## **Supporting information**

# Nitrate anion templated synthesis of a [2]rotaxane for selective nitrate recognition in organic–aqueous solvent media

Matthew J. Langton and Paul. D. Beer\*

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All reagents and solvents were purchased from commercial sources and used without further purification. Where necessary, solvents were dried by passing through a MBraun MPSP-800 column and degassed with nitrogen. Column chromatography was carried out on Merck® silica gel 60 under a positive pressure of nitrogen. Where mixtures of solvents were used, ratios reported are by volume. Triethylamine was distilled from and stored over potassium hydroxide. NMR spectra were recorded on a Bruker AVII 500 (with cryoprobe) and Bruker AVIII 500 spectrometers. Mass spectra were carried out on a Waters Micromass LCT and Bruker microTOF spectrometers.

#### Part 1 – Synthesis and characterisation

General procedure for acid chloride synthesis: To convert carboxylic acids to their acid chloride derivatives the following general procedure was used. To a suspension of acid (1 mmol) in dry  $CH_2Cl_2$  (10 mL) was added oxalyl chloride (2 mmol) dropwise under N<sub>2</sub>. A drop of DMF (~0.01 mL, cat.) was added and the reaction refluxed at 40 °C under N<sub>2</sub> until the solution became homogeneous. The solvent was removed *in vacuo* to leave a yellow solid. This was immediately re-dissolved in dry  $CH_2Cl_2$  and reacted on as desired. The yield was assumed to be quantitative.

Compounds  $1, 2, 3, 3, 8^4$  and  $13^1$  were prepared according to literature procedures.



**4.** To a suspension of **2** (320 mg, 1.77 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added EDC·HCl (372 mg, 1.95 mmol), HOBt (50 mg, 0.327 mmol) and DMAP (cat. ~1 mg). This was stirred for 1 hr under N<sub>2</sub> until the solution became homogeneous. To this was added dry triethylamine (0.26 mL, 1.95 mmol) and a solution of amine **1** (420 mg, 1.77 mmol). The reaction mixture was stirred for 2 days under N<sub>2</sub>, then washed with 10% citric acid (2 × 5 mL) and NaHCO<sub>3</sub> (2 × 5 mL). The organic layer was dried over MgSO<sub>4</sub> and the solvent removed *in vacuo*. The product was purified using silica gel column chromatography (75:20:5 CH<sub>2</sub>Cl<sub>2</sub>/acetone/CH<sub>3</sub>OH) to afford a white solid (450 mg, 60 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.40 (s, 1H, Ar*H*), 8.14 (d, <sup>3</sup>*J* = 8.6 Hz, 1H, Ar*H*), 8.02 (t, <sup>3</sup>*J* = 8.6 Hz, 1H, Ar*H*), 7.49 (t, <sup>3</sup>*J* =

8.6 Hz, 1H, Ar*H*), 6.84 (m, 4H, hydroquinone Ar*H*), 5.93 (m, 1H, *H*C=CH<sub>2</sub>), 5.31-5.18 (m, 2H, HC=C*H*<sub>2</sub>), 4.07 (m, 6H, *CH*<sub>2</sub>), 3.91 (s, 3H, *CH*<sub>3</sub>), 3.84 (m, 2H, *CH*<sub>2</sub>), 3.76 (m, 2H, *CH*<sub>2</sub>).<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ (ppm):166.8, 166.4, 153.4, 152.8, 134.6, 132.5, 131.9, 130.5, 128.9, 127.8, 117.3, 115.7, 115.5, 72.4, 68.6, 68.1, 67.3, 52.4, 39.8. HRMS (ES +ve) *m/z*: 422.1578 [M + Na]<sup>+</sup>, C<sub>22</sub>H<sub>25</sub>NO<sub>6</sub>Na requires 422.1574).



