Electronic Supplementary Information

Energetic transition metal complexes based on methyl carbazate and picric acid: syntheses, structures, physicochemical properties and catalysis on the thermal decomposition of ammonium perchlorate

Xiaoming Yang[a], Yanna Wang[a,b], Zhimin Li[*a], Jiang Du[c], Lin Wang[a] and Tonglai Zhang[*a]

[a] State Key Laboratory of Explosion Science and Technology, Beijing Institute of Technology, Beijing 100081, China.

[b] College of Chemistry and Chemical Engineering, Xingtai University, Xing tai 054001, China.

[c] North Automatic Control Technology Institute, Taiyuan 030006, China.

*Corresponding author: Tonglai Zhang and Zhimin Li

Email:

Tonglai Zhang: ztlbit@bit.edu.cn

Zhimin Li: lizm@bit.edu.cn

Xiaoming Yang: 649726360@qq.com

Table of contents

1. FT-IR spectra

FT-IR spectra of compounds **1~7**.

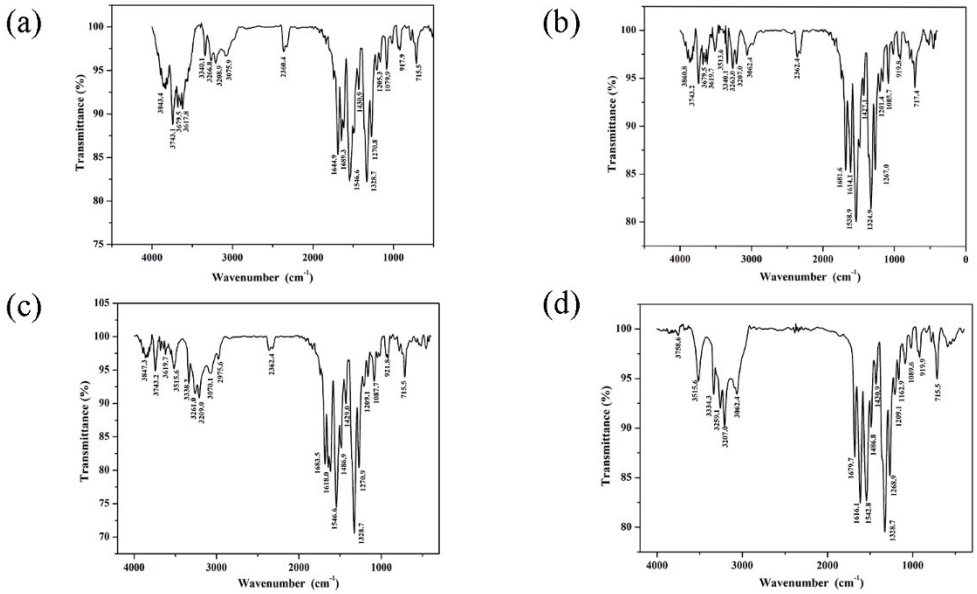

Fig. S1 The IR spectra of compounds **1**-**4**

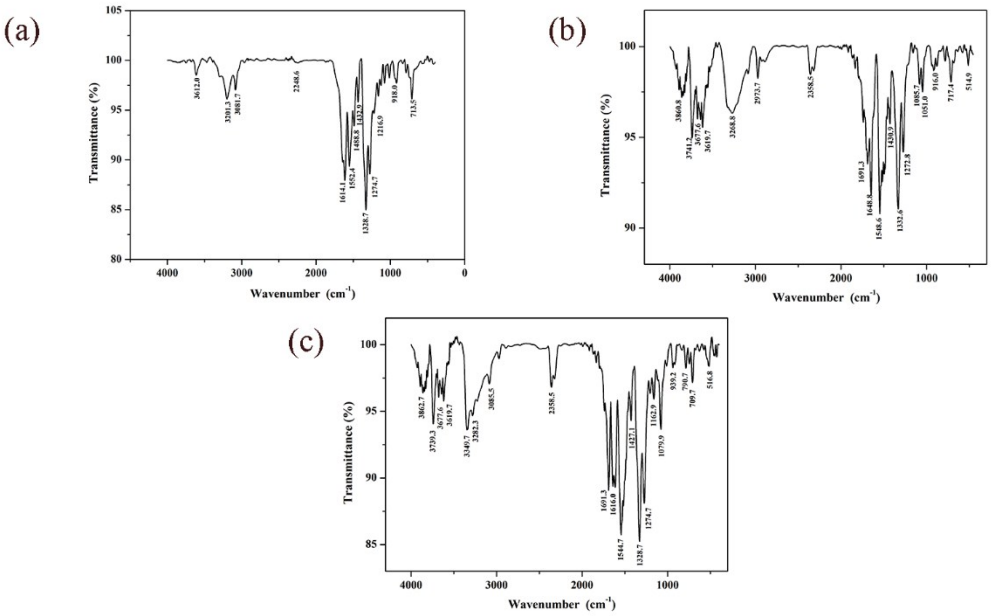

Fig. S2 The IR spectra of compounds **5**-**7**

2. Crystal data and structure refinement details of compounds 1~7

Table S1 Crystallographic data for **1**~**7**

	1	**2**	**3**	**4**	**5**	**6**	**7**
Formula	$C_{16}H_{20}MnN_{10}O_{20}$	$C_{16}H_{20}FeN_{10}O_{20}$	$C_{16}H_{20}CoN_{10}O_{20}$	$C_{16}H_{20}N_{10}NiO_{20}$	$C_{16}H_{20}CuN_{10}O_{20}$	$C_{16}H_{20}N_{10}O_{20}Zn$	$C_{16}H_{30}CdN_{10}O_{25}$
Form. mass/g mol^{-1}	727.36	728.27	731.35	731.13	735.96	737.79	874.90
Temperature/K	153.15	153.15	153.15	153.15	153.15	153.15	153.15
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	C2/c	C2/c	C2/c	C2/c	P-1	P-1	C2/c
a/Å	14.417 (3)	14.392(3)	14.361 (3)	14.276 (3)	7.1087 (14)	7.1016	12.551 (3)
b/Å	7.9325 (16)	7.9132 (16)	7.9175 (16)	7.9662 (16)	14.163 (3)	7.9404 (16)	8.5075 (17)
c/Å	24.414 (5)	24.259 (5)	24.317(5)	24.212 (5)	15.289 (3)	12.364 (3)	30.293 (6)
α/°	90	90	90	90	112.32 (3)	96.25(3)	90
β/°	101.44(3)	101.34(3)	101.49(3)	101.04(3)	100.42 (3)	92.51(3)	99.02(3)
γ/°	90	90	90	90	103.26 (3)	105.12 (3)	90
Volume/$Å^3$	2736.5	2708.9	2709.5	2702.5	1323.2	667.2	3194.6
Z	4	4	4	4	2	1	4
ρ_{calc}/g cm^{-3}	1.766	1.786	1.793	1.797	1.847	1.836	1.819
μ/mm^{-1}	0.594	0.669	0.746	0.831	0.941	1.035	0.800
F(000)	1484.0	1488.0	1492.0	1496.0	750.0	376.0	1776.0
Crystal size/mm^3	0.21 × 0.2 × 0.12	0.23 × 0.2 × 0.19	0.13 × 0.12 × 0.1	0.23 × 0.2 × 0.17	0.12 × 0.11 × 0.08	0.21 × 0.2 × 0.15	0.13 × 0.11 × 0.02
λ(Mo Kα)/ Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
2Θ range /°	6.088, 62.728	5.774 , 54.974	5.904, 54.972	5.816, 63.07	3.344, 54.984	5.356 , 54.98	5.446, 54.954
flections collected	18765	10572	9140	11532	9808	6521	12527
Independent reflections	4165	3080	3086	4027	5940	3012	3619
Data/restraints/ parameters	4165/0/214	3080/0/214	3086/0/214	4027/0/214	5940/0/425	3012/18/225	3619/0/237
Goodness-of-fit on F^2	1.131	1.112	1.070	1.082	1.143	1.068	1.117
