

# Ionic Liquid Mediated Sol-Gel Synthesis in the Presence of Water or Formic Acid: Which Synthesis for Which Material?

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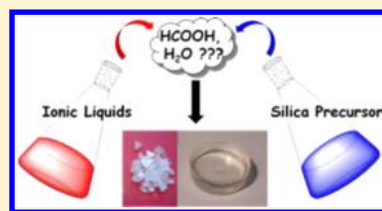
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## S Supporting Information

**ABSTRACT:** Sol-gel syntheses involving either neutral water or formic acid as a reactant have been investigated (1) to determine the best conditions to confine a maximum of ionic liquid (IL) inside silica-based matrixes and (2) to reach the highest porosity after removing the IL from the ion gels (washed gels). Several sets of ionogels were prepared from various 1-butyl-3-methylimidazolium ILs and various silica or organosilica sources. The study evidenced a critical effect of the anion on the morphology (monolith, powder) and texture of the resulting washed gels. Particularly, tetrafluoroborate anion led to monolith ionogels by a simple hydrolytic method, affording highly condensed mesoporous silicas with some fluorinated surface sites. Such sites have never been reported before and were evidenced by <sup>19</sup>F NMR. On the other hand, formic acid solvolysis turned out to be the only method to get non-exuding, crack-free, and transparent monoliths from ILs containing bis(trifluoromethylsulfonyl)imide [NTf<sub>2</sub>] anion, with promising applications in photochemistry or photosensing. With bulky imidazolium and pyridinium cations, removal of the IL led to highly porous silicas with pore diameters and pore volumes as high as 10–15 nm and 3 cm<sup>3</sup> g<sup>-1</sup>, respectively. These silicas could find applications as supports for immobilizing bulky molecules.

**KEYWORDS:** ionic liquids, non-aqueous sol-gel, organic-inorganic hybrid materials, mesoporous silica



## INTRODUCTION

Salts that have melting points below 100 °C are called ionic liquids (ILs). They consist of only ions, and their properties (such as negligible vapor pressure and, generally, thermal stability and nonflammability) are strikingly different from those of molecular liquids. For a given cation, their physicochemical properties can be tuned by the choice of the anion.<sup>1</sup> Accordingly, the choice of the anion is guided by the targeted application.

ILs have attracted the attention of electrochemists for a long time, as a result of their high ionic conductivity and their wide electrochemical potential window (up to 6 V).<sup>2</sup> More recently, ILs have been widely used as reaction media for organic synthesis, especially in the field of catalysis.<sup>3</sup> The use of ILs for the preparation of inorganic materials (including silicas, organosilicas, metal oxides, metal chalcogenides, metal salts) has been recently reviewed.<sup>4</sup> For material applications, there is currently a challenging need for immobilizing ILs in solid devices, while keeping their unique properties.<sup>5</sup> In this prospect, the sol-gel route was shown to give access to transparent crack-free silica monoliths (named ionogels or ion gels) in which the IL was kept confined.<sup>6–13</sup> Ionogels, which feature percolating conduction paths, are of interest as temperature-resistant electrolyte membranes in electrochemistry devices.<sup>14,15</sup> In this field of application, ILs containing

bis(trifluoromethylsulfonyl)-imide [NTf<sub>2</sub>] anion are widely used for their relatively low viscosity and high ionic mobility. Moreover, the confined IL may act as a catalyst,<sup>16,17</sup> an antibacterial agent,<sup>18</sup> or an active pharmaceutical ingredient in controlled release systems.<sup>19</sup> It was also reported that ILs acted as protective agents in the sol-gel immobilization of enzymes and enhanced their activity and stability.<sup>20</sup> The possibility to take advantage of both the transparency of ionogels and the ability of ILs in electrochromism, photochemistry, and sensing has been demonstrated.<sup>21–24</sup>

Porous materials with large mesopores and high connectivity (for a better internal diffusion) are of considerable interest as catalysts supports, adsorbents, and sensing devices.<sup>25</sup> It is worth underlining here that the IL could be removed from some ionogels by simple solvent washing to liberate a high mesoporosity,<sup>6</sup> thus confirming the three-dimensional (3-D) interconnected nanostructure of the confined IL phase. In such case the IL may be regarded as a recyclable templating agent avoiding the use of supercritical drying.<sup>26</sup> Note that (1) obtaining the complete encapsulation of an IL in a silica matrix requires that shrinkage and syneresis are minimized during

Received: April 6, 2012

Revised: July 25, 2012

Published: July 28, 2012

gelation and aging, whereas (2) achieving highly porous silicas implies a limited collapse of the pores during solvent extraction, and therefore a high degree of condensation before IL removal.

Different sol-gel methods can be used to synthesize ionogels.<sup>27</sup> Since the pioneering work of Dai et al.,<sup>6</sup> formic acid (FA) solvolysis was shown to give access to monolith ionogels using ILs derived from alkylmethylimidazolium [ $C_n$ MIm] or butylpyridinium [ $C_4$ Py] cations.<sup>14,15</sup> At the same time, the hydrolytic sol-gel synthesis of ionogels was reported by Deng et al. from [ $C_4$ MIm][ $BF_4$ ] and [ $C_4$ MIm][ $PF_6$ ] using HCl aqueous solutions,<sup>28</sup> and by Rogers et al. from [ $C_4$ MIm][Cl] using deionized water.<sup>9</sup> Since then, numerous articles reported the use of either formic acid solvolysis<sup>17,29–31</sup> or hydrolysis, generally in the presence of HCl catalyst<sup>19,32,33</sup> or of other acid catalysts.<sup>26,34,35</sup> However, to the best of our knowledge, a systematic comparison between the two sol-gel methods is still lacking to guide experimenters.

