Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Correlated translational motions in *pseudo*-rotaxane complexes controlled by a single chemical stimulus

Supplementary Information

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1. General Information.

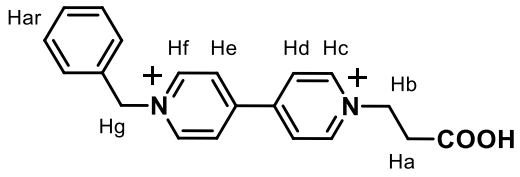
Chemical reagents were obtained from Sigma-Aldrich. All reactions were carried out in an open atmosphere and reagent grade solvents were used without additional purification.

NMR spectra were recorded on either JEOL ECA 500 MHz or Bruker AVANCE III 400 MHz spectrometers locked to the deuterated solvent. X-ray diffraction data were collected at 171 K on a Bruker D8 VENTURE diffractometer.
High-resolution mass spectra were obtained on an Agilent 6500 Series electrospray-ionization Q-TOF mass spectrometer. UV/Vis spectra were recorded on an Agilent 8453 spectrophotometer. Lauda R8 thermostat was used for fixing the temperature in the titrations.

Compounds [**1**][Br]$_2$ and [**2**][Br]$_2$ were synthesized by direct alkylation of 4,4'-bipyridine with the corresponding alkyl bromide derivative employing a previously described procedure[1].

Host [NMe_4]$_2$[**DSDB24C8**] was prepared and isolated as its *anti*-isomer according to our published method[2].

2. Non-symmetric viologen guest [**1**]Br_2



400 mg (1.22 mmol) of 1-benzyl-4,4'-bipyridynium bromide[3] was mixed with 3-bromopropionic acid (93 mg, 0.61 mmol) in 10 mL of acetonitrile. The mixture was stirred and heated at reflux temperature for 4 days. After the reaction period, the mixture was cooled down to room temperature (aprox. 20 °C) and acetone was added to obtain a yellow precipitate that was filtered off to yield 200 mg of compound [**1**][Br]$_2$ (68%).

^{1}H NMR (500 MHz, CD_3OD) δ ppm: 9.36 (d, *J* = 7.0 Hz, 2H, Hc), 9.35 (d, *J* = 7.0 Hz, 2H, Hf), 8.70 (d, *J* = 7.0 Hz, 2H, Hd), 8.67 (d, *J* = 7.0 Hz, 2H, He), 7.66 – 7.45 (m, 5H, Har), 5.99 (s, 2H, Hg), 5.00 (t, *J* = 6.2 Hz, 2H, Hb), 3.23 (t, *J* = 6.2 Hz, 2H, Ha).

^{13}C NMR (126 MHz, CD_3OD) δ 173.06 (COOH), 151.72 - 151.52 (CquatBipy), 147.87 - 147.06 (Cc – Cf), 134.32 (CquatAr), 131.26 - 130.82 - 130.44 (Car), 128.60 - 128.01 (Ce – Cd), 65.91 (Cg), 58.76 (Cb), 35.19 (Ca).

Molecular ion: [**1**-H]$^+$ $C20H19N2O2^+$ m/z: calc. 319.14410; exp. 319.14327; error: 2.6 ppm

a. 1D and 2D NMR spectra.

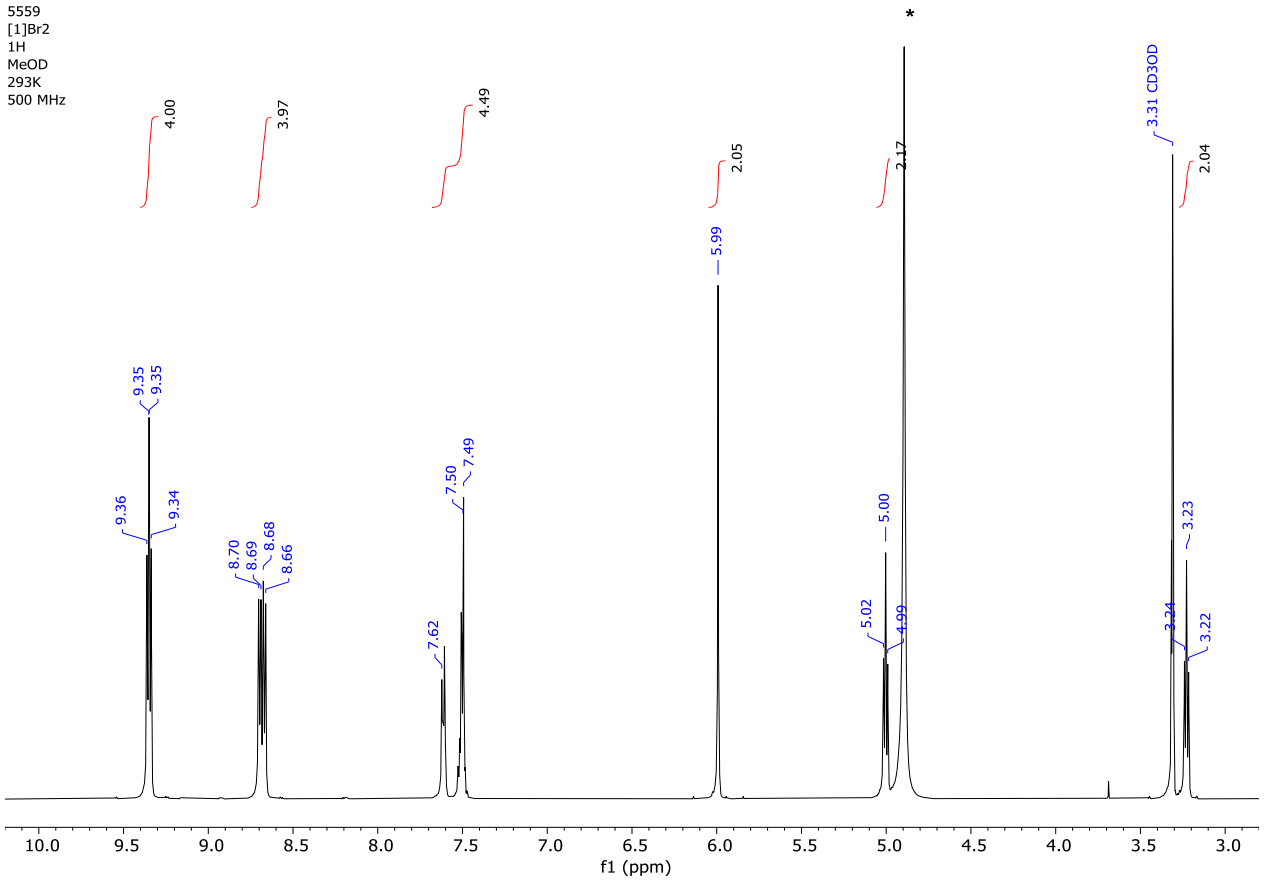
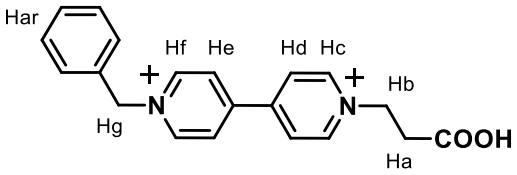


Figure S1. ^{1}H NMR spectrum of guest [**1**][Br]$_2$ (293 K, CD_3OD, 500 MHz, *H_2O).



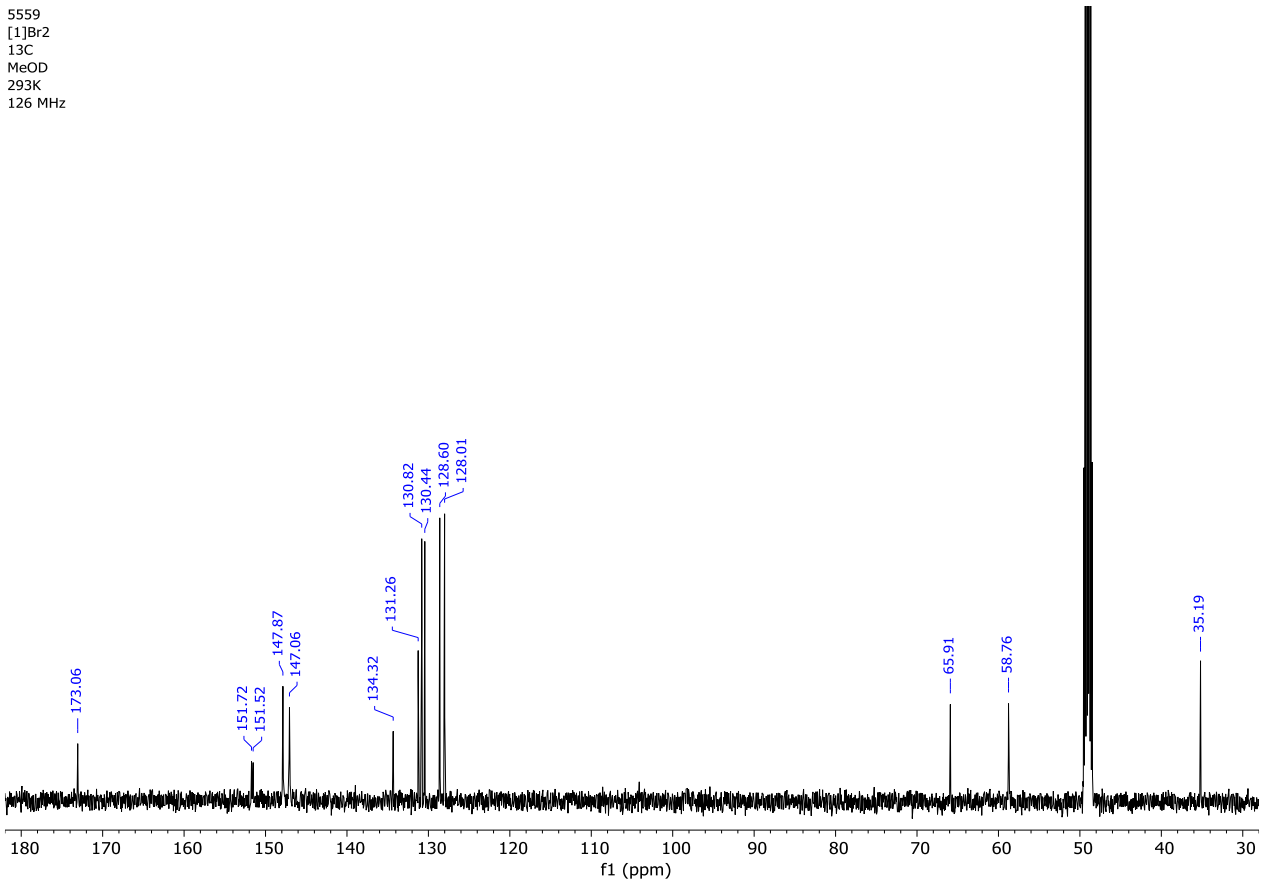
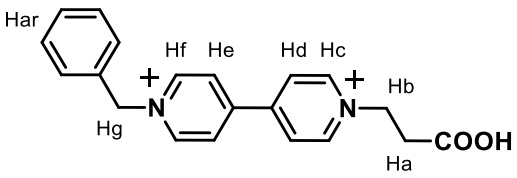


Figure S2. ^{13}C NMR spectrum of compound [**1**][Br]$_2$ (293 K, MeOD, 126 MHz).



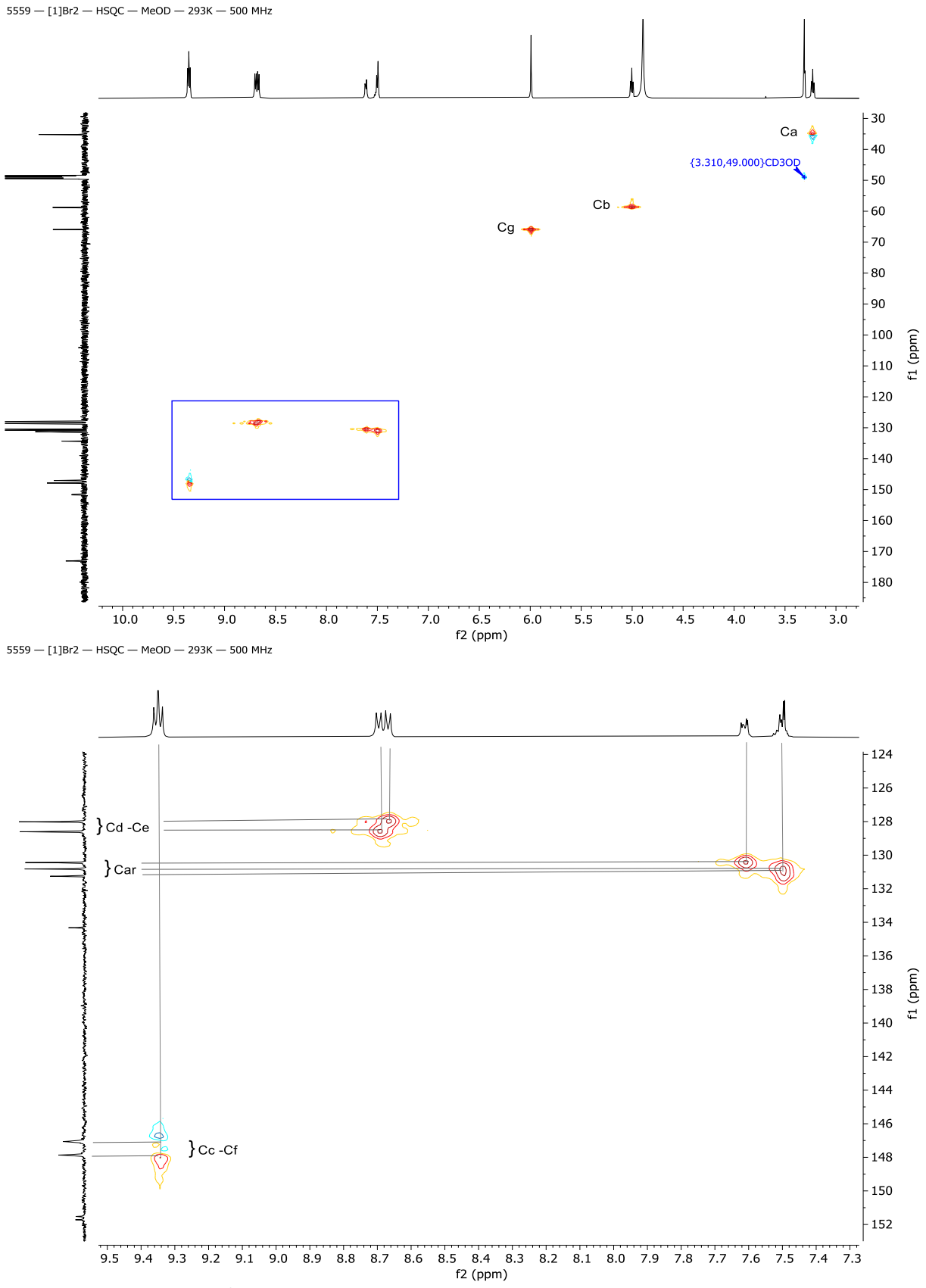


Figure S3. ^{1}H-^{13}C HSQC NMR spectrum of compound [**1**][Br]$_2$ (293 K, MeOD, 500 MHz).

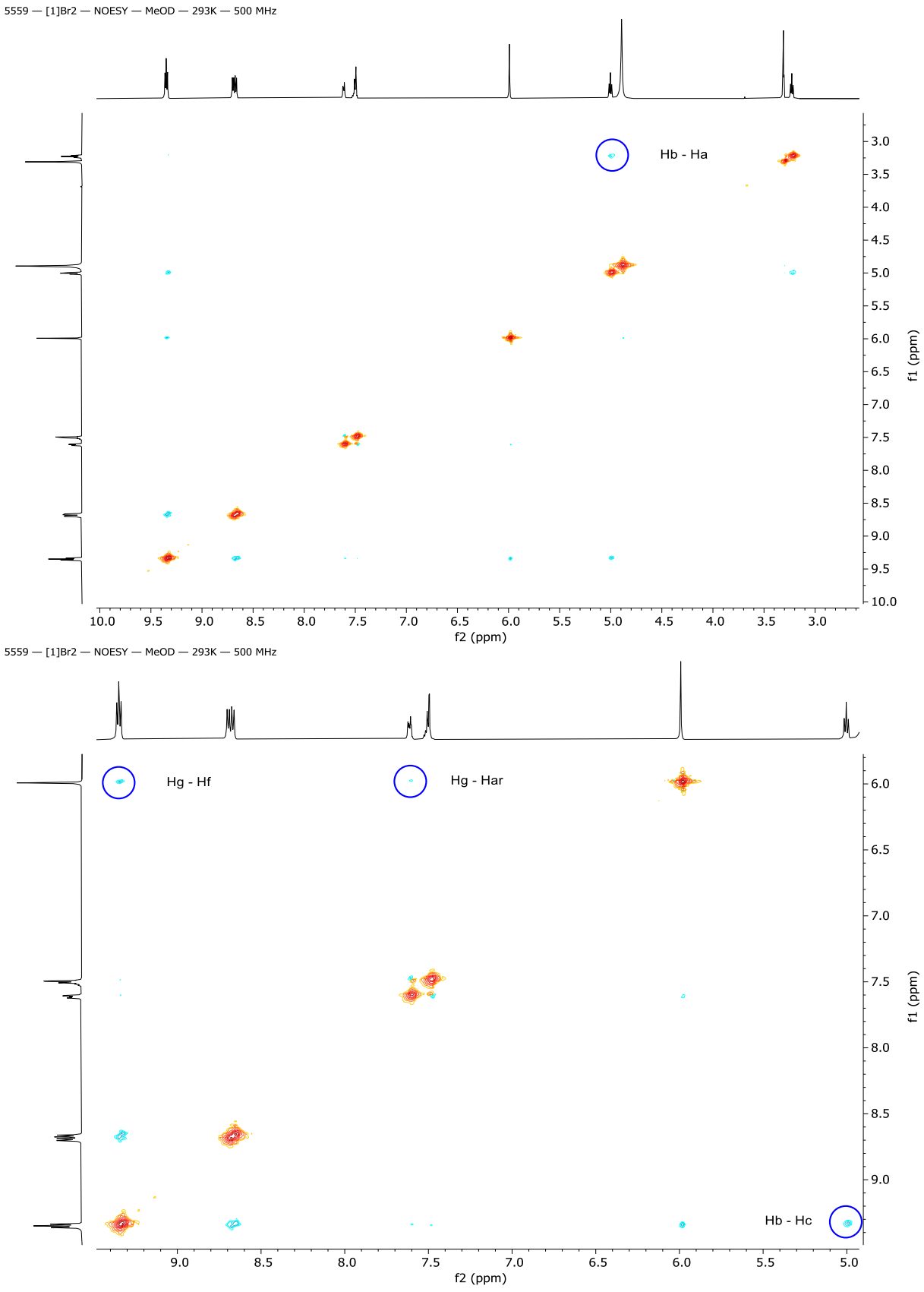


Figure S4. ^{1}H-^{1}H NOESY NMR spectrum of compound [**1**][Br]$_2$ (293 K, MeOD, 500 MHz).

b. ESI Q-TOF Mass Spectrometry.

