

Electronic Supplementary Information for:

Benzobis(imidazolium) salts as templates for the self-assembly of starburst [2₄]pseudorotaxanes and their corresponding carbene-based classic [2₂]pseudorotaxanes

Mathew W. Foster,^a Benjamin T. Mehl,^a Edward M. Treadwell,^a Radu F. Semeniuc,^{*a} and Kraig A. Wheeler^b

a) *Department of Chemistry and Biochemistry, Eastern Illinois University, Charleston, Illinois, 61920, United States.*

b) *Department of Chemistry, Whitworth University, Spokane, Washington, 99251, United States.*

Experimental details

General considerations

Operations requiring inert (nitrogen) atmosphere were carried out using standard Schlenk techniques and an MBraun LabStar dry-box. Solvents were dried by conventional methods and distilled under a dry N₂ atmosphere immediately prior to use. NMR spectra were recorded on a 400 MHz Bruker Avance FT-NMR Spectrometer. Electrospray ionization mass spectrometry data were obtained on a MicroMass QTOF spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. Bis-1,5-(dinaphtho)-38-crown-10 (15DN38C10)¹ and bis(paraphenylene)-34-crown-10 (BPP34C10)² crown ethers were prepared according to published procedures. Benzobis(imidazole) and tetraalkyl/tetraaryl-benzobis-(imidazolium) salts were prepared using modified reported synthetic procedures,³ as described below. All other reagents were commercially available and used without further purification.

Synthesis of benzobis(imidazole) (BBI)

A round bottom flask was charged with a magnetic stir bar, 1,2,4,5-benzenetetraamine tetrahydrochloride (2.84 g, 0.01 mol) and formic acid (88-99%, 75 mL). The flask was fitted with a condenser and mixture was heated at reflux overnight. Then, the condenser was replaced with a distillation head and the volume of the solution was reduced to approximately 10 mL. The remaining liquids were removed under vacuum and the resulting solid was dissolved in water and filtered to remove any solid impurities. The solution was brought to pH = 6.5 – 6.8 with 10% NaOH. The precipitate was collected *via* vacuum filtration on a frit, rinsed with cold water, and dried under vacuum over P₂O₅ to afford the desired benzobis(imidazole) (BBI, 1.36 g, 85 %) as a light brown solid. ¹H-NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.18 (s, 2H, C2-*H*), 7.69 (s, 2H, C₆*H*₂).

General procedure for the synthesis of benzobis(imidazolium) axles

A high-pressure vial was charged with a stirring bar, BBI (0.158 g, 1.0 mmol), Na₂CO₃ (0.424 g, 4.0 mmol), and anhydrous CH₃CN (50 mL). After the addition of the appropriate amount of the halo-derivative, the vial was sealed with a Teflon cap and the mixture was stirred in an oil bath at 100°C for 48 h. The mixture was then allowed to cool to room temperature, and the resulting white precipitate was filtered on a frit, washed with cold acetonitrile (15 mL) and diethyl ether (20 mL). The solids were taken in methanol (75 mL) and the solution filtered to remove the inorganic salts. After removal of methanol, the [BBI-H₂-R₄]²⁺ salts were dissolved in water and treated with an excess of a saturated aqueous solution of NH₄PF₆. The resulting precipitates were filtered, washed with water and dried over P₂O₅ to afford the desired axles as white powders.

[BBI-H₂-Me₄](PF₆)₂: Prepared using MeI (0.250 mL, 4.0 mmol). Yield 0.465 g (91 %). ¹H-NMR (400 MHz, acetone-*d*₆): δ (ppm) 9.83 (s, 2 H, C2-*H*), 8.88 (s, 2 H, C₆H₂), 4.43 (s, 12 H, Imd-CH₃).

[BBI-H₂-Bu₄](PF₆)₂: Prepared using BuBr (0.431 mL, 4.0 mmol). Yield 0.622 g (92 %). ¹H-NMR (400 MHz, acetone-*d*₆): δ (ppm) 10.12 (s, 2 H, C2-*H*), 9.13 (s, 2 H, C₆H₂), 4.85 (t, J = 7.36 Hz, 8 H, Imd-CH₂-), 2.17 (p, J = 5.36 Hz, 8 H, -CH₂-), 1.51 (sextet, J = 7.4 Hz, 8 H, -CH₂-), 0.99 (t, J = 7.36 Hz, 12 H, -CH₃).

[BBI-H₂-Bn₄](PF₆)₂: Prepared using BnBr (0.475 mL, 4.0 mmol). Yield 0.695 g (86 %). ¹H-NMR (400 MHz, acetone-*d*₆): δ (ppm) 10.15 (s, 2 H, C2-*H*), 8.67 (s, 2 H, C₆H₂), 7.57-7.54 (m, 8 H, C₆H₅), 7.45-7.42 (m, 12 H, C₆H₅), 5.99 (s, 8 H, Imd-CH₂-Ph).

[BBI-H₂-[CH₂Ph(3,5-*t*-Bu)₂]₄](PF₆)₂: Prepared using (3,5-*t*-Bu)₂PhCH₂Br (1.133 g, 4 mmol). Yield 1.028 g (82 %). ¹H-NMR (400 MHz, acetone-*d*₆): δ (ppm) 9.74 (s, 2 H, C2-*H*), 9.13 (s, 2 H, C₆H₂), 7.58 (t, J = 1.76 Hz, 4 H, C₆H₅), 7.48 (d, J = 1.76 Hz, 8 H, C₆H₅), 5.95 (s, 8 H, Imd-CH₂-Ph), 1.28 (s, 72 H, Ph-*t*-C₄H₉).

[BBI-H₂-[(CH₂)₃OH]₄](PF₆)₂: Prepared using 3-bromo-*n*-propanol (0.363 mL, 4 mmol). Yield 0.532 g (78 %). ¹H-NMR (400 MHz, acetone-*d*₆): δ (ppm) 9.96 (s, 2 H, C2-*H*), 9.03 (s, 2 H, C₆H₂), 4.96 (t, J = 6.8 Hz, 8 H, Imd-CH₂-Ph), 3.73 (t, J = 5.32, 8 H, -CH₂OH), 2.35 (p, J = 6.72 Hz, 8 H, -CH₂-).

[BBI-H₂-[(CH₂)₆Br]₄](PF₆)₂: Prepared using 1,6-dibromo-*n*-hexane (6.14 mL, 40 mmol). In this case, to minimize the formation of polymeric species, a 10-fold excess of the 1,6-dibromo-*n*-hexane starting material was used. Yield 0.783 g (71 %). ¹H-NMR (400 MHz, acetone-*d*₆): δ (ppm) 10.04 (s, 2 H, C2-*H*), 9.07 (s, 2 H, C₆H₂), 4.85 (t, J = 7.32 Hz, 8 H, Imd-CH₂-Ph), 3.49 (t, J = 6.70 Hz, 8 H, -CH₂-Br), 2.24-2.21 (m, 8 H, -CH₂-), 1.91-1.86 (m, 8 H, -CH₂-), 1.55 (br, 16 H, -CH₂-).

NMR studies

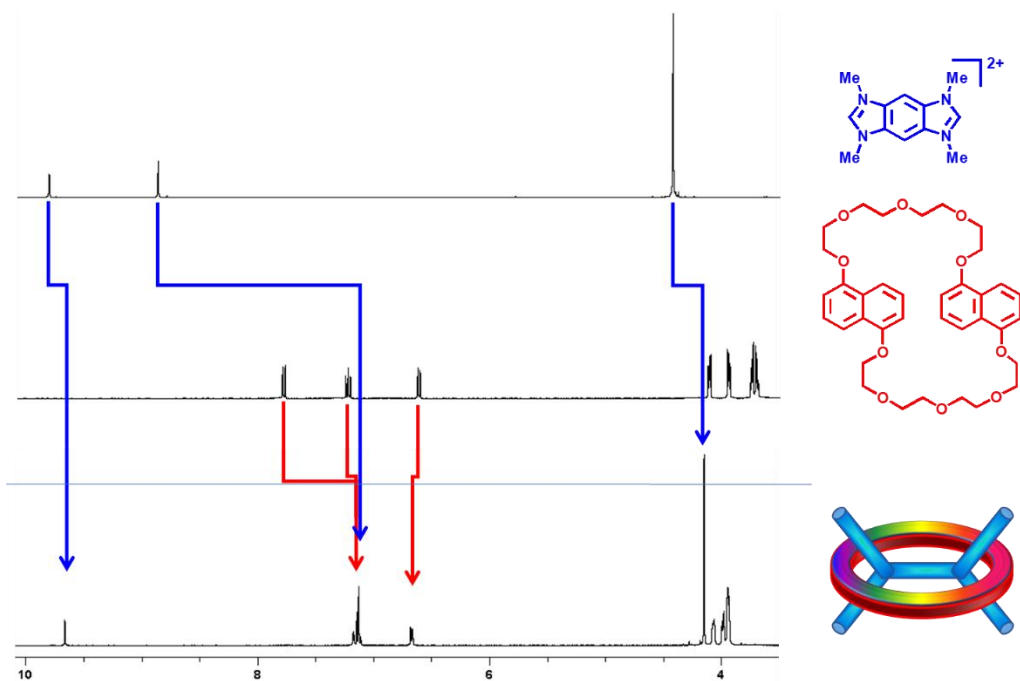


Fig. S1. ¹H-NMR spectra (acetone-d₆) of: [BBI-H₂-Me₄]²⁺ (top); 15DN38C10 (middle); and an equimolar mixture of the two components (bottom).

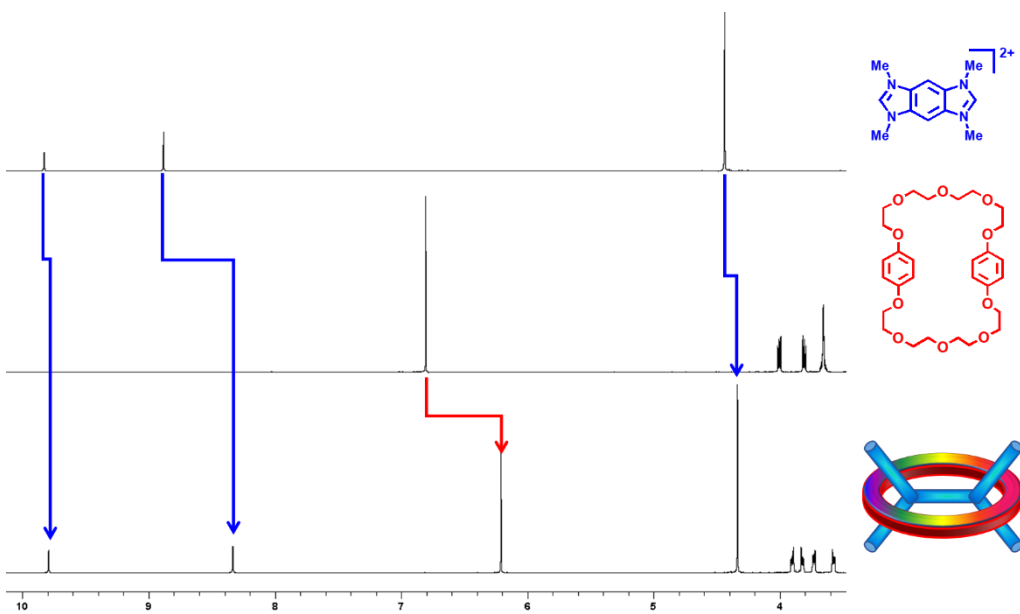


Fig. S2. ¹H-NMR spectra (acetone-d₆) of: [BBI-H₂-Me₄]²⁺ (top); BPP34C10 (middle); and an equimolar mixture of the two components (bottom).

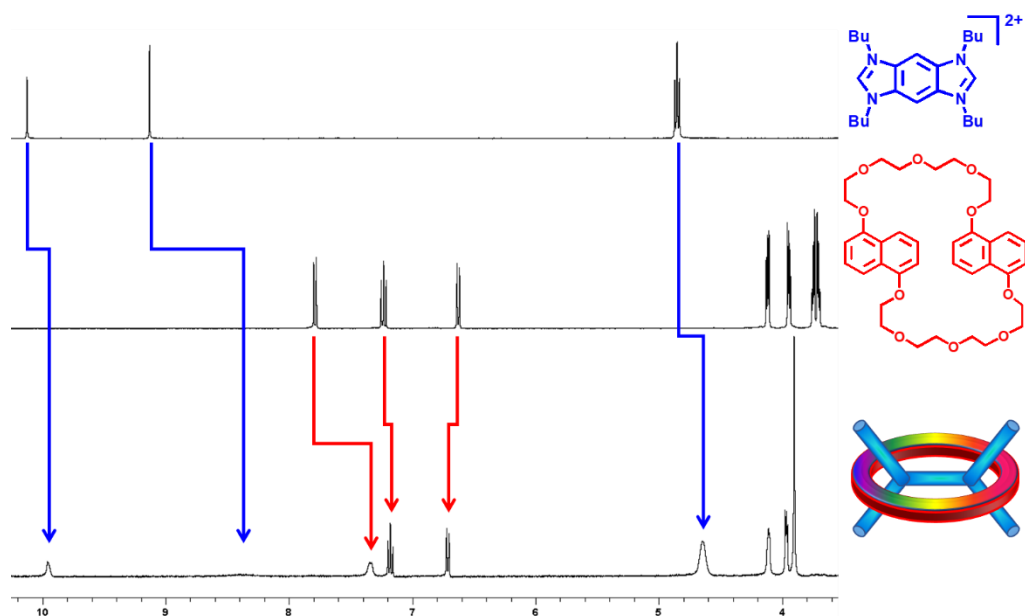


Fig. S3. ¹H-NMR spectra (acetone-d₆) of: [BBI-H₂-Bu₄]²⁺ (top); 15DN38C10 (middle); and an equimolar mixture of the two components (bottom).

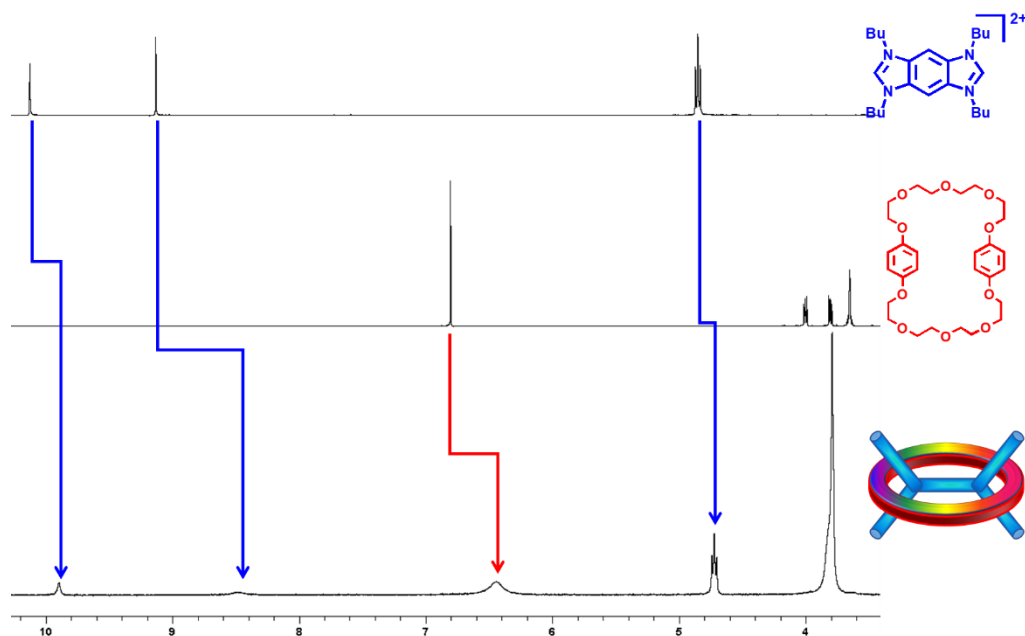


Fig. S4. ¹H-NMR spectra (acetone-d₆) of: [BBI-H₂-Bu₄]²⁺ (top); BPP34C10 (middle); and an equimolar mixture of the two components (bottom).

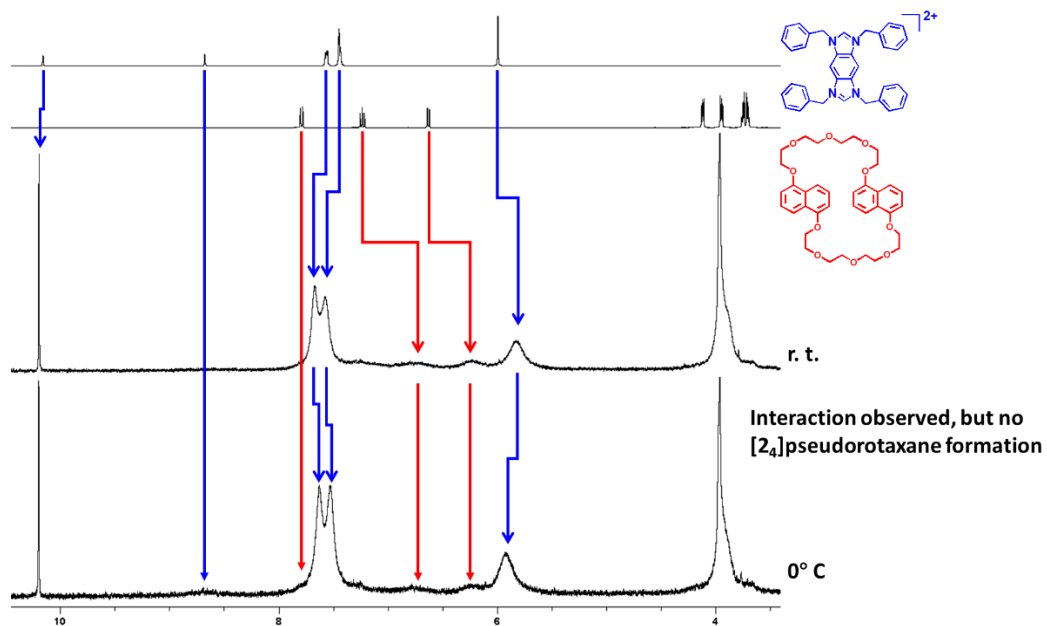


Fig. S5. ¹H-NMR spectra (acetone-d₆) of: [BBI-H₂-Bn₄]²⁺ (top); 15DN38C10 (middle); and an equimolar mixture of the two components at r. t. and 0° C (bottom). The spectra suggest an interaction of 15DN38C10 with the -CH₂-Ph side-arms of the axle, but not with the BBI²⁺ core.

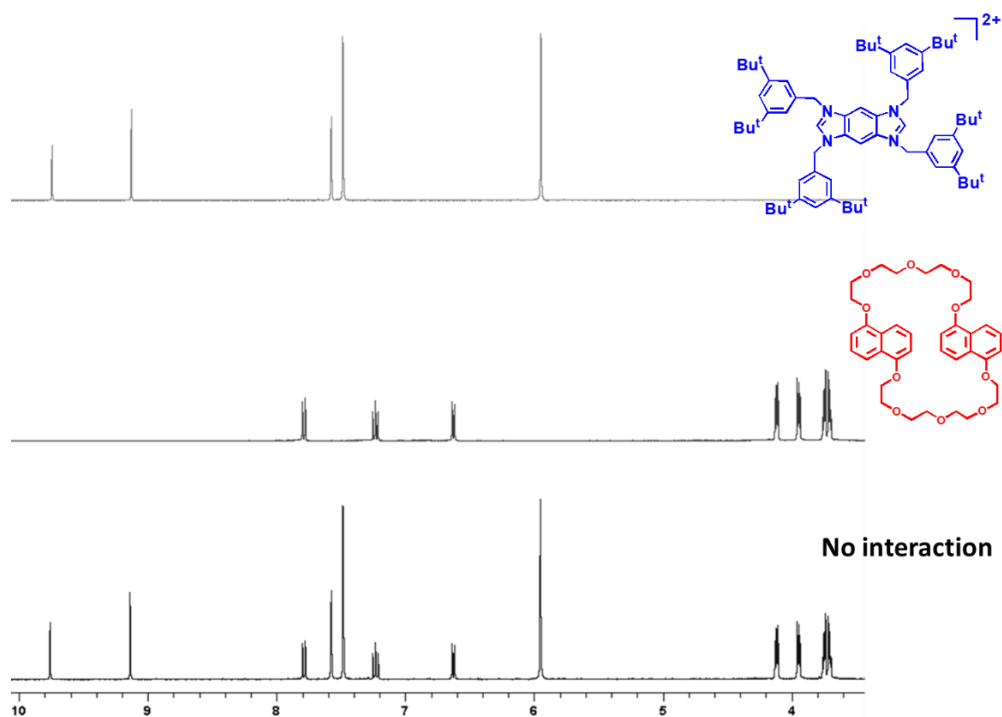


Fig. S6. ¹H-NMR spectra (acetone-d₆) of: [BBI-H₂-[CH₂Ph(3,5-*t*-Bu)₂]₄]²⁺ (top); 15DN38C10 (middle); and an equimolar mixture of the two components (bottom).

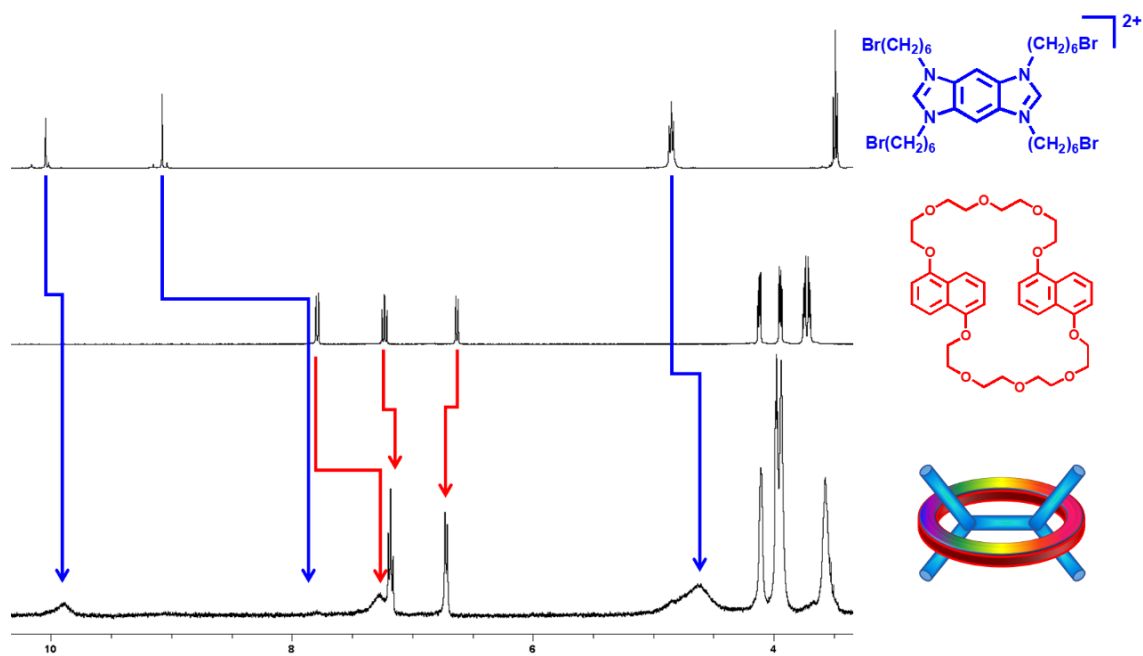


Fig. S7. ¹H-NMR spectra (acetone-d₆) of: [BBI-H₂-[(CH₂)₆Br]₄]²⁺ (top); 15DN38C10 (middle); and an equimolar mixture of the two components (bottom).

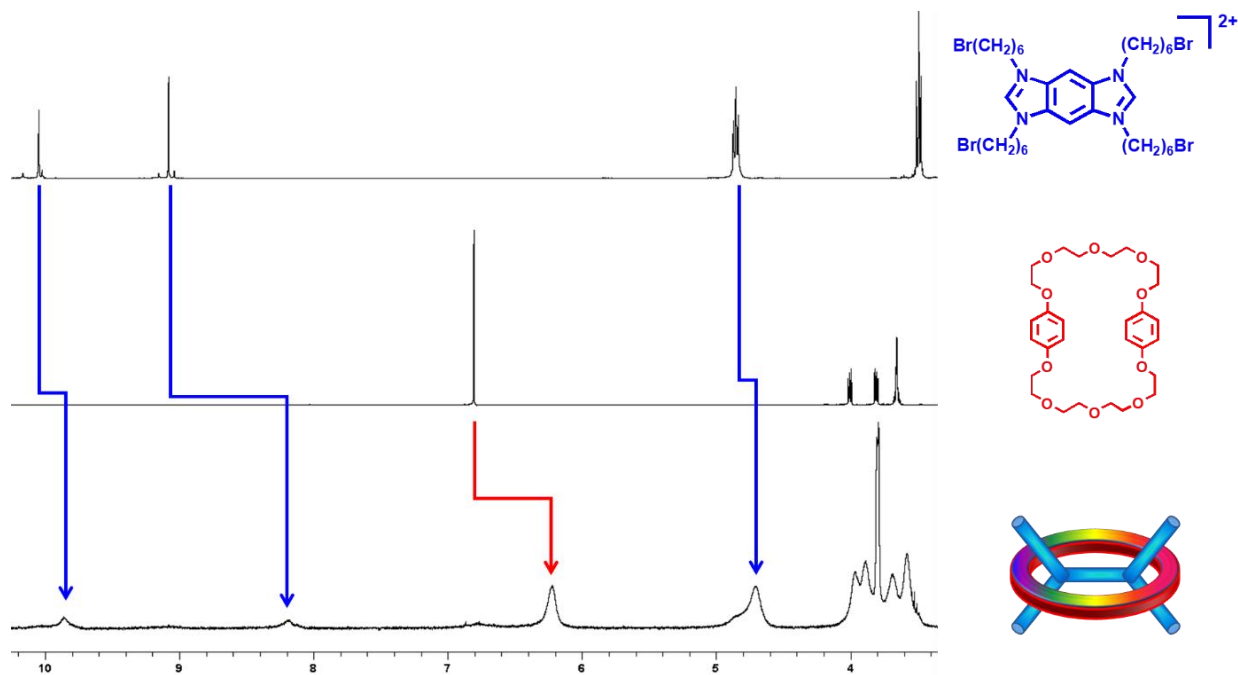


Fig. S8. ¹H-NMR spectra (acetone-d₆) of: [BBI-H₂-[(CH₂)₆Br]₄]²⁺ (top); BPP34C10 (middle); and an equimolar mixture of the two components (bottom).

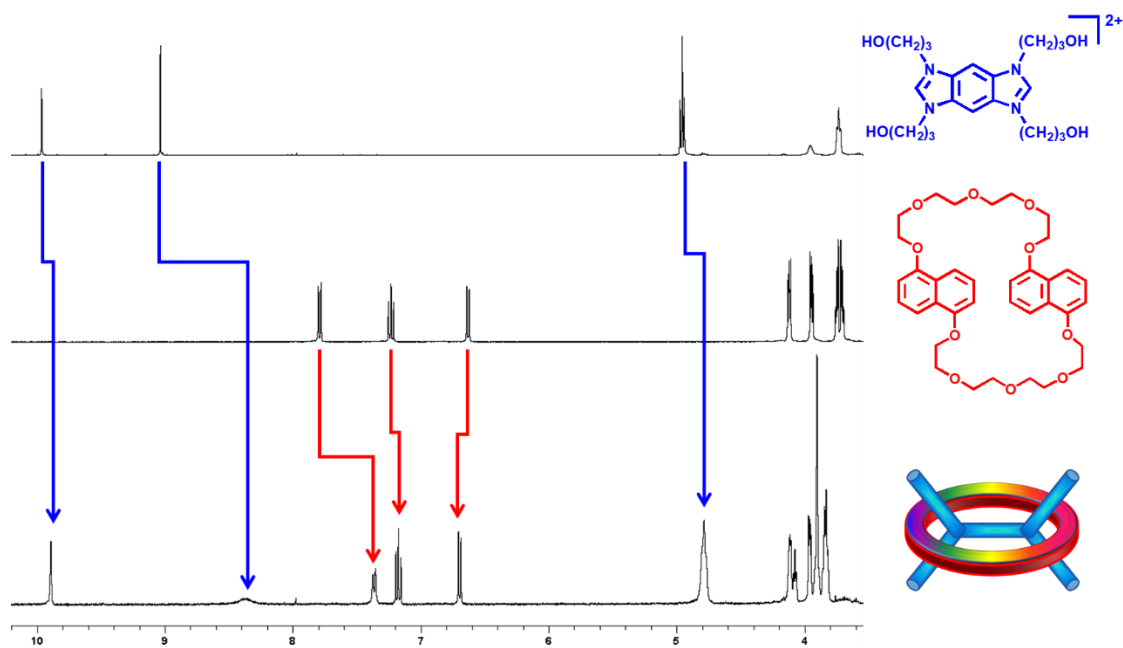


Fig. S9. $^1\text{H-NMR}$ spectra (acetone- d_6) of: $[\text{BBI-H}_2\text{-}[(\text{CH}_2)_3\text{OH}]_4]^{2+}$ (top); 15DN38C10 (middle); and an equimolar mixture of the two components (bottom).

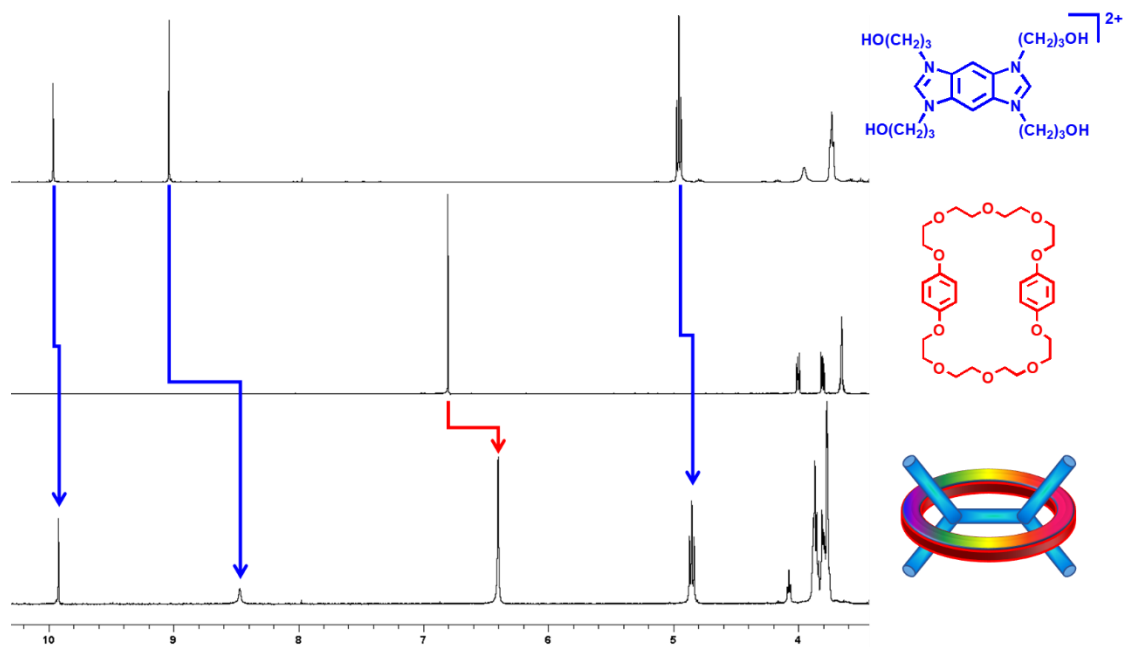


Fig. S10. $^1\text{H-NMR}$ spectra (acetone- d_6) of: $[\text{BBI-H}_2\text{-}[(\text{CH}_2)_3\text{OH}]_4]^{2+}$ (top); BPP34C10 (middle); and an equimolar mixture of the two components (bottom).

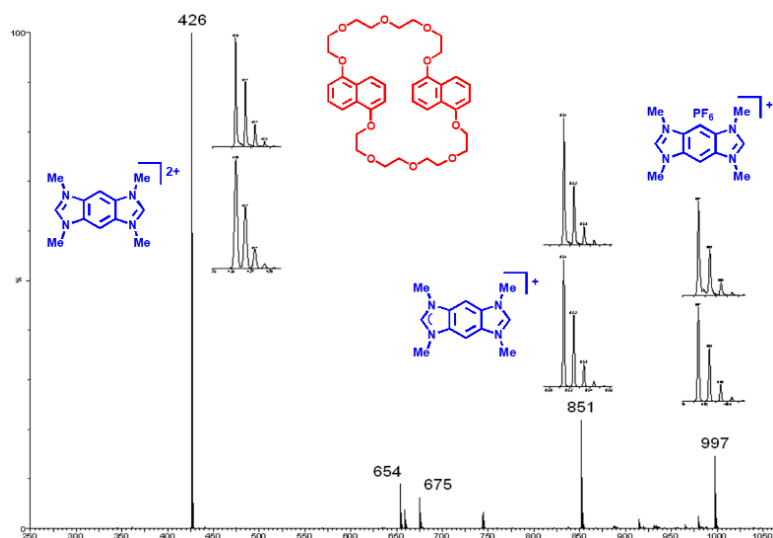


Fig. S11. ESI⁺/MS spectrum of a 1:1 mixture of [BBI-H₂-Me₄](PF₆)₂ and 15DN38C10.

Table S1. ESI⁺/MS data for equimolar mixtures of [BBI-H₂-R₄]²⁺ axles and crown ethers (m/z (%)).

R / Crown	{Axle⊂C} ²⁺	{[Axle⊂C](PF ₆) ⁺	{[Carbene]⊂C} ⁺
Me / 15DN38C10	426 (100)	997 (20)	851 (25)
Me / BPP34C10	376 (100)	897 (70)	751 (35)
Bu / 15DN38C10	510 (100)	1166 (20)	1020 (17)
Bu / BPP34C10	460 (70)	1066 (35)	920 (5)
Br / 15DN38C10	724 (70)	1593 (4)	-
Br / BPP34C10	674 (60)	1493 (5)	-
OH / 15DN38C10	514 (100)	1174 (17)	1028 (15)
OH / BPP34C10	464 (30)	1074 (3)	928 (5)

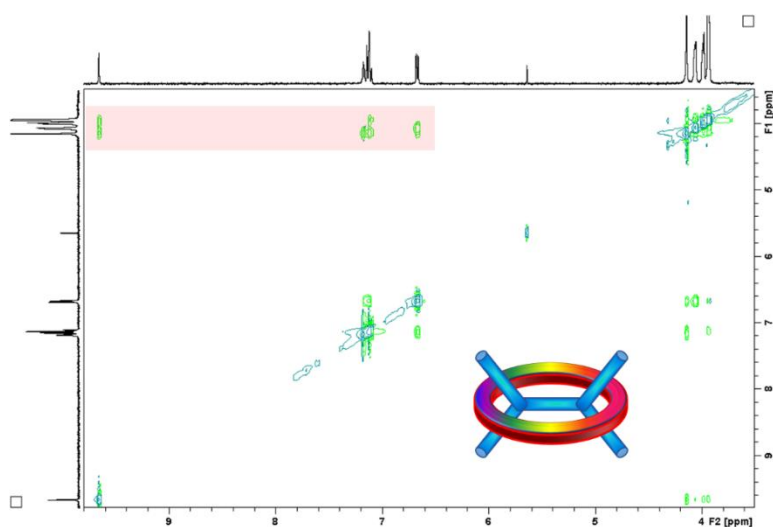


Fig. S12. ¹H-¹H NOESY spectrum (acetone-*d*₆) of the {[BBI-H₂-Me₄]⊂15DN38C10}²⁺ pseudorotaxane, displaying NOE correlations between the axle and the 15DN38C10 macrocycle.

NMR titrations

^1H -NMR titrations were conducted in acetone- d_6 at 293 K. To 500 μL of a solution of the BBI axle were added aliquots of the crown ethers (addition of 100 μL represented the addition of 0.2 equivalents). Thirteen titration points (for 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.5, and 3.0 equivalents of crown) were obtained in each case. The chemical shift of the protons situated on the imidazolium C2 atom and on the α - CH_2 -R (R = H for the Me derivative) bonded to the N atom of the imidazolium ring was monitored. The results were averaged and used for the determination of the K_a and ΔG^0 thermodynamic parameters.

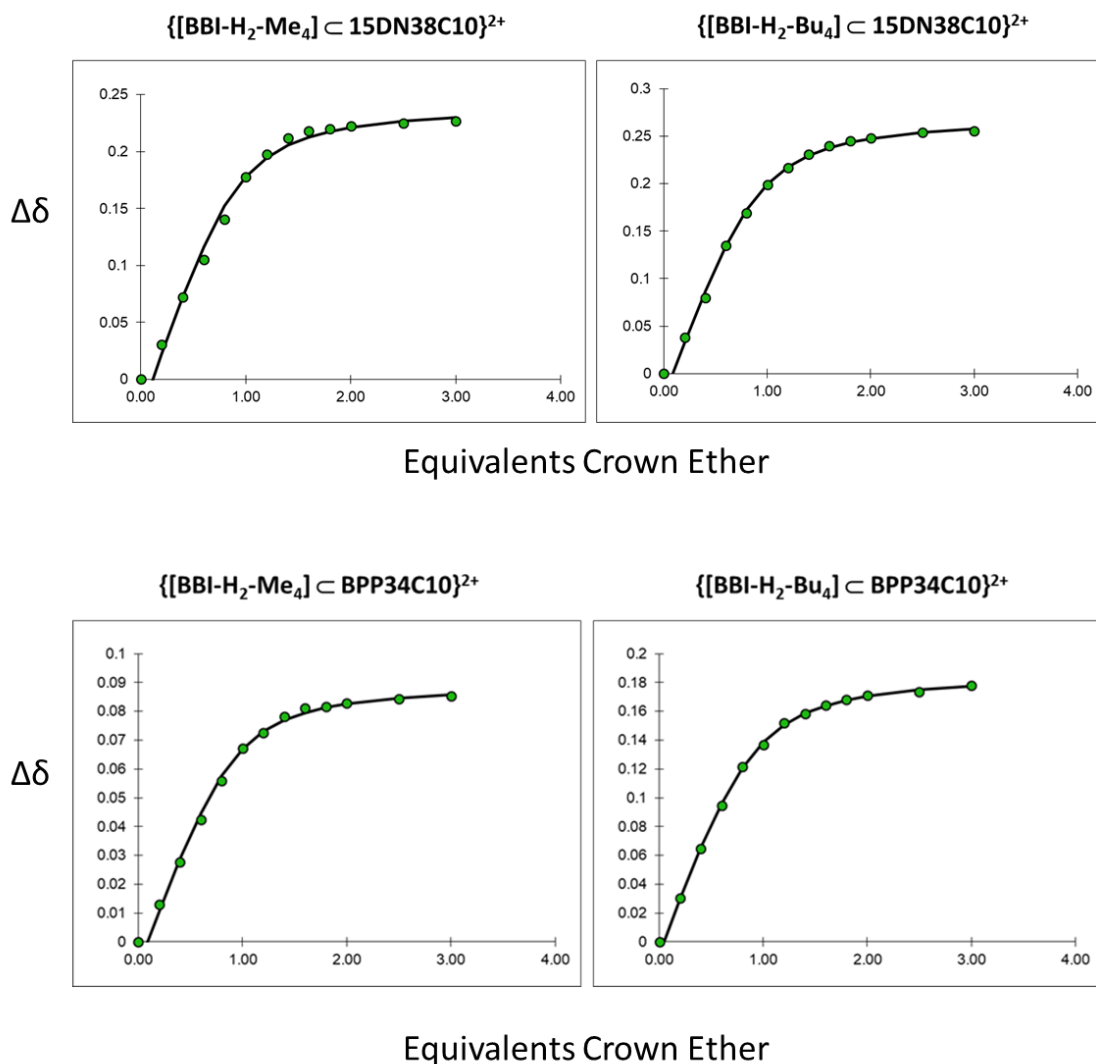


Fig. S13. ^1H -NMR titration curves $[\text{BBI-H}_2\text{-Me}_4] \subset 15\text{DN38C10}\}^{2+}$ (top left), $\{[\text{BBI-H}_2\text{-Bu}_4] \subset 15\text{DN38C10}\}^{2+}$ (top right), $\{[\text{BBI-H}_2\text{-Me}_4] \subset \text{BPP34C10}\}^{2+}$ (bottom left), and $\{[\text{BBI-H}_2\text{-Bu}_4] \subset \text{BPP34C10}\}^{2+}$ (bottom right).

Job plots were obtained from the titration data. The mole fractions of BBI axles (χ_{BBI}) were calculated for each data point by dividing the number of moles of the BBI axle by the total number of moles present in solution. The differences in the chemical shift of a given proton, $\Delta\delta$, were calculated for each point by subtracting the observed chemical shift from the chemical shift of that particular proton in the absence of the crown. The Job plots were then produced by plotting $\Delta\delta \cdot \chi_{\text{BBI}}$ against χ_{BBI} .

