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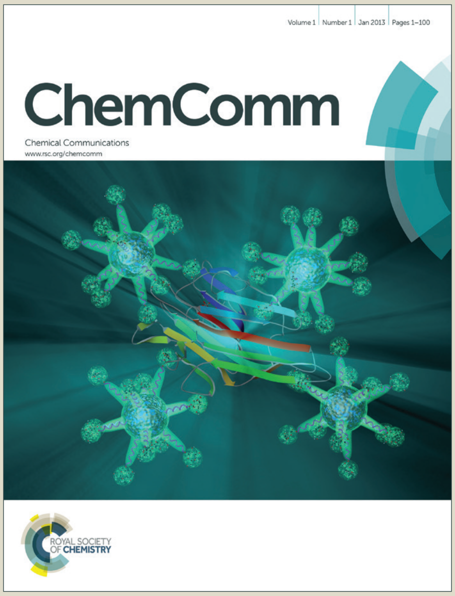

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**Xuzhou Yan**
Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China
TEL 86-571-87953189; FAX 86-571-87951895
E-mail: xzyan@zju.edu.cn

February 20, 2014

Prof. Jonathan W. Steed
Associate Editor, *Chemical Communications*
Durham University, UK
Re: CC-COM-02-2014-001091

Dear Prof. Steed,

We made the following corrections in response to the referees' comments.

1. *Reply to comment 1 made by Referee 1 "Page 4, right column, line 60, Fig. 2 caption, change "solutions" to "solution".*

   This was done.

2. *Reply to comment 2 made by Referee 1 "Page 5, left column, line 15, change "…superstructures which were…" to "…superstructure which was…".*

   This was done.

3. *Reply to comment 3 made by Referee 1 "change "16813–16816;" to "16813–16816."*

   This was done.

4. *Reply to comment made by Referee 2 "There are some grammar mistakes. For example, past tense should be used for "are mainly focusing on structural design by employing single host−guest interactions but pay less attention..." in Page 1, Line 56, and "we can easily and efficiently construct..." in Page 1, Line 63."*

   This was done and the text has been checked very carefully to avoid similar mistakes.

The "track changes" version was submitted as an "Editor Only" file. We appreciate all the valuable corrections suggested by you and the two reviewers. We are hopeful that this revised manuscript now meets your standards for publication in *Chemical Communications*. Thanks.

Best Regards,

Xuzhou Yan

*Enjoy the beauty of supramolecular chemistry*

Cite this: DOI: 10.1039/c0xx00000x

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COMMUNICATION

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

**Peifa Wei,[a] Binyuan Xia,[a] Yanyan Zhang,[b] Yihua Yu,[b] and Xuzhou Yan*[a]**

*Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX*

**DOI: 10.1039/b000000x**

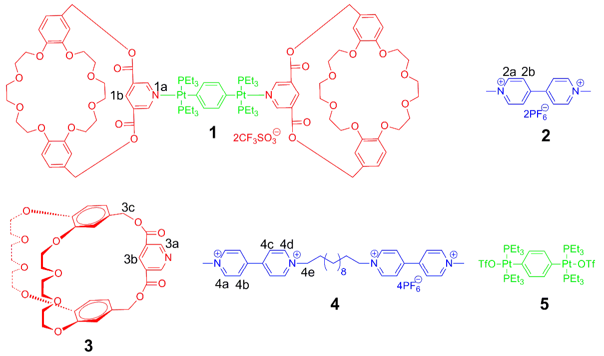
**Herein, a cation responsive linear supramolecular polymer was constructed in an orthogonal fashion by unifying the themes of coordination-driven self-assembly and cryptand-based host–guest interaction.**

Nature commonly exhibits elegant examples of integrating multiple simple interactions into complicated and functional ordered architectures.[1] Inspired by this, scientists are imitating to obtain elaborate artificial polymeric analogues by using various noncovalent interactions, such as hydrogen bonding,[2] host–guest interaction,[3] π–π interaction,[4] metal coordination,[5] *etc*. Supramolecular polymers are aggregate arrays based on low molecular weight monomers brought together by a series of noncovalent interactions instead of conventional covalent polymerization.[6] The relatively low activation energy required for breaking weak noncovalent interactions endows these materials with characteristics of self-healing and adaption.[7] The responsiveness to external stimuli, such as pH, temperature, electric/magnetic fields, enables their potential applications in the fields of smart devices and engineers the polymers with unprecedented macroscopic properties.[8]

Orthogonal self-assembly, a particularly attractive principle in the construction of multiple-code supramolecular polymers, has witnessed its superiority in recent years.[9] Under the principle of orthogonal self-assembly, we can not only carefully design each unique interaction but also simultaneously incorporate various noncovalent bonds to a hierarchical assembly process. Up to now, this methodology has been utilized for the fabrication of supramolecular polymers with various chain topologies such as linear, star-type, cross-linked, hyperbranched, and dendronized polymers.[10]

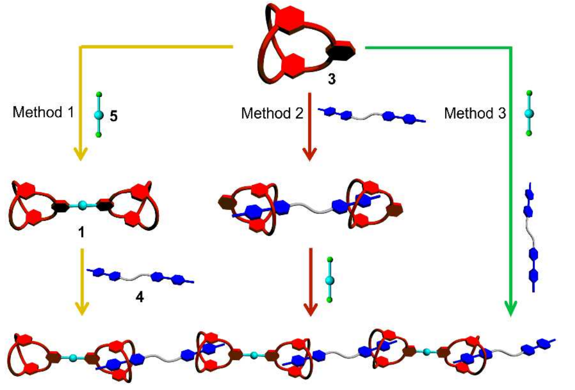
Metal-coordination is a valuable methodology to construct supramolecular coordination complexes (SCCs) based on the spontaneous formation of metal−ligand bonds.[11] Cryptands have been proved to be much better hosts for paraquat derivatives than the corresponding simple crown ethers because of the incorporation of additional binding sites, better preorganization of complexation conformations, and higher association constants.[12] To the best of our knowledge, supramolecular polymers constructed by cryptand-based molecular recognitions are still rare. In 2010, Huang and co-workers realized the reversible metal coordination mediated transition from linear to crosslinked supramolecular polymers by utilization of host–guest interactions between bis(*meta*-phenylene)-32-crown-10 (BMP32C10)-based cryptand and paraquat derivative.[13] In 2011, Gibson and co-workers reported the preparation of AA-BB-type linear supramolecular polymers (LSP) *via* the self-assembly of BMP32C10-based biscryptand and a bisparaquat derivative.[14] The two examples ~~are~~ were mainly focusing on structural design by employing single host–guest interactions but ~~pay~~ paid less attention on the responsiveness, hierarchical orthogonal self-assembly, and functionalities of the cryptand-based supramolecular polymers. Herein, by unifying the themes of coordination-driven self-assembly and *cis*-dibenzo-24-crown-8 (DB24C8) cryptand-based molecular recognition through hierarchical orthogonal strategies, we ~~can~~ could easily and efficiently construct functional LSP with stimuli-responsiveness and structural novelty.