R1; wR2 [I>=2σ (I)]	0.0541; 0.1274	0.0427; 0.1009	0.0397, 0.0973	0.0551, 0.1232	0.0842, 0.1541	0.0432, 0.0916	0.0442, 0.0895
R1; wR2 [all data]	0.0605; 0.1323	0.0456, 0.1029	0.0419, 0.0989	0.0648, 0.1306	0.1026, 0.1677	0.0443, 0.0925	0.0481, 0.0916
Resd. dens. (e $Å^{-3}$)	0.9/-0.61	0.51/-0.49	0.45/-0.41	0.56/-0.69	0.53/-0.88	0.28/-0.49	1.06/-0.83
CCDC	1881671	1881672	1881673	1881674	1882305	1881675	1881676

3. X-ray crystallography

Table S2 Selected bond lengths (Å) and band angles (°) of compound **1**

Selected bond lengths (Å)		
Mn1-O9 2.1830(15)	Mn1-O8 2.1382(16)	Mn1-N4 2.2832(18)
Selected band angles (°)		
O9-Mn1-O9 97.95 (9)	O9-Mn1-N4 73.43(6)	O9-Mn1-N4 85.24(6)
O8-Mn1-O9 89.99(6)	O8-Mn1-O9 172.00(6)	O8-Mn1-O8 82.09(9)
O8-Mn1-N4 106.47(6)	O8-Mn1-N4 98.02(6)	N4-Mn1-N4 147.43(9)

Table S3 Selected bond lengths (Å) and band angles (°) of compound **2**

Selected bond lengths (Å)		
Fe1-O9 2.1337(15)	Fe1-O10 2.0921(15)	Fe1-N5 2.2147(15)
Selected band angles (°)		
N5-Fe1-O9 75.41(6)	N5-Fe1-O10 105.87(6)	N5-Fe1-N5 151.06(10)
O9-Fe1-O9 95.76 (9)	O10-Fe1-O9 172.37(6)	O10-Fe1-O10 80.54(8)
O10-Fe1-O9 91.86(6)	O9-Fe1-N5 85.22(6)	O10-Fe1-N5 96.20(6)

Table S4 Selected bond lengths (Å) and band angles (°) of compound **3**

Selected bond lengths (Å)		
Co1-O1 2.0635(14)	Co1-O2 2.0994(14)	Co1-N1 2.1602(17)
Selected band angles (°)		
O1-Co1-O1 82.59(8)	O1-Co1-O2 172.88(5)	O1-Co1-O2 90.29(6)
O1-Co1-N1 95.18(6)	O1-Co1-N1 103.53(6)	O2-Co1-O2 96.83 (8)
O2-Co1-N1 86.32(6)	O2-Co1-N1 77.16(6)	N1-Co1-N1 155.08(9)

Table S5 Selected bond lengths (Å) and band angles (°) of compound **4**

Selected bond lengths (Å)		
Ni1-O1 2.0485(17)	Ni1-O3 2.0390(17)	Ni1-N1 2.107(17)
Selected band angles (°)		
O1-Ni1-O1 94.72(10)	O1-Ni1-N1 87.63(7)	O1-Ni1-N1 79.36(7)
O3-Ni1-O1 91.64(7)	O3-Ni1-O1 173.57(7)	O3-Ni1-O3 82.0(1)
O3-Ni1-N1 100.07(7)	O3-Ni1-N1 94.42(7)	N1-Ni1-N1 160.79(11)

Table S6 Selected bond lengths (Å) and band angles (°) of compound **5**

Selected bond lengths (Å)		
Cu01-O9 1.933(3)	Cu01-O10 2.297(3)	Cu01-O11 2.390(4)
Cu01-O12 1.980(3)	Cu01-N5 2.004(4)	Cu01-N6 2.019(4)
Selected band angles (°)		
O9-Cu01-O10 82.81(13)	O9-Cu01-O11 96.33(14)	O9-Cu01-N5 83.28(15)
O9-Cu01-N6 98.52(15)	O10-Cu01-O11 177.91(13)	O12-Cu01-O9 178.01
O12-Cu01-O10 95.54(14)	O12-Cu01-O11 85.29(14)	O12-Cu01-N5 95.54(15)
O12-Cu01-N6 82.64(15)	N5-Cu01-O10 86.77(15)	N5-Cu01-O11 91.24(15)
N5-Cu01-N6 178.06(16)	N6-Cu01-O10 92.73(15)	N6-Cu01-O11 89.27(15)

Table S7 Selected bond lengths (Å) and band angles (°) of compound **6**

Selected bond lengths (Å)		
Zn1-O8 2.0975(15)	Zn1-O10 2.1116(15)	Zn1-N5 2.1307(18)
Selected band angles (°)		
O8-Zn1-O8 180.000	O8-Zn1-O10 96.64(6)	O8-Zn1-O10 83.36(6)
O8-Zn1-N5 79.60(6)	O8-Zn1-N5 100.40(6)	O10-Zn1-O10 180.00(8)
O10-Zn1-N5 87.37(7)	O10-Zn1-N5 92.63(7)	N5-Zn1-N5 180.000

