Electronically Supplementary Information for:

Fast proton conductors for low humidity: hydrophilic sulfonated and phosphonated polysilsesquioxanes with Al–O–P crosslinks

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Experimental procedure

Dilute hydrochloric acid was added at once promptly to a mixture of (3-sulphanylpropyl)trimethoxysilane (3-SPTMS, 8 mmol, Tokyo Chemical Industry) and (2-diethylphosphatoethyl)triethoxysilane (DPTES, 2 mmol, Gelest) at a 3-SPTMS : DPTES : H_2O : HCl molar ratio of 0.8 : 0.2 : 3 : 0.002 and stirred in a sealed container at 20 °C for 3 h. The resulting solution was aged at 80 °C for 1 day without stirring, followed by drying at 60 °C for 3 h in air and 1 day under vacuum. The resulting viscous liquid **1** was oxidized by mixing with 30 wt% hydrogen peroxide (Fujifilm Wako Pure Chemical) at an S : H_2O_2 molar ratio of 1 : 5 and stirring the mixture at 20 °C for 2 days. Afterward, excess H_2O_2 was decomposed by immersing a Pt plate in this solution, which was subsequently dried to obtain **2** in powder form. Aluminum (III) chloride hexahydrate (Fujifilm Wako Pure Chemical) and phosphoric acid (PA, Fujifilm Wako Pure Chemical) were dissolved in water and **2** was added at a Si : Al : PA molar ratio of 1 : z_{Al} : z_{PA}. The mixture was heated at 100 °C for 2 days in a sealed container, followed by drying at 100 °C for 1 day in air. The samples used for the conductivity measurements were obtained by dissolving the resulting solid in water and drying the solution at 60 °C for 1 day in air. The resulting samples were referred to as the combination of z_{Al} and z_{PA}, i.e., (z_{Al}, z_{PA}).

As reference materials for X-ray diffraction (XRD) and attenuated total reflection Fourier transform infrared (ATR-FT-IR) measurements, poly(R-SQ)s with 3-sulphanylpropyl groups (poly(3-SP-SQ)) and n-propyl groups (poly(Pr-SQ)) were prepared. Dilute hydrochloric acid was added to 3-SPTMS or n-propyltrimethoxysilane (Tokyo Chemical Industry) at an alkoxysilane : H_2O : HCl molar ratio of 1 : 3 : 0.002, followed by stirring, aging, and drying under the same conditions as those used for the preparation of **1**.

Liquid-state ^1H, ^{29}Si, and ^{31}P nuclear magnetic resonance (NMR, JNM-ECS300, JEOL) spectra were recorded in a single pulse sequence with pulse flip angles of 45, 30, and 30°, respectively, and relaxation delays of 5, 20, and 5 s, respectively. Gel permeation chromatography (GPC) was performed using a Shodex KF-804L column, refractive index detector (RID-10A, Shimadzu), and tetrahydrofuran as the eluent (flow rate of 1.0 mL min^{-1}). Molar mass distribution curves were derived using standard polystyrene samples and were used to calculate

