Electronic Supporting Information

Hypergolic Ionic Liquids to Mill, Passivate, Suspend, and Ignite Boron Nanoparticles

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I. Materials and Methods

Chemicals. 1-methylimidazole, 1-chlorobutane, sodium dicyanamide, silver nitrate, 4-amino-1,2,4-triazole, methyl iodide, 1-ethyl-3-methylimidazolium acetate, potassium carbonate, and acetone were purchased from either Sigma-Aldrich (St. Louis, MO) or Alfa Aesar (Ward Hill, MA). 1-methylimidazole was redistilled and kept under vacuum prior to use while all other chemicals were used without any further purification. Feedstock boron particles (2 µm in diameter, 97%) were purchased from C.R. Supply Company (West Wills, CA). White Fuming Nitric Acid (98%) was purchased from Alfa Aesar and stored in a refrigerator until ready for use.

Preparation of Boron Nanoparticles. Following a modified protocol developed by Anderson et al.,[1,2] boron with an average diameter of 2 µm was ball-milled using a planetary ball mill (Spex-CertiPrep 800 M, Metuchen, NJ) with tungsten carbide milling jar and 1/8” diameter spherical balls to create B nanoparticles (60 nm in diameter). The boron feedstock (2 g) was first milled for a total of 12 h (80:1 ball-to-powder mass ratio; 300 rpm) to break the particles and expose more reactive surfaces. Subsequently the B was milled in the presence of surfactant or IL for an additional 6 h, and then another 6 h with acetonitrile (200 mL) as a dispersive solvent. Boron feedstock was milled with either no ligand, a combination of oleic acid and oleyl amine (1.5 mL, 1:1 v/v), or [MAT] [DCA] (1.5 mL). In the case where B was milled without ligand, the surfactant milling step was omitted from the procedure. Acetonitrile was added in the last milling step to help reduce viscosity, disperse the particles, and to allow easy transfer the newly milled nanoparticles.

Thermogravimetric Analysis (TGA). All experiments were done on a TA Instruments (New Castle, DE) model 2950 thermogravimetric analyzer. The instrument’s internal temperature was calibrated by observing the Curie point of Nickel (358.15ºC). In order to investigate the decomposition profile of the boron loaded ILs, samples of 5-25 mg were analyzed on a platinum pan under a purge of argon and measured *via* dynamic heating. Samples were heated from room temperature to 75 ºC at 5 ºC/min and held as an isothermic temperature for 30 min in order to ensure excess volatiles or residual solvents were removed. Following the isotherm, samples were heated to 800 ºC at 5 ºC/min. Decompositions temperatures are recorded as the onset to 5% weight mass loss ($T_{5\%dec}$).

Combustion Microcalorimetry. The heat of combustion was determined using a Parr (Moline, IL) (series 1425) semimicro oxygen bomb calorimeter. The substances were burned in an oxygen atmosphere at a pressure of 30 atm. Each sample was loaded into a crucible and placed in the bomb with a 5 five turn nichrome wire dipped into the liquid sample. The energy equivalent of the calorimeter was determined with a standard reference sample of benzoic acid. Each sample was run twice and the values averaged. The ΔH_c was determined to be -30970 J/g for the neat [BMIM][DCA], which compares with the literature results of ΔH_c= -30605 ± 4.4 J/g.[3]

Spectroscopy. All Nuclear Magnetic Resonance (NMR) spectra were recording utilizing a Bruker Avance Spectrometer Bruker/Magnex UltraShield 500 MHz magnet (Madison, WI) or a Bruker Spectrospin DRX 400 MHz UltrashieldTM spectrometer (Madison, WI). ^{1}H (500 MHz) and ^{13}C (125 MHz) were collected using DMSO-*d6* as the solvent with TMS as the standard and shifts reported in δ (ppm). Infrared (IR) spectra were collected using a Bruker α-FTIR by direct measurement *via* attenuated total reflection of the neat samples (or loaded with boron nanoparticles) on a diamond crystal.

