Electronic Supplementary Information

Enzyme-mediated free radical polymerization of acrylamide in deep-eutectic solvents

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HRP characterization (activity, structure and stability)

HRP activity

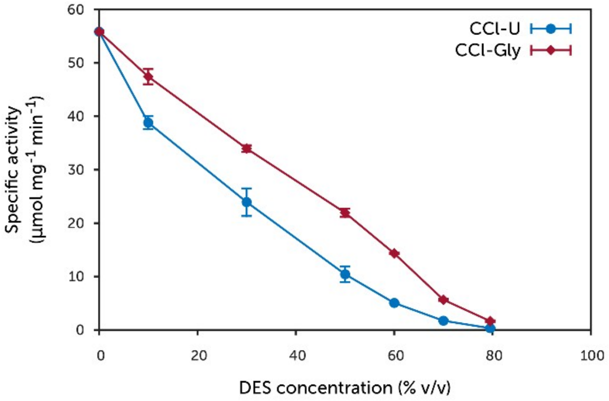

Fig. S1 Specific activity of HRP in DESs-aqueous mixtures at RT and different DES concentrations. Experiments were at least triplicated and the standard deviation error bars for each point are shown.

HRP Structure (Fluorescence)

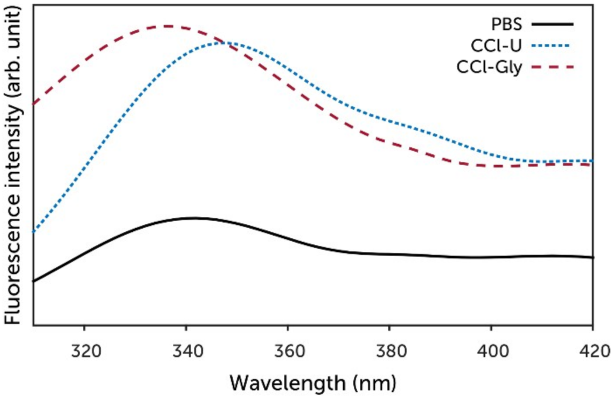

Fig. S2 Raw tryptophan fluorescence emission spectra of HRP (excitation wavelength 295 nm) in PBS (0.1M, pH 7) and DESs aqueous mixtures (80 % v/v DES) at RT.

HRP Structure (UV-Visible Spectroscopy)

