# Supporting Information

## Solid-liquid equilibria of binary mixtures of fluorinated ionic liquids

Ana Rita R. Teles[a], Helga Correia[a], Guilherme J. Maximo[b], Luís P. N. Rebelo[c], Mara G. Freire[a], Ana B. Pereiro[c*] andJoão A. P. Coutinho[a]


[a] CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal.

[b] Laboratory of Extraction, Applied Thermodynamics and Equilibrium, School of Food Engineering, University of Campinas, Campinas, São Paulo, Brazil

[c] Instituto de Tecnologia Química e Biológica António Xavier (www.itqb.unl.pt), UNL, Av. República, Apartado 127, 2780-901 Oeiras, Portugal.

**Table S1**. Experimental data for the melting temperatures, enthalpies of fusion, transition temperatures, and enthalpies of transition for the system $x$ [C$_4$C$_1$pyr] [N(C$_4$F$_9$SO$_2$)$_2$] + (1-$x$) [C$_4$C$_1$pyr] [C$_4$F$_9$SO$_3$].

| $x_{[C4C1pyr][N(C4F9SO2)2]}$ | $T_{fus}$ / K | $\Delta_{fus}H$ / KJ·mol$^{-1}$ | $T_{Tr1}$/K | $\Delta_{Tr1}H$/KJ·mol$^{-1}$ |
|---|---|---|---|---|
| 0.00 | 361 | 13 | - | - |
| 0.07 | 358 | 21 | - | - |
| 0.17 | 348 | 12 | 305 | 1.9 |
| 0.29 | 334 | 6.3 | 307 | 3.3 |
| 0.38 | 323 | 2.0 | 305 | 5.9 |
| 0.48 | 312 | 0.28 | 306 | 9.2 |
| 0.59 | 315 | 0.22 | 306 | 7.2 |
| 0.69 | 332 | 2.6 | 305 | 2.9 |
| 0.74 | 339 | 1.7 | 305 | 1.8 |
| 0.79 | 348 | 2.6 | - | - |
| 0.84 | 356 | 4.7 | - | - |
| 0.89 | 363 | 5.5 | - | - |
| 0.93 | 368 | 7.6 | - | - |
| 1.00 | 374 | 6.0 | - | - |

**Table S2**. Experimental data for the melting temperatures, enthalpies of fusion, transition temperatures, and enthalpies of transition for the system $x$ [C$_2$C$_1$pyr] [N(C$_4$F$_9$SO$_2$)$_2$] + (1-$x$) [C$_2$C$_1$pyr] [CF$_3$SO$_3$].

| $x_{[C2C1pyr][N(C4F9SO2)2]}$ | $T_{fus}$/ K | $\Delta_{fus}H$/KJ.mol$^{-1}$ | $T_{Tr1}$/K | $\Delta_{Tr1}H$/ KJ.mol$^{-1}$ |
|---|---|---|---|---|
| 0.00 | 384 | 6.7 | - | - |
| 0.09 | 372 | 18 | 355 | 6.9 |
| 0.21 | 365 | 8.5 | 357 | 13 |
| 0.27 | 361 | 5.0 | 357 | 17 |
| 0.33 | 360 | 1.8 | 357 | 18 |
| 0.38 | 357 | 18 | 357 | 18 |
| 0.46 | 365 | 2.5 | 356 | 15 |
| 0.59 | 377 | 6.2 | 356 | 10 |
| 0.67 | 387 | 2.8 | 355 | 6.1 |
| 0.77 | 399 | 3.6 | 353 | 4.1 |
| 0.89 | 417 | 2.7 | 348 | 0.54 |
| 1.00 | 431 | 7.9 | - | - |

**Table S3**. Experimental data for the melting points and enthalpies of fusion for the system $x$ [C$_4$C$_1$pyr] [N(C$_4$F$_9$SO$_2$)$_2$] + (1-$x$) [C$_2$C$_1$pyr] [N(C$_4$F$_9$SO$_2$)$_2$].

| $x_{[C4C1pyr][N(C4F9SO2)2]}$ | $T_{fus}$/ K | $\Delta_{fus}H$/KJ.mol$^{-1}$ |
|---|---|---|
| 0.00 | 431 | 16 |
| 0.10 | 425 | 16 |
| 0.24 | 411 | 14 |
| 0.39 | 401 | 13 |
| 0.49 | 395 | 13 |
| 0.59 | 391 | 13 |
| 0.74 | 384 | 12 |
| 0.89 | 380 | 12 |
| 1.00 | 373 | 12 |

