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Design and Characterization of a Polarized Coordination Polymer of a Zinc(II) Biphenyldicarboxylate Bearing a Sulfone Group

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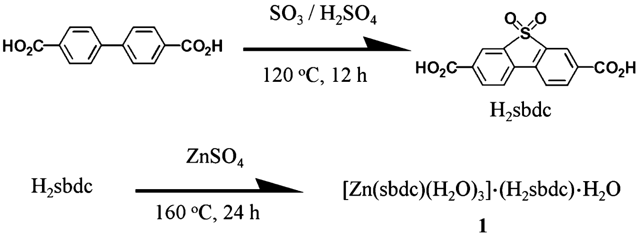
A novel coordination polymer of zinc(II) biphenyldicarboxylate bearing a sulfone group, $[Zn(sbdc)(H_2O)_3]\cdot(H_2sbdc)\cdot H_2O$ (H_2sbdc: sulfone biphenyldicarboxylic acid), has been synthesized. It is composed of a one-dimensional chain structure of alternating Zn(II) cations and sbdc anions. This coordination polymer possesses noncoordinating uncharged acid H_2sbdc existing between the chains with hydrogen-bonding networks. The proton conductivity of $[Zn(sbdc)(H_2O)_3]\cdot(H_2sbdc)\cdot H_2O$ strongly depended on the relative humidity (RH), being $2.5 \times 10^{-7}\,S\,cm^{-1}$ at 95% RH. The activation energy for proton conductivity was estimated to be 0.32 eV at 95% RH.



Scheme 1. Schematic outline of the syntheses of H_2sbdc ligand and coordination polymer **1**.

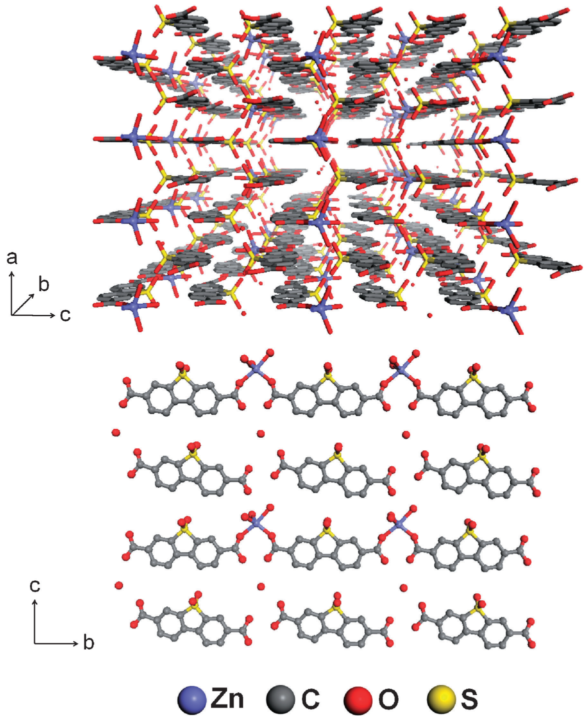


Figure 1. Crystal structure of coordination polymer **1**.

The design and synthesis of metal–organic frameworks (MOFs) have been intensively studied over the past decade because of their attractive applications in gas storage, molecular adsorption, catalytic reactions, and molecular sensing.[1–5] The performance of the MOFs strongly depends on the size of the cavity inside the frameworks. To date, many research groups have focused on controlling the cavity size of the frameworks, an effective way being to change the organic ligands and metal ions.[6–10] On the other hand, few examples have been reported for the control of polarity of frameworks because of the difficulty of synthesizing ligands bearing polarizing groups.[11] By the design and synthesis of a framework bearing polarizing groups, we can control not only physical properties such as ionic conductivity but also chemical properties such as catalytic activity.[12–15]

Biphenyldicarboxylic acid (H_2bpdc) is well designed for the construction of one-dimensional coordination polymers and MOFs because H_2bpdc has a simple linear structure. For example, coordination polymers with oxalic acid and 2,5-dihydroxybenzoquinone have been reported.[16,17] We tried to introduce electron-donating or electron-withdrawing moieties onto the framework. The sulfone group is an excellent substituent to introduce polarity to organic ligands because it is expected to be a strong electron-withdrawing group. However, the insertion reaction of sulfone to a MOF backbone has not been reported. Here, we first report the syntheses of sulfone biphenyldicarboxylic acid (H_2sbdc) and the novel coordination polymer $[Zn(sbdc)(H_2O)_3]\cdot(H_2sbdc)\cdot H_2O$ (**1**) and discuss the crystal structure and proton conductivity of **1**.

The H_2sbdc ligand was synthesized as follows (Scheme 1). Fuming sulfuric acid (5 mL) was added to H_2bpdc (0.50 g, 2.1 mmol), and the mixture was reacted at 120 °C for 12 h in air. After cooling to room temperature, the mixture was poured onto ice (10 g). The yellow-white solid was filtered and dried (90% yield). The H_2sbdc was characterized by ^{1}H NMR, IR, and elemental analysis (EA).[18] The MOF was made by mixing H_2sbdc (1 mmol) and zinc(II) sulfate hexahydrate (2 mmol) in distilled water (30 mL) at 160 °C for 24 h in a Teflon-lined autoclave by a hydrothermal method. After cooling to room temperature, the mixture was washed with THF and water to remove the unreacted ligand and metal ion. Colorless crystals were obtained and used for the single-crystal X-ray diffraction measurement, EA, thermogravimetry, and water uptake and electrical conductivity measurements.

