General and Greener Synthesis of Diverse Functional Organic Salts through Schiff Base Chemistry

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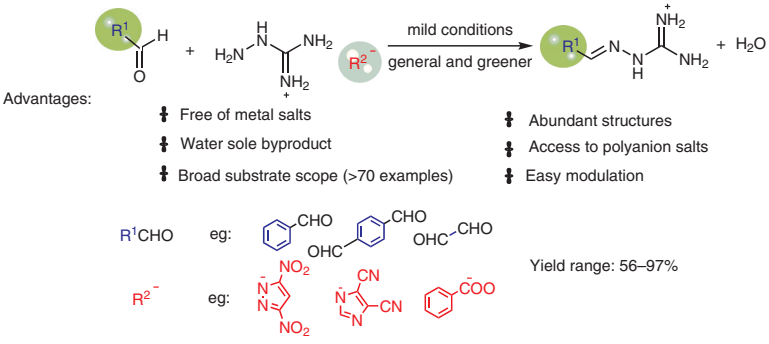

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Abstract We report a greener and more-general organic method for the synthesis of functional organic salts containing organic anions through a Schiff base reaction between readily available aldehydes and simple aminoguanidinium salts. This reaction is operationally simple, free of metal salts, and forms water as the sole byproduct. The broad scope and good functional-group compatibility of this method permit its use to provide ready access to a library of more than 70 distinct organic salts, including those of heterocyclic anions, complex pharmaceutical anions, and polyanions, which are difficult to obtain through classical inorganic methods. Moreover, choosing different aldehydes and organic anions provides a convenient method for modulating or improving the functional properties of the designed organic salts, such as their melting points, fluorescence, and energetic properties. We therefore expect that this method will open new opportunities for the discovery and functionalization of a wide variety of organic salts and functional materials.

Key words organic salts, Schiff base reaction, functional materials

Organic salts are a versatile and important class of molecules that typically consist of organic cations and inorganic or organic anions. Their unique nature, in that they consist entirely of ions, renders them useful various fields including organic synthesis (e.g., aryldiazonium salts), ionic dyes, ionic conductivity, and ionic liquids.[1–8] Recently, organic salts containing organic anions such as alkyl, arene, heterocyclic (e.g., azolate anions), or pharmaceutical anions have attracted growing interest because, in comparison with conventional inorganic anions such as Cl^-, NO_3^-, or BF_4^-, organic anions contain several carbon atoms that can be functionalized, thereby facilitating the expansion of the range of structures of these salts or tuning of their proper-

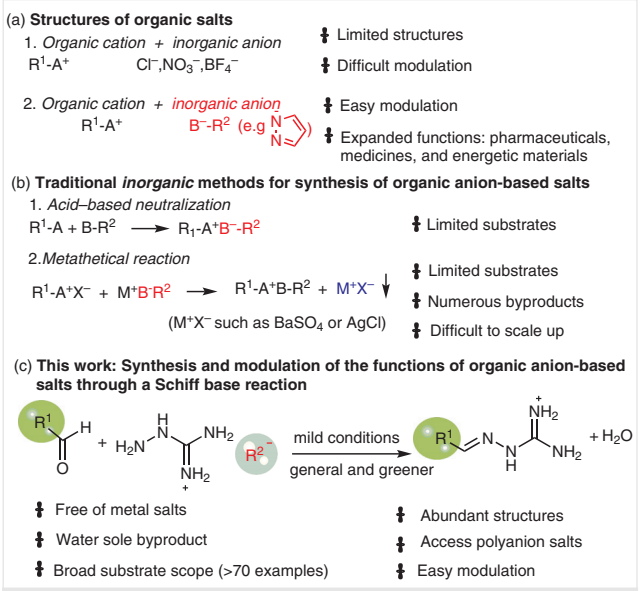


Figure 1 (a) Comparison of organic salts containing organic anions with analogues containing inorganic anions. (b) Conventional inorganic methods for synthesizing organic salts containing organic anions. (c) The proposed organic method for synthesizing organic salts containing organic anions and for modulating their functions. R^1, R^2 = alkyl, aryl, hetaryl, etc.

ties through the introduction of various functional groups [Figure 1(a)].[9,10] Moreover, such salts have found new applications as pharmaceuticals, medicines, nonlinear optical materials, lubricants, or energetic materials.[11–21] Despite the importance of these organic salts, a broadly applicable methodological approach to their synthesis remains elusive.

