Transition of cellulose crystalline structure in biodegradable mixtures of renewably-sourced levulinate alkyl ammonium ionic liquids, γ-valerolactone and water

Florent Boissou, Andrea Mühlbauer, Karine De Oliveira Vigier, Loïc Leclercq, Werner Kunz, Sinisa Marinkovic, Boris Estrine, Véronique Nardello-Rataj and François Jérôme

Chemicals : Microcrystalline cellulose AVICEL PH-200 (Lot. No. 40739C) was purchased to FMC Biopolymer. γ-valerolactone was bought to Sigma-Aldrich. All reagents were obtained from Aldrich at the highest purity available and used without further purification. $CDCl_3$ and CD_3OD (99.95% isotopic purity) were obtained from Euriso-top. In all experiments, the water used was Millipore (18.2 MΩ·cm; Simplicity 185).

Apparatus:

- IR spectra were recorded on a FT-IR Perkin Elmer (spectrum one) using ATR technology.
- The degree of polymerization (DP) of cellulose samples were determined by intrinsic viscosity measurements using copper ethylenediamine complex as solvent for dissolving MCC (normalized method: AFNOR NF G 06-037).
- XRD patterns of cellulose were recorded on a Bruker D5005 Bragg–Brentano (θ-θ) diffractometer operated with a copper tube powered at 40 kV and 40 mA ($Cu_{K\alpha1}$ = 1.54060 A˚ and $Cu_{K\alpha2}$ = 1.54443 A˚). Measurements were performed from 2θ = 10° to 60° in step mode, with steps of 0.068 and a fixed acquisition time of 10 s/step.
- ^{1}H- and ^{13}C-NMR spectra were recorded in the indicated solvents on a Bruker Avance 300 spectrometer. Chemical shifts (δ) are expressed in parts per million (ppm). Chemical shifts are given in ppm (δ) and measured relative to the HOD signal or the deuterated solvent chemical shift. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet.

The thermogravimetric analysis (TGA) of prepared salts was performed using a TGA Q5000 apparatus (TA Instruments) unit under a nitrogen atmosphere to determine decomposition temperatures. Samples between 2 and 10 mg were placed in aluminum pans and heated from 25 to 300 °C at a heating rate of 10 °C min^{-1}.

- Thermal transitions were determined by differential scanning calorimetry (DSC) with a DSC Q100 calorimeter (TA Instruments) unit under a nitrogen atmosphere, calibrated with a standard sample of indium. Samples between 5 and 10 mg were sealed in aluminum pans and

measured over a temperature range of -80 °C until ca. 20 °C under the beginning of degradation with a rate of 10 °C min^{-1}; the samples were cooled with an intercooler.

- Viscosity measurements were carried out with a Malvern Kinexus rotational rheometer with cone plate geometry (CP 20/2°), which was equipped with a Peltier temperature-controlled plate. Shear rates were determined over a shear stress ramp between 1 and 2000 Pa. To study the temperature dependence of the viscosity the measurements were carried out at 25 and 80 °C. Samples were dried under lyophilisation, and rapidly transferred to the plates of the rheometer. Measurements were started as quickly as possible to minimize the water absorption.
- The surface tension measurements of pure ILs were performed using a Krüss-K11 tensiometer equipped with plate geometry. They were carried out in the temperature range from 25 to 80 °C at atmospheric pressure. The temperature was thermo-regulated thanks to a double-jacketed glass cell by means of a water bath using a Lauda RC6 circulator to control the temperature.

Biodegradability experiments: Biodegradadion of ILs was performed following the OECD 301F standard, which requires the biological oxygen consumption (BOC) and the theoretical oxygen demand (ThOD). The ThOD (in mg of oxygen per mg of product) corresponds to the amount of oxygen necessary to oxidize the compound into its final oxidation products. Sodium acetate was used as a reference. With the average number of each element in the structure and the average molar weight (MW) of the compound, the ThOD can be calculated according to the equation 1 when no nitrification occurs.

$$\mathrm{ThOD} = \frac{2\mathrm{C} + 0.5(\mathrm{H} - \mathrm{Cl} - 3\mathrm{N}) + 3\mathrm{S} + 2.5\mathrm{P} + 0.5\mathrm{Na} - \mathrm{O}}{\overline{\mathrm{MW}}} \quad (1)$$

The biological oxygen consumption (BOC) was determined by means of an IBUK respirometer, which identifies the oxygen consumption all along the degradation process. Experiments were conducted at 20 °C over a period of 28 days in a medium containing various mineral substances (sodium and potassium phosphates, ammonium, calcium and iron chlorides, magnesium sulfate) and bacteria collected from a local wastewater treatment plant. The starting pH was 7.4. The percentage of biodegradation or biodegradability (% B) values were obtained according to the following equation (Eq. 2):

$$\%\mathrm{B} = \frac{\mathrm{BOC}}{\mathrm{ThOD}} \cdot 100 \quad (2)$$

The reliability of the experiment depends on 3 parameters. The first one is the degradation of the reference molecule (sodium acetate). Its degradation has to reach 60% after 14 days. Secondly, the mineral medium has to exhibit oxygen consumption below 60 mg L^{-1} (ideally between 20 and 30 mg L^{-1}) after 28 days. Finally, after 28 days, the pH should be between 6 and 8.5.

