

*Electronic Supporting Information (ESI) for*

**A catenane host system containing integrated triazole C-H  
hydrogen bond donors for anion recognition**

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## Synthesis:

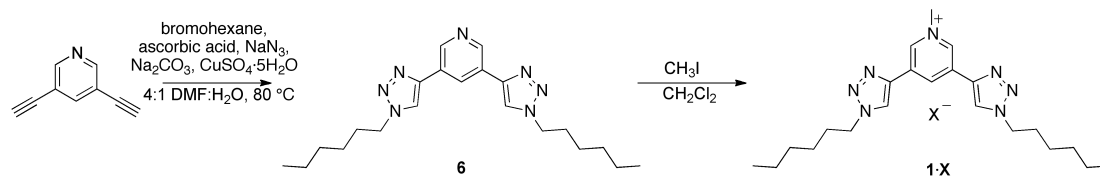
### *General Remarks*

2-(4-(2-(Allyloxy)ethoxy)phenoxy)ethanamine,<sup>S1</sup> and the isophthalamide macrocycles **2**<sup>S2</sup> and **2**<sup>tBu S3</sup> were synthesized as previously described. 3,5-Diethynylpyridine was prepared by deprotecting 3,5-bis(trimethylsilylethynyl) pyridine<sup>S4</sup> using KOH in methanol.<sup>S5</sup> Imidazole sulfonyl azide·HCl was prepared as described,<sup>S6</sup> although since using this reagent, the authors have published an addendum to their paper highlighting safety risks with the hydrochloride salt, and suggesting the use of other, less hygroscopic salts.

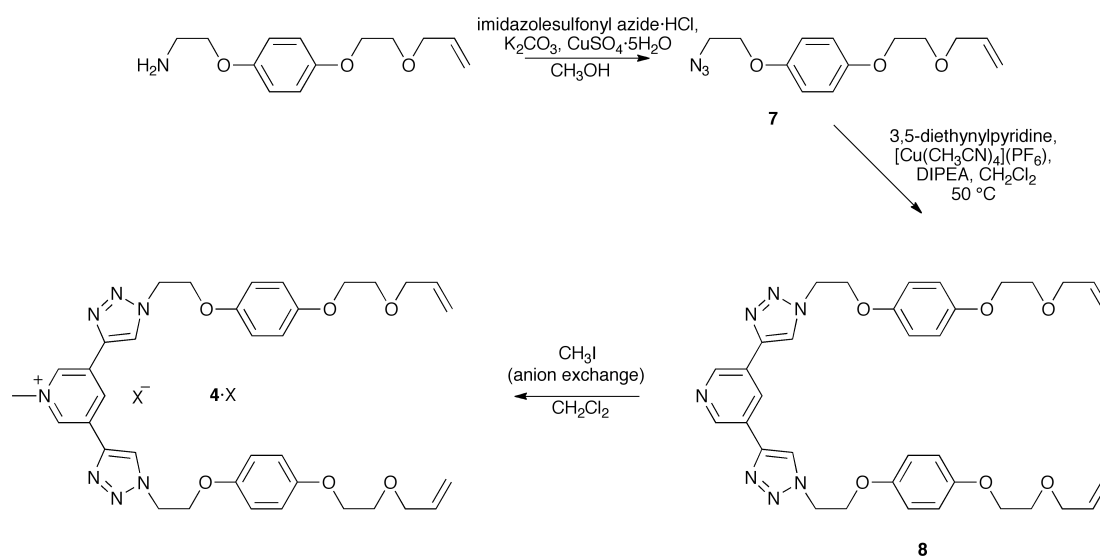
Other chemicals were available commercially and used as received. Where solvents are specified as “dry,” they were purged with nitrogen and passed through an MBraun MPSP-800 column. Water was de-ionised and microfiltered using a Milli-Q® Millipore machine. Tetrabutylammonium salts were stored in a vacuum dessicator. All chromatography was performed on silica gel (particle size: 40--63 µm).

Routine NMR spectra were recorded on a Varian Mercury 300 spectrometer with <sup>1</sup>H NMR operating at 300 MHz, <sup>13</sup>C at 75.5 MHz. Spectra for <sup>1</sup>H NMR titrations were recorded on a Varian Unity Plus 500 spectrometer with <sup>1</sup>H operating at 500 MHz. Mass spectra were recorded on a Bruker microTOF spectrometer.

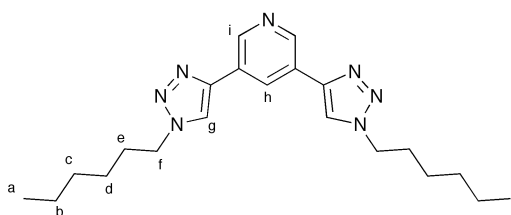
### Synthesis of 1



### Synthesis of 4

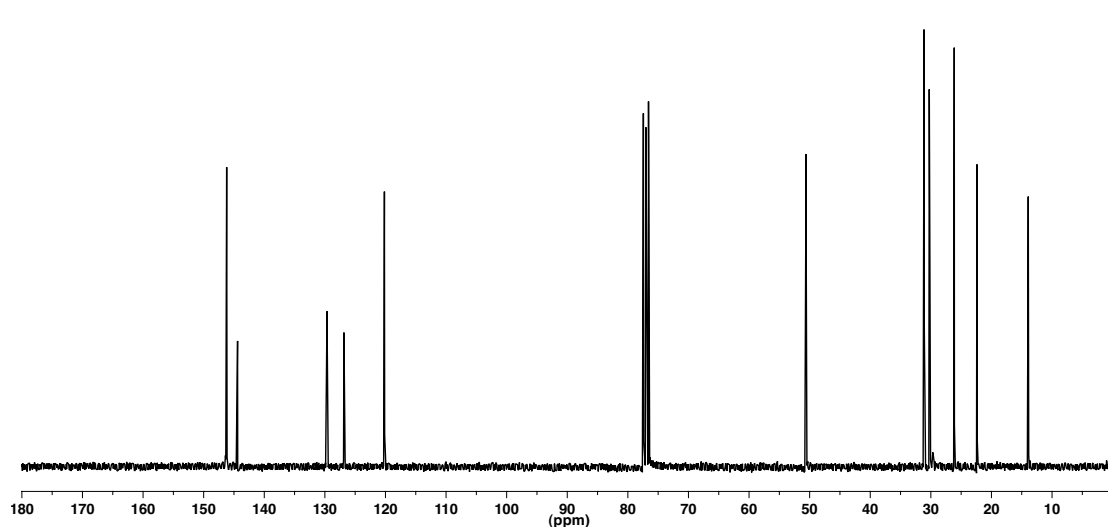
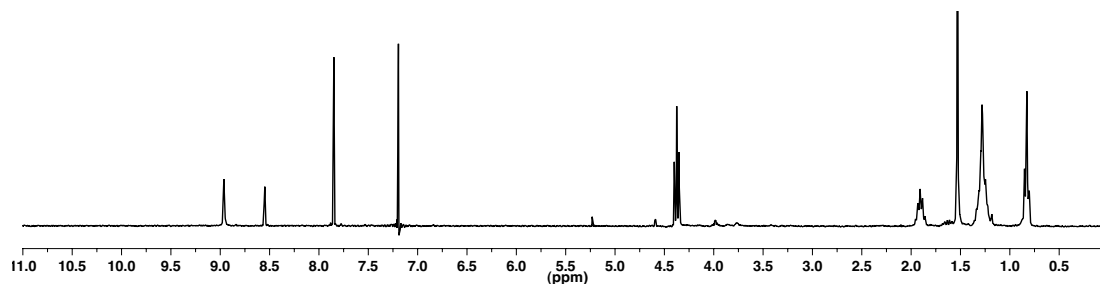


### Neutral pyridine bis-triazole receptor **6**

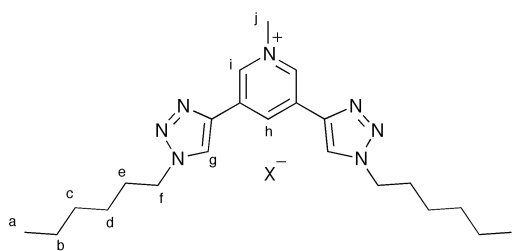


Sodium azide (0.156 g, 2.40 mmol), sodium carbonate (0.106 g, 1.00 mmol), ascorbic acid (0.176 g, 1.00 mmol) and copper sulfate pentahydrate (0.015 g, 0.060 mmol) were added to a solution of 3,5-diethynylpyridine (0.127 g, 1.00 mmol) in 4:1 DMF:water (15 mL). Bromohexane (0.31 mL, 0.36 g, 2.2 mmol) was added and the yellow solution heated to 80 °C under a nitrogen atmosphere over the weekend. The reaction was cooled to room temperature and partitioned between ethyl acetate (50 mL) and aqueous ammonium hydroxide/EDTA (50 mL). The aqueous layer was extracted with further ethyl acetate (50 mL) and the combined organic fractions washed with water (50 mL), brine (50 mL) and dried (magnesium sulfate). The clear, pale yellow solution was taken to dryness under reduced pressure, and purified by column chromatography (3% methanol in dichloromethane) to yield **6** as a white powder. Yield: 0.301 g (79%).