**Table S4**. Experimental data for the melting temperatures, enthalpies of fusion, transition temperatures, and enthalpies of transition for the system $x$ [C$_4$C$_1$pyr] [C$_4$F$_9$SO$_3$] + (1-$x$) [N$_{1112(OH)}$] [C$_4$F$_9$SO$_3$].

| $x_{[C4C1pyr][N(C4F9SO2)2]}$ | $T_{fus}$/ K | $\Delta_{fus}H$/KJ.mol$^{-1}$ | $T_{Tr1}$/ K | $\Delta_{Tr1}H$/KJ.mol$^{-1}$ | $T_{Tr2}$/ K | $T_{Tr3}$/ K |
|---|---|---|---|---|---|---|
| 0.00 | 449 | 3.7 | - | 1.4 | 406 | 378 |
| 0.06 | 436 | 7.2 | 367 | 2.1 | 408 | 373 |
| 0.09 | 429 | 6.1 | 360 | 2.9 | 406 | 374 |
| 0.15 | 417 | 2.3 | 358 | 3.0 | 404 | - |
| 0.21 | 403 | 1.7 | 358 | 1.7 | - | 371 |
| 0.22 | 400 | 1.4 | 356 | 1.4 | - | 374 |
| 0.24 | 400 | 1.2 | 359 | 1.1 | - | 375 |
| 0.28 | 390 | 4.9 | 359 | 5.6 | - | 379 |
