Supporting Information

Local Coordination and Dynamics of a protic Ammonium based Ionic Liquid Immobilized in Nano-porous Silica probed by Raman and NMR Spectroscopy

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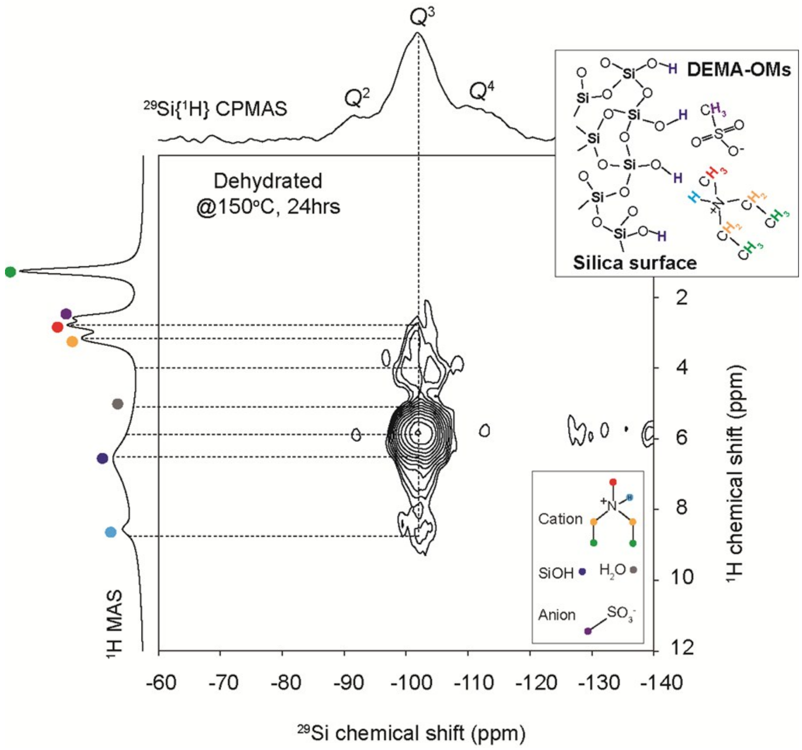

Fig. SI1 2D solid-state $^{29}Si\{^{1}H\}$ HETCOR NMR spectrum of the silica/DEMA-OMs gel with ΦSiO_2 = 0.68, or 25% pore filling, dehydrated at 150 °C for 24 hours. NMR spectra were collected on a Varian NMR spectrometer at a magnetic field of 14.1 T and at a MAS rate of 10 kHz.

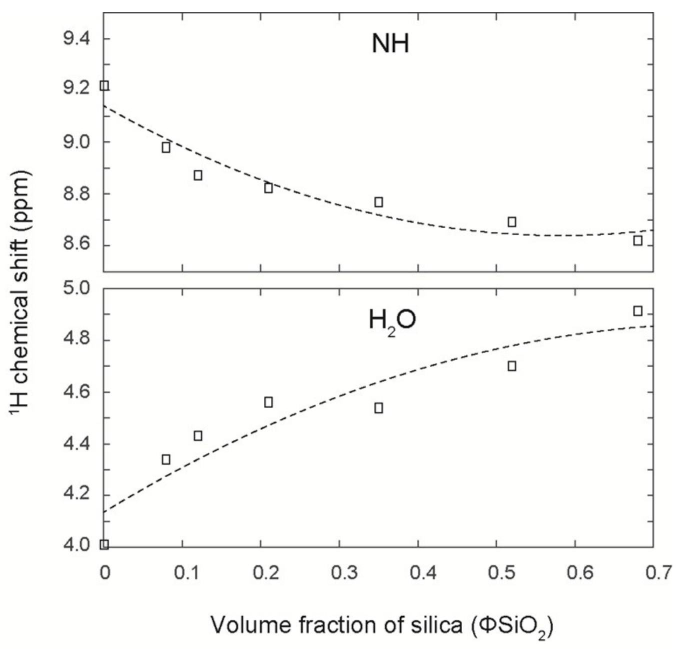

Fig. SI2 ^1H NMR chemical shifts of the NH and H_2O NMR peaks plotted against the volume fraction of silica (ΦSiO_2).

