Electronic Supplementary Information

Acid/base controllable complexation of triptycene-derived macrotricyclic host and protonated 4,4'-bipyridinium/pyridinium salts

Ying Han,* Zheng Meng, and Chuan-Feng Chen*

Beijing National Laboratory for Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

E-mail: cchen@iccas.ac.cn; hanying463@iccas.ac.cn

Contents

1. Synthetic procedures for guests **2-5**---S2

2. Copies of ^{1}H NMR and ^{13}C NMR spectra of new compounds --------------------------S4

3. ^{1}H NMR spectroscopic titrations of the complexes--S8

4. ^{1}H-^{1}H COSY and ROESY NMR spectra of the complexes-----------------------------S10

5. Determination of the association constants---S18

6. ESI MS spectra of the complexes--S30

7. Crystal packings of the complexes ---S33

8. Acid/base controllable binding and release of the guests in **1**·**2** and **1**·**5**$_2$-------------S35

9. References --S37

1. Synthetic procedures for guests 2-5

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. MALDI-TOF mass spectra were obtained on a BIFLEXIII mass spectrometer. Materials obtained commercially were used without further purification. Host **1** and guest **6** were prepared according to the published procedure.[S1]

General procedure for the synthesis of guests 2, 4 and 5. To a stirred solution of 4,4'-bipyridine or substituted pyridines (5 mmol) in CH_3CN (50 mL) was added excessive HCl. The reaction mixture was stirred for 12 h. The resulting mixture was concentrated under reduced pressure, and yellow oil was obtained, which was dissolved in acetone and treated with NH_4PF_6. The solution was stirred at ambient temperature until clear. After acetone was removed, the solid precipitate was collected by filtration, washed with water, and dried under vacuum.

2: White solid, yield 85.6%. Mp: >300 °C. ^{1}H NMR (300 MHz, CD_3CN): δ 8.49 (d, *J* = 6.3, 4H), 9.06 (d, *J* = 6.3 Hz, 4H), 9.37 (s, 2H). ^{13}C NMR (75 MHz, CD_3CN): δ 117.9, 127.0, 143.9. HRESI-MS: *m/z* calcd for $[M-H-PF_6^-]^+$ $C_{10}H_9N_2$, 157.0760, found 157.0757.

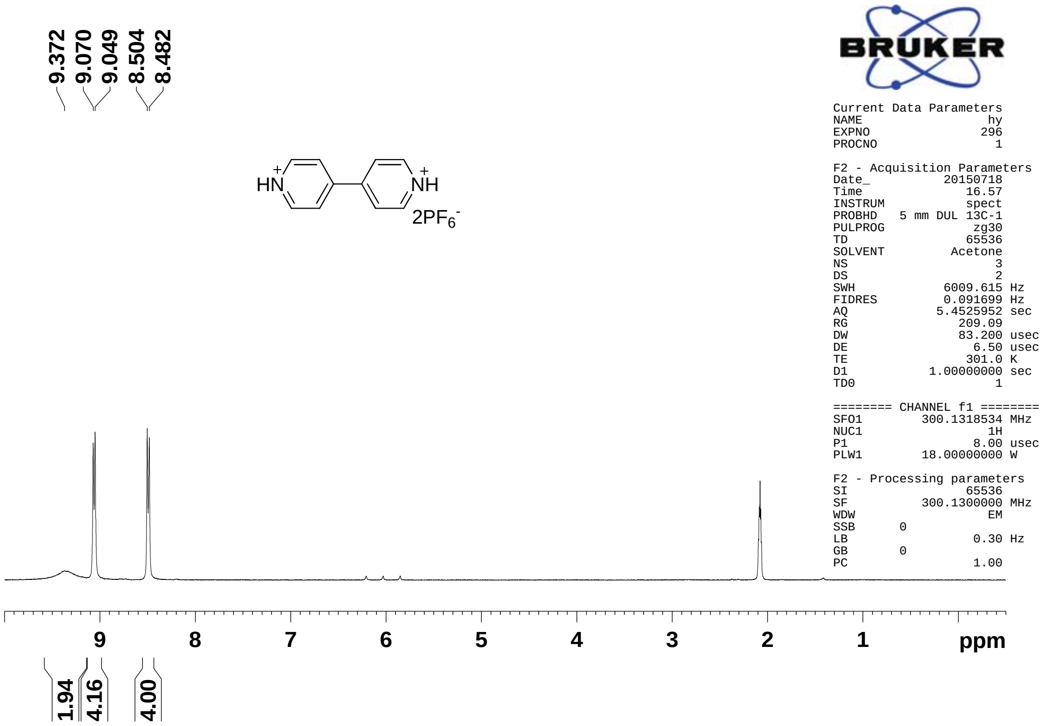
4: White solid, yield 80.3%. Mp: >300 °C. ^{1}H NMR (300 MHz, CD_3CN): δ 7.71 (m, 3H), 7.96 (m, 2H), 8.07 (d, *J* = 6.3 Hz, 2H), 8.81 (d, *J* = 6.3 Hz, 2H). ^{13}C NMR (75 MHz,

CD_3CN): δ 117.9, 123.6, 128.1, 130.1, 131.3, 136.8, 146.6. HRESI-MS: *m/z* calcd for $[M-PF_6^-]^+$ $C_{11}H_{10}N$, 156.0808, found 156.0806.

5: White solid, yield 87.2%. Mp: 206~207 °C. ^{1}H NMR (300 MHz, CD_3CN): δ 3.91 (s, 3H), 7.17 (d, *J* = 9.0 Hz, 2H), 7.94 (d, *J* = 9.0 Hz, 2H), 8.20 (d, *J* = 6.9 Hz, 2H), 8.60 (d, *J* = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, CD_3CN): δ 56.1, 115.9, 117.9, 123.1, 130.6, 141.7, 158.0, 164.0. HRESI-MS: *m/z* calcd for $[M-PF_6^-]^+$ $C_{12}H_{12}NO$, 186.0913, found 186.0913.

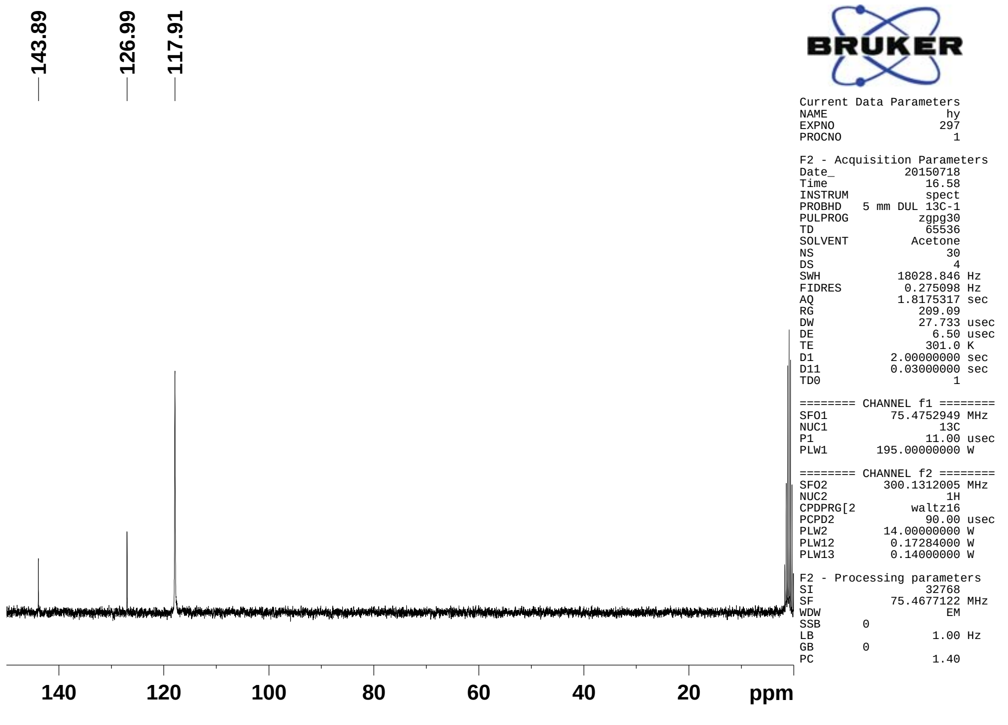
Synthesis of guest 3. To a stirred solution of 4,4'-bipyridine (5 mmol) in CH_3CN (50 mL) was added HCl (2 mmol). The reaction mixture was stirred for 12 h. The resulting mixture was concentrated under reduced pressure, and yellow oil was obtained, which was dissolved in acetone and treated with NH_4PF_6. The solution was stirred at ambient temperature until clear. After acetone was removed, the solid precipitate was collected by filtration, which was then washed with water, and dried under vacuum to give compound **3** (0.4 g, 66.6%) as a white solid. Mp: >300 °C. ^{1}H NMR (300 MHz, CD_3CN): δ 7.53 (s, 1H), 8.19 (d, *J* = 6.6 Hz, 4H), 8.97 (d, *J* = 6.6 Hz, 4H). ^{13}C NMR (75 MHz, CD_3CN): δ 117.9, 124.3, 147.3, 149.4. HRESI-MS: *m/z* calcd for $[M-PF_6^-]^+$ $C_{10}H_9N_2$, 157.0760, found 157.0756.

2. ^{1}H NMR and ^{13}C NMR spectra of new compounds



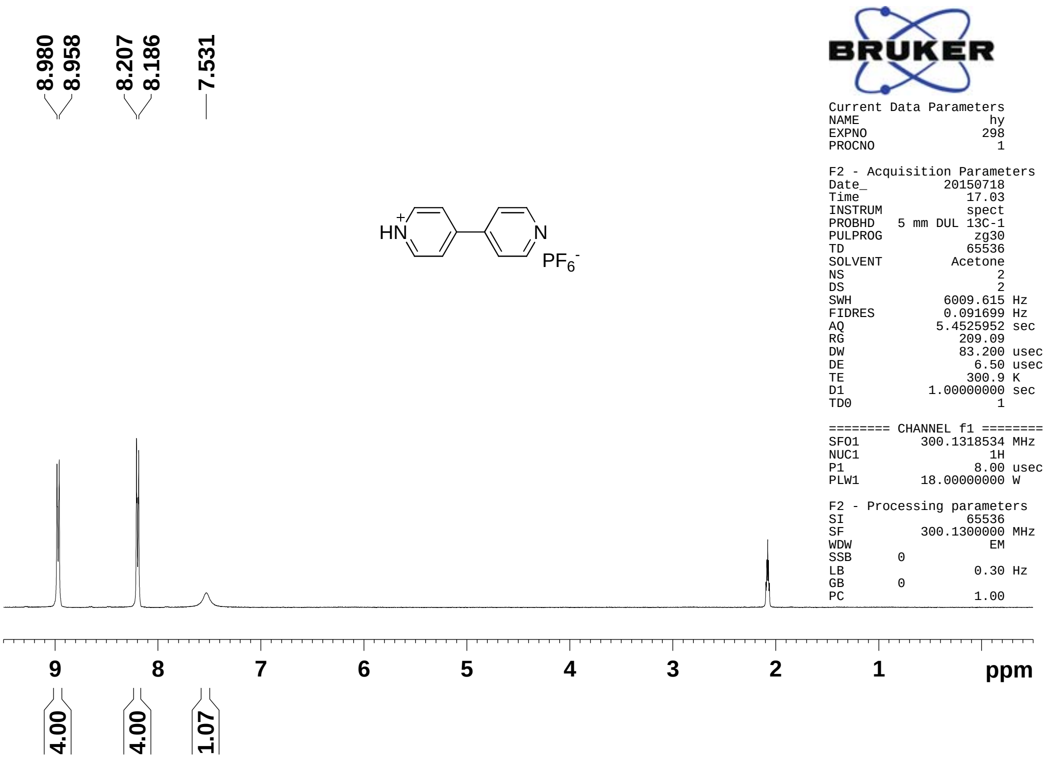
```
Current Data Parameters
NAME                    hy
EXPNO                  296
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150718
Time                 16.57
INSTRUM              spect
PROBHD   5 mm DUL 13C-1
PULPROG               zg30
TD                   65536
SOLVENT            Acetone
NS                       3
DS                       2
SWH               6009.615 Hz
FIDRES            0.091699 Hz
AQ               5.4525952 sec
RG                  209.09
DW                  83.200 usec
DE                    6.50 usec
TE                   301.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           300.1318534 MHz
NUC1                    1H
P1                    8.00 usec
PLW1           18.00000000 W

F2 - Processing parameters
SI                   65536
SF             300.1300000 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

Fig. S1. ^{1}H NMR spectrum (300 MHz, CD_3CN) of **2**.



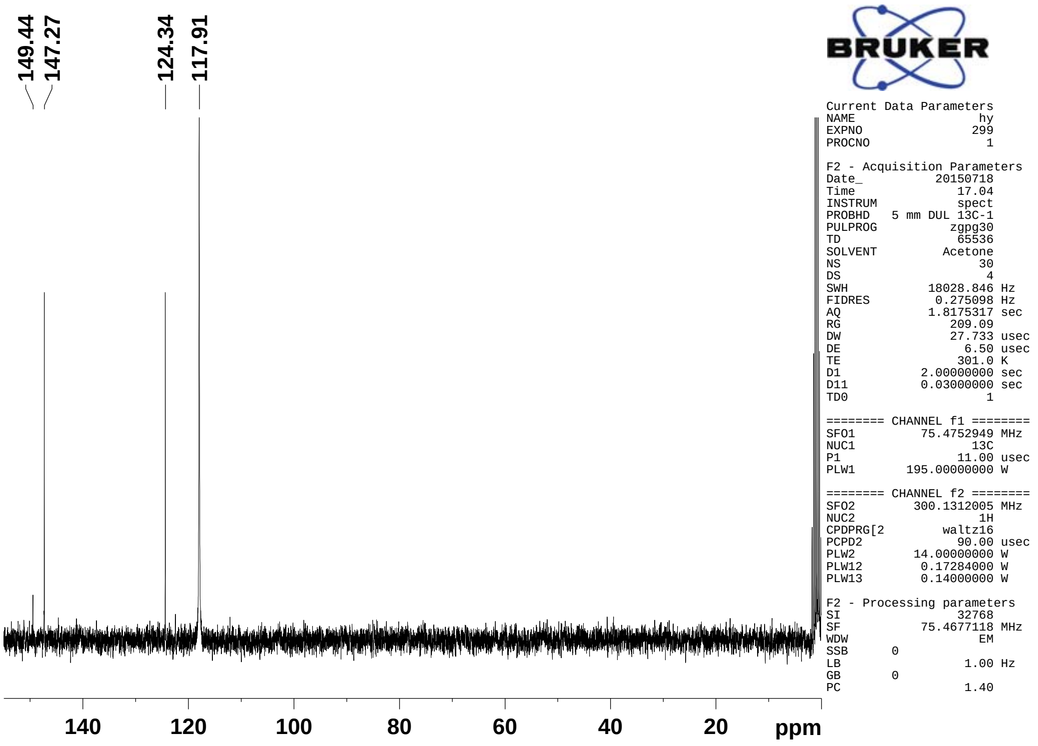
```
Current Data Parameters
NAME                    hy
EXPNO                  297
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150718
Time                 16.58
INSTRUM              spect
PROBHD   5 mm DUL 13C-1
PULPROG             zgpg30
TD                   65536
SOLVENT            Acetone
NS                      30
DS                       4
SWH              18028.846 Hz
FIDRES            0.275098 Hz
AQ               1.8175317 sec
RG                  209.09
DW                  27.733 usec
DE                    6.50 usec
TE                   301.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            75.4752949 MHz
NUC1                   13C
P1                   11.00 usec
PLW1          195.00000000 W

======== CHANNEL f2 ========
SFO2           300.1312005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           14.00000000 W
PLW12           0.17284000 W
PLW13           0.14000000 W

F2 - Processing parameters
SI                   32768
SF              75.4677122 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

Fig. S2. ^{13}C NMR spectrum (75 MHz, CD_3CN) of **2**.



