Electronic supplementary information

Self-Assembly of [2]Pseudorotaxanes Based on Pillar[5]arene and Bis(imidazolium) Cations

Chunju Li,*[a] Liu Zhao,[a] Jian Li,[a] Xia Ding[b], Songhui Chen,[a] Qiaolin Zhang[a], Yihua Yu[b] and Xueshun Jia*[a]

[a] *Department of Chemistry, Shanghai University, Shanghai, 200444, P. R.China*

E-mail: cjli@shu.edu.cn, xsjia@mail.shu.edu.cn

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

Contents

Re-design of bis(imidazolium) and bis(benzimidazolium) axles.

We were wondering if a similar dications, 1,4-bis(benzimidazolium)butane (**BBImB**$^{2+}$, See Fig. S1), could penetrate the **P5A**'s cavity to produce [2]pseudorotaxane. However, no obvious NMR changes of the **BBImB** guest were observed upon addition of the host, (Fig. S17) indicating that P5A did not form inclusion complex with **BBImB**•2PF_6 or at least had very weak interaction. This is likely because benzimidazolium group was a little more bulky than imidazolium and pyridinium, and couldn't thread through the cavity of P5A.[S1,S2] (Fig. S1)

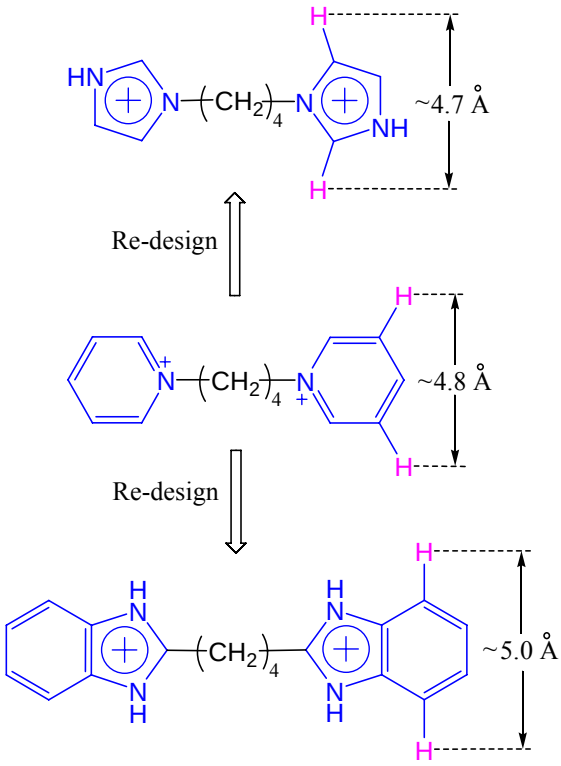
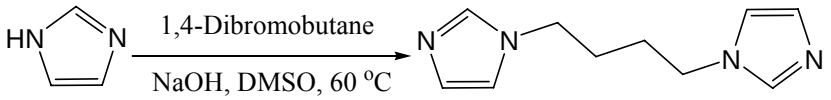


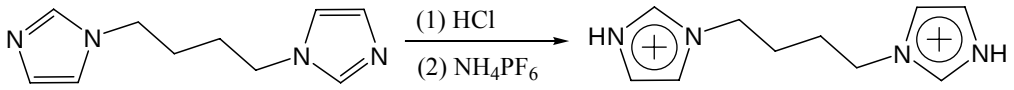
Figure S1. Re-design of bis(imidazolium) and bis(benzimidazolium) axles.

Synthesis.



1

1,4-Bis(imidazole-1-yl)butane **1**[S5]: A mixture of imidazole (4.1 g, 60 mmol) and NaOH (2.4 g, 60 mmol) in DMSO (20 mL) was stirred at 60 °C for 2h, and then 1,4-dibromobutane (6.0 g, 28 mmol) was added. After stirring at 60 °C for 2 h, the reaction mixture was cooled to room temperature and then poured into 200 mL of water. A white solid formed immediately, which was isolated by filtration in 86% yield (4.1 g) after drying in air.

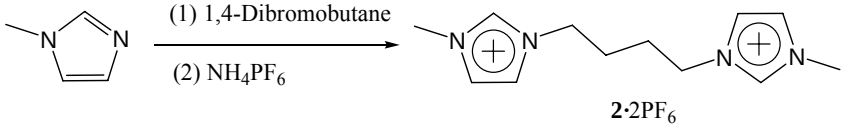


1 [**1**-2H]·2PF$_6$ or [**1**-2H]·2ClO$_4$

[**1**-2H]·2Cl: To compound **1** (0.57 g, 3.0 mmol) dissolved in MeOH (10 mL) was added conc. HCl to adjust pH 1~2, and the solvent was then evaporated off under reduced pressure. The residue was washed with acetone (5 ml) and dried under reduced pressure to give [**1**-2H]·2Cl as a white solid (0.75 g, 95%).

[**1**-2H]·2PF$_6$ and [**1**-2H]·2ClO$_4$: [**1**-2H]·2Cl (0.53 g, 2.0 mmol) was dissolved in deionized H_2O (10 mL), and a saturated aqueous solution of NH_4PF_6 or $NaClO_4$ was added until no further precipitation was observed. The mixture was then filtered, washed with deionized H_2O (10 ml) and Et_2O (3 ml) and dried under reduced pressure

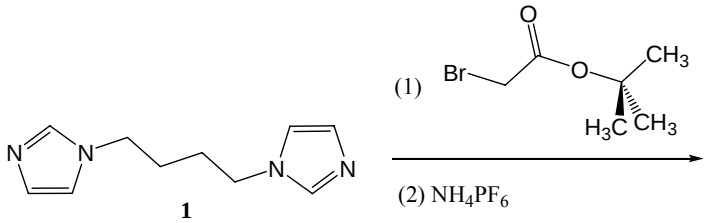
to give [**1**-2H]·2PF_6 (0.85 g, 88%) or [**1**-2H]·2ClO_4 (0.48 g, 61%) as a white solid.



2·2PF_6

2·2Br: **2**·2Br was prepared according to the literature procedure.[S6]. 1,4-Dibromobutane (2.16 g, 10.0 mmol) was mixed with 1-methylimidazole (1.80 g, 21.8 mmol) and the reaction mixture was kept at room temperature for 48 h. The resulting dark solid was crushed under acetone, filtered, washed with small portions of acetone and dried under reduced pressure, leaving **2**·2Br as yellow solid. (2.67 g, 70 % yield)

2·2PF_6: The same procedure as for [**1**-2H]·2PF_6 was used. **2**·2Br (0.76 g, 2.0 mmol) in deionized H_2O (10 mL) was added a saturated aqueous solution of NH_4PF_6 to produce a white solid **2**·2PF_6 (0.93 g, 91 % yield).



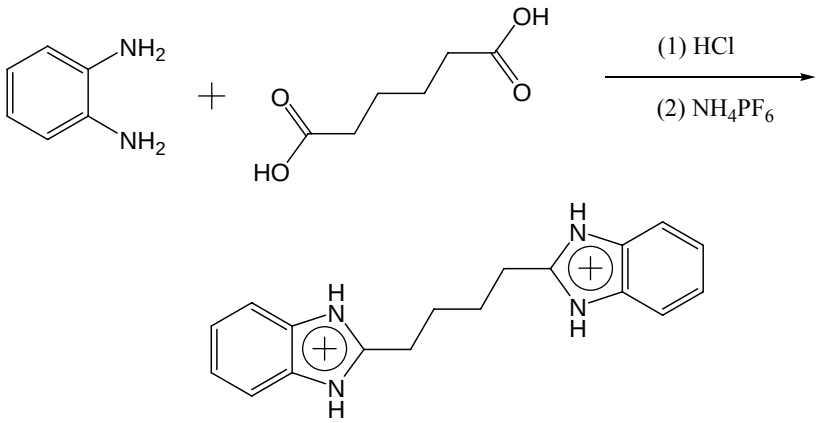
1

3·2PF_6

3·2Br: A solution of **1** (0.57 g, 3.0 mmol) and tert-Butyl bromoacetate (1.56 g, 8.0

mmol) in MeCN (6 mL) was refluxed for two days. The precipitate was then filtered, washed with tetrahydrofuran and dried to give **3**·2Br as colorless crystalline. (1.37 g, 78%)

3·2PF_6: The same procedure as for [**1**-2H]·2PF_6 was used. **3**·2Br (1.17 g, 2.0 mmol) in deionized H_2O (10 mL) was added a saturated aqueous solution of NH_4PF_6 to produce **3**·2PF_6 (1.25 g, 87 % yield).



BBImB·2PF_6.[S7] Phenylenediamine (5.4 g, 50 mmol) and adipic acid (3.65 g, 25 mmol) were added to 4M hydrochloric acid (60 mL), and the mixture was refluxed for 40 hours then gradually cooled to room temperature. The light green precipitate was filtered, washed with water then acetone and air dried to give **BBImB**·2Cl. **BBImB**·2Cl was dissolved in deionized H_2O, and a saturated aqueous solution of NH_4PF_6 was added until no further precipitation was observed. The mixture was then filtered, washed with H_2O and Et_2O and dried to give **BBImB**·2PF_6 as a white solid (10.3 g, 70 % yield).

