

## Electronic Supplementary Information

### Boron-Based Rotaxanes by Multicomponent Self-Assembly

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**General:** 1,2-di(4-pyridyl)ethylene, 4,4'-dipyridine, catechol, dibenzo-30-crown-10, and 3,5-bis(trifluoromethyl)phenylboronic acid were purchased from Acros or from Fluka. The crown ethers 1,5-dinaphtho-38-crown-10<sup>1</sup> and bis-*p*-phenylene-34-crown-10<sup>2</sup> were prepared as described in the literature. The multicomponent reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The <sup>1</sup>H, <sup>13</sup>C and <sup>11</sup>B spectra were recorded on a Bruker Advance DPX 400 spectrometer using the residual protonated solvents (<sup>1</sup>H, <sup>13</sup>C) as internal standards or BF<sub>3</sub>•OEt<sub>2</sub> (<sup>11</sup>B) as an external standard. <sup>19</sup>F NMR spectra were recorded on a Bruker Advance 200 spectrometer using CFCl<sub>3</sub> as an external standard. All spectra were recorded at room temperature and at a concentration of 10 mM. Elemental analyses were performed on a CE Instruments EA 1110 CHN instrument.

**Rotaxane 1:** A suspension of 3,5-bis(trifluoromethyl)benzeneboronic acid (5.2 mg, 20 μmol), catechol (2.2 mg, 20 μmol), 1,2-di(4-pyridyl)ethylene (1.8 mg, 10 μmol) and 1,5-dinaphtho-38-crown-10 (6.4 mg, 10 μmol) in toluene (30 mL) was heated under reflux using a Dean-Stark trap. After 1 h, 25 mL of solvent was distilled. After cooling to room temperature, the volume of the solvent was further reduced to 2 mL. This resulted in the precipitation of an orange solid, which was filtered, washed with pentane, and dried under vacuum. Yield: 10.2 mg, 67 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) : δ 3.76 (b, 16 H, CE), 3.81 (b,

16 H, CE), 6.17 (b, 4 H, CE), 6.85 (dd,  $^3J = 6$  Hz,  $^4J = 3$  Hz, 4 H, catechol), 6.95-7.02 (m, 8 H, CE+catechol), 7.32 (m, 4 H, CE), 7.59 (d,  $^3J = 7$  Hz, 4 H, pyridyl), 7.84 (s, 2 H, phenyl), 8.16 (s, 4 H, phenyl), 8.70 (d,  $^3J = 7$  Hz, 4 H, pyridyl);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) :  $\delta$  67.75, 69.90, 71.12, 71.18, 105.23, 111.08, 114.37, 120.73, 122.42 (b), 123.35, 123.92 (q,  $^1J_{\text{CF}} = 273$  Hz), 125.05, 126.50, 130.93 (q,  $^2J_{\text{CF}} = 33$  Hz), 132.26 (b), 145.08 (b), 146.92, 150.58, 154.10;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ ) :  $\delta$  14.5;  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ ) :  $\delta$  -63.01. Anal. Calcd. For  $\text{C}_{76}\text{H}_{68}\text{B}_2\text{F}_{12}\text{N}_2\text{O}_{14} \cdot 0.5 \text{C}_7\text{H}_8$ : C 62.45 H 4.75 N 1.83. Found: C 62.76 H 4.95 N 1.87. Crystals were obtained by slow evaporation of a solution of **1** in chloroform.

