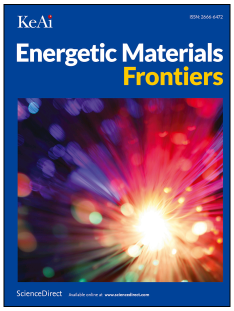

Molecular perovskites as a new platform for designing advanced multi-component energetic crystals

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Molecular perovskites as a new platform for designing advanced multi-component energetic crystals

Wei-Xiong Zhang,* Shao-Li Chen, Yu Shang, Zhi-Hong Yu, and Xiao-Ming Chen*

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China.

*E-mail: zhangwx6@mail.sysu.edu.cn (W.X.Z.); cxm@mail.sysu.edu.cn (X.M.C.)

Abstract

Molecular perovskite energetic crystals, as an emerging family of promising practicable energetic materials, have attracted increasing attentions in the past few years. Different from the mainstream strategies focusing on the intra-molecular designs and modifications on fused-ring energetic molecules/ions, molecular perovskites rely on the self-assembly of diverse molecular components into specified ternary crystal structures, hence generally could be prepared *via* an easy scale-up process at a low cost. As a kind of ternary salts, they have some unique advantages on the energetic-material designs in terms of optimizing oxygen balance, increasing pack efficiency (and crystal density), and decreasing hygroscopicity, hence could achieve improved detonation performances meanwhile overcome some technical weaknesses of traditional energetic binary salts. In this review, we summarize the current findings and understandings on molecular perovskite energetic crystals, and provide an outlook for the new opportunities brought by this new and promising material family towards advanced multi-component energetic crystals.

Keywords

Molecular perovskites, Energetic materials, Single explosive, Crystal engineering, Multi-component crystals

Abbreviations

TNT = 2,4,6-trinitrotoluene

PETN = pentaerythrite tetranitrate

RDX = 1,3,5-trinitro-1,3,5-triazacyclohexane

HMX = 1,3,5,7-tetranitro-1,3,5,7-tetrazocane

CL-20 = hexanitrohexaazaisowurtzitane

ONC = octanitrocubane

AP = ammonium perchlorate

AN = ammonium nitrate

ADN = ammonium dinitramide

KDN = potassium dinitramide

TKX-50 = dihydroxylammonium 5,5’-bistetrazole-1,1’-diolate

FOX-7 = 1,1-diamino-2,2-dinitroethylene

H_2dabco^{2+} = 1,4-diazabicyclo[2.2.2]octane-1,4-diium

$H_2odabco^{2+}$ = 1-hydroxyl-1,4-diazabicyclo[2.2.2]octane-1,4-diium

$H_2mdabco^{2+}$ = 1-methyl-1,4-diazabicyclo[2.2.2]octane-1,4-diium

H_2pz^{2+} = piperazine-1,4-diium

H_2mpz^{2+} = 1-methyl-piperazine-1,4-diium

H_2hpz^{2+} = homopiperazine-1,4-diium

$Hdabco^{+}$ = 1,4-diazabicyclo[2.2.2]octan-1-ium

1. Introduction

Energetic materials are of significant importance in military devices and civil industry,[1-10] as they have a unique capability of releasing large amount of heat and gas to output a work on the substances they contacted in a very short time. To achieve a fast release of the chemical energy and gas products, a well-known strategy is to covalently bond both oxidizing and reducing groups into a single molecule, which has been greatly successful in producing many classic organic energetic compounds, such as TNT, PETN, RDX, HMX, Cl-20, and ONC.[11] Their explosive performances are escalated with increasing the number of nitro-groups and the structural tension of carbon skeleton, but unfortunately, they become increasingly instable, sensitive, and costly along with the generation. Hunting more powerful, stable, reliable, and low-cost energetic crystals is an unending theme in the field of energetic materials.

The past decades have witnessed a fast growth of advanced energetic materials, especially the emergence of numerous energetic crystals designed by different strategies, such as the nitrogen-rich or all-nitrogen fused-ring energetic molecules/ions,[12-23] and the relevant energetic cocrystals,[24] ionic liquids,[25-26] binary salts,[27-31] or coordination polymers.[32-39] Some of these energetic crystals have find good balance between the detonation performance and stability, however, most of them are facing a complicated syntheses or expensive costs and thus hardly to have practical usages. Different from traditional design focusing on the intra-molecular functional groups, we proposed a strategy focusing on inter-molecular assembly in a specified crystal structure, *i.e.*, integrating low-cost fuel and oxidizer into ternary perovskite crystals.[40] This strategy have yielded a new sort of energetic materials, *i.e.*, molecular perovskite energetic crystals,[41] which have attracted increasing attentions and underwent a fast growth in the past years.

In this review, we will survey the current progress on the emerging molecular perovskite energetic crystals. A background of molecular perovskites will be briefly introduced in Section 2, especially on the perovskite structural feature and some highly-relative structural models. Then the current progresses on the design, syntheses and characterizations of molecular perovskite energetic crystals are introduced in Section 3. Our understanding on the characteristics or advantages of molecular perovskite energetic crystals distinguishing from other energetic materials are presented in Section 4, in which the discussions concern on the energy-releasing way, oxygen balance, packing efficiency, crystal density, self-assembly, scale-up synthesis, and hygroscopicity. Finally, we give a brief summary and an outlook for molecular perovskite energetic crystals.

2. A brief background of molecular perovskites

The term "perovskite" was firstly associated with the mineral $CaTiO_3$, which was found in Ural Mountains and was structural described by V. Goldschmidt in 1926, and then became the epitome of a large family of inorganic perovskites ABO_3, in which A and B is the divalent and 4-valent metal ion, respectively. The perovskite structure generally describes a cubic prototype structure (possessing $Pm\overline{3}m$ symmetry in the ideal model) with a general formula of ABX_3, in which the A-site cation have a larger size than the B-site one, and each B-site cation is six coordinated by X-site anions to form BX_6 octahedra (Figure 1a) those are further corner-shared to form a three-dimensional structure (Figure 1b). As the simplest and high-symmetric structural model of ternary salts, together with diverse compatible components, this cubic prototype endows perovskite crystals with various structural distortions and versatile functionalities.[42]

Besides the cubic prototype, the classification of perovskite has been extended to cover some important structures having a formula of ABX_3 and highly relating with cubic prototype. For example, a hexagonal perovskite describes a structure with $BaNiO_3$ prototype ($P6_3/mmc$ symmetry in ideal model),[43] in which the BX_6 octahedra are face-shared to form one-dimensional chains spaced by the A-site cations (Figure 1c). A postperovskite describes a structural prototype with *Cmcm* symmetry possessed by $MgSiO_3$ in an ultra-high pressure (> 125 GPa), in which the BX_6 octahedra are both edge- and corner-shared to form two-dimensional layers separated by the A-site cations (Figure 1d).[44-46] With these crystal structures based on the linked BX_6 octahedra and filled A-site ions, when two mixed ions are involved in A, B, or X sites, usually in an alternately ordered way, the term double perovskites could be used to describe such a large group of materials. When the charges of components are reversed, *i.e.*, A and B are anions while X is cations, such X_3BA materials are called as anti-perovskites. With the original cubic prototype and various extended structural models, inorganic perovskites represent a great success in the past century to serve as fundamental materials in diverse fields, such as ferroelectric, piezoelectric, colossal magneto-resistance, and superconductivity.

