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Textural control of Ionosilicas by Ionic Liquid templating

Nicole Abdou[1], Philippe Dieudonné-George[2], Nicolas Brun[1], Ahmad Mehdi[1], and Peter Hesemann[1]**

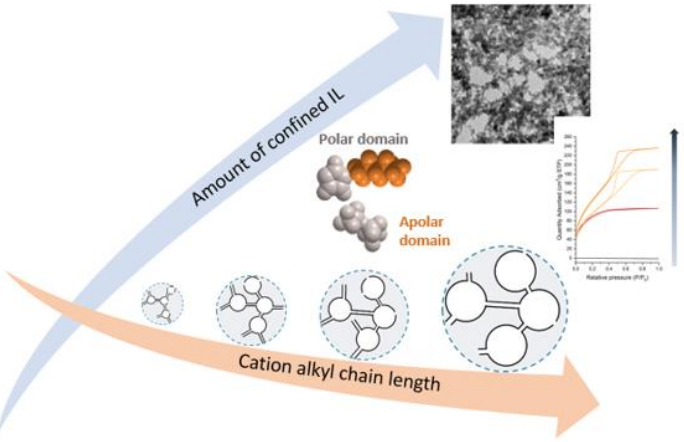
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KEYWORDS

Ionosilica, mesoporosity, sol-gel process, template directed synthesis, Ionic liquids.

Graphical Abstract



Ionic liquids were used as templates for the synthesis of mesoporous ionosilica phases. The textures of the formed solids can efficiently be controlled by the quantity of IL and the length of the alkyl chain of the IL.

ABSTRACT

Due to their unique self-assembly properties, ionic liquids (ILs) are versatile soft templates for the formation of mesoporous materials. Here, we report the use of ionic liquids as soft templates for the straightforward formation of mesoporous ionosilica phases. Ionosilicas are highly polyvalent functional materials that are constituted of ionic building block that are covalently immobilized within a silica hybrid matrix. Ionosilicas attracted significant interest in the last few years due to their high potential for applications in water treatment and upgrading, separation and drug delivery. The straightforward and reproducible formation of mesoporous ionosilica phases is therefore highly desirable. In this context, we report the formation of mesoporous ionosilica phases via non-hydrolytic sol-gel procedures in the presence of ionic liquids. Ionic liquids appear as particularly versatile templates for mesoporous ionosilicas due to the high chemical similarity and affinity between ILs and silylated ionic precursors. We therefore studied the textures of the resulting ionosilica phases, after IL elimination, using nitrogen sorption, small angle X-ray scattering (SAXS) and transmission and scanning electron microscopy. All these techniques give concordant results and show that the textures of the ionosilica scaffolds in terms of specific surface area, pore size, pore size distribution and connectivity, can efficiently be controlled by the nature and the quantity of the ionic liquid that is used in the ionothermal sol-gel procedure.

Introduction

Ionic liquids (ILs) have been widely investigated over the last decades for their unique properties such as high ionic conductivity and chemical stability, low vapor pressure and low flammability. ILs are salts with melting point below 100 °C.[1] They are known as "designer solvents" since one can tailor their properties choosing distinct cation/anion combination that matches the requirements of a given application. ILs with specific properties have been developed for applications in various domains such as energy storage[2-3], catalysis[4-5], gas adsorption[6] *etc*. Besides, ILs, and in particular imidazolium based ILs, show a very particular self-organization behavior.[7-10] On the one side, ILs form structured phases in the liquid state *via* the formation of extended hydrogen bonded networks.[11] On the other side, ILs phases display nanoscale segregation in polar and non-polar domains.[12] This segregation is the more pronounced the longer the alkyl chain of the IL is. ILs therefore display heterogeneities on the nanoscopic level that linearly scale with the length of the alkyl chain.[12] The nanoscale segregation increases with the length of the alkyl chain, resulting in liquid-crystalline (LC) behavior for long chain substituted ILs.[13] Besides the length of the alkyl chain, the nature of the counter anion is also of prime importance for the formation of ionic liquid crystal phases. Whereas long-chain (>C12) substituted imidazolium halides form LC-phases, the corresponding *bis*-triflimides do not.[14-15] Altogether, ILs display a unique self-aggregation behavior on various levels, that results either from their ability to form H-bonded networks, nanoscale segregation in polar/nonpolar domains or even highly organized and ordered lyotropic phases.[16] Due to all these features, ILs should therefore be considered as 'supramolecular' solvents.[17]

This unique self-organizing behavior makes that ILs are efficient soft templates for the synthesis of mesoporous materials. Following the IUPAC nomenclature, mesoporous materials are porous

compounds with pore size between 2 and 50 nm[18] that display some interesting properties such as high specific surface area and high pore volume. These features ensure enhanced diffusivity of large molecules throughout the material, diffusion being the dominant mass transport mechanism in mesopores.[19] Due to their textural features combining high specific surface area, tunable pore size and pore volume, mesoporous materials are potentially advantageous for applications in catalysis,[20] separation and energy storage.[21]

The first example of a mesoporous material synthesized in the presence of ILs goes back to the work of Dai *et al.* who reported the formation of a silica aerogel following an non-hydrolytic ionothermal sol-gel procedure.[22] Several years later, Antonietti *et al.* reported the synthesis of mesoporous silica using the IL $[C_4MIM]BF_4$. Elimination of the confined IL from the host matrix *via* washing led to a mesoporous silica material displaying a worm-like architecture.[23] The authors postulated a cooperative hydrogen bonding-π-π stacking mechanism to be responsible for the generation of mesoporosity and the formation of moderately ordered phases within this material. Finally, long-chain substituted imidazolium salts which were used for their lyotropic properties. These compounds have successfully been used in hydrolysis polycondensation processes following classical templating strategies.[24-25]

