Electronic Supplementary Information

Nitrogen-Rich Energetic Salts of 5,5'-Dinitramino-3,3'-Methylene-1H-1,2,4-Bistriazolate: powerful alliance towards good thermal stability and high performance

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1. X-ray crystallography determinations

Table S1 X-ray Crystallographic Data for $(DAG)_2(DNAMT)\cdot 4H_2O$(**1**) and $(NH_2OH)_2(DNAMT)\cdot H_2O$(**2**)

Compound	$(DAG)_2(DNAMT)\cdot 4H_2O$(**1**)	$(NH_3OH)(DNAMT)$ (**2**)
CCDC	1939348	2422609
Formula	$C_7H_{28}N_{20}O_8$	$C_5H_9N_{11}O_5$
M (g·mol^{-1})	520.49	303.2
Cryst. Syst.	monoclinic	monoclinic
Space Group	C2/c	$P2_1/c$
a (Å)	21.170(4)	4.2790(4)
b (Å)	4.5087(9)	8.6368(8)
c (Å)	23.576(5)	30.854(3)
β (deg.)	103.79(3)	92.692(3)
V (Å^3)	2185.5(8)	1139.01(18)
Z	4	4
ρ (g·cm^{-3})	1.582	1.768
F(000)	1096	624

Table S2 Selected Bond Lengths for $(DAG)_2(DNAMT)\cdot 4H_2O$(**1**)

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.249(2)	N5	C2	1.322(3)
O2	N1	1.260(2)	C3	C21	1.495(3)
N4	N5	1.372(2)	C3	C2	1.495(3)
N4	C1	1.334(3)	N8	N7	1.412(3)
N1	N2	1.320(2)	N9	C4	1.325(3)
N3	C1	1.342(2)	N9	N10	1.409(3)
N3	C2	1.361(3)	C4	N6	1.325(3)
N2	C1	1.380(3)	C4	N7	1.334(3)

Table S3 Selected Bond Angles for $(DAG)_2(DNAMT)\cdot 4H_2O$(**1**)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	N1	O2	121.24(18)	C4	N9	H9	122.00
O2	N1	N2	116.52(18)	N10	N9	H9	118.00
O1	N1	N2	122.25(18)	N9	N10	H10B	112.00
N1	N2	C1	117.30(18)	N9	N10	H10A	107.00
C1	N3	C2	103.04(17)	N2	C1	N3	118.35(17)
N5	N4	C1	110.07(17)	N3	C1	N4	109.77(18)
N4	N5	C2	102.47(17)	N2	C1	N4	131.88(19)
N5	N4	H4	120.00	N3	C2	N5	114.66(19)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N4	H4	130.00	N3	C2	C3	122.88(17)
N8	N7	C4	117.67(18)	N5	C2	C3	122.46(18)
N10	N9	C4	119.08(19)	C2	C3	C2_a	113.3(2)
C4	N6	H6A	119.00	C2	C3	H3B	109.00
C4	N6	H6B	121.00	C2	C3	H3A	109.00
C4	N7	H7	119.00	C2_a	C3	H3B	109.00
N8	N7	H7	123.00	C2_a	C3	H3A	109.00
N7	N8	H8A	106.00	N6	C4	N7	119.5(2)
N7	N8	H8B	106.00	N6	C4	N9	121.2(2)
H6A	N6	H6B	120.00	N7	C4	N9	119.3(2)

Table S4 Selected Torsion Angles for $(DAG)_2(DNAMT)\cdot 4H_2O$(**1**)

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N4	N5	C2	N3	0.1(2)	O1	N1	N2	C1	1.6(3)
N4	N5	C2	C3	179.51(18)	O2	N1	N2	C1	-178.27(18)
N1	N2	C1	N4	-6.0(3)	C1	N4	N5	C2	-0.2(2)
N1	N2	C1	N3	174.40(18)	C1	N3	C2	N5	0.1(2)
N5	N4	C1	N3	0.3(2)	C1	N3	C2	C3	-179.33(19)
N5	N4	C1	N2	-179.3(2)	C2	N3	C1	N4	-0.3(2)
N9	C4	N7	N8	-2.2(3)	C2	N3	C1	N2	179.43(18)
N10	N9	C4	N6	2.8(3)	C2	C3	C2	N3	-60.84(17)
N10	N9	C4	N7	-175.0(2)	C2	C3	C2	N5	119.8(2)
N6	C4	N7	N8	179.9(2)					

