Articles

Strategies Toward Syntheses of Triazolyl- or Triazolium-Functionalized Unsymmetrical Energetic Salts

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Triazolyl-functionalized monocationic energetic salts (**2a−m**) were prepared through reactions of 1-(chloromethyl)-1H-1,2,4-triazole with 1-methylimidazole, 1-methyl-1,2,4-triazole, or 4-amino-4H-1,2,4-triazole in the presence of NaI, followed by metathetical reactions with equivalent silver salts. Subsequent protonation with corresponding acids gave rise to triazolium-functionalized diquaternary salts (**3a−c**). Direct treatment of neutral 1-(1*H*-imidazole-1-yl)methylene-1*H*-1,2,4-triazole, which was prepared by reaction of 1-(chloromethyl)-1H-1,2,4-triazole with imidazole in the presence of a base, with acids in methanol or metathesis with silver salts after quaternization with methyl iodide gave rise to the corresponding diquaternary energetic salts **5a−c** and **7a−d**, respectively. All of the energetic salts were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and density determinations. The majority of them exhibit good thermal stability and relatively high density. The synergistic effect of two energetic rings in cations and the effect of anions on their preparation and physicochemical properties were examined and are discussed. The densities, standard enthalpies of formation, detonation pressures, detonation velocities, and specific impulse values for the unsymmetric dicationic energetic salts were calculated.

Introduction

There is significant interest in the development of new energetic compounds for use as aerospace propellants and fuels for explosives.[1−6] Much effort has been focused on the design and synthesis of high-energy density materials (HEDM) with higher performance and/or enhanced insensitivity to thermal shock, friction, and electrostatic discharge. In the context, nitrogen-containing heterocyclic compounds, such as imidazole, triazole, and tetrazole, have attracted considerable attention because their energy is directly attributable to the large number of inherently energetic N−N and C−N bonds.[2] Accordingly, compared with traditional energetic compounds, such as TNT, HMX, and RDX, their energy is derived from their high positive heat of formation rather than from the combustion of the carbon backbone or the ring/cage strain.[3] Perhaps most interestingly, the nitrogen-containing heterocycles are easily quarternized or protonized at nitrogen to form energetic cations, which give highly energetic salts when paired with energetic anions. The salts usually possess advantages over nonionic molecules because of their lower vapor pressures and higher densities.[4] In addition, their properties are readily varied and tuned through the modification of the cationic and/or anionic components. Substitution of hydrogen in the heterocyclic rings with nitro, cyano, or other electron-withdrawing energetic groups is a well-established strategy for the design and optimization of energetic cations,[5] but these groups decrease the susceptibility to protonation or quarternization, and thus the formation of salts was suppressed. Although polyazido-subsituted heterocycles possess more energetic content, they tend to be

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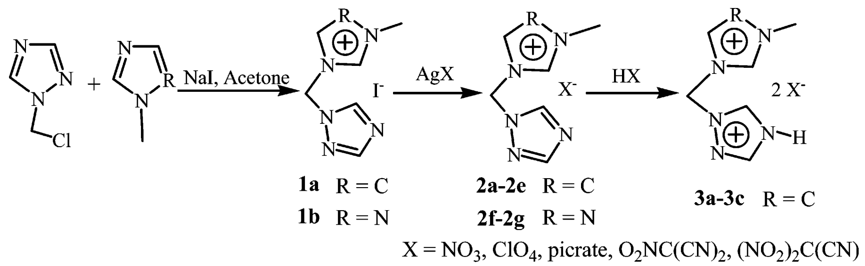
Scheme 1



extremely sensitive to spark, friction, impact, and heat.[6] Thus, an alternative way is needed to develop new energetic materials.

Triazole is a versatile and widely used starting material in the synthesis of a wide range of energetic molecules and salts.[7] It has a high positive standard heat of formation ($\Delta H_f{}^0{}_{(cryst)} = 109$ kJ/mol).[8a] Various triazolium-based monocationic salts paired with inorganic anions (nitrate, perchlorate, and dinitramide)[8] or organic anionic (picrate, 3,5-dinitro-1,2,4-triazolate) were reported,[9] but the modification of salts were largely restricted to substitution of hydrogen in the triazolium ring. The direct introduction of triazole into energetic salts as a functional group has rarely received attention despite the fact that the triazolyl group in the salts might be further quarternized to form dicationic salts. Recent research suggests di- and polycationic salts usually demonstrate wider liquid ranges, higher densities, and greater thermal stabilities than their monocationic analogues.[10] Moreover, it was anticipated that advantages of triazolyl or triazolium in this kind of salt could be imparted to resulting energetic salts, which not only makes salts with combined properties of both functional groups, but also allows the production of a much larger collection of energetic salts. As an extension of our research programs in the heterocycle-based energetic salts,[9,11] we became interested in unsymmetric energetic salts containing different heterocyclic rings. Therefore, in this paper, we wish to report the syntheses and characterization of a series of triazolyl- or triazolium-functionalized unsymmetric energetic salts.

Results and Discussion

The synthetic pathway to triazolyl- or triazolium-functionalized energetic salts is depicted in Schemes 1−3. Reaction of 1-(chloromethyl)-1H-1,2,4-triazole with 1-methylimidazole in the presence of NaI gave rise to **1a**; subsequent metathetical reactions with equivalent silver salts led to the formation of monocationic salts **2a**−**e** in good yield. As expected, the protonation of triazolyl-functionalized monocationic salts (**2a**−**c**) with corresponding acids generated triazolium-functionalized diquaternary salts (**3a**−**c**) in almost quantitative yield (Scheme 1).

To gain insight into the scope and limitation of the strategy, we examined triazolium- and 4-aminotriazolium-based salts. In general, introduction of the third nitrogen atom in the 1,2,4-triazole ring makes the species slightly more acidic and more resistant toward electrophilic attack than the 1,3-imidazole ring; hence, the difficulty of quaternization is increased. Encouragingly, triazolium-based iodide salt **1b** was obtained through treatment of 1-(chloromethyl)-1H-1,2,4-triazole, 1-methyl-1,2,4-triazole and NaI. The resulting salts (**2f** and **2g**) were generated through metathesis with equivalent silver perchlorate and silver picrate, respectively (Scheme 1), but metathesis with silver nitrate under identical conditions gave rise only to a contaminated syrup. It was impossible to remove the contaminants by washing or recrystallization using various solvents, although various triazolium-based monocationic nitrate salts have been prepared using similar protocols.[8,9,11] Attempts to protonize **2f** and **2g** with perchloric acid and picric acid by following the same synthetic procedures as used for **3a**−**c** failed, resulting only in the recovery of **2f** and **2g**. When harsh reaction conditions, such as higher temperatures, extended reaction times, and excess of picric acid, were employed in the reaction of **2g** with picric acid, only small amounts of the desirable dicationic salt were detected by NMR. This suggests that the basicity of the triazolyl ring is significantly reduced by the triazolium group.