Molecular ion: [**1**-H]$^+$ C20H19N2O2$^+$ m/z: calcd. 319.14410; exp. 319.14327; error: 2.6 ppm

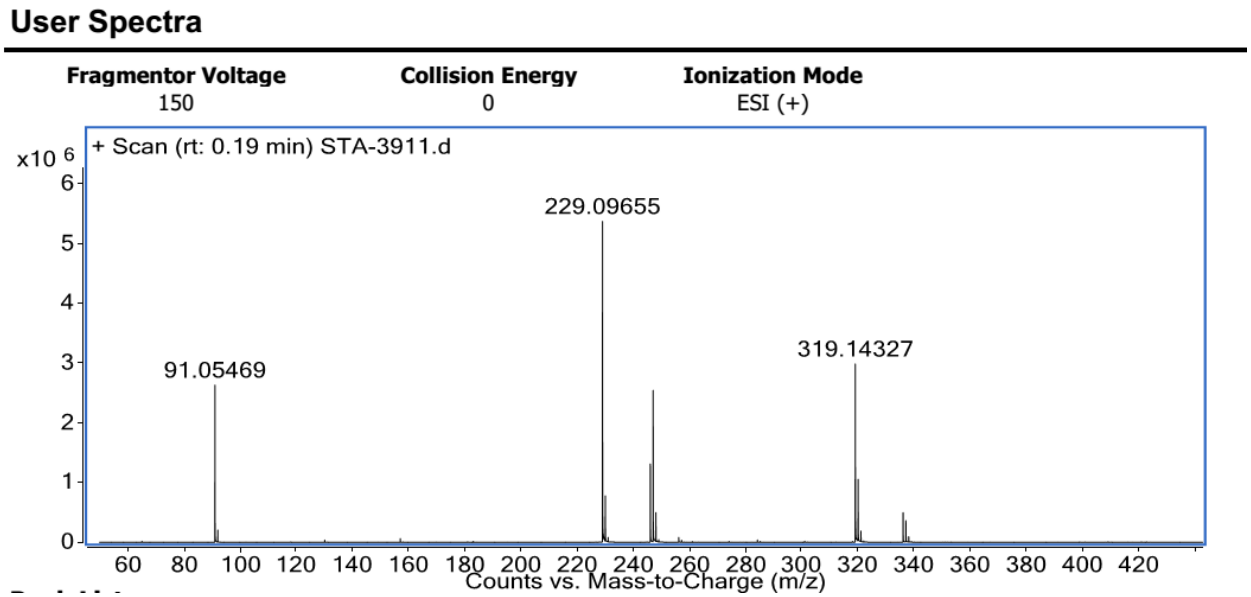
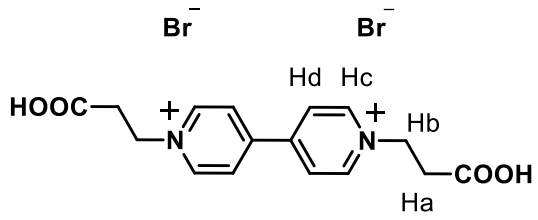
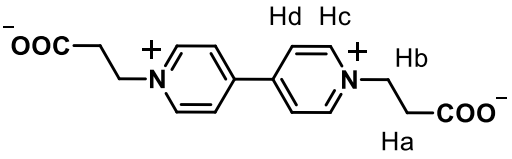


Figure S5. ESI Q-TOF Mass spectra of compound [**1**-H]$^+$.

3. Symmetric viologen compounds [**2**]Br_2 and [**3**].



[**2**][Br]$_2$



[**3**]

Compound [**2**][Br]$_2$ was formerly described.[4] 156 mg (1.0 mmol) of bipyridine was mixed with 3-bromopropionic acid (319 mg, 2.1 mmol) in 10 mL of acetonitrile. The mixture was stirred and heated at reflux temperature for 24 h. A yellowish precipitate was filtered off and washed with cold acetonitrile. Recrystallization from hot ethanol yielded 276 mg of yellow crystals of compound [**2**][Br]$_2$ (60%).

Compound [**3**] was generated *in situ* by the addition of 4 equivalents of diisopropylethylamine (DIEA) to a solution containing compound [**2**][Br]$_2$. NMR spectra contain the corresponding proton signals from DIEA.

NMR spectra from compounds [**2**][Br]$_2$ and [**3**] synthesized in this work are shown below.

Compound [**2**][Br]$_2$

^{1}H NMR (400 MHz, MeOD) δ 9.34 (d, *J* = 6.5 Hz, 4H, Hc), 8.67 (d, *J* = 6.5 Hz, 4H, Hd), 5.01 (t, *J* = 6.2 Hz, 4H, Hb), 3.23 (t, *J* = 6.2 Hz, 4H, Ha).
^{13}C NMR (100 MHz, MeOD) δ 173.05 (COOH), 151.59 (Cquat), 147.88 (Cc), 127.98 (Cd), 58.78 (Cb), 35.19 (Ca).

Molecular ion: [**2**-H]$^+$ C16H17N2O4$^+$ m/z: calcd. 301.11828; exp. 301.11799; error: 1.0 ppm

Compound [**3**]

^{1}H NMR (400 MHz, MeOD) δ 9.34 (d, *J* = 6.8 Hz, 4H, Hc), 8.67 (d, *J* = 6.8 Hz, 4H, Hd), 5.01 (t, *J* = 6.2 Hz, 4H, Hb), 3.23 (4H, Ha). 3.74 (DIEA-CH), 3.2 (DIEA- CH_2), 1.38 (DIEA-CH_3).
^{13}C NMR (100 MHz, MeOD) δ 173.05 (COO), 151.58 (Cquat), 147.87 (Cc), 127.98 (Cd), 58.83 (Cb), 35.29 (Ca). 13.19 – 17.31 – 18.75 (DIEA-CH_3), 43.85 (DIEA-CH_2), 55.89 (DIEA-CH).

a. 1D and 2D NMR spectra.

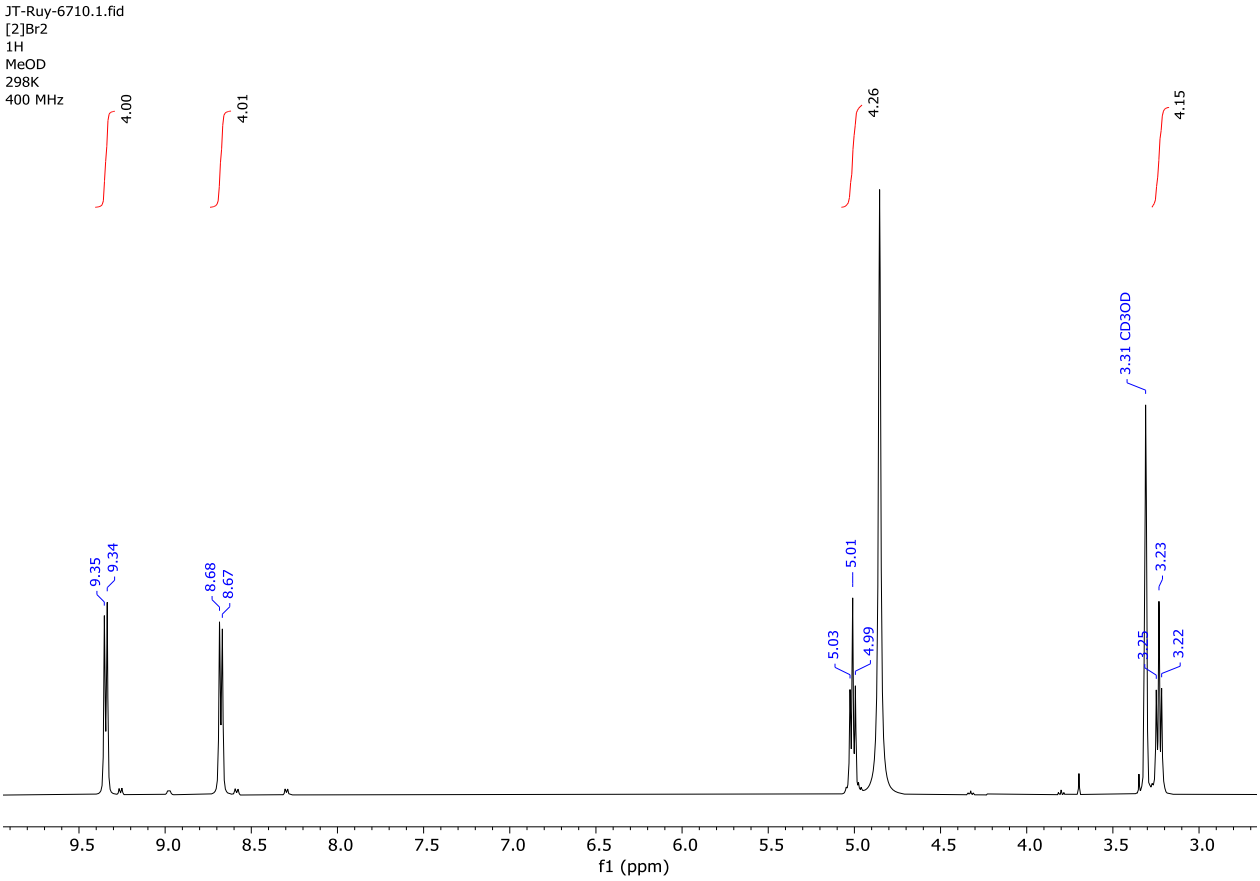
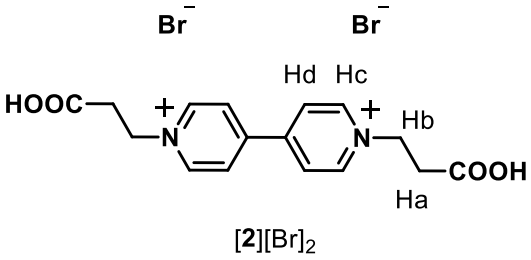


Figure S6. ^{1}H NMR spectrum of compound [**2**][Br]$_2$ (298 K, MeOD, 400 MHz, *H_2O).



[**2**][Br]$_2$

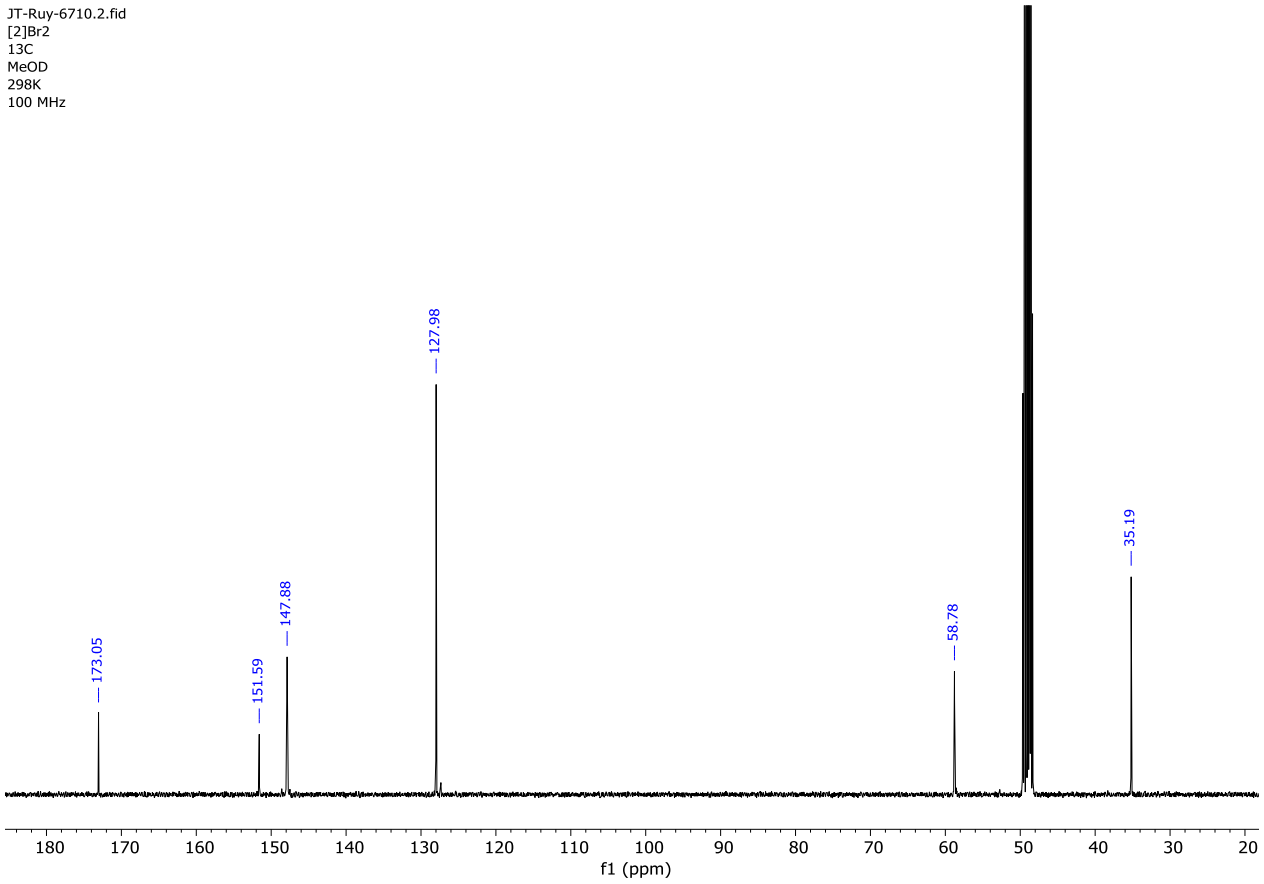
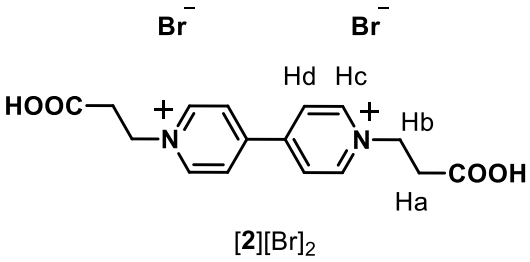


Figure S7. ^{13}C NMR spectrum of compound [**2**][Br]$_2$ (298 K, MeOD, 100 MHz).



[**2**][Br]$_2$

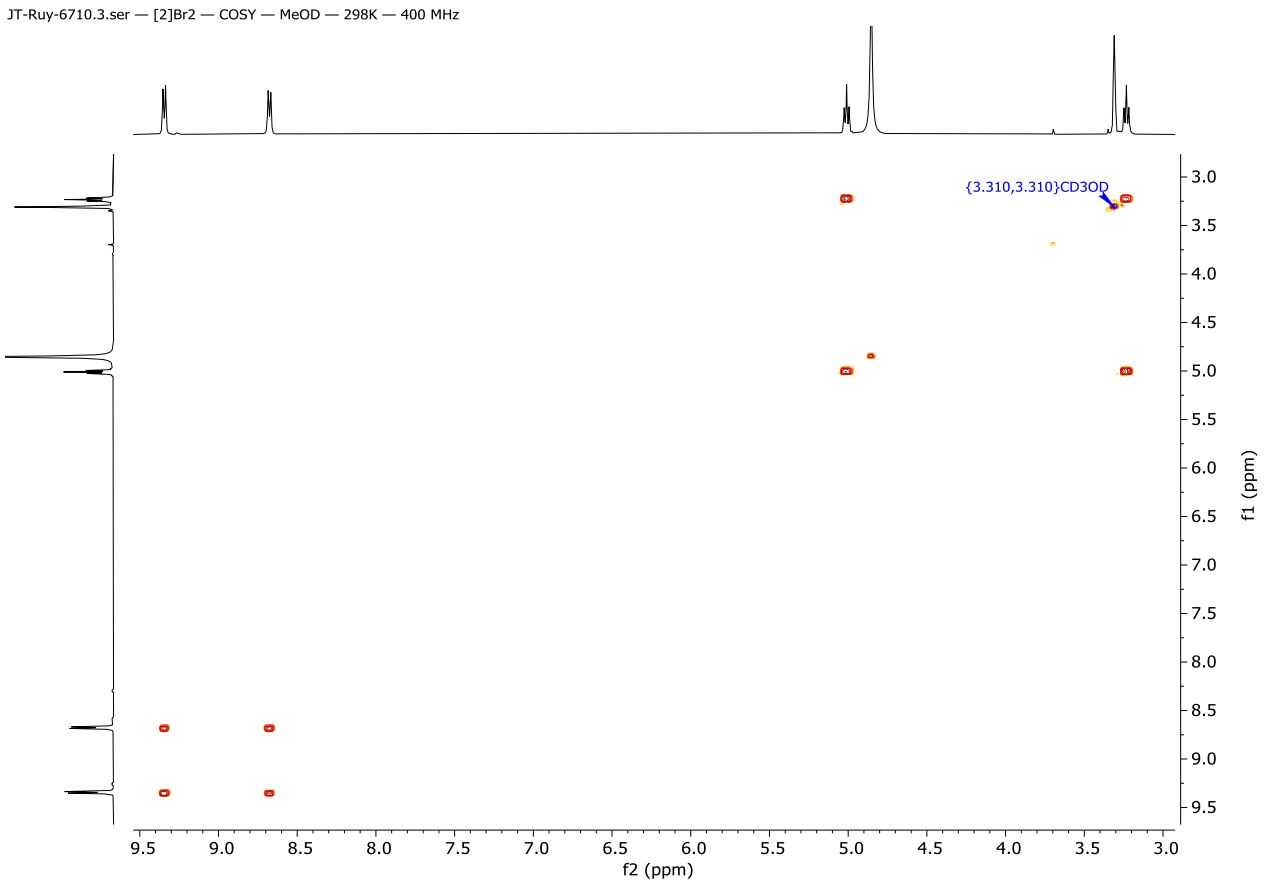
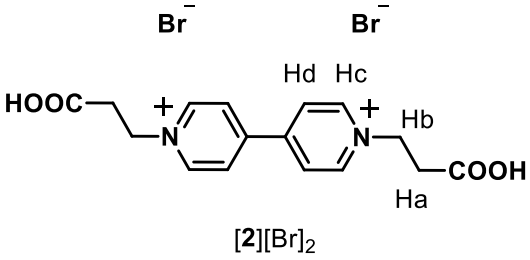


Figure S8. ^{1}H-^{1}H COSY NMR spectrum of compound [**2**][Br]$_2$ (298 K, MeOD, 400 MHz).



