Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Solvation structure of poly-*m*-phenyleneisophthalamide (PMIA) in ionic liquids

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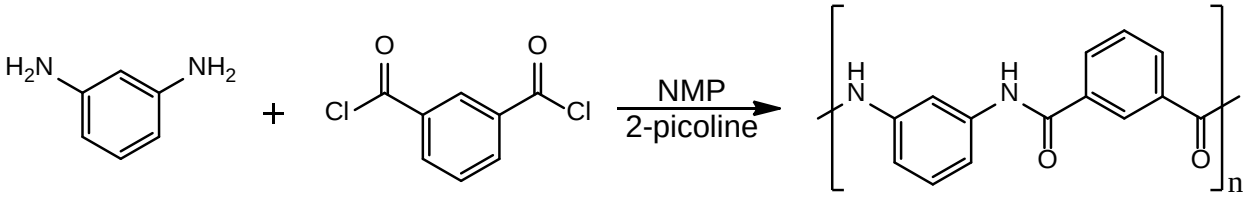
Electronic Supplementary Information (ESI)

1. Synthesis of PMIA, N-methylated PMIA and aramid model compounds

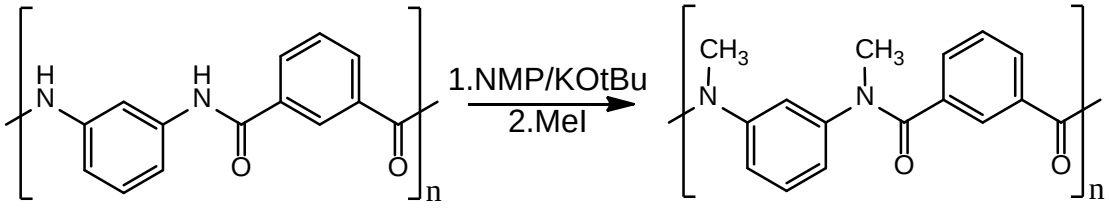
1.1 Poly-*m*-phenyleneisophthalamide (PMIA)



Dry NMP (20 g) was added to a dried 3-neck flask flushed with N_2. *m*-Phenylenediamine (1.0 eq, 19.4 mmol, 2.09 g) was added under a gentle N_2 flow. The monomer was dissolved by shaking for roughly 10 min. The solution was then put on an ice bath and 2-picoline (2.1 eq, 40.7 mmol, 3.79 g) was added using a syringe. An overhead stirrer (4 cm collapsible two-blade impeller fitted in a Cowie universal stirrer guide) was then placed on the flask under N_2 flow, and the reaction mixture was stirred at a rate of 200 rpm. The ice bath was replaced with a cooling bath containing dry ice and isopropanol, and the stirring rate was increased to 500 rpm. Isophthaloyl chloride (1.0 eq, 19.4 mmol, 3.94 g) was added under N_2 flow. The viscosity of the reaction mixture rapidly increased, creating a thick white gel. The stirring rate was further increased to 1000 rpm, and stirring continued for 15 min. Water was added to precipitate the polymer, which was removed from the 3-neck flask and subsequently washed with water and briefly dried in a vacuum oven at 50 °C. The polymer chunks were redissolved in 100 mL of NMP at 50 °C. When dissolution was complete, the polymer was again precipitated by adding water dropwise to the solution while under heavy stirring. This way a fine white powder could be obtained. The polymer powder was filtrated, washed with water, further purified via 12 h of Soxhlet extraction with methanol and finally dried overnight in a vacuum oven at 50 °C. The yield was quantitative. The inherent viscosity, using a PMIA/sulfuric acid (96%) solution with a

concentration of 0.5 g dL^{-1}, was determined to be 2.11 dL g^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 10.5 (1H, s), 8.55 (1H, s), 8.40 (1H, s), 8.15 (2H, d, *J* = 7.0 Hz), 7.69 (1H, t, *J* = 8.0 Hz), 7.54 (2H, d, *J* = 8.0 Hz), 7.35 (1H, t, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6, δ/ppm): 165.6, 139.7, 135.6, 131.2, 129.2, 129.0, 127.6, 116.6, 113.3. FTIR (ATR, ν_{max}/cm^{-1}): 3310 (N-H stretch), 1647 (amide I), 1532 (amide II), 652.

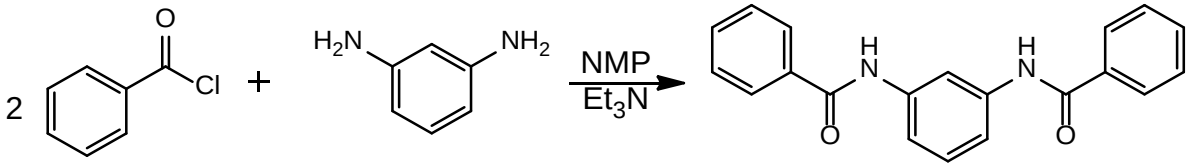
1.2 N-methylated PMIA



Poly-*m*-phenyleneisophthalamide (1.0 eq, 2.10 mmol, 0.50 g) was dissolved in 15 mL of dry NMP in a dried 3-neck flask flushed with N_2. Potassium *tert*-butoxide (2.1 eq, 4.46 mmol, 0.50 g) was added under N_2 flow, and the reaction mixture was stirred at 55 °C. After stirring for 1 h, the reaction mixture turned dark red, and was cooled to room temperature. Methyl iodide (3.0 eq, 6.30 mmol, 0.89 g) was added with a syringe, and stirred for 2 h, which turned the reaction mixture bright pink. Methanol was added dropwise under heavy stirring, in order to precipitate the methylated PMIA as a white powder. The product was filtrated, washed with methanol and cold acetone and dried overnight in a vacuum oven at 40 °C. Full conversion of N-H to N-CH_3 was confirmed with disappearance of the N-H stretch peak in the IR spectrum, and the disappearance of the NH signal and appearance of another CH_3 signal in the ^{1}H NMR spectrum. Yield: 0.47 g, 84%. ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 7.33 (1H, s), 7.14 (1H, s), 6.92 (4H, m), 6.65 (1H, s), 6.63 (1H, s), 3.14 (6H, s). ^{13}C NMR (100 MHz, DMSO-d_6, δ/ppm): 169.0,

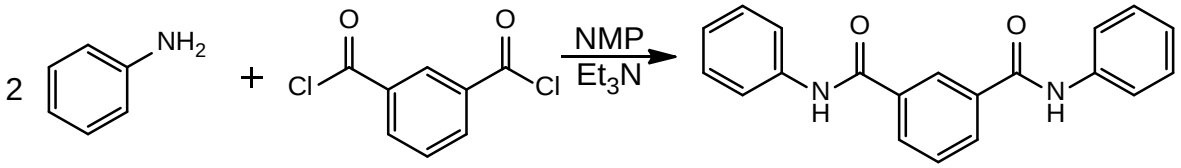
145.2, 136.3, 129.6, 129.3, 127.5, 125.5, 37.9. FTIR (ATR, ν_{max}/cm^{-1}): 2925 (C-H stretch), 1641 (carbonyl stretch), 1351, 702.

1.3 *m*-Trimer N (MTN)



Triethylamine (2.1 eq, 77.7 mmol, 7.86 g) and *m*-phenylenediamine (1.0 eq, 37.0 mmol, 4.0 g) were dissolved in 60 mL of dry NMP in a dried 3-neck flask flushed with N_2. The solution was put in an ice bath and benzoyl chloride (2.1 eq, 78.6 mmol, 10.9 g) was added dropwise under stirring. After 30 min, water was added to precipitate the product. The solid *m*-trimer N was isolated via filtration, washed with water and dried in a vacuum oven at 50 °C overnight, yielding a white solid. Yield: 11.3 g, 97%. ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 10.3 (2H, s), 8.34 (1H, t, *J* = 2.0 Hz), 7.96 (4H, m), 7.54 (8H, m), 7.32 (1H, m). ^{13}C NMR (100 MHz, DMSO-d_6, δ/ppm): 166.0, 139.8, 135.4, 132.0, 128.8, 128.6, 128.2, 116.5, 113.4. FTIR (ATR, ν_{max}/cm^{-1}): 3267 (N-H stretch), 3129, 3060, 3029 (C-H stretch), 1639 (amide I), 1518 (amide II), 792, 710. Melting point: 248 °C.

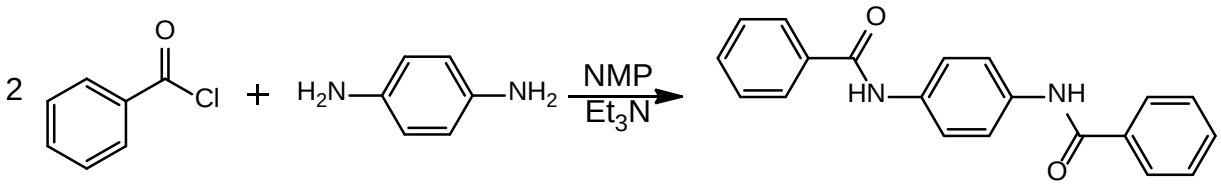
1.4 *m*-Trimer O (MTO)



Triethylamine (2.1 eq, 41.4 mmol, 4.18 g) and isophthaloyl chloride (1.0 eq, 19.7 mmol, 4.0 g) were dissolved in 60 mL of dry NMP in a dried 3-neck flask flushed with N_2. The solution was put in an ice bath and aniline (2.5 eq, 49.3 mmol, 4.58 g) was added dropwise under stirring.

After 30 min, water was added to precipitate the product. The solid *m*-trimer O was isolated via filtration, washed with water and dried in a vacuum oven at 50 °C overnight, yielding a white solid. Yield: 5.9 g, 95%. ^{1}H NMR (300 MHz, DMSO-d$_6$, δ/ppm): 10.44 (2H, s), 8.53 (1H, t, *J* = 1.6 Hz), 8.14 (2H, dd, *J* = 7.8 , *J* = 1.7 Hz), 7.79 (4H, m), 7.70 (1H, t, *J* = 7.8 Hz), 7.38 (4H, m), 7.12 (2H, m). ^{13}C NMR (100 MHz, DMSO-d$_6$, δ/ppm): 165.5, 139.5, 135.7, 131.1, 129.2, 129.1, 127.5, 124.3, 120.8. FTIR (ATR, ν_{max}/cm^{-1}): 3256 (N-H stretch), 3130, 3061, 3041 (C-H stretch), 1638 (amide I), 1545 (amide II), 1028, 688. Melting point: 291 °C.

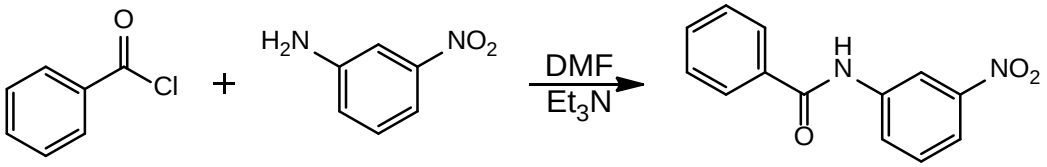
1.5 *p*-Trimer N (PTN)



Triethylamine (2.1 eq, 77.7 mmol, 7.8 g) and *p*-phenylenediamine (1.0 eq, 37.0 mmol, 4.0 g) were dissolved in 60 mL of dry NMP in a dried 3-neck flask flushed with N_2. The solution was put in an ice bath and benzoyl chloride (2.1 eq, 78.6 mmol, 10.9 g) was added dropwise under stirring. After 30 min, water was added to precipitate the product. The solid *p*-trimer N was isolated via filtration, washed with water and cold acetone and dried in a vacuum oven at 50 °C overnight, yielding a light yellow solid. Yield: 11.1 g, 95%. ^{1}H NMR (300 MHz, DMSO-d$_6$, δ/ppm): 10.32 (2H, s), 7.86 (4H, d, *J* = 7.2 Hz), 7.67 (4H, s), 7.44 (6H, m). ^{13}C NMR (100 MHz, DMSO-d$_6$, δ/ppm): 165.7, 135.5, 135.4, 131.9, 128.8, 128.1, 121.1. FTIR (ATR, ν_{max}/cm^{-1}): 3331 (N-H stretch), 3148, 3110, 3087, 3052 (C-H stretch), 1646 (amide I), 1536 (amide II), 653. Melting point: 325 °C.

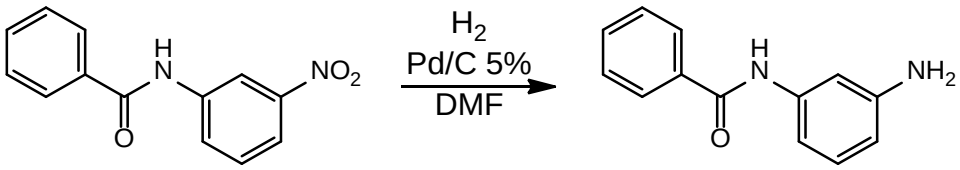
1.6 PMIA pentamer model compound

Step 1:



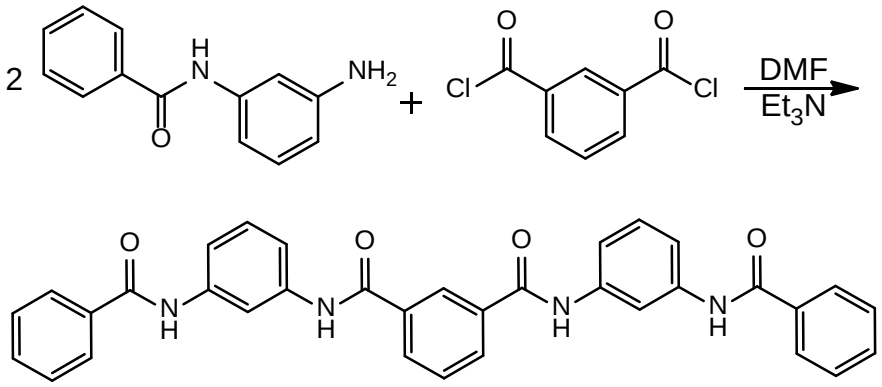
Triethylamine (1.0 eq, 36.2 mmol, 3.66 g) and 3-nitroaniline (1.0 eq, 36.2 mmol, 5.0 g) were dissolved in 60 mL of dry NMP in a dried 3-neck flask flushed with N_2. The solution was put in an ice bath and benzoyl chloride (1.0 eq, 36.2 mmol, 5.09 g) was added dropwise under stirring. After 30 min, water was added to precipitate the product. The white solid was isolated via filtration, washed with water and dried in a vacuum oven at 50 °C overnight. Yield: 8.6 g, 98%. ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 10.71 (1H, s), 8.82 (1H, t, *J* = 2.1 Hz), 8.20 (1H, m), 7.99 (3H, m), 7.61 (4H, m). Melting point: 158 °C.

Step 2:



The product from step 1 (2.3 g) was dissolved in 20 mL of dry DMF in a dried 3-neck flask flushed with N_2. The catalyst Pd/C (5%) (0.1g) was added, and the flask was again flushed with N_2. A balloon filled with H_2 was attached, and the reaction mixture was stirred at 80 °C for 24h. The reaction was considered complete due to the disappearance of signals of the starting product in the crude ^{1}H NMR spectrum of the reaction mixture. The solution was filtered using a syringe filter (pore size 0.45 µm), and the flask and filter washed again using 10 mL of dry DMF. The filtered solution was used directly for step 3.

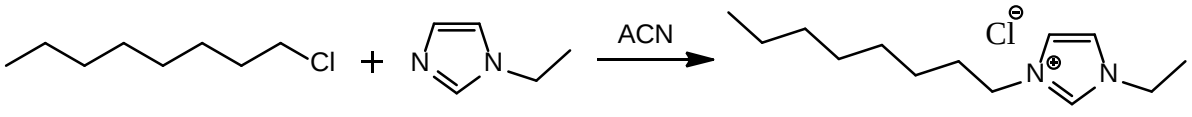
Step 3:



An aliquot of 20 mL containing the product of step 2 (2.2 eq, 9.49 mmol, 2.01 g) was added to a dried 3-neck flask flushed with N_2. Triethylamine (2.2 eq, 9.49 mmol, 0.96 g) was added and the solution was put on an ice bath. Isophthaloyl chloride (1.0 eq, 4.32 mmol, 0.88 g) was added under N_2 flow. The reaction mixture was stirred for 1 h, and precipitated with water. The solid pentamer model compound was isolated by filtration, washed with water and cold acetone. The product was further purified by recrystallization from NMP/H_2O and finally dried overnight in a vacuum oven at 50 °C, resulting in a yellow powder. Yield: 1.6 g, 67%. ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 10.50 (2H, s), 10.34 (2H, s), 8.55 (1H, s), 8.36 (2H, s), 8.16 (2H, d, *J* = 7.0 Hz), 7.98 (4H, d, *J* = 7.0 Hz), 7.70 (1H, t, J = 7.0 Hz), 7.54 (10H, m), 7.34 (2H, t, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, DMSO-d_6, δ/ppm): 166.0, 165.6, 139.9, 139.7, 135.6, 135.4, 132.0, 131.2, 129.1, 129.0, 128.8, 128.2, 127.6, 116.7, 116.5, 113.4. FTIR (ATR, ν_{max}/cm^{-1}): 3316 (N-H stretch), 1645 (amide I), 1532 (amide II), 687. Melting point: 332 °C.

