



# Use of Ionic Liquid as Template for Hydrothermal Synthesis of the MCM-41 Mesoporous Material

José Arnaldo Santana Costa<sup>1,2</sup> · Priscila Vedovello<sup>2</sup> · Caio Marcio Paranhos<sup>2</sup>

Received: 14 January 2019 / Accepted: 21 February 2019 / Published online: 13 March 2019  
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## Abstract

In this study the MCM-41 mesoporous material was first prepared by using hydrothermal method in the presence of 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([BMMIM]PF<sub>6</sub>) ionic liquid (IL) as template. The IL presented the average yields between 67 and 76%. The obtained MCM-41 showed the main structural parameters associated with the formation of condensed silica (Si–O–Si), a hexagonal mesostructure with a compact arrangement of cylindrical tubes and agglomerated spherical particles.

**Keywords** Ionic liquid · Template · Mesoporous material · MCM-41

## 1 Introduction

Ionic liquids (ILs) can be defined as organic salts in which at room temperature are in the molten state. They consist of inorganic anions asymmetrically arranged with organic cations and are important because of their physicochemical properties such as: low volatility and flammability, high thermal stability, and high ionic conductivity [1, 2].

Recently, ILs have attracted considerable interest in the development and research of their properties and applications in materials science not only as solvents and catalysts for green chemistry, but also in polymer science and as surfactant (template) [1–5]. There are some examples of the use of ionic liquids in the preparation of porous materials such as zeolites, MCM-41, and moreover studies have shown that ILs are viable template in the synthesis of micro/mesoporous materials [6–9]. Wang et al. [6] prepared the MCM-41 from the use of 1-

hexadecyl-3-methylimidazolium chloride IL as template and NaOH as the catalyst, however the synthesis gel obtained at 45 °C was hydrothermally treated for 3 days. Sanaeishoar et al. [10] used a mixture of templates for the synthesis of MCM-41 micro-mesoporous, in this work the ILs (*N*-butyl-Dabco bromide, *N*-butylpyridinium bromide, and *N*-butyl-hexamethylenetetramine bromide) were used as co-templates and the main template was cetyltrimethylammonium bromide (CTAB).

On the other hand, Kumar et al. [11] prepared the ordered mesoporous aluminosilicate (AIIITM-41) from the use of 1-hexadecyl-3-methylimidazolium chloride IL as template in the presence of aluminum sulphate and fumed silica (silica source), and Liu et al. [12] used 1-cethyl-3-methylimidazolium bromide to prepare the Al-MCM-41 on 7 days of crystallization. However, the synthesis of pure MCM-41 with the 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([BMMIM]PF<sub>6</sub>) IL as template has not been found in the literature.

Several methods have been proposed for synthesis of mesoporous materials. However, the hydrothermal method is more efficient and the most used in the literature [13–17]. This method was proposed from the traditional sol-gel method, so the aqueous solution obtained is transferred to a reactor and placed under heat treatment. However, to obtain this solution, it is necessary to use a catalyst in aqueous media (acid or basic), a silica source, and a surfactant (template); the latter is responsible for directing the final structure of the mesoporous material.

## Highlights

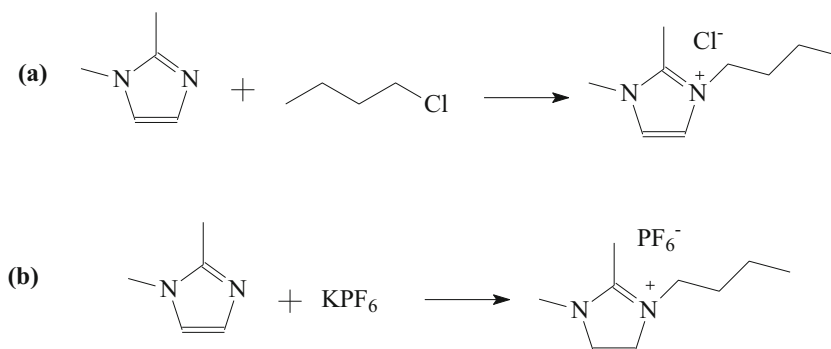
- The IL presented the average yields between 67–76%.
- The [BMMIM]PF<sub>6</sub> IL was used as template to prepare the MCM-41;
- The MCM-41 presented a hexagonal matrix.