the number- and mass-average molar masses (M_n and M_m, respectively). X-ray diffractometers (RINT-TTR III, Rigaku and NanoViewer, Rigaku) were used to measure XRD and small-angle X-ray scattering (SAXS) patterns with Cu $K\alpha$ radiation. The resulting diffraction patterns were plotted as a function of scattering vector $Q = 4\pi \sin\theta / \lambda$. ATR-FT-IR measurements were conducted at room temperature with a FT-IR spectrometer (FT/IR-6100, JASCO) and an ATR attachment with a diamond prism (ATR PRO670H-S). Before the ATR-FT-IR measurements, several samples were subjected to heat treatment up to 200 °C for 24 h in air. Simultaneous thermogravimetric and differential thermal analyses (TG-DTA, STA-7300, Hitachi) were performed at a heating rate of 10 °C min^{-1} in air in a platinum pan containing ~8 mg of powdered sample. The ac conductivity was evaluated using an electrochemical analyzer (SP-200, Bio-Logic) with a frequency range from 200 kHz to 1 Hz and an ac amplitude of 50 mV. Temperature was maintained between 40 and 120 °C in a conventional air-circulating oven (DKM300, Yamato) in air without humidity control (relative humidity of ~20 %RH at 40 °C and ~1 %RH at 120 °C). The sample (~1–2 mm thick) was sandwiched with Au electrodes (5 mmϕ) and equilibrated at each temperature by maintaining 1 h prior to the measurement. Resistance R was obtained from the intercept of the extrapolation of the Nyquist plot on the real axis, and ac conductivity σ_{ac} was calculated from the equation $\sigma_{ac} = t/(RA)$, where t is sample thickness and A is electrode area.
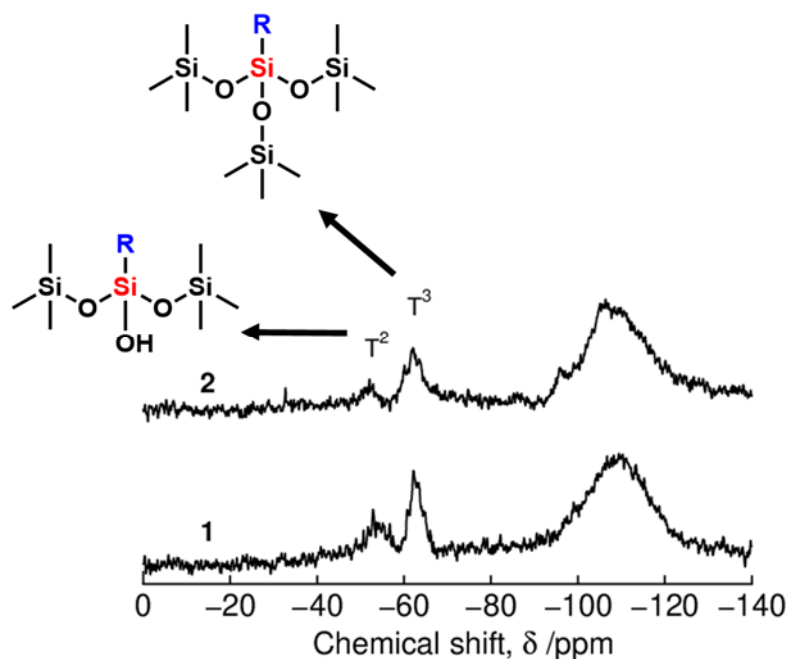
Fig. S1 ^{29}Si NMR spectra of **1** (59.6 MHz, CDCl$_3$) and **2** (59.6 MHz, D$_2$O). The broad signal peaked at −110 ppm originates from the silica sample tube. The superscripts in T denote the number of bridging oxygen atoms bonded to the respective T (or SQ) units.

Table S1 Fractions of T^1, T^2, and T^3 units (f_{T1}, f_{T2}, and f_{T3}, respectively), average number of bridging oxygen atoms per Si ($<m>$) evaluated from the equation $<m> = f_{T1} + 2f_{T2} + 3f_{T3}$, fractions of residual SiOMe, SiOEt, and SiOH groups (f_{SiOMe}, f_{SiOEt}, and f_{SiOH}, respectively) of **1** and **2**. The fraction of SiOH groups (f_{SiOH}) was calculated based on the prediction that oxygen atoms bonded to Si belong to either the bridging oxygen atoms, residual SiOMe or SiOEt groups, or SiOH groups ($f_{SiOH} = 1 − <m>/3 − 0.8f_{SiOMe} − 0.2f_{SiOEt}$).

