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

Using hydrogenated and perfluorinated gases to probe the interactions and structure of fluorinated ionic liquids

Luiz Fernando Lepre,[a] Laure Pison,[b] Ines Otero,[b] Arnaud Gautier,[b] Julien Dévemy,[b] Pascale Husson,[b] Agilio Padua[a] and Margarida Costa Gomes [*a]

** margarida.costa-gomes@ens.lyon.fr*

[a] Laboratoire de Chimie de l'ENS de Lyon, CNRS and ENS de Lyon, 69007 Lyon, France

[b] Institut de Chimie de Clermont-Ferrand, CNRS and Université Clermont Auvergne, Aubière, France

Supplementary Information

Synthesis of the ionic liquids

The toluene, 1-bromo hexane and 1-iodo-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro octane samples were used for the synthesis as received. The ethyl acetate, dichloromethane and *N*-methyl imidazole samples were distilled prior to their use.

Synthesis of 1-octyl-3-methylimidazolium bromide, [C_8C_1Im][Br]:

1-bromo hexane (27.8 g, 145 mmol, 1.18 equ.) was dissolved in 30 mL of toluene. *N*-methyl imidazole (10 g, 122 mmol, 1.0 equ.) dissolved in 20 mL of toluene was added and argon was bubbled for 30 minutes through the solution. The reaction was heated at 50°C for 48h under argon atmosphere. After cooling to room temperature, ethyl acetate (100 mL) was added, the solution was stirred for 30 minutes and the two observed layers were separated. The resulting product was left under high vacuum at 50°C for one day to furnish 28.4 g (85% yield) of a pale brownish liquid. ^{1}HNMR(dmso-d_6, 400MHz) δ(ppm)= 9.09 (t, J^4=1.8Hz, 1H); 7.76(t, J^4=1.8Hz, 1H); 7.69(t, J^4=1.8Hz, 1H); 4.14(t, J^3=7.3Hz, 2H); 3.84 (s, 3H); 1.77(m, 2H); 1.25(m, 10H); 0.86(t, J^3=6.8Hz, 3H).

Synthesis of 1-octyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)amide, [C_8C_1Im][BETI]:

[C_8C_1Im][Br] (4.81 g, 17.5 mmol, 1.0 eq.) was dissolved in 20 mL of bi-distilled water and then boiled in presence of 75-100 mg of charcoal for 30 minutes under argon atmosphere. After cooling to room temperature, the solution was filtered over a plug of celite and washed with 20 mL of bi-distilled water to furnish a colorless solution. [Li][BETI] (7.8 g, 20.15 mmol, 1.15 equ.) dissolved in 30 mL of bi-distilled water was then added under stirring. The solution was heated at 60°C for 2h and left at room temperature overnight. Bi-distilled water (50 mL) was added and the solution was extracted 5 times with dichloromethane (150 mL). The organic layer was dried over $MgSO_4$, and then evaporated. The resulting product was dried under high vacuum at 60°C for two days to furnish 8.4 g of a colorless liquid (yield: 78%). ^{1}HNMR(dmso-d_6, 400MHz) δ (ppm)= 9.09 (t, J^4=1.8Hz, 1H); 7.76(t, J^4=1.8Hz, 1H); 7.69(t, J^4=1.8Hz, 1H); 4.14(t, J^3=7.3Hz, 2H); 3.84 (s, 3H); 1.77(m, 2H); 1.25(m, 10H); 0.86(t, J^3=6.8Hz, 3H).

Synthesis of 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium iodide, [$C_8H_4F_{13}C_1$Im][I]:

N-Methyl Imidazole (3.77 g, 46.0 mmol, 1.0 equ.) was dissolved in 36 mL of toluene. 1-iodo(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro)octane (24.0 g, 50.6 mmol, 1.1 equ.) was added and argon was bubbled through the solution for 30 minutes. The reaction flask was capped, heated for 2 days at 75°C and cooled to room temperature before being placed at -20°C for 4-6 hours to form yellow crystals. The solid was filtered, washed 3 times with ether (20 mL), one time with the pentane (20 mL) and dried on air to furnish 15.9 g of a yellow solid (62% yield) of melting point of 51-52°C. ^{1}H NMR (400 MHz, dmso-d_6) δ (ppm): 9.21 (s, 1H); 7 .89 (t, J^3=1.7Hz, 1H); 7.74 (t, J^3=1.8Hz, 1H); 4.57 (t, J^3= 7.0, 2H); 3.02 (m, 2H); 3.88 (s, 3H). ^{13}C NMR (100 MHz, acetone-d_6) δ (ppm): 139.0;

124.9; 123.8; 122-108: multiple untreatable signal (CF_2), see Fig S0 ; 42.7 (t, J^3= 5,4Hz); 37.4 ; 31.3 (t, J= 21.5Hz).

Synthesis of 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, [$C_8H_4F_{13}C_1Im$][NTf_2], and 1-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-3-methylimidazolium bis(pentafluoroethylsulfonyl)amide, [$C_8H_4F_{13}C_1Im$][BETI]:

