Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic supporting information

Ionic liquids as solvents for PPTA oligomers

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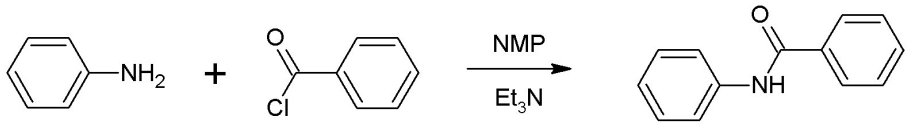
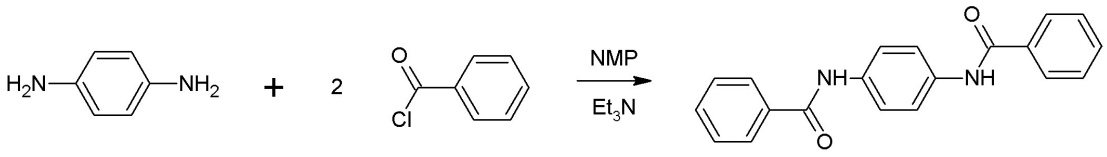
1. Synthesis of oligomers

1.1 Benzanilide (dimer)



Aniline (1.0 eq, 64.4 mmol, 6.0 g), triethylamine (1.2 eq, 77.3 mmol, 12.7 g) and dry *N*-methylpyrrolidone (20 ml) were added to a dried 3-neck flask flushed with argon. The flask was placed in an ice bath. With a syringe, benzoyl chloride (1.1 eq, 70.8 mmol, 10.0 g) was added dropwise. The reaction mixture was further stirred at room temperature for 2 hours after all the acid chloride was added. Water was added to precipitate the product. The product was filtrated off, washed with water, cold acetone and afterwards dried in a vacuum oven, yielding a white powder. Yield: 10.15 g, 80%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 10.2 (2H, s), 7.96 (2H, m), 7.79 (2H, m), 7.55 (3H, m), 7.36 (2H, m), 7.10 (1H, m). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 168.3, 139.1, 137.5, 131.8, 128.9, 128.5, 127.7, 123.8, 120.1. Elemental analysis for $C_{13}H_{11}NO$ (M= 197.2 g/mol) expected (%): C: 79.16, H: 5.62, N: 7.10; found (%)**:** C: 78.97, H: 6.01, N: 7.05. FTIR (ATR, ν_{max}/cm^{-1}): 3343 (NH-stretch), 1654 (amide carbonyl stretch), 1524 (N-H bend), 1436, 748, 689, 643. MS (ESI) (*m/z*): 197, 105, 77, 51. Melting point: 157 °C (lit. 160 °C[1]).

1.2 *N,N'-p*-phenylenebisbenzamide (trimer)

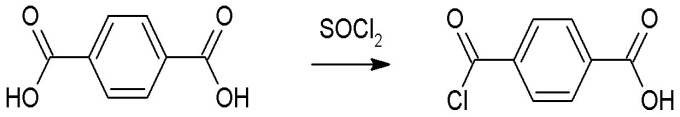


p-Phenylenediamine (1.0 eq, 37.0 mmol, 4.0 g) was added to a dried 3-neck flask flushed with argon. Dry *N*-methylpyrrolidone (60 ml) and triethylamine (2.2 eq, 81.3 mmol, 8.20 g) were added with a syringe. Benzoyl chloride (2.1 eq, 78.6 mmol, 10.92 g) was added dropwise while stirring in an ice bath. An additional stirring was done for 2 hours at room temperature. Water was added to precipitate the product. The product was filtrated off, washed with water, dichloromethane and acetone and dried in a vacuum oven, yielding a white solid. Yield: 11.51 g, 98%. ^{1}H NMR (300 MHz,

DMSO-d_6, δ): 10.25 (2H, s), 7.97 (4H, d, J = 7.1 Hz), 7.75 (4H, s), 7.55 (6H, m). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 167.7, 135.1, 131.8, 129.0, 127.9, 121.3. Elemental analysis for $C_{20}H_{16}N_2O_2$ (M= 316.4 g/mol) expected (%): C: 75.93, H: 5.10, N: 8.85; found (%)**:** C: 75.42, H: 5.53, N: 8.56. FTIR (ATR, ν_{max}/cm^{-1}): 3332 (NH-stretch), 1647 (amide carbonyl stretch), 1536 (N-H bend), 653. MS (ESI) (*m/z*): 316, 105, 77, 51. Melting point: 323 °C (lit. 315-345 °C[2]).

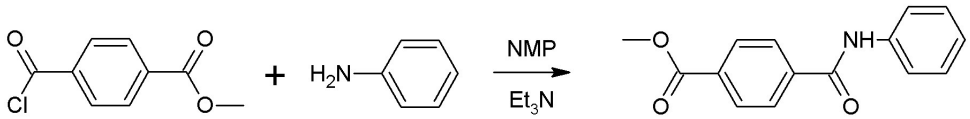
1.3 *N*-[4-(benzoylamino)phenyl]-*N*'-phenyl-1,4-benzenedicarboxamide (tetramer)

Step 1: Synthesis of *p*-(methoxycarbonyl)benzoyl chloride[3]



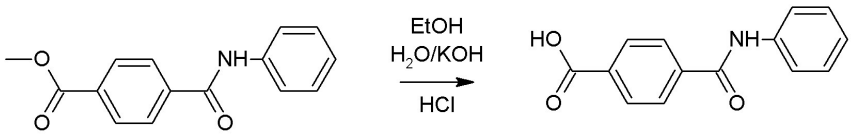
Mono-methylterephthalate (1.0 eq, 27.8 mmol, 5.0 g) was dissolved in thionyl chloride (58 ml). The reaction mixture was stirred for 45 min at 80 °C. The remaining thionyl chloride was evaporated to obtain the product as a slight, yellow solid. Yield: 5.5 g, 100%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 8.18 (4H, m), 4.00 (3H, s).

Step 2: Synthesis of 4-[(phenylamino)carbonyl]benzoic acid methyl ester



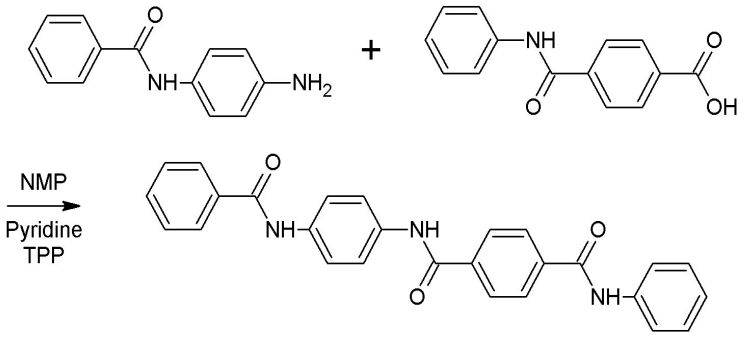
Aniline (1.0 eq, 10.95 mmol, 1.02 g), triethylamine (1.1 eq, 12.1 mmol, 1.22 g) and dry *N*-methylpyrrolidone (10 ml) were added to a dried 3-neck flask flushed with argon. To the solution was added with a syringe 4-(methoxycarbonyl)benzoyl chloride (1.1 eq, 12.1 mmol, 2.4 g) dissolved in *N*-methylpyrrolidone (10 ml). The product was precipitated by pouring the solution into water. The product was filtrated off and dried in a vacuum oven, yielding a white powder. Yield: 2.42 g, 86%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 10.45 (1H, s), 8.09 (4H, m), 7.79 (2H, m), 7.38 (2H, m), 7.13 (1H, m), 3.90 (3H, s).

Step 3: Synthesis of 4-[(phenylamino)carbonyl]benzoic acid[4]



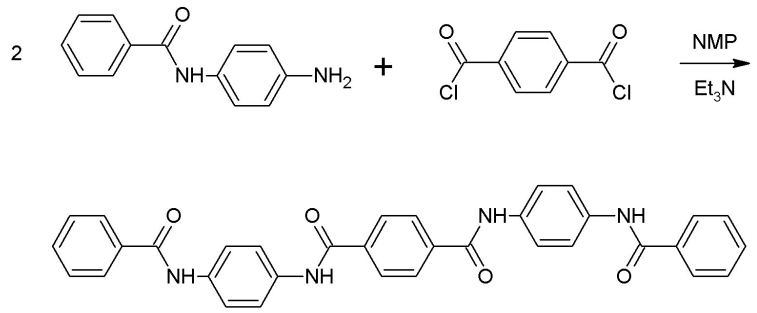
N-phenyl-4-carbomethoxybenzamide (1.0 eq, 9.5 mmol, 2.42 g), water (72 ml), ethanol (34 ml) and potassium hydroxide (2.2 eq, 20.9 mmol, 1.17 g) were added to a flask. The reaction mixture was refluxed for 24 hours. The solution was poured into water and HCl was added to neutralize the product. The product was filtrated off and washed with water and afterwards dried in a vacuum oven, yielding a white powder. Yield: 2.09 g, 91 %. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 10.45 (1H, s), 8.09 (4H, s), 7.79 (2H, m), 7.38 (2H, m), 7.13 (1H, m). Melting point: 317 °C (lit.[5] >300 °C).

Step 4: Synthesis of tetramer[6]



To a dried 3-neck flask flushed with argon were added 4-[(phenylamino)carbonyl]benzoic acid (1.0 eq, 2.1 mmol, 0.50 g) and *N*-(4-aminophenyl)benzamide (1.0 eq, 2.1 mmol, 0.44 g). With a syringe was added dry *N*-methylpyrrolidone (20 ml), pyridine (30 eq, 64.0 mmol, 5.18 g) and triphenylphosphite (1.06 eq, 2.20 mmol, 0.68 g). The reaction mixture was stirred under an inert atmosphere at 115 °C for 4 hours. Afterwards water was added to precipitate the product. The product was recrystallized from *N*-methylpyrrolidone, filtrated off and dried in a vacuum oven, yielding a white powder. Yield: 0.54 g, 58%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 10.4 (2H, s), 10.3 (1H, s), 8.12 (4H, s), 8.04 (2H, m), 7.84 (4H, s), 7.66 (3H, m), 7.43 (2H, m), 7.11 (1H, m). ^{1}H NMR (300 MHz, D_2SO_4, δ): 8.29 (4H, m), 7.93 (2H, t, J = 8.0 Hz), 7.88 (5H, m), 7.71 (2H, t, J= 8.0 Hz), 7.59 (4H, s). ^{13}C NMR (75 MHz, D_2SO_4, δ): 166.57, 164.71, 129.12, 128.94, 128.37, 127.76, 127.10, 124.40, 121.18, 120.60. FTIR (ATR, ν_{max}/cm^{-1}): 3332 (N-H stretch), 1646 (amide carbonyl stretch), 1543 (N-H bend). MS (EI) (*m/z*): 435, 224, 105, 77. Melting point: 367 °C.

