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ESI

Dissolution of oligo(tetrafluoroethylene) and preparation of poly(tetrafluoroethylene)-based composites by using fluorinated ionic liquids

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Materials

Precursors of ionic liquids (ILs) such as 2-bromoethanol (>95.0%), trihexylphosphine (>90.0%), trifluoromethanesulfonic acid (≥98.0%), nonafluorobutanesulfonic acid (≥98.0%), heptadecafluorooctanesulfonic acid (>98.0%), and lithium bis(pentafluoroethanesulfonyl)imide (Li[Pf_2N], >98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. 1-Methylimidazole (99%) and 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl iodide (≥99%) were purchased from Sigma Aldrich Co. LLC. 1-Bromobutane (min. 98%, from Kanto Chemical Co., Inc.), lithium bis(nonafluorobutanesulfonyl)imide (Li[Nf_2N], 97.0+%, from Wako Pure Chemical Industries, Ltd.), and 1,2-dimethylimidazole (98%, from Acros Organics) were purchased from each companies. Lithium bis(trifluoromethanesulfonyl)imide (Li[Tf_2N], 98%) and lithium bis(fluorosulfonyl)imide (Li[FSI]) were kindly donated from Sumitomo 3M. Co. and Dai-Ichi Kogyo Seiyaku Co. Ltd., respectively.

ILs such as 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim]BF_4, min. 95%), 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim]PF_6, min. 97%), and trihexyl(tetradecyl)phosphonium chloride ([$P_{666,14}$]Cl, >95%) were purchased from Kanto Chemical Co., Inc. Tributyl(methyl)ammonium bis(trifluoromethanesulfonyl)imide ([N_{4441}][Tf_2N], >98%), 1-butylpyridinium bromide ([C_4py]Br, >98.0%), and 1-butyl-1-methylpiperidinium bromide ([Pip_{14}]Br, >97.0%) were purchased from Tokyo Chemical Industry Co., Ltd. 1-Butyl-1-methylpyrrolidinium bromide ([Pyr_{14}]Br, ≥99.0%, from Sigma Aldrich Co. LLC.), 1-butyl-3-methylimidazolium bromide ([C_4mim]Br, 99%, from IoLiTec GmbH), and 1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl, ≥98.0%, from Merck Ltd.) were purchased from each companies. Tributyl(hexyl)phosphonium bromide ([P_{4446}]Br) was kindly donated from Hokko Chemical Industry Co., Ltd. 1-Ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([C_2mim][FAP], ≥98.0 %) was kindly donated from Merck Ltd. Other ILs were synthesised as follows. Structures of the ILs were determined by ^{1}H NMR (α-400 or α-500, both from JEOL). In the case of novel ILs, such as trihexyl(heptadecafluoroundecyl)phosphonium bis(trifluoromethanesulfonyl)imide ([P_{666F}][Tf_2N]) and trihexyl(heptadecafluoroundecyl)phosphonium heptadecafluorooctanesulfonate ([P_{666F}]$C_8F_{17}SO_3$) , ^{13}C NMR, ^{19}F NMR, and elemental analysis were performed.

Synthesis of ILs

1-(2-Hydroxyethyl)-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_2OHmim][Tf_2N])
First, [C_2OHmim]Br was prepared as follow. To 1-methylimidazole diluted tenfold with acetonitrile, 2-bromoethanol (1.2 molar of 1-methylimidazole) was added dropwise at room temperature under N_2 atmosphere. The resulting mixture was heated up to 70 °C and stirred for 48 h. Removal of acetonitrile and unreacted precursors by evaporation yielded a yellow solid. The resulting solid was recrystallised from ethyl acetate/methanol 2/1 (v/v) solution. Recrystallisation was repeated to give a colourless solid. [C_2OHmim]Br synthesised and Li[Tf_2N] were then diluted tenfold with Milli-Q water. To the aqueous solution of [C_2OHmim]Br, the aqueous solution of Li[Tf_2N] (1.1 molar of the bromide salt) was added. The resulting solution was mixed with dichloromethane, and the dichloromethane fraction was collected. The dichloromethane fraction containing [C_2OHmim][Tf_2N] was washed with Milli-Q water for 3 times, then evaporated to remove dichloromethane. The remaining liquid was again diluted with dichloromethane and passed through a short column filled with activated aluminum oxide. After the evaporation of dichloromethane, the remaining liquid was dried well under vacuum at 60 °C for at least 3 h to give colourless liquids. ^{1}H-NMR (400MHz, DMSO-d_6, δ/ppm relative to Me_4Si): 3.73 (2H, q, J = 5.3 Hz, NCH_2CH_2), 3.87 (3H, s, NCH_3), 4.21 (t, 2H, J = 4.0 Hz, NCH_2), 5.17 (1H, t, J = 6.0 Hz, OH), 7.68 and 7.72 (2H, d, J = 2.0 and 2.0 Hz, NCHCHN), 9.07 (1H, s, NCHN).