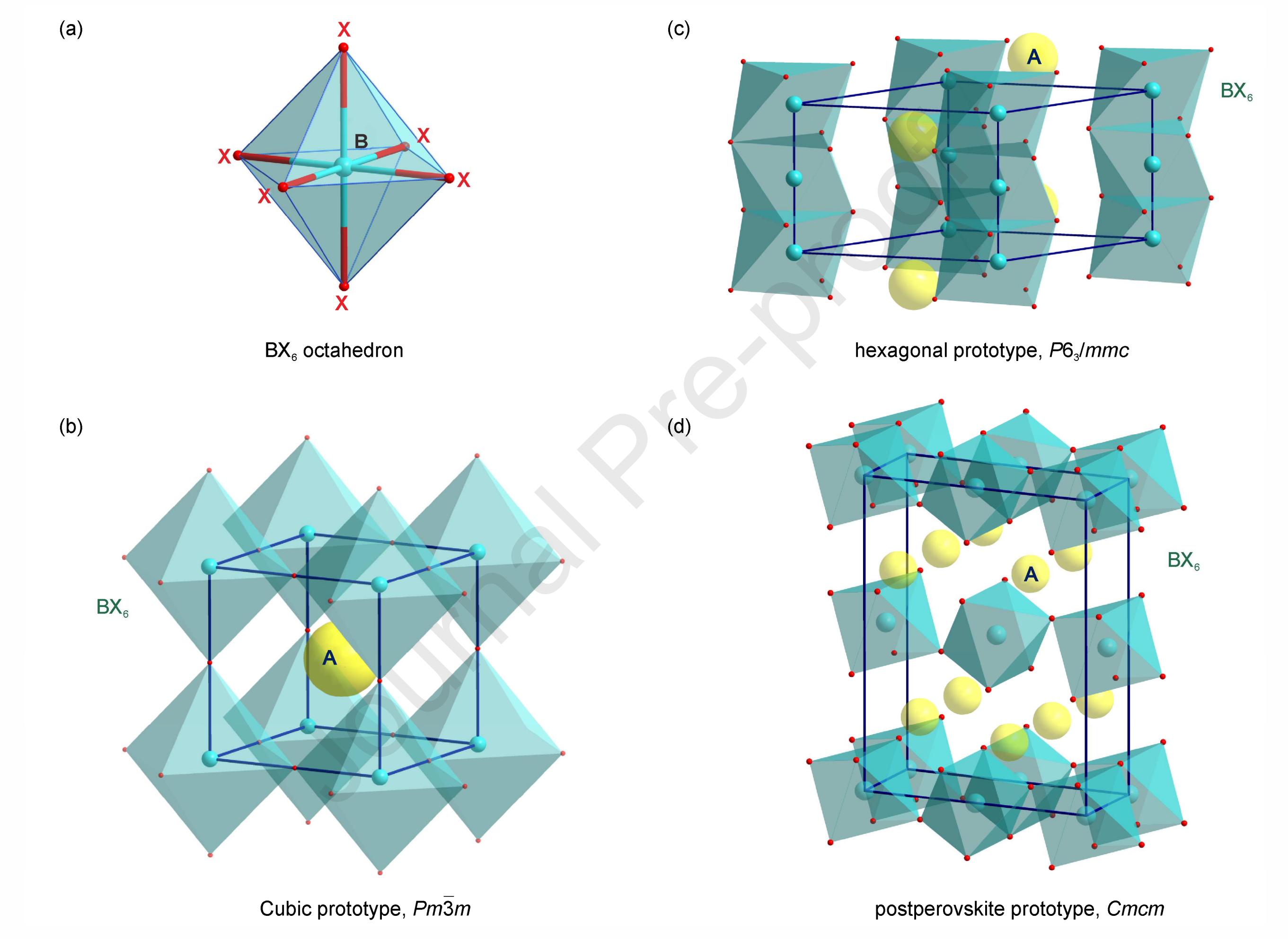


Figure 1. The BX_6 octahedral unit and the three typical perovskite structures based on different linkages of BX_6 octahedra.

In the past decades, there is a trend to construct perovskite crystals by partially or fully using molecular components, especially the organic ones, and such continued trend have yielded a large family of crystalline materials called as molecular perovskites, *aka.* organic-inorganic hybrid perovskites when organic component is involved.[47-50] Those molecular perovskites are topologically mimicking the traditional perovskite oxides with aforementioned structural features by using molecular components, usually on the A and/or X sites. Different from the perovskite oxides, by taking the advantage of diverse molecular components, such molecular perovskites are rich in exotic features, *e.g.*, in term of synthesis, an easy solution preparation process under ambient condition; in term of structure, an easy way to introduce forbidden distortion, structural chirality, and mechanical flexibility; and in term of functionality, a capable of hosting versatile functionalities particularly those hardly compatible with traditional perovskite oxides, such as solar absorption,[51-52] flexible ferroelectric,[53-55] optoelectronic materials,[56] and the energetic property concerned in this review.

3. Progress on molecular perovskites energetic crystals

Our efforts in the past few years on designing new molecular perovskite energetic crystals have yielded 20 compounds, as listed in Table 1 and Table 2, including 11 metal-containing members and 9 metal-free members; or 18 perchlorates and 2 nitrates; or 16 members in cubic-type structure and 4 members in hexagonal-type structure. More and more new molecular perovskite energetic crystals will emerge in the future with the persistent efforts on designing this new sort of interesting materials by self-assembling diverse potential molecular components through crystal engineering. For such a large family of compounds with a complicated full name, giving them simple and easy-pronounceable abbreviations is a good way to make convenient communication. According to their molecular components, as shown in Table 1, we abbreviated these compounds by using three capital letters, an en-dash, a number, and optionally a pre-number capital letter(s) to address the additional information. In the pre-endash term, the first letter indicates the A-site component, such as "D" to stand for 1,4-diazabicyclo[2.2.2]octane-1,4-diium (H_2dabco^{2+}) or its derivatives, and "P" to stand for piperazine-1,4-diium (H_2pz^{2+}), its derivatives or homopiperazine-1,4-diium; the last letter indicates the X-site components, such as "P" for perchlorate, and "N" for nitrate. The middle letter "A" together with the number indicates different B-site components, and we used 1, 2, ..., 7 to indicate Na^+, K^+, Rb^+, NH_4^+, Ag^+, NH_3OH^+, $NH_3NH_2^+$, respectively. An optional letter(s) inserted in between the en-dash and number is used to indicate additional information when the A-site is the derivatives of H_2dabco^{2+} or H_2pz^{2+}, *e.g.*, "M" indicates a methyl group, "O" indicates a hydroxyl group, "H" indicates homo-type piperazine. In this section, we will briefly describe the current findings for these compounds, such as their components, structures, stabilities, sensitivities, predicted (or measured) detonation performance, and structural phase transitions.

Table 1. Some A-site and B-site cations used for construction of perchlorate perovskite energetic crystals, and the resulted crystals with abbreviations.

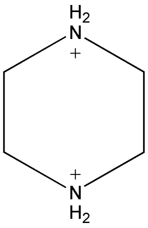
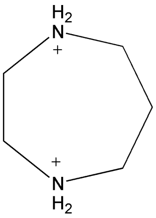
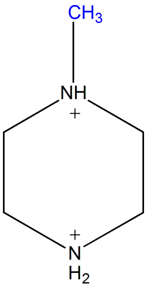
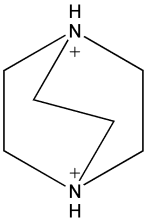
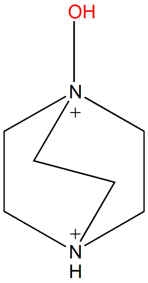
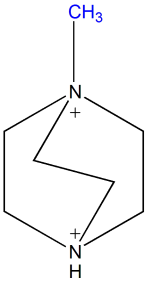
	A-site					
B-site	 H_2pz^{2+}	 H_2hpz^{2+}	 H_2mpz^{2+}	 H_2dabco^{2+}	 $H_2odabco^{2+}$	 $H_2mdabco^{2+}$
Na^+	PAP-1	/	/	DAP-1	/	/
K^+	/	PAP-H2	/	DAP-2	DAP-O2	/
Rb^+	/	/	/	DAP-3	/	/
NH_4^+	PAP-4	PAP-H4	PAP-M4	DAP-4	DAP-O4	DAP-M4
Ag^+	PAP-5	PAP-H5	PAP-M5	DAP-5	/	/
NH_3OH^+	/	/	/	DAP-6	/	/
NH_3NH^{2+}	/	/	/	DAP-7	/	/

Table 2 The selected parameters for molecular perovskite energetic crystals and some classic energetic crystals.

Compound	ρ/g ·cm^{-3}	T_d/°C	Q^e/kJ·g^{-1}	D^e/km·s^{-1}	p^e/GPa	ΔH_f/kJ·mol^{-1}	I_{sp}/s	OB/%	IS/J	FS/N
TNT	1.65[3]	290	3.74	6.897	20.0	−288.04	182	−74.0	15	353
RDX	1.82[3]	210[28]	5.59	8.634	33.3	−92.70	251	−21.6	7.5	120
HMX	1.90[3]	279[28]	5.57	8.892	36.2	−126.57	251	−21.6	7.5	112
CL-20	2.04[3]	215[28]	6.23	9.507	43.1	200.17	265	−11.0	4	48
DAP-1[40,59]	2.02^a	344^c	6.39	8.781	36.5	/	/	−22.0	17	36
PAP-1[59]	2.07^a	371^c	5.77	8.917	38.2	/	/	−3.9	20	5
DAP-2[40,59]	2.04^a	364^c	6.12	8.591	35.2	/	/	−21.3	16	42
DAP-O2[59]	1.98^a	329^c	5.69	8.327	32.5	/	/	−17.1	11	14
PAP-H2[61]	1.96^a	367^d	5.32	8.172	31.1	/	/	−15.6	27.5	7
DAP-3[40]	2.19^a	352^c	5.58	8.425	35.1	/	/	−19.3	22	28
DAP-4[40,60]	1.87^a	358^d	5.87	8.806	35.2	−484.0^f	254^h	−27.9	23	36
DAP-O4[60]	1.85^a	352^d	6.21	8.900	35.7	−436.1^f	262^h	−23.3	17.5	≤5
DAP-M4[60]	1.78^a	364^d	4.99	8.085	28.8	−839.0^f	225^h	−37.8	7.5	10
PAP-4[60]	1.74^b	288^d	6.00	8.629	32.4	−537.7^f	264^h	−9.9	/	/
PAP-M4[60]	1.77^a	323^d	5.14	8.311	30.3	−859.9^f	241^h	−21.0	30	≤6
PAP-H4[60]	1.83^a	348^d	5.76	8.756	34.3	−600.4^f	255^h	−21.0	27.5	6
DAP-5[61]	2.42^a	307^d	4.76	8.534	37.9	/	/	−18.4	3	≤5
PAP-5[61]	2.50^a	340^d	4.88	8.961	42.4	/	/	−3.2	≤10	≤5
PAP-M5[61]	2.37^a	307^d	5.42	8.778	39.7	/	/	-12.6	/	≤5
PAP-H5[61]	2.37^a	328^d	5.36	8.756	39.5	/	/	-12.6	/	≤5
DAP-6[62]	1.90^a	246^d	6.35	9.123	38.1	−373.7^f	265^h	−23.3	12	≤5
DAP-7[62]	1.87^a	375^d	6.00	8.883	35.8	−362.1^f	257^h	−28.7	27.5	≤5

DAN-2[41]	1.68^b	179^c	5.40	7.651	23.9	−339.1^g	/	−49.5	29	>360
DAN-4[41]	1.68^b	189^c	4.18	8.163	25.5	−677.8^g	212^h	−60.3	15	>360

ρ: crystal density; Q: detonation heat; D: detonation velocity; p: detonation pressure; ΔH_f: enthalpy of formation; I_{sp}: specific impulse; IS: impact sensitivity; FS: friction sensitivity; OB: Oxygen balance based on CO_2, for $C_aH_bN_cCl_dO_e$: OB = $1600[e - 2a - (b - d)/2]/M_W$, where M_W is molecular weight.

a,*b*) The crystal densities estimated from capillary powder X-ray diffraction data collected at room temperature (*a*) or single-crystal X-ray diffraction data (*b*).

c,*d*) The onset decomposition temperatures evaluated from DSC (*c*) and DTA (*d*).

e) The detonation parameters for molecular perovskite energetic crystals are calculated by DFT calculation and K-J equation for perchlorate-containing molecular perovskite energetic crystals (for details, see the cited references and their supplementary materials), and by using EXPLO5 v6.04.02 code based on formation enthalpies for the nitrate-containing compounds.

f) The enthalpies of formation for the metal-free perchlorate-containing compounds were roughly estimated by a back-calculation method from assumed detonation reactions,[60,62] and thus have lower precision.

g) The enthalpies of formation calculated from heat of combustion tested by oxygen bomb for the nitrate-containing compounds.

h) Specific impulses calculated by EXPLO5 v6.04.02 code based on enthalpies of formation.