Ignition Delay and Burn Duration. A Redlake Motion Pro® HS 4 (Tallahassee, FL) was utilized to capture the hypergolic process at 1000 fps at either 1280 X 1024 or 512 X 512 resolution depending on the size of the flame. Although the same vial size and procedures were utilized in the study of both [BMIM][DCA] and [MAT][DCA], the camera resolution and frame size had to be adjusted for the recording of the [MAT][DCA] studies due to the larger flame size. The resulting images make the vial sizes appear to be different, when in fact they are the same. The ignition delay was determined by counting the frames from which the fuel hit the oxidizer until the first signs of a visible flame. Burn duration was determined to be the time from the first signs of visible ignition until the last visible flame. Each sample was run three times and averaged.

II. Synthesis

Synthesis of [BMIM][Cl]

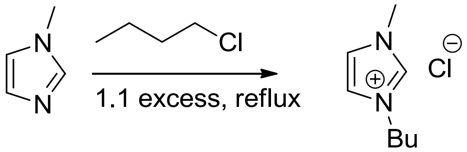

Figure S1. Synthesis of [BMIM][Cl].

1-methylimidazole (150.00 g, 1.83 mol) was distilled directly into the reaction flask and a 1.1 molar excess of 1-chlorobutane (204.64 g, 2.00 mol) was added and the reaction was refluxed under Argon through Schlenk-line techniques. The reaction was monitored by NMR until all traces of 1-methylimidazole were no longer visible, or 96 h. The remaining excess of 1-chlorobutane was removed under reduced pressure and the product was slowly cooled to a white crystalline solid. ^{1}H NMR (360 MHz, *DMSO-d$_6$*) δ ppm: 9.124 (1H, s), 7.929 (1H, s), 7.847 (1H, s), 4.223 (2H, t, *J* = 7.132 Hz), 3.898 (3H, s), 1.773 (2H, quintet, *J* = 7.427 Hz), 1.250 (2H, sextet, *J* = 7.538 Hz), 0.890 (3H, t, *J* = 7.310 Hz).

Synthesis of [MAT][I][4]

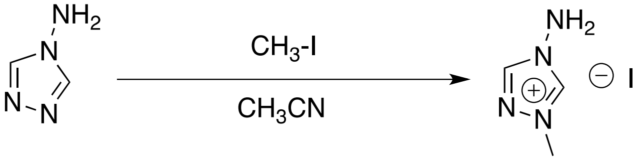

Figure S2. Synthesis of [MAT][I].

4-amino-1,2,4-triazole (400 g, 4.76 mol) was weighed out and piecewise added into a 6 L jacketed filter reaction flask containing 2 L of reagent grade acetonitrile while agitating with a glass stir shaft and Teflon paddle. The jacket was slowly heated to 35 °C during the addition. When the 4-amino-1,2,4-triazole was inside the reactor an additional 2 L - 2.5 L of acetonitrile was added with continued stirring at 35 °C until all of the solids dissolved (3 h to achieve dissolution). The reactor was covered to minimize light exposure. While at 35 °C, the methyl iodide was added slowly dropwise 1688 g (11.9 mol) over ~ 2 h, keeping the temperature of the solution under 40 °C during the addition. At the end of the methyl iodide addition, the chiller was turned off, and the reaction mixture allowed to cool down while agitating overnight. The reaction was monitored by TLC (7:3; ethyl acetate/methanol). When the reaction was complete, the jacket was cooled (chiller set to 0 °C) with ensuing solid precipitation. The solids were then filtered directly through the reactor filter via nitrogen pressure (< 5 psi) and removed to obtain 1300 g crude product. The crude solids were divided into 600 g – 700 g quantities and each recrystallized in 3000 mL quantities of absolute ethanol to yield a white crystalline solid. Melting point 98 °C; ^{1}H NMR (360 MHz, DMSO-*d6*) δ ppm: 10.115 (1H, s), 9.161 (1H, s), 6.938 (2H, s), 4.024 (3H, s); ^{13}C NMR (125 MHz, DMSO-*d6*) δ ppm: 145.109 (s), 143.002 (s), 39.107 (s).