Table S8 Selected bond lengths (Å) and band angles (°) of compound **7**

Selected bond lengths (Å)		
Cd1-O1 2.426(2)	Cd1-O11 2.270(2)	Cd1-O11 2.269(2)
Cd1-O12 2.457(3)	Cd1-N2 2.363(3)	
Selected band angles (°)		
O1-Cd1-O1 71.83(10)	O1-Cd1-O12 144.08(5)	O11-Cd1-O1 89.45(8)
O11-Cd1-O1 86.64(8)	O11-Cd1-O11 175.18(13)	O11-Cd1-O12 92.41(6)
O11-Cd1-N2 96.86(9)	O11-Cd1-N2 84.39(9)	N2-Cd1-O1 140.70(8)
N2-Cd1-O1 69.09(8)	N2-Cd1-O12 75.09(6)	N2-Cd1-N2 150.17(13)

4. The stacking crystal structures of compounds 1~6

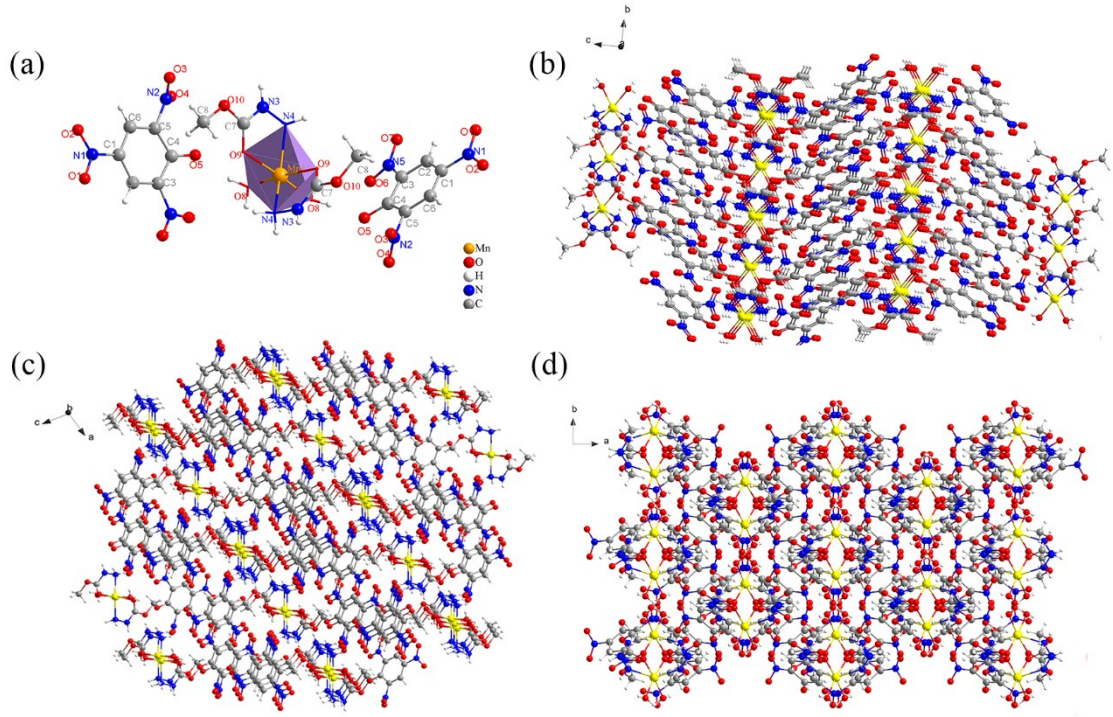

Fig. S3 (a) A view of the molecular unit of compound **1**. (b) The stacking crystal structure of compound **1** viewed down the *a* axis. (c) The stacking crystal structure of compound **1** viewed down the *b* axis. (d) The stacking crystal structure of compound **1** viewed down the *c* axis.

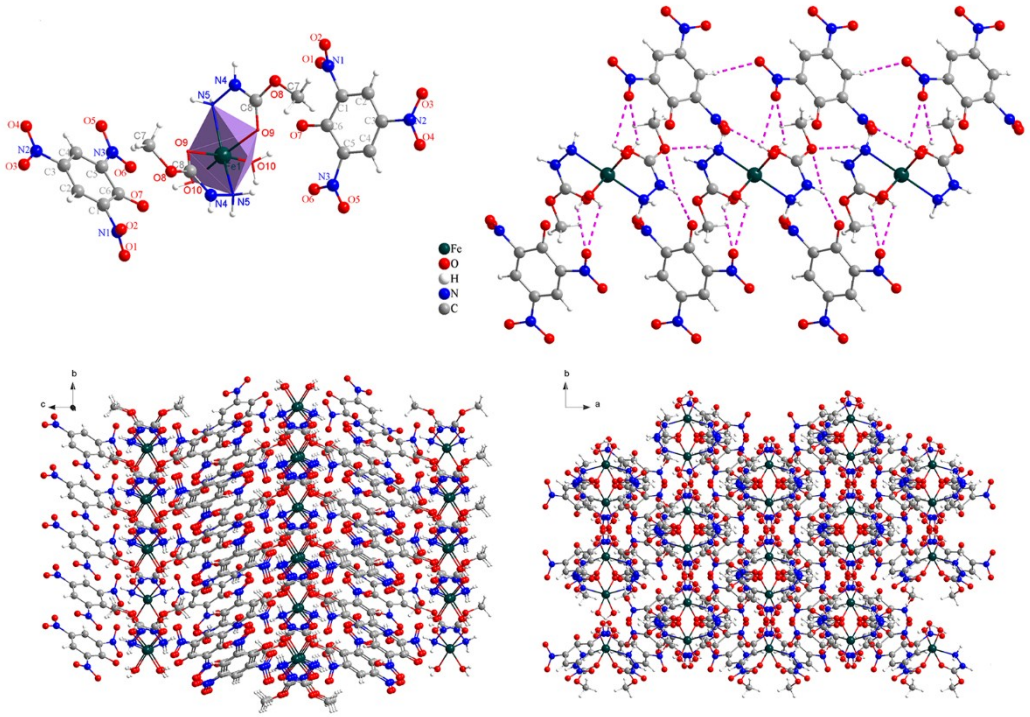

Fig. S4 (a) A view of the molecular unit of compound **2**. (b) The stacking crystal structure of compound **2** viewed down the *a* axis, the dashed lines indicate hydrogen bonding. (c) The stacking crystal structure of compound **2** viewed down the *b* axis. (d) The stacking crystal structure of compound **2** viewed down the *c* axis.

