

Supramolecular assembly and host–guest interaction of crown ether with inorganic acid and organic amine containing carboxyl groups†

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Four rotator–stator assembly complexes: benzoic-4-methylammonium-tetrafluoroborate-15-crown-5 ($[\text{C}_8\text{H}_{10}\text{NO}_2\text{-(15-crown-5)}]^+[\text{BF}_4]^-$, **1**); benzoic-4-methylammonium-perchlorate-15-crown-5 ($[\text{C}_8\text{H}_{10}\text{NO}_2\text{-(15-crown-5)}]^+[\text{ClO}_4]^-$, **2**); benzoic-4-methylammonium-tetrafluoroborate-18-crown-6 ($[\text{C}_8\text{H}_{10}\text{NO}_2\text{-(18-crown-6)}]^+[\text{BF}_4]^-$, **3**); benzoic-*m*-ammonium-tetrafluoroborate-18-crown-6 ($[\text{C}_7\text{H}_8\text{NO}_2\text{-(18-crown-6)}]^+[\text{BF}_4]^-$, **4**), for the investigation of the supramolecular assembly and host–guest interaction of crown ethers, have been synthesized and characterized. The results revealed that the variation of crown ethers, the substituent position of carboxyl group, as well as the different kinds of inorganic anions all can lead to quite another geometry and directionality of both the anilinium rotors and crown ether stators, which lead to entirely different supramolecular architectures. It is interesting that the optimal distances from the mean O-plane where found for the 18-crown-6 macrocycle with the ammonium cation, and the conformation of the macrocycle was badly affected in complexes with shorter or longer distances. We also studied the Raman spectroscopy of the five complexes, which give further inspection of the intermolecular interactions.

Introduction

As one of the well-known symbols in supramolecular chemistry, crown ethers have been the subject of various studies in supramolecular chemistry and crystal engineering in recent years,^{1–6} especially for the investigation of host–guest interactions in the construction of supramolecular architectures.^{7–9} In these, crown ethers acted as macrocyclic hosts, serving as building blocks to create a variety of molecularly assembled architectures with complementary guest molecules. The assembled architectures were constructed by multiple noncovalent interactions, such as hydrogen bonding, $\pi \cdots \pi$ stacking, charge transfer, and hydrophobic interactions between two complementary compounds, which leads not only to good binding affinity, but also to the formation of complexes with a fixed host–guest geometry and directionality.¹⁰

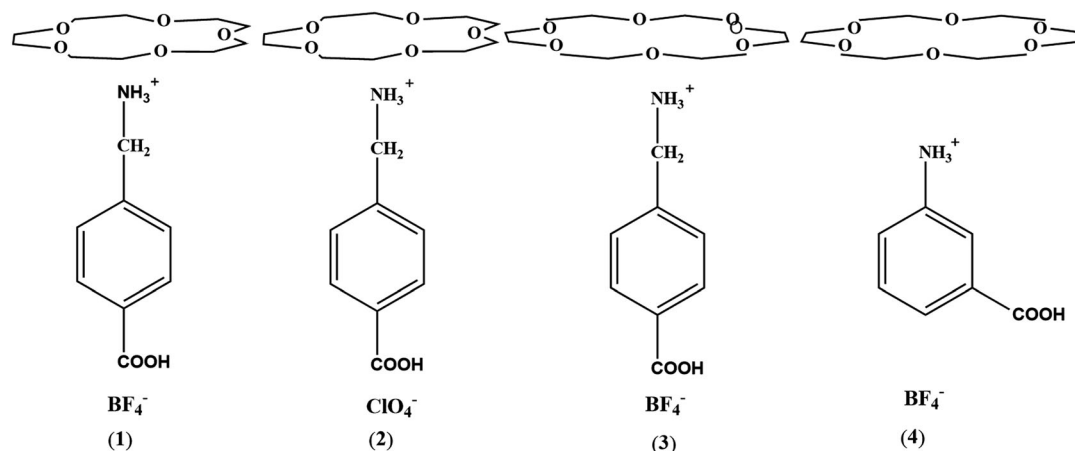
Crown ethers also have been used to construct stable complexes with alkali and transition-metal ions and hydrogenate cations *via* hydrogen bonds, which act as ideal candidates for the formation of molecular stators for the design of phase change materials and ferroelectric molecular materials.^{11,12} To date, numerous derivatives and complexes based on crown ethers have been synthesized and