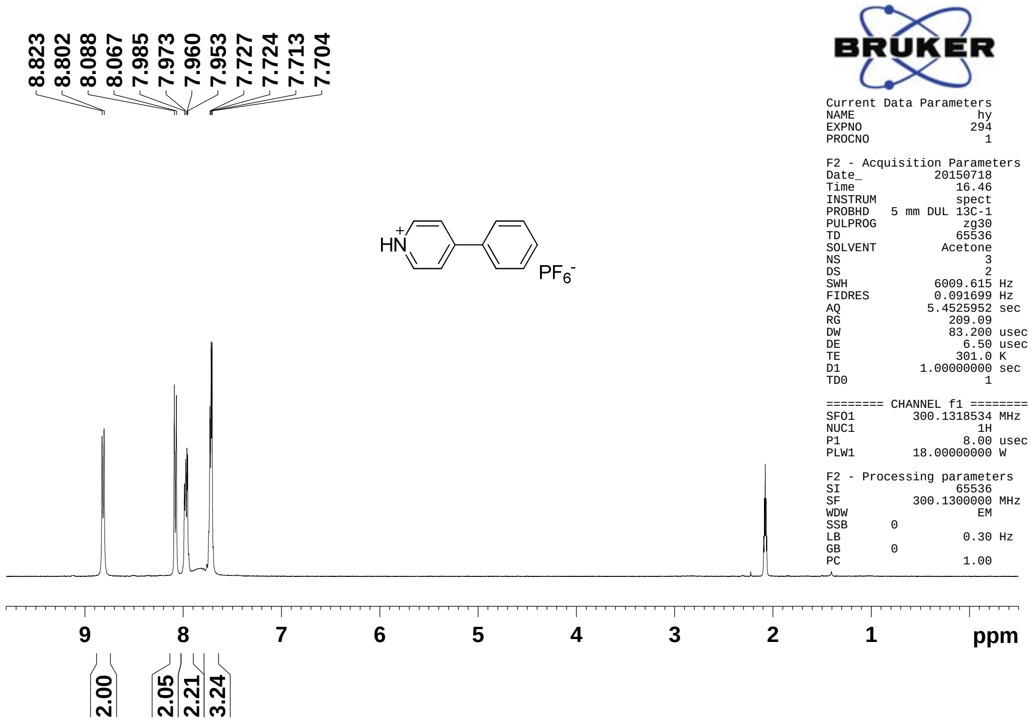
```
Current Data Parameters
NAME                  hy
EXPNO                298
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150718
Time               17.03
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT          Acetone
NS                     2
DS                     2
SWH             6009.615 Hz
FIDRES          0.091699 Hz
AQ             5.4525952 sec
RG                209.09
DW                83.200 usec
DE                  6.50 usec
TE                 300.9 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                  1H
P1                  8.00 usec
PLW1         18.00000000 W

F2 - Processing parameters
SI                 65536
SF           300.1300000 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

Fig. S3. ^{1}H NMR spectrum (300 MHz, CD_3CN) of **3**.



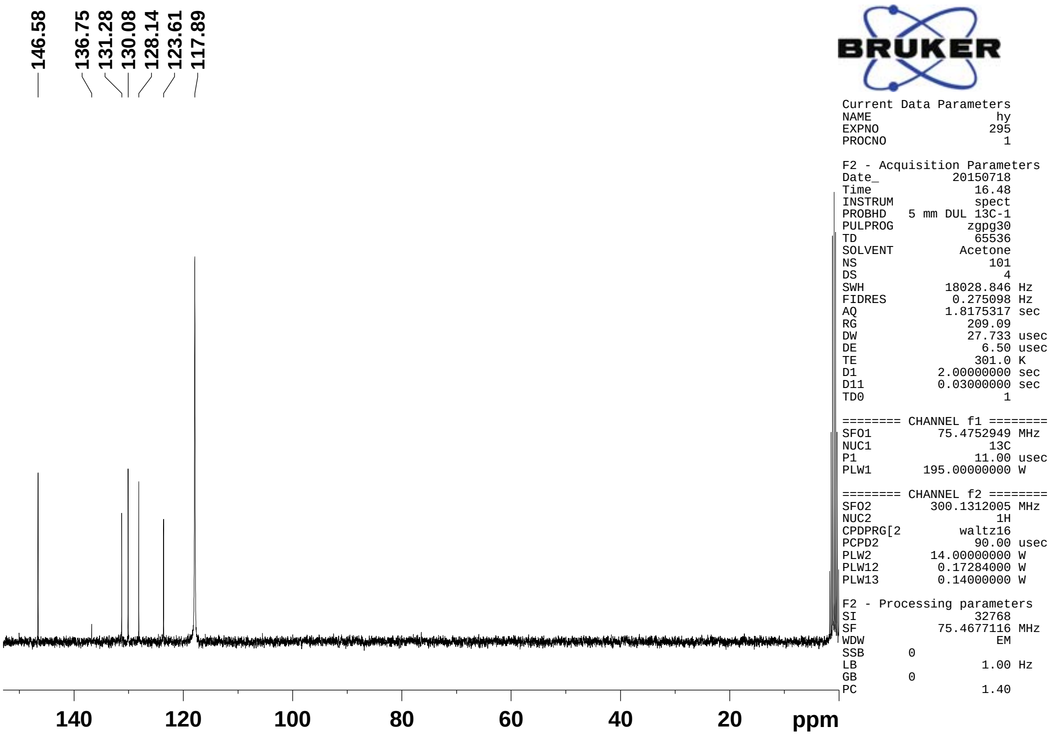
```
Current Data Parameters
NAME                  hy
EXPNO                299
PROCNO                 1

F2 - Acquisition Parameters
Date_           20150718
Time               17.04
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT          Acetone
NS                    30
DS                     4
SWH            18028.846 Hz
FIDRES          0.275098 Hz
AQ             1.8175317 sec
RG                209.09
DW                27.733 usec
DE                  6.50 usec
TE                 301.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          75.4752949 MHz
NUC1                 13C
P1                 11.00 usec
PLW1        195.00000000 W

======== CHANNEL f2 ========
SFO2         300.1312005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         14.00000000 W
PLW12         0.17284000 W
PLW13         0.14000000 W

F2 - Processing parameters
SI                 32768
SF            75.4677118 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

Fig. S4. ^{13}C NMR spectrum (75 MHz, CD_3CN) of **3**.



```
Current Data Parameters
NAME                    hy
EXPNO                  294
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150718
Time                 16.46
INSTRUM              spect
PROBHD   5 mm DUL 13C-1
PULPROG               zg30
TD                   65536
SOLVENT            Acetone
NS                       3
DS                       2
SWH               6009.615 Hz
FIDRES            0.091699 Hz
AQ               5.4525952 sec
RG                  209.09
DW                  83.200 usec
DE                    6.50 usec
TE                   301.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1           300.1318534 MHz
NUC1                    1H
P1                    8.00 usec
PLW1           18.00000000 W

F2 - Processing parameters
SI                   65536
SF             300.1300000 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

Fig. S5. ^{1}H NMR spectrum (300 MHz, CD_3CN) of **4**.



```
Current Data Parameters
NAME                    hy
EXPNO                  295
PROCNO                   1

F2 - Acquisition Parameters
Date_             20150718
Time                 16.48
INSTRUM              spect
PROBHD   5 mm DUL 13C-1
PULPROG             zgpg30
TD                   65536
SOLVENT            Acetone
NS                     101
DS                       4
SWH              18028.846 Hz
FIDRES            0.275098 Hz
AQ               1.8175317 sec
RG                  209.09
DW                  27.733 usec
DE                    6.50 usec
TE                   301.0 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1            75.4752949 MHz
NUC1                   13C
P1                   11.00 usec
PLW1          195.00000000 W

======== CHANNEL f2 ========
SFO2           300.1312005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           14.00000000 W
PLW12           0.17284000 W
PLW13           0.14000000 W

F2 - Processing parameters
SI                   32768
SF              75.4677116 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```

Fig. S6. ^{13}C NMR spectrum (75 MHz, CD_3CN) of **4**.

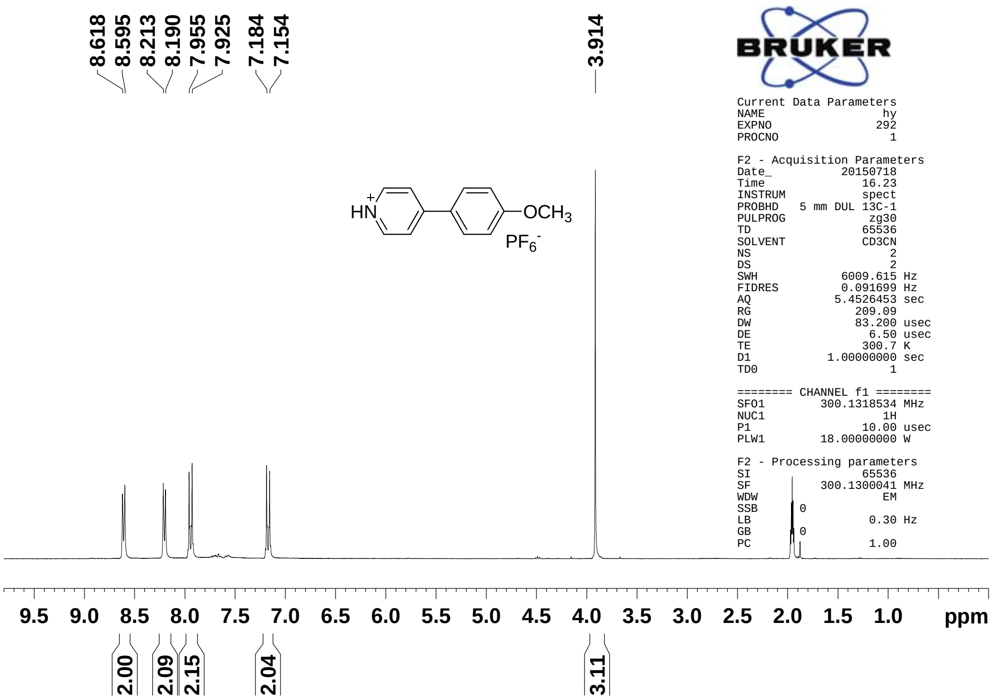


Fig. S7. ^{1}H NMR spectrum (300 MHz, CD_3CN) of **5**.

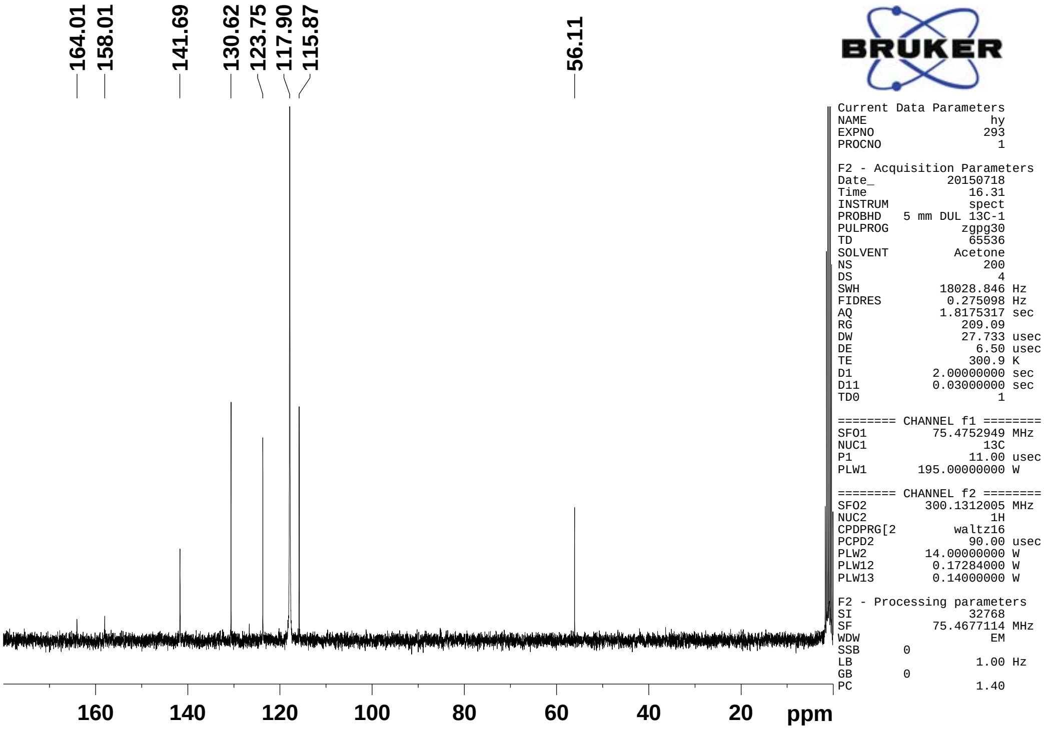


Fig. S8. ^{13}C NMR spectrum (75 MHz, CD_3CN) of **5**.

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

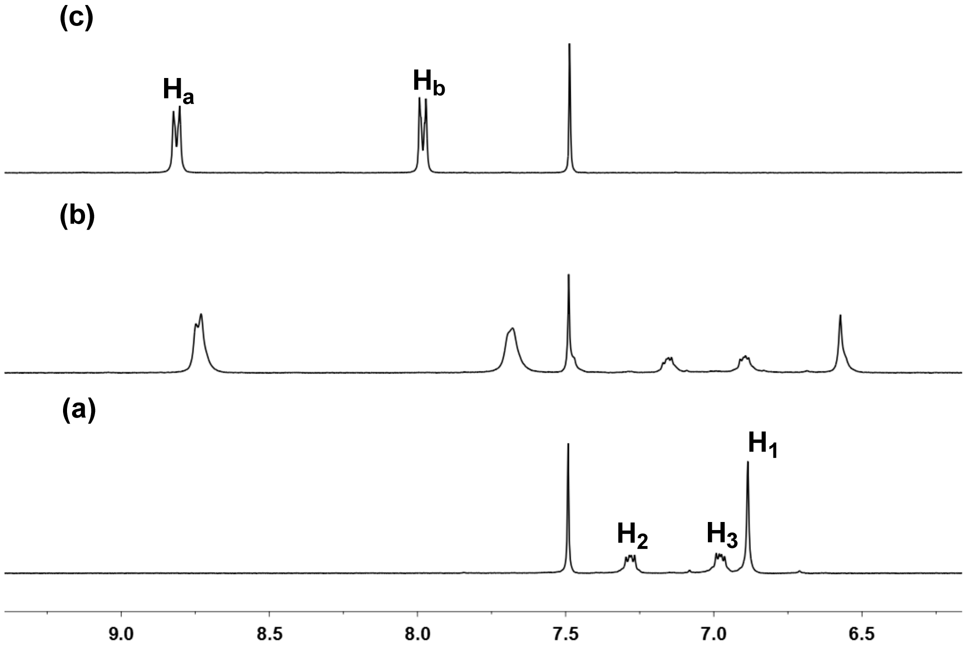


Fig. S9. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3 = 1:1$, 298 K) of (a) free **1**, (b) **1** and 2.0 equiv of **3**, (c) free **3**. $[\mathbf{1}]_0 = 3.0$ mM.

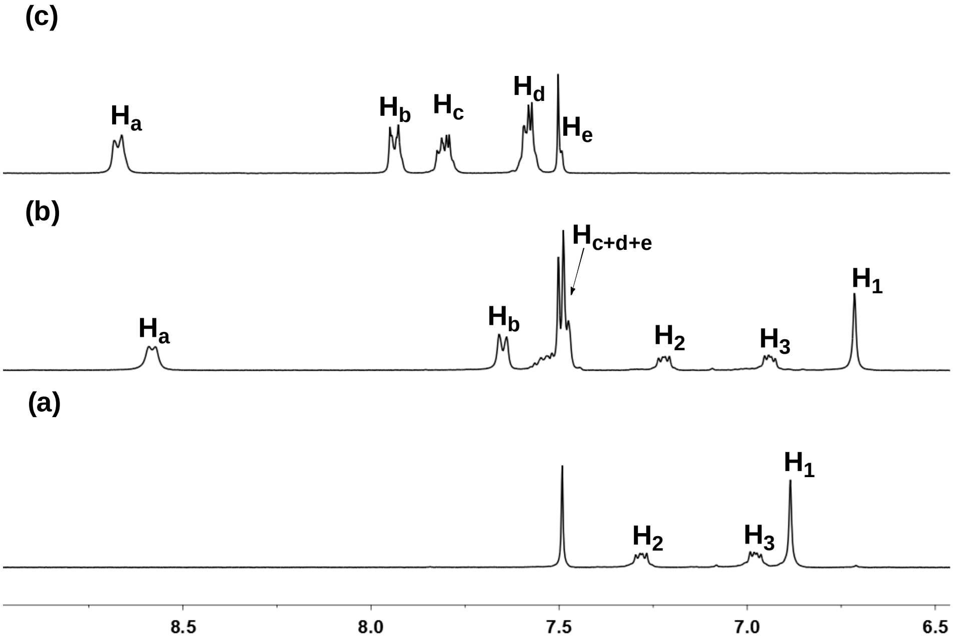


Fig. S10. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3 = 1:1$, 298 K) of (a) free **1**, (b) **1** and 2.0 equiv of **4**, (c) free **4**. $[\mathbf{1}]_0 = 3.0$ mM.

