Chemical Science

Topological isomerism in a chiral handcuff catenane

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SUPPORTING INFORMATION

Table of Contents

S1. 2D ^{1}H NMR Spectroscopy

Through analysis of 2D ^{1}H NMR spectra, it is possible to assign partially resonances to the protons of the handcuff catenane (Figure S1). The protons α to the nitrogens on the bipyridinium units can be related (Figure S2) to their vicinal protons β to the nitrogens on the bipyridinium units by 2D COSY NMR spectroscopy. Two-bond correlations can also be established between protons $H_{A\text{-}H}$ residing on methylene carbons (Figure S3), and three-bond correlations can be observed (Figures S3 and S4) between protons *ortho* to each other on the DNP units. We conclude that $H_{\alpha 1}$ and $H_{\alpha 7}$ are present on the same pyridinium ring; the same can also be said for $H_{\alpha 2/6}$, $H_{\alpha 3/4}$ and $H_{\alpha 5/8}$, which are established by four-bond correlations (Figures S5 and S6) between the two α or the two β protons on the same pyridinium ring, as well as the presence of through-space correlations (Figure S7), observed from 2D ROESY NMR spectra, between the methylene $H_{A\text{-}H}$ and α protons. Through-space correlations (Figure S8) between H_{i4} and H_1, and H_{i8} and $H_{2/3}$ confirm that H_{i4} is directed towards the center of the handcuff catenane, while H_{i8} points towards the terminal para-xylylene units. 2D COSY and ROESY ^{1}H NMR spectroscopy enabled us to identify that $H_{\alpha 2/6,3/4}$ reside in close proximity to the central benzenoid ring owing to the detection of through-space correlations between H_1 and H_B and H_D (Figure S7) that consequently display (Figure S3) through-bond correlations with H_A and H_C, respectively. These methylene protons show further through-space correlations with the protons α to the nitrogens on the pyridinium rings closest to the central benzenoid ring. The same analytical process was used to verify that $H_{\alpha 1/7,5/8}$ reside on the pyridinium rings furthest away from the central benzenoid ring.

The 2D ^{1}H EXSY spectra (Figures S9 and S10) reveals the presence of, not only site exchange between the α protons (and their respective β protons) on the same pyridinium ring, but also

between these protons on *opposite* sides of the cyclophane. In order to understand this phenomenon, the mechanism of the DNP reorientation has to be considered. Although the presence of the co-conformation wherein both DNP units reside in different orientations in the *meta-meta* isomer is not observed by ^{1}H NMR spectroscopy, it is possible for the DNP units to undergo an inversion process (Figure 8) provided they both leave the cavities of the cyclophanes, experience a pedaling motion and return inside the cavities in a concerted fashion. The co-conformations generated by this inversion process are degenerate. This degeneracy can be appreciated by rotating the original co-conformation by 180° around one of two different axes – one running through the center of the molecule intersecting all three phenylene rings, and the other one lying within the plane of the central benzenoid ring, but perpendicular to the C_2 axis shown in Figure S1. This degeneracy, which is illustrated in Figure 8, explains the site exchanges between the $H_{\alpha 1,7,5,8}$ protons (Figure S9). The site exchanges involving these protons are also mirrored more clearly between methylene protons on opposite sides of the cyclophanes, e.g., H_B and H_D are undergoing site exchange with each other (Figure S10) although 2D ^{1}H COSY NMR spectroscopy (Figure S3) reveals that these protons do not possess a through-bond correlation — i.e., they are not bound to the same methylene carbon — and therefore must be on opposite sides of the cyclophane, since both H_B and H_D have through-space correlations (Figure S7) with H_1.

The 2D EXSY spectra (Figures S9 and S10) also inform us that there is no site exchange between protons on the *ortho-ortho* isomer and those associated with the *meta-meta* isomer. Hence, it can be concluded that these two species are two distinct isomers that are not in equilibrium with each other. 2D DOSY (Figure S11) reveals that the *meta-meta* and *ortho-ortho* isomers have near identical diffusion properties in CD_3CN, confirming that the molecules constituting these two isomers have very similar sizes and charges.

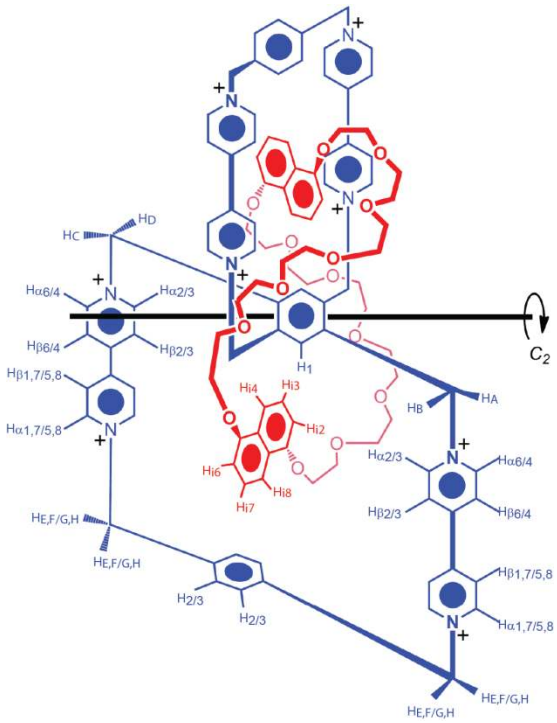

Figure S1. Structural formula of handcuff catenane **HC**$^{8+}$. Protons on the structural formula are labelled in keeping with their corresponding ^{1}H NMR assignments.

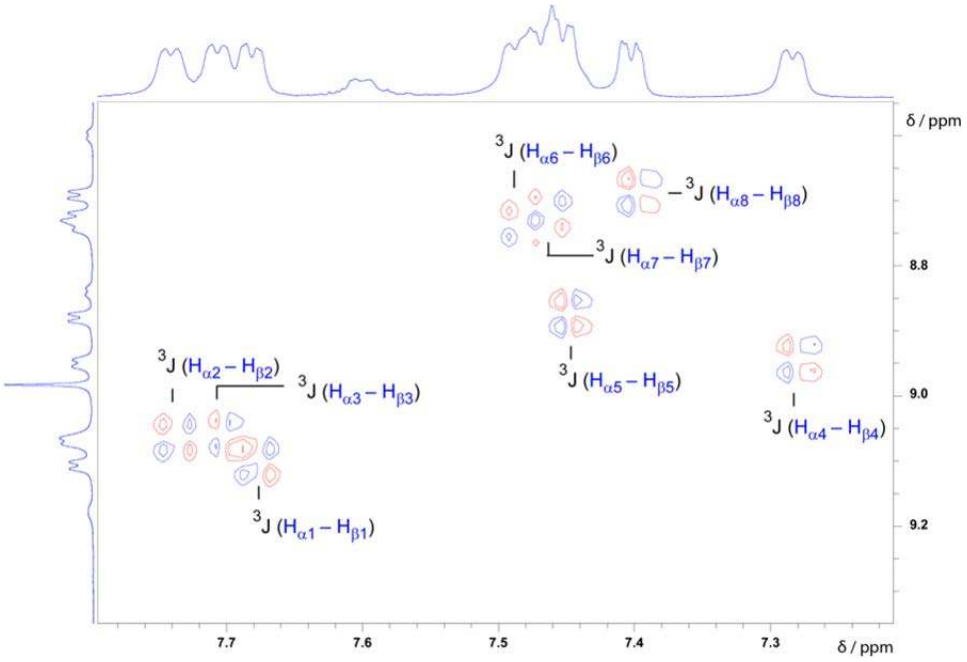

Figure S2. Partial ^{1}H–^{1}H gDQF COSY (600 MHz, CD_3CN, 298 K) spectrum of **HC**•8PF_6 with selected correlations labelled.

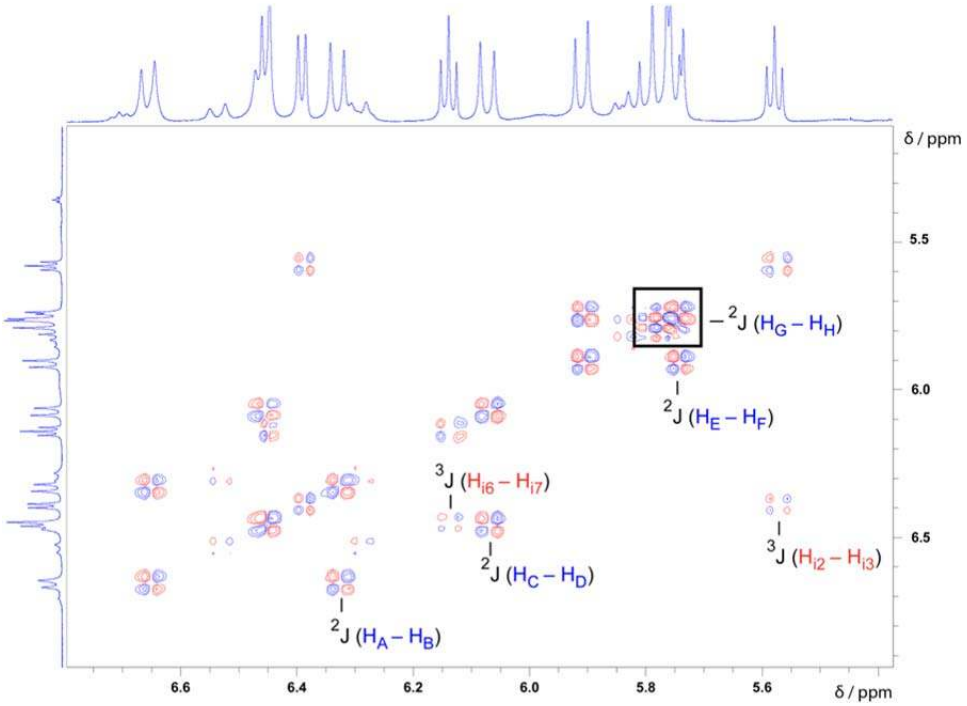

Figure S3. Partial ^{1}H–^{1}H gDQF COSY (600 MHz, CD_3CN, 298 K) spectrum of **HC**•8PF_6 with selected correlations labelled.

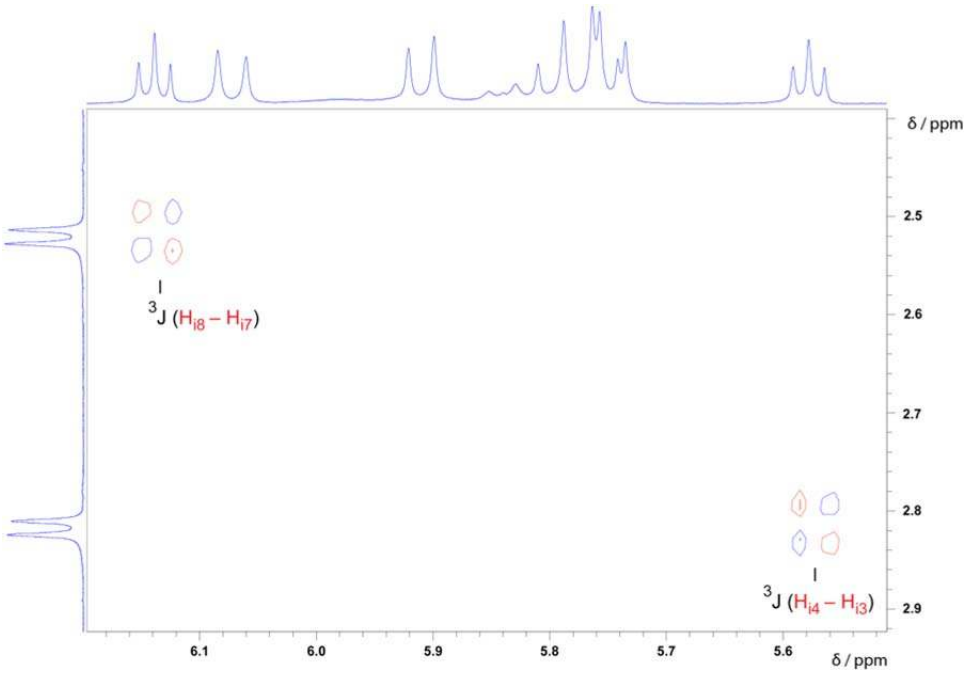

Figure S4. Partial ^{1}H–^{1}H gDQF COSY (600 MHz, CD_3CN, 298 K) spectrum of **HC**•8PF_6 with selected correlations labelled.

