

Archetype of hydrogen bonding observed in cationic dimers of carboxy-functionalized ionic liquids by means NMR solid state spectroscopy – Similarities to salt bridges, peptides and DNA

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I. Synthesis

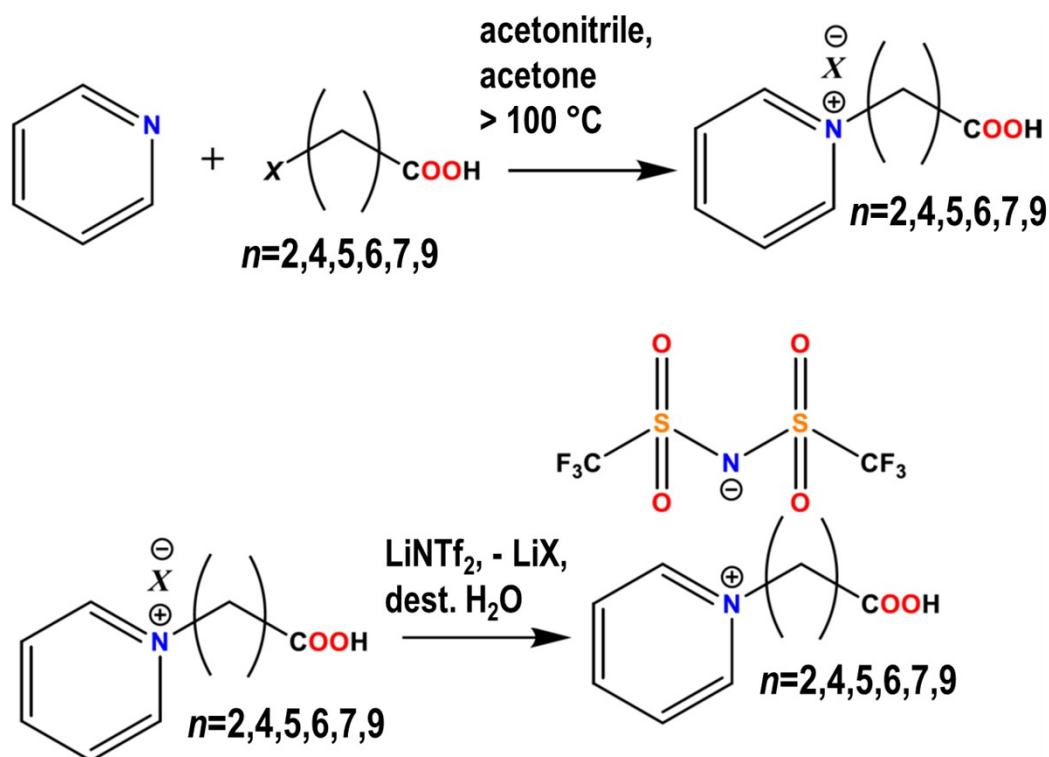


Figure S11. Reaction scheme for the synthesis of the ionic liquids 1-(carboxyalkyl)pyridinium bis(trifluoromethylsulfonate) [HOOC-(CH₂)_n-py][NTf₂] with $n=2,4,5,6,7,9$. X symbolizes the halogens Cl or Br.

We prepared the 1-(n-carboxyalkyl)pyridinium bromides with $n=2,4,5,6,7,9$ as follows: Pyridine was dissolved in acetonitrile and the solution was added dropwise to solid n-bromocarboxylic acids under vigorous stirring at 278 K. The resulting crystalline compounds were filtered and washed several times with acetonitrile and acetone. Then, they were dried under vacuum at 333 K and kept under argon. In the subsequent metathesis reaction, equimolar amounts of lithium bis(trifluoromethanesulfonyl)imide and the n-(carboxyalkyl) pyridinium bromides were dissolved in water, resulting in an upper aqueous and a lower organic layer. The latter includes the 1-(n-carboxyalkyl)pyridinium bis(trifluoromethylsulfonate) product and trace amounts of lithium bromide, which has been removed by washing several times with water. The residual amount of the Br-anion was determined using the reaction with silver nitrate.

