals for Z-L have been assigned twice due to a signal shift at higher temperatures.

To investigate the thermal stability of *Z-L* at room temperature, an NMR sample containing *E-T* / *E-L* mixture in a ratio of 78:22 was irradiated with 365 nm for 5 min to obtain *Z-L*. The sample was then stored in an amberised NMR tube wrapped in aluminium foil in an air-conditioned room at 22 °C to prevent any disruption caused by either temperature or ambient light. ¹H NMR spectra were measured at irregular intervals over a period of more than one year (Figure S73).

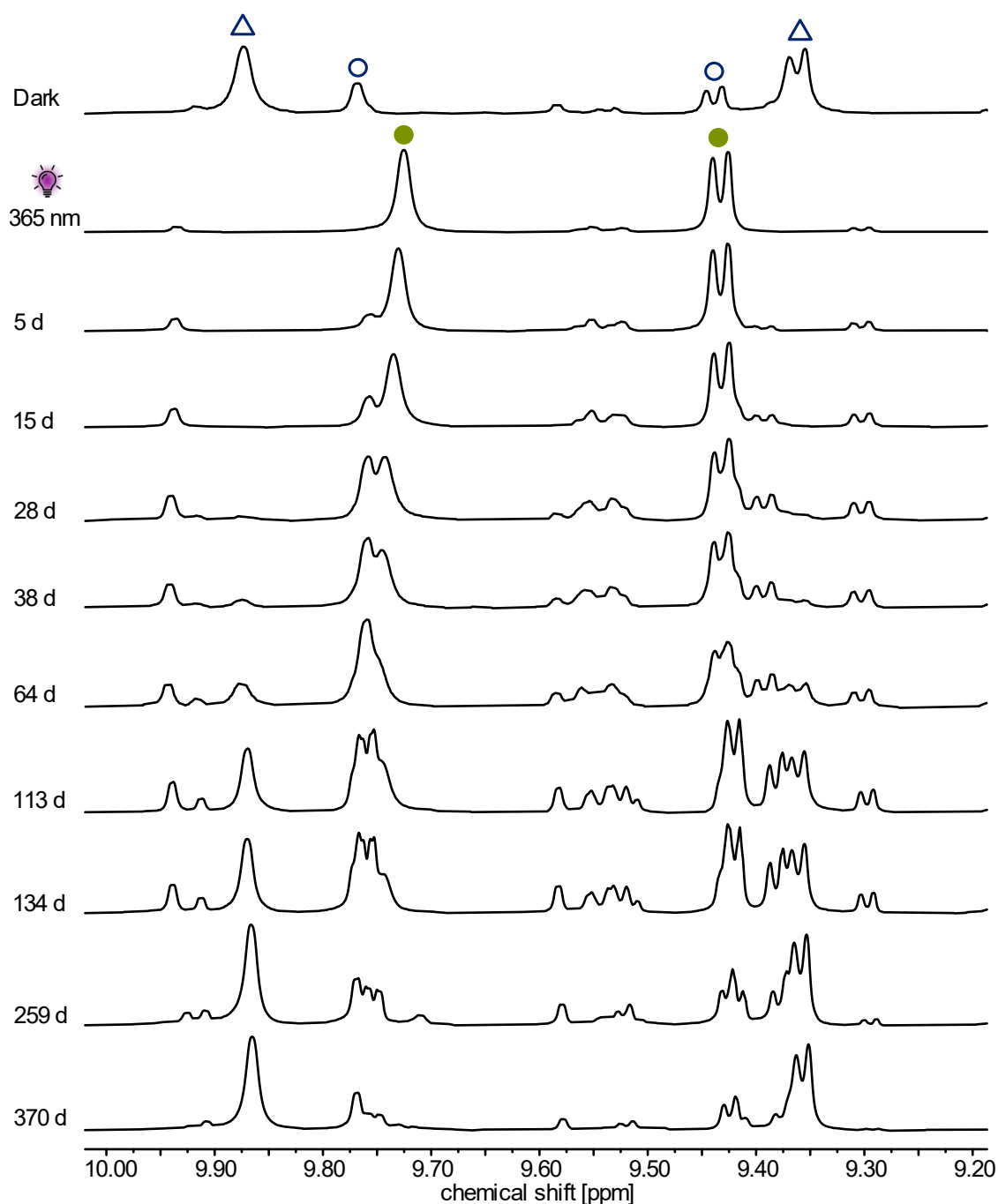


Figure S73. ¹H NMR (500 MHz, DMSO-*d*₆, 298 K) spectra under light exclusion (*E-T*: *E-L*, 78:22) following irradiation with 365 nm light (5 min; 0 d) to form *Z-L* and kept at 22 °C under light exclusion over a period of 370 d. *E-T* is denoted with Δ, *E-L* is denoted with ○, and *Z-L* is denoted with ●.

Comparison of the lantern-scrambling experiments presented in Section S2.8 and the thermal relaxation of **Z-L** shown above (Figure S73) revealed some of the tentatively assigned signals for lanterns with mixed ligand configurations, namely *Z,E,E,E-L*, *cis-Z,Z,E,E-L*, *trans-Z,Z,E,E-L*, and *Z,Z,Z,E-L*, to be present as intermediates during thermal relaxation.

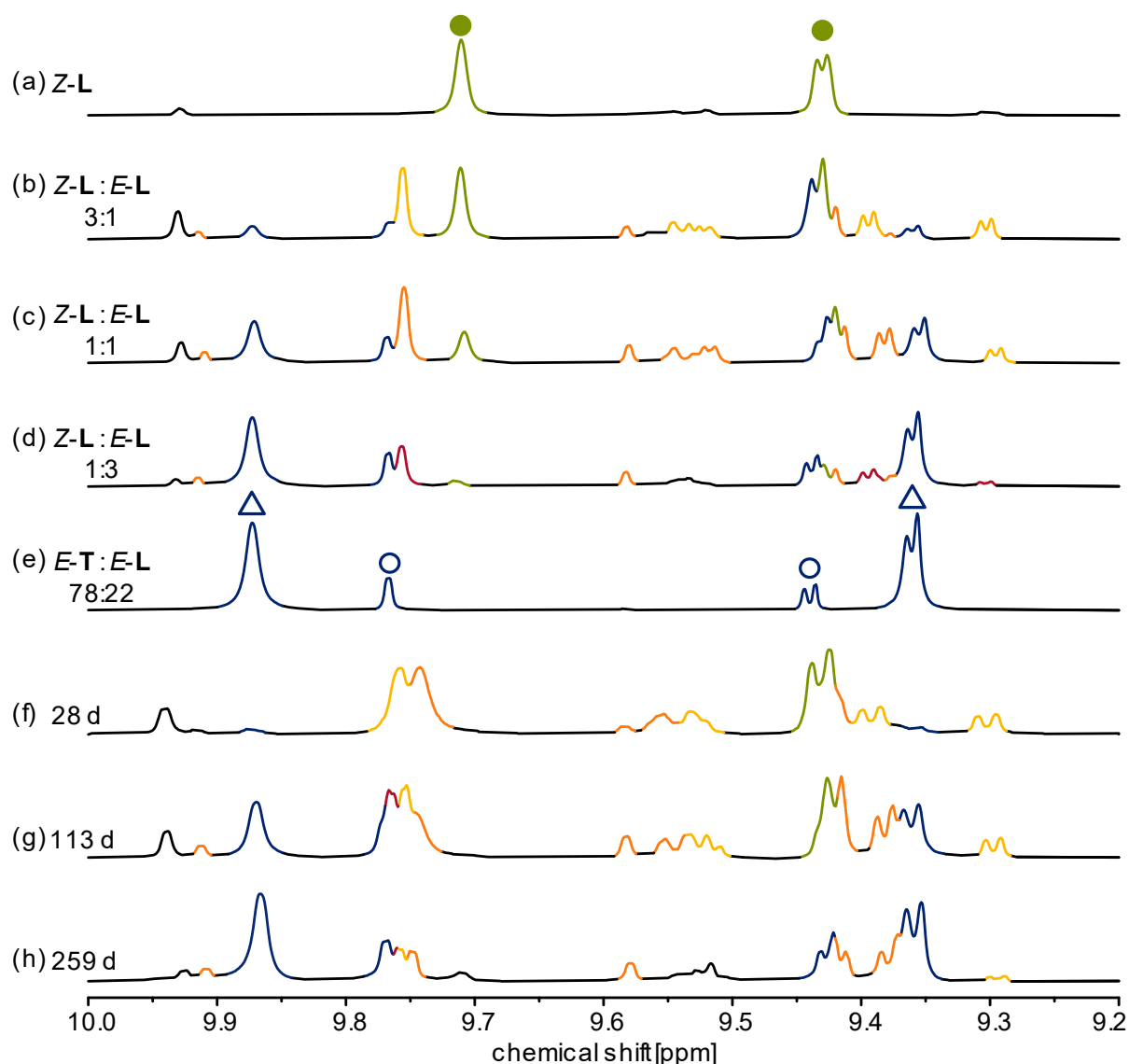


Figure S74. ^1H NMR (500/700 MHz, $\text{DMSO}-d_6$, 298 K) spectra of (a) **Z-L** and (e) **E-T** / **E-L** mixture under light exclusion (**E-T**: **E-L**, 78:22) for reference and of lantern-scrambling experiment after 13 h with **Z-L** / **E-L** ratios of (b) 3:1, (c) 1:1, and (d) 1:3; thermal relaxation of **Z-L** at 22 °C after (f) 28 d, (g) 113 d, and (h) 259 d. **E-T** is denoted with Δ , **E-L** is denoted with $\circ$, and **Z-L** is denoted with $\bullet$. Newly emerged signals are tentatively highlighted in yellow, orange, and red, respectively, depending on whether they were predominantly found in the 1:3, 1:1 or 3:1 **E-L** / **Z-L** mixtures.

S5.2 Kinetic investigation of the molecular ratchet

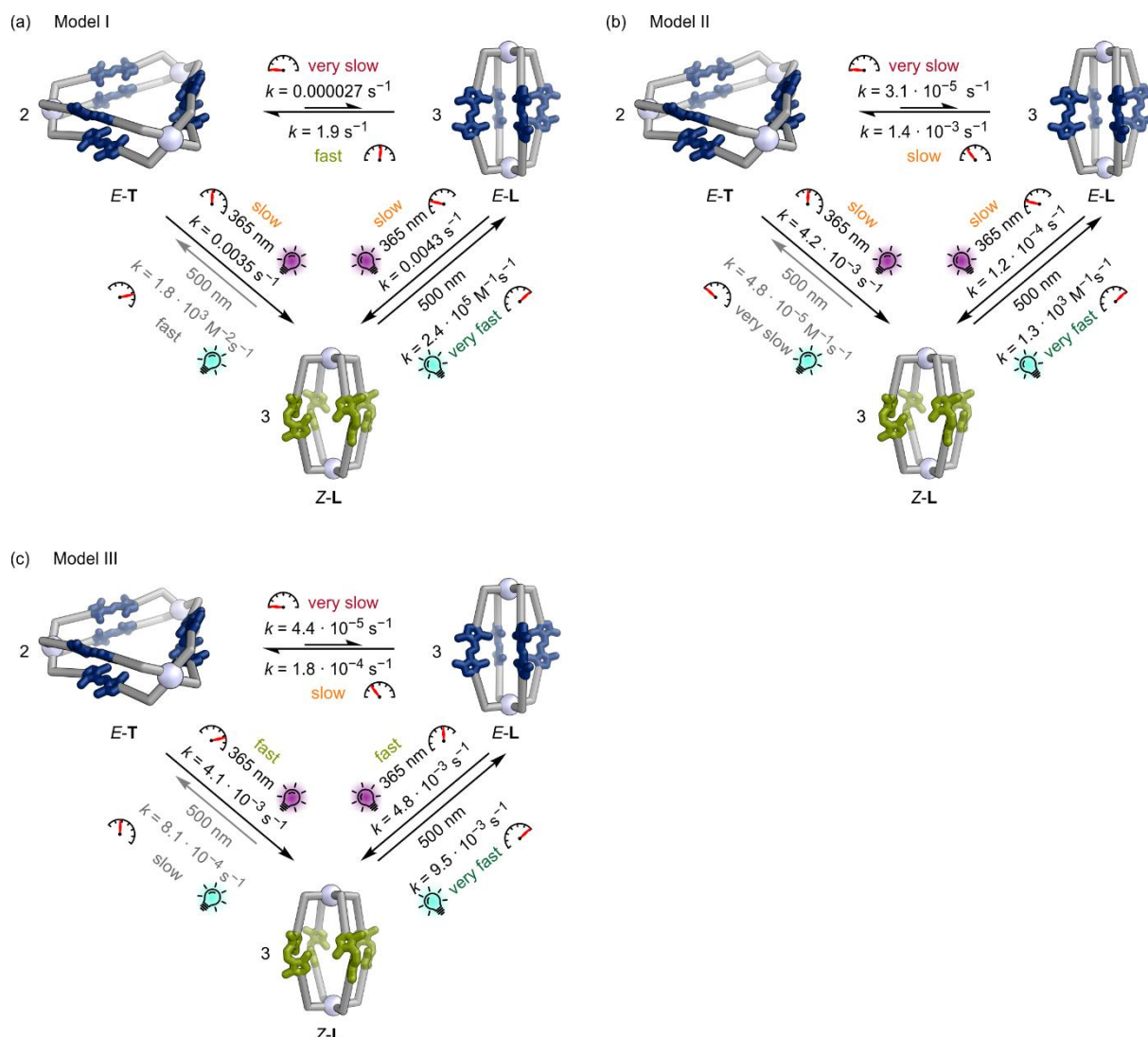


Figure S75. Schematic representation of the molecular ratchet governing the $E\text{-T} / E\text{-L} \rightarrow Z\text{-L}$ switching cycle, with the rate constants of the rate-determining steps indicated alongside the reaction arrows as determined by (a) Model I, (b) Model II, and (c) Model III. Note that for Models I and II, both photoswitching transformations involve a photoisomerisation and a capsule rearrangement step, which involve different reactant stoichiometries and therefore follow different reaction orders. For 365 nm irradiation, the rate-determining step is photoisomerisation (first order), while for 500 nm irradiation, it is rearrangement (second order). With only the rate-determining steps displayed in this scheme, this leads to apparent different reaction orders for forward and backward reactions of reciprocal processes (e.g. $E\text{-L} \rightarrow Z\text{-L}$ and $Z\text{-L} \rightarrow E\text{-L}$).

Clearly distinguishable signals for each species — triangle $E\text{-}\mathbf{T}$, lantern $E\text{-}\mathbf{L}$ and lantern $Z\text{-}\mathbf{L}$ — allowed the isomerisation kinetics of the complete photoisomerisation cycle (Figure S75) to be investigated using ^1H NMR spectroscopy (500 MHz or 700 MHz, $\text{DMSO-}d_6$, 298 K or 348 K):

- i) The triangle $E\text{-}\mathbf{T}$ / lantern $E\text{-}\mathbf{L}$ equilibrium.
- ii) The photoswitching of the triangle $E\text{-}\mathbf{T}$ / lantern $E\text{-}\mathbf{L}$ mixture to lantern $Z\text{-}\mathbf{L}$ under irradiation with 365 nm light.
- iii) The photoswitching of lantern $Z\text{-}\mathbf{L}$ to lantern $E\text{-}\mathbf{L}$ under irradiation with 500 nm light and subsequent equilibration to the triangle $E\text{-}\mathbf{T}$ / lantern $E\text{-}\mathbf{L}$ mixture.

While some intermediates could be detected, which we tentatively assigned to be the partly switched lantern structures, i.e. $Z,Z,Z,E\text{-}\mathbf{L}$, $Z,Z,E,E\text{-}\mathbf{L}$, and $Z,E,E,E\text{-}\mathbf{L}$ (see Figure S74 and Section S8.2), these intermediates were minor and could not be clearly identified. Hence, we excluded them from the kinetic investigation of the switching cycle.

Prior to investigation, all samples were stored in the dark in an air-conditioned room at 22 °C to prevent any disruption caused by either temperature or ambient light, so that the absolute concentrations of the species could be calculated from the ^1H NMR integrals based on the initial amount of ligand in the NMR sample and the assumption that all species were visible in ^1H NMR. The resulting concentrations were plotted against time and fitted using the software COPASI (version 4.44).⁹

Kinetic investigation of these processes is non-trivial, and similar systems have rarely been investigated.^{10–14} The kinetic data suggest that all transformations within the photoswitching cycle (Figure S71) follow (*pseudo*-) first-order kinetics. However, the transformation of triangle $E\text{-}\mathbf{T}$ to lantern $E\text{-}\mathbf{L}$, for example, does formally require two molecules of triangle $E\text{-}\mathbf{T}$ that form three molecules of lantern $E\text{-}\mathbf{L}$. This reaction would not follow first-order rate laws. Therefore, the apparent (*pseudo*-) first-order kinetics for all transformations indicate that their rate-determining steps depend solely on the concentrations of a single supramolecular species. We tentatively assume these rate-determining steps to be either (partial) capsule opening, in case of the equilibration between triangle $E\text{-}\mathbf{T}$ / lantern $E\text{-}\mathbf{L}$, or photoswitch isomerisation (both photochemically or thermally), in case of the photoswitch isomerisation steps. All other processes involved in these transformations are not rate-limiting.

