Translational Dynamics of a Non-degenerate Molecular Shuttle Imbedded in a Zirconium Metal-Organic Framework

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Materials and Methods

Anhydrous ethanol was purchased from Sigma-Aldrich. 24-Crown-8 ether (24C8) was purchased from TCI chemicals. THF was dried using an Innovative Technologies Solvent Purification System. Compounds, 3,6-di(4-ethoxycarbonylphenyl)-1,2-phenylenediamine,^{S1} $[H1][BF_4],$ 2-(4formylphenyl)-4,7-bis(4-ethoxycarbonylphenyl)benzimidazolium tetrafluoroborate, ^{S1} [H1*][BF₄], ¹³C 2-(4-formylphenyl)-4,7-bis(4-ethoxycarbonylphenyl)benzimidazolium enriched tetrafluoroborate^{S1} and 3.6-dibromo-1,2-phneylenediamine^{S2} were synthesised following literature procedures. Deuterated solvents were obtained from Cambridge Isotope Laboratories and used as received. ¹H, ¹³C, and 2D NMR spectra were recorded on a Brüker Avance 500 III spectrometer. Samples were locked to the deuterated solvent and all chemical shifts reported in ppm referenced to tetramethylsilane. Mass spectra were recorded on a Waters Xevo G2-XS instrument. Solutions with concentrations of 0.001 molar were prepared in methanol and injected for analysis at a rate of 5 μ L/min using a syringe. Melting point measurements were performed on MPA100 melting point apparatus. PXRD measurements were performed on a PROTO AXRD benchtop diffractometer for 2 to 30° 2theta values. VT measurements were performed using an Anton Paar BTS500 stage with temperatures ramped at 10 K min⁻¹ and allowed to stabilise for 2 minutes. TGA was performed using a TA TGA5500 and samples were allowed to isotherm for 10 min at ambient temperature unless otherwise stated and then heated at 10 °C min⁻¹ to 600 °C under a nitrogen atmosphere. IR measurements were performed using a Bruker Alpha FT-IR with the following abbreviations: weak, w medium, m strong, s and broad, br. Single crystal X-ray diffraction was performed on a Bruker D8 Venture diffractometer equipped with a PHOTON 100 detector, Kappa goniometer and collected using a CuK_{α} (λ = 1.54178 Å) high brilliance IµS microfocus source. Crystals were frozen in paratone oil inside a cryoloop under a cold stream of N₂. Reflection data were integrated from frame data using APEX III software. The raw area detector data frames were reduced and corrected for absorption effects using the SAINT+ and SADABS programs.^{S3} 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 intrinsic phasing with SHELXT.⁵⁴ Subsequent difference Fourier calculations and full-matrix least-squares refinement against |F²| were performed with SHELXL-2014^{S5} using OLEX2.^{S6} All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in idealized positions and refined using a riding model. SSNMR spectra were acquired using a Varian Infinity Plus console equipped with a 9.4 T Oxford magnet at a resonance frequency of 100.5 MHz for ¹³C experiments were conducted using a Chemagnetics 4 mmHX MAS probe. Samples were packed into zirconia rotors and temperatures calibrated using the ²⁰⁷Pb isotropic shift of PbNO₃. The program Materials Studio was used to create the model structure of UWDM-11 shown in Fig. 3. The starting point was the *cif* file for **PCN-57**.⁵⁷ The symmetry was changed from $Fm\overline{3}m$ to P1 in order to build the rotaxane appendage within Materials Studio and the structure optimized using the Forcite function.^{S8} A single H-bond between the benzimidazole NH and a 24C8 ether O-atom was used to tether the macrocycle to the axle.

Synthesis of Compound 2



[H1][BF₄] (314 mg, 0.52 mmol) and 24-crown-8 ether (365 mg, 1.0 mmol) were dissolved in chloroform (40 mL) at room temperature and stirred for 30 min. 3,6-Dibromo-1,2phenylenediamine (138 mg, 0.52 mmol) and ZrCl₄ (12.1 mg, 0.052 mmol) were added and the resulting yellow solution was stirred at room temperature exposed to air for 24 h. The solution was then filtered, and the solvent removed under reduced pressure. The resulting yellow oil was washed with diethyl ether (2 x 20 mL) and the residue was dissolved in acetonitrile (50 mL) and heated at reflux for 30 min. The cloudy solution was cooled to room temperature and filtered. The filtrate was reduced in volume and triethyl amine (0.5 mL) was added resulting in the formation of a pale brown precipitate which was separated via filtration and air dried (267 mg, 0.24 mmol, 46%). Slow evaporation of a DCM/methanol solution gave single crystals of $2 \cdot CH_3OH$ suitable for single crystal X-ray diffraction. Vapour diffusion of diethyl ether into the acetonitrile solution of [H2][BF₄] gave single crystals suitable for single crystal X-ray diffraction. M.P. 290 – 295 °C, ¹H NMR (CD₂Cl₂, 500 MHz) δ 11.76 (1H, br. s), 10.62 (1H, s), 8.79 (2H, d, J = 8.48 Hz), 8.43 (2H, d, J = 8.45 Hz), 8.35 (2H, d, J = 8.17 Hz), 8.22 (4H, m), 7.84 (2H, d, J = 8.08 Hz), 7.63 (1H, d, J = 7.69 Hz), 7.44 (1H, d, J = 7.70), 7.34 (1H, br. s), 7.28 (1H, br. s), 4.42 (4H, q, J = 7.13 Hz), 3.45 (16H, m), 3.28 (16H, m), 1.44 (6H, t, J = 7.13), ¹³C NMR (CD₂Cl₂, 101 MHz) δ 153.48, 152.63, 130.81, 130.17, 129.43, 128.36, 127.09, 123.34, 122.12, 69.88, 61.09, 14.13, IR (*u*_{cm-1}): 3200 (br. w), 2868 (w), 1710 (s), 1605 (m), 1565 (w), 1479 (m), 1439 (m), 1398 (w), 1359 (m), 1267 (s), 1179 (m), 1100 (br. s), 1021 (m), 946 (m), 926 (w), 861 (m), 816 (w), 792 (w), 768 (m), 702 (m), 637 (w), 569 (w), 533 (w), 511 (w), ESI-MS: [M+H]⁺, [C₅₄H₆₁Br₂N₄O₁₂]⁺ calc. 1117.2627 meas. 1117.2634