characterized.^{13–16} For example, Luo¹⁶ and his co-workers utilized dichloroacetate as the pendulum-like motions combined with the 18-crown-6 molecular rotor, which formed a novel supra-molecular potassium hydrogen bis(dichloroacetate)-18-crown-6 displaying a reversible phase transition. Xiong¹⁷ and his co-workers have introduced 4-methoxyanilinium into the cavity of 18-crown-6 and obtained a novel supra-molecular bola-like second-order ferroelectric phase-transition material. In the field of molecular machine design, the crown ethers often act as good molecular stators which can easily anchor the protonated R-NH_3^+ cation (R = aryl ring) into the cavity of crown ethers, and the utilization of the R group as a molecular rotor or pendulum unit to create desirable properties has also been investigated.¹⁷ However, the influence of R group containing carboxyl groups on the supra-molecular assembly behaviour of host–guest geometry and the directionality of crown ethers still remains unexplored.

Hence, in this work, we studied detailed the influences of R group containing carboxyl groups on the supra-molecular assembly behaviour of crown ethers, and we obtained four supra-molecular architectures (Scheme 1): benzoic-4-methylammonium-tetrafluoroborate-15-crown-5 ($[\text{C}_8\text{H}_{10}\text{NO}_2\text{-(15-crown-5)}]^+[\text{BF}_4]^-$, **1**); benzoic-4-methylammonium-perchlorate-15-crown-5 ($[\text{C}_8\text{H}_{10}\text{NO}_2\text{-(15-crown-5)}]^+[\text{ClO}_4]^-$, **2**); benzoic-4-methylammonium-tetrafluoroborate-18-crown-6 ($[\text{C}_8\text{H}_{10}\text{NO}_2\text{-(18-crown-6)}]^+[\text{BF}_4]^-$, **3**); benzoic-*m*-ammonium-tetrafluoroborate-18-crown-6 ($[\text{C}_7\text{H}_8\text{NO}_2\text{-(18-crown-6)}]^+[\text{BF}_4]^-$, **4**). We found that the variation of the crown ethers as well as the substituent position of

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Scheme 1 Molecular structure of complexes 1–4.

the carboxyl group leads to quite another geometry and directionality of the anilinium rotors, which resulted in entirely different supramolecular architectures. We also studied the Raman spectroscopy of the four complexes, which provided supporting evidence for the conclusions. These results are of importance not only for the evaluation of the specific case of these crown ethers' systems, but also for other host–guest systems where fascinating structures and properties are possible. The influence of the R group containing carboxyl groups on the dielectric properties will be investigated in the future.

Results and discussion

Supramolecular assembly of 4-aminomethyl benzoic acid with 15-crown-5 and 18-crown-6

Complexes 1 (benzoic-4-methylammonium-tetrafluoroborate-15-crown-5), 2 (benzoic-4-methylammonium-perchlorate-15-crown-5)

and 3 (benzoic-4-methylammonium-tetrafluoroborate-18-crown-6) were selected in this section. The only difference between 1 and 2 is in the lattice inorganic anions (Fig. 1). Crystal structural determinations revealed that 1 and 2 were all crystallized in the monoclinic $P2_1/n$ space group, the basic unit of 1 was composed of one $[C_8H_{10}NO_2-15\text{-crown-5}]^+$ complex cation and one BF_4^- anion, and the basic unit of 2 is similar to 1 with a ClO_4^- anion instead of a BF_4^- anion. For complex 1, the protonated benzoic-4-methylammonium cation joins with one 15-crown-5 molecule to form a rotator–stator assembly through four $N-H\cdots O$ hydrogen-bonding interactions (distances are within the common range of 3.015 (7) and 2.913 (7) Å, Table 1). It is interesting that the 15-crown-5 macrocycle in complex 1 showed nearly “chair like” conformations with O1, O2, O4, and O5 forming a mean O-atom plane, (O1 and O4 atoms are located above the mean O-atom plane with distances