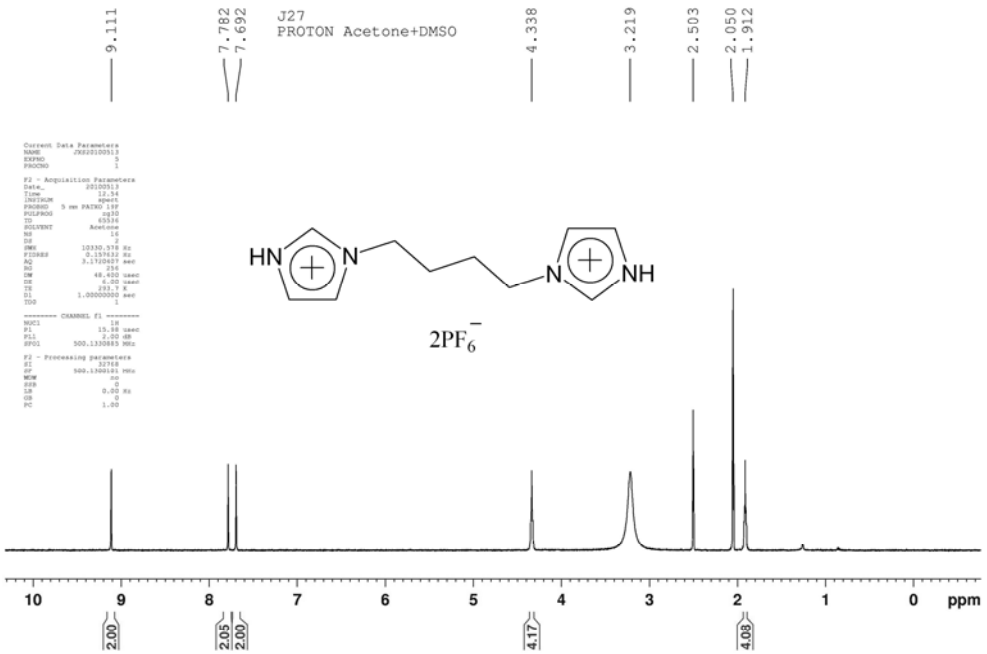


Figure S2. ^{1}H NMR spectrum (500 MHz) of [**1**-2H]·2PF_6 in acetone-d_6 and DMSO-d_6 (3:2, v:v).

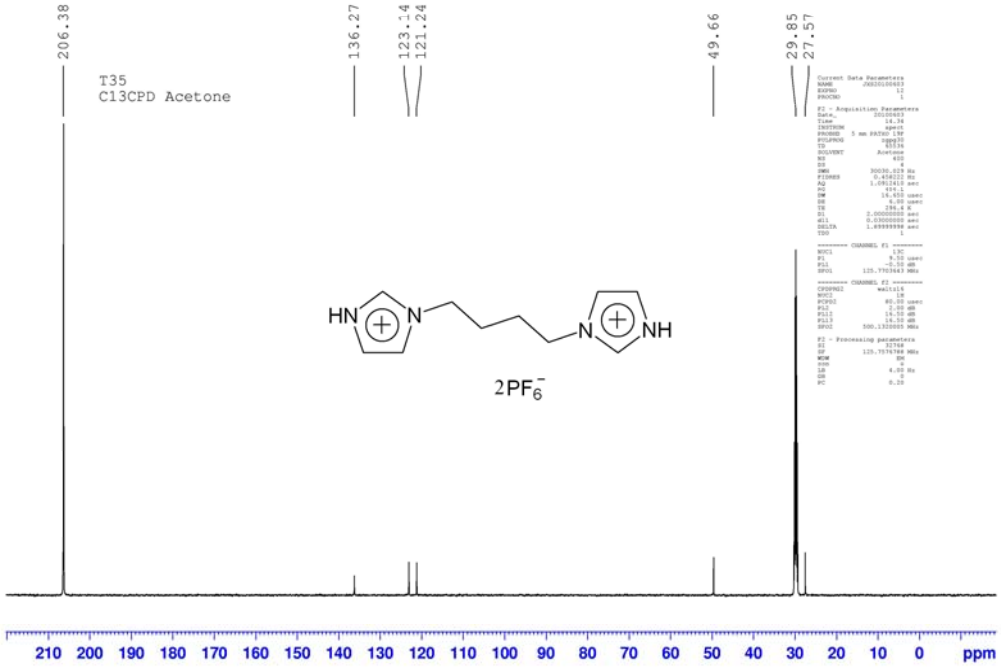


Figure S3. ^{13}C NMR spectrum (500 MHz) of [**1**-2H]·2PF_6 in acetone-d_6.

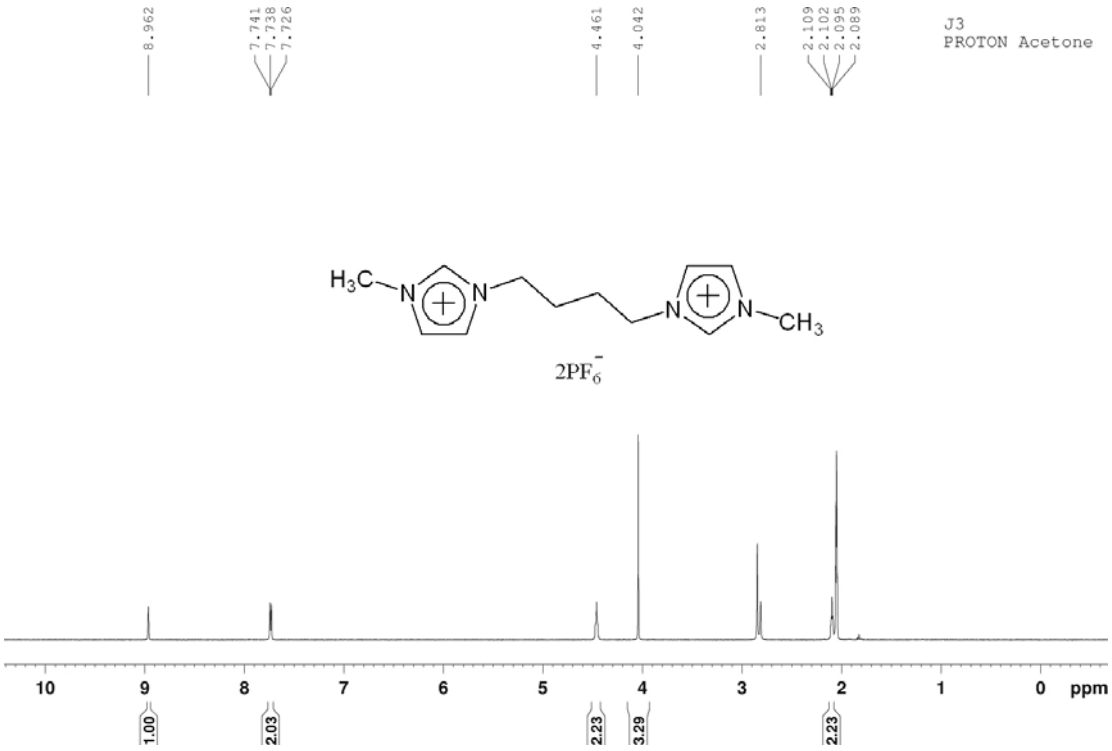


Figure S4. ^{1}H NMR spectrum (500 MHz) of **2**·2PF_6 in acetone-d_6.

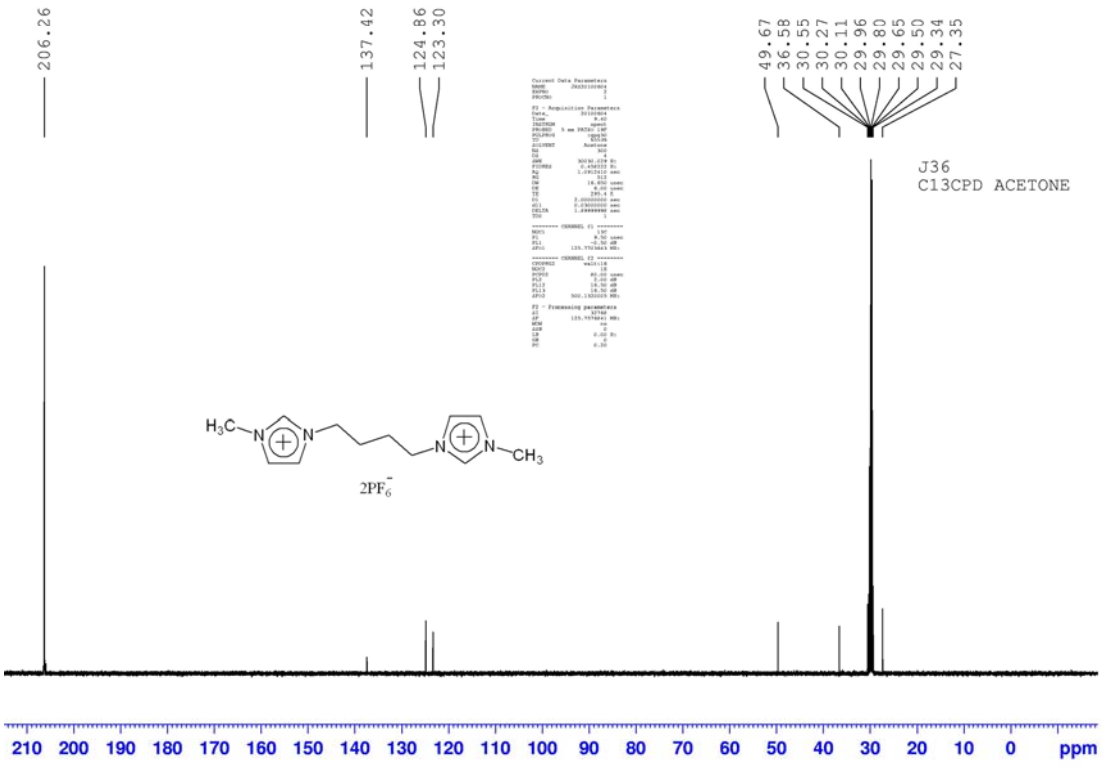


Figure S5. ^{13}C NMR spectrum (500 MHz) of **2**·2PF_6 in acetone-d_6.

