Supporting Information

Experimental section:

Solvents used were reagent grade purchased from Mallinckrodt Chemical Co. and were used without further purification. Imidazole was purchased from R. D. H. Alkyl halides were obtained from TCI. The ^{1}H NMR spectra were recorded on a Bruker AC-F300 and/ or BRUKER 600 UltraShield^{TM} equipped with a 5 mm BBO inverse probe in $CDCl_3$ with tetramethylsilane as an internal standard at 298 K. Elemental microanalyses were performed by the Taiwan Instrumentation Center. Optical characterization was performed by using covered microscope slides on an Olympus BH-2 polarizing microscope equipped with Mettler FP 82 Hot Stage and Mettler FP 90 Central Processor. Transition temperatures and heats of fusion were determined by differential scanning calorimetry using a Perkin-Elmer DSC-7 calorimeter, calibrated with indium and tin standards in conjunction with a Perkin-Elmer 7700 thermal analysis data station. X-Ray powder diffraction (XRD) studies were performed on an INEL MPD-diffractometer with a 2.0 kW Cu-Kα X-ray source equipped with an INEL CPS-120 position sensitive detector and a variable temperature capillary furnace with an accuracy of 0.10 °C in the vicinity of the capillary tube. The detector was calibrated using mica and silicon standards. The

powder samples were charged in Lindemann capillary tubes (80 mm long and 1/100 mm thick) from Charles Supper Co. with an inner diameter of 0.10 or 0.15 mm.

Synthesis of the salts: The $[C_nVIm]Br$ and $[C_nVIm]I$ series salts can be readily prepared by refluxing a mixture of *N*-vinylimidazole and corresponding alkyl bromide or iodide in a solvent-less reaction condition. These vinylimidazolium salts are reasonably soluble in polar solvents like dichloromethane, chloroform, and acetone, but insoluble in non polar solvents like *n*-hexane and ether; the solubility of these salts decreases with increasing chain length. Saturated congeners, namely, $[C_{16}EIm]Br$ and $[C_{16}EIm]I$ were prepared similarly, starting from *N*-ethylimidazole. The $[C_{16}VIm]PF_6$ and $[C_{16}VIm]BF_4$ series salts were prepared from $[C_nVIm]Br$ through anion metathesis.

General procedure for synthesis of $[C_nVIm]Br{\cdot}H_2O$ salts: 1-vinlyl-3-alkylimidazolium bromide salts have been prepared from the *N*-alkylation of 1-vinylimidazole with the corresponding alkyl halides. Under dry nitrogen atmosphere and vigorous stirring, freshly distilled alkyl halide was added drop-wise over a period of 2 h to reaction mixture. After the addition is complete the reaction mixture was kept refluxing for about 3 hours till consumption of vinylimidazole is complete as indicated by TLC. The crude product was washed with diethyl ether to remove unreacted starting materials if any. Further, the crude product was

recrystallized from DCM/ether to gives a product with a yield > 90%. All the salts were reasonably soluble in dichloromethane, chloroform and acetone, and insoluble in n-hexane and ether. The solubility decreased with increase in the alkyl chain length.

1-Vinyl-3-octadecylimidazolium bromide, [C_{18}VIm]Br·H_2O: Light yellow solid, yield 98%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.86 (t, J^3 = 6.3 Hz, 3H, CH_3), 1.04-1.32 (m, 30H, CH_2), 1.84-2.00 (m, 2H, CH_2), 4.39 (t, J^3 = 7.38, 2H, CH_2), 5.38–5.98 (m, 2H, CH_2), 7.44 (s, 1H, CH), 7.46-7.53 (q, H, CH), 7.74 (s, 1H, CH), 10.98 (s, 1H, CH). Anal. Calculated for $C_{23}H_{45}N_2OBr$: C, 62.01; H, 10.18; N, 6.29. Found: C, 62.13; H, 10.21; N, 6.19.

1-Vinyl-3-hexadecylimidazolium bromide, [C_{16}VIm]Br·H_2O: Light yellow solid, yield 97%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.86 (t, J^3 = 6.4 Hz, 3H, CH_3), 1.17-1.31 (m, 26H, CH_2), 1.88-2.00 (m, 2H, CH_2), 4.39 (t, J^3 = 7.35, 2H, CH_2), 5.37-6.00 (m, 2H, CH_2), 7.36-7.53 (q, H, CH), 7.48 (s, 1H, CH), 7.83 (s, 1H, CH), 10.87 (s, 1H, CH). Anal. Calculated for $C_{21}H_{41}N_2OBr$: C, 60.42; H, 9.90; N, 6.71. Found: C, 60.51; H, 10.09; N, 6.51.

1-Vinyl-3-tetradecylimidazolium bromide, [C_{14}VIm]Br·H_2O: Light yellow solid, yield 98%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.86 (t, J^3 = 4.4 Hz, 3H, CH_3), 1.23-1.32 (m, 22H, CH_2), 1.94-2.00 (m, 2H, CH_2), 4.40 (t, J^3 = 7.50, 2H, CH_2), 5.38-5.98 (m, 2H, CH_2), 7.46 (s, 1H, CH), 7.49-7.54 (q, H, CH), 7.76 (s, 1H, CH), 10.93 (s, 1H, CH). Anal.

Calculated for $C_{19}H_{37}N_2OBr$: C, 58.71; H, 9.58; N, 7.19. Found: C, 58.46; H, 9.19; N, 6.91.

1-Vinyl-3-dodecylimidazolium bromide, $[C_{12}VIm]Br{\cdot}H_2O$: Light yellow solid, yield 99%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.85 (t, J^3 = 6.3 Hz, 3H, CH_3), 1.22-1.32 (m, 18H, CH_2), 1.91-1.95 (m, 2H, CH_2), 4.38 (t, J^3 = 7.35, 2H, CH_2), 5.36-6.01 (m, 2H, CH_2), 7.45-7.53 (q, H, CH), 7.54 (s, 1H, CH), 7.87 (s, 1H, CH), 10.87 (s, 1H, CH). Anal. Calculated for $C_{17}H_{33}N_2OBr$: C, 56.50; H, 9.20; N, 7.75. Found: C, 56.93; H, 9.27; N, 7.77.

1-Vinyl-3-decylimidazolium bromide, $[C_{10}VIm]Br{\cdot}H_2O$: Brown liquid, yield 92%. ^{1}H NMR(ppm, $CDCl_3$): δ 0.85 (t, J^3 = 6.5 Hz, 3H, CH_3), 1.23-1.32 (m, 14H, CH_2), 1.88-1.98 (m, 2H, CH_2), 4.38 (t, J^3 = 7.29, 2H, CH_2), 5.36-5.99 (m, 2H, CH_2), 7.45-7.53 (q, H, CH), 7.50 (s, 1H, CH), 7.83 (s, 1H, CH), 10.86 (s, 1H, CH). Anal. Calculated for $C_{15}H_{29}N_2OBr$: C, 54.05; H, 8.77; N, 8.40. Found: C, 53.21; H, 9.01; N, 9.24.

1-Vinyl-3-octaylimidazolium bromide, $[C_8VIm]Br{\cdot}H_2O$: Brown liquid, yield 93%. ^{1}H NMR(ppm, $CDCl_3$): δ 0.82 (t, J^3 = 6.4 Hz, 3H, CH_3), 0.80-0.84 (m, 10H, CH_2), 1.21-1.29 (m, 2H, CH_2), 4.36 (t, J^3 = 7.4, 2H, CH_2), 5.33-6.00 (m, 2H, CH_2), 7.41-7.49 (q, H, CH), 7.57 (s, 1H, CH), 7.91 (s, 1H, CH), 10.90 (s, 1H, CH). Anal. Calculated for $C_{13}H_{25}N_2OBr$: C, 51.15; H, 8.25; N, 9.18. Found: C, 51.66; H, 8.32; N, 9.46.

1-Vinyl-3-hexylimidazolium bromide, $[C_6VIm]Br{\cdot}H_2O$: Brown liquid, yield

96%. ^{1}H NMR(ppm, $CDCl_3$): δ 0.79 (t, J^3 = 6.4 Hz, 3H, CH_3), 1.21-1.31 (m, 6H, CH_2), 1.82-1.92 (m, 2H, CH_2), 4.32 (t, J^3 = 7.5, 2H, CH_2), 5.29-5.98 (m, 2H, CH_2), 7.37-7.45 (q, H, CH), 7.60 (s, 1H, CH), 7.92 (s, 1H, CH), 10.73 (s, 1H, CH). Anal. Calculated for $C_{11}H_{21}N_2OBr$: C, 50.97; H, 7.39; N, 10.81. Found: C, 49.60; H, 7.92; N, 10.52.

