Electronic Supplementary Information

Triptycene-derived macrotricyclic polyether containing anthracene unit as a powerful host for 1,2-bis(pyridium)ethane, diquat and 2,7-diazapyrenium salt

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Contents

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

Binding studies by proton ^{1}H NMR. Science binding was a fast exchange process, the association constants were determined by titrating a solution (3.0×10^{-3} M) of host **1** in $CD_3CN/CDCl_3$ (1:1, v/v) with the increased amount of a solution (0.3 M in CD_3CN) of guests **2a-2c**. Deuterated acetonitrile was used as the lock, and TMS was employed as the internal standard. Chemical shifts were reported in parts per million (ppm). Fitting of chemical shifts of proton H_1 of **1** was performed a nonlinear regression algorithm using MATLAB.

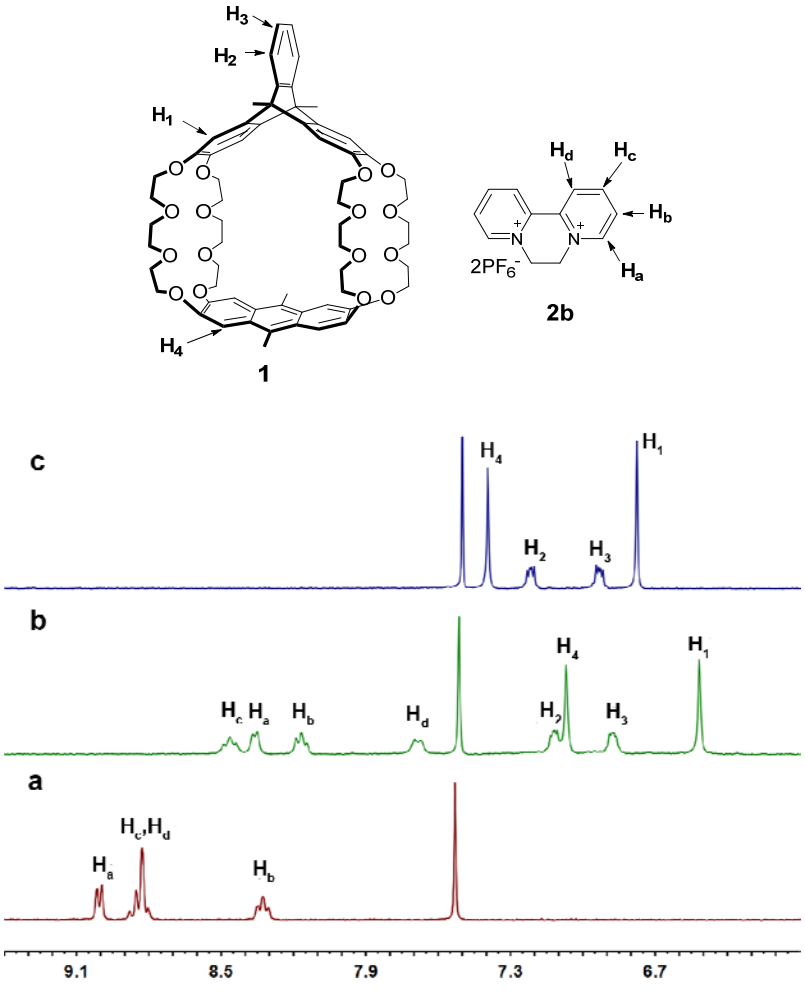


Figure S1. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$=1:1, v/v, 295K) of (a) free guest **2b**, (b) **1** and 1.0 equiv. of **2b**, and (c) free host **1**. $[\mathbf{H}]_0$ = 3.0 mM.

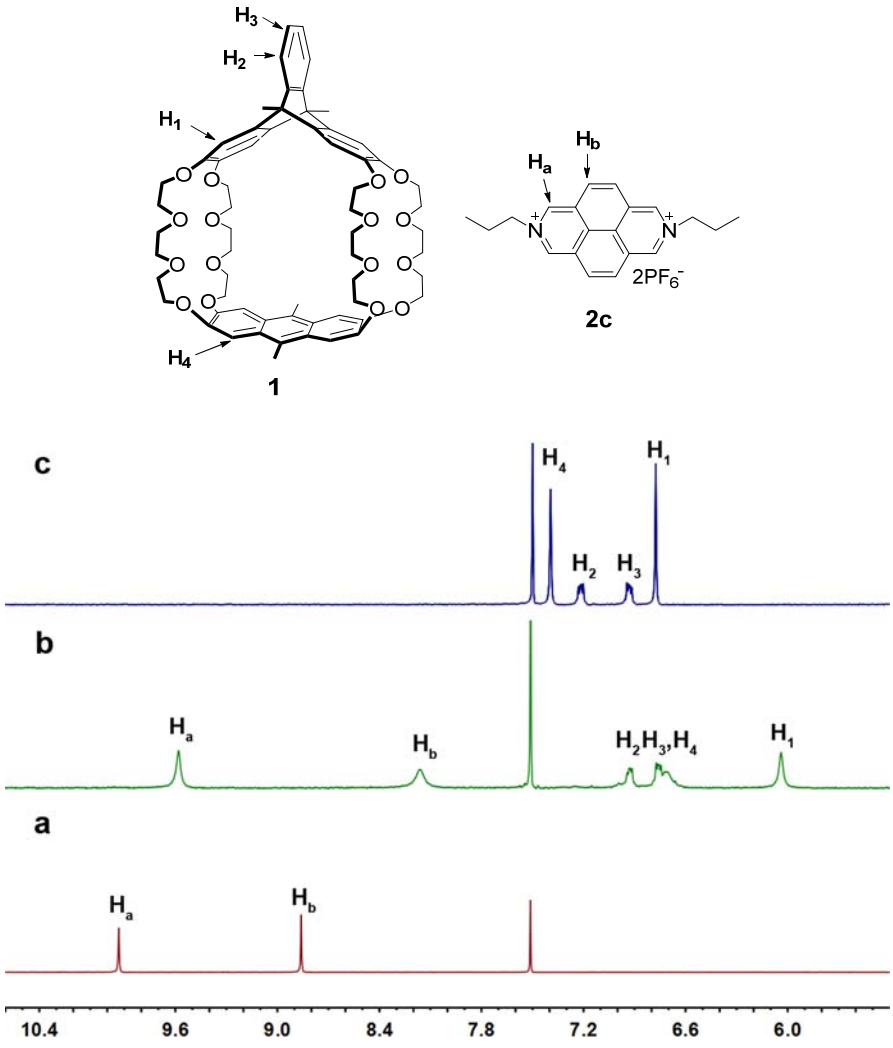


Figure S2. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$=1:1, v/v, 295K) of (a) free guest **2c**, (b) **1** and 1.0 equiv. of **2c**, and (c) free host **1**. $[\mathbf{1}]_0$ = 3.0 mM.

