Supplementary Information

Controllable synthesis of perovskite solid solutions as novel energetic materials via thermodynamic equilibrium

Min Li,[a] Dandan Han,*[a] Zheng Lin,[b] Xiujuan Qi,[c] Honglei Xia,*[b] Zhao Wang,[a] Qinghua Zhang,*[b] and Junbo Gong[a]

[a] M. Li, D. Han, Z. Wang, J. Gong
State Key Laboratory of Chemical Engineering
School of Chemical Engineering and Technology
Tianjin University, Tianjin 300072, People's Republic of China
E-mail: handandan@tju.edu.cn; xia_honglei@nwpu.edu.cn; qinghuazhang@nwpu.edu.cn

[b] Z. Lin, H. Xia, Q. Zhang
National Key Laboratory of Solid Propulsion
School of Astronautics
Northwestern Polytechnical University, Xi'an 710072, People's Republic of China

[c] X. Qi
School of Chemistry and Chemical Engineering
Northwestern Polytechnical University, Xi'an 710129, People's Republic of China

Table of contents

Table S1. Crystallographic data and structural refinements of $(H_2dabco)(NH_4)_{0.715}Na_{0.285}(ClO_4)_3$.

Complex	$(H_2dabco)(NH_4)_{0.715}Na_{0.285}(ClO_4)_3$
Formula	$C_6H_{16.86}O_{12}Cl_3N_{2.715}Na_{0.285}$
Formula weight	431.854
Temperature (K)	100
Crystal system	cubic
Space group	$Pa\bar{3}$
a (Å)	14.3319(3)
Volume ($Å^3$)	2943.82(19)
Density (g/cm^3)	1.946
R_{int}	0.0243
R_1 [$I>2\sigma(I)$]	0.0368
wR_2 [$I>2\sigma(I)$]	0.0975
R_1 (all data)	0.0376
wR_2 (all data)	0.0980
CCDC number	2465024

Table S2. The information for $(H_2dabco)(NH_4)_{(1-x)}Na_x(ClO_4)_3$ solid solutions.

Feeding molar ratio of DAP-4 and NaCl	Concentration of NaCl (mol/L)	Weight content of Na[a]	x	Effective tolerance factor t_{eff}	Cell parameter[b] [Å]
1 : 0.1	0.01	0.20%	0.037	0.966	14.481
1 : 0.3	0.04	0.52%	0.098	0.970	14.439
1 : 0.5	0.07	0.81%	0.153	0.973	14.384
1 : 1	0.14	1.43%	0.268	0.980	14.340
1 : 5	0.70	2.16%	0.407	0.989	14.285
1 : 10	1.39	2.36%	0.444	0.992	14.285
1 : 20	2.79	2.75%	0.517	0.997	14.284
1 : 40	5.58	2.89%	0.544	0.998	14.284
1 : 45.5[c]	6.34	3.09%	0.583	1.001	14.282

[a)] The weight content of Na was measured by ICP-MS. [b)] The cell parameter was calculated based on the PXRD data. [c)] The concentration of NaCl reached saturation at room temperature.

Table S3. The information for the DAP-4 and DAP-1 prepared in this work.

Sample	Formula	Weight content of Na	Tolerance factor *t*	Cell parameter[a] [Å]
DAP-4	$(H_2dabco)(NH_4)(ClO_4)_3$	0	0.964	14.479
DAP-1	$(H_2dabco)Na(ClO_4)_3$	5.28%	1.029	14.118

[a] The cell parameter was calculated based on the experimental PXRD data.