[$C_8H_4F_{13}C_1Im$][I] (14.0 g, 25.2 mmol, 1.0 equ.) was dissolved in 130 mL of bi-distilled water and the solution was heated at 60°C and 1.2 equ. of [Li][NTf_2] or [Li][BETI], dissolved in 85 mL of bi-distilled water, were added dropwise under vigorous stirring. The solution was stirred for 2 hours at 60°C to furnish two layers. After cooling to room temperature, 550 mL of dichloromethane and 250mL of bi-distilled water were added, the solution was vigorously stirred for 20 minutes then the layers were separated. The organic layer was washed 5 times with bi-distilled water – when silver test of the aqueous phase becomes negative. The organic layer was dried over $MgSO_4$, evaporated and then dried under high vacuum for two days to furnish a pale yellow liquid that spontaneously solidify after several days. This procedure rendered 11.0 g of [$C_8H_4F_{13}C_1Im$][NTf_2] (yield: 60%) or 13.1 g of [$C_8H_4F_{13}C_1Im$][BETI] (yield: 63%). $C_8H_4F_{13}C_1Im$][NTf_2] and [$C_8H_4F_{13}C_1Im$][BETI] ^{1}H NMR (400 MHz, acetone-d_6) δ (ppm): 9.28 (s, 1H); 7.78 (t, J^3=1,8Hz, 1H); 7.95 (t, J^3=1.8Hz, 1H); 4.85 (t, J^3=7,3Hz, 2H); 4.09 (s, 3H); 3.13 (m, 2H). [$C_8H_4F_{13}C_1Im$][NTf_2], ^{13}C NMR (100 MHz, dmso-d_6) δ (ppm): 137.8; 124.0; 122.9; 120.0 (q, J^1 = 320Hz); 120-108: multiple untreatable signal (CF_2), see Fig S0; 41.8 (t, J = 5.4Hz, CH_2); 35.9; 31.0 (t, J = 21.5Hz). [$C_8H_4F_{13}C_1Im$][BETI], ^{13}C NMR (100 MHz, acetone-d_6) δ (ppm): 137.7; 124.9; 123.2; 125-108: multiple untreatable signal (CF_2), see Fig S0; 42.3 (t, J = 5.4Hz, CH_2); 36.8; 31.5 (t, J = 21.5Hz).

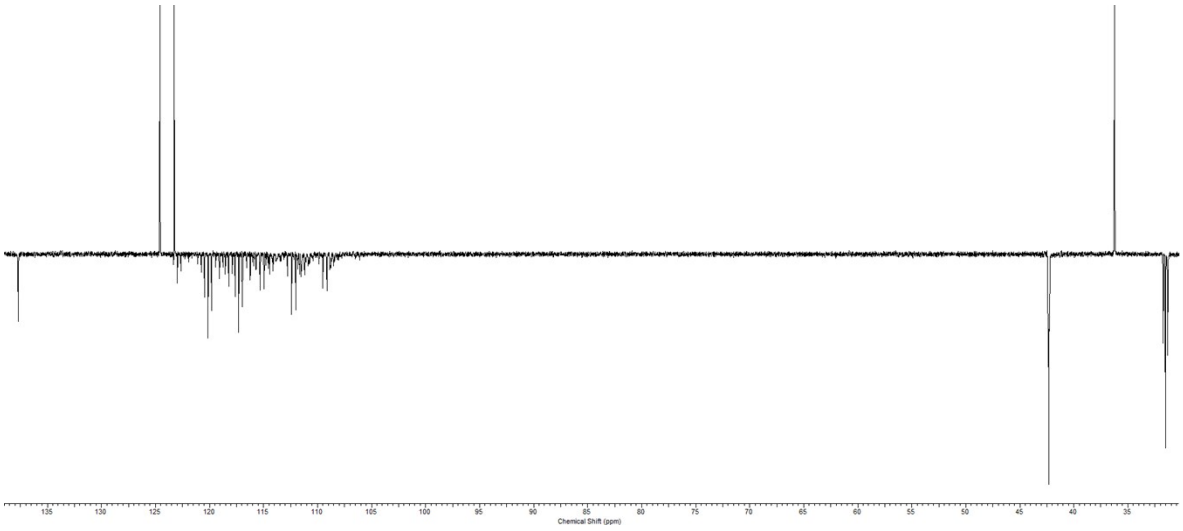

Figure S0. ^{13}C spectrum of synthesized [$C_8H_4F_{13}C_1Im$][BETI] in acetone-d_6.

Table S1. Density of the pure ionic liquids and of the mixtures studied.

T / K	ρ / g cm^{-3}	T / K	ρ / g cm^{-3}	T / K	ρ / g cm^{-3}
[C_8C_1Im][NTf_2]		[$C_8H_4F_{13}C_1$Im][NTf_2]		[C_8C_1Im][BETI]	
293.15	1.324821	293.15	1.728094	293.15	1.400916
303.15	1.315904	303.15	1.715452	303.15	1.391097
313.15	1.307060	313.15	1.702909	313.15	1.381319
323.15	1.298274	323.15	1.690449	323.15	1.371608
333.15	1.289546	333.15	1.677993	333.15	1.361959
343.15	1.280871	343.15	1.665606	343.15	1.352366
353.15	1.272243	353.15	1.653294	353.15	1.342818
293.15	1.324786			293.15	1.400910
303.15	1.315890			303.15	1.391096
313.15	1.307045			313.15	1.381317
323.15	1.298262			323.15	1.371608
333.15	1.289535			333.15	1.361956
343.15	1.280859			343.15	1.352365
353.15	1.272230			353.15	1.342819
[C_8C_1Im]$_x$[$C_8H_4F_{13}C_1$Im]$_{(1-x)}$[NTf_2]				[$C_8H_4F_{13}C_1$Im][BETI]	
x = 0.8996		x = 0.6025			
293.15	1.368592	293.15	1.493303	318.15	1.723065
298.15	1.363935	298.15	1.488086	323.15	1.716578
303.15	1.359284	303.15	1.482862	333.15	1.703584
313.15	1.350033	313.15	1.472442	343.15	1.690584
323.15	1.340850	323.15	1.462095	353.15	1.677639
333.15	1.331725	333.15	1.451823	318.15	1.723079
343.15	1.322657	343.15	1.441613	313.15	1.729653
353.15	1.313638	353.15	1.431460		

Table S2. Parameters A_0 and A_1 for linear fitting of density as a function of temperature as $\rho(gcm^{-3}) = A_0 + A_1 T(K)$. σ stands for the standard deviation of the resulting fit.

