

Interpretation of phase behavior of ionic liquids using the tool of theoretical chemistry

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What are ionic liquids?

Chemical species composed of molecular ions, being liquid at ambient temperatures, or at least below 100 °C. In other words, low-melting (in)organic salts.

What valuable properties do the ionic liquids possess?

Vast tunability of their chemical structure enables a tailored design of their extremely low volatility, high electrochemical stability, selective reactivity etc.

What potential applications can be ionic liquids suitable media for?

Electrolytes in supercapacitors and batteries; Gas capture, storage and metamorphosis; Biomass processing media

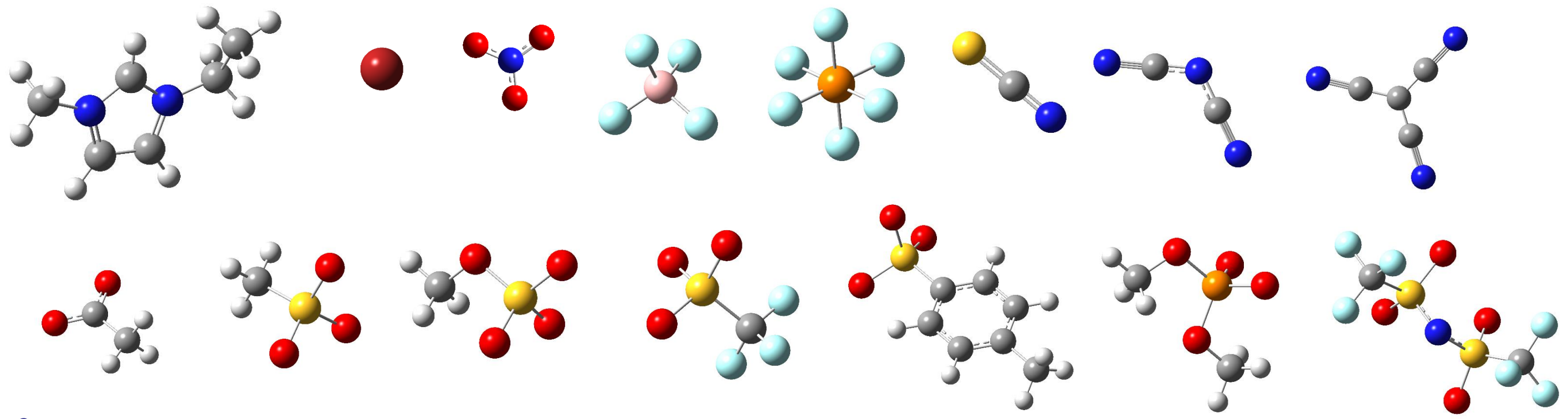
What are the challenges related to investigation of ionic liquids?

For experimentalists – high viscosity, limited availability.

For theoreticians – massive cohesive interactions, slow internal dynamics.

What factors impede broader exploitation of ionic liquids in chemical technologies?

Prevailing higher price, limited availability of their physico-chemical properties and insufficient understanding of their behavior.