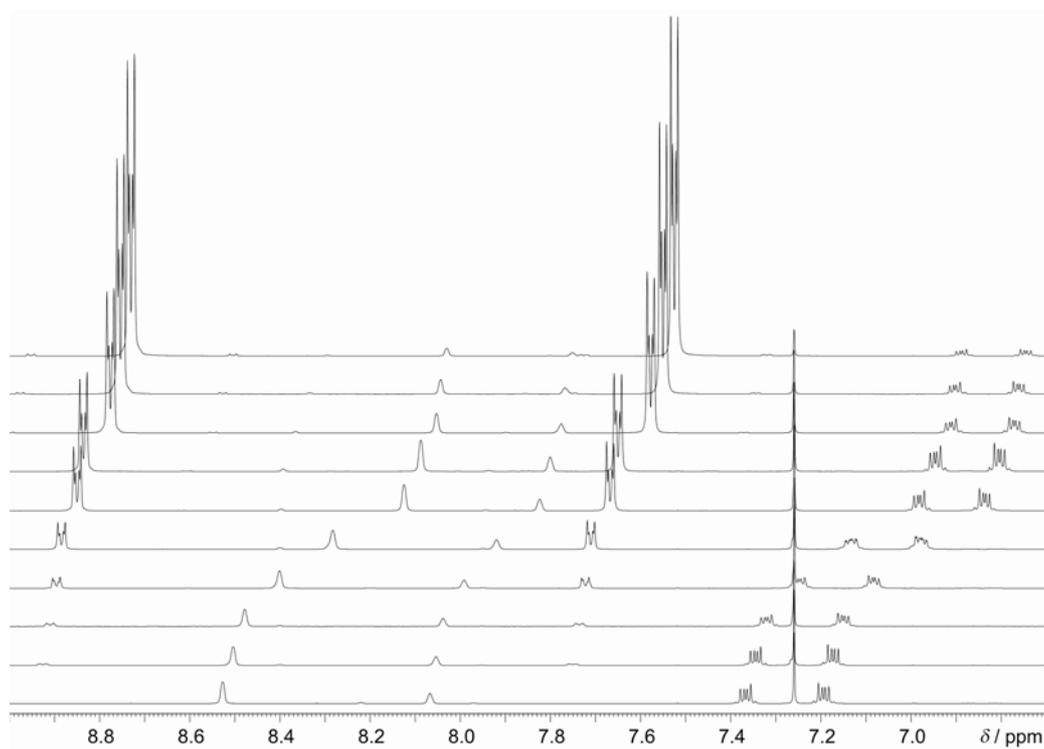
**Rotaxane 2:** A suspension of 3,5-bis(trifluoromethyl)benzeneboronic acid (12.9 mg, 50  $\mu\text{mol}$ ), catechol (5.5 mg, 50  $\mu\text{mol}$ ), 1,2-di(4-pyridyl)ethylene (4.6 mg, 25  $\mu\text{mol}$ ) and bis-*p*-phenylene-34-crown-10 (13.4 mg, 25  $\mu\text{mol}$ ) in benzene (30 mL) was heated under reflux using a Dean-Stark trap. After 1 h, 25 mL of solvent was distilled. After cooling to room temperature, the yellow solution was placed in a fridge for 1 h. This resulted in the formation of a yellow precipitate, which was isolated, washed with pentane, and dried under vacuum. Yield: 21.9 mg, 63 %.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) :  $\delta$  3.65-3.74 (m, 16 H, CE), 3.80-3.87 (m, 8 H, CE), 3.93-4.01 (m, 8 H, CE), 6.73 (s, 8 H, CE), 6.87 (dd,  $^3J = 6$  Hz,  $^4J = 3$  Hz, 4 H, catechol), 7.01 (dd,  $^3J = 6$  Hz,  $^4J = 3$  Hz, 4 H, catechol), 7.32 (s, 2 H, ethylene), 7.65 (d,  $^3J = 7$  Hz, 4 H, pyridyl), 7.84 (s, 2 H, phenyl), 8.14 (s, 4 H, phenyl), 8.78 (d,  $^3J = 7$  Hz, 4 H, pyridyl);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) :  $\delta$  68.29, 69.94, 70.89, 71.03, 111.32, 115.64, 121.04, 122.83 (bt,  $^3J_{\text{CF}} = 4$  Hz), 123.20, 123.82 (q,  $^1J_{\text{CF}} = 273$  Hz), 131.03 (q,  $^2J_{\text{CF}} = 33$  Hz), 132.47 (b), 133.22, 145.93, 147.03, 150.22, 153.21;  $^{11}\text{B}$  NMR (128 MHz,  $\text{CDCl}_3$ ) :  $\delta$  16.1;  $^{19}\text{F}$  NMR (188 MHz,  $\text{CDCl}_3$ ) :  $\delta$  -63.09. Anal. Calcd. For  $\text{C}_{68}\text{H}_{64}\text{B}_2\text{F}_{12}\text{N}_2\text{O}_{14}$ : C 59.06 H 4.66 N 2.03. Found: C 58.85 H 4.81 N 1.90. Crystals were obtained by slow diffusion of pentane into a solution of **2** in toluene.

