

Supporting Information for the article:

Role of the ionic liquid $C_6C_1\text{ImTFSI}$ in the sol-gel synthesis of silica studied by *in situ* SAXS and Raman spectroscopy[‡]

Moheb Nayeri^{*a} Kim Nygård,^b Maths Karlsson,^c Manuel Marechal,^d Manfred Burghammer,^e Michael Reynolds,^e and Anna Martinelli^{*a}

In what follows seven supplementary figures (Fig. SI-I – Fig. SI-VII) are provided, which are referred to in the main text of the manuscript.

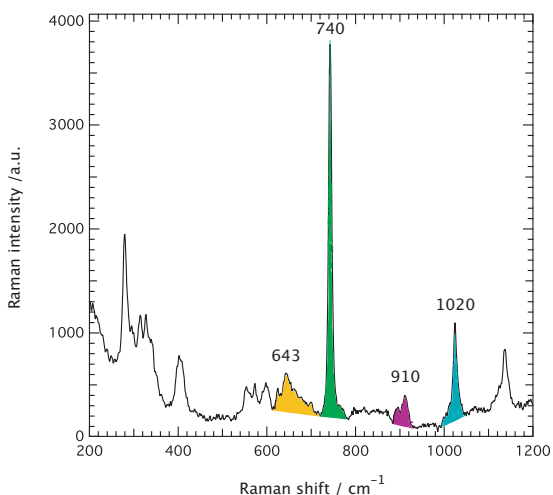


Fig. SI-I. This figure shows the typical Raman spectrum of an ionogel containing the ionic liquid 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, $C_6C_1\text{ImTFSI}$. The Raman vibrations arising from TMOS (643 cm^{-1}), the TFSI anion (740 cm^{-1}), methyl formate (910 cm^{-1}), and methanol (1020 cm^{-1}) are emphasized in color. The colored areas correspond to the integrated Raman intensities, which we monitor as a function of time to investigate the reaction evolution.

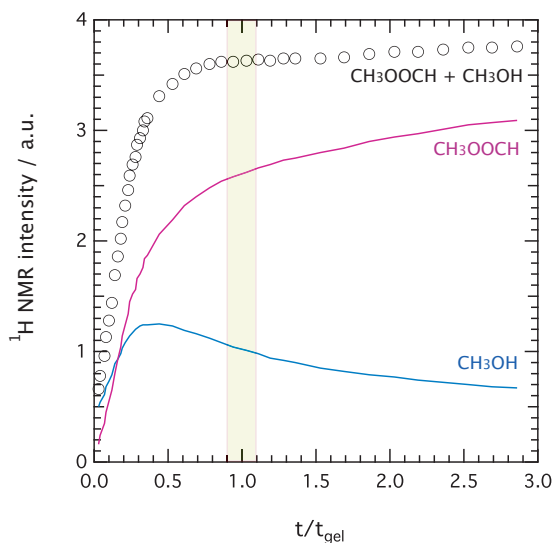


Fig. SI-II. This figure shows the ^1H NMR intensities previously reported in reference [19] for $x=1$ and here revisited to show the dependence on time of the added intensities (black) of the polar molecules methanol (blue) and methyl formate (purple).

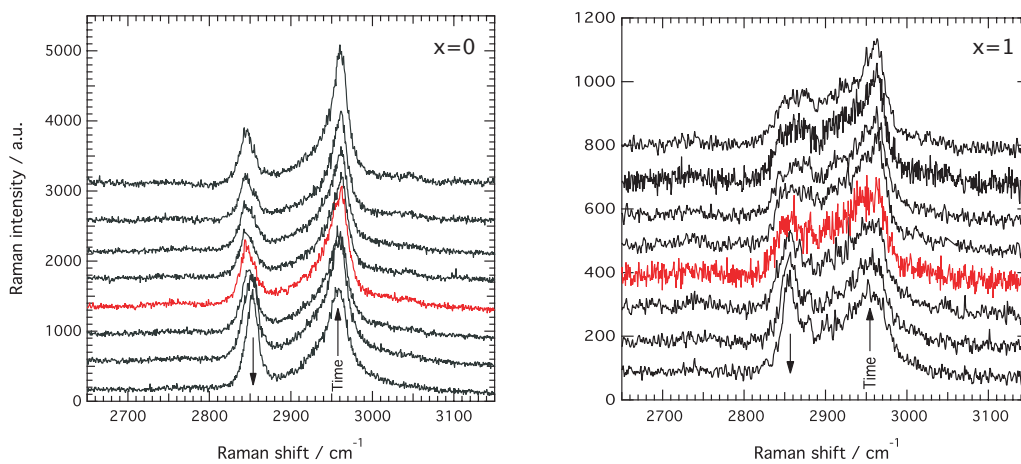


Fig. SI-III. This figure shows the time evolution of the Raman spectra recorded for $x=0$ and $x=1$ in the C–H stretching region. As reaction time progresses (see arrows), the low-frequency component mainly attributed to TMOS decreases with respect to the high-frequency one, which contains also contributions from methanol and methyl formate. Raman spectra recorded at the time of gelation are shown in red.

