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Metal-free Molecular Perovskite High-energetic Materials

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ABSTRACT: Metal-free energetic materials generally have the advantages of high gas yield and metal-free residue after combustion or explosion, enabling them to be widely used as explosives and propellant components. As part of a series of our investigations on ABX_3 molecular perovskite high-energetic materials, here we report five new metal-free members, $(H_2A)[NH_4(ClO_4)_3]$, by using different organic cations H_2A^{2+} , *i.e.*, 1-hydroxy-1,4-diazabicyclo[2.2.2]octane-1,4-dium for DAP-O4, piperazine-1,4-dium for PAP-4, 1-methyl-piperazine-1,4-dium for PAP-M4, homopiperazine-1,4-dium for PAP-H4 and 1-methyl-1,4-diazabicyclo[2.2.2]octane-1,4-dium for DAP-M4, respectively. Together with the previously-reported member, $(H_2dabco)[NH_4(ClO_4)_3]$ (DAP-4, $H_2dabco^{2+} = 1,4-diazabicyclo[2.2.2]octane-1,4-dium$), these six metal-free molecular perovskite high-energetic materials provide nice instances to fine-tune oxygen balance, crystal density, thermal stability, and detonation performance, by changing the A-site organic cations solely. The DFT calculations and K-J equation suggested that improving oxygen balance meanwhile keeping spherical shape of organic cations to well match the anionic cage in these metal-free energetic materials facilitate to obtain a better detonation performance, providing an important clue for designing advanced practicable high-energetic materials. It is worth noting that, three compounds (PAP-4, PAP-H4 and DAP-O4) are expected to exceed the performances of RDX as both explosive and propellant, in which DAP-O4 has the highest detonation heat (6.21 kJ mol^{-1}), detonation velocity (8.900 km s^{-1}), and detonation pressure (35.7 GPa), as well as a higher specific impulse value (262 s).

KEYWORDS: energetic materials, explosive, propellant, metal-free, molecular perovskite

INTRODUCTION

The design and synthesis of energetic materials, such as explosives, propellants, and pyrotechnics, have been widely concerned because of their extensive applications in military and civil fields.¹⁻⁴ Thanks to the efforts of researchers around the world, the amount of explosives has experienced a rapid increase in the past few decades, especially on energetic cyclopentazolate salts,⁵⁻⁹ nitrogen-rich organic energetic molecules,¹⁰⁻¹⁵ energetic salts,¹⁶⁻²³ energetic cocrystals,²⁴⁻³⁰ and energetic metal-organic frameworks or coordination compounds.³¹⁻³⁷ However, for most energetic compounds, excellent detonation performance is often contradictory to high stability and low production costs, excluding them from practical use. It is urgent but still a big challenge to design practicable energetic compounds with outstanding comprehensive performance, simple synthetic route, low cost and easy scale-up.

Recently, we demonstrated a promising strategy, *i.e.*, assembling low-cost molecular oxidizer and fuel components into molecular perovskites, to yield a family of high-energetic materials featuring detonation performances comparable to RDX/HMX but with higher stability and lower cost. Such ABX_3 -type perovskites, as a unique type of materials standing at the forefront of materials science,³⁸⁻⁴⁶ have a unique ternary crystal structure that gives an alternate and dense packing of A-site fuel cations with triple X-site oxidative anions at molecular level, and hence achieve an ultimate uniformity in a single explosive to facilitate a fast and effective denotation reaction. Moreover, the facile one-pot solution reaction under ambient condition endows the molecular perovskites to be low cost and easily scaled up. Recently, we have studied the effect

of B-site cations on detonation performance, by four members with different B-site cations, $(H_2dabco)[M(ClO_4)_3]$ ($H_2dabco^{2+} = 1,4-diazabicyclo[2.2.2]octane-1,4-dium$, $M = Na^+, K^+, Rb^+$, and NH_4^+ for DAP-1, -2, -3, and -4, respectively),⁴⁷⁻⁵⁰ and roughly the influence of A-site organic fuel cations on oxygen balance by another two compounds $(H_2pz)[Na(ClO_4)_3]$ (PAP-1, $H_2pz^{2+} = piperazine-1,4-dium$) and $(H_2dabco-O)[K(ClO_4)_3]$ (DAP-O2, $H_2dabco-O^{2+} = 1-hydroxy-1,4-diazabicyclo[2.2.2]octane-1,4-dium$).⁵¹ Among them, DAP-4 is unique as the only metal-free energetic compound, and has attracted great attentions.⁵²⁻⁵³

