Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Tailoring the properties of acetate-based ionic liquids using the tricyanomethanide anion

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Supplementary Information

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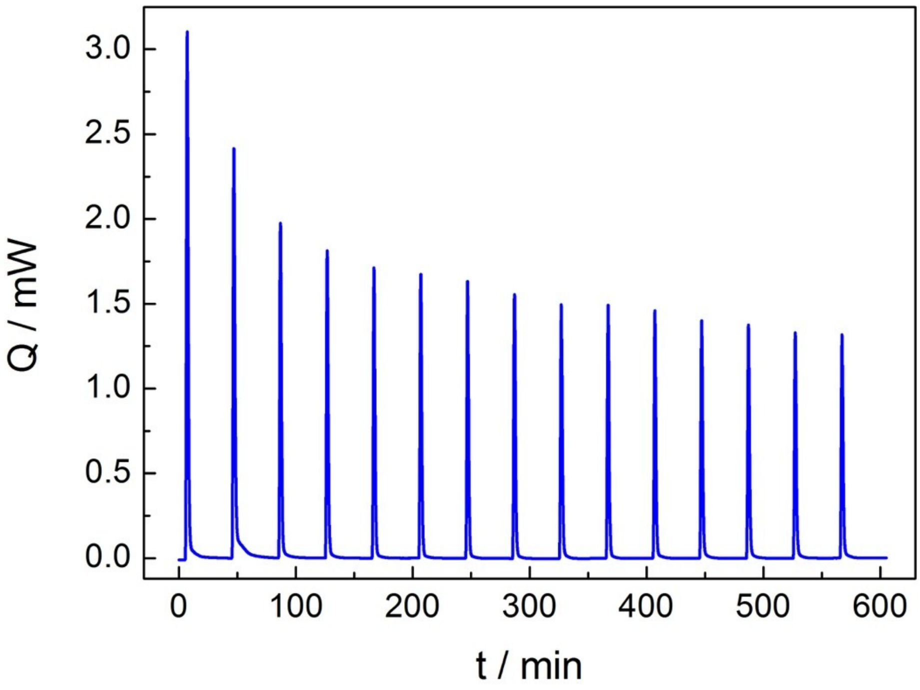

Figure S1. Calorimetric signals obtained in an ITC measurement upon mixing [C_4C_1Im][OAc] with [C_4C_1Im][C(CN)$_3$]. Each peak correspond to the heat effect involved in 10μL injections of a [C_4C_1Im][OAc]$_{(1-x)}$[C(CN)$_3$]$_x$ mixture ($x_{C(CN)3}$=0.2400) in pure [C_4C_1Im][C(CN)$_3$] at 318K. During the course of the experiment the sample in the measuring cell was stirred at 90 rpm. Each injection was done during 60 s allowing 40 min interval between consecutive injections.

Table S1. Experimental densities of $[C_4C_1Im][OAc]$, $[C_4C_1Im][C(CN)_3]$ and their mixtures between 293 K and 353 K at ambient pressure.

T / K	ρ / g cm^{-3}	δ / %	T / K	ρ / g cm^{-3}	δ / %
$[C_4C_1Im][OAc]$			$[C_4C_1Im][C(CN)_3]$		
293.15	1.054289	-0.009	293.15	1.049579	-0.015
298.15	1.051196	-0.003	298.15	-	-
303.15	1.048154	0.000	303.15	1.042796	0.000
313.15	1.042046	0.005	313.15	1.036081	0.009
323.15	1.035958	0.010	323.15	1.029431	0.012
333.15	1.029930	0.008	333.15	1.022843	0.009
343.15	1.023966	0.000	343.15	1.016318	-0.001
353.15	1.018046	-0.013	353.15	1.009847	-0.016
$[C_4C_1Im][OAc]_{0.7476}[C(CN)_3]_{0.2524}$			$[C_4C_1Im][OAc]_{0.4993}[C(CN)_3]_{0.5007}$		
293.15	1.052409	-0.010	293.15	1.050421	-0.012
298.15	1.049243	-0.003	298.15	1.047158	-0.003
303.15	1.046097	0.000	303.15	1.043939	0.002
313.15	1.039808	0.009	313.15	1.037524	0.010
323.15	1.033578	0.011	323.15	1.031167	0.011
333.15	1.027410	0.008	333.15	1.024865	0.009
343.15	1.021291	0.000	343.15	1.018614	0.000
353.15	1.015220	-0.013	353.15	1.012410	-0.013
$[C_4C_1Im][OAc]_{0.2501}[C(CN)_3]_{0.7499}$					
293.15	1.049400	-0.012			
298.15	1.042775	-0.004			
303.15	1.036215	0.001			
313.15	1.029712	0.009			
323.15	1.023269	0.012			
333.15	1.016880	0.008			
343.15	1.010542	0.000			
353.15	1.046067	-0.014			