Considering *cis*-DB24C8-based cryptand can often response to the $K^+$ cation, we want to synthesize a novel *cis*-DB24C8-based cryptand (**3**) with its pyridine nitrogen atom outside the third arm which facilitates its further self-assembly by metal coordination (Schemes 1 and S1, ESI†). Then, we studied the host–guest complexation of cryptand **3** with model guest **2**. Equimolar solution (1.00 mM) of cryptand **3** with guest **2** in $CH_2Cl_2/CH_3CN$ (1:1, *v*/*v*) is yellow because of charge-transfer interactions, direct evidence for host–guest complexation. A Job plot based on UV−vis spectroscopy absorbance data confirmed that $\mathbf{3}\supset\mathbf{2}$ was of 1:1 stoichiometry in $CH_2Cl_2/CH_3CN$ (1:1, *v*/*v*) (Fig. S4, ESI†). Electrospray ionization mass spectrometry (ESI-MS) further confirmed this: *m*/*z* 970.4 (100%) for $[\mathbf{3}\supset\mathbf{2} - PF_6]^+$ (Fig. S5, ESI†). No peaks with other complexation stoichiometries were found. The association constant ($K_a$) is determined in $CH_2Cl_2/CH_3CN$ (1:1, *v*/*v*) by using a UV−vis titration method to be $(2.27 \pm 0.10) \times 10^3$ $M^{-1}$ for $\mathbf{3}\supset\mathbf{2}$ (Fig. S6, ESI†). Moreover, the formation of the [2]pseudorotaxane based on cryptand **3** and paraquat **2** can be reversibly controlled by adding and removing potassium cation because $K^+$ can form a much more stable complex with cryptand **3**. However, when enough dibenzo-18-crown-6 (DB18C6) is added to trap the $K^+$, the complex $\mathbf{3}\supset\mathbf{2}$ forms again. This cation-induced reversible complexation was confirmed by proton NMR experiments (Fig. S7, ESI†) and it also paves the way for the design of responsive supramolecular polymers.



**Scheme 1.** Compounds used in this study.

Stirring a mixture of cryptand ligand **3** (10.0 mM) and 180° organoplatinum(II) acceptor **5** (5.00 mM) in a 2:1 ratio in $CD_2Cl_2$ at room temperature for 30 min resulted in the formation of the self-assembled bis-cryptand host **1** (Scheme S2, ESI†). $^1H$ and $^{31}P$ NMR analyses of the reaction mixtures supported the formation of desired symmetric species (Figs. S10–S14, ESI†). Then we construct a responsive LSP using the molecular recognition of host **1** to a homoditopic bisparaquat derivative **4**. The formation of LSP was first investigated by the proton NMR spectra of equimolar **1** and **4** solutions in $CD_2Cl_2/CD_3CN$ (1:1, *v*/*v*) recorded at concentrations in the range of 0.500–200 mM (Fig. 1). The concentration-dependent $^1H$ NMR spectra indicates the involvement of fast-exchanging noncovalent interactions in solution. The splitting and large chemical shift change (~0.80 ppm) of $H_{4b,4c}$ of biparaquat derivative **4** demonstrated that the percentage of complexed species was concentration-dependent, and it was favored to form supramolecular polymers at high concentrations. What is more, when the concentration is very high, all the proton signals became broad, further indicating the formation of high-molecular-weight polymeric structures.



**Scheme 2**. Cartoon representation of the formation of LSP by hierarchical orthogonal strategies.

To further substantiate the formation of LSP, 2D diffusion-ordered $^1H$ NMR spectroscopy (DOSY) was performed to test the dimensions of polydispersed supramolecular aggregates. As the concentration of equimolar solutions of **1** and **4** increased from 25.0 to 200 mM, the measured weight average diffusion coefficient *D* decreased from 4.73 × $10^{-10}$ to 1.75 × $10^{-10}$ $m^2s^{-1}$ (Fig. 2c). The result also indicates that concentration exerts a significant impact on the supramolecular polymerization process. Then dynamic light scattering (DLS) measurements were used to investigate the size distributions of the LSP at different concentrations. As the concentration increased from 12.5 to 50.0 mM, the average hydrodynamic diameter ($D_h$) increased from 220 to 1275 nm, indicating a concentration dependence on LSP sizes (Fig. 2b). Moreover, scanning electron microscopy (SEM) studies showed that long rod-like fibers could easily be drawn from concentrated solutions of LSP in $CH_3CN/CH_2Cl_2$ (1:1, *v*/*v*), while no fibers could be drawn from the individual highly concentrated solutions of monomers **1** and **4**, respectively, reflecting significant chain extension to generate the desired high moleular polymeric aggregates through orthogonal cryptand-based molecular recognition and coordination-driven self-assembly (Fig. 2d).

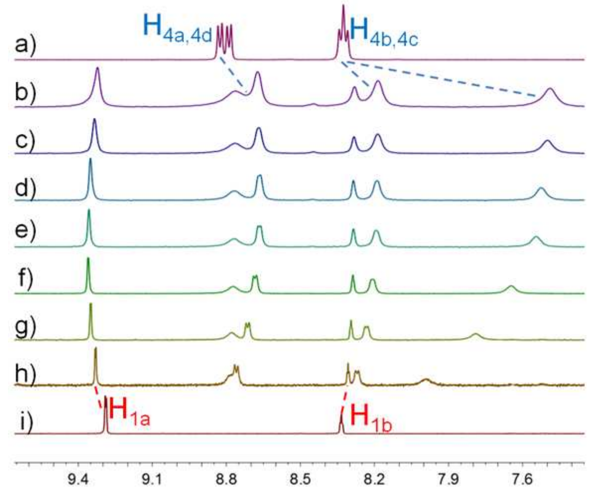


**Fig. 1** Partial $^1H$ NMR spectra [500 MHz, $CD_3CN/CD_2Cl_2$ (1:1, *v*/*v*), 293 K]: (a) **4**; (b–h) solutions of **1** and **4** with 1:1 molar ratio at concentrations of (b) 200, (c) 150, (d) 80.0, (e) 25.0, (f) 6.25, (g) 2.00, and (h) 0.500 mM; (i) **1**.

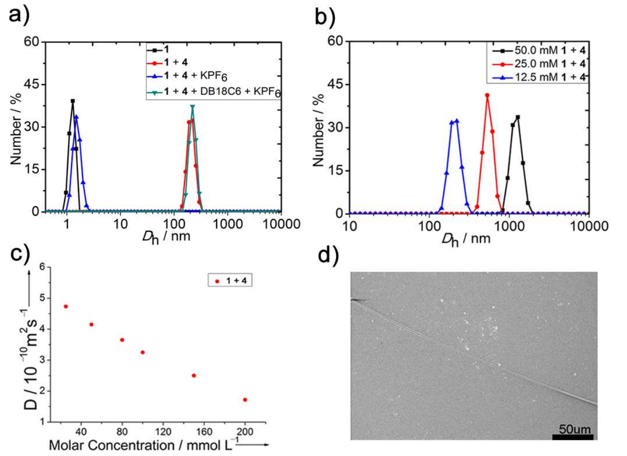


**Fig. 2** Size distributions: (a) LSP before and after addition of $KPF_6$ (*c* = 12.5 mM), (b) LSP at different concentrations, (c) concentration dependence of diffusion coefficient *D* [500 MHz, $CD_3CN/CD_2Cl_2$ (1:1, *v*/*v*), 298 K)] of LSP, and (d) SEM image of (gold coated) fiber drawn from concentrated solution~~s~~ of LSP in $CH_3CN/CH_2Cl_2$ (1:1, *v*/*v*).

The LSP can be also constructed based on an alternative stepwise method by exchanging the self-assembly sequence (Scheme 2, method 2) or a one-pot reaction (Scheme 2, method 3). Stirring a 2:1 mixture of host **3** and guest **4** in $CD_2Cl_2/CD_3CN$ (1:1, *v*/*v*) yielded [3]pseudorotaxane $\mathbf{3}_2\supset\mathbf{4}$. Chemical shift changes and the splitting of $H_{4b,4c}$ manifest the complexation between **3** and **4** (Fig. S15, ESI†). This intermediate $\mathbf{3}_2\supset\mathbf{4}$ was also well evidenced by ESI-MS: *m*/*z* 1039.3 (100%) for $[\mathbf{3}_2\supset\mathbf{4} - 2PF_6]^{2+}$ (Fig. S16, ESI†). Then, 1.00 equiv of **5** was introduced into this system, which resulted in the formation of LSP. The same features of multinuclear NMR ($^1H$ and $^{31}P$) analyses of the reaction mixtures revealed the feasibility of this alternative stepwise procedure. Except for two of the stepwise strategies, one-pot fashion was also explored to best demonstrate the power of this orthogonal procedure. Just mixing a 2:1:1 ratio for components **3**, **4**, **5** (Scheme 2, method 3) also produced the well-controlled superstructures which ~~were~~ was characterized by multinuclear NMR ($^1H$ and $^{31}P$) analyses. Thus, LSP can be prepared in three methods by utilizing the noninterfering orthogonal nature of coordination-driven self-assembly and host−guest interactions.