Metal-free energetic materials generally have the advantages of high gas yield and metal-free residue after combustion or explosion, and hence widely applied in many fields, particularly in explosives and propellant components.⁵⁵⁴⁻⁵⁵ To design more advanced metal-free energetic materials for practical use and to understand the relationship between the structural detail and property, as a continuing work, herein we focus on assembling metal-free molecular perovskite energetic compounds, by using ClO_4^- as X-bridges, NH_4^+ as B-site cation, and different organic A-site cations (Figure 1). We obtained five new metal-free molecular perovskites, $(H_2A)[NH_4(ClO_4)_3]$, where $H_2A = H_2pz^{2+}$ for PAP-4, 1-methyl-piperazine-1,4-dium (H_2mpz^{2+}) for PAP-M4, homopiperazine-1,4-dium (H_2hpz^{2+}) for PAP-H4, $H_2dabco-O^{2+}$ for DAP-O4 and 1-methyl-1,4-diazabicyclo[2.2.2]octane-1,4-dium ($H_2mdabco^{2+}$) for DAP-M4, respectively. As shown in Figure 1, employment of the five organic cations to replace H_2dabco^{2+} in DAP-4 could be regarded as modifying DAP-4 in three strategies: (1) “adding O atom” into H_2dabco^{2+}

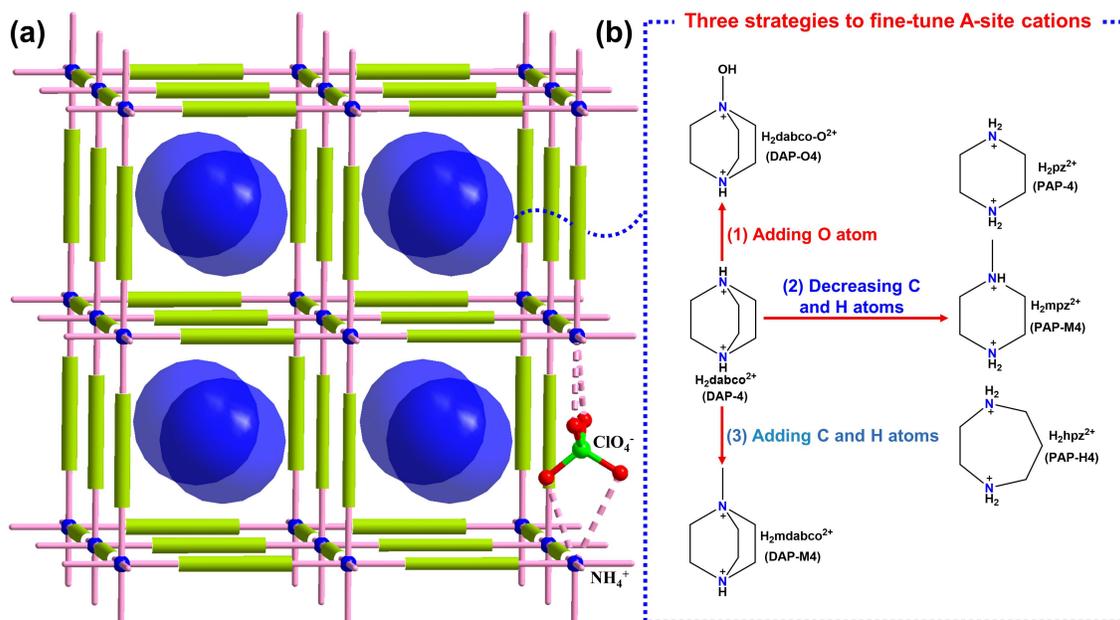


Figure 1. (a) The structures of metal-free perovskite compounds. For clarity, only one X-site ClO_4^- anion are shown, while A-site cations and X-site anions are presented as light-blue spheres and yellow-green cylinders, respectively. (b) Three strategies for fine-tuning A-site organic fuel cations.