The alkyl chain length of the IL has indeed significant impact on the segregation in nano-domains within the IL and therefore also on the template effect in ionosilica syntheses. We consider that silica or ionosilica precursors, as polar components, have particular affinities toward the polar nano-domains of the IL, and that the non-polar domains particularly contribute to the formation of the texture of the materials. The size of the alkyl groups of the IL therefore has a direct influence on the textures of the materials formed in the presence of IL phases.[26-27]

These examples highlight the templating behavior of ILs and clearly indicate that the structuration of ILs can be transcribed to solid phases. ILs are therefore not only structured but also structuring phases, with high potential in the area of materials chemistry and in particular for the elaboration of materials via bottom-up approaches.[28-32]

Since several years, our special concern is the elaboration of ionosilica phases with particular morphologies and architectures. We define ionosilicas as silica hybrid materials constituted of ionic building blocks.[33] Ionosilicas are highly modulable functional materials featuring a large range of surface and interface properties.[34-35] They found applications in water treatment and upgrading,[36-37] separation[38-39] and drug delivery.[40-42] Due to the high chemical similarity between ionosilicas and ILs and with the aim to study the confinement of ILs within an ionosilica matrix, we recently focused on the formation of nanocomposites via hydrolysis-polycondensation reactions of ionosilica precursors in the presence of ILs.[43] For this purpose, we synthesized various ionosilica ionogels, and we could demonstrate particular confinement effects between the ionic host and guest. More specifically, we were able to show that an IL confined within an ionic host matrix forms two distinct populations: (*i*) the first one interacting with the pore walls via electrostatic interactions; and (*ii*) the second one, forming bulk-like IL domains.[44-45] As a particularity of these all-ionic composites, we could access free-standing and mechanically robust ionosilica ionogel monoliths containing up to 80 wt.% of IL by this approach what can be explained by the high affinity between ionic host and guest

However, a systematic study of the textural properties of the ionosilica scaffolds formed in the presence of ILs is missing so far. That's why we describe here how the textural properties of ionosilica scaffold can be tuned as a function of the IL, *i.e.* via the amount of the used imidazolium

bis-triflimide IL and the length of its cation alkyl chain. We demonstrate that ILs allow an efficient control of the texture of ionosilicas in terms of specific surface area, pore size and pore volume.

Experimental section

Chemicals. The ionosilica precursor *tris*(3-(trimethoxysilyl)propyl)amine (TTA) was synthesized following previously described protocols.[33] All imidazolium-based ionic liquids [C_xMIM]TFSI (x = 2, 4, 6, 8, 12 and 16) were purchased from IoLiTec. Formic acid (p.a.) was purchased from VWR. All chemicals were used as received.

Synthesis of ionosilica materials. The synthesis of various ionosilica ionogels was performed in one-pot syntheses involving the ionosilica precursor **TTA**, formic acid and ionic liquid. Various imidazolium TFSI ILs with variable alkyl chain length were used: [C_xMIM]TFSI (x = 2, 4, 6, 8, 12 and 16). The ionosilica matrices were formed via a non-hydrolytic sol-gel procedure from the *tris*(3-(trimethoxysilyl) propyl) amine precursor **TTA** in the presence of the IL. First, 3.0 g of **TTA** precursor were mixed and vigorously stirred for three minutes with various molar amount of IL in a Pyrex glass tube using a vortex apparatus. Then the polycondensation reaction was initiated by adding 2.0 mL of formic acid to the mixture. The exact quantities of the reactants in the ionosilica syntheses are given in table 1. Gelation results from transesterification-polycondensation reactions undergone by the trimethoxysilyl groups of the TTA precursor. Note that the protonation of the precursor occurs during the sol-gel process yielding the ionic building blocks of the ionosilica matrix. Colorless monoliths were obtained after 24 h at room temperature and kept under static conditions at 80 °C overnight. The ionosilica monoliths were obtained after extraction of the IL with ethanol using a Soxhlet apparatus. Finally, the materials were dried at 80 °C under vacuum (0.01 mbar) during 24 h. The ionosilica monoliths are labelled $\mathbf{TS}_{\mathbf{z}}^{\boldsymbol{C_x}}$, where C_x is the length of the cation alkyl chain (x = 2, 4, 6, 8, 12, 16) and **z** is quantity of IL in mmoles.

Table 1 Used quantities for the synthesis of ionosilica ionogels materials.

	TTA		[C_xMIM]TFSI	HCOOH
	m(g)	n(mmol)	n(mmol)	V(mL)
$TS_3^{C_x}$	3.0	6.0	3.0	2.0
$TS_{10}^{C_x}$	3.0	6.0	10.0	2.0
$TS_{20}^{C_x}$	3.0	6.0	20.0	2.0
$TS_{41}^{C_x}$	3.0	6.0	41.0	2.0

Nitrogen Sorption isotherms were recorded at 77 K on a Micromeritics TriStar volumetric apparatus by admitting doses of N_2 in a measurement cell after an outgassing treatment of the samples at 120 °C under vacuum overnight. The BET surface area of each sample was determined using the Brunauer-Emmett-Teller (BET) method[46] on the linear range of the isotherms typically at p/p_0 = 0.05-0.15. The pore size distribution was calculated with the Barret-Joyner-Halenda (BJH) method[47] from the adsorption isotherm. The total pore volume of the materials was determined at p/p_0 = 0.99.

Small angle X-ray scattering (SAXS) experiments were performed with an in-house setup of the Laboratoire Charles Coulomb, Université de Montpellier, France. A high brightness low power X-ray tube, coupled with aspheric multilayer optic (GeniX^{3D} from Xenocs) was employed. It delivers an ultralow divergent beam (0.5 mrad, λ=0.15418 nm). Scatterless slits were used to give a clean 0.6 mm beam diameter with a flux of 35 Mphotons/s. We worked in a transmission configuration where the scattered intensity was measured by a 2D "Pilatus" 300 K pixel and detected by Dectris detector (490*600 pixels) with a pixel size of 172×172 μm^2, placed at a 1.9 m

distance from the sample. All intensities were corrected by transmission and the empty cell contribution (glass capillary) was subtracted.