With similar protocols, treatment of 1-(chloromethyl)-1H-1,2,4-triazole, NaI, and 4-amino-4H-1,2,4-triazole in acetone and acetonitrile produced Schiff-based salt **1c** and the desired iodide salt **1d**, respectively (Scheme 2). The formation of **1c** was confirmed by the presence of the methyl group resonances at 2.29 and 2.12 ppm, as well as the absence of the resonance for the amino group at 7.33 ppm in the ^{1}H NNR spectra. In the ^{13}C NMR spectrum, the signal for the carbon atom of C═N in **1c** appears at 185.5 ppm, which is a characteristic peak for Schiff-based complexes. Similarly, the impurities in products of equivalent reaction of **1c** or **1d** with silver nitrate are difficult to remove, whereas **2h**−**m** were readily available via metathetical reactions with equivalent silver salts. The protonation of **2h** with perchloric acid led to its hydrolysis and the formation of **2j**. The failure of

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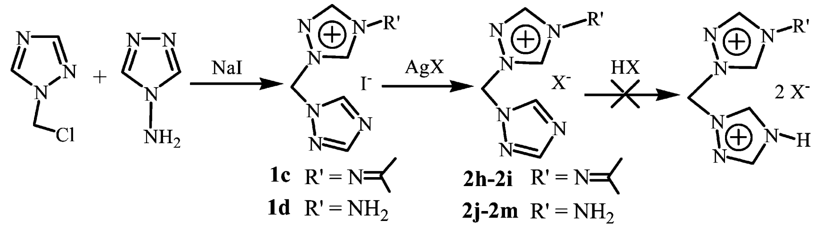
Scheme 2



Scheme 3

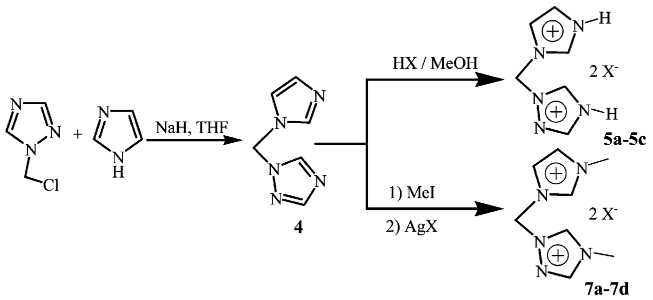


Table 1. Physical Properties of Unsymmetric Energetic Salts

compd	X	T_m[a] (°C)	T_d[b] (°C)	D_{expt}[c] (g/cm³)	d_{calcd}[d] (g/cm³)
2a	NO_3	116	242	1.45	1.47
2b	ClO_4	126	294	1.60	1.60
2c	picrate	149	271	1.55	1.59
2d	$O_2NC(CN)_2$	89	274	1.41	1.45
2e	$(O_2N)_2C(CN)$	124	251	1.48	1.50
2f	ClO_4	176	232	1.62	1.65
2g	picrate	165	213	1.60	1.62
2h	ClO_4	167	228	1.53	1.55
2i	$(O_2N)_2C(CN)$	189	202	1.53	1.49
2j	ClO_4	144	229	1.67	1.72
2k	picrate	164	199	1.65	1.66
2l	$O_2NC(CN)_2$	107	206	1.48	1.51
2m	$(O_2N)_2C(CN)$	170	215	1.62	1.59
3a	NO_3	103	245	1.59	1.53
3b	ClO_4	111	299	1.69	1.73
3c	picrate	140	191	1.61	1.66
5a	NO_3	135	167	1.63	1.58
5b	ClO_4	156	291	1.74	1.78
5c	picrate	148	189	1.67	1.68
7a	ClO_4	159	260	1.67	1.69
7b	picrate	176	234	1.60	1.63
7c	$O_2NC(CN)_2$	95	220	1.43	1.47
7d	$(O_2N)_2C(CN)$	123	167	1.54	1.53

[a] Melting point. [b] Thermal degradation. [c] Experimental density. [d] Calculated density.

protonation of **2j** and **2k** with perchloric acid and picric acid, respectively, is also not surprisingbecause of the stronger electron-withdrawing ability of 4-aminotriazolium.

As a comparison, the successful protonation of triazolyl-functionalized imidazolium-based salts **2a**−**e** encouraged us to prepare diquaternary salts bearing the same hydrogen or methyl substituents on both the imidazolium and triazolium rings. Neutral compound **4** was prepared by reaction of 1-(chloromethyl)-1H-1,2,4-triazole with imidazole in the presence of base.[10b] Direct reactions with acids in methanol or metathesis with silver salts after quaternization with methyl iodide gave rise to corresponding diquaternary salts **5a**−**c** and **7a**−**d**, respectively (Scheme 3). It should be mentioned that a previous study revealed a significant similarity between nitrate and its pseudochalogen analogue, nitrodicyanomethanide $[O_2NC(CN)_2]^-$, concerning their electronic structures and electrochemical and ligation properties,[12] but **7c** was successfully isolated by the reaction of 1-(3-methylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium) diiodide (**6**) with silver(I) nitrodicyanomethanide. However, the product from reaction of **6** and silver nitrate contained unremovable concomitants.

All of the unsymmetric energetic salts are stable in air and moisture. Remarkably, although anhydrous picric acid tends to be sensitive to impact and friction and is required to be stored in water,[13] the monocationic (**2c**, **2g, 2k**) and dicationic (**3c**, **5c**, **7b**) picrate salts are stable; moreover, they have poor solubility in most solvents except hot water, hot methanol, and high polar solvents such as DMF and DMSO. The remainder of the salts are soluble in water and are insoluble in less-polar solvents, such as hexane, diethyl ether, chloroform, and ethyl acetate.

The IR spectra of the nitrodicyanomethanide salts exhibit two strong stretching absorption bands of cyanide in the 2197−2211 cm^{-1} region, whereas dinitrocyanomethanide salts show one strong stretching absorption peak of cyanide in the 2208−2216 cm^{-1} region. The UV−vis spectra of nitrodicyanomethanide and dinitrocyanomethanide salts show the maximum absorbance around 317 and 343 nm, respectively. A red shift was observed for dinitrocyanomethanide salts.

The structures of these energetic salts were confirmed by the data from ^1H and ^{13}C NMR spectra and elemental analyses. In their ^1H and ^{13}C NMR spectra, two nitrogen-containing heterocyclic rings in each salt show two sets of signals even for diquaternary salts bearing the same substituents **5a**−**c** and **7a**−**d**, which indicates their nonequivalence and confirms the proposed unsymmetry of the salts. The chemical shifts of protons of the methylene bridge (NCH_2N) are in the range 6.65−6.89 ppm. There was minimal or no change in the chemical shifts of monoquaternary salts **2a**−**m** when compared with those of their respective precursors **1a**−**d**. For the triazolyl and triazolium-functionalized imidazolium-based salts **2a**−**c** and **3a**−**c**, the cations display the same patterns in their ^1H and ^{13}C spectra, which indicates that protonation of triazole has little effect on their chemical shifts. However, an obvious downfield shift was observed in diprotonated salts **5a**−**c** when compared with their precursor **4**. The chemical shift of the triazolium acidic proton H5 (NCHN) in triazolium-based salts **2f**−**m** is at 10.25−10.75 ppm, which is at much a lower field than the 9.34−9.39 ppm for the imidazolium acidic proton H2 (NCHN) in

