# Linking [2]rotaxane wheels to create a new type of metal organic rotaxane framework

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## General Experimental Details

Sodium tetrafluoroborate, 1,2-dibromoethane, 3,5-dimethylbenzoic acid, oxine, 3-pyridinemethanol, 4-pyridinemethanol, **DB24C8**, and tributylphosphine were purchased from Sigma-Aldrich and used as received. [4-(Pyridin-4-yl)phenyl]methanol, and 4-*tert*-butylbenzoic anhydride were synthesized from literature procedure. Deuterated solvents were obtained from Cambridge Isotope Laboratories and used as received. Solvents were dried using an Innovative Technologies Solvent Purification System. Thin Layer Chromatography (TLC) was performed using Merck Silica gel 60 $F_{254}$ plates and viewed under UV light. Column chromatography was performed using Silicycle Ultra Pure Silica Gel (230–400 mesh). $^1$H NMR experiments were performed on a Bruker Avance 500 instrument using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. High-resolution mass spectrometry experiments were performed on a Micromass LCT electrospray ionization, time of flight, mass spectrometer in lockmass mode. Solutions of 50 – 100 ng $\mu L^{-1}$ were prepared in MeCN–$H_2O$ (1 : 1) (unless otherwise indicated) and injected for analysis at a rate of 5 $\mu L\ min^{-1}$ using a syringe pump.

## Preparation of crown ether, 1

**DB24C8** (2.00 g, 4.45 mmol) and paraformaldehyde (3.17g, 20 mmol) was added to 1:1 mixture $CHCl_3$/AcOH (20 mL) and heated to 60°C. A solution 47% HBr (4 mL) in AcOH (5 mL) was then added. The reaction was heated at 60°C for 2 days, during which time a white solid formed. The reaction was then poured over ice, and washed with $CHCl_3$ (2 x 20 mL). The organic layer was isolated, dried over $MgSO_4$(anh) and then solvent evaporated. The residue was recrystallized twice from $CHCl_3$. Yield 1.50 g (50%). MP: 202-205°; $^1$H NMR (500 MHz, $CD_2Cl_2$): δ 6.86 (4H, s), 4.62 (8H, s), 4.12 (8H, m), 3.85 (8H, m), 3.37 (8H, m).

**Preparation of crown ether, 2**

Oxine (0.798 g, 4.88 mmol) was add to a solution of NaH (132 mg, 5.50 mmol) in dry THF (30 mL) and stirred for 2 h at room temperature. **1** (1.00 g, 1.21 mmol) and DMF (2 mL) were then added and the mixture refluxed for 1.5 days. The reaction mixture was cooled to room temperature and water (4 mL) added. The THF was removed, the oil dissolved in $CH_2Cl_2$ (50 mL) and this solution washed with 1*M* $NaHCO_3$ (3 x 50 mL) and $H_2O$ (50 mL), dried with $MgSO_4$, filtered, and concentrated. The resulting solid was recrystallized twice from $CH_3CN$ to give a reddish solid. Yield: 0.830 mg (63%); MP: 133-136; $^1$H NMR (500MHz $CD_2Cl_2$) δ 8.86 (4H, d, J = 2.47), 8.11 (4H, d, J = 8.26), 7.40 (4H, m), 7.37-7.37 (8H, m), 7.18 (4H, s), 7.14 (4H, d, J = 6.93), 5.49 (8H, s), 4.15 (8H, m), 3.83 (8H, m), 3.79 (8H, m); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) 155.1,149.4, 149.2, 141.2, 136.2, 130.0, 129.2, 127.1, 122.1, 120.5, 116.3, 110.7, 71.6, 70.3, 70.0, 69.4; HR-ESI-MS: *m/z* [**2** + H]$^+$ calc. 1077.4286, found 1077.4332.

**Preparation of crown ether, 3**

3-Pyridinemethanol (0.545 g, 4.99 mmol) was added to a solution of KH (0.066 g, 2.74 mmol) in dry DMF (30 mL) and this mixture stirred for 2 h at room temperature. **1** (1.00 g, 1.21 mmol) was added and the mixture refluxed for 1.5 days. The reaction mixture was then cooled to room temperature and water (4 mL) added. The solvents were removed, the oil dissolved in $CH_2Cl_2$ (50 mL) and washed with 1*M* $NaHCO_3$ (3 x 50 mL), and $H_2O$ (50 mL), dried with $MgSO_4$, filtered and concentrated. Yield: 0.837g (74%); MP: 82-85°C; $^1$H NMR (500 MHz $CD_2Cl_2$) δ 8.54 (4H, s), 8.50 (4H, d, J = 4.2), 7.63 (4H, dd, J = 7.6, 4.9), 7.24 (4H, m), 6.91 (4H, s), 4.51 (8H, s), 4.48 (8H, s), 4.06 (8H, m), 3.78 (8H, m), 3,68 (8H, m); $^{13}$C NMR (75 MHz,

$CD_2Cl_2$) 149.6, 149.4, 148.9, 136.0, 134.4, 123.9, 115.9, 71.5, 70.1, 70.3, 69.9; HR-ESI-MS: *m/z* [**3** + Na]$^+$ calc. 955.4099, found 955.4147.