II. NMR

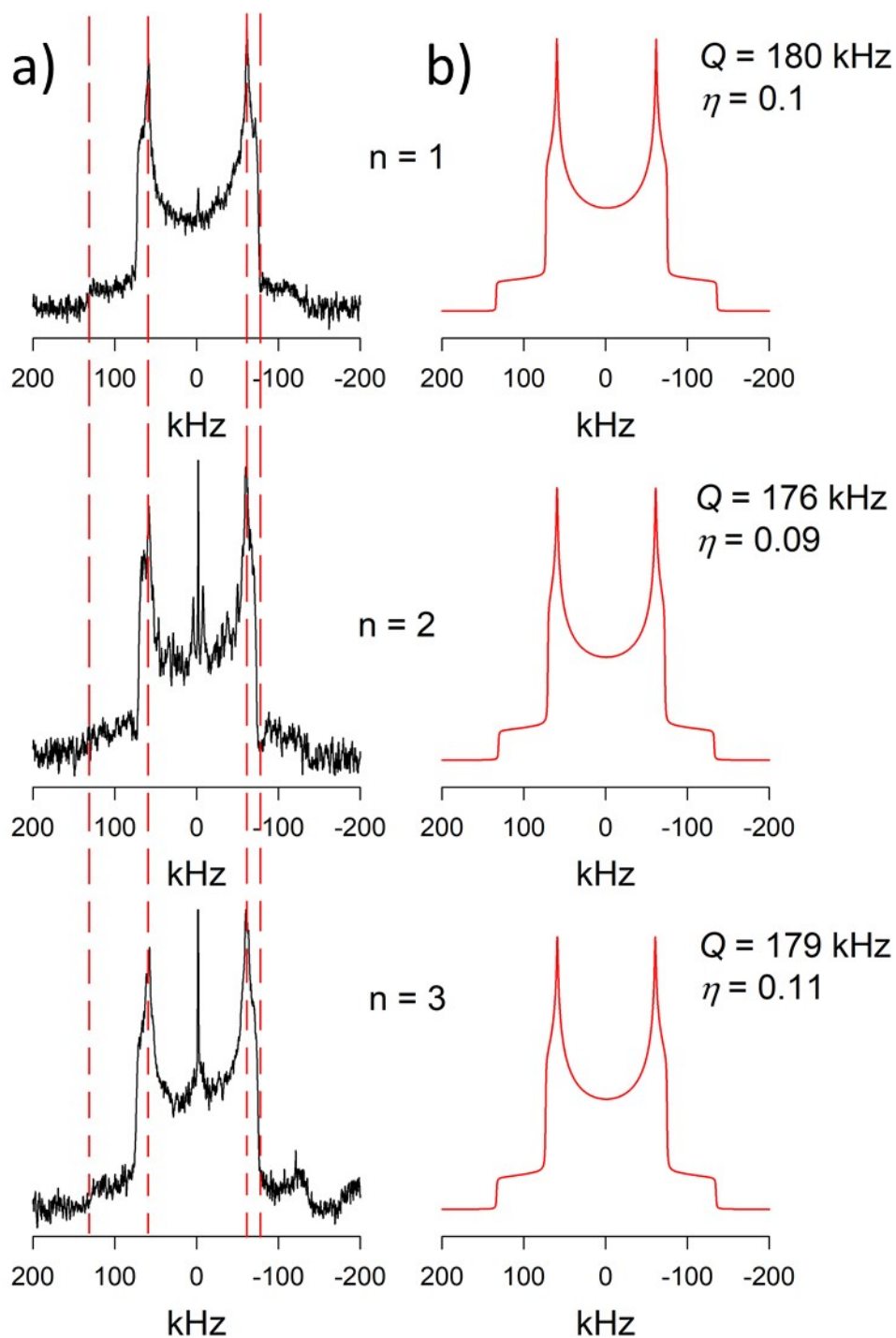


Figure SI2. ^2H NMR spectra and line shape analysis for phenylacetic acid ($n=1$), phenylpropanoic acid ($n=2$) and phenylbutanoic acid ($n=3$). (a) measured spectra and (b) simulated spectra. Q denote the DQCCs and η the asymmetry parameters. DQCCs of 180 kHz, 176 kHz and 179 kHz are only slightly higher than those observed for the corresponding carboxy-functionalized ILs.