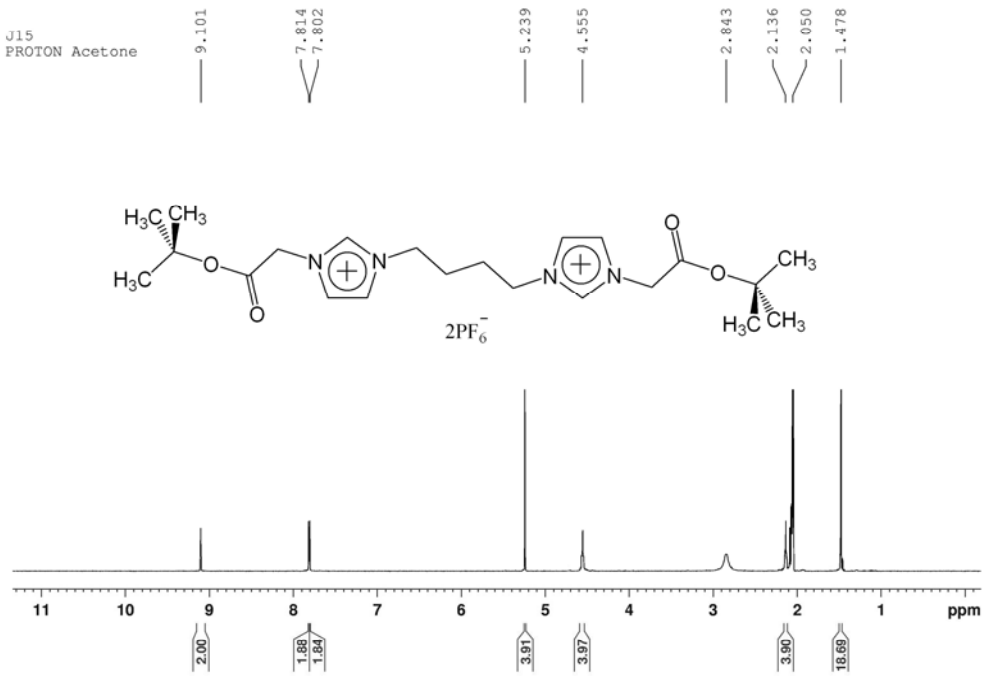


Figure S6. ^{1}H NMR spectrum (500 MHz) of **3**·2PF_6 in acetone-d_6.

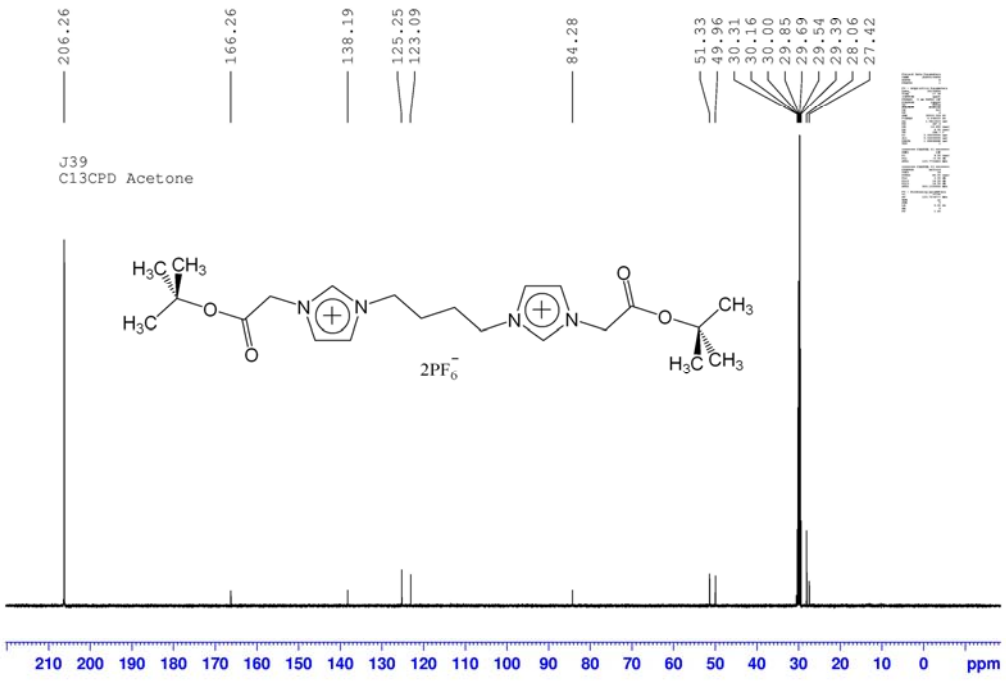


Figure S7. ^{13}C NMR spectrum (500 MHz) of **3**·2PF_6 in acetone-d_6.

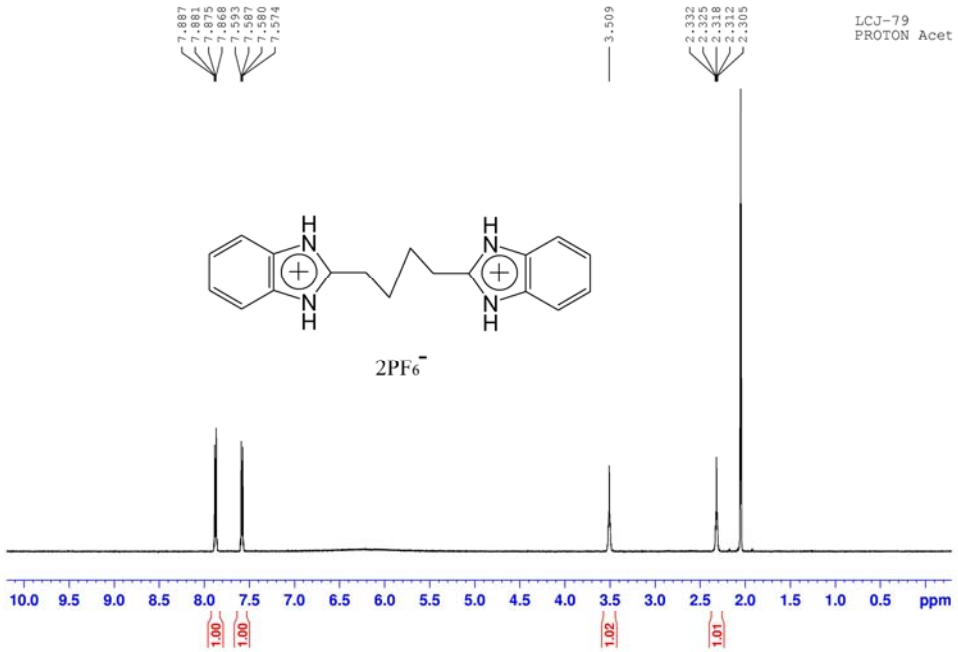


Figure S8. ^{1}H NMR spectrum (500 MHz) of **BBImB**·2PF$_6$ in acetone-d_6.

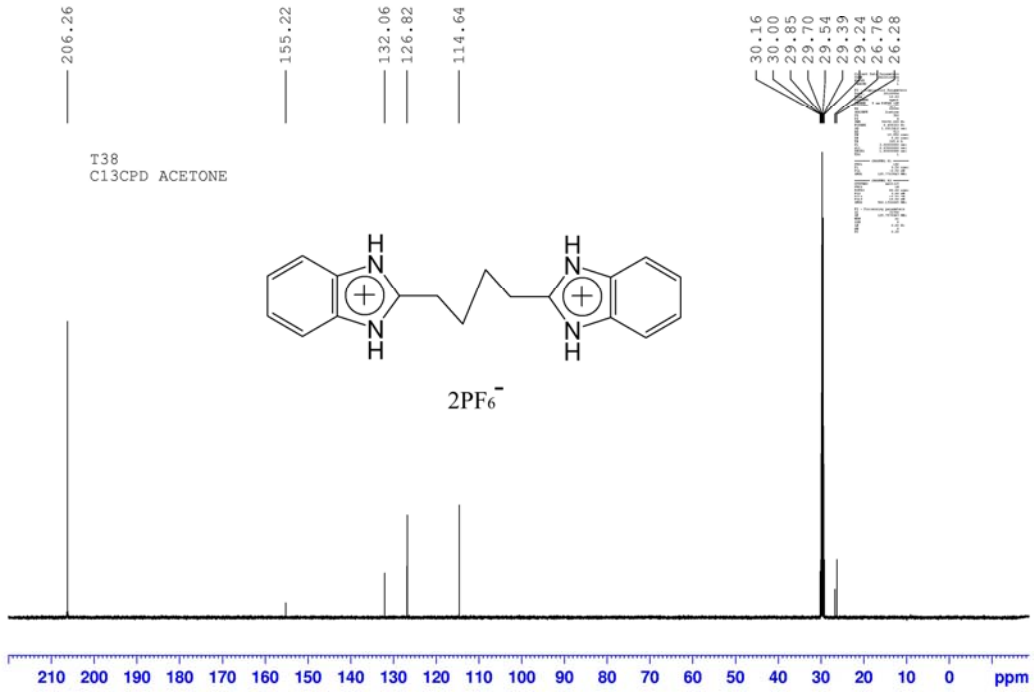


Figure S9. ^{13}C NMR spectrum (500 MHz) of **BBImB**·2PF$_6$ in acetone-d_6.

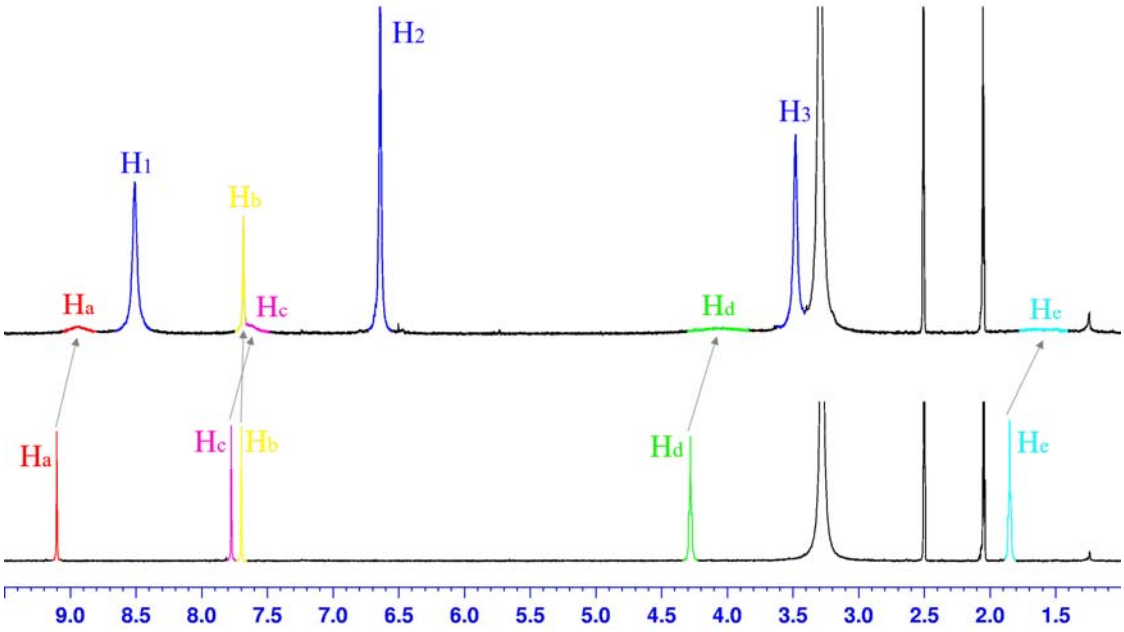


Figure S10. ^{1}H NMR spectrum (500 MHz) of [**1**-2H]·2PF_6 (6.3 mM) in the absence (lower) and presence (upper) of **P5A** host (6.6 mM) in acetone-d_6 and DMSO-d_6 (3:7, v:v).

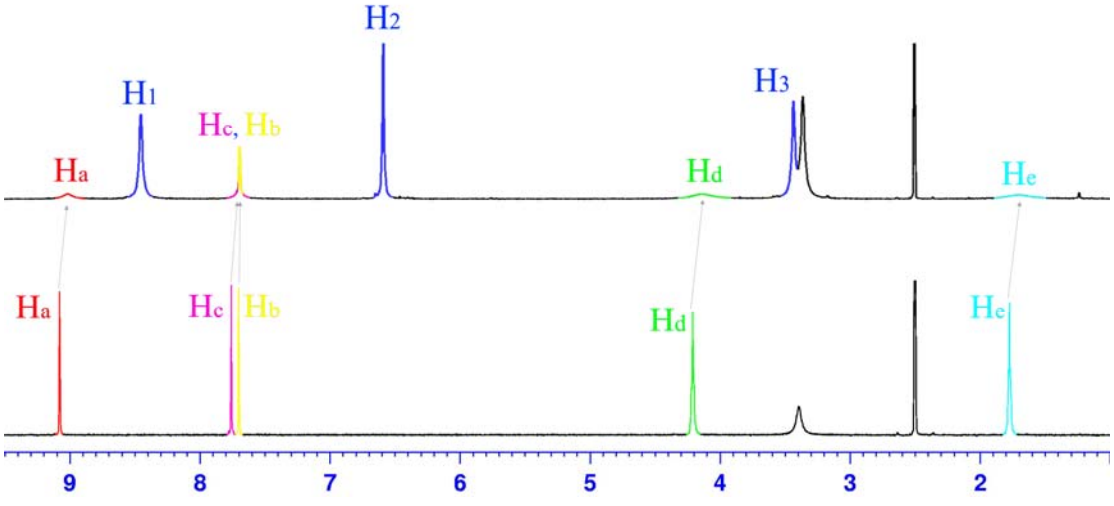


Figure S11. ^{1}H NMR spectrum (500 MHz) of [**1**-2H]·2PF_6 (6.2 mM) in the absence (lower) and presence (upper) of **P5A** host (6.5 mM) in DMSO-d_6.

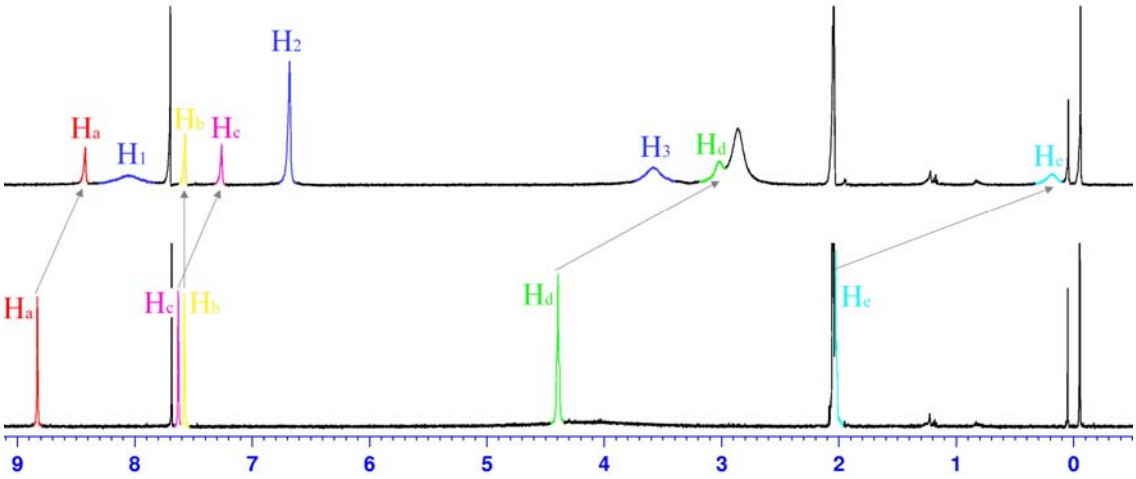


Figure S12. ^{1}H NMR spectrum (500 MHz) of [**1**-2H]·2PF_6 (4.4 mM) in the absence (lower) and presence (upper) of **P5A** host (4.1 mM) in acetone-d_6 and $CDCl_3$ (1:1, v:v).

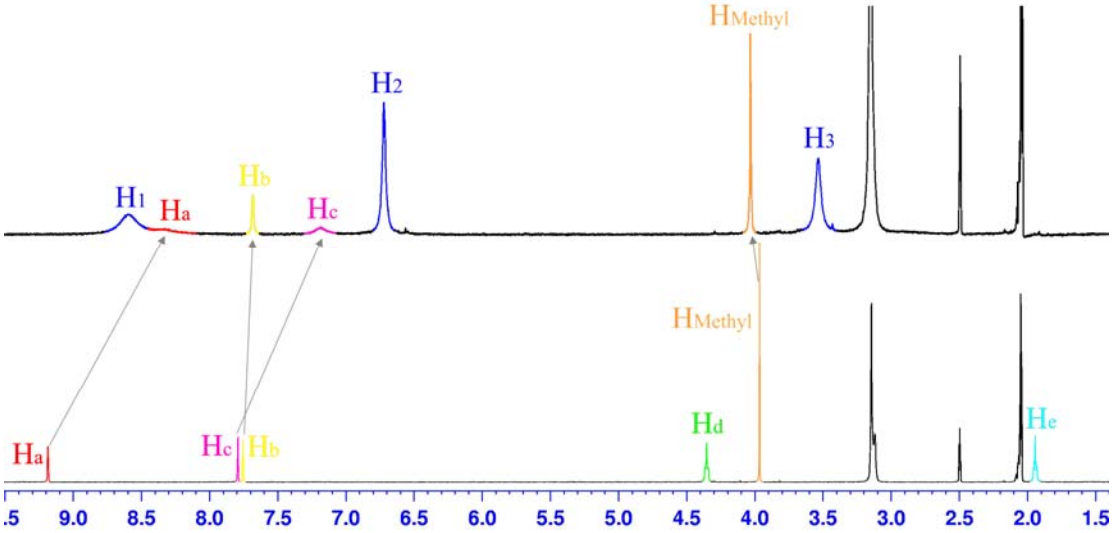


Figure S13. ^{1}H NMR spectrum (500 MHz) of **2**·2PF_6 (6.3 mM) in the absence (lower) and presence (upper) of **P5A** host (6.7 mM) in acetone-d_6 and DMSO-d_6 (3:2, v:v).

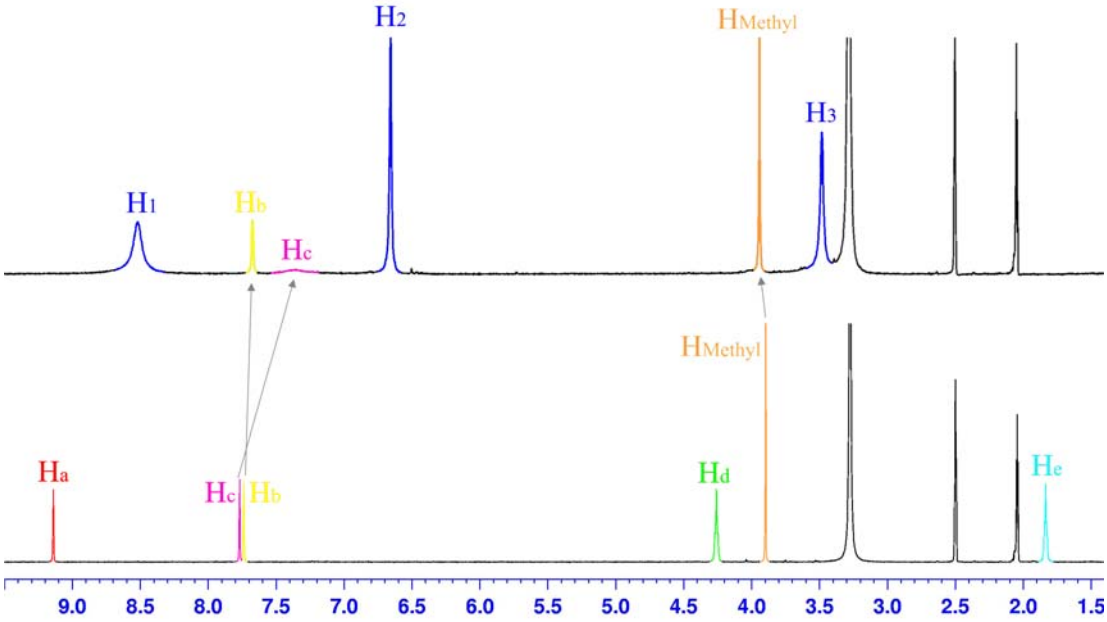


Figure S14. ^{1}H NMR spectrum (500 MHz) of **2**·2PF$_6$ (5.8 mM) in the absence (lower) and presence (upper) of **P5A** host (6.3 mM) in acetone-d_6 and DMSO-d_6 (3:7, v:v).