1-Vinyl-3-butylimidazolium bromide, [C_4VIm]Br·H_2O: Brown liquid, yield 95%. ^{1}H NMR(ppm, $CDCl_3$): δ 0.92 (t, J^3 = 7.2 Hz, 3H, CH_3), 1.32-1.40 (m, 2H, CH_2), 1.86-1.93 (m, 2H, CH_2), 4.38 (t, J^3 = 7.4, 2H, CH_2), 5.33-6.02 (m, 2H, CH_2), 7.41-7.49 (q, H, CH), 7.63 (s, 1H, CH), 7.92 (s, 1H, CH), 10.81 (s, 1H, CH). Anal. Calculated for $C_9H_{17}N_2OBr$: C, 12.12; H, 46.77; N, 6.54. Found: C, 11.54; H, 45.16; N, 7.90.

General procedure for synthesis of [C_nVIm]I: All salts in this series were prepared by using the same procedure used for preparation of bromide series salts. All product were recrystallized from CH_2Cl_2/ether to obtain a solid product with a yield >90%. All the salts are reasonably soluble in dichloromethane, chloroform and acetone, but do not dissolve in n-hexane and ether. The solubility decreased with increasing alkyl chain length.

1-Vinyl-3-octadecylimidazolium Iodide, [C_{18}VIm]I: Light yellow solid, yield 99%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.85 (t, J^3 = 6.3 Hz, 3H, CH_3), 1.22-1.32 (m, 30H, CH_2), 1.89-1.96 (m, 2H, CH_2), 4.40 (t, J^3 = 7.38, 2H, CH_2), 5.39-6.02 (m, 2H, CH_2), 7.56 (s, 1H , CH), 7.37-7.46 (q, H, CH), 7.83 (s, 1H, CH), 10.51 (s, 1H, CH). Anal. Calculated

for $C_{23}H_{43}N_2I$: C, 62.01; H, 10.18; N, 6.29. Found: C, 62.13; H, 10.21; N, 6.19.

1-Vinyl-3-hexadecylimidazolium Iodide, [C_{16}VIm]I: Light yellow solid, yield 97%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.86 (t, J^3 = 6.4 Hz, 3H, CH_3), 1.23-1.34 (m, 26H, CH_2), 1.90-1.97 (m, 2H, CH_2), 4.40 (t, J^3 = 7.35, 2H, CH_2), 5.40-6.01 (m, 2H, CH_2), 7.38-7.46 (q, H, CH), 7.54 (s, 1H, CH), 7.79 (s , 1H, CH), 10.56 (s, 1H, CH). Anal. Calculated for $C_{21}H_{39}N_2I$: C, 60.42; H, 9.90; N, 6.71. Found: C, 60.17; H, 9.48; N, 6.40.

1-Vinyl-3-tetradecylimidazolium Iodide, [C_{14}VIm]I: Light yellow solid, yield 95%. ^{1}H NMR (ppm, $CDCl_3$): δ = 0.88 (t, 3J = 6.4 Hz, 3H, CH3), 1.20-1.30 (m, 26H, CH_2), 1.92-1.97 (m, 2H, CH_2), 4.42 (t, J3 = 7.3 Hz, 2H, CH_2), 5.45-5.97 (m, 2H, CH_2), 7.38-7.58 (q, H, CH), 7.32 (s, 1H, CH), 7.90 (s , 1H, CH), 10.94 (s, 1H, CH). Anal. Calculated for $C_{19}H_{35}N_2I$: C, 54.54; H, 8.43; N, 6.70. Found: C, 54.93; H, 8.14; N, 6.24.

1-Vinyl-3-dodecylimidazolium Iodide, [C_{12}VIm]I: Light yellow solid, yield 98%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.84 (t, J^3 = 6.3 Hz, 3H, CH_3), 1.21-1.31 (m, 18H, CH_2), 1.88-1.96 (m, 2H, CH_2), 4.39 (t, J^3 = 7.35, 2H, CH_2), 5.38-6.02 (m, 2H, CH_2), 7.37-7.45 (q, H, CH), 7.60 (s, 1H, CH), 7.87 (s, 1H, CH), 10.50 (s, 1H, CH). Anal. Calculated for $C_{17}H_{31}N_2I$: C, 52.31; H, 8.00; N, 7.18. Found: C, 52.64; H, 7.63; N, 7.23.

