



Molecular perovskite high-energetic materials

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Since the black powder, the first known explosive, was discovered by ancient Chinese in the seventh century, people have been finding powerful, stable, reliable and low-cost energetic materials for military equipment and civil industry. To obtain a better explosive performance, an efficient strategy is to load unstable chemical bonds [1–3], as well as to combine fuel with oxidizer components in a proper ratio for achieving sufficient combustion and rapid detonation [4–6]. An effective way is to incorporate fuel and oxidizer properties into a single molecule [7], as demonstrated by a series of classical organic nitro group/nitrogen-rich molecules, such as trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), cyclotrimethylene trinitramine (RDX), cyclotetramethylene tetranitramine (HMX), hexanitrohexaazaisowurtzitane (CL-20) and octanitrocubane (ONC) (Fig. S1). Loading more nitro groups and higher structural tension into a single molecule does improve explosive performance, but usually leads to complicated and not cost-effective synthetic procedures. By a trade-off of detonation performance and cost, HMX is regarded as the best military high-energetic explosives nowadays [7], although it is neither the most powerful one nor the cheapest one.

Parallel to the intensive studies on molecule engineering on the backbone of nitrogen-rich organic energetic molecules [8,9], the exploration of advanced energetic materials extends to the crystal engineering on their energetic co-crystals [10–13], energetic salts [14–20], as well as coordination polymers or metal-organic frameworks [21–27]. The essential strategy is to control the intermolecular packing/linkage of the energetic organic fuel and oxidizer components in crystals by non-covalent interactions to modify/enhance the explosive performance and/or to reduce the sensitivity to a practicable level. However, for a specific energetic molecular component, it is highly challenging to predict/engineer the

crystal structure of its co-crystals, salts, or metal-organic frameworks [10], and the examples with good detonation performance, high stability and low cost are still scarce.

Here we present a promising solution, i.e., assembly of both low-cost organic fuel and oxidizer components into a closely packed, high-symmetry ternary compounds (*vide infra*), to achieve advanced energetic materials with a nice combination of high explosive power, high stability, and low cost. The presented materials belong to the so-called molecular perovskites [28] with a general formula of ABX_3 , which topologically mimic the cubic structure of the very well-known inorganic perovskites, the simplest high-symmetry structure for ternary compounds, but have at least one organic molecular component (usually A component). Recently, molecular perovskites have attracted growing attention, as illustrated by the extensive studies on methyl-ammonium lead iodide for high performance solar cells [29–32], and the phase transitions together with the relevant switching physical properties [33–35]. In the course of our investigation on relevant molecular perovskites [36], we discovered that, the well-known, low-cost oxidative perchlorate anion as X component, and compatible fuel organic cation as A component, can be easily assembled into molecular perovskites by one-pot reaction. Such simple synthetic approach led to a new class of high-energetic materials, $(H_2dabco)[M(ClO_4)_3]$ (DAPs, dabco = 1,4-diazabicyclo[2.2.2]octane, $M = Na^+, K^+, Rb^+$ and NH_4^+ for DAP-1, -2, -3 and -4, respectively). This sort of low-cost materials not only has very different structures and components compared with the well-known high-energetic explosives, but also has a high detonation performance comparable to HMX and even CL-20, and a much higher thermal stability than them.

Non-hygroscopic powders of DAPs were obtained in a high yield (>90%) by separating the precipitate product from the one-pot reactions of mixing aqueous solutions

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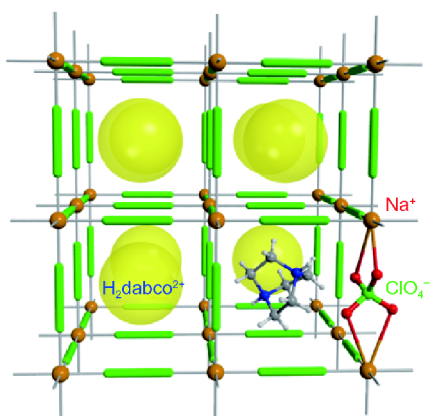


