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Ion-controlled switchable complexation between pentiptycene-based tweezer-like hosts and self-folding guests

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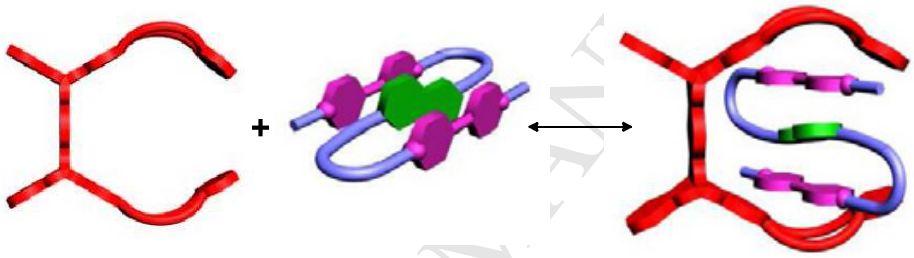
Ying Han,[a,b] Jia-Bin Guo,[a] Jing Cao[a] and Chuan-Feng Chen[a,*]

[a]*Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.* [b]*University of Chinese Academy of Sciences, Beijing 100049, China.*



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Ion-controlled switchable complexation between pentiptycene-based tweezer-like hosts and self-folding guests

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Abstract—A couple of self-folding A-D-A guests were synthesized, and it was found that the guests could be included by the pentiptycene-based tweezer-like hosts to form stable 1:1 complexes in solution, which have been evidenced by the ^{1}H NMR, ROESY 2D NMR and ESI MS spectra. Moreover, a potassium ion-controlled switchable process between the host and the self-folding guest was further achieved. © 2013 Elsevier Science. All rights reserved

1. Introduction

In host-guest chemistry, a permanent and challenging topic is to develop novel hosts with the capability of binding specific substrate species strongly and selectively.[1] During the past decades, chemists have designed and synthesized various macrocyclic hosts, including crown ethers,[2] cryptands,[3] calix[n]arenes,[4] cucurbit[n]urils,[5] and other macrocycles.[6] Undoubtedly, a new synthetic host could often provide a lot of opportunities in molecular recognition and self-assembly.

On the other hand, it was known that paraquat derivatives[7] have become some of the most common guests, and they have also been utilized for construction of different kinds of interlocked assemblies, such as pseudorotaxanes, rotaxanes, and catenanes. In addition, the foldamers have attracted much attention during the past two decades for they could not only mimic the structural features of biological macromolecules, but are also important in materials science.[8,9] However, the applications of the foldamers as guests in host-guest chemistry are still very limited. It might be because that the foldamer used as a guest is too large to complex with a classic macrocyclic host. Consequently, tweezer-like hosts[10] could be utilized for the purpose of inclusion with foldamer guests with large structures.

Recently, we found that the pentipytcene derivatives might be utilized as useful building blocks for the design and synthesis of novel hosts with specific structures and properties.[11] As a result, two pentiptycene-based tweezer-like hosts **1** and **2** (Figure 1) were synthesized.[12] They showed open central cavities, and thus could form stable complexes with tetracationic cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$) in different complexation modes.[12b] To further study the complexation of these synthetic hosts with large open cavities towards different kinds of organic guests, we herein report the complexation between two pentiptycene-based tweezer-like hosts **1** and **2** with self-folding A-D-A guests **3** and **4** in solution in details. Thus, we found that they could form 1:1 stable complexes respectively, in which the guests with '*S*' folding structures could all be included inside the central cavities of the hosts (Figure 1). Formation of the complexes was all proved by the ^{1}H NMR, ROESY 2D NMR, and ESI MS spectra. Moreover, it was also found that the binding and release of the guests in the complexes could be easily controlled by the addition and removal of potassium ions.

Keywords: Pentiptycene; Complexation; Tweezer-like host; Self-folding guest; Ion-controlled.

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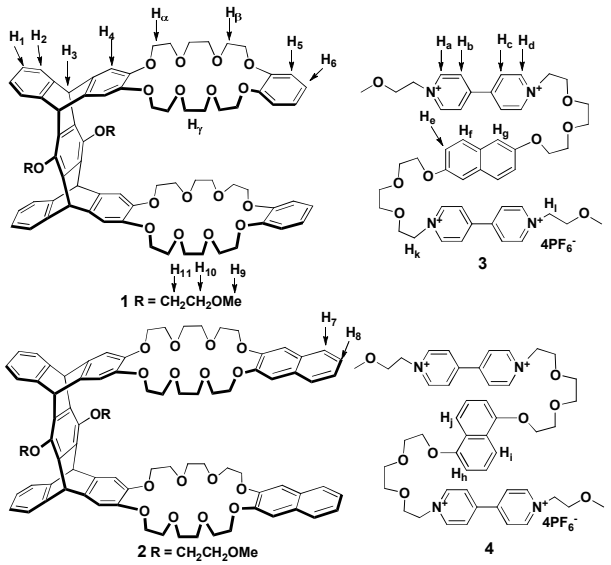
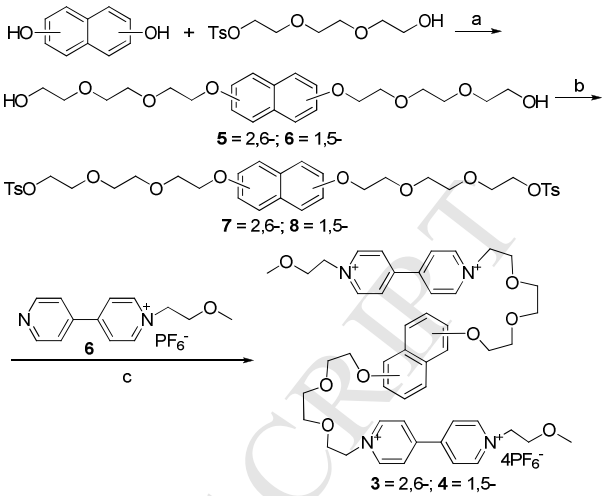


Figure 1. Structures and proton designations of hosts **1**, **2** and guests **3**, **4**.

2. Results and discussion

2.1 Synthesis of self-folding A-D-A guests 3 and 4. Synthesis of guests **3** and **4** is outlined in Scheme 1. Starting from the dihydroxynaphthalene, the self-folding A-D-A guests **3** and **4** linked by polyether chains could be conveniently synthesized in three steps. First, the reaction of dihydroxynaphthalene with 2-(2-(2-hydroxyethoxy)-ethoxy)ethyl 4-methylbenzenesulfonate in CH_3CN in the presence of K_2CO_3 could give compound **5** or **6**. Then, the reaction of **5** or **6** and tosyl chloride in the presence of Et_3N and DMAP gave bistosylate **7** or **8**, which was further reacted with 1-(2-methoxyethyl)-4-(pyridin-4-yl)pyridinium **6** to afford the target compound **3** or **4**. Compounds **3** and **4** were all characterized by the ^{1}H NMR, ^{13}C NMR, MS spectra, elemental analysis, and X-ray crystal structures.



Scheme 1. Synthesis of guests **3** and **4**. Reagents and conditions: (a) K_2CO_3, CH_3CN, reflux; (b) *p*-TsCl, Et_3N, DMAP, CH_2Cl_2, reflux; (c) (i) CH_3CN, reflux; (ii) NH_4PF_6, acetone.

2.2 Complexation between pentiptycene-based tweezer-like hosts and self-folding A-D-A guests in solution. Complexation between pentiptycene-based tweezer-like hosts and the self-folding A-D-A guests were first studied in solution by the ^{1}H NMR spectroscopic method. When we mixed the host **1** (3.0 mM) and 1.0 equiv of **3** in 1:1 (v/v) $CD_3CN/CDCl_3$, a deep orange solution formed immediately because of charge transfer between the electron-rich aromatic rings of the host and the electron-poor pyridinium rings of the guest.[13] As shown in Figure 2, the ^{1}H NMR spectrum of a 1:1 mixture of **1** and **3** showed only one set of different signals from those of the separated host and guest, which suggested that a new complex **1·3** was formed, and the complexation between **1** and **3** was a fast exchange process. Especially, it was found that the protons H_a, H_b, H_c and H_d of the paraquat ring showed a upfield shift due to the shielding effect of aromatic rings in **1**, and H_4 proton signals of the host also shifted upfield. These observations suggested that a stable complex between host **1** and guest **3** might be formed in solution. The ^{1}H NMR spectroscopic titrations further afforded a quantitative estimate for the complexation between host **1** and guest **3** by monitoring the changes of the chemical shift of the proton H_4 of **1**. The results showed that 1:1 complex between **1** and **3** was formed by a mole ratio plot. Accordingly, the apparent association constant $K_{a,exp}$ was calculated to be $0.5(\pm0.01)\times10^3$ M^{-1} by the Scatchard plot.[13, 14]

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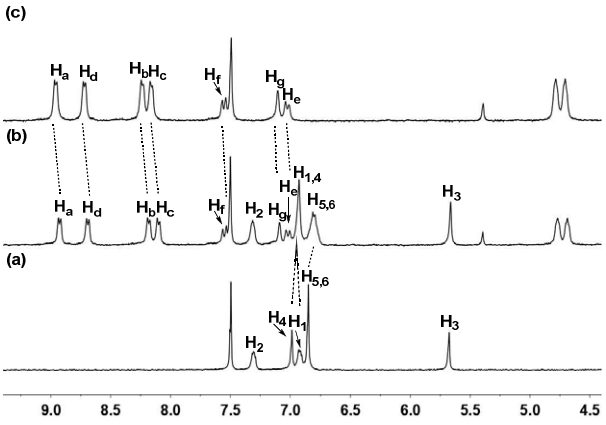

Figure 2. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, v/v, 295K) of (a) free host **1**, (b) **1** and 1.0 equiv. of **3**, (c) free guest **3**. $[\mathbf{1}]_0$ = 2.0 mM.

Moreover, we identified all protons of pentiptycene-based tweezer-like host **1** and the self-folding A-D-A guest **3** by the ^{1}H-^{1}H COSY spectrum.[13] The 2D ROESY spectral experiment[13] of complex **1·3** was further carried out to investigate the complexation between the host and the guest. The results showed that the cross-peaks between protons H_a and H_d in the bipyridinium ring of **3** and the proton H_γ in crown ether units, H_{10} in R group of **1** were found (Figure 3), which suggested that the guest could thread the central cavity of host **1** to form a 1:1 complex. Meanwhile, the cross-peaks between protons H_k and H_l in the guest **3** and the protons H_γ, H_β in crown ether units, H_{10} in R group of **1** were also found, and we still found the cross-peaks between the proton of guest **3** and H_5, H_6 in host **1**. This result also showed a stable complex formed between pentiptycene-based tweezer-like host **1** and self-folding A-D-A guest **3**.

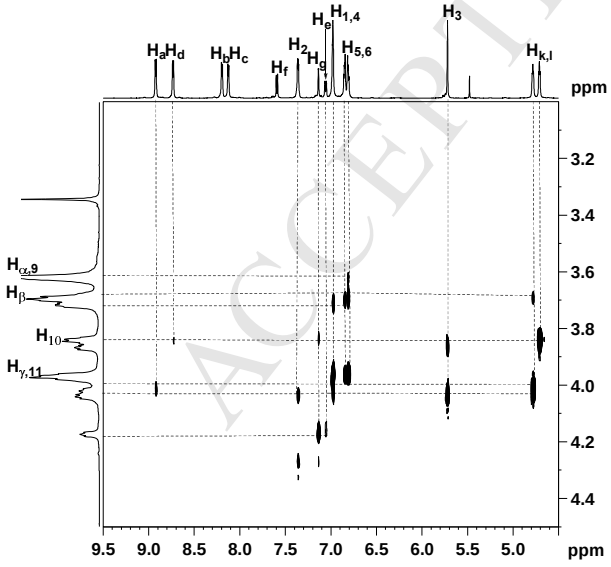

Figure 3. ^{1}H-^{1}H ROESY spectrum (300 MHz, CD_3CN, v/v, 295 K) of **1** and 1.0 equiv. of **3**. $[\mathbf{1}]_0$ = 2.0 mM.

