

Electronic Supporting Information

Enhanced Anion Recognition by Ammonium [2]Catenane Functionalisation of a Halogen Bonding Acyclic Receptor

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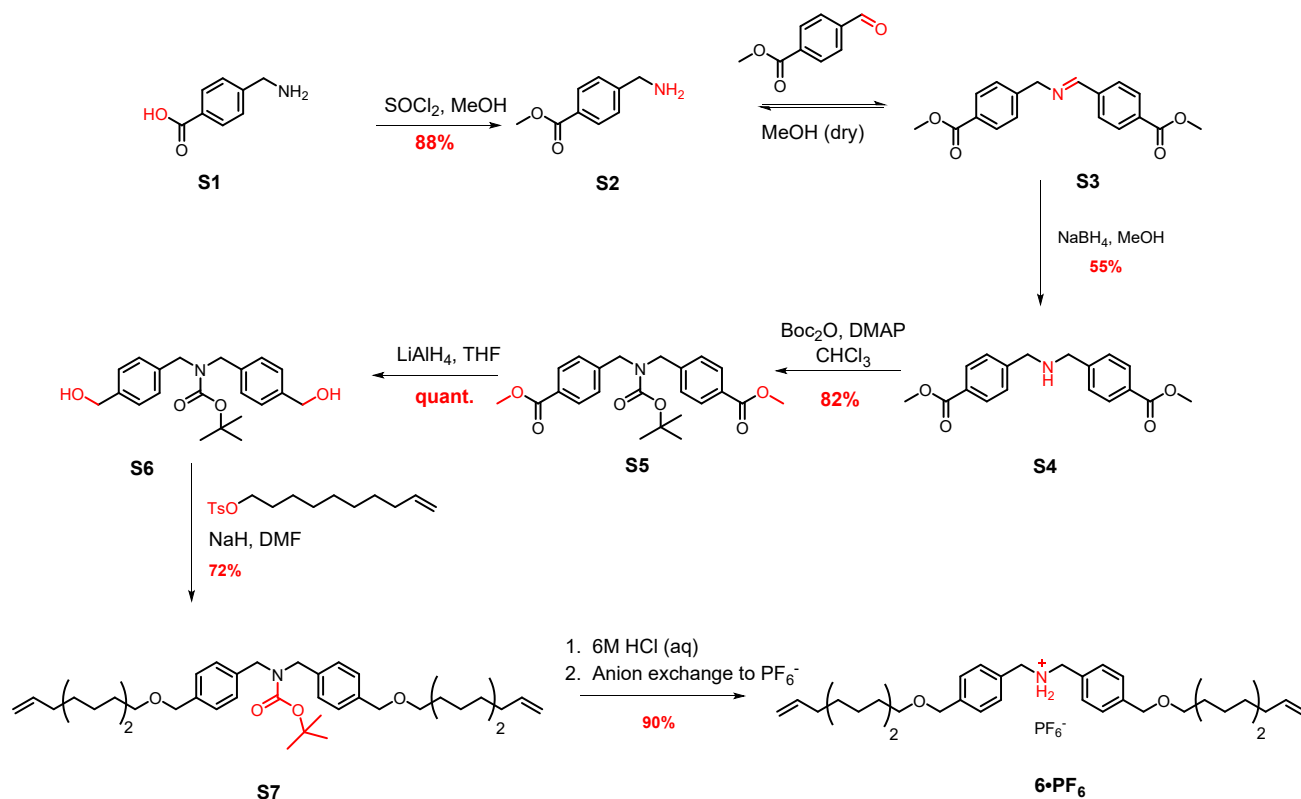
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1. Synthetic Methods

1.1 Synthesis of the bis-vinyldibenzyl ammonium thread **6**·PF₆

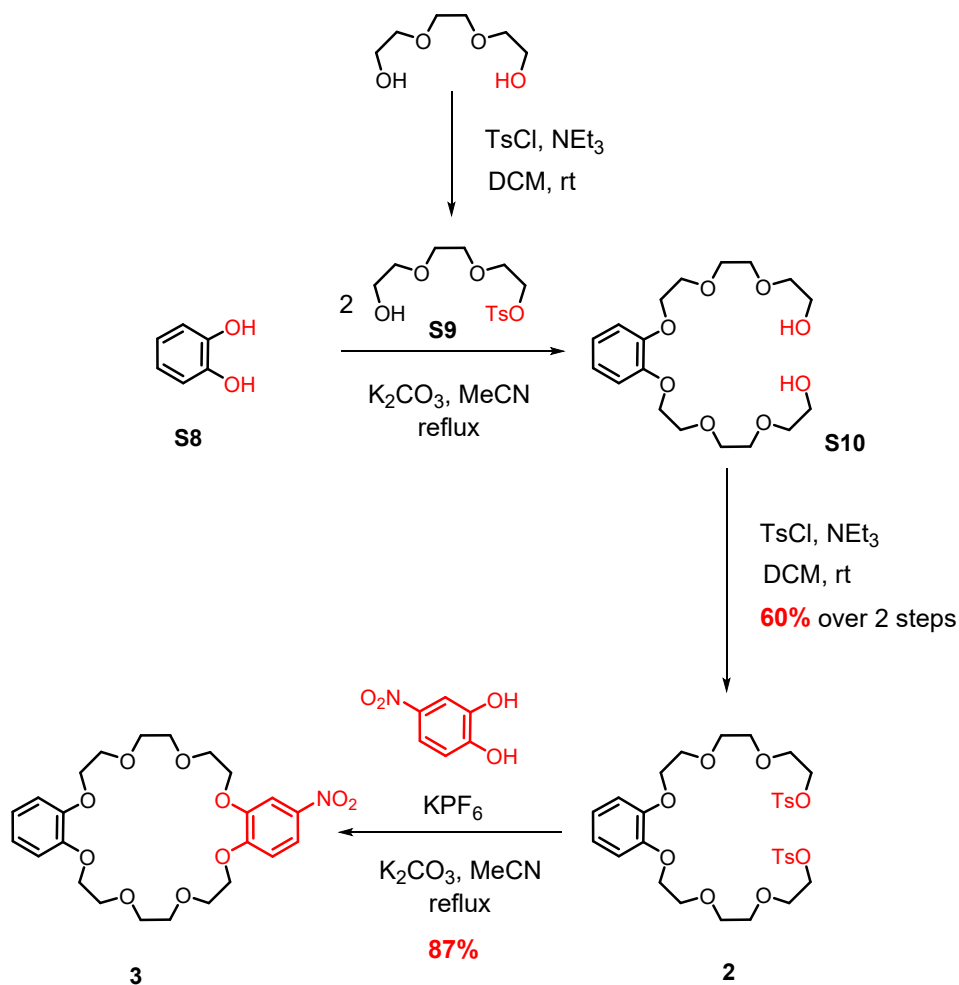
Before embarking upon the azide catenane synthesis, it was necessary to prepare the appropriate bis-alkene thread, using a modified procedure reported by Stoddart and Iwamoto (Scheme S1).^{1,2} Firstly, esterification of commercially available 4-aminomethyl benzoic acid **S1** with thionyl chloride and methanol afforded the methyl 4-aminomethyl benzoate **S2** in 88% yield. An equivalent of 4-formylmethylbenzoate was reacted with **S2** in dry methanol overnight to form imine **S3**, which was subsequently reduced using NaBH₄ to obtain the secondary amine **S4** without further purification. The reaction of **S4** with *tert*-di-*tert*-butyl dicarbonate in the presence of a catalytic amount DMAP gave the Boc-protected secondary amine **S5** in 82% yield. Reduction of the methyl ester group using LiAlH₄ was achieved in quantitative yield to obtain the bis-alcohol **S6**. A S_N2 reaction of **S6** and decenyl tosylate in the presence of NaH in DMF afforded the bis-alkene **S7** in 72% yield. Deprotection of the Boc group using acid gave the bis-alkene ammonium thread **6**·PF₆ in 90% yield after anion exchange.



Scheme S1 Synthesis of bis-vinyldibenzyl ammonium thread **6**·PF₆.

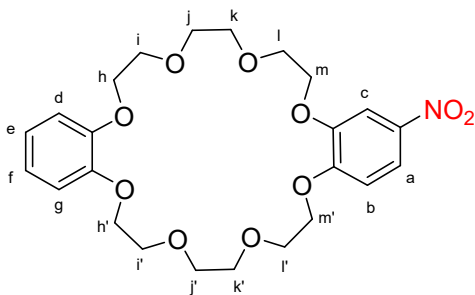
1.2 Synthesis of the nitro-dibenzo[24]crown-8 macrocycle **3**

Macrocycle precursors **S8**, **S9**, **S10**, and **2** were synthesised according to previously reported procedures (Scheme 2). Subsequent etherification of **2** with 4-nitrocatechol led to the formation of NO₂-Dibenzo[24]crown-8 **3**.^{3,4}



Scheme S2 Synthesis of a novel nitro-dibenzo[24]crown-8 macrocycle **3**.

(a) NO₂-Dibenzo[24]crown-8 (**3**)



Ditosylate **2** (2.87g, 4.2 mmol), 2-nitrocatechol (653 mg, 4.2 mmol), and KPF₆ (928 mg, 5.04 mmol) were mixed in MeCN (140 ml), and then degassed throughout a solution. K₂CO₃ (2.32g, 16.8 mmol) was added to a reaction mixture which was refluxed in the absence of light for 72 hours. After cool down to room temperature and removing solid residues, the reaction was dried and re-dissolved in DCM. The organic residue was washed with pyridine hydrochloride solution (3 times) and water (3 times), and subsequently dried over MgSO₄. Solvent was removed to obtain a yellow solid product of **2** in 90% yield.

¹H-NMR (400 MHz, CDCl₃) δ = 7.87 (H_a, dd, *J* = 8.9, 2.6 Hz, 1H), 7.72 (H_c, d, *J* = 2.6 Hz, 1H), 6.88 (H_b and H_{d-g}, q, *J* = 5.2, 4.6 Hz, 5H), 4.23 (H_{m,m'}, dt, *J* = 7.6, 4.0 Hz, 4H), 4.15 (H_{h,h'}, t, *J* = 4.3 Hz, 4H), 3.99 – 3.88 (H_{i,i'} and H_{l,l'}, m, 8H), 3.83 (H_{j,j'} and H_{k,k'}, d, *J* = 2.8 Hz, 8H).

¹³C-NMR (101 MHz, CDCl₃) δ = 154.46, 148.93, 148.85, 148.47, 141.57, 121.64, 121.57, 118.18, 114.17, 114.06, 111.47, 108.54, 71.47, 71.28, 69.95, 69.88, 69.73, 69.55, 69.49, 69.43, 69.30.

HRMS (ESI+ve) *m/z*: 511.22855 ([M+NH₄]⁺, C₂₄H₃₅N₂O₁₀ requires 511.22862)

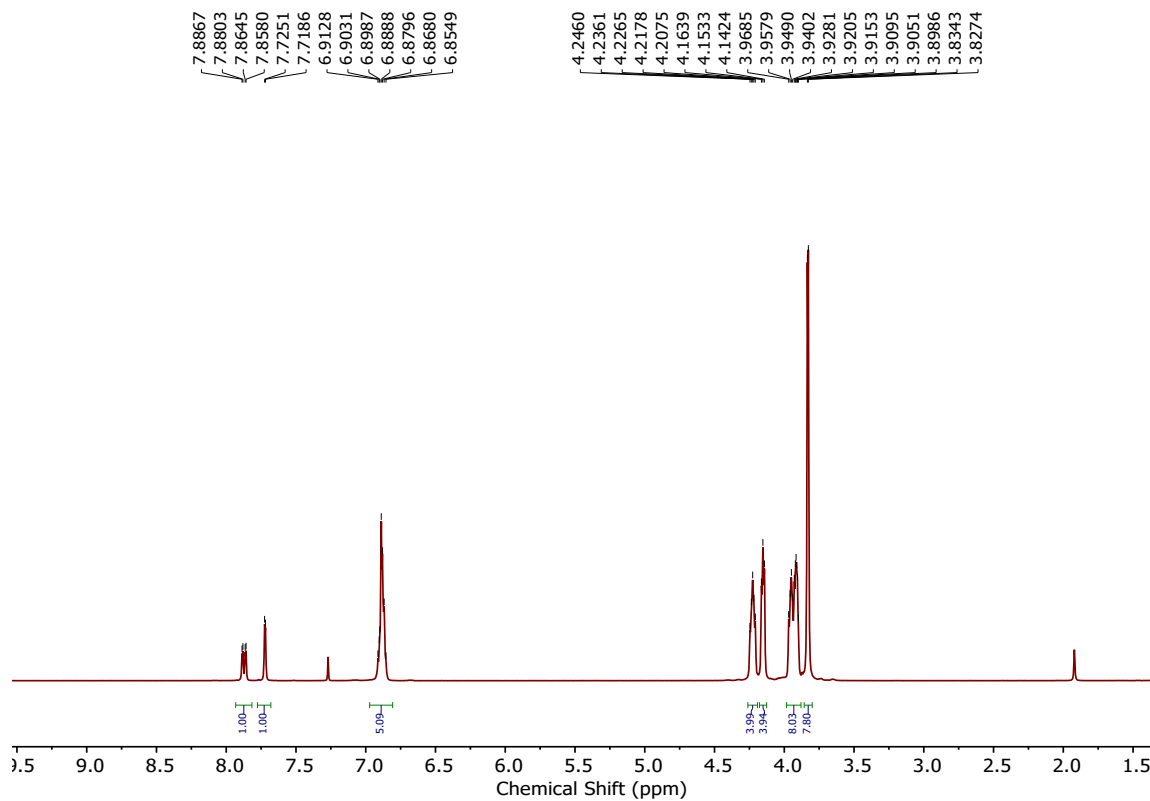


Figure S1 $^1\text{H-NMR}$ spectrum of **3** (400 MHz, CDCl_3)