In the present study, several sets of silica ionogels were prepared from imidazolium and pyridinium ILs with typical anions (tetrafluoroborate, hexafluorophosphate, bis-(trifluoromethylsulfonyl)imide, chloride and acetate) using either water (pure  $H_2O$  or acid aqueous solutions) or formic acid (FA) as a reactant with tetramethoxysilane (TMOS) or mixtures of TMOS and methyltrimethoxysilane (MTMS). The two sol-gel methods (hydrolysis and FA solvolysis) were compared on the basis of both (1) the morphology (monolith or powder) and the IL content of the ionogels and (2) the pore diameter, surface area, and pore volume of the mesoporous silicas obtained after solvent extraction of the IL. Finally, inspired by previous works of Sharp et al.,<sup>36</sup> FA solvolysis was extended to mixtures of TMOS and organically bridged precursors, 1,2-bis(triethoxysilyl)ethane, and 1,4-bis(triethoxysilyl)benzene.

## EXPERIMENTAL SECTION

**Chemicals.** 1-Butyl-3-methylimidazolium chloride [ $C_4$ MIm][Cl] and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [ $C_4$ MIm][ $NTf_2$ ] were synthesized according to the literature.<sup>37,38</sup> 1-Butyl-2,3,4,5-tetramethylimidazolium bromide [ $C_4M_4$ Im][Br] was synthesized by reaction of 1,2,3,4-tetramethylimidazole (purchased from TCI Europe) and butyl bromide (purchased from Acros). 1-Butyl-2,3,4,5-tetramethylimidazolium bis(trifluoromethylsulfonyl)imide [ $C_4M_4$ Im][ $NTf_2$ ] was synthesized by anion metathesis from [ $C_4M_4$ Im][Br] and lithium bis(trifluoromethylsulfonyl)imide [Li][ $NTf_2$ ] (purchased from Fluka). 1-Butyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide [ $C_4MePy$ ][ $NTf_2$ ] and 1-butylpyridinium bis(trifluoromethylsulfonyl)imide [ $C_4Py$ ][ $NTf_2$ ] were also obtained by anion metathesis from [ $C_4MePy$ ][Cl] and [ $C_4Py$ ][Cl], respectively, according to the literature.<sup>39</sup> The following chemicals were purchased and used as received: 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium hexafluorophosphate, and 1-butyl-3-methylimidazolium acetate ([ $C_4$ MIm][ $BF_4$ ], [ $C_4$ MIm][ $PF_6$ ], [ $C_4$ MIm][OAc], respectively) from Solvionic, TMOS from Fluka, methyltrimethoxysilane (MTMS) from Alfa Aesar, 1,2-bis(triethoxysilyl)ethane (BTESE), and 1,4-bis(triethoxysilyl)benzene (BTESB) from ABCR. Before each synthesis, the ILs were thoroughly dried for 24 h at 70 °C under reduced pressure.

**Synthesis of Ionogels. Hydrolytic Method.** In a Teflon vial, the IL was dissolved under stirring in an equivolume ethanol/water solution (0.5/0.5 mL) for 3 min before adding TMOS in molar ratio: 1 TMOS/0.5 IL/4  $H_2O$ /1.2 EtOH. The resulting solution was stirred at room temperature for 10 min. Syntheses were performed by using 6.72 mmol of silica precursor. Gel times depended on the IL. The Teflon vial was kept closed for 48 h and then opened. The aging process was followed by the weight loss over time and complete aging was reached when no more weight variation was noticed (around 15

days were found to be necessary). Hydrolysis in the presence of HCl catalyst was performed by replacing water by 0.1 N HCl solution. Organo-silica ionogels were obtained according to the same procedure by replacing half TMOS by MTMS to give a mixture with molar ratio: 0.5 TMOS/0.5 MTMS/0.5 IL/4  $H_2O$ /1.2 EtOH. The extent of condensation was assessed by quantitative <sup>29</sup>Si solid state NMR spectroscopy before extracting the IL.

**FA Solvolytic Method.** In a Teflon vial, the IL and formic acid (FA) were stirred at room temperature for 10 min before adding TMOS (molar ratio: 1 TMOS/0.5 IL/7.8 FA). The resulting solution was stirred at room temperature for 10 min. Syntheses were performed by using 6.72 mmol of silica. Gelation and aging were performed as described above for the hydrolytic method. The extent of condensation was also followed by <sup>29</sup>Si OPMA S NMR spectroscopy before extracting the IL. Ionogels containing organic-bridged precursors were obtained according to the same procedure by replacing 6 molar % of TMOS by organic-bridged precursor (molar ratio 0.94 TMOS/0.06 BTESE or BTESB/0.5 IL/7.8 FA).

**IL Extraction (Washed Gels).** The removal of IL was performed by means of a Soxhlet extractor with refluxing acetonitrile (or refluxing ethanol in the case of [ $C_4$ MIm][OAc]). The efficiency of the extraction was checked by thermal gravimetric analysis (TGA) and IR spectroscopy. A 48-h extraction was shown to be generally needed. Usually the extraction resulted in the crumbling of gels.