by using $\text{H}_2\text{dabco-O}^{2+}$ to give DAP-O4; (2) “decreasing C and H atoms” from $\text{H}_2\text{dabco}^{2+}$ by using H_2pz^{2+} , $\text{H}_2\text{mpz}^{2+}$ and $\text{H}_2\text{hpz}^{2+}$ to generate PAP-4, PAP-M4 and PAP-H4, respectively; and (3) “adding C and H atoms” into $\text{H}_2\text{dabco}^{2+}$ by using $\text{H}_2\text{mdabco}^{2+}$ to give DAP-M4. Namely, together with DAP-4, these six metal-free members provide nice instances for systematically investigating the tunability of molecular perovskite high-energetic materials, *i.e.*, fine-tuning oxygen balance, crystal density, thermal stability, and detonation performance, etc. by adjusting the A-site organic cations solely.

RESULTS AND DISCUSSION

Single-crystal Structures. The colorless block single crystals of DAP-O4, PAP-4, PAP-M4, PAP-H4 and DAP-M4 for X-ray diffraction were obtained by slow evaporation of the solution after several days. The single-crystal X-ray diffraction indicates that they all have ABX_3 type perovskite structures, by regarding $\text{H}_2\text{dabco-O}^{2+}$, H_2pz^{2+} , $\text{H}_2\text{mpz}^{2+}$, $\text{H}_2\text{hpz}^{2+}$ and $\text{H}_2\text{mdabco}^{2+}$ as A-site fuel cations, NH_4^+ as B-site cation and ClO_4^- as X-bridges. All ClO_4^- anions are tetrahedral, with the O–Cl–O angles range between 109° and 111° . Each NH_4^+ ion interacts with twelve oxygen atoms from six adjacent ClO_4^- anions, while each ClO_4^- anion connects two adjacent NH_4^+ ions, *via* N–H \cdots O hydrogen bonds, resulting in a three-dimensional anionic framework hosting the fuel cations (Figures 1 and 2). It is worth to note that, the average N \cdots O atomic distances for N–H \cdots O hydrogen bonds in PAP-4 and DAP-4 are 3.030 and 3.020 Å, respectively, both are shorter than those in PAP-M4 (3.150 Å) and DAP-M4 (3.135 Å), respectively, implying the larger methylated A-site cations, *i.e.*, $\text{H}_2\text{mpz}^{2+}$ and $\text{H}_2\text{mdabco}^{2+}$, could significantly enlarge the anionic framework (*vide infra*).

PAP-4 and DAP-O4 are isomorphous and crystallizes in the cubic space group $Fm\bar{3}c$ at 298 K (Table 1 and Figure 2a). As H_2pz^{2+} in PAP-4 is significantly smaller than $\text{H}_2\text{dabco-O}^{2+}$ in DAP-O4, the average N \cdots Cl atomic distance (N and Cl atoms from NH_4^+ and ClO_4^- , respectively) in PAP-4 (3.641 Å, see

Table S5) is slightly shorter than that in DAP-O4 (3.691 Å), indicating a contracted anionic framework in PAP-4. Compared with H_2pz^{2+} in PAP-4, $\text{H}_2\text{mpz}^{2+}$ cation has lower symmetry and is larger, so that the anionic framework in PAP-M4 becomes distorted, and the PAP-M4 crystallizes in an orthorhombic space group rather than in a cubic one at 298 K (Figure 2c). The distorted framework can fit the non-spherical $\text{H}_2\text{mpz}^{2+}$ cations in a more compact way, making the density of PAP-M4 (1.755 g cm $^{-3}$) slightly higher than that of PAP-4 (1.740 g cm $^{-3}$).

Similarly, the lower symmetry of A-site cations makes PAP-H4 crystallizing in monoclinic space groups $P2_1/n$ and DAP-M4 crystallizing in monoclinic space groups $P2_1$ at 223 K. The noncentrosymmetric structure of DAP-M4 was further confirmed by second-harmonic generation (SHG) test at room temperature, which give a SHG signal being 0.18 times of KDP (see Figure S6). Compared with DAP-4 encapsulating $\text{H}_2\text{dabco}^{2+}$ cations, PAP-H4 and DAP-M4 have a slightly-larger anionic framework propped up by the cations, whose longest non-hydrogen atomic distances (3.286 and 4.006 Å for $\text{H}_2\text{hpz}^{2+}$ and $\text{H}_2\text{mpz}^{2+}$, respectively) is longer than that of $\text{H}_2\text{dabco}^{2+}$ (2.991 Å), as indicated by the increase of average N \cdots Cl atomic distances in PAP-H4 (3.636 Å) and DAP-M4 (3.737 Å) than that in DAP-4 (3.611 Å) at 223 K.

