Supporting Information for:

Molecular motion of Donor-Acceptor catenanes in water

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NMR spectra were recorded on a 500 MHz Brucker cryo-NMR spectrometer.

Nomenclature - NDI: naphthalenedimide; DN: dialkoxynaphthalene.

1. 2D exchange spectroscopy (EXSY)

1.1. Determination of kinetic parameters for catenane **1a•6**

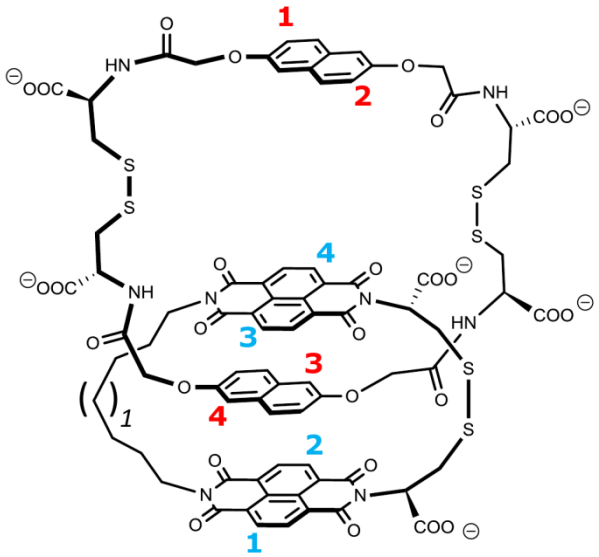

Fig. S1 Chemical structure of the [2]catenane **1a•6**. The numbers shown in blue depict protons on the acceptor NDI building block and the numbers shown in red depict protons on the donor DN building block.

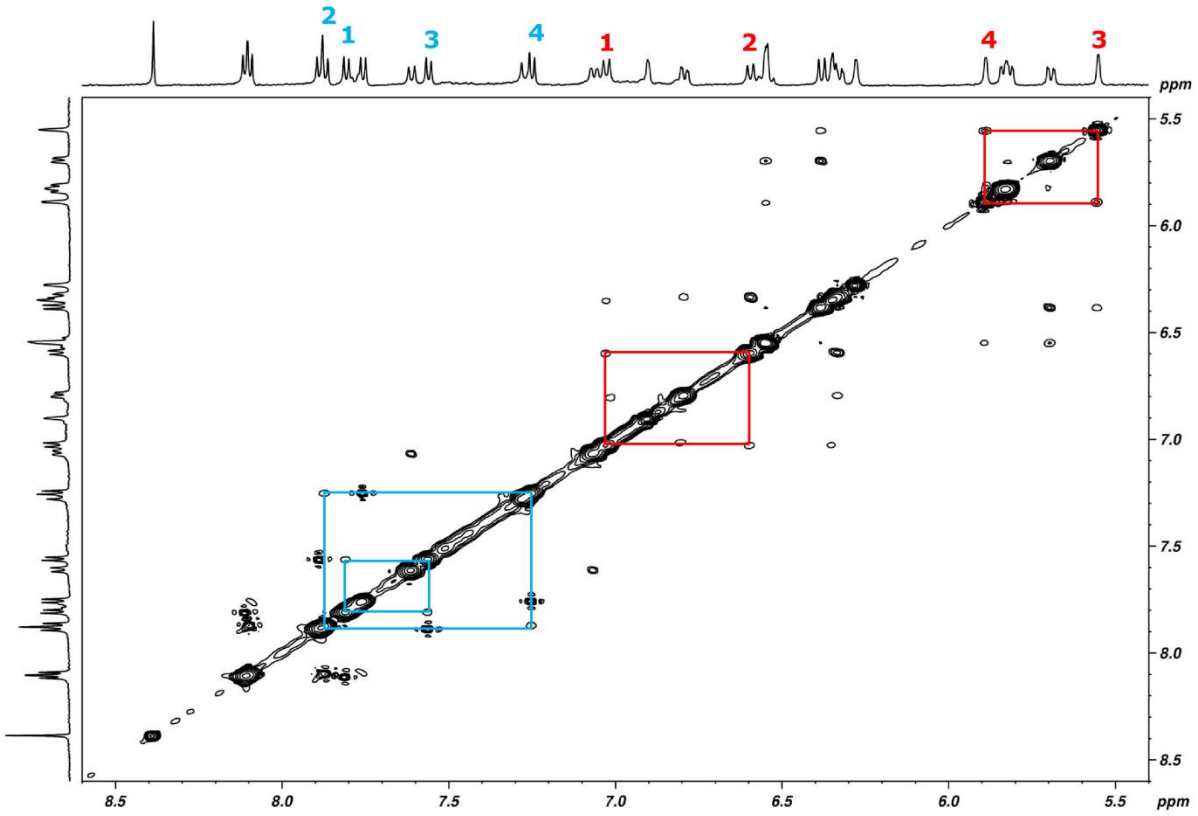

Fig. S2 Partial 2D NOESY spectrum of the [2]catenane **1a•6** (D_2O, 298 K, 500 MHz, d8 = 200 ms). The blue and the red boxes correspond to the exchange peaks between the acceptor protons and the donor protons respectively. Full NMR characterisation of this catenane was given in reference 1.

