

## SUPPORTING INFORMATION

### **Bio Ionic Liquids: Room Temperature Ionic Liquids Composed Wholly of Biomaterials**

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#### **MATERIALS AND INSTRUMENTS**

*N,N*-dimethylethanolamine was purchased from Tokyo Chemical Ind. Co., Ltd, and dried over *p*-toluenesulfonyl chloride and distilled before use. Iodomethane was purchased from Tokyo Chemical Ind. Co., Ltd, and were dried over K<sub>2</sub>CO<sub>3</sub> and CaCl<sub>2</sub> and distilled before use. Other commercially available solvents were used as received. Unless otherwise noted, synthesis and purification of choline iodide ([Ch][I]) was carried out in light shielding glassware. To toluene solution of *N,N*-dimethylethanolamine, freshly distilled iodomethane in toluene was added dropwise under argon gas atmosphere at 0°C. The reaction mixture was stirred at room temperature for 24h. The resulting precipitate was filtered off, washed with an excess amount of diethyl ether. Then the product was recrystallized from ethyl acetate/2-propanol solution. The resulting product was separated from the solution by filtration, and dried under reduced pressure at room temperature for 48h to give [Ch][I] as white crystal in 90% yield.

The measurements of <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were carried out on a JEOL ECX-400. Electro spray ionization-time-of-flight-mass (ESI-TOF-MAS) spectrometry was made on JEOL JMS-T100LC. The amount of water was confirmed by Karl Fischer coulometric titration (Kyoto Electronics MKC-510N). The differential scanning calorimetry (DSC) measurements were carried out using DSC-6200 (SEIKO Instruments) at a scanning rate for both heating and cooling of 1°Cmin<sup>-1</sup> in the temperature range -100°C to 100°C. The thermogravimetric analysis (TGA) was made on SEIKO TG/DTA 220 instrument with heating rate of 10°Cmin<sup>-1</sup> from 25°C to 400°C under nitrogen. Visible spectrum was measured using SHIMAZU UV 2450. The viscosity measurement was carried out with Brookfield DV-I + viscometer from 20°C to 95°C at interval of 5°C under nitrogen gas.

## CHARACTERIZATION OF IONIC LIQUIDS

The chemical structure for a series of ionic liquids prepared in this study was confirmed by  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR. Purity of ionic liquids was estimated as follows. In the  $^1\text{H}$ -NMR spectra, there were no peaks assigned to impurities. We examined halide impurities especially  $\Gamma^-$  in resulting ionic liquids by means of mass spectroscopy as well as  $\text{AgNO}_3$  titration. After addition of  $\text{AgNO}_3$  aqueous solution to the IL, no white precipitation of  $\text{Ag}\Gamma$  was observed. In the ESI-TOF-mass spectra, no peaks were observed due to  $\Gamma^-$  anion.

### Characterization of Choline Salts with Monocarboxylic Acid Anion

#### Choline acetate ([Ch][acetate])

$\delta_{\text{H}}$ (400 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ) 1.60 (3 H, s,  $\text{CH}_3\text{CO}$ ), 3.15 (9 H, s,  $3 \times \text{CH}_3\text{N}$ ), 3.43-3.45 (2 H, m,  $\text{CH}_2\text{CH}_2\text{OH}$ ), 3.82-3.86 (2 H, m,  $\text{CH}_2\text{OH}$ );  $\delta_{\text{C}}$  (100 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ) 25.7 (s,  $\text{CH}_3\text{CO}$ ), 53.0 ( $3 \times \text{t}$ ,  $3 \times \text{CH}_3\text{N}$ ), 54.9 (s,  $\text{CH}_2\text{OH}$ ), 67.3 (t,  $\text{CH}_2\text{N}$ ), 173.6 (s, CO); ESI-TOF-MS: Calcd for  $\text{C}_7\text{H}_{17}\text{NO}_3$   $[\text{M}]^+$ :  $m/z = 104.17$ ; Found: 104.43,  $[\text{M}]^-$ :  $m/z = 59.04$ ; Found: not detected.