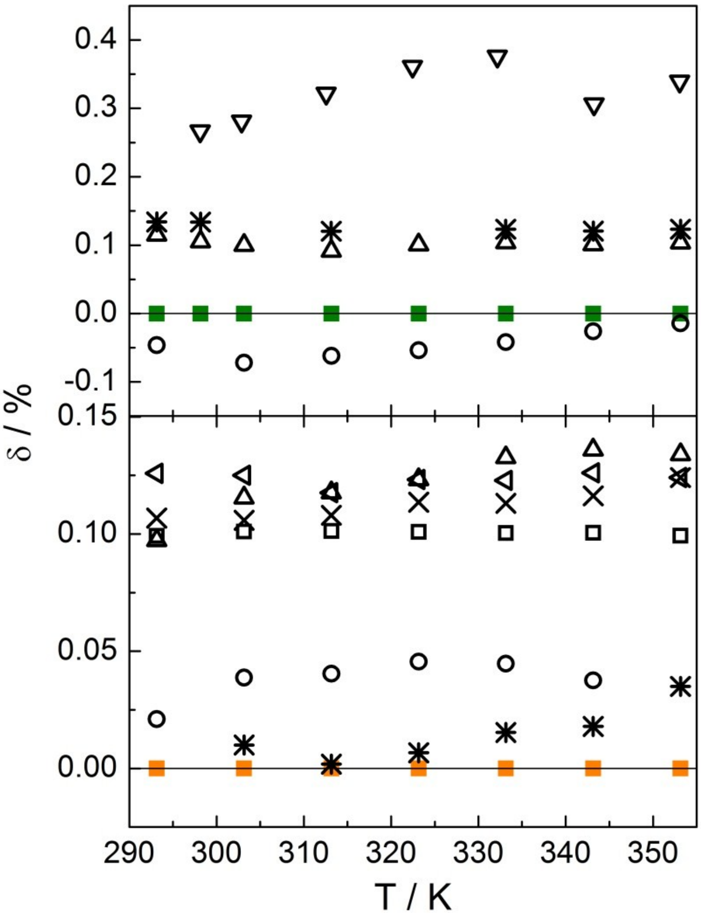

Figure S2. Comparison of experimental densities with those reported in the literature. Reported data for $[C_4C_1Im][OAc]$ (○, upper plot) were obtained from Stevanovic *et al.* [1] (♦), Almeida *et al.* [2] (❐), Higara *et al.* [3] (❧) and Safarov *et al*. [4] (→). For $[C_4C_1Im][C(CN)_3]$ (○, lower plot) reported data were obtained from Carvalho *et al*. [5] (❐), Koller *et al*. [6] (◉), Zubeir *et al*. [7] (→ and ❖ for 0.003 and 0.11 H_2O wt%), Lukoshko *et al*. [8] (❧) and Romanos *et al*. [9] (❦). $\delta = 100*(\rho_{lit}-\rho_{exp})/\rho_{exp}$.

Table S2. Excess molar volumes V^E for $[C_4C_1Im][OAc]_{(1-x)}[C(CN)_3]_x$ mixtures as a function of the composition, expressed in mole fraction of $[C_4C_1Im][C(CN)_3]$, $x_{C(CN)3}$, and as a function of temperature.

$x_{C(CN)3}$	V^E / cm^3 mol^{-1}	$x_{C(CN)3}$	V^E / cm^3 mol^{-1}	$x_{C(CN)3}$	V^E / cm^3 mol^{-1}
T = 293.15 K		T = 303.15 K		T = 313.15 K	
0.0000	0.000	0.0000	0.000	0.0000	0.000
0.2524	0.103	0.2524	0.103	0.2524	0.106
0.5007	0.258	0.5007	0.261	0.5007	0.260
0.7499	0.247	0.7499	0.247	0.7499	0.246
1.0000	0.000	1.0000	0.000	1.0000	0.000
T = 323.15 K		T = 333.15 K		T = 343.15 K	
0.0000	0.000	0.0000	0.000	0.0000	0.000
0.2524	0.104	0.2524	0.101	0.2524	0.102
0.5007	0.256	0.5007	0.254	0.5007	0.253
0.7499	0.245	0.7499	0.243	0.7499	0.244
1.0000	0.000	1.0000	0.000	1.0000	0.000
T = 353.15 K					
0.0000	0.000				
0.2524	0.102				
0.5007	0.254				
0.7499	0.245				
1.0000	0.000				

Table S3. Heat effects from ITC experiments with the system $[C_4C_1Im][OAc]$(1) + $[C_4C_1Im][C(CN)_3]$(2) at 318K. The subscripts c and d stands for cell (or container) and dispenser (or syringe), respectively.

