

Supplementary Materials

Synthesis and Characterization of Fluorinated Phosphonium Ionic Liquids to use as New Engineering Solvents

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1. Synthesis procedure, NMR and elemental analysis

[P₆₆₆₁₄][C₄F₉SO₃] synthesis: 3.84 g of [P₆₆₆₁₄]Cl was dissolved in ethanol and transformed into hydroxide by the use of an anionic exchange resin. Then, the prepared hydroxide was neutralized with C₄F₉SO₃H (2.29 g dissolved in ethanol). The solution was then evaporated in a rotavapor. The colourless liquid was washed with a solution of 90% acetonitrile in ethanol. The oil obtained was dried in a vacuum line and was obtained into a light-yellow liquid.

[P₆₆₆₁₄][C₄F₉SO₃]: ¹H RMN δ_H (400 MHz, (CD₃)₂CO): 0.80-0.93 (m, 12H, 3xPCH₂(CH₂)₂CH₃ and CH₃(CH₂)₁₂CH₂P), 1.16-1.53 (m, 48H, 3xPCH₂(CH₂)₄CH₃ and CH₃(CH₂)₁₂CH₂P), 2.10-2.24 (m, 8H, 3xPCH₂(CH₂)₂CH₃ and CH₃(CH₂)₁₂CH₂P). ¹⁹F NMR δ_F (376 MHz, (CD₃)₂CO): -80.46 (m, 3F, CF₃), -114.84 (m, 2F, CF₂SO₃), -121.39 (m, 2F, CF₃CF₂), -125.75 (m, 2F, CF₃CF₂CF₂). Elemental analysis calculated (found): %C 55.23 (53.32); %H 8.75 (8.42); %S 4.10 (4.11).

[P₆₆₆₁₄][C₄F₉CO₂] synthesis: 3.70 g of [P₆₆₆₁₄]Cl was dissolved in ethanol and transformed into hydroxide by the use of an anionic exchange resin. Then, the prepared hydroxide was neutralized with C₄F₉CO₂H (1.82 g dissolved in ethanol). The solution was then evaporated in a rotavapor. The colourless liquid was washed with a solution of 90% acetonitrile in ethanol. The oil obtained was dried in a vacuum line and was obtained into a colourless liquid.

[P₆₆₆₁₄][C₄F₉CO₂]: ¹H RMN δ_H (400 MHz, (CD₃)₂CO): 0.81-0.94 (m, 12H, 3xPCH₂(CH₂)₂CH₃ and CH₃(CH₂)₁₂CH₂P), 1.17-1.59 (m, 48H, 3xPCH₂(CH₂)₄CH₃ and CH₃(CH₂)₁₂CH₂P), 2.11-2.27 (m, 8H, 3xPCH₂(CH₂)₂CH₃ and CH₃(CH₂)₁₂CH₂P). ¹⁹F NMR δ_F (376 MHz, (CD₃)₂CO): -80.61 (m, 3F, CF₃), -115.57 (m, 2F, CF₂SO₃), -122.75 (m, 2F, CF₃CF₂), -125.51 (m, 2F, CF₃CF₂CF₂). Elemental analysis calculated (found): %C 59.50 (57.09); %H 9.18 (8.66).

[P₄₄₄₁₄][C₄F₉SO₃] synthesis: 3.29 g of [P₄₄₄₁₄]Cl was dissolved in one solution of 30% ethanol in water and transformed into hydroxide by the use of an anionic exchange resin. The solution was added with a few portions of ethanol during the process because the solution become cloudy. Then, the prepared hydroxide was neutralized with C₄F₉SO₃H (2.34 g dissolved in one solution of 30% ethanol in water). The solution was then evaporated in rotavapor. The light-yellow liquid was washed with a solution of

90% acetonitrile in ethanol. The oil obtained was dried in a vacuum line and was obtained into an orange liquid.

[P₄₄₄₁₄][C₄F₉SO₃]: ¹H RMN δ_H (400 MHz, (CD₃)₂CO): 0.83-0.98 (m, 12H, 3xPCH₂(CH₂)₂CH₃ and CH₃(CH₂)₁₂CH₂P), 1.18-1.54 (m, 36H, 3xPCH₂(CH₂)₂CH₃ and CH₃(CH₂)₁₂CH₂P), 2.11-2.26 (m, 8H, 3xPCH₂(CH₂)₂CH₃ and CH₃(CH₂)₁₂CH₂P). ¹⁹F NMR δ_F (376 MHz, (CD₃)₂CO): -80.45 (m, 3F, CF₃), -114.83 (m, 2F, CF₂SO₃), -121.37 (m, 2F, CF₃CF₂), -125.66 (m, 2F, CF₃CF₂CF₂). Elemental analysis calculated (found): %C 51.56 (48.49); %H 8.08 (7.68); %S 4.59 (4.90).

