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## ARTICLE TYPE

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## A long-chain protic ionic liquid inside silica nanopores: enhanced proton mobility due to efficient self-assembly and decoupled proton transport<sup>†</sup>

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We report enhanced protonic and ionic dynamics in a imidazole/protic ionic liquid mixture confined within the nanopores of silica particles. The ionic liquid is 1-octylimidazolium bis(trifluoromethanesulfonyl)imide ([HC<sub>8</sub>Im][TFSI]), while the silica particles are microsized and characterized by internal well connected nanopores. We demonstrate that the addition of imidazole is crucial to promote a proton motion decoupled from molecular diffusion, which occurs due to the establishment of new N-H...N hydrogen bonds and fast proton exchange events in the ionic domains, as evidenced by both infrared and <sup>1</sup>H NMR spectroscopy. An additional reason for the decoupled motion of protons is the nanosegregated structure adopted by the liquid imidazole/[HCsIm][TFSI] mixture, with segregated polar and non-polar nano-domains, as clearly shown by WAXS data. This arrangement, promoted by the length of the octyl group and thus by significant chain-chain interactions, reduces the mobility of molecules (D<sub>mol</sub>) more than that of protons (D<sub>H</sub>), which is manifested by  $D_H/D_{mol}$  ratios greater than three. Once included into the nanopores of hydrophobic silica microparticles, the nanostructure of the liquid mixture seems to be preserved with slightly larger ionic domains, with slightly larger ionic domains but unclear effects on the non-polar ones. This results in a further enhancement of proton motion with localised paths of conduction. These results demonstrate a significant progress in the design of proton conducting materials via tailor-made molecular structures as well as by smart exploitation of confinement effects. Compared to other imidazole-based proton conducting materials that are crystalline up to 90 °C or above, the gel materials that we propose are useful for applications from room temperature, and can thus find applications in e.g. intermediate temperature proton exchange fuel cells.

## 1 Supporting Information File

In this file, additional figures that complement the discussion presented in the main text are provided. These figures summarise data achieved by wide angle x-ray scattering, vibrational (infrared and Raman) spectroscopy, and solid-state NMR. A comprehensive table with observed <sup>1</sup>H NMR chemical shifts as well as self-diffusion values for the [HC<sub>8</sub>Im][TFSI] IL, the imidazole/[HC<sub>8</sub>Im][TFSI] mixture and the imidazole/[HC<sub>8</sub>Im][TFSI]/C<sub>8</sub>-SiO<sub>2</sub> gel is also provided.





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<sup>†</sup> Electronic Supplementary Information (ESI) available: [The Electronic Supplementary Information file contains additional and complementary data achieved by wide angle x-ray scattering, vibrational (infrared and Raman) spectroscopy, and solid-state NMR. A comprehensive table with observed <sup>1</sup>H NMR chemical shifts as well as self-diffusion values for the [HC<sub>8</sub>Im][TFSI] IL, the imidazole/[HC<sub>8</sub>Im][TFSI] mixture and the imidazole/[HC<sub>8</sub>Im][TFSI]/C<sub>8</sub>-SiO<sub>2</sub> gel is also provided.]. See DOI: 10.1039/b000000x/

**Table S1:** <sup>1</sup>H chemical shifts (in ppm) and self-diffusion coefficients (in  $10^{-12} \text{ m}^2/\text{s}$ ) obtained at 30 °C from PFG NMR experiments. The assignment of each chemical shift to a specific proton is given in parenthesis. <sup>*a*</sup>This value was deduced from assuming the same  $D_{NH}/D_{Im}$  and  $D_{Im}/D_{cat}$  ratios as in the liquid Im/[HC<sub>x</sub>Im][TFSI] mixture

