Electronic Supplementary Information

Ionic Liquids with Metal Chelate Anions

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Scheme and Figure

Scheme S1, A general method for the preparation of Ionic Liquids with Metal Chelate Anions

\[
\text{F}_3\text{C} \quad \text{R-acac} \quad \xrightarrow{\text{NH}_3\text{H}_2\text{O}} \quad \text{CH}_3\text{CN} \quad \text{NH}_4^+ \quad \text{MCl}_2\text{H}_2\text{O} \quad \xrightarrow{\text{MCl}_2\text{H}_2\text{O}} \quad \text{NH}_4^+\text{[M(R-acac)$_3$]}^- + \text{NH}_4\text{Cl}\dagger \\
\text{M}=\text{Cu, Co, Mn, Ni}
\]

\[
\text{C}^+\text{[M(R-acac)$_3$]}^- + \text{NH}_4\text{Cl}\dagger
\]

\[
\text{C}^+_1 = \text{N}^{+4,4,4,4} \\
\text{C}^+_2 = \text{N}^{+1,1,1,16} \\
\text{C}^+_3 = \text{P}^{+\text{Ph}_3\text{Bu}} \\
\text{C}^+_4 = \text{C}^{14\text{Py}^+} \\
\text{C}^+_5 = \text{C}^{10\text{min}^+}
\]

Electronically Supplementary Material (ESI) for Chemical Communications

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Figure S1. Five Runs to test the reusability of \([C_{10}\text{mim}][\text{Co(F}_6\text{-acac)}_3]\). Reaction conditions: cyclohexene (0.082 g, 1 mmol), \([C_{10}\text{mim}][\text{Co(F}_6\text{-acac)}_3]\) (recovered, 1 mL), 60 °C, 6 h, O\(_2\) 1 atm.
Experimental Section

Materials and general methods

All chemicals were obtained in the highest purity grade possible, and were used as received unless otherwise stated. All Ionic Liquids (ILs) samples were dried under vacuum at 60 °C for 24 h to reduce possible traces of water. 1H NMR spectra were recorded on a Bruker spectrometer (500MHz) in DMSO-d6 with tetramethylsilane as the standard. FT-IR spectra were recorded on a Nicolet 470 FT-IR spectrometer. Melting point and decomposition temperatures were measured with a DSC Q 100 meter and a TGA 2100 series of TA Instrument with a heating rate of 10°C/min, respectively. The density was the mean of three measurement values, which were determined by measuring the weight of three separate samples (1.0 mL) at 25°C. The relative standard uncertainty of the mean density was less than 5%. ESI-MS analysis was performed on a Bruker Esquire 3000 (Bruker–Franzen Analytik, Bermen, Germany) equipped with an ion trap analyzer system. All GC experiments were carried out and recorded using a SHIMADZU GC-2010 with FID detector. The structure of products and by-products was identified using HP6890 GC/MS spectrometer by comparing retention times and fragmentation patterns with authentic samples. The viscosities of these ILs were measured using a viscometer (Anton Paar Automated Microviscometer). These prepared ionic liquids at 30 °C are so viscous that only two viscosity values can be obtained. ([C10mim][Mn(F6-acac)3]: 268 mPa s, [C10mim][Co(F3-Phbdo)3]: 177 mPa s)

Preparation of ILs with Metal Chelate Anions

All the ILs were synthesized by a three-step method as shown in Scheme S1.