1-Butylpyridinium bis(trifluoromethanesulfonyl)imide ([C_4py][Tf_2N])
The titled compound was prepared by the same procedure as that for [C_2OHmim][Tf_2N] with the corresponding halide salt [C_4py]Br. ^{1}H-NMR (400MHz, $CDCl_3$, δ/ppm relative to Me_4Si): 0.88-0.99 (3H, m, $N(CH_2)_3CH_3$), 1.31-1.44 (2H, m, $N(CH_2)_2CH_2$), 1.92-2.02 (2H, m, NCH_2CH_2), 4.54-4.62 (2H, m, NCH_2), 8.00-8.07 (2H, m, CHCHNCHCH), 8.48 (1H, q, J = 8.2 Hz, NCHCHCH), 8.80 (2H, t, J = 5.7 Hz, CHNCH).

1-Ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C_2mim][Tf_2N])
The IL was synthesised by the same procedure as described for [C_2OHmim][Tf_2N] but with the halide salt [C_2mim]Cl. ^{1}H-NMR (400MHz, DMSO-d_6, δ/ppm relative to Me_4Si): 1.41 (3H, t, J = 7.4 Hz, NCH_2CH_3), 3.84 (3H, s, NCH_3), 4.19 (2H, q, J = 7.3 Hz, NCH_2), 7.69 and 7.77 (2H, t, J = 1.6 and 1.8 Hz, NCHCHN), 9.10 (1H, s, NCHN).

1-Butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ([C_4mmim][Tf_2N])
[C_4mmim]Br was prepared as follow. To 1,2-dimethylimidazole diluted tenfold with acetonitrile, 1-bromobutane (1.2 molar of 1,2-dimethylimidazole) was added dropwise at room temperature under N_2 atmosphere. The mixture was stirred for 48 h at 70 °C. A yellow solid was obtained by the evaporation of acetonitrile and unreacted precursors. The solid obtained was repeatedly recrystallised from ethyl acetate/acetonitrile 2/1 (v/v) solution to give a white crystal. Then, bromide anion of this salt was replaced with [Tf_2N] anion using the same procedure as described above for [C_2OHmim][Tf_2N]. ^{1}H-NMR (500 MHz,

$CDCl_3$, δ/ppm relative to Me_4Si): 0.96 (3H, t, J = 7.5 Hz, $N(CH_2)_3CH_3$), 1.33-1.41 (2H, m, $N(CH_2)_2CH_2$), 1.74-1.80 (2H, m, NCH_2CH_2), 2.60 (3H, s, NCH_3N), 3.79 (3H, s, NCH_3), 4.04 (2H, t, J = 7.5 Hz, NCH_2), 7.17 and 7.20 (2H, d, J = 2.3 and 1.7 Hz, NC*H*C*H*N).

1-Butyl-1-methylpiperidinium bis(trifluoromethanesulfonyl)imide ([Pip_{14}][Tf_2N])
The salt was synthesised in the same manner as described for [C_2OHmim][Tf_2N] with the corresponding halide salt [Pip_{14}]Br. ^{1}H-NMR (400MHz, $CDCl_3$, δ/ppm relative to Me_4Si): 0.98 (3H, t, J = 7.4 Hz, $N(CH_2)_3CH_3$), 1.36 - 1.44 (2H, m, $N(CH_2)_2CH_2$), 1.63 - 1.78 (4H, m, $N(CH_2)_2CH_2$ in ring and NCH_2CH_2 in chain), 1.87 (4H, broad, $CH_2CH_2NCH_2CH_2$), 3.01 (3H, s, NCH_3), 3.24-3.28 (2H, m, NCH_2 in chain), 3.33 (4H, t, J = 5.8 Hz, CH_2NCH_2).

1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide ([Pyr_{14}][Tf_2N])
This salt was prepared by the same procedure as that for [C_2OHmim][Tf_2N] but with [Pyr_{14}]Br. ^{1}H-NMR (400MHz, $CDCl_3$, δ/ppm relative to Me_4Si): 0.99-1.07 (3H, m, $N(CH_2)_3CH_3$), 1.43-1.51 (2H, m, $N(CH_2)_2CH_2$), 1.76-1.82 (2H, m, NCH_2CH_2 in chain), 2.30 (4H, t, J = 12.6, $CH_2CH_2NCH_2CH_2$), 3.08 (3H, d, J = 24.4, NCH_3), 3.30-3.39 (2H, m, NCH_2 in chain), 3.52-3.59 (4H, m, CH_2NCH_2).

Trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonyl)imide ([$P_{666,14}$][Tf_2N])
The titled compound was prepared by the same procedure as that for [C_2OHmim][Tf_2N] with the corresponding halide salt [$P_{666,14}$]Cl. ^{1}H-NMR (400MHz, $CDCl_3$, δ/ppm relative to Me_4Si): 0.86-0.91 (12H, m, CH_3), 1.26 and 1.31 (32H, broad, $P(CH_2)_3(CH_2)_{10}$ and $P(CH_2)_3(CH_2)_2CH_3$), 1.48 (16H, broad, $PCH_2(CH_2)_2$), 2.09 (8H, broad, PCH_2).

1-Ethyl-3-methylimidazolium bis(fluorosulfonyl)imide ([C_2mim][FSI])
The IL was prepared by the same procedure as that for [C_2OHmim][Tf_2N] with the corresponding halide and lithium salt; [C_2mim]Cl and Li[FSI]. ^{1}H-NMR (400MHz, DMSO-d_6, δ/ppm relative to Me_4Si): 1.45 (3H, t, J = 7.2 Hz, NCH_2CH_3), 3.88 (3H, s, NCH_3), 4.24 (2H, q, J = 12.1 Hz, NCH_2), 7.72 and 7.80 (2H, t, J = 1.8 and 1.8 Hz, NC*H*C*H*N), 9.13 (1H, s, NC*H*N).

1-Ethyl-3-methylimidazolium bis(pentafluoroethanesulfonyl)imide ([C_2mim][Pf_2N])
This salt was prepared by the same method as described above for [C_2OHmim][Tf_2N] but with the corresponding halide and lithium salt; [C_2mim]Cl and Li[Pf_2N]. ^{1}H-NMR (400MHz, DMSO-d_6, δ/ppm relative to Me_4Si): 1.41 (3H, t, J = 7.4 Hz, NCH_2CH_3), 3.84 (3H, s, NCH_3), 4.19 (2H, q, J = 7.3 Hz, NCH_2), 7.69 and 7.77 (2H, d and t, J = 1.6 and 1.8 Hz, NC*H*C*H*N), 9.11 (1H, s, NC*H*N).

1-Ethyl-3-methylimidazolium bis(nonafluorobutanesulfonyl)imide ([C_2mim][Nf_2N])
The titled compound was prepared by the same procedure as that for [C_2OHmim][Tf_2N] with the corresponding halide and lithium salt; [C_2mim]Cl and Li[Nf_2N]. ^{1}H-NMR (400MHz, DMSO-d_6, δ/ppm relative to Me_4Si):

1.41 (3H, t, $J = 7.4$ Hz, NCH_2CH_3), 3.85 (3H, s, NCH_3), 4.19 (2H, q, $J = 7.3$ Hz, NCH_2), 7.69 and 7.78 (2H, t, $J = 2.0$ and 1.8 Hz, NC*H*C*H*N), 9.11 (1H, s, NC*H*N).