[**2**][Br]$_2$

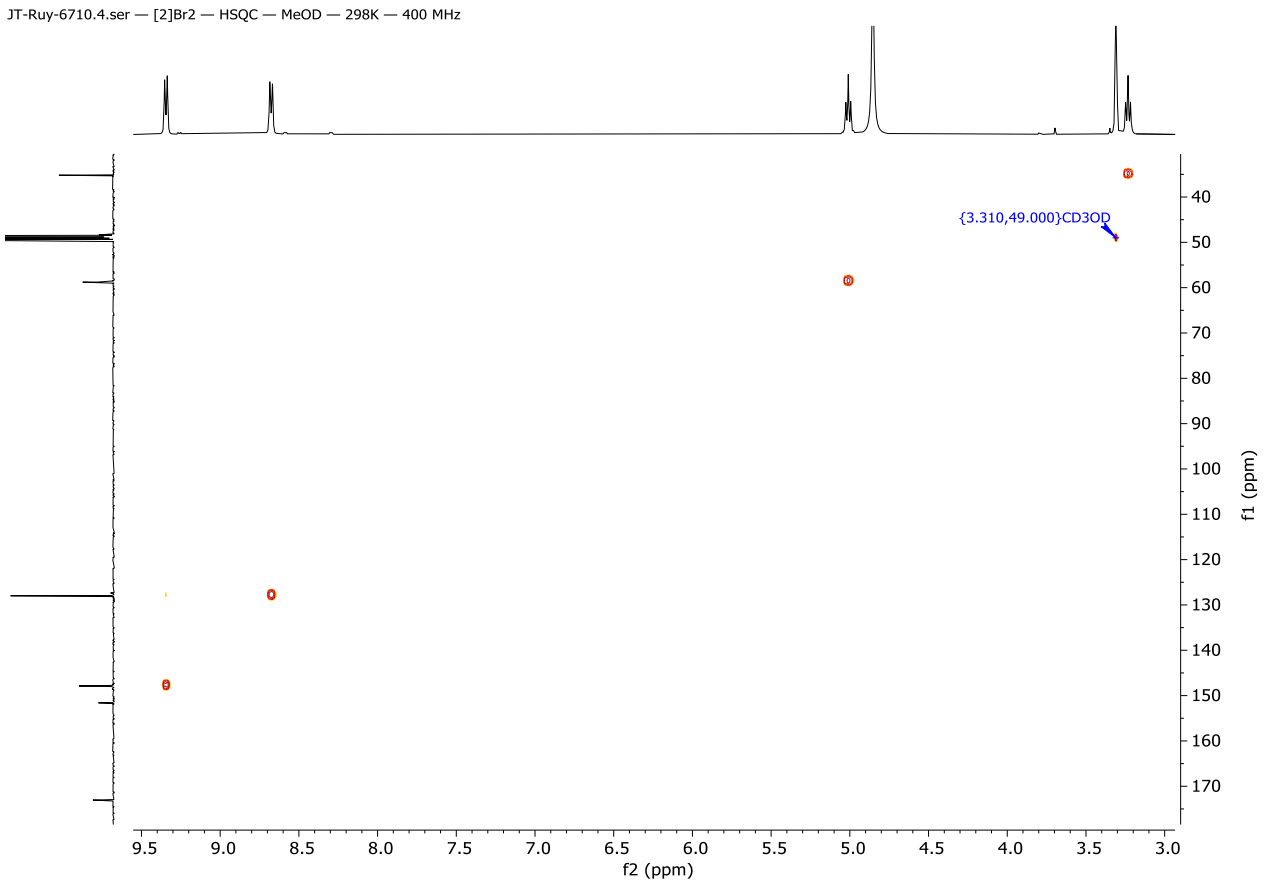
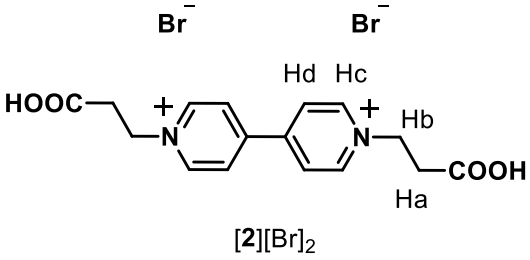


Figure S9. ^{1}H-^{13}C HSQC NMR spectrum of compound [**2**][Br]$_2$ (298 K, MeOD, 400 MHz).



[**2**][Br]$_2$

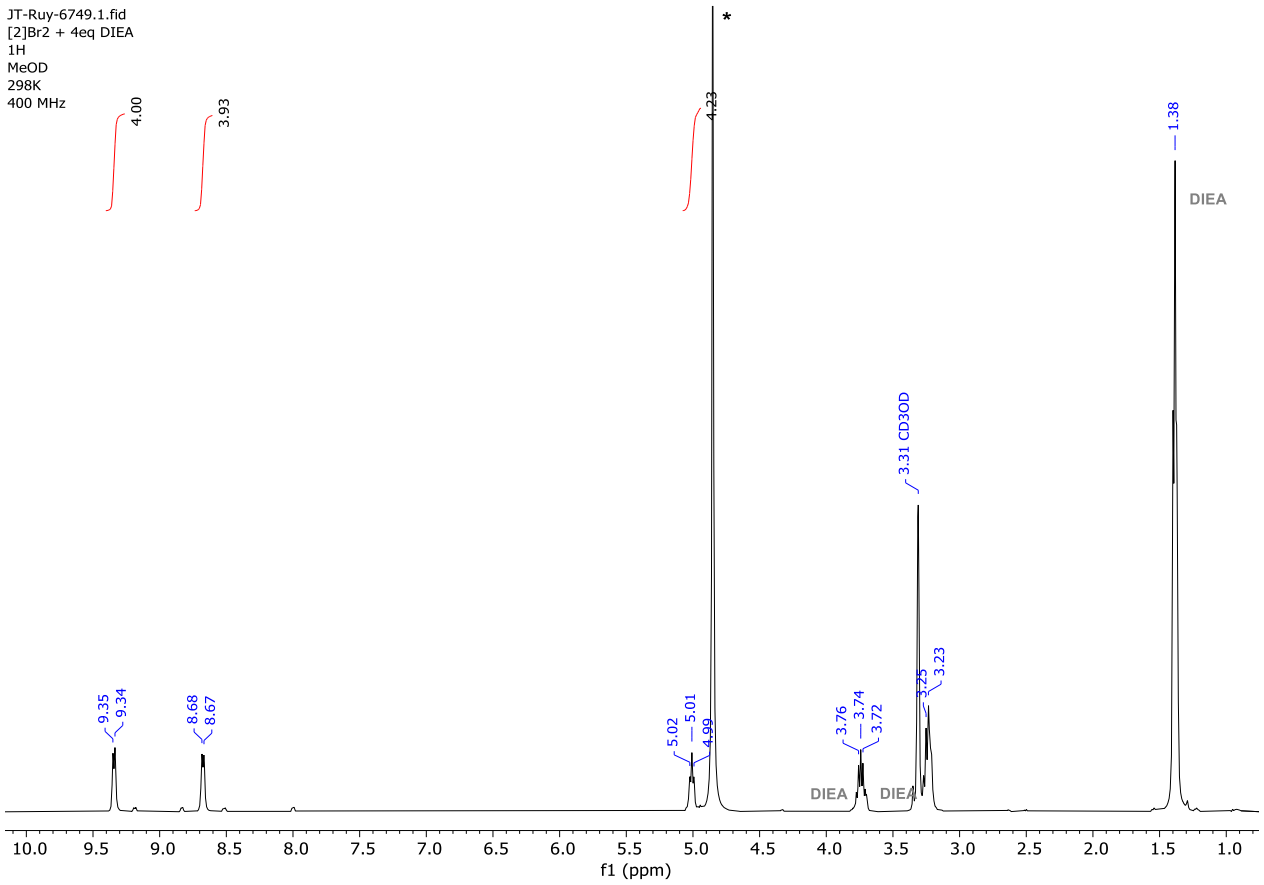
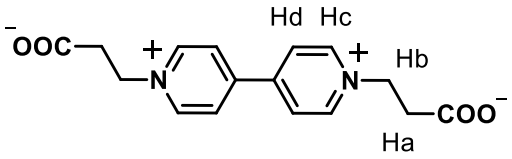


Figure S10. ^{1}H NMR spectrum of compound [**3**], prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution (298 K, MeOD, 400 MHz, *H_2O). DIEA proton signals are labeled in grey.



[**3**]

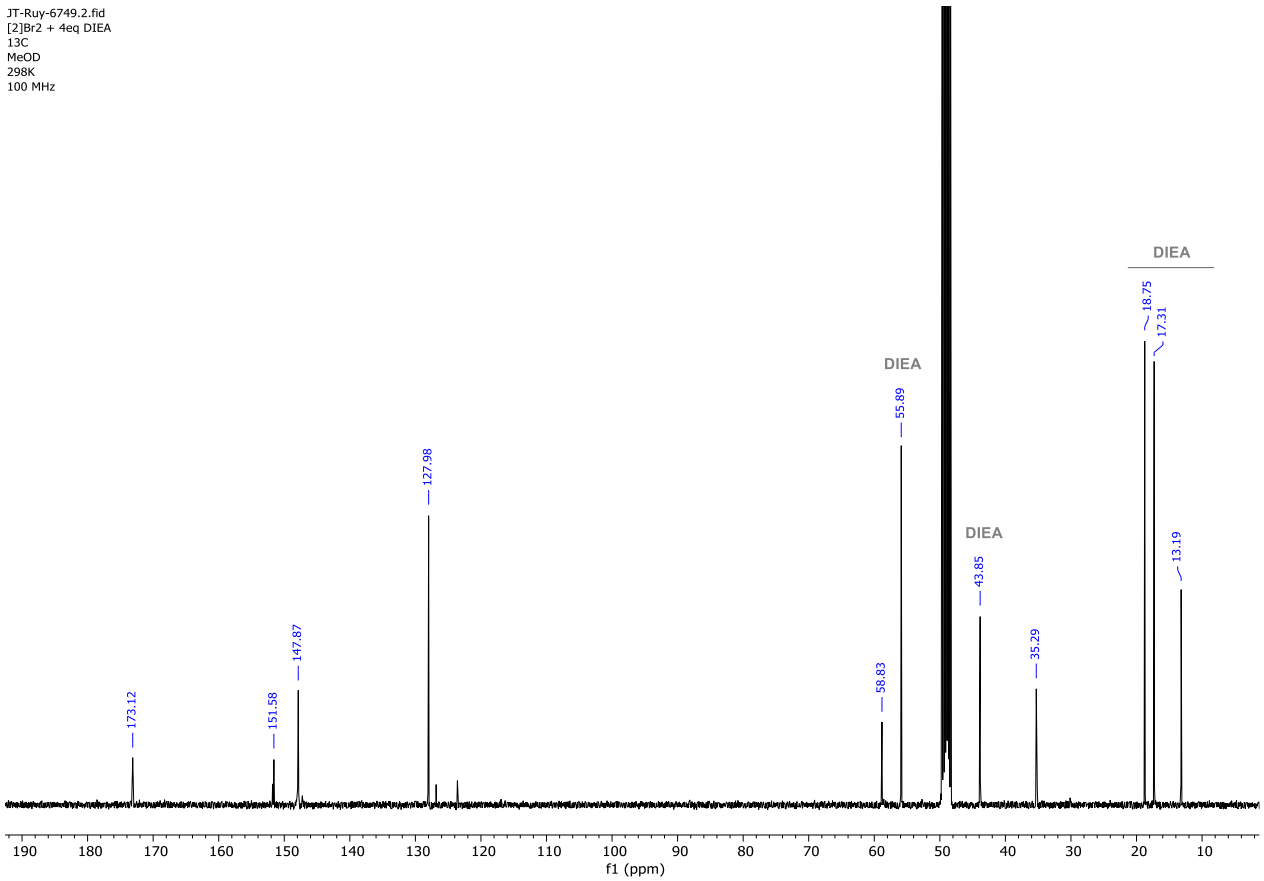
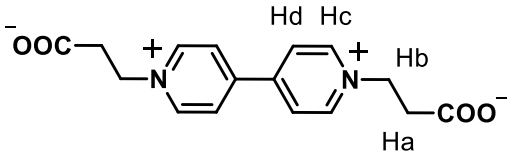


Figure S11. ^{13}C NMR spectrum of compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution (298 K, MeOD, 100 MHz). DIEA carbon signals are labeled in grey.



[**3**]

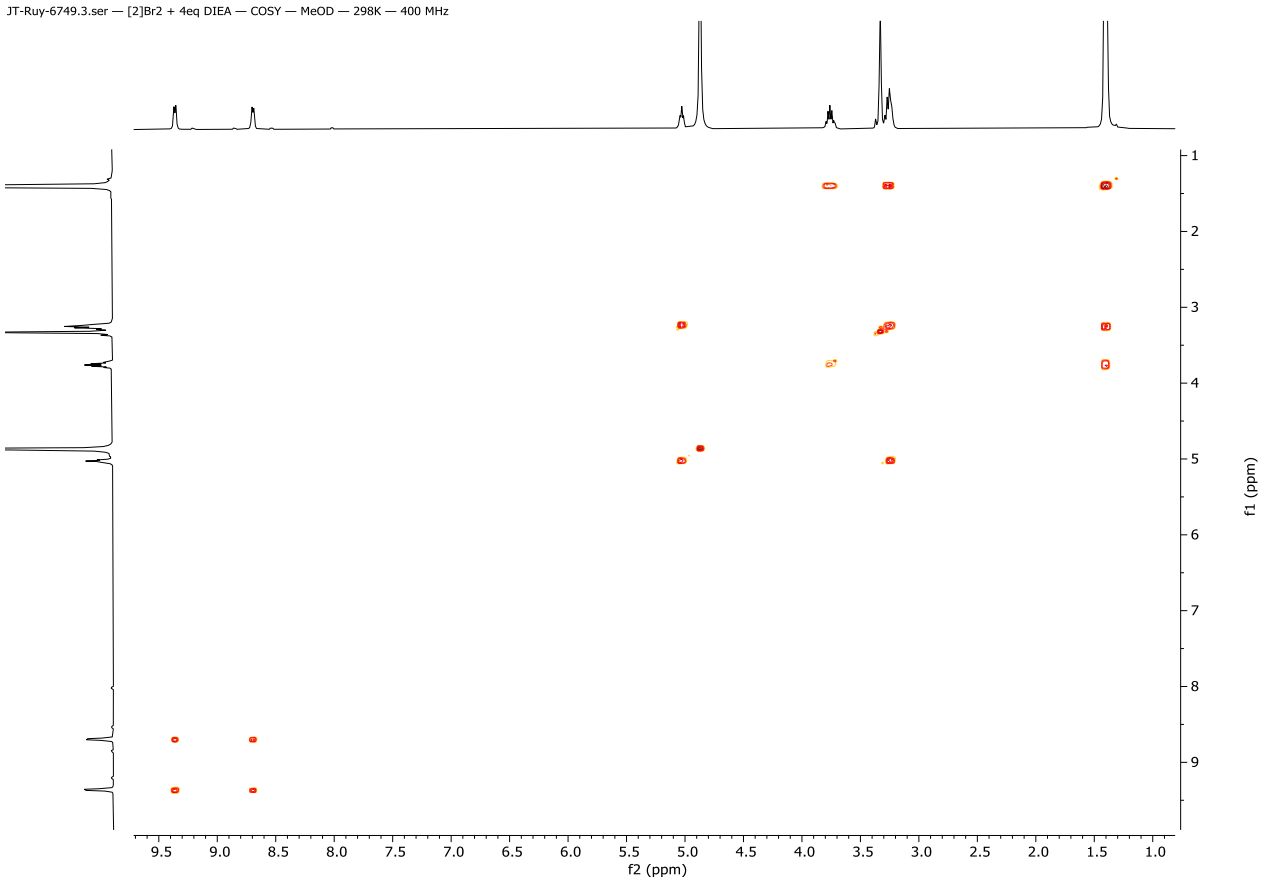
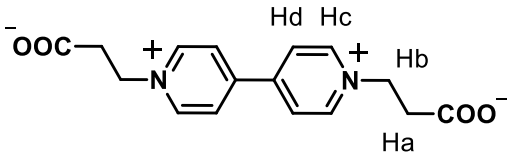


Figure S12. ^{1}H-^{1}H COSY NMR spectrum of compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution (298 K, MeOD, 400 MHz).



