Supplementary Information (SI) for New Journal of Chemistry.

Supplementary Information

Dinitromethyltetrazole (DNMT) Based Energetic Coordination Polymers (ECPs) as Lead-free Primary Explosives and Laser Initiator

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Table of Contents

1. Synthesis and crystallographic data for compound 1, DNMT, and ECPs.
2. The diagram of laser initiation device.
3. The TG-DSC of ECPs.
4. The FT-IR spectrogram of DNMT and ECPs.
5. The Mass spectrogram of compound 1 and DNMT.
6. Change of density after metal ions are replaced by H+
7. Computational details.

1. Synthesis and crystallographic data for compound 1, DNMT, and ECPs.

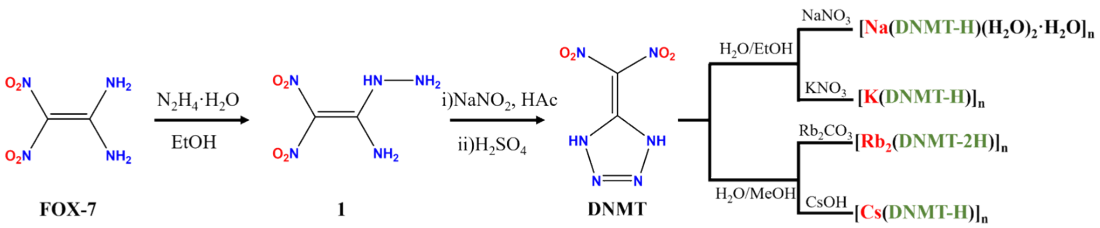

Fig. S1. Preparation process of ligand and four ECPs.

FOX-7, **1**, and DNMT were synthesized by the methods given in literature.[1,2]

X-ray crystallographic data was collected on XtaLAB diffractometer with Cu-K_α radiation. The data reduction and empirical absorption correction were carried in CrysAlisPro software. The crystal structures were refined by SHELX-2017 package.[3]

Table S1. Crystallographic data of four ECPs

Comp	**1**	**DNMT • H_2O**	**ECP 1**	**ECP 2**	**ECP 3**	**ECP 4**
empirical formula	$C_2H_5N_5O_4$	$C_2H_4N_6O_5$	$C_2H_7N_6O_7$Na	$C_2HN_6O_4$K	$C_2N_6O_4Rb_2$	$C_2HN_6O_4$Cs
formula weight	163.11	210.13	250.13	212.19	343.02	306.00
T (K)	295(2)	293	293(2)	298(2)	298(2)	293(2)
crystal system	Orthorhombic	orthorhombic	monoclinic	monoclinic	orthorhombic	triclinic
space group	Pnma	Pnma	$P2_1/n$	$P2_1$	Pbcn	P-1
a (Å)	6.2901(2)	10.3881(3)	3.5414(1)	4.81710(10)	10.0500(2)	4.9200(3)
b (Å)	7.7000(2)	15.7906(4)	30.1434(3)	9.1320(2)	9.42575(16)	8.9900(6)
c (Å)	12.2839(2)	5.0603(1)	8.6469(1)	7.61570(10)	9.12606(18)	9.6106(5)
α (deg)	90	90	90	90	90	65.390(6)

β (deg)	90	90	94.605(1)	92.019(2)	90	84.667(4)
γ (deg)	90	90	90	90	90	75.517(5)
V (Å^3)	594.96(3)	830.06(4)	920.08(3)	334.805(11)	864.50(3)	374.17(4)
Z	4	4	4	2	4	2
D_c (g·cm^{-3})	1.821	1.681	1.806	2.105	2.635	2.716
R_{int}	0.0305	0.034	0.067	0.0396	0.0205	0.1011
h, k, l	$-7 \leq h \leq 6$ $-9 \leq k \leq 9$ $-9 \leq l \leq 15$	$-12 \leq h \leq 12$ $-13 \leq k \leq 19$ $-6 \leq l \leq 6$	$-4 \leq h \leq 4$ $-35 \leq k \leq 37$ $-10 \leq l \leq 10$	$-6 \leq h \leq 5$ $-11 \leq k \leq 11$ $-9 \leq l \leq 8$	$-12 \leq h \leq 12$ $-11 \leq k \leq 11$ $-11 \leq l \leq 11$	$-6 \leq h \leq 6$ $-11 \leq k \leq 11$ $-11 \leq l \leq 11$
reflections collections	3261	3644	18235	3630	4639	9326
independent reflection	652	883	1889	1381	882	1515
R_1, wR_2 [$I > 2\sigma(I)$]	R_1=0.0393, wR_2=0.1199	R_1=0.0526, wR_2=0.1471	R_1=0.0393, wR_2=0.1094	R_1=0.0300, wR_2=0.0779	R_1=0.0278, wR_2=0.0768	R_1=0.0439, wR_2=0.1207
R_1, wR_2 (all data)	R_1=0.0415, wR_2=0.1227	R_1=0.0543, wR_2=0.1496	R_1=0.0427, wR_2=0.1226	R_1=0.0303, wR_2=0.0781	R_1=0.0285, wR_2=0.0774	R_1=0.0844, wR_2=0.1630
F(000)	336.0	432.0	12.0	212.0	640.0	284.0
CCDC	2337977	2340597	2336663	2336664	2336665	2336988

number

Table S2 Hydrogen Bonds (Angstrom, Deg) for: **1**

	d(D-H)	d(H-A)	d(D-A)	∠A-H-D
N2-H1..O1	0.904(8)	2.543(7)	3.3742(19)	153.3(7)
N2-H1..O2	0.904(8)	2.347(9)	3.1799(17)	153.2(9)
N1-HN1..O1	0.92(4)	2.31(3)	3.025(2)	134.6(10)
N1-HN1..O1	0.92(4)	2.31(3)	3.025(2)	134.6(10)
N3-H3A..N2	0.8600	2.3800	2.696(3)	102.00
N3-H3A..O1	0.8600	2.5300	3.235(2)	140.00
N3-H3A..O1	0.8600	2.5300	3.235(2)	140.00

Table S3 Hydrogen Bonds (Angstrom, Deg) for: **DNMT**

	d(D-H)	d(H-A)	d(D-A)	∠A-H-D
N2-HN1..O1	0.98(3)	2.11(2)	2.5610(19)	106.5(15)
N1-HN1..OW1	0.98(3)	1.77(3)	2.6997(17)	156.8(19)
OW1-HW1..O1	0.90(2)	2.06(2)	2.9611(18)	158.3(15)
OW1-HW2..OW1	0.900(18)	2.05(2)	2.9026(16)	157.2(16)
N3-H..OW1	0.899(7)	2.053(7)	2.9026(16)	157.2(4)
OW1-HW3.OW1	0.8600	2.5300	3.235(2)	140.00