Ionic liquid	A_0 / g cm^{-3}	A_1 / g cm^{-3} K^{-1}	σ / %
$[C_8C_1Im][NTf_2]$	1.58146	-0.87600×10^{-3}	0.01
$[C_8H_4F_{13}C_1Im][NTf_2]$	2.09334	-1.24647×10^{-3}	0.03
$[C_8C_1Im][BETI]$	1.68461	-0.96824×10^{-3}	0.01
$[C_8H_4F_{13}C_1Im][BETI]$	2.13657	-1.29963×10^{-3}	0.01

Table S3. Excess molar volumes, V^E, for $[C_8C_1Im]_x[C_8H_4F_{13}C_1Im]_{(1-x)}[NTf_2]$ mixtures as a function of temperature and composition.

x	V^E / cm^3 mol^{-1}							
	293 K	298 K	303 K	313 K	323 K	333 K	343 K	353 K
0.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.6025	1.217	1.243	1.271	1.322	1.355	1.368	1.364	1.344
0.8996	0.457	0.481	0.504	0.537	0.552	0.551	0.534	0.502
1.0000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

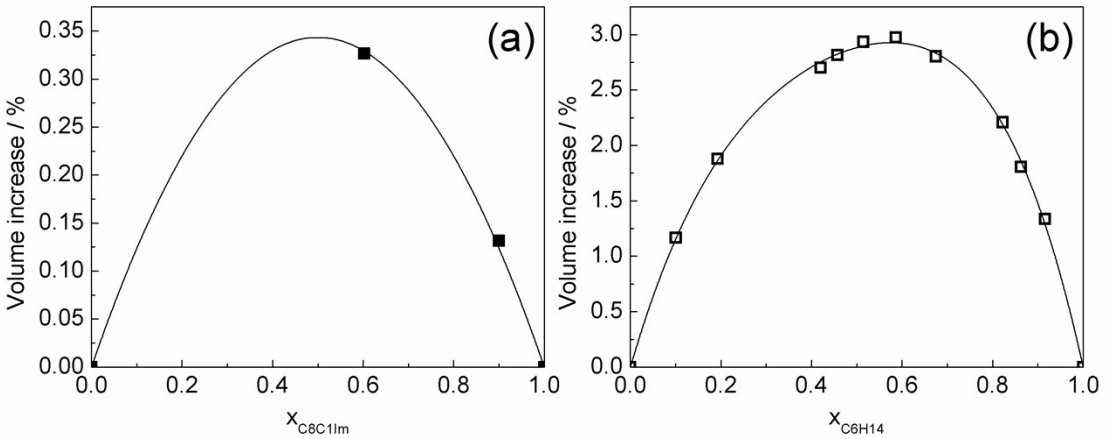

Figure S1. Volume increase upon mixing (a) $[C_8C_1Im][NTf_2]$ with $[C_8H_4F_{13}C_1Im][NTf_2]$ and (b) C_6H_{14} with C_6F_{14} at 298 K. For (b) density data were collected from Bedford and Dunlap. [1] Symbols represent experimental values while solid lines represent the best Redlich-Kister fittings.

Table S4. Stoichiometric data and heat effects of the calorimetry experiments with the system $[C_8H_4F_{13}C_1Im][NTf_2]$(1) + $[C_8C_1Im][NTf_2]$(2) at 313.15 K. 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
8.12949E-06	1.99434E-03	2.70983E-03	2.42805E-02	1.21E-03
1.08393E-05	2.01862E-03	2.70983E-03	2.42805E-02	1.15E-03
1.35492E-05	2.04290E-03	2.70983E-03	2.42805E-02	1.14E-03
1.62590E-05	2.06718E-03	2.70983E-03	2.42805E-02	1.04E-03
1.89688E-05	2.09146E-03	2.70983E-03	2.42805E-02	1.04E-03
2.16787E-05	2.11574E-03	2.70983E-03	2.42805E-02	9.4E-04
2.43885E-05	2.14002E-03	2.70983E-03	2.42805E-02	9.2E-04
2.70983E-05	2.16431E-03	2.70983E-03	2.42805E-02	9.7E-04
2.98081E-05	2.18859E-03	2.70983E-03	2.42805E-02	8.8E-04
3.25180E-05	2.21287E-03	2.70983E-03	2.42805E-02	9.3E-04
3.52278E-05	2.23715E-03	2.70983E-03	2.42805E-02	9.0E-04
3.79376E-05	2.26143E-03	2.70983E-03	2.42805E-02	8.2E-04
4.06475E-05	2.28571E-03	2.70983E-03	2.42805E-02	8.0E-04
4.33573E-05	2.30999E-03	2.70983E-03	2.42805E-02	7.7E-04
4.60671E-05	2.33427E-03	2.70983E-03	2.42805E-02	7.8E-04
4.87770E-05	2.35855E-03	2.70983E-03	2.42805E-02	6.8E-04
5.14868E-05	2.38283E-03	2.70983E-03	2.42805E-02	7.3E-04
8.12949E-06	2.00274E-03	2.70983E-03	2.42805E-02	1.13E-03
1.08393E-05	2.02702E-03	2.70983E-03	2.42805E-02	1.03E-03
1.35492E-05	2.05130E-03	2.70983E-03	2.42805E-02	1.10E-03
1.62590E-05	2.07558E-03	2.70983E-03	2.42805E-02	1.12E-03
1.89688E-05	2.09986E-03	2.70983E-03	2.42805E-02	1.02E-03
2.16787E-05	2.12414E-03	2.70983E-03	2.42805E-02	8.5E-04
2.43885E-05	2.14842E-03	2.70983E-03	2.42805E-02	9.2E-04
2.70983E-05	2.17271E-03	2.70983E-03	2.42805E-02	1.10E-03
2.98081E-05	2.19699E-03	2.70983E-03	2.42805E-02	9.2E-04
3.25180E-05	2.22127E-03	2.70983E-03	2.42805E-02	8.9E-04
3.52278E-05	2.24555E-03	2.70983E-03	2.42805E-02	9.3E-04
3.79376E-05	2.26983E-03	2.70983E-03	2.42805E-02	9.0E-04

