

**Table 1S.** Magnetic field inhomogeneity ( $\Delta B$ ) in the silica pore calculated from the line width of  $^{13}\text{C}$  NMR spectrum and  $T_2$  of **1**-Si<sub>M</sub>

Sites	$T_2$ ( $10^{-3}$ s)	Line width (Hz)	$T_2^*$ ( $10^{-4}$ s)	$\Delta B$ ( $10^{-5}$ Tesla)
2	5.67	365	8.73	2.9
6	8.89	367	8.68	3.1
10	23.52	365	8.73	3.3
7	10.78	365	8.73	3.1
8	13.09	365	8.73	3.2
9	62.02	321	9.92	3.0

## Captions for Supplemental Figures.

Figure 1S. (a)  $^1\text{H}$  PFG-NMR echo decay-dependent diffusion coefficient ( $D$ ) of H2 (solid) and H9 (open) of the  $[\text{C}_4\text{mim}]$  cation of **1** at 300 K. (b) Echo decay curves as a function of % echo decay. Keeping the maximum gradient strength constant and adjusting the lower gradient strength limit varied the decay range.

Figure 2S. The deconvoluted sub-spectra (green) of  $^1\text{H}$  NMR signal (black), obtained from  $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$  confined in silica (KIT-6) at 300 K as a function of a loading amounts of **1**: (a) **1-Si<sub>V</sub>**, (b) **1-Si<sub>M</sub>**, (c) **1-Si<sub>M/2</sub>**, (d) **1-Si<sub>M/4</sub>**. A broad probe background contribution (blue) of ca. 3 and 10 % intensity was removed from the **1-Si<sub>M/2</sub>** and **1-Si<sub>M/4</sub>** spectra, respectively, before deconvolution.

Figure 3S. The line width (a), chemical shift (b), and relative intensities (c) of the deconvoluted sub-spectra of the  $^1\text{H}$  NMR resonance bands of **1-Si** samples from Figure 2S.

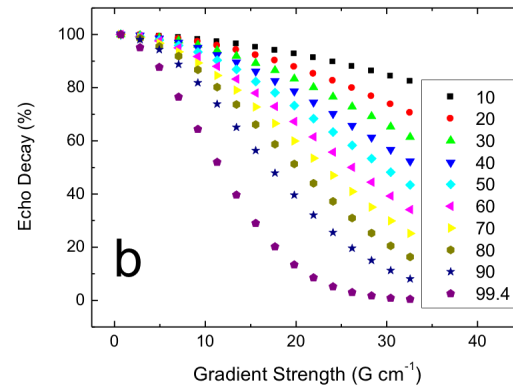
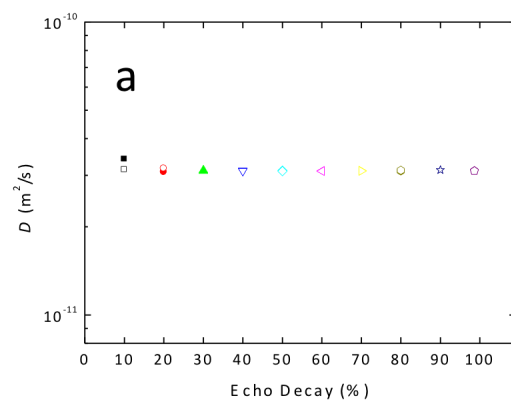


