A Proton Conductive Hydrogen-bonded Framework Incorporating 18-Crown-6-ether andDicarboxy-o-terphenyl Moieties

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To date, proton-conducting organic crystalline materials based on crown ethers are rarely integrated. In this work, we revealed that the flexible organic 18-crown-6 derivatives with one or two 4,4’-dicarboxy-o-terphenyl (CT) groups, formed four kinds of crystalline frameworks: 1CT-18C6-I (P21/n), 2CT-18C6-I (P-1), 2CT-18C6-II (P-1) and 2CT-18C6-III (Cm2c). Single crystal X-ray diffraction analysis clearly suggested the water molecules involved hydrogen-bonded network for all frameworks. In particular, a unique two-dimension (2D) water pathway had formed in 2CT-18C6-III and the activation energy was evaluated by Arrhenius plots to be 0.14 eV, indicating that the proton jumps from H2O+ to the neighboring H2O in the hydrogen-bonded network of 2CT-18C6-III.

Introduction

Under the concept of green sustainable development, new clean fuel sources are absolutely necessary. Proton exchange membrane fuel cells (PEMFCs) are one of the most optimal technologies to alternative the common fossil fuels.1 Proton exchange membranes (PEMs) with the ionic pathway for the protons are critical for the PEMFCs. Presently, organic conductive polymers, such as Nafion, sulfonated and phosphonic-based polyaromatics, polybenzimidazoles have been employed as the alternative PEMs materials.2-7 They exhibit the following features required for PEMs: (a) presence of proton-conducting functionalities,8-10 (b) poor electronic conductivities, and (c) good chemical and thermal stabilities. However, even the Nafion, achieving the outstanding proton conductivity of 10−1 S cm−1 at room temperature with 100% relative humidity (RH), still involves unavoidable defects. Thus, exploration of optimizing electrolyte materials have attracted much attention in this field. Highly crystalline materials with a periodic framework and infinite channels such as porous coordination polymers (PCPs) and metal-organic frameworks (MOFs) are, therefore, promising candidate of proton conductive materials.11

Proton conduction in PEMs related to two mechanism, namely, the Grothuss and vehicle mechanism.12-14 The vehicle mechanism indicates the diffusion of protons with the vehicles. While, the Grothuss mechanism always occurs in a water-based degenerated system consisting of H2O+ and H2O within an infinite network of hydrogen bonds. A proton jumps from H2O+ to a neighbouring H2O as well molecules rotations, which contribute to a high proton conductivity.

As well known, crown ether derivatives, such as dibenzo-18-crown-6-ether (DB18C6) with an excellent ability to bind alkali metal cations and water molecules,15,16 have drawn much attention as an ion conductive material.17 Theoretical calculation indicated that DB18C6 with H2O+ ions located in the cavities of the crown ether interact with water molecules.18-19 Therefore, crystalline frameworks composed of crown ethers are expected to show the conductivity with the Grothuss mechanism. In this connection, we were interested in hydrogen-bonded organic frameworks (HOFs),20-25 in which molecules are connected through non-covalent intermolecular interactions such as hydrogen bonds, because of their high crystallinity and high affinity toward proton. To date, some HOFs are reported to show proton conductivity.26-32 However, proton conductive HOFs based on crown ethers are hitherto unknown.

Herein, we newly designed 18-crown-6 derivatives with one and two 4,4’-dicarboxy-o-terphenyl (CT) groups, 1CT-18C6, and 2CT-18C6, respectively, as a building block molecule to develop proton conductive HOFs (Fig. 1). A working hypothesis is as follows: (1) The 18-crown-6 and carboxy groups can capture water molecules via hydrogen bonds; (2) The carboxy group also can form supramolecular synthony to organize the molecules into crystalline supramolecular frameworks;33 and (3) The rigid o-terphenyl moiety can form frameworks24,34,36 and provide space for H+ conducting. To date, 2CT-18C6 has been applied as an organic ligand of a metal-organic framework,37 an organic ligand is a metal-organic framework, and proton conductive molecular crystalline materials based on 2CT-18C6 are hitherto-unknown.