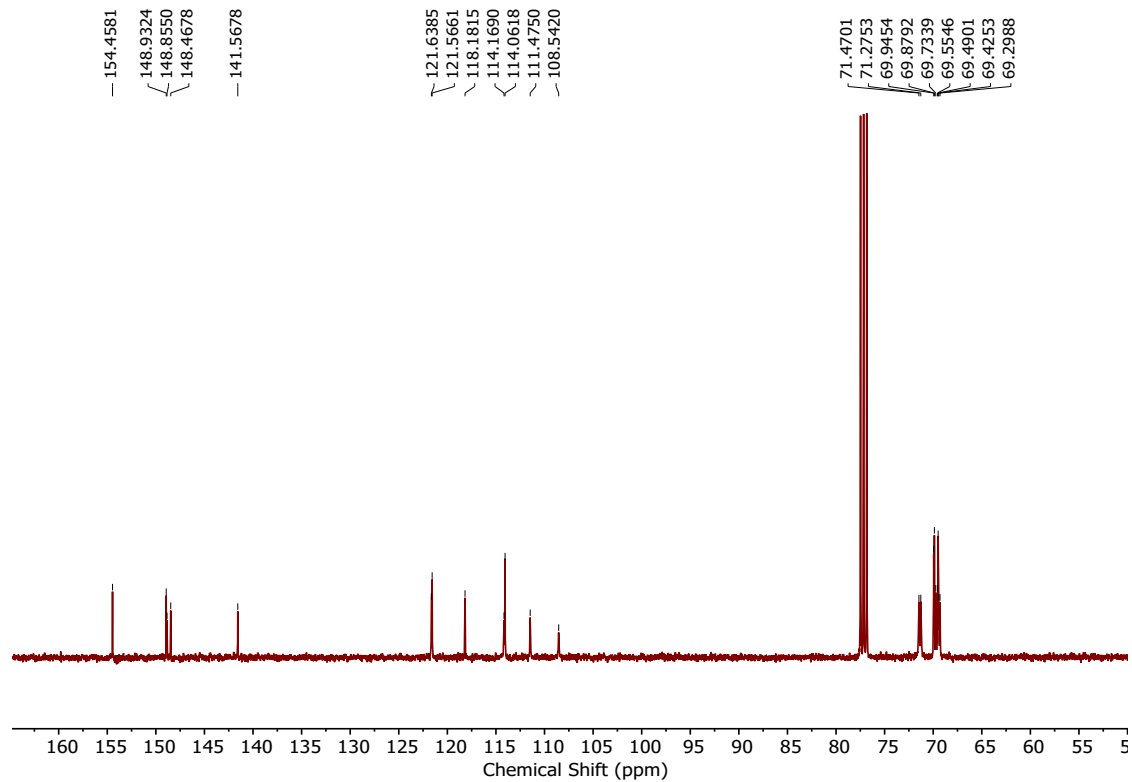
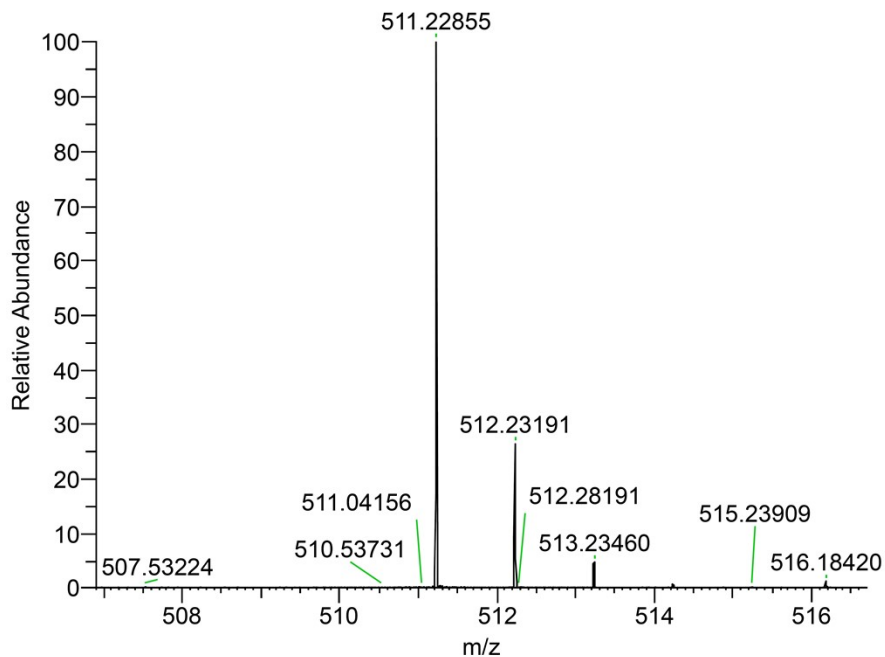
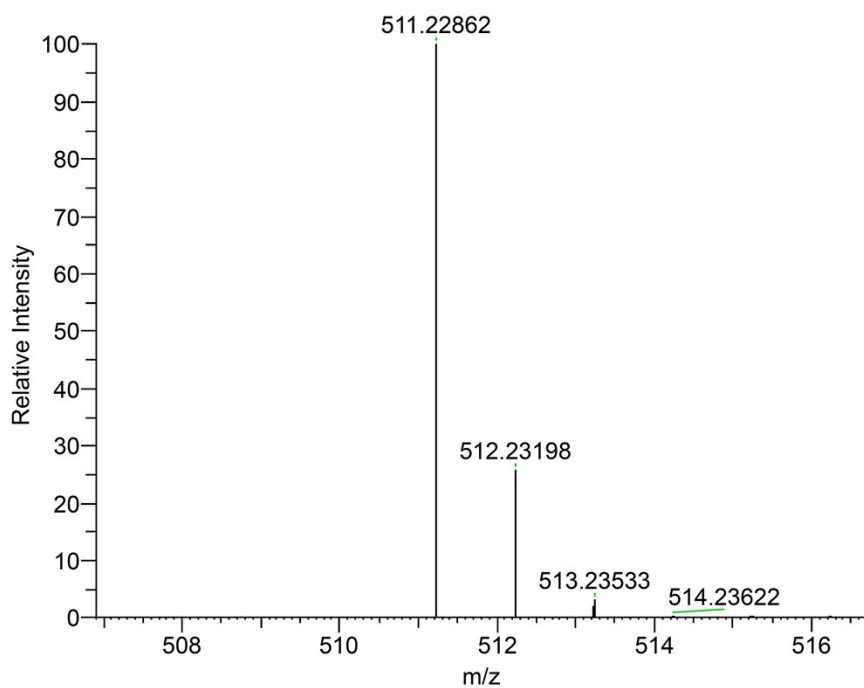


Figure S2 $^{13}\text{C-NMR}$ spectrum of **3** (101 MHz, CDCl_3)



NL: 3.01E7
 ESI61174 #14-27 RT: 0.17-0.31 AV: 7 NL:
 3.01E+007
 T: FTMS {1,1} + p ESI Full lock ms
 [80.00-1600.00]

Measured
Spectrum



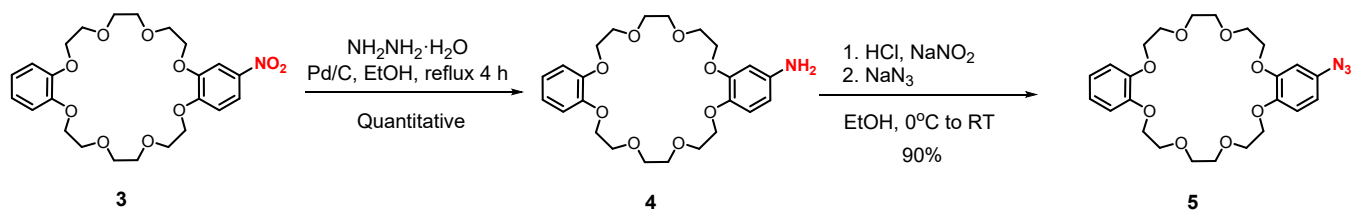
NL: 7.45E5
 C24H35O10N2: C₂₄H₃₅O₁₀N₂ Chrg 1 R:
 1000000 Res. Pwr. @FWHM

Theoretical
Spectrum

| m/z | Formula | RDB | Delta ppm | Theo. Mass |
|-----------|--|-----|-----------|------------|
| 511.22855 | C ₂₄ H ₃₅ O ₁₀ N ₂ | 8.5 | -0.15 | 511.22862 |

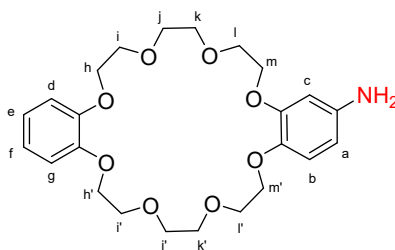
Figure S3 HRMS spectrum of 3

1.3 Synthesis of the azido-dibenzo[24]crown-8 macrocycle **5**



Scheme S3 Synthesis of a novel azide-dibenzo[24]crown-8 macrocycle **5**.

(a) NH_2 -Dibenzo[24]crown-8 (**4**)



To a solution of NO_2 -dibenzo[24]crown-8 **3** (1.07g, 2.03 mmol) in EtOH (10 ml) was added a suspension of 10%(w/w) Pd/C (100 mg) in water (0.5ml) and hydrazine monohydrate (5.5ml). The mixture was refluxed at 80°C for 5 hrs, followed by filtered through Celite® and removed solvent to afford a white solid in quantitative yield of **4**. Product can be used in the next step without further purification.

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 6.88 ($\text{H}_{\text{d-g}}$, d, J = 2.4 Hz, 4H), 6.70 (H_{b} , d, J = 8.4 Hz, 1H), 6.25 (H_{c} , d, J = 2.6 Hz, 1H), 6.18 (H_{a} , dd, J = 8.4, 2.6 Hz, 1H), 4.14 ($\text{H}_{\text{h,h'}}$, t, J = 4.3 Hz, 4H), 4.06 ($\text{H}_{\text{m,m'}}$, q, J = 5.0 Hz, 4H), 3.96 – 3.71 ($\text{H}_{\text{i-l}}$ and $\text{H}_{\text{i'-l'}}$, m, 16H).

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ = 150.22, 148.98, 148.95, 141.70, 141.55, 121.49, 121.46, 117.32, 114.25, 114.18, 107.20, 102.55, 71.19, 70.98, 70.65, 70.18, 69.91, 69.89, 69.86, 69.44, 69.33, 69.03.

HRMS (ESI+ve) m/z : 464.22760 ($[\text{M}+\text{H}]^+$, $\text{C}_{24}\text{H}_{34}\text{NO}_8$ requires 464.22789)

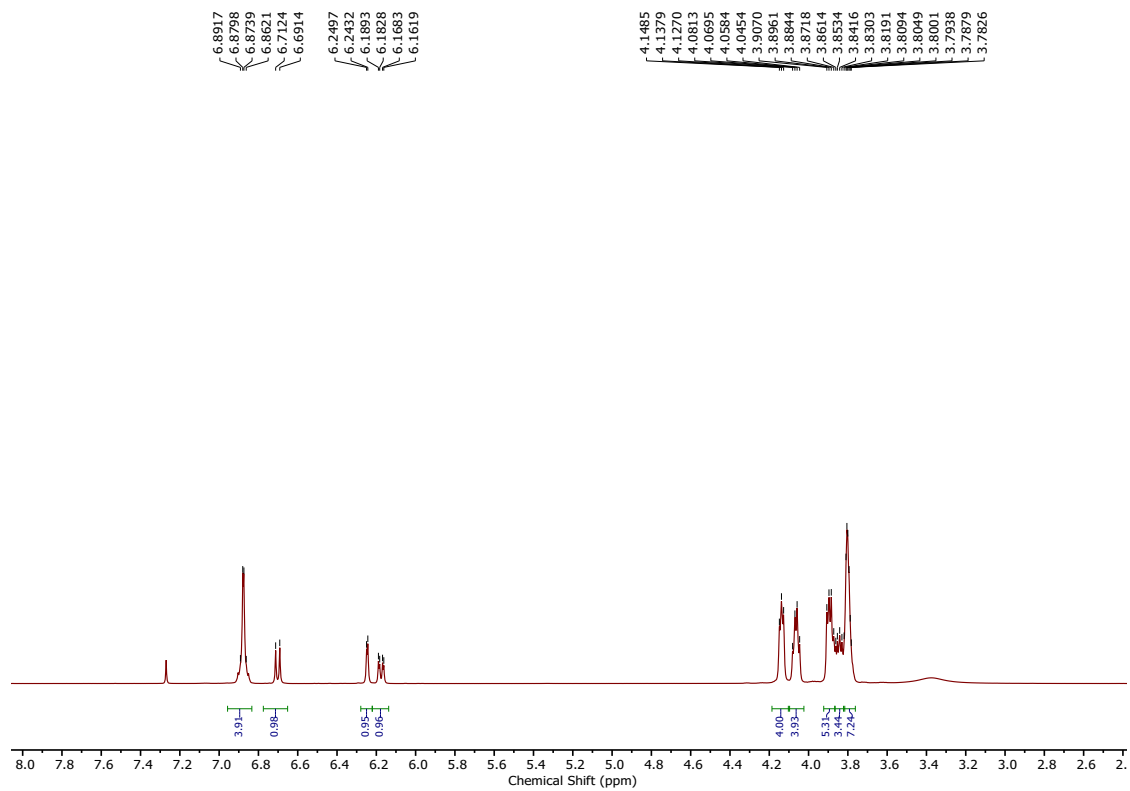


Figure S4 $^1\text{H-NMR}$ spectrum of **4** (400 MHz, CDCl_3)

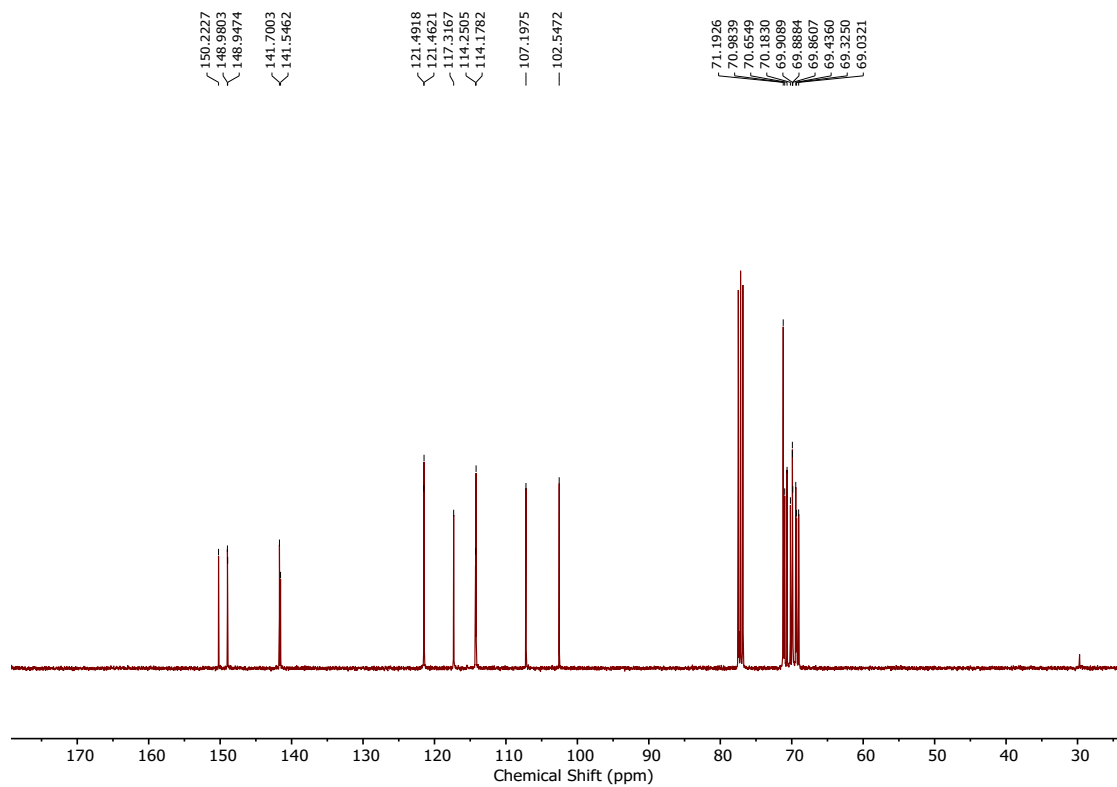
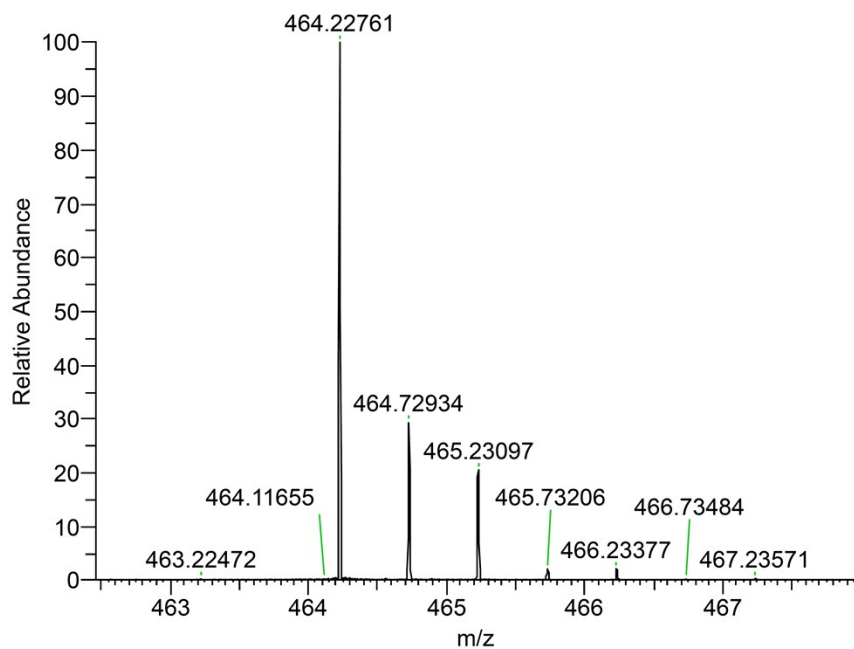
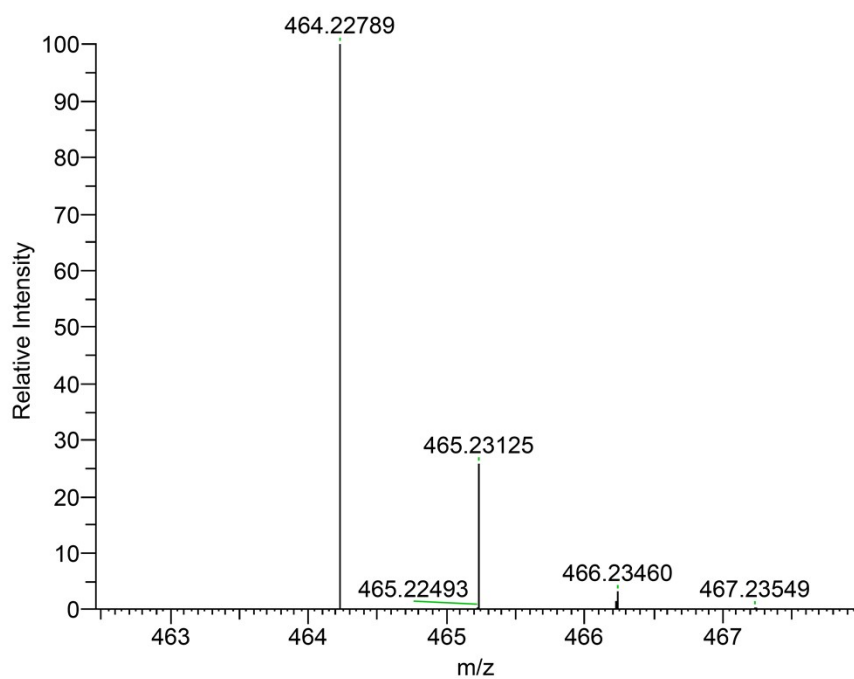


