Electronic Supplementary Information

Structural anchoring of highly reactive CBH^- for high-performance hypergolic coordination polymers with excellent thermal stability

Qin Wang,‡[a] Meng Cui,‡[b] Pin-Hao Wei,[a] Long-Chuan Li,[a] Ning-Ning Zhang,[c] Fei Tan,[a] Fa-Kun Zheng,*[b] Jian-Gang Xu,*[a,b] and Guo-Cong Guo[b]

[a] College of Material Engineering, Fujian Agriculture and Forestry University, Fuzhou, Fujian 350108, P. R. China

[b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, P. R. China

[c] School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng, Shandong 252000, P. R. China

‡Qin Wang and Meng Cui contributed equally to this work.

*Corresponding authors. E-mail addresses: zfk@fjirsm.ac.cn, jgxu@fafu.edu.cn

Index:

1. Experimental details

1.1 Synthesis

Synthesis of $[Mn(CBH)_2(BIM)_2]_n$ 2. Firstly, a solution of $Mn(NO_3)_2·4H_2O$ (0.2 mmol, 50.20 mg) dissolved in water (5 mL) was placed at the bottom of the test tube. Then, a mixture of acetonitrile and water (1:1, 5 mL) was slowly added to the top of the metal solution. Finally, a mixture of acetonitrile and water (2:1, 6 mL) containing BIM (0.4 mmol, 59.20 mg) and CBH (0.4 mmol, 25.14 mg) was added as the top layer. After 1 week, white crystals were obtained. Yield: 85% (based on BIM). Calcd for $C_{16}H_{24}N_{10}Mn$: C, 44.34; H, 5.54; N, 32.33%. Found: C, 44.33; H, 5.09; N, 32.46%. IR (KBr particle, cm^{-1}): 3113 vs, 3024 w, 2338 vs, 2230 w, 2192 vs, 1711 w, 1601 w, 1503 vs, 1391 s, 1285 s, 1234 vs, 1133 vs, 1086 vs, 1028 w, 932 s, 857 m, 754 vs, 711 s, 661 s, 612 w.

Synthesis of $[Zn(CBH)_2(BIM)_2]_n$ 3. Firstly, a solution of $Zn(NO_3)_2·6H_2O$ (0.2 mmol, 59.50 mg) dissolved in water (5 mL) was placed at the bottom of the test tube. Then, a mixture of acetonitrile and water (1:1, 5 mL) was slowly added to the top of the metal solution. Finally, a mixture of acetonitrile and water (2:1, 6 mL) containing BIM (0.4 mmol, 59.20 mg) and CBH (0.4 mmol, 25.14 mg) was added as the top layer. After 1 week, white crystals were obtained. Yield: 85% (based on BIM). Calcd for $C_{16}H_{24}N_{10}Zn$: C, 43.29; H, 5.41; N, 31.57%. Found: C, 42.98; H, 4.95; N, 31.43%. IR (KBr particle, cm^{-1}): 3115 m, 3023 w, 2337 vs, 2198 vs, 1719 w, 1597 w, 1502 vs, 1392 s, 1284 s, 1235 vs, 1194 w, 1133 vs, 1101 vs, 1027 w, 935 m, 859 m, 756 vs, 711 s, 663 s, 611 w.

1.2 Heat of combustion

The constant-volume combustion energies of the compounds were determined by a precise

oxygen bomb calorimetry (5E-AC8018, Changsha Kaiyuan Instrument Co., Ltd., China). Firstly, we adopted the certified benzoic acid (about 1.0 g, pellet), which has an isothermal heat of combustion close to −26.434 $J \cdot g^{-1}$ at 298.15 K, by the combustion in an oxygen atmosphere to calibrate the calorimeter. Then, 400 mg of the samples were prepared and mixed with certified benzoic acid (calculated: 1000 mg), which were pressed to form a pellet to ensure better combustion. Finally, the pellet was placed in combustion pots, which were subsequently burned in an atmosphere of pure oxygen.

