Molecular Assemblies and Physical Properties of Proton-Transferred Octaaminotetraphenylene Phosphate Salts

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Anhydrous solid-state proton conductors have attracted considerable attention as a new class of solid electrolytes for fuel cells. While polymer and porous materials have been mainly studied for this purpose anhydrous crystalline molecular proton conductors could offer an ideal platform due to well-defined molecular arrangements coupled with unique molecular properties. Organic acid (A) − base (HD) proton-transferred salt of $(HA^+)(D^-)$ have emerged as ideal conductive materials since the donors/acceptors of the building block can be regarded as proton sources.[1] In this work, *o*PD-COT, a saddle-shaped molecule with dynamic molecular motion, has been combined with H_3PO_4, to form a cation-anion hydrogen-bonding salt, and the dielectric and proton conducting properties were investigated.

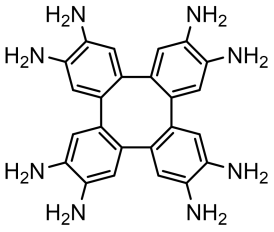

Fig. 1 Molecular structure of *o*PD-COT.

*o*PD-COT were synthesized according to the previous literature.[2] The proton-transferred salt showed thermal stability up to 440 K. DSC charts of *o*PD-COT·4(H_3PO_4) showed an irreversible peak at 360-370 K in the heating process. The XRD pattern showed the phosphonate anions as proton carriers form a three-dimensional network structure (Figs. 2a, b). The temperature (*T*) dependent dielectric responses of *o*PD-COT·4(H_3PO_4) showed anomalous frequency-dependent behavior in the *T*-range of 300−400 K. An imaginary part dielectric constant ε_2 showed a *T*-dependent dielectric peak. The *T*-dependence of the Cole-Cole plots also showed a semicircular trace over the entire *T*-range. The logσ–T^{-1} plots were obtained for *T* above 370 K, and the proton conductivity at 400 K was observed at 1.23×10^{-6} S cm^{-1} with the activation energy of 0.66 eV. Below 370 K, the short-range dynamic motion reflected in the frequency dependence of ε_2 behavior is thermally excited, whereas a change to long-range proton conduction occurred above 370 K, which corresponds to the DSC anomaly around 360−370 K.

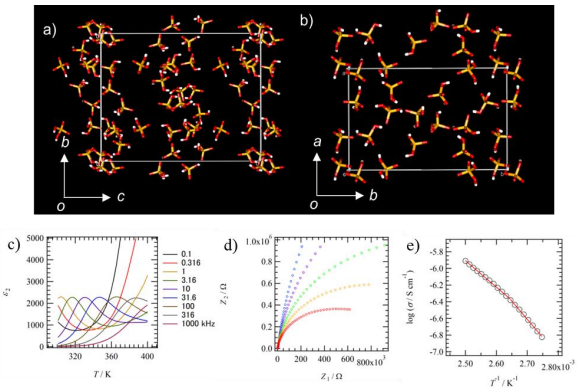

Fig 2. Array of phosphonate anions in *o*PD-COT·4(H_3PO_4) viewed along the a) *a*-axis and b) *c*-axis. c) *T*- and *f*-dependent ε_2. d) Cole-Cole plots and e) logσ–T^{-1} plots.

【References】

[1] G. Yuan et al. *J. Phys. Chem. C* **2020**, 124, 1861−1871.
[2] I. Ahmad et al. *J. Org. Chem.* **2021**, *86*, 14398−14403.