

## Supporting information

### High yield and isolation of 2,5 furandicarboxylic acid from HMF and sugars in ionic liquids, a new prospective for the establishment of a scalable and efficient catalytic route

Amir Al Ghatta<sup>†\*</sup> and Jason P. Hallett<sup>†\*</sup>

<sup>†</sup>Department of Chemical Engineering, Imperial College, South Kensington Campus, London SW7 2AZ.

e-mail: [a.al-ghatta16@imperial.ac.uk](mailto:a.al-ghatta16@imperial.ac.uk), [j.hallett@imperial.ac.uk](mailto:j.hallett@imperial.ac.uk)

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# 1 Materials and methods

## 1.1 Material

Manganese nitrate hexahydrate and urea for catalyst synthesis were supplied by Merck. 5-hydroxymethyl furfural, 2,5 furan dicarboxylic acid (FDCA) and 2,5 forfymfurancarboxylic acid (FFCA) used for standard calibration were supplied by Fluorochem. Ionic liquids [bmim]Cl and [bmim]Br were synthesized with the same procedure according to our previous publication.<sup>1</sup>

## 1.2 Synthesis of manganese oxide

Synthesis of  $\text{-MnO}_2$  using a urea precipitation method reported in literature. In brief, 1 gram of manganese nitrate (3.48 mmol) was dissolved in 10 ml of water followed by the addition of 10 eq. of urea (2.1 g). The mixture was heated up at 80 °C overnight. The solid precipitate was filtered and extensively washed with water and methanol. This was calcinated in a furnace at 400°C for 8 h. The catalyst was characterized by XRD, SEM, XPS, BET and TPD.

The surface area was calculated using Brunauer–Emmett–Teller (BET) analysis with a Tristar 3000 instrument with degassing at -20 °C with nitrogen for 1 h.

XRD was done using X'pert pro at a scan of 20 scans/min.

SEM was done using a Zeiss Gemini Sigma300.

XPS analysis was performed using a Thermo NEXSA XPS instrument fitted with a monochromated Al K $\alpha$  X-ray source (1486.7 eV), a spherical sector analyzer, a 3-multichannel resistive plate, and 128 channel delay line detectors. All data were recorded at 19.2 W and an X-ray beam size of 200 × 100  $\mu\text{m}$ . Survey scans were recorded at a pass energy of 160 eV, and high-resolution scans were recorded at a pass energy of 20 eV. Electronic charge neutralization was achieved using a dual-beam low-energy electron/ion source (Thermo Scientific FG-03). The ion gun current was 150  $\mu\text{A}$ , and the ion gun voltage was 45 V. All sample data were recorded at a pressure below 10–8 Torr and at room temperature (294 K).

For temperature programmed desorption experiments (TPD analysis), first a control experiment was carried to analyse the stability of the sample. The sample was conditioned at 400 °C for 30 min then cooled down. The sample was heated up at 10°/min under a flow of  $\text{N}_2$  of 30 ml/min and gas evolution was analysed by a thermoconductivity electrode (TCD). We observed that at 500°C gas evolution arises indicating that the material is undergoing to condensation and phase change. Therefore the TPD experiments were conducted up to a temperature of 400°C.

To measure the  $\text{CO}_2$  desorption, the sample was conditioned at 400 °C for 30 min then cooled down at room temperature and saturated with  $\text{CO}_2$  through a flow of 50 ml/min. The catalyst was then heated up in a furnace with a ramp of 10 °C/min with a  $\text{N}_2$  flow rate of 30 ml/min up to a temperature of 400°C and gas evolution analysed by TCD.