Interestingly, most organic salts containing organic anions are usually prepared by classical inorganic-type reactions such as acid–base neutralization or metathesis reactions [Figure 1(b)].[11–21] In the former case, the substrates are often limited to strong organic acids or bases such as hydrazine hydrate and phosphonium hydroxide. The metathesis reaction depends mainly on a difference in solubility between the reactants and the products. Consequently, this reaction is limited to substrates that are more soluble in the reaction solvent than are their corresponding products. Moreover, this reaction often results in the production of at least stoichiometric amounts of waste products such as AgCl or $BaSO_4$; it therefore has poor atom economy and suffers from difficulties in scalability and environmental pollution. Furthermore, although these classical methods readily give simple organic salts containing organic anions such as phosphonium,[22–24] ammonium, hydrazinium, or aminoguanidinium ions,[13–21] their structural diversity is relatively limited. The synthesis of organic salts with a variety of structures and versatile functions remains a significant challenge. This challenge can be attributed to the relatively low reactivity of inorganic-type reactions toward organic salts. Moreover, the larger sizes of organic anions compared with inorganic anions can introduce steric hindrance, preventing the formation of the corresponding organic salts.

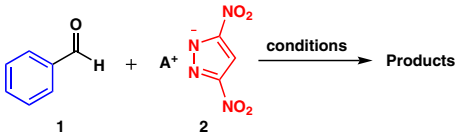
In considering ways to address the challenges associated with devising a more-efficient, greener, and more-general method for the synthesis of organic salts containing organic anions, our attention was drawn to the well-established Schiff base reaction.[25] This organic reaction involves condensation between an amine and aldehyde. It exhibits high reactivity, operational simplicity, mild reaction conditions, and, more importantly, water is the only byproduct. The Schiff base reaction has been widely used for the synthesis of various covalent compounds, including natural products, pharmaceuticals, agrochemicals, functional materials, and some salts containing inorganic anions.[26–32]

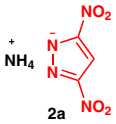
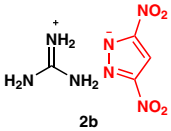
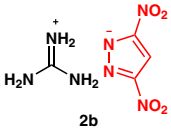
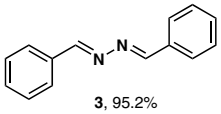
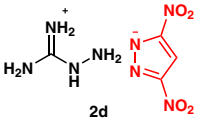
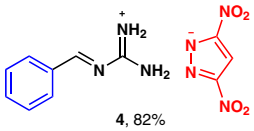
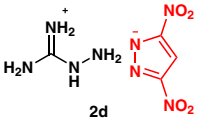
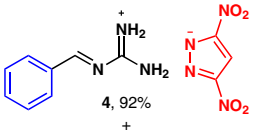
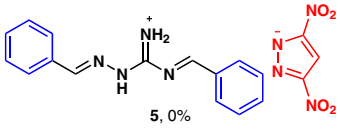
On the basis of the attractive characteristics of the Schiff base reaction, we hypothesized that this classical organic reaction might be developed as a novel method for the synthesis of organic salts containing organic anions if the anion contains a suitable amino-containing cation was present in a simple organic salt precursor containing an organic anion; this amino group would have to be able to condense with an aldehyde to form a new cation while retaining the original organic anion [Figure 1(c)]. Moreover, we envisioned that by choosing different aldehydes (with a functional unit R^1) and organic anions (with a functional unit R^2), the proposed method might be useful for preparing libraries of diverse organic salts, essential for structure–property relationship studies or for the modulation of their functions or properties. We hoped that, by taking advantage of the wide abundance of aldehydes and simple organic salts, the proposed organic reaction would be broadly useful and orthogonal to classical inorganic reactions.