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Scheme 4

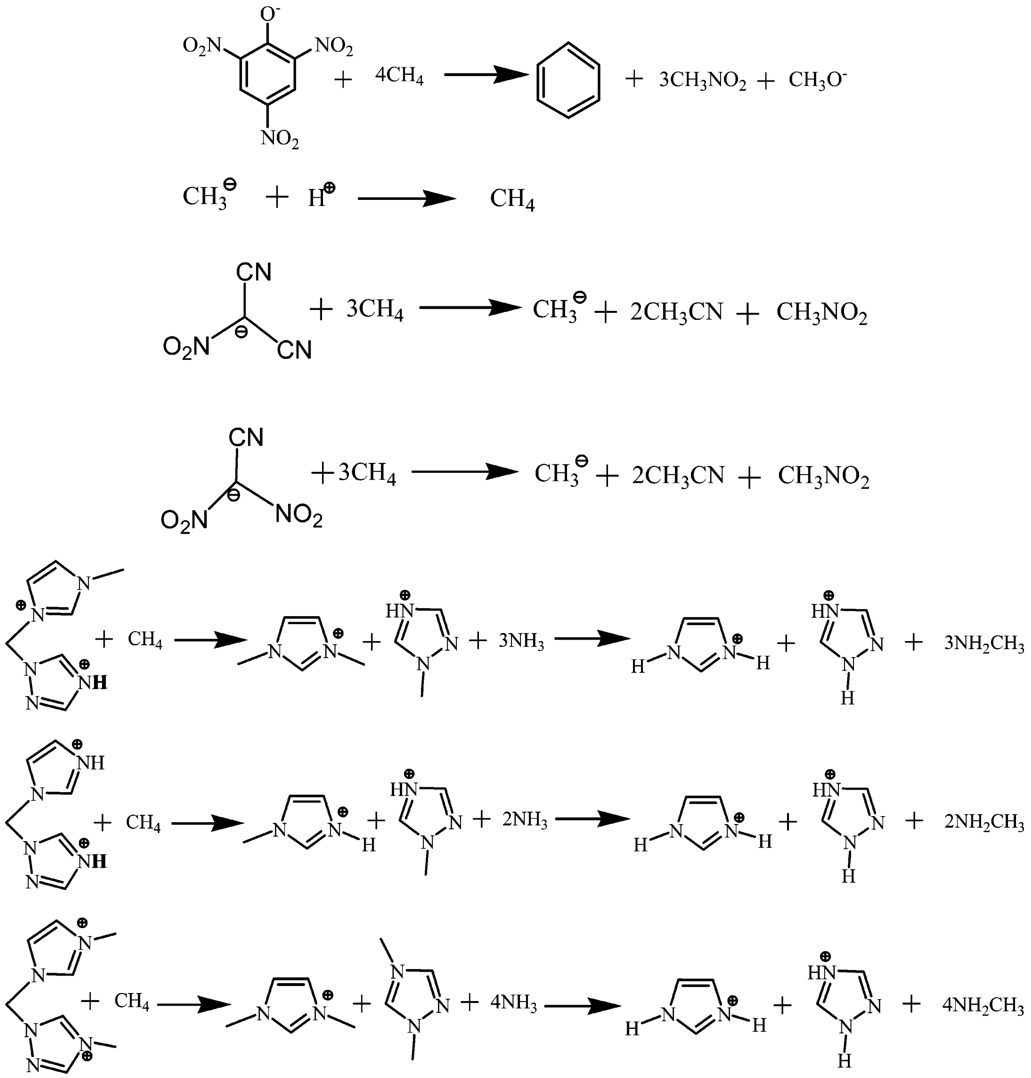

Table 2. Calculated Thermochemical Values for Unsymmetric Dicationic Energetic Salts

compd	X^-	Δ_fH_{Latt}[a]	Δ_fH_m[b] (cation)	Δ_fH_m[c] (anion)	Δ_fH_m[d] (salt)	P[e]	vd[f]	I_{sp}[g]
3a	NO_3	1566.7	1805.2	−307.9	−377.2	23.6	7725	237
3b	ClO_4	1501.2	1805.2	−277.8	−251.6	25.0	7428	246
3c	picrate	1301.9	1805.2	−108.5	286.3	19.0	7019	209
5a	NO_3	1596.7	1846.8	−307.9	−365.6	24.8	7609	243
5b	ClO_4	1527.2	1846.8	−277.8	−236.0	25.4	7717	255
5c	picrate	1320.5	1846.8	−108.5	309.3	15.3	6559	185
7a	ClO_4	1482.7	1760.9	−277.8	−277.3	20.6	7266	200
7b	picrate	1293.1	1760.9	−108.5	250.8	18.3	6964	205
7c	$O_2NC(CN)_2$	1407.7	1760.9	32.2	385.4	11.1	6063	170
7d	$(O_2N)_2C(CN)$	1400.4	1760.9	−127.7	105.1	16.7	6898	194

[a] Molar lattice energy (kJ/mol). [b] Molar enthalpy of formation of cation (kJ/mol). [c] Molar enthalpy of formation of anion (kJ/mol). [d] Molar enthalpy of formation of salt (kJ/mol). [e] Detonation pressure (GPa). [f] Detonation velocity (m s^{-1}). [g] Specific impulse (seconds).

2a−**e**, which clearly supports the higher acidity of the triazolium ring.

Physical Properties of the Unsymmetric Salts. Phase-transition temperatures and thermal stabilities of the unsymmetric energetic salts were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. As shown in Table 1, their melting points and thermal degradation temperatures are in the ranges 89−176 and 167−299 °C, respectively. Generally, the perchlorate salts and picrate salts have higher melting points and better thermal stability than the corresponding nitrate salts, but there is no clear relationship between perchlorate and picrate salts. Interestingly, nitrodicyanomethanide salts (**2d**, **2l**, **7c**) exhibit lower melting points than their nitrate, dinitrocyanomethanide, picrate, and perchlorate analogues. The melting points of **2d** and **7c** are below 100 °C and can thus be classified as ionic liquids.[14] This suggested that nitrodicyanomethanide is a promising anion in the area of energetic salts of lower melting points. Surprisingly, the melting points of triazolium-functionalized salts (**3a**−**c**) are

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lower than those of their triazolyl-functionalized analogues (**2a**−**c**). In the triazolium-based perchlorate salts, variation of *N*-substituents from methyl to N═CMe$_2$ to NH$_2$, the melting points decrease from 176 (**2f**) to 167(**2h**) to 144 °C (**2j**).

The densities of analogous energetic salts are in the order perchlorate > picrate > dinitrocyanomethanide > nitrate ∼ nitrodicyanomethanide. As expected, the diquaternary energetic salts show higher density than corresponding monocationic salts. It is not surprising that the densities of triazolium-functionalized salts (**3a**−**c**) are higher than those of triazolyl-functionalized analogues (**2a**−**c**) and lower than those of the diprotonated analogues (**5a**−**c**). Hence, the diprotonated perchlorate salt **5b** possesses the highest density (1.74 g/cm^3). The effect of substituents on density is observed in triazolium-based perchlorate salts: **2j** (1.67 g/cm^3) > **2f** (1.62 g/cm^3) > **2h** (1.53 g/cm^3). The densities were also estimated according to our newly tabulated volume parameters, which agreed reasonably with the experimental values within 5% deviation with the exception of **3a**.[15]

Thermochemical Properties of Unsymmetric Energetic Salts. The enthalpies of formation for unsymmetric dicationic energetic salts were calculated using Born−Haber energy cycles. On the basis of the cycle, we can simplify the heat of formation of an ionic salt by the formula

$$\Delta H_f^o(\text{ionic salt, 298 K}) = \Delta H_f^o(\text{cation, 298 K}) + \Delta H_f^o(\text{anion, 298 K}) - \Delta H_L$$

where ΔH_L is the lattice energy of the ionic salts, which could be predicted by the formula suggested by Jenkins et al.[16] as being

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \qquad \text{(A)}$$

where n_M and n_X depend on the nature of the ions M_p^+ and Xq^-, respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} (eq B) has the form

$$U_{POT}\ (\text{kJ mol}^{-1}) = \gamma(\rho_m/M_m)^{1/3} + \delta \qquad \text{(B)}$$

where ρ_m is density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g or mg), the coefficients γ (kJ mol^{-1}), and δ (kJ mol^{-1}) take the values from ref 16.

The calculated heats of formation of ClO$_4$ and NO$_3$ are −277.8 and −307.9 kJ/mol, respectively.[11f] The heats of formation of the other anions and the cations are computed using the method of isodesmic reactions[8c] (Scheme 4). The enthalpy of reaction ($\Delta H_r^o{}_{298}$) is obtained by combining the MP2(full)/6-311++G** energy difference for the reaction, the scaled zero-point energies (B3LYP/6-31 + G**), and other thermal factors. Thus, the heat of formation being investigated can be readily extracted.

As shown in Table 2, the heat of formation of anions and cations are in the order O$_2$NC(CN)$_2$ > picrate > (O$_2$N)$_2$C(CN) > ClO$_4$ > NO$_3$ and 1-(imidazolium-1-yl)methylene-(1,2,4-triazolium) > 1-(methylimidazolium-1-yl)methylene-(1,2,4-triazolium) > 1-(3-methylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium), respectively. A similar trend was observed for enthalpies of formation for dicationic energetic salts, which are in the range from 385.4 to −377.2 kJ/mol. It is noteworthy that the O$_2$NC(CN)$_2$ anion possesses a positive heat of formation (33.2 kJ/mol) and that its salt (**7c**) has a much higher enthalpy of formation than those of its analogues (**7a**, **7b**, **7d**). This suggests that O$_2$NC(CN)$_2$ is a promising anion in the field of high-energy materials. Salts with O$_2$NC(CN)$_2$, (O$_2$N)$_2$C(CN), and picrate anions have positive enthalpies of formation, whereas ClO$_4$ and NO$_3$ salts possess negative values. The negative results mainly result from large negative heats of formation of anions. It is not surprising that nitrate salts have the lowest enthalpies of formation in analogous salts.