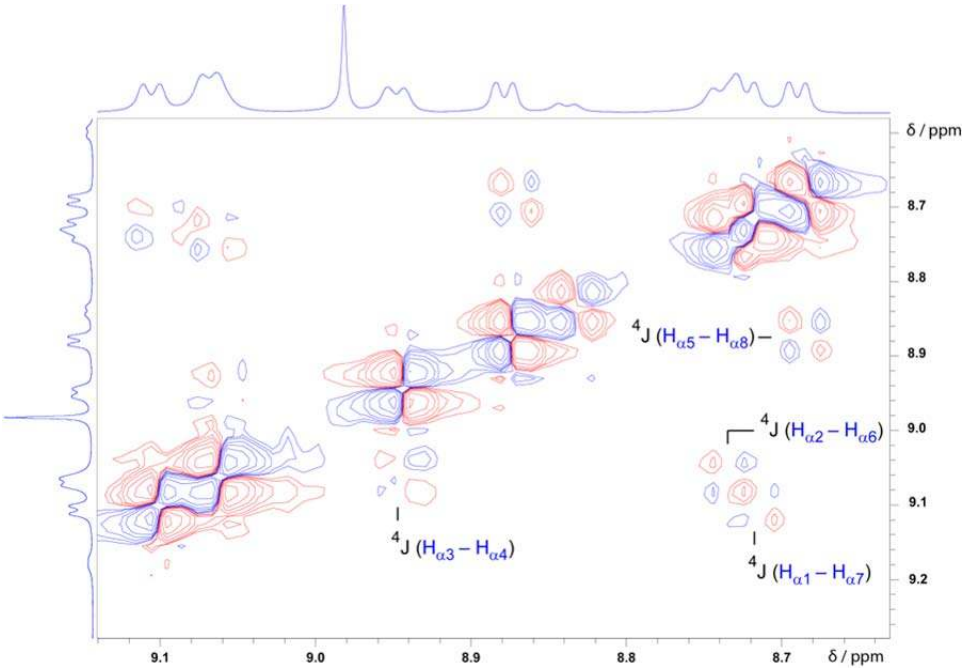

Figure S5. Partial ^{1}H–^{1}H gDQF COSY (600 MHz, CD_3CN, 298 K) spectrum of **HC**•8PF_6 with selected correlations labelled.

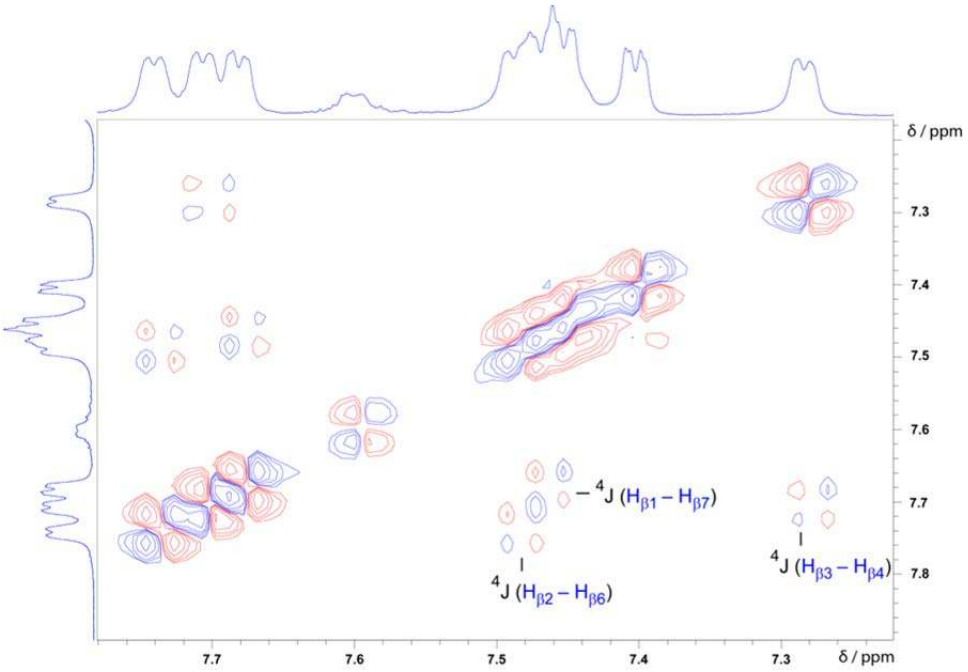

Figure S6. Partial ^{1}H–^{1}H gDQF COSY (600 MHz, CD_3CN, 298 K) spectrum of **HC**•8PF_6 with selected correlations labelled.

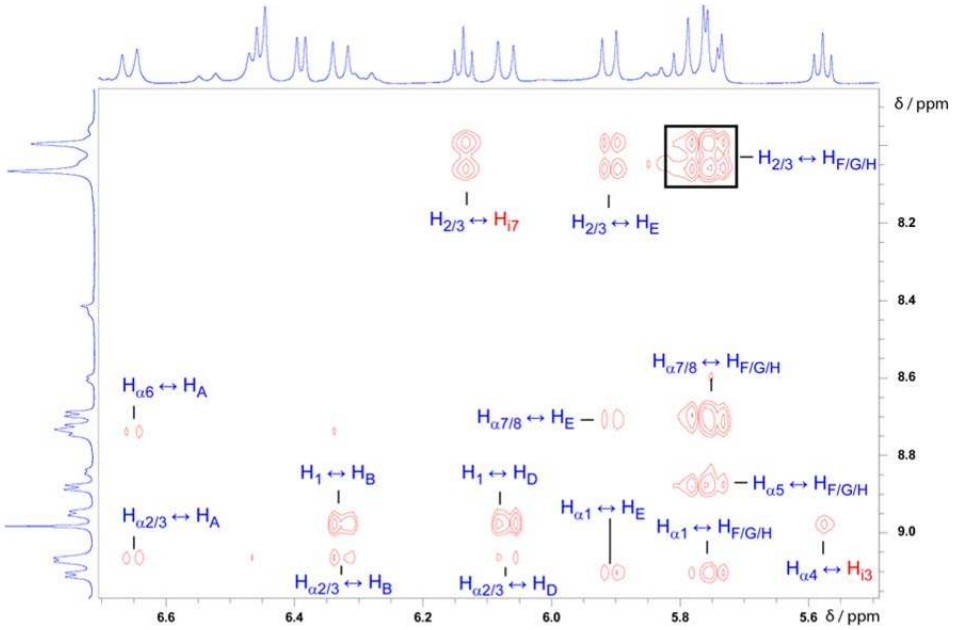

Figure S7. Partial ^{1}H ROESY (600 MHz, CD_3CN, 298 K) spectrum of **HC**•8PF_6 with selected correlations labelled.

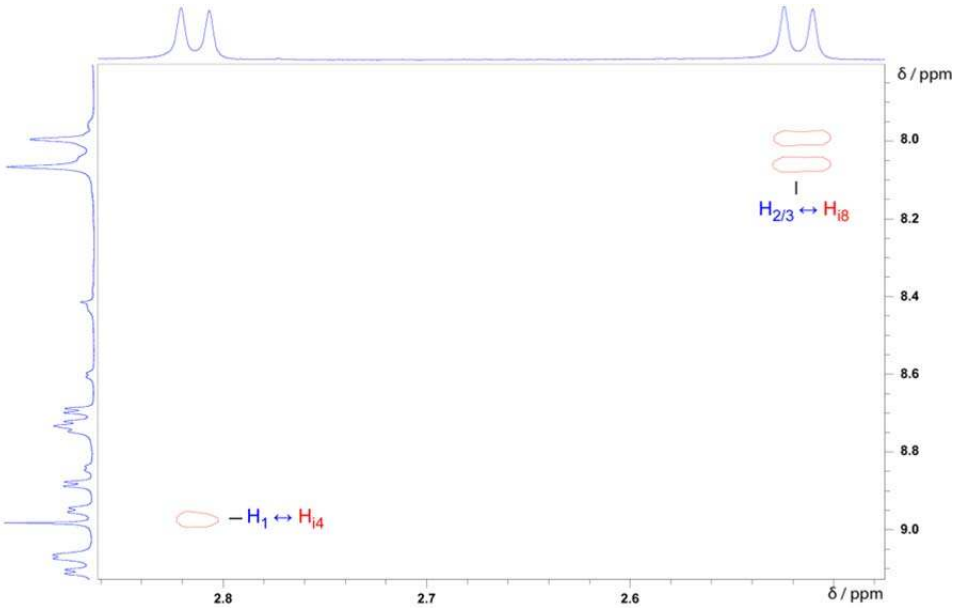

Figure S8. Partial ^{1}H ROESY (600 MHz, CD_3CN, 298 K) spectrum of **HC**•8PF_6 with selected correlations labelled.

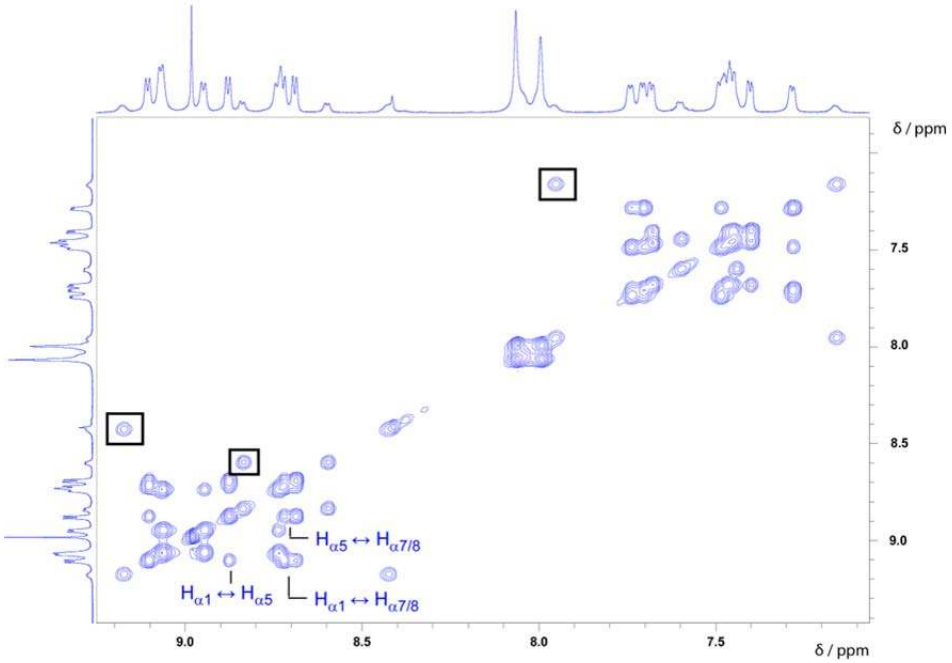

Figure S9. Partial 2D ^{1}H EXSY (600 MHz, CD_3CN, 298 K) spectrum of **HC**•$8PF_6$. Outlined crosspeaks show signals for the *ortho-ortho* isomer undergoing exchange with each other, but no signals are observed to suggest the *ortho-ortho* isomer undergoes exchange with the *meta-meta* isomer.

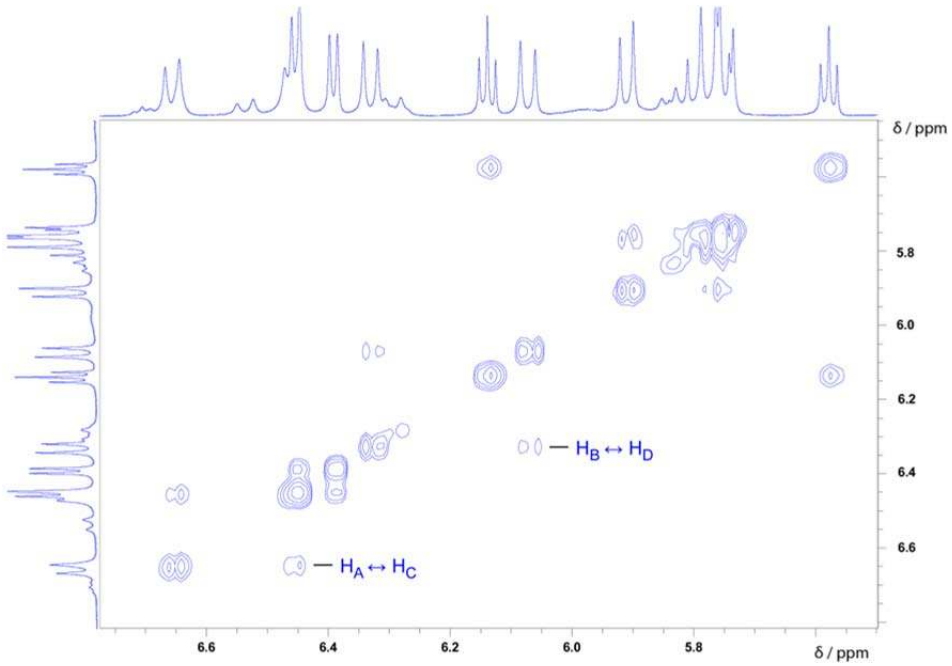

Figure S10. Partial 2D ^{1}H EXSY (600 MHz, CD_3CN, 298 K) spectrum of **HC**•$8PF_6$.

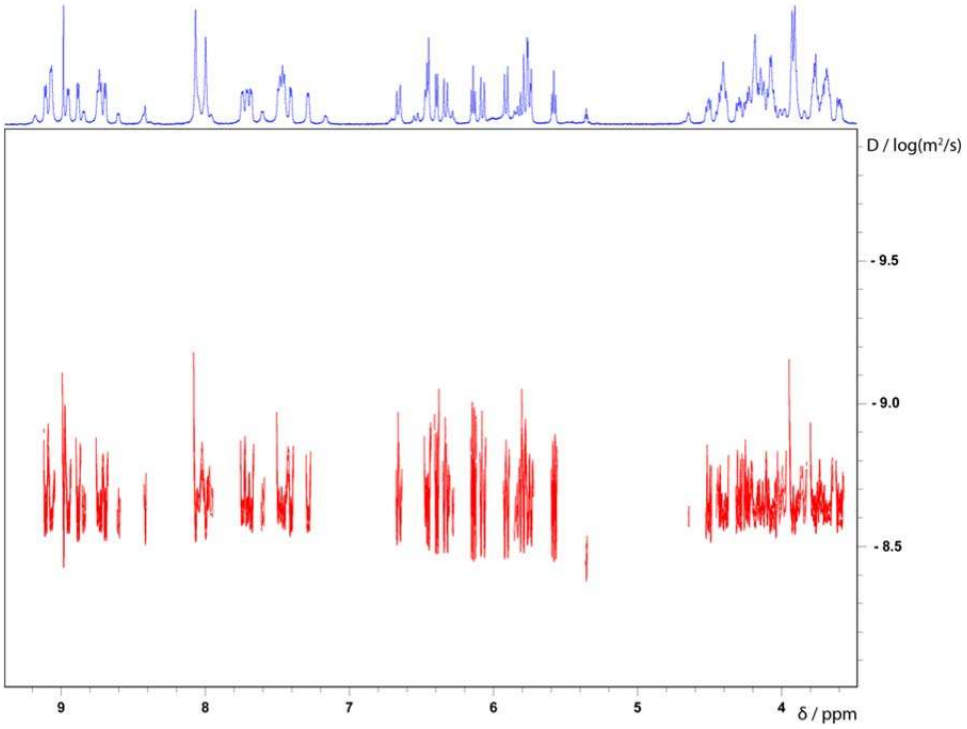

Figure S11. 2D ^{1}H DOSY (600 MHz, CD_3CN, 298 K) spectrum of **HC**•$8PF_6$

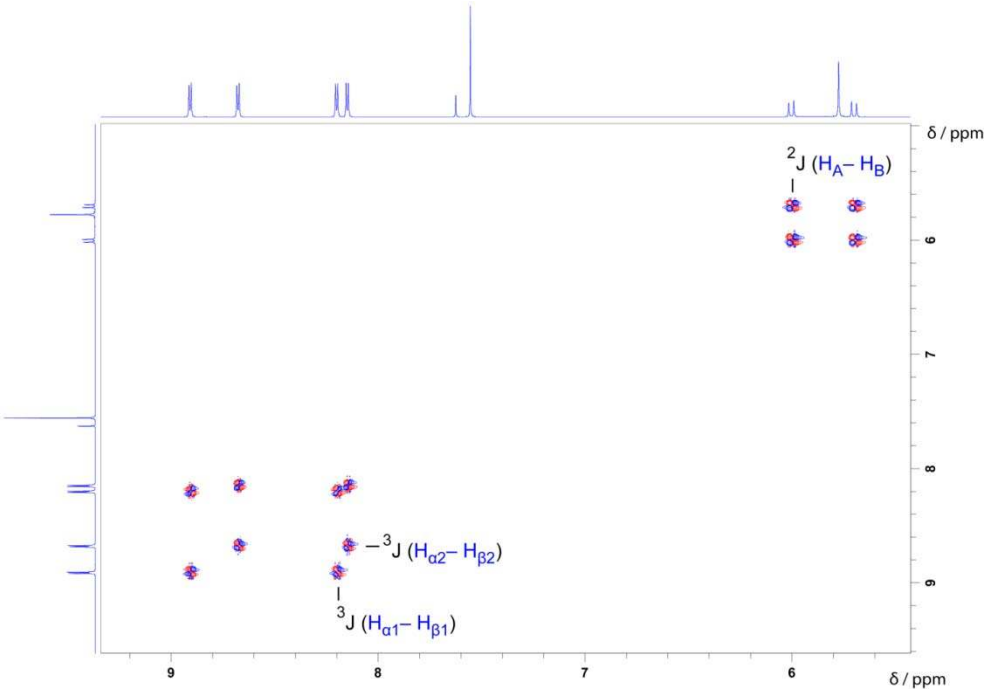

Figure S12. ^{1}H–^{1}H gDQF COSY (600 MHz, CD_3CN, 298 K) spectrum of **DBB**•$8PF_6$ with selected correlations labelled.

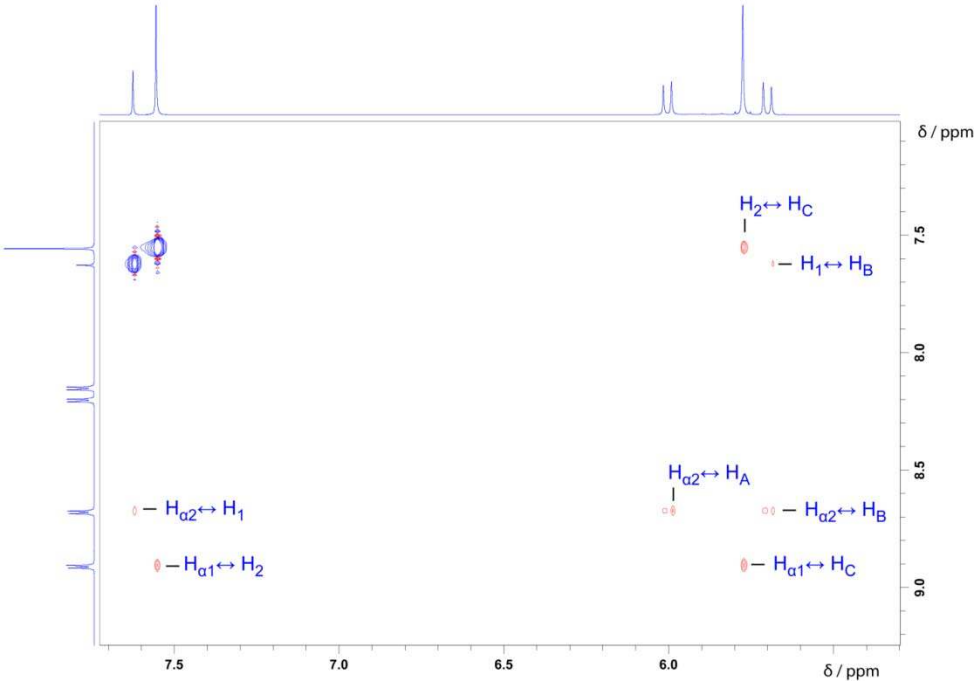

Figure S13. Partial NOESY (600 MHz, CD_3CN, 298 K) spectrum of **DBB**•$8PF_6$ with selected correlations labelled.

S2. Variable-Temperature ^{1}H NMR Spectroscopy

When the handcuff catenane $\mathbf{HC}^{8+}$ is heated to 363 K in CD_3SOCD_3 (Figure S14), no coalescence of the resonances for the *meta-meta* and *ortho-ortho* isomers is observed, supporting our claim that these two species exist as distinct isomer that are not in equilibrium with each other. Upon cooling the sample to 233 K, the signals in the ^{1}H NMR spectrum remain sharp (Figure S15), suggesting that slowing of DNP reorientation does not result in the detection of two co-conformations, and therefore the relative orientations of both DNP units is restricted by the length of the polyether chains; further evidence supporting our claim that DNP reorientation occurs in a concerted manner.

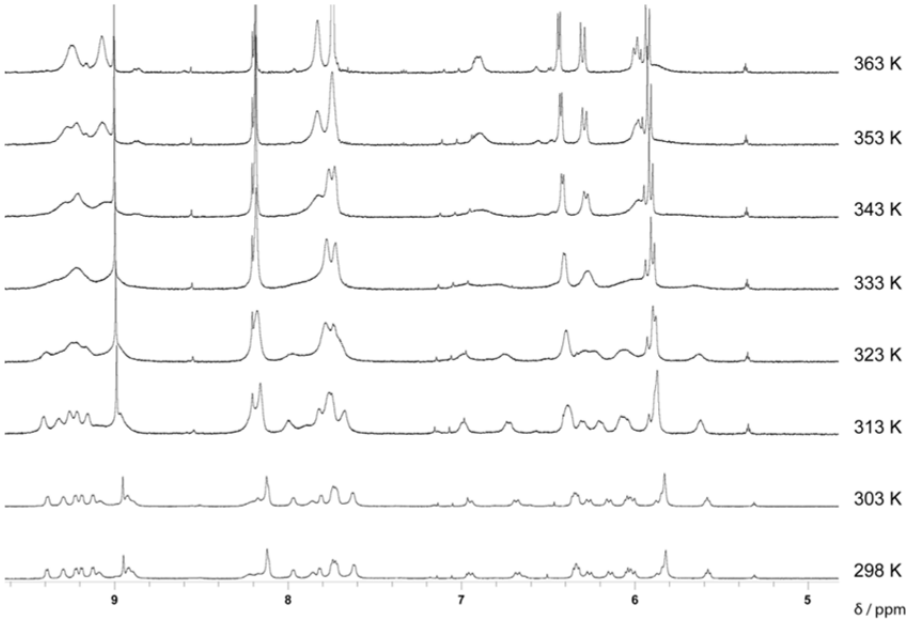

Figure S14. Partial ^{1}H NMR (600 MHz, $(CD_3)_2SO$) spectrum of **HC**•8PF_6. Signals for the *meta-meta* isomer appear to coalesce with increasing temperature. Signals for the *ortho-ortho* isomer, however, do not coalesce with those of the *meta-meta* isomer.

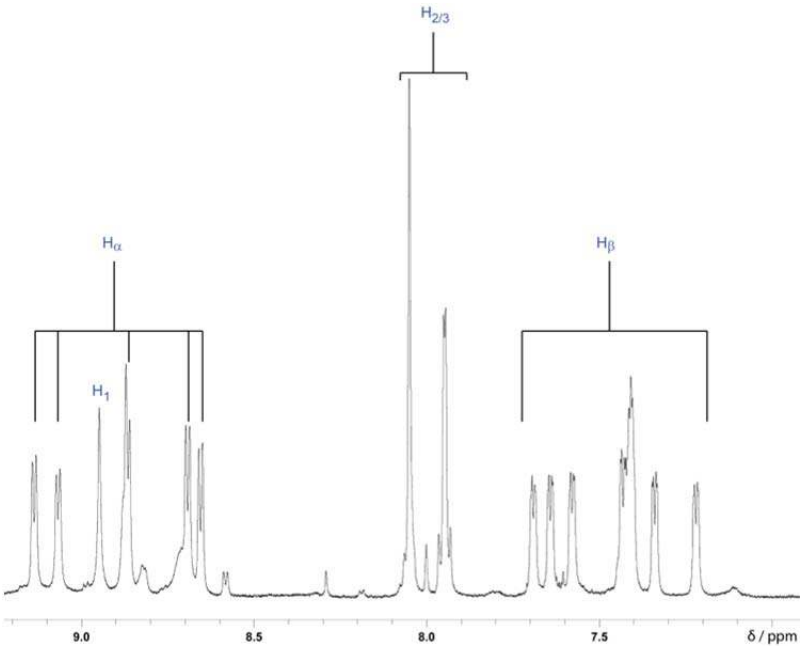

Figure S15. Partial ^{1}H NMR (600 MHz, CD_3CN, 233K) spectrum of **HC**•8PF_6. The signals for H_α, H_β and $H_{1,2,3}$ remain sharp, suggesting that upon cooling, two possible co-conformations of the *meta-meta* isomer that are dependent upon DNP orientation, are not in fast exchange on the ^{1}H NMR timescale and do not exist in solution.

S3. X-Ray Crystal Structures

Data were collected at 100 K using a Bruker d8-APEX II CCD diffractometer (Cu Kα radiation, λ=1.54178 Å). Intensity data were collected using ω and φ scans spanning at least a hemisphere of reciprocal space for all structures (data were integrated using SAINT). Absorption effects were corrected on the basis of multiple equivalent reflections (SADABS). Structures were solved by direct methods (SHELXS[S1]) and refined by full-matrix least-squares against F^2 (SHELXL[S1]). Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries, including those bound to oxygen, as no hydrogen atoms could be located in the difference Fourier map.

S3.1 X-Ray Crystal Structure of Handcuff Catenane HC•8PF_6

Crystals were grown by slow vapor diffusion of *i*-Pr_2O into a solution of **HC**•8PF_6 dissolved in MeCN. The presence of 'flat' and 'torqued' conformations of **HC**•8PF_6 are expressed in terms of disorder in the solid state. The crystal contains the 'flat' and 'torqued' conformations in a ratio of approximately, 7:3 respectively.

Crystal data for **HC**•8PF_6: $C_{110}H_{118}N_8O_{14}$•8(PF_6); purple prism, 0.191 × 0.174 × 0.096 mm^3; monoclinic, space group $P2_1/c$; a = 20.0951(4), b = 31.3942(6), c = 24.2862(5) Å; β = 94.082(1)°; V = 15282.6(5) $Å^3$; Z = 4; ρ_{calcd} = 1.276 gcm^{-3}; T = 100(2) K; $R_1(F^2 > 2\sigma F^2)$ = 0.0893; wR_2 = 0.2511. Out of 111556 reflections collected, a total of 25954 were unique. Crystallographic data (excluding structure factors) for the structures reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC–915345.

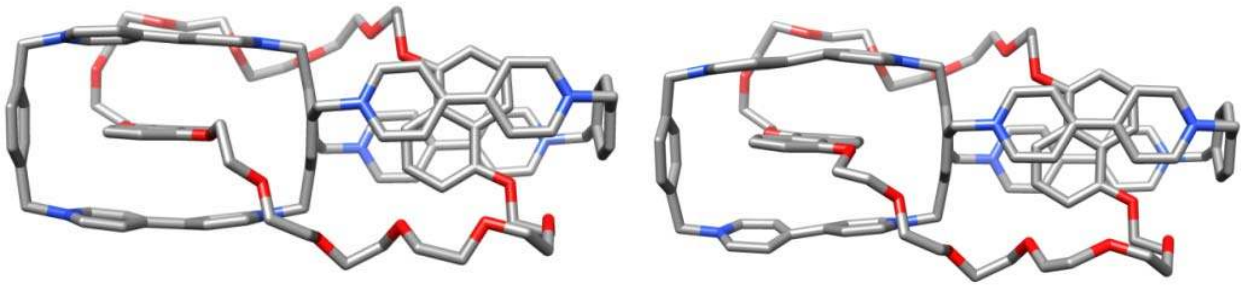

Figure S16. Crystal structure views left: 'flat' co-conformation, and right: 'torqued' co-conformation of **HC**•8PF_6. Hydrogen atoms omitted for the sake of clarity.

S3.2 X-Ray Crystal Structure of Ditopic Host DBB•8PF_6

Crystals were grown by slow vapor diffusion of *i*-Pr_2O into a solution of **DBB**•8PF_6 dissolved in MeCN.

Disordered PF_6^- anions were subjected to SADI restraints to effect an equivalent coordination environment around the P atom. Disordered and partially occupied MeCN solvent molecules were refined with SADI restraints to keep affected bonds equivalent. A global rigid bond (DELU) restraint was applied, and various SIMU restraints were applied to disordered PF_6^- and MeCN molecules. C24T C24S, N9S N9T C17T C18T C17S C18S, and N14S C27S C28S, were respectively refined with group displacement parameters. SOFs were allowed to refine freely, but were fixed (for the multiply-disordered PF_6^- and partially occupied MeCN) during the final refinement stages.

Crystal data for **DBB**•8PF_6: $C_{66}H_{58}N_8$•8(PF_6);6.86(C_2H_3N); colorless needle, 0.269 × 0.055 × 0.04 mm^3; triclinic, space group $P\bar{1}$; a = 16.6223(5), b = 22.9236(6), c = 29.6344(8) Å; α = 71.154(2), β = 78.075(2), γ = 73.175(2)°; V = 10149.1(5) $Å^3$; Z = 4; ρ_{calcd} = 1.574 gcm^{-3}; T = 100(2) K; $R_1(F^2 > 2\sigma F^2)$ = 0.0983; wR_2 = 0.2597. Out of 59810 reflections collected, a total of 24665 were unique. Crystallographic data (excluding structure factors) for the structures reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC–915343.

S3.3 X-Ray Crystal Superstructure of Inclusion Complex (**BHEEN**)$_2$ ⊂ **DBB**•8PF_6

Crystals were grown by slow vapor diffusion of *i*-Pr_2O into an MeCN solution containing **BHEEN** and **DBB**•8PF_6 in a ratio of 4:1, respectively.

Rigid bond restraints (esd 0.01) were imposed on the displacement parameters as well as restraints on similar amplitudes (esd 0.05) separated by less than 1.7 Å on the disordered fluorine and polyether chains. The disordered polyether chains were refined with distance restraints. Group anisotropic displacement parameters were refined for C79 C80 C79a C80a and also the C109 to O15 polyether chain. The solvent masking procedure as implemented in Olex2 was used to remove the electronic contribution of solvent molecules from the refinement. Only the atoms used in the refinement model are reported in the formula here. Total solvent accessible volume / cell = 487.7 $Å^3$ [6.6%] Total electron count / cell = 77.2.

Crystal data for (**BHEEN**)$_2$ ⊂ **DBB**•8PF_6: $C_{66}H_{58}N_8$•8(PF_6), 2.5($C_{18}H_{24}O_6$), 7(C_2H_3N); purple block, 0.153 × 0.115 × 0.066 mm^3; triclinic, space group $P\bar{1}$; a = 16.475(4), b = 18.609(5), c = 25.278(6) Å, α = 105.106(8), β = 99.281(7), γ = 93.008(6)°; V = 7348(3) $Å^3$, Z = 2; ρ_{calcd} = 1.469 gcm^{-3}; T = 100(2) K; $R_1(F^2 > 2\sigma F^2)$ = 0.0668; wR_2 = 0.1811. Out of 58131 reflections collected, a total of 23976 were unique. Crystallographic data (excluding structure factors) for the

structures reported in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC–915344.

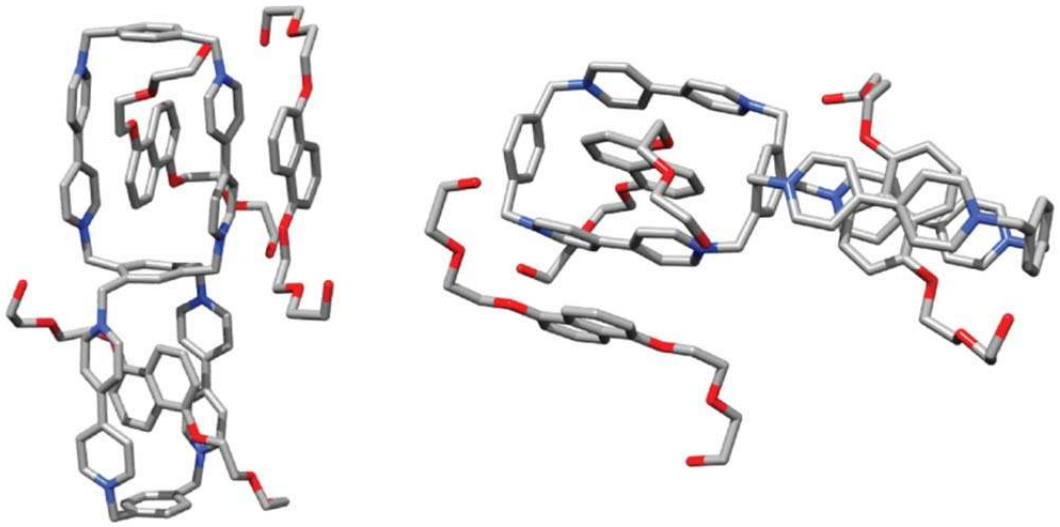

Figure S17. Crystal superstructure views of (**BHEEN**)$_2$ ⊂ **DBB**•8PF$_6$. Hydrogen atoms omitted for the sake of clarity.

S4. Quantum Mechanical Calculations

Density Functional Theory (DFT) calculations were performed with the B3LYP-D3 exchange-correlation functional[S2] using the Jaguar[S3] software package run in parallel on multiple processors. The pseudospectral[S4] methodology, which speeds up the SCF iterations significantly, was employed for all calculations. Ultra-fine DFT grids as implemented in Jaguar (specified with the keywords gdftmed=-13, gdftfine=-13 and gdftgrad=-13) were used for the calculations to improve the structural convergence during the geometry optimizations. All structures were optimized with the 6-31G** basis set in vacuum. Single-point calculations on the B3LYP-D3/6-31G** optimized structures were then performed with the larger 6-311G**++ basis set, while estimates for the solvation energies were computed with either the continuum Poisson Boltzman[S3] or the SM8[S5] solvent model implemented in Jaguar using solvent parameters for dimethylformamide at the B3LYP-D3/6-31G** level.

The calculated results indicate that in vacuum, the two topologies (*meta-meta*, co-conformation 2 and *ortho-ortho*, co-conformation 1) have very similar energies, which differ by less than 2.5 kcal/mol. Solvation seems to favour the experimentally preferred *meta-meta* isomer by several kcal/mol, however, with both solvation models (see Table S1).

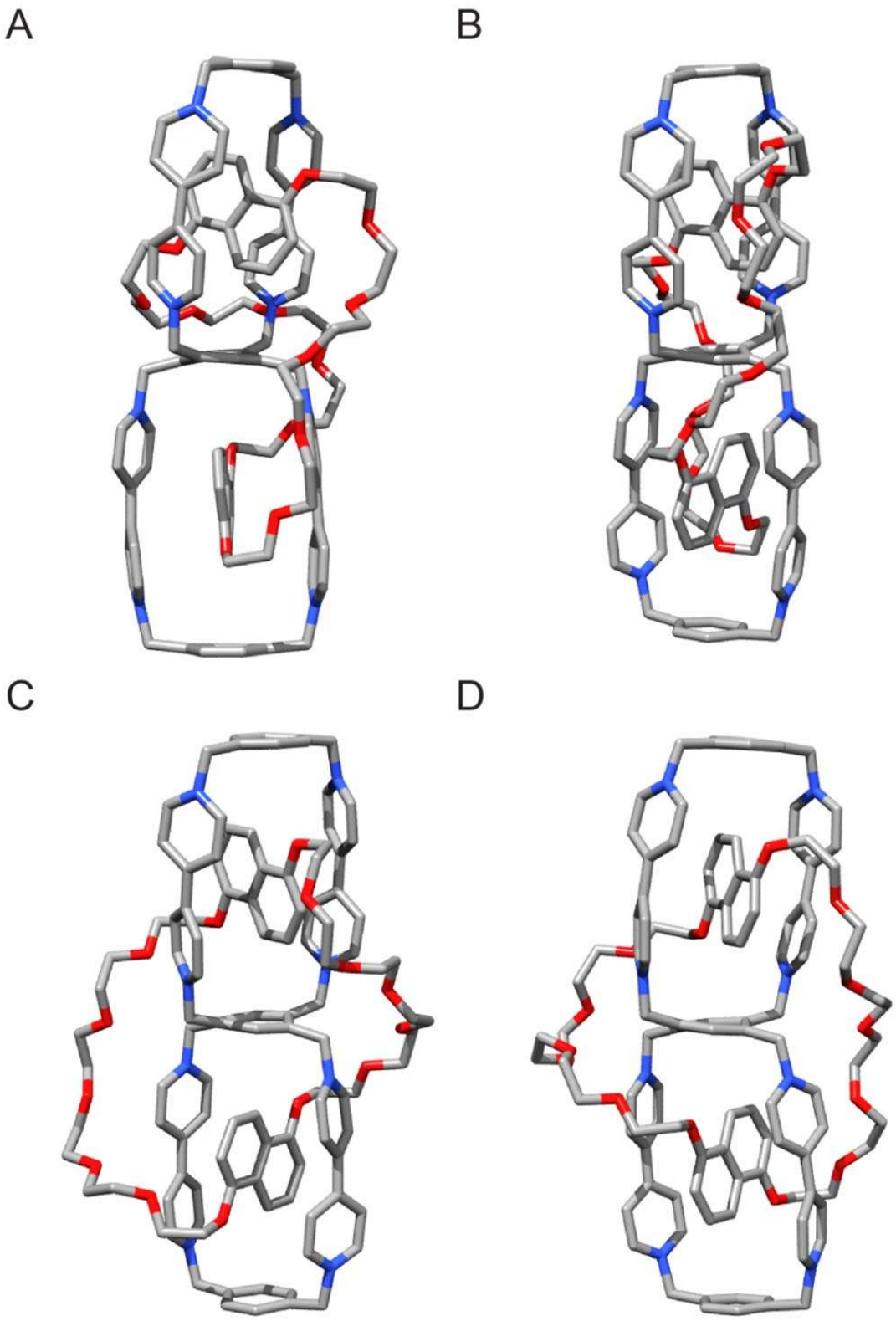

Figure S18. DFT-optimized structures of a) *meta-meta* isomer, co-conformation 1, b) *meta-meta* isomer, co-conformation 2, the experimentally observed structure, c) *ortho-ortho* isomer, co-conformation 1 and b) *ortho-ortho* isomer, co-conformation 2.

S4.1. DFT-Optimized Structures and Energies

The four different structures considered for DFT calculations are shown in Figure S18. These structures were chosen based on the two possible topologies – *meta-meta* and *ortho-ortho* – as well as the two possible combinations of DNP orientations within each cyclophane – co-conformations 1 and 2. Co-conformation 2 is the co-conformation that is observed by single-crystal X-ray diffraction.

Table S1. Relative Computed DFT-Energies (in kcal/mol) of the different Handcuff-Catenane Topologies.

	In Vacuum[a]	**PBF Solvation[b]**	**SM8 Solvation[c]**
(A) *Meta-Meta* isomer, Co-conformation 1	14.36	16.24	5.51
(B) *Meta-Meta* isomer, Co-conformation 2 (experimentally observed topology)	0.00	0.00	0.00
(C) *Ortho-Ortho* isomer, Co-conformation 1	**–2.44**	**5.94**	**2.37**
(D) *Ortho-Ortho* isomer, Co-conformation 2	6.40	10.23	7.61

[a] B3LYP-D3/6-311G**++//B3LYP-D3/6-31G** level. [b] Vacuum energies + solvation energies computed at the B3LYP-D3/6-31G** level with the Poisson-Boltzman solvation model. [c] Vacuum energies + solvation energies computed at the B3LYP-D3/6-31G** level with the SM8 solvation model.