| 0.32 | 378 | 6.8 | 358 | 0.92 | - | - |
| 0.38 | 377 | 7.6 | 358 | 1.8 | - | - |
| 0.48 | 378 | 9.8 | 361 | 1.7 | - | - |
| 0.58 | 377 | 12 | 364 | 2.2 | - | - |
| 0.68 | 377 | 13 | 365 | 3.9 | - | - |
| 0.78 | 374 | 18 | 361 | 3.2 | - | - |
| 0.85 | 369 | 19 | 356 | 5.4 | - | - |
| 0.94 | 361 | 20 | - | - | - | - |
| 1.00 | 361 | 25 | - | - | - | - |
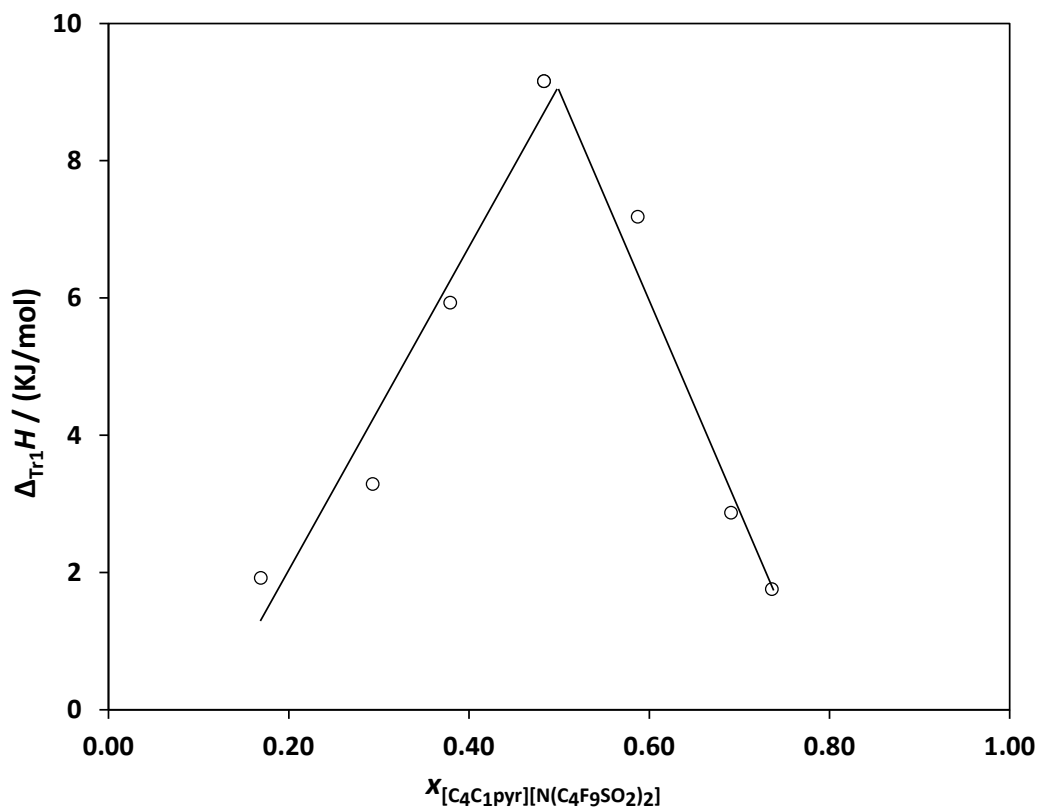
**Fig.S1**.Tamman plot for the binary system $x$ [C$_4$C$_1$pyr] [N(C$_4$F$_9$SO$_2$)$_2$] **+** (1-$x$) [C$_4$C$_1$pyr] [C$_4$F$_9$SO$_3$]:(O) enthalpy of the eutectic transition, $\Delta_{Tr1}H$, versus mole fraction of [C$_4$C$_1$pyr] [N(C$_4$F$_9$SO$_2$)$_2$]. Solid lines represent linear fits to the enthalpy values.
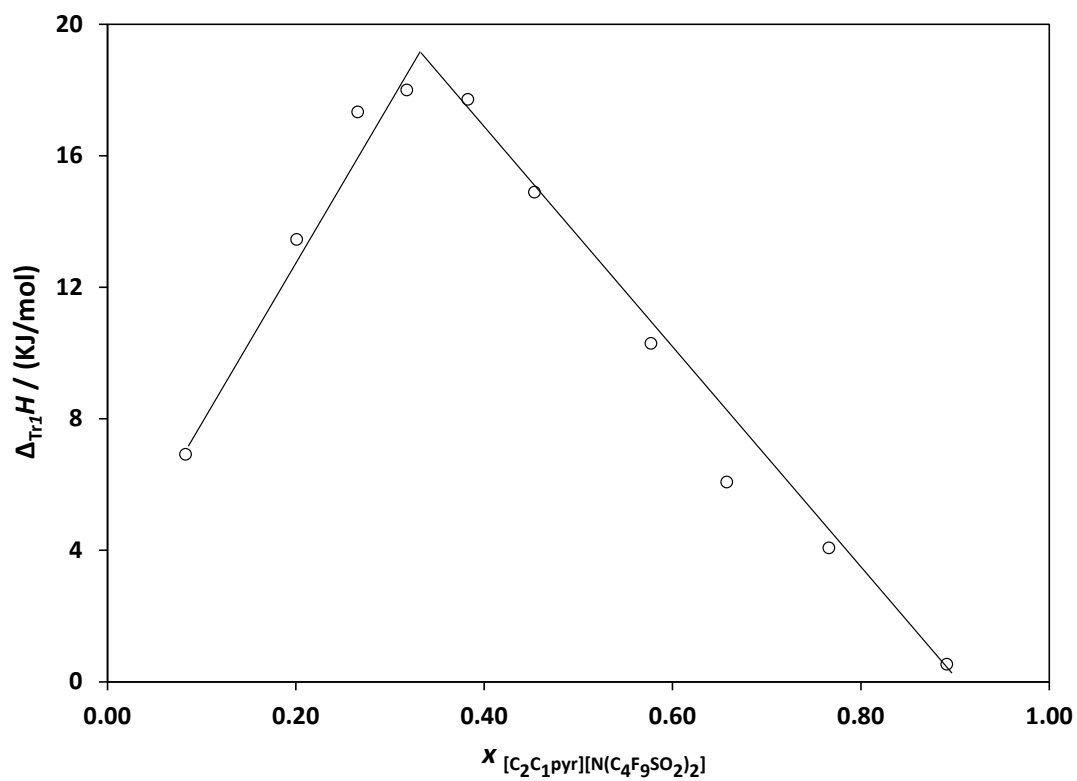


