Supporting information

Directional threading of a chiral porphyrin cage compound onto viologen guests

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1. Materials, instrumentation and methods

Acetonitrile and chloroform used in the binding and threading experiments were distilled from CaCl₂. All other solvents and chemicals were commercial products and used as received. UV-vis spectra were recorded on a Cary 100 Conc (Varian, Middelburg) UV-vis spectrometer. NMR spectra were measured using a Bruker Avance III 400 instrument (400 MHz, $^1$H and 2D-NMR spectra) equipped with a BBFO+ probe and a Bruker Avance III 500 instrument (500 MHz, $^1$H and 2D-NMR spectra) equipped with Prodigy BBO cryoprobe in deuterated chloroform (CDCl₃), unless stated otherwise. Chemical shifts are reported in ppm and referenced to tetramethylsilane. Fluorescence experiments were performed on a Perkin-Elmer LS5B luminescent spectrometer equipped with a thermostated cuvette holder. Cells with an optical path length of 1 cm were employed. Computational studies were performed by using the molecular modelling program Spartan’14 and the energy minimization calculations were performed using the semi-empirical PM3 method.

2. Syntheses of (±)-H₂2 and V₄

**Synthesis of (±)-H₂2:** This compound was synthesized according to a previously published procedure.$^{51}$ $^1$H NMR (500 MHz, CD₃CN/CDCl₃ 1:1 (v/v)) $\delta$ 8.89 – 8.54 (m, 8H), 8.33 (dd, $J = 7.4$, 1.7 Hz, 1H), 8.10 (dd, $J = 7.3$, 1.8 Hz, 1H), 8.03 (dd, $J = 7.2$, 1.8 Hz, 1H), 7.91 (dd, $J = 7.3$, 1.8 Hz, 1H), 7.80 (dddt, $J = 8.6$, 7.1, 3.1, 1.8 Hz, 4H), 7.54 – 7.51 (m, 1H), 7.46 – 7.38 (m, 5H), 7.35 (td, $J = 7.4$, 1.0 Hz, 1H), 7.32 (dd, $J = 8.4$, 1.1 Hz, 1H), 7.09 – 7.02 (m, 2H), 7.00 – 6.94 (m, 2H), 6.92 (td, $J = 7.6$, 1.5 Hz, 3H), 6.88 (dt, $J = 8.1$, 1.5 Hz, 1H), 6.80 (dddt, $J = 8.1$, 6.3, 1.6 Hz, 2H), 6.36 (s, 1H), 6.27 (s, 1H), 6.13 (s, 1H), 4.36 (d, $J = 15.8$ Hz, 1H), 4.31 – 4.21 (m, 2H), 4.21 – 4.13 (m, 6H), 4.09 – 4.04 (m, 1H), 4.00 (td, $J = 8.5$, 5.2 Hz, 1H), 3.90 (td, $J = 8.2$, 5.9 Hz, 1H), 3.80 (d, $J = 15.8$ Hz, 1H), 3.82 – 3.77 (m, 1H), 3.74 (d, $J = 15.8$ Hz, 1H), 3.74 (d, $J = 15.8$ Hz, 1H), 3.70 (d, $J = 16.7$ Hz, 1H), 3.65 – 3.57 (m, 2H), 3.49 – 3.34 (m, 2H), 3.28 – 3.07 (m, 2H), 2.67 – 2.55 (m, 1H), $\sim$2.77 (s, 2H) ppm. $^{13}$C($^1$H)-NMR (126 MHz, CD₃CN+CDCl₃) $\delta$ 159.00, 158.60, 158.48, 157.92, 157.55, 148.79, 146.50, 146.00, 143.91, 137.02, 135.86, 135.52, 135.35, 134.09, 132.83, 132.79, 131.47, 131.15, 130.83, 130.55, 130.49, 130.30, 130.00, 129.95, 129.83, 129.12, 128.69, 128.26, 128.18, 121.66, 120.82, 120.62, 120.18, 120.10, 117.44, 115.19, 115.08, 112.59,
111.96, 111.81, 85.50, 84.98, 72.39, 69.10, 68.35, 67.74, 67.56, 66.81, 65.96, 44.39, 43.91, 38.31 ppm. MS (HR-MALDI-TOF) \( m/z \): 1390.46 [(M)\(^{+}\), calcd for \( C_{84}H_{63}N_{9}O_{12} \): 1390.46]. HRMS (ESI): m/z, calcd for \( C_{84}H_{63}N_{9}O_{12} \), 1389.46744, found: 1390.46369 [M+H]\(^{+}\).