Supramolecular polymers that can response to external stimuli are always attractive. Herein, LSP are cation-responsive because of the introduction of *cis*-DB24C8-based cryptand motifs (**3**) which owns $K^+$ cation-induced assembly/disassembly behaviors. The $^1H$ NMR experiment demonstrated this reversible process (Fig. S17, ESI†). Upon adding $K^+$ to the equimolar solutions of **1** and **4**, almost all complexed signals disappeared and the chemical shifts corresponding to $H_{4b,4c}$ and $H_{4a,4d}$ restore to their uncomplexed values, indicating that the complexation between **1** and bisparaquat salt was essentially quenched (Fig. S17c, ESI†). Subsequent addition of enough DB18C6 leads to the considerable reduction of characteristic complexed signals (Fig. S17d, ESI†). These reversible conversions can also be monitored by DLS. By adding and removing potassium cation, the average $D_h$ of LSP (12.5 mM) decreases from 220 nm to 1.50 nm and then recovers (Fig. 2a).

In summary, a linear supramolecular polymer was constructed by unifying the themes of coordination-driven self-assembly and cryptand-based molecular recognition in a hierarchical orthogonal fashion. Two stepwise self-assembly behaviors as well as a one-pot interaction for the preparation of LSP were addressed. Cation-induced dynamic properties make the resulting polymer promising candidate for applications in degradable materials. Given the high efficiency of constructing the SCCs and favorable properties induced by host−guest interactions, the unification of these two orthogonal interactions paves an interesting way to construct novel functional materials.

This work was supported by the National Natural Science Foundation of China (21125417) and the Fundamental Research Funds for the Central Universities.

## Notes and references

[a]*Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China. E-mail: xzyan@zju.edu.cn*

[b]*Shanghai Key Laboratory of Magnetic Resonance, Department of Physics, East China Normal University, Shanghai 200062, P. R. China*

*†Electronic Supplementary Information (ESI) available: Synthetic procedures, characterizations, and other materials. See DOI: 10.1039/b000000x/*

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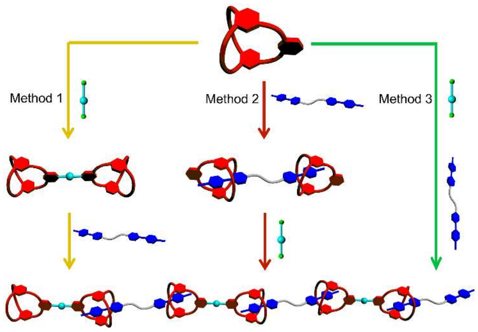
**ToC Graphic:**



A cation responsive linear supramolecular polymer was constructed by unifying the themes 5 of coordination-driven self-assembly and cryptand-based molecular recognition in a hierarchical orthogonal fashion.

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

Peifa Wei,[a] Binyuan Xia,[a] Yanyan Zhang,[b] Yihua Yu,[b] and Xuzhou Yan*[a]

[a] *Department of Chemistry, Zhejiang University, Hangzhou 310027, P. R. China*

*Email: xzyan@zju.edu.cn.*

[b] *Shanghai Key Laboratory of Magnetic Resonance, Department of Physics, East China Normal University, Shanghai 200062, P. R. China*

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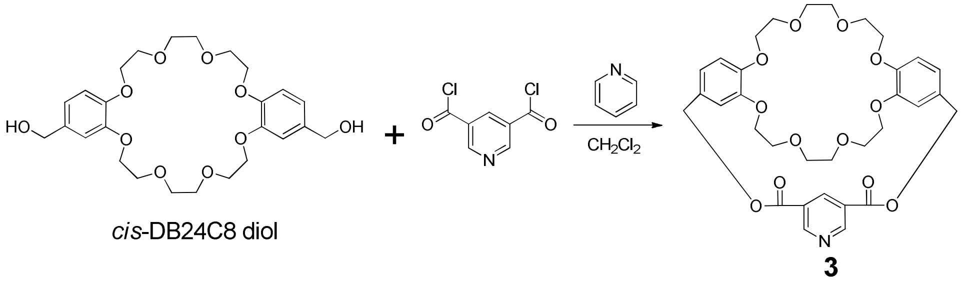
## *1. Materials and Methods*

*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. $^1$H and $^{13}$C NMR chemical shifts are reported relative to residual solvent signals, and $^{31}$P{$^1$H} NMR chemical shifts are referenced to an external unlocked sample of 85% $H_3PO_4$ ($\delta$ 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**



**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 ºC. The $^1$H NMR spectrum of **3** is shown in Figure S1. $^1$H NMR (400 MHz, chloroform-*d*, 293 K) $\delta$ (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) $\delta$ (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%) $[M + Na]^+$. HRESIMS: *m*/*z* calcd for $[M]^+$ $C_{33}H_{37}NO_{12}$ 639.2316, found 639.2317, error 0.2 ppm.