The constant volume heat of combustion ($\Delta_c U$) was determined by oxygen bomb calorimetry, and the experimental values of compounds **1-3** are −25.32, −28.61 and −26.23 $kJ \cdot g^{-1}$, respectively. The enthalpy of combustion ($\Delta_c H$) is calculated from $\Delta_c U$ and the gas volume correction ($\Delta_c H = \Delta_c U + \Delta nRT$), where Δn is the change in the number of gas components during the reaction, R = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$, T = 298.15 K. The combustion reaction is shown in formulas **1**, **2**, and **3**:

$$C_{16}H_{24}N_{10}B_2Cd(s) + 24O_2(g) \rightarrow CdO(s) + B_2O_3(s) + 16CO_2(g) + 12H_2O(l) + 5N_2(g) \quad (1)$$

$$C_{16}H_{24}N_{10}B_2Mn(s) + 24O_2(g) \rightarrow MnO(s) + B_2O_3(s) + 16CO_2(g) + 12H_2O(l) + 5N_2(g) \quad (2)$$

$$C_{16}H_{24}N_{10}B_2Zn(s) + 24O_2(g) \rightarrow ZnO(s) + B_2O_3(s) + 16CO_2(g) + 12H_2O(l) + 5N_2(g) \quad (3)$$

The $\Delta_c H$ values of **1-3** are –12515.24, −12379.68 and –11624.88 $kJ \cdot mol^{-1}$. According to the Hess thermochemical cycle reaction, the standard enthalpies of formation ($\Delta_f H^o$) of **1-3** can be calculated, and the Hess thermochemical cycle reactions are given by the following formula:

$$\Delta_f H^o [\mathbf{1}, s] = \Delta_f H^o [CdO, s] + \Delta_f H^o [B_2O_3, s] + 16\Delta_f H^o [CO_2, g] + 12\Delta_f H^o [H_2O, l] - \Delta_c H^o [\mathbf{1}, s] \quad (4)$$

$\Delta_f H^o$ [**2**, s] = $\Delta_f H^o$ [MnO, s] + $\Delta_f H^o$ [B_2O_3, s] + 16$\Delta_f H^o$ [CO_2, g] + 12$\Delta_f H^o$ [H_2O, l] – $\Delta_c H^o$ [**2**, s] (5)

$\Delta_f H^o$ [**3**, s] = $\Delta_f H^o$ [ZnO, s] + $\Delta_f H^o$ [B_2O_3, s] + 16$\Delta_f H^o$ [CO_2, g] + 12$\Delta_f H^o$ [H_2O, l] – $\Delta_c H^o$ [**3**, s] (6)

The $\Delta_f H^o$ values of ZnO, CdO, MnO, B_2O_3, CO_2 and H_2O are –350.5, –258.4, –384.9, –1271.94, –393.51 and 285.83 kJ·mol^{-1}, respectively. The $\Delta_f H^o$ values of **1-3** were calculated as 1258.78, 996.72 and 276.32 kJ·mol^{-1}, respectively.

1.3 Sensitivities Test

The mechanical sensitivities of the compounds were determined according to the BAM (German: Bundesanstalt für Materialforschung und Prüfung) standard for friction and impact. The classification of the tested compounds results from the 'UN Recommendations on the Transport of Dangerous Goods'.[1] Test conditions: 29 ℃ (temperature); 36% (relative humidity).

Impact sensitivity (IS). The impact sensitivity was tested on a BAM fall hammer BFH-12 produced by OZM Research. Impact sensitivity tests were carried out according to STANAG 4489. A weight was dropped from a set height onto a 10 mg sample placed on a copper cap. Each subsequent test was made at the next lower height if explosion occurred and at the next higher height if no explosion happened until the value of 50% probability of the explosion is obtained. After dozens of experiments, the IS values of **1-3** were all greater than 40 J.