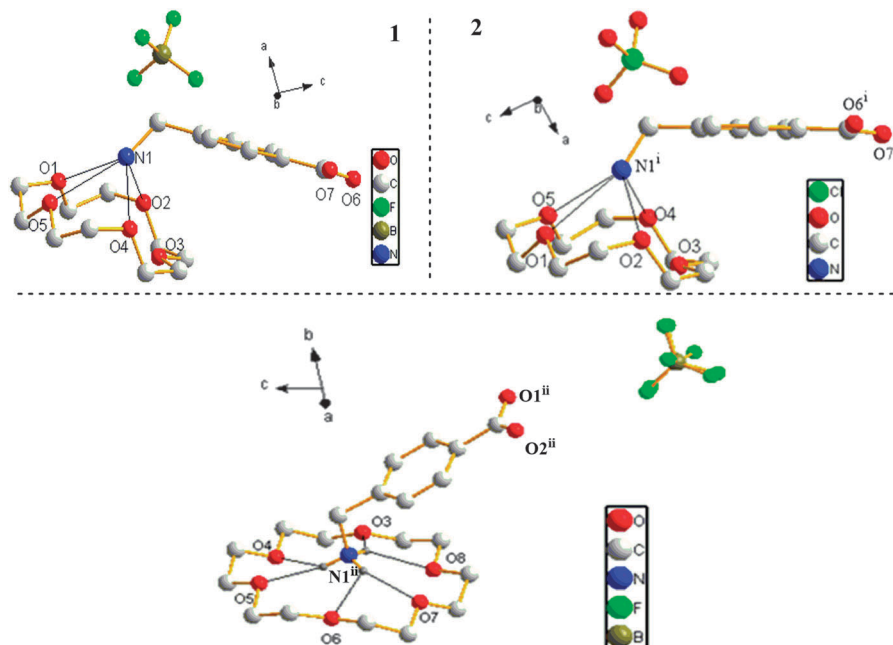


Fig. 1 The basic unit of complexes 1–3, hydrogen atoms were omitted for clarity ((i) $-1/2 + x, 1/2 - y, -1/2 + z$; (ii) $x, -y, -1/2 + z$).

Table 1 Geometrical parameters for hydrogen bonds in complexes 1–4

Complex	D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	∠ D–H...A (deg)	Symmetry operation
1	N1–H1C...O3	0.89	2.27	3.097(7)	154	–x + 1, –y + 1, –z + 1
	N1–H1C...O2	0.89	2.34	3.015(7)	132	
	N1–H1D...O6	0.89	2.30	2.997(7)	135	
	N1–H1D...O1	0.89	2.28	2.913(7)	128	
	N1–H1E...O4	0.89	2.29	2.934(8)	129	x + 1/2, –y + 3/2, z – 1/2
	N1–H1E...F3	0.89	2.27	2.924(8)	130	
2	O6–H6C...O11	0.82	2.08	2.903(9)	179	–x + 1, –y + 1, –z + 1
	N1–H1C...O3	0.89	2.19	3.074(6)	173	x + 1/2, –y + 1/2, z + 1/2
	N1–H1D...O5	0.89	2.13	2.936(8)	150	x + 1/2, –y + 1/2, z + 1/2
	N1–H1E...O9	0.89	2.26	3.061(11)	149	
3	N1–H1A...O3	0.89	2.02	2.866(7)	159	x, –y, z + 1/2
	N1–H1A...O8	0.89	2.36	2.927(7)	122	x, –y, z + 1/2
	N1–H1B...O5	0.89	2.11	2.898(7)	148	x, –y, z + 1/2
	N1–H1C...O7	0.89	2.02	2.896(9)	168	x, –y, z + 1/2
4	O2–H2...O1	0.82	1.88	2.675(6)	165	–x, –y + 1, –z + 1
	N1–H2A...O3	0.89	2.07	2.952(6)	173	–x + 1, –y + 1, –z + 1
	N1–H2B...O7	0.89	2.03	2.909(7)	169	–x + 1, –y + 1, –z + 1
	N1–H2C...O5	0.89	2.00	2.885(7)	176	–x + 1, –y + 1, –z + 1

