

## Supplementary Information for:

### Controllable explosion: Fine-tuning the sensitivities of the high-energetic complexes

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#### Part 1 Experimental Section

##### 1.1 Synthesis

**1,5-diaminotetrazole (DAT)** has been prepared according to the literature <sup>1</sup>.

A solvent of the perchloric acid (20 mL, 4 mol/L) was heated to 40 °C and stirred, then added slowly with the powder of metal carbonate into the solvent. After the evolution of gas was complete, the mixture was filtered to obtain the relevant solution of metal perchlorate. Then the solution of metal perchlorate was added drop wise to a stirred solution of DAT (0.12 mol) in hot water (40 mL, 80 °C). After that, the solution was stirred for an additional 2 hours at 80 °C. The solvent was removed in vacuum and the raw product (while precipitate) crystallized by slowly cooling a water solution to the room temperature.

**[Mn(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Yield: 88%. Elemental analysis (%) calcd for C<sub>6</sub>H<sub>18</sub>N<sub>36</sub>O<sub>8</sub>Cl<sub>2</sub>Mn (M<sub>r</sub> = 848.29): N 58.99, C 8.43, H 2.81; found N 59.18, C 8.45, H 2.82. IR (KBr) ν<sub>N-H</sub>: 3324, 3256 cm<sup>-1</sup>; δ<sub>N-H</sub>: 1660 cm<sup>-1</sup>; ν<sub>C-N</sub>: 1332 cm<sup>-1</sup>; ν<sub>ClO<sub>4</sub></sub>: 1097, 628 cm<sup>-1</sup> (1097 cm<sup>-1</sup>, Cl-O stretching; 628 cm<sup>-1</sup>, O-Cl bending).

**[Co(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Yield: 86%. Elemental analysis (%) calcd for C<sub>6</sub>H<sub>18</sub>N<sub>36</sub>O<sub>8</sub>Cl<sub>2</sub>Co (M<sub>r</sub> = 852.28):

N 58.71, C 8.39, H 2.79; found N 58.94, C 8.44, H 2.82. IR (KBr)  $\nu_{\text{N-H}}$ : 3322, 3258  $\text{cm}^{-1}$ ;  $\delta_{\text{N-H}}$ : 1678  $\text{cm}^{-1}$ ;  $\nu_{\text{C-N}}$ : 1316  $\text{cm}^{-1}$ ;  $\nu_{\text{ClO}_4}$ : 1098, 627  $\text{cm}^{-1}$  (1098  $\text{cm}^{-1}$ ,  $\text{ClO}_4$  stretching; 627  $\text{cm}^{-1}$ ,  $\text{OClO}_3$  bending).

**[Zn(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Yield: 78%. Elemental analysis (%) calcd for  $\text{C}_6\text{H}_{18}\text{N}_{36}\text{O}_8\text{Cl}_2\text{Zn}$  ( $M_r = 858.76$ ): N 58.28, C 8.33, H 2.77; found N 58.49, C 8.37, H 2.79. IR (KBr)  $\nu_{\text{N-H}}$ : 3325, 3240  $\text{cm}^{-1}$ ;  $\delta_{\text{N-H}}$ : 1657  $\text{cm}^{-1}$ ;  $\nu_{\text{C-N}}$ : 1330  $\text{cm}^{-1}$ ;  $\nu_{\text{ClO}_4}$ : 1110, 629  $\text{cm}^{-1}$  (1110  $\text{cm}^{-1}$ ,  $\text{ClO}_4$  stretching; 629  $\text{cm}^{-1}$ ,  $\text{OClO}_3$  bending).

**[Cd(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**: Yield: 72%. Elemental analysis (%) calcd for  $\text{C}_6\text{H}_{18}\text{N}_{36}\text{O}_8\text{Cl}_2\text{Cd}$  ( $M_r = 905.76$ ): N 55.27, C 7.90, H 2.63; found N 55.47, C 7.93, H 2.64. IR (KBr)  $\nu_{\text{N-H}}$ : 3326, 3263  $\text{cm}^{-1}$ ;  $\delta_{\text{N-H}}$ : 1660  $\text{cm}^{-1}$ ;  $\nu_{\text{C-N}}$ : 1332  $\text{cm}^{-1}$ ;  $\nu_{\text{ClO}_4}$ : 1086, 628  $\text{cm}^{-1}$  (1086  $\text{cm}^{-1}$ ,  $\text{ClO}_4$  stretching; 628  $\text{cm}^{-1}$ ,  $\text{OClO}_3$  bending).

## 1.2 Crystal structure determination

CCDC-704380, CCDC-783306<sup>2a</sup>, CCDC-742791, CCDC-671286<sup>2b</sup> contain the supplementary crystallographic data for the paper. These data can be obtained from the Cambridge Crystallographic Data Centre via the website of <http://www.ccdc.cam.ac.uk/>. All the single crystals were analyzed by Bruker Smart 1000 CCD diffractometer with graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by the programs of SHELXS-97. With the program of SHELXL-97, all the atoms except for hydrogen were obtained from the Difference Fourier Map and further refined by the least squares method based on  $F^2$ . All the hydrogen atoms of  $[\text{M}(\text{DAT})_6](\text{ClO}_4)_2$  were observed at the calculated positions.

**[Mn(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**: measurement at 113 K ( $\text{MoK}\alpha$ ,  $1.985^\circ \leq \theta \leq 27.85^\circ$ ), formula  $\text{C}_6\text{H}_{24}\text{MnCl}_2\text{N}_{36}\text{O}_8$ , trigonal, space group  $P\bar{3}c1$ ,  $a = b = 11.8435 \text{ \AA}$  (17),  $c = 13.081 \text{ \AA}$  (3),  $\gamma = 120^\circ$ ,  $V = 1589.1(5) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.786 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 0.188 \text{ mm}^{-1}$ , 10563 measured reflections, 1258 independent ( $R_{\text{int}} = 0.0295$ ),  $R_1 = 0.0262$ ,  $wR_2 [I > 2\sigma(I)] = 0.0678$ , GOF = 1.08, min/max residual = -0.409/0.278.