$^1\text{H}$  NMR ( $d_6$ -acetone): 9.02 (d,  $^4J_{h,i} = 2.1$  Hz, 2H,  $2 \times H_i$ ), 8.69 (t,  $^4J_{h,i} = 2.1$  Hz, 1H,  $H_h$ ), 8.59 (s, 2H,  $H_g$ ), 4.51 (t,  $^3J_{e,f} = 7.1$  Hz, 4H,  $4 \times H_f$ ), 1.92–2.06 (m, 4H,  $4 \times H_e$ ), 1.25–1.45 (m, 12H,  $4 \times H_b$ ,  $4 \times H_c$ ,  $4 \times H_d$ ), 0.88 (t,  $^3J_{a,b} = 7.0$  Hz, 6H,  $6 \times H_a$ ).  
 $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 146.3, 144.6, 129.8, 127.0, 120.3, 50.8, 31.3, 30.4, 26.3, 22.5, 14.1. HRESI-MS (pos.): 404.2530, calc. for  $[\text{C}_{21}\text{H}_{31}\text{N}_7\text{Na}]^+ = 404.2533$ .



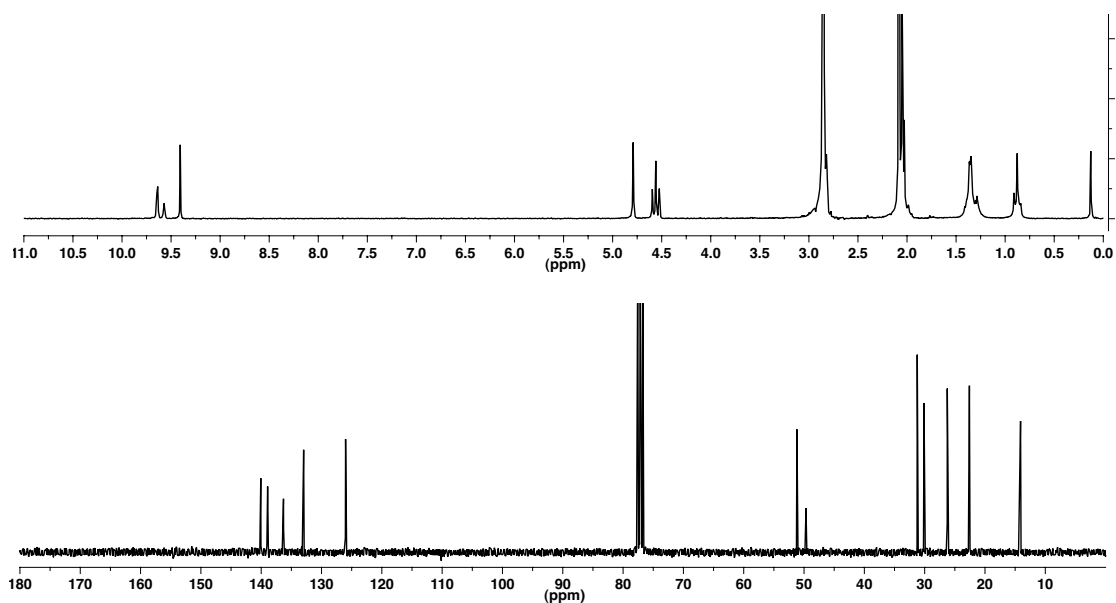
### Pyridinium bis-triazole receptor **1**



#### Iodide salt, **1-I**

The pyridine bis-triazole thread **6** (0.057 g, 0.15 mmol) was dissolved in dry dichloromethane (10 mL). Methyl iodide (0.23 mL, 0.53 g) was added and the reaction stirred for 3 days under a nitrogen atmosphere. It was taken to dryness and purified by preparative thin layer chromatography (3% methanol in dichloromethane) to give **1-I** as a golden yellow powder. Yield: 0.064 g (81%).

$^1\text{H}$  NMR ( $d_6$ -acetone): 9.64 (d,  $^4J_{h,i} = 1.3$  Hz, 2H,  $2 \times H_i$ ), 9.57 (t,  $^4J_{h,i} = 1.3$  Hz, 1H,  $H_h$ ), 9.41 (s, 2H,  $2 \times H_g$ ), 4.79 (s, 3H,  $3 \times H_j$ ), 4.56 (t,  $^3J_{e,f} = 7.1$  Hz, 4H,  $4 \times H_f$ ), 1.95–obscured by acetone solvent signal ( $4 \times H_e$ ), 1.25–1.43 (m, 12H,  $4 \times H_b$ ,  $4 \times H_c$ ,  $4 \times H_d$ ), 0.88 (t,  $^3J_{a,b} = 6.9$  Hz, 6H,  $6 \times H_a$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 140.1, 138.9, 136.3, 133.0, 126.0, 51.2, 49.7, 31.2, 30.1, 26.2, 22.6, 14.1. HRESI-MS (pos.): 396.2859, calc. for  $[\text{C}_{22}\text{H}_{34}\text{N}_7]^+ = 396.2870$ .



### Chloride salt, **1**·Cl

The iodide salt, **1**·I (0.042 g, 0.080 mmol) was dissolved in dichloromethane (10 mL). It was stirred vigorously with aqueous ammonium chloride (1 mol L<sup>-1</sup>, 10 mL) for half an hour. The organic layer was washed with further aqueous ammonium chloride (1 mol L<sup>-1</sup>, 5 × 10 mL), brine (10 mL), dried (magnesium sulfate), and taken to dryness to give **1**·Cl as a yellow powder. Yield: 0.034 g (98%).

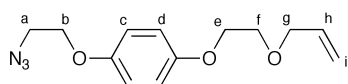
<sup>1</sup>H NMR (d<sub>6</sub>-acetone): 9.97 (t, <sup>4</sup>J<sub>h,i</sub> = 1.5 Hz, 1H, H<sub>h</sub>), 9.78–9.80 (m, 4H, 2 × H<sub>g</sub>, 2 × H<sub>i</sub>), 4.78 (s, 3H, 3 × H<sub>j</sub>), 4.52 (t, <sup>3</sup>J<sub>e,f</sub> = 7.1 Hz, 4H, 4 × H<sub>f</sub>), 1.95—obscured by acetone solvent signal (4 × H<sub>e</sub>), 1.29–1.42 (m, 12H, 4 × H<sub>b</sub>, 4 × H<sub>c</sub>, 4 × H<sub>d</sub>), 0.88 (t, <sup>3</sup>J<sub>a,b</sub> = 7.1 Hz, 6H, 6 × H<sub>a</sub>). LRESI-MS (pos.): 396.32, calc. for [C<sub>22</sub>H<sub>34</sub>N<sub>7</sub>]<sup>+</sup> = 396.29.

### Hexafluorophosphate salt, **1**·PF<sub>6</sub>

The iodide salt, **1**·I (0.105 g, 0.200 mmol) was dissolved in dichloromethane (25 mL). It was stirred vigorously with aqueous ammonium hexafluorophosphate (0.1 mol L<sup>-1</sup>, 25 mL) for half an hour, during which time the biphasic mixture changed colour from bright yellow to essentially colourless. The organic layer was washed with further aqueous ammonium hexafluorophosphate (0.1 mol L<sup>-1</sup>, 6 × 10 mL), and then water (2 × 10 mL), and taken to dryness under reduced pressure to give **1**·PF<sub>6</sub> as a very pale yellow powder. Yield: 0.096 g (89%).