Figure 1 shows the crystal structure of **1**, consisting of one-dimensional chains of sbdc ligand and zinc ion.[19] **1** has

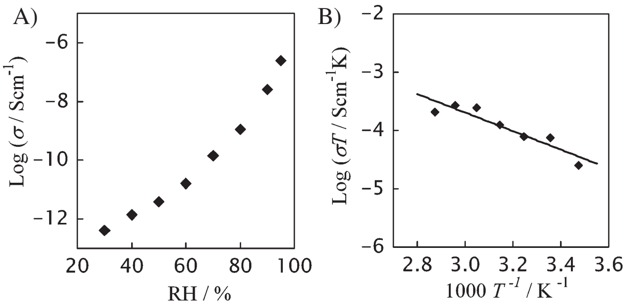


Figure 2. A) Plot of conductivity vs. relative humidity of $[Zn(sbdc)(H_2O)_3]\cdot(H_2sbdc)\cdot H_2O$ at 25 °C. B) Plot of conductivity vs. temperature of $[Zn(sbdc)(H_2O)_3]\cdot(H_2sbdc)\cdot H_2O$ at 95% RH.

uncoordinating H_2sbdc, and this H_2sbdc is sandwiched by chains. This unique structure is formed by the strong electron-withdrawing nature of the sulfone group. Titration plots show that the pK_a of H_2sbdc (6.59) is lower than that of H_2bpdc (8.25).[20] The difference between the pK_a values of the RCO_2H groups affects the coordination reaction between ligand and zinc ion. Therefore, both coordinating and uncoordinating ligands were included in the system of H_2sbdc. It is also noted that this crystal has two types of water molecules. Three water molecules coordinate to the zinc ion, and the other is uncoordinating water located between ligands constructing hydrogen-bonding networks into the MOF. Two carboxyl groups coordinate to the zinc ion so that this zinc has five coordination bonds and adopts a trigonal bipyramidal configuration.

From the presence of uncoordinating uncharged H_2sbdc and water molecules, it is expected that **1** would exhibit high proton conduction. The proton conductivity of **1** was measured by ac impedance.[21] Figure 2A shows plots of the logarithm of conductivity vs. relative humidity (RH). The conductivity strongly depends on the humidity. The change in conductivity was greater than six orders of magnitude, from 4.1×10^{-13} (30% RH) to 2.5×10^{-7} S cm^{-1} (95% RH). As we noted above, one water molecule in the crystal is located as water of crystallization; therefore, the uncoordinating ligands probably acted as proton sources. The activation energy was estimated to be 0.32 eV from the slope shown in Figure 2B. The possible mechanism of the conductivity is proton hopping through the hydrogen-bonding network in the crystal. The distance between the water molecules coordinating to the Zn metal center and hydroxy group of the uncoordinating ligand is 2.743 Å, indicating the existence of hydrogen bonding.[22,23]

In summary, we have carried out the synthesis and characterization of a novel coordination polymer **1**. The structure of this compound is a one-dimensional chain, and the proton conductivity strongly depends on the humidity. This conductivity is thought to originate from H_2sbdc as a proton source and from hydrogen bonding as a proton pathway. Because the change in proton conductivity of **1** is greater than six orders over a range of humidity, this material is suitable for highly sensitive humidity sensors.

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18 ^{1}H NMR (DMSO): δ_H 8.35 (d, 2H), 8.38 (s, 2H), 8.43 (d, 2H), 13.8 (s, 2H). IR [KBr/cm^{-1}]: 3591, 3487, 2995, 2625, 2534, 1724, 1678, 1606, 1398, 1240, 1169, 1140, 1117, 1074, 908, 762, 717, 648, 588, 559, 532, 426. Elemental analysis calcd for $C_{14}H_8O_6S$ (304.3): C, 55.26; H, 2.65%. Found: C, 54.90, H, 2.72%.

19 Crystal data were as follows: $C_{28}H_{22}O_{16}S_2Zn$, triclinic, space group $P\bar{1}$(no. 2), $a = 6.7486$ Å, $b = 13.902(3)$ Å, $c = 14.842(5)$ Å, $\alpha = 89.995(6)°$, $\beta = 88.158(4)°$, $\gamma = 84.556(4)°$, $V = 1385.5(5)$ Å^3, $Z = 2$, $R_1 = 0.0710$, $wR_2 = 0.2135$, and GOF = 1.133. Elemental analysis Calcd for $C_{28}H_{14}O_{12}S_2Zn\cdot 4H_2O$ (744.0): C, 45.20; H, 2.98%. Found: C, 45.30, H, 2.99%. Details of the crystal structure of the compound are available free of charge via Cambridge Crystallographic Data Centre under deposition number CCDC-749400.

20 The values of pK_a were estimated in a mixture of H_2O/DMSO because the solubility of these ligands in water was poor. The values in a mixture of water and organic solvent are higher than in water.

21 For the electrical conductivity study, the powdered sample was compressed to approximately 0.5 mm in thickness and 2.5 mm in diameter. Both sides of the pellet were attached to gold wires with gold paste. The conductivity measurement was carried out using a Solartron 1260 impedance/gain-phase analyzer by a quasi-four-probe method in the frequency range 10 MHz to 1 Hz. Proton conductivity was calculated from the diameter of the semicircle. Samples were placed in a temperature–humidity-controlled chamber (SH221, ESPEC Corp.) during the measurement.

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