1. Introduction

Achieving high proton conductivity in solid state materials is one of the current biggest challenges in materials science. Of emerging interest are porous solid materials like zeolites, ordered mesoporous silica and crystalline covalent organic frameworks, impregnated with a suitable proton conducting substance.\textsuperscript{1,2} Central to these materials is that large pores do not simply cause the flow of charge carriers but can, if smartly designed, also sustain the transport of the hydrogen ion, \textit{i.e.} the proton.\textsuperscript{3} Imidazole is a classic example of a proton conducting substance that, by providing both proton-acceptor and proton-donor sites, is able to support fast proton motion \textit{via} the Grotthuss mechanism, which involves a sequence of proton hopping and molecular reorientations.\textsuperscript{3} This mechanism of proton conduction is also displayed by other aromatic molecules like triazole or pyrazole, water, and hydrated strong acids like phosphoric or sulphuric acids, which have in common the ability to form an extended hydrogen bonded network. Although water-based systems have the advantage of high proton density and high proton mobility, they are limited to
usage at low temperatures due to evaporation and thus dehydra-
tion (close to or above 100 °C). By contrast, an amphoteric aro-
matic molecule can display high proton mobility at much
higher temperatures, but have a lower temperature limit defined
by the solid-to-liquid transition (which is 90 °C for imidazole).

In this context, protic ionic liquids (ILs) have emerged as a
new class of potentially good proton conductors, that also
provide a negligible volatility and are chemically stable up to
temperatures as high as 300 °C. Protic ILs are obtained by
the reaction (AH + B) to a Bronsted base (B), where the ΔpK_a of the acid–base pair determines whether
the reaction AH + B → A^- + BH^+ proceeds to completion. ILs
with a ΔpK_a value larger than 10 typically result in a low ionic
association (or high ionicity), and vice versa. Highly ionic ILs
display a superior thermal stability, and have exchangeable
protons more strongly bound to the cation. This results in
higher molar ionic conductivities, as can be revealed by
Walden plots, but limits the decoiled motion of the acidic
protons. Diffusion NMR experiments have shown that in pure
imidazolium-based ionic liquids like 1-ethylimidazolium tri-
flate [[HC2Im][TFO^-]] or 1-ethylimidazolium bis(trifluo-
methanesulfonyl)imide [[HC2Im][TFSI^-]] the self-diffusion
of the most acidic proton (D_{cat}) is not significantly different from
that of other aromatic or aliphatic protons (D_{cat}), as would be the
case if the Grothuss mechanism of proton motion
occurred. In some ammonium-based ILs, the proton affinity of
the acid may be so large that the exchangeable proton appears
to diffuse together with the anion. Moreover, the correlation
observed between the proton affinity of the acid used to
produce the protic ILs and the ^1H NMR chemical shift of the
exchangeable proton enables one to predict the diffusional
properties of an IL from its ^1H NMR spectrum. The diffusional
properties of ILs are also correlated with their local
structure, as nicely shown for a series of ammonium-based
protic ILs by pulsed field gradient (PFG) and heteronuclear
(HOESY) NMR experiments.

Interestingly, protic ILs prepared with non-equimolar
amounts of an acid and a base, more precisely in the composi-
tional range of excess base, can show an enhanced proton
hopping mechanism as revealed in the case of imidazole: bis(trifluoromethanesulfonyl)imide [[(HIm^-):[TFSI^-]] mix-
tures. Excess proton mobilities with D_{cat}/D_{cat} ratios in the
range of 1.1–1.4 could thus be measured between 20 and 120 °C. In our group, we have recently measured an enhanced proton mobility upon addition of imidazole, at low concentra-
tions, to the protic IL [HC2Im][TFSI^-]. By combining NMR and infrared spectroscopy with MD simulations, we
could explain this enhancement by the establishment of new
hydrogen bonds between imidazole and both cations and
anions. These results give rise to the question whether a selec-
tive proton mobility could be further enhanced by choosing a
more appropriate molecular structure for the IL, for instance
one that provides intrinsic nano-structuration.