Temperature (T)	Rate constant (k)	ln (k/T)	1/T
298.1	0.19	-7.38	0.00335
308.1	0.50	-6.43	0.00325
317.1	1.03	-5.73	0.00315

Table S1 Rate constant of the motion observed for catenanes **1a•6** at different temperatures obtained from 2D EXSY in D_2O. Rate constants were calculated using the software EXSYCalc developed my Mestrelab research.

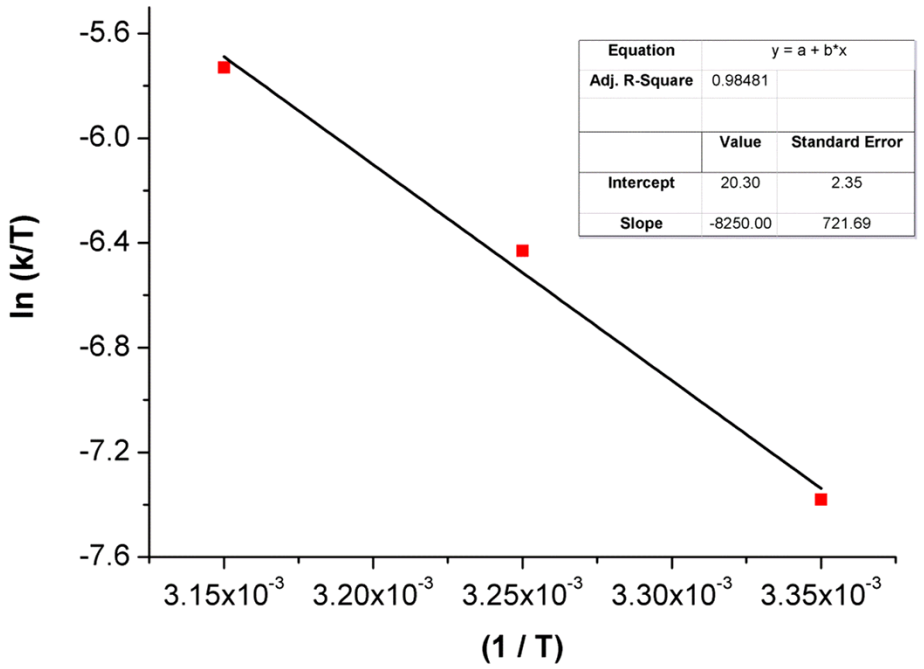

Fig. S3 A plot of ln(k/T) vs. (1/T) for the [2]catenane **1a•6**

$\Delta H^{\ddagger}$	68597.98	J/mol	=	16.38	kcal/mol
$\Delta S^{\ddagger}$	-28.67	J/mol K			
$\Delta G^{\ddagger}$ (at 298.1 K)	77145.88	J/mol	=	18.43	kcal/mol

Table S2 Kinetic parameters of the motion observed for catenanes **1a•6** obtained from Eyring equation.

1.2. Determination of kinetic parameters for catenane **1b•6**

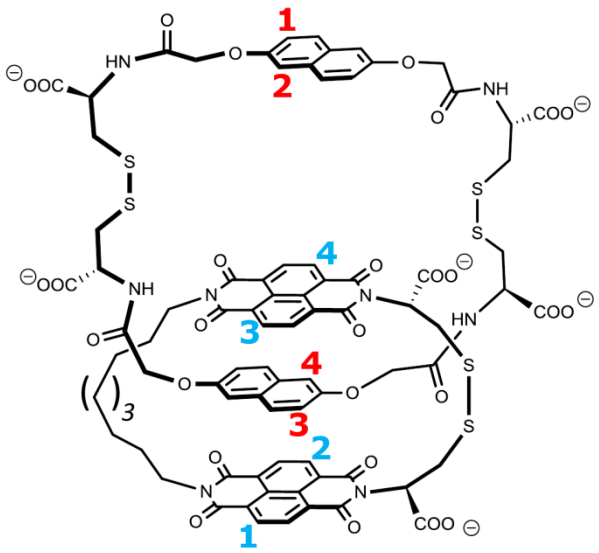

Fig. S4 Chemical structure of the [2]catenane **1b•6**. The numbers shown in blue depict protons on the acceptor NDI building block and the numbers shown in red depict protons on the donor DN building block.