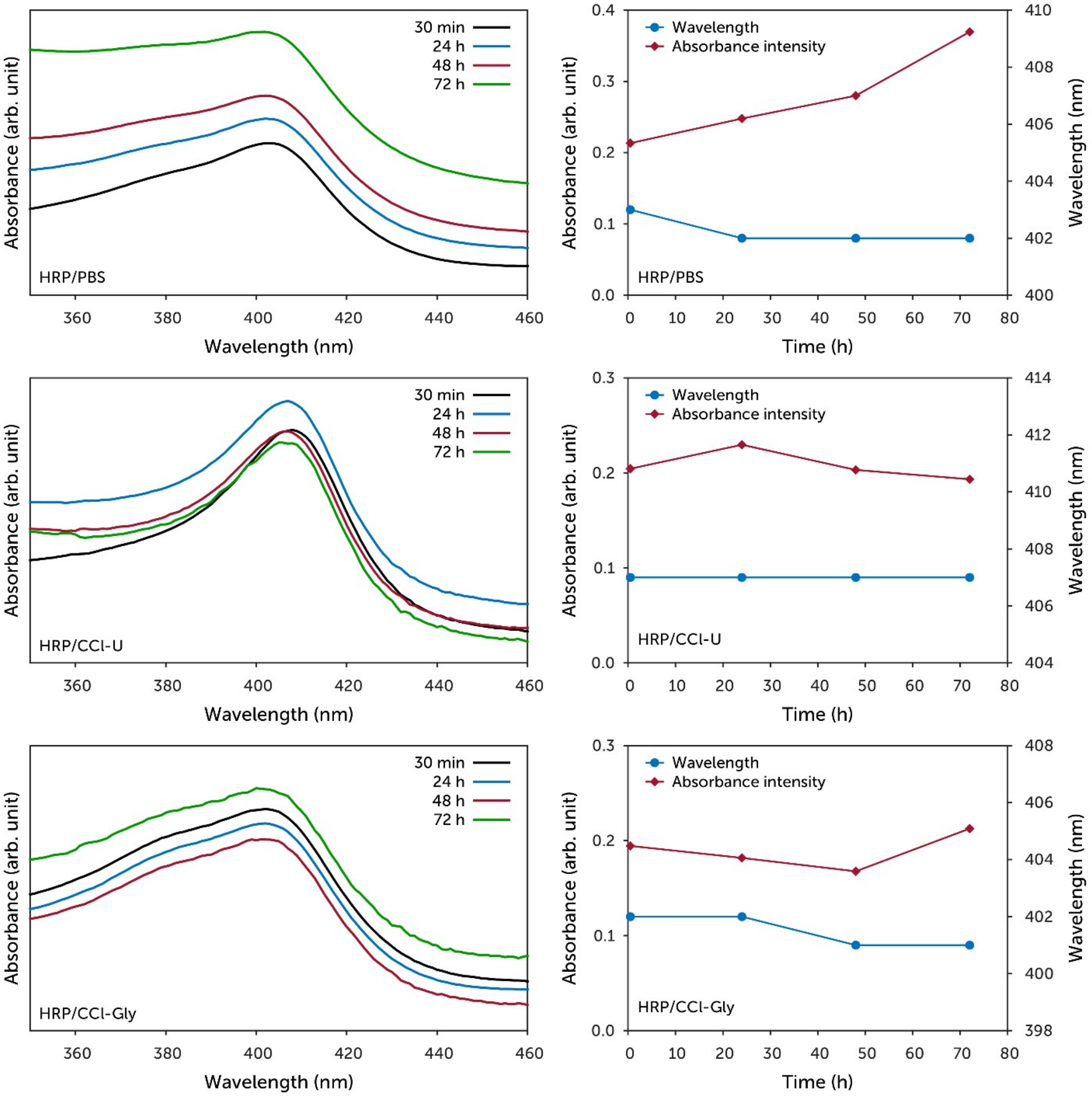

Fig. S3 Left: UV-Visible spectroscopy spectra of the Soret region of HRP at RT in DESs-aqueous mixtures with 80% v/v DES concentration after different times of incubation. Right: Changes in absorbance intensity and wavelength of the Soret band of HRP as a function of incubation time in the different solvents.

Polyacrylamide characterization

ATR – FTIR

ATR-FTIR spectra of HRP-mediated synthesized PAA in DESs-aqueous mixtures and water showed the characteristic bands for PAA (Fig. S4). The bands at 3335 cm^{-1} and 3196 cm^{-1} correspond to the stretching modes of the NH_2 group, and bands at 1660 cm^{-1} and 1620 cm^{-1} to the stretching of C=O and bending of NH_2 groups, respectively.[1]

