

# Crystallization of amino acids at the chiral ionic liquid/water interface

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## Supporting Information

### **1) Characterization of the N,N,N-trimethyl-L-leucine methyl ester iodide:**

$C_{10}H_{22}INO_2$ ,  $M_w = 315 \text{ g.mol}^{-1}$  (188+127).

NMR spectroscopy ( $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ ) and mass spectrometry indicated a pure product.

**$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):**  $\delta$  4.53 (dd, 12, 3 Hz, 1H), 3.90 (s, 3H), 3.60 (s, 9H), 1.96 (td, 12, 4 Hz, 1H), 1.87 (td, 10, 3 Hz, 1H), 1.58 (m, 1H), 1.10 (d, 1.5 Hz, 3H), 1.04 (d, 1.5 Hz, 3H).

**$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 600 MHz):**  $\delta$  168.10 (C), 73.48 (CH), 53.67 (CH<sub>3</sub>), 52.70 (3×CH<sub>3</sub>), 35.64 (CH<sub>2</sub>), 25.56 (CH), 23.50 (CH<sub>3</sub>), 21.50 (CH<sub>3</sub>).

**MS**  $m/z$  ( $\text{ES}^+$ ) 188 ( $[\text{M-I}]^+$ , 100).

**HRMS** ( $\text{CI}^+$ ):  $m/z$  for (M-Me): calculated 174.1409; experimental 174.1419. For (M-Me<sub>3</sub>): calculated 114.1283; experimental 114.1282.

## **2) Characterization of N,N,N-trimethyl-L-leucine methyl ester NTf<sub>2</sub>:**

$C_{12}H_{22}F_6N_2O_6S_2$ ,  $M_W = 468.43 \text{ g}\cdot\text{mol}^{-1}$  (188+280).

NMR spectroscopy ( $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR,  $^{19}\text{F}$ -NMR), mass spectrometry and elemental analysis indicate a very clean product. The shift of the  $\alpha$  peak from 4.53 ppm for the reagent to 4.02 ppm for the product, as well as the shift of the trimethyl peak from 3.6 ppm to 3.24 ppm, is proof of anion substitution.

**$^1\text{H}$ -NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  4.02 (dd, 12, 3 Hz, 1H), 3.88 (s, 3H), 3.24 (s, 9H), 1.97 (td, 12, 4 Hz, 1H), 1.72 (td, 10, 3 Hz, 1H), 1.53 (m, 1H), 1.02 (s, 3H), 0.99 (s, 3H).

**$^{13}\text{C}$ -NMR (CDCl<sub>3</sub>, 400 MHz):**  $\delta$  167.70 (C), 119.76 (2CF<sub>3</sub>), 73.73 (CH), 53.60 (CH<sub>3</sub>), 52.46 (3 $\times$ CH<sub>3</sub>), 35.43 (CH<sub>2</sub>), 25.35 (CH), 23.24(CH<sub>3</sub>), 20.64 (CH<sub>3</sub>).