**5.** To a suspension of acid **3** (300 mg, 1.66 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added EDC·HCl (348 mg, 1.82 mmol), HOBt (50 mg, 0.327 mmol) and DMAP (cat. ~1 mg). This was stirred for 1 hr under N<sub>2</sub> until the solution became homogeneous. To this was added dry triethylamine (0.25 mL, 1.82 mmol) and a solution of amine **1** (390 mg, 1.66 mmol). The reaction mixture was stirred for 2 days under N<sub>2</sub> and washed with 10 % citric acid (2 × 5 mL) and NaHCO<sub>3</sub> (2 × 5 mL). The organic layer was dried over MgSO<sub>4</sub> and the solvent removed *in vacuo*. The product was purified using silica gel column chromatography (75:20:5 CH<sub>2</sub>Cl<sub>2</sub>/acetone/CH<sub>3</sub>OH) to afford a white solid (290 mg, 45 %). %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 9.26 (d, <sup>3</sup>J = 2.2 Hz, 1H, pyridine ArH), 9.19 (d, <sup>3</sup>J =

2.2 Hz, 1H, pyridine Ar*H*), 8.65 (t,  ${}^{3}J$  = 2.2 Hz, 1H, pyridine Ar*H*), 6.80 (m, 4H, hydroquinone Ar*H*), 5.96 (m, 1H, *H*C=CH<sub>2</sub>), 5.30-5.22 (m, 2H, HC=CH<sub>2</sub>), 4.10-4.04 (m, 6H, CH<sub>2</sub>), 3.94 (s, 3H, CH<sub>3</sub>), 3.85 (q,  ${}^{3}J$  = 4.8 Hz, 2H, CH<sub>2</sub>), 3.75 (t,  ${}^{3}J$  = 4.8 Hz, 2H, CH<sub>2</sub>).  ${}^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 165.0, 165.0, 153.4, 152.9, 152.7 152.1, 135.8, 134.6, 129.9, 125.8, 117.3, 115.7, 72.4, 68.6, 68.0, 67.1, 52.6, 39.9. HRMS (ES +ve) *m/z*: 423.1530 [M + Na]<sup>+</sup>, C<sub>21</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>Na requires 423.1527).



**6.** Ester **4** (450 mg, 1.13 mmol) was dissolved with KOH (95 mg, 1.70 mmol) in MeOH (15 mL). The reaction mixture was stirred under N<sub>2</sub> for 16 hrs. The solvent removed *in vacuo* and re-dissolved in H<sub>2</sub>O (50 mL) and washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The aqueous layer was neutralised with 10% citric acid and the resulting precipitate was collected by vacuum filtration and washed with H<sub>2</sub>O (10 mL), CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and dried to give a white solid. (380 mg, 87 %). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sup>6</sup>)  $\delta$  (ppm): 8.89 (t, <sup>3</sup>*J* = 5.5, 1H, Ar*H*), 8.45 (s, 1H, Ar*H*), 8.09 (d, <sup>3</sup>*J* = 7.9 Hz, 2H, Ar*H*), 7.60 (t, <sup>3</sup>*J* = 7.9 Hz, 1H, Ar*H*), 6.87 (m, 4H, hydroquinone Ar*H*), 5.89 (m, 1H, *H*C=CH<sub>2</sub>), 5.31-5.19 (m, 2H, HC=CH<sub>2</sub>), 4.08 (m, 6H, CH<sub>2</sub>), 3.66 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 167.4, 166.3, 153.1, 153.0,

135.7, 135.1, 132.4, 132.0, 131.7, 129.3, 128.6, 117.0, 115.9, 71.6, 68.7, 68.0, 66.9. HRMS (ES +ve) *m/z*: 408.1415 [M+Na]<sup>+</sup>, C<sub>21</sub>H<sub>23</sub>NO<sub>6</sub>Na requires 408.1418).



