1D1a Development of a molecular transistor operated by solid-state ion exchange

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A transistor is the fundamental electronic device used for switching or amplifying electric signals. On the conventional transistor, the electric gate is controlled by the external stimuli such as an electric field,[1] a magnetic field[2], light irradiation[1] and so on. In this study, we aimed the development of a molecular transistor which is operated by solid-state ion exchange. In order to switch the electrical resistivity, we focused on $[Ni(dmit)_2]^{\delta-}$ complex which exhibited magnetic (δ = 1, S = 1/2) and electrical ($0 < \delta < 1$) properties.

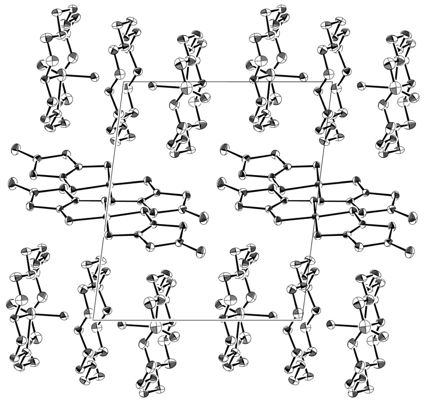

Figure 1. The crystal structure of **1** viewed along the *a*-axis.

Recently, we prepared a crystal, $Li_2([18]crown\text{-}6)_3[Ni(dmit)_2]_2(H_2O)_4$ (**1**, Figure 1), which is containing ion channel configuration composed of Li^+, [18]crown-6, and crystalline water molecules, and Li^+ ion conduction in ion channels was observed.[3] When the crystals of **1** were soaked in a molar KCl aqueous solution, the complete ion exchange of Li^+ in **1** with K^+ in solution occurred while keeping the crystalline state.

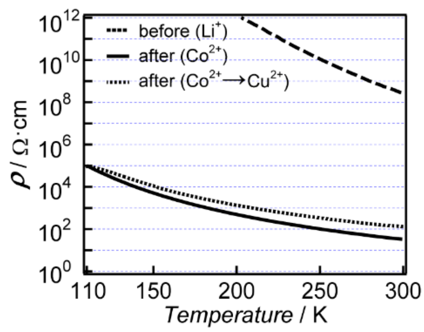

Figure 2. The temperature dependence of electrical resistivity of initial, Co^{2+}-exchanged, and twice ion-exchanged compounds.

In this study, we aimed to control the electrical resistivity through the solid-state ion exchange. For example, if Co^{2+} entered the crystal through the ion channel, the electron transfer from Co^{2+} to $[Ni(dmit)_2]^-$ (i.e. reduction of $[Ni(dmit)_2]^-$) was expected. On the other hand, the oxidation of $[Ni(dmit)_2]^-$ was anticipated by ion exchange of Li^+ with Cu^{2+}. In order to realize the switching of electrical resistivity, we carried out repeated ion exchange of Co^{2+} and Cu^{2+}. In fact, the electrical resistivity of the crystal was decreased by seven orders of magnitude through ion exchange of Li^+ with Co^{2+}. Furthermore, the electrical resistivity increased by one order of magnitude by ion exchange of Co^{2+} with Cu^{2+}. In the presentation, the control of electronic state and physical properties will be discussed in detail.

[1] T. L. Floyd, *Electronic Devices*, 9th Ed., Pearson Education, Inc. (2012); [2] T. Tsuchiya *et al.*, *Sci. Rep.* **2017**, *7*, 10534; [3] K. Ichihashi, S. Nishihara *et al.*, *Chem. Mater.* **2018**, *30*, 7130.