**Characterization.** Infrared spectra were recorded on a Thermo Nicolet Avatar 320-FT-IR spectrometer and Smart Orbit ATR accessory with a diamond crystal with a resolution of 4  $cm^{-1}$ . The nitrogen adsorption-desorption isotherms at 77 K were measured using a Micromeritics Tristar surface area and porosity analyzer on monolith pieces degassed under vacuum at 120 °C for 12 h. The mesopore size distribution was evaluated by the Barrett-Joyner-Halenda (BJH) method applied to the desorption branch of the  $N_2$  adsorption-desorption isotherm. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 409 PC Luxx by using alumina crucibles under an air flow, with a heating rate of 5 °C/min up to 850 °C followed by an isotherm at 850 °C for 30 min. Quantitative <sup>29</sup>Si solid-state NMR was performed on ground samples on a Varian VNMR S 300 spectrometer (7.05 T) and using a 3.2 mm T3MAS probe. Spectra were acquired using a  $\pi/6$  single pulse with proton decoupling and a 60 s recycling delay. Samples were spun in  $ZrO_2$  rotors at 6 kHz. Samples were spun at the magic angle using  $ZrO_2$  rotors. Percentages of  $Q_2$  (Si(OSi)<sub>2</sub>(OR)<sub>2</sub>) (−92 ppm),  $Q_3$  (Si(OSi)<sub>3</sub>(OR)) (−101 ppm), and  $Q_4$  (Si(OSi)<sub>4</sub>) (−110 ppm) silicon environments were estimated using DMFIT 2011.<sup>40</sup> <sup>19</sup>F and <sup>19</sup>F–<sup>29</sup>Si CPMAS NMR were recorded on a Varian VNMR S600 (14.09 T) with a 3.2 mm T3MAS probe. <sup>19</sup>F MAS spectra was acquired using a single pulse followed by two  $\pi$  pulses for background signal suppression (DEPTH filter). Samples were spun at 15 kHz. <sup>19</sup>F–<sup>29</sup>Si CPMAS spectra were acquired under <sup>19</sup>F decoupling using a ramped 500  $\mu s$  contact time and a 5 s recycling delay. Samples were spun at 6 kHz. <sup>29</sup>Si chemical shifts were reference to tetramethylsilane and <sup>19</sup>F chemical shift were referenced to  $Na_2SiF_6$  ( $\delta^{19}F = -153$  ppm).

## RESULTS

In the hydrolytic method, the lack of miscibility of some ILs either with TMOS or water was overcome by adding ethanol as a cosolvent. On the other hand, in the FA solvolytic method, FA acted both as a reactant and a solvent. The molar ratio IL/Si was set at 0.5 for the whole study.

**Hydrolytic Method.** Neutral hydrolysis was applied to the preparation of ionogels from [ $C_4$ MIm] ILs with five typical anions: acetate, chloride, tetrafluoroborate, hexafluorophosphate, and bis(trifluoromethylsulfonyl)imide (Table 1). The nature of the anion had a major influence on the gelation rate (Table 1), on the morphology (monolith or powder) of the ionogels (Table 2), and on the porosity of the mesoporous silicas obtained after IL extraction (Figure 1). Monolithic ionogels showing no exudation of IL were obtained within a

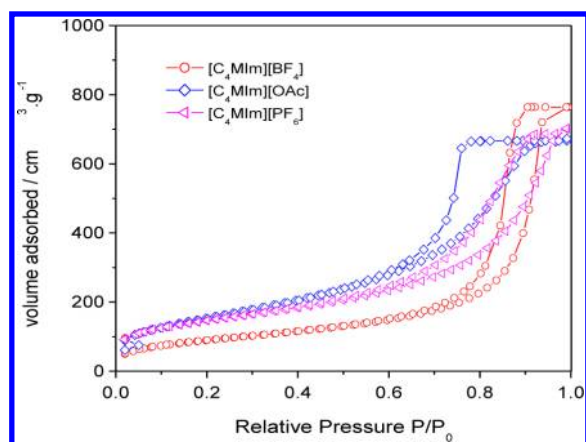
**Table 1. Influence of Anion in Hydrolytic Method: Brunauer–Emmett–Teller (BET) Specific Surface Area, Specific Pore Volume, Mean Pore Diameter from the Maximum of BJH Pore Size Distribution, and Gel Time**

anion	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_p$ ( $\text{cm}^3 \text{g}^{-1}$ )	$D_{\text{BJH}}$ (nm)	gel time
$[\text{BF}_4]$	330	1.21	11.7	few min
$[\text{OAc}]$	564	0.99	5.9	few min
$[\text{PF}_6]$	524	1.05	7.9	15 h
$[\text{Cl}]$	460	0.27	2.5	2 days
$[\text{NTf}_2]$	660	0.66	4.1	4 days

**Table 2. Monolithic Morphology of the Ionogel As a Function of the Sol-Gel Methods: Hydrolysis in Neutral Water or in Aqueous HCl, Solvolysis in Formic Acid**

anion	neutral $\text{H}_2\text{O}$	aq. HCl	FA
$[\text{BF}_4]$	yes	yes	no
$[\text{OAc}]$	yes	yes	yes
$[\text{PF}_6]$	yes	yes	no
$[\text{Cl}]$	yes	no	yes
$[\text{NTf}_2]$	no	yes <sup>a</sup>	yes

<sup>a</sup>Extensive syneresis.



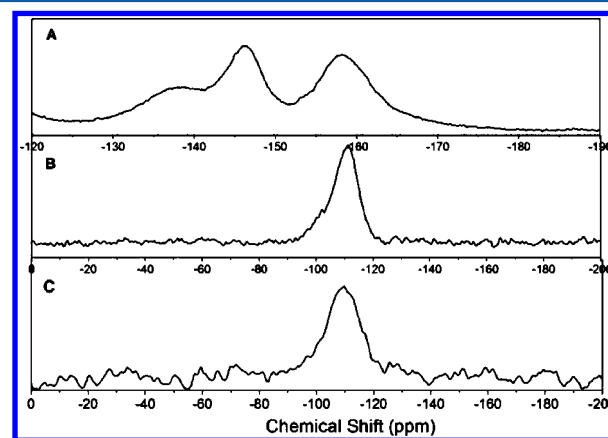
**Figure 1.** Influence of anion in the hydrolytic method:  $\text{N}_2$  sorption isotherms at 77 K of washed gels arising from  $[\text{C}_4\text{MIm}]$  ILs using TMOS precursor.