#### Choline propionate ([Ch][propionate])

$\delta_{\text{H}}$ (400 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ) 0.90 (3 H, t,  $J = 7.56$  Hz,  $\text{CH}_3\text{CH}_2$ ), 1.85 (2 H, q,  $J = 7.63$  Hz,  $\text{CH}_2\text{CO}$ ), 3.16 (9 H, s,  $3 \times \text{CH}_3\text{N}$ ), 3.46 (2 H, t,  $J = 4.81$  Hz,  $\text{CH}_2\text{CH}_2\text{OH}$ ), 3.85 (2 H, s,  $\text{CH}_2\text{OH}$ );  $\delta_{\text{C}}$ (100 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ) 11.4(s,  $\text{CH}_3\text{CH}_2$ ), 31.3 (s,  $\text{CH}_2\text{CO}$ ), 53.0 ( $3 \times \text{t}$ ,  $3 \times \text{CH}_3\text{N}$ ), 54.9 (s,  $\text{CH}_2\text{OH}$ ), 67.3 (t,  $\text{CH}_2\text{N}$ ), 176.8 (s, CO); ESI-TOF-MS: Calcd for  $\text{C}_8\text{H}_{19}\text{NO}_3$   $[\text{M}]^+$ :  $m/z = 104.17$ ; Found: 104.43,  $[\text{M}]^-$ :  $m/z = 73.07$ ; Found: not detected

#### Choline benzoate ([Ch][benzoate])

$\delta_{\text{H}}$ (400 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ) 3.16 (9 H, t,  $J = 16.94$  Hz,  $3 \times \text{CH}_3\text{N}$ ), 3.47 (2 H, dd,  $J = 5.50, 4.12$  Hz,  $\text{CH}_2\text{CH}_2\text{OH}$ ), 3.90 (2 H, d,  $J = 3.66$  Hz,  $\text{CH}_2\text{OH}$ ), 7.26 (3 H, dd,  $J = 6.64, 2.98$  Hz, Ph(H)), 7.83-7.85 (2 H, m, Ph(H));  $\delta_{\text{C}}$ (100 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ) 53.1 ( $3 \times \text{t}$ ,  $3 \times \text{CH}_3\text{N}$ ), 55.0 (s,  $\text{CH}_2\text{OH}$ ), 67.3 (t,  $\text{CH}_2\text{N}$ ), 127.0-140.9 ( $6 \times \text{s}$ , Ph), 169.0 (s, CO); ESI-TOF-MS: Calcd for  $\text{C}_{12}\text{H}_{19}\text{NO}_3$   $[\text{M}]^+$ :  $m/z = 104.17$ ; Found: 104.43,  $[\text{M}]^-$ :  $m/z = 121.11$ ; Found: 120.94.

#### Choline glycolate ([Ch][glycolate])

$\delta_{\text{H}}$ (400 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ) 3.14 (9 H, s,  $3 \times \text{CH}_3\text{N}$ ), 3.43 (2 H, td,  $J = 5.04, 1.68$  Hz,  $\text{CH}_2\text{CH}_2\text{OH}$ ), 3.85 (2 H, td,  $J = 4.81, 2.75$  Hz,  $\text{CH}_2\text{OH}$ ), 5.47 (1 H, br s, OH), 6.06 (2 H, d,  $J = 1.83$  Hz,  $\text{CH}_2(\text{OH})\text{CO}$ );  $\delta_{\text{C}}$ (100 MHz; DMSO- $d_6$ ;  $\text{Me}_4\text{Si}$ ) 53.2 ( $3 \times \text{t}$ ,  $3 \times \text{CH}_3\text{N}$ ), 55.2 (s,  $\text{CH}_2\text{OH}$ ), 67.0

(t, CH<sub>2</sub>N), 136.2 (s, CH<sub>2</sub>CO), 167.4 (s, CO); ESI-TOF-MS: Calcd for C<sub>7</sub>H<sub>17</sub>NO<sub>4</sub> [M]<sup>+</sup>: m/z = 104.17; Found: 104.40, [M]<sup>-</sup>: m/z = 75.04; Found: not detected.

#### **Choline tiglinate ([Ch][tiglate])**

$\delta_{\text{H}}$ (400 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 1.58 (3 H, d, J = 6.87 Hz, CH<sub>3</sub>CH=C), 1.65 (3 H, s, CH<sub>3</sub>C(CO)=C), 3.16 (9 H, s, 3 × CH<sub>3</sub>N), 3.46 (2 H, t, J = 4.81 Hz, CH<sub>2</sub>CH<sub>2</sub>OH), 3.85-3.88 (2 H, m, CH<sub>2</sub>OH), 6.26-6.31 (1 H, m, CH=C(CO));  $\delta_{\text{C}}$ (100 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 13.7 (s, CH<sub>3</sub>CH), 13.9 (s, CH<sub>3</sub>C(CO)), 53.0 (3 × t, 3 × CH<sub>3</sub>N), 55.0 (s, CH<sub>2</sub>OH), 67.3 (t, CH<sub>2</sub>N), 126.0 (s, CH=C(CO)), 136.6 (s, C(CO)=CH), 171.6 (s, CO); ESI-TOF-MS: Calcd for C<sub>10</sub>H<sub>21</sub>NO<sub>3</sub> [M]<sup>+</sup>: m/z = 104.17; Found: 104.43, [M]<sup>-</sup>: m/z = 99.11; Found: not detected.