Figure S5 $^{13}\text{C-NMR}$ spectrum of **4** (101 MHz, CDCl_3)



NL: 1.70E8
 ESI61364 #13-27 RT: 0.15-0.31 AV: 8 NL:
 1.70E+008
 T: FTMS {1,1} + p ESI Full ms
 [80.00-1600.00]

Measured
Spectrum



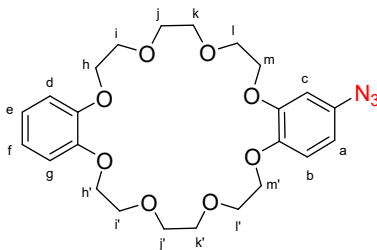
NL: 7.52E5
 C24H34O8N1: C₂₄ H₃₄ O₈ N Chrg 1 R:
 1000000 Res. Pwr. @FWHM

Theoretical
Spectrum

| m/z | Formula | RDB | Delta ppm | Theo. Mass |
|-----------|--|-----|-----------|------------|
| 464.22760 | C ₂₄ H ₃₄ O ₈ N | 8.5 | -0.63 | 464.22789 |

Figure S6 HRMS spectrum of 4

(b) N₃-Dibenzo[24]crown-8 (5)



A solution of NH₂-Dibenzo[24]crown-8 **4** (139 mg, 0.3 mmol) in EtOH (5ml) was cooled down and added 1:1 HCl (37%)/H₂O. NaNO₂ (62 mg, 0.9 mmol) was subsequently added to a reaction mixture, then stirring at 0°C for 1 hour. After addition of NaN₃ (59 mg, 0.9 mmol), the reaction was left stirring overnight, followed by dilute with water. An aqueous solution was extracted using Et₂O, the organic layer was dry over MgSO₄ and removed solvent to obtain the target product **5** as a brown solid in 90% yield.

¹H-NMR (400 MHz, CDCl₃) δ = 6.94 – 6.80 (H_{d-g} and H_a m, 5H), 6.58 (H_b, dd, *J* = 8.5, 2.6 Hz, 1H), 6.52 (H_c, d, *J* = 2.6 Hz, 1H), 4.14 (H_{m,m'} and H_{h,h'}, dt, *J* = 8.6, 4.0 Hz, 8H), 3.90 (H_{i,i'} and H_{l,l'}, q, *J* = 6.2, 5.3 Hz, 8H), 3.82 (H_{j,j'} and H_{k,k'}, s, 8H).

¹³C-NMR (101 MHz, CDCl₃) δ = 150.09, 148.99, 148.96, 146.34, 133.45, 121.61, 115.45, 114.32, 114.26, 111.27, 105.57, 71.19, 70.00, 69.90, 69.70, 69.47, 69.45, 69.39.

HRMS (ESI+ve) *m/z*: 512.20007 ([M+Na]⁺, C₂₄H₃₁N₃O₈ requires 512.20034)

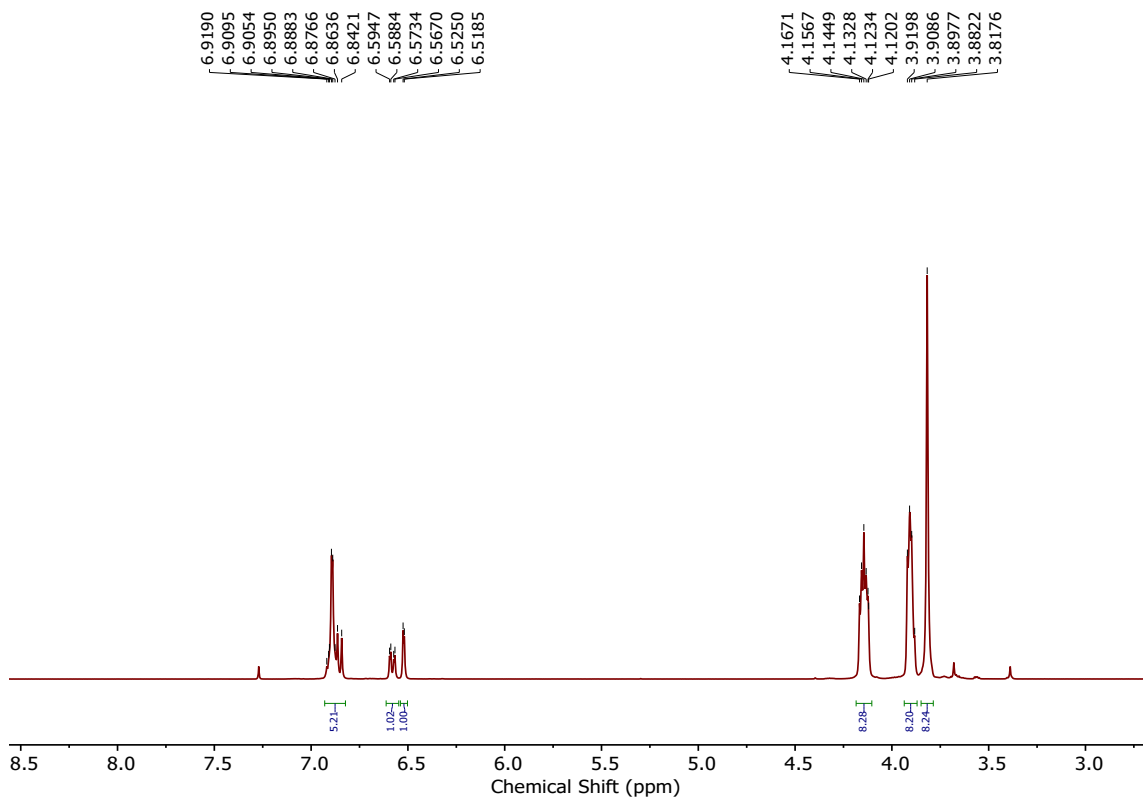


Figure S7 $^1\text{H-NMR}$ spectrum of **5** (400 MHz, CDCl_3)

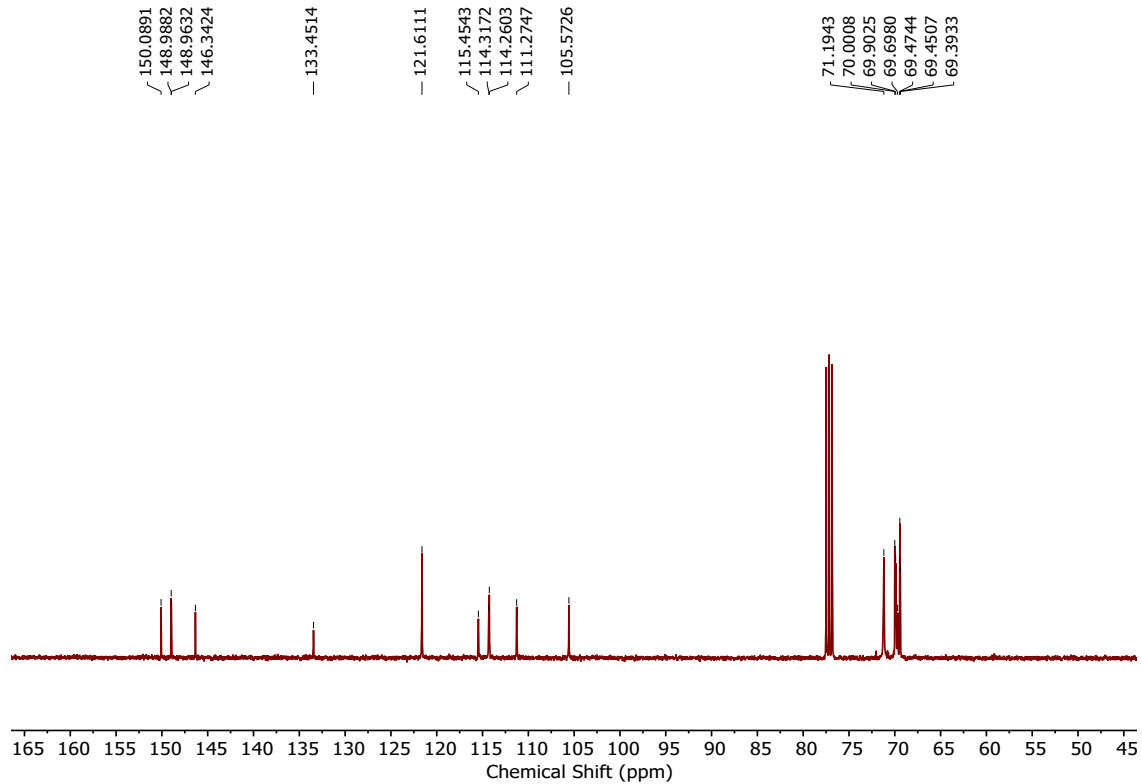
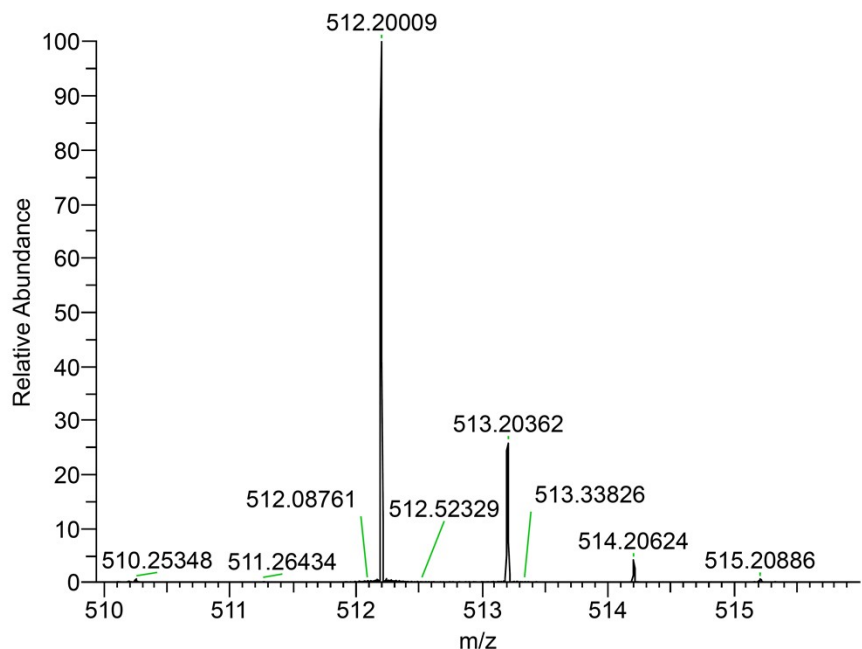
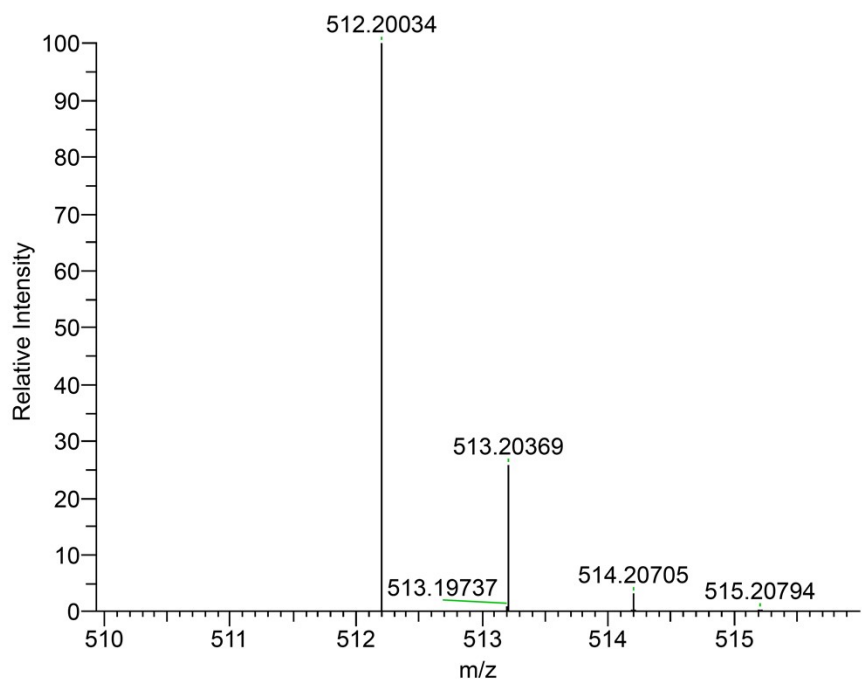


Figure S8 $^{13}\text{C-NMR}$ spectrum of **5** (101 MHz, CDCl_3)



NL: 2.57E7
 ESI61403 #13-27 RT: 0.15-0.31 AV: 8 NL:
 2.68E+007
 T: FTMS {1,1} + p ESI Full lock ms
 [80.00-1600.00]

Measured
Spectrum



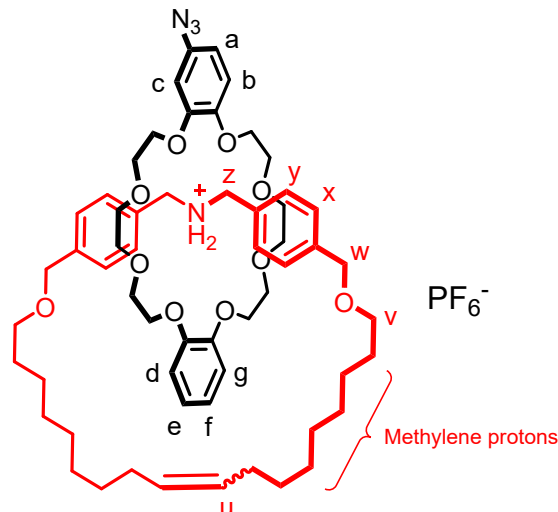
NL: 7.47E5
 C₂₄H₃₁O₈N₃Na1: C₂₄H₃₁O₈N₃Na Chrg
 1 R: 1000000 Res. Pwr. @FWHM

Theoretical
Spectrum

| m/z | Formula | RDB | Delta ppm | Theo. Mass |
|-----------|--|------|-----------|------------|
| 512.20007 | C ₂₄ H ₃₁ O ₈ N ₃ ²³ Na | 10.5 | -0.51 | 512.20034 |

Figure S9 HRMS spectrum of 5

1.4 Synthesis of Azido-catenane ($8 \cdot \text{PF}_6^-$)



A solution of N₃-dibenzo[24]crown-8 (100 mg, 0.204 mmol) in dry and degassed DCM (100 ml) was added the bis-vinyl thread (139 mg, 0.204 mmol). After stirring at room temperature for 30 minutes, the first-generation Grubbs' catalyst (35 mg, 0.043 mmol) was added to a reaction mixture and refluxed at 40°C for 48 hours. The crude mixture was stirred with activated charcoal (1 g) then filtered through Celite® and the organic residue was collected. The mixture was purified by silica gel column chromatography (5% MeOH/DCM) followed by passing through the size exclusion chromatography to obtain the desire product in 16% yield.

¹H-NMR (500 MHz, 1:1 CDCl₃/MeOD) δ = 7.30 (H_y, dd, J = 8.2, 2.0 Hz, 4H), 7.19 (H_x, dd, J = 8.0, 3.1 Hz, 4H), 6.91 – 6.87 (H_d and H_g, m, 2H), 6.86 – 6.75 (H_e, H_f, and H_a m, 3H), 6.60 (H_b, ddd, J = 8.7, 4.0, 2.5 Hz, 1H), 6.44 (H_c, dd, J = 4.1, 2.5 Hz, 1H), 5.33 – 5.22 (H_u, m, 2H), 4.41 (H_w, d, J = 3.6 Hz, 4H), 4.18 – 4.03 (H_{crown}, m, 8H), 3.84 – 3.70 (H_{crown}, m, 8H), 3.54 – 3.35 (H_{crown} and H_v, m, 12H), 1.90 (H_{methylene}, dq, J = 16.8, 6.3 Hz, 4H), 1.58 (H_{methylene}, hept, J = 7.4 Hz, 5H), 1.38 – 1.32 (H_{methylene}, m, 4H), 1.31 – 1.18 (H_{methylene}, m, 18H).

Note

1. H_z proton signals are hidden under the peak of water in MeOD at the chemical shift around 4.6 ppm.
2. H_{crown} represents proton signals of methylene protons derived from the dibenzo[24]crown-8 macrocycle.

¹³C-NMR (126 MHz, 1:1 CDCl₃/MeOD) δ = 149.20, 149.19, 147.98, 147.95, 147.93, 145.68, 145.66, 140.78, 140.75, 134.39, 134.35, 131.52, 130.92, 130.31, 130.03, 129.94, 128.47,

128.39, 122.45, 122.42, 122.40, 114.30, 113.36, 113.34, 113.31, 113.29, 111.83, 111.80,
105.10, 105.07, 72.64, 72.59, 71.29, 71.23, 71.19, 70.92, 70.89, 70.83, 70.77, 70.71, 70.68,
69.30, 69.24, 68.97, 68.93, 68.91, 68.86, 68.81, 52.79, 32.97, 30.39, 30.24, 30.20, 30.16, 30.06,
29.88, 29.71, 29.67, 29.25, 27.71, 26.97, 26.88.

HRMS (ESI+ve) m/z: 995.60962 ([M-PF₆]⁺, C₅₈H₈₃N₄O₁₀ requires 995.61037)

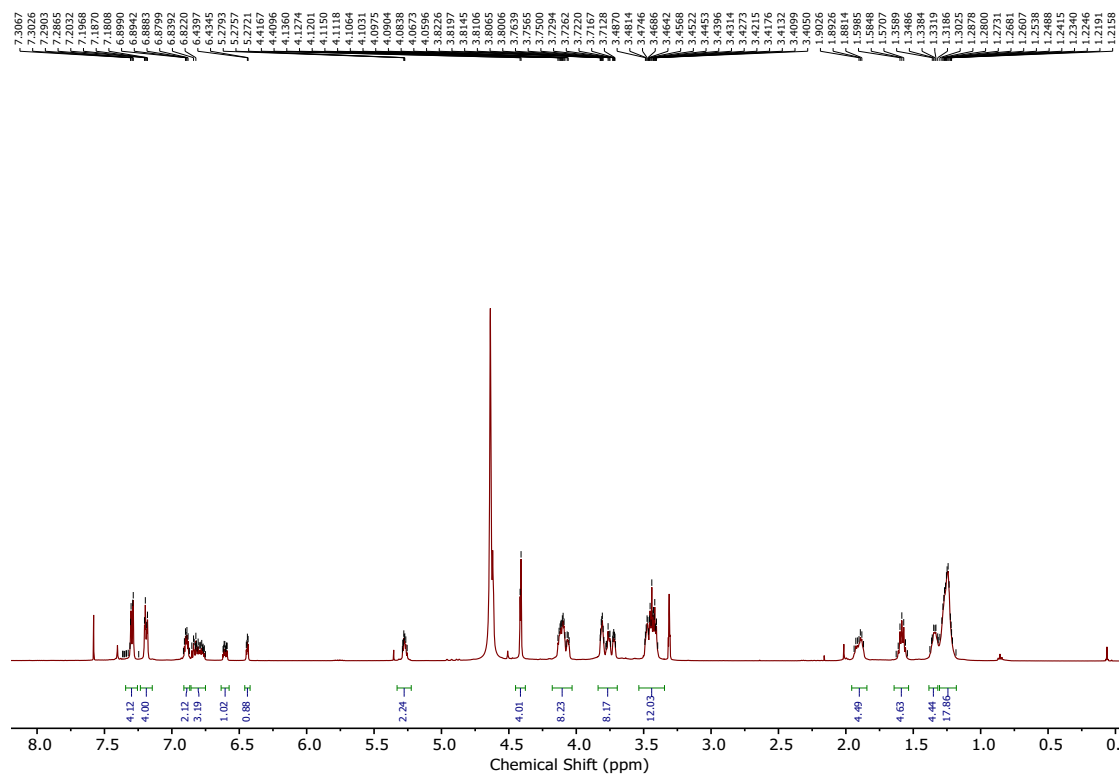


Figure S10 $^1\text{H-NMR}$ spectrum of $(\mathbf{8}\text{-PF}_6)$ (400 MHz, CDCl_3)

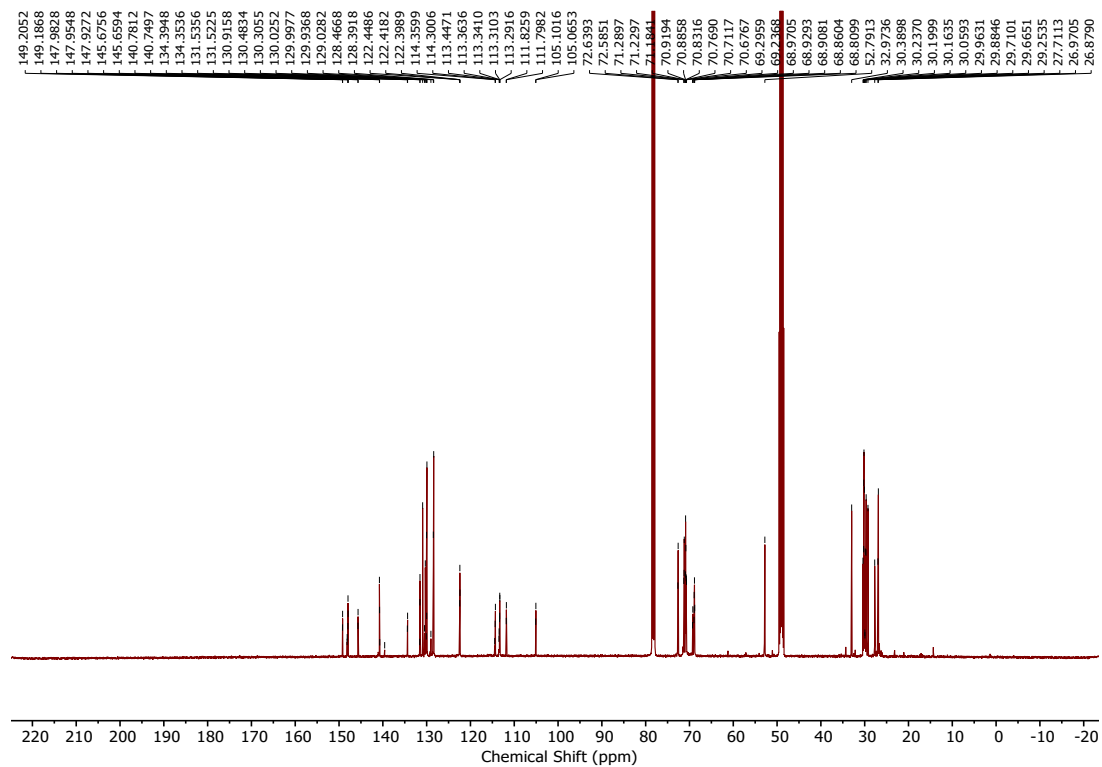


Figure S11 $^{13}\text{C-NMR}$ spectrum of $(\mathbf{8}\text{-PF}_6)$ (126 MHz, CDCl_3)

Further evidence of the interlocked nature of **8**·PF₆ was observed by ¹H-¹H ROESY NMR spectroscopy (**Figure S12**), in which through space interactions between proton resonances of the two macrocycles (H_a and H_c from the dibenzyl ammonium macrocycle with H_{crown ether}) are observed. In addition, strong through space coupling between H_c and methylene protons from the crown ether group indicates that the secondary ammonium group is stabilised in the cavity of dibenzo[24]crown-8.

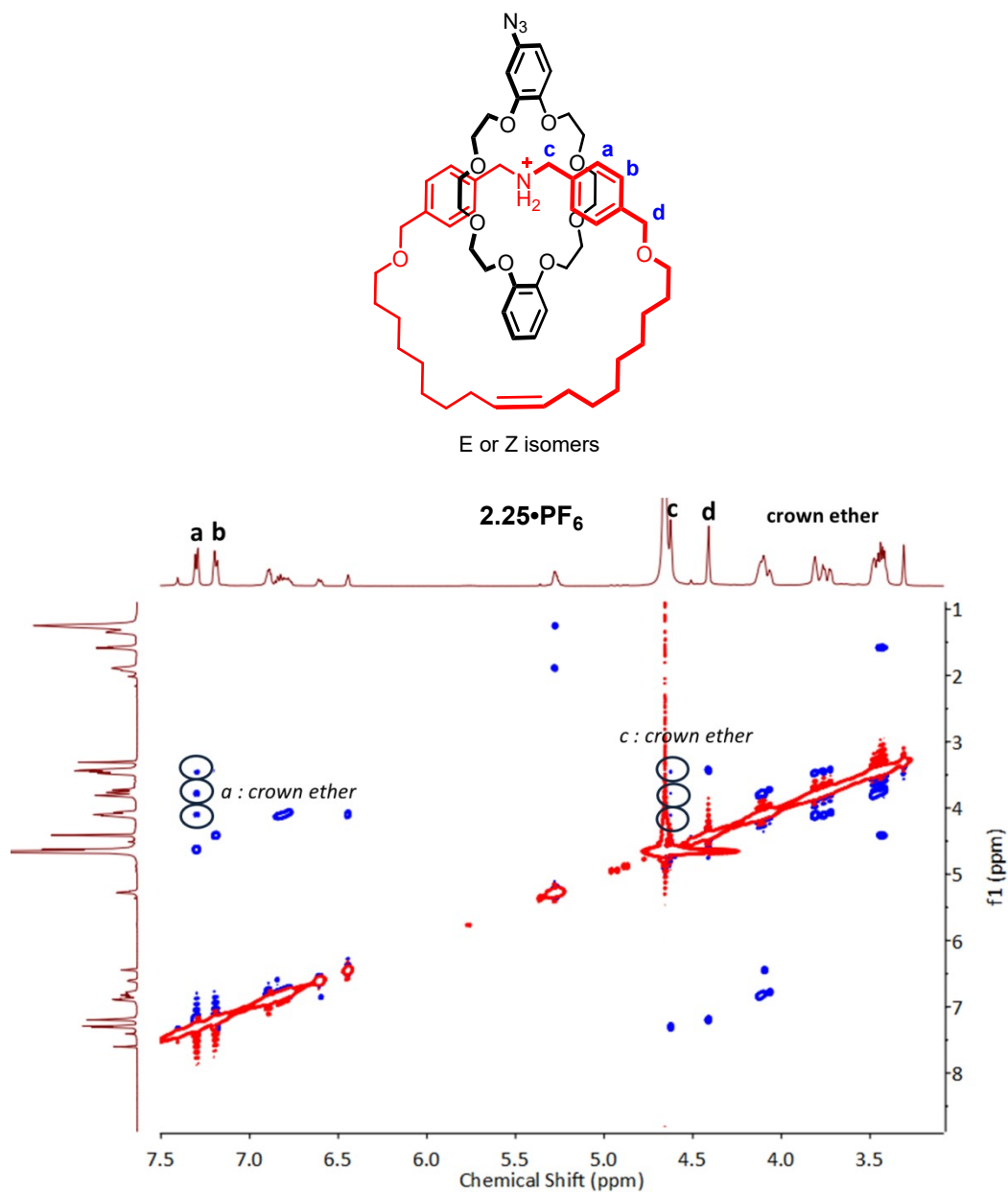
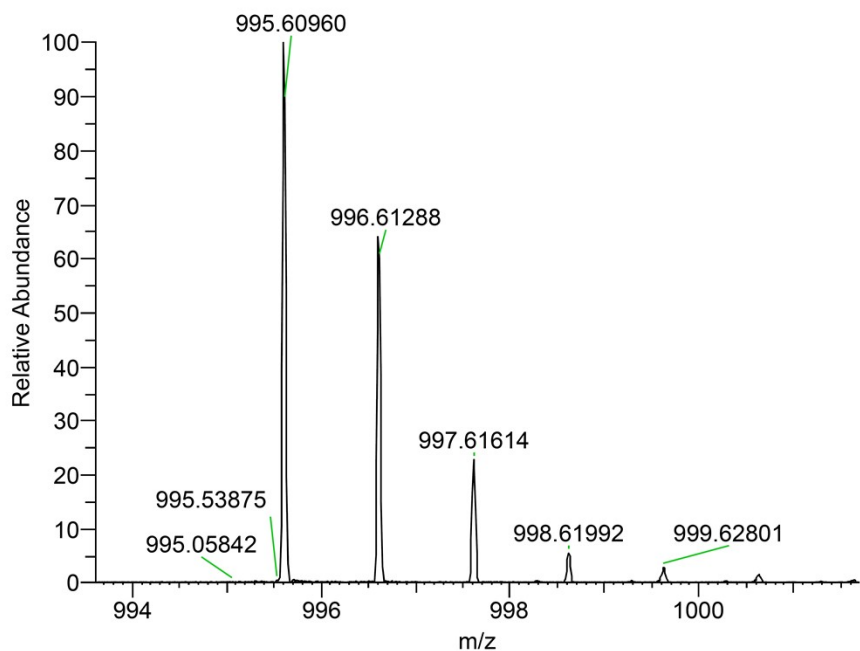
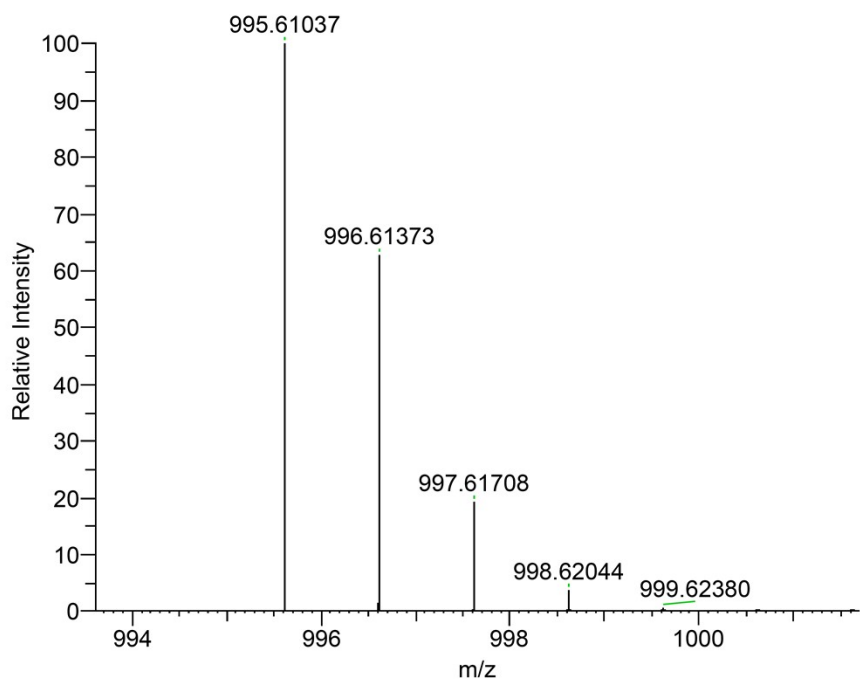


Figure S12 ROESY ¹H-NMR spectrum of the azido-[2]catenane **8**·PF₆ in 1:1 CD₃OD/CDCl₃ (298K, 500 MHz).



NL: 1.83E7
 ESI63708 #15-24 RT: 0.17-0.27 AV: 5 NL:
 1.83E+007
 T: FTMS {1,1} + p ESI Full lock ms
 [80.00-1600.00]

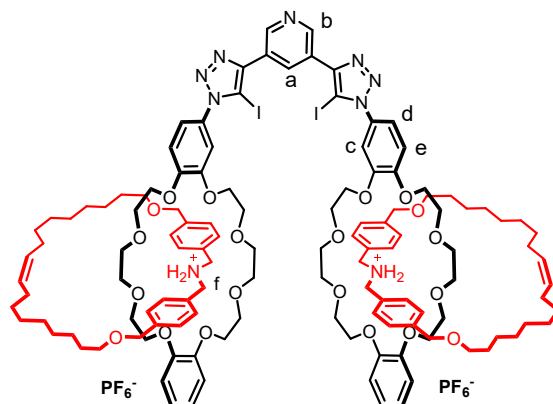


NL: 5.10E5
 C58H83O10N4: C₅₈H₈₃O₁₀N₄ Chrg 1 R:
 1000000 Res. Pwr. @FWHM

| m/z | Formula | RDB | Delta ppm | Theo. Mass |
|-----------|--|------|-----------|------------|
| 995.60962 | C ₅₈ H ₈₃ O ₁₀ N ₄ | 19.5 | -0.76 | 995.61037 |

Figure S13 HRMS spectrum of 8·PF₆

1.5 Synthesis of Ammonium catenane functionalised XB Receptor ($1 \cdot (\text{PF}_6)_2$)



A mixture of $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (2.3 mg, 0.006 mmol) and TBTA (2.4 mg, 0.005 mmol) was stirred in dry and degassed DCM (0.5 ml) at room temperature for 15 minutes. 3,5-Diiodoethynylpyridine (5.7 mg, 0.015 mmol) was added to a solution mixture, followed by azido-catenane $8 \cdot \text{PF}_6$ (36 mg, 0.036 mmol). The reaction was stirred at room temperature for 72 hours prior to purify by preparative plate chromatography in 3% MeOH/DCM to afford a pure product in 85% yield after anion exchange to PF_6^- salt.

$^1\text{H-NMR}$ (500 MHz, 1:1 $\text{CDCl}_3/\text{MeOD}$) δ = 7.37(m, 1H), 7.31 (d, J = 7.8 Hz, 8H), 7.24 – 7.14 (m, 8H), 7.10 (s, 3H), 6.99 (d, J = 7.2 Hz, 4H), 6.87 (q, J = 4.5 Hz, 5H), 6.74 (dd, J = 6.5, 3.7 Hz, 4H), 5.26 (dt, J = 9.7, 4.3 Hz, 4H), 4.68 (d, J = 3.0 Hz, 8H), 4.39 (d, J = 3.5 Hz, 8H), 4.21 (d, J = 22.7 Hz, 8H), 4.05 (q, J = 6.2, 5.7 Hz, 8H), 3.91 (s, 8H), 3.73 (t, J = 7.5 Hz, 8H), 3.61 – 3.51 (m, 8H), 3.51 – 3.43 (m, 8H), 3.40 (dt, J = 11.4, 6.1 Hz, 8H), 1.89 (dq, J = 16.8, 6.2 Hz, 8H), 1.55 (p, J = 6.5 Hz, 8H), 1.37 – 1.10 (m, 40H).

$^{13}\text{C-NMR}$ (126 MHz, 1:1 $\text{CDCl}_3/\text{MeOD}$) δ 149.76, 148.46, 147.62, 140.74, 131.36, 130.84, 130.67, 130.24, 129.84, 129.75, 128.46, 128.39, 122.29, 120.30, 113.01, 111.75, 72.55, 72.49, 71.32, 71.09, 70.86, 70.81, 70.67, 69.21, 68.62, 52.73, 32.90, 30.32, 30.16, 30.13, 30.09, 29.99, 29.87, 29.81, 29.64, 29.59, 29.19, 27.65, 26.90, 26.81.

HRMS (ESI+ve) m/z : 1185.02466 ($[\text{M}-2\text{PF}_6]^{2+}$, $\text{C}_{125}\text{H}_{169}\text{N}_9\text{O}_{20}\text{I}_2$ requires 1185.02811)

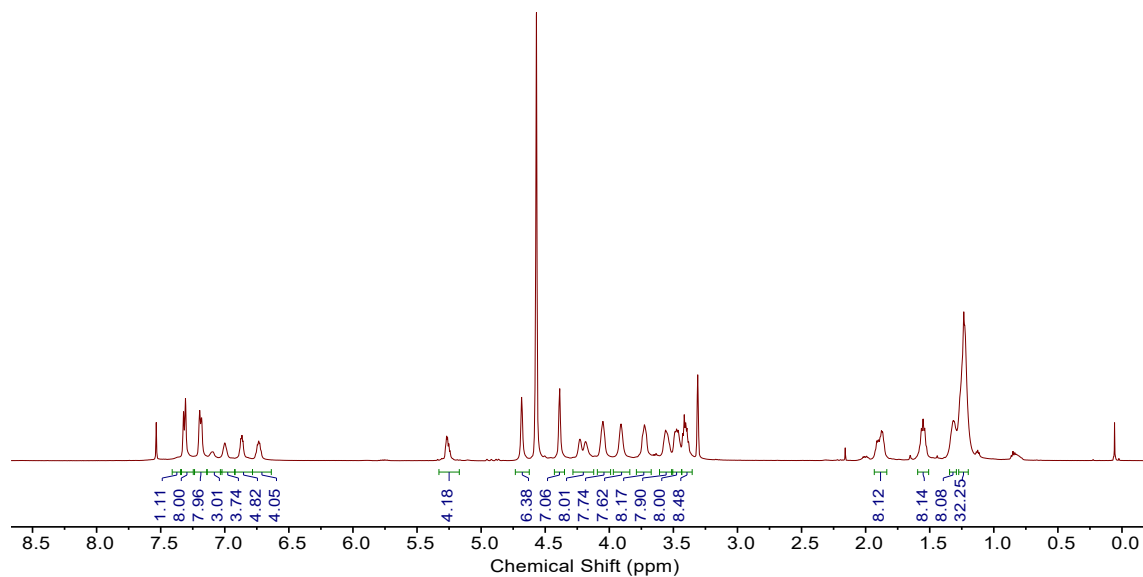


Figure S14 $^1\text{H-NMR}$ spectrum of $1\cdot(\text{PF}_6)_2$ (500 MHz, 1:1 $\text{CDCl}_3/\text{MeOD}$)

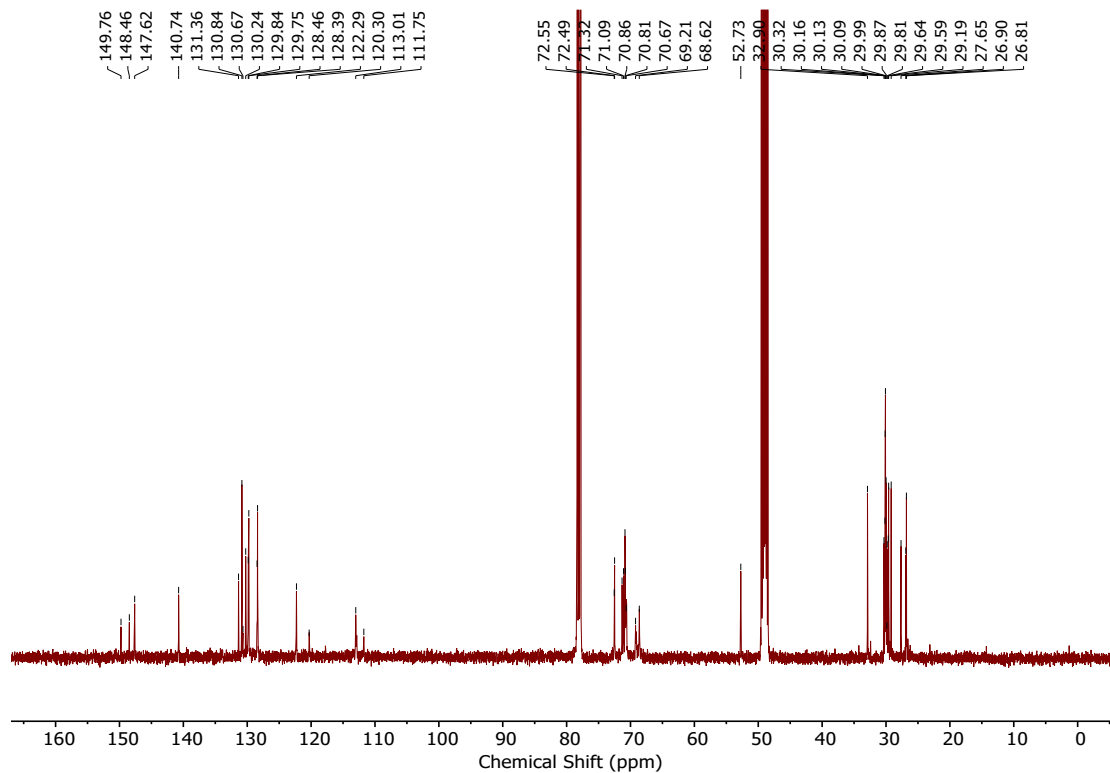
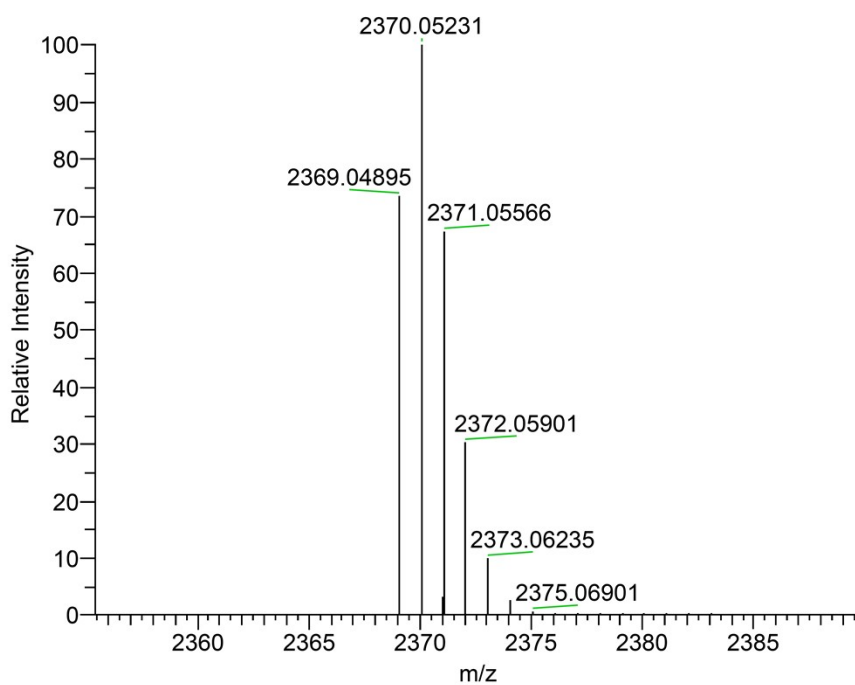
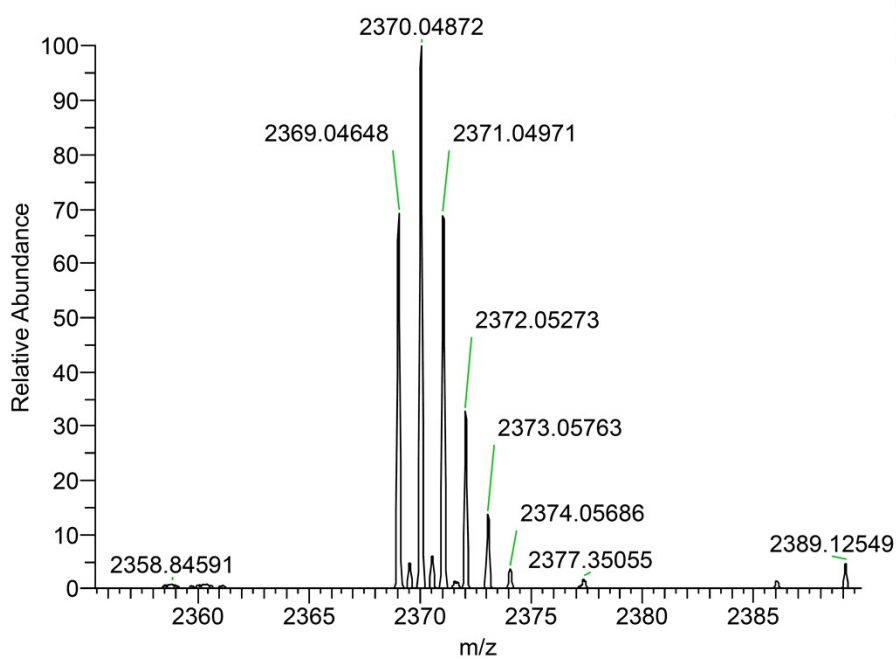


