

Electronic Supplementary Information

For

Extraordinary stable ammonium ion complex of a noncyclic crown-
type polyether: solid and solution studies

Ki-Min Park,^{*a} Hyun Jee Kim,^a Suk-Hee Moon,^b Jagadese J. Vittal,^{a,c}
Jong Hwa Jung,^a and Shim Sung Lee^{*a}

^a *Department of Chemistry and Research Institute of Natural Sciences, Gyeongsang National University, Jinju 660-701, S. Korea*

^b *Subdivision of Food Science, Kyungnam College of Information and Technology, Busan, 616-701, S. Korea*

^c *Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore*

Experimental

Synthesis of $[\text{L}\cdot\text{NH}_4]\text{PF}_6$

1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecan (**L**) was purchased from Merck and used without further purification. Equimolar amount of NH_4PF_6 in acetonitrile was added to the solution of **L** in acetonitrile. The reaction mixture was stirred for 1h. The single crystals suitable for X-ray analysis were obtained by slow evaporation of the reaction mixture. Found: C, 50.82; H, 5.40; N, 6.75%. Calc for $\text{C}_{26}\text{H}_{32}\text{F}_6\text{N}_3\text{O}_5\text{P}$: C, 51.07; H, 5.27; N, 6.87%. IR (KBr, cm^{-1}): 3198, 2909, 2360, 1619, 1579, 1505, 1457, 1379, 1322, 1263, 1105, 949, 842, 790, 556. MS-FAB m/z 466 ($[\text{L}\cdot\text{NH}_4]^+$).

Physical measurements

NMR spectra were recorded on a Bruker Avance-300 spectrometer (300 MHz). The IR spectrum was recorded on a VERTEX 80v FT-IR spectrometer with KBr pellet in the range $4000 \sim 400 \text{ cm}^{-1}$. Elemental analysis was carried out on a CHNS-932 elemental analyser. Thermogravimetric analysis (TGA) was performed under nitrogen on a SDT Q600 thermogravimetric analyser. The sample was heated using a $10^\circ\text{C}/\text{min}$ heating rate from 25 to 700°C . The solid and solution state emission spectra were performed on a RF-5301 spectrophotometer. The pulsed excitation source was generated using the 302 nm of the Xenon lamp. Photoluminescent spectra for **L** and $[\text{NH}_4\text{-L}]\text{PF}_6$ in solution state were obtained using the concentrations in the range of $30 \mu\text{M}$. FAB mass spectra were recorded on a JEOL JSM-700 spectrometer.

Crystallographic Structure Determinations

All data were collected on a Bruker Smart diffractometer equipped with a graphite monochromated $\text{Mo } K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation source and a CCD detector. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. A total of 1271 frames of two-dimensional diffraction images were collected, each of which was measured for 5 sec. Decay was monitored by 50 standard data frames measured at the beginning and end of data collection. The crystal showed no significant decay. The frame data were processed to give structure factors using the SAINT-plus.^{Srefl} The structure was solved by direct methods and refined by full matrix

least squares methods on F^2 for all data using SHELXTL software.^{Sref2} The non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms for ammonium ion were located from the difference electron density maps, and refined isotropically. All others were placed in calculated positions, and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the parent atom. Crystallographic data and structural refinement data for $[\text{L}\cdot\text{NH}_4]\text{PF}_6$ is summarized in Table S1.

References

- Sref1. Bruker, SMART (*ver. 5.625*) and SAINT-plus (*ver. 6.22*): *Area Detector Control and Integration Software*; Bruker AXS Inc.: Madison, Wisconsin, 2000.
- Sref2. Bruker, SHELXTL (*ver. 6.10*): *Program for Solution and Refinement of Crystal Structures*; Bruker AXS Inc.: Madison, Wisconsin, 2000.

Table S1. Crystal data and structure refinement for [L·NH₄]PF₆.

Empirical formula	C ₂₆ H ₃₂ F ₆ N ₃ O ₅ P	
Formula weight	611.52	
Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 9.7803(6) Å	α = 90°.
	b = 18.3376(12) Å	β = 101.6080(10)°.
	c = 16.0545(11) Å	γ = 90°.
Volume	2820.4(3) Å ³	
Z	4	
Density (calculated)	1.440 Mg/m ³	
Absorption coefficient	0.179 mm ⁻¹	
F(000)	1272	
Crystal size	0.3 x 0.4 x 0.5 mm ³	
Theta range for data collection	1.71 to 27.10°.	
Index ranges	-12 ≤ h ≤ 12, -23 ≤ k ≤ 23, -20 ≤ l ≤ 9	
Reflections collected	17031	
Independent reflections	6178 [R(int) = 0.0435]	
Completeness to theta = 27.10°	99.1 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6178 / 0 / 387	
Goodness-of-fit on F ²	1.041	
Final R indices [I > 2σ(I)]	R1 = 0.0537, wR2 = 0.1501	
R indices (all data)	R1 = 0.0826, wR2 = 0.1706	
Extinction coefficient	0.0068(10)	
Largest diff. peak and hole	0.443 and -0.364 e.Å ⁻³	