From the values of the heats of formation and density of energetic salts, the expected detonation pressures (*P*), detonation velocities (*D*), and specific impulse I_{sp} (s) were calculated on the basis of the traditional Chapman-Jouget thermodynamic detonation theory using Cheetah 4.0.[17] For all the salts, the calculated detonation pressures lie in the range from 11.1 (**7c**) to 25.4 (**5b**) GPa. Most of the pressures are higher than that of tetranitromethane (14.4 GPa) and are comparable to that of the trinitrophenylmethylnitramine (22.1 GPa).[18] Detonation velocities are in the range from 6063 (**7c**) to 7725 m s^{-1} (**3a),** which are comparable to that of 1,3,5-triamino-2,4,6-trinitrobenzene (7660 m s^{-1}).[18] Generally, the detonation pressure and specific impulse of analogous salts are in the order ClO$_4$ > NO$_3$ > picrate, but there is no clear relationship for detonation velocities.

Conclusions

We have developed a novel approach for the rational design and synthesis of the unsymmetric heterocycle-based energetic salts. These salts can be regarded as being the replacement of the hydrogen atom of a methyl group in corresponding imidazolim-, triazolium, 4-aminotrizolium-based salts by triazolyl or triazolium functional groups. The synergistic effect between triazolyl or triazolium and the other azolium ring on their synthesis and their physicochemical properties were examined. The relationship between their structures and melting points, thermal stabilities, densities, standard enthalpies of formation, detonation pressures, detonation velocities, and specific impulse was determined. Most of the energetic salts show good thermal stability. Their densities range between 1.41 and 1.74 g/cm^3. The densities of triazolium-functionalized diquaternary energetic salts are higher than those of the triazolyl-functionalized monocationic analogues. The effect of cations on density and enthalpies

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of formation of analogous energetic salts are in the order 1-(imidazolium-1-yl)methylene-(1,2,4-triazolium) > 1-(methylimidazolium-1-yl)methylene-(1,2,4-triazolium) > 1-(3-methylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium). Among them, $O_2NC(CN)_2$ is a promising anion for design and synthesis of energetic materials, because its salts exhibit lower melting points and higher enthalpies of formation than their analogues. In conclusion, this research has demonstrated that nitrogen-containing heterocycle-functionalized energetic salts are a promising pathway toward the design and synthesis of high-energy-density materials.

Experimental Section

Caution: Although we have experienced no difficulties with the shock and friction sensitivity of these compounds with high nitrogen content and rather high heats of formation, they should be synthesized in millimolar amounts and handled with extreme care.

General Methods. 1-(1*H*-Imidazole-1-yl)methylene-1*H*-1,2,4-triazole (**4**)[10b] and 1-(3-methylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium) diiodide (**6**),[10b] silver(I) nitrodicyanomethanide,[12a] silver(I) dinitrocyanomethanide,[19] and silver picrate[20] were prepared as reported previously. The other chemicals were obtained commercially and used as received. A standard Schlenk line system was used for handling the air- and moisture-sensitive reactions under nitrogen. IR spectra were recorded using a KBr plate on a BIORAD model 3000 FTS spectrometer. UV−vis spectra were measured in acetonitrile on an Ocean Optics USB 2000 UV−vis spectrophotometer in the 250−600 nm region. ^1H and ^{13}C spectra were recorded on spectrometers at 300 and 75 MHz, respectively, using DMSO-d_6 as a locking solvent except where otherwise indicated. Chemical shifts are reported in parts per millions relative to TMS. GC/MS spectra were determined using an appropriate instrument. Densities were measured at 25 °C using a Micromeritics Accupyc 1330 gas pycnometer. Differential scanning calorimetry (DSC) measurements were performed using a calorimeter equipped with an auto-cool accessory and calibrated using indium. The following procedure was used in experiments for each sample: cooling from 40 to −80 °C and heating to 400 or 500 °C at 10 °C/min. The transition temperature, T_m, was taken as peak maximum. Thermogravimetric analysis (TGA) measurements were carried out by heating samples at 10 °C/min from 25 to 500 °C in a dynamic nitrogen atmosphere (flow rate = 70 mL/min). Elemental analyses were performed on a CE-440 Elemental Analyzer.

Theoretical Study. Computations were performed with the Gaussian03 (revision D.01) suite of programs.[21] The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses were carried out using B3-LYP functional with 6-31+G** basis set,[22] and single-energy points were calculated at the MP_2(full)/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

1-(Methylimidazolium-1-yl)methylene-(1,2,4-triazole) Iodide (1a). To a solution of 1-(chloromethyl)-1H-1,2,4-triazole (1.18 g, 10.0 mmol) in acetone (30 mL) was added 1-methylimidazole (0.91 g, 11.0 mmol) and sodium iodide (1.65 g, 11.0 mmol). After the mixture was stirred for 2 days at 25 °C, the solution was filtered and the solvent was evaporated slowly to afford a colorless solid. The solid was washed three times with Et_2O (3 × 20 mL) and then recrystallized from acetone to afford a colorless solid. Yield: 2.3 g (79%). ^1H NMR: δ 9.39 (s, 1H), 8.89 (s, 1H), 8.14 (s, 1H), 7.90 (s, 1H), 7.74 (s, 1H), 6.70 (s, 2H), 3.88 (s, 3H). ^{13}C NMR: δ 152.9, 145.5, 137.3, 124.2, 121.9, 58.7, 36.2.

1-(Methyltriazolium-1-yl)methylene-(1,2,4-triazole) Iodide (1b). The procedures were similar to those for the synthesis of **1a** except 1-methylimidazole was replaced by 1-methyl-1,2,4-triazole (0.92 g, 11.0 mmol). Colorless solid, yield: 2.0 g (68%). ^1H NMR (CD_3OD): δ 10.35 (s, 1H), 9.31 (s, 1H), 8.97 (s, 1H), 8.18 (s, 1H), 6.94 (s, 2H), 4.22 (s, 3H). ^{13}C NMR (CD_3OD): δ 154.9, 147.6, 146.1, 145.4, 59.9, 40.7.

1-(4-Dimethylketiminetriazolium-1-yl)methylene-(1,2,4-triazole) Iodide (1c). The procedure was similar to that for the synthesis of **1a** except 1-methylimidazole was replaced by 4-amino-4H-1,2,4-triazole (0.93 g, 11.0 mmol). Colorless solid, yield: 2.8 g (84%). ^1H NMR: δ 10.71 (s, 1H), 9.45 (s, 1H), 8.96 (s, 1H), 8.14 (s, 1H), 6.90 (s, 2H), 2.29 (s, 3H), 2.12 (s, 3H). ^{13}C NMR: δ 185.5, 152.8, 146.2, 141.8, 140.4, 61.60, 25.39, 20.52.

1-(4-Aminotriazolium-1-yl)methylene-(1,2,4-triazole) Iodide (1d). The compound was synthesized using 1-(chloromethyl)-1H-1,2,4-triazole (1.18 g, 10.0 mmol), 4-amino-4H-1,2,4-triazole (0.93 g, 11.0 mmol), and sodium iodide (1.65 g, 11.0 mmol) in acetonitrile (30 mL) through following the procedures of **1a**. Colorless solid, yield: 1.6 g (55%). ^1H NMR: δ 10.78 (s, 1H), 9.27 (s, 1H), 9.00 (s, 1H), 8.12 (s, 1H), 7.33 (s, 2H), 6.91 (s, 2H). ^{13}C NMR: δ 152.9, 146.2, 145.5, 143.5, 61.1.