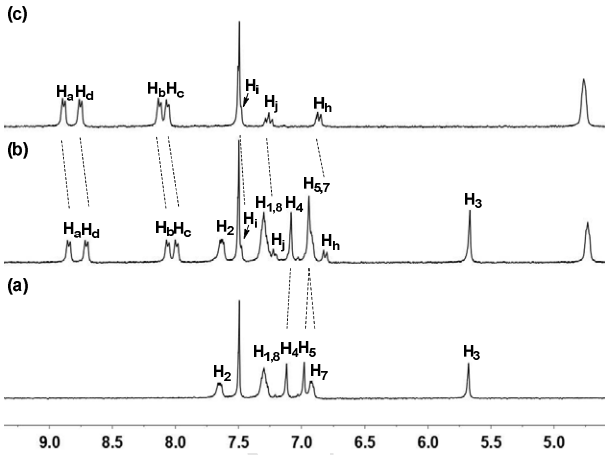

Figure 4. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, v/v, 295K) of (a) free host **2**, (b) **2** and 1.0 equiv. of **4**, (c) free guest **4**. $[\mathbf{2}]_0$ = 2.0 mM.

Similarly, we found that the complexation between host **2** and guest **4** was also a fast exchange process.[13] Correspondingly, the protons H_a, H_b, H_c and H_d of the paraquat ring showed an upfield shift due to the shielding effect of aromatic rings in **2**, while H_4 proton signals also shifted upfield (Figure 4). Moreover, the stoichiometry of the complex was determined to be 1:1 by a mole ratio plot, and the association constant K_a for the complex was calculated to be $0.4(\pm0.01)\times10^3$ M^{-1} by the Scatchard plot. This result was similar to the complexation between **1** and **3**, which could form 1:1 stable complex.

We also tested the complexation between host **1** and guest **4**; host **2** and guest **3** in solution by the NMR spectroscopy. The results showed that similar to the complexation modes described above, and the self-folding A-D-A guests **4** or **3** could also thread the central cavity of the pentiptycene-based tweezer-like host **1** or **2**, respectively, to form 1:1 complex. Moreover, the association constants for the complexes were all calculated by the Scatchard plot, and the results were summarized in Table 1. It was found that almost no obvious differences between the association constants of the complexes were shown for the small structural differences of the hosts and the guests.

Table 1. Summary of the stoichiometries and association constants of the complexes

Compound	Stoichiometry (H/G)	K_a $[M^{-1}]^a$
1·3	1:1	$0.5(\pm0.01)\times10^3$
1·4	1:1	$0.5(\pm0.01)\times10^3$
2·3	1:1	$0.4(\pm0.01)\times10^3$
2·4	1:1	$0.4(\pm0.01)\times10^3$

[a] From the ^{1}H NMR titration experiments in $CD_3CN/CDCl_3$ (1:1, v/v).

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2.3 Conformations of self-folding A-D-A guests in the solid state. We tried our best to obtain a single crystal suitable for X-ray diffraction analysis.[13] However after trying several times, we didn't obtain single crystals of the complexes between the pentiptycene-based tweezer-like host and the self-folding A-D-A guest. It might be due to the flexibility of the pentiptycene-based tweezer-like hosts so that the molecules could pack difficultly. Instead, we obtained the crystal structures of self-folding A-D-A guests **3** and **4**, which provided us an opportunity to investigate their structures in the solid state.

First, we obtained a single crystal of guest **3** suitable for X-ray diffraction analysis by vapor diffusion of diisopropyl ether into a solution of **3** in CH_3CN. As shown in Figure 5, since the bipyridinium ring was an electron-dificient group, while the naphthalene ring was an electron-rich group, π-π interactions between them existed which could result in the guest **3** to take a '*S*' conformation. There still existed multiple C-H···F hydrogen bonding interactions between the protons of the bipyridinium rings of the guests and PF_6^- counterions with the distances of 2.596 (a), 2.594 (b) and 2.597 Å (c), respectively, which might play an important role in formation of the self-folding structure of the guest as well. In addition, it was found that the two pyridinium rings of the guest were all distorted by the dihedral angle of 40.72˚, and the plane composed by bipyridinium rings was almost vertical to the plane of naphthalene ring.

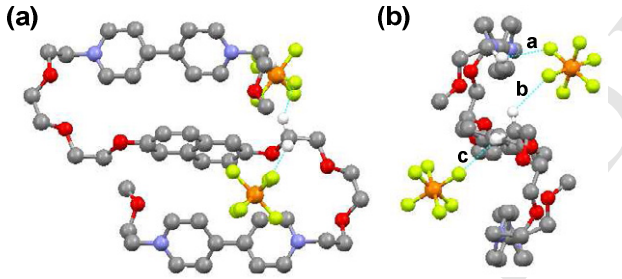

Figure 5. Top view (a) and side view (b) of the crystal structure of guest **3**. Blue lines denote the non-covalent interactions between the guest and PF_6^- counterions. Solvent molecules and hydrogen atoms not involved in the non-covalent interactions were omitted for clarity.

Similarly, we also obtained the single crystal of guest **4** suitable for X-ray diffraction analysis from the CH_3CN solution of **4**. As shown in Figure 6, it was found that the guest **4** also took a '*S*' conformation probably due to the π-π interaction between the electron-dificient bipyridinium ring and the electron-rich of naphthalene group. But it was found that the plane composed by bipyridinium rings in **4** was parallel to the plane of the naphthalene ring, and the two pyridinium rings of guest were distorted by the dihedral angle of 18.85˚, which are different from those of molecule **3**. Moreover, there also existed C-H···F hydrogen bonding interactions between the protons of the bipyridinium rings and the fluorine atoms of PF_6^- counterions with the distances of 2.448 (a) and 2.310 Å (b), respectively.

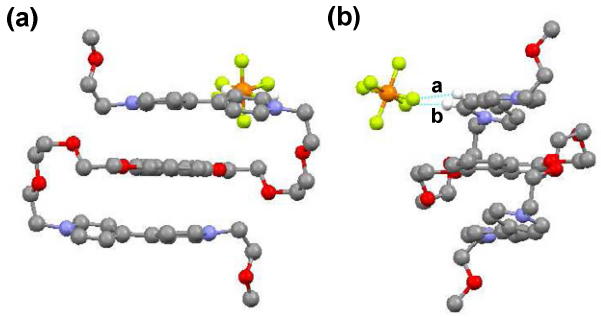

Figure 6. Top view (a) and side view (b) of the crystal structure of guest **4**. Blue lines denote the non-covalent interactions between the guest and PF_6^- counterions. Solvent molecules and hydrogen atoms not involved in the non-covalent interactions were omitted for clarity.

2.4 ESI MS studies on formation of the complexes. The electrospray ionization (ESI) mass spectrometry was also used to characterize the complexes between pentiptycene-based tweezer-like hosts and self-folding A-D-A guests.[13] Consequently, the strongest peak at *m/z* 535.57 for [**1**·**3**-$4PF_6$]$^{4+}$, 762.25 for [**1**·**3**-$3PF_6$]$^{3+}$ and 1215.95 for [**1**·**3**-$2PF_6$]$^{2+}$ were found by using the solution of **1** and **3** in 1:1 (v/v) chloroform and acetonitrile, which provided another support for formation of 1:1 stable complex between host **1** and self-folding A-D-A guest **3**. Similarly, formation of the 1:1 complexes between pentiptycene-based tweezer-like hosts and self-folding A-D-A guests were also evidenced by the ESI mass spectra, in which the strong peaks at *m/z* 535.50, 762.26, 1215.84, 560.55, 795.61, 1266.05, 560.54, 795.65 and 1266.05 for [**1**·**4**-$4PF_6$]$^{4+}$, [**1**·**4**-$3PF_6$]$^{3+}$, [**1**·**4**-$2PF_6$]$^{2+}$, [**2**·**3**-$4PF_6$]$^{4+}$, [**2**·**3**-$3PF_6$]$^{3+}$, [**2**·**3**-$2PF_6$]$^{2+}$, [**2**·**4**-$4PF_6$]$^{4+}$, [**2**·**4**-$3PF_6$]$^{3+}$ and [**2**·**4**-$2PF_6$]$^{2+}$, respectively, were all observed.[13]

2.5 K^+ ion-controlled binding and release of the guest in the complex. According to the previous work of our group,[15] we found that DB30C10 moieties could bind potassium ions to form the stable complex, and the consequent complexation of cations would introduce extra electrostatic repellent force to the cationic organic guest molecules and dissociate the previously formed host-guest complex. Thus, the result made us further investigate the potassium ion-controlled release and binding process of the guest molecule in the complex of pentiptycene-based tweezer-like host **1** and self-folding A-D-A guest **3** by a series of ^{1}H NMR experiments.

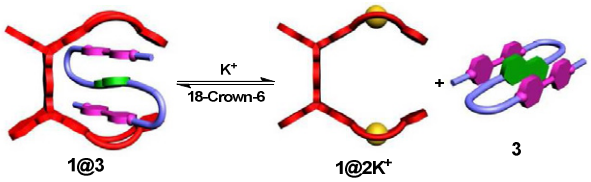

Figure 7. Cartoon description of the K^+ ion-controlled switchable complexation.

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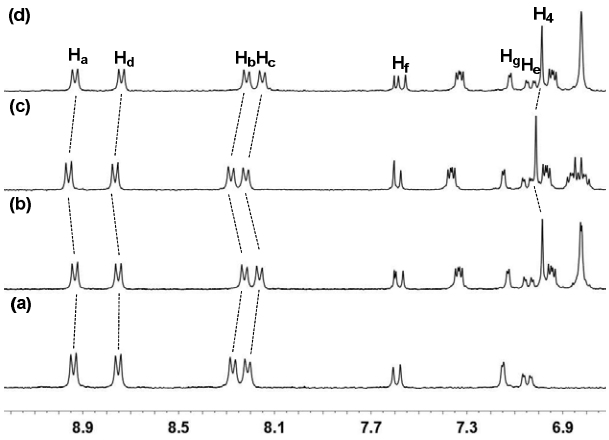

Figure 8. Partial ^{1}H NMR spectra (CD_3CN, 300 MHz) of (a) free guest **3**, (b) **1** and 1.0 equiv. of **3**, (c) to the solution of b was added 4.0 equiv. of KPF_6, and (d) to the solution of c was added 6.0 equiv. of [18]-crown-6, $[\mathbf{1}]_0$ = 2.0 mM.

As shown in Figure 8c, when 4.0 equiv. of KPF_6 were added into solution of a complex **1·3**, the proton signals of the complex disappeared, while the proton signals of the decomplexated species were observed. But when 6.0 equiv. of 18-crown-6 ether was added into the above system, the proton signals of complex **1·3** were recovered (Figure 8d). Thus, the ion-controlled binding and release of guest **3** in the complex could be easily performed by adding and removing the potassium ions.

3. Conclusions

In conclusion, we have synthesized a couple of new guests **3** and **4** with the self-folding A-D-A structures, and demonstrated that the pentiptycene-based tweezer-like hosts **1** and **2** could form 1:1 stable complexes with guests **3** and **4** in solution. The formation of the complexes was proved by the ^{1}H NMR, ROESY 2D NMR, and ESI MS spectra. Moreover, it was found that the binding and release of the guests in the complexes could be easily controlled by the addition and removal of potassium ions. Based on these developed host-guest complexation, our further studies will focus on the applications of the novel synthetic host in molecular assembly and molecular machines, which are now in progress.