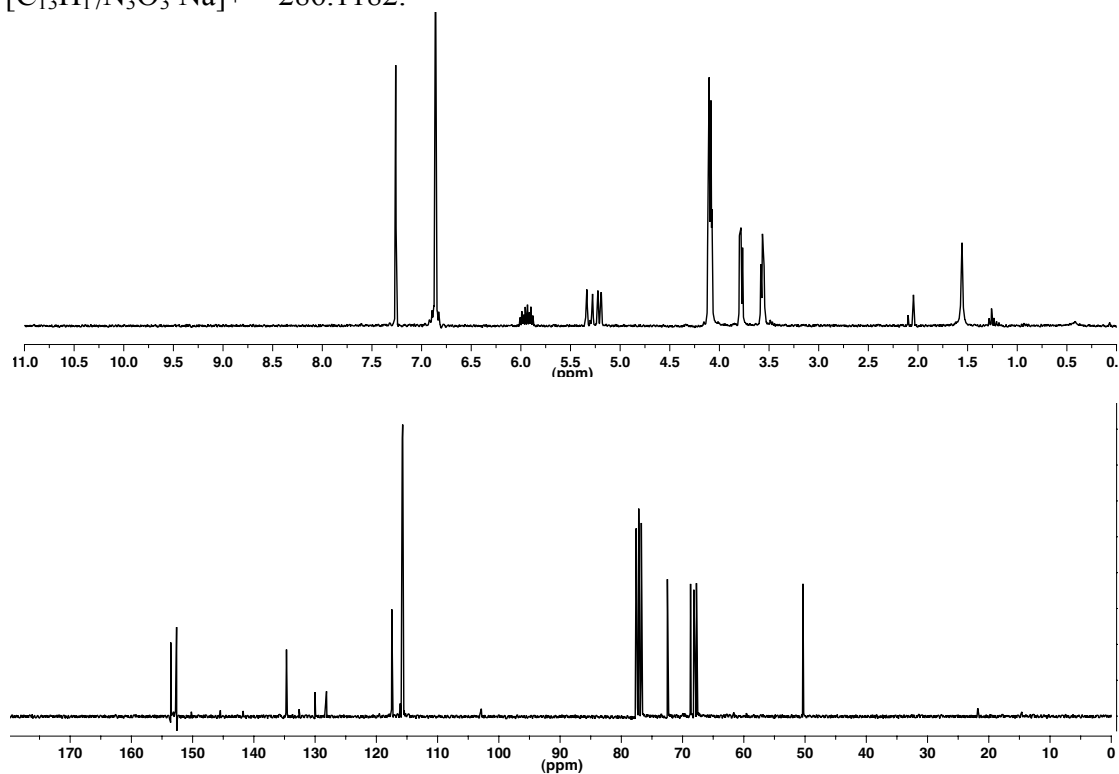
<sup>1</sup>H NMR (d<sub>6</sub>-acetone): 9.55 (d, <sup>4</sup>J<sub>h,i</sub> = 1.4 Hz, 2H, 2 × H<sub>i</sub>), 9.38 (t, <sup>4</sup>J<sub>h,i</sub> = 1.4 Hz, 1H, H<sub>h</sub>), 8.92 (s, 2H, 2 × H<sub>g</sub>), 4.80 (s, 3H, 3 × H<sub>j</sub>), 4.60 (t, <sup>3</sup>J<sub>e,f</sub> = 7.1 Hz, 4H, 4 × H<sub>f</sub>), 1.97–2.03 (m, 4H, 4 × H<sub>e</sub>), 1.27–1.41 (m, 12H, 4 × H<sub>b</sub>, 4 × H<sub>c</sub>, 4 × H<sub>d</sub>), 0.86 (t, <sup>3</sup>J<sub>a,b</sub> = 7.1 Hz, 6H, 6 × H<sub>a</sub>). LRESI-MS (pos.): 396.28, calc. for [C<sub>22</sub>H<sub>34</sub>N<sub>7</sub>]<sup>+</sup> = 396.29; 937.60, calc. for [(C<sub>22</sub>H<sub>34</sub>N<sub>7</sub>)<sub>2</sub>·PF<sub>6</sub>]<sup>+</sup> = 937.54.

### Vinyl-appended azide 7

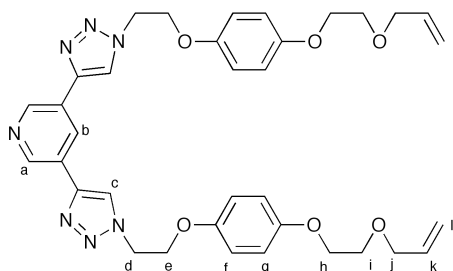


2-(4-(2-(Allyloxy)ethoxy)phenoxy)ethanamine (1.42 g, 6.00 mmol) was dissolved in methanol (60 mL). Imidazole sulfonylazide·HCl (1.95 g, 7.20 mmol), potassium carbonate (2.07 g, 15.0 mmol) and copper(II) sulfate pentahydrate (0.015 g, 0.060 mmol) were added and the white suspension stirred at room temperature under a nitrogen atmosphere overnight. It was concentrated to approximately 5 mL under reduced pressure, diluted with 10% HCl<sub>(aq)</sub> (100 mL) and extracted with ethyl acetate (3 × 100 mL). The combined organic fractions were washed with brine (100 mL), dried (magnesium sulfate) and taken to dryness under reduced pressure. Column chromatography (silica, 2:1 petrol:ethyl acetate) gave **7** as a colourless oil. Yield: 1.36 g (86%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 6.86 (s, 8H, 4 × H<sub>c</sub>, 4 × H<sub>d</sub>), 5.85–6.04 (m, 1H, H<sub>h</sub>), 5.17–5.36 (m, 2H, H<sub>i</sub>), 4.07–4.13 (m, 6H, 2 × H<sub>b</sub>, 2 × H<sub>e</sub>, 2 × H<sub>g</sub>), 3.78 (t, <sup>3</sup>J<sub>e,f</sub> = 4.9 Hz, 2H, 2 × H<sub>f</sub>), 3.56 (t, <sup>3</sup>J<sub>a,b</sub> = 5.0 Hz, 2H, 2 × H<sub>a</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 152.5, 134.6, 129.9, 128.0, 117.4, 115.7, 72.4, 68.6, 68.1, 67.6, 50.2. HRESI-MS (pos.): 286.1183, calc. for [C<sub>13</sub>H<sub>17</sub>N<sub>3</sub>O<sub>3</sub>·Na]<sup>+</sup> = 286.1182.

