High Proton-Conductivity in Covalently Linked Polyoxometalate-Organoboronic Acid-Polymers

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Abstract: The controlled bottom-up design of polymers with metal oxide backbones is a grand challenge in materials design, as it could give unique control over the resulting chemical properties. Herein, we report a 1D-organo-functionalized polyoxometalate polymer featuring a purely inorganic backbone. The polymer is self-assembled from two types of monomers, inorganic Wells–Dawson-type polyoxometalates, and aromatic organo-boronates. Their covalent linkage results in 1D polymer strands, which combine an inorganic oxide backbone (based on B=O and Nb–O linkages) with functional organic side-chains. The polymer shows high bulk proton conductivity of up to 1.59×10⁻² S cm⁻¹ at 90°C and 98% relative humidity. This synthetic approach could lead to a new class of organic–inorganic polymers where function can be designed by controlled tuning of the monomer units.

Molecular metal oxides, so-called polyoxometalates (POMs) are molecular analogues of solid-state metal oxides. They combine structural and chemical tunability on the atomic level with classic solid-state metal oxide functionalities including catalysis, electron storage or bioactivity. As such, POMs are ideal molecular prototypes to explore and mimic structure and function of more complex solid-state oxide materials. This has led to applications of POMs in diverse fields including functional nanostructures, energy conversion and storage, molecular electronics and bio-medicine. However, to deploy POMs in technological settings it is critical to establish heterogenization routes which enable their deposition on functional supports such as electrodes, semiconductors, or polymers. Traditionally, this is often achieved using harsh or unselective deposition routes including thermal or ultrasonication treatments, which often lead to POM degradation and formation of solid-state oxides.

One elegant alternative to overcome these challenges would be to devise strategies for the oligomerization and polymerization of polyoxometalates taking inspiration from organic and supramolecular chemistry. Pioneering studies have demonstrated that 3D linkage of POMs with metal cations gives polyoxometalate open frameworks (POM-OFs) with unique electronic and catalytic properties. More recently, the bottom-up assembly of POMs into supramolecular 1D chains has become a key area of POM development:

Pioneering studies by Cronin and colleagues demonstrated that octamolybdate-anions can be linked into 1D crystalline polymers using intricate silver linkages which utilize argentophilic interactions. The authors provided initial mass spectrometric analyses to study the oligomeric species formed during chain assembly. Nyman and co-workers used sophisticated in situ small angle X-ray scattering to rationalize oligomerization reactions of niobate clusters. The study demonstrated that pH value, concentration and type of counter-cation are the prime factors which control the aggregation processes. Building on these seminal studies, Streb and colleagues used organic ligands to link metal-functionalized polyoxovanadates into 1D polymeric chains. The authors reported the improved performance of the polymeric compounds as cathodes in lithium ion batteries.

Very recently, Weinstock and colleagues demonstrated that the direct linkage of tungstate Keggin anions is possible by incorporating Nb–O–Nb connectors. Their study explored the step-growth polymerization resulting in linear polymers with inorganic backbones, comprising up to 140000 repeat units.

Notably, the oligomerization or polymerization of POMs into chains typically uses metal linkage by oxo, hydroxo or solvent ligands. In contrast, to-date, to the best of our knowledge the covalent functionalization of POMs with organic groups has not been used as a means to access polymeric POM aggregates. However, this approach holds enormous potential as it could lead to polymers.
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type of organoboronic acid dimer has not been reported before, and it could be a first glimpse at possible applications of organoboronic acid-functionalized POMs for dynamic covalent chemistry, similar to pioneering studies using organoboronic acid esters in organic supramolecular chemistry.\[40,44]\n
In addition, we note that formation of this dimer is highly pH-sensitive (optimum pH 1.2–1.5), as no dimer is observed at higher or lower pH values (vide supra). We suggest that this observation could be related to a pH-sensitive equilibrium between boronic acid condensation and hydrolysis.\[45]\n
The [(4PBA)_2]O dimers in 1 connect neighbouring Dawson anions by the formation of Nb–O–B–O–B–O–Nb linkages, each boron centre retains one non-coordinated hydroxyl group, identified by BVS (Figure 1c and SI, Table S2). As a result, inorganic 1D chains are formed along the crystallographic a-axis, where the “polymer backbone” is purely based on metal oxo linkages (Nb–O or B–O, respectively) (Figure 2a). The organic moieties of 4PBA point away from the polymer backbone and form organic side-chains reminiscent of classical organic polymers such as polystyrene.

In the crystal lattice, the chains stack in the b-c plane and are linked by an extensive network of hydrogen interactions between the Dawson anion (surface OH groups), the boronic acid OH functions and lattice water molecules. We observe close intermolecular contacts indicative of OH–N hydrogen bonds (2.8–2.9 Å) between the 4PBA nitrogen atom and a cluster-based oxygen atom in the [Nb]_2-cap. This provides intra- and inter-chain structural stabilization (SI, Figure S4–S6 and Table S3). We expect that these hydrogen bonds play an important role for the structural stability of 1. This is supported by reference experiments where 4PBA was replaced by other boronic acids, including phenylboronic acid, 4-nitrobenzeneboronic acid and 3-pyridineboronic acid, where under identical experimental conditions, no related polymers were formed.