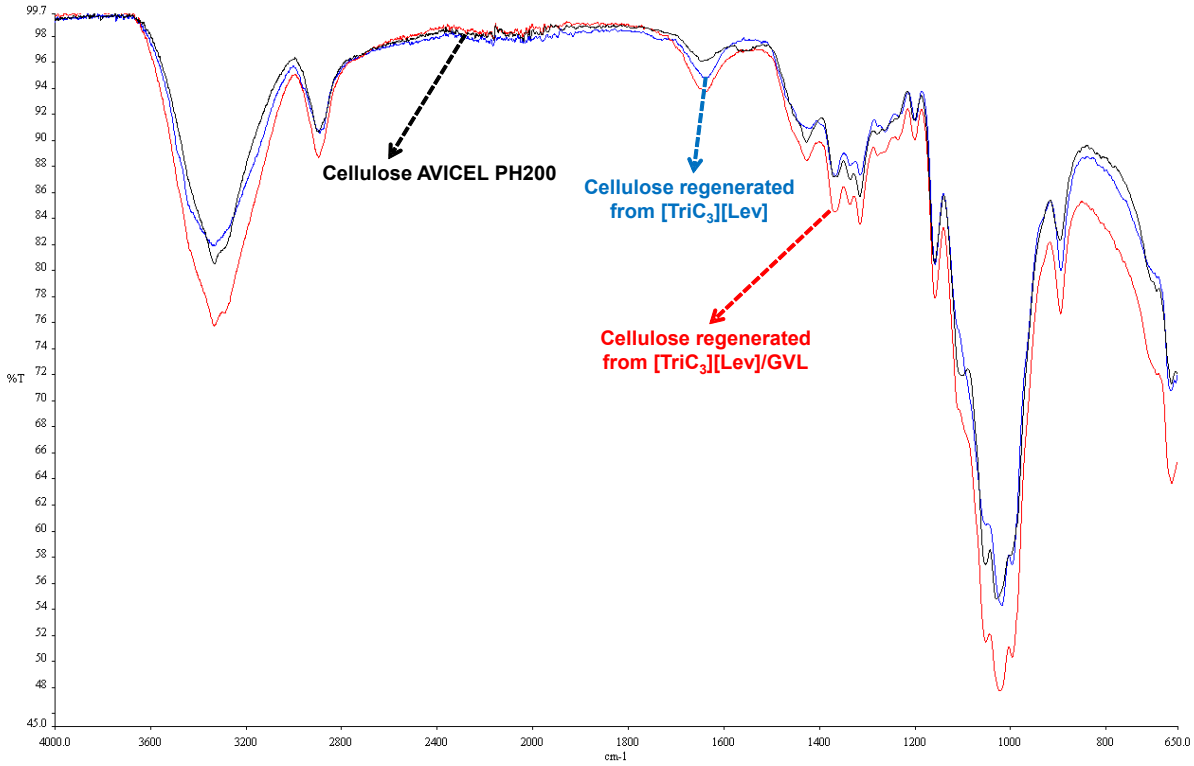


Figure S1: FT-IR spectra of cellulose AVICEL PH 200 and cellulose regenerated from $[TriC_3][Lev]$ and from $[TriC_3][Lev]$/GVL