4.06475E-05	2.29411E-03	2.70983E-03	2.42805E-02	8.0E-04
4.33573E-05	2.31839E-03	2.70983E-03	2.42805E-02	7.2E-04
4.60671E-05	2.34267E-03	2.70983E-03	2.42805E-02	8.0E-04
4.87770E-05	2.36695E-03	2.70983E-03	2.42805E-02	7.8E-04
5.14868E-05	2.39123E-03	2.70983E-03	2.42805E-02	6.6E-04
7.01400E-04	1.14572E-03	0.00000E+00	2.74741E-02	1.350E-02
7.01400E-04	1.17320E-03	0.00000E+00	2.74741E-02	1.334E-02
7.01400E-04	1.20067E-03	0.00000E+00	2.74741E-02	1.289E-02
7.01400E-04	1.22814E-03	0.00000E+00	2.74741E-02	1.243E-02
7.01400E-04	1.25562E-03	0.00000E+00	2.74741E-02	1.225E-02
7.01400E-04	1.28309E-03	0.00000E+00	2.74741E-02	1.182E-02
7.01400E-04	1.31057E-03	0.00000E+00	2.74741E-02	1.140E-02
7.01400E-04	1.33804E-03	0.00000E+00	2.74741E-02	1.093E-02
7.01400E-04	1.36552E-03	0.00000E+00	2.74741E-02	1.090E-02
7.01400E-04	1.39299E-03	0.00000E+00	2.74741E-02	1.057E-02
7.01400E-04	1.42046E-03	0.00000E+00	2.74741E-02	1.039E-02
7.01400E-04	1.44794E-03	0.00000E+00	2.74741E-02	9.71E-03
7.01400E-04	1.47541E-03	0.00000E+00	2.74741E-02	9.26E-03
7.01400E-04	1.50289E-03	0.00000E+00	2.74741E-02	8.92E-03
7.01400E-04	1.53036E-03	0.00000E+00	2.74741E-02	8.91E-03
7.01400E-04	1.55783E-03	0.00000E+00	2.74741E-02	9.10E-03
7.01400E-04	1.58531E-03	0.00000E+00	2.74741E-02	8.90E-03
7.20000E-04	1.17392E-03	0.00000E+00	2.74741E-02	1.315E-02
7.20000E-04	1.20140E-03	0.00000E+00	2.74741E-02	1.312E-02
7.20000E-04	1.22887E-03	0.00000E+00	2.74741E-02	1.269E-02
7.20000E-04	1.25634E-03	0.00000E+00	2.74741E-02	1.260E-02
7.20000E-04	1.28382E-03	0.00000E+00	2.74741E-02	1.232E-02
7.20000E-04	1.31129E-03	0.00000E+00	2.74741E-02	1.202E-02
7.20000E-04	1.33877E-03	0.00000E+00	2.74741E-02	1.150E-02
7.20000E-04	1.36624E-03	0.00000E+00	2.74741E-02	1.124E-02
7.20000E-04	1.39372E-03	0.00000E+00	2.74741E-02	1.078E-02
7.20000E-04	1.42119E-03	0.00000E+00	2.74741E-02	1.073E-02
7.20000E-04	1.44866E-03	0.00000E+00	2.74741E-02	1.059E-02
7.20000E-04	1.47614E-03	0.00000E+00	2.74741E-02	1.035E-02
7.20000E-04	1.50361E-03	0.00000E+00	2.74741E-02	9.75E-03

7.20000E-04	1.53109E-03	0.00000E+00	2.74741E-02	9.56E-03
7.20000E-04	1.55856E-03	0.00000E+00	2.74741E-02	9.17E-03
7.20000E-04	1.58603E-03	0.00000E+00	2.74741E-02	8.96E-03
7.20000E-04	1.61351E-03	0.00000E+00	2.74741E-02	8.88E-03

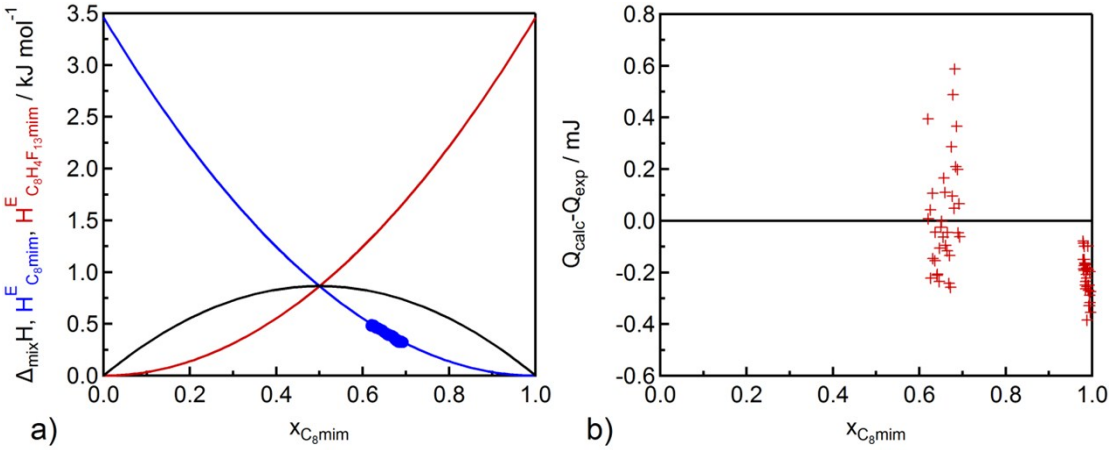

Figure S2. a) Partial molar enthalpies, H^E_i, of the components of the mixture $[C_8C_1Im]_x[C_8H_4F_{13}C_1Im]_{(1-x)}[NTf_2]$ and enthalpy of mixing, $\Delta_{mix}H$. Lines are fitting curves and ● are experimental data. In b) are plotted the differences between the experimental heat effects, Q_{exp}, and the ones calculated using the fitting parameter, Q_{calc}, as described in Mateolli *et al.*[2]