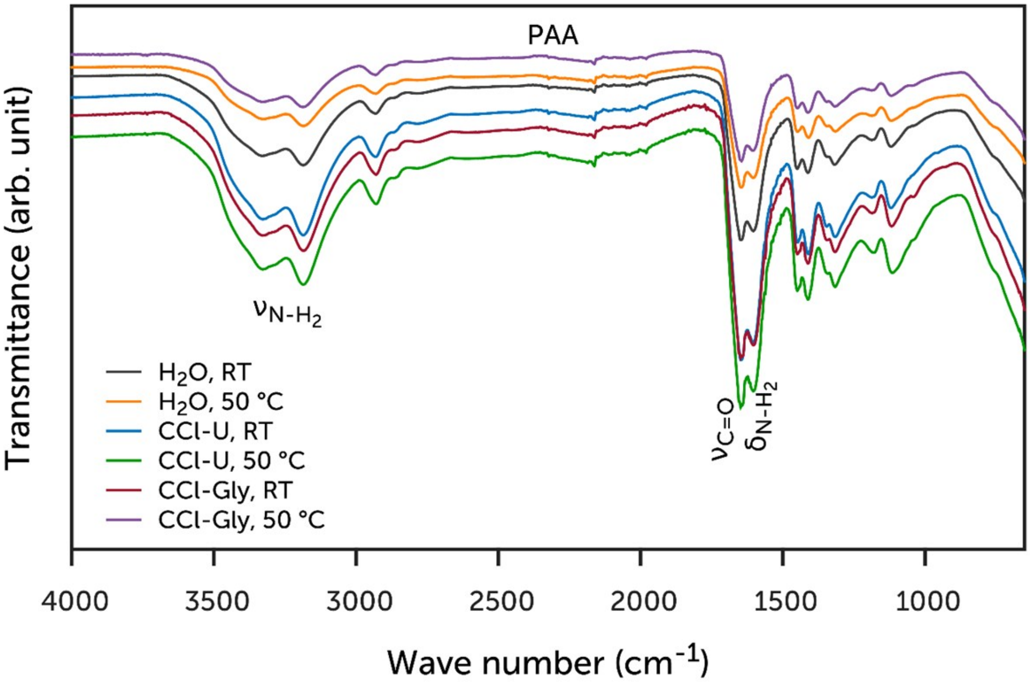

Fig. S4 ATR-FTIR spectra of HRP-mediated synthesized PAA in DESs-aqueous mixtures and H_2O at RT and 50 °C.

^{1}H-NMR

The proton spectrum of PAA samples showed two signals for methylene proton between 2.35 to 2.1 ppm and other two signals with small multiplicity for methylene protons between 1.8 to 1.4 ppm (Fig. S5). The splitting observed for these two groups is due to tacticity splitting in small range, as results of the low viscosity associate to the relativity low molecular weight. The integral relation between methylene and methyne proton is 2/1 in accordance to the expected value. The NH_2 groups are missed, due to exchange with deuterium from water. No signals for free monomer (AA) were detected. Depending on the protocol of PAA synthesis the corresponding spectrum shows: CCl, CCl-U or CCl-Gly in low quantities as contaminants coming from the solvent (note the narrow a well defined signals of the solvents *vs*. broad signals from the PAA).

