

**Responsive supramolecular polymer formed by
orthogonal metal-coordination and cryptand-based
host–guest interaction**

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Electronic Supplementary Information (17 pages)

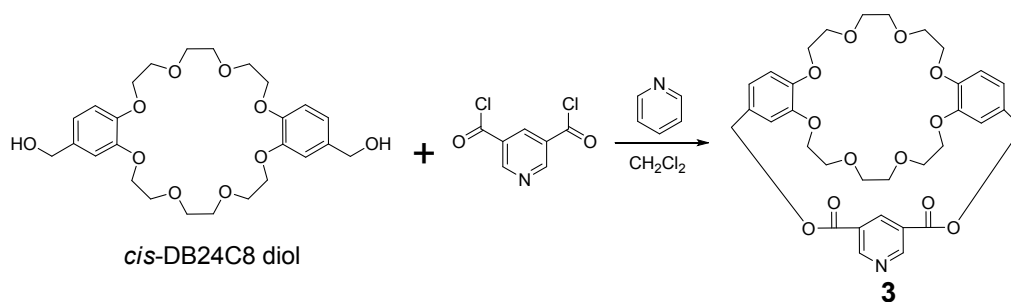
1.	<i>Materials and Methods</i>	S2
2.	<i>Synthesis of 3</i>	S3
3.	<i>Job plot of 3⇌2 based on UV-vis spectroscopy data in CH₂Cl₂/CH₃CN (1:1, v/v)</i>	S6
4.	<i>ESIMS of host 3 with guest 2 in CH₂Cl₂/CH₃CN (1:1, v/v)</i>	S7
5.	<i>Association constant of complex 3⇌2 in CH₂Cl₂/CH₃CN (1:1, v/v)</i>	S8
6.	<i>Cation-responsive complexation between 3 and 2</i>	S10
7.	<i>¹H NMR spectra of 4 and 5</i>	S11
8.	<i>Synthesis of bis-cryptand 1</i>	S12
9.	<i>Comparison of Partial ¹H NMR spectra of 1 and 3</i>	S14
10.	<i>Partial ¹H NMR spectra of 3₂⇌4</i>	S15
11.	<i>LRESI mass spectrum of 3₂⇌4</i>	S16
12.	<i>K⁺ cation responsive NMR of LSP</i>	S17
	<i>References</i>	S17

1. Materials and Methods

Cis-DB24C8 diol^{S1}, **4**^{S2}, and **5**^{S3} were synthesized according to literature procedures. All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. ¹H and ¹³C NMR chemical shifts are reported relative to residual solvent signals, and ³¹P{¹H} NMR chemical shifts are referenced to an external unlocked sample of 85% H₃PO₄ (δ 0.0). The two-dimensional diffusion-ordered (2D DOSY) NMR spectra were recorded on a Bruker DRX500 spectrometer. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system or a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH, Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. UV-vis spectroscopy was performed on a Shimadzu UV-2550 instrument at room temperature. The melting point was collected on a SHPSIC WRS-2 automatic melting point apparatus. Dynamic light scattering (DLS) was carried out on a Malvern Nanosizer S instrument at room temperature. Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument.

2. Synthesis of **3**

Scheme S1. Synthesis of cryptand **3**



To a solution of carbonyl chloride (1.22 g, 6.00 mmol) and pyridine (5.00 mL) in CH_2Cl_2 (1.50 L) was added *cis*-DB24C8 diol (2.03 g, 4.00 mmol) in CH_2Cl_2 (50.0 mL) *via* a syringe pump at 0.750 mL/h. After addition, the reaction mixture was stirred at room temperature for 4 days. After the solvent was evaporated by rotary evaporation, the residue was purified by flash column chromatography (dichloromethane/ethyl acetate, 6:1 v/v) to afford **3** as a white solid (1.10 g, 43%). Mp 180.5–181.6 °C. The ^1H NMR spectrum of **3** is shown in Figure S1. ^1H NMR (400 MHz, chloroform-*d*, 293 K) δ (ppm): 9.45 (s, 2H), 8.53 (s, 1H), 6.93 (d, 4H, $J = 4.0$ Hz), 6.82 (d, 2H, $J = 8.0$ Hz), 5.22 (s, 4H), 4.17 (m, 4H), 4.04 (m, 4H), 3.92 (m, 8H), and 3.79 (m, 8H). The ^{13}C NMR spectrum of **3** is shown in Figure S2. ^{13}C NMR (125 MHz, chloroform-*d*, 293 K) δ (ppm): 68.24, 68.86, 69.41, 69.47, 69.55, 70.65, 71.12, 112.48, 115.38, 122.61, 125.61, 127.01, 136.76, 148.63, 149.57, 154.91, and 164.45. LRESIMS is shown in Figure S3: m/z 662.5 (100%) $[\text{M} + \text{Na}]^+$. HRESIMS: m/z calcd for $[\text{M}]^+ \text{C}_{33}\text{H}_{37}\text{NO}_{12}$ 639.2316, found 639.2317, error 0.2 ppm.