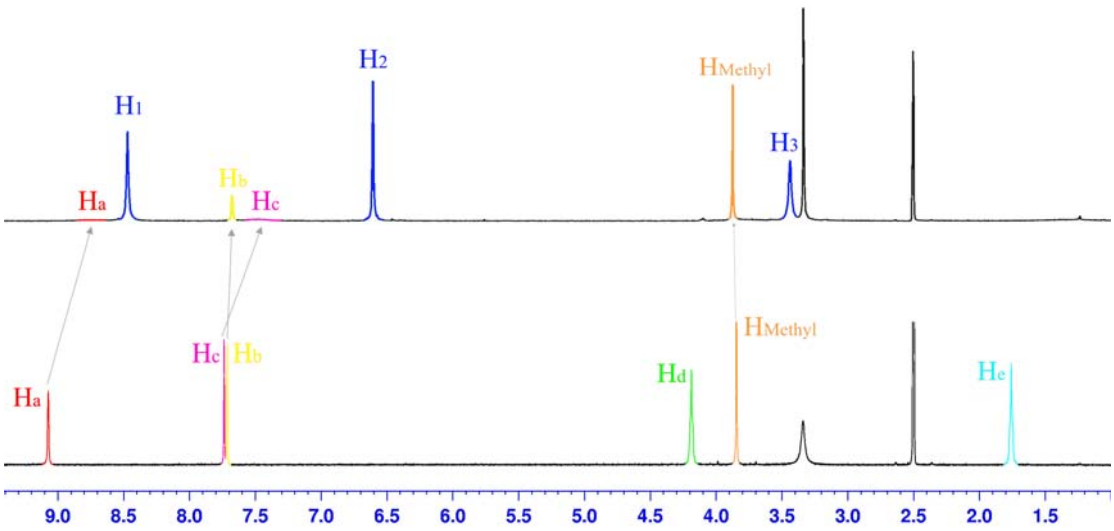


Figure S15. ^{1}H NMR spectrum (500 MHz) of **2**·2PF$_6$ (6.0 mM) in the absence (lower) and presence (upper) of **P5A** host (6.0 mM) in DMSO-d_6.

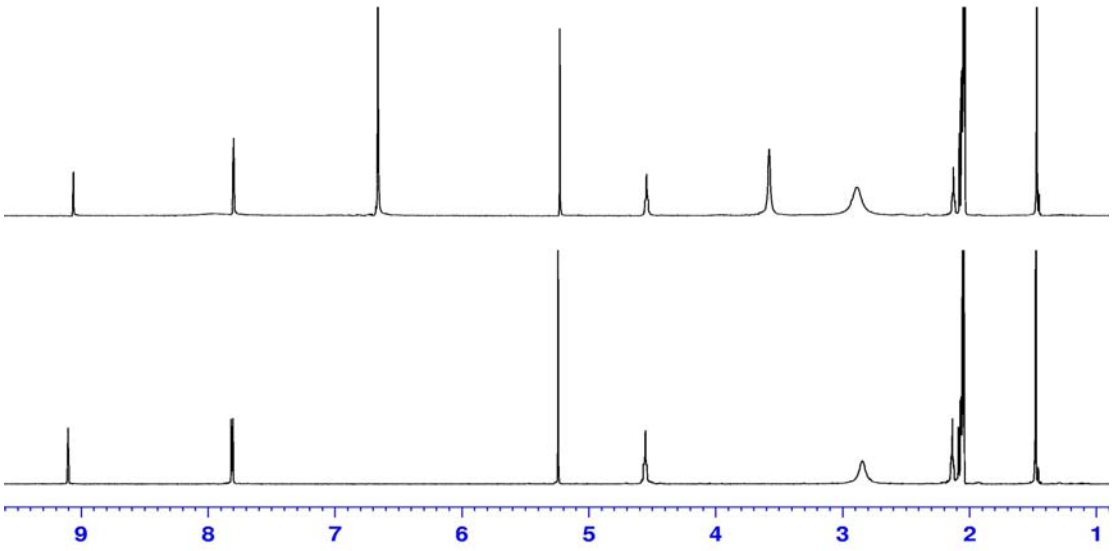


Figure S16. ^{1}H NMR spectrum (500 MHz) of **3**·2PF$_6$ (5.9 mM) in the absence (lower) and presence (upper) of **P5A** host (6.9 mM) in acetone-d_6.

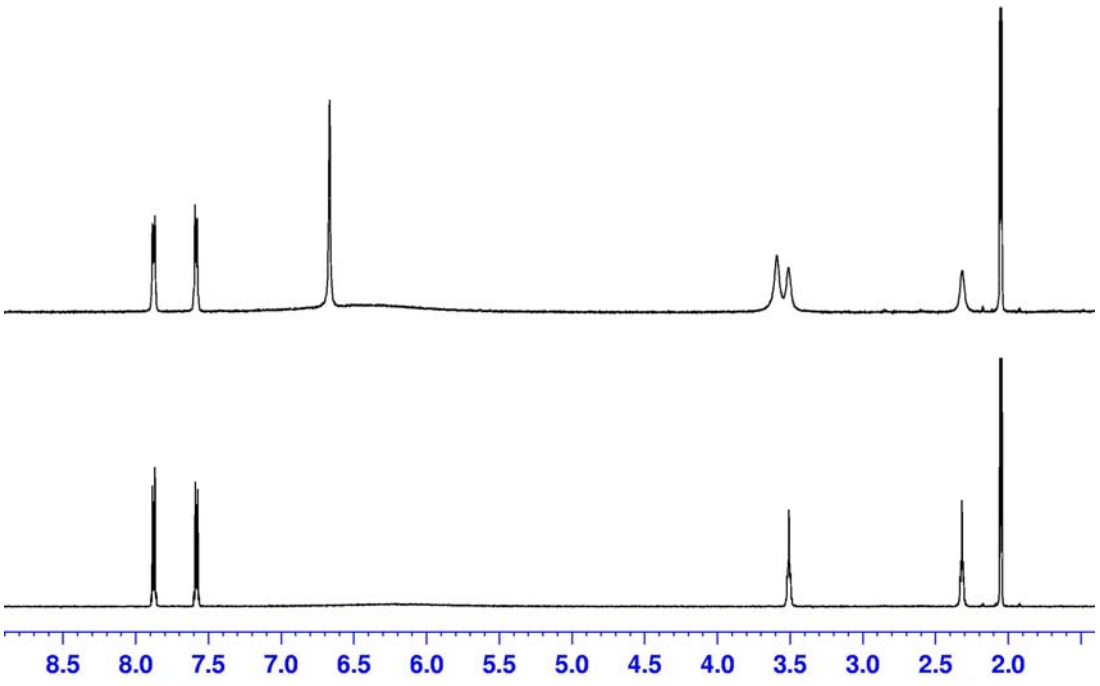


Figure S17. ^{1}H NMR spectrum (500 MHz) of **BBImB**·2PF$_6$ (4.8 mM) in the absence (lower) and presence (upper) of **P5A** host (4.7 mM) in acetone-d_6.

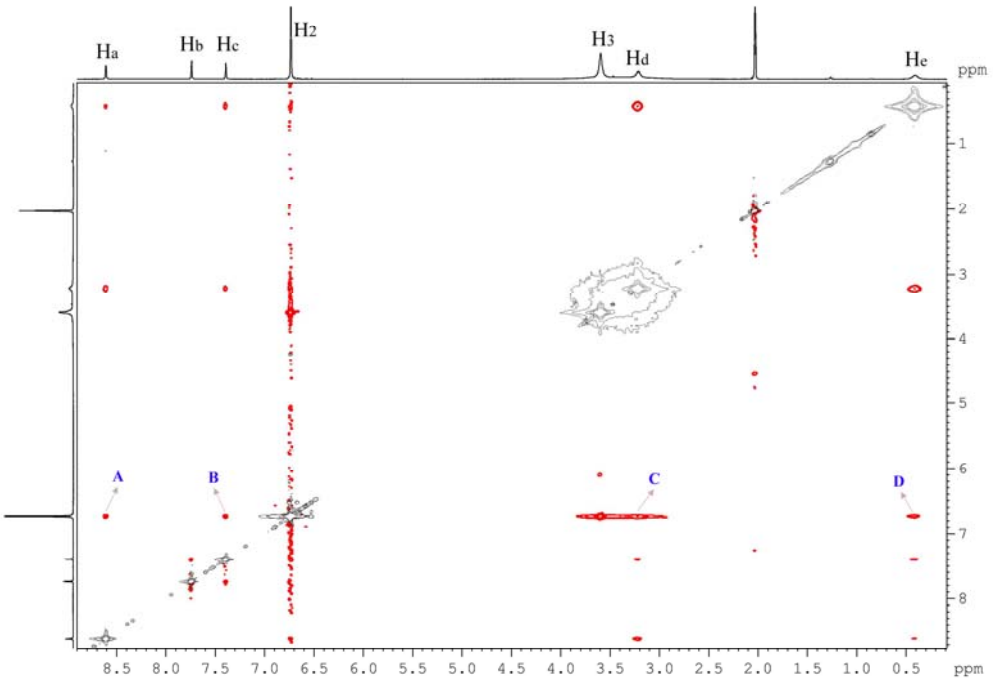
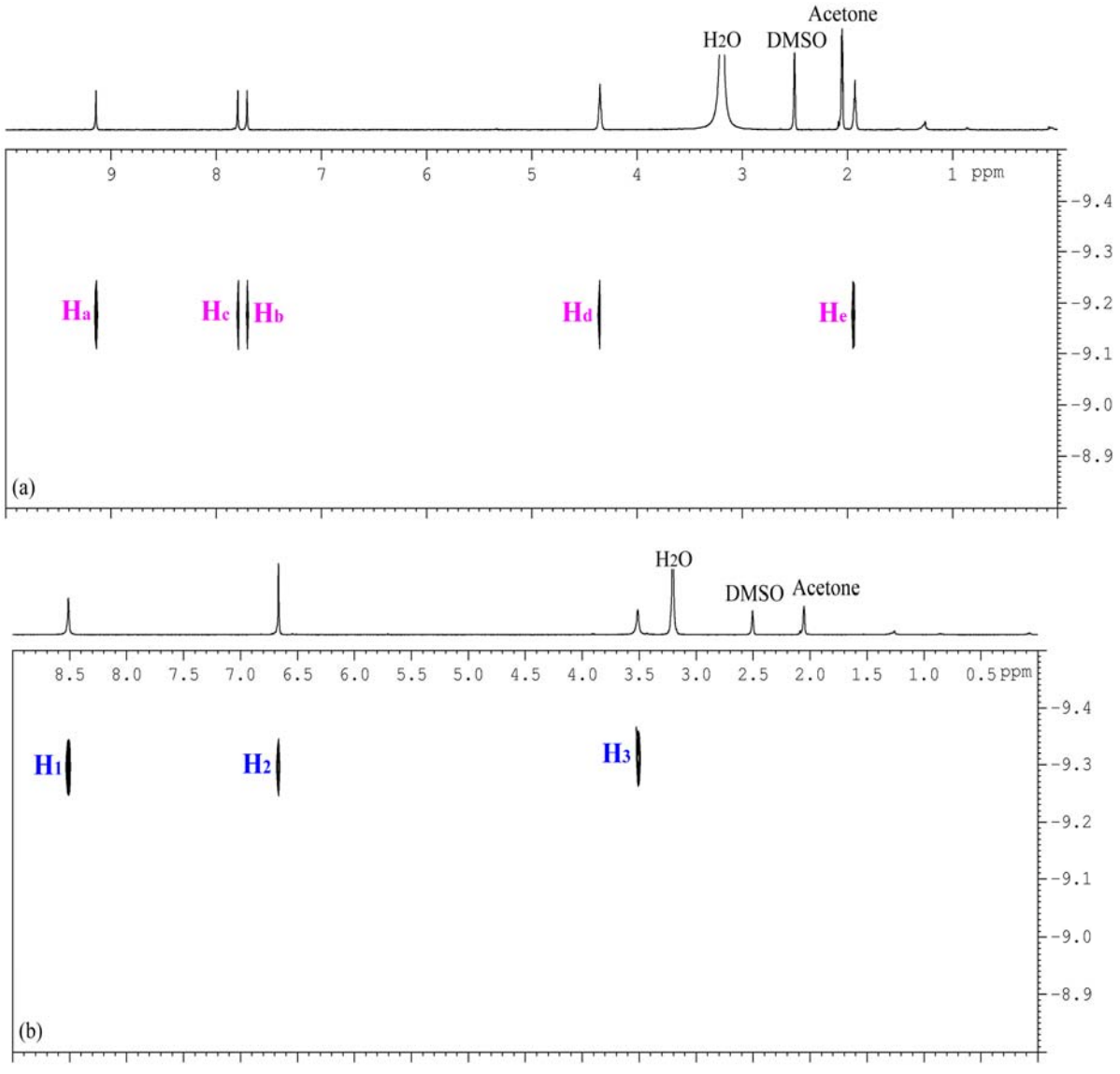


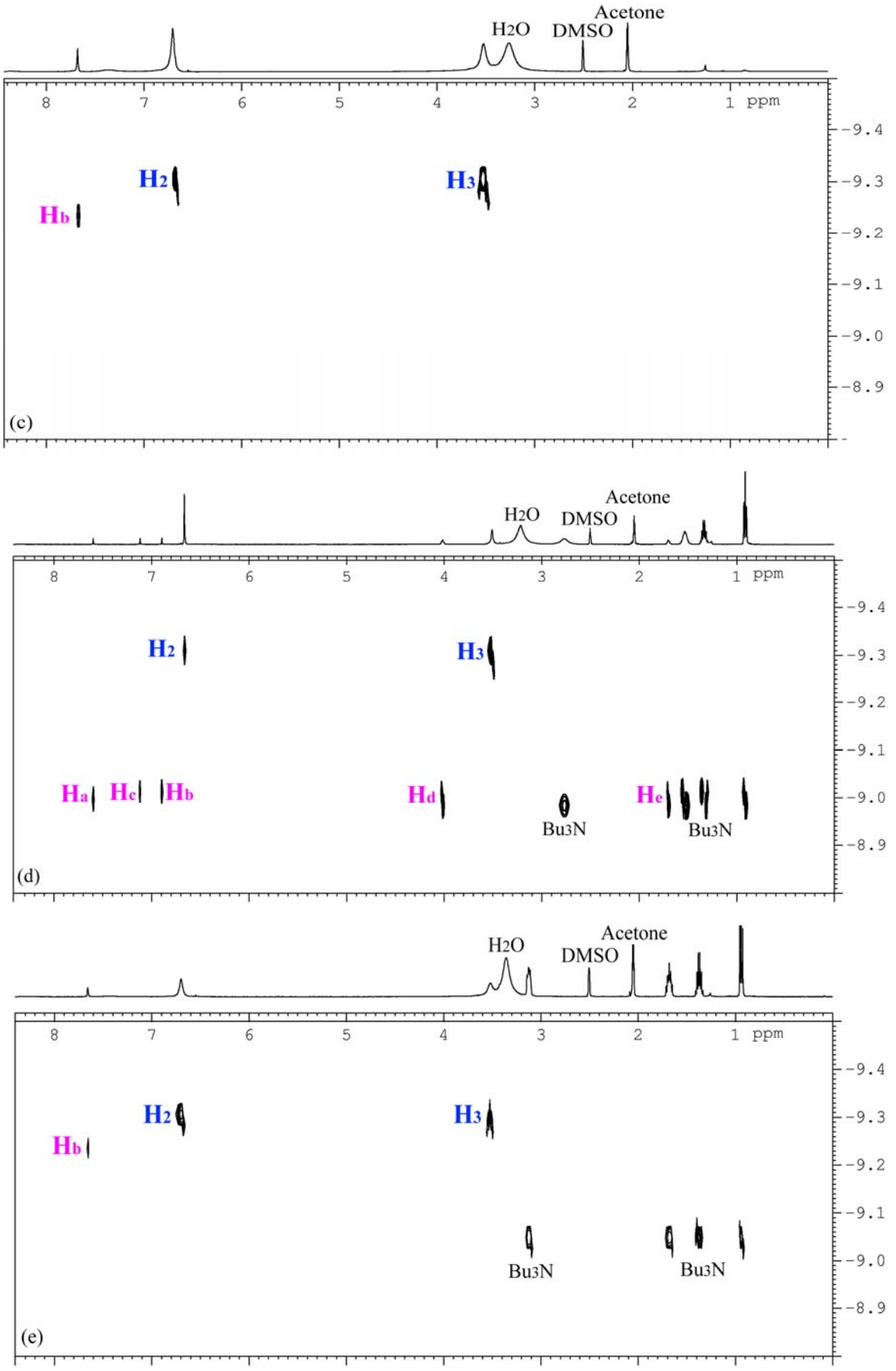
Figure S18. 2D NOESY analysis of [**1**-2H]•2PF_6 with **P5A** in acetone-d_6 with a mixing time of 600 ms at 25 °C. The concentrations of both host and guest are about 10 mM.

DOSY spectra.

Diffusion-ordered spectroscopy (DOSY) NMR experiments were performed to demonstrate the pseudorotaxane formation and the pH-controllable dethreading/rethreading process. The corresponding spectra were shown in Figure S19. Upon addition of **P5A** host, the diffusion coefficient of [**1**-2H]$^{2+}$ (D_{guest}) in 3:2 acetone-d_6:DMSO-d_6 decreased from 6.61×10^{-10} to 5.81×10^{-10} $m^2 \cdot s^{-1}$, although it is not completely reduced to that of the macrocycle (4.97×10^{-10} $m^2 \cdot s^{-1}$). This confirms the formation of host-guest complex with a free/bound equilibrium. Taking into account that the studied system is under fast equilibrium on NMR scale, the diffusion coefficients for the guest are the average values of the free and bound species. It should also be pointed out that H_a, H_c, H_d and H_e signals of the guest in the presence of **P5A** can not be observed in the DOSY spectrum due to the very remarkable complexation-induced broadening effects. (Figure S19c) On the other hand, the diffusion coefficient of **P5A** did not change very much. It's well known that the diffusion coefficient depends on the shape and size of the molecules. [**1**-2H]$^{2+}$ is significantly smaller than **P5A** and the guest is mostly trapped in the cavity of the host, without significantly affecting the size and shape of the **P5A** host. Therefore, it is reasonable that the diffusion coefficient of the **P5A** host is not greatly perturbed upon complexation with the axle.[S8] Using the well-established methodology[S8e,f, S9], we can estimate the association constant ($K_a \approx 250$ M^{-1}), which is in agreement with the value determined through the NMR titration and the indirect NMR methods (Table 1 & S1).

Upon addition of ~ 2.2 eq. of *n*-Bu_3N, D_{guest} increases to 9.77 × 10^{-10} $m^2 \cdot s^{-1}$ (resembling the value of free guest) showing that guest **1** has been released from the cavity of **P5A**. Upon addition of CF_3COOH again, the D_{guest} value (5.84 × 10^{-10} $m^2 \cdot s^{-1}$) restore the original value, indicating the rethreading process.




Acetone
H2O
DMSO
8
7
6
5
4
3
2
1 ppm
-9.4
-9.3
-9.2
-9.1
-9.0
-8.9
H2
H3
Hb
(c)
Acetone
H2O
DMSO
H2
H3
Ha
Hc
Hb
Hd
Bu3N
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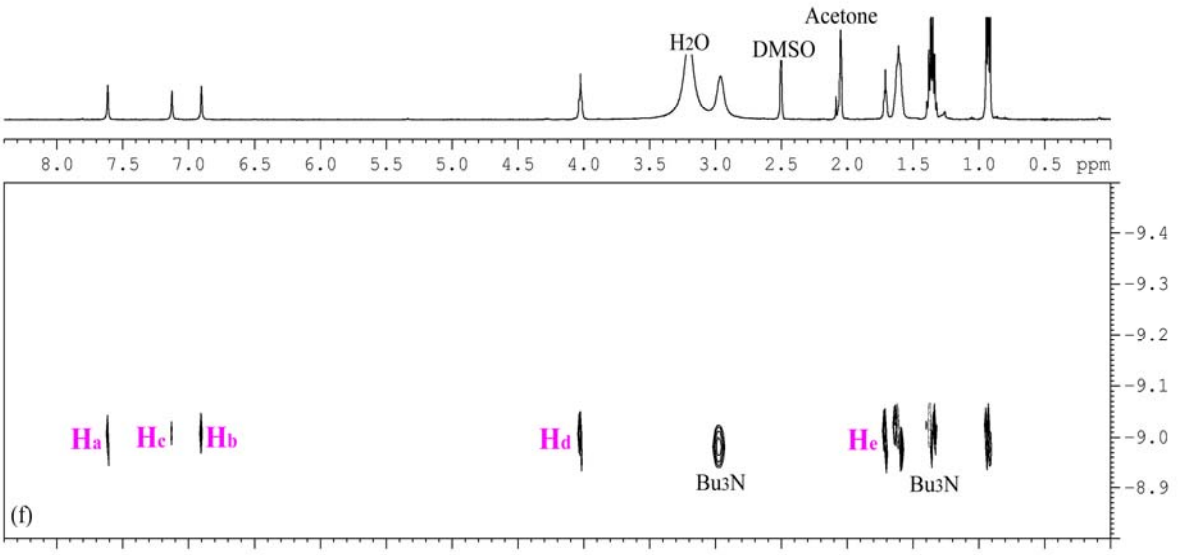
H2
H3
Hb
Bu3N
Bu3N
(e)



Fingre S19. DOSY spectra of (a) [**1**-2H]•2PF_6, (b) **P5A**, (c) **P5A** + [**1**-2H]•2PF_6, (d) **P5A** + [**1**-2H]•2PF_6 + *n*-Bu_3N, (e) **P5A** + [**1**-2H]•2PF_6 + *n*-Bu_3N + CF_3COOH, (f) [**1**-2H]•2PF_6 + *n*-Bu_3N, in 3:2 (v:v) acetone-d_6:DMSO-d_6 at 25°C. The concentrations of **P5A** and [**1**-2H]•2PF_6 were 6.2–6.8 mM; the concentrations of *n*-Bu_3N and CF_3COOH were 13.6–14.5 mM.

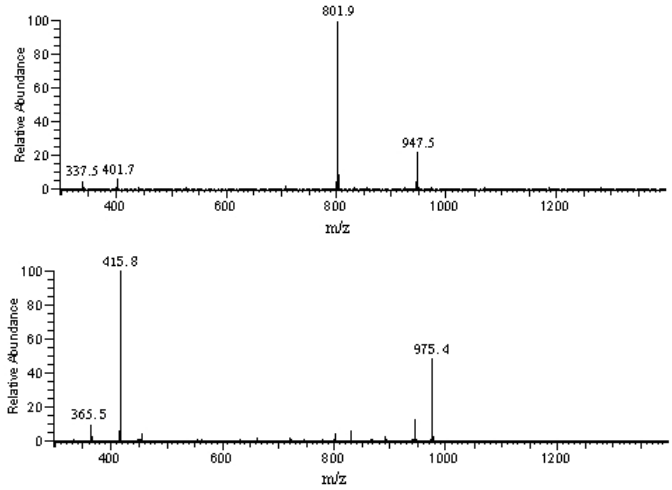


Figure S20. ESI mass spectra of [**1**-2H]·2PF_6 (upper) and **2**·2PF_6 (lower) in the presence of 1.2 eq **P5A** in methanol solution.

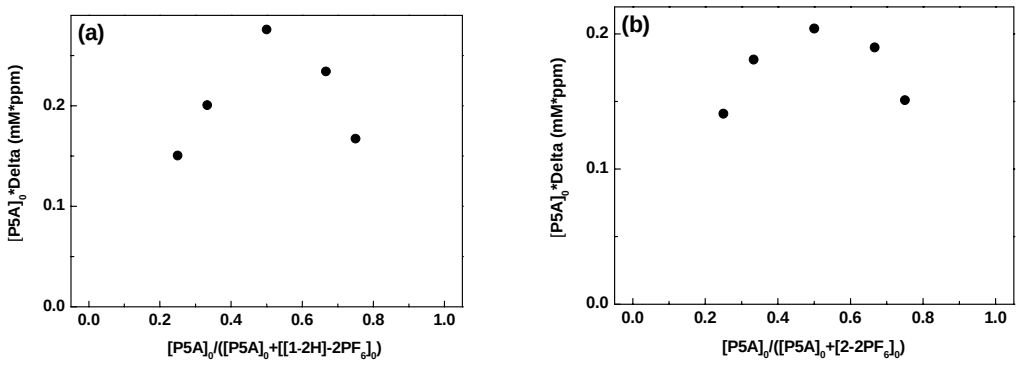


Figure S21. Job plots showing the 1:1 stoichiometries of the complexes between **P5A** and [**1**-2H]·2PF_6 in acetone-d_6 (a) and between **P5A** and **2**·2PF_6 in 3:2 acetone-d_6:DMSO-d_6 (b). For all solutions, the sum of initial concentrations of the **P5A** host and bis(imidazolium) guest was 8.0 mM. Delta is the chemical shift change for H2 of **P5A**.

Determination of the association constants.

(1). To determine the association constant (K_a), NMR titrations were done with solutions which had a constant concentration of **P5A** and varying concentrations of guest. Using the nonlinear curve-fitting method, the association constant was obtained for each host-guest combination from the following equation[S10]:

$$A = (A_\infty/[\ P5A]_0)\ (0.5[G]_0 + 0.5([P5A]_0+1/K_a)-(0.5\ ([G]_0^2+(2[G]_0(1/K_a - [P5A]_0)) + (1/K_a + [P5A]_0)^2)^{0.5}))$$

Where A is the chemical shift change of H2 on **P5A** host at $[G]_0$, A_∞ is the chemical shift change of H2 when the host is completely complexed, $[P5A]_0$ is the fixed initial concentration of the host, and $[G]_0$ is the initial concentration of guest.

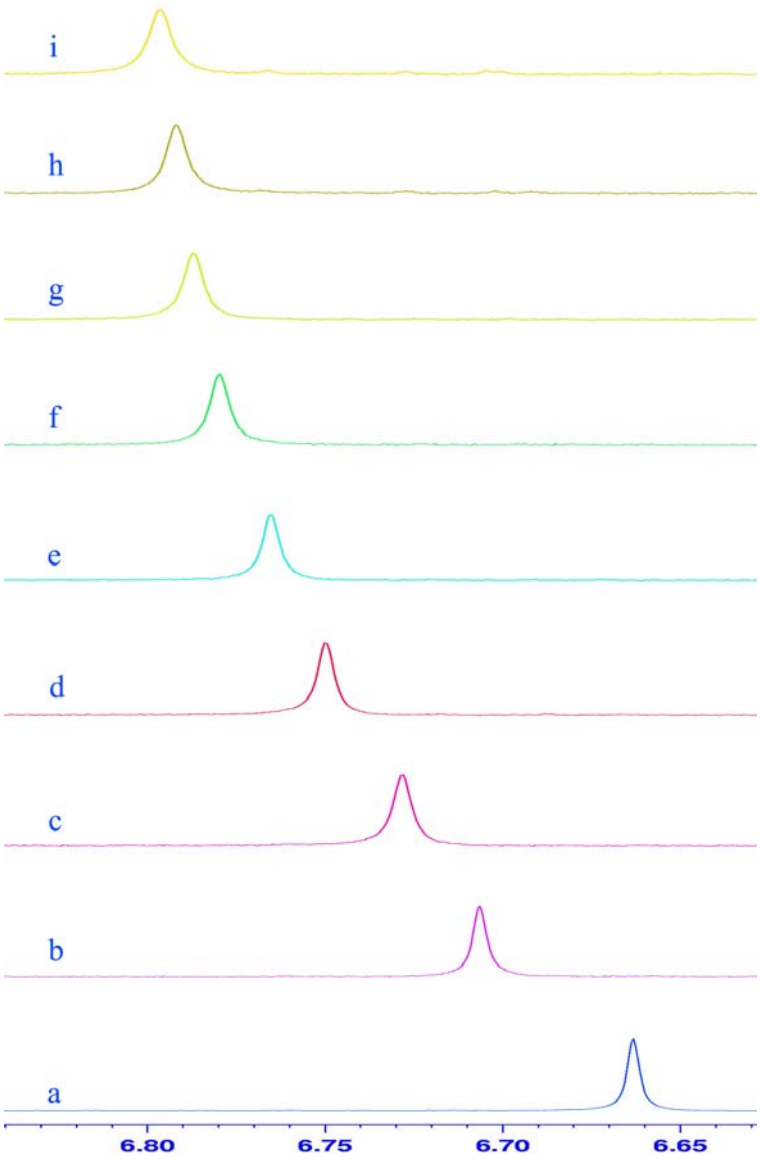


Figure S22. Partial ^{1}H NMR spectra (500 MHz, acetone-d_6, 25^{o}C) of **P5A** at a concentration of 1.2 mM upon addition of [**1**-2H]·2PF_6: (a) 0 mM, (b) 1.1 mM, (c) 2.4 mM, (d) 3.9 mM, (e) 5.9 mM, (f) 8.4 mM, (g) 10.6 mM, (h) 12.9 mM, and (i) 17.5 mM.