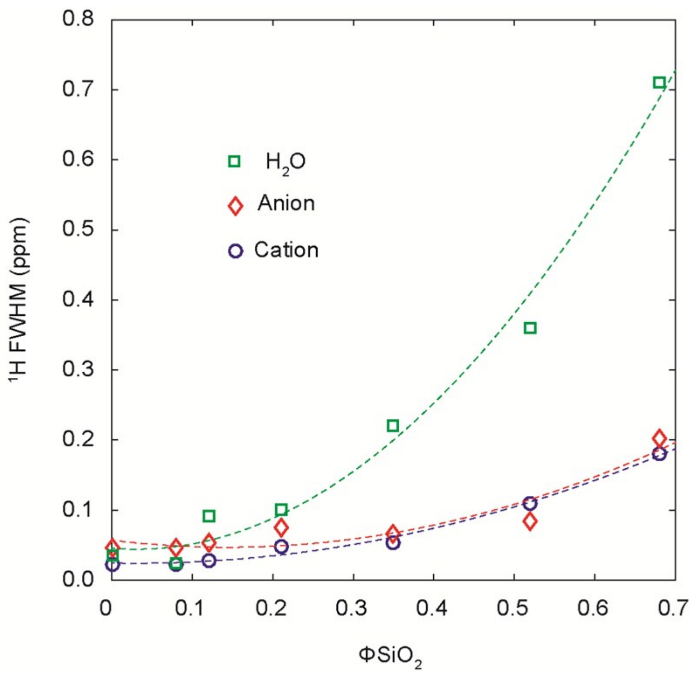

Fig. SI3 ^1H NMR full width at half maximum (FWHM) of the NMR peaks assigned to H_2O, anion, and cation (average) plotted against the volume fraction of silica (ΦSiO_2).

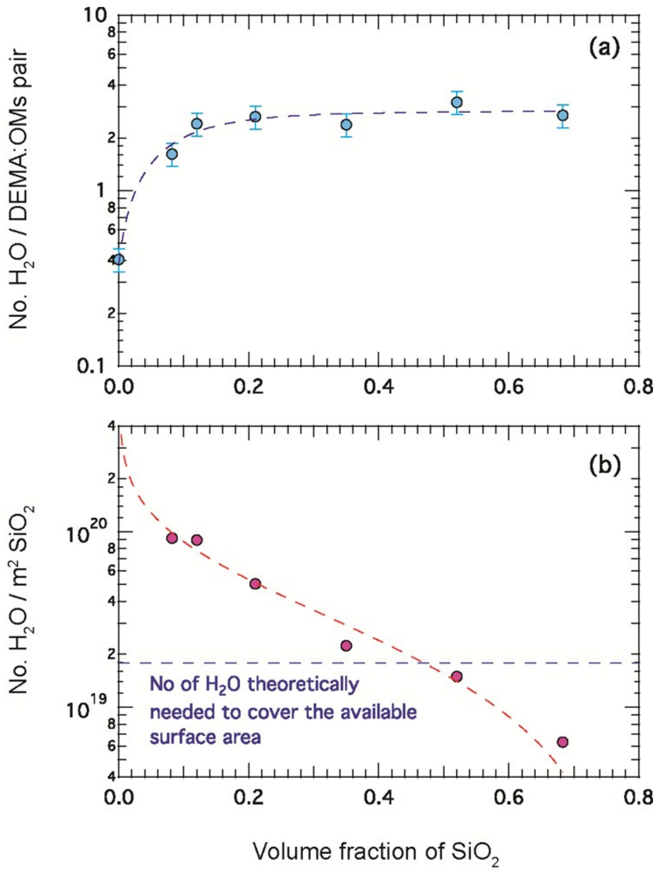

Fig. SI4 Number of water molecules actually present in the gels as estimated from the integrated areas in the ^{1}H solid-state NMR spectra, shown as number of H_2O molecules per DEMA:OMs pair (a) and converted to number of H_2O molecules per surface area of silica (b).