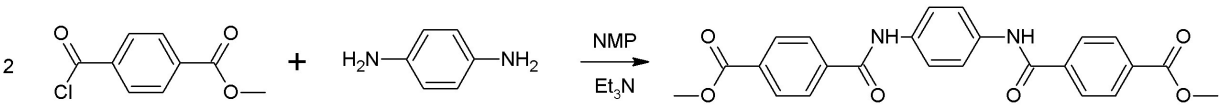
1.4 *N,N'*-Bis(4-benzamidophenyl)terephthalamide (pentamer)



To a dried 3-neck flask flushed with argon were added *N*-(4-aminophenyl)benzamide (2.0 eq, 1.41 mmol, 0.30 g), triethylamine (2.1 eq, 1.58 mmol, 0.16 g) and dry *N*-methylpyrrolidone (20 ml). The flask was placed in an ice bath. With a syringe, terephthaloyl chloride dissolved in dichloromethane (5 ml) was added dropwise. An additional stirring was done for 2 hours at 50 °C. Water was added to precipitate the product. The product was filtrated off, washed with water, dichloromethane and dried in a vacuum oven, yielding a white powder. Yield: 0.35 g, 83 %. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 10.4 (2H, s), 10.3 (2H, s), 8.10 (4H, s), 7.96 (4H, m), 7.78 (8H, s), 7.55 (6H, m). ^{1}H NMR (300 MHz, D_2SO_4, δ): 8.31 (4H, s), 7.96 (4H, t, J = 8.0 Hz), 7.91 (14H, m), 7.73 (4H, t, J = 8.0 Hz). ^{13}C NMR (75 MHz, D_2SO_4, δ): 189.5, 169.9, 167.8, 130.6, 129.2, 128.5, 126.9, 125.2, 122.2, 120.8. FTIR (ATR, ν_{max}/cm^{-1}): 3335 (N-H stretch), 1645 (amide carbonyl stretch), 1541 (N-H bend), 1518 (N-H bend), 825. Melting point: >450 °C.

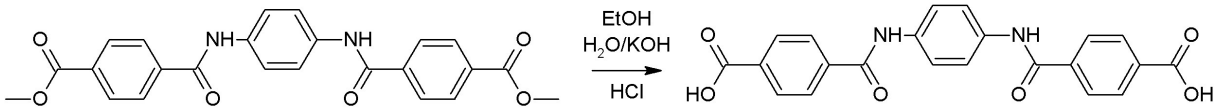
1.5 Heptamer

Step 1: Preparation of 4,4'-[1,4-phenylenebis(iminocarbonyl)]bis benzoic acid 1,1'-dimethyl ester (methylester end-functionalized trimer)



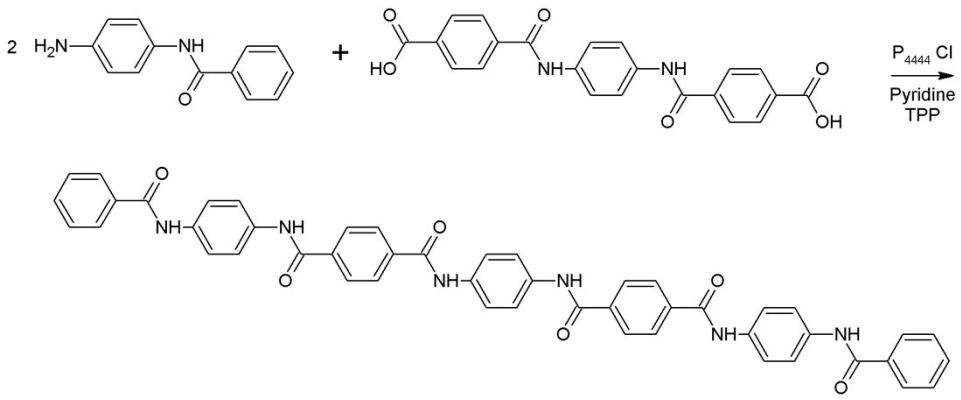
p-Phenylenediamine (1.0 eq, 7.31 mmol, 0.79 g) and triethylamine (2.2 eq, 15.8 mmol, 1.6 g) were dissolved in *N*-methylpyrrolidone (50 ml) in a dried 3-neck flask flushed with argon. The flask was placed in an ice bath. *p*-(Methoxycarbonyl)benzoyl chloride dissolved in dry *N*-methylpyrrolidone (20 ml) was added dropwise. The reaction mixture was further stirred for 1 h at 50 °C. Water was added to precipitate the product. The product was filtrated off, washed with water, dichloromethane and dried in a vacuum oven, yielding a white powder. Yield: 2.18 g, 74%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 10.48 (2H, s), 8.10 (8H, s), 7.78 (4H, s), 3.90 (6H, s). Melting point: 348 °C.

Step 2: Preparation of 4,4'-[1,4-phenylenebis(iminocarbonyl)]bis benzoic (carboxylic acid end-functionalized trimer) [3]



Methylester end-functionalized trimer (1.0 eq, 5.0 mmol, 2.0 g), ethanol (36 ml), water (17 ml) and potassium hydroxide (2.2 eq, 10.8 mmol, 0.6 g) were added to a flask. The reaction mixture was stirred for 10 hours. Afterwards the solution was poured into water. HCl was added to neutralize the compound. Product was filtrated off and washed with water and dried in a vacuum oven, yielding a white powder. Yield: 1.52 g, 86%. ^{1}H NMR: (300 MHz, DMSO-d_6, δ): 10.42 (2H, s), 8.04 (8H, s), 7.75 (4H, s). ^{1}H NMR (300 MHz, D_2SO_4, δ): 8.41 (4H, d, J = 7.7 Hz), 8.11 (4H, d, J= 7.7 Hz), 7.85 (4H, s). ^{13}C NMR (75 MHz, D_2SO_4, δ): 171.7, 168.2, 129.9, 129.1, 128.4, 128.2, 126.2, 122.1. Elemental analysis for $C_{22}H_{16}N_2O_6$ (M= 404.4 g/mol) expected (%): C: 65.34, H: 3.99, N: 6.93; found (%)**:** C: 65.21, H: 4.43, N: 6.90. FTIR (ATR, ν_{max}/cm^{-1}): 3327 (N-H stretch), 1745 (carboxylic acid stretch), 1612 (amide carbonyl stretch), 1510 (N-H bend). Melting point: 449 °C.

Step 3: Synthesis of heptamer



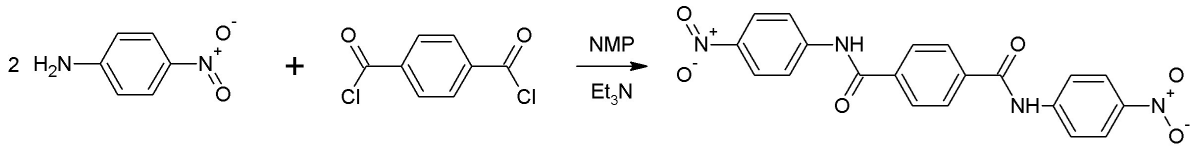
To a dried 3-neck flask flushed with argon were added *N*-(4-aminophenyl)benzamide (2.0 eq, 8.3 mmol, 1.76 g), carboxylic acid end-functionalized trimer (1.0 eq, 4.15 mmol, 1.68 g) and 12 g dry tetrabutylphosphonium chloride. With a syringe both pyridine (30 eq, 18.2 mmol, 1.44 g) and triphenylphosphite (2.1 eq, 8.72 mmol, 2.70 g) were added . The reaction mixture was stirred under an inert atmosphere at 110 °C for 24 hours. After the reaction water was added. The precipitate was filtrated off, washed with water and dimethyl sulfoxide and dried in a vacuum oven at 60 °C, resulting in a slight brown solid. Yield: 2.0 g, 58%. ^{1}H NMR (300 MHz, D_2SO_4, δ): 7.66 (10H, s), 7.26 (18H, m), 7.07 (4H, m). ^{13}C NMR (75 MHz, D_2SO_4, δ): 166.70, 164.82, 128.97, 128.37, 127.70, 127.10, 121.18. FTIR (ATR, ν_{max}/cm^{-1}): 3327 (N-H stretch), 1644 (amide carbonyl stretch), 1542 (N-H bend). Melting point: >450 °C.

1.6 COOH-trimer

See paragraph 3.5, synthetic steps 1 and 2.

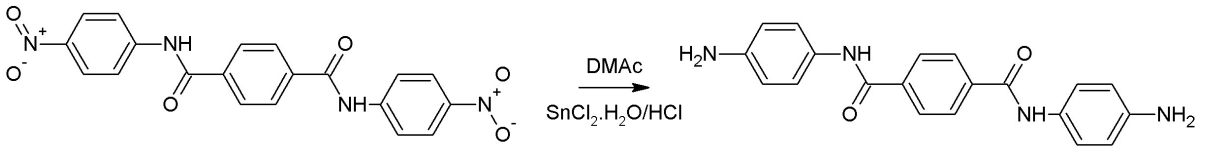
1.7 NH_2-trimer[3]

Step 1: synthesis of *N,N*-bis(4-nitrophenyl)-1,4-benzenedicarboxamide (nitro end-functionalized trimer)



p-Nitroaniline (2.0 eq, 27 mmol, 3.71 g) and triethylamine (2.1 eq, 29 mmol, 3.0 g) were dissolved in *N*-methylpyrrolidone (100 ml) in a dried 3-neck flask flushed with argon. The flask was placed in an ice bath. Terephthaloylchloride (1.1 eq, 15 mmol, 3.0 g) dissolved in dry *N*-methylpyrrolidone (20 ml) was added dropwise. The reaction mixture was further stirred for 1 h at 50 °C. Water was added to precipitate the product. The product was filtrated off, washed with water, dichloromethane and dried in a vacuum oven, yielding a slight yellow powder. Yield: 4.1 g, 75%. ^{1}H NMR: (300 MHz, DMSO-d_6, δ): 11.0 (2H, s), 8.31 (4H, d, J = 8.3 Hz), 8.16 (4H, s), 8.10 (4H, d, J = 8.3 Hz). Elemental analysis for $C_{20}H_{14}N_4O_6$ (M= 406.4 g/mol) expected (%): C: 59.12, H: 3.47, N: 13.79; found (%)**:** C: 59.32, H: 3.71, N: 13.48. FTIR (ATR, ν_{max}/cm^{-1}): 3350 (N-H stretch), 1665 (amide carbonyl stretch), 1553 (N-H bend), 1508 (assym. stretch NO_2), 1404, 1360 (sym. stretch NO_2), 890. Melting point: 366 °C. (lit.[9] 355 °C)