1-(Methylimidazolium-1-yl)methylene-(1,2,4-triazole) Nitrate (2a). To a stirring solution of **1a** (0.2911 g, 1.0 mmol) in MeOH (20 mL) was added dropwise a solution of $AgNO_3$ (0.1699, 1mmol) in MeOH (15 mL); the resulting solution was stirred at 25 °C for 1 h. After removal of AgI, the solvent was evaporated in vacuo and the residue was washed three times with Et_2O (10 mL) to give colorless solids. Yield: 0.19 g (84%). IR: 3096 (w, br), 1739 (vw), 1631 (w), 1578 (w), 1559 (m), 1510 (s), 1433 (s), 1321 (vs), 1277 (m), 1317 (s), 1277 (m), 1216 (w), 1168 (s), 1125 (vw), 1016 (vw), 837 (vw), 777 (m), 732 (m), 677 (w), 623 (w) cm^{-1}. ^1H NMR: δ 9.38 (s, 1H), 8.85 (s, 1H), 8.14 (s, 1H), 7.89 (s, 1H), 7.74 (s, 1H), 6.68 (s, 2H), 3.87 (s, 3H). ^{13}C NMR: δ 153.0, 145.6, 137.5, 124.3, 122.0, 58.7, 36.1. Anal. Calcd for $C_7H_{10}N_6O_3$ (226.19): C, 37.17; H, 4.46; N, 37.15. Found: C, 37.12; H, 4.38; N, 37.20.

1-(Methylimidazolium-1-yl)methylene-(1,2,4-triazole) Perchlorate (2b). The procedure was similar to that for the synthesis of **2a** except $AgNO_3$ was replaced by $AgClO_4$ (0.2073 g, 1.0 mmol). Colorless solids, yield: 0.23 g (87%). IR: 3113 (m), 1710 (s), 1631 (vw), 1578 (w), 1552 (m), 1511 (s), 1435 (m), 1367 (w), 1316 (vw), 1285 (m), 1217 (m), 1165 (s), 1136 (s), 1103 (vs), 1086 (vs), 877 (vw), 775 (m), 731 (w), 671 (w), 625 (s), cm^{-1}. ^1H NMR: δ 9.34 (s, 1H), 8.83 (s, 1H), 8.14 (s, 1H), 7.86 (s, 1H), 7.71 (s, 1H), 6.65 (s, 2H), 3.87 (s, 3H). ^{13}C NMR: δ 152.9, 145.6, 137.4, 124.3, 122.0, 58.7, 36.1. Anal. Calcd for $C_7H_{10}ClN_5O_4$ (263.64): C, 31.89; H, 3.82; N, 26.56. Found: C, 31.58; H, 3.85; N, 27.04.

1-(Methylimidazolium-1-yl)methylene-(1,2,4-triazole) Picrate (2c). The compound was synthesized using **1a** (0.2911 g, 1.0 mmol) and silver picrate (0.3360 g, 1.0 mmol) in DMF (20 mL) by following the procedures for **2a**. The yellow needle solid was obtained by recrystallization in MeOH (10 mL) and H_2O (10 mL). Yield: 0.30 g (76%). IR: 3146 (w), 3101 (w), 3035 (m), 1663 (s), 1608 (s), 1560 (s), 1491 (w), 1433 (w), 1366 (m), 1335 (s), 1319 (s), 1273 (s), 1163 (m), 1076 (vw), 1015 (vw), 905 (vw), 868 (vw),

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777 (w), 737 (w), 706 (m), 669 (w), 629 (w) cm^{-1}. ^{1}H NMR: δ 9.37 (s, 1H), 8.83 (s, 1H), 8.58 (s, 2H), 8.13 (s, 1H), 7.87 (t, 1H, $J = 1.8$ Hz), 7.72 (t, 1H, $J = 1.7$ Hz), 6.67 (s, 2H), 3.87 (s, 3H). ^{13}C NMR: δ 160.8, 152.9, 145.5, 141.8, 137.4, 125.1, 124.2, 122.0, 58.7, 36.1. Anal. Calcd for $C_{13}H_{12}N_8O_7$ (392.28): C, 39.80; H, 3.08; N. 28.56. Found: C, 39.64; H, 2.98; N, 28.02.

1-(Methylimidazolium-1-yl)methylene-(1,2,4-triazole) Nitrodicyanomethanide (2d). The compound was synthesized using **1a** (0.2911 g, 1.0 mmol) and silver nitrodicyanomethanide (0.2180 g, 1.0 mmol) in MeCN (25 mL) by following the procedures for **2a**. Colorless solids, yield: 0.23 g (88%). IR: 3148 (w), 3120 (w), 3037 (vw), 2208 (s), 2198 (s), 1712 (vs), 1630 (vw), 1582 (vw), 1558 (w), 1509 (m), 1413 (s), 1360 (s), 1334 (s), 1271 (w), 1224 (m), 1208 (w), 1161 (m), 1130 (w), 1093 (vw), 1033 (vw), 1003 (w), 952 (vw), 875 (w), 850 (vw), 780 (w), 737 (m), 676 (m), 621 (m) cm^{-1}. UV−vis (λ_{max}): 317 nm. ^{1}H NMR: δ 9.35 (s, 1H), 8.83 (s, 1H), 8.14 (s, 1H), 7.87 (t, 1H, $J = 1.8$ Hz), 7.71 (d, 1H, $J = 1.7$ Hz), 6.66 (s, 2H), 3.87 (s, 1H).^{13}C NMR: δ 153.0, 145.5, 137.4, 124.2, 122.0, 116.3, 58.7, 36.1. Anal. Calcd for $C_{10}H_{10}N_8O_2$ (274.24): C, 43.80; H, 3.68; N, 40.86. Found: C, 43.73; H, 3.60; N, 40.80.

1-(Methylimidazolium-1-yl)methylene-(1,2,4-triazole) Dinitrocyanomethanide (2e). The procedure was similar to that for the synthesis of **2d** except silver nitrodicyanomethanide was replaced by silver dinitrocyanomethanide (0.2379 g, 1.0 mmol). Colorless solid, yield: 0.27 g (92%). IR: 3157 (s), 3123 (s), 3091 (s), 2208 (s), 1583 (m), 1565 (m), 1504 (s), 1442 (w), 1414 (s), 1378 (w), 1358 (w), 1333 (m), 1287 (s), 1260 (s), 1207 (s), 1168 (s), 1152 (s), 1136 (s), 1035 (m), 1011 (m), 953 (w), 909 (vw), 876 (m), 780 (m), 765 (s), 739 (s), 674 (m), 624 (m) cm^{-1}. UV−vis (λ_{max}): 258, 343 nm. ^{1}H NMR: δ 9.35 (s, 1H), 8.83 (s, 1H), 8.14 (s, 1H), 7.87 (t, 1H, $J = 1.8$ Hz), 7.72 (s, 1H), 6.66 (s, 2H), 3.87 (s, 1H).^{13}C NMR: δ 153.0, 145.5, 137.4, 124.2, 122.0, 116.3, 58.7, 36.1. Anal. Calcd for $C_9H_{10}N_8O_4$ (294.23): C, 36.74; H, 3.43; N, 38.08. Found: C, 36.58; H, 3.41; N, 38.22.

1-(Methyltriazolium-1-yl)methylene-(1,2,4-triazole) Perchlorate (2f). The procedure was similar to that for the synthesis of **2b** except **1a** was replaced by **1b** (0.2921 g, 1.0 mmol). Colorless solid, yield: 0.24 g (91%). IR: 3443 (w), 3138 (m), 3044 (w), 2962 (vw), 1734 (s), 1714(vs), 1638 (vw), 1580 (s), 1510 (s), 1439 (m), 1432 (m), 1387 (s), 1364 (s), 1280 (m), 1218 (m), 1156 (s), 1121 (s), 1089 (vs), 1020 (m), 971 (w), 874 (vw), 783 (m), 743 (m), 670 (m), 623 (s), cm^{-1}. ^{1}H NMR: δ 10.50 (s, 1H), 9.51 (s, 1H), 8.98 (s, 1H), 8.15 (s, 1H), 6.89 (s, 2H), 4.07 (s, 3H).^{13}C NMR: δ 153.0, 145.9, 144.2, 143.3, 57.2, 30.6. Anal. Calcd for $C_6H_9ClN_6O_4$ (264.63): C, 27.23; H, 3.43; N, 31.76. Found: C, 27.20; H, 3.31; N, 31.38.