Figure S15 $^{13}\text{C-NMR}$ spectrum of $1\cdot(\text{PF}_6)_2$ (101 MHz, 1:1 $\text{CDCl}_3/\text{MeOD}$)



| m/z | Formula | RDB | Delta ppm | Theo. Mass |
|------------|--|------|-----------|------------|
| 2369.04639 | C ₁₂₅ H ₁₆₈ O ₂₀ N ₉ ¹²⁷ I ₂ | 45.5 | -1.08 | 2369.04895 |

Figure S16 HRMS spectrum of 1·(PF₆)₂

2. Pseudorotaxane Complexation of 5 with 6·PF₆ in d₂-dichloromethane

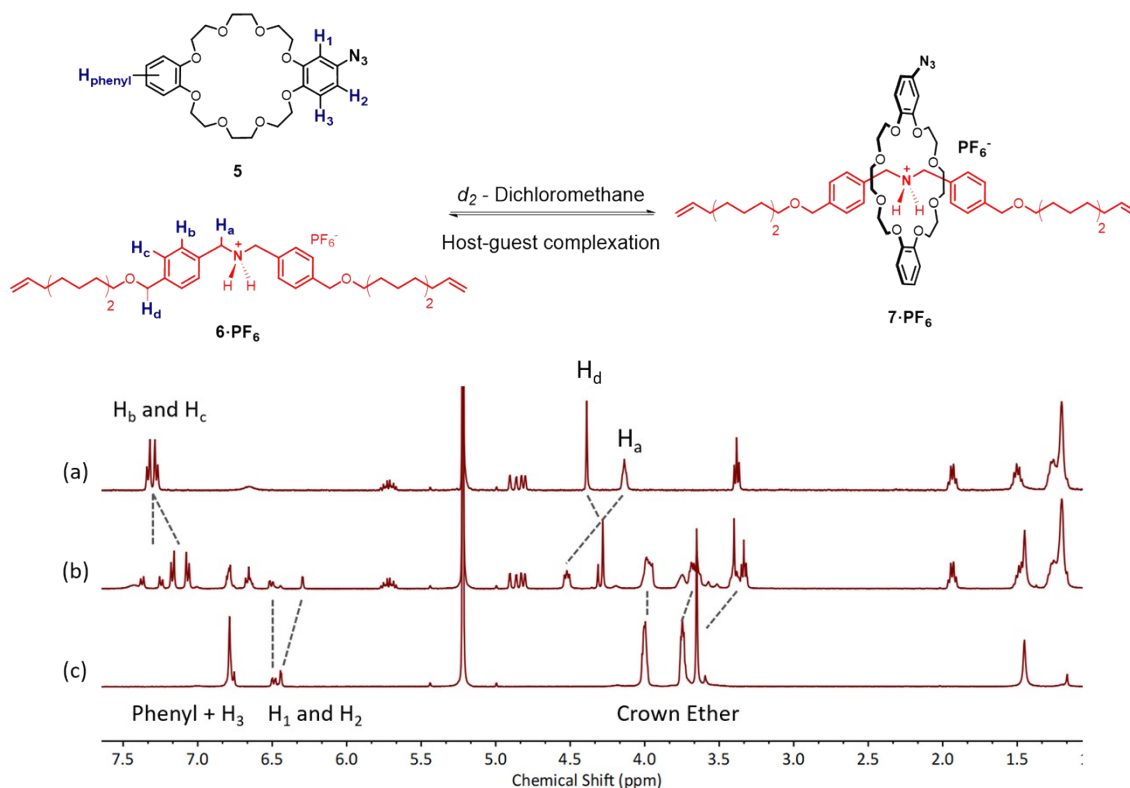


Figure S17 Comparative truncated ¹H-NMR spectra of (a) a thread **6**·PF₆, (b) an equimolar mixture of **6**·PF₆ and **5**, and (c) a macrocycle **5** in d₂-dichloromethane at room temperature.

3. Anion binding in organic and aqueous-organic mixture

Spectra for ¹H NMR titrations were recorded at 293 K on a Varian Unity Plus 500 spectrometer with ¹H operating at 500 MHz. Initial sample volumes were 0.50 mL and concentrations were 2.0 mM of host in all cases. Anion solution (100 mM) as the tetrabutylammonium salts 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 of anion. In all cases where association constants were calculated, bound and unbound species were found to be in fast exchange on the NMR timescale. In all cases where association constants were calculated, bound and unbound species were found to be in fast exchange on the NMR timescale. Association constants were obtained by analysis of the resulting binding isotherm data monitoring aryl proton a using WinEQNMR2 and Bindfit v.05.⁵⁻⁷

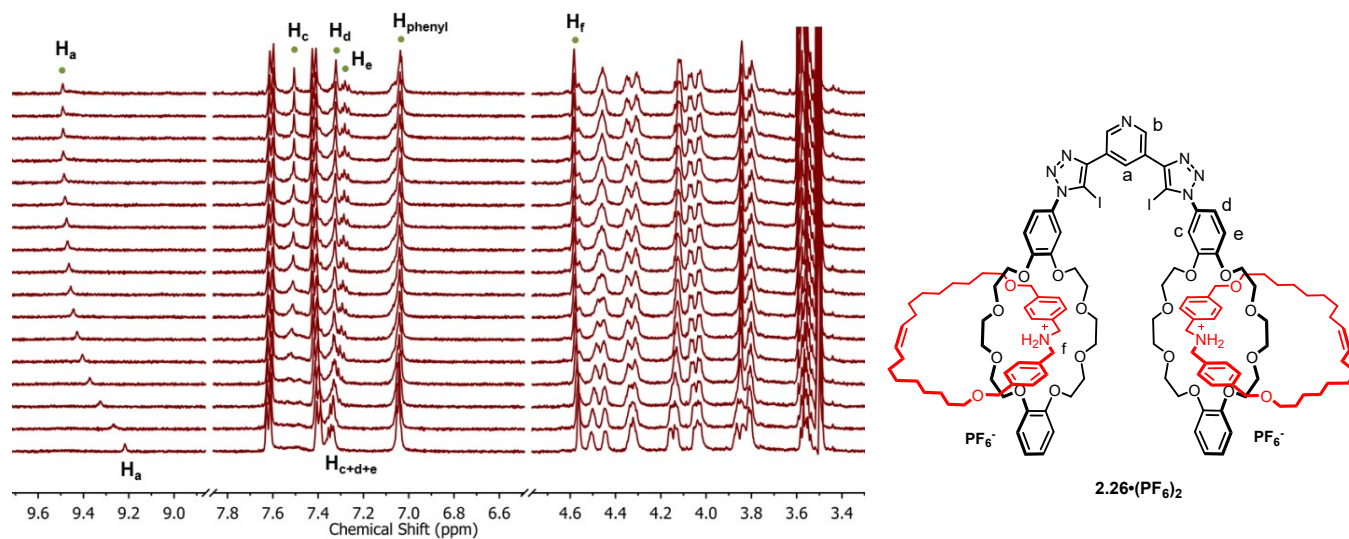


Figure S18 Truncated $^1\text{H-NMR}$ spectra of $1 \cdot (\text{PF}_6)_2$ in $5\% \text{D}_2\text{O}/\text{d}_6\text{-acetone}$ upon addition of TBAI (T=298K, 500 MHz).

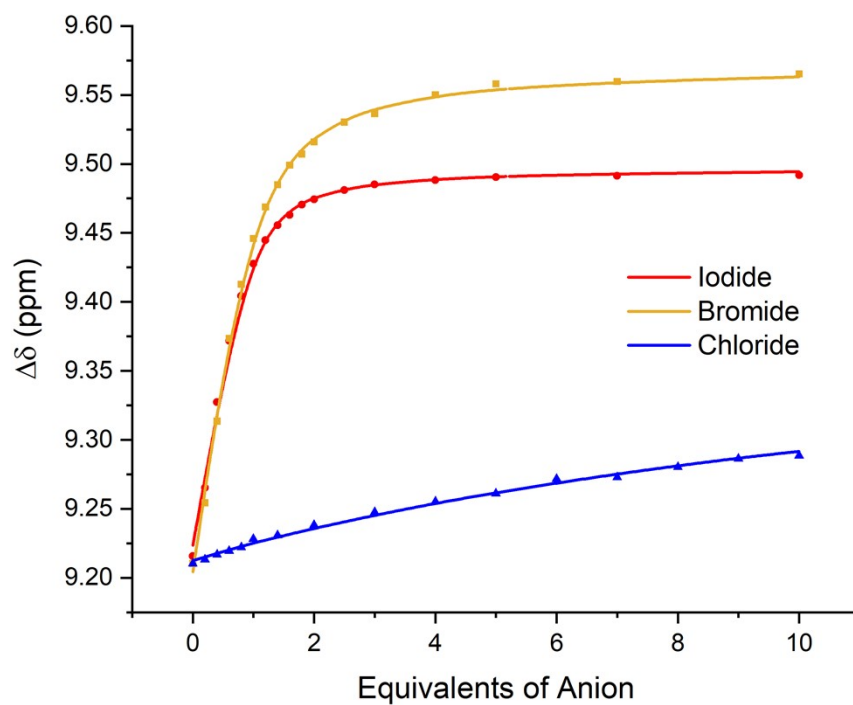


Figure S19 Anion binding isotherm of $1 \cdot (\text{PF}_6)_2$, [host] = 2mM and [guest] = 100 mM ($5\% \text{D}_2\text{O}/\text{d}_6\text{-Acetone}$, 500MHz, 298K)

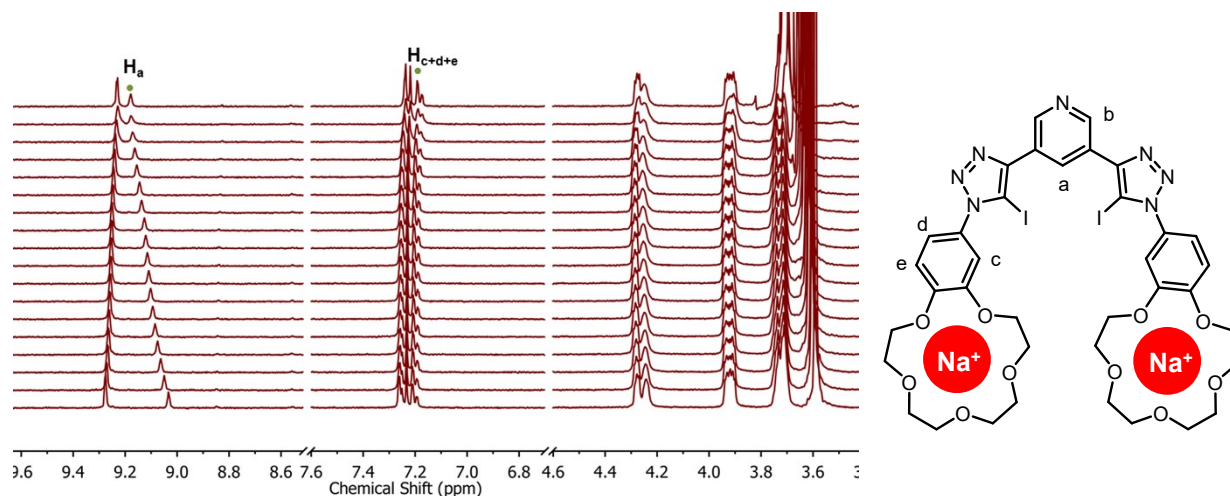


Figure S20 Truncated ^1H -NMR spectra of $\text{XB9}\cdot 2\text{NaPF}_6$ in 5% $\text{D}_2\text{O}/\text{d}_6$ -acetone upon addition of TBAI (T=298K, 500 MHz), counter-anions in the structure are omitted for clarity.

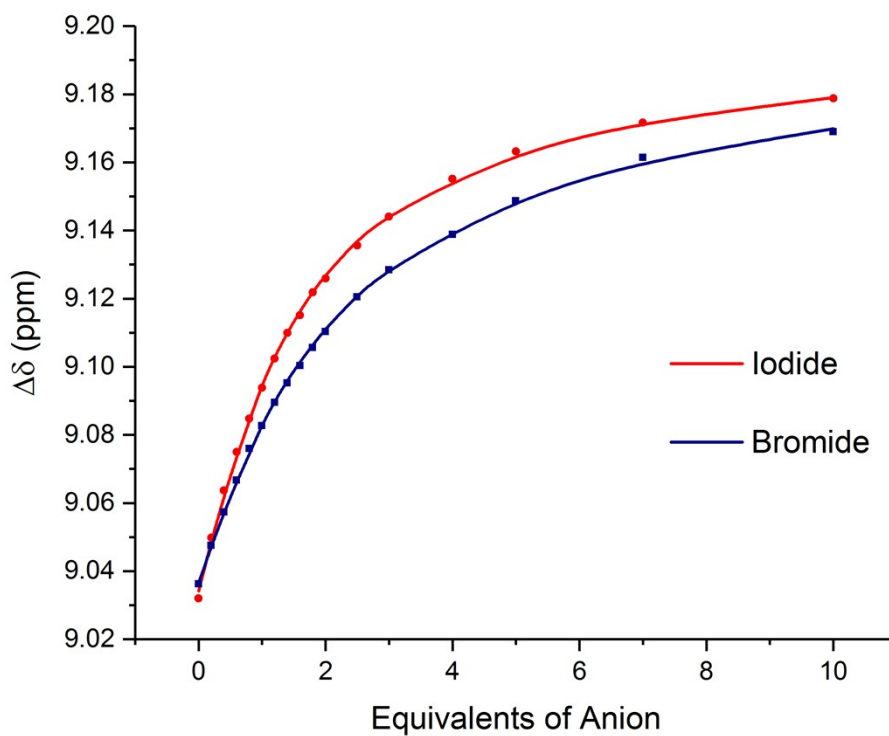


Figure S21 Anion binding isotherm of $\text{XB9}\cdot 2\text{NaPF}_6$, [host] = 2mM and [guest] = 100 mM (5% $\text{D}_2\text{O}/\text{d}_6$ -Acetone, 500MHz, 298K)

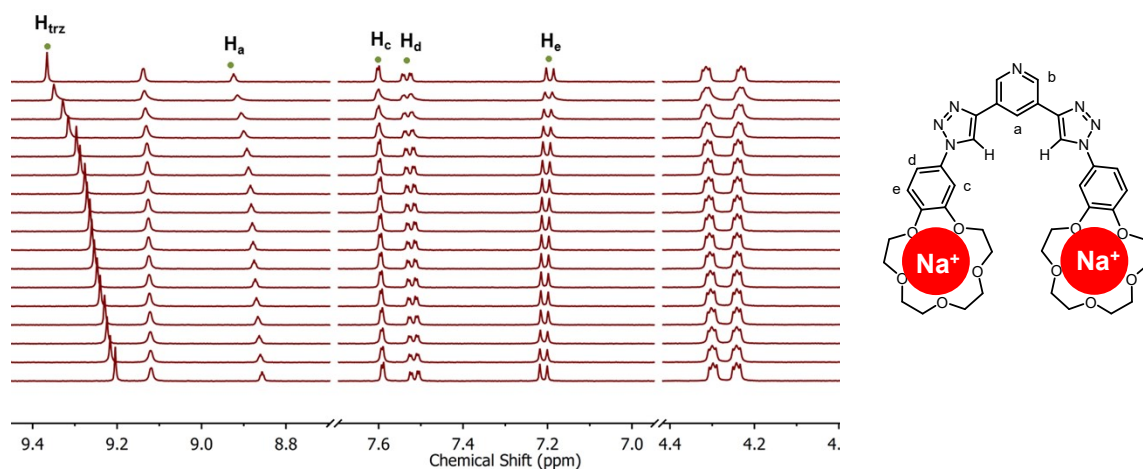


Figure S22 Truncated ^1H -NMR spectra of $\text{HB10}\cdot 2\text{NaPF}_6$ in 5% $\text{D}_2\text{O}/\text{d}_6$ -acetone upon addition of TBAI (T=298K, 500 MHz), counter-anions in the structure are omitted for clarity.