**[Co(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**: measurement at 294 K ( $\text{MoK}\alpha$ ,  $3.09^\circ \leq \theta \leq 26.29^\circ$ ), formula  $\text{C}_6\text{H}_{24}\text{CoN}_{36}\text{O}_8$ , trigonal, space group  $P\bar{3}$ ,  $a = b = 11.8610 \text{ \AA}$  (2),  $c = 6.5833 \text{ \AA}$  (17),  $\gamma = 120^\circ$ ,  $V = 802.1(3) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_c = 1.777 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 0.800 \text{ mm}^{-1}$ , 4506 measured reflections, 1092 independent ( $R_{\text{int}} = 0.0506$ ),  $R_1 = 0.0347$ ,  $wR_2 [I > 2\sigma(I)] = 0.0906$ , GOF = 1.104, min/max residual = -0.318/0.426.

**[Zn(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**: measurement at 293 K ( $\text{MoK}\alpha$ ,  $3.44^\circ \leq \theta \leq 26.34^\circ$ ), formula  $\text{C}_6\text{H}_{24}\text{ZnCl}_2\text{N}_{36}\text{O}_8$ , trigonal, space group  $P\bar{3}$ ,  $a = b = 11.8398 \text{ \AA}$  (9),  $c = 6.5700 \text{ \AA}$  (10),  $\gamma = 120^\circ$ ,  $V = 797.6(15) \text{ \AA}^3$ ,  $Z = 1$ ,  $D_c = 1.801 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 1.036 \text{ mm}^{-1}$ , 4613 measured reflections, 1091

independent ( $R_{\text{int}} = 0.0343$ ),  $R_1 = 0.0289$ ,  $wR_2 [I > 2\sigma(I)] = 0.0748$ ,  $\text{GOF} = 1.064$ , min/max residual = -0.484/0.332.

**[Cd(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**: measurement at 293 K ( $\text{Mo}_{K\alpha}$ ,  $3.08^\circ \leq \theta \leq 26.34^\circ$ ), formula  $\text{C}_6\text{H}_{24}\text{CdCl}_2\text{N}_{36}\text{O}_8$ , trigonal, space group  $P\bar{3}c1$ ,  $a = b = 11.9445 \text{ \AA}$  (7),  $c = 13.2162 \text{ \AA}$  (14),  $\gamma = 120^\circ$ ,  $V = 1633.0(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.855 \text{ g}\cdot\text{cm}^{-3}$ ,  $\mu(\text{Mo}_{K\alpha}) = 0.929 \text{ mm}^{-1}$ , 8699 measured reflections, 1124 independent ( $R_{\text{int}} = 0.0290$ ),  $R_1 = 0.0228$ ,  $wR_2 [I > 2\sigma(I)] = 0.0682$ ,  $\text{GOF} = 0.951$ , min/max residual = -0.373/0.426.

### 1.3 Thermal decomposition

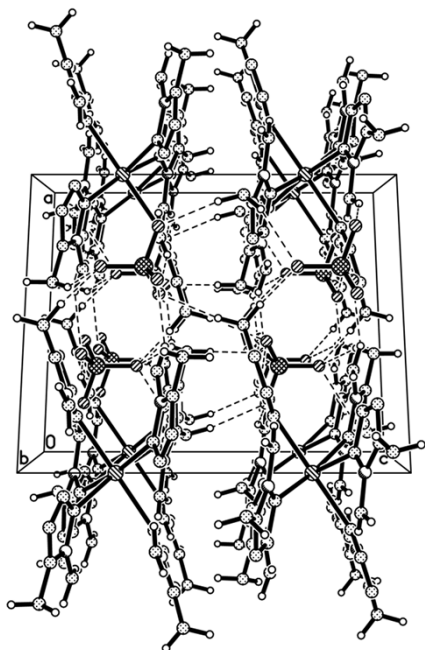
Decomposition of all the samples was investigated using Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA) techniques. DSC for the title compounds is measured at  $5 \text{ }^\circ\text{C}/\text{min}$  to  $600 \text{ }^\circ\text{C}$ . TGA weight loss is measured at  $5 \text{ }^\circ\text{C}/\text{min}$  to  $600 \text{ }^\circ\text{C}$  in nitrogen gas flowing with the rate of  $20 \text{ mL}/\text{min}$ .

### 1.4 Flame Sensitivity test

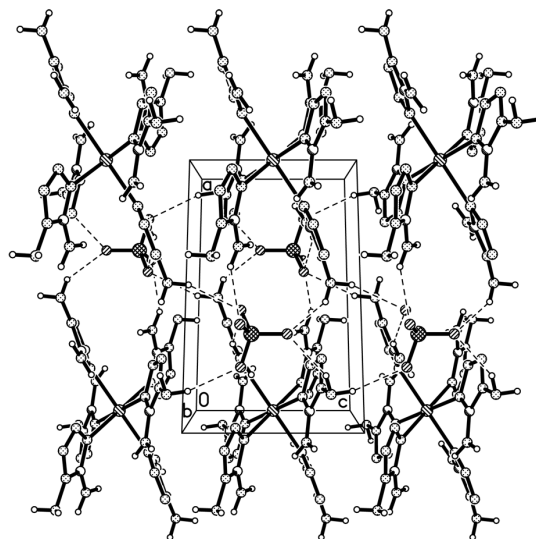
All the samples are tested at the temperature of  $20 \pm 5^\circ\text{C}$  with the humidity of 50%~65%.

Flame sensitivity was analyzed according to the Lao's literature<sup>3</sup> (HGY-1 Flame sensitivity instrument). 20 mg samples for each are compacted into a copper cap under the pressure of 39.2 Mpa for the prepare. Then the samples were ignited by the column of black powder above the sample. The flame sensitivity was determined by using the results of 50% ignition height .