Transmission Electron Microscopy (TEM) measurements were performed with a FEG JEOL 2200 FS–200 KV electron microscope equipped a CCD GATAN USC camera with 4092 × 4092 pixels and an electron gun of 200kV. The probe diameter in STEM mode is about 1 nm with a resolution able to attain 0.1 nm.

Scanning electron microscopy (SEM) images were taken with a Hitachi S-4800 microscope, Japan. 2 kV acceleration voltage was applied on grounded IL free samples.

Results and discussion

Nonhydrolytic sol-gel reactions of silylated precursors in the presence of ionic liquids result in the formation of silica based ionogels, where an ionic liquid is trapped within a silica matrix.[22] Following this strategy, we recently reported ionosilica ionogels, a special case of all-ionic composite materials,[43] formed from ionosilica precursors. Whereas the confinement of the IL was investigated and strong interactions between ionic host and guest could be demonstrated, the texture of the formed ionosilica scaffolds that are formed in this non-hydrolytic sol-gel approach has not been investigated so far. In this work, we therefore focused on the characteristics of the formed ionosilica scaffolds formed by non-hydrolytic sol-gel approach, obtained after IL elimination by washing. We determined in particular the textural characteristics of the ionosilicas as a function the reaction parameters, in particular of the quantity and the constitution of the used IL. We investigated the characteristics of the ionosilica materials as a function of two parameters: (1) the amount of ILs [C_xMIM]TFSI in the hydrolysis-polycondensation mixture and (2) the length of alkyl chain on the imidazolium cation.

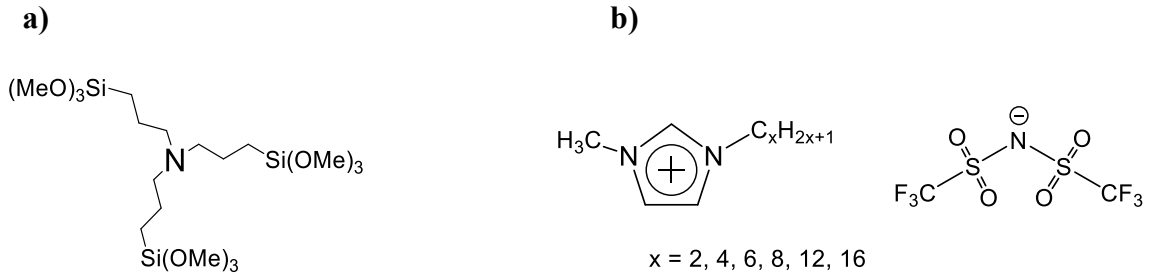


Figure 1 *(a):* molecular structure of the ionosilica precursor *tris*(3-(trimethoxysilyl)propyl)amine (**TTA**); *(b)*: molecular structure of the used imidazolium-based ionic liquids [C_xMIM]TFSI.

More specifically, the ionosilica materials were obtained from the *tris*-trialkoxysilylated amine precursor **TTA** (figure 1a) in the presence of various methyl-alkylimidazolium *bis*-triflimides (figure 1b) *via* non-hydrolytic sol-gel reactions in the presence of formic acid.[48] Ionosilica ionogels monoliths are formed at room temperature after several hours. After aging at 80 °C and IL elimination by washing, we obtained ionosilica phases that are labelled $\mathbf{TS}_{\mathbf{z}}^{\boldsymbol{C_x}}$, where **z** is quantity of the IL in mmoles and $\boldsymbol{C_x}$ is the length of the cation alkyl chain (x = 2, 4, 6, 8, 12 and 16). Here, we focused particularly on the impact of two parameters on the texture of the formed ionosilicas: (*i*) the quantity of the IL and (*ii*) the length of the alkyl chain of the methyl-alkyl imidazolium cation, and we studied the textural properties of the obtained materials *via* nitrogen sorption, small-angle X-ray scattering (SAXS), scanning and transmission electron microscopy (SEM and TEM).

Nitrogen sorption measurements at 77 K allowed determining the textural properties of the materials in terms of specific surface area S_{BET}, pore volume V_p and pore size D_p. The results are summarized in table 2, and a histogram of specific surface area data of the materials is given in figure 2. Histograms displaying the pore size and pore volumes are given in the ESI (figures S1 and S2).

Table 2 BET surface area, pore volumes and pore diameters of ionosilica monoliths synthesized in the presence of [C_xMIM]TFSI ionic liquids. The sets of materials that are discussed in detail in the text are in bold.

	S_{BET} (m^2/g)				Total pore volume Vp (cm^3/g)[a]				Pore diameter Dp (Å)[b]			
z (mmol)	3	10	**20**	41	3	10	**20**	41	3	10	**20**	41
$TS_z^{C_2}$	< 1	76	**444**	358	n.d.	0.04	**0.31**	0.31	n.d.	23	**30**	36
$\boldsymbol{TS_z^{C_4}}$	**< 1**	**310**	**463**	**306**	**n.d.**	**0.17**	**0.35**	**0.30**	**n.d.**	**24**	**31**	**34**
$TS_z^{C_6}$	< 1	306	**463**	353	n.d.	0.16	**0.36**	0.30	n.d.	24	**32**	35
$TS_z^{C_8}$	< 1	402	**525**	500	n.d.	0.22	**0.52**	0.50	n.d.	25	**39**	39
$TS_z^{C_{12}}$	< 1	516	**577**	520	n.d.	0.39	**0.81**	0.70	n.d.	32	**55**	52
$TS_z^{C_{16}}$	356	520	**600**	590	0.22	0.50	**0.78**	0.77	27	34	**52**	50

[a]Determined at p/p_0 0.99. [b]Calculated following the Harkins and Jura equation.[49]