Meta-Meta Isomer, Co-Conformation 1 (XYZ-Coordinates in Å, Total Charge: +8)

B3LYP-D3/6-311G**++//B3LYP-D3/6-31G** energy = -5752.37084 a.u.
Solvation Energy at the B3LYP-D3/6-31G** level with the PBF solvation model = -1251.38 kcal/mol
Solvation Energy at the B3LYP-D3/6-31G** level with the SM8 solvation model = -1342.25 kcal/mol

H	-0.76950	0.90240	-0.02950
C	-0.64800	1.12310	1.02730
C	-0.50920	1.65120	3.71060
C	-0.47470	0.04800	1.91320
C	-0.72530	2.45740	1.44880
C	-0.46800	2.72770	2.81320
C	-0.59690	0.31390	3.29910
H	-0.49160	1.88430	4.77070
C	-0.11960	-1.30530	1.30880
H	-0.49030	-2.15310	1.88360
H	-0.53800	-1.38440	0.30200
C	-0.16160	4.10910	3.38080
H	-0.59510	4.23490	4.37370
H	-0.54260	4.91640	2.76040
C	-1.16120	3.50820	0.43080
H	-0.96320	3.21170	-0.59970
H	-0.68140	4.47730	0.54680
C	-0.88120	-0.74720	4.36020
H	-0.61570	-1.75610	4.04370
H	-0.33280	-0.54510	5.28190
N	1.37900	-1.50680	1.20490
C	4.17770	-1.76990	1.11550
C	2.02800	-2.28350	2.10820
C	2.09340	-0.89700	0.22270
C	3.47060	-1.02570	0.15290
C	3.40220	-2.43420	2.08420
H	1.41890	-2.79600	2.84270
H	1.53330	-0.30050	-0.48510
H	3.99120	-0.48900	-0.63010
H	3.85210	-3.08920	2.82170
N	1.32310	4.33810	3.49100
C	4.11690	4.65470	3.58380
C	1.99710	4.09990	4.64510
C	2.00440	4.74490	2.39130
C	3.36730	4.94430	2.42650
C	3.37760	4.22920	4.70330
H	1.41640	3.82700	5.51930
H	1.45800	4.87880	1.46710
H	3.82040	5.30680	1.51500
H	3.84480	3.93210	5.63250
N	-2.34540	-0.80290	4.74480
C	-5.09860	-0.77670	5.35280
C	-3.23580	-1.45330	3.95220
C	-2.79850	-0.17290	5.85780
C	-4.14430	-0.15700	6.18280
C	-4.58830	-1.46370	4.23470
H	-2.83640	-1.95410	3.08210
H	-2.05690	0.31440	6.47890
H	-4.43260	0.34380	7.09940
H	-5.24310	-1.96870	3.53610
N	-2.64670	3.74040	0.51440
C	-5.41340	4.17850	0.66580
C	-3.48840	2.98800	-0.23320
C	-3.14660	4.71350	1.31430
C	-4.50070	4.95630	1.40660
C	-4.86000	3.19190	-0.16830
H	-3.04180	2.24230	-0.88660
H	-2.43250	5.30560	1.86910
H	-4.82220	5.74900	2.07160
H	-5.48320	2.54110	-0.76880
C	5.61020	4.74870	3.58800
N	8.41710	4.63320	3.53810
C	6.37070	4.67030	4.76810
C	6.33980	4.87990	2.39340
C	7.72210	4.81660	2.39410
C	7.75550	4.60120	4.71710
H	5.90640	4.64510	5.74400
H	5.85750	4.96910	1.43140
H	8.29890	4.86980	1.47930
H	8.36030	4.51270	5.61210
C	5.67060	-1.78170	1.16950
N	8.44840	-1.51860	1.38810
C	6.48150	-1.62410	0.03450
C	6.32440	-1.87460	2.41080
C	7.69950	-1.74240	2.49150
C	7.85980	-1.49230	0.17200
H	6.07020	-1.61110	-0.96880
H	5.77600	-1.99150	3.33740
H	8.22480	-1.77740	3.43750
H	8.51120	-1.36060	-0.68500
C	-6.88800	4.36980	0.81950
N	-9.63840	4.48720	1.33780
C	-7.40080	5.05680	1.93430
C	-7.82790	3.82020	-0.06790
C	-9.18660	3.88530	0.21590
C	-8.76250	5.09690	2.16830
H	-6.75290	5.51710	2.66830
H	-7.53550	3.33130	-0.98960
H	-9.93230	3.45090	-0.44070
H	-9.18210	5.57810	3.04220
C	-6.56840	-0.64140	5.58750
N	-9.32710	-0.19650	5.81870
C	-7.08320	0.46900	6.28070
C	-7.50620	-1.54980	5.06940
C	-8.86910	-1.30170	5.19140
C	-8.44930	0.66710	6.37810
H	-6.43700	1.22850	6.70170
H	-7.20870	-2.46800	4.57590
H	-9.61280	-1.98280	4.79250
H	-8.86980	1.53230	6.87480
C	9.90610	4.31600	3.45700
H	10.31900	4.47010	4.45520
H	10.35280	5.05250	2.78540
C	9.93230	-1.19940	1.55530
H	10.40530	-1.37090	0.58700
H	10.32940	-1.93550	2.25680
C	10.07760	2.88820	2.96890
C	10.08900	0.22700	2.05030
C	10.19870	2.60930	1.60070
C	10.06960	1.82350	3.88020
C	10.08220	0.50460	3.42510
C	10.19750	1.28950	1.14420
H	10.31140	3.41660	0.88160
H	10.06330	2.01680	4.94920
H	10.10270	-0.30510	4.14950
H	10.29970	1.09630	0.07950
C	-11.09570	4.36340	1.76500
H	-11.40530	5.34710	2.12470
H	-11.67230	4.13430	0.86830
C	-10.81170	0.16310	5.79570
H	-11.07070	0.47490	6.80930
H	-11.35650	-0.75600	5.57400
C	-11.20070	3.28560	2.82850
C	-11.05300	1.25600	4.77180
C	-11.37960	1.94360	2.46740
C	-11.06300	3.61140	4.18460
C	-10.98880	2.60470	5.14830
C	-11.30610	0.93670	3.43130
H	-11.58210	1.67500	1.43390
H	-11.03480	4.65070	4.50060
H	-10.90630	2.88040	6.19640
H	-11.45340	-0.09730	3.13050
H	7.49320	1.97890	0.45520
C	6.55840	1.86780	0.99330
H	7.51560	1.42210	2.85530
C	6.57870	1.54800	2.33260
C	4.14390	1.94570	0.96870
C	5.35840	1.38210	3.03830
C	5.34360	2.09470	0.30200
C	4.11910	1.52290	2.34020
C	5.32670	1.05260	4.43930
H	5.37910	2.39210	-0.73920
H	1.97080	1.32600	2.45810
C	4.12010	0.76840	5.05930
H	4.07830	0.56510	6.11930
C	2.92230	0.83900	4.32150
H	1.98970	0.61530	4.83270
C	2.90100	1.22990	2.99980
H	-7.21520	-0.51820	0.98480
C	-6.95360	0.23570	1.71710
C	-5.63740	0.52920	2.01100
C	-7.71900	1.90260	3.32010
C	-5.30770	1.53860	2.97780
C	-7.98900	0.92990	2.38470
C	-6.37310	2.23410	3.63020
C	-3.96210	1.85590	3.28980
H	-9.01710	0.68370	2.14860
H	-8.52600	2.41850	3.82270
C	-3.69040	2.81010	4.24700
H	-3.16750	1.34920	2.76030
H	-2.66870	3.06930	4.50330
C	-4.72060	3.50320	4.90800
H	-4.44650	4.28510	5.59600
C	-6.04150	3.25610	4.58630
O	6.54040	1.02570	5.04140
O	2.90260	2.13920	0.42350
O	-4.56040	-0.09980	1.44670
O	-7.10720	3.91220	5.11910
C	-4.80470	-1.12870	0.47120
H	-5.28160	-0.70090	-0.41860
H	-5.47670	-1.89310	0.88360
C	-3.47410	-1.77130	0.11650
H	-2.94820	-2.02240	1.04550
H	-3.66500	-2.71420	-0.41300
C	-6.91780	5.01990	6.03930
H	-6.14100	4.78090	6.77300
H	-7.86950	5.09650	6.57110
C	-6.63810	6.33870	5.32400
H	-7.42150	6.52210	4.57990
H	-6.70780	7.15480	6.05430
O	-5.37850	6.34660	4.64370
O	-2.61600	-0.91740	-0.63010
C	-4.35380	7.09540	5.32070
H	-4.37650	6.89730	6.40140
H	-4.53070	8.16990	5.17880
C	-2.98310	6.72750	4.75510
H	-2.29780	7.57410	4.88860
H	-3.08560	6.55200	3.67890
O	-2.40890	5.53070	5.31230
C	-1.69080	5.76600	6.53090
H	-2.25760	6.42930	7.19760
H	-0.72970	6.25830	6.32190
C	-1.46740	4.46630	7.27550
H	-2.41770	3.92170	7.37530
H	-1.11210	4.71580	8.28180
O	-0.50770	3.62440	6.60280
C	-0.07220	2.52610	7.42020
H	0.33830	1.77290	6.73370
H	-0.93590	2.08660	7.94250
C	0.99760	2.85920	8.44900
H	1.05290	2.01240	9.15090
H	0.70740	3.73960	9.04210
O	2.25710	3.06450	7.81760
C	3.28200	3.15920	8.82700
H	3.30220	2.23110	9.41490
H	3.06410	3.99160	9.51120
C	4.65250	3.38190	8.22710
H	5.35590	3.50830	9.06120
H	4.67460	4.31580	7.64100
O	5.00900	2.26500	7.40930
C	6.40660	2.01150	7.32890
H	6.81980	1.80710	8.32780
H	6.95330	2.87260	6.91560
C	6.67000	0.78540	6.46720
H	7.71550	0.49390	6.58780
C	2.80520	-1.05970	-2.05480
H	-3.85860	-0.90630	-2.31960
H	-2.51630	-2.07230	-2.36720
C	-1.96550	-0.03790	-2.78210
H	-0.91550	-0.09080	-2.44250
H	-1.97380	-0.29360	-3.85010
O	-2.50290	1.26390	-2.57050
C	-2.12630	2.18800	-3.60870
H	-2.35640	1.74720	-4.58770
H	-1.04710	2.39450	-3.56730
C	-2.89610	3.48280	-3.47680
H	-3.97050	3.27720	-3.36130
H	-2.76580	4.04560	-4.40940
O	-2.40710	4.24100	-2.36470
C	-2.52180	5.65490	-2.57210
H	-3.57430	5.97410	-2.56360
H	-2.09690	5.92230	-3.54800
C	-1.75560	6.39610	-1.49480
H	-2.19930	6.22360	-0.49730
H	-1.82190	7.47460	-1.69770
O	-0.41330	5.93610	-1.52390
C	0.49090	6.68970	-0.74280
H	0.47160	7.75770	-1.00530
H	0.24680	6.61670	0.33720
C	1.87830	6.14740	-1.01910
H	2.63760	6.74990	-0.50040
H	2.06880	6.20750	-2.09740
O	1.93330	4.77390	-0.58370
C	2.98980	4.03820	-1.18420
H	3.96950	4.35630	-0.79500
H	3.00610	4.20300	-2.27120
C	2.76510	2.55280	-0.94940
H	1.72930	2.31340	-1.20550
H	3.42640	1.96590	-1.59790
H	6.04360	-0.05660	6.77870

Meta-Meta Isomer, Co-Conformation 2 (XYZ-Coordinates in Å, Total Charge: +8)

B3LYP-D3/6-311G**++//B3LYP-D3/6-31G** energy = -5752.39372 a.u.
Solvation Energy at the B3LYP-D3/6-31G** level with the PBF solvation model = -1253.26 kcal/mol
Solvation Energy at the B3LYP-D3/6-31G** level with the SM8 solvation model = -1333.40 kcal/mol