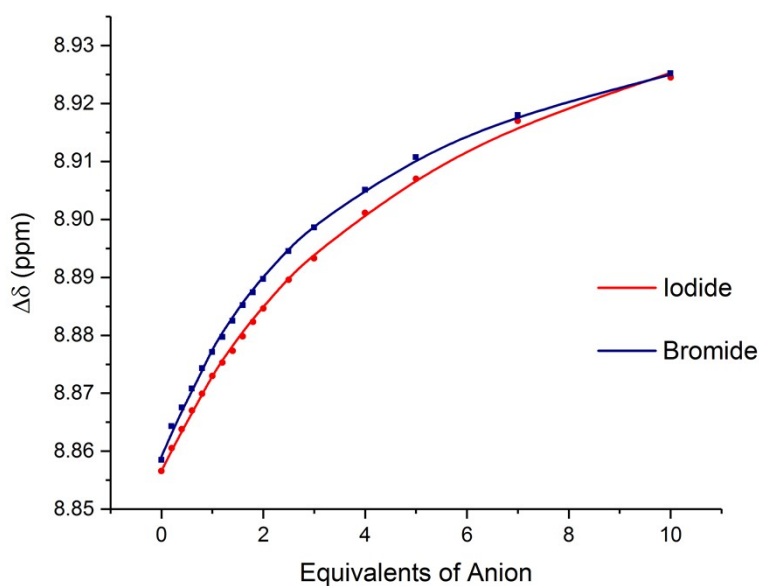
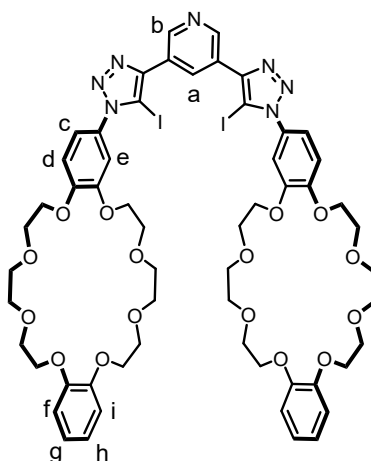


Figure S23 Anion binding isotherm of $\text{HB10}\cdot 2\text{NaPF}_6$, [host] = 2mM and [guest] = 100 mM (5% $\text{D}_2\text{O}/\text{d}_6$ -Acetone, 500MHz, 298K)

4. Comparative anion binding studies of XB11

4.1 Synthesis of XB11



A mixture of $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (15 mg, 0.04 mmol) and TBTA (7 mg, 0.013 mmol) was stirred in dry and degassed THF (1.0 ml) at room temperature for 15 minutes. 3,5-Diiodoethynylpyridine (50.3 mg, 0.013 mmol) was added to a solution mixture, followed by an azide **5** (143 mg, 0.29 mmol). The reaction was stirred at room temperature for 48 hours prior to purify by diluting with DCM, stirring with EDTA solution to remove copper residues, and washing the organic solution with water twice. After concentrating the solution, MeOH was added to crash out the product. The solid residue was collected by a vacuum filtration and washed with cold MeOH. The product was obtained as an off-white solid in 44 %yield.

$^1\text{H-NMR}$ (500 MHz, CDCl_3) δ = 9.34 (H_b , d, J = 2.1 Hz, 2H), 8.98 (H_a , t, J = 2.1 Hz, 1H), 7.17 – 6.96 (H_c , H_d , and H_e , 6H), 6.96 – 6.85 (H_f , H_g , H_h , and H_i , 8H), 4.31 – 4.13 (m, 8H), 4.04 – 3.89 (m, 8H), 3.85 (m, 16H).

$^{13}\text{C-NMR}$ (126 MHz, CDCl_3) δ = 150.52, 149.19, 149.00, 148.50, 147.42, 126.39, 121.67, 119.67, 114.23, 71.44, 70.03, 69.79, 69.48 ppm.

HRMS (ESI +ve) m/z : 1380.2457 ($[\text{M}+\text{Na}]^+$, $\text{C}_{57}\text{H}_{65}\text{N}_7\text{O}_{16}\text{I}_2\text{Na}^+$ requires 1380.2469).

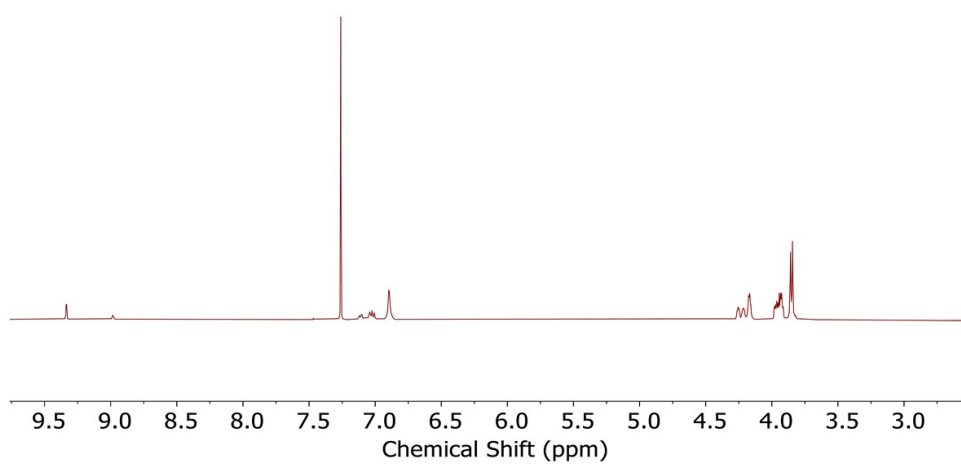


Figure S24 ¹H-NMR spectrum of **XB11** (500 MHz, CDCl₃)

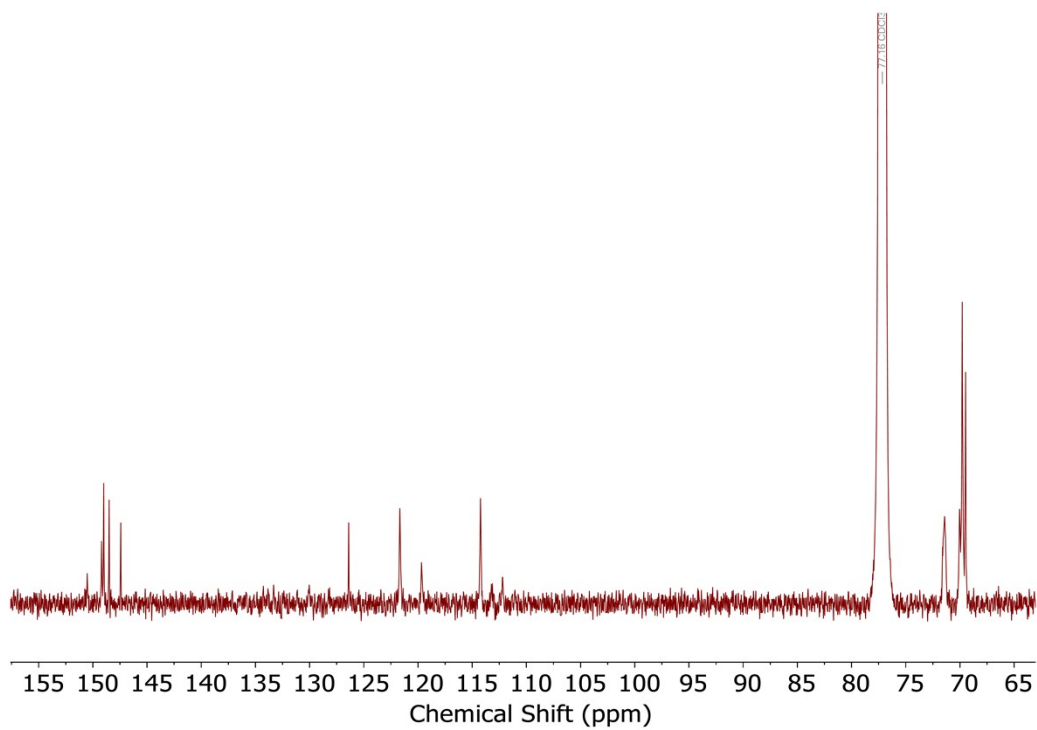
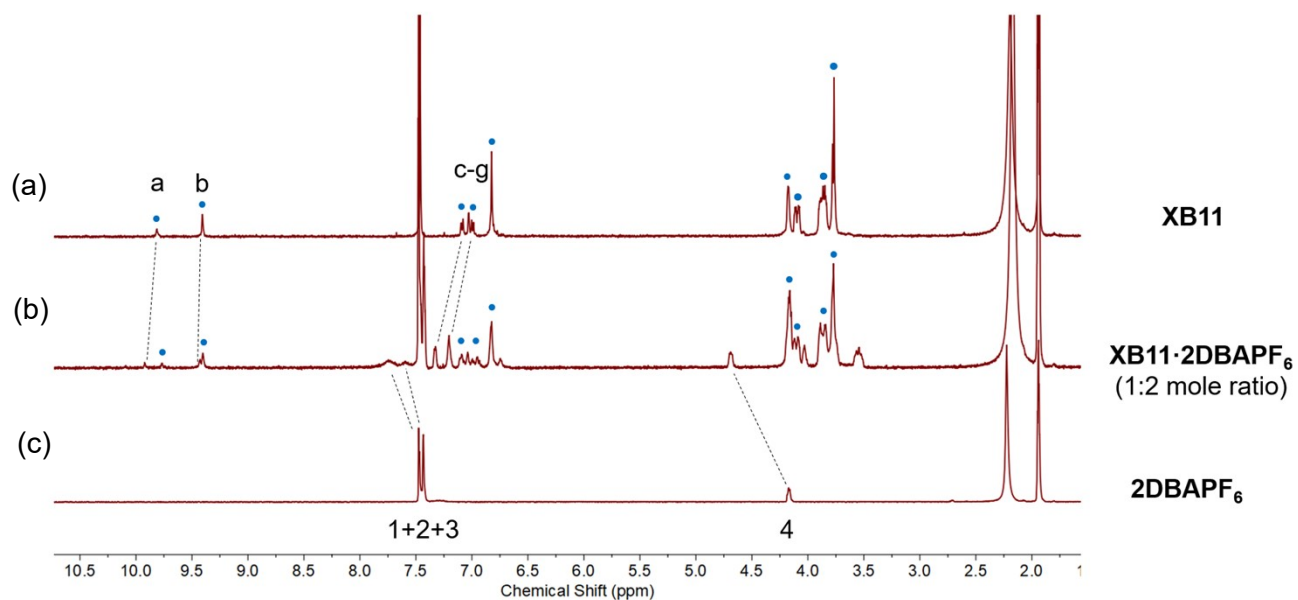
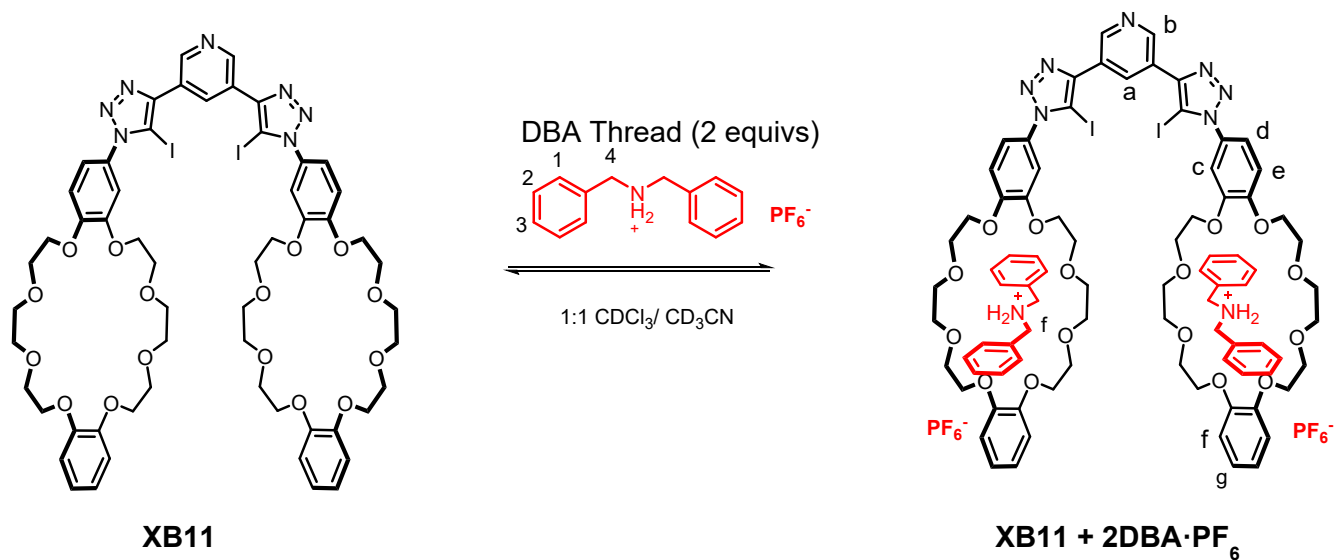


Figure S25 ¹³C-NMR spectrum of **XB11** (126 MHz, CDCl₃)

4.2 Anion Binding Studies of XB11 in the presence of DBAPF₆ (2 equivalents)



• Uncomplex **XB11**

Figure S26 Stacking of truncated ¹H-NMR spectra of (a) **XB11**, (b) **XB11·2DBAPF₆** and (c) **2DBAPF₆** in 1:1 CDCl₃:CD₃CN, (400 MHz, 298 K)

