

## Electronic Supplementary Information

### Janus bifunctional periodic mesoporous organosilica

Majid Vafaezadeh,<sup>\*a</sup> Kristin Weber,<sup>a</sup> Anna Demchenko,<sup>b</sup> Philipp Lösch,<sup>c</sup> Paul Breuninger,<sup>c</sup> Andrea Lösch,<sup>a</sup> Michael Kopnarski,<sup>b</sup> Sergiy Antonyuk,<sup>c</sup> Wolfgang Kleist<sup>a</sup> and Werner R Thiel<sup>\*a</sup>

<sup>a</sup> Fachbereich Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Str. 54, 67663 Kaiserslautern, Germany; E-mail: majidvafaezadeh@yahoo.com, thiel@chemie.uni-kl.de

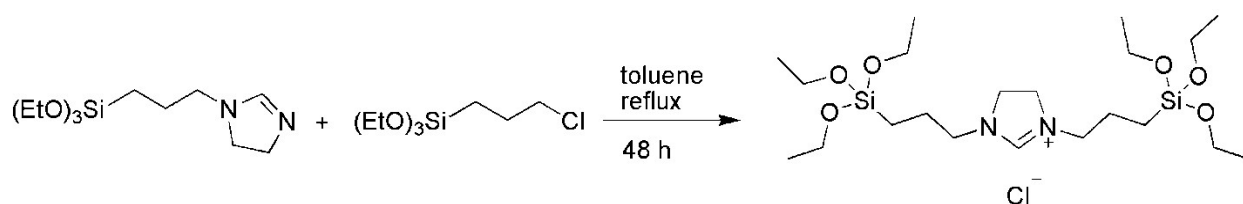
<sup>b</sup> Institut für Oberflächen- und Schichtanalytik (IFOS), Technische Universität Kaiserslautern, Trippstadter-Str. 120, 67663 Kaiserslautern (Germany)

<sup>c</sup> Fachbereich Maschinenbau und Verfahrenstechnik, Mechanische Verfahrenstechnik, Technische Universität Kaiserslautern, Gottlieb-Daimler-Str. 44, 67663 Kaiserslautern (Germany)

## 1. Experimental section

### 1.1. Materials and instruments

All chemicals and solvents were purchased from the suppliers and used without further purifications except toluene, which were dried before use. Solid state  $^{13}\text{C}$  and  $^{29}\text{Si}$  CP-MAS NMR spectra were measured with a 500 MHz BRUKER Avance III spectrometer with 2.5 mm tube under cross polarization conditions with a spinning frequency of 11000 Hz for both  $^{13}\text{C}$  and  $^{29}\text{Si}$  and with scan numbers of 15000 respectively 2500. High resolution  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were measured with 600 MHz BRUKER DPX spectrometers. SEM images were taken by means of JSM-6490LA JEOL instrument. The dispersion analysis was performed with an analytical photocentrifuge apparatus (LUMiSizer, LUM). The transmission electron microscope (TEM) images were taken by means of JEOL 2010 in analytical design (JEOL Ltd., Tokio, Japan) with a LaB6 cathode, operating at 197 kV. The TEM was equipped with Gatan imaging filter "863 GIF Tridiem" (Gatan Inc., Pleasanton, CA, USA). TEM imaging was accomplished in energy-filtered mode (EFTEM). For collecting and analyzing TEM images, the software "Digital Micrograph" (Gatan Inc., Pleasanton, CA, USA) was used.



### 1.2 Synthesis of the ionic liquid precursor

In a 50 mL vacuum-dried flask equipped with a condenser, 10 mmol (3-chloropropyl)triethoxysilane (2.4 mL, 2.41 g) and 10 mmol triethoxy-3-(2-imidazolyl)propylsilane (2.7 mL, 2.74 g) were added and refluxed in dry toluene (5 mL) for two days. At the end of reaction, the solvent was removed under vacuum and the resulted viscose oil was washed with dry *n*-pentane (4 × 15 mL) and then dried to afford

quantitative yield.  $^1\text{H}$  NMR (600.1 MHz,  $\text{CDCl}_3$ ): 9.65 (s, 1H), 3.76 (s, 4H), 3.57-3.53 (m, 12H), 3.39 (t, 4H), 1.52-1.47 (m, 4H), 0.96 (t, 18H) and 0.35-0.32 (t, 4H) ppm.  $^{13}\text{C}$  NMR (150.6 MHz,  $\text{CDCl}_3$ ): 158.5, 58.1, 50.0, 47.8, 20.8, 17.9 and 6.81 ppm. Elemental analysis: calcd. C: 48.95%, H: 9.19%, N: 5.44%; found: C: 47.94%, H: 8.94%, N: 5.53%.

