

Supplementary Information

**Optimizing the Oxygen Balance by Changing the A-site Cations in
Molecular Perovskite High-energetic Materials**

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Experimental details:

1. Powder X-Ray diffraction (PXRD) and Density Measurements

The PXRD patterns (Cu-K α) for identifying the phase purity were collected on Bruker Advance D8 θ - 2θ diffractometer by Bragg-Brentano geometry.

Capillary powder X-ray diffraction: The measurements were performed on the capillary samples on Bruker Advance D8 θ - 2θ diffractometer at 298 K. The powder samples were loaded in capillaries with diameter of 0.8 mm, and then the step-scanned PXRD data were recorded in the 2θ range of 5-80 $^\circ$ with 2θ step size of 0.02 $^\circ$. The Pawley refinements for the PXRD patterns were performed on unit-cell parameters, zero point, background terms with Pseudo-Voigt profile function and Berar-Baldinozzi asymmetry correction function, by using the Reflex module of Material Studio 5.0. The final Pawley refinements yielded the following parameters:

For PAP-1, $a = 10.1638(5)$ Å. $b = 9.7292(5)$ Å. $c = 13.3027(7)$ Å. $\beta = 92.0119(6)$ $^\circ$. $R_p = 1.30\%$ and $R_{wp} = 1.74\%$. The corresponding density is 2.07 g/cm 3 .

For DAP-O2, $a = 14.6345(10)$ Å. $R_p = 2.30\%$ and $R_{wp} = 3.40\%$. The corresponding density is 1.98 g/cm 3 .

2. The estimation on detonation performance for DAPs.

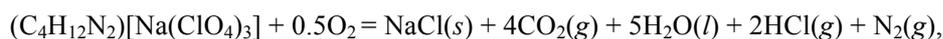
To estimate the detonation performances for DAPs, two different methods were employed: (1) using EXPLO5 based on enthalpy of formation measured by oxygen bomb calorimetry, and (2) using density functional theory (DFT) calculation and extended Kamlet-Jacob's equation. The results are listed in Table S4 and Table 2, respectively.

As the combustion product hydrochloric acid could corrode the container, producing extra heat release that overestimate the heat of formation for halogen-contained compounds, the method 1 would significantly overestimate the detonation performance for the halogen-contained DAPs (Table S4). To avoid overestimate the detonation performances for DAPs, the results obtained by method 2 were used instead in our discussion in the main text. Nevertheless, it should be pointed out that, the real detonation reactions are very complicated, therefore, these calculations could only roughly estimate the detonation performances as it is based on assumed detonation reaction and empirical K-J equation with low precision. It is necessary to accurately measure the detonation parameters by experiments for molecular perovskite materials in the next stage.

(1) Using EXPLO5 Based on enthalpy of formation measured by oxygen bomb calorimetry

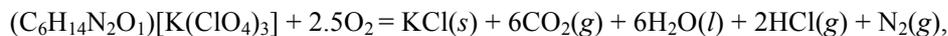
Oxygen bomb calorimetry was applied to approximate the enthalpy of formation of PAP-1 and DAP-O2. A big Oxygen bomb calorimeter (No. 24391170) with a volume of about 5.0 L and calorie limit of 203 kJ, which was made by Xi'an Modern Chemistry Research Institute (Xi'an, China), was used for the combustion of the samples. The calorimeter was calibrated by the combustion of certified benzoic acid (*ca.* 0.5 g per pellet, 12 pellets) in a dioxygen atmosphere at a pressure of 6 bar. The sample (*ca.* 4 g each) powders were loose with benzoic acid (*ca.* 3 g each) and placed in a combustion pot and burned in a 6 bar atmosphere of pure dioxygen. The enthalpies of combustion were calculated according to the formula $\Delta_c H = \Delta_c U + \Delta nRT$, ($\Delta n = n$ (gaseous products) - n (gaseous reactants)), $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and $T = 298.15 \text{ K}$) with the combustion reaction equations listed as follows:

For PAP-1:



$$\Delta_f H (\text{PAP-1}) = \Delta_f H (\text{NaCl}) + 4\Delta_f H (\text{CO}_2) + 5\Delta_f H (\text{H}_2\text{O}) + 2\Delta_f H (\text{HCl}) - \Delta_c H (\text{PAP-1})$$