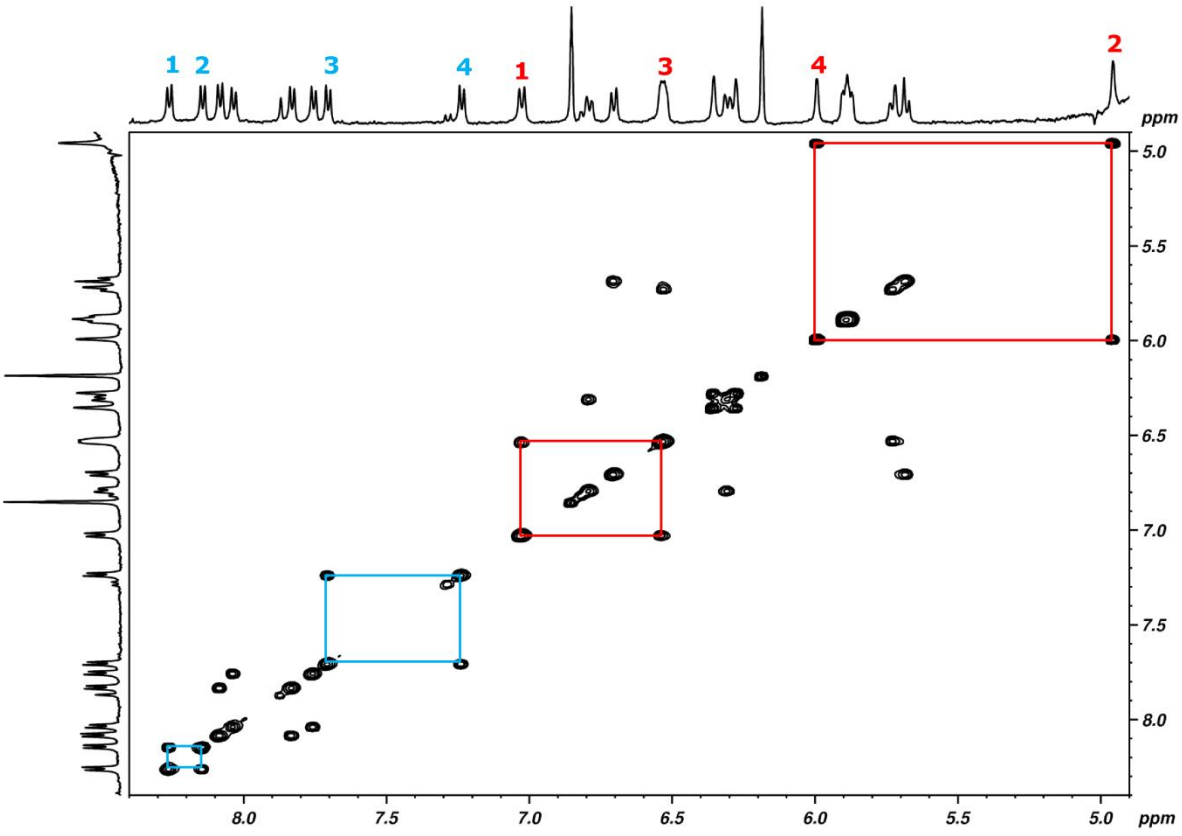

Fig. S5 Partial 2D NOESY spectrum of the [2]catenane **1b•6** (D_2O, 298 K, 500 MHz, d8 = 200 ms). The blue and the red boxes correspond to the exchange peaks between the acceptor protons and donor protons respectively. Full NMR characterisation of this catenane was given in reference 1.

Temperature (T)	Rate constant (k)	ln (k/T)	1/T
288.1	1.59	-5.20	0.00347
298.1	5.30	-4.03	0.00335
308.1	11.21	-3.31	0.00325

Table S3 Rate constant of the motion observed for catenanes **1b•6** at different temperatures obtained from 2D EXSY in D_2O. Rate constants were calculated using the software EXSYCalc developed my Mestrelab research.