✉ José Arnaldo Santana Costa  
josearnaldo@ua.pt

<sup>1</sup> CICECO, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

<sup>2</sup> Polymer Laboratory, Department of Chemistry, Federal University of São Carlos, 13565-905, São Carlos, São Paulo, Brazil

**Fig. 1** Synthesis reaction of **a** 1-butyl-2,3-dimethylimidazolium chloride [BMMIM]Cl and **b** 1-butyl-2,3-dimethylimidazolium hexafluorophosphate [BMMIM]PF<sub>6</sub>



In previous studies [13–15, 18, 19], our research group has synthesized different types of mesoporous materials from the use of cetyltrimethylammonium bromide (CTABr) as template. However, in the present study the 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([BMMIM]PF<sub>6</sub>) ionic liquid was synthesized and used as template in the synthesis of MCM-41 mesoporous material. From our knowledge, there are no previous works reporting the use of [BMMIM]PF<sub>6</sub> as molecular template to MCM-41 mesoporous material.

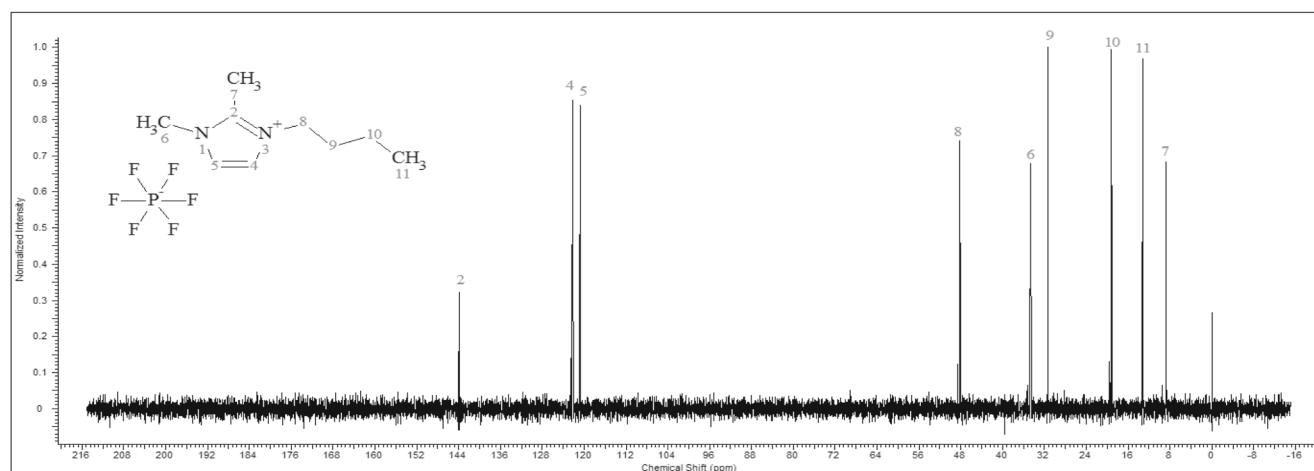
## 2 Materials and Methods

### 2.1 Standards, Solvents, and Reagents

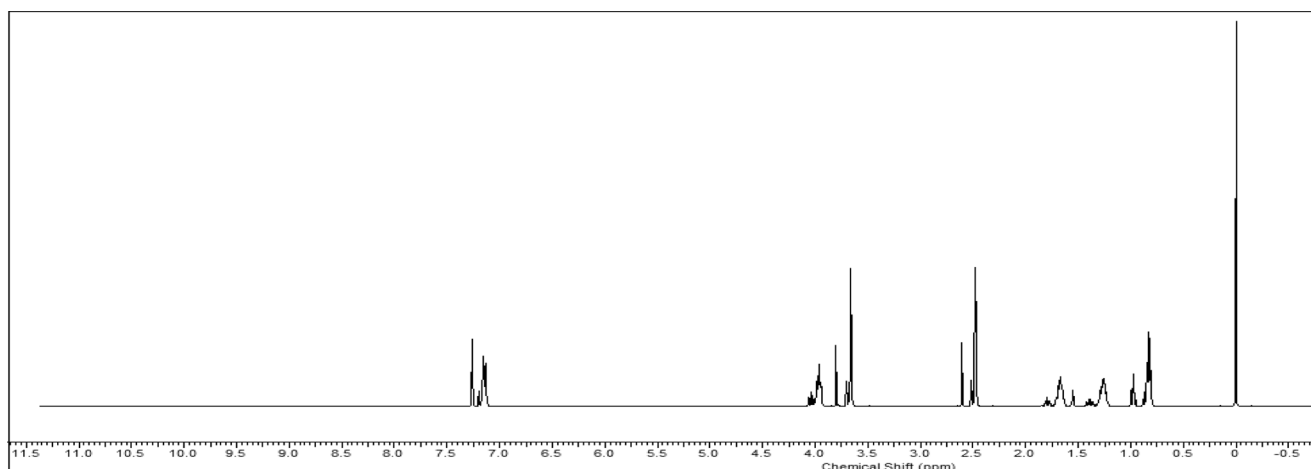
The 1,2-dimethyl imidazoline (Aldrich), toluene (Synth), 1-chlorobutane (Aldrich), acetonitrile (Synth), ethyl acetate (Synth), potassium hexafluorophosphate (KPF<sub>6</sub>, Aldrich), deuterated chloroform (Aldrich), tetraethylorthosilicate (TEOS, 98.0%, Aldrich), and ammonia monohydrate (NH<sub>3</sub>·H<sub>2</sub>O, Synth) were used without further purification.