To test the validity of our hypothesis, our initial investigations focused on the reaction of benzaldehyde (**1**), which contains a few carbon atoms that can be functionalized, as a model substrate for reaction with various simple dinitropyrazolide salts containing various amino-group containing cations (Table 1). The reaction of benzaldehyde (**1**) with ammonium 3,5-dinitropyrazolide (**2a**) did not proceed at room temperature or at 85 °C (Table 1, entries 1 and 2); instead, we simply recovered the starting materials. Guanidinium 3,5-dinitropyrazolide (**2b**), which contains more amino groups, was then tested, and this too showed no reaction (entries 3 and 4). It is appeared that the amino groups in these substrates were not sufficiently reactive. Hydrazinium 3,5-dinitropyrazolide (**2c**), which contains more-reactive amino groups, was then used, but this gave a stoichiometric amount of the covalent product PhCH=N-N=CHPh (**3**) through coupling of benzaldehyde and hydrazine with loss of the 3,5-dinitropyrazolide anion (entry 5); it therefore failed to give the desired product. It is possible that the positive charge resides on the reactive amino group of the hydrazinium cation; when the condensation reaction occurs, the positive charge is removed and the corresponding counteranion is lost.

On the basis of the above results, a salt with an amino-group-containing cation in which the positive charge is separated from the reactive amino group would be expected to react in the desired manner. We therefore designed and synthesized the aminoguanidinium 3,5-dinitropyrazolide (**2d**), in which the positive charge is separated from the reactive hydrazine group and resides on another amino group. Gratifyingly, we found that **2d** reacted smoothly with **1** to form the desired salt **4** in 82% yield at room temperature, with water as the only byproduct (Table 1, entry 6). Note that the disubstituted organic salt **5** was not obtained, even when the reaction was performed at 65 °C for seven hours (entry 7). It is possible that the hydrazine group of the aminoguanidinium cation is more reactive than the amino group in **2d**, which facilitates condensation.[33] According to a Gaussian calculation, the lengths of the C1–N2 (1.33 Å), C1–N4 (1.34 Å), and C1–N7 (1.35 Å) bonds are between the values for C–N (1.47 Å) and C=N (1.22 Å) bonds, showing that electron delocalization occurs in the amino group of the aminoguanidinium cation. This makes the amino group more stable than a hydrazine group[34] (see Supporting Information). The optimized con-

Table 1 Evaluation of Dinitropyrazolide Salts Containing Various Amino-Group-Containing Cations **2** for the Condensation Reaction with Benzaldehyde (**1**)[a]

