

# Electronic Supporting Information:

## Cellulose solubilities in carboxylate-based ionic liquids

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







































Table 1 The water content of ionic liquids before dissolving cellulose

| IL                  | 1a   | 1b | 1c   | 1d   | 1f   | 2a | 2b   | 2c   | 2d   |
|---------------------|------|----|------|------|------|----|------|------|------|
| Water content / ppm | -    | -  | 2089 | 1880 | 2141 | -  | 1262 | 2047 | 2666 |
| IL                  | 2e   | 2f | 2g   | 2h   | 2i   | 3b | 3d   | 3f   |      |
| Water content / ppm | 3257 | *  | *    | *    | -    | -  | -    | 1806 |      |

- They are solid, no water content.

\* No water content, due to the high viscosity.

Table 2 Appearance of synthesized carboxylate-based structures

| Cation \ Anion  |    |    |    |    |    |    |    |    |    |  |
|---|---|---|---|---|---|--|---|---|---|---|
|   | 1a  | 1b  | 1c  | 1d  | 1e  | 1f *   | 1g *  | 1h *  | 1i *  |   |
|  |   |   |   |   |   |   |   |   |   |   |
|  |  |  |  |  |  |  |  |  |  |   |
|  |  |  |  |  |  |  |  |  |  |   |

\* Not IL as m.p. > 373 K

### Experimental details and characterisation of carboxylate-based structures:

To get the intermediate 1,3-dimethylimidazolium-2-carboxylate, a few modifications was made according to the literature [J. D. Holbrey, W. M. Reichert, I. Tkatchenko, E. Bouajila, O. Walter, I. Tommasi, R. D. Rogers, *Chemical Communications* **2003**, 28.]. 10  
 15 mL 1,3-dimethylimidazole, 15 mL dimethylcarbonate and 20 mL methanol were added into a 75 mL autoclave, then heated up to 373 K  
 for 24 h. After removing low boiling point compounds in vacuum and washing with acetone, 10.5 g the pure intermediate 1,3-  
 dimethylimidazolium-2-carboxylate was obtained, yield: 59.7 %. Generally, 2.8 g intermediate was dissolved with 20 mL water or  
 ethanol-water (10 mL-10 mL) as solvent, then 20 mmol carboxylic acid was added. At 343 K, the solution was stirred over 3 hours. After  
 removal of the solvent, pure product was obtained quantitatively.

1,3-Dimethylimidazolium-2-carboxylate

<sup>1</sup>H-NMR(400 MHz; D<sub>2</sub>O; δ/ppm) : 3.97 (s, 6H, NCH<sub>3</sub>), 7.35 (s, 2H, NCHCHN). It conforms the literature.

1,3-Dimethylimidazolium formate 1a : <sup>1</sup>H-NMR(400 MHz; DMSO-*d*<sub>6</sub>; δ/ppm): 3.86 (s, 6H, NCH<sub>3</sub>), 7.79 (d, <sup>3</sup>J(H,H)=1.6 Hz, 2H,  
 25 NCHCHN), 8.60 (s, 1H, HCOO), 9.70 (s, 1H, NCHN)

$^{13}\text{C}$ -NMR(100 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 35.43 (NCH<sub>3</sub>), 123.38 (NCHCHN), 137.76 (NCHN), 165.47 (HCOO).

1,3-Dimethylimidazolium acetate 1b :  $^1\text{H}$ -NMR(400 MHz; DMSO- $d_6$ ;  $\delta$ /ppm) : 1.57 (s, 3H, OOCCH<sub>3</sub>), 3.83 (s, 6H, NCH<sub>3</sub>), 7.80 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 2H, NCHCHN), 10.02(1H, s, NCHN).

$^{13}\text{C}$ -NMR(100 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 26.23 (OOCCH<sub>3</sub>), 35.35 (NCH<sub>3</sub>), 123.34 (NCHCHN), 138.27 (NCHN), 173.08 (CH<sub>3</sub>COO).