### 2.2 Synthesis of 1-Butyl-2,3-Dimethylimidazolium Hexafluorophosphate ([BMMIM]PF<sub>6</sub>)

The method was based on the work described by Cammarata et al. [20]: The 1,2-dimethyl imidazoline (60.08 g) was added in a 3-necked flask containing toluene (62.5 mL, 0 °C, N<sub>2</sub> atmosphere), then 1-chlorobutane (72 mL) was added to the flask, which was refluxed for 24 h at 110 °C. After this time, the flask was placed in a cooler (20 °C, 14 h) for decantation and removal of toluene, then acetonitrile was added for crystallization. Subsequently, a further crystallization was carried out with ethyl acetate (40 °C, 24 h). Finally, the 1-butyl-2,3-dimethylimidazolium chloride ([BMMIM]Cl) (Fig. 1a) obtained was placed in a petri dish and dried under vacuum for 24 h. Then, to Ionic exchange of [BMMIM]Cl: Potassium hexafluorophosphate (KPF<sub>6</sub>) (88.2 g) was added to a solution of [BMMIM]Cl with dichloromethane (138 mL) under stirring for 24 h. The suspension was filtered to remove the precipitated chloride salt and the organic phase was washed a few times with water until complete precipitation of the AgCl into the aqueous phase from the addition of an AgNO<sub>3</sub> solution. The organic phase was then washed twice more with water for complete removal of the chloride salt and the solvent was



**Fig. 2** <sup>13</sup>C-NMR spectrum of 1-butyl-2,3-dimethylimidazolium hexafluorophosphate [BMMIM]PF<sub>6</sub>.



**Fig. 3**  $^1\text{H-NMR}$  spectrum of 1-butyl-2,3-dimethylimidazolium hexafluorophosphate [BMMIM] $\text{PF}_6$ .

removed under vacuum to provide the 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ([BMMIM] $\text{PF}_6$ ) (Fig. 1b).