**7**. Ester **5** (180 mg, 0.45 mmol) was dissolved with KOH (40 mg, 0.68 mmol) in MeOH (10 mL). The reaction mixture was stirred under N<sub>2</sub> for 16 hrs. The solvent removed *in vacuo* and re-dissolved in H<sub>2</sub>O (50 mL) and washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL). The aqueous layer was neutralised with 10% citric acid and the resulting precipitate was collected by vacuum filtration and washed with H<sub>2</sub>O (10 mL), CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and dried to give a white solid. (150 mg, 85 %).<sup>1</sup>H NMR (500 MHz, DMSO- $d^6$ )  $\delta$  (ppm): 13.54 (br s, 1H, COO*H*), 9.21 (s, 1H, pyridine Ar*H*), 9.18 (s, 1H, pyridine Ar*H*), 9.11 (s, 1H, N*H*), 8.70 (s, 1H, pyridine Ar*H*), 6.89 (m, 4H, hydroquinone Ar*H*), 5.90 (m, 1H, *H*C=CH<sub>2</sub>), 5.30-5.14 (m, 2H, HC=CH<sub>2</sub>), 4.08 (t, <sup>3</sup>J = 5.7 Hz 2H, CH<sub>2</sub>), 4.01 (m, 4H, CH<sub>2</sub>), 3.67 (m, 4H, CH<sub>2</sub>). <sup>13</sup>C NMR (101 MHz,

CDCl<sub>3</sub>) δ (ppm): 166.4, 164.7, 153.1, 153.0, 152.8, 152.5, 136.0, 135.7, 130.0, 117.0, 116.0, 115.8, 71.6, 68.7, 67.9, 66.8. HRMS (ES -ve) *m/z*: 385.1416 [M-H]<sup>-</sup>, C<sub>20</sub>H<sub>21</sub>N<sub>2</sub>O<sub>6</sub> requires 385.1405).



**9.** To a suspension of acid **6** (370 mg, 0.96 mmol) in  $CH_2Cl_2$  (20 mL) was added EDC·HCl (200 mg, 1.06 mmol) and DMAP (cat. ~1 mg). This was stirred for 1 hr under N<sub>2</sub> until the solution became homogeneous. To this was added dry triethylamine (0.26 mL, 1.95 mmol) and a solution of **8** (170 mg, 0.96 mmol). The reaction mixture was stirred for 2 days under N<sub>2</sub> and washed with NaHCO<sub>3</sub> (2 × 5 mL). The organic layer was dried over MgSO<sub>4</sub> and the solvent removed *in vacuo*. The product was purified using silica gel column chromatography (75:20:5 CH<sub>2</sub>Cl<sub>2</sub>/acetone/CH<sub>3</sub>OH) to afford an off-white oil (230mg, 45

%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 8.26 (s, 1H, Ar*H*), 7.96 (d, <sup>3</sup>*J* = 8.3 Hz, 2H, Ar*H*), 7.53 (br s, 1H, N*H*), 7.48 (t, <sup>3</sup>*J* = 8.3 Hz, 1H, Ar*H*), 7.05 (bs, 1H, N*H*), 6.82 (m, 4H, hydroquinone Ar*H*), 5.93 (m, 1H, *H*C=CH<sub>2</sub>), 5.30-5.20 (m, 2H, HC=C*H*<sub>2</sub>), 4.07 (m, 6H, C*H*<sub>2</sub>), 3.81 (t, <sup>3</sup>*J* = 5.0 Hz, 2H, C*H*<sub>2</sub>), 3.76 (t, <sup>3</sup>*J* = 5.0 Hz, 2H, C*H*<sub>2</sub>), 3.47 (q, <sup>3</sup>*J* = 5.9 Hz, 2H, C*H*<sub>2</sub>), 3.20 (bs, 2H, N*H*<sub>2</sub>), 1.68 (quintet, <sup>3</sup>*J* = 5.9 Hz, 2H, C*H*<sub>2</sub>), 1.43 (s, 3H, C*H*<sub>3</sub>). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 167.0, 166.8, 157.0, 153.3, 152.8, 134.8, 134.5, 130.4, 130.1, 129.0, 125.3, 117.4, 115.7, 115.5, 79.7, 72.4, 68.6, 68.1, 67.2, 39.8, 30.0, 28.4. HRMS (ES +ve) *m*/*z*: 564.2686 [M+Na]<sup>+</sup>, C<sub>29</sub>H<sub>39</sub>N<sub>3</sub>O<sub>7</sub>Na requires 564.2680).