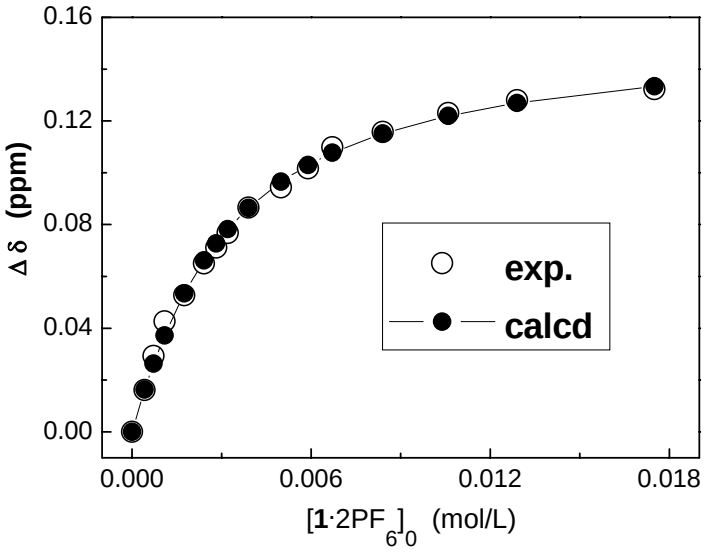


Figure S23. The non-linear curve-fitting (NMR titrations) for the complexation of **P5A** host (1.2 mM) with [**1**-2H]·2PF$_6$ in acetone-d_6 at 25°C. The concentration of **1**·2PF$_6$ was 0, 0.4, 0.7, 1.1, 1.8, 2.4, 2.8, 3.2, 3.9, 5.0, 5.9, 6.7, 8.4, 10.6, 12.9, 17.5 mM.

The K_a values of [**1**-2H]·2PF$_6$ and **2**·2PF$_6$ by **P5A** in different solvents are listed in Table 1 & 2 in the manuscript.

(2). The association constants (K_a) have also been determined using the indirect method.[S11] A previously reported guest 1,3-bis(4,4'-dipyridyl)propane bis(hexafluorophosphate) (**G**$_{ref}$·2PF$_6$, see ref S12 and Fig. S24) that exhibits slow exchange kinetics and an excess of [**1**-2H]·2PF$_6$ or **2**·2PF$_6$ are allowed to compete for a limiting quantity of **P5A**. The association constants between **G**$_{ref}$·2PF$_6$ and **P5A** are (1.2±0.2) × 10^2,[S12] (2.0±0.3) × 10^2, and (1.0±0.2) × 10^3 M^{-1} in DMSO-d_6, 3:7 acetone-d_6:DMSO-d_6, and 3:2 acetone-d_6:DMSO-d_6 respectively. Although **2**·2PF$_6$

has good solubility in acetone-d_6 and 1:1 acetone-d_6:$CDCl_3$, precipitation occurred immediately when mixing it and **P5A**. Therefore, the K_a values of $\mathbf{G_{ref}}$ and **P5A** can't be determined in these two solvents.

The integration of the resonances for the free and bound guest then allow for a calculation of the association constant. In the three component system:

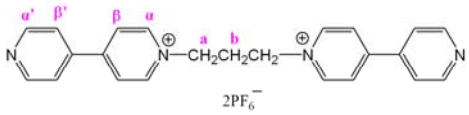
$$K_{a\ ref} = \frac{[P5A{\cdot}G_{ref}]_c}{[P5A]_{uc}[G_{ref}]_{uc}}$$

$$\therefore\ [P5A]_{uc} = \frac{[P5A{\cdot}G_{ref}]_c}{[G_{ref}]_{uc}K_{a\ ref}}$$

So the unknown K_a could be determined using the following equation:

$$K_a = \frac{[P5A{\cdot}G]_c}{[P5A]_{uc}[G]_{uc}} = \frac{[P5A]_0 - [P5A]_{uc} - [P5A{\cdot}G_{ref}]_c}{[P5A]_{uc}([G]_0 - [P5A{\cdot}G]_c)}$$

$$= \frac{[P5A]_0 - [P5A]_{uc} - [P5A{\cdot}G_{ref}]_c}{[P5A]_{uc}\{[G]_0 - ([P5A]_0 - [P5A]_{uc} - [P5A{\cdot}G_{ref}]_c)\}}$$



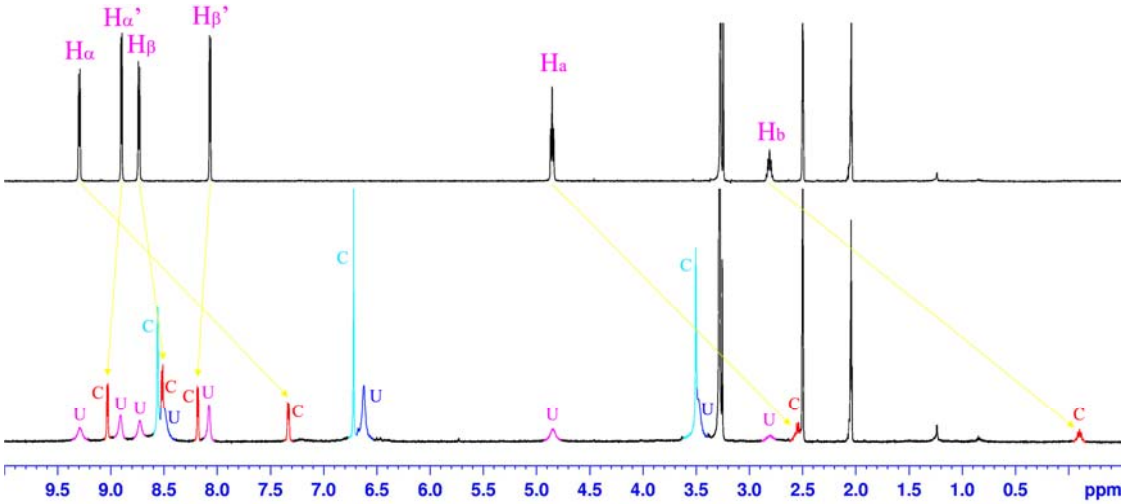


Figure S24. ^{1}H NMR spectrum (500 MHz) of $\mathbf{G_{ref}}\cdot 2PF_6$ (6.0 mM) in the absence (upper) and presence (lower) of **P5A** host (6.2 mM) in acetone-d_6 and DMSO-d_6 (3:7, v:v).

As shown in Table S1, the K_a values for **P5A** with [**1**-2H]·2PF$_6$ and **2**·2PF$_6$ systems determined using the indirect method are almost accordant with those from NMR titration.

TABLE S1. Association constant (K_a/M^{-1}) for complexation of host P5A with [1-2H]·2PF$_6$ and 2·2PF$_6$ at 25^{o}C using different methods.

Guest	Solvent [a]	K_a [b]	K_a [c]
[**1**-2H]·2PF$_6$	DMSO-d_6	(5.5±0.2) × 10	[d]
[**1**-2H]·2PF$_6$	acetone-d_6:DMSO-d_6 3:7	(1.2±0.4) × 10^2	1.4 × 10^2
[**1**-2H]·2PF$_6$	acetone-d_6:DMSO 3:2	(2.7±0.3) × 10^2	2.6 × 10^2
[**1**-2H]·2PF$_6$	acetone-d_6	(4.6±0.6) × 10^2	[e]
[**1**-2H]·2PF$_6$	acetone-d_6:CDCl$_3$ 1:1	(3.1±0.5) × 10^3	[e]
2·2PF$_6$	DMSO-d_6	(1.4±0.2) × 10^2	1.5 × 10^2
2·2PF$_6$	acetone-d_6:DMSO-d_6 3:7	(3.3±0.4) × 10^2	3.8 × 10^2
2·2PF$_6$	acetone-d_6:DMSO-d_6 3:2	(1.0±0.2) × 10^3	1.3 × 10^3
2·2PF$_6$	acetone-d_6	[f]	[e, f]
2·2PF$_6$	acetone-d_6:CDCl$_3$ 1:1	[f]	[e, f]

[a] v:v. [a] NMR titration. [b] The indirect method. [d] The K_a value was too small (< 80 M^{-1})

to be calculated accurately using the indirect method. [e] Could not be determined due to the poor solubility of the **P5A-G$_{ref}$**·2PF$_6$ complex in these solvents. [f] Could not be determined due to the poor solubility of the **P5A**-[**1**-2H]·2PF$_6$ or **P5A-2**·2PF$_6$ complex in these solvents.

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[S1] According to 1,4-dimethoxy**P5A**'s X-ray crystal structure, the diameter of the cavity of **P5A** was calculated to ca. 5 Å, (T. Ogoshi, S. Kanai, S. Fujinami, T. Yamagishi and Y. Nakamoto, *J. Am. Chem. Soc.* 2008, **130**, 5022–5023) which was similar with the largest H–H longitudinal distance in **BBImB** dication (~ 5.0 Å) and larger than that in 1,4-bis(pyridinium)butane (~ 4.8 Å) and [**1**-2H]$^{2+}$ (~4.7 Å). (Fig. S1)

[S2] It should be noted that suitable benzimidazolium derivative, 1,2-bis(benzimidazolium)ethane dications, can thread through the cavity of a larger dibenzo-24-crown-8 macrocycle (around 6.0 Å, ref S3) to form [2]pseudorotaxanes. (ref S3)

[S3] Cavity size of dibenzo-24-crown-8 macrocycle was estimated to be around 6 Å by taking into consideration the narrowest portion of the macrocycle. See: P. R. Ashton, P. J. Campbell, E. J. T. Chrystal, P. T. Glink, S. Menzer, D. Philp, N. Spencer, J. F. Stoddart, P. A. Tasker and D. J. Williams, *Angew. Chem. Int. Ed.*, 1995, **34**, 1865–1869.

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