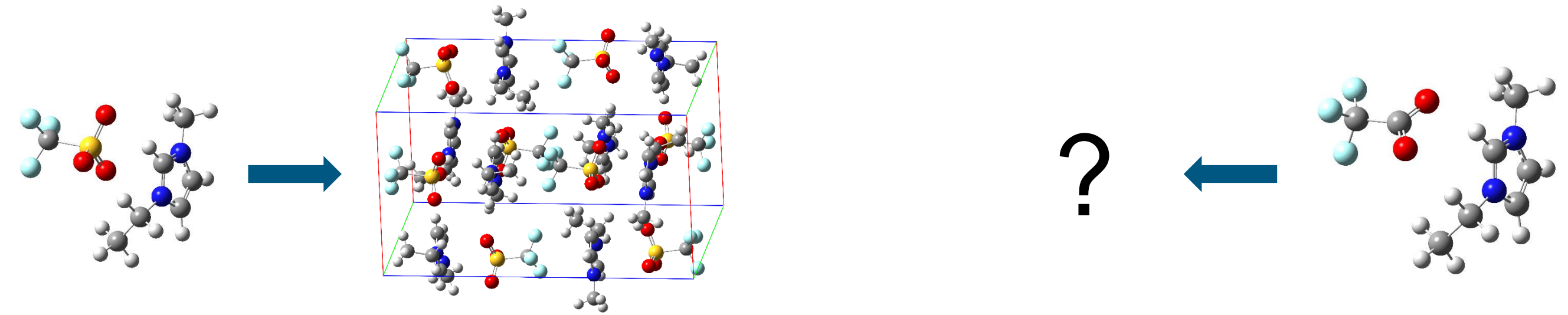


Project motivation

Phase behavior of 20 1-ethyl-3-methylimidazolium ionic liquids has been investigated calorimetrically in a related experimental project

Only 11 out of 20 species were found to crystallize routinely, additional 5 species crystallized rarely and irreproducibly while 4 species did not crystallize at any conditions and experimental setups

Computational interpretation of the tendency of the given ionic liquids to crystallize was looked for using structural, energetic and transport properties accessible from molecular-dynamics simulations or quantum-chemical calculations



Computational details

Liquid phase treated by classical non-polarizable molecular dynamics in LAMMPS using all-atom OPLS-like CL&P force-field model

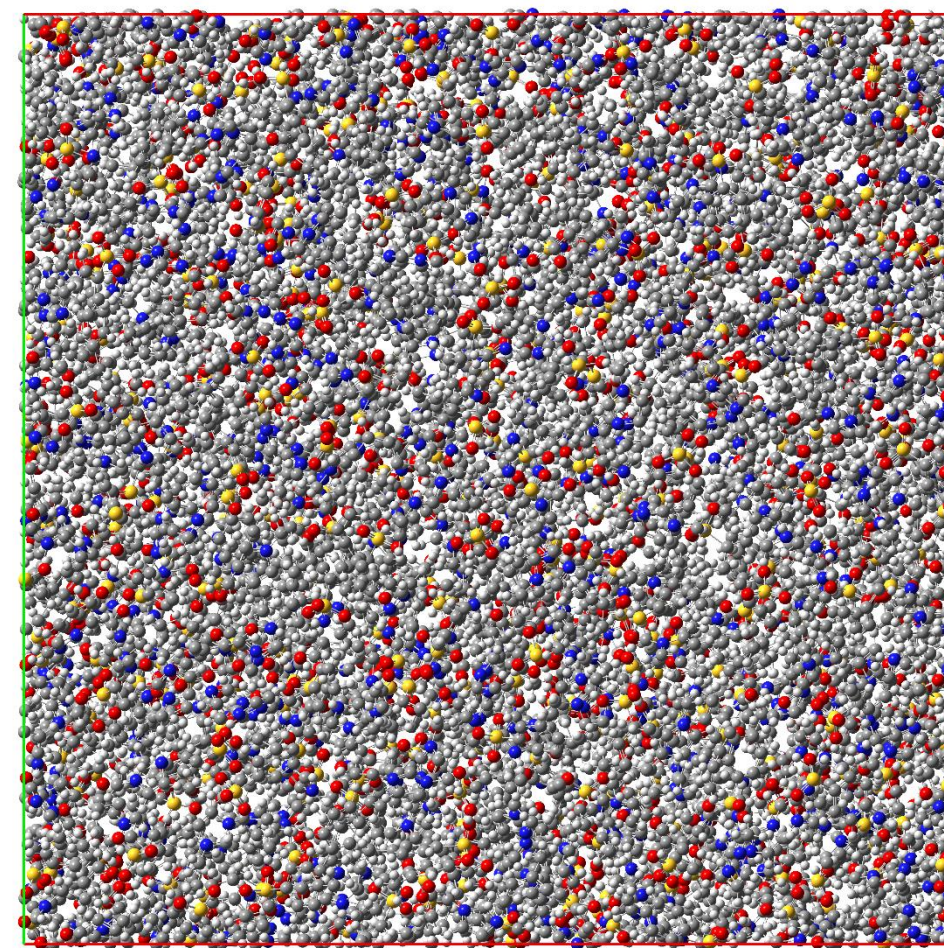
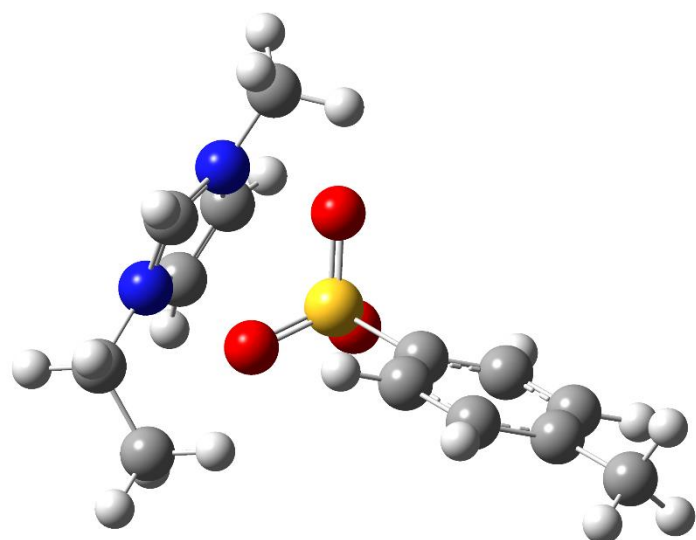
Trajectories initiated from random positions of 500 ion pairs maintained at 400 K and 1 bar