4.3 Anion Binding Studies of XB11

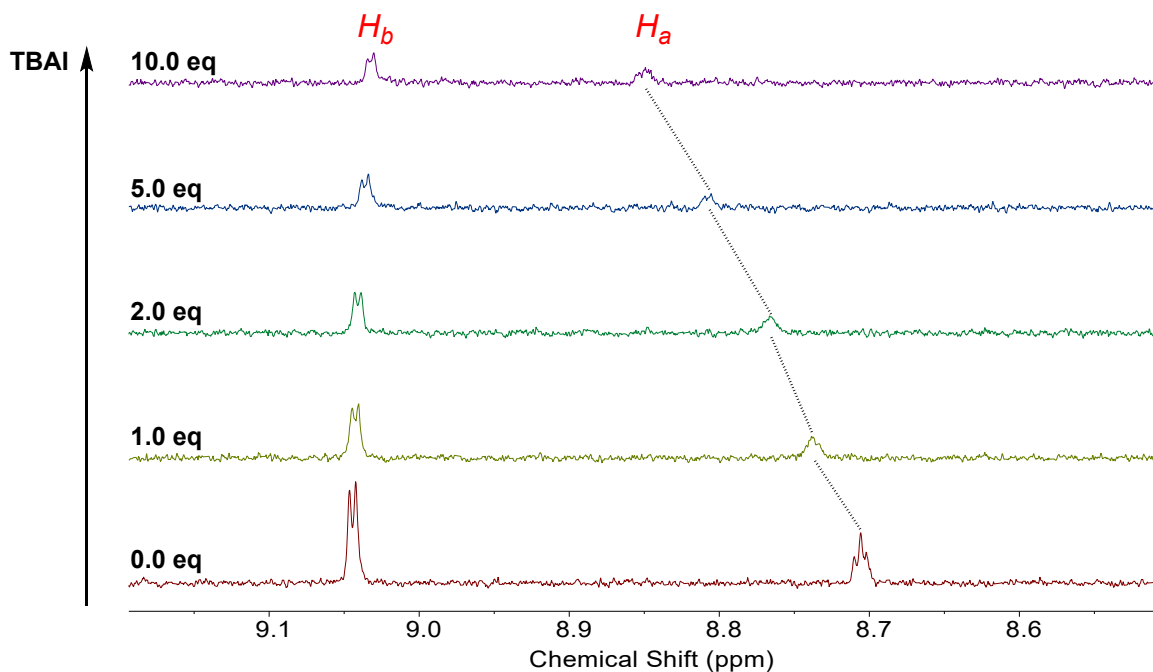
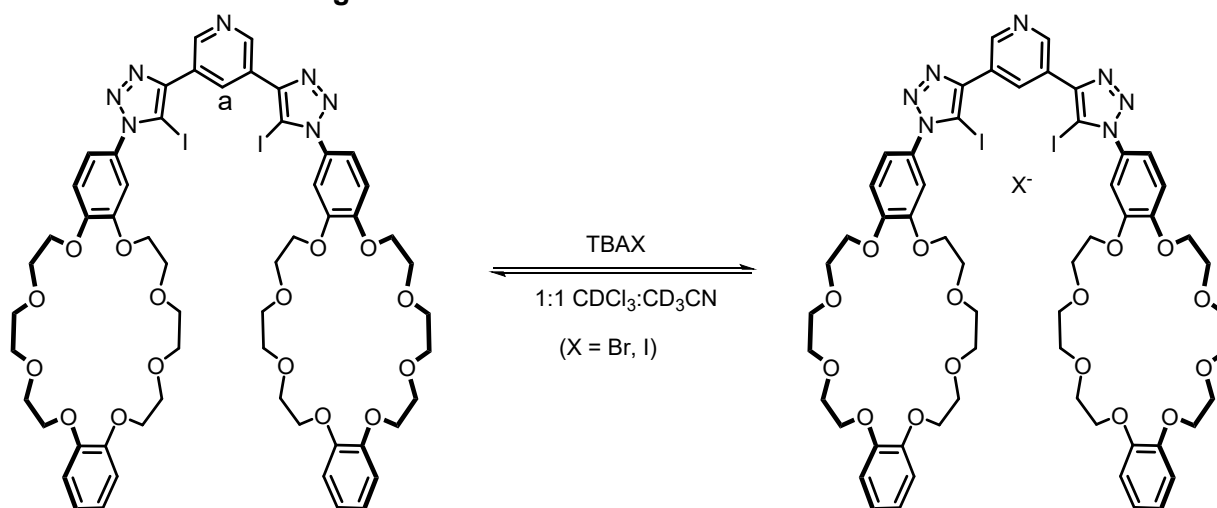


Figure S27 Truncated $^1\text{H-NMR}$ titration spectra of **XB11** upon addition of 0-10 equivalents of TBAI (500 MHz, 298 K, 1:1 CDCl_3 : CD_3CN , $[\text{XB11}] = 1.0 \text{ mM}$).

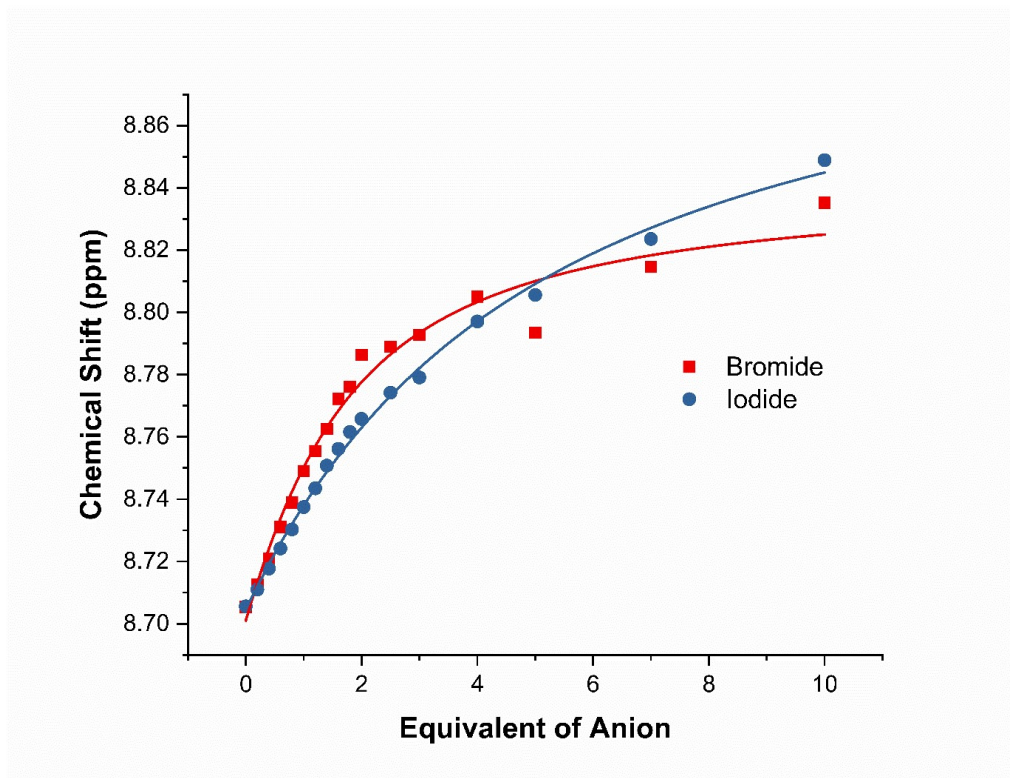


Figure S28 Changes in chemical shift of the internal pyridine proton b of **XB11** upon addition of halide anions as their TBA salts (1:1 $\text{CDCl}_3:\text{CD}_3\text{CN}$, 298K). Experimental titration data (squares, circles), and fitted binding isotherms (solid lines) by *Bindfit*.

4.4 Anion Binding Studies of XB11 complexed with DBAPF₆

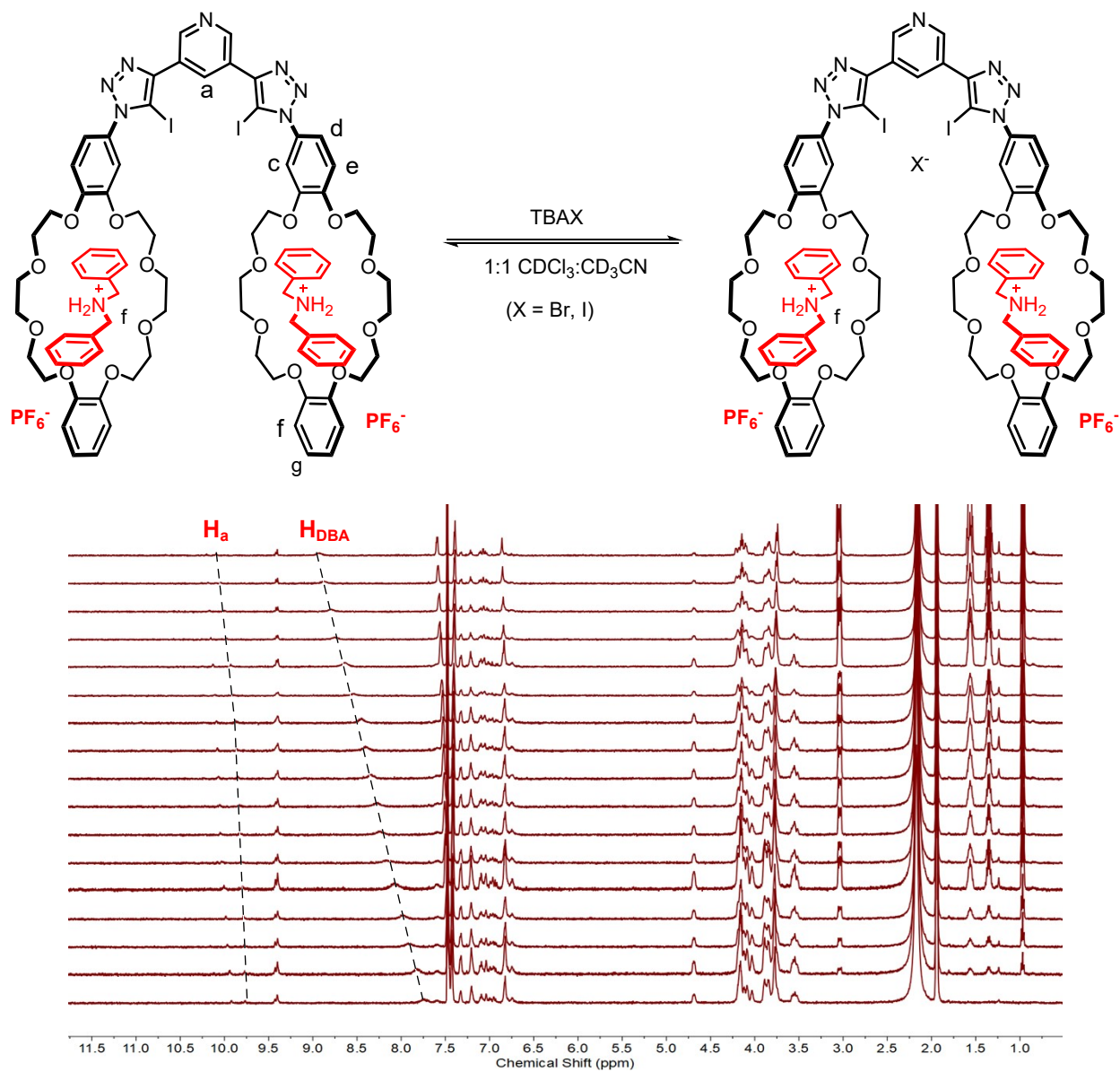


Figure S29 Truncated ¹H-NMR titration spectra of **XB11·2DBAPF₆** upon addition of 0-10 equivalents of TBABr (500 MHz, 298 K, 1:1 CDCl₃:CD₃CN, [XB11 + 2DBA·PF₆] = 1.0 mM).

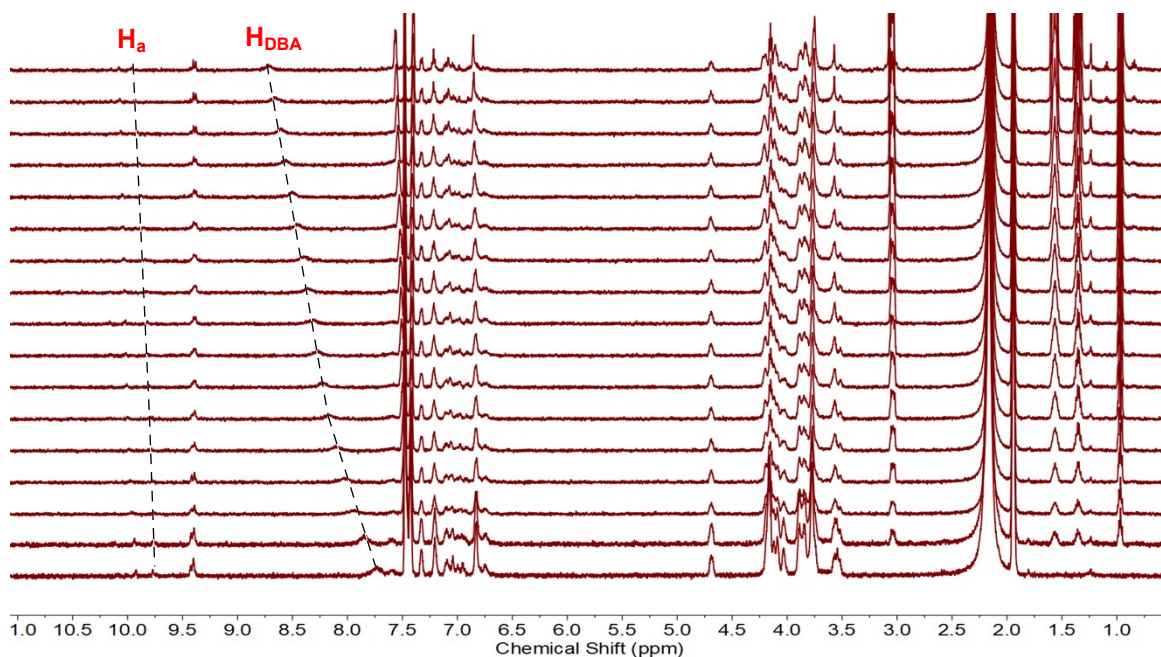


Figure S30 Truncated ^1H -NMR titration spectra of $\text{XB11}\cdot 2\text{DBAPF}_6$ upon addition of 0-10 equivalents of TBAI (500 MHz, 298 K, 1:1 $\text{CDCl}_3:\text{CD}_3\text{CN}$, $[\text{XB11} + 2\text{DBA}\cdot\text{PF}_6] = 1.0 \text{ mM}$).

Table S1 Anion association constants of XB11 and XB11 complexed with 2 equivalents of $\text{DBA}\cdot\text{PF}_6$ ($\text{XB11}\cdot 2\text{DBAPF}_6$) in 1:1 $\text{CDCl}_3/\text{CD}_3\text{CN}$, 298 K.^{a,b}

| Anion | Association Constant (K_a , M^{-1}) ^a | |
|---------------|---|------------------------------------|
| | XB11 | $\text{XB11}\cdot 2\text{DBAPF}_6$ |
| Br^- | 3640 ^b | 779 ^c |
| I^- | 853 | 1752 ^d |

^a K_a values obtained by fitting the binding isotherm (monitored chemical shift changes of H_a) to a host-guest 1:1 stoichiometric binding model using Bindfit v.05 error ($\pm 10\%$); each anion added as its tetrabutylammonium (TBA) salt. ^b Bindfit v.05 error ($\pm 15\%$); Quantitative binding data could not be determined from Bindfit analysis of the TBACl titration isotherms.

^c Binding data can be access via <http://app.supramolecular.org/bindfit/view/d5be64e8-5869-422f-9190-dac8e466bd86>

^d Binding data can be access via <http://app.supramolecular.org/bindfit/view/0e0e364b-4641-4632-b7f0-08d640115bea>

5. References

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