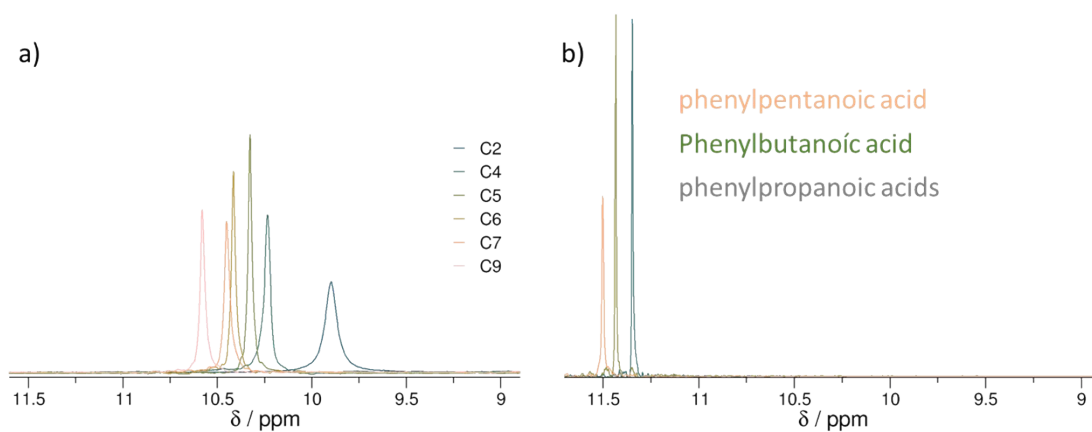


Figure SI3. Proton chemical shifts ^1H of a) the carboxy-functionalized ILs $\text{C}_n=2,4,5,6,7,9$ and b) phenylpropanoic acid, phenylbutanoic acid and phenylpentanoic acids, representing the molecular analogues of the IL cations for $n=2,3,4$.

III. DSC thermograms

We studied the thermal behavior of the ionic liquids 1-(carboxyalkyl)pyridinium bis(trifluoromethylsulfonyl)imide $[\text{HOOC}-(\text{CH}_2)_n\text{-py}][\text{NTf}_2]$ with $n=2,4,5,6,7,9$ by means of Differential Scanning Calorimetry (DSC). DSC measures temperatures and heat flows associated with thermal transitions in the ILs. We measured the DSC diagrams using the calorimeter Mettler Toledo DSC 823e coupled with Huber TC125MT cooler. The samples were placed in the standard non-pinned aluminum pan of 40 μl volume. All handling operations with sample were carried out in a glove-box under nitrogen atmosphere (residual concentrations of oxygen 1.0 ppm and water 0.3 ppm). Pans and samples were weighted with Sartorius MSE3.6P-000-DM microbalances with the standard uncertainty of $5 \cdot 10^{-6}$ g. The calibration of Mettler Toledo DSC 822e was checked with melting behaviour of the reference indium sample. The temperature of fusion agreed with recommended value better than 0.5 K. The temperature profiles of the DSC run included heating and cooling rates at 2 $\text{K} \cdot \text{min}^{-1}$, 5 $\text{K} \cdot \text{min}^{-1}$ and 10 $\text{K} \cdot \text{min}^{-1}$. The DSC studies of the thermal behavior of the ILs were repeated twice with the samples of the same batch.