To account for these (*pseudo*-) first-order kinetics and fit the data to the correct stoichiometries, we developed three independent models to determine the rate-determining steps of the transformations:

- (i) In Model I (Figure S75a), we deconstructed all triangle *E-T* to lantern *E-L* rearrangements into two-step processes with “Pd $\mathbf{1}_2$ *pseudo*-intermediates” (Figure S76, Figure S78, Figure S79). We do not propose “Pd $\mathbf{1}_2$ ” as an actual intermediate in the respective reaction mechanisms, which would be far more complex, but instead use this *pseudo*-intermediate “Pd $\mathbf{1}_2$ ” to separate the rate-determining *pseudo*-first-order reaction step from the complex capsule rearrangement. We chose this model because it imposes the fewest restrictions on the potential reaction mechanism, which is too complex to resolve with the available data. However, this model results in second and third-order reaction kinetics for all rearrangement steps of triangle *E-T* and lanterns *E-L* and *Z-L*, respectively, which makes comparison of the rate constants within the reaction cycle of the molecular ratchet difficult.
- (ii) In Model II (Figure S75b), we again made use of the “Pd $\mathbf{1}_2$ *pseudo*-intermediates”, however, for all transformations involving triangle *E-T*, we introduced lantern *L* as a second intermediate. Hiraoka and coworkers previously demonstrated,^{13,14} that smaller supramolecular assemblies are likely intermediates in the self-assembly of larger structures. Hence, we believe this to be a reasonable restriction on the reaction mechanism. Crucially, all transformation steps from triangle to lantern follow second-order rate laws and can therefore be compared.
- (iii) In Model III (Figure S75c), we normalised the data, so that each transformation can be described mathematically as a first-order process, effectively removing the complex stoichiometries of the conversions, allowing us to directly compare the rate constants. In Models I and II, these complex stoichiometries result in first and second-order rate constants, which complicate the comparison of individual reaction steps. To normalise the data, we calculated percentages for the three components at each timestep by dividing each component’s concentration by the total concentration of all species at that time.

We chose to present all three models here because, most importantly, they produce similar results at a fundamental level.

S5.2.1 Model I

The necessary first step to investigate was the thermal interconversion of triangle *E-T* and lantern *E-L* at 298 K and 348 K. For this, an NMR sample containing 78:22 triangle *E-T* / lantern *E-L* mixture was irradiated with 365 nm light for 5 min to obtain *Z-L*. The sample was then immediately irradiated with 500 nm light for 5 min to obtain a sample that contains almost exclusively *E-L* lantern. The equilibration between triangle *E-T* and lantern *E-L* was followed over time by ^1H NMR spectroscopy (500 MHz, $\text{DMSO}-d_6$, 298 K or 348 K; Figure S77).

Fixing the formation of triangle *E-T* or lantern *E-L* from *pseudo*-intermediate “Pd1₂” as an arbitrarily fast reaction ($k = 10^6$ or 10^8 , close to the diffusion limit in DMSO) allowed us to determine rate constants for the rate-determining steps that describe the triangle *E-T* / lantern *E-L* equilibrium at 298 K and 348 K, respectively (Figure S78 and Figure S79).

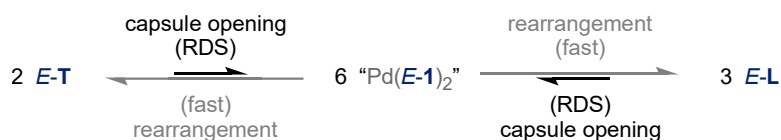


Figure S76. Schematic overview of the simplified kinetic model (within Model I) used for the interconversion between *E-T* and *E-L*. Note that the “Pd(*E-1*)₂” species is a *pseudo*-intermediate and not a real compound.

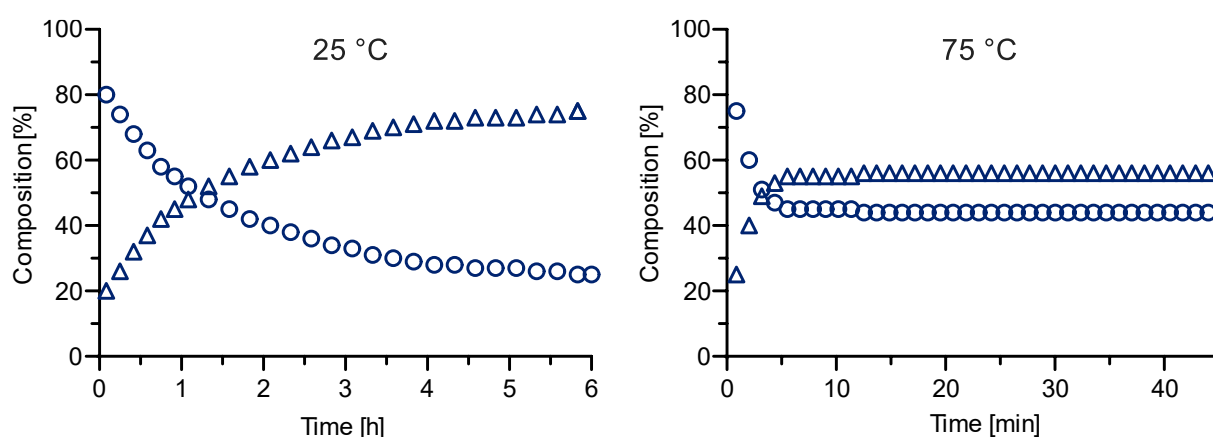


Figure S77. At room temperature, *Z-L* was irradiated with 500 nm for ca. 5 min to induce *Z*→*E* isomerisation. *Left*: ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 298 K) was measured every 5 min for 6 h to monitor the equilibrium between *E-T* triangle and *E-L* at 298 K. Between 0 h and 1 h, every second data point was removed for clarity, between 1 h and 6 h, only every third data point was plotted (kinetic fitting in **Figure S41**). *Right*: ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 348 K) was measured every 70 s for 45 min to monitor the equilibrium between *E-T* and *E-L* at 348 K (kinetic fitting in **Figure S42**). *E-T* is denoted with Δ , *E-L* is denoted with $\circ$.

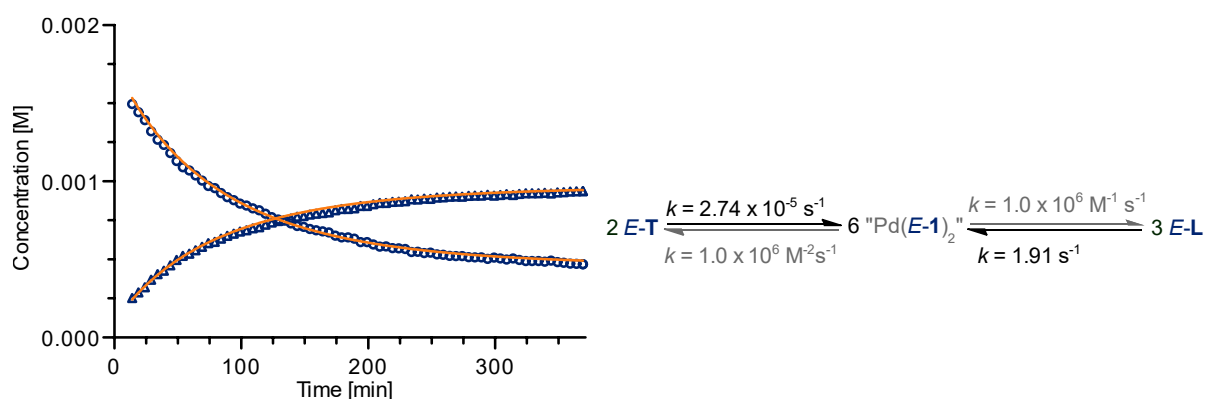


Figure S78. Kinetic plot of the equilibrium between $E-T$ and $E-L$ at $25\text{ }^{\circ}\text{C}$. $E-T$ is denoted with Δ and $E-L$ is denoted with $\circ$. The resulting reaction rates are provided within the reaction scheme on the right.

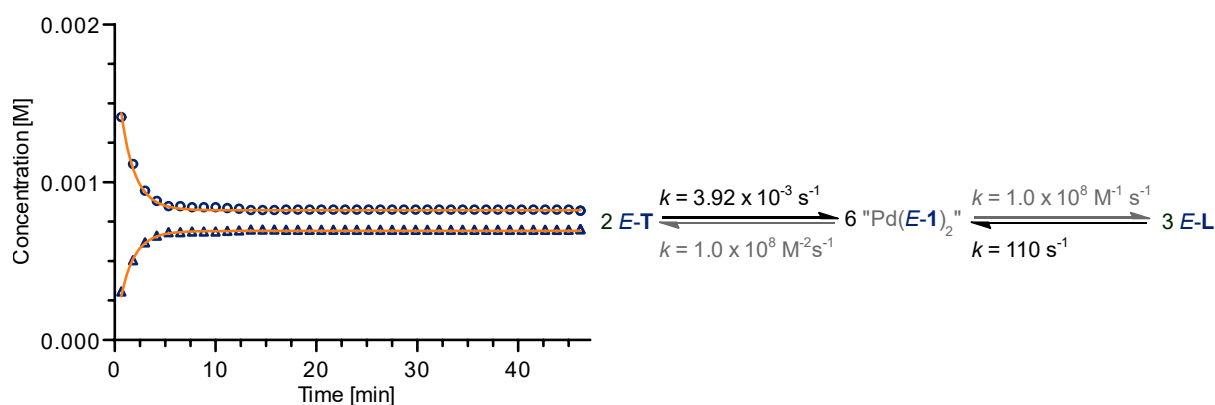


Figure S79. Kinetic plot of the equilibrium between $E-T$ and $E-L$ at $75\text{ }^{\circ}\text{C}$. $E-T$ is denoted with Δ and $E-L$ is denoted with $\circ$. The resulting reaction rates are provided within the reaction scheme on the right.

To investigate the $E \rightarrow Z$ and $Z \rightarrow E$ isomerisations of the capsules, a sample containing 78:22 triangle E -**T** / lantern E -**L** mixture was subjected to *in-situ* illuminated ^1H NMR spectroscopy (700 MHz, DMSO- d_6 , 298 K), using 365 nm (10% LED power) and later 500 nm light (2% LED power). The power of the LEDs had to be turned to a lower setting to ensure enough data points could be measured (Figures S62–S64).

The data obtained from these experiments (Figure S62a) were fitted to a model using three different “Pd1₂” species (“Pd(E -1)₂”, “Pd(Z -1)₂”, and “Pd(E -1)₂”*) with the kinetic data previously determined for the triangle E -**T** / lantern E -**L** equilibrium fixed within the model (Figure S80). Just like before, the capsule rearrangement was separated into two steps, in this case, a photoisomerisation (and capsule opening) step and a rearrangement step from the *pseudo*-intermediates “Z-Pd1₂” and “E-Pd1₂”*, respectively.

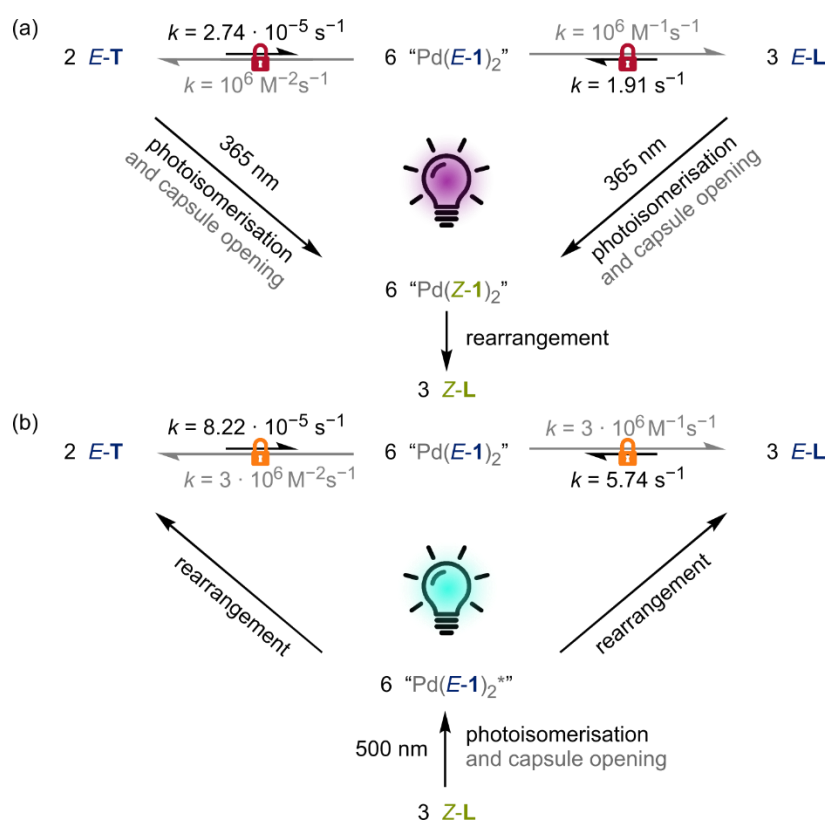


Figure S80. Kinetic models (within Model I) used for the fitting of the kinetic data of (a) $E \rightarrow Z$ photoisomerisation of triangle E -**T** / lantern E -**L** mixture under irradiation with 365 nm light and (b) $Z \rightarrow E$ photoisomerisation of lantern Z -**L** under irradiation with 500 nm light. Note that all “Pd1₂” species are *pseudo*-intermediates and not real compounds. The previously determined rate constants of the triangle E -**T** / lantern E -**L** equilibrium were fixed during fitting in (a), whereas continuous irradiation likely accelerates the equilibration in (b), and the rate constants determined under thermal conditions could not be used to fit the data. We therefore multiplied the equilibrium rate constants by a factor of three to account for this. This change affects how fast the equilibrium is reached, but does not affect the equilibrium distribution.

For the *in-situ* irradiation of the triangle *E-T* / lantern *E-L* mixture using 365 nm light, Model I suggests similar reaction rates for the photoswitching of triangle *E-T* and lantern *E-L*, indicating that both structures can photoswitch on a similar time scale to form the lantern *Z-L* (Figure S80a and Figure S81, also Section S4.3).

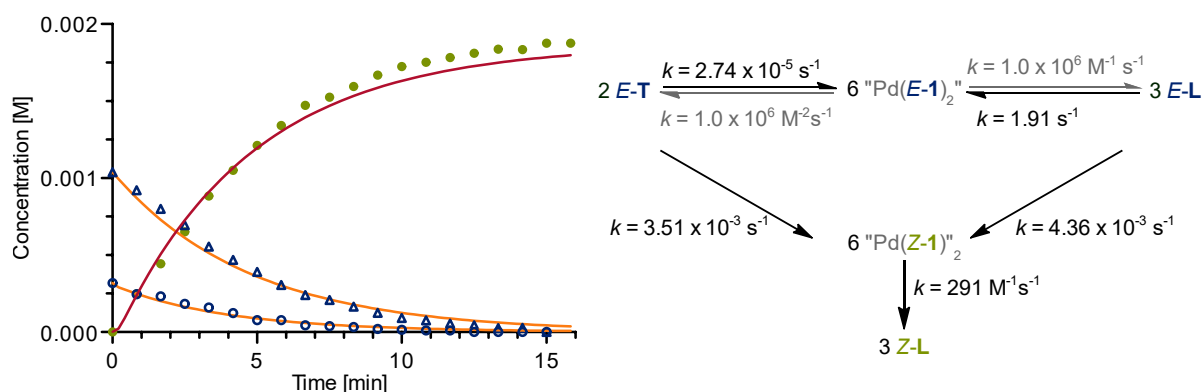


Figure S81. Kinetic plot of the formation of *Z-L* over time under *in-situ* illumination with 365 nm light (10% LED power) from a sample of *E-T*: *E-L* (78:22, respectively). *E-T* is denoted with Δ , *E-L* is denoted with $\circ$, and *Z-L* is denoted with $\bullet$. The resulting reaction rates are provided within the reaction scheme on the right.

The kinetic model for the irradiation of lantern **Z-L** with 500 nm light suggests that the formation of lantern **E-L** from lantern **Z-L** is significantly faster than the formation of triangle **E-T** from lantern **Z-L** (Figure S80b and Figure S82, also Section S4.3), suggesting kinetic asymmetry between the two photoisomerisation reactions. Hence, the main reaction pathway to form triangle **E-T** is via photoisomerisation from lantern **Z-L** to lantern **E-L** and subsequent thermal equilibration from lantern **E-L** to triangle **E-T**, indicating that lantern **Z-L** will hardly form the triangle **E-T** directly. For this fit to converge, it was necessary to multiply the equilibrium rate constants of the thermal isomerisation between triangle **E-T** and lantern **E-L** by a factor of three. We assume that continuous irradiation imparts additional energy to the system, thereby accelerating isomerisation rates. We multiplied both the forward and backward reaction rates of the equilibrium by the same factor. Therefore, this change does not affect the final equilibrium population; it only changes how fast it is reached.

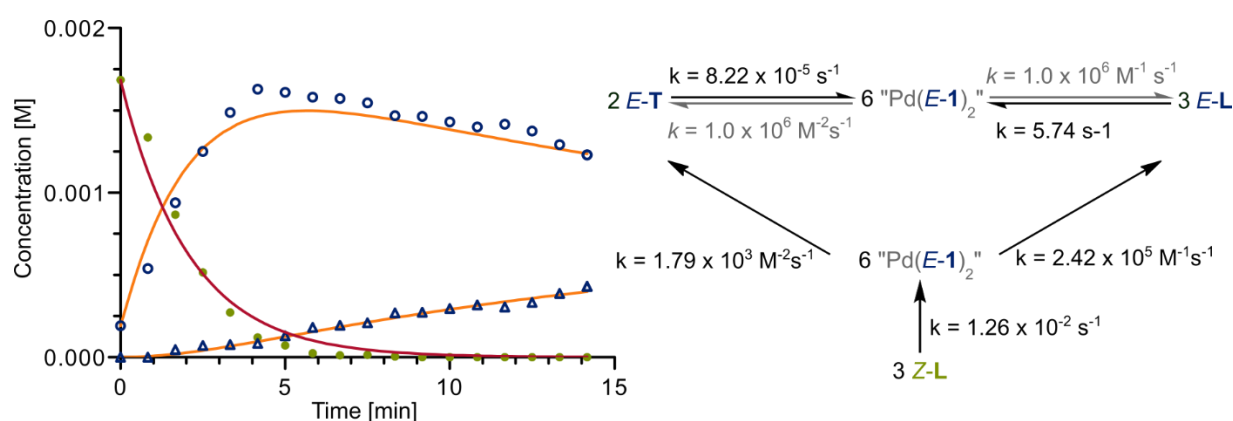


Figure S82. Kinetic plot of the formation of **E-T** and **E-L** over time under *in-situ* illumination with 500 nm light (2% LED power) from a sample of **Z-L**. **E-T** is denoted with Δ , **E-L** is denoted with $\circ$, and **Z-L** is denoted with $\bullet$. The resulting reaction rates are provided within the reaction scheme on the right.