0.062 (7) and 0.0379 (7) Å, while O2 and O5 atoms are below the plane with distances 0.0371 (7) and 0.0628 (7) Å, respectively), and the O3 atom was located 0.9848 (7) Å lower than the plane (Fig. 1). The N1 atom of the benzoic-4-methylammonium cation is in the perching position, lying 1.6052 (10) Å higher than the best plane of the oxygen atoms of the crown ring, rather than in the nesting position. The torsion angle between the aminomethyl group and the normal to the best plane is 165.02 (6)°. For complex 2, the deviations of the oxygen atoms were found to be 0.0669 (5) and 0.0385 (5) Å above the mean O-atom plane for O1 and O4 atoms, while the O2 and O5 atoms were 0.0396 (5) and 0.0659 (5) Å below the mean O-atom plane, respectively (Table 2). These deviations were larger than in 1, while the O3 atom was located 0.9819 (5) Å lower than the plane, a distances that is shorter than in 1. The N1 atom of the benzoic-4-methylammonium cation lies 1.600 (10) Å higher than the best plane of the oxygen atoms, and the torsion angle between the aminomethyl group and the normal to the best plane is 112.93 (10)°, which was also much smaller than that in 1. From these results we can conclude that the ClO₄[–] anion leads to more distortion of the crown macrocycle and the ammonium cation than the BF₄[–] anion due to its larger steric effect, and this conclusion was in accordance with the lattice volume: the volume of 1 and 2 were found to be 2242.3 (8) and 2287.7 (8) Å³, respectively.

Complex 3 crystallizes in the monoclinic *C2/c* space group; the basic unit is composed of one [C₈H₁₀NO₂-18-crown-6]⁺

complex cation, one BF₄[–] anion, and one water molecule (Fig. 1). The protonated benzoic-4-methylammonium cation joins with one 18-crown-6 molecule to form a rotator-stator assembly through six N–H...O hydrogen-bonding interactions (distances are within the common range of 2.950 (9) and 2.866 (7) Å, which are shorter than those in 1 and 2, Table 1). The symmetry of the 18-crown-6 in 3 was found to be nearly an ideal crown “round” “D_{3d} like” conformation, where oxygen atoms of the 18-crown-6 in the structure are, as a rule, displaced alternately above and below the median plane of the ring, forming two approximately parallel and nearly equilateral triangles, with O3, O5, and O8 atoms are located below the mean O-atom plane (0.2143 (9), 0.2106 (9), and 0.1217 (9) Å, respectively), and O4, O6, and O8 atoms above the plane (0.2459 (9), 0.1470 (9) and 0.1537 (9) Å, respectively). The N1 atom of the benzoic-4-methylammonium cation lies 1.1442 (10) Å higher than the best plane of the oxygen atoms of the crown ring, which is much shorter than that for 15-crown-5. The torsion angle between the aminomethyl group and the normal to the best plane is 144.94 (8)°.

Shown in Fig. 2 are the connecting and stacking motif of complexes 1 and 2. The adjacent complex cations in 1 were connected with each other through N–H...O hydrogen-bonding interactions (distances of 2.997 (7) Å) into infinite 1D chain structure in ...ABAB... fashion) and the BF₄[–] anions were distributed in the two sides of the chain (Fig. 2a and b).