Figure 1S

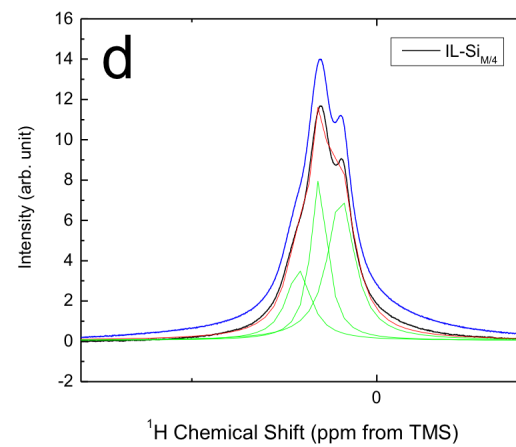
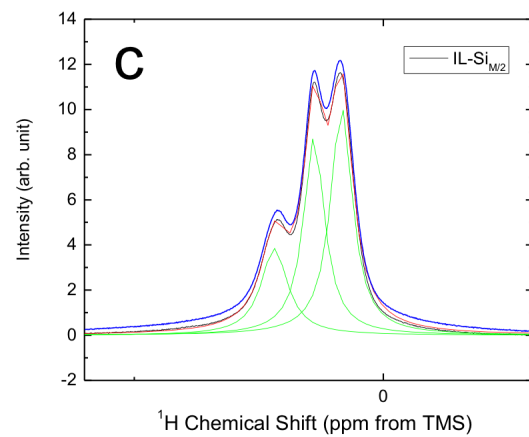
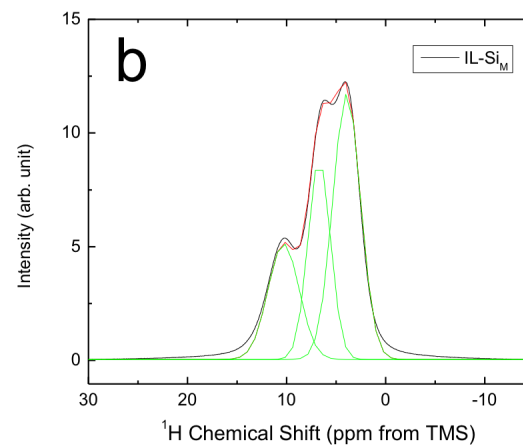
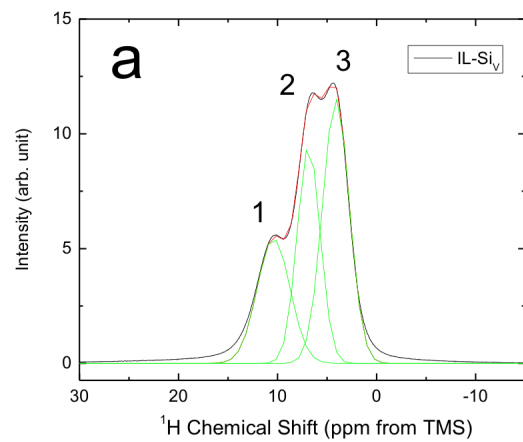


Figure 2S

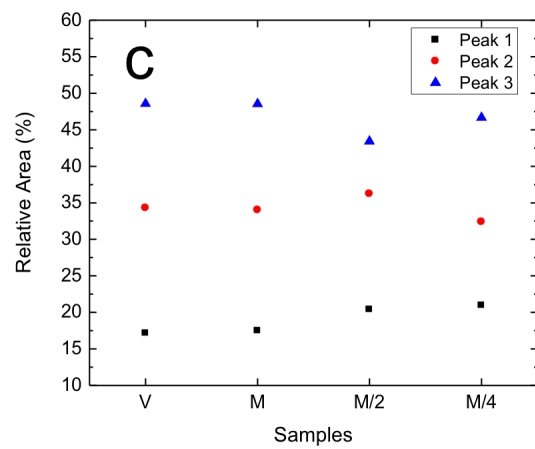
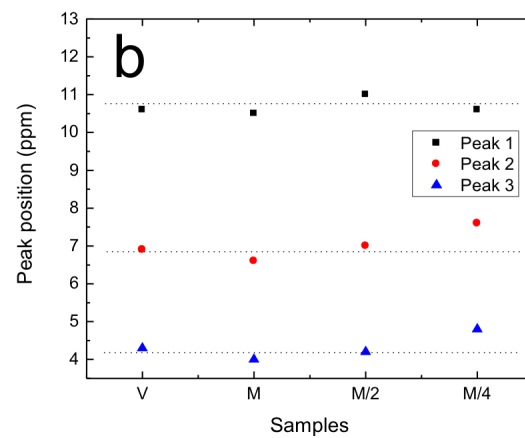
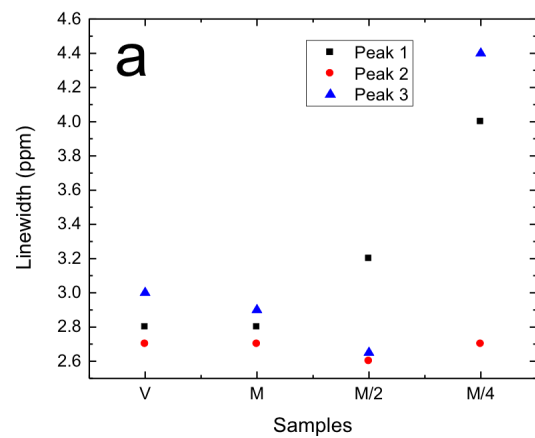


Figure 3S