Thermal stability. The thermal stabilities of these metal-free molecular perovskites were investigated by differential thermal analysis (DTA) with a heating rate of 5 °C min $^{-1}$. As shown in Table 2, the onset decomposition temperatures (T_d) of six metal-free molecular perovskites are between 288 and 364 °C, which are higher than those of HMX (279 °C) and RDX (210 °C), owing to the stable intra-ionic covalent bonds and the inter-ionic attractive Coulomb interactions. The thermal stabilities of PAP-M4 (323 °C) and DAP-M4 (364 °C) are higher than those of PAP-4 (288 °C) and DAP-4 (359 °C), respectively, which could be ascribed to the methylation on the organic cations.

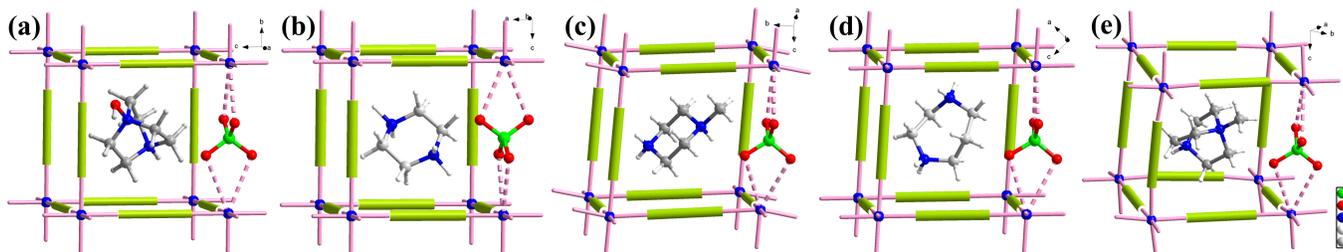


Figure 2. The structures of DAP-O4 (a), PAP-4 (b), PAP-M4 (c), PAP-H4 (d) and DAP-M4 (e). For clarity, only one X-site perchlorate anion was shown, and the remaining X-site anions are presented as yellow-green cylinders.

Table 1. Crystallographic data and structural refinements for six metal-free molecular perovskite high-energetic materials

Compound	DAP-O4	PAP-4	PAP-M4	PAP-H4	DAP-M4	DAP-4 ^[c]
Formula	C ₆ H ₁₈ Cl ₃ N ₃ O ₁₃	C ₄ H ₁₆ Cl ₃ N ₃ O ₁₂	C ₅ H ₁₈ Cl ₃ N ₃ O ₁₂	C ₅ H ₁₈ Cl ₃ N ₃ O ₁₂	C ₇ H ₂₀ Cl ₃ N ₃ O ₁₂	C ₆ H ₁₈ Cl ₃ N ₃ O ₁₂
Formula weight	446.56	404.56	418.57	418.57	444.61	430.56
<i>T</i> /K	298(2)	298(2)	298(2)	223(2)	223(2)	223(2)
Crystal system	Cubic	Cubic	Orthorhombic	Monoclinic	Monoclinic	Cubic
Space group	<i>Fm</i> $\bar{3}$ <i>c</i>	<i>Fm</i> $\bar{3}$ <i>c</i>	<i>Pnma</i>	<i>P2</i> ₁ / <i>n</i>	<i>P2</i> ₁	<i>Pa</i> $\bar{3}$
<i>a</i> /Å	14.7627(1)	14.5631(3)	10.2673(2)	19.7404(5)	10.1520(2)	14.4264(1)
<i>b</i> /Å	14.7627(1)	14.5631(3)	14.7004(2)	14.3294(5)	10.9824(2)	14.4264(1)
<i>c</i> /Å	14.7627(1)	14.5631(3)	20.9914(3)	21.2948(8)	14.7774(2)	14.4264(1)
β /°	90	90	90	90.075(3)	89.856(1)	90
<i>V</i> /Å ³	3217.34(7)	3088.6(2)	3168.32(8)	6023.6(4)	1647.58(5)	3002.44(6)
<i>D_c</i> /g cm ⁻³	1.852	1.740	1.755	1.846	1.792	1.905
<i>R</i> _{int}	0.0373	0.0889	0.0381	0.0487	0.0324	0.0353
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.0317	0.0711	0.0533	0.0776	0.0354	0.0275
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^[b]	0.0959	0.2567	0.1501	0.1574	0.0839	0.0793
<i>R</i> ₁ (all data)	0.0325	0.0733	0.0562	0.1399	0.0404	0.0330
<i>wR</i> ₂ (all data)	0.0970	0.2646	0.1521	0.1936	0.0880	0.0818