3.1 The first series of molecular perovskite energetic crystals

In 2018, we reported the first series of molecular perovskite energetic crystals, *i.e.*, $(H_2dabco)B(ClO_4)_3$ (B = $Na^+/K^+/Rb^+/NH_4^+$ for DAP-1/2/3/4), all of which possess a cubic-type perovskite structure.[40] Our initial interest on such perchlorate perovskites was their structural phase transitions and relevant functional switching materials. The room-temperature structure of DAP-2 firstly described by Jin et al. in 2003 catched our attention.[57] Our consequent study revealed that DAP-1, DAP-2, and DAP-3 undergo reversible order-disorder structural phase transitions at 479/473, 395/393, and 288/286 K in a heating/cooling run, respectively, accompanying with a space group change from $Pa\bar{3}$ at low-temperature phase to $Fm\bar{3}c$ at high-temperature phase and a relatively-large latent heat of 80.5, 25.1, and 11.9 $J\cdot g^{-1}$, respectively.[58] A destructive and explosive decomposition of *ca.* 7 mg sample of DAP-1 occurred in a thermogravimetry measurement inspired us to consider the potential as energetic materials for these perchlorate perovskites. Consequently, we designed and synthesized a metal-free member, *i.e.*, DAP-4, by using NH_4^+ as B-site cation, in consideration of metal-free residue after decomposition.[40]

On the basis of the formation heats calculated from combustion heats obtained by oxygen-bomb calorimetry, the detonation heats were initially estimated by EXPLO5 V6.04.02 as 8.89, 7.09, and 10.38 $kJ\cdot g^{-1}$, for DAP-1, DAP-2 and DAP-4, respectively, all of them are higher than that of CL-20 (6.22 $kJ\cdot g^{-1}$).[40] But those detonation heats were overestimated probably owing to the corrosion on the oxygen bomb after the decomposition of such halogen-containing compounds. Later on, we employed an alternate method, by using density functional theory, to revaluate the detonation heats, and obtained more reasonable detonation heats of 6.39, 6.12, and 5.87 kJ·g^{-1}, for DAP-1, DAP-2 and DAP-4, respectively.[59-60] Such values are in agreement with a direct measurements on detonation heats by laser-igniting the test samples (*ca.* 1.5 g) performed about one year later in Xi'an Modern Chemistry Research Institute. The directly measured detonation heats are 5.83 and 5.69 kJ·g^{-1} for DAP-1 and DAP-4, respectively, both are comparable to those of RDX and HMX estimated by the same method. The consequently revaluated and updated detonation velocity and pressure for DAP-1, DAP-2, and DAP-4 are listed in Table 2, suggesting that their overall detonation performances are comparable with RDX or HMX.

3.2 The first trial on changing A-site components in molecular perovskite energetic crystals

To briefly demonstrate the tunability of molecular components and thereby to manipulate the oxygen balance (based on CO_2) for molecular perovskite energetic crystals, we changed the A-site components from H_2dabco^{2+} by two strategies to manipulate oxygen balance: (i) trimming the C and H atoms by using H_2pz^{2+} to yield PAP-1, and (ii) adding an oxygen atom by using $H_2odabco^{2+}$ to yield DAP-O2.[59] Compared with its H_2dabco^{2+} analogues, *i.e.*, DAP-1 (oxygen balance is −22.0%) and DAP-2 (−21.3%), respectively, PAP-1 and DAP-O2 have improved oxygen balances of −3.9% and −17.1%, respectively. Together with the increased crystal density from 2.02 to 2.07 g·cm^{-3}, the significantly-improved oxygen balance endows an improved detonation performance for PAP-1. In contrast, the larger $H_2odabco^{2+}$ cation only gives a slight-improved oxygen balance from −21.3% (DAP-2) to −17.1% (DAP-O2), but causes a decreased crystal density from 2.04 to 1.98 g·cm^{-3}, and eventually results in a decreased detonation performance for DAP-O2. These facts suggested an intrinsic trade-off relationship between optimizing oxygen balance and increasing crystal density in such molecular perovskite crystals.

3.3 A series of metal-free molecular perovskite energetic crystals

In consideration of the advantage of metal-free residues and possibility to produce more gas products, metal-free energetic materials are of particular interest for application especially as propellant. Based on the first metal-free molecular perovskite energetic material, *i.e.*, DAP-4, we changed the A-site components and successfully added five metal-free members.[60] They could be viewed as the derivated crystals in three different branches from the truncal DAP-4, *i.e.*, adding fuel, trimming fuel, and adding oxygen. By and large, as the oxygen balance of DAP-4 is negative (−27.9%), adding fuel on DAP-4 results in a more negative oxygen balance, *e.g.*, −37.8% in DAP-M4, and not surprisingly, leading to a reduced detonation performance. By contrast, taking PAP-4 as example, trimming fuel on DAP-4 could significantly improves the oxygen balance, *e.g.*, −9.9% in PAP-4, but a smaller cation filling the cage decreases the crystal density by 7%. These two factors eventually result in an increased detonation heat but decreased detonation velocity and pressure in PAP-4. The third strategy that adding oxygen atom on H_2dabco^{2+} gave an improved oxygen balance of −23.3% and only about 1% reduced crystal density, thus results in a slightly improved detonation performance for DAP-O4.

From the comparison of DAP-O4 and DAP-M4, it is worth to note that, compared with the introduction of a larger methyl group, introducing a smaller hydroxyl group not only gives a better oxygen balance, but also facilitates to give a denser crystal packing. In this sense, similar to the circumstances in organic energetic molecules, the introduction of compact oxygen-containing groups, such as hydroxyl, hydroperoxy, and nitro groups, is a promising approach for enhancing the detonation performance of perovskite-type or other multi-component energetic crystals.

PAP-M4 and PAP-H4 present a pair of nice instances to demonstrate the influence of the shape of A-site cations, as H_2mpz^{2+} and H_2hpz^{2+} are isomeric cations with different shapes. With a methyl group, the skeleton of H_2mpz^{2+} is branched and deviates significantly a symmetric dish-like shape, resulting in a lower packing efficient and crystal density (1.77 $g\cdot cm^{-3}$) in PAP-M4. By contrast, H_2hpz^{2+} has a seven-membered ring structure with many easy-adoptable conformations to fit well the cage units, and hence furnishing a higher packing efficient and crystal density (1.83 $g\cdot cm^{-3}$) in PAP-H4.

3.4 A series of silver(I) perovskite energetic materials

To extend the types of B-site cation, we have attempted to use other monovalent metal ions. As the silver(I)-based energetic crystals, such as silver azide, usually have good initiation capabilities, while perchlorate molecular perovskites usually have high thermal stability and potential capable to produce very rapid explosive reaction, the potential of silver(I)-based perchlorate molecular perovskites as heat-resistant primary explosives would be an interesting topic. Our attempts have successfully yielded four new silver(I) perchlorate perovskites, *i.e.*, PAP-5, PAP-M5, PAP-H5, and DAP-5 (see Tables 1 and 2).[61]

Compared with the aforementioned perovskite crystals constructed by B-site alkali ions (*i.e.*, Na^+, K^+, and Rb^+), which have a less or negligible direction characteristic on coordination interactions, the silver(I)-based molecular perovskite energetic crystals reveal a different structural flexibility on their inorganic coordination framework, because the silver(I) cation has a much noticeable coordination direction characteristic to interact with six adjacent perchlorate ions. Accordingly, the size and symmetry of A-site organic cations have a different influence on the crystal structures of the silver(I)-based crystals. For instance, being different from the case that PAP-M4 and PAP-H4 are both isomeric and iso-structural, PAP-M5 and PAP-H5 are isomeric but not iso-structural at room temperature. Specifically speaking, PAP-M5 adopts a cubic prototype structure in the space group *Pnma*, in which the coordination framework become highly distorted to host crystallographically ordered H_2mpz^{2+} with a branched skeleton. In contrast, PAP-H5 adopts a distorted hexagonal prototype structure in the space group $P2_1/n$, in which the more flexible H_2hpz^{2+} cations are crystallographically disordered to fulfill the inter-chain space. Such phenomenon that a little change on A-site cation results in different structural models well reflects a delicate and sensitive inter-component cooperativity for silver(I)-based molecular perovskite crystals. Density function theory (DFT) calculations suggested that, these four silver(I)-based molecular perovskites have good detonation performances, though such calculations may overestimate the performances using a high crystal density of heavy-atom-containing compound and their detonation heats in unit mass are lower than those of the alkali analogues. Interestingly, the silver(I) ion endow them with relatively-higher impact sensitivities (< 10 J) and friction sensitivities (< 5 N), making these compounds as potential primary explosives. Moreover, the differential thermal analyses indicated that these four silver(I)-based molecular perovskites are capable of violently decomposing with a possible self-acceleration processes in the vicinity of peak decomposition temperatures ranging from 308.3 to 339.5 ^{o}C, which is slightly reduced when comparing with those of the alkali analogues, but are close to, or higher than, that of $Pb(N_3)_2$ (315.0 ^{o}C). Such a high thermal stability, together with a relatively-high mechanical sensitivity and a fast decomposition, implies these silver(I) compounds to be promising candidates as heat-resistant primary explosives, and a further study is undergoing.