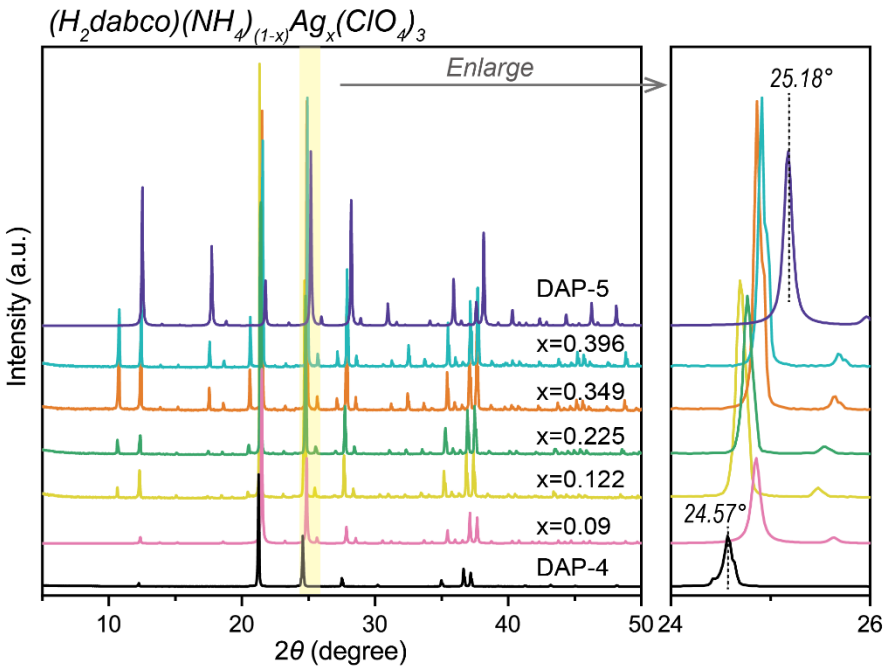

Figure S1. PXRD patterns of $(H_2dabco)(NH_4)_{(1-x)}Ag_x(ClO_4)_3$, DAP-4 and DAP-5.

Table S4. The information for $(H_2dabco)(NH_4)_{(1-x)}Ag_x(ClO_4)_3$ solid solutions.

Feeding molar ratio of DAP-4 and $AgClO_4$	Concentration of $AgClO_4$ (mol/L)	Weight content of Ag[a]	x	Effective tolerance factor t_{eff}	Cell parameter[b] [Å]
1 : 1	0.139	3.24%	0.122	0.974	14.406
-	0.249	5.85%	0.225	0.983	14.366
1 : 5	0.697	8.83%	0.349	0.994	14.309
1 : 10	1.394	9.94%	0.396	0.999	14.283

Table S5. Crystallographic data and structural refinements of $(H_2dabco)(NH_4)_{0.91}Ag_{0.09}(ClO_4)_3$.

Complex	$(H_2dabco)(NH_4)_{0.91}Ag_{0.09}(ClO_4)_3$
Formula	$C_6H_{17.64}O_{12}Cl_3N_{2.91}Ag_{0.09}$
Formula weight	438.66
Temperature (K)	100
Crystal system	cubic
Space group	$Pa\bar{3}$
a (Å)	14.3168(3)
Volume (Å^3)	2934.53(18)
Density (g/cm^3)	1.986
R_{int}	0.0239
R_1 [I>2σ(I)]	0.0323
wR_2 [I>2σ(I)]	0.0826
R_1 (all data)	0.0470
wR_2 (all data)	0.0905
CCDC number	2465025