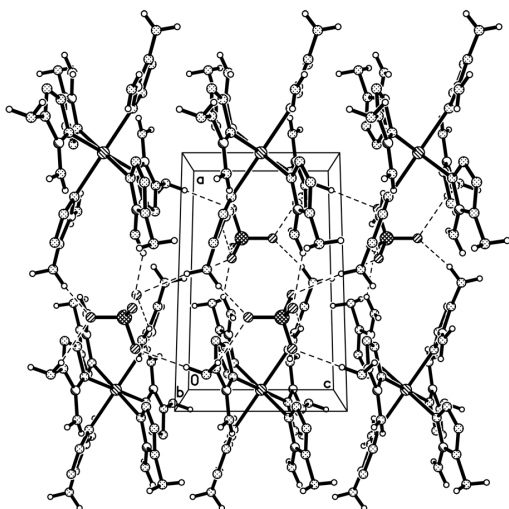
Figure (Part 1)



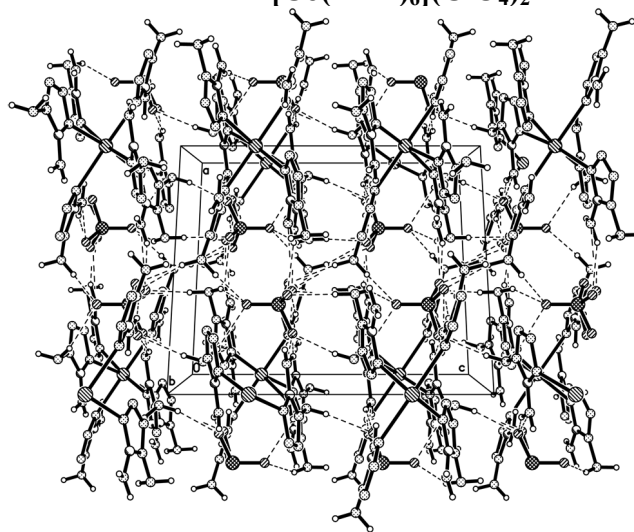
**[Mn(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**



**[Co(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**



**[Zn(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**



**[Cd(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>**

Fig S1 Packing diagrams of four [M(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub>

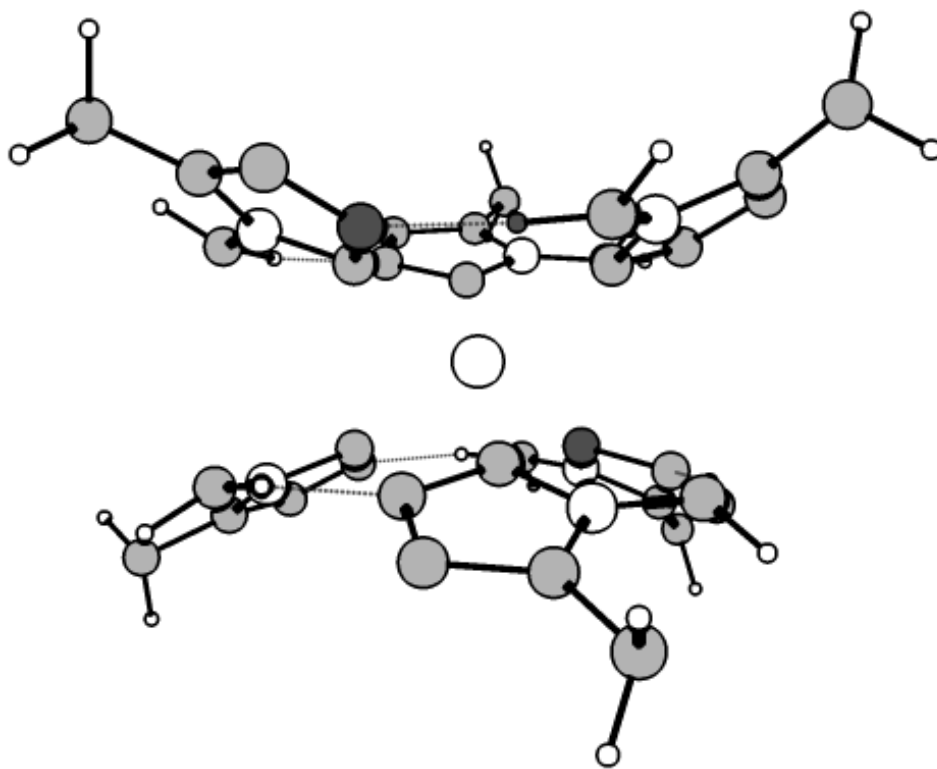


Figure S2 The intra molecular hydrogen bonds which cross-link the DAT molecules to form the layer-like structure