4. Experimental

4.1. General

Melting points, taken on an electrothermal melting point apparatus, are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a DMX300 NMR. Tetramethylsilane (TMS) was used as an internal standard, with chemical shifts expressed in parts per million (ppm) downfield from the standard. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. ESI mass spectra were obtained on a Finnigan Surveyor MSQ Plus mass spectrometer. Elementary analyses were performed in the Analytic Laboratory of this Institute. Flash column chromatography was carried out with silica gel (100-200 mesh). Other reagents and solvents were purchased from common commercial sources, and were used as received or purified by distillation from appropriate drying agents.

Compounds **5-8**[16-17] were prepared according to the published procedures.

4.2. General procedure for the synthesis of 3 and 4

A mixture of naphthalene dimethylbenzenesulfonate (0.5 mmol) and 1-(2-methoxyethyl)-[4,4'-bipyridin]-1-ium hexafluorophosphate(V) (1.0 mmol) in CH_3CN (30 mL) was heated under reflux for 3 days, and then the solvent was removed under reduced pressure. The residue was dissolved in acetone, and then added a concentrated aqueous solution of NH_4PF_6. After 2 h, the solvent was removed, and the solid was washed with water to give crude hexafluorophosphate, which was further recrystallized from CH_2Cl_2 and CH_3CN to give the target product.

4.2.1. Compound 3: Yellow solid, 85% yield. Mp 175~178 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 9.36 (d, J = 6.4 Hz, 4H), 9.16 (d, J = 6.4 Hz, 4H), 8.65 (d, J = 6.3 Hz, 4H), 8.59 (d, J = 6.3 Hz, 4H), 7.61 (d, J = 8.9 Hz, 2H), 7.20 (s, 2H), 7.06 (d, J = 8.8 Hz, 2H), 5.13-5.09 (m, 4H), 5.07-4.95 (m, 4H), 4.25-4.20 (m, 8H), 4.08-3.94 (m, 4H), 3.89-3.87 (m, 4H), 3.82-3.70 (m, 8H), 3.35 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6): δ 156.3, 150.8, 147.4, 147.1, 130.6, 129.3, 127.5, 120.0, 108.0, 100.9, 71.2, 71.1, 71.0, 70.4, 69.7, 68.5, 62.6, 59.1, 55.0. MALDI-TOF MS: *m/z* 820.7 for $[M\text{-}4PF_6^-]^{4+}$, 965.7 for $[M\text{-}3PF_6^-]^{3+}$. Elemental analysis calcd for $C_{48}H_{60}F_{24}N_4O_8P_4\cdot 3H_2O$: C 39.63, H 4.57, N 3.85; found: C 40.01, H 4.36, N 3.98.

4.2.2. Compound 4: Purple solid, 11% yield. Mp 167~169 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ 8.83 (d, J = 6.6 Hz, 4H), 8.73 (d, J = 6.6 Hz, 4H), 8.12 (d, J = 6.3 Hz, 4H), 8.05 (d, J = 6.3 Hz, 4H), 7.47 (d, J = 8.4 Hz, 2H), 7.25 (m, 2H), 6.87 (d, J = 7.8 Hz, 2H), 4.75 (s, 8H), 4.27-4.23 (m, 4H), 4.03-3.89 (m, 12H), 3.73 (m, 8H), 3.33 (s, 6H). ^{13}C NMR (75 MHz, acetone-d_6): δ 155.1, 150.5, 147.1, 146.8, 127.4, 127.3, 127.1, 126.9, 114.9, 107.2, 71.5, 71.1, 70.8, 70.6, 69.4, 69.1, 62.6, 62.5, 59.4. ESI MS: *m/z* 205.6 for $[M\text{-}4PF_6^-]^{4+}$, 322.4 for $[M\text{-}3PF_6^-]^{3+}$, 555.8 for $[M\text{-}2PF_6^-]^{2+}$. Elemental analysis calcd for $C_{48}H_{60}F_{24}N_4O_8P_4$: C 41.15, H 4.32, N 4.00; found: C 41.06, H 4.37, N 4.11.

4.3. CCDC 923288 (**3**) and CCDC 923289 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

4.3.1 Crystal data for **3**: $C_{24}H_{30}F_{12}N_2O_4P_2$, M_w = 700.44, crystal size 0.32 x 0.21 x 0.20 mm^3, triclinic, space group *P-1*, a = 8.345 (3) Å, b = 13.498 (4) Å, c = 13.974 (4) Å, α = 71.754 (10)° β = 84.234 (12)° γ = 76.011 (11)°, V =

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1450.0 (7) Å^3, Z = 2, D_c = 1.604 Mg/m^3, T = 173 (2) K, μ = 0.262 mm^{-1}, 12846 reflections measured, 6584 unique (R_{int} = 0.0495), final R indices [I > 2σ(I)]: R_1 = 0.0759, wR_2 = 0.2194, R indices (all data): R_1 = 0.0856, wR_2 = 0.2267.

4.3.2 Crystal data for **4**: $C_{56}H_{66}F_{24}N_6O_8P_4{\cdot}CH_3CN$, M_w = 1482.99, crystal size 0.52 x 0.40 x 0.35 mm^3, triclinic, space group *P-1*, a = 10.789 (2) Å, b = 11.294 (2) Å, c = 13.711 (3) Å, α = 95.52 (3)° β = 108.99 (3)° γ = 93.16 (3)°, V = 1565.8 (5) Å^3, Z = 1, D_c = 1.573 Mg/m^3, T = 173(2) K, μ = 0.249 mm^{-1}, 11449 reflections measured, 5434 unique (R_{int} = 0.0271), final R indices [I > 2σ(I)]: R_1 = 0.0431, wR_2 = 0.1097, R indices (all data): R_1 = 0.0458, wR_2 = 0.1118.

Acknowledgments

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Supplementary material

Copies of ^{1}H and ^{13}C NMR spectra for new compounds. ^{1}H-^{1}H COSY spectra and ROESY spectra for the complexes. Determination of the association constants. ESI-MS spectra for the complexes. This material associated with this article can be found, in the online version, at doi: 10.1016/j.tet. 2013.xx.xxx.

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Supplementary materials

Ion-controlled switchable complexation between pentiptycene-based tweezer-like hosts and self-folding guests

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Contents

1. Characterization data of new compounds

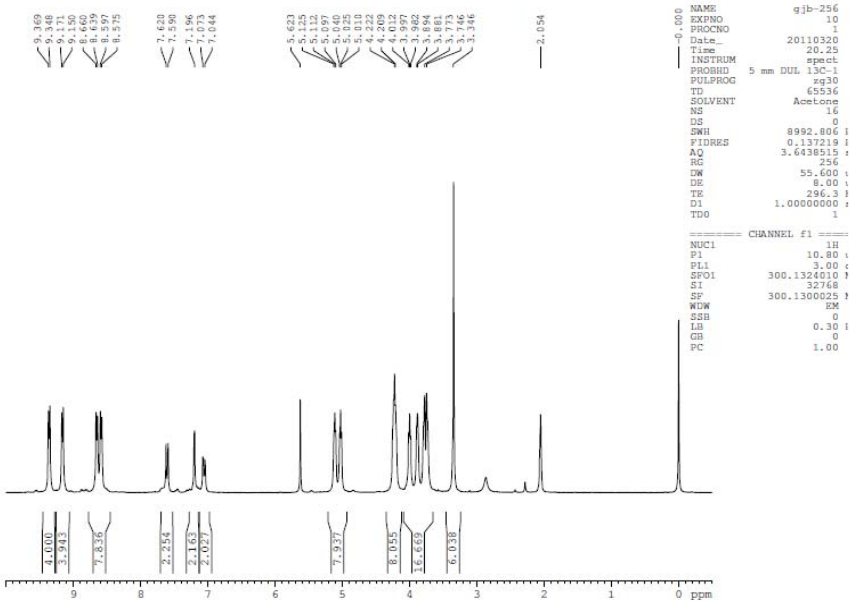


Figure S1. ^{1}H NMR spectrum (300 MHz, acetone-d_6) of **3**.

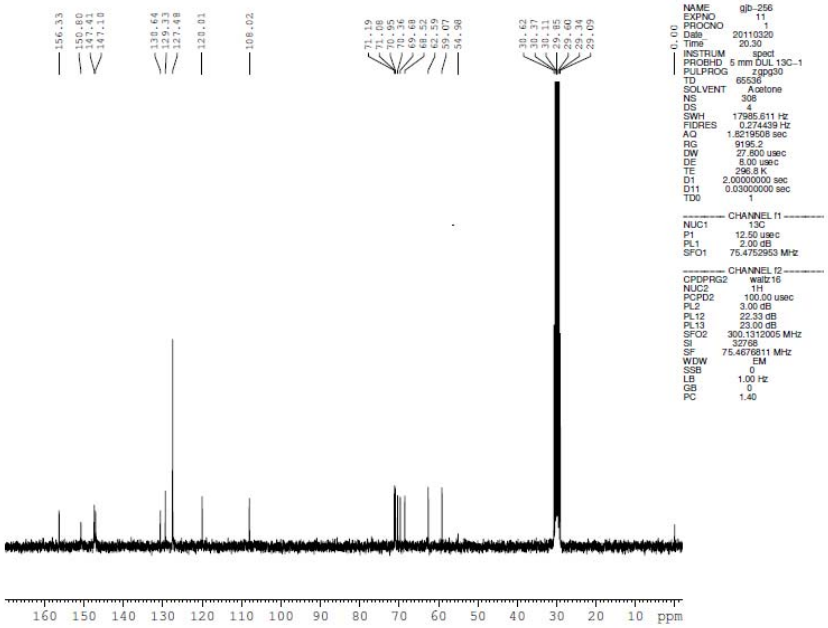


Figure S2. ^{13}C NMR spectrum (75 MHz, acetone-d_6) of **3**.

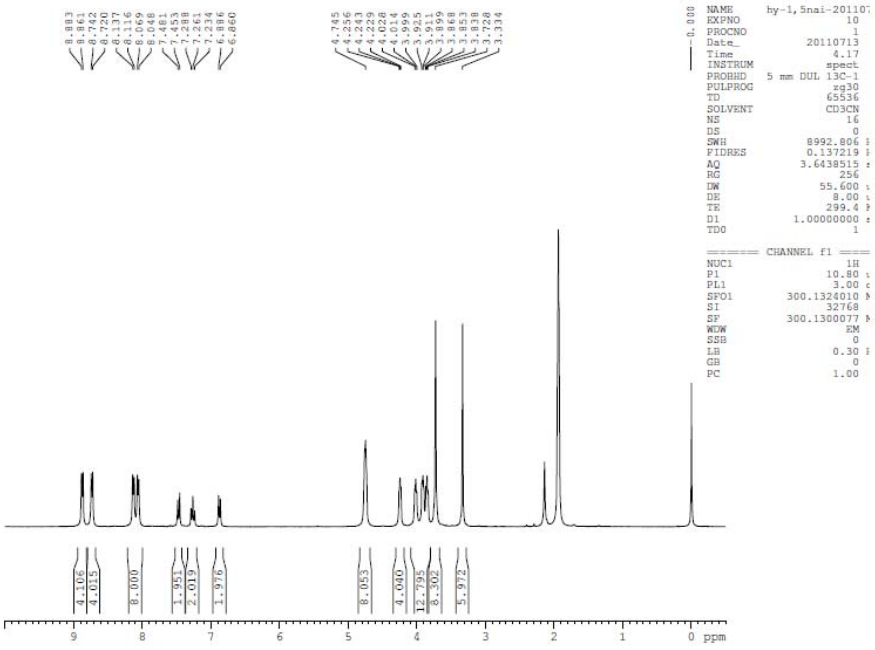


Figure S3. ^{1}H NMR spectrum (300 MHz, CD_3CN) of **4**.