Friction sensitivity (FS). The friction sensitivity was determined using a FSKM-10 BAM friction apparatus produced by OZM Research based on STANAG 4487. The FS values of **1-3** are greater than 360 N. The above results indicate that compounds **1-3** are classified as insensitive energetic materials

1.4 Specific impulse and thrust coefficient.

The specific impulse is an ideal indicator for judging whether the propellant is suitable for the task, and the specific impulse is proportional to the thrust generated.[2] The specific impulse is determined by the formula $I_{sp} = CF \cdot C^*/g$, where CF represents the inference coefficient and C^* represents the characteristic velocity (m/s), g = 9.8 $m \cdot s^{-2}$. In this work, CEA, as a chemical equilibrium application developed by NASA researchers, was used to calculate the specific impulse of compounds. In the calculation, we chose HNO_3 as the oxidant, with an ambient temperature (T_a) of 298.15 K. The fuel-to-oxidant ratio (O/F) ranges from 1.0 to 5.0, the combustion chamber pressure (P_c) is 25 atm, and the ambient pressure (P_e) is 1 atm. The expansion ratio, represented by the outlet-to-throat area ratio (Ae/At), ranges from 2 to 4, assuming freezing flow conditions during expansion. The results showed that compound **1** exhibited the I_{sp} value of 223 s with Ae/At = 4.1016, CF=1.4466. Compound **2** show the highest specific impulse I_{sp} = 225 s with Ae/At = 4.0756, CF = 1.4393. Compound **3** was collected at Ae/At = 4.0923 with I_{sp} = 219 s.

1.5 Theoretical calculation.

The electrostatic potential and density of states of the compounds were calculated using Materials Studio 2019. Compounds **1-3** were optimized using the DMol3 module and select the GGA-BLYP functional in the function to calculate the electrostatic potential of **1-3**. The density of states (DOS) and band gaps were determined by using the CASTEP code and the geometry optimization and the calculation of DOS maps and band gaps employed the GGA/PBE functional.

2. Tables

Table S1 Crystal data.

Compound	**1**	**2**	**3**
CCDC	Ref.[3]	2329590	2329589
Empirical formula	$C_{16}H_{24}B_2CdN_{10}$	$C_{16}H_{24}B_2MnN_{10}$	$C_{16}H_{24}B_2ZnN_{10}$
M_r *(g mol^{-1})*	490.47	433.01	443.44
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Cmce*	*Cmce*	*Cmce*
Z	4	4	4
a/Å	9.4128(2)	9.3100(2)	9.1756(2)
b/Å	15.0618(3)	15.0016(3)	14.8590(3)
c/Å	15.6238(3)	15.4922(3)	15.4234(3)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
V/Å^3	2215.04(8)	2163.72(8)	2102.83(7)
D_c/g cm^{-3}	1.471	1.329	1.401
Temperature (K)	293(2)	293(2)	293(10)
F(000)	992.0	900.0	920.0
Reflns	3714	3647	3673
GOF *on* F^2	1.095	1.092	1.165
R_1 $(I > 2\sigma(I))^a$	0.0248	0.0269	0.0290
wR_2 $(I > 2\sigma(I))^b$	0.0654	0.0694	0.0787
R_1 (all data)^a	0.0277	0.0303	0.0325
wR_2 (all data)^b	0.0677	0.0711	0.0807

^{a} $R_1 = \sum(F_o - F_c)/\sum F_o$; ^{b} $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table S2 Selected bond distances (Å) and bond angles (°).

