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Short communication

Inorganic anion regulated phase transition in a supramolecular adduct: 4-Trifluoromethoxyanilinium hexafluorophosphate-18-crown-6

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ABSTRACT

A new supramolecular adduct 4-trifluoromethoxyanilinium hexafluorophosphate-1,4,7,10,13,16-hexaoxacyclooctadecane ($[C_7H_7NOF_3\text{–}(18\text{-crown-}6)]^+[PF_6]^-$) was synthesized and separated as crystals. DSC measurement detected that this compound undergoes a reversible phase transition at about 158 K with a heat hysteresis of 4.8 K. The single crystal X-ray diffraction data obtained at 213 K and 113 K suggest that the phase transition undergoes from a high temperature phase with a space group of *Pnma* to a low temperature one with a space group of $P2_1/n$, the symmetry breaking occurs with an Aizu notation of *mmmF*2/*m*. The driving force of the transition may be ascribed to the order–disorder transformation of the inorganic PF_6^- anion. Broad peak dielectric anomaly observed at 157 K further confirms this phase transition.

Searching for a new kind of solid-to-solid phase transition (SSPT) compound induced by temperature is of great importance not only for the potential application of new functional materials but also for better understanding of the relationship between structure and property [1–10]. In particular, energy harvesting can be achieved during the phase change process and the variation of related physical quantities enables phase transition materials as smart sensors. Recent researches on phase transition in a supramolecular adduct based on 18-crown-6 are of great interest due to its ability to form supramolecular host–guest compounds with ammonium cations, especially with the protonated $R\text{–}NH_3^+$ cation ($R =$ aromatic group) [11–15]. To design such supramolecular crystals which can undergo a phase transition, the common strategy lies in the utilization of the guest molecular ($R\text{–}NH_3^+$) which can reorient along with the external stimuli. As a result, for most of the current existing supramolecular adducts based on 18-crown-6 with phase transition, the driving force can be ascribed to the motional changes of the $R\text{–}NH_3^+$ guest cation [16–18]. On the other hand, the supramolecular adduct asymmetric unit also contains one counter inorganic anion, and some ball-like anions (e.g. BF_4^-, ClO_4^-, ReO_4^-, etc.) are frequently used to design phase transition materials due to their relatively smaller volume and higher symmetry which can easily tend to reorient in the close-packing crystal structure. So can we introduce such an inorganic anion as the counter anion into the crown ether complex to trigger phase transition? To answer this question, another condition must be taken into consideration, i.e. the inorganic anion must adopt a disordered conformation at a relatively higher temperature with higher symmetry, and accompanying with temperature decrease, the anion can reorient to an ordered state which may lead to symmetry breaking. However, for most of the current existing supramolecular adducts based on 18-crown-6 with phase transition, the anions with tetrahedral configuration do not make any significant contributions to the phase transition. So we tried to make an effort to find out other suitable geometric anions which also adopt small volume and high symmetry to regulate potential structure phase transition. Taking these considerations into account, as a continuation of a study on structure phase transitions, we obtained a supramolecular adduct: 4-trifluoromethoxyanilinium hexafluorophosphate-18-crown-6, $[(C_7H_7NOF_3)\cdot(C_{12}H_{24}O_6)][PF_6]$ (**1**) with an octahedral inorganic anion which plays a great role in the origin of the phase transition. Herein we report the synthesis, differential scanning calorimetry (DSC) measurements, variable-temperature single crystal X-ray diffraction analyses and dielectric measurement of **1**.

Compound **1** was obtained as colorless block crystals by slow evaporation of the methanol solution containing equal molar 4-trifluoromethoxyaniline, $HPF_6\text{–}H_2O$ (65%, w/w) and 18-crown-6 at room temperature. The IR spectrum of **1** shows a strong vibration peak at 836 cm^{-1}, indicative of the presence of hexafluorophosphate anion (see Supplementary Material Fig. S1). The powder XRD patterns of **1** measured at 213 and 113 K match very well with the patterns simulated from the corresponding single-crystal structure (see Supplementary Material Fig. S2), indicating the pure phase of the bulk crystal.

