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Conductive Organic Crystals

Phosphonated Hexaphenylbenzene: A Crystalline Proton Conductor

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Proton conductivity has been widely studied because of its importance in biological and chemical processes.[1] A fuel cell (FC) is a promising device that can provide electrical energy with high efficiency and low environmental impact. A critical issue that severely hampers FC performance is the synthesis of proton-exchange membranes (PEMs) that simultaneously provide high proton conductivity that is constant over temperature. In the case of automotive applications, a guideline of close to 1×10^{-1} S cm^{-1} for the proton conductivity of the membrane at 120 °C and 50 % relative humidity (RH) was established by the U.S. Department of Energy as target operating conditions.[2] State-of-the-art polymeric electrolytes are sulfonic acid based perfluorinated polymers such as Nafion. These electrolytes present high but temperature-dependent proton conductivity, since proton transport is governed by the vehicle mechanism that is based on the diffusion of proton-containing groups.[3] Alternatively, phosphonic acid has been suggested as a protogenic group for intrinsically conducting separator materials because of its amphoteric properties.[4] It has been demonstrated that a high concentration of these acidic groups, which are able to aggregate, is required for a high intrinsic proton conductivity.[4b] Inorganic crystals (solid acid proton conductors) have been proposed as alternative materials to polymer electrolytes.[5] However, despite their high intrinsic conductivities (10^{-2}–10^{-3} S cm^{-1}; Grotthuss-type mechanism), these crystals have certain disadvantages, such as poor mechanical properties, water solubility, and high-temperature operating conditions (above 230 °C under atmospheric pressure for CsH_2PO_4).[6]

Although research has focused to date on increasing the flexibility of the protogenic groups, for example, by introducing spacers or by adding small molecules,[7] we have followed a different approach, in which we proposed to increase proton mobility by using a self-assembly and preorganization concept.

Herein, organic crystals of small molecules are suggested as an alternative to common polymeric electrolytes and inorganic crystals employed as PEM in FC systems. Although a lot of effort has been made to investigate inorganic crystals, very little information on entirely organic crystals has been reported to date.[8] The crystal structure of hexaphenylbenzene (HPB) and its derivatives have been known for a long time.[9] Most recently, crystallographic studies on acidic derivatives have been carried out.[10] It was found that almost all the molecules present multiple hydrogen bonds in the molecular plane and additionally form hydrogen bonds between adjacent sheets in such a way that columnar supramolecular networks are formed.

Inspired by the properties of phosphonic acids, as well as by the supramolecular self-assembly of HPB derivatives, we introduced phosphonic acid groups into the nonplanar structure of HPB. Hexakis(*p*-phosphonatophenyl)benzene (*p*-6PA-HPB) was synthesized in a three-step reaction (Scheme 1).

Powder X-ray measurements at different temperatures and RH values were performed (see Figure 1 and Figures S4 and S5 in the Supporting Information). It was found that *p*-6PA-HPB is crystalline and that the local order is only slightly affected by changing these parameters. These changes are attributed to small local packing variations probably caused by the evaporation of water (see Figure 1).

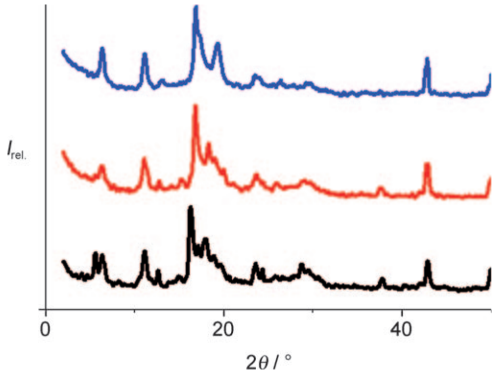

Figure 1. X-ray diffractogram of *p*-6PA-HPB at 33 % RH and RT, 100, and 200 °C (black, red, and blue lines respectively).