Step 2: Synthesis of *N,N*-bis(4-aminophenyl)-1,4-benzenedicarboxamide



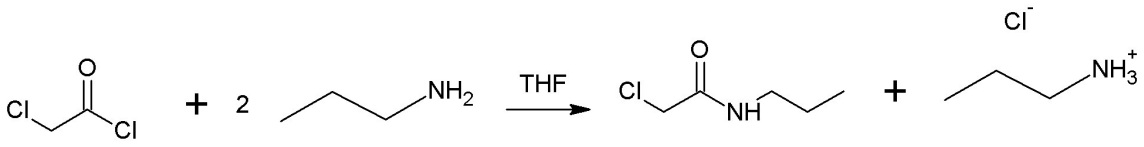
Nitro-end-functionalized trimer (1 eq, 8.6 mmol, 3.5 g) was added to a dried 3-neck flask flushed with argon. Dimethylacetamide (35 ml) was added with a syringe. Tin chloride dihydrate (7.2 eq, 62 mmol, 14 g) was dissolved in 25 ml HCl (37%) and added to the flask with a syringe. The reaction mixture was refluxed for 15h at 100 °C under argon atmosphere. Afterwards, the product was filtered off and washed with water, saturated sodium hydrogen carbonate and again water. The filtrate was dried in a vacuum oven, yielding a bright yellow powder. Yield: 3.01 g, 100 %. ^{1}H NMR: (300 MHz, DMSO-d_6, δ): 10.0 (2H, s), 8.03 (4H, s), 7.39 (4H, d, J = 7.2 Hz), 6.56 (4H, d, J = 7.2 Hz), 4.97 (4H, s). ^{13}C NMR (75 MHz, D_2SO_4, δ): 172.19, 134.44, 132.40, 131.05, 129.90, 129.75, 126.92, 125.95. Elemental analysis for $C_{20}H_{14}N_4O_2$ (M= 346.4 g/mol) expected (%): C: 69.35, H: 5.24, N: 16.17; found (%)**:** C: 68.92, H:

5.22, N: 16.26. FTIR (ATR, ν_{max}/cm^{-1}): 3350 (N-H stretch), 1639 (amide carbonyl stretch), 1530 (N-H bend), 890. Melting point: 366 °C. (lit.[9] 355 °C)

2. Synthesis of ionic liquids

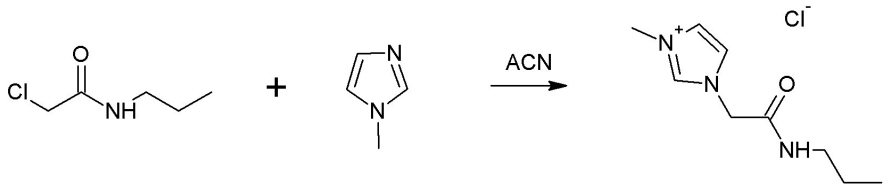
2.1 3-Methyl-1-*N*-propyl-acetamideimidazolium chloride, [$C_1IMCH_2CONHPr$] [Cl]

Step 1: Synthesis of 2-chloro-*N*-propylacetamide[7]



2-Chloroacetyl chloride (1.0 eq, 26.6 mmol, 3.0 g) was dissolved in dry tetrahydrofuran (20 ml) in a dried 3-neck flask flushed with argon. The flask was placed in an ice bath. With a syringe, propylamine (2.0 eq, 53 mmol, 3.13 g) was added dropwise. The reaction was further stirred at room temperature for 12 h. Afterwards, the formed amine salt was filtrated off and the solvent evaporated. A yellow liquid was obtained. Yield: 5.1 g, 87%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 4.10 (2H, s), 3.21 (2H, t, J = 7.0 Hz), 1.53 (2H, q, J_1 = 7.2 Hz and J_2 = 7.0 Hz), 0.87 (3H, t, J = 7.2 Hz).

Step 2: Quaternization reaction

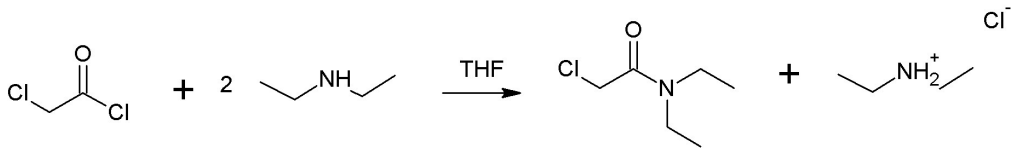


2-Chloro-*N*-propylacetamide (1.0 eq, 20.1 mmol, 3,0 g) was dissolved in acetonitrile (30 ml). To this solution, 1-methylimidazole (1.0 eq, 20.1 mmol, 1.65 g) was added. The reaction mixture was refluxed for 24 h at 82 °C. The solvent was removed by evaporation and the excess acetamide was removed by water/dichloromethane extraction. The product was obtained by drying the water layer

and by further drying on a vacuum line. A very viscous orange liquid was obtained. Yield: 4.1 g, 88%. ^{1}H NMR (300 MHz, D_2O, δ): 8.71 (1H, s), 7.41 (1H, s), 7.39 (1H, s), 5.00 (2H, s), 3.86 (3H, s), 3.13 (2H, t, J = 7.0 Hz), 1.46 (2H, m), 0.81 (3H, t, J = 7.5 Hz). ^{13}C NMR (75 MHz, D_2O, δ): 167.3, 124.4, 123.8, 50.7, 41.5, 35.9, 21.7, 10.6. Elemental analysis for $C_9H_{16}N_3OCl$ (M= 217.7 g/mol) expected (%): C: 42.66, H: 7.41, N: 19.30; found (%)**:** C: 42.93, H: 7.72, N: 19.78. FTIR (ATR, ν_{max}/cm^{-1}): 3065 (N-H stretch band), 2964 (C-H stretch), 1673 (amide carbonyl stretch), 1563 (N-H bend), 1174, 622.

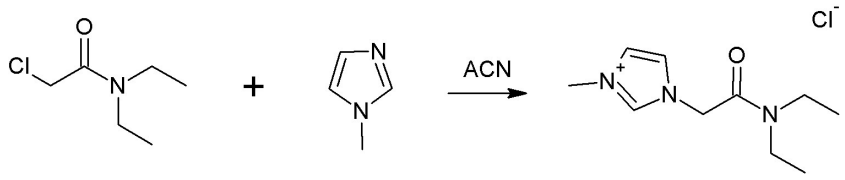
2.2 3-Methyl-1-*N,N*-diethyl-acetamideimidazolium chloride, [$C_1IMCH_2CON(Et)_2$][Cl]

Step 1: Synthesis of 2-chloro-*N,N*-diethylacetamide[8]



2-Chloroacetyl chloride (1.0 eq, 53 mmol, 5.99 g) was dissolved in tetrahydrofuran (40 ml) in a dried 3-neck flask flushed with argon. The flask was placed in an ice bath. With a syringe diethylamine (2.0 eq, 106 mmol, 7.90 g) was added dropwise. The reaction was further stirred at room temperature for 2 h. Afterwards the formed ammonium chloride was filtrated off and the solvent evaporated. A yellow liquid was obtained. Yield: 11.9 g, 87%. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 4.07 (2H, s), 3.38 (4H, m), 1.29 (3H, t, J = 7.1 Hz), 1.15 (3H, t, J = 7.1 Hz).

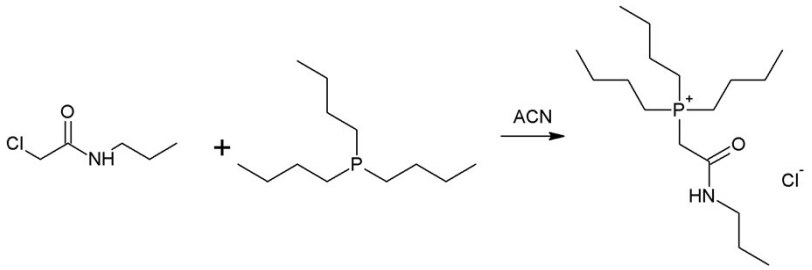
Step 2: Quaternization reaction



2-Chloro-*N,N*-diethylacetamide (2.0 g, 13 mmol, 1.1 eq) was dissolved in acetonitrile (30 ml). To this solution *N*-methylimidazole (1 eq, 12 mmol, 1.0 g) was added. The reaction mixture was refluxed for 24 h at 82 °C. The solvent was removed by evaporation and the excess of acetamide was removed by

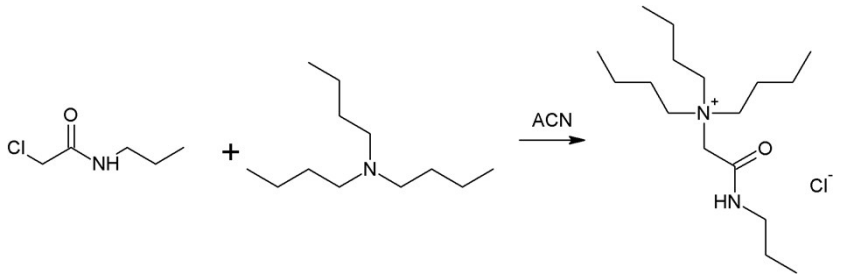
water/dichloromethane extraction. The product was obtained by drying the water layer via evaporation and further drying on vacuum line. An orange glass was obtained. Yield: 2.73 g, 91%. ^{1}H NMR (300 MHz, D_2O, δ): 8.63 (1H, s), 7.40 (1H, s), 7.31 (1H, s), 5.19 (s, 2H), 3.84 (s, 3H), 3.31 (4H, J = 7.5 Hz), 1.01 (3H, t, J = 7.1 Hz), 0.93 (3H, t, J = 7.1 Hz). ^{13}C NMR (75 MHz, D_2O, δ): 166.8, 138.0, 124.2, 123.7, 50.1, 41.9, 41.5, 36.0, 13.0, 12.2. Elemental analysis for $C_{10}H_{18}N_3OCl + 1H_2O$ (M= 247.7 g/mol) expected (%): C: 48.09, H: 8.07, N: 16.83; found (%)**:** C: 48.53, H: 8.32, N: 17.06. FTIR (ATR, ν_{max}/cm^{-1}): 2973 (C-H stretch), 1643 (amide carbonyl stretch), 1430 (C-N stretch), 1145, 623.

2.3 Tributyl-*N*-propylacetamidephosphonium chloride, [$P_{444}CH_2CONHPr$][Cl]



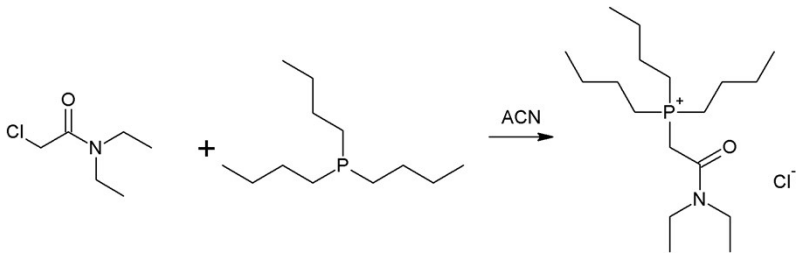
2-chloro-*N*-propylacetamide (1.1 eq, 14 mmol, 1.83 g) and acetonitrile (30 ml) were added with a syringe to a 3-neck flask purged with argon. Tributylphosphine (1.0 eq, 15 mmol, 3.0 g) was added. The reaction mixture was refluxed under argon atmosphere for 24 h at 82 °C. The solvent was removed by evaporation and the excess of acetamide was removed by water/dichloromethane extraction. The product was obtained by drying the water layer via evaporation and further drying on a vacuum line. A slight yellow solid was obtained. Yield: 3.12 g, 65%. ^{1}H NMR (300 MHz, D_2O, δ): 3.36 (2H, d, J = 14.0 Hz), 3.16 (2H, t, J = 6.9 Hz), 2.25 (6H, m), 1.50 (14H), 0.89 (12H, m). ^{13}C NMR (75 MHz, D_2O, δ): 41.7, 23.1, 22.7, 21.6, 18.8, 18.1, 12.5, 10.9. ^{31}P NMR (242,92 MHz, D_2O): δ (ppm) 34.90. Elemental analysis for $C_{17}H_{37}NOClP$ (M= 337.9 g/mol) expected (%): C: 60.43, H: 11.04, N: 4.15; found (%)**:** C: 60.41, H: 11.08, N: 4.03. FTIR (ATR, ν_{max}/cm^{-1}): 2961 (C-H stretch), 1668 (amide carbonyl stretch), 1549 (N-H bend), 918. Melting point: 82 °C.

2.4 Tributyl-*N*-propylacetamideammonium chloride, [$N_{444}CH_2CONHPr$][Cl]



N-Propyl-2-chloroacetamide (1.1 eq, 16 mmol, 2.2 g) was dissolved in acetonitrile (30 ml). Tributylamine (1.0 eq, 3.0 g, 15 mmol) was added. The reaction mixture was refluxed for 24 h at 82 °C. The solvent was removed by evaporation and the excess of acetamide was removed by water/dichloromethane extraction. The product was obtained by drying the water layer via evaporation and further drying on a vacuum line. An orange solid was obtained. Yield: 2.76 g, 53%. ^{1}H NMR (300 MHz, D_2O, δ): 3.91 (2H, s), 3.36 (6H, m), 3.11 (2H, t, J = 6.6 Hz), 1.62 (6H, m), 1.45 (2H, m), 1.29 (6H, m), 0.86 (12H, m). ^{13}C NMR (75 MHz, D_2O, δ): 165.2, 59.8, 57.8, 41.3, 23.4, 21.6, 19.1, 12.8, 10.7. Elemental analysis for $C_{17}H_{37}N_2OCl$ (M= 320.9 g/mol) expected (%): C: 63.62, H: 11.62, N: 8.73; found (%)**:** C: 63.41, H: 11.13, N: 8.46. FTIR (ATR, ν_{max}/cm^{-1}): 2962 (C-H stretch), 1668 (amide carbonyl stretch), 1548 (N-H bend), 918. Melting point: 78 °C.

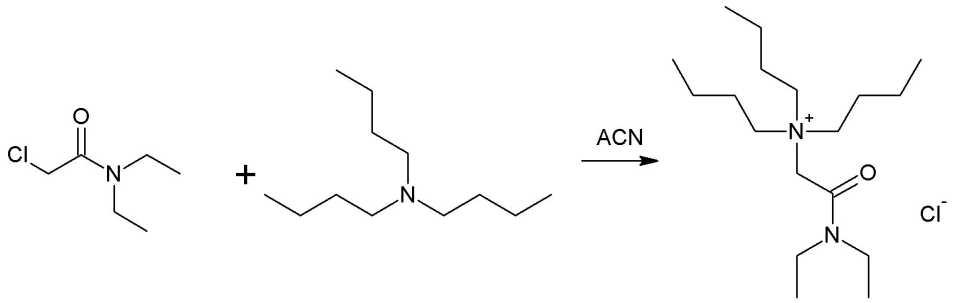
2.5 Tributyl-*N,N*-diethylacetamidephosphonium chloride, [$P_{444}CH_2CON(Et)_2$][Cl]



N,N-diethyl-2-chloroacetamide (1.1 eq, 12 mmol, 1.8 g) and acetonitrile (30 ml) were added with a syringe to a 3-neck flask purged with argon. Tributylphosphine (1.0 eq, 11 mmol, 2.2 g) was added. The reaction mixture was refluxed under argon atmosphere for 24 h at 82 °C. The solvent was

removed by evaporation and the excess of acetamide was removed by water/dichloromethane extraction. The product was obtained by drying the water layer via evaporation and further drying on a vacuum line. A transparent liquid was obtained. Yield: 3.04 g, 83%. ^{1}H NMR (300 MHz, D_2O, δ): 3.60 (2H, d, J = 14 Hz), 3.33 (4H, m), 2.20 (6H, m), 1.42 (12H, m), 1.15 (3H, J= 7.1 Hz, t), 1.06 (3H, J= 7.1 Hz, t), 0.84 (9H, J= 7.1 Hz, t). ^{13}C NMR (75 MHz, D_2O, δ): 165.2, 43.8, 41.2, 23.2, 23.0, 19.2, 18.6, 13.2, 12.6. ^{31}P NMR (242,92 MHz, D_2O): δ (ppm) 34.75. Elemental analysis for $C_{18}H_{39}NOPCl$ + 1 H_2O (M= 369.9 g/mol) expected (%): C: 58.44, H: 11.17, N: 3.79; found (%)**:** C: 58.62, H: 11.03, N: 3.96. FTIR (ATR, ν_{max}/cm^{-1}): 2960 (C-H stretch), 1629 (amide carbonyl stretch), 1463 (C-N stretch), 918.

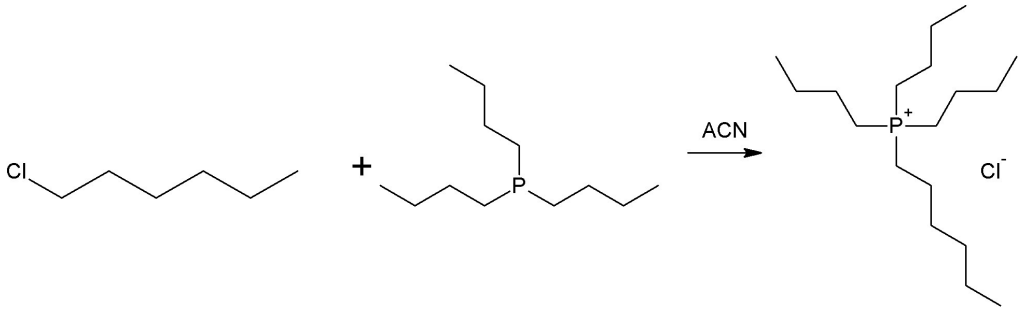
2.6 Tributyl-*N,N*-diethylacetamideammonium chloride, [$N_{444}CH_2CON(Et)_2$][Cl]



N,N-diethyl-2-chloroacetamide (1.1 eq, 18 mmol, 2.6 g) was dissolved in acetonitrile (30 ml). Tributylamine (1 eq, 16 mmol, 3 g) was added. The reaction mixture was refluxed for 24 h at 82 °C. The solvent was removed by evaporation and the excess of acetamide was removed by water/dichloromethane extraction. The product was obtained by drying the water layer via evaporation and further drying on a vacuum line. An orange, viscous liquid was obtained. Yield: 2.54 g, 45 %. ^{1}H NMR (300 MHz, D_2O, δ): 3.90 (2H, s), 3.23 (6H, m), 3.06 (4H, m), 1.35 (6H, m), 1.04 (6H, m), 0.84 (6H, J= 6.7 Hz), 0.62 (9H, m). ^{13}C NMR (75 MHz, D_2O, δ): 164.1, 60.0, 52.7, 42.0, 25.1, 23.7, 19.0, 12.8. Elemental analysis for $C_{18}H_{39}N_2OCl$ + 2 H_2O (M= 405.9 g/mol) expected (%): C: 58.27, H: 11.68, N: 7.55; found (%)**:** C: 58.57, H: 12.03, N: 7.48. FTIR (ATR, ν_{max}/cm^{-1}): 2961 (C-H stretch), 1645 (amide carbonyl stretch), 1461 (C-N stretch), 875.