[**3**]

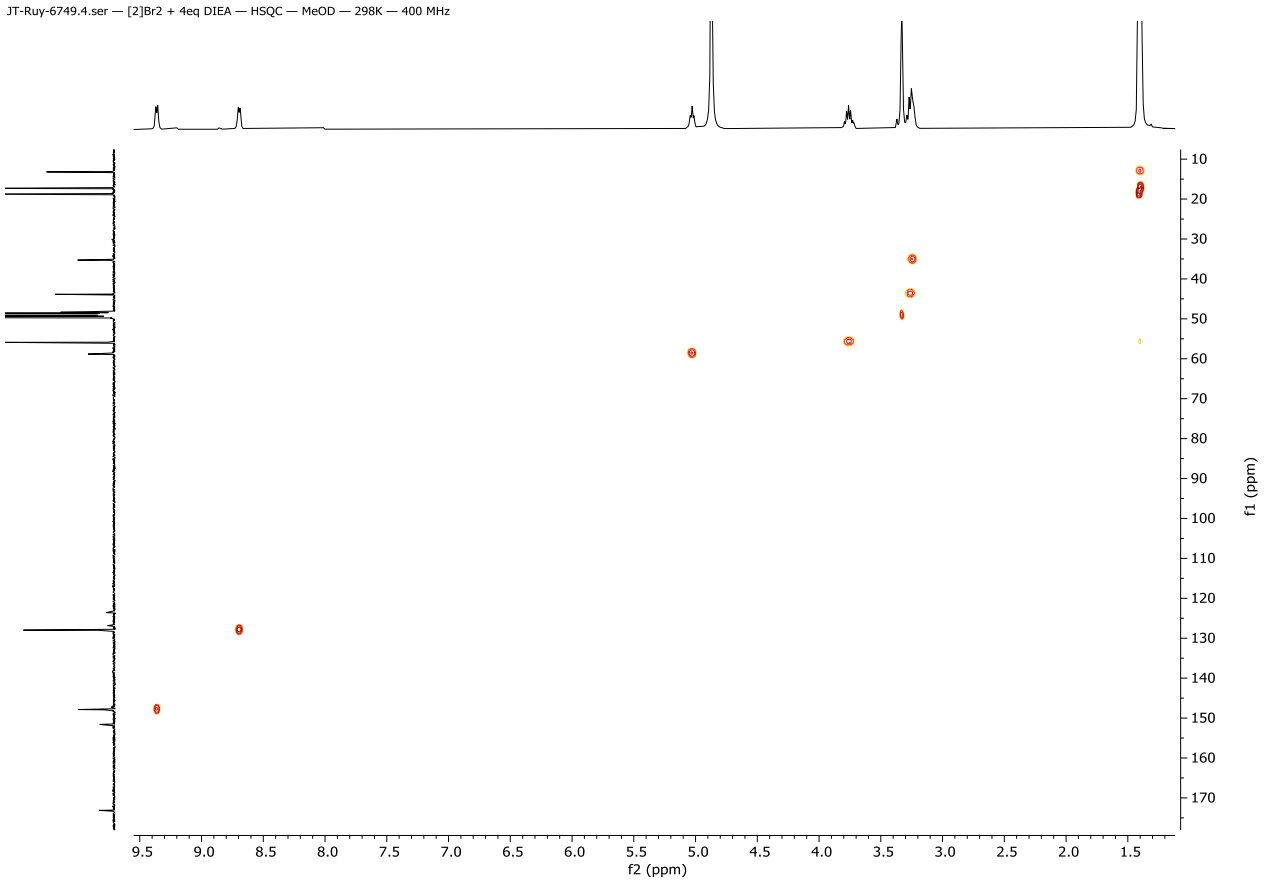
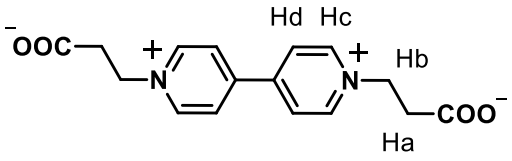


Figure S13. ^{1}H-^{13}C HSQC NMR spectrum of compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution (298 K, MeOD, 400 MHz).



[**3**]

b. ESI Q-TOF Mass Spectrometry**.**

Molecular ion: [**2**-H]$^+$ C16H17N2O4$^+$ m/z: calcd. 301.11828; exp. 301.11799; error: 1.0 ppm

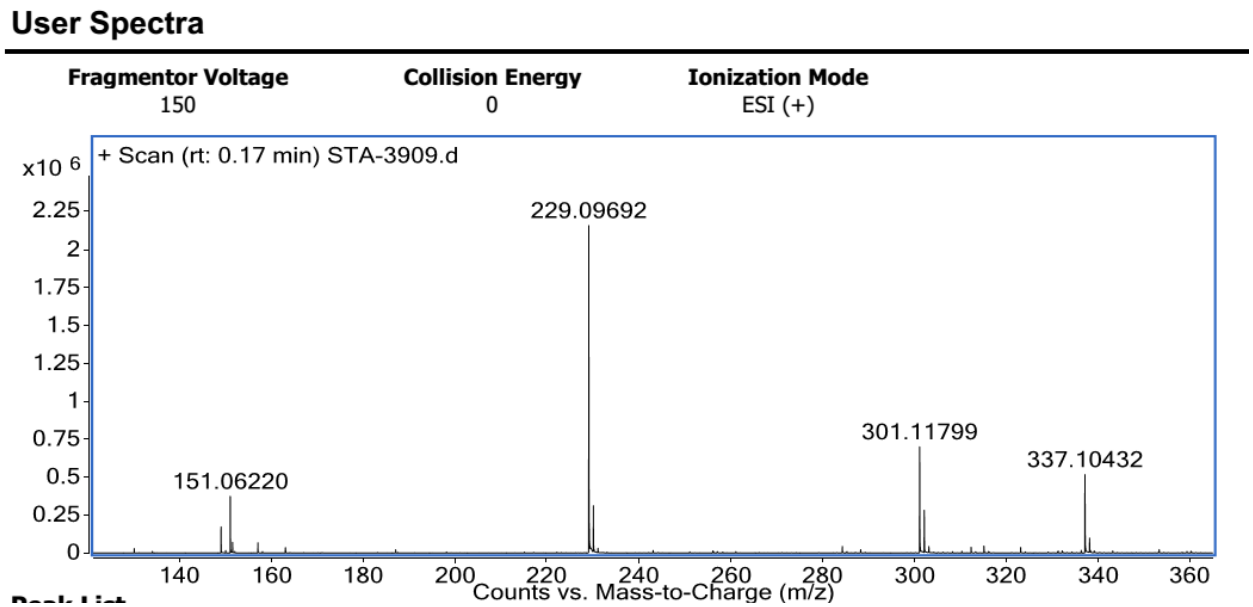


Figure S14. ESI Q-TOF Mass spectra of compound [**2**-H]$^+$.

4. [2]*pseudo*-rotaxanes [**1**⊂**DSDB24C8**], [**2**⊂**DSDB24C8**], and [**3**⊂**DSDB24C8**]$^{2-}$.

a. Stacked ^{1}H NMR spectra.

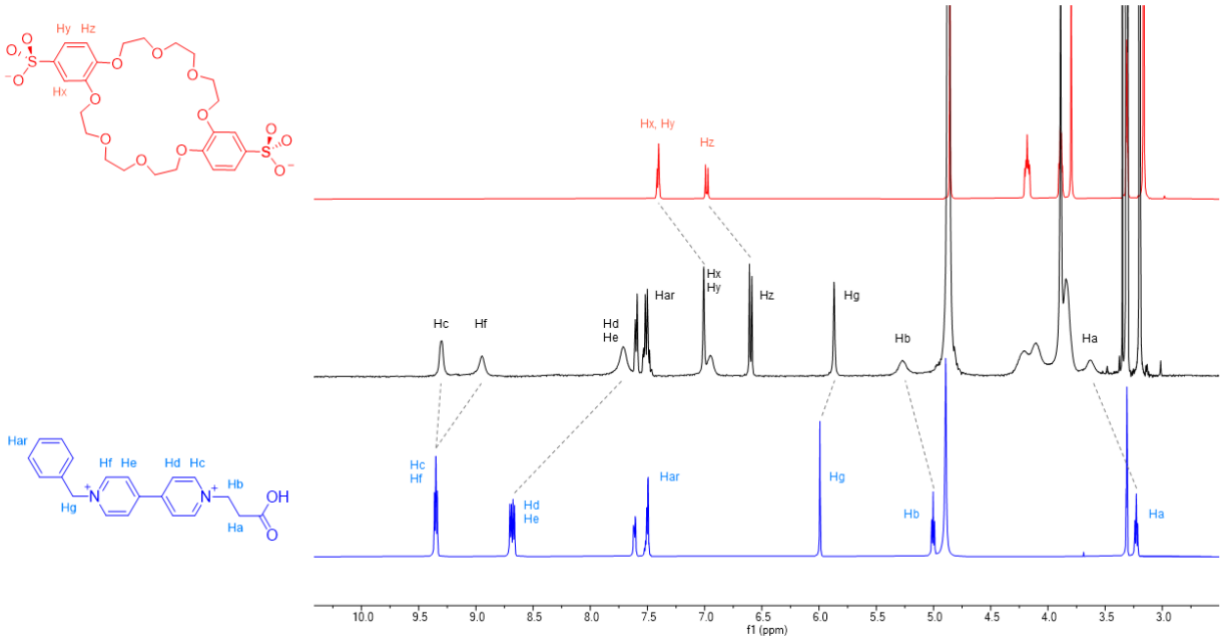


Figure S15. ^{1}H NMR stacked spectra (293 K, MeOD, 500 MHz) of free compound [**DSDB24C8**]$^{2-}$ (top), an equimolar (5 mM) mixture of [**1**]$^{2+}$ and [**DSDB24C8**]$^{2-}$ (middle), and free compound [**1**]$^{2+}$ (bottom).

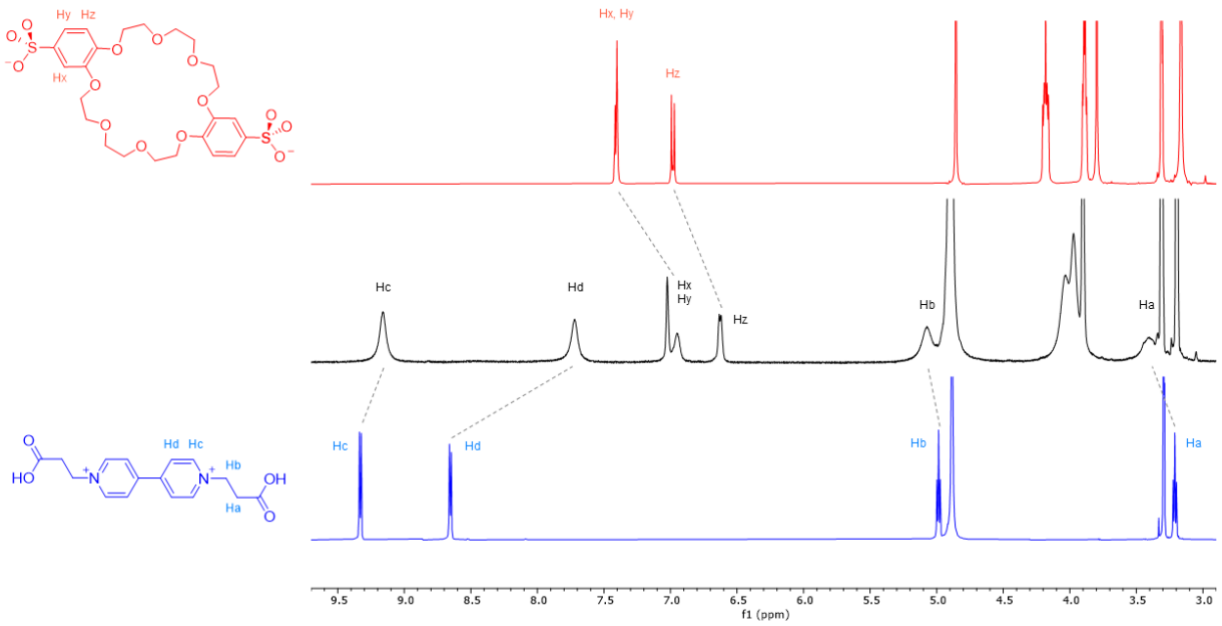


Figure S16. ^{1}H NMR stacked spectra (293 K, MeOD, 500 MHz) of free compound [**DSDB24C8**]$^{2-}$ (top), an equimolar (5 mM) mixture of [**2**]$^{2+}$ and [**DSDB24C8**]$^{2-}$ (middle), and free compound [**2**]$^{2+}$ (bottom).

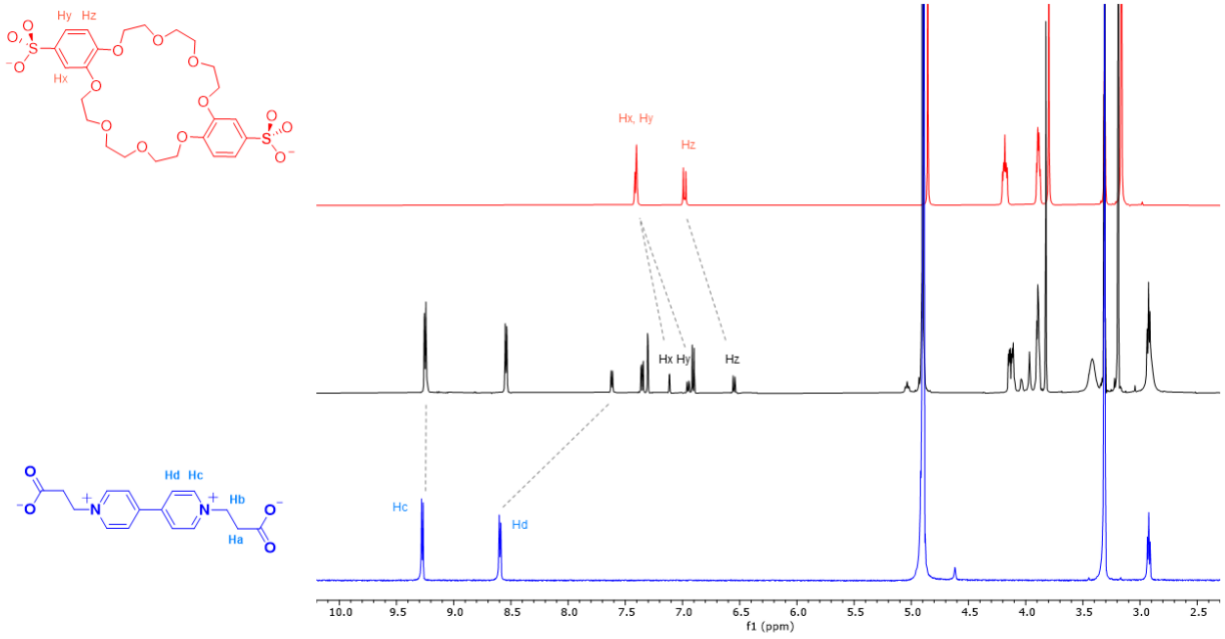


Figure S17. ^{1}H NMR stacked spectra (293 K, MeOD, 500 MHz) of free compound [**DSDB24C8**]$^{2-}$ (top), an equimolar (5 mM) mixture of [**3**] and [**DSDB24C8**]$^{2-}$ (middle), and free compound [**3**] (bottom).

b. ^{1}H NMR Variable Temperature experiments.

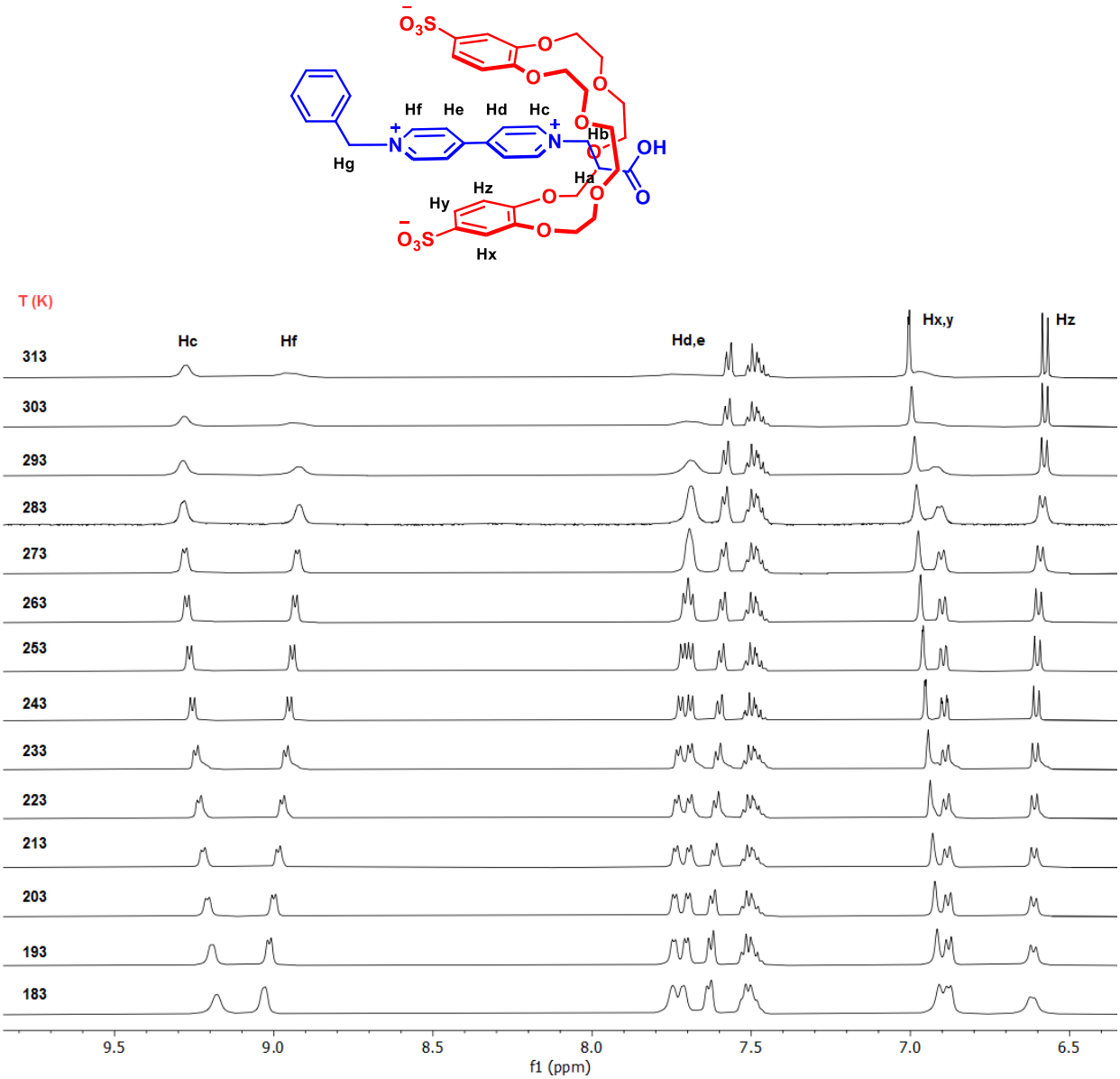


Figure S18. Partial ^{1}H NMR-VT stacked spectra from 313 to 183 K (500 MHz, 5 mM, MeOD) for a 1:1 mixture of $[NMe_4]_2$[**DSDB24C8**] and [**1**][Br]$_2$.