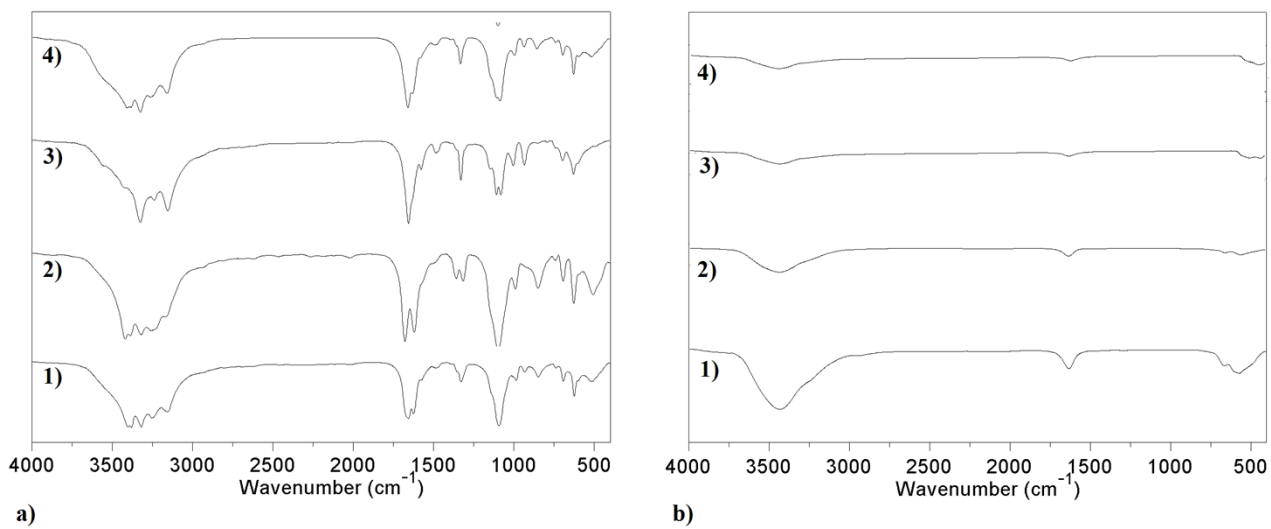
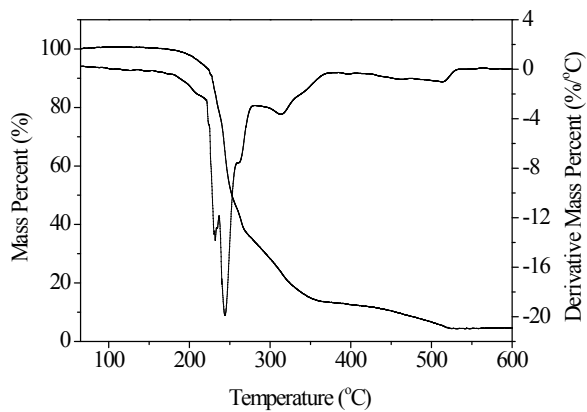
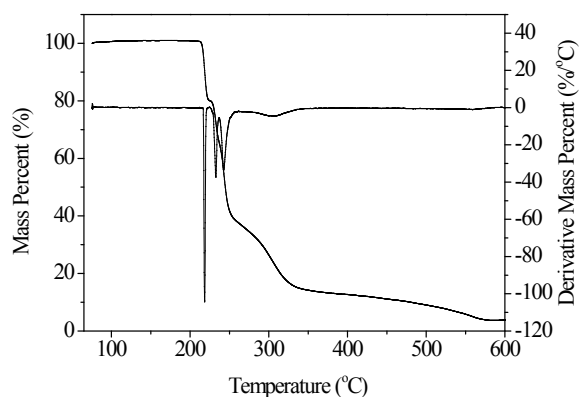


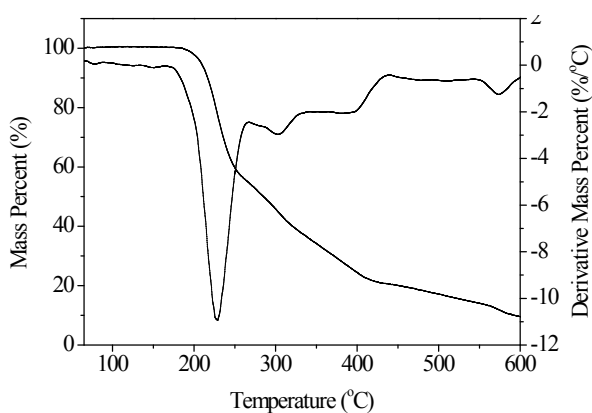
Figure S3 FTIR spectrum of the four  $[M(\text{DAT})_6](\text{ClO}_4)_2$  at 298K (a) and the products at 600K (b). 1):  $[\text{Mn}(\text{DAT})_6](\text{ClO}_4)_2$ , 2):  $[\text{Co}(\text{DAT})_6](\text{ClO}_4)_2$ , 3):  $[\text{Zn}(\text{DAT})_6](\text{ClO}_4)_2$ , 4):  $[\text{Cd}(\text{DAT})_6](\text{ClO}_4)_2$



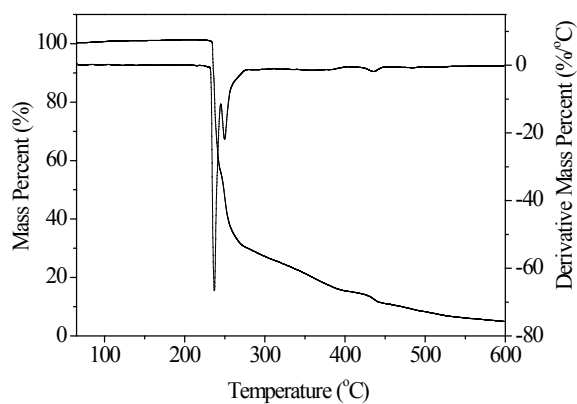
[Mn(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (1)



[Co(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (2)



[Zn(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (3)



[Cd(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> (4)

Figure S4 TG-DTG spectra of [M(DAT)<sub>6</sub>](ClO<sub>4</sub>)<sub>2</sub> TGA weight loss for the title compounds is measured at 5°C/min to 600°C in nitrogen gas flowing with the rate of 20mL/min.

Table (Part 1)