**10.** To a solution of **9** (130 mg, 0.24 mmol) in  $CH_2Cl_2$  (5 mL) at 0 °C was added trifluoroacetic acid (1 mL) dropwise. The reaction mixture was allowed to warm to room temperature and stirred under N<sub>2</sub>. The solvent was removed *in vacuo* and redissolved in CH<sub>3</sub>OH which was subsequently again removed *in vacuo*. This was repeated until all the excess TFA had been removed to give the trifluoroacetate salt of the product (136 mg, 99 %). <sup>1</sup>H NMR (400 MHz, 1:1 CDCl<sub>3</sub>/CD<sub>3</sub>OD)  $\delta$  (ppm):

8.21 (s, 1H, Ar*H*), 7.92 (d,  ${}^{3}J$  = 8.5 Hz, 2H, Ar*H*), 7.46 (t,  ${}^{3}J$  = 8.5 Hz, 1H, Ar*H*), 6.78 (m, 4H, hydroquinone Ar*H*), 5.85 (m, 1H, *H*C=CH<sub>2</sub>), 5.26-5.12 (m, 2H, HC=C*H*<sub>2</sub>), 4.01 (m, 6H, C*H*<sub>2</sub>), 3.71 (t,  ${}^{3}J$  = 7.2 Hz, 2H, C*H*<sub>2</sub>), 3.43 (t,  ${}^{3}J$  = 7.2 Hz, 2H, C*H*<sub>2</sub>), 1.89 (quintet,  ${}^{3}J$  = 7.2 Hz, 2H, C*H*<sub>2</sub>).  ${}^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 168.7, 167.7, 153.2, 153.0, 134.4, 134.3, 133.7, 130.7, 130.5, 129.0, 125.6, 117.5, 72.3, 68.6, 68.0, 67.0, 39.7, 36.7, 36.2, 27.1. HRMS (ES +ve) *m*/z: 442.2335 [M-CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>]<sup>+</sup>, C<sub>24</sub>H<sub>32</sub>N<sub>3</sub>O<sub>5</sub> requires 442.2336).



**11.** To a suspension of **7** (95 mg, 0.246 mmol) in  $CH_2Cl_2$ (10 mL) was added EDC·HCl (52 mg, 0.271 mmol), HOBt (25 mg, 0.160 mmol) and DMAP (cat. ~1 mg). This was stirred for 1 hr under N<sub>2</sub> until the solution became homogeneous. To this was added dry triethylamine (0.1 mL, 0.780 mmol) and a solution of **10** (136 mg, 0.246 mmol) in dry DMF (3 mL). The reaction mixture was stirred for 7 days under N<sub>2</sub> and washed with 10 % citric acid, before the solvent was removed *in* 

*vacuo*. The product was purified using silica gel column chromatography (75:20:5 CH<sub>2</sub>Cl<sub>2</sub>/acetone/CH<sub>3</sub>OH) to afford a white solid (70 mg, 35 %). <sup>1</sup>H NMR (500 MHz, 1:1 CDCl<sub>3</sub>/CD<sub>3</sub>OD)  $\delta$  (ppm): 9.05 (br s, 1H, Ar*H*), 8.57 (s, 1H, Ar*H*), 8.21 (s, 1H, Ar*H*), 7.91 (t, <sup>3</sup>*J* = 7.6 Hz, 2H, Ar*H*), 7.46 (m, 2H, Ar*H*), 6.77 (m, 8H, hydroquinone Ar*H*), 5.82 (m, 2H, *H*C=CH<sub>2</sub>), 5.24-5.11 (m, 4H, HC=C*H*<sub>2</sub>), 4.02 (m, 12H, C*H*<sub>2</sub>), 3.71 (m, 8H, C*H*<sub>2</sub>), 3.43 (q, <sup>3</sup>*J* = 6.4 Hz, 4H, C*H*<sub>2</sub>), 1.84 (quintet, <sup>3</sup>*J* = 6.4 Hz, 2H, C*H*<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 168.7, 166.4, 153.8, 153.6, 151.2, 151.0, 135.1, 135.0, 134.8, 131.0, 130.9, 129.5, 126.3, 118.0, 116.3, 116.0, 72.9, 69.1, 68.6, 67.6, 67.4, 40.5, 40.3, 37.6, 30.2, 29.4. 14 peaks missing, presumed overlapped due to apparent symmetry. HRMS (ES +ve) *m/z*: 832.3524 [M + Na]<sup>+</sup>, C<sub>44</sub>H<sub>51</sub>N<sub>5</sub>O<sub>10</sub>Na requires 832.3528).



