

Supporting material

Hydrophobic Ionic Liquids with Strongly Coordinating Anions

Hasan Mehdi, Koen Binnemans*, Kristof Van Hecke, Luc Van Meervelt,
Peter Nockemann*

Experimental details:

General techniques. Elemental analyses (carbon, hydrogen, nitrogen) were performed using a CE Instruments EA-1110 elemental analyzer. ^1H NMR spectra were recorded on a Bruker Avance 400 spectrometer (operating at 400 MHz for ^1H). The water content of the ionic liquids was determined by a coulometric Karl Fischer titrator (Mettler Toledo Coulometric Karl Fischer Titrator, model DL39). The viscosity of the ionic liquids was measured at room temperature by the falling ball method (Gilmont Instruments). Differential scanning calorimetry (DSC) measurements were carried out on a Mettler-Toledo DSC822e module (scan rate of $10\text{ }^\circ\text{C min}^{-1}$ under helium flow). All chemicals were obtained from ACROS Organics, Aldrich-Sigma or IoLiTec.

Crystallography.

X-ray intensity data for $[\text{C}_{18}\text{mim}][\text{hfac}]$, $[\text{C}_4\text{mim}]_2[\text{Na}(\text{hfac})_3]$, $[\text{C}_4\text{mim}][\text{Nd}(\text{hfac})_4]$, $[\text{C}_4\text{mim}][\text{Co}(\text{hfac})_3]$ and $[\text{C}_4\text{mim}][\text{Cu}(\text{hfac})_3]$ were collected at 100 K on a SMART 6000 diffractometer equipped with CCD detector using $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54178\text{ \AA}$). The images were interpreted and integrated with the program SAINT from Bruker.ⁱ All five structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXTL program package.ⁱⁱ Non-hydrogen atoms were anisotropically refined and the hydrogen atoms in the riding mode with isotropic temperature factors fixed at 1.2 times $U(\text{eq})$ of the parent atoms (1.5 times for methyl groups). For the structures $[\text{C}_4\text{mim}]_2[\text{Na}(\text{hfac})_3]$, $[\text{C}_4\text{mim}][\text{Nd}(\text{hfac})_4]$, $[\text{C}_4\text{mim}][\text{Co}(\text{hfac})_3]$ and $[\text{C}_4\text{mim}][\text{Cu}(\text{hfac})_3]$, additional restraints had to be used to model the disorder of several hfac CF_3 groups and C_4mim butyl chains. CCDC

742062-066 contain the supplementary crystallographic data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk). The crystallographic data of the compounds is summarized in Table S1 and S2.

	[C ₁₈ mim][hfac]	[C ₄ mim] ₂ [Na(hfac) ₃]	[C ₄ mim][Nd(hfac) ₄]
Formula	C ₂₇ H ₄₄ F ₆ N ₂ O ₂	C ₃₁ H ₃₃ F ₁₈ N ₄ NaO ₆	C ₂₈ H ₁₉ F ₂₄ N ₂ NdO ₈
<i>M_r</i> (g mol ⁻¹)	542.64	922.66	1111.69
Crystal dimensions (mm ³)	0.3 × 0.25 × 0.2	0.35 × 0.25 × 0.2	0.4 × 0.25 × 0.2
Crystal system	triclinic	monoclinic	orthorhombic
Space group	<i>P</i> -1 (No. 2)	<i>P</i> 2 ₁ /n (No. 14)	<i>P</i> bca (No. 61)
<i>a</i> (Å)	7.7419(2)	11.6351(5)	16.4109(3)
<i>b</i> (Å)	9.9974(2)	16.6309(7)	21.9547(5)
<i>c</i> (Å)	37.1893(7)	20.594(1)	43.1651(8)
<i>α</i> (°)	93.990(1)	90.00	90.00
<i>β</i> (°)	91.607(1)	103.070(2)	90.00
<i>γ</i> (°)	91.107(1)	90.00	90.00
<i>V</i> (Å ³)	2869.7(1)	3881.8(3)	15552.2(5)
<i>Z</i>	4	4	16
<i>ρ</i> _{calc} (g cm ⁻³)	1.256	1.579	1.899
<i>μ</i> _{CuKα} (mm ⁻¹)	0.892	1.590	11.734
Absorption correction	multi-scan	multi-scan	multi-scan
<i>F</i> (000)	1160	1872	8656
Measured reflections	43326	32095	134988
Unique reflections	11016	7162	15060
Obs. reflections (<i>I</i> ₀ > 2σ(<i>I</i> ₀))	8955	6124	12984
<i>R</i> _{int}	0.0597	0.0708	0.0878
Parameters refined	671	697	1251
Goodness-of-fit on <i>F</i> ²	1.054	1.033	1.014
<i>R</i> ₁	0.0484	0.0449	0.0529
<i>wR</i> ₂	0.1226	0.1202	0.1342
<i>R</i> ₁ (all data)	0.0606	0.0526	0.0616
<i>wR</i> ₂ (all data)	0.1351	0.1282	0.1425

	[C ₄ mim][Co(hfac) ₃]	[C ₄ mim][Cu(hfac) ₃]
Formula	C ₂₃ H ₁₈ CoF ₁₈ N ₂ O ₆	C ₂₃ H ₁₈ CuF ₁₈ N ₂ O ₆
<i>M_r</i> (g mol ⁻¹)	819.32	823.94
Crystal dimensions (mm ³)	0.4 × 0.25 × 0.15	0.3 × 0.2 × 0.15
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1 (No. 2)	<i>P</i> -1 (No. 2)
<i>a</i> (Å)	9.0040(6)	9.0624(2)
<i>b</i> (Å)	17.737(1)	17.4690(3)
<i>c</i> (Å)	20.161(1)	20.1946(4)
α (°)	74.172(3)	73.527(1)
β (°)	87.160(4)	86.288(1)
γ (°)	89.240(4)	89.106(1)
<i>V</i> (Å ³)	3094.0(3)	3059.4(1)
<i>Z</i>	4	4
ρ_{calc} (g cm ⁻³)	1.759	1.789
$\mu_{CuK\alpha}$ (mm ⁻¹)	5.768	2.443
Absorption correction	multi-scan	multi-scan
<i>F</i> (000)	1628	1636
Measured reflections	29476	43008
Unique reflections	11258	11449
<i>R</i> _{int}	0.0819	0.0617
Obs. reflections (<i>I</i> ₀ > 2σ(<i>I</i> ₀))	8050	9555
Parameters refined	990	999
Goodness-of-fit on <i>F</i> ²	1.076	1.041
<i>R</i> ₁	0.0599	0.0455
<i>wR</i> ₂	0.1407	0.1108
<i>R</i> ₁ (all data)	0.0870	0.0570
<i>wR</i> ₂ (all data)	0.1571	0.1190

Details on synthesis and characterization of the ionic liquids

Synthesis of ammonium hexafluoroacetylacetonate :

Hexafluoroacetylacetonone (Hhfac) was dissolved in hexane and cooled in an ice-bath. Bubbling dry ammonia gas into the solution resulted in the evolution of fume and solid precipitation during a very exothermic reaction. When no more fume formation was observed, the suspension was filtered, washed with hexane to obtain a white solid which was dried on air then *in vacuo* at room temperature. White solid. Yield: 95%. ¹H NMR (400.13 MHz, dms_o-d₆, δ/ppm): 7.28 (s, 4H, broad), 5.43 (s, 1H). ¹³C NMR (100.62 MHz, dms_o-d₆, δ/ppm): 172.0 (q, *J*= 30 Hz), 118.1 (q, *J*= 293 Hz), 83.2.

General methods for the synthesis of hexafluoroacetylacetonate ionic liquids:

Using an ammonia solution:

Hexafluoroacetylacetonone (1 eqv.) was added slowly via a syringe to a cooled ammonia solution sealed in a flask. A white solid precipitated which redissolved while the mixture was allowed to warm up to room temperature. An aqueous solution of the appropriate halide ionic liquid (bromide or chloride salt) was added. Immediate phase separation was observed. Dichloromethane was added to the reaction mixture, aqueous phase was separated and the organic layer was washed with water three or more times till the AgNO₃ test gave no precipitation with the aqueous fraction. Solvent and residual water were removed under reduced pressure.

Using ammonium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (NH₄[hfac]) in water:

Ammonium hexafluoroacetylacetonate (1 eqv.) was dissolved in water (5 ml of water for 1 g of NH₄[hfac]) and an aqueous solution of 1 eqv. of the halide ionic liquid (bromide or chloride salt) in water was added. The reaction mixture immediately became turbid and a second layer formed upon stopping with stirring. Dichloromethane was added to the reaction

mixture, the aqueous phase was separated and the organic layer was washed with water three or more times till the AgNO_3 test gave no precipitation with the aqueous phase fraction. Solvent and residual water was removed under reduced pressure.