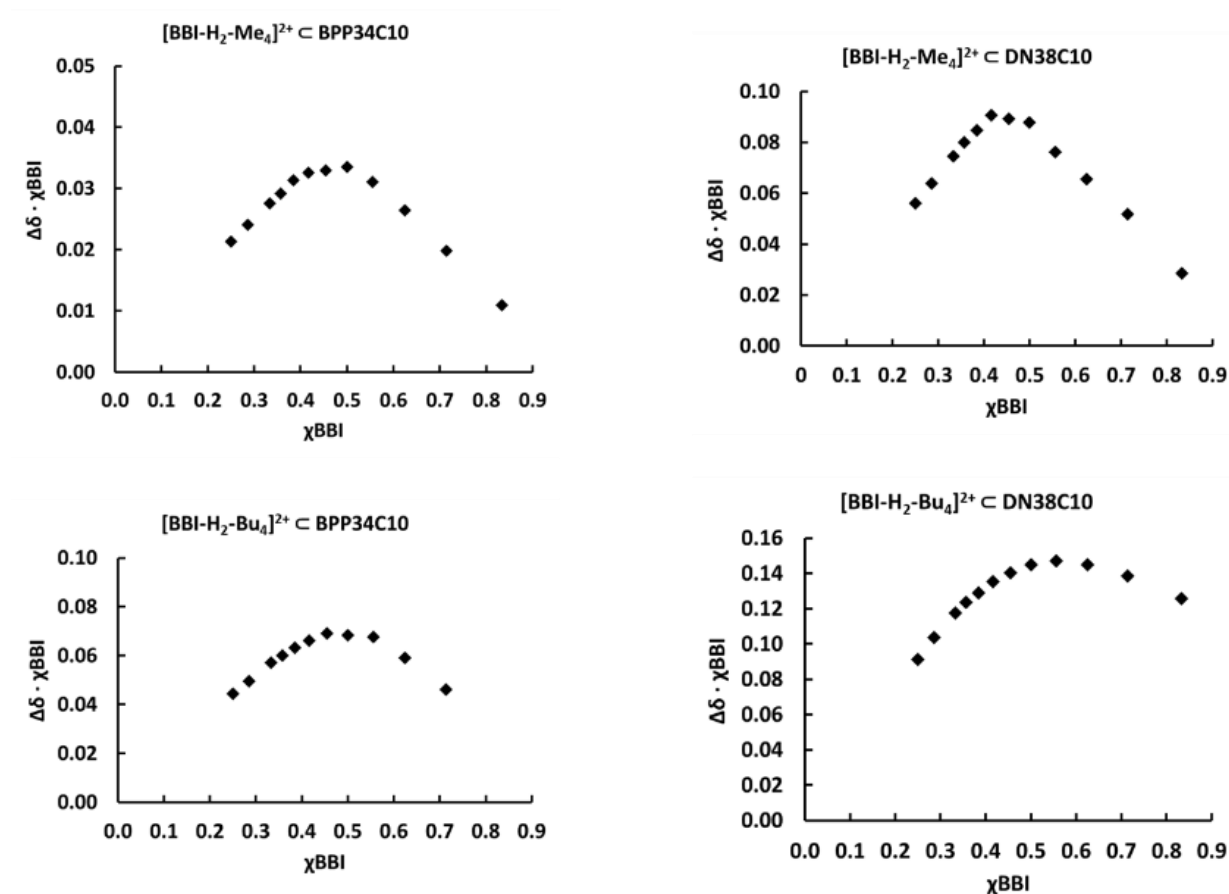


Fig. S14. Job plots for $\{[\text{BBI-H}_2\text{-Me}_4]\text{C}[\text{BPP34C10}]\}^{2+}$ (top left), $\{[\text{BBI-H}_2\text{-Me}_4]\text{C}[\text{DN38C10}]\}^{2+}$ (top right), $\{[\text{BBI-H}_2\text{-Bu}_4]\text{C}[\text{BPP34C10}]\}^{2+}$ (bottom left), and $\{[\text{BBI-H}_2\text{-Bu}_4]\text{C}[\text{DN38C10}]\}^{2+}$ (bottom right).

Crystallographic studies

The $[2_4]$ pseudorotaxanes were prepared by mixing equimolar solutions of the axle and crown ethers in acetone. Vapor diffusion of diethyl ether into an acetone solution of the components yielded single crystals which were subjected to X-ray diffraction studies. The X-ray data were collected at 100 K on a Bruker SMART APEXII CCD diffractometer equipped with Cu K α radiation. Intensities were collected using phi and omega scans and were corrected for Lorentz polarization and absorption effects. The *X-SEED* software

platform,⁴ equipped with *SHELXS* and *SHELXL* modules on a PC computer,⁵ was used for all structure solution and refinement calculations and molecular graphics. The structure was solved by direct methods and refined by anisotropic full-matrix least-squares for all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions and refined using a riding model with fixed thermal parameters. Crystallographic details for these compounds are summarized in Table S2.

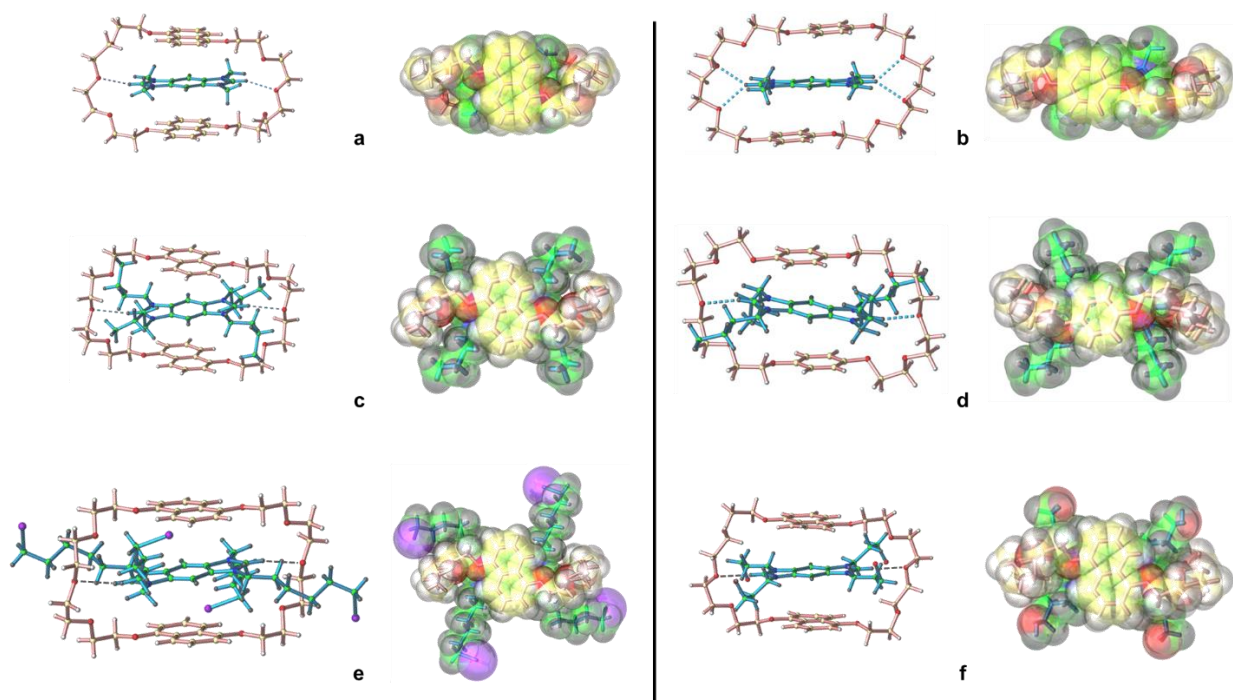


Fig S15. X-ray structures (ball and stick and space filling representations) of: a) $\{[\text{BBI-H}_2\text{-Me}_4]\text{C}15\text{DN}38\text{C}10\}^{2+}$; b) $\{[\text{BBI-H}_2\text{-Me}_4]\text{C}15\text{PP}34\text{C}10\}^{2+}$; c) $\{[\text{BBI-H}_2\text{-Bu}_4]\text{C}15\text{DN}38\text{C}10\}^{2+}$; d) $\{[\text{BBI-H}_2\text{-Bu}_4]\text{C}15\text{PP}34\text{C}10\}^{2+}$; e) $\{[\text{BBI-H}_2\text{-}((\text{CH}_2)_6\text{Br})_4]\text{C}15\text{DN}38\text{C}10\}^{2+}$; f) $\{[\text{BBI-H}_2\text{-}((\text{CH}_2)_3(\text{OH})_4)\text{C}15\text{DN}38\text{C}10\}^{2+}$ dications; color code: axle – carbon = green, hydrogen = black; wheel – carbon = yellow, hydrogen = white. The dashed lines depict de hydrogen bonding interactions between the C2-H atom on the BBI^{2+} axle and O atoms on the crown ether molecules.