Table S5. Heat effects of mixing perfluorooctane(1) + octane(2) at 353.15 K. 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
3.3413E-03	1.1353E-04	0.0000E+00	4.5662E-02	6.1089E-01
3.3413E-03	1.5919E-04	0.0000E+00	4.5662E-02	5.8444E-01
3.3413E-03	2.0486E-04	0.0000E+00	4.5662E-02	5.6130E-01
3.3413E-03	2.5052E-04	0.0000E+00	4.5662E-02	5.3956E-01
3.3413E-03	2.9618E-04	0.0000E+00	4.5662E-02	5.2003E-01
3.3413E-03	3.4184E-04	0.0000E+00	4.5662E-02	5.0592E-01
3.3413E-03	3.8751E-04	0.0000E+00	4.5662E-02	4.8060E-01
3.3413E-03	4.3317E-04	0.0000E+00	4.5662E-02	4.6632E-01
3.3413E-03	4.7883E-04	0.0000E+00	4.5662E-02	4.5023E-01
3.3413E-03	5.2449E-04	0.0000E+00	4.5662E-02	4.3617E-01
3.3413E-03	5.7015E-04	0.0000E+00	4.5662E-02	4.1786E-01
2.9603E-05	5.1629E-03	2.9681E-02	0.0000E+00	4.9650E-01
5.9284E-05	5.1629E-03	2.9681E-02	0.0000E+00	4.7854E-01
8.8966E-05	5.1629E-03	2.9681E-02	0.0000E+00	4.6344E-01
1.1865E-04	5.1629E-03	2.9681E-02	0.0000E+00	4.5152E-01
1.4833E-04	5.1629E-03	2.9681E-02	0.0000E+00	4.3880E-01
1.7801E-04	5.1629E-03	2.9681E-02	0.0000E+00	4.2719E-01
2.0769E-04	5.1629E-03	2.9681E-02	0.0000E+00	4.2046E-01
2.3737E-04	5.1629E-03	2.9681E-02	0.0000E+00	3.9741E-01
2.6705E-04	5.1629E-03	2.9681E-02	0.0000E+00	3.9608E-01
2.9674E-04	5.1629E-03	2.9681E-02	0.0000E+00	3.7061E-01
3.2642E-04	5.1629E-03	2.9681E-02	0.0000E+00	3.5995E-01
2.0710E-03	2.0266E-03	2.9681E-02	0.0000E+00	9.2160E-02
2.1007E-03	2.0266E-03	2.9681E-02	0.0000E+00	9.1430E-02
2.1304E-03	2.0266E-03	2.9681E-02	0.0000E+00	9.1650E-02
2.1600E-03	2.0266E-03	2.9681E-02	0.0000E+00	8.9940E-02
2.1897E-03	2.0266E-03	2.9681E-02	0.0000E+00	8.8000E-02
2.2194E-03	2.0266E-03	2.9681E-02	0.0000E+00	8.8130E-02
2.2491E-03	2.0266E-03	2.9681E-02	0.0000E+00	8.5590E-02
2.2788E-03	2.0266E-03	2.9681E-02	0.0000E+00	8.4710E-02
2.3085E-03	2.0266E-03	2.9681E-02	0.0000E+00	8.4410E-02
2.3381E-03	2.0266E-03	2.9681E-02	0.0000E+00	8.3420E-02
2.3678E-03	2.0266E-03	2.9681E-02	0.0000E+00	8.2130E-02
1.1381E-03	3.4467E-03	0.0000E+00	3.4275E-02	4.1473E-02
1.1381E-03	3.4810E-03	0.0000E+00	3.4275E-02	4.0577E-02
1.1381E-03	3.5153E-03	0.0000E+00	3.4275E-02	3.9421E-02
1.1381E-03	3.5495E-03	0.0000E+00	3.4275E-02	3.9883E-02
1.1381E-03	3.5838E-03	0.0000E+00	3.4275E-02	3.9366E-02
1.1381E-03	3.6181E-03	0.0000E+00	3.4275E-02	3.8985E-02
1.1381E-03	3.6524E-03	0.0000E+00	3.4275E-02	3.8286E-02
1.1381E-03	3.6866E-03	0.0000E+00	3.4275E-02	3.8114E-02

Table S6. Parameters A_i of the Redlich-Kister equation (equation 9 in main text) and the partial molar enthalpies at infinite dilution ($\overline{H}^{E,\infty}_i$) for mixing perfluorooctane(1) + octane(2) at 353.15 K.