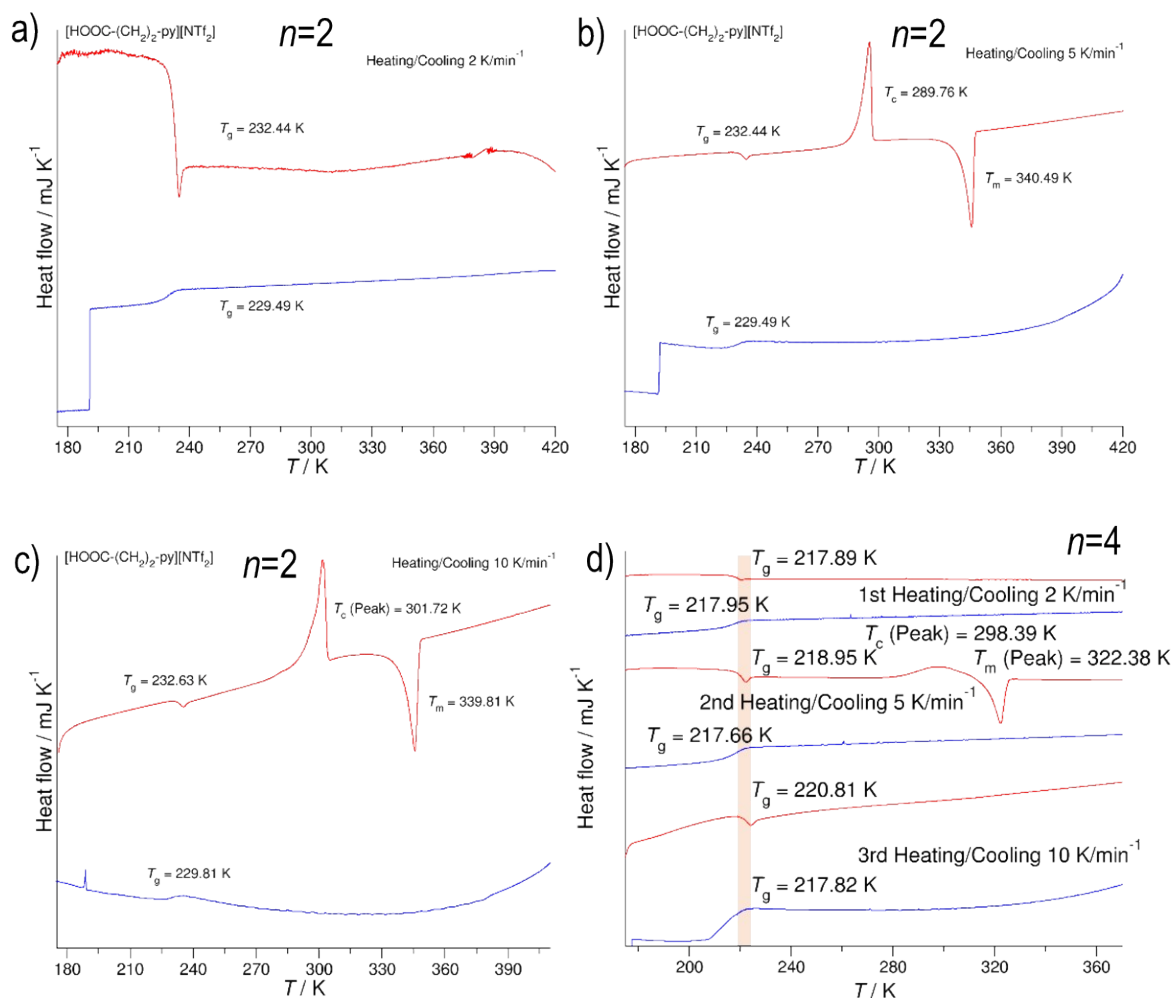
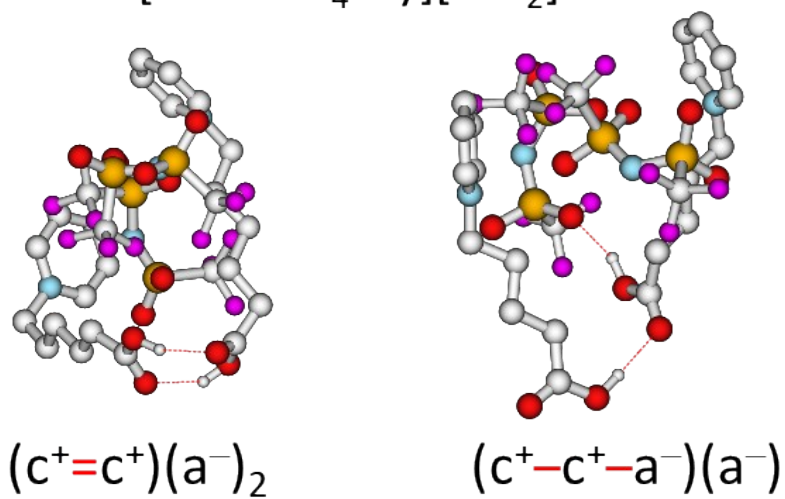
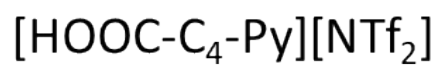
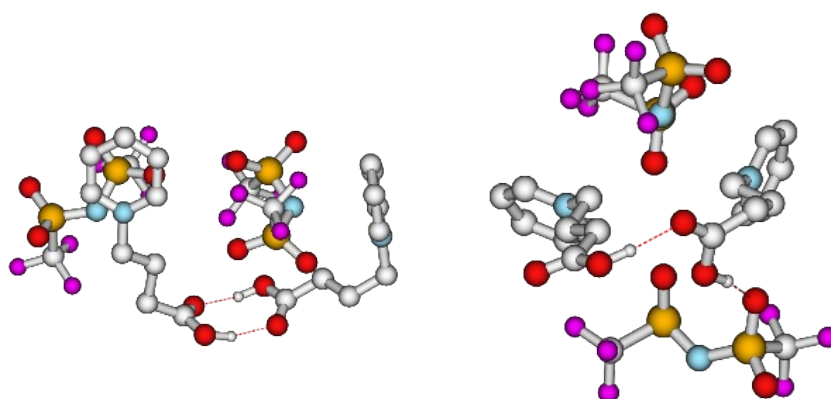
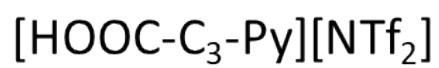
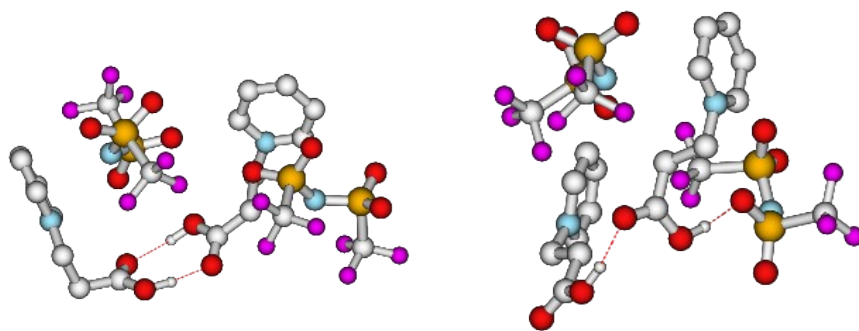
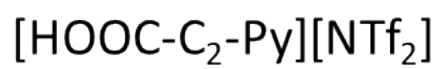
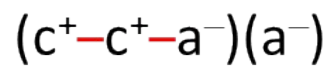
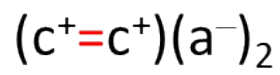
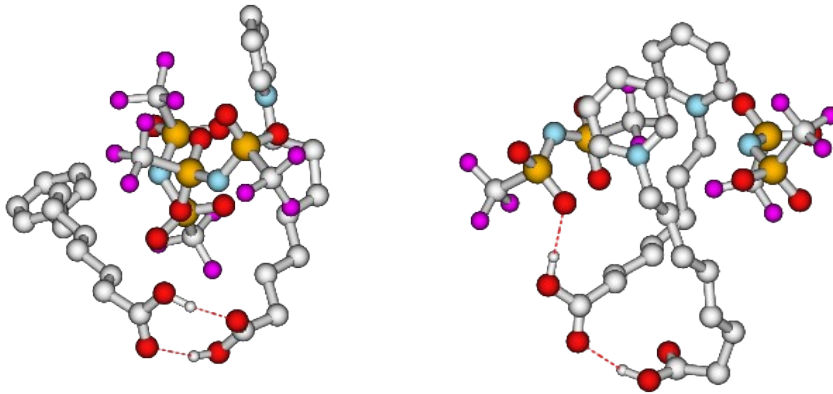
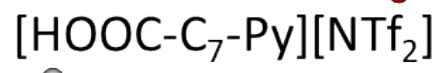
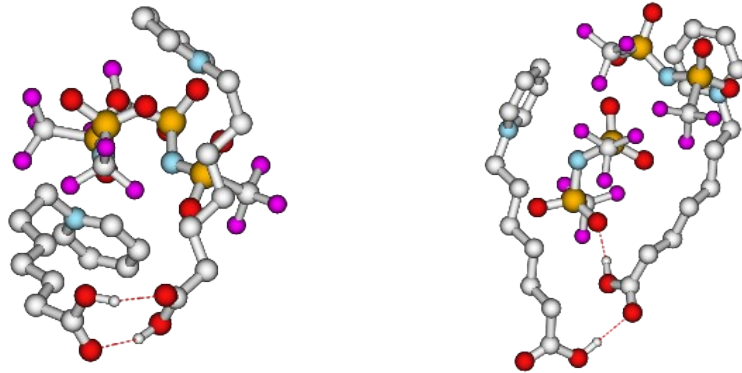
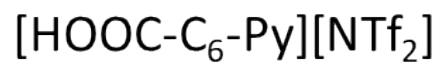
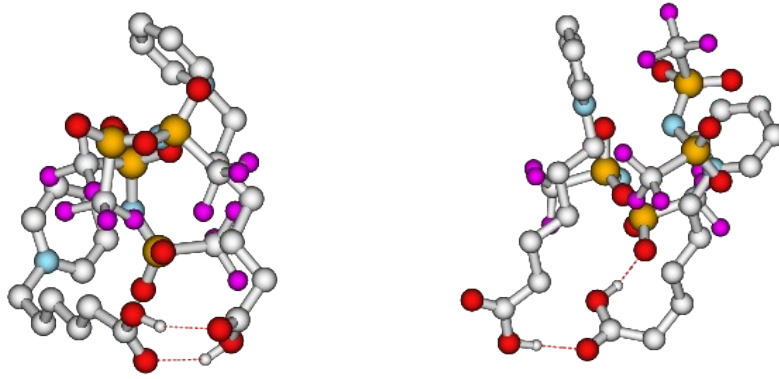
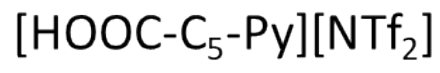


Figure SI4. The DSC thermograms of the IL [HOOC-(CH₂)_n-py][NTf₂] not shown in Figure 1 of the main article: a,b,c) [HOOC-(CH₂)₂-py][NTf₂] for heating and cooling rates at 2 K·min⁻¹, 5 K·min⁻¹ and 10 K·min⁻¹ and d) [HOOC-(CH₂)₄-py][NTf₂] for heating and cooling rates at 2 K·min⁻¹, 5 K·min⁻¹ and 10 K·min⁻¹.

IV. DFT calculated clusters

We calculated neutral-complexes $(c^+=c^+)(a^-)_2$ and $(c^+-c^+-a^-)(a^-)$ of the carboxy-functionalized ILs using the B3LYP-D3/6-31+G(d) level of theory considering Grimme's D3-dispersion correction.[1-4] The doubly hydrogen bonded cations in the $(c^+=c^+)(a^-)_2$ complexes are present throughout but differ in the way that the anion is solvated by the alkyl chains and the pyridinium rings of cations. In the open structures the ring motif of the doubly hydrogen bonded cations ($c^+=c^+$) is opened and replaced by H-bond complexes $(c^+-c^+-a^-)$ with one remaining H-bond ($c-c$) and an additional H-bond ($c-a$) between cation and anion.





