

Supporting Information

Imidazolium Ionic Liquids carrying pendant Terpyridine ligands

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200 (^1H), 300 (^1H) and 75.5 MHz (^{13}C) NMR spectra were recorded at room temperature using perdeuterated solvents as internal standards. Differential Scanning Calorimetry (DSC) was performed on a Netzsch DSC 200 PC/1/M/H Phox[®] instrument equipped with an intracooler, allowing measurements from $-65\text{ }^\circ\text{C}$ up to $450\text{ }^\circ\text{C}$. The samples were examined at a scanning rate of 10 K min^{-1} by applying two heating and one cooling cycles. The apparatus was calibrated with indium ($156.6\text{ }^\circ\text{C}$). Phase behavior was studied by polarized light optical microscopy (POM) on a Leica DMLB microscope with a Linkam LTS350 hot-stage and a Linkam TMS94 central processor. Trace metal analyses were performed using an Agilent 7500ce ICP-MS, equipped with a Peltier cooled Scott spray chamber and a Shield Torch System. The nebulizer was a MicroMist system (0.1 mL min^{-1} , Glass Expansion) and the optimized operating conditions were RF Power: 1550 W ; Carrier gas: 0.9 L min^{-1} ; Make-up gas: 0.21 L min^{-1} ; Spray chamber temperature: $2\text{ }^\circ\text{C}$; Detector mode: Pulse Counting and Integration time: 0.3 s . Microwave irradiation experiments were performed using a multi-mode MARS System from CEM Corporation using standard teflon vessels (capacity 50 mL). The temperature profiles for microwave experiments were recorded using a fiber-optic probe protected by a sapphire immersion well inserted directly into the reaction mixture.

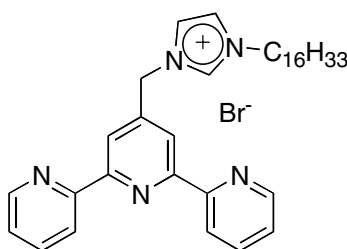
Material. 4'-(Bromomethyl)-2,2':2'',6'-terpyridine^[1] and alkyl-imidazol^[2] ($n = 4, 6, 8, 12, 16$) was synthesized as previously described. Sodium tetrafluoroborate and potassium hexafluorophosphate were purchased from Fluka and used as received. Lithium bis(trifluoromethanesulfonyl) Imide was purchased from TIC and used as received.

¹ F. Camerel, B. Donnio, C. Bourgogne, M. Schmutz, D. Guillon, P. Davidson, R. Ziessel, *Chem. Eur. J.*, **2006**, *12*, 4261.

² M. Tosoni, S. Lashat, A. Baro, *Helv. Chim. Acta*, **2004**, *87*, 2742.

General procedure for the synthesis of terpyridine imidazolium bromide salt

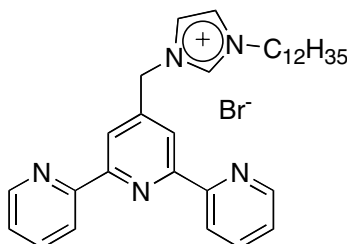
[C_nterpim]Br: To a solution of 4'-(Bromomethyl)-2,2':2'',6'-terpyridine (40 mg, 0.12 mmol) dissolved in 10 mL of THF was added two equivalents of the corresponding alkyl-imidazol (0.24 mmol). The mixture was subsequently heating under microwave irradiations at 130°C (1200W) during 1 hour in a 50 mL Teflon reactor Vial (4-5 bars). The solvent was evaporated under reduced pressure. The resulting oil was purified by repetitive precipitation from CH₂Cl₂/Et₂O mixtures. The resulting solid was centrifuged and dried under vacuum.



N-Hexadecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide

([C₁₆terpim]Br): The general procedure was followed using N-hexadecyl-imidazol (70 mg, 0.24 mmol). The product was obtained as a white solid (61 mg, 0.10 mmol, 83 %).

¹H NMR (300 MHz, CDCl₃): δ 11.06 (s, 1H), 8.67 (d, 2H, ³J = 4.13 Hz), 8.59 (d, 2H, ³J = 7.92 Hz), 8.40 (s, 2H), 7.86 (dt, 2H, ³J = 9.51 Hz, ⁴J = 1.68 Hz), 7.35 (ddd, 2H, ³J = 7.53 Hz, ³J = 4.89 Hz, ⁴J = 1.85 Hz), 7.28 (d, 2H), 5.89 (s, 2H), 4.35 (t, 2H, ³J = 7.53 Hz), 1.96 (q, 2H, ³J = 6.21 Hz), 1.36-1.18 (m, 26H), 0.87 (t, 3H, ³J = 6.21 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 156.38, 154.98, 149.20, 143.43, 138.68, 137.11, 124.38, 121.84, 121.63, 121.53, 120.01, 52.68, 50.56, 31.90, 30.13, 29.66, 29.56, 29.47, 29.34, 28.95, 26.29, 22.67, 14.09; EI-MS m/z (nature of peak, relative intensity): 538.3 ([M]⁺, 100); Anal. Calcd for C₃₅H₄₈N₅Br: C, 67.95; H, 7.82, N, 11.32. Found C, 67.75; H, 7.60; N, 11.09.

