

## Synthesis, Structural Characterization, and Physical Properties of Alkylammonium Derivative Complex with Acyclic Crown Ether Analog

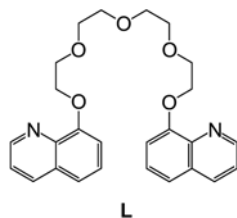
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**Key Words** : Host-guest chemistry, Dipodal ligand, Alkylammonium derivative, Hydrogen bonds, Crystal structure

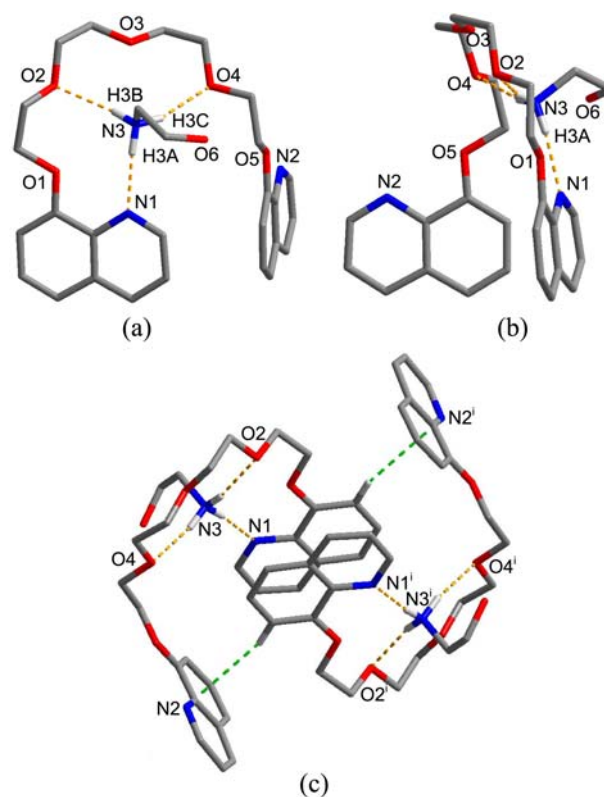
The complexation abilities of cyclic or acyclic crown-type polyethers toward metal cations, ammonium (or alkylammonium) ion, and neutral molecules have attracted much attention during the last four decades because of their contributions to stereoselective complexation, cation transport, and enzyme chemistry.<sup>1-9</sup> It is well-known that the cyclic polyethers such as 18-crown-6 show the excellent complexing ability and selectivity for the guest species with or without the charge.<sup>2,3</sup> On the other hand, the complexation abilities of the acyclic polyethers are weaker because of their conformational freedom as well as much less effective complexation process. However, the complexing abilities of the dipodal type acyclic polyethers are improved remarkably when they have rigid aromatic donor end-groups at the both ends of the oligo(ethylene glycol) backbone.<sup>4-8</sup> Among these, 1,13-bis-(8-quinoly)-1,4,7,10,13-pentaoxatridecane (**L**)<sup>4</sup> is representative and has already been extensively investigated for its complexation ability toward several cationic or neutral guests because **L** has the attractive characteristics forming the pseudo-cyclic complexes with guest species in a manner similar to 18-crown-6.<sup>5-9</sup> However, the crystal structures reported for complexation between **L** and the guest species, especially organic guests, are still rare.<sup>7,9</sup>



Recently, we have firstly reported the crystal structure of  $\text{NH}_4^+$  complex with **L**, in which the  $\text{NH}_4^+$  is wrapped around by **L** in a helical manner through the unique tetrahedral-type hydrogen bonds.<sup>9</sup> As an ongoing efforts for the complexation of **L**,<sup>8,9</sup> we were able to isolate the crystalline complex **1** obtained from the reaction of **L** with ethanolanionium ion ( $^+\text{NH}_3\text{-(CH}_2)_2\text{OH}$ ). Herein, we report the preparation, crystal structure, and physical properties of **1**.