For DAP-O2:



$$\Delta_f H (\text{DAP-O2}) = \Delta_f H (\text{KCl}) + 6\Delta_f H (\text{CO}_2) + 6\Delta_f H (\text{H}_2\text{O}) + 2\Delta_f H (\text{HCl}) - \Delta_c H (\text{DAP-O2})$$

(2) Using Density functional theory (DFT) calculation and extended Kamlet-Jacob's equation

DFT was employed to compute the energy of detonation (ΔE_{det}), performing with the code DMol3^[S1] under 3D periodic boundary conditions accompany with the Monkhorst-Pack multiple K-point sampling of the Brillouin zone^[S2] and the Perdew-Becke-Ezerhoff (PBE) exchange-correlation function^[S3]. The heat of detonation (ΔH_{det}) was estimated from ΔE_{det} by a linear correlation equation :

$$\Delta H_{\text{det}} = 1.127\Delta E_{\text{det}} + 0.046, r = 0.968. \quad \text{Eq. S1}$$

Detonation velocity and pressure were estimated by a method using extended Kamlet-Jacob's equation for metal-containing explosives^[S4]:

$$D = 1.01 \Phi^{1/2} (1+1.30\rho) \quad \text{Eq. S2}$$

$$P = 1.558 \Phi \rho^2 \quad \text{Eq. S3}$$

$$\Phi = 31.68 N(MQ)^{1/2} \quad \text{Eq. S4}$$

Here, ρ represents the density of explosive (g cm^{-3}). N , M are the characteristic parameters of the detonation products. N is the moles of detonation gases per gram of explosive and M is the average molecular weight of these gases. Q is the heat of detonation (ΔH_{det} , kcal g^{-1}), D is the detonation velocity (km s^{-1}) and P is the detonation pressure (GPa).

The detonation products of non-metal components can be described as dinitrogen, water, carbon dioxide, carbon and hydrogen chloride, while the metal atoms were assumed to form metal chlorides. Accordingly, the complete detonation reactions are as follows:

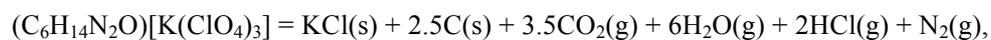
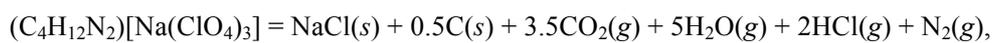


Table S1. Crystallographic data and structural refinements of PAP-1 and DAP-O2.

Complex	PAP-1	PAP-1	DAP-O2	DAP-O2
Formula	C ₄ H ₁₂ Cl ₃ N ₂ NaO ₁₂	C ₄ H ₁₂ Cl ₃ N ₂ NaO ₁₂	C ₆ H ₁₄ Cl ₃ KN ₂ O ₁₃	C ₆ H ₁₄ Cl ₃ KN ₂ O ₁₃
Formula weight	409.50	409.50	467.64	467.64
<i>T</i> /K	223(2)	293(2)	223(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Cubic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Fm</i> $\bar{3}$ <i>c</i>
<i>a</i> /Å	10.1521(2)	10.1689(4)	14.6921(5)	14.745(3)
<i>b</i> /Å	9.7195(2)	9.7312(4)	10.4526(4)	/
<i>c</i> /Å	13.1621(3)	13.2985(6)	10.0448(3)	/
β ^o	91.900(2)	91.993(4)	91.171(3)	/
<i>V</i> /Å ³	1298.03(5)	1315.17(9)	1542.26(9)	3206(2)
<i>Z</i>	4	4	4	8
<i>D</i> _c /g cm ⁻³	2.095	2.0679	2.014	1.938
reflns coll.	13462	11329	13406	650
unique reflns	8275	2722	6075	165
<i>R</i> _{int}	0.0296	0.1187	0.0563	0.0281
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^[a]	0.0505	0.0731	0.0759	0.0412
<i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^[b]	0.1171	0.2007	0.2048	0.1041
<i>R</i> ₁ (all data)	0.0808	0.0788	0.1002	0.0679
<i>wR</i> ₂ (all data)	0.1403	0.2103	0.2242	0.1251
GOF on <i>F</i> ²	1.043	1.029	1.052	1.052
Completeness	0.997	1.000	1.000	0.910
CCDC number	1860907	1872452	1872410	1860906

^[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^[b] $wR_2 = \{\sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2\}^{1/2}$. The structure of PAP-1 at room temperature^[S7] were previously reported without any concern on the energetic properties.