Table 2 Summary of the deviations (Å) of oxygen atoms from the median O-plane of 18-crown-6 in complexes 1–4 and the distances (Å) of N atoms from the median O-plane

Complex	Deviations above		Deviations below		Average	Distances
1	0.062(7)	0.0379(7)	0.0371(7)	0.0628(7)	0.1974(7)	1.6052(7)
2	0.0669(5)	0.0385(5)	0.0396(5)	0.0659(5)	0.1988(5)	1.6(5)
3	0.2143(9)	0.2106(9)	0.1217(9)	0.2459(9)	0.1537(9)	1.1442(9)
4	0.5803(6)	0.504(6)	0.0532(6)	0.4834(6)	0.0237(6)	0.5714(6)

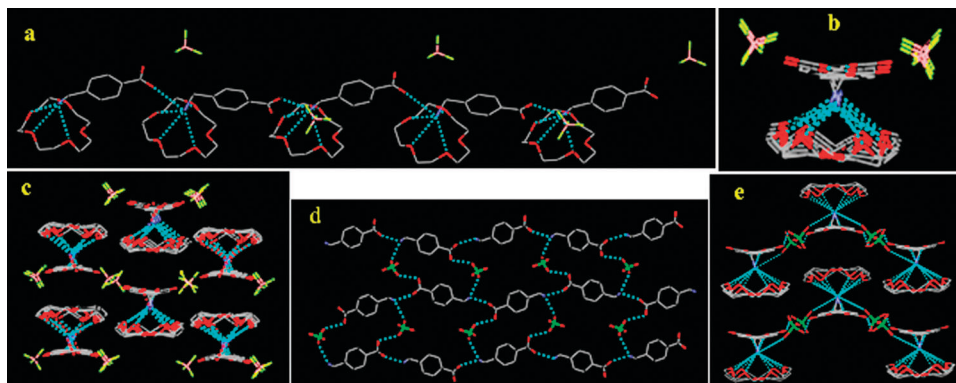


Fig. 2 Connecting and stacking motif of complexes **1** and **2**; hydrogen atoms were omitted for clarity and hydrogen bonds were shown in dashed lines. (a) 1D chain connecting motif of **1**; (b) diagram of 1D chain viewed from one end; (c) 3D stacking motif of **1**; (d) 2D wave plane of complex **2**; (e) 3D stacking motif of **2**.

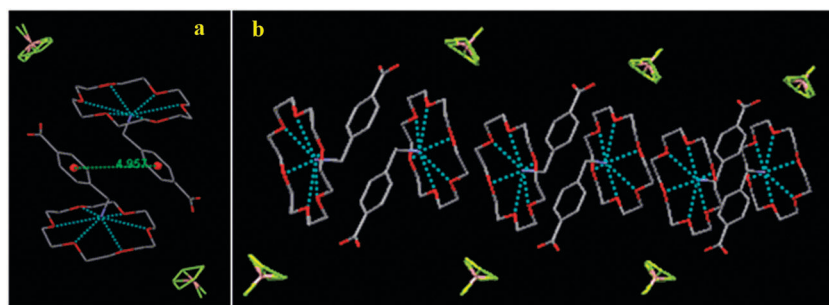


Fig. 3 (a) Packing motif of the double-component unit of **3**, the plane separation is highlighted; (b) 1D stacking motif of the double-component units.

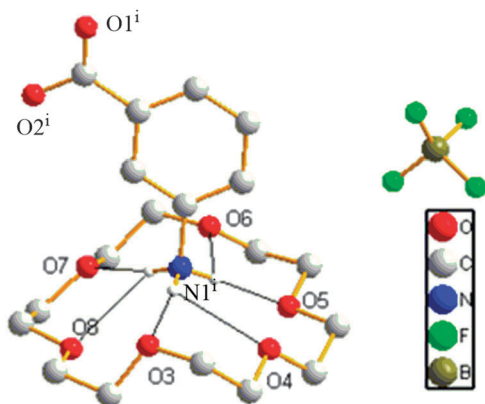


Fig. 4 The basic unit of complex **4**, hydrogen atoms was omitted for clarity ((i) $1 - x$, $1 - y$, $1 - z$).

The different 1D chains then further stack with each other into a 3D motif (Fig. 2c). For complex **2**, the primary 1D motif was identical to **1** (Fig. S1, ESI[†]). It is interesting that the benzoic-4-methylammonium cations and ClO_4^- anions constructed a 2D wave plane *via* an $R_4^2(26)$ and $R_4^2(38)$ motif (Fig. 2d), and the 15-crown-5 macrocycles hang on the two sides of the wave plane, then the 2D structures interact with each other *via* the macrocycles into a 3D motif (Fig. 2e).