few minutes in the case of  $[\text{BF}_4]$  and  $[\text{OAc}]$  anions, while using  $[\text{PF}_6]$  gelation occurred within 15 h. After extraction of these ILs, all washed gels presented  $\text{N}_2$  sorption isotherms of type IV (IUPAC) characteristic of mesoporous materials (Figure 1). The highest pore volume was reached for the silica prepared from  $[\text{C}_4\text{MIm}][\text{BF}_4]$  with a pore volume of  $1.21 \text{ cm}^3 \text{ g}^{-1}$  and a pore size of 11.7 nm. The acetate anion led to similar gel times, suggesting a comparable activity; however, the pore volume and pore diameter were lower ( $0.99 \text{ cm}^3 \text{ g}^{-1}$  and 5.9 nm, respectively). The longer gel time observed with  $[\text{PF}_6]$  anion was associated with a broader pore size distribution centered around 8 nm. The small-angle X-ray scattering (SAXS) curves of these samples are shown on Supporting Information, Figure S1. The SAXS patterns of the washed gels prepared from  $[\text{C}_4\text{MIm}][\text{OAc}]$  and  $[\text{C}_4\text{MIm}][\text{BF}_4]$  look very similar even if in the latter case, the size distribution of the particles seems narrower. The radii of gyration ( $R_g$ ) of constituent particles were determined by Guinier Analysis. They range from 5.2 to 7.4 nm for the  $\text{BF}_4^-$  anion and from  $5.2 < R_g < 9.2$  nm for the acetate anion. The SAXS pattern of the silica obtained using

$[\text{C}_4\text{MIm}][\text{PF}_6]$  showed a broader aggregates distribution with smaller particles and larger structures.

Chloride and  $[\text{NTf}_2]$  anions led to much longer gel times, 2 and 4 days, respectively. The resulting ionogels using chloride showed very poor mechanical properties while those obtained with  $[\text{NTf}_2]$  were extensively fractured. The washed gels obtained with these anions showed poor textural properties (Supporting Information, Figure S2). However in the case of chloride, performing the synthesis in pure water (i.e., replacing ethanol by water to keep the volume constant) allowed to reach higher surface area, pore volume, and pore diameter ( $600 \text{ m}^2 \text{ g}^{-1}$ ,  $0.7 \text{ cm}^3 \text{ g}^{-1}$ , and 4.5 nm, respectively) but still showing poor mechanical stability. In the case of  $[\text{NTf}_2]$ , the use of HCl aqueous solutions, instead of neutral water, led to monoliths; however, extensive exudation took place and the silica matrixes showed again very poor textural properties.

$^{29}\text{Si}$  single pulse NMR spectra displayed broad peaks at  $-101$  and  $-110$  ppm, attributed to the  $\text{Q}_{3\text{OR}}$  ( $\text{Si}(\text{OSi})_3(\text{OR})$ ) ( $\text{R} = \text{Me}$  or  $\text{H}$ ) and  $\text{Q}_4$  ( $\text{Si}(\text{OSi})_4$ ) silicon sites, respectively (Supporting Information, Table S1). One supplementary peak at  $-92$  ppm, attributed to  $\text{Q}_2$  ( $\text{Si}(\text{OSi})_2(\text{OR})_2$ ) silicon sites, was observed with  $[\text{Cl}]$  anion. Ionogels prepared with  $[\text{OAc}]$ ,  $[\text{Cl}]$ , and  $[\text{NTf}_2]$  show medium condensation state of silica with condensation degrees  $C$  between 87 and 90% ( $C = 1/4 (2\% \text{Q}_2 + 3\% \text{Q}_3 + 4\% \text{Q}_4)$  ( $\text{Q}_4$  between 55 and 61%). In the case of fluoride containing anions, extremely high condensation states of silica are obtained with condensation degrees  $C$  of 97 and 95% ( $\text{Q}_4$  of 88 and 80%) for  $[\text{BF}_4]$  and  $[\text{PF}_6]$ , respectively. This unusually high condensation degree is only apparent and is in fact accounted for by the presence of  $\text{Q}_{3\text{F}}$  ( $\text{Si}(\text{OSi})_3\text{F}$ ) silicon sites (Figure 2) arising from in situ fluorination reactions

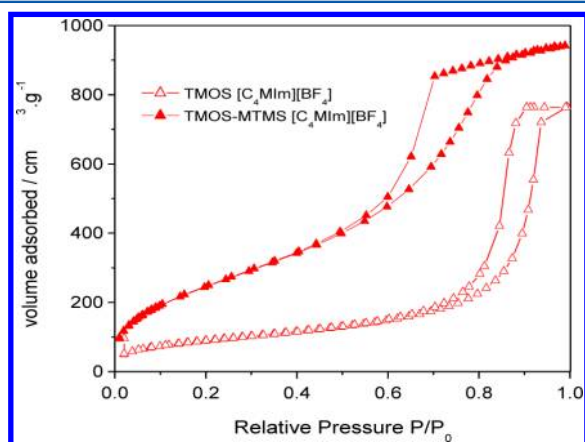


**Figure 2.**  $^{19}\text{F}$  MAS NMR spectrum (A),  $^{29}\text{Si}$  single pulse MAS NMR spectrum (B) and  $^{19}\text{F}$ – $^{29}\text{Si}$  CP MAS NMR spectrum of washed gels obtained using  $[\text{C}_4\text{MIm}][\text{BF}_4]$  (C).

and giving rise to an NMR  $^{29}\text{Si}$  peak at  $-106$  ppm.<sup>41</sup> The  $^{19}\text{F}$  NMR spectrum of silica obtained after extraction of  $[\text{C}_4\text{MIm}][\text{BF}_4]$  displayed three resonances at  $-138$ ,  $-146$ , and  $-158$  ppm revealing the presence of fluorine species in three different environments<sup>41</sup> (Figure 2 A). No signal at  $-151$  ppm attributed to remaining  $[\text{C}_4\text{MIm}][\text{BF}_4]$  was observed. According to Hartmeyer et al.<sup>41</sup> and Lataste et al.<sup>42</sup> who studied silica fluorinated in aqueous ( $\text{NH}_4\text{F}$ ) and in gas ( $\text{F}_2$ ) phases, respectively, the signals at  $-158$  ppm and at  $-146$  ppm are attributed to tetrahedral  $\text{O}_{3/2}\text{SiF}$  as “isolated species” and as species close to other groups of the same type, respectively.