1-(Methyltriazolium-1-yl)methylene-(1,2,4-triazole) Picrate (2g). The procedure was similar to that for the synthesis of **2c** except **1a** was replaced by **1b** (0.2921 g, 1.0 mmol). Yellow solid, yield: 0.32 g (81%). IR: 3150 (vw), 3119 (w), 3040 (m), 1628 (s), 1602 (s), 1582 (m), 1555 (s), 1508 (s), 1429 (m), 1368 (m), 1326 (s), 1317 (s), 1269 (s), 1206 (m), 1162 (m), 1132 (m), 1080 (w), 1020 (w), 978 (vw), 911 (vw), 890 (vw), 780 (w), 745 (m), 719 (w), 708 (m), 669 (w), 612 (w) cm^{-1}. ^{1}H NMR: δ 10.25 (s, 1H), 9.37 (s, 1H), 8.81 (s, 1H), 8.57 (s, 2H), 8.17 (s, 1H), 6.76 (s, 2H), 4.07 (s, 3H). ^{13}C NMR: δ 160.9, 153.1, 145.8, 144.2, 143.3, 141.9, 125.2, 57.3, 38.7. Anal. Calcd for $C_{12}H_{11}N_9O_7$ (393.27): C, 36.65; H, 2.82; N, 32.05. Found: C, 36.45; H, 2.82; N, 32.02.

1-(Dimethylketiminetriazolium-1-yl)methylene-(1,2,4-triazole) Perchlorate (2h). The procedure was similar to that for the synthesis of **2b** except **1a** was replaced by **1c** (0.3331 g, 1.0 mmol). Colorless solid, yield: 0.25 g (81%). IR: 3113 (vw), 3078 (w), 3015 (vw), 2975 (w), 1632 (m), 1554 (w), 1514 (m), 1432 (m), 1362 (w), 1307 (m), 1273 (m), 1205 (s), 1137 (vs), 1083 (vs), 864 (vw), 774 (vw), 724 (m), 669 (m), 626 (s), 522 (w) cm^{-1}. ^{1}H NMR: δ 10.61 (s, 1H), 9.38 (s, 1H), 8.90 (s, 1H), 8.16 (s, 1H), 6.85 (s, 2H), 2.29 (s, 3H), 2.08 (s, 3H); ^{13}C NMR: δ 185.6, 152.9, 146.2, 142.0, 140.5, 61.5, 25.2, 20.0. Anal. Calcd for $C_8H_{12}ClN_7O_4$ (305.68): C, 31.43; H, 3.96; N 32.08. Found: C, 31.05; H, 3.97; N, 32.30.

1-(Dimethylketiminetriazolium-1-yl)methylene-(1,2,4-triazole) Dinitrocyanomethanide (2i): The procedure was similar to the synthesis of **2e** except **1a** was replaced by **1c** (0.3331 g, 1.0 mmol). Colorless solid, yield: 0.30 g (89%); IR: 3150 (w), 3122 (s), 3086 (w), 2976 (vw), 2214 (s), 1632 (m), 1557 (s), 1501 (s), 1437 (m), 1389 (w), 1322 (w), 1310 (m), 1258 (s), 1209 (s), 1142 (s), 1084 (s), 1053 (vw), 1024 (vw), 995 (w), 953 (w), 787 (w), 770 (m), 736 (s), 670 (s), 637 (m), 621 (w) 521 (vw) cm^{-1}. UV−vis (λ_{max}): 256, 332 nm. ^{1}H NMR: δ 10.61 (s, 1H), 9.37 (s, 1H), 8.90 (s, 1H), 8.16 (s, 1H), 6.86 (s, 2H), 2.29 (s, 3H), 2.08 (s, 3H). ^{13}C NMR: δ 185.6, 153.0, 146.2, 142.0, 140.5, 116.3, 61.6, 25.2, 20.1. Anal. Calcd for $C_{10}H_{12}N_{10}O_4$ (336.27): C, 35.72; H, 3.60; N, 41.65. Found: C, 35.48; H, 3.49; N, 41.52.

1-(4-Aminotriazolium-1-yl)methylene-(1,2,4-triazole) Perchlorate (2j). The procedure were similar to that for the synthesis of **2b** except **1a** was replaced by **1d** (0.2931 g, 1.0 mmol). Colorless solid, yield: 0.23 g (86%). IR: 3109 (s), 3038 (s), 2023 (vw), 1632 (m), 1564 (w), 1510 (s), 1443 (m), 1394 (w), 1364 (w), 1333 (w), 1278 (s), 1210 (s), 1153 (vs), 1081 (vs, br), 1028 (s), 1015 (vw), 984 (w), 958 (w), 882 (vw), 784 (m), 750 (m), 674 (s), 634 (s), 626 (s) cm^{-1}. ^{1}H NMR: δ 10.74 (s, 1H), 9.25 (s, 1H), 8.98 (s, 1H), 8.11 (s, 1H), 7.30 (s, 2H), 6.89 (s, 2H). ^{13}C NMR: δ 152.9, 146.2, 145.5, 143.5, 61.1. Anal. Calcd for $C_5H_8ClN_7O_4$ (265.61): C, 22.61; H, 3.04; N, 36.91. Found: C, 22.47; H, 2.81; N, 36.76.

1-(4-Aminotriazolium-1-yl)methylene-(1,2,4-triazole) Picrate (2k). The procedure was similar to that for the synthesis of **2c** except **1a** was replaced by **1d** (0.2931 g, 1.0 mmol). Yellow solid, yield: 0.31 g (79%). IR: 3327 (w), 3114 (w), 3045 (w), 1640 (s), 1616 (s), 1568 (s), 1532 (s), 1501 (m), 1480 (vw), 1436 (w), 1366 (s), 1330 (s), 1320 (s), 1261 (s), 1209 (m), 1169 (w), 1148 (w), 1076 (w), 1024 (vw), 998 (w), 958 (vw), 916 (vw), 869 (vw), 785 (vw), 748 (w), 708 (w), 673 (w), 639 (w), 610 (w) cm^{-1}. ^{1}H NMR: δ 10.51 (s, 1H), 9.25 (s, 1H), 8.92 (s, 1H), 8.61 (s, 2H), 8.17 (s, 1H), 7.05 (s, 2H), 6.84 (s, 2H). ^{13}C NMR: δ 160.8, 153.0, 146.2, 145.7, 143.8, 141.8, 125.1, 124.1, 57.2. Anal. Calcd for $C_{11}H_{10}N_{10}O_7$ (394.26): C, 33.51; H, 2.56; N, 35.53. Found: C, 33.34; H, 2.30; N, 35.74.

1-(4-Aminotriazolium-1-yl)methylene-(1,2,4-triazole) Nitrodicyanomethanide (2l). The procedure was similar to that for the synthesis of **2d** except **1a** was replaced by **1d** (0.2931 g, 1.0 mmol). Colorless solid, yield: 0.24 g (87%). IR: 3292 (vw), 3117 (s), 3025 (w), 2211 (s), 2200 (s), 1631 (vw), 1572 (vw), 1509 (m), 1440 (s), 1404 (s), 1356 (vs), 1337 (vs), 1290 (m), 1211 (vw), 1161 (s), 1134 (m), 1074 (vw), 1031 (w), 997 (w), 953 (vw), 889 (w), 785 (w), 747 (m), 672 (w), 640 (w), 628 (m) cm^{-1}. UV−vis (λ_{max}): 317 nm. ^{1}H NMR: δ 10.48 (s, 1H), 9.22 (s, 1H), 8.89 (s, 1H), 8.14 (s, 1H), 7.02 (s, 2H), 6.81 (s, 2H). ^{13}C NMR: δ 153.0, 146.2, 145.8, 143.8, 115.1, 61.3. Anal. Calcd for $C_8H_8N_{10}O_2$ (276.21): C, 34.79; H, 2.92; N, 50.71. Found: C, 34.66; H, 2.68; N, 50.13.