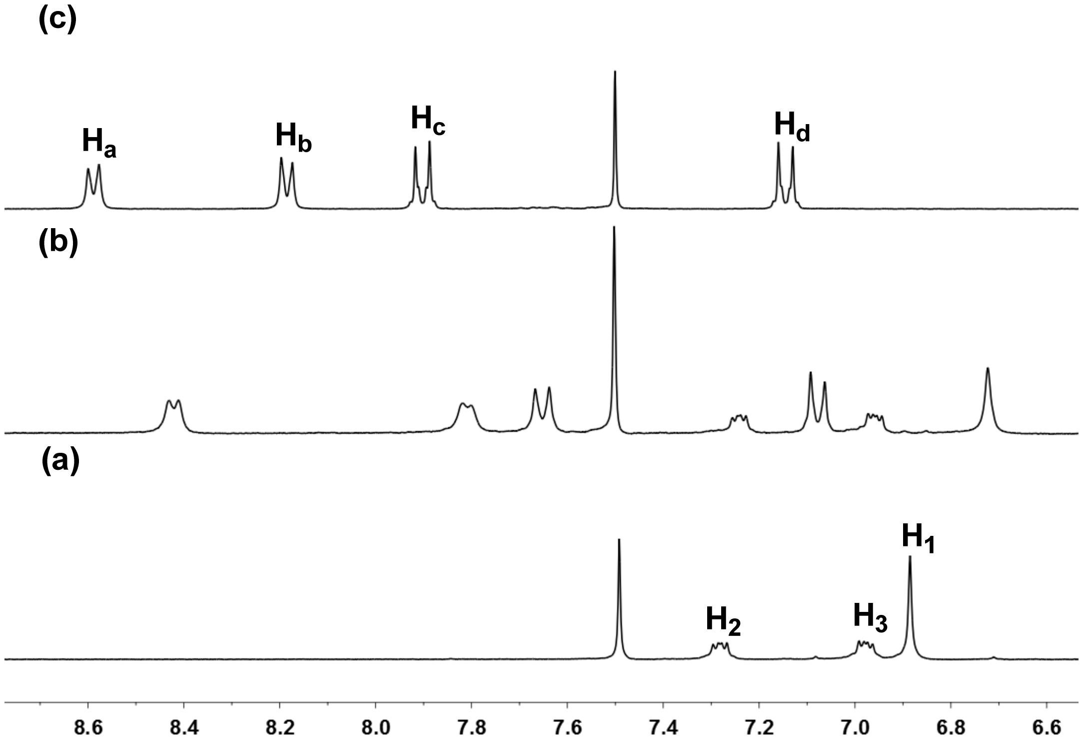
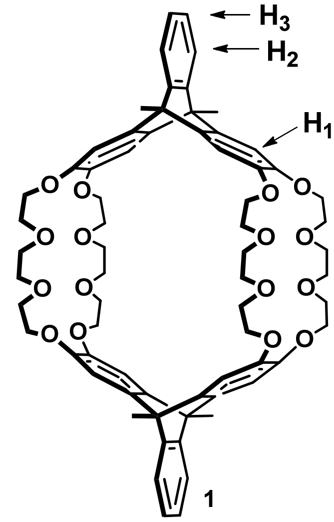
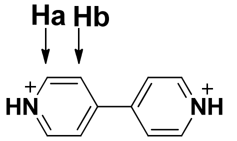


Fig. S11. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3 = 1:1$, 298 K) of (a) free **1**, (b) **1** and 2.0 equiv of **5**, (c) free **5**. $[\mathbf{1}]_0 = 3.0$ mM.

4. ^{1}H-^{1}H COSY and ROESY NMR spectra of the complexes



1



2 $2PF_6^-$

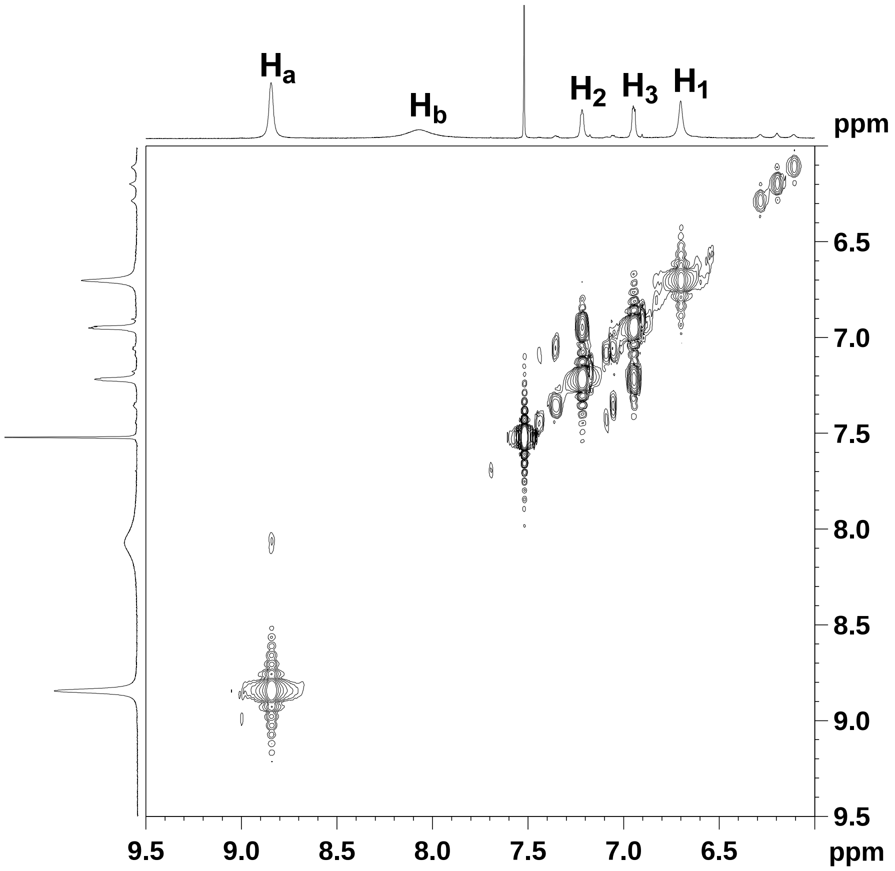
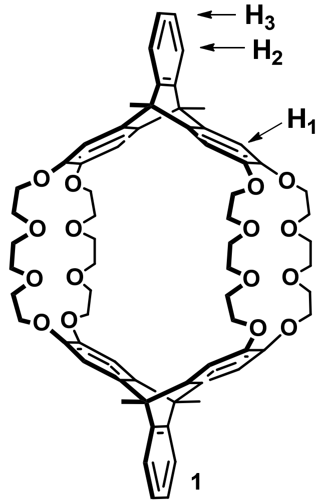
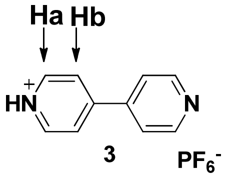


Fig. S12. ^{1}H-^{1}H COSY spectrum (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of **1** and 1 equiv of **2**. $[\mathbf{1}]_0$ = 3.0 mM.



1



3

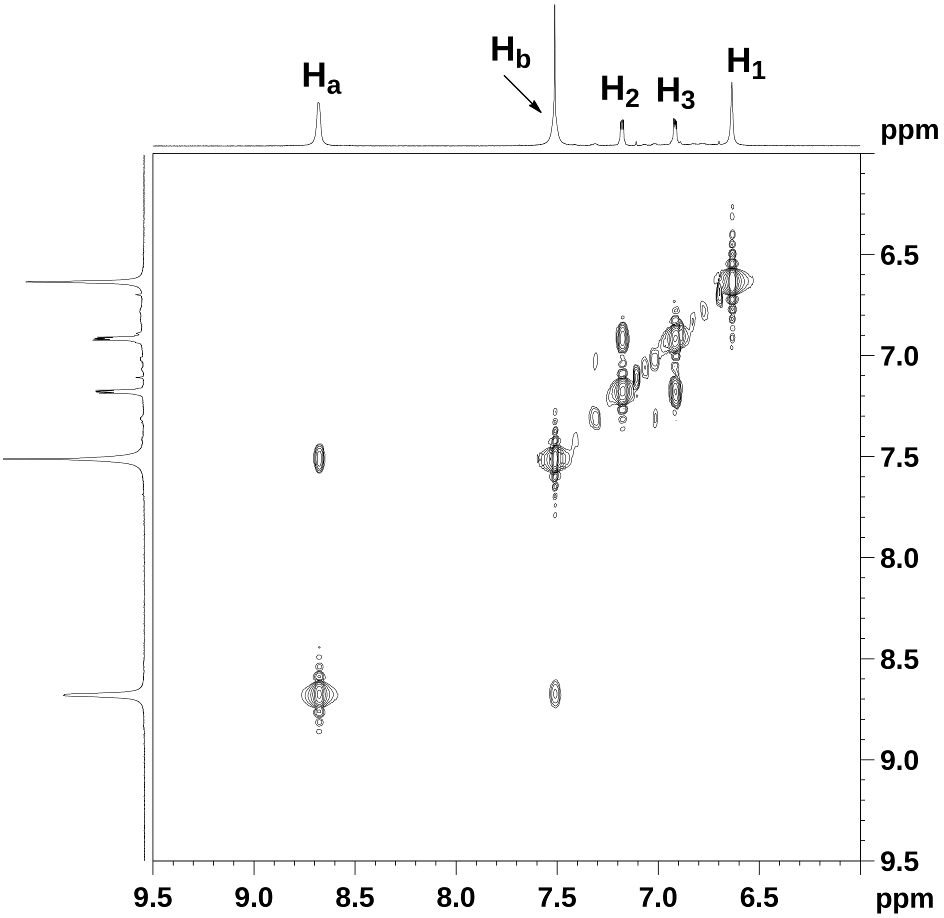
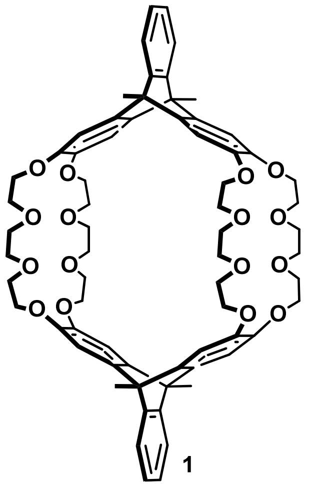
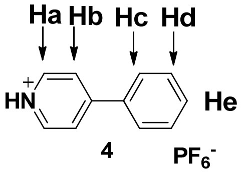


Fig. S13. ^{1}H-^{1}H COSY spectrum (300 MHz, CD$_3$CN/CDCl$_3$ = 1:1, 298 K) of **1** and 2 equiv of **3**. [**1**]$_0$ = 3.0 mM.



1



4

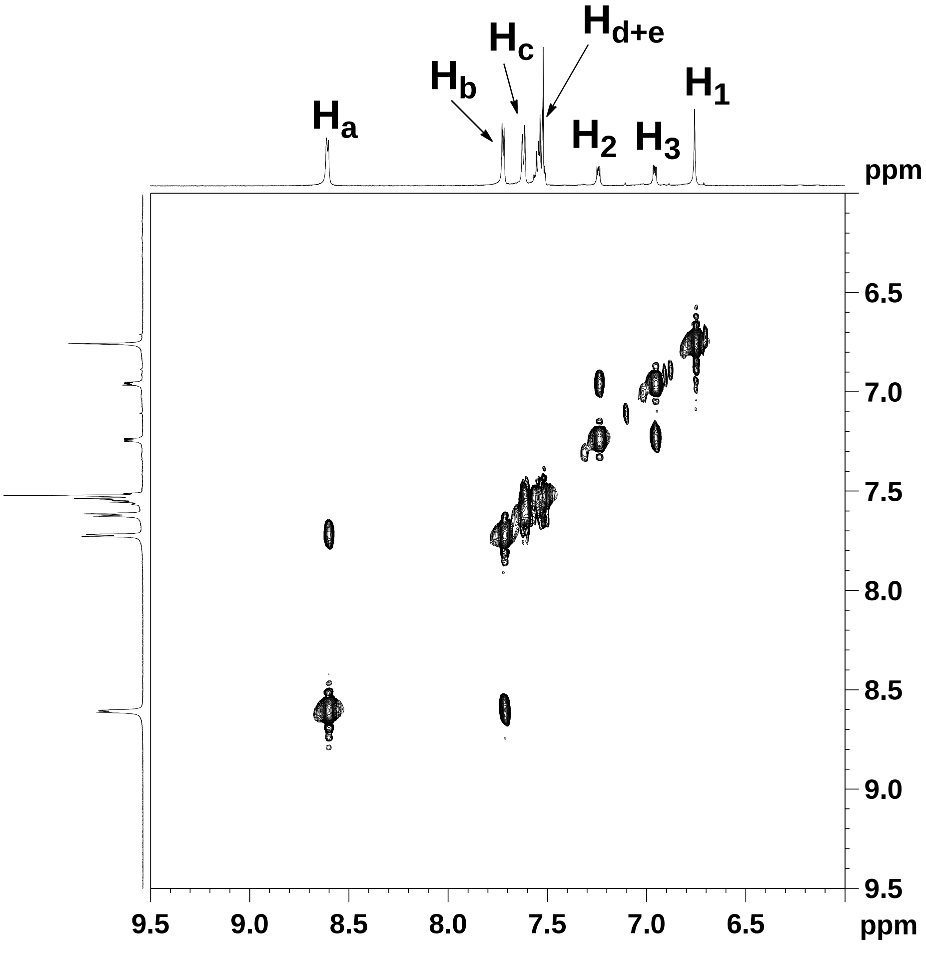
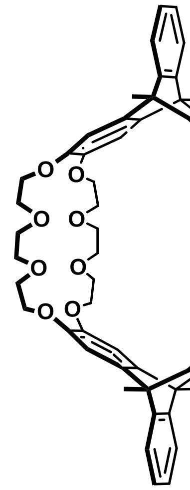
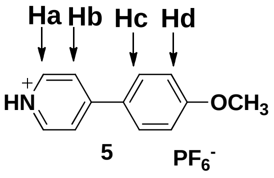


Fig. S14. ^{1}H-^{1}H COSY spectrum (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of **1** and 2 equiv of **4**. [**1**]$_0$ = 3.0 mM.