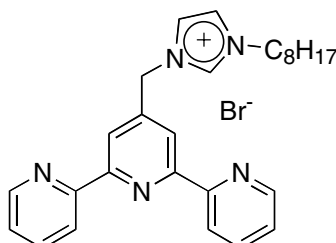


N-dodecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide ([C₁₂terpim]Br):

The general procedure was followed using N-dodecyl-imidazol (57 mg, 0.24 mmol). The product was obtained as a white solid (57 mg, 0.10 mmol, 83 %).

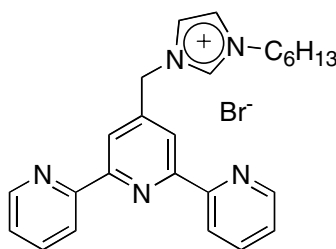
¹H NMR (300 MHz, CDCl₃): δ 10.71 (s, 1H), 8.60 (d, 2H, ³J = 4.32 Hz), 8.50 (d, 2H, ³J = 7.92 Hz), 8.30 (s, 2H), 7.80 (dt, 2H, ³J = 7.49 Hz, ⁴J = 1.72 Hz), 7.48 (s, 1H), 7.39 (s, 1H), 7.29 (ddd, 2H, ³J = 7.53 Hz, ³J = 4.89 Hz, ⁴J = 1.85 Hz), 5.84 (s, 2H), 4.29 (t, 2H, ³J = 7.53

Hz), 1.90 (q, 2H, $^3J = 7.35$ Hz), 1.27-1.17 (m, 18H), 0.87 (t, 3H, $^3J = 6.42$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 156.50, 154.89, 149.05, 143.76, 137.70, 136.96, 124.23, 122.51, 122.07, 121.38, 119.75, 52.33, 50.37, 31.79, 30.06, 29.55, 29.47, 29.39, 29.25, 29.22, 28.88, 26.18, 22.57, 14.01; EI-MS m/z (nature of peak, relative intensity): 482.2 ($[\text{M}]^+$, 100); Anal. Calcd for $\text{C}_{31}\text{H}_{40}\text{N}_5\text{Br}$: C, 66.18; H, 7.17, N, 12.45. Found C, 65.92; H, 7.04; N, 12.22.



N-octyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide ($[\text{C}_8\text{terpim}]\text{Br}$): The general procedure was followed using N-octyl-imidazol (43 mg, 0.24 mmol). The product was obtained as a white solid (52 mg, 0.10 mmol, 83 %).

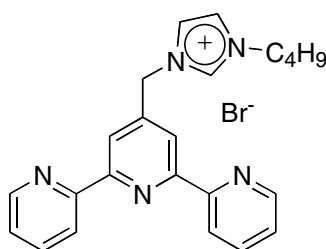
^1H NMR (300 MHz, CDCl_3): δ 10.81 (s, 1H), 8.62 (d, 2H, $^3J = 4.89$ Hz), 8.54 (d, 2H, $^3J = 7.92$ Hz), 8.34 (s, 2H), 7.45-7.43 (m, 3H), 7.38 (s, 1H), 7.31 (dt, 2H, $^3J = 7.53$ Hz, $^4J = 1.86$ Hz), 5.86 (s, 2H), 4.31 (t, 2H, $^3J = 7.38$ Hz), 1.92 (q, 2H, $^3J = 7.27$ Hz), 1.31-1.20 (m, 10H), 0.85 (t, 3H, $^3J = 6.39$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 156.46, 154.79, 149.02, 143.75, 137.88, 137.14, 124.32, 122.39, 122.01, 121.51, 119.89, 52.38, 50.47, 31.58, 30.08, 28.92, 28.85, 26.20, 22.48, 13.97; EI-MS m/z (nature of peak, relative intensity): 426.1 ($[\text{M}]^+$, 100); Anal. Calcd for $\text{C}_{27}\text{H}_{32}\text{N}_5\text{Br}$: C, 64.03; H, 6.37, N, 13.83. Found C, 63.81; H, 6.20; N, 13.69.



