Electronic Supplementary Information for:

Influence of axle length on the rate and mechanism of shuttling in rigid H-shaped [2]rotaxanes

Ghazale Gholami,^a Kelong Zhu,^{*b} Giorgio Baggi^a, Eduardo Schott^{*c}, Ximena Zarate^{*d}, Stephen J. Loeb^{*a}

^aDepartment of Chemistry & Biochemistry, University of Windsor, Windsor, Ontario, N9B 3P4, Canada ^bSchool of Chemistry, Sun Yat-Sen University, Guangzhou, 510275, P. R. China

^cDepartamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Avenida Vicuña Mackenna, 4860, Santiago, Chile.

^dInstituto de Ciencias Químicas Aplicadas, Facultad de Ingeniería, Universidad Autónoma de Chile. Avenida Pedro de Valdivia 641, Santiago, Chile

Table of Contents	Page
General Comments	S2
Synthetic Steps	S3
Synthesis, ¹ H and ¹³ C NMR spectra of 2	S5
Synthesis, ¹ H and ¹³ C NMR spectra of 3	S7
Synthesis, ¹ H and ¹³ C NMR spectra of [3 -H][BF ₄]	S9
Synthesis, ¹ H and ¹³ C NMR spectra of R_2	S11
Synthesis, ¹ H and ¹³ C NMR spectra of [R ₂ -H ₂][BF ₄] ₂	S13
Synthesis, ¹ H and ¹³ C NMR spectra of 4	S15
Synthesis, ¹ H and ¹³ C NMR spectra of [4 -H][BF ₄]	S17
Synthesis, ¹ H and ¹³ C NMR spectra of R_3	S19
Synthesis, ¹ H and ¹³ C NMR spectra of [R ₃ -H ₂][BF ₄] ₂	S21
Synthesis, ¹ H and ¹³ C NMR spectra of 5	S23
Synthesis, ¹ H and ¹³ C NMR spectra of 5b	S25
Synthesis, ¹ H and ¹³ C NMR spectra of [5b -H][BF ₄]	S27
Synthesis, ¹ H and ¹³ C NMR spectra of R ₄	S29
Synthesis, ¹ H and ¹³ C NMR spectra of [R ₄ -H ₂][BF ₄] ₂	S31
Synthesis, ¹ H and ¹³ C NMR spectra of 6	S33
Synthesis, ¹ H and ¹³ C NMR spectra of [6 -H][BF ₄]	S35
Synthesis, ¹ H and ¹³ C NMR spectra of R ₅	S37
Synthesis, ¹ H and ¹³ C NMR spectra of [R ₅ -H ₂][BF ₄] ₂	S40
Determination of Shuttling Rates for Neutral Molecular Shuttles	S43
Determination of Shuttling Rates for Dicationic Molecular Shuttles	S52
Details of Single-Crystal X-ray Structure Determinations	S56
Methods and Computational Details	S60
References	S62

General Comments

4,7-Di(4'-t-butylphenyl)-benzothiodiazole^{S1}, 1,2-diamino-3,6-di(4'-t-butylphenyl)-benzene (1)^{S2}, terphenyl-4,4'-dicarbaldehyde^{S3}, 4'-bromo-4-triphenylbenzaldehyde^{S4} and naphthalene-2,6-dicarbaldehyde^{S5} were synthesized according to literature methods. Dibenzo[24]crown-8 ether **DB24C8** was purchased from TCI Chemical. 4,4'-Dibromobiphenyl, 1,4-dibromobenzene and 4-t-butylphenylboronic acid were purchased from Sigma-Aldrich. The solvents were dried and distilled prior to use. Deuterated solvents were obtained from Cambridge Isotope Laboratories and used as received. ¹H, ¹³C, and 2D NMR spectra were recorded on Brüker Avance 500 or 300 instruments. All peak positions are listed in ppm relative to TMS. Melting point measurements were performed on MPA100 melting point apparatus. Column chromatography was performed using Silicycle Ultra-Pure Silica Gel (230–400 mesh).



Scheme S1. Synthetic steps involved in the preparation of precursor aldehydes (n = 1-4, Np).



Scheme S2. Synthesis of neutral [2]rotaxanes and dicationic [2]rotaxanes (n = 1-4, Np)

Synthesis of 2

ZrCl₄ (3.20 mg, 0.0136 mmol) was added to a round bottom flask containing **1** (505 mg, 0.136 mmol). Bromobenzaldehyde (25.3 mg. 0.136 mmol) was diluted with CHCl₃ in a small vial and then transferred to the round bottom flask containing **1**. The orange solution was stirred for 24 h at room temperature. Solvents were removed and a white solid residue was obtained. Yield 96% (70.0 mg). Mp: 257-259 °C. ¹H NMR (300 MHz, CDCl₃, 298 K) δ = 1.45 (s, 18H), 7.50 (s, 2H), 7.63, (m, 8H, *J* = 7.6 Hz), 7.97, (d, 4H, *J* = 7.9 Hz), 9.52 (br s, 1H).¹³CNMR (300 MHz, CDCl₃ 298K) δ = 31.51, 34.79, 123.01, 124.57, 128.29, 128.52, 128.72, 132.23, 135.52, 150.37, 150.74. IR (neat): 3358, 3031, 2691, 2902, 2866, 1602, 1493, 1474, 1461, 1425, 1260 cm⁻¹. HR-MS (ESI): calcd for [M+H]⁺, [C₃₃H₃₃BrN₂]⁺, m/z = 537.1906, found m/z = 537.1905.



S1. ¹H NMR spectrum of **2** (300 MHz, CDCl₃, 298 K).



S2. ¹³C NMR spectrum of **2** (125 MHz, CDCl₃, 298 K).

Synthesis of 3

2 (100 mg, 0.178 mmol), 4-formylphenylboronic acid (69.46 mg, 0.3909 mmol) and [Pd(PPh₃)₄] (20.5 mg, 0.0178 mmol) were added to a 100 mL Schlenk flask, degassed and backfilled with N₂. A solution of 2M Na₂CO₃ (11 mL, 120 eq.) and THF (11 mL, 120 eq.) were added and the yellow solution was refluxed (80 °C) for 24 h. The solution was cooled to room temperature, the organic layer was extracted with ethyl acetate (2 x 50 mL) and then dried over anhydrous MgSO₄. CH₃CN (20 mL) was added, the solution heated to reflux and then cooled to room temperature. The resulting solids were filtered and air dried producing a yellow solid. Yield 75% (91 mg). Mp: 191-194°C. ¹H NMR (500 MHz, CDCl₃, 298 K) δ = 1.41 (s, 18H), 7.38 (d, 1H, *J* = 7.7 Hz), 7.55 (d, 1H, *J* = 7.7 Hz), 7.56 (d, 2H, *J* = 7.5), 7.60 (d, 2H, *J* = 8.5 Hz), 7.64 (d, 2H, *J* = 8.5 Hz), 7.75 (d, 2H, *J* = 8.6) 7.80(d, 2H, *J* = 8.2 Hz), 7.97 (d, 2H, *J* = 8.45), 7.12(d, 2H, *J* = 8.5), 8.18 (d, 2H, *J* = 8.5), 9.63(s, 1H) 10.08(s, 1H). ¹³C NMR (126 MHz, CDCl₃) δ = 191.94, 150.91, 150.29, 146.10, 142.30, 140.96, 135.67, 135.46, 133.26, 131.43, 130.37, 129.97, 128.98, 127.72, 127.63, 127.41, 126.32, 125.47, 124.44, 123.39, 122.28, 34.64, 31.41. HR-MS (ESI): calcd for [M+H]⁺, [C₄₀H₃₈N₂O]⁺, m/z = 563.3018, found m/z = 563.3032.