Using ammonium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ($\text{NH}_4[\text{hfac}]$) in acetonitrile:

Ammonium hexafluoroacetylacetonate (1 eqv.) was dissolved in dry acetonitrile (5 ml of acetonitrile for 1 g of $\text{NH}_4[\text{hfac}]$) and a concentrated solution of 1 eqv. of the halide ionic liquid (bromide or chloride salt) in dry acetonitrile was added. A white solid immediately precipitated and the reaction mixture was stirred for additional 10 minutes. The solid was filtered and washed with DCM. Some additional ammonium chloride precipitated on addition of DCM and the solution was filtered again. The liquid obtained after removal of solvents was redissolved in DCM and filtered again to obtain a clear solution. This solution was washed with a small amount of water. The aqueous phase was tested for its halide content by the AgNO_3 test. Solvent and residual water were removed under reduced pressure.

Synthesis of 1-ethyl-3-methylimidazolium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ($[\text{C}_2\text{mim}][\text{hfac}]$):

The ionic liquid $[\text{C}_2\text{mim}][\text{hfac}]$ was prepared by reaction of 1-ethyl-3-methylimidazolium chloride and ammonium hexafluoroacetylacetonate in dry acetonitrile. A green-yellow liquid was obtained that solidified slowly at room temperature to give an off-white solid. mp.: 33 °C. Yield: 59%. Anal. Calcd for $\text{C}_{11}\text{H}_{12}\text{F}_6\text{N}_2\text{O}_2$: C, 41.52; H, 3.80; N, 8.80. Found: C, 40.53; H, 2.58; N, 8.53. ^1H NMR (400.13 MHz, $\text{dms}\text{-d}_6$, δ /ppm): 9.55 (s, 1H), 7.82 (s, 1H), 7.73 (s, 1H), 5.46 (s, 1H), 4.25 (q, 2H, $J = 7.3$ Hz), 3.92 (s, 3H), 1.42 (t, 3H, $J = 7.3$ Hz). ^{13}C NMR (100.62 MHz, $\text{dms}\text{-d}_6$, δ /ppm): 171.9 (q, $J = 29$ Hz), 137.1, 123.6, 122.0, 118.2 (q, $J = 293$ Hz), 82.8, 44.2, 35.4, 14.9.

Synthesis of 1-butyl-3-methylimidazolium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ($[\text{C}_4\text{mim}][\text{hfac}]$):

The ionic liquid $[\text{C}_4\text{mim}][\text{hfac}]$ was prepared by reaction of 1-butyl-3-methylimidazolium chloride and ammonium hexafluoroacetylacetonate in dry acetonitrile.

Green-yellow liquid. Yield: 85%. Anal. calcd for $C_{13}H_{16}F_6N_2O_2$: C, 45.09; H, 4.66; N, 8.09. Found: C, 44.88; H, 4.44; N, 8.16. 1H NMR (400.13 MHz, dms o - d_6 , δ /ppm): 9.57 (s, 1H), 7.83 (s, 1H), 7.74 (s, 1H), 5.44 (s, 1H), 4.20 (t, 2H, $J = 7.3$ Hz), 3.92 (s, 3H), 1.77 (m, 2H), 1.27 (m, 2H), 0.89 (t, 3H, $J = 7.4$ Hz). ^{13}C NMR (100.62 MHz, dms o - d_6 , δ /ppm): 171.6 (q, $J = 29$ Hz), 137.3, 123.5, 122.3, 118.1 (q, $J = 293$ Hz), 82.6, 48.5, 35.4, 31.6, 18.7, 12.8. ^{19}F NMR (564.7 MHz, $CFCl_3$ as reference at 0 ppm, dms o - d_6 , δ /ppm): -75.7. The density of [C $_4$ mim][hfac] was measured with a pycnometer and was found to be 1.290 g/cm 3 at 20°C. Dynamic viscosity was measured with a falling sphere viscometer, $\eta = 65$ cP (20 °C). [C $_4$ mim][hfac] is not miscible with water and hexane, but it is miscible with DMSO, methanol, ethanol, dichloromethane and it is even miscible with diethyl ether, tetrahydrofuran and toluene.

Synthesis of 1-butyl-2,3-dimethylimidazolium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate [C $_4$ dmim][hfac]:

The ionic liquid [C $_4$ dmim][hfac] was prepared by reaction of 1-butyl-2,3-dimethylimidazolium chloride and ammonium hexafluoroacetylacetonate in dry acetonitrile (see example 2). Green-yellow liquid. mp.: 16-17 °C. Yield: 82 %. Anal. Calcd for $C_{14}H_{18}F_6N_2O_2$: C, 46.67; H, 5.04; N, 7.78. Found: C, 46.27; H, 4.09; N, 8.09. 1H NMR (400.13 MHz, dms o - d_6 , δ /ppm): 7.80 (s, 1H), 7.72 (s, 1H), 5.46 (s, 1H), 4.14 (t, 2H, $J = 7.5$ Hz), 3.85 (s, 3H), 2.65 (s, 3H), 1.73 (m, 2H), 1.33 (m, 2H), 0.93 (t, 3H, $J = 7.4$ Hz). ^{13}C NMR (100.62 MHz, dms o - d_6 , δ /ppm): 171.7 (q, $J = 29$ Hz), 144.1, 122.4, 121.1, 118.2 (q, $J = 293$ Hz), 82.6, 47.6, 34.3, 31.3, 18.9, 12.7, 8.6.

Synthesis of 1-hexyl-3-methylimidazolium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ([C $_6$ mim][hfac]):

The ionic liquid [C $_6$ mim][hfac] was prepared by reaction of 1-hexyl-3-methylimidazolium chloride and ammonium hexafluoroacetylacetonate in dry acetonitrile.

Green-yellow liquid. Yield is 89%. Anal. Calcd for $C_{15}H_{20}F_6N_2O_2$: C, 48.13; H, 5.39; N, 7.48. Found: C, 47.73; H, 4.08; N, 7.86. 1H NMR (400.13 MHz, dms o - d_6 , δ /ppm): 9.79 (s, 1H), 7.83 (s, 1H), 7.72 (s, 1H), 5.56 (s, 1H), 4.23 (t, 2H, $J = 7.4$ Hz), 3.96 (s, 3H), 1.80 (m, 2H),

1.28 (m, 6H), 0.86 (t, 3H, $J = 6.7$ Hz). ^{13}C NMR (100.62 MHz, dms -d_6 , δ /ppm): 172.3 (q, $J = 30$ Hz), 137.7, 123.5, 122.3, 118.2 (q, $J = 293$ Hz), 83.2, 49.0, 35.3, 30.6, 29.9, 25.3, 21.9, 13.2.

Synthesis of 1-methyl-3-octylimidazolium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ([C₈mim][hfac]):

The ionic liquid [C₈mim][hfac] was prepared by reaction of 1-methyl-3-octylimidazolium chloride and ammonium hexafluoroacetylacetonate in dry acetonitrile.

Green liquid. mp.: 17-18 °C. Yield: 93%. Anal. Calcd for C₁₇H₂₄F₆N₂O₂: C, 50.74; H, 6.01; N, 6.96. Found: C, 50.59; H, 6.37; N, 7.27. ^1H NMR (400.13 MHz, CDCl₃, δ /ppm): 9.85 (s, 1H), 7.16 (s, 1H), 7.14 (s, 1H), 5.47 (s, 1H), 4.01 (t, 2H, $J = 7.4$ Hz), 3.79 (s, 3H), 1.64 (m, 2H), 1.10 (m, 10H), 0.69 (t, 3H, $J = 6.5$ Hz). ^{13}C NMR (100.62 MHz, CDCl₃, δ /ppm): 173.4 (q, $J = 30$ Hz), 138.1, 122.8, 121.4, 117.9 (q, $J = 292$ Hz), 84.1, 49.5, 35.5, 31.1, 29.8, 28.4, 28.3, 25.6, 22.0, 13.4.

Synthesis of 1-decyl-3-methylimidazolium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ([C₁₀mim][hfac]):

The ionic liquid [C₁₀mim][hfac] was prepared by reaction of 1-decyl-3-methylimidazolium chloride and ammonium hexafluoroacetylacetonate in dry acetonitrile.

A green liquid, which crystallized out upon standing was obtained. mp.: 33 °C. Yield: 93%. Anal. Calcd for C₁₉H₂₈F₆N₂O₂: C, 53.02; H, 6.56; N, 6.51. Found: C, 52.74; H, 5.36; N, 6.89. ^1H NMR (400.13 MHz, dms -d_6 , δ /ppm): 9.83 (s, 1H), 7.83 (s, 1H), 7.73 (s, 1H), 5.57 (s, 1H), 4.23 (t, 2H, $J = 7.4$ Hz), 3.96 (s, 3H), 1.81 (m, 2H), 1.28 (m, 14H), 0.89 (t, 3H, $J = 6.8$ Hz). ^{13}C NMR (100.62 MHz, dms -d_6 , δ /ppm): 172.4 (q, $J = 30$ Hz), 137.8, 123.4, 122.5, 118.2 (q, $J = 293$ Hz), 83.2, 48.9, 35.3, 31.5, 30.0, 29.1, 29.0, 28.9, 28.5, 25.7, 22.2, 13.4.

Synthesis of 1-hexadecyl-3-methylimidazolium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ([C₁₆mim][hfac]):

The ionic liquid [C₁₆mim][hfac] was prepared by reaction of 1-hexadecyl-3-methylimidazolium chloride and ammonium hexafluoroacetylacetonate in dry acetonitrile. White solid. mp.: 66 °C. Yield: 91%. Anal. Calcd for C₂₅H₄₀F₆N₂O₂: C, 58.35; H, 7.83; N, 5.44. Found: C, 58.23; H, 8.75; N, 5.25. ¹H NMR (400.13 MHz, dms_o-d₆, δ /ppm): 9.38 (s, 1H), 7.80 (s, 1H), 7.72 (s, 1H), 5.33 (s, 1H), 4.16 (t, 2H, *J* = 7.2 Hz), 3.88 (s, 3H), 1.76 (m, 2H), 1.23 (m, 26H), 0.84 (t, 3H, *J* = 6.8 Hz). ¹³C NMR (100.62 MHz, dms_o-d₆, δ /ppm): 170.9 (q, *J* = 29 Hz), 136.8, 123.4, 122.1, 117.9 (q, *J* = 294 Hz), 82.0, 48.6, 35.5, 31.2, 29.4, 29.0, 28.9, 28.8, 28.7, 28.6, 28.3, 25.4, 22.0, 13.6.

Synthesis of 1-methyl-3-octadecylimidazolium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ([C₁₈mim][hfac]):

The ionic liquid [C₁₈mim][hfac] was prepared by reaction of 1-methyl-3-octadecylimidazolium chloride and ammonium hexafluoroacetylacetonate in dry acetonitrile. White solid, mp.: 72-73°C. Yield: 91%. Anal. Calcd for C₂₇H₄₄F₆N₂O₂: C, 59.76; H, 8.17; N, 5.16; Found: C, 59.83; H, 8.94; N, 4.96. ¹H NMR (400.13 MHz, dms_o-d₆, δ /ppm): 9.33 (s, 1H), 7.79 (s, 1H), 7.72 (s, 1H), 5.31 (s, 1H), 4.15 (t, 2H, *J* = 6.8 Hz), 3.87 (s, 3H), 1.76 (m, 2H), 1.23 (m, 30H), 0.85 (t, 3H, *J* = 6.2 Hz). ¹³C NMR (100.62 MHz, dms_o-d₆, δ /ppm): 170.8 (q, *J* = 29 Hz), 136.7, 123.4, 122.1, 117.9 (q, *J* = 294 Hz), 82.0, 48.6, 35.2, 31.2, 29.4, 29.0, 28.9, 28.7, 28.7, 28.6, 28.3, 25.4, 22.0, 13.7.

Synthesis of N-butyl-N-methylpyrrolidinium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ([C₁C₄pyrr][hfac]):

The ionic liquid [C₁C₄pyrr][hfac] was prepared by reaction of *N*-butyl-*N*-methylpyrrolidinium bromide and ammonium hexafluoroacetylacetonate in dry acetonitrile. A pale yellow liquid that solidified slowly at room temperature to give an off-white solid was obtained. mp.: 0 °C. Yield is 71 %. Anal. Calcd for C₁₄H₂₁F₆NO₂: C, 48.14; H, 6.06; N, 4.01. Found: C, 46.99; H, 4.36; N, 4.36. ¹H NMR (400.13 MHz, dms_o-d₆, δ /ppm): 5.43 (s, 1H), 3.53 (m, 4H), 3.34 (m, 2H), 3.05 (s, 3H), 2.12 (m, 4H), 1.68 (m, 2H), 1.32 (m, 2H), 0.93 (t, 3H, *J* = 7.4 Hz). ¹³C NMR (100.62 MHz, dms_o-d₆, δ /ppm): 171.5 (q, *J* = 29 Hz), 118.1 (q, *J* = 294 Hz), 82.4, 63.4, 63.2, 47.3, 25.0, 21.0, 19.2, 12.9.

Synthesis of N-butyl-N-hexylpyrrolidinium bromide ([C₄C₆pyrr]Br):

1-Bromohexane (9.467 g, and 58.4 mmol) and *N*-butylpyrrolidine (6.834 g, 53.7 mmol) were mixed in a round-bottomed flask and sealed. The mixture was stirred and heated at 80 °C for two days. The colorless homogeneous mixture became turbid and yellow in half an hour and subsequently a second phase was formed. After two days a viscous brown mixture was obtained which solidified at room temperature. Diethyl ether was added to the solid and filtered quickly to obtain 13.4 g of white, very hygroscopic solid (85%). The solid was dried under vacuum at room temperature.

¹H NMR (400.13 MHz, dms_o-d₆, δ /ppm): 3.52 (m, 4H), 3.38-3.15 (m, 4H), 2.04 (m, 4H), 1.60 (m, 4H), 1.28 (m, 8H), 1.05-0.65 (m, 6H). ¹³C NMR (100.62 MHz, dms_o-d₆, δ /ppm): 61.9, 58.5, 58.2, 30.5, 25.3, 24.3, 22.3, 21.7, 21.2, 19.0, 13.6, 13.3.

Synthesis of N-butyl-N-hexylpyrrolidinium 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate ([C₄C₆pyrr][hfac]):

The ionic liquid ([C₄C₆pyrr][hfac]) was prepared by reaction between *N*-butyl-*N*-hexylpyrrolidinium bromide and hexafluoroacetylacetonate. White solid, mp.: 48 °C. Yield: 96%. Anal. Calcd for C₁₉H₃₁F₆NO₂: C, 54.41; H, 7.45; N, 3.34. Found: C, 54.08; H, 5.62; N, 3.27. ¹H NMR (400.13 MHz, dms_o-d₆, δ /ppm): 5.43 (s, 1H), 3.59 (m, 4H), 3.25 (m, 4H), 2.12 (m, 4H), 1.63 (m, 4H), 1.42-1.24 (m, 8H), 0.95 (t, 3H, *J* = 7.3 Hz), 0.89 (t, 3H, *J* = 6.1 Hz). ¹³C NMR (100.62 MHz, dms_o-d₆, δ /ppm): 171.3 (q, *J* = 29 Hz), 118.1 (q, *J* = 294 Hz), 82.3, 62.0, 58.9, 58.6, 30.6, 25.4, 24.5, 22.4, 21.8, 21.3, 19.0, 13.1, 12.8.

Table S1: Melting points of the ionic liquids.

Compound	Melting point (°C)*
[C ₂ mim][hfac]	33
[C ₄ mim][hfac]	--
[C ₆ mim][hfac]	--
[C ₈ mim][hfac]	17-18
[C ₁₀ mim][hfac]	33
[C ₁₆ mim][hfac]	66
[C ₁₈ mim][hfac]	72-73
[C ₄ dmim][hfac]	15-16
[C ₁ C ₄ pyrr][hfac]	0
[C ₄ C ₆ pyrr][hfac]	48

* Melting points were determined by DSC.
No freezing was observed for [C₄mim][hfac] and [C₆mim][hfac].

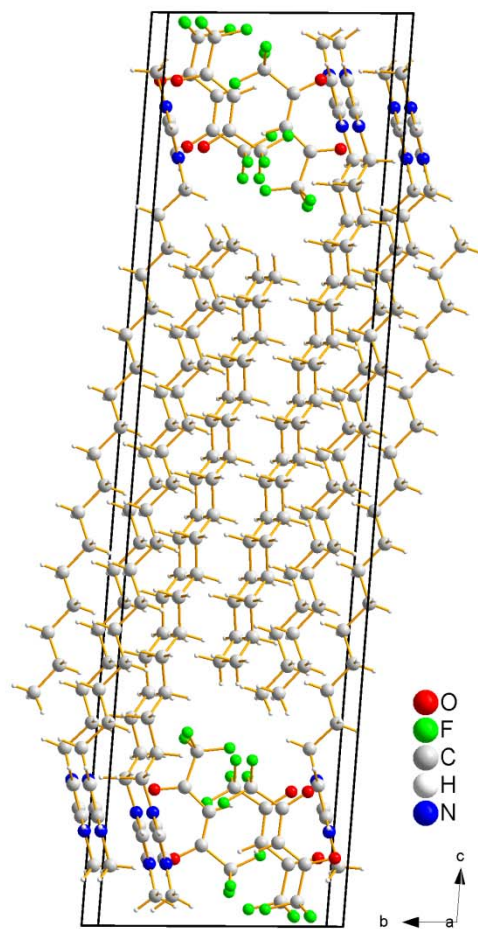


Figure S1: Packing in the crystal structure of [C₁₈mim][hfac].

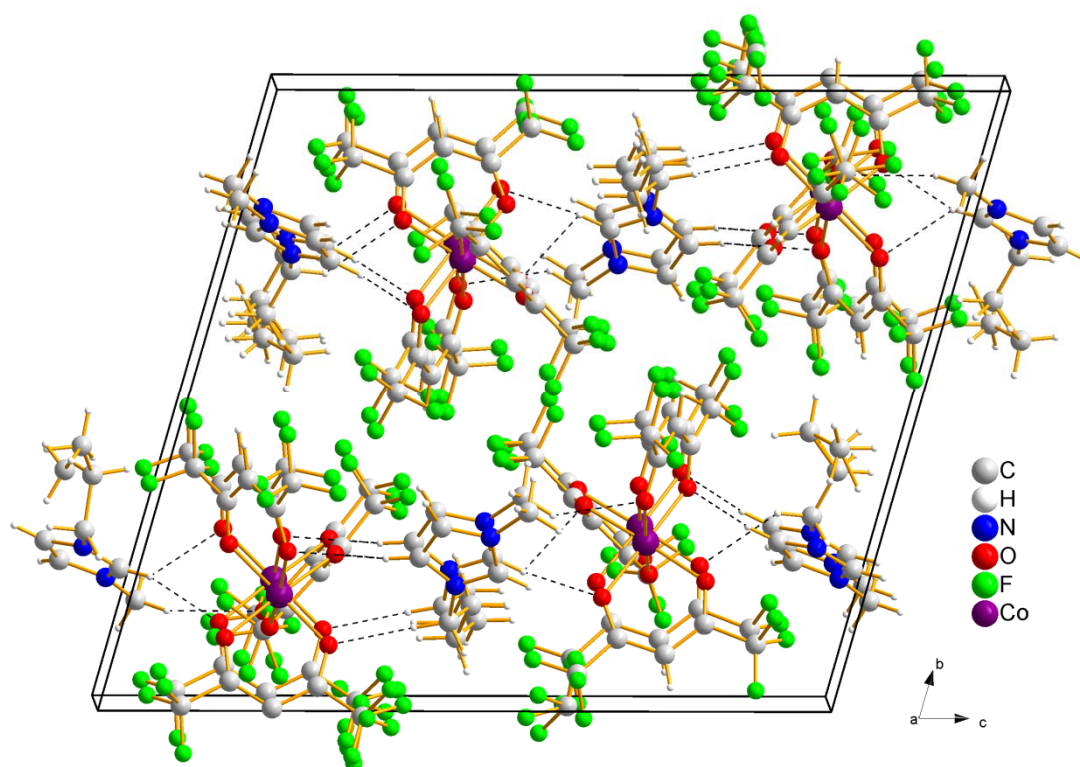


Figure S2: Packing in the crystal structure of $[\text{C}_4\text{mim}][\text{Co}(\text{hfac})_3]$.

⁽ⁱ⁾ SAINT, Bruker Analytical X-ray Systems Inc., Madison, WI, Manual Version 5/6.0, 1997.

⁽ⁱⁱ⁾ SHELXTL-PC, Bruker Analytical X-ray Systems Inc., Madison, WI, Manual Version 5.1, 1997.