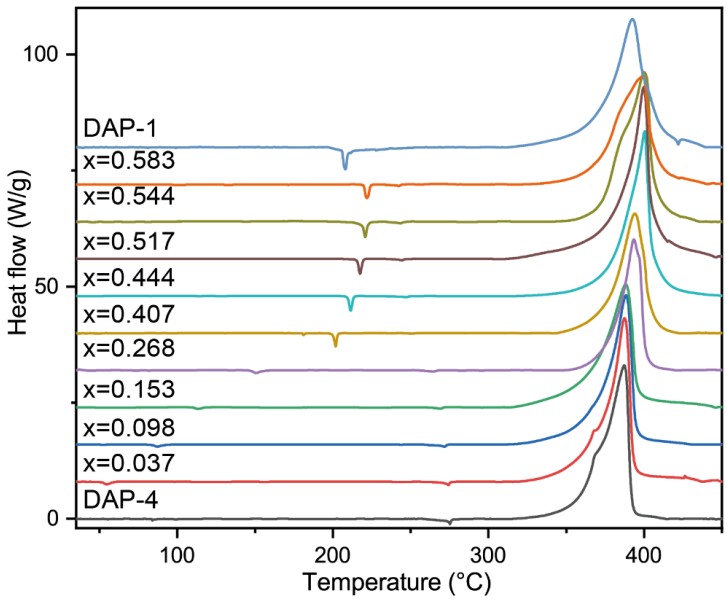

Figure S2. DSC curves of DAP-4, DAP-1, and $(H_2dabco)(NH_4)_{(1-x)}Na_x(ClO_4)_3$ solid solutions.

Thermal Analysis

Based on the experimental DSC data under differen heating rates of 5, 10, 15, and 20 K/min, the kinetics of thermal decomposition was calculated using Kissinger's method as follows (H. E. Kissinger, *Anal. Chem.* 1957, *29*, 1702-1706).

$$\ln\frac{\beta}{T_p^2} = \ln\frac{AR}{E} - \frac{E}{RT_p} \quad \text{(S1)}$$

where Tp is the peak temperature of thermal decomposition, β refers to the heating rate, E_k means the apparent activation energy, A_k is the pre-exponential factor, and R is the molar gas constant. The kinetic parameters were obtained by fitting the curve of $1/T_p$ and $\ln[\beta/T_p^2]$.

The values (T_{p0}) of the peak temperature (T_p) corresponding to $\beta \rightarrow 0$ were obtained by Eq. (S2).

$$T_p = T_{p0} + a\beta_i + b\beta_i^2 + c\beta_i^3, i = 1\sim4 \quad \text{(S2)}$$

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$) and free energy of activation ($\Delta G^{\neq}$) corresponding to $T = T_{p0}$, were obtained by Eq. (S3-5), respectively.[1-2]

$$A = \frac{k_B T}{h} e^{\frac{\Delta S^{\neq}}{R}} \quad \text{(S3)}$$

$$A\exp\left(-\frac{E}{RT}\right) = \frac{kT}{h}\exp\left(\frac{\Delta S^{\neq}}{R}\right)\exp\left(-\frac{\Delta H^{\neq}}{RT}\right) \quad \text{(S4)}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \quad \text{(S5)}$$

Where k_B is the Boltzmann constant and h is the Planck constant.