#### **Characterization of Choline Salts with Hydrogen dicarboxylic Acid Anion**

In the <sup>1</sup>H-NMR spectra, the peaks assigned to free COOH protons were not observed. Moreover, we observed on COO carbons in <sup>13</sup>C-NMR spectra except for the case of [Ch][H-malate]. These might be due to the quick proton exchange. Therefore we were unable to confirm that only one COOH group is in the deprotonated form by NMR measurements. However, aqueous solution of the prepared bio-ILs with hydrogen dicarboxylate acid anions was acidic after diluting with pure water. Moreover, when we neutralized [Ch][OH] with melecic acid or fumaric acid ([Ch][OH] : acid = 2 : 1 by mol), unstable solids were obtained. They were quickly colored to brown. The equimolar mixture of [Ch][OH] with melecic acid or fumaric acid gave the salt we expected.

#### **Choline hydrogen malate ([Ch][H-malate])**

$\delta_{\text{H}}$ (400 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 2.31 (2H, dd, J = 15.57, 2.75 Hz, CH<sub>2</sub>CO), 3.11 (9 H, s, 3 × CH<sub>3</sub>N), 3.40 (2 H, t, J = 5.27 Hz, CH<sub>2</sub>CH<sub>2</sub>OH), 3.81-3.86 (3 H, m, CH<sub>2</sub>OH + CH(OH)CO);  $\delta_{\text{C}}$ (100 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 42.1 (s, CH<sub>2</sub>CH(OH)), 53.2 (3 × t, 3 × CH<sub>3</sub>N), 55.2 (s, CH<sub>2</sub>OH), 65.7 (s, CH(OH)CH<sub>2</sub>), 67.0 (t, CH<sub>2</sub>N), 172.2 (s, COCH<sub>2</sub>), 176.9 (s, COCH(OH)); ESI-TOF-MS: Calcd for C<sub>9</sub>H<sub>19</sub>NO<sub>6</sub> [M]<sup>+</sup>: m/z = 104.17; Found: 104.44, [M]<sup>-</sup>: m/z = 133.08; Found: 132.93.

#### **Choline hydrogen maleate ([Ch][H-maleate])**

$\delta_{\text{H}}$ (400 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 3.14 (9 H, s, 3 × CH<sub>3</sub>N), 3.36 (2 H, d, J = 0.92 Hz, 2 × CH=CH), 3.44 (2 H, t, J = 4.81 Hz, CH<sub>2</sub>CH<sub>2</sub>OH), 3.85 (2 H, dt, J = 9.46, 2.52 Hz, CH<sub>2</sub>OH);  $\delta_{\text{C}}$ (100 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 53.1 (3 × t, 3 × CH<sub>3</sub>N), 55.0 (s, CH<sub>2</sub>OH), 61.6 (2 × s, 2 × CH=CH), 67.1 (t, CH<sub>2</sub>N), 174.3 (2 × s, 2 × CO); ESI-TOF-MS: Calcd for C<sub>9</sub>H<sub>17</sub>NO<sub>5</sub> [M]<sup>+</sup>: m/z = 104.17; Found: 104.40, [M]<sup>-</sup>: m/z = 115.06; Found: 114.91.

**Choline hydrogen succinate ([Ch][H-succinate])**

$\delta_{\text{H}}$ (400 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 2.19 (4H, s, 2 × CH<sub>2</sub>CO), 3.14 (9 H, s, 3 × CH<sub>3</sub>N), 3.43 (2 H, t, J = 4.81 Hz, CH<sub>2</sub>CH<sub>2</sub>OH), 3.84 (2 H, q, J = 4.88 Hz, CH<sub>2</sub>OH);  $\delta_{\text{C}}$ (100 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 33.6 (2 × s, CH<sub>2</sub>CO), 53.1 (3 × t, 3 × CH<sub>3</sub>N), 55.0 (s, CH<sub>2</sub>OH), 67.1 (t, CH<sub>2</sub>N), 176.0 (2 × s, 2 × CO); ESI-TOF-MS: Calcd for C<sub>9</sub>H<sub>19</sub>NO<sub>5</sub> [M]<sup>+</sup>: m/z = 104.17; Found: 104.40, [M]<sup>-</sup>: m/z = 117.08; Found: 116.93.