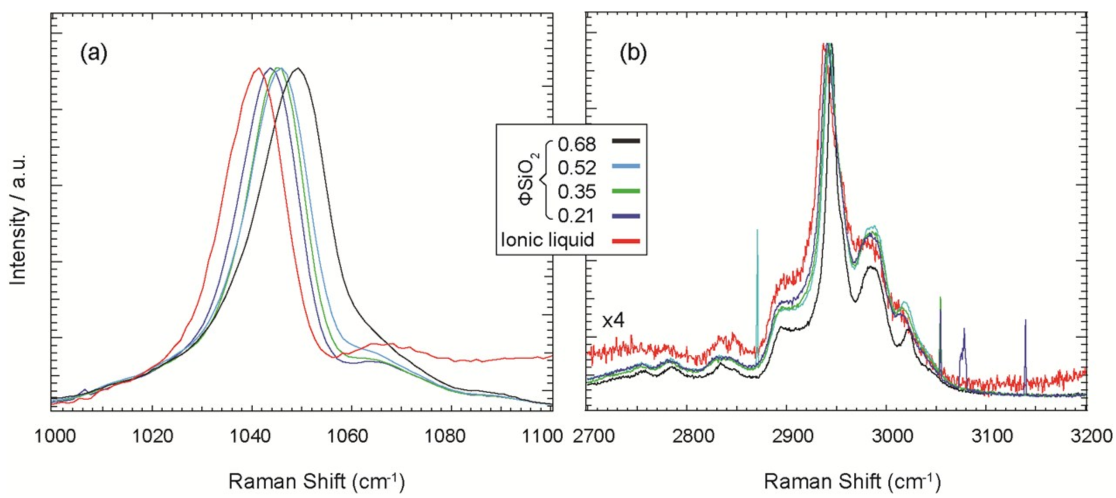

Fig. SI5 Raman spectra of silica/DEMA-OMs gels in the region of (a) 1000-1100 cm^{-1} and (b) 2700-3200 cm^{-1}.