Equilibration 5 ns, 20 ns production runs, step 1 fs

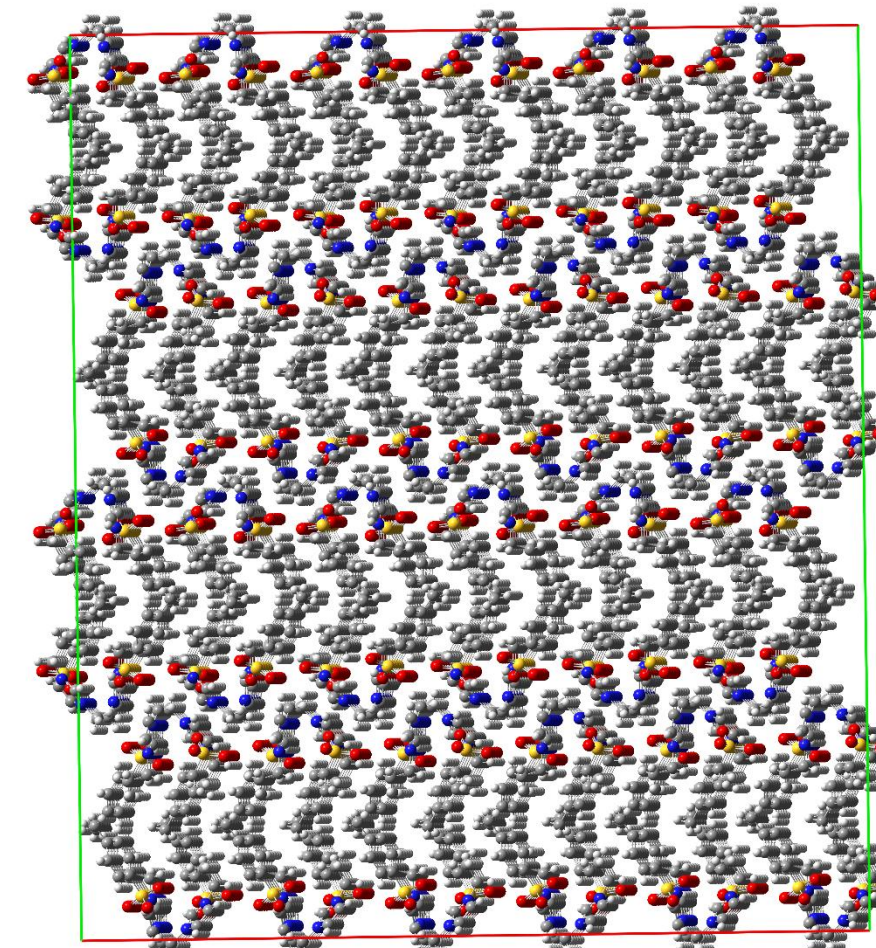
Simulated annealing used to determine the ion pair geometry corresponding to the global potential energy of the ion pair

Pair interaction energies and their decompositions calculated with sSAPT0/jun-pVDZ

Geometry of the 1-ethyl-3-methylimidazolium p-toluenesulfonate [emim][OTs] corresponding to its global minimum of the potential energy.



Chaotic structure of the liquid phase of ionic liquid 1-ethyl-3-methylimidazolium p-toluenesulfonate [emim][OTs].



Ordered crystal structure of the monoclinic polymorph of [emim][OTs].

Crystal phase treated by quantum-chemical density-functional theory (DFT) using the PBE-D3(BJ) functional, PAW basis sets and periodic boundary conditions in VASP

Geometry of unit cells containing 2-8 ion pairs optimized with DFT

Isolated ion pairs relevant for the gaseous phase mimicked within periodic DFT calculations with fixed 30 Å cubic cells

Static electronic cohesive energies computed as the difference of energies of an ion pair in the crystalline and gaseous phases

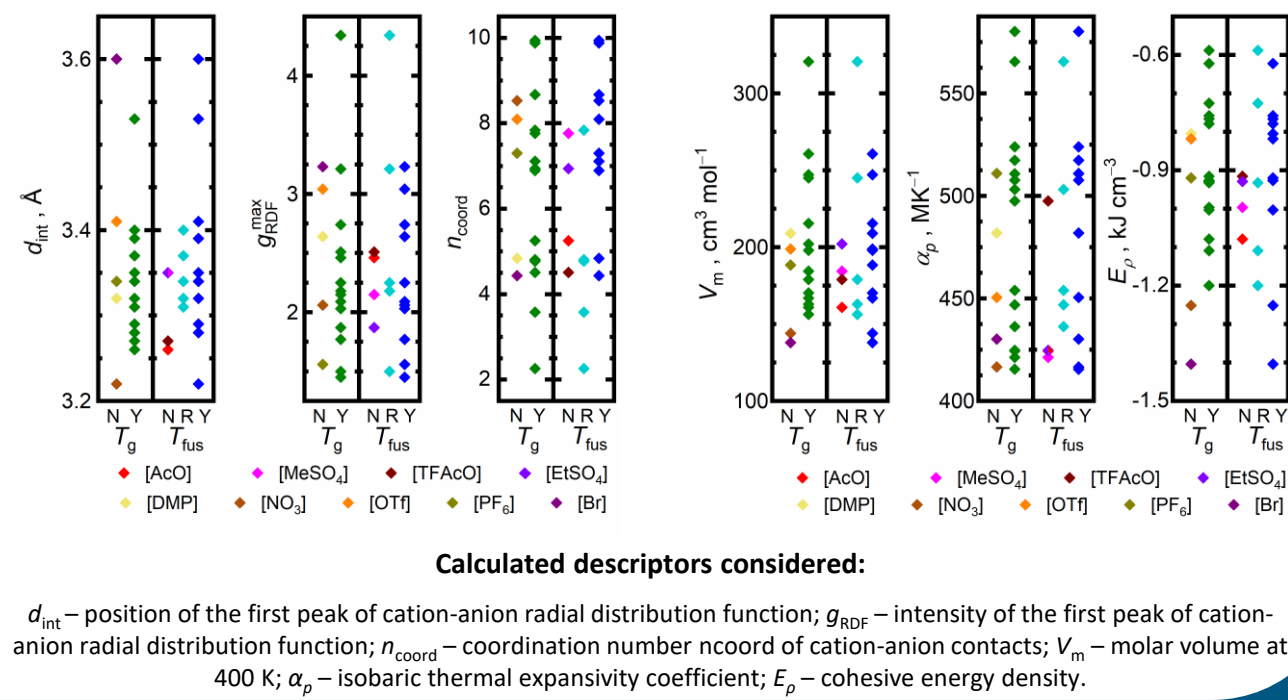
Structural aspects

Ionic liquids not reported to crystallize exhibit shorter ion contact distance in the liquid and its lower ordering

Molar volumes or the cohesive energy density cannot be used to predict the crystallizability of investigated ILs

Lower thermal expansivity seems to impede the crystallizability

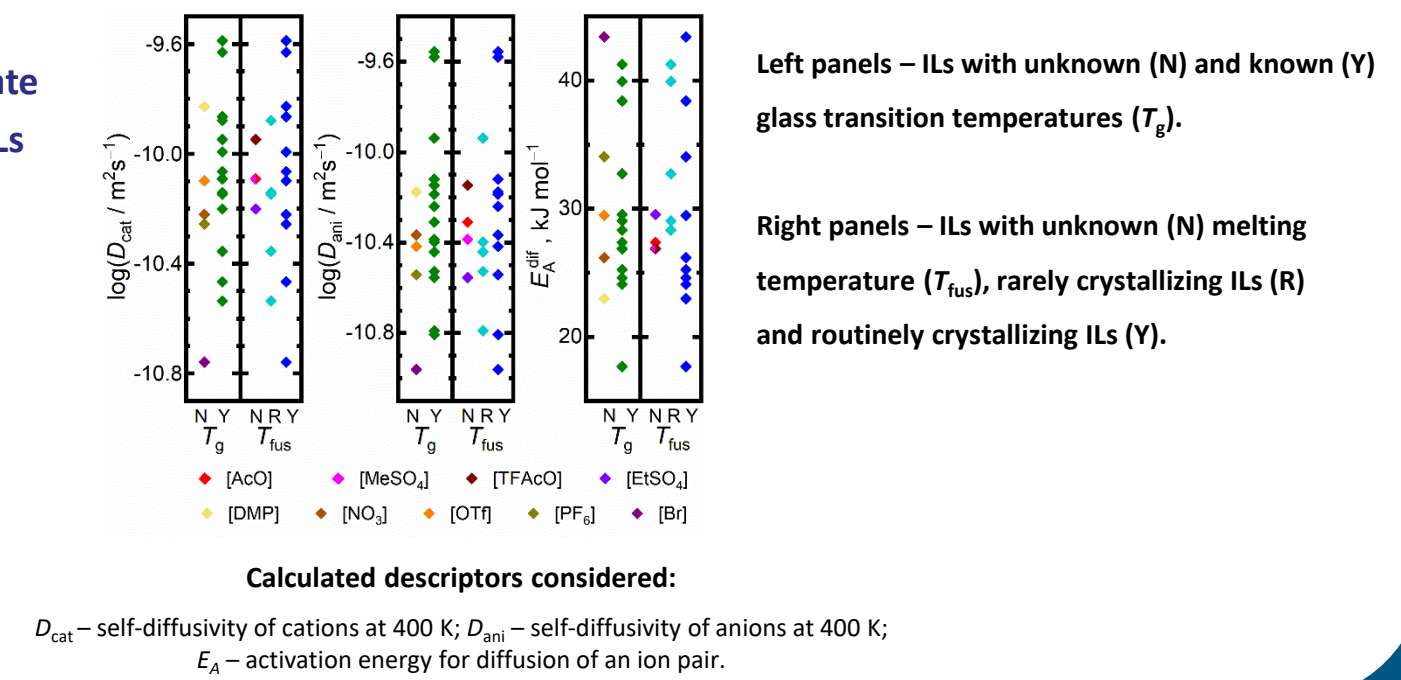
Structural parameters were found to be uncorrelated with T_g and T_{fus} values



Diffusion aspects

Transport properties do not discriminate crystallizing and yet non-crystallizing ILs

Self-diffusivities yield reasonable correlations with T_g and T_{fus} , enabling estimates of these quantities for compounds with unavailable physico-chemical data



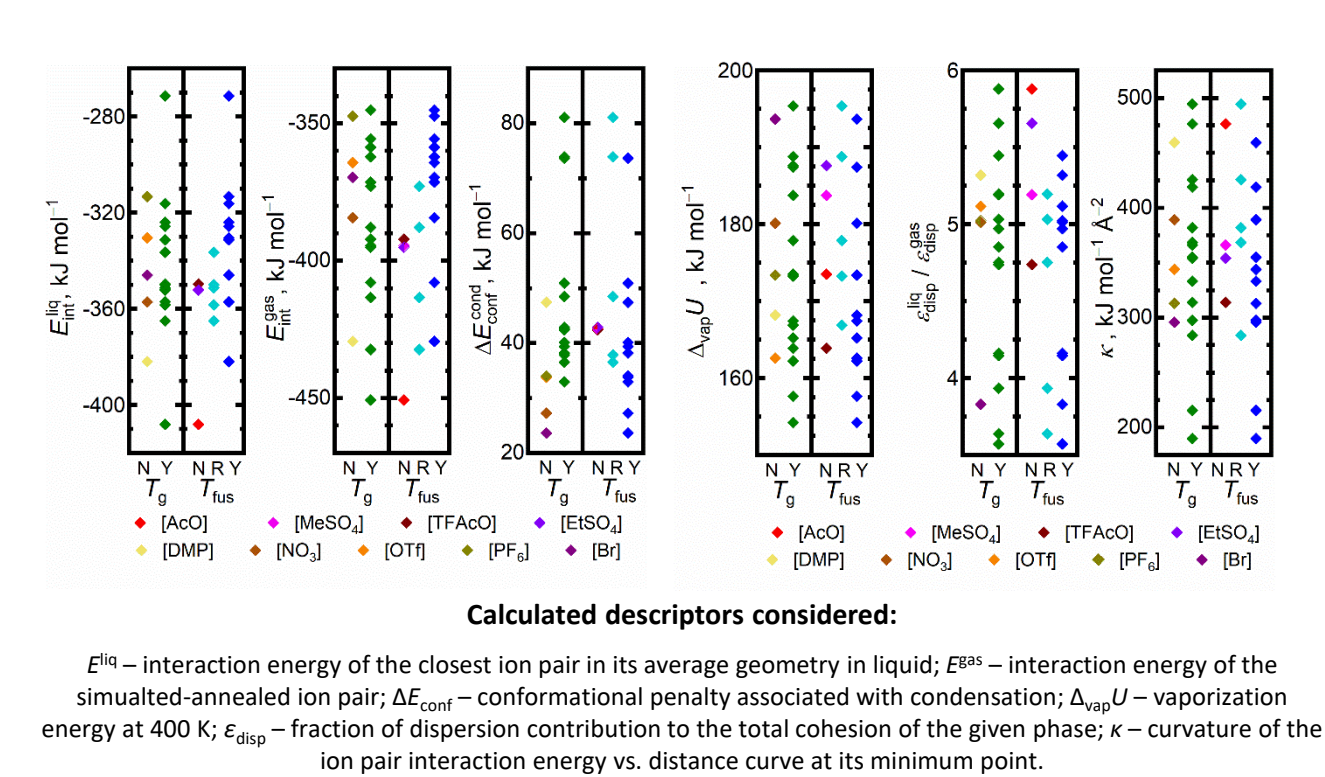
Energetic aspects

Pair interaction energies are the most relevant descriptors for assessment of the crystallizability

Out of 11 species exhibiting $|E^{ic}|$ above 350 kJ·mol⁻¹, only 3 crystallize routinely

Vaporization energy and its conformational component do not discriminate crystallizing and yet non-crystallizing ILs

Significant dispersion interactions in the liquid and large curvature of the interaction energy vs. distance curves impede the crystallizability