N-hexyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide ($[\text{C}_6\text{terpim}]\text{Br}$): The general procedure was followed using N-hexyl-imidazol (36 mg, 0.24 mmol). The product was obtained as a white solid (50 mg, 0.10 mmol, 83 %).

^1H NMR (300 MHz, CDCl_3): δ 11.07 (s, 1H), 8.66 (d, 2H, $^3J = 4.17$ Hz), 8.59 (d, 2H, $^3J = 7.92$ Hz), 8.40 (s, 2H), 7.86 (dt, 2H, $^3J = 7.74$ Hz, $^4J = 1.89$ Hz), 7.35 (ddd, 2H, $^3J = 7.49$ Hz, $^3J = 4.91$ Hz, $^4J = 1.83$ Hz), 7.30 (s, 2H), 5.89 (s, 2H), 4.34 (t, 2H, $^3J = 7.38$ Hz), 1.96 (q, 2H, $^3J = 7.32$ Hz), 1.41-1.25 (m, 6H), 0.85 (t, 3H, $^3J = 6.42$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 156.67, 154.87, 149.11, 143.60, 138.43, 137.18, 124.38, 122.02, 121.81, 121.57, 121.04, 52.57, 50.51, 31.02, 30.05, 25.92, 22.32, 13.87; EI-MS m/z (nature of peak, relative

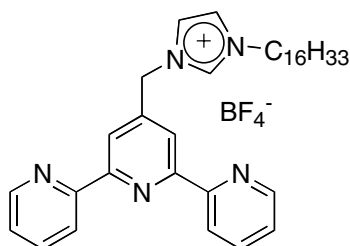
intensity): 398.2 ($[M]^+$, 100); Anal. Calcd for $C_{25}H_{28}N_5Br$: C, 62.76; H, 5.90, N, 14.64. Found C, 62.59; H, 5.69; N, 14.38.



N-butyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide ($[C_4\text{terpim}]Br$): The general procedure was followed using N-butyl-imidazol (30 mg, 0.24 mmol). The product was obtained as a white solid (49 mg, 0.11 mmol, 92 %).

1H NMR (300 MHz, $CDCl_3$): δ 11.10 (s, 1H), 8.69 (d, 2H, $^3J = 4.14$ Hz), 8.62 (d, 2H, $^3J = 7.92$ Hz), 8.41 (s, 2H), 7.89 (dt, 2H, $^3J = 7.71$ Hz, $^4J = 1.71$ Hz), 7.37 (ddd, 2H, $^3J = 7.49$ Hz, $^3J = 4.71$ Hz, $^4J = 1.03$ Hz), 7.35-7.31 (m, 2H), 5.89 (s, 2H), 4.36 (t, 2H, $^3J = 7.35$ Hz), 2.13-1.95 (m, 2H), 1.46 (s, 2H, $^3J = 7.53$ Hz), 1.00 (t, 3H, $^3J = 6.42$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.67, 154.87, 149.11, 143.60, 138.52, 137.19, 124.39, 122.05, 121.79, 121.56, 119.99, 52.58, 50.26, 31.97, 19.53, 13.42; EI-MS m/z (nature of peak, relative intensity): 370.2 ($[M]^+$, 100); Anal. Calcd for $C_{23}H_{24}N_5Br$: C, 61.34; H, 5.37; N, 15.55. Found C, 61.22; H, 5.17; N, 15.27.

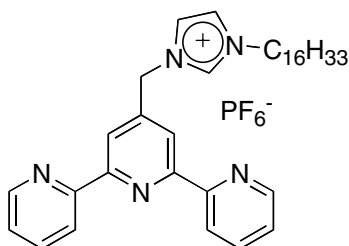
General procedure for the anions metathesis: To a solution of N-alkyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide (0.15 mmol) dissolved in 5 mL of Acetone or water/acetone was added two equivalent of the corresponding salt (0.30 mmol). The mixture was stirred at room temperature during 2 hours. 10 mL of CH_2Cl_2 was added and the organic layers were extracted with CH_2Cl_2 (3 x 10 mL). The solvents were removed under vacuum. Product purified by repetitive precipitation from CH_2Cl_2/Et_2O mixtures. The resulting solid was centrifuged and dried under vacuum.



N-Hexadecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium tetrafluoroborate ($[C_{16}\text{terpim}]BF_4$): The general procedure was followed using N-Hexadecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide (93 mg, 0.15 mmol) and sodium tetrafluoroborate

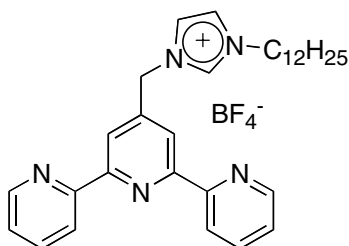
(33 mg, 0.30 mmol). The product was obtained as a white sticky solid (87 mg, 0.14 mmol, 93 %).

