Electronic Supporting Information

Electronic Supporting Information

Gating the photochromism of an azobenzene by strong host-guest interactions in a divalent pseudo[2]rotaxane

M. Lohse,^{*a*} K. Nowosinski,^{*b*} Nora L. Traulsen,^{*b*} Andreas J. Achazi,^{*b*} L. K. S. von Krbek,^{*b*} Beate Paulus,^{*,*b*} Christoph A. Schalley^{*,*b*} and Stefan Hecht^{*,*a*}

^a Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany ^b Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany

Email: b.paulus@fu-berlin.de; christoph@schalley-lab.de; sh@chemie.hu-berlin.de

Contents

1.	General methods	2
2.	Synthesis	3
	2.1 Synthesis of <i>E</i> -1	3
	2.2 Synthesis of <i>E</i> / <i>Z</i> -2	15
3.	Complex characterisation	21
	3.1 Characterisation of the <i>E</i> -1@3 complex	21
	3.2 Characterisations of E-2@3 and Z-2@3	24
	3.3 Isothermal titration calorimetry (ITC)	25
	3.4 Competition Experiment of Z-2@3 with E-1	27
	3.5. Theoretical Calculation	28
4.	Photoisomerisation studies	30
	4.1 Photoisomerisation of 1	30
	4.2 Quantum yield determination for the $E \rightarrow Z$ isomerisation of 1	30
	4.3 Thermal $Z \rightarrow E$ isomerisation of 1	31
	4.4 Thermal $Z \rightarrow E$ isomerisation of 1@3	32
	4.5 Reference Experiments	32
	4.6 Fluorescence Experiments	33
5.	References	34

1. General methods

Solvents were either employed as purchased or dried prior to use by usual laboratory methods. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel plates (Merck 60F-254) using UV light for visualisation. Silica gel (Merck 60, particle size 0.040–0.063 mm) was used for column chromatography.

NMR spectra were recorded on a Bruker 300 MHz (75 MHz for ¹³C) spectrometer using residual protonated solvent signals as the internal standard (¹H NMR: δ (CDCl₃) = 7.26 ppm, δ (DMSO-*d*₆) = 2.50 ppm; ¹³C NMR: δ (CDCl₃) = 77.2 ppm, δ (DMSO-*d*₆) = 39.5 ppm). Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quadruplet (q), quintet (quint), multiplet (m), and broad (br).

Ultraperformance liquid chromatography coupled to mass spectrometry (UPLC-MS) was performed with a Waters Alliance system equipped with Acquity UPLC columns(gradient mixtures of acetonitrile/water). The Waters systems consisted of a Waters Separations Module 2695, a Waters Diode Array detector 996, a LCT Premier XE mass spectrometer, and a Waters Mass Detector ZQ 2000.

The electrospray-ionisation Fourier-transform ion-cyclotron-resonance (ESI-FTICR) mass spectrometric experiments were performed with a Varian/IonSpec QFT-7 FTICR mass spectrometer equipped with a superconducting 7 Tesla magnet and a micromass Z-spray ESI ion source.

UV-visible absorption spectra were recorded using quartz cuvettes either on a Cary 60 or a Cary 50 spectrophotometer equipped with a Peltier-thermostated cell holder (temperature accuracy \pm 0.1 °C). The solvents used were of spectrophotometric grade. Irradiation experiments were performed using a Hg/Xe lamp with monochromomator (slide length 2 nm). The photostationary state (PSS) was generated by irradiation a 2*10⁻³ M solution NMR-sample in a Rayonet photoreactor at 350 nm.

Synthesis of **3**¹, **13**², **14**², **15**³ have been described in the literature.

2. Synthesis

2.1 Synthesis of E-1



Scheme S1: Synthesis of *E*-1.

N-(4-nitrobenzylidene) N-benzyl amine 5



Benzylamine (1.2 mL, 11.0 mmol, 1 eqiv.) was added drop-wise to a stirred solution of pnitrobenzaldehyde (1.66 g, 11.0 mmol, 1 eqiv.) in trimethylorthoformate (20 mL) and the mixture was stirred at rt for 18 h. DCM was added and the organic phase was washed twice with sat. NaHCO₃-solution, and brine, dried over MgSO₄ and concentrated under reduced pressure. A yellow solid crystallises under high vacuum (2.56 g, 10.7 mmol, 96% yield).

¹**H NMR** (500 MHz, CDCl₃): δ = 8.48 (s, 1H, H–5), 8.27 (d, ⁴J-HH = 8.7 Hz, 2H, H–2), 7.96 (d, ⁴J-HH = 8.7 Hz, 2H, H–3), 7.38 (m, 5H, H–8, 9, 10), 4.90 (s, 2H, H–6). ¹³**C NMR** (125.75 MHz, CDCl₃): δ = 159.4, 149.0, 138.4, 128.8, 128.6, 128.0, 127.2, 123.8, 65.1 ppm.



Figure S1 $^1\mathrm{H}$ NMR spectrum (500 MHz, CDCl_3, 298K) of compound 5.



Figure S2 ¹³C NMR spectrum (126MHz, CDCl₃, 298K) of compound 5.