Figure S3. ¹H NMR spectrum of 3 (500 MHz, CDCl₃, 298 K).



Figure S4. ¹³C NMR spectrum of 3 (125 MHz, CDCl₃, 298 K).

Synthesis of [3-H][BF₄]

3 (118 mg, 0.220 mmol) was dissolved in diethyl ether (100 mL). Tetrafluoroboric acid diethyl ether complex (22 μ L, 0.24 mmol) was added in a dropwise fashion. The resulting yellow solid was vacuum filtered and washed with ether. Yield 74% (87 mg). Mp: 214-217°C. ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 1.42 (s, 18H), 7.69 (s, 10H), 7.95 (d, 2H, *J* = 8.3 Hz), 8.01 (dd, 4H, *J* = 8.03Hz), 8.15 (d, 2H, *J* = 8.6Hz), 10.10(s, 1H), 12.60 (br s, 2H). ¹³C NMR (125 MHz, CD₃CN) δ = 192.32, 152.26, 151.06, 144.45, 132.50, 132.50, 130.41, 130.20, 129.94, 128.53, 128.21, 128.06, 127.59, 127.14, 126.43, 121.66, 121.66, 34.48, 30.60. HR-MS (ESI): calculated for [M+H] ⁺, [C₄₀H₃₈N₂O]⁺, m/z = 563.3062, found m/z = 563.3063.



S6. ¹³C NMR spectrum of [**3**-H][BF₄] (125 MHz, CD₃CN).

Synthesis of R₂

DB24C8 (179 mg, 0.399 mmol) was added to [**3**-H][BF₄] (65 mg, 0.0997 mmol) in a round bottom flask. CHCl₃ (30 mL) was added and stirred at room temperature until a clear solution formed. 1,2-Diamino-3,6-di(4-t-butylphenyl)benzene **1** (41 mg, 0.1097 mmol) was added, followed by ZrCl₄ (26 mg, 0.1097 mmol) and the yellow solution was stirred at room temperature for 24 h. The solution was filtered, solvents were evaporated and CH₃CN (30 mL) was added to dissolve the solids. Et₃N (0.2 mL) was slowly added and the formation of crystals was observed. The solution was filtered and air dried producing a white solid. Yield 45% (65 mg). Mp >300°C. ¹H NMR (500 MHz, CD₂Cl₂, 298 K) *δ* = 1.29 (d,36H), 2.62 (s,8H), 3.45 (s, 8H), 4.01 (s, 8H), 6.91 (m, 4H), 6.98 (m,4H), 7.30 (d, 2H, *J*= 5.7 Hz), 7.32 (d, 4H, *J*= 8.4 Hz), 7.37 (d, 4H, *J*= 8.4 Hz), 7.55 (d, 2H, *J*= 7.3 Hz), 7.57 (d, 4H, *J*= 8.6 Hz), 7.80 (d, 4H, *J*= 8.4 Hz), 8.23 (d, 4H, *J*= 8.2 Hz), 8.66 (d, 4H, *J*= 8.5 Hz), 10.7 (s, 2H). ¹³C NMR (300 MHz, CDCl3, 298K) *δ* = NMR (125 MHz, CD₂Cl₂) *δ* 152.46, 150.51, 148.86, 142.83, 135.93, 130.89, 129.66, 129.34, 128.18, 126.81, 126.23, 125.54, 123.43, 121.55, 121.26, 112.12, 69.38, 68.91, 68.60, 34.81, 31.53, 31.43. HR-MS (ESI): calcd for [M+H]⁺, [C₉₀H₉₈N₄O₈]⁺, m/z = 1363.7463, found m/z = 1363.7483.



Synthesis of [R₂-H₂][BF₄]₂

Tetrafluoroboric acid (2.8 µL, 0.0322 mmol) was added dropwise to **R**₂ which was dissolved in CH₃CN (1 mL). After 30 min, the CH₃CN was removed and diethyl ether (20 mL) was added. The solution was sonicated and vacuum filtered. Yield 66% (13.7 mg). Mp: 217-220°C. ¹H NMR (500 MHz, CD₃CN, 298 K) δ =1.44 (s,36H), 2.95 (m,4H), 3.36 (m, 8H), 3.52 (m, 4H), 3.65 (m, 8H), 6.63 (m, 4H), 6.62 (m,4H), 7.10 (s,1H),7.43 (d, 4H, *J*= 7.3 Hz), 7.62 (d, 4H, *J*= 7.3 Hz), 7.72 (d, 10H, *J*= 7.6 Hz), 8.12 (m, 4H, *J*= 8.1 Hz), 8.23 (d, 2H, *J*= 8.2 Hz), 8.54 (d, 2H, *J*= 8.5 Hz), 12.32 (s, 2H), 12.89 (s, 2H). ¹³C NMR (75 MHz, CD₃CN, 298 K) δ = 152.36, 152.11, 151.13, 150.95, 147.34, 142.23, 132.61, 132.33, 130.60, 129.96, 129.28, 128.75, 128.64, 128.10, 127.31, 126.72, 126.54, 126.34, 125.90, 124.91, 120.84, 112.49, 69.98, 69.74, 67.86, 34.55, 30.68. HR-MS (ESI): calculated for [M+H]²⁺, [C₉₀H₁₀₀N₄O₈]²⁺, m/z = 682.3765, found m/z = 682.3756.



Figure S9. ¹H NMR spectrum of [R₂-H₂][BF₄]₂ (500 MHz, CD₃CN, 298 K).



Figure S10. ¹³C NMR spectrum of [R₂-H₂][BF₄]₂ (75 MHz, CD₃CN, 298 K).