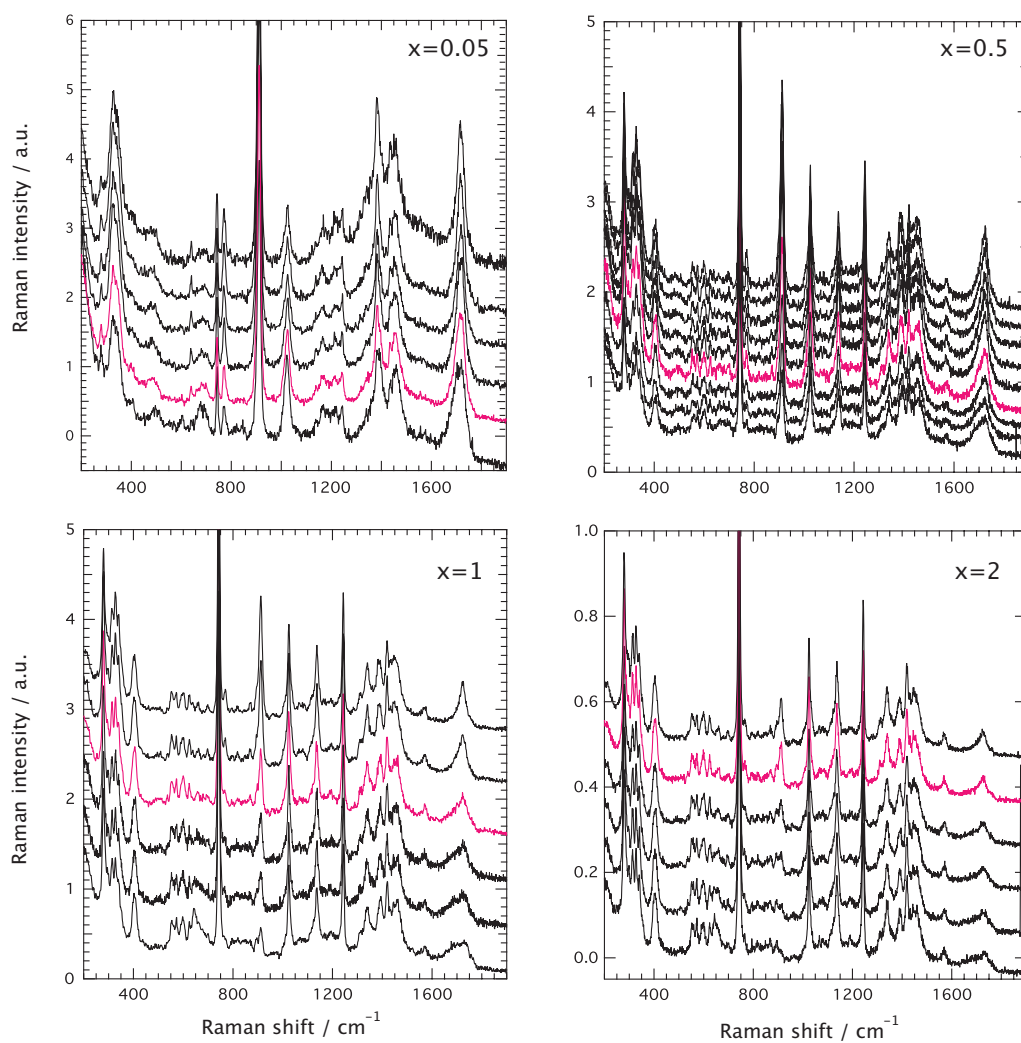


Fig. SI-IV. This figure shows the time evolution of the Raman spectra recorded for solutions with different ionic liquid content, *i.e.* for $x=0.05$ (top-left), $x=0.5$ (top-right), $x=1$ (bottom-left), and $x=2$ (bottom-right). The Raman spectra recorded at the time of gelation, that is at t_{gel} , are shown in red.