### 1.3. Synthesis of hollow JPMO 2

In a 500 mL flask, 0.644 g (1.77 mmol) of cetyltrimethylammonium bromide (CTAB) were dissolved a solution of 215.6 mL of  $\text{H}_2\text{O}$  and 0.4 mL of aqueous ammonia (25 weight-%). In a 250 mL flask (the second flask), a solution of 0.5 mL of *n*-decane and 102 g of ethanol was prepared, and added to the first one. Then, the first 500 mL flask was placed for 15 min in an ultrasonic bath at a temperature of 35 °C. Afterward, 3 mmol (1.11 mL, 1.06 g) of 1,2-bis(triethoxysilyl)ethane (BTSE) and 19.2 mmol (4.00 g, 4.26 mL) of tetraethylorthosilicate (TEOS) were added to this solution. The mixture was vigorously stirred at 35 °C for 60 minutes. Then, 2 mmol (1.03 g) of the IL derivative (from section 1.2) was dissolved in 1 mL ethanol and dropwise added to this mixture while continuing the stirring for 23 h. At the end of reaction, the white solid was collected by centrifugation (2 min at 5000 rpm) and was washed several times with ethanol and dried in oven at 80 °C overnight. Yield: 2.11 g. Elemental analysis: C: 15.34%, H: 3.62%, N: 2.23%.

### 1.4. Synthesis of JPMO 3

At the first step, hollow JPMO 2 was crushed by a simple and mild grinding method using mortar and pestle for 30 min. To remove the template (CTAB), the crushed material was transferred into a 250 mL flask containing a mixture of 200 mL of EtOH and 0.25 mL of concentrated hydrochloric acid (37%). The suspension was stirred for 3 h at 60 °C. This procedure was repeated two times to ensure the complete removal of CTAB. At the end, the solid was separated by centrifugation, washed several times with deionized water/ethanol until the solvent reached to the neutral pH value. The resulted material was dried at 80 °C for 12 h. Yield: 2.0 g. Elemental analysis: C: 17.31%, H: 3.37%, N: 2.51%.

### **1.5. Immobilization of BTSE and IL on the surface of commercially silica gel (1 in Fig. S8)**

In a 25 mL flask equipped with a condenser, 0.5 g of commercially SiO<sub>2</sub> was dispersed in dry toluene (10 mL) and the mixture was stirred at room temperature. Then, 0.27 mL of BTSE and 0.25 mL of the IL were added to the flask and the mixture was refluxed for 24 h under N<sub>2</sub> atmosphere. At the end of reaction, the flask was cooled down to room temperature and the solid was separated with centrifuging of the mixture followed by washing several times with toluene, ethanol and acetone. The final material was dried at 80 °C for 16 h.