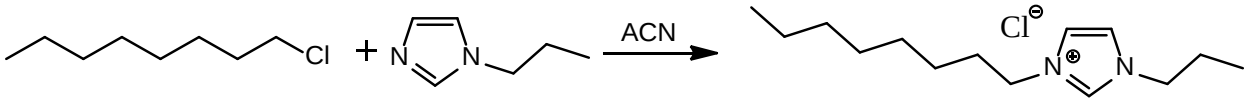
2. Synthesis of ionic liquids

2.1 1-Ethyl-3-octylimidazolium chloride



1-Ethylimidazole (1.0 eq, 90.6 mmol, 8.70 g) was dissolved in acetonitrile (ACN) (50 mL). 1-Chlorooctane (1.2 eq, 109 mmol, 16.2 g) was added, and the reaction mixture was put under N_2 atmosphere to prevent discoloration during the reaction. After refluxing for 48 h at 82 °C, the solvent was removed on a rotary evaporator, and the excess 1-chlorooctane was removed via H_2O/Et_2O extraction. The water layer was dried on a rotary evaporator and further dried on a vacuum line, yielding a viscous light yellow liquid. Yield: 20.6 g, 93%. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 10.7 (1H, s), 7.86 (1H, s), 7.60 (1H, s), 4.47 (2H, q, *J* = 7.4 Hz), 4.35 (2H, t, *J* = 7.4 Hz), 1.93 (2H, m), 1.62 (3H, t, *J* = 7.3 Hz), 1.28 (10H, m), 0.87 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 137.0, 122.1, 121.9, 49.9, 45.0, 31.6, 30.2, 28.9, 28.8, 26.2, 22.4, 15.6, 13.9. FTIR (ATR, ν_{max}/cm^{-1}): 3131, 3045 (aromatic C-H stretch), 2955, 2925, 2856 (alkyl C-H stretch), 1562, 1459, 1166.

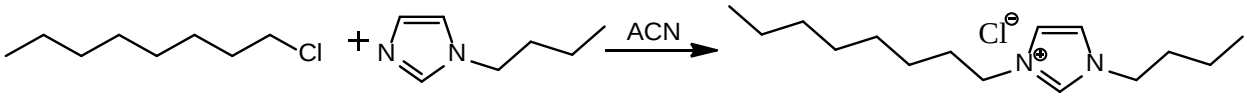
2.2 1-Octyl-3-propylimidazolium chloride



1-Propylimidazole (1.0 eq, 63.6 mmol, 7.0 g) was dissolved in ACN (50 mL). 1-Chlorooctane (1.2 eq, 76.3 mmol, 11.4 g) was added, and the reaction mixture was put under N_2 atmosphere to prevent discoloration during the reaction. After refluxing for 48 h at 82 °C, the solvent was

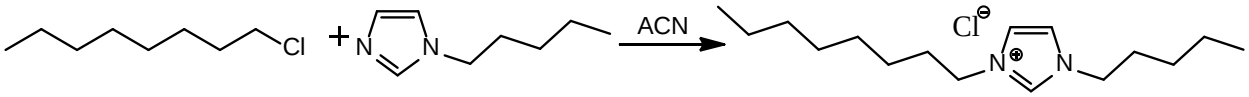
removed on a rotary evaporator, and the excess was 1-chlorooctane removed via H_2O/Et_2O extraction. The water layer was dried on a rotary evaporator and further dried on a vacuum line, yielding a viscous light yellow liquid. Yield: 14.7 g, 89%. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 10.7 (1H, s), 7.73 (1H, s), 7.61 (1H, s), 4.36 (4H, t, *J* = 7.4 Hz), 1.98 (4H, m), 1.28 (10H, m), 0.99 (3H, t, *J* = 7.4 Hz), 0.87 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 137.2, 122.3, 122.0, 51.2, 49.9, 31.5, 30.2, 28.9, 28.8, 26.1, 23.6, 22.4, 13.9, 10.6. FTIR (ATR, ν_{max}/cm^{-1}): 3131, 3049 (aromatic C-H stretch), 2958, 2926, 2856 (alkyl C-H stretch), 1562, 1463, 1166.

2.3 1-Butyl-3-octylimidazolium chloride



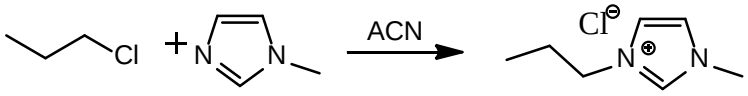
1-Butylimidazole (1.0 eq, 49.1 mmol, 6.08 g) was dissolved in ACN (50 mL). 1-Chlorooctane (1.2 eq, 58.9 mmol, 8.78 g) was added, and the reaction mixture was put under N_2 atmosphere to prevent discoloration during the reaction. After refluxing for 48 h at 82 °C, the solvent was removed on a rotary evaporator, and the excess 1-chlorooctane was removed via H_2O/Et_2O extraction. The water layer was dried on a rotary evaporator and further dried on a vacuum line, yielding a viscous light yellow liquid. Yield: 12.6 g, 94%. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 10.7 (1H, s), 7.71 (1H, s), 7.64 (1H, s), 4.38 (4H, q, *J* = 7.6 Hz), 1.93 (4H, m), 1.32 (12H, m), 0.96 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 137.1, 122.3, 122.1, 49.8, 49.5, 32.0, 31.5, 30.2, 28.8, 28.7, 26.1, 22.4, 19.3, 13.9, 13.3. FTIR (ATR, ν_{max}/cm^{-1}): 3130, 3044 (aromatic C-H stretch), 2956, 2926, 2856 (alkyl C-H stretch), 1562, 1463, 1166.

2.4 1-Octyl-3-pentylimidazolium chloride



1-Pentylimidazole (1.0 eq, 35.8 mmol, 4.94 g) was dissolved in ACN (50 mL). 1-Chlorooctane (1.2 eq, 42.9 mmol, 6.40 g) was added, and the reaction mixture was put under N_2 atmosphere to prevent discoloration during the reaction. After refluxing for 48 h at 82 °C, the solvent was removed on a rotary evaporator, and the excess 1-chlorooctane was removed via H_2O/Et_2O extraction. The water layer was dried on a rotary evaporator and further dried on a vacuum line, yielding a viscous light yellow liquid. Yield: 8.63 g, 84%. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 10.5 (1H, s), 7.66 (1H, s), 7.62 (1H, s), 4.37 (4H, m), 1.94 (4H, m), 1.32 (14H, m), 0.87 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 136.7, 122.2, 122.1, 49.6, 49.5, 31.3, 30.0, 29.6, 28.7, 28.6, 27.9, 25.9, 22.2, 21.7, 13.7, 13.5. FTIR (ATR, ν_{max}/cm^{-1}): 3219, 3041 (aromatic C-H stretch), 2955, 2925, 2856 (alkyl C-H stretch), 1562, 1459, 1166.

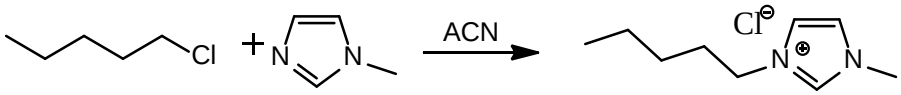
2.5 1-Methyl-3-proylimidazolium chloride



1-Methylimidazole (1.0 eq, 137 mmol, 11.2 g) was dissolved in ACN (50 mL). 1-Chloropropane (1.2 eq, 164 mmol, 12.8 g) was added, and the reaction mixture was put under N_2 atmosphere to prevent discoloration during the reaction. After refluxing for 48 h at 82 °C, the solvent and excess 1-chloropropane were removed on a rotary evaporator. The ionic liquid was further dried on a vacuum line, yielding a viscous light yellow liquid. Yield: 20.7 g, 94%. ^{1}H NMR (300

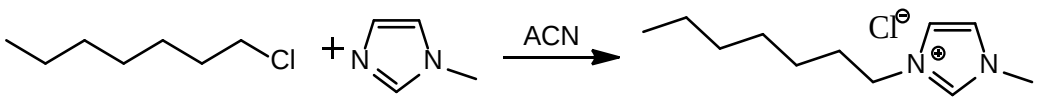
MHz, $CDCl_3$, δ/ppm): 10.1 (1H, s), 7.46 (1H, s), 7.34 (1H, s), 3.94 (2H, t, *J* = 7.3 Hz), 3.76 (3H, s), 1.58 (2H, m), 0.59 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 137.0, 123.5, 122.0, 50.9, 36.1, 23.3, 10.4. FTIR (ATR, ν_{max}/cm^{-1}): 3138, 3042 (aromatic C-H stretch), 2964, 2876 (alkyl C-H stretch), 1568, 1171, 622.

2.6 1-Methyl-3-pentylimidazolium chloride



1-Methylimidazole (1.0 eq, 100 mmol, 8.20 g) was dissolved in ACN (50 mL). 1-Chloropentane (1.2 eq, 120 mmol, 12.8 g) was added, and the reaction mixture was put under N_2 atmosphere to prevent discoloration during the reaction. After refluxing for 48 h at 82 °C, the solvent and excess 1-chloropentane were removed on a rotary evaporator. The ionic liquid was further dried and remaining traces of 1-chloropentane were removed on a vacuum line, yielding a viscous light yellow liquid. Yield: 17.6 g, 93%. ^1H NMR (300 MHz, $CDCl_3$, δ/ppm): 10.1 (1H, s), 7.53 (1H, s), 7.35 (1H, s), 4.06 (2H, t, *J* = 7.4 Hz), 3.86 (3H, s), 1.65 (2H, m), 1.05 (4H, m) 0.60 (3H, t, *J* = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 137.4, 123.7, 121.9, 49.8, 36.4, 29.8, 28.1, 21.9, 13.7. FTIR (ATR, ν_{max}/cm^{-1}): 3139, 3053 (aromatic C-H stretch), 2956, 2932, 2861 (alkyl C-H stretch), 1568, 1459, 1168, 623.

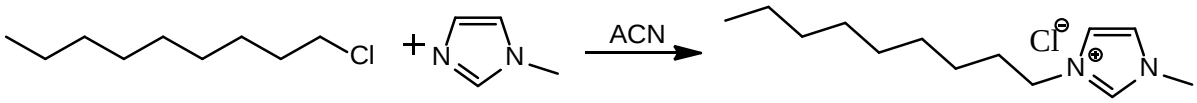
2.7 1-Heptyl-3-methylimidazolium chloride



1-Methylimidazole (1.0 eq, 24.4 mmol, 2.00 g) was dissolved in ACN (15 mL). 1-Chloroheptane (1.2 eq, 29.3 mmol, 3.94 g) was added, and the reaction mixture was put under N_2 atmosphere to

prevent discoloration during the reaction. After refluxing for 48 h at 82 °C, the solvent was removed on a rotary evaporator, and the excess 1-chloroheptane was removed via H_2O/Et_2O extraction. The water layer was dried on a rotary evaporator and further dried on a vacuum line, yielding a viscous light yellow liquid. Yield: 4.70 g, 89%. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 10.5 (1H, s), 7.80 (1H, s), 7.57 (1H, s), 4.33 (2H, t, *J* = 7.4 Hz), 4.14 (3H, s), 1.92 (2H, m), 1.30 (6H, m) 0.87 (3H, t, *J* = 6.7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 137.6, 123.8, 121.9, 49.9, 36.5, 31.4, 30.2, 28.5, 26.1, 22.4, 13.9. FTIR (ATR, ν_{max}/cm^{-1}): 3138, 3045 (aromatic C-H stretch), 2954, 2927, 2856 (alkyl C-H stretch), 1569, 1460, 1169, 624.

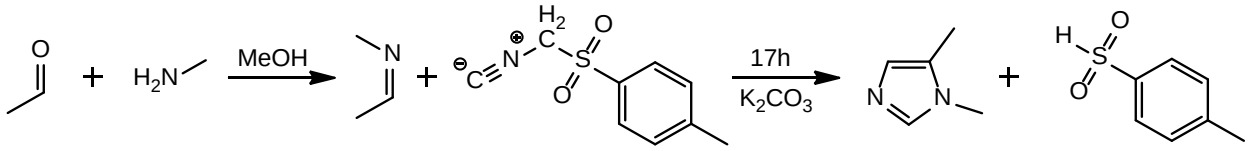
2.8 1-Methyl-3-nonylimidazolium chloride



1-Methylimidazole (1.0 eq, 24.4 mmol, 2.00 g) was dissolved in ACN (15 mL). 1-Chlorononane (1.2 eq, 29.3 mmol, 4.76 g) was added, and the reaction mixture was put under N_2 atmosphere to prevent discoloration during the reaction. After refluxing for 48 h at 82 °C, the solvent was removed on a rotary evaporator, and the excess 1-chlorononane was removed via H_2O/Et_2O extraction. The water layer was dried on a rotary evaporator and further dried on a vacuum line, yielding a viscous light yellow liquid. Yield: 5.42 g, 91%. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 10.5 (1H, s), 7.77 (1H, s), 7.54 (1H, s), 4.33 (2H, t, *J* = 7.4 Hz), 4.14 (3H, s), 1.91 (2H, m), 1.30 (8H, m) 0.87 (3H, t, *J* = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 137.7, 123.7, 121.9, 50.0, 36.5, 31.7, 30.3, 29.2, 29.0, 28.9, 26.2, 22.5, 14.0. FTIR (ATR, ν_{max}/cm^{-1}): 3139, 3052 (aromatic C-H stretch), 2955, 2924, 2854 (alkyl C-H stretch), 1569, 1465, 1169, 623.

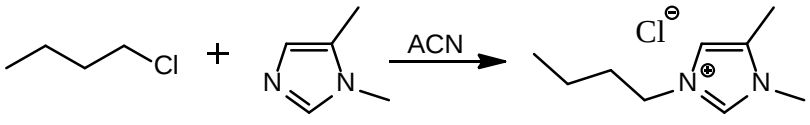
2.9 1-Butyl-3,4-dimethylimidazolium chloride

Step 1: Van Leusen imidazole synthesis[1]



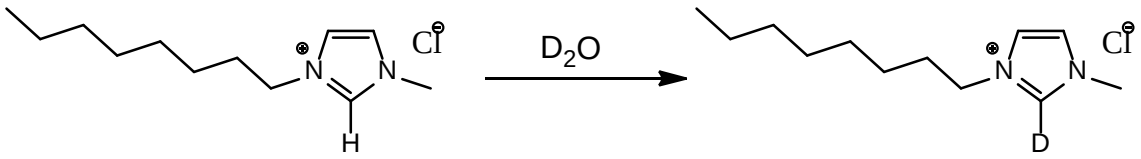
Acetaldehyde (1.5 eq, 37.5 mmol, 1.65 g) was added to a solution of $MeNH_2$ (1.6 eq, 40.0 mmol, 1.24 g) in MeOH (20 mL), and the reaction mixture was stirred for 1 h at room temperature. Tosylmethyl isocyanide (TosMIC) (1.0 eq, 25.0 mmol, 4.88 g), K_2CO_3 (1.0 eq, 25.0 mmol, 3.45 g) and an additional 20 mL of MeOH were added. After stirring for 17 h at room temperature, the solvent was evaporated on a rotary evaporator. The brown residue was dissolved in 30 mL of ethyl acetate (EtOAc), and washed with 20 mL of a saturated $NaHCO_3$ solution and 10 mL of distilled water. The aqueous phases were collected and extracted twice with 15 mL of EtOAc. The organic phases were then collected and the solvent evaporated. Distilled water was added to the resulting brown oil, upon which some dark brown impurities precipitated which were removed by filtration. The water was again evaporated, and the brown oil again dissolved in EtOAc. The solution was poured on a 1 cm layer of silica, which was washed with more EtOAc. A small dark brown initial fraction was discarded. Only when the eluent had a light yellow color, the fraction was collected. The silica layer was washed further with copious EtOAc. The solvent was finally evaporated to obtain a dark yellow transparent oil. Yield: 0.70 g, 29%. ^{1}H NMR (300 MHz, DMSO-d_6, δ/ppm): 7.57 (1H, s), 6.66 (1H, s), 3.51 (3H, s), 2.14 (3H, s).