n_{1c} / mol	n_{2c} / mol	n_{1d} / mmol	n_{2d} / mmol	Q / J
3.6669E-03	6.2638E-04	0	2.2488E-02	-0.14267
3.6669E-03	6.4887E-04	0	2.2488E-02	-0.14213
3.6669E-03	6.7136E-04	0	2.2488E-02	-0.14102
3.6669E-03	6.9384E-04	0	2.2488E-02	-0.13908
3.6669E-03	7.1633E-04	0	2.2488E-02	-0.13926
3.6669E-03	7.3882E-04	0	2.2488E-02	-0.13751
3.6669E-03	7.6131E-04	0	2.2488E-02	-0.13667
3.6669E-03	7.8379E-04	0	2.2488E-02	-0.13448
3.6669E-03	8.0628E-04	0	2.2488E-02	-0.13326
3.6669E-03	8.2877E-04	0	2.2488E-02	-0.13459
3.6669E-03	8.5126E-04	0	2.2488E-02	-0.12763
3.6669E-03	8.7374E-04	0	2.2488E-02	-0.12903
3.6669E-03	8.9623E-04	0	2.2488E-02	-0.12681
3.6669E-03	9.1872E-04	0	2.2488E-02	-0.12640
3.6669E-03	9.4121E-04	0	2.2488E-02	-0.12534
3.6669E-03	9.6369E-04	0	2.2488E-02	-0.12416
3.6669E-03	9.8618E-04	0	2.2488E-02	-0.12261
3.6669E-03	1.0087E-03	0	2.2488E-02	-0.12119
3.6669E-03	1.0312E-03	0	2.2488E-02	-0.12381
3.6669E-03	1.0536E-03	0	2.2488E-02	-0.11635
3.6669E-03	1.0761E-03	0	2.2488E-02	-0.11864
3.6669E-03	1.0986E-03	0	2.2488E-02	-0.11634
3.6669E-03	1.1211E-03	0	2.2488E-02	-0.11572
3.6674E-03	6.2638E-04	0	2.2488E-02	-0.14565
3.6674E-03	6.4887E-04	0	2.2488E-02	-0.14329
3.6674E-03	6.7136E-04	0	2.2488E-02	-0.14204
3.6674E-03	6.9384E-04	0	2.2488E-02	-0.14043
3.6674E-03	7.1633E-04	0	2.2488E-02	-0.13873
3.6674E-03	7.3882E-04	0	2.2488E-02	-0.13744
3.6674E-03	7.6131E-04	0	2.2488E-02	-0.13528
3.6674E-03	7.8379E-04	0	2.2488E-02	-0.13318
3.6674E-03	8.0628E-04	0	2.2488E-02	-0.13147
3.6674E-03	8.2877E-04	0	2.2488E-02	-0.13086
3.6674E-03	8.5126E-04	0	2.2488E-02	-0.12985
3.6674E-03	8.7374E-04	0	2.2488E-02	-0.12853
3.6674E-03	8.9623E-04	0	2.2488E-02	-0.12704
3.6674E-03	9.1872E-04	0	2.2488E-02	-0.12518
3.6674E-03	9.4121E-04	0	2.2488E-02	-0.12442
3.6674E-03	9.6369E-04	0	2.2488E-02	-0.12374
3.6674E-03	9.8618E-04	0	2.2488E-02	-0.12184
3.6674E-03	1.0087E-03	0	2.2488E-02	-0.12056
3.6674E-03	1.0312E-03	0	2.2488E-02	-0.11970
3.6674E-03	1.0536E-03	0	2.2488E-02	-0.11857
3.6674E-03	1.0761E-03	0	2.2488E-02	-0.11732
3.6674E-03	1.0986E-03	0	2.2488E-02	-0.11541
3.6674E-03	1.1211E-03	0	2.2488E-02	-0.11481
3.6674E-03	1.1436E-03	0	2.2488E-02	-0.11390
3.6674E-03	1.1661E-03	0	2.2488E-02	-0.11237
3.6674E-03	1.1886E-03	0	2.2488E-02	-0.11135

3.6674E-03	1.2111E-03	0	2.2488E-02	-0.11071
3.6674E-03	1.2335E-03	0	2.2488E-02	-0.10902
1.7855E-03	1.7848E-03	0	2.2488E-02	-0.03940
1.7855E-03	1.8073E-03	0	2.2488E-02	-0.03949
1.7855E-03	1.8298E-03	0	2.2488E-02	-0.03803
1.7855E-03	1.8523E-03	0	2.2488E-02	-0.03812
1.7855E-03	1.8748E-03	0	2.2488E-02	-0.03747
1.7855E-03	1.8972E-03	0	2.2488E-02	-0.03683
1.7855E-03	1.9197E-03	0	2.2488E-02	-0.03616
1.7855E-03	1.9422E-03	0	2.2488E-02	-0.03590
1.7855E-03	1.9647E-03	0	2.2488E-02	-0.03504
1.7855E-03	1.9872E-03	0	2.2488E-02	-0.03425
1.7855E-03	2.0097E-03	0	2.2488E-02	-0.03344
1.7855E-03	2.0322E-03	0	2.2488E-02	-0.03301
1.7855E-03	2.0547E-03	0	2.2488E-02	-0.03274
1.7855E-03	2.0771E-03	0	2.2488E-02	-0.03207
1.7855E-03	2.0996E-03	0	2.2488E-02	-0.03143
1.7855E-03	2.1221E-03	0	2.2488E-02	-0.03093
1.7855E-03	2.1446E-03	0	2.2488E-02	-0.03015
1.7855E-03	2.1671E-03	0	2.2488E-02	-0.02989
1.7855E-03	2.1896E-03	0	2.2488E-02	-0.02948
1.7855E-03	2.2121E-03	0	2.2488E-02	-0.02878
1.7855E-03	2.2346E-03	0	2.2488E-02	-0.02857
1.7855E-03	2.2570E-03	0	2.2488E-02	-0.02814
1.7855E-03	2.2795E-03	0	2.2488E-02	-0.02771
1.7855E-03	2.3020E-03	0	2.2488E-02	-0.02726
1.7855E-03	2.3245E-03	0	2.2488E-02	-0.02681
1.7855E-03	2.3470E-03	0	2.2488E-02	-0.02624
1.7855E-03	2.3695E-03	0	2.2488E-02	-0.02590
1.7855E-03	2.3920E-03	0	2.2488E-02	-0.02557
1.7855E-03	2.4145E-03	0	2.2488E-02	-0.02526
1.7855E-03	2.4369E-03	0	2.2488E-02	-0.02476
1.7855E-03	2.4594E-03	0	2.2488E-02	-0.02451
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1.7855E-03	2.6393E-03	0	2.2488E-02	-0.02178
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1.7855E-03	2.6843E-03	0	2.2488E-02	-0.02130
1.7855E-03	2.7068E-03	0	2.2488E-02	-0.02102
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1.7855E-03	2.8417E-03	0	2.2488E-02	-0.01936
1.7855E-03	2.8642E-03	0	2.2488E-02	-0.01905
1.7855E-03	2.8867E-03	0	2.2488E-02	-0.01883
1.7855E-03	2.0980E-03	0	2.2488E-02	-0.03183
1.7855E-03	2.1205E-03	0	2.2488E-02	-0.03165
1.7855E-03	2.1430E-03	0	2.2488E-02	-0.03116