### **1.6. Synthesis of un-functionalized crushed hollow silica (2 in Fig. S8)**

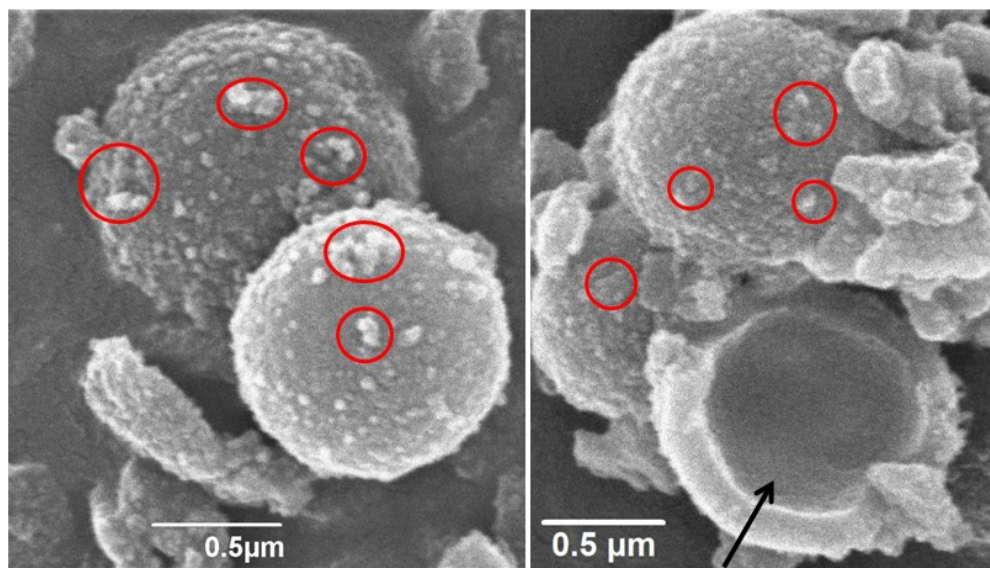
This material was prepared according to section 1.3 without addition of BTSE and the IL at 35 °C for 24 h. The final material was crushed as described in section 1.4.

### **1.7. Synthesis of crushed hollow silica with BTSE group in one face (3 in Fig. S8)**

This material was prepared according to section 1.3 without addition of the IL at 35 °C for 24 h. The final material was crushed as described in section 1.4.

### **1.8. The dispersion analysis**

The dispersion analysis was performed with an analytical photocentrifuge (LUMiSizer, LUM). 16 mg of JPMO **3** was dispersed in 6 ml water (sample 1), 6 ml toluene (sample 2) and a biphasic mixture of 3 ml toluene and 3 ml water (sample 3) each and dispersed by a rotor stator disperser in 5 minutes. From each sample two measuring cuvettes were prepared with 0.4 ml dosage. For the sedimentation analysis, the measuring cuvettes were accelerated with a rotational speed between 200 and 500 rpm passing a light source (wavelength 870 nm) and the detectors. This leads to a time- and space-resolved extinction of the transmitted light across the complete sample. Due to the different transmission signals of solid or liquid material, the sedimentation behavior could be determined.



**Fig. S1** The SEM images of the half-crushed JPMO **3**, which was labelled with  $\text{Fe}_3\text{O}_4$ @citrate. The outer surface strongly interacted with the labelling agent while the inner face almost remained untouched.

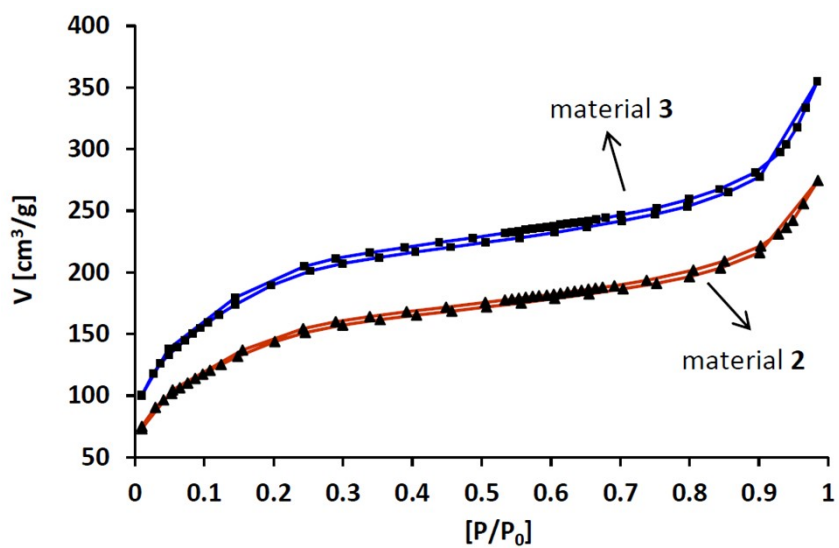


Fig. S2 N<sub>2</sub> adsorption-desorption isotherms of JPMO material 2 and 3.