Table S2. Crystal and refinement data for the compounds described in this work

	{[BBI-H ₂ -Me ₄] ⊂ 15DN38C10}(PF ₆) ₂	{[BBI-H ₂ -Me ₄] ⊂ BPP34C10}(PF ₆) ₂	{[BBI-H ₂ -Bu ₄] ⊂ 15DN38C10}(PF ₆) ₂	{[BBI-H ₂ -Bu ₄] ⊂ BPP34C10}(PF ₆) ₂
Crystal data				
Chemical formula	C ₄₈ H ₆₀ F ₁₂ N ₄ O ₁₀ P ₂	C ₄₀ H ₅₆ F ₁₂ N ₄ O ₁₀ P ₂	C ₆₀ H ₈₃ F ₁₂ N ₄ O ₁₀ P ₂	C ₅₅ H ₈₆ F ₁₂ N ₄ O ₁₁ P ₂
<i>M_r</i>	1142.94	1042.83	1310.24	1269.22
Crystal system, space group	Tetragonal, <i>I</i> 2 <i>d</i>	Triclinic, <i>P</i>	Triclinic, <i>P</i>	Triclinic, <i>P</i>
Temperature (K)	100	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	22.7748 (2), 22.7748 (2), 22.9902 (3)	8.4853 (13), 11.6056 (17), 12.1927 (18)	10.8478 (2), 12.9719 (2), 12.9821 (2)	11.0528 (4), 16.2715 (6), 17.9174 (6)
<i>α</i> , <i>β</i> , <i>γ</i> (°)	90, 90, 90	84.209 (7), 73.935 (6), 83.516 (7)	75.025 (1), 67.442 (1), 69.602 (1)	92.546 (2), 97.823 (2), 107.791 (2)
<i>V</i> (Å ³)	11924.8 (3)	1143.4 (3)	1564.75 (5)	3027.05 (19)
<i>Z</i>	8	1	1	2
<i>μ</i> (mm ⁻¹)	1.46	1.85	1.47	1.51
Crystal size (mm)	0.43 × 0.27 × 0.21	0.36 × 0.27 × 0.03	0.50 × 0.35 × 0.15	0.34 × 0.23 × 0.11
Data collection				
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan SADABS (Bruker, 2009)	Multi-scan SADABS (Bruker, 2010)	Multi-scan SADABS (Bruker, 2010)	Multi-scan SADABS (Bruker, 2010)
<i>T_{min}</i> , <i>T_{max}</i>	0.537, 0.737	0.554, 0.943	0.527, 0.815	0.543, 0.881
No. of measured, independent and observed reflections	64801, 5414, 4530 { <i>I</i> > 2σ(<i>I</i>)}	11844, 3476, 2007 { <i>I</i> > 2σ(<i>I</i>)}	31447, 5501, 4033 { <i>I</i> > 2σ(<i>I</i>)}	62977, 10685, 7142 { <i>I</i> > 2σ(<i>I</i>)}
<i>R_{int}</i>	0.109	0.098	0.095	0.107
(sin θ/λ) _{max} (Å ⁻¹)	0.601	0.594	0.600	0.601
Refinement				
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.062, 0.187, 1.06	0.064, 0.166, 1.03	0.054, 0.170, 1.07	0.049, 0.119, 1.02
No. of reflections	5414	3476	5501	10685
No. of parameters	348	310	410	763
No. of restraints	27	0	0	0
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.86, -0.34	0.47, -0.28	0.43, -0.37	0.72, -0.44

Table S2 (continued). Crystal and refinement data for the compounds described in this work

	{[BBI-H ₂ -[(CH ₂) ₃ OH] ₄] c 15DN38C10}(PF ₆) ₂	{[BBI-H ₂ -[(CH ₂) ₆ Br] ₄] c 15DN38C10}(PF ₆) ₂	{[BBI-Me ₄ -(AuPPh ₃) ₂] c 15DN38C10}(PF ₆) ₂
Crystal data			
Chemical formula	C ₅₆ H ₇₂ F ₁₂ N ₄ O ₁₄ P ₂	C ₆₈ H ₉₆ Br ₄ F ₁₂ N ₄ O ₁₀ P ₂	C ₈₈ H ₉₈ Au ₂ F ₁₂ N ₄ O ₁₁ P ₄
<i>M_r</i>	1315.11	1739.07	2133.51
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>n</i>	Triclinic, <i>P</i>	Triclinic, <i>P</i>
Temperature (K)	100	100	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.2760 (4), 12.8324 (4), 21.9878 (7)	10.9879 (4), 13.5898 (4), 13.7145 (4)	8.8880 (3), 12.0830 (5), 21.1375 (7)
α, β, γ (°)	90, 90.158 (2), 90	78.086 (2), 79.356 (2), 67.925 (2)	77.868 (2), 84.721 (2), 75.319 (2)
<i>V</i> (Å ³)	3181.58 (18)	1843.89 (10)	2145.08 (14)
<i>Z</i>	2	1	1
μ (mm ⁻¹)	1.49	3.84	7.8
Crystal size (mm)	0.43 × 0.42 × 0.30	0.52 × 0.48 × 0.28	0.44 × 0.32 × 0.13
Data collection			
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD	Bruker <i>SMART APEX II</i> CCD
Absorption correction	Multi-scan <i>SADABS</i> (Bruker, 2009)	Multi-scan <i>SADABS</i> (Bruker, 2010)	Numerical <i>SADABS v2.05</i> (Bruker, 2010)
<i>T_{min}</i> , <i>T_{max}</i>	0.534, 0.753	0.239, 0.417	0.130, 0.430
No. of measured, independent and observed reflections	42964, 5712, 4382 { <i>I</i> > 2σ(<i>I</i>)}	37174, 6432, 5812 { <i>I</i> > 2σ(<i>I</i>)}	42232, 7522, 6986 { <i>I</i> > 2σ(<i>I</i>)}
<i>R_{int}</i>	0.038	0.041	0.062
(sin θ/λ) _{max} (Å ⁻¹)	0.600	0.6	0.6
Refinement			
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.191, 0.548, 2.55	0.047, 0.121, 1.04	0.048, 0.124, 1.12
No. of reflections	5712	6432	7522
No. of parameters	614	456	628
No. of restraints	620	0	99
Δρ _{max} , Δρ _{min} (e Å ⁻³)	2.04, -0.68	1.72, -1.16	3.90, -0.98

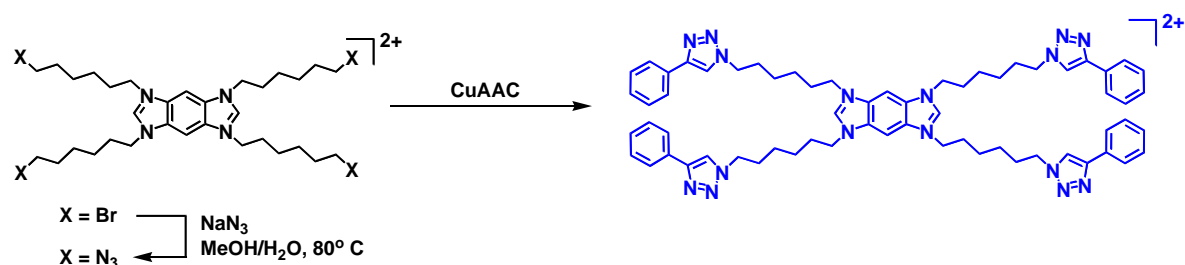
Table S3. Essential non-covalent interactions holding together the pseudorotaxane assemblies.^a

	C2-H...O _{crow} (Å)	C2...O _{crow} (Å)	C2-H-O _{crow} (°)	π-π stacking, ⊥ dist. (Å)	[N-C-N] ⁺ ...O dist. (Å)
{[BBI-H ₂ -Me ₄] ⊂ 15DN38C10}(PF ₆) ₂	2.328	3.235(6)	159.68	3.3511(14)	3.334 – 3.998
{[BBI-H ₂ -Me ₄] ⊂ BPP34C10}(PF ₆) ₂	2.365 2.292	3.154(7) 3.116(6)	140.16 144.74	3.505(2)	3.154 – 4.146
{[BBI-H ₂ -Bu ₄] ⊂ 15DN38C10}(PF ₆) ₂	2.692	3.576(4)	159.15	3.6293(14)	3.148 – 3.829
{[BBI-H ₂ -Bu ₄] ⊂ BPP34C10}(PF ₆) ₂	2.383	3.241(4)	150.37	3.3309(14)	3.140 – 3.847
{[BBI-H ₂ -[(CH ₂) ₃ OH] ₄] ⊂ 15DN38C10}(PF ₆) ₂	2.308 2.495	3.239(7) 3.410(8)	166.09 161.48	3.489(3)	3.083 – 3.773
{[BBI-H ₂ -[(CH ₂) ₆ Br] ₄] ⊂ 15DN38C10}(PF ₆) ₂	2.420	3.340(4)	162.56	3.5038(15)	3.251 – 3.747
{[BBI-Me ₄ -(AuPPh ₃) ₂] ⊂ 15DN38C10}(PF ₆) ₂	-	-	-	3.3843(19)	-

a) Calculated using Platon software⁶

Synthesis of the [BBI-H₂-(PhTz)₄](PF₆)₂ axle

The “clicked” BBI axle was prepared following a one-pot, two-step procedure as shown below.



{[BBI-H₂-[(CH₂)₆Br]₄]}(PF₆)₂ (0.110 g, 0.1 mmol) was taken in 75 mL of a MeOH : H₂O mixture (1 : 1 v/v). To the resulting suspension NaN₃ was added (0.033 g 0.5 mmol), and the mixture was stirred overnight at 50° C. Then, Ph-C≡CH (0.055 μL, 0.5 mmol) was added, followed by sodium ascorbate (0.020 g, 20 mol %), and CuSO₄ · 5 H₂O (0.013 g, 10 mol %). The reaction mixture was stirred at 50° C for 24 hours, then diluted with 75 mL ice cold water. After stirring for another hour, the precipitate was collected on a frit and air dried. Yield 0.108 g, 79 %. ¹H-NMR (400 MHz, acetone-*d*₆): δ (ppm) 10.03 (s, 2 H, C2-*H*), 9.04 (s, 2 H, C₆H₂), 8.30 (s, 4H, Triazole-*H*), 7.85 (d, J = 7.08 Hz, 8H, *Ph*), 7.42 (t, J = 4.96 Hz, 8H, *Ph*), 7.34 (t, J = 1.96 Hz, 4H, *Ph*), 4.83 (t, J = 7.24 Hz, 8 H, Imd-CH₂-), 4.43 (t, J = 6.76 Hz, 8 H, -CH₂-Br), 2.21-2.17 (m, 8 H, -CH₂-), 1.97-1.93 (m, 8 H, -CH₂-), 1.57-1.49 (m, 8 H, -CH₂-), 1.44-1.37 (m, 8 H, -CH₂-).

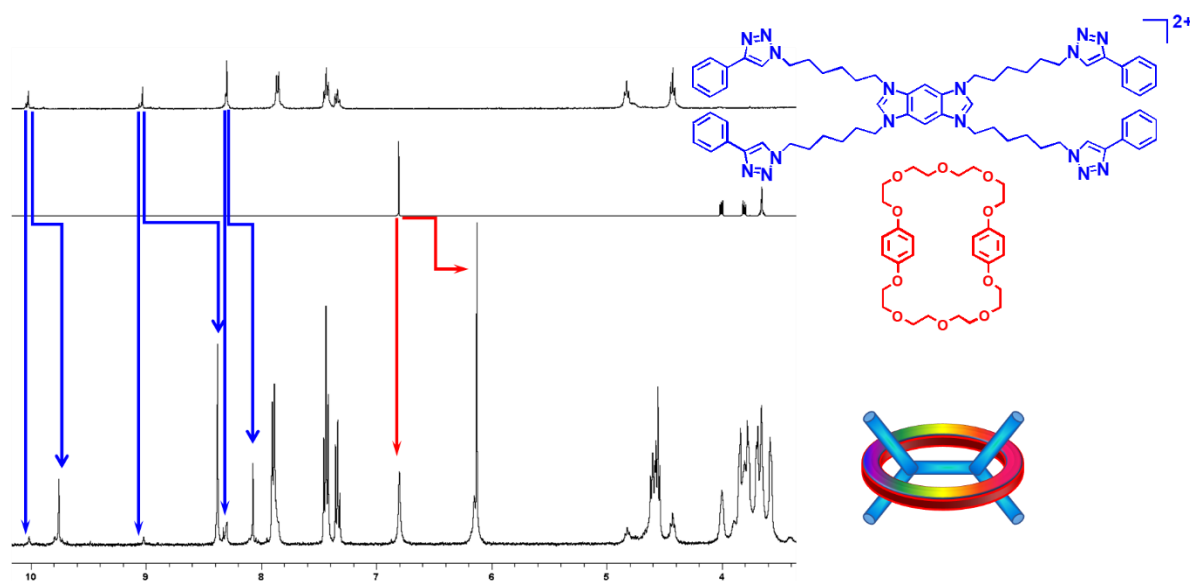


Fig S16. $^1\text{H-NMR}$ spectra (acetone- d_6) of: $[\text{BBI-H}_2\text{-PhTz}_4]^{2+}$ (top); BPP34C10 (middle); and an equimolar mixture of the two components (bottom); the K_a and ΔG^0 parameters for this compound are $3.34 \cdot 10^3 \text{ M}^{-1}$ and $-4.81 \text{ kcal} \cdot \text{mol}^{-1}$, respectively.

General procedure for the preparation of gold(I) carbene compounds.

A 100 mL round bottom flask was charged with a stirring bar, $[\text{BBI-H}_2\text{-R}_4](\text{PF}_6)_2$ ($\text{R} = \text{Me, Bu, 0.1 mmol}$), $[\text{Au}(\text{acac})\text{PPh}_3]$,⁷ (0.112 g, 0.2 mmol) and acetone (50 mL). The mixture was stirred for 2 hours at room temperature, then the solvent and the formed acetylaceton by-product were removed under reduced pressure. Recrystallization of the residue from acetone - diethyl ether produced the desired compounds as white powders.

$[\text{BBI-Me}_4\text{-(AuPPh}_3)_2](\text{PF}_6)_2$: 0.092 g, 65 %; $^1\text{H-NMR}$ (400 MHz, acetone- d_6): δ (ppm) 7.92-7.74 (m, 32H, PPh_3 overlapped with C_6H_2), 4.42 (s, 12H, $-\text{CH}_3$).

$[\text{BBI-Bu}_4\text{-(AuPPh}_3)_2](\text{PF}_6)_2$: 0.106 g, 67 %; $^1\text{H-NMR}$ (400 MHz, acetone- d_6): δ (ppm) 7.86-7.65 (m, 32H, PPh_3 overlapped with C_6H_2), 4.64 (t, $J = 7.52 \text{ Hz}$, 8 H, Imd-CH_2 -), 2.21 (p, $J = 5.61 \text{ Hz}$, 8 H, $-\text{CH}_2$ -), 1.39 (sextet, $J = 7.48 \text{ Hz}$, 8 H, $-\text{CH}_2$ -), 0.97 (t, $J = 7.51 \text{ Hz}$, 12 H, $-\text{CH}_3$).

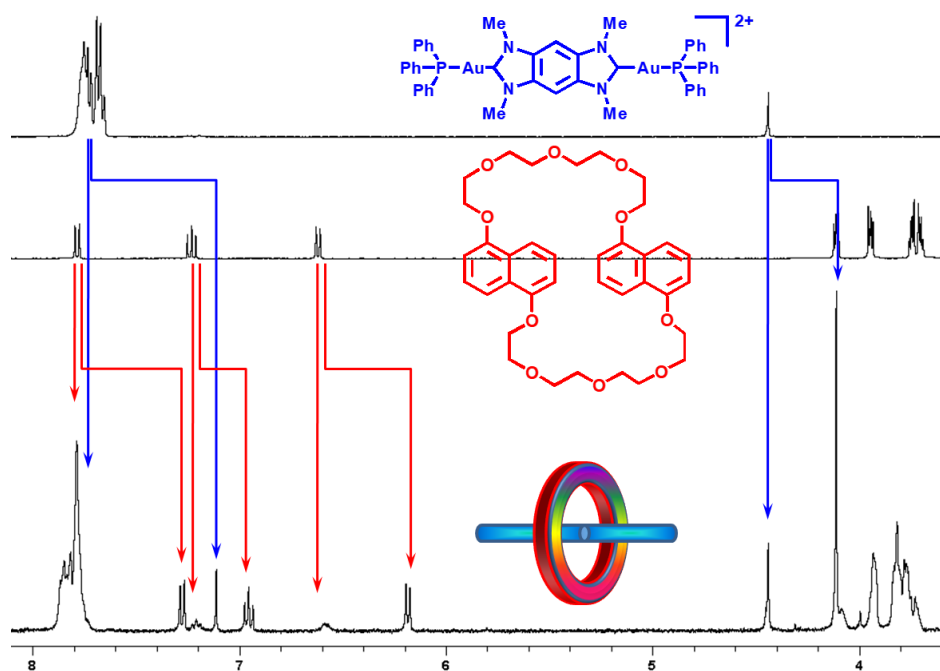


Fig. S17. $^1\text{H-NMR}$ spectra (acetone- d_6) of: $[\text{BBI-Me}_4\text{-(AuPPh}_3)_2]^{2+}$ (top); 15DN38C10 (middle); and an equimolar mixture of the two components (bottom).

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