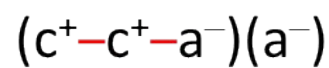
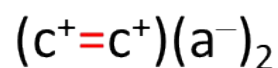
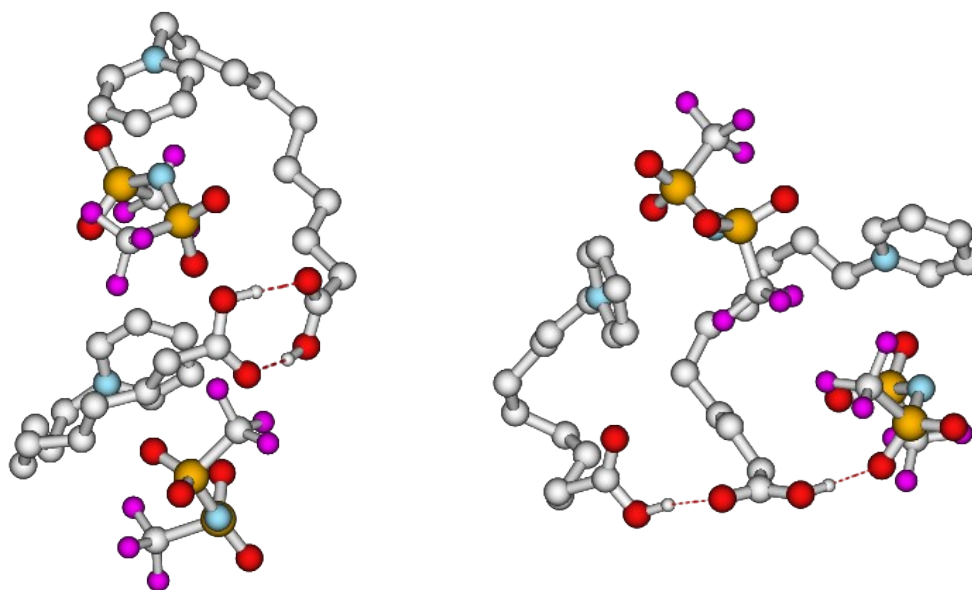
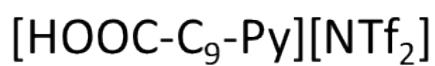
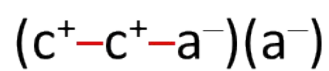
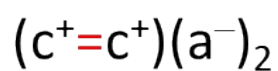
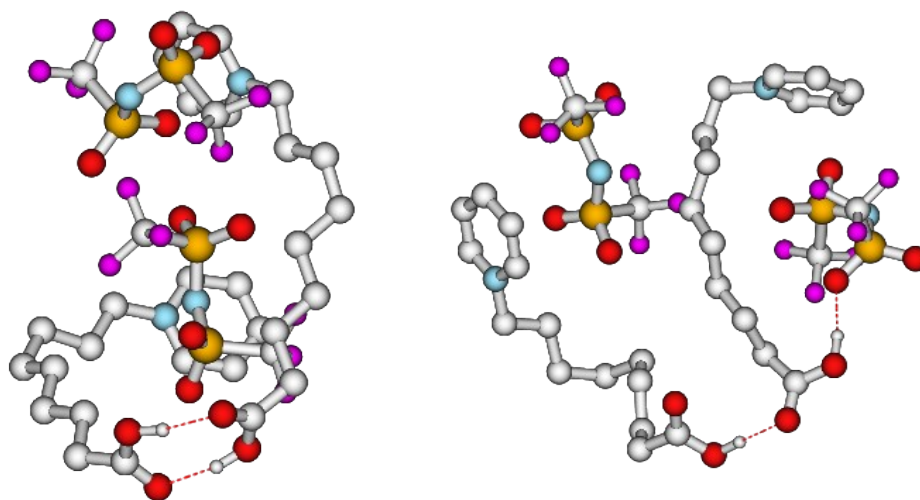
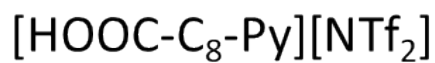
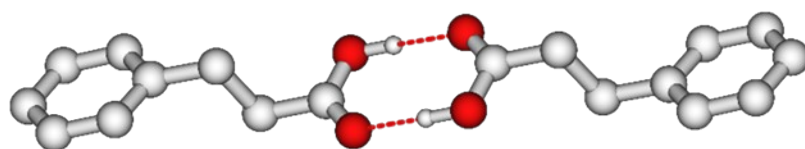
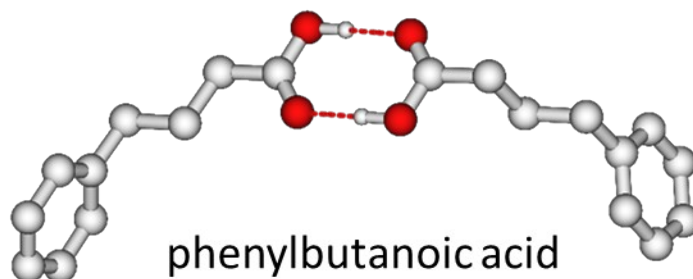