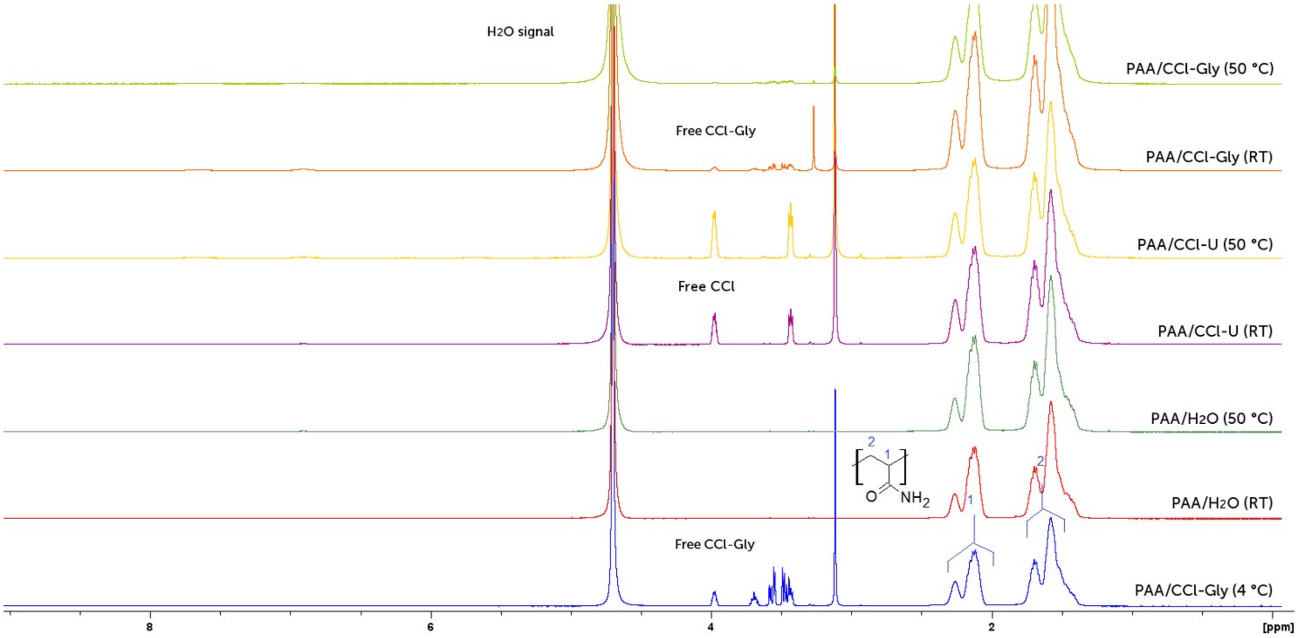

Fig. S5 ^{1}H-NMR spectra of PAA samples synthesized in DESs-aqueous mixtures and H_2O at RT, 50 °C and 4 °C.

Monomer and polymer-DES interactions

ATR-FTIR

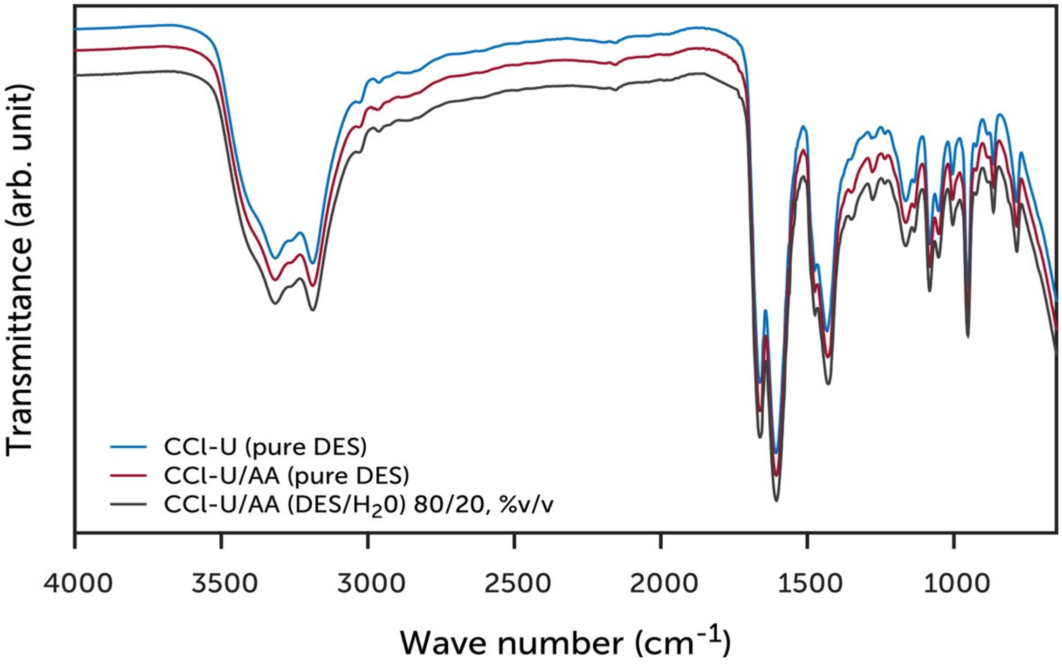

Fig. S6 ATR-FTIR spectra of CCl-U in its pure state, CCl-U/AA (0.64 M) and CCl-U/AA (0.64 M) at 80% v/v DES concentration.

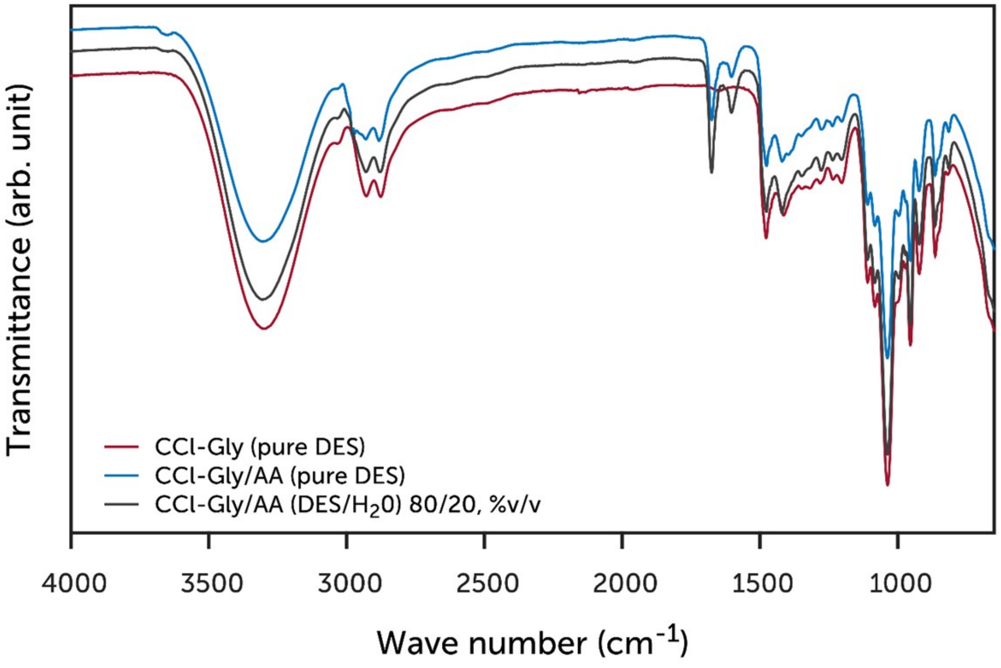

Fig. S7 ATR-FTIR spectra of CCl-Gly in its pure state, CCl-Gly/AA (0.64 M) and CCl-Gly/AA (0.64 M) at 80% v/v DES concentration.

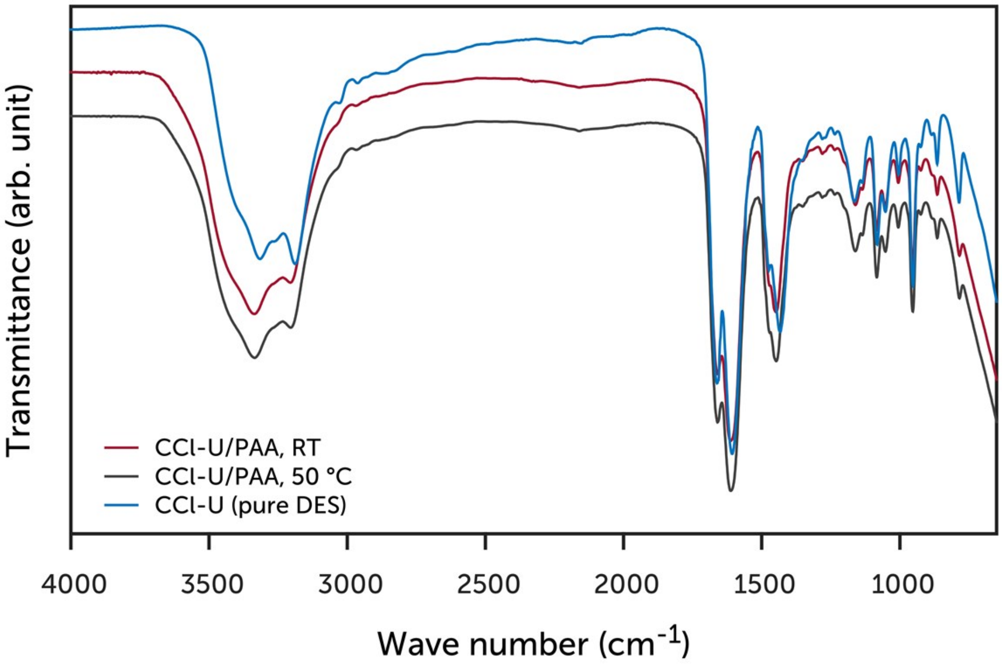

Fig. S8 ATR-FTIR spectra of CCl-U in its pure state and PAA solutions in CCl-U aqueous mixtures at 80% v/v DES concentration synthesized at RT and 50 °C.

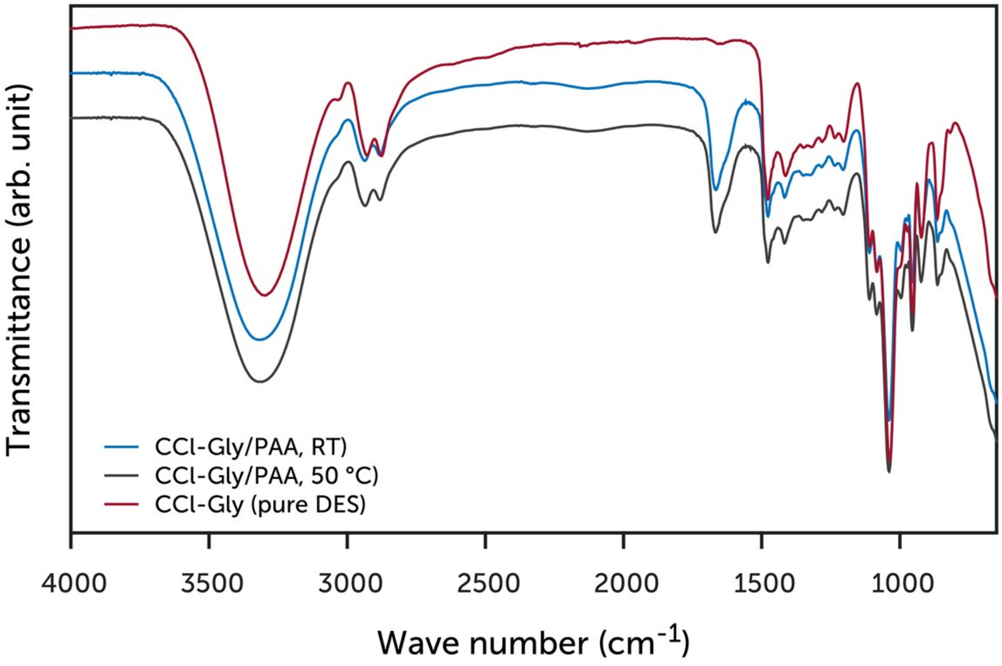

Fig. S9 ATR-FTIR spectra of CCl-Gly in its pure state and of PAA solutions in CCl-Gly aqueous mixtures at 80% v/v DES concentration synthesized at RT and 50 °C.