Step 2: Quaternization



1,5-Dimethylimidazole (1.0 eq, 7.29 mmol, 0.70 g) was dissolved in ACN (5 mL). 1-Chlorobutane (1.5 eq, 10.9 mmol, 1.02 g) was added, and the reaction mixture put under N_2 atmosphere to prevent discoloration during the reaction. After refluxing for 48 h at 82 °C, the solvent and excess 1-chlorobutane were removed on a rotary evaporator. The ionic liquid was further purified via H_2O/Et_2O extraction and dried on a vacuum line, yielding a viscous brown liquid. Yield: 1.07 g, 78%. ^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): 9.91 (1H, s), 7.29 (1H, s), 4.15 (2H, t, *J* = 7.3 Hz), 3.84 (3H, s), 2.27 (3H, s), 1.87 (2H, m), 1.27 (2H, m), 0.87 (3H, t, *J* = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 134.8, 129.7, 117.2, 47.5, 31.6, 30.1, 17.5, 11.5, 7.2. FTIR (ATR, ν_{max}/cm^{-1}): 3124, 3085 (aromatic C-H stretch), 2961, 2934, 2874 (alkyl C-H stretch), 1670 (C=C stretch), 1569, 1453, 1156, 637.

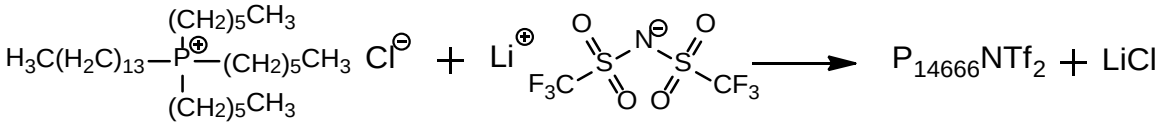
2.10 C_2-deuterated 1-methyl-3-octylimidazolium chloride



1-Octyl-3-methyl imidazolium chloride (10 g) was dissolved in D_2O (50 mL) and stirred at room temperature under N_2 atmosphere. After 72 h, the proton on the C_2 position was completely exchanged for deuterium, as was confirmed by ^{1}H NMR. The D_2O was evaporated using a rotary evaporator. The C_2-deuterated ionic liquid was dried on a vacuum line and stored under N_2 atmosphere. Yield: quantitative. ^{1}H NMR (300 MHz, D_2O, δ/ppm): 7.45 (2H, s), 4.16 (2H, t, *J* = 7.0 Hz), 3.85 (3H, s), 1.78 (2H, m), 1.16 (10H, m), 0.72 (3H, m). ^{13}C NMR (100 MHz, D_2O,

δ/ppm): 135.8 (**C**D, t, *J* = 34.1 Hz), 123.8, 122.2, 49.6, 36.0, 31.6, 29.8, 28.9, 28.8, 25.9, 22.4, 13.8. FTIR (ATR, ν_{max}/cm^{-1}): 3048 (aromatic C-H stretch), 2954, 2925, 2855 (alkyl C-H stretch), 2241 (C-D stretch), 1544, 1454, 560.

2.11 Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide



Trihexyltetradecylphosphonium chloride (1.0 eq, 52.0 mmol, 27.2 g) and lithium bis(trifluoromethylsulfonyl)imide (1.0 eq, 52.0 mmol, 15.0 g) were added to a flask containing 60 mL of DCM and 60 mL of distilled water. The reaction mixture was stirred heavily at room temperature overnight. The aqueous layer was separated and extracted two more times with 20 mL of DCM. The organic fractions were collected and the solvent evaporated, yielding trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide as a transparent oily liquid, which was further dried a vacuum line. Yield: 38.9 g, 98%. ^{1}H NMR (300 MHz, $CDCl_3$, δ/ppm): 2.10 (8H, m), 1.48 (16H, m), 1.26 (24H, m), 0.90 (12H, m). ^{13}C NMR (100 MHz, $CDCl_3$, δ/ppm): 119.9 (**C**F_3, q, *J* = 320.6 Hz), 31.9, 30.8, 30.5, 30.3, 30.2, 30.0, 29.6, 29.5, 29.4, 29.3, 29.2, 28.7, 22.6, 22.2, 21.4, 21.3, 18.7, 18.3, 14.0, 13.7. FTIR (ATR, ν_{max}/cm^{-1}): 2956, 2926, 2856 (alkyl C-H stretch), 1349, 1183, 1056.

3. Calculating the inherent viscosity

GPC measurements are difficult to perform on polyaramids due to their low solubility in conventional solvents. For this reason, the average molar mass of polyaramids in generally expressed in terms of inherent viscosity (η_{inh}). The inherent viscosity of a polymer is defined as the natural logarithm of the relative viscosity (η_{rel}) of a polymer solution, divided by the mass concentration (c) of that solution (Equation 1). The relative viscosity is determined by using an Ubbelohde viscometer to measure the flow time of the pure solvent ($t_{solvent}$) and of the polymer solution ($t_{solution}$).

$$\eta_{inh} = \frac{\ln \eta_{rel}}{c} \quad (1)$$

$$\eta_{rel} = \frac{t_{solution}}{t_{solvent}} \quad (2)$$

The mass concentration of the PMIA/sulfuric acid solution was 0.5 g dL^{-1}. The flow times of the concentrated sulfuric acid (96 %) and the PMIA/sulfuric acid solution were determined to be 89.9 s and 258.8 s respectively. Therefore the inherent viscosity of the PMIA sample is 2.11 dL g^{-1}, which is on par with the industrial standard.[2]

4. Comparing *p*-aramid PPTA and *m*-aramid PMIA

Imidazolium cations are better solvents for PMIA than quaternary phosphonium cations, while our earlier work showed the opposite was true for PPTA.[3] This discrepancy was suspected to be the result of using a pentamer model compound to determine solubility trends of PPTA in ILs. The use of this model compound was necessary, however, as high molar mass PPTA is only truly soluble in concentrated sulfuric acid. PMIA polymer, on the other hand, is readily soluble in ionic liquids. To compare the two aramids, a PMIA pentamer model compound was synthesized,

and it's solubility in several ionic liquids was compared to that of both PMIA polymer and PPTA pentamer. These results can be found in Table S1.

Table S1: Solubility of PMIA and PPTA pentamer model compounds in ionic liquids

	Solubility (mol%)	
Ionic Liquid	PMIA pentamer[a]	PPTA pentamer[b]
$[P_{2444}][Et_2PO_4]$	36	7.6
$[P_{4444}][Cl]$	22	3.2
$[P_{44414}][Cl]$	33	3.1
$[N_{8881}][Cl]$	19	2.9
$[C_4MIm][OAc]$	8.9	1.6
$[C_4MIm][Cl]$	7.6	0.7

a. *The solubility in mol% was calculated using the molar mass of the pentamer which is 555 g mol^{-1}. This is higher than the molar mass of the repeating unit of PMIA polymer, being 238 g mol^{-1}. This may give the false impression that in some cases the polymer is more soluble than the pentamer. b. Data taken from ref 3.*

Contrary to PMIA polymer, the pentamer model compound could easily be dissolved in phosphonium and ammonium containing ionic liquids. Furthermore, the phosphonium and ammonium cations were able to dissolve much larger amounts of PMIA pentamer than the imidazolium counterparts. The reason for this possibly lies in the microscopic structure of the ionic liquids. As mentioned earlier, imidazolium-based ionic liquids form an ordered network of hydrogen bonded cations and anions, whereas quaternary phosphonium cations are more disordered, having more free volume and being more loosely bound to their counter anions. The oligomers are thus more free to interact with the anions in a phosphonium ionic liquid, while in imidazoliums they need to break up the hydrogen bond network and have to compete with the cation for interaction with the anion. However, for larger polymers to remain in solution, they require a stable solvation shell in order to separate the chains. The weak interactions between phosphonium cations and their counter anions are not able to create a sufficiently stable solvation shell, making the ionic liquid unable to keep the polymer in solution.

This reverse trend in solubility indicates that solubility data for these aramid pentamers cannot be directly extrapolated to aramid polymers. However, we know that imidazolium-based ionic liquids are much better solvents for the synthesis of PPTA polymer than phosphonium ionic liquids.[4,5] It is therefore more likely that the solution structure of PPTA polymer in ionic liquids closely resembles that of PMIA polymer, and that its solubility is governed by the same principles.

5. ^{13}C NMR and HMBC spectra of [C_8MIm][Cl]

^{13}C NMR (100 MHz) spectra were recorded with a Bruker Avance 400 MHz spectrometer at 90 °C, using TMSPA sodium salt dissolved in D_2O as internal reference.

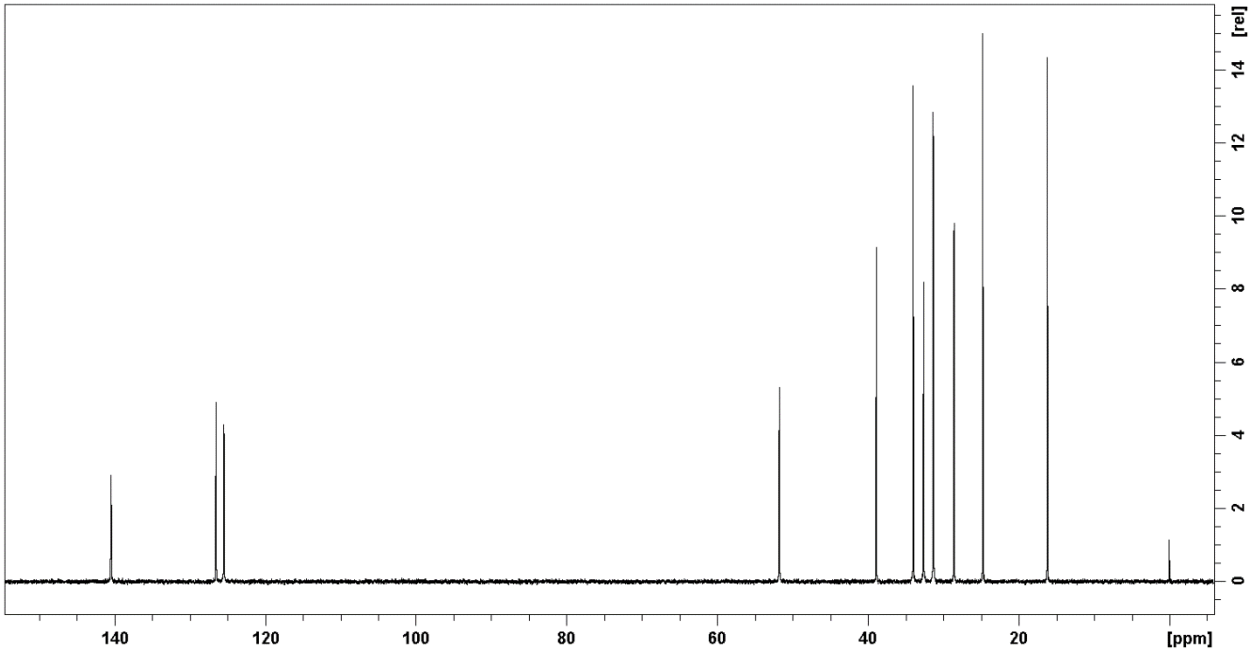


Figure S1: ^{13}C NMR spectrum of neat [C_8MIM][Cl].

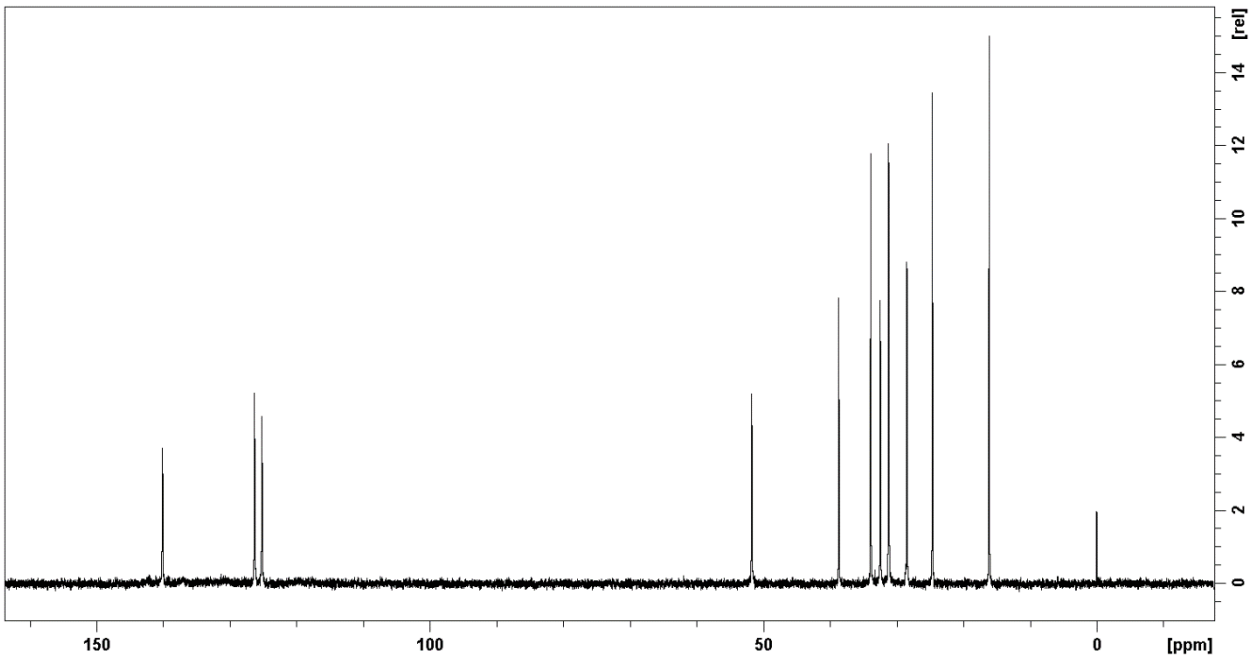


Figure S2: ^{13}C NMR spectrum of [C_8MIM][Cl] containing 20 wt% PMIA.

The peaks at 126.47 ppm and 125.42 ppm were assigned using an HMBC (Heteronuclear Multiple Bond correlation) experiment. The spectrum was recorded with a Bruker Avance 600 MHz spectrometer at room temperature, using $CDCl_3$ as deuterated solvent. The spectrum shown in Figure S3 indicates that the peak at 126.47 ppm in the ^{13}C spectrum shows long range correlation with the peak at 3.74 ppm in the ^{1}H spectrum. This proton peak integrates as 3H and can be assigned to the CH_3 group directly bonded to the imidazolium. The ^{13}C peak at 125.42 ppm shows long range correlation with the ^{1}H peak at 3.95 ppm, which integrates as 2H and can be assigned to the CH_2 group of the alkyl chain directly bonded to the imidazolium. Using this information, the peak at 126.47 ppm can be assigned to C_4 and the peak at 125.42 ppm to C_5.