N-Benzyl N-(4-nitrobenzyl) amine 6



NaBH₄ (337 mg, 8.9 mmol, 2 eqiv.) was slowly added to a stirred ice-cooled solution of **5** (1.069 g, 4.5 mmol, 1 eqiv.) in MeOH (50 mL). The mixture was allowed to gain rt and stirred for additional 2h. After TLC showed a full conversion of starting material, excess NaBH₄ was quenched by adding water to the mixture. MeOH was removed under reduced pressure before EtOAc was added the slurry mixture and the aqueous phase was extracted thrice with EtOAc. The combined organic phases were washed with water and brine, dried over MgSO₄ and dried under reduced pressure to obtain the desired product as a colourless oil (0.912 g, 3.8 mmol, yield 84%).

¹**H** NMR (500 MHz, CDCl₃): δ = 8.21 (d, ⁴J-HH = 8.7 Hz, 2H, H–2), 7.56 (d, ⁴J-HH = 8.7 Hz, 2H, H-3), 7.36 (m, 5H, H–8, 9, 10), 3.94 (s, 2H, H–5), 3.84 (s, 2H, H–6), 1.80 (s, 1H, H–11). ¹³C NMR (125.75 MHz, CDCl₃): δ = 148.1, 146.9, 139.7, 128.6, 128.4, 128.0, 127.1, 123.5, 53.1, 52.2 ppm. MS (ESI+): m/z = 243.10 (calcd. 243.11 for [C₁₄H₁₅N₂O₂]⁺).



Figure S3 ${\rm ^1H}$ NMR spectrum (500 MHz, CDCl_3, 298K) of compound 6.



Figure S4 ¹³C NMR spectrum (126 MHz, CDCl₃, 298K) of compound 6.

tert-Butyl-benzyl(4-nitrobenzyl)carbamate 7



N,N-Dimethylaminopyridine (DMAP)(226 mg, 1.9 mmol, 0.5 eqiv.) was added in small portions to a stirred solution of bocanhydride (4.038 g, 18.5 mmol, 5 eqiv.) and **6** (0.896 g, 3.7 mmol, 1 eqiv.) in ACN. The mixture was stirred for 2 h at rt before the solvent was removed under reduced pressure and the remaining crude product was purified by column chromatography (SiO₂, eluent Petroloium ether : EtOAc 9:1) to obtain the pure product as a colourless oil (0.9 g, 2.6 mmol, yield 71%).

¹**H** NMR (500 MHz, CDCl₃): δ = 8.20 (m, 2H, H–2), 7.33 (m, 7H, H–3, 8, 9, 10), 4.48 (br, 4H, H–5, 6), 1.52 (s, 9H, H–13). ¹³**C** NMR (125.75 MHz, CDCl₃): δ = 147.2, 137.4, 128.7, 128.4, 128.3, 128.0, 127.6, 123.8, 80.7, 28.4 ppm. MS (ESI+): m/z = 287.09 (caldc. 287.10 for [C₁₅H₁₅N₂O₄]⁺).



Figure S5 ¹H NMR spectrum (500 MHz, CDCl₃, 298K) of compound 7.



Figure S6 ¹³C NMR spectrum (126 MHz, CDCl₃, 298K) of compound 7.

tert-Butyl-4-aminobenzyl(benzyl)carbamate 8



A mixture of **7** (342 mg, 1.0 mmol, 1 eqiv.) and Pd/C (34 mg, 10 wt%) was stirred in EtOAc under hydrogen atmosphere (1 atm) for 2 h. After a full consumption of the substrate, the mixture was filtered through a plug of celite (eluent: EtOAc) and concentrated under reduced pressure to obtain the pure product (300 mg, 9.6 mmol 96% yield) which was used without further purification.

¹H-NMR (500 MHz, CDCl₃): δ = 7.32 (m, 5H, H–8, 9, 10), 7.04 (m, 2H, H–3), 6.71 (m, 2H, H–2), 7.32 (br, 4H, H– 5, 6), 1.51 (s, 9H, H–13) ppm. ¹³C NMR (125.75 MHz, CDCl₃): δ = 156.0, 145.7, 149.5, 149.4, 128.5, 127.7, 127.1, 115.1, 79.9, 48.5, 28.4 ppm. MS (ESI+): m/z = 257.11 (calcd. 257.11 for [C₁₅H₁₇N₂O₂]⁺).



Figure 7 ¹H NMR spectrum (500 MHz, CDCl₃, 298K) of compound 8.



Figure 8 ¹³C NMR spectrum (500 MHz, CDCl₃, 298K) of compound 8.

(E)-Bis(BOC-4-benzylaminomethyl)azobenzene E-9



Pyridine (0.05 mL, 0.6 mmol, 0.1 eqiv.) was added to a solution of **8** (2.00 g, 6.4 mmol, 1 eqiv.) and CuBr (28 mg, 0.2 mmol, 0.03 eqiv.) in 30 mL of toluene. The reaction mixture was stirred under oxygen atmosphere for 3 days before it was concentrated under reduced pressure and purified by column chromatography (SiO₂, eluent petrolether : EtOAc 9:1) to obtain an orange oil that solidifies upon standing (1.30 g, 2.09 mmol, yield: 65 %).