1



5

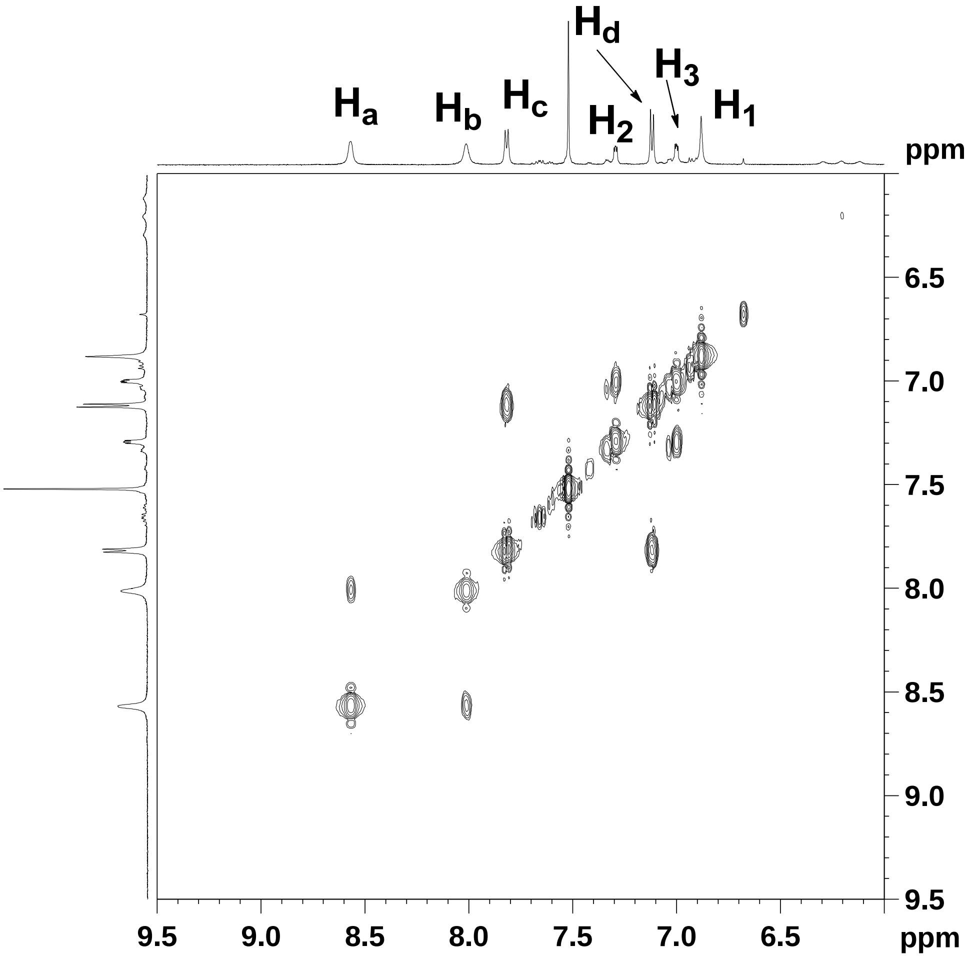
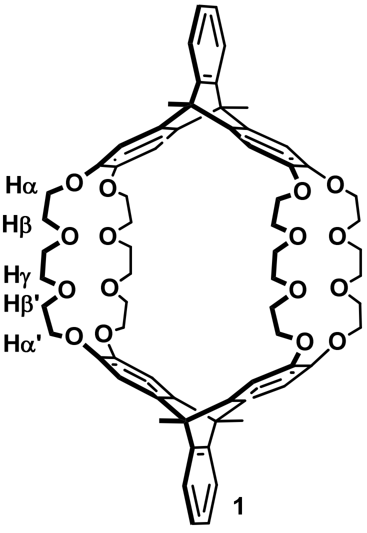
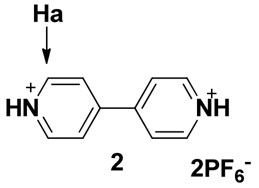


Fig. S15. ^{1}H-^{1}H COSY spectrum (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of **1** and 2 equiv of **5**. $[\mathbf{1}]_0$ = 3.0 mM.



1



2

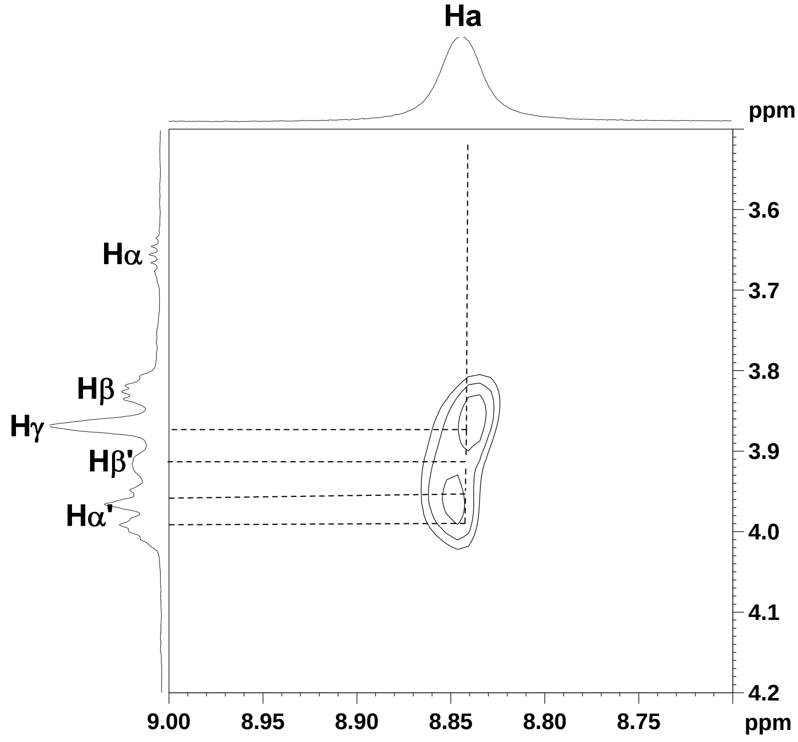
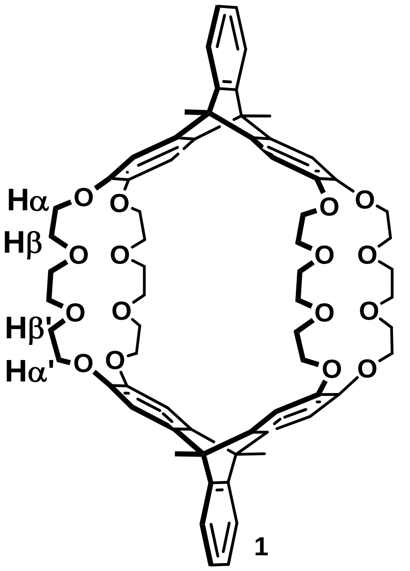
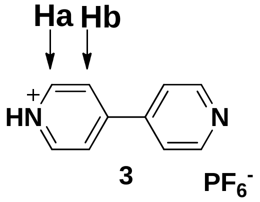


Fig. S16. ^{1}H-^{1}H ROESY spectrum (600 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of **1** and 1 equiv of **2**. $[\mathbf{1}]_0$ = 3.0 mM.



1



3

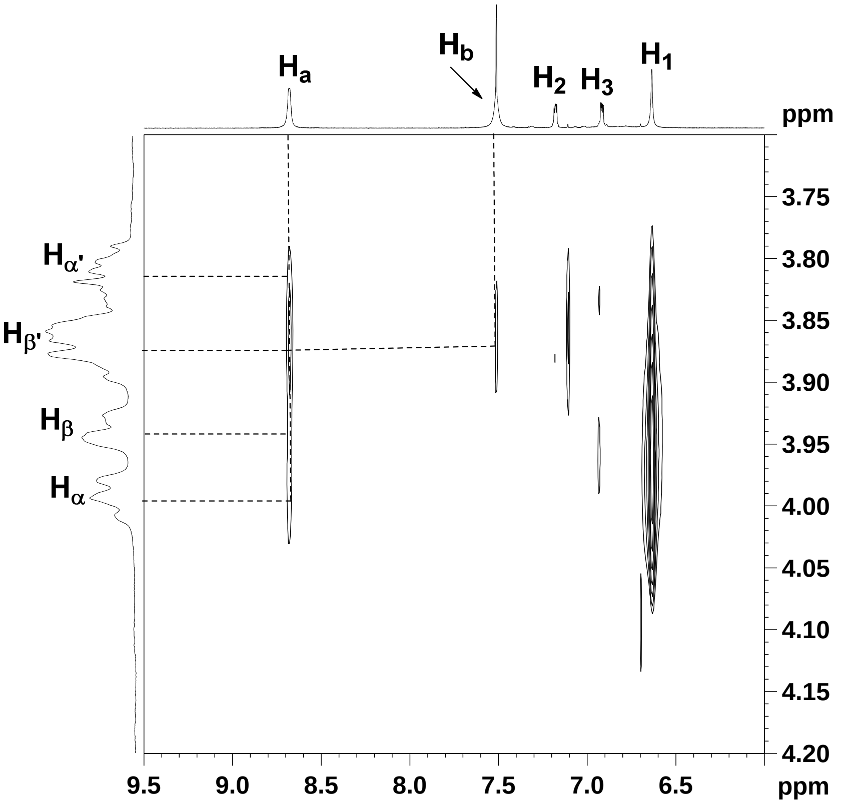
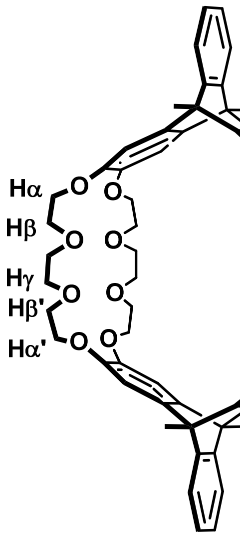
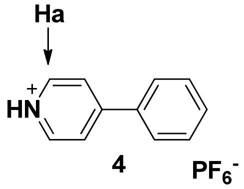


Fig. S17. ^{1}H-^{1}H ROESY spectrum (600 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of **1** and 2 equiv of **3**. [**1**]$_0$ = 3.0 mM.



1



4

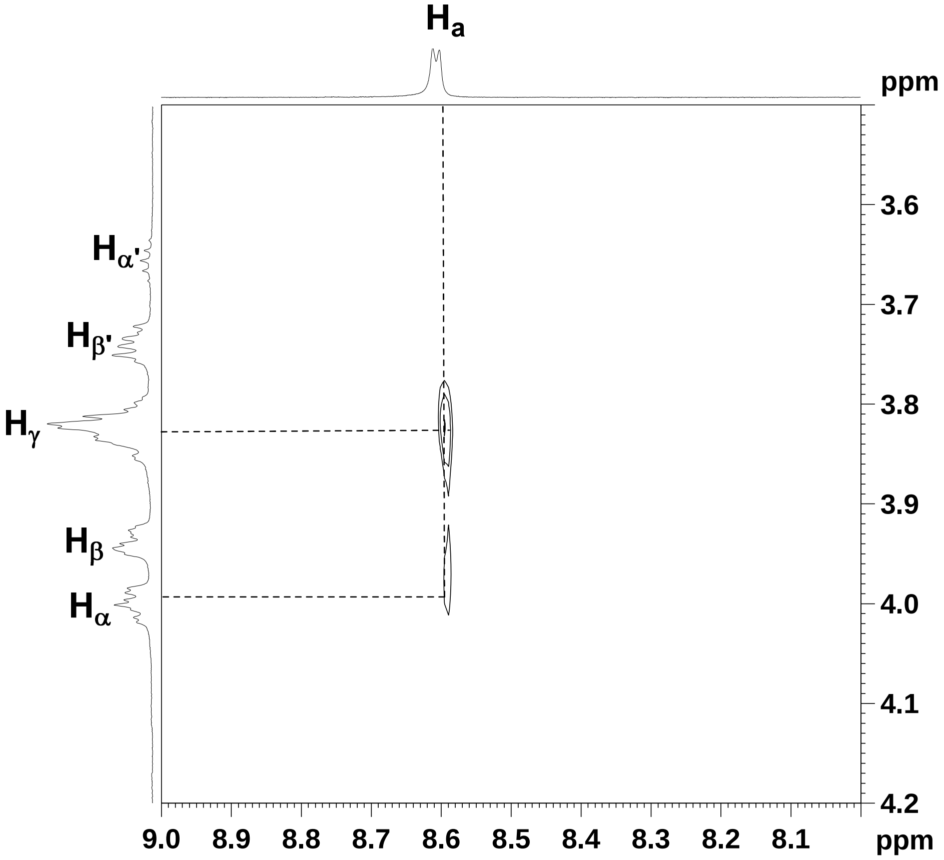
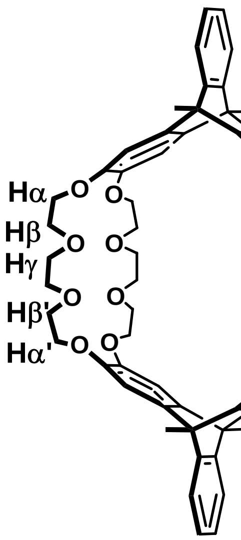
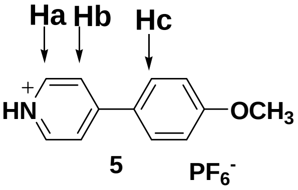


Fig. S18. ^1H-^1H ROESY spectrum (600 MHz, $CD_3CN/CDCl_3 = 1:1$, 298 K) of **1** and 2 equiv of **4**. $[\mathbf{1}]_0 = 3.0$ mM.



1



5

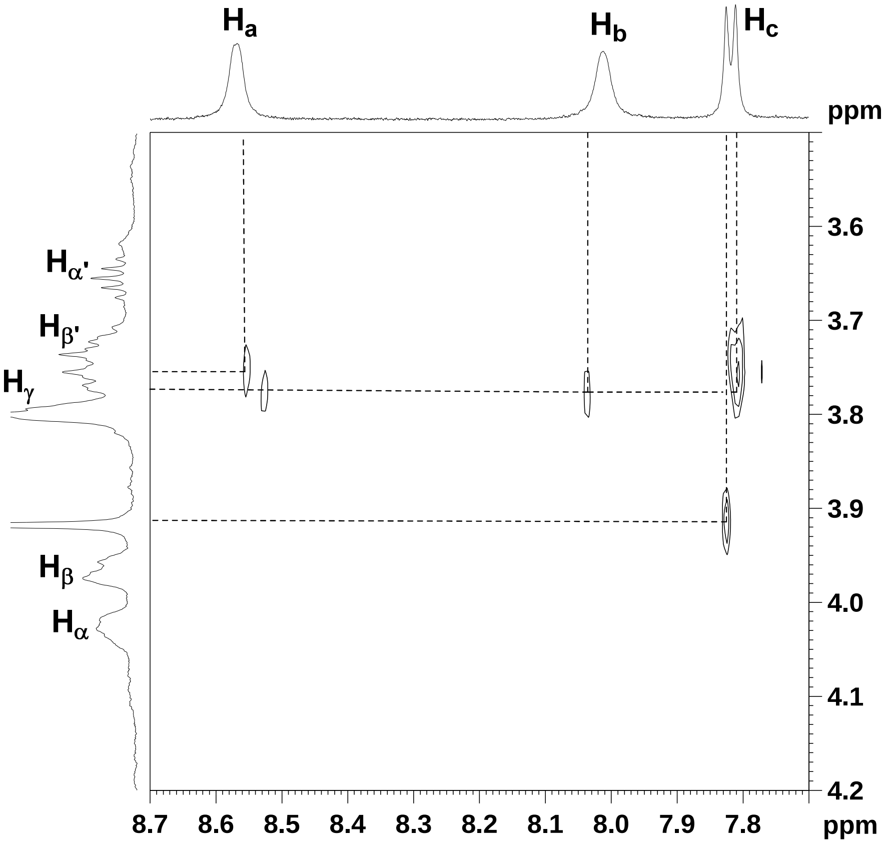


Fig. S19. ^{1}H-^{1}H ROESY spectrum (600 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of **1** and 2 equiv of **5**. [**1**]$_0$ = 3.0 mM.

5. Determination of the association constants of the complexes

In the ^{1}H NMR titrations, a 1:1 (v/v) $CD_3CN/CDCl_3$ solvent was chosen to dissolve the host and the guests. CD_3CN was used as the lock, and TMS was employed as the internal standard. Chemical shifts were reported in parts per million (*ppm*). Δ is the observed chemical shift change relative to uncomplexed species, and Δ_0 is calculated chemical shift change of fully complexed species, and is determined by extrapolation of a plot of Δ vs $1/[\text{guest}]_0$ in the high initial concentration range of the guest. The complex fraction (p) value was calculated from $p=\Delta/\Delta_0$, and the [guest] values were calculated from $[\text{guest}]_0 - p[\mathbf{1}]_0$. A plot of $p/[\text{guest}]$ vs p was used to determine the average association constant K_{av}, which is the average value of the slope and the intercept.[S2] The average association constants (K_{av}) for complexes $\mathbf{1}\cdot\mathbf{3}_2$, $\mathbf{1}\cdot\mathbf{4}_2$ and $\mathbf{1}\cdot\mathbf{5}_2$ were calculated to be $4.0(\pm0.1)\times10^2$, $7.5(\pm0.1)\times10^2$ and $4.5(\pm0.1)\times10^2$ M^{-1}, respectively, by the Scatchard plot. By a nonlinear curve-fitting method,[S3] the association constants between the host and the guests were further calculated, and the results were shown in text.