^[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^[b] $wR_2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2 \}^{1/2}$; ^[c] From reference 47.

Such methylation effect beneficial to thermal stability was similarly observed in high-energetic materials with nitrogen-containing heterocycles, such as triazole and tetrazole.⁵⁶⁻⁵⁸

The detonation parameters. As the heats of formations of halogen-containing compounds measured by oxygen bomb calorimetry were generally overestimated as well as the accompanied calculated explosive performances.⁵¹ Herein, we used density function theory (DFT) and extended K-J equation (see ESI) to calculate the detonation parameters for these six metal-free molecular perovskites. Based on the calculation results listed in Table 2, the effects on detonation performance by tuning oxygen balance, shape and size of A-site cations in these six metal-free molecular perovskites were discussed.

(1) By a hydroxyl modification on A-site components, the oxygen balance of the entire compounds would be further improved, but the density would probably decrease as the shape deviation from sphere, hence, the detonation performance may not change significantly. For example, DAP-O4 has one more hydroxyl group than DAP-4, and thus has better oxygen balance (−27.9% for DAP-4 vs. −23.3% for DAP-O4), but has a slightly-reduced density (1.87 vs. 1.85 g cm⁻³), and hence only giving rise to slightly-improved detonation heat (5.87 vs. 6.21 kJ g⁻¹), detonation velocity (8.806 vs. 8.900 km s⁻¹) and detonation pressure (35.2 vs. 35.7 GPa).

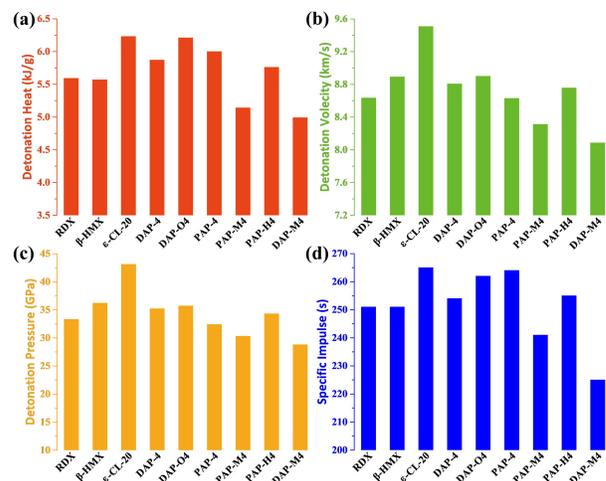


Figure 3. Bar chart representation of detonation heat (a), detonation velocity (b), detonation pressure (c), and specific impulse (d) for six metal-free molecular perovskite high-energetic materials, and the classical organic explosives RDX, β-HMX and ε-CL-20.

Table 2. Detonation properties of some classical explosives and six metal-free molecular perovskite high-energetic materials