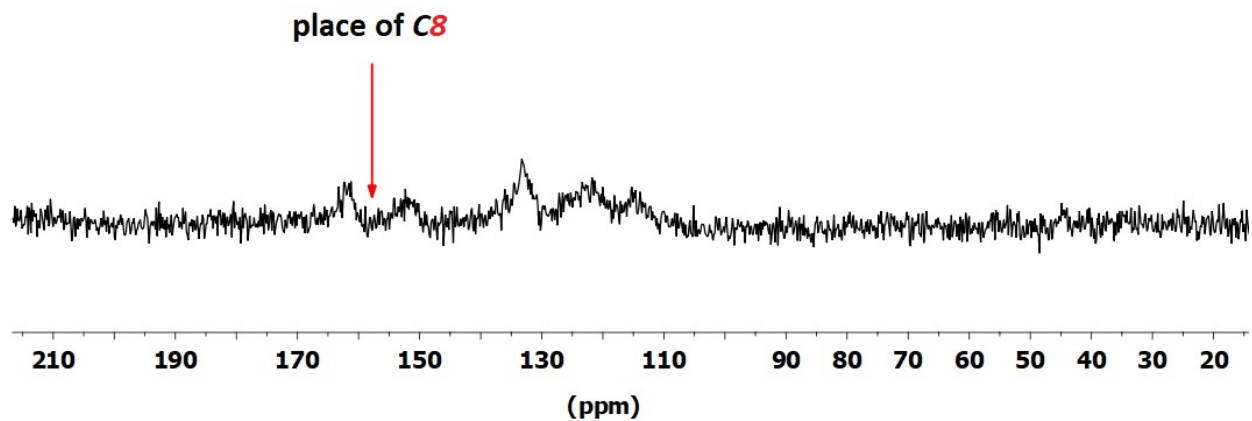
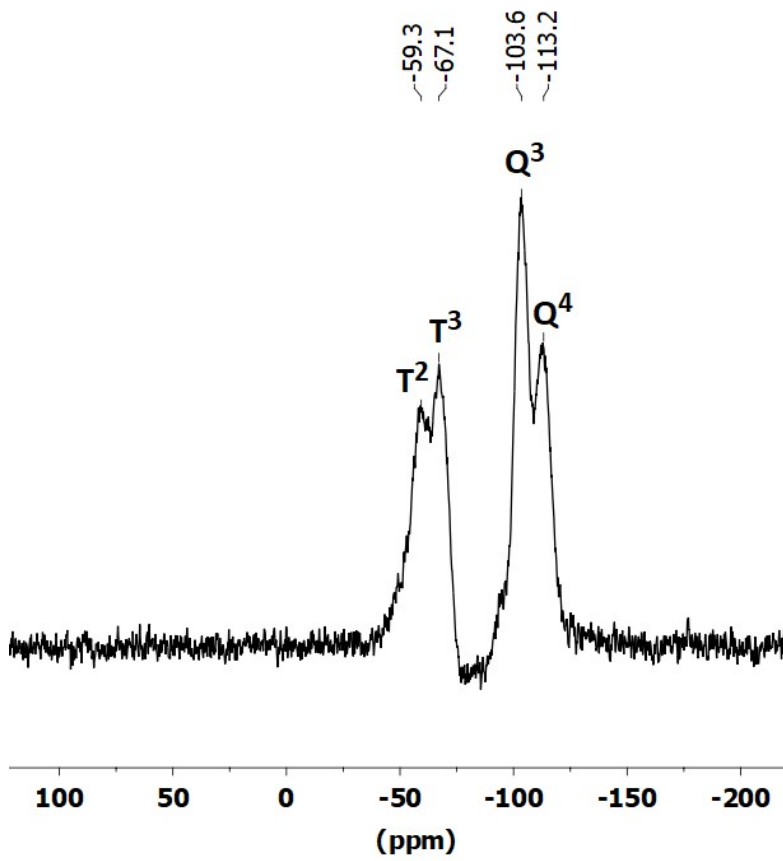
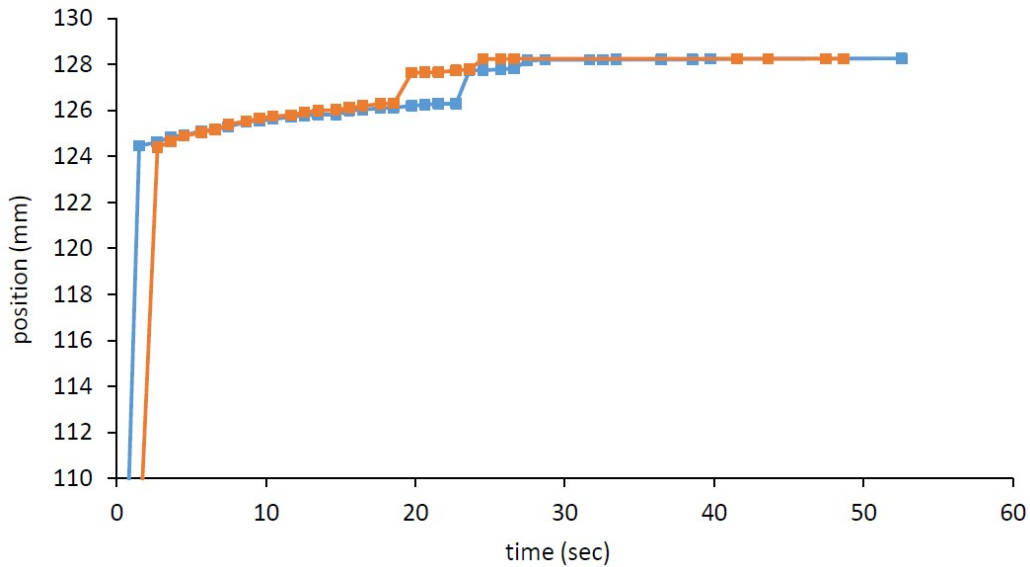