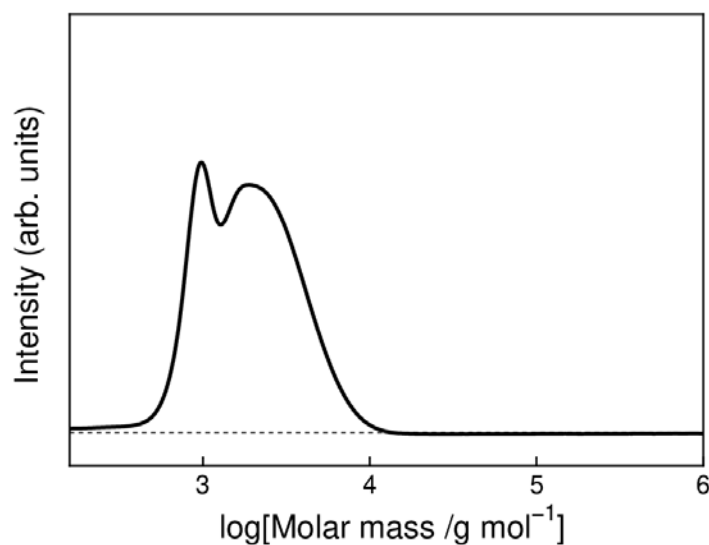| Sample	f_{T1}	f_{T2}	f_{T3}	$<m>$	f_{SiOMe}	f_{SiOEt}	f_{SiOH}
1	–	0.35	0.65	2.65	0.01	0.06	0.10
2	–	0.32	0.68	2.68	0.00	0.00	0.11

Fig. S2 Polystyrene-equivalent molar mass distribution curve of **1**.

Table S2 The peak assignments of ^{31}P NMR spectra shown in Fig. 3(a) on the basis of the assignments reported in refs. 1 and 2.

Peak	Assignment
A	Free phosphoric acid molecules and ions, H_3PO_4, $H_2PO_4^-$, $H_6P_2O_8$, $H_5P_2O_8^-$
B	P nuclei in H_3PO_4 molecules bonded to Al and hydrogen-bonded to other H_3PO_4 molecules, $[Al(H_3PO_4)(H_3PO_4)_n]^{m+}$, ($n \geq 1$, m is undetermined)
C	P nuclei in $H_2PO_4^-$ ligands complexed to Al, $[Al(H_2PO_4)]^{2+}$ and $[Al(H_2PO_4)_2]^+$
D	P nuclei in H_3PO_4 complexed to Al, $[Al(H_3PO_4)]^{3+}$
B'	P nuclei in $RPO(OH)_2$ groups bonded to Al and hydrogen-bonded to other $RPO(OH)_2$ groups and H_3PO_4 molecules, $[Al(RPO(OH)_2)(RPO(OH)_2)_n(H_3PO_4)_l]^{m+}$, ($n + l \geq 1$, m is undetermined)
C'	P nuclei in $RPO_2(OH)^-$ ligands bonded to Al, $[Al(RPO_2(OH))]^{2+}$, $[Al(RPO_2(OH))_2]^+$, and $[Al(RPO_2(OH))(HPO_4)]^+$
D'	P nuclei in $RPO(OH)_2$ groups complexed to Al, $[Al(RPO(OH)_2)]^{3+}$

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Table S3 Appearances of samples prepared at various (z_{Al}, z_{PA}) values; −: brittle, +: flexible but not tough, ++: flexible and tough, L: liquid. The sample denoted as (z_{Al}, z_{PA}) = (0, 0) is identical to **2**.

z_{Al}	z_{PA}					
	0	0.2	0.3	0.4	0.5	0.6
0	−	+			L	
0.2		++	++	++	++	L
0.3		−	++	++	++	
0.4	−	−	++	++	++	