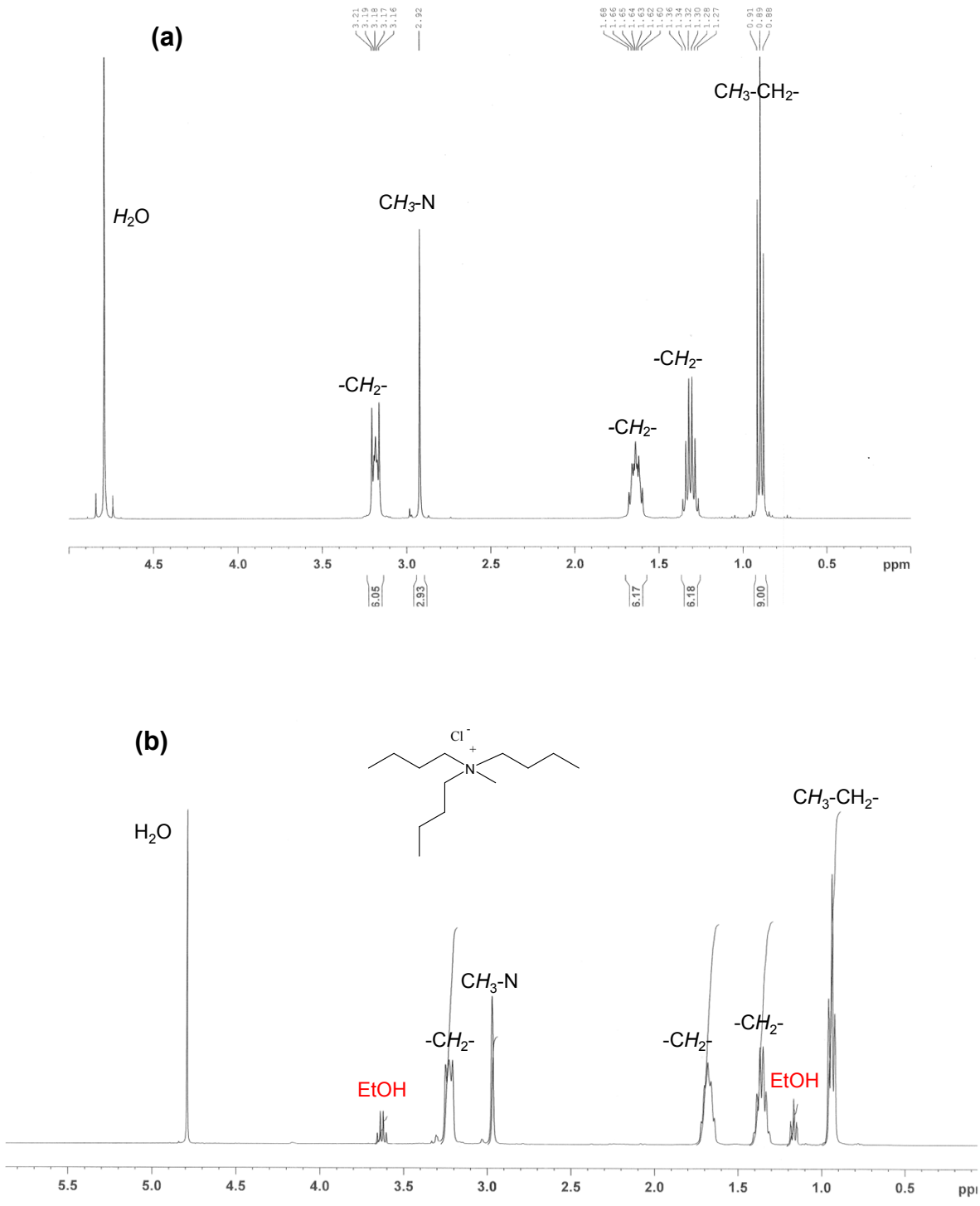


Figure S2: (a) ^{1}H NMR of fresh [TriC$_4$][Cl] and (b) ^{1}H NMR of recycled [TriC$_4$][Cl] after regeneration of cellulose with ethanol (EtOH)

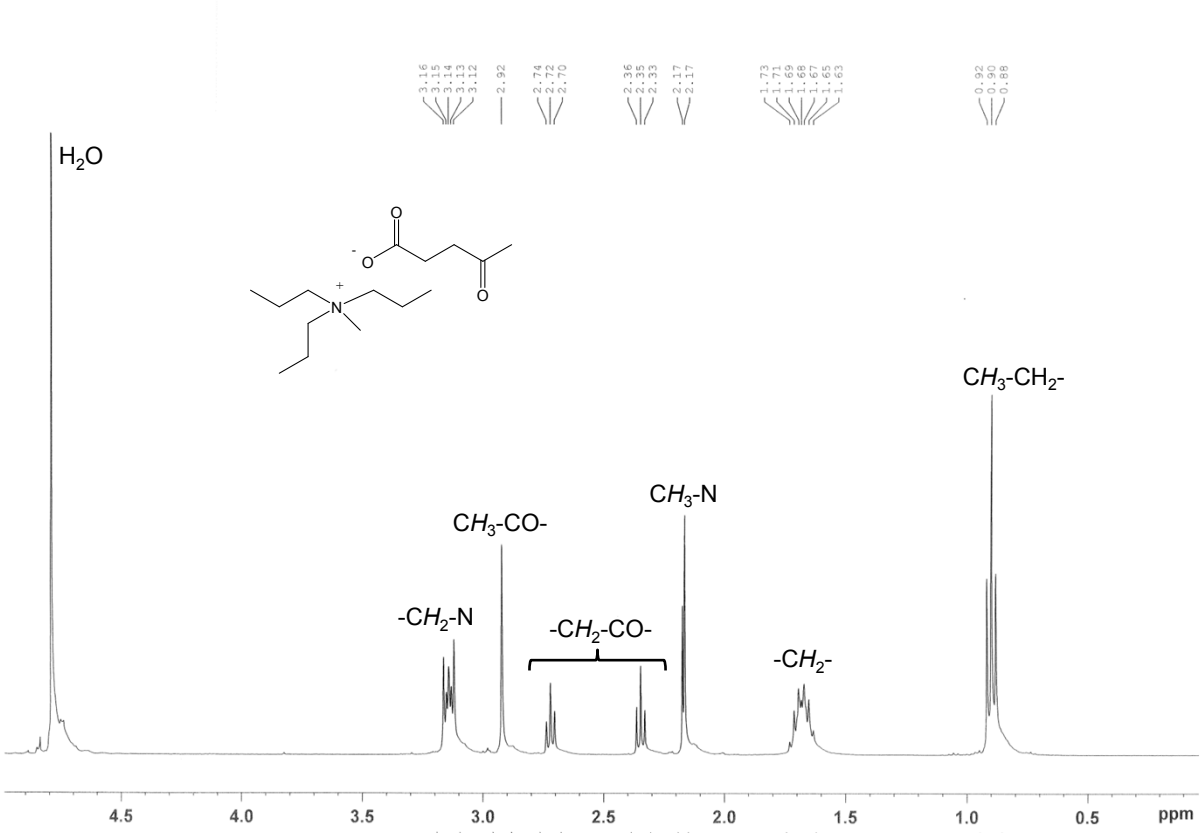
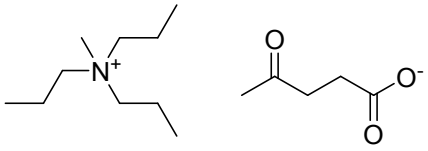


Figure S3: ^{1}H NMR of recycled [TriC_3][Lev]

NMR-Analysis of [TriC3][Lev]

Methyltripropylammonium levulinate, [TriC$_3$][Lev]: [$C_{10}H_{24}N^+$][$C_5H_7O_3^-$], M=273.41 g/mol



^{1}H-NMR (CDCl$_3$): δ(ppm): 0.93 (t, *J*=7.4 Hz, 9H), 1.57-1.73 (m, 6H), 2.07 (s, 3H), 2.31 (t, *J*=6.9 Hz, 2H), 2.59 (t, *J*=6.9 Hz, 2H), 3.09 (s, 3H), 3.15-3.23 (m, 6H)

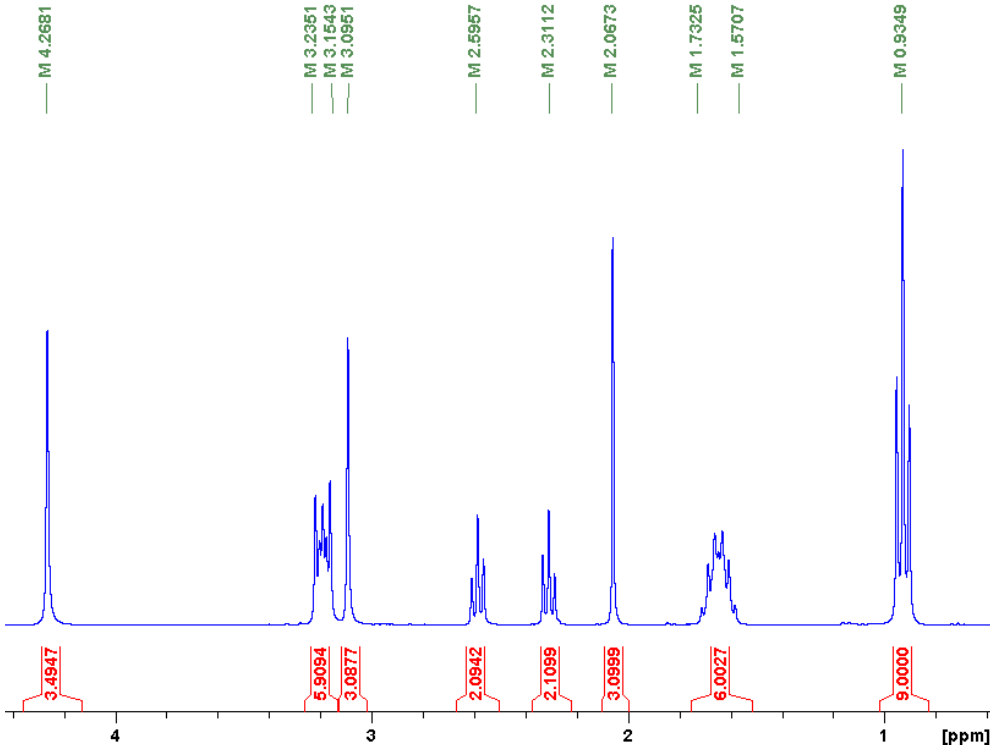


Fig. S4 ^{1}H NMR spectrum of [TriC3][Lev]

^{13}C-NMR (CDCl$_3$): δ(ppm): 10.7 (CH_3), 15.9 (CH_2), 30.2 (CH_3), 32.1 (CH_2), 40.4 (CH_2), 48.9 (CH_3), 62.9 (CH_2), 177.1 (C), 210.0 (C)

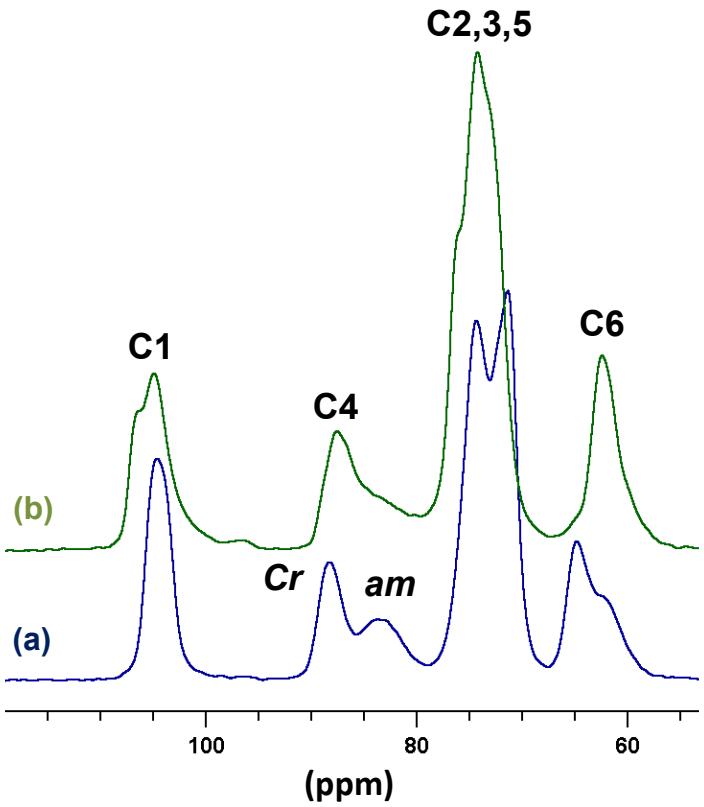
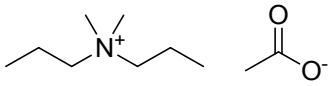


Fig. S5. ^{13}C CP/MAS NMR spectrum of PH-AVICEL cellulose (cellulose I) and regenerated cellulose (cellulose II) (Cr=crystalline and am = amorphous). For comparison with data in the current literature, please see reference 26 of the manuscript

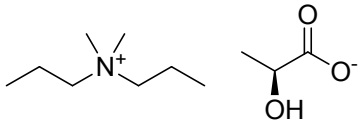
Analytical data for all other tested ILs

Dimethyldipropylammonium acetate, **[DiC$_3$][Ace]**: [$C_8H_{20}N^+$][$C_3H_2O_2^-$], M=189.29 g/mol



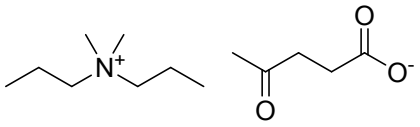
^{1}H-NMR (CDCl$_3$): δ(ppm): 0.93 (t, *J*=6.3 Hz, 6H), 1.74-1.57 (m, 4H), 1.81 (s, 3H), 3.19 (s, 6H), 3.22-3.32 (m, 4H)
^{13}C-NMR (CDCl$_3$): δ(ppm): 10.7 (CH_3), 16.2 (CH_2), 25.3 (CH_3), 51.1 (CH_3), 65.1 (CH_2), 176.8 (C)

Dimethyldipropylammonium lactate, **[DiC$_3$][Lac]**: [$C_8H_{20}N^+$][$C_3H_5O_3^-$], M=219.32 g/mol



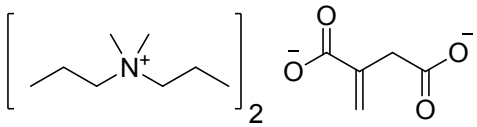
^{1}H-NMR (CDCl$_3$): δ(ppm): 0.96 (t, *J*=7.3 Hz, 6H), 1.26 (d, *J*=6.8 Hz, 3H), 1.62-1.78 (m, 4H), 3.17 (s, 6H), 3.21-3.29 (m, 4H), 3.84 (q, *J*=6.5 Hz, 1H)
^{13}C-NMR (CDCl$_3$): δ(ppm): 10.8 (CH_3), 16.3 (CH_2), 21.6 (CH_3), 51.2 (CH_3), 65.4 (CH_2), 68.3 (CH), 179.6 (C)

Dimethyldipropylammonium levulinate, **[DiC$_3$][Lev]**: [$C_8H_{20}N^+$][$C_5H_7O_3^-$], M=245.36 g/mol



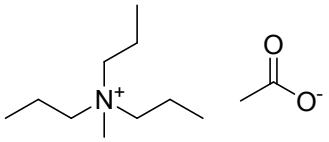
^{1}H-NMR ($CDCl_3$): δ(ppm): 0.95 (t, *J*=7.3 Hz, 6H), 1.62-1.77 (m, 4H), 2.10 (s, 3H), 2.33 (t, *J*=6.7 Hz, 2H), 2.61 (t, *J*=6.7 Hz, 2H), 3.15 (s, 6H), 3.19-3.27 (m, 4H)
^{13}C-NMR ($CDCl_3$): δ(ppm): 10.8 (CH_3), 16.1 (CH_2), 30.1 (CH_3), 31.7 (CH_2), 40.1 (CH_2), 51.2 (CH_3), 65.1 (CH_2), 177.4 (C), 210.0 (C)

Di-(dimethyldipropylammonium) itaconate, **[DiC_3]$_2$[Ita]**: $[C_8H_{20}N^+]_2[C_5H_4O_4^{2-}]$, M=388.59g/mol



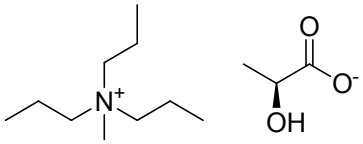
^{1}H-NMR ($CDCl_3$): δ(ppm): 1.04 (t, *J*=6.7 Hz, 12H), 1.69-1.85 (m, 8H), 3.25 (s, 12H), 3.30 (s, 2H), 3.30-3.39 (m, 8H), 5.33 (s, 1H), 5.91 (s, 1H)
^{13}C-NMR ($CDCl_3$): δ(ppm): 10.7 (CH_3), 16.6 (CH_2), 43.6 (CH_2), 51.2 (CH_3), 65.4 (CH_2), 122.3 (CH_2), 141.2 (C), 172.9 (C), 175.3 (C)

Methyltripropylammonium acetate, **[$TriC_3$][Ace]**: $[C_{10}H_{24}N^+][C_3H_2O_2^-]$, M=217.35 g/mol



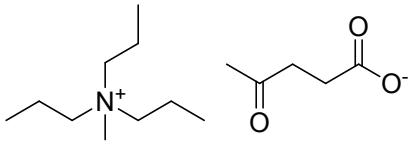
^{1}H-NMR ($CDCl_3$): δ(ppm): 0.89 (t, *J*=6.7 Hz, 9H), 1.53-1.68 (m, 6H), 1.75 (s, 3H), 3.07 (s, 3H), 3.11-3.19 (m, 6H)
^{13}C-NMR ($CDCl_3$): δ(ppm): 10.7 (CH_3), 15.8 (CH_2), 24.8 (CH_3), 48.8 (CH_3), 62.9 (CH_2), 177.1 (C)

Methyltripropylammonium lactate, **[$TriC_3$][Lac]**: $[C_{10}H_{24}N^+][C_3H_5O_3^-]$, M=247.37 g/mol



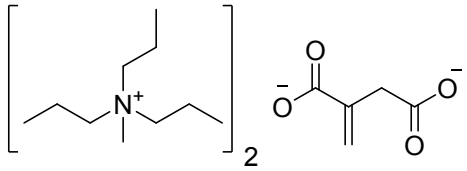
^{1}H-NMR ($CDCl_3$): δ(ppm): 0.96 (t, *J*=7.3 Hz, 9H), 1.26 (d, *J*=6.8 Hz, 3H), 1.60-1.75 (m, 6H), 3.12 (s, 3H), 3.16-3.25 (m, 6H), 3.85 (q, *J*=6.8 Hz, 1H)
^{13}C-NMR ($CDCl_3$): δ(ppm): 10.7 (CH_3), 15.9 (CH_2), 21.6 (CH_3), 48.8 (CH_3), 63.1 (CH_2), 68.1 (CH), 179.8 (C)