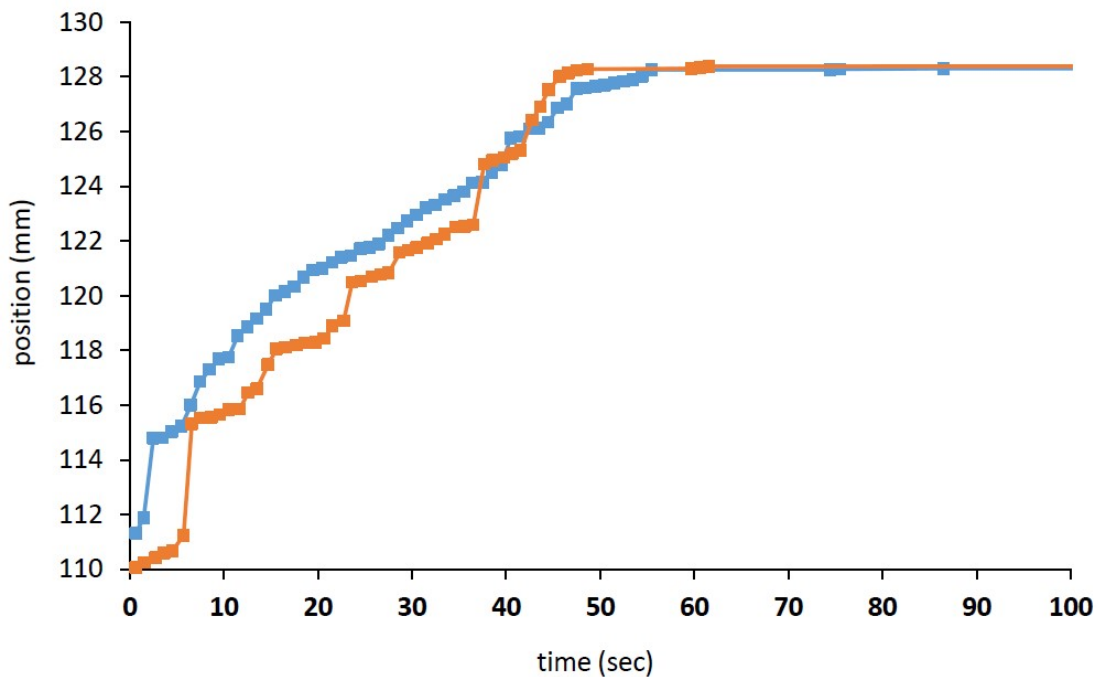
Fig. S3 The solid-state <sup>13</sup>C CP-MAS NMR spectrum of the empty tube. There is no overlap for the C8 with the background peaks.