Table S4 Hydrogen Bonds (Angstrom, Deg) for: **ECP 1**

	d(D-H)	d(H-A)	d(D-A)	∠A-H-D
OW1-HW1...O2	0.88(3)	2.10(3)	2.976(2)	178(4)
OW1-HW2...O2	0.80(3)	2.27(3)	3.023(2)	157(3)
Ow1-HW2..O3	0.80(3)	2.31(3)	2.924(2)	135(3)
N4-H4..O4	0.8600	2.0300	2.5558(18)	119.00
N4-H4..N2	0.8600	2.2600	3.0453(19)	152.00
O5-H5A..N1	0.9700	2.0000	2.8627(18)	146.00
O5-H5B..N3	0.9700	2.2000	3.0005(19)	139.00
O6-H6A..OW1	0.9700	1.9500	2.843(2)	153.00
O6-H6B..OW1	0.9700	1.9900	2.837(2)	145.00

Table S5 Hydrogen Bonds (Angstrom, Deg) for: **ECP 2**

	d(D-H)	d(H-A)	d(D-A)	∠A-H-D
OW1-HW1...O2	0.88(3)	2.10(3)	2.976(2)	178(4)
OW1-HW2...O2	0.80(3)	2.27(3)	3.023(2)	157(3)
Ow1-HW2..O3	0.80(3)	2.31(3)	2.924(2)	135(3)
N4-H4..O4	0.8600	2.0300	2.5558(18)	119.00
N4-H4..N2	0.8600	2.2600	3.0453(19)	152.00
O5-H5A..N1	0.9700	2.0000	2.8627(18)	146.00

O5-H5B..N3	0.9700	2.2000	3.0005(19)	139.00
O6-H6A..OW1	0.9700	1.9500	2.843(2)	153.00
O6-H6B..Ow1	0.9700	1.9900	2.837(2)	145.00

Table S6 Hydrogen Bonds (Angstrom, Deg) for: **ECP 2**

	d(D-H)	d(H-A)	d(D-A)	∠A-H-D
N4-H4..O1	0.8600	2.0100	2.542(4)	119.00
N4-H4..O2	0.8600	2.1500	2.961(4)	156.00

Table S7 Hydrogen Bonds (Angstrom, Deg) for: **ECP 4**

	d(D-H)	d(H-A)	d(D-A)	∠A-H-D
N1-H1..O1	0.8600	2.3000	2.662(11)	106.00
N1-H1..N4	0.8600	2.0100	2.786(11)	149.00
N4-H4..O4	0.8600	2.3900	2.723(12)	104.00
N4-H4..N1	0.8600	1.9700	2.786(11)	158.00

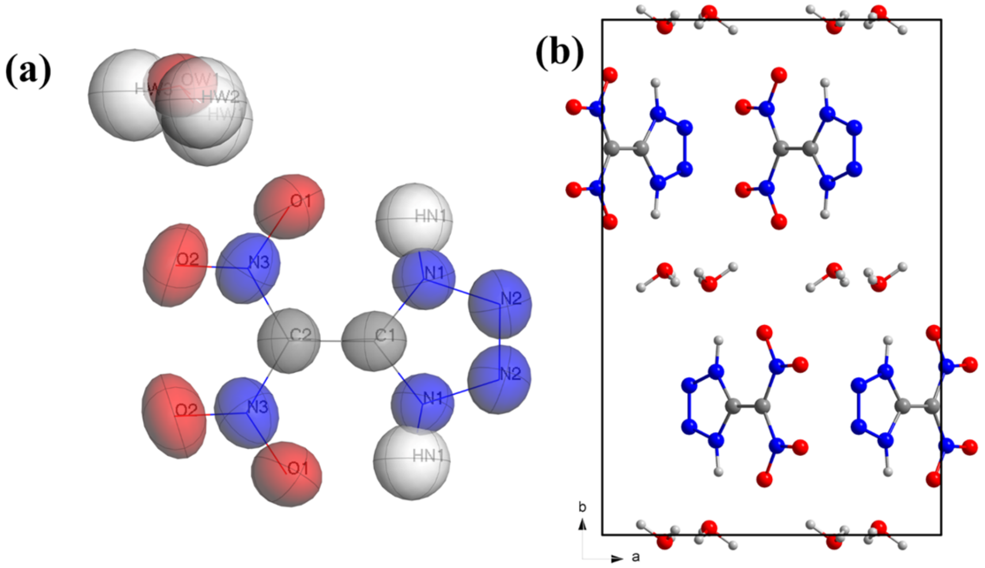

Fig. S2 The minimum asymmetric unit (a) and crystal structure diagram (b) of **DNMT・H_2O**.

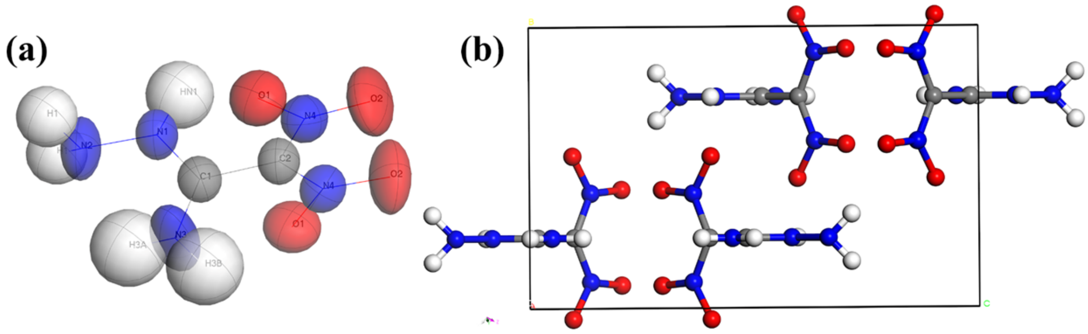

Fig. S3 The minimum asymmetric unit (a) and crystal structure diagram (b) of **1**.

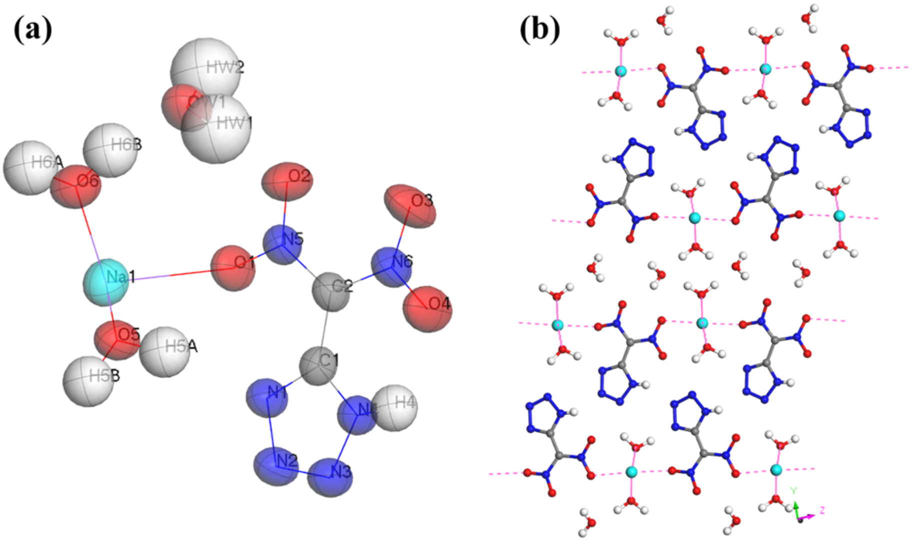

Fig. S4 The minimum asymmetric unit (a) and crystal structure diagram (b) of **ECP 1**.