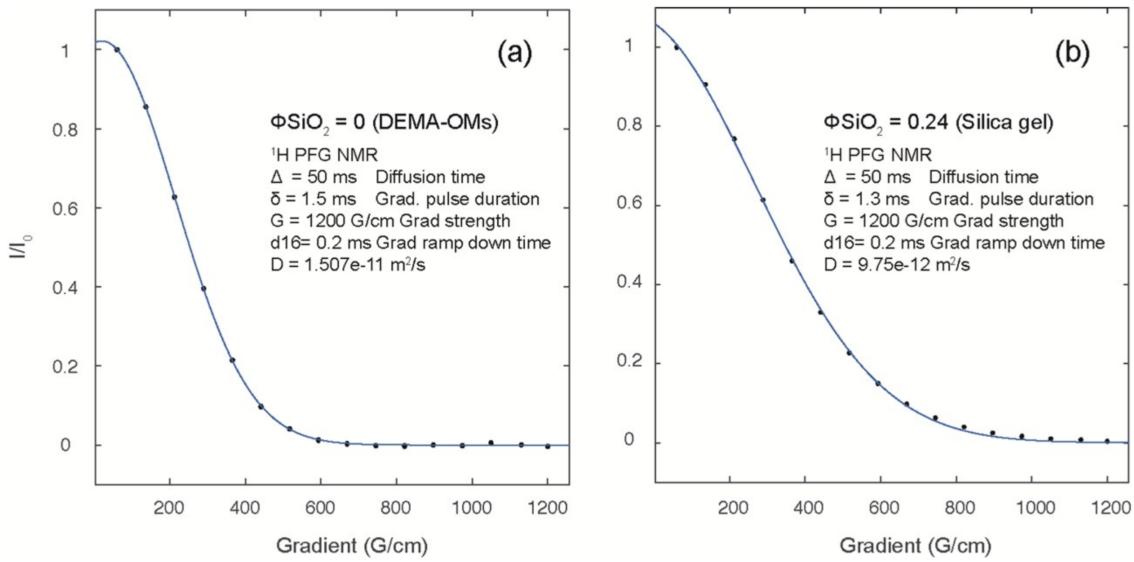

Fig. SI6 A representative plot of I/I_0 vs G of (a) DEMA-OMs and (b) silica gel (ΦSiO_2=0.24) extracted from ^{1}H peak at 1.3 ppm that is assigned to the methyl group of the cation. Detailed experimental conditions are also given. The diffusion measurements were performed on a 600 MHz Bruker NMR spectrometer.

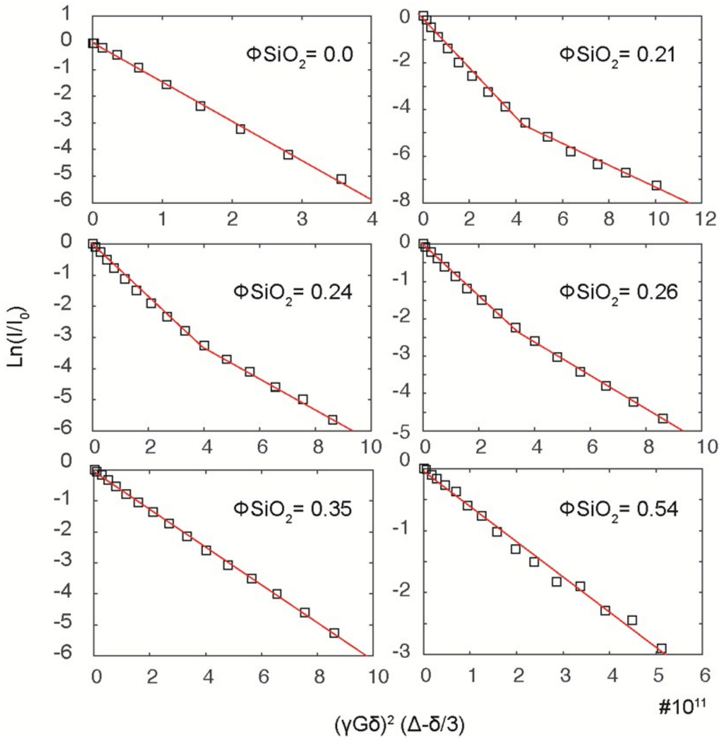

Fig. SI7 Plot of the attenuated intensity versus gradient component showing a bi-exponential dependence for gels with ΦSiO_2 = 0.21, 0.24, and 0.26, and a single exponential dependence for the gels with ΦSiO_2 = 0, 0.35 and 0.54.