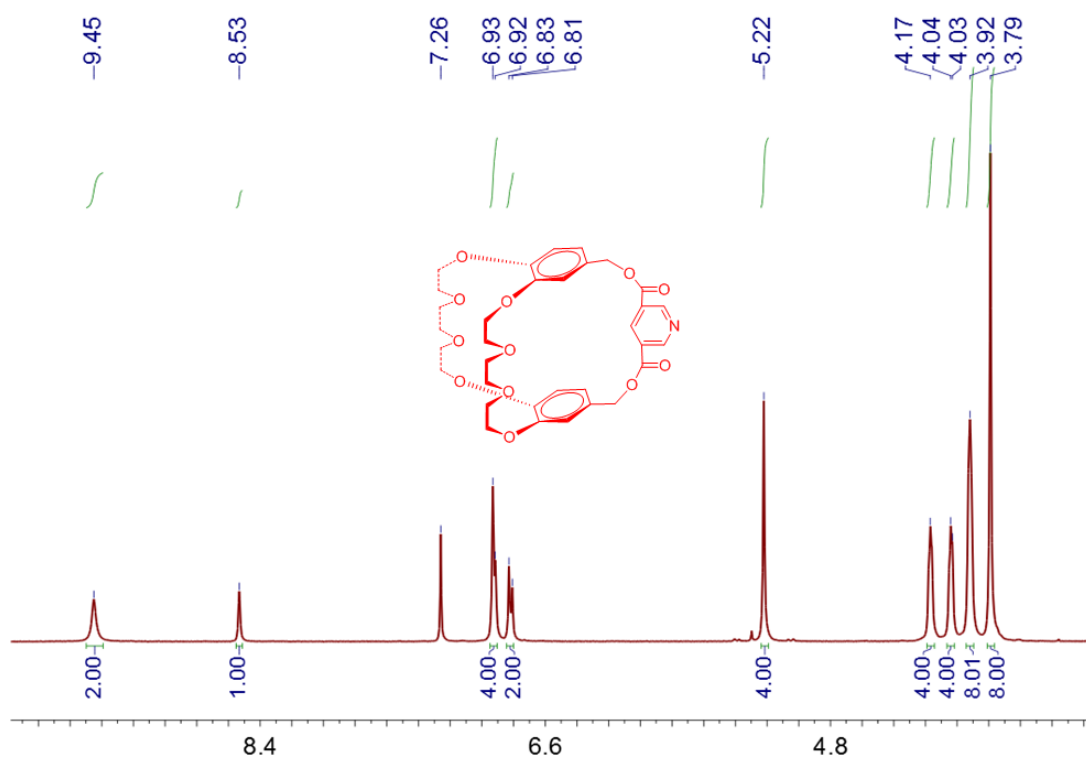


Figure S1. ^1H NMR spectrum (400 MHz, chloroform-*d*, 293 K) of **3**.

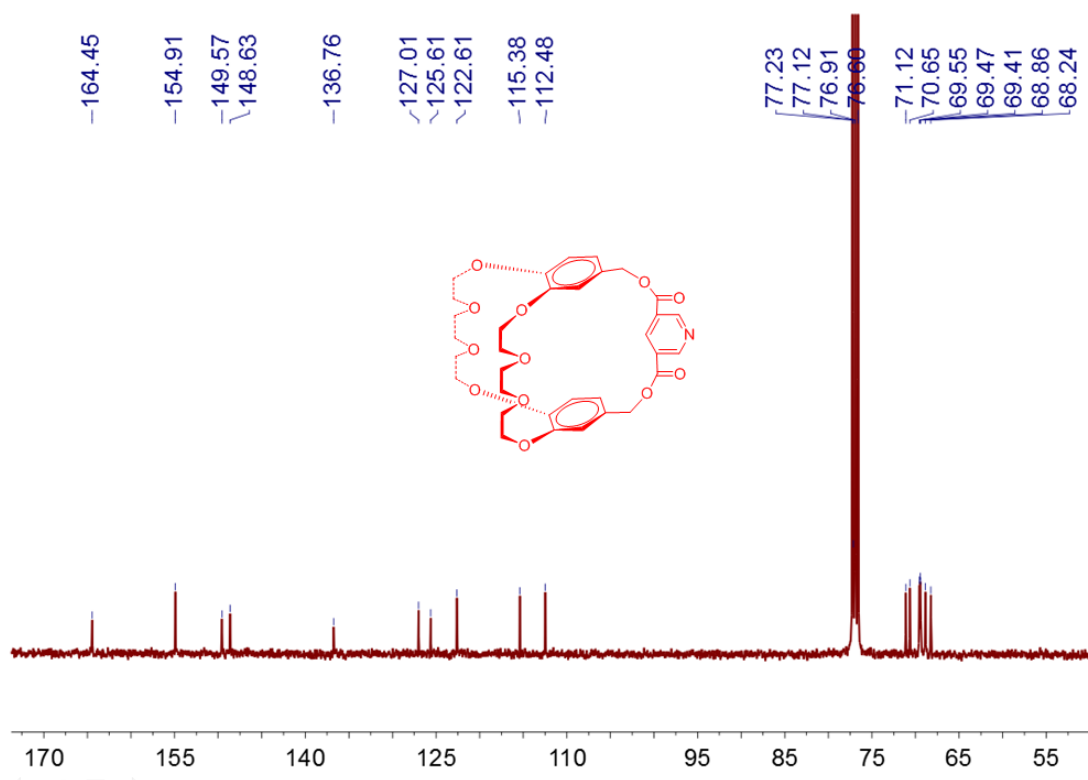


Figure S2. ^{13}C NMR spectrum (125 MHz, chloroform-*d*, 293 K) of **3**.

Spectrum 1A Plot - 2011-12-13 18:11

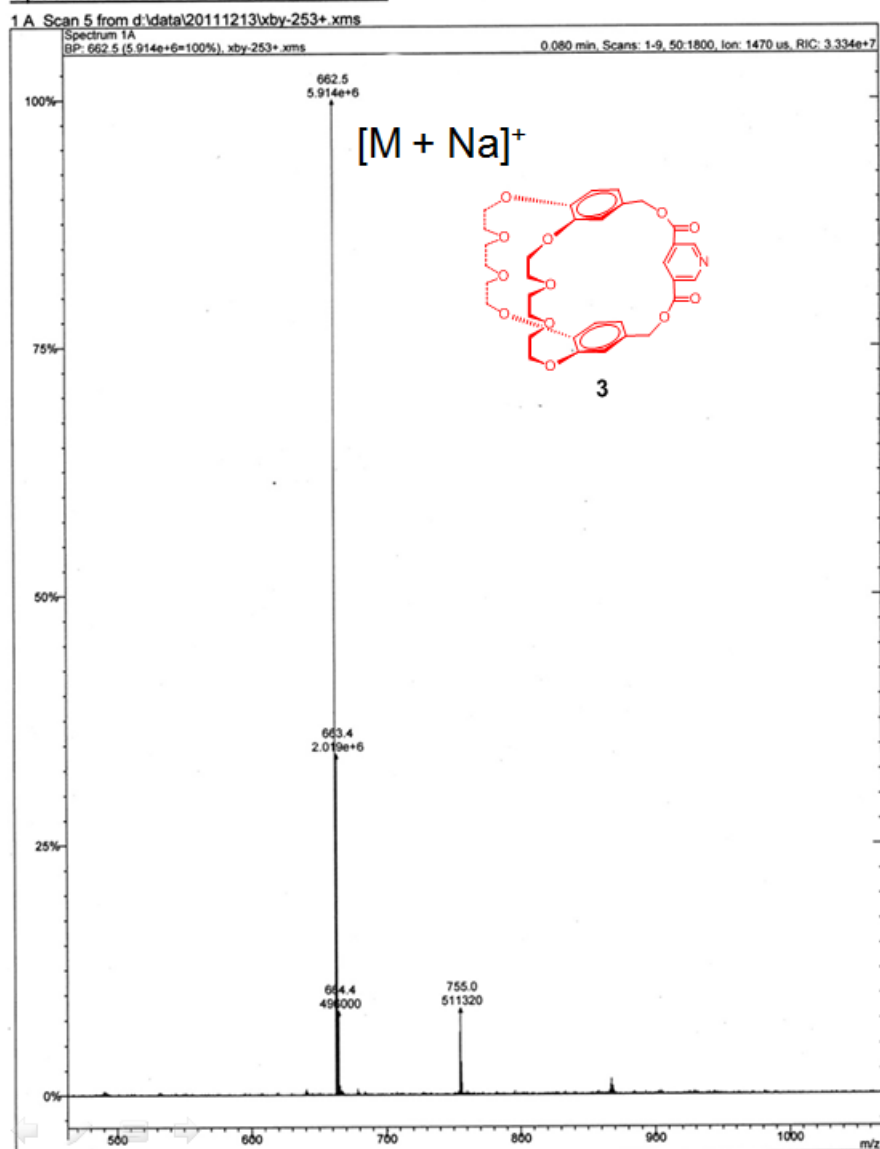


Figure S3. LRESI mass spectrum of **3**.

