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

Electronic Supplementary Information

Insights into the influence of the molecular structure of Fluorinated Ionic Liquids on their thermophysical properties. A soft-SAFT based approach.

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Table S1. Symbols, molecular weight, soft-SAFT molecular parameters from literature and reparametrized, correlations of molecular parameters and absolute average deviation (AAD) for the densities of all ionic liquids studied in this work.

Symbol	Ionic Liquid	M_w [g mol^{-1}]	m	σ [Å]	ε/k_B [K]	$m\sigma^3$ [Å^3]	$m\varepsilon/k_B$ [K]	ε^{HB}/k_B [K]	κ^{HB} [Å^3]	AAD [%]	REF
★	$[C_2C_1Im][C_4F_9CO_2]$	374.21	7.233	3.762	338.8	385	2451	3850	2250	0.008	1
☆	$[C_2C_1py][C_4F_9CO_2]$	385.23	7.233	3.836	349.2	408	2526	3850	2250	0.005	1
⊗	$[C_2C_1py][C_4F_9SO_3]$	421.28	7.320	3.889	359.4	431	2631	3850	2250	0.019	1
□	$[C_2C_1Im][C_4F_9SO_3]$	410.31	7.320	3.816	343.4	407	2514	3850	2250	0.053	2
△	$[C_4C_1Im][C_4F_9SO_3]$	438.31	7.685	3.919	349.4	463	2685	3850	2250	0.033	2
○	$[C_6C_1Im][C_4F_9SO_3]$	466.33	8.050	4.006	355.4	518	2861	3850	2250	0.074	2
◇	$[C_8C_1Im][C_4F_9SO_3]$	494.42	8.429	4.078	357.4	572	3013	3850	2250	0.017	2
▽	$[C_{10}C_1Im][C_4F_9SO_3]$	522.43	8.812	4.126	359.4	619	3167	3850	2250	0.091	2
⬡	$[C_{12}C_1Im][C_4F_9SO_3]$	550.48	9.178	4.194	360.2	677	3306	3850	2250	0.036	2
✚	$[C_2C_1Im][CF_3SO_3]$	260.24	4.495	4.029	420.0	294	1888	3450	2250	-	This work
✖	$[C_4C_1Im][CF_3SO_3]$	288.29	4.149	4.375	378.0	347	1568	3650	2400	0.116	3
▬	$[C_2C_1Im][CF_3CO_2]$	224.18	4.225	3.998	417.1	270	1762	3450	2250	-	This work
▮	$[C_4C_1Im][CF_3CO_2]$	252.33	4.180	4.256	360.7	322	1508	3725	2400	0.016	3
⊞	$[C_1C_1Im][N(CF_3SO_2)_2]$	377.29	5.947	3.992	391.1	378	2326	3450	2250	–	4
■	$[C_2C_1Im][N(CF_3SO_2)_2]$	391.32	6.023	4.069	394.6	406	2377	3450	2250	–	4
⊕	$[C_3C_1Im][N(CF_3SO_2)_2]$	405.33	6.101	4.143	397.0	434	2422	3450	2250	–	4
●	$[C_4C_1Im][N(CF_3SO_2)_2]$	419.34	6.175	4.211	399.4	461	2466	3450	2250	–	4
⛬	$[C_5C_1Im][N(CF_3SO_2)_2]$	433.35	6.247	4.277	401.8	489	2510	3450	2250	–	4
▲	$[C_6C_1Im][N(CF_3SO_2)_2]$	447.36	6.338	4.334	404.2	516	2562	3450	2250	–	4
⊕	$[C_7C_1Im][N(CF_3SO_2)_2]$	461.45	6.418	4.395	407.6	545	2616	3450	2250	–	4
◆	$[C_8C_1Im][N(CF_3SO_2)_2]$	475.48	6.489	4.45	410.0	572	2660	3450	2250	–	4
⛛	$[C_9C_1Im][N(CF_3SO_2)_2]$	489.49	6.575	4.501	411.7	600	2707	3450	2250	–	4
▼	$[C_{10}C_1Im][N(CF_3SO_2)_2]$	503.5	6.653	4.551	414.0	627	2754	3450	2250	–	4
⊕	$[C_{12}C_1Im][N(CF_3SO_2)_2]$	531.52	6.810	4.645	418.5	683	2850	3450	2250	–	4
⬢	$[C_{14}C_1Im][N(CF_3SO_2)_2]$	559.54	6.967	4.731	422.7	738	2945	3450	2250	–	4
⬓	$[C_2C_1py][N(CF_3SO_2)_2]$	402.33	6.023	4.125	378.4	423	2279	3450	2250	0.017	This work
◒	$[C_3C_1py][N(CF_3SO_2)_2]$	416.37	6.101	4.194	380.2	450	2320	3450	2250	0.062	This work
◒	$[C_4C_1py][N(CF_3SO_2)_2]$	430.39	6.175	4.257	378.9	476	2340	3450	2250	0.042	This work
⬙	$[C_6C_1py][N(CF_3SO_2)_2]$	458.44	6.338	4.375	380.2	531	2410	3450	2250	0.028	This work
⊠	$[C_8C_1py][N(CF_3SO_2)_2]$	486.49	6.489	4.483	402.4	585	2611	3450	2250	0.112	This work
◔	$[C_2py][N(CF_3SO_2)_2]$	388.3	5.947	4.044	368.2	393	2190	3450	2250	0.036	This work
◑	$[C_3py][N(CF_3SO_2)_2]$	402.33	6.023	4.119	378.4	421	2279	3450	2250	0.040	This work
⬘	$[C_4py][N(CF_3SO_2)_2]$	416.37	6.101	4.193	378.5	450	2309	3450	2250	0.025	This work
⬗	$[C_5py][N(CF_3SO_2)_2]$	430.38	6.175	4.248	378.2	473	2335	3450	2250	0.015	This work
⬒	$[C_6py][N(CF_3SO_2)_2]$	444.42	6.247	4.305	379.2	498	2369	3450	2250	0.048	This work
◪	$[C_8py][N(CF_3SO_2)_2]$	472.48	6.418	4.429	386.4	558	2480	3450	2250	0.066	This work
⬙	$[C_{10}py][N(CF_3SO_2)_2]$	500.52	6.575	4.529	382.5	611	2515	3450	2250	0.023	This work
◐	$[C_{12}py][N(CF_3SO_2)_2]$	528.57	6.732	4.622	387.7	665	2610	3450	2250	0.036	This work