Table S2 Hydrogen bonding geometry (Å, °) for [L·NH₄]PF₆

D-H...A	D-H(Å)	H...A(Å)	D...A(Å)	∠ D-H...A(°)
N3-H3A...N1	0.91(3)	2.02(4)	2.849(3)	151(3)
N3-H3A...O1	0.91(3)	2.56(3)	3.032(3)	113(2)
N3-H3B...O2	0.87(3)	2.13(3)	2.991(3)	170(3)
N3-H3B...O3	0.87(3)	2.50(3)	2.924(3)	111(2)
N3-H3C...O3	0.94(4)	2.56(4)	2.924(3)	103(3)
N3-H3C...O4	0.94(4)	1.96(4)	2.898(3)	172(3)
N3-H3D...O5	0.84(3)	2.61(3)	3.061(3)	115(2)
N3-H3D...N2	0.84(3)	2.09(3)	2.842(3)	148(2)
C7-H7...F3 ⁱ	0.93	2.50	3.386(4)	159
C14-H14B...F3 ⁱⁱ	0.97	2.62	3.540(4)	158
C19-H19...F6	0.93	2.58	3.367(3)	143
C20-H20...F2	0.93	2.57	3.268(4)	132

Symmetry codes: (i) 1-x, 1/2+y-1, 1/2-z+1; (ii) x-1, y, z.

Table S3. Selected torsion angles (°) for [L·NH₄]PF₆

O(1)–C(10)–C(11)–O(2)	-62.4(3)	C(10)–C(11)–O(2)–C(12)	-168.5(2)
C(11)–O(2)–C(12)–C(13)	-175.3(2)	O(2)–C(12)–C(13)–O(3)	70.8(3)
C(12)–C(13)–O(3)–C(14)	-179.6(2)	C(13)–O(3)–C(14)–C(15)	-178.3(2)
O(3)–C(14)–C(15)–O(4)	-64.8(3)	C(14)–C(15)–O(4)–C(16)	-173.7(2)
C(15)–O(4)–C(16)–C(17)	-71.5(3)	O(4)–C(16)–C(17)–O(5)	-57.2(3)