The thermal relaxation of lantern **Z-L** to the triangle **E-T** / lantern **E-L** mixture was investigated by ^1H NMR spectroscopy (500 MHz, $\text{DMSO-}d_6$, 348 K). An NMR sample containing 78:22 triangle **E-T** / lantern **E-L** mixture was irradiated with 365 nm light for 5 min to obtain lantern **Z-L**. The sample was then immediately inserted into the NMR spectrometer at 348 K and a spectrum measured every 127 s (Figure S72).

The data obtained from these experiments were fitted to a model using two different “ Pd1_2 ” species (“ $\text{Pd}(\text{E-1})_2$ ” and “ $\text{Pd}(\text{E-1})_2^*$ ”) with the kinetic data previously determined for the triangle **E-T** / lantern **E-L** equilibrium fixed within the model (Figure S83). Just like before, the capsule rearrangement was separated into two steps, in this case, a thermal relaxation (and capsule opening) step and a rearrangement step from the *pseudo*-intermediate “ E-Pd1_2^* ”.

Using the kinetic data of the **E-T** / **E-L** equilibrium at 348 K, which we fitted previously (Figure S79), the model determined the main pathway of the thermal relaxation of lantern **Z-L** to be the formation of the lantern **E-L** from lantern **Z-L** (Figure S84). The fastest reaction pathway to form triangle **E-T** is the isomerisation from lantern **E-L**, indicating that lantern **Z-L** will only slowly (or not at all) form triangle **E-T** via thermal relaxation.

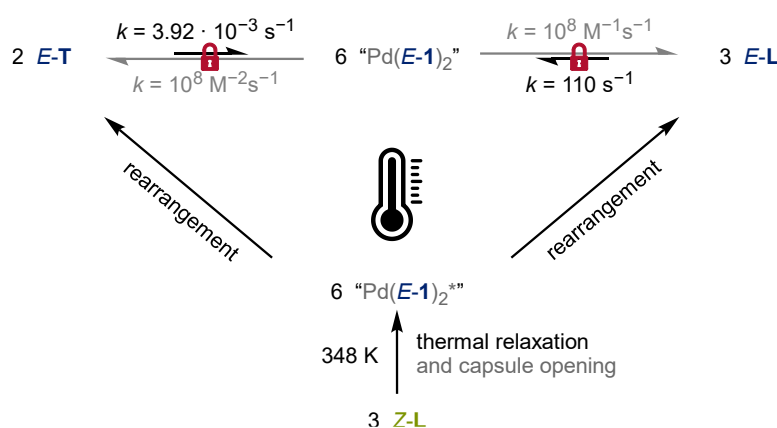


Figure S83. Kinetic model (within Model I) used for the fitting of the kinetic data of the thermal relaxation of lantern **Z-L** at 348 K. Note that all “ Pd1_2 ” species are *pseudo*-intermediates and not real compounds. The previously determined rate constants of the triangle **E-T** / lantern **E-L** equilibrium were fixed during fitting.

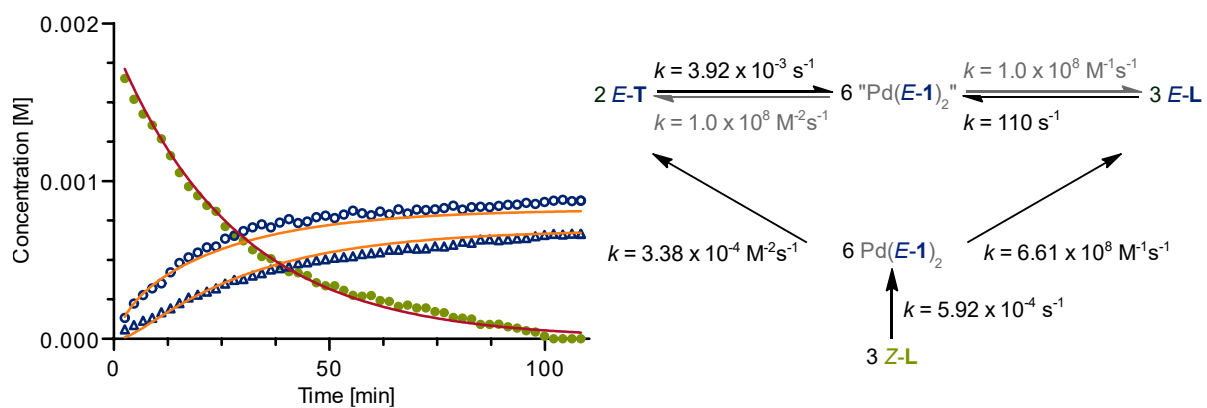


Figure S84. Kinetic plot of the thermal relaxation of Z-L at 348 K. $E-T$ is denoted with Δ , $E-L$ is denoted with $\circ$, and $Z-L$ is denoted with $\bullet$. The resulting reaction rates are provided within the reaction scheme on the right.

S5.2.2 Model II

Model II was fitted to the same experimental data as Model I. The respective experiments are detailed in Section 5.2.1.

For the equilibration between triangle $E\text{-T}$ or lantern $E\text{-L}$, Model II assumes triangle $E\text{-T}$ to open into lantern $E\text{-L}$ and *pseudo*-intermediate “Pd1₂”. In contrast to Model I, all involved reaction steps could be fitted and allowed us to determine rate constants for the rate-determining steps that describe the triangle $E\text{-T}$ / lantern $E\text{-L}$ equilibrium at 298 K and 348 K, respectively (Figure S85–87).

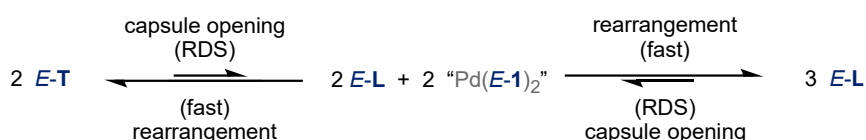


Figure S85. Schematic overview of the simplified kinetic model (within Model II) used for the interconversion between $E\text{-T}$ and $E\text{-L}$. Note that the “Pd($E\text{-1}$)₂” species is a *pseudo*-intermediate and not a real compound.

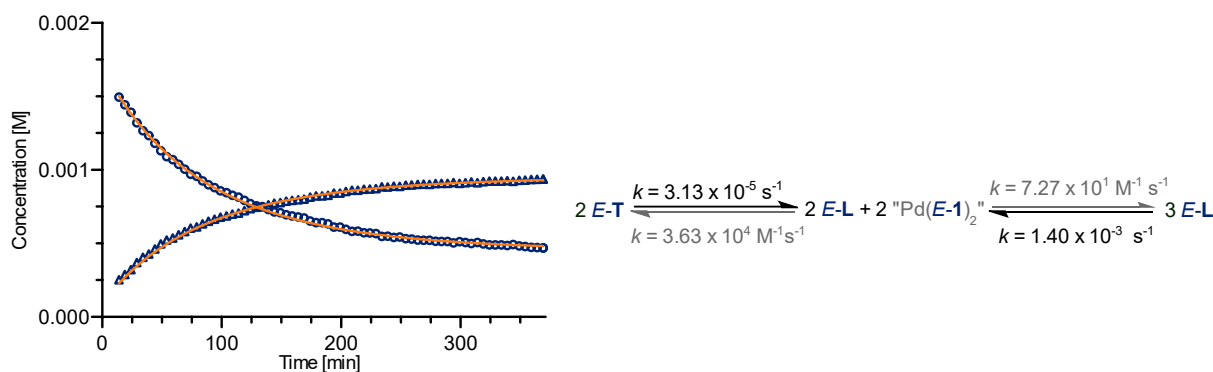


Figure S86. Kinetic plot of the equilibrium between $E\text{-T}$ and $E\text{-L}$ at 25 °C. $E\text{-T}$ is denoted with Δ and $E\text{-L}$ is denoted with $\circ$. The resulting reaction rates are provided within the reaction scheme on the right.

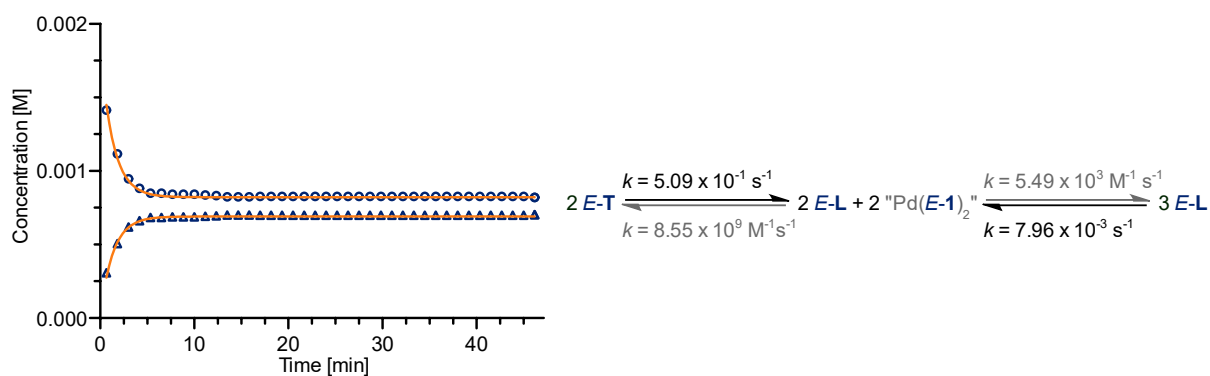


Figure S87. Kinetic plot of the equilibrium between $E-T$ and $E-L$ at 75 °C. $E-T$ is denoted with Δ and $E-L$ is denoted with $\circ$. The resulting reaction rates are provided within the reaction scheme on the right.

To investigate the $E \rightarrow Z$ and $Z \rightarrow E$ isomerisations, the data obtained from the illumination experiments (Figure S62a) were fitted to a model using three different “Pd1₂” species (“Pd(*E*-1)₂”, “Pd(*Z*-1)₂”, and “Pd(*E*-1)₂”*) with the kinetic data previously determined for the triangle E -**T** / lantern E -**L** equilibrium fixed within the model (Figure S88). Just like before, the capsule rearrangement was separated into two steps, in this case, a photoisomerisation (and capsule opening) step and a rearrangement step from the *pseudo*-intermediates “Z-Pd1₂” and “E-Pd1₂”, respectively. Additionally, in Model II, Z -**L** and E -**L** act as further intermediates for all transformations involving triangle E -**T**.

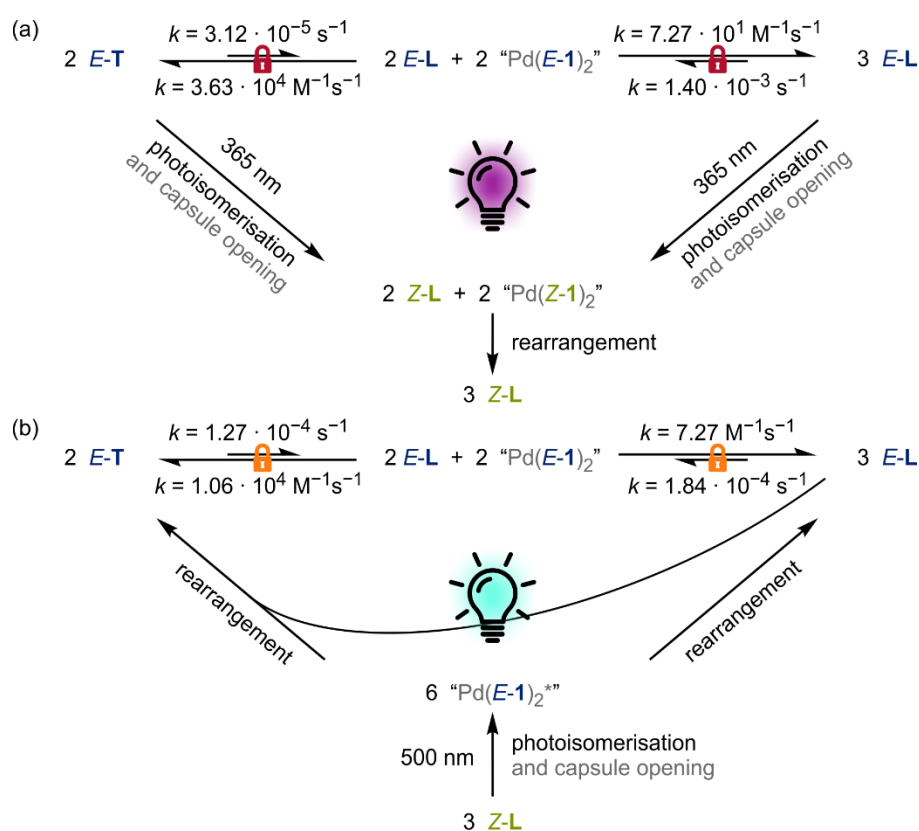


Figure S88. Kinetic models (within Model II) used for the fitting of the kinetic data of (a) $E \rightarrow Z$ photoisomerisation of triangle E -**T** / lantern E -**L** mixture under irradiation with 365 nm light and (b) $Z \rightarrow E$ photoisomerisation of lantern Z -**L** under irradiation with 500 nm light. Note that all “Pd1₂” species are *pseudo*-intermediates and not real compounds. Starting from Z -**L**, E -**T** would be formed from 2 “Pd(*E*-1)₂” and 1 E -**L** via the direct reaction pathway. The previously determined rate constants of the triangle E -**T** / lantern E -**L** equilibrium were fixed during fitting in (a), whereas irradiation likely elevated the sample temperature in (b), which is why the rate constants were given one order of magnitude of freedom to allow the fit to converge.

For the *in-situ* irradiation of the triangle *E-T* / lantern *E-L* mixture using 365 nm light, similar to Model I, Model II suggests similar reaction rates (deviating by one order of magnitude) for the photoswitching of triangle *E-T* and lantern *E-L*, indicating that both structures can photoswitch on similar timescales to form the lantern *Z-L*, with *E-L* switching faster than *Z-L* by one order of magnitude (Figure S88a and Figure S89, also Section S4.3).

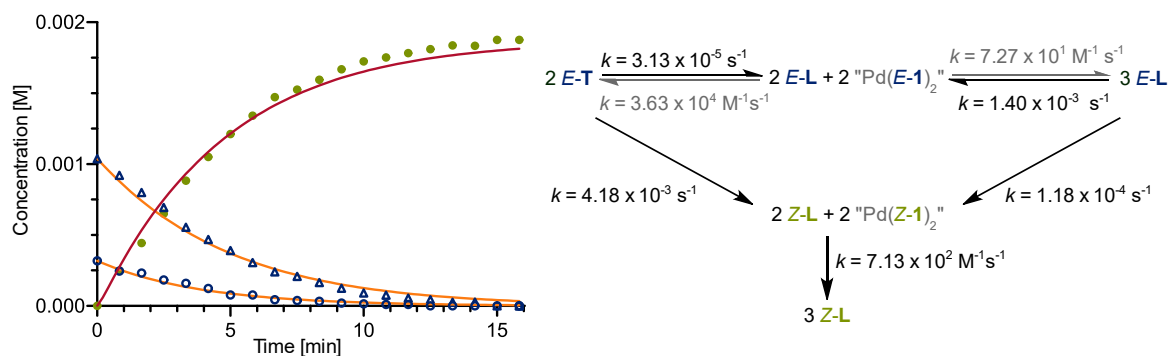


Figure S89. Kinetic plot of the formation of *Z-L* over time under *in-situ* illumination with 365 nm light (10% LED power) from a sample of *E-T*: *E-L* (78:22, respectively). *E-T* is denoted with Δ , *E-L* is denoted with $\circ$, and *Z-L* is denoted with $\bullet$. The resulting reaction rates are provided within the reaction scheme on the right.

As in Model I, Model II for the irradiation of lantern **Z-L** with 500 nm light suggests that the formation of lantern **E-L** from lantern **Z-L** is significantly faster than the formation of triangle **E-T** from lantern **Z-L** (Figure S88b and Figure S90, also Section S4.3). The fastest reaction pathway to form triangle **E-T** is via photoisomerisation from lantern **Z-L** to lantern **E-L** and subsequent thermal equilibration from lantern **E-L** to triangle **E-T**, indicating that lantern **Z-L** will only slowly (or not at all) form the triangle **E-T** directly. For this fit to converge, it was necessary to give the model the freedom to slightly modify the rate constants of the thermal isomerisation between triangle **E-T** and lantern **E-L**. We assume that the continuous green-light irradiation required during the measurements to form lantern **Z-L** had slightly heated the sample, which in turn minimally altered the equilibrium and, therefore, the corresponding rate constants.

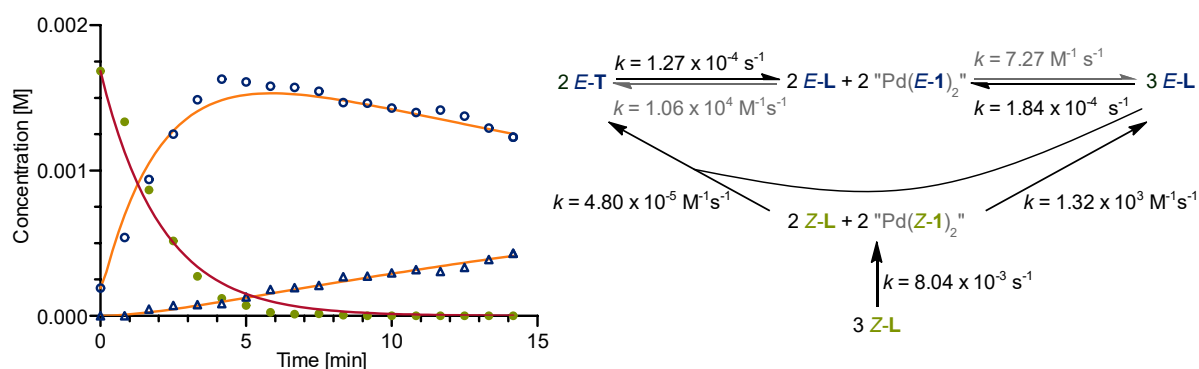


Figure S90. Kinetic plot of the formation of **E-T** and **E-L** over time under *in-situ* illumination with 500 nm light (2% LED power) from a sample of **Z-L**. **E-T** is denoted with Δ , **E-L** is denoted with $\circ$, and **Z-L** is denoted with $\bullet$. The resulting reaction rates are provided within the reaction scheme on the right.