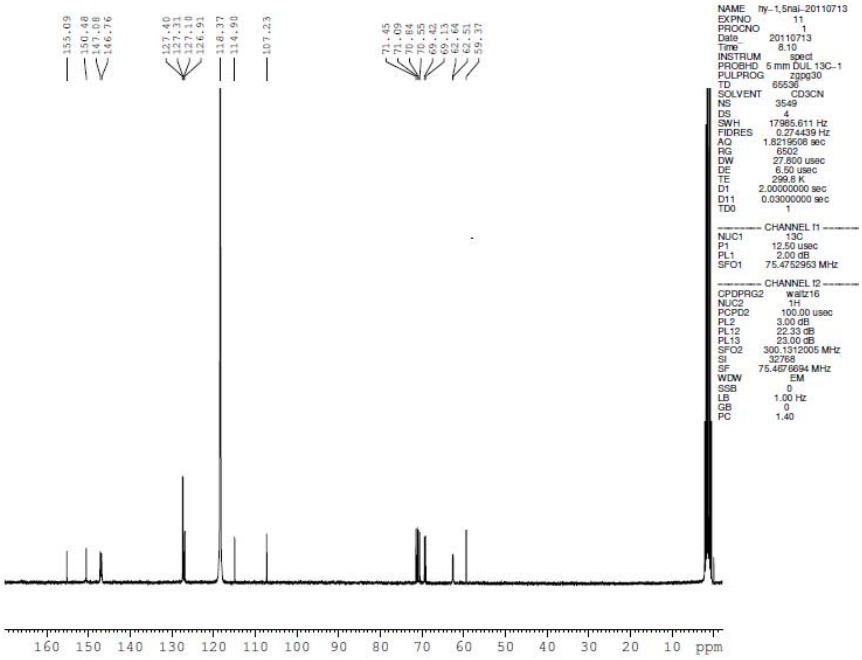


Figure S4. ^{13}C NMR spectrum (75 MHz, CD_3CN) of **4**.

2. ^{1}H-^{1}H COSY and 2D ROESY NMR spectra of the complexes

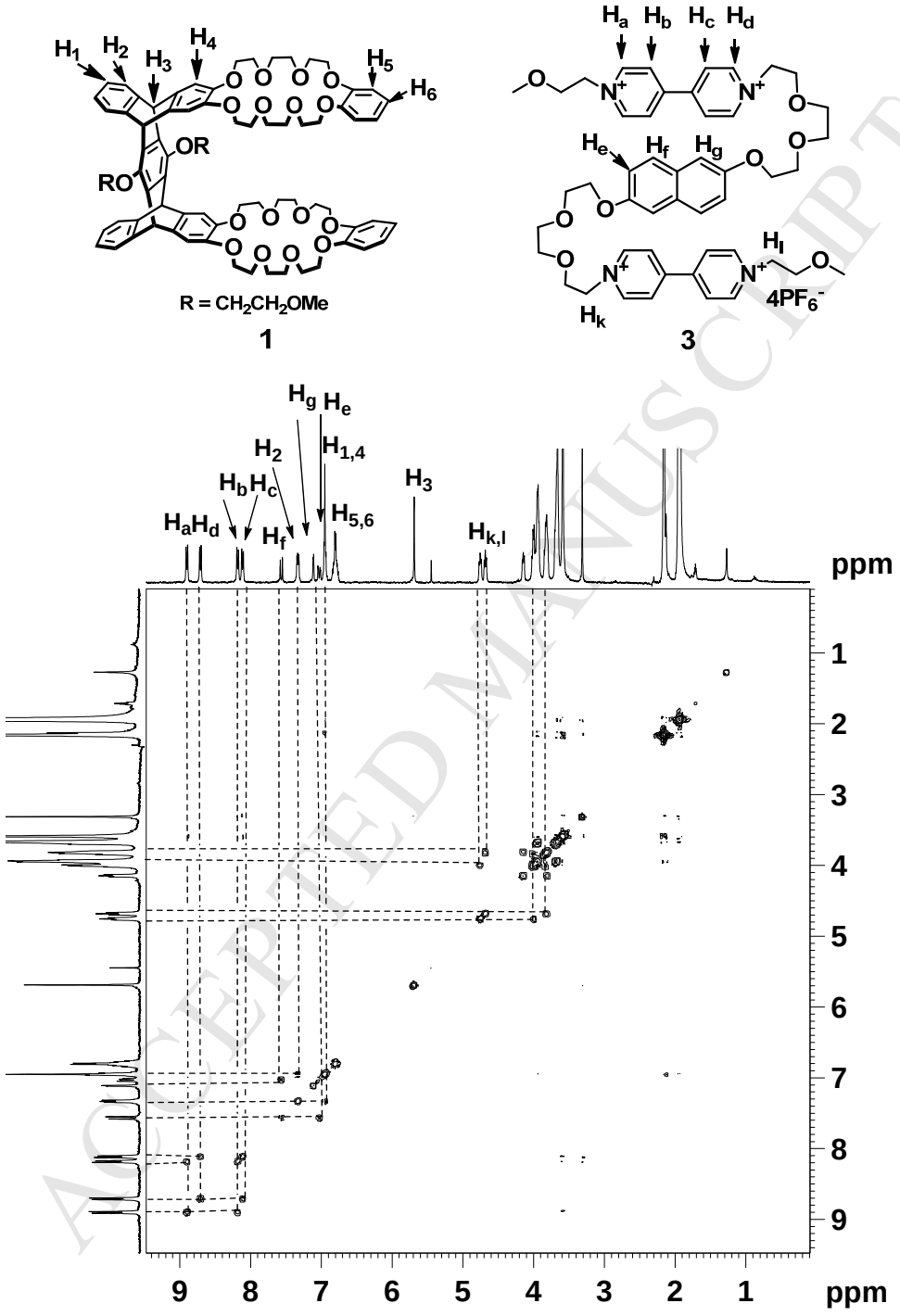


Figure S5. ^{1}H-^{1}H COSY spectrum (300 MHz, CD_3CN, v/v, 295 K) of **1** and 1.0 equiv. of **3**. $[\mathbf{1}]_0$ = 2.0 mM.

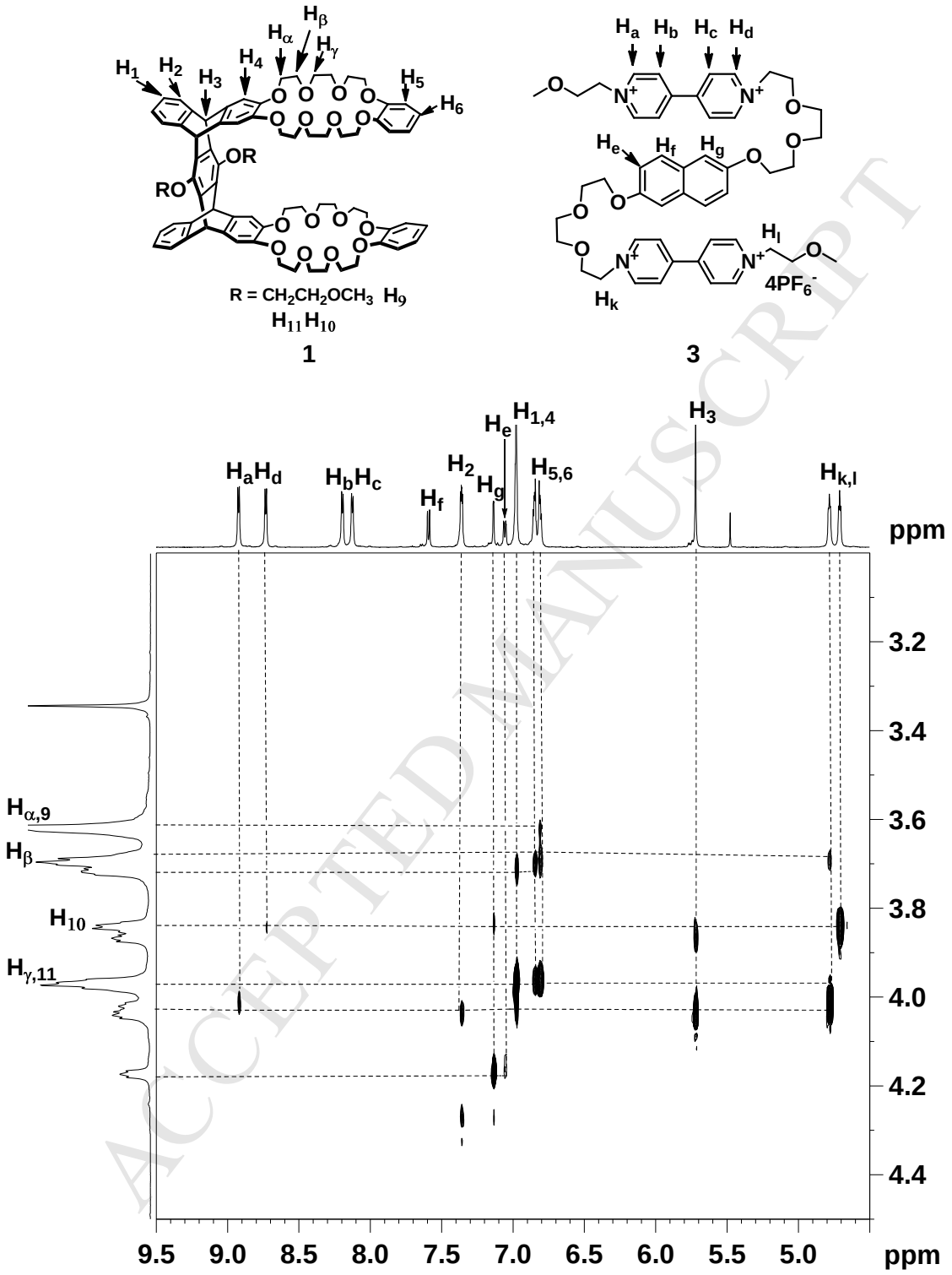


Figure S6. ^{1}H-^{1}H ROESY spectrum (300 MHz, CD_3CN, v/v, 295 K) of **1** and 1.0 equiv. of **3**. $[\mathbf{1}]_0$ = 2.0 mM.