## 1.3 Oxidation reaction of HMF into FDCA

For screening purpose the reactions were carried at small scale in a parallel high pressure reactor. A batch solution of ionic liquid and HMF (1.26 % in weight) was prepared. As an example, 8 g of ionic liquid were mixed with 2 g of water and 126 mg of HMF. The mixture was mixed through a vortex mixer until the mixture turns into a homogeneous solution. 250 mg of the mixture were placed in a glass vial followed with the addition of 5 mg of  $\text{MnO}_2$  with a stirrer bar. The vial was then placed in a reactor slot and pressurized with an oxygen cylinder at 10 bar (previous three time purging). All

conditions were repeated in triplicate. The reactor was covered with a glass wool and heated in a hot plate at 130°C for 6 h. The reaction mixture was analysed using a Shimadzu Prominence preparative HPLC (Shimadzu, Kyoto, Japan) with refractive index (RI) and ultraviolet (UV) detectors and equipped with an Aminex HPX-87H column using 0.005 M H<sub>2</sub>SO<sub>4</sub> as the mobile phase at 55 °C and flow rate of 0.6 mL min<sup>-1</sup>. Since the mobile phase is acidic the [dbmim]FDC was eluting as FDCA. Quantification of the compounds was done by external standard. Quantification of [dbmim]FDC was done by calibrating FDCA in mM scale.

In large scale the reaction was performed in a Parr autoclave. The quantities were scaled up at 10 g scale and mixing was done by overhead stirring. The scale up proved to give the same results as the small-scale experiments. For product isolation, after the reaction was completed the reaction mixture was placed in a rotovap at 60 °C under vacuum to remove all the water. The 10 ml of ethanol were added, and the mixture was placed in the fridge (3°C) to complete the precipitation of [dbmim]FDC as a white solid. The product was collected by centrifugation and washed 3 times with 50 ml of ethanol to assure that all the ionic liquid was removed.

The product could be converted into FDCA by treating [dbmim]FDC at acidic conditions. NMR spectra of the final products are reported in Figure S. 11, S. 12. HPLC analysis of [dbmim]FDC confirmed that the final product has a purity over 98 %.

The ionic liquid phase was recovered by evaporation of the ethanol phase and analysed by NMR and mass spec to assess its stability. The spectra are reported in Figures S. 8, S. 9, S. 10 . The NMR of the recovered ionic liquid resulted broader compared the original one due to the leaching of manganese which lead to paramagnetism which leads to poorer resolution of the NMR and disappearance of the multiplicities. However no new peaks and no shift was observed the used ionic liquids indicating stability of this solvent under the reacting conditions.

#### 1.4 Conversion of fructose into [dbmim]FDC

The reaction was performed in two-steps at large scale. 200 mg of fructose were dissolved in 9 g of [bmim]Cl and 1 ml of water. Followed the addition of HCl (5 % in mol respect to fructose). The mixture was placed in a preheated heating block at 80°C for 15 min. The amount of HMF formed was evaluated by HPLC. In the second step, HCl was neutralized at pH 7 with a diluted solution of [bmim]OH and water content adjust to achieve 20 % then 200 mg of MnO<sub>2</sub> were loaded. The vial was placed in the Parr Autoclave and pressurized at 10 bar of O<sub>2</sub>. From this point, the reaction and work-up was the same as the one described previously. The ionic liquid phase was neutralized with a diluted solution of [bmim]OH.

#### 1.5 Conversion of glucose into [dbmim]FDC

The reaction was performed in two steps at large scale. 200 mg of glucose were dissolved in 9.5 g of [bmim]Cl and 0.5 ml of water followed by the addition of CrCl<sub>3</sub>·6H<sub>2</sub>O (7 % in mol respect glucose). The reaction mixture was placed in a preheated heating block at 120°C for 30 min. The amount of HMF formed was evaluated by HPLC. In the second step, 1.875 ml of water was added to achieve 20 % water content, from the catalyst loading, conditions and work-up are the same as describe in the previous Zein Test.

#### 1.6 Synthesis of [bmim][OH]

[bmim]OH was used as neutralizing agent. In brief, 5 g of [bmim]Cl were diluted in 100 ml of water and passed through an anion exchange resin Amberlite IRN78. In order to avoid degradation, the ionic liquid was used at diluted conditions previous control that pH is higher than 8.

## 2 CHARACTERIZATION

### 2.1 Characterization catalyst

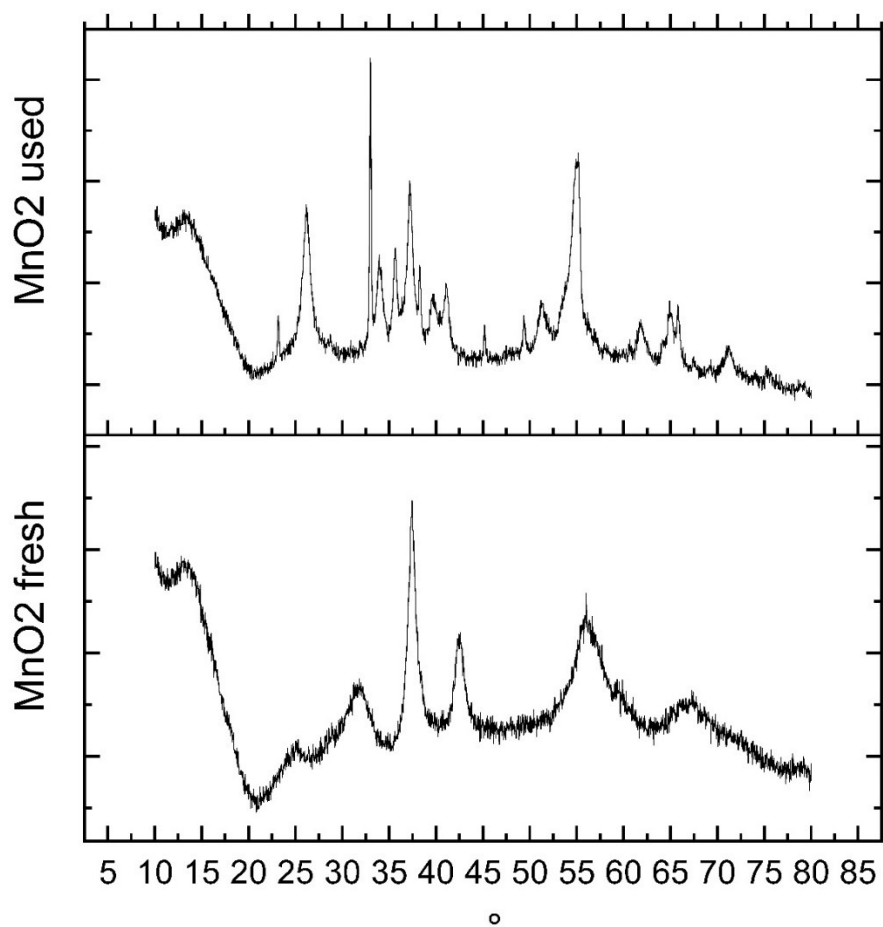


Figure S. 1 XRD fresh and spent catalyst

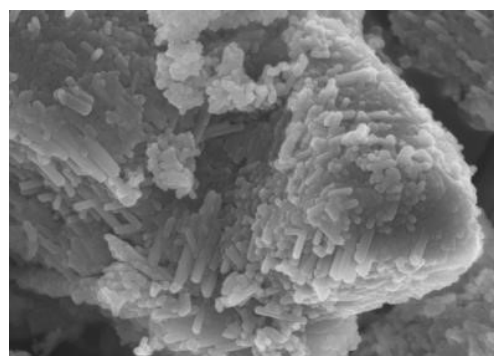


Figure S. 2 SEM fresh( left) and spent catalyst (right)

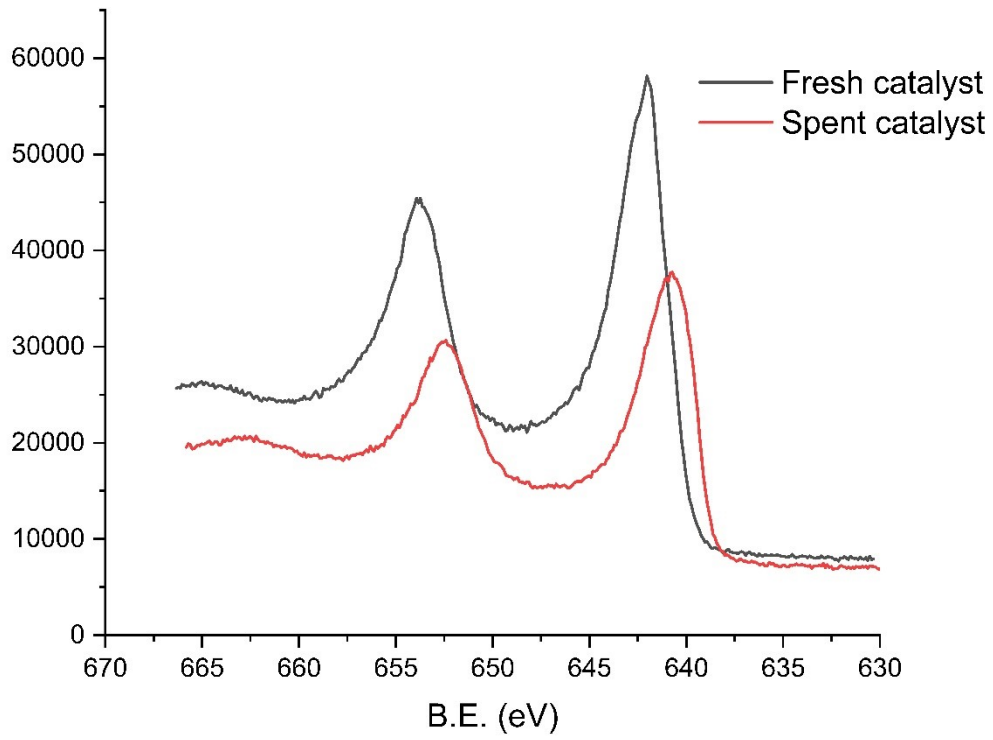


Figure S. 3 XPS fresh and spent catalyst

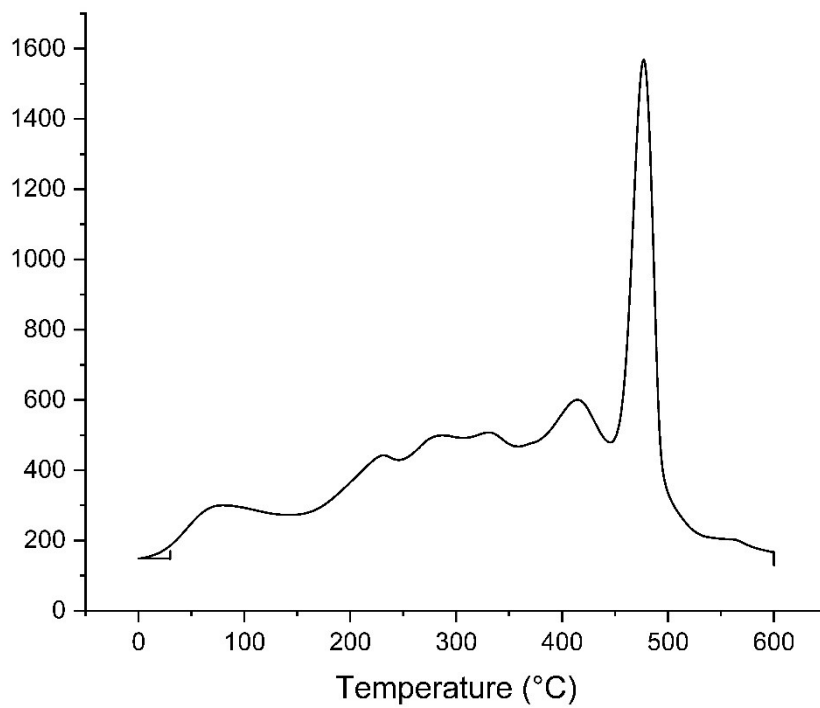


Figure S. 4 TPD control of fresh MnO<sub>2</sub>

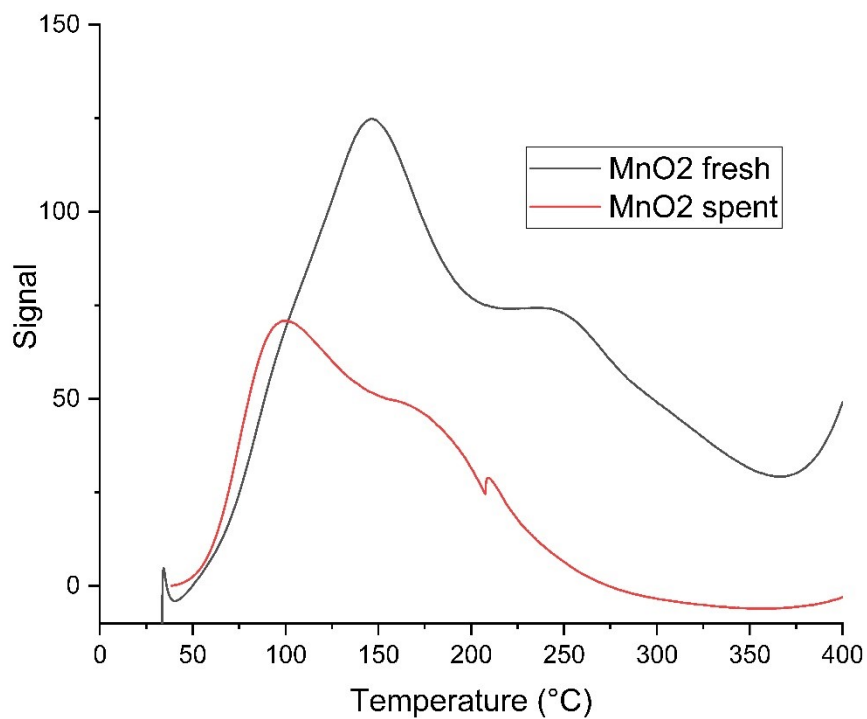


Figure S. 5 TPD of fresh and spent catalyst

## 2.2 Ionic Liquid and final product

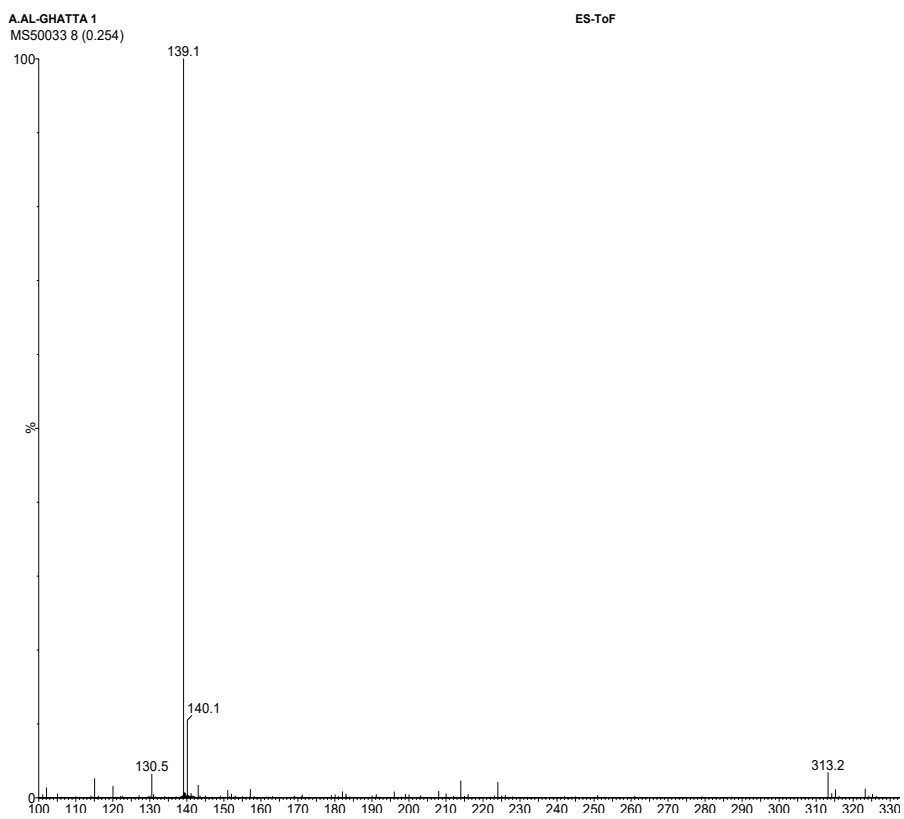


Figure S. 6 MS fresh ionic liquid

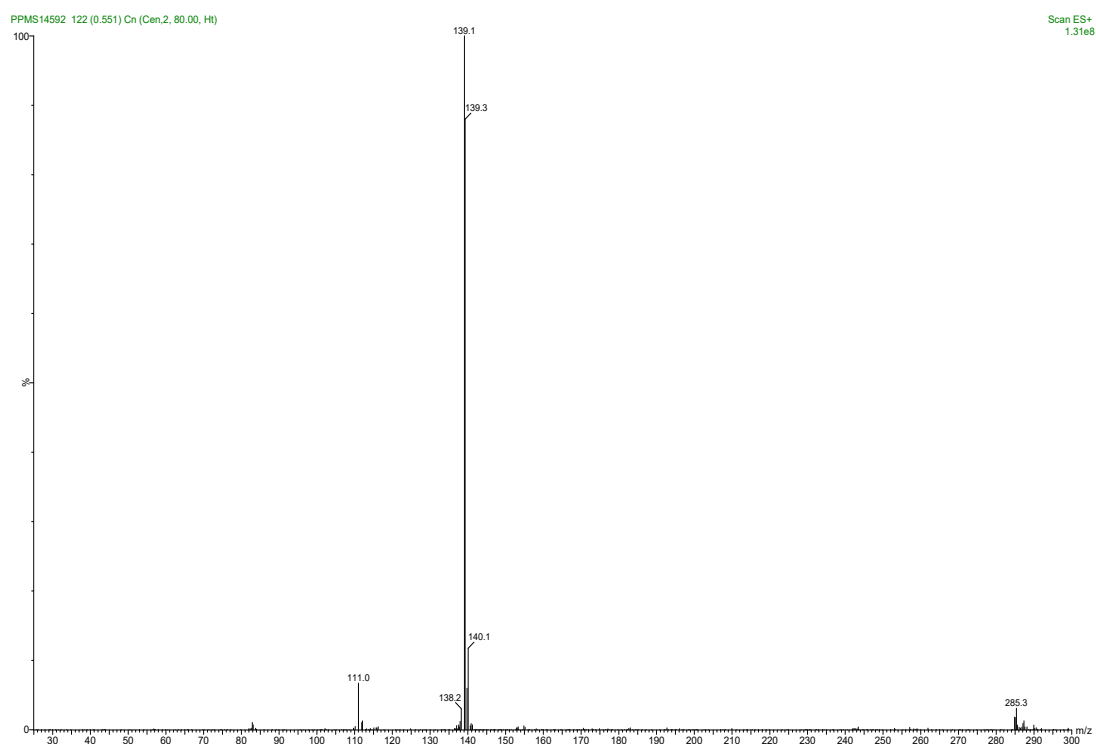


Figure S. 7 MS spent ionic liquid

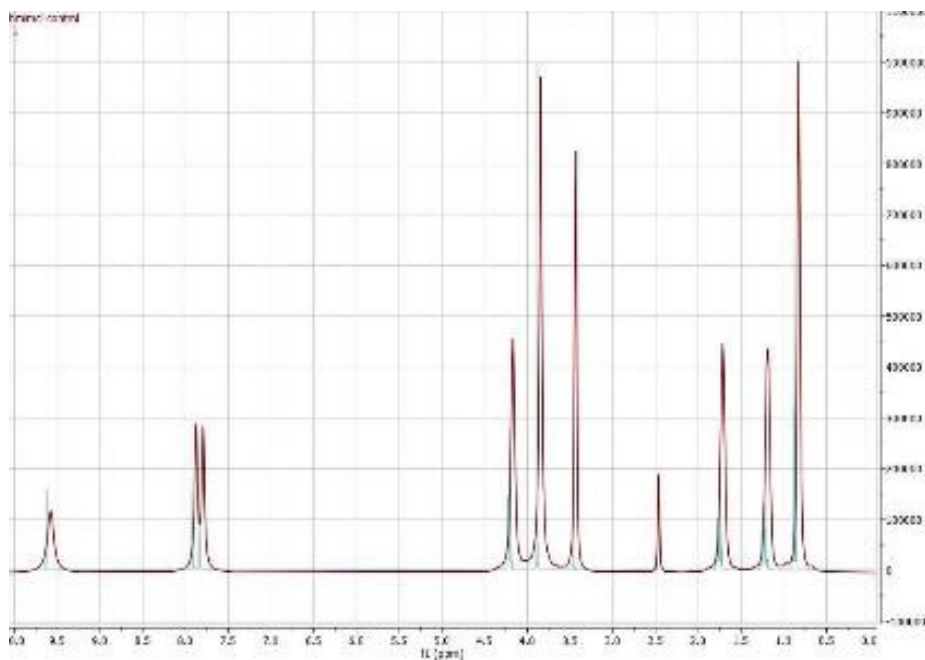


Figure S. 8 Comparison  $^1\text{H-NMR}$  fresh and used  $[\text{bmim}]\text{Cl}$ . Blue fresh, Red used

$^1\text{H NMR}$  ( $\text{DMSO-d}_6$ ):  $\delta$  9.62 (s, 1H,  $\text{N}_2\text{CH}$ ), 7.92, 7.84 (m x 2, 2 x 1H, 2 x N-CH), 4.20 (t, 2H, N-CH<sub>2</sub>-CH<sub>2</sub>,  $J_{\text{HH}} = 7.2$  Hz), 3.88 (s, 3H, N-CH<sub>3</sub>), 1.77, 1.24 (m x 2, 2 x 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 0.87 (t, 3H, -CH<sub>2</sub>-CH<sub>3</sub>,  $J_{\text{HH}} = 7.3$  Hz) ppm.  $m/z=139.1$  ( $[\text{bmim}]^+$ )

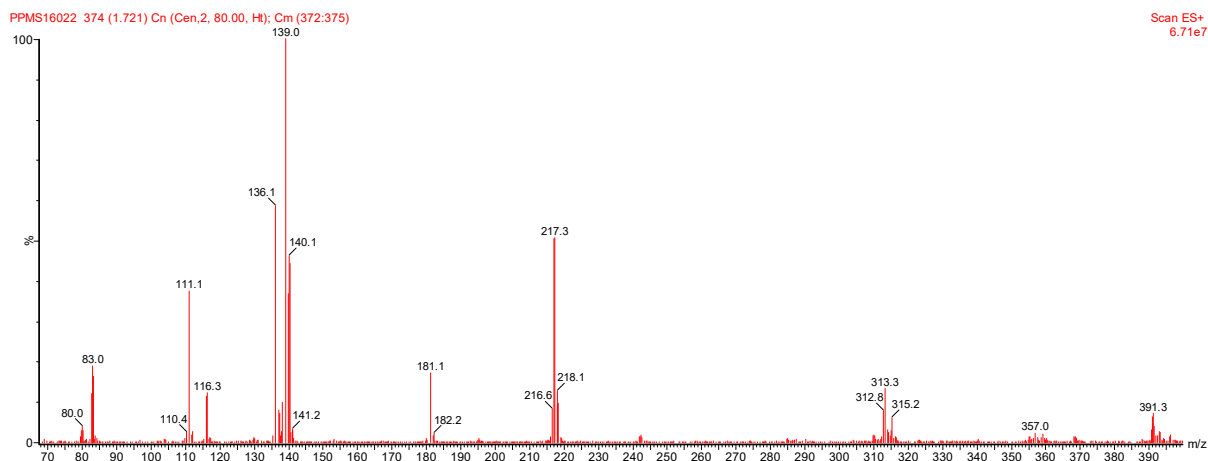


Figure S 9 MS [dbmim][FDC]

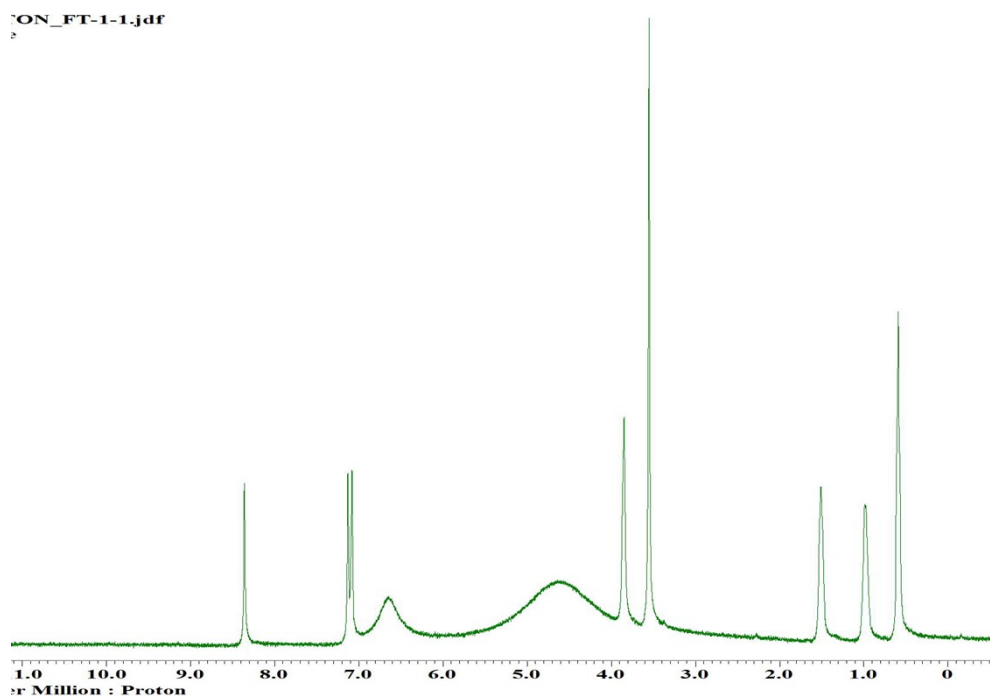


Figure S. 10 H-NMR [dbmim][FDC]

$^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  8.1 (s, 1H, N<sub>2</sub>CH), 7.2-7.1 (2 x 1H, 2 x N-CH), 3.9 (2H, N-CH<sub>2</sub>-CH<sub>2</sub>), 3.50 (3H, N-CH<sub>3</sub>), 1.77, 1.3-1 (2 x 2H, N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), 0.87 (3H, -CH<sub>2</sub>-CH<sub>3</sub>) ppm.  $m/z=139.0$  ([bim]<sup>+</sup>)



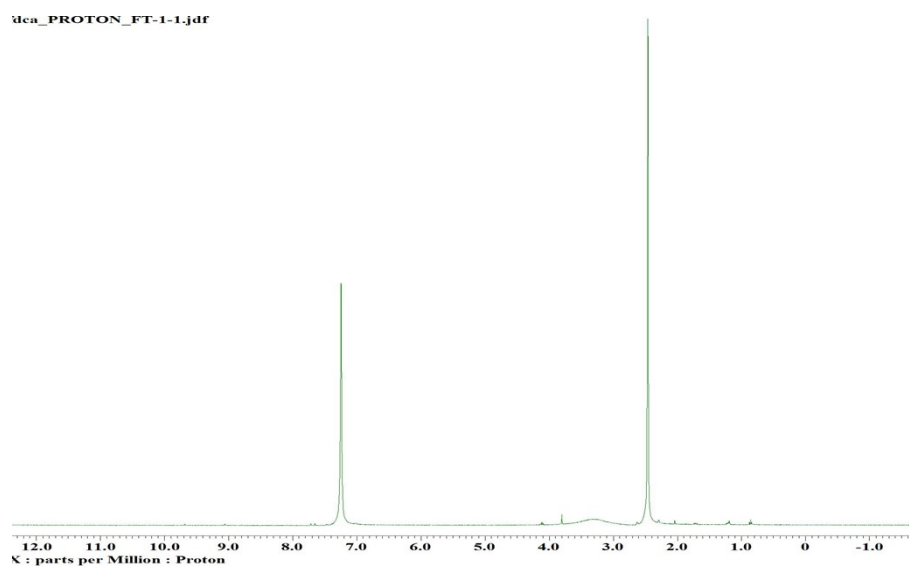


Figure S. 11  $^1\text{H}$ -NMR FDCA obtained after acidification of [dbmim]FDC

$^1\text{H}$  NMR (DMSO- $d_6$ ):  $\delta$  7.1 (s, 1H,C-CH-C)