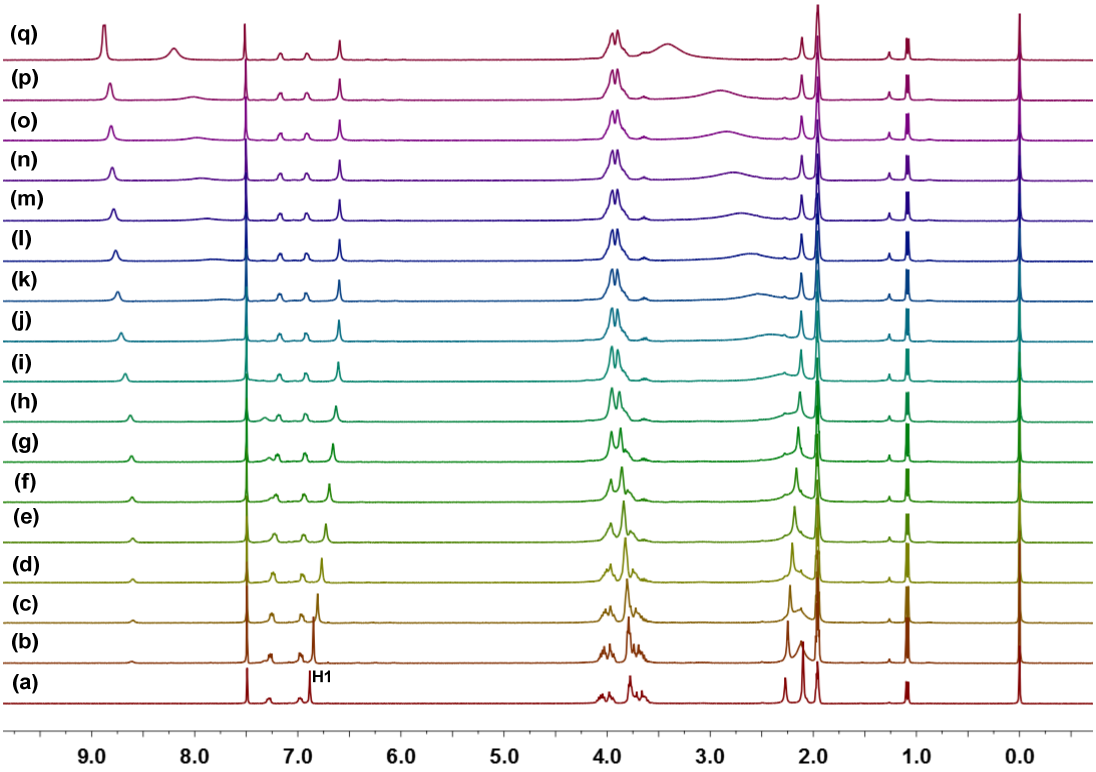


Fig. S20. ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of **1** at a concentration of 3.0 mM with different concentrations of **2**: (a) 0.00 mM; (b) 0.6 mM; (c) 0.9 mM; (d) 1.2 mM; (e) 1.5 mM; (f) 1.8 mM; (g) 2.1 mM; (h) 2.4 mM; (i) 3.0 mM; (j) 3.6 mM; (k) 4.2 mM; (l) 4.8 mM; (m) 5.4 mM; (n) 6.0 mM; (o) 6.6 mM; (p) 7.2 mM; (q) 15.0 mM.

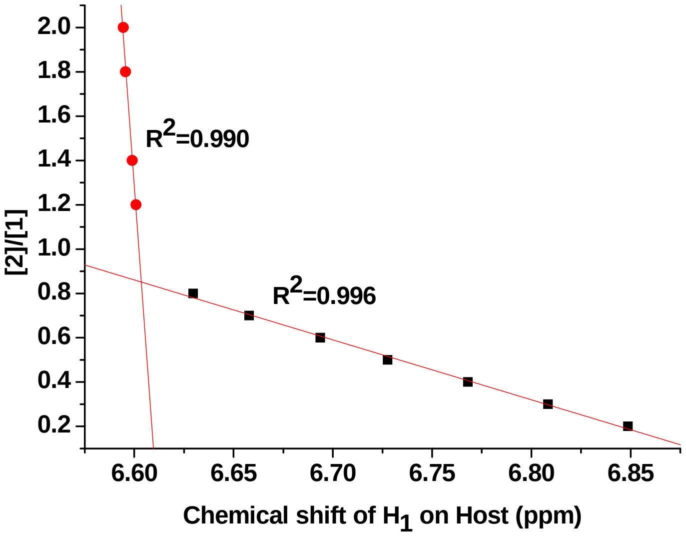


Fig. S21. Mole ratio plot for the complexation of **1** and **2** in $CD_3CN/CDCl_3$ = 1:1 at 298 K.

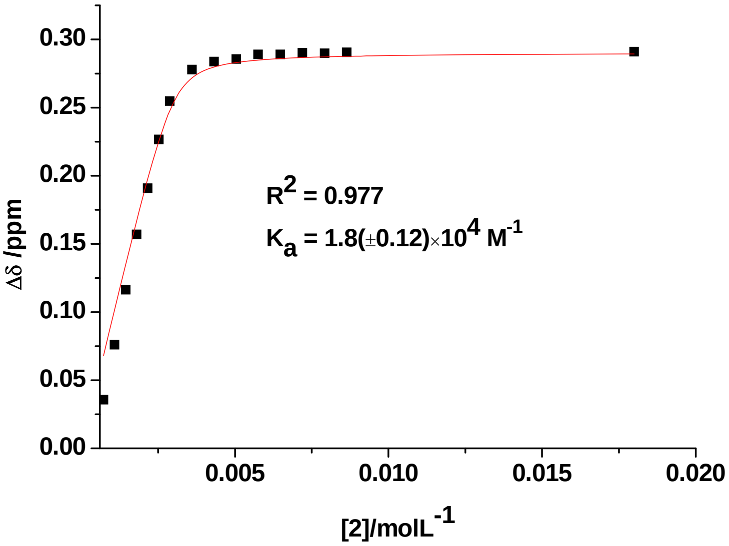


Fig. S22. Plot of $\Delta\delta$ (ppm) for the bridgehead proton H_1 of **1** vs **2** concentration in $CD_3CN/CDCl_3$ = 1:1 at 298 K.

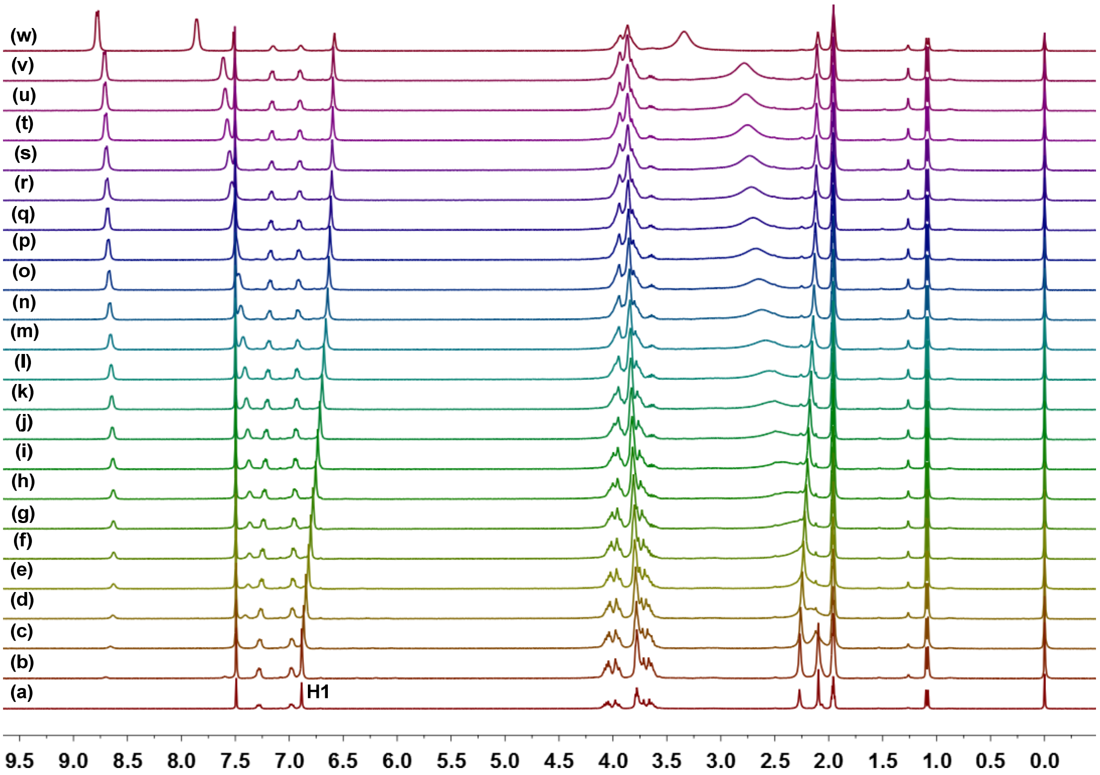


Fig. S23. ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of **1** at a concentration of 3.0 mM with different concentrations of **3**: (a) 0.00 mM; (b) 0.6 mM; (c) 1.2 mM; (d) 1.8 mM; (e) 2.4 mM; (f) 3.0 mM; (g) 3.6 mM; (h) 4.2 mM; (i) 4.8 mM; (j) 5.4 mM; (k) 6.0 mM; (l) 6.6 mM; (m) 7.2 mM; (n) 7.8 mM; (o) 8.4 mM; (p) 9.0 mM; (q) 9.6 mM; (r) 10.2 mM; (s) 10.8 mM; (t) 11.4 mM; (u) 12.0 mM; (v) 12.6 mM; (w) 30.0 mM.

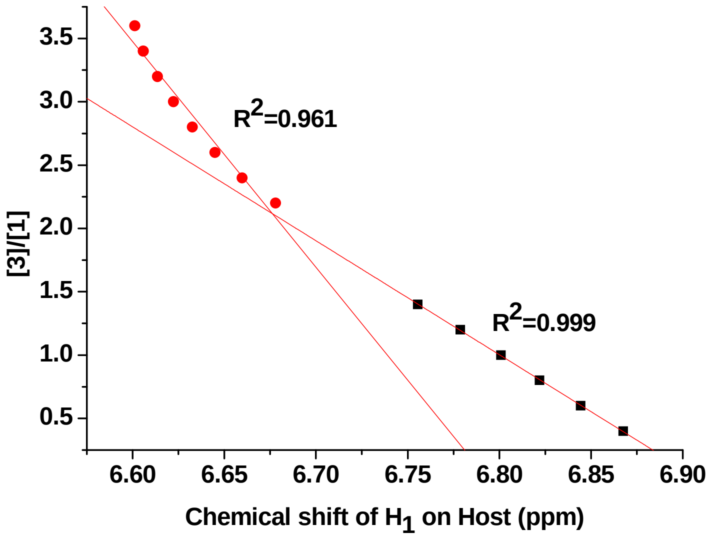


Fig. S24. Mole ratio plot for the complexation of **1** and **3** in $CD_3CN/CDCl_3$ = 1:1 at 298 K.

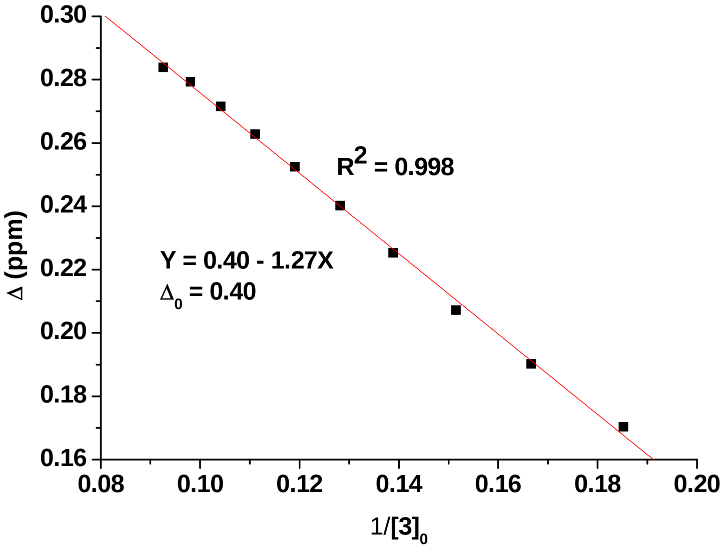


Fig. S25. Determination of Δ_0 of H_1 for the complexation between **1** and **3** in $CD_3CN/CDCl_3$ = 1:1 at 298 K. [**1**]$_0$ = 3.0 mM.

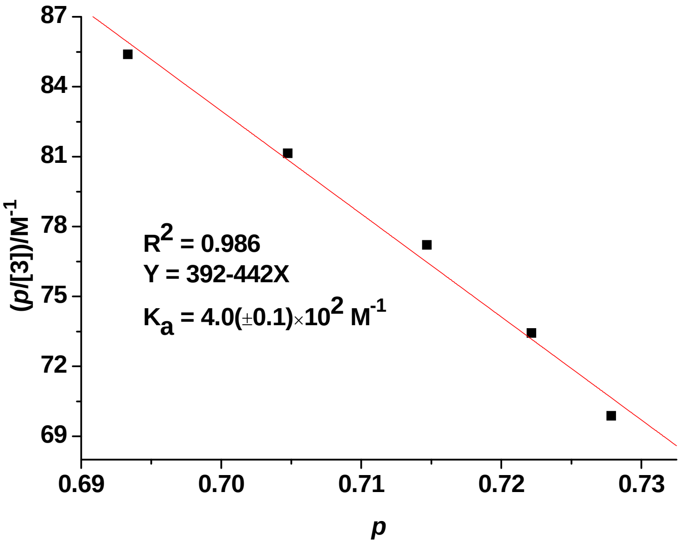


Fig. S26. Scatchard plot for the complexation between **1** and **3** in $CD_3CN/CDCl_3 = 1:1$ at 298 K. $[\mathbf{1}]_0 = 3.0$ mM.

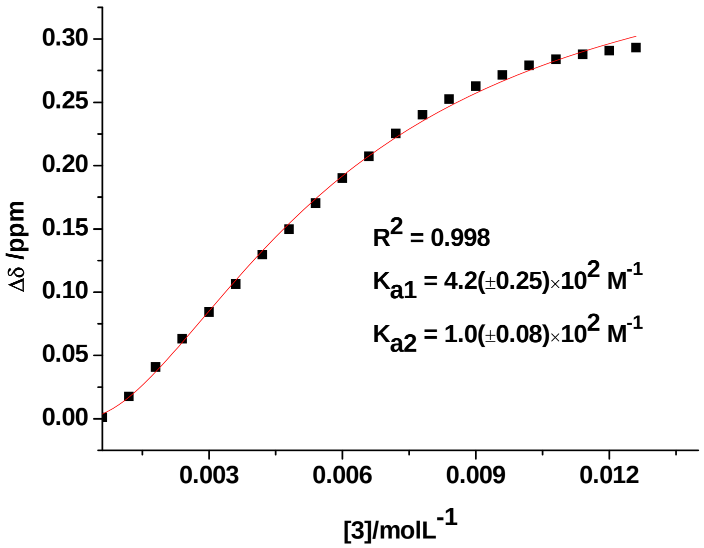


Fig. S27. Plot of Δδ (ppm) for the bridgehead proton H_1 of **1** vs **3** concentration in $CD_3CN/CDCl_3 = 1:1$ at 298 K.