3. ^{1}H NMR spectroscopic titrations of the complexes

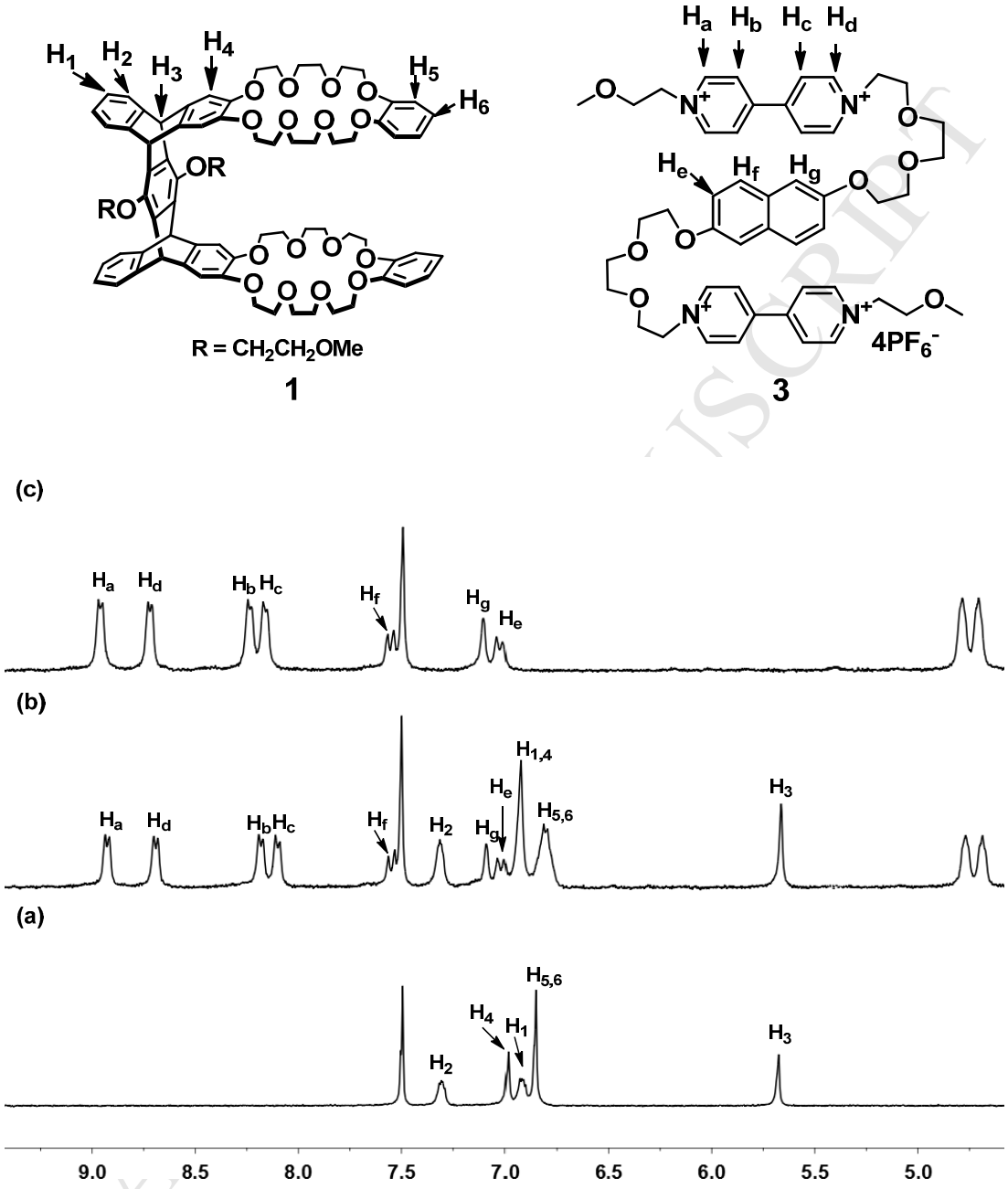


Figure S7. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$=1:1, v/v, 295K) of (a) free host **1**, (b) **1** and 1.0 equiv. of **3**, (c) free guest **3**. $[\mathbf{1}]_0$ = 2.0 mM.

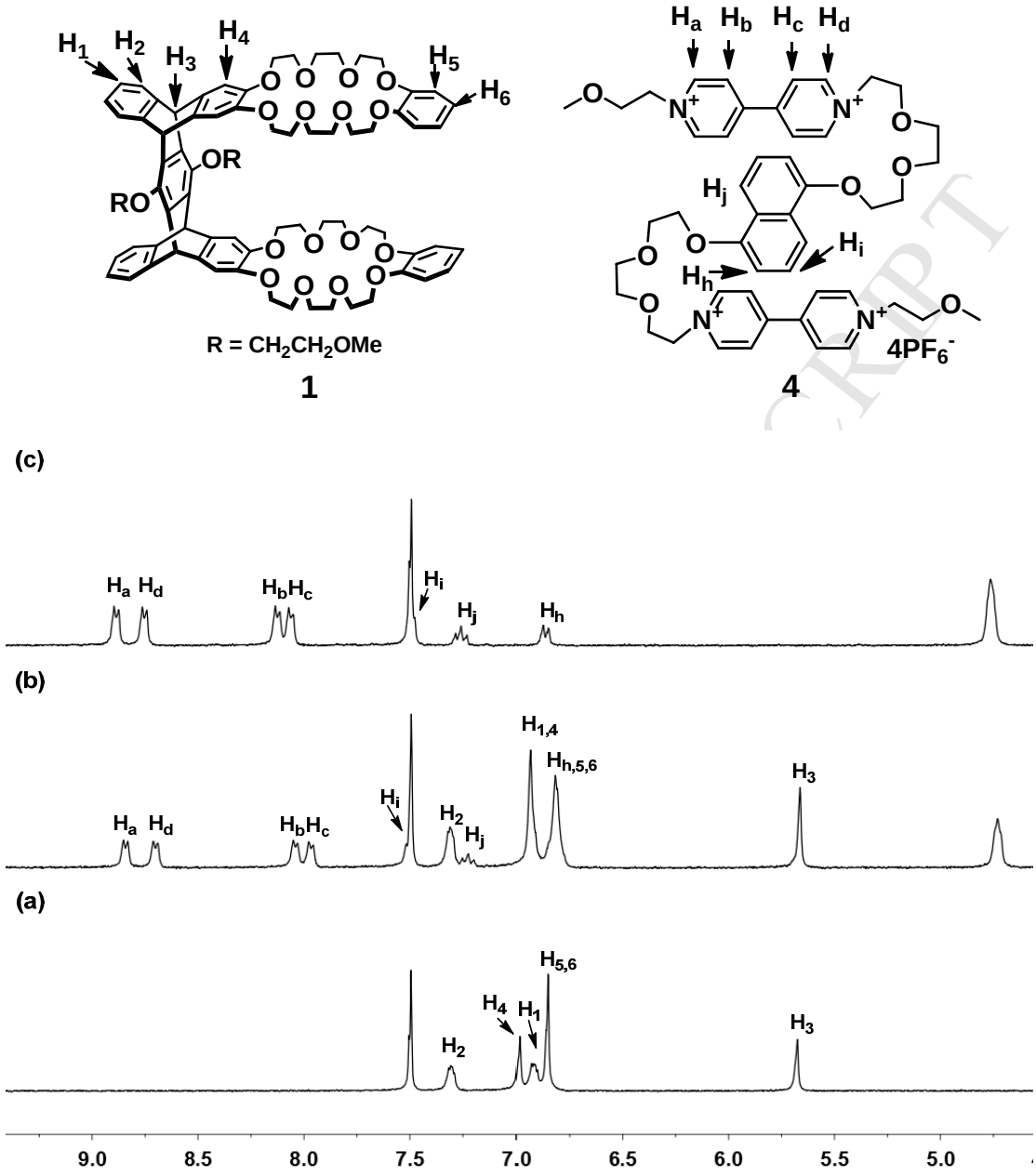


Figure S8. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$=1:1, v/v, 295K) of (a) free host **1**, (b) **1** and 1.0 equiv. of **4**, (c) free guest **4**. $[\mathbf{1}]_0$ = 2.0 mM.

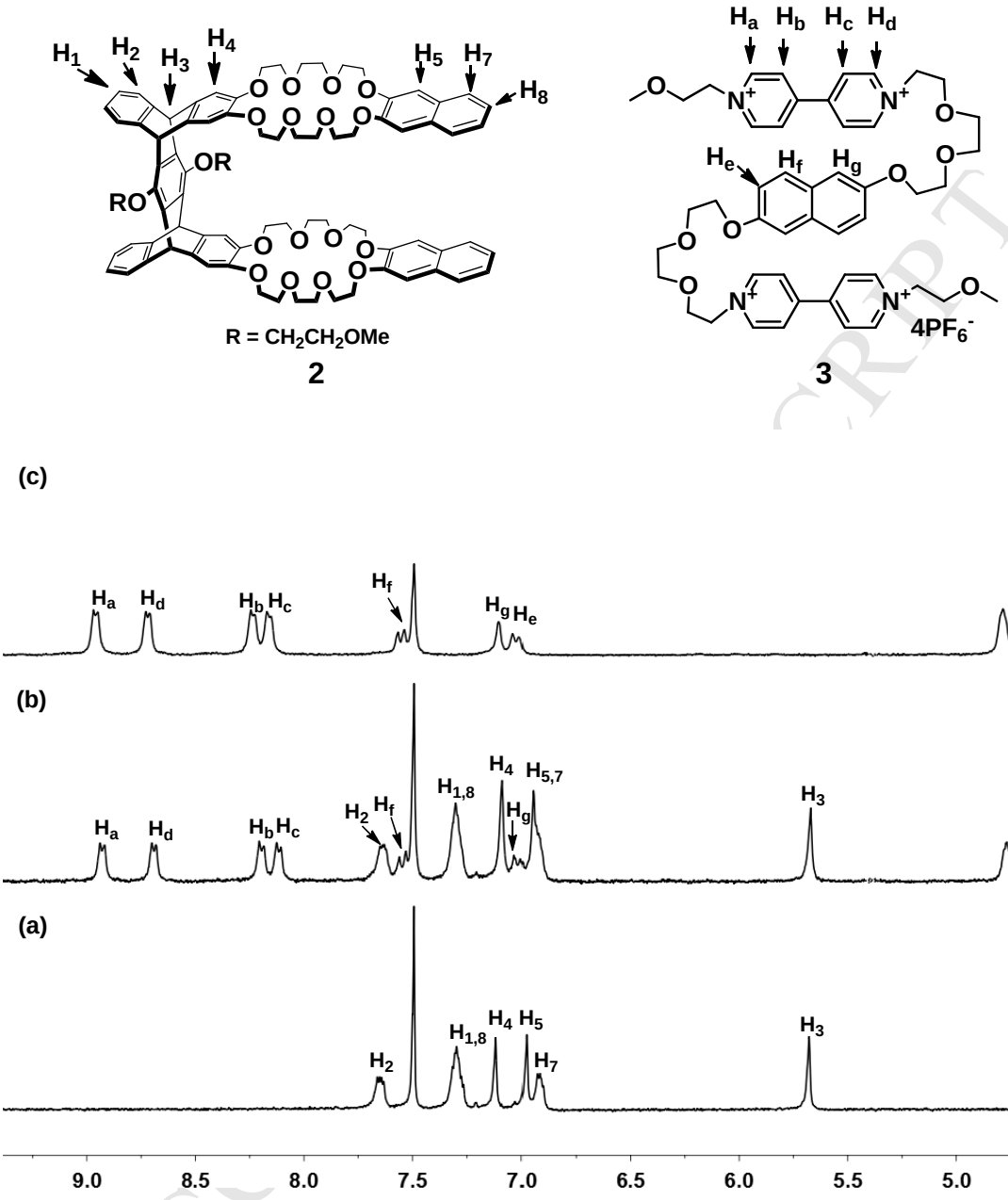


Figure S9. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$=1:1, v/v, 295K) of (a) free host **2**, (b) **2** and 1.0 equiv. of **3**, (c) free guest **3**. $[\mathbf{2}]_0$ = 2.0 mM.