[P₄₄₄₁₄][C₄F₉CO₂] synthesis: 3.50 g of [P₄₄₄₁₄]Cl was dissolved in one solution of 30% ethanol in water and transformed into hydroxide by the use of an anionic exchange resin. The solution was added with a few portions of ethanol during the process because the solution become cloudy. Then, the prepared hydroxide was neutralized with C₄F₉CO₂H (2.21 g dissolved in one solution of 30% ethanol in water). The solution was then evaporated in a rotavapor. The colourless liquid was washed with a solution of 90% acetonitrile in ethanol. The oil obtained was dried in a vacuum line and was obtained into a colourless liquid.

[P₄₄₄₁₄][C₄F₉CO₂]: ¹H RMN δ_H (400 MHz, (CD₃)₂CO): 0.80-0.96 (m, 12H, 3xPCH₂(CH₂)₂CH₃ and CH₃(CH₂)₁₂CH₂P), 1.17-1.54 (m, 36H, 3xPCH₂(CH₂)₂CH₃ and CH₃(CH₂)₁₂CH₂P), 2.09-2.25 (m, 8H, 3xPCH₂(CH₂)₂CH₃ and CH₃(CH₂)₁₂CH₂P). ¹⁹F NMR δ_F (376 MHz, (CD₃)₂CO): -80.52 (m, 3F, CF₃), -115.35 (m, 2F, CF₂SO₃), -122.67 (m, 2F, CF₃CF₂), -125.49 (m, 2F, CF₃CF₂CF₂). Elemental analysis calculated (found): %C 56.18 (53.89); %H 8.52 (8.13).

[P₄₄₄₄][C₄F₉SO₃] synthesis: 3.29 g of [P₄₄₄₄]Br was dissolved in water and transformed into hydroxide by the use of an anionic exchange resin. The solution was added with a few portions of ethanol during the process because the solution become cloudy. Then, the prepared hydroxide was neutralized with C₄F₉SO₃H (3.00 g dissolved in water). The solution was then evaporated in a rotavapor. The liquid was washed with a solution of 90% acetonitrile in ethanol. The oil obtained was dried in a vacuum line and was obtained as a solid.

[P₄₄₄₄][C₄F₉SO₃]: ¹H NMR δ_H (400 MHz, (CD₃)₂CO): 0.88-1.00 98 (m, 12H, 4xPCH₂(CH₂)₂CH₃), 1.33-1.56 (m, 16H, 4xPCH₂(CH₂)₂CH₃), 2.11-2.26 (m, 8H, 4xPCH₂(CH₂)₂CH₃). ¹⁹F NMR δ_F (376 MHz, (CD₃)₂CO): -80.52 (m, 3F, CF₃), -114.86 (m, 2F, CF₂SO₃), -121.37 (m, 2F, CF₃CF₂), -125.70 (m, 2F, CF₃CF₂CF₂). Elemental analysis calculated (found): %C 43.01 (40.09); %H 6.50 (6.12); %S 5.74 (6.07).

[P₄₄₄₄][C₄F₉CO₂] synthesis: 3.42 g of [P₄₄₄₁₄]Br was dissolved in water and transformed into hydroxide by the use of an anionic exchange resin. The solution was added with a few portions of ethanol during the process because the solution become cloudy. Then, the prepared hydroxide was neutralized with C₄F₉CO₂H (2.77g dissolved in water). The solution was then evaporated in a rotavapor. The colourless liquid was washed with a solution of 90% acetonitrile in ethanol. The oil obtained was dried in a vacuum line and was obtained into a colourless solid.

[P₄₄₄₄][C₄F₉CO₂]: ¹H NMR δ_H (400 MHz, (CD₃)₂CO): 0.87-0.98 98 (m, 12H, 4xPCH₂(CH₂)₂CH₃), 1.33-1.55 (m, 16H, 4xPCH₂(CH₂)₂CH₃), 2.11-2.25 (m, 8H, 4xPCH₂(CH₂)₂CH₃). ¹⁹F NMR δ_F (376 MHz, (CD₃)₂CO): -80.57 (m, 3F, CF₃), -115.48 (m, 2F, CF₂CO₂), -122.73 (m, 2F, CF₃CF₂), -125.50 (m, 2F, CF₃CF₂CF₂). Elemental analysis calculated (found): %C 48.28 (44.69); %H 6.95 (6.49).