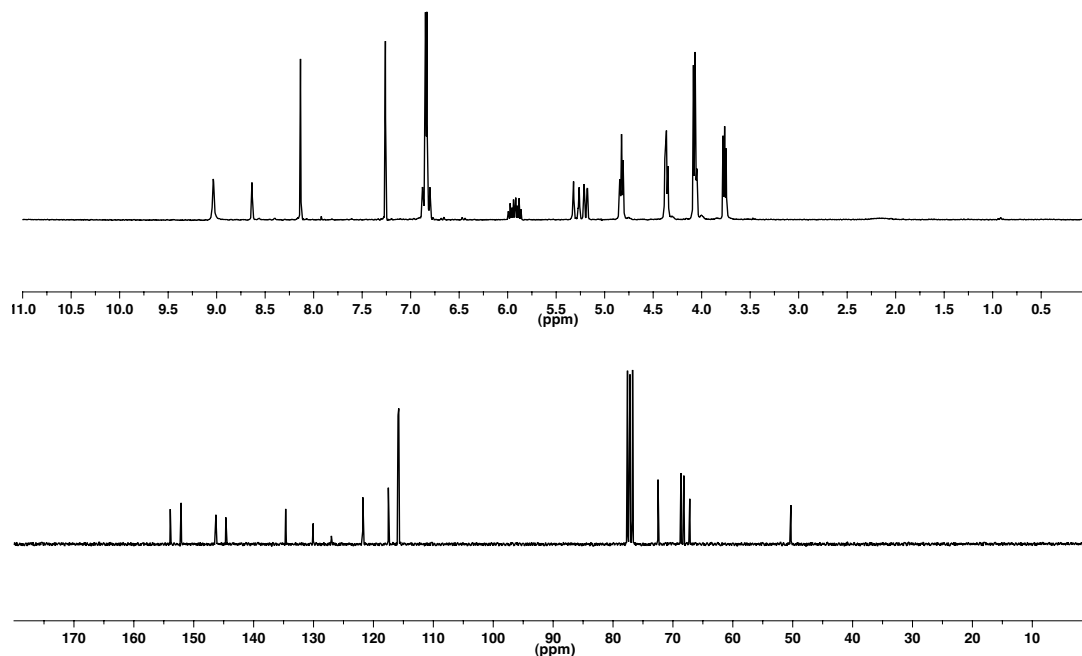


### Pyridine bis(triazole) precursor **8**



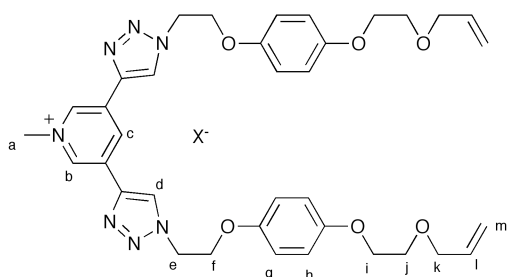
The vinyl-appended azide **7** (0.663 g, 2.52 mmol) and 3,5-diethynyl pyridine (0.153 g, 1.20 mmol) were dissolved in dichloromethane (15 mL). DIPEA (0.54 mL, 0.39 g, 3.0 mmol) was added, followed by  $[\text{Cu}(\text{CH}_3\text{CN})_4](\text{PF}_6)$  (0.089 g, 0.24 mmol) and the mixture heated to 50 °C for four days in a sealed vial. Aqueous EDTA/ammonium hydroxide solution (20 mL) was added, the organic layer taken and the aqueous layer extracted with further dichloromethane ( $2 \times 20$  mL). The combined organic fractions were washed with brine (30 mL), dried (magnesium sulfate), taken to dryness under reduced pressure and purified by column chromatography (3% methanol in dichloromethane) to give **8** as a white powder. Yield: 0.640 g (82%).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 9.01 (d,  $^4J_{a,b} = 2.0$  Hz, 2H,  $2 \times H_a$ ), 8.59 (t,  $^4J_{a,b} = 2.0$  Hz, 1H,  $H_b$ ), 8.12 (s, 2H,  $2 \times H_c$ ), 6.78–6.86 (m, 8H,  $4 \times H_f$ ,  $4 \times H_g$ ), 5.85–5.98 (m, 2H,  $2 \times H_k$ ), 5.16–5.31 (m, 4H,  $4 \times H_l$ ), 4.80 (t,  $^3J_{d,e} = 4.8$  Hz, 4H,  $4 \times H_d$ ), 4.34 (t,  $^3J_{d,e} = 4.8$  Hz, 4H,  $4 \times H_e$ ), 4.03–4.07 (m, 8H,  $4 \times H_h$ ,  $4 \times H_j$ ), 3.75 (t,  $^3J_{h,i} = 4.8$  Hz, 4H,  $4 \times H_i$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 153.9, 152.1, 146.3, 144.6, 134.7, 130.1, 127.0, 121.8, 117.5, 115.9, 115.8, 72.5, 68.7, 68.2, 67.2, 50.3. HRESI-MS (pos.): 676.2839, calc. for  $[\text{C}_{35}\text{H}_{39}\text{N}_7\text{O}_6 \cdot \text{Na}]^+ = 676.2854$ .





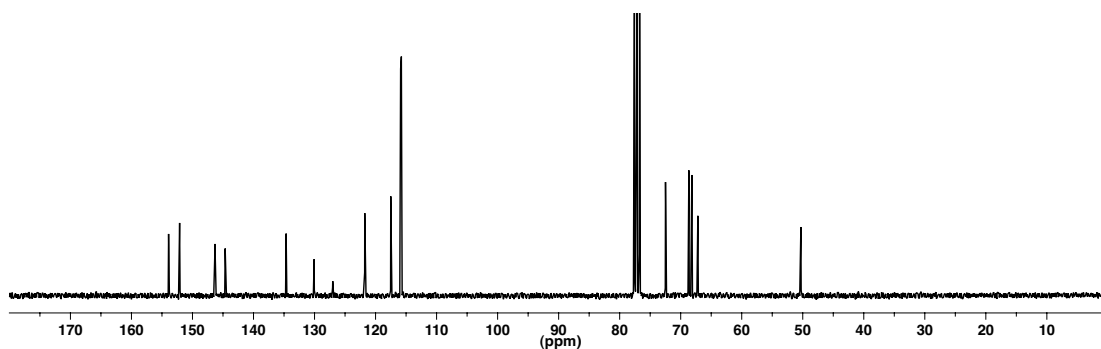
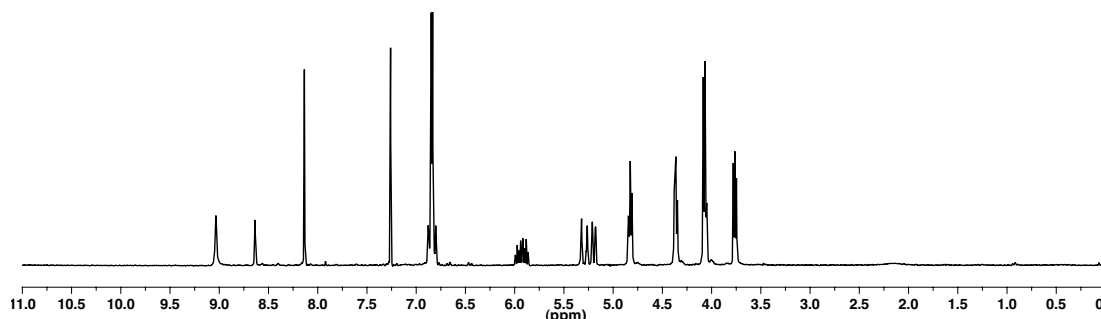
*Pyridinium bis(triazole) precursor iodide 4*



**Iodide salt, 4-I**

**8** (0.261 g, 0.400 mmol) was dissolved in dry dichloromethane (15 mL) in a vial. Methyl iodide (0.62 mL, 1.4 g, 10 mmol) was added, the vial sealed and the colourless solution stirred at room temperature for 7 days, during which time a yellow precipitate developed. The mixture was diluted with methanol (15 mL), taken to dryness under reduced pressure, and purified by column chromatography (5–12% methanol in chloroform) to give **4-I** as a lemon yellow powder. Yield: 0.289 g (91%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.49 (br. s, 2H, 2 × H<sub>b</sub>), 9.46 (br. s, 1H, H<sub>c</sub>), 9.33 (s, 2H, 2 × H<sub>d</sub>), 6.80–6.92 (m, 8H, 4 × H<sub>g</sub>, 4 × H<sub>h</sub>), 5.86–5.99 (m, 2H, 2 × H<sub>i</sub>), 5.16–5.33 (m, 4H, 4 × H<sub>m</sub>), 4.81 (t, <sup>3</sup>J<sub>e,f</sub> = 4.8 Hz, 4H, 4 × H<sub>e</sub>), 4.59 (s, 3H, 3 × H<sub>a</sub>), 4.39 (t, <sup>3</sup>J<sub>e,f</sub> = 4.8 Hz, 4H, 4 × H<sub>f</sub>), 4.02–4.09 (m, 8H, 4 × H<sub>i</sub>, 4 × H<sub>k</sub>), 3.75 (t, <sup>3</sup>J<sub>i,j</sub> = 4.8 Hz, 4H, 4 × H<sub>j</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 153.8, 152.2, 140.4, 139.4, 136.2, 134.7, 132.5, 126.6, 117.5, 116.1, 115.7, 72.5, 68.7, 68.1, 66.8, 50.7, 29.8. HRESI-MS (pos.): 668.3192, calc. for [C<sub>36</sub>H<sub>42</sub>N<sub>7</sub>O<sub>6</sub>]<sup>+</sup> = 668.3191.



### Chloride salt, 4·Cl

The iodide salt 4·I (0.080 g, 0.10 mmol) was dissolved in 4:1 acetone:water (50 mL). It was passed down a chloride-loaded Amberlite<sup>®</sup> column five times in this solvent, and the column washed with more of the same solvent. All solvent was removed under reduced pressure, and the resulting waxy solid taken up in 5% methanol in dichloromethane (50 mL), it was dried (magnesium sulfate), filtered and taken to dryness under reduced pressure to give 4·Cl as a pale yellow powder. Yield: 0.063 g (89%).