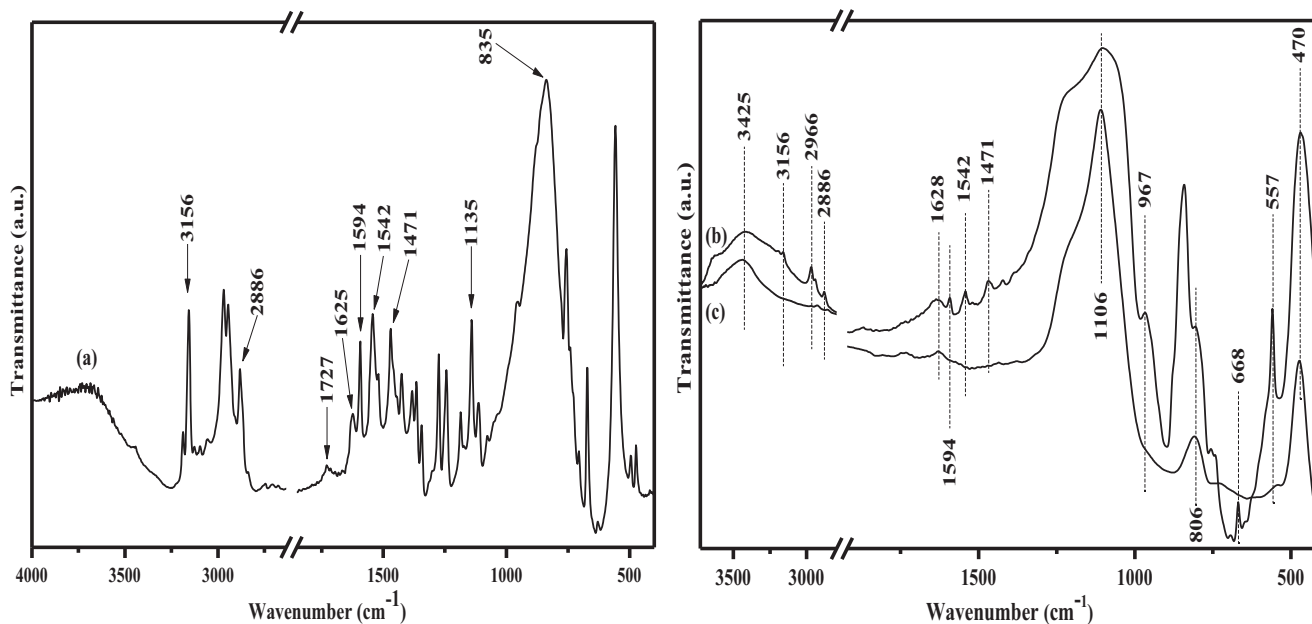
### 2.3 Synthesis of MCM-41 Mesoporous Material

The synthesis of MCM-41 was performed according to the methodology described previously [19], with modifications: The [BMMIM] $\text{PF}_6$  IL (2.0 g) was dissolved in  $\text{NH}_3\cdot\text{H}_2\text{O}$  (12 mL), followed by addition of  $\text{H}_2\text{O}$  (26 mL) and TEOS (5.5 mL). After, the mixture obtained was agitated for 48 h at ambient temperature and then transferred to a Teflon-lined stainless steel autoclave (100 °C, 48 h). The solid product was separated by filtration, washed with deionized water, and air-dried at 100 °C for 12 h. The IL template was removed from the synthesized material by calcination at 550 °C for 5 h