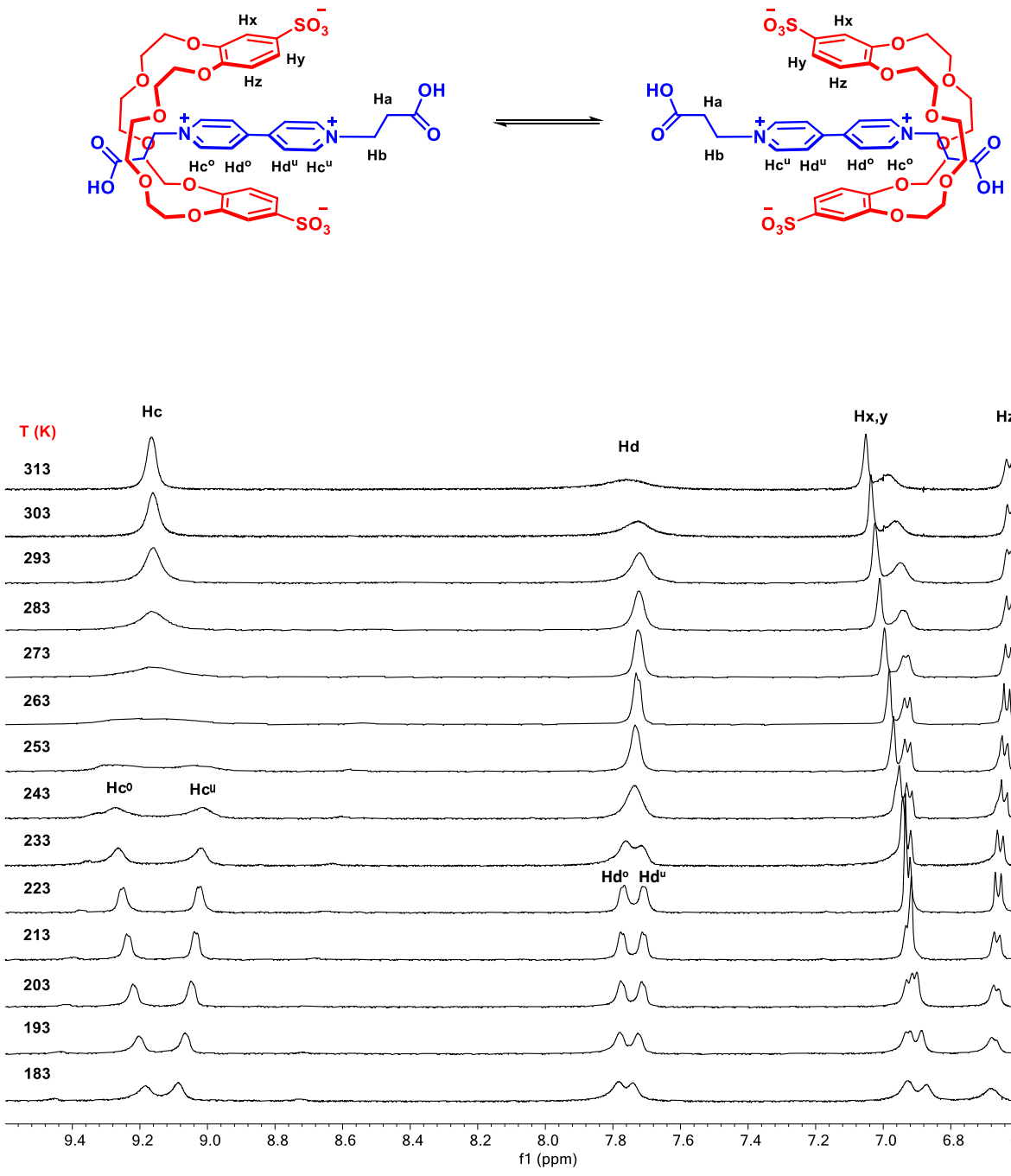


Figure S19. Partial ^{1}H NMR-VT stacked spectra from 313 to 183 K (500 MHz, 5 mM, MeOD) for a 1:1 mixture of $[NMe_4]_2$[**DSDB24C8**] and [**2**]$[Br]_2$.

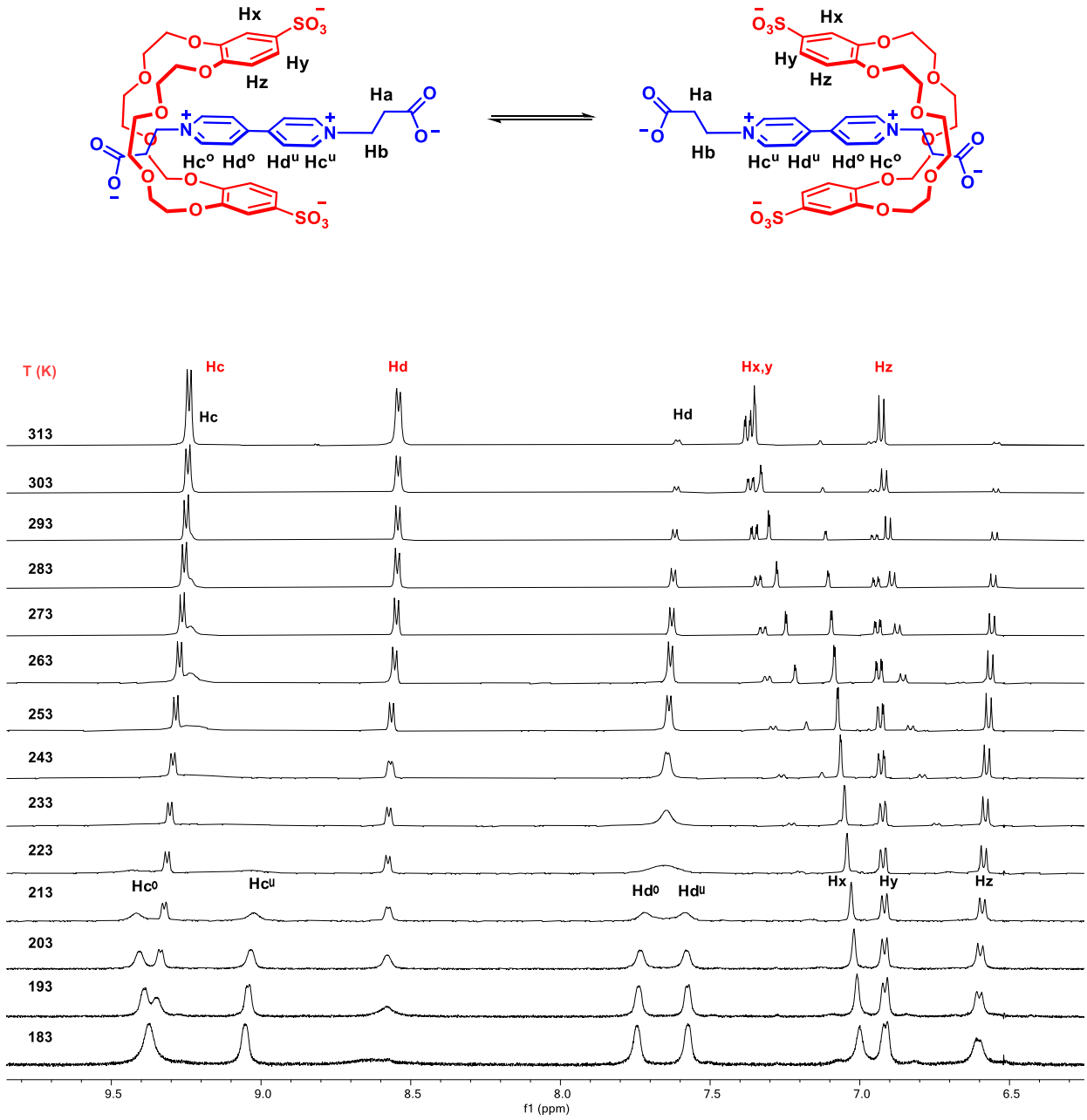


Figure S20. Partial ^{1}H NMR-VT stacked spectra from 313 to 183 K (500 MHz, 5 mM, MeOD) for an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**], prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution. Resonances for uncomplexed host and guest are shown in red, and those for complex in black.

c. ESI Q-TOF Mass Spectrometry of [**1**⊂**DSDB24C8**] and [**2**⊂**DSDB24C8**].

[**1**⊂**DSDB24C8**]

Molecular ion: [**1**⊂ **DSDB24C8**+H]$^+$ C44H51N2O16S2$^+$ m/z: calcd. 927.26745; exp. 927.26758; error: 0.1 ppm

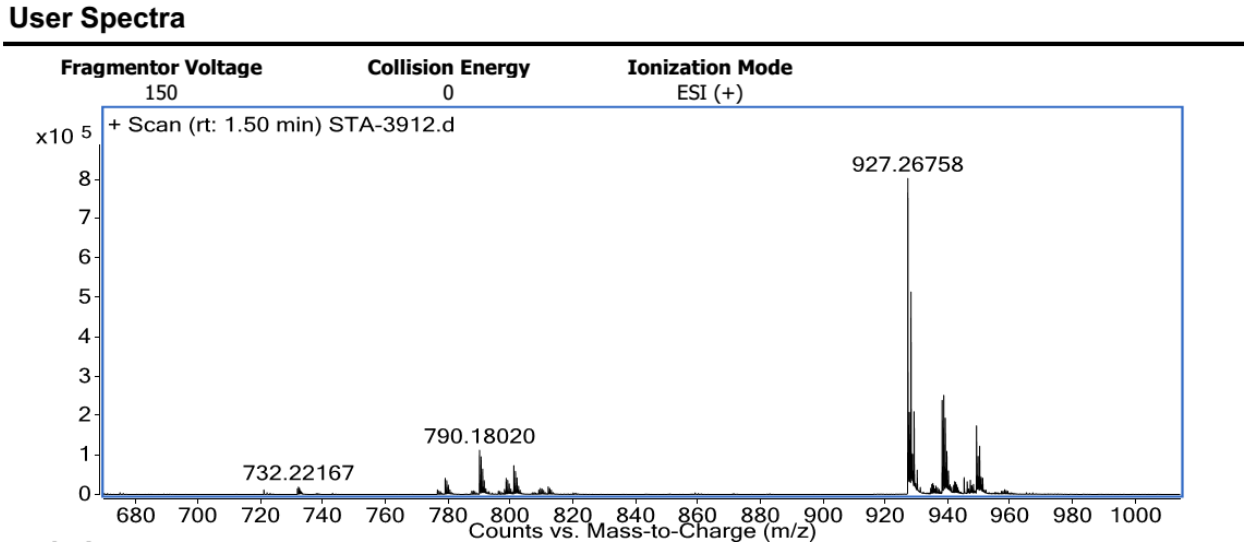


Figure S21. ESI Q-TOF Mass spectra of compound [**1**⊂ **DSDB24C8**+H]$^+$.

[**2**⊂**DSDB24C8**]

Molecular ion: [**2**⊂ **DSDB24C8**+H]$^+$ C40H49N2O18S2$^+$ m/z: calcd. 909.24163; exp. 909.24109; error: 0.6 ppm

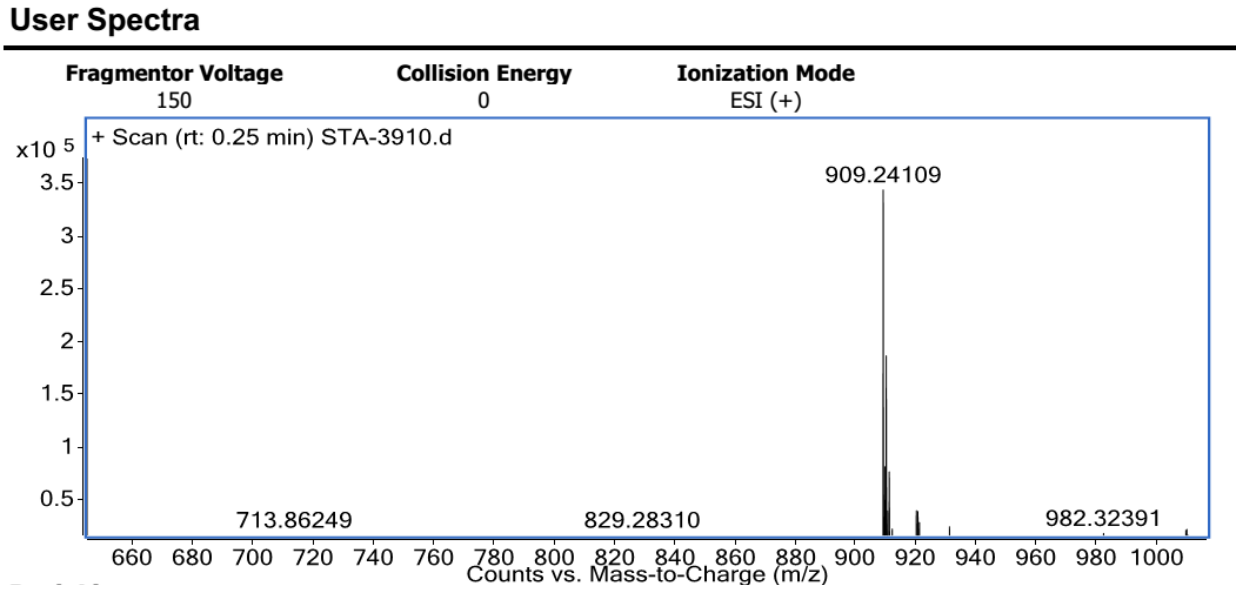


Figure S22. ESI Q-TOFMass spectra of compound [**2**⊂ **DSDB24C8**+H]$^+$.

d. Crystallographic information of [**1**⊂**DSDB24C8**].

Single crystals were grown by slow evaporation of saturated aqueous solutions of compounds [**1**][Br]$_2$ and [NMe$_4$]$_2$[**DSDB24C8**]. X-ray diffraction data were collected at 171 K on a Bruker D8 VENTURE diffractometer fitted with a CPAD-based detector using MoKα radiation (λ=0.71073 Å). The structure was solved by direct methods using SHELXL-2019. Least-squares refinement based on F^2 was carried out by the full-matrix method of SHELXL-2019.[5] The crystal was refined as a 2-component twin. Disorder in a phenyl ring, a sulfonate group, and fragments of the ethylene glycol chains were modeled in two different positions with 66:33 occupancy. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and refined with an isotropic fixed thermal parameter by using a riding model. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for Crystallography.[6] Molecular structure drawings were generated by using CrystalMaker® for Windows.[7]

CCDC- 2278846 [**1**][Br]$_2$ contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. X-ray crystallographic data collection and refinement statistics.

Identification code	jtk130 (compound [**1**][Br]$_2$)	
Empirical formula	C_{44} H_{55} N_2 O_{19} S_2	
Formula weight	980.02	
Temperature	171(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P* -1	
Unit cell dimensions	a = 10.6348(3) Å b = 14.9932(5) Å c = 15.9123(4) Å	α = 83.694(2)° β = 73.596(2)° γ = 73.516(2)°
Volume	2332.68(12) Å^3	
Z	2	
Density (calculated)	1.395 mg/m^3	
Absorption coefficient	0.194 mm^{-1}	
F(000)	1034	
Crystal size	0.35 × 0.23 × 0.12 mm^3	
2Θ range for data collection	2.983 to 27.584°	
Index ranges	-13 ≤ *h* ≤ 13, -19≤ *k* ≤ 19, -20 ≤ *l* ≤ 20	
Reflections collected	10559	
Refinement method	Full-matrix least-squares on F^2	
Goodness-of-fit on F^2	1.047	
*R*1	0.1096	
w*R*2	0.2926	

5. Determination of association constants and standard free energy for [2]pseudorotaxanes.

Association constants for compounds [**1**⊂**DSDB24C8**] and [**2**⊂**DSDB24C8**] were obtained by UV-vis titration in methanol. A thermostated (293 K) solution of guest ([**1**]$^{2+}$ 0.2 mM ; [**2**]$^{2+}$ 0.6 mM) was titrated with a concentrated [**DSDB24C8**]$^{2-}$ solution (1.3 and 6.0 mM respectevely) by subsequent addition of aliquots until saturation is reached. The working absorbance was recorded at 380 nm. Dilution correction was applied and fitting analysis was performed using OpenDataFit website Supramolecular.org[8]

Association constant for compound [**3**⊂**DSDB24C8**]$^{2-}$ was measured using the single point method based on ^{1}H NMR spectra. Error is estimated to be 10 % or less.

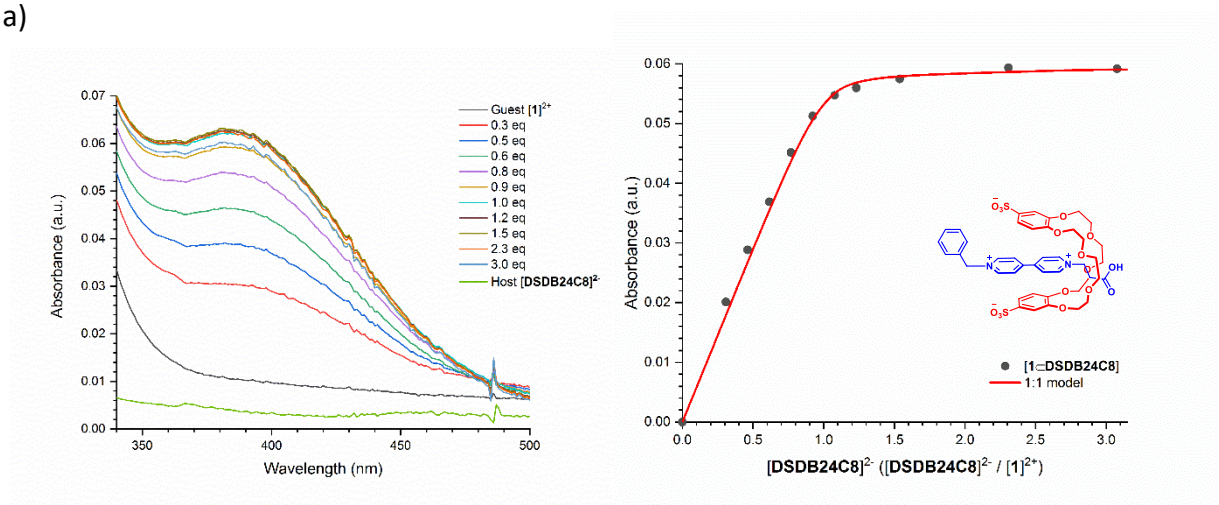
Derived standard free energy was obtained by $\Delta G^{o} = -RTlnK_{a}$.