Synthesis of 4

1 (65 mg, 0.174mmol) and terphenyl-4,4'-dicarbaldehyde (0.25 g, 0.873 mmol) were dissolved in CHCl₃. ZrCl₄ (4 mg, 0.0174mmol) was added. After 24 h stirring, the solution was filtered and solvent removed. The crude product was purified by column chromatography (SiO₂, dichloromethane). Yield: 100 mg, 89%. Mp: 185-190 °C. ¹H NMR (300 MHz, CDCl₃, 298 K) δ = 1.42 (s, 18H), 7.47 (s, 2H), 7.58 (d, 4H, *J*= 7.5 Hz), 7.76 (m, 8H), 7.97 (d, 2H *J*= 7.9 Hz), 8.1 (d, 2H *J*= 8 Hz), 10.07 (s, 1H). ¹³C NMR (126 MHz, CDCl₃, 298 K) δ = 192.00, 151.12, 151.05, 146.58, 142.12, 141.89, 140.37, 139.69, 139.16, 135.63, 135.40, 130.46, 129.20, 127.98, 127.77, 127.66, 127.54, 127.33, 34.77, 31.50. H-MS (ESI): calcd for [M+H]⁺, [C₄₆H₄₃N₂O]⁺, *m/z* = 639.3370, found *m/z* = 639.3375.



Figure S12. ¹³C NMR spectrum of **4** (125 MHz, CDCl₃, 298 K).

Synthesis of [4-H][BF₄]

4 (100 mg, 0.16 mmol) was dissolved in THF (15 mL) and tetrafluoroboric acid diethyl ether complex (24 μ L, 0.176 mmol) was added. The resulting yellow solid was vacuum filtered and washed with diethyl ether. Yield 83% (93 mg). Mp: >300°C, ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 1.44 (s, 18H), 7.72 (m, 10H), 7.93 (m, 2H), 7.98 (s, 2H), 8.03 (d, 1H, *J* = 6.5 Hz), 8.07 (m, 2H, 10.07), 8.17 (m, 2H), 10.08(s, 1H), 12.45(s, 2H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 153.12, 133.39, 131.25, 130.99, 130.76, 129.40, 128.94, 128.82, 128.64, 128.41, 128.01, 127.30, 71.00, 35.35, 31.45, 27.22. H-MS (ESI): calcd for [**M** - BF₄] ⁺, [C₄₆H₄₃N₂O] ⁺, *m/z* =639.3370, found *m/z* = 639.3375.



Figure S13. ¹H NMR spectrum of [**4**-H][BF₄]; THF and Et₂O (500 MHz, CD₃CN, 298 K).



Figure S14. ¹³C NMR spectrum of [4-H][BF₄] (125 MHz, CD₃CN, 298 K).

Synthesis of R₃

DB24C8 (0.25 g, 0.56 mmol) was added to [4-H][BF₄] (90 mg, 0.14 mmol) in a round bottom flask. CHCl₃ (20 mL) was added and the mixture stirred at room temperature until a clear solution formed. 1,2-Diamino-3,6-di(4-t-butylphenyl)benzene **1** (52.4 mg, 0.14 mmol) was added, followed by ZrCl₄ (32.6 mg, 0.014 mmol) and the yellow solution was stirred at room temperature for 24 h. The solution was filtered, solvents were evaporated and CH₃CN (20 mL) was added to dissolve the solids. Et₃N (0.2 mL) was slowly added and formation of a solid was observed. The solution was filtered and air dried producing a white solid. Yield 50% (110 mg). Mp: 230-235°C. ¹H NMR (500 MHz, CD₂Cl₂, 298 K) *δ* = 1.31 (s, 36H), 2.64(s, 8H), 3.48(s, 8H), 4.03(s, 8H), 6.93(m, 4H), 7.01(m, 4H), 7.32 (m, 10H), 7.55(d, 2H, *J*= 7.7), 7.59 (d, 4H, *J*= 8.2), 7.79(d, 8H, *J*= 7.8), 8.26 (d, 4H, *J*= 8.2), 8.7(d, 4H, *J*= 8.1), 10.77(s, 2H). ¹³C NMR (125 MHz, CD₂Cl₂, 298 K) *δ* = 30.82, 30.92, 34.19, 68.00, 68.27, 68.74, 111.48, 120.63, 120.92, 122.79, 124.92, 125.61, 126.16, 127.00, 127.56, 128.72, 128.97, 129.14, 130.24, 135.31, 135.54, 139.27, 140.22, 148.25, 149.85,150.12, 151.86. HR-MS (ESI): calcd for [M+H]⁺, [C₃₆H₁₀₃N4O8]⁺, *m*/*z* =1439.7770, found *m*/*z* = 1439.7786.



Figure S16. ¹³C NMR spectrum of R₃ (125 MHz, CD₂Cl₂, 298 K).

Synthesis of [R₃-H₂][BF₄]₂

Tetrafluoroboric acid was added dropwise to **R**₃ which was dissolved in DCM. After 30 min, the DCM was removed and diethyl ether was added. The solid was filtered and recrystallized from CH₃CN. Yield 70% (12mg). Mp: >300°C. ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 1.44 (d, 36H), 2.96 (dd, 4H), 3.15 (m, 4H), 3.34 (m, 8H), 3.55 (m, 8H), 6.34 (m, 4H), 6.63 (m, 4H), 7.08 (s, 2H), 7.44 (d, 4H, *J*= 8.35 Hz), 7.64 (d, 4H, *J*= 8.35 Hz), 7.72 (m, 12H), 8.01 (m, 4H), 8.11 (m, 4H), 8.18 (d, 2H, *J*= 8.5 Hz), 8.53 (d, 2H, *J*= 8.4 Hz), 12.33 (s, 2H), 12.91 (s, 2H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 31.41, 35.26, 68.56, 70.44, 70.65, 113.19, 121.50, 121.76, 125.30, 125.49, 126.57, 126.95, 127.20, 127.87, 128.33, 128.50, 128.68, 128.81, 129.32, 129.45, 130.00, 130.73, 131.16, 132.93, 133.37, 139.57, 144.11, 148.05, 151.93, 152.05, 152.77, 153.01. HR-MS (ESI): calcd for [M-(BF₄)₂]²⁺, [C₉₆H₁₀₄N₄O₈]²⁺, *m/z* =1440.7843, found *m/z* = 1440.7831.





Figure S18. ¹³C NMR spectrum of [R₃-H₂][BF₄]₂ (125 MHz, CD₃CN, 298 K).

Synthesis of 5

1 (300 mg, 0.805mmol) and 4'-bromo-4-triphenylbenzaldehyde (271mg, 0.805 mmol) were dissolved in CHCl₃. ZrCl₄ (18.7 mg, 0.08mmol) was added. After 24 h stirring, the solution was filtered and solvent removed. The crude product was purified by recrystallization with ethyl acetate. Yield 90% (500 mg). Mp: 238-240°C. ¹H NMR (500 MHz, CDCl₃, 298 K) δ =1.42 (s, 18H), 7.45 (s, 2H), 7.52 (d, 2H, *J*= 7.5 Hz), 7.58 (d, 2H, *J*= 7.5 Hz), 7.65 (d, 3H *J*= 7.6 Hz),7.72 (dd, 4H *J*= 7.7 Hz), 7.8 (s,3H), 8.19 (d, 2H, *J*= 8.1 Hz), 10.01 (s, 1H). ¹³C NMR (125 MHz, CDCl₃, 298 K) δ = 31.50, 34.81, 121.91, 123.29, 126.09, 127.35, 127.47, 127.65, 128.40, 128.71, 132.09, 135.16, 139.47, 139.61, 142.37, 150.85, 150.99. H-MS (ESI): calcd for [M+H], [C₄₅H₄₂BrN₂]⁺, *m/z* =689.2526, found *m/z* = 689.2531.