Table S2. Selected atomic distances (Å) in DAP-1, PAP-1, DAP-2 and DAP-O2 measured at 223 K.

	DAP-1 ^{b)}	PAP-1	DAP-2 ^{b)}	DAP-O2
M1–O1 ^{a)}	3.411(1)	2.630(2)	3.241(1)	2.982(3)
M1–O2	2.548(1)	2.811(2)	2.776(1)	3.082(3)
M1–O3	/	2.724(2)	/	3.228(3)
M1–O4	/	2.730(2)	/	2.847(3)
M1–O5	/	2.429(2)	/	3.117(3)
M1–O6	/	3.372(2)	/	2.825(3)
M1–O7	/	3.281(2)	/	/
M1–O8	/	2.827(2)	/	/
M1–O9	/	2.500(2)	/	/
M1–O10	/	3.316(2)	/	/
M1–O11	/	3.317(2)	/	/
M1–O12	/	2.741(2)	/	/
average M1–O	2.980	2.890	3.008	3.014
M2–O3	3.072(1)	/	2.999(1)	/
M2–O4	2.864(1)	/	2.934(1)	/
M2–O7	/	/	/	3.545(3)
M2–O8	/	/	/	2.869(3)
M2–O9	/	/	/	2.836(3)
M2–O10	/	/	/	3.357(4)
M2–O11	/	/	/	2.987(3)
M2–O12	/	/	/	2.991(3)
average M2–O	2.968	/	2.966	3.098
average M–O	2.974	2.890	2.988	3.056
M1···Cl1	3.551(1)	3.464(1)/3.614(1)	3.598(1)	3.616(9)
M1···Cl2	/	3.464(1)/3.585(1)	/	3.588(0)
M1···Cl3	/	3.287(1)/3.304(1)	/	/
M2···Cl1	3.551(1)	/	3.559(1)	/
M2···Cl2	/	/	/	3.791(9)
M2···Cl3	/	/	/	3.683(3)
average M···Cl	3.551	3.453	3.578	3.670

^{a)} M represents Na in DAP-1 and PAP-1, K in DAP-2 and DAP-O2, respectively.

^{b)} From reference 52.

Table S3. The combustion heat and enthalpies of formation of PAP-1 and DAP-O2, and the relevant combustion products.

	CO ₂ (g)	H ₂ O(l)	N ₂ (g)	HCl(g)	NaCl(s)	KCl(s)
$\Delta_f H$, kJ mol ⁻¹	-393.51	-285.83	0	-92.31	-411.12	-436.68
	PAP-1	DAP-O2				
$\Delta_c U$, kJ mol ⁻¹	-4261.56	-7228.78				
$\Delta_c H$, kJ mol ⁻¹	-4245.45	-7212.67				
$\Delta_f H$, kJ mol ⁻¹	646.52	2515.33				

^[a] the enthalpies of formation ($\Delta_f H$) of the products were derived from NIST.

Table S4. Detonation properties of some well-known explosives and series of molecular perovskite high-energetic materials estimated by using EXPLO5 v6.04.02.

Compound	ρ (g cm ⁻³)	ΔH_f (kJ mol ⁻¹)	Q^e (kJ g ⁻¹)	D^e (km s ⁻¹)	P^e (GPa)	OB ^d (%)
TNT ^c	1.65	-59.3	4.36	6.915	19.4	-74.0
RDX ^c	1.80	70.3	5.74	8.817	34.9	-21.6
HMX ^c	1.91	74.8	5.72	9.152	39.1	-21.6
CL-20 ^c	2.04	397.8	6.22	9.598	45.9	-11.0
DAP-1	2.02 ^a	1013.7 ^b	8.89	9.306	48.3	-22.0
PAP-1	2.07 ^a	646.5 ^b	8.79	9.420	46.0	-3.9
DAP-2	2.04 ^a	247.3 ^b	7.09	9.224	44.2	-21.3
DAP-O2	1.98 ^a	2515.3 ^b	11.87	10.000	55.5	-17.1

^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 density and heat of formation of well-known explosives were collected from EXPLO5 v6.04.02. The detonation parameters were calculated by EXPLO5 v6.04.02; ^d Oxygen Balance based on CO₂ for C_aH_bN_cM_dCl_eO_f; M as alkali metal ion, were calculated by: OB[%] = 1600[f-2a-(b-e+d)/2]/M_w, where M_w is molecular weight.