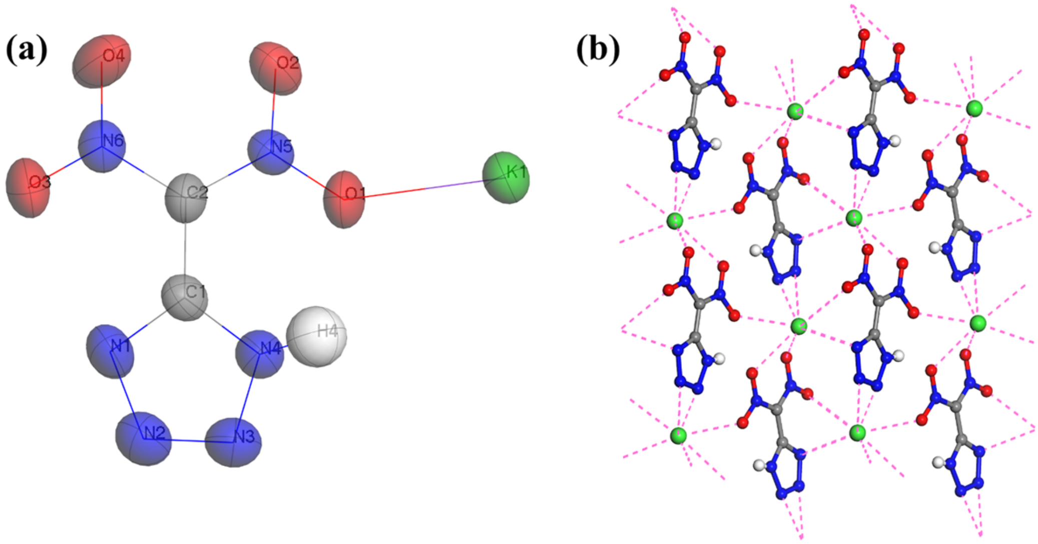

Fig. S5 The minimum asymmetric unit (a) and crystal structure diagram (b) of **ECP 2**.

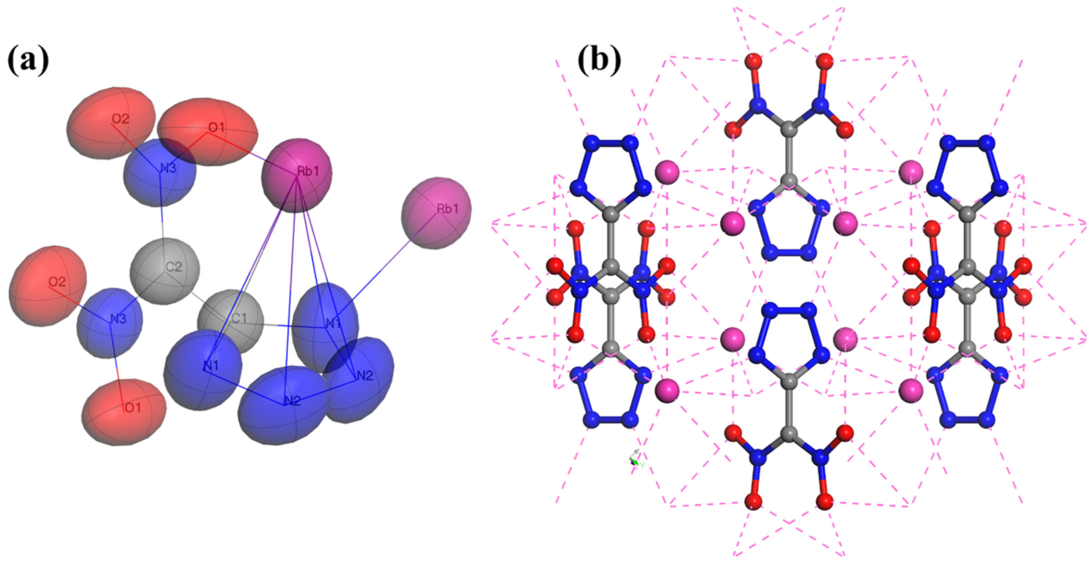

Fig. S6 The minimum asymmetric unit (a) and crystal structure diagram (b) of **ECP 3**.

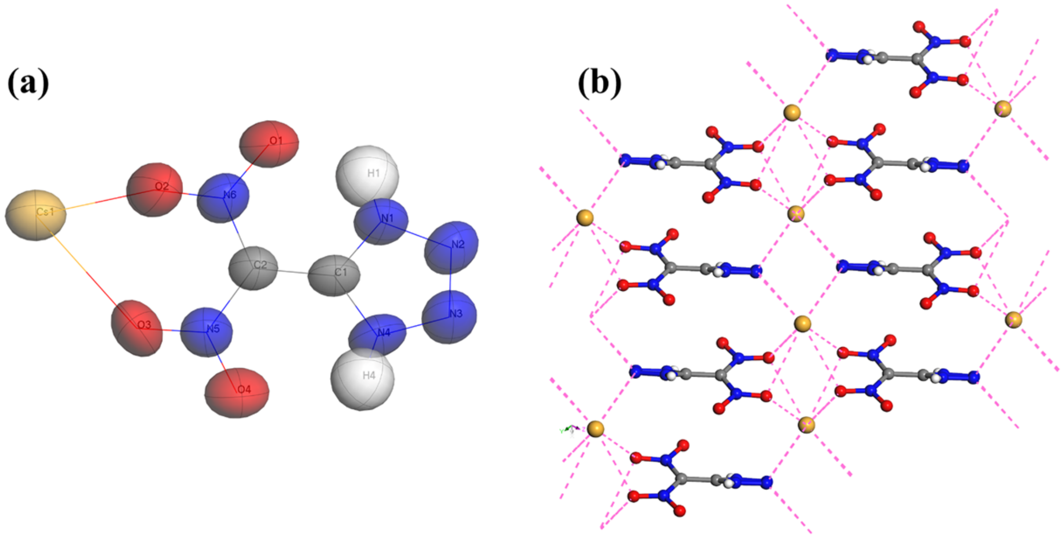

Fig. S7 The minimum asymmetric unit (a) and crystal structure diagram (b) of **ECP 4**.