1-Butyl-3-methylimidazolium trifluoromethanesulfonate ([C_4mim]CF_3SO_3)

[C_4mim]Br was diluted tenfold with Milli-Q water, and passed through a column filled with anion exchange resin (Amberlite IRN-78) to give an aqueous solution of [C_4mim]OH. To the resulting solution, an aqueous solution of trifluoromethanesulfonic acid was added dropwise. The neutralised solution was concentrated by evaporation. The crude material was dissolved in acetone and then passed through a short column filled with activated aluminum oxide. Acetone was removed by evaporation and the resulting liquid was dried under vacuum at 60 °C for at least 3 h. The purpose material was obtained as a colourless liquid. ^{1}H-NMR (400MHz, DMSO-d_6, δ/ppm relative to Me_4Si): 0.91 (3H, t, $J = 7.4$ Hz, $N(CH_2)_3CH_3$), 1.24-1.30 (2H, m, $N(CH_2)_2CH_2$), 1.74-1.80 (2H, m, NCH_2CH_2), 3.85 (3H, s, NCH_3), 4.17 (2H, t, $J = 7.2$ Hz, NCH_2), 7.70 and 7.77 (2H, t, $J = 1.7$ and 1.7 Hz, NC*H*C*H*N), 9.10 (1H, s, NC*H*N).

1-Ethyl-3-methylimidazolium nonafluorobutanesulfonate ([C_2mim]$C_4F_9SO_3$)

The IL was prepared in the same manner as described above for [C_4mim]CF_3SO_3 but with the corresponding halide salt and acid; [C_2mim]Cl and nonafluorobutanesulfonic acid. ^{1}H-NMR (400MHz, DMSO-d_6, δ/ppm relative to Me_4Si): 1.41 (3H, t, $J = 7.4$ Hz, NCH_2CH_3), 3.84 (3H, s, NCH_3), 4.19 (2H, q, $J = 7.3$ Hz, NCH_2), 7.69 and 7.78 (2H, t, $J = 2.0$ and 1.6 Hz, NC*H*C*H*N), 9.10 (1H, s, NC*H*N).

1-Ethyl-3-methylimidazolium heptadecafluorooctanesulfonate ([C_2mim]$C_8F_{17}SO_3$)

The titled compound was prepared by the same procedure as described for [C_4mim]CF_3SO_3 with the corresponding halide salt and acid; [C_2mim]Cl and heptadecafluorooctanesulfonic acid. ^{1}H-NMR (400MHz, DMSO-d_6, δ/ppm relative to Me_4Si): 1.35-1.39 (3H, m, NCH_2CH_3), 3.80 (3H, d, $J = 0.8$ Hz, NCH_3), 4.12-4.18 (2H, m, NCH_2), 7.66 and 7.74 (2H, d, $J = 1.6$ and 2.0 Hz, NC*H*C*H*N), 9.07 (1H, s, NC*H*N).

Trihexyl(tetradecyl)phosphonium heptadecafluorooctanesulfonate ([$P_{666,14}$]$C_8F_{17}SO_3$)

This IL was prepared by the same procedure as described above for [C_4mim]CF_3SO_3 with the corresponding halide salt and acid; [$P_{666,14}$]Cl and heptadecafluorooctanesulfonic acid. ^{1}H-NMR (400MHz, $CDCl_3$, δ/ppm relative to Me_4Si) $\delta_H = 0.88$-0.93 (12H, m, CH_3), 1.27-1.34 (32H, m, $P(CH_2)_3(CH_2)_{10}$ and $P(CH_2)_3(CH_2)_2CH_3$), 1.50-1.58 (16H, m, $PCH_2(CH_2)_2$), 2.19-2.26 (8H, m, PCH_2).

Tributyl(hexyl)phosphonium heptadecafluorooctanesulfonate ([P_{4446}]$C_8F_{17}SO_3$)

The salt was prepared in the same manner as described above for [C_4mim]CF_3SO_3 with corresponding halide salt and acid; [P_{4446}]Br and heptadecafluorooctanesulfonic acid. ^{1}H-NMR (400MHz, $CDCl_3$, δ/ppm relative to Me_4Si) $\delta_H = 0.89$ (3H, t, $J = 6.9$ Hz, $P(CH_2)_5CH_3$), 0.97 (9H, t, $J = 4.7$ Hz, $P(CH_2)_3CH_3$), 1.29-1.35 (4H, m, $P(CH_2)_3(CH_2)_2$), 1.48-1.55 (16H, m, $PCH_2(CH_2)_2$), 2.16-2.24 (8H, m, PCH_2).

Trihexyl(heptadecafluoroundecyl)phosphonium bis(trifluoromethanesulfonyl)imide ($[P_{666F}][Tf_2N]$)

To 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl iodide, 1.2 molar of trihexylphosphine was added at room temperature under N_2 atmosphere. The resulting mixture was heated up to 120 °C and stirred for 24 h. The crude iodide salt was obtained as solid when it reached room temperature. The solid was washed with hexane to remove the residual of trihexylphosphine. The resulting solid was mixed with activated carbon in ethyl acetate for 1 night. The final iodide salt was obtained by the filtration of carbon and evaporation of the solvent. The iodide anion was then replaced with $[Tf_2N]$ anion in the same manner as described for $[C_2OHmim][Tf_2N]$. ^{1}H-NMR (400MHz, $CDCl_3$, δ/ppm relative to Me_4Si) $\delta_H = 0.90$ (9H, q, $J = 4.0$ Hz, $C\mathit{H_3}$), 1.31 (12H, broad, $P(CH_2)_3(C\mathit{H_2})_2$), 1.49-1.60 (12H, m, $PCH_2(C\mathit{H_2})CH_2$), 1.84 -1.91 (2H, m, $C\mathit{H_2}CF_2$), 2.11-2.18 (6H, m, $PC\mathit{H_2}(CH_2)_4CH_3$), 2.26 -2.35 (4H, m, $P(C\mathit{H_2})_2CH_2CF_2$). ^{13}C-NMR (400MHz, $CDCl_3$, δ/ppm relative to Me_4Si): 121.5 (s), 118.3 (s), 30.9 (s), 30.2 (d, $J = 30.5$), 22.3 (s), 21.5 (d, $J = 7.6$), 18.8 (d, $J = 28.6$), 18.3 (d, $J = 34.3$), 13.8 (s), 13.5 (s). ^{19}F-NMR (400MHz, $CDCl_3$, δ/ppm relative to C_6F_6): -129.3 (2F, s, $CH_2C\mathit{F_2}$), -126.7 (2F, s, $CH_2CF_2C\mathit{F_2}$), -125.9 (2F, s, $CH_2(CF_2)_2C\mathit{F_2}$), -125.1 (4F, s, $CH_2(CF_2)_3(C\mathit{F_2})_2$), -124.9 (2F, s, $CH_2(CF_2)_5C\mathit{F_2}$), -117.4 (2F, s, $CH_2(CF_2)_6C\mathit{F_2}$), -84.0 (3F, s, $CH_2(CF_2)_7C\mathit{F_3}$), -82.1 (2F, s,$SCF_3$). Elemental analysis: Calculated for $C_{31}H_{45}F_{23}NO_4PS_2$: C, 36.23; H, 4.41; N, 1.36. Found: C, 36.67; H, 4.41; N, 1.34. Glass transition temperature: -69.1 °C. Thermal decomposition temperature: 397 °C.

Trihexyl(heptadecafluoroundecyl)phosphonium heptadecafluorooctanesulfonate ($[P_{666F}]C_8F_{17}SO_3$)

The titled compound was prepared by the same procedure as described above for $[C_4mim]CF_3SO_3$ with the corresponding halide salt and acid; $[P_{666F}]I$ and heptadecafluorooctanesulfonic acid. ^{1}H-NMR (400MHz, $CDCl_3$, δ/ppm relative to Me_4Si) $\delta_H = 0.88$ (9H, q, $J = 4.0$ Hz, $C\mathit{H_3}$), 1.30 (12H, broad, $P(CH_2)_3(C\mathit{H_2})_2$), 1.46-1.54 (12H, m, $PCH_2(C\mathit{H_2})CH_2$), 1.80 -1.86 (2H, m, $C\mathit{H_2}CF_2$), 2.18 -2.25 (6H, m, $PC\mathit{H_2}(CH_2)_4CH_3$), 2.29 -2.49 (4H, m, $P(C\mathit{H_2})_2CH_2CF_2$). ^{13}C-NMR (400MHz, $CDCl_3$, δ/ppm relative to Me_4Si): 31.0 (s), 30.4 (d, $J = 30.5$), 22.3 (s), 21.7 (d, $J = 9.5$), 18.9 (d, $J = 30.5$), 18.4 (d, $J = 36.2$), 13.8 (s), 13.6 (s). ^{19}F-NMR (400MHz, $CDCl_3$, δ/ppm relative to C_6F_6): -129.3 (2F, s, $CH_2C\mathit{F_2}$), -126.7 (2F, s, $CH_2CF_2C\mathit{F_2}$), -125.9 (2F, s, $CH_2(CF_2)_2C\mathit{F_2}$), -125.1 (4F, s, $CH_2(CF_2)_3(C\mathit{F_2})_2$), -124.9 (2F, s, $CH_2(CF_2)_5C\mathit{F_2}$), -117.4 (2F, s, $CH_2(CF_2)_6C\mathit{F_2}$), -84.0 (3F, s, $CH_2(CF_2)_7C\mathit{F_3}$), -82.1 (2F, s,$SCF_3$). Elemental analysis: Calculated for $C_{37}H_{45}F_{34}O_3PS$: C, 35.65; H, 3.64; N, 0.00. Found: C, 35.93; H, 3.27; N, 0.06. Thermal decomposition temperature: 374 °C.

Evaluation of fluorophilicity

Fluorophilicity was evaluated based on the mole fraction of perfluorohexane (χ_{PFH}) dissolved in the ILs. Perfluorohexane (PFH) was purchased from Tokyo Chemical Industry. PFH and ILs were mixed in a ratio of 150:150 (μl/μl) under semi-dry condition (RH < 20 %) and shaken using a vortex mixer until they form an opaque monophase. These mixtures were kept from 1 day to 1 week until they separated into PFH- and IL-rich transparent phases. The amount of PFH dissolved in the IL-rich phase ($\%W_{PFH}$) was quantified with thermogravimetric analysis (TGA), because PFH has the boiling temperature around 60 °C. The IL-rich phases were heated to 70 °C at a rate of 10 °C min^{-1}, and they were kept at that temperature for 1 h. The weight loss after the isothermal step was defined as $\%W_{PFH}$, and this value was used to calculate χ_{PFH} as follows.

$$\chi_{PFH}\,(mmol\,mol^{-1}) = \frac{\%W_{PFH} \,/\, M_{w \cdot PFH}}{\%W_{PFH} \,/\, M_{w \cdot PFH} \;+\; (100 - \%W_{PFH}) \,/\, M_{w \cdot ILs}} \times 1000$$

The water content of each samples were confirmed to be less than 0.1 % by using Karl-Fischer titration (MKC-510N, from Metrohm AG).

Effect of Kamlet-Taft parameters and fluorine content of ILs on χ_{PFH}

The Kamlet-Taft parameters were evaluated as reported in the literature (Y. Fukaya *et. al*, Green Chem., 2008, **10**, 44). In the case of the [Tf_2N] salts, χ_{PFH} is affected by the α value of Kamlet-Taft parameters which is an index of hydrogen bond acidity of ILs (Figure S1, left). The linear correlations are found when these are plotted individually for the [Tf_2N] salts containing aliphatic and aromatic cations. Meanwhile, a clear correlation is not found between the fluorine content (%F) and χ_{PFH} of the ILs. In the case of the [C_2mim] salts, effect of the β value of Kamlet-Taft parameters, an index of the hydrogen bond basicity of ILs, on χ_{PFH} was analysed because the α value of the ILs was found to be similar due to their identical cation structure. The series of [C_2mim] salts exhibits better correlation between χ_{PFH} and %F than χ_{PFH} and β value.

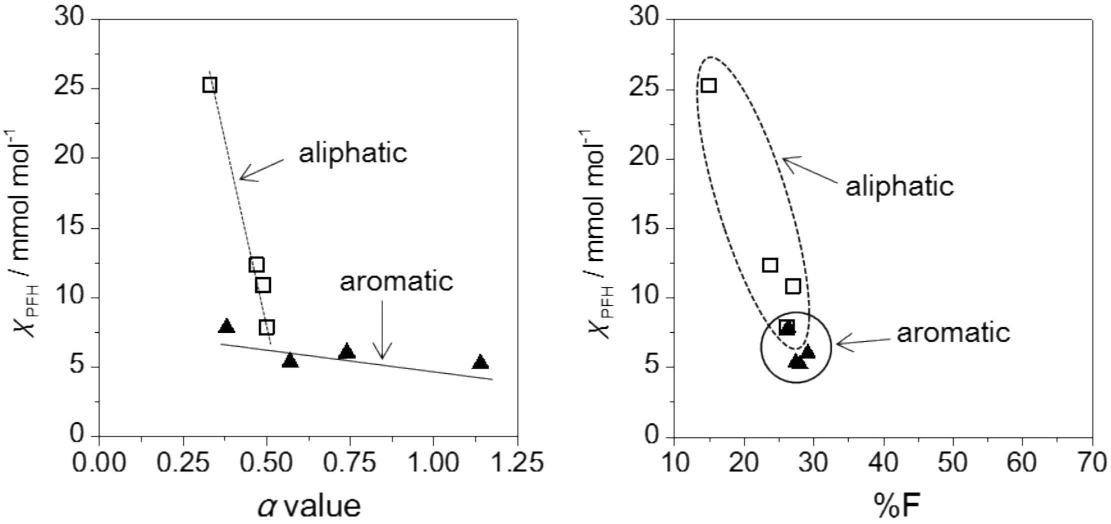

Figure S1. Plots of χ_{PFH} *versus* α value (left) and %F (right) of [Tf_2N] salts.

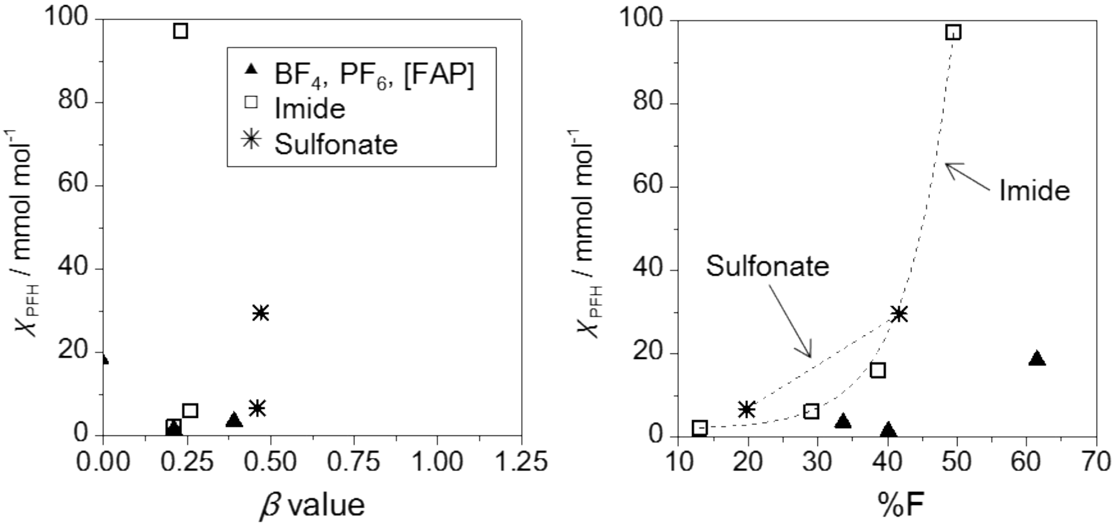

Figure S2. Plots of χ_{PFH} *versus* β value (left) and %F (right) of [C_2mim] salts

Composites based on PTFE

The ILs and PTFE were mixed in a ratio of 1:1 (w/w) at room temperature. These were mixed with a spatula until they became homogenous. These procedures were carried out in a N_2 filled glove box. When the equivalent weight of [C_2mim][Tf_2N] was added to PTFE, these components repelled each other and a homogeneous composite was not obtained. On the other hand, the homogeneous composite was obtained when the ILs functionalised with perfluorinated-octyl chains such as [P_{666F}]$C_8F_{17}SO_3$ were used. In Figure S3, the ILs are dyed with methyl red to visualise the presence of the ILs.

[C_2mim][Tf_2N]-PTFE

[P_{666F}]$C_8F_{17}SO_3$-PTFE

Figure S3. Pictures of the PTFE composites with [C_2mim][Tf_2N] and [P_{666F}]$C_8F_{17}SO_3$.

Contact angle of PTFE and the ILs

Contact angle was evaluated by using Contact Angle Meter: DMs-401 (from Kyowa Interface Science Co. Ltd.). The droplet of the ILs (1.0 ± 0.1 μL) was deposited on the PTFE plate. The contact angle was recorded after 30 min of the deposition so as to obtain static contact angles. As summarized in Table S1, the contact angle decreased by modifying the anion with a perfluoro-octyl chain. Further improvement was found when a perfluoro-octyl chain is also inserted to the cation structure. The smallest contact angle was found for

[P_{666F}]$C_8F_{17}SO_3$.

Table S1. Contact angle of the ILs with PTFE plate.

ILs	Contact angle / °
[C_2mim][Tf_2N]	62.4
[$P_{666,14}$][Tf_2N]	45.9
[$P_{666,14}$]$C_8F_{17}SO_3$	30.0
[P_{666F}][Tf_2N]	22.5
[P_{666F}]$C_8F_{17}SO_3$	20.8

Differential scanning calorimetry of PTFE and PTFE/[P_{666F}]$C_8F_{17}SO_3$

Differential scanning calorimetry (DSC-120, Seiko Instruments Inc.) was taken from 25 °C to 350 °C with a rate of 5 °C min^{-1}. Both samples, pure PTFE and PTFE/[P_{666F}]$C_8F_{17}SO_3$ composites, exhibited melting temperature around 325 °C. However, the drift of heat flow started 285 °C and 300 °C for the pure PTFE and the PTFE/[P_{666F}]$C_8F_{17}SO_3$ composite, respectively. This suggests that a part of PTFE interact with the ILs. Consequently, it can be concluded that, in PTFE and [P_{666F}]$C_8F_{17}SO_3$ composites, some parts of PTFE were just disperses in the IL and some PTFE chains were solvated and dissolved in the IL.

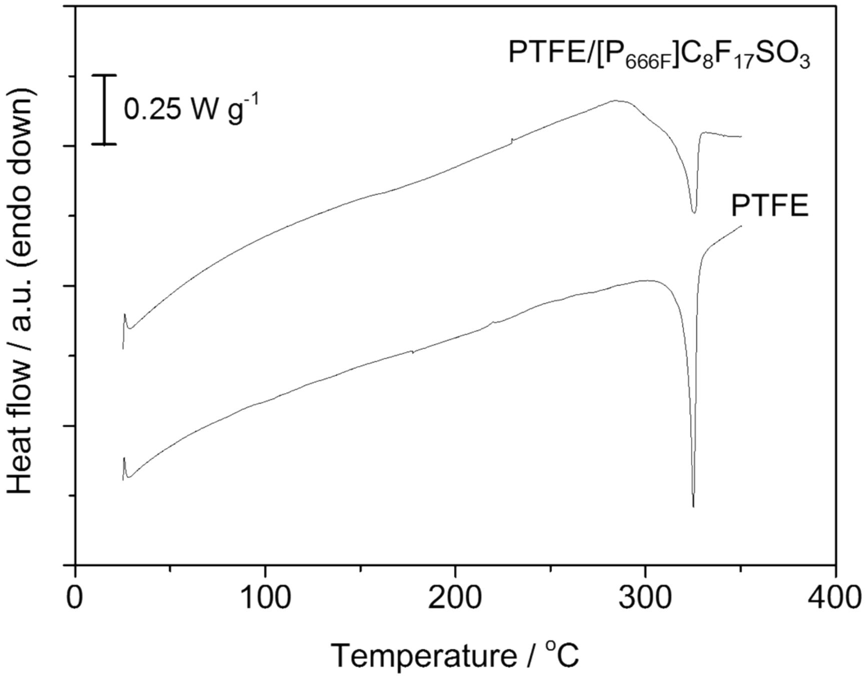

Figure S4. DSC curves of PTFE/[P_{666F}]$C_8F_{17}SO_3$ composite (upper) and pure PTFE (lower).