Table S5. Calculated parameters in the detonation reactions of series molecular perovskite compounds.

Explosives	N ₂	H ₂ O	CO ₂	HCl	C	MCl	
DAP-1	-2790.152	-109.449	-76.379	-188.479	-460.638	-38.084	-622.376 (NaCl)
DAP-2	-3227.699	-109.449	-76.379	-188.479	-460.638	-38.084	-1059.916 (KCl)
PAP-1	-2712.942	-109.449	-76.379	-188.479	-460.638	-38.084	-622.376 (NaCl)
DAP-O2	-3302.932	-109.449	-76.379	-188.479	-460.638	-38.084	-1059.916 (KCl)

1 hartree = 627.51 kcal·mol⁻¹

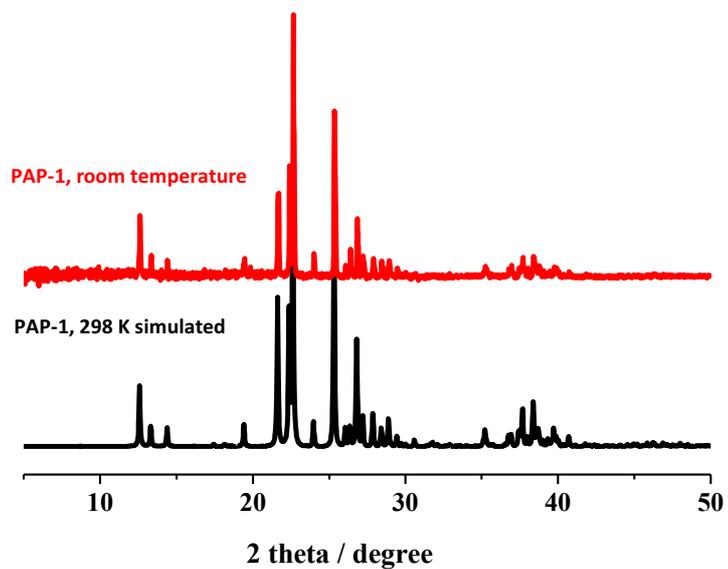


Figure S1. PXRD patterns of PAP-1.

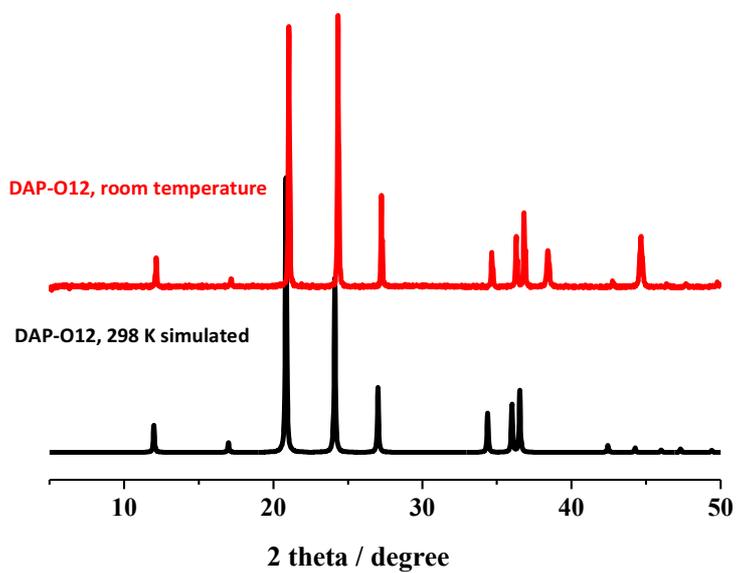


Figure S2. PXRD patterns of DAP-O2.