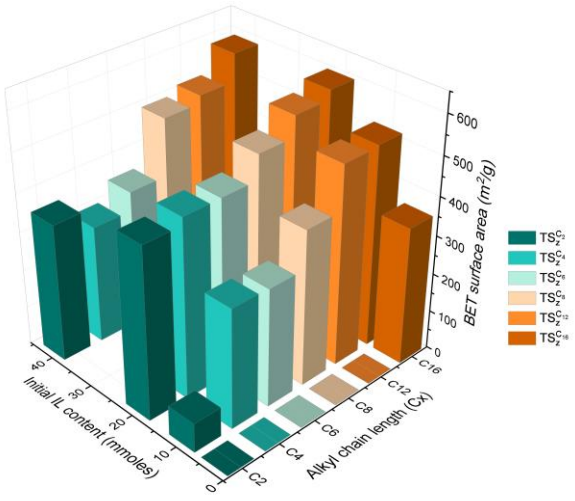


Figure 2 Histograms of the BET surface areas of the IL-free ionosilica ionogels $\mathbf{TS_z^{C_x}}$, synthesized in the presence of different volumes of imidazolium IL [C_xMIM]TFSI (x = 2, 4, 6, 8, 12 and 16).

At a first glance, the formed monoliths are moderately to highly porous materials, with specific surface areas in the range of 300-600 m^2/g. The materials are mostly mesoporous with pore

diameters in the range of 25-55 Å, except those that are synthesized with the lowest amount of IL, *i.e.*, the $\mathbf{TS_3^{C_x}}$ series obtained with 3 mmoles of IL. These latter materials are non-porous with specific surface areas $S_{BET} < 1$ m^2/g. It should be mentioned that all $\mathbf{TS_z^{C_x}}$ materials (z = 10, 20 and 41) display large pore size distribution (figures S3 - S8).

In order to highlight the impact of the two investigated parameters, *i.e.,* the quantity of the IL and the substitution the alkyl chain of the methyl-alkyl imidazolium cation, on the textures and architectures of the formed ionosilica phases, we discuss more in detail two sets of materials:

i) the ionosilicas $\mathbf{TS_z^{C_4}}$, synthesized in the presence of variable amounts of the IL [C$_4$MIM]TFSI on the one side,

ii) the ionosilicas $\mathbf{TS_{20}^{C_x}}$, synthesized in the presence of 20 mmoles of different methyl-alkylimidazolium *bis*-triflimides with different alkyl chain length on the other side. The nitrogen sorption isotherms of both series of materials are given in figures 3a and 3b.

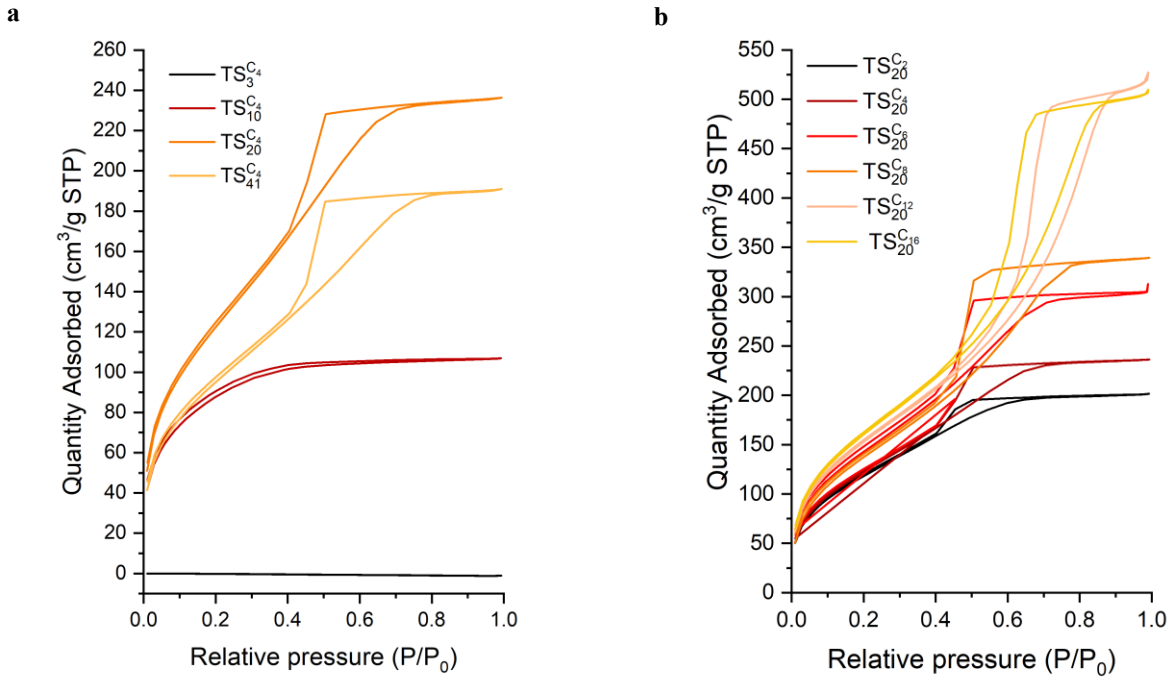


Figure 3 (*a*) Nitrogen sorption isotherms of monoliths synthesized in the presence of variable amounts of [C_4MIM]TFSI; (*b*) Nitrogen sorption isotherms of the ionosilica monoliths synthesized in the presence of 20 mmoles of methyl-alkylimidazolium *bis*-triflimides [C_xMIM]TFSI with variable alkyl chain length (x = 2, 4, 6, 8, 12 and 16).

In the series of ionosilicas $\mathbf{TS_z^{C_4}}$, formed in the presence of variable amounts of [C_4MIM]TFSI, our results indicate low porosity for the material $\mathbf{TS_3^{C_4}}$ that is synthesized in the presence of the lowest quantity of IL (3 mmoles). For the materials $\mathbf{TS_{10}^{C_4}}$ and $\mathbf{TS_{20}^{C_4}}$, a significant increase of the specific surface area was observed, to reach a maximum value for the material $\mathbf{TS_{20}^{C_4}}$. Finally, the material $\mathbf{TS_{41}^{C_4}}$, synthesized in the presence of the highest quantity of IL, shows slightly lower specific surface area compared to material $\mathbf{TS_{20}^{C_4}}$. This general trend can be found in all other series of ILs, synthesized in the presence of variable amounts of a given IL.

The evolution of the pore volume in the series of the materials $\mathbf{TS_z^{C_4}}$ follows an identical trend. We found increasing values up to the material $\mathbf{TS_{20}^{C_4}}$**.** This material shows the highest pore volume in this series. The pore volume slightly decreased when the IL quantity is further increased, *i.e.,* in the case of the material $\mathbf{TS_{41}^{C_4}}$.

In contrast, the pore diameter progressively increases in this series of materials. This evolution can clearly be seen in the nitrogen sorption via the shape of the isotherms (figure 3a). Whereas material $\mathbf{TS_3^{C_4}}$ displays low porosity, the material $\mathbf{TS_{10}^{C_4}}$ gives rise to a type I isotherm, evidencing the presence of supermicropores (wide micropores of width between 7 and 20 Å). The isotherms of the materials $\mathbf{TS_{20}^{C_4}}$ and $\mathbf{TS_{41}^{C_4}}$ show type IV isotherms with H2(a) type hysteresis loops, attesting the presence of narrow mesopores with a diameter of 30 and 35 Å, respectively. The very steep

decrease in the desorption branch at a relative pressures of ca. 0.4 is typical of cavitation-induced evaporation (the pore body empties while the pore neck remains filled) and suggests the presence of bottle-neck type mesopores.[50]

Regarding the series of materials $\mathbf{TS}_{\mathbf{20}}^{\boldsymbol{C_x}}$, synthesized in the presence of 20 mmoles of methyl-alkylimidazolium *bis*-triflimides, we observed an increase of specific surface area, pore size and pore diameter for the materials with ethyl, butyl, hexyl, octyl and dodecyl groups (figure 3b). The specific surface area levels off for the material $\mathbf{TS}_{\mathbf{20}}^{\mathbf{C_{16}}}$. In contrast, whereas the use of short-chain substituted ILs (C_2-C_6) results in the formation of materials with similar pore size, the use of long-chain substituted ILs (C_{12}/C_{16}) led to materials with significantly larger pores, as indicated by the different shape of the nitrogen sorption isotherms (figure 3b, table 2 - *pore diameter*). This latter result indicates a particular templating behavior of long chain substituted ILs, namely of dodecyl- and hexadecyl-methylimidazolium *bis*-triflimide.

Our results therefore reveal a clear correlation between the nature and the amount of the IL on the textures of the formed materials. They indicate that the supramolecular aggregation of imidazolium based *bis*-triflimide ILs in hydrophilic and hydrophobic domains has a direct impact on the texture of the formed ionosilicas in terms of specific surface area, pore size and pore volume. The porosity of the ionosilica matrix can be well tuned both *via* the amount of confined IL and the length of the cation alkyl chain.

We then performed small angle X-ray scattering (SAXS) in order to get a more detailed insight in the pore architecture of the materials. Similarly to the results of nitrogen sorption experiments, we discuss here more in detail the same sets of materials: *i*) the ionosilicas $\mathbf{TS}_{\mathbf{z}}^{\boldsymbol{C_4}}$, synthesized in the presence of variable quantities of the IL [C_4MIM]TFSI on the one side, and *ii*) the ionosilicas $\mathbf{TS}_{\mathbf{20}}^{\boldsymbol{Cx}}$, synthesized in the presence of 20 mmoles of different methyl-

alkylimidazolium *bis*-triflimides with different alkyl chain length on the other side. The SAXS patterns of the $\mathbf{TS}_{\mathbf{z}}^{\mathbf{C_4}}$ materials are given in figure 4, and the patterns of the series $\mathbf{TS}_{\mathbf{20}}^{\boldsymbol{Cx}}$ are shown in figure S13.

Similar SAXS profiles were obtained for all materials of the $\mathbf{TS}_{\mathbf{z}}^{\mathbf{C_4}}$ series (figure 4), synthesized in the presence of different quantities of ILs. However, the patterns show some significant evolutions namely in the high q (q = ~0.5-1 nm^{-1}) and low q domains (q = ~ 0.15-0.4 nm^{-1}). At q values in the range of ~0.5-1 nm^{-1}, the SAXS intensity profiles show a cross over, whose position clearly shifts toward lower q values as a function of the molar fraction **z** of ionic liquid used to prepare the $\mathbf{TS}_{\mathbf{z}}^{\boldsymbol{C_x}}$ samples. This q region profile should be characteristic of the form factor of pores in mesoporous solids. In the case of wormlike ink-bottle pores, we can estimate, from the q-position of the cross over (see dash lines in figure 4), the order of magnitude of the average pore diameter d (nm) using the equation 1:

$$d\ (\text{nm}) \sim 2/q(\text{nm}^{-1}) \qquad (1)$$

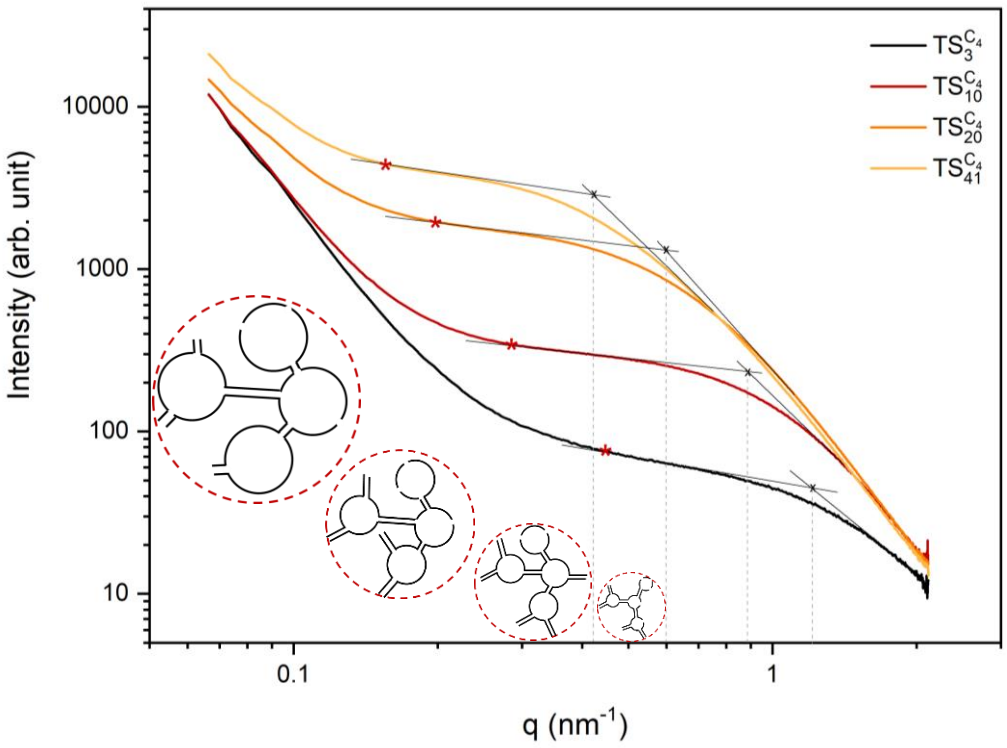


Figure 4 SAXS patterns of the $\mathbf{TS_z^{C_4}}$ monoliths synthesized in the presence of variable amount of [C_4MIM]TFSI (z= 3, 10, 20 and 41).

The shift of the cross over toward lower q values as a function of **z** (figure 4), from 1.188 nm^{-1} for $\mathbf{TS_3^{C_4}}$ to 0.420 nm^{-1} for $\mathbf{TS_{41}^{C_4}}$, clearly indicates an increase of the pore diameter values obtained by SAXS, from ~17 to ~48 Å, respectively (Table 3). The increase in the quantity of [C_4MIM]TFSI therefore promotes the formation of larger confined ionic liquid domains within the host matrix, resulting in the formation of larger pores within the ionosilica scaffold after IL elimination. Interestingly, the values of the pore diameters obtained from nitrogen sorption and SAXS measurements are in good agreement (Table 3). The slightly higher values obtained by SAXS compared to those obtained by nitrogen sorption can be explained by limited pore filling in the case of closed porosity or interconnected pores with too narrow openings in nitrogen sorption

experiments. Furthermore, some pores could also not be completely filled with nitrogen, depending on the pore surface curvature distribution (convex/concave).[51] Comparatively, the SAXS scattering signal only depends on the real volumetric distribution of density fluctuations inside the monolith, regardless of the pore architecture and connectivity. Therefore, the pore sizes obtained by nitrogen sorption are then often underestimated compared to SAXS values, as also observed here.

At lower q values (in the ~ 0.15-0.4 nm^{-1} q range), a second cross-over can be observed for all samples (figure 4). This type of SAXS profile suggests the aggregation of individual pores into primary pore clusters. Pores are interconnected by narrow paths to form larger pore domains in accordance with "ink-bottle" shape deduced from the mentioned H2 type isotherms observed in figures 3a and 3b. Such primary porous clusters can be interconnected to form larger pore aggregates (at the 100-1000 nm scale), as suggested by the significant increase of the scattering intensity observed at lower q values on figure 4 for all samples. A characteristic size d' (nm) of the primary clusters can also be deduced from relation (1). A shift toward lower q values of the primary cluster cross-over as a function of z is observed in figure 4. It can be seen that d' increases proportionally to z value from ~40 Å ($\mathbf{TS_3^{C_x}}$) to ~125 Å ($\mathbf{TS_{41}^{C_x}}$) that corresponds to 2-3 times the size of individual pore size.

Table 3 Small-angle X-ray scattering data of $\mathbf{TS_z^{Cx}}$ monoliths with different ratio of [C_xMIM]TFSI ionic liquid.

	Pore diameter (Å)[a]				*Pore diameter (Å)*[b]			
n (mmol)	3	10	***20***	41	3	10	***20***	41
$TS_z^{C_2}$	14	22	***34***	47	n.d.	23	***30***	36
$\mathbf{TS_z^{C_4}}$	***17***	***22***	***33***	***48***	n.d.	***24***	***31***	***34***
$TS_z^{C_6}$	16	26	***35***	47	n.d.	24	***32***	35
$TS_z^{C_8}$	19	24	***39***	49	n.d.	25	***39***	39
$TS_z^{C_{12}}$	n.d	n.d	***48***	n.d	n.d.	32	***55***	52
$TS_z^{C_{16}}$	n.d	n.d	***42***	n.d	27	34	***52***	50

[a]Determined by SAXS using relation (1). [b]Calculated by Harkins and Jura equation from nitrogen sorption analysis.[49]

Regarding the second series of materials $\mathbf{TS_{20}^{Cx}}$, we also studied the effect of the length of the cation alkyl chain on the textural properties of the obtained material *via* SAXS measurements. As discussed earlier, the alkyl chains of the IL tend to aggregate into nonpolar domains whereas the imidazolium ring and the anion form polar domains.[52] The increase of the length of the alkyl chain of the cation is expected to enlarge the nonpolar IL domains.[15] The SAXS profiles (figure S13) show the presence of two evolution domains as function of the length of the cation alkyl chain (C_x), similarly to the results discussed in figure 4 (*vide supra*). The average size of pores and pore primary-clusters clearly increases with the increase of the length of the cation alkyl chain for x > 8. SAXS experiments therefore indicate the same trend as observed in nitrogen sorption measurements and confirm that only long-chain substituted imidazolium ILs (C12 and C16) led to an increase of the pore diameters, whereas no significant increase of the pore size could be observed for short chain substituted species (C<10). These results therefore highlight a particular

self-aggregation behavior of dodecyl- and hexadecyl-imidazolium *bis*-triflimides, as already described earlier.[53]

Finally, morphologies and textures of the materials were studied via scanning and transmission electron microscopy (SEM and TEM). Figure 5 shows SEM images of the materials $\mathbf{TS}_{\mathbf{20}}^{\mathbf{C_2}}$, $\mathbf{TS}_{\mathbf{20}}^{\mathbf{C_8}}$ and $\mathbf{TS}_{\mathbf{20}}^{\mathbf{C_{16}}}$, all synthesized in the presence of 20 mmoles of [C_xMIM]TFSI (x = 2, 8 and 16).

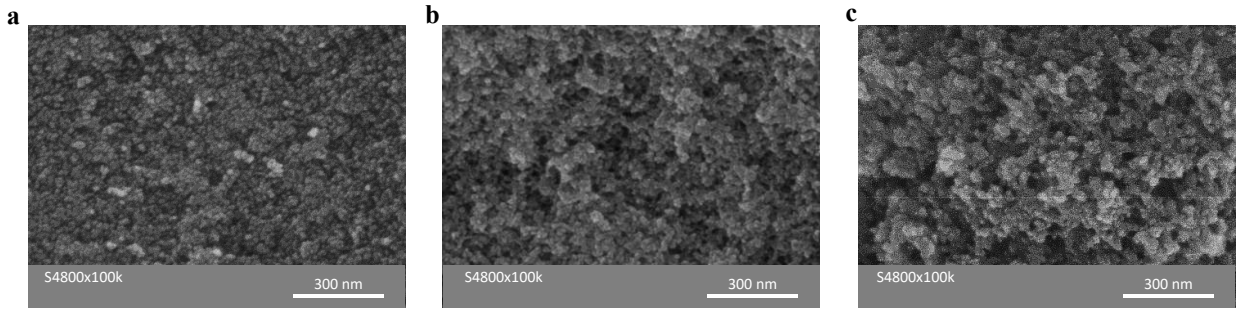


Figure 5 Scanning electron microscopy (SEM) images of $\mathbf{TS}_{\mathbf{20}}^{\mathbf{C_2}}$, $\mathbf{TS}_{\mathbf{20}}^{\mathbf{C_8}}$ and $\mathbf{TS}_{\mathbf{20}}^{\mathbf{C_{16}}}$monoliths with 20 mmoles of (a) [C_2MIM]TFSI (b) [C_8MIM]TFSI and (c) [C_{16}MIM]TFSI. Scale bars: 300 nm.

The SEM images show that the materials consist of agglomerated primary particles of nanometric size (at the 10-100nm scale). The diameter of the primary particles depends on the nature of the used IL and increases with increasing alkyl chain length. Hence, the utilization of long chain (C_{16}) substituted imidazolium *bis*-triflimides led to the formation of a material displaying a widened architecture, larger pores and larger granulometry compared to the two other materials as shown in figure 5 (a-c). All formed ionosilicas show interconnected pore architectures ensuring good diffusion throughout the whole material. SEM images seem to reveal the existence of macropores that cannot be detected neither by gas sorption nor by SAXS techniques.

The texture of the materials was then observed by transmission electron microscopy (TEM). The TEM images of the of the materials $\mathbf{TS_{20}^{C_2}}$, $\mathbf{TS_{20}^{C_8}}$ and $\mathbf{TS_{20}^{C_{16}}}$, all synthesized in the presence of 20 mmoles of [C_xMIM]TFSI (x = 2, 8 and 16) are displayed in figure 6.

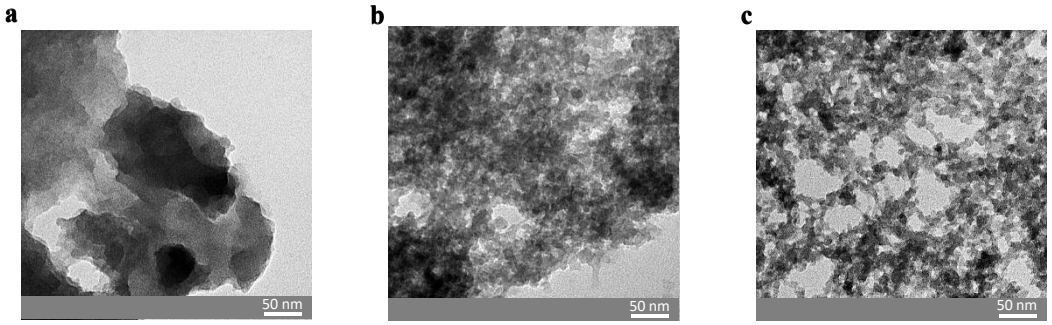


Figure 6 Transmission electron microscopy (TEM) images of the materials $\mathbf{TS_{20}^{C_2}}$, $\mathbf{TS_{20}^{C_8}}$ and $\mathbf{TS_{20}^{C_{16}}}$

TEM imaging of the materials also show that the nature of the used IL has a direct impact on the texture and directly affects the morphology of the formed materials. The TEM image of material $\mathbf{TS_{20}^{C_2}}$ shows a dense matrix indicating the presence of a low porous or mesoporous material (figure 6a), whereas the TEM images of $\mathbf{TS_{20}^{C_8}}$ and $\mathbf{TS_{20}^{C_{16}}}$ (figures 6b and 6c)-reveal a macroporosity with increasing pore widths. These results confirm the meso-macroporous character of these materials and an increase of both macroporosity and macropores size of the materials with the length of the cation alkyl chain of the ionic liquid. The interconnected macropores form pore domains of about 50 nm width for $\mathbf{TS_{20}^{C_{16}}}$ (figure 6c).

To sum up, nitrogen sorption and SAXS measurements of the ionosilica materials give a complete and concordant image of the mesoporous textures and architectures (at the 1-10nm scale) of the ionosilica materials formed in the presence of ionic liquids (figure 7). Both investigated

parameters, the quantity of IL used for the sol-gel procedure on the one side (figure 7 - *vertical*) and the alkyl chain length of the imidazolium cation on the other side (figure 7 - *horizontal*), contribute to the evolution of the texture and morphology of the formed ionosilica materials. The increase in the amount of the IL leads to an increase of the specific surface area and enlarged mesopore diameter and primary clusters within the ionosilica scaffold. On the other side, the increase of the alkyl chain length of the cation also contributes to increasing specific surface areas. However, a significant increase of the pore diameters could only be observed with long-chain substituted ILs, *i.e.,* imidazolium cations bearing dodecyl or hexadecyl groups. The texture of ionosilicas formed in non-hydrolytic sol-gel syntheses involving room-temperature ionic liquids, can therefore efficiently be controlled by the two studied parameters.

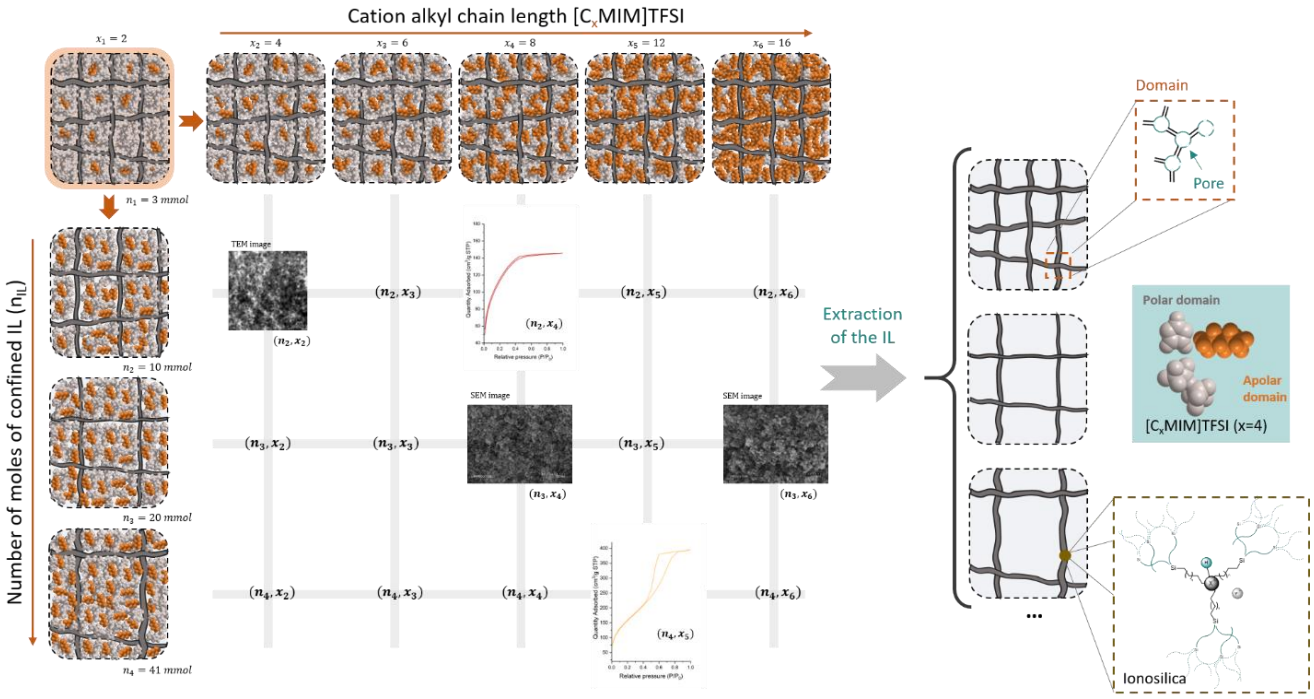


Figure 7 Scheme resuming the mesoporosity control via the number of moles of confined IL and the cation alkyl chain length.

Conclusion

We report ionosilica materials obtained via a non-hydrolytic sol-gel procedure in the presence of various methyl-alkylimidazolium *bis*-triflimide ILs. The aim was to study the effect of the amount of confined IL and the length of its cation alkyl chain on the morphological and textural properties of the ionosilica scaffold after the extraction of the IL. This study clearly shows a clear correlation between both investigated parameters and the textural properties of the ionosilica scaffold. It also reveals for our ionolica monoliths, the existence of both macro and mesoporosity. Electron microscopies indicate that the ionosilica scaffolds show a tunable interconnected macroporosity. Nitrogen sorption and SAXS measurements give concordant results and show that by increasing the quantity of a given IL, an increase of the mesoporosity in terms of the specific surface area, pore volume and pore diameter could be observed, with a maximum for the materials synthesized in the presence of 20 mmoles of IL. Regarding materials obtained in the presence of a specific amount of IL [C_xMIM]TFSI bearing different alkyl chain length (x = 2, 4, 6, 8, 12 and 16), an increase of the specific surface area could be detected. However, different substitution of the imidazolium cation leads to increasing pore size only with long-chain substituted ILs (C>8), thus highlighting a particular self-aggregation behavior of imidazolium *bis*-triflimides bearing dodecyl or hexadecyl groups. Our results indicate that the supramolecular aggregation of imidazolium based *bis*-triflimide ILs in hydrophilic and hydrophobic domains has a direct impact on the texture of the formed ionosilicas.

Supporting Information

Electronic supplementary information (ESI) available. See DOI: 10.1039/xxxx:

- Supplementary Nitrogen sorption isotherms and BJH adsorption pore distribution
- Supplementary SAXS diffractograms

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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