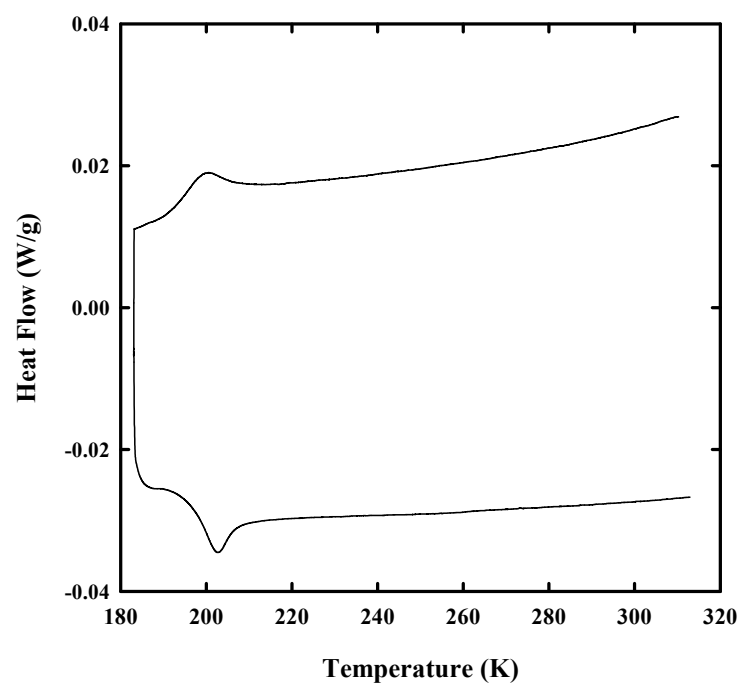


Figure S1. Differential scanning calorimetry curves at 1 K/min of $[P_{66614}][C_4F_9SO_3]$.

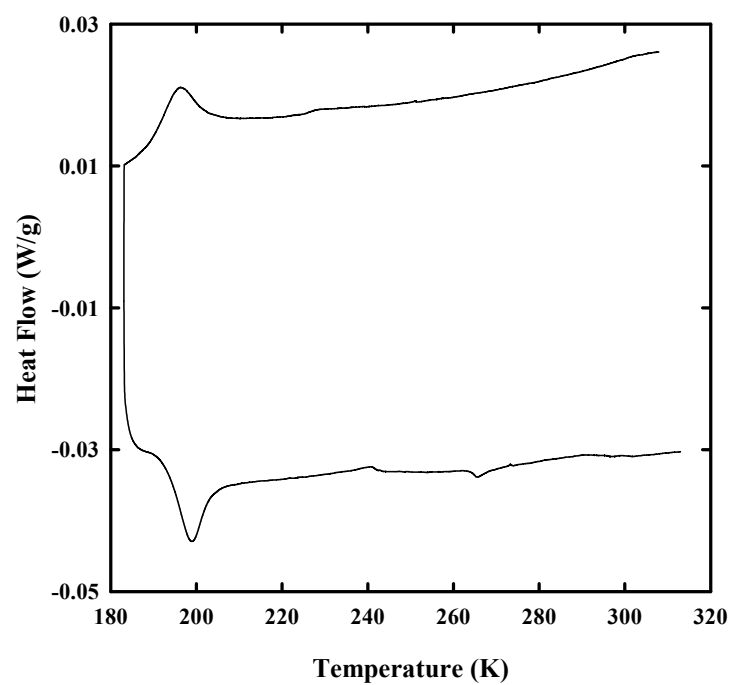


Figure S2. Differential scanning calorimetry curves at 1 K/min of $[P_{66614}][C_4F_9CO_2]$.

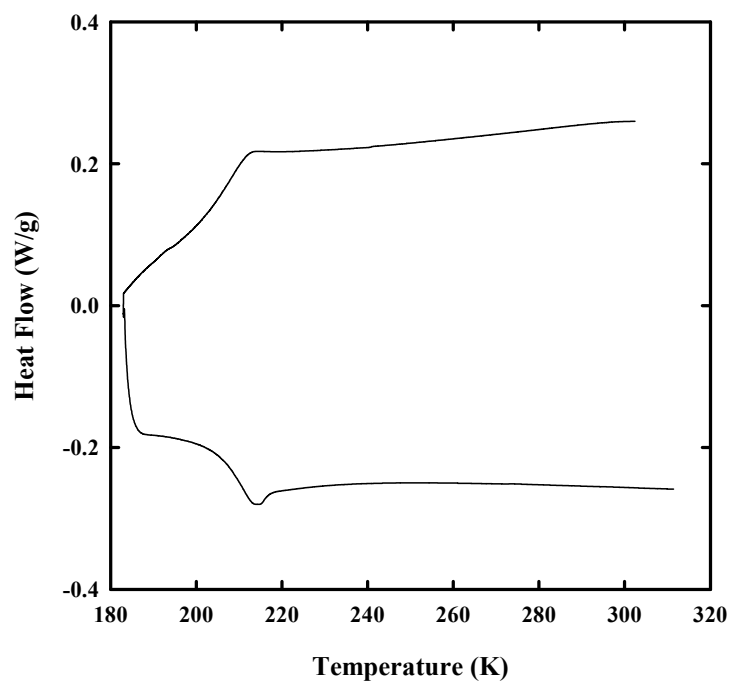


Figure S3. Differential scanning calorimetry curves at 10 K/min of [P₄₄₄₁₄][C₄F₉SO₃].