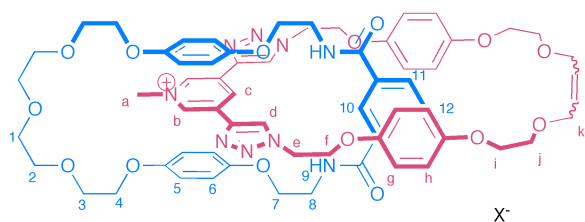
<sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.61 (br. s, 2H, 2 × H<sub>b</sub>), 9.53 (br. s, 1H, H<sub>c</sub>), 9.22 (s, 2H, 2 × H<sub>d</sub>), 6.78–6.85 (m, 8H, 4 × H<sub>g</sub>, 4 × H<sub>h</sub>), 5.83–5.96 (m, 2H, 2 × H<sub>l</sub>), 5.15–5.30 (m, 4H, 4 × H<sub>m</sub>), 4.87 (br. s, 4H, 4 × H<sub>e</sub>), 4.58 (s, 3H, 3 × H<sub>a</sub>), 4.37 (br. s, 4H, 4 × H<sub>f</sub>), 4.01–4.05 (m, 8H, 4 × H<sub>i</sub>, 4 × H<sub>k</sub>), 3.73 (t, <sup>3</sup>J<sub>i,j</sub> = 4.7 Hz, 4H, 4 × H<sub>j</sub>). LRESI-MS (pos.): 668.30, calc. for [C<sub>36</sub>H<sub>42</sub>N<sub>7</sub>O<sub>6</sub>]<sup>+</sup> = 668.32.

### Hexafluorophosphate salt, 4·PF<sub>6</sub>

The iodide salt 4·I (0.056 g, 0.070 mmol) was taken up in 5% methanol in dichloromethane (20 mL). It was washed with 0.1 M NH<sub>4</sub>PF<sub>6(aq)</sub> (6 × 20 mL) and water (2 × 20 mL), dried (magnesium sulfate) and taken to dryness to give a pale yellow solid. Yield: 0.054 g (95%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.06 (br. s, 2H, 2 × H<sub>b</sub>), 9.01 (br. s, 1H, H<sub>c</sub>), 8.60 (s, 2H, 2 × H<sub>d</sub>), 6.77–6.84 (m, 8H, 4 × H<sub>g</sub>, 4 × H<sub>h</sub>), 5.86–5.99 (m, 2H, 2 × H<sub>l</sub>), 5.17–5.32 (m, 4H, 4 × H<sub>m</sub>), 4.77 (t, <sup>3</sup>J<sub>e,f</sub> = 4.4 Hz, 4H, 4 × H<sub>e</sub>), 4.43 (s, 3H, 3 × H<sub>a</sub>), 4.33 (t, <sup>3</sup>J<sub>e,f</sub> = 4.4 Hz, 4H, 4 × H<sub>f</sub>), 4.00–4.08 (m, 8H, 4 × H<sub>i</sub>, 4 × H<sub>k</sub>), 3.74 (t, <sup>3</sup>J<sub>i,j</sub> = 4.7 Hz, 4H, 4 × H<sub>j</sub>). LRESI-MS (pos.): 668.30, calc. for [C<sub>36</sub>H<sub>42</sub>N<sub>7</sub>O<sub>6</sub>]<sup>+</sup> = 668.32, 1481.61, calc. for [C<sub>72</sub>H<sub>84</sub>N<sub>14</sub>O<sub>12</sub>·PF<sub>6</sub>]<sup>+</sup> = 1481.60.

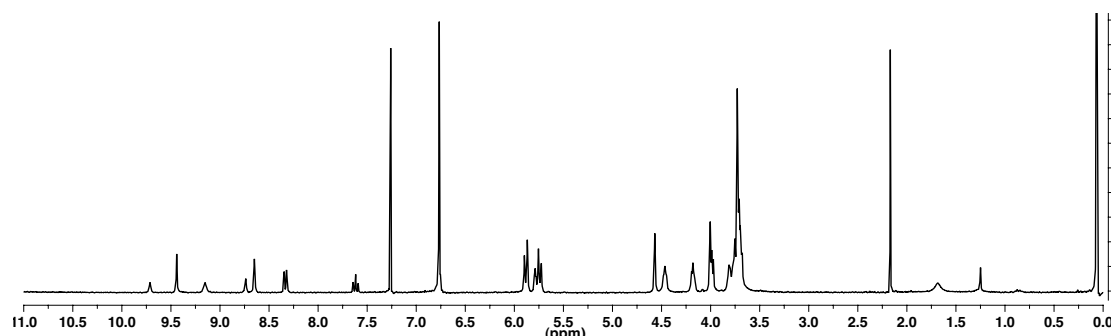
### Catenane **5**



### Chloride salt, **5**·Cl

The isophthalamide macrocycle **2** (0.018 g, 0.030 mmol) and **4**·Cl (0.025 g, 0.036 mmol) were dissolved in dry dichloromethane (6 mL). Grubbs' II catalyst (0.0025 g, 10% by weight) was added and the mixture stirred at room temperature under a nitrogen atmosphere for four days. It was taken to dryness, and then purified by preparative TLC (5% methanol in dichloromethane) to give **5**·Cl as a pale yellow powder. Yield: 0.024 g (64%).

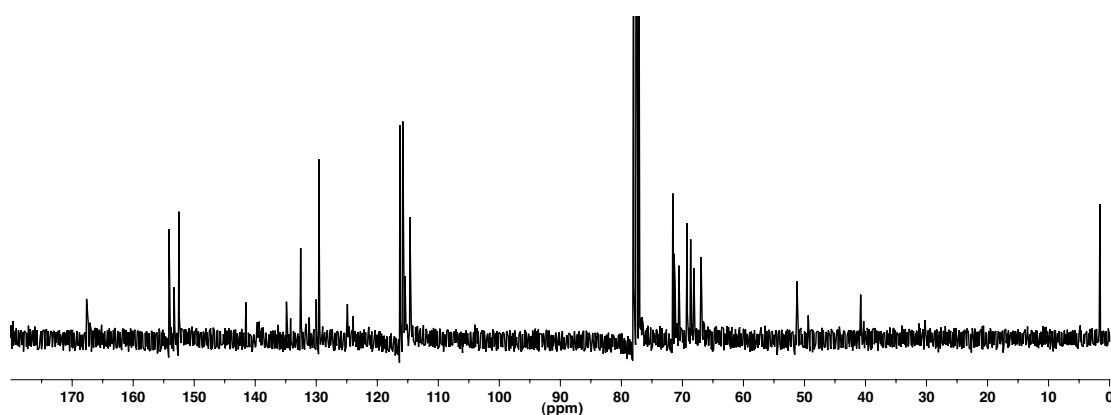
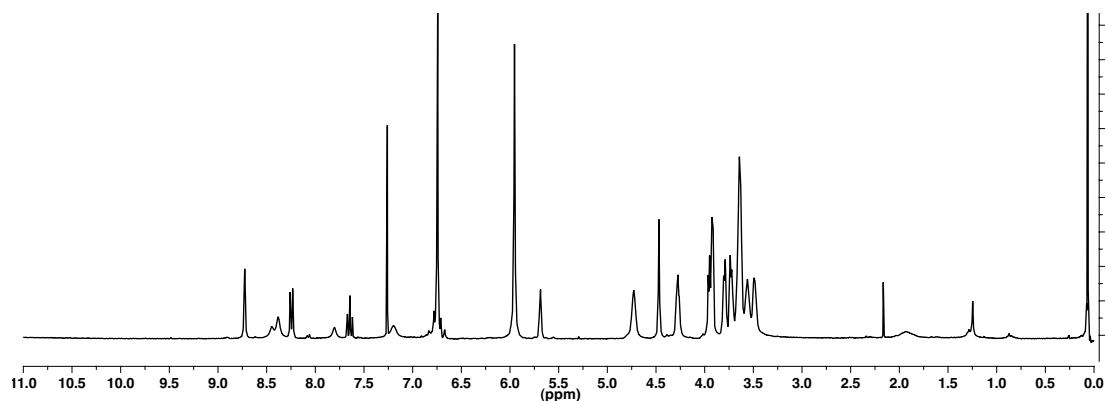
$^1\text{H}$  NMR ( $\text{CDCl}_3$ ): 9.71 (s, 1H,  $H_c$ ), 9.44 (s, 2H,  $2 \times H_b$ ), 9.15 (br. s, 2H,  $2 \times H_9$ ), 8.73 (s, 1H,  $H_{10}$ ), 8.65 (s, 2H,  $2 \times H_d$ ), 8.33 (d,  $^3J_{11,12} = 7.8$  Hz, 2H,  $2 \times H_{11}$ ), 7.62 (t,  $^3J_{11,12} = 7.8$  Hz, 1H,  $H_{12}$ ), 6.77 (s, 8H,  $4 \times H_g$ ,  $4 \times H_h$ ), 5.73–5.90 (m, 10H,  $4 \times H_5$ ,  $4 \times H_6$ ,  $2 \times H_i$ ), 4.57 (s, 3H,  $3 \times H_a$ ), 4.47 (t,  $^3J_{e,f} = 4.2$  Hz, 4H,  $4 \times H_e$ ), 4.18 (t,  $^3J_{e,f} = 4.2$  Hz, 4H,  $4 \times H_f$ ), 3.97–4.01 (m, 8H,  $4 \times H_7$ ,  $4 \times H_i$ ), 3.68–3.83 (m, 24H,  $4 \times H_1$ ,  $4 \times H_2$ ,  $4 \times H_3$ ,  $4 \times H_4$ ,  $4 \times H_j$ ,  $4 \times H_k$ ). HRESI-MS (pos.): 1234.5432, calc. for  $[\text{C}_{66}\text{H}_{76}\text{N}_9\text{O}_{15}]^+$  = 1234.5455.