3. Job plot of **3** ⇌ **2** based on UV-vis spectroscopy data in CH₂Cl₂/CH₃CN (1:1, v/v)

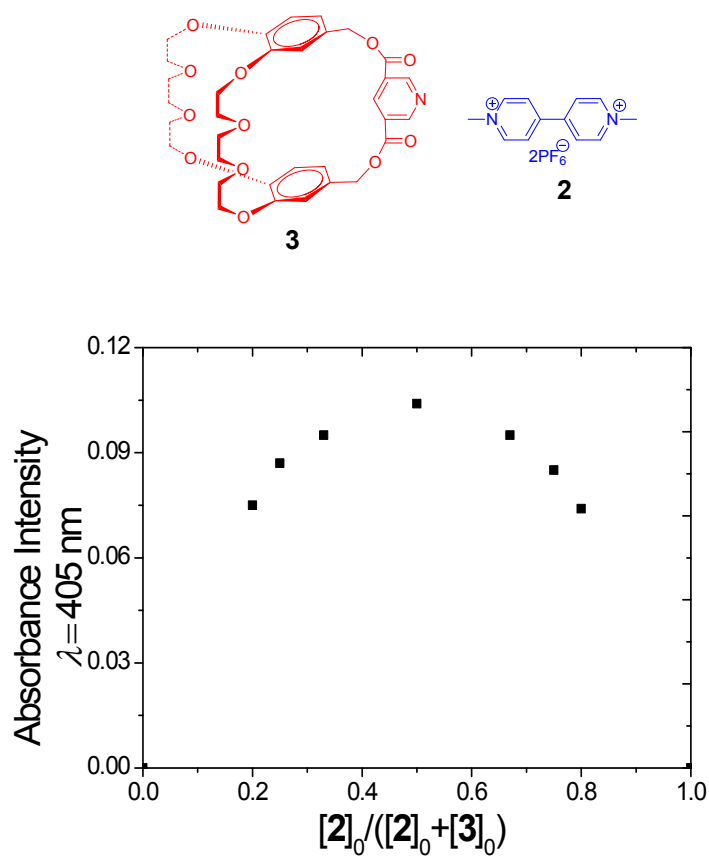


Figure S4. Job plot showing the 1:1 stoichiometry of the complex between **3** and **2** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1, v/v): $[\mathbf{3}]_0 + [\mathbf{2}]_0 = 1.00 \text{ mM}$; $[\mathbf{3}]_0$ and $[\mathbf{2}]_0$ are the initial concentrations of **3** and **2**.

4. ESIMS of host **3** with guest **2** in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1, v/v)

Spectrum 1A Plot - 2013-12-14 12:30

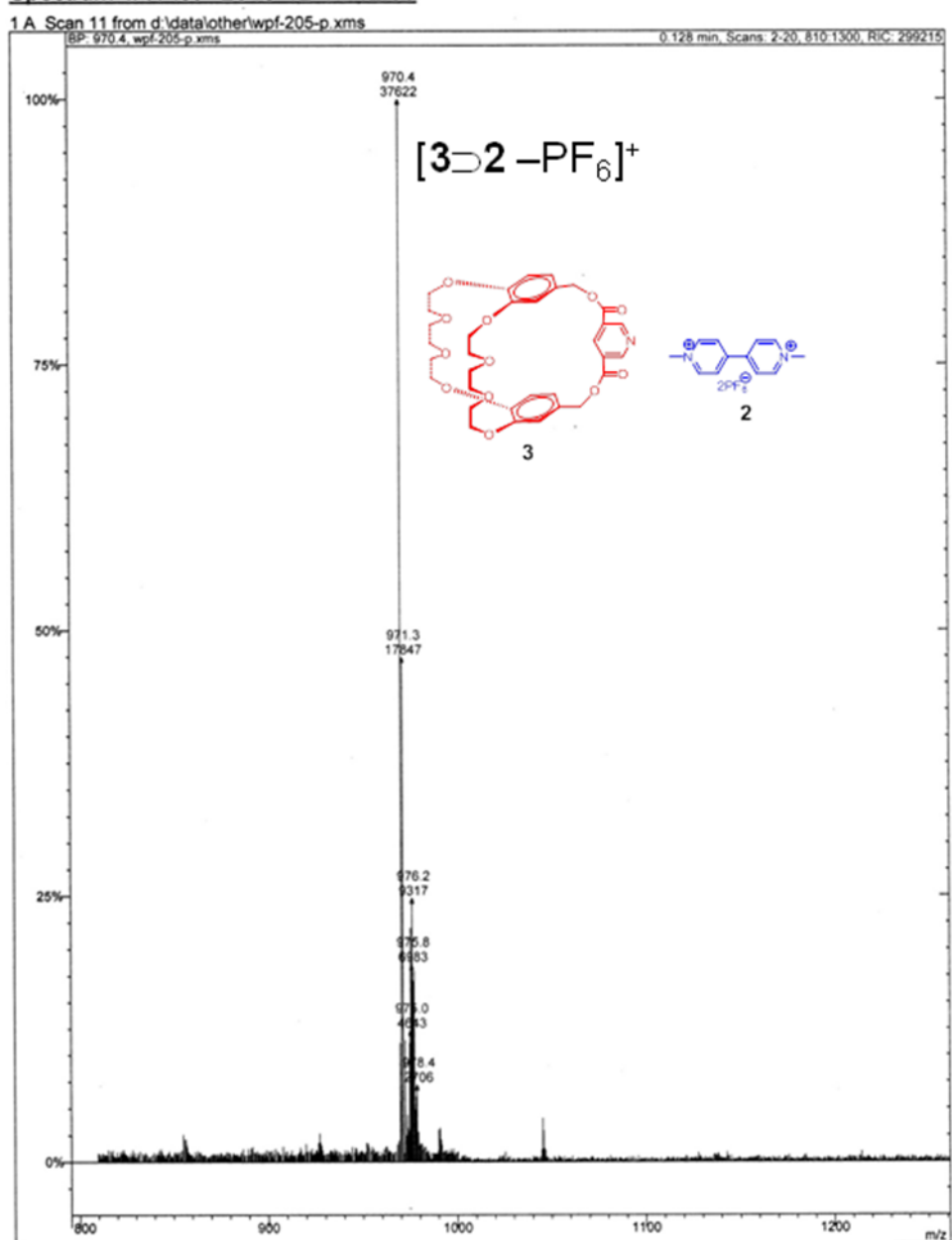


Figure S5. The positive electrospray ionization mass spectrum of an equimolar mixture of **3** and **2** in CH₂Cl₂/CH₃CN (1:1, v/v). Mass fragment at *m/z* 970.4 for [3⊃2 - PF₆]⁺ confirmed the 1:1 complexation stoichiometry between **3** and **2**.