To verify this possibility, we have focused this study on the
combination of an imidazole with a long-chain protic IL, i.e.
1-octylimidazolium bis(trifluoromethanesulfonyl)imide
[[HC8Im][TFSI^-]] that is supposed to provide a close proximity
between the cationic head and imidazole in the polar domains
and, simultaneously, promote nano-structuration by aggrega-
tion of the alkyl chains in the non-polar domains. We
hypothesise that in such a binary mixture the mobility of the
cation (D_{cat}) can be reduced more effectively than that of the
exchangeable protons (D_{cat}). Moreover, to meet the quest of
proton conducting materials in the solid state, we have investi-
gated the diffusional properties of an imidazole/
[HC8Im][TFSI^-] mixture confined in silica nanopores, with
pores having a diameter of 10 nm and the pore walls being
functionalized with triocylsilyl groups to provide hydrophobi-
city, and thus reduce interfacial friction. The structural prop-
erties and molecular dynamics of the hypothetically proton
conducting materials, i.e. the imidazole/[HC8Im][TFSI^-]
liquid mixture and the imidazole/[HC8Im][TFSI^-]/silica solid-
like gel, were investigated by ^1H NMR and vibrational spec-
troscopy and wide angle X-ray scattering (WAXS), as well as
diffusion and solid-state ^1H NMR techniques. The results show interesting confinement effects, which depend on the
relationship between the size of the nanopores and the nano-
segregated structure of the selected IL. The study that we
present thus bridges the fields of confined self-organised
crystal ILs and the nanoconfinement of ILs. We find these
results relevant not only for the field of fuel cells, that operate
upon proton conduction, but also for other electrochemically
related fields where the use of ILs as electrolytes is seen as the
future solution (for example, batteries or super-capacitors) or
for applications based on controlled release from porous struc-
tures (e.g. in drug delivery).

2. Experimental

2.1 Synthesis of the ionic liquids

The Bronsted base 1-octylimidazole (here abbreviated as C8Im)
with a purity higher than 98% was purchased in liquid
form from IoLiTec (Ionic Liquids Technologies) GmbH,
whereas the acid H-bis(trifluoromethanesulfonyl)imide (here
abbreviated as HTFSI) with a purity higher than 99% was pur-
chased from Acros Organics. The synthesis of the protic ionic
liquid 1-octylimidazolium bis(trifluoromethanesulfonyl)imide
(in this paper abbreviated as [HC8Im][TFSI^-]) was carried out
under inert conditions in a glove bag (Atmosbag) purchased
from Sigma-Aldrich Co. by mixing equimolar quantities of the
base and acid according to the following stoichiometric
reaction:

\[
\text{C}_8\text{Im} + \text{HTFSI} \rightarrow \text{HC}_8\text{Im}^+ + \text{TFSI}^- \tag{1}
\]

The Karl Fischer titration revealed that water uptake for the
protic IL [HC8Im][TFSI^-] was 0.003% w/w. The molecular struc-
tures of the 1-octylimidazolium cation and the TFSI anion are
sketched in Fig. 1.
2.2 Synthesis of the nanoporous silica

As already described in ref. 20, the nanoporous silica micro-particles were synthesized following an established emulsion solvent evaporation procedure that results in a tunable pore volume and pore size distribution. The results from the Brunauer–Emmett–Teller (BET) analysis reveal that the average pore size in these silica particles is 10 nm and that the surface area is 338 m$^2$ g$^{-1}$. The average particle size is estimated to be $\sim 10 \mu$m, with a narrow size distribution that fulfills the requirement of a $dV_{90}/dV_{10}$ ratio smaller than 1.5. To provide hydrophobic surfaces, and in this way reduce interfacial friction, the as synthesized silica particles were functionalized with the trioctylsilyl (TOS) groups. New BET analyses revealed that the functionalized silica particles have a surface area reduced to 220 m$^2$ g$^{-1}$ and can provide a free volume equal to 0.55 cm$^3$ per gram, a value that is crucial to define the degree of filling of the pores by the ionic liquid, given in % (vide infra). In addition, after functionalization, the pore diameter distribution shows a maximum at 8.5 nm, as a consequence of the volume taken up by the TOS groups. A SEM image of this type of nanoporous silica particle, as well as the pore diameter distribution, is given in Fig. SI-1.†