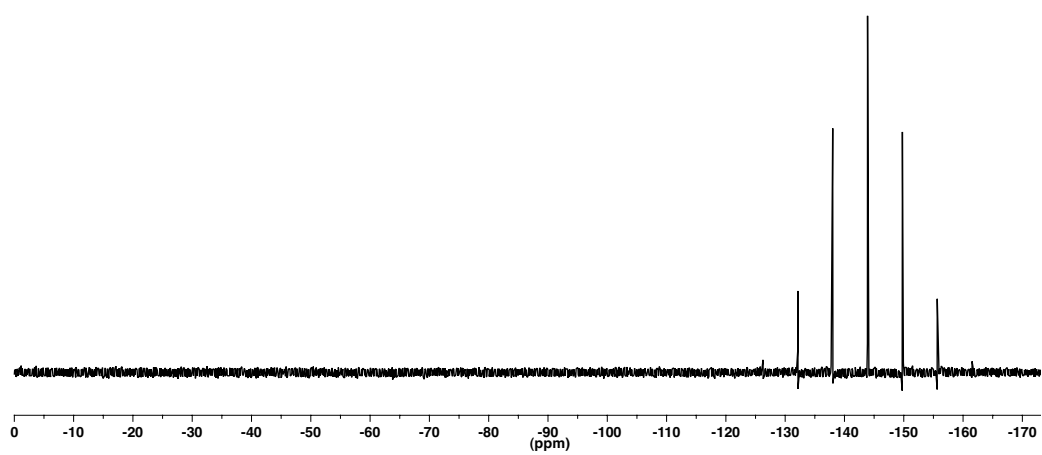
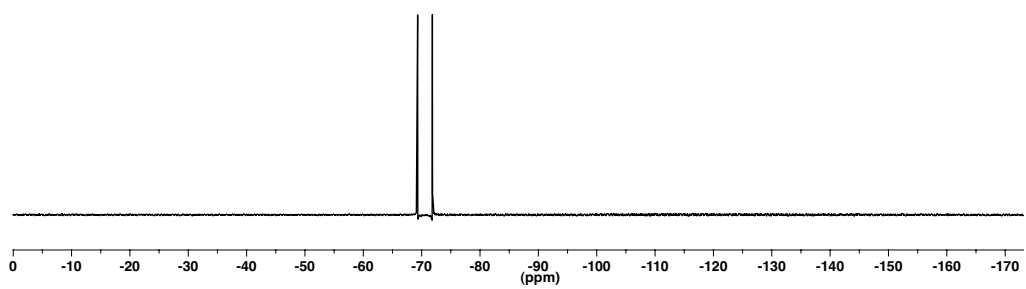


### Hexafluorophosphate salt, **5**·PF<sub>6</sub>

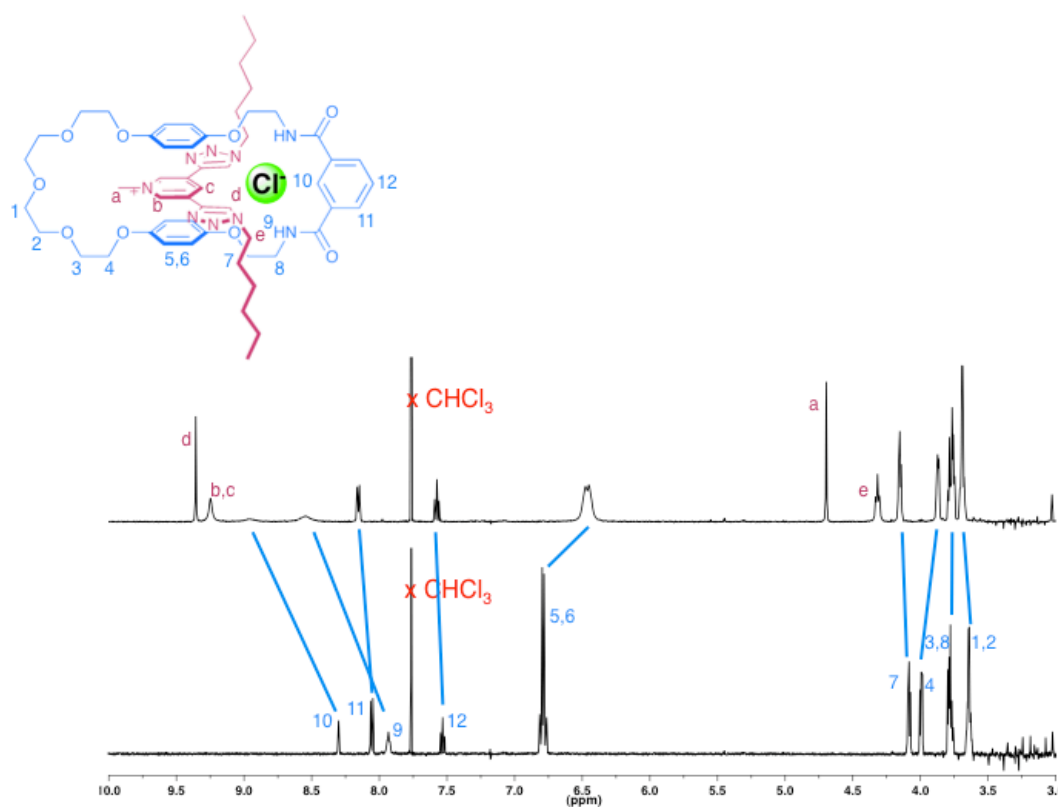
The chloride salt of **5** (0.019 g, 0.015 mmol) was taken up in dichloromethane (20 mL). It was washed with 0.1 M NH<sub>4</sub>PF<sub>6(aq)</sub> (7 × 20 mL) and water (3 × 20 mL), and taken to dryness under reduced pressure. Drying thoroughly in vacuo gave **5**·PF<sub>6</sub> as a white powder. Yield: 0.015 g (71%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.74 (s, 2H, 2 × H<sub>b</sub>), 8.34–8.46 (2 overlapping br. s, 3H, 2 × H<sub>d</sub>, H<sub>c</sub>), 8.25 (d, <sup>3</sup>J<sub>11,12</sub> = 7.8 Hz, 2H, 2 × H<sub>11</sub>), 7.77 (br. s, 1H, H<sub>10</sub>), 7.65 (t, <sup>3</sup>J<sub>11,12</sub> = 7.8 Hz, 1H, H<sub>12</sub>), 7.18 (br. s, 2H, 2 × H<sub>9</sub>), 6.75 (s, 8H, 4 × H<sub>g</sub>, 4 × H<sub>h</sub>), 5.95 (s, 8H, 4 × H<sub>5</sub>, 4 × H<sub>6</sub>), 5.70 (br. s, 2H, H<sub>i</sub>), 4.73 (br. s, 4H, 4 × H<sub>e</sub>), 4.48 (s, 3H, H<sub>a</sub>), 4.28 (br. s, 4H, 4 × H<sub>f</sub>), 3.91–3.96 (m, 8H, 4 × H<sub>4</sub>, 4 × H<sub>i</sub>), 3.72–3.80 (m, 8H, 4 × H<sub>7</sub>, 4 × H<sub>8</sub>), 3.63–3.66 (m, 12H, 4 × H<sub>2</sub>, 4 × H<sub>3</sub>, 4 × H<sub>j</sub>), 3.44–3.60 (m, 8H, 4 × H<sub>1</sub>, 4 × H<sub>k</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 167.2, 153.7, 152.9, 152.2, 152.1, 141.1, 139.2, 134.5, 133.8, 132.1, 130.7, 129.6, 129.2, 124.5, 123.5, 115.9, 115.4, 115.0, 114.2, 71.2, 70.9, 70.8, 70.1, 68.8, 68.2, 67.7, 66.5, 50.8, 49., 40.4. <sup>19</sup>F NMR (CDCl<sub>3</sub>): -70.6 (d, J<sub>P,F</sub> = 714 Hz). <sup>31</sup>P NMR (CDCl<sub>3</sub>): -143.9 (sept., J<sub>P,F</sub> = 714 Hz) LRESI-MS (pos.): 1234.54, calc. for [C<sub>66</sub>H<sub>76</sub>N<sub>9</sub>O<sub>15</sub>]<sup>+</sup> = 1234.55.