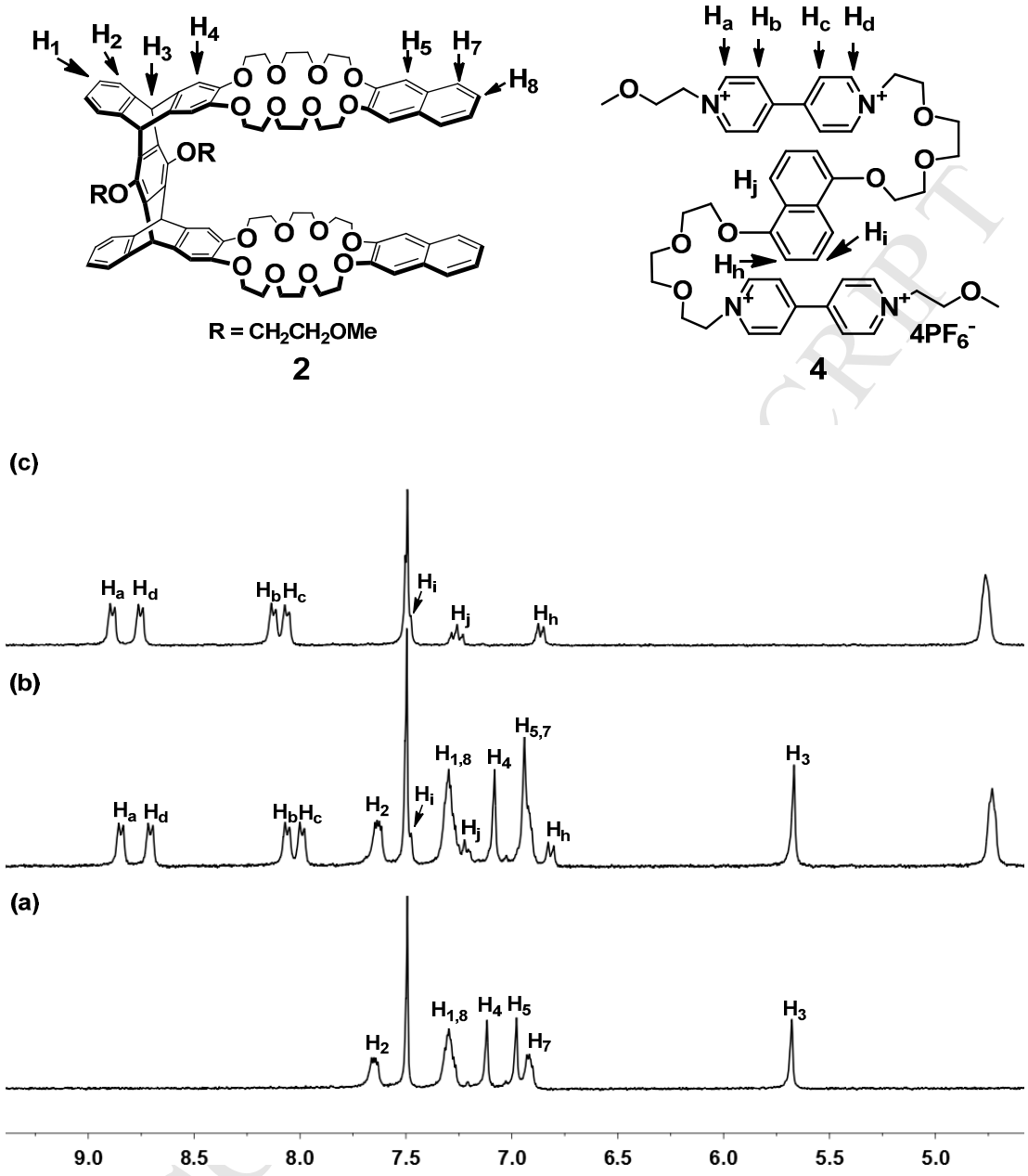


Figure S10. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$=1:1, v/v, 295K) of (a) free host **2**, (b) **2** and 1.0 equiv. of **4**, (c) free guest **4**. $[\mathbf{2}]_0$ = 2.0 mM.

4. Determination of the association constants of the complexes

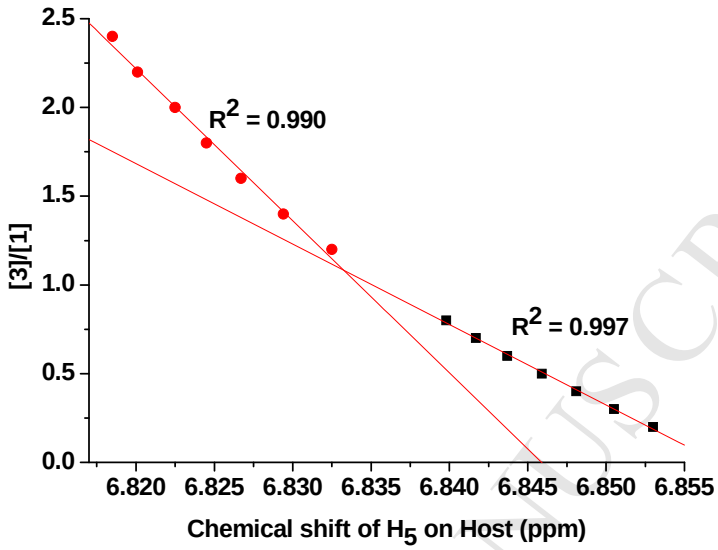


Figure S11. Mole ratio plot for the complexation between **1** and **3** in $CD_3CN/CDCl_3$ (1:1, v:v) at 295 K. $[\mathbf{1}]_0$ = 2.0 mM.

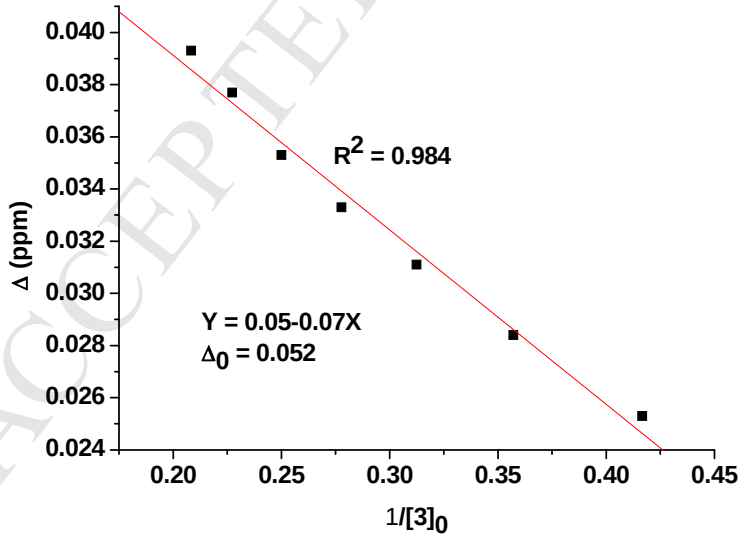


Figure S12. Determination of Δ_0 of H_4 for the complexation between **1** and **3** in $CD_3CN/CDCl_3$ (1:1, v:v) at 295 K. $[\mathbf{1}]_0$ = 2.0 mM.

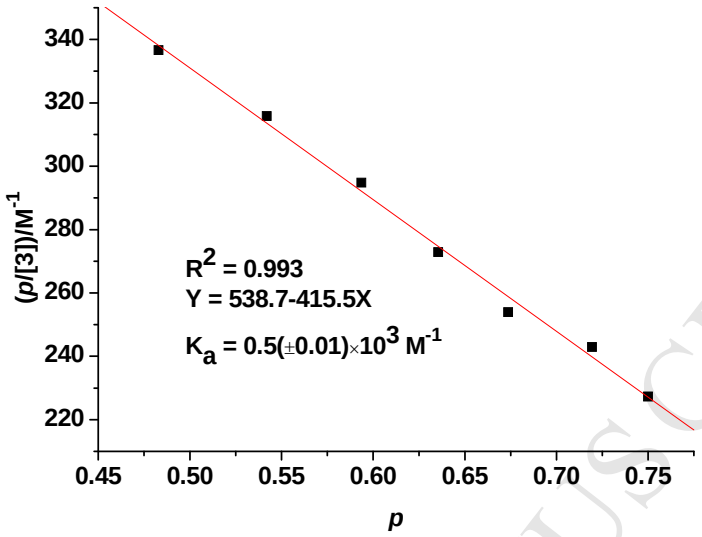


Figure S13. Scatchard plot for the complexation between **1** and **3** in $CD_3CN/CDCl_3$ (1:1, v:v) at 295 K. $[\mathbf{1}]_0$ = 2.0 mM.

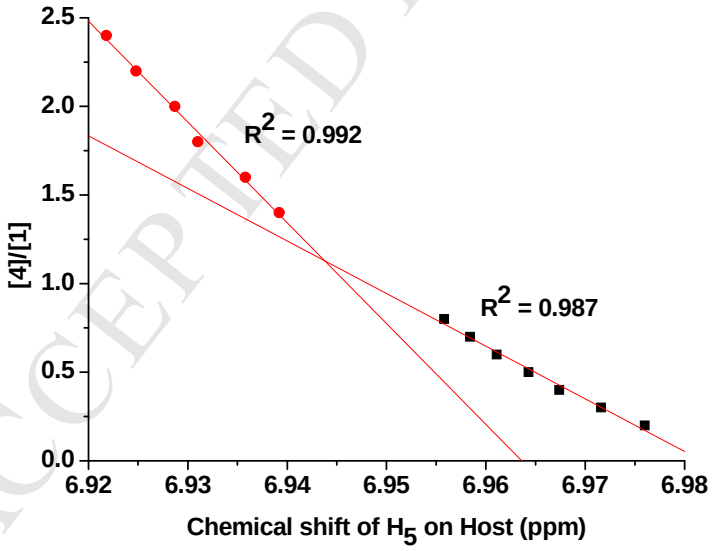
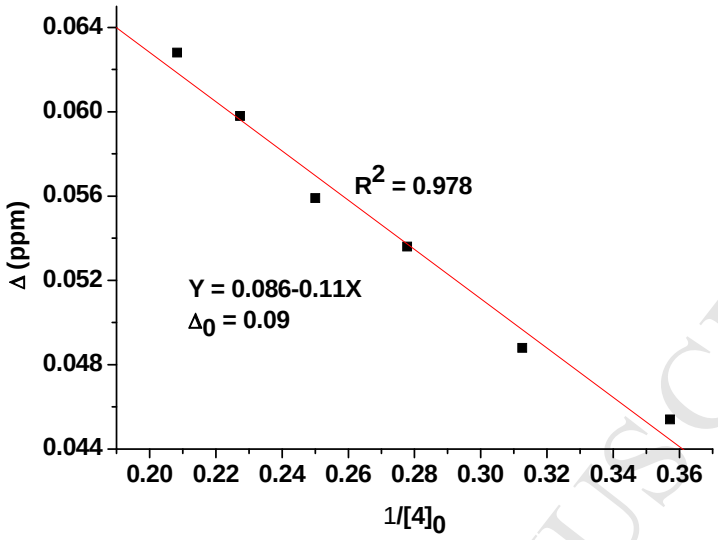


Figure S14. Mole ratio plot for the complexation between **1** and **4** in $CD_3CN/CDCl_3$ (1:1, v:v) at 295 K. $[\mathbf{1}]_0$ = 2.0 mM.