Compound	ρ (g cm ⁻³)	T_d (°C)	Q ^{e)} (kJ g ⁻¹)	D ^{e)} (km s ⁻¹)	P ^{e)} (GPa)	H_f ^{f)} (kJ mol ⁻¹)	I_{sp} ^{g)} (s)	OB ^{h)} (%)
RDX	1.82 ^{a)}	210.0 ^{e)}	5.59	8.634	33.3	-92.70	251	-21.6
β -HMX	1.90 ^{a)}	279.0 ^{e)}	5.57	8.892	36.2	-126.57	251	-21.6
ϵ -CL-20	2.04 ^{a)}	215.0 ^{e)}	6.23	9.507	43.1	200.17	265	-11.0
DAP-4	1.87 ^{b)}	358.4 ^{d)}	5.87	8.806	35.2	-483.96	254	-27.9
DAP-O4	1.85 ^{b)}	351.6 ^{d)}	6.21	8.900	35.7	-436.08	262	-23.3
PAP-4	1.74 ^{b)}	288.0 ^{d)}	6.00	8.629	32.4	-537.68	264	-9.9
PAP-M4	1.77 ^{b)}	323.0 ^{d)}	5.14	8.311	30.3	-859.90	241	-21.0
PAP-H4	1.83 ^{b)}	348.3 ^{d)}	5.76	8.756	34.3	-600.38	255	-21.0
DAP-M4	1.78 ^{b)}	363.7 ^{d)}	4.99	8.085	28.8	-839.05	225	-37.8

^{a)} The crystal densities reported in Ref.3 ; ^{b)} The crystal densities calculated from capillary powder X-ray diffraction at room temperature, except that of PAP-4 calculated from single-crystal X-ray diffraction at 298 K; ^{c)} The onset decomposition temperatures (T_D) obtained from Ref. 17; ^{d)} The onset decomposition temperatures (T_d) evaluated from DTA (5 °C min⁻¹); ^{e)} Q is the heat of detonation, D is the detonation velocity, and P is the detonation pressure. The detonation parameters calculated by DFT calculation and K-J equation; ^{f)} The heat of formation back-calculated from assumed detonation reactions (see ESI for detail); ^{g)} Specific impulses calculated by EXPLO5 v6.04.02 code; ^{h)} Oxygen balance based on CO₂ for C_aH_bN_cCl_dO_e: OB[%] = 1600[e-2a-(b-d)/2]/M_w, where M_w is molecular weight.

(2) When the organic fuel cations are methylated, although the thermal stability is enhanced, both the oxygen balance and the stacking density of the compound decreases owing to the increase of carbon and hydrogen content as well as a shape deviation from sphere in the A-site components. As a result, the comprehensive performance become worse. For example, PAP-M4 and DAP-M4 have one more methyl group than PAP-4 and DAP-4, respectively. As showed in Figure 3, the methylated organic cation H₂mpz²⁺ makes PAP-M4 has a reduced performance than PAP-4 on detonation heat (6.00→5.14 kJ g⁻¹), detonation velocity (8.629→8.311 km s⁻¹) and detonation pressure (32.4 → 30.3 GPa). Similarly, from DAP-4 to DAP-M4, the detonation heat is significantly reduced from 5.87 to 4.99 kJ g⁻¹, so are the detonation velocity (8.806 → 8.085 km s⁻¹) and detonation pressure (35.2 → 28.8 GPa).

3) It is well known that the oxygen balance of energetic compounds has a great influence on the detonation heat. Compared with H₂dabco²⁺, H₂zp²⁺ is too small in the anionic framework constructed by NH₄⁺ and ClO₄⁻, which seems too loose in a cubic structure. Although the density of PAP-4 (1.74 g cm⁻³) is lower than that of DAP-4 (1.87 g cm⁻³), the oxygen balance of PAP-4 (-9.9%) is much superior to DAP-4 (-27.9%), and the detonation heat of PAP-4 (6.00 kJ g⁻¹) is higher than that of DAP-4 (5.87 kJ g⁻¹). However, PAP-4 have a slightly-decreased detonation velocity (8.629 km s⁻¹) and detonation pressure (32.4 GPa) than DAP-4 (8.806 km s⁻¹ and 35.2 GPa, respectively), which is the result of the combined effects of density and detonation heat.