For the thermal relaxation of lantern **Z-L** to the triangle **E-T** / lantern **E-L** mixture, the obtained data were fitted to a model using two different “Pd $\mathbf{1}_2$ ” species (“Pd(**E-1**) $_2$ ” and “Pd(**E-1**) $_2^*$ ”) with the kinetic data previously determined for the triangle **E-T** / lantern **E-L** equilibrium fixed within the model (Figure S87). Just like before, the capsule rearrangement was separated into two steps, in this case, a thermal relaxation (and capsule opening) step and a rearrangement step from the *pseudo*-intermediate “E-Pd $\mathbf{1}_2^*$ ”. Additionally, in Model II, **Z-L** and **E-L** act as further intermediates for all transformations involving triangle **E-T**.

Using the kinetic data of the **E-T** / **E-L** equilibrium at 348 K, which we previously fitted (Figure S83), Model II identified the main pathway of the thermal relaxation of lantern **Z-L** as the formation of lantern **E-L** from lantern **Z-L** (Figure S88), which was also observed for Model I. The fastest reaction pathway that forms triangle **E-T** is again the isomerisation from lantern **E-L**, indicating that lantern **Z-L** will only slowly (or not at all) form triangle **E-T** by thermal relaxation.

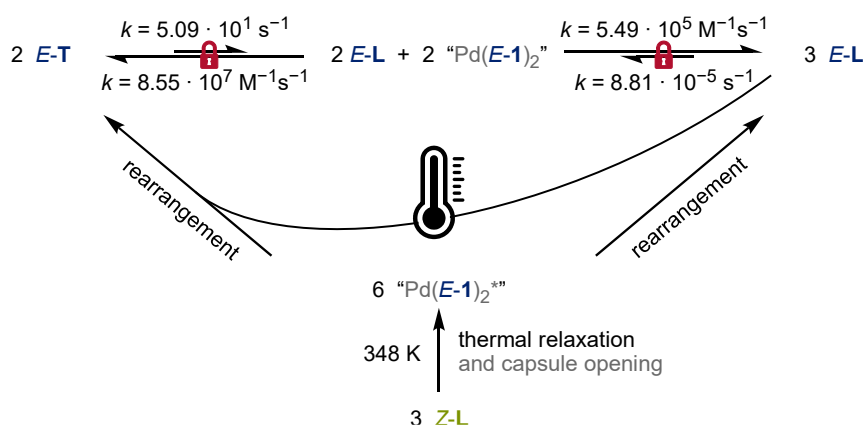
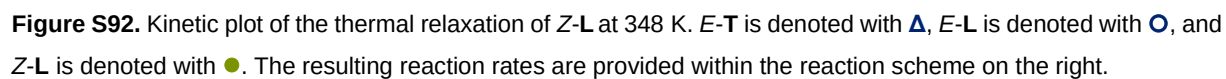


Figure S91. Kinetic model (within Model II) used for the fitting of the kinetic data of the thermal relaxation of lantern **Z-L** at 348 K. Note that both “Pd $\mathbf{1}_2$ ” species are *pseudo*-intermediates and not real compounds. Starting from **Z-L**, **E-T** is formed from 2 “Pd(**E-1**) $_2^*$ ” and 1 **E-L**. The previously determined rate constants of the triangle **E-T** / lantern **E-L** equilibrium were fixed during fitting.



S5.2.3 Model III

Model III uses the same experimental data as Models I and II. The respective experiments are detailed in Section 5.2.1.

Instead of plotting the concentration directly, for Model III, we calculated the percentage ratio of each species by dividing each compound's concentration by the total concentration at each time step. The data conversion for lantern $E\text{-}\mathbf{L}$ is exemplified in Equation S5. This conversion standardises the data and ensures all transformations follow direct first-order kinetics, allowing us to compare the kinetics of the individual reaction steps.

$$E\text{-}\mathbf{L}^{\%}(t) = 100 \times \frac{[E\text{-}\mathbf{L}](t)}{[E\text{-}\mathbf{L}](t) + [E\text{-}\mathbf{T}](t) + [Z\text{-}\mathbf{L}](t)} \quad (\text{S5})$$

$E\text{-}\mathbf{L}^{\%}(t)$ = percentage of lantern $E\text{-}\mathbf{L}$ at time t

$[E\text{-}\mathbf{L}](t)$ = concentration of lantern $E\text{-}\mathbf{L}$ at time t

$[E\text{-}\mathbf{T}](t)$ = concentration of triangle $E\text{-}\mathbf{T}$ at time t

$[Z\text{-}\mathbf{L}](t)$ = concentration of lantern $Z\text{-}\mathbf{L}$ at time t

For the equilibration between triangle $E\text{-}\mathbf{T}$ or lantern $E\text{-}\mathbf{L}$, Model III assumes direct first-order interconversion between triangle $E\text{-}\mathbf{T}$ and lantern $E\text{-}\mathbf{L}$ (Equation S6). This direct fit allowed us to determine equilibrium rate constants at 298 K and 348 K, respectively (Figure S93–94).

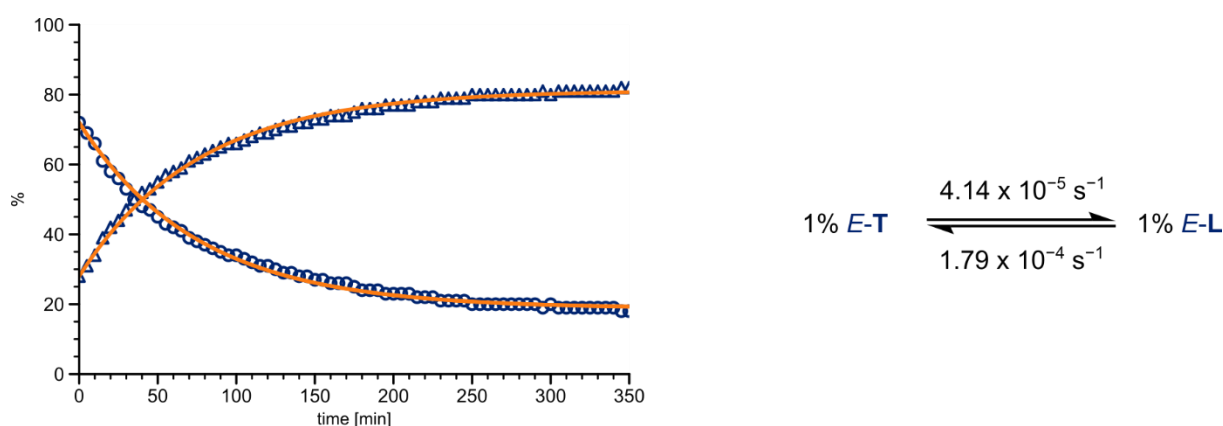


Figure S93. Kinetic plot of the equilibrium between $E\text{-}\mathbf{T}$ and $E\text{-}\mathbf{L}$ at 25 °C. $E\text{-}\mathbf{T}$ is denoted with Δ and $E\text{-}\mathbf{L}$ is denoted with $\circ$. The resulting reaction rates are provided within the reaction scheme on the right.

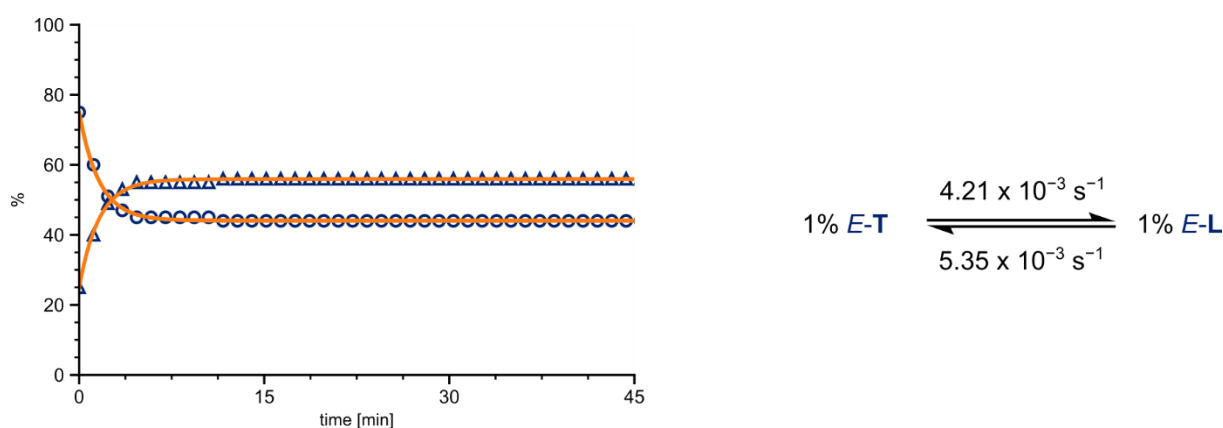


Figure S94. Kinetic plot of the equilibrium between $E\text{-}\mathbf{T}$ and $E\text{-}\mathbf{L}$ at 75 °C. $E\text{-}\mathbf{T}$ is denoted with Δ and $E\text{-}\mathbf{L}$ is denoted with $\circ$. The resulting reaction rates are provided within the reaction scheme on the right.

To investigate the $E \rightarrow Z$ and $Z \rightarrow E$ isomerisations, the normalised data obtained from the illumination experiments (Figure S62a) was fitted to a simple first-order model with the kinetic data previously determined for the triangle $E\text{-T}$ / lantern $E\text{-L}$ equilibrium fixed within the model (Figure S96).

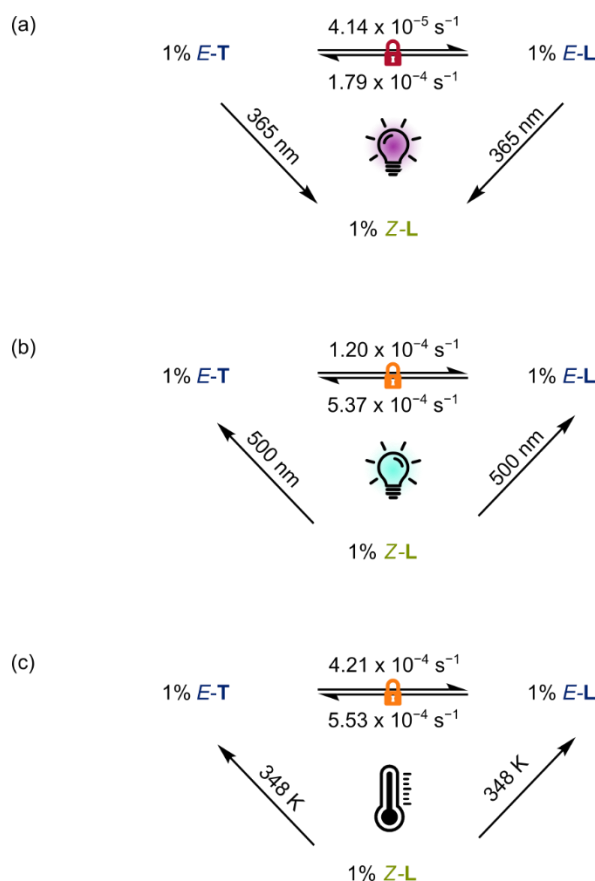


Figure S95. Kinetic models (within Model III) used for the fitting of the kinetic data of (a) $E \rightarrow Z$ photoisomerisation of triangle $E\text{-T}$ / lantern $E\text{-L}$ mixture under irradiation with 365 nm light, (b) $Z \rightarrow E$ photoisomerisation of lantern $Z\text{-L}$ under irradiation with 500 nm light and (c) thermal relaxation of lantern $Z\text{-L}$ at 348 K. The previously determined rate constants of the triangle $E\text{-T}$ / lantern $E\text{-L}$ equilibrium were fixed during fitting in (a), whereas continuous irradiation likely accelerates the equilibration in (b), and the rate constants determined under thermal conditions could not be used to fit the data. We therefore multiplied the equilibrium rate constants by a factor of three to account for this. In (c), we multiplied the equilibrium rate constants by 0.1 for similar reasons. This change affects how fast the equilibrium is reached but does not affect the equilibrium distribution.

For the *in-situ* irradiation of the triangle *E-T* / lantern *E-L* mixture using 365 nm light, all three models suggest similar reaction rates for the photoswitching of triangle *E-T* and lantern *E-L*, indicating that both structures can photoswitch on a similar time scale to form lantern *Z-L* (Figure S80, Figure S81, Figure S89 also Section S4.3).

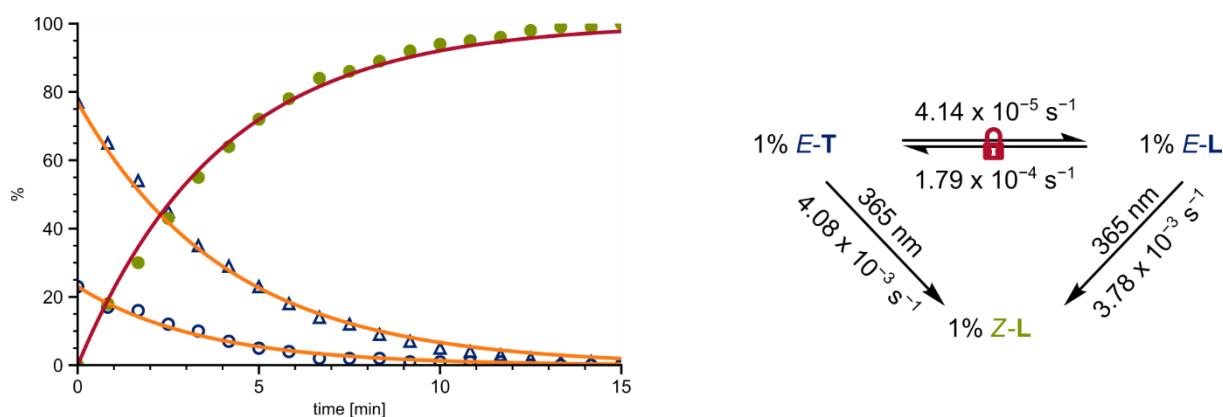


Figure S96. Kinetic plot of the formation of Z-L over time under *in-situ* illumination with 365 nm light (10% LED power) from a sample of *E-T*: *E-L* (78:22, respectively). *E-T* is denoted with Δ , *E-L* is denoted with $\circ$, and Z-L is denoted with $\bullet$. The resulting reaction rates are provided within the reaction scheme on the right.

As in Models I and II, the irradiation of lantern **Z-L** with 500 nm light suggests that the formation of lantern **E-L** from lantern **Z-L** is significantly faster than the formation of triangle **E-T** from lantern **Z-L** (Figure S80, Figure S82, Figure S90, also Section S4.3), indicating kinetic asymmetry in the two photoisomerisation pathways (Section S5.3). Hence, the main reaction pathway to form triangle **E-T** is via photoisomerisation from lantern **Z-L** to lantern **E-L** and subsequent thermal equilibration from lantern **E-L** to triangle **E-T**, indicating that lantern **Z-L** will hardly form the triangle **E-T** directly.

Just as in Model I, the equilibrium rate constants for thermal isomerisation between triangle **E-T** and lantern **E-L** had to be multiplied by a factor of three in Model III; the same factor that was used in Model I. We multiplied both the forward and backward reaction rates of the equilibrium by the same factor. Therefore, this change does not affect the final equilibrium population; it only changes how fast it is reached. We assume that continuous irradiation adds energy to the system, thereby accelerating isomerisation rates.

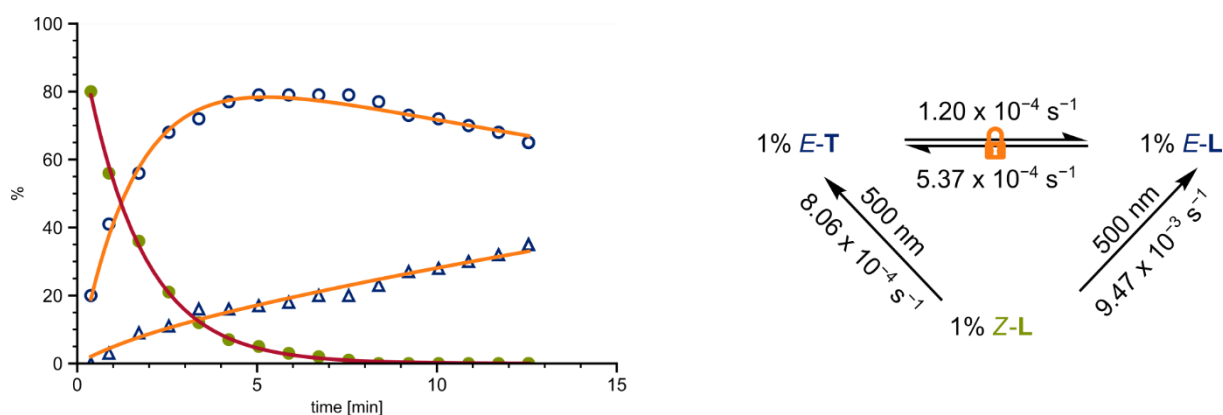


Figure S97. Kinetic plot of the formation of **E-T** and **E-L** over time under *in-situ* illumination with 500 nm light (2% LED power) from a sample of **Z-L**. **E-T** is denoted with Δ , **E-L** is denoted with $\circ$, and **Z-L** is denoted with $\bullet$. The resulting reaction rates are provided within the reaction scheme on the right.

Using Model III and the data from Figure S62b, we not only investigated and fitted the isomerisation kinetics for 500 nm light at 2% LED power, but also at 100% LED power. This showed a much larger difference in rate constants, indicating that greater light intensity increases the kinetic asymmetry of the information ratchet (Figure S100).