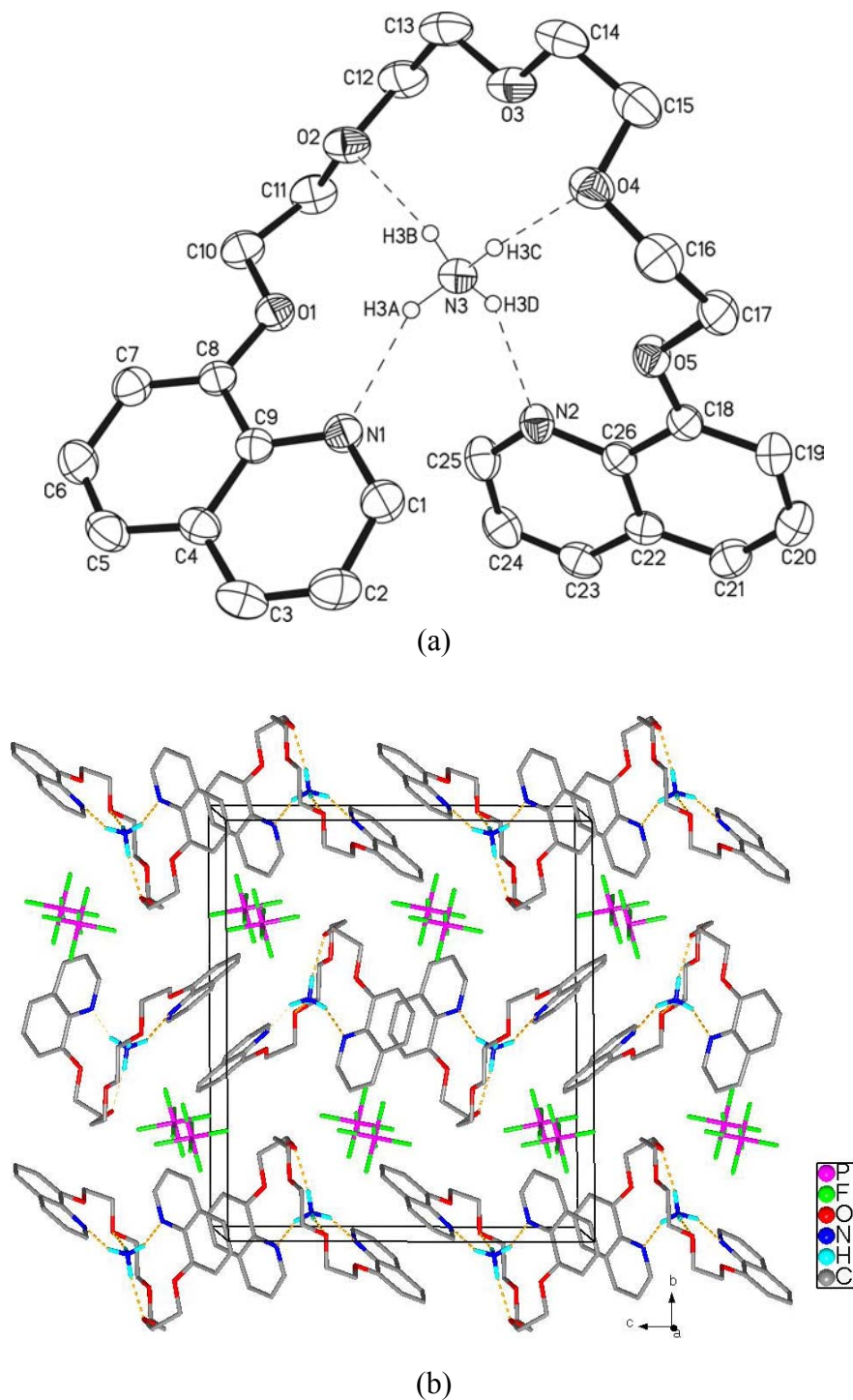
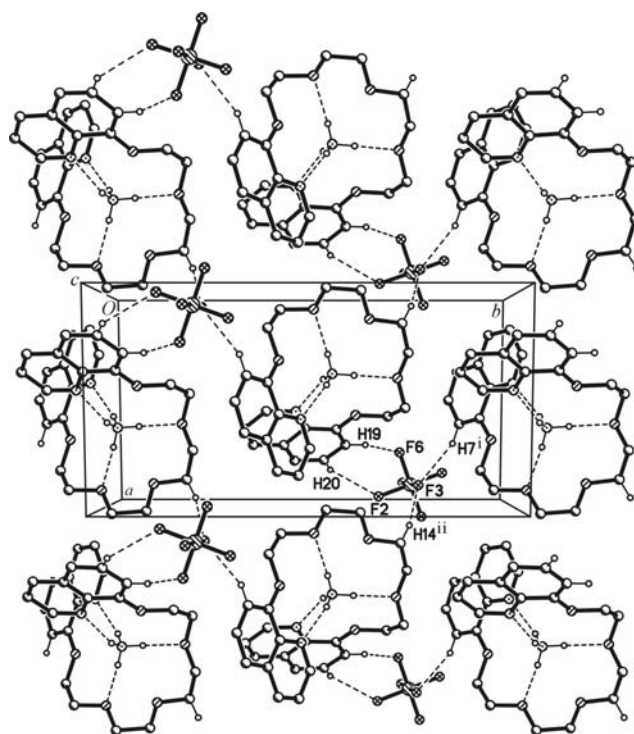
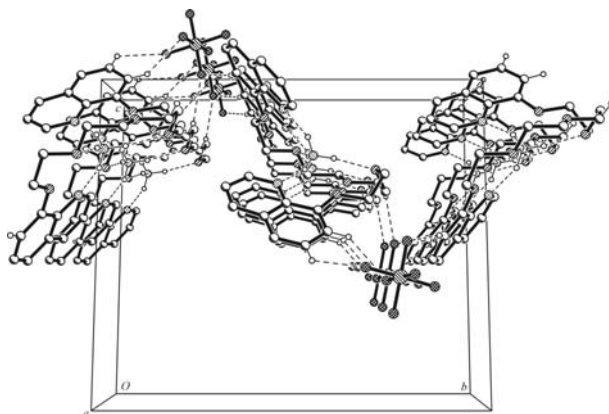


Fig. S1 (a) A view of the molecular structure of $[\text{L}\cdot\text{NH}_4]\text{PF}_6$ with the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level and H atoms are shown as small spheres of arbitrary radii. H atoms of **L** and the anion have been omitted for clarity. Dash lines represent the reasonable hydrogen bonds. (b) Packing diagram representing intermolecular $\pi\cdots\pi$ interactions between quinoline moieties. Dash lines (brown) represent the reasonable hydrogen bonds.



(a)



(b)

Fig. S2 (a) Top and (b) side views of [L·NH₄]PF₆ representing the puckered 2-D network induced by the C-H...F hydrogen bonds (dash lines). For the sake of clarity, only H atoms participating in the C-H...F hydrogen bonds have been plotted. [Symmetry codes: (i) 1-x, 1/2+y, 3/2-z; (ii) 1+x, y, z.]