Table S5 Hydrogen bond lengths /Å and angles /º of $(DAG)_2(DNAMT)\cdot 4H_2O$(**1**)

D-H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
O3-H3C···O2	0.8400	2.0700	2.891(3)	167.00
O3-H3D···N5	0.8400	2.1100	2.939(3)	169.00
N4-H4···O1	0.8500	2.1700	2.574(2)	109.00
N4-H4···O1	0.8500	2.0400	2.820(2)	152.00
O4-H4A···O3	0.8400	2.1000	2.918(3)	163.00
O4-H4B···O4	0.8400	2.2900	2.797(3)	119.00
N6-H6A···N10	0.8500	2.3600	2.699(3)	104.00
N6-H6A···N10	0.8500	2.3200	3.011(3)	139.00
N6-H6B···N2	0.8500	2.0600	2.907(3)	174.00
N7-H7···N3	0.8500	2.0500	2.899(3)	176.00
N8-H8B···O3	0.8500	2.2800	3.039(3)	150.00
N9-H9···O4	0.8500	2.0000	2.799(3)	156.00
N9-H9···N8	0.8500	2.3300	2.640(3)	102.00
N10-H10A···N2	0.8500	2.6000	3.433(3)	168.00

Table S6 Selected Bond Lengths for (NH_3OH)(DNAMT)(**2**)

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
C1	H1A	0.9700	N6	N7	1.389(4)
C1	H1B	0.9700	N7	C5	1.336(5)
N1	C2	1.329(5)	N7	H7	0.8600
N1	N2	1.386(4)	N8	C5	1.347(4)
N2	C3	1.331(5)	N8	C4	1.375(5)
N2	H2	0.8600	N8	H8	0.8600
N3	C3	1.352(4)	N9	N10	1.323(5)
N3	C2	1.356(5)	N9	C5	1.368(5)
N4	N5	1.329(4)	N10	O4	1.240(4)
N4	C3	1.385(5)	N10	O3	1.258(4)
N5	O2	1.257(4)	N11	O5	1.420(5)
N5	O1	1.273(4)	N11	H11A	0.8900
N6	C4	1.315(5)	N11	H11B	0.8900
C1	C4	1.495(5)	N11	H11C	0.8900
C1	C2	1.512(5)	O5	H5	0.8200

Table S7 Selected Bond Angles for (NH_3OH)(DNAMT)(**2**)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5	N11	H11A	109.5	N6	C4	C1	124.7(3)
O5	N11	H11B	109.5	N5	N4	C3	115.6(3)
O5	N11	H11C	109.5	N3	C2	C1	121.9(3)
O4	N10	N9	116.2(3)	N3	C3	N4	117.8(3)
O4	N10	O3	121.9(4)	N2	C3	N3	109.5
O3	N10	N9	121.8(3)	N2	C3	N4	132.7(3)
O2	N5	N4	123.8(3)	N11	O5	H5	109.5
O2	N5	O1	120.6(3)	N10	N9	C5	117.0(3)
O1	N5	N4	115.6(3)	N1	N2	H2	125
N8	C5	N9	134.6(3)	C5	N8	C4	106.8(3)
N8	C4	C1	123.5(3)	C5	N7	N6	111.6(3)
N7	C5	N8	106.4(3)	C4	N6	N7	103.4(3)
N7	C5	N9	119.0(3)	C3	N2	H2	125
C2	C1	H1B	109.3	C2	N1	N2	102.4(3)

Table S8 Selected Torsion Angles for (NH_3OH)(DNAMT)(**2**)

A	B	D	C	Angle/°	A	B	D	C	Angle/°
C2	N1	N2	C3	-0.6(4)	C2	N3	C3	N2	0.3(4)
C3	N4	N5	O2	1.5(6)	C2	N3	C3	N4	179.4(3)
C3	N4	N5	O1	-177.0(3)	N5	N4	C3	N2	-9.1(6)
C4	N6	N7	C5	-1.6(4)	N5	N4	C3	N3	172.1(3)
C5	N9	N10	O4	-175.9(3)	N7	N6	C4	N8	0.9(4)
C5	N9	N10	O3	6.1(5)	N7	N6	C4	C1	178.8(3)