3.5 Hexagonal perovskites with NH_3OH^+ or $NH_3NH_2^+$ as B-site components

Our efforts have also been extended to cover derivatives of ammonium as B-site cations, resulting in the isolations of two hexagonal perovskites, *i.e.*, DAP-6 and DAP-7, with NH_3OH^+ and $NH_3NH_2^+$ as B-site components, respectively.[62-63] These two cations, comparing with NH_4^+, have higher formation enthalpies and are capable to form more hydrogen-bonding interactions, and thus are favored for designing energetic salts, especially those with nitrogen-rich or full-nitrogen energetic anions.[64-65] Moreover, they have larger sizes and rod-shapes with pesudo-C_3 symmetry along the N−O/N bond, when compared with T_d-symmetric NH_4^+, so that they are more compatible to a hexagonal perovskite structure rather than a cubic one adopted by DAP-4. The deviations from a real C_3 symmetry on the B-site cations lead DAP-6 and DAP-7 to possess a monoclinic structure (Figure 2) at room temperature caused by a symmetry breaking from the ideal hexagonal structure.

With a hexagonal perovskite structure, DAP-6 and DAP-7 have higher crystal densities (1.90 and 1.87 g·cm^{-3}, respectively), and also have higher formation enthalpies (−373.68 and −362.14 kJ·mol^{-1}, respectively) than that of DAP-4 (−483.96 kJ·mol^{-1}), and eventually possess detonation performances prior to DAP-4. It is worth to point out that, DAP-6 and DAP-O4 could be regarded as two isomers modified from DAP-4 by adding oxygen atoms on B-site cation and A-site cation, respectively (Table 1). DAP-6 (B-site modification) has an overall energetic performance superior to DAP-O4 (A-site modification), and hence reached a new record on energetic performance in the known molecular perovskites to date. However, it should also be noted that, as NH_3OH^+ cation has a relatively low thermal stability, DAP-6 has an onset decomposition temperatures of 245.9 °C, which is higher than those of RDX (210 °C) and CL-20 (215 °C) but much lower than those of most molecular perovskite energetic crystals (> 300 °C).

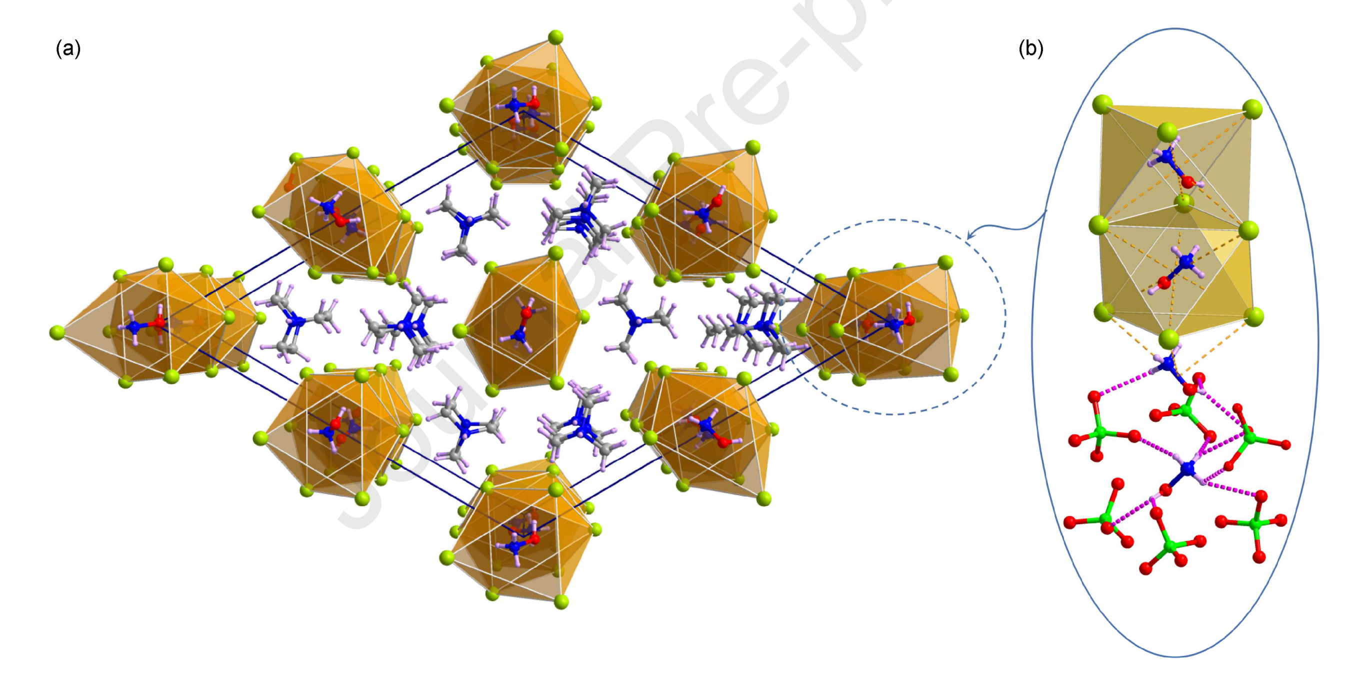


Figure 2. (a) The three-dimensional molecular packing of DAP-6 in the monoclinic space group $P2_1$ deviated from the ideal hexagonal perovskite. (b) The $(BX_3)_n^{n-}$ supramolecular chain consisting of face-sharing BX_6 octahedra. For clarity, only six perchlorate ions are shown, and the rest ones are represented as yellow green spheres as vertexes of octahedra.

3.6 Comprehensive studies on $(H_2dabco)(NH_4)(ClO_4)_3$ (DAP-4)

Molecular perovskite energetic crystals have gained growing attention, such as on the decomposition performance,[66-71] elastic property,[72] phase transition,[58,73,74] crystal morphology,[75,76] hygroscopicity,[77] and formula design.[78] Among them, DAP-4, as the first metal-free member, has attracted particular attention, and its important physical properties have been studied comprehensively.[68-71,76-78] Recently, we have achieved scale-up preparation of pure and uniform DAP-4 sample on a 100 g scale, and will achieve a kilogram scale soon. A measurement on 1.5 g DAP-4 sample indicated its detonation heat is 5.69 $kJ\cdot g^{-1}$, comparable with RDX. Consequently, its detonation velocity, pressure, and volume were estimated as 9.21 $km\cdot s^{-1}$, 38.5 GPa, and 858 $L\cdot kg^{-1}$, respectively. In other words, DAP-4 has an overall detonation performance comparable to RDX and HMX.

The mechanical sensitivity tests according to the Chinese GJB772A-97 standard indicated that DAP-4 has a possibility of 28% to be explored upon impact of 10 kg hammer from a height of 25 cm, a characteristic height (H_{50}) of 77.6 cm (5 kg hammer), and a possibility of 88% to be explored upon friction (3.92 MPa, 90°). These results consist with the previous ones measured by BAM apparatus,[40] and indicate that DAP-4 is not sensitive to an impact stimulus but is relatively sensitive to a friction stimulus. The underlying mechanism of mechanical sensitivity is thought to be related to multiscale structures at least including molecular stability, stacking mode, crystal morphology, and interfacial features.[79] The different responses of DAP-4 to impact and friction has not been well known, and might be highly associated with the intrinsic characteristic of perchlorate ions and the relatively-rigid cubic perovskite structure. In addition, an electrostatic sensitivity test according to the Chinese GJB5891.27-2006 standard indicated that no explosive occurred in 30 trials, using 10000 pF capacity with an output voltage of 10.0 kV, under four different experiment conditions (0.12 mm, 0 Ω; 0.25 mm, 0 Ω; 0.18 mm, 100 kΩ; and 0.50 mm, 100 kΩ). Such a low sensitivity to the electrostatic stimuli probably benefits from the ionic characteristic of molecular components in DAP-4 that is beneficial for dispersing electrostatic charge.

Different from the most perchlorate-containing salts, DAP-4 has a very low hygroscopicity. Our studies indicated that, according to the Chinese GJB772A-97 test standard, the samples of DAP-4 showed only *ca.* –0.01% weight change (*i.e.*, almost unchanged) under the relative humility of 91% at 30 ^{o}C for 3 days. A comparison study reported by Cao et al. revealed that the hygroscopicity of DAP-4 is only about 10% of that of AP under the same condition (*vide infra*).[77] Storage of a unit mass of DAP-4 under vacuum at 90/100 ^{o}C for 40 hours only produced 0.04/0.05 mL gaseous products. Moreover, when mixing DAP-4 with one of some commonly-used materials in energetic formulas, such as RDX, Cl-20, HMX, TNT, Al, AP, NC-NG, and DINA, very few gaseous product was detected after storage of these two-component mixtures at 100 ^{o}C for 40 hours, namely, DAP-4 is compatible with these materials individually. These results indicated a rather high stability and a good compatibility for DAP-4, implying a large room for formula design based on DAP-4.