Synthesis of Compound H₂3



Compound **2** (240 mg, 0.21 mmol) was dissolved in THF (20 mL) and ethanol (40 mL). 1 M sodium hydroxide (40 mL) was added and the resulting solution was heated at reflux overnight. The organic solvents were then removed under reduced pressure and the residue acidified to pH 7 with 1 M HCl resulting in an off-white precipitate. The precipitate was separated via filtration, washed with water (4 x 10 mL) and then dried under vacuum (190 mg, 0.18 mmol, 86%). Slow evaporation of a DMF solution gave crystals suitable for single crystal X-ray diffraction. M.P. 326 – 336 °C (decomposition), ¹H NMR (d₆-DMSO, 500 MHz) δ 12.72 (1H, s), 12.58 (1H, s), 8.66 (4H, m), 8.39 (2H, d, *J* = 8.20 Hz), 8.15 (4H, q, *J* = 7.42 Hz), 7.88 (2H, d, *J* = 8.06 Hz), 7.64 (1H d, *J* = 7.81 Hz), 7.40 (3H, m, *J* = 5.19 Hz), 3.34 – 3.22 (31.5H, overlaps with H₂O peak, m), ¹³C NMR (d₆-DMSO, 101 MHz) δ 167.80, 167.65, 153.84, 153.54, 143.02, 142.76, 142.65, 135.31, 133.91, 130.51, 130.21, 129.86, 129.72, 129.58, 129.38, 128.61, 126.78, 126.12, 125.61, 123.97, 122.12, 111.52, 102.65, 69.56, IR (u_{cm-1}): 3086 (br. w), 2870 (br. w), 1712 (m), 1638 (w), 1610 (m), 1471 (m), 1434 (w), 1392 (w), 1350 (m), 1249 (s), 1175 (m), 1092 (s), 1016 (s), 952 (m), 932 (m), 861 (m), 828 (w), 776 (s), 704 (m), 661 (w), 640 (w), 598 (w), 569 (w), 538 (m), ESI-MS: [M+H]⁺, [C₅₀H₅₃Br₂N₄O₁₂]⁺ calc. 1061.2001 meas. 1061.2013

Synthesis of Compound 2*



[H1*][BF₄] (300 mg, 0.50 mmol) and 24-crown-8 ether (350 mg, 1.0 mmol) were dissolved in chloroform (30 mL) at room temperature and stirred for 30 minr. 3,6-Dibromo-1,2phenylenediamine (132 mg, 0.50 mmol) and ZrCl₄ (11.6 mg, 0.050 mmol) were added and the resulting yellow solution was stirred at room temperature exposed to air for 24 h. The solution was then filtered, and the solvent removed under reduced pressure. The resulting yellow oil was washed with diethyl ether (2 x 20 mL) and the residue was re-dissolved in acetonitrile (50 mL) and heated at reflux for 30 min. The cloudy solution was cooled to room temperature and filtered. The filtrate was reduced in volume and triethyl amine (0.5 mL) was added resulting in the formation of a pale brown precipitate which was separated via filtration and air dried (225 mg, 0.2 mmol, 40%).MP. 292 – 296 °C, ¹H NMR (CD₂Cl₂, 500 MHz) δ 11.08 (1H, br. s), 10.72 (1H, s), 8.83 (2H, d, J = 8.3 Hz), 8.46 (2H, dd, J = 8.47, 4.2 Hz), 8.39 (2H, d, J = 8.30 Hz), 8.27 (4H, dd, J = 11.98, 8.44 Hz), 7.88 (2H, d, J = 8.20 Hz), 7.66 (1H, d, J = 7.70 Hz), 7.48 (1H, d, J = 7.75 Hz), 7.37 (1H, br. s), 7.32 (1H, br. s), 4.46 (4H, q, J = 7.17 Hz), 3.48 (16H, m), 3.32 (16H, m), 1.48 (6H, t, J = 7.17 Hz), ¹³C NMR (CD₂Cl₂, 101 MHz) δ 153.50, 153.61, 152.20, 130.29, 130.18, 129.91, 129.42, 129.32, 128.38, 127.13, 126.06, 125.68, 124.94, 123.34, 122.10, 69.87, 69.10, 60.86, IR (*u*_{cm-1}): 3624 (w), 3437 (br., w), 3195 (br., w), 2867 (br., w), 1709 (s), 1604 (m), 1554 (w), 1469 (m), 1435 (m), 1395 (w), 1353 (m), 1265 (s), 1177 (m), 1098 (s), 1018 (m), 946 (m), 923 (m), 857 (m), 816 (m), 792 (w), 767 (m), 700 (m), 659 (w), 636 (w), 567 (w), 531 (w), 510 (w), 468 (w), 433 (w), ESI-MS: [M+H]⁺, [¹³C₁C₅₃H₆₁Br₂N₄O₁₂]⁺ calc. 1118.2661 meas. 1118.2668