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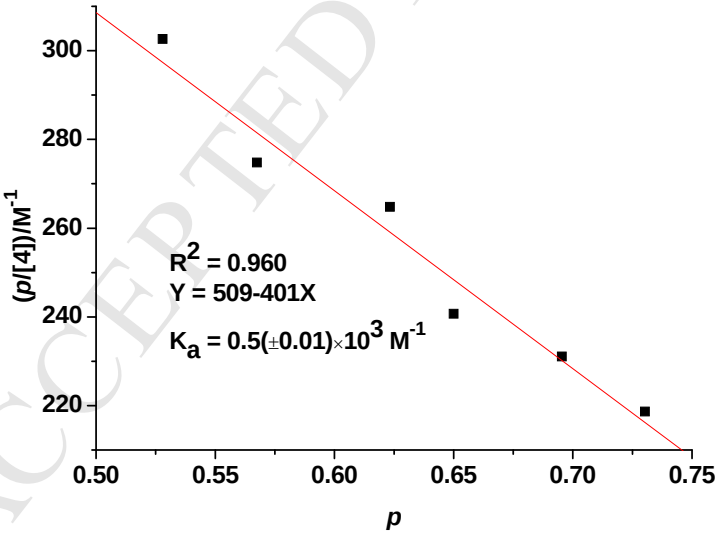

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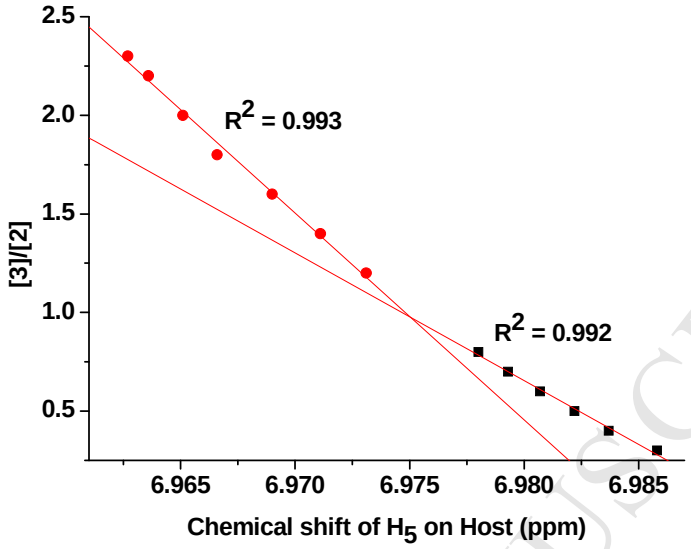

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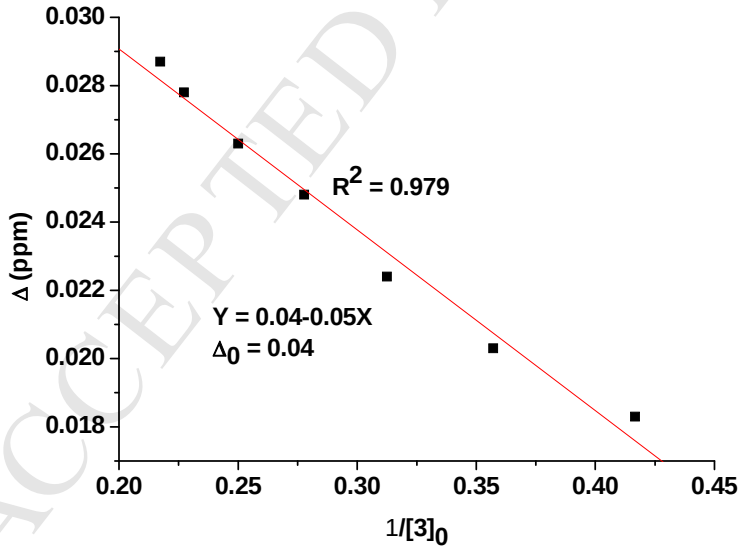

Figure S18. Determination of Δ_0 of H_4 for the complexation between **2** and **3** in $CD_3CN/CDCl_3$ (1:1, v:v) at 295 K. $[\mathbf{2}]_0$ = 2.0 mM.

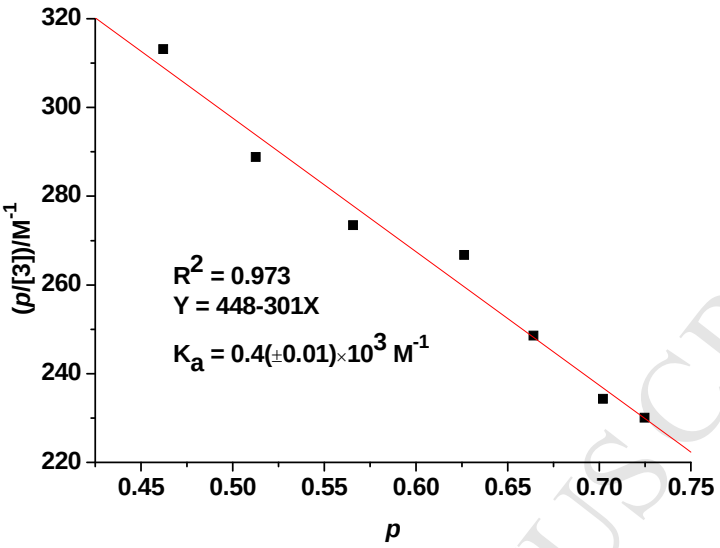

Figure S19. Scatchard plot for the complexation between **2** and **3** in $CD_3CN/CDCl_3$ (1:1, v:v) at 295 K. $[\mathbf{2}]_0$ = 2.0 mM.

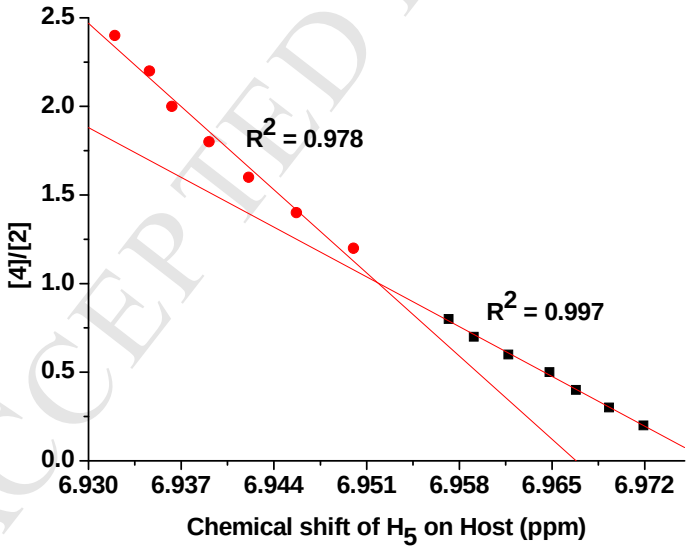

Figure S20. Mole ratio plot for the complexation between **2** and **4** in $CD_3CN/CDCl_3$ (1:1, v:v) at 295 K. $[\mathbf{2}]_0$ = 2.0 mM.

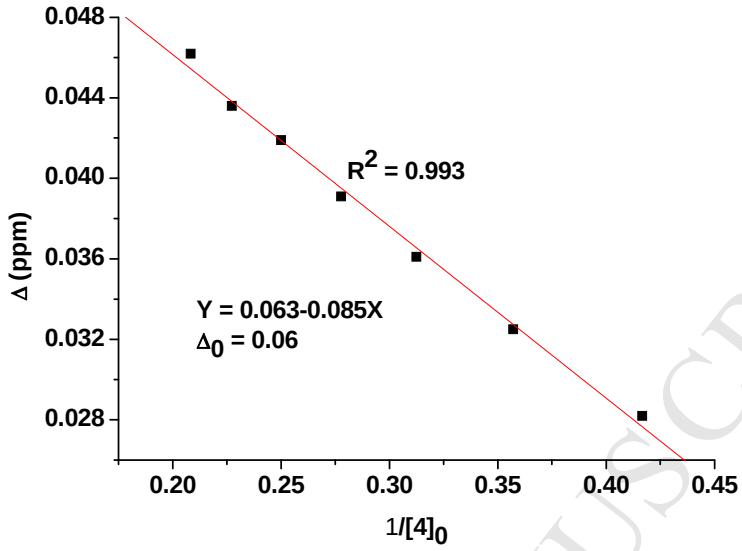

Figure S21. Determination of Δ_0 of H_4 for the complexation between **2** and **4** in $CD_3CN/CDCl_3$ (1:1, v:v) at 295 K. $[\mathbf{2}]_0$ = 2.0 mM.

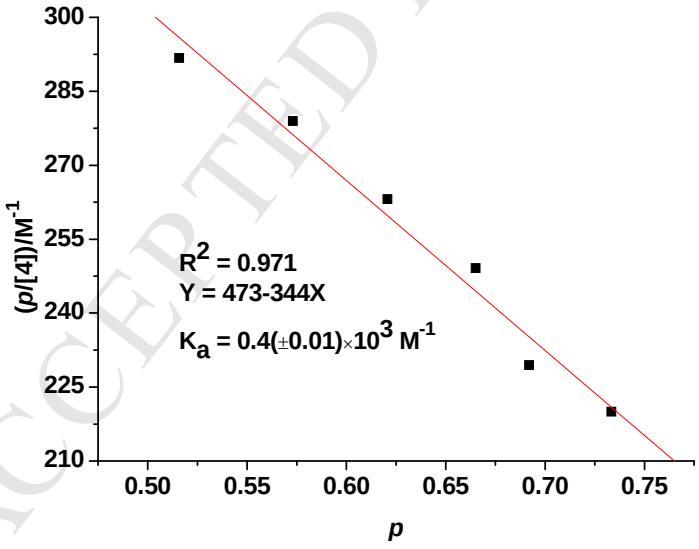

Figure S22. Scatchard plot for the complexation between **2** and **4** in $CD_3CN/CDCl_3$ (1:1, v:v) at 295 K. $[\mathbf{2}]_0$ = 2.0 mM.

5. ESI MS spectra of the complexes

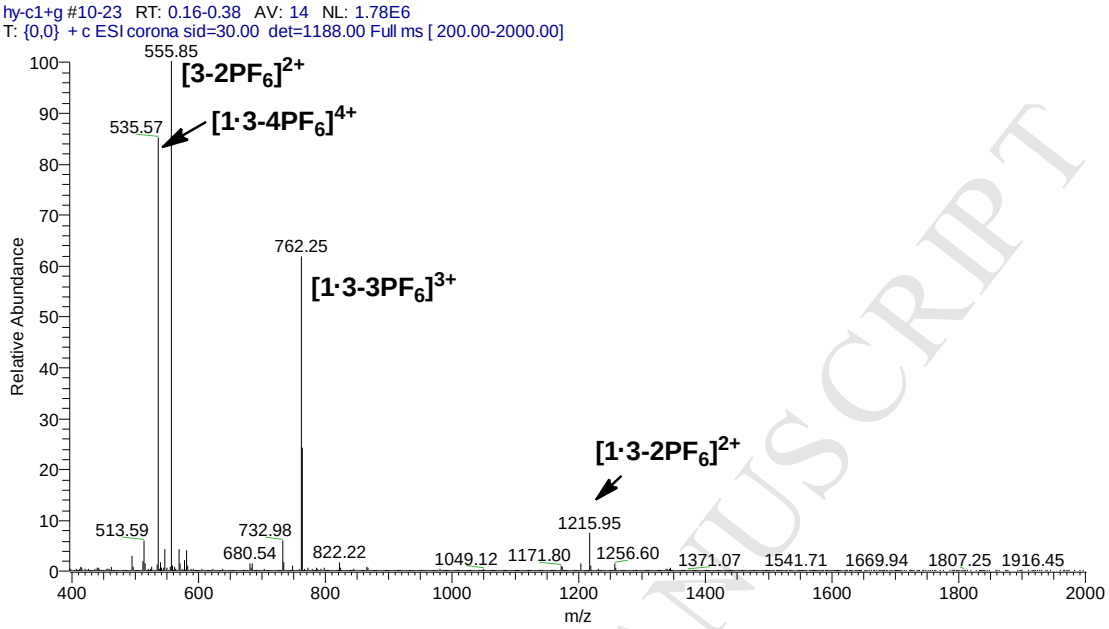

Figure S23. ESI MS of a solution of **1** and **3** in acetonitrile-chloroform (1:1, v:v).