[HC <sub>8</sub> Im][TFSI]		Im/[HC <sub>8</sub> Im][TFSI]		Im/[HC <sub>8</sub> Im][TFSI]/C <sub>8</sub> SiO <sub>2</sub>	
<sup>1</sup> H chemical shift	Self-diff. coeff.	<sup>1</sup> H chemical shift	Self-diff. coeff.	<sup>1</sup> H chemical shift	Self-diff. coeff.
(-1 <sup>2</sup> )					
$0.85 (C^{13}H_3)$	7.98	$0.82 (C^{13}H_3)$	8.62		
$1.30 (C^{8-12}H_2)$	8.03	$1.27 (C^{8-12}H_2)$	8.63	$0.5-2.5 (C^{7-13}H_2)$	14.5
1.92 (C <sup>7</sup> H <sub>2</sub> )	8.01	$1.88 (C^7 H_2)$	8.61		
4.29 (C <sup>6</sup> H <sub>2</sub> )	8.04	4.24 (C <sup>6</sup> H <sub>2</sub> )	8.61	3.5–4.5 (C <sup>6</sup> H <sub>2</sub> )	
7.44 (C <sup>5</sup> H)	8.10	7.39 (C <sup>5</sup> H)	n.a.	7–8 (C <sup>4,5</sup> H)	
7.54 (C <sup>4</sup> H)	n.a.	7.47 (C <sup>4</sup> H)	n.a.		
		8.50 (C <sup>2'</sup> H)	12.40	8–9 (C <sup>2,2′</sup> H)	$22.0^{a}$
8.66 (C <sup>2</sup> H)	8.00	8.58 (C <sup>2</sup> H)	8.50		
11.81 (N <sup>3</sup> H)	7.91	12.04 (N <sup>3,3'</sup> H)	13.50	11.5–12.5 (N <sup>3,3'</sup> H)	24.0



**Figure SI-1:** From left to right: picture of a gel based on nanoporous silica particles filled with a imidazole/[HC<sub>8</sub>Im][TFSI) liquid mixture; SEM image of functionalized silica microparticles; enlargement showing the nanoporosity of silica; pore size distribution as obtained by BET measurements.



**Figure SI-2:** WAXS intensities recorded for the aprotic ionic liquid  $[C_1C_8Im][TFSI]$  (as previously reported in reference [12]) and the protic ionic liquid  $[HC_8Im][TFSI]$  at focus in the present work.



**Figure SI-3:** Left: Example of the peak fitting procedure used to analyse infrared spectra. Right: Dependence of the N–H stretching frequency on the state of the ionic liquid, i.e. neat and bulk (blue), mixed with imidazole (green), or mixed with imidazole and confined in nanopores of silica (red).



**Figure SI-4:** Close up of Raman spectra in the 700–780 cm<sup>-1</sup> range where the expansion-contraction mode of TFSI appears. The Raman spectra of the Im-[HC<sub>8</sub>Im][TFSI] mixture (green) and the same when confined in nanopores of silica (red) are shown. The peak position recorded for the pure ionic liquid [HC<sub>8</sub>Im][TFSI] but using a FT-Raman spectrometer and the 1064 nm excitation source (due to luminescence while using the 785 nm or the 532 nm lines) is indicated as a blue dashed line for comparison.



**Figure SI-5:** Solid-State 2D <sup>29</sup>Si(<sup>1</sup>H) HETCOR NMR experiments performed on a 400 MHz spectrometer at 5 kHz spinning speed, at room temperature.



**Figure SI-6:** <sup>1</sup>H NMR spectra recorded with a liquid state spectrometer for the neat  $[HC_8Im][TFSI]$  ionic liquid (blue), the imidazole/ $[HC_8Im][TFSI]$  mixture (green) and the imidazole/ $[HC_8Im][TFSI]/C_8-SiO_2$  gel (red). The latter shows broader lines.



**Figure SI-7:** Peak fit analysis of the WAXS diffraction pattern recorded for an imidazole/[HC<sub>8</sub>Im][TFSI] mixture inside nanopores of silica. Left: Fit that does not include a diffraction peak at q<sub>1</sub>; Center: Fit that does include a diffraction peak at q<sub>1</sub>; Right: The contribution from the IL only (now shown on a linear scale on the y-axis).



**Figure SI-8:** X-Ray scattering patterns in the lower q-range of the bare functionalized silica particles (C<sub>8</sub>-SiO<sub>2</sub>) and of the same after filling with the imidazole/[HC<sub>8</sub>Im][TFSI] liquid mixture (C<sub>8</sub>-SiO<sub>2</sub>/PIL-Im). Characteristic correlation lengths associated to the pore walls' thickness (~6.5 nm) and to the pores' diameter (8.5 nm; and 8.5 nm + ~6.5 nm = ~15 nm) can be identified. The close to  $q^{-2}$  dependence found in this q-range indicates a locally flat (2D) geometry, which could be the manifestation of the walls' interfaces or of the layers of ionic liquids formed close to the walls. Nevertheless, a more precise description cannot be given at this point. These structural features, together with the results from BET analysis and SEM images, suggest that the pores have an average concave shape.