$(z_{Al}, z_{PA}) =$ (0, 0) (**2**) (0.4, 0.2) (0, 0.2) (0.2, 0.2) (0.2, 0.5)
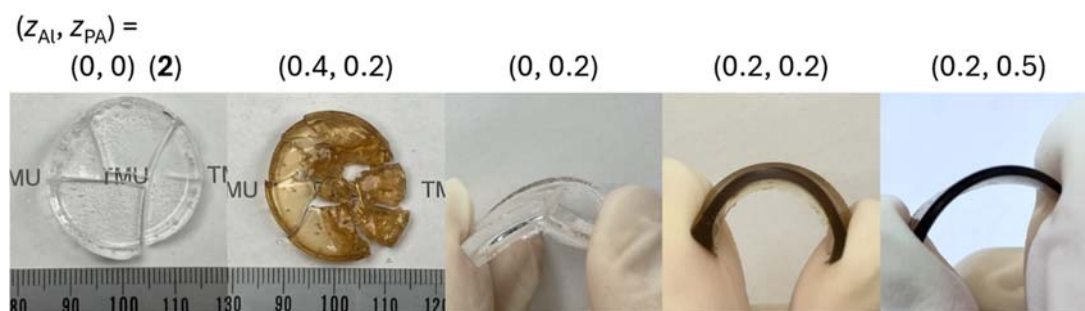
Fig. S3 Typical appearance of samples listed in Table S3. The samples prepared at (z_{Al}, z_{PA}) = (0, 0) (**2**) and (0.4, 0.2) were brittle and fractured easily. The sample prepared at (z_{Al}, z_{PA}) = (0.2, 0) was soft but not tough, and split upon bending. The samples prepared at (z_{Al}, z_{PA}) = (0.2, 0.2) and (0.2, 0.5) were flexible and tough.
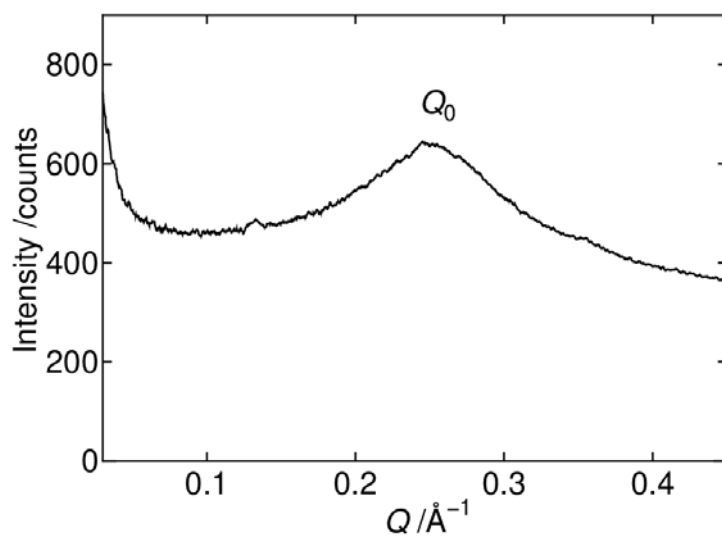
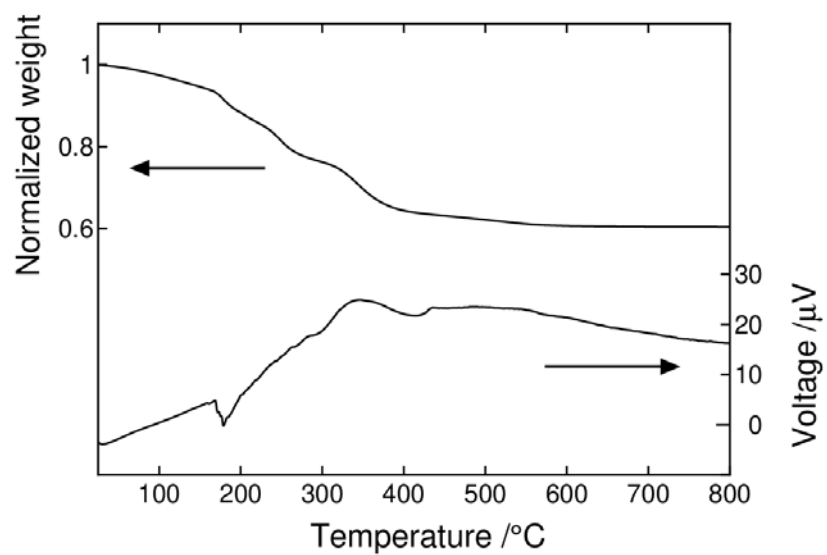**Fig. S4** SAXS pattern of the sample prepared at (z_{Al}, z_{PA}) = (0.2, 0.5).