**Synthesis of viologen V4:**

\[
\begin{align*}
\text{Br} & \quad \text{OH} \quad + \quad \text{COOH} \\
& \Rightarrow \\
\text{Br} & \quad \text{OH} \quad + \quad \text{COOH}
\end{align*}
\]

**Synthesis of adamantane-1-carboxylic acid 11-bromo-undecyl ester (7)**

11-Bromo-1-undecanol (125.8 mg, 0.5008 mmol), adamantane-1-carboxylic acid (111 mg, 0.616 mmol) and \( p \)-toluenesulfonic acid (20 mg, 0.13 mmol) were dissolved in toluene (15 mL). The solution was heated at reflux temperature under argon over a Dean-Stark trap for 16 h. After cooling, the solution was evaporated to dryness. The product was purified by column chromatography (Silica 60H, CHCl\(_3\)) to give compound 7 as a colourless oil in a yield of 181.4 mg (88%).

\(^{1}\text{H NMR} (500.135 \text{ MHz, CDCl}_3) \delta 4.03 (t, 2H, \(^3J = 6.5 \text{ Hz}) , 3.41 (t, 2H, \(^3J = 7.0 \text{ Hz}) , 2.01 (m, 3H), 1.89-1.81 (m, 8H), 1.76-1.66 (m, 6H), 1.61 (m, 2H), 1.42 (m, 2H), 1.38-1.24 (m, 12H) \text{ ppm.} \)
\(^{13}\text{C NMR} (125 \text{ MHz, CDCl}_3) \delta 177.89, 129.09, 128.28, 64.24, 40.77, 38.94, 36.61, 34.10, 32.89, 29.50, 29.26, 28.82, 28.69, 28.23, 28.05, 25.97 \text{ ppm.} \)

MALDI-TOF \( m/z \) 414 [M+H]\(^{+}\).
Figure S1: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 7.

Figure S2: $^{13}$C{$^1$H} NMR spectrum (500 MHz, CDCl$_3$) of compound 7.
Synthesis of adamantane-1-carboxylic acid 11-{1’-[5-(3,5-di-tert-butyl-phenoxy)-pentyl]-[4,4’]bipyridinium-1-yl}-undecyl ester dihexafluorophosphate (V4)

Compounds 7 (179.4 mg, 0.435 mmol) and 8\(^{82}\) (61 mg, 0.11 mmol) were dissolved in degassed DMF (2 mL). The mixture was heated at 100 °C for 64 h. After cooling, 10 mL of diethyl ether was added and a precipitate formed. The mixture was stirred for 10 min and then filtered. The residue was washed with diethyl ether (50 mL) and dissolved in acetonitrile (2 mL). The resulting yellow solution was added dropwise to a stirred saturated aqueous NH\(_4\)PF\(_6\) solution (20 mL). A precipitate formed which was filtered off. It was dissolved in CHCl\(_3\)/CH\(_3\)CN (1:1 v/v, 1 mL), and this solution was added dropwise to stirred diethyl ether (20 mL). The resulting precipitate was filtered off and dried under vacuum to yield compound V4 (55 mg, 49%) as an off-white solid.

\(^1\)H NMR (500.135 MHz, CDCl\(_3\);CD\(_3\)CN (1:1, v/v)) δ 8.92 (d, 2H, \(^3\)J = 6.5 Hz), 8.91 (d, 2H, \(^3\)J = 7.0 Hz), 8.44-8.39 (m, 4H), 7.02 (t, 1H, \(^3\)J = 1.6 Hz), 6.73 (d, 2H, \(^3\)J = 1.6 Hz), 4.67 (t, 2H, \(^3\)J = 7.5 Hz), 4.61 (t, 2H, \(^3\)J = 7.5 Hz), 4.03-3.95 (m, 4H), 2.18-2.07 (m, 6H), 2.06-1.96 (m, 3H), 1.89-1.82 (m, 8H), 1.78-1.66 (m, 6H), 1.65-1.55 (m, 4H), 1.44-1.24 (m, 30H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\);CD\(_3\)CN (1:1, v/v)) δ 176.50, 151.37, 149.00, 144.73, 126.45, 114.02, 107.93, 66.19, 63.06, 61.49, 61.36, 39.73, 37.97, 35.52, 33.96, 30.36, 30.25, 30.12, 28.46, 28.31, 28.20, 27.94, 27.75, 27.66, 27.12, 24.92, 21.37 ppm. MALDI-TOF m/z 766 [M−2PF\(_6\)]\(^+\).
**Figure S3:** $^1$H NMR spectrum (500 MHz, CDCl$_3$:CD$_3$CN (1:1, v/v)) of compound V4.