2. The diagram of laser initiation device.

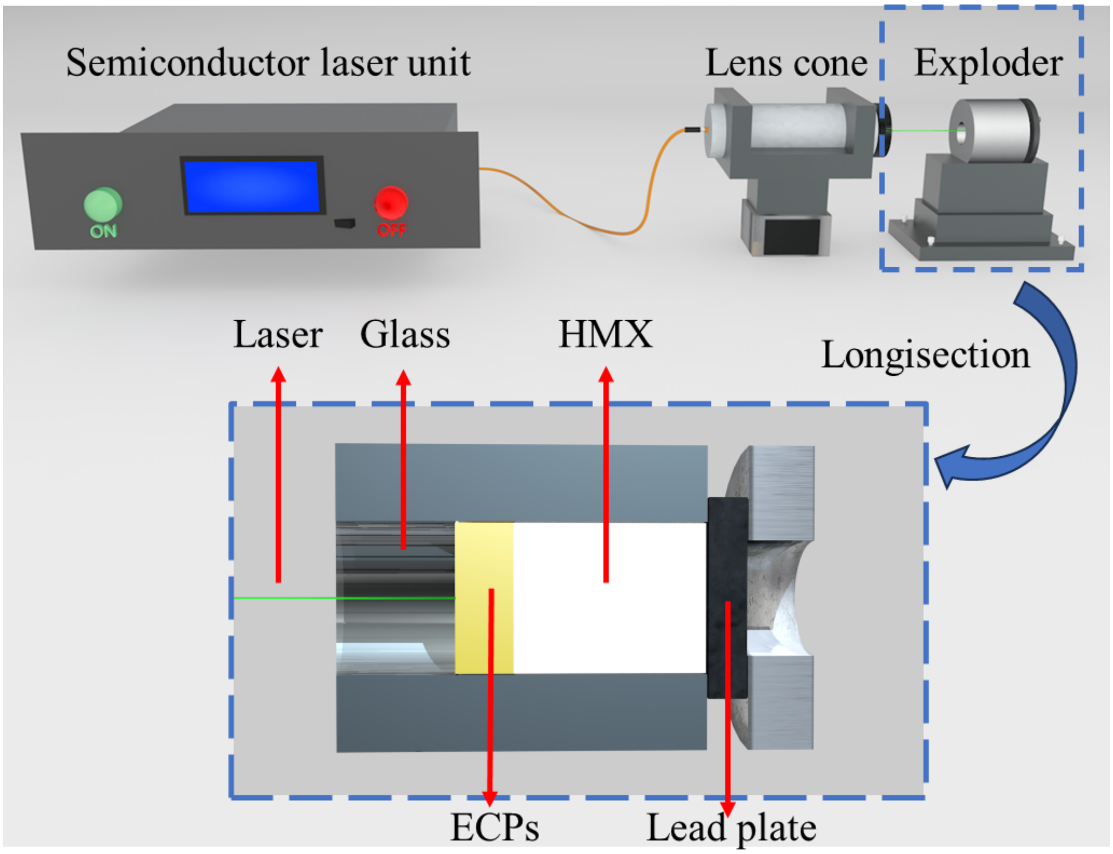

Fig. S8 The diagram of laser initiation devices

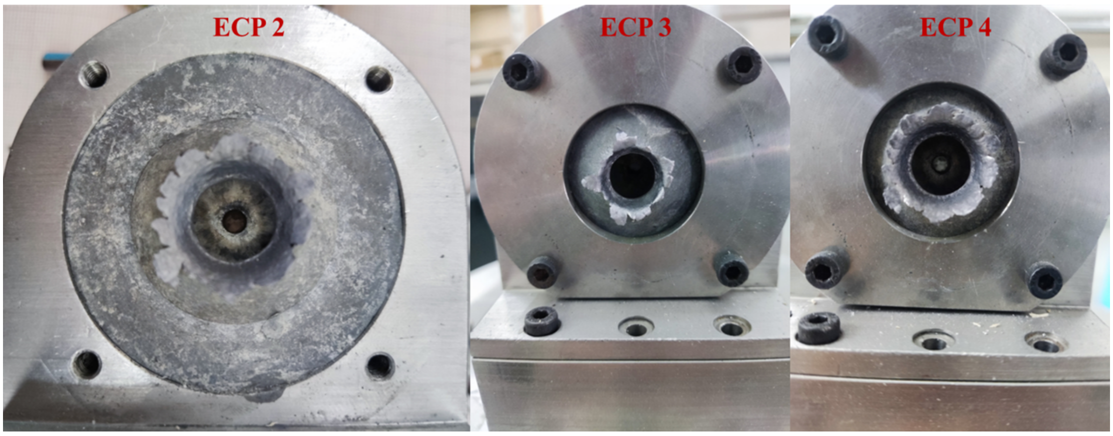

Fig. S9 The lead plate experimental results of ECPs

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3. The TG-DSC of ECPs

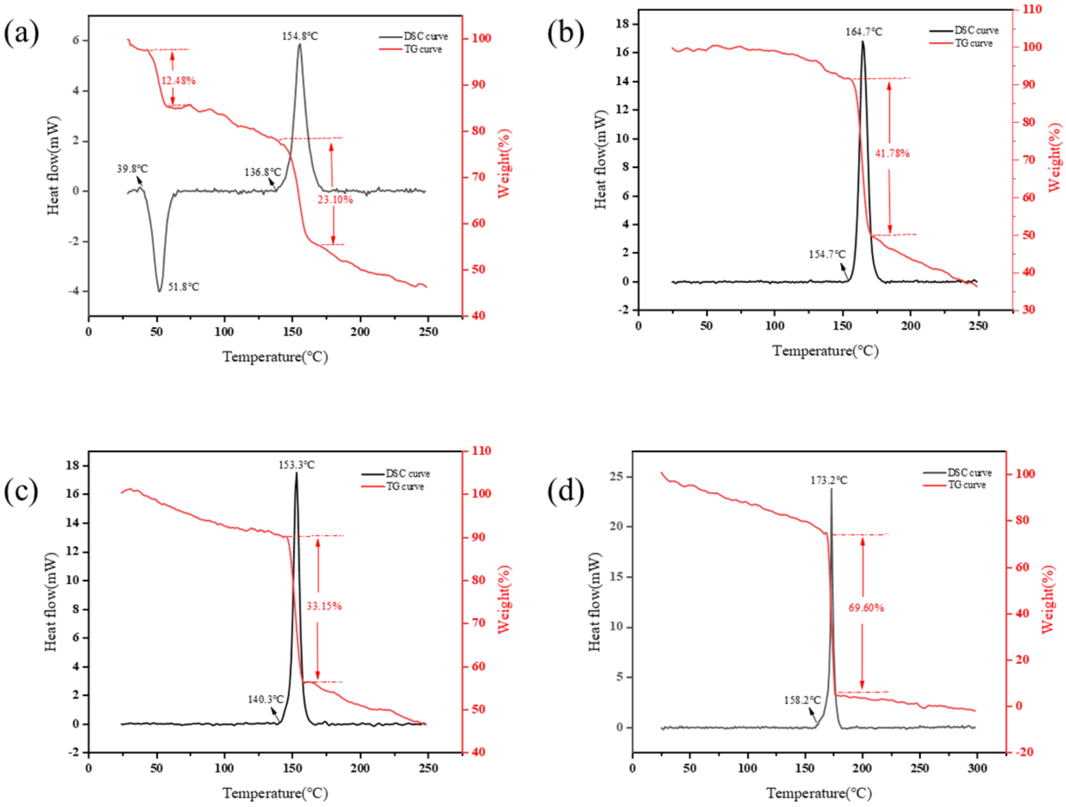


Fig. S10 The TG-DSC of ECPs: (a)**ECP 1**; (b) **ECP 2**; (c) **ECP 3**; (d) **ECP 4**.