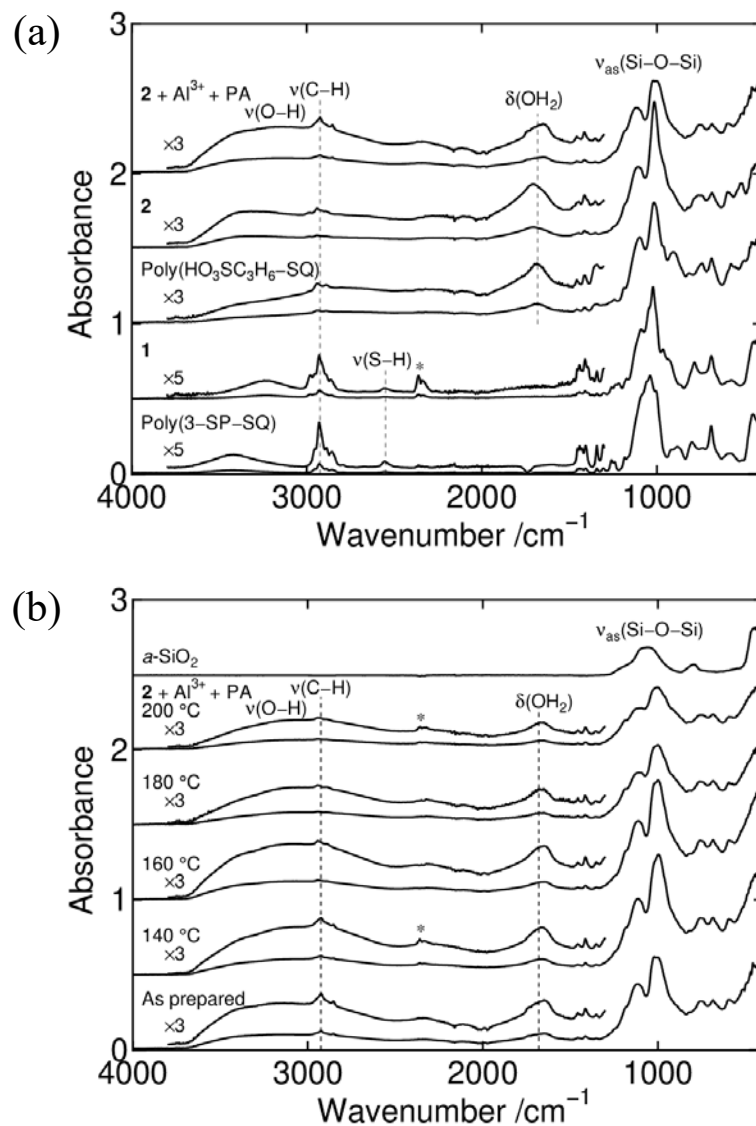**Fig. S5** TG-DTA curves of the sample prepared at (z_{Al}, z_{PA}) = (0.2, 0.5).