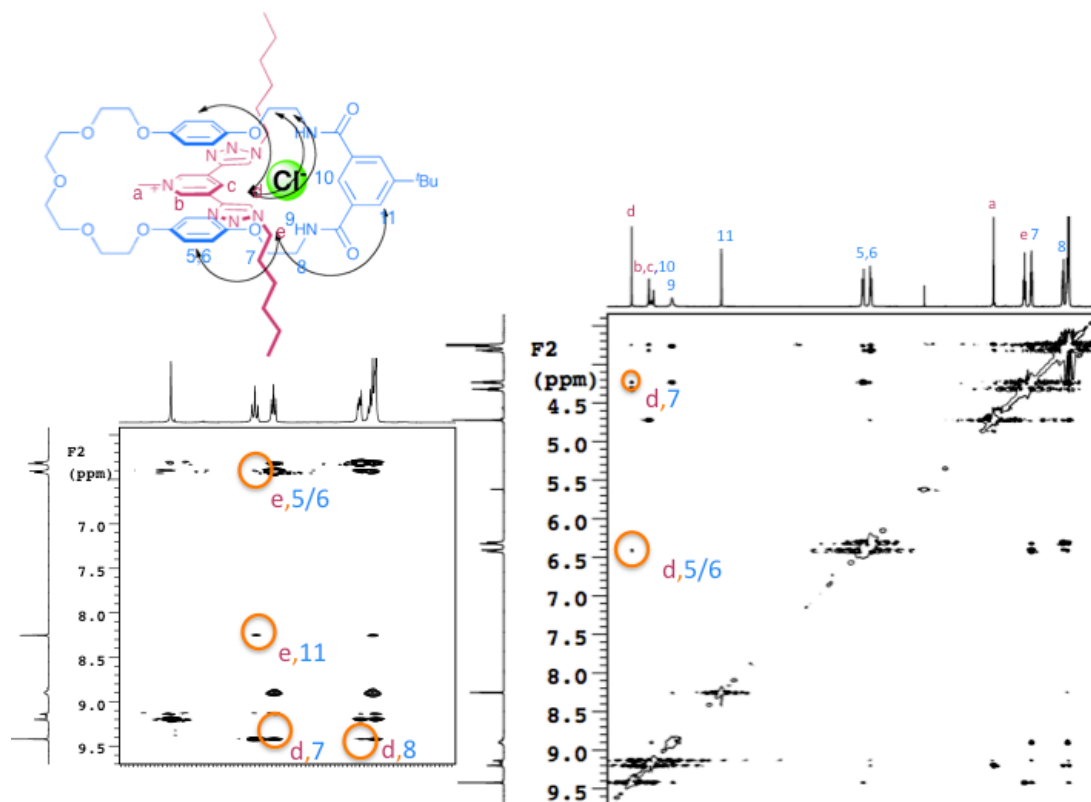




### $^1\text{H}$ NMR and $^1\text{H}$ - $^1\text{H}$ ROESY NMR Spectra of $1\cdot\text{Cl}\cdot 2$

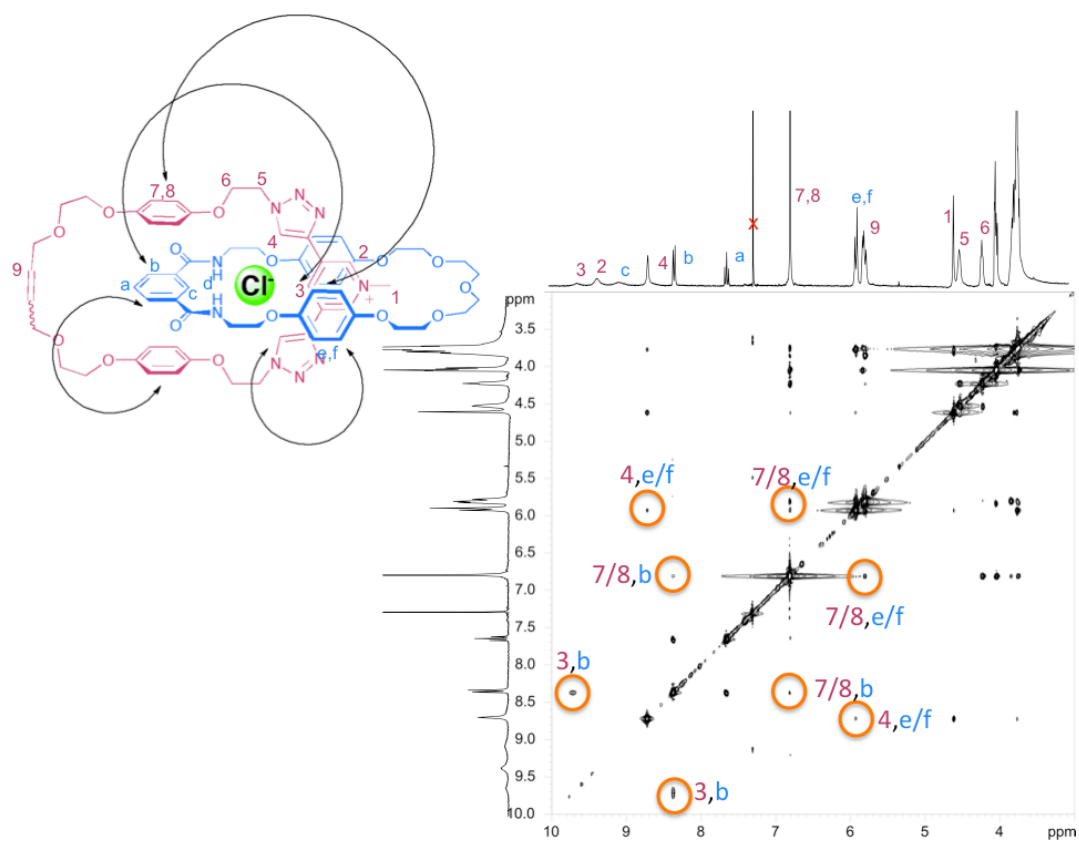


**Figure S1.** Truncated  $^1\text{H}$  NMR spectra of **2** (bottom) and  $1\cdot\text{Cl}\cdot 2$  (top). 2.0 mM in 1:1  $\text{CDCl}_3$ : $d_6$ -acetone (293 K, 500 MHz).



**Figure S2.** Truncated 2D ROESY NMR spectrum of  $1 \cdot \text{Cl} \cdot 2^{t\text{Bu}}$  in  $d_6$ -acetone showing selected intermolecular couplings (293 K, 500 MHz).