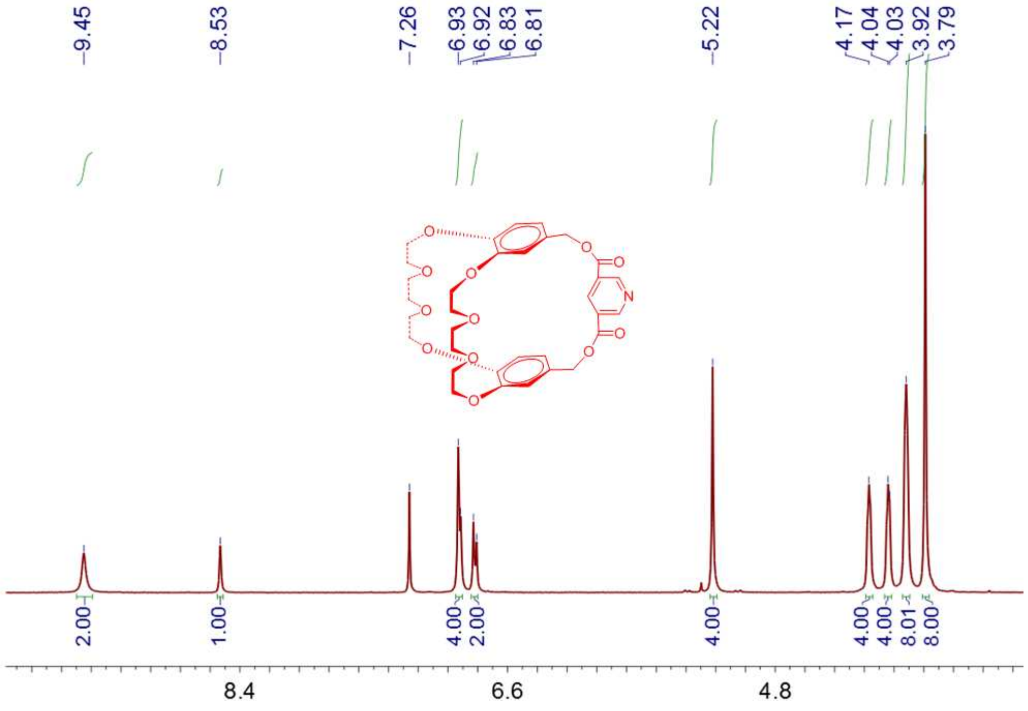


**Figure S1.** $^1$H NMR spectrum (400 MHz, chloroform-*d*, 293 K) of **3**.

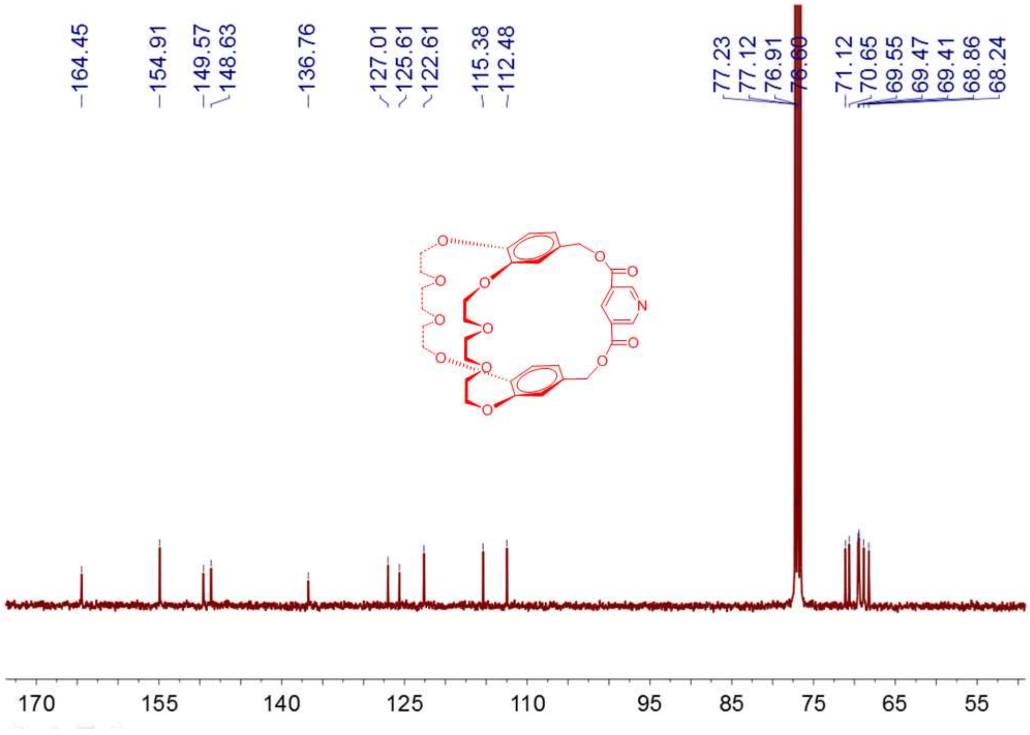


**Figure S2.** $^{13}$C NMR spectrum (125 MHz, chloroform-*d*, 293 K) of **3**.

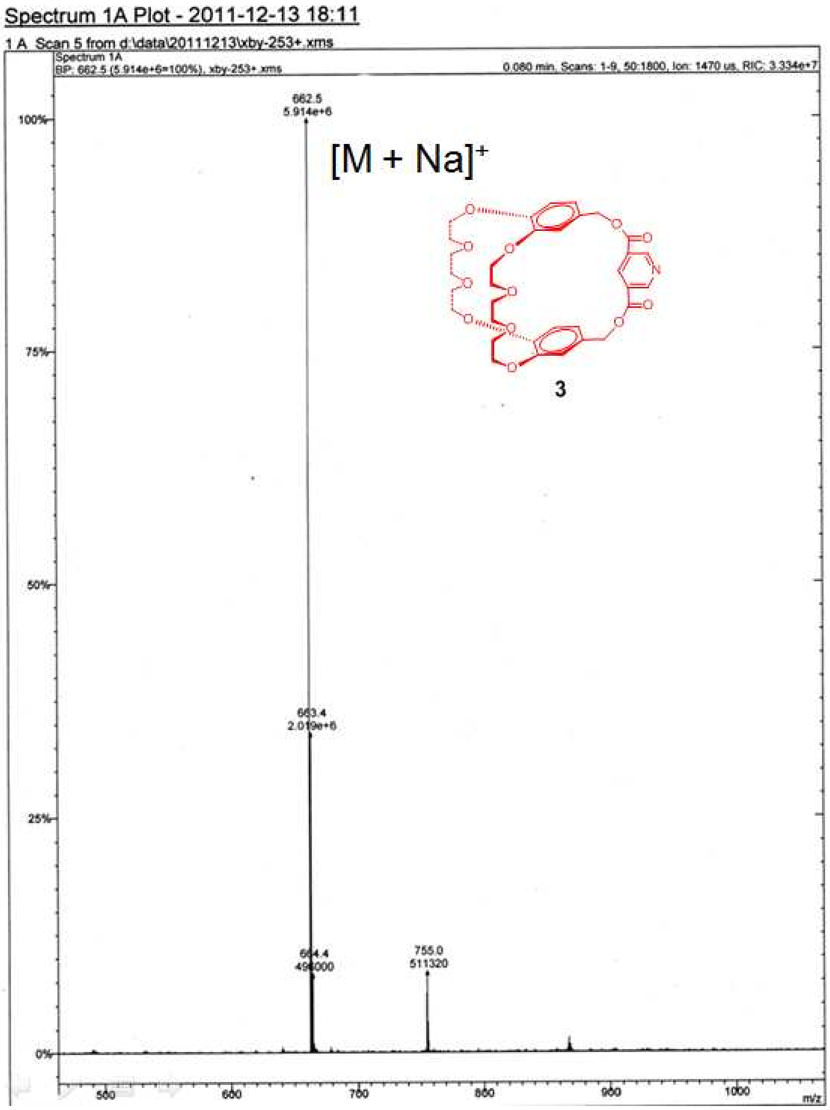
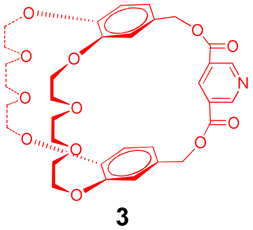
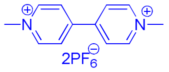


**Figure S3.** LRESI mass spectrum of **3**.

### *3. Job plot of* ***3*** *⊐* ***2*** *based on UV-vis spectroscopy data in* $CH_2Cl_2/CH_3CN$ *(1:1, v/v)*



**3**



**2**

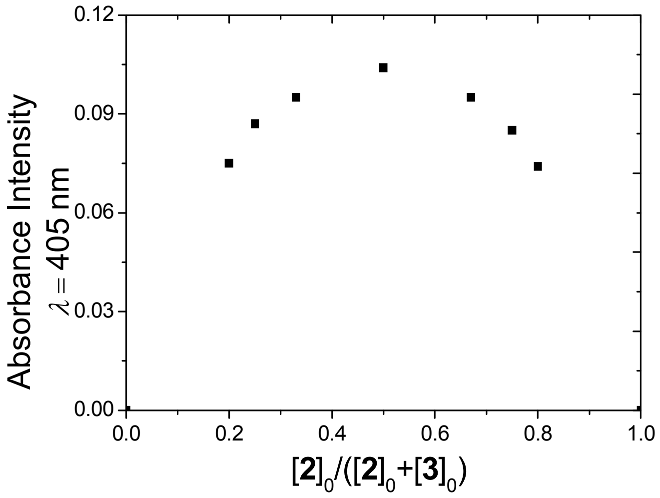


**Figure S4.** Job plot showing the 1:1 stoichiometry of the complex between **3** and **2** in $CH_2Cl_2/CH_3CN$ (1:1, *v*/*v*): $[\mathbf{3}]_0$ + $[\mathbf{2}]_0$ = 1.00 mM; $[\mathbf{3}]_0$ and $[\mathbf{2}]_0$ are the initial concentrations of **3** and **2**.