N	11.82810	23.62140	23.58820
N	11.22500	23.83580	30.62550
N	15.58550	18.97130	30.98000
N	15.47300	18.49840	23.94170
N	15.57970	23.35570	19.80890
N	15.94670	22.83500	12.77270
N	11.47970	18.09440	13.04930
N	11.77570	18.32260	20.11120
C	10.85210	22.89470	24.19590
H	10.27730	22.20700	23.58970
C	10.59090	23.02030	25.55030
H	9.79070	22.40470	25.94890
C	11.34450	23.90190	26.34790
C	12.30530	24.68320	25.67470
H	12.92100	25.40510	26.19610
C	12.52890	24.52260	24.32300
H	13.26860	25.11350	23.79780
C	11.19870	23.95140	27.83230
C	10.54500	22.92180	28.52930
H	10.01600	22.11190	28.03910
C	10.58140	22.88520	29.91410
H	10.10760	22.06880	30.45040
C	11.78780	24.88970	29.99190
H	12.24280	25.65350	30.61250
C	11.78300	24.97120	28.60720
H	12.23930	25.84820	28.16450
C	11.40230	23.63250	32.11960
H	10.42020	23.38270	32.52620
H	11.70910	24.59060	32.54070
C	12.42570	22.53610	32.35410
C	12.01700	21.21120	32.54870
H	10.96210	20.97780	32.66230
C	12.96010	20.18390	32.62540
H	12.62250	19.16670	32.80650
C	14.32690	20.46660	32.50540
C	14.73890	21.80270	32.40110
H	15.79690	22.05160	32.39530
C	13.79650	22.82810	32.32860
H	14.13650	23.85860	32.26740
C	15.34500	19.34410	32.44080
H	15.00820	18.43540	32.94460
H	16.31300	19.62410	32.85970
C	14.63510	18.27120	30.32040
H	13.79200	17.92680	30.90560
C	14.72440	18.05000	28.95790
H	13.90860	17.52730	28.47480
C	15.80420	18.56910	28.22310
C	16.80610	19.23640	28.94450
H	17.70430	19.61120	28.46640
C	16.67340	19.42020	30.31640
H	17.42640	19.93520	30.90270
C	15.79590	18.48310	26.73300
C	15.19260	17.40870	26.05380
H	14.83820	16.53020	26.58170
C	15.04240	17.44260	24.67870
H	14.57890	16.62330	24.14220
C	16.11540	19.52320	24.56050
H	16.45380	20.36180	23.96230
C	16.29470	19.52510	25.93370
H	16.76620	20.39470	26.37410
C	15.22990	18.53400	22.44270
H	14.79940	17.56780	22.18460
H	16.21850	18.59890	21.98180
C	14.37220	19.71990	22.01370
C	12.96280	19.73030	21.84220
C	12.32110	20.97390	21.85240
H	11.23390	20.98380	21.84900
C	13.00150	22.20030	21.86710
C	14.40370	22.16730	21.68530
C	15.04940	20.93190	21.83830
H	16.13760	20.91240	21.82550
C	12.14130	23.43570	22.12130
H	12.60840	24.36300	21.78880
H	11.18510	23.33260	21.59950
C	15.30560	23.33390	21.29090
H	14.88880	24.30900	21.54120
H	16.26700	23.23930	21.80190
C	16.57060	22.60120	19.26070
H	17.20900	22.02770	19.92630
C	16.76780	22.56820	17.88800
H	17.56510	21.92960	17.52510
C	15.95160	23.31910	17.02290
C	14.96780	24.12360	17.63160
H	14.29180	24.73530	17.04780
C	14.79830	24.11600	18.99910
H	14.03720	24.71680	19.48000
C	16.05220	23.21570	15.53740
C	16.66730	22.10990	14.92780
H	17.19050	21.34010	15.48520
C	16.59410	21.94270	13.55360
H	17.03310	21.07060	13.07680
C	15.42110	23.95630	13.31550
H	14.96350	24.66640	12.63580
C	15.46630	24.17020	14.68500
H	15.04460	25.09690	15.05570
C	15.72330	22.49370	11.31070
H	15.42720	23.41390	10.80590
H	16.68720	22.17920	10.90570
C	14.66890	21.40620	11.21300
C	15.04310	20.05700	11.18030
H	16.09100	19.78340	11.09490
C	14.07330	19.05440	11.23610
H	14.38300	18.01420	11.17670
C	12.71480	19.38520	11.33120
C	12.33730	20.73360	11.27410
H	11.28610	21.00940	11.25930
C	13.30660	21.73530	11.21280
H	12.99330	22.77410	11.15150
C	11.67300	18.30460	11.54940
H	10.69670	18.56330	11.13670
H	11.96970	17.33880	11.13430
C	12.43790	17.44190	13.74490
H	13.24450	17.00700	13.16880
C	12.40230	17.37570	15.12530
H	13.22960	16.88820	15.62390
C	11.36500	17.99570	15.84380
C	10.34800	18.60260	15.09010
H	9.47340	19.04420	15.55390
C	10.43150	18.64100	13.70250
H	9.66760	19.11220	13.09400
C	11.41680	18.05330	17.33540
C	12.13680	17.10440	18.08470
H	12.57030	16.22420	17.62440
C	12.31180	17.26840	19.44600
H	12.87620	16.55260	20.03130
C	11.01650	19.22340	19.43130
H	10.57830	20.04280	19.99070
C	10.82950	19.10290	18.06450
H	10.26200	19.88140	17.57030
C	12.06750	18.52140	21.58410
H	12.48520	17.58090	21.94300
H	11.09790	18.66360	22.06460
O	14.95620	22.65550	25.18650
O	17.46340	22.33240	23.80970
O	18.40270	20.46930	21.72600
O	18.68170	20.46670	18.81390
O	19.25780	20.60840	15.89590
O	18.04500	19.36730	13.48760
O	15.59250	18.77210	14.89940
O	12.24810	22.32650	18.36210
O	9.76510	22.32180	19.88590
O	9.02150	20.37360	21.86490
O	8.50510	21.00890	24.66970
O	7.85070	21.50770	27.52310
O	9.03420	20.41310	30.02460
O	11.57310	19.52960	29.01490
C	14.57310	22.30830	26.45820
C	15.05550	22.86890	27.62320
H	15.82290	23.63400	27.60960
C	14.54050	22.43500	28.86820
H	14.92390	22.88490	29.77700
C	13.56890	21.46200	28.94870
H	13.17930	21.15200	29.90930
C	13.08070	20.84940	27.76510
C	13.59610	21.26020	26.50010
C	13.16760	20.60510	25.31680
H	13.56180	20.93090	24.36690
C	12.29290	19.54800	25.40040
H	12.00640	19.01370	24.49910
C	11.74010	19.13710	26.63230
H	11.04050	18.31160	26.65330
C	12.08760	19.80290	27.79730
C	15.87520	23.73310	24.95610
H	15.77000	24.52190	25.70810
H	15.57470	24.15450	23.99310
C	17.32040	23.28550	24.86960
H	17.93400	24.17730	24.68180
H	17.65820	22.84970	25.82120
C	18.83880	22.20740	23.37890
H	19.51740	22.42620	24.21250
H	19.03830	22.93520	22.58240
C	19.14220	20.80440	22.90840
H	20.22040	20.75730	22.70660
H	18.93170	20.07710	23.70800
C	19.03760	19.40310	20.99700
H	18.90350	18.44370	21.52140
H	20.11720	19.58810	20.93910
C	18.44870	19.30800	19.59930
H	18.84040	18.40050	19.11790
H	17.36090	19.20390	19.66430
C	19.98710	20.53940	18.19700
H	20.75220	20.10140	18.84890
H	20.21190	21.60330	18.08380
C	20.03920	19.86430	16.83590
H	21.09090	19.82970	16.52270
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C	19.79880	20.62660	14.56230
H	20.88750	20.76030	14.58970
H	19.37980	21.51270	14.07630
C	19.46350	19.38230	13.75510
H	20.01560	19.39270	12.80760
H	19.75900	18.48100	14.30620
C	17.41570	18.09350	13.51230
H	18.12330	17.27950	13.31720
H	16.66290	18.06990	12.71750
C	16.74330	17.88620	14.85840
H	16.40870	16.85150	14.99970
H	17.44720	18.16050	15.65100
C	15.10940	19.19640	16.08530
C	15.50330	18.70070	17.31810
H	16.22850	17.90000	17.38680
C	14.96160	19.25490	18.49780
H	15.27750	18.85210	19.45520
C	14.05510	20.28820	18.46290
H	13.66210	20.72080	19.37000
C	13.60070	20.78450	17.21420
C	14.10530	20.22710	16.00220
C	13.60730	20.69180	14.75670
H	13.99520	20.27250	13.83670
C	12.63320	21.66490	14.72950
H	12.24330	22.00630	13.77740
C	12.12430	22.23940	15.91870
H	11.35460	22.99840	15.84450
C	12.61880	21.82570	17.13890
C	11.33290	23.42900	18.44840
H	11.41870	24.09530	17.58490
H	11.64200	23.99450	19.33180
C	9.89620	22.97920	18.62380
H	9.24210	23.86190	18.57680
H	9.60140	22.30890	17.80180
C	8.39420	21.97810	20.16380
H	7.74040	22.84270	19.98470
H	8.07040	21.16300	19.50100
C	8.25440	21.56390	21.60960
H	7.19150	21.38530	21.80810
H	8.57450	22.37510	22.27490
C	8.40200	19.44430	22.77340
H	8.72770	18.43860	22.47860
H	7.31250	19.47130	22.65550
C	8.81580	19.69660	24.21960
H	8.37260	18.92190	24.86080
H	9.90400	19.60900	24.30090
C	7.17960	21.18340	25.22150
H	6.43290	20.67380	24.59950
H	6.98330	22.25750	25.18030
C	7.05030	20.69890	26.65680
H	5.98870	20.77130	26.92920
H	7.33050	19.63820	26.74300
C	7.31830	21.62790	28.85460
H	6.23380	21.79160	28.82230
H	7.76620	22.53010	29.28190
C	7.61960	20.42910	29.74140
H	7.05140	20.50370	30.67680
H	7.32080	19.49890	29.24120
C	9.60190	19.14380	30.32800
H	8.83830	18.39750	30.57590
H	10.25300	19.25050	31.20170
C	10.40790	18.66640	29.13360
H	10.74080	17.62830	29.24650
H	9.78560	18.75820	28.23870

Ortho-Ortho Isomer, Co-Conformation 1 (XYZ-Coordinates in Å, Total Charge: +8)

B3LYP-D3/6-311G**++//B3LYP-D3/6-31G** energy = -5752.39761 a.u.
Solvation Energy at the B3LYP-D3/6-31G** level with the PBF solvation model = -1244.88 kcal/mol
Solvation Energy at the B3LYP-D3/6-31G** level with the SM8 solvation model = -1328.59 kcal/mol