1.7855E-03	2.1655E-03	0	2.2488E-02	-0.03048
1.7855E-03	2.1880E-03	0	2.2488E-02	-0.03035
1.7855E-03	2.2104E-03	0	2.2488E-02	-0.02953
1.7855E-03	2.2329E-03	0	2.2488E-02	-0.02967
1.7855E-03	2.2554E-03	0	2.2488E-02	-0.02903
1.7855E-03	2.2779E-03	0	2.2488E-02	-0.02772
1.7855E-03	2.3004E-03	0	2.2488E-02	-0.02781
1.7855E-03	2.3229E-03	0	2.2488E-02	-0.02750
1.7855E-03	2.3454E-03	0	2.2488E-02	-0.02728
1.7855E-03	2.3679E-03	0	2.2488E-02	-0.02643
1.7855E-03	2.3903E-03	0	2.2488E-02	-0.02604
1.7855E-03	2.4128E-03	0	2.2488E-02	-0.02544
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1.7855E-03	2.4578E-03	0	2.2488E-02	-0.02493
1.7855E-03	2.4803E-03	0	2.2488E-02	-0.02469
1.7855E-03	2.5028E-03	0	2.2488E-02	-0.02414
1.7855E-03	2.5253E-03	0	2.2488E-02	-0.02402
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1.7855E-03	2.5702E-03	0	2.2488E-02	-0.02338
1.7855E-03	2.5927E-03	0	2.2488E-02	-0.02265
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1.7855E-03	2.6377E-03	0	2.2488E-02	-0.02230
1.7855E-03	2.6602E-03	0	2.2488E-02	-0.02186
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1.7855E-03	2.7277E-03	0	2.2488E-02	-0.02092
1.7855E-03	2.7501E-03	0	2.2488E-02	-0.02070
1.7855E-03	2.7726E-03	0	2.2488E-02	-0.02046
1.7855E-03	2.7951E-03	0	2.2488E-02	-0.02010
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1.7855E-03	2.8401E-03	0	2.2488E-02	-0.01972
1.7855E-03	2.8626E-03	0	2.2488E-02	-0.01960
1.7855E-03	2.8851E-03	0	2.2488E-02	-0.01903
1.7855E-03	2.9076E-03	0	2.2488E-02	-0.01882
7.0353E-04	2.7897E-03	0	2.2488E-02	-0.00427
7.0353E-04	2.8122E-03	0	2.2488E-02	-0.00442
7.0353E-04	2.8347E-03	0	2.2488E-02	-0.00419
7.0353E-04	2.8572E-03	0	2.2488E-02	-0.00426
7.0353E-04	2.8797E-03	0	2.2488E-02	-0.00403
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7.0353E-04	3.0596E-03	0	2.2488E-02	-0.00375
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7.0353E-04	3.1720E-03	0	2.2488E-02	-0.00350
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7.0353E-04	3.2170E-03	0	2.2488E-02	-0.00344
7.0353E-04	3.2395E-03	0	2.2488E-02	-0.00344

7.0353E-04	3.2619E-03	0	2.2488E-02	-0.00340
7.0353E-04	3.2844E-03	0	2.2488E-02	-0.00341
7.0353E-04	3.3069E-03	0	2.2488E-02	-0.00337
7.0353E-04	3.3294E-03	0	2.2488E-02	-0.00334
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7.0353E-04	3.4868E-03	0	2.2488E-02	-0.00330
7.0353E-04	3.5093E-03	0	2.2488E-02	-0.00328
7.0353E-04	3.5318E-03	0	2.2488E-02	-0.00328
7.0353E-04	3.5543E-03	0	2.2488E-02	-0.00327
7.0353E-04	3.5768E-03	0	2.2488E-02	-0.00327
7.0353E-04	3.5993E-03	0	2.2488E-02	-0.00318
7.0353E-04	3.6217E-03	0	2.2488E-02	-0.00321
7.0353E-04	3.6442E-03	0	2.2488E-02	-0.00313
7.0353E-04	3.6667E-03	0	2.2488E-02	-0.00315
7.0353E-04	3.6892E-03	0	2.2488E-02	-0.00306
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3.4483E-04	3.7027E-03	3.8314E-02	1.2099E-02	-0.16820
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4.2146E-04	3.7269E-03	3.8314E-02	1.2099E-02	-0.15954
4.5977E-04	3.7390E-03	3.8314E-02	1.2099E-02	-0.15885
4.9809E-04	3.7511E-03	3.8314E-02	1.2099E-02	-0.15922
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1.9157E-04	3.6391E-03	3.8314E-02	1.2099E-02	-0.18105
2.2989E-04	3.6512E-03	3.8314E-02	1.2099E-02	-0.17260
2.6820E-04	3.6633E-03	3.8314E-02	1.2099E-02	-0.16824
3.0652E-04	3.6754E-03	3.8314E-02	1.2099E-02	-0.16581
3.4483E-04	3.6875E-03	3.8314E-02	1.2099E-02	-0.16194
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4.9809E-04	3.7359E-03	3.8314E-02	1.2099E-02	-0.15496
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1.5326E-04	3.6318E-03	3.8314E-02	1.2099E-02	-0.19720
1.9157E-04	3.6439E-03	3.8314E-02	1.2099E-02	-0.18670