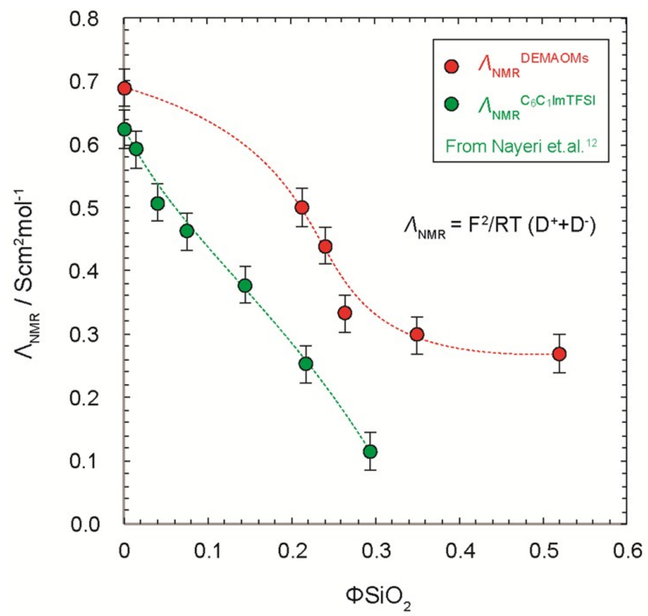

Fig. SI8 Molar conductivity (Λ_{NMR}) of silica gels (red) plotted against ΦSiO_2 and calculated from the self-diffusion coefficients (D) using the Nernst-Einstein equation. For comparison, Λ_{NMR} values calculated from the D values of C_6C_1ImTFSI in sol-gel prepared silica gels (Nayeri et.al. reference 12) are also reported (green). Red and green short-dashed lines are guide to the eye.

Volume fraction of silica (φ_{Sio_2})

$$\varphi_{Sio_2} = \frac{V_{SiO_2}}{V_{SiO_2} + V_{IL}}$$

ρ_{SiO_2} = 2.2 g/cm^3 and ρ_{IL+H_2O} = 1.096 g/cm^3

Conversion from pore filling (%) to volume fraction (φ_{SiO2}).

Silica particles contain 65% of free space, and 35% of dense silica matrix.

V_{SiO_2} = 35, V_{IL} => $V_{Free\ space}$ = n 65, where n = % of pore filling

For 200% pore filling, $\varphi_{Sio_2} = \dfrac{35}{35 + \frac{200}{100}65} = 0.21$

For 100% pore filling, $\varphi_{Sio_2} = \dfrac{35}{35 + \frac{100}{100}65} = 0.35$

For 50% pore filling, $\varphi_{Sio_2} = \dfrac{35}{35 + \frac{50}{100}65} = 0.51$

For 25% pore filling, $\varphi_{Sio_2} = \dfrac{35}{35 + \frac{25}{100}65} = 0.68$

Percentage of pore filling

Silica particles contain 65% of free space, and 35% of dense silica matrix.

Nanoporous silica => x grams ρ_{SiO_2} = 2.2 g/cm^3
DEMA-OMs => y cm^3

Dense volume = x g/2.2 gcm^{-3}
From above: Free space/Dense volume = 65/35 => Free space = 65/35 (x g/ 2.2 gcm^{-3})

Hence, the amount of DEMA-OMs (in cm^3) required for complete pore filling (i.e. 100% pore filling) would be

$$y = \frac{65\ (x/2.2)}{35} \Rightarrow 0.8441 \cdot x\ (\text{cm}^3)$$

Amount of DEMA-OMs required 200% pore filling => $y = 1.6882 \cdot x$ (cm^3)
Amount of DEMA-OMs required 50% pore filling => $y = 0.422 \cdot x$ (cm^3)
Amount of DEMA-OMs required 25% pore filling => $y = 0.211 \cdot x$ (cm^3)

Conductivity of silica gels (σ_{NMR})

$$\Lambda_{NMR} = \frac{F^2}{RT}(D^+ + D^-)$$

$$\text{Molarity (M)} = \frac{\text{Moles of ionic liquid}}{\text{Volume of ionic liquid}} \times 1000\ /\text{litre}$$

$$= \frac{\dfrac{\text{Mass of ionic liquid}}{\text{Molecular weight}}}{\text{Volume of ionic liquid}} \times 1000\ /\text{litre}$$

$$\text{Molarity (M)} = \frac{\text{Density } (\rho)}{\text{Molecular weight}} \times 1000\ /\text{litre}$$

$$\sigma_{NMR} = \Lambda_{NMR}\, M \cdot \text{ionicity}$$

Faraday's constant (F) = 96485.3365 s A / mol
Gas constant (R) = 8.31446 J/Kmol
Room temperature (T) = 298 K
Density (ρ) g/cm^3
Diffusion coefficients (D) m^2/s
Molarity (M) moles/litre
Molar conductivity (Λ_{NMR}) $S.cm^2/mol$
Conductivity (σ_{NMR}) mS/cm
Ionicity = 0.6 (from reference 32)