Table S2 summarizes these thermodynamic parameters at 293 K.

Table S2. Association constants and derived standard free energy for [2]pseudorotaxanes.

	[**1**⊂**DSDB24C8**]	[**2**⊂**DSDB24C8**]	[**3**⊂**DSDB24C8**]$^{2-}$
K_a (M^{-1}) @ 293 K	8.9(0.9) × 10^5	7.2(0.7) × 10^5	8.1(0.8) × 10^1
ΔG^o (kJmol^{-1}) @ 293 K	-33.4(0.3)	-32.9(0.3)	-10.7(0.1)

a)



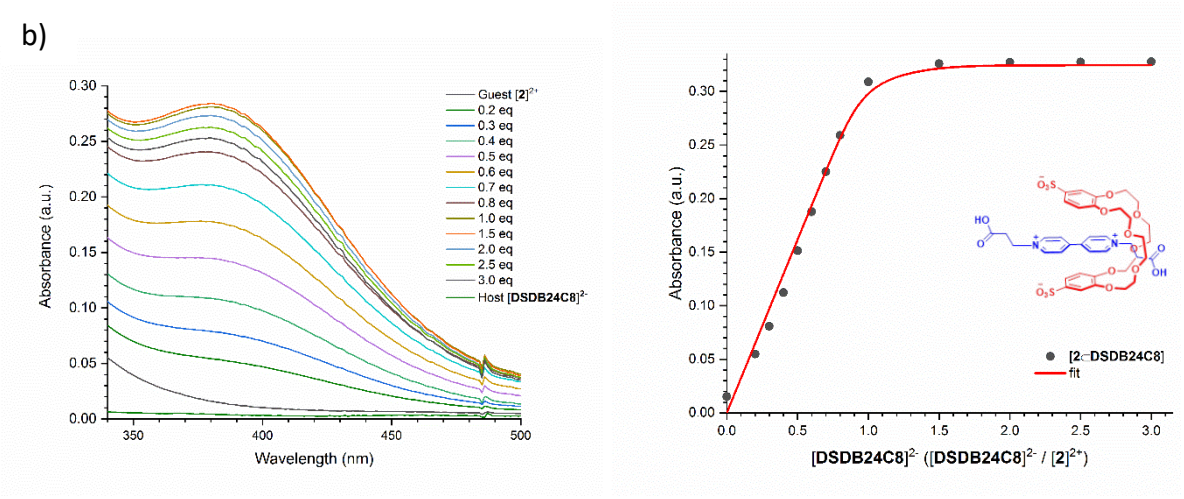


Figure S23. Absorbance changes at 380 nm as a function of the concentration of [**DSDB24C8**]$^{2-}$ for the titrations of guests: a) [**1**]$^{2+}$ and b) [**2**]$^{2+}$ in methanol at 293 K.

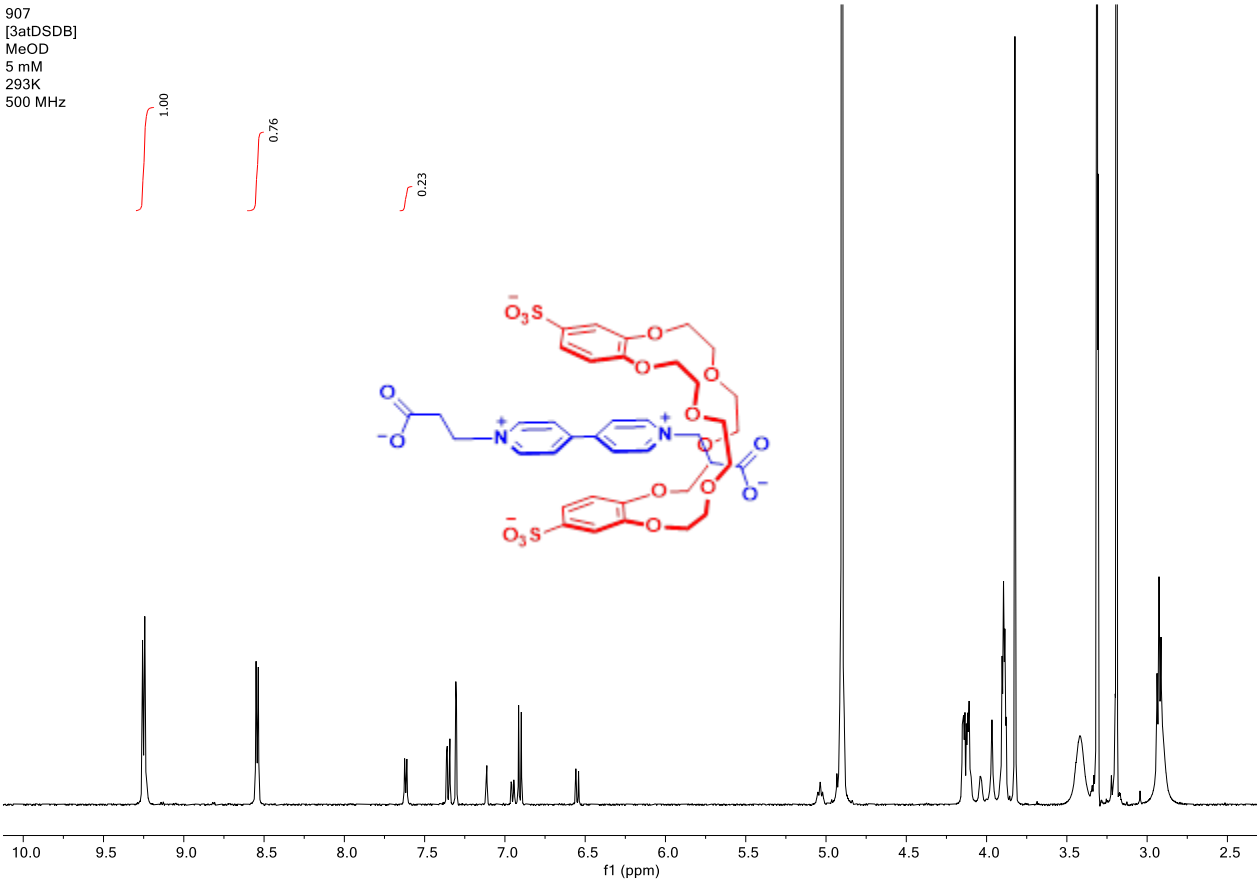


Figure S24. ^{1}H NMR spectrum (293 K, MeOD, 500 MHz, 5 mM)) for an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**], prepared in situ by addition of four equivalents of DIEA to the solution.

6. Determination of rate constants for threading process by ROESY NMR spectroscopy.

EXSY measurements were carried out with ROESY pulse sequence. The k values, which represent rate constants, were determined by using the following equations:

$$G_{free} + H_{free} \underset{k_{off}}{\overset{k_{on}}{\rightleftharpoons}} C$$

$$K_a = \frac{k_{on}}{k_{off}}$$

An exchange involving a bimolecular event (2nd order rate constant) cannot be analyzed directly however, from the perspective of the observed nucleus, the system is still just in two site exchange between free and bound states.

$$G_{free} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$$

$$k = k_1 + k_{-1}$$
$$k = k_{on}[H_{free}] + k_{off}$$

$$k = \left(\frac{1}{\tau_{mix}}\right) ln\left(\frac{\gamma + 1}{\gamma - 1}\right)$$

Where τ_{mix} represents the mixing time and γ is defined by the following equation:

$$\gamma = \frac{4X_A X_B (I_{AA} + I_{BB})}{(I_{AB} + I_{BA}) - (X_A - X_B)^2}$$

Where X_A and X_B are the mole fraction of free and complex species, respectively, I_{AB} and I_{BA} are the intensities of the cross peaks between the free and complex peaks, respectively, and I_{AA} and I_{BB} are the intensities of the diagonal signals.

The exchange process free energy of activation was obtained from the Eyring equation:

$$\Delta G^{\ddagger}_{on} = -RTln\frac{k_{on}h}{k_B T}$$

Where k_B is the Boltzmann constant, T is the absolute temperature, h is Plank's constant, and $\Delta G^{\neq}_{on}$ is the free energy of activation.

Table S3. Kinetic parameters for [2]pseudorotaxanes at 293 K.

Compound	k_{on} ($M^{-1}s^{-1}$)	k_{off} (s^{-1})	$t_{1/2}$ (s)	$\Delta G^{\ddagger}_{on}$ ($kJmol^{-1}$)	$\Delta G^{\ddagger}_{off}$ ($kJmol^{-1}$)
[**2**⊂**DSDB24C8**]	2.5×10^{6}	3.5	0.2	36.4	69.3
[**3**⊂**DSDB24C8**]$^{2-}$	5.1×10^{1}	6.2×10^{-1}	1.1	62.2	72.9

a. ROESY of [**2**⊂ **DSDB24C8**].

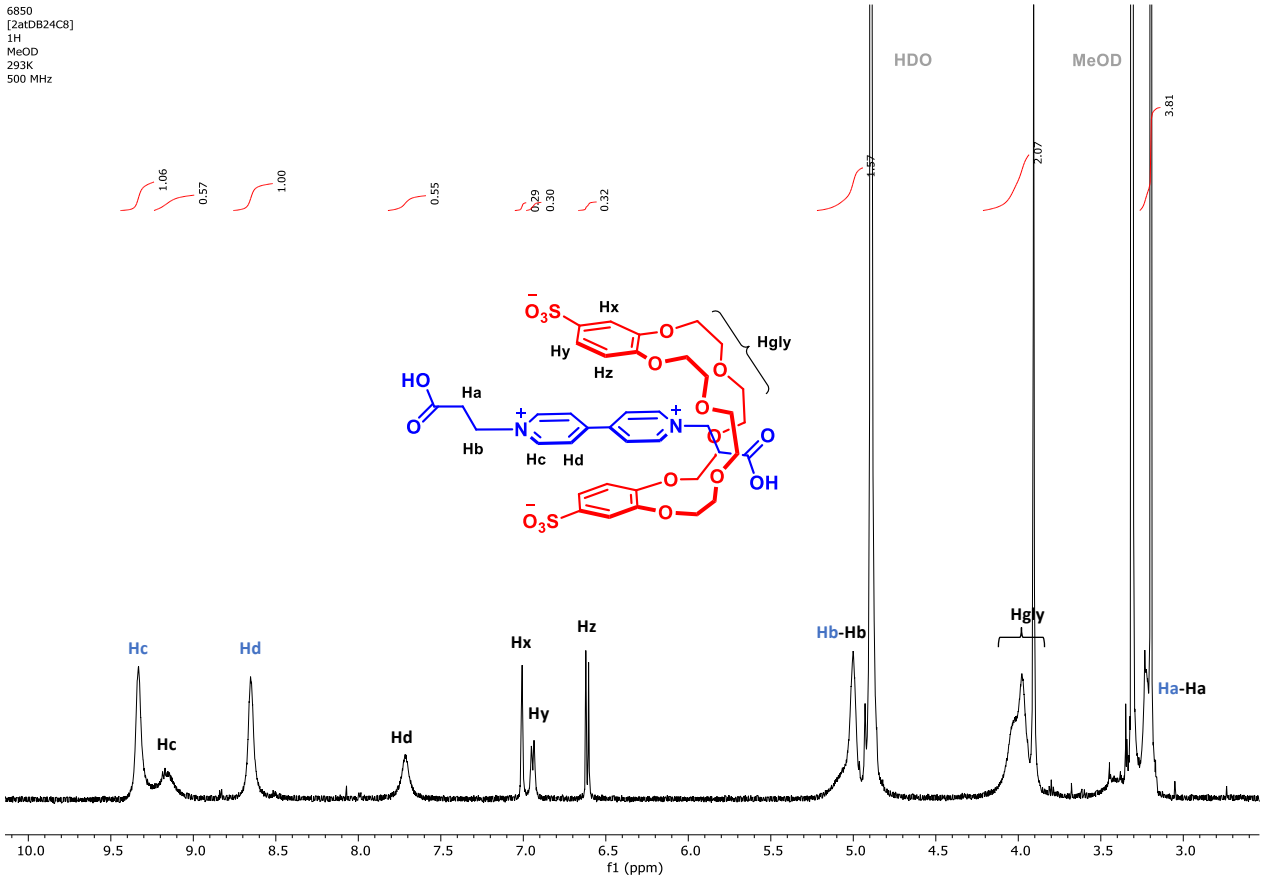


Figure S25 ^{1}H NMR spectrum (293 K, MeOD, 500 MHz) of a mixture of [**2**]$^{2+}$ (5 mM) and [**DSDB24C8**]$^{2-}$ (2 mM). Mole fractions X_A and X_B were determined from Hd resonance integrals. [**2**]$^{2+}$ blue labels; [**2**⊂**DSDB24C8**] black.

Table S4. Relative peak intensities, mole fractions, γ, and mixing times for [**2**⊂**DSDB24C8**] ROESY at 293 K.

	I_{AA}	I_{BB}	I_{AB}	I_{BA}	X_A	X_B	γ	τ_{mix} (s)
293 K	1.00	3.99	1.94	1.86	0.36	0.64	1.236	0.2
	1.00	4.48	2.18	2.31	0.36	0.64	1.145	0.3
	1.00	5.75	2.58	2.62	0.36	0.64	1.215	0.5
	1.00	5.20	2.39	2.7	0.36	0.64	1.140	0.6

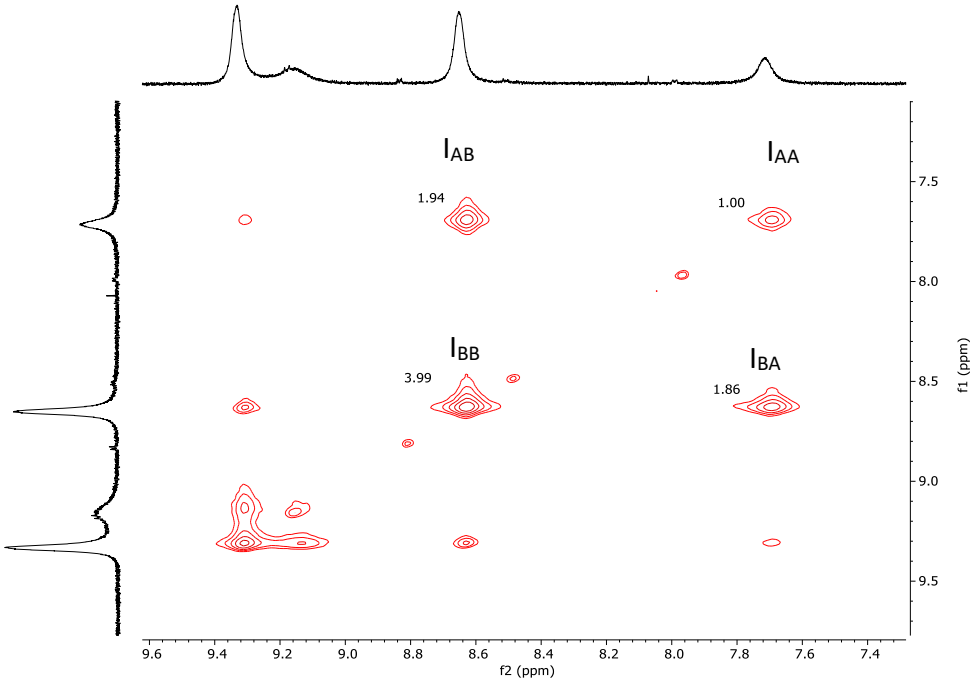


Figure S26 Partial ROESY NMR spectrum (293 K, MeOD, 500 MHz, τ_{mix} = 0.2 s) of an mixture of [**2**]$^{2+}$ (5 mM) and [**DSDB24C8**]$^{2-}$ (2 mM).

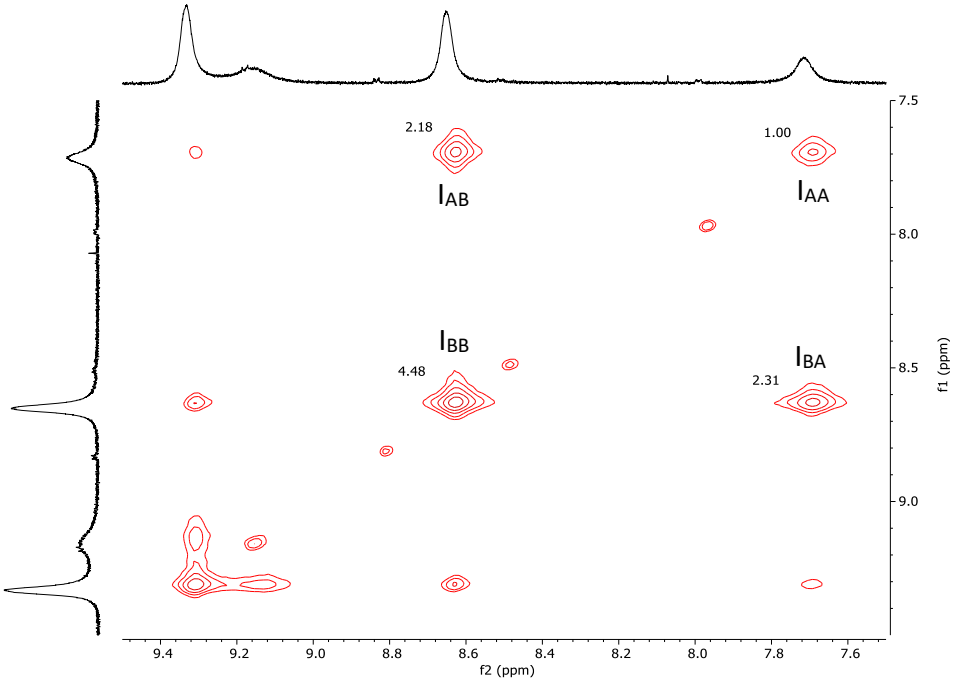


Figure S27 Partial ROESY NMR spectrum (293 K, MeOD, 500 MHz, τ_{mix} = 0.3 s) of an mixture of [**2**]$^{2+}$ (5 mM) and [**DSDB24C8**]$^{2-}$ (2mM).