A	B	D	C	Angle/°	A	B	D	C	Angle/°
N2	N1	C2	N3	0.9(4)	C5	N8	C4	N6	0.1(4)
N2	N1	C2	C1	-177.7(3)	C5	N8	C4	C1	-177.8(3)
C3	N3	C2	N1	-0.8(4)	C2	C1	C4	N6	-113.1(4)
C3	N3	C2	C1	177.8(3)	C2	C1	C4	N8	64.5(5)
C4	C1	C2	N1	-147.9(4)	N6	N7	C5	N8	1.7(4)
C4	C1	C2	N3	33.7(5)	N6	N7	C5	N9	-177.5(3)
N1	N2	C3	N3	0.2(4)	C4	N8	C5	N7	-1.0(4)
N1	N2	C3	N4	-178.7(4)	C4	N8	C5	N9	177.9(4)
N10	N9	C5	N7	179.3(3)	N10	N9	C5	N8	0.4(7)

Table S9 Hydrogen bond lengths /Å and angles /º of (NH_3OH)(DNAMT)(**2**)

D-H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠DHA**
N2-H2···O2	0.86	2.11	2.585 (4)	114.00
N2-H4···O1	0.86	2.1	2.848(4)	145
O5-H5···N1	0.82	1.97	2.792(4)	177
N7-H7···N9	0.86	2.18	2.614(4)	111
N8-H8···N3	0.86	1.96	2.758(4)	154
N11-H11A···N4	0.89	2.33	3.211(5)	172
N11-H11B···O3	0.89	1.99	2.860(5)	167
N11-H11C···O1	0.89	2.24	3.056(4)	152
N11-H11C···O2	0.89	2.23	3.032(5)	149
N11-H11C···N5	0.89	2.57	3.465(5)	179
C1-H1B···O4	0.97	2.33	2.962(5)	122

2. FT-IR spectrums

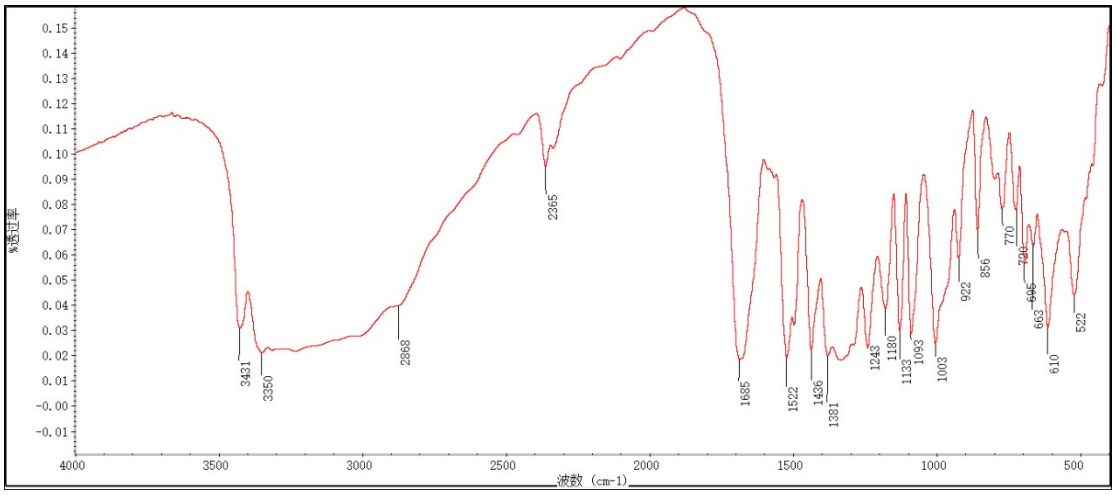

Fig.S1 FT-IR spectra of $(DAG)_2(DNAMT)\cdot 4H_2O$(**1**)

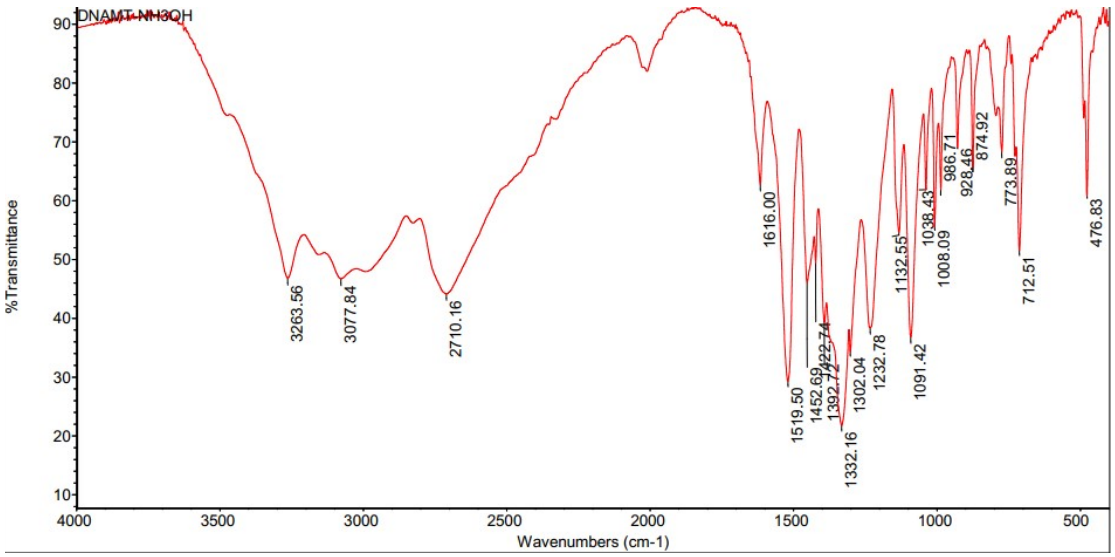

Fig.S2 FT-IR spectra of $(NH_2OH)(DNAMT)$(**2**)