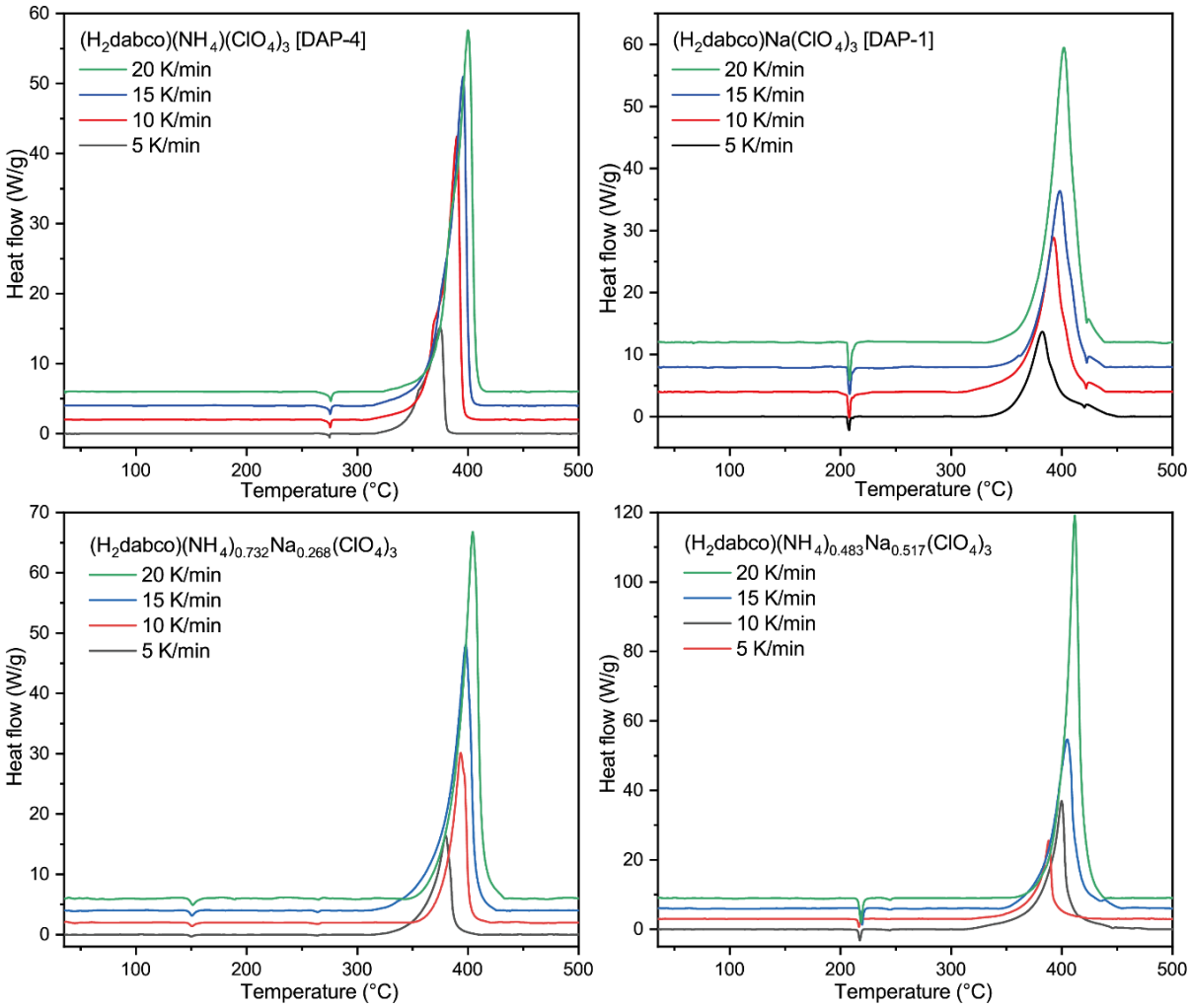

Figure S3. DSC curves of the four samples with varied heating rates.

Table S6. Thermal analysis for $(H_2dabco)(NH_4)(ClO_4)_3$ (DAP-4), $(H_2dabco)Na(ClO_4)_3$ (DAP-1), $(H_2dabco)(NH_4)_{0.732}Na_{0.268}(ClO_4)_3$ and $H_2dabco)(NH_4)_{0.483}Na_{0.517}(ClO_4)_3$.

Sample	Crystallinity[c]	T_{onset}[d] [°C]	T_p[d] [°C]	E [kJ/mol]	LgA	R^2	T_{p0} [°C]	$\Delta H^{\neq}$ [kJ/mol]	$\Delta S^{\neq}$[J/(s·mol)]	$\Delta G^{\neq}$ [kJ/mol]
DAP-4	93.8%	360.07	386.64	236.99	18.59	0.987	360.83	236.99	104.72	170.60
DAP-1	93.2%	373.28	391.70	265.93	20.76	0.999	364.91	265.93	146.23	172.63
x=0.268[a]	92.3%	366.12	393.14	203.03	15.69	0.984	341.40	203.03	49.43	172.36
x=0.517[b]	91.5%	377.98	399.95	219.40	16.82	0.986	358.40	219.40	70.81	174.68

[a] It represents the $(H_2dabco)(NH_4)_{0.732}Na_{0.268}(ClO_4)_3$. [b] It refers to $(H_2dabco)(NH_4)_{0.483}Na_{0.517}(ClO_4)_3$. [c] The crystallinity is calculated based on PXRD data. [d] T_{onset} and T_p are the onset temperature and peak temperature obtained at 10 K/min.