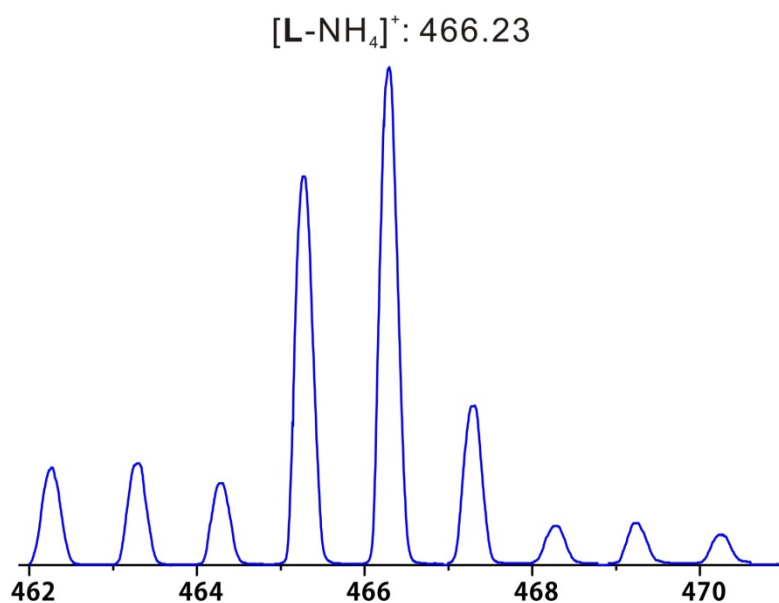


Fig. S3 FAB mass spectrum of $[\text{L}\cdot\text{NH}_4]\text{PF}_6$.

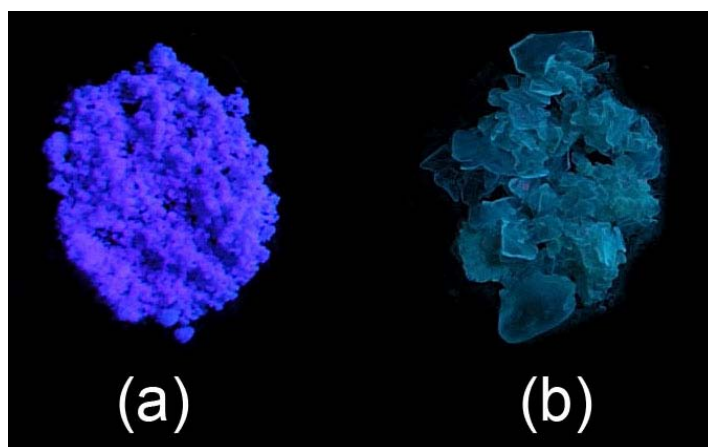


Fig. S4. Photos of (a) L and (b) $[\text{L}\cdot\text{NH}_4]\text{PF}_6$ at room temperature after excitation.

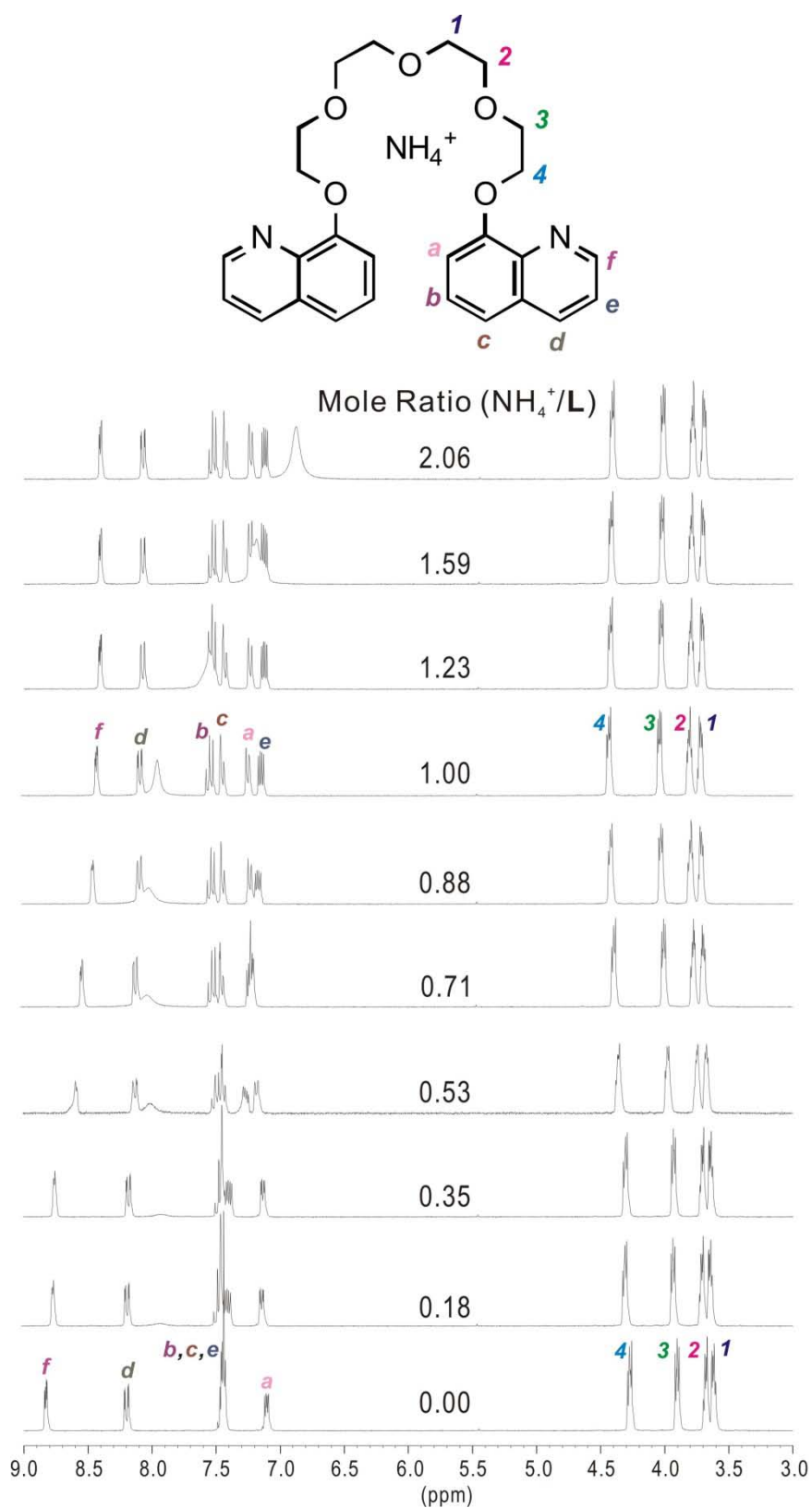
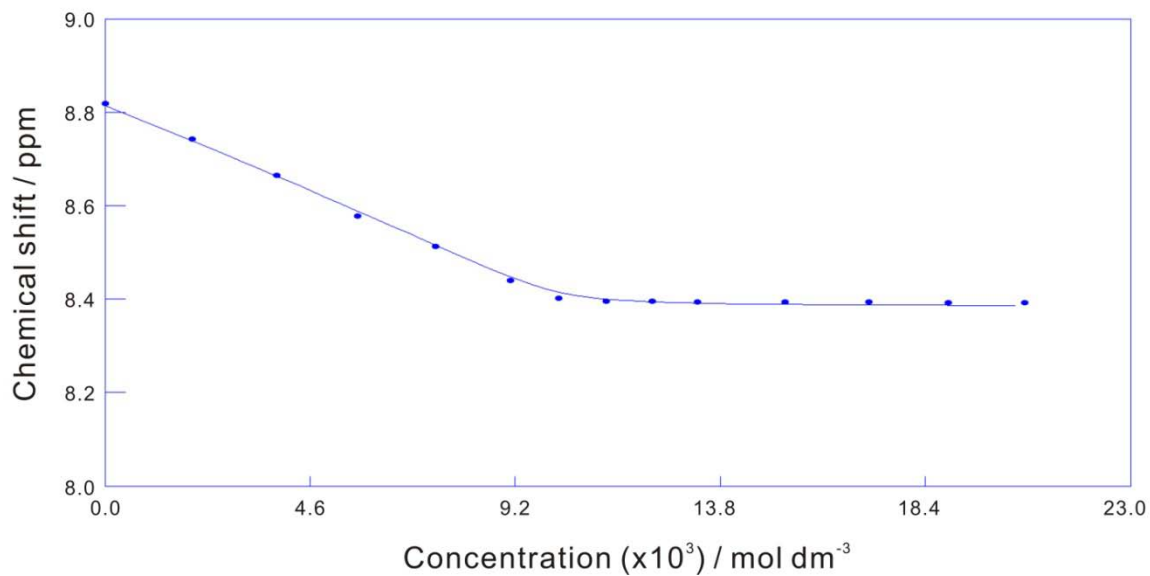
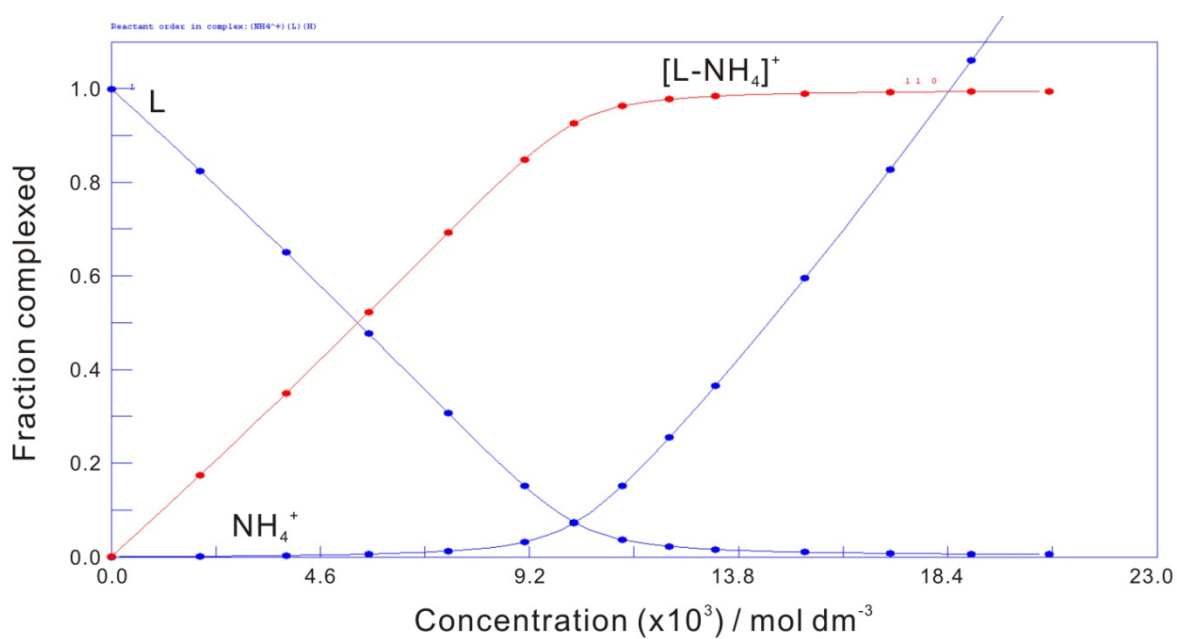