4. The FT-IR spectrogram of DNMT and ECPs.

IR spectra were recorded on a FT-IR spectrometer (*Thermo Nicolet 6700*) with Attenuated Total Refraction mode.

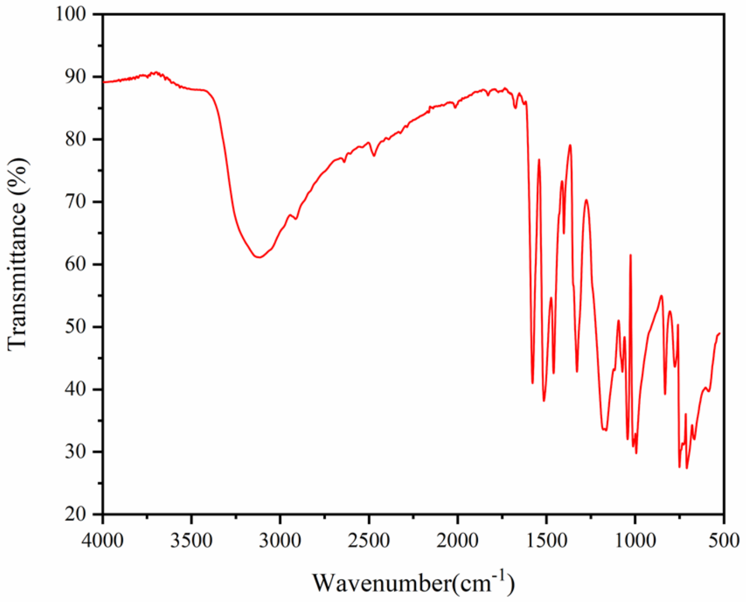


Fig. S11 IR spectra of **DNMT•$2H_2O$**

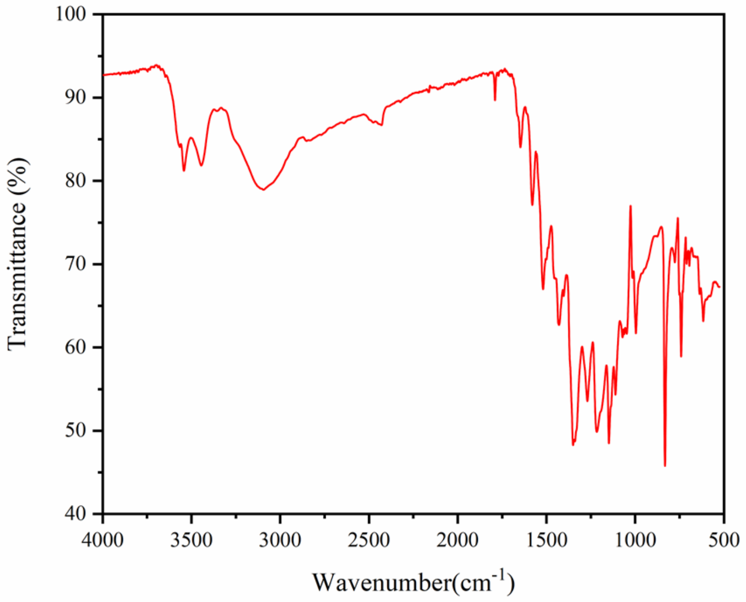


Fig. S12 IR spectra of **ECP 1**.

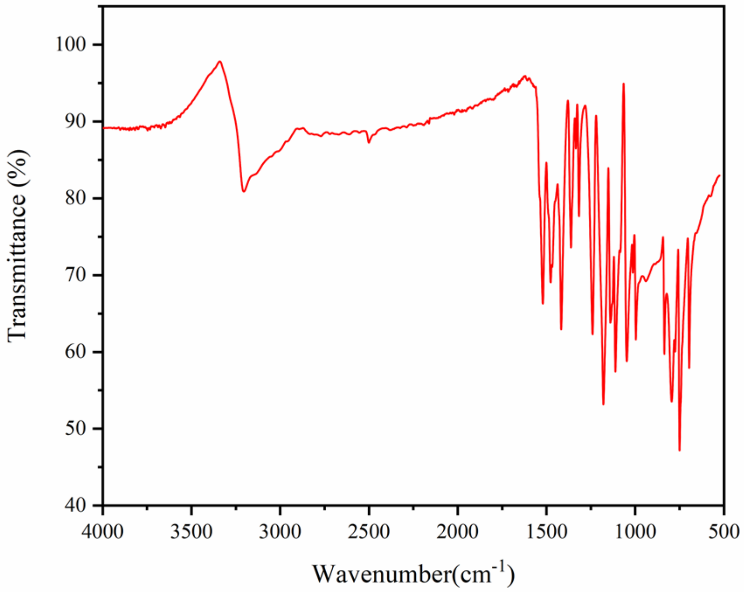


Fig. S13 IR spectra of **ECP 2**.

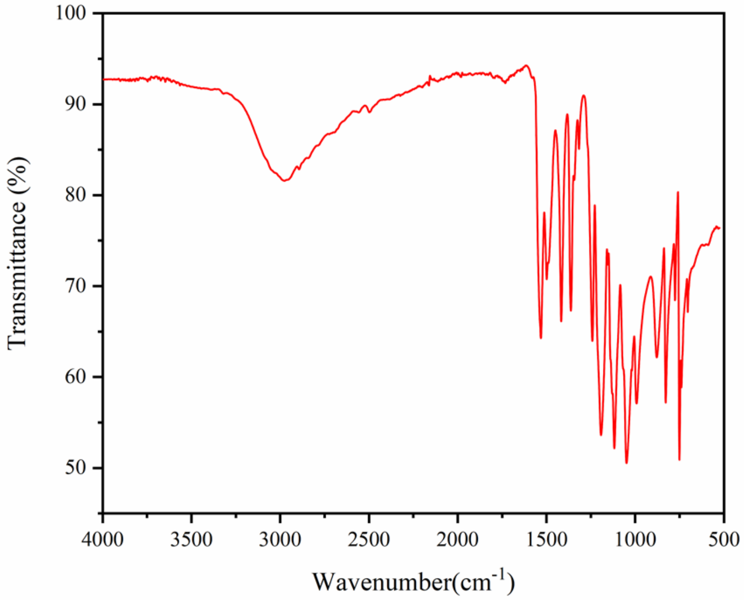


Fig. S14 IR spectra of **ECP 3**.

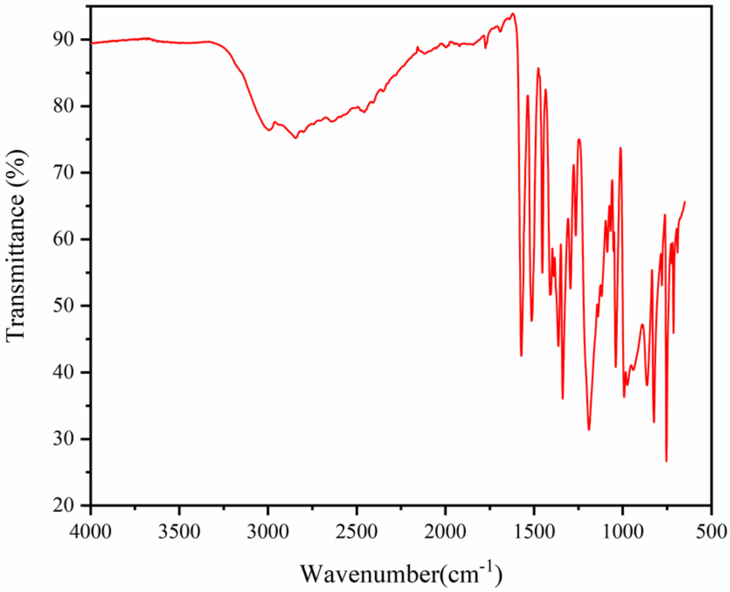


Fig. S15 IR spectra of **ECP 4**.