**$^{19}\text{F}$ -NMR (CDCl<sub>3</sub>, 400 MHz):** -79.44 (s).

**MS m/z (ES<sup>+</sup>)** 188 ([M-An]<sup>+</sup>, 100).

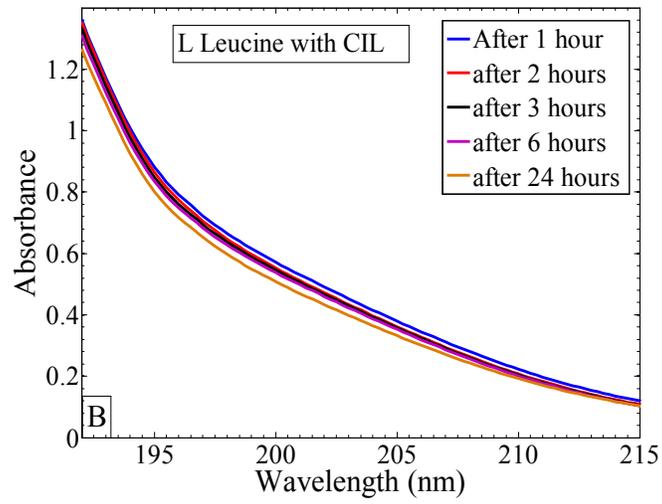
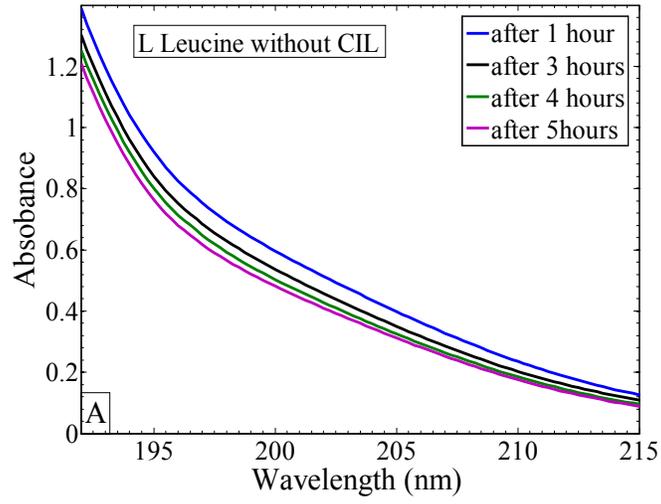
**MS m/z (ES<sup>-</sup>)** 280 (An<sup>-</sup>, 100).

**Elemental analysis:** calculated (%) for  $C_{12}H_{22}F_6N_2O_6S_2$  (468.44): C 30.77, H 4.73, N 5.98; experimental: C 30.46, H 4.39, N 6.10.

## **3) Figures**



Figure S11: Photograph of the biphasic system: supersaturated solution of L-leucine/chiral ionic liquid (CIL).



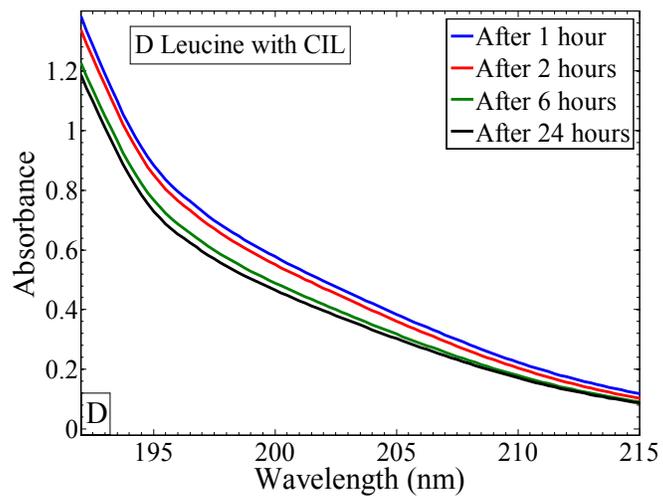
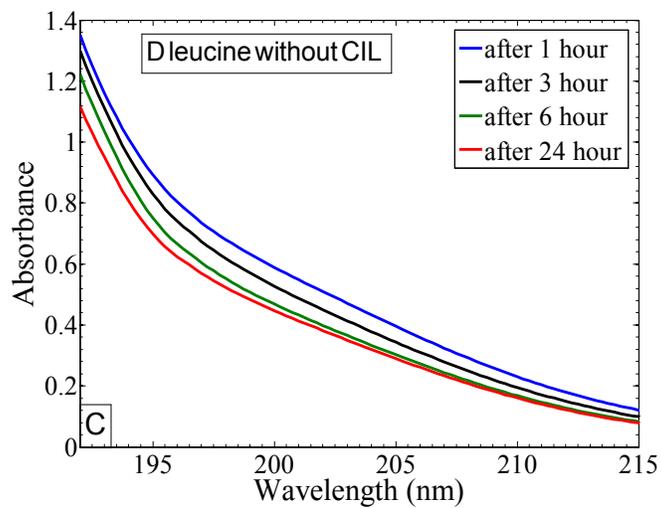


Figure SI2: UV-visible spectra at different times for the crystallization of L-leucine with and without CIL (A and B), and for the crystallization of D-leucine with and without CIL (C and D). About 200 mg of each solution was extracted and diluted 50 times at different times.