Figure 1 The perovskite structure of DAP-1. For clarity, only one ClO_4^- bridge and one $\text{H}_2\text{dabco}^{2+}$ cation are shown, while the others are represented by green bars and yellow spheres, respectively.

of dabco, perchloric acid, and the corresponding perchlorate salt in a molar ratio of 1:2:1 at room temperature. The single-crystal X-ray diffraction at 232 K indicates that DAPs are isomorphous and crystallized in the cubic space group $Pa\bar{3}$ (No. 206). As shown in Fig. 1, the structure of DAPs can be simply described as perovskite type, by regarding $\text{H}_2\text{dabco}^{2+}$ as A-site cation, M^+ as B-site cation and ClO_4^- as X-bridges. Each M^+ ion is surrounded by twelve oxygen atoms from six ClO_4^- anions, while each ClO_4^- anion bridges two M^+ ions, forming a three-dimensional anionic framework consisting of cages that are filled by $\text{H}_2\text{dabco}^{2+}$ cations. It is worth noting that, although DAP-1, -2 and -3 have B-site alkali ions with significantly different ion radius (coordination number = 12): Na^+ (1.39 Å) < K^+ (1.64 Å) < Rb^+ (1.72 Å)[37], their average $\text{M}\cdots\text{Cl}$ atomic distances vary in a narrow range of 3.551(1)–3.616(1) Å (Table S2). That is to say, the size of cage unit is almost independent of the M^+ ions, because the steric requirement of $\text{H}_2\text{dabco}^{2+}$ cations prevents the further contraction of anionic framework. In this sense, such perovskite structure leads to significant structural tension in DAPs, and the smaller M^+ ion is, the stronger structural tension is.

As shown in Fig. 2 and Table 1, the decomposition temperatures (onset) of DAPs range from 344 to 365°C, which are much higher than those of the famous single explosives such as HMX (280°C), RDX (204°C), and CL-20 (210°C). Such high thermal stability of DAPs should be ascribed to the steady covalent bonds of molecular components as well as the structure reinforcement by strong Coulombic interactions between the alternately-packed cations and anions in the unique perovskite

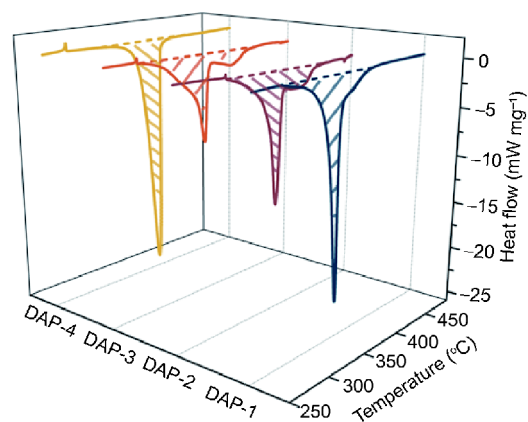


Figure 2 Differential scanning calorimetry graphs of DAPs.

Table 1 Thermal data of DAPs from DSC measurements

Compounds	T_d^a (°C)	T_p^b (°C)	Q_{DSC} (kJ g ⁻¹)
DAP-1	344	361	4.40
DAP-2	364	377	4.08
DAP-3	352	369	3.80
DAP-4	365	383	5.18

a) The onset decomposition temperatures. b) The peak decomposition temperatures. c) The decomposition heat recorded by DSC.

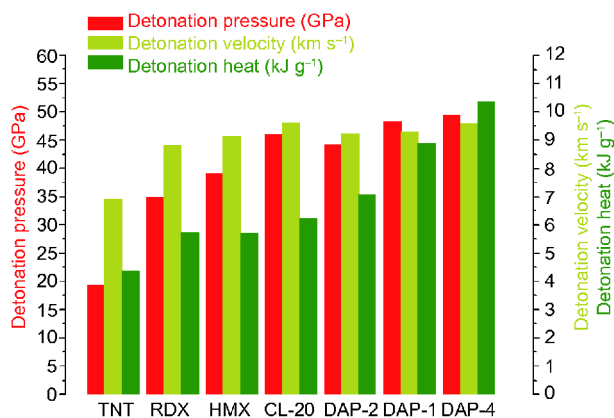


Figure 3 Bar chart representation of detonation parameters calculated by EXPLO5 V6.04.02, for DAP-1, DAP-2, DAP-4, and the well-known explosive materials including TNT, RDX, HMX and CL-20.

structure.