**Fig.S2**.Tamman plot for the binary system $x$ [C$_2$C$_1$pyr] [N(C$_4$F$_9$SO$_2$)$_2$] + (1-$x$) [C$_2$C$_1$pyr] [CF$_3$SO$_3$]: (O) enthalpy of the eutectic transition, $\Delta_{Tr1}H$, versus mole fraction of [C$_2$C$_1$pyr] [N(C$_4$F$_9$SO$_2$)$_2$]. Solid lines represent linear fits to the enthalpy values.

## Viscosity and density measurements

### Experimental methods

Viscosity and density measurements of mixtures composed of $[C_4C_1pyr]$ $[N(C_4F_9SO_2)_2]$ + $[C_4C_1pyr]$ $[C_4F_9SO_3]$ with mole fraction of 0.40, 0.50 and 0.60, were performed in the temperature range between 328.15and 363.15 K, at atmospheric pressure, using an automated SVM 3000 Anton Paar rotational Stabinger viscometer-densimeter. The SVM 3000 uses Peltier elements for fast and efficient thermostability. The relative uncertainty for the dynamic viscosity values is 0.5 % and the absolute uncertainty for the density values is 0.0005 g·cm$^{-3}$.

### Results and discussion

The density and dynamic viscosity of mixtures close to the eutectic point for the binary system $[C_4C_1pyr]$ $[N(C_4F_9SO_2)_2]$ + $[C_4C_1pyr]$ $[C_4F_9SO_3]$ were determined, at atmospheric pressure and as a function of temperature, in order to better characterize this mixture. The experimental results are reported in Table S5 of ESI and displayed in Figure S3. The molar volumes for these mixtures were also calculated from density data and are plotted in Figure S4.

These measurements show that the increment of the amount of $[C_4C_1pyr]$ $[N(C_4F_9SO_2)_2]$ for a specific temperature implies an increment in both the density and molar volume, and a decrease in the viscosity. It is important to note that, generally, the mixing of two ionic liquids involves the mixing of four ions (in this case only three ions because this mixture has a common ion, the $[C_4C_1pyr]^+$ cation). Therefore, the mixtures' physical properties reflect the amounts present of different chemical moieties, in this case the presence of either the $[N(C_4F_9SO_2)_2]^-$ or the $[C_4F_9SO_3]^-$ anion. The incorporation of the $[N(C_4F_9SO_2)_2]^-$ anion increases the volume of the fluorinated domains in the binary mixture, thus causing a decrease in the intensity of the Coulombic interactions. These facts might justify the decrease of the dynamic viscosity with the increasing incorporation of this anion. Furthermore, the greater number of fluor atoms causes an increment in the density and also justifies the increment of molar volume when the amount of $[C_4C_1pyr]$ $[N(C_4F_9SO_2)_2]$ increases. The number of fluor atoms and the volume of the $[N(C_4F_9SO_2)_2]^-$ anion is obviously higher than that of the $[C_4F_9SO_3]^-$ anion.

**Table S5**. Experimental data for the viscosity and density measurements for the system $[C_4C_1pyr]$ $[N(C_4F_9SO_2)_2]$ + $[C_4C_1pyr]$ $[C_4F_9SO_3]$ in the eutectic region.