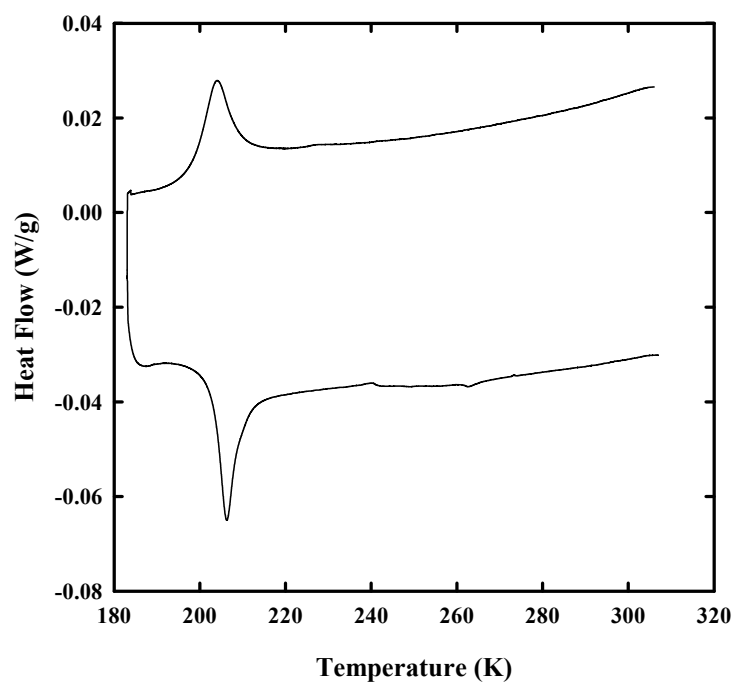


Figure S4. Differential scanning calorimetry curves at 1 K/min of [P₄₄₄₁₄][C₄F₉CO₂].

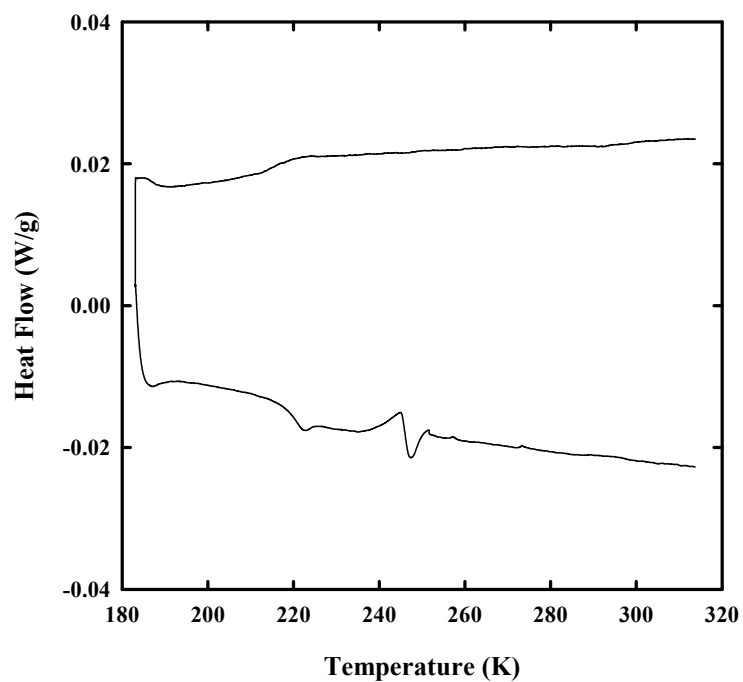


Figure S5. Differential scanning calorimetry curves at 1 K/min of $[P_{4444}][C_4F_9SO_3]$.