Nevertheless, it's worth noting that, although PAP-M4 and PAP-H4 are isomers with the same oxygen balance, and their organic cations have similar enthalpies of formation (1555.9 and 1558.6 kJ mol⁻¹ for H₂mpz²⁺ and H₂hpz²⁺, respectively, see Table S4), their detonation heats differ greatly (5.14 and 5.76 kJ g⁻¹ for PAP-M4 and PAP-H4, respectively, see Table 2), probably owing to their difference on lattice energy. In addition, PAP-M4 has a lower crystal density (1.77 g cm⁻³)

than that of PAP-H4 (1.83 g cm⁻³), as the shape of H₂mpz²⁺ is more deviated from the sphere than H₂hpz²⁺. As a result, PAP-H4 has a better detonation velocity (8.756 km s⁻¹) and detonation pressure (34.3 GPa) than PAP-M4 (8.311 km s⁻¹ and 30.3 GPa). These facts well suggest that a cation with a more spherical shape, *i.e.*, H₂hpz²⁺ in the presented cases, is better for increasing crystal packing efficiency, lattice energy and hence the detonation performance for molecular perovskite energetic materials.

Specific impulse. The specific impulse (I_{sp}), a key parameter of the performance of solid propellants or binders, was also calculated for these six compounds, by using EXPLO5 v6.04.02 code based on the heat of formation back-calculated from the assumed detonation reactions (see ESI for detailed calculation methods). As listed in Table 2 and Figure 3, the calculated specific impulse values of PAP-4 (264 s), PAP-H4 (255 s) and DAP-O4 (262 s) are higher than those of DAP-4 (254 s), RDX (251 s) and β -HMX (251 s), enabling these three metal-free molecular perovskites to be promising candidates as solid propellant components. In particular, in spite of its undistinguished detonation velocity and pressure, PAP-4 has the highest specific impulse, and comparable to ϵ -CL-20 (265 s). Such fact well demonstrates an advantage of molecular perovskite high-energetic materials that they may be designed and finely tuned for different application purposes.

CONCLUSIONS

In summary, based on the metal-free molecular perovskite high-energetic material DAP-4, five new metal-free members were elaborately designed and prepared utilizing the intermolecular self-assembly in solution under ambient conditions, by changing A-site cations solely based modifying H₂dabco²⁺ via three strategies, *i.e.*, “adding O atom”, “decreasing C and H atoms”, and “adding C and H atoms”. Then the structure-property relationship in the six metal-free energetic materials was systematically investigated, especially the influence of the oxygen balances, the shape and size of A-site cations on the

crystal density and the consequent effects on the detonation velocity and pressure. We demonstrated that improving the oxygen balance meanwhile keeping the spherical shape of organic cations to well match the anionic cages in these metal-free molecular perovskites tends to obtain a better comprehensive detonation performance, providing an important clue for the design of more advanced practical high-energy materials. It is worth noting that, among these metal-free molecular perovskites assembled by fine-tuned A-site organic fuel cations, DAP-O4 has the highest detonation heat (6.21 kJ mol⁻¹), detonation velocity (8.900 km s⁻¹), and detonation pressure (35.7 GPa), whereas PAP-4 has the highest specific impulse (264 s), which is comparable to CL-20 (265 s). The outstanding performances, together with the high optimizability for different application purposes, make this type of metal-free molecular perovskites to be a new sort of energetic material candidates for practical usages such as explosives and propellants, and the advanced energetic materials with enhanced performances based on metal-free molecular perovskites are well worth further exploration.

EXPERIMENTAL SECTION

Cautions. Although it was safe in the course of this research, these energetic materials need to be handled with extremely care.

Materials and methods. All chemicals were obtained from commercial sources and used without further purification. Decomposition temperatures were measured *via* differential thermal analysis (DTA) with an OZM Research DTA 552-Ex instrument at a heating rate of 5 °C min⁻¹ and in a temperature range from room temperature to 450 °C. The PXRD patterns (Cu-K α) for identifying the phase purities were collected on Bruker Advance D8 diffractometer by Bragg-Brentano geometry. The second-harmonic generation test for DAP-M4 was performed with a KDP reference at room temperature. Detonation parameters were calculated by DFT calculation and extended Kamlet-Jacob's equation. Impact sensitivity was tested on a BFH 10 BAM impact apparatus. Friction sensitivity was tested on a FSKM 10 BAM friction apparatus.