[BMIM][DCA][5]

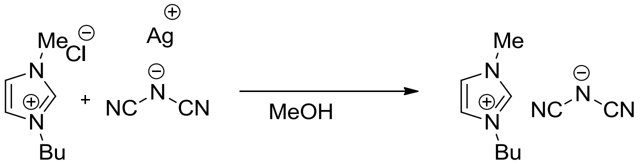

Figure S3. Metathesis of [BMIM][DCA].

Synthesis of [Ag][DCA]

Sodium dicyanamide (13.35 g, 150 mmol) was dissolved in 20 mL DI water and added dropwise to a solution of silver nitrate (25.48 g, 150 mmol) in a 100 mL round bottom flask with a Teflon stirbar. The mixture was stirred overnight in darkness at room temperature, and the resulting white solid was vacuum filtered and washed with DI water followed by methanol. The solid was dried in a vacuum oven at 70 °C for 24 h.

Metathesis

[BMIM][Cl] (12.482 g, 71.46 mmol) stored in separate vials was dissolved in 25 mL of dry methanol and transferred to a 250 mL round bottom flask containing a 1.1 molar excess of [Ag][DCA] (13.670 g, 78.61 mmol) as synthesized above containing 175 mL of dried methanol. An excess of [Ag][DCA] was used to ensure complete conversion due to the limited solubility in methanol. The flask was covered with aluminum foil and stirred for 3 days. AgCl and remaining [Ag][DCA] was filtered and the solvent removed through reduced pressure. The resulting clear oil was dissolved in the minimum amount of methanol and filtered again to remove trace amounts of AgCl dissolved in the IL. The methanol was removed through reduced pressure. The IL was dried by high vacuum drying and freeze thawed to remove remaining gas. A clear nonviscous liquid was obtained. TGA: $T_{dec5\%}$ = 257 °C; ^{1}H NMR (360 MHz, *DMSO-d6*) δ ppm: 9.082 (1H, s), 7.737 (1H, s), 7.670 (1H, s), 4.164 (2H, s), 3.853 (3H, s), 1.775 (2H, quintet (triplet of triplets)), 1.267 (2H, sextet), 0.898 (3H, t); ^{13}C NMR (125 MHz, *DMSO-d_6*) δ ppm: 136.950 (s), 124.028 (s), 122.691 (s), 119.550 (s), 49.065 (s), 36.183 (s), 31.813 (s), 19.255 (s), 13.647 (s).

[MAT][DCA][5]

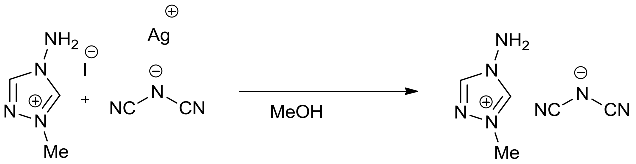

Figure S4. Metathesis of [MAT][DCA].

[MAT][I] (50.0 g, 221 mmol) was dissolved in methanol with a 1.1 molar equivalent of [Ag][DCA] (42.27 g, 243.1 mmol). An excess of [Ag][DCA] was used to ensure complete conversion due to the limited solubility in methanol. AgCl and any remaining [Ag][DCA] was filtered and the solvent removed through reduced pressure to yield a colorless liquid. TGA: $T_{dec5\%}$ = 161 °C; ^{1}H NMR (500 MHz, neat liquid) δ ppm: 10.67 (1H, s), 9.74 (1H, s), 7.39 (2H, s, NH_2), 5.00(3H, s, CH_3); ^{13}C NMR (125 MHz, neat liquid) δ ppm: 146.2 (s), 144.0 (s), 120.1 (s), 40.4 (s); ^{15}N NMR(400 MHz, neat liquid) δ ppm: 86.3 (s), -169.3 (s), -189.5 (s), -305.4(t, $^{1}J_{Hz}$ 72), -218.5(s), -368.2 (s).