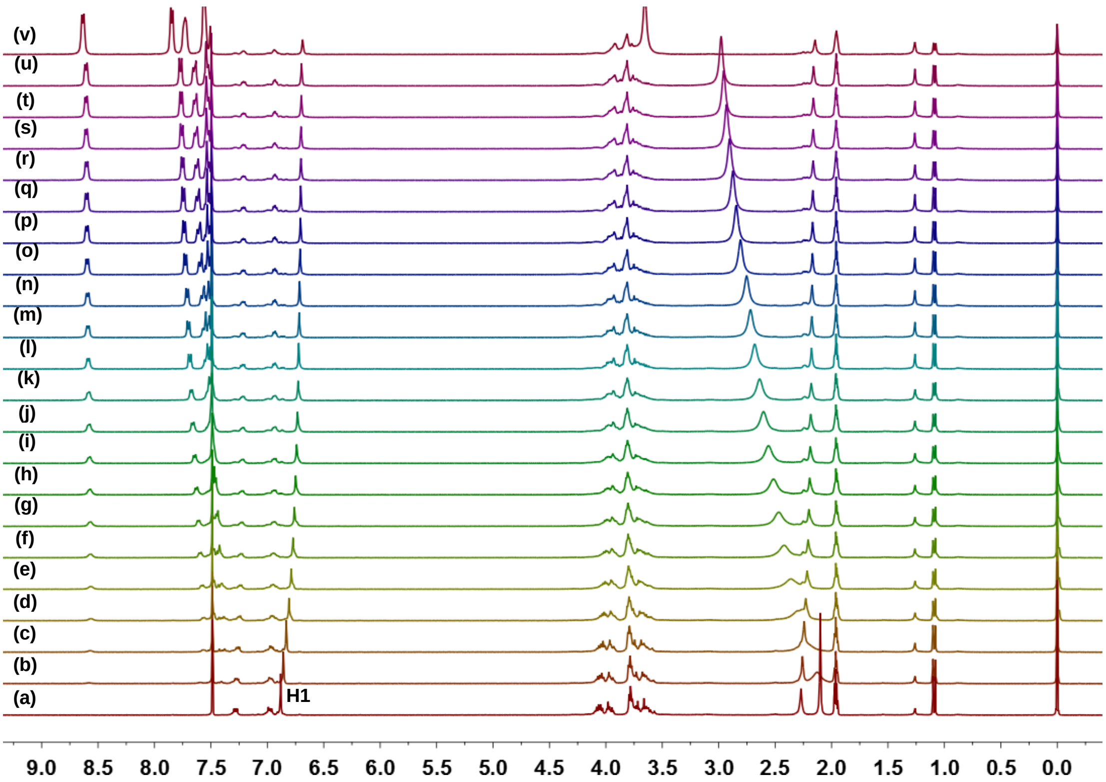


Fig. S28. ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of **1** at a concentration of 3.0 mM with different concentrations of **4**: (a) 0.00 mM; (b) 0.6 mM; (c) 1.2 mM; (d) 1.8 mM; (e) 2.4 mM; (f) 3.0 mM; (g) 3.6 mM; (h) 4.2 mM; (i) 4.8 mM; (j) 5.4 mM; (k) 6.0 mM; (l) 6.6 mM; (m) 7.2 mM; (n) 7.8 mM; (o) 9.0 mM; (p) 9.6 mM; (q) 10.2 mM; (r) 10.8 mM; (s) 11.4 mM; (t) 12.0 mM; (u) 12.6 mM; (v) 30.0 mM.

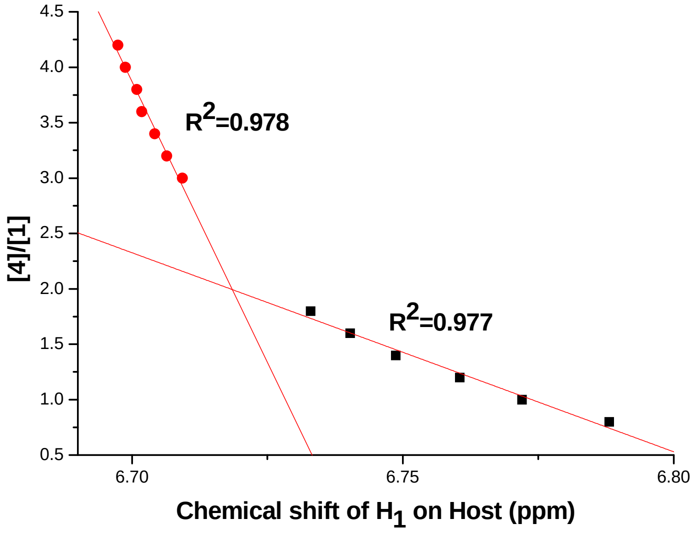


Fig. S29. Mole ratio plot for the complexation of **1** and **4** in $CD_3CN/CDCl_3$ = 1:1 at 298 K.

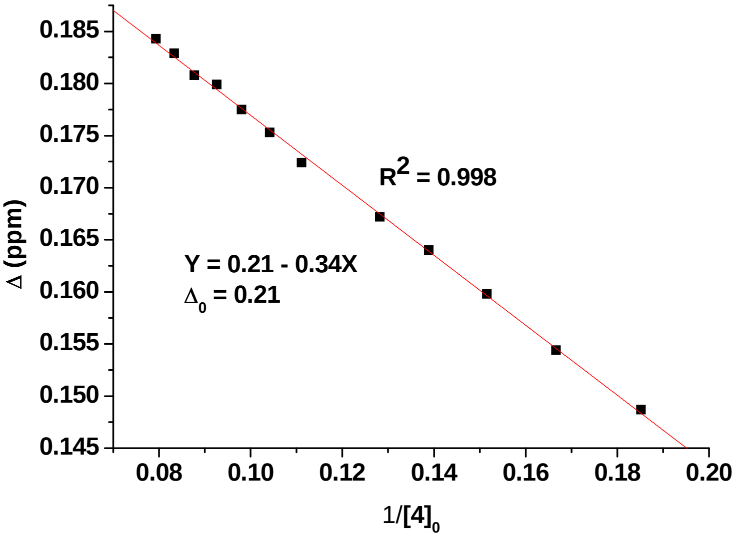


Fig. S30. Determination of Δ_0 of H_1 for the complexation between **1** and **4** in $CD_3CN/CDCl_3$ = 1:1 at 298 K. [**1**]$_0$ = 3.0 mM.

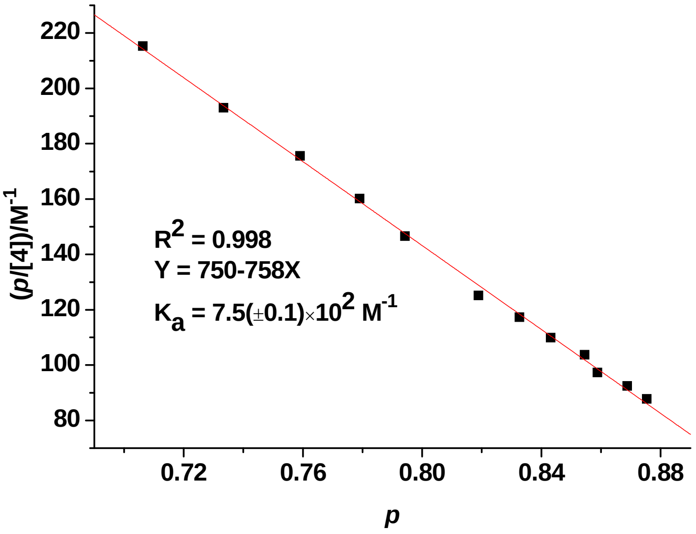


Fig. S31. Scatchard plot for the complexation between **1** and **4** in $CD_3CN/CDCl_3 = 1:1$ at 298 K. $[\mathbf{1}]_0 = 3.0$ mM.

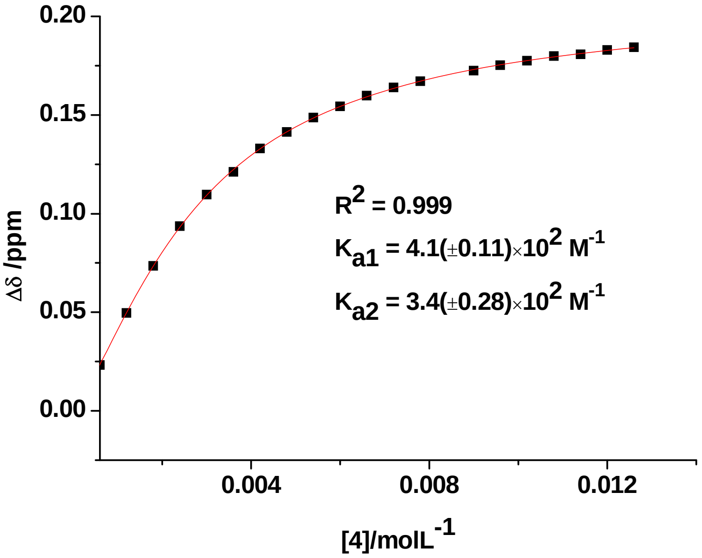


Fig. S32. Plot of Δδ (ppm) for the bridgehead proton H_1 of **1** vs **4** concentration in $CD_3CN/CDCl_3 = 1:1$ at 298 K.

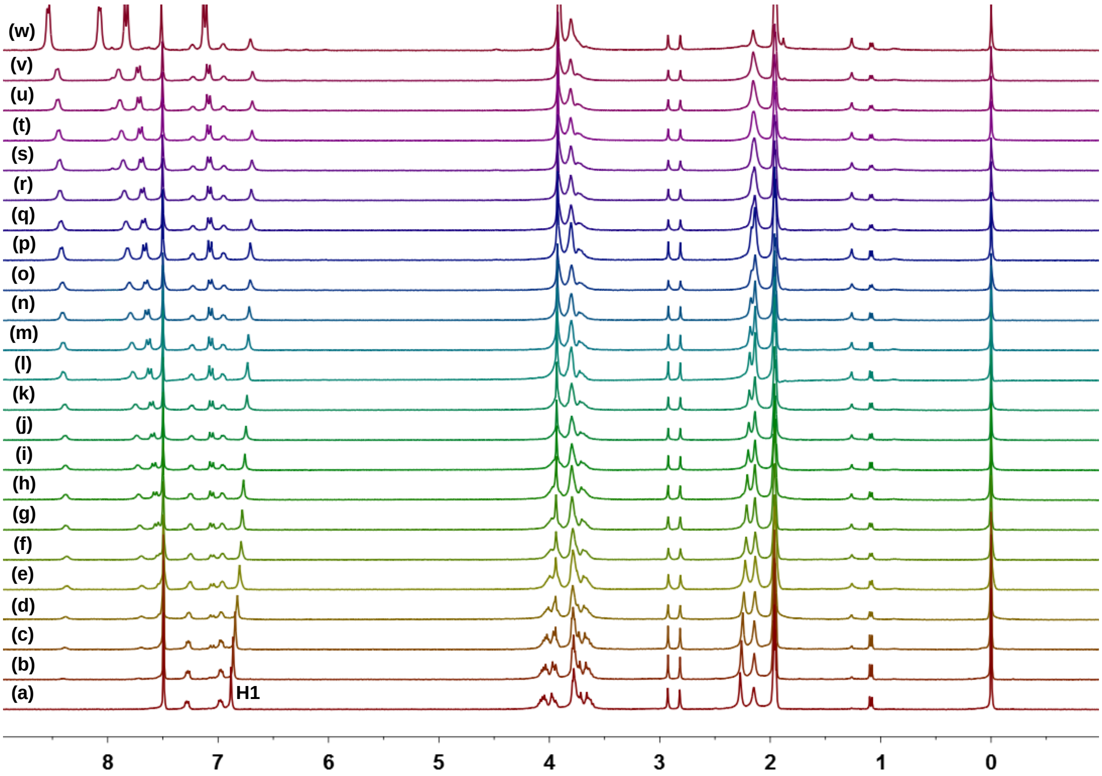


Fig. S33. ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of **1** at a concentration of 3.0 mM with different concentrations of **5**: (a) 0.00 mM; (b) 0.6 mM; (c) 1.2 mM; (d) 1.8 mM; (e) 2.4 mM; (f) 3.0 mM; (g) 3.6 mM; (h) 4.2 mM; (i) 4.8 mM; (j) 5.4 mM; (k) 6.0 mM; (l) 6.6 mM; (m) 7.2 mM; (n) 7.8 mM; (o) 8.4 mM; (p) 9.0 mM; (q) 9.6 mM; (r) 10.2 mM; (s) 10.8 mM; (t) 11.4 mM; (u) 12.0 mM; (v) 12.6 mM; (w) 30.0 mM.

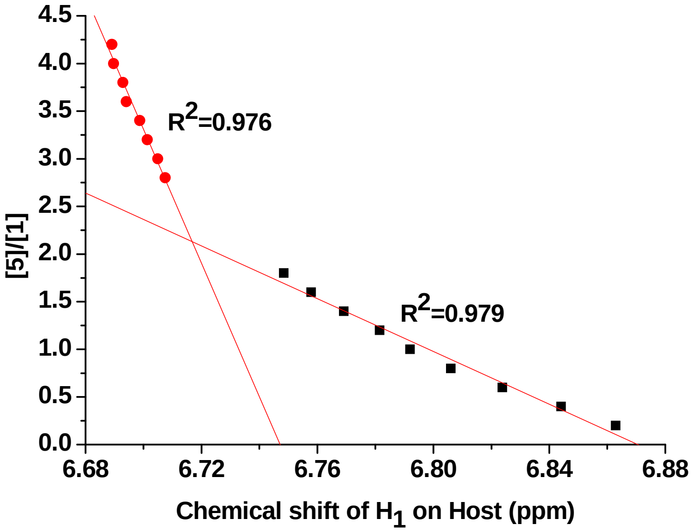


Fig. S34 Mole ratio plot for the complexation of **1** and **5** in $CD_3CN/CDCl_3$ = 1:1 at 298 K.

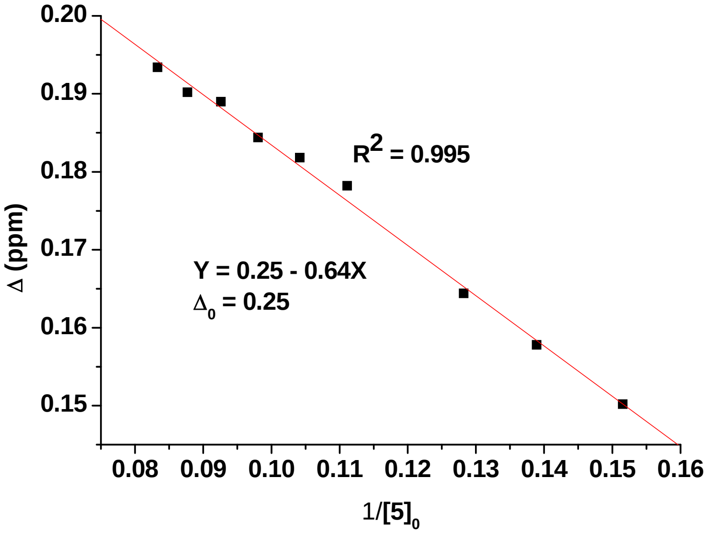


Fig. S35. Determination of Δ_0 of H_1 for the complexation between **1** and **5** in $CD_3CN/CDCl_3$ = 1:1 at 298 K. $[\mathbf{1}]_0$ = 3.0 mM.

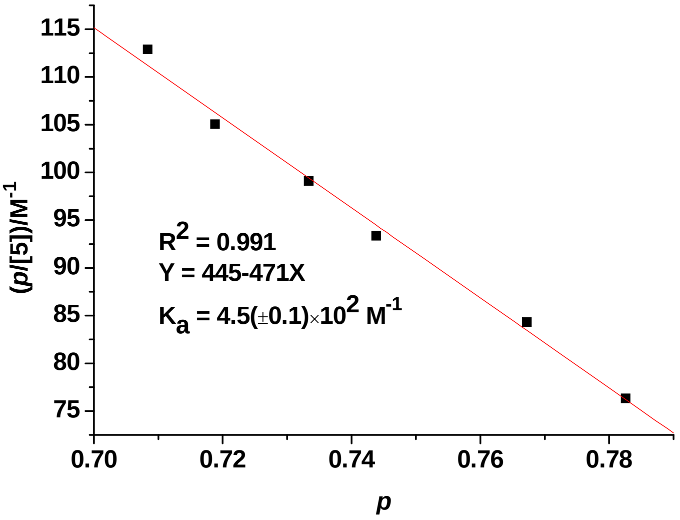


Fig. S36. Scatchard plot for the complexation between **1** and **5** in $CD_3CN/CDCl_3$ = 1:1 at 298 K. $[\mathbf{1}]_0$ = 3.0 mM.

