

Supplementary information for:

Effect of choline amino acid ionic liquids on maize seed germination and endogenous plant hormone levels

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Table of contents:

Preparation and characterization of cholinium amino acid ionic liquids

Spectroscopic data for seven [Chl][AA] ILs

References

Preparation and characterization of choline amino acid ionic liquids

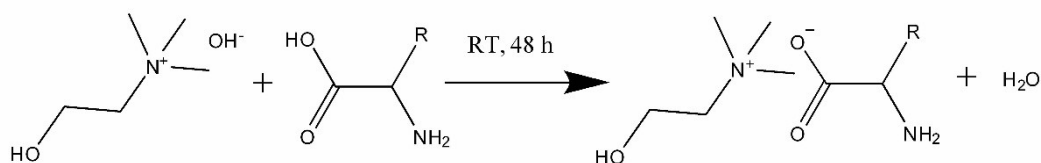


Fig. S1. The synthesis of choline amino acid ionic liquids

R: the group differing in different amino acids

Choline amino acid ILs were synthesized according to previously described methods [1, 2] with some modifications (Fig. S1). An aqueous solution of choline hydroxide was added drop wise to aqueous solutions of amino acids in a 1:1 molar ratio. The mixtures were stirred for 48 h at 20°C, followed by evaporation of the water under reduced pressure at 60°C, and were subsequently stored under moisture-free conditions until utilization. This one-step procedure is a typical atom-economic reaction that does not yield any toxic by-products. All seven ILs were in liquid form at room temperature, and with the exception of choline tryptophan ([Chl][Trp]), these ILs exhibited hues ranging from light yellow to yellowish brown (Fig. S2). These colors tended to deepen with increased temperature and time.

The [Chl][AA] ILs thus obtained were characterized by means of proton nuclear magnetic resonance (¹H NMR) analysis carried out in D₂O using a Bruker AVANCE Digital 500 MHz spectrometer, with tetramethylsilane used as an internal standard. The yields of all the desired products were found to be greater than 95% (Table S1).



Fig. S2. The seven choline amino acid ionic liquids ([Chl][AA] ILs) synthesized in this study.

[Chl][Val]: choline valine, [Chl][Leu]: choline leucine, [Chl][Ser]: choline serine, [Chl][Asp]: choline aspartic acid, [Chl][Asn]: choline asparagine, [Chl][Phe]: choline phenylalanine, [Chl][Trp]: choline tryptophan.

¹H NMR spectra for seven choline amino acid ionic liquids

Table S1 ¹H NMR data of seven [Chl][AA]

ILs	δ /ppm
[Chl][Val]	0.83 (t, J = 9.44 Hz, 3H), 0.89 (d, J = 6.53 Hz, 3H), 1.89 (td, J = 12.62, 6.22 Hz, 1H), 3.01 (d, J = 4.48 Hz, 1H), 3.16 (s, 9H), 3.47 (d, J = 3.64 Hz, 2H), 4.01 (s, 2H)
[Chl][Leu]	0.86 (m, 6H), 1.34 (m, 1H), 1.44 (td, J = 13.34, 6.64 Hz, 1H), 1.61 (qd, J = 12.49, 6.36, 6.06 Hz, 1H), 4.02 (s, 2H), 3.47 (d, J = 3.94 Hz, 2H), 3.16 (s, 9H), 3.23 (m, 1H)
[Chl][Ser]	3.13 (s, 9H), 3.29 (s, 1H), 3.45 (s, 2H), 3.67 (dd, J = 24.92, 8.34 Hz, 2H), 3.99 (s, 2H)
[Chl][Asp]	2.62 (dd, J = 17.39, 8.86 Hz, 1H), 2.76 (d, J = 17.39 Hz, 1H), 3.15 (s, 9H), 3.46 (s, 2H), 3.84 (d, J = 8.69 Hz, 1H), 4.01 (s, 2H)
[Chl][Asn]	2.39 (dd, J = 14.72, 9.06 Hz, 1H), 2.63 (dd, J = 14.88, 4.27 Hz, 1H), 3.15 (s, 9H), 3.46 (d, J = 3.98 Hz, 2H), 3.54 (dd, J = 8.40, 4.50 Hz, 1H), 4.01 (s, 2H)
[Chl][Phe]	2.79 (dd, J = 12.99, 7.61 Hz, 1H), 2.94 (dd, J = 13.16, 3.89 Hz, 1H), 3.08 (s, 9H), 3.39 (s, 2H), 3.45 (t, J = 5.73 Hz, 1H), 3.95 (s, 2H), 7.27 (m, 5H)
[Chl][Trp]	2.97(m, 1H), 3.01 (s, 9H), 3.13 (m, 1H), 3.30 (s, 2H), 3.53 (t, J = 5.60 Hz, 1H), 3.89 (s, 2H), 7.11 (t, J = 7.18 Hz, 1H), 7.18 (m, 2H), 7.44 (d, J = 8.07 Hz, 1H), 7.67 (d, J = 7.84 Hz, 1H)

References

1. Moriel, P., E.J. Garcia-Suarez, M. Martinez, A.B. Garcia, M.A. Montes-Moran, V. Calvino-Casilda, and M.A. Banares, Synthesis, characterization, and catalytic activity of ionic liquids based on biosources. *Tetrahedron Letters*, 2010. **51**(37): p. 4877-4881.
2. Liu, Q.P., X.D. Hou, N. Li, and M.H. Zong, Ionic liquids from renewable biomaterials: synthesis, characterization and application in the pretreatment of biomass. *Green Chemistry*, 2012. **14**(2): p. 304-307.