^1H NMR (300 MHz, CDCl_3) : δ 9.41 (s, 1H), 8.65 (d, 2H, $^3J = 3.24$ Hz), 8.60 (d, 2H, $^3J = 5.85$ Hz), 8.39 (s, 2H), 7.89 (dt, 2H, $^3J = 8.53$ Hz, $^4J = 1.32$ Hz), 7.39-7.35 (m, 2H), 7.27-7.25 (m, 2H), 5.61 (s, 2H), 4.23 (t, 2H, $^3J = 5.55$ Hz), 1.92 (q, 2H, $^3J = 6.21$ Hz), 1.33-1.33 (m, 26H), 0.87 (t, 3H, $^3J = 6.21$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 156.26, 154.26, 148.80, 143.72, 137.73, 137.25, 124.62, 122.32, 122.20, 121.82, 120.33, 52.55, 50.59, 31.91, 29.92, 29.69, 29.67, 29.64, 29.63, 29.57, 29.48, 29.35, 29.32, 29.13, 28.92, 26.24, 22.67, 14.10; Anal. Calcd for $\text{C}_{35}\text{H}_{48}\text{N}_5\text{BF}_4$: C, 67.20; H, 7.73, N, 11.19. Found C, 66.92; H, 7.49; N, 10.83.



N-Hexadecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium hexafluoro phosphate ([C₁₆terpim]PF₆): The general procedure was followed using N-Hexadecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide (93 mg, 0.15 mmol) and potassium hexafluorophosphate (55 mg, 0.30 mmol). The product was obtained as a white solid (95 mg, 0.14 mmol, 93 %).

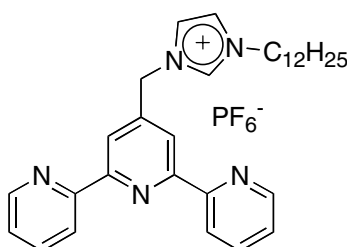
^1H NMR (300 MHz, CDCl_3) : δ 9.00 (s, 1H), 8.68 (d, 2H, $^3J = 4.14$ Hz), 8.60 (d, 2H, $^3J = 7.92$ Hz), 8.36 (s, 2H), 7.89 (dt, 2H, $^3J = 7.71$ Hz, $^4J = 1.50$ Hz), 7.40-7.36 (m, 2H), 7.30-7.27 (m, 2H), 5.55 (s, 2H), 4.22 (t, 2H, $^3J = 7.53$ Hz), 1.92 (q, 2H, $^3J = 5.58$ Hz), 1.33-1.22 (m, 26H), 0.87 (t, 3H, $^3J = 6.19$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 156.66, 154.67, 149.20, 144.13, 138.14, 137.66, 125.03, 122.56, 122.30, 122.08, 121.59, 52.64, 50.60, 31.91, 29.82, 29.67, 29.64, 29.63, 29.60, 29.58, 29.48, 29.35, 29.34, 29.30, 28.89, 26.20, 22.67, 14.10; Anal. Calcd for $\text{C}_{35}\text{H}_{48}\text{N}_5\text{PF}_6$: C, 61.48; H, 7.08, N, 10.24. Found C, 61.25; H, 6.79; N, 10.04.



N-dodecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium tetrafluoroborate ([C₁₂terpim]BF₄): The general procedure was followed using N-dodecyl-N'-(4'-(methyl)-

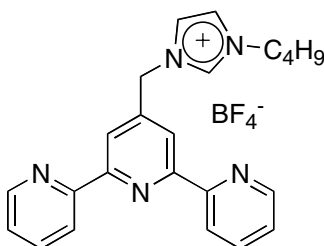
2,2':2'',6'-terpyridyl)imidazolium bromide (84 mg, 0.15 mmol) and sodium tetrafluoroborate (33 mg, 0.30 mmol). The product was obtained as a white solid (78 mg, 0.14 mmol, 93 %).