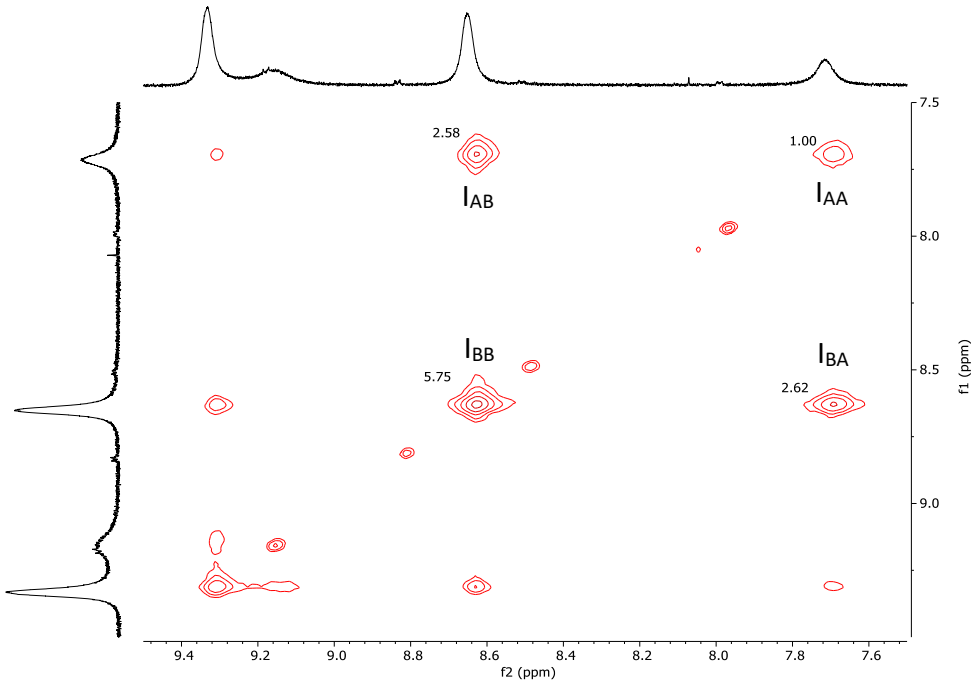


Figure S28 Partial ROESY NMR spectrum (293 K, MeOD, 500 MHz, τ_{mix} = 0.5 s) of an mixture of [**2**]$^{2+}$ (5 mM) and [**DSDB24C8**]$^{2-}$ (2 mM).

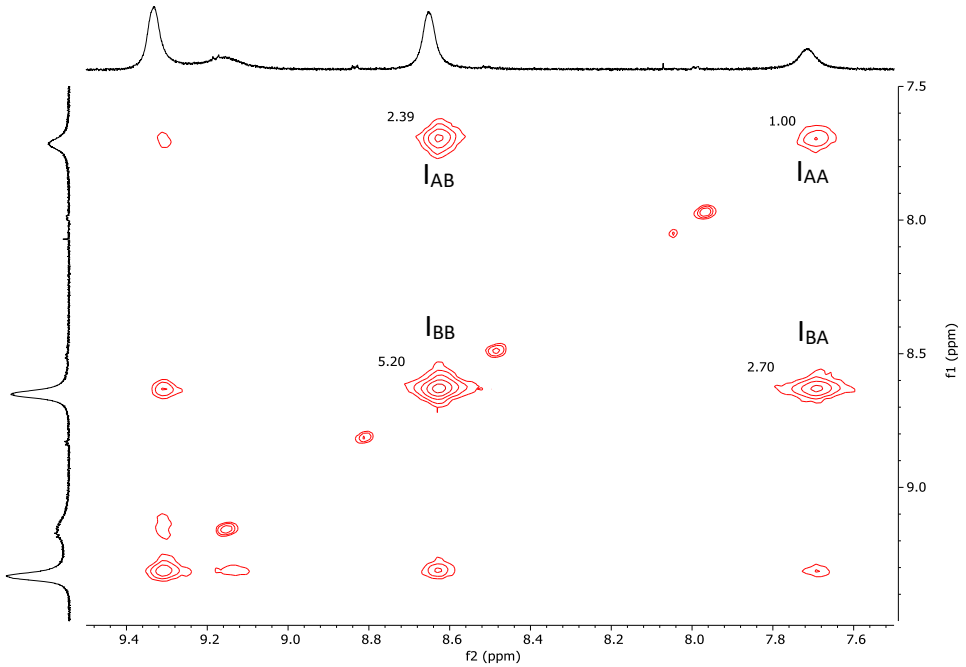


Figure S29 Partial ROESY NMR spectrum (293 K, MeOD, 500 MHz, τ_{mix} = 0.6 s) of an mixture of [**2**]$^{2+}$ (5 mM) and [**DSDB24C8**]$^{2-}$ (2 mM).

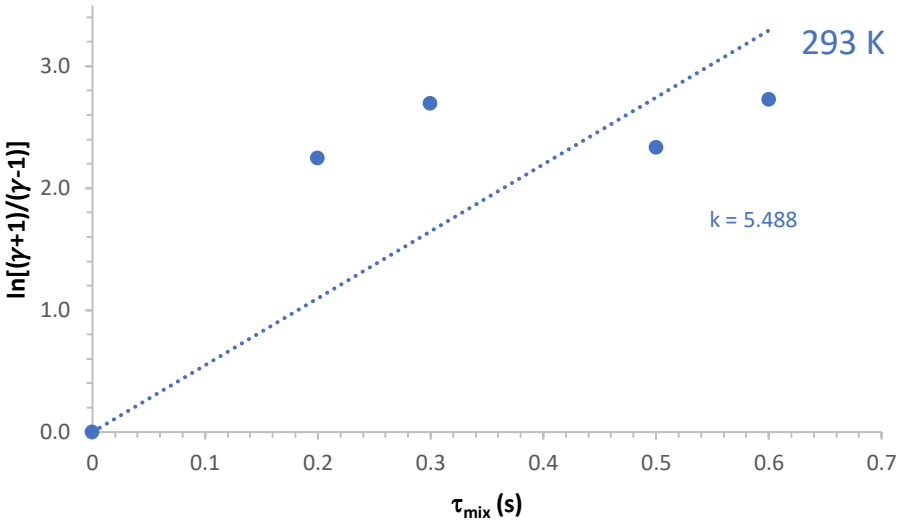


Figure S30 Plot of ln[(γ+1)/(γ-1)] as a function of mixing time at 293 K for [**2**⊂[**DSDB24C8**] with the corresponding value of k_{obs}. (R^2 = 0.8843)

b. ROESY of [**3**⊂ **DSDB24C8**] $^{2-}$.

Table S5. Relative peak intensities, mole fractions, γ, and mixing times for [**3**⊂[**DSDB24C8**]$^{2-}$ ROESY at different temperatures.

	I_{AA}	I_{BB}	I_{AB}	I_{BA}	X_A	X_B	γ	τ_{mix} (s)
293 K	5.70	13.28	1.00	1.00	0.74	0.26	8.25	0.50
	3.35	7.79	1.00	0.97	0.74	0.26	4.92	0.75
	2.02	4.38	1.00	1.00	0.74	0.26	2.78	1.25
298 K	2.79	7.82	1.00	0.94	0.76	0.24	4.61	0.50
	2.10	6.23	1.00	1.09	0.76	0.24	3.32	0.75
	1.47	4.20	1.00	0.81	0.76	0.24	2.67	1.25
303 K	1.30	6.31	1.00	0.92	0.83	0.17	2.86	0.50
	0.83	4.63	1.00	1.05	0.83	0.17	1.89	0.75
	0.37	3.87	1.00	0.99	0.83	0.17	1.52	1.25

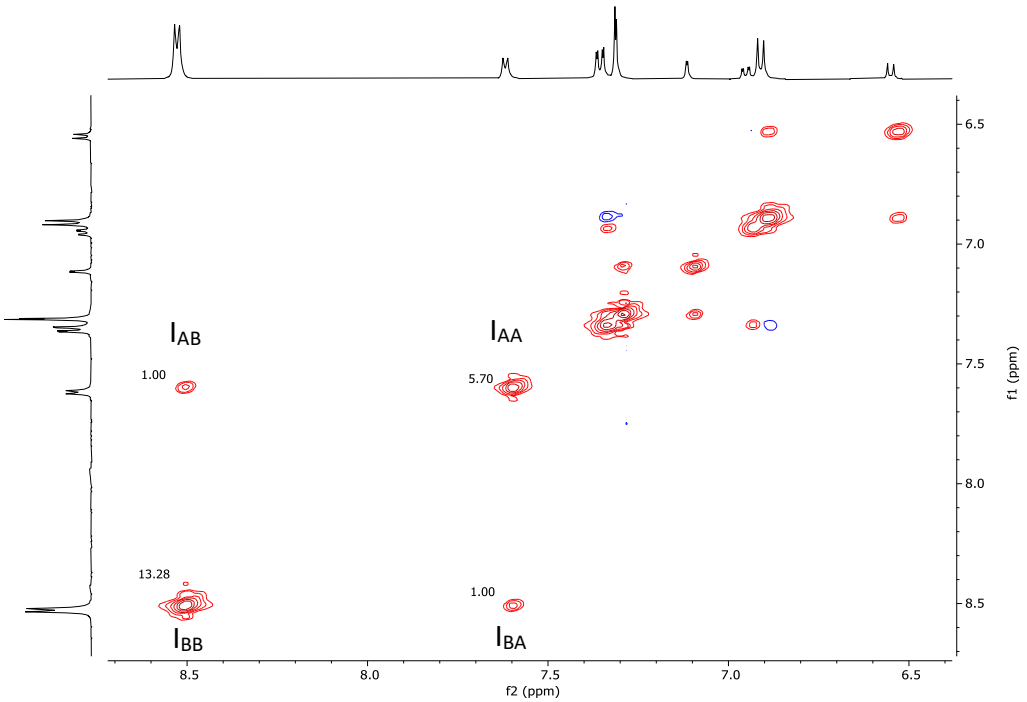


Figure S31 Partial ROESY NMR spectrum (293 K, MeOD, 500 MHz, 5 mM, τ_{mix} = 0.50 s) of an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution.

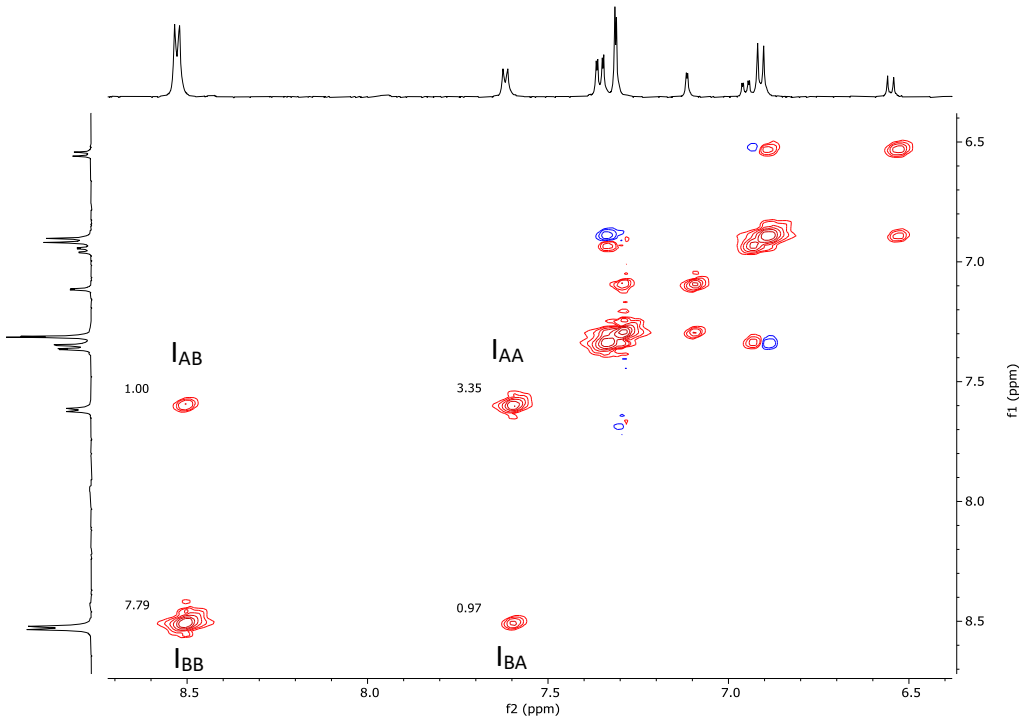


Figure S32 Partial ROESY NMR spectrum (293 K, MeOD, 500 MHz, 5 mM, τ_{mix} = 0.75 s) of an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution.

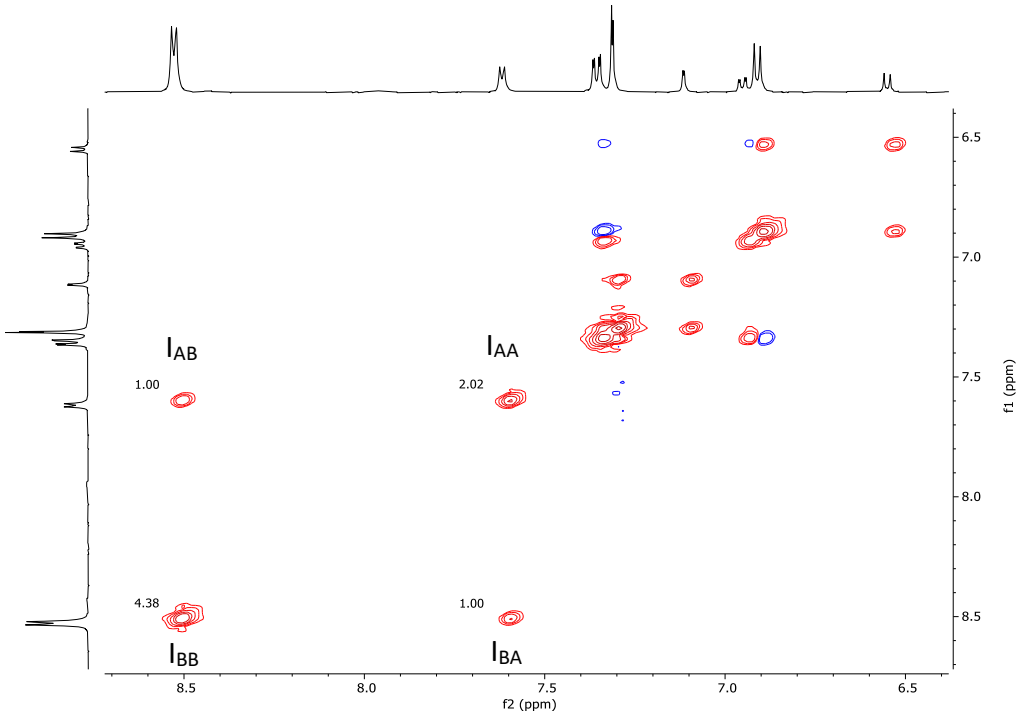


Figure S33 Partial ROESY NMR spectrum (293 K, MeOD, 500 MHz, 5 mM, τ_{mix} = 1.25 s) of an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution.

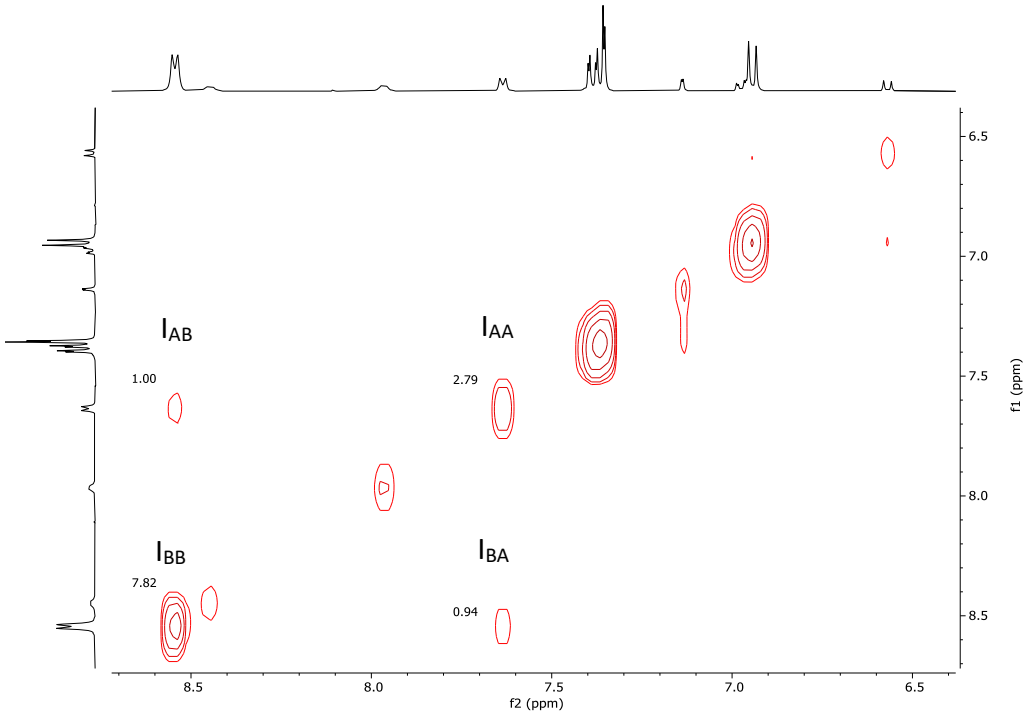


Figure S34 Partial ROESY NMR spectrum (298 K, MeOD, 500 MHz, 5 mM, τ_{mix} = 0.50 s) of an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution.