2.3 Synthesis of the silica-based gels

The IL filled silica-based gels were prepared according to the following procedure, which is equivalent to the one recently reported in ref. 20 except for the addition of the imidazole to the protic IL [HC$_8$Im][TFSI]. An appropriate amount of imidazole (i.e. 0.03 grams, $M_w = 68$ g mol$^{-1}$) was added to 1.30 grams of the protic IL [HC$_8$Im][TFSI] ($M_w = 461$ g mol$^{-1}$) under magnetic stirring to obtain an imidazole/IL mixture with a molar fraction of the imidazole, $\chi$, equal to 0.15. This value was chosen from a previous study of imidazole/[HC$_8$Im][TFSI] mixtures that revealed more pronounced proton mobilities at low concentrations of imidazole. Part of this solution was kept aside for further characterisation, but a calculated volume of this mixture was added to a weighed amount of the functionalised silica powder to achieve the desired pore filling factor. This is given in percent (%) and represents the fraction of the whole available free space provided by the particles actually filled by the liquid mixture. For example, a 50% pore filling represents silica powder with half of the available empty volume filled by the liquid. A sealed NMR tube containing the functionalized silica powder and the liquid mixture was then centrifuged for the time necessary (about 30 minutes) to obtain a homogeneous gel-like material (see the image in Fig. SI-1†).

2.4 Vibrational spectroscopy

Raman spectra of the pure protic IL and the imidazole/IL mixture were collected using the 785 nm line from a near infrared diode laser as the excitation source. The Raman spectrum of the protic IL, however, resulted in a significant luminescence effect, wherefore better quality spectra were also collected with an FT Raman spectrometer using the 1064 nm laser line. Good Raman spectra of the silica gels, on the other hand, could be recorded using the 532 nm laser line, which also provides a suitable wavelength to perform highly confocal mapping experiments. These were performed along vertical lines along the z-axis penetrating the whole volume of silica microparticles, and over x-y surface sectioning particles at their half-diameter height. Scanning steps of 0.5 μm were used to reproduce the contours of the particles and thus monitor the presence of the liquid phase inside the microparticles’ nanopores. For monitoring purposes, the integrated intensity underlying the Raman signal at 742 cm$^{-1}$ was chosen, which was then converted into a gradient of colours between red (high intensity) and black (low intensity) to visualise the mapping results. The use of the 532 nm line was coupled with a grating of 2400 l mm$^{-1}$, which provides a spectral resolution better than 1 cm$^{-1}$.
Infrared spectra were collected using a PerkinElmer spectrometer using the attenuated total reflection (ATR) mode and pouring the solutions, or gels, over a single reflectance diamond crystal. For each sample, 32 scans were averaged achieving a nominal spectral resolution of 2 cm\(^{-1}\). The full spectral range 400–4000 cm\(^{-1}\) was investigated. For a more detailed analysis of the 3000–4000 cm\(^{-1}\) spectral region where the N–H stretching modes appear, the software Igor Pro from WaveMetrics was employed to make a peak fitting analysis based on a linear background and Gaussian components.

2.5 Liquid state \(^1\)H NMR spectroscopy

All NMR measurements were carried out on a Bruker Avance 600 spectrometer, equipped with a Bruker Diff30 probe with a 5 mm 1H/2H RF double coil insert and connected to a 40 A gradient amplifier. The relaxation times were obtained by standard inversion recovery (\(T_1\)) and CPMG (\(T_2\)) pulse sequences. All NMR signals, in both liquid and gel-like samples, revealed strict mono-exponential behaviour for the relaxation recovery. Regarding the NMR self-diffusion studies of the liquid samples, the standard stimulated echo sequence was used with a gradient pulse length, \(g\), equal to 1 ms and diffusion time, \(D\) equal to 100 ms. In each experiment, the gradient strength, \(g\), was ramped uniformly in 16 steps from 0.1 to 12 T m\(^{-1}\). The experiments were carried out at 30 °C, collecting data at each gradient value with a sum of 8 acquisitions, and using a 7 s recycle delay time to ensure complete longitudinal relaxation of all signals. For the gel-like samples (i.e. the liquid mixture inside the nanopores of silica), the stimulated echo sequence using bipolar pulses was used to suppress the influence of internal background gradients. Due to fast spin–spin relaxation, a gradient pulse length \(d\) equal to 0.37 ms was used, while the diffusion time \(D\) was set to 300 ms. In each experiment, the gradient strength \(g\) was ramped uniformly in 16 steps from 0.1 to 17 T m\(^{-1}\). The experiments were carried out at 30 °C, collecting data at each gradient value with a sum of 16 acquisitions, and using a 7 s recycle delay time to ensure complete longitudinal relaxation of all signals. The gradient strength was calibrated with the self-diffusion coefficient of HDO traces in a standard sample of pure D\(_2\)O. For all samples, a strict one-component attenuation of the logarithmic NMR signal intensity against \(k\) was noted, where \(k\) is equal to \((gd)^2(D−d/3)\) and the \(^1\)H gyromagnetic ratio is denoted \(γ\).