X-ray Crystallography. For PAP-4, PAP-M4 and DAP-O4, the diffraction intensities were collected on a Rigaku XtaLAB P300DS diffractometer with graphite-monochromated Cu-K α radiation ($\lambda = 1.54184$ Å). For PAP-H4 and DAP-M4, the single-crystal X-ray diffraction experiments were performed on a SuperNova AtlasS2 diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by SHELXS structure solution program using direct methods and refined with SHELXL refinement package using a full-matrix least-squares technique. Anisotropic atom displacement parameters were applied to all non-hydrogen atoms. All the hydrogen atoms were generated geometrically, taking account the possible hydrogen bonds. Crystallographic data are summarized in Table 1. The CIFs were deposited in Cambridge Crystallographic Data Center, CCDC numbers: 1956808, 1956805, 1956806, 1956807 and 1956809 for DAP-O4, PAP-4, PAP-M4, PAP-H4 and DAP-M4, respectively.

Synthesis of (H₂dabco-O)[NH₄(ClO₄)₃] (DAP-O4). Dabco-O (N-oxide-triethylenediamine) was synthesized according to the literature.⁵⁹ Ammonium perchlorate (2 mmol) and 70% perchloric acid solution (0.7 mL) were added to H₂O (5 mL), then an aqueous solution (2 mL) of dabco-O (2 mmol) was added into the above mixed solution slowly. White solid was then collected by filtration and washed three times with ethanol, and the yield was 85% based on NH₄ClO₄.

Synthesis of (H₂pz)[NH₄(ClO₄)₃] (PAP-4). Ammonium perchlorate (2 mmol) and 70% perchloric acid solution (1.5 mL) were added to H₂O (5 mL) with stirring and heating at 80 °C, then an aqueous solution of piperazine (2 mmol, 2 mL) was slowly added into the above solution. After 1.5 hours, the solution was cooled slowly to

room temperature and the white solid was obtained by filtration, in a yield of 80 % based on NH₄ClO₄.

Synthesis of (H₂mpz)[NH₄(ClO₄)₃] (PAP-M4). Ammonium perchlorate (2 mmol) and 70% perchloric acid solution (0.7 mL) were added to H₂O (5 mL), then aqueous solution (2 mL) of 1-methyl-piperazine (2 mmol) was added into the above solution slowly. The white solid was collected by filtration and washed three times with ethanol. The yield was 80% based on NH₄ClO₄.

Synthesis of (H₂hpz)[NH₄(ClO₄)₃] (PAP-H4). Same to the synthesis of PAP-M4, except using aqueous solution (2 mL) of homopiperazine (2 mmol) instead of 1-methyl-piperazine (2 mmol). The white solid was obtained in a yield of 80% based on NH₄ClO₄.

Synthesis of (H₂dabco)[NH₄(ClO₄)₃] (DAP-M4). 1-methyl-1,4-diazabicyclo[2.2.2]octane-1,4-diium Iodide was synthesized according to literature.⁶⁰ Ammonium perchlorate (2 mmol) and 70% perchloric acid solution (0.7 mL) were added to H₂O (5 mL), then aqueous solution (2 mL) of 1-methyl-1,4-diazabicyclo[2.2.2]octane-1,4-diium Iodide (2 mmol) was added into the above solution slowly. The white solid was obtained by filtration and washed three times with ethanol (70% yield based on NH₄ClO₄).

SUPPORTING INFORMATION

The Supporting Information is available free of charge on the ACS Publications website. Powder X-ray diffraction (PXRD) and density measurements, the estimation on detonation performance, impact and friction sensitivities, and supporting tables and figures (Table S1-S5 and Figures S1-S6).

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Notes

The authors declare no competing financial interest.

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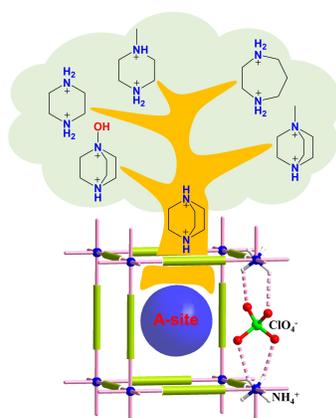
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Metal-free Molecular Perovskite High-energetic Materials

Yu Shang, Rui-Kang Huang, Shao-Li Chen,* Chun-Ting He, Zhi-Hong Yu, Zi-Ming Ye, Wei-Xiong Zhang* and Xiao-Ming Chen



The oxygen balance, density, thermal stability and detonation performance were fine-tuned by changing A-site organic fuel cations solely in six metal-free molecular perovskite high-energetic materials.