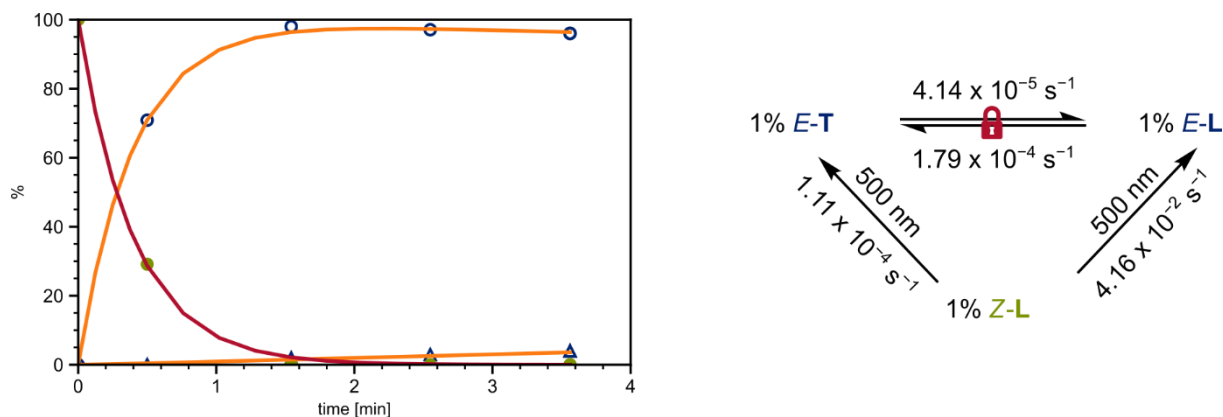


Figure S98. Kinetic plot of the formation of *E*-T and *E*-L over time under *in-situ* illumination with 500 nm light (**100% LED power**) from a sample of *Z*-L. *E*-T is denoted with Δ , *E*-L is denoted with $\circ$, and *Z*-L is denoted with $\bullet$. The resulting reaction rates are provided within the reaction scheme on the right.

For the thermal relaxation of lantern **Z-L** to the triangle **E-T** / lantern **E-L** mixture, the obtained data were fitted to Model III (Figure S99). The kinetic data previously determined for the triangle **E-T** / lantern **E-L** equilibrium was adjusted by a factor of 0.1, as the fit would not converge otherwise. Just like before, this change does not influence the equilibrium distribution.

Using the kinetic data of the **E-T** / **E-L** equilibrium at 348 K, which we previously fitted (Figure S94), Model III identified the formation of lantern **E-L** from lantern **Z-L** to be faster than the direct formation of triangle **E-T** from lantern **Z-L**, indicating that lantern **Z-L** will only slowly form triangle **E-T** by thermal relaxation, again indicating kinetic asymmetry in the reaction pathways (Section S5.3).

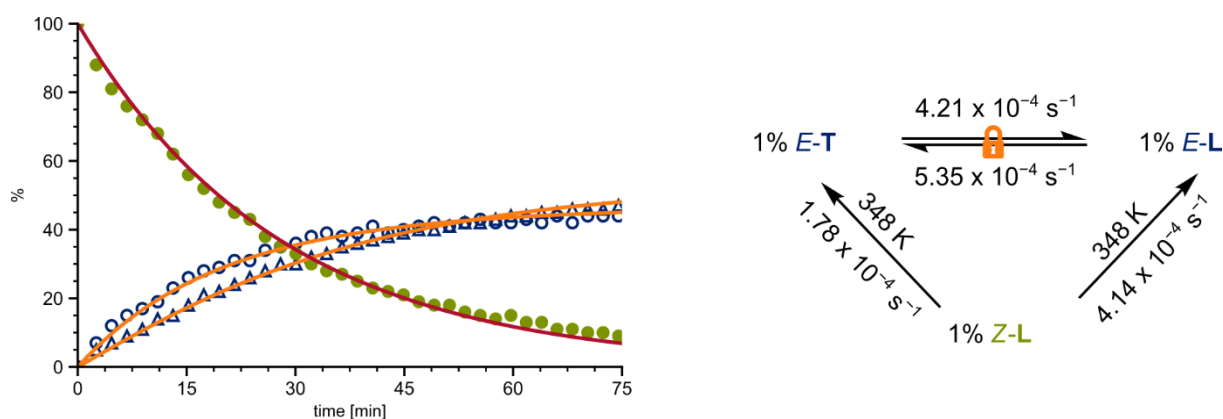


Figure S99. Kinetic plot of the thermal relaxation of **Z-L** at 348 K. **E-T** is denoted with Δ , **E-L** is denoted with $\circ$, and **Z-L** is denoted with $\bullet$. The resulting reaction rates are provided within the reaction scheme on the right.

S5.3 Determination of kinetic asymmetry

Due to the simplicity of Model III and the fact that all reactions were first order transformations, we tentatively used the fitted rate constants to evaluate the kinetic asymmetry for the isomerisation processes by comparing the rate constants of competing reactions (Table S4). Furthermore, we calculated $\Delta\Delta G^\ddagger$ using Equation S2.

$$\Delta\Delta G^\ddagger = -RT \ln \left(\frac{k_1}{k_2} \right) \quad (\text{S2})$$

For **Z** → **E** switching, the kinetic asymmetry is lowest for the thermal isomerisation at 2.3 : 1 or -2.5 kJ mol⁻¹. Irradiation with 500 nm light at 2% power increases the kinetic asymmetry to 12 : 1 or -6.3 kJ mol⁻¹. An even greater kinetic asymmetry was observed at 100% LED power, at which kinetic asymmetry reaches 375 : 1 or -14.6 kJ mol⁻¹. This shows that the kinetic asymmetry in this light-driven information ratchet can be adjusted by the intensity of the light source.

For **E** → **Z** switching, there is essentially no kinetic asymmetry as the two competing rate constants are almost identical.

Table S4. Kinetic asymmetry and $\Delta\Delta G^\ddagger$ for the preferential formation of **E-L** over **E-T** from **Z-L** under different reaction conditions as calculated from rate constants of model III.

	$K_{Z-L \rightarrow E-L}$ [s ⁻¹]	$K_{Z-L \rightarrow E-T}$ [s ⁻¹]	kinetic asymmetry $K_{Z-L \rightarrow E-L} : K_{Z-L \rightarrow E-T}$	$\Delta\Delta G^\ddagger$ [kJ mol ⁻¹]
in situ 500 nm @100% LED power	4.2 × 10 ⁻²	1.1 × 10 ⁻⁴	375 : 1	-14.6
in situ 500 nm @2% LED power	9.5 × 10 ⁻³	8.1 × 10 ⁻⁴	12 : 1	-6.3
thermal relaxation @75 °C	4.1 × 10 ⁻⁴	1.8 × 10 ⁻⁴	2.3 : 1	-2.5
in situ 365 nm @10% LED power	3.9 × 10 ⁻³	4.1 × 10 ⁻³	0.93 : 1	0.4

S5.4 Determination of energy storage and efficiency

Considering the energy difference between triangle *E-T* and lantern *E-L* of $\Delta G = -27.8 \pm 13.0 \text{ kJ mol}^{-1}$ and the triangle *E-T* / lantern *E-L* ratios before (78:22) and after light irradiation (365 nm and 500 nm: 2:98; white light: 34:66), consecutive irradiation with 365 nm and 500 nm light stores

$$\Delta G_{\text{iterative}} = (0.98-0.22) \cdot 27.8 \text{ kJ mol}^{-1} = 21.1 \text{ kJ mol}^{-1}$$

of light as chemical energy in the system, whereas the continuous operation of the information ratchet with white light stores

$$\Delta G_{\text{white light}} = (0.66-0.22) \cdot 27.8 \text{ kJ mol}^{-1} = 12.2 \text{ kJ mol}^{-1}.$$

This information ratchet benefits from highly selective reactions with excellent yields, which in turn enable a comparatively large energy storage that is more than twenty times larger than that of a fuel-driven disequilibrium process published by the Leigh group¹⁵ with $\Delta G = 1.05 \text{ kJ mol}^{-1}$ and a photochemical deracemisation reported by the groups of Miller and Knowles¹⁶ with $\Delta G = 1.76 \text{ kJ mol}^{-1}$.

Based purely on the electrical power consumed by the 2 W LED during the 5.5 hours of continuous white light irradiation (= 40 kJ) needed to disequilibrate 0.5 mL of a 1.75 mM triangle *E-T* / lantern *E-L* solution at 12.2 kJ mol^{-1} (= 0.011 J), we estimate the information ratchet operates at a low efficiency of just $3 \cdot 10^{-5} \%$. This is likely due to the low overlap between the UV-vis spectra of the involved species and the white-light emission spectrum, as well as the thermally activated equilibrium between *E-T* and *E-L* at room temperature, which necessitates numerous cycles.

However, targeted iterative irradiation occurs on a much faster timescale (minutes instead of hours). When consecutively irradiating the triangle *E-T* / lantern *E-L* mixture with 365 nm and 500 nm light, we observe much higher efficiency due to reduced impact of the thermally activated *E-T* and *E-L* equilibration and improved spectral overlap. In this case, we irradiated the sample for 4.5 minutes at a light intensity of 170 mW (= 45 J) and stored 21.1 kJ mol^{-1} in 0.5 mL of a 1.75 mM solution (= 0.019 J) for a single cycle efficiency of 0.04%.

The single-cycle efficiency of the iterative irradiation with 365 nm and 500 nm light is in line with those calculated for comparable photochemical disequilibria ranging from 0.3%^{15,17} to 0.03%^{15,16}. While fuel-driven

systems typically boast a higher first cycle efficiency of, for example 0.3%, the efficiency often drops off dramatically in the second cycle to just 0.03% with further reductions in subsequent cycles due to waste accumulation.¹⁸

Both the experiment under continuous white light irradiation, as well as the iterative sequential photoswitching (no fatigue was observed over 10 switching cycles, see Figure S57) confirm excellent stability over multiple cycles of the system. Hence, cycle efficiency is expected to remain constant over numerous cycles.

Since our system is light-driven and the emission of light can be fine-tuned to some degree, the efficiency of our system could likely be improved through an optimised emission spectrum, increased light intensity, and reduced operating temperatures to slow thermal *E-T* and *E-L* isomerisation.

S6 Autonomous information ratchet

To investigate, whether the molecular ratchet could operate autonomously under white light irradiation, two different experiments were conducted (Figure S101). In the first experiment, an NMR sample of the 78:22 triangle *E-T* / lantern *E-L* mixture was left next to a window on a sunny spring day for 7 h (Figure S101d). The second experiment involved monitoring the changes in composition observed over time when an NMR sample of the 78:22 triangle *E-T* / lantern *E-L* mixture was irradiated *in situ* inside the NMR spectrometer with a white LED for 5.5 h (Figure S102 and Figure S103). Both experiments yielded a mixture enriched with lantern *E-L*.

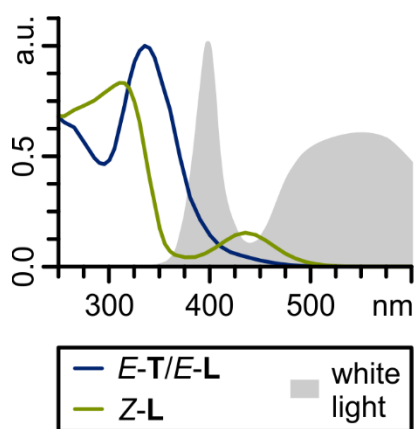


Figure S100. UV-vis spectrum of the *E-T* / *E-L* mixture after irradiation with 365 nm (green: *Z-L*) and 500 nm light (blue: *E-T/E-L*; 1 min each) with an overlay of the normalised emission spectrum of the white light LED (grey).

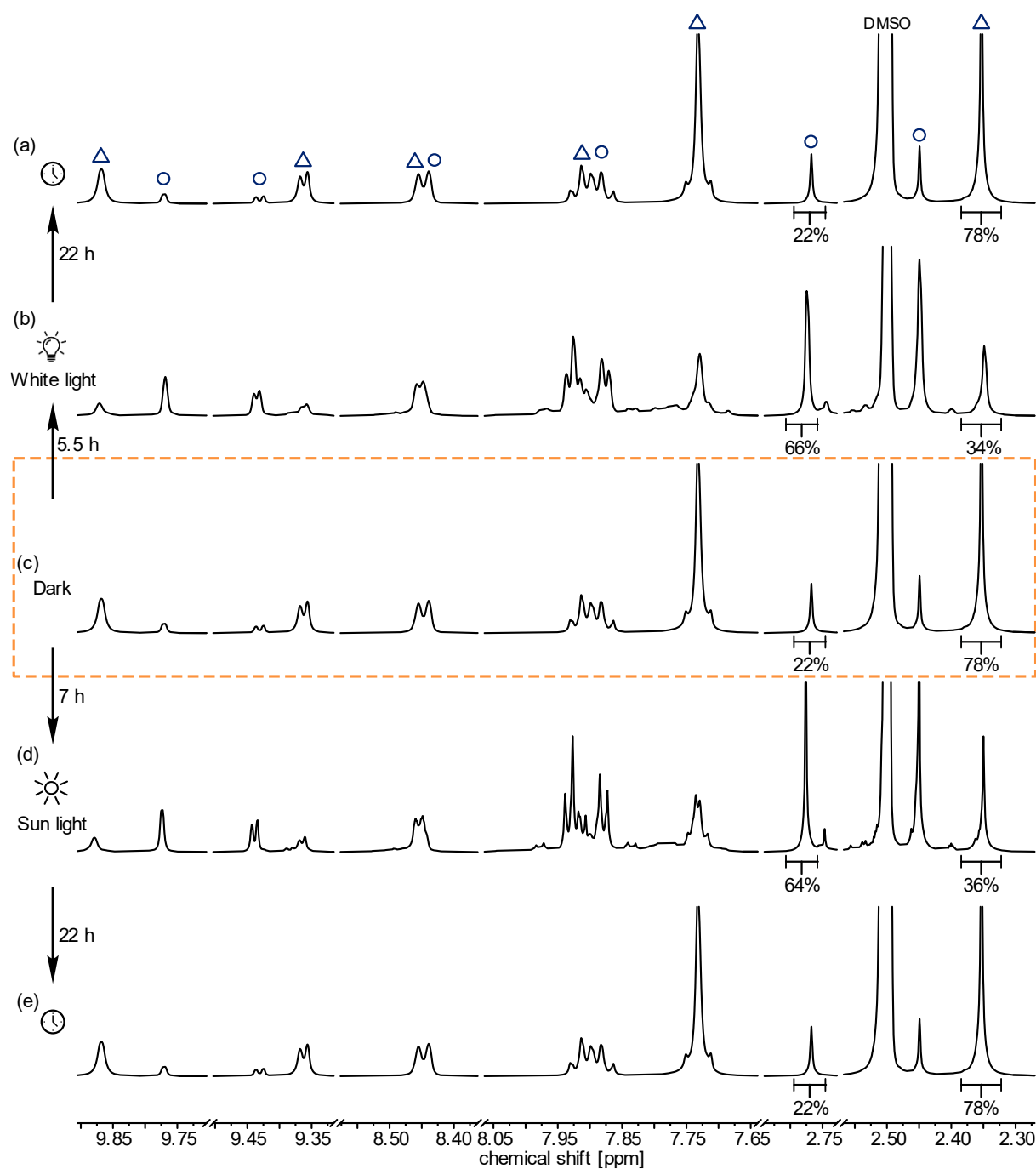


Figure S101. ^1H NMR (700 MHz, $\text{DMSO}-d_6$, 298 K) of (c) an *E-T*: *E-L* mixture under light exclusion (*E-T*: *E-L*, 78:22), (b) after *in-situ* irradiation with white light for 5.5 h (*E-T*: *E-L*, 34:66), (d) after leaving the initial NMR sample next to a window on a sunny spring day for 7 h (*E-T*: *E-L*, 36:64), and (a/e) after 22 h equilibrating in an amberised NMR tube wrapped in aluminium foil in an air-conditioned room (22 $^{\circ}\text{C}$, *E-T*: *E-L*, 78:22). *E-T* is denoted with Δ , *E-L* is denoted with $\circ$.

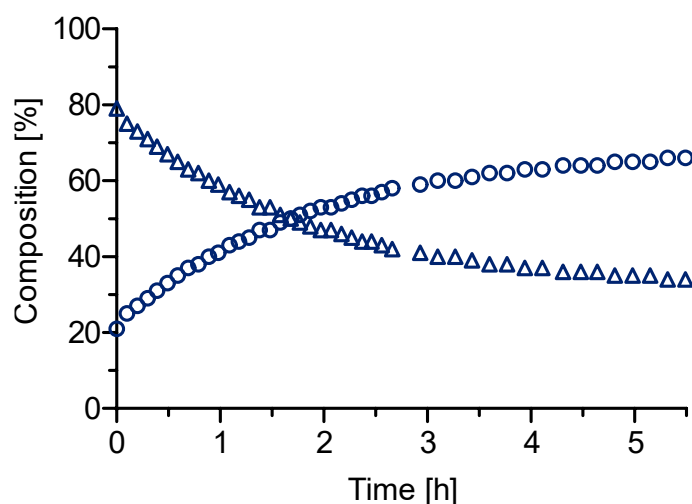


Figure S102. Changes in composition of *E*-T and *E*-L upon irradiation with white light, measured by *in-situ* illumination ^1H NMR (700 MHz, $\text{DMSO}-d_6$, 298 K) over 5.5 h (Figure S96). For the first 2.66 h a spectrum was recorded every 6 min. At 2.9 h, a gap of 18 min is observed due to changes made to the NMR time parameters; from 2.93 h onwards, a spectrum was measured every 10 min. *E*-T is denoted with Δ , *E*-L is denoted with $\circ$.