**Preparation of crown ether, 4**

4-Pyridinemethanol (0.545 g, 4.99 mmol) was added to a solution of KH (0.066 g, 2.74 mmol) in dry DMF (30 mL) and this mixture stirred for 2 h at room temperature. **1** (1.00 g, 1.21 mmol) was then added and the mixture refluxed for 1.5 days. The reaction mixture was the cooled to room temperature and water (4 mL) was added. The solvents were then removed, the oil dissolved in $CH_2Cl_2$ (50 mL) and washed 1*M* $NaHCO_3$ (3 x 50 mL) and $H_2O$ (50 mL), then dried with $MgSO_4$, filtered, and concentrated. Yield: 0.837 g (74%); MP: 97-100°C; $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 8.44 (8H,d, J = 4.5), 7.15 (8H, d, J = 5.1), 6.88 (4H, s), 4.69 (8H, s), 4.43 (8H, s), 4.06 (8H, m), 3.78 (8H, m), 3,68 (8H, m); $^{13}$C NMR (75 MHz, $CD_2Cl_2$) 150.0, 148.9, 148.2, 129.8, 122.3, 115.9, 71.5, 69.9, 70.7, 70.4, 70.2; HR-ESI-MS: *m/z* [**4** + Na]$^+$ calc. 955.4099, found 955.4147.

**Preparation of axle, $[5][BF_4]_2$**

[4-(Pyridin-4-yl)phenyl]methanol (85 mg, 4.59 mmol) was combined with 1,2-dibromoethane (245 mg, 1.31 mmol) in MeCN (6 mL) and allowed to reflux for 72 h. The solution was filtered while hot to form a white precipitate. The bromide salt was dissolved in a minimum amount of distilled water and an excess amount of 65 NaBF4 was added. The solution was cooled and filtered to give **3**[BF4]2. Yield: 51 mg, 88%. 1H NMR (CD3CN) 8.59 (d, 4H, 3J = 5.2 Hz), 8.31 (d, 4H, 3J = 5.2 Hz), 7.93 (d, 4H, 3J = 6.9 Hz), 7.61 (d, 4H, J = 7.2 Hz), 5.06 (s, 4H), 4.71 (s, 4H), 3.48 (s, 2H). HR-ESI-MS: m/z {[**3**][BF4]}+ calc.: 485.2018, 70 found: 485.2023.

**Preparation of [2]rotaxane, 6[$BF_4$]$_2$**

[**5**][$BF_4$]$_2$ (0.088 g, 0.154 mmol) was combined with **2** (0.05 4g, 0.874 mmol) and 3,5-dimethylbenzoic anhydride (0.032 g, 0.524 mmol) in MeCN/$CH_2Cl_2$ (10 mL). Tri-butylphosphine (5 µL) was added as a catalyst and the mixture was allowed to stir for 72 h at room temperature. The solvent was removed under pressure and the product was stirred in anhydrous ethanol for 30 min. A column chromatography was performed using MeOH/$CH_2Cl_2$ (4:1). The solvent was removed and the residue dissolved in MeCN. *iso*-Propyl ether was allowed to diffuse into the solution to precipitate a yellow solid. Yield 0.030 g, (32%). $^1$H NMR (500 MHz $CD_3CN$) δ 9.03 (4H, d, J = 6.7), 8.81 (4H, d, J = 5.5), 8.20 (4H, d, J = 7.3), 8.04 (4H, d, J = 6.7), 7.71 (4H, J = 8.2) 7.46 (12H, m), 7.40 (4H, d, 8.1), 7.36 (4H, dd, J = 8.1, 7.7), 7.10 (4H, d, J = 7.5), 7.05 (2H, s), 6.99 (4H, s), 5.48 (4H, s), 5.32 (4H, s), 4.88 (4H, s), 4.09-4.00 (24H, m). 2.07 (12H, s); ESI-MS: *m/z* [**1** + $BF_4$]$^+$ calc. 869.3671, found 869.3685.