Synthesis of Compound H₂3*



Compound **2*** (192 mg, 0.172 mmol) was dissolved in THF (20 mL) and ethanol (40 mL). 1 M sodium hydroxide (40 mL) was added and the resulting solution was heated at reflux overnight. The organic solvents were then removed under reduced pressure and the residue acidified to pH 7 with 1 M HCl resulting in an off-white precipitate. The precipitate was separated via filtration, washed with water (4 x 10 mL) and then dried under vacuum (174 mg, 0.164 mmol, 95%). MP. 324 – 337 °C (decomposition),¹H NMR (d₆-DMSO, 500 MHz) δ 12.74 (1H, br. s), 12.58 (1H, br. s), 8.66 (4H, m) 8.38 (2H, d, *J* = 6.96 Hz), 8.14 (4H, m), 7.87 (2H, d, *J* = 6.75 Hz), 7.64 (1H, d, *J* = 6.60 Hz), 7.39 (3H, m), 3.35 – 3.20 (32H, overlaps with H₂O peak, m), ¹³C 1467.85, 167.74, 153.08, 142.97, 142.65, 133.97, 132.11, 131.15, 130.62, 130.52, 130.22, 129.88, 129.57, 129.35, 128.65, 125.65, 123.97, 122.13, 69.58, IR (ν_{cm-1}): 3060 (br., w), 2878 (br., w), 1704 (w), 1634 (w), 1608 (w), 1571 (w), 1493 (w), 1454 (w), 1380 (w), 1350 (m), 713 (m), 714 (w), 659 (w), 538 (m), 494 (w), 448 (w), ESI-MS: [M+H]⁺, [¹³C₁C₄9H₅₃Br₂N₄O₁₂]⁺ calc. 1062.2035 meas. 1062.2030

Comparison of Fluorescence of 2 and [H2][BF₄]



Figure S1. The fluorescence of **2** and $[H2][BF_4]$ in CD_2Cl_2 solution under long and short UV light. The change in fluorescence upon addition of one equivalent of HBF_4 ·Et₂O is used to confirm the protonation state of **2** and **2*** during NMR experiments. This change in fluorescence is accompanied by the halting of the molecular shuttling.



¹H 1D, COSY and 2D ROESY Experiments for Compound 2

Figure S2. Schematic of the partially assigned ¹H NMR spectrum for **2** (CD₂Cl₂/CD₃CN, 298 K, 500 MHz), highlighting the four distinct parts of the molecular shuttle and selected ¹H chemical environments: terphenyl stopper (blue and red), axle (black), bromo stopper (pale blue and orange) and crown ether macrocycle (grey). The two carboxy-phenyl rings are not chemically equivalent due to the tautomerism of the benzimidazole being slower than the NMR timescale. Therefore, there are 4 different chemical environments for these protons. The protons •H and •H have very different chemical shifts as •H can form a C-H…N interaction resulting in a downfield shift. The protons •H and •H along with •H and •H are assigned based on the assignment in related T-axle benzimidazole molecules.^{S9}



Figure S3. Partial COSY spectrum for **2** (CD_2Cl_2 , 298 K, 500 MHz) reveals five through bond coupling systems; the axle protons, the two chemically non-equivalent carboxy phenyl rings and the two benzimidazole rings.



Figure S4. Partial ROESY spectrum for **2** (CD_2Cl_2 , 298 K, 500 MHz) showing through space coupling of the axle protons to the crown ether protons.

¹H 1D and 2D ROESY Experiments for [H2][BF₄]

Compound **2** (9.8 mg, 8.8 μ mol) was dissolved in CD₂Cl₂. HBF₄·Et₂O was added (1.2 μ L, 8.8 μ mol) resulting in the formation of a small amount of white precipitate which dissolved upon the addition of several drops of CD₃CN. An identical procedure was used to synthesise [H**2***][BF₄].