For complex **3**, the primary structure is double-components of the basic unit, which was packed *via* $\pi \cdots \pi$ interactions

(distances of 4.957 (6) Å) in a $\cdots \text{A-A} \cdots$ fashion, with the BF_4^- anions located in the upper left and lower right positions (Fig. 3a). The different double-component units then stacked parallel into a 1D motif with a distance of 4.957 (5) Å between adjacent 18-crown-6 macrocycles (Fig. 3b). The different 1D motif further stacked in parallel into a 3D structure (Fig. S2, ESI[†]).

Supramolecular assembly of *m*-aminobenzoic acid with 18-crown-6

m-Aminobenzoic acid was selected for the investigation of the influence of the substituent-position of the carboxyl group on the supramolecular assembly fashion of the crown ether complex. Crystal structural determinations reveal that complexes **4** (benzoic-*m*-ammonium-tetrafluoroborate-18-crown-6) crystallize in a triclinic $P\bar{1}$ space group, the basic unit is composed of one $[\text{C}_7\text{H}_8\text{NO}_2\text{-18-crown-6}]^+$ complex cation and one BF_4^- anion (Fig. 4). In the complex cation, the protonated benzoic-*m*-ammonium cation joins with one 18-crown-6 molecule to form a rotator-stator assembly *via* six $\text{N-H} \cdots \text{O}$ hydrogen-bonding interactions (distances are within the common range of 3.003 (6) and 2.856 (7) Å, Table 1). It is interesting that the 18-crown-6 stator in **4** demonstrates a “boat” rather than “ D_{3d} like” conformation, with O3 and O6 atoms located on both ends of the “boat” and deviate 0.5803 (6) and 0.5040 (6) Å above the mean O-atom plane of 18-crown-6, respectively, while the O4, O5, O7 and O8 atoms are located on the bottom of the “boat” and

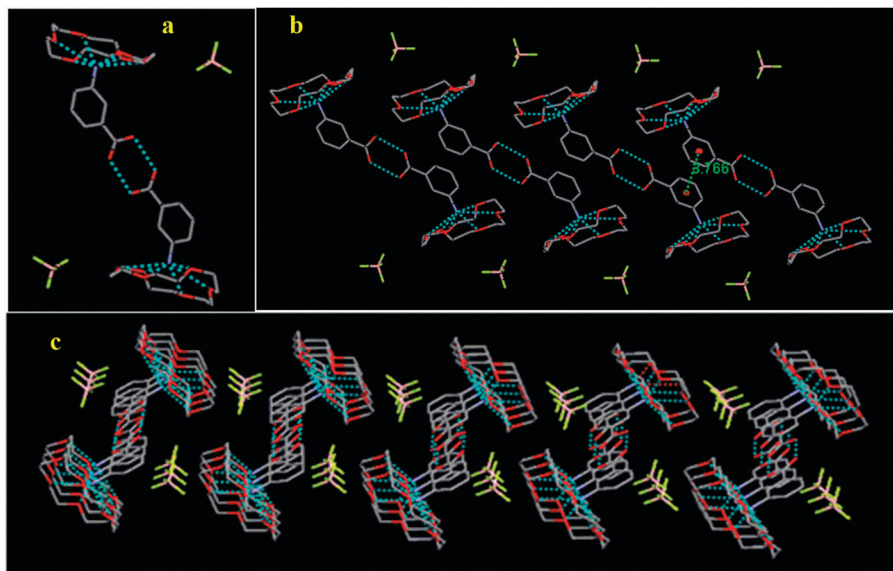


Fig. 5 Connecting and stacking motif of complex **4**, hydrogen atoms were omitted for clarity and hydrogen bonds were shown in dashed lines. (a) Connecting motif of the dimer unit of **4**; (b) 1D packing motif of **4**, $\pi \cdots \pi$ interactions were highlighted; (c) 3D stacking motif of **4**.