As evaluated by using EXPLO5 V6.04.02 program [38] (Fig. 3 and Table 2), DAP-1, -2 and -4 have excellent detonation performances superior to HMX and comparable to CL-20. Their detonation heats in a descending order are: 10.38 kJ g⁻¹ (DAP-4) > 8.89 kJ g⁻¹ (DAP-1) >

Table 2 Detonation properties of well-known explosives and DAPs

Compound	ρ^a (g cm ⁻³)	ΔH_f^b (kJ mol ⁻¹)	Q^c (kJ g ⁻¹)	D^e (km s ⁻¹)	P^e (GPa)	IS (J)	FS (N)	OB ^e (%)
TNT	1.65	-59.3	4.36	6.915	19.4	15	353	-24.7
RDX	1.80	70.3	5.74	8.817	34.9	7.4	120	0
HMX	1.91	74.8	5.72	9.152	39.1	7.5	112	0
CL-20	2.04	397.8	6.22	9.598	45.9	4	48	11.0
DAP-1	2.02 ^a	1013.7 ^b	8.89	9.306	48.3	17	36	0
DAP-2	2.04 ^a	247.3 ^b	7.09	9.224	44.2	16	42	0
DAP-3 ^d	2.16 ^a	/	/	/	/	22	28	0
DAP-4	1.87 ^a	1904.2 ^b	10.38	9.588	49.4	23	36	-5.6

a) ρ is the density of powder sample measured by capillary powder X-ray diffraction at room temperature; b) ΔH_f is the heat of formation calculated from heat of combustion tested by oxygen bomb; c) Q is the heat of detonation, D is the detonation velocity, and P is the detonation pressure. The detonation parameters were calculated by EXPLO5 V6.04.02; d) since EXPLO5 doesn't cover rubidium element, the detonation parameters of DAP-3 could not be calculated; e) oxygen balance based on CO for $C_xH_yN_zM_eCl_fO_p$, M as alkali metal ion, were calculated by: $OB[\%] = 1600[f-a-(b-e+d)/2]/M_w$, where M_w is molecular weight.

7.09 kJ g⁻¹ (DAP-2), and all are higher than those of classic high explosives such as RDX (5.74 kJ g⁻¹), HMX (5.72 kJ g⁻¹) and CL-20 (6.22 kJ g⁻¹). The detonation velocities of DAPs are in range of 9.224–9.588 km s⁻¹, higher than that of HMX (9.152 km s⁻¹) and close to that of CL-20 (9.598 km s⁻¹), meanwhile their detonation pressures (44.2–49.4 GPa) are much higher than that of HMX (39.1 GPa), and particularly, both of DAP-4 (49.4 GPa) and DAP-1 (48.3 GPa) are even higher than that of CL-20 (45.9 GPa).

It is worth noting that the large difference in denotation heats (3,872 – 3,202 = 670 kJ mol⁻¹) between DAP-1 and DAP-2 is mainly ascribed to their large difference in combustion heats (5,685 – 4,945 = 740 kJ mol⁻¹). Meanwhile, their combustion products only differ in metal chlorides, in which NaCl has an enthalpy of formation (-411.1 kJ mol⁻¹) slightly higher than that of KCl (-436.7 kJ mol⁻¹), and the smaller Na⁺ ions lead to the stronger structural tension of the anionic framework in DAP-1 than that in DAP-2. These facts strongly imply that, the released detonation heats of DAPs do not just come from the breaking and recombination of covalent bonds during the denotation reaction, but also are notably contributed by the structural tension in the perovskite structure. Thus, such perovskite structure plays an important role in enhancing the denotation heat for DAPs.

