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Synthesis and Structure of Supramolecular Compound with Ethyl 2-(4-Aminophenoxy)acetate Based on 18-Crown-6[†]

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The title ammonium compound ethyl 2-(4-aminophenoxy)acetate ($C_{10}H_{13}NO_3$, **I**) and its crown ether inclusion complex {$[(C_{10}H_{14}NO_3)\cdot(\text{18-crown-6})]^+[PF_6]^-$, **II**} (18-crown-6=1,4,7,10,13,16-hexaoxacyclo-octadecane) were synthesized. The ammonium compound **I** was determined by ^{1}H NMR, IR and ESI-MS techiniques. X-ray crystallography reveals that compound **I** crystallizes in the triclinic system with space group of *P*-1, all the atoms in **I** are almost coplanar except H, and N—H···O hydrogen bonds lead to the formation of one dimensional chain. The rotator-stator-like compound **II** was crystallizes in the centrosymmetric monoclinic system with space group of *P*21/*c*. The supramolecular was formed via N—H···O hydrogen-bond interactions. Temperature-dependent dielectric constants of compound **II** were measured.

Keywords solid-phase synthesis, crystal structure, crown ether, phase transition

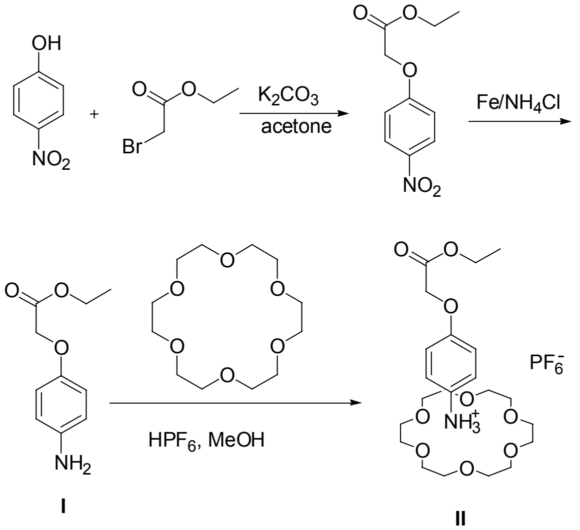
Introduction

Owing to their widespread applications in resonators, filters, and other key components in microwave communication systems, much attention has been devoted to the preparation of suitable materials displaying excellent dielectric constant.[1,2] The temperature-dependent dielectric response, especially in relatively high frequency range, is very useful in searching for phase transitions materials.[3,4] There are only a limited number of materials which approximately meet the stringent dielectric constant requirements. While there have been a variety of studies on pure inorganic compounds,[5,6] examples on supramolecular compounds (which would possess the preponderant properties of both inorganic and organic compounds) as dielectric materials have remained a significant challenge.

Great deals of interest were devoted to crown ethers due to their ability to form non covalent and hydrogen-bonded complexes with ammonium cations. Charge transfer and hydrogen-bonded interactions of crown ethers play an important role in various template, recognition and complexation phenomena in supramolecular chemistry.[7,8] Crown ether's complexation process can accelerate salt solubility and anion reactivity in nonaqueous solvents, enabling their potential application in fields of mediated ion transport, molecular recognition,[9] self-assembly,[10] crystal engineering and anion-activated catalysis.[11] It is therefore vital to design and synthesize novel crown ether complexes and to explore their various properties.

As one part of our continuing studies on crown ethers-based dielectric-ferroelectric materials,[12-16] we report here the synthesis (Scheme 1), structural characterization of the title ammonium compound and its crown ether inclusion complex.

Scheme 1 Synthesis of the compounds **I** and **II**



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Experimental

Materials and instruments

Commercially available reagents were used as received without further purification. Infrared spectra were taken on a Bruker Vector 22 spectrophotometer as KBr pellets in the 4000—400 cm^{-1} region. Elemental analysis (C, N, and H) was performed with a Perkin-Elmer 2400 elemental analyzer. The ^1H NMR spectrum was obtained with a Bruker Am-300 spectrometer operating at 300 MHz using $CDCl_3$ as solvent at room temperature. The crystal structures were determined by a Rigaku SCX mini diffraction meter. Dielectric capacitance and dielectric loss measurements were performed with pure compounds powder using an automatic impedance TongHui2828 Analyzer.