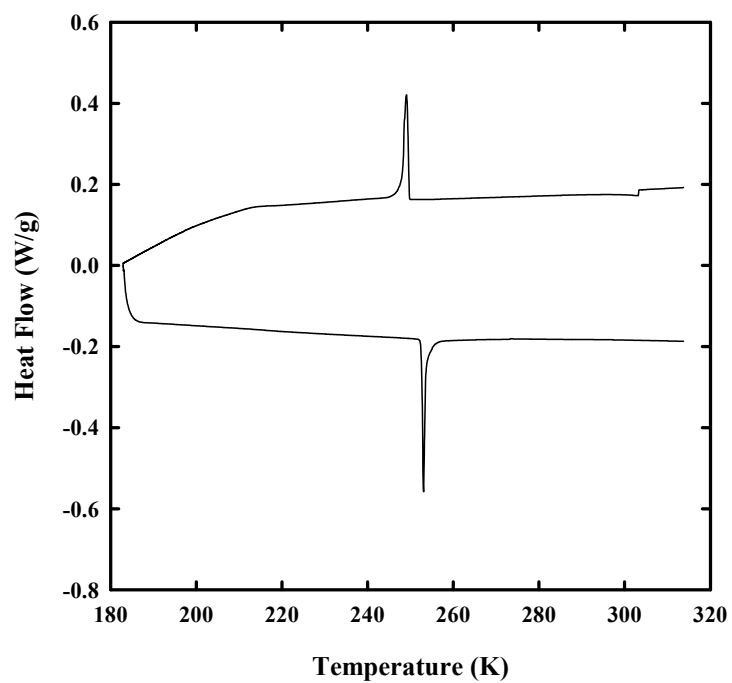


Figure S6. Differential scanning calorimetry curves at 10 K/min of $[P_{4444}][C_4F_9CO_2]$.

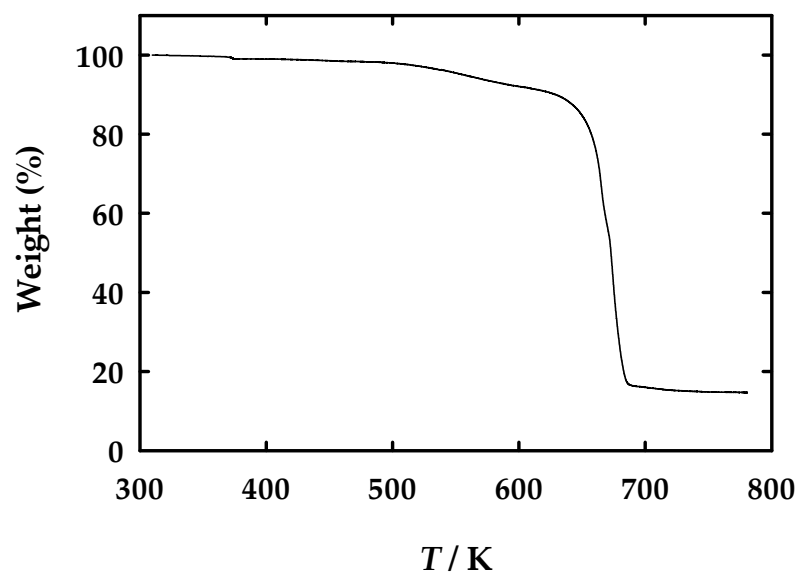


Figure S7. Thermogravimetric curves at 1 K/min of $[P_{66614}][C_4F_9SO_3]$.

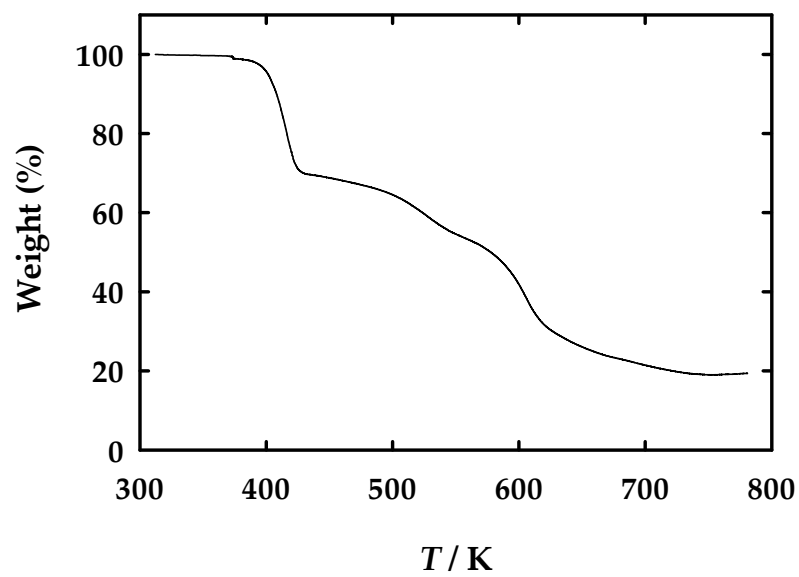


Figure S8. Thermogravimetric curves at 1 K/min of $[P_{66614}][C_4F_9CO_2]$.

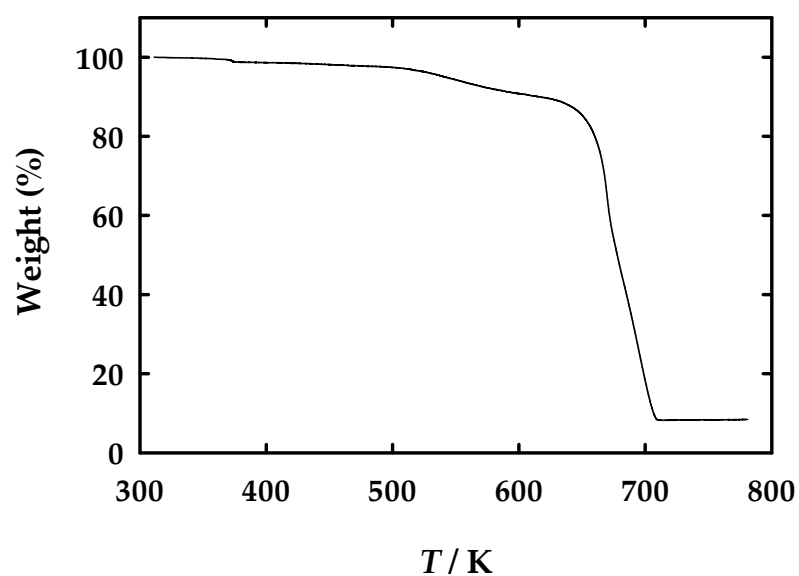


Figure S9. Thermogravimetric curves at 1 K/min of $[P_{44414}][C_4F_9SO_3]$.

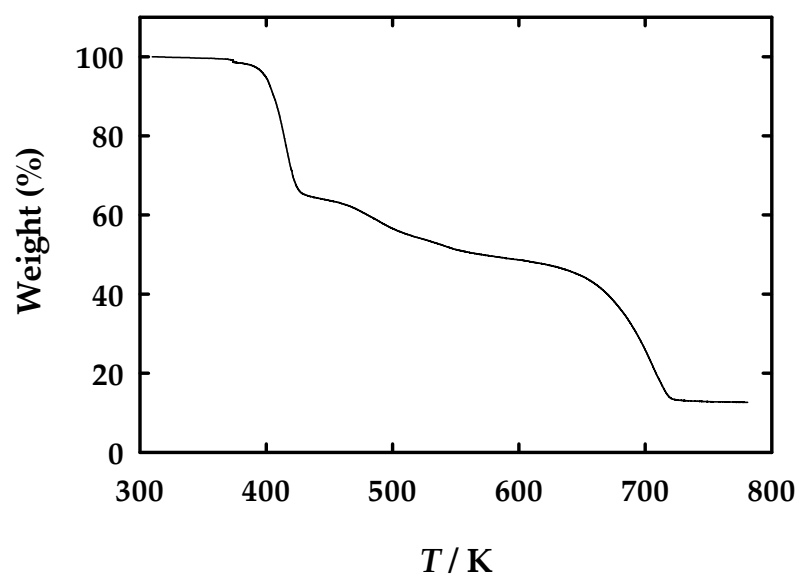


Figure S10. Thermogravimetric curves at 1 K/min of $[P_{44414}][C_4F_9CO_2]$.

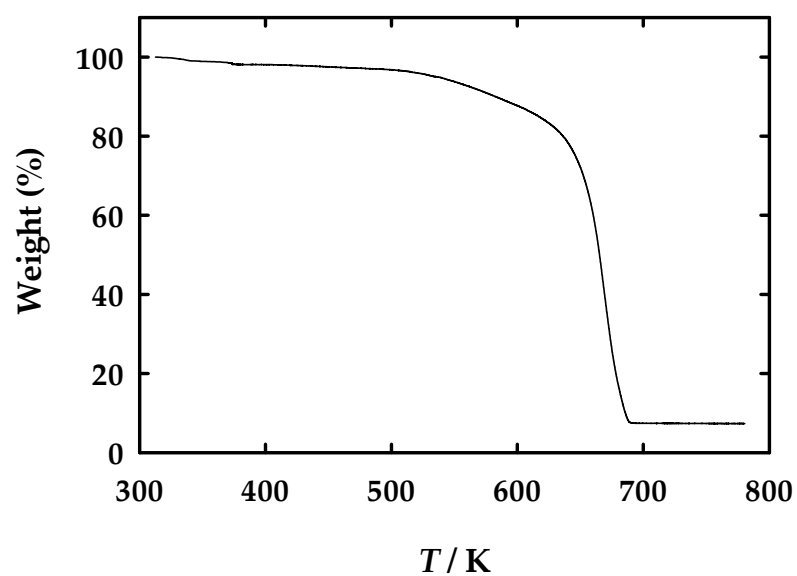


Figure S11. Thermogravimetric curves at 1 K/min of $[P_{444}][C_4F_9SO_3]$.

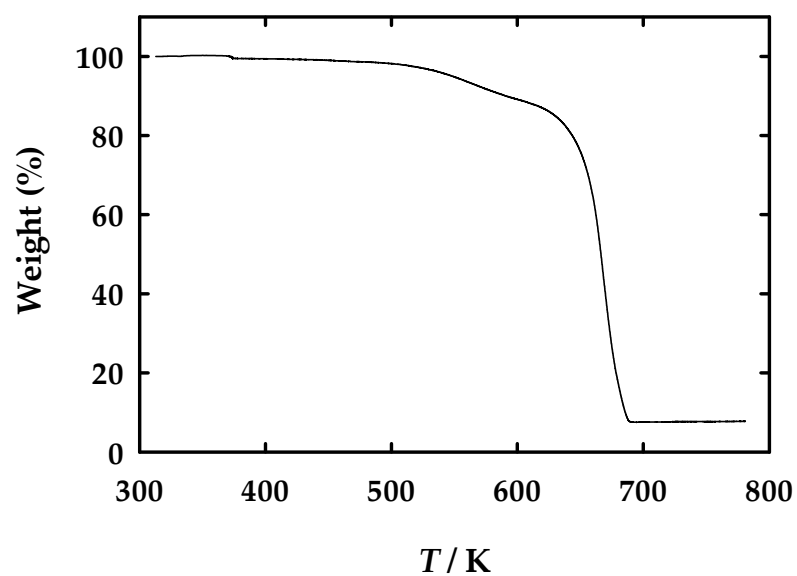


Figure S12. Thermogravimetric curves at 1 K/min of $[P_{444}][C_4F_9CO_2]$.

Table S1. Density, ρ , dynamic viscosity, η , refractive index, n_D , and ionic conductivity, k , of the fluorinated ionic liquids as a function of temperature.

FIL	T/K	$\rho/g\cdot cm^{-3}$	$\eta/mPa\cdot s$	n_D	$k/mS\cdot cm^{-1}$
[P ₆₆₆₁₄][C ₄ F ₉ SO ₃]	293.15	1.0686	947.18	1.4368	0.0140
	298.15	1.0647	662.21	1.4353	0.0201
	303.15	1.0607	473.41	1.4337	0.0276
	308.15	1.0566	345.17	1.4321	0.0373
	313.15	1.0526	256.50	1.4305	0.0491
	318.15	1.0483	193.99	1.4289	0.0640
	323.15	1.0440	149.16	1.4273	0.0817
	328.15	1.0395	116.41	1.4258	-
	333.15	1.0355	92.166	1.4242	-
	338.15	-	73.897	1.4227	-
	343.15	-	59.990	1.4211	-
	348.15	-	49.254	1.4196	-
	353.15	-	40.850	1.4180	-
[P ₆₆₆₁₄][C ₄ F ₉ CO ₂]	293.15	1.0692	247.70	1.4361	0.0319
	298.15	1.0649	185.13	1.4344	0.0428
	303.15	1.0609	141.17	1.4328	0.0563
	308.15	1.0567	109.43	1.4311	0.0725
	313.15	1.0526	86.140	1.4295	0.0923
	318.15	1.0485	69.059	1.4278	0.115
	323.15	1.0447	55.617	1.4262	0.145
	328.15	1.0408	45.526	1.4246	-
	333.15	1.0371	37.684	1.4230	-
	338.15	-	31.518	1.4213	-
	343.15	-	26.601	1.4198	-
	348.15	-	22.654	1.4182	-
	353.15	-	19.459	1.4166	-
[P ₄₄₄₁₄][C ₄ F ₉ SO ₃]	293.15	1.1482	1934.5	1.4327	0.0132
	298.15	1.1442	1289.0	1.4312	0.0197
	303.15	1.1402	882.29	1.4296	0.0281
	308.15	1.1362	618.10	1.4281	0.0394
	313.15	1.1321	442.55	1.4265	0.0539
	318.15	1.1280	323.29	1.4250	0.0724
	323.15	1.1242	240.53	1.4235	0.0949
	328.15	1.1203	182.03	1.4219	-
	333.15	1.1166	139.94	1.4204	-
	338.15	-	109.11	1.4189	-
	343.15	-	86.446	1.4174	-
	348.15	-	69.357	1.4159	-
	353.15	-	56.216	1.4144	-
[P ₄₄₄₁₄][C ₄ F ₉ CO ₂]	293.15	1.1067	297.97	1.4303	0.0518
	298.15	1.1026	219.32	1.4286	0.0704
	303.15	1.0985	164.46	1.4270	0.0934
	308.15	1.0944	125.50	1.4253	0.122
	313.15	1.0905	97.330	1.4237	0.160
	318.15	1.0868	76.670	1.4221	0.202
	323.15	1.0830	61.250	1.4205	0.252
	328.15	1.0793	49.580	1.4189	-
	333.15	1.0757	40.617	1.4173	-

338.15	-	33.652	1.4157	-
343.15	-	28.350	1.4141	-
348.15	-	23.942	1.4126	-
353.15	-	20.450	1.4110	-

Table S2. Fitting parameters for the density, ρ , dynamic viscosity, η , refractive index, n_D , and ionic conductivity, k , as a function of temperature for fluorinated ionic liquids. Standard deviations, S.D., are also shown.