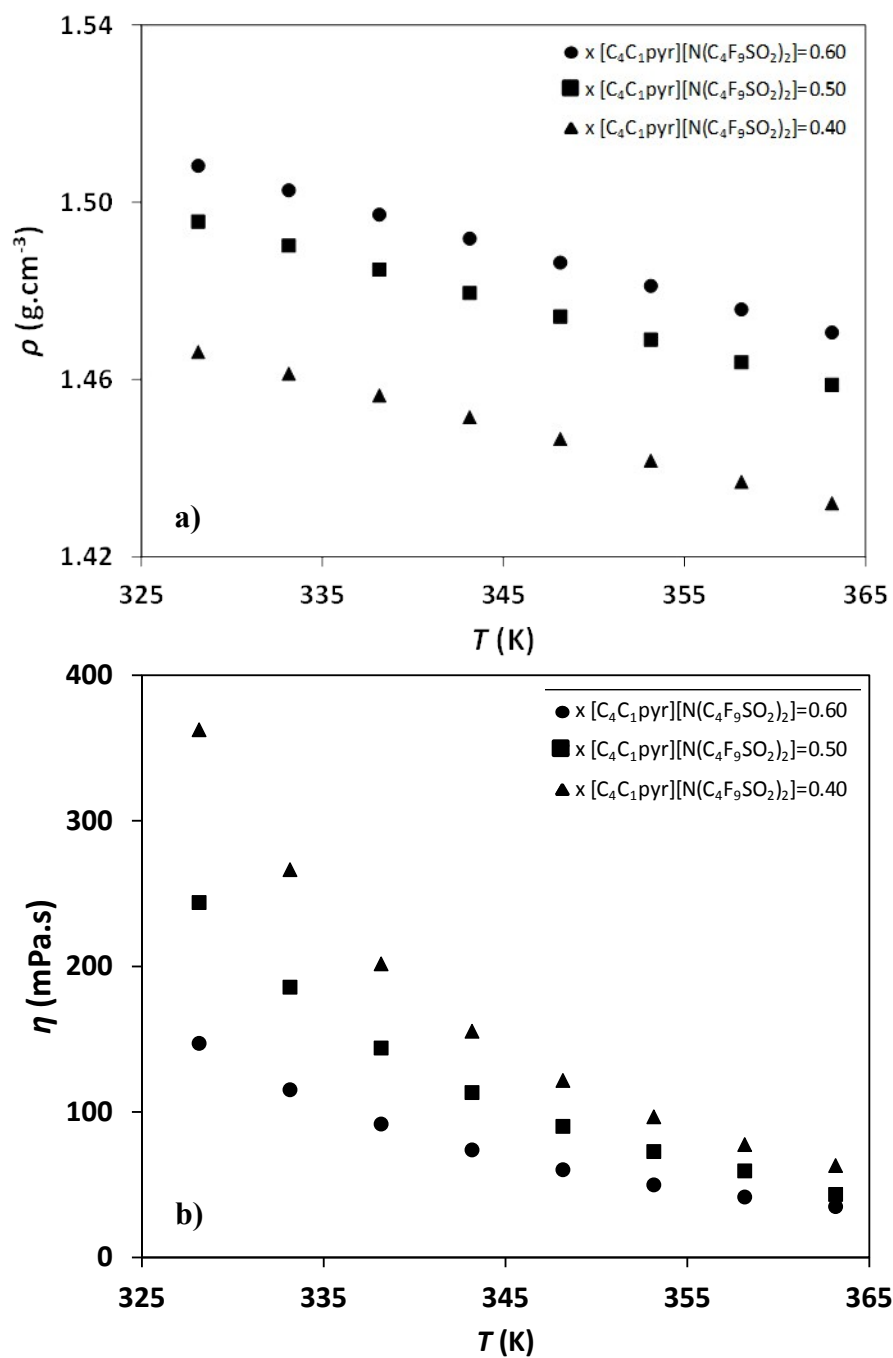| $T$/ K | $x_{[C4C1pyr][N(C4F9SO2)2]} = 0.38$ | | $x_{[C4C1pyr][N(C4F9SO2)2]} = 0.48$ | | $x_{[C4C1pyr][N(C4F9SO2)2]} = 0.59$ | |
| --- | --- | --- | --- | --- | --- | --- |
| | $\eta$/ mPa·s | $\rho$/ g.cm$^{-1}$ | $\eta$/ mPa·s | $\rho$/ g.cm$^{-1}$ | $\eta$/ mPa·s | $\rho$/ g.cm$^{-1}$ |
| 328.15 | 147.1 | 1.4662 | 155.3 | 1.4848 | 143.8 | 1.4972 |
| 333.15 | 115.2 | 1.4613 | 121.5 | 1.4795 | 113.2 | 1.4918 |
| 338.15 | 91.59 | 1.4564 | 96.55 | 1.4742 | 89.99 | 1.4864 |
| 343.15 | 73.87 | 1.4515 | 77.55 | 1.4690 | 72.67 | 1.4811 |
| 348.15 | 60.28 | 1.4466 | 63.17 | 1.4639 | 59.42 | 1.4758 |
| 353.15 | 49.78 | 1.4417 | 52.06 | 1.4588 | 43.19 | 1.4706 |
| 358.15 | 41.50 | 1.4369 | 43.34 | 1.4538 | 36.02 | 1.4655 |
| 363.15 | 34.97 | 1.4321 | 36.42 | 1.4489 | 30.28 | 1.4604 |

