

Supporting Information:

Investigation of Confined Ionic Liquid in Nanostructured Materials by a Combination of SANS, Contrast-Matching SANS and Nitrogen Adsorption

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1. Preparation of 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF₆]

a) Synthesis of 1-butyl-3-methylimidazolium chloride, [bmim][Cl]

The synthesis procedure was based on published data with minor changes.¹⁻³ To (23.4 mmol) of 1-methyl-imidazole, (28.7 mmol, 1.2 eq) of 1-chlorobutane was added in a round bottomed flask fitted with a reflux condenser and the mixture was allowed under stirring to react in reflux conditions and N₂ atmosphere for 48 hr. The viscous yellow-orange liquid obtained was washed with EtOAc (2x30 ml) and dried under vacuum at 363 K to give 3.9 g (95% w/w) of 1-butyl-3-methylimidazolium chloride.

b) Ion exchange step

The ion exchange step was based on published data with slight changes.³⁻⁵ (1.05 g, 6.04 mmol) of 1-butyl-3-methylimidazolium chloride were dissolved in 6 ml CH₂Cl₂ and to the solution it was added (1.14 g, 6.78 mmol) of sodium hexafluorophosphate in 4 ml CH₃CN.

The milky solution was left under stirring at room temperature for 14 hr and then it was cooled at $-15\text{ }^{\circ}\text{C}$ for 10 min and centrifuged at 9000 rpm for 20 min to remove sodium chloride produced during ion exchange. To the organic phase 10 ml of dichloromethane were added and organic phase was washed with deionized water until AgNO_3 test was negative. Back washing with dichloromethane of the water phase used was not performed. The organic phase was concentrated and the remaining liquid obtained was dried first by azeotropic removal of water with toluene (3x15 ml) and then by high vacuum at 353 K to give a less viscous light yellow to colorless liquid (197.9 g, 41% w/w). In Figure S1 the H-NMR spectrum of the as above synthesised $[\text{bmim}][\text{PF}_6]$ in comparison to the commercial ionic liquid (Sigma-Aldrich) is shown.

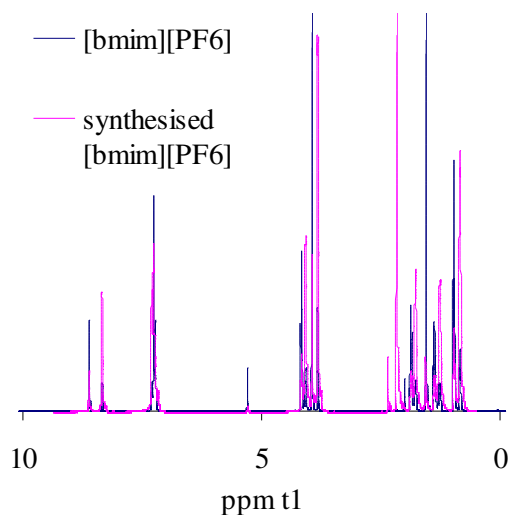


Figure S1. H-NMR spectra of synthesised and commercial $[\text{bmim}][\text{PF}_6]$ in CDCl_3 .

2. Pore filling process by physical imbibition

A vacuum assisted physical imbibition method was involved in order to facilitate the pore filling process. More specific crimp top-flat bottom headspace vials of 20 ml were appropriately modified to permit the application of high vacuum (10^{-3} mbar) into their

internal space. The modification consisted on the welding of the common port of a high vacuum three-way glass valve (ACE 8145-06 three-way stopcock) on the sidewall of the vials close to their bevelled neck. About 200 mg of the SBA-15 and MCM-41 powders, having an absolute pore volume of 0.19 and 0.25 cm³ respectively, were placed on the bottom of the vials together with a stirring magnet and the vials were tightly sealed by means of crimp caps and PTFE/black butyl molded septa. The three-way valve was then turned to the vacuum working port and the vials were in parallel heated to 200 °C to allow the removal of the adsorbed water phase from the solid surface. After 24 hr, the temperature was decreased to 60 °C the valve was turned to the off position and a binary mixture of [bmim][PF₆⁻] and methanol (v/v) 1:1 (5 ml solution) was injected on the powder by means of a glass syringe that perforated the septa. The powder suspension was left for another 24 hr under stirring to assist the infiltration of the ionic liquid solution into the pores. In order to break the vacuum and avoid the direct contact with the air moisture the three-way valve was turned to the gas working port permitting the introduction of 1 bar of argon into the vial. After several hours without stirring the supernatant aliquot was suctioned by means of the glass syringe and replaced with pure methanol. The washing with methanol was repeated 5 times to remove most of the excess ionic liquid before proceeding with the solvent evaporation (rota-vapor) to yield the IL impregnated solid powder.

References

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