**Host-guest complex 3:** A suspension of 3,5-bis(trifluoromethyl)benzeneboronic acid (20.6 mg, 80  $\mu\text{mol}$ ), catechol (8.8 mg, 80  $\mu\text{mol}$ ), 4,4'-dipyridyl (6.2 mg, 40  $\mu\text{mol}$ ) and dibenzo-30-crown-10 (21.5 mg, 40  $\mu\text{mol}$ ) in toluene (30 mL) was heated under reflux using a Dean-Stark trap. After 1 h, 25 mL of solvent was distilled. After cooling to room temperature, the volume of solvent was further reduced to 2 mL and the yellow solution was placed in a freezer for 12 h. This resulted in the formation of X-ray quality crystals, which were isolated, washed with pentane and dried under vacuum. Yield: 35.5 mg, 60 %.  $^1\text{H}$  NMR (400 MHz,

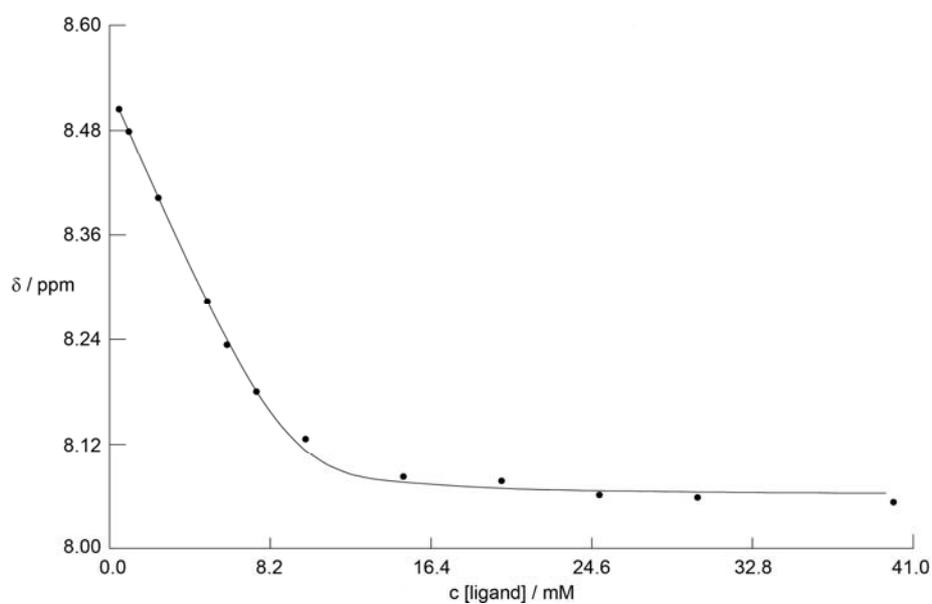
CDCl<sub>3</sub>) :  $\delta$  3.65-3.70 (m, 8 H, CE), 3.73-3.79 (m, 8 H, CE), 3.86 (t, <sup>3</sup>J = 5 Hz, 8 H, CE), 4.11 (t, <sup>3</sup>J = 5 Hz, 8 H, CE), 6.82-6.91 (m, 8 H, CE), 6.96 (dd, <sup>3</sup>J = 6 Hz, <sup>4</sup>J = 3 Hz, 4 H, catechol), 7.11 (dd, <sup>3</sup>J = 6 Hz, <sup>4</sup>J = 3 Hz, 4 H, catechol), 7.70-7.76 (m, 4 H, pyridyl), 7.91 (s, 2 H, phenyl), 8.26 (s, 4 H, phenyl), 8.87-8.92 (m, 4 H, pyridyl); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) :  $\delta$  69.23, 69.94, 70.87, 71.04, 111.83, 114.62, 121.66, 121.76, 123.10, 123.68 (bt, <sup>3</sup>J<sub>CF</sub> = 4 Hz), 123.70 (q, <sup>1</sup>J<sub>CF</sub> = 273 Hz), 131.26 (q, <sup>2</sup>J<sub>CF</sub> = 33 Hz), 133.10 (b), 147.56 (overlap), 149.12, 149.65; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) :  $\delta$  20.4; <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) :  $\delta$  -63.15. Anal. Calcd. For C<sub>66</sub>H<sub>62</sub>B<sub>2</sub>F<sub>12</sub>N<sub>2</sub>O<sub>14</sub>•1.2C<sub>7</sub>H<sub>8</sub>: C 60.90 H 4.92 N 1.91. Found: C 61.36 H 4.95 N 2.23.