^1H NMR (300 MHz, CDCl_3): δ 9.27 (s, 1H), 8.60 (d, 2H, $^3J = 3.96$ Hz), 8.49 (d, 2H, $^3J = 7.92$ Hz), 8.25 (s, 2H), 7.80 (dt, 2H, $^3J = 7.71$ Hz, $^4J = 1.86$ Hz), 7.40-7.39 (m, 1H), 7.34-7.32 (m, 1H), (ddd, 2H, $^3J = 7.49$ Hz, $^3J = 4.71$ Hz, $^4J = 1.03$ Hz), 5.54 (s, 2H), 4.19 (t, 2H, $^3J = 7.35$ Hz), 1.88-1.83 (m, 2H), 1.26-1.17 (m, 18H), 0.99 (t, 3H, $^3J = 6.39$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 156.55, 154.83, 149.07, 143.59, 137.00, 136.69, 124.29, 122.79, 122.31, 121.38, 119.66, 52.35, 50.39, 31.83, 29.87, 29.64, 29.52, 29.44, 29.26, 28.88, 26.14, 22.61, 14.05; Anal. Calcd for $\text{C}_{31}\text{H}_{40}\text{N}_5\text{BF}_4$: C, 65.38; H, 7.08; N, 12.30. Found C, 65.41; H, 7.27; N, 12.50.



N-dodecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium hexafluorophosphate ([C₁₂terpim]PF₆): The general procedure was followed using N-dodecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide (84 mg, 0.15 mmol) and potassium hexafluorophosphate (55 mg, 0.30 mmol). The product was obtained as a white solid (88 mg, 0.14 mmol, 93 %).

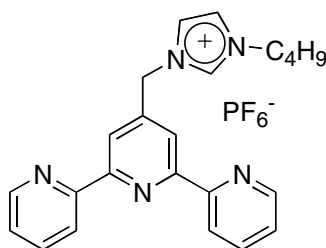
^1H NMR (300 MHz, CDCl_3): δ 9.33 (s, 1H), 8.67 (d, 2H, $^3J = 4.14$ Hz), 8.58 (d, 2H, $^3J = 8.07$ Hz), 8.25 (s, 2H), 7.87 (dt, 2H, $^3J = 7.92$ Hz, $^4J = 1.71$ Hz), 7.38-7.29 (m, 4H), 5.60 (s, 2H), 4.24 (t, 2H, $^3J = 7.53$ Hz), 1.97-1.87 (m, 2H), 1.32-1.22 (m, 18H), 0.87 (t, 3H, $^3J = 6.57$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 156.50, 154.62, 148.98, 143.50, 137.43, 137.22, 124.49, 122.38, 122.15, 121.64, 120.08, 52.62, 50.59, 31.87, 29.90, 29.64, 29.56, 29.47, 29.31, 29.10, 28.91, 26.24, 22.66, 14.08; Anal. Calcd for $\text{C}_{31}\text{H}_{40}\text{N}_5\text{PF}_6$: C, 59.32; H, 6.42; N, 11.16. Found C, 59.28; H, 6.44; N, 10.89.



N-butyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium tetrafluoroborate ([C₄terpim]BF₄): The general procedure was followed using N-butyl-N'-(4'-(methyl)-

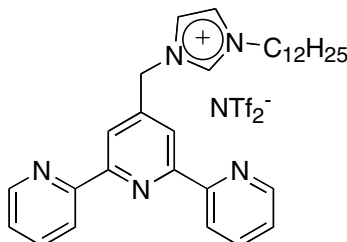
2,2':2'',6'-terpyridyl)imidazolium bromide (68 mg, 0.15 mmol) and sodium tetrafluoroborate (33 mg, 0.30 mmol). The product was obtained as a white solid (64 mg, 0.14 mmol, 93 %).

^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ 9.44 (s, 1H), 8.76-8.74 (m, 2H), 8.56 (d, 2H, $^3J = 7.92$ Hz), 8.36 (s, 2H), 8.09-8.03 (m, 3H), 7.97 (t, 1H, $^3J = 1.86$ Hz), 7.57-7.52 (m, 2H), 5.94 (s, 2H), 4.50 (t, 2H, $^3J = 7.14$ Hz), 2.12-1.97 (m, 2H), 1.46 (st, 2H, $^3J = 7.35$ Hz), 0.99 (t, 3H, $^3J = 7.35$ Hz); ^{13}C NMR (75 MHz, Me_2CO): δ 157.02, 155.65, 149.88, 146.10, 138.08, 137.60, 125.28, 124.04, 121.79, 120.55, 120.14, 52.76, 50.43, 32.43, 19.79, 13.46; Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{N}_5\text{BF}_4$: C, 60.41; H, 5.29; N, 15.32. Found C, 60.12; H, 4.99; N, 15.04.