2.2989E-04	3.6560E-03	3.8314E-02	1.2099E-02	-0.18030
2.6820E-04	3.6681E-03	3.8314E-02	1.2099E-02	-0.17414
3.0652E-04	3.6802E-03	3.8314E-02	1.2099E-02	-0.16959
3.4483E-04	3.6923E-03	3.8314E-02	1.2099E-02	-0.16575
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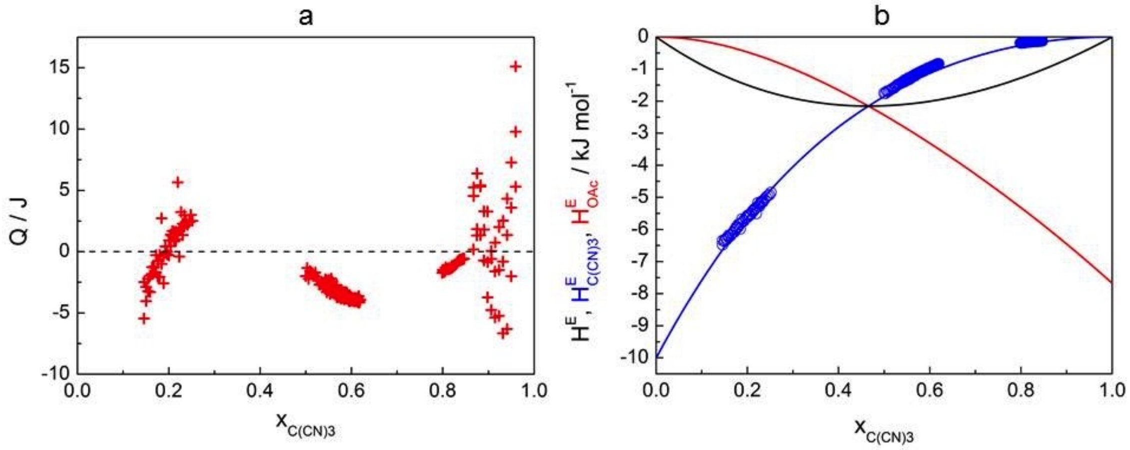

Figure S3. (a) Absolute deviation of experimental ITC data from the adjusted Redlich-Kister curve and (b) partial excess enthalpy for both ILs (H^{E}_{OAc} and $H^{E}_{C(CN)3}$ for [C_4C_1Im][OAc] and [C_4C_1Im][$C(CN)_3$], respectively) together with excess enthalpy of the mixture (H^E) after ITC data treatment.

Table S4. Parameters obtained from fitting experimental data of partial excess enthalpies upon mixing $[C_4C_1Im][An1]$ with $[C_4C_1Im][An2]$ to form the mixture $[C_4C_1Im][An1]_{(1-x)}[An2]_x$. The parameters A_i are in kJ mol^{-1} and the partial molar excess enthalpies at infinite dilution ($\overline{H}_{IL}^{E,\infty}$ / kJ mol^{-1}) for IL1 and IL2.

$[C_4C_1Im][An1]_{(1-x)}[An2]_x$	A_0	A_1	A_2	$\overline{H}_{IL1}^{E,\infty}$	$\overline{H}_{IL2}^{E,\infty}$
$[C_4C_1Im][OAc]_{(1-x)}[CCN)_3]_x$	−8.580	−1.168	−0.265	−7.677	−10.012
$[C_4C_1Im][NTf_2]_{(1-x)}[PF_6]_x$	1.656	−0.211	0.088	1.955	1.533
$[C_4C_1Im][BF_4]_{(1-x)}[PF_6]_x$	−0.486	0.120	0.271	−0.335	−0.095
$[C_4C_1Im][MeSO_4]_{(1-x)}[BF_4]_x$	-1.425	0.085	0.577	−0.933	−0.763

Table S5. Experimental viscosities (η) of $[C_4C_1Im][OAc]_{(1-x)}[C(CN)_3]_x$ mixtures as a function of the composition, expressed in mole fraction of $[C_4C_1Im][C(CN)_3]$, $x_{C(CN)3}$, and as a function of temperature.

$[C_4C_1Im][OAc]_{(1-x)}[C_4C_1Im][C(CN)_3]_x$					
$x_{C(CN)3}$	η / mPa.s	$x_{C(CN)3}$	η / mPa.s	$x_{C(CN)3}$	η / mPa.s
T = 293.15 K		T = 298.15 K		T = 303.15 K	
0.0000	551.01	0.0000	370.9	0.0000	255.37
0.2524	249.29	0.2524	174.13	0.2524	125.49
0.5007	111.43	0.5007	81.864	0.5007	62.111
0.7499	55.097	0.7499	42.515	0.7499	33.895
1.0000	32.977	1.0000		1.0000	21.767
T = 313.15 K		T = 323.15 K		T = 333.15 K	
0.0000	133.77	0.0000	77.166	0.0000	48.416
0.2524	70.732	0.2524	43.743	0.2524	28.976
0.5007	38.197	0.5007	25.349	0.5007	18.11
0.7499	22.605	0.7499	16.423	0.7499	12.165
1.0000	15.67	1.0000	11.657	1.0000	9.0056
T = 343.15 K		T = 353.15 K			
0.0000	32.291	0.0000	22.704		
0.2524	20.317	0.2524	15.167		
0.5007	13.425	0.5007	10.266		
0.7499	9.3253	0.7499	7.3853		
1.0000	6.7708	1.0000	5.5259		

Table S6. Correlation parameters of the VFT equation (A, k and T0) with the average absolute deviation of the fit (AAD) for the viscosity of the ILs mixtures.

IL	**A /10^{-3} mPa.s.$K^{-1/2}$**	**k / K**	**T_0 / K**	**AAD /%**
$[C_4C_1Im][OAc]$	2.99	1006.92	184.7	-0.51
$[C_4C_1Im][OAc]_{0.75}[C(CN)_3]_{0.25}$	6.00	785.42	192.4	-0.12
$[C_4C_1Im][OAc]_{0.50}[C(CN)_3]_{0.50}$	9.71	637.58	195.2	-0.03
$[C_4C_1Im][OAc]_{0.25}[C(CN)_3]_{0.75}$	1.17	573.10	191.1	0.20
$[C_4C_1Im][C(CN)_3]$	4.86	795.75	160.1	0.13

Table S7. Deviations of viscosity from the linear average ($\Delta\eta = \eta_{mix} - \sum_{i=1}^{n} x_i \eta_i$) of $[C_4C_1Im][OAc]_{(1-x)}[C(CN)_3]_x$ mixtures as a function of the composition, expressed in mole fraction of $[C_4C_1Im][C(CN)_3]$, $x_{C(CN)3}$, and as a function of temperature.

		$[C_4C_1Im][OAc]_{(1-x)}[C(CN)_3]_x$			
$x_{C(CN)3}$	Δη / mPa.s	$x_{C(CN)3}$	Δη / mPa.s	$x_{C(CN)3}$	Δη / mPa.s
T = 293.15 K		T = 303.15 K		T = 313.15 K	
0.0000	0.0	0.0000	0.0	0.0000	0.0
0.2524	-171.0	0.2524	-70.9	0.2524	-33.2
0.5007	-180.2	0.5007	-76.3	0.5007	-36.4
0.7499	-107.4	0.7499	-46.3	0.7499	-22.6
1.0000	0.0	1.0000	0.0	1.0000	0.0
T = 323.15 K		T = 333.15 K		T = 343.15 K	
0.0000	0.0	0.0000	0.0	0.0000	0.0
0.2524	-16.9	0.2524	-9.5	0.2524	-5.5
0.5007	-19.0	0.5007	-10.6	0.5007	-6.1
0.7499	-11.6	0.7499	-6.7	0.7499	-3.8
1.0000	0.0	1.0000	0.0	1.0000	0.0
T = 353.15 K					
0.0000	0.0				
0.2524	-3.2				
0.5007	-3.8				
0.7499	-2.4				
1.0000	0.0				

Table S8. Experimental self-diffusion coefficients of $C_4C_1Im^+$, OAc^- and $C(CN)_3^-$ in $[C_4C_1Im][OAc]_{(1-x)}[C(CN)_3]_x$ mixtures at 323 K as a function of anion composition.

$x_{C(CN)3}$	D / 10^{-11} m^2 s^{-1}		
	$C_4C_1Im^+$	OAc^-	$C(CN)_3^-$
0.00	2.00	2.02	---
0.25	3.68	3.37	4.76
0.50	5.97	5.31	7.19
0.75	9.31	7.33	10.7
1.00	13.4	---	14.3

Table S9. Experimental ionic conductivity of $[C_4C_1Im][OAc]$, $[C_4C_1Im][C(CN)_3]$ and their mixtures at 298 K as a function of composition.

$x_{C(CN)3}$	κ / mS cm^{-1}
0.0000	0.83
0.2524	1.41
0.5007	2.88
0.7499	6.13
1.0000	11.23

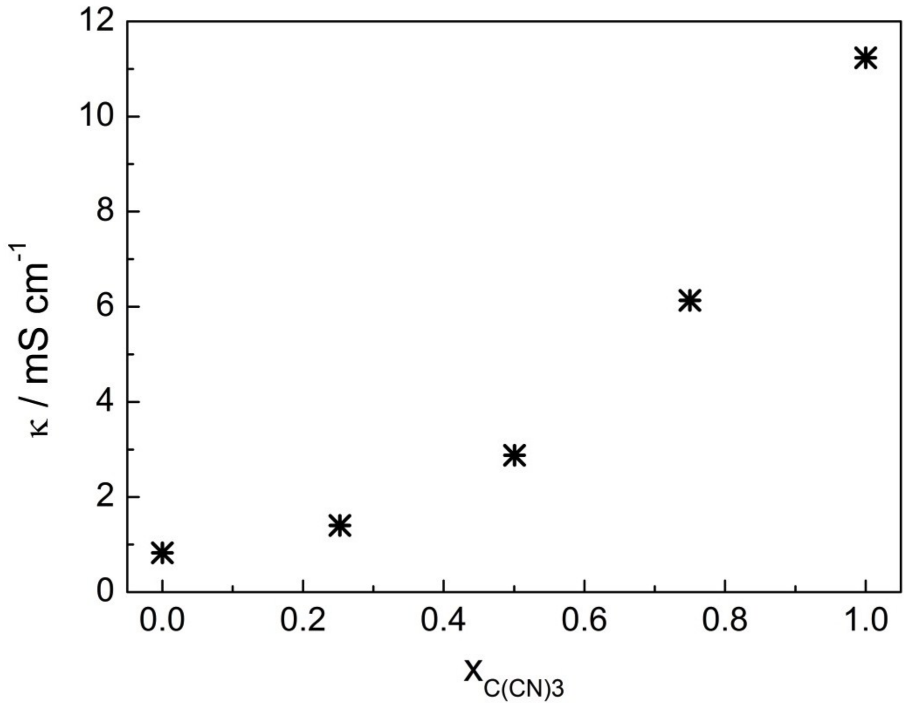

Figure S4. Ionic conductivity $[C_4C_1Im][OAc]_{(1-x)}[C(CN)_3]_x$ mixtures as a function of $C(CN)_3^-$ at 298.15 K.

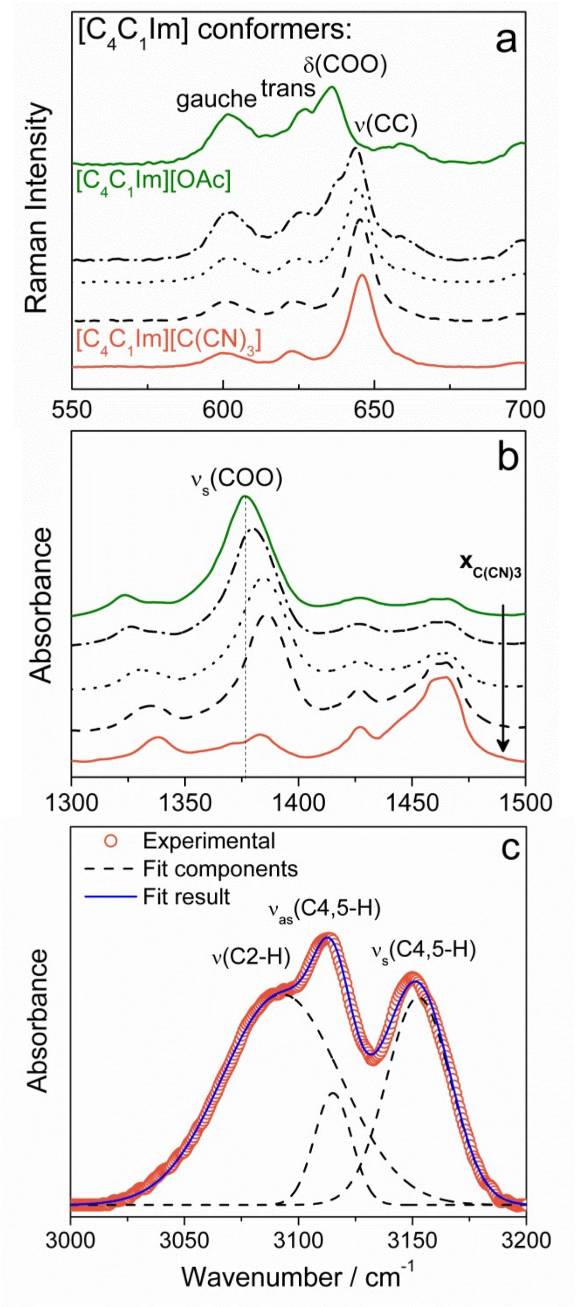

Figure S5. (a) Raman spectra of the pure $[C_4C_1Im][OAc]$ (green line), pure $[C_4C_1Im][C(CN)_3]$ (orange line) and their mixtures in the region of *gauche* and *trans* conformers of $C_4C_1Im^+$ cation. Infrared spectra of (b) pure ILs and their mixtures in the range of COO symmetric stretching, ν_s(COO), and (c) $[C_4C_1Im][C(CN)_3]$ in the region of C-H bands of the imidazolium ring.

Table S10. ^{1}H chemical shifts observed for $[C_4C_1Im][OAc]_{(1-x)}[C(CN)_3]_x$ mixtures at 298 K as a function of anion composition.

$x_{C(CN)3}$	δ / ppm		
	H(C2)	H(C4)	H(C5)
0.0000	10.42	8.08	8.23
0.2512	9.99	7.56	7.66
0.5007	9.67	7.32	7.37
0.7499	9.27	7.35	7.39
1.0000	8.45	7.2	7.26

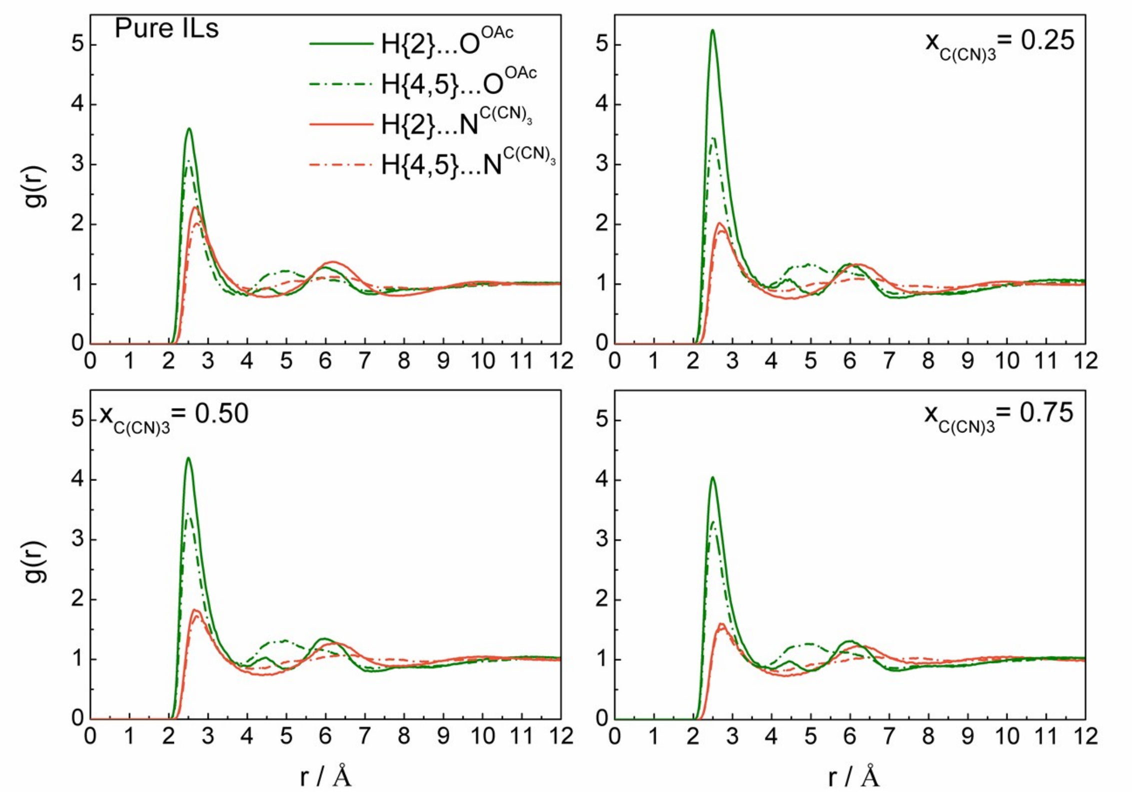

Figure S6. Site-site radial pair distribution functions, g(r), of $[C_4C_1Im][OAc]_{(1-x)}[C(CN)_3]_x$ mixtures. H{2} and H{4,5} correspond to the hydrogen bond donors positioned in C2, C4 and C5 of the imidazolium ring, respectively. O and N correspond to the hydrogen bond acceptors (oxygen and nitrogen atoms) in the OAc^- and $C(CN)_3^-$ anions, respectively.