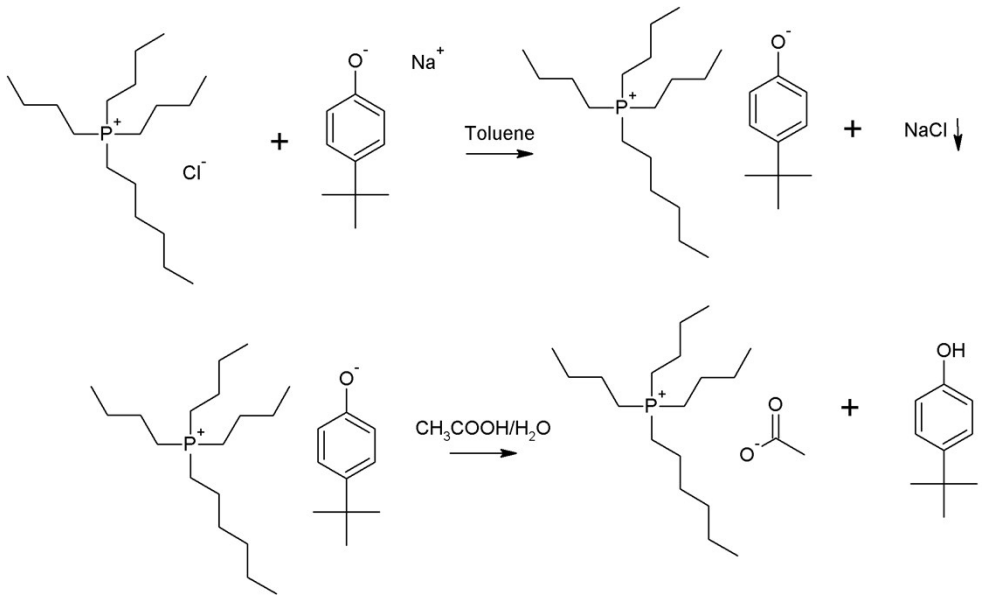
2.7 Tributylhexylphosphonium acetate, $[P_{4446}][CH_3COO]$

Step 1: Synthesis of tributylhexylphosphonium chloride



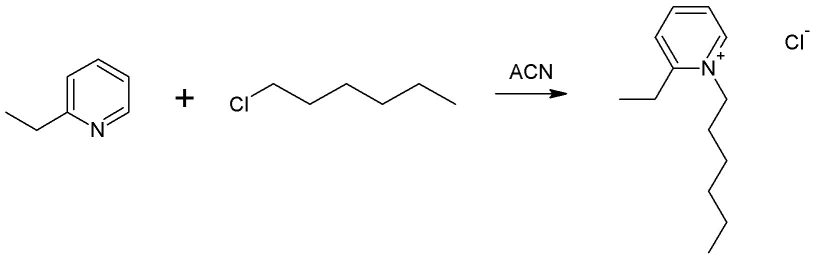
1-chlorohexane (1.2 eq, 18 mmol, 2.2 g) and acetonitrile (20 ml) were added with a syringe to a 3-neck flask purged with argon. Tributylphosphine (1 eq, 15 mmol, 3.0 g) was added. The reaction mixture was refluxed under argon atmosphere for 48 h at 82 °C. The solvent was removed by evaporation. The product was further purified on a Schlenk line at 110 °C to allow the removal of excess 1-chlorohexane. A transparent liquid was obtained. Yield: 3.1 g, 87%. ^{1}H NMR (300 MHz, D_2O, δ): 2.06 (8H, m), 1.35 (20H, m), 0.81 (12H, m). ^{13}C NMR (75 MHz, D_2O, δ): 26.1, 25.2, 23.2, 22.8, 22.7, 21.7, 18.0, 17.3, 12.8, 12.5. ^{31}P NMR (242.92 MHz, D_2O): δ (ppm) 33.87. Elemental analysis for $C_{18}H_{40}N_0PCl$ + 1 H_2O (M= 340.9 g/mol) expected (%): C: 63.41, H: 12.42, N: 0; found (%)**:** C: 62.98, H: 12.15, N: 0.

Step 2: Metathesis reaction[10]



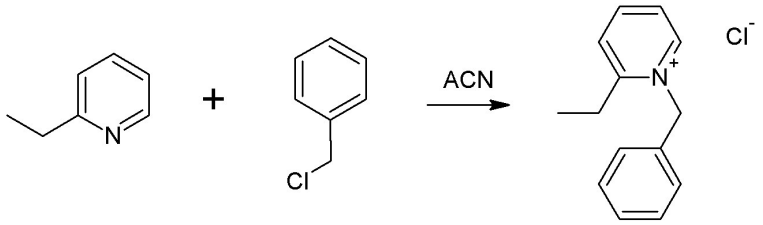
Tributylhexylphosphonium chloride (1.0 eq, 4 g, 0.012 mol) and *p*-tert-butylphenolate (2.13 g, 1.0 eq, 12 mmol) were dried beforehand and added to a dry 3-neck flask flushed with argon. Dry toluene (100 ml) was added with a syringe to the flask. The reaction mixture was stirred for 18 h at room temperature. The formed precipitate (NaCl) was filtered off through Celite. To the filtrate, acetic acid (3 eq, 0.036 mol, 2.2 g) in 200 ml water was added and the mixture was stirred vigourously for 4 h. The organic phase was washed with 50 ml water. All water phases were collected and dried to obtain the product as a brown liquid. Yield: 2.8 g, 82%. ^{1}H NMR (300 MHz, D_2O, δ): 2.13 (8H, m), 1.93 (3H, s), 1.43 (20H, m), 0.90 (12H, m). ^{13}C NMR (75 MHz, D_2O, δ): 178.8, 30.2, 29.4, 23.4, 23.2, 22.7, 21.7, 21.6, 17.9, 17.3, 13.2, 12.5. ^{31}P NMR (242.92 MHz, D_2O): δ (ppm) 34.10. Elemental analysis for $C_{20}H_{43}N_0O_2P$ + 2 H_2O (M= 382.57 g/mol) expected (%): C: 62.79, H: 12.38, N: 0; found (%)**:** C: 62.43, H: 12.61, N: 0. FTIR (ATR, ν_{max}/cm^{-1}): 1602 (C=O of carboxylate).

2.8 2-ethyl-1-hexylpyridinium chloride [C_2C_6Pyr][Cl]



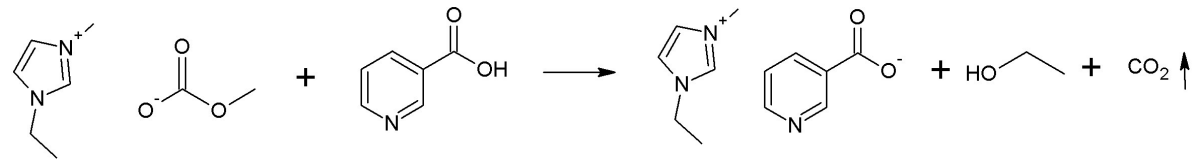
2-ethylpyridine (1.0 eq, 37.3 mmol, 4.0 g) was dissolved in acetonitrile (30 ml). To this solution 1-chlorohexane (1.0 eq, 22 mmol, 1.65 g) was added. The reaction mixture was refluxed for 24 h at 82 °C. The solvent and excess alkylchloride were removed by evaporation. The product was further dried on a vacuum line. Yield: 6.35 g, 71%. ^{1}H NMR (300 MHz, D_2O, δ): 9.89 (2H, d, J = 6.6 Hz), 9.13 (2H, d, J = 6.6 Hz), 5.79 (2H, t, J = 7.3 Hz), 4.20 (2H, q, J_1 = 7.6 and J_2 = 7.5 Hz), 3.22 (2H, m), 2.55 (9H, m), 2.08 (3H, m). ^{13}C NMR (75 MHz, D_2O, δ): 12.7, 29.8, 54.6, 128.2, 128.4, 128.7, 129.4, 129.6 144.8, 145.3. Elemental analysis for $C_{13}H_{22}NCl$ (M= 227.7 g/mol) expected (%): C: 68.55, H: 9.74, N: 6.15; found (%)**:** C: 68.21, H: 9.69 N: 6.51. FTIR (ATR, ν_{max}/cm^{-1}): 3436, 2977, 736. Melting point: 91 °C.

2.9 2-Ethyl-1-benzylpyridinium chloride [BenzylC_2Pyr][Cl]



Benzylchloride (1 eq, 16 mmol, 2.0 g) was dissolved in acetonitrile (20 ml). To the solution 2-ethylpyridine (1.1 eq, 1.9 g, 18 mmol) was added. The reaction mixture was refluxed for 24 h at 82 °C. The solvent and excess 2-ethylpyridine were removed by evaporation. The product was obtained by further drying on a vacuum line, yielding a brown solid. Yield: 66%, 2.44 g. ^{1}H NMR (300 MHz, D_2O, δ): 8.70 (1H, d, J = 5.0 Hz), 8.41 (1H, t, J = 7.0 Hz), 7.94 (1H, d, J = 7.0 Hz), 7.82 (1H, m), 7.38 (3H, s), 7.16 (2H, s), 5.77 (2H, s), 3.02 (2H, q, J= 7.0 Hz), 1.22 (3H, t, J= 7.0 Hz). ^{13}C NMR (75 MHz, D_2O, δ): 160.2, 146.4, 145.0, 132.8, 130.8, 129.1, 128.7, 127.6, 125.9, 60.6, 25.8, 11.1. Elemental analysis for $C_{14}H_{16}NCl$ (M= 233.7 g/mol) expected (%): C: 71.94, H: 6.90, N: 5.99; found (%)**:** C: 71.81, H: 9.69 N: 6.51. FTIR (ATR, ν_{max}/cm^{-1}): 1630, 1440, 762. Melting point: 112 °C.

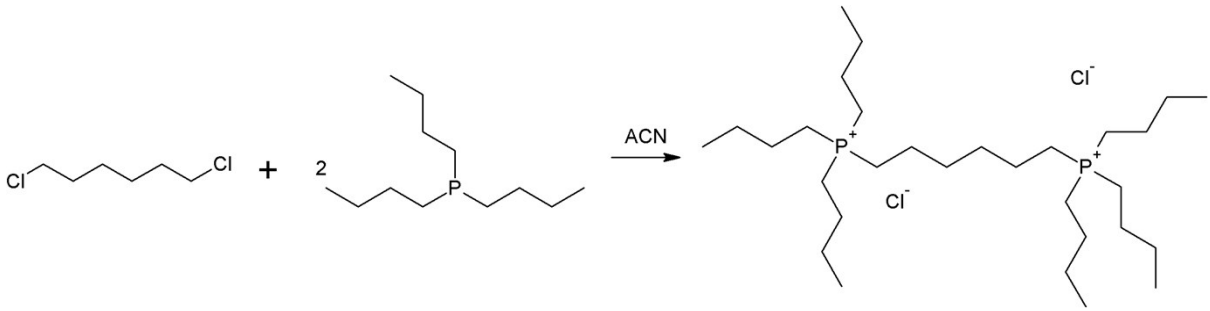
2.10 1-Ethyl-3-methylimidazolium nicotinate, [C_2MIM][Nicot]



A 30 wt% mixture of 1-ethyl-3-methylimidazolium methylcarbonate (1.0 eq, 12.2 mmol, 7.57 g) was added to a flask. To the flask nicotinic acid (1.0 eq, 12.2 mmol, 2.31 g) dissolved in methanol was added dropwise. The reaction mixture was stirred for 2 h under vacuum to release the formed CO_2. The methanol was evaporated and the resulting product further dried on a vacuum line, resulting in a dark red liquid. Yield: 2.13 g, 75%. ^{1}H NMR (300 MHz, D_2O, δ): 8.82 (1H, s), 8.57 (1H, s), 8.50 (1H, d, J = 5.0 Hz), 8.15 (1H, d, J = 7.9 Hz), 7.42 (1H, dd, J_1 = 5.1 Hz, J_2 = 7.9 Hz), 7.35 (1H, s), 7.29 (1H, s), 4.10 (2H, q, J = 7.4 Hz), 3.77 (3H, s), 1.38 (3H, t, J = 7.4 Hz). ^{13}C NMR (75 MHz, D_2O, δ): 173.2, 150.8, 149.6,

138.2, 135.6, 133.9, 124.0, 123.4, 122.3, 44.9, 35.7, 14.5. Elemental analysis for $C_{12}H_{15}N_3O_2$ + 2 H_2O (M= 233.3 g/mol) expected (%): C: 53.32, H: 7.46, N: 15.55; found (%): C: 53.91, H: 7.81, N: 15.28. FTIR (ATR, vmax/cm-1): 1602 (C=O of carboxylate), 826, 756.