5. Association constant of complex 3⊃2 in CH₂Cl₂/CH₃CN (1:1, v/v)

The association constant (K_a) of complex **3**⊃**2** was determined by probing the charge-transfer band of the complex by UV-vis spectroscopy and employing a titration method. Progressive addition of a CH₂Cl₂/CH₃CN (1:1, v/v) solution with high guest concentration and low host concentration to a CH₂Cl₂/CH₃CN (1:1, v/v) solution with the same host concentration resulted in an increase of the intensity of the charge-transfer band of the complex. Treatment of the collected absorbance data with a non-linear curve-fitting program afforded the corresponding association constant (K_a): $2.27 (\pm 0.10) \times 10^3 \text{ M}^{-1}$ for **3**⊃**2**. The non-linear curve-fitting was based on the equation:

$$A = (A_\infty/[H]_0) (0.5[G]_0 + 0.5([H]_0 + 1/K_a) - 0.5 ([G]_0^2 + (2[G]_0(1/K_a - [H]_0) + (1/K_a + [H]_0)^2)^{0.5}))$$

(Eq. S1)

Wherein A is the absorption intensity of the charge-transfer band at $[G]_0$, A_∞ is the absorption intensity of the charge-transfer band when the host is completely complexed, $[H]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of the guest.

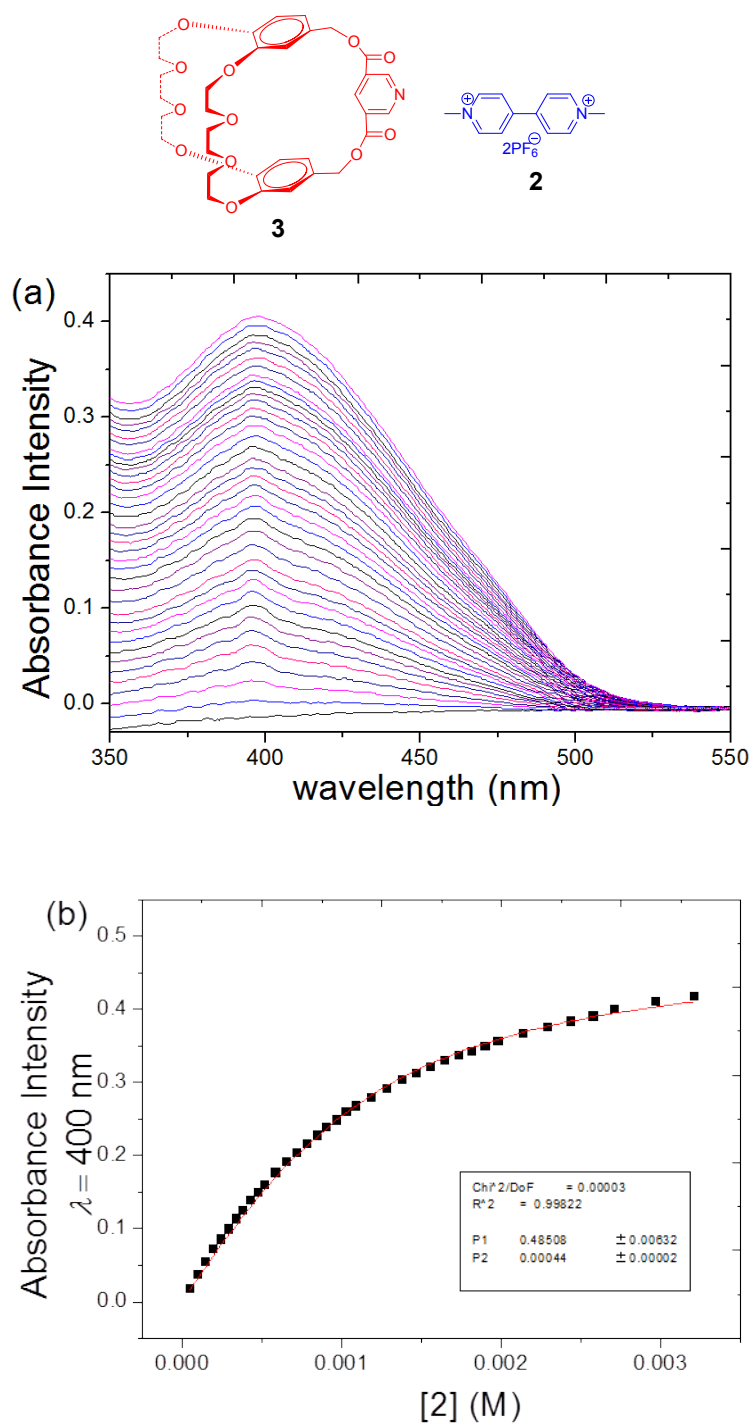


Figure S6. (a) The absorption spectral changes of **3** (1.00 mM) upon addition of **2** and (b) the absorbance intensity change at $\lambda = 400$ nm upon addition of **2** (from 0 to 6.79 mM). The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

