Support information

The electronic energies and structures of ILs and IL⋯CO_2 complex in the gas phase were calculated by full optimization without any geometrical constraints with Gaussian 09 software package[1] using the density functional theory and the B3LYP hybrid exchange-correlation functional[2,3] with the 6-31+G(d,p) basis set.[4] All stationary point species were verified by calculating their vibrational frequencies.[5,6]

For [RMIm][TCM], geometric optimization was conducted as follows: the imidazolium group of the 1-alkyl-3-methylimidazolium cation was found to have a planar aromatic structure in its energy minimum. A methyl group was added to one of the N atoms to produce methylimidazolium and was optimized. The binding of an ethyl group to the other N atom resulted in a stable [EMIm] cation structure. Optimized [BMIm] and [HMIm] cations were obtained using a similar procedure. A [TCM] anion was then added mainly at four different positions, including the top and bottom of the planar imidazolium cation and vertically as well as horizontally to the planar structure of imidazolium, and these structures were optimized.

For [EMIm][TCM]⋯CO_2, eight initial configurations were constructed for geometric optimization. In each of the configurations, the CO_2 molecule was placed at a different location between the cation and anion of the IL, horizontally and vertically for the plane made by the cation and anion of the IL. The formation of these complexes is diffusion controlled with no activation energy.

The B3LYP structures of [BMIm][TCM]⋯CO_2 and [HMIm][TCM]⋯CO_2 were obtained

using a similar method, and an optimized structure was obtained with CO_2 in a position similar to the position of CO_2 in [EMim][TCM]. For all complexes, the oxygen atoms of the CO_2 molecule are bent outward to reduce the repulsive interaction with the electronegative N of $C(CN)_3^-$.

The complexation energy (ΔE_c) is defined as the difference between the energy of the [RMIm][TCM]$\cdots CO_2$ adduct and the sum of the energies of the separate [RMIm][TCM] and CO_2 species in the gas phase. Although calculations with the basis set superposition error correction by the Boys-Bernardi counterpoise method[7] would provide results that are more consistent with the experimental data,[8] for computational efficiency we considered only the uncorrected complexation energy between the molecules because our objective here was to see the trend in this system.

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