1,3-Dimethylimidazolium propionate 1c :  $^1\text{H}$ -NMR (400 MHz; DMSO- $d_6$ ;  $\delta$ /ppm) : 0.87 (t,  $^3\text{J}(\text{H,H})=7.6$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.82 (q,  $^3\text{J}(\text{H,H})=7.6$  Hz,  $^3\text{J}=11.4$  Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>), 3.87 (s, 6H, NCH<sub>3</sub>), 7.84 (s, 2H, NCHCHN), 10.17 (1H, s, NCHN).

$^{13}\text{C}$ -NMR (100 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 11.49 (CH<sub>2</sub>CH<sub>3</sub>), 31.67 (CH<sub>3</sub>CH<sub>2</sub>), 35.30 (NCH<sub>3</sub>), 123.34 (NCHCHN), 138.45 (NCHN), 176.42 (CH<sub>2</sub>COO).

1,3-Dimethylimidazolium butyrate 1d :  $^1\text{H}$ -NMR (400 MHz; DMSO- $d_6$ ;  $\delta$ /ppm) : 0.79 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 3H, CH<sub>3</sub>CH<sub>2</sub>), 1.40 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 1.79 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>), 3.87 (s, 6H, NCH<sub>3</sub>), 7.76 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 2H, NCHCHN), 10.14 (s, 1H, NCHN).

$^{13}\text{C}$ -NMR (100 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 14.56 (CH<sub>2</sub>CH<sub>3</sub>), 19.87 (CH<sub>3</sub>CH<sub>2</sub>), 35.40 (NCH<sub>3</sub>), 41.35 (OOCCH<sub>2</sub>), 123.32 (NCHCHN), 138.22 (NCHN), 175.29 (CH<sub>2</sub>COO).

1,3-Dimethylimidazolium *iso*-butyrate 1e :  $^1\text{H}$ -NMR (400 MHz; DMSO- $d_6$ ;  $\delta$ /ppm) : 0.90 (d,  $^3\text{J}(\text{H,H})=6.8$  Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.97 (septet,  $^3\text{J}(\text{H,H})=6.8$  Hz, 1H, CHCOO), 3.87 (s, 6H, NCH<sub>3</sub>), 7.80 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 2H, NCHCHN), 10.14 (s, 1H, NCHN).

$^{13}\text{C}$ -NMR (100 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 20.98 (CH(CH<sub>3</sub>)<sub>2</sub>), 35.35 (NCH<sub>3</sub>), 36.80 ((CH<sub>3</sub>)<sub>2</sub>CH), 123.33 (NCHCHN), 138.46 (NCHN), 179.02 (CHCOO).

1,3-Dimethylimidazolium *mono*-maleate 1f :  $^1\text{H}$ -NMR (400 MHz; DMSO- $d_6$ ;  $\delta$ /ppm) : 3.85 (s, 6H, NCH<sub>3</sub>), 6.02 (s, 2H, CHCH), 7.68 (s, 2H, NCHCHN), 9.05 (s, 1H, NCHN).

$^{13}\text{C}$ -NMR (100 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 35.66 (NCH<sub>3</sub>), 123.45 (NCHCHN), 136.17 (CHCH), 137.07 (NCHN), 167.21 (CHCOO).

Bis(1,3-dimethylimidazolium) maleate 1g :  $^1\text{H}$ -NMR (400 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 3.89 (s, 12H, NCH<sub>3</sub>), 5.46 (s, 2H, CHCH), 7.72 (s, 4H, NCHCHN), 9.98 (s, 2H, NCHN).

$^{13}\text{C}$ -NMR (100 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 35.41 (NCH<sub>3</sub>), 123.10 (NCHCHN), 130.56 (CHCH), 139.12 (NCHN), 171.18 (CHCOO).

1,3-Dimethylimidazolium *mono*-succinate 1h :  $^1\text{H}$ -NMR (400 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 2.23 (s, 4H, CH<sub>2</sub>CH<sub>2</sub>), 3.85 (s, 6H, NCH<sub>3</sub>), 7.69 (s, 2H, NCHCHN), 9.08 (s, 1H, NCHN).