Figure S5. Schematic of the partially assigned ¹H NMR spectrum for [H**2**][BF₄] (CD₂Cl₂/CD₃CN, 298 K, 500 MHz), highlighting the four distinct parts of the molecular shuttle and selected ¹H chemical environments: terphenyl stopper (blue), axel (black), bromo stopper (pale blue and orange) and crown ether macrocycle (grey).



Figure S6. ROESY spectrum for $[H2][BF_4]$ (CD₂Cl₂/CD₃CN, 298 K, 500 MHz) showing ROE correlations between the terphenyl stopper protons and one face of the crown. A further ROE correlation between the axle proton of the terphenyl stopper end and the other face of the crown is observed.



Figure S7. Partial ROESY spectra showing through space correlations between the terphenyl stopper protons (left) and the two faces of the crown ether (right).

¹³C Variable Temperature Solution NMR for **2***

298 K	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	my hoursen man
280 K		human
270 K	Marine and the second and the second s	
260 K		
250 K		
240 K		
230 K		
220 K		
210 K		
159.5 159.0 158.5 158.0 157.5 157.0 156.5	156.0 155.5 155.0 154.5 154.0 153.5 (ppm)	153.0 152.5 152.0 151.5 151.0 150.5

Figure S8. A solution of **2**^{*} was cooled to 210 K and then heated to 280 K in 10 K increments and then heated back to 298 K (CD_2Cl_2 , 101 MHz).

Summary of Solution NMR Experiments



Figure S9. Comparison of ¹H NMR spectra (CD_2CI_2 , 298 K, 500 MHz) for **2*** (top) and [H**2***][BF₄] (bottom).



Figure S10. Comparison of ¹³C NMR spectra (CD_2Cl_2 , 298 K, 101 MHz) of the ¹³C enriched carbon of the benzimidazole for **2**^{*} (top) and [H**2**^{*}][BF₄] (bottom).

Single-Crystal X-Ray Diffraction Experiments

		-(6411106)
Compound	2·CH ₃ OH	$[H2][BF_4]\cdot\frac{1}{2}(CH_3CN)\cdot\frac{1}{2}(C_4H_{10}O)$
CCDC Number	2049899	2049901
Empirical formula	$C_{55}H_{64}Br_2N_4O_{13}$	C ₅₇ H _{67.5} BBr ₂ F ₄ N _{4.5} O _{12.5}
Formula weight	1148.92	1262.28
Temperature/K	170.0	170.00
Crystal system	triclinic	monoclinic
Space group	P-1	P21/c
a/Å	9.3936(9)	28.49(2)
b/Å	16.7830(16)	10.505(4)
c/Å	17.8687(17)	43.418(18)
α/°	75.171(4)	90
β/°	83.247(4)	106.34(5)
γ/°	84.427(4)	90
Volume/ų	2697.7(4)	12468(12)
Z	2	8
ρ _{calc} g/cm ³	1.414	1.345
µ/mm ⁻¹	2.464	2.270
F(000)	1192.0	5216.0
Crystal size/mm ³	$0.1 \times 0.01 \times 0.01$	$0.4 \times 0.4 \times 0.2$
Radiation	CuKα (λ = 1.54178)	CuKα (λ = 1.54178)
20 range for data collection/°	5.14 to 101.788	4.242 to 130.168
Index ranges	-9 ≤ h ≤ 9, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17	$-33 \le h \le 32, -12 \le k \le 11, -51 \le l \le 50$
Reflections collected	35147	98593
Independent reflections	5559 [R _{int} = 0.1374, R _{sigma} = 0.1289]	21024 [R _{int} = 0.0531, R _{sigma} = 0.0413]
Data/restraints/parameters	5559/408/671	21024/474/1512
Goodness-of-fit on F ²	1.341	1.041
Final R indexes [I>=2 σ (I)]	R ₁ = 0.1520, wR ₂ = 0.2536	R ₁ = 0.1139, wR ₂ = 0.2936
Final R indexes [all data]	R ₁ = 0.2112, wR ₂ = 0.2761	R ₁ = 0.1323, wR ₂ = 0.3088
Largest diff. peak/hole / e Å ⁻³	0.76/-0.57	2.02/-0.96

Table S1. SC XRD Data for $2 \cdot CH_3OH$ and $[H2][BF_4] \cdot \frac{1}{2}(CH_3CN) \cdot \frac{1}{2}(C_4H_{10}O)$



Figure S11. Hydrogen bonding interactions (·····) occurring in the asymmetric unit of **2**·CH₃OH.

Interaction	d(D-H…A) Å	d(D…A) Å	<(D-H…A) °	Symmetry code
N1-H1…O5	2.02(1)	2.90(2)	173.8(9)	x,y,z
O13-H13a…O8	2.08(1)	2.91(2)	168(1)	x,y,z
N3-H3…O13	2.21(2)	3.02(2)	152.1(9)	x,y,z

Table S2. Hydrogen Bonding Parameters for **2**·CH₃OH



Figure S12. π - π stacking interactions (·····) between the benzimidazole moieties of two neighbouring rotaxane axles (blue). π (centroid) ····· π (centroid) separation of the two crystallographically identical interactions is 3.75(1) Å of **2**·CH₃OH. Crown ether macrocycles are shown in red while hydrogen atoms and methanol molecules are omitted for clarity.