1-Vinyl-3-decylimidazolium Iodide, [C_{10}VIm]I: Brown liquid, yield 95%. ^{1}H NMR(ppm, $CDCl_3$): δ 0.87 (t, J^3 = 6.5 Hz, 3H, CH_3), 1.19-1.29 (m, 14H, CH_2),

1.91-2.01 (m, 2H, CH_2), 4.41 (t, J^3 = 7.29, 2H, CH_2), 5.25-6.06 (m, 2H, CH_2), 7.40-7.43 (q, H, CH), 7.47 (s, 1H, CH), 7.71 (s, 1H, CH), 10.53 (s, 1H, CH). Anal. Calculated for $C_{15}H_{27}N_2I$: C, 49.73; H, 7.51; N, 7.73. Found: C, 57.88; H, 8.83; N, 5.91.

1-Vinyl-3-octylimidazolium Iodide, [C_8VIm]I: Brown liquid, yield 94%. ^{1}H NMR(ppm, $CDCl_3$): δ 0.85 (t, J^3 = 6.4 Hz, 3H, CH_3), 1.24-1.33 (m, 10H, CH_2), 1.88-1.98 (m, 2H, CH_2), 4.40 (t, J^3 = 7.4, 2H, CH_2), 5.04-6.01 (m, 2H, CH_2), 7.40-7.47 (q, H, CH), 7.53 (s, 1H, CH), 7.78 (s, 1H, CH), 10.62 (s, 1H, CH). Anal. Calculated for $C_{13}H_{23}N_2I$: C, 46.72; H, 6.94; N, 8.38. Found: C, 44.35; H, 7.04; N, 7.99.

1-Vinyl-3-hexylimidazolium Iodide, [C_6VIm]I: Brown liquid, yield 97%. ^{1}H NMR(ppm, $CDCl_3$): δ 0.86 (t, J^3 = 6.4 Hz, 3H, CH_3), 1.28-1.38 (m, 6H, CH_2), 1.90-2.00 (m, 2H, CH_2), 4.41 (t, J^3 = 7.5, 2H, CH_2), 5.40-6.02 (m, 2H, CH_2), 7.38-7.46 (q, H, CH), 7.59 (s, 1H, CH), 7.88 (s, 1H, CH), 10.57 (s, 1H , CH). Anal. Calculated for $C_{11}H_{19}N_2I$: C, 43.15; H, 6.25; N, 9.15. Found: C, 42.72; H, 6.09; N, 8.80.

1-Vinyl-3-butylimidazolium Iodide, [C_4VIm]I·0.5H_2O: Brown liquid, yield 96%. ^{1}H NMR(ppm, $CDCl_3$):δ 0.95 (t, J^3 = 7.2 Hz, 3H, CH_3), 1.40-1.45 (m, 2H, CH_2), 1.92-1.97 (m, 2H, CH_2), 4.43 (t, J^3 = 7.4, 2H, CH_2), 5.40-6.01 (m, 2H, CH_2), 7.37-7.45 (q, H, CH), 7.60 (s, 1H, CH), 7.81 (s, 1H, CH), 10.54 (s, 1H, CH). Anal. Calculated for $C_9H_{15}N_2I$·0.5H_2O: C, 37.65; H, 5.62; N, 9.76. Found: C, 38.05; H, 5.95; N, 9.81.

General procedure for synthesis [C_nVIm]BF_4: [C_nVIm]BF_4 series salts were

prepared by anion metathesis of corresponding salt from bromide series, $[C_nVIm]Br \cdot H_2O$ salts, in MeOH-H_2O (20/80 v/v) solvent system using NH_4BF_4. The precipitates were isolated by filtration. The crude product obtained was washed with a lot of MeOH-H_2O (20/80 v/v). A light yellow product was obtained with about 70% yield.

1-Vinyl-3-octadecylimidazolium Tetrafluoroborate, $[C_{18}VIm]BF_4$: Colorless solid, ^{1}H NMR (ppm, $CDCl_3$): δ = 0.87 (t, J^3 = 6.4 Hz, 3H, CH3), 1.25-1.37 (m, 30H, CH_2), 1.89-1.91 (m, 2H, CH_2), 4.24 (t, J^3 = 7.3 Hz, 2H, CH_2), 5.37-5.84 (m, 2H, CH_2), 7.10-7.19 (q, H, CH), 7.40 (s, 1H, CH), 7.63 (s, 1H, CH), 9.12 (s, 1H, CH). Anal. Calculated for $C_{23}H_{43}N_2BF_4$: C, 63.59; H, 9.98; N, 6.45. Found: C, 63.20; H, 9.87; N, 6.03.

1-Vinyl-3-hexadecylimidazolium Tetrafluoroborate, $[C_{16}VIm]BF_4$: Colorless solid, ^{1}H NMR (ppm, $CDCl_3$): δ = 0.87 (t, J^3 = 6.5 Hz, 3H, CH3), 1.25-1.57 (m, 26H, CH_2), 1.87-1.91 (m, 2H, CH_2), 4.24 (t, J^3 = 7.3 Hz, 2H, CH_2), 5.38-5.83 (m, 2H, CH_2), 7.11-7.19 (q, H, CH), 7.38 (s, 1H, CH), 7.61 (s, 1H, CH), 9.14 (s, 1H, CH). Anal. Calculated for $C_{21}H_{39}N_2BF_4$: C, 62.07; H, 9.67; N, 6.89. Found: C, 61.98; H, 9.51; N, 6.51.

1-Vinyl-3-tetradecylimidazolium Tetrafluoroborate $[C_{14}VIm]BF_4$: Colorless solid, ^{1}H NMR (ppm, $CDCl_3$): δ = 0.88 (t, J^3 = 6.4 Hz, 3H, CH3), 1.25-1.38 (m, 22H,

CH_2), 1.87-1.92 (m, 2H, CH_2), 4.25 (t, J^3 = 7.5 Hz, 2H, CH_2), 5.38-5.85 (m, 2H, CH_2), 7.12-7.20 (q, H, CH), 7.40 (s, 1H, CH), 7.63 (s, 1H, CH), 9.15 (s, 1H, CH). Anal. Calculated for $C_{19}H_{35}N_2BF_4$: C, 60.32; H, 9.33; N, 7.40. Found: C, 60.07; H, 9.17; N, 7.09.

1-Vinyl-3-dodecylimidazolium Tetrafluoroborate [C_{12}VIm]BF_4: Colorless solid, ^{1}H NMR (ppm, $CDCl_3$): δ = 0.87 (t, J^3 = 6.5 Hz, 3H, CH_3), 1.23-1.44 (m, 18H, CH_2), 1.87-1.91 (m, 2H, CH_2), 4.25 (t, J^3 = 7.4 Hz, 2H, CH_2), 5.35-5.86 (m, 2H, CH_2), 7.13-7.24 (q, H, CH), 7.44 (s, 1H, CH), 7.69 (s, 1H, CH), 9.26 (s, 1H, CH). Anal. Calculated for $C_{17}H_{31}N_2BF_4$: C, 58.30; H, 8.92; N, 8.00. Found: C, 57.82; H, 8.84; N, 7.63.

General procedure for synthesis [C_nVIm]PF_6: [C_nVIm]PF_6 series salts were prepared by anion metathesis of corresponding salt from bromide series, [C_nVIm]Br·H_2O salts, in MeOH-H_2O (15/85 v/v) solvent system using NH_4PF_6. The precipitates were isolated by filtration. The crude product obtained was washed with a lot of MeOH-H_2O (15/85 v/v). A light yellow product was obtained with about 70% yield.

1-Vinyl-3-octadecylimidazolium Hexafluorophosphate, [C_{18}VIm]PF_6: Colorless solid, yield 86%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.88 (t, J^3 = 6.3 Hz, 3H, CH_3), 1.25-1.33 (m, 30H, CH_2), 1.87-1.92 (m, 2H, CH_2), 4.21 (t, J^3 = 7.38, 2H, CH_2),

5.40–5.80 (m, 2H, CH_2), 7.03-7.11 (q, H, CH), 7.33 (s, 1H, CH), 7.54 (s, 1H, CH), 8.84 (s, 1H, CH). Anal. Calculated for $C_{23}H_{43}N_2PF_6$: C, 56.08; H, 8.80; N, 5.69. Found: C, 56.25; H, 8.39; N, 5.64.

1-Vinyl-3-hexadecylimidazolium Hexafluorophosphate, $[C_{16}VIm]PF_6$: Colorless solid, yield 84%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.87 (t, J^3 = 6.4 Hz, 3H, CH_3), 1.17-1.34 (m, 26H, CH_2), 1.88-2.00 (m, 2H, CH_2), 4.21 (t, J^3 = 7.35, 2H, CH_2), 5.42–5.79 (m, 2H, CH_2), 7.03-7.11 (q, H, CH), 7.33 (s, 1H , CH), 7.53 (s, 1H, CH), 8.86 (s, 1H, CH). Anal. Calculated for $C_{21}H_{39}N_2PF_6$: C, 54.30; H, 8.46; N, 6.03. Found: C, 54.18; H, 8.54; N, 6.02.

1-Vinyl-3-tetradecylimidazolium Hexafluorophosphate, $[C_{14}VIm]PF_6$: Colorless solid, yield 84%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.88 (t, J^3 = 4.4 Hz, 3H, CH_3), 1.25-1.33 (m, 22H, CH_2), 1.87-1.92 (m, 2H, CH_2), 4.22 (t, J^3 = 7.50, 2H, CH_2), 5.41–5.80 (m, 2H, CH_2), 7.03–7.11 (q, H, CH), 7.34 (s, 1H, CH), 7.53 (s, 1H, CH), 8.85 (s, 1H, CH). Anal. Calculated for $C_{19}H_{35}N_2PF_6$: C, 52.29; H, 8.08; N, 6.42. Found: C, 52.25; H, 8.22; N, 6.36.

1-Vinyl-3-dodecylimidazolium Hexafluorophosphate, $[C_{12}VIm]PF_6$: Colorless solid, yield 80%. ^{1}H NMR (ppm, $CDCl_3$): δ 0.90 (t, J^3 = 6.3 Hz, 3H, CH_3), 1.23-1.35 (m, 18H, CH_2), 1.89-1.94 (m, 2H, CH_2), 4.24 (t, J^3 = 7.35, 2H, CH_2), 5.42–5.82 (m, 2H, CH_2), 7.05–7.13 (q, H, CH), 7.38 (s, 1H , CH), 7.58 (s, 1H, CH), 8.84 (s, 1H, CH). Anal.

Calculated for $C_{17}H_{31}N_2PF_6$: C, 50.00; H, 7.65; N, 6.86. Found: C, 50.15; H, 6.95; N, 6.87.

Synthesis of 1-Hexadecyl-3-ethylimidazolium Bromide, [C_{16}EIm]Br·H_2O: Ethylimidazole (0.5 g, 5.2 mmol) and 1-bromohexadecane (1.6 g, 5.2 mmol) were mixed in 50 mL round bottom flask and was refluxed at 90 ℃ for 3 h. After completion of reaction, crude product was recrystallized from CH_2Cl_2/ether to get Colorless crystalline solid with 96% yield. ^{1}H NMR (ppm, $CDCl_3$): δ = 0.84 (t, 3J = 5.2 Hz, 3H, CH_3), 1.20-1.29 (m, 26H, CH_2), 1.56 (t, J^3 = 5.9 Hz, 3H, CH_3), 1.88 (m, 2H, CH_2), 3.69 (t, J^3 = 1.8 Hz, 2H, CH_2), 4.28-4.33 (m, 2H, CH_2), 4.41-4.44 (m, 2H, CH2),7.37 (s, 1H, CH), 7.51 (s, 1H, CH), 10.34 (s, 1H, CH). Anal. Calculated for $C_{21}H_{40}N_2OBr$: C, 60.13; H, 10.33; N, 6.68. Found: C, 60.40; H, 10.60; N, 6.68.

Synthesis of 1-Hexadecyl-3-ethylimidazolium Iodide, [C_{16}EIm]I: Ethylimidazole (0.5 g, 5.2 mmol) and 1-iodohexadecane (5.2 mmol) were mixed in 50 mL round bottom flask and was refluxed at 90 ℃ for 3 h. After completion of reaction crude product was recrystallized from CH_2Cl_2/ether to get Colorless crystalline solid with 96% yield. ^{1}H NMR (ppm, $CDCl_3$) : δ = 0.86 (t, J^3 = 6.4Hz, 3H, CH_3), 1.23-1.32 (m, 26H, CH_2), 1.62 (t, J^3 = 7.4Hz, 3H, CH_3), 1.90-1.95 (m, 2H, CH_2), 4.33 (t, J^3 = 7.4

Hz, 2H, CH_2), 4.40-4.47 (m, 2H, CH_2), 7.34 (s, 1H, CH), 7.44 (s, 1H, CH), 10.23 (s, 1H, CH). Anal. Calculated for $C_{21}H_{40}N_2I$: C, 55.92; H, 9.12; N, 6.12. Found: C, 56.24; H, 9.21; N, 6.25.

Synthesis of 1-Hexadecyl-3-ethylimidazolium Hexafluorophosphate, [C_{16}EIm]PF_6: [C_{16}EIm]PF_6 salt was prepared by anion metathesis of [C_{16}EIm]Br·H_2O salt, in MeOH-H_2O (15/85 v/v) solvent system using $AgPF_6$. The precipitates were isolated by filtration. The crude product obtained was washed with a lot of MeOH-H_2O (15/85 v/v). A light yellow product was obtained with about 75% yield. ^{1}H NMR (ppm, $CDCl_3$) : δ = 0.87 (t, J^3 = 6.4Hz, 3H, CH_3), 1.26-1.34 (m, 27H, CH_2), 1.56 (t, J^3 = 7.4Hz, 3H, CH_3), 1.88 (t, 2H, CH_2), 4.29 (t, J^3 = 7.4 Hz, 2H, CH_2), 4.26 (q, 2H, CH_2), 7.28 (s, 1H, CH), 7.32 (s, 1H, CH), 8.89 (s, 1H, CH).

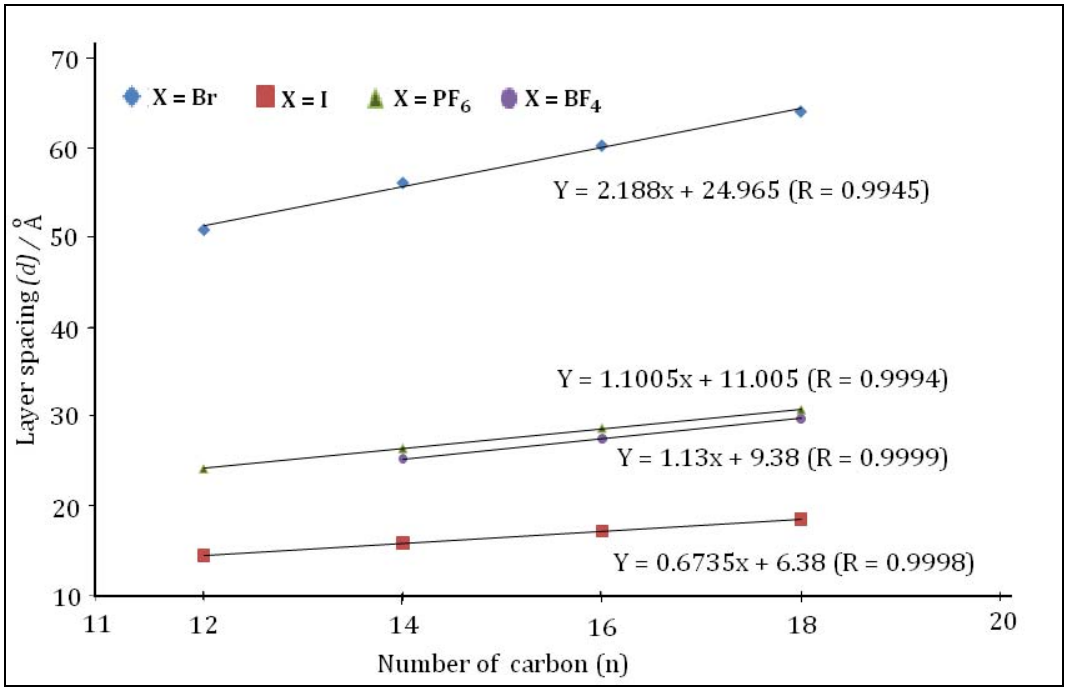

Figure S1. The dependence of layer spacing *d* on chain length *n*, along with the best fit linear equations for $[C_nVIm]X$ in the crystal phase.