**Macrocycle precursor 12'NO<sub>3</sub>.** Methyliodide (2 mL) was added to a solution of **11** (70 mg, 0.086 mmol) in DMF (2 mL) and stirred under N<sub>2</sub> for 16 hrs. The solvent was removed *in vacuo* to give compound **1** as the iodide salt. Ion exchange to the NO<sub>3</sub><sup>-</sup> salt was achieved passing down a nitrate loaded Amberlite® column in 9:1 acteone/water. The solvent was subsequently removed *in vacuo* to give **12'NO<sub>3</sub>**. (71 mg, 92 %). <sup>1</sup>H NMR (500 MHz, 1:1 CDCl<sub>3</sub>/CD<sub>3</sub>OD)  $\delta$ (ppm): 9.17 (*app* s, 3H, ArH), 8.38 (s, 1H, NH), 8.10 (s,

1H, N*H*), 7.85 (m, 3H, Ar*H*), 7.40 (t,  ${}^{3}J$  = 7.0 Hz, 1H, Ar*H*), 6.72 (m, 8H, hydroquinone Ar*H*), 5.83 (m, 2H, *H*C=CH<sub>2</sub>), 5.23-5.10 (m, 4H, HC=CH<sub>2</sub>), 4.34 (s, 3H, CH<sub>3</sub>), 3.98 (m, 12H, CH<sub>2</sub>), 3.69 (m, 8H, CH<sub>2</sub>), 3.39 (m, 4H, CH<sub>2</sub>), 1.80 (*app* t,  ${}^{3}J$  = 6.1 Hz, 2H, CH<sub>2</sub>).  ${}^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 168.5, 168.3, 161.9, 161.8, 161.7, 161.7, 153.8, 153.7, 153.5, 153.3, 146.8, 146.7, 141.9, 135.2, 135.1, 135.0, 134.8, 130.9, 130.8, 129.5, 126.0, 118.0, 116.2, 116.1, 72.8, 69.1, 68.6, 68.5, 67.5, 67.0, 40.8, 40.2, 38.2. 7 peaks missing, presumed overlapped due to apparent symmetry. HRMS (ES +ve) *m*/*z*: 824.3848 [M]<sup>+</sup>, C<sub>45</sub>H<sub>54</sub>N<sub>5</sub>O<sub>10</sub> requires 824.3865).



**Catenane 14'NO<sub>3</sub>. 12'NO<sub>3</sub>** (26 mg, 0.029 mmol) and macrocycle **13** (26 mg, 0.044 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub>(3 mL) under N<sub>2</sub>. Grubbs' 2<sup>nd</sup> generation catalyst (3 mg) was added and the reaction stirred for 48 hrs. The solvent was removed *in vacuo*, and the crude purified by preparative thin layer chromatography (95:5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH) to afford catenane **14'NO<sub>3</sub>** (7.5 mg, 20%). <sup>1</sup>H NMR (500 MHz, 1:1 CDCl<sub>3</sub>/CD<sub>3</sub>OD)  $\delta$  (ppm): 9.22 (s, 1H, pyridinium