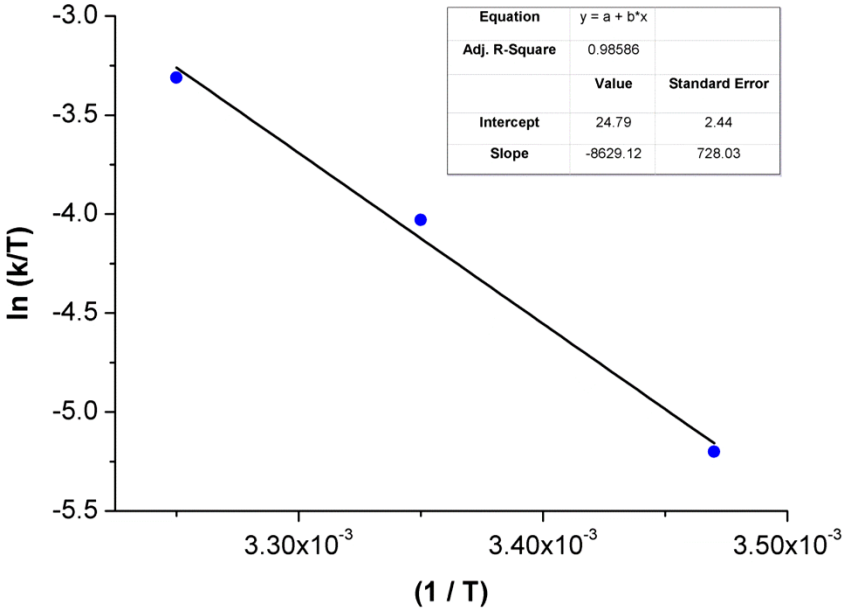

Fig. S6 A plot of ln(k/T) vs. (1/T) for the [2]catenane **1b•6**

$\Delta H^{\ddagger}$	69751.13	J/mol	=	16.66	kcal/mol
$\Delta S^{\ddagger}$	1.86	J/mol K			
$\Delta G^{\ddagger}$ (at 298.1 K)	69195.86	J/mol	=	16.53	kcal/mol

Table S4 Kinetic parameters of the motion observed for catenanes **1b•6** obtained from Eyring equation.

1.3. Determination of kinetic parameters for catenane **2•5**

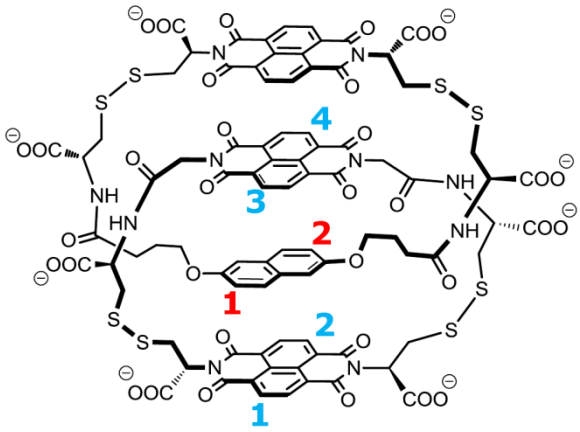

Fig. S7 Chemical structure of the [2]catenane **2•5**. The numbers shown in blue depict protons on the acceptor NDI building block and the numbers shown in red depict protons on the donor DN building block.

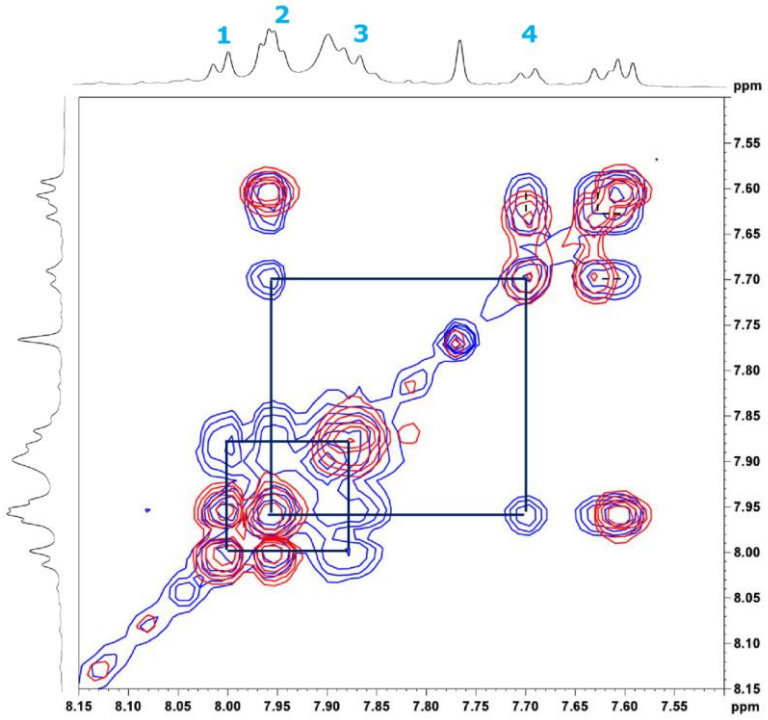

Fig. S8 Partial 2D NOESY spectrum of the [2]catenane **2•5** depicting the acceptor NDI region (D_2O, 298 K, 500 MHz, d8 = 800 ms). 2D COSY spectrum is overlaid and is coloured in red. The solid boxes correspond to the exchange peaks between the acceptor protons. Full NMR characterisation of this catenane was given in reference 2.