Two-dimensional wide-angle X-ray scattering (2D WAXS) experiments on mechanically oriented filaments show that *p*-6PA-HPB self-assembles into columnar structures in which the molecules are stacked on top of each other with a distance of 0.6 nm, and an intercolumnar distance of 1.4 nm (Figure 2). *p*-6PA-HPB shows a columnar alignment of the extruded filaments perpendicular to the alignment direction. This unusual orientation behavior has been recently observed for the first time in low-molecular-weight discotic molecules.[11] Strong hydrogen-bond interactions between

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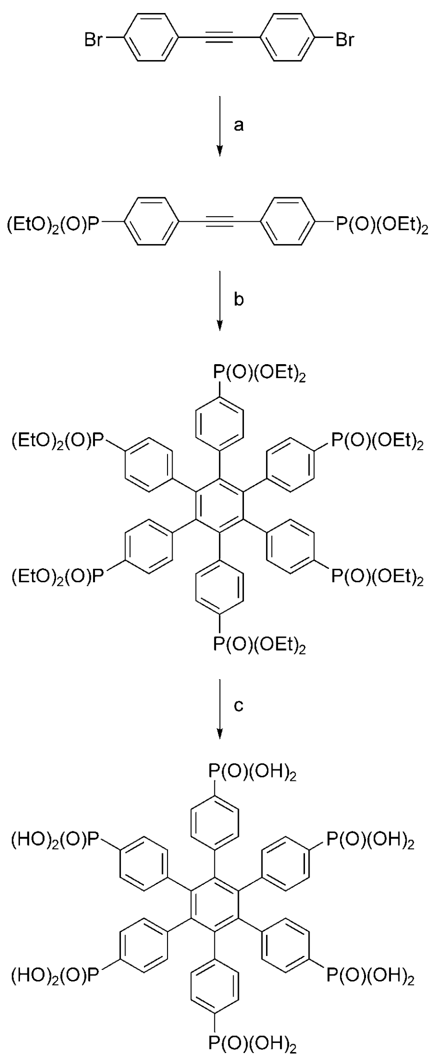

Scheme 1. Synthesis of *p*-6PA-HPB: a) HP(O)(OEt)$_2$, [Pd(PPh$_3$)$_4$], NEt$_3$, toluene, 60 °C, 12 h; b) [Co$_2$(CO)$_8$], dioxane, reflux, 12 h; c) 1. TMS-Br, CH$_2$Cl$_2$, RT, 3 days, 2. MeOH, RT, 3 days. TMS = trimethylsilyl.

phosphonic acid groups lead to a perpendicular orientation of the columnar structures. During extrusion, the molecules first assemble into a 2D network by hydrogen bonding between the phosphonic acid groups, and subsequently assemble into a 3D columnar structure.

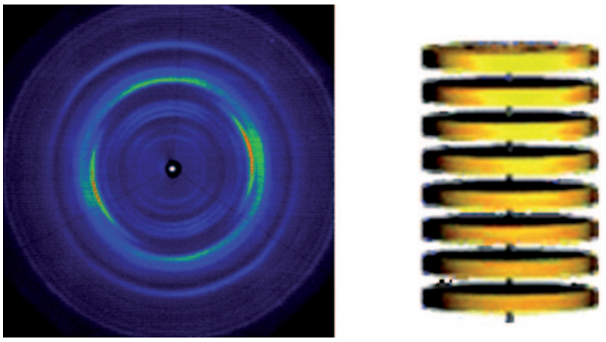

Figure 2. 2D WAXS pattern and representation of the columnar structure of *p*-6PA-HPB.

p-6PA-HPB possesses the characteristics of a hydrated crystal. Thermogravimetric analysis combined with mass spectrometry indicated that 8 wt % of water is released only at temperatures well above the boiling point of water (see Figure S2 in the Supporting Information). Moreover, water sorption and desorption isotherms at room temperature (Figure 3) indicate the stepwise hydration/dehydration and hysteresis characteristics of crystal hydrates.[12] Interestingly, in the case of the above-mentioned organic crystals, these steps involve close to integer multiples of water molecules per *p*-6PA-HPB molecule. The pronounced hysteresis isotherm predicts that a considerable amount of water remains in the crystalline material.

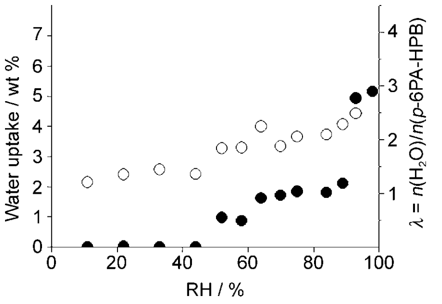

Figure 3. Water adsorption (●) and desorption (○) isotherms at RT.