[P ₆₆₆₁₄][C ₄ F ₉ SO ₃]	$\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.2986$	$A_1 = -7.91 \cdot 10^{-4}$	-	S.D. = $2.38 \cdot 10^{-4}$
	n_D	$A_0 = 1.5286$	$A_1 = -3.13 \cdot 10^{-4}$	-	S.D. = $3.67 \cdot 10^{-5}$
	$\eta/\text{mPa}\cdot\text{s}$	$\eta_0 = 0.0193$	$B = 1570.4$	$T_0 = 147.72$	S.D. = $3.03 \cdot 10^{-1}$
	$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 87.957$	$B' = 1041.2$	$T_0' = 174.06$	S.D. = $3.31 \cdot 10^{-3}$
[P ₆₆₆₁₄][C ₄ F ₉ CO ₂]	$\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.2906$	$A_1 = -7.64 \cdot 10^{-4}$	-	S.D. = $1.58 \cdot 10^{-4}$
	n_D	$A_0 = 1.5311$	$A_1 = -3.24 \cdot 10^{-4}$	-	S.D. = $5.31 \cdot 10^{-5}$
	$\eta/\text{mPa}\cdot\text{s}$	$\eta_0 = 0.0446$	$B = 1236.1$	$T_0 = 149.81$	S.D. = $7.88 \cdot 10^{-2}$
	$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 423.26$	$B' = 1510.3$	$T_0' = 133.99$	S.D. = $4.36 \cdot 10^{-3}$
[P ₄₄₄₁₄][C ₄ F ₉ SO ₃]	$\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.3438$	$A_1 = -7.01 \cdot 10^{-4}$	-	S.D. = $9.47 \cdot 10^{-5}$
	n_D	$A_0 = 1.5220$	$A_1 = -3.05 \cdot 10^{-4}$	-	S.D. = $3.47 \cdot 10^{-5}$
	$\eta/\text{mPa}\cdot\text{s}$	$\eta_0 = 0.0183$	$B = 1582.7$	$T_0 = 156.34$	S.D. = $1.21 \cdot 10^{-0}$
	$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 248.26$	$B' = 1179.8$	$T_0' = 173.25$	S.D. = $3.27 \cdot 10^{-3}$
[P ₄₄₄₁₄][C ₄ F ₉ CO ₂]	$\rho/\text{g}\cdot\text{cm}^{-3}$	$A_0 = 0.3094$	$A_1 = -7.10 \cdot 10^{-4}$	-	S.D. = $1.89 \cdot 10^{-4}$
	n_D	$A_0 = 1.5240$	$A_1 = -3.20 \cdot 10^{-4}$	-	S.D. = $5.27 \cdot 10^{-5}$
	$\eta/\text{mPa}\cdot\text{s}$	$\eta_0 = 0.0342$	$B = 1290.8$	$T_0 = 150.88$	S.D. = $1.56 \cdot 10^{-1}$
	$k/\text{mS}\cdot\text{cm}^{-1}$	$k_0 = 965.42$	$B' = 1533.1$	$T_0' = 137.24$	S.D. = $5.69 \cdot 10^{-3}$

Table S3. Values of calculated molar volume, V_m , and molar refraction, R_m , as a function of temperature for selected fluorinated ionic liquids.

FIL	T/K	$V_m/\text{cm}^3\cdot\text{mol}^{-1}$	$R_m/\text{cm}^3\cdot\text{mol}^{-1}$
[P ₆₆₆₁₄][C ₄ F ₉ SO ₃]	293.15	732.69	191.88
	298.15	735.37	191.97
	303.15	738.14	192.11
	308.15	741.01	192.24
	313.15	743.82	192.34
	318.15	746.87	192.51
	323.15	749.95	192.67
	328.15	753.20	192.91
	333.15	756.11	193.02
[P ₆₆₆₁₄][C ₄ F ₉ CO ₂]	293.15	698.55	182.65
	298.15	701.37	182.80
	303.15	704.02	182.86
	308.15	706.82	183.00
	313.15	709.57	183.08
	318.15	712.35	183.19
	323.15	714.94	183.26
	328.15	717.62	183.30
	333.15	720.18	183.35
[P ₄₄₄₁₄][C ₄ F ₉ SO ₃]	293.15	608.59	158.08
	298.15	610.72	158.15
	303.15	612.86	158.19
	308.15	615.02	158.26
	313.15	617.25	158.32
	318.15	619.49	158.40
	323.15	621.59	158.45
	328.15	623.75	158.47
	333.15	625.82	158.50
[P ₄₄₄₁₄][C ₄ F ₉ CO ₂]	293.15	598.84	154.76
	298.15	601.07	154.83
	303.15	603.31	154.90
	308.15	605.57	154.94
	313.15	607.73	154.98
	318.15	609.80	154.99
	323.15	611.94	154.99
	328.15	614.04	155.03
	333.15	616.10	155.03