III. Characterization Data

Infrared Spectroscopy. In the FT-IR spectra of [MAT][DCA] there is no change in the intensity of the DCA^- anion suggesting no change in dipole moment and thus no interaction with B. There is a change in the intensity of the N-H band due to the change in the dipole moment indicating there is an interaction of the cation. Moreover, in the C-N band from the DCA^- anion (~ 1300 cm^{-1}), there is no significant change in its intensity again indicating little or no interaction with B.

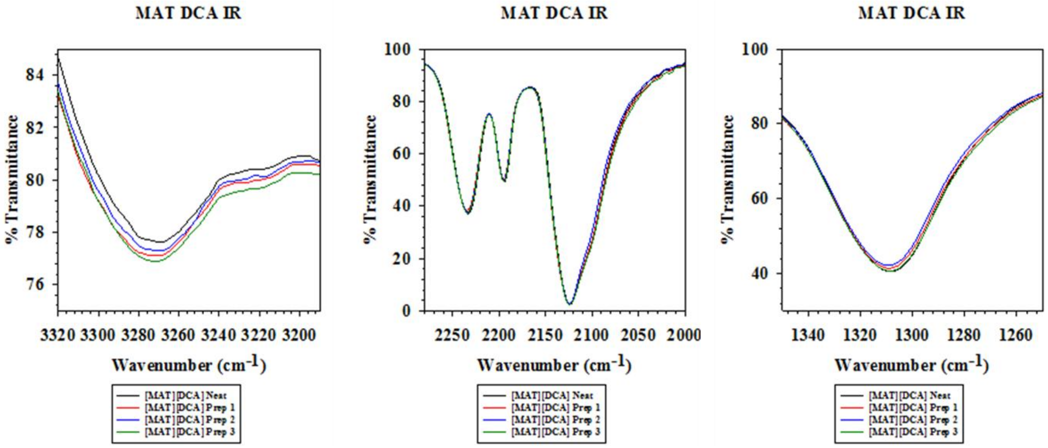

Figure S5. FT-IR spectra of [MAT][DCA] neat and with boron.

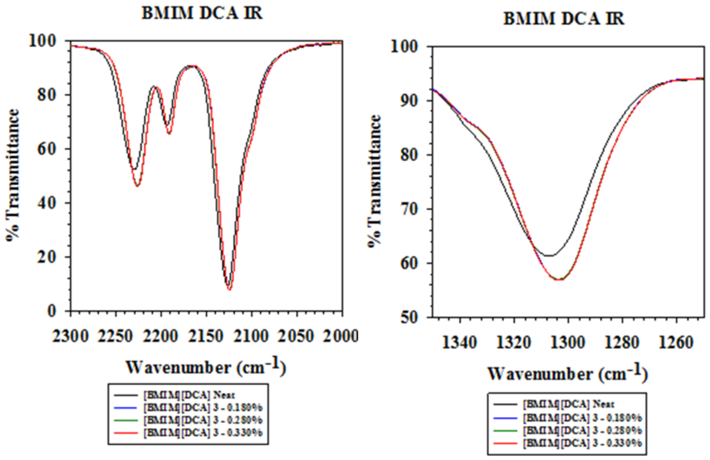

Figure S6. FT-IR spectra of [BMIM][DCA] neat and with boron.

In the FT-IR spectra of [BMIM][DCA] there is a change in the intensity of the DCA$^-$ bands, including a small shift which suggests a change in the dipole moment of this group because of interaction with B. Also, in the region where the N-C band appears (~1300) for the B loaded samples there is a change in the intensity and a shift for this band when compared to the neat IL suggesting a change in the dipole moment and interaction of DCA$^-$ with B.

Thermogravimetric Analysis. The decomposition profiles remain largely unaffected by the addition of boron particles based on any of the three milling conditions, the IL it was suspended in, or the concentration at which it was loaded.