Methyltripropylammonium levulinate, **[$TriC_3$][Lev]**: $[C_{10}H_{24}N^+][C_5H_7O_3^-]$, M=273.41 g/mol



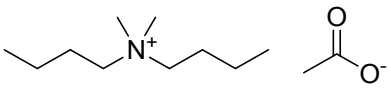
^{1}H-NMR ($CDCl_3$): δ(ppm): 0.93 (t, *J*=7.3 Hz, 9H), 1.57-1.73 (m, 6H), 2.07 (s, 3H), 2.31 (t, *J*=6.9 Hz, 2H), 2.60 (t, *J*=6.9 Hz, 2H), 3.09 (s, 3H), 3.14-3.24 (m, 6H)
^{13}C-NMR ($CDCl_3$): δ(ppm): 10.7 (CH_3), 15.9 (CH_2), 30.2 (CH_3), 32.1 (CH_2), 40.4 (CH_2), 48.8 (CH_3), 62.8 (CH_2), 177.1 (C), 210.0 (C)

Di-(methyltripropylammonium) itaconate, **[TiC$_3$]$_2$[Ita]**: [$C_{10}H_{24}N^+$]$_2$[$C_5H_4O_4^{2-}$], M=444.69g/mol



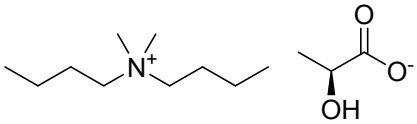
^{1}H-NMR (CDCl$_3$): δ(ppm): 0.99 (t, *J*=7.3 Hz, 18H), 1.63-1.78 (m, 12H), 3.17 (s, 6H), 3.19-3.28 (m, 12H+2H), 5.19 (s, 1H), 5.80 (s, 1H)
^{13}C-NMR (CDCl$_3$): δ(ppm): 10.7 (CH_3), 15.9 (CH_2), 43.4 (CH_2), 49.1 (CH_3), 62.8 (CH_2), 119.4 (CH_2), 145.0 (C), 173.5 (C), 177.1 (C)

Dibutyldimethylammonium acetate, **[DiC$_4$][Ace]**: [$C_{10}H_{24}N^+$][$C_3H_2O_2^-$], M=217.35 g/mol



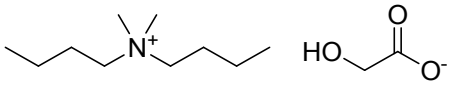
^{1}H-NMR (CDCl$_3$): δ(ppm): 0.96 (t, *J*=7.3 Hz, 6H), 1.31-1.45 (m, 4H), 1.57-1.69 (m, 4H), 1.85 (s, 3H), 3.21 (s, 6H), 3.32-3.40 (m, 4H)
^{13}C-NMR (CDCl$_3$): δ(ppm): 13.7 (CH_3), 19.7 (CH_2), 24.6 (CH_2), 25.2 (CH_3), 51.1 (CH_3), 63.3 (CH_2), 177.3 (C)

Dibutyldimethylammonium lactate, **[DiC$_4$][Lac]**: [$C_{10}H_{24}N^+$][$C_3H_5O_3^-$], M=247.37 g/mol



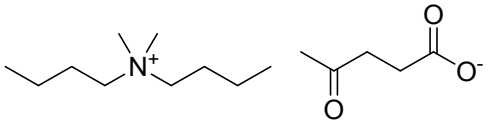
^{1}H-NMR (CDCl$_3$): δ(ppm): 0.98 (t, *J*=7.3 Hz, 6H), 1.31 (d, *J*=6.7 Hz, 3H), 1.33-1.45 (m, 4H), 1.57-1.70 (m, 4H), 3.22 (s, 6H), 3.31-3.40 (m, 4H), 3.91 (q, *J*=6.8 Hz, 1H)
^{13}C-NMR (CDCl$_3$): δ(ppm): 13.6 (CH_3), 19.6 (CH_2), 21.7 (CH_3), 24.7 (CH_2), 51.2 (CH_3), 63.6 (CH_2), 68.0 (CH), 179.8 (C)

Dibutyldimethylammonium glycolate, **[DiC$_4$][Gly]**: [$C_{10}H_{24}N^+$][$C_2H_3O_3^-$], M=233.35 g/mol



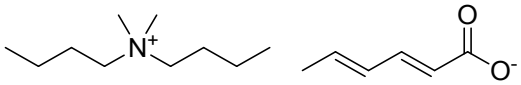
^{1}H-NMR (CDCl$_3$): δ(ppm): 0.90 (t, *J*=7.3 Hz, 6H), 1.25-1.38 (m, 4H), 1.52-1.65 (m, 4H), 3.13 (s, 6H), 3.21-3.30 (m, 4H), 3.68 (s, 2H)
^{13}C-NMR (CDCl$_3$): δ(ppm): 13.7 (CH_3), 19.5 (CH_2), 24.4 (CH_2), 50.9 (CH_3), 62.3 (CH_2), 63.7 (CH_2), 176.6 (C)

Dibutyldimethylammonium levulinate, **[DiC$_4$][Lev]**: [$C_{10}H_{24}N^+$][$C_5H_7O_3^-$], M=273.41 g/mol



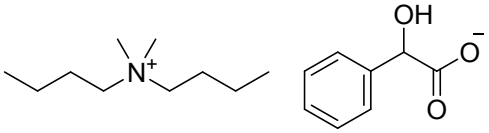
^{1}H-NMR (CDCl$_3$): δ(ppm): 0.95 (t, *J*=7.3 Hz, 6H), 1.30-1.45 (m, 4H), 1.57-1.70 (m, 4H), 2.11 (s, 3H), 2.36 (t, *J*=6.8 Hz, 2H), 2.63 (t, *J*=6.8 Hz, 2H), 3.19 (s, 6H), 3.25-3.34 (m, 4H)
^{13}C-NMR (CDCl$_3$): δ(ppm): 13.8 (CH_3), 19.9 (CH_2), 24.6 (CH_2), 30.4 (CH_3), 32.1 (CH_2), 40.4 (CH_2), 51.4 (CH_3), 63.6 (CH_2), 177.5 (C), 210.4 (C)

Dibutyldimethylammonium sorbate, **[DiC$_4$][Sor]**: [$C_{10}H_{24}N^+$][$C_6H_7O_2^-$], M=269.42 g/mol



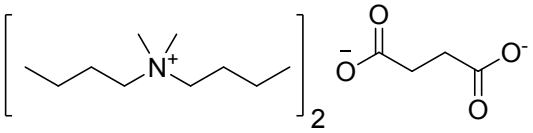
^{1}H-NMR (CD$_3$OD): δ(ppm): 1.05 (t, *J*=7.3 Hz, 6H), 1.44 (sext*a*, *J*=7.4 Hz, 4H), 1.68-1.79 (m, 4H), 1.83 (d, *J*=6.8 Hz, 3H), 3.09 (s, 6H), 3.25-3.43 (m, 4H), 5.83 (d, *J*=15.3 Hz, 1H), 6.02 (dq, *J*=15.1 Hz, *J*=6.7 Hz, 1H), 6.20 (dd, *J*=15.1 Hz, *J*=10.8 Hz, 1H),7.01 (dd, *J*=15.4 Hz, *J*=10.5 Hz, 1H)
^{13}C-NMR (CD$_3$OD): δ(ppm): 13.9 (CH_3), 18.5 (CH_3), 20.7 (CH_2), 25.4 *(*CH_2), 51.1 (CH_3), 65.2 (CH_2), 127.6 (CH), 131.9 (CH), 135.9 (CH), 141.4 (CH), 175.9 (C)

Dibutyldimethylammonium mandelate, **[DiC$_4$][Mand]**: [$C_{10}H_{24}N^+$][$C_8H_7O_3^-$], M=309.44 g/mol



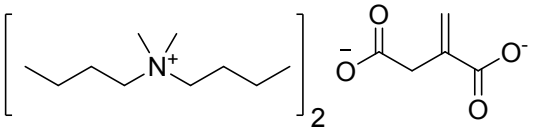
^{1}H-NMR (CDCl$_3$) : δ(ppm): 0.89 (t, *J*=7.3 Hz, 6H), 1.16-1.29 (m, 4H), 1.32-1.46 (m, 4H), 2.77 (s, 6H), 2.89-2.98 (m, 4H), 4.79 (s, 1H), 7.10-7.29 (m, 3H), 7.46 (d, *J*=7.3 Hz, 2H)
^{13}C-NMR (CDCl$_3$) : δ(ppm): 13.7 (CH_3), 19.5 (CH_2), 24.1 (CH_2), 50.9 (CH_3), 63.4 (CH_2), 74.5 (CH), 126.87 – 128.04 (5xCH), 143.2 (C), 176.3 (C)

Di-(dibutyldimethylammonium) succinate, **[DiC$_4$]$_2$[Suc]**: [$C_{10}H_{24}N^+$]$_2$[$C_4H_4O_4^{2-}$], M=432.68 g/mol



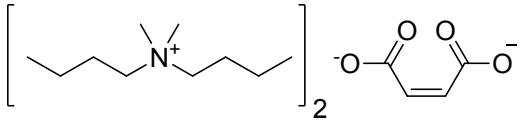
^{1}H-NMR (CDCl$_3$) : δ(ppm): 0.88 (t, *J*=7.3 Hz, 12H), 1.23-1.39 (m, 8H), 1.49-1.64 (m, 8H), 2.29 (s, 4H), 3.15 (s, 12H), 3.19-3.29 (m, 8H, NCH_2)
^{13}C-NMR (CDCl$_3$) : δ(ppm): 13.7 (CH_3), 19.5 (CH_2), 24.4 (CH_2), 35.5 (CH_2), 51.2 (CH_3), 63.1 (CH_2), 179.2 (C)

Di-(dibutyldimethylammonium) itaconate, **[DiC$_4$]$_2$[Ita]**: [$C_{10}H_{24}N^+$]$_2$[$C_5H_4O_4^{2-}$], M=444.69 g/mol



^{1}H-NMR (CDCl$_3$) : δ(ppm): 0.92 (t, *J*=7.3 Hz, 12H), 1.25-1.40 (m, 8H), 1.51-1.66 (m, 8H), 3.02 (s, 2H), 3.14 (s, 12H), 3.18-3.28 (m, 8H), 5.12 (s, 1H), 5.73 (s, 1H)
^{13}C-NMR (CDCl$_3$) : δ(ppm): 13.7 (CH_3), 19.8 (CH_2), 24.4 (CH_2), 43.6 (CH_2), 51.5 (CH_3), 63.4 (CH_2), 119.6 (CH_2), 144.9 (C), 173.4 (C), 176.9 (C)

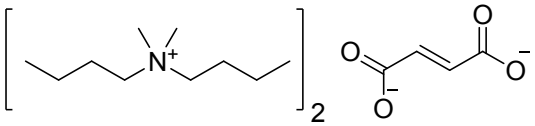
Di-(dibutyldimethylammonium) maleate,**[DiC$_4$]$_2$[Male]**: [$C_{10}H_{24}N^+$]$_2$[$C_4H_2O_4^{2-}$], M=430.66g/mol