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

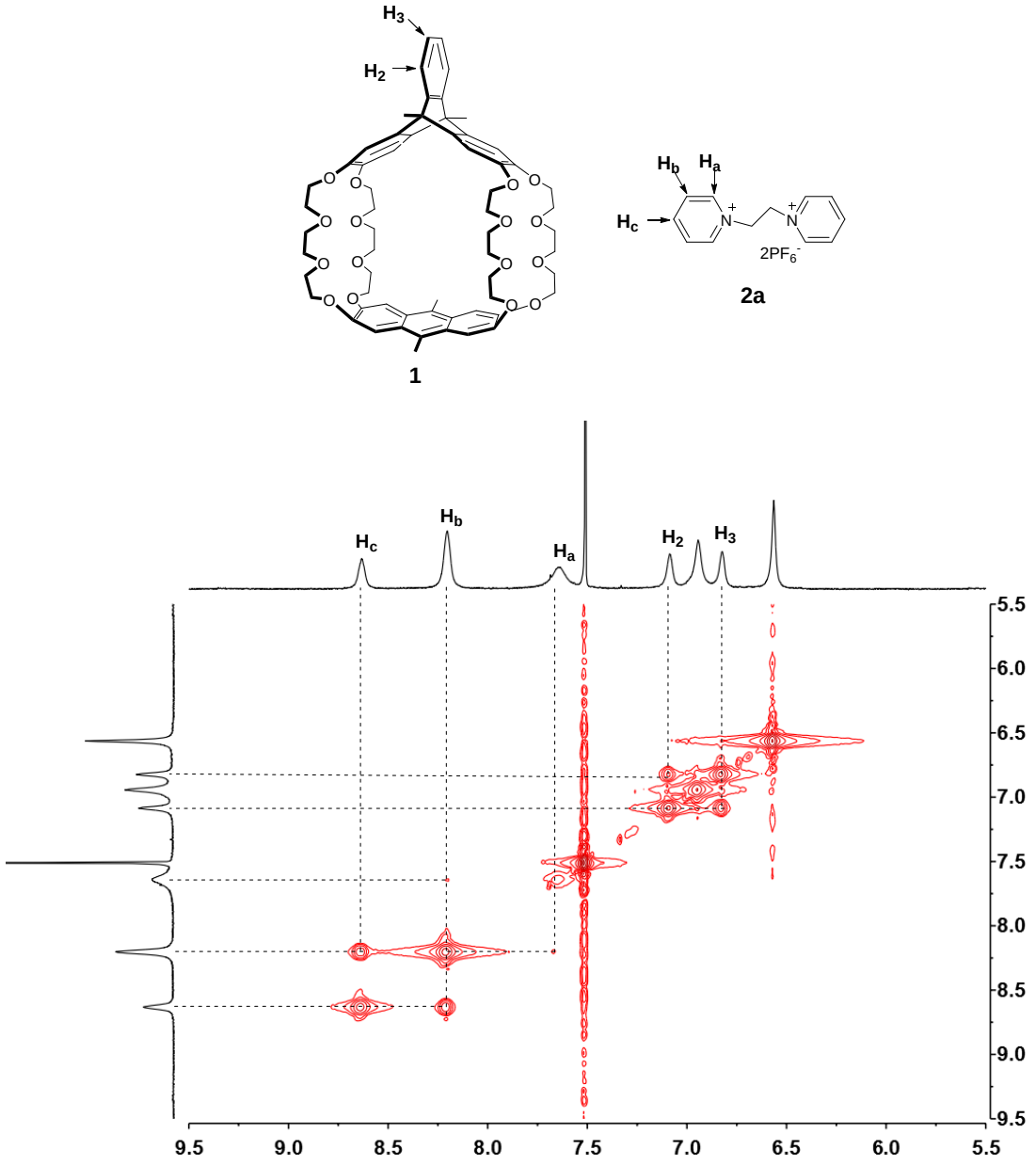


Figure S3. ^{1}H-^{1}H COSY spectrum (300 MHz, $CD_3CN/CDCl_3$=1:1, v/v, 295 K) of host **1** and 1.0 equiv. of **2a**. $[1]_0$ = 3.0 mM.

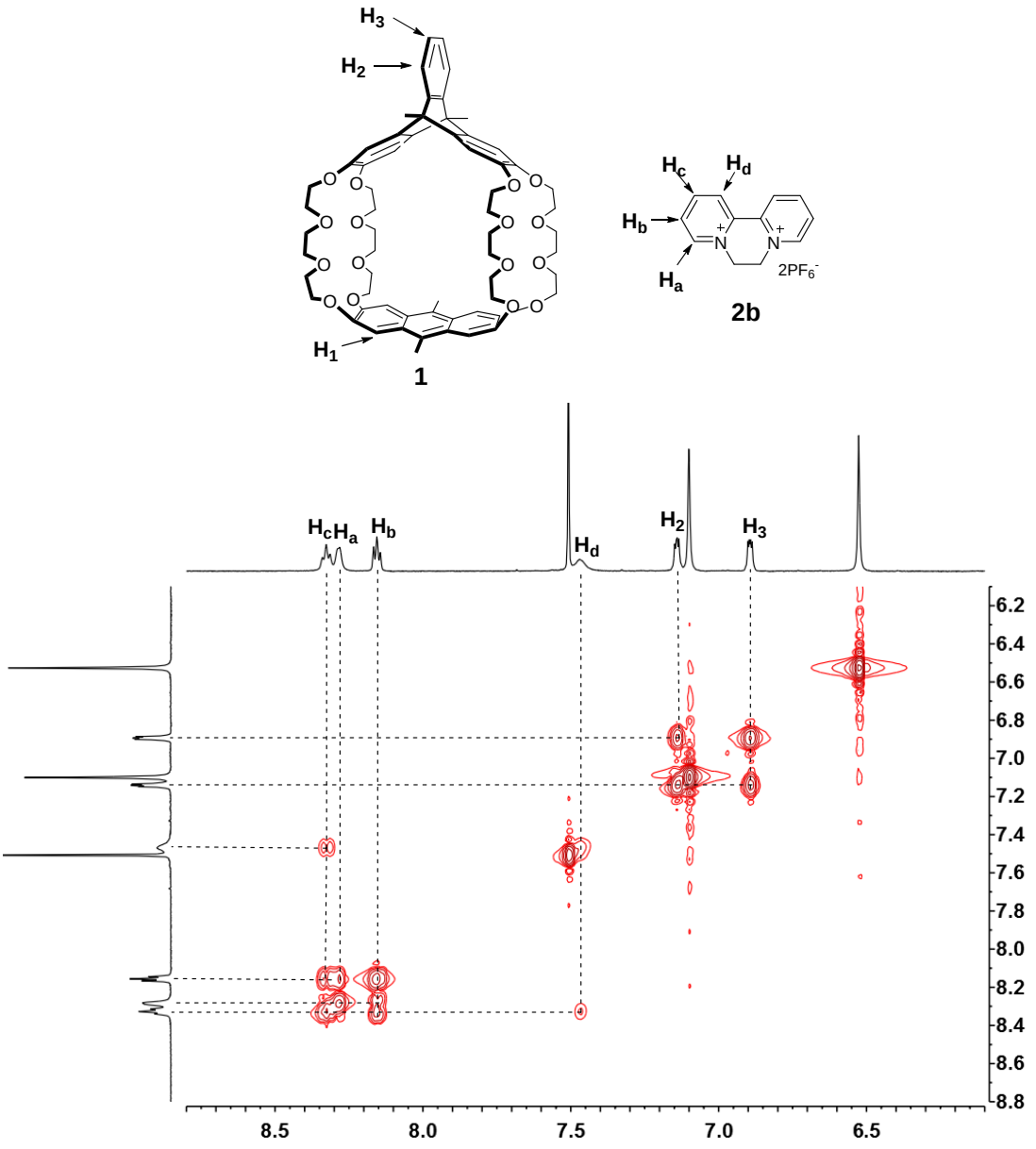


Figure S4. ^{1}H-^{1}H COSY spectrum (300 MHz, $CD_3CN/CDCl_3$=1:1, v/v, 295 K) of host **1** and 1.0 equiv. of **2b**. $[1]_0$ = 3.0 mM.

