Direct, Atom Efficient, and Halide-Free Syntheses of Azolium Azolate Energetic Ionic Liquids and Their Eutectic Mixtures, and Method for Determining Eutectic Composition

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We report i) the successful halide free, efficient syntheses of azolium azolates by reaction of 1,3-dimethylimidazolium-2-carboxylate with neutral azoles, ii) the development of a facile, low sample demand method for ready determination of the eutectic point compositions of mixtures of these salts, and iii) the application of the new synthetic techniques for the direct preparation of the eutectic mixtures. This work is illustrated here with the synthesis of 1,3-dimethylimidazolium 4,5-dinitroimidazolate and 1,3-dimethylimidazolium 4-nitro-1,2,3-triazolate (via a one-pot synthesis with an easy to remove byproduct ($CO_{2(g)}$), thus avoiding halide and metal impurities) and the determination of their eutectic composition and its direct synthesis.

The ever growing list of applications for the unique physical, chemical, and biological property sets available from ionic liquids (ILs) calls for an increased emphasis on the preparation of ILs in more elegant and, more importantly, cleaner ways. The specifications needed for many new applications (e.g., energetic materials,[1,2] catalysis,[3] and pharmaceuticals[4]) often require synthetic products free of inorganic salts and other impurities which are commonly observed in current IL preparation techniques such as metathesis reactions. At the same time it is readily apparent that ILs may require formulation with other ionic or molecular components to achieve the often stringent physical properties these applications require.[5]

With the introduction of dialkylsulfates[6,7] and dialkylcarbonates,[8] and more recently the use of alcohols in Mitsunobu alkylation reactions[9] and alkanesulfonates as alkylating agents[10] for the synthesis of alkylated imidazolium salts, halide-free IL materials were successfully prepared. These salts, though halide free, were then typically used as precursors for further ion-exchange reactions. Ideally, in order to obtain pure IL salts, the synthesis would have to be carried out directly with routes that are byproduct-free or that allow facile removal of byproducts by their evaporation, rather than by extraction. The zwitterionic dialkylimidazolium-2-carboxylate, for example, can be decarboxylated with a protic acid to form pure imidazolium salts with only $CO_{2(g)}$ as byproduct.[11,12]

Our group,[2,13,14] as well as others,[1,15] have been interested in transferring the synthetic techniques demonstrated for the dialkylimidazolium-based ILs to the azolate class of anions in the development of energetic azolium azolate materials. The structural similarity to the azolium cations used in many ILs, suggested that similar degrees of functionalization in azolate anions would lead to a diverse new range of ILs with interesting physical and chemical properties. To that end, we demonstrated that the combination of the 1-butyl-3-methylimidazolium cation ([1-Bu-3-MeIm]$^+$) with a variety of azolate anions resulted in the formation of low melting salts with glass transitions as low as $-82\,°C$ (for [1-Bu-3-MeIm][tetrazolate]) and no observable melting point.[14] Moreover the thermal stabilities of these new salts are high which can be beneficial for many IL applications.

Others have also reported the utilization of azolate-based anions in attempts to form ILs, with the majority of these salts prepared via ion exchange,[16,17] or by protonation of neutral azoles (when differences in the pK_a values of the substrates permitted) via Brønsted acid–base neutralization reactions.[15,17,18] The only exception to this approach was presented by Ohno and co-workers,[15] where the azolate salts were formed by the reaction of a hydroxide precursor with neutral azoles. Unfortunately, this latter approach is limited to cations that are stable as hydroxide salts.