Fig. S5. ^1H NMR titration spectra of **L** by stepwise addition of NH_4PF_6 in CD_3CN .



(a)



(b)

Fig. S6. (a) A plot of raw and fitted data based on complexation-induced chemical shift for H_f of L and (b) species distribution curves in WinEQNMR.

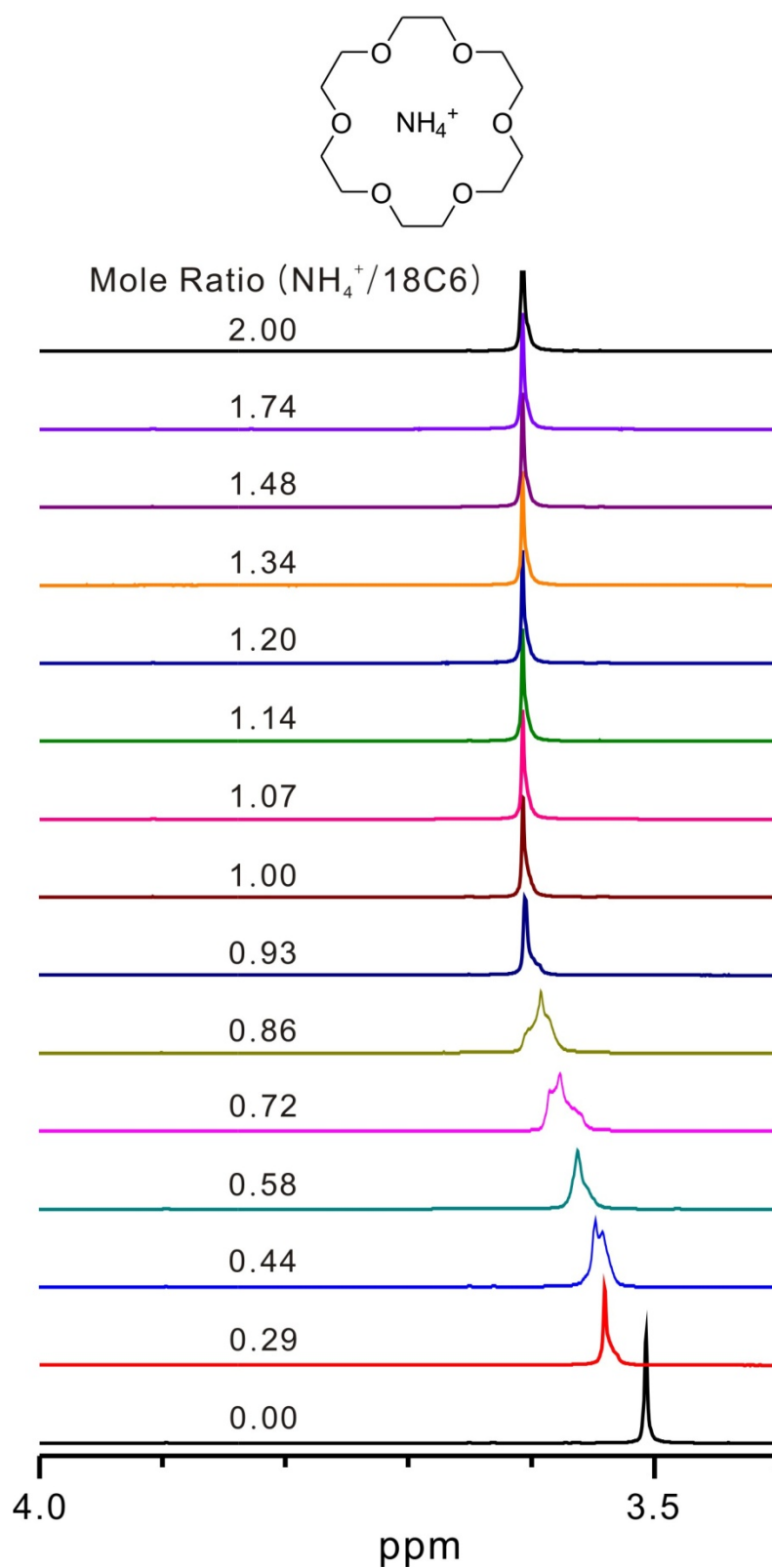
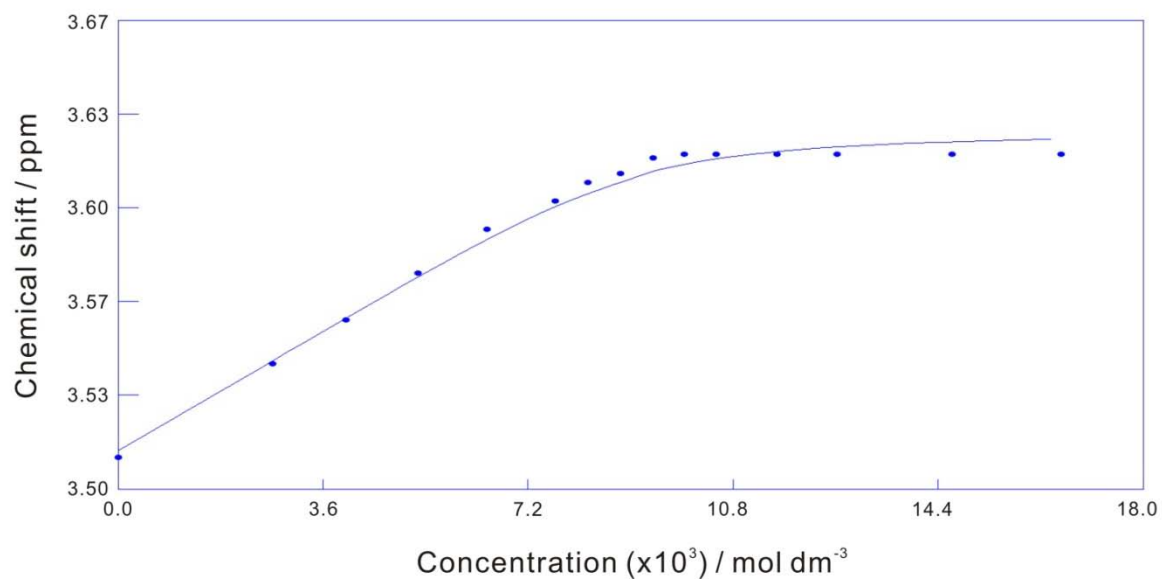
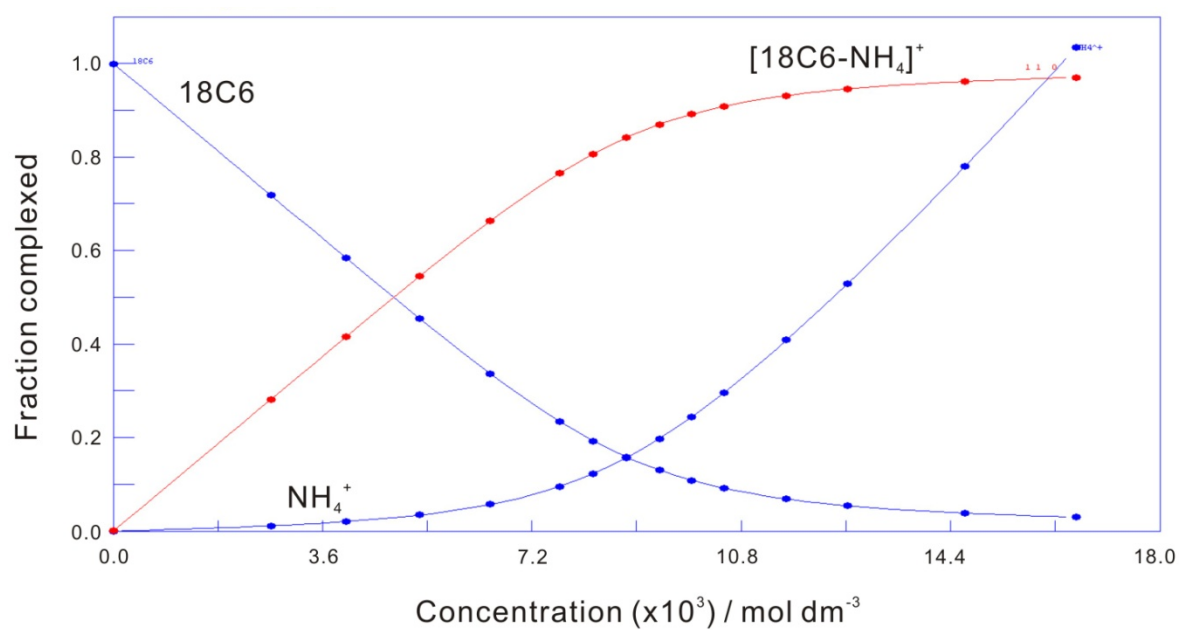