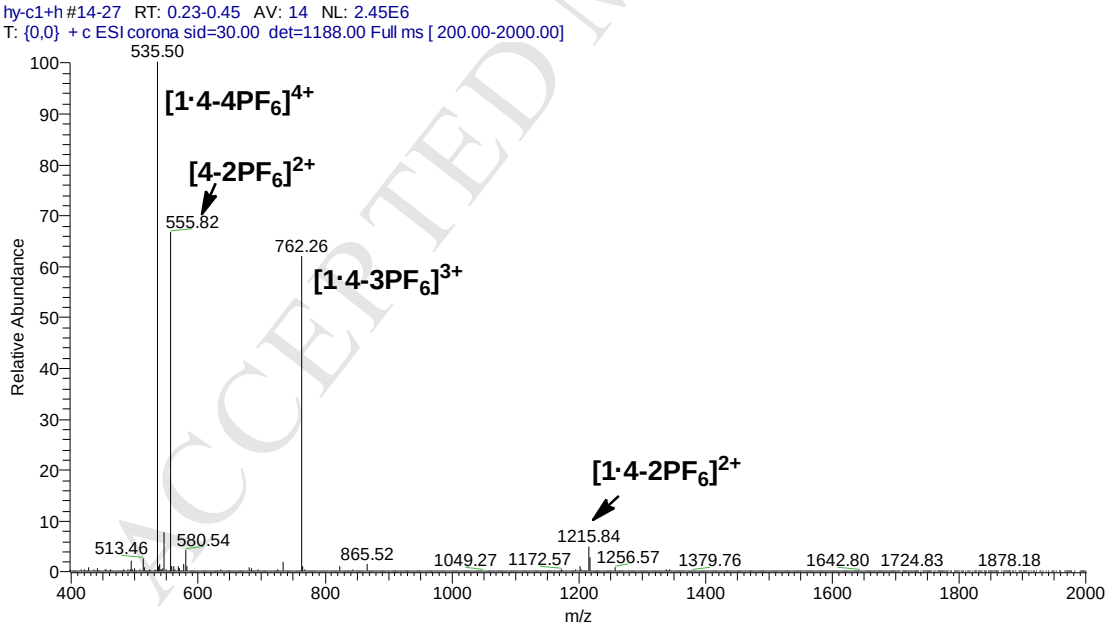

Figure S24. ESI MS of a solution of **1** and **4** in acetonitrile-chloroform (1:1, v:v).

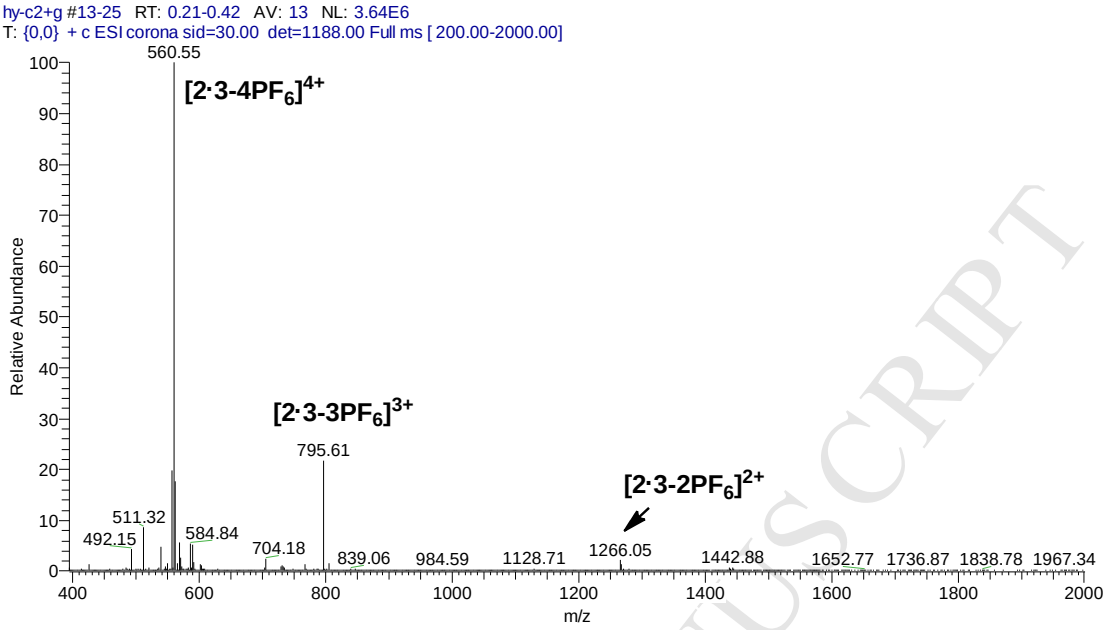

Figure S25. ESI MS of a solution of **2** and **3** in acetonitrile-chloroform (1:1, v:v).

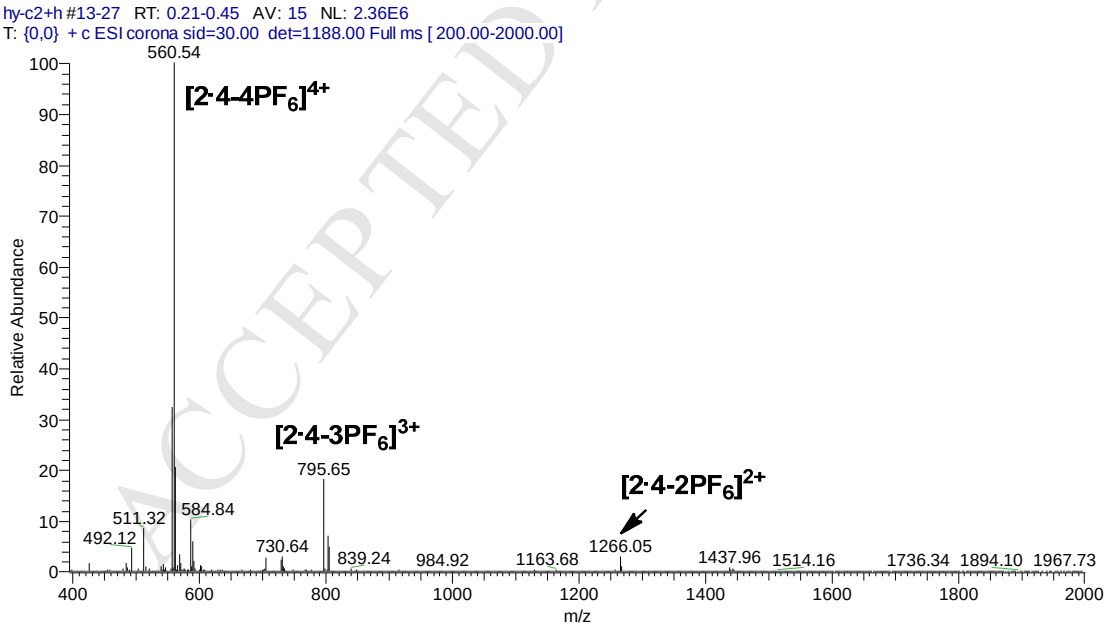

Figure S26. ESI MS of a solution of **2** and **4** in acetonitrile-chloroform (1:1, v:v).

6. Crystal data of guests

Table S1. Crystal data for **3**

Identification code	mx938
Empirical formula	$C_{24}H_{30}F_{12}N_2O_4P_2$
Formula weight	700.44
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	*a* = 8.345(3) Å alpha = 71.754(10)˚
	b = 13.498(4) Å beta = 84.234(12)˚
	c = 13.974(4) Å gamma = 76.011(11)˚
Volume	1450.0(7) $Å^3$
Z, Calculated density	2, 1.604 Mg/m^3
Absorption coefficient	0.262 mm^{-1}
F(000)	716
Crystal size	0.32 x 0.21 x 0.20 mm
Theta range for data collection	1.53 to 27.49˚
Limiting indices	-10<=h<=10, -17<=k<=17, -18<=l<=18
Reflections collected / unique	12846/6584 [R(int)=0.0495]
Completeness to theta = 25.35	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9494 and 0.9208
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6584/0/397
Goodness-of-fit on F^2	1.552
Final R indices [I>2sigma(I)]	R_1 = 0.0759, wR_2 = 0.2194
R indices (all data)	R_1 = 0.0856, wR_2 = 0.2267
Largest diff. peak and hole	1.179 and -0.805 e.$Å^{-3}$

Table S2. Crystal data for **4**

Identification code	a
Empirical formula	$C_{56}H_{66}F_{24}N_6O_8P_4$
Formula weight	1482.99
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	*a* = 10.789(2) Å alpha = 95.52(3)˚
	b = 11.294(2) Å beta = 108.99(3)˚
	c = 13.711(3) Å gamma = 93.16(3)˚
Volume	1565.8(5) $Å^3$
Z, Calculated density	1, 1.573 Mg/m^3
Absorption coefficient	0.249 mm^{-1}
F(000)	760
Crystal size	0.52 x 0.40 x 0.35 mm
Theta range for data collection	2.55 to 25.00˚
Limiting indices	-12<=h<=12, -10<=k<=13, -16<=l<=16
Reflections collected / unique	11449/5434 [R(int)=0.0271]
Completeness to theta = 25.35	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8019
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5434/0/426
Goodness-of-fit on F^2	1.099
Final R indices [I>2sigma(I)]	R_1 = 0.0431, wR_2 = 0.1097
R indices (all data)	R_1 = 0.0458, wR_2 = 0.1118
Largest diff. peak and hole	0.404 and -0.329 e.$Å^{-3}$

7. K^+ ion-controlled switchable complexation between 1 and 3

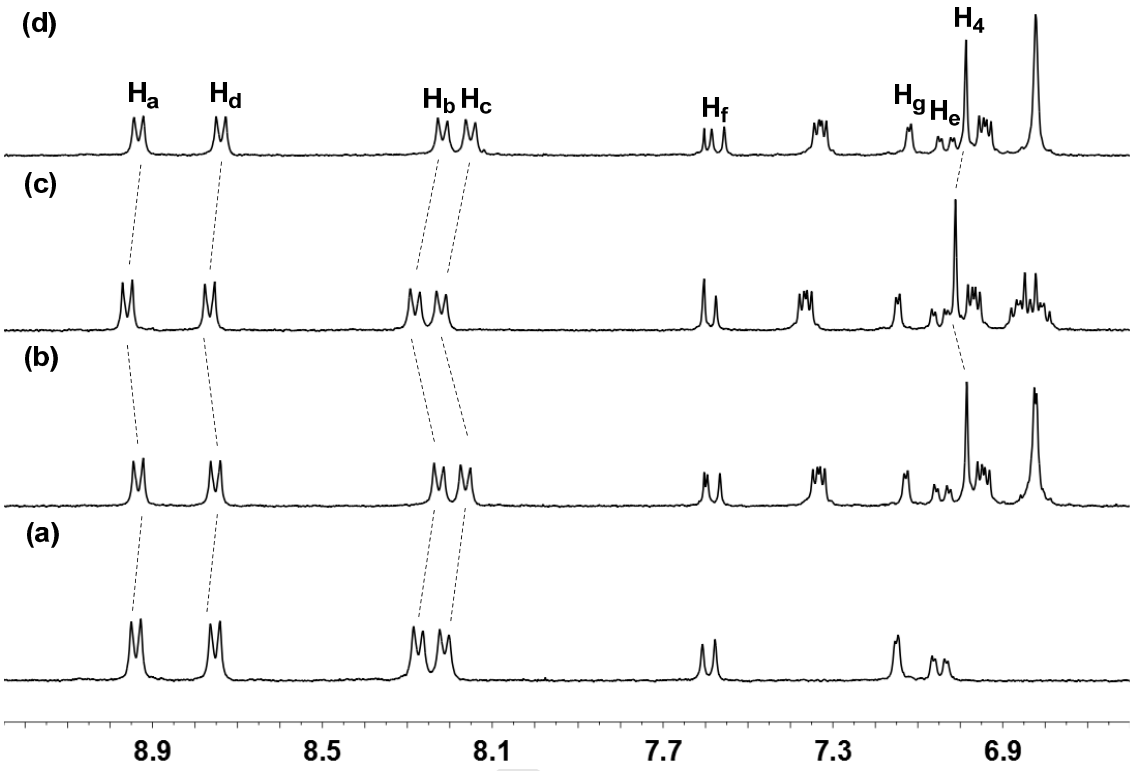

Figure S27. Partial ^{1}H NMR spectra (CD_3CN, 300 MHz) of (a) free guest **3**, (b) **1** and 1.0 equiv. of **3**, (c) to the solution of b was added 4.0 equiv. of KPF_6, and (d) to the solution of c was added 6.0 equiv. of [18]-crown-6, $[\mathbf{1}]_0$ = 2.0 mM.

ACCEPTED