1-(4-Aminotriazolium-1-yl)methylene-(1,2,4-triazole) Dinitrocyanomethanide (2m). The procedure was similar to that for the synthesis of **2e** except **1a** was replaced by **1d** (0.2931 g, 1.0 mmol). Colorless solid, yield: 0.25 g (84%). IR: 3329 (s), 3120 (s), 3032 (m), 2984 (w), 2216 (s), 1638 (vw), 1572 (w), 1505 (s), 1449 (w), 1427 (m), 1391 (w), 1357 (w), 1331 (w), 1290 (m), 1257 (s, br), 1151 (s), 1128 (s), 1074 (w), 1028 (m), 991 (w), 953 (m), 886 (w), 785 (m), 767 (m), 745 (s), 672 (s), 645 (w), 616 (m), 565 (vw)

cm^{-1}. UV−vis (λ_{max}): 258, 343 nm. ^1H NMR: δ 10.47 (s, 1H), 9.21 (s, 1H), 8.89 (s, 1H), 8.14 (s, 1H), 7.01 (s, 2H), 6.80 (s, 2H). ^{13}C NMR: δ 153.0, 146.2, 145.8, 143.8, 116.3, 61.3. Anal. Calcd for $C_7H_8N_{10}O_4$ (296.07): C, 28.38; H, 2.72; N, 47.29. Found: C, 28.35; H, 2.50; N, 47.26.

1-(Methylimidazolium-1-yl)methylene-(1,2,4-triazolium) Dinitrate (3a). To a stirring solution of **2a** (0.1131 g, 0.5 mmol) in methanol (20 mL) was added concentrated nitric acid (70 wt %, 0.054 g, 0.6 mmol) in methanol (5 mL); the resulting solution was stirred at 50 °C for 5 h. After the solvent was removed under reduced pressure, the residue was washed three times with Et_2O (10 mL) to give colorless solids. Yield: 0.14 g (97%). IR: 3124 (w), 3097 (m), 2973 (w), 1714 (s), 1627 (vw), 1572 (m), 1383 (vs), 1317 (s), 1223 (m), 1172 (s), 1104 (m), 1034 (m), 962 (vw), 825 (m), 777 (m), 724 (w), 657 (w), 621 (s) cm^{-1}. ^1H NMR: δ 9.39 (s, 1H), 8.88 (s, 1H), 8.15 (s, 1H), 7.87 (s, 1H), 7.72 (s, 1H), 6.68 (s, 2H), 3.86 (s, 3H). ^{13}C NMR: δ 152.8, 145.6, 137.6, 124.3, 122.0, 58.8, 36.1. Anal. Calcd for $C_7H_{11}N_7O_6$ (289.21): C, 29.07; H, 3.83; N, 33.90. Found: C, 29.05; H, 3.71; N, 33.73.

1-(Methylimidazolium-1-yl)methylene-(1,2,4-triazolium) Diperchlorate (3b). The compound was synthesized using **2b** (0.1318 g, 0.5 mmol) and perchloric acid (70 wt %, 0.072 g, 0.5 mmol) by following the procedures for **3a**. Colorless solid, yield: 0.17 g (93%). IR: 3097 (w), 1627 (w), 1585 (w), 1563 (m), 1511 (w), 1389 (w), 1308 (w), 1278 (m), 1139 (m), 1141 (s), 1107 (vs), 1086 (vs), 848 (vw), 777 (m), 724 (m), 669 (m), 625 (s) cm^{-1}. ^1H NMR: δ 9.35 (s, 1H), 8.83 (s, 1H), 8.14 (s, 1H), 7.87 (s, 1H), 7.72 (s, 1H), 6.66 (s, 2H), 3.87 (s, 3H).^{13}C NMR: δ 152.7, 145.5, 137.4, 124.2, 121.9, 58.7, 36.1. Anal. Calcd for $C_7H_{11}Cl_2N_5O_8$ (364.10): C, 23.09; H, 3.05; N, 19.23. Found: C, 23.04; H, 3.03; N, 19.17.

1-(Methylimidazolium-1-yl)methylene-(1,2,4-triazolium) Dipicrate (3c). The compound was synthesized using **2c** (0.1961 g, 0.5 mmol) and picric acid (0.1260 g, 0.55 mmol) in DMF (20 mL) by following the procedures of **3a**. Yellow solid, yield: 0.30 g (97%). IR: 3063 (w, br), 1648 (s), 1610 (s), 1566 (s), 1539 (s), 1492 (m), 1435 (m), 1361 (s), 1319 (vs), 1269 (vs), 1163 (m), 1121 (vw), 1079 (w), 1006 (vw), 912 (m), 787 (vw), 742 (m), 703 (s), 624 (w) cm^{-1}. ^1H NMR: δ 9.36 (s, 1H), 8.84 (s, 1H), 8.58 (s, 4H), 8.14 (s, 1H), 7.87 (t, 1H, $J = 1.8$ Hz), 7.72 (t, 1H, $J = 1.7$ Hz), 6.66 (s, 2H), 3.87 (s, 3H). ^{13}C NMR: δ 160.6, 152.9, 145.5, 141.8, 137.4, 125.1, 124.3, 122.0, 58.7, 36.1. Anal. Calcd for $C_{19}H_{15}N_{11}O_{14}$ (621.39): C, 36.72; H, 2.43; N, 24.80. Found: C, 36.66; H, 2.34; N, 24.02.

1-(Imidazolium-1-yl)methylene-(1,2,4-triazolium) Dinitrate (5a). To a stirring solution of **4** (0.1492 g, 1.0 mmol) in methanol (20 mL) was added concentrated nitric acid (70 wt %, 0.189 g, 2.1 mmol) in methanol (5 mL); the resulting solution was stirred at 50 °C for 5 h. After the solvent was removed under reduced pressure, the residue was washed three times with Et_2O (3 × 10 mL) to give rise to colorless solid. Yield: 0.26 g (95%). IR: 3124 (s), 3047 (s), 2968 (s), 2871 (s), 2743 (s), 2662 (s), 2561 (m), 1754 (vw), 1656 (vw), 1568 (m), 1552 (w), 1534 (m), 1384 (vs), 1342 (w), 1257 (m), 1263 (s), 1148 (w), 1113 (m), 1003 (vw), 968 (w), 895 (w), 853 (m), 825 (s), 772 (s), 714 (vw), 660 (w), 622 (s) cm^{-1}. ^1H NMR: δ 9.40 (s, 1H), 8.86 (s, 1H), 8.15 (s, 1H), 7.89 (d, 1H, $J =$ 1.4 Hz), 7.72 (d, 1H, $J = 1.3$ Hz), 6.68 (s, 2H). ^{13}C NMR: δ 152.8, 145.5, 136.5, 121.6, 120.6, 58.6. Anal. Calcd for $C_6H_9N_7O_6$ (275.18): C, 26.19; H, 3.30; N, 35.63. Found: C, 26.04; H, 2.97; N, 35.28.

1-(Imidazolium-1-yl)methylene-(1,2,4-triazolium) Diperchlorate (5b). The procedure was similar to that for the synthesis of **5a** except HNO_3 was replaced by $HClO_4$ (70 wt %, 0.286 g, 2.0 mmol). Colorless solid, yield: 0.34 g (97%). IR: 3263 (vw), 3097 (w), 3017 (m), 2975 (w), 2870 (w), 2727 (m), 2654 (w), 2560 (w), 1713 (m), 1564 (m), 1517 (w), 1432 (m), 1372 (w), 1300 (m), 1265 (vw), 1144 (s), 1112 (s), 1086 (vs), 845 (vw), 766 (w), 721 (vw), 667 (w), 624 (s) cm^{-1}. ^1H NMR: δ 9.38 (s, 1H), 8.88 (s, 1H), 8.17 (s, 1H), 7.87 (d, 1H, $J = 1.4$ Hz), 7.71 (d, 1H, $J = 1.4$ Hz), 6.68 (s, 2H);. ^{13}C NMR: δ 152.8, 145.5, 136.5, 121.7, 120.6, 58.7. Anal. Calcd for $C_6H_9Cl_2N_5O_8$ (350.07): C, 20.59; H, 2.59; N, 20.01. Found: C, 20.32; H, 2.48; N, 19.78.

1-(Imidazolium-1-yl)methylene-(1,2,4-triazolium) Dipicrate (5c). The procedure was similar to that for the synthesis of **5a** except HNO_3 was replaced by picric acid (0.481 g, 2.1 mmol). Yellow solid, yield: 0.58 g (95%). IR: 3152 (w), 3083 (w), 1647 (s), 1611 (s), 1568 (s), 1535 (s), 1490 (m), 1425 (m), 1346 (s), 1322 (s), 1276 (s), 1166 (m), 1123 (w), 1082 (m), 1033 (vw), 974 (w), 917 (m), 877 (w), 837 (w), 783 (vw), 744 (m), 708 (s), 654 (vw), 617 (w) cm^{-1}. ^1H NMR: δ 9.40 (s, 1H), 8.88 (s, 1H), 8.58 (s, 4H), 8.15 (s, 1H), 7.87 (t, 1H, $J = 1.8$ Hz), 7.70 (t, 1H, $J = 1.7$ Hz), 6.69 (s, 2H). ^{13}C NMR: δ 160.6, 152.7, 145.5, 141.8, 136.6, 121.7, 120.6, 58.7. Anal. Calcd for $C_{18}H_{13}N_{11}O_{14}$ (607.36): C, 35.60; H, 2.16; N, 25.37. Found: C, 35.45; H, 2.06; N, 24.88.

1-(3-Methylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium) diperchlorate (7a). To a stirring solution of **6** (0.2165 g, 0.5 mmol) in H_2O (20 mL) was added $AgClO_4$ (0.2073 g, 1.0 mmol) dropwise in H_2O (5 mL); the resulting solution was stirred at 25 °C for 1 h. After removal of AgI, the solvent was evaporated in vacuo and the residue was washed three times with Et_2O (10 mL) to give colorless solids. Yield: 0.16 g (85%). IR: 3395 (br, w), 3063 (w), 2980 (vw), 1632 (vw), 1583 (m), 1551 (w), 1506 (vw), 1428 (vw), 1389 (w), 1342 (w), 1333 (w), 1161 (s), 1149 (s), 1111 (s), 1084 (s), 956 (vw), 931 (vw), 906 (vw), 845 (vw), 770 (m), 732 (w), 683 (vw), 646 (m), 627 (s). ^1H NMR: δ 10.21 (s, 1H), 9.36 (s, 1H), 9.23 (s, 1H), 7.87 (t, 1H, $J = 1.7$ Hz), 7.77 (s, 1H), 6.86 (s, 2H), 3.94 (s, 1H), 3,90 (s, 1H). ^{13}C NMR: δ 146.4, 145.1, 138.2, 124.2, 122.6, 60.2, 36.2, 34.4. Anal. Calcd for $C_8H_{13}Cl_2N_5O_8$ (378.12): C, 25.41; H, 3.47; N, 18.52. Found: C, 25.26; H, 3.35; N, 18.15.

1-(3-Methylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium) Dipicrate (7b). The compound was synthesized using **6** (0.2165 g, 0.5 mmol) and silver picrate (0.3360 g, 1.0 mmol) in DMF (20 mL) by following the procedures of **7a**. Yellow solid, yield: 0.21 g (66%). IR: 3136 (w), 3080 (m), 1637 (s), 1612 (s), 1583 (m), 1557 (s), 1531 (m), 1491 (s), 1435 (m), 1364 (s), 1336 (s), 1307 (s), 1270 (s), 1161 (s), 1076 (m), 1039 (vw), 1013 (vw); 972 (vw), 908 (w), 785 (m), 744 (m), 708 (m), 648 (w), 621 (w) cm^{-1}. ^1H NMR: δ 10.22 (s, 1H), 9.37 (s, 1H), 9.23 (s, 1H), 8.58 (s, 4H), 7.87 (t, 1H, $J = 1.7$ Hz), 7.78 (t, 1H, $J = 1.7$ Hz), 6.86 (s, 2H), 3.93 (s, 3H), 3.91 (s, 3H). ^{13}C NMR: δ 160.9, 146.4, 145.2, 141.7, 138.3, 125.3, 124.3, 122.6, 60.2, 36.2, 34.4. Anal. Calcd for $C_{20}H_{17}N_{11}O_{14}$ (635.41): C, 37.80; H, 2.70; N, 24.25. Found: C, 37.95; H, 2.66; N, 23.80.

1-(3-Methylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium) Di(nitrodicyanomethanide) (7c). The compound was synthesized using **6** (0.2165 g, 0.5 mmol) in H_2O (20 mL) and silver nitrodicyanomethanide (0.2180, 1.0 mmol) in MeCN (5 mL) by following the procedures of **7a**, Colorless solid, yield: 0.16 g (80%). IR: 3155 (w), 3120 (w), 3049 (vw), 2977 (vw), 2208 (s), 2197 (s), 1589 (w), 1558 (w), 1426 (s), 1415(s), 1336 (vs), 1289 (m), 1165 (m), 1009 (vw), 876 (w), 781 (w), 748 (m), 646 (m), 619 (m) cm^{-1}. ^1H NMR: δ 10.22 (s, 1H), 9.36 (s, 1H), 9.22 (s, 1H), 7.87 (t, 1H, $J = 1.8$ Hz), 7.76 (t, 1H, $J = 1.7$ Hz), 6.86 (s, 2H), 3.94 (s, 3H), 3.91 (s, 3H). ^{13}C NMR: δ 146.4, 145.1, 138.2, 124.2, 122.6, 115.1, 60.2, 36.2, 34.4. UV−vis (λ_{max}): 317 nm. Anal. Calcd for $C_{14}H_{13}N_{11}O_4$ (399.32): C, 42.11; H, 3.28; N, 38.58. Found: C, 42.07; H, 3.13; N, 38.69.

1-(3-Methylimidazolium-1-yl)methylene-(4-methyl-1,2,4-triazolium) Di(dinitrocyanomethanide) (7d). The procedure was similar to the synthesis of **7c** except silver nitrodicyanomethanide was replaced by silver dinitrocyanomethanide (0.2379 g, 1.0 mmol). Colorless solid, yield: 0.20 g (91%). IR: 3135 (m), 3045 (w), 3000 (vw), 2215 (s), 1586 (m), 1554 (m), 1509 (s), 1418 (w), 1387 (w), 1357 (w), 1330 (w), 1259 (vs, br), 1164 (s), 1146 (s), 1064 (w), 1012 (w), 965 (vw), 873 (vw), 847 (w), 781 (w), 763 (m), 746 (m), 678 (vw), 645 (w), 621 (m) cm^{-1}. ^{1}H NMR: δ 10.22 (s, 1H), 9.36 (s, 1H), 9.22 (s, 1H), 7.88 (t, 1H, J = 1.8 Hz), 7.76 (t, 1H, J = 1.7 Hz), 6.86 (s, 2H), 3.94 (s, 3H), 3.91 (s, 3H). ^{13}C NMR: δ 146.4, 145.1, 138.2, 124.2, 122.6, 60.2, 36.2, 34.4. UV−vis (λ_{max}): 258, 343 nm. Anal. Calcd for $C_{12}H_{13}N_{11}O_8$ (439.30): C, 32.81; H, 2.98; N, 35.07. Found: C, 32.73; H, 2.79; N, 34.94.

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