Detailed analysis of the protonation of the Dawson anion by BVS calculations suggest that in the bulk, the protons are not localized on specific (thermodynamically favoured) positions but are distributed across the complete oxo-shell of the cluster. The presence of an extensive H-bonding network along the 1D chains in 1a (Figure 2b) further led us to suggest that the protons in the compound could show mobility.

Recently, crystalline molecular materials including POMs\[36–38\] and coordination polymers (e.g. metal-organic frameworks)\[46\] have received immense attention as solid-state proton-conductors, owing to their possible role as solid-state electrolytes. However, the proton conductivity of covalently linked POM polymers has not been reported yet. To this end, we studied the proton conduction of 1 using alternating current electrochemical impedance spectroscopy (AC-EIS).\[37\] As proton conductivity is highly dependent on temperature and relative humidity (RH), we studied variations of these parameters (T = 20 °C to 90 °C, RH = 30% to 98%) on the resulting performance.\[42\] The values of bulk (R_{bulk}) and grain boundary resistances (R_{gb}) were obtained by fitting the EIS Nyquist plots using suitable equivalent circuit models (details see SI, Figure S1).\[43\] The bulk conductivity (\sigma_{bulk}) and total conductivity (\sigma_{total}) of 1 were calculated according to \( \sigma = h/(S \times R) \), where \( R \) is the resistance (Ohm), \( h \) is the thickness (in cm) of the sample pellet, and \( S \) is the cross-sectional area (in cm²) of the sample pellet. Further details see SI.

As shown in Figure 3a, at 98% RH and 20 °C, \( \sigma_{total} \) of 1 is 1.64 x 10⁻³ S cm⁻¹, while at 90 °C, \( \sigma_{bulk} \) is 1.59 x 10⁻³ S cm⁻¹ (\( \sigma_{total} = 7.78 \times 10^{-2} \) S cm⁻¹). As shown in the SI, Table S6, these values are amongst the highest proton conductivities for POM-based materials reported to-date. The temperature-dependent proton conductivity of 1 is summarized in Figure 3b, Figure S7 and Table S4: at RH = 98 %, the conductivity increases by more than two orders of magnitude when the temperature is increased from 20 to 90 °C. Both at 70°C and 20°C, the proton conductivity of 1 increases when RH is increased from 30 % to 98 %, see Figure 3c,d, S8 and S9. These results demonstrate that the proton conductivity of 1 is improved by increasing humidity as well as temperature. This suggests that the hydrogen bonding network and the lattice water molecules play a key role in the proton conduction in 1 (vide infra).

Next, we analysed the activation energy \( (E_a) \) of the proton transport in 1 based on the slope of the Arrhenius plot (Figure 3b) using the equation \( \sigma = \sigma_0 \exp(-E_a/kT) \). \( \sigma_0 \) is the pre-exponential factor and \( k \) is the Boltzmann constant. An activation energy of \( E_a = 0.66 \) eV was obtained. This value

Figure 2. a) Simplified rationalization of the inorganic polymer backbone of 1a showing the Dawson anions (teal) and boronic acid linkages (pink). Note that all linkages shown are M-O-M bridges (M = Nb or B). b) Example of the extended hydrogen-bonding network formed by water molecules (red spheres) around the B-OH groups (light blue spheres) of 4PBA. Red dashed lines: hydrogen bonds identified by intermolecular distances smaller than the sum of the van der Waals distance. Color Scheme see Figure 1, H-atoms have been omitted for clarity.
suggests that the proton transfer pathway of 1 is based on a so-called vehicle mechanism, that is, protons are transported by diffusion of “carrier molecules”, such as H$_3$O$^+$. This is also in line with the observation of increasing proton conduction at elevated temperature and humidity. In addition, we propose that the presence of a large number of cluster-bound protons (i.e. surface OH groups) as well as OH groups on the organoboronic acids could contribute to the high proton conductivity reported.

Finally, no change of the proton conductivity of 1 was observed over a monitoring period of 28 h (T = 90°C, RH = 98 %, see SI, Figure S10), indicating the stability of 1 under harsh conditions. This stability assessment is further supported by experimental data from IR, Raman and UV/Vis Diffuse reflectance spectroscopies (Figure S11–S15), powder X-ray diffraction (Figure S16), thermal analyses (Figure S17), XPS (Figure S18) and SEM/TEM images (Figure S19–21) of 1 before and after proton conduction experiments. All data suggest that the structural integrity of 1 is retained.

In summary, we demonstrate how organoboronic acids can be used to enable the polymerization of polyoxometalates into 1D chains in the solid-state. Initial insights into the polymerization processes are provided by spectroscopic and crystallographic analysis. The hybrid polymer features a purely inorganic polymer backbone with organic side-chains, which can in principle be further functionalized. The extensive hydrogen-bonding network in the crystal lattice is used as a basis for proton conduction in the crystal lattice, leading to high, temperature- and humidity-dependent proton conductivities. In future works, we will use in situ analyses to gain more detailed understanding of the self-assembly polymerization mechanisms and explore how further chemical modification of the organic moieties can be used to control material properties for applications including electrocatalysis, light-driven energy conversion and redox-switchable polymers.

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** boronic acid · organo-functionalization · polyoxometalate · self-assembly · supramolecular chemistry

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Polyoxometalate polymers with high proton conductivity are accessed for the first time by controlled covalent polymerization of Wells–Dawson-type niobotungstate and organoboronic acid monomers. The resulting polymer features a purely inorganic backbone, organic sidechains, and acts as a solid-state proton conductor.