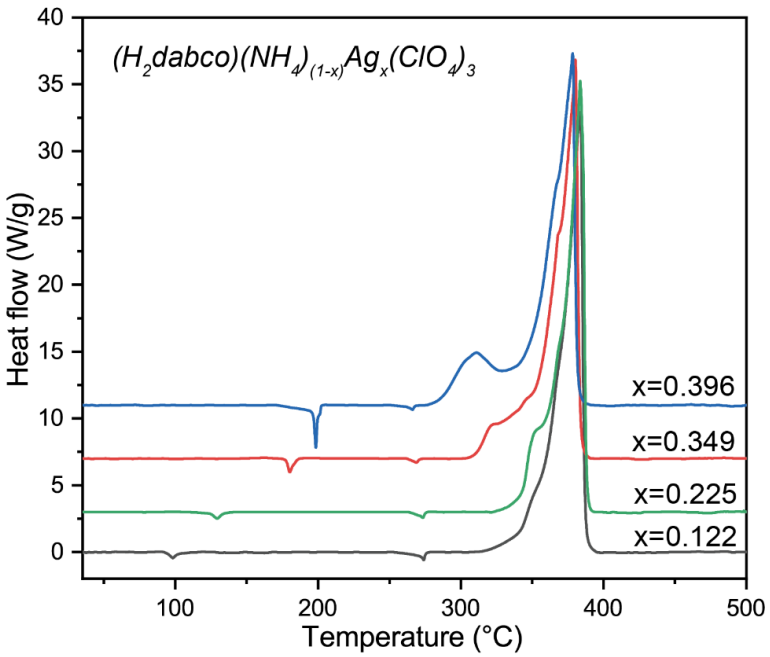

Figure S4. DSC curves of $(H_2dabco)(NH_4)_{(1-x)}Ag_x(ClO_4)_3$ solid solutions.

Table S7. The properties of the samples involved in this work.

Samples	T_{onset}[b] [°C]	T_p[b] [°C]	Density[c] [g/cm^3]	Friction sensitivity[d] [N]	Impact sensitivity[e] [J]
$(H_2dabco)(NH_4)(ClO_4)_3$ [DAP-4]	360.07	386.64	1.884	36	>40
$(H_2dabco)Na(ClO_4)_3$ [DAP-1]	373.28	391.70	2.055	48	>40
$(H_2dabco)(NH_4)_{0.963}Na_{0.037}(ClO_4)_3$	360.68	389.46	1.884	36	>40
$(H_2dabco)(NH_4)_{0.902}Na_{0.098}(ClO_4)_3$	366.02	388.58	1.902	42	>40
$(H_2dabco)(NH_4)_{0.847}Na_{0.153}(ClO_4)_3$	370.50	391.71	1.921	36	>40
$(H_2dabco)(NH_4)_{0.732}Na_{0.268}(ClO_4)_3$	371.72	393.14	1.945	40	>40
$(H_2dabco)(NH_4)_{0.593}Na_{0.407}(ClO_4)_3$	375.71	393.21	1.971	32	>40
$(H_2dabco)(NH_4)_{0.556}Na_{0.444}(ClO_4)_3$	377.08	400.85	1.972	48	>40
$(H_2dabco)(NH_4)_{0.483}Na_{0.517}(ClO_4)_3$	377.98	399.95	1.974	48	>40
$(H_2dabco)(NH_4)_{0.456}Na_{0.544}ClO_4)_3$	370.56	399.46	1.974	36	>40
$(H_2dabco)(NH_4)_{0.417}Na_{0.583}(ClO_4)_3$	368.77	398.76	1.976	48	>40
$(H_2dabco)(NH_4)_{0.878}Ag_{0.122}(ClO_4)_3$	347.20	383.82	1.961	14	>40
$(H_2dabco)(NH_4)_{0.775}Ag_{0.225}(ClO_4)_3$	342.60	383.65	2.019	20	>40
$(H_2dabco)(NH_4)_{0.651}Ag_{0.349}(ClO_4)_3$	309.45	380.27	2.094	12	>40
$(H_2dabco)(NH_4)_{0.604}Ag_{0.396}(ClO_4)_3$	285.99	378.39	2.125	14	>40
$(H_2dabco)Ag(ClO_4)_3$ [DAP-5][a]	313.2	313.6	2.42	≤5	3

[a)] The data of DAP-5 were from the reference (Y. Shang, S.-L. Chen, Z.-H. Yu, R.-K. Huang, C.-T. He, Z.-M. Ye, W.-X. Zhang, X.-M. Chen, *Inorg. Chem.* 2022, *61*, 4143-4149), while other data were from this work. [b)] T_{onset} and T_p are the onset temperature and peak temperature obtained at 10 K/min. [c)] The measurements of friction sensitivity were carried out using a BAM friction tester. [d)] The impact sensitivity was measured on a standard BAM Fallhammer, during which the sample is placed in the plunger assembly, consisting of two steel rollers, a hollow steel collar, and a centering ring for fixation (note that to avoid the influence of friction, the sample should not touch the wall of the hollow steel collar).

Detonation performance

The standard enthalpy of formation ($\Delta_f H_m^\theta$) of explosive samples was calculated based on the constant-volume combustion energy ($\Delta_c U$). The $\Delta_c U$ of the six samples involved in Table 1 (besides DAP-5, since it is highly sensitive to mechanical stimulus) was measured on an oxygen calorimeter (ZDHW-HN7000, HUANENG, China), using the average value of three measurements of each sample. The sample mass of each test was around 0.2 g.

$$\Delta_c H_m^\theta = \Delta_c U + \Delta nRT \tag{S6}$$

where $\Delta_c H_m^\theta$ represents the standard molar enthalpy of combustion, Δn = n (gaseous products) – n (gaseous reactants), R is 8.314 J·mol^{-1}K^{-1}, and T is 298.15 K.

$$\Delta_f H_m^\theta(\text{explosives}) = \sum n\Delta_f H_m^\theta(\text{product}) - n\Delta_f H_m^\theta(O_2, \text{reactant}) - \Delta_c H_m^\theta \tag{S7}$$

The modified K-J equation was applied to estimate detonation performance (detonation heat, detonation pressure, and detonation velocity). The equations are as follows.[3-4]

$$D = 1.01\left(NM^{\frac{1}{2}}Q^{\frac{1}{2}}\right)^{\frac{1}{2}}(1 + 1.30\rho_0) \tag{S8}$$

$$P = 1.55\rho_0^2 M^{\frac{1}{2}}Q^{\frac{1}{2}} \tag{S9}$$

$$Q = \frac{-[\Delta_f H(\text{detonation products}) - \Delta_f H(\text{explosive})}{\text{formula weight of explosives}} \tag{S10}$$

where D is detonation velocity (km/s), P is detonation pressure (GPa), Q is detonation heat (cal/g), ρ_0 represents the density of explosive (g cm^{-1}), N is the moles of detonation gases per gram of explosive (mol/g), and M is the average molecular weight of the gases (g/mol).

The possible detonation reactions are assumed as in Table S8. Given the enthalpies of formation of the products in Table S9, the calculated detonation parameters are listed in Table S10.

Table S8. The assumed combustion reactions of the six samples involved in Table 1.

Reactants		Products					
Compounds	O_2 (g)	CO_2 (g)	H_2O (l)	HCl (g)	N_2 (g)	NaCl (s)	AgCl (s)
$(C_6H_{14}N_2)(NH_4)(ClO_4)_3$ [DAP-4][a]	3.75[b]	6	7.5	3	1.5	0	0
$(C_6H_{14}N_2)Na(ClO_4)_3$ [DAP-1]	3	6	6	2	1	1	0
$(C_6H_{14}N_2)(NH_4)_{0.732}Na_{0.268}(ClO_4)_3$	3.549	6	7.098	2.732	1.366	0.268	0
$(C_6H_{14}N_2)(NH_4)_{0.483}Na_{0.517}(ClO_4)_3$	3.362	6	6.725	2.483	1.242	0.517	0
$(C_6H_{14}N_2)(NH_4)_{0.878}Ag_{0.122}(ClO_4)_3$	3.659	6	7.317	2.878	1.439	0	0.122
$(C_6H_{14}N_2)(NH_4)_{0.651}Ag_{0.349}(ClO_4)_3$	3.489	6	6.977	2.651	1.326	0	0.349

[a] $(C_6H_{14}N_2)^{2+}$ is $(H_2dabco)^{2+}$. [b] The dimensionless parameters are the stoichiometry ratios of reactions of one equivalent of explosive compound.

Table S9. Enthalpy of formation of the product (derived from NIST).

Compounds	CO_2 (g)	H_2O (l)	H_2O (g)	HCl (g)	N_2 (g)	NaCl (s)	AgCl (s)
$\Delta_f H_m^\theta$ (kJ/mol)	-393.51	-285.83	-241.83	-92.31	0	-411.12	-127.01

Table S10. The assumed detonation reactions determined by the K-J equation.

Reactants	Products						
	C (s)	CO_2 (g)	H_2O (g)	HCl (g)	N_2 (g)	NaCl (s)	AgCl (s)
$(C_6H_{14}N_2)(NH_4)(ClO_4)_3$ [DAP-4]	3.75	2.25	7.5	3	1.5	0	0
$(C_6H_{14}N_2)Na(ClO_4)_3$ [DAP-1]	3	3	6	2	1	1	0
$(C_6H_{14}N_2)(NH_4)_{0.732}Na_{0.268}(ClO_4)_3$	3.549	2.451	7.098	2.732	1.366	0.268	0
$(C_6H_{14}N_2)(NH_4)_{0.483}Na_{0.517}(ClO_4)_3$	3.362	2.638	6.725	2.483	1.242	0.517	0
$(C_6H_{14}N_2)(NH_4)_{0.878}Ag_{0.122}(ClO_4)_3$	3.659	2.341	7.318	2.878	1.439	0	0.122
$(C_6H_{14}N_2)(NH_4)_{0.651}Ag_{0.349}(ClO_4)_3$	3.489	2.511	6.978	2.651	1.326	0	0.349

Table S11. The calculated detonation parameters of the samples prepared in this work.

Compounds[a]	ρ[b] (g/cm^3)	$\Delta_c U$ (kJ/mol)	$\Delta_f H_m^\theta$ kJ/mol	N (mol/g)	M (g/mol)	Q (kJ/g)	P (GPa)	D (km/s)
$(C_6H_{14}N_2)(NH_4)(ClO_4)_3$ [DAP-4]	1.88	-4884.60	86.15	0.03310	27.0526	7.11	39.07	9.2836
$(C_6H_{14}N_2)Na(ClO_4)_3$ [DAP-1]	2.05	-4567.38	-119.28	0.02756	28.4167	7.14	39.77	9.1393
$(C_6H_{14}N_2)(NH_4)_{0.732}Na_{0.268}(ClO_4)_3$	1.95	-4909.52	141.04	0.03161	27.3741	7.38	40.74	9.3937
$(C_6H_{14}N_2)(NH_4)_{0.483}Na_{0.517}(ClO_4)_3$	1.97	-4589.35	-151.30	0.03023	27.6992	6.82	38.82	9.1314
$(C_6H_{14}N_2)(NH_4)_{0.878}Ag_{0.122}(ClO_4)_3$	2.02	-4721.83	-28.43	0.03166	27.1943	6.67	39.32	9.2067
$(C_6H_{14}N_2)(NH_4)_{0.651}Ag_{0.349}(ClO_4)_3$	2.14	-4720.41	59.97	0.02916	27.4749	6.55	41.12	9.2468

[a] All the samples were self-prepared. [b] The density was calculated based on the PXRD data.