### $^1\text{H}$ - $^1\text{H}$ ROESY NMR Spectra of $5\cdot\text{Cl}$



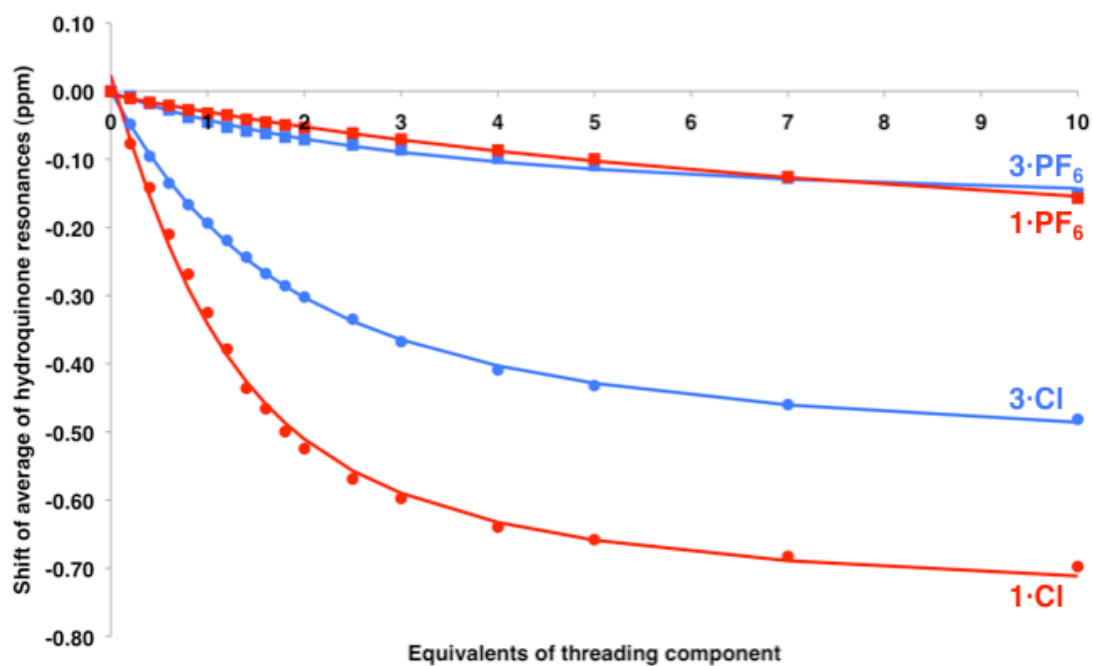
**Figure S3.** Truncated 2D ROESY NMR spectrum of  $5\cdot\text{Cl}$  in  $\text{CDCl}_3$  showing selected intermolecular couplings (293 K, 500 MHz).



## NMR Titration Protocol

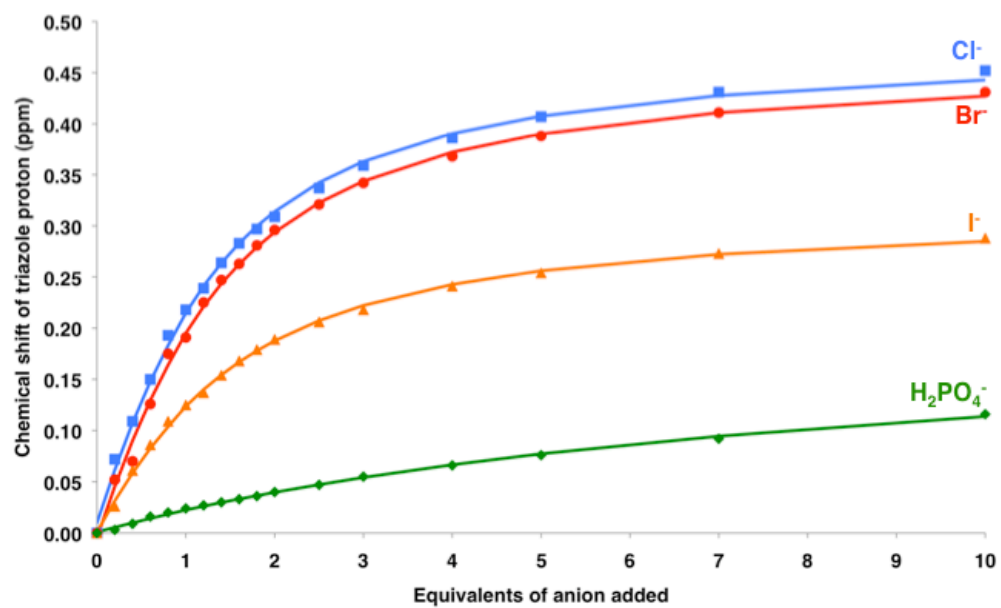
Initial sample volumes were 0.50 mL and concentrations were 2.0 mmol L<sup>-1</sup> of host. Solutions (100 mmol L<sup>-1</sup>) of anions as their tetrabutylammonium salts, or threading components as the appropriate salt were added in aliquots, the samples thoroughly shaken and spectra recorded. Spectra were recorded at 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 equivalents. Stability constants were obtained by analysis of the resulting data using the WinEQNMR2<sup>S7</sup> computer program, following the triazole C-H protons for anion association experiments, and the centre of gravity of the hydroquinone resonance for pseudorotaxane assembly experiments.

### Binding Isotherms for Pseudorotaxane Assembly Experiments



**Fig S4.** Observed data (solid points) and fitted isotherms<sup>S7</sup> (lines) for addition of amide (blue) or triazole (red) based threading components as either the hexafluorophosphate (squares) or chloride (circles) salts (293 K, 1:1 CDCl<sub>3</sub>:d<sub>6</sub>-acetone, 500 MHz).

### Binding Isotherms for Anion Association of $5 \cdot \text{PF}_6$



**Fig S5.** Observed data (solid points) and fitted isotherms<sup>S7</sup> (lines) for addition of anions as their TBA salts to  $5 \cdot \text{PF}_6$  (293 K, 1:1  $\text{CDCl}_3$ : $\text{CD}_3\text{OD}$ , 500 MHz).

## X-ray crystallography

Single crystals of **1**·Cl·2<sup>t</sup>Bu were grown by vapour diffusion of diethyl ether into a 1:1 mixture of the two components in d<sub>6</sub>-acetone. Data were collected using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) on a Nonius Kappa CCD diffractometer equipped with a Cryostream N<sub>2</sub> open-flow cooling device,<sup>S8</sup> and the data were collected at 150(2) K. Series of  $\omega$ -scans were performed in such a way as to collect all unique reflections to a maximum of 0.80  $\text{\AA}$ . Cell parameters and intensity data (including inter-frame scaling) were processed using the DENZO-SMN package.<sup>S9</sup>

Single crystals of **5**·Cl were grown by vapour diffusion of diisopropyl ether into a mixture of **5**·PF<sub>6</sub> and ten equivalents of TBA·Cl in 1:1 CDCl<sub>3</sub>:CD<sub>3</sub>OD. Data were collected using graphite monochromated Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) on an Oxford Diffraction SuperNova diffractometer. The diffractometer was equipped with a Cryostream N<sub>2</sub> open-flow cooling device,<sup>S8</sup> and the data were collected at 150(2) K. Series of  $\omega$ -scans were performed in such a way as to collect all unique reflections to a maximum of 0.80  $\text{\AA}$ . Cell parameters and intensity data (including inter-frame scaling) were processed using CrysAlis Pro.<sup>S10</sup>

The structures were solved by charge-flipping methods using SUPERFLIP<sup>S11</sup> and refined using full-matrix least-squares on  $F^2$  within the CRYSTALS suite.<sup>S12</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were generally visible in the difference map and their positions and displacement parameters were refined using restraints prior to inclusion into the model using riding constraints.<sup>S13</sup>

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC: 885861 and 885862. Copies of these data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data/\\_request/cif](http://www.ccdc.cam.ac.uk/data/_request/cif).

**Table S1.** Selected X-ray structural data.

	<b>1·Cl·2<sup>t</sup>Bu</b>	<b>5·Cl·1.5(C<sub>4</sub>H<sub>10</sub>O)</b>
empirical formula	C <sub>58</sub> H <sub>80</sub> N <sub>9</sub> O <sub>9</sub> Cl	C <sub>72</sub> H <sub>90</sub> N <sub>9</sub> O <sub>16.5</sub> Cl
crystal system	triclinic	triclinic
space group	P -1	P -1
radiation type	molybdenum ( $\lambda = 0.71073 \text{ \AA}$ )	copper ( $\lambda = \text{ \AA}$ )
<i>a</i> (Å)	9.3945(5)	11.4693(3)
<i>b</i> (Å)	17.0675(10)	16.2473(5)
<i>c</i> (Å)	18.9451(12)	20.3444(8)
$\alpha$ (°)	109.827(3)	97.255(3)
$\beta$ (°)	96.627(3)	105.022(3)
$\gamma$ (°)	93.298(2)	99.338(2)
<i>V</i> (Å <sup>3</sup> )	2823.3(3)	3556.2(2)
<i>Z</i>	2	2
$\rho_{\text{calc}}$ (mg mm <sup>-3</sup> )	1.274	1.290
$\mu$ (mm <sup>-1</sup> )	0.132	1.088
crystal size (mm)	0.02 × 0.08 × 0.32	0.03 × 0.28 × 0.32
total reflections	23720	37560
unique reflections	11935	14781
<i>R</i> <sub>int</sub>	0.111	0.030
goodness of fit	0.9711	0.9666
<i>R</i> <sub>1</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0694	0.0760
w <i>R</i> <sub>2</sub>	0.1832	0.2233
CCDC deposit no.	885861	885862

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