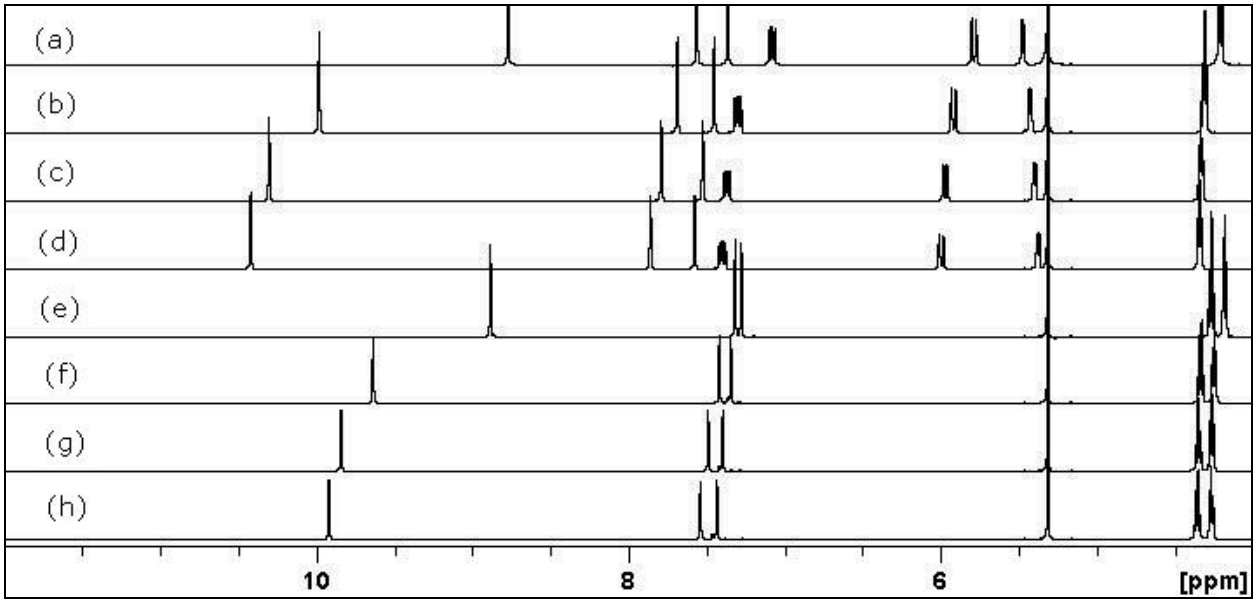

Figure S2. Downfield region of ^1H NMR spectra (600 MHz) in CD_2Cl_2 of (a) $[C_{16}VIm]PF_6$, (b) $[C_{16}VIm]PF_6$+ TBAI (1:1), (c) $[C_{16}VIm]PF_6$ + TBAI (1:2), (d) $[C_{16}VIm]PF_6$ + TBAI (1:3), (e) $[C_{16}EIm]PF_6$, (f) $[C_{16}EIm]PF_6$ + TBAI (1:1), (g) $[C_{16}EIm]PF_6$ + TBAI (1:2), (h) $[C_{16}Eim]PF_6$ + TBAI (1:3).

Table S1: NMR peak values for the $[C_{16}Vim]PF_6$ and $[C_{16}EIm]PF_6$ protons.

Salt	Additive	Equivalence	Chemical shift for the corresponding proton in CD_2Cl_2 (δ ppm)							
			H^2	H^4	H^5	H^7	H^6	H^a	H^b	H^c
$[C_{16}EIm]PF_6$	None	-	8.89	7.32	7.28	4.30	4.20	-	-	-
$[C_{16}EIm]PF_6$	TBAI	1:1	9.64	7.42	7.35	4.34	4.25	-	-	-
$[C_{16}EIm]PF_6$	TBAI	1:2	9.85	7.50	7.40	4.38	4.30	-	-	-
$[C_{16}EIm]PF_6$	TBAI	1:3	9.92	7.54	7.44	4.35	4.27	-	-	-
$[C_{16}VIm]PF_6$	None	-	8.77	7.37	7.56	-	4.21	5.48	5.79	7.08

$[C_{16}VIm]PF_6$	TBAI	1:1	9.98	7.29	7.69	-	4.31	5.43	5.65	7.29
$[C_{16}VIm]PF_6$	TBAI	1:2	10.31	7.53	7.79	-	4.34	5.40	5.97	7.37
$[C_{16}VIm]PF_{16}$	TBAI	1:3	10.43	7.58	7.86	-	4.34	5.38	5.99	7.40