Table S1 Crystal data and structural refinements of the complexes

	1	2	3	4
Empirical formula	C <sub>6</sub> H <sub>24</sub> MnCl <sub>2</sub> N <sub>36</sub> O <sub>8</sub>	C <sub>6</sub> H <sub>24</sub> C <sub>12</sub> CoN <sub>36</sub> O <sub>8</sub>	C <sub>6</sub> H <sub>24</sub> C <sub>12</sub> N <sub>36</sub> O <sub>8</sub> Zn	C <sub>6</sub> H <sub>24</sub> CdCl <sub>2</sub> N <sub>36</sub> O <sub>8</sub>
Mass	854.45	858.44	864.88	911.91
Temperature (K)	113(2)	294(2)	293(2)	293(2)
syngony	trigonal	trigonal	trigonal	trigonal
Space group	$P\bar{3}c1$	$P\bar{3}c1$	$P\bar{3}$	$P\bar{3}$
<i>a</i> (Å)	11.8435(17)	11.861(2)	11.8398(9)	11.9445(7)
<i>b</i> (Å)	11.8435(17)	11.861(2)	11.8398(9)	11.9445(7)
<i>c</i> (Å)	13.081(3)	6.5833(17)	6.5700(10)	13.2162(14)
$\gamma$ (°)	120	120	120	120
<i>V</i> (Å <sup>3</sup> )	1589.1(5)	802.1(3)	797.60(15)	1633.0(2)
<i>Z</i>	2	1	1	2
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.786	1.777	1.801	1.855
$\mu$ (MoK $\alpha$ ) (1/mm)	0.683	0.8	1.036	0.929
<i>F</i> (000)	870	437	440	916
$\theta$ range for the data collection(°)	3.44~27.85	1.98~26.37	1.99~26.34	1.97~26.37
h/k/l range	-13≤h≤15, -15≤k≤13, -17≤l≤12	-8≤h≤14, -14≤k≤14, -8≤l≤7	-14≤h≤14, -14≤k≤14, -8≤l≤2	-10≤h≤14, -14≤k≤14, -16≤l≤16
Reflection measured	10563	4506	4613	8699
Independent reflection	1258 [ <i>R</i> <sub>int</sub> = 0.0295]	1092 [ <i>R</i> <sub>int</sub> = 0.0506]	1091 [ <i>R</i> <sub>int</sub> = 0.0343]	1124 [ <i>R</i> <sub>int</sub> = 0.0290]
S (fitting on <i>F</i> <sup>2</sup> )	1258/6/97	1092/12/82	1091/12/87	1124/35/90
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2σ( <i>I</i> )]	<sup>a1</sup> <i>R</i> <sub>1</sub> = 0.0262, <i>wR</i> <sub>2</sub> = 0.0678	<sup>a2</sup> <i>R</i> <sub>1</sub> = 0.0347, <i>wR</i> <sub>2</sub> = 0.0906	<sup>a3</sup> <i>R</i> <sub>1</sub> = 0.0289, <i>wR</i> <sub>2</sub> = 0.0748	<sup>a4</sup> <i>R</i> <sub>1</sub> = 0.0228, <i>wR</i> <sub>2</sub> = 0.0682
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all) <sup>a</sup>	<sup>a1</sup> <i>R</i> <sub>1</sub> = 0.0285, <i>wR</i> <sub>2</sub> = 0.0691	<sup>a2</sup> <i>R</i> <sub>1</sub> = 0.0476, <i>wR</i> <sub>2</sub> = 0.0991	<sup>a3</sup> <i>R</i> <sub>1</sub> = 0.0355, <i>wR</i> <sub>2</sub> = 0.0795	<sup>a4</sup> <i>R</i> <sub>1</sub> = 0.0294, <i>wR</i> <sub>2</sub> = 0.0756
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e/Å <sup>3</sup> )	0.278, -0.409	0.426, -0.318	0.332, -0.484	0.426, -0.373

<sup>a1</sup>:  $w = 1/[\sigma^2(F_o^2) + (0.0355p)^2 + 0.7016p]$ , where  $p = (F_o^2 + 2F_c^2)/3$ ;  
<sup>a2</sup>:  $w = 1/[\sigma^2(F_o^2) + (0.0461p)^2 + 0.4483p]$ , where  $p = (F_o^2 + 2F_c^2)/3$ ;  
<sup>a3</sup>:  $w = 1/[\sigma^2(F_o^2) + 0.0372p^2 + 0.4534p]$ , where  $p = (F_o^2 + 2F_c^2)/3$ ;  
<sup>a4</sup>:  $w = 1/[\sigma^2(F_o^2) + (0.0534p)^2 + 0.9373p]$ , where  $p = (F_o^2 + 2F_c^2)/3$ .



Table S2 Peak temperature under different heating rates of the first exothermic stage and the kinetic parameters

parameter	$T_p$				
	1	2	3	4	
$\beta$ (K)	2	492.05	483.45	483.05	505.45
	5	507.75	492.85	498.85	516.65
	10	515.95	502.75	510.65	522.45
	20	526.55	513.05	519.05	530.35
$K^{-1}$	$E_k$ (kcal/mol)	32.63	37.18	29.55	47.78
	$\ln(A_k/s^{-1})$	11.81	14.25	10.66	18.12
	$R_k$ (kcal/mol)	-0.24	-0.24	-0.24	-0.24
$O^{-2}$	$E_0$ (kcal/mol)	32.94	37.22	30.00	47.39
	$R_0$ (kcal/mol)	-0.24	-0.24	-0.24	-0.24

1. Kissinger's method; 2. Ozawa-Doyle's method

## Part 2 Theoretical Section

Figure (Part 2)

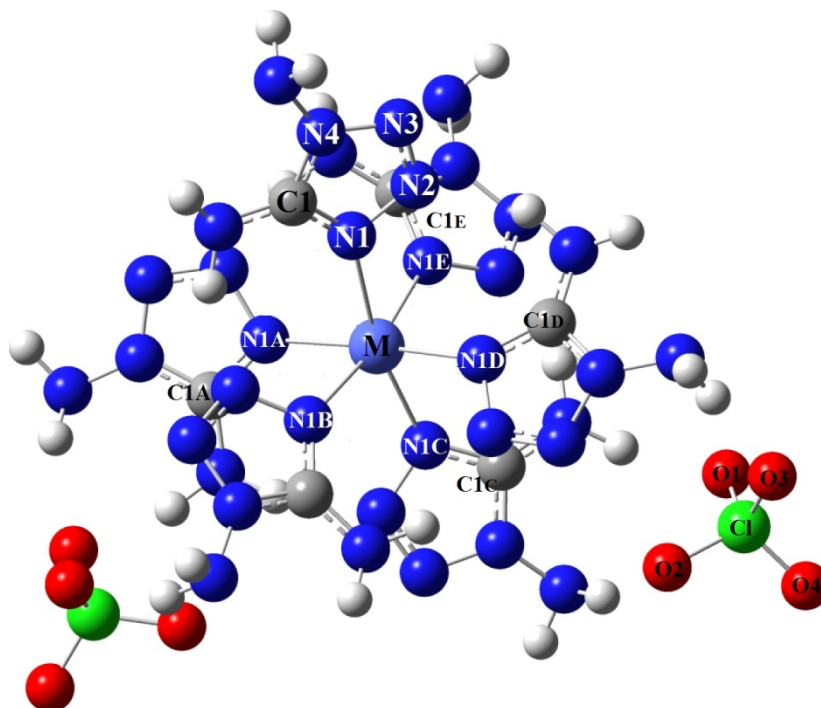


Figure S5. The optimized structure of  $[M(\text{DAT})_6](\text{ClO}_4)_2$  by Gaussian 09. Here, M represents the metal cation  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . The deep blue atom means nitrogen, green means chlorine, red means oxygen.

### Theoretical method for the solidate calculation

First-principles calculations were carried out within the DFT calculations using the projector augmented wave (PAW) method <sup>4</sup>, which is implemented in the CASTEP code <sup>5</sup>. The generalized gradient approximation <sup>6</sup> of Perdew, Burke and Erzerhof <sup>7</sup> (GGA-PBE) for the exchange-correlation function has been used throughout. The Vanderbilt-type ultrasoft pseudopotentials <sup>8</sup> with valence states  $3d^5 4s^2$  for Mn,  $3d^7 4s^2$  for Co,  $3d^{10} 4s^2$  for Zn,  $4d^{10} 5s^2$  for Cd,  $3s^2 3p^5$  for Cl,  $2s^2 2p^2$  for C,  $2s^2 2p^4$  for O,  $2s^2 2p^3$  for N, and  $1s^1$  for H were used to describe the core electrons. A plane wave basis set with an energy cutoff of 600eV has been used. The Brillouin-zone integration of  $[\text{Mn}(\text{DAT})_6](\text{ClO}_4)_2$ ,  $[\text{Co}(\text{DAT})_6](\text{ClO}_4)_2$ ,  $[\text{Zn}(\text{DAT})_6](\text{ClO}_4)_2$  and  $[\text{Co}(\text{DAT})_6](\text{ClO}_4)_2$  were done by using  $5 \times 5 \times 4$ ,  $5 \times 5 \times 8$ ,  $4 \times 4 \times 3$ ,  $5 \times 6 \times 2$  Monkhorst-Pack meshes <sup>9</sup> respectively. Structural relaxations of atomic positions, cell shapes and cell volume were carried out by BFGS method <sup>10</sup> until the residual forces and stresses were less than  $0.005 \text{ eV/\AA}$  and  $0.05 \text{ Gpa}$ .

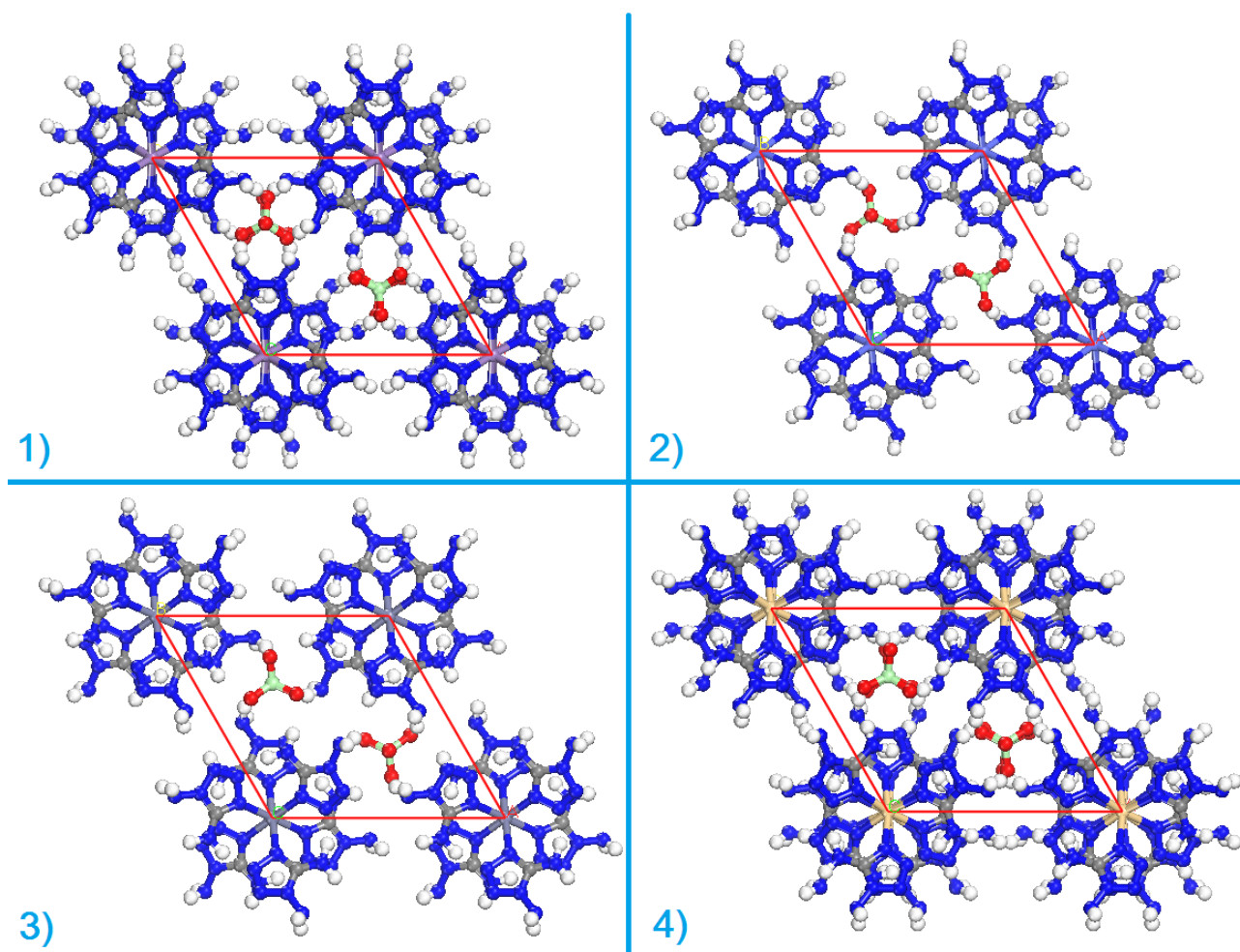


Figure S6 The optimized structures of solidate 1~4.

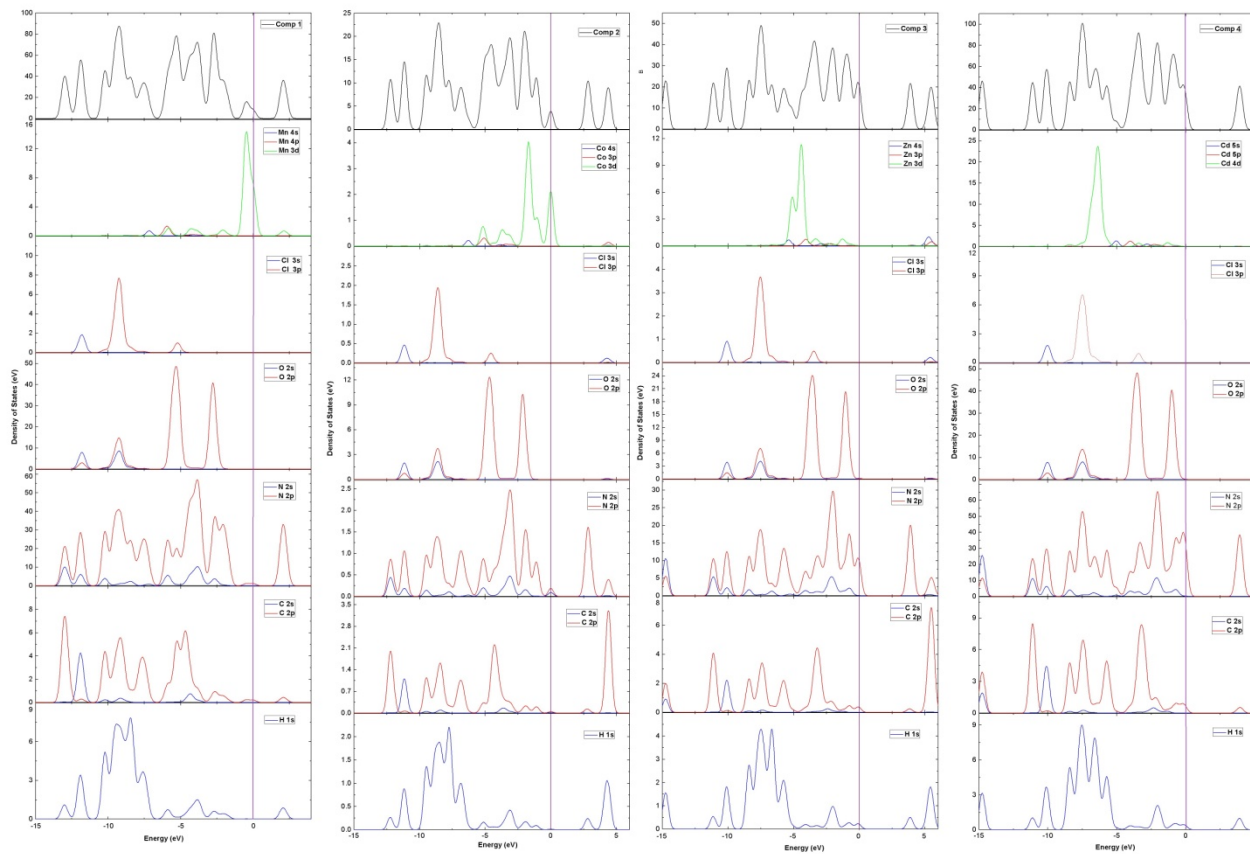


Figure S7 The DOS and pDOS map of the for compounds.

**Table (Part 2)**

Table S2. The selected experimental and theoretical bond lengths (Å)

Bond	1			2			3			4		
	Cal <sup>1</sup>	Cal <sup>2</sup>	Expt	Cal <sup>1</sup>	Cal <sup>2</sup>	Expt	Cal <sup>1</sup>	Cal <sup>2</sup>	Expt	Cal <sup>1</sup>	Cal <sup>2</sup>	Expt
M-N1	2.32	2.13	2.29	2.25	2.20	2.22	2.28	2.26	2.22	2.42	2.41	2.37
M-N1A	2.32	2.13	2.29	2.24	2.19	2.21	2.28	2.26	2.22	2.42	2.41	2.37
M-N1B	2.32	2.13	2.29	2.24	2.19	2.21	2.28	2.26	2.22	2.42	2.41	2.37
M-N1C	2.32	2.13	2.29	2.25	2.20	2.22	2.28	2.26	2.22	2.42	2.41	2.37
M-N1D	2.32	2.13	2.29	2.24	2.19	2.21	2.28	2.26	2.22	2.42	2.41	2.37
M-N1E	2.32	2.13	2.29	2.24	2.19	2.21	2.28	2.26	2.22	2.42	2.41	2.37
N1-N2	1.37	1.39	1.38	1.37	1.38	1.38	1.37	1.38	1.37	1.37	1.38	1.37
N1A-N14	1.37	1.39	1.38	1.37	1.38	1.38	1.37	1.38	1.37	1.37	1.38	1.37
N1B-N25	1.37	1.39	1.38	1.37	1.38	1.38	1.37	1.38	1.37	1.37	1.38	1.37
N1C-N36	1.37	1.39	1.38	1.37	1.38	1.38	1.37	1.38	1.37	1.37	1.38	1.37
N1D-N47	1.37	1.39	1.38	1.37	1.38	1.38	1.37	1.38	1.37	1.37	1.38	1.37
N1E-N58	1.37	1.39	1.38	1.37	1.38	1.38	1.37	1.38	1.37	1.37	1.38	1.37
N1-C1	1.34	1.36	1.34	1.34	1.36	1.34	1.34	1.35	1.33	1.34	1.35	1.33
N1A-C1A	1.34	1.36	1.34	1.34	1.36	1.34	1.34	1.35	1.33	1.34	1.35	1.33
N1B-C1B	1.34	1.36	1.34	1.34	1.36	1.34	1.34	1.35	1.33	1.34	1.35	1.33
N1C-C1C	1.34	1.36	1.34	1.34	1.36	1.34	1.34	1.35	1.33	1.34	1.35	1.33
N1D-C1D	1.34	1.36	1.34	1.34	1.36	1.34	1.34	1.35	1.33	1.34	1.35	1.33
N1E-C1E	1.34	1.36	1.34	1.34	1.36	1.34	1.34	1.35	1.33	1.34	1.35	1.33

Cal<sup>1</sup> means the results from gaussian 09; Cal<sup>2</sup> means the results from castep.

Table S3. The second order stabilized energies (kcal/mol) associated with delocalizations of  $\sigma_{N-N} \rightarrow \sigma^*_{N-M}/n_M$  and  $\sigma_{N-C} \rightarrow \sigma^*_{N-M}/n_M$

Delocalization (kcal /mol)	Mn	Co	Zn	Cd
$\sigma_{N1-N2} \rightarrow \sigma^*_{N1-M}/n_M$	2.96	1.18	3.12	2.71
$\sigma_{N1A-N2A} \rightarrow \sigma^*_{N1A-M}/n_M$	3.02	1.22	3.13	2.70
$\sigma_{N1B-N2B} \rightarrow \sigma^*_{N1B-M}/n_M$	2.93	1.21	3.11	2.68
$\sigma_{N1C-N2C} \rightarrow \sigma^*_{N1C-M}/n_M$	2.92	1.21	3.12	2.71
$\sigma_{N1D-N2D} \rightarrow \sigma^*_{N1D-M}/n_M$	2.93	1.22	3.13	2.69
$\sigma_{N1E-N2E} \rightarrow \sigma^*_{N1E-M}/n_M$	3.00	1.22	3.12	2.68
$\sigma_{N1-C1} \rightarrow \sigma^*_{N1-M}/n_M$	4.35	3.05	4.23	3.73
$\sigma_{N1A-C1A} \rightarrow \sigma^*_{N1A-M}/n_M$	4.35	3.03	4.65	3.72
$\sigma_{N1B-C1B} \rightarrow \sigma^*_{N1B-M}/n_M$	4.23	3.04	4.62	3.73
$\sigma_{N1C-C1C} \rightarrow \sigma^*_{N1C-M}/n_M$	4.24	3.06	4.65	3.74
$\sigma_{N1D-C1D} \rightarrow \sigma^*_{N1D-M}/n_M$	4.26	3.05	4.66	3.72
$\sigma_{N1E-C1E} \rightarrow \sigma^*_{N1E-M}/n_M$	4.23	3.04	4.64	3.72

Table S4. Different energetic performances caused by the different electronic configuration of the center metals.

The series of Azido Metal salts of ethandiamine complexes (M(en)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>)<sup>11a</sup>

Complexes	Electronic Configuration of center metal	Impact sensitivities (J)
Mn(en) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>5</sup>	14.12
Ni(en) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>8</sup>	1.38
Cu(en) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>9</sup>	7.81
Zn(en) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>10</sup>	- (> 4 J)

The series of Azido Metal salts of propanediamine complexes (M(pn)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>)<sup>11a</sup>

Complexes	Electronic Configuration of center metal	Impact sensitivities (J)
Mn(pn) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>5</sup>	- (> 25 J)
Ni(pn) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>8</sup>	4.38
Cu(pn) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>9</sup>	2.56
Zn(pn) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>10</sup>	- (> 25 J)
Cd(pn) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	4d <sup>10</sup>	- (> 25 J)

The series of Azido Metal salts of 1,5-Diaminotetrazole complexes (M(DAT)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>)<sup>11b</sup>

Complexes	Electronic Configuration of center metal	Impact sensitivities (J)
Mn(DAT) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>5</sup>	11.03
Co(DAT) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>7</sup>	8.62
Ni(DAT) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>8</sup>	10.39
Zn(DAT) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	3d <sup>10</sup>	- (> 25 J)
Cd(DAT) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	4d <sup>10</sup>	- (> 25 J)
Pb(DAT) <sub>2</sub> (N <sub>3</sub> ) <sub>2</sub>	5d <sup>10</sup> 6s <sup>2</sup> 6p <sup>2</sup>	- (> 25 J)

The series of Perchlorate Metal salts of 1,5-Diaminotetrazole complexes (M(DAT)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub>)

Complexes	Electronic Configuration of center metal	Impact sensitivities (J)
Mn(DAT) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	3d <sup>5</sup>	3.6
Co(DAT) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	3d <sup>8</sup>	0.6
Zn(DAT) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	3d <sup>10</sup>	- (> 4 J)
Cd(DAT) <sub>6</sub> (ClO <sub>4</sub> ) <sub>2</sub>	4d <sup>10</sup>	1.2

Table S5 The relationship between the theoretical band gap and the impact sensitivity

The series complexes of  $\alpha$ -Perchlorate Metal salts of carbohydrazide complexes ( $\alpha$ -MCP), where the metal coordinates with the oxygen atom<sup>11c,d</sup>

Compounds	band gap (eV)	Impact sensitivities (J)
$\alpha$ - [Fe(NH <sub>2</sub> NHCONHNH <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	4.44	0.75
$\alpha$ - [Co(NH <sub>2</sub> NHCONHNH <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	4.87	0.93
$\alpha$ - [Ni(NH <sub>2</sub> NHCONHNH <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	5.91	0.98
$\alpha$ - [Zn(NH <sub>2</sub> NHCONHNH <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6.27	1.83
$\alpha$ - [Cd(NH <sub>2</sub> NHCONHNH <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	6.33	1.55

The series complexes of  $\beta$ -Perchlorate Metal salts of carbohydrazide complexes ( $\beta$ -MCP), where the metal coordinates with the nitrogen atom<sup>11e</sup>

Compounds	band gap (eV)	Impact sensitivities (J)
$\beta$ - [Co(NH <sub>2</sub> NHCONHNH <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	4.55	4.31
$\beta$ - [Ni(NH <sub>2</sub> NHCONHNH <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	5.80	4.70
$\beta$ - [Cu(NH <sub>2</sub> NHCONHNH <sub>2</sub> ) <sub>3</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	3.59	0.86

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