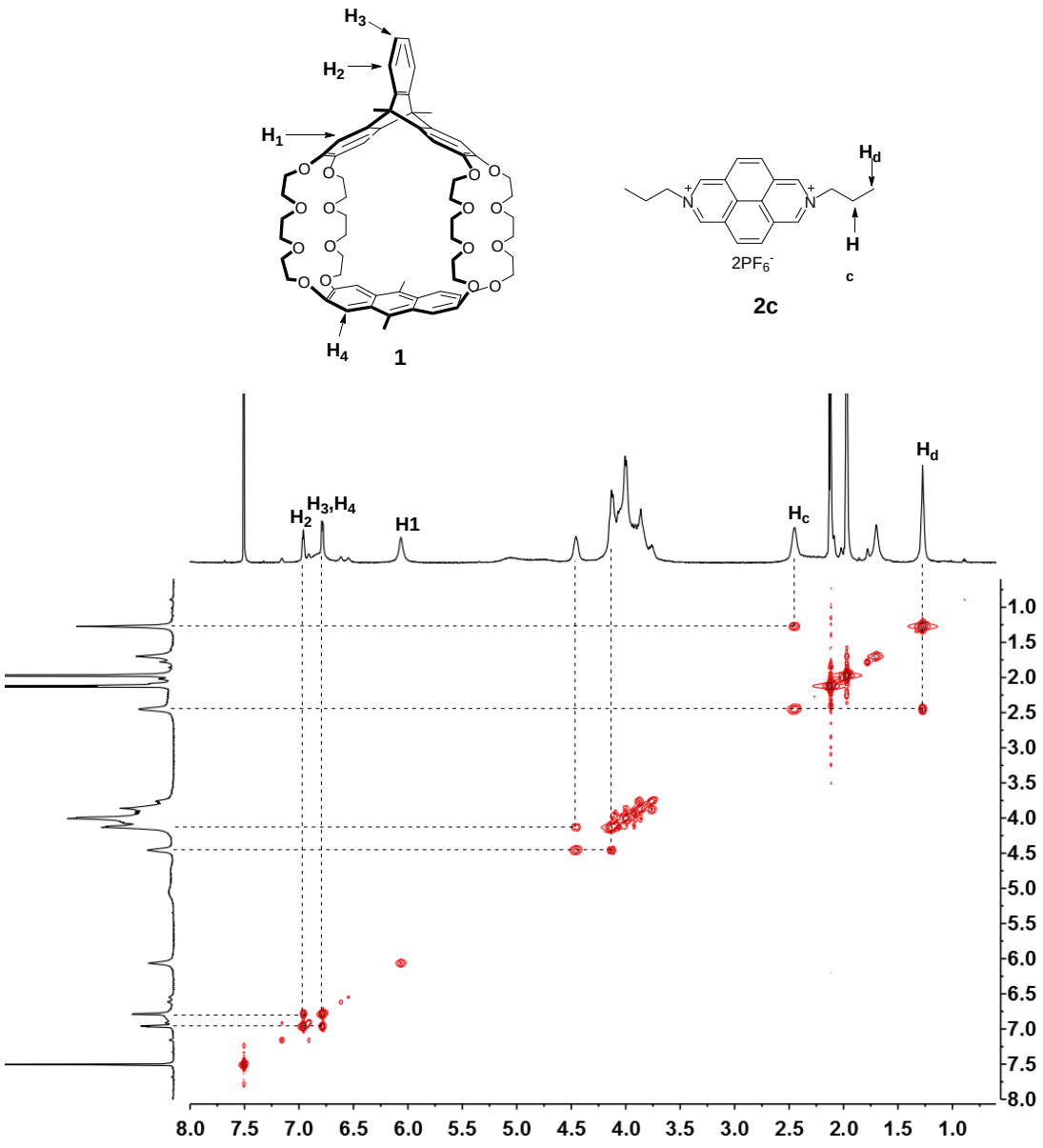


Figure S5. ^{1}H-^{1}H COSY spectrum (300 MHz, $CD_3CN/CDCl_3$=1:1, v/v, 295 K) of host **1** and 1.0 equiv. of **2c**. $[1]_0$ = 3.0 mM.

3. Mole ratio between the host and the guests of the complexes

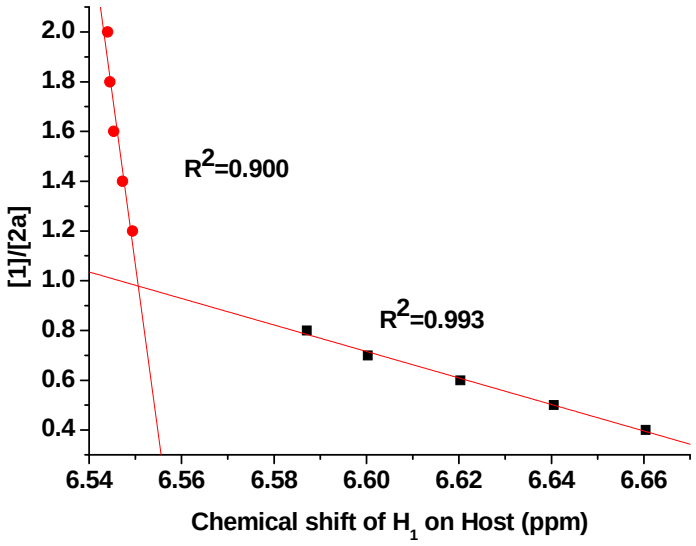


Figure S6. Mole ratio plot for the complexation between **1** and **2a** in $CD_3CN/CDCl_3$ (1:1, v/v) at 295 K. $[\mathbf{1}]_0$= 3.0 mM.

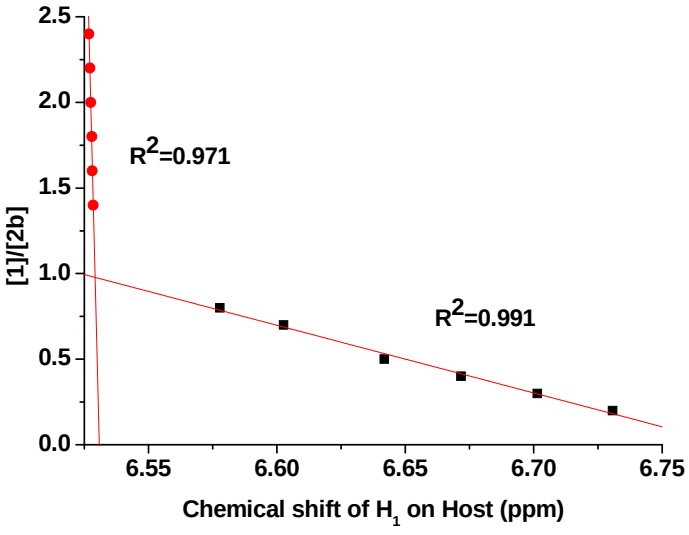


Figure S7. Mole ratio plot for the complexation between **1** and **2b** in $CD_3CN/CDCl_3$ (1:1, v/v) at 295 K. $[\mathbf{1}]_0$= 3.0 mM.

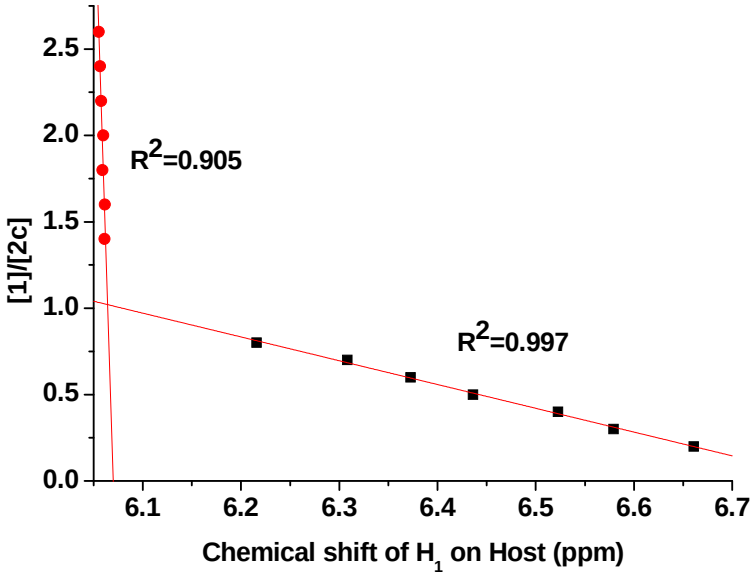


Figure S8. Mole ratio plot for the complexation between **1** and **2c** in $CD_3CN/CDCl_3$ (1:1, v/v) at 295 K. $[\mathbf{1}]_0$= 3.0 mM.

4. ESI MS spectra of the complexes

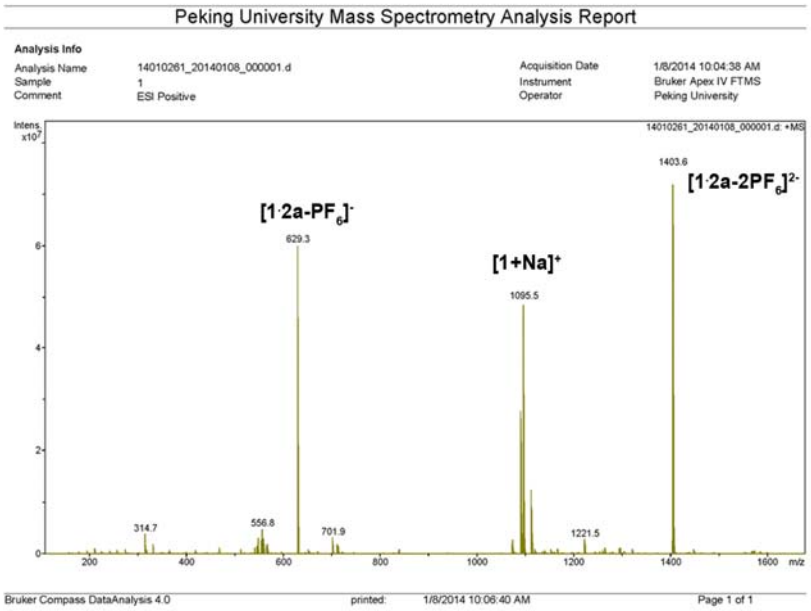


Figure S9. ESI MS of a solution of **1** and **2a** in acetonitrile-chloroform (1:1, v/v).

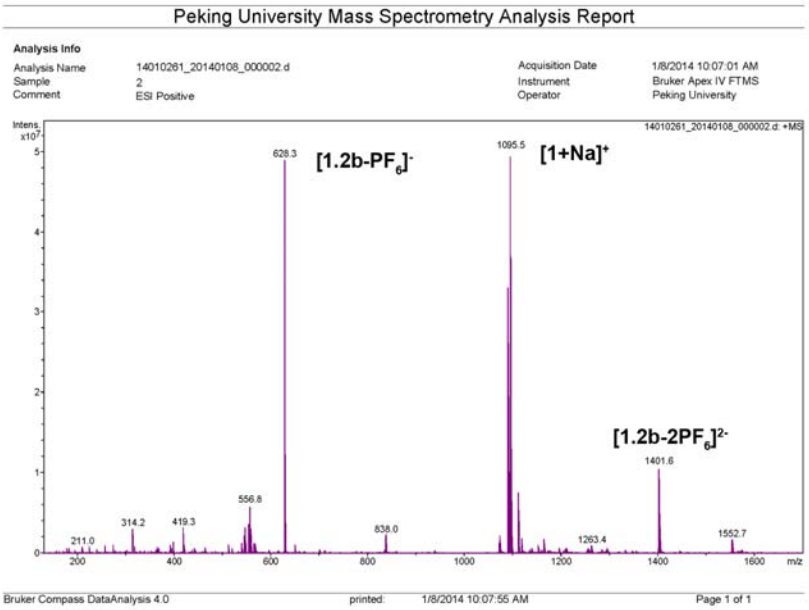


Figure S10. ESI MS of a solution of **1** and **2b** in acetonitrile-chloroform (1:1, v/v).

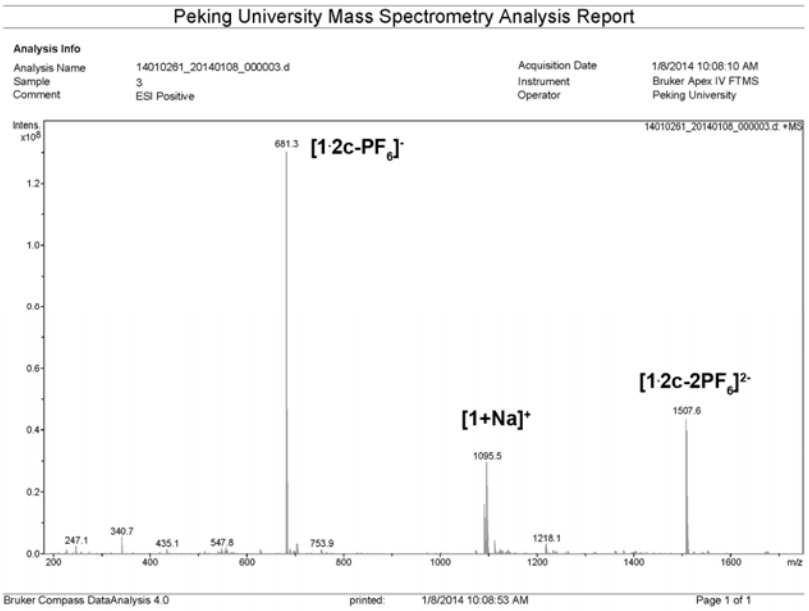


Figure S11. ESI MS of a solution of **1** and **2c** in acetonitrile-chloroform (1:1, v/v).

5. Crystal packing of the complexes

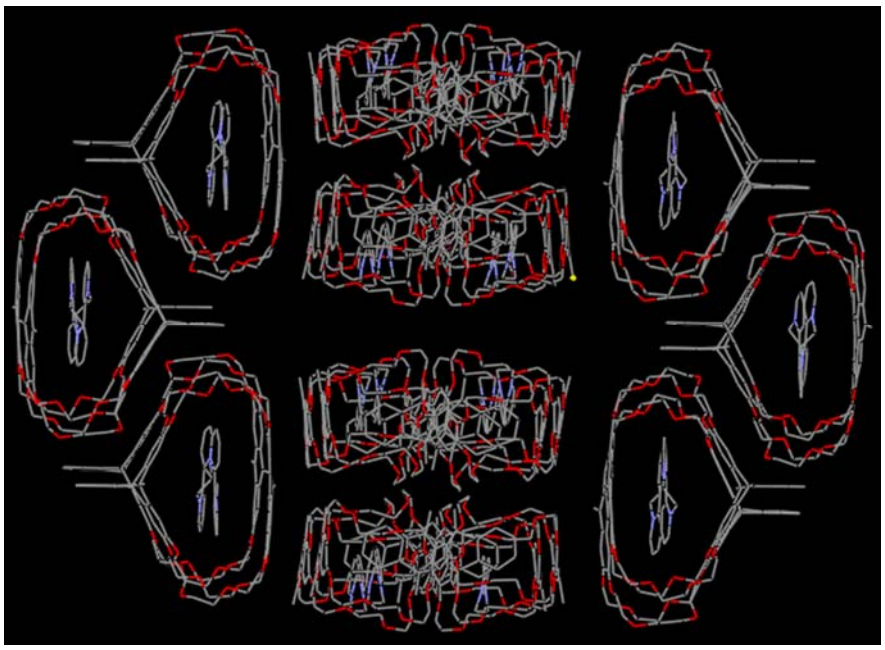


Figure S12. Crystal packing of complex **1·2b**. PF_6^- counterions and hydrogen atoms were omitted for clarity.

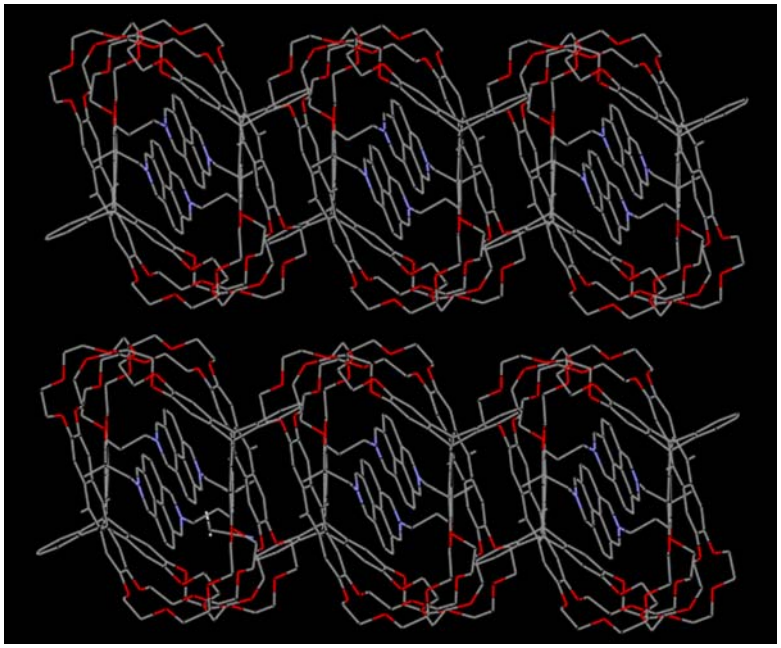


Figure S13. Crystal packing of complex **1·2c**. Solvent molecules, PF_6^- counterions and hydrogen atoms were omitted for clarity.

6. Structural parameters of the complexes

Table S1. Crystal data for **1·2a**

Empirical formula	$C_{158}\ H_{187}\ F_{24}\ N_9\ O_{32}\ P_4$
Formula weight	3304.05
Crystal size (mm)	0.28 × 0.34 × 0.27
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	*P-1*
a (Å)	17.928(4)
b (Å)	21.795(4)
c (Å)	26.597(5)
α (°)	68.93(3)
β (°)	79.43(3)
γ (°)	73.05(3)
V (Å^3)	9240(3)
Z	2
D_{calcd} (g cm^{-3})	1.188
Absorption coefficient(mm^{-1})	0.130
F (000)	3460
θ / (°)	1.38~ 27.48
Limiting indices	-23 ≦ h≦22 -27≦ k≦28 -34≦ l ≦ 30
Reflections collected / unique	86969/41863 [R(int) = 0.0542]
Data/restraints/parameters	41863/0/2056
Goodness of fit on F^2	1.293
R_1, wR_2 [I>2σ(I)]	0.0980, 0.2526
R_1, wR_2 [all data]	0.1368, 0.2765
Largest diff. peak and hole (e$^-$Å^{-3})	1.025 and -0.510

Table S2. Crystal data for **1·2b**

Empirical formula	$C_{148}H_{166}F_{24}N_4O_{32}P_4$
Formula weight	3092.73
Crystal size (mm)	0.35 × 0.28 × 0.21
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	*C2/c*
a (Å)	33.928(7)
b (Å)	26.606(5)
c (Å)	41.298(8)
α (°)	90.00
β (°)	112.64(3)
γ (°)	90.00
V (Å^3)	34407(12)
Z	8
D_{calcd} (g cm^{-3})	1.194
Absorption coefficient(mm^{-1})	0.135
F (000)	12912
θ / (°)	1.00~ 26.34
Limiting indices	-27≦ h≦40 -30≦ k≦31 -49≦ l ≦48
Reflections collected / unique	68412/30084 [R(int) = 0.0827]
Data/restraints/parameters	30084/85/1916
Goodness of fit on F^2	1.352
R_1, wR_2 [I>2σ(I)]	0.1200, 0.2932
R_1, wR_2 [all data]	0.1696, 0.3159
Largest diff. peak and hole (e$^-$Å^{-3})	1.942 and -0.563

Table S3. Crystal data for **1·2c**

Empirical formula	$C_{86}H_{102}F_{12}N_4O_{17}P_2$
Formula weight	1753.66
Crystal size (mm)	0.46 × 0.31 × 0.23
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	triclinic
Space group	*P-1*
a (Å)	12.547(2)
b (Å)	16.146(3)
c (Å)	21.955(4)
α (°)	109.304(4)
β (°)	91.346(3)
γ (°)	91.789(3)
V (Å^3)	4192.7(14)
Z	2
D_{calcd} (g cm^{-3})	1.389
Absorption coefficient(mm^{-1})	0.149
F (000)	1840
θ / (°)	0.98~ 25.00
Limiting indices	-14≦ h≦14 -18≦ k≦ 19 -26 ≦ l ≦26
Reflections collected / unique	31625/14622 [R(int) = 0.0567]
Params/ restraints	14622/51/1135
Goodness of fit on F^2	1.110
R_1, wR_2 [I>2σ(I)]	0.1017, 0.2583
R_1, wR_2 [all data]	0.1187, 0.2755
Largest diff. peak and hole (e$^-$Å^{-3})	0.965 and -0.493

7. Ellipsoid plot for crystal structures of the complexes

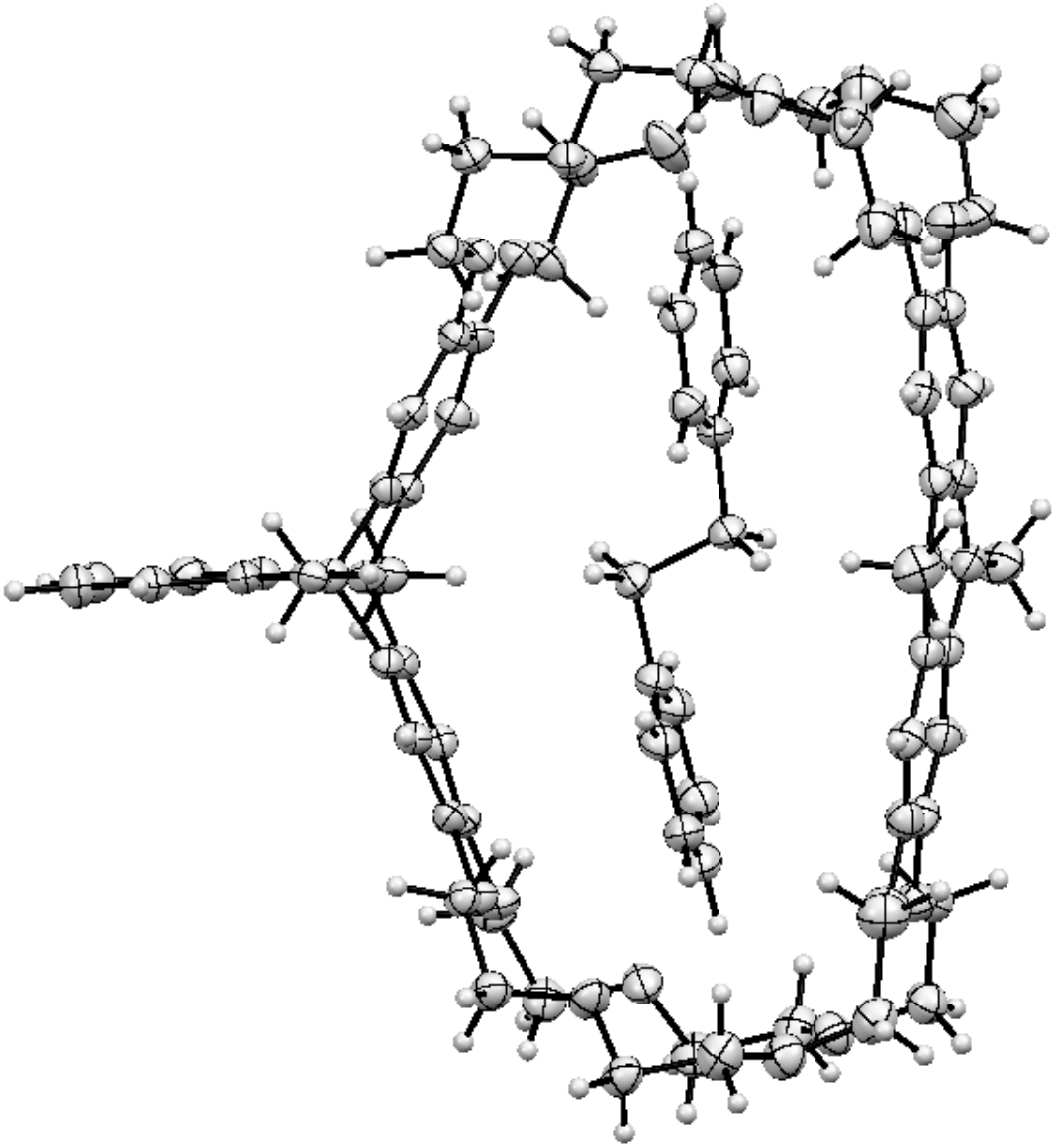


Figure S14. Ellipsoid plot for crystal structure of complex **1·2a** with probability level of 50%. Solvent molecules, and PF_6^- counterions were omitted for clarity.

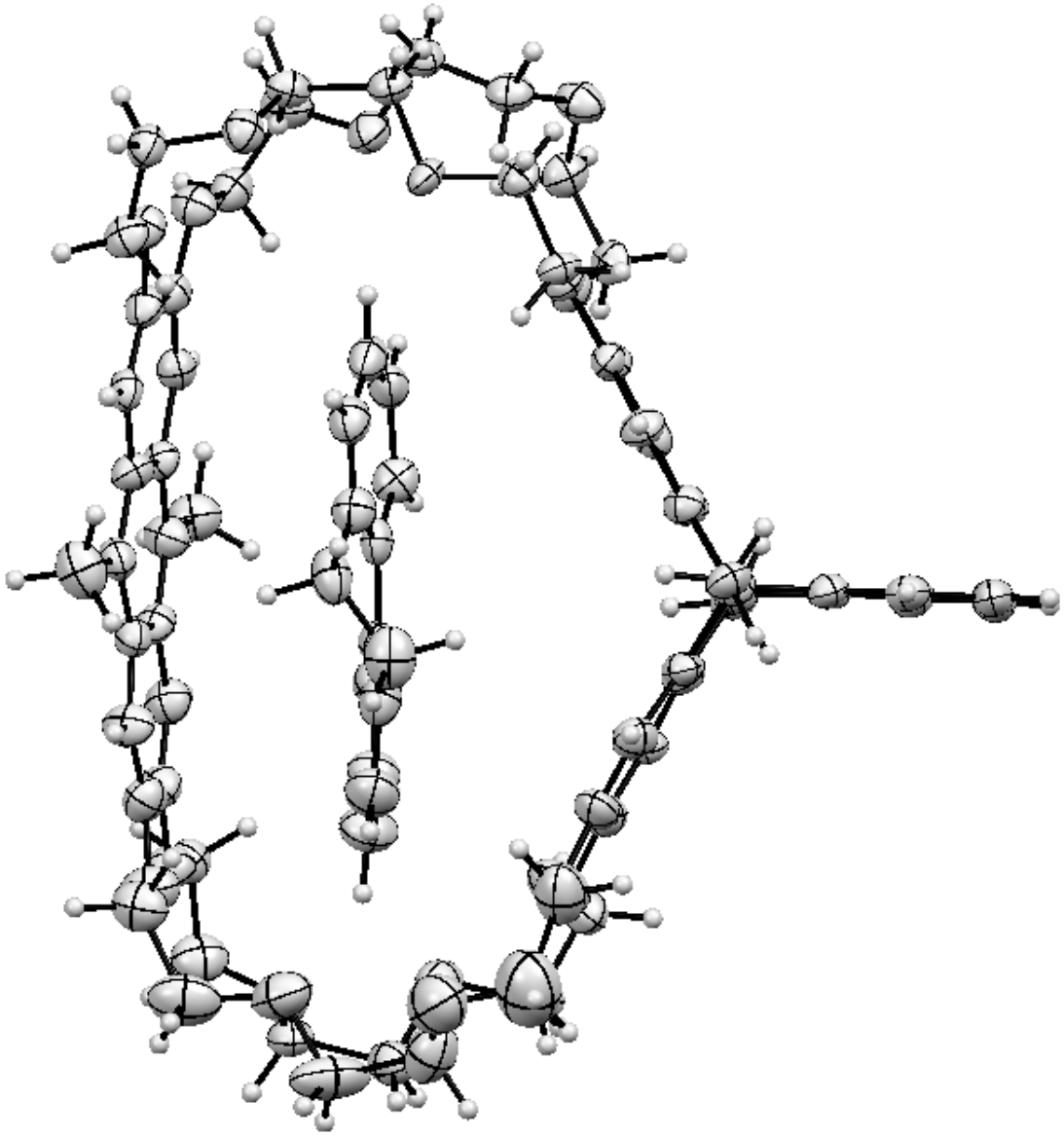


Figure S15. Ellipsoid plot for crystal structure of complex **1·2b** with probability level of 50%. Solvent molecules, and PF_6^- counterions were omitted for clarity.

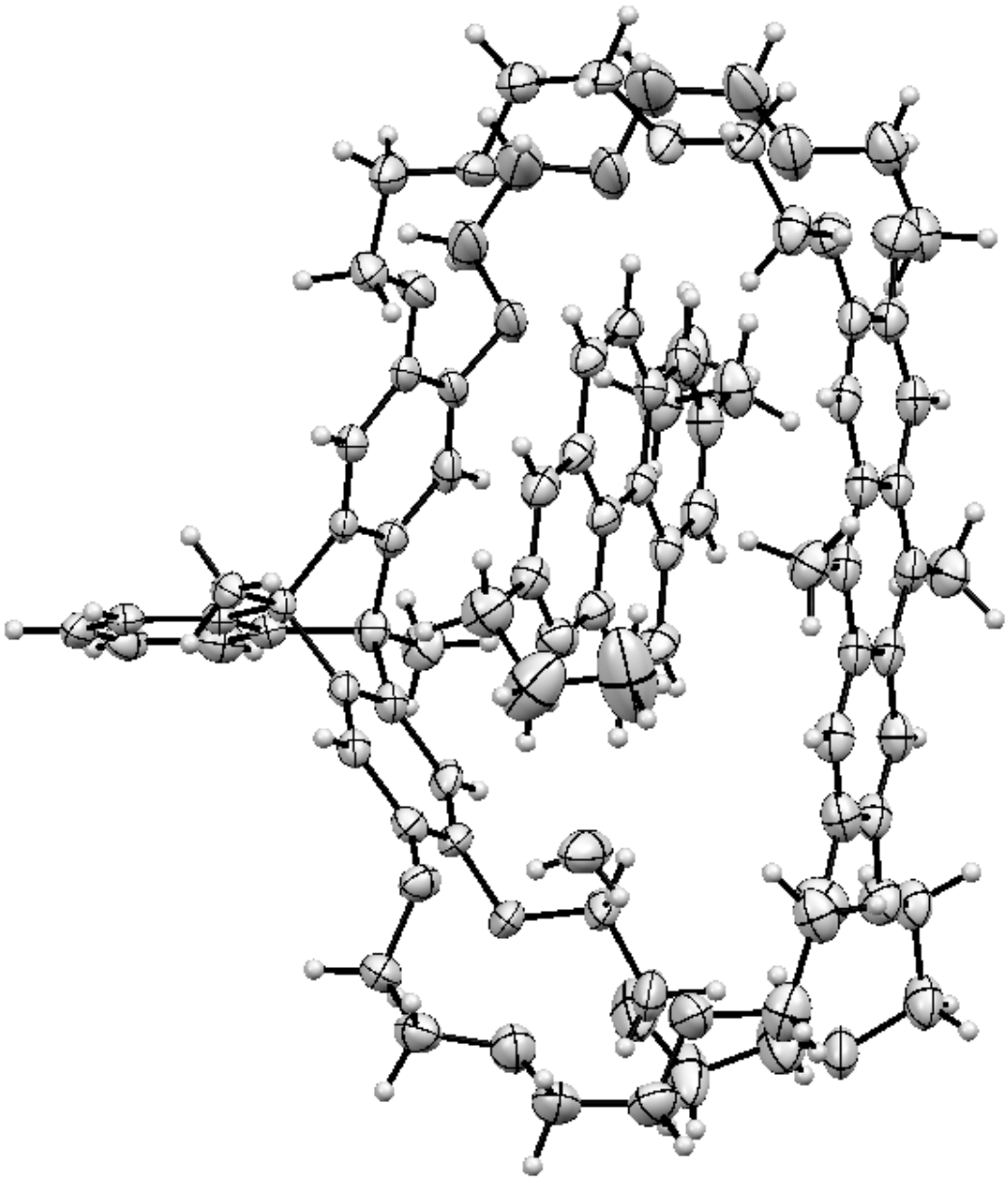


Figure S16. Ellipsoid plot for crystal structure of complex **1·2c** with probability level of 50%. Solvent molecules, and PF_6^- counterions were omitted for clarity.

8. K^+ Ion-controlled binding and release of guests in the complexes

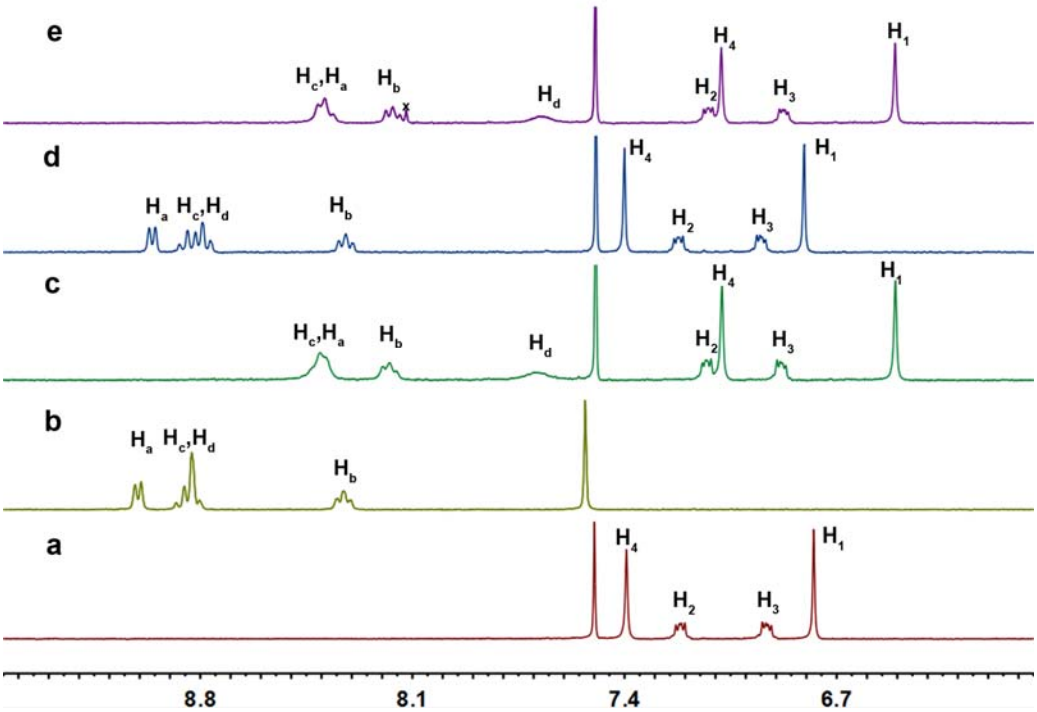


Figure S17. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$= 1:1, v/v, 295K) of (a) free Host **1**, (b) free guest **2b**, (c) **1** and 1.0 equiv. of **2b**, (d) to the solution of c was added 4.0 equiv. of KPF_6, and (e) to the solution of d was added 6.0 equiv. of [18]-crown-6. $[\mathbf{1}]_0$= 3.0 mM.

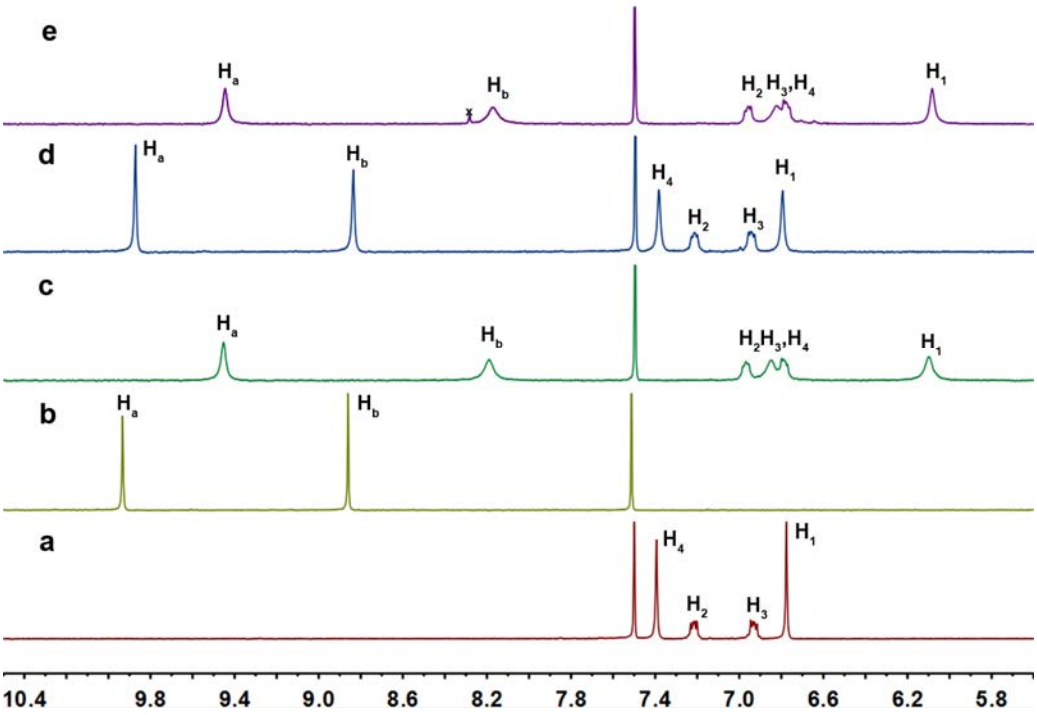


Figure S18. Partial ^{1}H NMR spectra (300 MHz, $CD_3CN/CDCl_3$= 1:1, v/v, 295K) of (a) free host **1**, (b) free guest **2c**, (c) **1** and 1.0 equiv. of **2c**, (d) to the solution of c was added 4.0 equiv. of KPF_6, and (e) to the solution of d was added 6.0 equiv. of [18]-crown-6. $[\mathbf{1}]_0$= 3.0 mM.

