

Supporting Information for:

Anhydrous Proton Conductivities of Squaric Acid Derivatives

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- I. General Information (S1-S2)
- II. Thermal Gravimetric Analysis (TGA) (S2)
- III. Differential Scanning Calorimetry (DSC) (S2-S3)
- IV. Proton Conductivity vs. time (S4)
- V. Cyclic Voltammetry (S5)

I. General Information

All reactions were carried out in oven-dried glassware (160 °C). The chemicals were purchased from major chemical suppliers and were used without further purification unless otherwise noted. Tetrahydrofuran was redistilled over sodium-benzophenone ketyl. Flash chromatography was performed using silica gel from Sorbent Technologies (Standard Grade, 60 Å, 40-63 μ m). Analytical thin layer chromatography was performed on pre-coated silica gel glass plate with visualization under UV light or staining in potassium permanganate solution. All ^1H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer and compared with the NMR, already reported in the literature (see main text).

TGA was carried out using a TA Instruments TGA 2950 thermogravimetric analyzer with a heating rate of 10 °C/min from room temperature to 500 °C under nitrogen.

Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo model DSC 822^c differential scanning calorimeter, where temperature and enthalpy were calibrated with In (430 K, 3.3 J/mol) and Zn (692.7 K, 12 J/mol) standard samples using sealed Al sample pans. Cooling and heating profiles were recorded and analyzed using the Mettler–Toledo STAR^c software system. Heating and cooling rates were 10 °C/min and 5 °C/min, respectively.

X-Ray scattering was done using an in-house setup from Molecular Metrology Inc. (presently sold as Rigaku S-Max3000). It uses a 30 W microsource (Bede) with a $30 \times 30 \mu\text{m}^2$ spot size matched to a Maxflux[®] optical system (Osmic) leading to a low-divergence beam of monochromatic CuK_α radiation (wavelength $\lambda=0.1542 \text{ nm}$). After passing beam defining and guard pinholes, the beam of about 0.4 mm diameter enters the sample chamber. Samples were placed within a hot stage connected to an Omega CN76000 temperature controller. WAXS is performed using an image plate (maximum resolution 50 μm) positioned in the sample chamber at a distance of 139 mm. The whole system is evacuated. The actual scattering angles are calibrated using the accurately known reflections from tricosane.

Impedance data were obtained using a Solartron 1260 frequency response analyzer in the range 0.1 Hz to 32MHz with a sinusoidal excitation voltage of 0.1 V root-mean-square amplitude. Vacuum dried samples were placed into a cavity ($L = 0.1 \text{ cm}$ long by $A = 0.07917 \text{ cm}^2$ cross-sectional area) between two custom brass electrodes, forming liquid seals at the ends of a PTFE tube. The sample's resistance to proton transport, R , was estimated by fitting a constant value to the plateau of impedance magnitude, which occurred within this frequency range. Conductivity was computed as $\sigma = L/(R \cdot A)$. Measurements were conducted with a home-built sample holder placed in a Cascade-TEK TVO-2 vacuum oven. Samples were heated under vacuum up to 120 °C, held for ~ 10 h, and allowed to cool to near ambient temperature, while conductivity was monitored at regular time intervals of ~ 0.5 h.

Cyclic voltammetry (CV) studies were done using a BAS CV-50 W instrument. CV was recorded with tetrabutylammonium hexafluorophosphate as a supporting electrolyte (0.1 M) in acetonitrile with platinum as the working electrode. The redox potentials were determined versus an Ag/Ag^+ reference electrode. The working and auxiliary electrodes were cleaned after each run. In these conditions, the redox potential of Fc/Fc^+ ($\text{Fc} =$ ferrocene) was +0.09 V *versus* Ag/Ag^+ .