Ar*H*), 9.16 (s, 1H, pyridinium Ar*H*), 9.10 (s, 1H, pyridinium Ar*H*), 9.00 (s, 1H, isophthalamide Ar*H*), 8.79 (s, 1H, N*H*), 8.16 (s, 1H, N*H*), 8.49 (s, 1H, isophthalamide Ar*H*), 8.05 (m, 2H, isophthalamide Ar*H*), 8.17 (d,  ${}^{3}J =$  7.9 Hz, 1H, isophthalamide Ar*H*), 8.16 (s, 1H, N*H*), 8.49 (s, 1H, isophthalamide Ar*H*), 8.05 (m, 2H, isophthalamide Ar*H*), 8.17 (d,  ${}^{3}J =$  7.9 Hz, 1H, isophthalamide Ar*H*), 7.67 (m, 2H, isophthalamide Ar*H*), 7.04 (d,  ${}^{3}J =$  9.0 Hz, 2H, hydroquinone Ar*H*), 6.91 (d,  ${}^{3}J =$  9.0 Hz, 2H, hydroquinone Ar*H*), 6.95 (d,  ${}^{3}J =$  9.0 Hz, 2H, hydroquinone Ar*H*), 6.91 (d,  ${}^{3}J =$  9.0 Hz, 2H, hydroquinone Ar*H*), 6.55 (d,  ${}^{3}J =$  9.0 Hz, 4H, hydroquinone Ar*H*), 6.32 (d,  ${}^{3}J =$  9.0 Hz, 4H, hydroquinone Ar*H*), 5.97 (s, 2H, *H*C=*CH*), 4.71 (s, 3H, *CH*<sub>3</sub>), 4.40 (br m, 2H, *CH*<sub>2</sub>), 4.33 (br m, 2H, *CH*<sub>2</sub>), 4.28 (br m, 2H, *CH*<sub>2</sub>), 4.20 (br m, 4H, *CH*<sub>2</sub>), 4.20 (m, 2H, *CH*<sub>2</sub>), 4.05-3.73 (br m, 28H, *CH*<sub>2</sub>), 1.88 (quintet,  ${}^{3}J =$  6.6 Hz, 2H, *CH*<sub>2</sub>).  ${}^{13}$ C NMR (125 MHz, 1:1 CDCl<sub>3</sub>/CD<sub>3</sub>OD) 168.3, 168.0, 161.1, 161.1, 160.3, 160.2, 153.9, 153.5, 153.5, 153.3, 152.4, 145.8, 145.4, 134.8, 134.7, 133.9, 133.5, 133.3, 132.3, 131.6, 131.4, 129.9, 129.8, 129.6, 125.3, 124.9, 116.4, 116.2, 115.9, 115.8, 115.2, 114.9, 71.5, 71.4, 71.1, 70.5, 68.9, 68.7, 68.6, 67.5, 67.1, 65.6, 58.1, 50.1, 41.4, 40.8, 40.5, 38.2, 37.9, 32.4, 4 peaks missing presumed overlapped due to apparent symmetry. HRMS (ES +ve) *m*/*z*: 706.8010 [M-NO<sub>3</sub><sup>-</sup>+Na]<sup>2+</sup>, C<sub>75</sub>H<sub>88</sub>N<sub>7</sub>O<sub>10</sub>Na requires 706.8011).