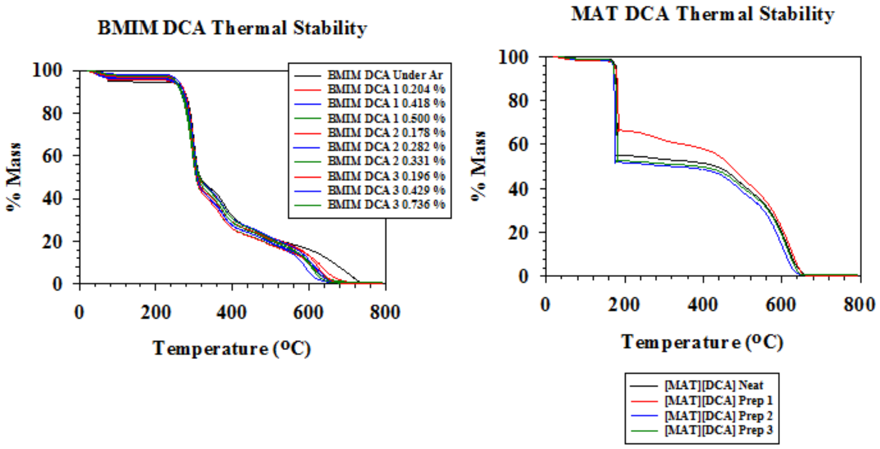

Figure S7. Thermogravimetric Analysis of [BMIM][DCA] (left) and [MAT][DCA] (right).

IV. Hypergolic Tests

Although the same vial size and procedures were utilized in the study of both [BMIM][DCA] and [MAT][DCA], the camera resolution and frame size had to be adjusted for the recording of the [MAT][DCA] studies due to the larger flame size. The resulting images make the vial sizes appear to be different, when in fact they are the same.

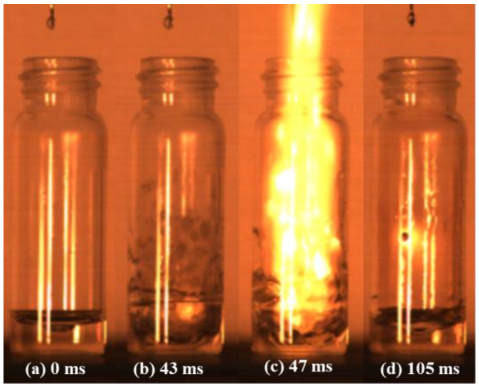

Figure S8. Hypergolic test of neat [BMIM][DCA] with 98 % WFNA: (a) drop hitting, (b) first sign of ignition, (c) burning, (d) last indication of burn.

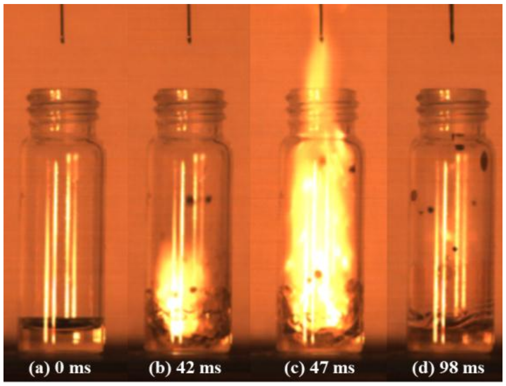

Figure S9. [BMIM][DCA] with Boron milled with no ligand: (a) drop hitting; (b) first sign of ignition; (c) burn ongoing; (d) last sign of burn**.**

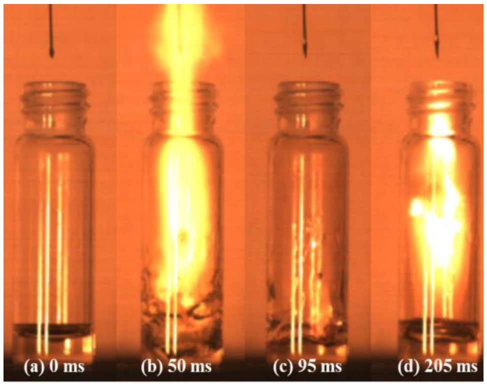

Figure S10. [BMIM][DCA] with B milled with oleic acid/oleyl amine: (a) drop hitting; (b) burn ongoing; (c) last sign of first flame; (d) second flame ending.