For the metal-free member, i.e., DAP-4, it could be regarded as the modification of ammonium perchlorate (AP), the most-commonly-used oxidizing component in solid rocket propellants. The replacement of alkali metal ions by NH₄⁺ ions enables DAP-4 to give a much better denotation performance than the metal-contained mem-

Table 3 Specific impulse of well-known oxidizing agents, explosives and DAP-4

Com-pound	AP	ADN	TNT	RDX	HMX	CL-20	DAP-4
I_{sp}^a (s)	157	202	206	267	266	272	344

a) The specific impulses were calculated by EXPLO5 V6.04.02.

bers, due to the extra oxidation of ammonium to release more denotation heat and gas products. Moreover, the denotation of DAP-4 gives an extremely high calculated specific impulse (I_{sp}) value of 344 s, much higher than those of RDX (267 s), HMX (266 s) and CL-20 (272 s) (Table 3). As an increase of about 10 s in I_{sp} can double the payload of a rocket [4], one could expect that DAP-4 may significantly improve the performance for the presently used propellants.

Distinguishing from the other high-energy-density materials which are mainly derived from nitrogen-rich heterocycles and their cations, DAPs present a new class of single explosives based on ternary compounds that are uniform versions of oxidants and fuels at molecular level, in which the size-matched fuel cations (H₂dabco²⁺) are tightly confined in the cubic cages composed of oxidative anions (ClO₄⁻) in a triple molar ratio. The design of molecular perovskite energetic materials retrospects the history of composite explosives from black powders to modern industrial emulsion explosives, at which pursuing better and better intimacy of oxidants and reductants is a direct means to achieve better detonation performance. But instead of making improvements of mechanical agitation, perovskite structure provides an alternative and dense packing of each fuel molecules with triple oxidant

groups at molecular level for achieving the ultimate uniform in a single explosive, resulting in good oxygen balances same with (or close to) those of HMX and RDX, high densities, and eventually, excellent detonation properties. The steady covalent bonds of molecular components, together with the structural reinforcement by strong Coulombic interactions between the cations and anions in perovskite structure, achieved high thermal stability for DAPs, as well as an isotropic response to the external stimuli [39] by the cubic symmetry to achieve low impact sensitivity (Table 2). In addition, different from their raw materials that are binary salts with serious hygroscopicity, DAPs are ternary ionic crystals without heavy-metal ions, and feature with non-hygroscopic, non-volatile, and non-weathering characteristics, which are beneficial for the storage and transportation.

Moreover, as demonstrated by DAPs with different B-site cations, the molecular perovskites provide an opportunity to tailor the performances by taking the tunable/modifiable characteristics of the three components. In fact, we have recently found several analogues of DAPs, by replacing $\text{H}_2\text{dabco}^{2+}$ with piperazine-1,4-dium cation on the A component, and/or replacing perchlorate with nitrate on the X component, and also some solid solutions of DAPs. A detailed study is now underway for these new materials. Regarding the diversities of the organic cations (especially lost-cost but high-calorific-value ones), oxidative anions and the high-symmetry crystal structure, the molecular design strategy illustrated by DAPs opens a new avenue for designing the advanced energetic materials for practical uses.

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Author contributions Zhang WX, Chen XM and Chen SL conceived the idea, designed the experiments and co-wrote the manuscript. Chen SL conducted synthetic experiments, calculations, and performed the DSC, TGA, PXRD measurements. Yang ZR, Wang BJ, Shang Y and Sun LY assisted the synthetic experiments. He CT assisted the calculations. Zhou HL performed the single-crystal XRD measurements. All authors discussed the results and commented on the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.



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分子钙钛矿含能材料

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摘要 设计合成兼具良好爆轰性能、高稳定性和低成本的含能化合物是发展实用含能材料的关键。本文报道了一类新型分子钙钛矿含能化合物, 它们可以通过使用低成本原料经简单一锅反应制备。作为氧化组分的高氯酸根阴离子和作为燃料组分的还原性有机阳离子交替紧密堆积于钙钛矿结构中, 使该类化合物不仅有比目前军用含能炸药(例如RDX和HMX)更优异的爆炸性能, 而且有更高的稳定性; 其中无金属组分的分子钙钛矿含能化合物具有与CL-20相当的爆炸性能以及更高的比冲(约344秒)。这种将低成本有机燃料组分和氧化剂组分组装在高对称性三元晶体结构的分子组装策略为设计有实用前景的含能材料提供了新思路。