

## **SUPPORTING INFORMATION**

### **Treatment of energetic materials contaminated wastewater using ionic liquids**

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## I) Synthesis of ionic liquids<sup>1-3</sup>

### General Remarks

The FT-IR of each synthesized ionic liquid was performed by using BRUKAR, ALPHA FT-IR spectrometer with Zn-Se ATR crystal and gold coated mirror. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Varian Mercury 300 MHz and 75 MHz spectrometer with tetramethylsilane as an internal standard and DMSO-d<sup>6</sup> as a solvent.

**1) 1-butyl 3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>]:** 5.01 g (0.0286 mol) of [BMIM][Cl] and 5.79 g (0.0314 mol) of lithium hexafluorophosphate were mixed in a round bottom flask containing 10 ml of water and stirred for 8 hrs at room temperature. The obtained product was washed by water (3 × 10 mL) and dissolved in 20 ml of dichloromethane. The solution was dried by magnesium sulfate and the solvent was evaporated by rotary vacuum evaporator. The resultant light-yellow liquid dried for 24 hr at 70 ° C under vacuum (yield: 70%).

FT-IR: 567.3 (s), 623.8 (w), 725.3 (w), 838.6 (s), 1111 (w), 1169.5 (m), 1468 (m), 1574 (m), 2878 (w), 2966.5 m, 3177.3 (w), 3169.3 (m).

<sup>1</sup>H-NMR: 0.90 (t, 3H), 1.27 (sex, 2H), 1.78 (p, 2H), 3.35 (s, 3H), 4.16 (t, 2H), 7.62 (t, 1H), 7.68 (t, 1H), 9.02 (s, 1H).

<sup>13</sup>C-NMR: 13.13, 18.79, 31.37, 35.64, 48.65, 122.20, 123.55, 136.51.

**2) 1-butyl 3-methylimidazolium bis(trifluoromethanesulfonyl)imide [BMIM][NTf<sub>2</sub>]:** 5.42 g (0.0310 mol) of [BMIM][Cl] and 9.79 g (0.03413 mol) of lithium bis(trifluoromethanesulfonyl)imide were mixed in a round bottom flask containing 10 ml of water and stirred for 8 hrs at room temperature. The obtained product was washed by water (3 × 10 mL) and dissolved in 20 ml of dichloromethane. The solution was dried by magnesium sulfate and solvent evaporated by rotary vacuum evaporator. The resultant light-yellow liquid dried for 24 hr at 70 ° C under vacuum, (yield: 75%).

FT-IR: 406.37 (w), 510 (s), 569 (s), 652 (s), 739 (s), 789 (m), 843 (w) 1051 (s), 1133 (s), 1178 (s), 1347 (m), 1466 (w), 1573 (w), 2880 (w), 2967 (m), 3121 (w), 3157 (m).

<sup>1</sup>H-NMR: 0.95 (t, 3H), 1.35 (sex, 2H), 1.84 (p, 2H), 3.93 (s, 3H), 4.16 (t, 2H), 7.27 (s, 1H), 7.31 (t, 1H), 8.73 (s, 1H)

<sup>13</sup>C-NMR: 12.93, 18.72, 31.35, 48, 60, 117.38, 121.64, 122.17, 123.55, 136.28

**3) 1-octyl-3-methylimidazolium chloride [OMIM][Cl]:** Three neck round bottom flask equipped with heating bath, nitrogen inlet adapter, magnetic stirrer and reflux condenser were used for the synthesis. The flask was flushed by nitrogen gas and charged with 5 g (0.061 mol) of 1-methyl imidazole and 10.86 g (0.073 mol) of 1-chlorooctane with 10 ml acetonitrile. The reaction mixture heated under reflux for 48 hr and cooled to room temperature. The volatile material was removed by rotary vacuum evaporator and remaining the light yellow oil was washed by dry ethyl acetate. The light yellow oil was dried under vacuum for 24 hr at 70 °C (Yield: 80%).

FT-IR: 612 (s), 653 (m), 766 (m), 870 (w), 1167 (s), 1464 (s), 1569 (s), 2856 (s), 2924 (s), 3035 (m), 3380 (m)

<sup>1</sup>H NMR: 0.73 (t, 3H), 1.22 (m, 6H), 1.72 (p, 2H), 3.89 (s, 3H), 4.22 (t, 2H), 8.0 (s, 1H), 8.10 (s, 1H), 9.93 (s, 1H)

<sup>13</sup>C NMR: 14.13, 22.39, 25.85, 28.89, 29.93, 31.53, 35.97, 48.84, 122.65, 123.82

**4) 1-octyl-3-methylimidazolium hexafluorophosphate [OMIM][PF<sub>6</sub>]:** 5 g (0.0211 mol) of [OMIM][Cl] and 4.417g (0.0239 mol) of lithium hexafluorophosphate were mixed in a round bottom flask containing 10 ml of water and stirred 8 hr at room temperature. The obtained product was washed by water (3 × 10 mL) and dissolved in 20 ml of dichloromethane. The solution was dried by magnesium sulfate and solvent evaporated by rotary vacuum evaporator. The resultant light-yellow liquid dried under vacuum for 24 hr at 70 °C, (yield: 80%).