2CT-18C6 are revealed to form three kinds of crystalline frameworks (2CT-18C6-I, -II, and -III). In particular, 2CT-18C6-III has a unique two-dimension (2D) water pathway and showed
the proton conductivity of $6.75 \times 10^{-8}$ S cm$^{-1}$ at 85% RH. Notably, the activation energy ($E_a$) was evaluated by Arrhenius plots to be 0.14 eV, suggesting that the proton jumps from H$_2$O$^+$ to the neighbouring H$_2$O in the H-bonding networks of 2CT-18C6-III. The thermogravimetric (TG) analysis also indicated that 2CT-18C6-III is stable up to 588 K. The present system is the first example for the tailoring structural features of crown ethers with a 2D water pathway.

Fig. 1 (a) A molecular structure of 2CT-18C6 and expected roles of the parts. (b) Related molecules 1CT-18C6, dibenzo-18-crown-6 (DB18C6), and 4,4’-dicarboxy-o-terphenyl (CT).

In this paper, we present synthesis of the crown ether derivatives, construction of crystalline frameworks, and evaluation of their H$^+$ conductivity. Moreover, the relationships between the structures of water pathways and proton conductivity are discussed.

Results and Discussion

Synthesis and crystallization. Synthesis of 1CT-18C6 and 2CT-18C6 is shown in Scheme 1. 4,5-Bis(methoxycarbonylphenyl)benzo-18-crown-6 (1) and 4,4’,5,5’-tetrakis(methoxycarbonylphenyl)dibenzo-18-crown-6 (2) were synthesised through a Suzuki-Miyaura cross-coupling reaction of 4-(methoxycarbonyl)phenylboronic acid and the corresponding brominated crown ether derivatives. Hydrolysis of 1 and 2 gave 1CT-18C6 and 2CT-18C6, respectively. Conditions to prepare frameworks are shown in Scheme 1b. 1CT-18C6 dissolved in EtOH at room temperature for 1 day afforded colourless block crystals (1CT-18C6-I). 2CT-18C6 forms three forms 2CT-18C6-I, -II, and -III. Slow evaporation of a mixed solution of N,N-dimethylformamide (DMF) and water at 85 °C for several days successfully obtained two kinds of block-shaped P-1 crystals (2CT-18C6-I and 2CT-18C6-II) concomitantly. 2CT-18C6 dissolved in EtOH at room temperature afforded a colourless block Cmc2$_1$ crystal (2CT-18C6-III).

Scheme 1. (a) Synthesis and (b) crystallization of 1CT-18C6 and 2CT-18C6. Reaction conditions: i) 4-(methoxycarbonyl)phenylboronic acid, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, THF, water, reflux; ii) KOH$_{aq.}$, THF, iii) HCl.

Fig. 2 Crystal structure of 2CT-18C6-I. (a) Anisotropic ellipsoid plot with 50% probability. (b) One-dimensional ribbon-like motifs formed through intermolecular hydrogen bonds. (c) Blanched Hydrogen bonded network formed by three carboxy groups. (d) Packing diagram, where the crown ether moiety and DMF molecules are coloured by purple and orange, respectively.
Crystallography. In 2CT-18C6-I crystal, a sodium cation is captured at the centre of the crown ether with a Na\(^+\)•••O distance ranging from 2.57 to 2.79 Å. Two DMF molecules are then coordinated to Na\(^+\) from axial directions. Because of the cation binding, the 18C6 moiety has a boat-shape conformation with bending angle of 76.4° (Fig. 2a), where the bending angle is defined as a dihedral angle between mean planes of the two benzene rings of dibenzo-18-crown-6-ether moiety. Three of the four carboxy groups form intermolecular hydrogen bonds and the one binds to a DMF molecule, resulting formation of a ribbon like motif (Fig. 2b). It is noteworthy that the carboxy groups form no self-complementary dimer, which is often observe in hydrogen bonded frameworks composed of highly-symmetric rigid π-conjugated molecules, but branched networks involving water molecule as shown in Fig. 2c. This result clearly indicates that flexibility and lower symmetry of 2CT-18C6-I crucially effects on a way of formation of a hydrogen bonded network. Packing of the boat shape molecules provides small inclusion spaces, in which water and DMF molecules are included. In this framework, however, there are no one-dimensional water alignment suitable for proton conduction. 2CT-18C6-II consists of crystallographically independent three molecules as well as water and DMF molecules. 2CT-18C6-II has almost the same structure with 2CT-18C6-I (Fig. S1).