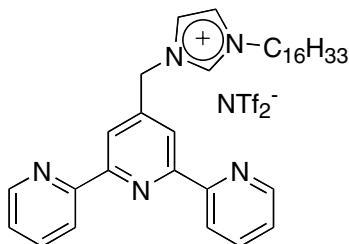
N-butyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium hexafluorophosphate ([C₄terpim]PF₆): The general procedure was followed using N-butyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide (66 mg, 0.15 mmol) and potassium hexafluorophosphate (55 mg, 0.30 mmol). The product was obtained as a white solid (72 mg, 0.14 mmol, 93 %).

^1H NMR (300 MHz, $(\text{CD}_3)_2\text{CO}$): δ 9.44 (s, 1H), 8.75-8.72 (m, 4H), 8.54 (s, 2H), 8.10-8.04 (m, 3H), 7.96 (t, 1H, $^3J = 1.79$ Hz), 7.53-7.49 (m, 2H), 5.90 (s, 2H), 4.46 (t, 2H, $^3J = 7.14$ Hz), 2.08-1.94 (m, 2H), 1.42 (st, 2H, $^3J = 7.71$ Hz), 0.95 (t, 3H, $^3J = 7.35$ Hz); ^{13}C NMR (75 MHz, $(\text{CD}_3)_2\text{CO}$): δ 157.00, 155.61, 149.83, 146.02, 138.11, 137.53, 125.29, 124.07, 124.01, 121.80, 120.56, 52.79, 50.44, 32.40, 19.77, 13.44. Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{N}_5\text{PF}_6$: C, 53.59; H, 4.69; N, 13.59. Found C, 53.64; H, 4.84; N, 13.75.



N-dodecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bis(trifluoromethanesulfonyl) imide ([C₁₂terpim]NTf₂): The general procedure was followed using N-dodecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide (84 mg, 0.15 mmol) and lithium bis(trifluoromethanesulfonyl) imide (86 mg, 0.30 mmol). The product was obtained as a brown oil (107 mg, 0.14 mmol, 93 %).

^1H NMR (300 MHz, CDCl_3) : δ 9.10 (s, 1H), 8.63 (d, 2H, $^3J = 4.89$ Hz), 8.56 (d, 2H, $^3J = 8.17$ Hz) 8.33 (s, 2H), 7.85 (dt, 2H, $^3J = 7.74$ Hz, $^4J = 1.68$ Hz), 7.376-7.31 (m, 4H), 5.57 (s, 2H), 4.24 (t, 2H, $^3J = 7.53$ Hz), 1.93-1.89 (m, 2H), 1.32-1.23 (m, 18H), 0.86 (t, 3H, $^3J = 7.42$ Hz) ; ^{13}C NMR (75 MHz, CDCl_3): δ 156.87, 154.77, 149.16, 143.07, 137.11, 136.37, 124.44, 122.75, 122.33, 121.89, 121.43, 119.75, 117.64, 52.67, 50.56, 31.85, 29.95, 29.52, 29.41, 29.28, 29.23, 28.83, 26.11, 22.63, 14.07; Anal. Calcd for $\text{C}_{33}\text{H}_{40}\text{F}_6\text{N}_6\text{O}_4\text{S}_2$: C, 51.96; H, 5.29; N, 11.02. Found C, 52.17; H, 5.48; N, 11.39.



N-hexadecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium

bis(trifluoromethanesulfonyl) imide ([C₁₆terpim]NTf₂): The general procedure was followed using N-hexadecyl-N'-(4'-(methyl)-2,2':2'',6'-terpyridyl)imidazolium bromide (93 mg, 0.15 mmol) and lithium bis(trifluoromethanesulfonyl) imide (86 mg, 0.30 mmol). The product was obtained as a brown oil (114 mg, 0.14 mmol, 93 %).

^1H NMR (300 MHz, CDCl_3): δ 9.08 (s, 1H), 8.65-8.63 (m, 2H), 8.55 (d, 2H, $^3J = 7.92$ Hz) 8.30 (s, 2H), 7.84 (dt, 2H, $^3J = 7.74$ Hz, $^4J = 1.89$ Hz), 7.37-7.29 (m, 4H), 5.50 (s, 2H), 4.20 (t, 2H, $^3J = 7.53$ Hz), 1.89-1.85 (m, 2H), 1.32-1.23 (m, 26H), 0.86 (t, 3H, $^3J = 7.42$ Hz); ^{13}C NMR (75 MHz, CDCl_3): δ 156.79, 154.74, 149.10, 143.06, 137.11, 136.22, 126.14, 124.41, 122.89, 122.34, 121.88, 121.41, 119.69, 117.62, 113.36; 52.58, 50.51, 31.87, 29.93, 29.63, 29.60, 29.52, 29.42, 29.31, 29.23, 28.82, 26.08, 22.64, 14.06; Anal. Calcd for $\text{C}_{37}\text{H}_{48}\text{F}_6\text{N}_6\text{O}_4\text{S}_2$: C, 54.27; H, 5.91; N, 10.26. Found C, 54.44; H, 6.19; N, 10.52.