2.6 Solid-state NMR spectroscopy

One-dimensional (1D) \(^1\)H and two-dimensional (2D) \(^{29}\)Si\(^{\text{i}}\)\(^{\text{H}}\) HETCOR NMR experiments were performed on a 400 MHz Bruker Avance DSX NMR spectrometer operating at a magnetic field of 9.4 T (with \(^1\)H and \(^{29}\)Si Larmor frequencies of 400.24 and 79.51 MHz, respectively) using a 7 mm double-resonance probe head. \(^1\)H NMR spectra were acquired over 8 scans with 5 seconds of recycling delay at room temperature (RT) and variable temperature (VT) from 290 K to 335 K. The sample was spun at 6 kHz. The \(^1\)H 90° pulse was calibrated to 12.5 μs. \(^{29}\)Si\(^{\text{i}}\)\(^{\text{H}}\) CPMAS NMR spectra were collected over 1024 scans with 2 seconds of recycling delay at a 5 kHz spinning speed, where RAMP shape was used to transfer polarization with 8 ms of contact time. The 2D spectra were collected under the same CP conditions. The signals were accumulated over 256 scans for each of 76 increments with 2.5 seconds of relaxation delay. The 2D NMR experiments were performed at room temperature. A saturation recovery and CPMG pulse sequences were used to measure \(^1\)H \(T_1\) and \(T_2\) relaxations as a function of temperature (290–335 K) while spinning the sample at 6 kHz. The \(^1\)H chemical shifts were externally referenced to those of isopropanol.

2.7 X-ray scattering

Wide- and small-angle X-ray scattering (WAXS and SAXS) experiments were performed on a Mat: Nordic instrument purchased from SAXSLAB, a Xenocs company, and available at the Chalmers Materials Analysis Laboratory (CML) at the Chalmers University of Technology. The X-ray source was generated using a Rigaku 003+ high brilliance microfocus Cu-radiation source, while the detector was a Pilatus 300K. Samples were inserted into thin capillaries with a wall diameter of 0.15 mm, and silver behenate was used as the standard to calibrate the q-range. All experiments were performed at room temperature. To collect WAXS and SAXS data, an accumulation time of 8 and 12 minutes, respectively, was used. Since the diffraction peaks of interest in this paper fell within the q-range covered by the WAXS setup, only these data will be presented and discussed.

2.8 Surface analysis

Nitrogen sorption analyses were performed using a TriStar 3000 instrument from Micromeritics Instrument Corporation. Prior to the measurements, the materials were outgassed overnight at 120 °C. The pore size distribution was calculated according to the BJH (Barrett–Joyner–Halenda) method, whereas the surface area was obtained using the BET (Brunauer–Emmett–Teller) method. The pore volume was calculated using a single point adsorption value at the relative pressure \((p/p_0)\) of 0.990. The obtained pore size distribution is shown in Fig. S1.†

3. Results and discussion

3.1. Chemistry and nanostructure of the protic ionic liquid

Upon complete proton transfer from the acid (HTFSI) to the base (C\(_4\)Im), a new N–H bond should be created in the cation, on site N\(^1\) according to the atom labelling given in Fig. 1. The formation of the N–H bond was straightforwardly demonstrated by infrared spectroscopy in the high frequency range where the N–H stretching modes typically appear, as shown in Fig. 2. The new N–H stretching mode appears at about 3265 cm\(^{-1}\), with a broad shape indicative of a wide distribution of the N–H bond lengths and thus of the establishment of hydrogen bonds with various strengths. This can be compared to the infrared spectrum of the analogous aprotic IL (i.e. [C\(_4\)C\(_8\)Im][TFSI]) that is featureless in the frequency region.
above 3200 cm\(^{-1}\). That the proton has been transferred to the base and is now residing on the 1-octylimidazolium cation is also demonstrated by \(^1\)H NMR spectroscopy, through the (N3)H proton resonance that appears at 11.81 ppm (Table S1†). This enhancement is attributed to the protonation of the imidazolium ring, which increases the polarity of the ionic domains thus promoting the segregation from the non-polar regions and increasing the contrast of scattering length densities between these domains.

Upon addition of an imidazole to [HC\(_8\)Im][TFSI], specific hydrogen bonds are formed that primarily involve the (N)H protons, as expected from two non-interacting molecular species (note that the (N\(^3\))H chemical shift of neat imidazole is expected to appear at 13.5 ppm). In the imidazole/[HC\(_8\)Im][TFSI] mixture, the aromatic and aliphatic protons shifts slightly upfield, see also Table S1.† These features reflect the proximity of the imidazole to the imidazolium ring as well as a fast proton exchange (on a time scale shorter than 1 ms), since only one narrow (N)H feature is observed in the \(^1\)H NMR spectrum, rather than two as expected from two non-interacting molecular species. In addition, the high ppm value observed for the merged (N)H feature in the liquid mixture is expected to appear at 13.5 ppm.

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explained, invoking the Stokes–Einstein relation $D = (k_B T)/(\eta r)$,\(\S\) by the smaller size of the imidazole compared to the bulkier octylimidazolium cation.

The most interesting result, however, is that the self-diffusion coefficient of the exchangeable (N\(^{3,3}\))H protons is the highest,\(\|$ indicating that they move faster than both imidazolium and imidazole. The implication of such an observation can only be discussed through a detailed analysis of all possible dynamical contributions. In a complex system like the one investigated here, three potential proton carriers must be considered, i.e. the octylimidazolium cation, the neutral imidazole, and the free proton H\(^+\), whereby the self-diffusion value measured from the (N\(^{3,3}\))H resonance ($D_{\text{NH}}$) is assumed to contain contributions from both the vehicular ($D_{\text{cat}}$ and $D_{\text{im}}$) and the Grotthuss ($D_H$) mechanisms of proton motion (eqn (2)):

$$D_H = \chi_1 D_H + \chi_2 D_{\text{im}} + \chi_3 D_{\text{cat}}$$

(2)

where $\chi_1$, $\chi_2$ and $\chi_3$ are the molar fractions of free protons, neutral imidazole and imidazolium cations, respectively. In our case, $\chi_1 = 0.15$ and $\chi_2 = 0.70$,\(\|$ while $D_{\text{NH}} = 13.5 \times 10^{-12}$ m\(^2\) s\(^{-1}\), $D_{\text{im}} = 12.4 \times 10^{-12}$ m\(^2\) s\(^{-1}\) and $D_{\text{cat}} = 8.6 \times 10^{-12}$ m\(^2\) s\(^{-1}\), as experimentally measured by PFG NMR. Implementing these values in eqn (2) we obtain that $D_H$ is equal to $37 \times 10^{-12}$ m\(^2\) s\(^{-1}\), and thus infer that some protons move about four times faster than the imidazolium cation and about three times faster than the imidazole.

Based on the observation that in the pure protic IL $D_H \approx D_{\text{cat}}$, the addition of imidazole appears to be a crucial approach to enhance proton mobility. This is a result of the amphoteric nature of the imidazole, which is able to create hydrogen bonded molecular networks by acting as both a hydrogen bond donor and acceptor. This property has already been discussed for imidazole added polymers\(^{25}\) (in which $D_H \approx 2.5 D_{\text{mol}}$ was measured), liquids and liquid crystals\(^{25,26}\) as well as for imidazole-containing complex compounds\(^{27,28}\). A proton diffusivity greater than that of the parent molecule has also been reported for imidazole:HTFSI mixtures at non-equimolar ratios ($D_H \approx 2 D_{\text{mol}}$),\(^9\) and pure imidazole ($D_H \approx 2 D_{\text{mol}}$).\(^29\)

From the above analysis, it turns out that the contribution of the Grotthuss mechanism of proton transport is more enhanced in the imidazole/[HC\(_8\)Im][TFSI] mixture ($D_H \approx 4 D_{\text{cat}}$) than in the imidazole/[HC\(_2\)Im][TFSI] mixture previously investigated by us,\(^10\) in which mobile protons were observed to diffuse about two times faster than the cations ($D_H \approx 2 D_{\text{cat}}$). This is explained by a more pronounced nano-segregation in [HC\(_8\)Im][TFSI] than in [HC\(_2\)Im][TFSI], due to the longer chain (octyl, C\(_8\), versus ethyl, C\(_2\)), yet the same chemical environment in the polar domains where imidazole and exchangeable protons reside. Hence, in both cases the decoupled proton motion is strictly related to the nature and strength of the hydrogen bonded network formed by the imidazole and imidazolium, whilst the molecular mobility is markedly reduced in [HC\(_8\)Im][TFSI] due to stronger chain–chain interactions. That the characteristic nanostructure with segregated polar and non-polar nanodomains is preserved even upon addition of imidazole is shown in Fig. 4, where the diffraction peaks $q_1$, $q_2$ and $q_3$ observed for the imidazole/
proximity of the imidazole to imidazolium cations. This is deduced from the phase close to the cations. Interactions, two effects that can co-exist only if imidazole resides in the ionic phase close to the cations.

This type of nanostructure-related proton motion is similar to that discussed in ref. 26 and 27, which, however, report the cases of non-ionic systems that require temperatures above 110 °C for good proton conductivities. With respect to a selective ionic motion, that is the enhancement of the mobility of either the cation or the anion compared to its counterion, reports are available on ILs that exhibit liquid-crystal like nanostructures. For instance, at temperatures below the liquid-crystal phase transition, i.e. below ~80 °C, a long-chain fan-shaped tri-nonylammonium-based ionic liquid displays diffusion values for the anion twice as large as those of the cations. On the other hand, in [C6H4C2Im][C4OS] the 1-ethyl-3-methylimidazolium cations diffuse two to three times faster than the octylsulfate anions in the rigid-gel phase, which sets in at temperatures between 20 and 25 °C depending on the level of hydration. These experimental findings are in great accordance with the molecular dynamics simulations recently provided by Erbas et al., who have demonstrated the pivotal role of nanomorphologies for enhanced counterion mobilities in ILs.

3.3. Enhanced dynamics inside the nanopores

Whether the structural properties and molecular dynamics of the liquid mixture are affected by nanoconfinement was a key question in this work. The 1H NMR and infrared spectroscopic studies as well as the WAXS experiments were therefore repeated for a gel prepared by filling the nanopores of the functionalised silica microparticles with the imidazole/[HC8Im][TFSI] mixture. Particular attention was thus paid to verify that the liquid mixture effectively penetrated the nanopores. This was verified by using confocal Raman spectroscopy, and collecting Raman spectra while scanning a large X-Y surface area containing the silica microparticles. To do so in the most precise way, a single layer of particles was isolated over a thin glass slide. Moreover, to avoid artefacts due to surface roughness, the confocal volume from where the Raman scattered light is collected was positioned at half-height with respect to the particles’ diameter (in the z-direction), see Fig. 5A for the details of this experimental setup. The presence, or absence, of the IL within the scanned area was verified by monitoring the integrated area of the vibrational mode at 742 cm−1, the strongest Raman signature of the neat [HC8Im][TFSI] IL.**

**The WAXS pattern of the imidazole/[HC8Im][TFSI] liquid also confirms the proximity of the imidazole to imidazolium cations. This is deduced from the slightly reduced intensity of peak q1, mainly related to intermolecular interactions, and the slight increase of peak qυ, mainly related to intramolecular interactions, two effects that can co-exist only if imidazole resides in the ionic phase close to the cations.

Fig. 5 Surface mapping experiments by confocal Raman spectroscopy performed over silica particles whose nanopores were 100% filled with the imidazole/PIL mixture. A: Experimental setup with the confocal point of the laser positioned at half-height with respect to the particles diameter. B: Integration of the most intense Raman signal in TFSI containing compounds, i.e. the expansion–contraction mode of the TFSI anion at 742 cm−1. C: Results from visualising the Raman intensity as in (B) on a colour scale, where red indicates strong intensity and black indicates low intensity. The net red spherical shapes reproduced in (C) confirm that the liquid mixture has penetrated the particles and fills the particles’ nanopores.
dynamics retardation can be a limit for the practical use of gels, especially in gel electrolytes whose functionality is based on a high and selective ionic mobility. Hence, with the aim to counteract the reduced dynamics, different strategies have been explored, which include e.g. surface modification of the walls in the host matrix or the selection of specific size domains that change the phase behaviour of the guest liquid.33,38–42 Nevertheless, ionic mobilities higher in the gel than in the bulk state have been reported in a few cases only, i.e. in directional nanochannels and/or carbon nanotubes,43,44 but never in nanoporous silica gels. By using the measured self-diffusion values and implementing eqn (2) as done above for the liquid mixture, we found that inside the nanopores the protons move about seven times faster than in the imidazolium cations ($D_{\text{H}} \approx 7 \cdot D_{\text{cat}}$), see also Table 1. This is, to the best of our knowledge, the greatest enhancement of proton mobility ever reported for nanoporous materials in the anhydrous state. Highly mobile protons inside the nanopores were also evidenced by solid state $^1$H NMR spectra recorded at increasing temperatures, from 290 to 335 K, as summarised in Fig. 6.†† Upon increasing the temperature, we observe a chemical shift down-field for the merged ($\text{N})$H resonance, from 11 to 12 ppm, and a concomitant narrowing of the line, with a FWHM varying from 313 to 206 Hz in the temperature range investigated. By comparison, the chemical shift and line width of other proton resonances, for instance the one at position C6, are not affected in the same way (the chemical shift change remains below 0.1 ppm and the line width decreases by only 15 Hz). Similar shift and line width effects with increased temperature had been observed in other imidazole-based proton conductors, indicating dynamic hydrogen bonds.45 Hence, the high-resolution solid state NMR experiments shown in Fig. 6 reveal that the hydrogen bond type

| Sample State (at 30 °C) | $D_{\text{cat}}$ ($10^{-11}$ m$^2$ s$^{-1}$) | $D_{\text{Im}}$ ($10^{-11}$ m$^2$ s$^{-1}$) | $D_{\text{NH}}$ ($10^{-11}$ m$^2$ s$^{-1}$) | $D_{\text{H}}/D_{\text{cat}}$ |
|------------------------|-----------------|-----------------|-----------------|-----------------|
| [HC$_8$Im][TFSI] Liquid | 0.80            | —               | 0.79            | 1               |
| 0.13Im/0.85[HC$_8$Im][TFSI] Liquid | 0.86 | 1.24            | 1.35            | 3.7             |
| 0.13Im/0.85[HC$_8$Im][TFSI]/C$_8$SiO$_2$ Gel | 1.45 | 2.2$^a$         | 2.4             | 7.0             |

$^a$This value was deduced from assuming the same $D_{\text{NH}}/D_{\text{Im}}$ and $D_{\text{Im}}/D_{\text{cat}}$ ratios as in the liquid Im/[HC$_8$Im][TFSI] mixture.

†† Fig. SI-6† shows broad lines for the liquid-state NMR spectra of the gel, which motivates the use of MAS solid-state NMR methods to achieve higher spectral resolution.
interactions established in the imidazole/[HC8Im][TFSI]
mixture are retained also inside the nanopores of silica.

An explanation for the observed molecular dynamics was
sought in the local structure adopted by the liquid in the
confined state, which can a priori be captured from the WAXS
data. Fig. 7 compares the WAXS intensities measured for the
imidazole/[HC8Im][TFSI] mixture in the bulk and inside the
nanopores. Distinct diffraction features are observed also for
the confined liquid, albeit shifted compared to the bulk case.
The peak at position $q_3$ appears shifted to higher $q$-values, but
this is an apparent effect due to the stronger contribution of
the silica particles with their characteristic peak at $\sim 1.6$ Å$^{-1}$.
The peak at position $q_2$, on the other hand, is shifted to lower
$q$-values, from 0.86 to 0.78 Å$^{-1}$, which corresponds to a corre-
lation length $d_2$ of 0.8 nm. Determining the position and
intensity of peak $q_1$ was a major challenge, due to the strong
interference in the low-$q$ range from the structural features of
the silica microparticles, i.e. the 10 nm large nanopores and
the pore wall thickness of $\sim 6$ nm. Thus, to best describe the
overall collected intensity in this range a power-law contri-
bution, as observed in the WAXS intensity of bare silica micro-
particles (C8-SiO2), was included. For the liquid-filled silica
gel, a power of $\sim 2.6$ was found (i.e. $I \propto q^{-2.6}$), which indicates
smooth pore wall surfaces and a planar-like (2D) distribution of
the ionic liquid, most likely as a consequence of a bilayer
formation towards the TOS groups. A power law contribution
decays strongly with $q$ and we found it unable to fit, on its
own, the experimental data of the gel for $q$-values between 0.2
and 0.5 Å$^{-1}$, see Fig. SI-7A.† By contrast, the fit is more consist-
ent if a contribution at a $q$-value between 0.33 and 0.35 Å$^{-1}$,
attributable to the non-polar domains, is considered, as shown in
Fig. SI-7B.† It is very important to mention, however, that
during the peak fit procedure both the intensity and position of
peak $q_1$ change slightly when small variations are imposed on
the power-law contribution. This makes conclusive state-
ments on the value of $d_1$ difficult. In all cases, though, the
intensity of peak $q_1$ is found to be less intense, when com-
pared to that of $q_2$, in the nanopores than in the bulk
(Fig. SI-7C†), which suggests a certain loss of the long-range
order. This could be an effect of the concave shape of the
pores or of a loose packing of the molecules. Additional struc-
tural data, in the lower $q$-range, supporting this argument can
be found in Fig. SI-8 of the ESI.†

Since these are the first experimentally measured X-ray
diffraction data for an IL in nanopores, it is difficult to use the
literature data as a benchmark for discussion. Nevertheless,
density fluctuations and order/disorder effects due to nano-
confine have recently been discussed in the context of MD simulations, e.g. by Ori et al.46 and by Shi et al.47
Accordingly, we hypothesize that a density change inside the
nanopores of this work could arise from a mismatch between
the real space available and the structural parameters of the
liquid, i.e. from the fact that the diameter of the pore is
different from an integer number of bilayers (diam$_{pore}$ $\neq$
$n(d_1 + d_2)$). A schematic representation of the local structure
plausibly adopted inside the nanopores is given in Fig. 7, from
different axial perspectives. This arrangement is in accordance
with the tendency of long-chain ILs to form bilayer structures
at confined interfaces, as Smith et al. have reported.48
The figure also shows that due to an efficient self-assembly,
preferred paths for the transport of protons are created, which is
in good agreement with the enhanced $D_{H2O}/D_{pore}$ ratios observed
in the gel phase and already discussed above.

4. Conclusions

To conclude, we have demonstrated a strategy for materials' design that results in an enhanced proton mobility
decoupled from molecular diffusion. One important factor
that enables this achievement is the intrinsic nanostructura-
tion of long-chain ionic liquids, with separated polar and
non-polar nanodomains. This property is here combined
with the protonation of the aromatic head, which provides
localised and acidic protic sites. Nevertheless, protons
diffuse independently of the parent molecules only upon
addition of an imidazole, an amphoteric molecule that
resides in the polar domains and promotes the formation of
an extended hydrogen bonded network. This finding is per se
of highest relevance, primarily in the field of fuel cells, since
it highlights the possibility of selective proton motion under
anhydrous conditions, as required for use in next-generation
devices. In addition, the liquid mixture reported here can
provide a high proton mobility over a wide temperature
range, that bridges over the upper limit of water-based elec-
trolytes (i.e. the dehydration temperature of 80 °C) and the
lower limit of aromatic proton conductors like imidazole (i.e.
the temperature for the solid–liquid transition of 90 °C or
above). In fact, the imidazole/[H3C][TFSI] mixture is fluid
at room temperature and is expected to be chemically stable
up to at least 200 °C. The inclusion of imidazolyl/[H3C][TFSI]
into the nanopores of silica microparticles revealed a further enhancement in ionic and protic mobili-
ties, which is a rare observation. The faster dynamics that
we observed are attributed partly to weak surface inter-
actions, thanks to the anchored TOS groups, and partly to
confinement effects that have an influence on the nano-
structure of the confined liquid. Here, the concave shape of
the pore walls may also play a role. A better understanding of
the structure and dynamics of ILs in the nanodomains is
also relevant to the fields of batteries and supercapacitors,
which foresee the use of electrolytes inside nanoporous elec-
trodes. Based on these results, future studies will focus on
confining a longer-chain ionic liquid inside silica particles
with smaller pores, with the aim to further localise the proto-
nic charges.

Conflicts of interest

There is no conflict to declare.

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