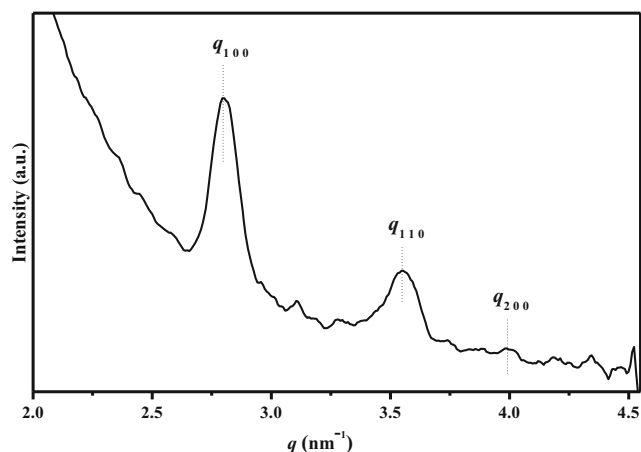
and the temperature was gradually increased to 550 °C at a rate of 1 °C  $\text{min}^{-1}$ .

### 2.4 Characterizations of IL and MCM-41

The MCM-41 was characterized by Fourier transform infrared spectroscopy (FTIR), with spectra obtained in the region 4000–400  $\text{cm}^{-1}$  using a Varian 3100 spectrophotometer operated at room temperature with resolution of 4  $\text{cm}^{-1}$  and 32 scans. The samples were prepared in the form of KBr pastilles. The SAXS analysis was obtained using the D2A beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil) according to the methodology described previously [19]. SEM analysis was obtained in a Phillips microscopy (FEG-XL), using an accelerator power of 3 kV and analyzed with the help of a secondary electron detector. The



**Fig. 4** FTIR spectra of **a** IL, **b** MCM-41 with IL surfactant, and **c** MCM-41 without IL surfactant



**Fig. 5** SAXS profile of the obtained MCM-41 mesoporous material

NMR spectra were obtained at room temperature using a Bruker Advance 400 spectrometer. The measures of  $^{13}\text{C}$  NMR were performed at 100 MHz, using deuterated water ( $\text{D}_2\text{O}$ ) as a solvent and the measures  $^1\text{H}$  NMR were performed at 400 MHz using deuterated chloroform ( $\text{CDCl}_3$ ) as the solvent. The chemical shifts were calculated from the internal standard TMS (tetramethylsilane).

### 3 Results and Discussion

The NMR spectra of  $^{13}\text{C}$  and  $^1\text{H}$  for the IL are illustrated in Figs. 2 and 3, respectively. The assignment of  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR resonance peaks evidence of the ionic liquid synthesis, as well as the average yields were between 67 and 76%. Finally, the product has the following spectral properties:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.97 (m, 3 H), 1.50 (m, 2 H), 2.1 (m, 2 H), 3.60 (s, 3 H), 3.90 (t, 2 H), 7.26 (s, 1 H), 7.16 (s, 1H), 2.61 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 13.24 (C11), 19.2 (C10), 31.4 (C9), 34.6 (C6), 48.1 (C8), 122.2 (C5), 122.0 (C4), 143.9 (C2) ppm, according to the work of Mehnert et al. [21].