Synthesis of ammonium hexafluoroacetylacetonate ([NH4][F6-acac]):

[NH4][F6-acac] was prepared by neutralizing of ammonium hydroxide (NH3·H2O) and hexafluoroacetylacetonate (F6-acac) as a weak proton donor. Equimolar ammonium hydroxide was added to the F6-acac solution in acetonitrile. The mixture was then stirred at room temperature for 24 h. Subsequently, acetonitrile and water were distilled off at 60
C under reduced pressure. Then, the solid was washed with n-hexane. The obtained white solid was dried in high vacuum for 24 h at room temperature. Yield: 92%. The structures of \([\text{NH}_4][\text{F}_6\text{-acac}]\) was confirmed by NMR, ESI-MS and IR spectroscopy. \(^1\)H NMR (500 MHz, d6-DMSO): 5.33 (s, 1H), 7.19 (s, 4H). ESI-MS: [F\(_6\)-acac] \(206.6\). FT-IR: 3134, 1670, 1529, 1508, 1400, 1257, 1196, 1146, 795, 663, 579 cm\(^{-1}\)

Synthesis of ammonium hexafluoroacetylacetonate ([NH\(_4\)][F\(_3\)-Phbdo]) and ([NH\(_4\)][F\(_3\)-Fubdo])

To synthesize [NH\(_4\)][F\(_3\)-Phbdo], equimolar ammonium hydroxide was added to the F\(_3\)-Phbdo solution in acetonitrile. The mixture was then stirred at room temperature for 24 h. Solid precipitation was observed and the suspension was filtered, washed with cold acetonitrile to obtain a white solid. The obtained white solid was dried in high vacuum at room temperature for 24 h. Yield: 81%. \(^1\)H NMR (500 MHz, d6-DMSO): 5.96 (s, 1H), 7.18 (s, 4H), 7.45-7.42 (m, 3H), 7.78 (d, 2H). ESI-MS: [F\(_3\)-Phbdo] \(214.7\). FT-IR: 2968, 1681, 1633, 1578, 1274, 1122, 758, 626, 569 cm\(^{-1}\)

[NH\(_4\)][F\(_3\)-Fubdo] was synthesized as the same method. Yield: 74%. \(^1\)H NMR (500 MHz, d6-DMSO): 6.09 (s, 1H), 6.56 (d, 1H), 7.12 (d, 1H), 7.24 (d, 4H), 7.51 (d, 1H). ESI-MS: [F\(_3\)-Fubdo] \(204.7\). FT-IR: 3136, 1633, 1574, 1390, 886, 763, 674 cm\(^{-1}\)

Synthesis of ([N\(_{4,4,4,4}\)][M(F\(_6\)-acac)\(_3\)], [N\(_{1,1,1,1,1,1}\)][M(F\(_6\)-acac)\(_3\)], [C\(_{14}\)Py][M(F\(_6\)-acac)\(_3\)], [C\(_{10}\)mim][M(F\(_6\)-acac)\(_3\)] and [PPh\(_3,4\)][M(F\(_6\)-acac)\(_3\)])

MCl\(_2\) (1/3 eqv.) was added to [NH\(_4\)][F\(_6\)-acac] (1 eqv.) solution in acetonitrile and the mixture was vigorously stirred at room temperature for 12 h. After filtering the solid precipitation (NH\(_4\)Cl), 1/3 eqv. of the halide ionic liquid (chloride salt) was added to the solution. Then, after stirring for 12h at room temperature, the mixture was filtered. The solvent was removed under reduced pressure at 60 °C and the residue (crude product) was extracted with Et\(_2\)O. The extracted organic layer was washed with H\(_2\)O for three or more times till AgNO\(_3\) test gave no precipitation with the aqueous fraction. The solvent was
removed under reduced pressure 90 °C and the obtained ILs was dried in high vacuum for 24 h to remove possible trace of water. The structures of these chelate-based ILs was confirmed by ESI-MS, IR spectroscopy and Atomic Absorption Spectroscopy (AAS).