The lower intensity signal at  $-138$  ppm has not been yet attributed (Figure 2). However a signal at  $-137$  ppm was observed in highly postfluorination silica and was attributed to pentahedral  $O_{2/2}SiF_3$  species giving rise to a low intensity peak in  $^{29}Si$  NMR at  $-132$  ppm.<sup>41,42</sup> Moreover,  $^{19}F$ - $^{29}Si$  CPMAS NMR spectra recorded with short contact times ( $500 \mu s$ ) exhibited a unique resonance at  $-109$  ppm (Figure 2 C). A bump at around  $-130$  ppm could arise for  $O_{2/2}SiF_3$  but it is difficult to conclude given the very low signal-to-noise ratio. The apparent high condensation degree obtained with  $[C_4MIm][PF_6]$  ( $C = 95\%$ ), could also come from fluorination of silica (in a less extent) but was difficult to observe by  $^{19}F$  NMR.

It has been reported that incorporation of a hydrophobic group on the silica surface using a mixture of TMOS/MTMS silica precursor allowed to obtain ionogels stable over time toward water.<sup>15</sup> Moreover, besides the utilization of ILs as protective agent, catalytic efficiency of encapsulated enzymes could be enhanced by the presence of hydrophobic alkyl groups in the sol-gel matrix.<sup>43</sup> Accordingly, the effect of added methylated precursor (MTMS) was evaluated in the hydrolytic method. Figure 3 displays the  $N_2$  sorption isotherms of washed gels arising from  $[C_4MIm][BF_4]$  and a TMOS-MTMS precursor mixture (50/50 molar ratio).

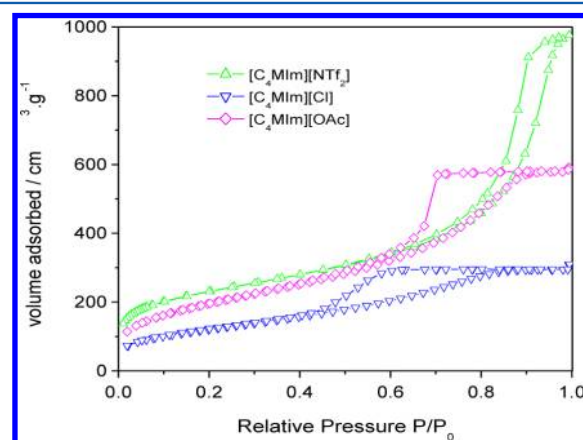


**Figure 3.** Effect of the addition of a methylated precursor in the hydrolytic method:  $N_2$  sorption isotherms at 77 K of washed gels arising from  $[C_4MIm][BF_4]$  and 50/50 TMOS-MTMS precursor mixture.

The addition of MTMS led to an increase of the surface area ( $889 \text{ m}^2 \text{ g}^{-1}$ ) and to a significant decrease of pore size and broadening of the pore size distribution, without affecting the pore volume ( $1.42 \text{ cm}^3 \text{ g}^{-1}$ ). The addition of MTMS was found to be markedly beneficial to the pore volume in the case of washed gels arising from  $[C_4MIm][NTf_2]$  (Supporting Information, Figure S3).

**Formic Acid Solvolytic Method.** FA solvolysis was tested with the same set of  $[C_4MIm]$  ILs, to evaluate again the effect of the anion. This sol-gel method, which involved non aqueous conditions, appeared quite complementary to the hydrolysis method (Table 2). Thus, with  $[BF_4]$  and  $[PF_6]$  anions, FA solvolysis method led to very fast reaction rates and precipitation of non porous solids (Table 2). Conversely, with  $[NTf_2]$  and chloride anions, FA solvolysis turned out to be a much better method than hydrolysis to cast crack-free monoliths. The porous structures obtained with acetate anion were found to be close in the two sol-gel methods. However,

inspection of the FT-IR spectra demonstrated partial protonation of the acetate to form acetic acid (apparition of a new band attributed to  $\nu COOH$  at  $1708 \text{ cm}^{-1}$  see Supporting Information, Figure S4). Note that  $[NTf_2]$  anion led to high open mesoporosity (Figure 4), with specific surface area of



**Figure 4.** Formic acid solvolysis:  $N_2$  sorption isotherms at 77 K of washed gels arising from  $[C_4MIm]$  ILs using TMOS precursor.

about  $780 \text{ m}^2 \text{ g}^{-1}$ , pore volume of about  $1.5 \text{ cm}^3 \text{ g}^{-1}$  and large mesopores of  $10 \text{ nm}$  (Table 3). On the basis of  $^{29}Si$  MAS NMR, condensation rates were very close to those obtained by hydrolytic method ( $87$ – $89\%$ ; Supporting Information, Table S2).