Proton conductivity studies have been carried out above 100 °C under 1 bar H_2O atmosphere. These investigations show high proton conductivity values (Figure 4), especially when compared to inorganic hydrates or some phosphonic acid containing polymers.[13] Even though the proton conductivity of *p*-6PA-HPB is inferior to that observed for some sulfonated polysulfones,[14] *p*-6PA-HPB presents certain advantages since its proton conductivity is temperature-independent. Contrary to Nafion 117[15] and the above-mentioned polymers, this rather rigid system has an almost constant proton conductivity (3.2×10^{-3} S cm^{-1}) with increasing temperature (Figure 4). *p*-6PA-HPB exhibits higher values of proton conductivity than Nafion 117 above 160 °C. Nafion 117 suffers from the loss of water in the proton-conducting channels (vehicle mechanism),[3] whereas the steplike water desorption isotherm of *p*-6PA-HPB is the most likely reason for the flat temperature response of the crystalline material. The RH value, which is set by a H_2O atmosphere at 1 bar, decreases with increasing temperature. Proton conductivity measurements were realized under 1 bar

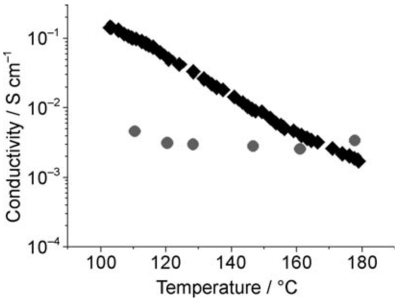

Figure 4. Plots of the proton conductivity vs. temperature under 1 bar H_2O atmosphere for *p*-6PA-HPB (●) and Nafion 117 (◆).

H_2O atmosphere above 100 °C, which corresponds to a RH lower than 50 %. As can be seen in the desorption isotherm, *p*-6 PA-HPB accommodates about two water molecules in its crystalline structure above 50 % RH. It is therefore assumed that these immobilized water molecules act as proton donor and acceptor instead of being diffusible carrier molecules.[16] This absence of any significant temperature dependence has been also observed for a phosphonated fully aromatic polymer,[17,4b] which presents slightly inferior proton conductivity values. This result is proof that derivative aggregation is more important than local flexibility in the case of phosphonic acids. The aggregation of *p*-6 PA-HPB is assisted by the preorganization of the HPB moieties.

Investigations at room temperature as a function of RH have been performed and compared to water uptake studies (Figure 5). Contrary to the adsorption isotherm, there is a constant increase in conductivity when starting with a well-dried material. This result is probably due to the pellet's macroporous morphology, which enables proton transport along water molecules that are adsorbed on the pore surfaces. At around 50 % RH, a step in conductivity is observed, which is in agreement with the plateau of the water uptake study. At room temperature and 95 % RH, *p*-6 PA-HPB has a conductivity of 2.5×10^{-2} S cm^{-1}, which is comparable to that of mixtures of inorganic acids.[18]

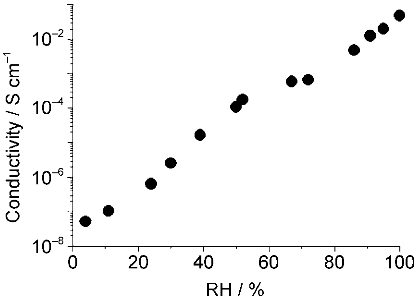

Figure 5. Plot of the proton conductivity of *p*-6 PA-HPB vs. relative humidity (RH) at RT.

We have presented a crystalline organic material in which proton conductivity is not a water-based diffusion process, as in common amorphous polymer electrolytes. *p*-6 PA-HPB can be seen as an inverse-proton-conducting cable because its columnar structure contains a proton-conducting periphery and an insulating core. Proton conductivity through the crystalline material is possible because of the amphoteric character, high concentration, and preorganization/aggregation of the phosphonic acid groups, and also because of the transport pathways within from the self-assembled columns. Moreover, proton transport is assisted by the presence of immobilized water in the crystal hydrate. In contrast to state-of-the-art polymers and inorganic crystals, *p*-6 PA-HPB provides high and furthermore temperature-independent proton conductivity, thus satisfying one of the prerequisites for new separator materials in FC systems.

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