5. The Mass spectrogram of compound 1 and DNMT.

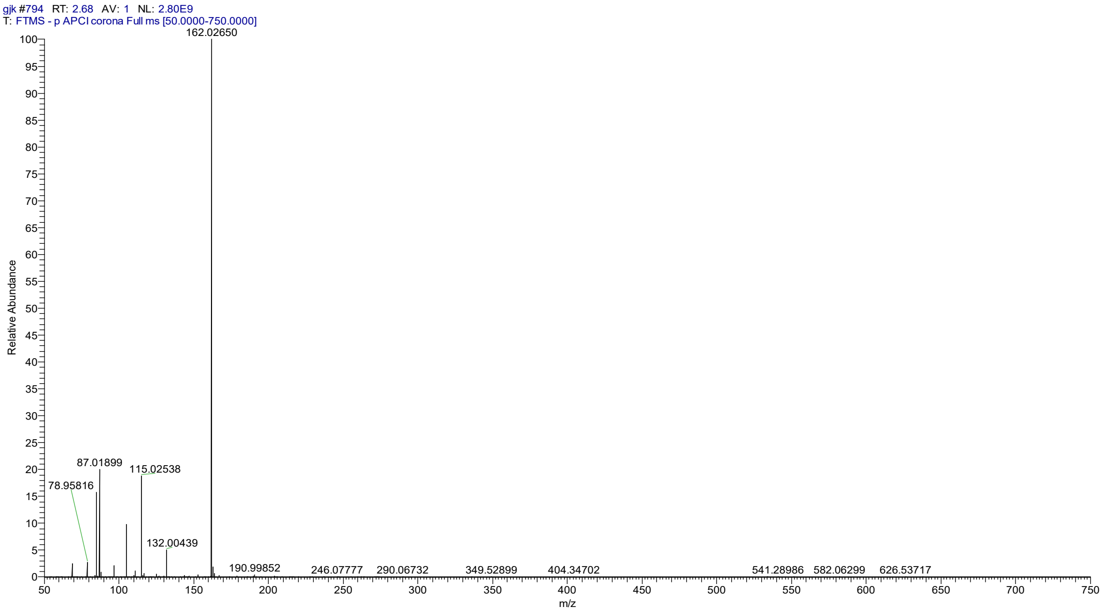


Fig. S16 Mass spectra of **1**

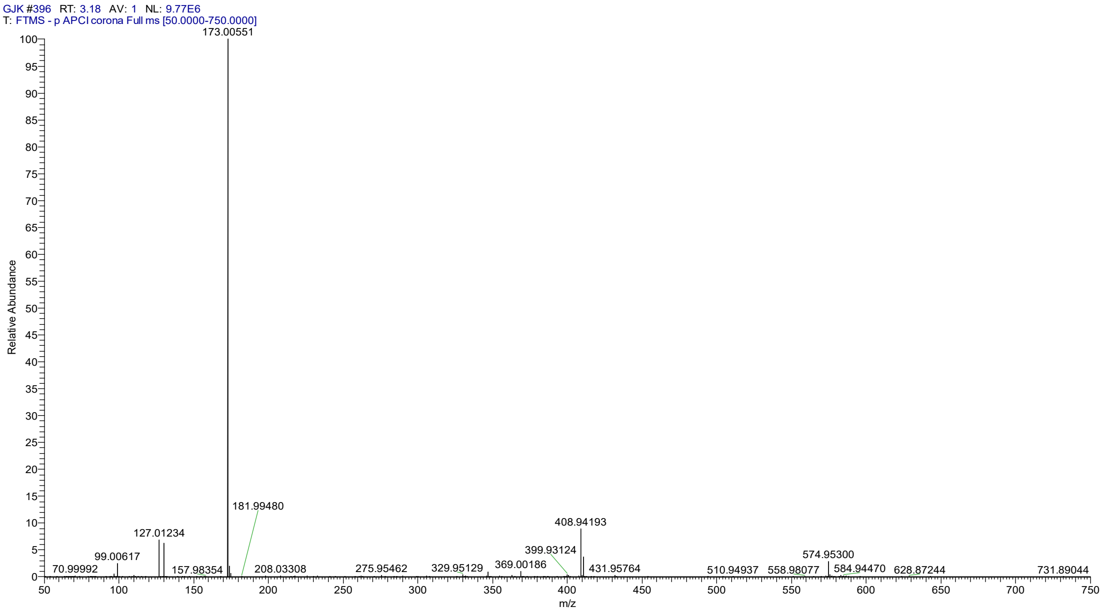


Fig. S17 Mass spectra of **DNMT**

6. Change of density after metal ions are replaced by H+

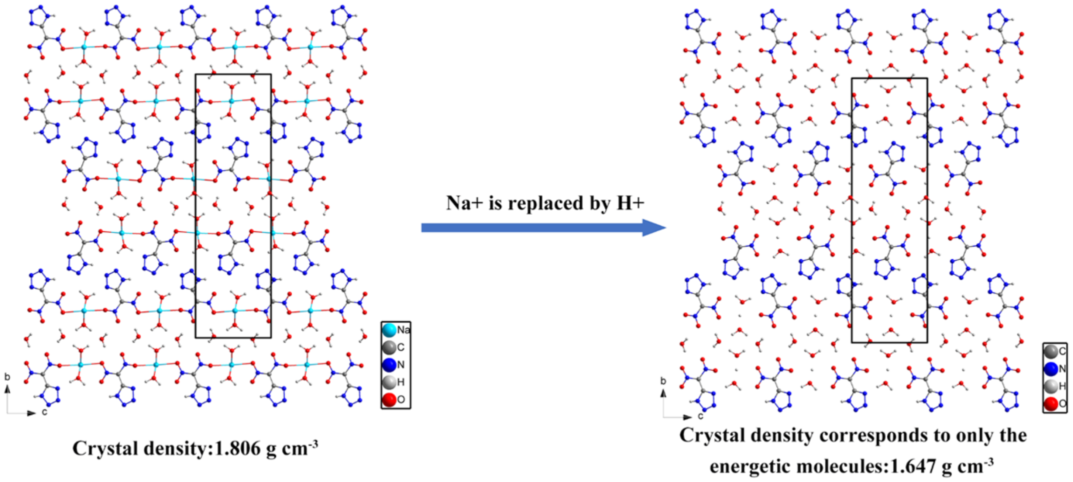


Fig. S18 Change of density of **ECP 1** after Na^+ is replaced by H^+.

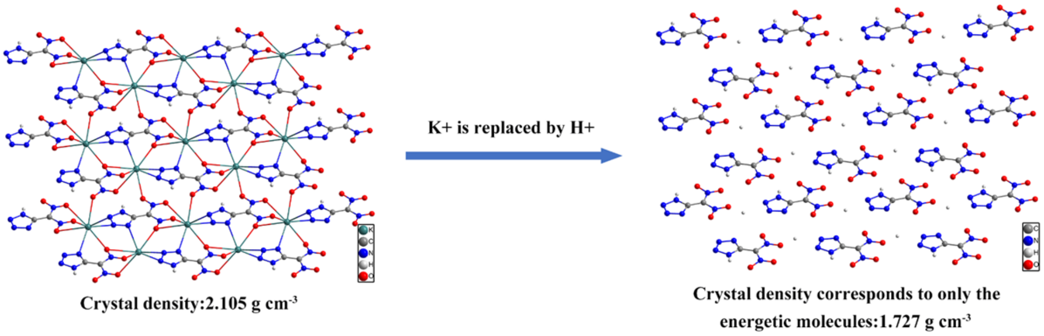


Fig. S19 Change of density of **ECP 2** after K^+ is replaced by H^+.

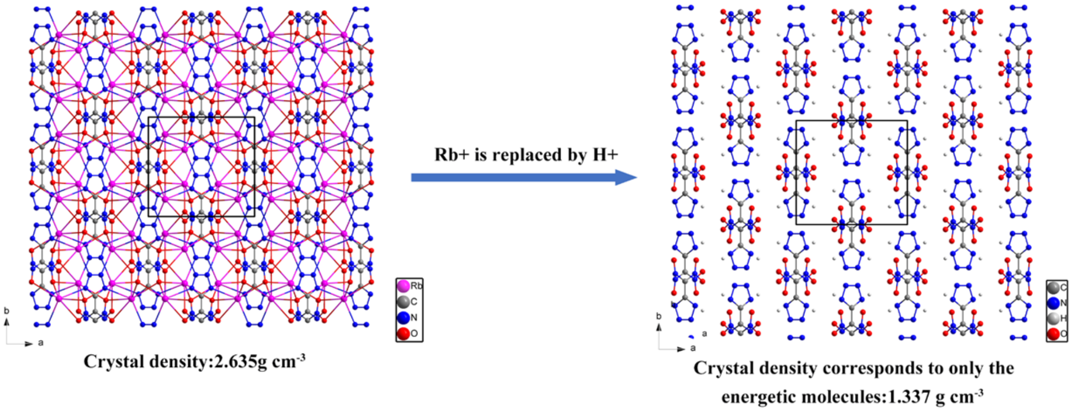
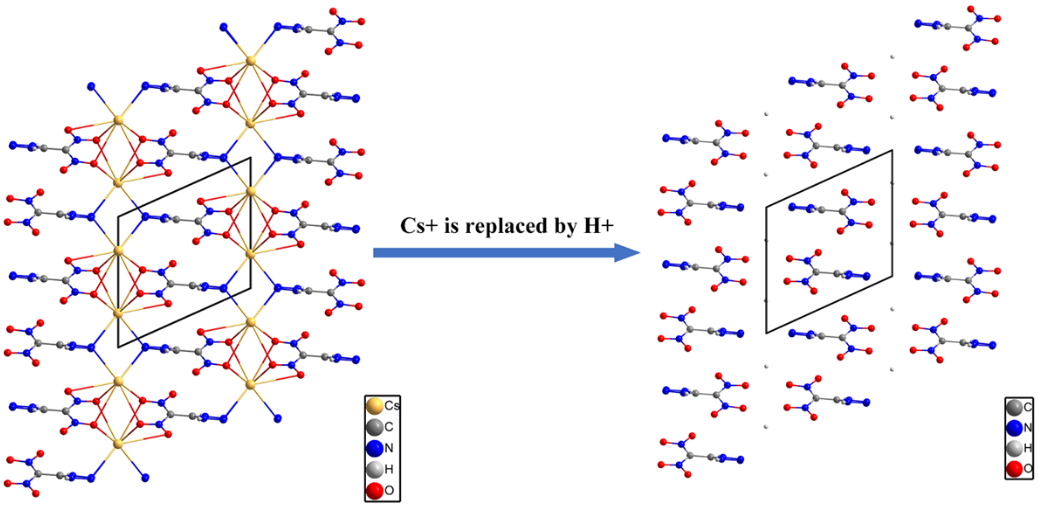


Fig. S20 Change of density of **ECP 3** after Rb^+ is replaced by H^+.



Crystal density:2.716 g cm^{-3}

Crystal density corresponds to only the energetic molecules:.1.545 g cm^{-3}

Fig. S21 Change of density of **ECP 4** after Cs^{+} is replaced by H^{+}.

7. Computational details.

In this work, computations were performed by using the Gaussian 09 programs. The DFT / B3LYP method were used, combined with the 6-311g** basis set. The geometric optimization calculation of DNMT, DNMT-H, DNMT-2H was carried out and the total energy of the ground state was obtained. Based on the vibration analysis, the zero-point energy and thermal correction energy were obtained. On this basis, the formation enthalpy was obtained by atomization reaction. All the structures are confirmed to be the minima on the potential energy surface.