Figure S20. ¹³C NMR spectrum of 5 (125 MHz, CDCl₃, 298 K).

Synthesis of 5b

5 (300 mg, 0.43 mmol), 4-formylphenylboronic acid (65.2 mg, 0.43 mmol) and [Pd(PPh₃)₄] (34 mg, 0.0294 mmol) were added to a 100 mL Schlenk flask, degassed and backfilled with N₂. A solution of 2M Na₂CO₃ (100 mL) and THF (100 mL) were added and the yellow solution refluxed (80 °C) for 24 h. The solution was cooled to room temperature, the organic layer was extracted with DCM (2 x 50 mL) and the solution was dried over anhydrous MgSO₄. The product was recrystallized from acetonitrile to give a yellow solid, Yield 85% (260 mg). Mp: 185-190, ¹H NMR (500 MHz, CD₂Cl₂, 298 K) δ =1.42 (s, 18H), 7.39 (d, 1H, *J*= 7.7 Hz), 7.52 (d, 1H, *J*= 7.7 Hz), 7.58 (d, 2H, *J*= 8.4 Hz), 7.64 (dd, 4H *J*= 8.4 Hz), 7.80 (d, 4H *J*= 8.6 Hz), 7.81 (s,4H), 7.85 (dd, 4H, *J*= 6.5 Hz), 7.97 (d, 2H, *J*= 8.3 Hz), 8.08 (d, 2H, *J*= 8.4 Hz), 8.18 (d, 2H, *J*= 8.4 Hz), 9.7 (s, 1H), 10.06 (s, 1H). ¹³C NMR (125 MHz, CD₂Cl₂ 298K) δ =192.04, 150.71, 135.89, 130.50, 129.26, 128.13, 127.82, 127.79, 127.71, 127.39, 126.79, 125.63, 124.80, 123.38, 122.28, 70.78, 34.94, 31.42. HR-MS (ESI): calcd for [M+H]⁺, [C₅₂H₄₇N₂O]⁺, *m/z* =715.3683, found *m/z* = 715.3688.



Figure S22. ¹³C NMR spectrum of 5b (125 MHz, CD₂Cl₂ 298K).

Synthesis of [5b-H][BF₄]

Tetrafluoroboric acid was added dropwise to **5b** which was dissolved in DCM. After 30 min, the DCM was removed and diethyl ether was added. The solid was filtered and recrystallized from CH₃CN. Yield 75% (150 mg) Mp: 235-240. ¹H NMR (500 MHz, CD₃CN, 298 K) δ =1.45 (s, 18H) 7.73 (m, 10H), 7.8 (d, 4H, *J*= 7.8 Hz), 7.93 (d, 4H *J*= 8.4 Hz), 7.96 (d, 2H *J*= 8.3 Hz), 8.01 (d, 2H *J*= 8.4 Hz), 8.06 (d, 2H, *J*= 8.6 Hz), 8.1 (d, 2H, *J*= 8.5 Hz), 10.08 (s, 1H), 12.33 (s, 2H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 193.21, 153.23, 152.19, 146.79, 146.50, 141.38, 140.87, 139.78, 139.00, 136.61, 133.49, 131.30, 131.07, 130.83, 129.53, 128.85, 128.82, 128.60, 128.52, 128.46, 128.10, 127.43, 121.59, 35.47, 31.58. HR-MS (ESI): calcd for [M-BF₄]⁺, [C₅₂H₄₇N₂O]⁺, *m/z* = 715.3688, found *m/z* = 715.3688.



Figure S24. ¹³C NMR spectrum of [5b-H][BF₄] (125 MHz, CD₃CN, 298 K).

Synthesis of R4

DB24C8 (0.25 g, 0.56 mmol) was added to [**5b**-H][BF₄] (90 mg, 0.14 mmol) in a round bottom flask. CHCl₃ (20 mL) was added and the mixture stirred at room temperature until a clear solution formed. 1,2-Diamino-3,6-di(4-t-butylphenyl)benzene **1** (52.4 mg, 0.14 mmol) was added, followed by ZrCl₄ (32.6 mg, 0.014 mmol) and the yellow solution was stirred at room temperature for 24 h. The solution was filtered, solvents were evaporated and CH₃CN (20 mL) was added to dissolve the solids. Et₃N (0.2 mL) was slowly added and formation of a solid was observed. The solution was filtered and air dried producing a white solid. Yield 60% (120mg). Mp: >300°C. ¹H NMR (500 MHz, CD₂Cl₂, 298 K) *δ* = 1.32 (36H), 2.62 (s, 8H), 3.46 (s,8H), 4.01 (s, 8H), 6.92 (m, 4H), 6.98 (m, 4H), 7.30 (dd,6H *J*= 7.7 Hz), 7.37 (d, 4H, *J*= 8.4Hz), 7.53 (d, 2H, *J*= 7.7 Hz), 7.57 (d, 4H, *J*= 8.3 Hz), 7.76 (m, 12H), 8.24 (d, 4H, *J*= 8.4Hz), 8.69 (d, 4H, *J*= 8.1 Hz), 10.76 (s, 2H). ¹³C NMR (125 MHz, CD₂Cl₂, 298 K) *δ* = 30.13, 31.03, 31.47, 31.57, 34.85, 53.43, 53.65, 53.86, 54.08, 54.30, 68.66, 68.94, 69.41, 112.15, 121.29, 121.58, 123.45, 125.17, 125.58, 126.27, 126.84, 127.68, 127.73, 128.22, 129.39, 129.83, 130.93, 135.97, 136.21, 139.87, 140.00, 142.89, 148.92, 150.52, 152.53. HR-MS (ESI): calcd for [M+H]⁺, [C₁₀₂H₁₀₇N₄O₈]⁺, *m/z* =1516.8117, found *m/z* = 1516.8123.



Figure S26. ¹³C NMR spectrum of R₄ (* = grease) (125 MHz, CD₂Cl₂, 298 K).