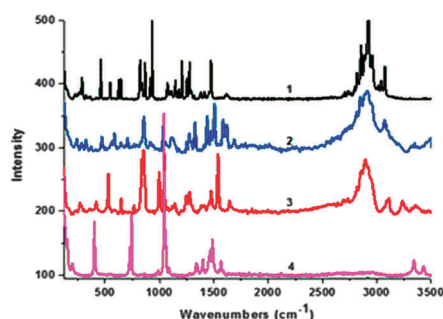


Fig. 6 Raman spectroscopy of complexes **1–4**.

deviate 0.0532 (6), 0.4834 (6), 0.0237 (6) and 0.5714 (6) Å below the mean O-atom plane, respectively. The distances of the oxygen atoms above and below the median O-plane of the three complexes are summarized in Table 2. The N1 atom of the benzoic-*m*-ammonium cation lies 0.9957 (9) Å from the best plane of the oxygen atoms of the crown ring, which is much shorter than the same distance in **1–3** (Table 2). The benzene ring is almost vertical to the median O-plane with dihedral angle of 77.26 (10)°.

The complex cation in **4** formed a dimer unit *via* O–H \cdots O hydrogen-bonding interactions (distances of 2.675 (6) Å) between the adjacent carboxyl group (Fig. 5a), then the different dimer units packed by $\pi \cdots \pi$ interactions between two of the

Table 3 Crystal data and structure refinement for complexes **1–4**

Complex	1	2	3	4
Formula	C ₁₈ H ₃₀ BF ₄ NO ₇	C ₁₈ H ₃₀ ClNO ₁₁	C ₂₀ H ₃₄ BF ₄ NO ₈	C ₁₉ H ₃₂ BF ₄ NO ₈
Formula weight	459.24	471.88	503.29	489.27
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.5060(19)	9.5970(19)	23.270(5)	9.3105(19)
<i>b</i> /Å	15.001(3)	15.241(3)	12.926(3)	10.982(2)
<i>c</i> /Å	15.777(3)	15.677(3)	19.947(4)	11.809(2)
α /°	90.00	90.00	90.00	82.80(3)
β /°	94.68(3)	93.90(3)	117.76(3)	89.03(3)
γ /°	90.00	90.00	90.00	85.61(3)
<i>V</i> /Å ³	2242.3(8)	2287.7(8)	5309(2)	1194.4(4)
<i>Z</i>	4	4	8	2
<i>D</i> calc. (Mg m ^{−3})	1.360	1.370	1.304	1.360
<i>T</i> /K	293(2)	293(2)	293(2)	293(2)
μ (mm ^{−1})	0.122	0.224	0.117	0.122
Cryst. dimensions	0.3 × 0.2 × 0.1	0.3 × 0.2 × 0.1	0.2 × 0.1 × 0.1	0.2 × 0.2 × 0.2
No. of reflns collected	4112	4212	4882	5434
No. of unique reflns	1646	2129	1922	1621
No. of params	260	281	357	300
Goodness-of-fit on <i>F</i> ²	1.025	1.075	1.020	0.942
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0847, 0.1971	0.0948, 0.2520	0.0789, 0.1651	0.1125, 0.2889
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1399, 0.1500	0.1670, 0.3016	0.1678, 0.2047	0.2934, 0.3904
CCDC no.	946942	946943	946956	946959

benzene rings in adjacent dimer units (distance of 3.766 (9) Å) into a 1D structure along *b* axis (Fig. 5b). The different 1D structures further stacked into a 3D motif (Fig. 5c).

Table 2 summarizes the distances that the oxygen atoms deviate from the median O-plane of the crown ether (15-crown-5 and 18-crown-6) and the distances of the N1 atoms from the median O-plane for complexes 1–4. From the comparison between the average value of the deviation and the distances of N1 atoms from the median O-plane, we may conclude that the anilinium showed closer interaction with 18-crown-6 than with 15-crown-5, and the distances of N1 atoms from the median O-plane of 18-crown-6 showed an optimum value of around 1.14 (9) Å, with which, the 18-crown-6 macrocycle displays minimum distortion. Distances shorter or longer than this value all lead to more distortion of the 18-crown-6 macrocycle. These results were in accordance with the distances of the hydrogen bonds in Table 1.