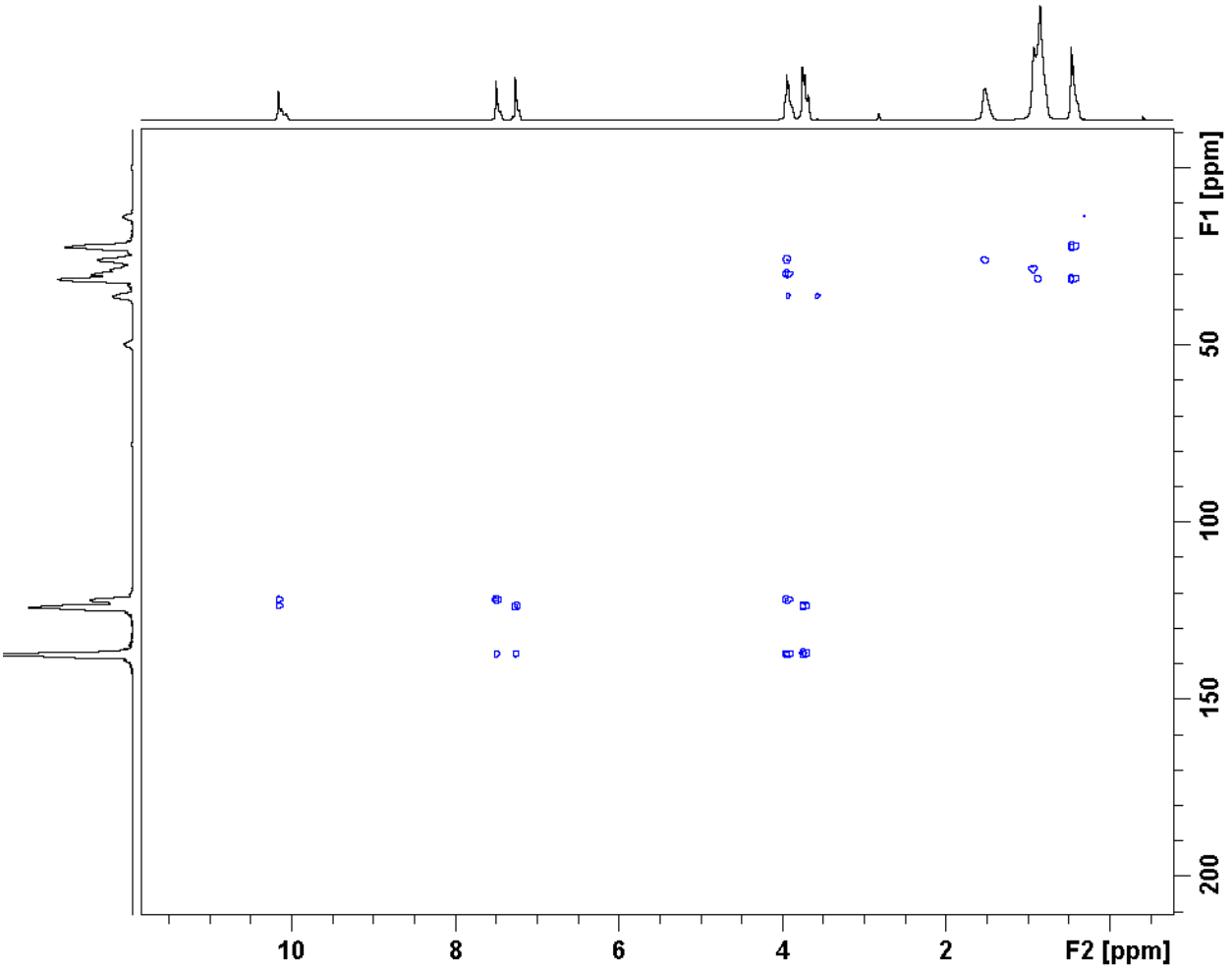
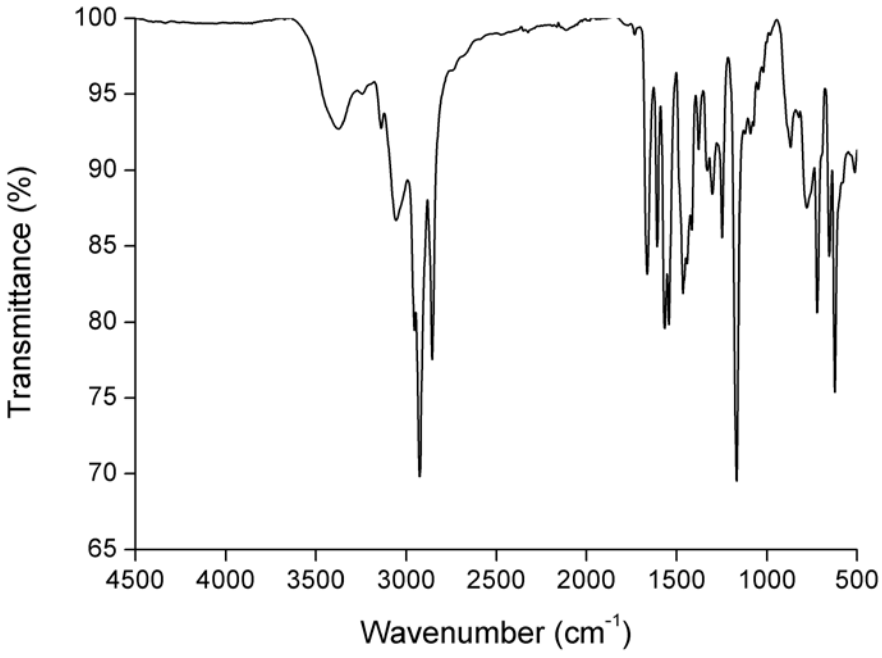


Figure S3: HMBC spectrum of [C_8MIm][Cl]

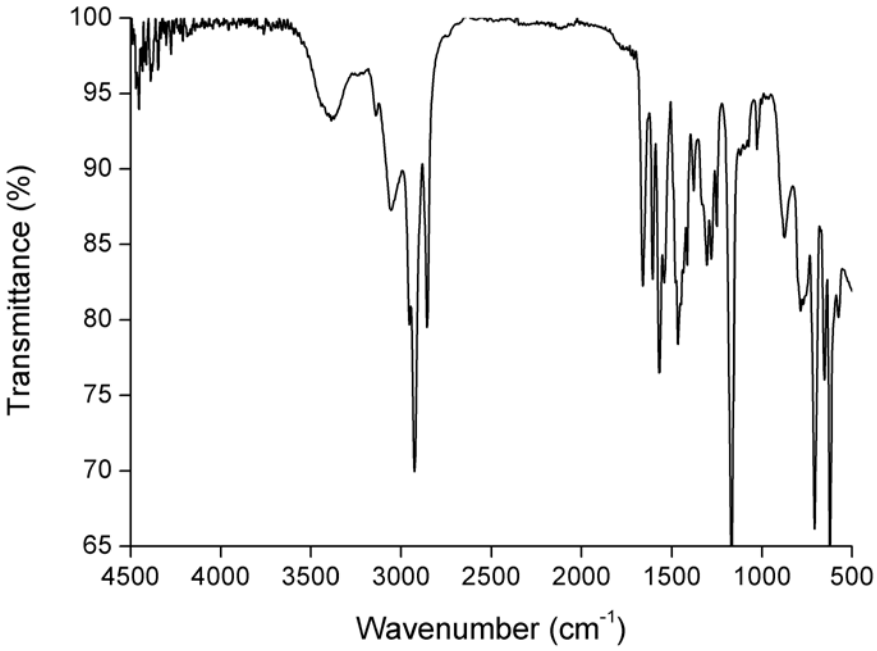
6. FTIR spectra

The FTIR spectra used in the study of hydrogen bond interactions between the cation and the amide carbonyl are listed below. The concentration of PMIA/aramid model compound in all was 20 wt%, or less in case of lower solubility.