¹**H** NMR (500 MHz, CD₂Cl₂): δ = 7.89 (m, 4H, H–2), 7.34 (m, 14H, H–3, 8, 9, 10), 4.45 (br, 8H, H-5, 6), 1.51 (s, 18H, H–13). ¹³C NMR (125.75 MHz, CD₂Cl₂): δ = 156.4, 152.5, 142.3, 138.7, 129.1, 128.7, 128.4, 128.1, 127.8, 123.5, 121.2, 80.6, 28.7 ppm. HRMS (ESI+): m/z = 621.335 (calcd. 621.345 for [C₃₈H₄₅N₄O₄]⁺).



Figure S9 ¹H NMR spectrum (500 MHz, CD₂Cl₂, 298K) of compound 9.



Figure S10 ¹³C NMR spectrum (126 MHz, CD₂Cl₂, 298K) of compound 9.

(E)-Bis(4-benzylaminomethyl)azobenzene E-10



Trifluoroacetic acid (TFA, 5 mL) was added drop-wise to a stirred solution of **9** (320 mg, 0.5 mmol) in 20 mL of CH_2Cl_2 . The mixture was stirred for 2 h until all starting material was consumed before the solvent was removed under reduced pressure and the pure product was collected as an orange solid (300 mg, 0.7 mmol, 96% yield).

¹**H-NMR** (500 MHz, DMSO-d6): δ = 9.53 (br, 4H, NH), 7.97 (m, 4H, H–2), 7.73 (m, 4H, H–3), 7.52 (m, 4H, H–8), 7.44 (m, 6H, H–9, 10), 4.31 (br, 4H, H–5), 4.23 (br, 4H, H–6). ¹³**C NMR** (125.75 MHz, DMSO-d6): δ =148.4, 158.2, 151.9, 131.2, 130.0, 129.1, 128.7, 122.8, 50.2, 49.5 ppm. **HRMS (ESI+)**: m/z = 421.244 (calcd. 421.239 for $[C_{28}H_{29}N_4]^+$).



Figure S11 ¹H NMR spectrum (500 MHz, DMSO-d6, 298K) of compound 10.



Figure S12 ¹³C NMR spectrum (126 MHz, DMSO-d6, 298K) of compound 10.

(E)-Bis(4-benzylaminomethyl)azobenzene bis(hexafluorophosphate) E-1



 NH_4PF_6 (572 mg, 3.5 mmol, 2.5 eqiv.) was added to a stirred solution of **10** (590 mg, 1.4 mmol, 1 eqiv.) in 100 mL of acetonitrile. The solution was stirred for 30 min while argon was bubbled through the solution. Water was added and the precipitate collected. The desired compound was obtained by recrystallisation from MeOH/water as an orange solid (500 mg, 1.2 mmol, 85% yield).

¹**H** NMR (500 MHz, CD₃CN): δ = 7.97 (m, 4H, H-2), 7.67 (m, 4H, H-3), 7.48 (m, 10H, H-8, 9, 10), 4.31 (s, 4H, H-5), 4.26 (s, 4H, H-6). ¹³C NMR (125.75 MHz, CD₃CN): δ = 154.0, 135.4, 132.4, 131.2, 130.8, 130.2, 124.4, 118.4, 52.8, 52.1 ppm. **HRMS (ESI+)**: m/z = 211.282 (calcd. 211.281 for [C₂₈H₃₀N₄]²⁺).



Figure S13 ¹H NMR spectrum (500 MHz, CD₃CN, 298K) of compound E-1.



Figure S14 ¹³C NMR spectrum (126 MHz, CD₃CN, 298K) of compound *E*-1.

2.2 Synthesis of *E*/*Z*-2



(Z)-Bis(4-benzylaminomethyl)stilbene Z-17



A solution of bisbenzaldehyde Z-15 and benzylamine was stirred overnight in trimethylorthoformate. The product was obtained and used without further purification. NaBH₄ (0.102 g, 2.7 mmol, 2 eqiv.) was added to a stirred ice-cooled solution of Z-16 (0.560 g, 1.4 mmol, 1 eqiv.) in a 1:1 mixture of THF and MeOH (20 mL each). The mixture was stirred over night until no starting material was left. The solution was concentrated under reduced pressure and the crude product was redissolved in EtOAc. Non soluable impurities were filtered off through a celite plug using EtOAc and the organic solution was concentrated again. The pure product was obtained by column chromatography (SiO₂, solvent: petroleum ether : EtOAc) as a colourless oil (0.340 g, 0.8 mmol, 60% yield).

¹**H** NMR (500 MHz, CD₂Cl₂): δ = 7.35 (m, 8H), 7.25 (m, 10H), 6.58 (s, 2H), 3.79 (s, 4H), 3.75 (s, 4H). ¹³**C** NMR (125.75 MHz, CD₂Cl₂): δ = 141.1, 140.0, 136.3, 130.1, 129.1, 128.6, 128.4, 128.3, 127.1, 53.2 ppm. MS (ESI+): m/z = 419.25 (calcd. for 419.24 [C₃₀H₃₁N₂]⁺).



Figure S15 ¹H NMR spectrum (500 MHz, CD₂Cl₂, 298K) of compound Z-17.



FigureS 16 ¹³C NMR spectrum (126 MHz, CD₂Cl₂, 298K) of compound Z-17.

(Z)-Bis(4-benzylaminomethyl)stilbene bis(hexafluorophosphate) Z-2



 NH_4PF_6 (0.331 g, 2.0 mmol, 2.5 eqiv.) was added to a stirred solution of *Z*-**17** (0.340 g, 0.8 mmol, 1 eqiv.) in 10 mL of acetonitrile. The mixture was stirred for 30 min while argon was purged through the solution. Upon addition of water, the product precipitated as a white solid which was collected and dried (0.370 g, 0.5 mmol, 64% yield).

¹**H NMR** (500 MHz, CD₃CN): δ = 7.48 (m, 10H), 7.31 (m, 8H), 6.75 (s, 2H), 4.16 (s, 4H), 4.13 (s, 4H). ¹³**C NMR** (125.75 MHz, CD₃CN): δ = 139.0, 133.2, 132.2, 131.2, 130.9, 130.8, 130.3, 130.2, 130.0, 52.6, 52.3. ¹⁹**F-NMR** (470 MHz, CD₃CN) δ =71.48, 72.98 ppm. **MS (ESI+)**: m/z = 419.23 (calcd. for 419.24 [C₃₀H₃₁N₂]⁺).



Figure S17 ¹H NMR spectrum (500 MHz, CD₃CN, 298K) of compound Z-2.



Figure S18 ¹³C NMR spectrum (126 MHz, CD₃CN, 298K) of compound Z-2.

(E)-Bis(4-benzylaminomethyl)stilbene E-16



A solution of (E)-bisbenzaldehyde *E*-**15** (0.050 g, 0.212 mmol, 1 eqiv.) and benzylamine (0.045 g, 0.423 mmol, 2 eqiv.) were stirred overnight in 3 mL trimethylorthoformate. After concentrating the solution under reduced pressure the product was obtained and used without further purification. NaBH₄ (0.016 g, 0.424 mmol, 2 eqiv.) was added to a stirred ice-cooled solution of *E*-**16** (0.088 g, 0.212 mmol, 1 eqiv.) in a 1:1 mixture of THF and MeOH (3 mL each). The mixture was stirred over night until no starting material was left. The solution was concentrated under reduced pressure and the crude product redissolved in EtOAc. The remaining insoluable impurities were filtered off through a celite plug using EtOAc and the organic solution was concentrated again. The pure product was obtained by column chromatography (SiO₂, solvent: petroleum ether : EtOAc) as a colourless oil (0.07 g, 0.17 mmol, 79% yield).

¹**H NMR** (500 MHz, CD_2Cl_2): δ = 7.50 (m, 4H, H–3), 7.35 (m, 14H, H–4,9,10,11), 7.12 (s, 2H, H–1), 3.80 (s, 4H, H–6,7) ¹³**C NMR** (125.75 MHz, CD_2Cl_2): δ = 140.7, 140.3, 136,0, 128.5, 128.3, 128.1, 127.9, 126.8, 126.4, 53.1, 52.9 ppm. **MS (ESI+)**: m/z = 419.24 (calcd. 419.24 for [C₃₀H₃₁N₂]⁺).



Figure S19 ¹H NMR spectrum (500 MHz, CD₂Cl₂, 298K) of compound *E*-17.



Figure 20 ¹³C NMR spectrum (500 MHz, CDCl₃, 298K) of compound *E*-17.

(E)-Bis(4-benzylaminomethyl)stilbene bis(hexafluorophosphate E-2



 NH_4PF_6 (0.056 g, 0,358 mmol, 2.5 eqiv.) was added to a stirred solution of *E*-**16** (0.060 g, 0.143 mmol, 1 eqiv.) in 10 mL acetonitrile. Everything was stirred for 30 min while argon was purged through the solution. Upon addition of water the product precipitated as a white solid which was collected and dried (0.08 g, 0.11 mmol, 80% yield).

¹**H** NMR (500 MHz, CD₃CN): δ = 7.66 (m, 4H, H–3), 7.48 (m, 14H, H–4,9,10,11), 7.30 (s, 2H, H–1), 4.25 (s, 2H, H–6/7), 4.24 (s, 2H, H–6/7). ¹³C NMR (125.75 MHz, CD₃CN): δ = 139.6, 131.8, 131.4, 131.2, 130.9, 130.8, 130.1, 130.0, 128.1, 52.5, 52.2. ¹⁹F NMR (470 MHz, CD₃CN) δ = -71.51, 73.02 ppm. MS (ESI+): m/z = 419.24 (calcd. 419.24 for [C₃₀H₃₁N₂]⁺).



Figure S21 ¹H NMR spectrum (500 MHz, CD₃CN, 298K) of compound *E*-2.



figure S22 ¹³C NMR spectrum (126 MHz, CD₃CN, 298K) of compound E-2.