**Figure S4:** $^{13}$C ($^1$H) NMR spectrum (500 MHz, CDCl$_3$:CD$_3$CN (1:1, v/v)) of compound V4.
3. NMR studies: Host-guest complexation

CDCl₃/CD₃CN solutions (1:1 (v/v)) containing (±)-H₂2 and 1.5 equivalents of the different viologen guests were prepared except for V4, which was prepared via preformation of the complex followed by chromatographic purification. The samples were then investigated by ¹H NMR (500 MHz, 298 K unless indicated otherwise).

3.1: (±)-H₂2/V1

Figure S5: ¹H NMR spectrum (500 MHz, 243 K) of pseudorotaxane (±)-H₂2/V1 in CD₂Cl₂ at −30 °C.
**Figure S6**: $^1$H NMR spectrum (500 MHz, 203 K) of pseudorotaxane (±)-H$_2$/V1 in CD$_2$Cl$_2$ at $-70$ °C.

### 3.2: H$_2$/V2

**Figure S7**: $^1$H NMR spectra (500 MHz, 298 K) of a) (±)-H$_2$, b) V2, c) pseudorotaxane (±)-H$_2$/V2 in CDCl$_3$:CD$_3$CN 1:1 v/v.
Key ROESY correlations for the assignment of directional threading of V2 in H\textsubscript{2}2

![Diagram of molecular structure]

**Figure S8:** 2D ROESY spectrum of pseudorotaxane (±)-H\textsubscript{2}2/V2 in CDCl\textsubscript{3}:CD\textsubscript{3}CN 1:1 v/v. BA = NCH\textsubscript{2}Ar proton signal; EG = OCH\textsubscript{2}CH\textsubscript{2}O proton signal; SW = sidewall.
Assignment of $^1$H (black) and $^{13}$C resonances (red) of bound V2 in H$_2$2 based on 2D COSY, ROESY, HSQC and HMBC Data

Figure S9: Expanded region of the COSY spectrum of pseudorotaxane (±)-H$_2$2/V2 in CDCl$_3$:CD$_3$CN 1:1 v/v.
Figure S10: HMBC spectrum of pseudorotaxane (±)-H₂2/V2 in CDCl₃:CD₃CN 1:1 v/v.
Figure S11: Multiplicity edited HSQC spectrum of pseudorotaxane (±)-H₂2/V₂ in CDCl₃:CD₃CN 1:1 v/v (Blue: + CH and CH₃, Red – CH₂).
Figure S12: NMR spectra of guest V2 (VAd) threading through (+)-H22 in CDCl3:CD3CN 1:1 v/v. A) 1H NMR spectrum of the host-guest complex. b) 1D extracts from the 2D ROESY spectrum. BA = NCH2Ar proton signal; EG = OCH3CH2O proton signal; SW = sidewall; VAd_o = ortho pyridinium proton of VAd; VAd_m = meta pyridinium proton of VAd; VAd-Ad = adamantane proton of V2; VAd-N+CH2 = N+CH2 in V2 linker; X = artifact from t1 noise.
3.3: (±)-H₂₂/V₃

Figure S13: $^1$H NMR spectra (500 MHz, 298 K) of a) (±)-H₂₂, b) V₃, c) pseudorotaxane (±)-H₂₂/V₃ in CDCl₃:CD₃CN 1:1 v/v.
Key ROESY correlations for the assignment of directional threading of V3 in H$_2$2

**Major Species**

**Minor Species**

![Diagram showing ROESY correlations for the assignment of directional threading of V3 in H$_2$2](image-url)
Figure S14: Expanded region of the 2D ROESY spectrum of pseudorotaxane (±)-H₂/V₃ in CDCl₃:CD₃CN 1:1 v/v. BA = NCH₂Ar proton signal; EG = OCH₂CH₂O proton signal; SW = sidewall.