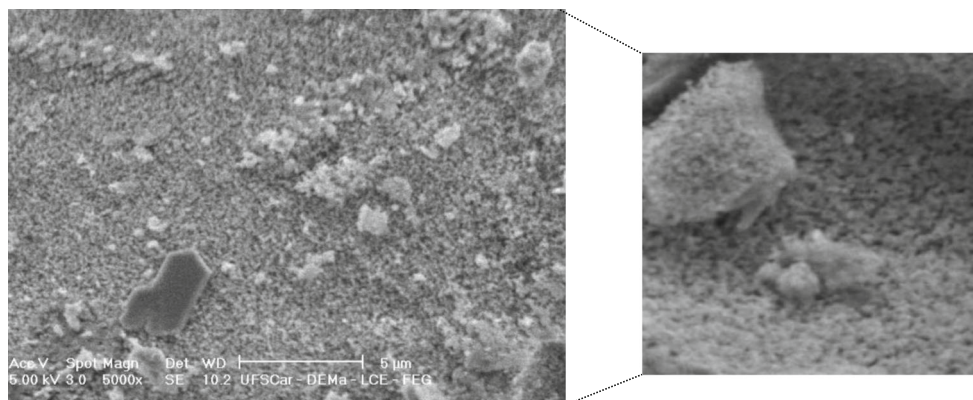
Figure 4 shows the spectra for the IL and mesoporous material, before and after removal of the IL template. The IL presented its main bands, as can be seen in Fig. 4a. The bands at around 3156 and 1727  $\text{cm}^{-1}$  corresponded to C–H and C=N stretching vibrations of the ring, respectively. The band at around 2886  $\text{cm}^{-1}$  is attributed to C–H stretching vibration in the aliphatic chain. Bands at 1625, 1594, 1542, and 1471  $\text{cm}^{-1}$  are attributed to C=C and C=N symmetrical axial deformation in the ring and the band centered at 1135  $\text{cm}^{-1}$  corresponded to C–N axial deformation. The band at 853  $\text{cm}^{-1}$  is attributed to C–H angular deformation [22, 23].

Figure 4b and c show the absorption band at 3425  $\text{cm}^{-1}$  corresponded to stretching of the O–H bond of  $\text{H}_2\text{O}$  molecules and a narrow band at around 1637  $\text{cm}^{-1}$  which is attributed to the flexion vibration of  $\text{H}_2\text{O}$  molecules imprisoned on the MCM-41 [19, 24]. The characteristic bands associated with the formation of condensed silica (Si–O–Si) in the MCM-41 can be observed at 1106 ( $\nu_{as}$ , Si–O), 806 ( $\nu_s$ , Si–O), and 470  $\text{cm}^{-1}$  ( $\delta$ , Si–O–Si) [13, 15, 18, 19]. The bands centered at around 3156, 2966, 2886, 1542, 1471, 967, 668, and 557  $\text{cm}^{-1}$  are attributed to the IL template (Fig. 4b). However, these bands were absent in the spectra of MCM-41 without IL template (Fig. 4c), confirming the efficiency of elimination of the template by calcination.

SAXS measurement can be used to prove the synthesis of the mesoporous materials. The SAXS profile obtained for the MCM-41 is shown in Fig. 5. The MCM-41 presented a hexagonal matrix, typical of the M41S family, with the distinct Bragg diffraction peaks, which can be indexed as (100), (110), and (200). These peaks are related to  $q_{100}$ ,  $q_{110}$ , and  $q_{200}$  of hexagonal mesostructures (P6 mm) characterized by a compact arrangement of cylindrical tubes, thus confirming the success of synthesis of the MCM-41 from the use of IL as a template [14, 18, 19, 25, 26].

The SEM image obtained for the MCM-41 mesoporous material is shown in Fig. 6. The SEM image was used to determine the morphology of the synthesized mesoporous material. The MCM-41 showed good homogeneity and

**Fig. 6** Scanning electron micrograph of the MCM-41 mesoporous material



agglomerated spherical particles which that are a typical feature of the M41S family [13, 14].

## 4 Conclusions

In the present study, the [BMMIM]PF<sub>6</sub> ionic liquid was satisfactorily prepared and the average yields were between 67 and 76%. The hydrothermal method was efficient in the synthesis of MCM-41 from the use of the [BMMIM]PF<sub>6</sub> as a template. The FTIR spectra showed the main characteristic bands of the ionic liquid, as well as the corresponding bands of the amorphous silica framework, which are typical of the mesoporous materials of the M41S family. Finally, the MCM-41 presented a hexagonal matrix and agglomerated spherical particles, according to SAXS and SEM results.