3. Complex characterisation

3.1 Characterisation of the E-1@3 complex



Figure S23: ¹H NMR (500 MHz, 298K, CDCl₃:CD₃CN = 2:1, 1.4 mM) of (top) *E*-**1**, (middle) *E*-**1**@**3** and (bottom) **3** after 21 h showing clear evidence for the complexation. The dotted lines indicate the shifting of the protons upon complex formation. The increase of signals in the crown ether region is due to the formation of diasterotopic protons upon complexation.



Figure S24: ¹H,¹H COSY NMR (500 MHz, 298K, CDCl₃:CD₃CN = 2:1, 1.4 mM) of *E*-1@3.

ESI-FTICR Mass Spectrum of E-1@3



formation of the desired 1:1 complex.

3.2 Characterisations of *E*-2@3 and *Z*-2@3



Figure S26: ¹H NMR (500 MHz, 298K, CDCl₃:CD₃CN = 2:1, 1.4 mM) of (top) *E*-**2**, (middle) *E*-**2**@**3** and (bottom) **3** after 21h showing clear evidence for the complexation. The increase of signals in the crown ether region is due to the formation of diasterotopic protons upon complexation.



Figure S27: ¹H NMR (500 MHz, 298K, CDCl₃:CD₃CN = 2:1, 1.4 mM) of (top) *Z*-**2**, (middle) *Z*-**2**@**3** and (bottom) **3** after 21h showing no clean spectrum indicating a non-discrete aggregate.

3.3 Isothermal titration calorimetry (ITC)

Titration experiments were carried out in $CH_3CN/CHCl_3$ 2.2 : 1 (v/v) at 25 °C on a TAM III microcalorimeter (Waters GmbH, TA Instruments, Eschborn, Germany). High purity solvents were used as purchased (LGC Standarts GmbH, Optigrade®, solvents for HPLC). For this reason, literature-known binding data of some complexes like **4@5** are slightly different.⁴ In a typical experiment, an 800 µL of a 2 mM solution of the crown ether was placed in the sample and 200 µL of a solution of the ammonium salt (40 mM in the same solvent) was placed in the injection syringe. The titrations consisted of 20 consecutive injections between 8-10 µL each with a 10 min interval between injections. Heats of dilution, measured by titration of the ammonium salt into the sample cell with blank solvent, were subtracted from each data set. All solutions were degassed prior to titration. The data were analysed using the instrument's software package and fitted with a 1:1 or 1:2 binding model. In case of **5@3** and **1@4**, the following model was used: $[H] + [G] \rightarrow [H \cdot G]; [H \cdot G] + [G] \rightarrow [H \cdot G_2] (H = host, G = Guest). Errors are smaller than ±10%.$



Figure S28: Double mutant cycle for the equilibrium in eq 1. Divalent pseudorotaxanes exhibiting strongly positive chelate cooperativity shift this equilibrium further (large negative $\Delta\Delta G$ and high *EM* values) to the product side than that of weakly cooperative systems.

For calculating the effective molarity (*EM*) of the *E*-**1**@**3** complex the dissociation equilibrium

$$(b) + (c) \rightleftharpoons (a) + (d) \tag{eq 1}$$

was considered.⁴ EM can be calculated considering the overall association constant K for this reaction

$$K = \frac{K^{a}K^{d}}{K^{b}K^{c}} = EM$$
 (eq 2)

with *K*ⁿ representing the single association constants a-d (see Figure S28).



Figure S29: ITC Experiments: Titration plots (heat flow versus time and heat/volume versus guest/host ratio) obtained from ITC experiments of crown ethers with ammonium hexafluorophosphate salts. Labels (a), (b), (c) and (d) according to Figure S5.

Table S1: Thermodynamic binding data as obtained from ITC experiments (CHCl₃/CH₃CN = 2.2:1, 298 K). labels (a), (b), (c) and (d) refer to the complexes shown in Figure S6.

0,00	Ċ	1	0		
		<i>K</i> a [M ⁻¹]	ΔG [kJ mol ⁻¹]	ΔH [kJmol ⁻¹]	Τ ΔS [kJmol ⁻¹]
(a)	Ka	200,000 ± 20,000	-30.3 ± 0.2	-52.1	-21.8
(b)	$K_1^{\rm b}$	3,100 ± 300	-19.9 ± 0.3	-27.6	-7.7
	K_2^{b}	870 ± 90	-16.8 ± 0.2	-35.0	-18.1
(c)	K ₁ ^c	3,700 ± 400	-20.4 ± 0.2	-26.3	-5.9
	K_2^{c}	170 ± 20	-12.7 ± 0.3	-32.9	-20.2
(d)	K ^d	1,800 ± 200	-18.6 ± 0.2	-39.3	-20.6

3.4 Competition Experiment of Z-2@3 with E-1



Figure S30: ¹H NMR (500 MHz, 298K, CDCl₃:CD₃CN = 2:1, 1.4 mM) of (left) an equimolar mixture of *Z*-**2** and **3**, (right top) *E*-**1**@**3**, (right middle) an equimolar mixture of *E*-**1**, *Z*-**2** and **3** and (right bottom) *Z*-**2** showing the rapid and exclusive formation of *E*-**1**@**3** in the presence of *Z*-**2** giving evidence to a strong preference for the formation of the *E* complex.