Raman spectroscopy of the complexes 1–4

Fig. 6 shows the Raman spectroscopy of complexes 1–4 in the region of 3500–50 cm^{−1}. The region around 2900 cm^{−1} may be attributed to the nearly ideal crown “round” “D_{3d} like” conformations of the crown ether macrocycles, and this was absent for the Raman spectroscopy of 4 due to the “boat” conformation of the 18-crown-6 macrocycle in it. The region between 1500–50 cm^{−1} can be attributed to the organic anilinium and inorganic anions, and there were no visible differences between the complexes 1–3 within this region.

Conclusions

In conclusion, the influences of different kinds of crown ethers, the substituent position of carboxyl group, and different kinds of inorganic anions on the supramolecular assembly and host–guest interaction of crown ethers rotator–stator complexes have been investigated detailed. The host–guest interaction of 15-crown-5 with 4-methylamino benzoic acid resulted in a 1D chain *via* N–H...O hydrogen-bonding interactions, while 18-crown-6 with 4-methylamino benzoic acid packed by $\pi\cdots\pi$ intermolecular interactions. The *meta*-position of the carboxyl group (*m*-amino benzoic acid) leads to dimer units *via* O–H...O hydrogen-bonding interactions and a “boat” conformation of 18-crown-6 rather than “D_{3d} like” conformation as seen with 4-methylamino benzoic acid. It is interesting that the optimal distances from the mean O-plane were found for the 18-crown-6 macrocycle with the ammonium cation, and the conformation of the macrocycle was badly affected in complexes with shorter or longer distances. This was confirmed by the Raman spectroscopy. These results are important not only for the evaluation of the specific case of this work, but also for other host–guest systems with crown ethers.

Experimental

Materials and physical measurements

18-Crown-6, 4-methylamino benzoic acid, *m*-amino benzoic acid, HClO₄, and HBF₄ were all commercially available from

Sigma Aldrich and used as received without further purification. Methanol was commercially available from Sinopharm Chemical Reagent Co., Ltd and used as received without further purification. Elemental analyses were performed using a Vario-EL III elemental analyzer for carbon, hydrogen, and nitrogen of the complexes 1–4. Raman spectra were recorded using a Raman microscope (Kaiser Optical Systems, Inc., Ann Arbor, MI, USA) with 785 nm laser excitation. The spectra were obtained for one 2 min exposure of the CCD detector in the wavenumber range 50–3500 cm^{−1}.

Preparation of the complexes

The preparation of complexes 1–4 was performed using a slow evaporation technique; a 35 mL methanol–water (2 : 1 v/v) system was used. They were all obtained from a methanol–water solvent system using 1 : 1 : 1 stoichiometric mixtures of 18-crown-6, organic amines and inorganic acids. Complex 1, elemental analysis anal. calcd (%): C, 47.03; N, 3.05; H, 6.53. Found: C, 48.30; N, 3.48; H, 7.01. Complex 2, elemental analysis anal. calcd (%): C, 45.77; N, 2.97; H, 6.36. Found: C, 44.68; N, 2.31; H, 6.76. Complex 3, elemental analysis anal. calcd (%): C, 46.04; N, 2.68; H, 6.91. Found: C, 45.07; N, 2.45; H, 7.15. Complex 4, elemental analysis anal. calcd (%): C, 46.60; N, 2.86; H, 6.54. Found: C, 47.07; N, 2.25; H, 6.15.

X-ray crystallographic study

The single-crystal X-ray diffraction data of the complexes 1–4 were collected at 293 K with graphite-monochromated Mo-K α radiation (λ = 0.071073 nm) equipped with Rigaku SCXmini diffractometer.¹⁸ The lattice parameters were integrated using vector analysis and refined from the diffraction matrix. The absorption correction was carried out using a Bruker SADABS program with a multi-scan method.¹⁹ The crystallographic data, data collection, and refinement parameters for complexes 1–4 were given in Table 3. The structures were solved by a full-matrix least-squares methods on all *F*² data, and the SHELXS-97 and SHELXL-97 programs²⁰ were used for structure solution and refinement respectively. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were geometrically fixed.

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