**Acknowledgments** The authors thank FAPESP (Research Support Foundation of the State of São Paulo) (Grants 2014/05679-4, 2017/06775-5, 2015/00609-0, and 2018/18894-1), CAPES (Coordination for the Improvement of Higher Education Personnel) (Grant 309342/2010-4), and CDMF (Center for the Development of Functional Materials) (Grant 2013/07296-2) for the financial support.

## Compliance with Ethical Standards

**Conflicts of Interest** The authors declare that they have no conflict of interest.

## References

- Welton T (1999) Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem Rev* 99:2071–2084. <https://doi.org/10.1021/cr980032t>
- Lu J, Yan F, Texter J (2009) Advanced applications of ionic liquids in polymer science. *Prog Polym Sci* 34:431–448. <https://doi.org/10.1016/j.progpolymsci.2008.12.001>
- Hanamertani AS, Pilus RM, Idris AK, Irawan S, Tan IM (2017) Ionic liquids as a potential additive for reducing surfactant adsorption onto crushed Berea sandstone. *J Pet Sci Eng* 162:480–490. <https://doi.org/10.1016/j.petrol.2017.09.077>
- Meksi N, Moussa A (2017) A review of progress in the ecological application of ionic liquids in textile processes. *J Clean Prod* 161:105–126. <https://doi.org/10.1016/j.jclepro.2017.05.066>
- Livi S, Duchet-Rumeau J, Pham TN, Gérard J-F (2011) Synthesis and physical properties of new surfactants based on ionic liquids: improvement of thermal stability and mechanical behaviour of high density polyethylene nanocomposites. *J Colloid Interface Sci* 354:555–562. <https://doi.org/10.1016/j.jcis.2010.10.058>
- Wang T, Kaper H, Antonietti M, Smarsly B (2007) Templating behavior of a long-chain ionic liquid in the hydrothermal synthesis of mesoporous silica. *Langmuir* 23:1489–1495. <https://doi.org/10.1021/la062470y>
- Cooper ER, Andrews CD, Wheatley PS, Webb PB, Wormald P, Morris RE (2004) Ionic liquids and eutectic mixtures as solvent and template in synthesis of zeolite analogues. *Nature* 430:1012–1016. <https://doi.org/10.1038/nature02860>
- Adams CJ, Bradley AE, Seddon KR (2001) The synthesis of mesoporous materials using novel ionic liquid templates in water. *Aust J Chem* 54:679–681
- Martínez Blanes JM, Szyja BM, Romero-Sarria F et al (2013) Multiple zeolite structures from one ionic liquid template. *Chem Eur J* 19:2122–2130. <https://doi.org/10.1002/chem.201202556>
- Sanaeishoar H, Sabbaghan M, Mohave F (2015) Synthesis and characterization of micro-mesoporous MCM-41 using various ionic liquids as co-templates. *Microporous Mesoporous Mater* 217:219–224. <https://doi.org/10.1016/j.micromeso.2015.06.027>
- Kumar MA, Krishna NV, Selvam P (2019) Novel ionic liquid-templated ordered mesoporous aluminosilicates: synthesis, characterization and catalytic properties. *Microporous Mesoporous Mater* 275:172–179. <https://doi.org/10.1016/j.micromeso.2018.08.033>
- Liu C, Yu X, Yang J, He M (2007) Preparation of mesoporous Al-MCM-41 with stable tetrahedral aluminum using ionic liquids as a single template. *Mater Lett* 61:5261–5264. <https://doi.org/10.1016/j.matlet.2007.04.043>
- Costa JAS, de Jesus RA, da Silva CMP, Romão LPC (2017) Efficient adsorption of a mixture of polycyclic aromatic hydrocarbons (PAHs) by Si-MCM-41 mesoporous molecular sieve. *Powder Technol* 308:434–441. <https://doi.org/10.1016/j.powtec.2016.12.035>