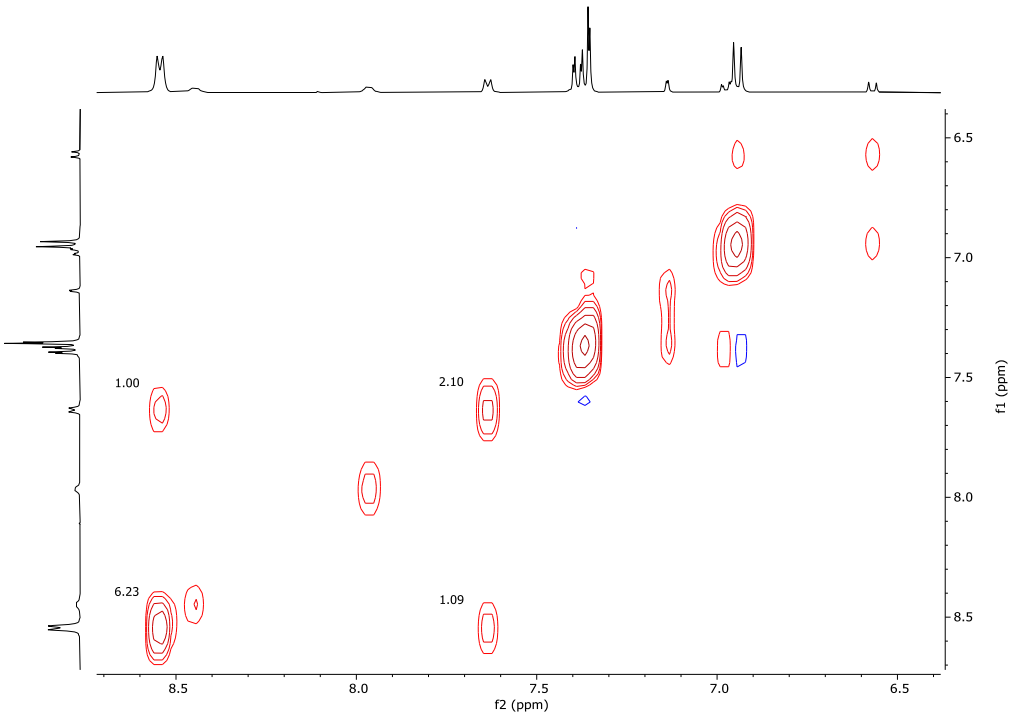


Figure S35 Partial ROESY NMR spectrum (298 K, MeOD, 500 MHz, 5 mM, τ_{mix} = 0.75 s) of an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution.

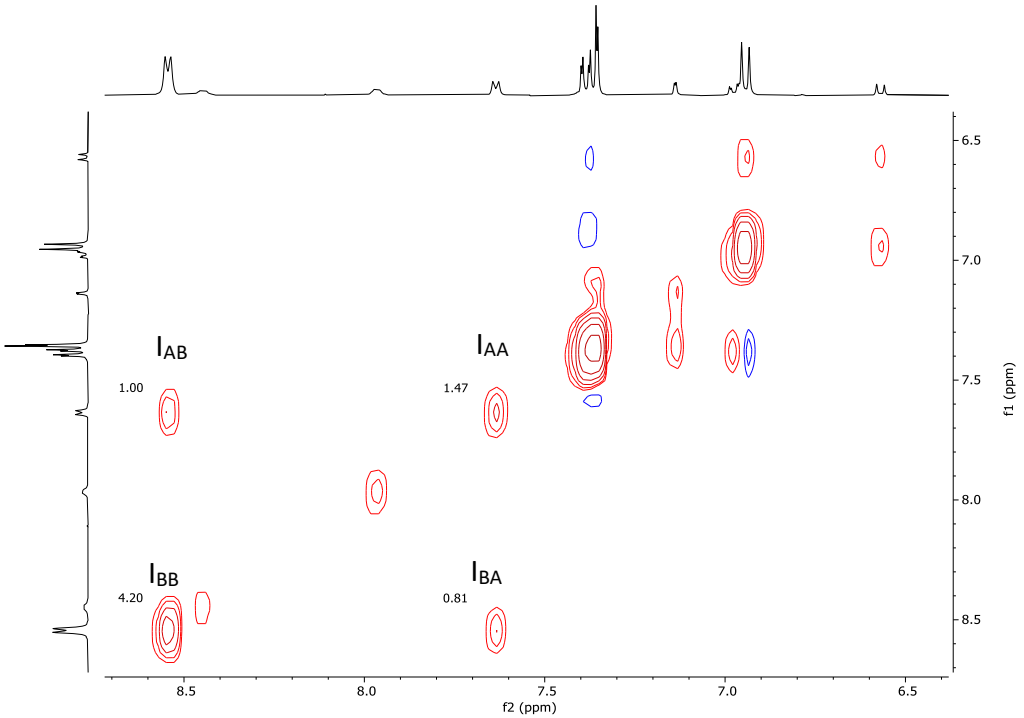


Figure S36 Partial ROESY NMR spectrum (298 K, MeOD, 500 MHz, 5 mM, τ_{mix} = 1.25 s) of an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution.

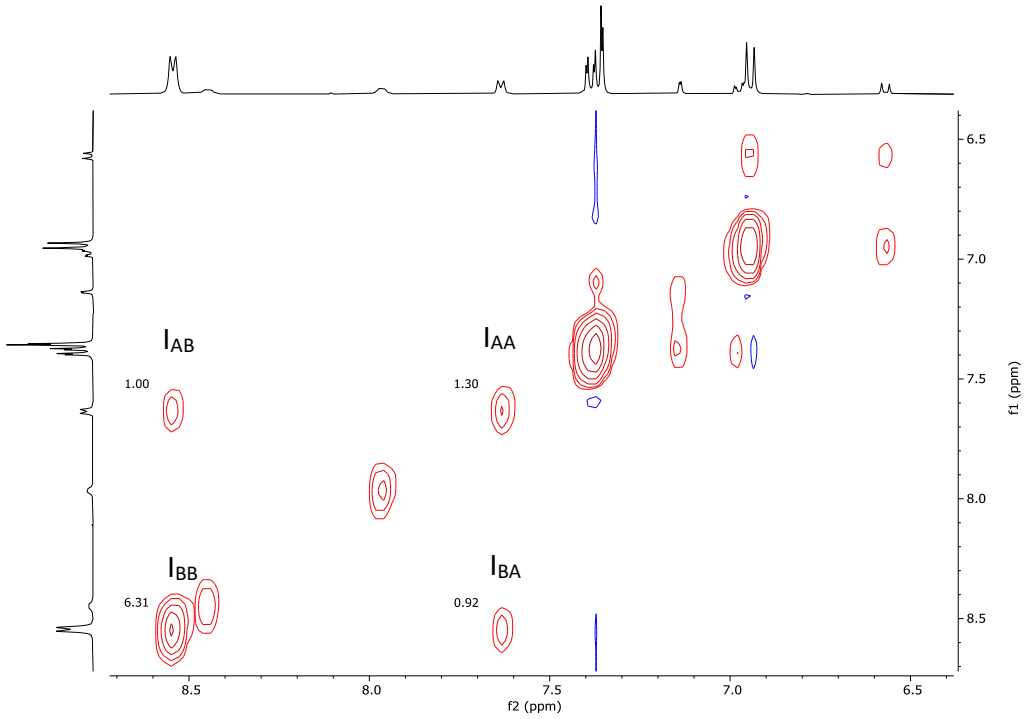


Figure S37 Partial ROESY NMR spectrum (303 K, MeOD, 500 MHz, 5 mM, τ_{mix} = 0.50 s) of an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution.

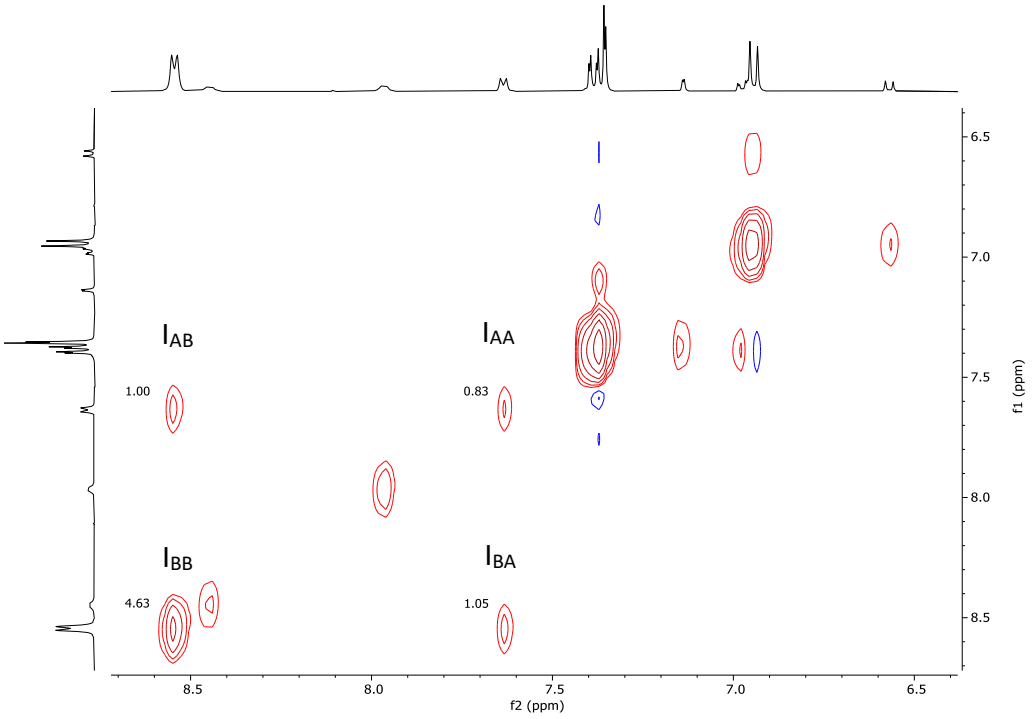


Figure S38 Partial ROESY NMR spectrum (303 K, MeOD, 500 MHz, 5 mM, τ_{mix} = 0.75 s) of an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution.

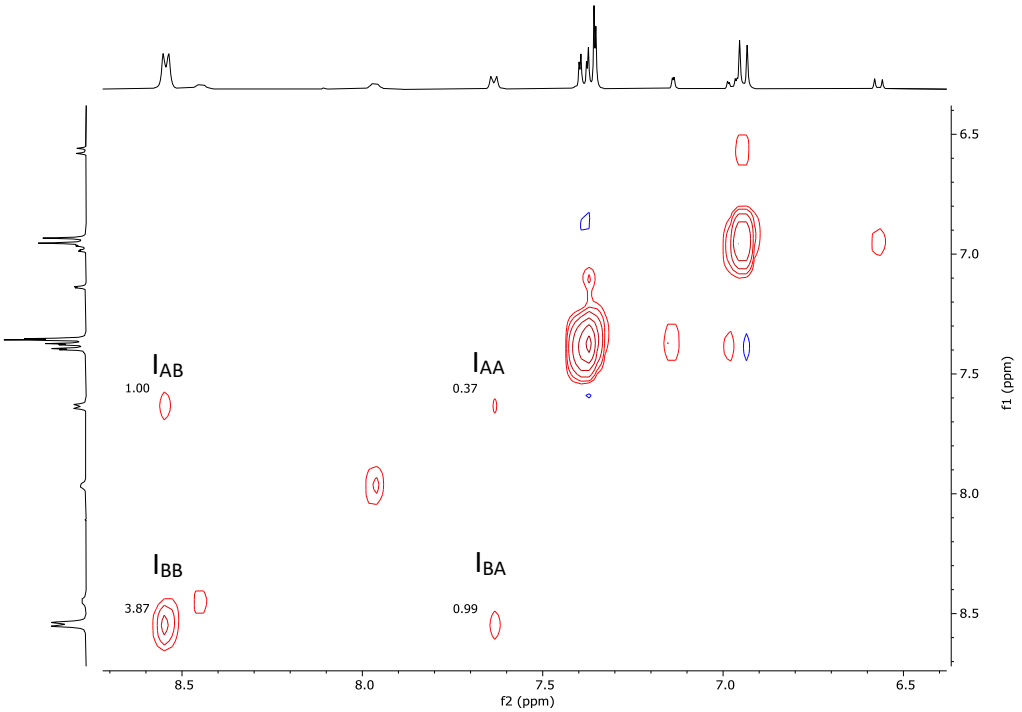


Figure S39 Partial ROESY NMR spectrum (303 K, MeOD, 500 MHz, 5 mM, τ_{mix} = 1.25 s) of an equimolar mixture of [**DSDB24C8**]$^{2-}$ and compound [**3**] , prepared in situ by addition of four equivalents of DIEA to a [**2**][Br]$_2$ solution.

Kinetic rate constants k_{on}/k_{off} were derived as follows:

$$k = k_1[H]_{free} + k_{-1} \quad (1)$$

$$K = \frac{k_1}{k_{-1}} \quad (2)$$

Rearranging equations (1) and (2) we obtain k_1

$$k_1 = \frac{k}{\left([H]_{free} + \frac{1}{K}\right)} \quad (3)$$

And then k_{-1} value was obtained from equation (2).

$$k_{-1} = \frac{k_1}{K} \quad (2)$$

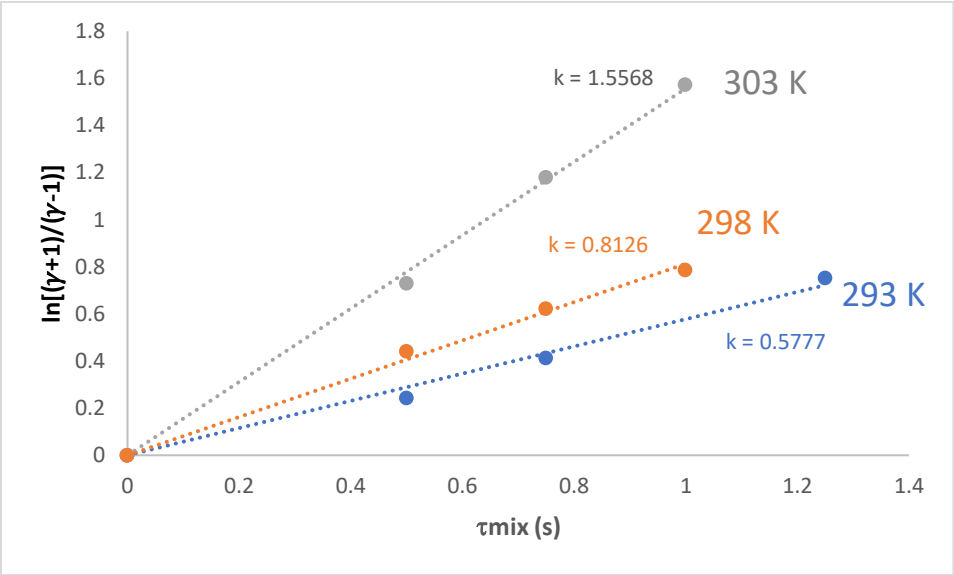


Figure S40 Plot of ln[(γ+1)/(γ-1)] as a function of mixing time at different temperatures for [**3**⊂[**DSDB24C8**]$^{2-}$ with the corresponding value of k_{obs}. (R^2 = 0.9957 (293 K); R^2 = 0.9983 (298 K); R^2 = 0.9994 (303 K).

7. Determination of shuttling energy barriers (ΔG$^{\neq}$) in [2]pseudorotaxanes.

Shuttling rates were determined by a coalescence temperature method using the equation:

$$k_c = \frac{\pi \Delta v}{\sqrt{2}}$$

where k_C is the rate of shuttling at coalescence temperature, $\Delta\nu$ is the limiting chemical shift -in Hz- between the exchanging proton resonances and can be determined by variable-temperature NMR. Eyring equation

$$\Delta G^{\ddagger} = -RT_c ln \frac{k_c h}{k_B T_c}$$

was used to estimate $\Delta G^{\ddagger}$ and extrapolate the rate of shuttling to other temperatures. T_c is the coalescence temperature, R the gas constant, h Planck's constant, and k_B Boltzmann's constant.

Table S6. Shuttling free energies for [2]pseudorotaxanes.

Compound	Proton	occupied (ppm)	unoccupied (ppm)	$\Delta\nu$ (Hz)	k_c (s^{-1})	T_c (K)	$\Delta G^{\ddagger}_{shuttling}$ ($kJmol^{-1}$)	Error
[**2**⊂**DSDB24C8**]	*ortho*-N^+	9.27	9.01	130	288.8	263	51.7	1.2
	meta-N^+	7.77	7.71	30	66.6	243	50.6	1.7
	NCH_2	5.22	4.88	170	377.6	263	51.2	1.2
[**3**⊂**DSDB24C8**]$^{2-}$	*ortho*-N^+	9.42	9.02	200	444.3	243	46.8	1.3
	meta-N^+	7.74	7.57	85	188.8	223	44.4	1.3
	NCH_2	5.22	4.81	205	455.4	243	46.7	1.1

$t_{1/2} = \ln(2) / k_{off}$

SN is the average number of shuttling cycles before the macrocycle is dethreaded, it was determined by multiplying $k_{shuttling}$ by $t_{1/2}$.

Table S7. Summary of kinetic and shuttling parameters for [2]pseudorotaxanes at 293 K; *SF* = shuttling frequency; *SN* = shuttling number.

Compound	k_{on} ($M^{-1}s^{-1}$)	k_{off} (s^{-1})	$t_{1/2}$ (s)	$\Delta G^{\ddagger}_{shuttling}$ ($kJmol^{-1}$)	*SF* (s^{-1})	*SN*
[**2**⊂**DSDB24C8**]	2.5×10^{6}	3.5	0.2	51 (1)	4.6×10^{3}	9.8×10^{2}
[**3**⊂**DSDB24C8**]$^{2-}$	5.1×10^{1}	6.2×10^{-1}	1.1	46 (1)	3.9×10^{4}	4.3×10^{4}

8. References

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