The phase transition of **1** was first detected in the differential scanning calorimetry (DSC) measurement. Upon cooling and then heating, as shown in Fig. 1, two heat anomalies are shown at 158.0 K and

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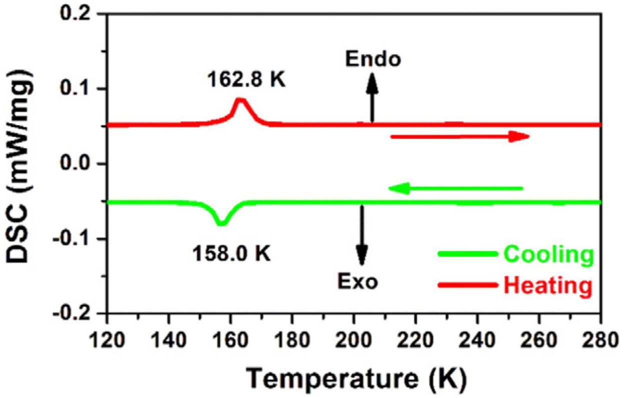

Fig. 1. DSC curves for 1 obtained on heating–cooling cycle.

Table 1
Summary of crystallographic data and structural refinement details of **1**.

	T213	T113
Empirical formula	$C_{19}H_{31}F_9NO_7P$	$C_{19}H_{31}F_9NO_7P$
Formula weight	587.42	587.42
Temperature (K)	213(2)	113(2)
Radiation type	Mo–K_α (0.71073 Å)	Mo–K_α(0.71073 Å)
Crystal system, space group	Orthorhombic, *Pnma*	Monoclinic, $P2_1/n$
Unit cell dimensions	a = 17.274(6) Å b = 11.117(4) Å c = 13.782(5) Å	a = 11.081(4) b = 17.017(6) c = 13.734(5) β = 90.013(6)
Volume (Å^3), *Z*	2646.6(16), 4	2589.8(16), 4
Density (cald) ($g \cdot cm^{-3}$)	1.474	1.507
Absorption coefficient (mm^{-1})	0.205	0.210
Absorption correction	Multi-scan	Multi-scan
Crystal size/mm	0.30 × 0.24 × 0.20	0.30 × 0.24 × 0.20
F(000)	1216	1216
T_{min}/T_{max}	0.943/0.960	0.941/0.959
θ range for data collection	2.35–27.44°	2.65–27.52°
Limiting indices	$-22 \le h \le 20$ $-14 \le k \le 14$ $-17 \le l \le 17$	$-14 \le h \le 14$ $-22 \le k \le 21$ $-17 \le l \le 16$
No. of measured, independent and observed [$I > 2\,(I)$] reflections	18,658, 3169, 2483	18,930, 5831, 5471
R_{int}	0.0560	0.0332
Completeness to θ (%)	99.6	97.7
Goodness-of-fit on F^2	1.149	1.063
$R_1[I > 2\sigma(I)]$	0.1177	0.0343
$wR_2[I > 2\sigma(I)]$	0.3148	0.0795
No. of reflections	3169	5831
No. of parameters	215	345

162.8 K respectively. This couple of exothermic and endothermic peaks represents a reversible phase transition with a 4.8 K hysteresis. Both the small thermal hysteresis and the round-like shape of the peaks indicate the characteristics of a second-order phase transition. From the DSC curve, the enthalpy change of $\Delta H = 0.2555$ J/g and the entropy change of $\Delta S = 0.9499$ J/(mol K) can be obtained. According to the Boltzmann equation, $\Delta S = R\ln(N)$, where R is the gas constant and N represents possible configurations, it is found that N = 1.12, indicating that the phase transition of the system is an order–disorder character and is probably related to the change of reorientational dynamics of the PF_6^- anions.

The microscopic details of the structural phase transition were investigated by the determination of variable-temperature crystal structures. The structure of the high temperature phase (HTP) at 213 K is orthorhombic, space group *Pnma*, a = 17.27, b = 11.12, c = 13.78 Å, V = 2646.6 Å^3 and Z = 4. When the temperature decreases to 113 K, namely the low temperature phase (LTP), the crystal becomes monoclinic, space group $P2_1/n$, a = 11.08, b = 17.02, c = 13.73 Å, $\beta = 90.013(6)°$, V = 2589.8 Å^3 and Z = 4. The unit cell volume decreases from 2646.6 Å^3 in the orthorhombic phase to 2589.8 Å^3 in the monoclinic phase. The corresponding calculated density changes from 1.474 $g \cdot cm^{-3}$ to 1.507 $g \cdot cm^{-3}$. Crystallographic data and details of the data collection and refinement for the structures at 213 and 113 K are given in Table 1.