- Costa JAS, Garcia ACFS, Santos DO et al (2014) A new functionalized MCM-41 mesoporous material for use in environmental applications. *J Braz Chem Soc* 25:197–207. <https://doi.org/10.5935/0103-5053.20130284>
- Santos DO, Santos MLN, Costa JAS et al (2013) Investigating the potential of functionalized MCM-41 on adsorption of Remazol red dye. *Environ Sci Pollut Res* 20:5028–5035. <https://doi.org/10.1007/s11356-012-1346-6>
- Wang J, Lu J, Yang J, Xiao W, Wang J (2012) Synthesis of ordered MCM-48 by introducing economical anionic surfactant as co-template. *Mater Lett* 78:199–201. <https://doi.org/10.1016/j.matlet.2012.03.040>
- Santos LFS, de Jesus RA, Costa JAS, Gouveia LGT, de Mesquita ME, Navickiene S (2019) Evaluation of MCM-41 and MCM-48 mesoporous materials as sorbents in matrix solid phase dispersion method for the determination of pesticides in soursop fruit (*Annona muricata*). *Inorg Chem Commun* 101:45–51. <https://doi.org/10.1016/j.inoche.2019.01.013>
- Costa JAS, de Jesus RA, Dorst DD, Pinatti IM, Oliveira LMR, de Mesquita ME, Paranhos CM (2017) Photoluminescent properties of the europium and terbium complexes covalently bonded to functionalized mesoporous material PABA-MCM-41. *J Lumin* 192:1149–1156. <https://doi.org/10.1016/j.jlumin.2017.08.046>
- Costa JAS, Garcia ACFS, Santos DO, Sarmento VHV, de Mesquita ME, Romão LPC (2015) Applications of inorganic-organic mesoporous materials constructed by self-assembly processes for removal of benzo[k]fluoranthene and benzo[b]fluoranthene. *J Sol-Gel Sci Technol* 75:495–507. <https://doi.org/10.1007/s10971-015-3720-6>
- Cammarata L, Kazarian SG, Salter PA, Welton T (2001) Molecular states of water in room temperature ionic liquids. Electronic supplementary information available. *Phys Chem Chem Phys* 3:5192–5200. <https://doi.org/10.1039/b106900d> <http://www.rsc.org/suppdata/cp/b1/b106900d/>
- Mehnert CP, Dispenziere NC, Cook RA (2005) Method for preparing high-purity ionic liquids. 1–10
- Pilli SR, Banerjee T, Mohanty K (2014) 1-Butyl-2,3-dimethylimidazolium hexafluorophosphate as a green solvent for the extraction of endosulfan from aqueous solution using supported liquid membrane. *Chem Eng J* 257:56–65. <https://doi.org/10.1016/j.cej.2014.07.019>
- Hunt PA (2007) Why does a reduction in hydrogen bonding lead to an increase in viscosity for the 1-Butyl-2,3-dimethyl-imidazolium-

- based ionic liquids? *J Phys Chem B* 111:4844–4853. <https://doi.org/10.1021/jp067182p>
24. Costa JAS, Paranhos CM (2018) Systematic evaluation of amorphous silica production from rice husk ashes. *J Clean Prod* 192: 688–697. <https://doi.org/10.1016/j.jclepro.2018.05.028>
25. Cao Q-Y, Chen Y-H, Liu J-H, Gao X-C (2009) Novel luminescent europium(III) complexes covalently bonded to bis(phosphino)amine oxide functionalized MCM-41. *Inorg Chem Commun* 12:48–51. <https://doi.org/10.1016/j.inoche.2008.10.024>
26. Wongsakulphasatch S, Kiatkittipong W, Saiswat J, Oonkhanond B, Striolo A, Assabumrungrat S (2014) The adsorption aspect of  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  on MCM-41 and SDS-modified MCM-41. *Inorg Chem Commun* 46:301–304. <https://doi.org/10.1016/J.INOCHE.2014.06.029>

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