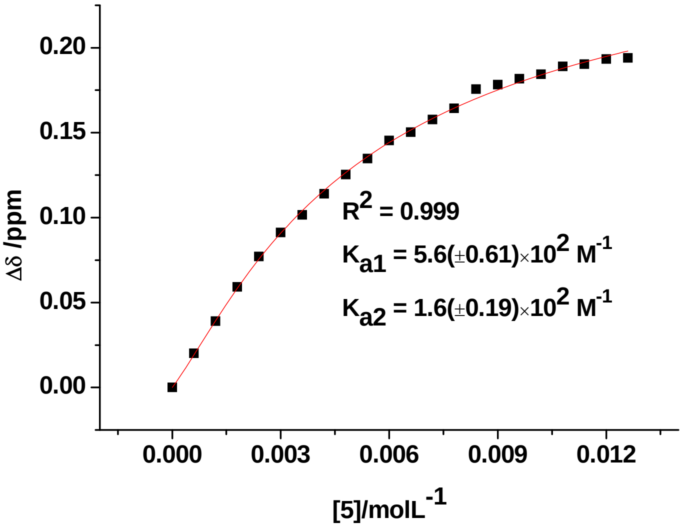


Fig. S37. Plot of Δδ (ppm) for the bridgehead proton H_1 of **1** vs **5** concentration in $CD_3CN/CDCl_3$ = 1:1 at 298 K.

6. ESI-MS spectra of the complexes

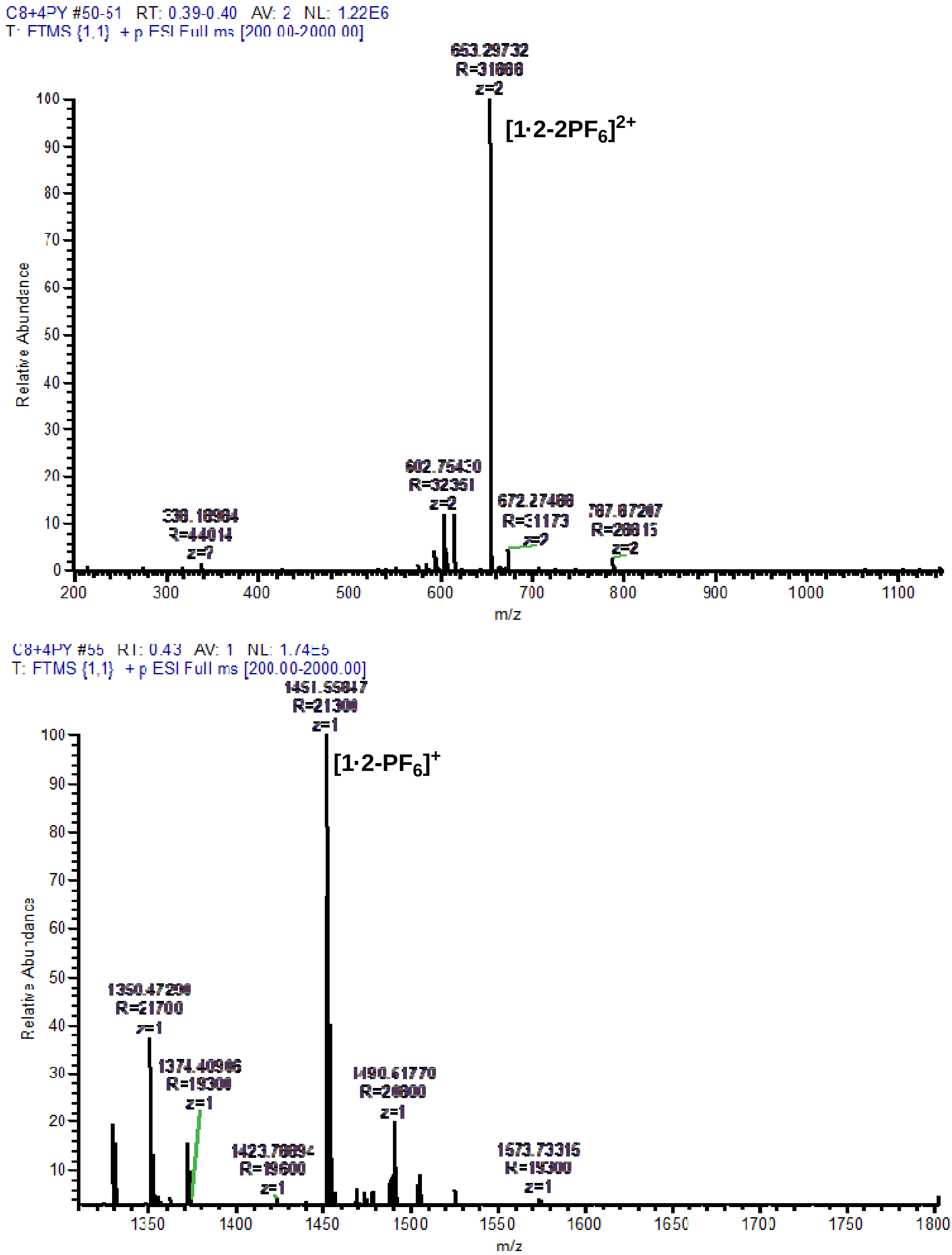


Fig. S38. ESI-MS spectrum of complex **1**·**2**.

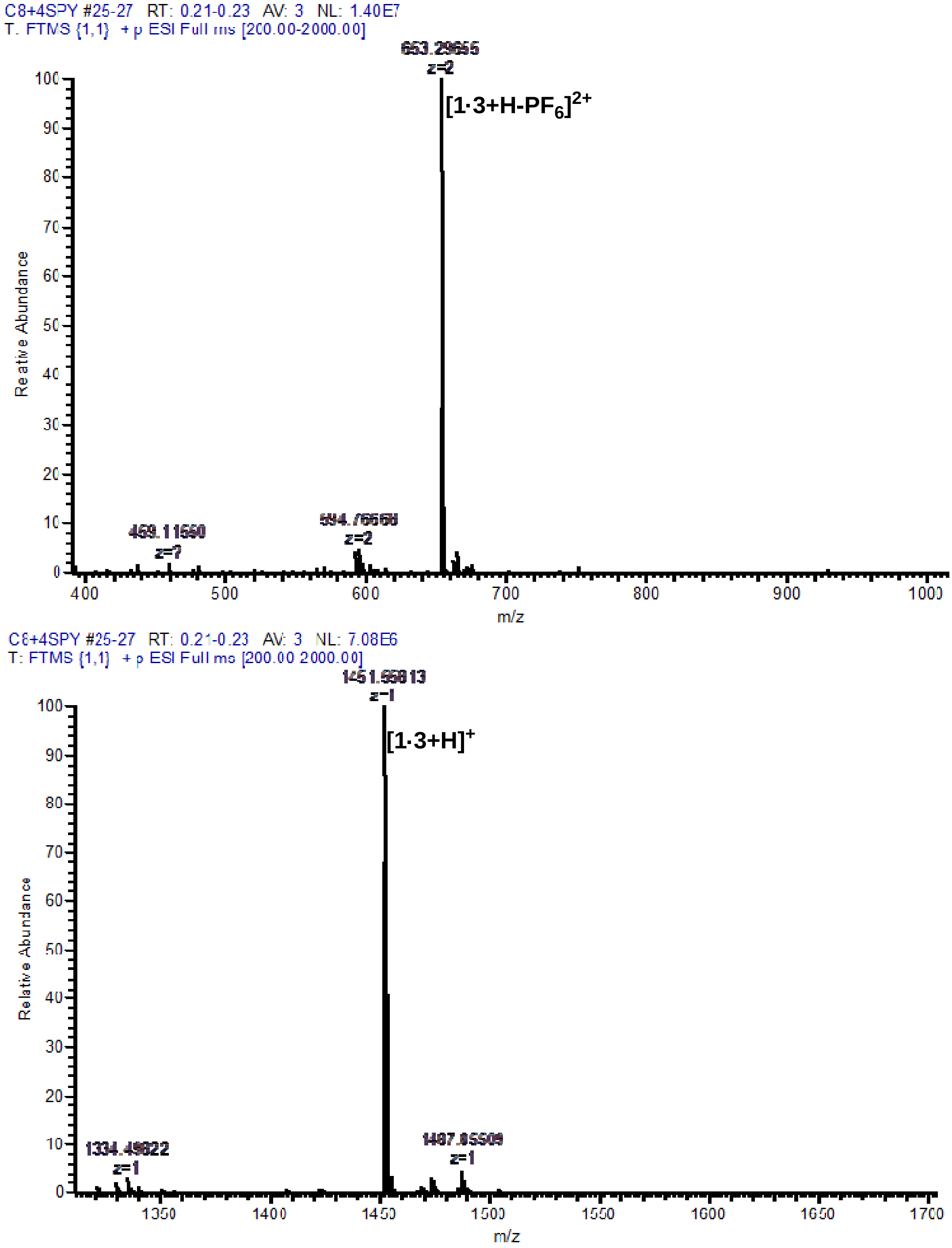


Fig. S39. ESI-MS spectrum of complex **1·3**$_2$.

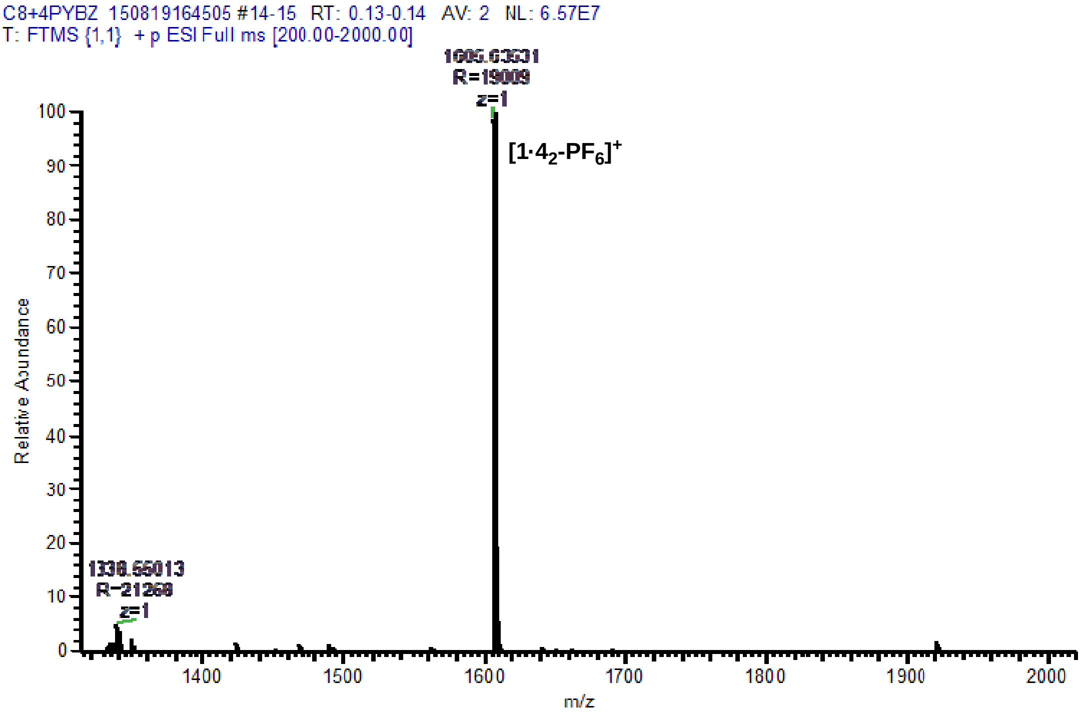


Fig. S40. ESI-MS spectrum of complex **1**·**4**$_2$.

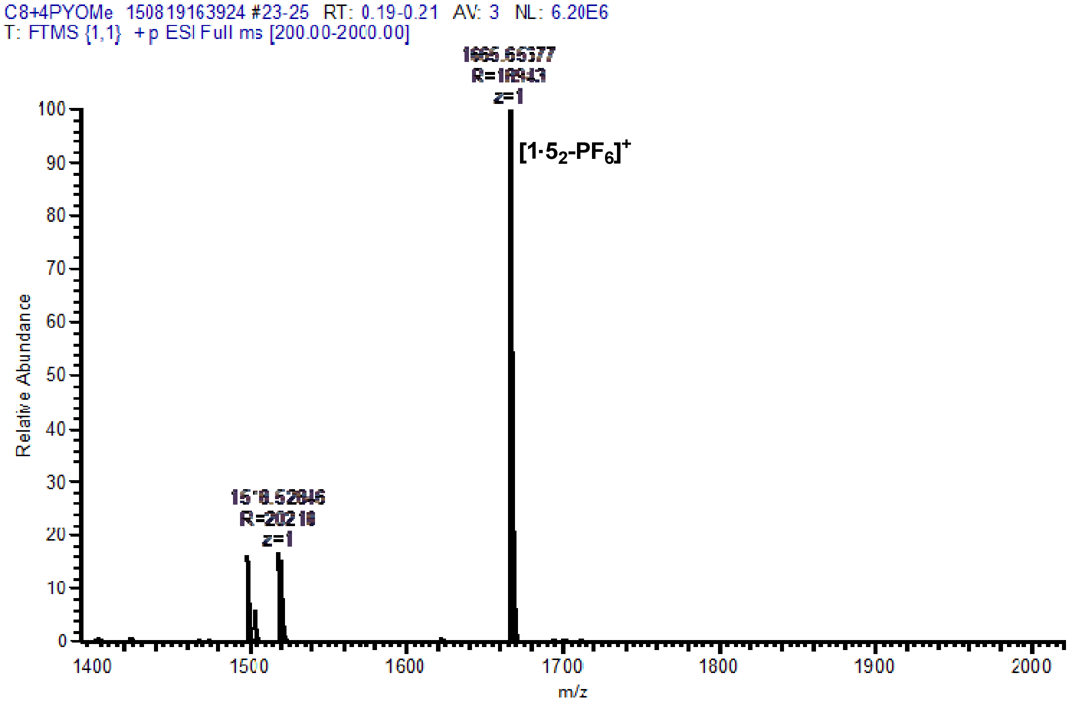


Fig. S41. ESI-MS spectrum of complex **1**·**5**$_2$.

7. Crystal packings of the complexes

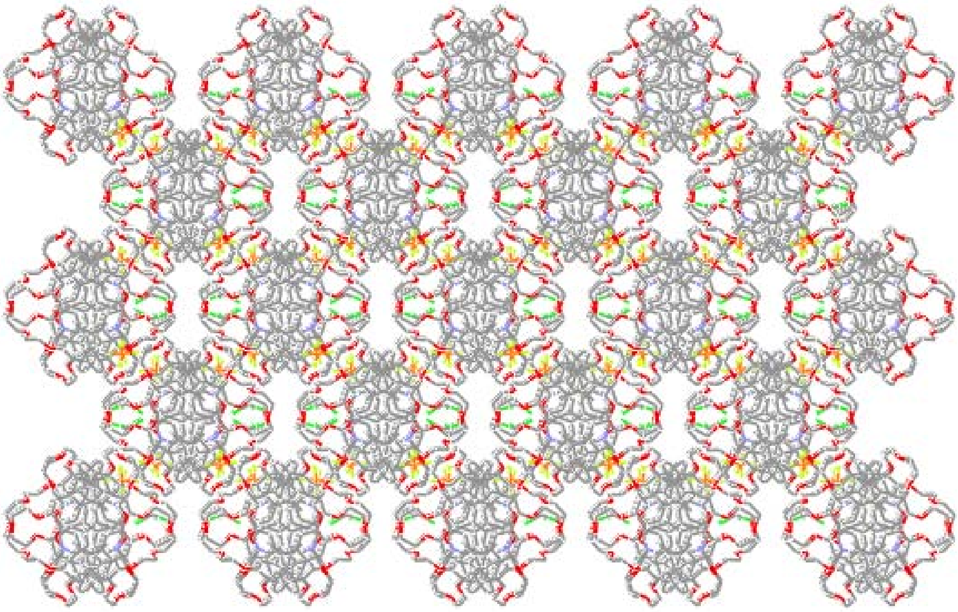


Fig. S42. Packing of complex **1**·**2**. Hydrogen atoms were omitted for clarity.