Figure S13. The hydrogen bonding interactions (.....) for the N-H moieties of the benzimidazole and benzimidazolium moieties for the two crystallographically unique rotaxanes (left and right) in the asymmetric unit of for $[H2][BF_4] \cdot 0.5(CH_3CN) \cdot 0.5(C_4H_{10}O)$.

Interaction	d(D-H…A) Å	d(D…A) Å	<(D-H…A) °	Symmetry code
N1-H1…O25	2.001(6)	2.878(8)	174.1(4)	х,у,z
N3-H3…O9	2.062(6)	2.885(7)	155.2(4)	х,у,z
N4-H4…O5	2.152(6)	2.945(7)	149.6(3)	х,у,z
N5-H5a…F2	1.969(5)	2.847(7)	175.9(4)	x,y,z, -x,1-y,1-z
N7-H7…O17	2.160(7)	2.927(8)	145.2(4)	x,y,z
N7-H7…O24	2.189(8)	2.891(9)	136.4(4)	х,у,z
N8-H8…O20	2.039(6)	2.783(8)	141.6(4)	х,ү,z
N8-H8…O21	2.326(6)	3.016(8)	135.4(3)	х,у,z

Table S3. Hydrogen Bonding Parameters for [H2][BF₄]·0.5(CH₃CN)·0.5(C₄H₁₀O)



Figure S14. Representation of the voids present in the unit cell of [H2][BF4]·0.5(CD₃CN)·0.5(C₄H₁₀O) calculated in Mercury with a probe radius of 1.2 Å and a grid spacing of 0.7 Å. The two crystallographically unique rotaxanes in the asymmetric unit are shown in blue (axle) and red (macrocycle) while solvent molecules and anions are omitted for clarity. (top) The voids calculated as the contact surface which constitute a total of 649.91 Å³ which is 5.2% of the unit cell. (bottom) The voids were calculated as the solvent accessible voids which constitute a total of 1569.29 Å³ which is 1.3% of the unit cell.

Table 3	S4.	SC-XRD	Data	for	3
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Identification code	3
CCDC Number	2049900
Empirical formula	$C_{50}H_{52}Br_2N_4O_{12}$
Formula weight	1060.77
Temperature/K	170
Crystal system	Monoclinic
Space group	P21/n
a/Å	19.889(5)
b/Å	18.209(4)
c/Å	33.691(7)
α/°	90
β/°	105.93(2)
γ/°	90
Volume/ų	11733(5)
Z	8
$\rho_{calc}g/cm^3$	1.201
µ/mm⁻¹	2.214
F(000)	4368.0
Crystal size/mm ³	$0.2 \times 0.1 \times 0.1$
Radiation	CuKα (λ = 1.54184)
20 range for data collection/°	4.676 to 100.858
Index ranges	-19 ≤ h ≤ 19, -18 ≤ k ≤ 18, -33 ≤ l ≤ 33
Reflections collected	111138
Independent reflections	12204 [$R_{int} = 0.4617$, $R_{sigma} = 0.1686$]
Data/restraints/parameters	12204/1052/1180
Goodness-of-fit on F ²	1.350
Final R indexes [I>=2σ (I)]	$R_1 = 0.2005$, $wR_2 = 0.4848$
Final R indexes [all data]	$R_1 = 0.2789$, w $R_2 = 0.5352$
Largest diff. peak/hole / e Å ⁻³	0.75/-0.62



Figure S15. Asymmetric unit of **3** containing two crystallographically unique rotaxanes. The low resolution and poor-quality data prevent further analysis of the supramolecular interactions. The structure is sufficient to provide connectivity for the system and illustrate the binding location of the **24C8** macrocycle.

Synthesis and Characterisation of MOFs

UWDM-11: ZrCl₄ (52.7 mg, mmol) was sonicated in DMF (9.5 mL) to give a cloudy solution. TFA (24 drops) was added and the cloudy solution was heated at 80 °C for 30 min. Ligand H₂**3** (40 mg, mmol) and H₂**TTDC** (70.6 mg, mmol) were added and the resulting cloudy solution sonicated and heated gently until all solids dissolved to give a pale-yellow solution which was placed in a preheated oven at 100 °C for 48h. This resulted in the formation of a white precipitate which was cooled to room temperature and washed with DMF (2 x 10 mL) and ethanol (10 mL) the soaked in an ethanol solution of proton sponge (60 mg in 4 mL ethanol) for 3 days with the solvent exchanged every 12h. The solid was then soaked in DCM for 2 days with the solvent exchanged every 12h and then activated by heating at 120 °C under vacuum for 3h. IR (v_{cm-1}): 2874 (w), 1601 (br. w), 1546 (w), 1519 (w), 1412 (br. s), 1178 (w), 1156 (w), 1100 (w), 1020 (w), 991 (w), 875 (w), 778 (m), 738 (w), 709 (m), 690 (w), 662 (m), 5522 (w), 467 (s), ¹H NMR: A sample of **UWDM-11** was sonicated in a saturated D₂O solution of K₃PO₄, d₆-DMSO was added and the solution gently heated until all solid dissolved. The d₆-DMSO solution was removed and a ¹H spectra was collected.