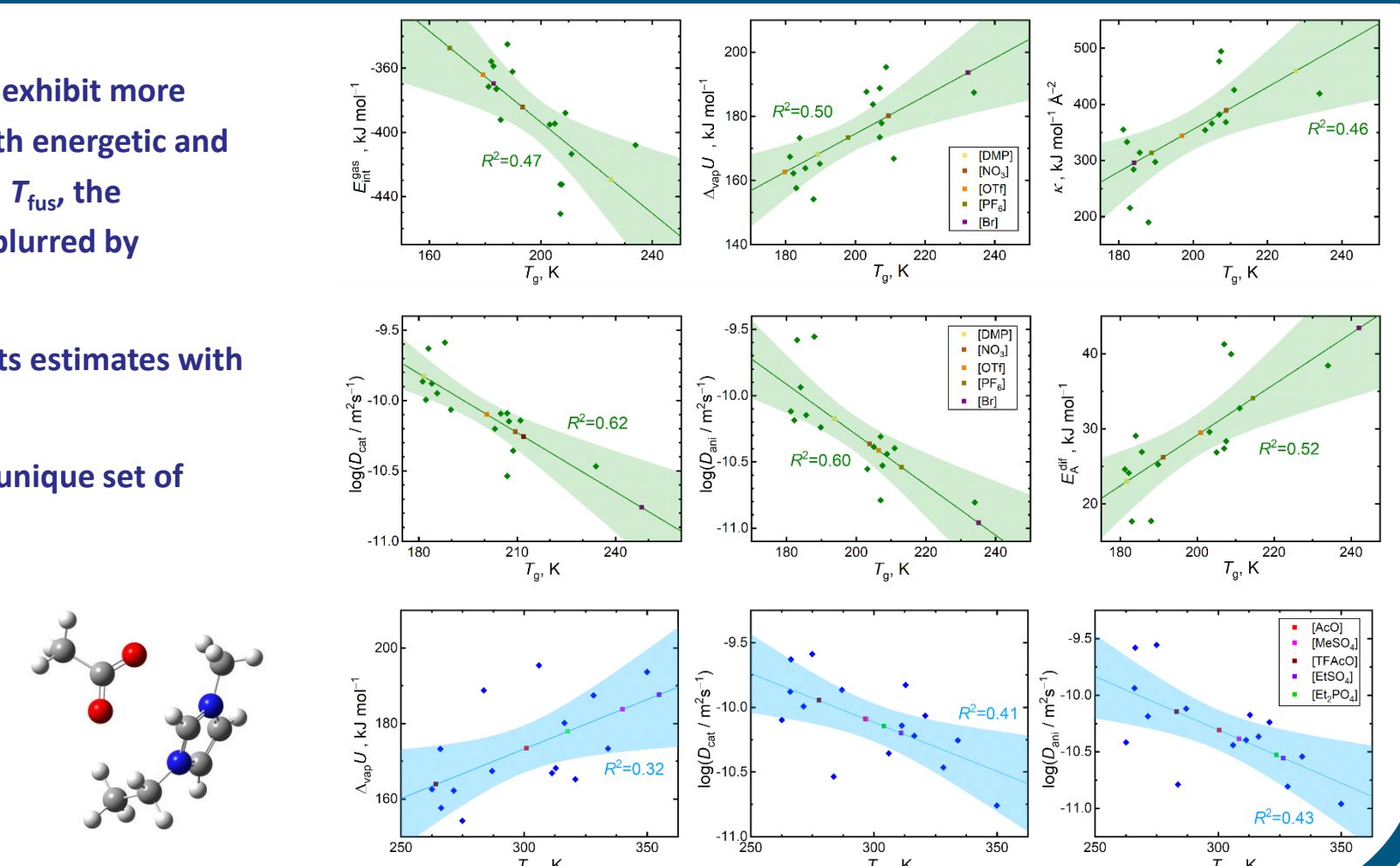


Relevant correlations

Rather enthalpy-driven T_g exhibit more significant correlations with energetic and transport descriptors than T_{fus} , the correlations of which are blurred by entropic contributions

Correlations of T_g enable its estimates with an uncertainty 10-20 K

[emim][AcO] possesses a unique set of outlying characteristics, possibly rendering its crystallization extremely hard, yet not impossible



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