Table S2. Molecular weight and molecular parameters of carbon dioxide, methanol and water used in this work.

Compound	M_w [g mol^{-1}]	m	σ [Å]	ε/k_B [K]	ε^{HB}/k_B [K]	κ^{HB} [Å^3]	Q (C m^2)	x_p	REF
CO_2	44.01	1.571	3.184	160.2	–	–	4.4×10^{-40}	1/3	5
CH_3OH	32.04	1.491	3.375	220.4	3213	4847	–	–	6,7
H_2O	18.01	1.000	3.154	365.0	2388	2932	–	–	8

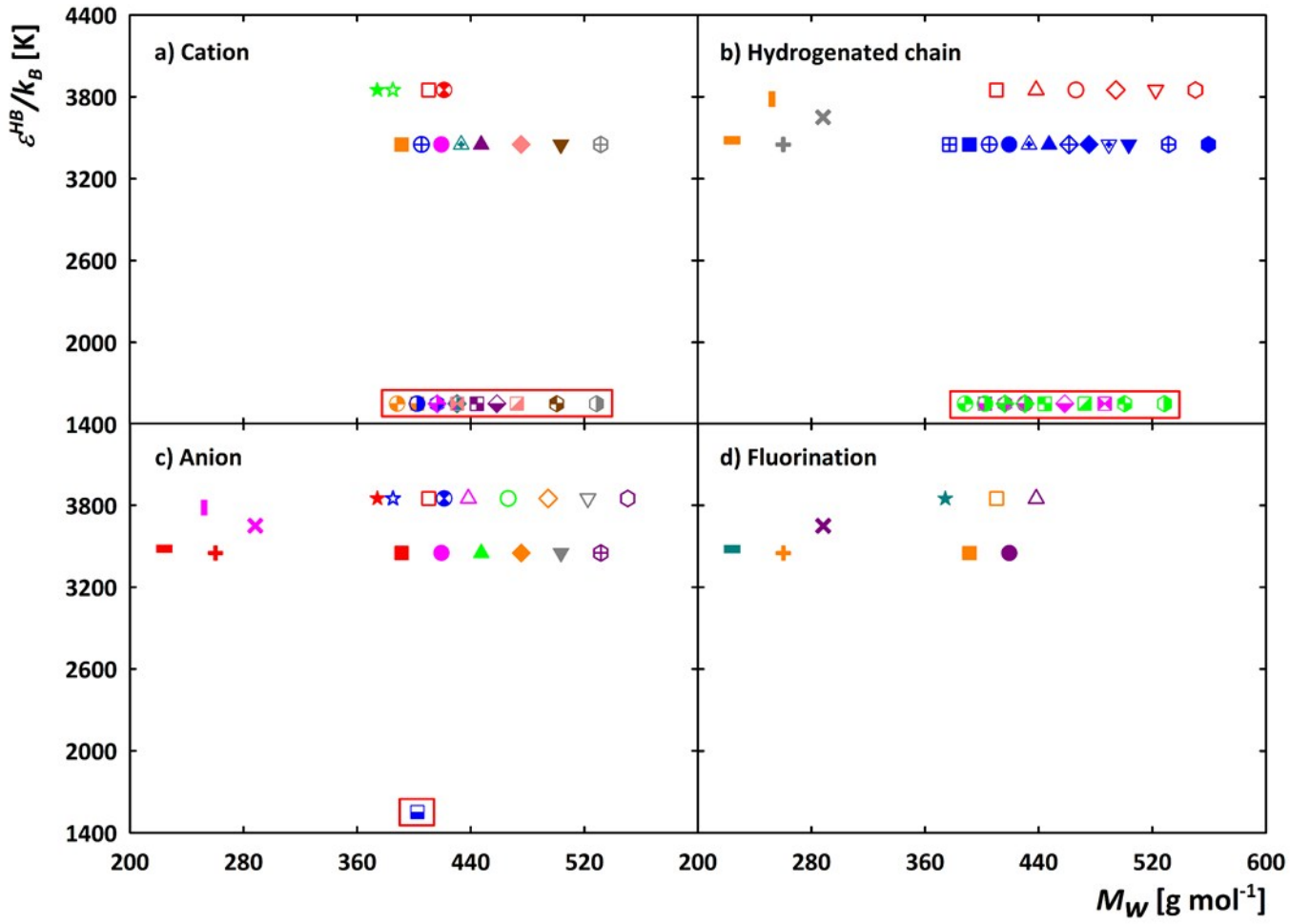

Figure S1. Values of the association parameter ε^{HB} *versus* molecular weight of the studied ionic liquids, where: a) the influence of cations; b) increment of cation hydrogenated alkyl side chain; c) anions; and d) increment of fluorination. The comparisons are grouped by colours. These values illustrate the trends from the reference 5 before any reparameterization process of $[C_nC_1py][N(CF_3SO_2)_2]$ and $[C_npy][N(CF_3SO_2)_2]$ families. Herein, one can identify the "outliers" values, around 1550 K, highlighted by the red box in the comparisons a), b) and c). Symbols are described in Table S1.