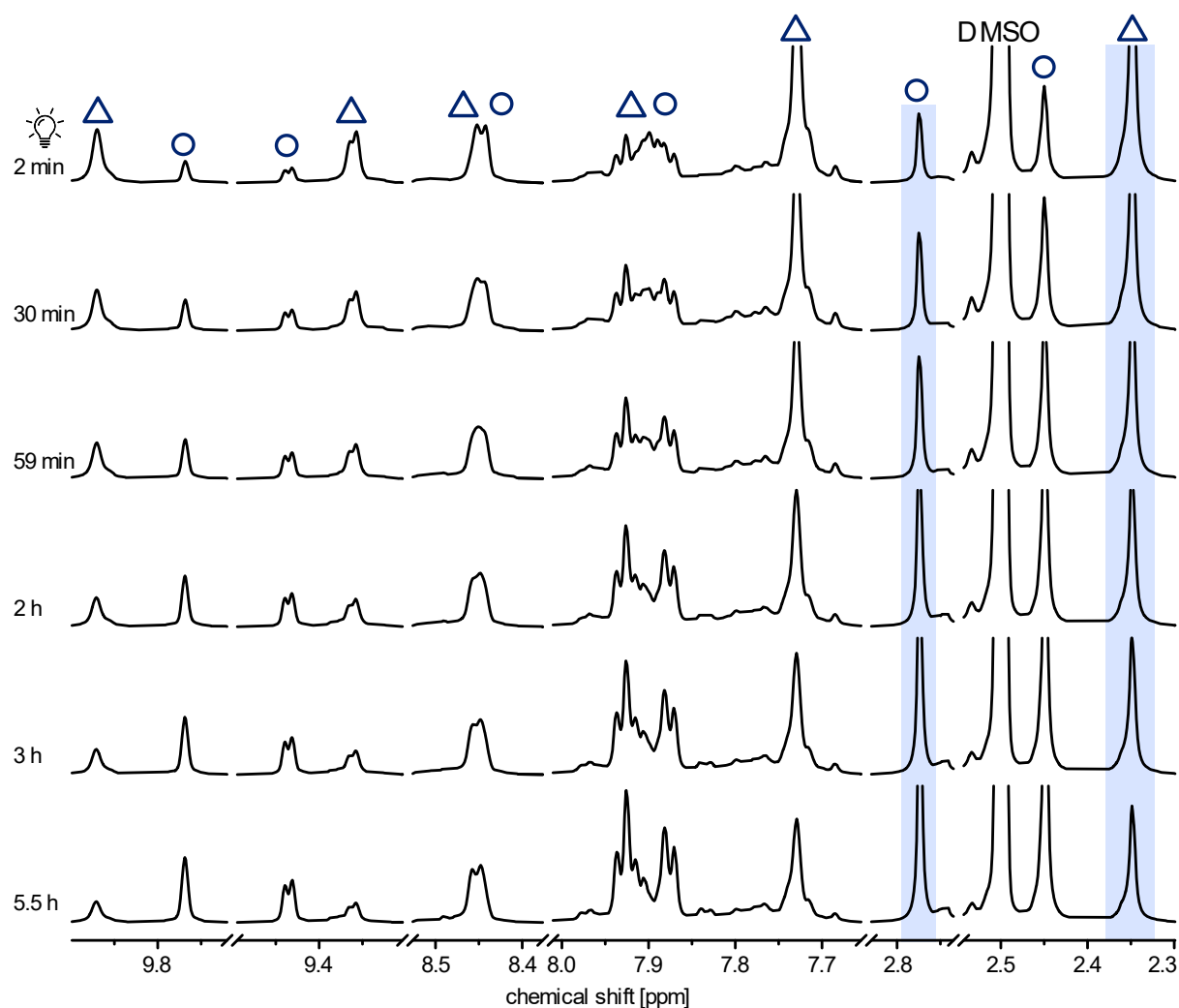


Figure S103. ^1H NMR (700 MHz, $\text{DMSO}-d_6$, 298 K) spectral changes during *in-situ* illumination with white light. The signals highlighted in blue were chosen to be line-fitted and plotted to display changes in composition between triangle *E*-T and lantern *E*-L (Figure S102). *E*-T is denoted with Δ , *E*-L is denoted with $\circ$.

S7 X-ray crystallography

Crystals of *E*-**1** were obtained by slow solvent evaporation of a saturated solution in dichloromethane at ambient temperature. Crystals of *E*-**L** were obtained by slow diffusion of ethyl acetate into a DMSO solution of the 78:22 triangle *E*-**T** / lantern *E*-**L** mixture.

A colourless plate-like specimen of *E*-**1** (0.18 x 0.08 x 0.02 mm) and a clear yellow plate of *E*-**L** (0.16 x 0.03 x 0.02 mm) were mounted on a Bruker D8 Venture 4-circle Kappa-diffractometer equipped with a low-temperature device (100(2) K, Oxford Cryostream 800er series, Oxford Cryosystems) by using Cu- K_{α} -radiation ($\lambda = 1.54186$ Å, Helios mirror optics, *E*-**1**) or Mo- K_{α} -radiation ($\lambda = 0.71073$ Å, Helios mirror optics, *E*-**1**) and a PHOTONIII/C14 CMOS detector system. Intensities were measured by fine-slicing φ - and ω -scans and corrected for background, polarisation and Lorentz effects. A semi-empirical absorption correction from equivalent reflections (multi-scan type) was performed using SADABS.¹⁹

Structure solution was done using intrinsic phasing methods included in the SHELXT program system²⁰ and refined by full matrix least-squares/difference Fourier synthesis with ShelXL-2019/3).²¹ All non-hydrogen atoms were refined anisotropically; hydrogen atoms were placed in geometrically calculated positions and included using a riding model on the bound carbon atoms and relative isotropic displacement parameters. Olex2 was used for graphical representations of the molecular structures.²²

CCDC numbers CCDC-2488074 (*E*-**1**), CCDC-2488075 (*E*-**L**) contain the supplementary crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

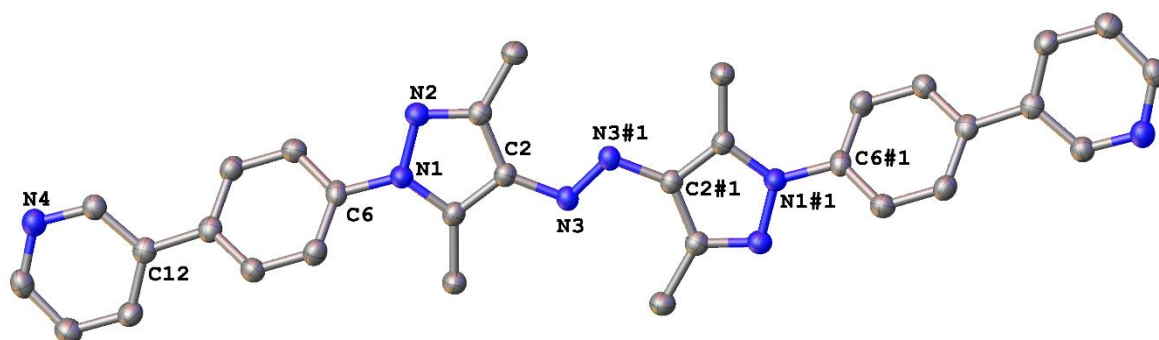


Figure S104. Solid-state structure of *E*-1. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are set to 50% probability level. The crystallographic inversion centre is located at the midpoint of the N3 – N3#1 bond.

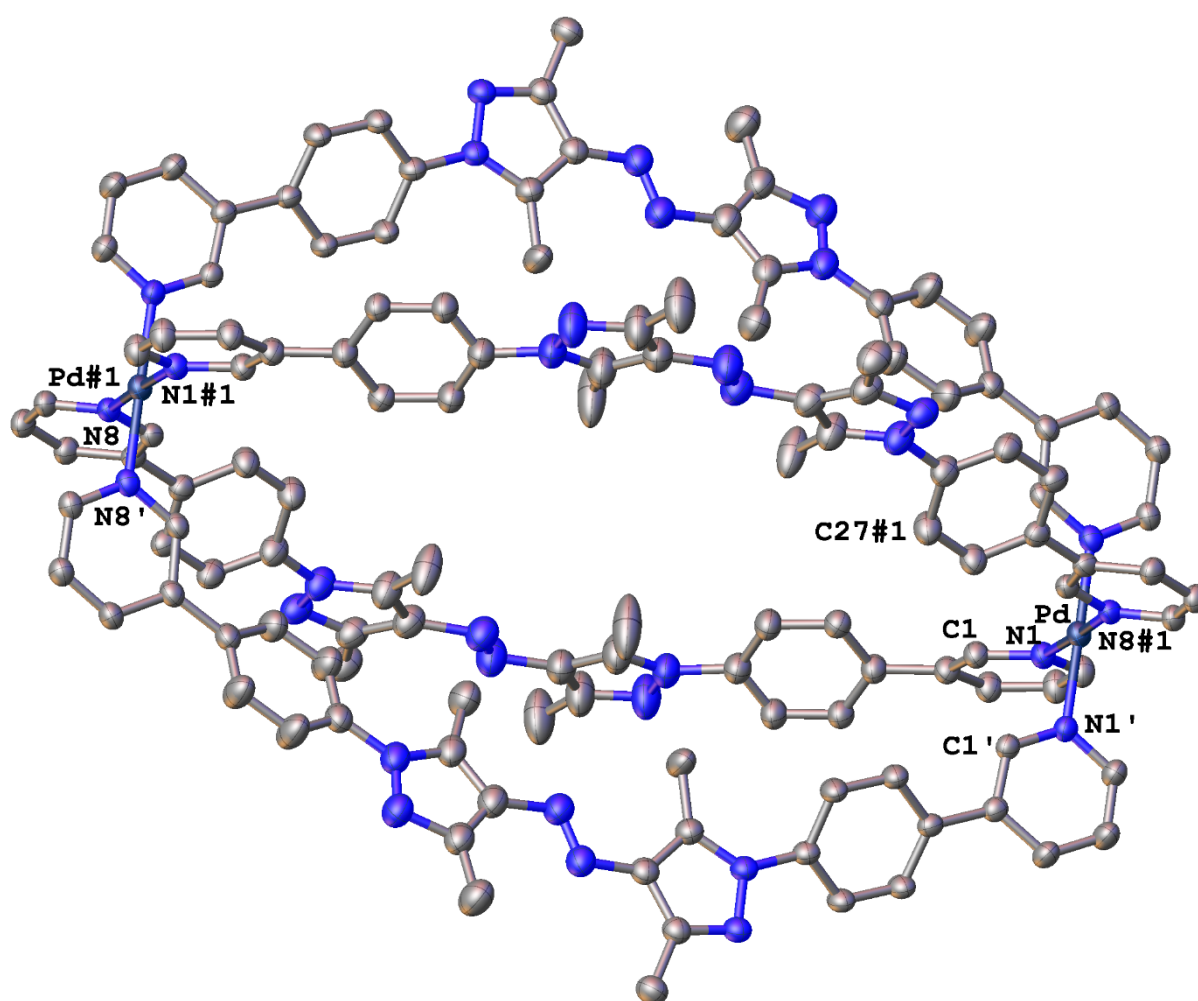


Figure S105. Solid-state structure of *E*-L. Hydrogen atoms, co-crystallised solvent molecules and anions are omitted for clarity. Thermal ellipsoids are set to 40% probability level. The crystallographic inversion centre is located at the midpoint of the Pd – Pd#1 vector. The contribution of some solvent molecules and anions in the cage to the overall scattering factor had to be modelled by using the squeezing methodology implemented in the Olex program system.²³

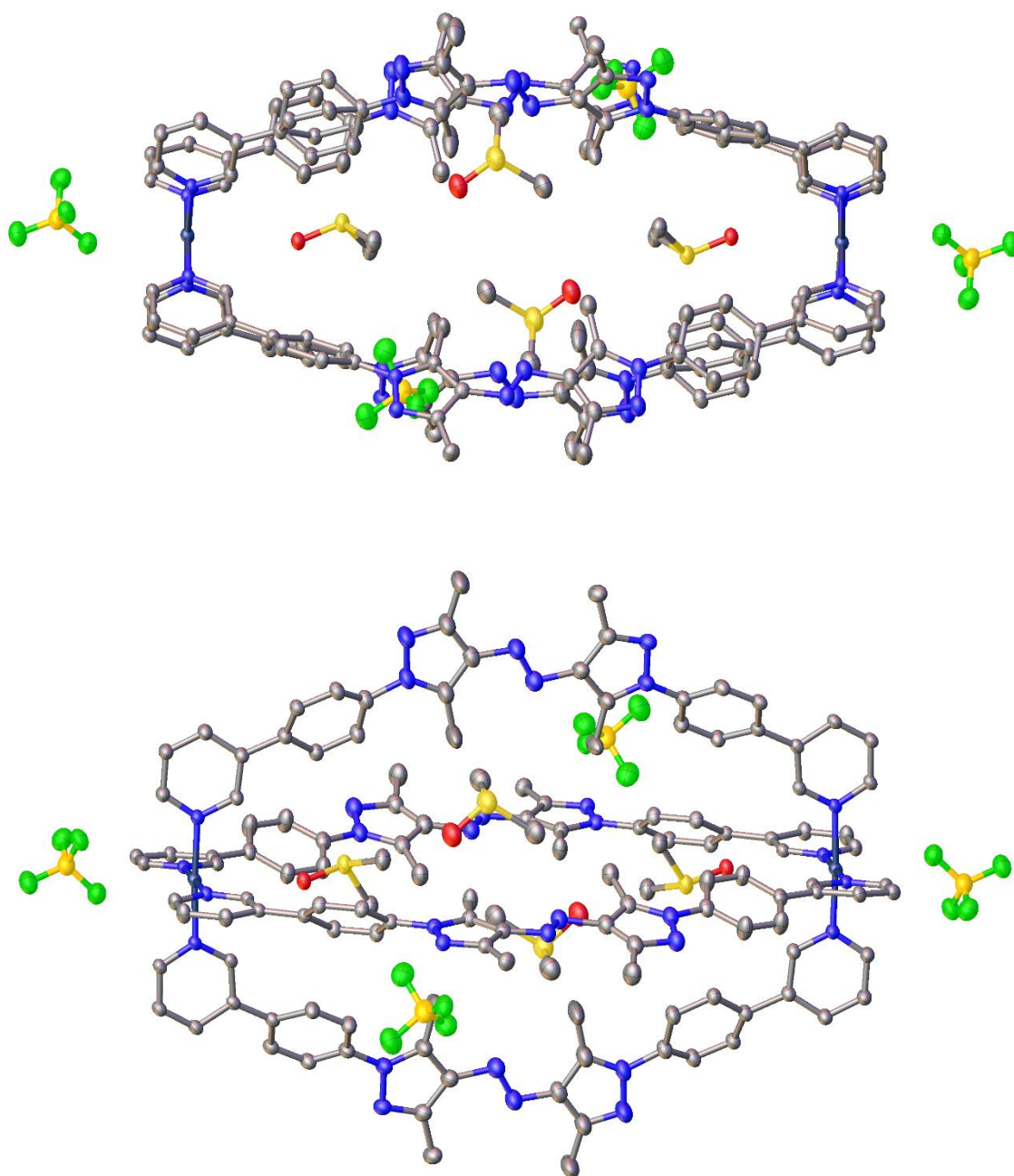


Figure S106. Solid-state structure of *E-L*, including four BF_4^- counterions and four DMSO solvent molecules located within the capsule cavity. Hydrogen atoms and additional co-crystallised solvent molecules are omitted for clarity. Thermal ellipsoids are set to 40% probability level. The crystallographic inversion centre is located at the midpoint of the Pd–Pd vector. The contribution of some solvent molecules and anions in the cage to the overall scattering factor had to be modelled by using the squeezing methodology implemented in the Olex program system.²³

S8 Computational studies

S8.1 Computational Details

Due to the extended system size and flexibility of the investigated structures, solvent molecules and anions were not considered explicitly in the calculations unless stated otherwise. Thus, the lantern structures carry a formal charge of +4, while the triangle structures carry a charge of +6. These charges will not be indicated in subsequent figures or tables unless they differ from the values stated above.

For all computed structures, the energetically most favourable conformer was searched using meta-dynamics (MTD)-based²⁴ Conform-Rotamer Ensemble Sampling Tool (CREST)²⁵ (v. 3.0.2), employing the semi-empirical quantum mechanical (SQM) method GFN2-xTB.^{26,27} Solvation effects were accounted for using the implicit solvation model ALPB (DMSO).²⁸

The respective lowest conformers found were then optimised using the ω B97X-3c²⁹ composite DFT method, while considering solvation effects using the CPCM implicit solvation model.³⁰ Final single-point calculations were performed using the ω B97X-3c method in combination with the more sophisticated SMD solvation model.³¹ For all structures, thermal corrections were computed at a GFN2-xTB [ALPB: DMSO] level of theory using the modified rigid-rotor-harmonic-oscillator approximation (mRRHO)³² as implemented in the xTB software package (v. 6.6.1).³³

Gibbs-free energies were then computed as follows:

$$G = E_{\text{gas}} + G_{\text{thermo}} + \delta G_{\text{solv}}$$

With E_{gas} being the gas-phase electronic energy (using ω B97X-3c), G_{thermo} being the thermal corrections (using GFN2-xTB), and δG_{solv} being the solvation contributions (considered by SMD model).

All density functional calculations were performed using the ORCA³⁴ software package (v. 6.0.1). Model systems were constructed using the Avogadro program,² while the ChimeraX³⁵ software suite was used for the visualisation of structures in this section.

All structures discussed in the main manuscript and the supporting information can be found in the file “structures.zip”.

S8.2 Free Ligand & Lantern – $E \rightarrow Z$ Isomerisation

The free energy for the $E \rightarrow Z$ Isomerisation of the free ligand **1** (implicitly solvated by DMSO) was computed to be:

$$\Delta G_{E \rightarrow Z} = G(E-1) - G(Z-1) = -47.4 \text{ kJ mol}^{-1} = -11.3 \text{ kcal mol}^{-1}.$$

The respective structures are depicted in Figure S107.