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We have now successfully prepared two new energetic azolium azolate ionic liquids (1,3-dimethylimidazolium 4,5-dinitroimidazolate ([1,3-diMeIm][4,5-diNO$_2$-Im]) and 1,3-di-methylimidazolium 4-nitro-1,2,3-triazolate ([1,3-diMeIm][4-NO$_2$-Tri])) via a one-pot synthesis with an easy to remove byproduct (CO$_{2(g)}$)—avoiding halide and metal impurities (Scheme 1) by applying a recently developed synthetic route to ILs.[11] This synthetic route involves a solvent promoted decarboxylation reaction of dialkylimidazolium-2-carboxyl-ate (similar to, or based on, the Krapcho reaction)[19–24] in the presence of protic acid, evolution of CO$_{2(g)}$ as the only byproduct, and protonation of the C2 ring position with a proton from the acid. This simple, low-temperature, and moderately fast reaction in aqueous ethanol resulted in almost quantitative yields with the reaction easily monitored by the evolution of CO$_{2(g)}$ which formed instantly during addition of the reactants.
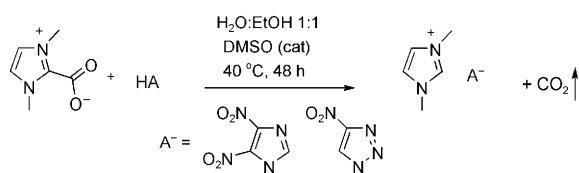
Scheme 1. One-pot synthesis of [1,3-diMeIm][4-NO$_2$-Tri] and [1,3-diMeIm][4,5-diNO$_2$-Im] salts.

Having successfully prepared the azolium azolates, we set out to develop methods to determine and prepare their eutectic mixtures. It is well known, that in order for an organic salt to exhibit low-melting or glass-transition temperature, modifications to the structure of the cation or the anion must be made, usually to lower the symmetry and increase charge de-localization of the ions.[25] Unfortunately, in many cases this requires redesign of not only the individual ions, but also of the salt itself and its method of preparation since changes in ion structure may also change other important properties (e.g., viscosity, density). It is therefore interesting to note, that in the growing number of IL applications, the presence of a pure IL (one cation and one anion) may often not be necessary; one could merely use an entirely ionic fluid.

Specific applications such as liquid mirrors,[26] electrolytes,[27] solvents for dissolution of biomass,[28] and energetic materials,[1] simply do not require a single cation and anion composition to perform at their best. One such example, where the mixtures of quaternary ammonium salts with glycerol have been used to extract excess glycerol from biodiesel, was recently presented by Abbott et al.[29] Moreover, we

believe, that by formation of mixtures of ILs, multifunctional capabilities, possibly having synergistic effects, can be introduced by means of the combination of different properties brought together by different ion components in the mixture (Figure 1). More importantly, however, by proper selection of ions in the mixture, and their relative concentrations, eutectic mixtures can be envisioned which allow for further depression in the melting point and ready modification of the other physical properties. It is thus surprising that the topic of eutectic mixtures composed entirely of multiple ILs has been relatively neglected in the IL field. (We note that eutectic mixtures of IL or similar salts with neutral solutes such as water, alcohols, hydrocarbons, have been studied,[30–33] but much of this work (e.g., Abbott's elegant work with deep eutectic solvents[34]) tends to be excluded from the IL community, reputedly because of the presence of neutral "molecules" in the system.)

Generally, a eutectic mixture of solutes is defined as mixture of two or more phases at the proper molar ratio that causes the global maximum in melting point depression of the mixture.[35–37] The main characteristic of a eutectic mixture is that the resulting melting point is usually lower than that of any single component of the mixture, and that the components simultaneously crystallize from molten solution at this temperature. Eutectic mixtures can be formed by mixing a variety of solutes miscible with each other, including mixtures of two or more neutral compounds, neutral compounds and salts, or salts.
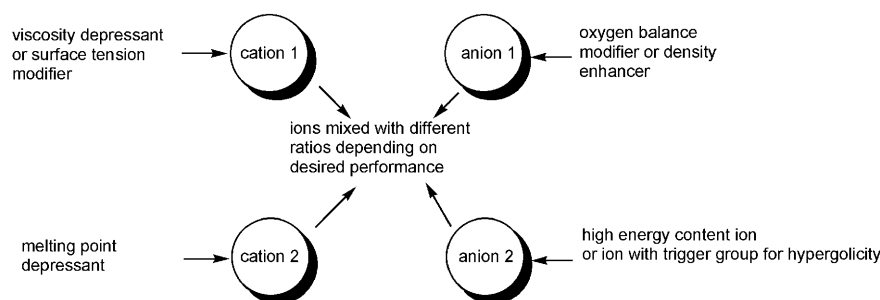

Figure 1. Synthetic strategy to form eutectic mixtures of ILs to tune bulk properties.