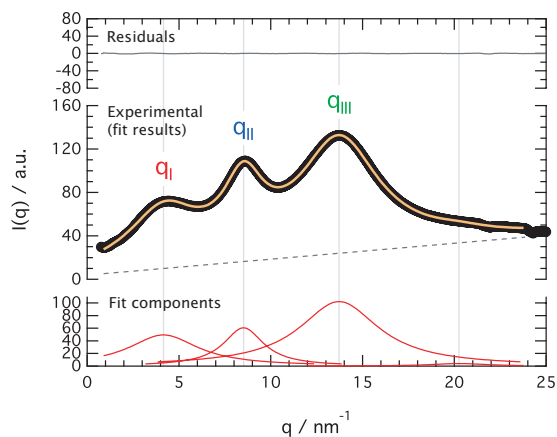


Fig. SI-V. This figure shows the peak-fit procedure employed to model the x-ray diffraction pattern of the ionic liquid $C_6C_1ImTFSI$. Three Lorentzian functions are used to account for the three peaks (q_I , q_{II} , and q_{III}) associated to non-polar and polar domains, and to tail-to-tail correlations, respectively. As can be deduced from the residual trace, this model describes very well the experimental data.

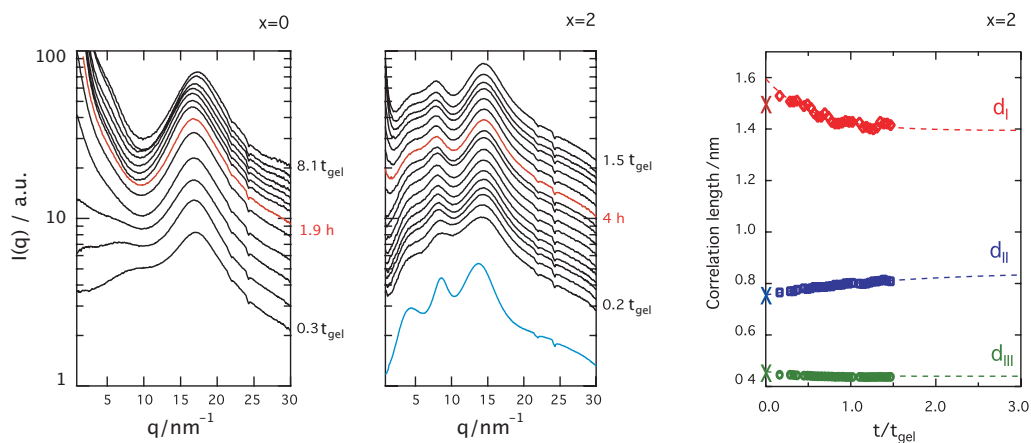


Fig. SI-VI. This figure shows the time evolution of the SAXS pattern for the sample with no ionic liquid ($x=0$) and a sample with $x=2$. For the latter, the correlation lengths are also shown (right-most plot).

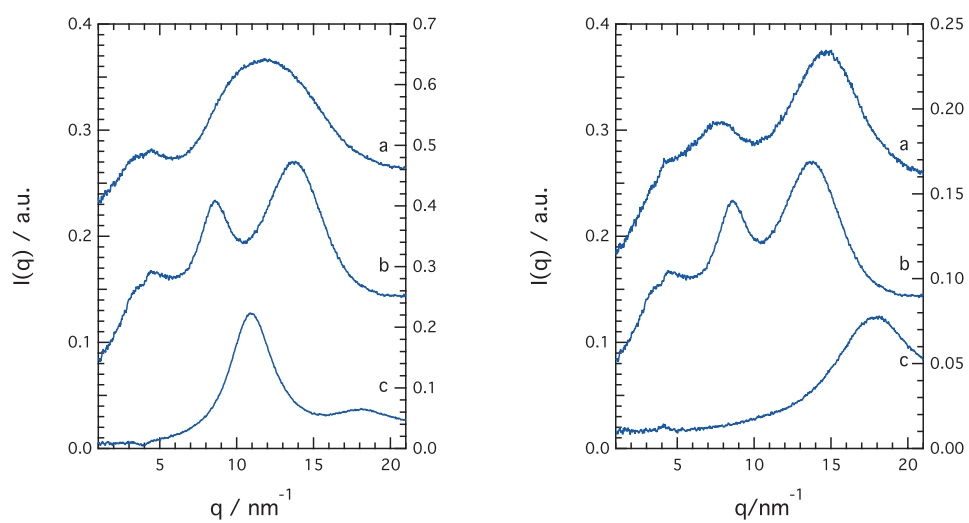


Fig. SI-VII. This figure shows the x-ray diffraction patterns recorded for the binary mixture $C_6C_1\text{ImTFSI:TMOS}$ (left, a) and $C_6C_1\text{ImTFSI:FA}$ (right, a). For comparison, the patterns of the pure ionic liquid (b, right and left), and TMOS (c, left) and formic acid (c, right) are also included.