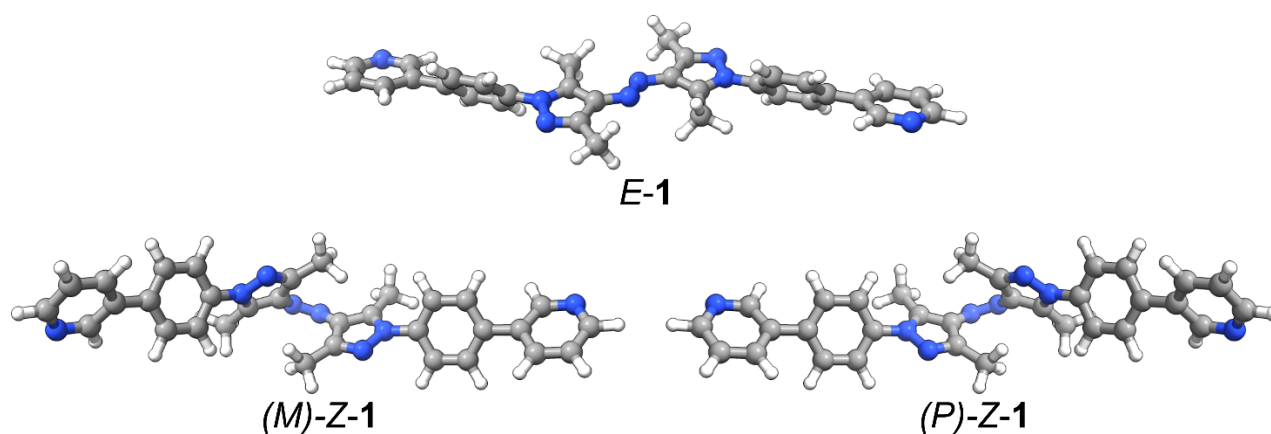


Figure S107. Lowest conformations found by CREST for the studied ligand **1** in E and Z (both enantiomers) configuration, respectively. Structures are optimised at the ω B97X-3c [CPCM: DMSO] level of theory. Atom colour code: H (white), C (grey), N (blue).

Note that Z -**1** is helically chiral. It can exist in either its P or M form.

Since each lantern structure contains four ligands, each of which can adopt either the *E*- or *Z*-configuration, *E*-**1** and *Z*-**1**, respectively, a total of six distinct lantern motifs can be constructed: *E,E,E,E*-**L** (or *E*-**L**), *Z,E,E,E*-**L**, *cis-Z,Z,E,E*-**L**, *trans-Z,Z,E,E*-**L**, *Z,Z,Z,E*-**L**, and *Z,Z,Z,Z*-**L** (or *Z*-**L**; Figure S108). All six motifs were investigated computationally. While only *E*-**L** and *Z*-**L** could be experimentally characterised in detail, tentative ^1H NMR evidence for the existence of *Z,E,E,E*-**L**, *cis-Z,Z,E,E*-**L**, *trans-Z,Z,E,E*-**L**, and *Z,Z,Z,E*-**L** in solution could be obtained by mixing *E*-**L** and *Z*-**L** in different ratios (Section S2.8) or during thermal relaxation of *Z*-**L** (Figure S74). The obtained structures are depicted in Table S5. The computed free energies relative to *E*-**L** reveal that each conversion of a ligand from the *E*- to the *Z*-configuration incurs an energetic penalty. Dividing the relative energy differences of each lantern by the number of ligands in *Z* configuration highlights this systematic trend, providing an average penalty of 47.8 kJ mol $^{-1}$. This value correlates closely with the computed free energy difference between free ligand **1** in its *E* and *Z* configurations (47.4 kJ mol $^{-1}$).

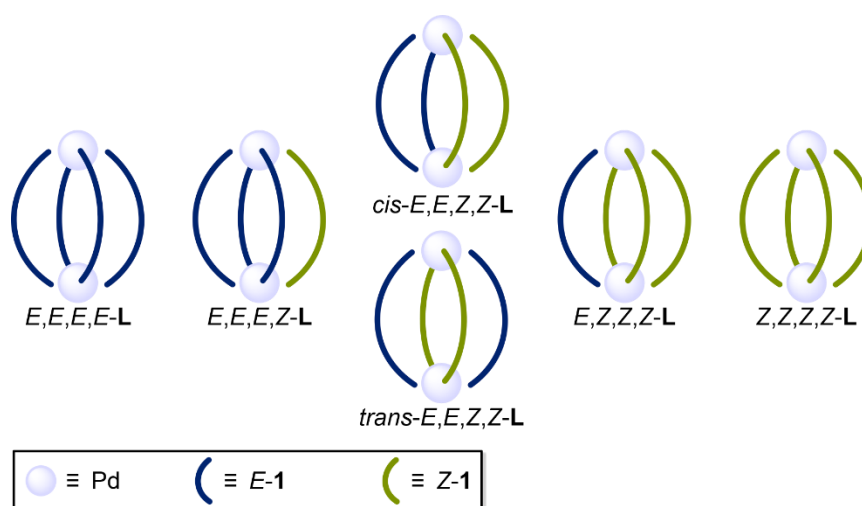
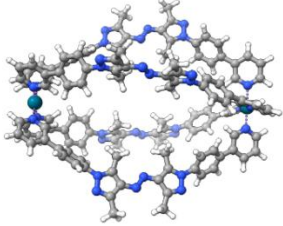
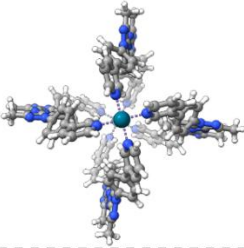
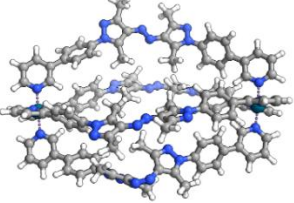
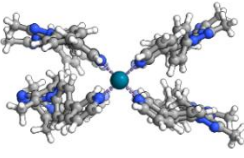
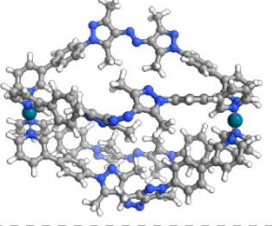
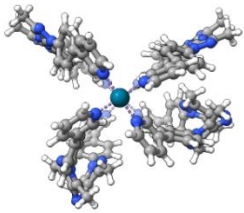
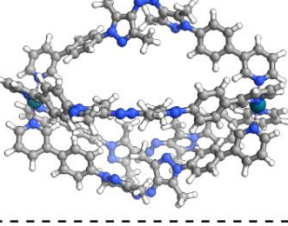
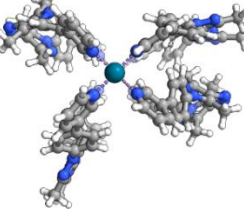
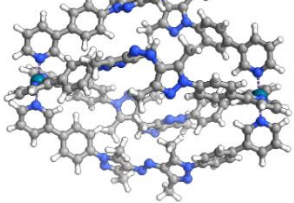
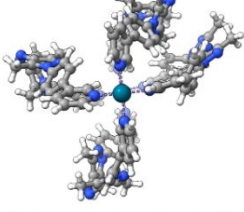
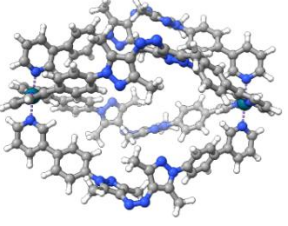
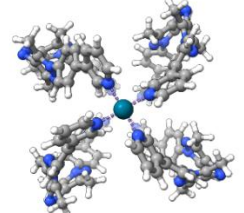


Figure S108. Cartoon representation of the six distinct lantern motifs derived from combining the two different ligand configurations, *E*-**1** and *Z*-**1**, within the same lantern structure: *E,E,E,E*-**L** (or *E*-**L**), *Z,E,E,E*-**L**, *cis-Z,Z,E,E*-**L**, *trans-Z,Z,E,E*-**L**, *Z,Z,Z,E*-**L**, and *Z,Z,Z,Z*-**L** (or *Z*-**L**).

Table S5. Side and top views of the lowest-energy conformers of all possible lantern motifs defined by the *E/Z* configurations of the four ligands. The motifs shown (top to bottom) are: *E,E,E,E-L* (or *E-L*), *Z,E,E,E-L*, *cis-Z,Z,E,E-L*, *trans-Z,Z,E,E-L*, *Z,Z,Z,E-L*, and *Z,Z,Z,Z-L* (or *Z-L*). Relative free energies with respect to *E-L* ($\Delta G_{w.r.t. E-L}$) along with values normalised by the number of ligands in the *Z*-configuration ($\Delta G_{w.r.t. E-L} / \# \text{ of } Z$). Energies are given in kJ mol^{-1} . Structures are optimised at the $\omega\text{B97X-3c}$ [CPCM: DMSO] level of theory; free energies were computed at the $\omega\text{B97X-3c}$ [SMD: DMSO] level with thermal corrections obtained from GFN2-xTB [APLB: DMSO]. Atom colour code: H (white), C (grey), N (blue), Pd (teal).

Structure	Side View	Top View	$\Delta G_{w.r.t. E-L}$ [kJ mol^{-1}]	$\Delta G_{w.r.t. E-L} / \# \text{ of } Z$ [kJ mol^{-1}]
<i>E,E,E,E-L</i> (<i>E-L</i>)			0.0	–
<i>Z,E,E,E-L</i>			39.6	39.6
<i>cis-Z,Z,E,E-L</i>			97.0	48.5
<i>trans-Z,Z,E,E-L</i>			99.8	49.9
<i>Z,Z,Z,E-L</i>			146.1	48.7
<i>Z,Z,Z,Z-L</i> (<i>Z-L</i>)			209.3	52.3

S8.3 Isomers of Z-L

Six diastereomers of Z-L exist, differing in the chirality of their ligands **1**, i.e. (*P*)-Z-**1** and (*M*)-Z-**1**, respectively: (*M,M,M,M*)-Z-L and its enantiomer (*P,P,P,P*)-Z-L, (*P,M,M,M*)-Z-L and its enantiomer (*P,P,P,M*)-Z-L, (*cis-P,P,M,M*)-Z-L, and (*trans-P,P,M,M*)-Z-L (Figure S109).

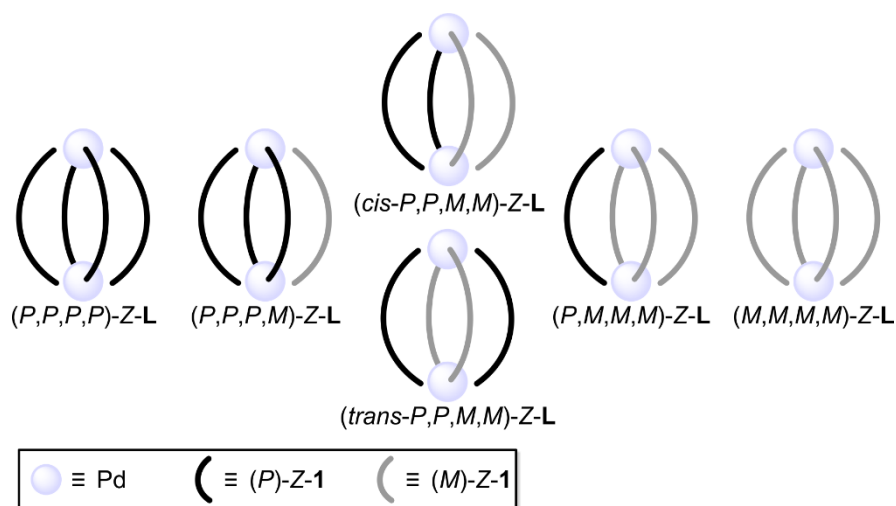


Figure S109. Cartoon representations of the six diastereomers of Z-L: (*M,M,M,M*)-Z-L and its enantiomer (*P,P,P,P*)-Z-L, (*P,M,M,M*)-Z-L and its enantiomer (*P,P,P,M*)-Z-L, (*cis-P,P,M,M*)-Z-L, and (*trans-P,P,M,M*)-Z-L.

To help visualise these isomers systematically, the cage is oriented such that the Pd atom with the lower index in the xyz file is placed at the bottom and the other at the top. If the upper methyl group adjacent to the azo bridge (tilted downwards) points to the left, the respective ligand is the *M* enantiomer (*M*)-Z-**1**; if it points to the right, it is the *P* isomer (*P*)-Z-**1**. This procedure is applied to all ligands in a structure to obtain an unambiguous classification of each isomer. An example of the procedure is shown in Figure S110. This convention is arbitrary and serves only to provide a consistent differentiation between isomers. Based on this scheme, the following Z-L configurations were constructed and investigated:

(*M,M,M,M*)-Z-L and its enantiomer (*P,P,P,P*)-Z-L, (*P,M,M,M*)-Z-L and its enantiomer (*P,P,P,M*)-Z-L, (*cis-P,P,M,M*)-Z-L, and (*trans-P,P,M,M*)-Z-L.

The xyz-files of all isomers can be found in the file “structures.zip

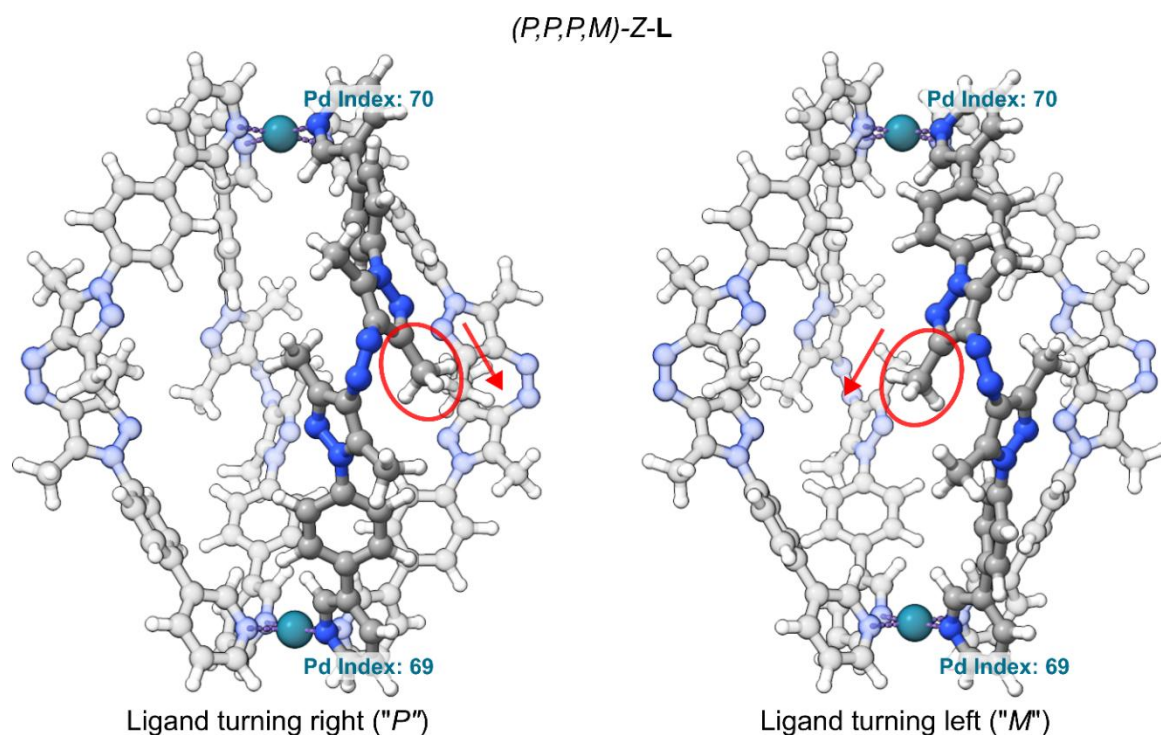


Figure S110. Illustration of the classification applied for (*P*)-**Z-1** and (*M*)-**Z-1** on two ligands within the structure of (*P,P,P,M*)-**Z-L**. The Pd atom with the lower index is positioned at the bottom of the lantern, and the defining upper methyl group adjacent to the azo bridge (tilted downwards, highlighted with a red circle) points either to the right (*P* isomer) or to the left (*M* isomer). Atom colour code: H (white), C (grey), N (blue), Pd (teal).

TM

The computed relative free energies with respect to (M,M,M,M) -Z-L are summarised in Table S6. The largest absolute difference is 5.0 kJ mol⁻¹, which is likely within the error margin of the computational approach. One limitation of the method is evident in the energy differences between enantiomers, (M,M,M,M) -Z-L and its enantiomer (P,P,P,P) -Z-L as well as (P,M,M,M) -Z-L and its enantiomer (P,P,P,M) -Z-L, respectively, which ideally should be identical but deviate up to 1.0 kJ mol⁻¹ for the considered pairs. Consequently, we focus on the general conclusion that all computed configurations are energetically similar, indicating that multiple isomers could coexist.

Table S6. Relative free energies of the investigated Z-L isomers with respect to (M,M,M,M) -Z-L ($\Delta G_{w.r.t. (M,M,M,M)-Z-L}$). Enantiomeric pairs are highlighted in blue or purple. Energies are computed at a $\omega B97X-3c$ [CPCM: DMSO] // $\omega B97X-3c$ [SMD: DMSO] level of theory with thermal corrections obtained at the GFN2-xTB [APLB: DMSO] level. Energies are given in kJ mol⁻¹. The corresponding structures can be found in the file “structures.zip”.

Z-L isomer	$\Delta G_{w.r.t. (M,M,M,M)-Z-L}$ [kJ mol ⁻¹]
(M,M,M,M) -Z-L	0.0
(P,M,M,M) -Z-L	-0.6
$(cis-P,P,M,M)$ -Z-L	-5.0
$(trans-P,P,M,M)$ -Z-L	-2.7
(P,P,P,M) -Z-L	-0.1
(P,P,P,P) -Z-L	-1.0

S8.4 Isomers of *E*-L

As already mentioned in Section S2.6, lantern *E*-L can adopt six isomers, because ligand *E*-1 is not C_2 symmetric (Figure S13 and Figure S111).