Since the detonation parameters in Table S11 were calculated through the same method, their relative relations can be of reference significance for the initial assessment of explosive properties for energetic perovskite solid solutions.

For the case of $(C_6H_{14}N_2)(NH_4)_{(1-x)}Na_x(ClO_4)_3$ solid solutions, the comparisons of the involved four samples concerning detonation parameters (*Q*, *P*, and *D*) are listed below.

Q: $(C_6H_{14}N_2)(NH_4)_{0.732}Na_{0.268}(ClO_4)_3$ > DAP-4 > DAP-1 > $(C_6H_{14}N_2)(NH_4)_{0.483}Na_{0.517}(ClO_4)_3$

P: $(C_6H_{14}N_2)(NH_4)_{0.732}Na_{0.268}(ClO_4)_3$ > DAP-4 > DAP-1 > $(C_6H_{14}N_2)(NH_4)_{0.483}Na_{0.517}(ClO_4)_3$

D: $(C_6H_{14}N_2)(NH_4)_{0.732}Na_{0.268}(ClO_4)_3$ > DAP-4 > DAP-1 > $(C_6H_{14}N_2)(NH_4)_{0.483}Na_{0.517}(ClO_4)_3$

For the case of $(C_6H_{14}N_2)(NH_4)_{(1-x)}Ag_x(ClO_4)_3$ solid solutions, the comparisons of the involved samples concerning detonation parameters (*Q*, *P*, and *D*) are listed below.

Q: DAP-4 > $(C_6H_{14}N_2)(NH_4)_{0.878}Ag_{0.122}(ClO_4)_3$ > $(C_6H_{14}N_2)(NH_4)_{0.651}Ag_{0.349}(ClO_4)_3$

P: $(C_6H_{14}N_2)(NH_4)_{0.651}Ag_{0.349}(ClO_4)_3$ > $(C_6H_{14}N_2)(NH_4)_{0.878}Ag_{0.122}(ClO_4)_3$ > DAP-4

D: DAP-4 > $(C_6H_{14}N_2)(NH_4)_{0.878}Ag_{0.122}(ClO_4)_3$ > $(C_6H_{14}N_2)(NH_4)_{0.651}Ag_{0.349}(ClO_4)_3$

In addition, it should be noted that the calculated detonation parameters in Table S11 are not comparable to the previously reported values in Table S12 since different calculation methods were used. The previously reported detonation parameters were obtained through DFT calculations coupled with the K-J equation.[5-6]

Table S12. The previously reported detonation parameters of DAP-4, DAP-1, and DAP-5.

Compounds[a]	*Q*' (kJ/g)	*P*' (GPa)	*D*' (km/s)
DAP-4	5.87	35.2	8.806
DAP-1	6.39	36.5	8.781
DAP-5	4.76	37.9	8.534

[a] All the detonation data are derived from the reported literature.[5-6]

References

1. H. Ma, B. Yan, Z. Li, Y. Guan, J. Song, K. Xu, R. Hu, *J. Hazard. Mater.* 2009, *169*, 1068-1073.
2. An, S. Chen, X. Li, Y. Tan, X. Cao, P. Deng, *Can. J. Chem.* 2021, *100*, 328-337.
3. M. J. Kamlet and S. J. Jacobs, *J. Chem. Phys.*, 1968, **48,** 23-35.
4. Y. Wang, J. Zhang, H. Su, S. Li, S. Zhang and S. Pang, *J. Phys. Chem. A*, 2014, **118,** 4575-4581.
5. W.-X. Zhang, S.-L. Chen, Y. Shang, Z.-H. Yu and X.-M. Chen, *Energ. Mater. Front.*, 2020, **1,** 123-135.
6. Y. Shang, S.-L. Chen, Z.-H. Yu, R.-K. Huang, C.-T. He, Z.-M. Ye, W.-X. Zhang and X.-M. Chen, *Inorg. Chem.*, 2022, **61,** 4143-4149.