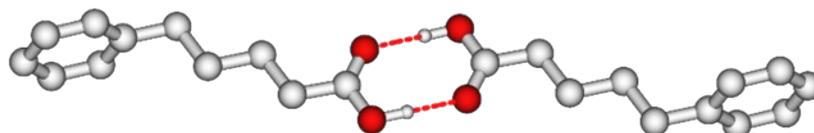
Figure SI5. Calculated neutral-complexes $(c^+=c^+)(a^-)_2$ and $(c^+-c^+-a^-)(a^-)$ of the carboxy-functionalized ILs using the B3LYP-D3/6-31+G(d) level of theory considering Grimme's D3-dispersion correction.



phenylpropanoic acid



phenylbutanoic acid



phenylpentanoic acid

Figure SI6. Calculated molecular dimers of phenylpropanoic acid, phenylbutanoic acid and phenylpentanoic acid using the B3LYP-D3/6-31+G(d) level of theory considering Grimme's D3-dispersion correction.

V. DFT calculated DQCC and asymmetry parameters η

We calculated the DQCC, χ_D , for each deuteron present in the $(c^+=c^+)(a^-)_2$ and $(c^+-c^+-a^-)(a^-)$ complexes. The DQCC describes the coupling between the nuclear quadrupole moment, eQ , and the principle component of the electric field gradient tensor, eq_{zz} at the deuteron nucleus. It could be shown that the relation between χ_D and eq_{zz} is given by the equation

$$\chi_D = \left(\frac{eQeq_{zz}}{h} \right) (\text{kHz}) = 2.3496 eQ \left(\frac{\text{fm}^2}{e} \right) eq_{zz} (\text{a.u.}) \quad (1)$$

where the factor 2.3496 takes care of the units. In principle, the DQCC can be obtained by multiplying the calculated principle component of electric field gradient tensor, eq_{zz} , of the OD hydroxyl groups in the $(c^+=c^+)(a^-)_2$ and $(c^+-c^+-a^-)(a^-)$ complexes with a calibrated nuclear quadrupole moment, eQ . The calibrated eQ is obtained by plotting the measured gas phase quadrupole coupling constants from microwave spectroscopy versus the calculated electric field gradients for small molecules, such as H_2O , CH_3OH , H_2CO_2 etc., as described by Huber et al.[5-7]. The slope gives a reasonable value of $eQ = 295.5 \text{ fm}^2$, which should be used for calculating DQCCs at the B3LYP-D3/6-31+G* level of theory. It could be also shown for this set of molecules that the principal axis of the deuteron electric field gradient is nearly axially symmetric and lies along the direction of the O-D bonds. We cannot expect that the calculated DQCCs of $(c^+=c^+)(a^-)_2$ and $(c^+-c^+-a^-)(a^-)$ complexes to represent the measured NMR values in the crystalline or glassy state of the ILs. Thus, we focus on the differences of the χ_D values in $(c^+=c^+)(a^-)_2$ relative to those obtained for the $(c^+-c^+-a^-)(a^-)$ complexes, which can be compared to $\Delta\chi_D [(c^+-c^+-a^-)(a^-)-(c^+=c^+)(a^-)_2]$ and $(c^+-c^+-a^-)(a^-)$ complexes obtained from the NMR experiment.