9. Computational methods and coordinates for the guests

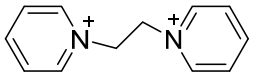
Computational methods

All calculations were performed using the Gaussian 03 suite of programs.[1] Optimized gas-phase structures were obtained using the density functional theory (DFT) method B3LYP, a combination of Becke's three-parameter hybrid exchange functional,[2-3] as implemented[4] in Gaussian 03, and the correlation functional of Lee, Yang and Parr,[5] in conjunction with the 6-31G(d,p) basis set.

Coordinates for guests 2a-2c

B3LYP/6-31G(d,p) optimized geometries (in Cartesian coordinate form) and their B3LYP/6-31G(d,p) electronic energies, enthalpies and free energies for the three guests are listed below for gas phase.

1,2-bis(pyridium) ethane (BPE^{2+}) (2a)

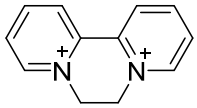


gas phase
B3LYP/6-31G(d,p)
SCF Energy (no zpe)= -574.423860 au; Energy + zpe (0K)= -574.412295 au
Enthalpy (298K)= -574.411351 au; Gibbs free energy (298K)= -574.463826 au

C	-3.889554000	-1.206552000	-0.082394000
C	-2.536838000	-1.182333000	0.204582000
C	-2.536732000	1.182278000	0.204957000
C	-3.889439000	1.206707000	-0.082005000
C	-4.580514000	0.000129000	-0.229684000
H	-4.391792000	-2.162613000	-0.178598000
H	-1.954396000	-2.085098000	0.346328000
H	-1.954200000	2.084936000	0.347000000
H	-4.391606000	2.162835000	-0.177905000
H	-5.643736000	0.000221000	-0.448396000
C	-0.422587000	-0.000193000	0.647714000
C	0.422421000	-0.000044000	-0.647466000
H	-0.209054000	-0.881614000	1.255907000
H	-0.208960000	0.881043000	1.256143000
H	0.209152000	-0.881362000	-1.255892000
H	0.209069000	0.881380000	-1.255708000
C	2.536753000	-1.182305000	-0.204591000
C	2.536775000	1.182329000	-0.204896000
C	3.889522000	-1.206597000	0.082208000

H	1.954215000	-2.085007000	-0.346299000
C	3.889543000	1.206660000	0.081888000
C	1.954248000	2.085002000	-0.346826000
C	4.580563000	0.000043000	0.229459000
H	4.391737000	-2.162683000	0.178319000
H	4.391789000	2.162756000	0.177748000
H	5.643807000	0.000070000	0.448042000
N	-1.876957000	-0.000084000	0.341248000
N	1.876992000	-0.000002000	-0.341033000

Diquat (DQ^{2+}) (2b)

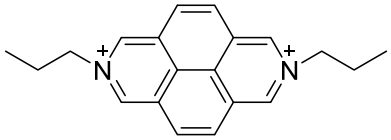


gas phase
B3LYP/6-31G(d,p)
SCF Energy (no zpe)= -573.217833 au; Energy + zpe (0K)= -573.208305 au
Enthalpy (298K)= -573.207360 au; Gibbs free energy (298K)= -573.253400 au

C	-3.539594000	-0.375401000	0.000010000
C	-2.787666000	0.784058000	-0.000127000
C	-0.741012000	-0.426109000	0.000040000
C	-1.476493000	-1.614739000	0.000216000
C	-2.870030000	-1.598966000	0.000204000
C	-0.768274000	2.088344000	-0.000236000
C	0.741012000	-0.426109000	-0.000031000
C	0.768274000	2.088344000	0.000260000
C	2.787666000	0.784058000	0.000111000
H	3.239625000	1.769807000	0.000234000
C	3.539594000	-0.375401000	-0.000030000
C	2.870030000	-1.598966000	-0.000210000
C	1.476493000	-1.614739000	-0.000209000
H	-1.131619000	2.615046000	-0.884775000
H	-4.621976000	-0.310082000	-0.000021000
H	-3.239625000	1.769807000	-0.000256000
H	-0.969841000	-2.569135000	0.000384000
H	-3.421278000	-2.533917000	0.000345000
H	1.131618000	2.615031000	0.884808000
H	4.621976000	-0.310082000	-0.000013000
H	3.421278000	-2.533917000	-0.000351000
H	0.969841000	-2.569135000	-0.000368000

N	-1.429489000	0.752813000	-0.000095000
N	1.429489000	0.752813000	0.000096000
H	1.132134000	2.615485000	-0.883805000
H	-1.132133000	2.615469000	0.883838000

2,7-diazapyrenium (DAP^{2+}) (2c)



gas phase
B3LYP/6-31G(d,p)
SCF Energy (no zpe)= -884.052080 au; Energy + zpe (0K)= -884.033822 au
Enthalpy (298K)= -884.032878 au; Gibbs free energy (298K)= -884.099139 au

C	-2.933573000	0.840376000	0.000191000
C	-1.551232000	1.054739000	0.000104000
C	-0.703058000	-0.083886000	0.000015000
C	-1.259206000	-1.393569000	-0.000024000
C	-2.648903000	-1.505161000	0.000041000
C	-0.970715000	2.372601000	0.000112000
C	0.703059000	0.083887000	-0.000040000
C	1.259206000	1.393569000	0.000010000
C	0.382793000	2.536374000	0.000080000
C	2.648904000	1.505161000	-0.000009000
H	3.154333000	2.464107000	0.000041000
C	2.933574000	-0.840376000	-0.000146000
C	1.551233000	-1.054739000	-0.000132000
C	0.970715000	-2.372601000	-0.000197000
C	-0.382792000	-2.536374000	-0.000148000
H	-0.813091000	-3.532536000	-0.000205000
H	1.625379000	-3.238036000	-0.000297000
H	-1.625379000	3.238037000	0.000160000
H	-3.640060000	1.658057000	0.000191000
H	-3.154333000	-2.464106000	0.000048000
H	0.813092000	3.532536000	0.000110000
H	3.640061000	-1.658056000	-0.000219000
C	4.944724000	0.653756000	-0.000065000
C	5.827010000	-0.588437000	0.000002000
H	5.137932000	1.263832000	0.886775000
H	5.137956000	1.263753000	-0.886953000
C	7.307218000	-0.172666000	-0.000010000

H	5.624697000	-1.199219000	0.887803000
H	5.624699000	-1.199305000	-0.887740000
H	7.940307000	-1.061969000	-0.000007000
H	7.558799000	0.415425000	-0.887290000
H	7.558811000	0.415441000	0.887256000
C	-4.944723000	-0.653755000	0.000538000
C	-5.827012000	0.588436000	0.000051000
H	-5.137889000	-1.263472000	0.887646000
H	-5.137997000	-1.264113000	-0.886080000
C	-7.307222000	0.172662000	-0.000452000
H	-5.625157000	1.199385000	0.887838000
H	-5.624243000	1.199138000	-0.887704000
H	-7.940311000	1.061965000	-0.001414000
H	-7.558344000	-0.416054000	-0.887446000
H	-7.559267000	-0.414802000	0.887116000
N	3.445178000	0.408625000	-0.000078000
N	-3.445177000	-0.408623000	0.000198000

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