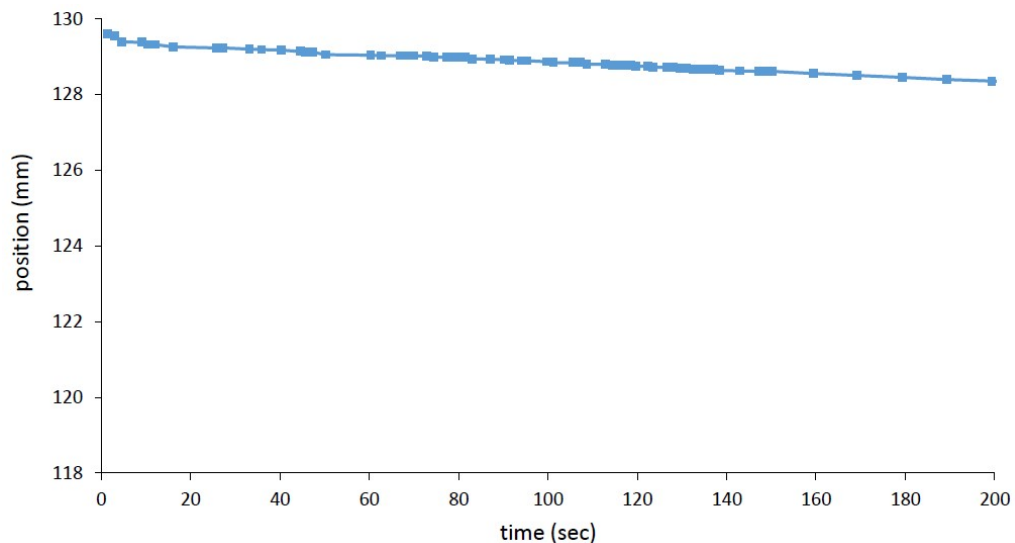
**Fig. S4** The solid-state  $^{29}\text{Si}$  CP-MAS NMR spectrum of JP MO 3



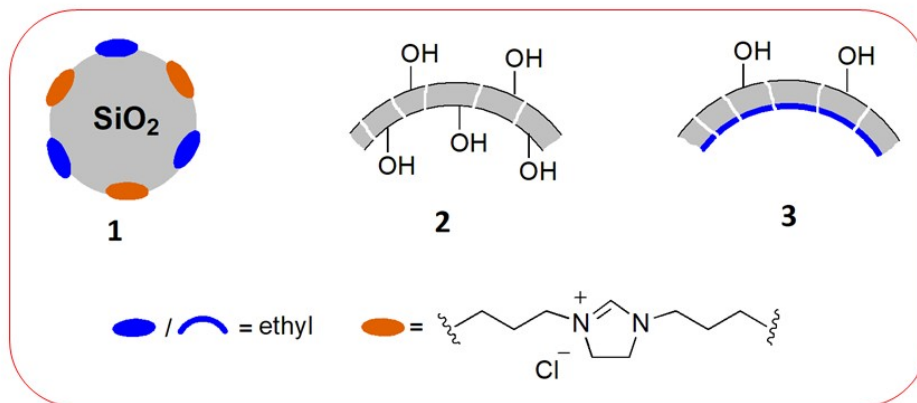
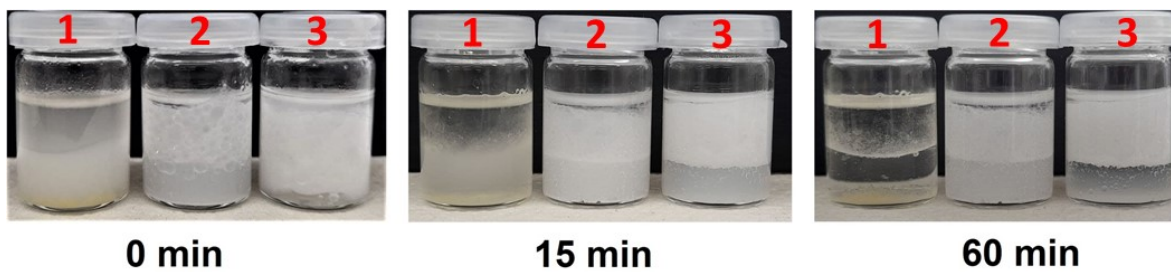
**Fig. S5** Deposition analysis of JP MO 3 in toluene with 200 rpm speed (the analysis was repeated two times).



**Fig. S6** Deposition analysis of JPMO 3 in water with 200 rpm speed (the analysis was repeated two times).

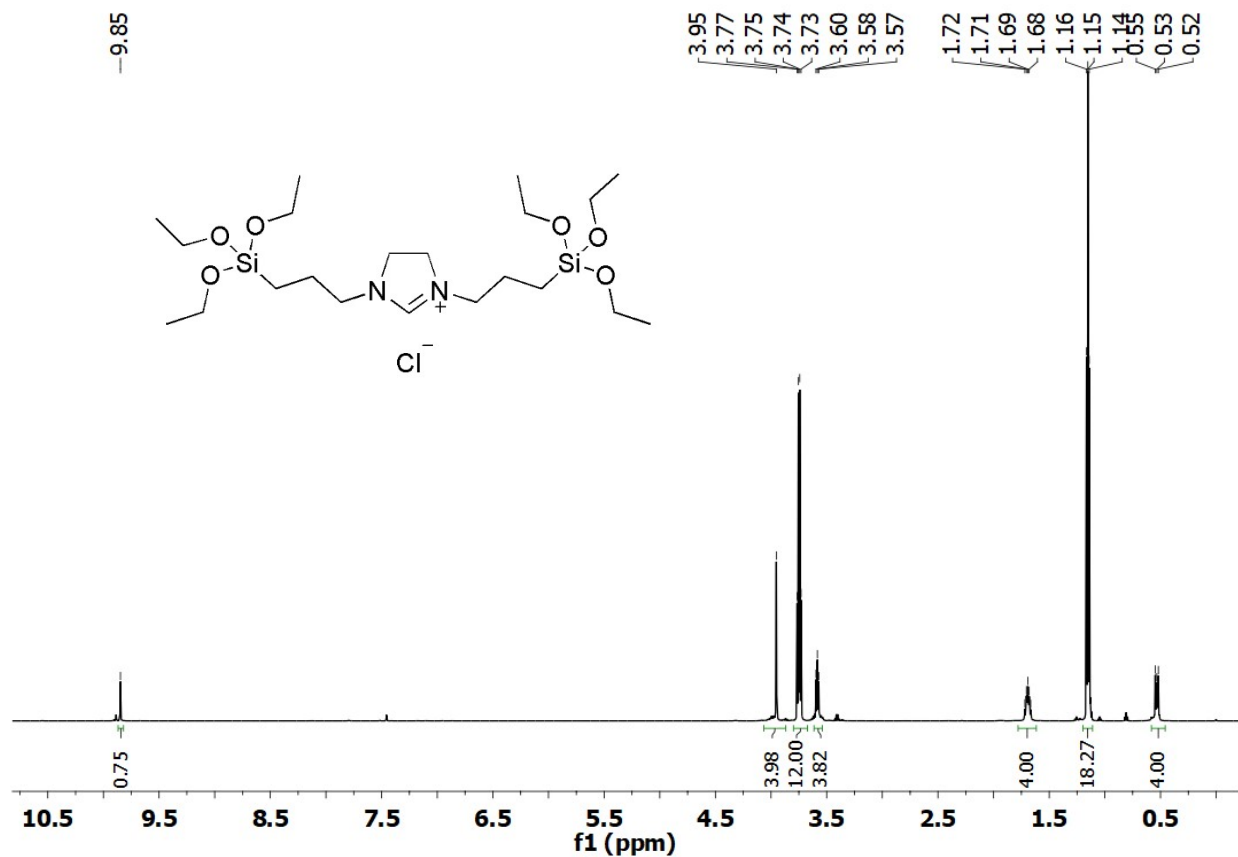


**Fig. S7** Deposition analysis of JPMO 3 in water/toluene with 200 rpm speed.





**Fig. S8** details of the control experiments for formation of Pickering emulsion using commercially available silica particles, which was randomly functionalized with **BTSE** and **IL** groups (**1**), unfunctionalized crushed hollow silica (**2**) and crushed hollow silica with **BTSE** group in one face (**3**).



**Fig. S9**  $^1\text{H}$  NMR of the ionic liquid in  $\text{CDCl}_3$ .



Fig. S10 <sup>13</sup>C NMR of the ionic liquid in CDCl<sub>3</sub>.