Investigation of the proton conductivity switching using metal complex with multi light-responsive units

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Ion conductivity switching materials have attracted great attention toward the application in memory or sensor via the reversibility or responsibility. In the previous research, ion conductivity switching has been investigated by using various external stimuli such as temperature, electromagnetic field and light.¹ However, the on/off ratios of the ion conductivity are far from that of the electron conductivity, *i.e.*, transistor, where more than 10⁶ on/off ratio is required. In this research, we aimed at the high ion conductivity switching by utilizing the concerted effect of multiple light-responsive units.

A novel metal complex 1 composed of Fe^{III} ions and imidazole-based ligand containing two light-responsive groups, (i) azo and (ii) *o*-nitrobenzaldehyde groups (**Figure (a)**) was synthesized, and the structure before the light irradiation was determined by the single-crystal X-ray structural analysis at 100 K. From the ultraviolet-visible spectroscopy of 1 in the solid state, it was clarified that (i) azo and (ii) *o*-nitrobenzaldehyde groups were isomerized at 470 nm and 340 nm, respectively (**Figure (b**)). Based on this, proton conductivity with or without light irradiation was investigated. We found that when either of the two light-responsive units was isomerized, on/off ratio of the ion conductivity was relatively low (~10²), although the enhancement of the proton conductivity was observed. By contrast, high proton conductivity of 5.5×10^{-3} S/cm was achieved when two light-responsible units were simultaneously isomerized, resulting in high on/off ratio up to 10^5 due to the concerted effect (**Figure (c)**).



Figure. (a) Chemical structure of 1. (b) Isomerization wavelengths of azo and *o*-nitrobenzaldehyde groups of 1 in the solid state. (c) Proton conductivity of 1 with or without light irradiation at 298 K. The values in the parentheses denote the on/off ratios at 95% relative humidity.
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