Synthesis of [R₄-H₂][BF₄]₂

Tetrafluoroboric acid was added dropwise to \mathbf{R}_4 which was dissolved in DCM. After 30 min, the DCM was removed and diethyl ether was added. The solid was filtered and recrystallized from CH₃CN. Yield 80% (13.5mg). Mp >300°C. ¹H NMR (500 MHz, CD₃CN, 298 K) δ =1.43 (36H), 2.95 (m, 4H), 3.33 (m,8H), 3.55 (m, 4H), 3.65 (m, 8H), 6.32 (m, 4H), 6.61 (m,4H), 7.07 (s, 2H), 7.43 (d, 4H, *J* = 8.3 Hz), 7.62 (d, 4H, *J* = 8.3 Hz), 7.69 (m, 12H), 7.92 (m, 8H), 8.06 (m, 4H), 8.16 (d, 2H, *J* = 8.5 Hz), 8.51 (d, 2H, *J* = 8.3 Hz), 12.29 (s, 2H), 12.90 (s, 2H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 31.47, 35.34, 68.65, 70.54, 70.75, 113.28, 121.59, 125.55, 126.67, 126.96, 127.07, 127.33, 128.00, 128.40, 128.55, 128.59, 128.78, 129.43, 129.54, 130.11, 130.75, 131.25, 133.01, 133.40, 133.48, 139.03, 140.75, 146.42, 148.14, 152.12, 152.86, 153.12. 31.4. HR-MS (ESI): calcd for [M-(BF₄)₂]²⁺, [C₁₀₂H₁₀₈N₄O₈]²⁺, *m/z* =1516.8156, found *m/z* = 1516.8153.



Figure S27. ¹H NMR spectrum of [R₄-H₂][BF₄]₂ (500 MHz, CD₃CN, 298 K).



Figure S28. ¹³C NMR spectrum of [R₄-H₂][BF₄]₂ (* = Et₂O) (125 MHz, CD₃CN, 298 K).

Synthesis of 6

1,2-Diamino-3,6-di(4'-t-butylphenyl)benzene (130 mg, 0.36 mmol), naphthalene-2,6-dicarbaldehyde (330 mg, 1.8 mmol), and ZrCl₄ (4.2 mg, 0.018 mmol) were added to 50 mL of CH₃CN. The mixture was stirred in open air at room temperature for 24 h. Trimethylamine (0.5 mL) and chloroform (20 mL) were added and the mixture was filtered. The solvents of the filtrate were removed on a rotary evaporator. The residue was purified by column chromatography using dichloromethane as eluent. Further washing with acetonitrile gave the pure product as a pale yellow solid. Yield: 162 mg, 84%. Mp: 280-283 °C. ¹H NMR (300 MHz, DMSO-*d*₆, 298 K) δ = 12.93 (s, 1H), 10.18 (s, 1H), 9.03 (s, 1H), 8.64 (s, 1H), 8.58 (d, 1H, *J* = 8.7 Hz), 8.30 (d, 1H, *J* = 8.7 Hz), 8.18 (d, 1H, *J* = 8.7 Hz), 8.14 (d, 2H, *J* = 8.4 Hz), 7.96 (d, 1H, *J* = 8.7 Hz), 7.70 (d, 2H, *J* = 8.4 Hz), 7.60 (d, 2H, *J* = 8.4 Hz), 7.57 (d, 2H, *J* = 8.4 Hz), 7.50 (d, 1H, *J* = 8.4 Hz), 7.31 (d, 1H, *J* = 8.4 Hz), 1.39 (s, 9H), 1.37 (s, 9H). ¹³C NMR (75 MHz, DMSO-*d*₆, 298 K) δ = 193.5, 152.2, 150.5, 150.1, 142.7, 136.3, 135.9, 135.6, 135.0, 134.7, 134.3, 133.3, 131.1, 130.4, 130.1, 129.2, 128.7, 127.2, 126.7, 126.3, 125.7, 125.5, 124.2, 123.7, 121.8, 31.7, 31.7. HR-MS (ESI): calcd for [M+H]⁺, [C₃₈H₃₇N₂O]⁺, *m*/*z* = 537.2861, found *m*/*z* = 537.2907.





Figure S30. ¹³C NMR spectrum of **6** (75 MHz, DMSO-*d*₆, 298 K).

Synthesis of [6-H][BF₄]

Tetrafluoroboric acid diethyl ether complex (36 μ L, 0.26 mmol) was added to a mixture of **6** (130 mg, 0.24 mmol) in diethyl ether (100 mL) with stirring. After stirred for 10 min, the resulting white solid was filtered, rinsed with diethyl ether and air dried. Yield: 141 mg, 93%. Mp 240–243 °C. ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 12.45 (br s, 2H), 10.21 (s, 1H), 8.76 (s, 1H), 8.60 (s, 1H), 8.38 (d, 1H, *J* = 8.5 Hz), 8.23 (d, 1H, *J* = 8.5 Hz), 8.15 (d, 1H, *J* = 8.5 Hz), 8.08 (d, 1H, *J* = 8.5 Hz), 7.72 (s, 2H), 7.70 (m, 8H), 1.42 (s, 18H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 192.4, 152.3, 150.9, 136.6, 135.1, 134.75, 133.8, 132.4, 131.4, 130.9, 130.2, 130.0, 128.6, 127.6, 127.3, 126.5, 125.9, 124.5, 121.7, 34.5, 30.6. HR-MS (ESI): calcd for [M-BF₄]⁺, [C₃₈H₃₇N₂O]⁺, *m*/*z* = 537.2900, found *m*/*z* = 537.2908.



Figure S31. ¹H NMR spectrum of [**6**-H][BF₄] (* = diethyl ether) (500 MHz, CD₃CN, 298 K).



Figure S32. ¹³C NMR spectrum of [**6**-H][BF₄] (* = diethyl ether) (125 MHz, CD₃CN, 298 K).

Synthesis of R₅

[6-H][BF₄] (94 mg, 0.15 mmol) and **DB24C8** (135 mg, 0.30 mmol) were stirred in CHCl₃ (20 mL) until a clear solution resulted. 1,2-Diamino-3,6-di(4'-t-butylphenyl)benzene (57 mg, 0.154 mmol) was added followed by ZrCl₄ (3.6 mg, 0.015 mmol). The mixture was stirred at room temperature overnight, filtered and the filtrate was concentrated under vacuum. The residue was washed with diethyl ether twice and air dried. The dried solid was dissolved in CH₃CN (30 mL) and filtered. Et₃N (0.2 mL) was added to the filtrate. The mixture was heated to reflux and allowed to cool to room temperature. The pale yellow solid was filtered, washed with CH₃CN, and air dried. Yield: 171 mg, 85%. Mp> 300 °C. ¹H NMR (500 MHz, CD₂Cl₂, 298 K) δ = 10.70 (br s, 1H), 9.08 (s, 2H), 8.70 (d, 2H, J = 4.2 Hz), 8.22 (d, 4H, J = 8.5 Hz), 7.81 (d, 2H, J = 4.2 Hz), 7.54 (d, 4H, J = 8.5 Hz), 7.49 (d, 2H, J = 8.4 Hz), 7.32 (m, 10H), 6.96 (m, 8H), 3.97 (s, 8H), 3.36 (s, 8H), 2.44 (s, 8H), 1.25 (s, 36H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 192.4, 152.3, 150.9, 136.6, 135.1, 134.75, 133.8, 132.4, 131.4, 130.9, 130.2, 130.0, 128.6, 127.6, 127.3, 126.5, 125.9, 124.5, 121.7, 34.5, 30.6. ¹³C NMR (75 MHz, CD₂Cl₂) δ 152.47, 150.45, 150.13, 148.53, 142.57, 135.77, 135.56, 133.53, 133.42, 130.62, 129.03, 128.64, 128.27, 127.82, 126.99, 125.93, 125.18, 124.77, 123.10, 121.20, 121.03, 111.87, 69.08, 68.55, 68.34, 34.50, 34.45, 31.18, 31.11. HR-MS (ESI): calcd for [M+H]⁺, $[C_{88}H_{97}N_4O_8]^+$, m/z = 1337.7301, found m/z = 1337.7306.

Figure S33. ¹H NMR spectrum of R₅ (500 MHz, CD₂Cl₂, 298 K).

Figure S34. ¹³C NMR spectrum of **R**₅ (125 MHz, CD₃CN, 298 K).

Figure S35. ¹H NMR spectrum of R₅ (500 MHz, CD₂Cl₂, 298 K).

Synthesis of [R₅-H₂][BF₄]₂

Tetrafluoroboric acid diethyl ether complex (28 μ L, 0.20 mmol) was added to a mixture of **R**₅ (67 mg, 0.05 mmol) in dichloromethane (10 mL) with stirring. The solvent of the mixture was removed under vacuum. The residue was washed by diethyl ether and air dried. Yield: 70 mg, 92%. Mp> 300 °C. ¹H NMR (500 MHz, CD₃CN, 298 K) δ = 12.99 (br s, 2H), 12.46 (br s, 2H), 9.13 (s, 1H), 8.87 (s, 1H), 8.65 (d, 1H, *J* = 4.1 Hz), 8.44 (d, 1H, *J* = 4.1 Hz), 8.34 (d, 1H, *J* = 4.1 Hz), 8.21 (d, 1H, *J* = 4.1 Hz), 7.71-7.77 (m, 6H), 7.65 (d, 4H, *J* = 8.5 Hz), 7.44 (d, 4H, *J* = 8.5 Hz), 7.13 (s, 2H), 8.38 (d, 1H, *J* = 8.5 Hz), 8.23 (d, 1H, *J* = 8.5 Hz), 8.15 (d, 1H, *J* = 8.5 Hz), 8.08 (d, 1H, *J* = 8.5 Hz), 7.13 (s, 2H), 6.64 (m, 4H), 6.37 (m, 4H), 3.66-3.35 (m, 8H), 3.60 (m, 4H), 3.48 (m, 4H), 3.39 (m, 4H), 2.75 (m, 4H), 1.43 (s, 36H). ¹³C NMR (125 MHz, CD₃CN, 298 K) δ = 152.31, 152.15, 150.85, 150.57, 147.34, 133.72, 133.53, 132.51, 132.47, 132.23, 131.64, 130.26, 130.06, 129.30, 129.23, 128.89, 128.83, 128.57, 127.69, 127.37, 126.53, 126.44, 126.13, 126.02, 125.92, 125.13, 121.30, 120.88, 112.55, 69.93, 69.82, 67.83, 34.51, 30.66, 30.64. HR-MS (ESI): calcd for [M-BF4]⁺, [C44H₅₀N₂O4]⁺, *m/z* = 670.3765, found *m/z* = 670.3732.

Figure S36. ¹H NMR spectrum of [R₅-H₂][BF₄]₂ (500 MHz, CD₃CN, 298 K).

Figure S37. ¹³C NMR spectrum of [R₅-H₂][BF₄]₂ (125 MHz, CD₃CN, 298 K).

Figure S38.¹H NMR (500 MHz, 298K, CD₂Cl₂); rotaxane (top) and dumbbell thread (bottom)

Determination of Shuttling Rates for Neutral [2]Rotaxane Molecular Shuttles $R_2 - R_5$

Figure S39. Variable temperature ¹H NMR of R₂ (500 MHz, CD₂Cl₂)

Figure S40. Comparison of the experimental and simulation ¹H NMR data

Figure S41. Eyring plot generated from the simulated data for R₂

Figure S43. Comparison of the experimental and simulation ¹H NMR data

Figure S44. Eyring plot generated from the simulated data (right) for R₃

Figure S45. Variable temperature ¹H NMR of R₄ (500 MHz, CD₂Cl₂)

Figure S46. Comparison of the experimental and simulation ¹H NMR data (left)

Figure S47. Eyring plot generated from the simulated data (right) for R4

Figure S48. Variable temperature ¹H NMR of R₅ (500 MHz, CD₂Cl₂)

Figure S49. Comparison of the experimental and simulation ¹H NMR data

Figure S50. Eyring plot generated from the simulated data (right) for R₅

The shuttling rates were calculated from a line shape analysis of the NMR spectra using the program DNMR71.EXE.^{S6}

$$k_{\rm c} = (\pi \Delta v)/2^{1/2}$$

 k_c is the rate of shuttling at coalescence temperature. Δv is the limiting chemical shift (in Hz) between the exchanging proton resonances and can be determined by variable-temperature NMR. The Eyring equation,^{S7} $\Delta G_c^{\neq} = -RT_c \ln(k_c h/k_B T_c)$, was used to estimate ΔG_c^{\neq} and extrapolate the rate of shuttling to other temperatures. T_c is the coalescence temperature, R is the gas constant, h is Planck's constant, and k_B is Boltzmann's constant.

The neutral species **R**₁ could not be cooled down far enough to attain the limiting chemical shifts. We observed the coalescence temperature at 183 K, but nothing further. This data has been published^{S8} and the VT spectra are available in the ESI of that article. By assuming the separation of the limiting peaks to be approximately 1000 Hz – this is about the average of the other (n = 2,3,4) samples – we roughly estimated an upper value for ΔG_c^{\star} to be 7.73 kcal/mol.

shuttle	⊿v(Hz)	Т _с (К)	<i>k</i> _c (s⁻¹)	<i>k</i> _(298 к) (s ⁻¹)	ΔG c [≠] (kcal/mol)	ΔG (298) [≠] (kcal/mol)
R ₂	1080	222	6200	4.20 × 10 ⁶	9.01	8.41
R ₃	932	228	3264	4.03 × 10 ⁶	9.56	8.44
R ₄	999	223	4650	3.80 × 10 ⁶	9.18	8.47
R₅	609	233	3100	4.26 × 10 ⁶	9.80	8.40

Table S1 Summary of Shuttling Rates for Neutral [2] Rotaxane Molecular Shuttles

Determination of Shuttling Rates for Dicationic Molecular Shuttles $[R_1-H_2]^{2+} - [R_5-H_2]^{2+}$

Figure S51. 2D ¹H-¹H EXSY (300 MHz, 295 K, CD₃CN) spectrum of [R₂-H₂][BF₄]₂

Figure S52. 2D ¹H-¹H EXSY (300 MHz, 295 K, CD₃CN) spectrum of [R₃-H₂][BF₄]₂

NH': Complexed, NH: Uncomplexed

Figure S54. 2D ¹H-¹H EXSY (500 MHz, 298K, CD₃CN) spectrum of [R₅-H₂][BF₄]₂

shuttle	I _{AA}	I _{BB}	I _{AB}	I _{BA}	k (s ⁻¹)	ΔG [≠] (kcal/mol)	Т (К)
[R₂-H 2][BF4]2	0.3421	0.0887	0.0013	0.00001	0.0061	20.21	295
[R ₃ -H ₂][BF ₄] ₂	1.7451	1.3902	0.0094	0.0033	0.0078	20.07	295
[R ₄ -H ₂][BF ₄] ₂	0.3385	0.3464	0.0016	0.0016	0.0090	19.83	293
[R 5-H2][BF4]2	0.9899	1.0000	0.0060	0.0063	0.0124	20.05	298

Table S2 Shuttling Rates for Dicationic [2] Rotaxane Molecular Shuttles

Details of Single X-ray Crystal Structure Determinations

X-ray Crystallography

General: Crystals were frozen in paratone oil inside a cryoloop under a cold stream of N₂. X-ray intensity data were collected at 173(2) K using a Bruker APEX diffractometer equipped with an APEX area detector. The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.⁵⁹ Final unit cell parameters were determined by least-squares refinement taken from the data set. Diffraction data and unit-cell parameters were consistent with the assigned space groups. The structures were solved by direct methods with SHELXT.⁵¹⁰ Subsequent difference Fourier calculations and full-matrix least-squares refinement against |F²| were performed with SHELXL-2014^{S10} using OLEX2.⁵¹¹ All non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in idealized positions and refinement details. Complete details of the structures can be obtained from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk for CCDC accession numbers 1563641, 1563642, 1563643 and 1563644.

X-ray structure of [2]Rotaxane R₅

Single crystals were obtained from slow evaporation of a DMF solution of **R**₅. Crystals of formula $\mathbf{R}_5(\text{DMF})_2$ were of good quality. Data was collected using MoK α radiation ($\lambda = 0.71073$ Å). The asymmetric unit contained one molecule of the [2]rotaxane ($C_{88}H_{96}N_4O_8$) and two molecules of DMF. The structure was solved in the triclinic space group P-1 (#2). One of the *t*Bu groups was disordered and modelled with occupancies of 81:19 using PART and FVAR. See Table S1 for details.

X-ray structure of [2]Rotaxane [R₅-H₂][BF₄]₂

Single crystals were obtained from slow evaporation of a toluene solution of R_5 -H₂][BF₄]₂. Crystals of formula [R_5 -H₂][BF₄]₂(toluene)₄ were of good quality. Data was collected using MoK α radiation ($\lambda = 0.71073$ Å). The asymmetric unit contained one molecule of the dicationic [2]rotaxane (C₈₈H₉₈N₄O₈), two BF₄ anions, three molecules of toluene and one water molecule. The structure was solved in the triclinic space group P-1 (#2). Two of the *t*Bu groups were disordered and both modelled with occupancies of 53:47 using PART and FVAR. Both anions were disordered and restrained with SAME & SIMU commands and modelled with occupancies of 84:16 and 79:21 respectively using PART and FVAR. The toluene molecules were included as rigid groups using a combination of SADI restraints. See Table S1 for details.

X-ray structure of [2]Rotaxane R₂ from THF

Single crystals were obtained from slow evaporation of a THF solution of R_2 . Crystals of formula R_2 (THF)₄ were of good quality. Data was collected using CuK α radiation ($\lambda = 1.54178$ Å). The asymmetric unit contained half a molecule of the [2]rotaxane (C₉₀H₉₈N₄O₈) and two molecules of THF. The structure was solved in the triclinic space group P-1 (#2). Both *t*Bu groups were disordered and modelled as rigid groups using SADI and SIMU with occupancies of 54:46 and 68:32 respectively using PART and FVAR. One of the THF molecules was disordered modelled with occupancies of 75:25 using PART and FVAR. See Table S1 for details.

X-ray structure of [2]Rotaxane R₁-Br

Single crystals were obtained from slow evaporation of an ethyl acetate solution of **R**₁-**B**_r. Crystals of formula **R**₁-**B**_r were of good quality. Data was collected using MoK α radiation (λ = 0.71073 Å). The asymmetric unit contained half a molecule of the [2]rotaxane (C₃₆H₄₂Br₄N₄ O₈); no anions, no solvent. The structure was solved in the triclinic space group P-1 (#2). No restraints were required. See Table S1 for details.

CCDC No.	1563641	1563642
Compound	R ₅ (DMF) ₂	$[\mathbf{R}_{5}-H_{2}][\mathbf{BF}_{4}]_{2}(H_{2}O)(toluene)_{3}$
Formula	$C_{94}H_{110}N_6O_{10}$	$C_{109}H_{124}B_2F_8N_4O_9$
<i>M</i> [gmol ⁻¹]	1483.87	1807.73
Crystal system	Triclinic	Triclinic
Space group	P-1 (No. 2)	P-1 (No. 2)
a [Å]	14.3220(13)	14.2079(9)
b [Å]	15.9818(16)	18.9576(11)
<i>c</i> [Å]	20.0611(16)	20.1063(13)
α[°]	107.703(4)	97.249(3)
β[°]	90.106(4)	100.114(3)
γ[°]	110.238(4)	108.536(3)
V [ų]	4074.8(7)	4957.8(5)
Z	2	2
D_{calcd} . [gcm ⁻³]	1.209	1.211
μ [mm ⁻¹]	0.078	0.086
Reflections	8510	20185
R _{int}	0.1148	0.0518
Parameters	1007	1400
Restraints	114	328
<i>R</i> 1 [I > 2σ(I)]ª	0.1041	0.1057
R1 (all data)	0.2001	0.1744
<i>wR</i> 2 [I > 2σ(I)] ^b	0.2151	0.2079
wR2 (all data)	0.2713	0.2555
GoF (<i>F</i> ²)	1.026	1.106
Δρ [e Å ^{–3}]	+0.39 (-0.41)	+0.63 (-0.63)

Table S1. Single-crystal X-ray data collection, solution and refinement detailsfor R_5 and $[R_5-H_2][BF_4]_2$.