Crystallographic measurement conditions:

Data collection³ was carried out using a graphite-monochromated Mo-K α ($\lambda = 0.71069$ Å) radiation on an ENRAF-NONIUS KappaCCD diffractometer. Crystal unit-cell and orientation parameters were derived from the autoindexing procedure, as implemented in DENZO-HKL2000,⁴ Intensities recorded up to a diffraction angle of 22.6° were integrated with Denzo-HKL2000,⁴ scaled, corrected for instrumental factors, polarization effects, X-ray absorption

³ Nonius, B. V. (1999). *COLLECT*, data collection software.

⁴ Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Volume **276**, Macromolecular Crystallography, part A, edited by C.W. Carter, Jr. & R.M. Sweet, 307-326, 1997, New York: Academic Press.

by multi-scan method and then reduced in Scalepack-HKL2000⁴ after postrefinement of the unit-cell parameters.

The structure was solved by direct methods using SIR97⁵ and refined by full-matrix least-squares techniques on F^2 using SHELX-L 97.⁶ All non-hydrogen atoms were anisotropically and fully refined at the calculated positions. All hydrogen atoms (located in difference Fourier syntheses or geometrically calculated for the disordered atoms) were refined as riding to maximize the data/parameter ratio, with C—H = 0.93-0.97 Å and with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ or 1.5 (methyl C). The butyl chain exhibits positional disorder and was refined with split positions for C21-C22 atoms of occupancy fixed at the refined values 0.65 and 0.35. The PF₆ anion appeared disordered by rotation around one F—P—F axis. The occupancy factors of the F atom in the corresponding equatorial plane were refined to values (circa 0.25:0.75). The P—F distances and atomic displacement parameters were restrained to be approximately equal with respect to the octahedric PF₆ geometry.

The data was only collected out to 22.57° because no diffraction could be detected beyond 22.6°, likely related to high dynamic molecular disorder inside the crystal at room temperature.

Crystals with different sizes were tested. Choice for a crystal with a long dimension (parallel to b axis), mainly maintained perpendicular to the incident radiation during the data collection, was selected in order to maximize diffraction resolution limits.

Separation experiment:

After extraction, the [C₁₂terpim][NTf₂] functional ionic liquid and the [Fe(C₁₂terpim)₂(NTf₂)₂](ClO₄)₂ iron complex were easily separated over a pad (length : 10 cm, diameter : 3 cm) of aluminium oxide (Figure S1). After deposition of the organic phase containing the C₁₂terpim][NTf₂] and the [Fe(C₁₂terpim)₂(NTf₂)₂](ClO₄)₂ salts from a dichloromethane solution, the ionic liquid was first eluted with a solvent mixture CH₂Cl₂/MeOH (98/2 %v/v) (250 mL). After evaporation of the solvent, the ionic liquid was isolated as a colorless oil. The iron complex [Fe(C₁₂terpim)₂][NTf₂]₂(ClO₄)₂ can be eluted with a more polar solvent mixture CH₂Cl₂/MeOH (95/5 %v/v) (250 mL) and after removal of the solvent, the iron salt was isolated as a violet solid.

⁵ Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.*, **32**, 115-119.

⁶ Sheldrick, G.M. (2008). *Acta Cryst.* **A64**, 112-122.

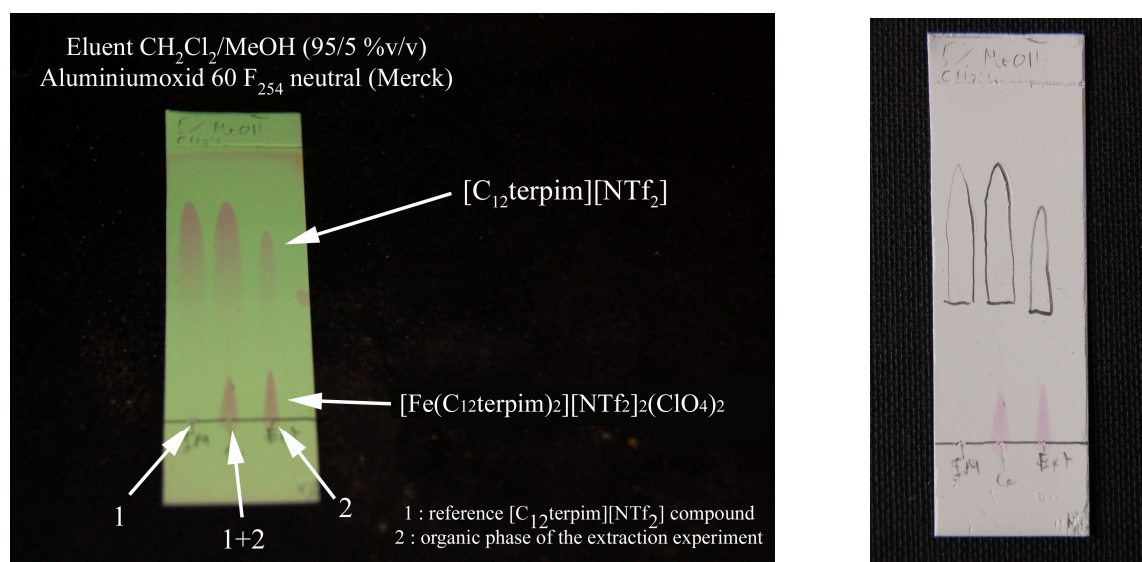


Figure S1. (Left) TLC under UV irradiation showing the facile separation of the iron salt from the ionic liquid. (Right) day light image.

Decomplexation experiment:

After extraction, the organic phase containing $[\text{C}_{12}\text{terpim}][\text{NTf}_2]$ functional ionic liquid and the $[\text{Fe}(\text{C}_{12}\text{terpim})_2(\text{NTf}_2)_2](\text{ClO}_4)_2$ iron complex was dissolved in 20 mL of THF and 10 mL of H_2O . To this solution, 30 equ. of EDTA (éthylène-diamine-tétraacétique acid) were added and pH was adjusted to 11 with an aqueous solution of NaOH (1M). After stirring for 12 hours at room temperature, the violet solution turn to a colourless solution, testifying the efficient decomplexation of the iron cation from the terpyridine fragments. Evaporation of the THF from the mixture allows the precipitation of the uncomplexed terpyridine functionalized imidazolium cation (insoluble in pure water) as a colorless oil. The same process can be applied on the solid $[\text{Fe}(\text{C}_{12}\text{terpim})_2][\text{NTf}_2]_2(\text{ClO}_4)_2$ complex isolated after the filtration on aluminium oxide (vide supra). NMR experiments performed on the isolated oil confirm that the terpyridine functionalized imidazolium cation did not degrade during the decomplexation process.

S11

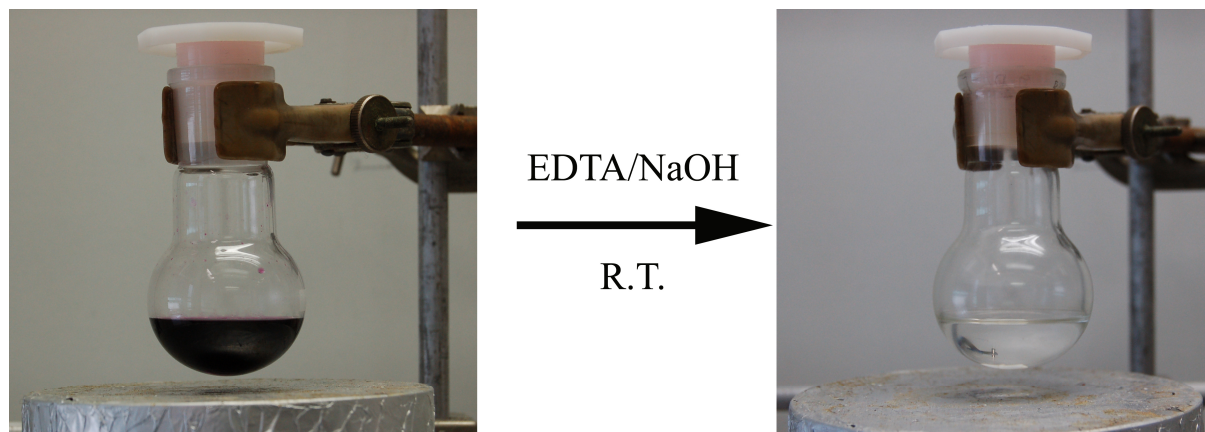


Figure S2. a) Photograph of a solution of the iron complex $[\text{Fe}(\text{C}_{12}\text{terpim})_2][\text{NTf}_2]_2(\text{ClO}_4)_2$ in a THF/ H_2O mixture and b) Same solution, 12 hours, after the addition of 30 equiv. of EDTA and adjusting the pH to 11 with a 1M sodium hydroxide aqueous solution.