6. Cation-responsive complexation between **3** and **2**

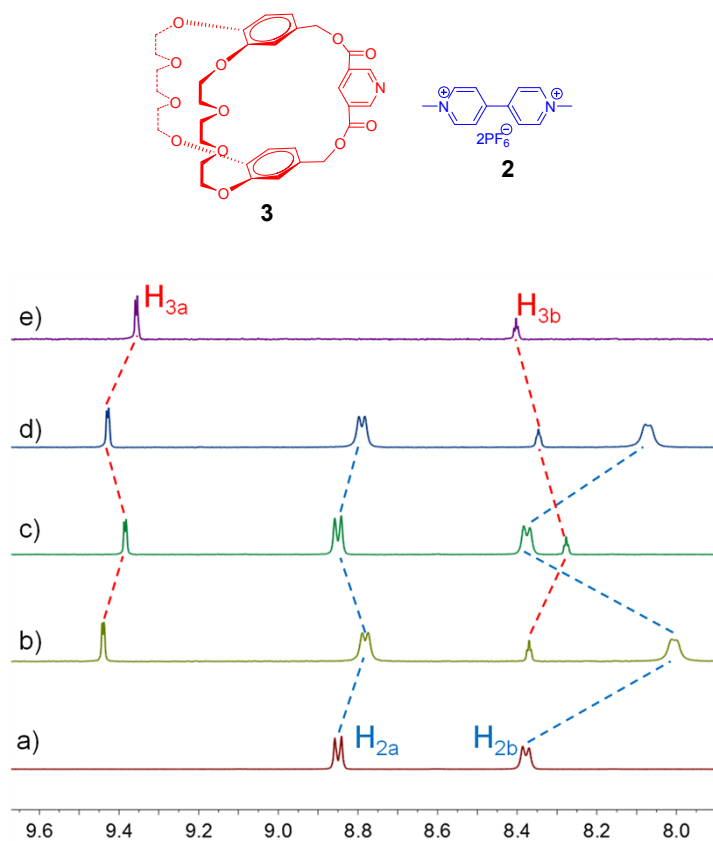


Figure S7. Partial ¹H NMR spectra (400 MHz, dichloromethane-*d*₂/acetonitrile-*d*₃ (1:1, v/v), 293 K): (a) 2.00 mM **2**; (b) 2.00 mM **3** + 2.00 mM **2**; (c) after addition 2.00 equiv of KPF₆ to b; (d) after addition 2.00 equiv of DB18C6 to c; (e) 2.00 mM **3**.

7. ^1H NMR spectra of **4** and **5**

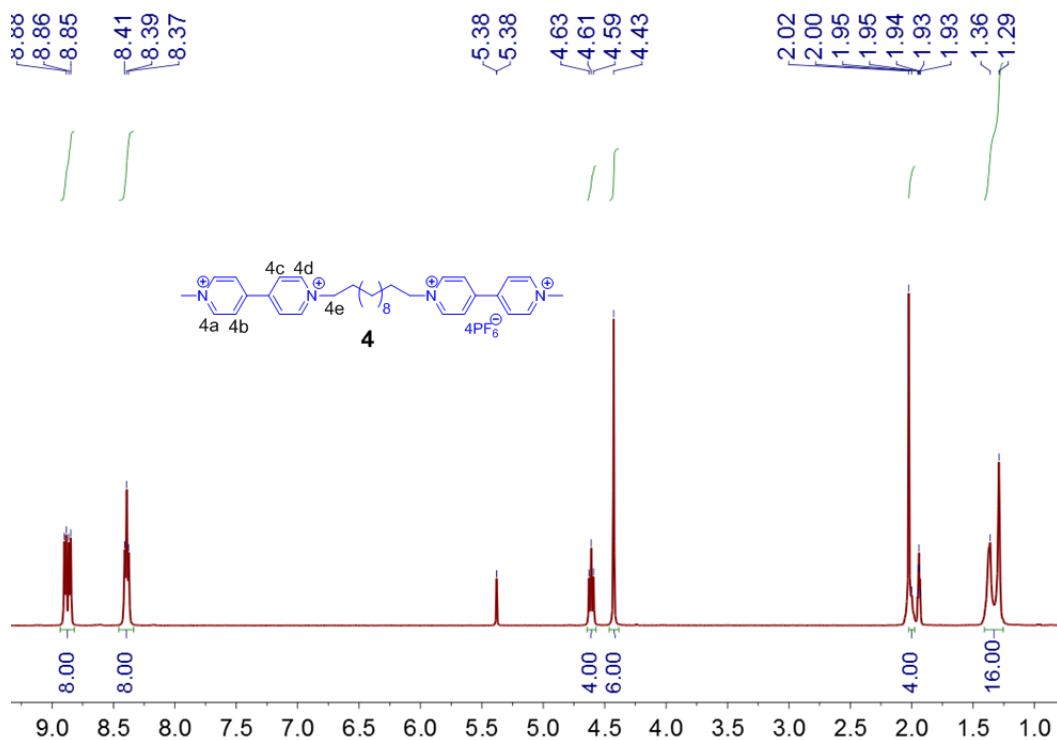


Figure S8. ^1H NMR spectrum (400 MHz, dichloromethane- d_2 /acetonitrile- d_3 (1:1, v/v), 293 K) of **4**.

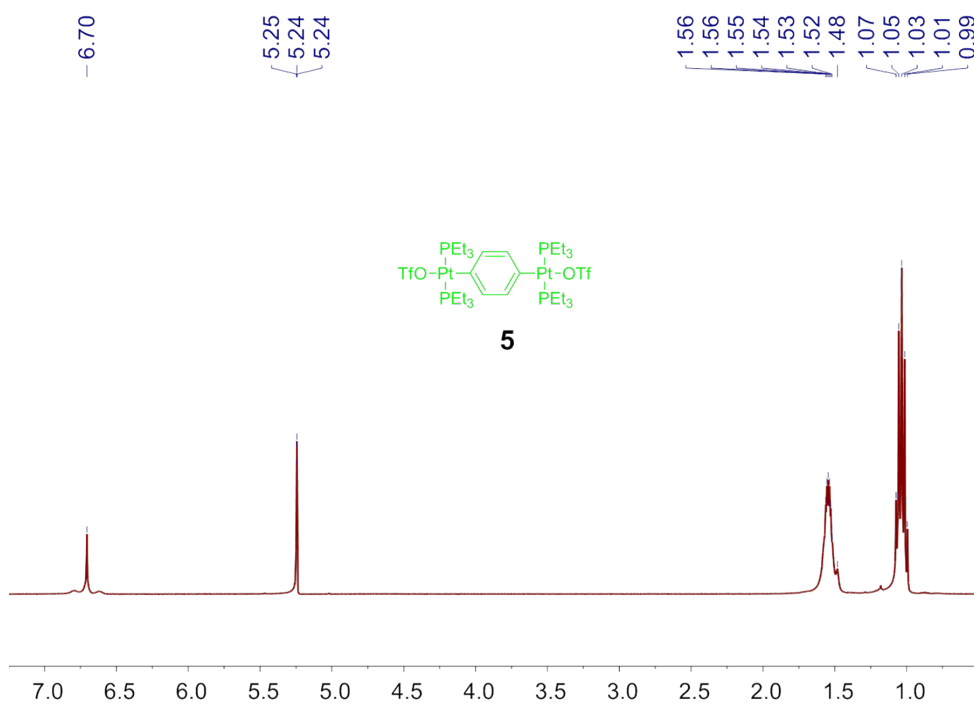
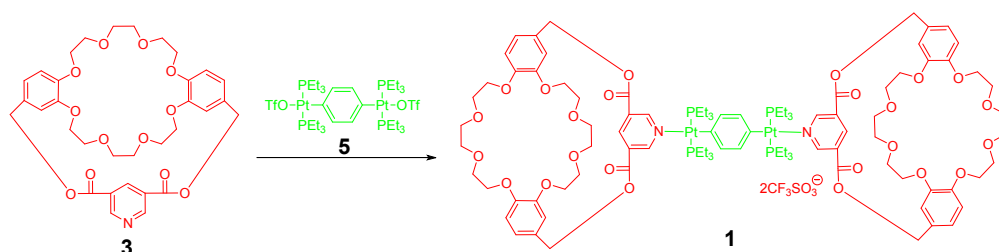


Figure S9. ^1H NMR spectrum (400 MHz, dichloromethane- d_2 , 293 K) of **5**.

8. Synthesis of bis-cryptand **1**

Scheme S2. Synthesis of bis-cryptand host **1**



Cryptand **3** (6.39 mg, 10.0 mM) and **5** (6.18 mg, 5.00 mM) were mixed together in CD_2Cl_2 at room temperature for 30 minutes to give host **1**. The ^1H NMR spectrum of **1** is shown in Figure S10. ^1H NMR (400 MHz, dichloromethane- d_2 , 293 K) δ (ppm): 9.35 (d, 4H, $J = 2.0$ Hz), 8.61 (t, 2H, $J = 3.2$ Hz), 7.01 (s, 2H), 6.86–6.91 (m, 10H), 6.78 (s, 1H), 6.76 (s, 1H), 5.23 (s, 8H), 4.05–4.08 (m, 8H), 3.96–3.98 (m, 8H), 3.77–3.80 (m, 16H), 3.66 (s, 16H), 1.26–1.29 (m, 24H), 1.02–1.09 (m, 36H). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** is shown in Figure S11. $^{31}\text{P}\{^1\text{H}\}$ NMR (s, 161.8 MHz, dichloromethane- d_2 , 293K) δ (ppm): 12.85 (s, ^{195}Pt satellites, $^1J_{\text{Pt-P}} = 2703.7$ Hz). ESI- TOF-MS for **1** is shown in Figure S12: m/z 1108.89 for $[\mathbf{1} - 2\text{OTf}]^{2+}$.

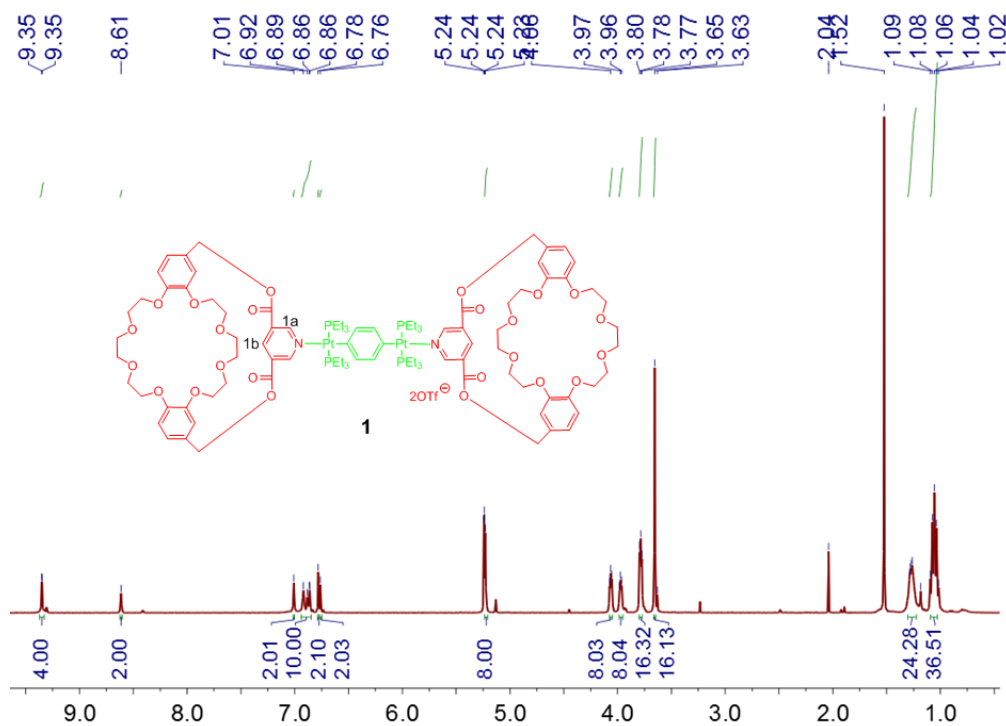


Figure S10. ^1H NMR spectrum (400 MHz, dichloromethane- d_2 , 293 K) of **1**.

-21.20

-12.85

-4.49

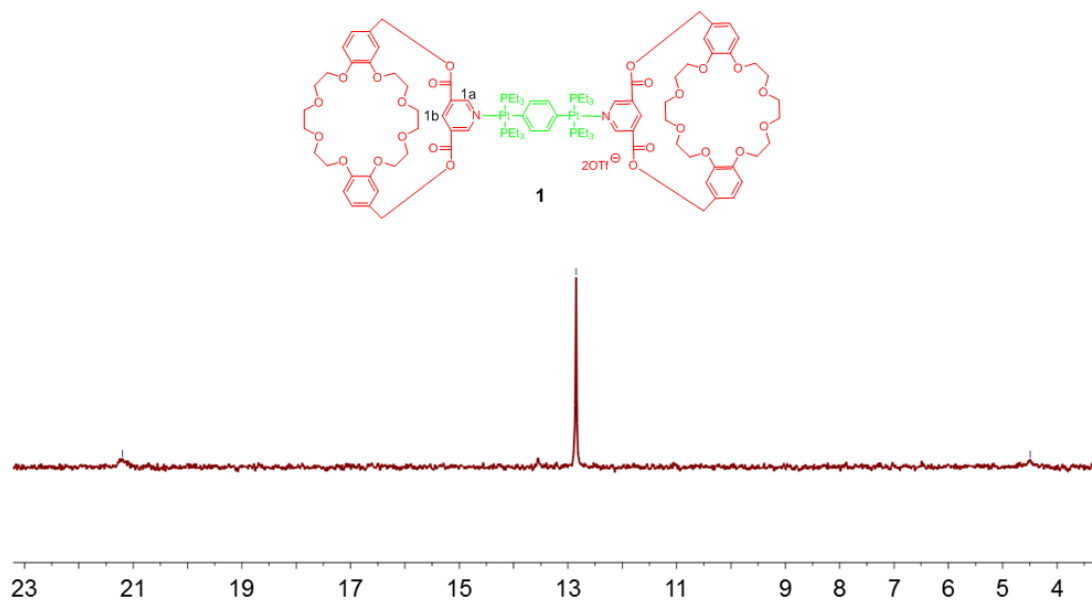


Figure S11. ³¹P{¹H} NMR spectrum (161.8 MHz, dichloromethane-*d*₂, 293 K) of **1**.

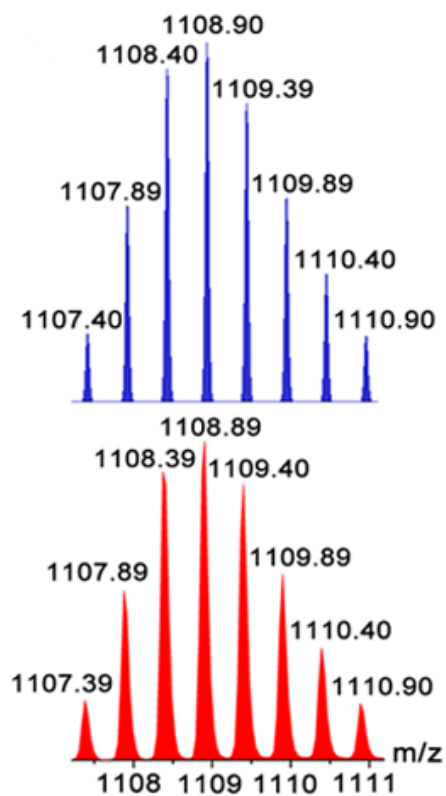


Figure S12. Experimental (red) and calculated (blue) ESI-TOF-MS spectra of **1** [M - 2OTf]²⁺.

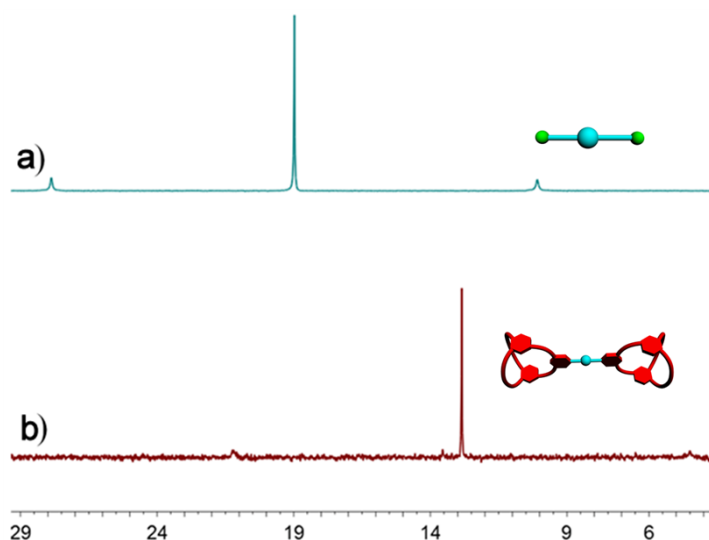


Figure S13. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (161.8 MHz, CD_2Cl_2 , 293 K) of (a) bis-arm acceptor **5**, (b) bis-cryptand host **1**.

9. Comparison of Partial ^1H NMR spectra of **1** and **3**

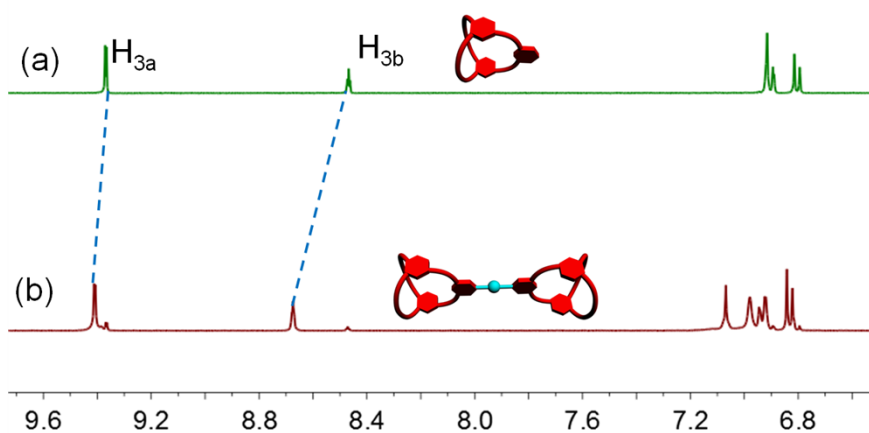


Figure S14. ^1H NMR spectra (400 MHz, dichloromethane- d_2 , 293 K) of (a) bis-cryptand host **1** and (b) **3**.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1**, for example, possesses a sharp singlet at ~ 12.85 ppm with concomitant ^{195}Pt satellites ($J_{\text{Pt-P}} = 2703.7$ Hz), consistent with a single phosphorus environment (Fig. S13, ESI †). This peak is shifted upfield relative to that of acceptor **5** by *ca.* 6.13 ppm. Moreover, in the ^1H NMR spectrum of **1**, the protons

of the pyridyl group (H_{3a} and H_{3b}) showed downfield shifts compared to those of **3** (Fig. S14, ESI[†]), in accordance with coordination of the *N*-atoms to platinum centers. Electrospray ionization time of flight mass spectrometry (ESI-TOF-MS) provides further evidence for the formation of bis-cryptand host **1**. The peak at $m/z = 1108.89$, corresponding to $[M - 2OTf]^{2+}$ was found to support the formation of bis-cryptand (Fig. S12, ESI[†]). The peak was isotopically resolved and agreed very well with the calculated theoretical distribution.