II. Thermal Gravimetric Analysis (TGA)

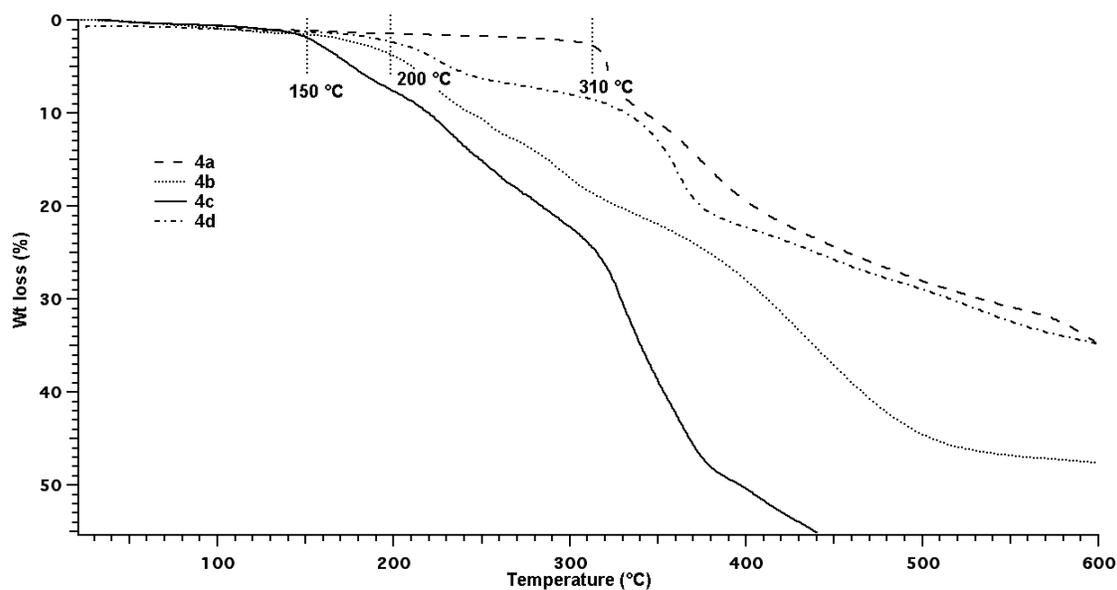
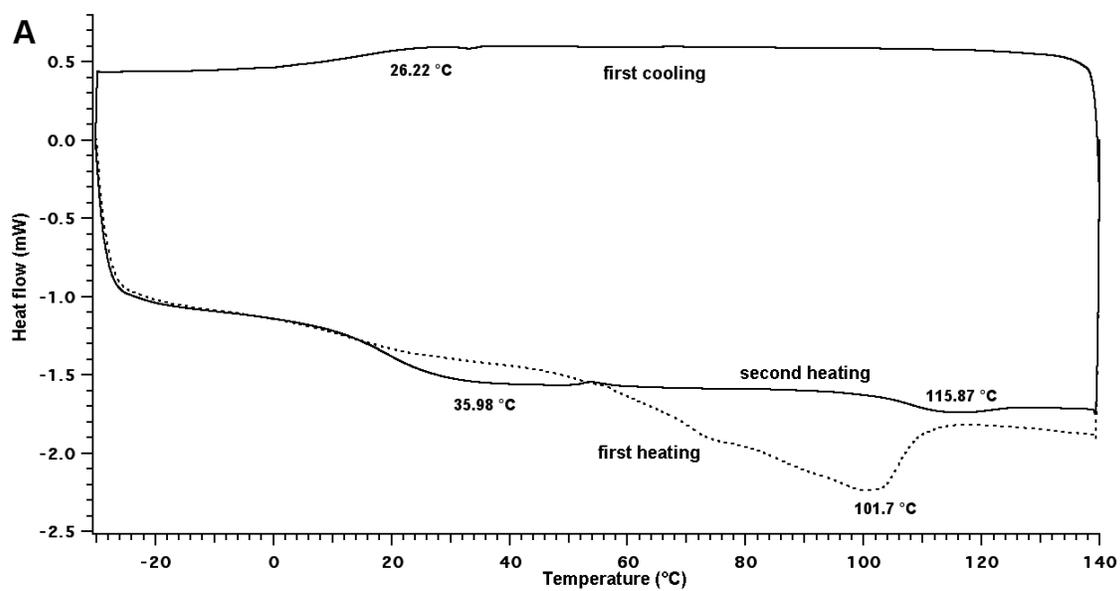


Fig. S1 Thermogravimetric Analysis (TGA) of **4a-4d** (heating rate 10 °C/min).