In order to determine the eutectic composition of the mixture of components, a binary phase diagram must be constructed, an analysis of which allows the determination of the eutectic melting point and composition.[38] Only a few examples of the determination of the eutectic composition of two organic salts have been reported, and interestingly these reports mark the genesis of the modern era of the field of ILs.[39–41] Wilkes et al.,[41] determined the common cation system 1-ethyl-3-methylimidazolium chloride/tetrachloroaluminate eutectic which exhibited melting point depression to about −96 °C. More recently, Dunstan et al.[42] reported formation of a common anion eutectic mixture of 1-ethyl-3-methylimidazolium/1-ethyl-2-methylpyrazolium hexafluorophosphate which exhibited an eutectic at a molar

composition of 47:53 (m.p. 23 °C). A few other examples of mixtures of ILs exist in the literature where the physical properties of organic salts were analyzed rather than the eutectic point itself.[43, 44]

Determination of the eutectic composition of a mixture of components (e.g., **A** and **B**) by DSC, normally involves the construction of an isobaric phase diagram, where the end of the melting transitions of various composition mixtures of **A**+**B** is found by DSC and these points are plotted versus the molar composition. A second method involves construction of a graph, where the enthalpy of the eutectic peak (heat of fusion) is plotted against the molar ratio of the components. Since the enthalpy of the eutectic peak should linearly increase (approaching the eutectic point composition), the extrapolation of the results allows for a quick estimate of the eutectic point composition (X_E).

The techniques previously reported for the eutectic point analysis,[45] even though using DSC instruments and samples sizes between 2 and 10 mg during each run, often require larger quantities (often >500 mg) of each component to be milled together prior to the analysis. This introduces i) the risk of non-homogenous mixing, ii) the possibility of partial compound spillage, introducing error to the calculated composition, iii) point overheating during the milling process which can cause partial decomposition, and iv) for samples that are hygroscopic (common for many ILs), inaccurate mass calculations of the weighed mixture. All of these can result in inaccurate determination of the enthalpy of the eutectic peak necessary for precise eutectic point identification.

Our modification of the general protocol for eutectic determination[46, 47] allows for the precise eutectic point analysis of mixtures of compounds that i) are either very difficult to obtain or expensive to purchase, ii) have hazardous properties that restricts their usage in larger scale due to safety issues, or iii) are shock sensitive (e.g., energetic compounds) which restricts the processing (e.g., milling) usually performed on samples prior to calorimetric analysis.

Since the ILs are composed of ions, in contrast to molecular compounds, they introduce two components to the system each time one salt is added which can make the determination of the eutectic point of the resulting mixture very difficult. Any time that the number of different ions in the mixture increases over three, the possibility of ion-exchange and the formation of new compounds makes the analysis more challenging. Bearing this in mind, we chose to study a eutectic mixture of two energetic ionic liquids (EILs) with a common cation.

The investigation of the eutectic composition of [1,3-diMeIm][4,5-diNO₂-Im] and [1,3-diMeIm][4-NO₂-Tri] started with the careful preparation of mixtures of the salts for DSC experiments according to the protocol described in the experimental section where various mole fractions of each salt were prepared by addition of the latter. Only data from the third DSC cycle were used for the analysis assuring that the analyzed samples retained their uniform character throughout the experiment (Figure 2, Table S2). Repetitions of the

heating/cooling cycles also assured that any possible non-reversible thermal transition peaks were eliminated.

Based on this data, two phase diagrams were constructed. The first involved analysis of the melting points of mixtures
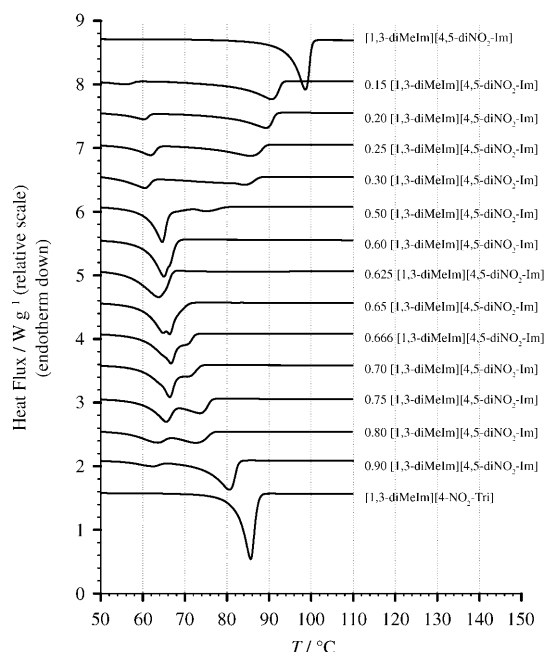

Figure 2. Thermal transitions of different mole fractions of mixtures of [1,3-diMeIm][4-NO₂-Tri] and [1,3-diMeIm][4,5-diNO₂-Im].

of increasing mole fraction of [1,3-diMeIm][4-NO₂-Tri] (Figure 3), the second plotting the enthalpy of the eutectic peak as a function of mole fraction of the same IL (Figure 4). The solidus line consists of the values for the recorded melting point minimums for the eutectic mixture.

The binary phase diagram (Figure 3) is composed of two sets of data; along liquidus and solidus lines. The liquidus line consists of the data from the depressed melting point of the component of the mixture used in excess to the eutectic composition. Two linear equations were fit to the melting points of the excess components as their melting point decreased. The R^2 values were in acceptable ranges of 0.99 for the melting points of [1,3-diMeIm][4,5-diNO₂-Im] and 0.97 for the melting points of [1,3-diMeIm][4-NO₂-Tri].

In our approach, the values for the melting point of the eutectic mixture were not constant and shifted from ≈ 56 °C on the left of the composition axis to ≈ 62 °C on the right, with the maximum at ≈ 66 °C at the eutectic composition. Such a drift of the eutectic point temperature may be associated with the interactions between any slight excesses of ionic components thus furthering melting-point depression.

The data show significant melting point depression for the eutectic in comparison with the pure components ([1,3-diMeIm][4,5-diNO₂-Im] m.p. 98.5 °C, and [1,3-diMeIm][4-NO₂-Tri] m.p. 85.7 °C). The intersection of the two linear equations constructed from the melting point of excess components in the mixture allowed determination of both the
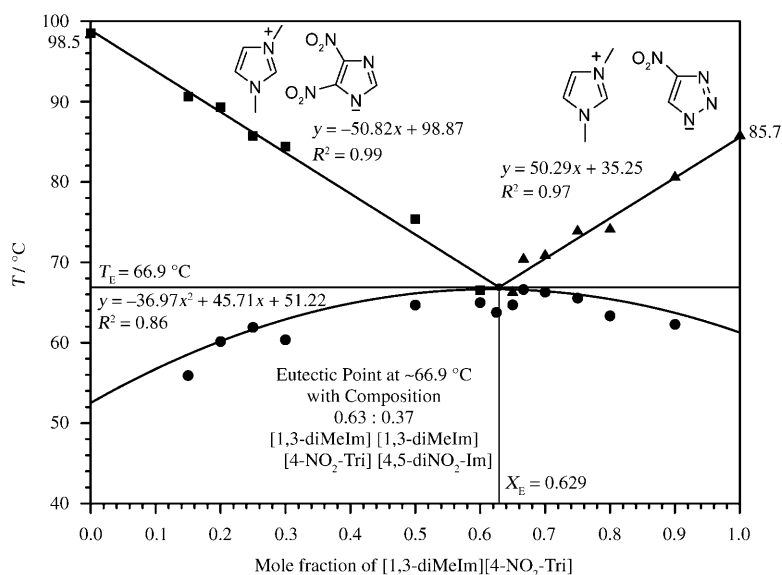
Figure 3. Two-component phase diagram for the mixture [1,3-diMeIm][4,5-diNO$_2$-Im] and [1,3-diMeIm][4-NO$_2$-Tri]: ●) melting point of the eutectic mixture; ■) depressed melting point of [1,3-diMeIm][4,5-diNO$_2$-Im] when used in excess to the eutectic composition; ▲) depressed melting point of the [1,3-diMeIm][4-NO$_2$-Tri] when used in excess to the eutectic composition.

quantitative yield. DSC analysis of the eutectic mixture of the salts gave a single melting-point transition at 66.5 °C (Figure 5) which corresponds closely to the value expected from the binary phase diagram (66.9 °C).

We have demonstrated a synthetic protocol for halide free formation of pure 1,3-dialkyli-midazolium salts which can also be utilized to directly prepare their eutectic mixtures. This easy to implement, synthetic protocol is applicable to a variety of imidazolium-based salts and can easily be extended to more complicated multiple ion systems. In order to determine the correct ion ratios for such multiple ion systems, we have also demonstrated a modified
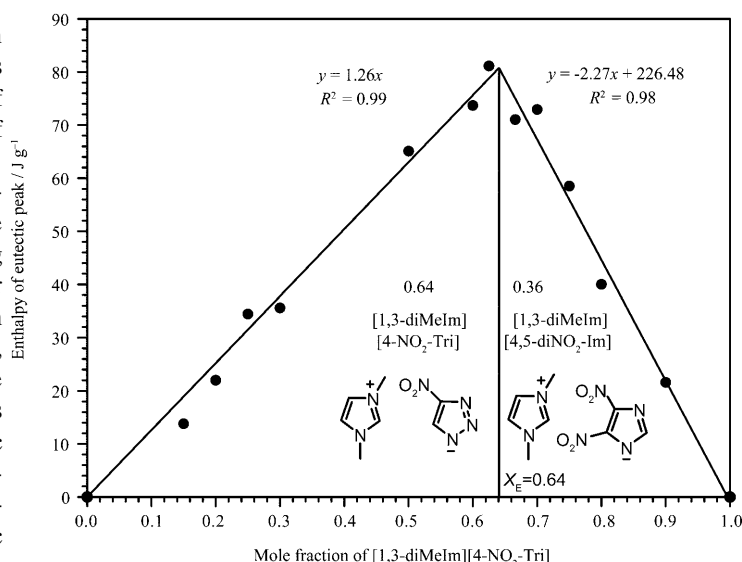
melting point for the eutectic mixture and the composition of this mixture. The melting point of the eutectic (T_E) was determined to be ≈ 69.9 °C at a eutectic composition (X_E) of ≈ 63 mol % of [1,3-diMeIm][4-NO$_2$-Tri] and 37 mol % of [1,3-diMeIm][4,5-diNO$_2$-Im].

On the other hand, evaluation of the mass-related enthalpy of the eutectic peak allows an exact determination of the eutectic composition of a pair of substances. By constructing a plot of the enthalpy of the eutectic peak against the molar composition of the mixed components, a linear correlation between both variables is expected. As shown in Figure 4, the linear relationship of the integrated peaks, with the changing ratios of the components in the mixture, allows quick determination of the composition of the eutectic peak. The R^2 values for the fitted equations were in acceptable ranges of 0.99 and 0.98 giving confidence that extrapolation of the results gives a good estimate for the eutectic point composition. The eutectic composition determined by this method was calculated to be 64 mol % of [1,3-diMeIm][4-NO$_2$-Tri] and 36 mol % of [1,3-diMeIm][4,5-diNO$_2$-Im]. The difference between the results of the two techniques in the determination of the eutectic point composition was approximately 1 mol %, providing confidence that the eutectic mixture is at approximately a 2:1 molar ratio and melts at ~67 °C.

With the eutectic composition in hand, we attempted the direct synthesis of the eutectic using the one-step, halide free approach used to prepare the individual EILs. One equivalent of [1,3-diMeIm-2-COO] was reacted with 0.64 equivalents of 4-nitro-1,2,3-triazole and 0.36 equivalents of 4,5-dinitroimidazole, in a 9:1 solution of EtOH and DMSO (Scheme 2). The eutectic mixture [1,3-diMeIm][4,5-diNO$_2$-Im]$_{0.36}$[4-NO$_2$-Tri]$_{0.64}$ was obtained as yellow solid in

Figure 4. Determination of eutectic mixture composition utilizing enthalpies of the eutectic peaks for mixtures of [1,3-diMeIm][4-NO$_2$-Tri] and [1,3-diMeIm][4,5-diNO$_2$-Im].

DSC technique for the determination of the eutectic composition which i) is simple in operation, ii) is quick, and iii) requires very small sample sizes (ca. 200 mg of each IL for the entire study) which minimizes the hazards associated with the usage of high quantities of energetic materials.