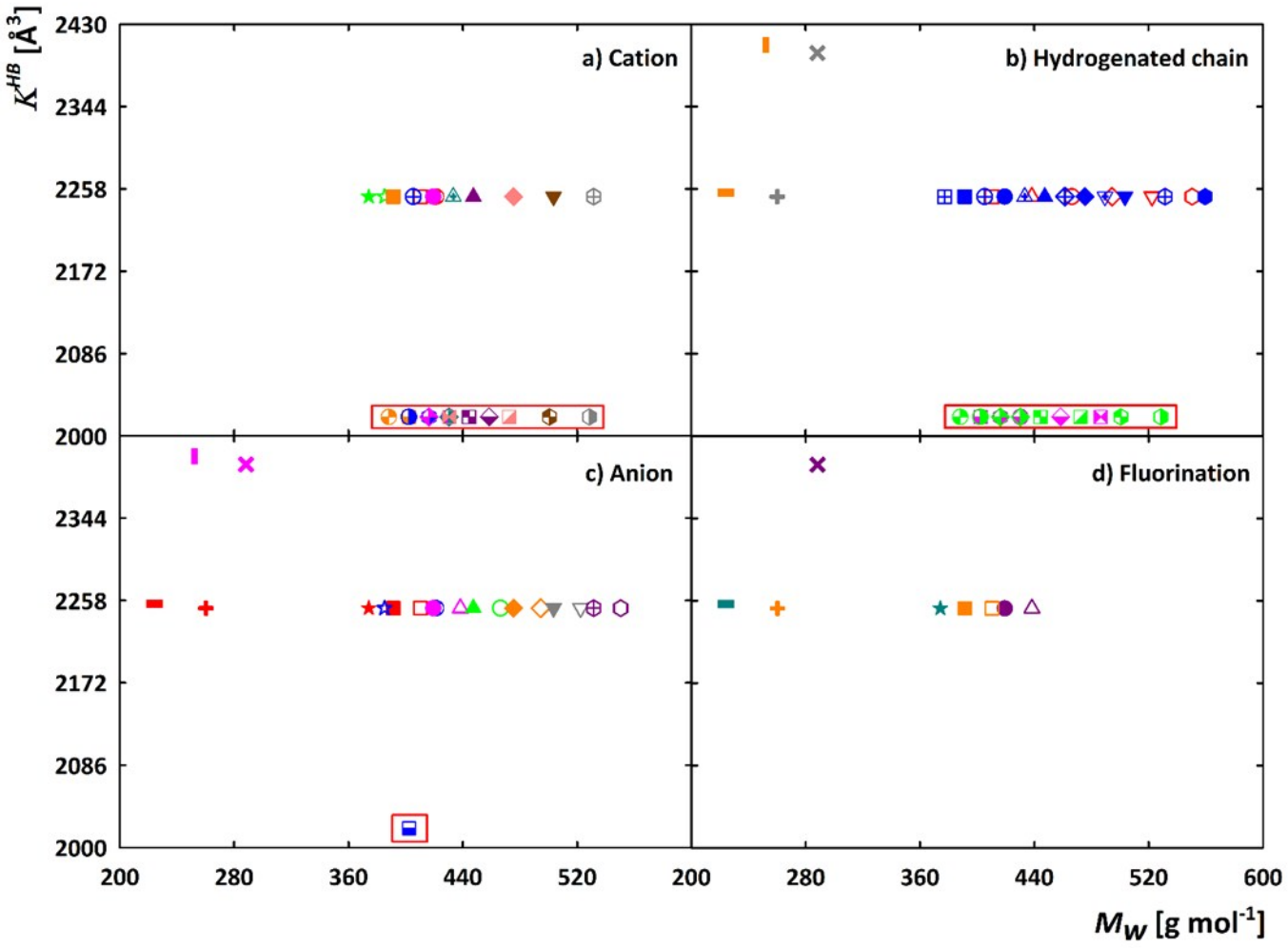

Figure S2. Values of the association parameter κ^{HB} *versus* molecular weight of the studied ionic liquids, where: a) influence of cations; b) increment of cation hydrogenated alkyl side chain; c) anions; and d) increment of fluorination. The comparisons are grouped by colours. These values illustrate the trends from the reference 5 before any reparameterization process of $[C_nC_1py][N(CF_3SO_2)_2]$ and $[C_npy][N(CF_3SO_2)_2]$ families. Herein, one can identify the "outliers" values, around 2020 Å^3, highlighted by the red box in the comparisons a), b) and c). Symbols are described in Table S1.

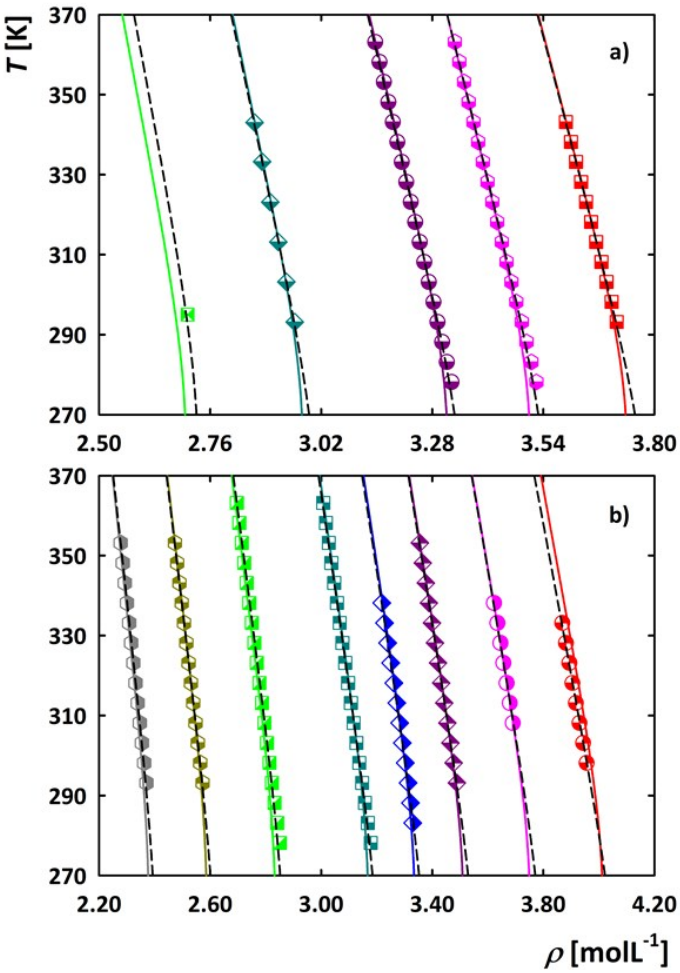

Figure S3. Temperature versus density diagram at 0.1 MPa for: a) $[C_nC_1py][N(CF_3SO_2)_2]$; and b) $[C_npy][N(CF_3SO_2)_2]$ for different alkyl chains (n = 2, red; n = 3, pink; n = 4, purple; n = 5, blue; n = 6, dark cyan; n = 8, green; n = 10, dark yellow; n = 12, grey). The solid lines represent the calculations obtained with the parameters from reference 5 whereas the dashed lines are the results obtained with the parameters optimized in this work. Symbols represent the experimental data[9-14] for each system (see Table S1 for more details).

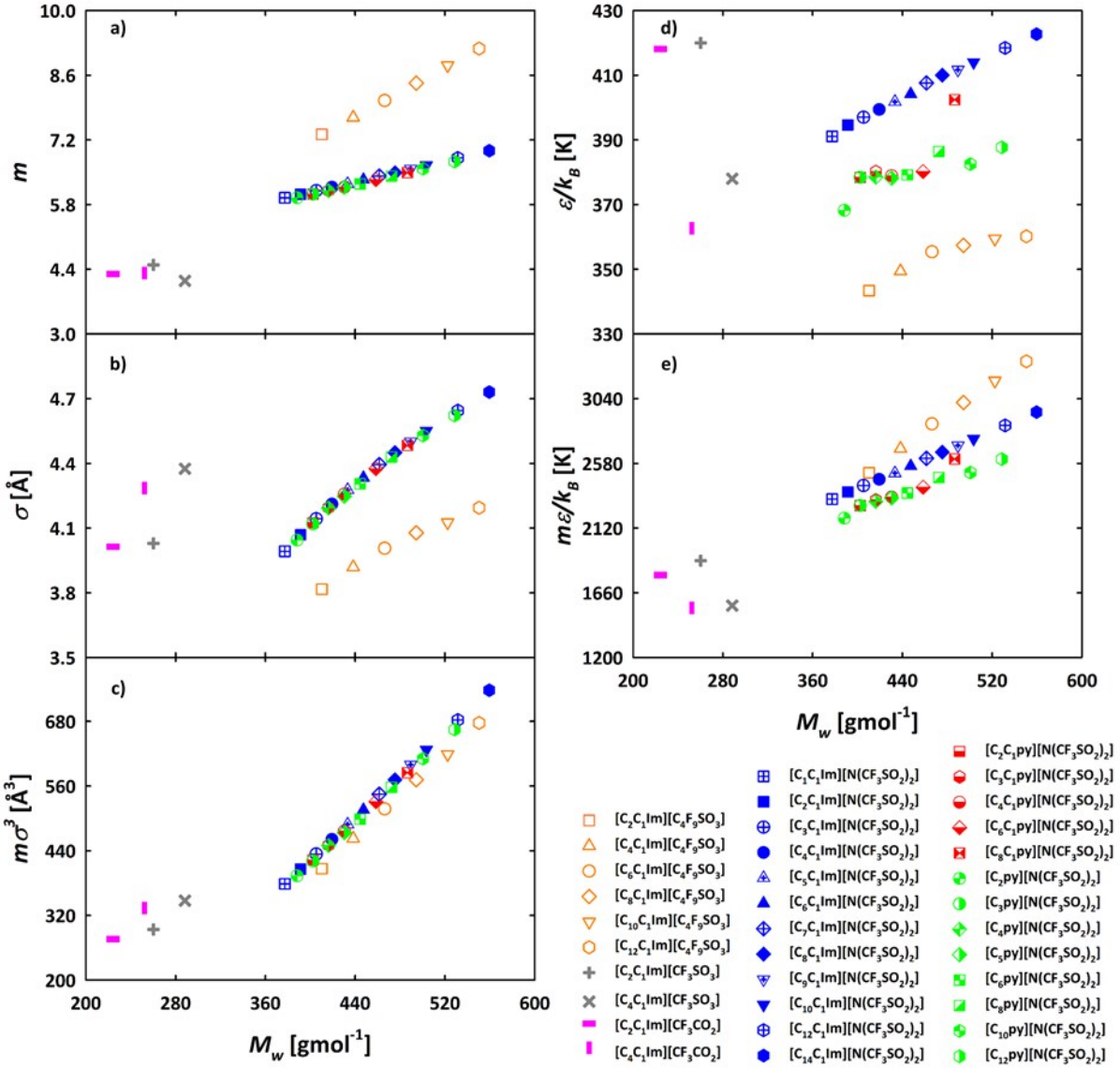

Figure S4. Molecular parameters values *versus* molecular weight for FILs with different hydrogenated alkyl side chains in the cation, where: a) m parameter; b) σ parameter; c) $m\sigma^3$ is a correlation of the volume of the molecules (anion + cation); d) ε/k_B parameter; and e) $m\varepsilon/k_B$ is a correlation representing the van der Waals energy of the molecules (anion + cation). The comparisons are grouped by colours.

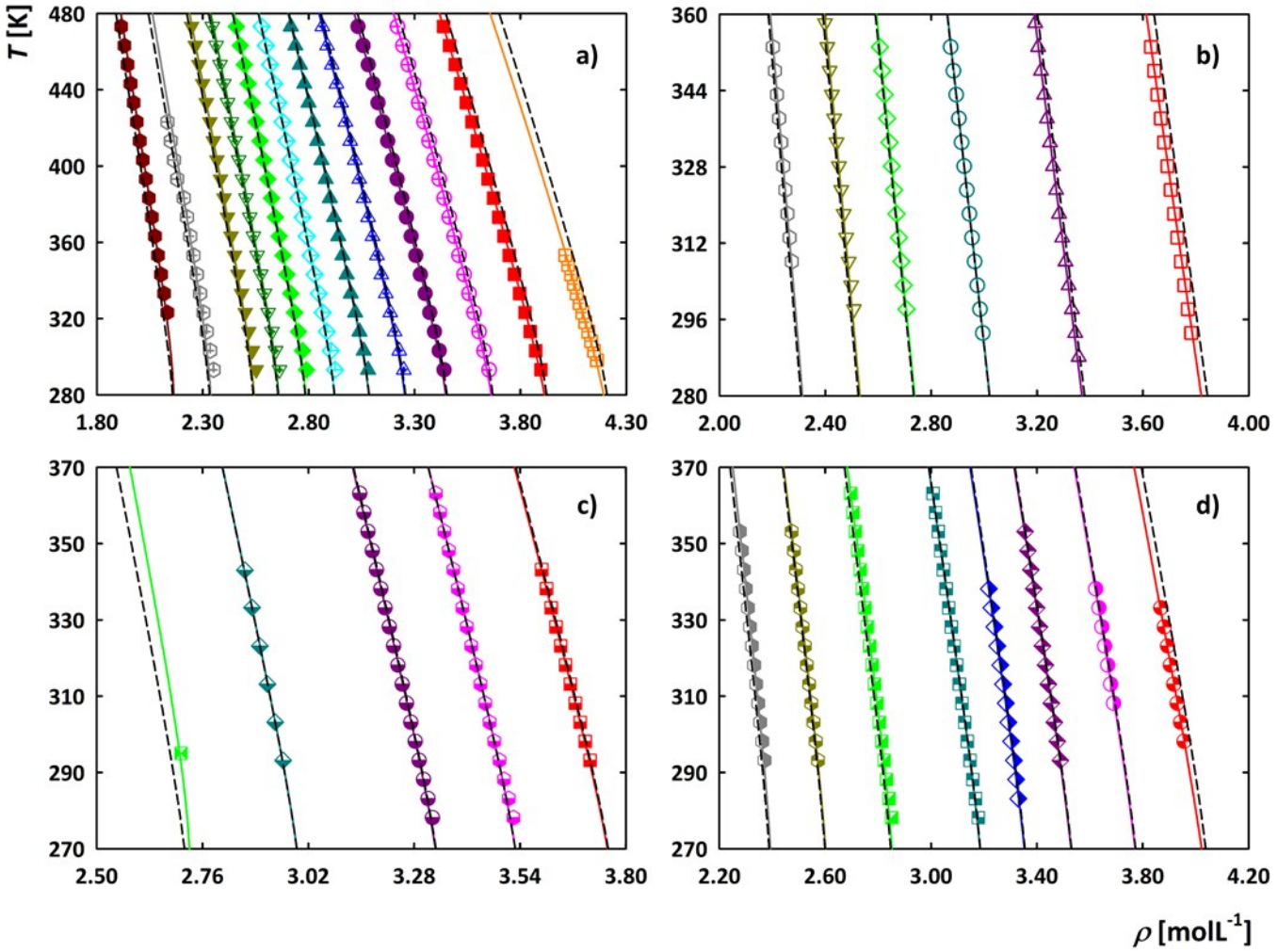

Figure S5. Temperature *versus* density diagrams at 0.1 MPa for: a) $[C_nC_1Im][N(CF_3SO_2)_2]$; b) $[C_nC_1Im][C_4F_9SO_3]$; c) $[C_nC_1py][N(CF_3SO_2)_2]$; and d) $[C_npy][N(CF_3SO_2)_2]$. The colour code is for the alkyl chain length of the cation: n=1, orange; n=2, red; n=3, pink; n=4, purple; n=5, blue; n=6, dark cyan; n=7, light cyan; n=8, light green; n=9, dark green; n=10, dark yellow; n=12, grey; n=14, dark red. The solid lines represent the calculations obtained with the optimized ε parameter for each IL (Table S1), and the dashed lines illustrate the calculations with the fixed ε/k_B parameter for each family at: a) 406 K, b) 355 K, c) and d) 380 K. Symbols represent the experimental data.[2,9-20]

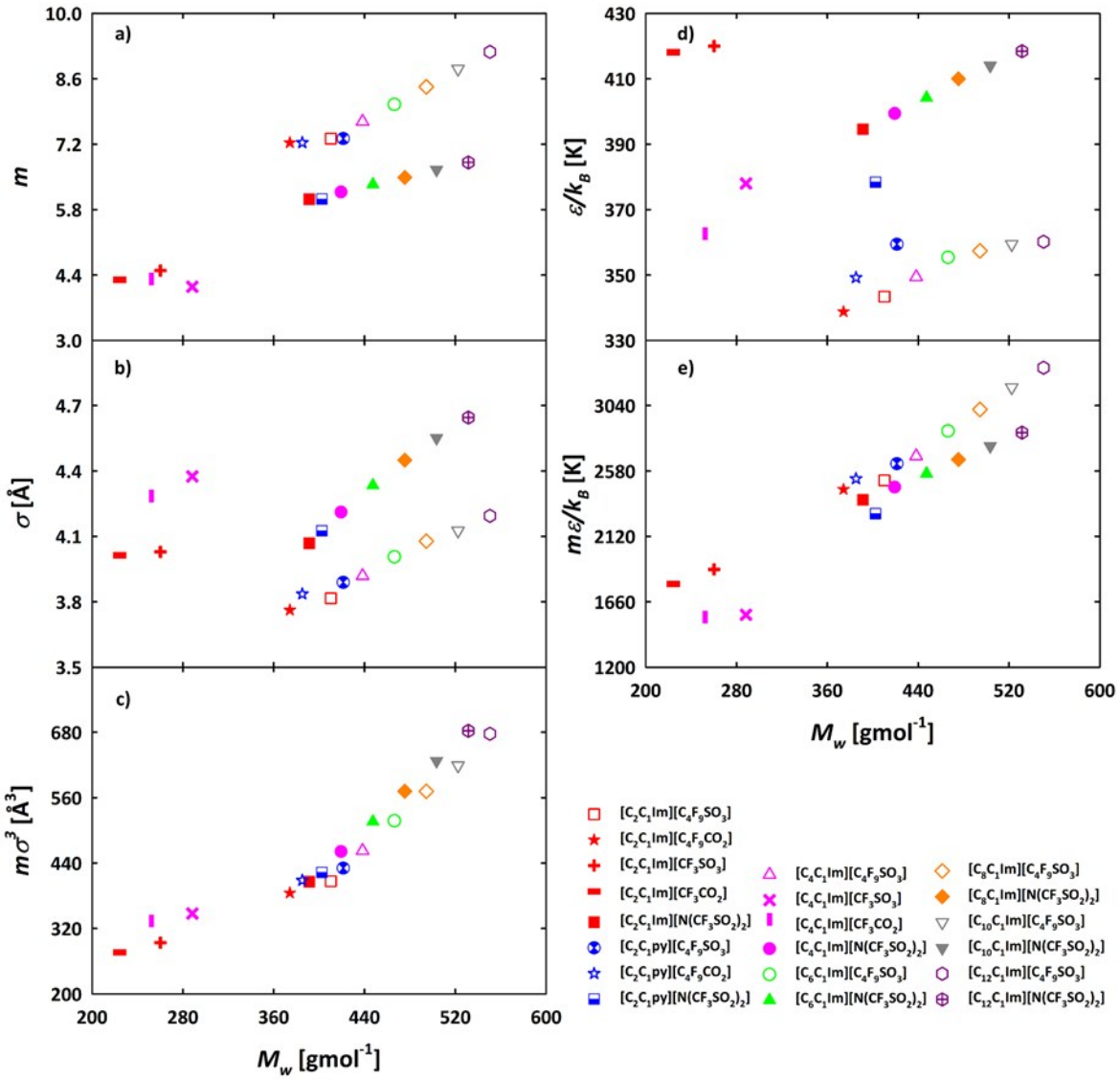

Figure S6. Molecular parameters values *versus* molecular weight for FILs with different anions, where: a) *m* parameter; b) σ parameter; c) $m\sigma^3$ is a correlation of the volume of the molecules (anion + cation); d) $^{\varepsilon}/k_B$ parameter; and e) m^{ε}/k_B is a correlation representing the van der Waals energy of the molecules (anion + cation). The comparisons are grouped by colours.