**Choline hydrogen fumarate ([Ch][H-fumarate])**

$\delta_{\text{H}}$ (400 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 3.13 (9 H, s, 3 × CH<sub>3</sub>N), 3.42 (2 H, t, J = 5.04 Hz, CH<sub>2</sub>CH<sub>2</sub>OH), 3.83-3.87 (2 H, m, CH<sub>2</sub>OH), 6.44 (2 H, s, 2 × CH=CH);  $\delta_{\text{C}}$ (100 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 53.1 (3 × t, 3 × CH<sub>3</sub>N), 55.1 (s, CH<sub>2</sub>OH), 67.1 (t, CH<sub>2</sub>N), 135.4 (2 × s, 2 × CH=CH), 168.4 (2 × s, 2 × CO); ESI-TOF-MS: Calcd for C<sub>9</sub>H<sub>17</sub>NO<sub>5</sub> [M]<sup>+</sup>: m/z = 104.17; Found: 104.44, [M]<sup>-</sup>: m/z = 115.06; Found: 114.93.

**Choline hydrogen tartarate ([Ch][H-tartarate])**

$\delta_{\text{H}}$ (400 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 3.11 (9 H, s, 3 × CH<sub>3</sub>N), 3.41 (2 H, t, J = 5.04 Hz, CH<sub>2</sub>CH<sub>2</sub>OH), 3.82-3.86 (4 H, m, CH<sub>2</sub>OH + 2 × CH(OH)CO);  $\delta_{\text{C}}$ (100 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 53.2 (3 × t, 3 × CH<sub>3</sub>N), 55.1 (s, CH<sub>2</sub>OH), 67.0 (t, CH<sub>2</sub>N), 71.2 (2 × s, 2 × CH(OH)CO), 174.4 (2 × s, 2 × CO); ESI-TOF-MS: Calcd for C<sub>9</sub>H<sub>19</sub>NO<sub>7</sub> [M]<sup>+</sup>: m/z = 104.17; Found: 104.44, [M]<sup>-</sup>: m/z = 149.08; Found: 148.91.

**MEASUREMENT OF THE KAMLET-TAFT PARAMETERS**

Measurement of the Kamlet-Taft parameters of a series of ionic liquids has been carried out as follows. The following three solvatochromic dyes with spectroscopic grade, (2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye 33) (Fluka), 4-nitroaniline (Tokyo Chemical Ind. Co., Ltd), and *N,N*-diethyl-4-nitroaniline (Kanto Chem.) were used as received. To 0.2 ml of ionic liquid, the dye was individually added as a concentrated dry methanol solution. The methanol was then carefully removed by vacuum drying at 40 °C for 6h. To avoid aggregation of dye molecules, the dye concentration in a series of ionic liquids was settled to show the absorbance between 0.15 and 0.30. These ionic liquid solutions were placed into quartz cells. Temperature of the sample was maintained at 25°C in the spectrometer. Spectroscopic measurements were carried out to calculate the following parameters such as  $\alpha$ : hydrogen bond acidity,  $\beta$ : hydrogen bond basicity,  $\pi^*$ : dipolarity. From the maximum absorption ( $\lambda_{\text{max}}$ ), we calculated the  $\alpha$ ,  $\beta$ , and  $\pi^*$  values with the following equations:

$$v_{(\text{dye})} = 1 / (\lambda_{\text{max}(\text{dye})} \times 10^{-4}) \quad (1)$$

$$E_{\text{T}}(30) = 0.9986 (28592 / \lambda_{\text{max}(\text{Reichardt's dye 33})}) - 8.6878 \quad (2)$$

$$\pi^* = 0.314(27.52 - v_{(N,N\text{-diethyl-4-nitroaniline})}) \quad (3)$$

$$\alpha = 0.0649 E_{\text{T}}(30) - 2.03 - 0.72 \pi^* \quad (4)$$

$$\beta = (1.035 v_{(N,N\text{-diethyl-4-nitroaniline})} + 2.64 - v_{(4\text{-nitroaniline})}) / 2.80 \quad (5)$$