\[ \text{N}_{4,4,4,4}\text{[Co(F}_6\text{-acac)}_3] \]: Yield: 82%. ESI-MS: \[\text{N}_{4,4,4,4}\] \text{ + 242.2; [Co(F}_6\text{-acac)}_3] \text{ - 680.2. FT-IR: 3437, 2976, 1647, 1528, 1255, 1195, 1150, 793, 665, 582 cm}^{-1}. \text{ AAS: Calc. for C}_{31}\text{H}_{39}\text{CoO}_{6}\text{NF}_{18}: \text{Co, 6.39%; Found: Co, 6.12%}. \]

\[ \text{N}_{4,4,4,4}\text{[Mn(F}_6\text{-acac)}_3] \]: Yield: 74%. ESI-MS: \[\text{N}_{4,4,4,4}\] \text{ + 242.2; [Mn(F}_6\text{-acac)}_3] \text{ - 676.1. FT-IR: 3422, 2970, 1643, 1557, 1530, 1506, 1480, 1253, 1197, 1149, 798, 664, 581 cm}^{-1}. \text{ AAS: Calc. for C}_{31}\text{H}_{39}\text{MnO}_{6}\text{NF}_{18}: \text{Mn, 5.99%; Found: Mn, 6.04%}. \]

\[ \text{N}_{4,4,4,4}\text{[Cu(F}_6\text{-acac)}_3] \]: Yield: 67%. ESI-MS: \[\text{N}_{4,4,4,4}\] \text{ + 242.3; [Cu(F}_6\text{-acac)}_3] \text{ - 683.9. FT-IR: 3440, 2987, 1646, 1528, 1253, 1194, 1149, 789, 667, 584 cm}^{-1}. \text{ AAS: Calc. for C}_{31}\text{H}_{39}\text{CuO}_{6}\text{NF}_{18}: \text{Cu, 6.89%; Found: Cu, 6.71%}. \]

\[ \text{N}_{1,1,1,16}\text{[Co(F}_6\text{-acac)}_3] \]: Yield: 71%. ESI-MS: \[\text{N}_{1,1,1,16}\] \text{ + 284.4; [Co(F}_6\text{-acac)}_3] \text{ - 680.2. FT-IR: 3455, 2922, 2854, 1643, 1521, 1500, 1253, 1200, 1149, 795, 670, 581 cm}^{-1}. \text{ AAS: Calc. for C}_{34}\text{H}_{45}\text{CoO}_{6}\text{NF}_{18}: \text{Co, 6.11%; Found: Co, 6.07%}. \]

\[ \text{C}_{14}\text{Py}[\text{Co(F}_6\text{-acac)}_3] \]: Yield: 64%. ESI-MS: \[\text{C}_{14}\text{Py}\] \text{ + 276.4; [Co(F}_6\text{-acac)}_3] \text{ - 680.2. FT-IR: 3447, 2926, 2851, 1654, 1637, 1560, 1508, 1257, 1200, 1143, 792, 669 cm}^{-1}. \text{ AAS: Calc. for C}_{34}\text{H}_{37}\text{CoO}_{6}\text{NF}_{18}: \text{Co, 6.16%; Found: Co, 6.01%}. \]

\[ \text{C}_{14}\text{Py}[\text{Mn(F}_6\text{-acac)}_3] \]: Yield: 80%. ESI-MS: \[\text{C}_{14}\text{Py}\] \text{ + 276.4; [Mn(F}_6\text{-acac)}_3] \text{ - 676.1. FT-IR: 3434, 2928, 2857, 1643, 1530, 1509, 1253, 1200, 1146, 798, 661, 584 cm}^{-1}. \text{ AAS: Calc. for C}_{34}\text{H}_{37}\text{MnO}_{6}\text{NF}_{18}: \text{Mn, 5.77%; Found: Mn, 5.75%}. \]

\[ \text{C}_{14}\text{Py}[\text{Cu(F}_6\text{-acac)}_3] \]: Yield: 59%. ESI-MS: \[\text{C}_{14}\text{Py}\] \text{ + 276.3; [Cu(F}_6\text{-acac)}_3] \text{ - 683.9. FT-IR: 3453, 2919, 1645, 1525, 1483, 1383, 1255, 1139, 797, 668, 586 cm}^{-1}. \text{ AAS: Calc. for C}_{34}\text{H}_{37}\text{CuO}_{6}\text{NF}_{18}: \text{Cu, 6.66%; Found: Cu, 6.61%}. \]
[C_{10}mim][Co(F_6-acac)_3]: Yield: 74%. ESI-MS: [C_{10}min]^+ 223.2; [Co(F_6-acac)_3]^− 680.2. FT-IR: 3444, 2935, 2855, 1654, 1554, 1498, 1259, 1200, 1146, 795, 668, 579 cm⁻¹. AAS: Calc. for C_{29}H_{30}CoO_6N_2F_{18}: Co, 6.53%; Found: Co, 6.37%.