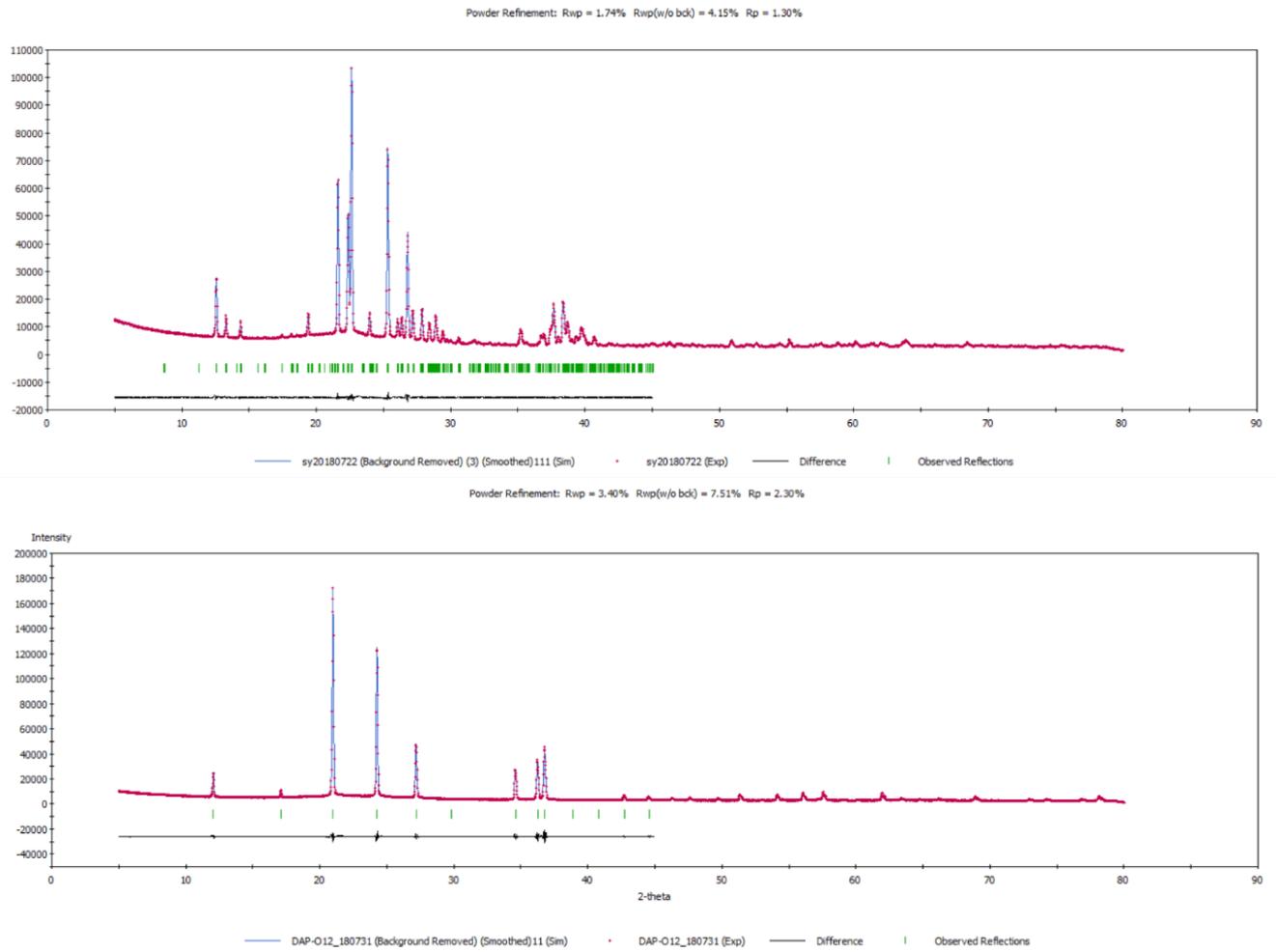


Figure S3. The Pawley refinement on the capillary PXRD patterns of PAP-1 and DAP-O2 at room temperature.