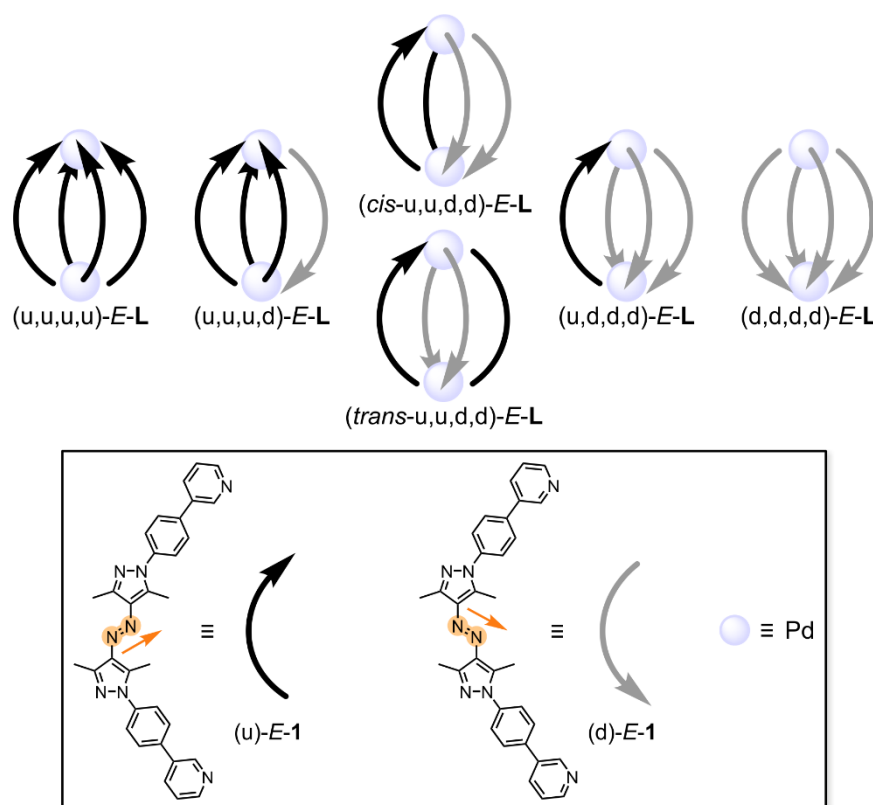


Figure S111. Cartoon representations of the different possible isomers of *E*-L. Ligand orientations are labelled “up” (u) and “down” (d), respectively, with respect to the orientations of the azo groups: If the N=N double bond of the azo bridge tilts slightly upward and into the concave side of the ligand (orange arrow), a ligand is assigned the “up” (u) orientation (black curved arrow); if it tilts slightly downward and into the concave side of the ligand (orange arrow), it is assigned the “down” (d) orientation (grey curved arrow). Note that the X-ray crystal structure showed the (*cis*-u,u,d,d)-*E*-L isomer (Section S7).

To systematically classify these isomers, the cage is oriented such that the Pd atom with the lower index in the xyz-file is at the bottom, with the other Pd atom on top. If the N=N double bond of the azo bridge points slightly upward and into the lantern, a given ligand is assigned the “up” (u) orientation; if it points slightly downward and into the lantern, it is assigned the “down” (d) orientation. This procedure is applied to all ligands in a structure to obtain an unambiguous classification of each isomer (Figure S112). These rules were arbitrarily chosen and serve solely to provide a

consistent differentiation between isomers. According to this nomenclature, the six possible isomers are:

(u,u,u,u)-*E-L* and its enantiomer (d,d,d,d)-*E-L*, (u,u,u,d)-*E-L* and its enantiomer (u,d,d,d)-*E-L*, (*cis*-u,u,d,d)-*E-L*, and (*trans*-u,u,d,d)-*E-L*.

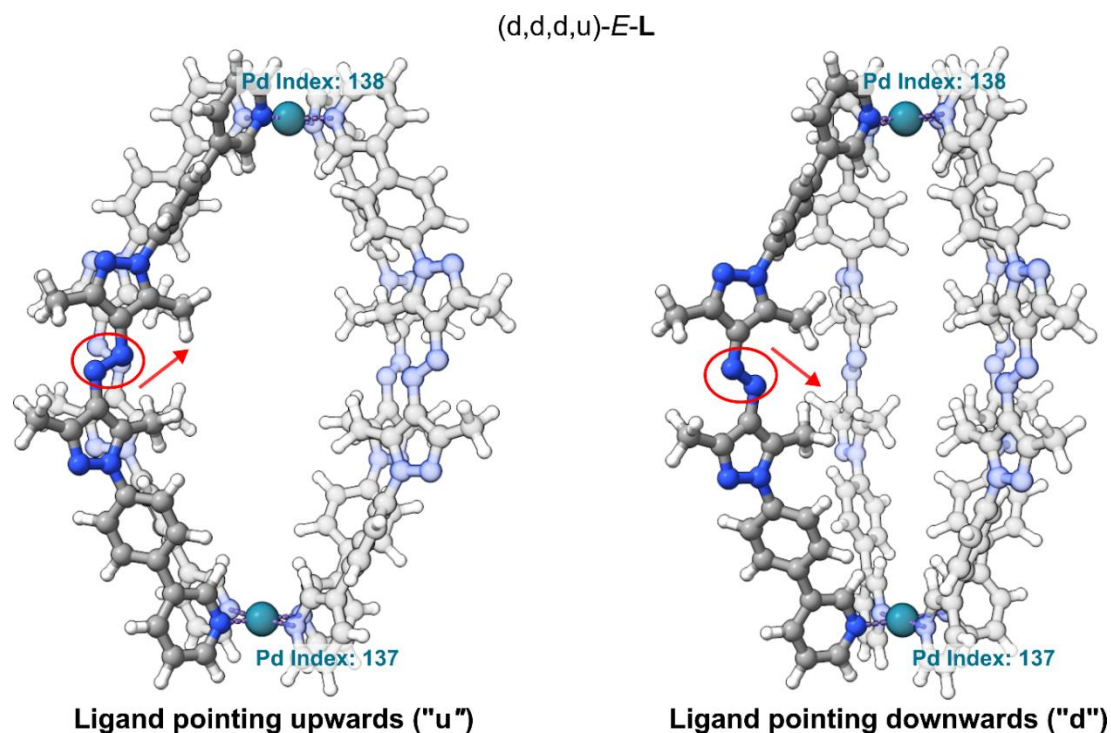


Figure S112. Illustration of the nomenclature scheme of *E-L* isomers for two ligands within the structure of (d,d,d,u)-*E-L*. The Pd atom with the lower index is positioned at the bottom of the lantern and the defining N=N double bond of the azo bridge (highlighted with a red circle) points into the lantern and either upwards or downwards, respectively. Atom colour code: H (white), C (grey), N (blue), Pd (teal).

The computed relative free energies with respect to (d,d,d,d)-*E-L* are summarised in Table S7. The results closely resemble those of the *Z-L* isomers. With absolute relative energy differences of up to 6.3 kJ mol⁻¹, all investigated isomers are predicted to be similarly stable. The computed energy difference of 4.2 kJ mol⁻¹ between the enantiomers (d,d,d,d)-*E-L* and (u,u,u,u)-*E-L* further highlights the limitations of the applied workflow, indicating that conclusions should be considered qualitative rather than quantitative.

Table S7. Relative free energies of the investigated *E-L* isomers with respect to (d,d,d,d)-*E-L* ($\Delta G_{\text{w.r.t. (d,d,d,d)-E-L}}$). Enantiomeric pairs are coloured blue or purple, respectively. Energies are computed at the ω B97X-3c [CPCM: DMSO] // ω B97X-3c [SMD: DMSO] level of theory, with thermal corrections obtained at the GFN2-xTB [APLB: DMSO] level. Energies are given in kJ mol⁻¹. The corresponding structures can be found in the file “structures.zip”.

<i>E-L</i> isomer	$\Delta G_{\text{w.r.t (d,d,d,d)-E-L}}$ [kJ mol⁻¹]
(d,d,d,d)- <i>E-L</i>	0.0
(d,d,d,u)- <i>E-L</i>	-6.3
(cis-d,d,u,u)- <i>E-L</i>	0.9
(trans-d,d,u,u)- <i>E-L</i>	-6.2
(d,u,u,u)- <i>E-L</i>	-3.1
(u,u,u,u)- <i>E-L</i>	4.2

S8.5 Comparison to the crystal structure of *E*-**L**

The experimentally obtained crystal structure provides a means to validate the previously applied computational approach. In the crystal structure, all ligands adopt the *E*-configuration, corresponding to *E*-**L**. Using the nomenclature introduced in Section S8.4, the lantern is classified as the (*cis*-u,u,d,d)-*E*-**L** isomer. A comparison of the crystal structure with the computationally predicted structure is shown in Figure S113. Overall, good agreement can be observed between the two structures. The Pd–Pd distance in the crystal is 20.6 Å, which is slightly longer than the predicted distance of 19.9 Å, and some portions of the structure exhibit minor differences in ligand orientation. Notably, the benzene rings adjacent to the azo bridges seem to adopt two preferred orientations, rotated by approximately 60° relative to each other. This can also partially be seen in the measured crystal structure, in which they exhibit respective static site disorder. Cases where the predicted structure deviates by a comparable rotation are still considered good agreement with the experiment. Using a bleeding-edge version of the CREST program, a permutation-invariant root-mean-square deviation (iRMSD) of 1.1 Å was obtained between the two structures (for more information, see ³⁶).

We conclude that the comparison demonstrates the computational approach is sufficient to reliably predict lantern structures, despite the omission of explicit solvent molecules or anions. This observation provides validation for the previously presented data.

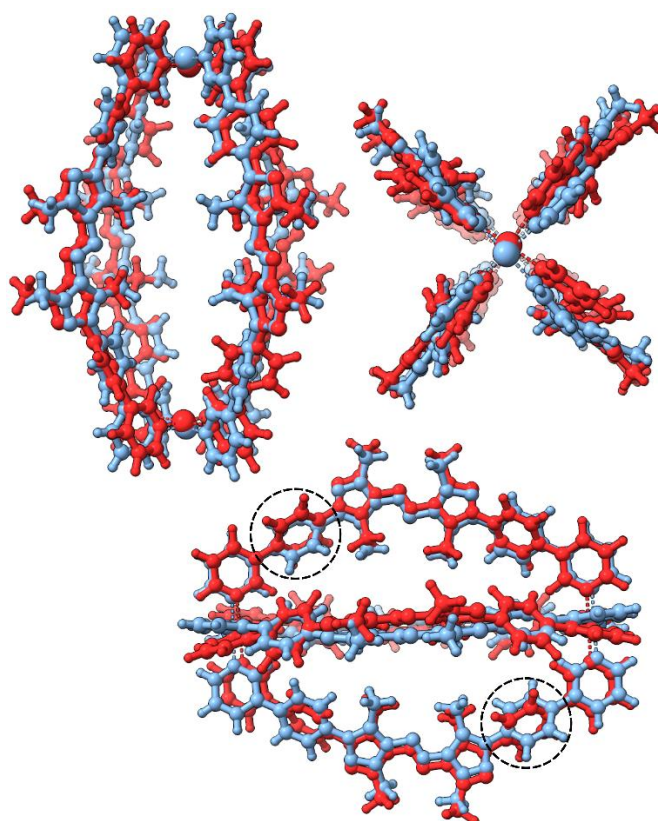


Figure S113. Overlay of the X-ray crystal structure of *E-L* (blue) with the computationally obtained structure (red) from CREST, reoptimized at the ω B97X-3c [CPCM: DMSO] level of theory. Following the nomenclature introduced in Section S8.4, the shown isomer is classified as (*cis-u,u,d,d*)-*E-L*. In the crystal structure, the benzene rings exhibit site disorder (main layer 55% occupancy), rotated by approximately 60°; black circles mark cases where the computed structure shows a similar rotation, which is therefore still considered good agreement. The structures have a permutation-invariant root-mean-square deviation (iRMSD) of 1.1 Å.

S8.6 Lantern models based on crystal structure

Analysis of the experimental crystal structure provided valuable information on the positions of solvent molecules and anions. A cutout of the crystal structure was used to construct a more sophisticated (but computationally more demanding) model, including four explicit DMSO molecules inside the lantern and two explicit BF_4^- anions coordinating the Pd^{II} cations in their octahedral positions outside the lantern. The cutout was relaxed at the $\text{r}^2\text{SCAN-3c}$ [CPCM: DMSO] level of theory.³⁷ The lower level of theory was necessary due to the extended system size to maintain feasible computation times; nonetheless, only negligible structural changes were observed upon relaxation.

Since no crystal structure could be obtained for $Z\text{-L}$, analogous model systems containing four DMSO and two BF_4^- anions in similar positions to those of $E\text{-L}$ were constructed for all possible isomers.

CREST was then employed to identify the lowest-energy conformer of each system, utilising the “subrmsd” setting. Due to the increased model complexity, several distinct low-lying conformers were manually selected and reoptimized at the $\text{r}^2\text{SCAN-3c}$ [CPCM: DMSO] level of theory. The energetically most favourable conformer was found to be a $(M,M,M,M)\text{-Z-L}$ isomer model system, which was subsequently used for further calculations. The resulting model systems for $E\text{-L}$ and $Z\text{-L}$ are shown in Figure S114.

Free energies were computed at the usual level of theory, yielding the following energy difference between $E\text{-L}$ and $Z\text{-L}$:

$$\Delta G_{E\text{-L}-Z\text{-L}} = G(E\text{-L}) - G(Z\text{-L}) = 181.2 \text{ kJ mol}^{-1} = 43.3 \text{ kcal mol}^{-1}.$$

This value is 12% lower than the previously computed value of $209.3 \text{ kJ mol}^{-1}$ (compare Table S5), which was obtained without explicit solvent molecules or anions. This indicates that explicit interactions between the lantern and its environment have a non-negligible effect, highlighting the limitations of the previously applied approximate model system.

However, due to the larger system size, the computational cost for a geometry optimisation increased from approximately 1 day to about 7 days, even with the use of a more efficient composite DFT method for the structures.

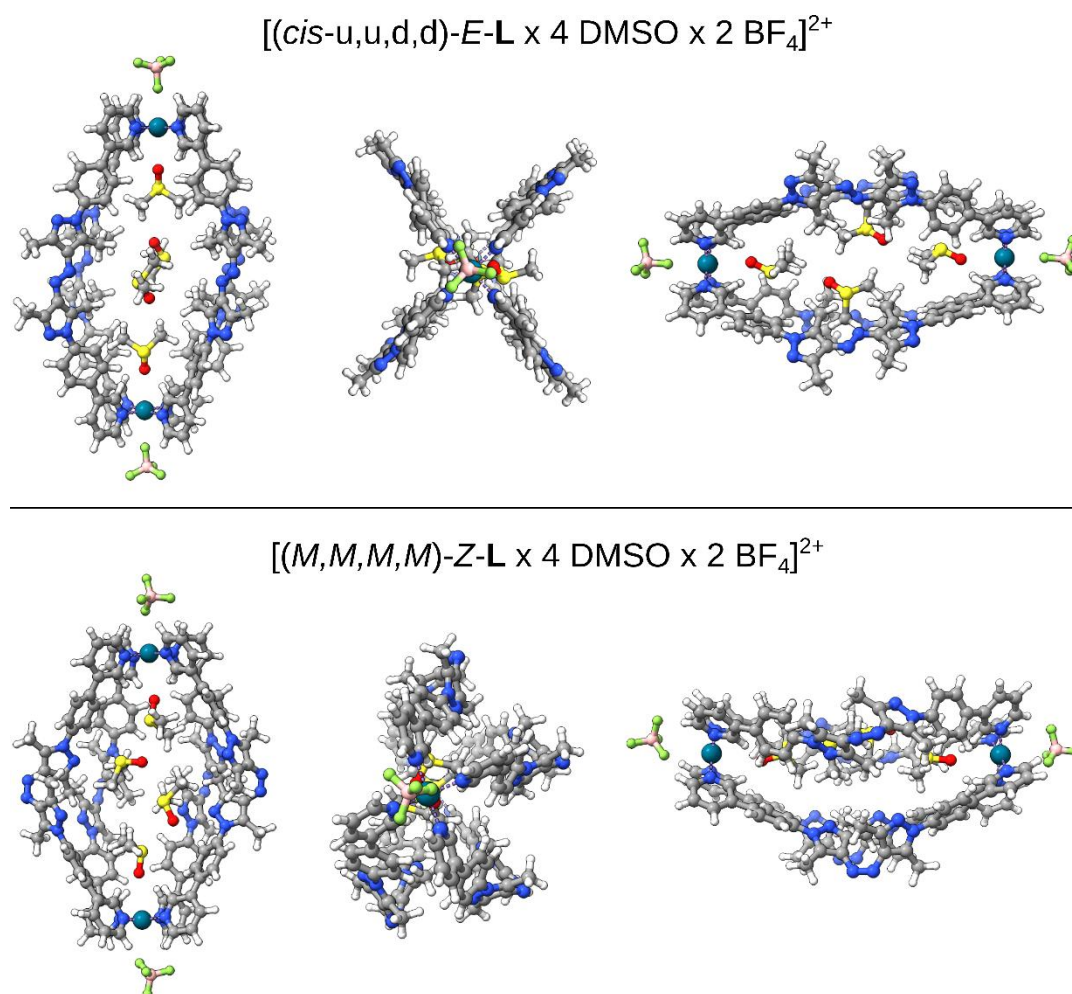


Figure S114. Model systems of *E*-L and *Z*-L, including four DMSO molecules and two BF_4^- anions. The *E*-L model was extracted from the experimental crystal structure and relaxed at the $\omega\text{B97X-3c}$ [CPCM: DMSO] level of theory. The given isomer is (*cis-u,u,d,d*)-*E*-L. The *Z*-L model was constructed analogously (for all isomers), and following conformational sampling, the lowest-energy conformer was relaxed at the same theory level. The given isomer is (*M,M,M,M*)-*Z*-L. Atom colour code: H (white), C (grey), N (blue), Pd (teal), O (red), S (yellow), F (green), B (pink).

S8.7 Investigation of *E-T* and *Z-T*

Model systems for the triangle complex with either all *E*-configured ligands (*E-T*) or all *Z*-configured ligands (*Z-T*) were constructed and conformationally sampled following the same procedure as for the lantern structures. However, technical difficulties arose, and the resulting low-lying conformers disagreed with the experimental NMR data presented in Section S2.6. This suggests that the combination of extended system size, flexibility, and high system charge (+6) renders the previously applied workflow unsuitable for obtaining reliable structures.

Based on the predicted lowest conformer of *E-T*, we attempted to reproduce the experimentally determined reaction energy for the transition of *E-L* to *E-T* ($-27.8 \text{ kJ mol}^{-1}$) but obtained a qualitatively incorrect result. The inclusion of six explicit DMSO molecules and three BF_4^- anions in the model did not help to resolve this discrepancy.

Consequently, a model of *E-T* consistent with the experimental NMR data was constructed and optimised at the GFN2-xTB [ALPB: DMSO] level of theory, which was only used for visualisation of *E-T* in the figures of this study and to approximate dimensions for comparison with the solvodynamic diameters obtained via DOSY NMR (Figure S23).

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