**Boronic ester 4:** A suspension of 3,5-bis(trifluoromethyl)benzeneboronic acid (103.2 mg, 40  $\mu$ mol) and catechol (44.0 mg, 40  $\mu$ mol) in toluene (60 mL) was heated under reflux using a Dean-Stark trap. After 1 h, 50 mL of solvent was distilled. After cooling to room temperature, the solvent was removed under vacuum and the white residue was sublimated under vacuum, producing crystals of the boronic ester. Yield: 81.9 mg, 62 %. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) :  $\delta$  7.20 (dd, <sup>3</sup>J = 6 Hz, <sup>4</sup>J = 3 Hz, 2 H, catechol), 7.37 (dd, <sup>3</sup>J = 6 Hz, <sup>4</sup>J = 3 Hz, 2 H, catechol), 8.07 (s, 1 H, phenyl), 8.53 (s, 2 H, phenyl); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) :  $\delta$  113.08, 122.63, 123.42 (q, <sup>1</sup>J<sub>CF</sub> = 273 Hz), 125.94 (sept, <sup>3</sup>J<sub>CF</sub> = 4 Hz), 131.81 (q, <sup>2</sup>J<sub>CF</sub> = 34 Hz), 134.91 (bd, <sup>3</sup>J<sub>CF</sub> = 3 Hz), 148.26; <sup>11</sup>B NMR (128 MHz, CDCl<sub>3</sub>) :  $\delta$  31.9; <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) :  $\delta$  -63.40. Anal. Calcd. For C<sub>14</sub>H<sub>7</sub>BF<sub>6</sub>O<sub>2</sub>: C 50.65 H 2.13. Found: C 51.27 H 2.11.

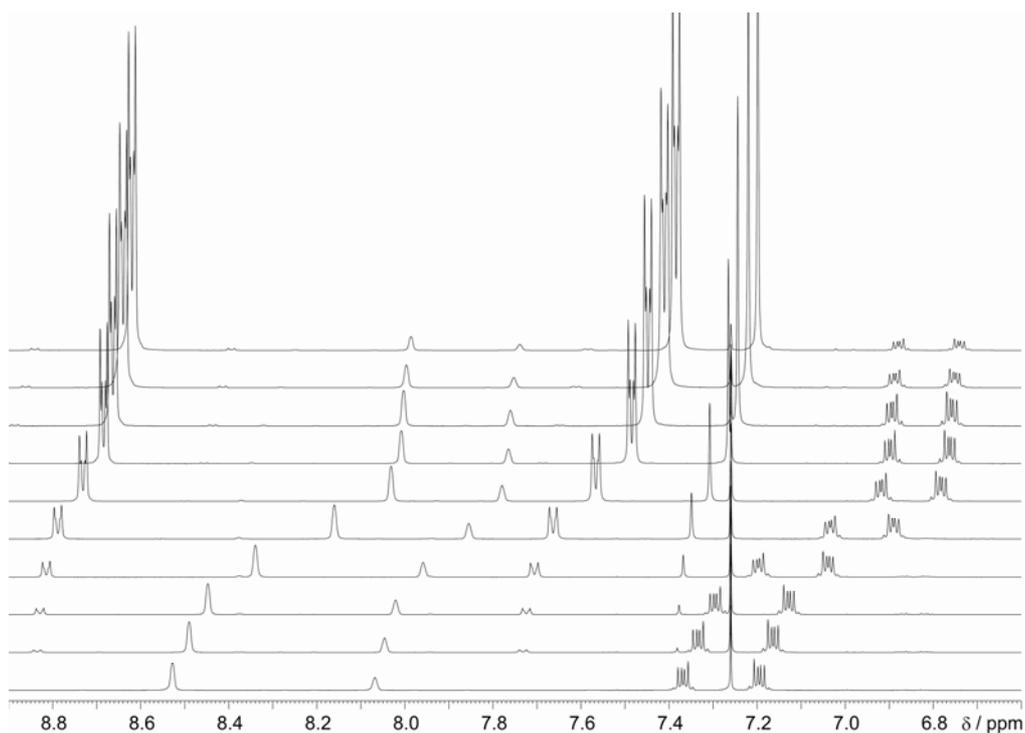
**Binding studies:** CDCl<sub>3</sub> stock solutions of ester **4** (100 mM), 4,4'-dipyridyl (50 mM) and 1,2-di(4-pyridyl)ethylene (50 mM) were prepared. 50  $\mu$ l of the stock solution of **4** were placed in an NMR tube and various amounts of ligand were added. The volume was then adjusted to 0.5 ml with CDCl<sub>3</sub> so that the final concentration of **4** was 10 mM. Thirteen <sup>1</sup>H NMR spectra were recorded corresponding to ligand concentrations of 0, 0.5, 1.0, 2.5, 5.0, 6.0, 7.5, 10.0, 15.0, 20.0, 25.0, 30.0 and 40.0 mM. The chemical shift values of the signal for the H<sup>2</sup> and H<sup>6</sup> atoms of the boronic ester phenyl ring were plotted versus the ligand concentration. The data was fitted with the non-linear least square curve-fitting program WinEQNMR<sup>3</sup> using a 2:1 binding model. An analogous experiment was performed using 4,4'-dipyridyl instead of 1,2-di(4-pyridyl)ethylene. Selected <sup>1</sup>H NMR spectra and the resulting binding curves are shown in the Figures S1 – S4.