[C_{10}mim][Mn(F_6-acac)_3]: Yield: 86%. ESI-MS: [C_{10}min]^+ 223.2; [Mn(F_6-acac)_3]^− 676.1. FT-IR: 3421, 2932, 1646, 1555, 1530, 1507, 1255, 1147, 796, 741, 664, 584 cm⁻¹. AAS: Calc. for C_{29}H_{30}MnO_6N_2F_{18}: Mn, 6.11%; Found: Mn, 6.05%.

[C_{10}mim][Ni(F_6-acac)_3]: Yield: 67%. ESI-MS: [C_{10}min]^+ 223.2; [Ni(F_6-acac)_3]^− 679.2. FT-IR: 3157, 3095, 2928, 2858, 1643, 1554, 1486, 1343, 1257, 1196, 1149, 793, 743, 673, 587 cm⁻¹. AAS: Calc. for C_{29}H_{30}NiO_6N_2F_{18}: Ni, 6.54%; Found: Ni, 6.40%.

[C_{10}mim][Cu(F_6-acac)_3]: Yield: 52%. ESI-MS: [C_{10}min]^+ 223.2; [Cu(F_6-acac)_3]^− 683.9. FT-IR: 3152, 2930, 2859, 1667, 1646, 1552, 1529, 1499, 1464, 1256, 1201, 1149, 795, 742, 669, 577 cm⁻¹. AAS: Calc. for C_{29}H_{30}CuO_6N_2F_{18}: Cu, 7.04%; Found: Cu, 7.32%.

[PPh_{3,4}][Co(F_6-acac)_3]: Yield: 93%. ESI-MS: [PPh_{3,4}]^+ 318.9; [Co(F_6-acac)_3]^− 680.2. FT-IR: 3416, 1640, 1521, 1506, 1441, 1250, 1203, 1143, 789, 667, 581, 524 cm⁻¹. AAS: Calc. for C_{37}H_{27}CoO_6PF_{18}: Co, 5.90%; Found: Co, 6.01%.

Synthesis of [C_{10}mim][M(F_3-Phbdo)_3] [C_{10}mim][Mn(F_3-Fubdo)_3]:

These chelate-based ILs were synthesized as the same method with above described method for [N_{4,4,4,4}][M(F_6-acac)_3], but acetone was used as the reaction medium.

[C_{10}mim][Co(F_3-Phbdo)_3]: Yield: 75%. ESI-MS: [C_{10}min]^+ 223.2; [Co(F_3-Phbdo)_3]^− 703.1. FT-IR: 3447, 3149, 2928, 1611, 1577, 1534, 1490, 1318, 1290, 1184, 1134, 762, 703, 641, 580 cm⁻¹. AAS: Calc. for C_{44}H_{45}CoO_6N_2F_{9}: Co, 6.37%; Found: Co, 6.33%.

[C_{10}mim][Ni(F_3-Phbdo)_3]: Yield: 86%. ESI-MS: [C_{10}min]^+ 223.2; [Ni(F_3-Phbdo)_3]^− 702.9. FT-IR: 3447, 3149, 2928, 2857, 1612, 1572, 1535, 1490, 1291, 1185, 1134, 944, 761, 719, 702, 646, 581 cm⁻¹. AAS: Calc. for C_{44}H_{45}NiO_6N_2F_{9}: Ni, 6.36%; Found: Ni, 6.38%.
[C_{10}mim][Mn(F_3-Fubdo)_3]: Yield: 62%. ESI-MS: [C_{10}min]^+ 223.2; [Mn(F_3-Fubdo)_3]^− 670.1. FT-IR: 3415, 2928, 2857, 1615, 1575, 1517, 1458, 1389, 1302, 1258, 1188, 1138, 1020, 790, 676, 641, 583 cm⁻¹. AAS: Calc. for C_{38}H_{39}MnO_{9}N_{2}F_{9}: Mn, 6.16%; Found: Mn, 6.18%.

**Typical Procedure for the Oxidation of Cyclohexene (in Table 1)**

The oxidation of cyclohexene was carried out in a three-necked glass-reactor (15mL for the entries 1-3; 3mL for the entries 4-6), which was fitted with an O₂ inlet tube and a reflux condenser. Cyclohexene and catalysts as described in the table were added to the reactor. Then the reaction was vigorously stirred at 60 °C in oil bath with O₂ flowing at a constant flow rate (10mL min⁻¹). After completion of the reaction, petroleum ether (5mL × 3 for the entries 1-3; 1mL × 3 for the entries 4-6) was added to extract the product. The extracted organic layer was separated and treated with excess Ph₃P for 2 h to reduce the alkyl hydroperoxide. The obtained solution was injected into GC for analysis.
The original ESI-MS spectras of all the cations and anions in our prepared chelate-based ionic liquids.

$[\text{N}_4,4,4,4]^+$:
[C$_{10}$mim]$^+$:
[C_{14}Py]^+:
\[ [N_{1,1,1,16}]^+ : \]

**Spectrum 1A Plot - 2010-11-2 20:21**

Print Date: 02 Nov 2010 20:21:55

\[ C_6H_5 - C_7H_4 - (\sigma) \]

Plot 1A, Scan 5 from d' data/20101102/c16-co+xms

Ion: 284.4 (4.114e+7=100%), c16-co+xms

0.062 min, Scans: 2.7, 100:1500, Ion 188 vs. RIC: 1.371e+6

m/z 200 250 300 350 400

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4.114e+7

285.4

8.163e+6

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[F₆-acac]:

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Page 1 of 1
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Acquisition Date 03/31/11 19:41:58
Operator Administrator
Instrument esquire3000plus

Acquisition Parameter
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Alternating Ion Polarity Off
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Skim 1 -40.0 Volt
Trap Drive 43.8
Accumulation Time 710 µs
Averages 5 Spectra
Auto MS/MS Off

Intens x10⁷

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1.0

0.5

0.0

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MS, 0.0-0.1min (R2-#10)

Bruker Daltonics DataAnalysis 3.1 printed: 03/31/11 20:24:57 Page 1 of 1
[Co(Fe-acac)₃]:

Print Date: 02 Nov 2010 20:22:40

Spectrum 1A Plot - 2010-11-2 20:22

Spectrum 1A

Spectrum 1A Plot from d:/data/20101102/c10min-co.xms

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207.1 257.60

561.1 305.68

1431.1 774.65

1467.6 1339.43

0% 100% 25% 50% 75%

0 250 500 750 1000 1250 1500 (m/z)

Electronic Supplementary Material (ESI) for Chemical Communications
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[Mn(F₆-acac)₃]⁺:
[Cu(F6-acac)3]−

Analysis Info
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Comment:

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Instrument: esquire3000plus

Acquisition Parameter
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Accumulation Time: 97 µs

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1.00
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0.50
0.25

521.6
660.8

Bruker Daltonics DataAnalysis 3.1 printed: 04/08/11 09:42:55 Page 1 of 1
[Ni(F_6-acac)_3]^{-}:
[Ni(F3-Phbdo)3]−:

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Bruker Daltonics DataAnalysis 3.1 printed: 04/08/11 09:44:22 Page 1 of 1
[Mn(F₃-fubdo)₃]⁺: