Use of 4,5-dicyanoimidazolate anion based Ionic Liquid for the Synthesis of Iron and Silver Nanoparticles

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\textit{Electronic Supplementary Information}
General procedure for the preparation of ILs [1-4(a-e)]: Anhydrous potassium carbonate was added to a solution of the appropriate imidazole in acetone. The mixture was stirred for 2–4 h at 25 °C. Solution of the appropriate [Q]chloride ([Q] = cation) in dichloromethane was added and the reaction mixture was stirred for 3–6 h. The resultant precipitate of potassium chloride was removed by filtration and the solvents were evaporated under vacuum. The product was extracted with acetone, the extract was filtered and solvent was removed to obtain the ILs.

Elemental analysis (C, H, N) was performed on Elementar Vario EL elemental analyzer. TG measurements was performed in a static air atmosphere from room temperature up to 850 °C with a Perkin Elmer TGA 4000 thermal analyzer. The heating rate was 10 °C min⁻¹. The samples were placed in ceramic pans. TG-MS measurements were performed with Linseis STA PT-1600 online coupled mass spectrometer. ¹H and ¹³C NMR spectra of all compound were performed on Bruker Advanced 300 spectrometer. Resonances for NMR spectra are reported relative to Me₄Si (δ = 0.0 ppm) and calibrated based on the solvent signal for ¹H and ¹³C. The ESI-MS spectra were recorded using a Micromass Q-TOF mass spectrometer in positive and negative electrospray mode.

Tetrabutylphosphonium 4,5-dicyano-2-methylimidazolate (4a): Light yellow liquid (yield: 95%); ¹H NMR (300 MHz, CDCl₃): δ = 0.93 (m, 12H), 1.52 (m, 8H), 2.29 (m, 8H), 2.73 (m, 8H) 2.99 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ= 13.9, 18.7, 19.3, 24.1, 27.6, 40.2, 116.9, 122.3, 158.0 ppm; ESI-MS: m/z (%): 259 (100) for cation, 131 (100) for anion; elemental analysis calcd (%) for C₂₂H₃₆N₄P (390.5): C 67.66, H 10.07, N 14.35; found: C 67.21, H 10.49, N 24.71.

Tetraethylammonium 4,5-dicyano-2-trifluoromethylimidazolate (1b): White solid (yield: 94%); ¹H NMR: δ = 1.41 (m, 12H), 1.36 (m, 4H), 3.3 ppm (m, 4H); ¹³C NMR: δ = 7.8, 53.0, 106.2, 115.9, 119.9, 144.2 ppm; ESI-MS: m/z (%): 130 (100) for cation, 185 (100) for anion; elemental analysis calcd (%) for C₁₄H₂₀N₅F₃ (315.1): C 53.32, H 6.39, N 22.21; found: C 53.04, H 6.79, N 22.49.

1-Butyl-3-methylimidazolium 4,5-dicyano-2-trifluoromethylimidazolate (2b): Colorless liquid (yield: 95%); ¹H NMR (300 MHz, CDCl₃): δ = 0.75 (t, J=7.3 Hz, 3H), 1.34 (sextet, J=7.5 Hz, 2H), 1.80 (pentet, J=7.4 Hz, 2H), 1.87 (pentet, J=7.4 Hz, 2H), 4.02 (s, 3H), 4.27 (t, J=7.3 Hz, 2H), 7.41 (d, 2 H), 9.64 ppm (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ= 13.7, 19.8, 32.4, 36.9, 50.2, 115.8, 119.4, 122.3, 123.9, 138.1 ppm; ESI-MS: m/z (%): 139 (100) for cation, 185 (100) for anion; elemental analysis calcd (%) for C₁₄H₁₅N₆F₃ (324.1): C 51.85, H 4.66, N 25.91; found: C 51.41, H 4.24, N 25.72.

3-Methyl-1-octylimidazolium 4,5-dicyano-2-trifluoromethylimidazolate (3b): Light yellow liquid (yield: 95%); ¹H NMR (300 MHz, CDCl₃): δ = 0.85 (t, J=6.7 Hz, 3H), 1.26–1.33 (m, 10H), 2.10 (m, 2H), 4.06 (s, 3 H), 4.17 (t, J=7.4 Hz, 2H), 7.28 (m, 2 H), 9.58 ppm (s, 1H); ¹³C NMR (75 MHz, CDCl₃): δ = 14.4, 22.9, 26.6, 29.3, 29.4, 50.6, 115.8, 117.3, 119.4, 122.2, 123.8, 138.4 ppm; ESI-MS: m/z (%): 195 (100) for cation, 185 (100) for anion; elemental analysis calcd (%) for C₁₈H₂₃N₆F₃ (380.4): C 56.83, H 6.09, N 22.09; found: C 58.67, H 6.53, N 22.32.

Tetrabutylphosphonium 4,5-dicyano-2-trifluoromethylimidazolate (4b): Light yellow semisolid (yield: 95%); ¹H NMR (300 MHz, CDCl₃): δ = 0.96 (m, 12H), 1.22 (m, 8H), 1.52 (m, 8H), 2.15 ppm (m, 8H); ¹³C NMR (CDCl₃): δ = 13.6, 19.3, 18.7, 24.2, 28.8, 116.0, 119.9 ppm; ESI-MS: m/z (%): 259 (100) for cation, 185 (100) for anion; elemental analysis calcd (%) for C₂₂H₃₈N₄PF₃ (444.5): C 59.44, H 8.16, N 12.60; found: C 59.78, H 7.98, N 12.87.
Tetraethylammonium 4,5-dicyano-2-pentafluoroethylimidazolide (1c): White solid (yield: 96 %); \( ^1 \)H NMR: \( \delta = 1.42 \) (m, 12H), 1.35 (m, 4H), 3.30 ppm (m, 4H); \( ^{13} \)C NMR: \( \delta = 7.4, 52.5, 117.1, 118.4, 126.2, 149.2 \) ppm; ESI-MS: \( m/z \) (%): 130 (100) for cation, 235 (100) for anion; elemental analysis calcd (%) for C\(_{15}\)H\(_{20}\)N\(_5\)F\(_5\) (365.3): C 49.31, H 5.52, N 19.17; found: C 49.01, H 5.83, N 18.96.

1-Butyl-3-methylimidazolide 4,5-dicyano-2-tetrafluoroethylimidazolide (2c): Light yellow liquid (yield: 97 %); \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 0.93 \) (t, \( J = 7.3 \) Hz, 3H), 1.34 (sextet, \( J = 7.5 \) Hz, 2H), 1.86 (pentet, \( J = 7.4 \) Hz, 2H), 2.14 (pentet, \( J = 7.4 \) Hz, 2H), 4.00 (s, 3H), 4.22 (t, \( J = 7.3 \) Hz, 2 H), 7.41 (d, 2 H), 9.27 ppm (s, 1H); \( ^{13} \)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 13.6, 19.7, 32.3, 36.9, 50.3, 115.8, 120.4, 122.9, 124.2, 136.4, 147.6 \) ppm; ESI-MS: \( m/z \) (%): 139 (100) for cation, 235 (100) for anion; elemental analysis calcd (%) for C\(_{15}\)H\(_{20}\)N\(_5\)F\(_5\) (374.3): C 48.13, H 4.04, N 22.45; found: C 48.39, H 3.83, N 22.09.

3-Methyl-1-octylimidazolide 4,5-dicyano-2-pentafluoroethylimidazolide (3c): Light yellow liquid (yield: 94 %); \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 0.86 \) (t, \( J = 6.7 \) Hz, 3H), 1.13−1.30 (m, 10H), 2.13 (m, 2H), 4.00 (s, 3 H), 4.21 (t, \( J = 7.4 \) Hz, 2H), 7.41 (m, 2 H), 10.32 ppm (s, 1H); \( ^{13} \)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 14.4, 22.8, 26.6, 29.2, 30.4, 32.0, 36.9, 50.8, 115.0, 117.3, 120.4, 122.9, 124.3, 136.1, 147.6 \) ppm; ESI-MS: \( m/z \) (%): 195 (100) for cation, 235 (100) for anion; elemental analysis calcd (%) for C\(_{15}\)H\(_{20}\)N\(_5\)F\(_5\) (430.4): C 53.02, H 5.39, N 19.53; found: C 53.42, H 5.13, N 19.31.