Taking a rather high thermal stability of DAP-4, *e.g.*, a burst temperature (5 seconds delay) of 370 ^{o}C (Woods' metal bath method) and a peak decomposition temperature of 404 ^{o}C (DSC method),[40] a heat-resistant explosive formula based on DAP-4 has been successfully designed and used for charging petroleum perforating bomb.[78] Recently, particular efforts have been devoted for studying on the thermal decomposition of DAP-4. With DSC measurements at different heating rates, Ding and Zhang et al. estimated an apparent activation energy of about 215 kJ·mol^{-1} for the decomposition,[68] a value close to that of RDX (211 kJ·mol^{-1}). By analyzing the *in-situ* variable-temperature FTIR spectra for both DAP-4 and AP, they suggested that a confined effect of the A-site cations, *i.e.*, the H_2dabco^{2+} cations being locked in the cage skeleton constructed by NH_4^+ and ClO_4^- ions, renders DAP-4 a superior thermal stability different from traditional organic energetic materials. Another investigation on the thermal decomposition and combustion of DAP-4 performed by Ren et al. showed a lower decomposition activation energy of 181 kJ·mol^{-1}.[69] They preformed an ignition test for DAP-4, and found that a sustained combustion process with violent flames can be observed from 10 to 350 ms. Such a short-time and fast reaction process well demonstrates a fierce energy-releasing effect for DAP-4.[69] In addition, Ren et al. found that mechanically mixing DAP-4 with 10 wt% graphene could enhance the combustion performance of DAP-4.[70] While Cao et al. found that mechanically mixing 1 wt% MoS_2 nanosheet could catalyze the decomposition of DAP-4, leading to a decrease of the initial decomposition temperature from 394 ^{o}C to 343 ^{o}C.[71] These investigations on decomposition and combustion of DAP-4 could give useful information for practical application of DAP-4 in composite propellants.

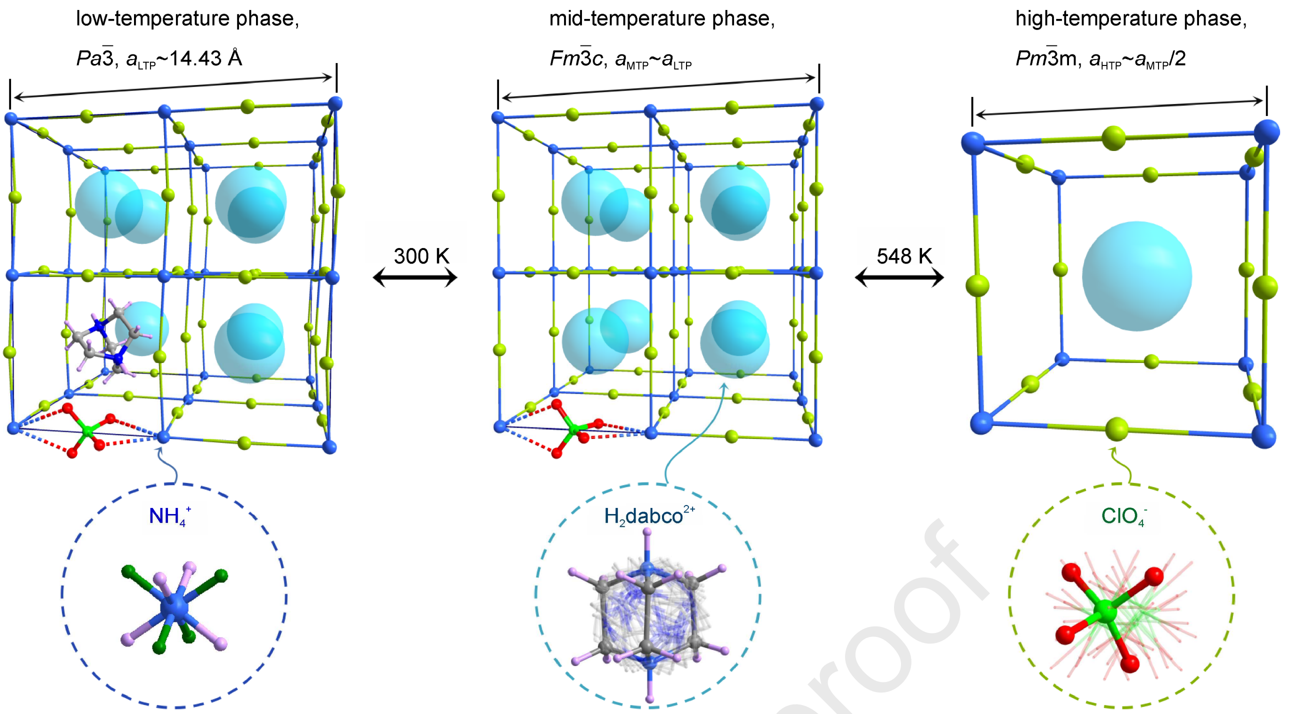


Figure 3. Structural scheme for the two-step phase transitions of DAP-4 arising from step-wise dynamically order-disorder transition of molecular components.

Our recent investigation on DAP-4 revealed that DAP-4 undergoes two-step reversible phase transitions at 300/299 K (T_{c1}) and 548/548 K (T_{c2}), respectively, during a heating/cooling cycle. Crystal X-ray diffraction indicated that these phase transitions are caused by two-step order-disorder dynamical change of the molecular components.[80] As shown in Figure 3a, at the low-temperature phase (below T_{c1}) in the cubic space group $Pa\bar{3}$, all molecular components except NH_4^+ cations are crystallographically ordered. For the mid-temperature phase (between T_{c1} and T_{c2}) in the space group $Fm\bar{3}c$, the organic cation, *i.e.*, H_2dabco^{2+}, become crystallographically 48-fold disordered owing to its relatively-weak inter-molecular interactions (Figure 4b). Upon heating to above T_{c2}, an additional phase transition occurs with a lager enthalpy change of 15.6 kJ·mol^{-1} (36.2 J·g^{-1}). It is difficult to structurally characterize the high-temperature phase by single-crystal X-ray diffraction, as it is hard to maintain the high-quality single crystallinity at such a high temperature. However, on the basis of the previous findings on the phase transitions in other similar molecular perovskites, especially the borofluoride (BF_4^-)-based ones, we proposed a structure model for the high-temperature phase that possesses the ideal cubic perovskite prototype ($Pm\bar{3}m$) with a halved cell length of the mid-temperature phase (Figure 3c). In this model, all molecular components become “melt-like” orientationally disordered but positional ordered, namely, being a plastic-crystal phase. Such plastic-crystal phase may have an easy deformablility that is good for shaping by applying an axial pressure.

As T_{c1} is near room temperature, the change of crystal volume during this phase transition may affect the mechanical properties of DAP-4. We recently performed an accurate measurement for the thermal expansion coefficient of DAP-4 by means of Pawley refinements on the powder X-ray diffraction patterns in a large temperature range of 173–353 K. We found the axial expansion coefficients of 57.1×10^{-6} and 81.4×10^{-6} K^{-1} for low-temperature and mid-temperature phases, respectively. Accordingly, the volumetric expansion coefficients are 173.5×10^{-6} and 245.5×10^{-6} K^{-1} for low-temperature and mid-temperature phases, respectively, both are close to those estimated for β-HMX (213.0×10^{-6} K^{-1} and 205.0×10^{-6} K^{-1} in temperature range of 5–350 K and 303–423 K,[81-82] respectively). Moreover, a noticeable volume change of 0.77% occurs in the vicinity of the near-room-temperature phase transition of DAP-4, suggesting a first-order characteristic for this phase transition, *i.e.*, super-cooling phenomenon and dual-phase coexistence are theoretically allowed for this transition. Such a near-room-temperature volume change should be paid attentions when performing formula design based on DAP-4. It should be noted that, although three crystalline phases have been identified for DAP-4 in a large temperature range, *i.e.*, from its decomposition temperature down to 173 K, this polymorphism is mainly caused by the aforementioned orientationally order-disorder transition (*i.e.*, step-wise dynamical change) of molecular components rather than by an inter-molecular rearrangement usually observed in other energetic crystals such as HMX.[83] Moreover, all these three crystalline phases possess cubic structures hence an isotropic expansibility rather than an anisotropic one observed in most of other energetic crystals.[79] Such isotropic characteristic on thermal expansion of DAP-4 may be propitious to reduce the adverse effect of its volume change on the formula design.

4. Discussions on molecular perovskites energetic materials

In this section, we present our understanding or opinions on the basis of the current findings in this new branch of energetic crystals, *i.e.*, molecular perovskites energetic crystals. Although some of them contains metal ions, they are not metal-organic framework because their X-site ligands are inorganic ones rather than organic ones. In view of the fact that molecular perovskites are formed by well-defined cationic and anionic components, they could be called as “ionic cocrystals”, in which the attributive “ionic” is used to distinguish them from the customarily-defined cocrystals those should be formed by charge neutral molecular components rather than ionic ones.[84] Some molecular perovskites could be regarded as “double salts”, similar to some well-known examples such as $(NH_4)_2Fe(SO_4)_2$ containing two kinds of cations. Nevertheless, in consideration of the capability on extending more components into perovskite structures, such as double perovskites ($A_2B'B''X_6$) mixing three different cations, we strongly recommend to use "multi-component salts" when only ionic components are involved, or "multi-component crystals" when neutral components are possibly involved, to emphasize an advantage of molecular perovskites, *i.e.*, a crystal engineering assembling ternary or more components into a specific crystal structure to tune the material properties toward advanced energetic crystals for different applications (*vide infra*).