We envision that the eutectic approach can be easily adapted to the modification of the melting points of many ILs when the targeted materials fall short of melting point (or other physical property) requirements and where the presence of multiple ions does not interfere with the specific application desired. The modified DSC protocol for the de-
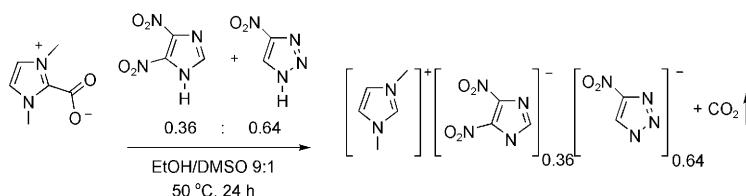
Scheme 2. One-pot synthesis of the eutectic mixture [1,3-diMeIm][4,5-diNO$_2$-Im]$_{0.36}$[4-NO$_2$-Tri]$_{0.64}$.
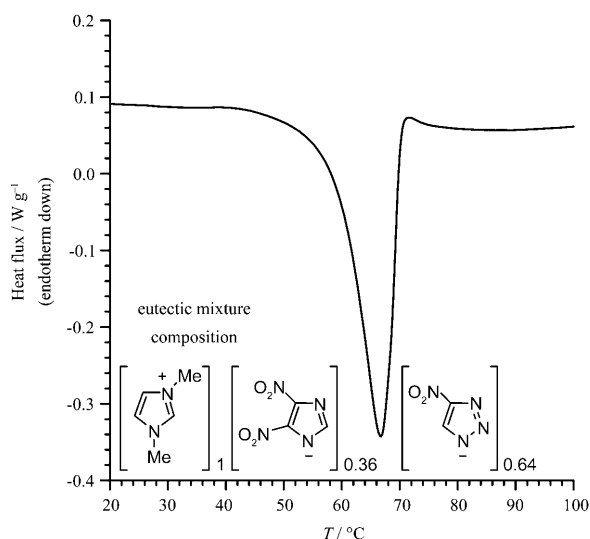

Figure 5. DSC analysis of the eutectic mixture.

termination of the eutectic point can be used in high throughput screening of binary and ternary mixtures of ILs leading to the ready identification of additional useful eutectic mixtures.

Experimental Section

5-Nitro-1H-1,2,3-triazole was purchased from Sigma–Aldrich (St. Louis, MO) and used as received.

4,5-Dinitroimidazole was supplied by the Professor Alan R. Katritzky group (University of Florida, Gainesville, FL).

1,3-Dimethylimidazolium-2-carboxylate: This zwitterion was obtained according to a literature procedure.[8] Colorless crystals of the product, with melting at the decomposition temperature, were obtained in 85% yield and >99% purity. The NMR data were consistent with literature data.

Synthesis of azolium azolate salts: To 4,5-dinitroimidazole or 5-nitro-1,2,3-triazole (0.5 mmol), dissolved in 50% aqueous ethanol (v/v), 1,3-dimethylimidazolium-2-carboxylate (0.5 mmol), dissolved in 50% aqueous ethanol (v/v, 2 mL) and DMSO (0.5 mL) was added dropwise. The reaction mixture was heated to 40°C for 48 h, after which the solvent was removed in vacuo at 90°C. Both samples were dried under high vacuum for 48 h at 50°C to ensure all moisture was removed. **[1,3-diMeIm][4,5-diNO$_2$-Im]**: Yellow, crystalline solid; m.p. 98.5°C; $T_{5\% \text{ decomp}}$ (onset to 5% decomposition) 215°C; ^{1}H NMR (360 MHz, [D$_6$]DMSO, 23°C, TMS): $\delta = 9.02$ (s, 1H; C2-H), 7.67 (s, 2H; C4/C5-H), 6.94 (s, 1H; C2'-H), 3.84 ppm (s, 6H; N-CH$_3$); ^{13}C NMR (90 MHz, [D$_6$]DMSO, 23°C, TMS): $\delta = 140.16$ (C4'/5'), 139.25 (C2'), 136.92 (C2), 123.33 (C4/C5), 35.55 ppm (N-CH$_3$). **[1,3-diMeIm][4-NO$_2$-Tri]**: Yellow, crystalline solid; m.p. 85.7°C; $T_{5\% \text{ decomp}}$ 187°C; ^{1}H NMR (360 MHz, [D$_6$]DMSO, 23°C, TMS): $\delta = 9.08$ (s, 1H; C2-H), 8.04 (s, 1H; C4'-H), 7.69 (d, 2H; C4/C5-H), 3.86 ppm (s, 6H; N-CH$_3$); ^{13}C NMR (90 MHz, [D$_6$]DMSO, 23°C, TMS): $\delta = 154.1$ (C4'), 136.99 (C2), 129.39 (C5'), 123.34 (C4/C5), 35.57 ppm (N-CH$_3$).

Synthesis of the eutectic mixture: 1,3-Dimethylimidazolium-2-carboxylate (100.0 mg, 0.714 mmol) was placed in a 10 mL round bottom flask and EtOH/DMSO 9:1 (2 mL) was added. To this solution, 4,5-dinitroimidazole (40.6 mg, 0.257 mmol) and 5-nitro-1,2,3-triazole (52.1 mg, 0.457 mmol) was added. The reaction was stirred for 24 h at 50°C, after which time the solvents were evaporated first on the rotary evaporator at 60°C, and then placed under high vacuum for an additional 12 h at 60°C. The product, a eutectic mixture with the formula [1,3-diMeIm][4,5-NO$_2$-Im]$_{0.36}$[4-NO$_2$-Tri]$_{0.64}$ was obtained as a yellow solid in quantitative yield. The sample was analyzed by NMR and the spectra corresponds to the spectra of [1,3-diMeIm][4,5-diNO$_2$-Im] and [1,3-diMeIm][4-NO$_2$-Tri] with the integration of peaks in the correct ratios for the ratio of starting materials. No carboxylate peak from the starting material was observed in the ^{13}C NMR.

DSC protocol: 1) Two separate solutions of the ILs were prepared by weighting 1 mmol of [1,3-diMeIm][4-NO$_2$-Tri] or 1 mmol [1,3-diMeIm][4,5-diNO$_2$-Im] in 5 mL volumetric flasks with dry N$_2$ gas blown over the sample and balance. The volumetric flasks were placed under high vacuum at 50°C for 6 h, after which time they were reweighed and water (polished to 18.1–18.2 MΩ cm (Nanopure, Barnstead, Dubuque, IA) was added. The drying and refilling cycle allowed determination of the true mass of the salts used, since this was difficult to establish during the first weighting due to extremely high hygroscopicity of the samples.

2) Homogenous solutions, containing various mole fractions (0.00, 0.15, 0.20, 0.25, 0.30, 0.50, 0.60, 0.625, 0.65, 0.666, 0.70, 0.75, 0.80, 0.90, 1.00) of [1,3-diMeIm][4-NO$_2$-Tri] and [1,3-diMeIm][4,5-diNO$_2$-Im] were prepared to yield a total of 50 μmol of each solution (Table S1).

3) The samples were concentrated by placement in a vacuum desiccator for 6 h at room temperature. Thereafter, concentrated solutions were transferred into pre-weighed DSC aluminum pans. The open pans were then dried under high vacuum for additional 12 h at 50°C, after which time the pans were closed and reweighed. The final mass of the mixture of ILs was designed to be between 9 and 13 mg in each pan.

4) The DSC protocol for determination of sample melting points involved three heating cycles and two cooling cycles. (The results of the first heating cycle were disregarded.) Each DSC cycle involved: i) initial heating to 120°C (heating rate 5°C min^{-1}), ii) isotherm at 120°C for 20 min to allow any possible water present in the sample to evaporate, iii) cooling to 0°C (heating rate 10°C min^{-1}), iv) isotherm at 0°C for 5 min, v) heating to 120°C (heating rate 2.5°C min^{-1}), vi) repeat steps ii)–v).

5) The results were taken from the third heating cycle, and were plotted as the molar ratio of [1,3-diMeIm][4-NO$_2$-Tri] to [1,3-diMeIm][4,5-diNO$_2$-Im] (Figures 3 and 4).

6) The melting transition peaks were integrated using PeakFit software (Systat Software, Inc, San Jose, CA, USA). The residuals procedure used for the determination initially places peaks by finding local maxima in a smoothed data stream. Hidden peaks are then optionally added where peaks in the residuals occur.

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