**Preparation of [2]rotaxane, 7[$BF_4$]$_2$**

[**5**][$BF_4$]$_2$ (0.088 g, 1.54 mmol) was combined with **3** (0.072 g, 0.077 mmol) and 3,5-dimethylbenzoic anhydride (0.03 2g, 0.524 mmol) in MeCN/$CH_2Cl_2$ (10 mL). Tri-butylphosphine (5 µL) was added as a

catalyst and the mixture was allowed to stir for 72 h at room temperature. The solvent was removed under pressure and the product was stirred in anhydrous ethanol for 30 min. A column chromatography was performed using MeOH/$CH_2Cl_2$ (4:1). The solvent was removed and the residue dissolved in MeCN. *iso*-Propyl ether was allowed to diffuse into the solution to precipitate a yellow solid. Yield 40 mg (30%). $^1$H NMR (500 MHz $CD_3CN$) δ 9.04 (4H, d, J = 6.8), 8.49 (4H, d, J = 4.4), 8.46 (4H, s), 7.98 (4H, d, J = 6.8), 7.70 (4H, s), 7.58 (8H, d, J = 8.0), 7.49 (4H, d, J = 8.2), 7.29 (6H, m), 6.68 (4H, s), 5.46 (4H, s), 5.37 (4H, s), 4.28 (16H, s), 4.08-4.03 (24H, m). 2.35 (12H, s); HR-ESI-MS: *m/z* [**2**+ H]$^{3+}$ calc. 531.9138, found 531.9134.

**Preparation of [2]rotaxane, 8[$BF_4$]$_2$**

[**5**][$BF_4$]$_2$ (0.088 g, 1.54 mmol) was combined with **4** (0.072 g, 0.077 mmol) and 3,5-dimethylbenzoic anhydride (0.032 g, 0.524 mmol) in MeCN/$CH_2Cl_2$ (10 mL). Tri-butylphosphine (5 µL) was added as a catalyst and the mixture was allowed to stir for 72 h at room temperature. The solvent was removed under pressure and the product was stirred in anhydrous ethanol for 30 min. The product was dissolved in MeCN and *iso*-propyl ether was allowed to diffuse into the solution to give a yellow solid. Yield 35 mg (26%). $^1$H NMR (500 MHz $CD_3CN$) δ 9.04 (4H, d, J = 6.9), 8.49 (4H, d, J = 5.0), 7.98 (4H, d, J = 7.0), 7.74 (4H, s), 7.58 (8H, d, J = 8.3), 7.51 (4H, d, 8.2), 7.27 (4H, m), 7.17 (8H, d, J = 8.0), 6.70 (4H, s), 5.46 (4H, s), 5.36 (4H, s), 4.29 (16H, s), 4.16-4.03 (24H, m). 2.36 (12H, s); HR-ESI-MS: *m/z* [**3** + H]$^{3+}$ calc. 531.9138, found 531.9134.

**Preparation of Complex, [(Cd(MeCN)$_2$($H_2O$))$_2$(6)][$BF_4$]$_6$**

To a solution of **6**[$BF_4$]$_6$ (30 mg) dissolved in MeCN (1 mL) was added to Cd(BF4)$_2$·6 $H_2O$ (9 mg) and the mixture stirred at room temperature overnight. Slow diffuse of *iso*-propyl ether into the solution gave brownish yellow crystals in quantitative yield. $^1$H NMR (500 MHz $CD_3CN$) δ 9.13 (4H, d, J = 3.34), 9.02 (4H, d, J = 5.4), 8.67 (4H, d J = 7.9), 7.88 (4H, m), 7.73 (4H, d, J = 7.9), 7.67, (4H, dd, J = 8.1, 7.8), 7.50 (4H,

s), 7.41 (4H, d, J = 7.2), 7.34 (4H, d, J = 7.5), 7.16 (2H, s), 7.00 (4H, d, 6.6), 6.93 (4H, s), 5.46 (4H, s) 4.97 (12H, m), 4.17-4.05 (24H, m), 2.13 (12H, s); HR-ESI-MS: *m/z* [**4** + $BF_4$]$^+$ calc. 869.3671, found 869.3685.

**Preparation of Complex, $[Cd_2Cl_4(H_2O)_4(7)][BF_4]_2$**

To a solution of **7**$[BF_4]_6$ (30 mg) dissolved in MeCN (1 mL) was added $Cd(BF4)_2 \cdot 6\ H_2O$ (9 mg;) and the mixture was stirred at room temperature for overnight. Slow diffuse of *iso*-propyl ether into the solution gave yellow crystals in quantitative yield.

**General Comments on X-ray Structure Determinations**

Crystals were frozen in paratone oil inside a cryoloop. Reflection data were integrated from frame data obtained from hemisphere scans on a Bruker APEX diffractometer with a CCD detector. Decay was monitored by 50 standard data frames measured at the beginning and end of data collection. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved by direct methods, completed by subsequent Fourier syntheses and refined using full-matrix least-squares methods against $|F^2|$ data. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as idealized contributions. Scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (Sheldrick, G. M., Madison, WI).

**Crystal data for $[8][BF_4]_2$**: $C_{96}H_{102}B_2F_8N_6O_{16}$, M = 1769.46, T = 173(2) K, triclinic, space group *P-1*, *a* = 12.403(3), *b* = 13.676(3), *c* = 14.347(4) Å, $\alpha$ = 101.628(4), $\beta$ = 101.186(4), $\gamma$ = 106.532(4), *V* = 2201.8(9) Å$^3$, $\rho_{calc}$ = 1.334 g cm $^{-3}$, $\mu$ = 0.101 mm$^{-1}$, Z = 1, reflections collected = 20669 ($R_{int}$ = 0.0995), final *R* indices [$I > 2\sigma I$]: *R*1 = 0.1312 , *wR*2 = 0.2013, *R* indices (all data): *R*1 = 0.2129. *wR*2 = 0.2302, GoF = 1.204 with data/variables/restraints = 7715/577/0.

**Crystal data for $[(Cd(MeCN)_2(H_2O))_2(6)][BF_4]_6.(MeCN)_9(H_2O)_2$**: $C_{134}H_{149}B_6Cd_2F_{24}N_{19}O_{20}$, M = 3091.40, T = 173(2) K, triclinic, space group *P-1*, *a* = 11.341(2), *b* = 16.817(2), *c* = 22.030(3) Å, $\alpha$ = 107.475(2), $\beta$ = 97.650(2), $\gamma$ = 107.379(2), *V* = 3708.5(9) Å$^3$, $\rho_{calc}$ = 1.384 g cm $^{-3}$, $\mu$ = 0.385 mm$^{-1}$, Z = 1, reflections collected = 34624 ($R_{int}$ = 0.0422), final *R* indices [$I > 2\sigma I$]: R1 = 0.0887 , wR2 = 0.2249, R indices (all data): R1 = 0.1091, wR2 = 0.2389, GoF = 1.139 with data/variables/restraints = 13000/964/75. Three MeCN solvent molecules were refined successfully with full site occupancy factors. One MeCN solvent

molecule was refined with a 0.5 site occupancy factor. Two MeCN were refined as a 2/3:1/3 disorder. SAME was used to restrain MeCN solvent molecules to a sensible geometry using the full occupancy molecule with the best metric and thermal parameters.

**Crystal data for $\{[Cd_2Cl_4(H_2O)_4(7)][BF_4]_2.8(MeNO_2)\}_x$**: $C_{104}H_{134}B_2Cd_2Cl_4F_8N_{14}O_{36}$, M = 2696.47, T = 173(2) K, monoclinic, space group $P2_1/c$, $a$ = 17.006(2), $b$ = 18.712(2), $c$ = 19.944(3) Å, $\beta$ = 102.151(2), $V$ = 6204.2(14) Å$^3$, $\rho_{calc}$ = 1.443 g cm $^{-3}$, $\mu$ = 0.523 mm$^{-1}$, Z = 2, reflections collected = 38654 ($R_{int}$ = 0.0456). Due to the severe disorder of solvent molecules in the lattice, we employed the program SQUEEZE to calculate the diffraction contribution of 16 disordered $CH_3NO_2$ solvent molecules. Before SQUEEZE: R1 = 0.1544, wR2 = 0.4371 [I>2σI], R1 = 0.1748, wR2 = 0.4650 [all data], GoF($F^2$) = 2.065. After SQUEEZE; $R$ indices [$I > 2\sigma I$]: $R1$ = 0.1195 , $wR2$ = 0.3443, $R$ indices (all data): $R1$ = 0.1342. $wR2$ = 0.3638, GoF = 1.537 with data/variables/restraints = 6488/640/6. The non-coordinating chloride anion is disordered over three positions which were modelled as 45%, 45% and 10% occupancy and restrained with SIMU to have comparable thermal parameters. There was also evidence of disorder at the $(H_2O)_2Cd(\mu\text{-}Cl)_2Cd(H_2O)_2$ core, but this could not be modelled satisfactorily. As a result, the final structure displays elongated thermal parameters for these atoms.