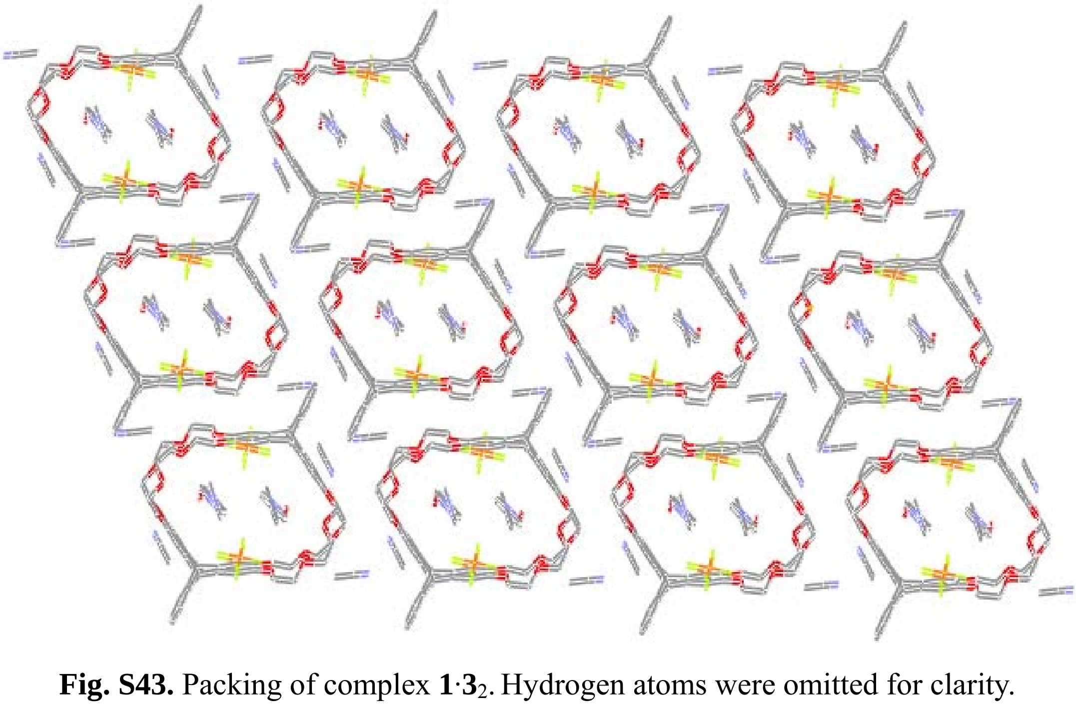


Fig. S43. Packing of complex **1**·$\mathbf{3}_2$. Hydrogen atoms were omitted for clarity.

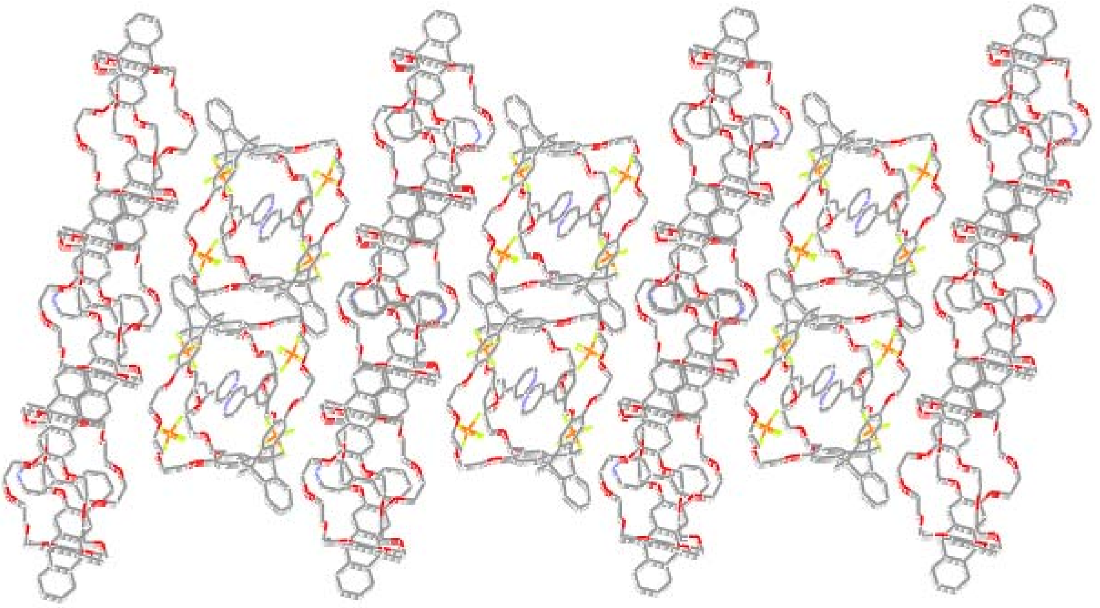


Fig. S44. Packing of complex **1**·**4**$_2$. Solvent molecules and hydrogen atoms were omitted for clarity.

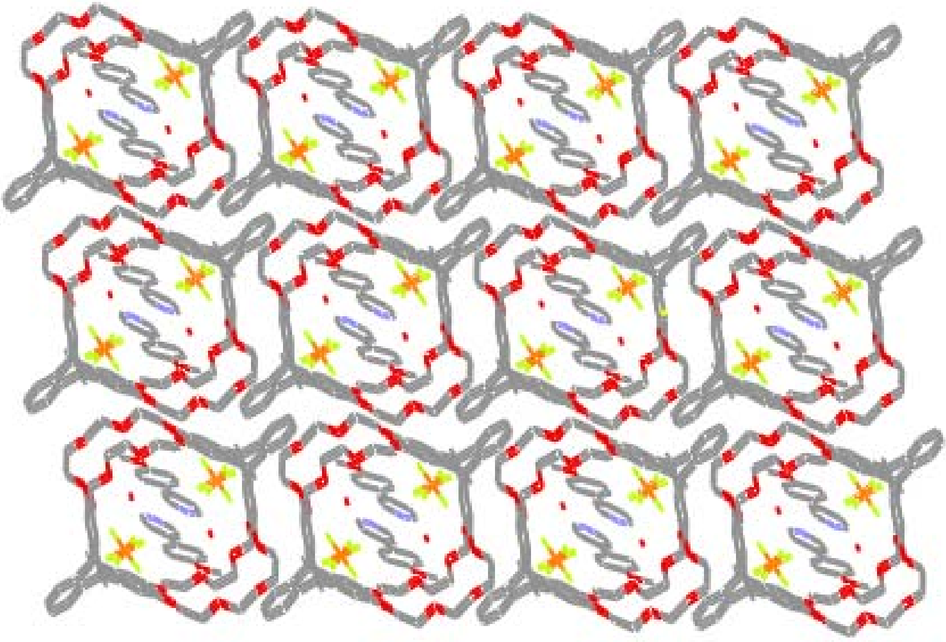
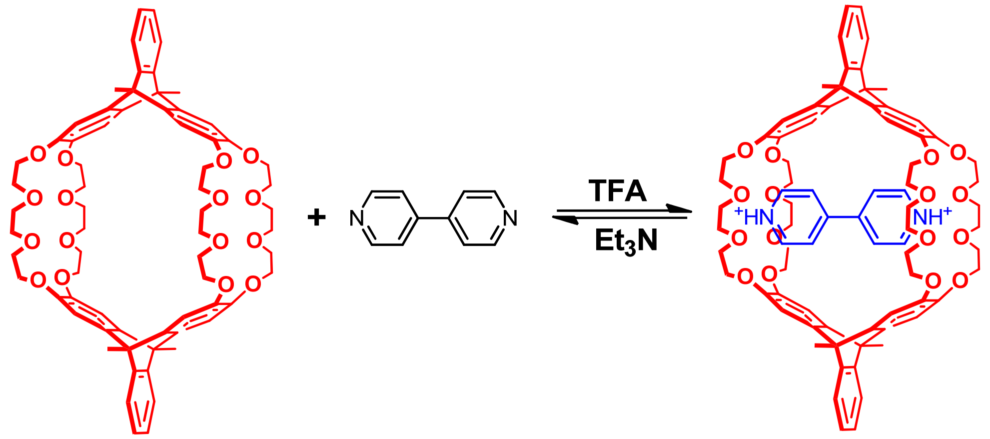


Fig. S45. Packing of complex **1**·**5**$_2$. Hydrogen atoms were omitted for clarity.

8. Acid/base controllable binding and release of the guests in 1·2 and 1·5_2



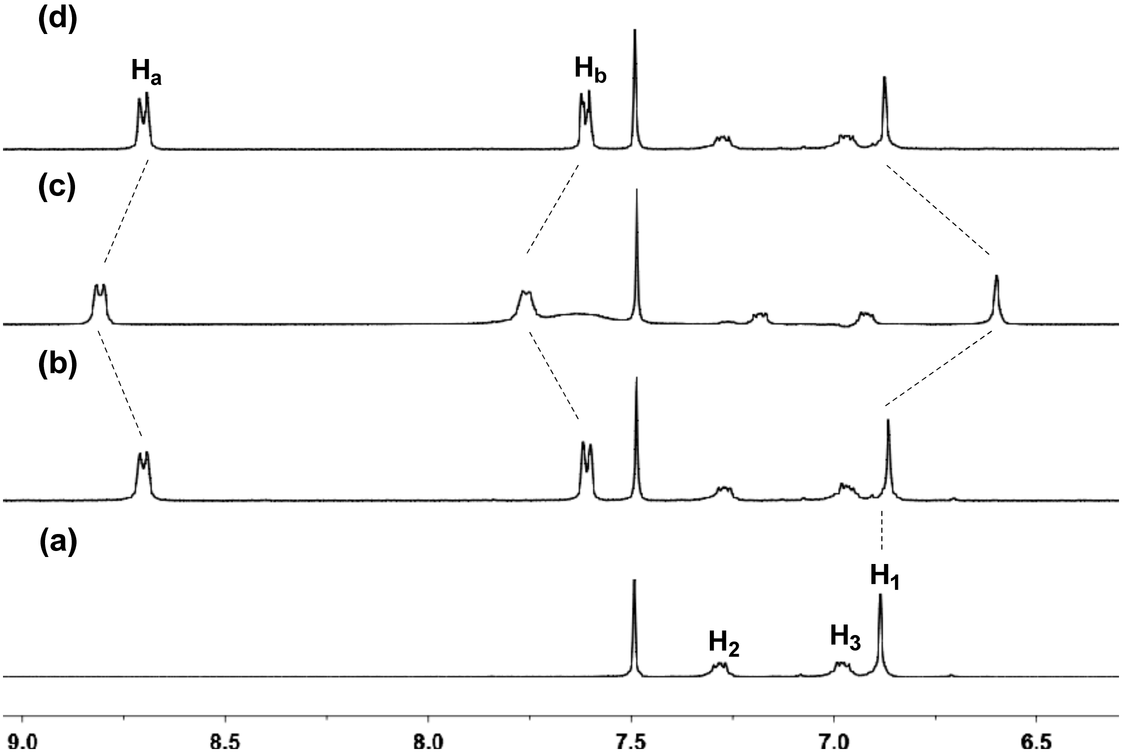


Fig. S46. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of (a) free **1**, (b) **1** and 1.0 equiv of 4,4'-bipyridine, (c) to the solution of b was added 4.0 equiv. of TFA, (d) to the solution of c was added 6.0 equiv. of Et_3N. $[\mathbf{1}]_0$ = 3.0 mM.

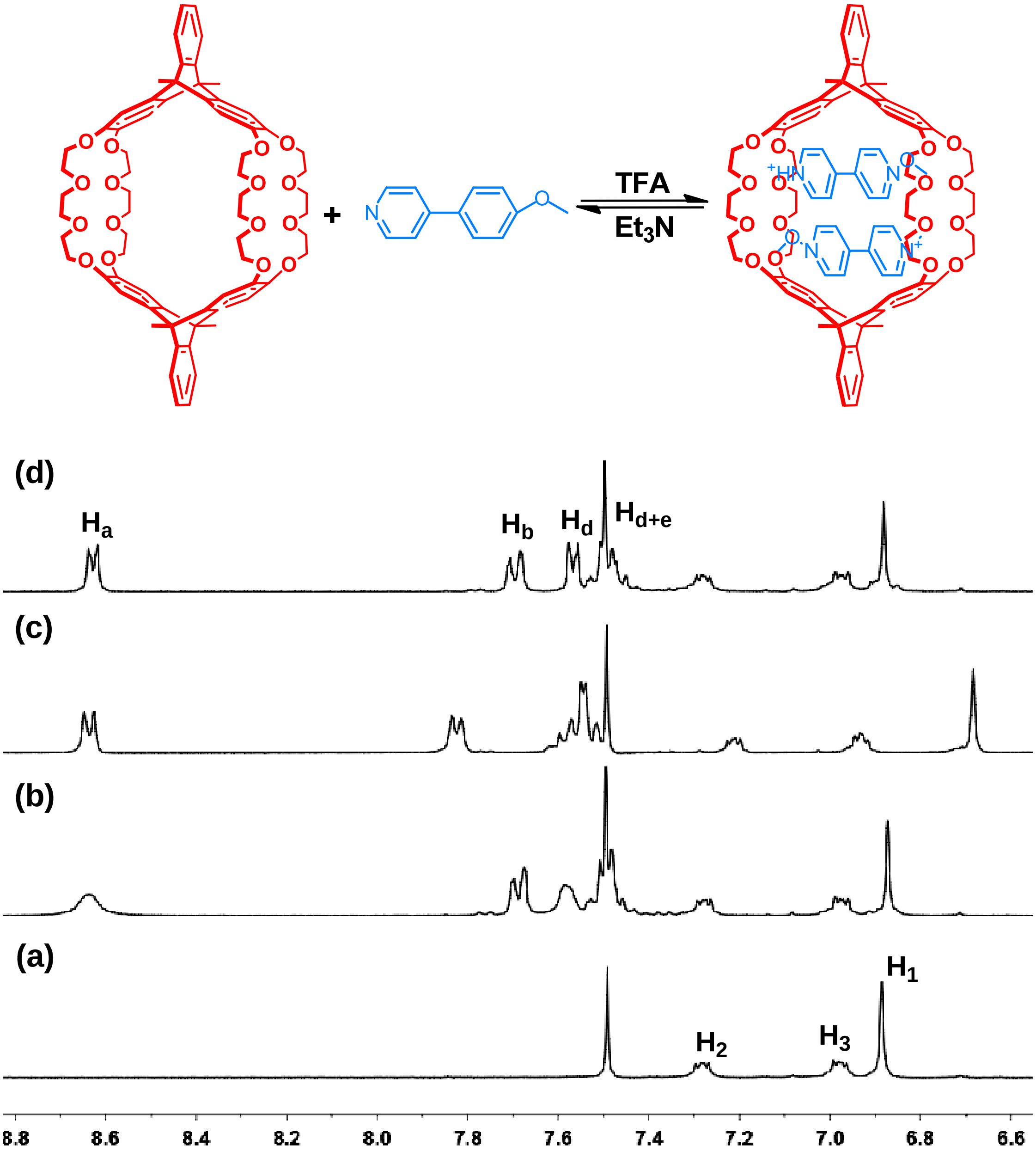


Fig. S47. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$ = 1:1, 298 K) of (a) free **1**, (b) **1** and 2.0 equiv of 4-(4-methoxyphenyl)pyridine, (c) to the solution of b was added 4.0 equiv. of TFA, (d) to the solution of c was added 6.0 equiv. of Et_3N. $[\mathbf{1}]_0$ = 3.0 mM.

9. References:

S1. Q.-S. Zong and C.-F. Chen, *Org. Lett.*, 2006, **8**, 211-214.

S2. F. H. Huang, J. W. Jones, C. Slebodnick and H. W. Gibson, *J. Am. Chem. Soc.*, 2003, **125**, 14458–14464.

S3. P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305–1323.