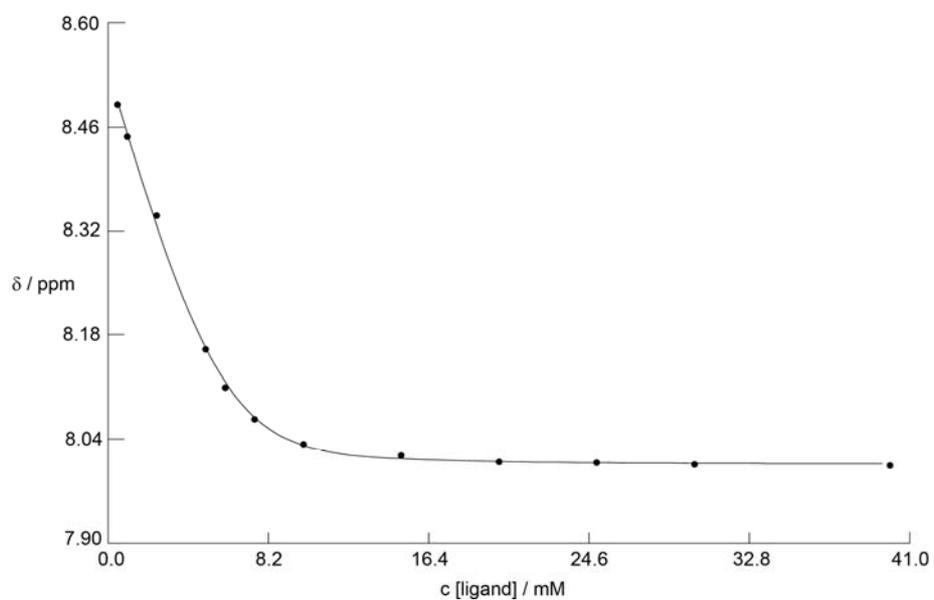
**Figure S1.** Selected  $^1\text{H}$  NMR spectra in the aromatic region for the titration of **4** with 4,4'-dipyridyl (the amount of 4,4'-dipyridyl increases from the bottom to the top).



**Figure S2.** Experimental points and fitting curve for the titration of **4** with 4,4'-dipyridyl.



**Figure S3.** Selected  $^1\text{H}$  NMR spectra in the aromatic and olefinic region for the titration of **4** with 1,2-di(4-pyridyl)ethylene (the amount of 1,2-di(4-pyridyl)ethylene increases from the bottom to the top).



**Figure S4.** Experimental points and fitting curve for the titration of **4** with 1,2-di(4-pyridyl)ethylene.

**Crystallographic analyses:** Data collections were performed at low temperature on different equipment: Bruker-Nonius APEX II CCD (**1**) and Oxford Diffraction Sapphire/KM4 CCD (**2**, **3**) both having kappa geometry. Data were reduced by means of EVALCCD<sup>4</sup> (**1**) and CrysAlis PRO (**2**, **3**)<sup>5</sup> and corrected for absorption. The structures were solved and refined using SHELXTL, release 6.1.4<sup>6</sup>. As stated briefly in the main article, crystals of **1** and **2** were weak but different attempts at crystallization and diffraction did unfortunately not improve the quality. For crystal structure **1**: disorder problems in the chains of the crown-ether were solved by a split model concerning atoms O7 and C21, some bonds dealing with this moiety were restrained by means of the DFIX card and the anisotropic refinement of the disordered part restrained by means of the SIMU card. A twin law [-1 0 0 0 -1 0 0.5 0 1] has been found by ROTAX and a BASF refined factor has been obtained [0.153(4)]. For crystal structure **2**: crystals were very weak and no diffraction can be seen beyond 0.91 Å (CrysAlis PRO gives for higher resolution data a ratio  $I/\sigma(I) < 1$ ). This means that the anisotropic refinement of light atoms can be problematic. The SIMU card has been employed in the refinement of all C and F atoms, and the ISOR card has been used for N1, C11 and C12. All CF<sub>3</sub> moieties have been treated by means of the DFIX card (C-F and F...F distances). Disorder problems were found for one CF<sub>3</sub> group (F4, F5, F6) and for one toluene molecule (C83, ..., C89) and then solved by the split model. For crystal structure **3**: disorder problems have been found once again in the chains of the crown-ether (O13, C65) and solved by the split model but no strong restraint has been applied to the corresponding bond distances.

## References:

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