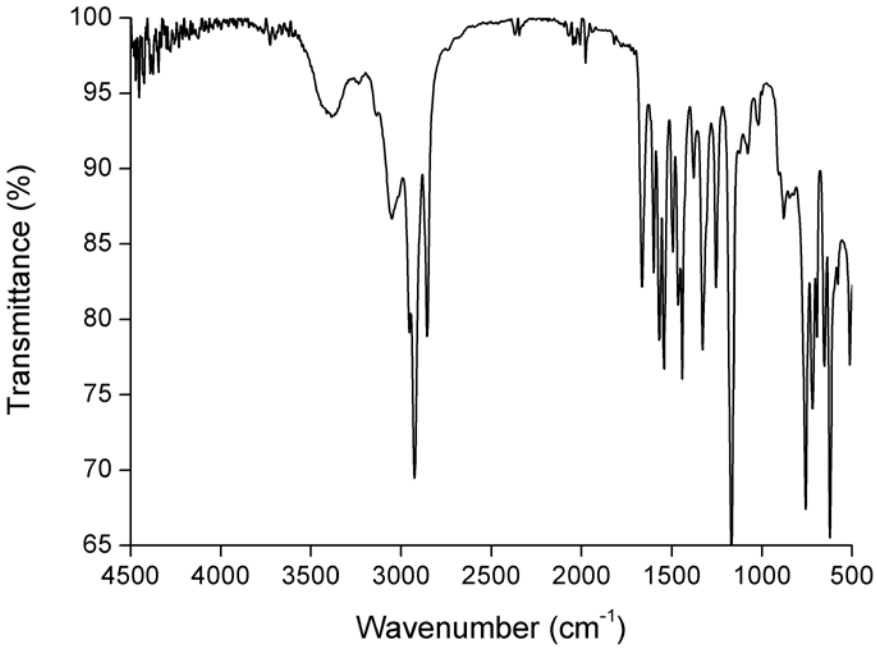
[C_8MIM][Cl] + 20 wt% PMIA



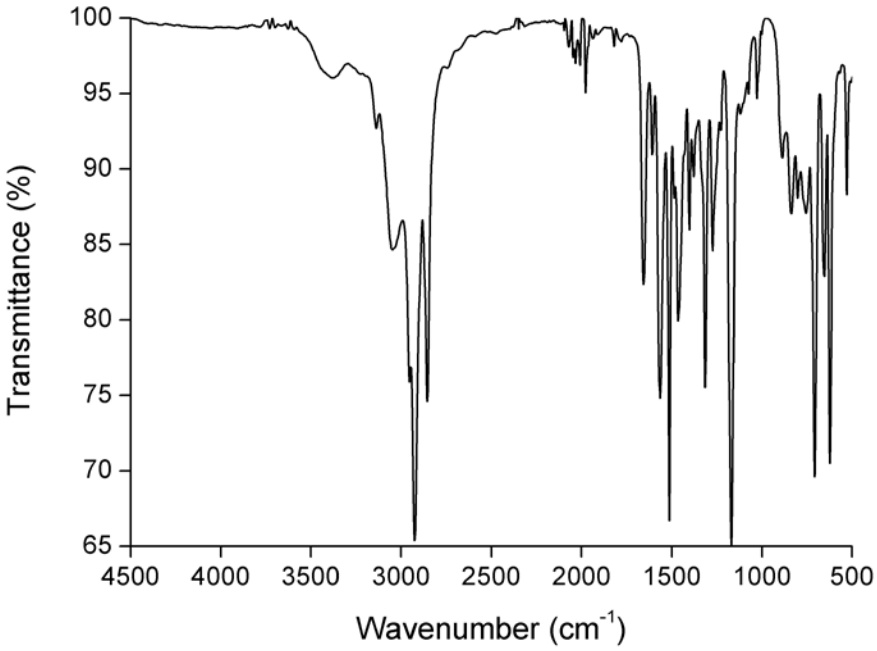
[C_8MIM][Cl] + 20 wt% MTN



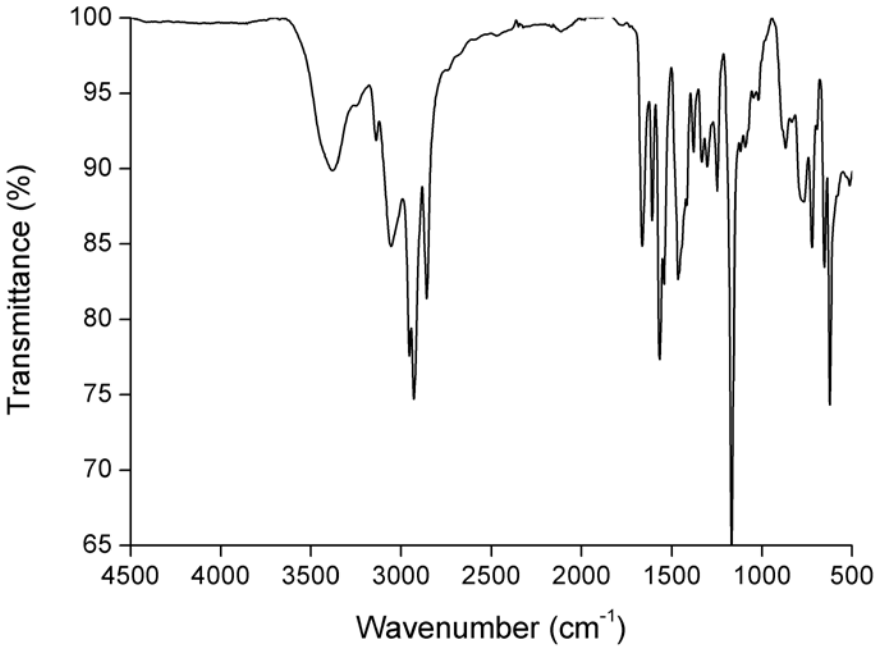
[C_8MIM][Cl] + 20 wt% MTO



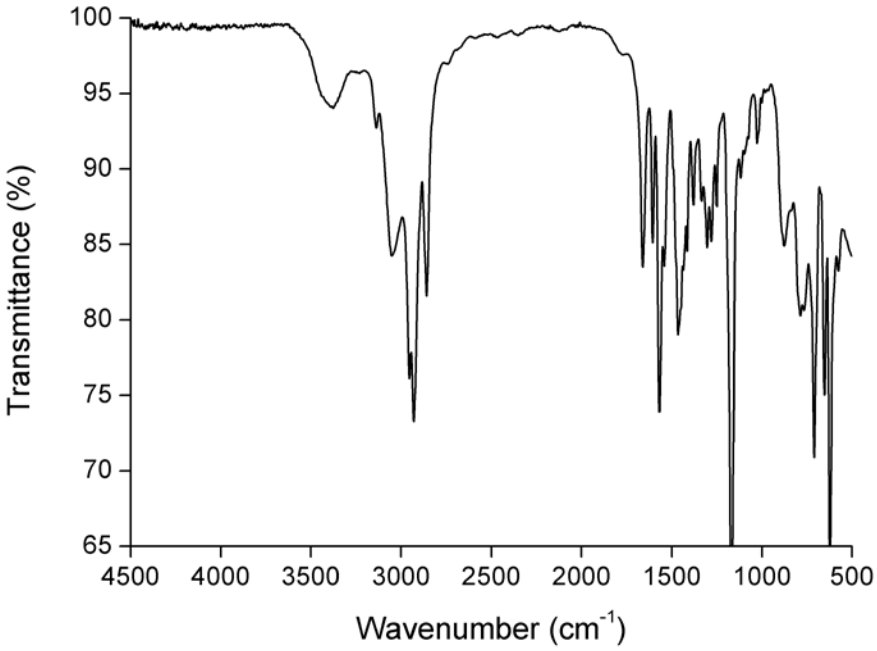
[C_8MIM][Cl] + 20 wt% PTN



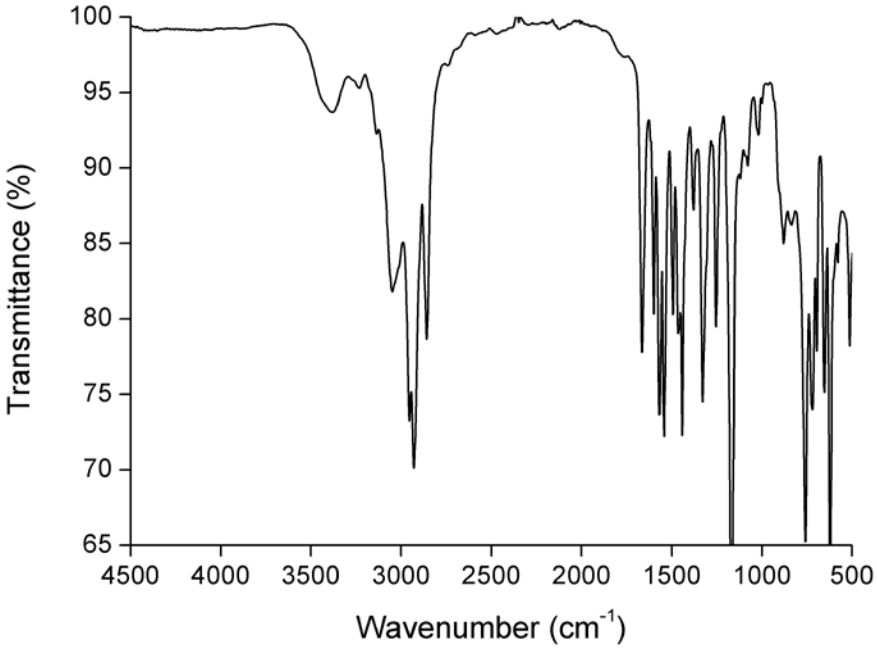
[C_6MIM][Cl] + 20 wt% PMIA



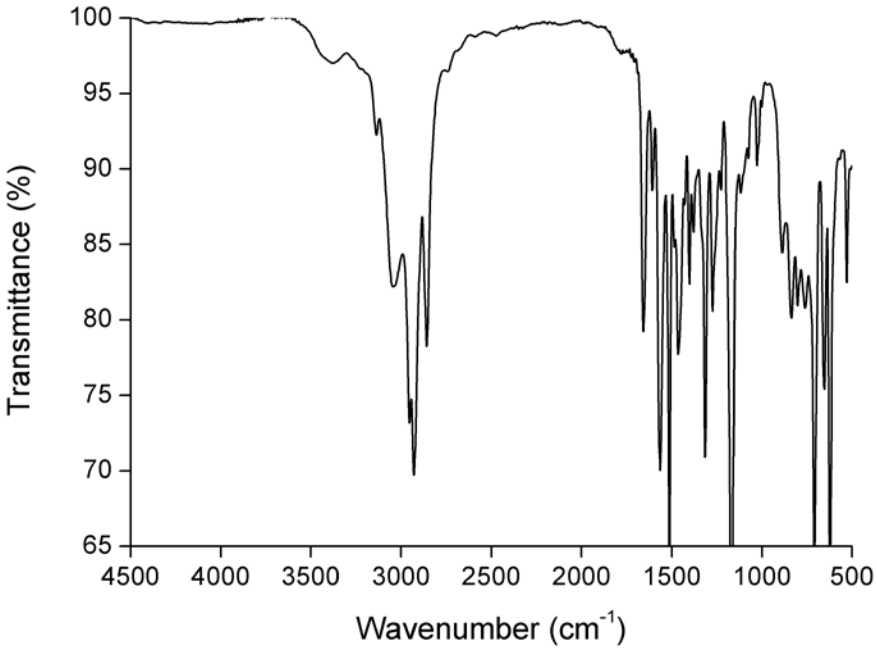
[C_6MIM][Cl] + 20 wt% MTN



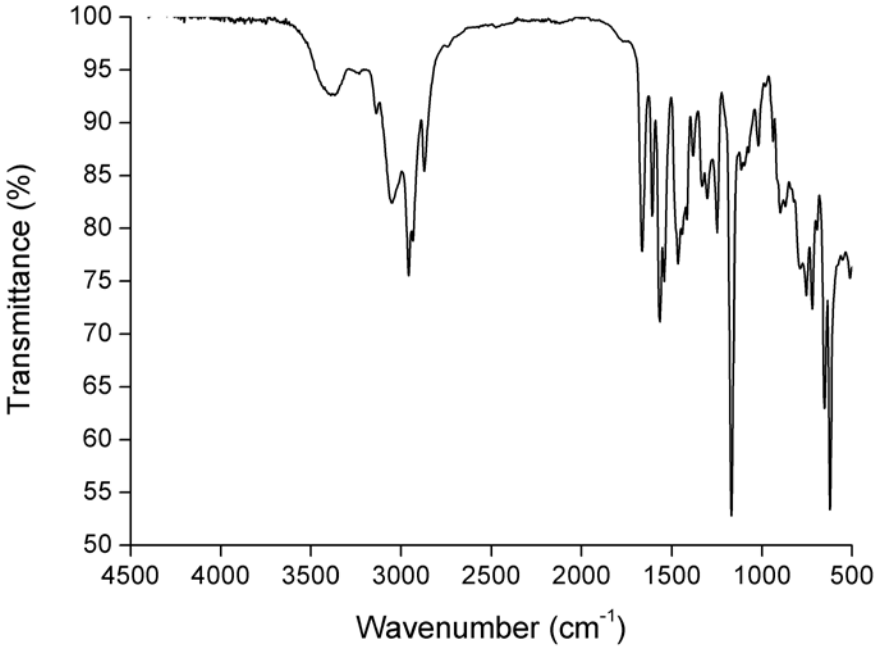
[C_6MIM][Cl] + 20 wt% MTO



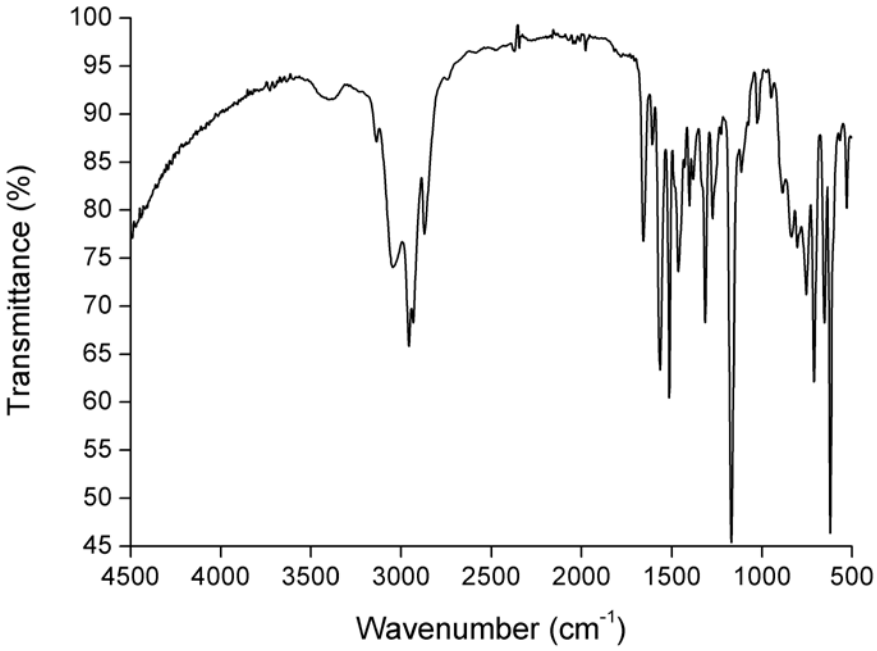
[C_6MIM][Cl] + 20 wt% PTN



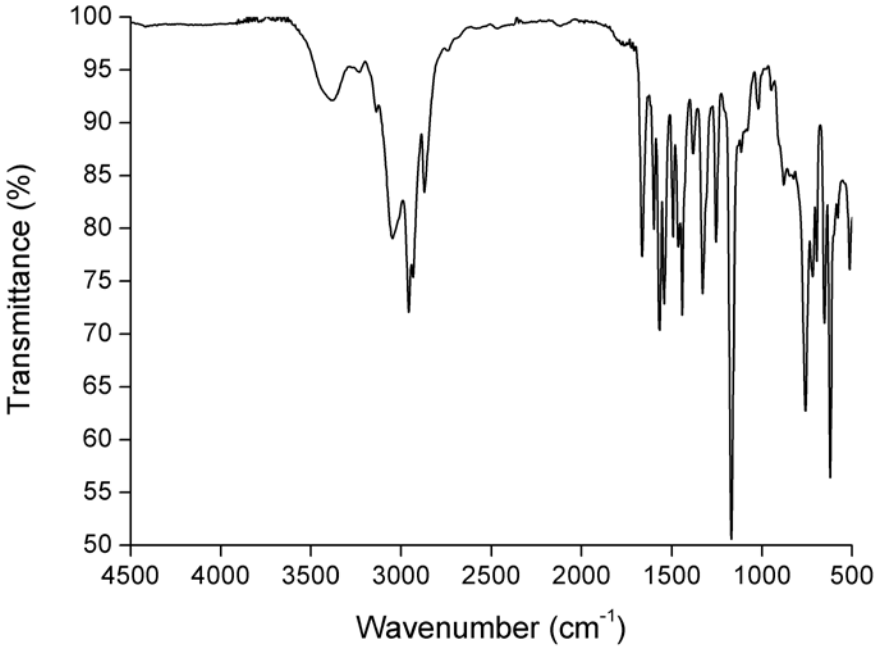
[C_4MIM][Cl] + 20 wt% PMIA



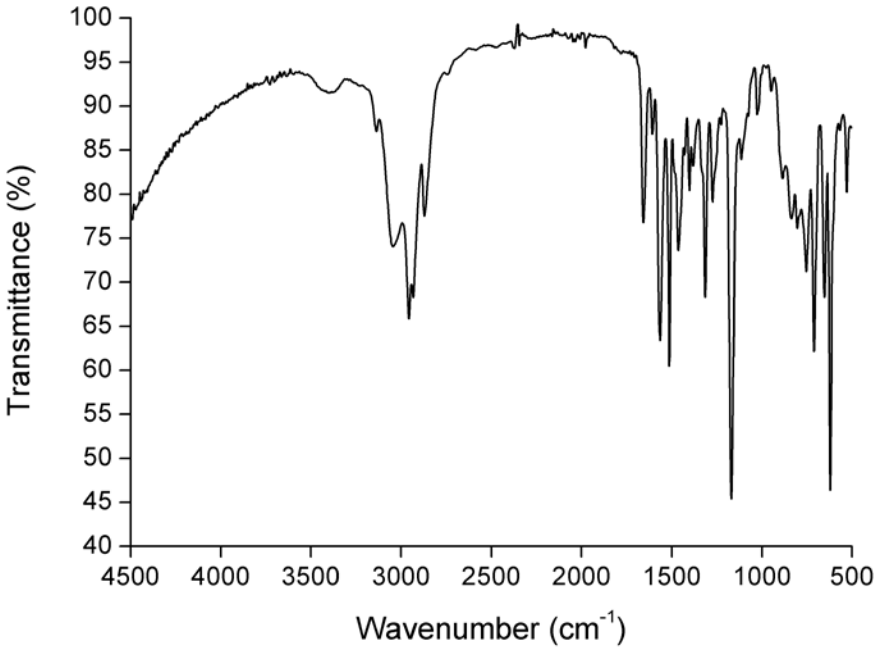
[C_4MIM][Cl] + 20 wt% MTN



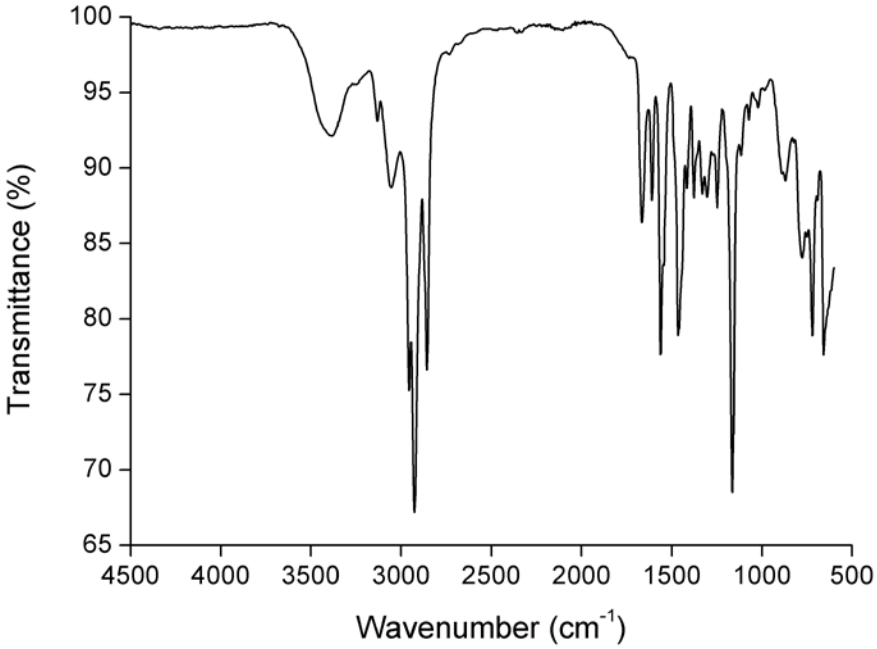
[C_4MIM][Cl] + 20 wt% MTO



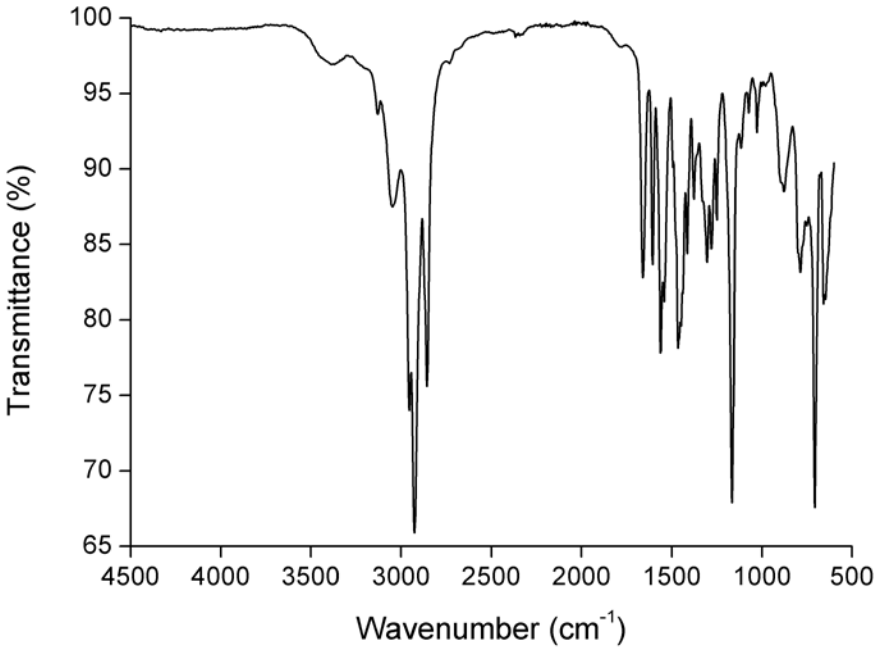
[C_4MIM][Cl] + 20 wt% PTN



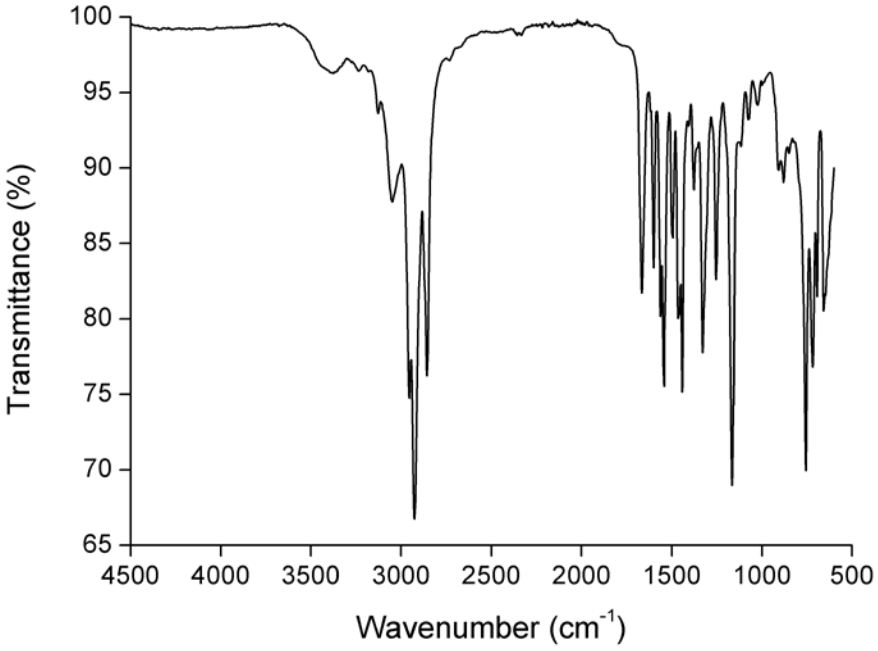
[C_8C_5IM][Cl] + 7 wt% PMIA



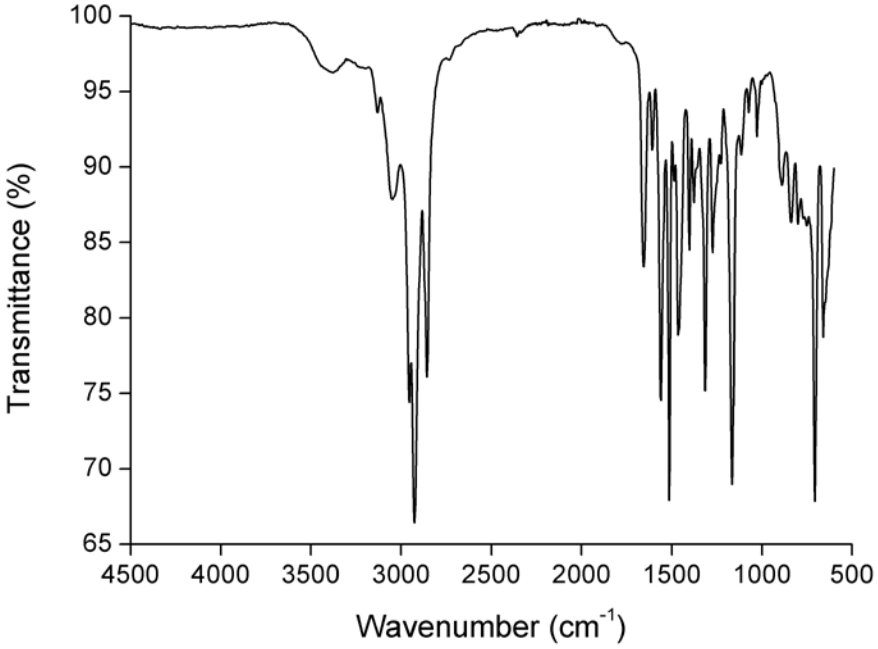
[C_8C_5IM][Cl] + 20 wt% MTN



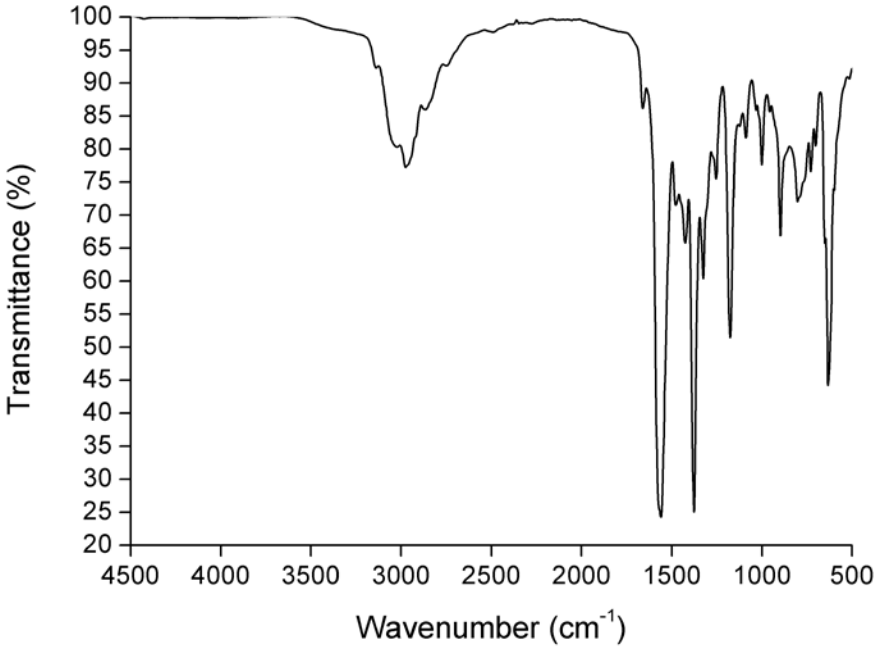
[C_8C_5IM][Cl] + 20 wt% MTO



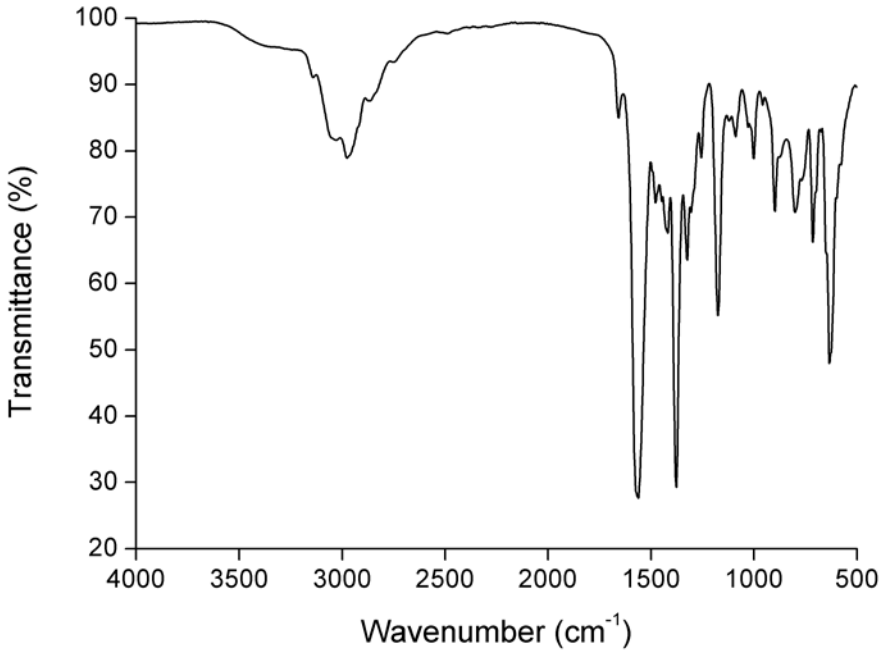
[C_8C_5IM][Cl] + 20 wt% PTN



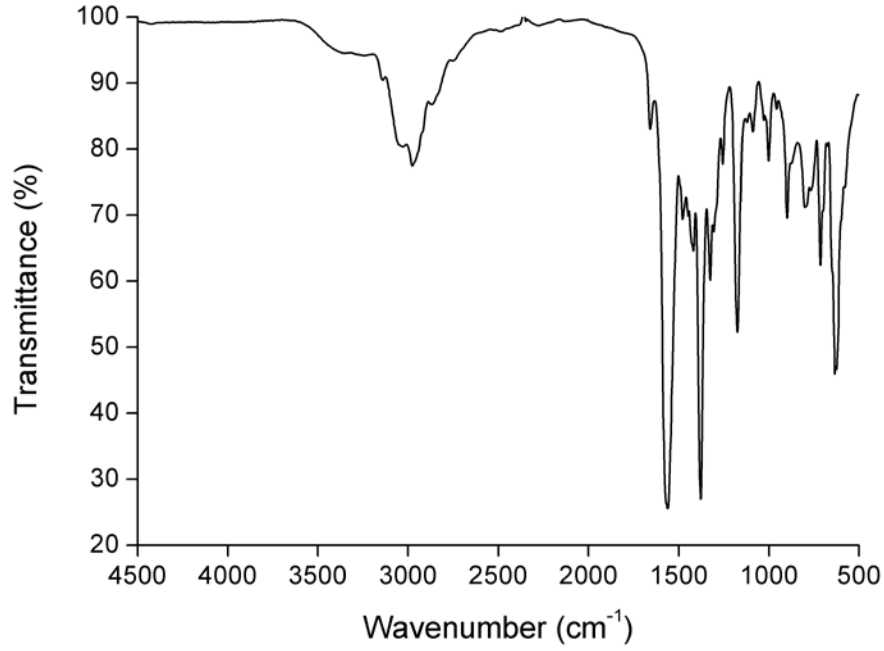
[C_2MIM][OAc] + 12 wt% PMIA



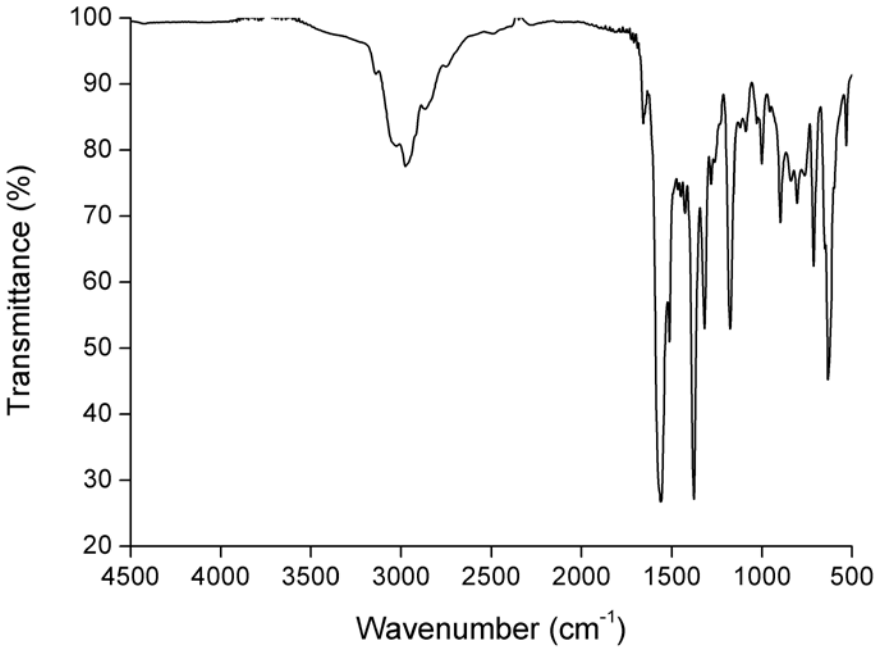
[C_2MIM][OAc] + 20 wt% MTN



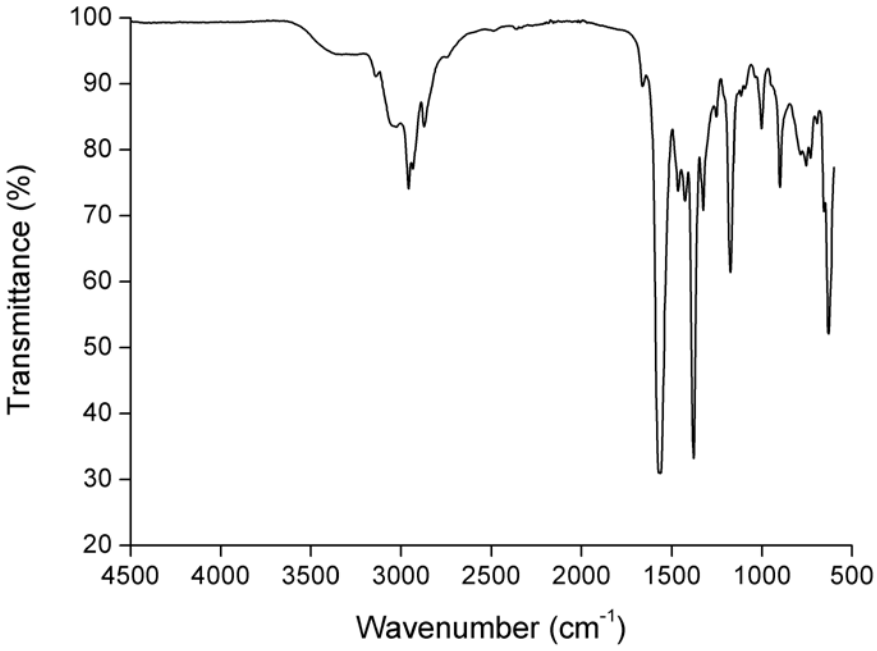
[C_2MIM][OAc] + 20 wt% MTO



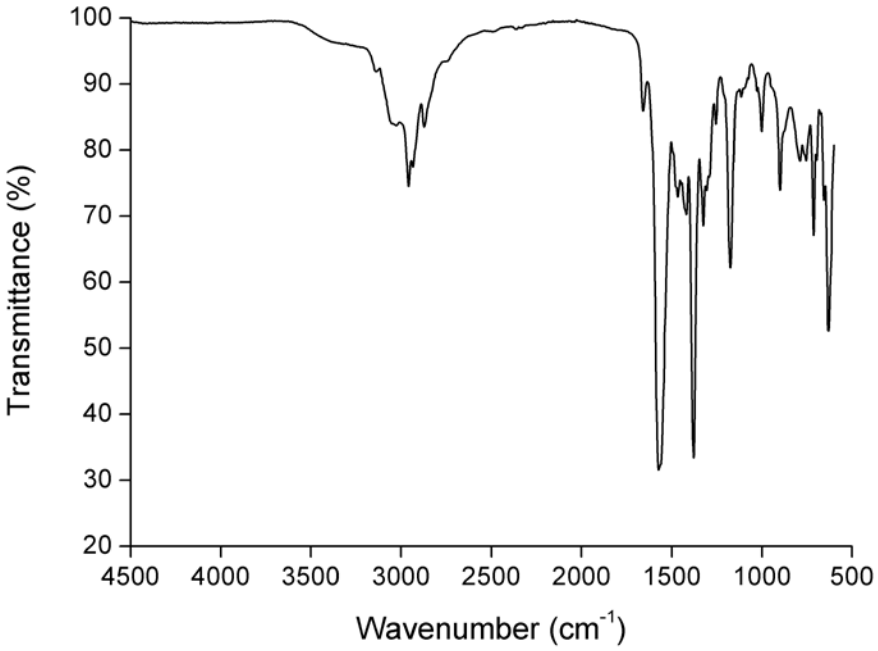
[C_2MIM][OAc] + 20 wt% PTN



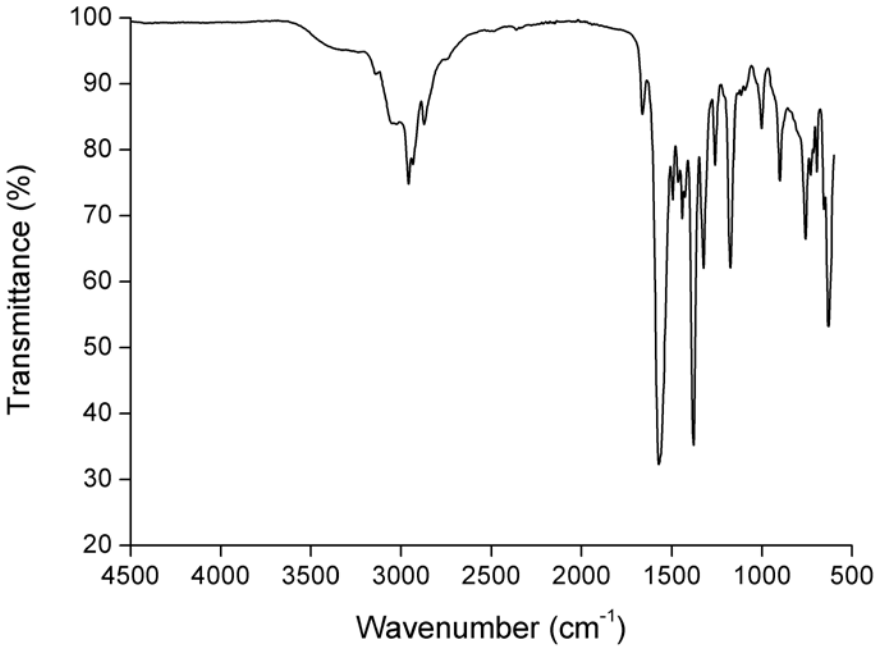
[C_4MIM][OAc] + 15 wt% PMIA



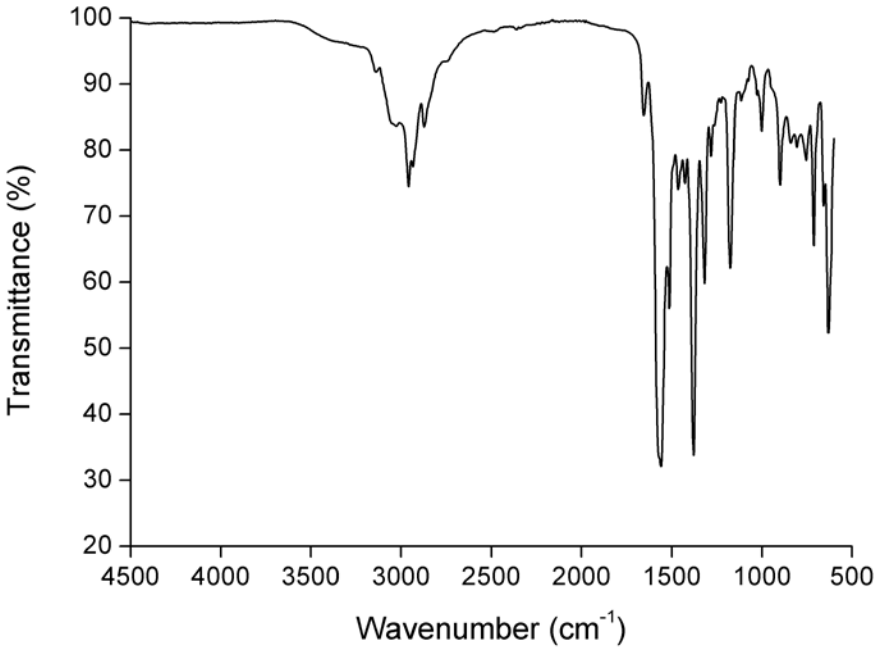
[C_4MIM][OAc] + 20 wt% MTN



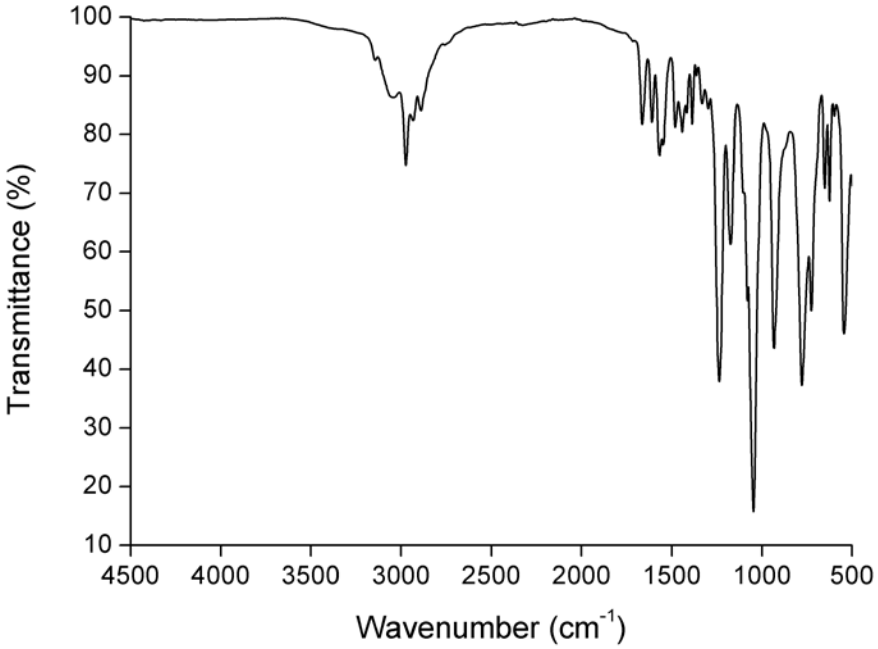
[C_4MIM][OAc] + 20 wt% MTO



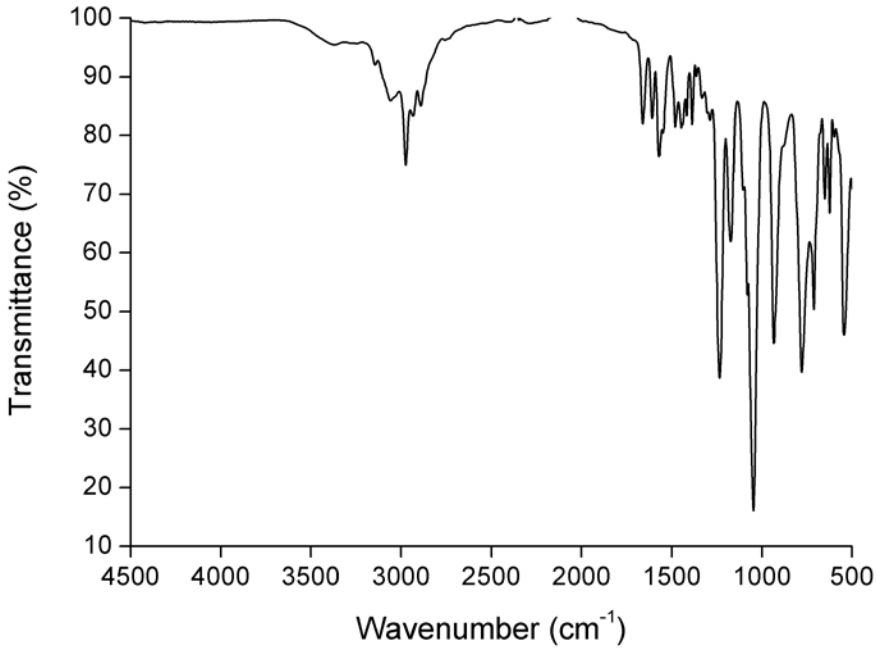
[C_4MIM][OAc] + 20 wt% PTN



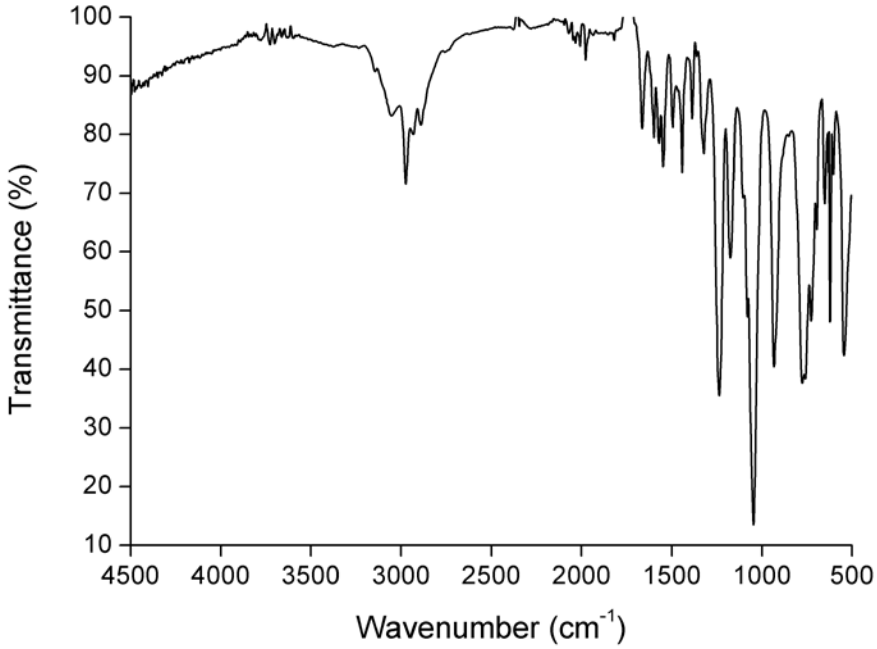
[C_2MIM][Et_2PO_4] + 17 wt% PMIA



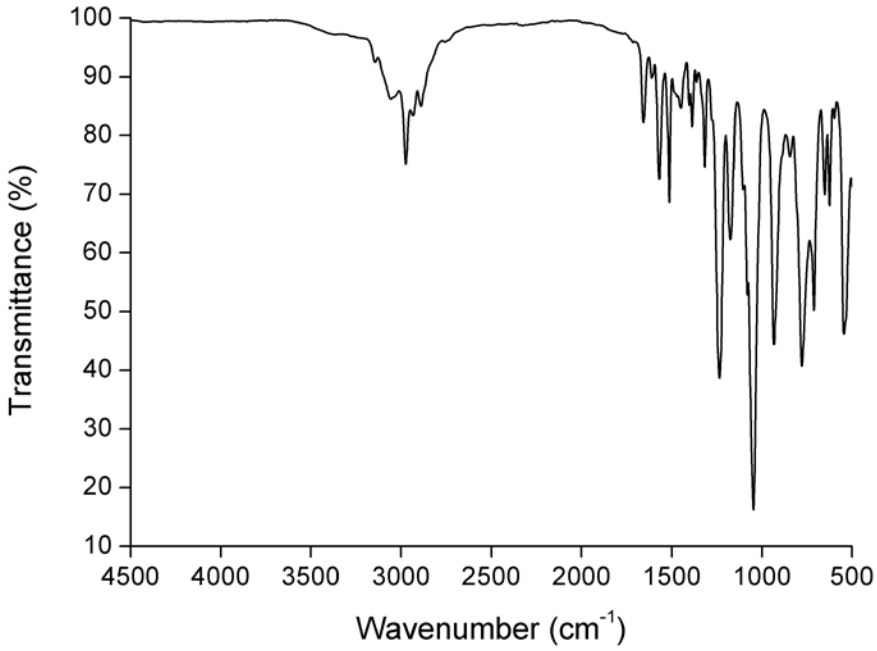
[C_2MIM][Et_2PO_4] + 20 wt% MTN



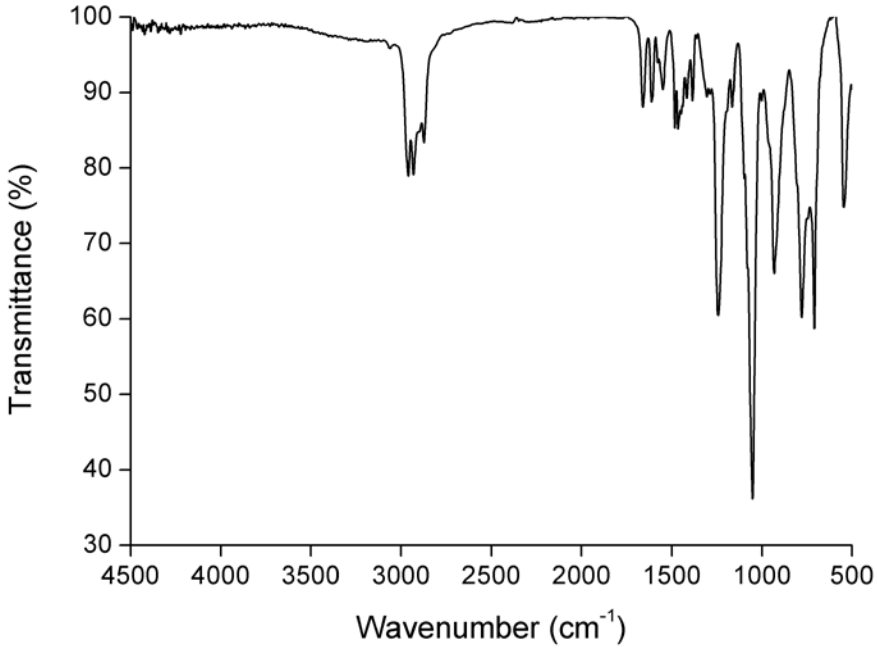
[C_2MIM][Et_2PO_4] + 20 wt% MTO



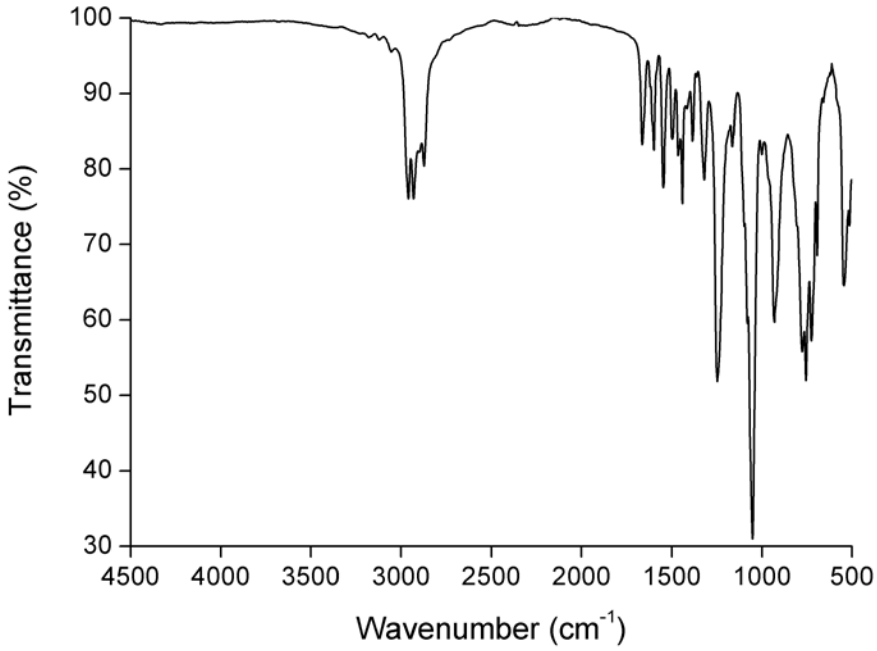
[C_2MIM][Et_2PO_4] + 20 wt% PTN



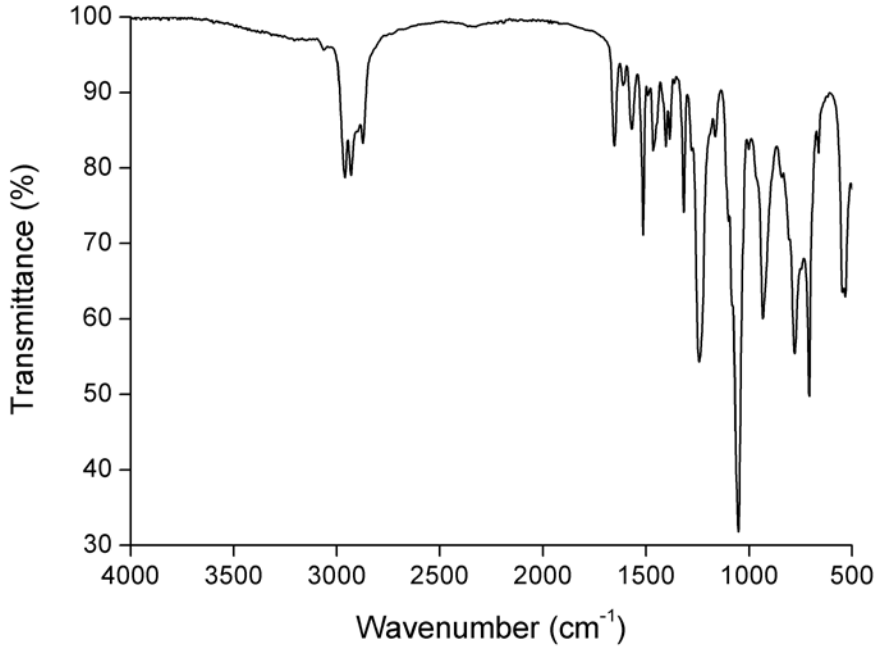
[P_{4442}][Et_2PO_4] + 20 wt% MTN



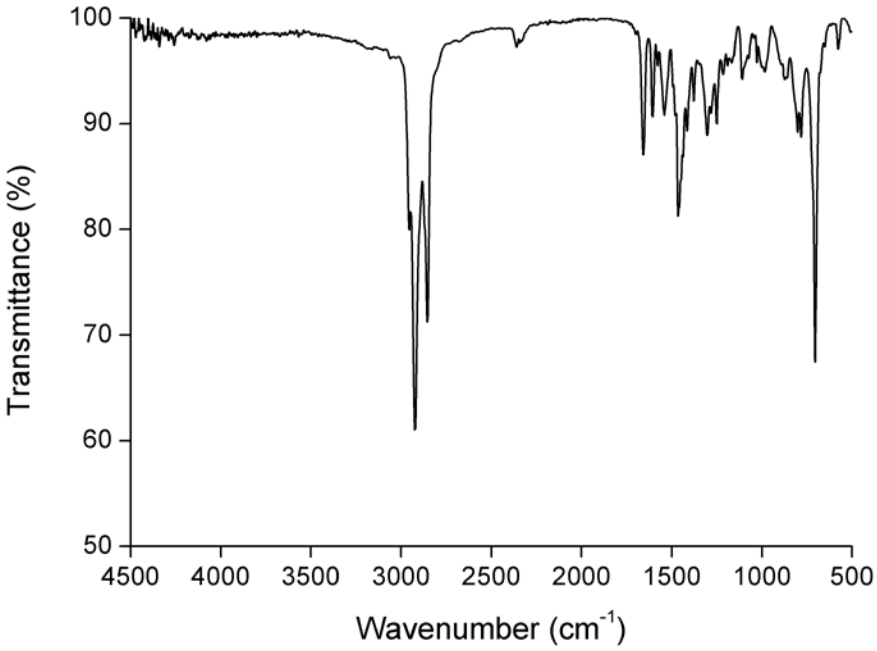
$[P_{4442}][Et_2PO_4]$ + 20 wt% MTO



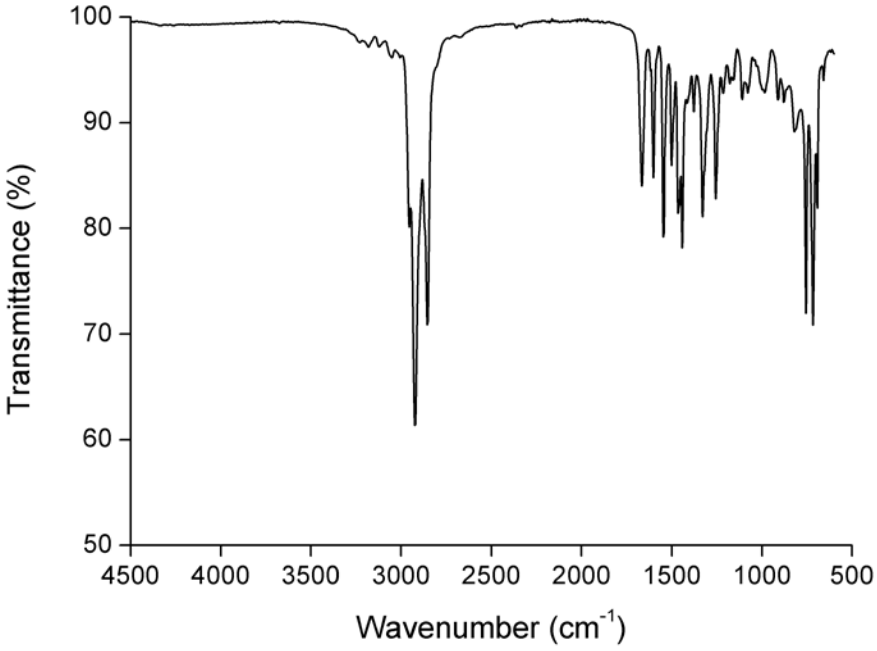
$[P_{4442}][Et_2PO_4]$ + 20 wt% PTN



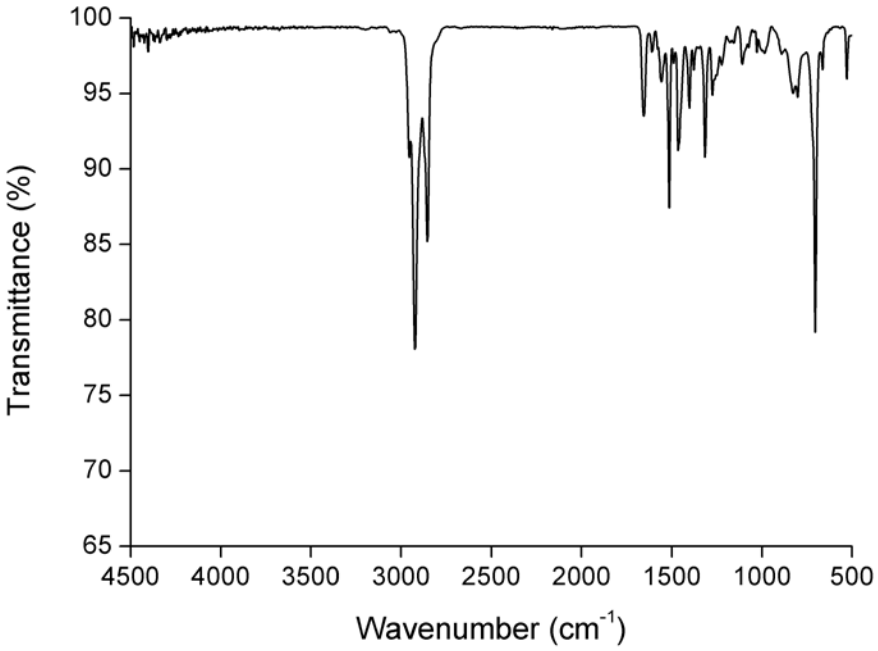
[P_{14666}][Cl] + 20 wt% MTN