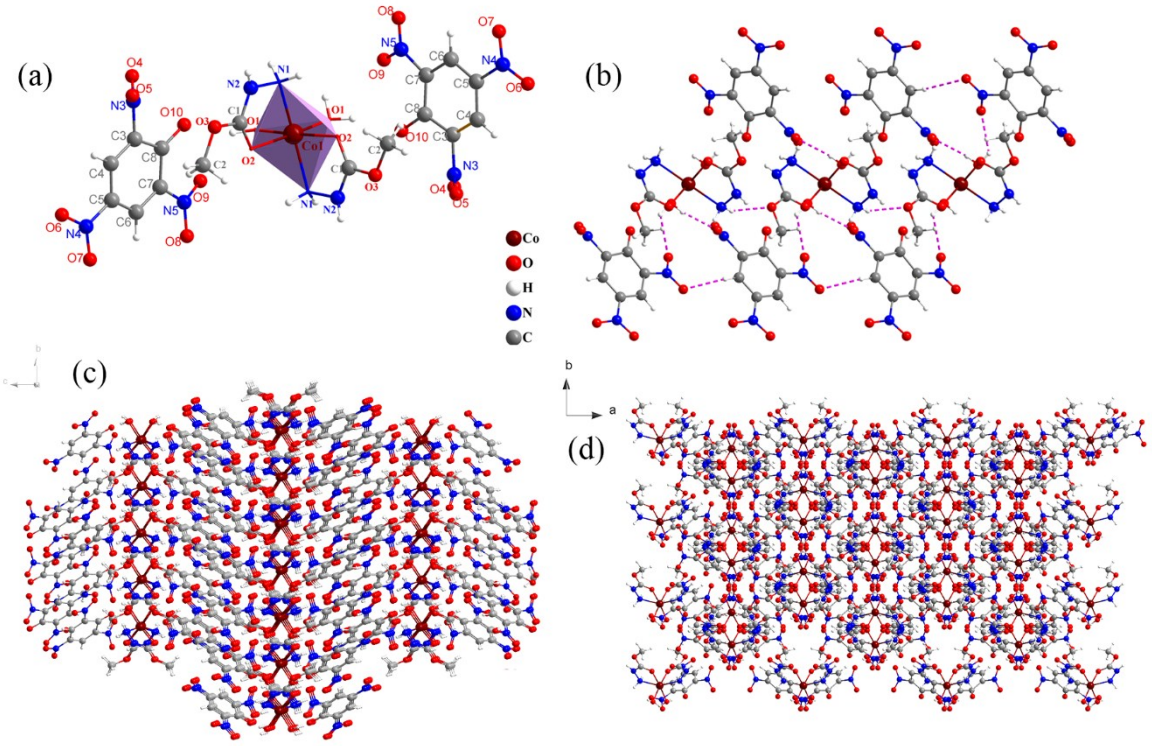

Fig. S5 (a) A view of the molecular unit of compound **3**. (b) The stacking crystal structure of compound **3** viewed down the *a* axis, the dashed lines indicate hydrogen bonding. (c) The stacking crystal structure of compound **3** viewed down the *b* axis. (d) The stacking crystal structure of compound **3** viewed down the *c* axis.

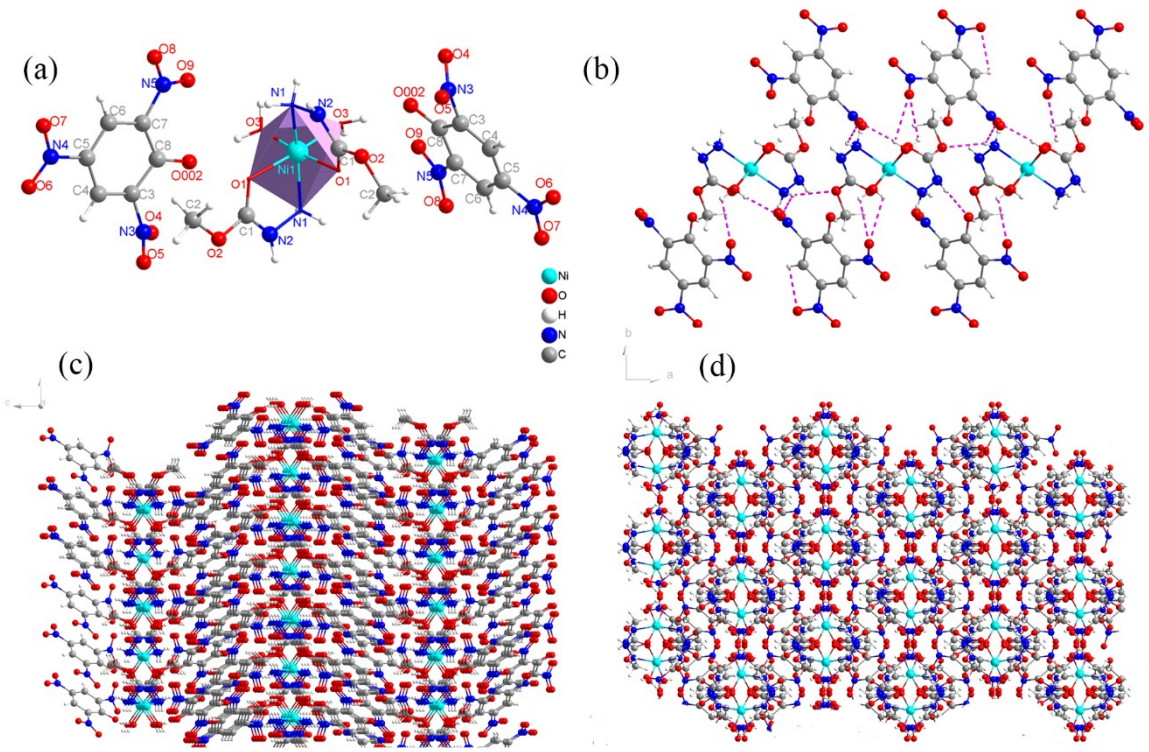

Fig. S6 (a) A view of the molecular unit of compound **4**. (b) The stacking crystal structure of compound **4** viewed down the *b* axis, the dashed lines indicate hydrogen bonding. (c) The stacking crystal structure of compound **4** viewed down the *a* axis. (d) The stacking crystal structure of compound **4** viewed down the *c* axis.

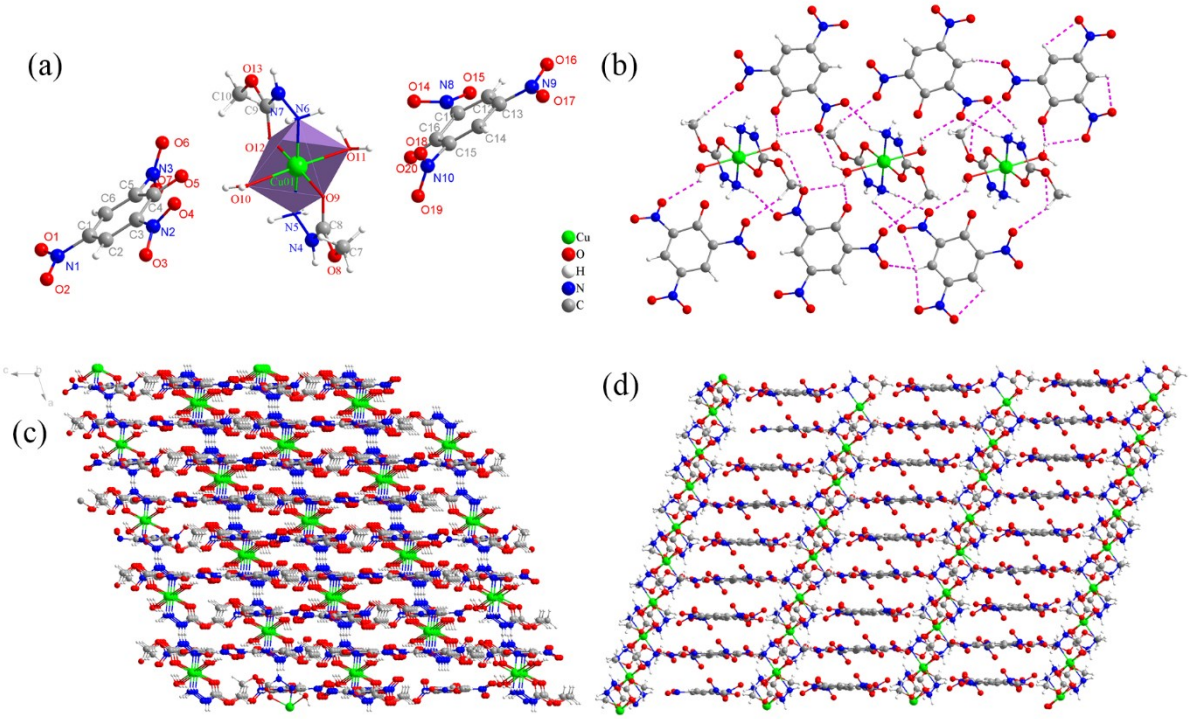

Fig. S7 (a) A view of the molecular unit of compound **5**. (b) The stacking crystal structure of compound **5** viewed down the *a* axis, the dashed lines indicate hydrogen bonding. (c) The stacking crystal structure of compound **5** viewed down the *b* axis. (d) The stacking crystal structure of compound **5** viewed down the *c* axis.

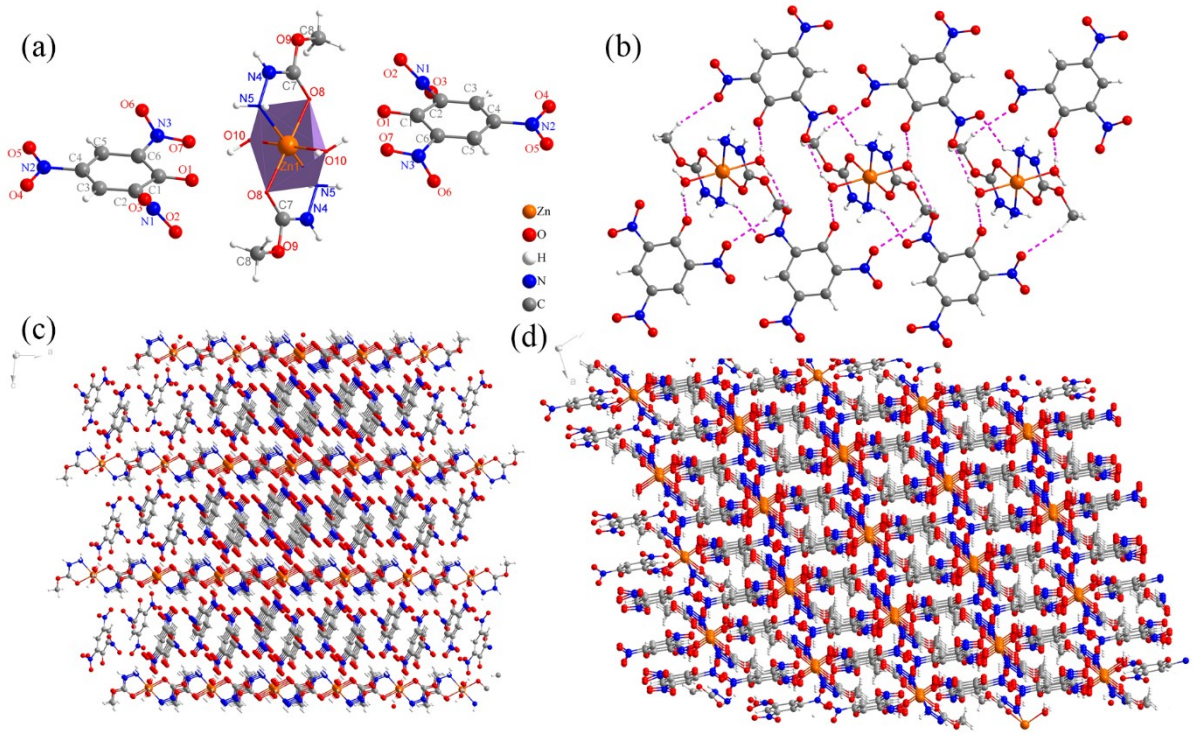

Fig. S8 (a) A view of the molecular unit of compound **6**. (b) The stacking crystal structure of compound **6** viewed down the *a* axis, the dashed lines indicate hydrogen bonding. (c) The stacking crystal structure of compound **6** viewed down the *b* axis. (d) The stacking crystal structure of compound **6** viewed down the *c* axis.

5. The distances of hydrogen bonds of compounds 1~7

Table S9 The distances of hydrogen bonds of compounds **1**~**7**

$[Mn(MCZ)_2(H_2O)_2]PA_2$(**1**)				
N3--H3⋯O5	0.8800	2.1600	2.9143	144.00
N4--H4A⋯O1	0.9100	2.2200	3.0961	162.00
N4--H4B⋯O3	0.9100	2.4100	3.0391	126.00
N4--H4B⋯O10	0.9100	2.3000	3.1051	147.00
O8--H8A⋯O5	0.8400	1.8400	2.6703	171.00
O8--H8A⋯O6	0.8400	2.4500	2.8795	112.00
O8--H8B⋯O6	0.8400	2.5600	2.8795	104.00
O8--H8B⋯O3	0.8400	2.2000	2.9140	144.00
C2--H2⋯O7	0.9500	2.3300	2.6568	100.00
C6--H6⋯O7	0.9500	2.5000	3.4187	163.00
$[Fe(MCZ)_2(H_2O)_2]PA_2$(**2**)				
N4--H4A⋯O7	0.8800	2.1900	2.9245	141.00
N5--H5A⋯O2	0.9100	2.3400	2.9909	128.00
N5--H5A⋯O8	0.9100	2.3400	3.1215	144.00
N5--H5B⋯O4	0.9100	2.2000	3.0891	164.00
O10--H10A⋯O6	0.8400	2.4300	2.9063	117.00
O10--H10A⋯O7	0.8400	1.8300	2.6540	165.00
O10--H10B⋯O6	0.8400	2.5200	2.9063	109.00
O10--H10B⋯O2	0.8400	2.1300	2.8865	150.00

C2--H2···O5	0.9500	2.4800	3.4076	164.00
C4--H4···O5	0.9500	2.3200	2.6532	100.00
C7--H7A···O6	0.9800	2.5900	3.0095	106.00
$[Co(MCZ)_2(H_2O)_2]PA_2$**(3)**				
N4--H4···O5	0.8800	1.9700	2.7931	155.00
N4--H4···O6	0.8800	2.4500	3.0091	122.00
N5--H5A···O16	0.9100	2.1500	3.0375	164.00
N5--H5A···O15	0.9100	2.5700	3.0618	115.00
N5--H5B···O14	0.9100	2.2600	3.0173	141.00
N6--H6A···O19	0.9100	2.5900	2.9859	107.00
N6--H6A···O3	0.9100	2.1900	2.9553	141.00
N6--H6B···O1	0.9100	2.4000	3.2196	150.00
N6--H6B···O2	0.9100	2.5200	3.3209	147.00
N7--H7···O19	0.8800	2.4700	2.9822	118.00
N7--H7···O20	0.8800	1.9800	2.8032	156.00
O10--H10A···O4	0.8400	2.5900	2.9983	111.00
O10--H10A···O4	0.8400	2.3400	2.9982	136.00
O10--H10B···O4	0.8400	2.4800	2.9983	121.00
O10--H10B···O5	0.8400	1.9600	2.7619	160.00
O11--H11A···O14	0.8400	2.5100	2.9697	116.00
O11--H11A···O20	0.8400	1.9000	2.7208	167.00
C7--H7B···O19	0.9800	2.4600	3.4047	161.00
C7--H7C···O17	0.9800	2.4400	2.7918	101.00
C10--H10C···O1	0.9800	2.5200	3.1132	119.00
C10--H10C···O14	0.9800	2.5600	3.3211	134.00
C10--H10E···O6	0.9800	2.4900	3.4240	159.00
C12--H12···O7	0.9500	2.5700	3.2413	128.00
$[Ni(MCZ)_2(H_2O)_2]PA_2$(**4**)				
N1--H1A···O5	0.8500	2.3000	2.9174	129.00
N1--H1B···O7	0.8500	2.2500	3.0796	167.00
N2--H2···O002	0.8500	2.0900	2.9347	173.00
N2--H2···O4	0.8500	2.5500	2.9648	111.00
O3--H3A···O9	0.8400	2.5600	2.9412	109.00
O3--H3A···O5	0.8400	2.1200	2.8765	150.00
O3--H3B···O002	0.8400	1.8100	2.6513	175.00
O3--H3B···O9	0.8400	2.5600	2.9412	109.00
C4--H4···O8	0.9500	2.4400	3.3640	163.00
$[Cu(MCZ)_2(H_2O)_2]PA_2$(**5**)				
N4--H4···O5	0.8800	1.9700	2.7931	155.00
N4--H4···O6	0.8800	2.4500	3.0091	122.00
N5--H5A···O16	0.9100	2.1500	3.0375	164.00
N5--H5A···O15	0.9100	2.5700	3.0618	115.00
N5--H5B···O14	0.9100	2.2600	3.0173	141.00
N6--H6A···O19	0.9100	2.5900	2.9859	107.00

N6--H6A···O3	0.9100	2.1900	2.9553	141.00
N6--H6B···O1	0.9100	2.4000	3.2196	150.00
N6--H6B···O2	0.9100	2.5200	3.3209	147.00
N7--H7···O19	0.8800	2.4700	2.9822	118.00
N7--H7···O20	0.8800	1.9800	2.8032	156.00
O10--H10A···O4	0.8400	2.5900	2.9983	111.00
O10--H10A···O4	0.8400	2.3400	2.9982	136.00
O10--H10B···O4	0.8400	2.4800	2.9983	121.00
O10--H10B···O5	0.8400	1.9600	2.7619	160.00
O11--H11A···O14	0.8400	2.5100	2.9697	116.00
O11--H11A···O20	0.8400	1.9000	2.7208	167.00
C7--H7B···O19	0.9800	2.4600	3.4047	161.00
C7--H7C···O17	0.9800	2.4400	2.7918	101.00
C10--H10C···O1	0.9800	2.5200	3.1132	119.00
C10--H10C···O14	0.9800	2.5600	3.3211	134.00
C10--H10E···O6	0.9800	2.4900	3.4240	159.00
C12--H12c···O7	0.9500	2.5700	3.2413	128.00
$[Zn(MCZ)_2(H_2O)_2]PA_2$(**6**)				
N4--H4···O1	0.8500	1.9800	2.8124	167.00
N5--H5A···O5	0.8500	2.3500	3.1685	162.00
N5--H5B···O6	0.8500	2.3400	2.8846	122.00
O10--H10A···O7	0.8400	2.1600	2.9443	155.00
O10--H10B···O1	0.8400	1.8400	2.6626	166.00
O10--H10B···O7	0.8400	2.4000	2.8864	117.00
C8--H8B···O4	0.9800	2.4400	2.9121	109.00
C8--H8C···O2	0.9800	2.5300	3.4603	159.00
$[Cd(MCZ)_2(H_2O)_3]PA_2 \cdot 4H_2O$(**7**)				
N1--H1···O3	0.8500	2.1800	3.0183	168.00
N1--H1···O5	0.8500	2.5900	3.0044	111.00
N2--H2A···O10	0.8400	2.1800	2.9374	150.00
N2--H2B···O6	0.8400	2.2800	3.1000	165.00
O10--H10A···O9	0.8400	1.9300	2.7592	171.00
O10--H10B···O5	0.8400	1.9900	2.7853	158.00
O11--H11A···O13	0.8400	1.8900	2.7174	170.00
O11--H11B···O6	0.8400	2.4400	3.0524	130.00
O11--H11B···O9	0.8400	2.0800	2.8381	150.00
O12--H12···O13	0.8400	2.0400	2.8427	159.00
O13--H13A···O1	0.8400	1.9800	2.8161	171.00
O13--H13B···O10	0.8400	1.8800	2.7115	170.00
C2--H2D···O4	0.9800	2.3600	3.2872	157.00

6. Thermo-stability measurements (DSC and TGA)

Furthermore, all of these compounds were investigated by thermal gravimetric analysis (TGA). What is noteworthy is

that the measurement of TG is under dry oxygen-free nitrogen atmosphere that different with DSC. The deviation of decomposition temperature is within acceptable scopes.

The TGA measurements revealed the same decomposition process. In addition, the decomposition residue amounts to only 8.5 % and 6.7 % for **2** and **3**, respectively. That is almost equal to its own metal content, this indicates that all nonmetallic substances transformed into gaseous products.

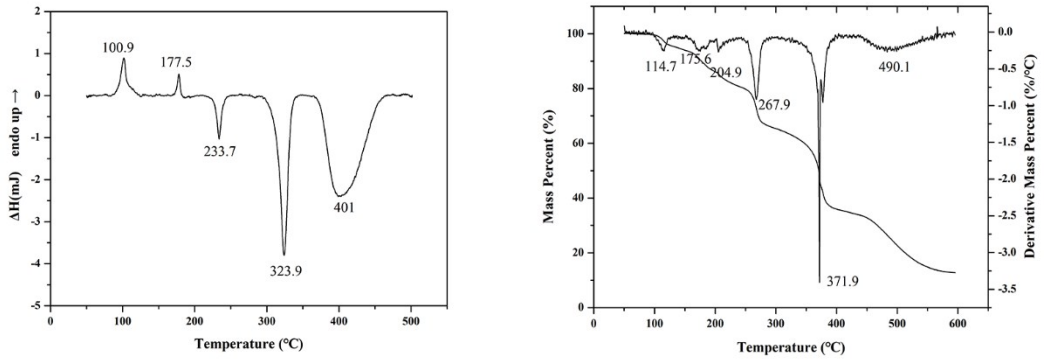

Fig. S9 The DSC and TG-DTG curves of compound **1** with a scanning rate of 10 K min^{-1}.

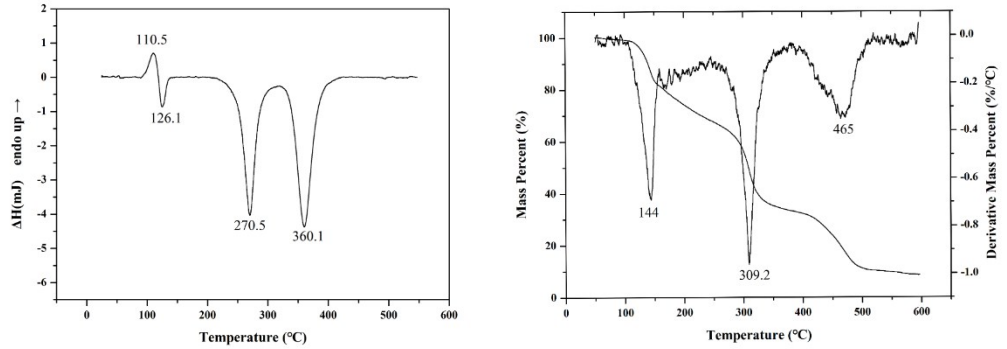

Fig. S10 The DSC and TG-DTG curves of compound **2** with a scanning rate of 10 K min^{-1}.

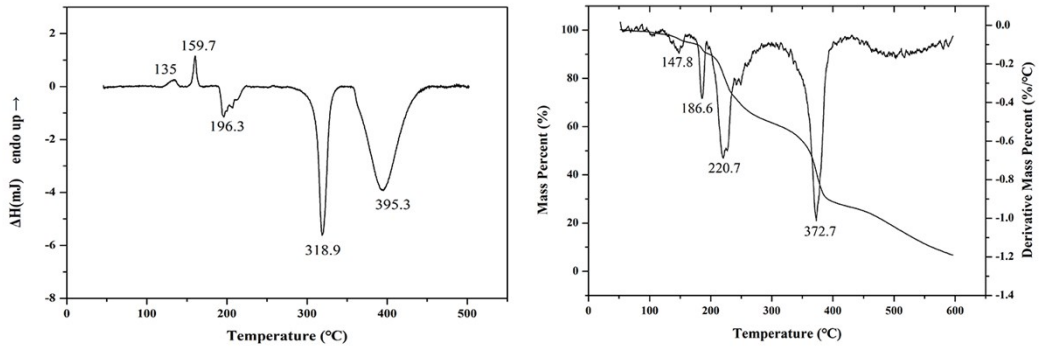

Fig. S11 The DSC and TG-DTG curves of compound **3** with a scanning rate of 10 K min^{-1}.

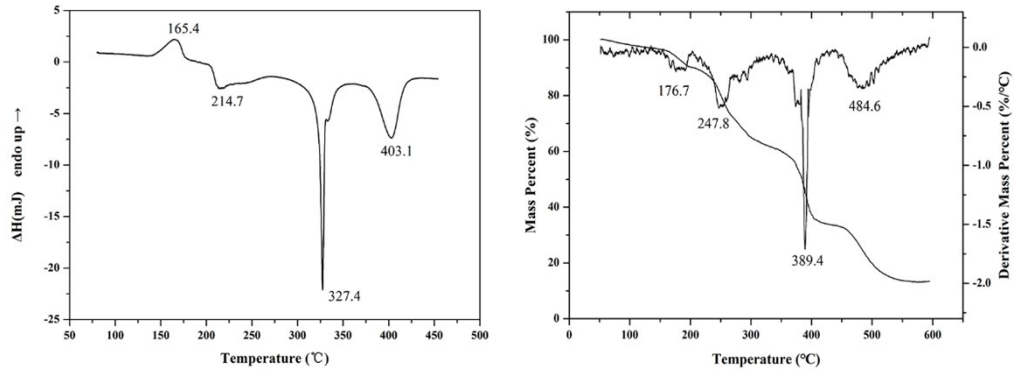

Fig. S12 The DSC and TG-DTG curves of compound **4** with a scanning rate of 10 K min^{-1}.

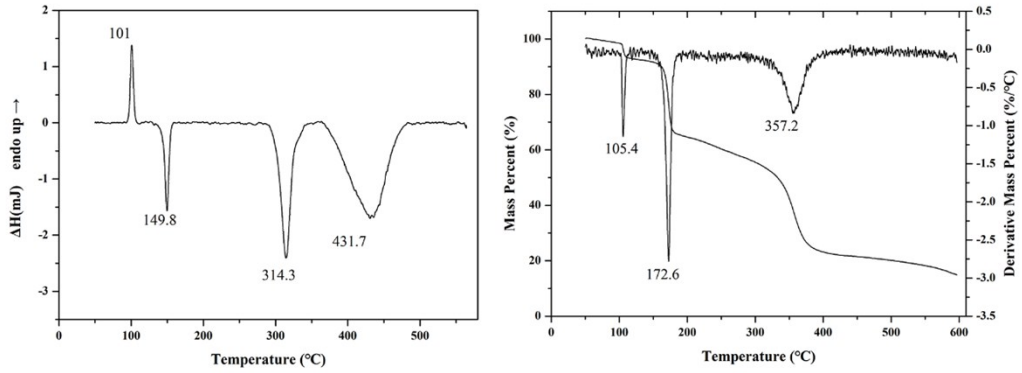

Fig. S13 The DSC and TG-DTG curves of compound **5** with a scanning rate of 10 K min^{-1}.

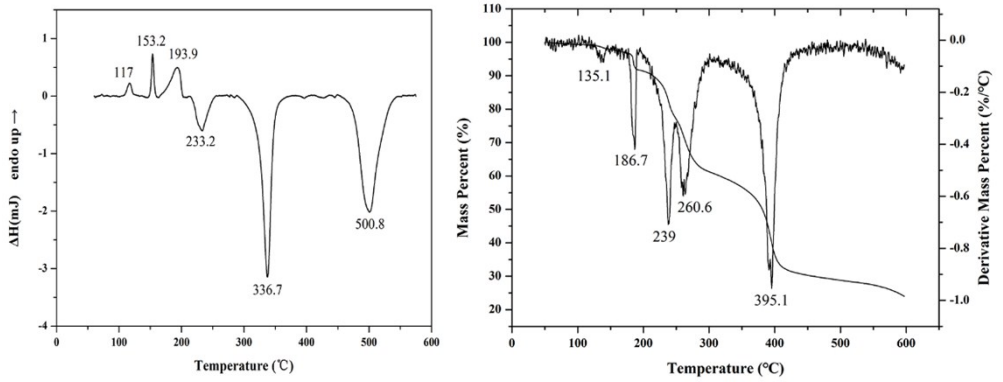

Fig. S14 The DSC and TG-DTG curves of compound **6** with a scanning rate of 10 K min^{-1}.

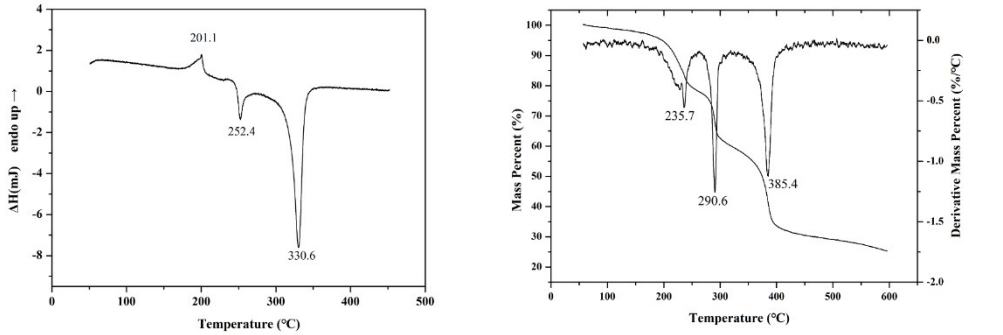

Fig. S15 The DSC and TG-DTG curves of compound **7** with a scanning rate of 10 K min^{-1}.

7. The first exothermic decomposition peak temperature with four heating rates

Table S10 The first exothermic decomposition peak temperature Tp with four heating rates (β=5, 10, 15, 20 K min^{-1})

β (K min^{-1})	Peaks temperatures Tp (K)						
	1	**2**	**3**	**4**	**5**	**6**	**7**
5	498.25	393.85	461.45	478.85	420.85	493.35	515.95
10	506.85	399.25	469.45	487.85	422.95	506.35	525.55
15	508.45	406.65	471.75	492.15	428.05	513.25	526.15
20	509.15	408.15	473.55	494.15	430.05	513.55	527.05

8. Non-isothermal kinetics analysis

The peak temperatures of first decomposition processes were used to calculated kinetics parameters (apparent activation energies (*E*a) and the pre-exponential factor (A)), by Kissinger's method[1] (Eq. (1)) and Ozawa-Doyle's method[2] (Eq. (2)).

$$ln\frac{\beta}{T_p^2} = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (1)$$

$$ln\beta + 0.4567\frac{E_a}{RT_p} = C \quad (2)$$

Where Tp is the peak temperature (K) of first reaction process (see in Table S8), A is the pre-exponential factor (s^{-1}), Ea is the apparent activation energy (kJ mol^{-1}), R is the gas constant (J mol^{-1} K^{-1}), β is the heating rate (K min^{-1}) and C is a constant. The results are listed in Table S11. The symbol "S" stands for the standard deviation. *E*a is equal to the average of E_k and E_o.

Table S11 Non-isothermal reaction kinetics parameters.

compound	Kissinger's method			Ozawa's method		E_a
	E_K	lgA_K	R_K	E_O	R_O	
1	231.1	22.2	-0.95	227.7	-0.95	229.4
2	111.8	12.7	-0.98	112.7	-0.98	112.3
3	193.3	19.8	-0.98	191.2	-0.98	192.3
4	159.7	15.3	-0.99	159.5	-0.99	159.6
5	194.9	22.3	-0.96	192.1	-0.96	193.5
6	122.6	10.7	-0.97	124.5	-0.98	123.6
7	234.5	21.7	-0.92	231.2	-0.93	232.9

9. 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	476.6	485.0	176.2	227.1	143.2
2	384.5	396.2	-3.9	108.6	110.1
3	442.6	451.4	130.9	189.6	131.7
4	462.8	474.5	44.3	155.9	135.3
5	417.2	424.9	179.2	191.4	116.7
6	474.8	491.2	-43.9	118.7	139.5
7	488.1	496.9	166.4	230.4	149.2

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.