H	-1.04030	1.91130	0.75490
C	-0.84260	2.06090	1.81360
C	-0.37840	2.43910	4.48070
C	-0.73110	0.93120	2.63350
C	-0.72560	3.37360	2.29340
C	-0.31030	3.55650	3.63330
C	-0.67110	1.14370	4.03080
H	-0.19590	2.58790	5.54250
C	-0.67680	-0.45320	1.99870
H	-0.96970	-1.23880	2.68740
H	-1.34340	-0.53480	1.13830
C	0.28240	4.85140	4.18480
H	0.12050	4.92230	5.26180
H	-0.11250	5.77550	3.76640
C	-1.11770	4.52360	1.37320
H	-0.75290	4.37040	0.35580
H	-0.73740	5.48650	1.71440
C	-0.95210	0.05830	5.06370
H	-0.63350	-0.92880	4.74750
H	-0.44080	0.26720	6.00430
N	0.71410	-0.81650	1.53240
C	3.33250	-1.41820	0.72170
C	1.60210	-1.31980	2.42330
C	1.08350	-0.65530	0.23610
C	2.36660	-0.94830	-0.19070
C	2.89530	-1.63200	2.03720
H	1.28020	-1.44890	3.45160
H	0.32460	-0.29330	-0.44640
H	2.59740	-0.81590	-1.24180
H	3.57710	-1.97920	2.80290
N	1.77270	4.87680	3.96380
C	4.53820	4.79700	3.50910
C	2.57640	4.12540	4.76270
C	2.32080	5.60320	2.95900
C	3.68470	5.56030	2.69720
C	3.93760	4.08270	4.56750
H	2.09390	3.56380	5.55120
H	1.66280	6.27070	2.41560
H	4.05370	6.18020	1.88180
H	4.51670	3.44670	5.22400
N	-2.42500	-0.04970	5.38610
C	-5.17550	-0.18770	5.90820
C	-3.15650	-1.07950	4.89380
C	-3.02230	0.89170	6.15870
C	-4.37410	0.84100	6.43680
C	-4.51730	-1.16740	5.14680
H	-2.63720	-1.81320	4.28480
H	-2.39690	1.69760	6.51980
H	-4.80450	1.64720	7.01810
H	-5.04750	-2.02050	4.74040
N	-2.61880	4.66390	1.27510
C	-5.40850	4.89100	1.13680
C	-3.29430	4.17180	0.20410
C	-3.29860	5.27580	2.27600
C	-4.67380	5.41870	2.20960
C	-4.67210	4.26270	0.11580
H	-2.70220	3.71990	-0.58240
H	-2.73990	5.63900	3.13740
H	-5.17020	5.88850	3.04930
H	-5.15730	3.85880	-0.76560
C	6.00580	4.68500	3.26120
N	8.69690	4.16600	2.70360
C	6.88660	4.20760	4.24970
C	6.55990	4.98680	2.00460
C	7.89500	4.71000	1.75940
C	8.21420	3.95000	3.94730
H	6.56840	4.02770	5.26920
H	5.95950	5.38110	1.19210
H	8.35150	4.89050	0.79540
H	8.90830	3.55970	4.68250
C	4.77020	-1.57550	0.34970
N	7.52210	-1.58180	-0.14490
C	5.34490	-0.73570	-0.62060
C	5.62890	-2.47340	1.00330
C	6.99360	-2.45520	0.73930
C	6.71000	-0.75300	-0.83970
H	4.75310	-0.01070	-1.16530
H	5.26210	-3.20190	1.71780
H	7.68360	-3.12840	1.23580
H	7.18890	-0.08600	-1.54450
C	-6.89850	4.92100	1.15520
N	-9.66090	4.79090	1.51340
C	-7.60720	5.97280	1.75820
C	-7.64300	3.83850	0.65880
C	-9.01180	3.79810	0.86470
C	-8.98240	5.88530	1.92310
H	-7.11160	6.87360	2.10210
H	-7.17070	2.98560	0.18170
H	-9.61630	2.95720	0.55460
H	-9.55910	6.67390	2.39380
C	-6.65960	-0.15400	6.06560
N	-9.43350	0.19070	6.13960
C	-7.29280	0.44770	7.16480
C	-7.48970	-0.64910	5.04590
C	-8.85690	-0.45760	5.10190
C	-8.67410	0.60710	7.17620
H	-6.73760	0.79420	8.02940
H	-7.07950	-1.12890	4.16730
H	-9.51830	-0.78750	4.31200
H	-9.19100	1.07760	8.00550
C	10.08550	3.68330	2.31670
H	10.67540	3.63390	3.23350
H	10.52400	4.45160	1.67620
C	9.03340	-1.42520	-0.29260
H	9.24860	-1.45420	-1.36320
H	9.48860	-2.30290	0.16870
C	9.96960	2.33930	1.62000
C	9.46280	-0.12530	0.35960
C	9.79200	2.27530	0.23210
C	9.98490	1.14770	2.35870
C	9.73170	-0.07390	1.73410
C	9.54290	1.05300	-0.39370
H	9.87410	3.17370	-0.37380
H	10.20630	1.16520	3.42240
H	9.75870	-0.98720	2.32240
H	9.44450	1.02100	-1.47600
C	-11.12770	4.59660	1.88090
H	-11.51140	5.57320	2.18040
H	-11.64640	4.29470	0.96830
C	-10.91860	0.53250	6.05770
H	-11.22430	0.85760	7.05330
H	-11.44310	-0.39810	5.82910
C	-11.22820	3.56020	2.98440
C	-11.12620	1.59950	4.99960
C	-11.46310	2.21480	2.67600
C	-11.03790	3.92850	4.32390
C	-10.98510	2.95660	5.32280
C	-11.41580	1.24230	3.67670
H	-11.71670	1.92020	1.66090
H	-10.94060	4.97620	4.59590
H	-10.84610	3.26250	6.35620
H	-11.64060	0.20930	3.42250
H	7.49120	0.09740	3.72080
C	6.52590	0.47670	3.40180
H	7.29700	1.35770	1.60780
C	6.42400	1.17700	2.22130
C	4.15740	0.70770	3.83210
C	5.16210	1.66780	1.79650
C	5.39410	0.23050	4.21810
C	4.00490	1.42940	2.60130
C	5.01190	2.40480	0.56950
H	5.52180	-0.33320	5.13480
H	1.87290	1.73000	2.78860
C	3.76470	2.84590	0.16580
H	3.66430	3.45490	-0.72100
C	2.63810	2.58140	0.97300
H	1.66970	2.94700	0.64340
C	2.74000	1.90320	2.16670
H	-5.95740	5.25120	6.33360
C	-6.06990	4.47030	5.59050
C	-4.97370	3.87500	4.99800
C	-7.58000	3.07650	4.27450
C	-5.14550	2.84670	4.01160
C	-7.37450	4.05300	5.22250
C	-6.47090	2.45430	3.64740
C	-4.02910	2.21420	3.40330
H	-8.22510	4.52500	5.70460
H	-8.58190	2.77360	4.00100
C	-4.23150	1.20400	2.49130
H	-3.03400	2.53540	3.67700
H	-3.39930	0.69520	2.01820
C	-5.52660	0.80030	2.11700
H	-5.62700	0.05520	1.34670
C	-6.62920	1.42880	2.65430
O	6.17030	2.60780	-0.11200
O	2.98420	0.54210	4.53040
O	-3.65700	4.17690	5.25330
O	-7.91880	1.14820	2.30480
C	-3.29050	5.14820	6.25430
H	-2.27880	4.86170	6.55500
H	-3.93740	5.06880	7.13470
C	-3.27830	6.58150	5.75030
H	-4.27050	6.87370	5.37430
H	-3.04700	7.23630	6.60230
C	-8.23740	-0.01150	1.49670
H	-9.27830	-0.23200	1.75010
C	-8.14590	0.20140	-0.01470
H	-8.58430	-0.68310	-0.49500
H	-8.77110	1.05310	-0.31280
O	-6.80890	0.42920	-0.44190
O	-2.29440	6.73210	4.71940
C	-6.26710	-0.51300	-1.38510
H	-6.54410	-0.23100	-2.40940
H	-6.67600	-1.51460	-1.20170
C	-4.74500	-0.52040	-1.27070
H	-4.37890	0.50900	-1.34270
H	-4.33210	-1.08880	-2.11490
O	-4.23820	-1.02000	-0.02110
C	-4.27620	-2.44440	0.11120
H	-3.48510	-2.91080	-0.49440
H	-5.23200	-2.85420	-0.24140
C	-4.13070	-2.81480	1.58130
H	-4.42180	-3.86370	1.72120
H	-4.81240	-2.18870	2.16780
O	-2.82270	-2.58250	2.12760
C	-1.87070	-3.64110	1.92700
H	-1.02620	-3.25320	1.34160
H	-2.30480	-4.46870	1.35470
C	-1.38020	-4.18110	3.25740
H	-0.69910	-5.02350	3.07910
H	-2.23160	-4.54810	3.84570
O	-0.69460	-3.13470	3.98230
C	-0.23280	-3.55490	5.28660
H	-0.41760	-4.62380	5.43640
H	-0.79950	-3.01330	6.05550
C	1.25120	-3.30220	5.46370
H	1.82290	-3.81560	4.67720
H	1.56110	-3.71240	6.43390
O	1.51060	-1.88450	5.41800
C	2.83100	-1.54830	5.85890
H	3.58950	-2.02540	5.22030
H	2.99250	-1.90990	6.88410
C	2.99180	-0.03690	5.85050
H	3.89420	0.24900	6.40000
H	2.13520	0.41340	6.36040
C	-2.13810	8.11590	4.32920
H	-1.71260	8.68580	5.16470
H	-3.12160	8.55080	4.09950
C	-1.26060	8.22180	3.08840
H	-1.63510	7.54500	2.30950
H	-1.35420	9.23900	2.68610
O	0.11120	7.89050	3.31050
C	0.87300	9.04560	3.74840
H	0.83120	9.81810	2.97110
H	0.43390	9.45060	4.66890
C	2.31950	8.69560	4.02420
H	2.38550	7.83690	4.71420
H	2.76210	9.55730	4.54190
O	3.00730	8.43010	2.80510
C	4.40500	8.74790	2.84840
H	4.95870	7.98310	3.41770
H	4.56280	9.71030	3.35290
C	4.95360	8.86890	1.44210
H	5.98340	9.24750	1.49970
H	4.35330	9.59480	0.87880
O	4.92550	7.59400	0.77940
C	5.42910	7.65430	-0.56120
H	5.17160	8.61460	-1.02760
H	6.52680	7.57790	-0.55960
C	4.79050	6.55120	-1.38360
H	5.04900	6.67920	-2.44190
H	3.70320	6.62040	-1.28480
O	5.13820	5.22470	-0.93600
C	6.26840	4.63330	-1.55970
H	7.20750	4.97580	-1.10070
H	6.32400	4.89240	-2.62680
C	6.16630	3.11740	-1.46830
H	5.28260	2.75540	-2.00410
H	7.05660	2.68080	-1.92930
H	-7.61470	-0.86250	1.79840

Ortho-Ortho Isomer, Co-Conformation 2 (XYZ-Coordinates in Å, Total Charge: +8)

B3LYP-D3/6-311G**++//B3LYP-D3/6-31G** energy = -5752.38352 a.u.
Solvation Energy at the B3LYP-D3/6-31G** level with the PBF solvation model = -1249.43 kcal/mol
Solvation Energy at the B3LYP-D3/6-31G** level with the SM8 solvation model = -1332.19 kcal/mol

H	-1.30610	3.38070	0.05810
C	-0.96740	2.88630	0.96550
C	-0.15510	1.65020	3.26800
C	-0.52530	1.55680	0.88310
C	-1.02970	3.60310	2.17060
C	-0.42590	3.02780	3.31070
C	-0.28480	0.87680	2.10210
H	0.17370	1.16180	4.18250
C	-0.35580	0.92760	-0.49970
H	-0.62830	-0.12610	-0.54900
H	-0.99450	1.43790	-1.22330
C	0.01070	3.86760	4.50980
H	-0.08840	3.34950	5.46550
H	-0.52860	4.80550	4.62500
C	-1.81980	4.90310	2.23150
H	-1.79070	5.42650	1.27580
H	-1.47050	5.62600	2.97510
C	-0.15100	-0.63890	2.20290
H	0.22040	-1.10620	1.29090
H	0.53420	-0.90620	3.00860
N	1.05070	1.03340	-1.03190
C	3.68500	1.27510	-1.96540
C	1.89050	-0.02940	-0.98000
C	1.48190	2.20280	-1.57260
C	2.76770	2.34150	-2.05430
C	3.19630	0.07710	-1.42850
H	1.50180	-0.97450	-0.61250
H	0.76980	3.01600	-1.59880
H	3.06300	3.30610	-2.44780
H	3.81070	-0.80250	-1.33090
N	1.45230	4.27050	4.34160
C	4.13890	4.94610	3.93740
C	2.43210	3.55790	4.94980
C	1.76900	5.35260	3.58990
C	3.09620	5.69840	3.37580
C	3.76390	3.87480	4.77360
H	2.11650	2.74080	5.58690
H	0.95740	5.92590	3.15710
H	3.29460	6.54060	2.72480
H	4.50040	3.28540	5.30680
N	-1.44370	-1.36380	2.50250
C	-3.80510	-2.80750	2.98720
C	-2.33200	-1.58460	1.50570
C	-1.69380	-1.87060	3.73840
C	-2.84160	-2.59570	3.99680
C	-3.50570	-2.28970	1.71690
H	-2.08990	-1.23380	0.51230
H	-0.94410	-1.69900	4.50130
H	-2.96160	-3.00690	4.99260
H	-4.17830	-2.36920	0.86600
N	-3.27920	4.61370	2.53490
C	-5.96090	3.91960	2.99760
C	-4.22690	4.87090	1.59980
C	-3.64890	4.07860	3.72750
C	-4.96950	3.74400	3.97910
C	-5.55590	4.54160	1.80420
H	-3.89490	5.34260	0.68270
H	-2.88330	3.87420	4.46890
H	-5.19230	3.27270	4.92830
H	-6.26360	4.78030	1.01930
C	5.57680	5.19390	3.61530
N	8.23560	5.51140	2.79540
C	6.48680	4.12180	3.62310
C	6.08090	6.44720	3.23320
C	7.40600	6.57800	2.83030
C	7.79190	4.30320	3.20820
H	6.17970	3.11830	3.88790
H	5.46840	7.34180	3.25090
H	7.82210	7.53270	2.52720
H	8.49720	3.48400	3.15660
C	5.12100	1.44920	-2.33440
N	7.82970	2.01940	-2.70540
C	5.54570	2.42110	-3.25560
C	6.11820	0.69990	-1.68520
C	7.45190	1.01840	-1.87830
C	6.89790	2.68610	-3.42230
H	4.84610	2.98580	-3.85990
H	5.88820	-0.08460	-0.96900
H	8.24440	0.51200	-1.34440
H	7.25650	3.44020	-4.11410
C	-7.34040	3.37100	3.16600
N	-9.79820	2.06750	3.45230
C	-7.98250	3.28900	4.41150
C	-8.01640	2.82450	2.06130
C	-9.22680	2.17350	2.23090
C	-9.20640	2.64070	4.52450
H	-7.55990	3.73710	5.30390
H	-7.58700	2.83520	1.06740
H	-9.74440	1.70330	1.40390
H	-9.73060	2.56510	5.47070
C	-5.11670	-3.46370	3.26810
N	-7.76040	-4.24950	3.73100
C	-5.66670	-3.46980	4.56160
C	-5.90930	-4.01170	2.24450
C	-7.22090	-4.38750	2.49920
C	-6.98100	-3.85880	4.76350
H	-5.11850	-3.10570	5.42100
H	-5.53500	-4.13060	1.23440
H	-7.87070	-4.77630	1.72340
H	-7.44970	-3.82170	5.73990
C	9.63850	5.61190	2.20290
H	10.32500	5.22010	2.95700
H	9.84970	6.67430	2.07100
C	9.28090	2.47810	-2.70430
H	9.44300	3.02830	-3.63290
H	9.90100	1.57990	-2.73130
C	9.69380	4.83740	0.89990
C	9.52540	3.32550	-1.46840
C	9.27930	5.43740	-0.29750
C	10.11510	3.50160	0.87930
C	10.02830	2.75030	-0.29510
C	9.19660	4.68860	-1.47090
H	9.03080	6.49530	-0.32330
H	10.53930	3.04500	1.77000
H	10.37910	1.72200	-0.29400
H	8.88630	5.17650	-2.39130
C	-11.05300	1.21970	3.61990
H	-11.55980	1.57850	4.51750
H	-11.69510	1.43880	2.76430
C	-9.26770	-4.34150	3.93000
H	-9.43750	-4.82290	4.89540
H	-9.65640	-4.99930	3.15060
C	-10.68440	-0.25080	3.70970
C	-9.84240	-2.93550	3.86110
C	-10.62300	-1.04290	2.55450
C	-10.39270	-0.83510	4.94950
C	-9.97800	-2.16630	5.02520
C	-10.20150	-2.37200	2.62900
H	-10.92970	-0.63790	1.59390
H	-10.51690	-0.26750	5.86800
H	-9.79380	-2.60790	6.00140
H	-10.18660	-2.97510	1.72490
H	4.91460	-0.38950	2.45900
C	4.66760	0.60160	2.10900
C	5.63030	1.39310	1.50470
C	2.94690	2.26310	1.65220
C	5.27130	2.66900	0.94420
C	3.33590	1.05630	2.18920
C	3.90560	3.08590	1.01140
C	6.22580	3.51020	0.31070
H	2.60420	0.41840	2.67730
C	5.82730	4.70270	-0.24910
H	6.55980	5.34100	-0.72960
C	4.47410	5.11930	-0.22130
H	4.20380	6.06200	-0.68290
C	3.52900	4.32170	0.38940
H	-5.30930	-0.04370	6.18090
C	-5.46580	0.02440	5.11100
C	-4.47890	0.49910	4.26890
C	-6.96300	-0.33930	3.21970
C	-4.72810	0.63370	2.86400
C	-6.71550	-0.37540	4.57190
C	-5.97030	0.16830	2.33830
C	-3.77930	1.22610	1.99680
H	-7.48890	-0.72480	5.24820
H	-7.91560	-0.66200	2.81730
C	-4.06220	1.38440	0.65700
H	-2.84760	1.57160	2.41690
H	-3.34540	1.86900	0.00220
C	-5.27660	0.91900	0.11660
H	-5.50410	1.02400	-0.93740
C	-6.19210	0.28990	0.93050
O	2.18390	4.59550	0.44470
O	6.94100	1.05700	1.36830
O	-3.22360	0.88800	4.64770
O	-7.37740	-0.15360	0.40310
C	-2.77340	0.66920	5.99620
H	-1.68240	0.64970	5.92350
H	-3.11260	-0.30690	6.36210
C	-3.17760	1.76400	6.96210
H	-4.27190	1.88310	6.99280
H	-2.85820	1.45830	7.96940
C	-7.39250	-1.52220	-0.07020
H	-8.44460	-1.72660	-0.28110
C	-6.59320	-1.78670	-1.33720
H	-6.91780	-2.75600	-1.74340
H	-6.83620	-1.01840	-2.08410
O	-5.18010	-1.80070	-1.07250
O	-2.54830	2.98040	6.58020
C	-4.40180	-2.02670	-2.26310
H	-4.97460	-1.72560	-3.14930
H	-4.18070	-3.09710	-2.37110
C	-3.12130	-1.19620	-2.24540
H	-3.35900	-0.18870	-1.88980
H	-2.73090	-1.11710	-3.26770
O	-2.09250	-1.70100	-1.36900
C	-1.21430	-2.66030	-1.98580
H	-0.47230	-2.14030	-2.60790
H	-1.78600	-3.32740	-2.64260
C	-0.52990	-3.53600	-0.95610
H	-0.04800	-4.35690	-1.50270
H	-1.27690	-3.97990	-0.28220
O	0.46400	-2.83000	-0.18320
C	1.35170	-3.76810	0.46730
H	1.74330	-4.47400	-0.27700
H	0.79400	-4.35270	1.21410
C	2.51350	-3.05810	1.14830
H	3.05740	-3.79970	1.74840
H	2.14710	-2.29480	1.84580
O	3.37280	-2.39090	0.23250
C	4.48960	-3.16240	-0.25220
H	4.69600	-2.80380	-1.26640
H	4.23750	-4.22690	-0.33370
C	5.73260	-3.00310	0.60670
H	6.53630	-3.60110	0.15640
H	5.56460	-3.38100	1.62540
O	6.09130	-1.61180	0.66070
C	7.42150	-1.36820	1.12250
H	8.09620	-1.25100	0.26250
H	7.80770	-2.20870	1.71390
C	7.46720	-0.13210	2.01310
H	8.51150	0.10400	2.23410
H	6.95170	-0.30250	2.96250
C	-2.71740	3.99060	7.59920
H	-2.47270	3.57320	8.58330
H	-3.76410	4.32870	7.61590
C	-1.80000	5.15740	7.31970
H	-1.93740	5.50910	6.28330
H	-2.10210	5.98140	7.97960
O	-0.45580	4.77410	7.55520
C	0.39130	5.81570	8.06830
H	-0.21130	6.61000	8.52460
H	1.01480	5.38650	8.85980
C	1.27680	6.37070	6.95880
H	1.99680	5.60680	6.65080
H	1.84890	7.23550	7.31890
O	0.51340	6.68900	5.78860
C	0.02280	8.03460	5.74260
H	0.81250	8.70840	5.38300
H	-0.29070	8.38370	6.73530
C	-1.17530	8.06540	4.81590
H	-1.54010	9.09350	4.72130
H	-1.98970	7.45990	5.23160
O	-0.81890	7.51790	3.53050
C	-0.99060	8.36760	2.39030
H	-1.85220	8.02280	1.80050
H	-1.19170	9.40190	2.69050
C	0.25970	8.35200	1.53950
H	1.11790	8.71650	2.12180
H	0.11680	9.02230	0.68070
O	0.50870	7.00640	1.08740
C	1.52300	6.96620	0.09050
H	2.49300	7.29080	0.49790
H	1.27740	7.64500	-0.74000
C	1.61580	5.55680	-0.46350
H	0.59790	5.20280	-0.65670
H	2.16540	5.56050	-1.41140
H	-7.06090	-2.18210	0.73940
H	1.92080	2.59820	1.70110
H	7.26340	3.20330	0.27150