In 2CT-18C6-III crystal, a Cs-symmetric 2CT-18C6 molecule has quite shallow boat conformation with a bending angle of 25.2° (Fig. 3a), which is significantly different from 2CT-18C6-I. The observed differences on the conformation probably causes by existence of strongly bound cationic species in the macrocycle. The carboxy groups form hydrogen bonds with only water molecules to give the crystal contains no solvent but water molecules with a host/guest ratio of 1 : 3 stoichiometry (Fig. 3b). One water molecule form hydrogen bonds with crown ether’s oxygen and the carboxy groups with 2.86 and 2.69 Å, respectively, and is isolated from neighbouring water molecules (yellow spheres). The other four molecules (red spheres), on the other hand, form hydrogen bonds with the carboxy groups (O•••O distances: 2.72, 2.89, and 2.94 Å) to form one-dimensional zig-zag alignment along the c axis (Fig. 3c). Distance between the oxygen atoms of the neighbouring water molecules is 2.97 and 3.74 Å (Fig. 3d).

1CT-18C6-I also contains only water molecules with a host/guest ratio of a 1 : 3 stoichiometry. Two water molecules are hydrogen bonded by the crown ether’s oxygen atoms and the other are by the carboxy groups. Totally, the water molecules are aligned one dimensionally along the b axis. The distance between oxygen atoms of the neighbouring water molecules ranges 2.77 to 3.68 Å. Although these distances are relatively shorter than that in the case of 2CT-18C6-III, the alignment crosses through crown ether ring.

Phase purity and thermal stability. The powder X-ray diffraction (PXRD) patterns of crystalline bulk samples of 1CT-
18C6-I and 2CT-18C6-III are in good agreement with the ones simulated from their single-crystal data respectively (Fig. 5), indicating high phase purity and good stability. In the TG curves, 1CT-18C6-I starts losing slowly from room temperature and displays 8.9% weight loss to 373 K, which corresponds to the loss of the water molecules (cal. 8.9%). Then the framework maintains until 588 K (Fig. 5a). Similarly, 2CT-18C6-III shows a 4.5% weight loss of water molecules from room temperature to 373 K (cal. 4.5%) and the framework also collapses after 588 K (Fig. 5b). On the other hand, variable temperature-PXRD plots show both 1CT-18C6-I and 2CT-18C6-III with an obvious change of structure with the increase of the temperature, which result from the reorganization of the hydrogen bonds connected with the loss of the water molecules (Fig. 5c, 5d).

**Proton Conductivity.** The structures of 1CT-18C6-I and 2CT-18C6-III were constructed by hydrophilic crown ether moiety, assembly of carboxy groups, and one-dimensional alignment of water molecules. In addition, TG and variable temperature-PXRD analyses suggested the frameworks of 1CT-18C6-I and 2CT-18C6-III maintained after the removal of water molecules. These results indicated that there were enough sites for water molecules supplied at higher relative humidity. These structural features could provide an orderly way for proton transport. Therefore, 1CT-18C6-I and 2CT-18C6-III are expected to show proton conductivity. Due to the limitation of the size of the samples, compressed pellet of the samples was used for the measurement of proton conductivity. As a reference, proton conductivity at the same condition was measured for pelletized samples of CT and DB18C6.

Temperature-dependent Nyquist plot under 85 RH% for four samples of 1CT-18C6-I, 2CT-18C6-III, CT, and DB18C6 were summarized in Figures 6a, 6b, S3, and S4, respectively.

The Nyquist plots (Figs. 6a, 6b and S3) of 1CT-18C6-I, 2CT-18C6-III, and CT were the sum of a straight line and a semicircle in the low and high frequency range, respectively. On the other hand, the each Nyquist diagram of DB18C6 was composed of a single semicircle (Fig. S4). Since the pellet sample was used to measure the proton conductivity, the Nyquist plot showed the proton conduction which are contributed from a bulk and an interface. Since bulk conduction is usually observed in the higher frequency range than the interface, the semicircles in the Nyquist diagram of 1CT-18C6-I, 2CT-18C6-III, and CT were attributed to bulk conduction. For the calculation of proton conductivity, we applied the equivalent circuit model. The model for the conductivity of DB18C6 is that a resistor and constant phase element (CPE) are arranged in parallel, while the model for that of 1CT-18C6-I, 2CT-18C6-III, and CT is that two parallel pairs of resistors and CPEs were lined up in series.

Regarding the conductivity estimated from the equivalent circuit model, an Arrhenius plot was summarized from the bulk conductivity of 1CT-18C6-I, 2CT-18C6-III, CT, and the conductivity of DB18C6, respectively. From the Arrhenius plot, the proton conductivities at room temperature and Ea of 1CT-18C6-I, 2CT-18C6-III, CT, and DB18C6 were estimated, and summarized in Table 1. The proton conductivity at room temperature was higher in the order of 2CT-18C6-III, 1CT-18C6-I, 2CT-18C6-III, CT, and DB18C6, and the Ea was also lower in the same order. The proton conductivities of MFM-511 and MFM-512, which are the MOF samples with the carboxy group involved in proton transport, are 4.0×10⁻⁷ (87 RH%) and 2.5×10⁻⁷ S cm⁻¹ (77 RH%) at 298 K, respectively. The value of proton conductivity from 2CT-18C6-III is in the similar order of MFM-511 and MFM-512.

Referring to the proton transport, proton conduction can be classified as the vehicle and the Grotthus mechanisms, which are divided by Ea = 0.4 eV. When Ea is larger and smaller than 0.4 eV, proton conductivity is estimated to be the vehicle and Grotthus mechanisms, respectively.
Since Ea of DB18C6 and CT are higher than 0.4 eV, proton conducting mechanism of DB18C6 and CT is attributed to the vehicle one. On the other hand, 1CT-18C6-I and 2CT-18C6-III had lower Ea than 0.4 eV, and therefore, the proton conduction of them is due to the Grotthus mechanism. Both 1CT-18C6-I and 2CT-18C6-III had continuous hydrogen-bonded networks, resulting in the effective proton-conducting pathways and corresponding to Grotthus mechanism. Notably, 2CT-18C6-III has two unique linear water pathways. Water molecules in 2CT-18C6-III were not only arranged along the one-dimensional array of the crown ether unit, but also arranged in the parts formed the hydrogen-bonded networks surrounded by carboxy group. Therefore, 2CT-18C6-III exhibited the highest proton conductivity of $3.43 \times 10^{-8}$ S cm$^{-1}$ under 85% RH at 300 K.

**Conclusions**

In this study, we newly applied 18-crown-6 derivatives with one or two 4,4’-dicarboxy-o-terphenyl (CT) moieties as building block molecules to develop organic crystalline materials with proton conductivity. The 18-crown-6 and carboxy groups capture water molecules via hydrogen bonds and constructed good self-adaptability to water molecules frameworks especially for 2CT-18C6-III with a unique 2D water pathway, which provide available space for H$^+$ conduction. Based on this study, it is available to develop a novel proton conductive flexible framework with good adaptability to guest molecules. In addition, the high chemical stability and superior thermal stability indicate a promising and potential application in PEMFCs.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

† Crystal Data for 1CT-18C6-I, C$_{30}$H$_{66}$O$_{13}$; Fw = 604.59; Monoclinic, P2$_1$/n (14), Z = 4, $a = 13.6633(2)$ Å, $b = 8.2601(10)$ Å, $c = 26.8789(6)$ Å, $\beta = 90.208(2)^\circ$, $V = 3033.54(9)$ Å$^3$, $T = 223$ K, $D = 1.324$ g cm$^{-3}$, 12904 collected, 5424 unique ($R_{int} = 0.031$) reflections, the final R1 and wR2 values are 0.058 [R>2.0σ(I)] and 0.184 (all data), respectively. CCDC-2057700. Crystal Data for 2CT-18C6-I, C$_{36}$H$_{54}$S$_{3}$N$_{35}$O$_{27}$NaO$_{17.5}$; Fw = 1119.62; Triclinic, P1$_1$ (2a), Z = 2, $a = 11.3113(2)$ Å, $b = 13.4267(2)$ Å, $c = 21.7047(4)$ Å, $\alpha = 104.103(2)^\circ$, $\beta = 95.267(1)^\circ$, $\gamma = 111.048(2)^\circ$, $V = 2924.57(1)$ Å$^3$, $T = 293$ K, $D = 1.271$ g cm$^{-3}$, 31008 collected, 11017 unique ($R_{int}$ = 0.026) reflections, the final R1 and wR2 values are 0.061 [R>2.0σ(I)] and 0.209 (all data), respectively. CCDC-2078832. Crystal Data for 2CT-18C6-II, C$_{38}$H$_{32}$Na$_{3}$O$_{27}$; Fw = 1082.07; Triclinic, P1 (2a), Z = 6, $a = 13.1094(8)$ Å, $b = 25.3403(16)$ Å, $c = 26.7457(16)$ Å, $\alpha = 105.281(5)^\circ$, $\beta = 90.128(5)^\circ$, $\gamma = 91.834(5)^\circ$, $V = 8565.89(9)$ Å$^3$, $T = 293$ K, $D = 1.259$ g cm$^{-3}$, 89237 collected, 32350 unique ($R_{int}$ = 0.116) reflections, the final R1 and wR2 values are 0.081 [R>2.0σ(I)] and 0.309 (all data), respectively. CCDC-2078834.

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**Table 1. Proton conductivity at 300 K and activation energy (Ea) of 1CT-18C6-I, 2CT-18C6-III, CT, and DB18C6, estimated from Arrhenius Plot.**

| Compound         | $\sigma$ at 300 K / S cm$^{-1}$ | $E_a$/ eV |
|------------------|---------------------------------|-----------|
| 1CT-18C6-I       | 1.95 x 10$^{-10}$               | 0.354     |
| 2CT-18C6-III     | 3.43 x 10$^{-8}$                | 0.140     |
| CT               | 8.69 x 10$^{-11}$               | 1.150     |
| DB18C6           | 3.97 x 10$^{-12}$               | 0.452     |
Crystal Data for 2CT-18C6-III, C4aH24O12; Fw = 890.81; Orthorhombic, Cmc21; (R36); Z = 4, a = 27.4687(10) Å, b = 20.3236(8) Å, c = 8.0251(16) Å, β = 90°, V = 4480.14(14) Å³, T = 298 K, D = 1.921 g/cm³, 29283 collected, 4181 unique (Rint = 0.128) reflections, the final R1 and wR2 values are 0.094 (>2.00(I)) and 0.287 (all data), respectively. CCDC-2078835.

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