Assignment of ¹H (black) and ¹³C resonances (red) of bound V₃ in H₂ based on 2D COSY, ROESY, HSQC and HMBC Data

**Major Species**

**Minor Species**
Figure S15: COSY spectrum of pseudorotaxane $(\pm)$-H$_2$/V3 in CDCl$_3$:CD$_3$CN 1:1 v/v.

Figure S16: Expanded region of the HMBC spectrum of pseudorotaxane $(\pm)$-H$_2$/V3 in CDCl$_3$:CD$_3$CN 1:1 v/v.
**Figure S17**: Multiplicity edited HSQC spectrum of pseudorotaxane (±)-H$_2$2/V3 in CDCl$_3$:CD$_3$CN 1:1 v/v (Blue: + CH and CH$_3$, Red: – CH$_2$).
3.4: \( \text{H}_2\text{2/V4} \)

**Synthesis of pseudorotaxane complex \( \text{H}_2\text{2/V4} \)**

Compounds (±)-H\(_2\text{2} \) (5.3 mg, 3.8 \( \mu \)mol) and V\(_4 \) (22.3 mg, 21.1 \( \mu \)mol) were dissolved in CHCl\(_3\)/CH\(_3\)CN (1:1 v/v, 6 mL). The mixture was heated at reflux temperature for 5 days. After cooling, the solution was evaporated to dryness. The crude product was purified by column chromatography (Silica 60, 3% MeOH in CHCl\(_2\) (v/v). The purple fraction was collected and evaporated to dryness. It was redissolved in a minimal amount of CHCl\(_3\) and this solution was added dropwise to rapidly stirred \( n \)-heptane (10 mL). The precipitate was collected by centrifugation and dried under vacuum. Yield: 8.0 mg (86%) of an inseparable mixture of two pseudorotaxane complexes between (±)-H\(_2\text{2} \) and V\(_4 \) as a purple solid.

\(^1\text{H} \) NMR (500.135 MHz, CDCl\(_3\):CD\(_3\)CN (1:1, v/v)): see Fig. S18. MALDI-TOF \( m/z \) 2155 [M−2PF\(_6\)]\(^+\).

**Figure S18** \(^1\text{H} \) NMR spectrum (500 MHz, 298 K) of the mixture of the two pseudorotaxanes (±)-H\(_2\text{2/V4} \) in CDCl\(_3\):CD\(_3\)CN 1:1 (v/v).
Figure S19 Numbering of relevant protons (in blue) and their assignments in the two pseudorotaxane isomers (±)-H$_2$2/V4 (left: structure of the isomer; right: relevant proton numbering in the respective thread components of the rotaxane isomers). Assignments in black are of the major product, assignments in red of the minor product. See also the assignments in the spectra in Figures S20 and S21.

Figure S20 Magnification of the aromatic region of the ¹H NMR spectrum (500 MHz, 298 K) of the mixture of the two pseudorotaxanes (±)-H$_2$2/V4 in CDCl$_3$:CD$_3$CN 1:1
(v/v). See Figure S19 for proton numbering. Black numbering indicates the major product, red numbering the minor product.

**Figure S21** Magnification of the aliphatic region of the $^1$H NMR spectrum (500 MHz, 298 K) of the mixture of the two pseudorotaxanes $\text{H}_2V^4$ in CDCl$_3$:CD$_3$CN 1:1 (v/v). See Figure S19 for proton numbering. Black numbering indicates the major product, red numbering the minor product.
**Figure S22:** COSY spectrum (expanded region) of the mixture of the two pseudorotaxanes (±)-H$_2$2/V4 in CDCl$_3$:CD$_3$CN 1:1 (v/v).

**Figure S23:** 2D-ROESY spectrum (expanded region) of the mixture of the two pseudorotaxanes (±)-H$_2$2/V4 in CDCl$_3$:CD$_3$CN 1:1 (v/v). See Figure S19 for proton numbering.
**Figure S24:** Multiplicity edited HSQC spectrum of the mixture of the two pseudorotaxanes (±)-H$_2$2/V4 in CDCl$_3$:CD$_3$CN 1:1 (v/v). (Blue: +CH and CH$_3$, Red: – CH$_2$).