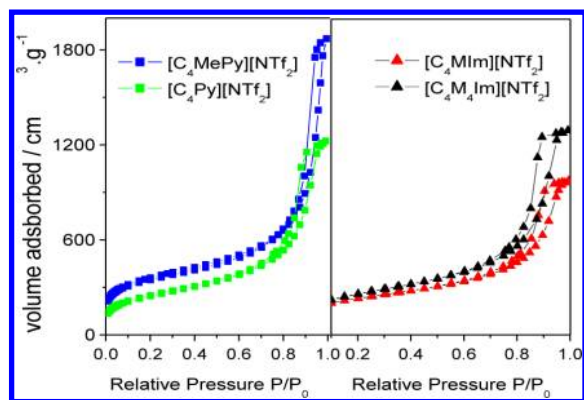
**Table 3.** Influence of Anion in FA Solvolytic Method: BET Specific Surface Area, Specific Pore Volume, Mean Pore Diameter from the Maximum of BJH Pore Size Distribution and Gel Time

anion	$S_{BET}$ ( $\text{cm}^2 \text{ g}^{-1}$ )	$V_p$ ( $\text{cm}^3 \text{ g}^{-1}$ )	$D_{BJH}$ (nm)	gel time
$[BF_4]$	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
$[OAc]$	713	0.91	4.7	2 h
$[PF_6]$	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>	NA <sup>a</sup>
$[Cl]$	436	0.46	3.5	2 h
$[NTf_2]$	773	1.5	10.1	1 h

<sup>a</sup>NA stands for non available as precipitation of non porous solids occurred.

The effect of the cation was further evaluated through two sets of ionogels arising from  $[NTf_2]$  ILs: one involving pyridinium cations (*N*-butylpyridinium  $[C_4Py]$  and *N*-butyl-4-methylpyridinium  $[C_4MePy]$ ), the other involving imidazolium cations (1-butyl-3-methylimidazolium  $[C_4MIm]$  and 1-butyl-2,3,4,5-tetramethyl imidazolium  $[C_4M_4Im]$ ) (Figure 5). In the two cases, after Soxhlet extraction, the pore volumes and mean diameters were found to increase with the molar volume of the IL (in relation with the bulkiness of the cation, pyridinium cations being bulkier than the imidazolium ones), reaching values comparable to those of aerogels (up to  $2.89 \text{ cm}^3 \text{ g}^{-1}$  and  $15 \text{ nm}$ , respectively, for  $[C_4MePy]$ , with a specific surface area of  $1300 \text{ m}^2 \text{ g}^{-1}$ ) (Table 4).<sup>44</sup>

Organic-bridged precursors, as ethylene bridged bis-(trialkoxysilane)s, have been reported to substantially toughen silica materials<sup>36</sup> and improve their hydrothermal stability.<sup>35</sup> As  $[C_4MIm][NTf_2]$  ionogels formed using formic acid and TMOS precursor presented the best structure in term of porosity (surface area and pore volume), a set of ionogels were prepared

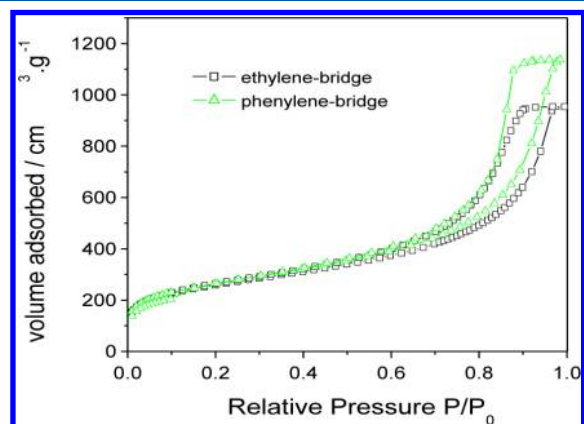


**Figure 5.** Formic acid solvolysis:  $N_2$  sorption isotherms at 77 K of washed gels arising from  $[NTf_2]$  ILs comprising different pyridinium (left) and imidazolium cations (right).

**Table 4.** Formic Acid Solvolysis: Effect of the Bulkiness of the Cation on the Porous Structure of Washed Gels Arising from  $[NTf_2]$  ILs

anion	$S_{BET}$ ( $m^2 g^{-1}$ )	$V_p$ ( $cm^3 g^{-1}$ )	$D_{BJH}$ (nm)
$[C_4Py]$	887	1.89	10.5
$[C_4MePy]$	1298	2.89	15.1
$[C_4MIm]$	773	1.50	10.1
$[C_4M_4Im]$	930	2.00	10.5

using this system incorporating a fraction of ethylene- and phenylene-bridged precursor (BTESE or BTESEB) in the starting formulation. The fraction of organic-bridged precursor was calculated to replace 9% of methoxy groups of TMOS with the ethoxy groups of this component, the idea being to keep the total number of hydrolyzable groups constant throughout the series (the molar ratio IL/Si was kept constant at 0.5). Despite the low molar content (BTESE/TMOS or BTESEB/TMOS = 0.066) of organic-bridged precursor, a significant enhancement of specific surface area and pore volume was observed (Figure 6, Table 5). Thus, on adding only 6.6% BTESEB, the surface area increased from 770 to 960  $m^2 g^{-1}$  and the pore volume from 1.5 to 1.8  $cm^3 g^{-1}$ . Moreover, some improvement of mechanical resistance was obtained with



**Figure 6.** Formic acid solvolysis:  $N_2$  sorption isotherms at 77 K of washed gels arising from  $[C_4MIm][NTf_2]$  and precursor mixtures in which 9% of methoxy groups of TMOS were replaced by the ethoxy groups of BTESE or BTESEB.

**Table 5.** Formic Acid Solvolysis: Effect of the Addition of BTESE or BTESEB Organic-Bridged Precursors on the Porous Structure of Washed Gels Arising from  $[C_4MIm][NTf_2]$

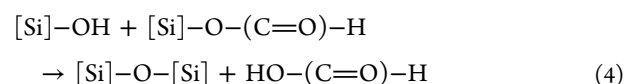
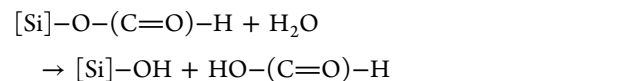
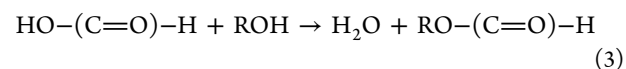
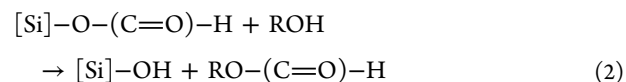
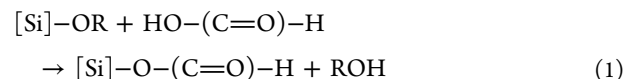
organic-bridged precursor	$S_{BET}$ ( $m^2 g^{-1}$ )	$V_p$ ( $cm^3 g^{-1}$ )	$D_{BJH}$ (nm)
ethylene	923	1.45	6.9
phenylene	961	1.76	8.1
no	773	1.50	10.1

BTESE, the use of bridging siloxane allowing the preservation of the monolith morphology during the Soxhlet extraction.

## DISCUSSION

### Comparison of FA Solvolysis and Hydrolysis Methods.

The FA solvolysis route, initially reported by Sharp,<sup>46</sup> involves the liberation of alcohol molecules by the exchange of formate and alkoxy groups on the silicon atom (eq 1), followed by the nonhydrolytic hydroxylation of formate derivatives (eq 2), as well as the esterification of FA, with in situ generation of water (eq 3).<sup>47</sup> Gelation is believed to result mainly from the high condensation rate of formate groups with silanol groups (eq 4).



Accordingly, the extensive loss of volatiles causes an extensive shrinkage of the monoliths. It is worth stressing that gels arising from the reaction of TEOS with neat FA (without IL) were found to be ultramicroporous, in relation to a considerable collapse of the porous structure on drying. Moreover, aging in FA in the absence of any IL, was shown to accelerate condensation of silanols, which causes an extensive syneresis.<sup>48</sup> This suggests that some ILs (typically those containing anions as  $NTf_2$  or acetate) are able to prevent the pore walls from direct interaction with FA and from collapsing.

On the other hand, the hydrolytic method (at least when minimizing the amount of water) involves a much lower release of volatile byproduct and, accordingly, induces a much lower shrinkage. This can be a choice criterion in the favor of this method. Moreover, neutral hydrolysis, which was found quite efficient in the presence of IL, is a milder method, quite suitable for the immobilization of enzymes for instance. Actually the catalytic activity of the IL anion is a key parameter. Thus, besides the special case of  $BF_4$  and  $PF_6$  anions, which will be discussed below, the catalytic activity of acetate anion (conjugate base of a weak acid) can be related to its basicity. Conversely, the weak catalytic activity of other anions (typically  $[NTf_2]$ , conjugate base of a very strong acid) is not surprising given their weak basicity. However, in the presence of large

amounts of water, a certain catalytic activity of chloride ILs was observed, as previously reported by Karout et al.<sup>49</sup> Besides the intrinsic catalytic activity of the anion, physical properties associated with the choice of anion, such as viscosity and water miscibility, most probably influence the whole sol–gel process. Some key properties of the anion should be its ability to form more or less compact (more or less organized) ion aggregates with the cation, its ability to stabilize the growing silica interface, and finally to provide a protecting film adsorbed on the pore walls.

**Special Case of Fluorinated Anions.** The critical effect of the anion on the kinetics of sol–gel reactions, which finally determines the morphology and structure of the resulting ionogel, is particularly outstanding in the case of fluorinated anions. Thus, FA solvolysis is the appropriate method to immobilize ILs containing  $[\text{NTf}_2]$  anions, which are used as electrolytes in electrochemical devices, whereas neutral hydrolysis is the efficient method to immobilize ILs containing  $[\text{BF}_4]$  or  $[\text{PF}_6]$ .

The efficiency of tetrafluoroborate ILs in preparing mesoporous silica and organosilica gels by the hydrolytic method has been yet reported by Deng et al., which used ethanol as a cosolvent and HCl aqueous solution as a catalyst.<sup>26</sup> Deng et al. ascribed the efficiency of  $[\text{BF}_4]$  anion to a templating effect, in relation to a specific H-bonded arrangement of  $[\text{BF}_4]$  anions along the silica pore walls.<sup>26</sup> Most authors implemented the sol–gel processing in the presence of a Brønsted acid catalyst.<sup>1,2,26,28,50</sup> However in the present study acid hydrolysis (HCl 0.1 N) did not bring about any significant changes with respect to neutral hydrolysis, indicating that the effect of  $[\text{BF}_4]$  anion predominates over other factors. Actually, as noted by Karout et al.,  $[\text{BF}_4]$  anion can act as a catalyst by itself.<sup>49</sup> Even though the point has most often been ignored in the IL literature,  $[\text{BF}_4]$  anion undergoes some hydrolysis in the presence of water, even at room temperature, and releases some  $\text{HF}$ ,<sup>51</sup> which is known as a very powerful catalyst for hydrolytic condensation of alkoxy silanes.<sup>52</sup>  $[\text{BF}_4]$  anion has even been reported as a better-behaved promoter than fluoride anion in aqueous media containing amphiphiles with onium ion headgroups as templates, affording ordered mesoporous silica with thick silicate walls associated with a higher extent of condensation, even without calcination.<sup>53</sup> Note that the hydrolysis for  $[\text{PF}_6]$  anion was shown to occur in imidazolium-based ILs to a much lower extent than with  $[\text{BF}_4]$  anion, at least at moderate temperatures and in the absence of an acidic promoter,<sup>51</sup> which is consistent with the lower catalytic activity observed in this comparative study.

In the hydrolysis method, the in situ formation of HF using  $\text{BF}_4$  anions led to some fluorination of the silica surface as observed by  $^{19}\text{F}$  MAS NMR. This results in an overestimation of the condensation degree as  $\text{Q}_{3\text{F}}$  resonances are expected in the region of  $\text{Q}_4$  resonances.

According to the condensation degree observed using  $[\text{C}_4\text{MIm}][\text{PF}_6]$ , fluorination might have occurred as well, but to a less extent. Importantly, we also observed the decomposition of  $\text{PF}_6^-$  anions in the presence of FA, which led to the formation of  $\text{PO}_3\text{F}_2^-$ ,  $\text{PO}_2\text{F}_2^-$ , and  $\text{PO}_4^{2-}$  species within 1 h (see Supporting Information, Figures S5, S6 and Table S3). The  $^{19}\text{F}$  NMR spectra also presented additional signals after 24 h of stirring at  $-129.7$  ppm ( $\text{SiF}_6^{2-}$ ) and  $-150.8$  ppm ( $\text{BF}_4^-$ ) attributed to the reaction of HF with the borosilicate glass of the vial.

**Preparation of Mesoporous Silica Supports.** When the whole IL is incorporated in the monolith, IL/Si ratio (here set at 0.5) could be thought to determine the pore volume of the final porous silica matrix after solvent extraction. Thus, pore volumes of 1.6 and  $2.4 \text{ cm}^3 \text{ g}^{-1}$  should be theoretically expected for the silicas prepared from  $[\text{C}_4\text{MIm}][\text{BF}_4]$ ,  $[\text{PF}_6]$ ,  $[\text{OAc}]$ , and  $[\text{C}_4\text{MIm}][\text{NTf}_2]$ , respectively. However, the solvent extraction entails some collapse of pores, despite the high condensation extents. Nevertheless, surface area as high as  $1300 \text{ m}^2 \text{ g}^{-1}$ , mesopore diameter of 10–15 nm, and pore volume as high as  $2.9 \text{ cm}^3 \text{ g}^{-1}$  were reached with the bulkier cations by FA solvolysis. Such silica and organosilica supports, which feature both transparency and a high porosity, with large mesopores suitable to host bulky molecules, are of interest to combine the activity of the functional guest with an optical stimulation.

Moreover, it is worth noting that residual IL content from 3 to 7% was determined by TGA (see Supporting Information, Figure S7). The highest amounts of residual IL were observed with the anions showing higher hydrogen bonding acceptor abilities ( $[\text{Cl}]$ ,  $[\text{OAc}]$  anions). These substantial IL films could be of interest for some applications such as catalysis<sup>54</sup> (even though it could be also removed by calcination if pure silica surface was required). Typically, this kind of material, produced under neutral conditions and with  $[\text{OAc}]$  anions, could be a useful method to immobilize or encapsulate enzymes and to protect them from inhibitors, since enzymes can undergo organic solvents when dissolved in ILs.<sup>20</sup>

## CONCLUSIONS

Several sets of silica and organosilica ionogels were prepared from imidazoliums and pyridiniums ILs with a range of typical anions by either hydrolysis or FA solvolysis of TMOS, or mixtures of TMOS and MTMS or TMOS and an organically bridged precursor. In the two methods, the occurrence of cracking or/and expulsion of IL (i.e., the collapse of the porous structure) on aging were shown to depend on the nature of the IL anion and to a lesser extent on the nature of silicon precursors. Accordingly the choice of the anion, which depends on the application area, dictates the choice of the sol–gel methods.

Actually, the two methods turned out to be complementary. FA solvolysis was confirmed to be a robust sol–gel method to get non-exuding crack-free mesoporous silica monoliths from TMOS and imidazolium (or pyridinium) ILs containing  $[\text{NTf}_2]$  anion, whereas neutral hydrolysis was found to be the proper sol–gel method with ILs containing  $[\text{BF}_4]$  and  $[\text{PF}_6]$  anions. Note that in the case of acetate anion, both methods could be used to obtain porous materials. However, neutral hydrolysis should be used instead of FA solvolysis to confine the IL without protonation of acetate (i.e., exchange for formate anion).

In the hydrolytic sol–gel method, the use of HCl aqueous solution as a catalyst brought no decisive advantage over neutral hydrolysis, which highlights the catalytic activity of most IL anions. More specifically, tetrafluoroborate anion showed an outstanding catalytic activity and led to highly condensed silica networks, with high mesoporosity and some fluorination of surface sites. The use of some methylsilane precursor led to textural improvements as well, while modifying the hydrophilic character of the mesopore walls.

In the FA solvolysis, transparent mesoporous silicas and organo-silicas featuring surface area as high as  $1300 \text{ m}^2 \text{ g}^{-1}$ , pore volume as high as  $2.9 \text{ cm}^3 \text{ g}^{-1}$ , and mesopore diameter as

high as 15 nm have been successfully prepared. They could be efficient supports for immobilizing bulky molecules (e.g., porphyrins, enzymes, organometallic compounds) for catalysis and separation, and other applications requiring transparent monoliths and light stimulation (e.g., photocatalysis, photosensing).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Five figures and two tables showing N<sub>2</sub> sorption isotherms, TGA, FT-IR, SAXS patterns, and condensation extent measurements of different ionogels. Two figures and one table showing <sup>19</sup>F and <sup>31</sup>P NMR of the mixture of [C<sub>4</sub>MIm]-[PF<sub>6</sub>] and FA. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

S.V. thanks the Regional Council of Languedoc-Roussillon for a financial grant.

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