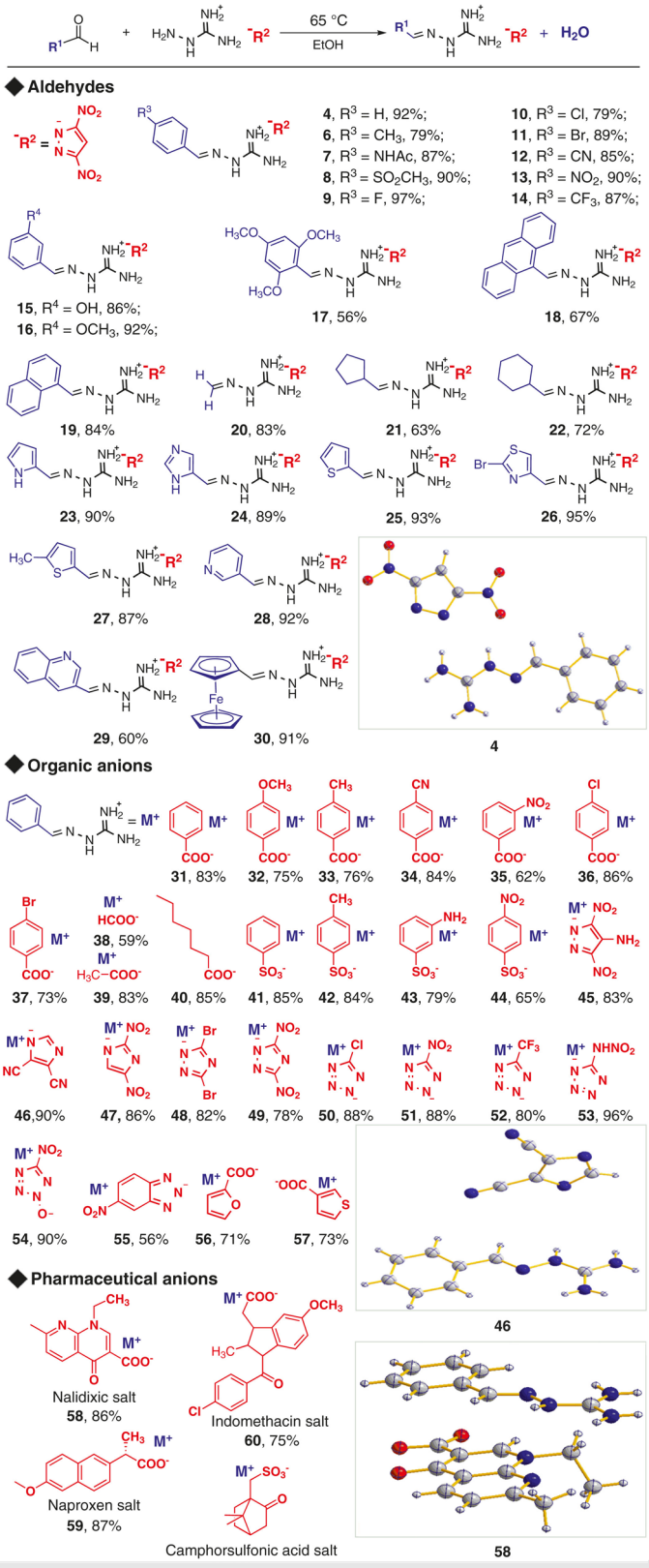


Entry	Reactant	Conditions	Products[b]
1	 **2a**	EtOH, 25 °C, 12 h	–
2	 **2a**	EtOH, 85 °C, 12 h	–
3	 **2b**	EtOH, 25 °C, 12 h	–
4	 **2b**	EtOH, 85 °C, 1 h	–
5	 **2c**	EtOH, 25 °C, 12 h	 **3**, 95.2%
6	 **2d**	EtOH, 25 °C, 7 h	 **4**, 82%
7	 **2d**	EtOH, 65 °C, 7 h	 **4**, 92% +  **5**, 0%

[a] Standard conditions: PhCHO (1.0 equiv), dinitropyrazolide salt (1.0 equiv), 1 mmol scale.
[b] Isolated yields are reported.

ditions were eventually identified as follows. Ethanol is the optimal the solvent, due to the high solubility of both the aminoguanidinium salts and aldehydes in this solvent, and the reaction is carried out at 65 °C for seven hours.

With the optimized conditions in hand, we attempted to explore the generality of this condensation protocol to enrich the range of structures of the organic salts. First, we investigated the scope of aldehyde substrate and we found



Scheme 1 Substrate scope. *Reaction conditions*: aldehyde (1.0 equiv), aminoguanidinium salt (1.0 equiv), 65 °C, 7 h (1 mmol scale). Isolated yields are reported.

that a variety of aldehydes could be successfully transformed into the corresponding products in modest to good yields (Scheme 1). The reaction showed good tolerance toward electron-donating groups such as amide, ether, or methyl, and to electron-withdrawing groups such as sulfonyl, nitro, cyano, or trifluoromethyl. Aryl halides were also compatible with the new transformation (**9**–**11**). It is interesting to note that the reaction even tolerated an unprotected OH group (**15**). The reaction with fused-ring aldehydes also proceeded smoothly (**18** and **19**).

Furthermore, aliphatic aldehydes also reacted to give reasonable quantities of the corresponding condensation products **20**–**22**. We were pleased to find that aldehydes containing various hetaryl moieties, such as pyrrolyl, imidazolyl, or thienyl groups, gave the desired products **23**–**29** in good yields with no byproducts from the elimination of the 3,5-dinitropyrazolide counteranion to form a covalent product. Ferrocene derivatives are an important class of organometallic compounds that exhibit a wide range of biological and electrochemical activities.[35–37] Ferrocenecarbaldehyde also afforded the desired product **30** in good yield. Furthermore, the reaction also tolerates a significant degree of steric hindrance; the reaction of **2d** with 2,4,6-trimethoxybenzaldehyde gave **17** in good yield. Interestingly, the condensation reaction was also expanded to a series of ketones at elevated temperatures. For example, acetone and acetophenone were readily transformed into afford the corresponding products in good yields (see Supporting Information).

Having studied the scope of the aldehyde substrate, we turned our attention to various organic anions containing simple aminoguanidinium salts by using benzaldehyde (**1**) as a model substrate (Scheme 1). The ready availability of these simple aminoguanidinium salts, either from commercial suppliers or by synthesis in a single step by methods described in literature, allowed us to perform the reaction on a synthetically useful 1 mmol scale. We found that the reaction was effective for a variety of benzoate (**31**–**37**) and benzenesulfonate anions (**41**–**44**). A wide range of functional groups, including ether, methyl, amino, nitro, cyano, chloro, and bromo were tolerated under mild reaction conditions. Furthermore, alkanoic acid anions were also suitable for this condensation reaction (**38**–**40**). Heterocyclic anions were also investigated, with the knowledge that organic salts containing heterocyclic anions are widely used as energetic materials, gas absorbents, and ionic liquids.[13–24] In addition to the pyrazolide anion, other heterocyclic anions such as imidazolide, triazolide, tetrazolide, and benzotriazolide also reacted smoothly (**45**–**55**). Thiophenecarboxylate and furancarboxylate anions were also compatible with the reaction.

The structures of seven as-synthesized organic salts, including **4** and **46**, were unambiguously confirmed by single-crystal X-ray diffraction analysis.[38] Most products were obtained in sufficiently pure form to permit straightforward isolation (e.g., by filtration). In addition, **42** and **46** were prepared on a gram scale under the standard reaction conditions in yields similar to those obtained from 1 mmol scale experiments, demonstrating both the scalability and practicality of this method. In contrast, attempts to prepare several products, including **34** and **46**, by classical metathesis reactions of their hydrochlorides with the corresponding metal salts were unsuccessful. It is likely that the organic anions of these compounds contain a few nitrogen or oxygen atoms that can readily coordinate to transition metal ion (e.g., Ag^+) to form an insoluble complex, resulting in difficulties in the reactions (see Supporting Information). The above features indicate that the present condensation method is complementary to classical reactions for the synthesis of organic salts with a wide range of structures.

The promising functional-group compatibility and broad substrate scope of this protocol encouraged us to evaluate this condensation method for complex pharmaceutical anions containing aminoguanidinium salts. The preparation of active pharmaceutical ingredients in an anionic form would permit an improvement in their physicochemical and biological properties, such as their solubility, lipophilicity, or toxicity.[11,39] The nalidixic anion, a well-known antibiotic ingredient used in the treatment of urinary-tract infections, when tested under the standard conditions gave the target product **58** in 86% yield. Moreover, the naproxen anion, a widely used nonsteroidal antiinflammatory ingredient, was amenable to this condensation reaction. Other active pharmaceutical ingredients, including indomethacin and camphorsulfonic acid salts, were also viable substrates. This transformation therefore offers good potential for the discovery of interesting new biologically active organic salts.

Having demonstrated the broad scope of this new reaction, we next sought to examine its application in modulating the functional properties of the new organic salts by selecting different aldehydes (R^1) and organic anions (R^2) containing aminoguanidinium salts (Scheme 1). For example, the melting point is a fundamental physical property of organic salts, and its modulation is important for gaining insight into the correlation between structure and melting point, and for various applications.[7,8,14] By simply changing the alkyl chain of the aldehyde substrate, the melting points of the corresponding product was modulated (Figure 2). For example, when the aldehyde substrate was changed from butanal to octanal, thermogravimetric/differential scanning calorimetry (TG/DSC) analysis unambiguously showed that the melting point of the corresponding products with the same anion decreased from 139 °C (**62**) to 77 °C (**63**). Note that the melting point of the organic salt **63** was 77 °C, whereas its decomposition temperature was 217 °C. This temperature difference of more than 100 °C between the melting point and the decomposition temperature suggests that **63** is potential useful as an ionic liquid.

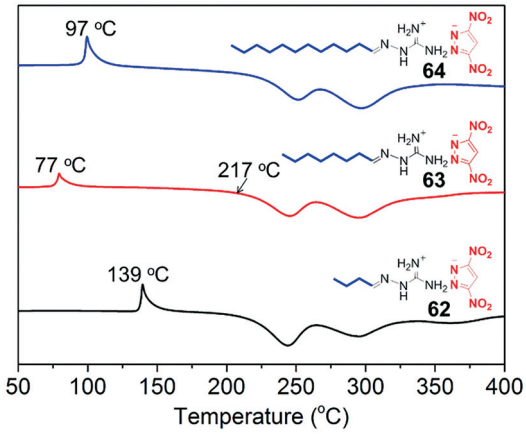


Figure 2 DSC curves of organic salts **62–64**

In addition to aldehydes, various organic anions can be also used to tune the properties of the products (Figure 3). Ionic fluorescent organic materials have attracted significant attention because of their various applications, for example in photovoltaics, ionic organic light-emitting diodes, and ionic liquid crystals.[4,40] When pyrene-1-carbaldehyde was treated with simple aminoguanidinium salts containing various organic anions, such as 4,5-dicyanoimidazolide or 3,3-dibromotriazolide, a series of ionic fluorescent salts were obtained in high yields. Interestingly, the 4,5-dicyanoimidazolide pyrene salt **65** and the 3,3-dibromotriazolide pyrene salt **66** both exhibited higher fluorescent intensities than that of the corresponding inorganic nitrate anion-based analogue **67** at the same concentration. It is possible that these organic anions have larger π-conjugated systems than inorganic anions, which could contribute to their enhanced fluorescence. Therefore, this approach provides a useful tool for the modulation or improvement of the properties of organic salts.

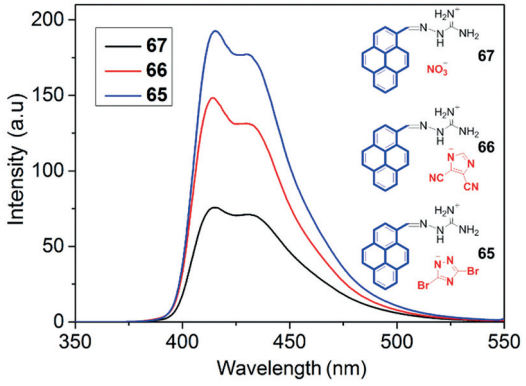


Figure 3 Fluorescence spectra of organic salts **65–67**. Excitation at 280 nm in MeOH (1 mmol/L).

In addition to organic salts containing single organic anions, complex organic salts containing polyanions also exhibited promising antimicrobial, and energetic properties, as polyanions usually enhance their unique properties.[13,41] The preparation of such compounds has relied mainly on inorganic metathesis reactions; however, the need to introduce several large organic anions into organic salts make this reaction more difficult, and it usually suffers from low yields and a limited substrate scope, thereby hindering the discovery of promising new scaffolds. To highlight the utility of our method, we attempt to employ this reaction to synthesize various organic salts containing polyanions with polyaldehydes as substrates. For example, glyoxal condensed smoothly with simple aminoguanidinium salts under our standard conditions to give the corresponding products **68–70** in high yields (Figure 4). Similarly, terephthalaldehyde and pyridine-2,6-dicarbaldehyde also worked well.

The nitrogen-rich organic salts based on glyoxal as a substrate **68–70** exhibited acceptable energetic properties (Table 2). In particular, organic salt **70** possesses a high decomposition temperature (241 °C), good detonation properties [detonation velocity (*D*): 8840 m/s; detonation pressure (*P*): 31.0 GPa] and extremely low sensitivities (impact sensitivity: >40 J; friction sensitivity: >360 N). Its detonation velocity and pressure are comparable to those of RDX (*D*, 8861 m/s; *P*, 34.5 GPa). Thus, the organic salt **70** might

Table 2 Physical Properties of As-Synthesized Organic Salts and RDX

Compound	**68**	**69**	**70**	**71**	RDX
ρ[a]	1.66	1.69	1.68	1.57	1.81
T_d[b]	257	282	241	246	210
N%[c]	63.0	65.1	58.3	47.3	37.8
Ω_{CO}[d]	-32.0	-33.5	-22.2	-21.6	-21.6
IS[e]	16	4.0	>40	>40	7.5
FS[f]	>360	>360	>360	>360	120
$\Delta_f H^{-}$[g]	112.8	9.8	536.8	–307.9	–307.9
$\Delta_f H^{+}$[h]	1811.6	1811.6	1811.6	1811.6	–307.9
$\Delta_f H$[i]	578.3	390.7	1448.1	–307.9	70.3
P[j]	23.0	22.8	31.0	19.3	34.5
D[k]	7694	7981	8840	7441	8861

[a] Density measured with a gas pycnometer (g/cm).
[b] Decomposition temperature (°C; onset).
[c] Nitrogen content.
[d] Oxygen balance.
[e] Impact sensitivity (J).
[f] Friction sensitivity (N).
[g] Heat of formation of anion.
[h] Heat of formation of cation.
[i] Heat of formation of salt.
[j] Detonation pressure.
[k] Detonation velocity. The detonation properties were calculated by using *EXPLO5* v6.01. The properties of RDX are taken from the work of Klapötke et al.[42]

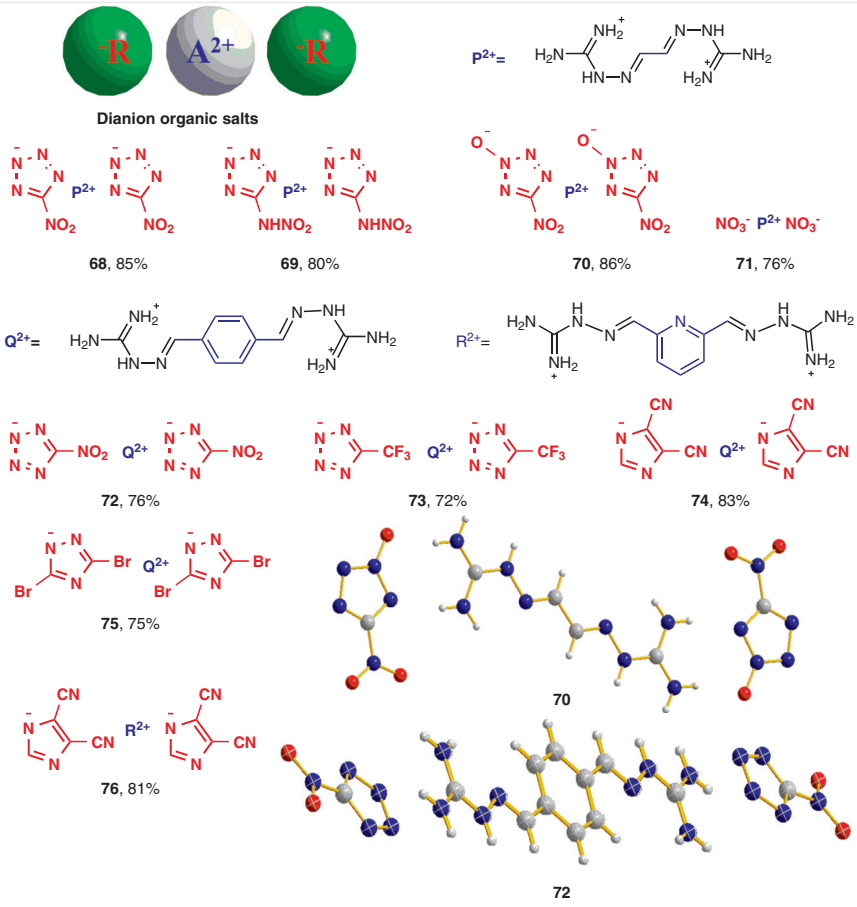


Figure 4 Preparation of polyanion salts through the condensation reaction. *Reaction conditions*: aldehyde (1.0 equiv), aminoguanidinium salt (2.0 equiv), 65 °C, 7 h.

be potentially useful as an insensitive energetic material. Moreover, these organic salts also display higher nitrogen contents, greater densities, higher heats of formation, and better detonation properties than those of their corresponding nitrate salt **71**. Remarkably, the heat of formation and detonation velocity of **70** are, respectively, more than 1700 kJ/mol and more than 1400 m/s higher than the corresponding values for **71** (1448.1 kJ/mol and 8840 m/s, respectively, for **70** versus –357.5 kJ/mol and 7441 m/s for **71**). It is possible that the nitrogen-rich anions of **68**–**70** have higher nitrogen contents, greater densities, and higher heats of formation than those of the inorganic nitrate anion (NO_3^-), resulting in better detonation properties. Therefore, our transformation might offer the potential for the discovery of promising functional organic salts containing polyanions.

In conclusion, we have developed a greener and more-general protocol for the synthesis of organic salts through a Schiff base reaction between simple aminoguanidinium salts and aldehydes.[43] Compared with conventional inorganic methods, this condensation method has several advantages including freedom from metal salts, the formation of water as the sole byproduct, and a remarkably broad scope that includes salts of heterocyclic anions, complex pharmaceutical anions, and polyanions. The usefulness of this method is also demonstrated by the fact that choosing different aldehydes and organic anions permits convenient modulation or improvement of the functional properties of the products, including their melting points, fluorescence, and energetic properties. In particular, the difference between the melting point and the decomposition temperature of organic salt **63** is more than 100 °C, making it potentially useful as an ionic liquid. Moreover, the nitrogen-rich organic salt **70** has a high decomposition temperature (241 °C), good detonation properties (*D*: 8840 m/s; *P*: 31.0 GPa), and extremely low sensitivities (impact sensitivity: >40 J; friction sensitivity: >360 N), and it might be useful as an insensitive energetic material. We therefore expect that our new method could open new opportunities for the discovery and functionalization of a wide variety of organic salts and functional materials, such as pharmaceuticals,

medicines, nonlinear optical materials, and energetic materials, in particular those that are difficult to access by conventional inorganic methods.

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The authors declare no competing financial interest.
B.P.H. performed the experiment. Q.R.S, F.P.L., P.C.Z., P.P.P., C.F.Z., Y.D., and H.S provided some help. S.H.L. and S.P.P. conceived the idea and provided funding support. S.H.L. and B.P.H. analyzed the data and wrote the manuscript.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611783.

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(43) **Amino(2-benzylidenehydrazino)methaniminium 3,5-Dinitropyrazolide (4); Typical Procedure**
A 50 mL round-bottomed flask was charged with PhCHO (0.106 g, 1 mmol) and EtOH (6 mL) A solution of aminoguanidinium 3,5-dinitropyrazolide (0.232 g, 1 mmol) in EtOH (20 mL) was added dropwise to the flask and the resulting mixture was stirred for 7 h at 65 °C. The solvent was then slowly removed under a vacuum, and the residue was crystallized from H_2O to give light-yellow needle crystals; yield: 0.294 g (92%); mp 174.32–174.96 °C.
IR (KBr): 759, 834, 1010, 1318, 1351, 486, 541, 1622, 1670, 3255

cm^{-1}. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.35 (s, 1 H, CH), 7.45 (s, 3 H, NH), 7.72 (t, J = 7.5 Hz, 3 H, CH), 7.87 (m, 2 H, CH), 8.22 (s, 1 H, CH,), 11.59 (s, 1 H, NH). ^{13}C NMR (150 MHz, DMSO-d_6): δ = 98.89 (s), 128.07 (s,), 129.13 (s), 130.98 (s), 133.85 (s), 147.75 (s), 155.57 (s), 156.81 (s). MS (ESI-MS): m/z = 163.05 ($C_8H_{11}N_4^+$, cation); 156.95 ($C_3HN_4O_4^-$, anion). Anal. Calcd: C 42.25, N 34.99, H 3.78. Found: C 42.82, N 34.52, H 3.96.