Tetrabutylphosphonium 4,5-dicyano-2-pentafluoroethylimidazolide (4c): Light yellow liquid (yield: 93 %); \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 0.87 \) (m, 12H), 0.95 (m, 8H), 1.78 (m, 8H), 2.14 ppm (m, 8H); \( ^{13} \)C NMR (CDCl\(_3\)): \( \delta = 13.6, 19.3, 18.7, 24.2, 28.8, 116.0, 119.9, 126, 142.4 \) ppm; ESI-MS: \( m/z \) (%): 250 (100) for cation, 235 (100) for anion; elemental analysis calcd (%) for C\(_{23}\)H\(_{36}\)N\(_4\)F\(_5\) (494.5): C 55.86, H 7.34, N 11.33; found: C 55.31, H 7.11, N 11.71.

Tetraethylammonium 4,5-dicyano-2-(N,N'-dimethyl)aminoimidazolide (1d): Light brown solid (yield: 93 %); \( ^1 \)H NMR: \( \delta = 0.58 \) (t, \( J = 12 \) Hz, 3H), 1.30−1.47 (m, 8H), 3.18 (m, 3H), 3.22 ppm (m, 3H); \( ^{13} \)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 13.9, 24.1, 27.6, 40.2, 118.0, 116.9 \) ppm; ESI-MS: \( m/z \) (%): 130 (100) for cation, 160 (100) for anion; elemental analysis calcd (%) for C\(_{15}\)H\(_{20}\)N\(_6\) (290.4): C 62.04, H 9.02, N 28.94; found: C 62.54, H 8.79, N 28.67.

1-Butyl-3-methylimidazolide 4,5-dicyano-2-(N,N'-dimethyl)aminoimidazolide (2d): Light brown liquid (yield: 93 %); \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 0.92 \) (t, \( J = 7.3 \) Hz, 3H), 1.25 (m, 2 H), 1.81 (pentet, \( J = 7.4 \) Hz, 2H), 3.02 (m, 3H), 3.16 (m, 3H), 3.95 (s, 3H), 4.36 (t, \( J = 7.3 \) Hz, 2 H), 7.81 (d, 2 H), 9.21 ppm (s, 1H); \( ^{13} \)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 13.7, 19.0, 29.4, 32.0, 36.9, 40.2, 50.4, 116.8, 117.9, 122.7, 136.7, 162.7, 164.5 \) ppm; ESI-MS: \( m/z \) (%): 139 (100) for cation, 160 (100) for anion; elemental analysis calcd (%) for C\(_{15}\)H\(_{20}\)N\(_2\) (299.4): C 60.18, H 7.07, N 32.75; found: C 60.45, H 7.14, N 32.41.

3-Methyl-1-octylimidazolide 4,5-dicyano-2-(N,N'-dimethyl)aminoimidazolide (3d): Light yellow liquid (yield: 95 %); \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 0.84 \) (t, \( J = 6.7 \) Hz, 3H), 1.16−1.30 (m, 10H), 1.88 (m, 2H), 3.10 (m, 3H), 3.19 (m, 3H), 4.06 (s, 3 H), 4.26 (t, \( J = 7.4 \) Hz, 2H), 7.37 (m, 2 H), 9.42 ppm (s, 1H); \( ^{13} \)C NMR (75 MHz, CDCl\(_3\)): \( \delta = 14.4, 22.9, 26.6, 29.3, 32.9, 30.6, 32.0, 36.9, 40.2, 50.6, 116.8, 118.0, 122.6, 124.1, 136.7, 164.5 \) ppm; ESI-MS: \( m/z \) (%): 195 (100) for cation, 160 (100) for anion; elemental analysis calcd (%) for C\(_{15}\)H\(_{20}\)N\(_2\) (355.2): C 64.20, H 8.22, N 27.58; found: C 63.88, H 8.01, N 28.11.

