Supporting information

Homooxacalix[3]arene-based Ditopic Receptor for Alkylammonium Ions Controlled by Ag^+ Ions

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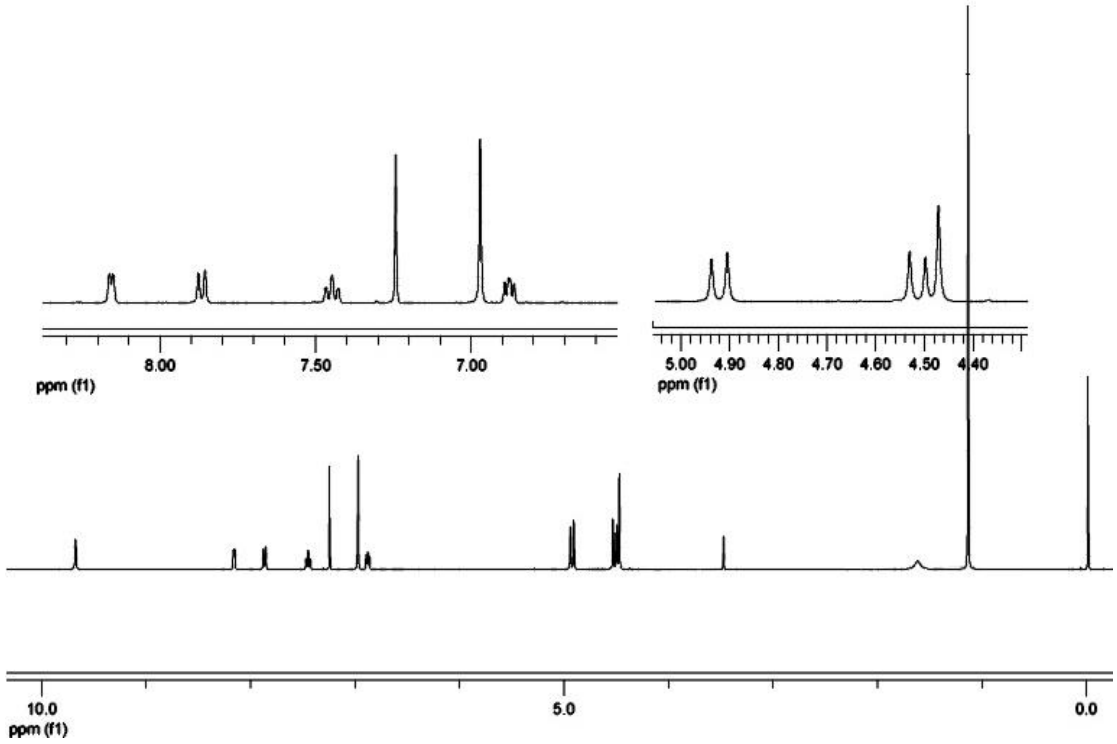


Figure S1. ^{1}H-NMR spectrum of receptor *cone*-**1** (300 MHz, $CDCl_3$, 293 K).

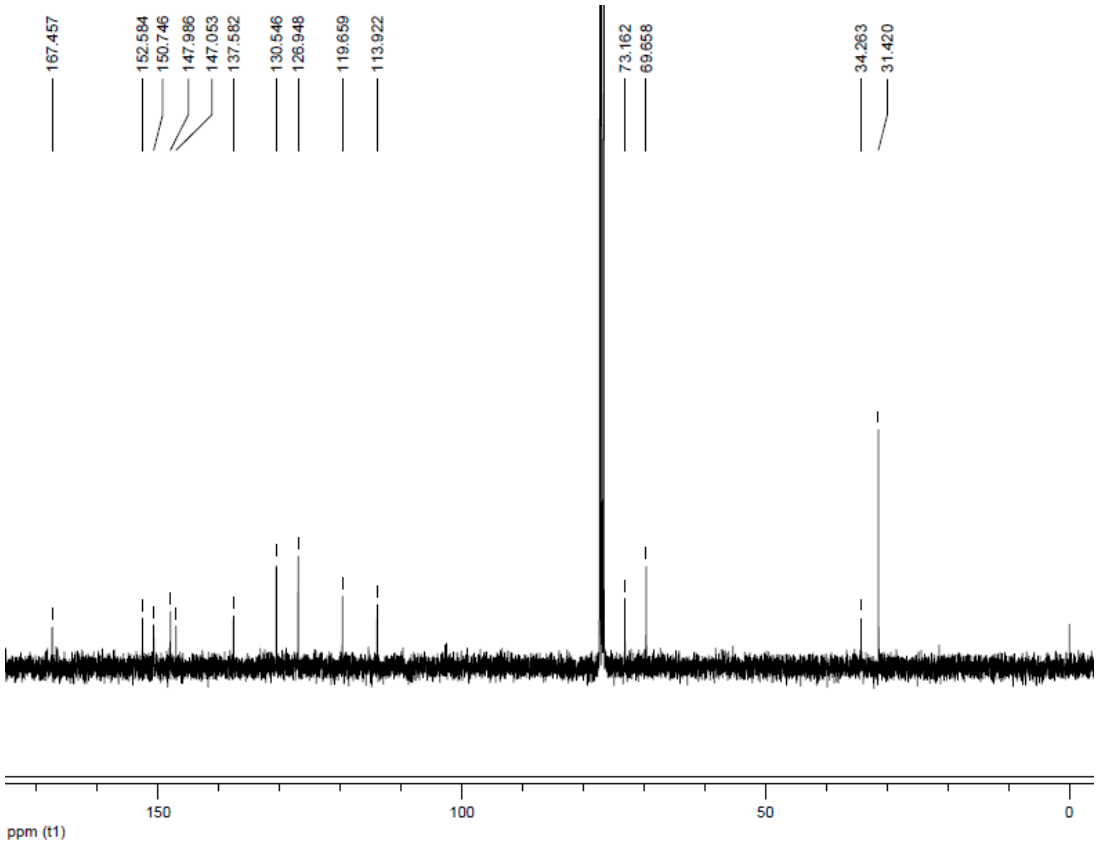


Figure S2. ^{13}C-NMR spectrum of receptor *cone*-**1** (100 MHz, $CDCl_3$, 293 K).

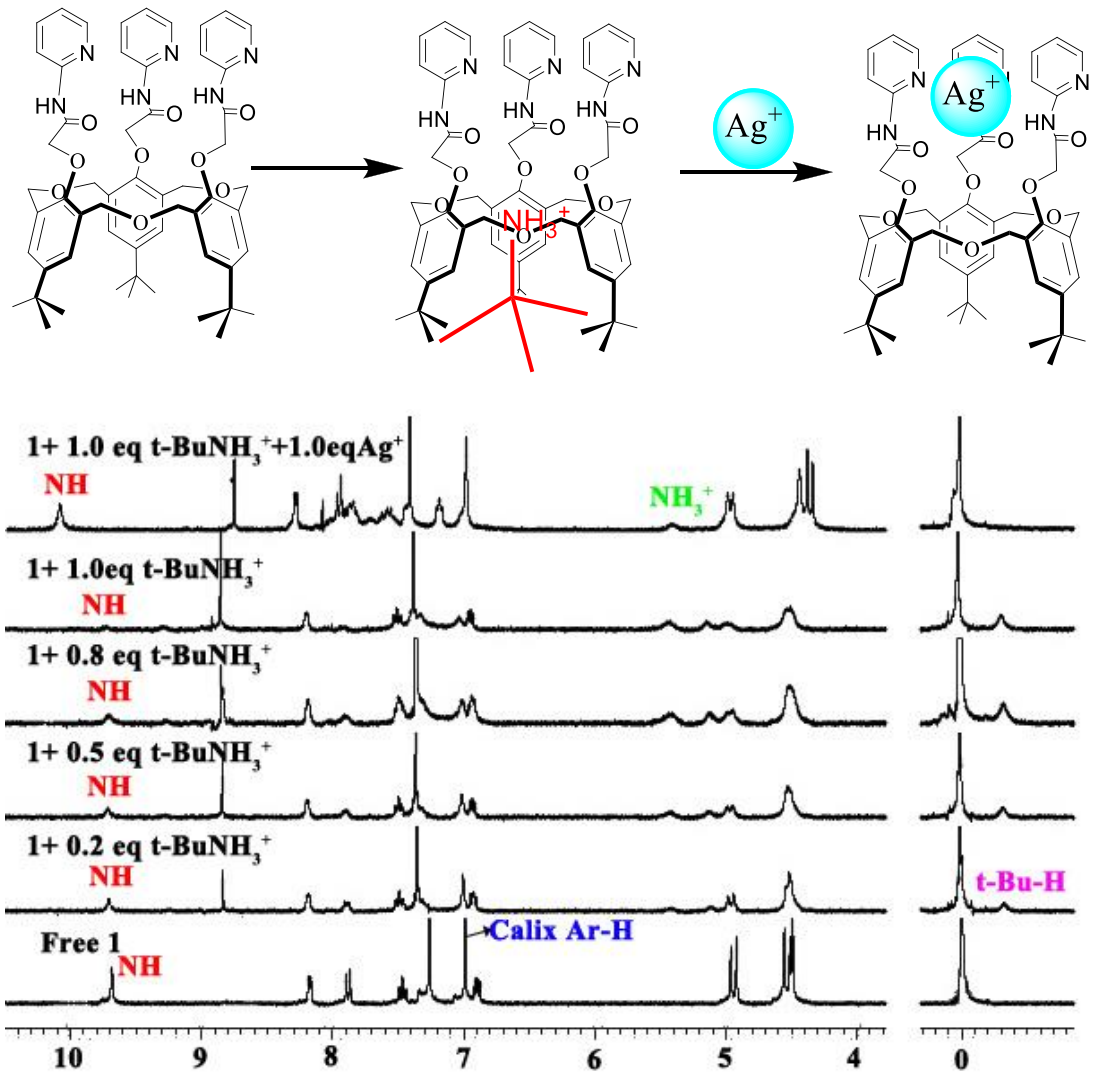


Figure S3. Partial ^{1}H-NMR spectral titration of receptor *cone*-**1**/*t*-BuNH$_3^+$ (H/G = 1:1); solvent: $CDCl_3/CD_3CN$ (10:1, v/v).

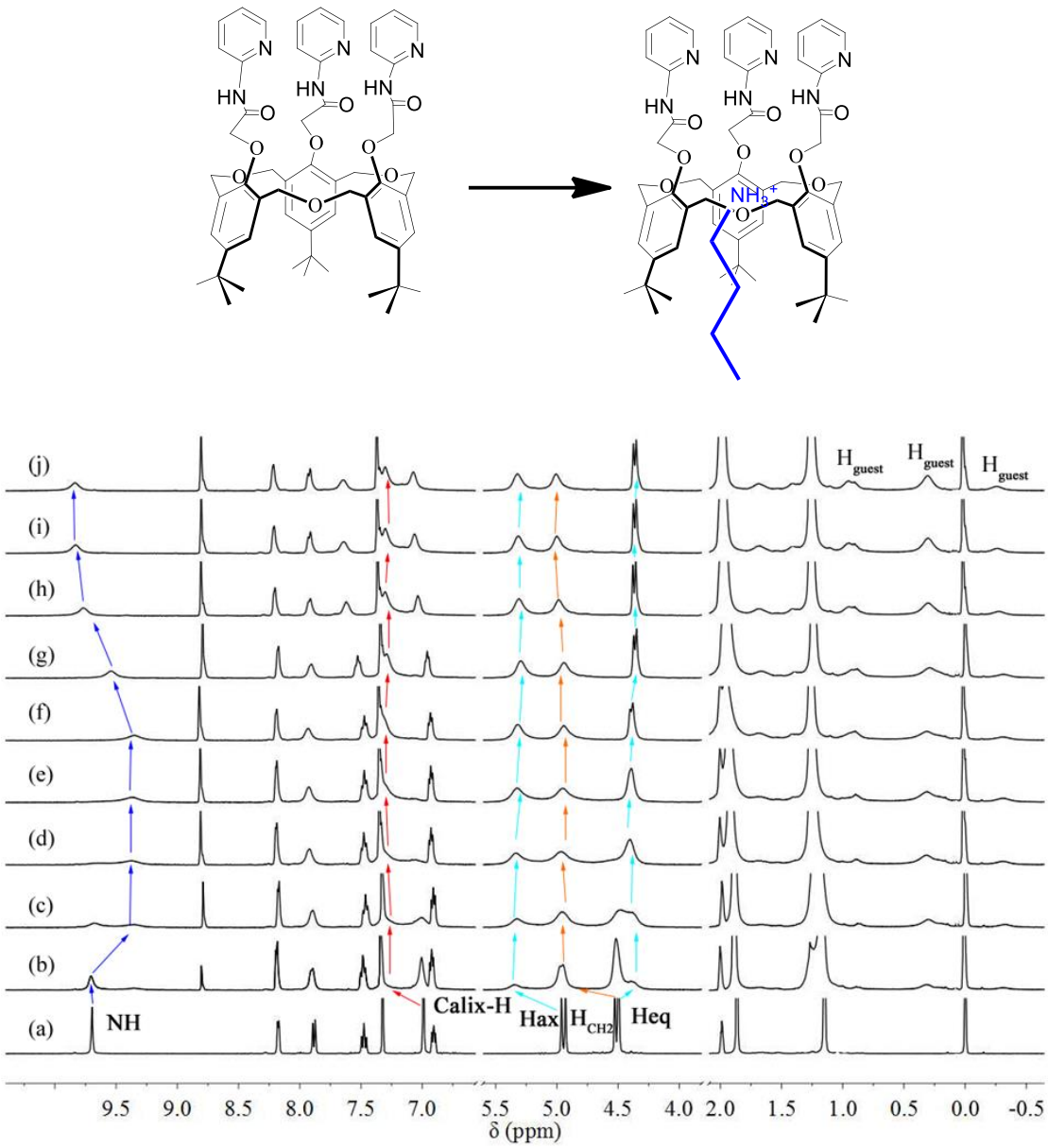


Figure S4. Partial ^{1}H-NMR spectral titration of receptor *cone*-**1**/guest complex (H/G = 1:1); a) free receptor *cone*-**1**; b) receptor *cone*-**1** ⊃ 0.2 equiv. of *n*-$BuNH_3^+$; c) receptor *cone*-**1** ⊃ 0.4 equiv. of *n*-$BuNH_3^+$; d) receptor *cone*-**1** ⊃ 0.6 equiv. of *n*-$BuNH_3^+$; e) receptor *cone*-**1** ⊃ 0.8 equiv. of *n*-$BuNH_3^+$; f) receptor *cone*-**1** ⊃ 1.0 equiv. of *n*-$BuNH_3^+$; g) receptor *cone*-**1** ⊃ 1.0 equiv. of *n*-$BuNH_3^+$ ⊃ 0.2 equiv. of Ag^+; h) receptor *cone*-**1** ⊃1.0 equiv. of *n*-$BuNH_3^+$ ⊃ 0.5 equiv. of Ag^+; i) receptor *cone*-**1** ⊃1.0 equiv. of *n*-$BuNH_3^+$ ⊃ 0.8 equiv. of Ag^+; j) receptor *cone*-**1** ⊃1.0 equiv.of *n*-$BuNH_3^+$ ⊃ 1.0 equiv. of Ag^+; solvent: $CDCl_3/CD_3CN$ (10:1, v/v).

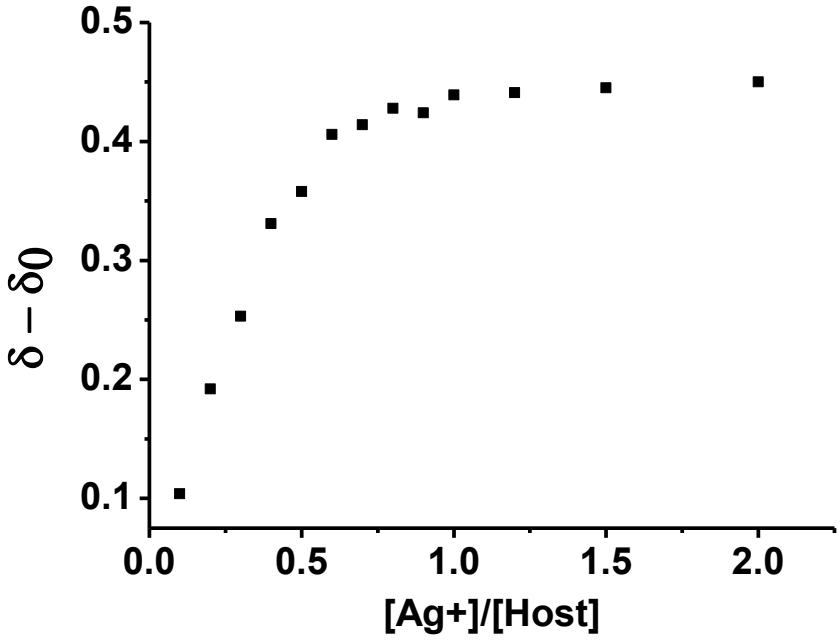


Figure S5. Molar ratio of Ag^+ with host receptor *cone*-**1**.

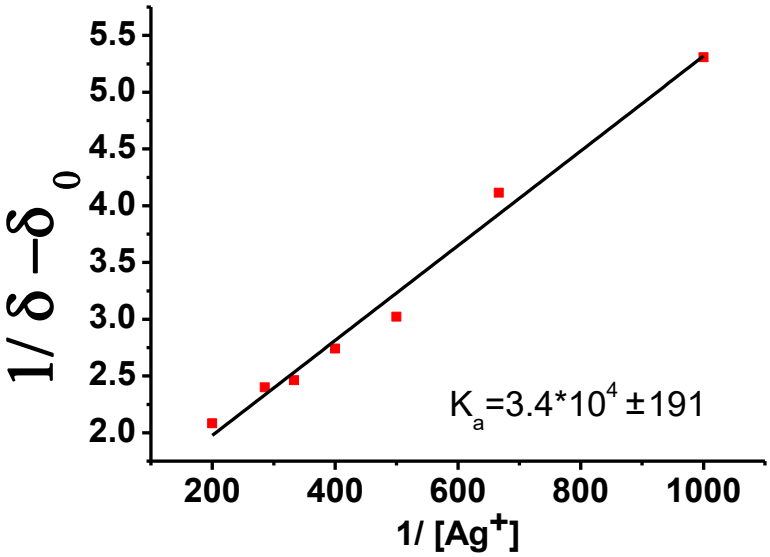


Figure S6. Bensei-Hilderbrand plot of receptor *cone*-**1** with varied concentrations of Ag^+ at 298 K. The associate constant (K_a) was calculated to be 3.4×10^4 M^{-1}.

X-ray crystallography

Table S1 Summary of crystal data for *cone*-**1**.[a,b]

Parameter	*cone*-**1**·3MeOH·H_2O	*cone*-**1**·2.5MeOH
Formula	$C_{57}H_{66}N_6O_9$ ·3(COH_4) ·H_2O	$C_{57}H_{66}N_6O_9$ ·2.5(COH_4)
Formula weight	1093.30	1059.26
Space group	*C*2/*c*	*C*2/*c*
a [Å]	26.1641(11)	26.308(2)
b [Å]	15.4995(6)	15.6159(14)
c [Å]	28.5153(11)	28.644(3)
β [°]	94.063(3)	94.1811(15)
Volume ($Å^3$)	11534.8(8)	11736.3(18)
Z	8	8
Wavelength [Å]	0.7085	0.71073
D(calc) [$g.m^{-3}$]	1.259	1.199
Temperature [K]	100(2)	150(2)
Measured reflns	113193	67896
Unique reflns	22109	17827
Obsd reflns [$I > 2\sigma(I)$]	16974	11159
Parameters	747	718
R_{int} [mm^{-1}]	0.074	0.053
R [$I>2\sigma(I)$][a]	0.067	0.059
wR [$I>2\sigma(I)$][b]	0.205	0.178
GOF on F^2	1.03	1.07

[a] Conventional R on F_{hkl}: $\Sigma ||Fo| - |Fc||/\sigma|Fo|$.

[b] Weighted R on $|F_{hkl}|^2$: $\Sigma [w(F_o^2 - F_c^2)^2]/ \Sigma [w(F_o^2)^2]^{1/2}$

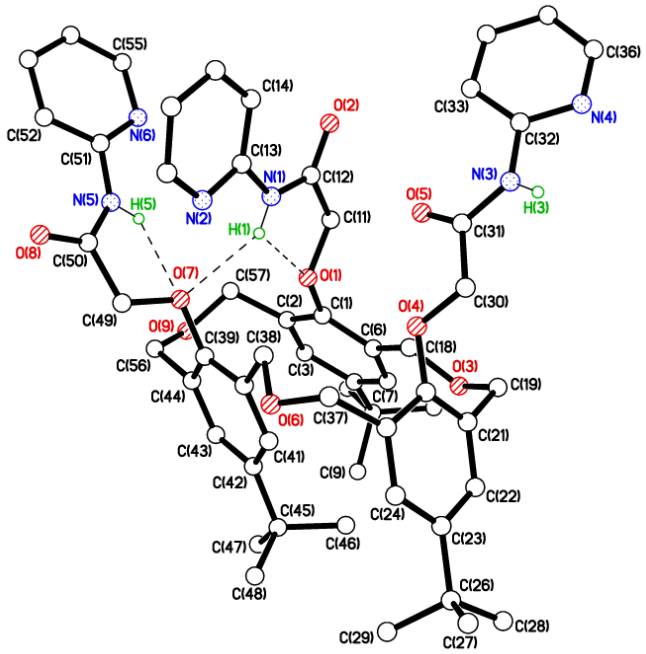


Figure S7. Crystal structure of *cone*-**1**·2.5MeOH; side view. MeOH of crystallization and H atoms not involved in H-bonding omitted for clarity.