$^{13}\text{C}$ -NMR (100 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 32.91 (CH<sub>2</sub>CH<sub>2</sub>), 35.65 (NCH<sub>3</sub>), 123.45 (NCHCHN), 137.11 (NCHN), 175.38 (CH<sub>2</sub>COO).

Bis(1,3-dimethylimidazolium) succinate 1i :  $^1\text{H}$ -NMR (400 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 1.97 (s, 4H, CH<sub>2</sub>CH<sub>2</sub>), 3.87 (s, 12H, NCH<sub>3</sub>), 7.75 (s, 4H, NCHCHN), 9.99 (s, 2H, NCHN).

$^{13}\text{C}$ -NMR (100 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 35.45 (NCH<sub>3</sub>), 37.00 (CH<sub>2</sub>CH<sub>2</sub>), 123.32 (NCHCHN), 138.42 (NCHN), 176.81 (CH<sub>2</sub>COO).

According to the method of synthesizing 1,3-dimethylimidazolium carboxylate and the literature [C. Rijkssen, R. D. Rogers, *The Journal of Organic Chemistry* **2008**, 73, 5582 & B. Bantu, G. M. Pawar, K. Wurst, U. Decker, A. M. Schmidt, M. R. Buchmeiser, *European Journal of Inorganic Chemistry* **2009**, 2009, 1970], 1-ethyl-3-methylimidazolium carboxylate was prepared. The procedure is: 10 mL 1-ethylimidazole, 20 mL dimethylcarbonate, and 20 mL methanol were added into a 75 mL autoclave. Then the solution was heated up to 393 K for 24 hours. After reaction, the solvent was removed with reduced pressure (keep it less than 40 °C). After washing with acetone (10 mL  $\times$ 3), the intermediate 1-ethyl-3-methylimidazolium-2-carboxylate was obtained, 8.1 g, yield: 50.5 %. Then 3.08 g intermediate was dissolved with 20 mL water or ethanol-water (10 mL-10 mL) as solvent, then 20 mmol carboxylic acid was added. At 343 K, the solution was stirred over 3 hours. After removal of the solvent, pure product was obtained quantitatively. Target molecules also can be prepared by replacing the intermediate with another compound, 1-ethyl-3-methylimidazolium hydrogen carbonate.

1-Ethyl-3-methylimidazolium-2-carboxylate

$^1\text{H}$ -NMR (400 MHz; D<sub>2</sub>O;  $\delta$ /ppm) : 1.40 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 3.92 (s, 3H, NCH<sub>3</sub>), 4.37 (d,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H, NCH<sub>2</sub>), 7.35 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 1H, NCH), 7.41 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 1H, NCH).

$^{13}\text{C}$ -NMR (100 MHz; D<sub>2</sub>O;  $\delta$ /ppm): 15.04 (CH<sub>2</sub>CH<sub>3</sub>), 36.43 (NCH<sub>3</sub>), 45.07 (NCH<sub>2</sub>), 121.19 (NCH), 123.12 (NCH), 139.57 (NCHN), 158.33 (CHCOO).

1-Ethyl-3-methylimidazolium hydrogen carbonate

1-Ethyl-3-methylimidazolium-2-carboxylate was dissolved in water, stirred at 313 K overnight. After removing water under reduced pressure and washing with acetone, pure product 1-ethyl-3-methylimidazolium hydrogen carbonate was obtained.

$^1\text{H}$ -NMR (400 MHz; D<sub>2</sub>O;  $\delta$ /ppm) : 1.43 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H, NCH<sub>2</sub>), 3H, CH<sub>2</sub>CH<sub>3</sub>), 3.82 (s, 3H, NCH<sub>3</sub>), 4.15 (d,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H, NCH<sub>2</sub>), 2H, NCH<sub>2</sub>), 7.35 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 1H, NCH), 7.42 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 1H, NCH), 8.65 (s, 1H, NCHN).

$^{13}\text{C}$ -NMR (100 MHz; D<sub>2</sub>O;  $\delta$ /ppm): 14.38 (CH<sub>2</sub>CH<sub>3</sub>), 35.47 (NCH<sub>3</sub>), 44.66 (NCH<sub>2</sub>), 121.73 (NCH), 123.32 (NCH), 160.17 (HOCOO).

1-Ethyl-3-methylimidazolium formate 2a :  $^1\text{H}$ -NMR (400 MHz; DMSO- $d_6$ ;  $\delta$ /ppm) : 1.39 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 3.87 (s, 3H, NCH<sub>3</sub>), 4.21 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H, CH<sub>3</sub>CH<sub>2</sub>), 7.82 (s, 1H, NCH), 7.92 (s, 1H, NCH), 8.63 (s, 1H, HCOO), 9.86 (s, 1H, NCHN).

$^{13}\text{C}$ -NMR (100 MHz; DMSO- $d_6$ ;  $\delta$ /ppm): 15.19 (CH<sub>2</sub>CH<sub>3</sub>), 35.53 (NCH<sub>3</sub>), 43.97 (NCH<sub>2</sub>), 122.04 (NCH), 123.57 (NCH), 137.16 (NCHN), 165.49 (HCOO).

1-Ethyl-3-methylimidazolium acetate 2b :  $^1\text{H-NMR}$  (400 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ) : 1.38 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.58 (s, 3H,  $\text{OOCCH}_3$ ), 3.89 (s, 3H,  $\text{NCH}_3$ ), 4.23 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H,  $\text{CH}_3\text{CH}_2$ ), 7.90 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 1H, NCH), 8.01 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 1H, NCH), 10.37 (s, 1H, NCHN).  
5  $^{13}\text{C-NMR}$  (100 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ): 15.27 ( $\text{CH}_2\text{CH}_3$ ), 26.29 ( $\text{OOCCH}_3$ ), 35.37 ( $\text{NCH}_3$ ), 43.85 ( $\text{NCH}_2$ ), 122.08 ( $\text{NCH}$ ), 123.58 ( $\text{NCH}$ ), 137.95 ( $\text{NCHN}$ ), 173.42 ( $\text{CH}_3\text{COO}$ ).

1-Ethyl-3-methylimidazolium propionate 2c :  $^1\text{H-NMR}$  (400 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ) : 0.87 (t,  $^3\text{J}(\text{H,H})=7.6$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.40 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 3H,  $\text{NCH}_2\text{CH}_3$ ), 1.79 (q,  $^3\text{J}(\text{H,H})=7.6$  Hz, 2H,  $\text{OOCCH}_2$ ), 3.88 (s, 3H,  $\text{NCH}_3$ ), 4.22 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H,  $\text{CH}_3\text{CH}_2$ ),  
10 7.78 (s, 1H, NCH), 7.88 (s, 1H, NCH), 10.11 (s, 1H, NCHN).  
 $^{13}\text{C-NMR}$  (100 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ): 11.60 ( $\text{CH}_2\text{CH}_3$ ), 15.27 ( $\text{NCH}_2\text{CH}_3$ ), 31.75 ( $\text{OOCCH}_2$ ), 35.47 ( $\text{NCH}_3$ ), 43.91 ( $\text{NCH}_2$ ), 121.92 ( $\text{NCH}$ ), 123.47 ( $\text{NCH}$ ), 137.60 ( $\text{NCHN}$ ), 176.00 ( $\text{CH}_2\text{COO}$ ).

1-Ethyl-3-methylimidazolium butyrate 2d :  $^1\text{H-NMR}$  (400 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ) : 0.79 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 3H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.40  
15 (m, 5H,  $\text{NCH}_2\text{CH}_3$ ,  $\text{OOCCH}_2\text{CH}_2$ ), 1.79 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H,  $\text{OOCCH}_2$ ), 3.88 (s, 3H,  $\text{NCH}_3$ ), 4.22 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H,  $\text{CH}_3\text{CH}_2$ ), 7.82 (s, 1H, NCH), 7.92 (s, 1H, NCH), 10.25 (s, 1H, NCHN).  
 $^{13}\text{C-NMR}$  (100 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ): 14.59 ( $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 15.24 ( $\text{NCH}_2\text{CH}_3$ ), 35.42 ( $\text{NCH}_3$ ), 41.42 ( $\text{OOCCH}_2$ ), 43.88 ( $\text{NCH}_2$ ), 121.95 ( $\text{NCH}$ ), 123.49 ( $\text{NCH}$ ), 137.79 ( $\text{NCHN}$ ), 175.44 ( $\text{CH}_2\text{COO}$ ).

1-Ethyl-3-methylimidazolium *iso*-butyrate 2e :  $^1\text{H-NMR}$  (400 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ) : 0.89 (d,  $^3\text{J}(\text{H,H})=6.8$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.41  
20 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 3H,  $\text{NCH}_2\text{CH}_3$ ), 1.95 (m,  $^3\text{J}(\text{H,H})=6.8$  Hz, 1H,  $(\text{CH}_3)_2\text{CH}$ ), 3.87 (s, 3H,  $\text{NCH}_3$ ), 4.22 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H,  $\text{CH}_3\text{CH}_2$ ), 7.76 (s, 1H, NCH), 7.86 (s, 1H, NCH), 10.03 (s, 1H, NCHN).  
 $^{13}\text{C-NMR}$  (100 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ): 15.21 ( $\text{NCH}_2\text{CH}_3$ ), 21.08 ( $\text{CH}(\text{CH}_3)_2$ ), 35.49 ( $\text{NCH}_3$ ), 36.85 ( $(\text{CH}_3)_2\text{CH}$ ), 43.94 ( $\text{NCH}_2$ ), 121.90 ( $\text{NCH}$ ), 123.46 ( $\text{NCH}$ ), 137.53 ( $\text{NCHN}$ ), 178.78 ( $\text{CHCOO}$ ).

1-Ethyl-3-methylimidazolium *mono*-maleate 2f :  $^1\text{H-NMR}$  (400 MHz;  $\text{D}_2\text{O}$ ; 1,4-dioxane;  $\delta/\text{ppm}$ ) : 1.44 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 3H,  $\text{NCH}_2\text{CH}_3$ ), 3.84 (s, 3H,  $\text{NCH}_3$ ), 4.16 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H,  $\text{CH}_3\text{CH}_2$ ), 6.21 (s, 2H,  $\text{CCHCHC}$ ), 7.36 (s, 1H, NCH), 7.43 (s, 1H, NCH), 8.66 (s, 1H, NCHN).  
25  $^{13}\text{C-NMR}$  (100 MHz;  $\text{D}_2\text{O}$ ; 1,4-dioxane;  $\delta/\text{ppm}$ ): 15.05 ( $\text{NCH}_2\text{CH}_3$ ), 36.17 ( $\text{NCH}_3$ ), 45.37 ( $\text{NCH}_2$ ), 122.47 ( $\text{NCH}$ ), 124.06 ( $\text{NCH}$ ), 134.49 ( $\text{CHCH}$ ), 136.15 ( $\text{NCHN}$ ), 172.17 ( $\text{CHCOO}$ ).

Bis(1-ethyl-3-methylimidazolium) melate 2g :  $^1\text{H-NMR}$  (400 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ) : 1.38 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 6H,  $\text{NCH}_2\text{CH}_3$ ), 3.89  
30 (s, 6H,  $\text{NCH}_3$ ), 4.25 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{CH}_3\text{CH}_2$ ), 5.41 (d, 2H,  $\text{CHCH}$ ), 7.67 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 2H, NCH), 7.75 (d,  $^3\text{J}(\text{H,H})=1.6$  Hz, 2H, NCH), 9.80 (s, 2H, NCHN).  
 $^{13}\text{C-NMR}$  (100 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ): 15.29 ( $\text{NCH}_2\text{CH}_3$ ), 35.53 ( $\text{NCH}_3$ ), 43.82 ( $\text{NCH}_2$ ), 121.47 ( $\text{NCH}$ ), 123.21 ( $\text{NCH}$ ), 138.08 ( $\text{NCHN}$ ), 171.06 ( $\text{CHCOO}$ ).

1-Ethyl-3-methylimidazolium *mono*-succinate 2h :  $^1\text{H-NMR}$  (400 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ) : 1.41 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 3H,  $\text{NCH}_2\text{CH}_3$ ),  
35 2.28 (t, 4H,  $\text{CH}_2\text{CH}_2$ ), 3.85 (s, 3H,  $\text{NCH}_3$ ), 4.19 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H,  $\text{CH}_3\text{CH}_2$ ), 7.71 (s, 1H, NCH), 7.80 (s, 1H, NCH), 9.22 (s, 1H, NCHN).  
 $^{13}\text{C-NMR}$  (100 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ): 15.11 ( $\text{NCH}_2\text{CH}_3$ ), 35.01 ( $\text{NCH}_3$ ), 35.68 ( $\text{CH}_2\text{CH}_2$ ), 44.12 ( $\text{NCH}_2$ ), 121.99 ( $\text{NCH}$ ), 123.58 ( $\text{NCH}$ ), 136.40 ( $\text{NCHN}$ ), 175.47 ( $\text{CH}_2\text{COO}$ ).

Bis(1-ethyl-3-methylimidazolium) succinate 2i :  $^1\text{H-NMR}$  (400 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ) : 1.39 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 6H,  $\text{NCH}_2\text{CH}_3$ ),  
40 1.97 (s, 4H,  $\text{CH}_2\text{CH}_2$ ), 3.88 (s, 6H,  $\text{NCH}_3$ ), 4.23 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{CH}_3\text{CH}_2$ ), 7.79 (s, 2H, NCH), 7.88 (s, 2H, NCH), 10.24 (s, 2H, NCHN).  
 $^{13}\text{C-NMR}$  (100 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ): 15.26 ( $\text{NCH}_2\text{CH}_3$ ), 35.44 ( $\text{NCH}_3$ ), 37.25 ( $\text{CH}_2\text{CH}_2$ ), 43.87 ( $\text{NCH}_2$ ), 121.87 ( $\text{NCH}$ ), 123.46 ( $\text{NCH}$ ), 137.89 ( $\text{NCHN}$ ), 176.96 ( $\text{CH}_2\text{COO}$ ).

50 According to the literature [Z. Q. Zheng, J. Wang, T. H. Wu, X. P. Zhou, *Advanced Synthesis & Catalysis* 2007, 349, 1095], a few modifications were made to get pure product. Under argon protection, 7.0 g *N,N*-diethylammonium chloride (it was prepared by diethylamine with HCl gas, before using), 11 mL dimethylcarbonate were added into a 75 mL autoclave, then heated up to 383 K overnight. After removing the low boiling point compounds under reduced pressure and washing with acetone, the pure intermediate *N,N*-diethyl-*N,N*-dimethylimidazolium chloride were obtained, 8.5 g, yield: 90.1 %. Then the intermediate went through the anion  
55 exchange resin IRA-400 (OH), to get the corresponding hydroxide. The hydroxide was neutralized with stoichiometric acid. After removal of water under reduced pressure, the target molecule was obtained.

*N,N*-Diethyl-*N,N*-dimethylammonium Chloride:

$^1\text{H-NMR}$  (400 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ) : 1.37 (m, 6H,  $\text{CH}_2\text{CH}_3$ ), 3.05 (s, 6H,  $\text{NCH}_3$ ), 3.40 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{NCH}_2$ ).

60 *N,N*-Diethyl-*N,N*-dimethylammonium formate 3a :  $^1\text{H-NMR}$  (400 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ) : 1.20 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 6H,  $\text{CH}_2\text{CH}_3$ ), 2.99 (s, 6H,  $\text{NCH}_3$ ), 3.34 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{NCH}_2$ ), 8.58 (s, 1H,  $\text{HCOO}$ ).

$^{13}\text{C-NMR}$  (100 MHz;  $\text{DMSO-}d_6$ ;  $\delta/\text{ppm}$ ): 7.75 ( $\text{CH}_2\text{CH}_3$ ), 48.74 ( $\text{NCH}_3$ ), 57.67 ( $\text{NCH}_2$ ), 164.97 ( $\text{HCOO}$ )

- N,N-Diethyl-N,N-dimethylammonium acetate 3b :  $^1\text{H-NMR}$  (400 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ) : 1.19 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 6H,  $\text{CH}_2\text{CH}_3$ ), 1.54 (s, 3H,  $\text{OOCCH}_3$ ), 3.00 (s, 6H,  $\text{NCH}_3$ ), 3.37 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{NCH}_2$ ).  
 $^{13}\text{C-NMR}$  (100 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ): 7.74 ( $\text{CH}_2\text{CH}_3$ ), 25.91 ( $\text{OOCCH}_3$ ), 48.65 ( $\text{NCH}_3$ ), 57.52 ( $\text{NCH}_2$ ), 172.52 ( $\text{CH}_3\text{COO}$ )
- 5 N,N-Diethyl-N,N-dimethylammonium propionate 3c :  $^1\text{H-NMR}$  (400 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ) : 0.85 (t,  $^3\text{J}(\text{H,H})=7.6$  Hz, 3H,  $\text{CH}_2\text{CH}_3$ ), 1.20 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 6H,  $\text{NCH}_2\text{CH}_3$ ), 1.77 (q,  $^3\text{J}(\text{H,H})=7.6$  Hz, 2H,  $\text{CH}_3\text{CH}_2$ ), 3.01 (s, 6H,  $\text{NCH}_3$ ), 3.36 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{NCH}_2$ ).  
 $^{13}\text{C-NMR}$  (100 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ): 7.74 ( $\text{NCH}_2\text{CH}_3$ ), 11.55 ( $\text{CH}_2\text{CH}_3$ ), 31.58 ( $\text{CH}_3\text{CH}_2$ ), 48.66 ( $\text{NCH}_3$ ), 57.55 ( $\text{NCH}_2$ ), 175.50 ( $\text{CH}_2\text{COO}$ ).
- 10 N,N-Diethyl-N,N-dimethylammonium butyrate 3d :  $^1\text{H-NMR}$  (400 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ) : 0.78 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 3H,  $\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.20 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 6H,  $\text{NCH}_2\text{CH}_3$ ), 1.36 (m, 2H,  $\text{OOCCH}_2\text{CH}_2$ ), 1.73 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 2H,  $\text{OOCCH}_2$ ), 3.00 (s, 6H,  $\text{NCH}_3$ ), 3.36 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{NCH}_2$ ).  
 $^{13}\text{C-NMR}$  (100 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ): 7.74 ( $\text{NCH}_2\text{CH}_3$ ), 14.66 ( $\text{CH}_2\text{CH}_3$ ), 20.00 ( $\text{OOCCH}_2\text{CH}_2$ ), 41.58 ( $\text{OOCCH}_2$ ), 48.69 ( $\text{NCH}_3$ ), 157.59 ( $\text{NCH}_2$ ), 174.58 ( $\text{CH}_2\text{COO}$ ).
- 15 N,N-Diethyl-N,N-dimethylammonium *iso*-butyrate 3e :  $^1\text{H-NMR}$  (400 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ) : 0.87 (d,  $^3\text{J}(\text{H,H})=6.8$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ), 1.20 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 6H,  $\text{NCH}_2\text{CH}_3$ ), 1.92 (m,  $^3\text{J}(\text{H,H})=6.8$  Hz, 1H,  $(\text{CH}_3)_2\text{CH}$ ), 2.99 (s, 6H,  $\text{NCH}_3$ ), 3.35 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{NCH}_2$ ).  
 $^{13}\text{C-NMR}$  (100 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ): 7.73 ( $\text{CH}_2\text{CH}_3$ ), 21.05 ( $\text{CH}(\text{CH}_3)_2$ ), 36.72 ( $(\text{CH}_3)_2\text{CH}$ ), 48.70 ( $\text{NCH}_3$ ), 57.61 ( $\text{NCH}_2$ ), 178.20 ( $\text{CHCOO}$ ).
- N,N-Diethyl-N,N-dimethylammonium *mono*-maleate 3f :  $^1\text{H-NMR}$  (400 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ) : 1.22 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 6H,  $\text{CH}_2\text{CH}_3$ ), 2.96 (s, 6H,  $\text{NCH}_3$ ), 3.30 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{NCH}_2$ ), 6.04 (s, 2H,  $\text{CHCH}$ ).  
25  $^{13}\text{C-NMR}$  (100 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ): 7.72 ( $\text{CH}_2\text{CH}_3$ ), 48.86 ( $\text{NCH}_3$ ), 57.93 ( $\text{NCH}_2$ ), 136.04 ( $\text{CHCH}$ ), 167.22 ( $\text{CHCOO}$ )
- Bis(N,N-diethyl-N,N-dimethylammonium) maleate 3g :  $^1\text{H-NMR}$  (400 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ) : 1.19 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 12H,  $\text{CH}_2\text{CH}_3$ ), 3.01 (s, 12H,  $\text{NCH}_3$ ), 3.38 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 8H,  $\text{NCH}_2$ ), 5.27 (s, 2H,  $\text{CHCH}$ ).  
30  $^{13}\text{C-NMR}$  (100 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ): 7.80 ( $\text{CH}_2\text{CH}_3$ ), 48.71 ( $\text{NCH}_3$ ), 57.45 ( $\text{NCH}_2$ ), 130.18 ( $\text{CHCH}$ ), 170.47 ( $\text{CHCOO}$ )
- N,N-Diethyl-N,N-dimethylammonium *mono*-succinate 3h :  $^1\text{H-NMR}$  (400 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ) : 1.22 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 6H,  $\text{CH}_2\text{CH}_3$ ), 2.22 (s, 4H,  $\text{CH}_2\text{CH}_2$ ), 2.96 (s, 6H,  $\text{NCH}_3$ ), 3.30 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{NCH}_2$ ).  
 $^{13}\text{C-NMR}$  (100 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ): 7.72 ( $\text{CH}_2\text{CH}_3$ ), 33.03 ( $\text{CH}_2\text{CH}_2$ ), 48.83 ( $\text{NCH}_3$ ), 57.87 ( $\text{NCH}_2$ ), 175.36 ( $\text{CH}_2\text{COO}$ )
- 35 Bis(N,N-diethyl-N,N-dimethylammonium) succinate 3i :  $^1\text{H-NMR}$  (400 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ) : 1.19 (t,  $^3\text{J}(\text{H,H})=7.2$  Hz, 12H,  $\text{CH}_2\text{CH}_3$ ), 1.86 (s, 8H,  $\text{CH}_2\text{CH}_2$ ), 3.01 (12H, s,  $\text{NCH}_3$ ), 3.37 (q,  $^3\text{J}(\text{H,H})=7.2$  Hz, 4H,  $\text{NCH}_2$ ).  
 $^{13}\text{C-NMR}$  (100 MHz; DMSO- $d_6$ ;  $\delta/\text{ppm}$ ): 7.76 ( $\text{CH}_2\text{CH}_3$ ), 37.62 ( $\text{CH}_2\text{CH}_2$ ), 48.63 ( $\text{NCH}_3$ ), 57.48 ( $\text{NCH}_2$ ), 176.37 ( $\text{CH}_2\text{COO}$ ).