4.1 The way to release heat

In the known molecular perovskite energetic crystals, it seems that only the X-site component, *i.e.*, perchlorate or nitrate, is energetically activating group, whereas both A-site and B-site cations are energetically inactivating components. One question is arisen that how those compounds can release a large amount of chemical energy in a short time. Different from the classical organic energetic molecules containing energetically activating group such as nitro and azido groups, the molecular perovskite energetic crystals release a large amount of heat by inter-molecular redox reactions in a single-phase material. Such an energy release way is almost same with the traditional binary salts prepared by simply mixing O-rich oxidizing energetic ions and C/H-rich reducing organic cations, such as ethylenediammonium perchlorate and ethylenediammonium nitrate.[85] In general, for such energetic salts consisting of components with a relatively low formation enthalpy, whatever binary ones or the present ternary ones (*i.e.*, molecular perovskites), the relatively strong attractive coulomb interactions between the adjacent cations and anions give a large lattice energy, and thus usually endow these salts with negative formation enthalpies, which seems not energetically favored for designing ultrahigh explosives. By contrast, one of the mainstream approaches to design advanced energetic materials is to synthesize nitrogen-rich or all-nitrogen crystals with a rather high positive enthalpy, such as more than 2000 $kJ \cdot mol^{-1}$.[30] It should be pointed out that, the chemical energy released from a decomposition reaction not only depends on the formation enthalpy of reactants but also on the formation enthalpies of decomposed product. In other words, the difference on their formation enthalpies matters (Figure 4). For nitrogen-rich or all-nitrogen compounds, the majority of the decomposed product is dinitrogen with a zero formation enthalpy. Whereas for the present energetic salts mixing O-rich oxidizing anions and C/H-rich fuel cations, the majority of the decomposed product is H_2O and CO_2/CO with a very negative formation enthalpy of −241.8 $kJ \cdot mol^{-1}$ (−13.4 $kJ \cdot g^{-1}$) and −393.5 $kJ \cdot mol^{-1}$ (−8.94 $kJ \cdot g^{-1}$) / −110.5 $kJ \cdot mol^{-1}$ (−3.94 $kJ \cdot g^{-1}$). Therefore, although the energetic salts have a negative formation enthalpy, about minus several hundred, even to minus one thousand $kJ \cdot mol^{-1}$, their decomposition reactions are capable of releasing a large amount of chemical energy, especially those with an oxygen balance (based on CO_2) close to zero for a theoretically complete combustion. For instance, based on an ideally-assumed decomposition reaction, one molar DAP-4 could yield 7.5 molar H_2O, 2.25 molar CO_2, and 3.0 molar HCl ($\Delta H_f = -92.3$ kJ·mol^{-1}), those products give a total energy decrease of *ca.* 2977 kJ if neglecting the volume work. Although DAP-4 has a negative formation enthalpy (*ca.* −484 kJ·mol^{-1}), its decomposition reaction has a large energy difference (~2491 kJ) between reactant and products, and hence could release a considerable chemical energy, ~5.78 kJ for a unit mass of DAP-4 by taking account of formula weigh (430.56 g·mol^{-1}).

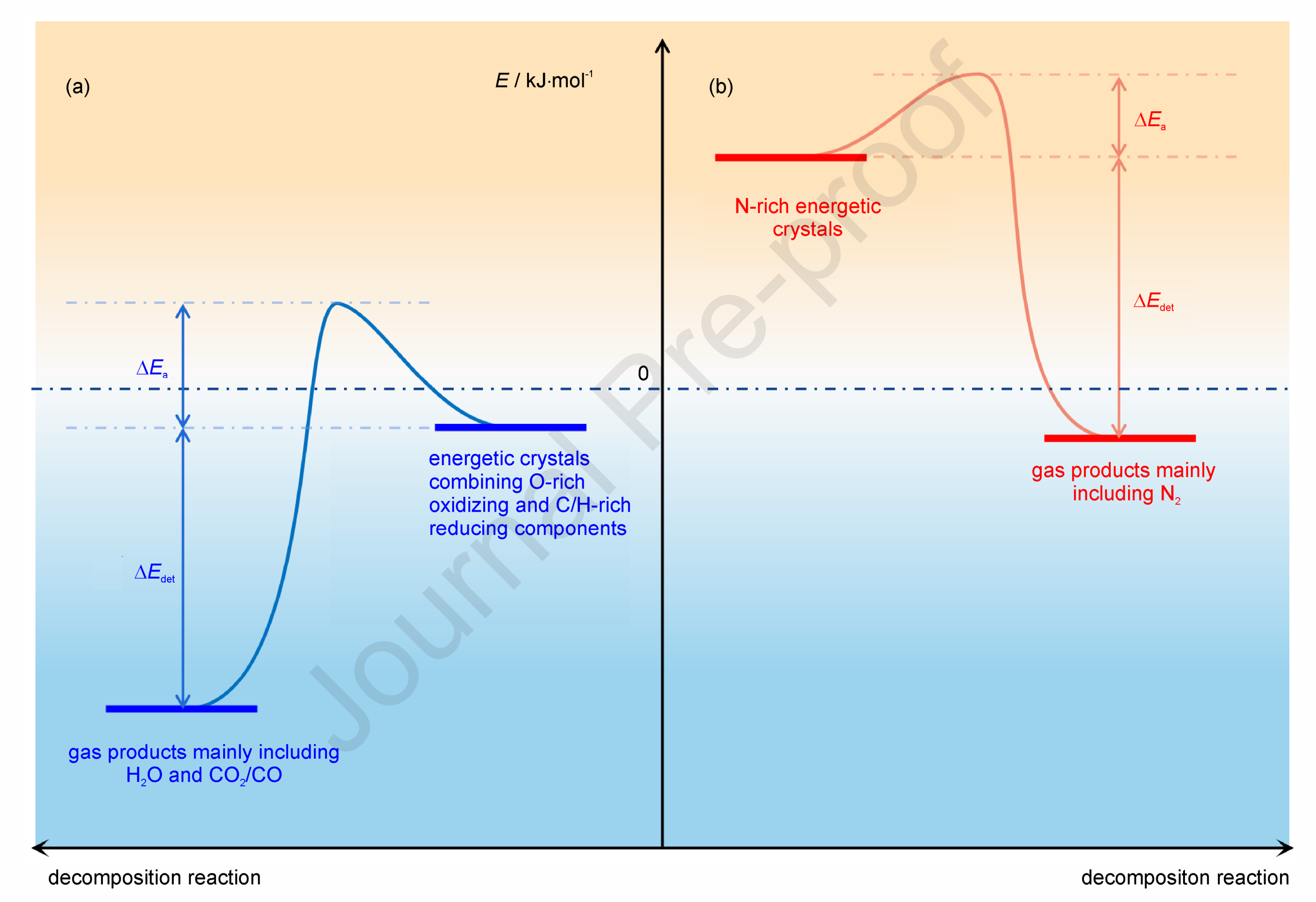


Figure 4. Scheme for the released chemical energy (ΔE_{det}) by decomposition of energetic crystals based on combining O-rich oxidizing and C/H-rich reducing components (a) and the N-rich energetic crystals (b).

4.2 Optimization on oxygen balance for self-redox reactions

In a thermodynamic view of the releasing chemical energy and gas products based on the self-redox reactions, the oxygen balance is a crucial parameter.[86-88] It is customary to desire a zero oxygen balance based on CO_2 for explosive, as in such case, the self-supplied oxygen element is exactly enough to convert all C and H elements into their thermal-dynamically most stable oxides, *i.e.*, CO_2 and H_2O, respectively. Whereas for the propellants that more favors gaseous products with a lower molecular weight to do more effective work, the zero oxygen balance based on CO rather than CO_2 is customarily desired. Therefore, oxygen balance is an important parameter needed to be optimized for different applications, and is considered as one of the most important parameters in the formula design of multi-phase energetic mixture, which is, in principle, an approach having capable of manipulate the oxygen balance in a successive way *via* finely changing the ratio between oxidizing and reducing reagents.

A detonation reaction generally finishes in a time shorter than micro-seconds, such that a thermodynamic equilibrium could not be fast established by a sufficient atomic/molecular diffusion and collision. The real combustion or detonation reaction is far from the thermodynamic prediction, but is much complicated and highly dependent on the phase composition and confined situation of the energetic materials. For a multi-phase mixture well mixing oxidizing reagent (*e.g.*, AP) and reducing reagent (*e.g.*, organic oil), as the effective redox reactions only occur on the boundary between the oxidizing and reducing reagents, a high percentage of intra-phase oxidizing (or reducing) molecules could not participate the redox reaction until they meet reducing (or oxidizing) molecules, eventually resulting in a kinetically delayed process. By contrast, in a view of the effective atomic/molecular collisions, the redox reactions in a single-phase energetic salt could be finished much fast and sufficient, because the oxidizing and reducing atomic/molecular components have been alternately packed in a domino-like way, *i.e.*, being ready for molecular collision to trigger a domino effect at high temperature. In this sense, molecular perovskite energetic crystals, as ternary single-phase crystalline materials, have a potential capable of finely optimizing the oxygen balance by changing the molecular, while having the advantage of single-phase energetic salts that enables the fast and sufficient redox reactions.

It should be pointed out that, many binary energetic salts mixing oxidizing anions and reducing organic cations are believed to be capable of releasing a large amount of chemical energy after sufficient combustion, especially those based C/H-rich alkylaminium cations having a high calorific value. However, in the most cases, the organic cations are monovalent or divalent ones, such that they can mix with only one or two stoichiometric oxidizing anions in their binary salts, resulting in relatively worse oxygen balances, low denotation heats, and eventually ordinary denotation performances close to TNT. A few exceptions based on low-carbon alkylaminium, such as ethylenediammonium perchlorate and ethylenediammonium nitrate, have better oxygen balances even close to zero, hence can reach a higher denotation performance, but their high hygroscopicities strongly limit their practice uses. By contrast, in the ABX_3 molecular perovskite energetic crystals, the addition of carbon-free B-site cations, *i.e.*, ammonium, hydrazinium, hydroxylammonium, or metal ions, enables the ratio between reducing A-site organic cation and oxidizing X-site anions to reach 1:3 and to yield good oxygen balances, most of which are close to that of RDX/HMX and even to that of CL-20, meanwhile maintain relatively high crystal densities (Figure 5). Such a strategy based ternary salts undoubtedly gives a huge potential to finely optimize oxygen balance in a large range, by changing not only the inter-component reducer/oxidizer ratio but also the intra-component element composition.