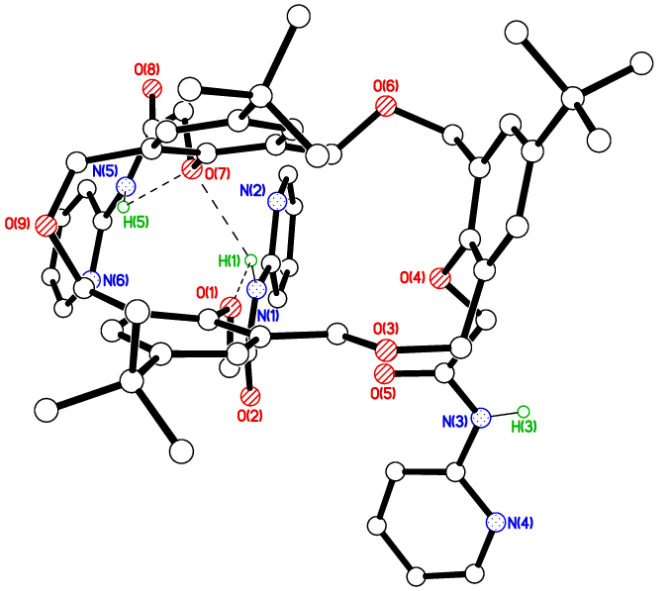
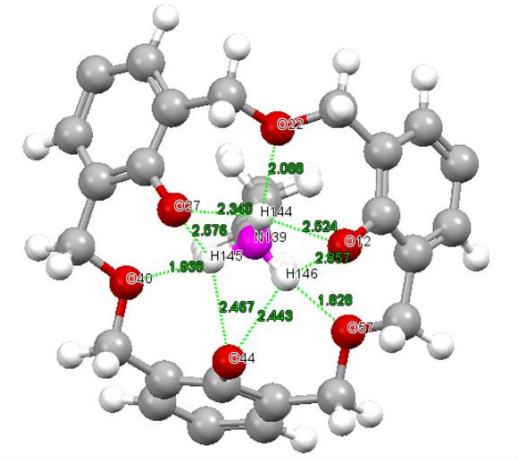


Figure S8. Crystal structure of *cone*-**1**·2.5MeOH; top view. MeOH of crystallization and H atoms not involved in H-bonding omitted for clarity.



Number	Object1	Object2	Length
1	O12	H144	2.5242
2	O12	H146	2.8573
3	O27	H144	2.3399
4	O27	H145	2.5755
5	O44	H145	2.4675
6	O44	H146	2.4428
7	O22	H144	2.0878
8	O40	H145	1.9378
9	O57	H146	1.8279

Figure S9. Geometry-optimized (PBE0/LANL2DZ) structures (Ball-and-stick) of *cone*-**1** and as its complex with *n*-$BuNH_3^+$. Top: view of the *cone*-**1**⊃ *n*-$BuNH_3^+$ complex (*tert*-butyl groups at the upper rim and the pyridyl groups at the lower rim have been omitted for clarity). For bond distance values, see Table S2.