*4. ESIMS of host **3** with guest **2** in $CH_2Cl_2/CH_3CN$ (1:1, v/v)*

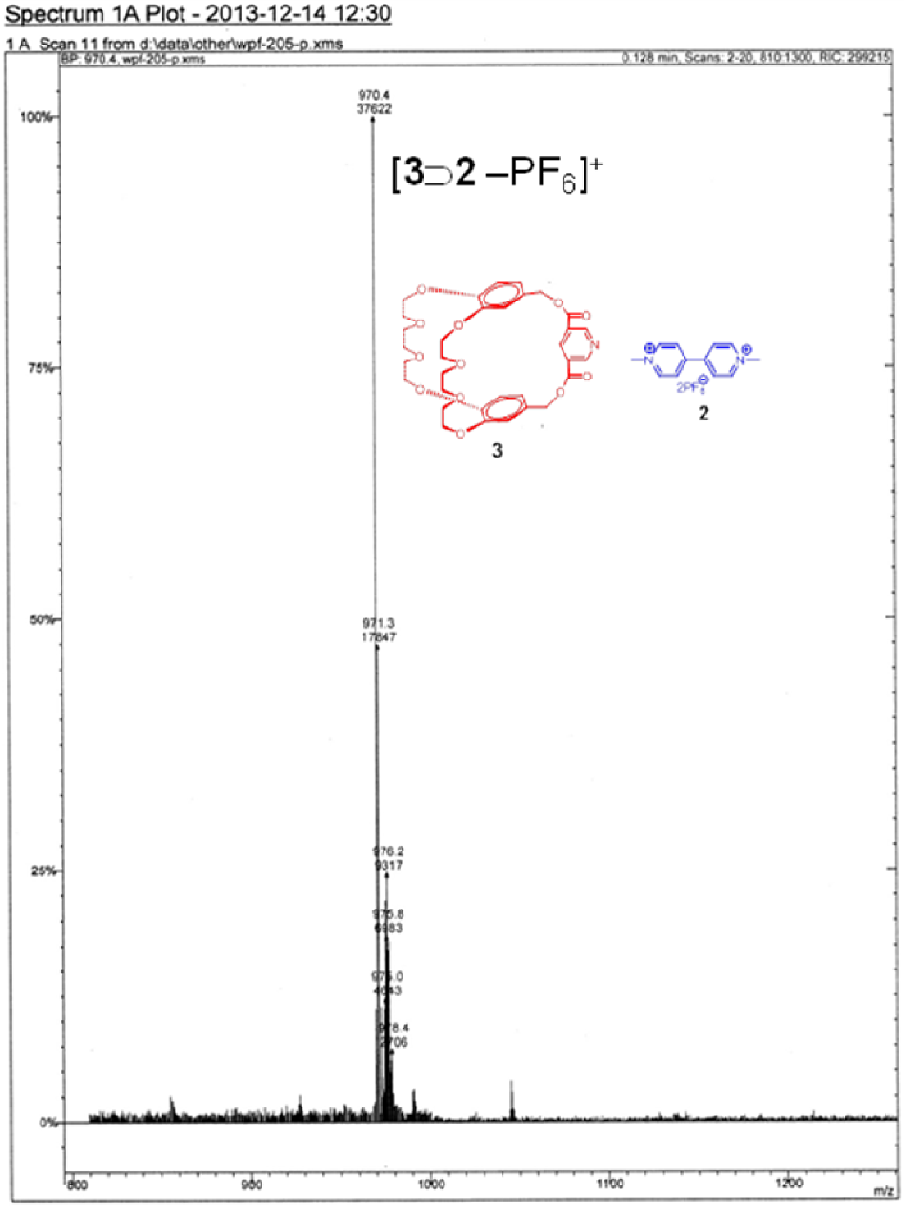


**Figure S5.** The positive electrospray ionization mass spectrum of an equimolar mixture of **3** and **2** in $CH_2Cl_2/CH_3CN$ (1:1, *v*/*v*). Mass fragment at *m/z* 970.4 for [**3**⊃**2** – $PF_6]^+$ confirmed the 1:1 complexation stoichiometry between **3** and **2**.

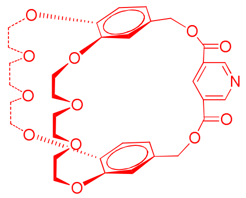
*5. Association constant of complex* ***3⊃2*** *in* $CH_2Cl_2/CH_3CN$ *(1:1, v/v)*

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 $CH_2Cl_2/CH_3CN$ (1:1, *v*/*v*) solution with high guest concentration and low host concentration to a $CH_2Cl_2/CH_3CN$ (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 (± 0.10) × $10^3$ $M^{-1}$ for **3⊃2**. The non-linear curve-fitting was based on the equation:

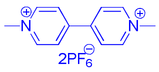
$$A = (A_\infty/[H]_0)\ (0.5[G]_0 + 0.5([H]_0+1/K_a)-(0.5\ ([G]_0^{\ 2}+(2[G]_0(1/K_a - [H]_0)) + (1/K_a + [H]_0)^2)^{\ 0.5}))$$

(Eq. S1)

Wherein $A$ is the absorption intensity of the charge-transfer band at $[G]_0$, $A_\infty$ 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.



**3**



**2**

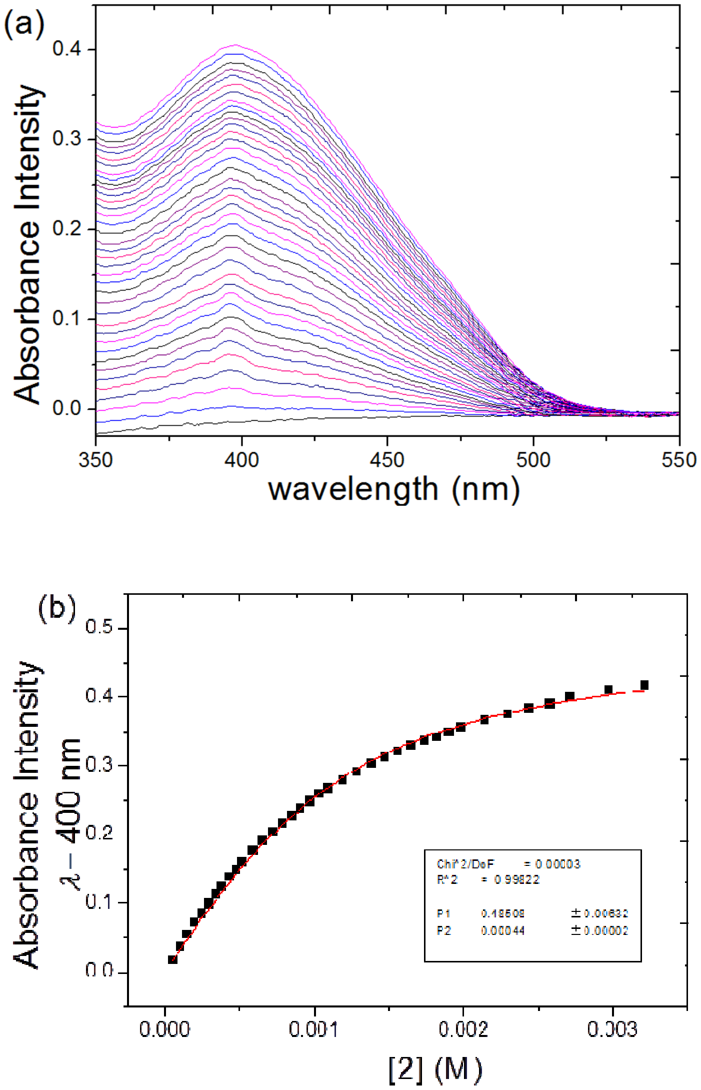


**Figure S6.** (a) The absorption spectral changes of **3** (1.00 mM) upon addition of **2** and (b) the absorbance intensity change at $\lambda$ = 400 nm upon addition of **2** (from 0 to 6.79 mM). The red solid line was obtained from the non-linear curve-fitting using Eq. S1.