3.5. Theoretical Calculation

For the calculation of the electronic energy *E* the meta-GGA-functional TPSS^{5, 6} was used together with the dispersion correction D3(BJ)^{7, 8} and the triple- ζ basis set def2-TZVP.^{9, 10} In a next step, the contributions of translation, rotation and vibration G_{RRHO}^T are included with an approach from Grimme.¹¹ In this approach, the low-lying vibrations are partially treated as hindered rotations (with TPSS-D3(BJ)/def2-SVP^{10, 12} for the vibrations). Solvation effects δG_{SE}^T have been included with the COSMO-RS solvent model^{13, 14}.

$$\Delta G = G_{\rm RRHO}^T + \delta G_{\rm SE}^T \tag{eq 3}$$

The influence of the counterion PF_{6} , G(ce), onto the Gibbs energy of association ΔG has been taken into account. We have recently described this approach in detail for similar systems and the computed results agree well with the experiment.¹⁵

$$\Delta G(\text{complex}) = G(\text{complex}) - G(\text{host}) - G(\text{guest}) - G(\text{ce}) \qquad (\text{eq 4})$$

$$G(ce) = G(guest \bullet PF_6^{-}) - G(guest) - G(PF_6^{-})$$
(eq 5)

The calculated Gibbs energy of association ΔG of *E*-**1**@**3** is -29.0 kJ mol⁻¹ (Table S2). It is the Gibbs energy that is released when *E*-**1** and **3** form a 1:1 complex. For *Z*-**1**@**3** the calculated Gibbs energy of association ΔG to form the 1:1 complex is +52.9 kJ mol⁻¹ (Table S2). Thus, *Z*-**1** and **3** do not form a doubly bound 1:1 complex. The reason is that host and guest are deformed, when forced to form a doubly bound 1:1-complex. This causes a substantial amount of strain, which overcompensates the association energy of the two binding sites. Hence, the experimentally observed complexes of *Z*-**1** and **3** are no doubly bound 1:1 complexes.

The difference between the calculated Gibbs energies of association ΔG for *E*-1@3 and *Z*-1@3 is +81.9 kJ mol⁻¹:

$$\Delta G(E-1@3) - \Delta G(Z-1@3) = [52.9 - (-29.0)] \text{ kJ mol}^{-1} = +81.9 \text{ kJ mol}^{-1}$$

$$= G(E-1@3) - G(3) - G(E-1) - [G(Z-1@3) - G(3) - G(Z-1)]$$

= $G(E-1@3) - G(E-1) - G(Z-1@3) + G(Z-1)$ (eq 6)

To obtain the isomerisation Gibbs energy of the complexed guest $\Delta G(E-1@3 \rightarrow Z-1@3)$, the isomerisation Gibbs energy of the free guest $\Delta G(E-1 \rightarrow Z-1)$ has to be added to equation 6, resulting $\Delta G(E-1@3 \rightarrow Z-1@3) = +110.7$ kJ mol⁻¹:

$$\Delta G (E-1@3 \rightarrow Z-1@3) = \Delta G(E-1@3) - \Delta G(Z-1@3) + \Delta G(E-1 \rightarrow Z-1)$$

= (52.9 - (-29.0) + 28.8) kJ mol⁻¹ = +110.7 kJ mol⁻¹
= G(E-1@3) - G(E-1) - G(Z-1@3) + G(Z-1) + \Delta G(E-1 \rightarrow Z-1) (eq 7)

with $\Delta G(E-1 \to Z-1) = G(E-1) - G(Z-1)$ (eq 8)

$$\Delta G (E-1@3 \rightarrow Z-1@3) = G(E-1@3) - G(E-1) - G(Z-1@3) + G(Z-1) + G(E-1) - G(Z-1)$$

= G(E-1@3) - G(Z-1@3) (eq 9)

As shown in equation 9, the isomerisation Gibbs energy of the complexed guest $\Delta G(E-1@3 \rightarrow Z-1@3)$ can be directly calculated from the absolute Gibbs energies of the complexes G(E-1@3) and G(Z-1@3), respectively, as well:

$$\Delta G (E-1@3 \rightarrow Z-1@3) = G(E-1@3) - G(Z-1@3) = +115.3 \text{ kJ mol}^{-1}$$
 (eq 10)

In principle both approaches shown in equation 7 and equation 10 should give the same isomerisation Gibbs energy $\Delta G(E-\mathbf{1}@\mathbf{3} \rightarrow Z-\mathbf{1}@\mathbf{3})$. If infinite basis sets could be applied, this would be the case. In the approach given in equation 7, systematic errors occur due to basis set superposition errors. The direct calculation with equation 10 suffers from the basis set superposition error, as well. However, due to the fact that $E-\mathbf{1}@\mathbf{3}$ and $Z-\mathbf{1}@\mathbf{3}$ have the same number of basis functions and a similar structure, the basis set superposition error is negligible compared to the approach in equation 7. Summarised the +115.3 kJ mol⁻¹ value contains less errors than the +110.7 kJ mol⁻¹ and was therefore reported. Nevertheless, the difference between the two approaches below 5% which indicates the reasonable quality of the used basis set.

Table S2: Computed Gibbs energies of association ΔG of *E*-1, *Z*-1, *E*-2, and *Z*-2 to 3 and ΔG for the *E*-*Z* isomerisation of 1 in the complex in CHCl₃ : CH₃CN = 2.2 : 1 at 298 K. Calculated with TPSS-D3(BJ)/def2-TZVP⁶⁻¹¹ and COSMO-RS.¹⁴

-	E-1@3	Z -1@3	E -2@3	Z-2@3	$E\textbf{-1@3} \rightarrow Z\textbf{-1@3}$	
ΔG [kJ mol ⁻¹] -29.0	+52.9	-19.0	+36.2	+115.3	

4. Photoisomerisation studies

4.1 Photoisomerisation of 1



Figure S31: a) $E \rightarrow Z$ isomerisation (CHCl₃: CH₃CN 2:1, 20 µM, $\lambda_{irr.}$ = 334 nm), b) $Z \rightarrow E$ (CHCl₃: CH₃CN 2:1, 20 µM, $\lambda_{irr.}$ = 436 nm) and c) the corresponding isomerisation cycles ($A_{obs.}$ = 350 nm) for the free guest **1**.





Figure S32: Isomerisation of **1** (20 μ M in CHCl₃/CH₃CN 2:1) upon irradiation at 334 nm (left) and the corresponding $E \rightarrow Z$ conversion (right). Irradiation time 60 min.

The quantum yield for the *E*-**1**→Z-**1** isomerisation was calculated using the initial slope method¹⁶ based on the equation $\frac{da}{dt} = 1000 \cdot I_0 \frac{1-10^{-E(t)}}{E(t)} (-\epsilon_A \Phi_{A \to B} \cdot a \cdot l + \epsilon_B \Phi_{B \to A} \cdot b \cdot l)$ with the light intensity I₀, the overall extinction at observed wavelength *E*(*t*), extinction coefficients ϵ_A and ϵ_B , the quantum yields $\Phi_{A \to B}$ and $\Phi_{B \to A}$, and the irradiation path length l = 1cm. During the first 10% of irradiation, the *Z*-**1**→*E*-**1** isomerisation is assumed to be zero ($\epsilon_B \Phi_{B \to A} \cdot b = 0$) resulting in a linear correlation (see Figure S10) and a quantum yield of 0.068 (±0.007) can be calculated. Light intensity I₀ at 334 nm was determined by potassium ferrioxalate actinometry.¹⁷ The "micro-version"¹⁸ consisting of irradiation of 3 mL of a fresh potassium ferrioxalate solution (0.006 M in 0.05 M H₂SO₄) in a cuvette for 2 – 4 min, subsequent addition of 0.5 mL of phenanthroline buffer (0.1 wt % in 0.5 M H₂SO₄/1.6 M NaOAc), and absorbance readout at 510 nm was applied.

4.3 Thermal $Z \rightarrow E$ isomerisation of 1

The thermal $Z \rightarrow E$ isomerisation follows 1st order reaction kinetics $A = A_0 e^{-kt}$. Thermal half life and activation parameters can be determined from temperature-dependent measurements. The initial photostationary state (PSS) was determined by irradiating 3 mg of **1** in 250 mL of CH₃CN in a photoreactor. After removing the solvent under reduced pressure at 20 °C, the sample was dissolved in CD₃CN and the PSS was calculated from the ratios of the *E*-**1** and *Z*-**1** integrals in ¹H NMR. The content of *Z* can be calculated following the equation $Z(%) = \frac{A_E - A_{obs}}{A_E - A_Z}$ with the absorption of the pure (*E*)- and (*Z*)-isomer A_E and A_Z , as well as the observed absorption A_{obs} . The absorption A_Z can be calculated from the PSS (known from NMR) following equation $A_Z = \frac{A_0 - A_E * x(t)}{y(t)}$ with the mole fraction x(t) (*E*-**1**) and y(t) (*Z*-**1**) and the absorption at the photostationary state A_0 .



Figure S33: Thermal *Z*-**1** \rightarrow *E*-**1** isomerisation observed by UV/Vis spectroscopy (CH₃CN, 20 μ M, A_{obs} = 321 nm): plot of -ln(Z%) (initial percentage of *Z*-**1** as determined by NMR) vs. time at different temperatures showing a linear decay of *Z*-**1**.



9.11 (±0.07)·10 ⁻⁵	7600 (±54)	106 (±4)	103 (±4)	-24 (±12)	110 (±7)

Figure S34: Thermal *Z*-**1** \rightarrow *E*-**1** isomerisation in CH₃CN: Arrhenius plot (left), Eyring-plot (right), and the corresponding kinetic data and activation parameters (298 K) as calculated using the Arrhenius and Eyring equations.

4.4 Thermal $Z \rightarrow E$ isomerisation of 1@3

To investigate the influence of the complexation on the thermal half-life of guest **1** was irradiated to its photostationary state upon which host **3** was added. After equilibration for 60 min, the time-dependent absorption change was monitored for three different temperatures (Figure S13). Note that no reasonable thermal half-life could be calculated as the $Z \rightarrow E$ isomerisation of E-**1**@**3** does not follow 1st or 2nd order reaction kinetics.



Figure S35: Thermal $Z \rightarrow E$ isomerisation observed by UV/Vis spectroscopy (CHCl₃:CH₃CN 2:1, 40 μ M, A_{obs} = 350 nm): plot of -ln(Z%) (initial percentage of Z-1 as determined by NMR) of 1 (red) and 1@3 (black) against the time (minutes) at different temperatures showing a slower thermal isomerisation in the complex compared to the free guest.

4.5 Reference Experiments

To investigate the influence of the divalent interaction in the *E*-1@3 complex several reference experiments have been performed: first, the influence of the threading of *E*-1 in a monovalent crown ether **4** (Figure S14 b), second, the presence of host **3**, while irradiating a non-binding model compound **10** (Figure S14 a, pure spectra of 10 see Figure S16), and third the influence of the polarity and the resulting binding strength (Figure S15). In all three cases a successful *E*-*Z* isomerisation was achieved. Additionally, the overlap of the individual species (Figure S16) shows that a selective irradiation of *E*-**1** in the presence of **3** is impossible.



Figure S36: a) Isomerisation of **10** in presence of **3** (20 μ M in CHCl₃/CH₃CN 2:1) and b) **1**@**4** (20 μ M in CHCl₃/CH₃CN 2:1) in CHCl₃/CH₃CN 2:1) in CHCl₃/CH₃CN 2:1 upon irradiation at 334 nm. Absorption changes indicate an *E* \rightarrow *Z* isomerisation of **10** and **2**.



Figure S37: a) Irradiation of Z-1 + 3 (25 μ M in CHCl₃/CH₃CN 2:1, λ_{irr} =436 nm) showing a clear Z-1 \rightarrow E-1 isomerisation; b) Irradiation of E-1@3 (20 μ M in CHCl₃/CH₃CN 1:14, λ_{irr} = 334 nm) in polar solvent showing a clear E-1 \rightarrow Z-1 isomerisation.



Figure S38: Absorption spectra (20 μ M in CHCl₃/CH₃CN 2:1) of **1**, **3**, **4** and **10** showing strong overlap in the UV region making a selective irradiation of **1**, respectively **10**, impossible.

4.6 Fluorescence Experiments

To investigate potential energy transfer in the E-1@3 complex, emission and excitation spectra have been recorded. The decrease in fluorescence of E-1@3 compared to free 3 clearly shows an energy transfer from the excited host to E-1 in the formed complex (Figures S17).



Figure S39: Excitation (λ_{em} = 426 nm, solid lines) and emission (λ_{ex} = 333 nm, dashed lines) spectra of **1**, **3** and *E*-**1@3** (CHCl₃: CH₃CN 2:1, 2 µM each).

5. References

- 1 W. Jiang and C. A. Schalley, *Proc. Natl. Acad. Sci. USA*, 2009, **106**, 10425-10429.
- 2 M. Linseis, S. Záliš, M. Zabel and R. F. Winter, *J. Am. Chem. Soc.*, 2012, **134**, 16671-16692.
- 3 T. Bosanac and C. S. Wilcox, *Org. Lett.*, 2004, **6**, 2321-2324.
- 4 W. Jiang, K. Nowosinski, N. L. Löw, E. V. Dzyuba, F. Klautzsch, A. Schäfer, J. Huuskonen, K. Rissanen and C. A. Schalley, *J. Am. Chem. Soc.*, 2011, **134**, 1860-1868.
- 5 TURBOMOLE V6.5 2013 a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, TURBOMOLE GmbH, since 2007; available from http://www.turbomole.com.
- 6 J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.
- 7 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 8 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456-1465.
- 9 F. Weigend, M. Häser, H. Patzelt and R. Ahlrichs, *Chem. Phys. Lett.*, 1998, **294**, 143-152.
- 10 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057-1065.
- 11 S. Grimme, Chem. Eur. J., 2012, 18, 9955-9964.
- 12 A. Schäfer, H. Horn and R. Ahlrichs, J. Chem. Phys., 1992, 97, 2571-2577.
- 13 F. Eckert and A. Klamt, *AIChE J.*, 2002, **48**, 369-385.
- 14 F. Eckert and A. Klamt, COSMOtherm, Version C3.0, Relase 13.01; COSMOlogic GmbH & Co. KG Leverkusen, Germany.
- 15 A. J. Achazi, L. K. S. von Krbek, C. A. Schalley, B. Paulus, *J. Comput. Chem.* **2015**, *accepted*.
- 16 M. Herder, B. M. Schmidt, L. Grubert, M. Pätzel, J. Schwarz and S. Hecht, *J. Am. Chem. Soc.*, 2015, **137**, 2738-2747.
- 17 C. G. Hatchard and C. A. Parker, A New Sensitive Chemical Actinometer. II. Potassium Ferrioxalate as a Standard Chemical Actinometer, 1956.
- 18 M. Montalti, A. Credi, L. Prodi, Gandolfi and M. T. In, *Handbook of Photochemistry*, CRC Press: Boca Raton, 2006.