3. ^{1}H NMR and ^{13}C NMR spectrum

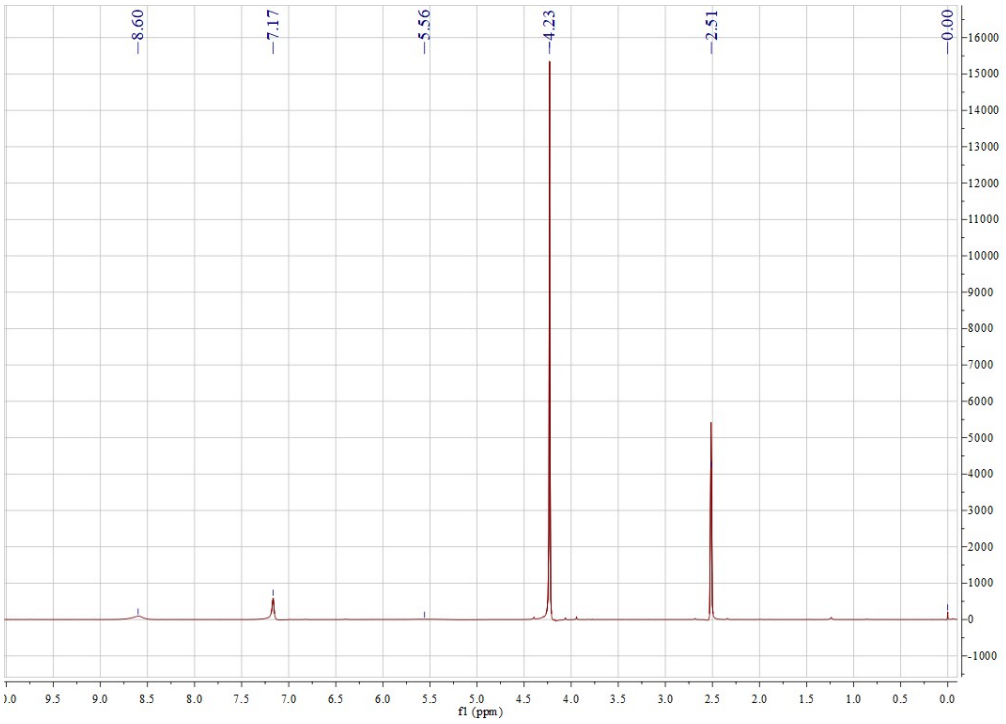

Fig.S3 ^{1}H NMR spectrum of **1**

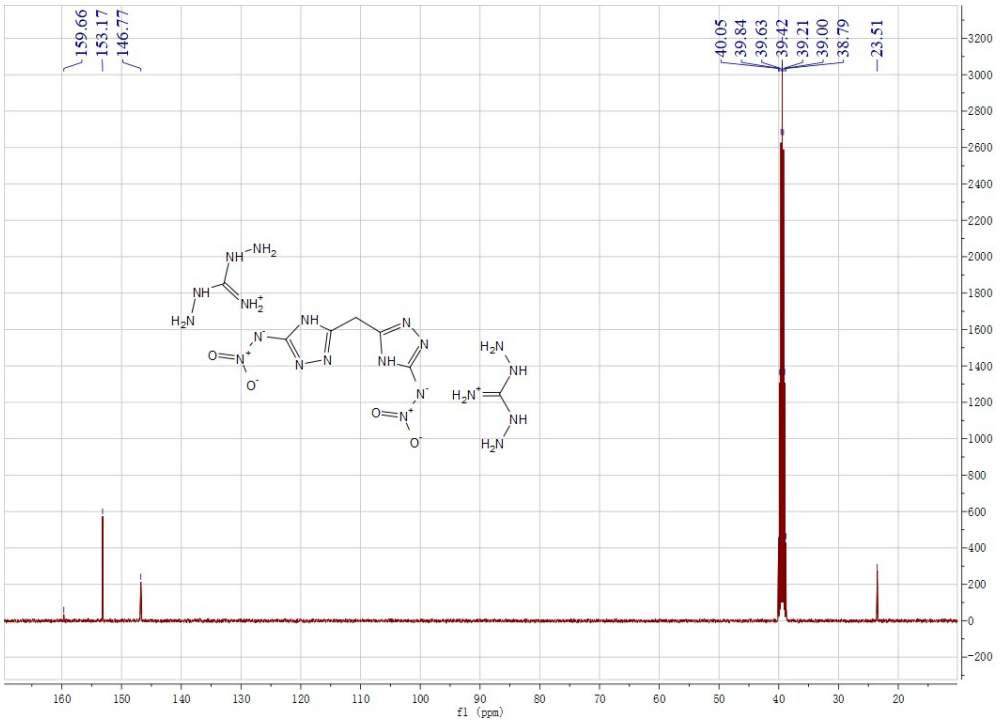

Fig.S4 ^{13}C NMR spectrum of **1**

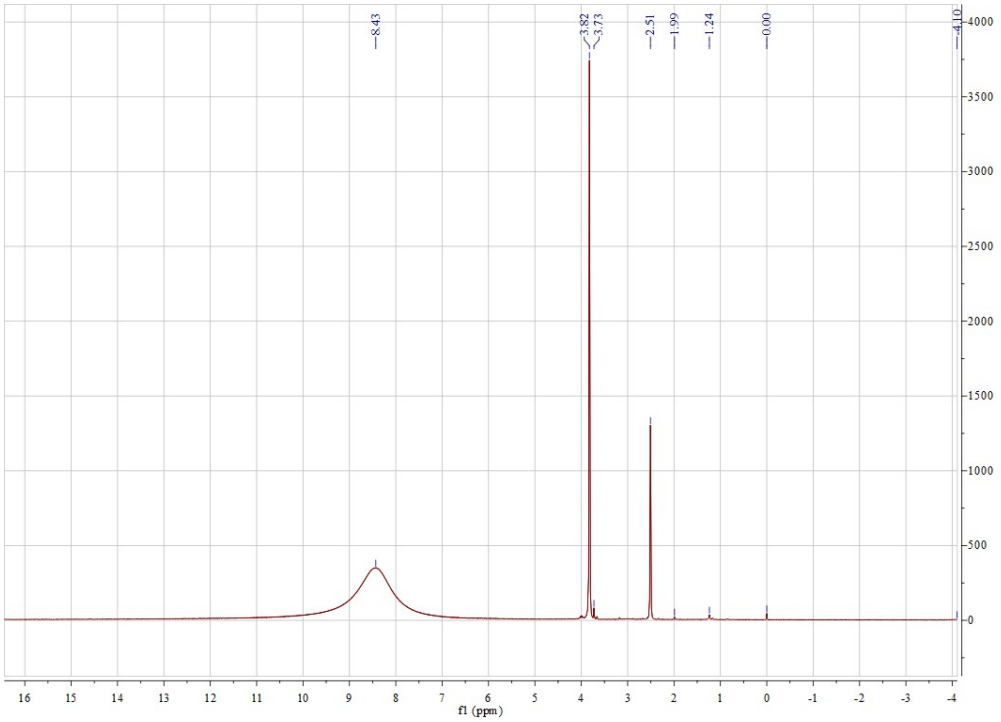

Fig.S5 ^{1}H NMR spectrum of **2**

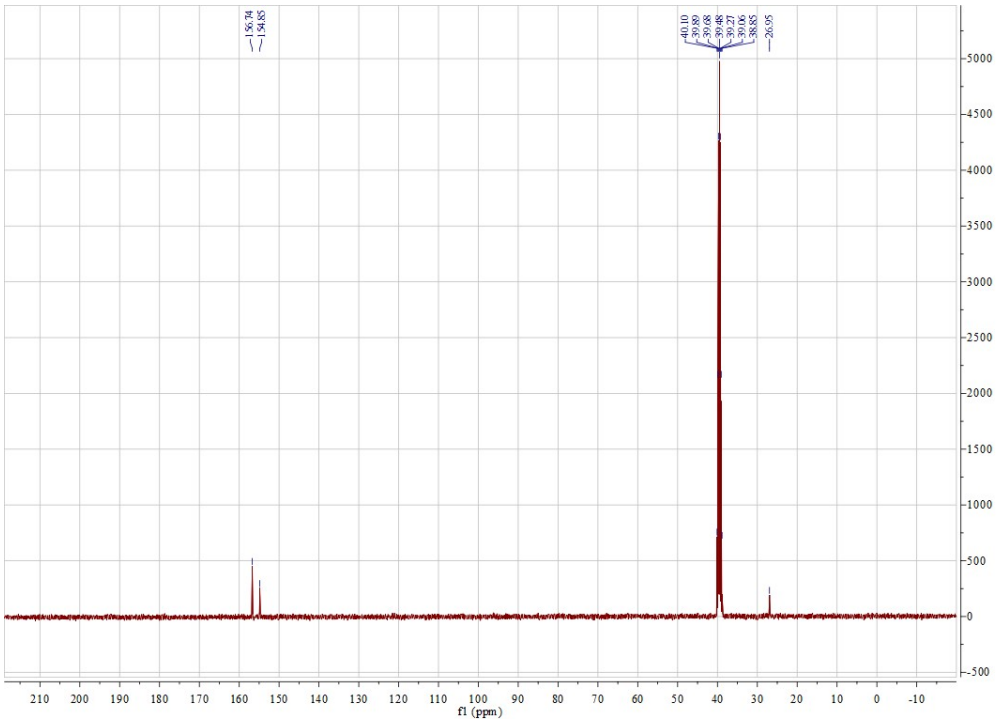

Fig.S6 ^{13}C NMR spectrum of **2**

5. Thermo-stability measurement (DSC)

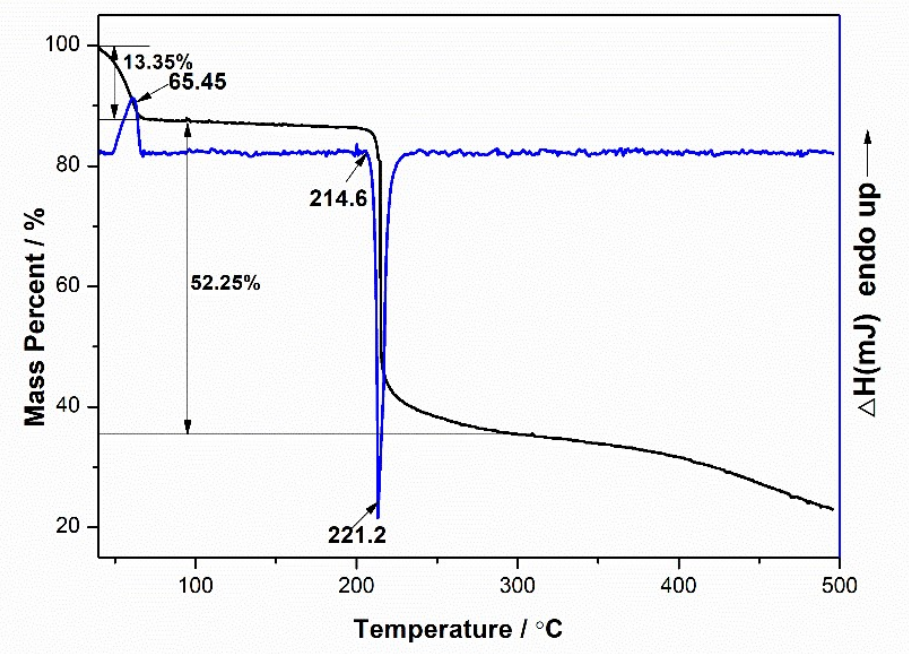

Fig.S7 DSC and TG curves of compound **1** (β=10 ℃·min^{-1})

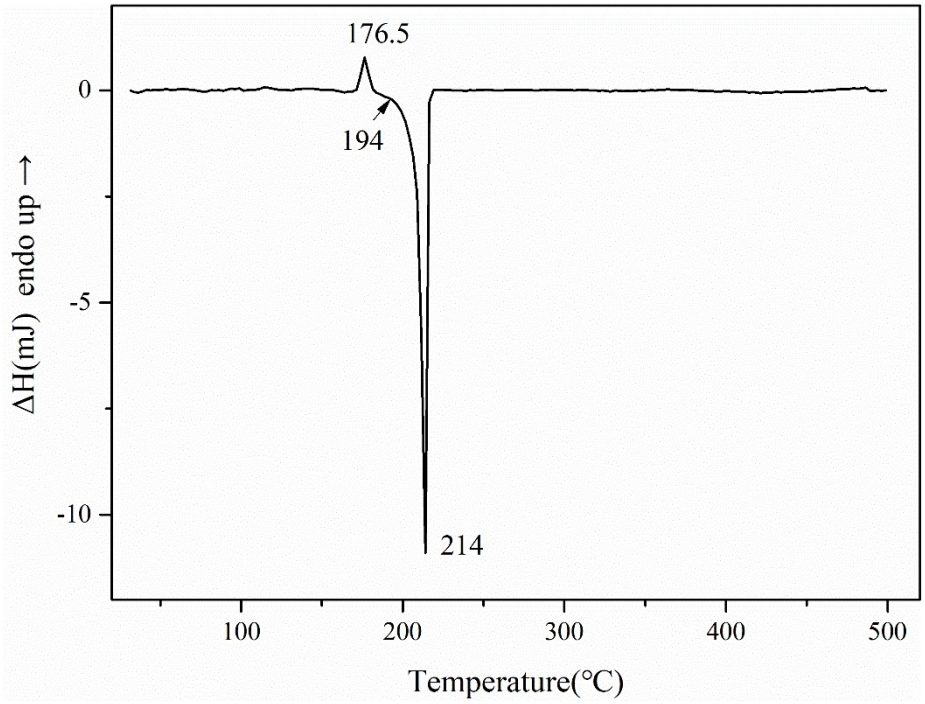

Fig.S8 DSC curves of compound **2** (β=10 ℃·min^{-1})

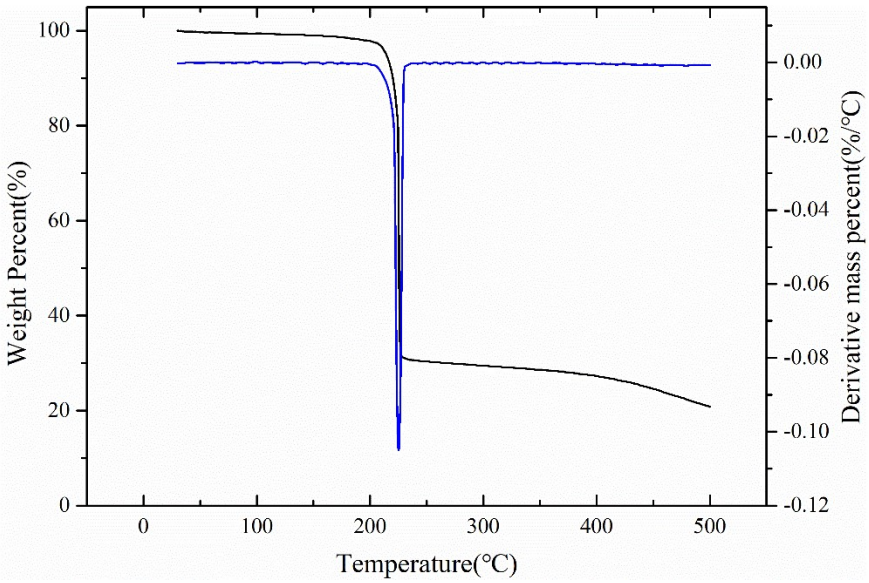

Fig.S9 TG and DTG curves of compound **2** (β=10 °C·min^{-1})

6. Non-isothermal kinetics analysis

The kinetics parameters, such as the apparent activation energy (*Ea*), the pre-exponential factor (*A*), were calculated by Kissinger's method[1] and the Ozawa's method[2] based on the exothermic decomposition peak temperature of different heating rates. The equations of the two methods (Eq. (1) to (2)) are as follows. where, T_p is the peak temperature (K), R is the gas constant 8.314 (J·mol^{-1}·K^{-1}), β is the linear heating rate (K·min^{-1}), C is a constant.

$$ln\frac{\beta}{T_P^2} = ln\frac{AR}{E_a} - \frac{E_a}{RT_P} \quad (1)$$

$$\lg\beta + 0.4567\frac{E_a}{RT_P} = C \quad (2)$$

Table S10 The peak temperature decomposition of compounds **1** and **2**.

β (K·min^{-1})	Compound **1**	Compound **2**
5 K·min^{-1}	487.65	479.65
10 K·min^{-1}	494.35	487.15
15 K·min^{-1}	498.75	487.95
20 K·min^{-1}	501.95	491.75

Table S11 Non-isothermal reaction kinetics parameters and thermo-dynamic parameters of compounds **1** and **2**

Compound	Kissinger's method				Ozawa's method		
	E_k (kJ·mol^{-1})	$\lg A_K$	R_K	S	E_O (kJ·mol^{-1})	R_O	S
1	189.2	18.17	-0.9999	0.0105	188.5	-0.9999	0.0045
2	218.9	21.82	-0.9752	0.1575	215.9	-0.9768	0.0068

7. The calculation of thermodynamics parameters

The thermodynamics parameters (T_{p0}, T_b, $\Delta S^{\neq}$, $\Delta H^{\neq}$, $\Delta G^{\neq}$) were obtained by the Zhang's calculation equations[3] (3)~(7) and the results listed in Table S12. The equations for these calculations are as follows:

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

$$T_b = (E_K - \sqrt{E_K{}^2 - 4E_K RT_{p0}})/2R \quad (4)$$

$$A = (k_B T_{p0}/h)exp(1 + \Delta S^{\neq}/R) \quad (5)$$

$$\Delta H^{\neq} = E_K - RT_{p0} \quad (6)$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T_{p0}\Delta S^{\neq} \quad (7)$$

Where a, b and c are coefficients, k_B is the Boltzmann constant (1.381 ×10^{-23} J K^{-1}) and h is the Planck constant (6.626 ×10^{-34} J s). T_{p0} is the values of the peak temperature corresponding to β→0, T_b is the corresponding critical temperature of thermal explosion, $\Delta S^{\neq}$ is the entropy of activation, $\Delta H^{\neq}$ is the enthalpy of activation, and $\Delta G^{\neq}$ is the free energy of activation.

Table S12 Calculation of critical temperatures of thermal explosion, $\Delta S^{\neq}$, $\Delta H^{\neq}$ and $\Delta G^{\neq}$.

compound	T_{p0}/K	T_b/K	$\Delta S^{\neq}$/ J K^{-1} mol^{-1}	$\Delta H^{\neq}$/ kJ mol^{-1}	$\Delta G^{\neq}$/ kJ mol^{-1}
1	477.6	488.0	99.01	185.2	137.9
2	455.8	463.9	169.3	215.1	138.0

8. References

1 H. E. Kissinger, *Anal. Chem.*, 1957, **29**, 1702-1706.

2 T. Ozawa, Bull. *Chem. Soc. Jpn.*, 1965, **38**, 1881-1886.

3. T. Zhang, R. Hu, X. Yi and F. Li, Thermochim Acta, 1994, **244**, 171–176.