Anion exchange to the hexaflurophosphate salt was achieved by washing a solution of **14**'NO<sub>3</sub> (7.5 mg, 0.005 mmol) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> with 8 × 10 mL of a 0.1M solution of aqueous ammonium hexafluorophosphate, followed by 2 × 10 mL H<sub>2</sub>O. The organic layer was dried over MgSO<sub>4</sub>, filtered and the solvent removed *in vacuo* to afford **14**'PF<sub>6</sub> in quantitative yield (8 mg). <sup>1</sup>H NMR (500 MHz, 1:1 CDCl<sub>3</sub>/CD<sub>3</sub>OD)  $\delta$  (ppm): 9.11 (s, 1H, pyridinium Ar*H*), 9.00 (s, 1H, pyridinium Ar*H*), 8.98 (s, 1H, pyridinium Ar*H*), 8.74 (s, 1H, N*H*), 8.60 (s, 1H, isophthalamide Ar*H*), 8.53 (s, 1H, N*H*), 8.46 (s, 1H, isophthalamide Ar*H*), 8.12 (m, 4H, isophthalamide Ar*H*), 7.67 (m, 2H, isophthalamide Ar*H*), 6.99 (app s 4H, hydroquinone Ar*H*), 6.92 (m, 4H, hydroquinone Ar*H*), 6.95 (d, <sup>3</sup>*J* = 9.0 Hz, 2H, hydroquinone Ar*H*), 6.39 (d, <sup>3</sup>*J* = 9.0 Hz, 4H, hydroquinone Ar*H*), 5.95 (s, 2H, *H*C=C*H*), 4.55 (s, 3H, C*H*<sub>3</sub>), 4.26-4.04 (br m, 14H, C*H*<sub>2</sub>), 4.26-4.04 (br m, 40H, C*H*<sub>2</sub>), 1.93 (quintet, <sup>3</sup>*J* = 6.6 Hz, 2H, C*H*<sub>2</sub>).



Figure SI-2. <sup>13</sup>C NMR spectrum of 14'NO<sub>3</sub> in 1:1 CDCl<sub>3</sub>/CD<sub>3</sub>OD (500 MHz, 298K)



**Figure SI-3.** <sup>1</sup>H ROESY NMR spectrum of **14**'NO<sub>3</sub> (1:1 CDCl<sub>3</sub>/CD<sub>3</sub>OD). Selected cross-peaks indicating through space interactions between the interlocked macrocycle components are highlighted. For atom labels see Scheme 2 in the main text.

### Part 2 – <sup>1</sup>H NMR titrations

<sup>1</sup>H NMR spectra were recorded on a Bruker AVIII 500 spectrometer. A solution of the anion guest, as the noncomplexing tetrabutylammonium (TBA) salt (or in the case of hydrogen carbonate, as the triethylammonium (TEA) salt), was added to a solution of the host at 298 K. The chemical shift of the pyridinium proton *3* was monitored for seventeen 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, 3.0, 4.0, 5.0, 7.0 and 10.0 equivalents of guest added). The resulting data were analysed using the WinEqNMR2<sup>5</sup> computer program. (In all experiments the association of guest and host was fast on the NMR timescale).

The anion guest was titrated into a solution of host species [2]catenane **14PF**<sub>6</sub> in 45:45:10 CDCl<sub>3</sub>/CD<sub>3</sub>OD/D<sub>2</sub>O, A 75 mM solution of anion was added to 0.5 mL of a 1.5 mM solution of [2]catenane. The volumes of salt solution added were 10 x 2  $\mu$ L, 2 x 5  $\mu$ L, 2 x 10  $\mu$ L, 1 x 20  $\mu$ L, and 1 x 30  $\mu$ L. The values of the observed chemical shift and the guest concentration were entered into winEQNMR2 for every titration point and estimates for the binding constant and limiting chemical shifts were made. The parameters were refined using non-linear squares analysis to obtain the best fit between observed and calculated chemical shifts for a 1:1 host-guest binding stoichiometry. The input parameters were varied until the best-fit values of the stability constants, and their errors, converged.



**Figure SI-4**. Changes in the <sup>1</sup>H NMR spectra of **14**·NO<sub>3</sub> in 45:45:10 CDCl<sub>3</sub>/CD<sub>3</sub>OD/D<sub>2</sub>O at 298 K upon addition of TBANO<sub>3</sub>.



**Figure SI-5**. Plots of change in chemical shift against anion concentration in  $45:45:10 \text{ CDCl}_3/\text{CD}_3\text{OD}/\text{D}_2\text{O}$ , at 298 K. Observed data (solid points) and fitted isotherms (lines), monitoring proton *3*.

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