^aR1 = $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; R2w = $[\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$ ^bw = $q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

CCDC No.	1563643	1563644
Compound	R ₂ (THF) ₄	R ₁ -Br
Formula	$C_{106}H_{130}N_4O_{12}$	$C_{36}H_{42}Br_4N_4O_8$
<i>M</i> [gmol ⁻¹]	1652.13	978.37
Crystal system	Triclinic	Triclinic
Space group	P-1 (No. 2)	P-1 (No. 2)
<i>a</i> [Å]	12.0595(2)	9.6346(14)
<i>b</i> [Å]	12.5637(3)	10.1658(15)
<i>c</i> [Å]	16.8685(3)	11.2070(17)
α[°]	74.7825(11)	68.379(2)
β[°]	76.6602(12)	82.740(2)
γ [°]	70.7332(11)	68.992(2)
<i>V</i> [Å ³]	2298.72(8)	10682(13)
Z	1	1
D_{calcd} . [gcm ⁻³]	1.193	1.706
μ [mm ⁻¹]	0.607	4.281
Reflections	8028	3839
R _{int}	0.0557	0.0518
Parameters	664	235
Restraints	100	0
$R1 [I > 2\sigma(I)]^a$	0.0584	0.0374
R1 (all data)	0.0962	0.0438
$wR2 [I > 2\sigma(I)]^{b}$	0.1379	0.0995
wR2 (all data)	0.1570	0.1042
GoF (<i>F</i> ²)	1.037	1.032
Δ <i>ρ</i> [e Å ⁻³]	+0.36 (-0.23)	+0.99 (-0.36)

Table S2. Single-crystal X-ray data collection, solution and refinementdetails for R_2 and R_1 -Br.

^aR1 = $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$; R2w = $[\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$ ^bw = $q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$.

Methods and Computational Details

Quantum mechanics calculations were carried out in the framework of the Density Functional Theory (DFT) methods incorporated in the GAUSSIAN09 package.^{S12} The ground state equilibrium structures and the transition state (TS) structures of the dibenzo[24]crown-8 (**DB24C8**) macrocycle and an H-shaped axle, forming a rotaxane, were fully optimized without symmetry restraints. The track length of the axle was varied in terms of the amount (n) of phenylene spacers, increasing from n=1 to n=4. The Becke-3-parameter-Lee-Yang–Parr hybrid functional (B3LYP),^{S13} which incorporates 20% of Hartree-Fock exact exchange, was employed as it has been reported to achieve good agreement with X-ray geometrical structures of even large molecular systems.^{S14} The Gaussian-type basis set 6-31G(d,p)^{S15} was employed for all atoms and the dispersion correction (DFT-D3) to the energy was included in all the calculations using the Grimme scheme.^{S16}

Molecular structures of the starting and finishing points for the shuttling of the rotaxane, which were constructed with the **DB24C8** macrocycle in each extreme of the axle, were optimized to find stationary point geometries. The structures of the TS between these geometries were optimized by applying Schlegel's synchronous-transit-guided quasi-Newton (QST3) method.^{S17} The nature of the found stationary points on the potential energy surface (PES) was characterized by the computation of the harmonic vibrational frequencies obtained by the examination of the Hessian matrix, which is constituted by the second derivative of energy with respect to the spatial coordinates of the systems. The transition states were verified to be first order saddle points with only one negative eigenvalue. Implicit solvation effects were taken into account by means of the Polarized Continuum Model (PCM) using dichloromethane (DCM, $\varepsilon = 8.93$).^{S18}

n	Charge	Start	TS	Finish	∆G[≠] (AU) ⊺h	ΔG [≠] (kcal mol⁻¹) _{Th}
1	0	-4077.19	-4077.17	-4077.19	0.018	11.1
2	0	-4308.18	-4308.15	-4308.18	0.027	17.1
3	0	-4539.17	-4539.14	-4539.17	0.033	20.5
4	0	-4770.17	-4770.14	-4770.17	0.033	20.9
1	+2	-4078.08	-4078.05	-4078.07	0.029	18.0
2	+2	-4309.08	-4309.02	-4309.07	0.054	34.1
3	+2	-4540.08	-4540.01	-4540.07	0.068	42.6
4	+2	-4771.07	-4771.00	-4771.06	0.074	46.4

Figure S55. Calculated TS structures for $R_1 - R_4$ and $[R_1-H_2]^{2+} - [R_4-H_2]^{2+}$.

References

- S1 H. Akpinar, A. Balan, D. Baran, E. Unver, L. Toppare, *Polymer*, **2010**, 51, 6123–6131.
- S2 K. Zhu, V. N. Vukotic, N. Noujeim, S. J. Loeb, *Chem. Sci.*, **2012**, *3*, 3265–3271.
- S3 M. Kozakova, M. Budesinsky, J. Hodacova, Synthetic Communication, 2005, 35, 161– 167.
- S4 H. C.hun Cheng, P. P. Yu Chen, Y. Oliver Su, *Dalton Trans.*, **2014**, *43*, 1424–1433.
- S5 G.-Y. Xie, L. Jiang, T.-B. Lu, *Dalton Trans.*, **2013**, *42*, 14092–14099.
- S6 DNMR71.EXE, Reich, H. J., J. Chem. Educ. Software, 1996.
- S7 I. O. Sutherland, Annu. Rep. NMR Spectrosc. **1971**, 4, 71.
- S8 K. Zhu, V. N. Vukotic, N. Noujeim, S. J. Loeb, Chem. Sci. 2012, **3**, 3265.
- S9 Bruker, SAINT+ and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA, 2012.
- S10 G. M. Sheldrick, Acta Cryst. 2015, C71, 3–8.
- S11 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Cryst., 2009, 42, 339–341.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O[°]. Farkas, J. B. Foresman, J. V. Ortiz and J. Cioslowski and D. J. Fox, *Gaussian 09, Revision E.01, Gaussian, Inc.*, Wallingford CT, 2009.
- S13 (a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648; (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 1994, 98, 11623.
- S14 (a) S. Tortorella, M. M. Talamo, A. Cardone, M. Pastore, F. De Angelis. J. Phys.: Condens. Matter. 2016, 28, 074005 (11 pp); (b) M Pastore, E Mosconi, F De Angelis, M. Grätzel. J. Phys. Chem. C. 2010, 114, 7205; (c) M. N. Glukhovtsev, R. D. Bach, C. J. Nagel. J. Phys. Chem. A. 1997, 101, 316.
- S15 M. J. Frisch, J. A. Pople, J. S. Binkley. J. Chem. Phys. 1984, 80, 3265.
- S16 S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 1541041 (19 pp).
- S17 C. Peng, H. B. Schlegel. Israel J. Chem. 1993, 33, 449.
- S18 M. Cossi, N. Rega, G. Scalmani and V. Barone, J. Comput. Chem., 2003, 24, 669.