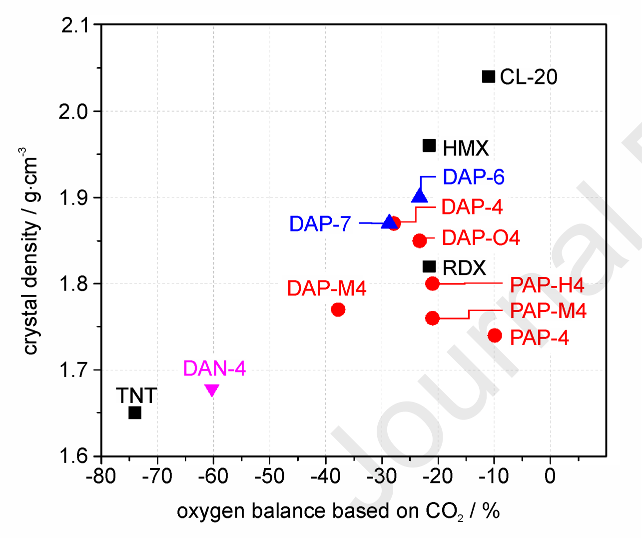
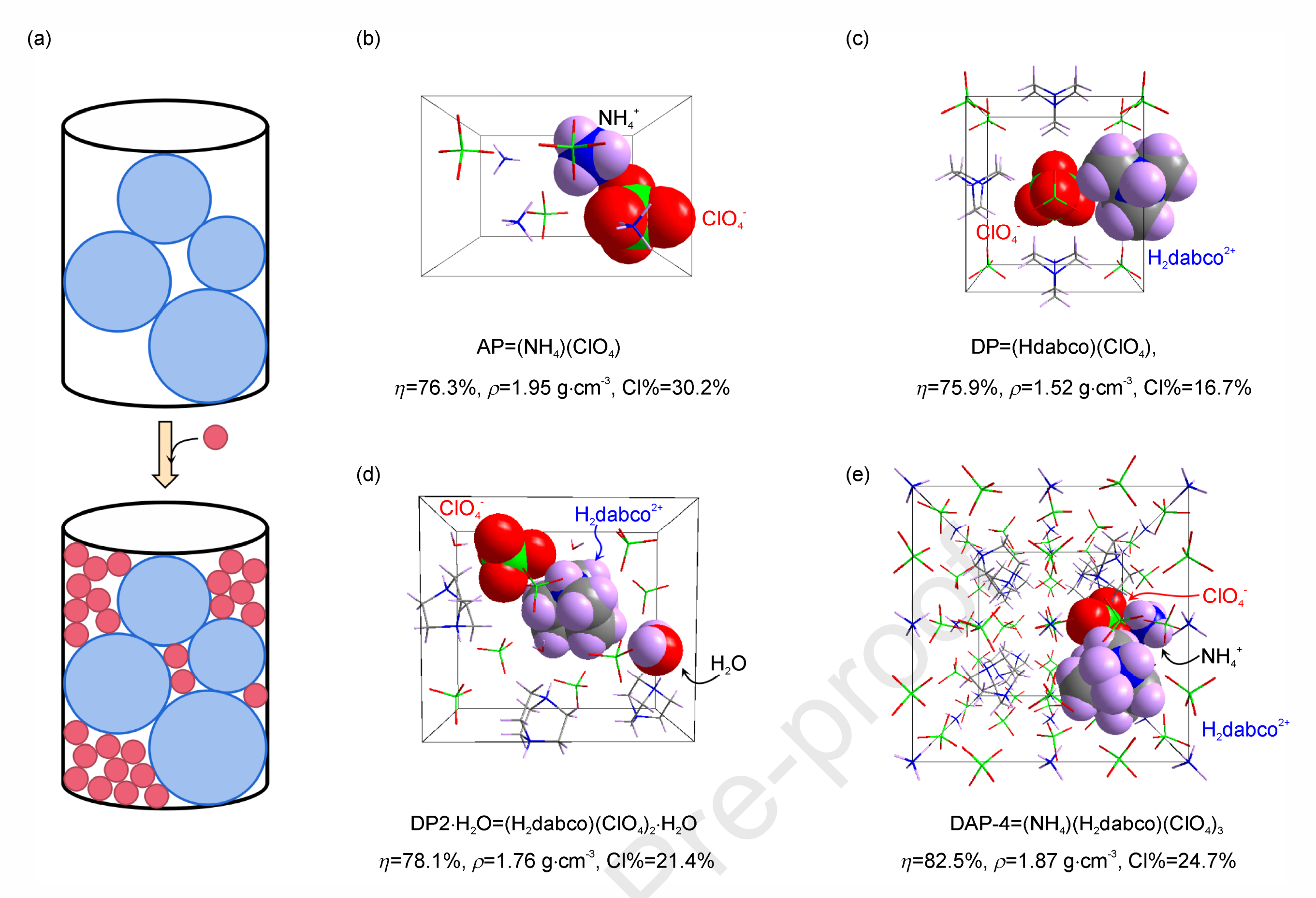


Figure 5. A scatter diagram for oxygen balance parameters based on CO_2 for the metal-free perovskite members and four classic organic energetic crystals.

4.3 Packing efficiency and crystal density

Crystal density (ρ) is one of the most important factors in crystalline energetic materials, as a denser structure, in principle, implies shorter atomic distances between atomic/molecular components that generally facilitates a faster reaction to propagate shock wave, *i.e.*, a faster detonation velocity. Given a same reaction, a higher density of energetic materials also implies that the same gas products could be confined in a smaller volume to yield a higher detonation pressure. In addition, a higher crystal density usually means a reduced apparently sensitizing free space in the crystal lattice hence facilitates to reduce impact sensitivity.[89]

For the energetic materials with significantly different chemical formulas or different element compositions, it is not straightforward to compare their crystal densities for discussing the influences on material performance, in particular, not suitable in the cases when comparing a heavy-atom-containing compound and a heavy-atom-free compound. Alternately, a packing efficiency (η) defined as the percentage of occupied spaces by atoms in the whole cell space is an appropriate and supplementary factor for discussing the energetic materials with significantly different chemical formulas, such as different cocrystals of HMX.[90]



AP=$(NH_4)(ClO_4)$
η=76.3%, ρ=1.95 g·cm^{-3}, Cl%=30.2%

DP=$(Hdabco)(ClO_4)$,
η=75.9%, ρ=1.52 g·cm^{-3}, Cl%=16.7%

DP2·H$_2$O=$(H_2dabco)(ClO_4)_2 \cdot H_2O$
η=78.1%, ρ=1.76 g·cm^{-3}, Cl%=21.4%

DAP-4=$(NH_4)(H_2dabco)(ClO_4)_3$
η=82.5%, ρ=1.87 g·cm^{-3}, Cl%=24.7%

Figure 6. (a) Scheme for a way to increase molecular packing efficiency (η) by adding small-size components. (b-e) The three-dimensional molecular packing structure in one unit-cell of AP (b), DP (c), DP2·H$_2$O (d), and DAP-4 (e).

Taking DAP-4 as an example, the ternary characteristic of perovskites enables optimization of the oxygen balance meanwhile maintaining a high packing efficiency by judicious choice of size-matched components (Figure 6a). As shown in Figures 6b-e, two binary salts, *i.e.*, AP,[91] and (Hdabco)(ClO$_4$) (DP),[92] and two ternary crystals, *i.e.*, (H$_2$dabco)(ClO$_4$)$_2$·H$_2$O (DP2·H$_2$O)[93] and DAP-4, are compared on their crystal packing efficiencies and crystal densities. AP has the highest crystal density (1.95 g·cm^{-3}), and then DAP-4 (1.87 g·cm^{-3}), DP2·H$_2$O (1.76 g·cm^{-3}), and DP (1.52 g·cm^{-3}). Such descending order in crystal density should be mainly ascribed to a decreased percentage of relatively-heavy chlorine element (Cl%), *i.e.*, AP (30.2%) > DAP-4 (24.7%) > DP2·H$_2$O (21.4%) > DP (16.7%). However, in view of packing efficiency, both ternary crystals have higher values (82.5% for DAP-4, and 78.1% for DP2·H$_2$O) than those of binary crystals (76.3% for AP, and 75.9% for DP). Such findings well suggested that importing size-suitable components (especially one with a small size) into the known binary crystals has a potential advantage to increase the packing efficiency, which could be a promising way to modify these binary crystals for application requirement.

Such advantage of ternary salt was also well demonstrated by DAP-6 and DAP-7, both of which adopt a hexagonal perovskite structure to pack the ternary components in a denser way, and have a high packing efficiency of 81.9% and 83.9%, respectively, and a high crystal density of 1.90 and 1.87 g·cm^{-3}, respectively.[62] In this sense, besides the element compositions of the molecular components, the matchable sizes of these components are also a key in judicious choice of the molecular components for assembling advanced multi-component energetic crystals with both an optimized oxygen balance and a high-enough packing efficiency.[94]

4.4 Self-assembly design and scale-up synthesis

Most molecular perovskites are prepared *via* a supramolecular self-assembly process, or so-called “one-pot” solution reaction by mixing the components in a proper chemically stoichiometric ratio. Such inter-molecular assembly into crystals does not concern breaking covalent bonds and could generate the product in a high yield under an ambient condition and a proper pH value. As most of the starting chemicals for preparations of the present molecular perovskites are not expensive, such an easy scale-up synthetic process under ambient condition endows these materials with a low cost, which is a very crucial for practical usages of the energetic materials.

It seems very easy to tune the molecular components for molecular perovskite energetic crystals, especially on the A-site organic cations, as well demonstrated by a family of ammonium-based compounds using different organic cations (Table 1). However, a crystallization process is a traditional method for purification, *i.e.*, inherently favors a single-component outcomes for neutral species, or a binary salt for ionic species.[95] It is not always an easy task to design and achieve a self-assembly process to import the third or more components into binary salts, in an order way, to yield a stoichiometric multi-component salts with a target structure, as the potential crystallization outcomes are too many to be easily predicted. Moreover, for the crystalline energetic materials, a desired crystallization process is essentially required to exclude the large amount of non-energetic solvent molecules (or its protonated form) into the target crystals, as the crystals containing such neutral small molecules (*e.g.*, DP2·H_2O) or protonated solvent molecule (*e.g.*, $(H_2dabco)(H_3O)(ClO_4)_3$)[96] usually have some technically undesired properties, such as a serious weathering, a lower thermal stability, and a lower energetic performance.