2.11 1,6-Hexanediylbis(tributyl)phosphonium dichloride, [Cl][P_{444}-C_6H_{12}-P_{444}][Cl]



1,6-Dichlorohexane (1.0 eq, 14 mmol, 2.2 g) and acetonitrile (30 ml) were added with a syringe to a 3-neck flask purged with argon. Tributylphosphine (2.1 eq, 30 mmol, 6.0 g) was added. The reaction mixture was refluxed under argon atmosphere for 48 h at 82 °C. The solvent was removed by evaporation. The product was further purified on a Schlenk line at 110 °C to allow the removal of excess tributylphosphine and formed tributylphosphine oxide, resulting in slightly yellow solid. Yield: 83%, 6.60 g. ^{1}H NMR (300 MHz, D_2O, δ): 2.05 (18H, m), 1.39 (32H, m), 0.81 (18H, m). ^{13}C NMR (75 MHz, D_2O, δ): 23.4, 23.2, 22.7, 22.6, 17.9, 17.3, 12.5. Elemental analysis for $C_{30}H_{66}N_0P_2Cl_2$ (MW= 559.7 g/mol) expected (%): C: 64.38, H: 11.89, N: 0; found (%): C: 63.89, H: 12.35, N: 0. FTIR (ATR, vmax/cm^{-1}): 2958, 2902 and 2870 (C-H stretching), 1461, 720. Melting point: 108 °C.

3. Schemes from results and discussion

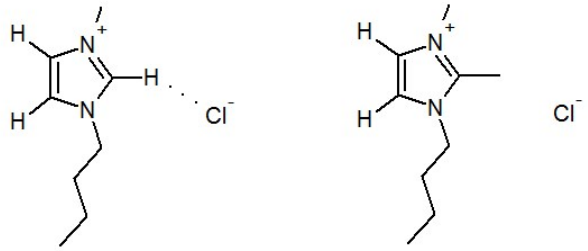


Fig. S1 Left: The structure of 1-butyl-3-methylimidazolium chloride with the hydrogen atoms on the heteroaromatic ring displayed. The dashed line represents a hydrogen bond interaction. Right: The structure of 1-butyl-2,3-dimethylimidazolium chloride.

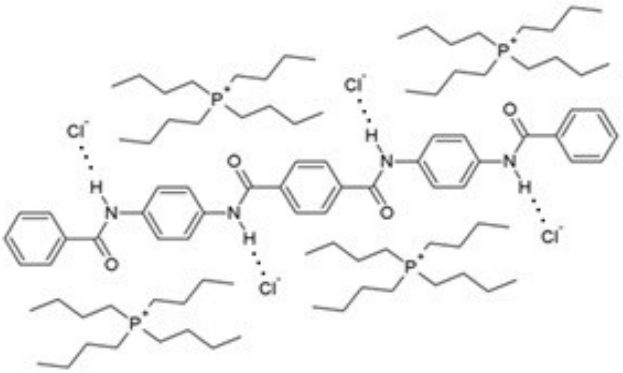


Fig. S2 Suggested interaction scheme of tetrabutylphosphonium chloride with the PPTA pentamer model compound.

4. Extended solubility tests

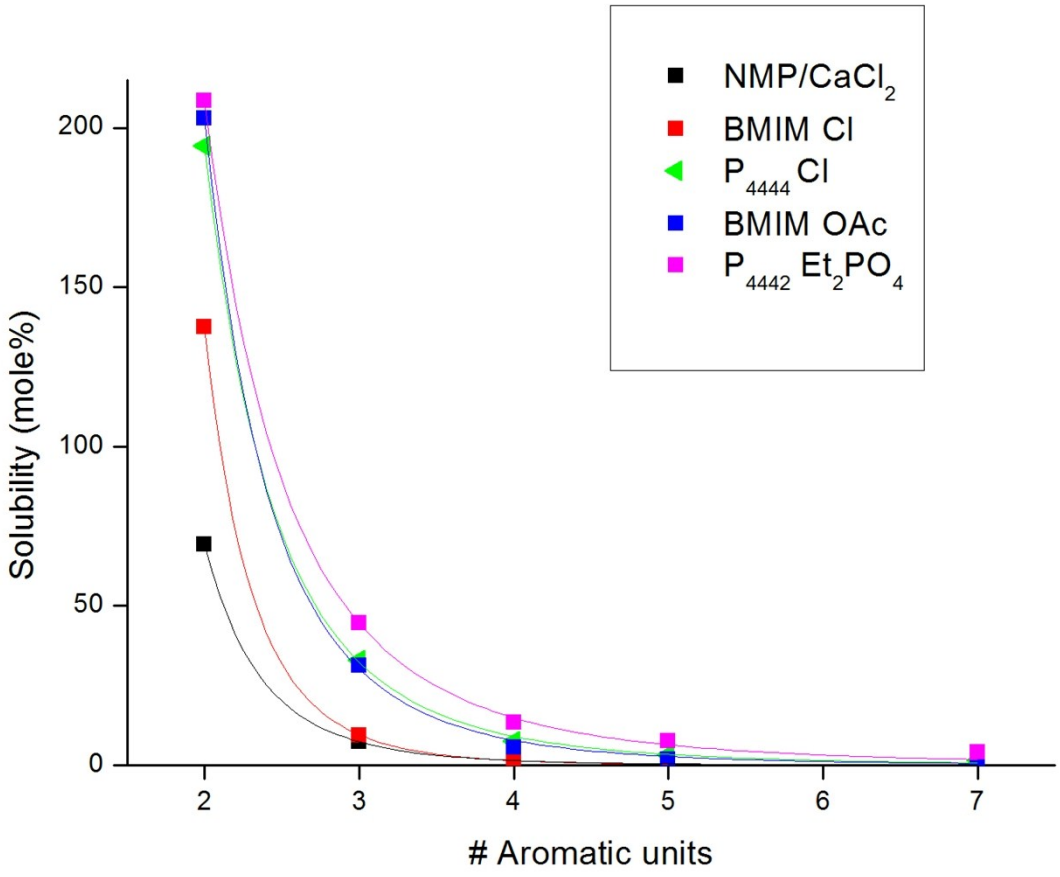


Fig. S3 Graphical representation of the solubility data of all the different oligomers in NMP/10wt% $CaCl_2$ (■), 1-butyl-3-methylimidazolium chloride (●), tetrabutylphosphonium chloride (▲),1-ethyl-3-methylimidazolium acetate (▼) and tributylethylphosphonium diethylphosphate (►).

The data points of the solubility of the dimer are omitted from this graph in order to have a more detailed look into solvent behavior at longer oligomer chains.

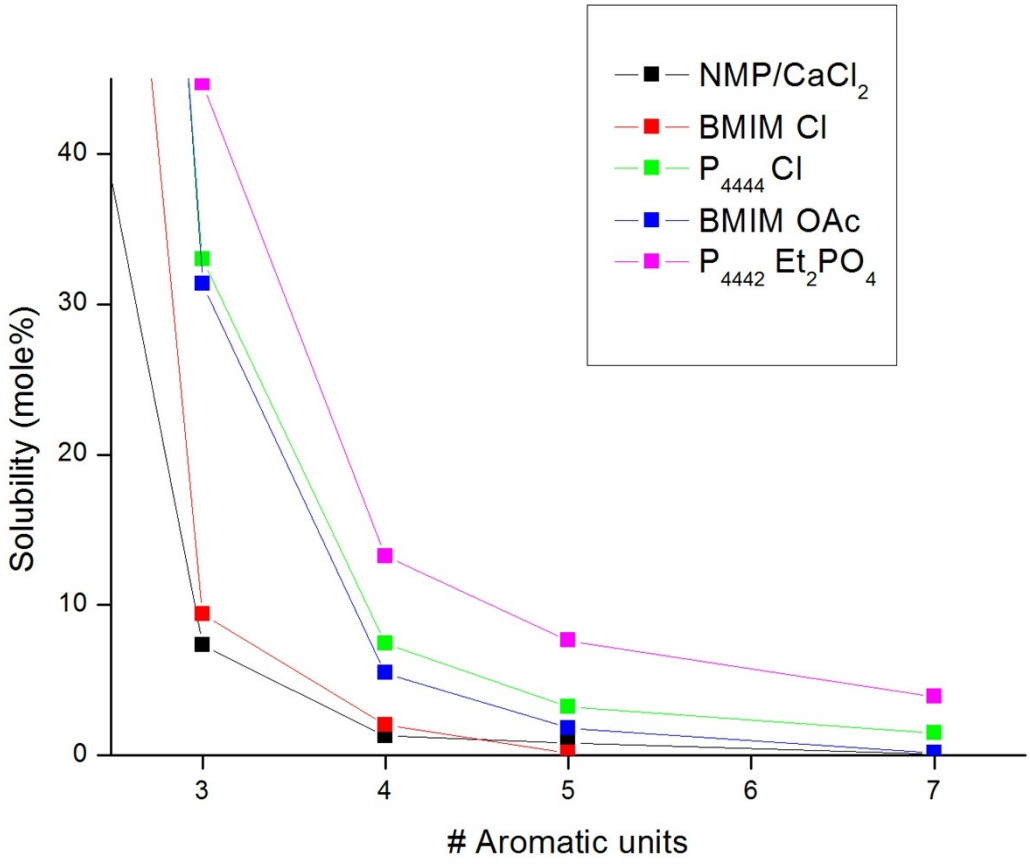


Fig. S4 Graphical representation of the solubility data of all the different oligomers in NMP/10wt% $CaCl_2$ (■), 1-butyl-3-methylimidazolium chloride (●), tetrabutylphosphonium chloride (▲), 1-ethyl-3-methylimidazolium acetate (▼) and tributylethylphosphonium diethylphosphate (►).

5. ^{13}C NMR spectra from the dissolution studies

^{13}C NMR (100 MHz) spectra with DMSO-d_6 as external reference for the dissolution studies were recorded with a Bruker Avance 400 MHz spectrometer at 70 °C.

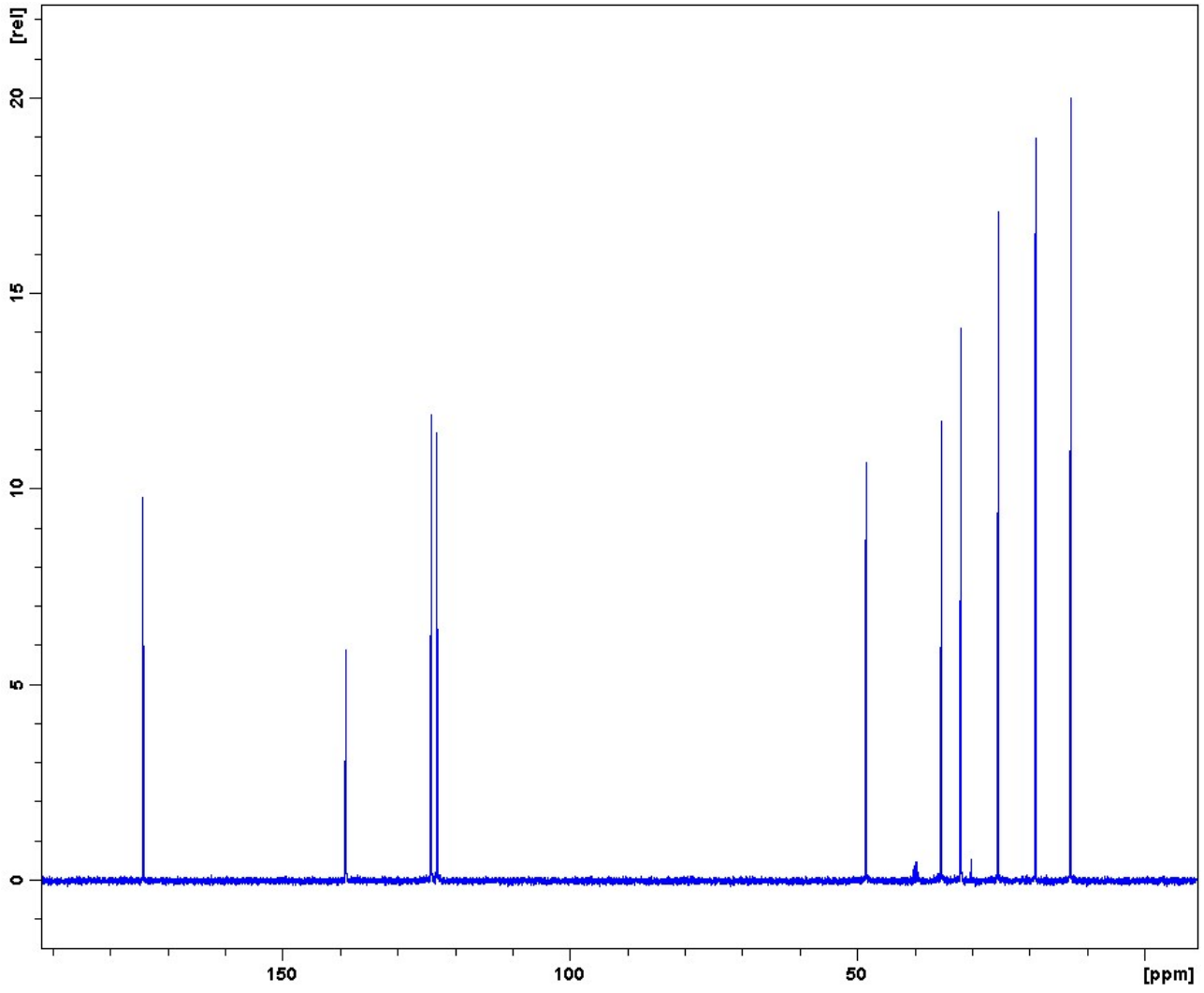


Fig. S5 Recorded spectrum of pure [C_4MIM][CH_3COO].

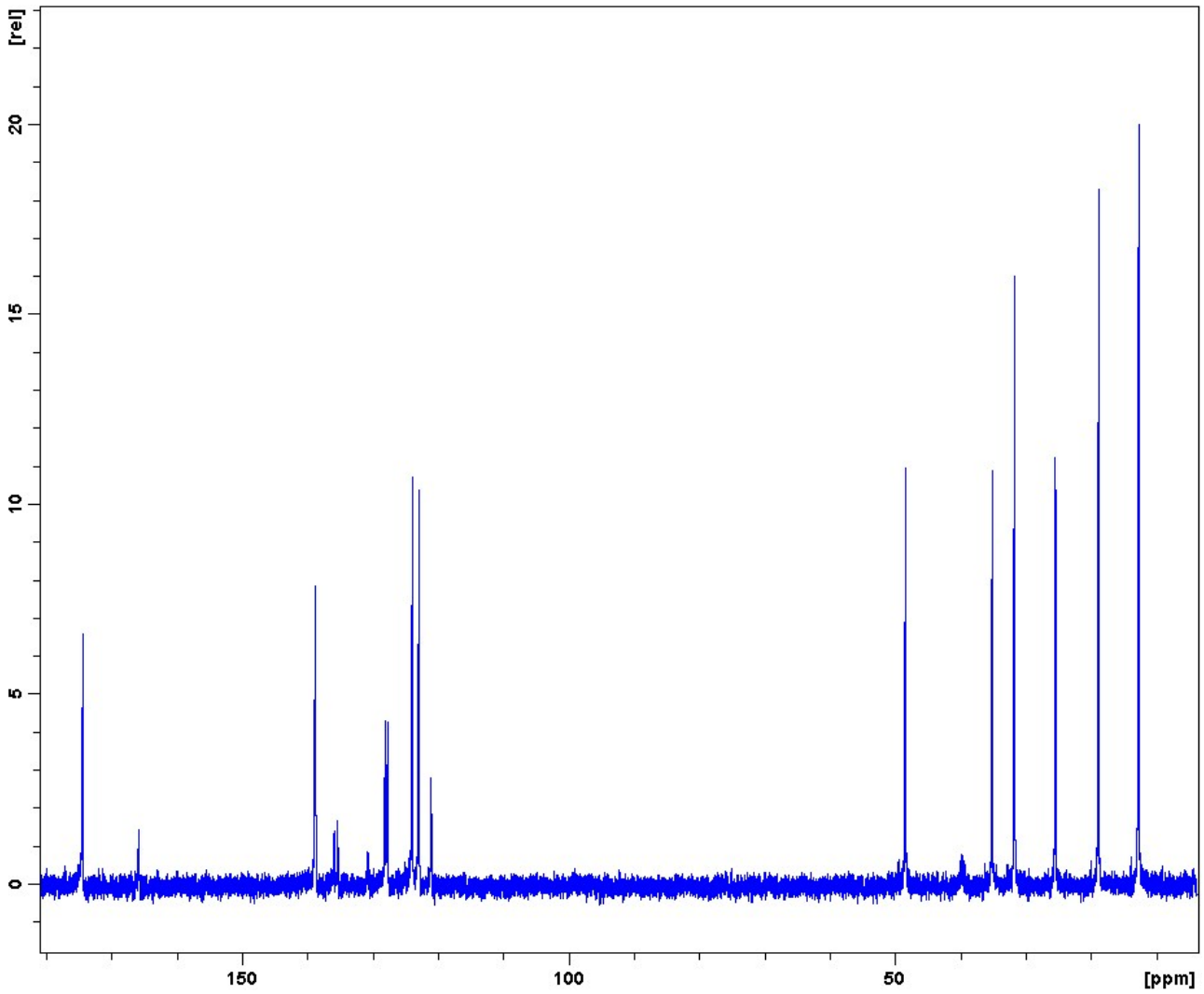


Fig. S6 Recorded spectrum of 20 wt% trimer model compound dissolved in $[C_4MIM][CH_3COO]$.

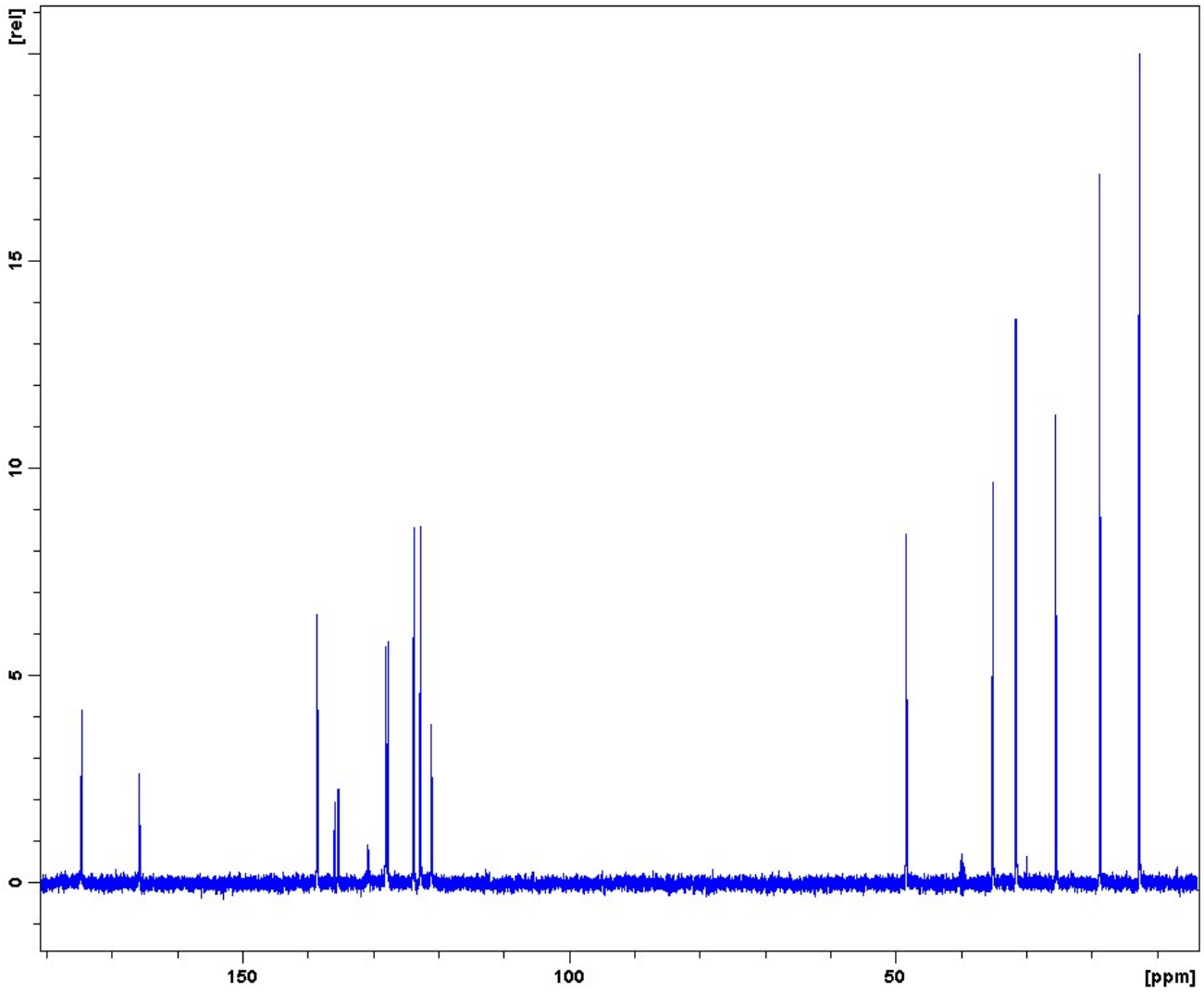


Fig. S7 Recorded spectrum of 40 wt% trimer model compound dissolved in $[C_4MIM][CH_3COO]$.

6. ^{15}N NMR spectra from the dissolution studies

^{15}N NMR (40.5 MHz) spectra with DMSO-d_6 as external reference for the dissolution studies were recorded with a Bruker Avance 600 MHz spectrometer at 70 °C over a whole weekend.

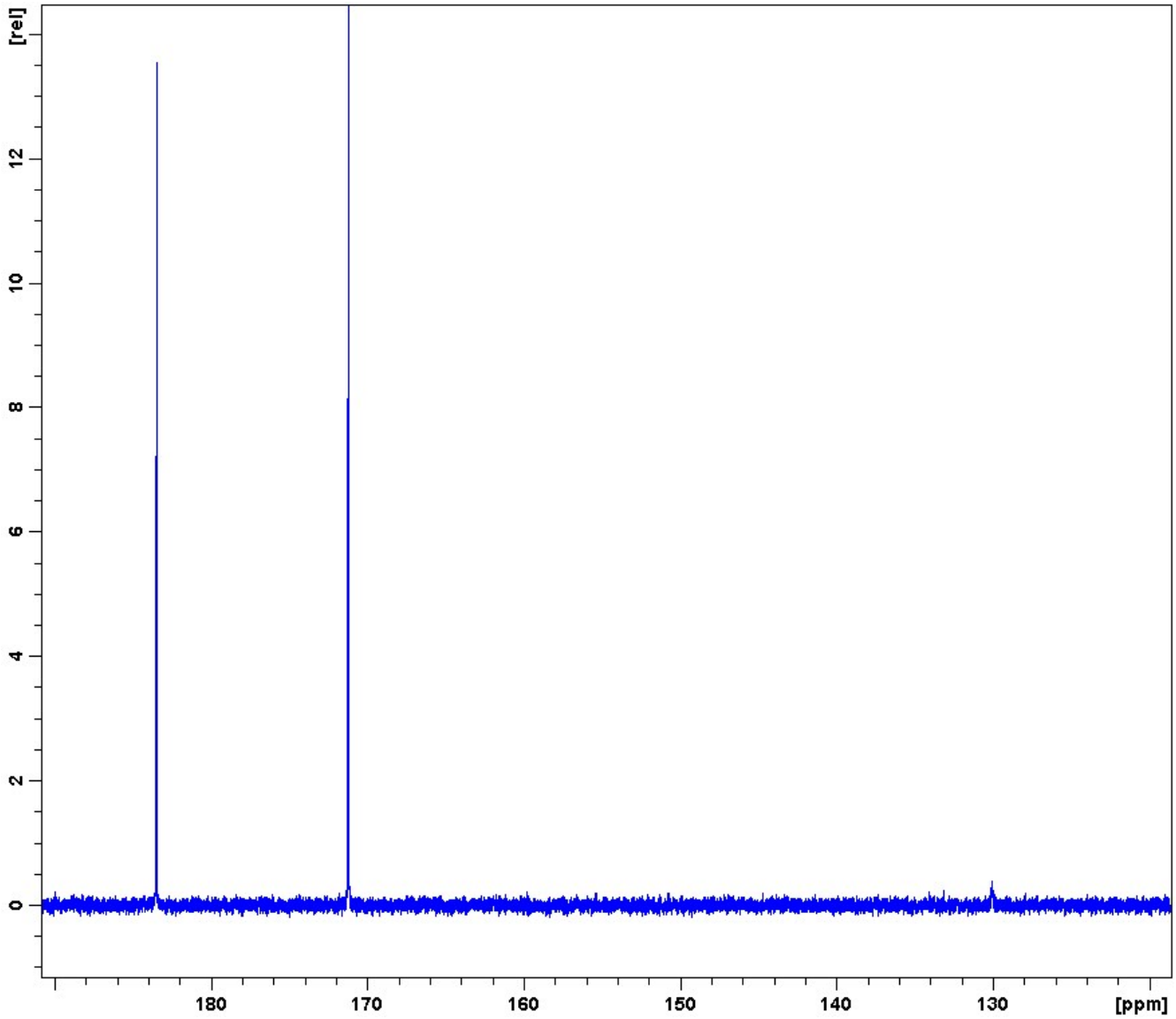


Fig. S8 Recorded spectrum of 20 wt% trimer model compound dissolved in [C_4MIM][CH_3COO].

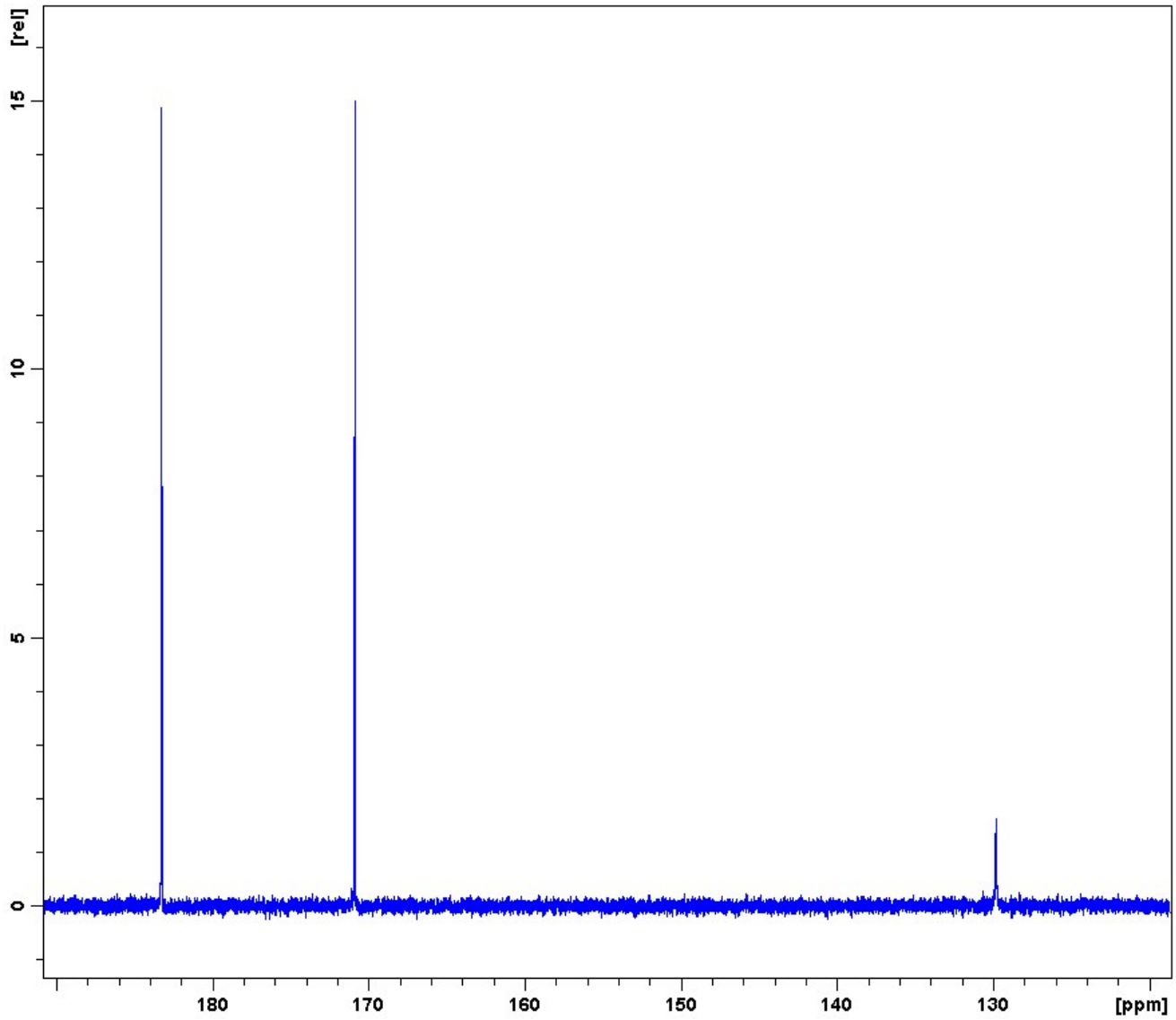


Fig. S9 Recorded spectrum of 40 wt% trimer model compound dissolved in $[C_4MIM][CH_3COO]$.

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