III. Differential Scanning Calorimetry (DSC)



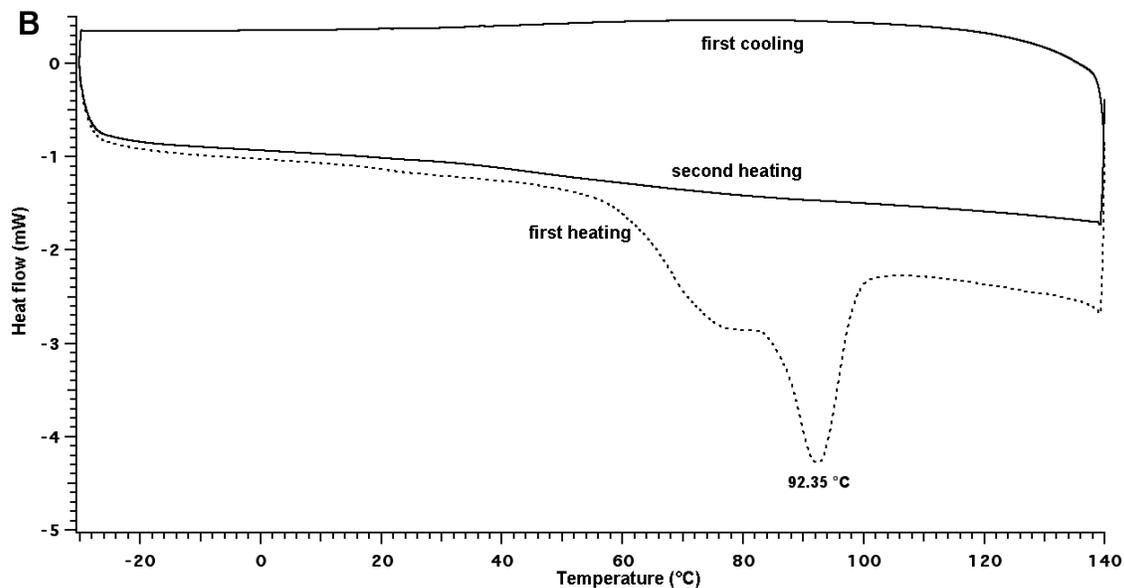


Fig. S2: a) Differential scanning calorimetric traces for compounds **4b** (A) and **4c** (B) from the first heating/cooling and second heating cycle. The heating and cooling rates were 10 °C/min and 5 °C/min, respectively.

IV. Proton Conductivity vs time

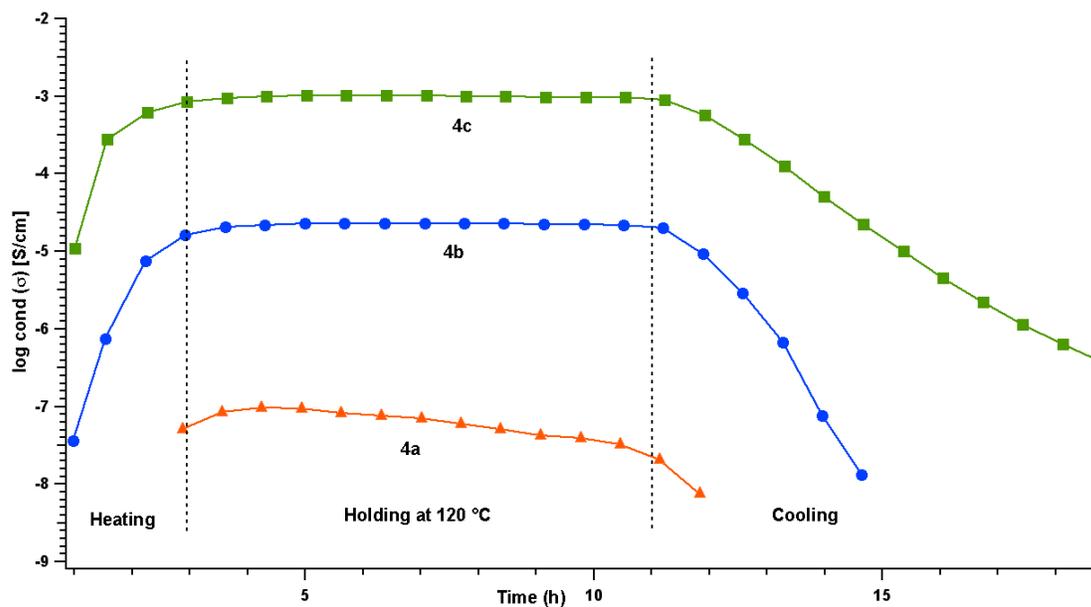


Fig. S3 Monitoring proton conductivities of **4a**, **4b** and **4c** vs. time.