Some strategies were proposed to rationally assemble multi-component molecular solids, especially the cocrystals based the neutral organic molecules, and have been successful in producing ternary cocrystals, quaternary cocrystals,[97] and even six-component solid solutions.[98] In principle, the inter-component matches on both size and interactions need to be highly concerned in self-assembly design. Based on similar consideration on the inorganic perovskites, an extended Goldschmidt tolerance factor was proposed to evaluate the ionic size mismatches for molecular perovskites using the empirical and effective molecular sizes,[99] and could undoubtedly be referred to exclude some combinations of A, B, and X components in crystal design. An overall understanding on the potential inter-molecular interactions of the chosen components, specifically the hydrogen bonds, coulomb force, van der Waals attractions, and possible coordination bonds for molecular perovskites, is of importance to promote the success of obtaining new perovskite energetic compounds. A careful balance of the inter-molecular interactions must be taken, on their strengths, directional characteristics, and distance falloff properties,[95] to design a proper complementary recognition between different components, to promote the self-assembly process, and to obtain multi-component energetic crystals in a high yield and high purity.

In addition, it should be noted that the most of the present molecular perovskite energetic crystals have a low or very low solubility in water and most organic solvents, so the re-crystallization method commonly-used for organic energetic compounds is not suitable for further purification of the molecular perovskite products in a large scale. In this sense, optimizing the reaction process, seeking the best technological parameters, and then well controlling the core reaction conditions become particularly important technical issues for preparing pure and uniform crystalline products, especially those with a specific crystal morphology and size.

4.5 Low hygroscopicity

Some organic perchlorate/nitrate binary salts possessing good energetic performances, high thermal stabilities, and low cost, such as ethylenediammonium perchlorate and ethylenediammonium nitrate, are likely promising candidates for practicable energetic materials. However, most of perchlorate salts, neither organic ones or inorganic ones, have a common disadvantage, *i.e.*, high hygroscopicity in high humidity (even at low humidity in some cases), causing difficulty in their storage and some safe problems when mixing then with other materials in formulas.[85] In this sense, it is a surprising and stirring fact that most of the present perchlorate perovskites, as ternary salts, have a low hygroscopicity in high humidity. Taking DAP-4 as example, when its 5.0 g samples were exposed at room temperature and relative humidity of 45%, 60%, 75%, and 90%, respectively, for 48 hours, the observed weight increases are only 0.046%, 0.044%, 0.040%, and 0.060%, respectively.[77] In contrast, at the same experimental conditions, the binary perchlorate salt, AP, a commonly-used oxidizer in rocket propellants, has a weight increase of 0.52%, 0.56%, 0.60%, and 0.58%, respectively, *i.e.*, about 10 times higher than those of DAP-4. A possible mechanism for explaining such low hygroscopicity of DAP-4 was ascribed to the unique perovskite structure that have a stronger coulomb forces between cations and anions on the surface of crystals.[77] Considering the fact that the family of perchlorate perovskites still have different performance on the hygroscopicity, the essential reasons related with such a low hygroscopicity are complicate and highly governed by the structural details, such as the complementary recognition between A, B, and X components, and the saturation degree of the inter-molecular interactions, especially the hydrogen bonds for perchlorate anions. The further in-depth studies, including experimental and theoretical ones, are urgent needed to uncover the mechanism and provide new clues to modify the other binary energetic salts (*e.g.*, ADN, KDN) for overcoming their high-hygroscopicity problems.

5. A brief perspective

In summary, we survey the current progresses on an emerging research topic, *i.e.*, molecular perovskite energetic crystals, which provide a new platform towards multi-component energetic crystals. Benefiting from molecular assembly by using diverse molecular components, these molecular perovskite energetic crystals have several advantages over the traditional organic energetic crystals or binary salts, in particular, the low cost benefited from an easy scale-up synthesis by using cheap chemicals under ambient condition, and the capability in finely manipulating important parameters (*e.g.*, oxygen balance, packing efficiency, and crystal density) to meet different application requirements.

Some important questions/problems should be addressed for promoting the further developments of molecular perovskite energetic crystals to achieve their practical applications. For the known compounds of molecular perovskites, accurate measurements of their important physical parameters or properties, such as the formation enthalpy, detonation performances, decomposition activated energy, thermal expansibility, and possible structural phase transition, are essentially important for evaluating their potential capabilites as energetic materials in different applications. For the members evaluated as promising materials, such as DAP-4 and other metal-free members, an optimized synthesis process to obtain pure and uniform crystalline sample on large scale, *e.g.*, kilogram scale, especially those with a specific crystal size and morphology, *e.g.*, globular crystals in several micrometers, is an important step towards the practical applications. It is also critical to investigate comprehensively their compatibility with other usual materials in formula, and if necessary, to seek a way to modify crystal surface to decrease the friction sensitivity, and/or to enhance compatibility/cooperation with other materials. Then the considerable efforts are needed to preform comprehensive formula design by utilizing molecular perovskite energetic crystals to meet different application requirements, such as heat-resistant explosives, rocket propellants, and fireworks. The joint efforts of scientists and engineers from different disciplines are highly necessary to promote the molecular perovskite energetic crystals towards their practical applications.

In view of basic science, besides the ABX_3-type molecular perovskite energetic crystals, there is a huge room to explore the other new family of multi-component energetic crystals with different crystal structures (especially the non-perovskite ones) based on diverse molecular components (especially the cheaper ones) by changing the component ratio (such as ABX_4, A_2BX_4, and AB_2X_5)[100-102] or changing the component member (such as quaternary and quinary salts). Some relevant layered perovskite structures, such as Ruddlesden-Popper phases with a general formula of $(A')_2(A)_{n-1}BX_{3n+1}$ found in Pb(II)-halide-based compounds,[103] may provide very important clues for new multi-component energetic crystals, *e.g.*, by replacing the halide ions with oxidizing ions such as ClO_4^-, NO_3^-, and $N(NO_2)_2^-$. Seeking the multi-component energetic crystals based on halogen-free oxidizing ions, *e.g.*, $N(NO_2)_2^-$, is particularly worth trying to develop “green” energetic crystals,[4] in consideration of the environmental concerns caused by the production and usage of perchlorate ions. In addition, it is urgently needed to extend or modify the existent models/methods, which have been successfully used for traditional CHNO-based energetic materials, to estimate the detonation performances in a more accurate way for the multi-component energetic crystals, especially those with heavy-metal elements. And the computer-aided methods based on these improved models undoubtedly find useful in the materials screening to improve the design efficiency. With continued efforts on developing multi-component energetic crystals following the present molecular perovskite energetic crystals, the fruitful results could be expected in the near future, not only in the emergence of new advanced energetic crystals but also the breakthrough in practical applications.

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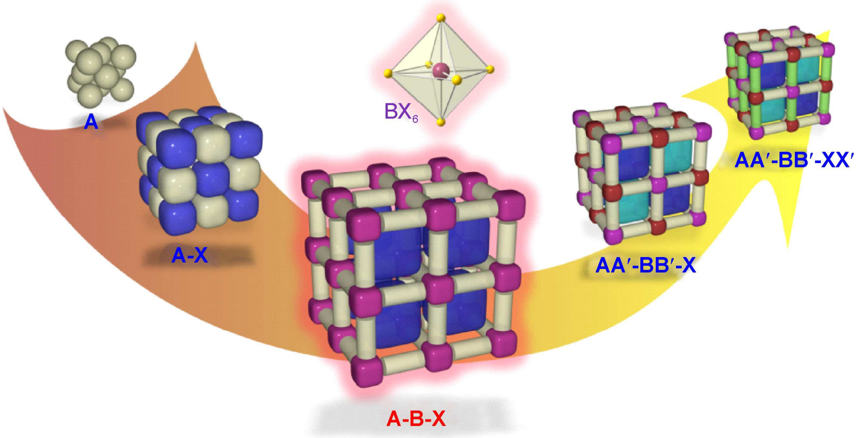
Graphic Abstract



By taking the advantage of tuneability on components, molecular perovskite provide a path towards advanced multi-component energetic crystals for practical usage.

Biography

Wei-Xiong Zhang obtained BSc in 2004 and Ph.D in 2009 from Sun Yat-Sen University (SYSU). He was a JSPS postdoctoral fellow in Tohoku University, Japan. He joined SYSU in 2012, and became professor in 2018. His current research interest is in crystal engineering of multi-component dense crystals, especially the structural-phase-transition functional crystals and energetic crystals.

Xiao-Ming Chen obtained his BSc in 1983 and M.S. in 1986 from Sun Yat-Sen University (SYSU), and his Ph.D. from Chinese University of Hong Kong in 1992. He then joined SYSU and became a professor in 1995. He was elected to CAS in 2009 and TWAS in 2013. His current research interest is in synthesis and crystal engineering of functional metal complexes and coordination polymers.

Highlights

- This review gives an overview of the current studies on molecular perovskite energetic crystals, which are prepared by self-assembling stable oxidizing and reducing components in a proper ratio and thus have advantages of high detonation performance, high stability, and low cost.

- As the simplest and high-symmetric structural model of ternary salts, perovskite structure gives a nice platform to design advanced multi-component salts with optimized oxygen balance, packing efficiency, and hence the energetic performance.

- Inspired by molecular perovskite energetic crystals, assembling multi-component salts by using diverse molecular components through crystal engineering is a very promising approach toward advanced energetic crystals for practical usage.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: