Electronic Supplementary Information

Structure and performance regulation of energetic complexes through multifunctional molecular self-assembly

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1. The method of synthesized dipotassium tetranitroethide

Tetraiodoethylene powder (20.0 g, 0.04 mol) was added to 50 ml of 96% HNO_3 in 0°C, with stirring. Then the solution heated quickly to 70°C. After 20 min, the mixture was poured onto 200 g of ice, and extracted with dichloromethane (100 mL). The solution was washed with $NaHSO_3$ solution (50 mL), brine (100 mL) and dried ($MgSO_4$). Removal of solvent gave 1,1-diiododinitroethylene, 8 g (50%) of a yellow solid. The solution of 1,1-diiododinitroethylene (8.0 g) in 50 mL of 60% aqueous methanol was added to a solution of KNO_2 (8.0 g) in 50 mL of 60% aqueous methanol. After 18h, the product, 5.5 g (90%), was gave by filtered and washed with methanol. Dipotassium tetranitroethide is a bright yellow solid, mp. 280°C.IR (KBr, cm^{-1}): 3446, 1534, 1472, 1385, 1349, 1261, 1197, 1141, 1007, 851, 796, 774, 727, 626 cm^{-1}. EA ($K_2C_2N_4O_8$, 286.24, %): calcd C, 8.39; N, 19.57. found: C, 8.35; N, 19.58.

Tetranitroethane (TNE). Concentrated sulfuric acid (10 mL) was added to a suspension of dipotassium tetranitroethide (4 mmol, 1.1 g) dichloromethane (30 mL) at -40°C and stirred for 1 h. Then the mixture was treated by a quick separation using a separating funnel, which gave the solution of tetranitroethane in dichloromethane.

2. The crystallographic data

Table S1. Crystallographic data and structure determination details for **EP-1**-**EP-4**.

Comp.	EP-1	EP-2	EP-3	EP-4
data_block name	200813f	200827g	200723d	200708b
Chemical formula	$CuC_2H_{12}N_8O_8$	$NiC_2H_{18}N_{10}O_8$	$CuC_6H_{18}N_8O_9$	$Ag_2C_6H_{18}N_8O_9$
Formula weight	340	369	410	562
Temperature /K	298(3)	298(3)	298(2)	298(3)
Crystal size /mm	0.46×0.17×0.14	0.43×0.40×0.35	0.45×0.4×0.17	0.3×0.11×0.06
Color/shape	green/needle	yellow/block	brown/block	yellow/needle
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	*C*2/*c*	*Fdd*2	$P2_1/n$	*P*2/*n*
a[Å]	12.9524(11)	21.9591(19)	9.0943(11)	18.9066(17)
b[Å]	10.4313(9)	35.049(3)	13.4408(15)	7.4881(9)
c[Å]	9.065(8)	7.6278(7)	12.7697(12)	21.104(3)
β[º]	108.793(4)	90	105.08(4)	111.826
Volume /Å^3	1159.48(18)	5870.6(9)	1507.1(3)	2773.7(5)
Z	4	16	4	4
ρ/g·cm^{-3}	1.946	1.67	1.806	2.505
μ/mm^{-1}	1.941	1.379	1.515	2.884
F(000)	692	3072	844	2032
θ/º	-	2.325~27.337	2.242~26.243	3.313~28.444
h	-15-10	-26-11	-10-9	-22-20
k	-12-9	-41-41	-15-13	-8-9
l	-10-10	-9-9	-15-15	-16-25
Reflections collected	2374	6666	7201	12033
Independent reflections	1007	2557	2648	5156
R_{int}	0.0845	0.0535	0.0725	0.0365
Parameters	89	190	217	416
S	1.073	1.072	1.146	1.055
R_1 (I＞2σ(I))	0.0525	0.0401	0.0566	0.0363
wR_2 (I＞2σ(I))	0.1386	0.1024	0.1559	0.0736
R_1 (all data)	0.0726	0.0459	0.0886	0.0492
wR_2 (all data)	0.1602	0.105	0.1734	0.079
CCDC	2330649	2330650	2330651	2330654

Table S2. Crystallographic data and structure determination details for **EP-5-EP-9**.

Compound	EP-5	EP-6	EP-7	EP-8	EP-9
data_block name	200728j	200910a	200826c	exp_6586	200827h
Chemical formula	$NiC_8H_{24}N_{10}O_8$	$ZnC_8H_{24}N_{10}O_8$	$NiC_5H_{18}N_{16}O_{11}$	$CoC_5H_{18}N_{16}O_{11}$	$Mn_8C_{36}H_{153}N_{120}O_{77}$
Formula weight	447	454	537	537	3938.87
Temperature /K	298(2)	298(2)	298(2)	119(3)	298(2)
Crystal size /mm	0.37×0.35×0.3	0.11×0.07×0.05	0.38×0.1×0.08	0.22×0.21×0.2	0.35×0.1×0.07
Color/shape	brown/block	yellow/block	green/needle	red/needle	yellow/needle
Crystal system	hexagonal	hexagonal	trigonal	trigonal	trigonal
Space group	$P6_1$	$P6_522$	$P3c1$	$P3c1$	$R3$
a[Å]	9.341(9)	9.4361(11)	18.6951(16)	18.751(6)	36.583(3)
b[Å]	9.341(9)	9.4361(11)	18.6951(16)	18.751(6)	36.583(3)
c[Å]	35.71(3)	36.237(3)	9.6219(7)	9.6642(4)	28.975(3)
Volume /$Å^3$	2698.4(4)	2794.2(5)	2912.4(4)	2942.71(17)	33582 (5)
Z	6	6	6	6	9
$\rho/g\cdot cm^{-3}$	1.651	1.618	1.837	1.819	1.713
μ/mm^{-1}	1.141	1.379	1.094	0.968	0.787
F(000)	1404	1416	1656	1650	17775
θ/º	2.518~24.196	2.555~27.23	3.039~25.268	3.915~26.517	3.067~28.458
h	-11-10	-9-11	-22-15	-19-19	-43-43
k	-11-10	-11-9	-21-22	-14-23	-43-28
l	-42-10	-41-43	-11-11	-11-6	-34-34
Reflections collected	13463	14235	13610	6427	54748
Independent reflections	1592	1656	3369	2864	26209
R_{int}	0.0556	0.1121	0.0795	0.044	0.1124
Parameters	135	127	298	298	2125
S	1.226	1.091	1.045	1.063	0.985
R_1 ($I>2\sigma(I)$)	0.0526	0.0591	0.0812	0.063	0.1036
wR_2 ($I>2\sigma(I)$)	0.1203	0.1203	0.2056	0.1651	0.1973
R_1 (all data)	0.0558	0.0726	0.113	0.0735	0.2167
wR_2 (all data)	0.1215	0.1273	0.2331	0.1764	0.2303

CCDC	2330655	2330656	2330658	2330659	2330931

3. The FT-IR spectra.

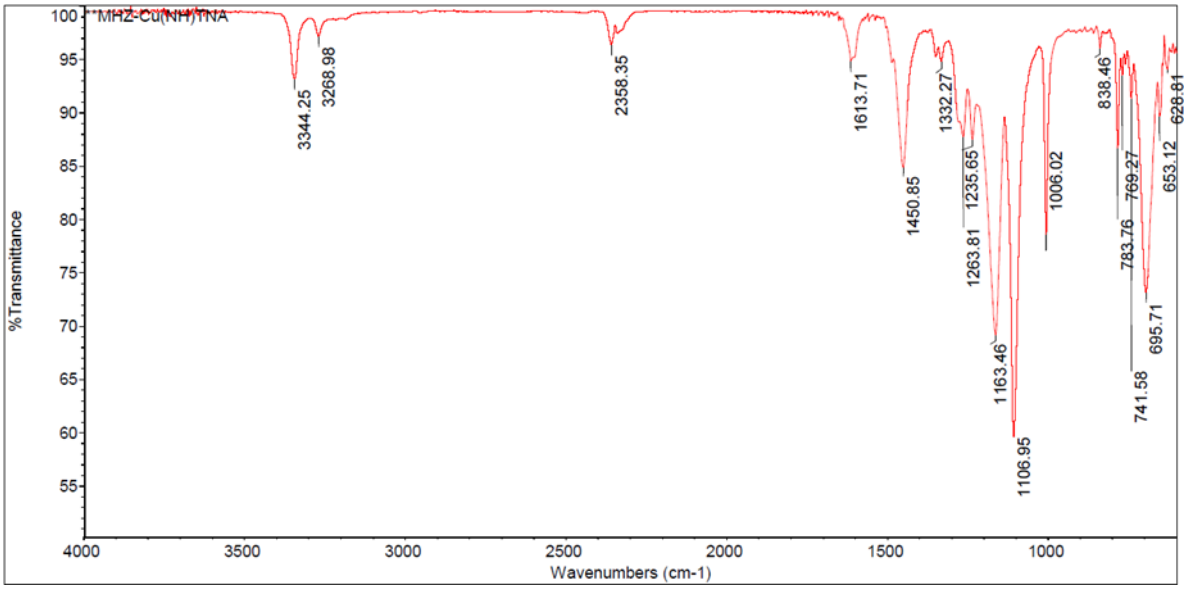

Figure S1. FT-IR spectra of salts **EP-1**.

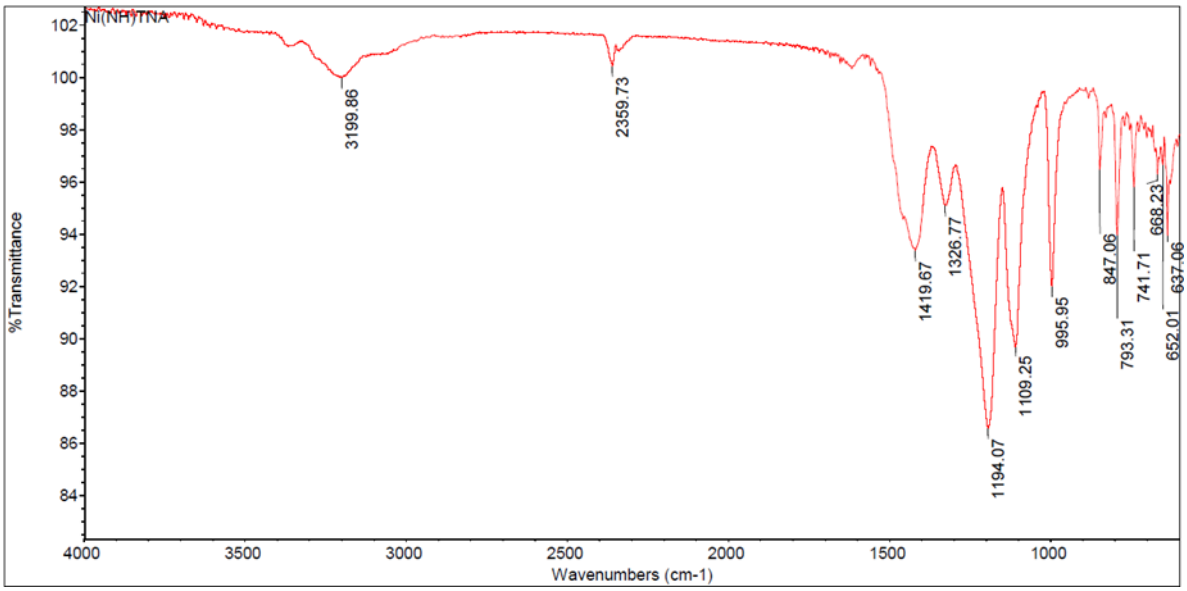

Figure S2. FT-IR spectra of salts **EP-2**.

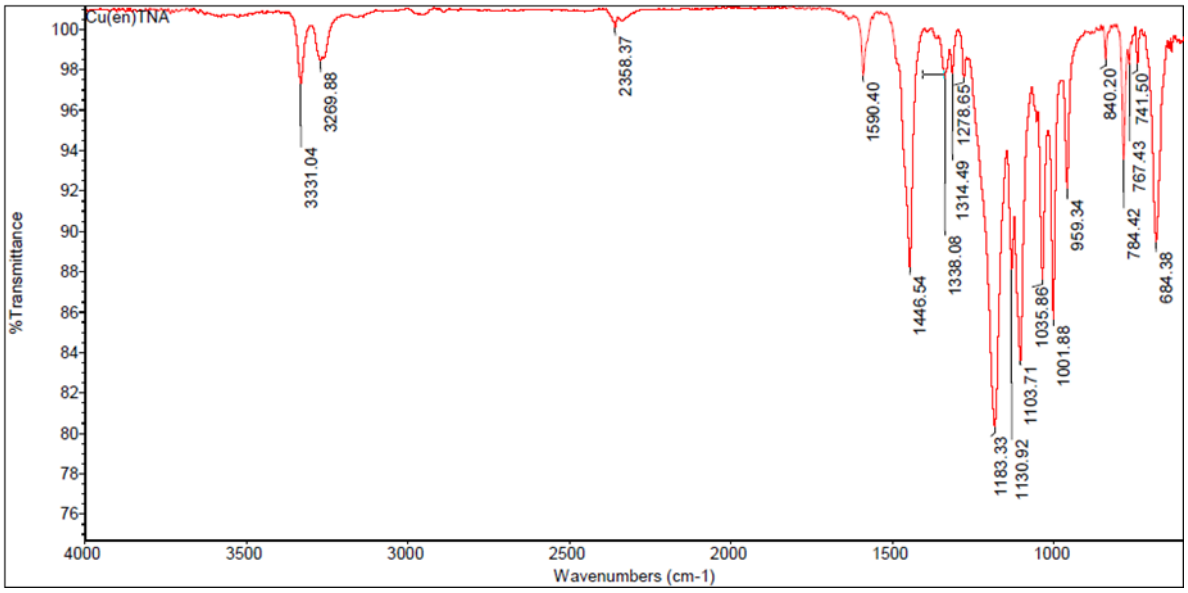

Figure S3. FT-IR spectra of **EP-3**.

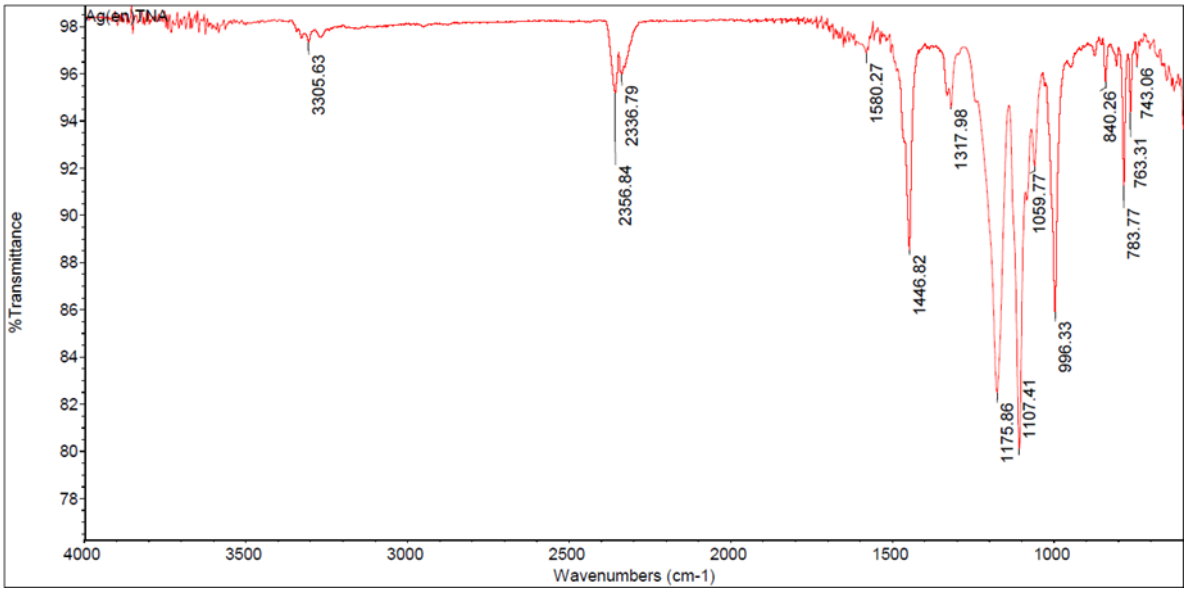

Figure S4. FT-IR spectra of salts **EP-4**.

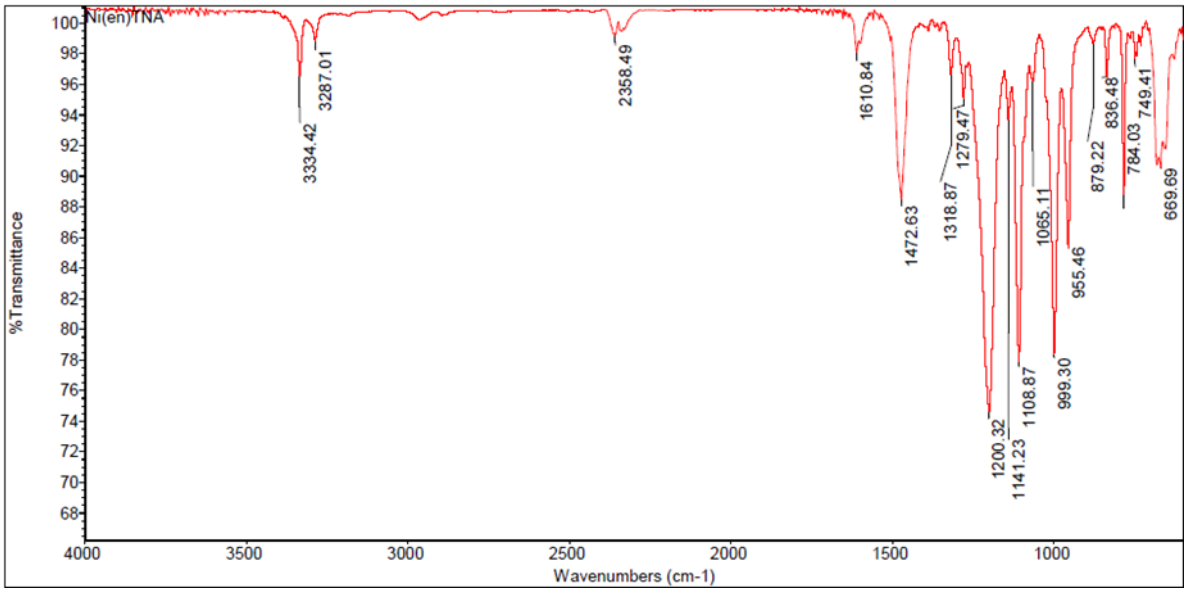

Figure S5. FT-IR spectra of salts **EP-5**.

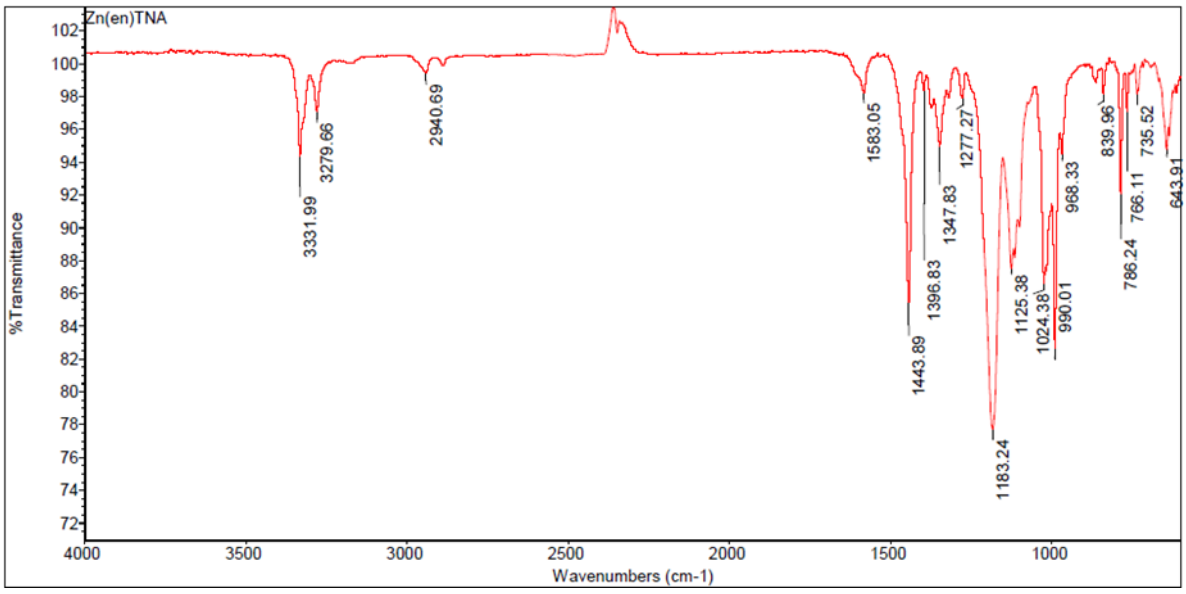

Figure S6. FT-IR spectra of **EP-6**.

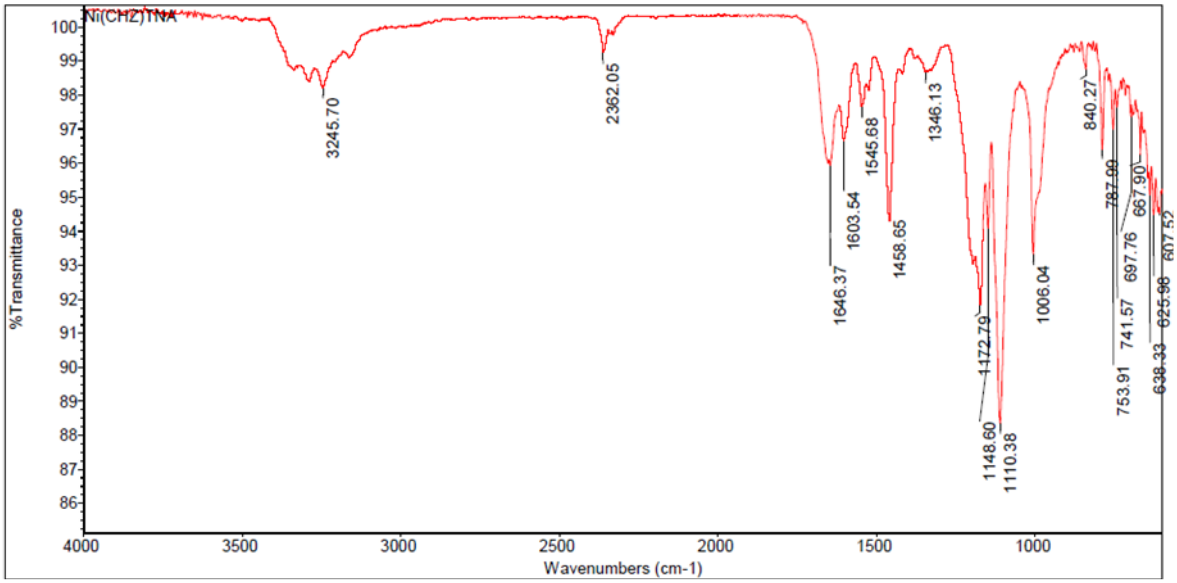

Figure S7. FT-IR spectra of **EP-7**.

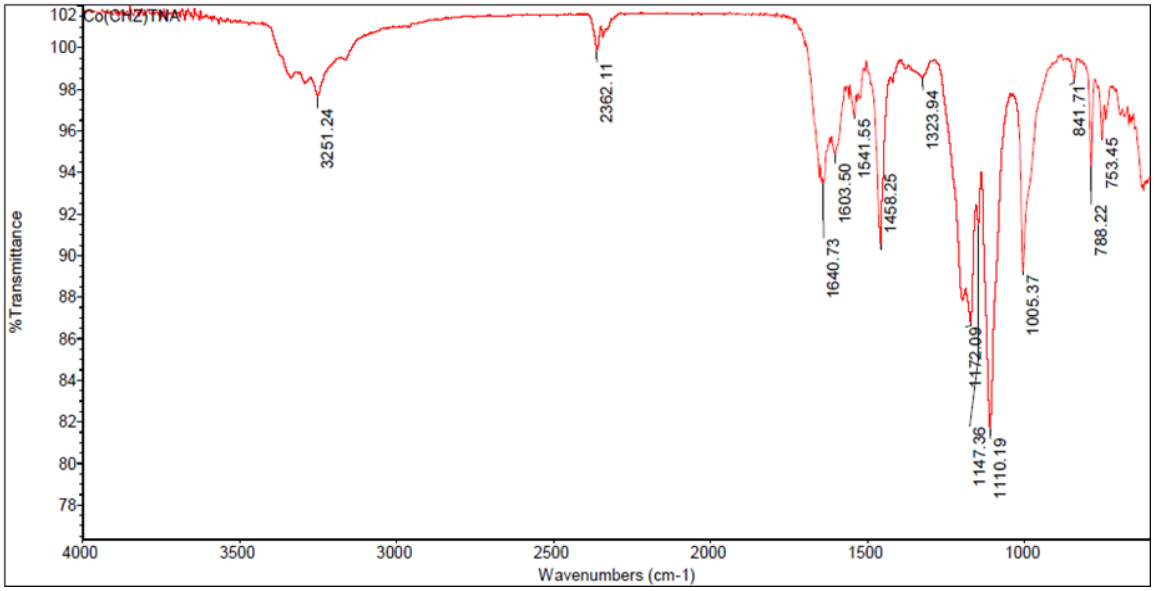

Figure S8. FT-IR spectra of **EP-8**.

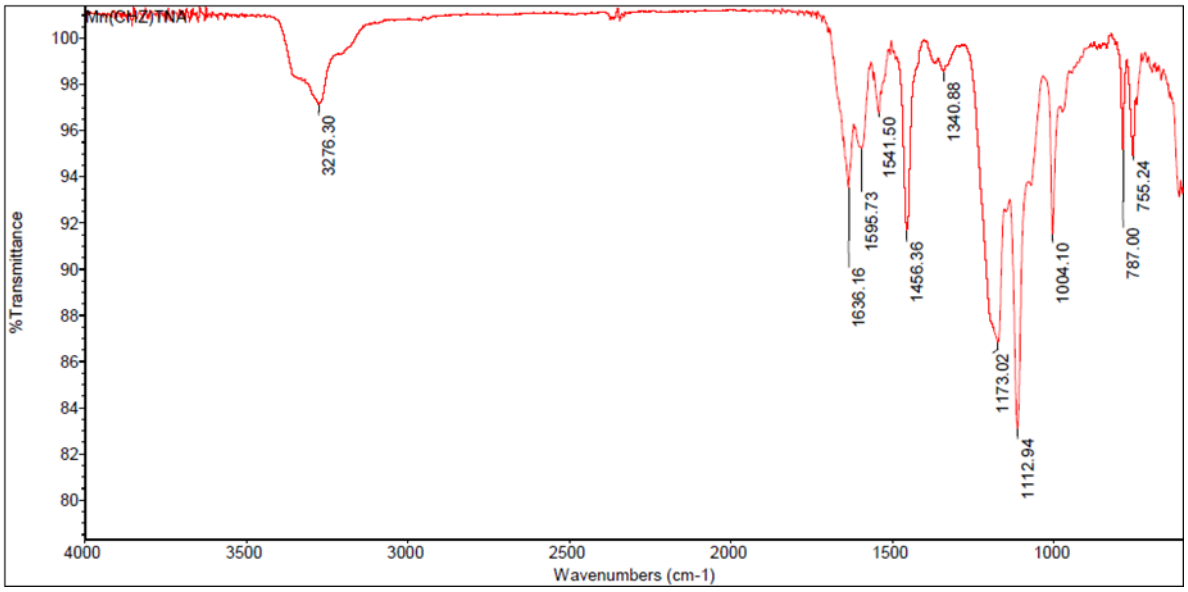

Figure S9. FT-IR spectra of **EP-9**.

4. Thermal stability analysis

To study the thermal decomposition reaction process of tetranitroethane energetic complexes, the thermal decomposition behavior of tetranitroethane energetic complexes at different heating rates was tested by differential calorimeter (DSC). The test conditions used in DSC were as follows: the heating rates were 5 $^{o}C \cdot min^{-1}$, 10 $^{o}C \cdot min^{-1}$, 15 $^{o}C \cdot min^{-1}$, and 20 $^{o}C \cdot min^{-1}$, the temperature range was 40-500^{o}C, the flow rate was 20 $mL \cdot min^{-1}$ with nitrogen atmosphere, and the stainless steel pressure sealed crucible. The detailed data of the peak temperature of the first exothermic decomposition peak of **EP-1-EP-9** at different heating rates were shown in and **Figure S10** and **Table S3**.

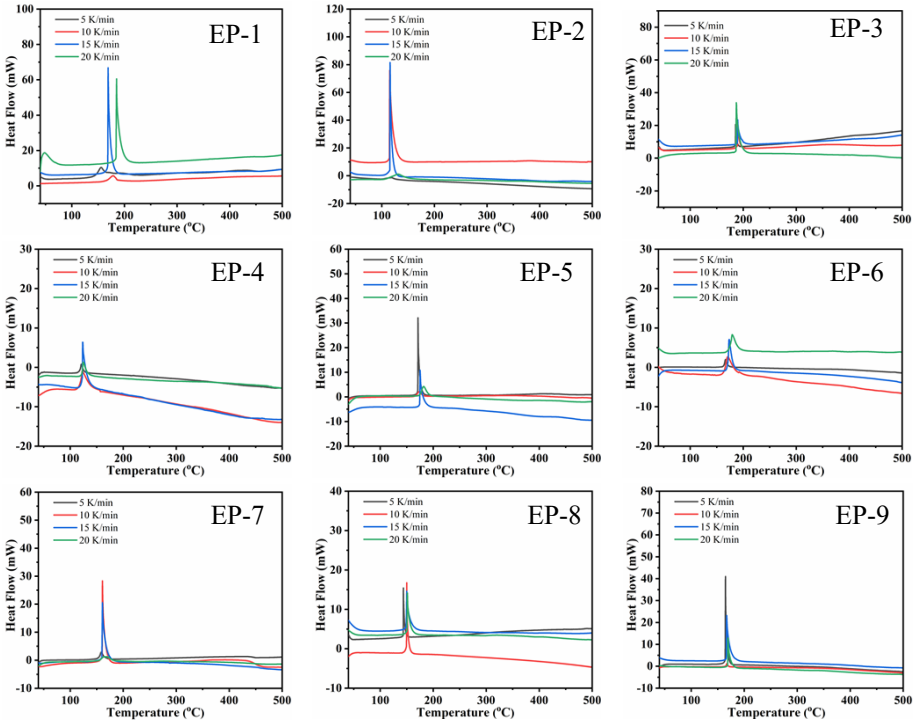

Figure S10. DSC curves of **EP-1-EP-9** at different heating rates.

Table S3. The first exothermic decomposition peak temperature of **EP-1-EP-9**.

Comp.	Heating rate ($^{o}C \cdot min^{-1}$); Peak temperature (^{o}C)			
	5	10	15	20
EP-1	179	181	184	188
EP-2	112	114	116	120
EP-3	187	191	195	199
EP-4	120	121	123	125
EP-5	171	173	175	181
EP-6	167	174	180	185
EP-7	159	162	162	166
EP-8	144	148	151	152
EP-9	164	168	170	172

To explore the decomposition mechanism of **EP-1-EP-9**, the kinetic parameters including apparent activation energy (E_a) and pre-exponential constant (A) are determined by the Kissinger's method and Ozawa-Doyle's method. The equations (Equation (S1) and Equation (S2)) of the two methods are as follows:

Kissinger's method：

$$\ln\frac{\varphi}{T_m^2}=\left[\ln A-\ln\frac{E_a}{R}\right]-\frac{E_a}{RT_m} \quad (S1)$$

Ozawa's method：

$$\lg\varphi=\lg\frac{AE_a}{RG(\alpha)}-2.315-0.4567E_a/RT \quad (S2)$$

Where T_p is the peak temperature (°C) of decomposition progress. R is the gas constant (8.314 J mol^{-1} K^{-1}), β is the linear heating rate (K min^{-1}). E_a is the apparent activation energy (kJ mol^{-1}). A represents the pre-exponential constant.

Table S4. Kinetic parameters of non-isothermal thermal decomposition reaction of **EP-1-EP-9**.

Comp.	Kissinger's method			Ozawa's method	
	E_K(kJ/mol)	r_K	lnA_K(1/s)	E_O(kJ/mol)	r_O
EP-1	245.1	-0.9588	65.00	240.3	-0.9611
EP-2	200.9	-0.9314	25.47	197.2	-0.9353
EP-3	194.8	-0.9822	50.44	192.6	-0.9922
EP-4	326.4	-0.9416	41.79	326.4	-0.9437
EP-5	201.0	-0.9055	21.78	198.3	-0.9100
EP-6	119.9	-0.9919	31.80	121.1	-0.9929
EP-7	293.0	-0.9275	81.55	285.6	-0.9306
EP-8	256.3	-0.9941	73.66	250.4	-0.9944
EP-9	276.9	-0.9989	31.26	270.3	-0.9990

To further estimate the rate constant of the initial decomposition process of **EP-1-EP-9**, the Arrhenius equation can be expressed as follows:

EP-1：$\ln k=65.00-245.1\times10^3/(RT)$

EP-2：$\ln k=306.02-991.9\times10^3/(RT)$

EP-3：$\ln k=50.44-194.8\times10^3/(RT)$

EP-4：$\ln k=148.96-486.6\times10^3/(RT)$

EP-5：$\ln k=176.19-650.4\times10^3/(RT)$

EP-6：$\ln k=31.80-119.8\times10^3/(RT)$

EP-7: $\ln k = 81.55 - 293.0 \times 10^3/(RT)$

EP-8: $\ln k = 73.66 - 256.3 \times 10^3/(RT)$

EP-9: $\ln k = 106.58 - 388.9 \times 10^3/(RT)$

In order to evaluate the thermal safety of **EP-1-EP-9**, the critical temperature of thermal explosion (T_{bp0}), entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) can be used to determine the corresponding strength of thermal stimulation. The calculation formulas are shown in

$$T_{pi} = T_{p0} + a\beta + b\beta^2 + c\beta^3 \quad \text{(S3)}$$

$$T_{bp} = \frac{E_O - \sqrt{E_O^2 - 4E_O RT_{p0}}}{2R} \quad \text{(S4)}$$

$$A = \frac{k_B T_{p0}}{h} e^{\left(1 + \Delta S^{\neq}/R\right)} \quad \text{(S5)}$$

$$\Delta H^{\neq} = E_k - RT_{p0} \quad \text{(S6)}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T_{p0}\Delta S^{\neq} \quad \text{(S7)}$$

Where a, b, c are constants. β is heating rate. E_O is the apparent activation energy corresponding to Ozawa equation. E_K is the apparent activation energy corresponding to Kissinger equation. k_B is Boltzmann constant (1.381×10^{-23} J K^{-1}), h is Planck constant (6.626×10^{-34} J·s), and $T = T_{p0}$, $A = A_k$, $E_a = E_k$. The calculated critical temperature and thermodynamic parameters were shown in **Table S5**.

Table S5. Thermal explosion critical temperature and thermodynamic parameters of **EP-1-EP-9.**

Comp.	T_{p0} (°C)	T_{bp} (°C)	$\Delta S^{\neq}$ (J·mol^{-1}·K^{-1})	$\Delta H^{\neq}$ (kJ·mol^{-1})	$\Delta G^{\neq}$ (kJ·mol^{-1})
EP-1	175	176	291.9	243.7	192.4
EP-2	116	116	2301.7	991.0	724.3
EP-3	184	185	1704	193.3	161.9
EP-4	119	119	994.1	485.6	367.6
EP-5	173	174	1217.6	648.9	437.9
EP-6	156	158	16.5	118.6	115.9
EP-7	147	148	431.2	291.8	228.2
EP-8	143	144	365.7	255.1	202.9
EP-9	168	168	638.4	387.6	280.6

5. Calculation of heats of formation

The constant-volume combustion energy of **EP-1-EP-9** were determined by an oxygen bomb calorimetry (OZM BAC500). The recorded data are the average of five single measurements. The calorimeter is calibrated by the combustion of certified benzoic acid in an oxygen atmosphere at a pressure of 30 bar. Under the experimental condition of 298 K, the constant volume combustion heat (Q_v) is measured with an oxygen bomb calorimeter, and the gas generated in the combustion process is treated as an ideal gas. For a closed system, there is a conversion between constant volume combustion heat and constant pressure combustion heat, as shown in **equation S8**.

$$Q_p = Q_v + \Delta nRT \quad (S8)$$

Where Δn is the change in the number of gas products during the reaction process, R is 8.314 $J \cdot mol^{-1} \cdot K^{-1}$, and T is 298.15 K.

The combustion equations for **EP-1-EP-9** are as follows:

$$CuC_2H_{12}N_8O_8(s) + 1.5\ O_2(g) \rightarrow CuO(s) + 2\ CO_2(g) + 6\ H_2O(l) + 4\ N_2(g) \quad (S9)$$

$$NiC_2H_{18}N_{10}O_8(s) + 3\ O_2(g) \rightarrow NiO(s) + 2\ CO_2(g) + 9\ H_2O\ (l) + 5\ N_2(g) \quad (S10)$$

$$CuC_6H_{16}N_8O_8(s) + 6.5\ O_2(g) \rightarrow CuO(s) + 6\ CO_2(g) + 8\ H_2O\ (l) + 4\ N_2(g) \quad (S11)$$

$$Ag_2C_6H_{18}N_8O_9(s) + 6.5\ O_2(g) \rightarrow Ag_2O(s) + 6\ CO_2(g) + 9\ H_2O(l) + 4\ N_2(g) \quad (S12)$$

$$NiC_8H_{24}N_{10}O_8(s) + 7\ O_2(g) \rightarrow NiO(s) + 8\ CO_2(g) + 5\ H_2O\ (l) + 5\ N_2(g) \quad (S13)$$

$$ZnC_8H_{24}N_{10}O_8(s) + 10\ O_2(g) \rightarrow ZnO(s) + 8\ CO_2(g) + 12\ H_2O\ (l) + 5\ N_2(g) \quad (S14)$$

$$NiC_5H_{18}N_{16}O_{11}(s) + 4.5\ O_2(g) \rightarrow NiO(s) + 5\ CO_2(g) + 9\ H_2O\ (l) + 8\ N_2(g) \quad (S15)$$

$$CoC_5H_{18}N_{16}O_{11}(s) + 4.5\ O_2(g) \rightarrow CoO(s) + 5\ CO_2(g) + 9\ H_2O\ (l) + 8\ N_2(g) \quad (S16)$$

$$MnC_5H_{18}N_{16}O_{11}(s) + 4.5\ O_2(g) \rightarrow MnO(s) + 5\ CO_2(g) + 9\ H_2O\ (l) + 8\ N_2(g) \quad (S17)$$

According to Gass law, the standard molar combustion heat and standard molar enthalpy of formation can be obtained.Based on $\Delta_f H_m^{\theta}{}_{298}(CO_2, g) = -393.5\ kJ \cdot mol^{-1}$, $\Delta_f H_m^{\theta}{}_{298}(H_2O, l) = -285.8\ kJ \cdot mol^{-1}$, the standard molar enthalpy of formation of compounds **EP-1-EP-9** can be calculated.

Table S6. Calculation of formation enthalpy of **EP-1-EP-9**.

Comp.	Heat of combustion (J/g)	Heat of formation (kJ/mol)
EP-1	-4575	-1092.5
EP-2	-3167	-2425.1
EP-3	-8719	-1221.5
EP-4	-8577	-36.7
EP-5	-12330	-1304.7

EP-6	-12424	-1294.0
EP-7	-8217	-350.8
EP-8	-8198	-354.4
EP-9	-8163	-553.5