The atomization method was used for the calculation of heats of formation (HOF).[4] The atomization used to derive HOF of compound DNMT, DNMT-H, and DNMT-2H were shown in equation 1-3.

$$C_2H_2N_6O_4 \rightarrow 2C + 2H + 6N + 4O \tag{1}$$

$$C_2HN_6O_4 \rightarrow 2C + H + 6N + 4O \tag{2}$$

$$C_2N_6O_4 \rightarrow 2C + 6N + 4O \tag{3}$$

The calculation process of HOF is as follows:

$$\Delta_f H^0(M, 0K) = \sum_{atoms} x\Delta_f H^0(X, 0K) - \left(\sum_{atoms} x\varepsilon_0(X) - (\varepsilon_0(M) + \varepsilon_{ZPE}M)\right) \tag{4}$$

$$\Delta_f H^0(M, g, 298K) = \Delta_f H^0(M, 0K) + H_{corr} - \varepsilon_{ZPE}(M) - \sum_{atoms} x((H_X^0(298K) - H_X^0(0K))) \tag{5}$$

Where $\Delta_f H^0(M, 0K)$ is the formation enthalpy of molecule in 0 K; $\sum_{atoms} x\Delta_f H^0(X, 0K)$ is the sum of formation enthalpy of atoms; $\sum_{atoms} x\varepsilon_0(X)$ is the sum of total energy of atoms; $\varepsilon_0(M)$ is the total energy of molecule; $\varepsilon_{ZPE}(M)$ is the zero-point energy of molecule; $\Delta_f H^0(M, g, 298K)$ is the formation enthalpy of molecule in gas state in 298 K; H_{corr} is the thermal correction to enthalpy; $\sum_{atoms} x((H_x^0(298K) - H_x^0(0K)))$ is the sum of thermal correction to enthalpy of atoms.

The HOF of salt $\Delta_f H^0(salt, 298K)$ of salt was calculated by equation (6):[5]

$$\Delta_f H^0(salt, 298K) = \Delta_f H^0(cation, 298K) + \Delta_f H^0(anion, 298K) - \Delta H_L \tag{6}$$

Where $\Delta_f H^0(cation, 298K)$ and $\Delta_f H^0(anion, 0K)$ are the HOF of cation and anion; ΔH_L is the lattice enthalpy of salt. The lattice energy is calculated by the equation (7):[6]

$$\Delta H_L = U_{pot} + (p(n_M/2 - 2) + q(n_X/2 - 2))RT \tag{7}$$

Where U_{pot} is the lattice energy; p and q are the charge of cation and anion; n_M and n_X nX are determined by the structural properties of cations and anions. Monoatomic ions take 3, linear polyatomic ions take 5, and nonlinear polyatomic ions take 6. *R* is the ideal gas constant; *T* is the temperature. The U_{pot} is calculated by the equation (8):[7]

$$U_{pot} = \gamma(\rho_m/M_m)^{1/3} + \delta \tag{8}$$

Where ρ_m is the density; M_m is the molar mass; For 1:1 type ionic salts, γ and δ are 1981.2 kJ·mol^{-1} and 103.8 kJ·mol^{-1}, respectively. For the 1:2 type ionic salt, γ and δ are 8375.6.2 kJ·mol^{-1} and -178.8 kJ·mol^{-1}, respectively.

The detonation velocity *D* (km s^{-1}) and detonation pressure *P* (GPa) were calculated by the K-J equation, as shown in equation (9) and (10):[8]

$$D = 1.01\left(N\bar{M}^{1/2}Q^{1/2}\right)^{1/2}(1 + 1.3\rho) \tag{9}$$

$$P = 1.558\rho^2 N\bar{M}^{1/2}Q^{1/2} \tag{10}$$

where *N* is moles of detonation gases per gram of explosive, *M* is average molecular weight of the gases, *Q* is the chemical energy of detonation (kcal g^{-1}) and *ρ* is the density (g cm^{-3}).

Table S8. The formation enthalpy of atoms in 0 K, calculated total energy, and thermal correction to enthalpy of C, H, O, and N.

	C	H	N	O
$\Delta_f H(0\,K)$ / kJ mol^{-1}	711.19	216.02	470.82	246.81
ε_0 / kJ mol^{-1}	-99390.90	-1318.41	-143348.48	-197136.68
$H^0(298K) - H^0(0K)$ / kJ mol^{-1}	1.05	4.23	4.35	4.35

Table S9. All the data in calculation process of the HOF of DNMT-H and DNMT-2H.

	DNMT-H in ECP 1	DNMT-H in ECP 2	DNMT-2H	DNMT-H in ECP 4
empirical formula	$C_2HN_6O_4$	$C_2HN_6O_4$	$C_2N_6O_4$	$C_2HN_6O_4$
$\sum_{atoms} x\Delta_f H^0(X, 0K)$ / kJ mol^{-1}	5450.56	5450.56	5234.54	5450.56
$\sum_{atoms} x\varepsilon_0(X)$ / kJ mol^{-1}	-1848737.78	-1848737.78	-1847419.37	-1848737.78

$\varepsilon_{ZPE}(M)$ / kJ mol^{-1}	31.92	91.97	0	32.26
$\varepsilon_0(M) + \varepsilon_{ZPE}(M)$ / kJ mol^{-1}	-1854154.60	-1854153.89	-1852403.74	-1854146.23
$\Delta_f H^0(M, 0K)$ / kJ mol^{-1}	33.74	34.45	250.17	42.11
H_{corr} / kJ mol^{-1}	42.19	42.22	9.92	42.56
$H_{corr} - \varepsilon_{ZPE}(M)$ / kJ mol^{-1}	10.27	10.25	9.92	10.30
$\sum_{atoms} x[\left(H_X^0 298K\right) - H_X^0(0$ / kJ mol^{-1}	49.83	49.83	45.61	49.83
$\Delta_f H^0(M,g,298K)$ / kJ mol^{-1}	-5.83	-5.14	214.48	2.58

Table S10. The lattice enthalpy and energetic properties of ECPs.

	ECP **1**	ECP **2**	ECP **3**	ECP **4**
ρ / g cm^{-3}	1.647	1.727	1.337	1.545
M / g mol^{-1}	228.12	174.08	174.08	174.08
γ / kJ mol^{-1}	1981.2	1981.2	8375.6	1981.2
δ / kJ mol^{-1}	103.8	103.8	-178.8	103.8
U_{pot} / kJ mol^{-1}	486.70	529.49	1473.91	514.00
ΔH_L / kJ mol^{-1}	487.94	530.73	1477.63	515.24
$\Delta_f H(cation, 298K)$ / kJ mol^{-1}	-5.83	-5.14	214.48	2.58
$\Delta_f H(anion, 298K)$ / kJ mol^{-1}	1536.2	1536.2	1536.2	1536.2
$\Delta_f H(salt, 298K)$ / kJ mol^{-1}	1042.43	1000.334	273.05	1023.54
Q / kJ mol^{-1}	1656.29	1746.20	1018.92	1769.41
DV / m s^{-1}	8503.72	8641.21	4827.23	6693.69

DP / GPa	30.36	32.30	8.49	18.05

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