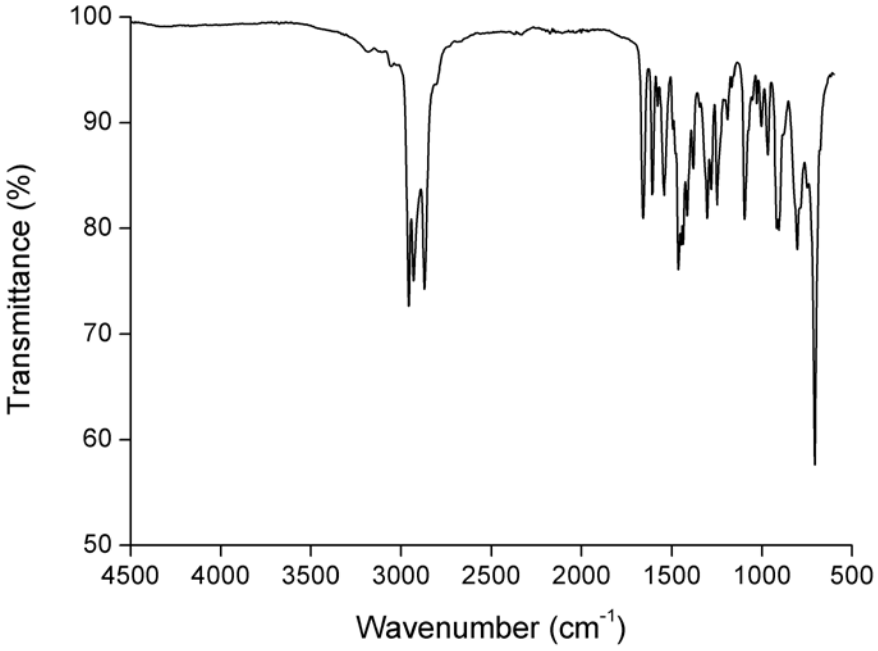
[P_{14666}][Cl] + 20 wt% MTO



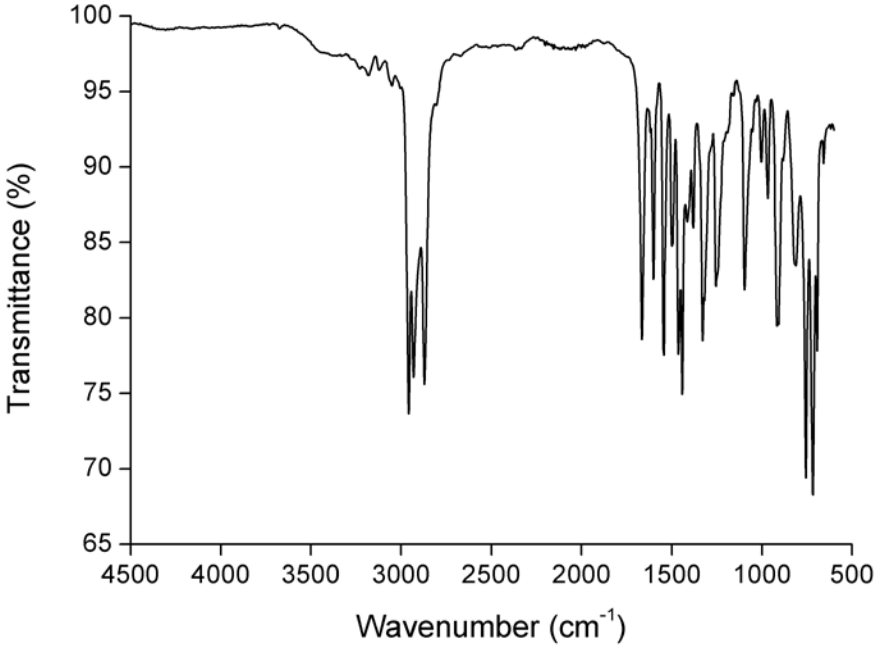
[P_{14666}][Cl] + 20 wt% PTN



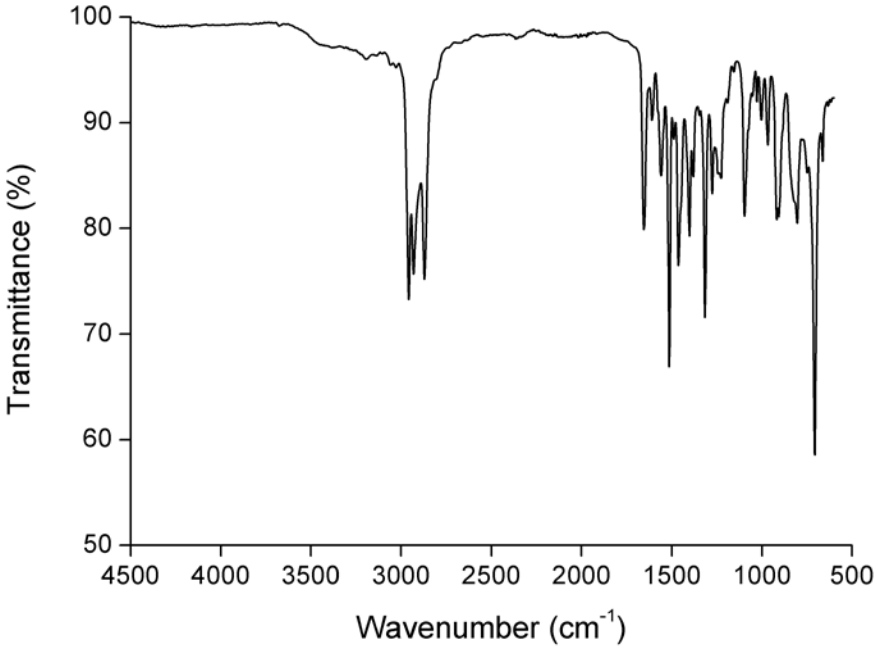
[P_{4444}][Cl] + 20 wt% MTN



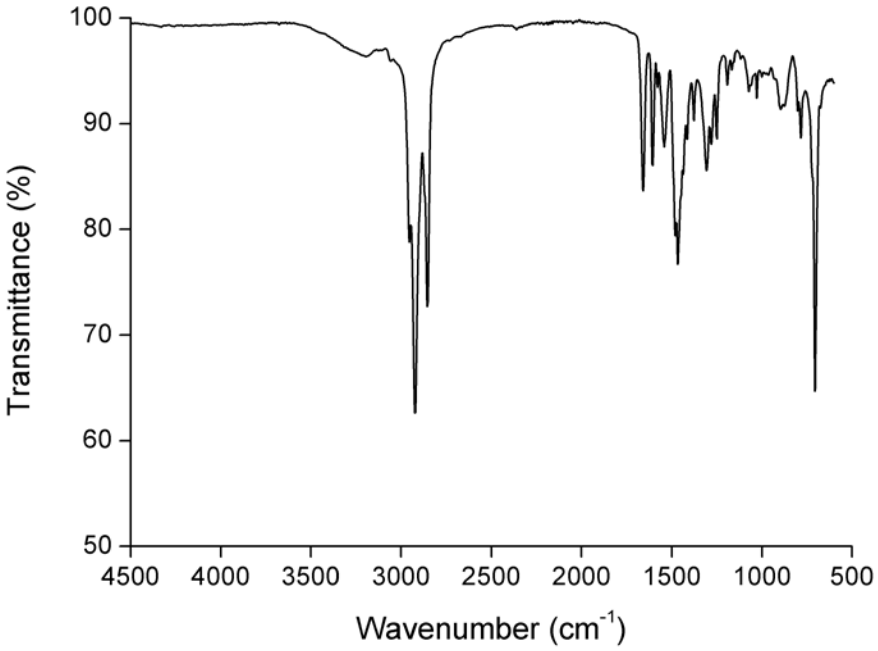
[P_{4444}][Cl] + 20 wt% MTO



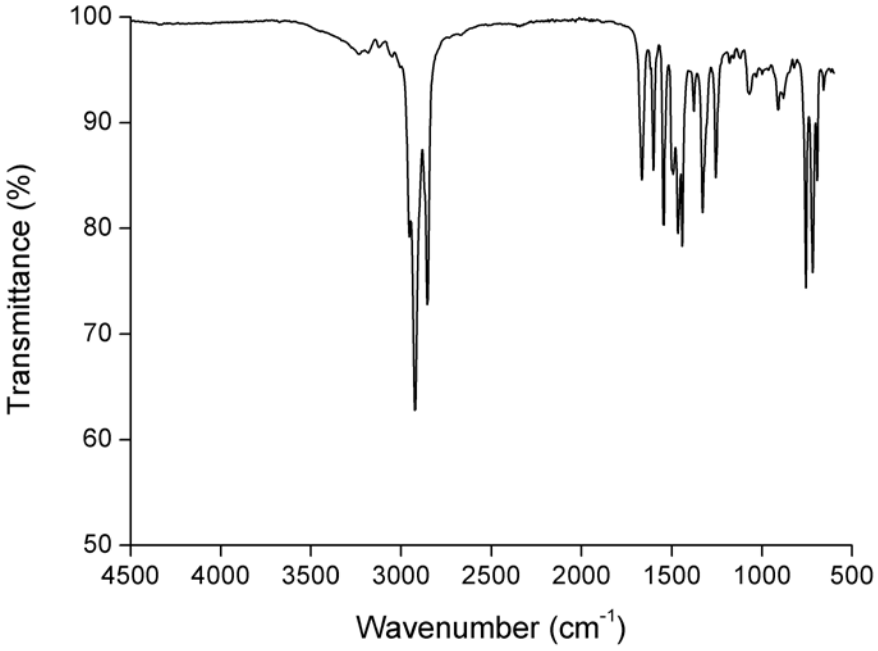
[P_{4444}][Cl] + 20 wt% PTN



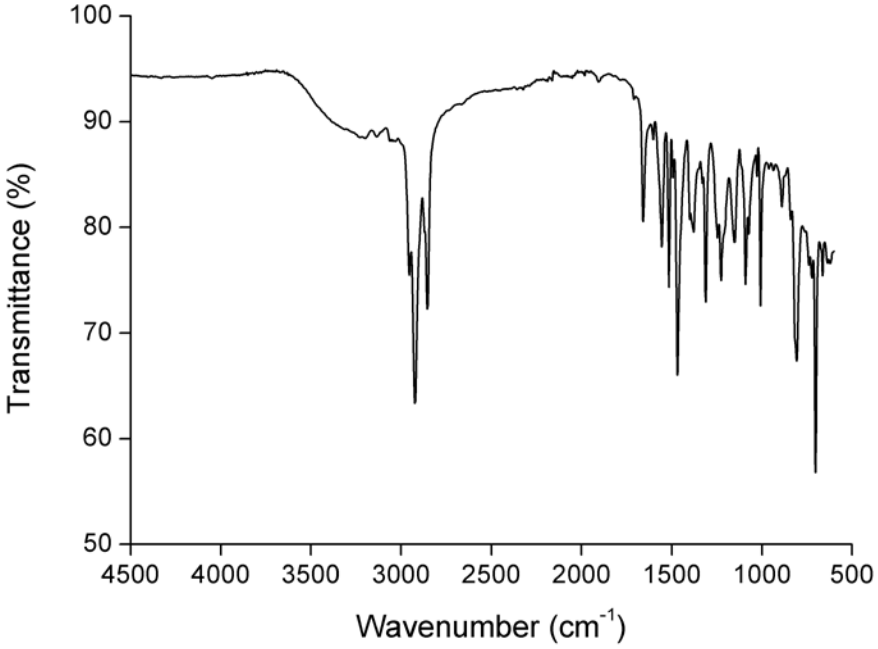
$[N_{8881}][Cl]$ + 20 wt% MTN



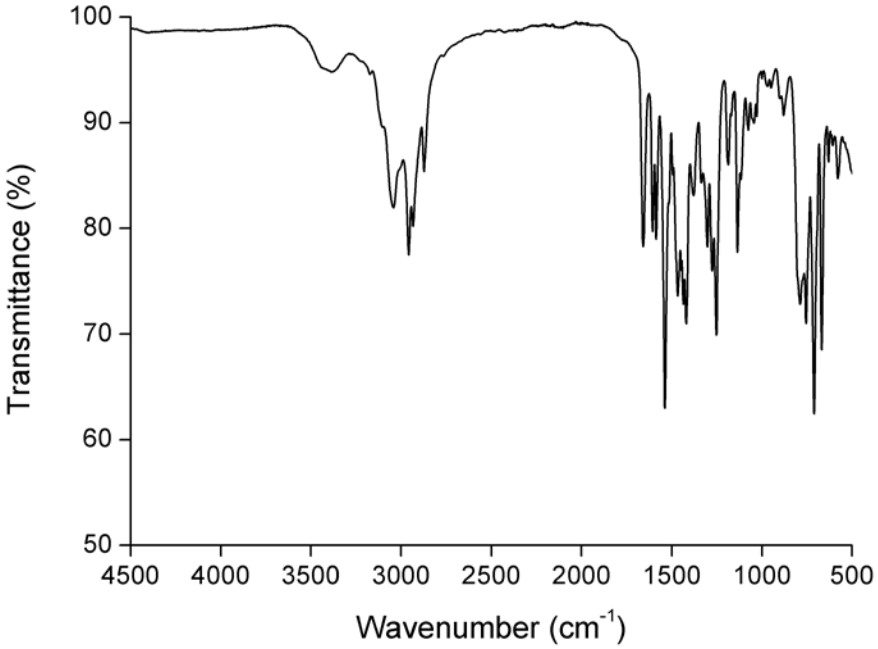
$[N_{8881}][Cl]$ + 20 wt% MTO



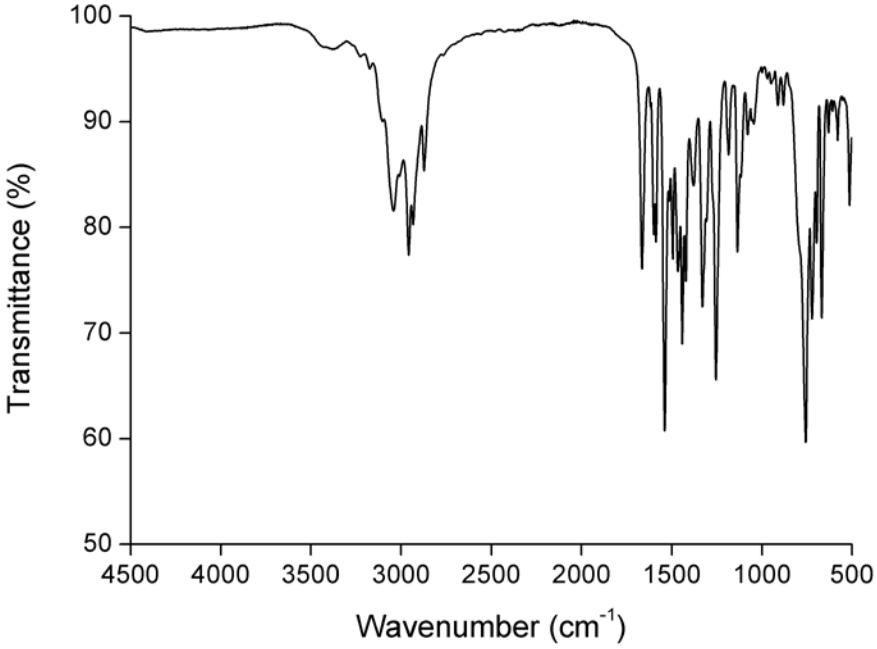
[N_{8881}][Cl] + 20 wt% PTN



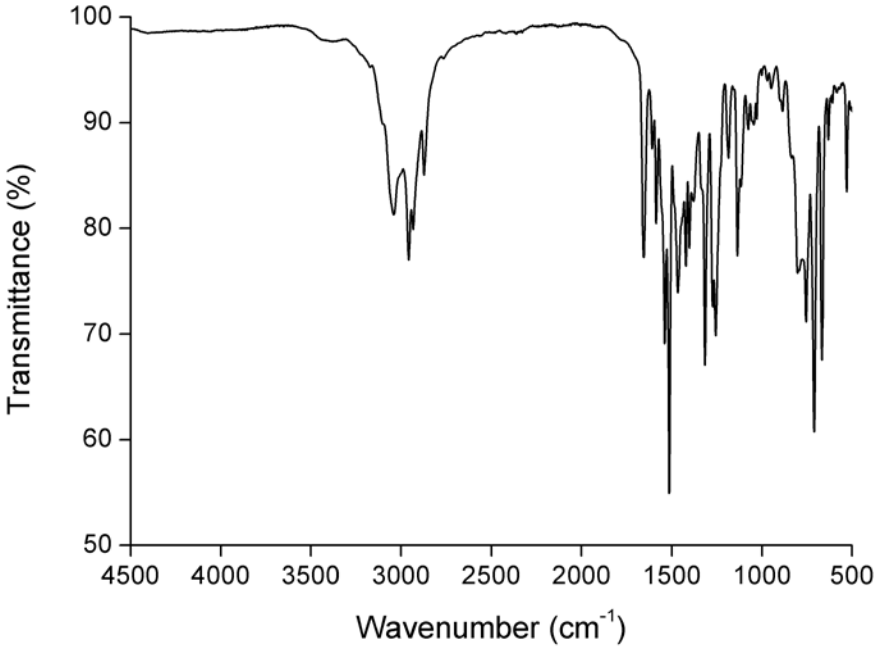
[2-Me-C_4MIM][Cl] + 20 wt% MTN



[2-Me-C_4MIM][Cl] + 20 wt% MTO



[2-Me-C_4MIM][Cl] + 20 wt% PTN



7. References

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