System	kJ mol^{-1}				
	A_0	A_1	A_2	$\overline{H}^{E,\infty}_{L1}$	$\overline{H}^{E,\infty}_{L2}$
C_8H_{18}/C_8F_{18}	12.59631	- 0.45752	3.44480	15.584	16.499

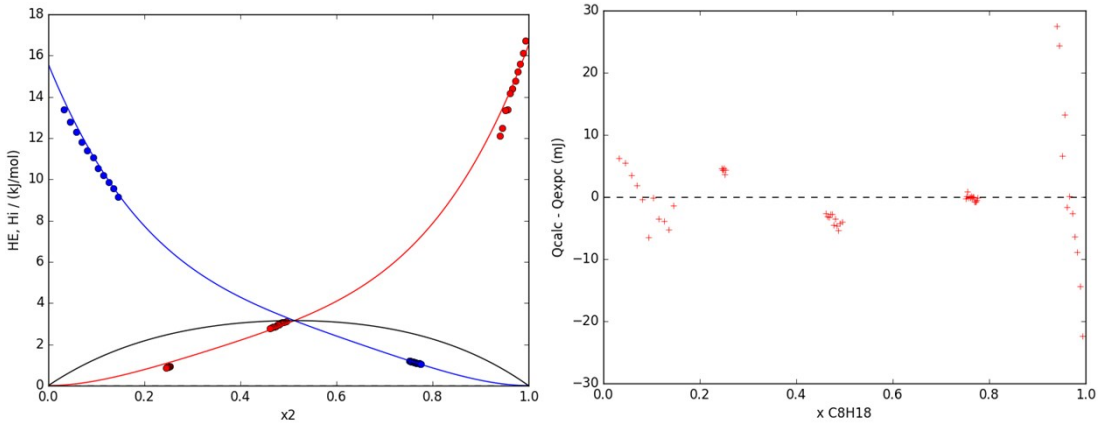

Figure S3. Left panel: Partial molar enthalpies, H^E_i, of C_8H_{18} (blue line) and C_8F_{18} (red line) of the mixture C_8H_{18} + C_8F_{18} and their enthalpy of mixing (black line). Symbols stand for the experimental data and solid lines represent fitting results. Right panel: Differences between the experimental heat effects, Q_{exp}, and those resulted from fitting, Q_{calc}.

Table S7. Experimental solubility of CF_4 and C_2F_6 in $[C_8C_1Im][NTf_2]$ expressed both as Henry's law constants, K_H and as gas mole fraction, x_{gas}, corrected for a partial pressure of solute of 0.1 MPa. p is the experimental equilibrium pressure and the per cent deviation is relative to the correlation of the data.

$\frac{T}{K}$	$\frac{p}{10^2 Pa}$	$\frac{K_H}{10^5 Pa}$	$\frac{x_{gas}}{10^{-3}}$	$\frac{dev}{\%}$
$CF_4 + [C_8C_1Im][NTf_2]$				
303.18	694.53	607.3	1.647	+ 1.2
303.18	703.15	633.5	1.579	– 3.0
303.18	760.26	605.2	1.652	+ 1.6
313.18	717.27	648.4	1.542	+ 1.1
313.18	726.10	663.2	1.508	– 1.2
313.19	785.22	655.3	1.526	+ 0.0
323.19	749.05	700.6	1.427	+ 1.4
323.19	740.00	692.6	1.444	+ 2.5
323.19	810.21	724.6	1.380	– 2.0
333.20	835.21	812.4	1.231	– 4.0
333.20	762.79	766.9	1.304	+ 1.6
342.76	784.56	851.9	1.174	+ 1.0
$C_2F_6 + [C_8C_1Im][NTf_2]$				
303.17	669.83	329.0	3.040	– 1.3
303.17	677.15	333.0	3.003	– 2.5
303.17	667.45	314.5	3.180	+ 3.3
313.18	689.69	348.6	2.869	+ 3.5
313.18	692.27	368.4	2.714	– 2.1
323.19	722.15	405.3	2.467	– 2.5
323.19	711.83	379.2	2.637	+ 4.3
323.19	714.59	405.1	2.468	– 2.4
333.19	734.09	429.5	2.328	– 0.4
343.19	759.41	456.4	2.191	+ 0.4

Table S8. Experimental solubilities of CF_4, C_2F_6 and C_3F_8 in $[C_8H_4F_{13}C_1Im][NTf_2]$ expressed both as Henry's law constants, K_H and as gas mole fraction, x_{gas}, corrected for a partial pressure of solute of 0.1 MPa. p is the experimental equilibrium pressure and the per cent deviation is relative to the correlation of the data.

$\frac{T}{K}$	$\frac{p}{10^2 Pa}$	$\frac{K_H}{10^5 Pa}$	$\frac{x_{gas}}{10^{-3}}$	$\frac{dev}{\%}$
$CF_4 + [C_8H_4F_{13}C_1Im][NTf_2]$				
303.16	682.48	221.8	4.508	− 0.8
303.17	688.93	219.9	4.548	+ 0.1
313.15	711.50	237.3	4.215	+ 1.6
313.16	705.02	241.3	4.145	− 0.1
323.16	727.64	267.4	3.739	− 1.2
323.17	734.16	259.9	3.847	+ 1.7
333.15	750.30	300.6	3.326	− 3.7
333.18	756.83	285.5	3.502	+ 1.4
343.16	779.36	313.2	3.193	+ 1.2
$C_2F_6 + [C_8H_4F_{13}C_1Im][NTf_2]$				
303.15	670.93	99.39	10.06	− 2.2
303.16	643.84	96.03	10.41	+ 1.2
303.16	628.00	95.38	10.48	+ 1.9
313.13	665.50	112.3	8.904	+ 0.7
313.14	650.10	111.9	8.938	+ 1.1
313.16	666.10	114.9	8.704	− 1.5
313.17	694.37	115.4	8.667	− 1.9
318.16	692.03	124.1	8.059	− 1.2
323.13	672.13	131.2	7.623	+ 1.3
323.14	687.47	130.3	7.676	+ 2.0
323.17	717.82	136.1	7.350	− 2.3
323.18	703.33	132.9	7.523	+ 0.1
333.04	725.48	152.6	6.554	+ 2.9
333.14	694.18	154.9	6.455	+ 1.5
333.16	741.20	161.3	6.201	− 2.4
343.19	716.45	189.2	5.284	− 1.1
$C_3F_8 + [C_8H_4F_{13}C_1Im][NTf_2]$				
303.16	618.08	39.39	25.38	+ 0.7
313.17	660.17	49.33	20.27	− 1.6
313.17	656.22	48.94	20.43	− 0.8
313.18	643.39	48.28	20.71	+ 0.6
323.13	680.21	59.22	16.89	+ 0.1
323.14	684.18	59.28	16.87	+ 0.0
323.19	668.17	58.83	17.00	+ 0.9
333.21	692.67	72.04	13.88	+ 0.5
343.21	716.75	88.30	11.32	− 0.4

Table S9. Experimental solubilities of CF_4, C_2F_6 and C_3F_8 in $[C_8C_1Im][BETI]$ expressed both as Henry's law constants, K_H and as gas mole fraction, x_{gas}, corrected for a partial pressure of solute of 0.1 MPa. p is the experimental equilibrium pressure and the per cent deviation is relative to the correlation of the data.