Figure S16. ¹H NMR spectrum of **UWDM-11** after digestion in saturated K_3PO_4/d_6 -DMSO (298 K, 300 MHz) showing the ratio of [**TTDC**]²⁻ and [**3**]² based on the integrals of the aromatic and crown ether protons.



Figure S17. TGA for activated **UWDM-11** heating from ambient temperature to 600 °C at 10 °C min⁻¹ under a nitrogen atmosphere.

Protonation of UWDM-11: UWDM-11 (9.8 mg, 3.13 µmol) was soaked in 1 mL of an ethanol solution of HBF₄·Et₂O (2.9 µL HBF₄·Et₂O in 10 mL of ethanol) for 12h. The solution was then replaced with 1 mL of fresh solution and soaked for a further 12h. The solution was then replaced with 1 mL of fresh solution and soaked for a further 6h, the solution was then replaced with 1 mL of DCM and soaked over night. The DCM was decanted and [**UWDM-11**-H][BF₄] was activated by heating at 120 °C under vacuum. IR (u_{cm-1}): 2930 (br. w), 1604 (m), 1549 (w), 1518 (w), 1417 (s), 1178 (w), 1098 (w), 1020 (w), 991 (w), 876 (w), 777 (m), 711 (m), 687 (m), 659 (s), 524 (s), IR peak at 524 cm⁻¹ corresponds to BF₄⁻ deformation.



Figure S18. Comparison of **UWDM-11** (neutral) and **[UWDM-11**-H][BF₄] (protonated) fluorescence under UV light.

UWDM-11(mesitylene): Samples of **UWDM-11** and ¹³C-**UWDM-11** were soaked in mesitylene (2 mL) with the solvent exchanged for fresh solvent every 12h for two days. The solid was then separated by filtration and allowed to air dry to give **UWDM-11**(mesitylene) as-synthesised followed by TGA/IR analysis. A sample was then kept in a capped vial at room temperature for 24h and a second TGA experiment was carried out on **UWDM-11**(mesitylene)-24h. IR (u_{cm-1}): 3014 (br., w), 2915 (br., w), 2891 (br., w), 1603 (m), 1590 (m), 1541 (m), 1514 (w), 1471 (w), 1402 (s), 1176 (w), 1099 (w), 1037 (w), 990 (w), 928 (w), 878 (w), 834 (s), 777 (m), 758 (w), 738 (w), 708 (m), 687 (s), 663 (m), 523 (m), 465 (s)



Figure S19. TGA for **UWDM-11**(mesitylene) as-synthesised and **UWDM-11**(mesitylene) 24h was performed between ambient temperature and 600 °C with a ramp rate of 10 °C min⁻¹ under a nitrogen atmosphere. The formula for **UWDM-11** (no solvent) is $[Zr_6O_4(OH)_4(3)_{0.667}(TTDC)_{5.334}]$ (MW = 3135.27 g mol⁻¹). A decrease in the weight % of 50 % for **UWDM-11**(mesitylene) assynthesised corresponds to the loss of 26 mesitylene molecules from $[UWDM-11] \cdot 26(C_9H_{12})$. A decrease in the weight % of 45 % for **UWDM-11**(mesitylene) 24h corresponds to the loss of 21 mesitylene molecules from $[UWDM-11] \cdot 21(C_9H_{12})$. It is important to note that a constant weight of **UWDM-11**(mesitylene) as-synthesised was not obtained prior to the measurement despite allowing the sample to isotherm for 30 min at ambient temperature (~22 °C). Therefore, the calculated number of mesitylene molecules is only a rough approximation. It is possible that the loss of mass at room temperature is due to surface adsorbed solvent which is lost upon standing over 24 h (**UWDM-11**(mesitylene) 24h).

Powder X-Ray Diffraction (PXRD)



Figure S20. Comparison of PXRD of **PCN-57**, **UWDM-11**, **[UWDM-11-H]**[BF₄] and **UWDM-11**(mesitylene) at 298 K for 2theta values of 2^o to 30^o.



Figure S21. Variable temperature PXRD for **UWDM-11** from 25 °C to 175 °C for 2Theta values of 2° to 30° Sample was heated under ambient atmosphere at 10 °C min⁻¹ and the temperature allowed to stabilise for 2 minutes prior to collection.

Solid State NMR (SSNMR) Analysis of UWDM-11 and UWDM-11(mesitylene)



f1 (ppm)

Figure S22. The ¹H-¹³C CP/MAS SSNMR spectrum of ¹³C-labelled **UWDM-11** at 298 K with * showing the peak corresponding to the ¹³C enriched site.



220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)

Figure S23. The ¹H-¹³C CP/MAS SSNMR spectrum of ¹³C-labelled **UWDM-11**(mesitylene) at 298 K with * showing the peak corresponding to the ¹³C-enriched site.



Figure S24. Partial ¹H-¹³C CP/MAS SSNMR spectra for a freshly activated sample of **UWDM-11** between 173 and 273 K showing the peak at ~151.4 ppm corresponding to the ¹³C-enriched site.



Figure S25. Partial ¹H-¹³C CP/MAS SSNMR spectra for a freshly activated sample of **UWDM-11**(mesitylene) between 173 and 423 K. At low temperature there is a peak at ~151.4 ppm with a shoulder at ~148.5 ppm indicating that two chemical environments for the ¹³C-enriched site are present. At higher temperatures (373 K and above) a single, increasingly symmetric, broad peak is observed, corresponding to an average ¹³C shift of 150.5 ppm resulting from fast shuttling of the macrocycle on the NMR timescale.

Fitting of the VT ¹³C SSNMR spectra for ¹³C enriched UWDM-11

A doublet composed of peaks a and b undergoing chemical exchange can be described by the following equilibrium: $a \rightleftharpoons b$, composed of the two individual processes: $a \stackrel{k_a}{\to} b$ and $b \stackrel{k_b}{\to} a$ with an equilibrium constant, K, where K = k_a/k_b and K = [b]/[a].

The ΔG^{\dagger} value of our previously reported molecular shuttle, which showed dynamics within the cavity of a MOF in the solid state,^{S1} was calculated by line fitting of the VT SSNMR spectra using DNMR71^{S10} to obtain the rates at each temperature. The ΔH^{\dagger} and ΔS^{\dagger} values were then extracted using an Eyring plot and used to calculate the ΔG^{\dagger} . This fitting can only be performed using a single rate constant and thus is only valid when $k_a = k_b$ in the case of a degenerate molecular shuttle where the translational motion can be described by a symmetrical double-well potential. As **UWDM-11** contains a non-degenerate molecular shuttle $k_a \neq k_b$ and this line fitting method is not valid.

An alternative approach to calculating the ΔG^{\dagger} at coalescence is known as the *coalescence method*. The coalescence of two singlets *a* and *b* into a single peak occurs when the following conditions are satisfied (Equation 1).^{S11}

Eq. 1 (a)
$$\Delta v \tau = \frac{\sqrt{2}}{2\pi}$$

Eq. 1 (b) $\frac{1}{\tau} = \frac{1}{\tau_a} + \frac{1}{\tau_b}$
Eq. 1 (c) $k = \frac{1}{2\tau}$

Equation 1. a) Conditions for coalescence of a doublet into a singlet where Δv is the difference in frequency of the two peaks at the slow exchange limit: chemical exchange slower than the NMR timescale. b) Definition of τ where τ_a and τ_b are the lifetimes of species *a* and *b*. c) the relationship between the lifetime (τ) and rate (k) of *a* and *b*

When $\tau_a = \tau_b$ which occurs for two equal singlets; $k_a = k_b$ resulting in Equations 2a and 2b.^{S12} This allows for the calculation of the rate of translation of the macrocycle of a rotaxane from site *a* to site *b* and vice versa at the point of coalescence.^{S13} However, this only applies in the case of a degenerate molecular shuttle where the rates k_a and k_b reaction are the same. Therefore, equations 2a and 2b are only valid when there are equal proportions of the two singlets below the coalescence point.^{S14}

Eq. 2 (a)
$$au = \frac{1}{2k_a}$$

Eq. 2 (b) $k_a = \frac{\pi \Delta v}{\sqrt{2}}$

Equation 2. a) The relationship between τ and rate constant for an equal doublet at coalescence. b) The calculation of the rate constant at coalescence using Δv at the low temperature limit. The shuttling of macrocycle from site a (terphenyl stoppered end) and site b (dibromo stoppered end) in **UWDM-11** is an example of a non-degenerate molecular shuttle where the rates k_a and k_b are different, and the translational motion cannot be described by a symmetrical double well potential. As site a is more energetically favourable than site b; $k_a < k_b$ resulting in two uneven singlets below the coalescence point, with a larger site a peak than site b peak. Therefore, equation 1a is not valid so equation 2b cannot be used to find the rate at coalescence.

A solution to this was provided by Lynden-Bell^{S15} and later refined by Shanan-Atidi and Bar-Eli who present the following (equation 3a).^{S12} By plotting all values of ΔP verses $x/2\pi$ for $0.0 < \Delta P < 1.0$ (see Fig. S25). The ΔP of a given system is simply calculated from there relative proportions of the two uneven singles and via Fig. S25, provides the value of $x/2\pi$. The x parameter is used to calculate τ (Equation 3b) from which the rates k_a and k_b can be elucidated (Equation 3c).

Eq. 3 (a) $\Delta P = \left(\frac{x^2 - 2}{3}\right)^{3/2} \frac{1}{x}$

Eq. 3 (b) $\tau = \frac{x}{2\pi\Delta\nu}$

Eq. 3 (c) $k_a = \frac{1}{2\tau}(1 - \Delta P);$ $k_b = \frac{1}{2\tau}(1 + \Delta P)$

Equation 3. a) Coalescence criteria for an uneven doublet where $\Delta P = P_a - P_b$ where P_a and P_b are the proportions of P_a and P_b respectively and $x = 2\pi\Delta\nu\tau$. b) Relationship between τ and x. c) calculation of rates k_a and k_b from τ and ΔP .