Fig. S7. (a) ^1H NMR titration spectra of $18\text{C}6$ by stepwise addition of NH_4PF_6 in CD_3CN .



(a)



(b)

Fig. S8. (a) A plot of raw and fitted data based on complexation-induced chemical shift of the proton of **18C6** and (b) species distribution curves in WinEQNMR.

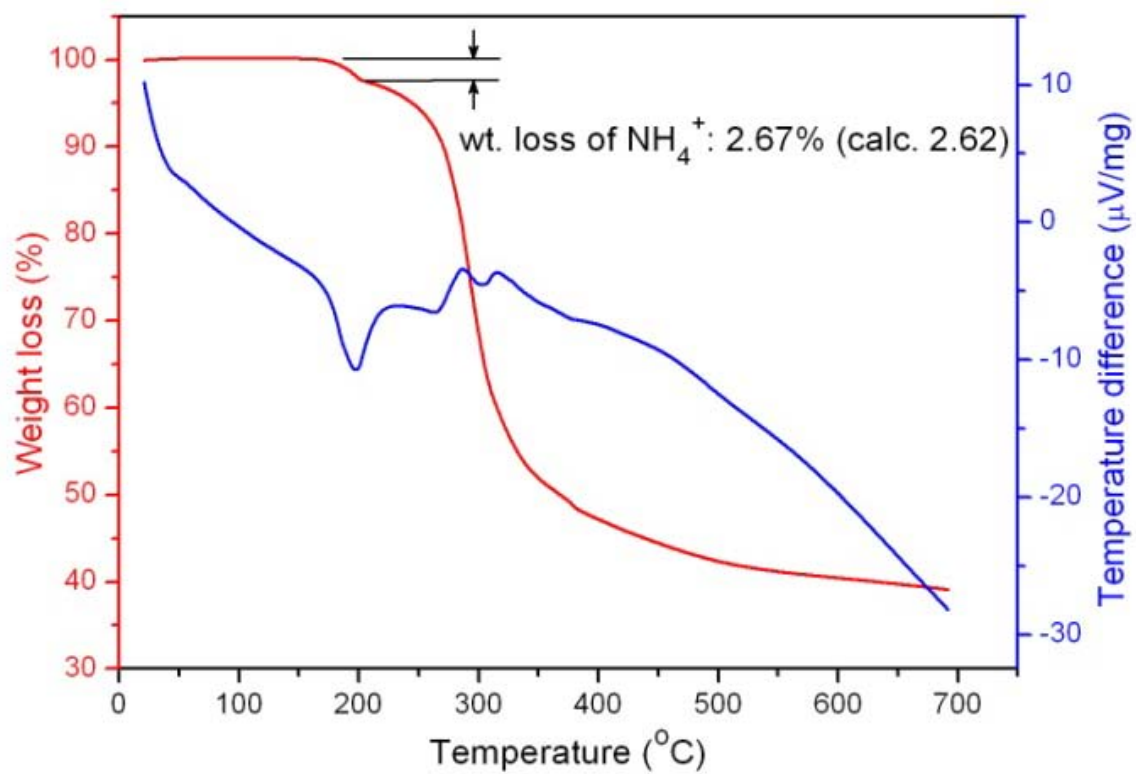


Fig. S9. TGA and DTA curves of $[\text{L}\cdot\text{NH}_4]\text{PF}_6$.