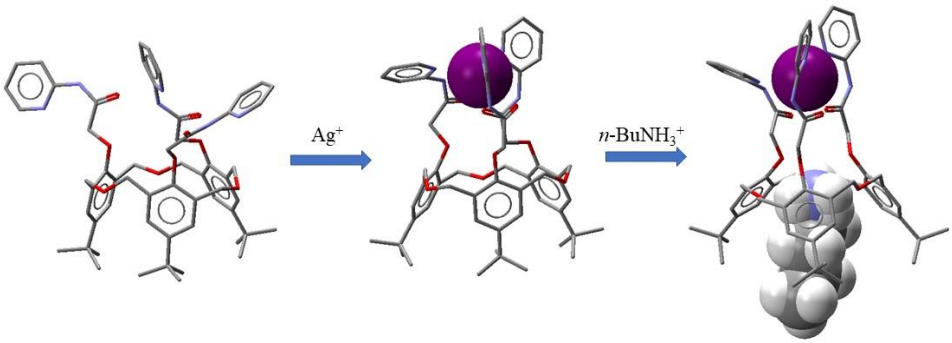
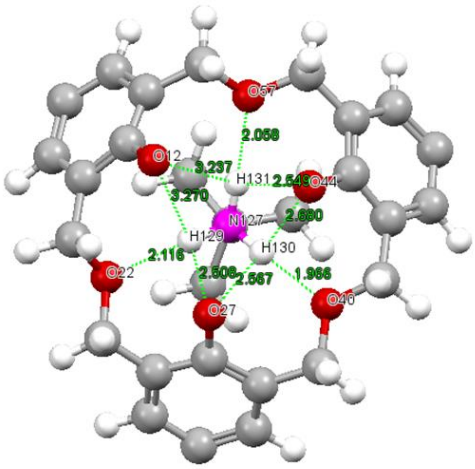


Figure S10. Geometry-optimized (PBE0/LANL2DZ) structures of *cone*-**1** and as its complex with *n*-$BuNH_3^+$. *Left*: The free *cone*-**1**. *Right*: 1:1 *cone*-**1**⊃ *n*-$BuNH_3^+$ complex. Colour code: carbon = drack grey, oxygen atom = red, nitrogen = blue and nitrogen (*n*-$BuNH_3^+$) = magenta. For bond distance values, see Table S2.



Number	Object1	Object2	Length
1	H129	O27	2.5084
2	H130	O44	2.6801
3	H131	O12	3.2373
4	H130	O40	1.9659
5	H129	O22	2.1162
6	H129	O12	3.2701
7	H131	O57	2.0577
8	H130	O27	2.5667
9	H131	O44	2.5494

Figure S11. Geometry-optimized (PBE0/LANL2DZ) structures (Ball-and-stick) of *cone*-**1** and as its complex with *tert*-$BuNH_3^+$. Top: view of the *cone*-**1** ⊃ *tert*-$BuNH_3^+$ complex (*tert*-butyl groups at the upper rim and the pyridyl groups at the lower rim have been omitted for clarity). For bond distance values, see Table S2.

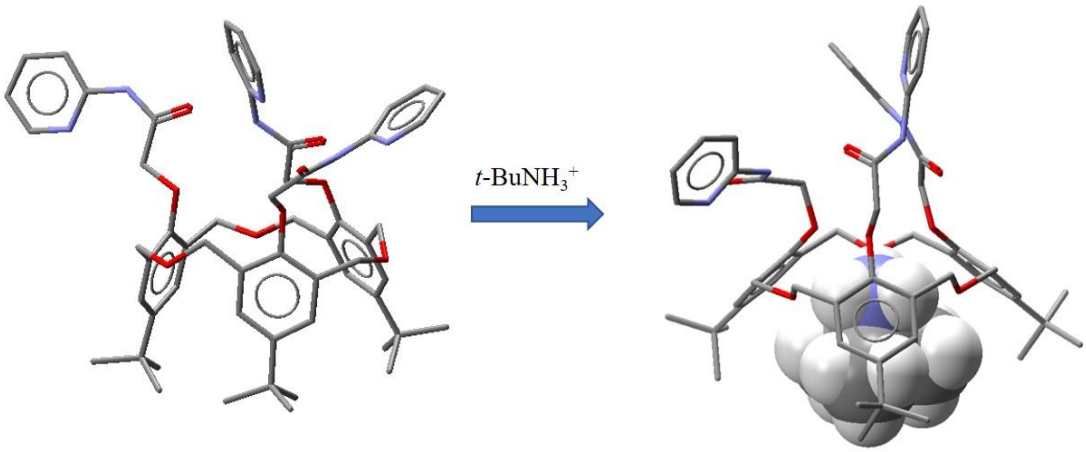


Figure S12. Geometry-optimized (PBE0/LANL2DZ) structures of *cone*-**1** and as its complex with *tert*-$BuNH_3^+$. *Left*: The free *cone*-**1**. *Right*: 1:1 *cone*-**1** ⊃ *tert*-$BuNH_3^+$ complex. Colour code: carbon = drack grey, oxygen atom = red, nitrogen = blue and nitrogen (*tert*-$BuNH_3^+$) = magenta. For bond distance values, see Table S2.

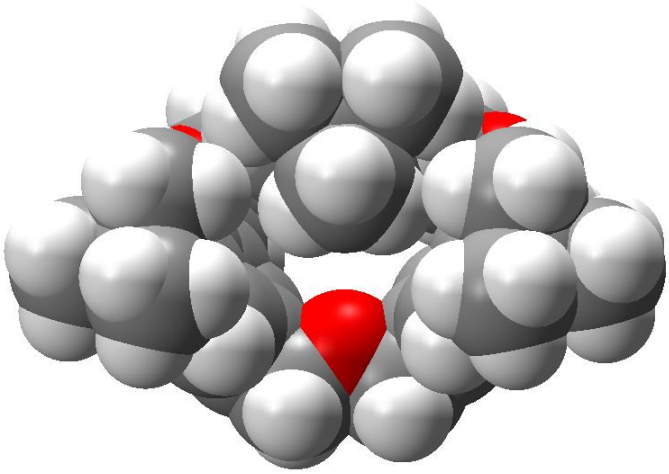


Figure S13. Geometry-optimized (PBE0/LANL2DZ) structures (space-filled) of *cone*-**1** and as its complex with Ag^+ from the wide-rim showing the compressed cavity entrance, due to the crowding of the three *tert*-butyl groups, in particular the one group which in pointing inwards towards an opposite aromatic ring.. The lower-rim functional groups of the *cone*-**1** Ag^+ complex have been have been omitted for clarity).

Table S2. The calculated distance for selected parameters for the backbones of the host *cone*-**1** and complexes with Ag^+ and *n*-$BuNH_3^+$ ions in the gas phase at PBE0/LANL2DZ basis set (Distance in Å).

Parameter	*cone*-**1** Distance **(**Å)	*cone*-**1⊃Ag**$^+$ Distance **(**Å)	*n*-$BuNH_3^+$⊂ [*cone*-**1⊃Ag**$^+$] Distance **(**Å)	*cone*-**1**⊃ *n*-$BuNH_3^+$ Distance **(**Å)	*cone*-**1**⊃*tert*-$BuNH_3^+$ Distance **(**Å)
$N_6 - N_{48}$	5.0247	4.2956	4.130	7.100	7.427
$N_6 - N_{132}$	8.3503	3.8462	3.991	4.989	4.932
$N_{48} - N_{132}$	13.111	3.768	3.761	8.006	7.936
$O_9 - O_{35}$	4.9912	3.1731	3.224	3.373	3.330
$O_9 - O_{33}$	4.9425	3.1865	3.000	4.940	4.920
$O_{35} - O_{53}$	8.1903	6.2554	5.862	7.239	6.983
$O_{12} - O_{27}$	4.7736	4.2434	3.532	5.053	5.099
$O_{12} - O_{44}$	4.2481	4.7334	4.674	5.054	5.281
$O_{27} - O_{44}$	5.182	4.8133	4.139	4.995	5.108
$O_{22} - O_{40}$	6.2249	6.0583	5.061	3.836	3.842
$O_{22} - O_{57}$	5.636	5.9854	5.113	3.875	3.730
$O_{40} - O_{57}$	7.0824	7.2396	4.950	3.748	3.684
$N_6 - Ag_{156}$	–	2.4331	2.448	–	–
$N_{48} - Ag_{156}$	–	2.3271	2.364	–	–
$N_{132} - Ag_{156}$	–	2.4413	2.468	–	–
$O_9 - Ag_{156}$	–	2.3706	2.360	–	–
$O_{35} - Ag_{156}$	–	4.693	4.494	–	–
$O_{53} - Ag_{156}$	–	2.7364	2.617	–	–
$H_{144} - O_{22}$	–	–	2.382	2.524	3.237
$H_{144} - O_{27}$	–	–	2.234	2.088	2.116
$H_{145} - O_{27}$	–	–	2.233	2.340	2.508
$H_{145} - O_{40}$	–	–	2.678	2.576	2.567
$H_{145} - O_{44}$	–	–	1.906	1.938	1.966
$H_{145} - O_{12}$	–	–	3.069	2.468	2.549
$H_{145} - O_{44}$	–	–	2.896	2.857	3.270
$H_{146} - O_{57}$	–	–	3.209	2.443	2.680
$H_{146} - O_{57}$	–	–	1.818	1.828	2.058