^{1}H-NMR

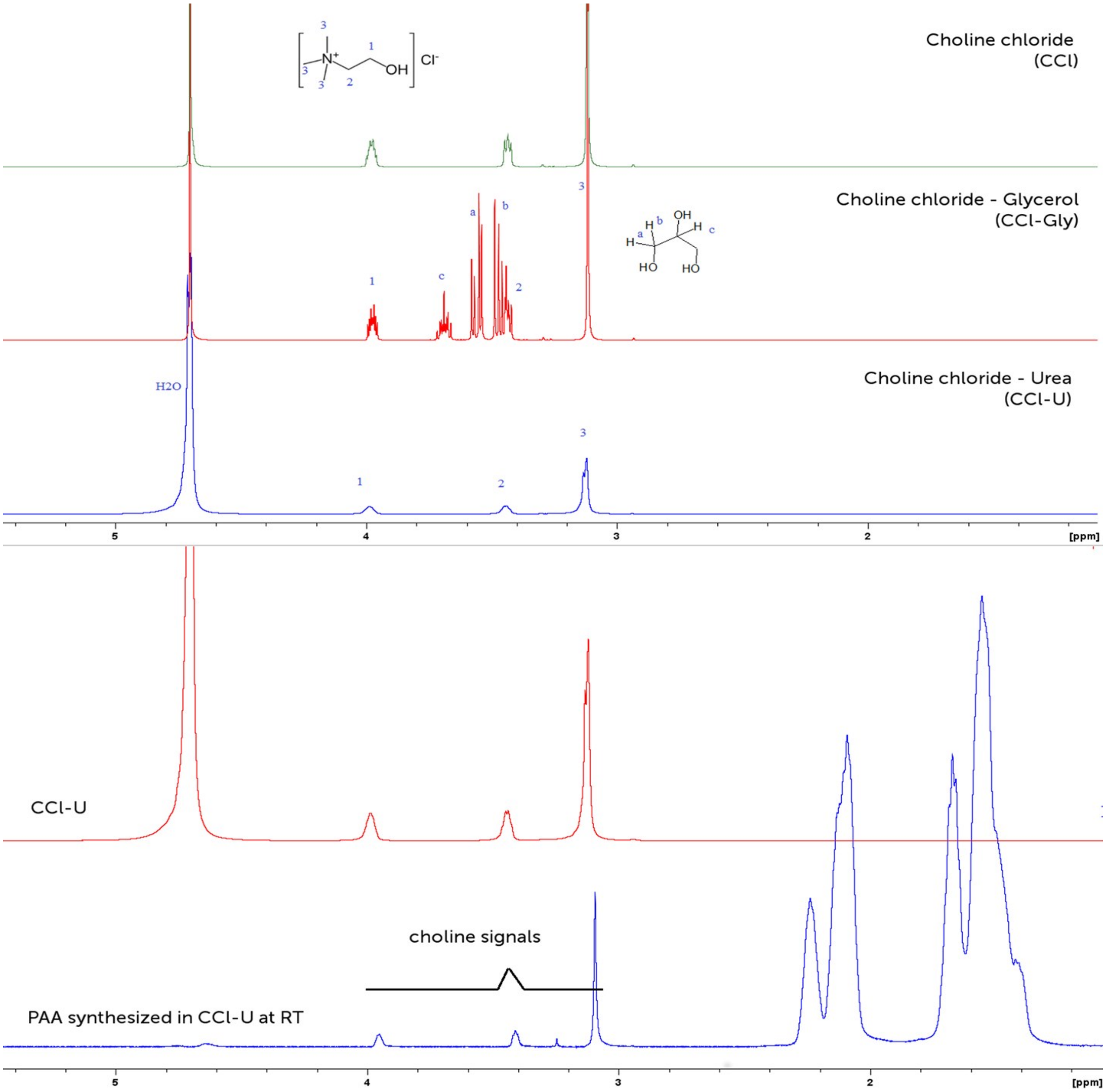

Fig. S10 ^{1}H-NMR spectra of CCl, CCl-Gly, CCl-U and PAA synthesized in CCl-U aqueous mixture at RT.

References

1 R. Murugan, S. Mohan and A. Bigotto, *J. Korean Phys. Soc.*, 1998, **32**, 505–512.