**Fig. S3.** Density and dynamic viscosity of some mixtures close to the eutectic region for the binary system $x$ [$C_4C_1$pyr] [$N(C_4F_9SO_2)_2$] + (1-$x$) [$C_4C_1$pyr] [$C_4F_9SO_3$].
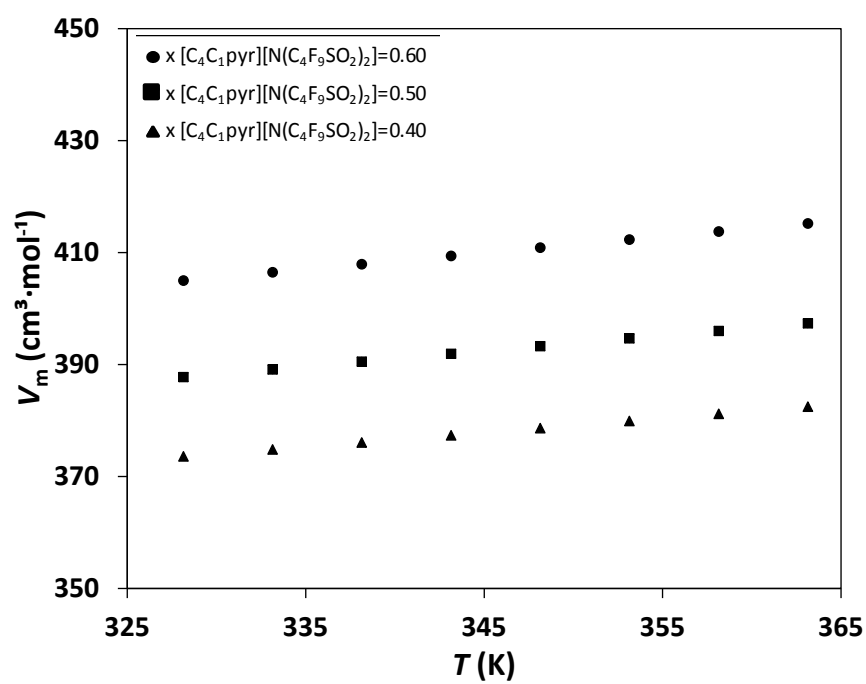
**Fig. S4**. Molar volume of some mixtures in the eutectic region for the system $x$ [$C_4C_1$pyr] [N($C_4F_9SO_2$)$_2$] + (1-$x$) [$C_4C_1$pyr] [$C_4F_9SO_3$].
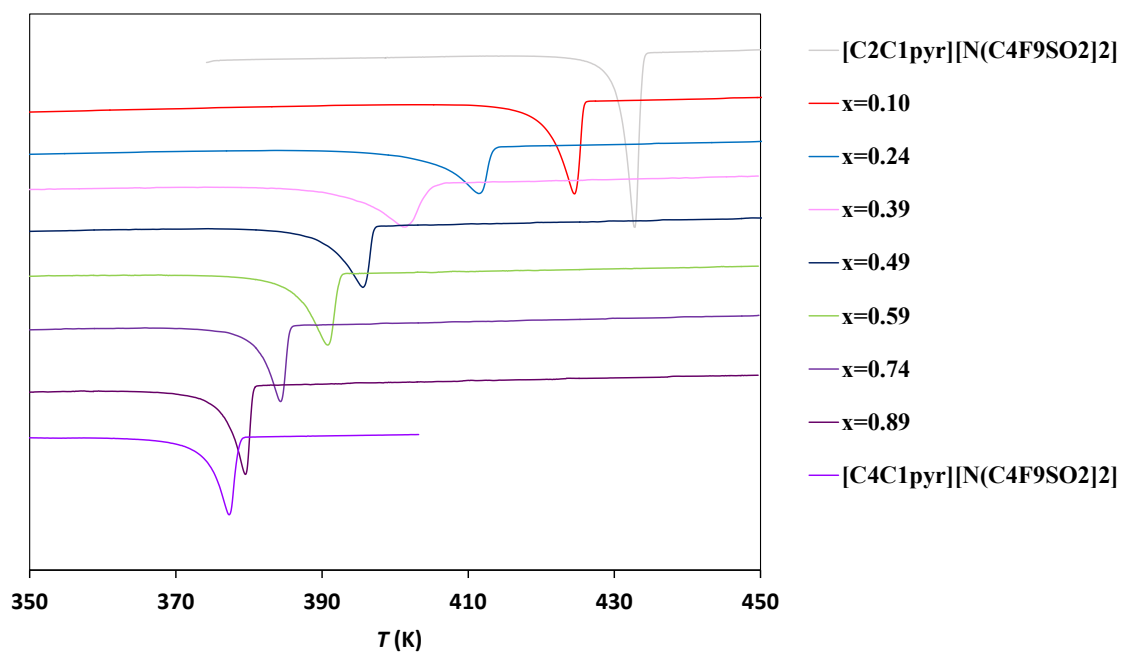
**Fig. S5**. DSC thermograms (heating run) for the binary mixture $x$ [$C_4C_1$pyr] [$N(C_4F_9SO_2)_2$] + (1-$x$) [$C_2C_1$pyr] [$N(C_4F_9SO_2)_2$].