**Figure S25:** HMBC spectrum (expanded region) of the mixture of the two pseudorotaxanes (±)-H$_2$2/V4 in CDCl$_3$:CD$_3$CN 1:1 (v/v).
3.5: $\text{H}_2/\text{V5}$

Figure S26: $^1$H NMR spectra (500 MHz, 298 K) of a) (±)-H$_2$2, b) V5, c) pseudorotaxane (±)-H$_2$2/V5 in CDCl$_3$:CD$_3$CN 1:1 v/v.
Key ROESY correlations for the assignment of directional threading of V5 in H$_2$2

**Figure S27**: Expanded region of the 2D ROESY spectrum of pseudorotaxane (±)-H$_2$2/V5 in CDCl$_3$:CD$_3$CN 1:1 v/v. BA = NCH$_2$Ar proton signal; EG = OCH$_2$CH$_2$O proton signal; SW = sidewall.
Assignment of $^1$H (black) and $^{13}$C resonances (red) of bound V5 in H$_2$2 based on 2D COSY, ROESY, HSQC and HMBC Data

Figure S28: COSY spectrum of pseudorotaxane (±)-H$_2$2/V5 in CDCl$_3$:CD$_3$CN 1:1 v/v.
Figure S29: Expanded region of the HMBC spectrum of pseudorotaxane (±)-H$_2$2/V5 in CDCl$_3$:CD$_3$CN 1:1 v/v.

Figure S30: Multiplicity edited HSQC spectrum of pseudorotaxane (±)-H$_2$2/V5 in CDCl$_3$:CD$_3$CN 1:1 v/v (Blue: +CH and CH$_3$, Red: – CH$_2$).
4. Variable-temperature $^1$H NMR spectra of (±)-H$_2$2/V5

**Figure S31.** a) Portion of $^1$H NMR spectral changes (400 MHz, CDCl$_3$/CD$_3$CN 1:1 (v/v)) during the threading experiment of (±)-H$_2$2 (0.68 mM) and V5 (1.4 mM, 2 equiv) as a function of time (from bottom to top) at 45 °C, revealing the disappearance of the resonances of (±)-H$_2$2 and V5 as a result of the formation of the oriented (pseudo-
rotaxane complex between (±)-H\textsubscript{2}2 and V5. The signals (mainly the side-wall benzene protons) belonging to free (±)-H\textsubscript{2}2 (α) and free V5 (X), and to (±)-H\textsubscript{2}2 (+) and V5 (*) in the rotaxane self-assembled structure are indicated. In the first and final spectrum, some of the proton signals of (±)-H\textsubscript{2}2 are assigned by \textsuperscript{1}H NMR spectral changes (500 MHz, CDCl\textsubscript{3}/CD\textsubscript{3}CN 1:1 (v/v)) during the threading experiment of (±)-H\textsubscript{2}2 (0.68 mM) and V5 (1.4 mM, 2 equiv) as a function of time (from bottom to top) at 45 °C.

5. Complexation of (±)-H\textsubscript{2}2 with V6

When no complexation of a viologen-substituted guest occurs inside the porphyrin cage, the fluorescence emission is not quenched.\textsuperscript{S3,S4} In order to study the effect of the blocking group, we used di-blocked viologen (V6) as the guest. As expected no complexation occurred inside the cavity. Fluorescence studies (Figure S32) revealed no quenching as a result of complex formation, even after prolonged standing of the host-guest mixture at elevated temperatures (50 °C) or upon the addition of 5 equivalents of the guest. NMR studies revealed that none of the proton signals of the cavity displayed shifts upon the addition of 1 equivalent of V6 (Figure S33). These studies confirm that the viologen guests V1-V5 must enter (±)-H\textsubscript{2}2 via the terminal side and not the blocked side.

![Chemical structure of (±)-H\textsubscript{2}2 and V5](image)

**Figure S32.** (a) Chemical structure of di-blocked viologen V6. (b) Fluorescence emission of (±)-H\textsubscript{2}2 upon the addition of V6. The number of added equivalents is indicated (c = 2 μM in CHCl\textsubscript{3}/CH\textsubscript{3}CN, 1:1, v/v, T = 295 K. λ\textsubscript{ex} = 421 nm).
Figure S33. $^1$H NMR spectra (500 MHz, 298 K, CDCl$_3$/CD$_3$CN, 1:1 (v/v)) of (a) (±)-H$_2$2, (b) V6, (c) (±)-H$_2$2 with 1 equivalent of V6, (d) idem, after 120 h at 20°C, (e) idem, after 3 h at 45°C.

6. Variable-temperature $^1$H NMR spectra of (±)-H$_2$2
Figure S34. $^1$H NMR spectral changes (500 MHz) of $(\pm)$-H$_2$2 in CDCl$_3$ at two different temperatures, 25 °C (purple) and 50 °C (green). Inset: pyrrole NH proton signals.

7. References