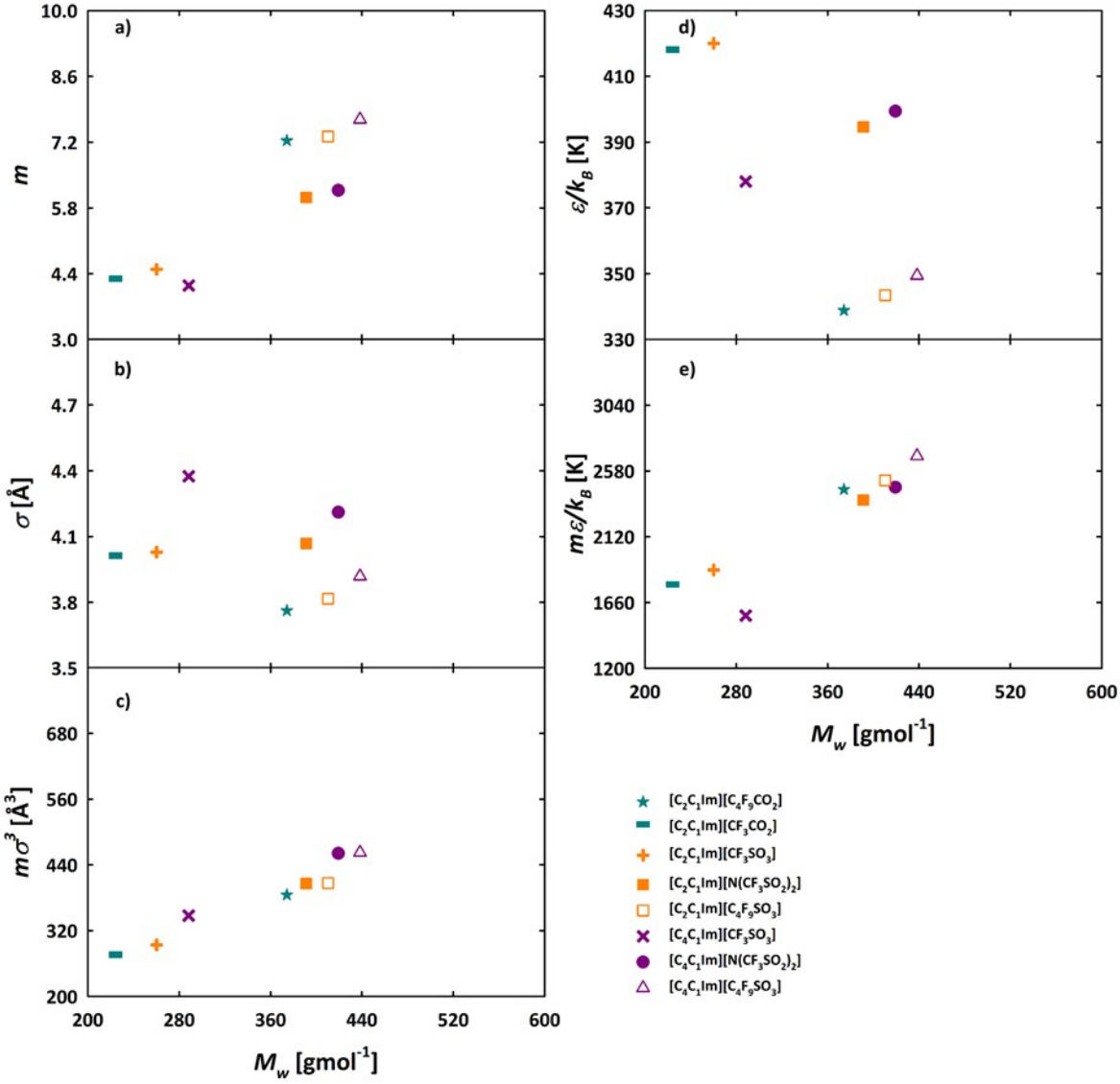

Figure S7. Molecular parameters values *versus* molecular weight for FILs with different anion fluorination, where: a) *m* parameter; b) σ parameter; c) $m\sigma^3$ is a correlation of the volume of the molecules (anion + cation); d) ε/k_B parameter; and e) $m\varepsilon/k_B$ is a correlation representing the van der Waals energy of the molecules (anion + cation). The comparisons are grouped by colours.

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