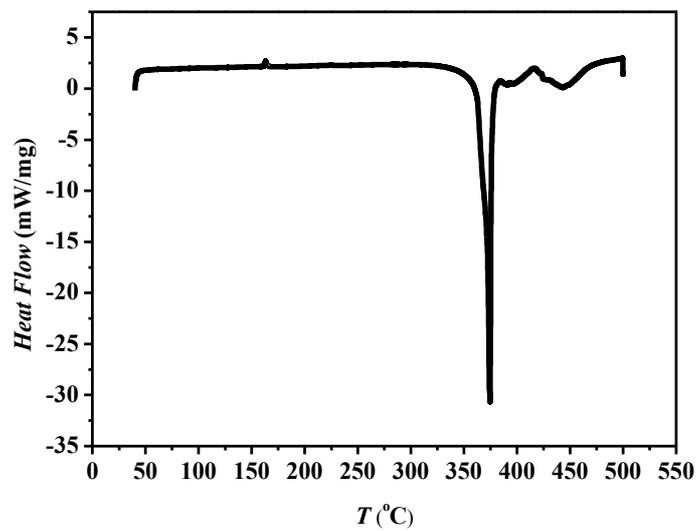


Figure S4. DSC graph of PAP-1.

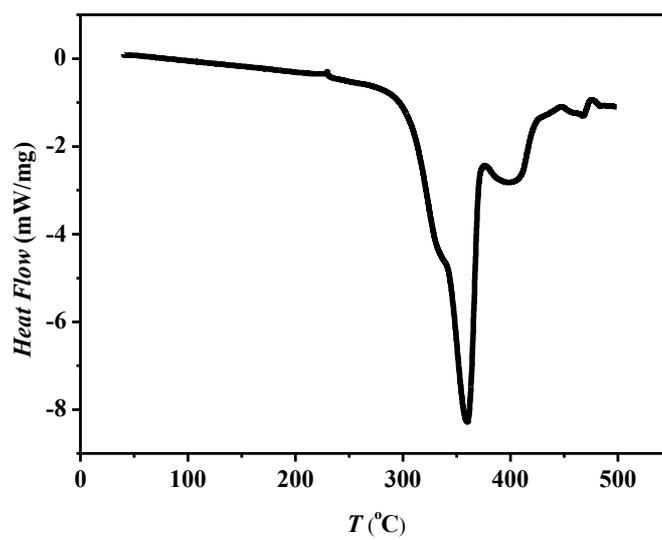


Figure S5. DSC graph of DAP-O2.

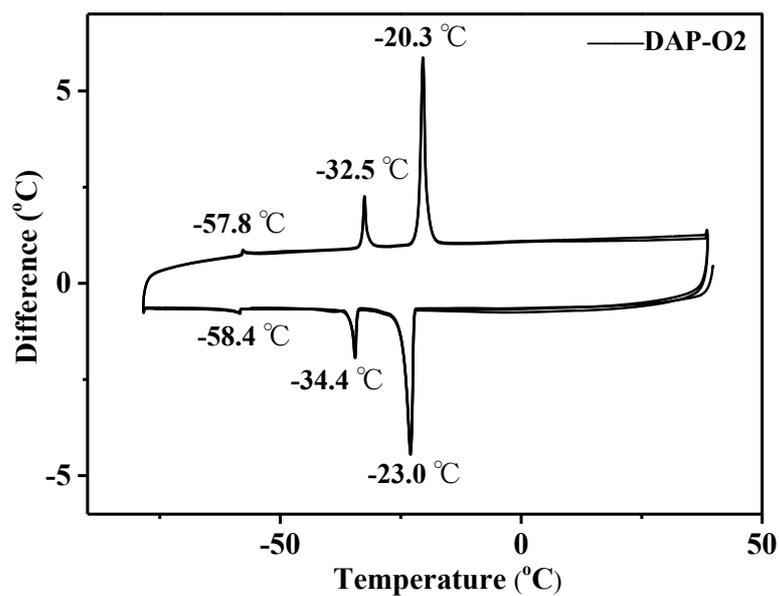


Figure S6. DSC graph of DAP-O2 measured in two cooling-heating cycles.

Reference:

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- [S4] Y. Wang, J.-C. Zhang, S. Hui, S.-H. Li, S.-W. Zhang, S.-P. Pang, *J. Phys. Chem. A.* **2014**, 118, 4575.
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- [S7] Y.-L. Sun, X.-B. Han, W. Zhang, *Chem. Eur. J.* **2017**, 23, 11126.