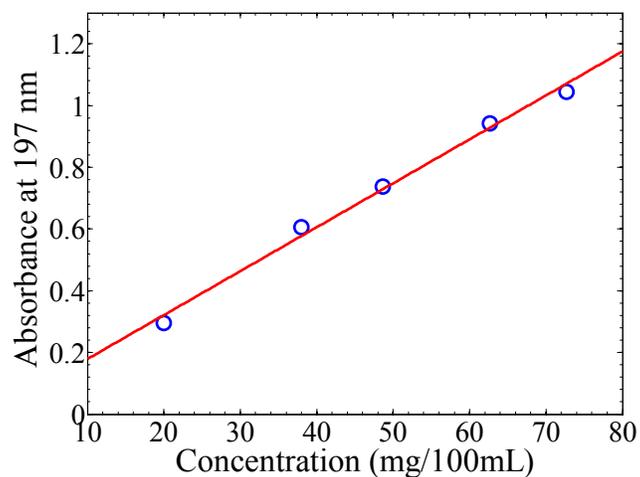


Figure SI3: Absorbance at 197 nm for solutions of L-leucine prepared at different concentrations. The absorbance of pure water at 197 nm was subtracted for all the points. The red line is a linear fit given by  $y = a x + b$ , where  $a = 1.4 \text{ mL/mg}$  and  $b = 0.037$ , demonstrating the Beer-Lambert law for L-leucine at 197 nm.

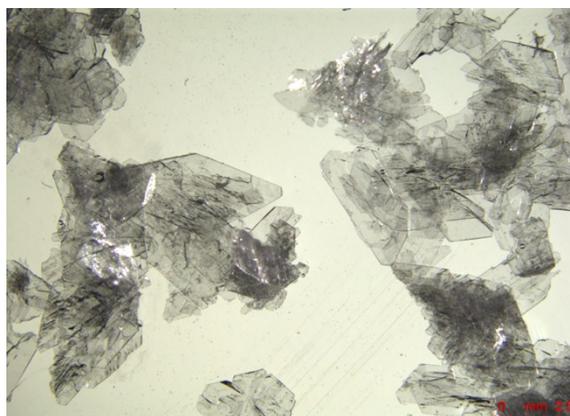


Figure SI4: Photograph of the DL-leucine crystals that were grown in the solution. Almost no DL-leucine crystals were grown on the CIL.

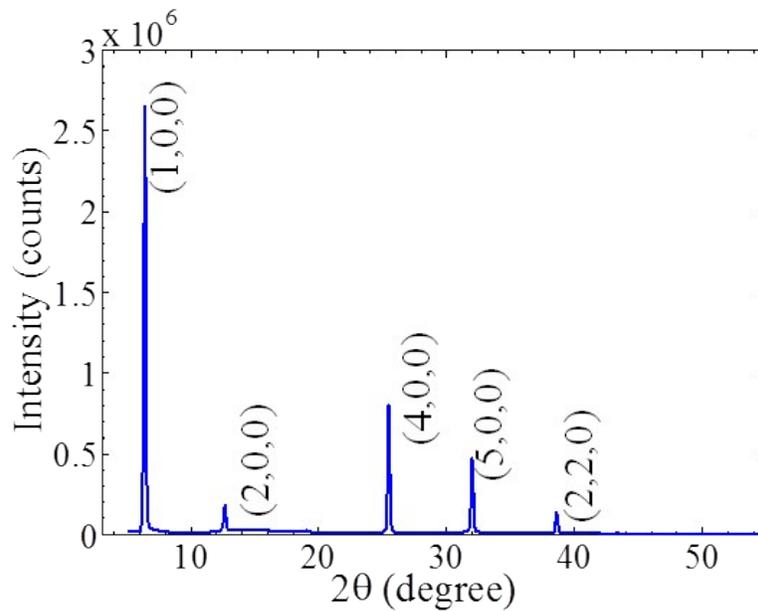


Figure SI5: X-ray diffraction pattern of the DL-leucine crystals, showing strong preferred orientation.

<b>C = 1.27 g/100 mL</b>	<b>Crystal yield after 2 days (%)</b>
DL-leucine reference	25.0
DL-leucine sample	20.1
Ratio Sample/Ref	80.4%

Figure SI6: Crystal yield for DL-leucine obtained from the overall crystal mass after 2 days, for a supersaturated concentration of 1.27 g/100 mL.