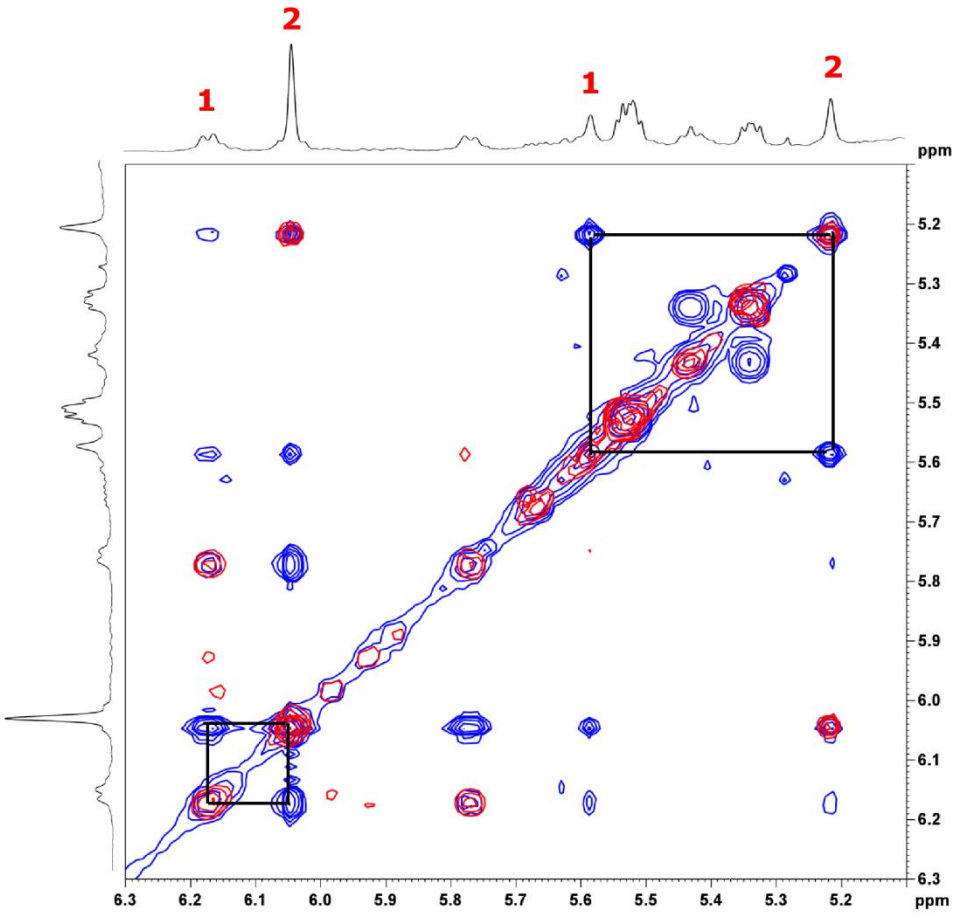

Fig. S9 Partial 2D NOESY spectrum of the [2]catenane **2•5** depicting the donor DN region (D_2O, 298 K, 500 MHz, d8 = 800 ms). 2D COSY spectrum is overlaid and is coloured in red. The black boxes correspond to the exchange peaks between the donor protons.

Temperature (T)	Rate constant (k)	ln (k/T)	1/T
288.1	0.58	-6.21	0.00347
298.1	2.21	-4.91	0.00335
308.1	6.74	-3.82	0.00325

Table S5 Rate constant of the motion observed for catenanes **2•5** at different temperatures obtained from 2D EXSY in D_2O. Rate constants were calculated using the software EXSYCalc developed my Mestrelab research.

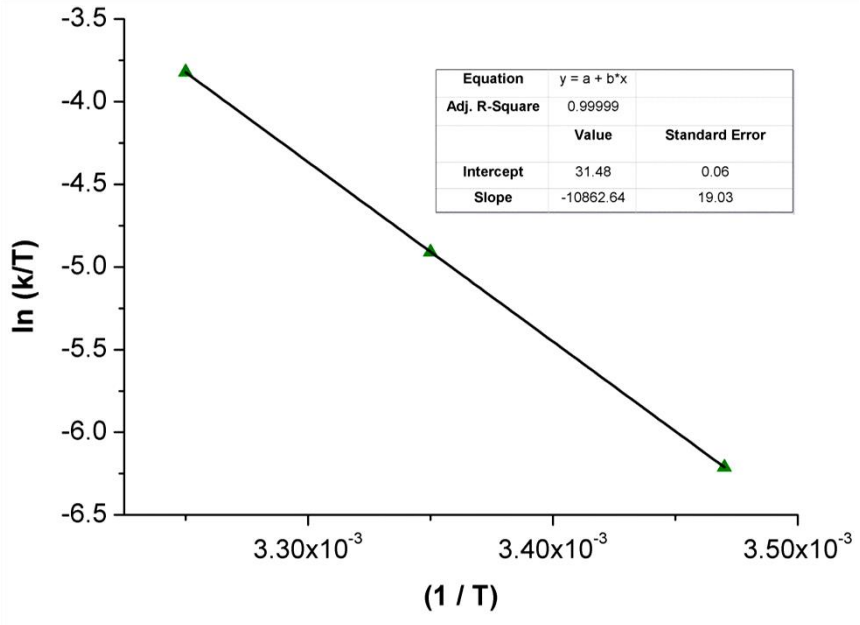

Fig. S10 A plot of ln(k/T) vs. (1/T) for the [2]catenane **2•5**

ΔH‡	88078.52	J/mol	=	21.04	kcal/mol
ΔS‡	56.74	J/mol K			
ΔG‡ (at 298.1 K)	71163.30	J/mol	=	17.00	kcal/mol