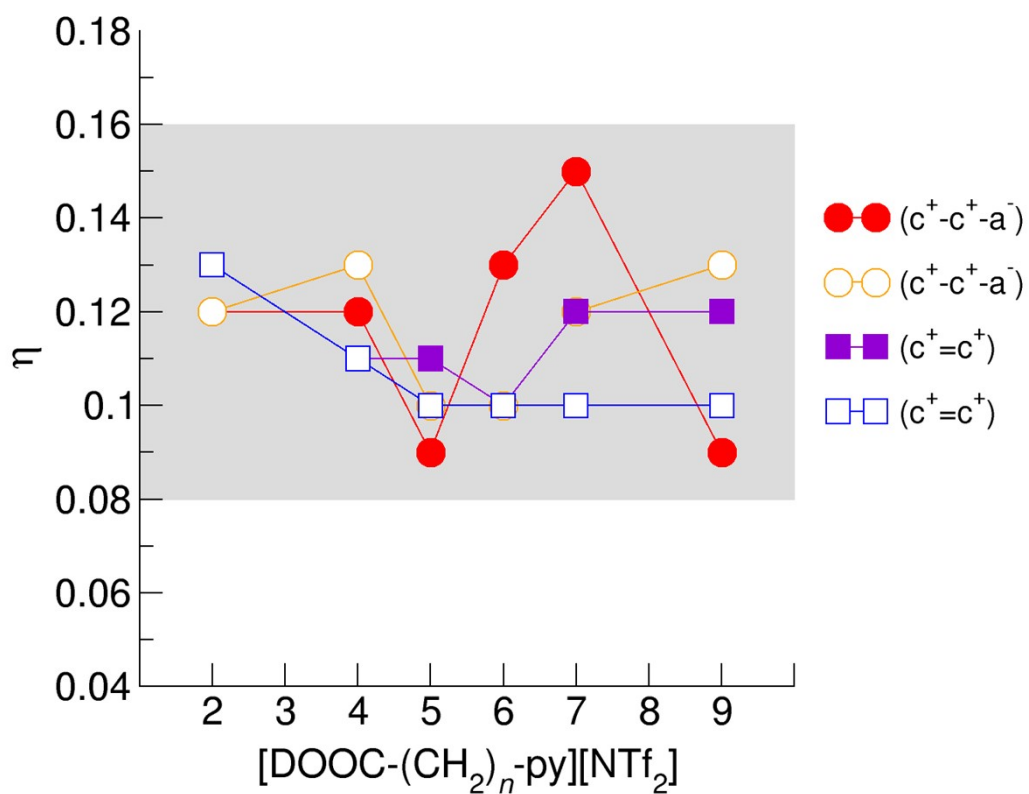


Figure SI7. Measured asymmetry parameters η of carboxy-functionalized ionic liquids $[\text{DOOC}-(\text{CH}_2)_n\text{-py}][\text{NTf}_2]$ with $n=2,4,5,6,7,9$ for temperatures 143 K (closed symbols) and 203 K (open symbols), respectively. The asymmetry parameters stay almost the same with n and only slightly decrease as expected for stronger H-bonds towards $n=9$.

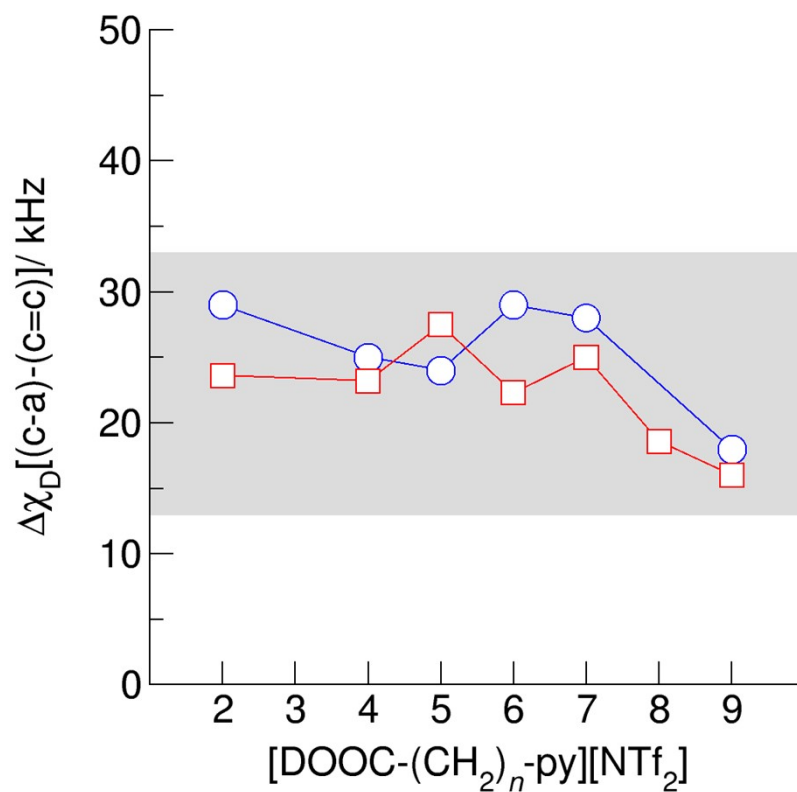


Figure SI8. Differences between the measured and calculated DQCCs $\Delta\chi_D$ obtained for the $(^+c=c^+)(a^-)_2$ and $(c^+-c^+-a^-)$ H-bond motifs. The differences range between 15 and 30 kHz for both, experiment and theory, finally supporting our interpretation for the H-bond motifs.

VI. References

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