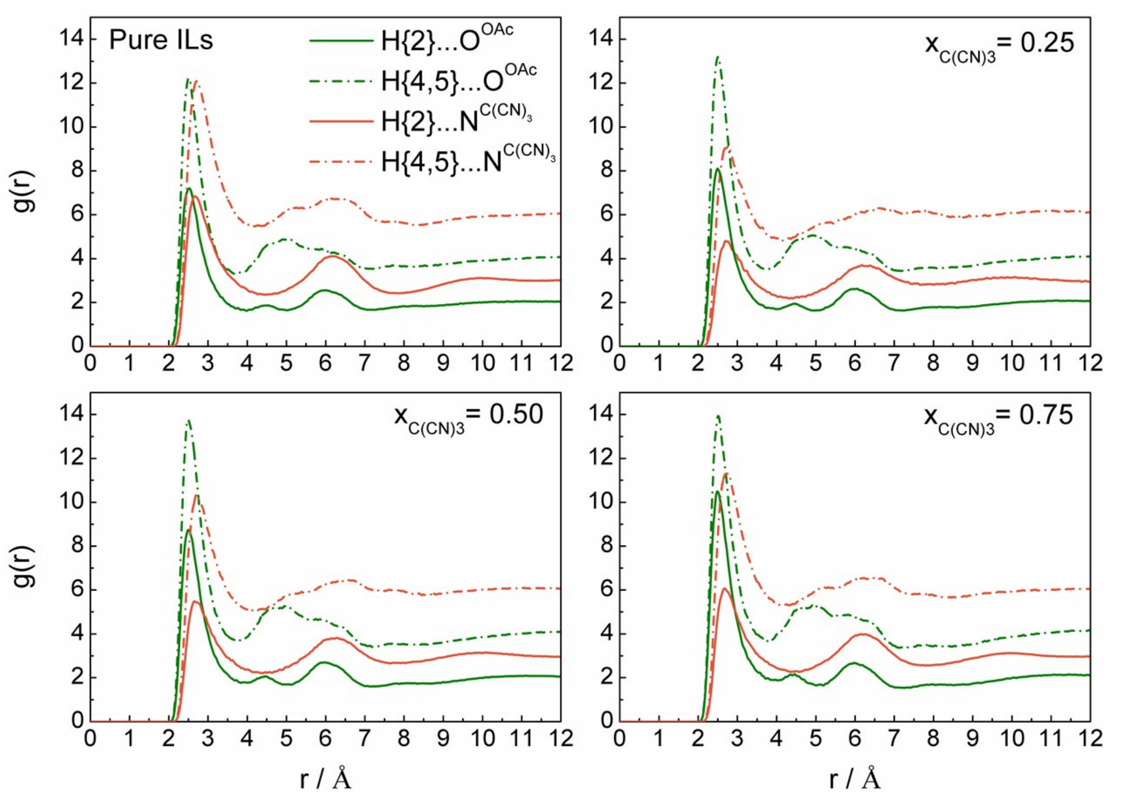

Figure S7. Un-normalized site-site radial distribution functions of $[C_4C_1Im][OAc]_{(1-x)}[C(CN)_3]_x$ mixtures with respect to the number of possible H-bonds between donor H atoms on the imidazolium cation and acceptor O or N atoms in the two anions (e.g., two possible H-bonds can occur between the H_2 and the two O atoms from acetate, but four possible H-bonds can occur between $H_{4,5}$ and O). This allows comparison of the height of the first peaks corresponding to the probability of different H-bonds.

Table S11. Total (E_{TOT}), Coulomb (E_{Coul}) and Van der Waals (E_{VDW}) energies, volume of the box (V), pV term, enthalpy (H) and calculated enthalpy (H_{calc}) of the system, and enthalpy of mixing (Δ_{mixH}).

$x_{C(CN)3}$	1.00	0.75	0.50	0.25	0.00
E_{TOT} / kJ mol^{-1}	-81.8 ± 2.8	-93.4 ± 2.8	-104.5 ± 2.8	-115.7 ± 2.7	-126.1 ± 2.8
E_{Coul} / kJ mol^{-1}	-207.2	-216.6	-225.5	-234.2	-242.4
E_{VDW} / kJ mol^{-1}	-84.9	-84.5	-84.1	-83.7	-83.3
V / Å^3 (100 ion pairs)	38730.5	37237.7	35761.8	34278.0	32881.0
pV / kJ mol^{-1}	2.3	2.3	2.1	2.1	2.0
H / kJ mol^{-1}	-79.4 ± 2.8	-91.2 ± 2.9	-102.3 ± 2.8	-113.6 ± 2.7	-124.1 ± 2.8
H_{calc} / kJ mol^{-1}		-90.6 ± 2.8	-101.8 ± 2.8	-112.9 ± 2.8	
$\Delta_{mix}H$ / kJ mol^{-1}		-0.6	-0.6	-0.7	

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