^{1}H-NMR (CD$_3$OD): δ(ppm): 1.05 (t, *J*=7.5 Hz, 12H), 1.44 (sext*a*, *J*=7.5 Hz, 8H), 1.68-1.82 (m, 8H), 3.09 (s, 12H), 3.26-3.59 (m, 8H), 5.97 (s, 2H)

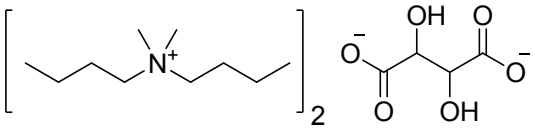
^{13}C-NMR (CD_3OD): δ(ppm): 13.9 (CH_3), 20.7 (CH_2), 25.5 (*(*CH_2), 51.3 (CH_3), 65.1 (CH_2), 132.4 (CH), 175.3 (C)

Di-(dibutyldimethylammonium)fumarate,**[DiC$_4$]$_2$[Fum]**: [$C_{10}H_{24}N^+]_2[C_4H_2O_4^{2-}]$, M=430.66g/mol



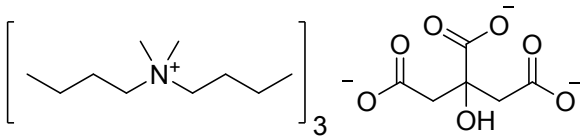
^{1}H-NMR (CD_3OD): δ(ppm): 1.04 (t, *J*=7.5 Hz, 12H), 1.42 (sext*a*, *J*=7.4 Hz, 8H), 1.68-1.82 (m, 8H), 3.08 (s, 12H), 3.26-3.35 (m, 8H), 6.67 (s, 2H)
^{13}C-NMR (CD_3OD): δ(ppm): 14.0 (CH_3), 20.8 (CH_2), 25.5 (CH_2), 51.2 (CH_3), 65.2 (CH_2), 137.2 (CH), 174.0 (C)

Di-(dibutyldimethylammonium) tartrate, **[DiC$_4$]$_2$[Tar]**: [$C_{10}H_{24}N^+]_2[C_4H_4O_6^{2-}]$, M=464.68 g/mol



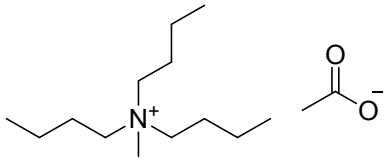
^{1}H-NMR ($CDCl_3$): δ(ppm): 0.95 (t, *J*=7.3 Hz, 12H), 1.35-1.49 (m, 8H), 1.59-1.74 (m, 8H), 3.20 (s, 12H, NCH_3), 3.30-3.39 (m, 8H), 4.19 (s, 2H)
^{13}C-NMR ($CDCl_3$): δ(ppm): 14.0 (CH_3), 19.9 (CH_2), 24.7 (CH_2), 51.9 (CH_3), 63.6 (CH_2), 73.7 (CH), 177.2 (C)

Tri-(dibutyldimethylammonium) citrate, **[DiC$_4$]$_3$[Cit]**: [$C_{10}H_{24}N^+]_3[C_6H_5O_7^{3-}]$, M=664.01 g/mol



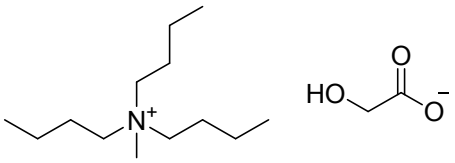
^{1}H-NMR ($CDCl_3$): δ(ppm): 0.93 (t, *J*=7.3 Hz, 18H), 1.29-1.43 (m, 12H), 1.55-1.68 (m, 12H), 2.61 (d, *J*=7.3 Hz, 4H), 3.22 (s, 18H, NCH_3), 3.26-3.35 (m, 12H)
^{13}C-NMR ($CDCl_3$): δ(ppm): 13.9 (CH_3), 19.6 (CH_2), 24.7 (CH_2), 46.7 (CH_2), 51.6 (CH_3), 63.3 (CH_2), 176.7 (2xC), 180.2 (C)

Tributylmethylammonium acetate, **[TriC$_4$][Ace]**: [$C_{13}H_{304}N^+$][$C_3H_2O_2^-$], M=259.43 g/mol



^{1}H-NMR ($CDCl_3$): δ(ppm): 0.94 (t, *J*=7.3 Hz, 9H), 1.29-1.43 (m, 6H), 1.53-1.67 (m, 6H), 1.84 (s, 3H), 3.15 (s, 3H), 3.19-3.29 (m, 6H)
^{13}C-NMR ($CDCl_3$): δ(ppm): 13.8 (CH_3), 19.6 (CH_2), 24.2 (CH_2), 25.2 (CH_3), 48.9 (CH_3), 61.3 (CH_2), 177.1 (C)

Tributylmethylammonium glycolate, **[DiC$_4$][Gly]**: [$C_{13}H_{304}N^+$][$C_2H_3O_3^-$], M=275.43 g/mol



^{1}H-NMR ($CDCl_3$): δ(ppm): 0.95 (t, *J*=7.3 Hz, 9H), 1.28-1.43 (m, 6H), 1.53-1.66 (m, 6H), 3.11 (s, 3H), 3.20-3.30 (m, 6H), 3.77 (s, 2H)
^{13}C-NMR ($CDCl_3$): δ(ppm): 13.8 (CH_3), 19.8 (CH_2), 24.3 (CH_2), 48.9 (CH_3), 61.3 (CH_2), 62.5 (CH_2), 176.9 (C)