V. Cyclic Voltammetry (CV)

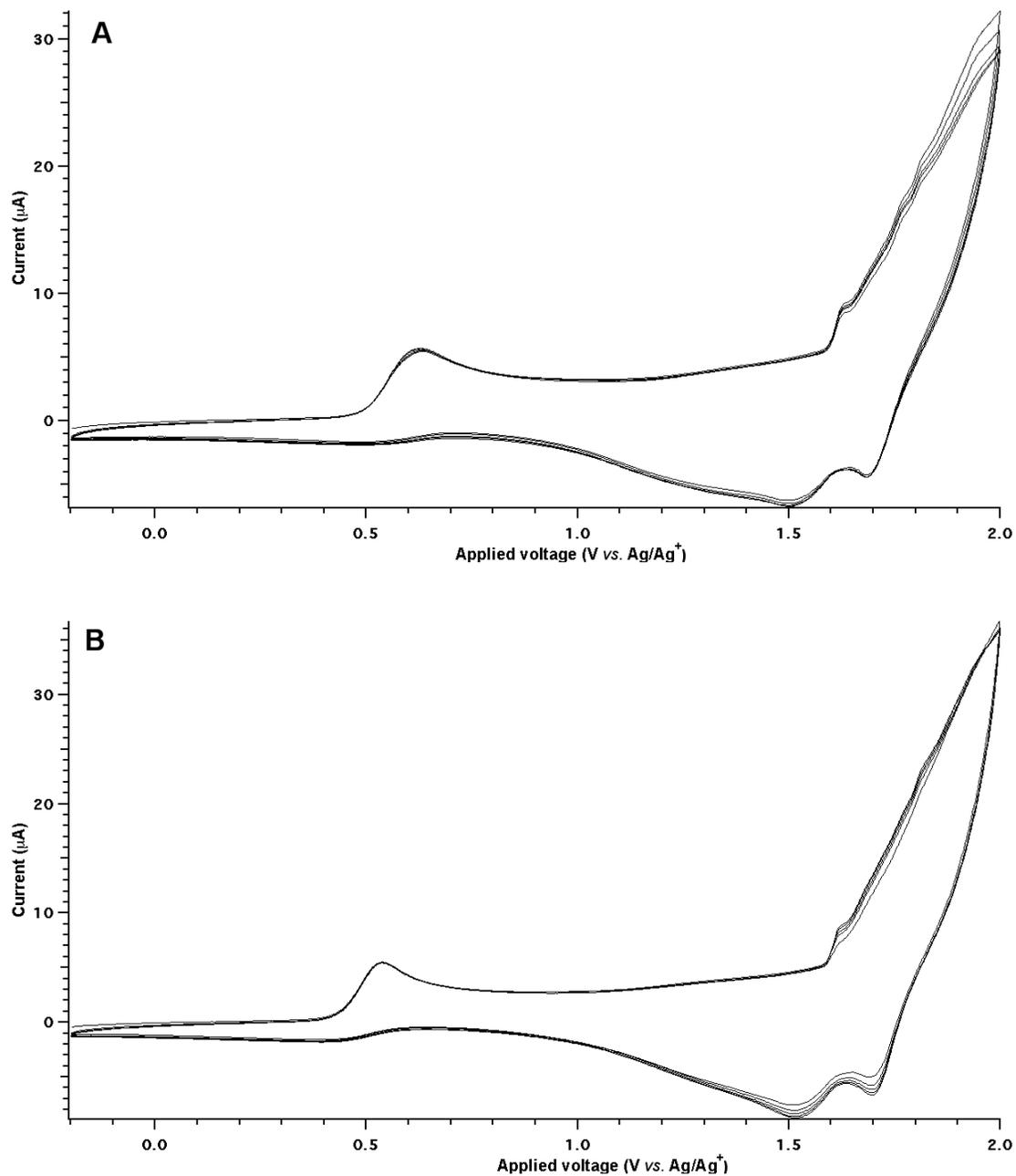


Fig. S4 Cyclic voltammograms of **4b** (A) and **4c** (B) were recorded at 1×10^{-3} M concentration in 0.1 M $\text{TBAPF}_6\text{-CH}_3\text{CN}$ solution at 25 °C. The scan rate was 100 and ten subsequent cycles were recorded.