Figure S26. The values of $x/2\pi$ for $0.0 < \Delta P < 1.0$ are plotted verses ΔP .

The values of the free energy of activation ΔG_a^{\ddagger} and ΔG_b^{\ddagger} at coalescence can then be calculated using the Eyring equation (Equation 4). The free energy of the equilibrium $\Delta G_{a\rightleftharpoons b}$ at coalescence can be calculated using the equilibrium constant K derived from k_a and k_b .

Eq. 4
$$\Delta G^{\ddagger} = -RT_c ln\left(\frac{kh}{k_B T_c}\right)$$

Equation 4. Eyring equation where h is Planck's constant, k_B is the Boltzmann constant T_c is the temperature at coalescence and k is k_a or k_b , the rates for $a \rightarrow b$ and $b \rightarrow a$ respectively at the coalescence temperature.

The values of Δv and P_a and P_b for **UWDM-11**(mesitylene) were obtained by line fitting the two peaks in the chemical shift range 160 to 146 ppm using DNMR71 (Figure S26).^{S10} Due to the overlapping nature, the integrals and thus P_a and P_b values cannot be elucidated directly. P_a and P_b along with Δv were then used to calculate k_b , k_a , K, ΔG_a^{\ddagger} , ΔG_b^{\ddagger} and $\Delta G_{a \rightleftharpoons b}$ (Table S5).



Figure S27. The simulated (red) and experimental ${}^{1}H{}^{-13}C$ CP/MAS SSNMR spectra for **UWDM**-**11**(mesitylene) at 173 K. The simulated spectrum is based on two peaks: *a* at 151.09 ppm (FWHH = 240 Hz) and *b* at 148.30 ppm (FWHH = 201 Hz) in a ratio of *a*:*b* of 78:22.

	Site <i>a</i> / reaction $a \rightarrow b$		Site <i>b</i> / reaction $b \rightarrow a$
Δv (Hz)		278.8	
P _a or P _b	0.78		0.22
k _a or k _b (s ⁻¹)	162.3		575.3
ΔG_a^{\ddagger} or ΔG_b^{\ddagger} (kcal mol ⁻¹)	13.2		12.5
К		3.55	
Tc		273	
$\Delta G_{a \rightleftharpoons b}$ (kcal mol ⁻¹)		1.52	

Using this method an upper limit for the ΔG_a^{\ddagger} or ΔG_b^{\ddagger} values for activated **UWDM-11** can also be estimated by assigning the highest possible temperature of coalescence to 173 K (the lowest temperature accessible for measurement). This estimate is based on two key assumptions. The first is that the limiting chemical shifts for the two peaks and thus Δv are the same in **UWDM-11** as they are in **UWDM-11**(mesitylene). The second assumption is that the relative proportions of site *a* and *b* are the same in **UWDM-11** as they are in **UWDM-11**(mesitylene). These assumptions are likely valid given that the only salient difference between **UWDM-11** and **UWDM-11**(mesitylene) is the presence of guest molecules which will have a negligible effect on the chemical shift of the ¹³C-enriched position of the benzimidazole moiety or the relative affinities for site *a* or *b* towards the macrocycle. Therefore, the following values for the upper limits of the free energies of activation can be estimated; $\Delta G_a^{\ddagger} = 8.19$ kcal mol⁻¹ and $\Delta G_b^{\ddagger} = 7.76$ kcal mol⁻¹.

	Energy barrier (kcal mol ⁻¹)		
	MOF (solvated)	MOF (activated)	
UWDM-4 ^{S16}	14.1	n/a	
UWDM-11	13.2, 12.5	<8.19, <7.76	

Table S6. (Comparison o	of energy	barriers in	UWDM-4	and U	WDM-11
10010 001 0	2011112011		Sarriers III			

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¹H and ¹³C Solution NMR Spectra for New Compounds



Figure S28. ¹H NMR spectrum for compound 2 (CD₂Cl₂, 500 MHz, 298 K)



Figure S29. ¹³C NMR spectrum for compound 2 (CD₂Cl₂, 101 MHz, 298 K)



13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 f1 (ppm)

Figure S30. ¹H NMR spectrum for compound 3 (d₆-DMSO, 500 MHz, 298 K)



Figure S31. ¹³C NMR spectrum for compound 3 (d₆-DMSO, 101 MHz, 298 K)



Figure S32. ¹H NMR spectrum for compound 2* (CD₂Cl₂, 500 MHz, 298 K)



Figure S33. ¹³C NMR spectrum for compound 2* (CD₂Cl₂, 101 MHz, 298 K)



Figure S34. ¹H NMR spectrum for compound **3*** (d₆-DMSO, 500 MHz, 298 K)



Figure S35. ¹³C NMR spectrum for compound 3* (d₆-DMSO, 101 MHz, 298 K)