T / K	p / 10^2Pa	K_H / 10^5Pa	x_{gas} / 10^{-3}	dev / %
CF_4 + $[C_8C_1Im][BETI]$				
303.16	724.97	315.8	3.167	− 1.4
303.17	707.29	305.0	3.279	+ 2.1
313.15	748.73	335.9	2.977	− 1.9
313.18	730.56	327.7	3.052	+ 0.6
323.16	772.52	359.0	2.786	− 1.3
323.18	753.77	348.7	2.868	+ 1.6
333.17	796.41	394.0	2.538	− 2.1
333.19	776.98	373.3	2.679	+ 3.4
343.16	820.29	438.5	2.281	− 3.2
343.20	800.36	413.9	2.416	+ 2.6
C_2F_6 + $[C_8C_1Im][BETI]$				
303.15	633.45	169.7	5.893	+ 0.1
303.15	656.58	169.8	5.889	+ 0.1
303.17	646.92	170.9	5.850	− 0.6
313.16	655.13	195.1	5.125	− 0.5
313.17	679.00	192.2	5.203	+ 1.1
313.20	669.04	195.1	5.126	− 0.4
323.16	676.72	222.5	4.495	+ 1.6
323.17	701.54	223.4	4.477	+ 1.2
323.21	691.27	229.0	4.368	− 1.2
333.12	698.42	265.4	3.768	+ 0.5
333.18	735.04	263.3	3.798	+ 1.4
333.18	713.55	278.9	3.586	− 4.3
343.18	746.63	311.6	3.209	+ 2.2
343.18	720.33	322.3	3.103	− 1.2
C_3F_8 + $[C_8C_1Im][BETI]$				
303.17	702.40	83.46	11.98	+ 0.3
303.18	663.17	84.16	11.88	− 0.5
313.16	727.99	97.50	10.26	+ 0.8
313.18	687.44	98.50	10.15	− 0.2
323.16	753.31	113.1	8.843	+ 0.4
323.17	711.39	114.0	8.773	− 0.3
333.14	735.04	130.9	7.640	− 1.0
333.14	778.25	129.1	7.749	+ 0.4
343.09	758.22	146.8	6.811	− 0.6
343.12	802.80	144.5	6.921	+ 1.0

Table S10. Experimental solubilities of CF_4, C_2F_6 and C_3F_8 in $[C_8H_4F_{13}C_1Im][BETI]$ expressed both as Henry's law constants, K_H and as gas mole fraction, x_{gas}, corrected for a partial pressure of solute of 0.1 MPa. p is the experimental equilibrium pressure and the per cent deviation is relative to the correlation of the data.

T / K	p / 10^2Pa	K_H / 10^5Pa	x_{gas} / 10^{-3}	dev / %
CF_4 + $[C_8H_4F_{13}C_1Im][BETI]$				
318.15	729.62	190.0	5.263	+ 2.5
318.19	726.10	200.8	4.981	– 3.0
323.13	741.05	202.4	4.940	+ 1.6
323.19	737.45	206.8	4.836	– 0.5
333.17	760.31	227.0	4.406	– 1.0
333.20	764.03	223.9	4.467	+ 0.4
343.07	782.73	239.0	4.185	+ 0.2
C_2F_6 + $[C_8H_4F_{13}C_1Im][BETI]$				
318.16	697.15	93.44	10.70	– 0.6
318.18	633.86	91.14	10.97	+ 2.0
318.20	710.33	93.43	10.70	– 0.5
323.15	708.62	100.7	9.929	– 0.4
323.18	722.12	102.5	9.758	– 2.1
323.19	644.39	99.38	10.06	+ 1.0
333.19	745.57	121.5	8.230	– 1.1
333.21	665.37	117.6	8.503	+ 2.3
343.12	755.05	150.7	6.636	– 1.6
343.23	769.31	151.1	6.619	– 1.6
343.24	686.52	144.6	6.916	+ 2.8
C_3F_8 + $[C_8H_4F_{13}C_1Im][BETI]$				
318.20	719.25	39.92	25.05	+ 1.0
318.18	692.66	39.87	25.08	+ 1.1
323.17	705.40	43.58	22.95	– 1.8
323.20	732.64	43.80	22.83	– 2.3
333.17	730.48	51.60	19.38	+ 1.5
333.22	758.73	51.72	19.33	+ 1.4
343.17	787.21	71.29	14.03	– 0.9

Table S11. Parameters of equation (5) used to smooth the experimental results on K_H from Tables 1, 2, 3, 4 along with the standard deviation of the fit, s.

Ionic liquid	A_0	A_1 / K	A_2 / K_2	S
		CF_4		
$[C_8C_1Im][NTf_2]$	+ 19.00	-7.128×10^3	-10.05×10^5	1.7
$[C_8H_4F_{13}C_1Im][NTf_2]$	+ 11.25	-2.708×10^3	$+2.831 \times 10^5$	1.3
$[C_8C_1Im][BETI]$	+ 17.63	-6.770×10^3	$+9.599 \times 10^5$	2.0
$[C_8H_4F_{13}C_1Im][BETI]$	− 2.58	$+6.169 \times 10^3$	-11.68×10^5	1.3
		C_2F_6		
$[C_8C_1Im][NTf_2]$	+ 5.140	$+1.427 \times 10^3$	$-3{,}737 \times 10^5$	2.3
$[C_8H_4F_{13}C_1Im][NTf_2]$	+ 19.15	-7.495×10^3	$+9.324 \times 10^5$	1.6
$[C_8C_1Im][BETI]$	+ 23.09	-9.758×10^3	$+13.08 \times 10^5$	1.2
$[C_8H_4F_{13}C_1Im][BETI]$	+ 34.95	-17.91×10^3	$+26.18 \times 10^5$	1.4
		C_3F_8		
$[C_8H_4F_{13}C_1Im][NTf_2]$	+ 15.54	-5.327×10^3	$+5.246 \times 10^5$	0.6
$[C_8C_1Im][BETI]$	+ 6.62	$+0.221 \times 10^3$	-2.686×10^5	0.6
$[C_8H_4F_{13}C_1Im][BETI]$	+ 73.89	-43.78×10^3	$+68.24 \times 10^5$	1.5

Figure S4. Mole fraction solubility of tetrafluoromethane (CF_4) in the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ionic liquids, $[C_nC_1Im][NTf_2]$, as a function of the alkyl-side chain in the cation. Symbols ♂ and ♾ stand for n = 6 and n = 8 in $[C_nC_1Im][NTf_2]$, respectively. CF_4 solubility data in the $[C_6C_1Im][NTf_2]$ were reported in ref [3].

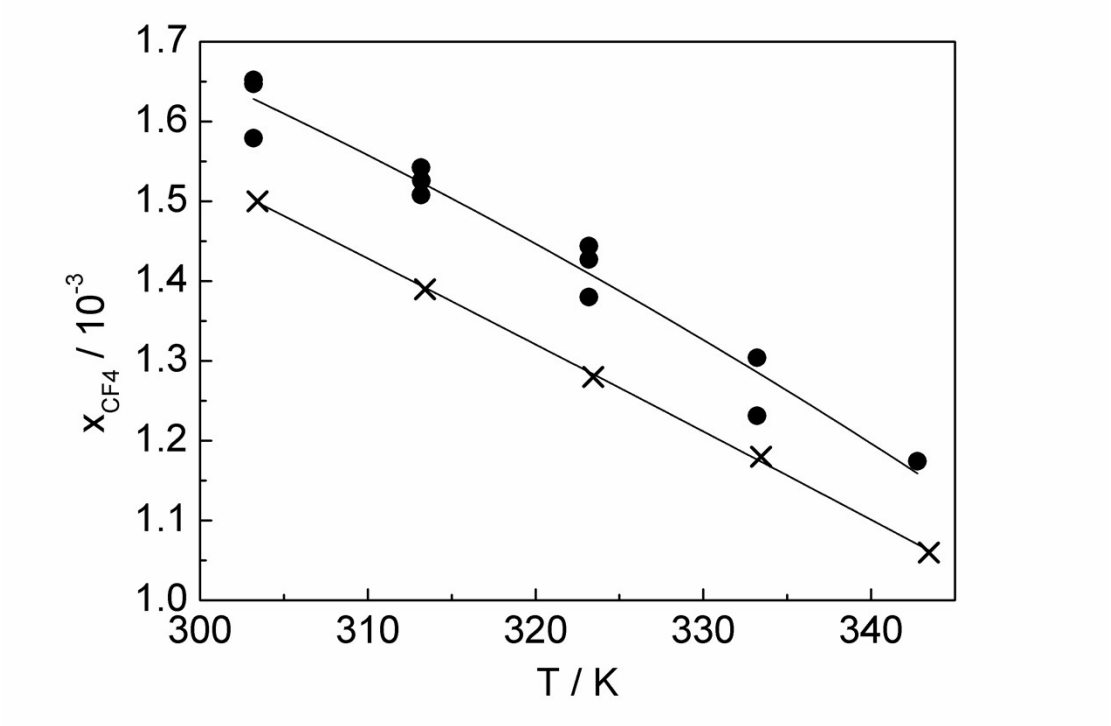

Table S12. Thermodynamic properties of CF_4, C_2F_6 and C_3F_8 solvation in the ionic liquids studied at 323 K.

Ionic liquid	$\Delta_{solv}H^{\infty}/\text{kJmol}^{-1}$	$T\Delta_{solv}S^{\infty}/\text{kJmol}^{-1}$
	CF_4	
$[C_8C_1Im][NTf_2]$	-7 ± 1	-25 ± 2
$[C_8H_4F_{13}C_1Im][NTf_2]$	-8 ± 1	-23 ± 1
$[C_8C_1Im][BETI]$	-7 ± 1	-23 ± 2
$[C_8H_4F_{13}C_1Im][BETI]$	-8.8 ± 0.8	-23.1 ± 0.5
	C_2F_6	
$[C_8C_1Im][NTf_2]$	-7.4 ± 0.4	-23.6 ± 0.1
$[C_8H_4F_{13}C_1Im][NTf_2]$	-14 ± 1	-27 ± 1
$[C_8C_1Im][BETI]$	-14 ± 2	-28 ± 2
$[C_8H_4F_{13}C_1Im][BETI]$	-14 ± 2	-30 ± 3
	C_3F_8	
$[C_8H_4F_{13}C_1Im][NTf_2]$	-17.3 ± 0.5	-28 ± 1
$[C_8C_1Im][BETI]$	-12.1 ± 0.3	-24.8 ± 0.2
$[C_8H_4F_{13}C_1Im][BETI]$	-13 ± 3	-23 ± 3

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