Synthesis and Proton Conductivity of Paddlewheel-Type Dinuclear Platinum(III) Complexes

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Pt-based paddlewheel unit is well known by its potential to have various valence state of Pt ions. If basic ligands that can serve as a proton hopping site coordinate to the Pt ions, the change in the valence state possibly affects the basic ability of the ligands to control the proton migration in the solid. In this study, the paddlewheel-type Pt(III) complex anion with squarate (sq^{2-}) ligands (pK_{a2} of H_2sq: 3.5; Fig. 1a) was combined with a protonated 1,2,4-triazolium (Htrz) cation (pK_a = 2.5) as a proton source; $(Htrz)_2[Pt_2(sq)_4(trz)_2]\cdot 2H_2O$ (**1**) and $(Bu_4N)_2[Pt_2(sq)_4(trz)_2]\cdot 3H_2O$ (**2**). Single-crystal X-ray structure analyses revealed that both complexes involved paddlewheel-type Pt dimer units, in which the valence state of Pt ions was estimated to be +3 based on XPS analyses. Proton conductivity of **1** under a certain condition was significantly higher than that of **2** because of the continuous hydrogen bond pathway including the Htrz cations (Fig. 1b); for example, σ = 1.00 x 10^{-4} S cm^{-1} for **1** and 8.53 x 10^{-8} S cm^{-1} for **2** at 25 ºC and 98% RH. This result indicates that the protonated triazolium cation has a great ability to form an infinite hydrogen bond pathway for enhancing the proton conductivity. The proton conductivity of **1** under 98% RH is more than 5 orders magnitude higher than that under 30% RH at 25 ºC, while the corresponding increase of **2** is only about 10^2 times. Although there is a large difference in proton conductivity, both showed comparable activation energies under 98% RH (E_a = 0.64 eV for **1** and 0.61 eV for **2**). The high E_a values may be associated with the possible inclusion of proton tautomeric process in the proton migration.

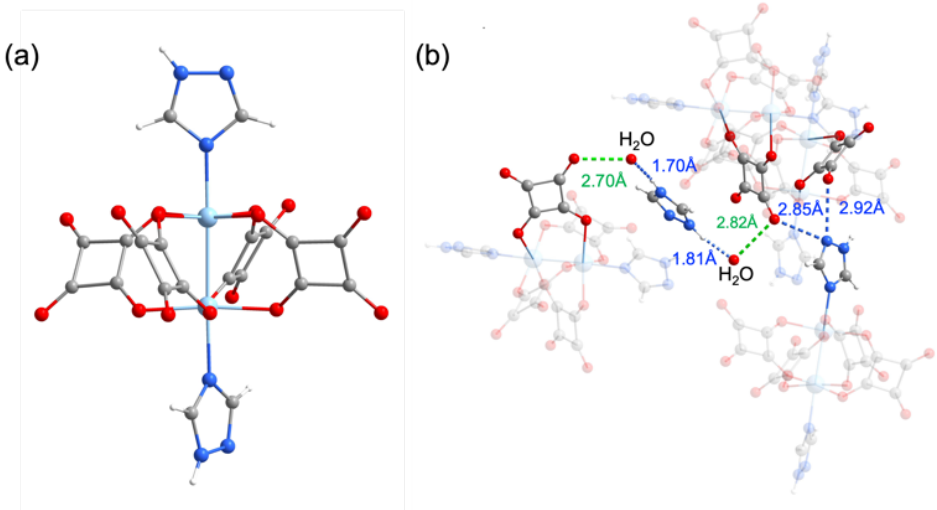

Figure 1. (a) Pt-based paddlewheel structure of **1**. (b) Hydrogen bond pathway composed of squarate, triazole, water, and triazolium cations in **1**. Atoms color: C, gray; H, white; N, blue; O, red; Pt, cyan. The green and blue dotted lines represent O…O and O…N hydrogen bonds.