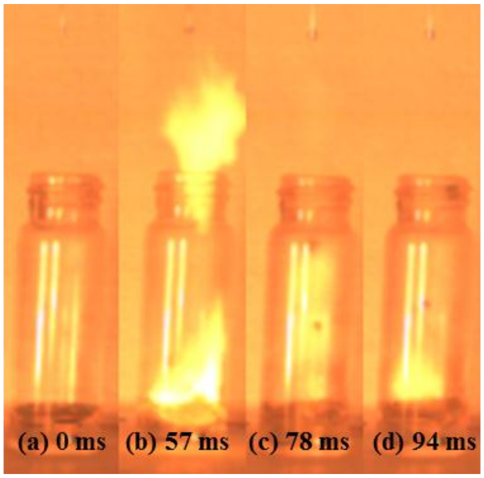

Figure S11. [MAT][DCA] with B milled with no ligand: (a) drop hitting; (b) first sign of ignition; (c) burn ongoing; (d) last sign of burn.

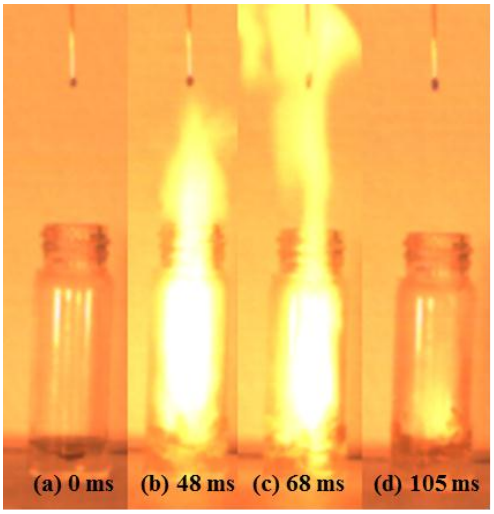

Figure S12. [MAT][DCA] with B milled with oleic acid/oleyl amine: (a) drop hitting; (b) burn ongoing; (c) burn continuing; (d) last signs of burn.

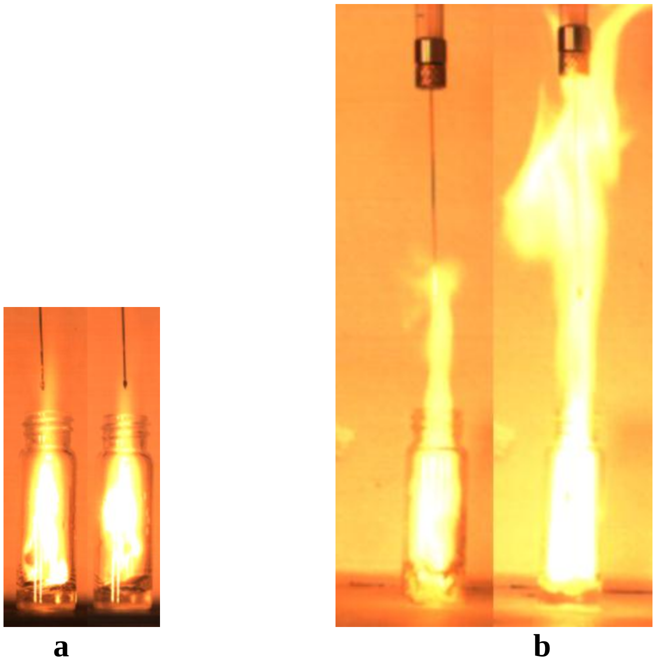

Figure. S13. Comparison of [BMIM][DCA] neat (image a – left) and containing IL-milled B (image a – right) indicating no enhanced performance, and of [MAT][DCA] neat (Image b – left) and containing IL-milled B (image b - right) indicating enhanced performance.

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[2] B. Van Devener, J. P. L. Perez, J. Jankovich, S. L. Anderson, *Energy Fuels* 2009, **23**, 6111.

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[4] T. Hawkins, S. Schneider, G. Vaghjiani, S. Chambreau, G. W. Drake, Hypergolic Fuels. US Patent 8034202, October 2011.

[5] S. Schneider, T. Hawkins, M. Rosander, G. Vaghjiani, S. Chambreau, G. W. Drake, *Energy Fuels*. 2008, **22**, 2871.