Preparation of substituted benzyl ammonium I

To a solution of 4-nitrophenol (6.95 g, 0.05 mol) in 50 mL of acetone was added potassium carbonate (7.59 g, 0.055 mol). The mixture was refluxed for 30 min with stirring. 8.5 g (0.051 mol) of ethyl 2-bromoacetate and 0.2 g of KI were added and the mixture was refluxed for 10 h. When the reaction finished by TLC monitoring, heating was stopped and the mixture was dumped into the ice water with violent stirring. The mixture was filtered and washed with cold water, dried in air, pale yellow ethyl 2-(4-nitrophenoxy) acetate was obtained. The product was used for next step without further purification.

5.35 g of NH_4Cl was added to the solution of 5.625 g (0.025 mol) of ethyl 2-(4-nitrophenoxy) acetate in 20 mL of 50% ethanol. The mixture was refluxed for 30 min with stirring, then 4.2 g (0.075 mol) of Fe powder was added separately and the mixture was refluxed for another 1 h. The mixture was hot filtered and the filter cake was washed with hot water. Red crystal product of compound **I** was obtained after the filtrate was cooled to room temperature. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.28—1.32 (m, 3H, CH_3), 3.37 (s, 2H, NH_2), 4.23—4.30 (m, 2H, O-CH_2-C), 4.55 (s, 2H, OC-CH_2), 6.64—6.67 (m, 2H, ArH), 6.76—6.80 (m, 2H, ArH); IR v: 3448 (w), 3346 (w), 2978 (w), 2908 (w), 1749 (s), 1626 (s), 1512 (s), 1442 (m), 1384 (m), 1332 (m), 1277 (s), 1217 (m), 1088 (w), 1024 (w), 821 (s), 794 (w), 601 (w) cm^{-1}; ESI-MS *m/z*: 196.40 $[M+H^+]$. Anal. calcd for $C_{10}H_{13}NO_3$: C 61.53, H 6.71, N 7.18; found C 61.49, H 6.76, N 7.15.

Synthesis of the complexes II

Compound **I** (2 mmol, 0.39 g) and 18-crown-6 (2 mmol, 0.528 g) were dissolved in methanol (20 mL), followed by hexafluorophosphate (2 mL). Single crystals of **II** suitable for X-ray diffraction analysis were obtained via slow evaporation from the methanol solution at room temperature over one week. Yield 62% (based on compound **I**). IR v: 3446 (w), 2916 (w), 1753 (m), 1670 (s), 1512 (s), 1452 (w), 1352 (w), 1247 (s), 1103 (m), 962 (m), 840 (s), 617 (w), 557 (w) cm^{-1}. Anal. calcd for $C_{22}H_{38}NO_9PF_6$: C 43.64, H 6.33, N 2.31, F 18.83, P 5.12, O 23.78; found C 43.62, H 6.36, N 2.29.

X-ray crystallography

X-ray diffraction experiment was carried out using a Rigaku SCX mini diffractometer with Mo Kα radiation (λ=0.71073 Å). Resolution of the detector is 13.6612 pixels•mm^{-1}. Data collection, cell refinement and data reduction: CrystalClear 1.4.0.[17] The structure was solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXL97 software package.[18] All non-hydrogen atoms were refined anisotropically, all H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. The crystal data and some details of the structure determination are summarized in Table 1.

Crystallographic data for the structure reported here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-890243, 890244). The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/perl/catreq.cgi (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: 0044-1223-336033; e-mail: deposit@ccdc.cam. ac.uk).

Dielectric constant measurements

Because of the difficulty in obtaining large crystals, the powderpressed pellets of compound **II** were used in dielectric studies of capacitance and dielectric loss factor measurements. The measuring AC voltage was 1 V. The pressed-powder sheet deposited with carbon conducting glue was used for dielectric studies. The samples have been placed inside a dielectric cell whose temperature-dependent dielectric constants were measured.

Results and Discussion

Upon condensation of 4-nitrophenol with ethyl 2-bromoacetate, the use of KI remarkably shortened the reaction time. The ratio of ethanol and water is the critical factor in the reduction reaction of the iron powder, and 50% gives the best result. The infrared spectrum of compound **I** exhibits the characteristic peaks at 3448 and 3346 cm^{-1}, which are assigned to the $v(NH_2)$. Strong peak at 1749 cm^{-1} refers to the $v(C=O)$, weak peaks at 2978 and 2908 cm^{-1} refer to the ethyl in ester group. The ^1H NMR and ESI-MS spectra for the compound **I** are consistent with the theoretical values.

Single crystals of **II** were grown by a standard evaporation method of a mixed solution of ethyl 2-(4-aminophenoxy)acetate, hexafluorophosphate and 18-crown-6 in CH_3OH at room temperature. In the infrared spectrum of compound **II**, characteristic peak of hexafluorophosphate appears at 840 cm^{-1}.

Table 1 Summary of crystallographic data for compounds **I** and **II**

	I	**II**
Molecular formula	$C_{10}H_{13}NO_3$	$C_{22}H_{38}NO_9PF_6$
Formular weigh	195.21	605.5
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/c$
Temperature/K	298	170(2)
a/Å	8.3456(17)	12.540(8)
b/Å	10.630(2)	14.585(8)
c/Å	11.977(2)	16.573(9)
α/(°)	101.13(3)	90.00
β/(°)	91.88(3)	108.100(12)
γ/(°)	104.20(3)	90.00
V/Å^3	1007.1(3)	2881(3)
Z	4	4
Calculated density/(Mg•m^{-3})	1.288	1.396
F(000)	416	1272
Crystal size/mm	0.37×0.32×0.24	0.33×0.24×0.20
h, *k*, *l* (min, max)	(−10, 10); (−13, 13); (−15, 15)	(−16, 16); (−18, 18); (−18, 18)
Completeness	99.4% (to è=27.48°)	99.7% (to è=27.44°)
GOF on F^2	1.008	1.096
Final *R* indices $[I>2\sigma(I)]^a$	$R_1=0.0612$, $wR_2=0.1413$	$R_1=0.0812$, $wR_2=0.2112$
R indices (all data)^a	$R_1=0.1377$, $wR_2=0.1732$	$R_1=0.1009$, $wR_2=0.2312$
Largest diff. peak and hole/(e•Å^{-3})	0.163 and −0.164	1.026 and −0.919

^{a} $R_1=\Sigma|F_o|-|F_c||/\Sigma F_o|$; $wR_2=\{\Sigma w(F_o^2-F_c^2)^2\}/\Sigma w(F_o^2)\}\}^{1/2}$.

As shown in Figure 1, compound **I** is composed of two same molecules (a and b) in each asymmetric unit. Nearly all the atoms of each molecule are in the same plane except H atoms. The mean deviation to the least square plane of molecular a is 0.0407 and 0.0655 Å of molecular b. The two molecules are almost coplanar with dihedral angles of 5.9°. Intramolecular and intermolecular N—H···O hydrogen bonds lead to the formation of one dimensional chain (Figure 2).

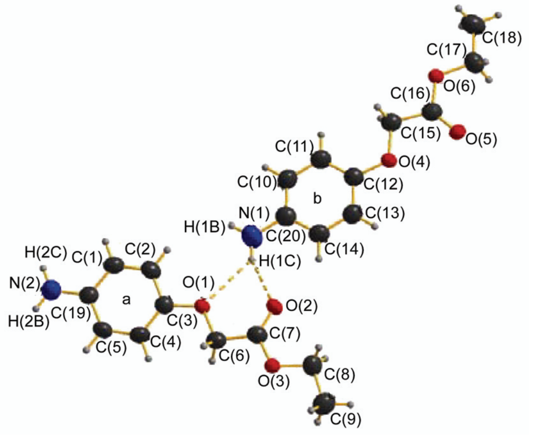

Figure 1 Asymmetric unit for compound **I**.

The asymmetric unit of compound **II** contains one substituted benzyl ammonium cation, one 18-crown-6 ether molecule and one PF_6^- anion (Figure 3). Atom F(3) shows somewhat disorder. The ether O atoms are nearly coplanar: O(4), O(6) and O(8) are located above the mean O-atom plane and O(3), O(5) and O(7) atoms below the plane. Supramolecular rotators were assembled between protonated aromatic amines $(C_{10}H_{14}O_3N)^+$ and 18-crown-6 via hydrogen-bonding interaction. The $—NH_3^+$ moiety interacts with the six oxygen atoms of crown ethers by six N—H···O hydrogen bonds (Table 2). The distances between the N atom and the three O atoms above the mean O-atom plane in the crown ether are short [2.843(3), 2.826(3), and 2.895(3) Å from

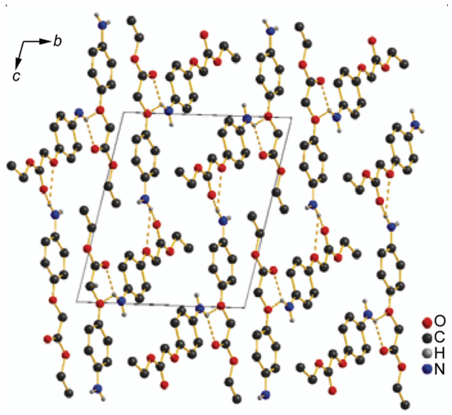

Figure 2 Packing diagram for compound **I**, viewing along *a* axis.

Table 2 Hydrogen bonded geometry, distances (Å) and angles (°) in compounds **I** and **II**

	D—H···A	*d*(D—H)	*d*(H···A)	*d*(D···A)	*θ*(D—H···A)
I	N(2)—H(2C)···O(4)#1	0.86	2.63	3.321(3)	138.3
	N(2)—H(2C)···O(5)#1	0.86	2.33	3.125(3)	153.1
	N(1)—H(1C)···O(1)	0.86	2.61	3.295(3)	136.9
	N(1)—H(1C)···O(2)	0.86	2.41	3.170(3)	147.2
II	N(1)—H(1A)···O(3)	0.89	2.34	2.995(4)	130.7
	N(1)—H(1B)···O(4)	0.89	2.01	2.843(3)	154.9
	N(1)—H(1B)···O(5)	0.89	2.42	3.024(3)	125.1
	N(1)—H(1C)···O(6)	0.89	2.01	2.826(4)	152.2
	N(1)—H(1C)···O(7)	0.89	2.35	2.939(3)	123.7
	N(1)—H(1A)···O(8)	0.89	2.08	2.895(3)	151.4

Symmetry code: #1: $x+1, y, z-1$.

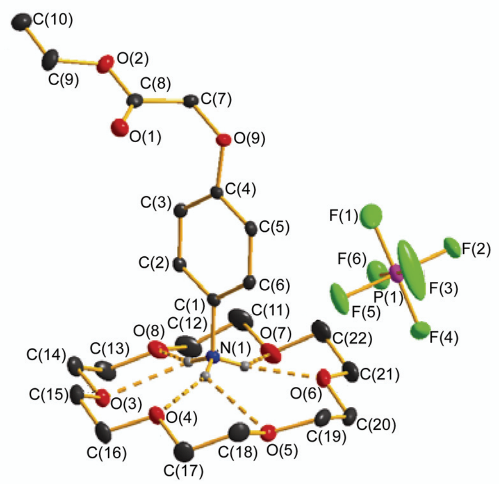

Figure 3 The interactions between the title ammonium compound and a crown ether molecule in compound **II**. Dashed lines indicate hydrogen bonds.

N(1) to O(4), O(6) and O(8), respectively], indicating strong dipolar attractions. Comparatively below the mean O-atom plane the distances are longer [2.995(4), 3.024(3), 2.939(3) Å from N(1) to O(3), O(5) and O(7), respectively]. The C—N bonds of the aromatic amines cation are almost perpendicular to the mean plane of the crown-ether O atoms. Atom N(1) of the aromatic amines cation is 0.8405(25) Å out of the plane. The long tail of the benzyl ammonium, unlike co-planer molecular of compound **I**, was bending along co-planer of O atoms from crown ether.

The PF_6^- anions are present as counter-ions to the supramolecular $[(C_{10}H_{14}O_3N\bullet(18\text{-crown-6}))]^+$. The P—F bond lengths range from 1.544(3) Å to 1.605(2) Å. The adjacent F-P-F bond angles range from 86.84(19)° to 95.7(3)° (Table 3). Owing to the obvious differences of the P—F distances and the F-P-F angles, the geometry of the anion could be regarded as a distorted octahedral (Figure 4).

Table 3 Selected distances (Å) and angles (°) for compounds **I** and **II**

I		**II**	
O(1)—C(3)	1.381(3)	P(1)—F(3)	1.544(3)
O(1)—C(6)	1.410(3)	P(1)—F(4)	1.569(3)
O(3)—C(7)	1.324(3)	P(1)—F(1)	1.574(3)
O(3)—C(8)	1.448(3)	P(1)—F(6)	1.585(3)
O(4)—C(12)	1.381(3)	P(1)—F(2)	1.595(2)
O(4)—C(15)	1.411(3)	P(1)—F(5)	1.605(2)
O(6)—C(16)	1.334(3)	O(9)—C(4)	1.374(3)
O(6)—C(17)	1.448(3)	O(9)—C(7)	1.425(3)
O(5)—C(16)	1.200(3)	O(1)—C(8)	1.200(4)
C(7)—O(2)	1.192(3)	O(2)—C(8)	1.332(4)
C(19)—N(2)	1.388(3)	O(2)—C(9)	1.479(4)
N(1)—C(20)	1.399(3)	O(3)—C(15)	1.416(4)
C(14)—C(20)	1.383(3)	O(6)—C(21)	1.442(5)
C(3)-O(1)-C(6)	117.76(17)	F(4)-P(1)-F(6)	86.84(19)
C(7)-O(3)-C(8)	116.30(19)	F(3)-P(1)-F(1)	88.5(3)
C(12)-O(4)-C(15)	117.44(18)	F(6)-P(1)-F(2)	91.27(14)
C(16)-O(6)-C(17)	115.69(19)	F(3)-P(1)-F(4)	95.7(3)
C(3)-C(2)-C(1)	121.0(2)	O(9)-C(7)-C(8)	111.9(2)
C(2)-C(3)-O(1)	115.3(2)	C(4)-O(9)-C(7)	117.8(2)
O(1)-C(3)-C(4)	125.5(2)	C(8)-O(2)-C(9)	114.2(3)
O(5)-C(16)-C(15)	126.1(2)	C(16)-O(4)-C(17)	111.1(3)
O(6)-C(16)-C(15)	109.7(2)	C(12)-O(8)-C(13)	113.1(3)
O(1)-C(6)-C(7)	107.60(18)	O(5)-C(18)-C(17)	108.4(3)
O(4)-C(12)-C(13)	115.4(2)	O(4)-C(16)-C(15)	109.7(3)
O(4)-C(12)-C(11)	125.7(2)	O(7)-C(22)-C(21)	108.1(3)

It is known that thermally actived molecular rotations can arise striking dielectric response. Temperature-

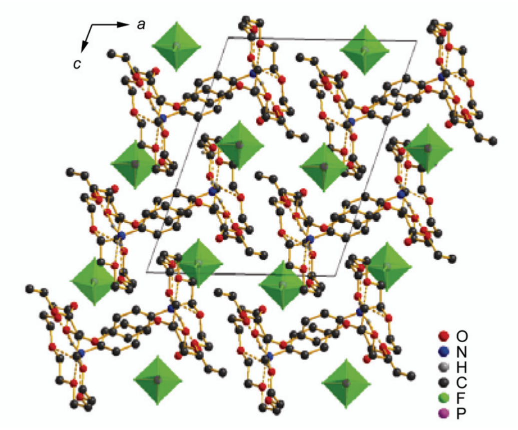

Figure 4 Packing diagram in the *ac* plane for compound **II**.

dependent dielectric constant of compound **II** was tested to systematically investigate the possibility of ferroelectric phase transitions. As shown in Figure 5, the real part (ε_1) of dielectric constant of compound **II** at a frequency of 1 MHz indicates that ε_1 remains small change; it increases smoothly from 1.5 to 3.5 within the measured temperature range, together with the dielectric loss ($\varepsilon_2/\varepsilon_1$) behavior. No evident heat hysteresis phenomenon (dielectric anomaly) occurred in the dielectric measurements on heating and cooling processes, suggesting that no distinct phase transition occurred within the measured temperature range for compound **II** at 1 MHz. Such a feature would probably because of the large molecule rotating slowly with electric field in low temperature. This case is similar to that found in 1∶1 complexes of 18-crown-6 with 4-methoxyanilinium hexafluorophosphate.[16] Further studies on these features are underway.

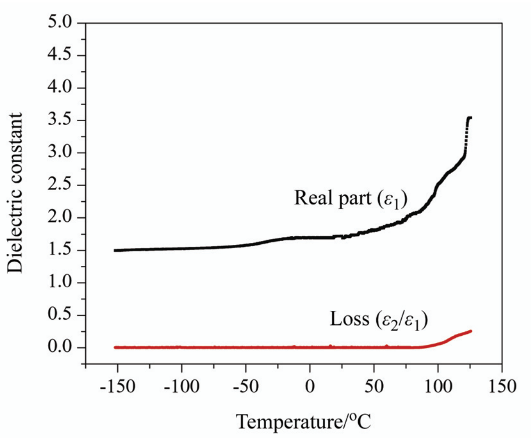

Figure 5 Temperature dependence of the dielectric constant.

Conclusions

The title ammonium compound ethyl 2-(4-aminophenoxy)acetate and its crown ether-based supramolecular structures have been synthesized successfully, by introducing the organic ammonium and 18-crown-6 as the combination of cation. This approach allows us to modulate the assembled molecule structures, and thus to obtain many useful properties. Temperature-dependent dielectric constants of compound **II** were also tested, suggesting no phase transition during the measured temperature range, probably because the molecular rotation is frozen at the temperature.

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