Tetrabutylphosphonium 4,5-dicyano-2-(N,N'-dimethyl)aminoimidazolide (4d): Light brown semisolid (yield: 93 %); Light brown liquid (yield: 95%); \( ^1 \)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 0.87 \) (m, 12H), 0.95 (m,
8H), 1.78 (m, 8H), 2.14 ppm (m, 8H), 3.10 (m, 8H), 3.19 ppm (m, 3H); $^{13}$C NMR (CDCl$_3$): $\delta = 13.9$, 18.7, 19.3, 24.1, 27.6, 40.2, 118.0, 116.9 ppm; ESI-MS: $m/z$ (%): 259 (100) for cation, 160 (100) for anion; elemental analysis calcd (%) for C$_{23}$H$_{42}$N$_5$P (419.6): C 65.84, H 10.09, N 16.69; found: C 65.51, H 10.39, N 16.42.

Tetraethylammonium 4,5-dicyano-2-nitroimidazolate (1e): Brown solid, (yield: 93 %); $^1$H NMR: $\delta = 0.58$ (t, 12H), 1.30-1.47 ppm (m, 8H); $^{13}$C NMR: $\delta = 7.4$, 52.5, 117.1, 118.4, 149.2 ppm; ESI-MS: $m/z$ (%): 130 (100) for cation, 162 (100) for anion; elemental analysis calcd (%) for C$_{13}$H$_{20}$N$_6$O$_2$ (292.3): C 62.04, H 9.02, N 28.94; found: C 62.38, H 8.81, N 28.77.

1-Butyl-3-methylimidazolium 4,5-dicyano-2-nitroimidazolate (2e): Light brown liquid (yield: 93%); $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.92$ (t, $J$=7.3 Hz, 3H), 1.34 (sextet, $J$=7.2 Hz, 2H), 1.85 (m, $J$=7.4 Hz, 2H), 4.05 (s, 3H), 4.27 (t, $J$=7.3 Hz, 2H), 7.41 (d, 2H), 9.19 ppm (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 13.7$, 19.8, 32.4, 36.9, 50.2, 115.8, 119.4, 123.9, 138.1, 153.2 ppm; ESI-MS: $m/z$ (%): 139 (100) for cation, 162 (100) for anion; elemental analysis calcd (%) for C$_{13}$H$_{15}$N$_7$O$_2$ (301.3): C 51.82, H 5.02, N 32.54; found: C 51.41, H 5.44, N 32.11.

3-Methyl-1-octylimidazolium 4,5-dicyano-2-nitroimidazolate (3e): Brown oil (yield: 92 %); $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 0.85$ (t, $J$=6.7 Hz, 3H), 1.34–1.67 (m, 10H), 2.37 (m, 2H), 4.00 (s, 3 H), 4.20 (t, $J$=7.4 Hz, 2H), 7.50 (m, 2 H), 10.09 ppm (s, 1H); $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta = 14.4$, 22.9, 26.6, 29.3, 29.4, 30.6, 32.0, 37.0, 50.7, 122.3, 114.5, 120.4, 123.8, 138.0, 152.6 ppm; ESI-MS: $m/z$ (%): 195 (100) for cation, 162 (100) for anion; elemental analysis calcd (%) for C$_{17}$H$_{23}$N$_7$O$_2$ (357.4): C 57.13, H 8.95, N 27.43; found: C 56.84, H 9.04, N 27.62.

Tetrabutylphosphonium 4,5-dicyano-2-nitroimidazolate (4e): Dark brown liquid (yield: 95%); $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 7.37$ (s, 1H), 7.56–7.64 (m, 8H), 7.71–7.78 (m, 8H), 7.87–7.92 ppm (m, 4H); $^{13}$C NMR (CDCl$_3$): $\delta = 116.9$, 117.2 (d, $J$= 89.4 Hz, 4C), 130.5 (d, $J$=13.2 Hz, 8C), 134.1 (d, $J$=10.3 Hz, 8C), 135.6 (d, $J$=3.4 Hz, 4C), 148.9, 148.9 ppm; ESI-MS: $m/z$ (%): 259 (100) for cation, 162 (100) for anion; elemental analysis calcd (%) for C$_{21}$H$_{36}$N$_5$O$_2$P (421.5): C 59.84, H 8.61, N 16.61; found: C 59.62, H 8.32, N 16.79.
Enlarged and additional TEM-images of Fe–NPs in 3a six weeks after synthesis (complementing Figure 4a in main text).
Figure S1. Enlarged and additional TEM-images of Fe–NPs in 3a six weeks after synthesis (complementing Figure 4a in main text).