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

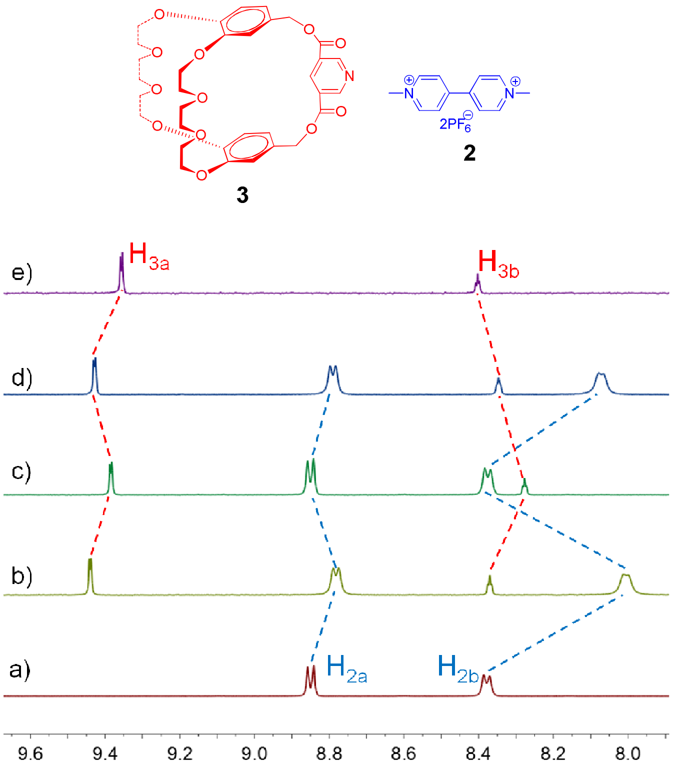


**Figure S7.** Partial $^1$H NMR spectra (400 MHz, dichloromethane-$d_2$/acetonitrile-$d_3$ (1:1, *v*/*v*), 293 K): (a) 2.00 mM **2**; (b) 2.00 mM **3** +2.00 mM **2**; (c) after addition 2.00 equiv of $KPF_6$ to b; (d) after addition 2.00 equiv of DB18C6 to c; (e) 2.00 mM **3**.

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

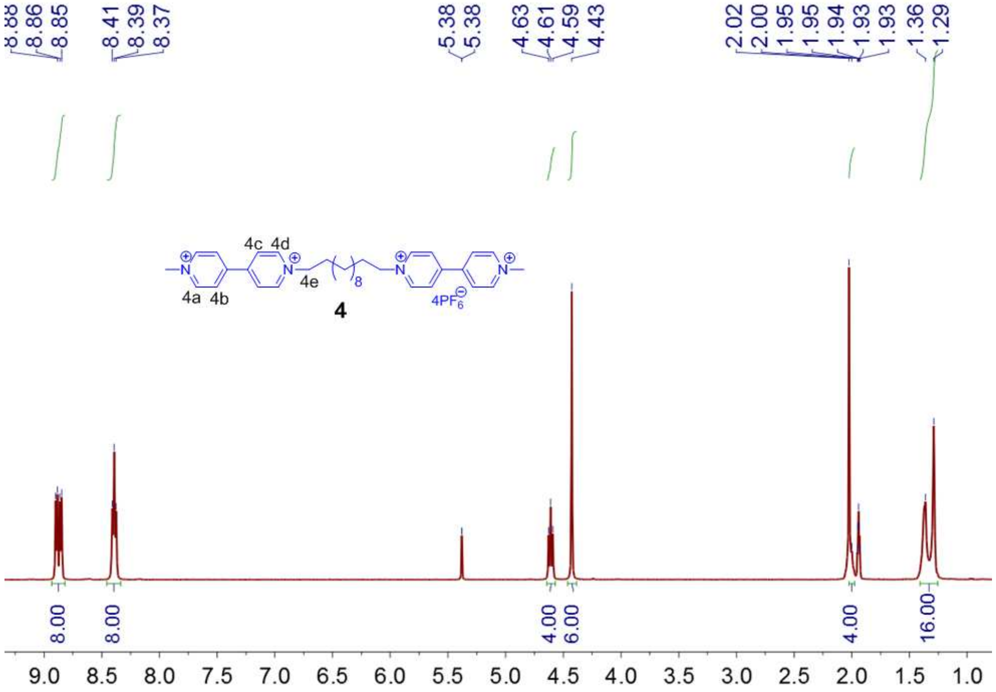


**Figure S8.** $^1$H NMR spectrum (400 MHz, dichloromethane-$d_2$/acetonitrile-$d_3$ (1:1, *v*/*v*), 293 K) of **4**.

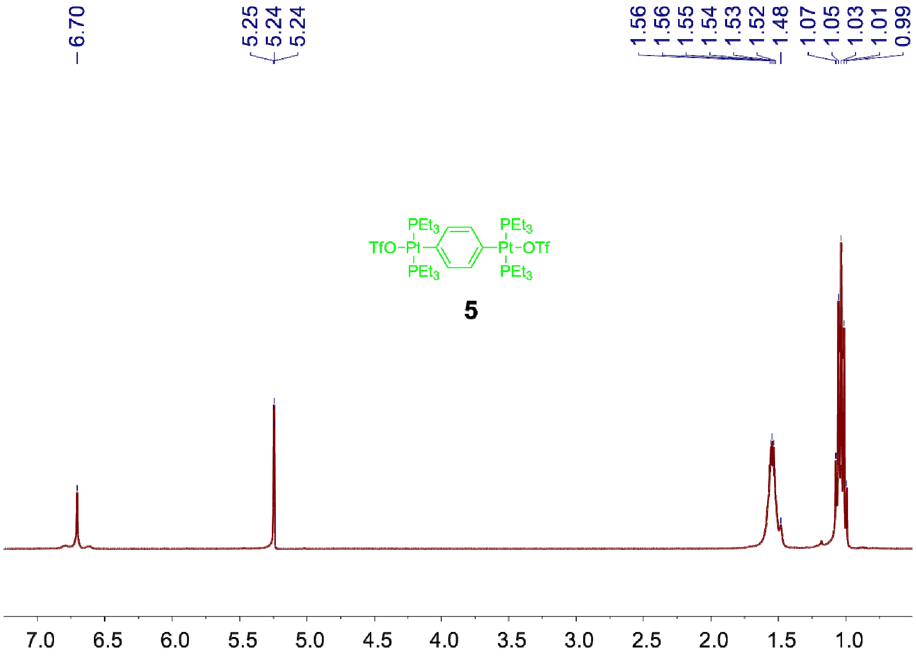
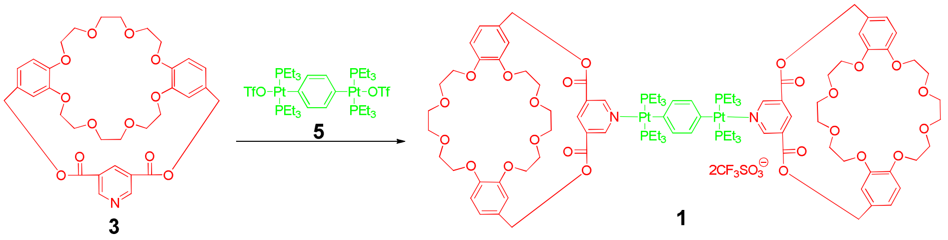


**Figure S9.** $^1$H NMR spectrum (400 MHz, dichloromethane-$d_2$, 293 K) of **5**.

### *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) $\delta$ (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 $^{31}P\{^1H\}$ NMR spectrum of **1** is shown in Figure S11. $^{31}P\{^1H\}$ NMR (s, 161.8 MHz, dichloromethane-$d_2$, 293K) $\delta$ (ppm): 12.85 (s, $^{195}Pt$ satellites, $^1J_{Pt\text{–}P}$ = 2703.7 Hz). ESI- TOF-MS for **1** is shown in Figure S12: $m/z$ 1108.89 for [**1** – 2OTf]$^{2+}$.

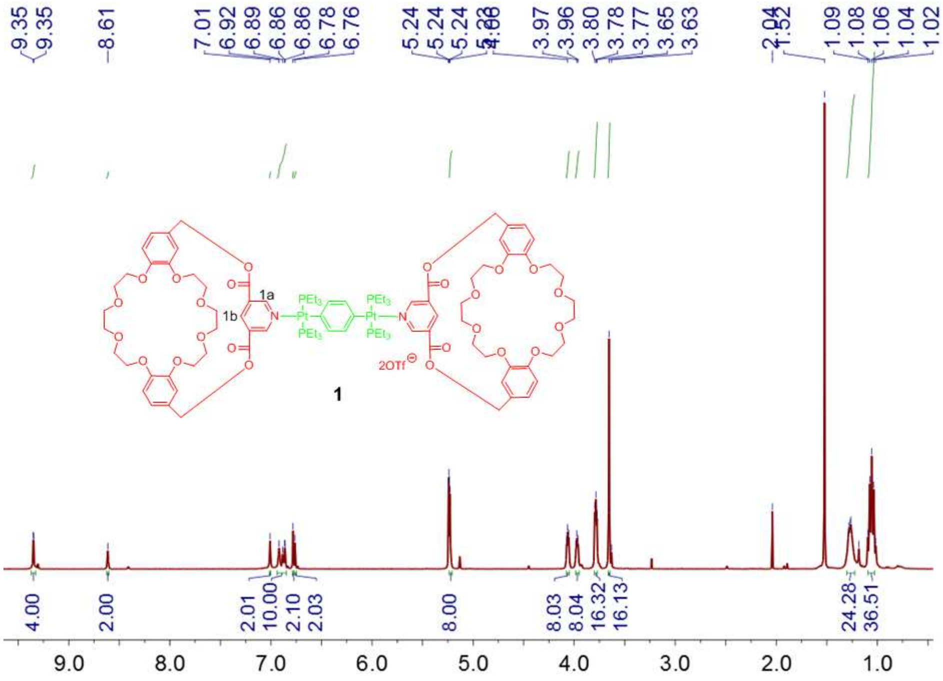


**Figure S10.** $^1H$ NMR spectrum (400 MHz, dichloromethane-$d_2$, 293 K) of **1**.

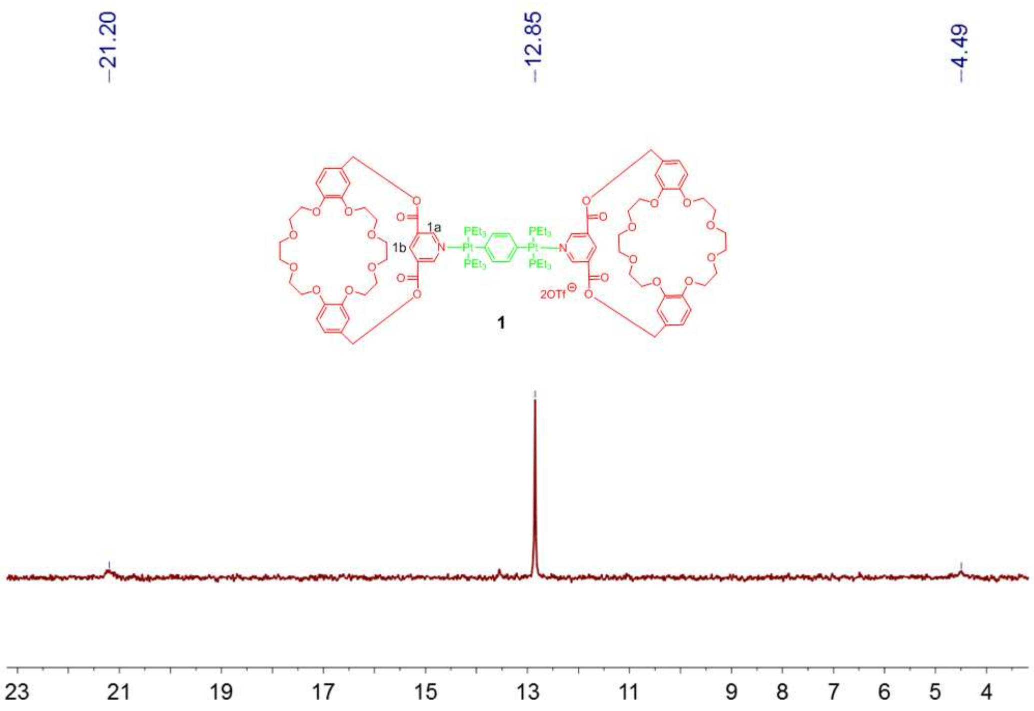


**Figure S11.** $^{31}P\{^{1}H\}$ NMR spectrum (161.8 MHz, dichloromethane-$d_2$, 293 K) of **1**.

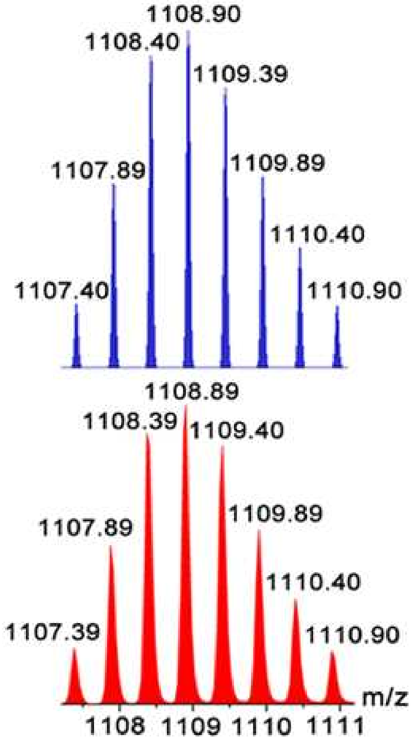


**Figure S12.** Experimental (red) and calculated (blue) ESI-TOF-MS spectra of **1** [M – $2OTf]^{2+}$.

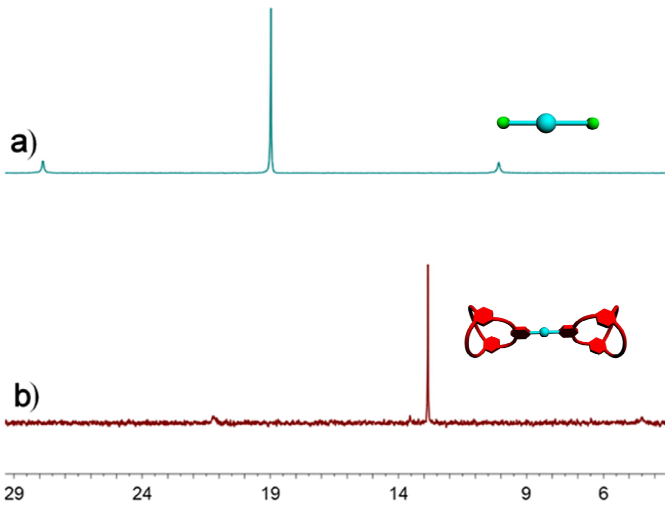


**Figure S13.** $^{31}P\{^{1}H\}$ NMR spectra (161.8 MHz, $CD_2Cl_2$, 293 K) of (a) bis-arm acceptor **5**, (b) bis-cryptand host **1**.