Crystal structural determination of **1** in the HTP structure reveals the asymmetric unit is composed of one half cationic ($CF_3O–C_6H_4–NH_3^+$)·(18-crown-6) moiety and one half disordered anionic PF_6^- (Fig. 2a). The protonated 4-trifluoromethoxyanilinium cation connects with the 18-crown-6 ring to form a supramolecular rotator–stator structure via intramolecular N–H···O interactions between the $–NH_3^+$ and oxygen atoms (O1, O2, O3, O4, O3^i and O2^i) on the crown ether with a symmetry transformation of (x, 1/2 − y, z). The N–H···O hydrogen-bond distances are within the normal range of 2.860(6)–2.940(4) Å (see Supplementary Material Table. S1). The symmetry of the 18-crown-6 macrocycle approximates to C_{3v}, corresponding to nearly ideal crown formation. The oxygen atoms of the 18-crown-6 in the structure are displaced alternately above and under the median plane of the ring, forming two approximately parallel and almost equilateral triangles. O2, O2^i and O4 atoms are located above the mean O-atom plane (0.1195, 0.1195, and 0.4056 Å, respectively), and O1, O3 and O3^i atoms are under the plane (0.1681, 0.1933 and 0.1933 Å, respectively). N1 atom of the 4-trifluoromethoxyanilinium cation is in the perching position, lying 0.7509(37) Å higher from the best plane of the oxygen atoms of the crown ring, rather than in the nesting position. The dihedral angle between aromatic ring and the crown ring is about 87.5°.

In the basic unit of the HTP crystal, all three components mentioned above lie on a perfect crystallographic mirror plane perpendicular to [010] as depicted in Fig. 3a. Furthermore, this mirror plane is also precisely normal to the best plane of the crown ether and the aromatic ring both with the same dihedral angles of 90.00°. Ten non-hydrogen atoms (C11, O5, C10, C7, N1, O1, O4, P1, F4 and F5) are locating in this mirror plane with an occupancy factor of 0.5, other atoms out of the mirror plane can be produced by the symmetry transformation of (x, 1/2 − y, z). Interestingly, the trifluoromethoxy group ($-OCF_3$) just adopts a disordered state across the mirror plane, which could be ascribed tothe trifluoromethoxy group swings around the two sides of the mirror plane at the same probability above the phase transition point. The most surprising is the hexafluorophosphate (PF_6^-) anion is highly orientationally disordered symmetrically over two sides of the crystallographic mirror plane with F1, F2 and F3 disordered over it to produce F1^i, F2^i and F3^i. Besides, the F1 atom is split into F1 and F1′ with occupation factors of 0.628(2) and 0.38(2) respectively. The same situation is for the F1^i atom in the other side of the mirror plane. No classical strong hydrogen bonds are found between the PF_6^- anion and ($CF_3O–C_6H_4–NH_3^+$)·(18-crown-6) moiety but for some weak ones. (see Supplementary Material Table. S1)

At the temperature of 113 K, the LTP asymmetric unit of **1** is doubled compared to the basic unit of HTP, that is, one cationic ($CF_3O–C_6H_4–NH_3^+$)·(18-crown-6) moiety and one ordered anionic PF_6^- (Fig. 2b). The conformation of the hydrogen-bond geometry and the 18-crown-6 structure in the cation moiety closely resemble those in the high-temperature structure. The hydrogen-bonding interaction between 4-trifluoromethoxyanilinium and 18-crown-6 is strong with the N–H···O hydrogen-bond distances falling into the range from 2.855(2) to 2.924(2) Å (see Supplementary Material Table. S2). The symmetry of the 18-crown-6 macrocycle approximates to C_{3v} with all C–O–C–C torsion angles being trans-geometry and all O atoms arranged alternately up and down in the median plane of the crown ring. O1, O3, and O5 atoms are located under the mean O-atom plane (0.2557, 0.2662, and 0.0852 Å, respectively), and O2, O4, and O6 atoms are above the plane (0.2912, 0.1582 and 0.1407(12) Å, respectively). The nitrogen atom of the $–NH^{3+}$ group is also in the perching position, with N1 lying 0.6485(13) Å higher from the macrocycle plane. The dihedral