Fig. S6 ATR-FT-IR spectra of samples measured at room temperature. Successive curves have shifted ordinates. Spectra magnified 3 or 5 times are also shown between 1300 and 3800 cm^{-1}. The asterisks at ~2350 cm^{-1} indicate the absorption band of CO_2 in air. (a) Poly(3-SP-SQ), **1**, poly(HO$_3$SC$_3$H$_6$-SQ) (oxidation product of poly(3-SP-SQ)), **2**, and the sample prepared by mixing **2** with Al^{3+} ions and PA at (z_{Al}, z_{PA}) = (0.2, 0.5). (b) The sample prepared by mixing **2** with Al^{3+} ions and PA at (z_{Al}, z_{PA}) = (0.2, 0.5); as prepared one and those subjected to heat treatment at designated temperatures for 24 h in air. A spectrum of amorphous SiO$_2$ (a-SiO$_2$) powder is also shown for comparison.
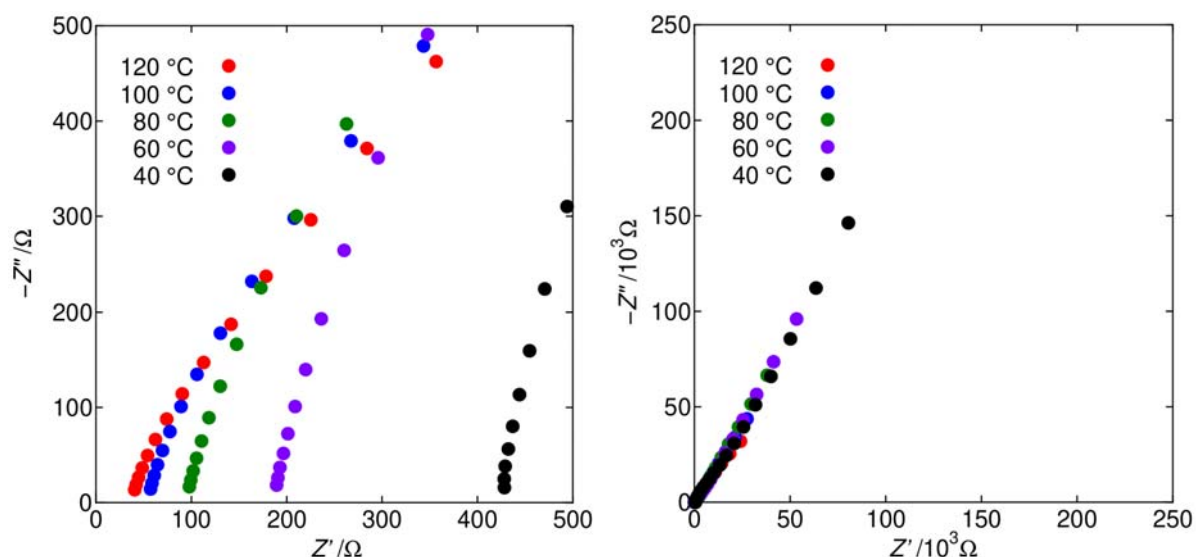
Fig. S7 Magnified (left) and full-range (right) Nyquist plots of the sample prepared at (z_{Al}, z_{PA}) = (0.2, 0.5).
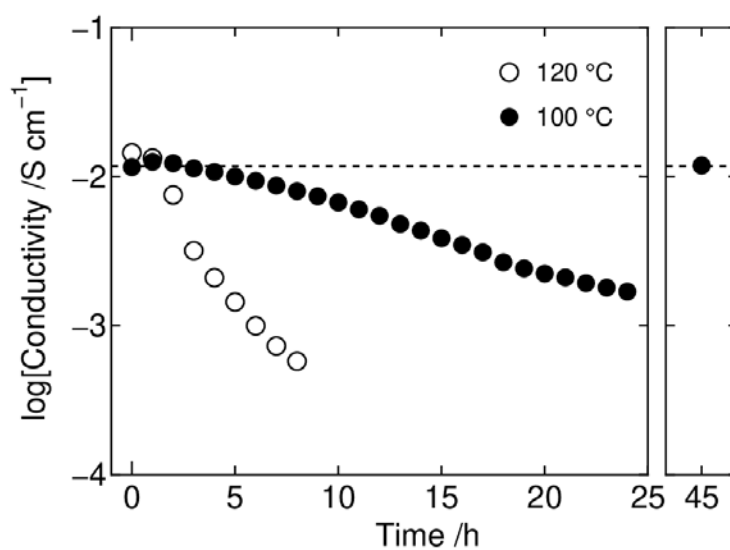

Fig. S8 Variation of ac conductivity at 100 and 120 °C with time of the samples prepared at (z_{Al}, z_{PA}) = (0.2, 0.5) similarly to the one shown in Fig. 4. The right panel shows the conductivity at 100 °C after rest at room temperature for ~20 h of the sample subjected to the conductivity measurement at 100 °C for 24 h (left panel). Prior to starting measurements at t = 0 and 45 h, each sample was equilibrated at respective temperature by maintaining for 1 h. At 120 °C, vapor bubbles were formed between the sample and Au electrodes at ~2 h. They deformed the sample, and resulted in the partial loss of electrical contact and a sudden conductivity decrease.

References

1 J. W. Akitt, N. N. Greenwood and G. D. Lester, *J. Chem. Soc. A*, 1971, 2450–2457.
2 R. F. Mortlock, A. T. Bell and C. J. Radke, *J. Phys. Chem.*, 1993, **97**, 767–774.