10. Partial 1H NMR spectra of **3**₂→**4**

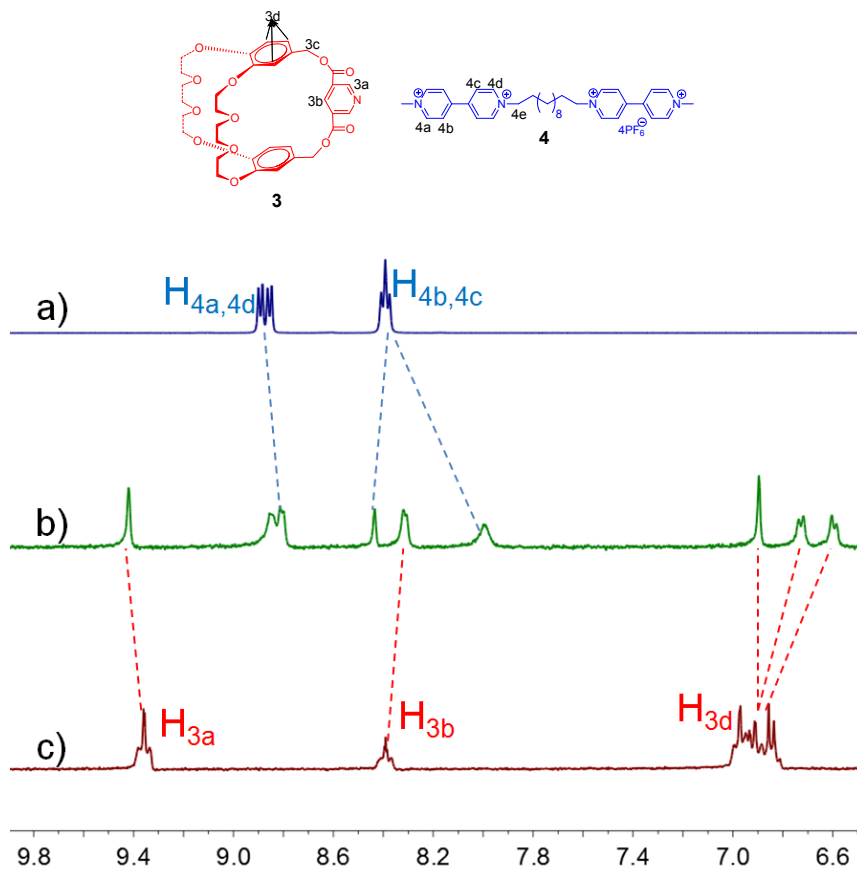


Figure S15. Partial ^1H NMR spectra (400 MHz, dichloromethane- d_2 /acetonitrile- d_3 (1:1, v/v), 293 K): (a) 4.00 mM **4**; (b) 8.00 mM **3** + 4.00 mM **4**; (c) 8.00 mM **3**.

11. LRESI mass spectrum of $3_2\text{D}4$

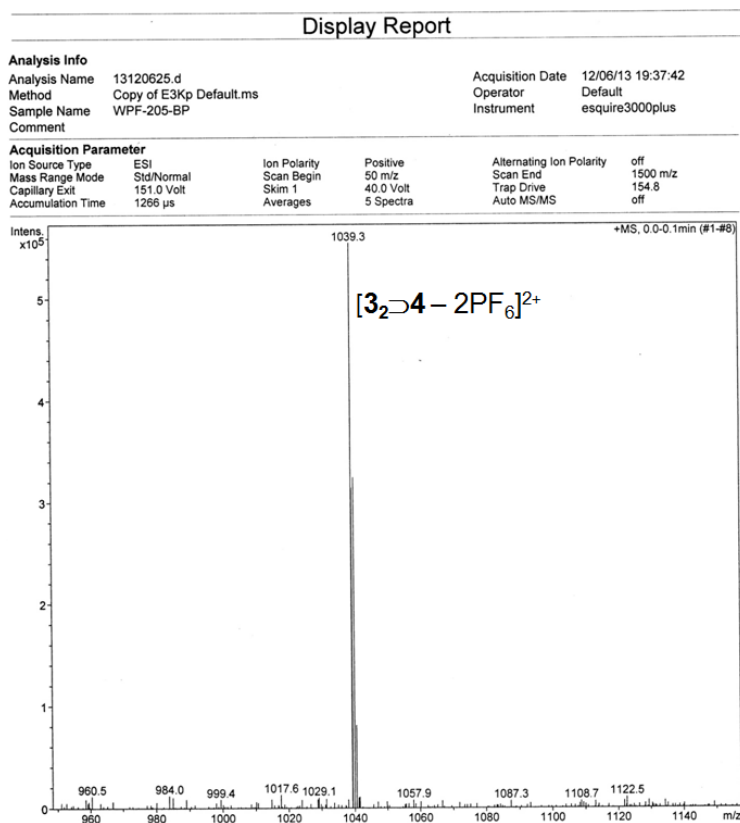


Figure S16. LRESI mass spectrum of $3_2\text{D}4$.

12. K^+ cation responsive NMR of LSP

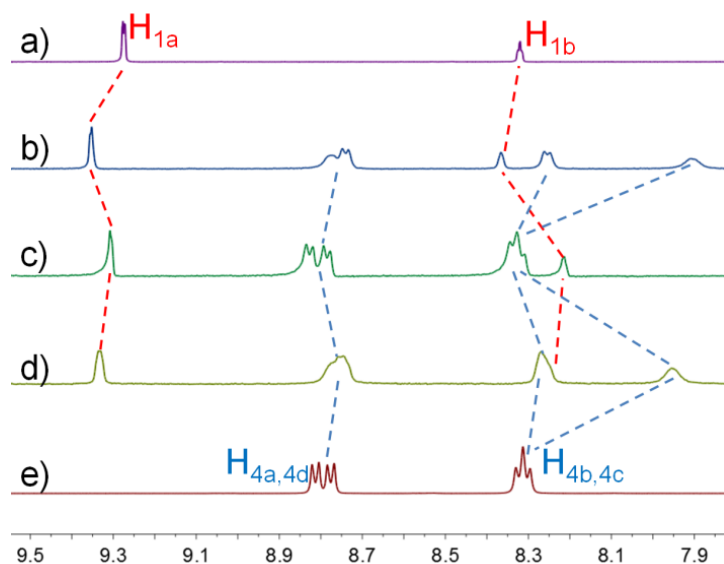


Figure S17. Partial ^1H NMR spectra [400 MHz, dichloromethane- d_2 /acetonitrile- d_3 (1:1, v/v), 293 K]: (a) 5.00 mM **1**; (b) 5.00 mM **1** + 5.00 mM **4**; (c) after addition 2.00 equiv of KPF_6 to b; (d) after addition 2.00 equiv of DB18C6 to c; (e) 5.00 mM **4**.

References:

- S1. H. W. Gibson, H. Wang, C. Slebodnick, J. Merola, W. S. Kassel and A. L. Rheingold, *J. Org. Chem.*, 2007, **72**, 3381–3393.
- S2. F. Wang, B. Zheng, K. Zhu, Q. Zhou, C. Zhai, S. Li, N. Li and F. Huang, *Chem. Commun.*, 2009, 4375–4377.
- S3. J. Li, P. Wei, X. Wu, M. Xue and X. Yan, *Org. Lett.*, 2013, **15**, 4984–4987.