S5. Analytical Reverse-Phase HPLC

Analytical reverse-phase HPLC was used to determine the purity of both the handcuff catenane **HC**$^{8+}$ (Figure S19) and the ditopic host **DBB**$^{8+}$ (Figure S20). Figure S19 shows a single peak in the chromatogram, indicating that the *meta-meta* and *ortho-ortho* isomers have very similar retention times. The two topological isomers could not be separated using HPLC techniques.

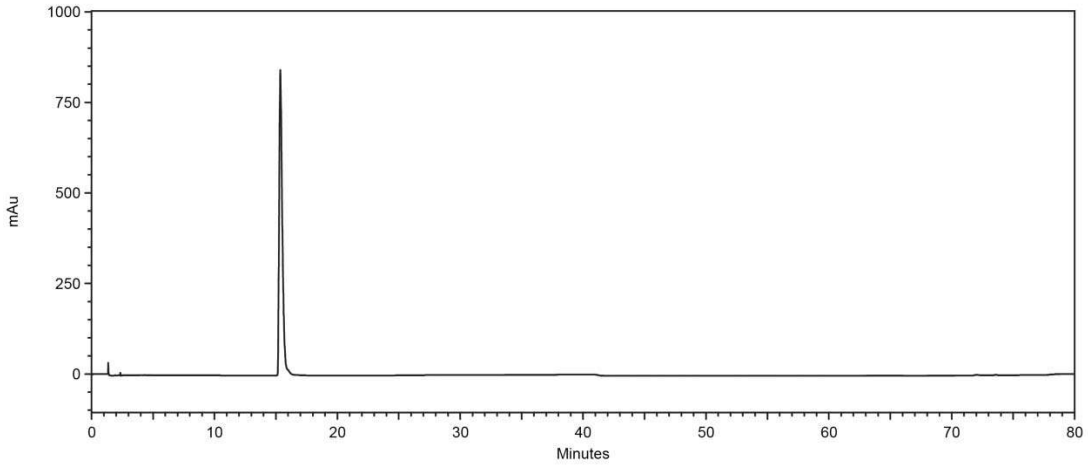

Figure S19. Analytical RP-HPLC trace (H_2O/0.1% TFA – MeCN/0.1% TFA, 0 – 50% in 65 mins → 100% MeCN/0.1% TFA after 80 mins) of handcuff catenane **HC**•8PF_6. The single peak represents two topological isomers.

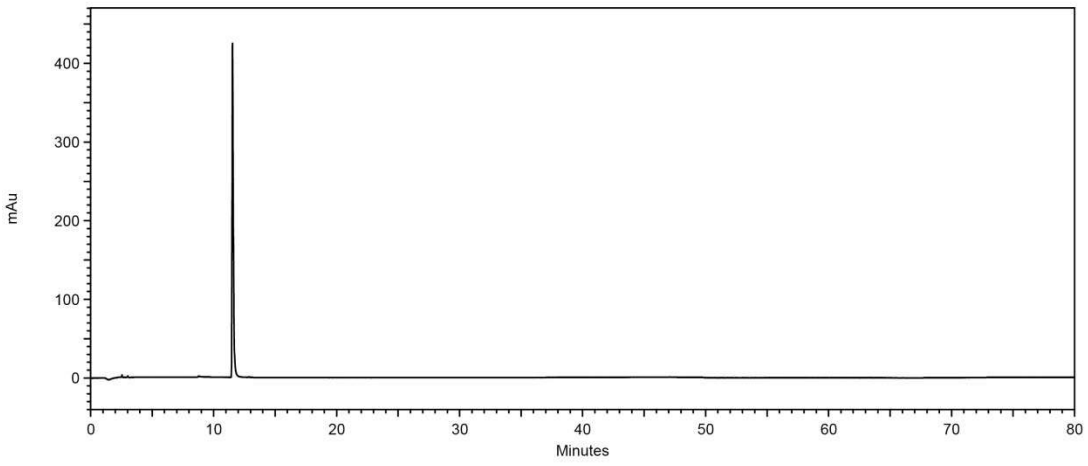

Figure S20. Analytical RP-HPLC trace (H_2O/0.1% TFA – MeCN/0.1% TFA, 0 – 50% in 65 mins → 100% MeCN/0.1% TFA after 80 mins) of **DBB**•8PF_6.

S6. Isothermal Titration Calorimetry (ITC)

ITC measurements (Figure S21) were performed in dry, degassed MeCN at 298 K. A solution of **DBB**•8PF_6 (0.75 mM) was used as the host solution. Solutions of **BHEEN** (15 mM) were added by injecting 5 μL of a titrant solution over 20 s, which was repeated 50 times with a 300 s interval between each injection. Experiments were repeated three times. Thermodynamic parameters were calculated using a sequential binding site model utilizing data from which the heat of dilution of **BHEEN** was subtracted, with the average of three runs reported, and the error represents the standard deviation calculated from those runs.

$$\boldsymbol{K_1 = 2047 \pm 249\ M^{-1}}$$
$$\Delta H_1 = -13.8 \pm 0.7\ \text{kcal}\cdot\text{mol}^{-1}$$
$$\Delta S_1 = -31.3 \pm 0.6\ \text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$
$$\Delta G_1 = -4.5 \pm 0.5\ \text{kcal}\cdot\text{mol}^{-1}$$

$$\boldsymbol{K_2 = 52 \pm 6\ M^{-1}}$$
$$\Delta H_2 = -34.8 \pm 6.5\ \text{kcal}\cdot\text{mol}^{-1}$$
$$\Delta S_2 = -109 \pm 18.7\ \text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$
$$\Delta G_2 = -2.3 \pm 0.3\ \text{kcal}\cdot\text{mol}^{-1}$$

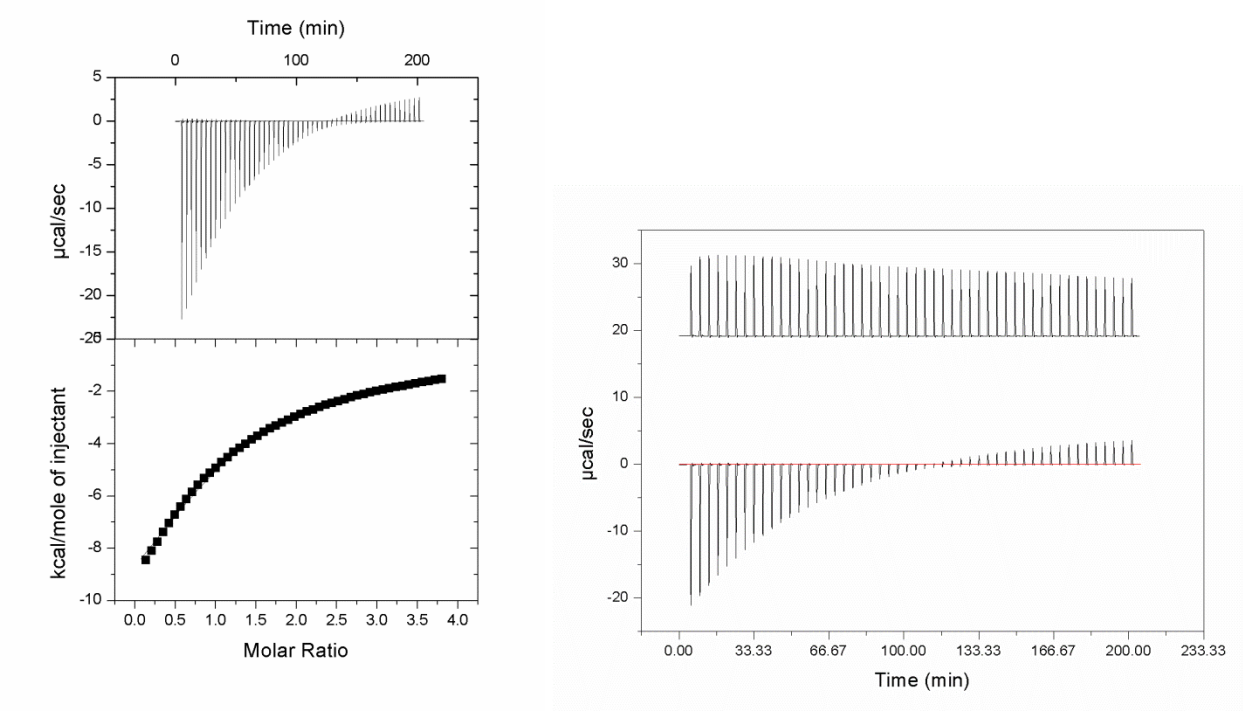

Figure S21. a) ITC trace of the (**BHEEN**)$_2$ ⊂ **DBB**•8PF_6 complex, b) ITC trace revealing large endothermic heat of dilution upon addition of **BHEEN** to MeCN.

S7. References

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