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

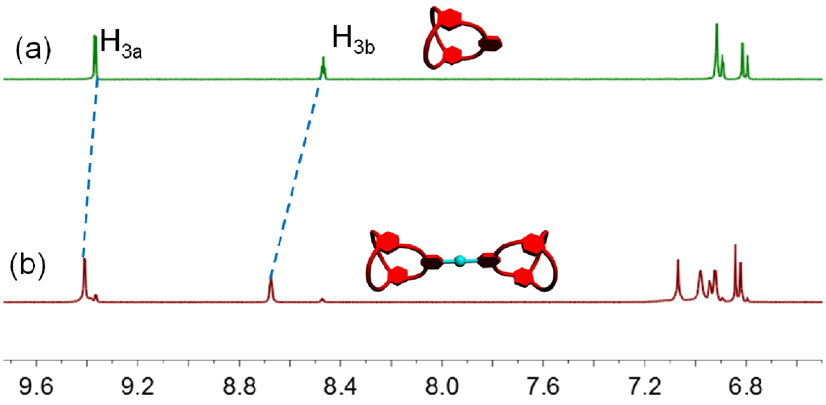


**Figure S14.** $^{1}H$ NMR spectra (400 MHz, dichloromethane-$d_2$, 293 K) of (a) bis-cryptand host **1** and (b) **3**.

The $^{31}P\{^{1}H\}$ NMR spectrum of **1**, for example, possesses a sharp singlet at ~12.85 ppm with concomitant $^{195}Pt$ satellites ($J_{Pt–P}$ = 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 $^{1}H$ 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 $[\mathrm{M} - 2\mathrm{OTf}]^{2+}$ 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 $^1$H NMR spectra of $\mathbf{3_2{\supset}4}$*

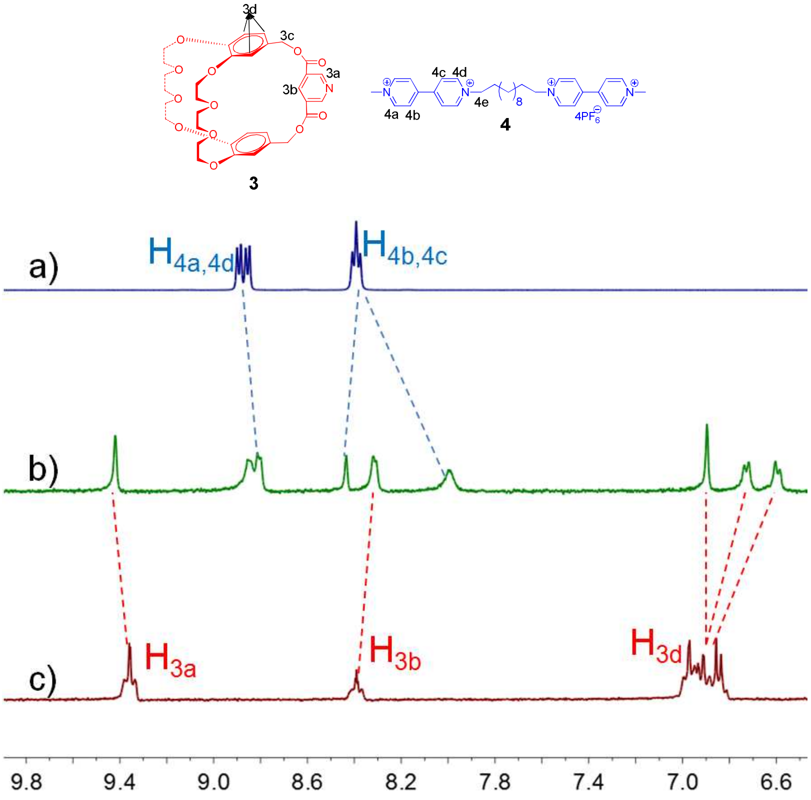
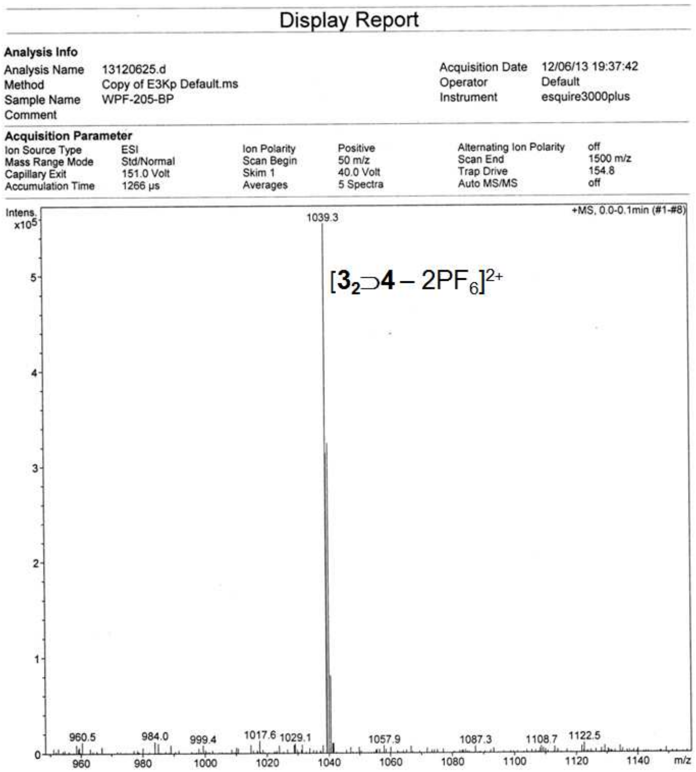


**Figure S15.** Partial $^1$H NMR spectra (400 MHz, dichloromethane-$d_2$/acetonitrile-$d_3$ (1:1, *v*/*v*), 293 K): (a) 4.00 mM **4**; (b) 8.00 mM **3** + 4.00 mM **4**; (c) ) 8.00 mM **3**.

### *11. LRESI mass spectrum of $\mathbf{3_2{\supset}4}$*



Display Report

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| Comment | | | |

**Acquisition Parameter**

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| Accumulation Time | 1266 µs | Averages | 5 Spectra | Auto MS/MS | off |

**Figure S16.** LRESI mass spectrum of $\mathbf{3_2{\supset}4}$.

## *12. $K^+$ caion responsive NMR of LSP*

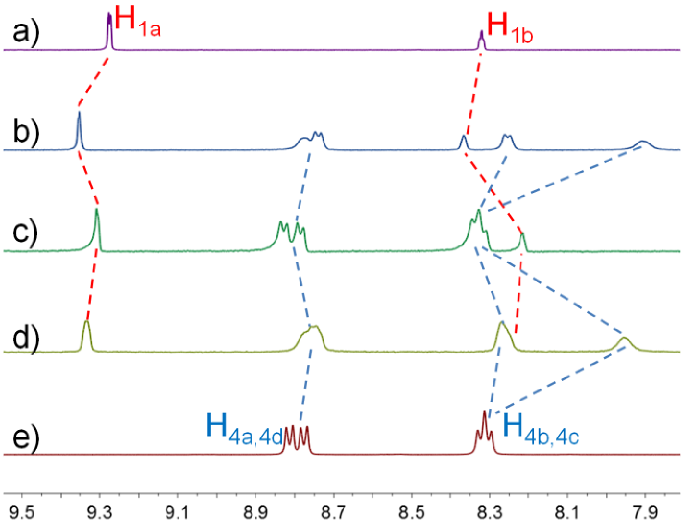

**Figure S17.** Partial $^1$H NMR spectra [400 MHz, dichloromethane-$d_2$/acetonitrile-$d_3$ (1:1, *v*/*v*), 293 K]: (a) 5.00 mM **1**; (b) 5.00 mM **1** + 5.00 mM **4**; (c) after addition 2.00 equiv of $KPF_6$ to b; (d) after addition 2.00 equiv of DB18C6 to c; (e) 5.00 mM **4**.

*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.