FT-IR: 623 (s), 650 (w), 740 (m), 817 (s), 1167 (m), 1467 (m), 1574 (m), 2858 (m), 2928 (m), 2956 (w), 3125 (w), 3170 (m).

<sup>1</sup>H NMR: 0.85 (t, 3H), 1.26 (sex, 2H), 1.80 (p, 2H), 3.85 (s, 3H), 4.15 (t, 2H), 7.67 (t, 1H), 7.68 (t, 1H), 9.02 (s, 1H).

<sup>13</sup>C NMR: 13.80, 22.18, 25.57, 28.46, 28.56, 29.46, 31.25, 35.69, 48.95, 122.17, 123.52, 136.48

**5) 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [OMIM][NTf<sub>2</sub>]:** 1.73 g (0.00753 mol) of [OMIM][Cl] and 2.378g (0.00828 mol) of lithium bis(trifluoromethanesulfonyl)imide were mixed in a round bottom flask containing 10 ml of water and stirred 8 hr at room temperature. The obtained product was washed by water (3 × 10 mL) and dissolved in 20 ml of dichloromethane. The solution was dried by magnesium sulfate

and solvent evaporated by rotary vacuum evaporator. The resultant light-yellow liquid dried under vacuum for 24 hr at 70 °C (Yield: 80%).

FT-IR: 612 (s), 739 (m), 789 (m), 845 (m), 1052 (s), 1133 (s), 1170 (s), 1348 (s), 1468 (m), 1572 (m), 2860 (m), 2930 (m), 2958 (w), 3121 (w), 3156 (m)

<sup>1</sup>H NMR: 0.88 (m), 1.27 (m), 1.80 (m), 2.52 (m), 3.87 (s), 4.17 (t), 7.71 (t), 7.77 (t), 9.12 (s).

<sup>13</sup>C NMR: 13.82, 21.99, 25.46, 28.41, 29.33, 31.11, 35.69, 48.78, 122.22, 122.68, 123.67, 136.45.

**TABLE 1S. Important Physico-chemical Properties of the Ionic Liquids**

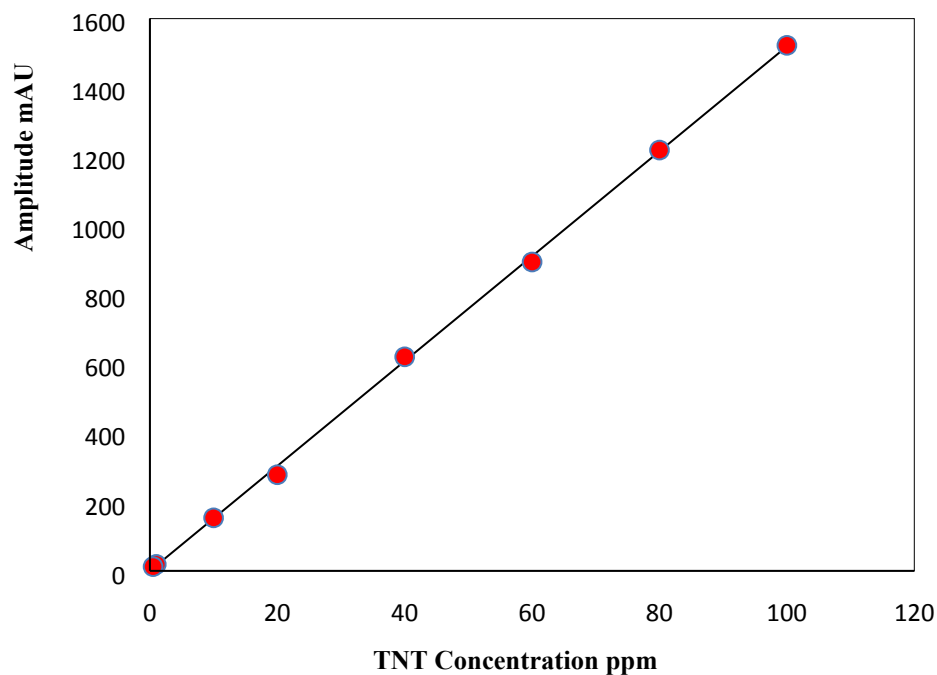
<b>ILs</b>	<b>Tg</b> <b>°C</b> [a,b]	<b>Td</b> <b>°C</b> [a,b]	<b>Density</b> <b>(g/cm<sup>3</sup>)</b> [c]	<b>η</b> <b>(cP)</b> [d] <sup>40,41</sup>	<b>Misc.</b> [e]	<b>Imm</b> <b>isc.</b> [e]
[BMIM][PF <sub>6</sub> ]	-80	349	1.3670	450	meth, ea, dm, dc, ac	w, h, de
[BMIM][NTf <sub>2</sub> ]	-104	439	1.4357	69	eth, meth, ea, dm, dc, ac	w, h, de
[OMIM][PF <sub>6</sub> ]	-82	376	1.2358	682	ea, dc, ac, eth, meth.	w, h, de
[OMIM][NTf <sub>2</sub> ]	-86	>300	1.3197	93	ea, dc, ac, eth, meth.	w, h, de

Tg - glass transition temperature, Td - decomposition temperature, η - Viscosity, Misc.- Miscible, Immisc. – Immiscible. [a] Ref. 40, [b] Ref. 39, [c] Density of ILs measured by Anton-paar density-meter., [d] Ref. 40, 41. [e] Observed complete solubilization (miscible) and non solubilization (immiscible) by adding solvent to a small amount of IL, where, water = w, hexane = h, ethyl acetate = ea, diethyl ether = de, ethanol= eth, acetone = ac, dichloromethane = dc, methanol = meth, chloroform = ch.

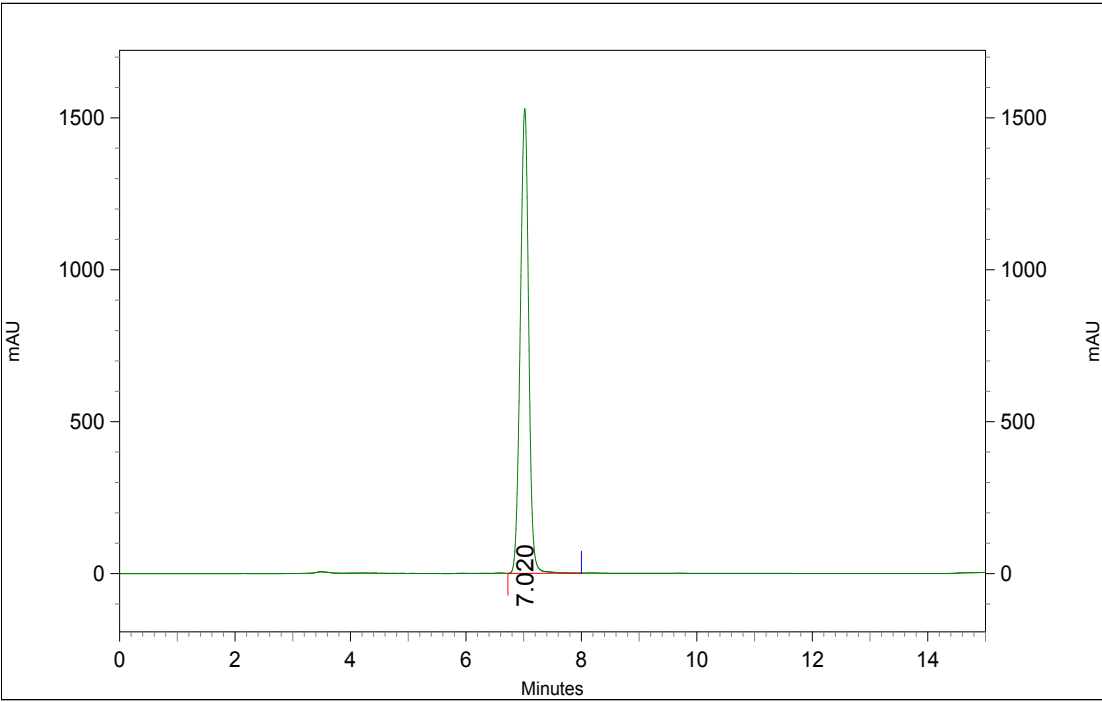
## II) Analysis of energetic materials

The EMs containing TNT, Tetryl and picric acid were analyzed as per the procedure described (USEPA method 8330)<sup>4</sup> by using HPLC (model Hitachi). The chromatographic reverse phase C<sub>18</sub> column was used with a size of 25 cm × 4.6 mm, 5 μm at 25 °C. A UV-Vis detector was used at wavelength 248 nm. The analytes were eluted isocratically at a flow rate of 0.5 mL/min, using an acetonitrile/water mobile phase (80/20, v/v). The sample injection volume used was 20 μL. The retention time (R<sub>t</sub>) of TNT, Tetryl and picric acid were obtained at 7.1, 6.6 and 3.2 min., respectively. The calibration of TNT, Tetryl and Picric acid gave linear regression curve, which was obtained by plotting amplitude (Y, mAU) against the concentration (X, ppm). The calibration curve exhibited good linearity; the data graph is given in ESI. All aqueous samples of EMs were analyzed by this method.

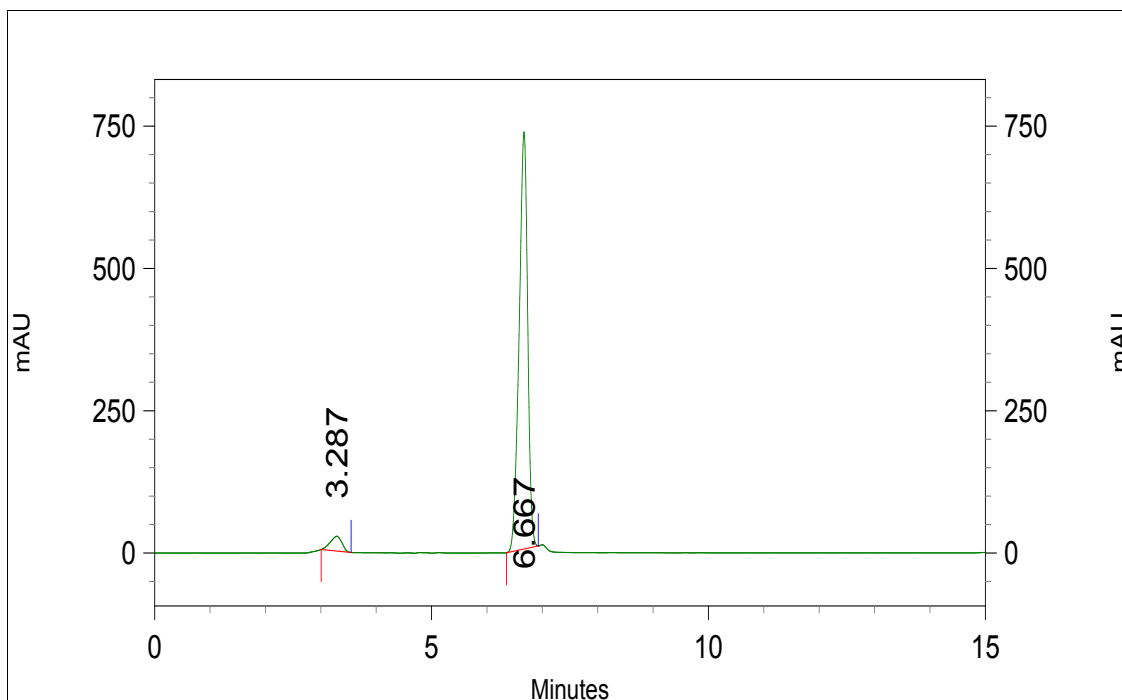
### Representative calibration graph and HPLC spectra



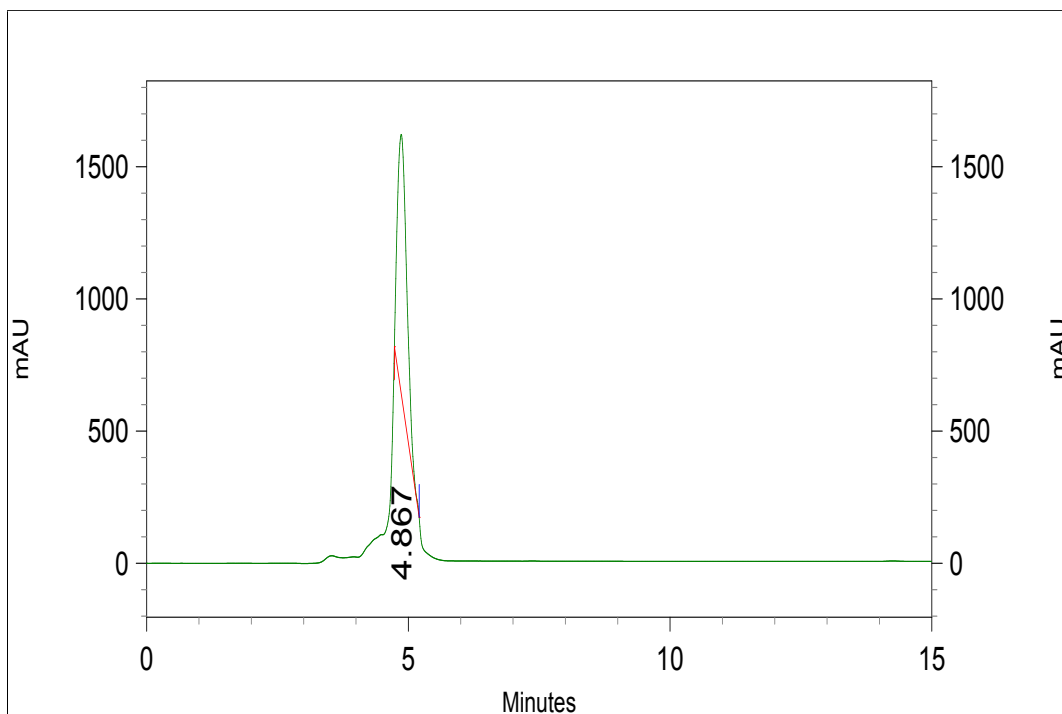
**Fig 1S.** Calibration curve of TNT



**Fig 2S.** HPLC spectrum of TNT

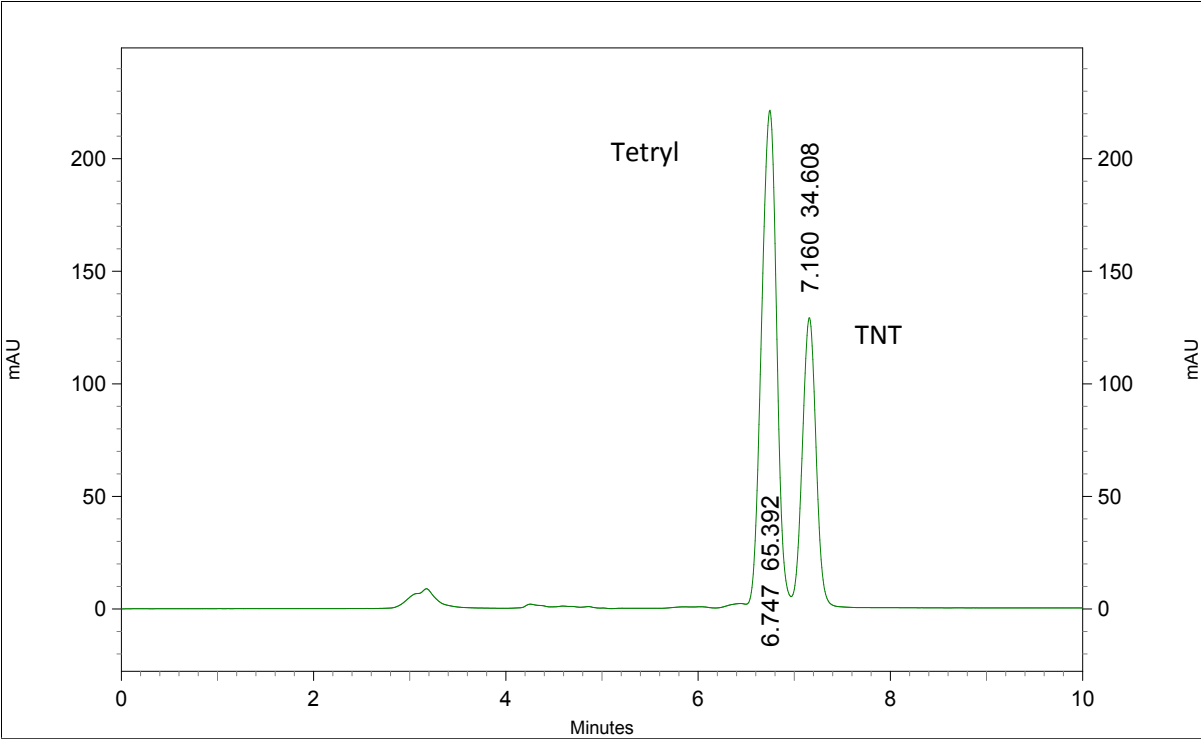


**Fig 3S.** HPLC spectrum of Tetryl



**Fig 4S.** HPLC spectrum of picric acid





**Fig 5S.** HPLC spectrum of Tetryl and TNT mixture

## References

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