Table S6 Kinetic parameters of the motion observed for catenanes **2•5** obtained from Eyring equation.

2. 1D NMR of the previously characterised catenanes

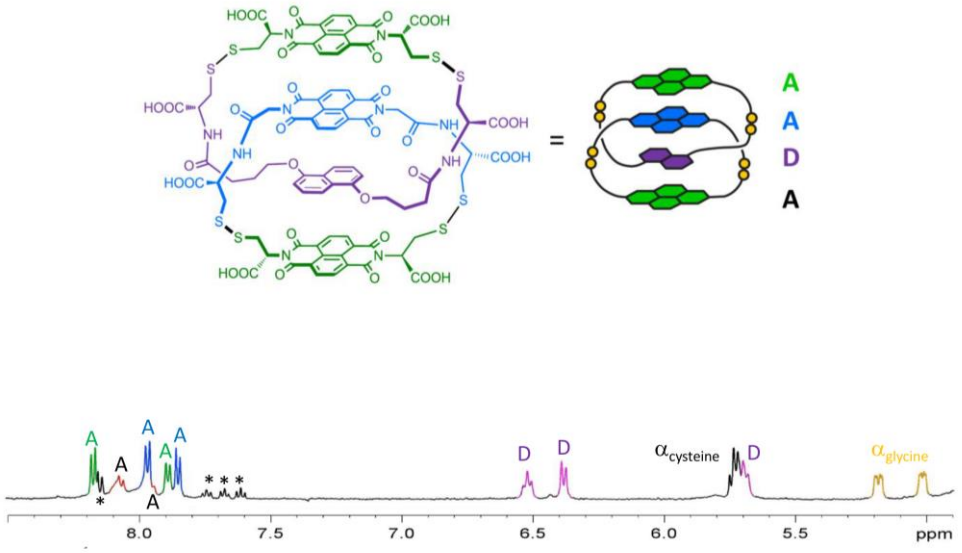

Fig. S11 Partial ^{1}H NMR spectrum (D_2O, 500 MHz) of catenane **2•4** at 298 K, showing the presence of a single conformation. An impurity was labelled by *, and the water peak was referenced at 4.79 ppm. Full NMR characterisation of this catenane was given in reference 2.

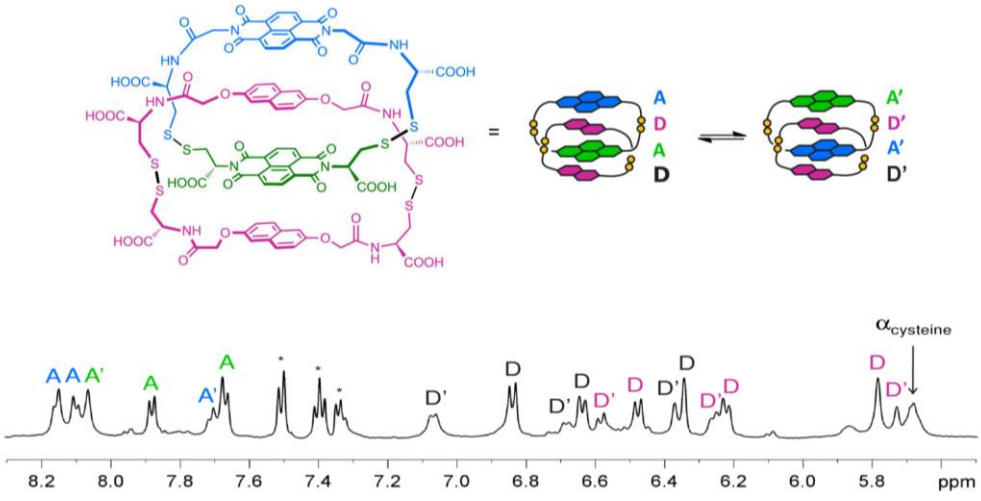

Fig. S12 Partial ^{1}H NMR spectrum (D_2O, 500 MHz) of catenane **2•6** at 298 K, showing the presence of two conformations. An impurity was labelled by *, and the water peak was referenced at 4.79 ppm. Full NMR characterisation of this catenane was given in reference 2.

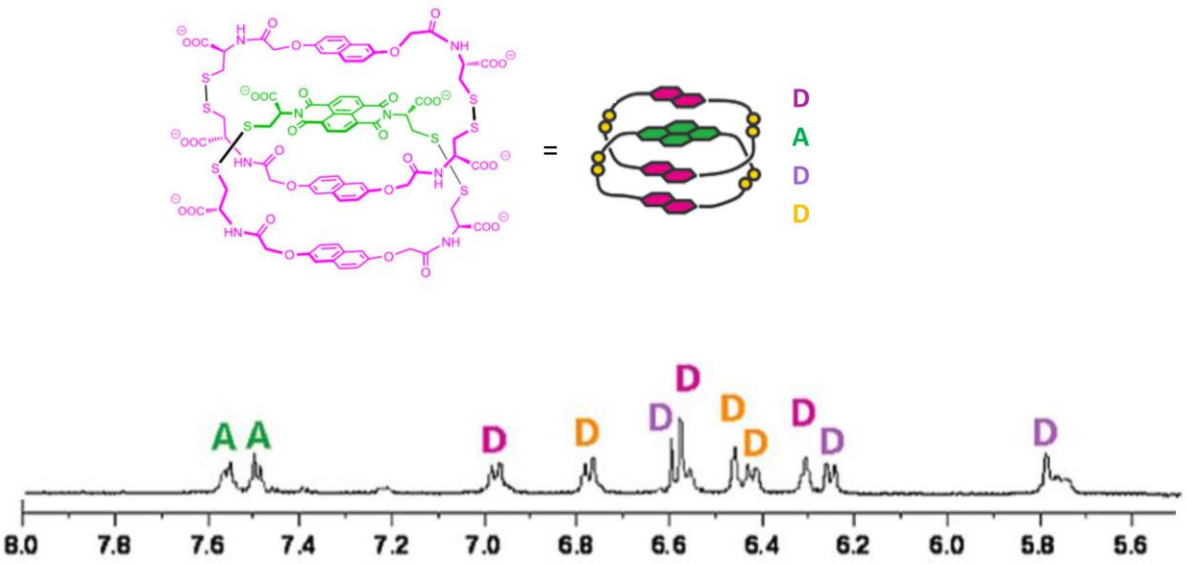

Fig. S13 Partial ^{1}H NMR spectrum (D_2O, 500 MHz) of catenane **3•6** at 300 K, showing the presence of a single conformation. Full NMR characterisation of this catenane was given in reference 3. The water peak was referenced at 4.79 ppm.

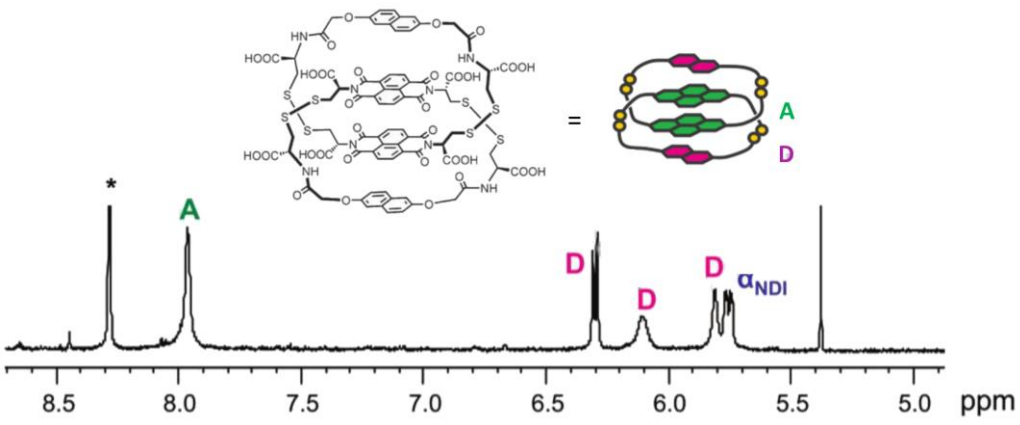

Fig. S14 Partial ^{1}H NMR spectrum (D_2O, 500 MHz) of catenane **3•3** at 300 K, showing the presence of a single conformation. Full NMR characterisation of this catenane was given in reference 3. The water peak was referenced at 4.79 ppm.

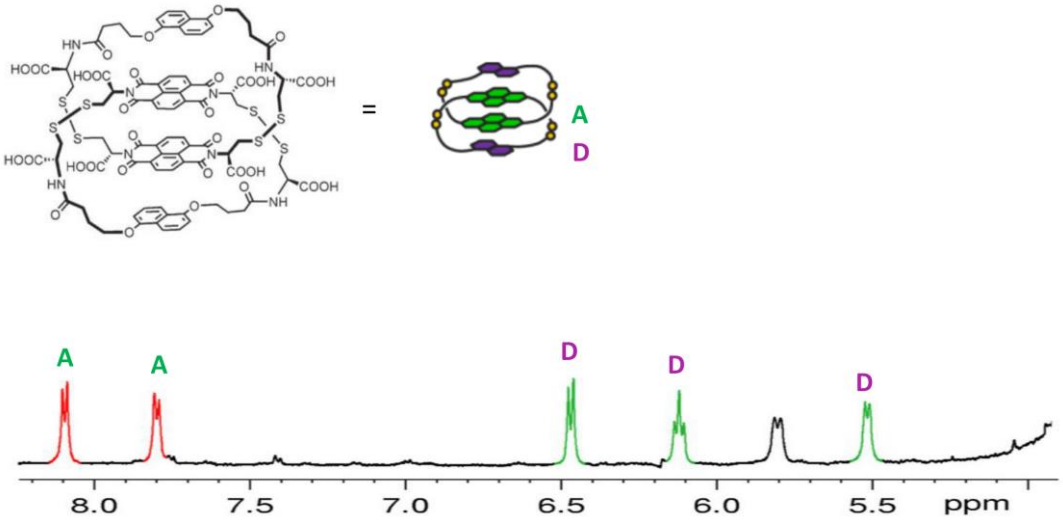

Fig. S15 Partial ^{1}H NMR spectrum (D_2O, 500 MHz) of catenane **4•4** at 300 K, showing the presence of a single conformation. Full NMR characterisation of this catenane was given in reference 4. TFA was labelled by * and the water peak was referenced at 4.79 ppm.

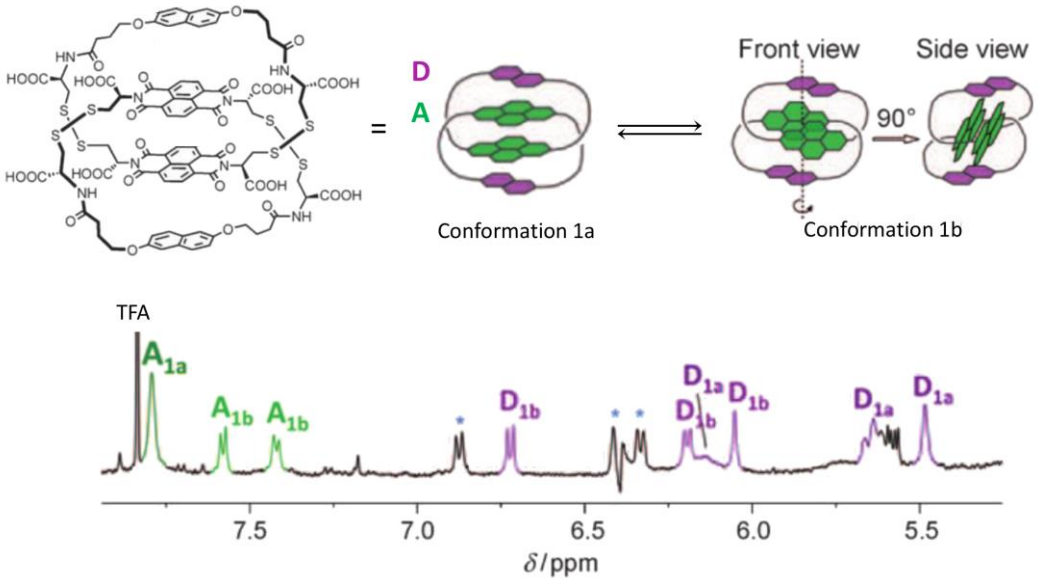

Fig. S16 Partial ^{1}H NMR spectrum (D_2O, 500 MHz) of catenane **5•5** at 300 K, showing the presence of two conformations, assigned as a fully stacked (1a) and a Gemini-like (1b) conformations. Full NMR characterisation of this catenane was given in reference 5. An impurity was labelled by *

3. References

(1) F. B. L. Cougnon, N. Ponnuswamy, N. A. Jenkins, G. D. Pantoş and J. K. M. Sanders, *J. Am. Chem. Soc.*, 2012, **134**, 19129.

(2) F. B. L. Cougnon, H. Y. Au-Yeung, G. D. Pantoş and J. K. M. Sanders, *J. Am. Chem. Soc.*, 2011, **133**, 3198.

(3) H. Y. Au-Yeung, G. D. Pantoş and J. K. M. Sanders, *J. Am. Chem. Soc.*, 2009, **131**, 16030.

(4) H. Y. Au-Yeung, G. D. Pantoş and J. K. M. Sanders, *Proc. Natl. Acad. Sci. USA.*, 2009, **106**, 10466.

(5) H. Y. Au-Yeung, G. D. Pantoş and J. K. M. Sanders, *Angew. Chem. Int. Ed.*, 2010, **49**, 5331.