Slow evaporation of the methanol solution with **L** and

ethanolamine under the acidic condition controlled by  $\text{HPF}_6$  afforded colorless crystals of **1** suitable for X-ray analysis. **1** crystallized in a 1:1 complex of formula  $[\text{L}\cdot\text{NH}_3\text{-(CH}_2)_2\text{OH}]\text{PF}_6$ , which was also confirmed by elemental analysis. In the crystal, as illustrated in Figure 1, **L** wraps around the  $-\text{NH}_3^+$  moiety of the guest molecule to form a pseudo-cycle through a unique tripodal-type  $\text{N-H}\cdots\text{X}$  ( $\text{X} = \text{N}$  or  $\text{O}$ ) hydrogen bonds. Since the  $-\text{NH}_3^+$  unit in **1** is in a perching position with respect to the pseudo-cycle of **L**, and the ammonium nitrogen atom is displaced by 0.831(3) Å from the mean plane of the pseudo-cycle. Notably, one



**Figure 1.** The crystal structure of **1**: (a) front view, (b) side view, and (c) stick model showing pair-wise intermolecular  $\pi$ - $\pi$  and  $\text{C-H}\cdots\pi$  interactions (green dotted lines).  $\text{PF}_6^-$  anion and hydrogen atoms except those related to intermolecular interactions are omitted for clarity. (Symmetry code: (i)  $1-x, 1-y, -z$ )

**Table 1.** Crystallographic data and structure refinement for **1**

Chemical formula	C <sub>28</sub> H <sub>36</sub> F <sub>6</sub> N <sub>3</sub> O <sub>6</sub> P
Formula weight	655.57
<i>T</i> (K)	173(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> (Å)	8.9026(14)
<i>b</i> (Å)	15.020(2)
<i>c</i> (Å)	23.198(4)
$\beta$ (°)	103.184(3)
<i>V</i> (Å <sup>3</sup> )	3020.3(8)
<i>Z</i>	4
Absorption coefficient (mm <sup>-1</sup> )	0.174
<i>F</i> (000)	1368
Crystal size (mm <sup>3</sup> )	0.10 × 0.10 × 0.45
$\theta$ range (°)	1.63 to 26.37
Reflections collected / Unique	17537 / 6148
No. variables	397
Refl./para. ratio	15.49
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.010
Final <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0530, 0.0900
(all data)	0.1422, 0.1261

hetero nitrogen (N1) and two oxygen atoms (O2 and O4) which participate in the hydrogen bonds are positioned alternately in the array of the donor set of **L** to fit the tripodal-type interaction. The hydrogen bond distances [O2···N3 3.011(3), O4···N3 3.023(3), N1···N3 2.865(3) Å] (Table 2) are slightly longer than those observed for [**L**·NH<sub>4</sub>]<sup>+</sup> we reported previously.<sup>9</sup>

The dihedral angle between the two quinoline end-groups

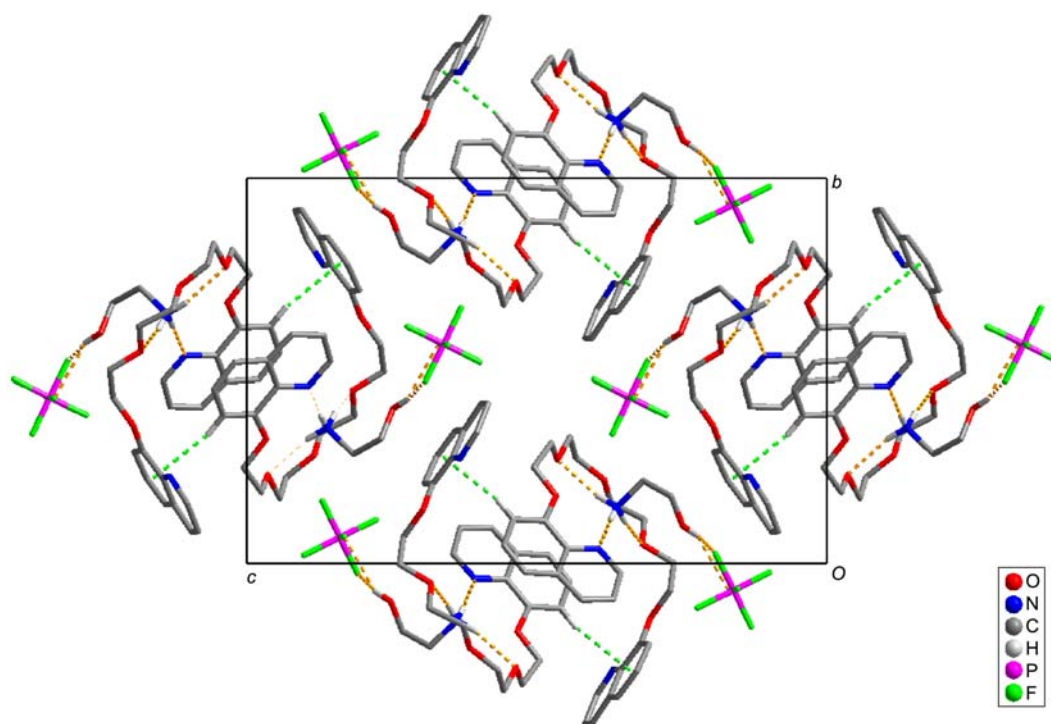
**Table 2.** Hydrogen bonds for **1** [Å and °]

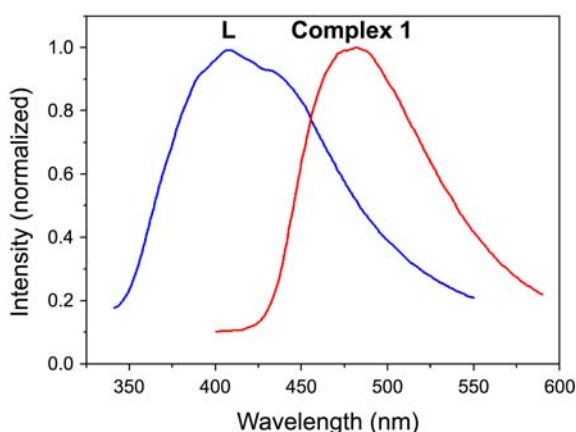
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N3-H3A···N1	0.91	1.96	2.865(3)	173.1
N3-H3B···O2	0.91	2.13	3.011(3)	161.6
N3-H3C···O4	0.91	2.14	3.023(3)	163.2
O6-H6A···F3	0.84	2.49	3.201(3)	142.5
O6-H6A···F6	0.84	2.15	2.908(3)	150.0
C1-H1···F4	0.96	2.69	3.325(4)	124.1
C2-H2···F4	0.96	2.72	3.325(4)	121.8

is 86.31(5)° but no intramolecular  $\pi$ - $\pi$  interaction was observed. Instead, as shown in Figure 1(c), the intermolecular  $\pi$ - $\pi$  interaction with the distance of 3.575(6) Å between two quinoline end-groups is observed. In addition, weak intermolecular C-H··· $\pi$  interactions (dashed line, 2.71 Å) between two perpendicular quinoline moieties from two different **L** exist. The counter anion (PF<sub>6</sub><sup>-</sup>) resides in the void and interacts with **1** through O-H···F and C-H···F hydrogen bonds (Table 2 and Figure 2).

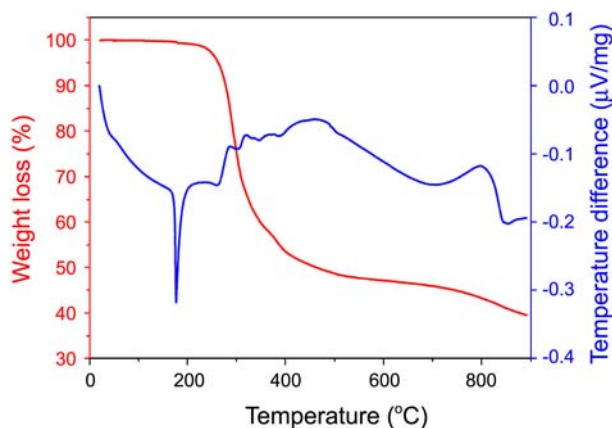
Solid-state photoluminescence studies were carried out for **L** and **1** at room temperature (Figure 3). **L** shows indigo-violet photoluminescence dominated by the emission at 407 nm which is likely due to a  $\pi$ - $\pi^*$  transition of the quinoline moiety. Meanwhile, an emission band of **1** was observed at 481 nm (bathochromic shift,  $\Delta\lambda_{em} = 74$  nm), indicating the presence of the intermolecular  $\pi$ - $\pi$  interactions between quinoline moieties in the solid state, as mentioned in the single-crystal structure (Figure 1(c)). This observation is consistent with a previous study on the photoluminescence properties for ammonium complex of **L** in the solid state.<sup>9</sup>

Thermogravimetric analysis (TGA) and differential thermal

**Figure 2.** Perspective molecular packing diagram of **1**, showing hydrogen bonds (brown dotted line), C-H··· $\pi$  (green dotted line), and  $\pi$ - $\pi$  interaction between quinoline end-groups.



**Figure 3.** Photoluminescence spectra of **L** (blue) and **1** (red) in the solid state ( $\lambda_{\text{ex}} = 302$  nm).



**Figure 4.** TGA and DTA curves for **1**.

analysis (DTA) were performed on **1** (Figure 4). The TGA curve shows **1** is stable up to 176 °C, at which the DTA curve also shows a sharp endothermic peak, indicating the melting of **1**. The high thermal stability of **1** is probably due to the multiple interactions such as hydrogen bonds,  $\pi \cdots \pi$  and C-H $\cdots\pi$  stacking interactions observed in the crystal structure of **1**.

In summary, we have achieved the preparation and structural characterization of the ethanolammonium complex **1** with acyclic crown-type polyether **L** from the assembly reaction under the acidic condition. The association of ethanolammonium ion and **L** is mainly provided by  $^+\text{N-H}\cdots\text{X}$  (X=O or N) hydrogen bonds with the tripod-type perching arrangement. Photoluminescence and TGA studies also support that **L** interacts efficiently with the ethanolammonium ion through the intermolecular interactions such as hydrogen bonds,  $\pi \cdots \pi$  and C-H $\cdots\pi$  stacking interactions. We believe the knowledge of such structural information and properties is an essential precondition for progress in the recognition of organic and biomolecules.

### Experimental Section

All commercial reagents including solvents were of analytical reagent grade where available. The IR spectra were

recorded on a VERTEX 80v FT-IR spectrometer with KBr pellet in the range 4000–400  $\text{cm}^{-1}$ . Elemental analysis was carried out on a CHNS-932 elemental analyzer. Thermogravimetric analysis (TGA) was performed under nitrogen on a SDT Q600 thermogravimetric analyzer. The sample was heated with 10 °C/min heating rate from 20 to 900 °C. The solid state emission spectrum was performed on a RF-5301 spectrophotometer. The pulsed excitation source was generated using the 302 nm of the Xenon lamp.

**Preparation of  $[\text{L}\cdot\text{NH}_3(\text{CH}_2)_2\text{OH}]\text{PF}_6$  (**1**).** 1,13-Bis(8-quinolyyl)-1,4,7,10,13-pentaoxatriecan (**L**) was purchased from Merck and used without further purification. A solution of ethanolamine (7 mL, 0.12 mmol) in methanol was added to a solution (5 mL) of **L** (52 mg, 0.12 mmol) in methanol and then the pH of the reaction mixture was adjusted at 4.0 by using  $\text{HPF}_6$ . Slow evaporation of the methanol solution afforded crystalline product **1** suitable for X-ray analysis (yield: 48%), mp 175–176 °C. IR (KBr pellet): 3433, 2941, 2904, 1620, 1505, 1474, 1379, 1321, 1263, 1105, 951, 842, 791, 557. Anal. Calcd for  $\text{C}_{28}\text{H}_{36}\text{F}_6\text{N}_3\text{O}_6\text{P}$ : C, 51.30; H, 5.54; N, 6.41. Found: C, 51.18; H, 5.82; N, 6.25%.

**X-ray Crystallography.** Single crystal diffraction data of **1** were collected on a Bruker Smart diffractometer equipped with a graphite monochromated Mo  $K\alpha$  ( $\lambda = 0.71073$  Å) radiation source and a CCD detector. Crystals were isolated from mother liquor and immediately immersed in paratone oil and then mounted. The 45 frames of two dimensional diffraction images were collected at 173 K 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.<sup>10</sup> The structure was solved by direct methods and refined by full matrix least squares methods on  $F^2$  for all data using SHELXTL software.<sup>11</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the nitrogen atoms (N3) of the ethanolammonium ion were located in difference electron density maps, and refined with a riding model. All the other hydrogen atoms were included in the calculated positions with isotropic thermal parameters 1.2 times those of the attached atoms. Crystallographic data and structural refinement data for **1** is summarized in Table 1.

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**Supplementary Material.** Supplementary crystallographic data associated to complex **1** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 821683. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK

(fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk), or electronically via [www.ccdc.cam.ac.uk/perl/catreq.cgi](http://www.ccdc.cam.ac.uk/perl/catreq.cgi).

**Supporting Information.** Supplementary table and figure of **1** are available via the internet at <http://www.kcsnet.or.kr/bkcs>.

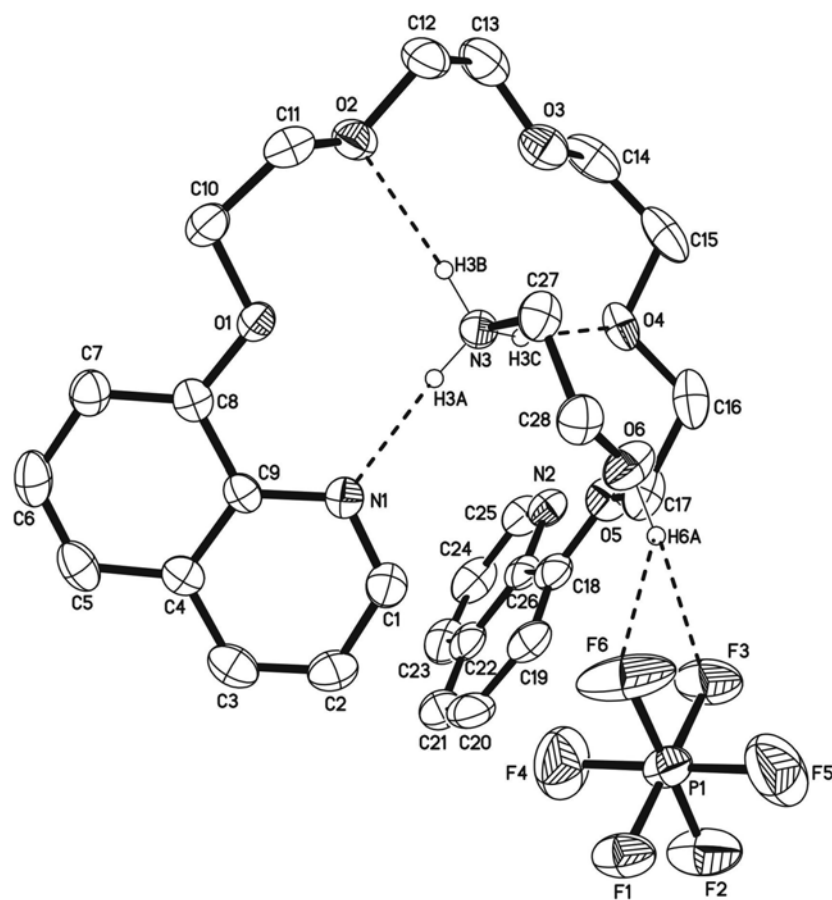
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## Supporting Information

Synthesis, Structural Characterization, and Physical Properties of  
Alkylammonium Derivative Complex with Acyclic Crown Ether AnalogEunji Lee, Suk-Hee Moon,<sup>†</sup> Shim Sung Lee,<sup>\*</sup> and Ki-Min Park<sup>\*</sup>*Department of Chemistry (WCU) and Research Institute of Natural Science, Gyeongsang National University,  
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Received April 15, 2011, Accepted April 26, 2011***Table S1.** Crystal data and structure refinement for **1**

Empirical formula	C <sub>28</sub> H <sub>36</sub> F <sub>6</sub> N <sub>3</sub> O <sub>6</sub> P	
Formula weight	655.57	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	$a = 8.9026(14)$ Å	$\alpha = 90^\circ$ .
	$b = 15.020(2)$ Å	$\beta = 103.184(3)^\circ$ .
	$c = 23.198(4)$ Å	$\gamma = 90^\circ$ .
Volume	3020.3(8) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.442 Mg/m <sup>3</sup>	
Absorption coefficient	0.174 mm <sup>-1</sup>	
F(000)	1368	
Crystal size	0.10 × 0.10 × 0.45 mm <sup>3</sup>	
Theta range for data collection	1.63 to 26.37°.	
Index ranges	-11 ≤ h ≤ 11, -18 ≤ k ≤ 18, -28 ≤ l ≤ 19	
Reflections collected	17537	
Independent reflections	6148 [R(int) = 0.0915]	
Completeness to theta = 26.37°	99.6%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	6148 / 0 / 397	
Goodness-of-fit on F <sup>2</sup>	1.010	
Final R indices [I > 2σ(I)]	R1 = 0.0530, wR2 = 0.0900	
R indices (all data)	R1 = 0.1422, wR2 = 0.1261	
Largest diff. peak and hole	0.286 and -0.252 e.Å <sup>-3</sup>	



**Figure S1.** Ortep diagram of **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms except those related to hydrogen bonds are omitted for clarity.