Compound **1**			
Cd(1)–N(11)#1	2.3477(16)	Cd(1)–N(11)#3	2.3477(16)
Cd(1)–N(11)	2.3478(17)	Cd(1)–N(21)	2.334(3)
Cd(1)–N(11)#2	2.3477(16)	Cd(1)–N(21)#1	2.334(3)
N(11)#1–Cd(1)–N(11)#2	86.14(8)	N(21)–Cd(1)–N(21)#1	180.0
N(11)#2–Cd(1)–N(11)#3	180.0	C(11)–N(12)–C(14)	126.5(2)
N(11)#1–Cd(1)–N(11)#3	93.86(8)	C(11)–N(12)–C(13)	106.94(18)
N(11)#1–Cd(1)–N(11)	180.0	C(13)–N(12)–C(14)	126.5(2)
N(11)#3–Cd(1)–N(11)	86.15(8)	C(11)–N(11)–Cd(1)	124.34(14)
N(11)#2–Cd(1)–N(11)	93.85(8)	C(11)–N(11)–C(12)	105.51(18)
N(21)–Cd(1)–N(11)#2	89.00(6)	C(12)–N(11)–Cd(1)	130.03(14)
N(21)#1–Cd(1)–N(11)#1	89.00(6)	C(21)–N(21)–Cd(1)	167.2(3)
N(21)#1–Cd(1)–N(11)	90.99(6)	N(12)#4–C(14)–N(12)	111.8(2)
N(21)#1–Cd(1)–N(11)#2	91.00(6)	N(11)–C(11)–N(12)	111.64(16)
N(21)–Cd(1)–N(11)#1	91.00(6)	N(21)–C(21)–B(21)	177.2(4)
N(21)–Cd(1)–N(11)#3	91.00(6)	C(12)–C(13)–N(12)	106.1(2)
N(21)#1–Cd(1)–N(11)#3	89.00(6)	C(13)–C(12)–N(11)	109.8(2)
N(21)–Cd(1)–N(11)	89.01(6)		
Compound **2**			
Mn(1)–N(11)#1	2.2694(12)	Mn(1)–N(11)#3	2.2694(12)
Mn(1)–N(11)#2	2.2694(12)	Mn(1)–N(21)	2.2134(18)

Mn(1)–N(11)	2.2694(12)	Mn(1)–N(21)#1	2.2134(18)
N(11)#1–Mn(1)–N(11)	180.0	N(21)–Mn(1)–N(21)#1	180.0
N(11)–Mn(1)–N(11)#2	86.41(6)	C(11)–N(12)–C(14)	126.44(13)
N(11)#1–Mn(1)–N(11)#2	93.59(6)	C(11)–N(12)–C(12)	106.74(12)
N(11)#1–Mn(1)–N(11)#3	86.41(6)	C(12)–N(12)–C(14)	126.82(14)
N(11)#2–Mn(1)–N(11)#3	180.0	C(11)–N(11)–Mn(1)	124.67(9)
N(11)–Mn(1)–N(11)#3	93.59(6)	C(11)–N(11)–C(13)	104.86(12)
N(21)–Mn(1)–N(11)	88.96(5)	C(13)–N(11)–Mn(1)	130.41(10)
N(21)#1–Mn(1)–N(11)#1	88.95(5)	C(21)–N(21)–Mn(1)	170.0(2)
N(21)#1–Mn(1)–N(11)#3	91.05(5)	N(11)–C(11)–N(12)	111.90(12)
N(21)#1–Mn(1)–N(11)	91.04(5)	N(21)–C(21)–B(21)	178.1(3)
N(21)–Mn(1)–N(11)#1	91.04(5)	N(12)–C(14)–N(21)#4	111.91(16)
N(21)–Mn(1)–N(11)#2	91.04(5)	C(12)–C(13)–N(11)	110.54(14)
N(21)#1–Mn(1)–N(11)#2	88.95(5)	C(13)–C(12)–N(12)	105.95(14)
N(21)–Mn(1)–N(11)#3	88.96(5)		
Compound **3**			
Zn(1)–N(11)	2.1777(14)	Zn(1)–N(11)#3	2.1777(14)
Zn(1)–N(11)#1	2.1777(14)	Zn(1)–N(21)#2	2.153(2)
Zn(1)–N(11)#2	2.1777(14)	Zn(1)–N(21)	2.153(2)
N(11)–Zn(1)–N(11)#1	180.0	N(21)#1–Zn(1)–N(21)	180.0
N(11)#1–Zn(1)–N(11)#2	93.26(8)	C(11)–N(12)–C(14)	126.31(17)

N(11)–Zn(1)–N(11)#2	86.74(8)	C(11)–N(12)–C(12)	107.08(15)
N(11)–Zn(1)–N(11)#3	93.26(8)	C(12)–N(12)–C(14)	126.60(17)
N(11)#2–Zn(1)–N(11)#3	180.0	C(11)–N(11)–Zn(1)	124.35(12)
N(11)#1–Zn(1)–N(11)#3	86.74(8)	C(11)–N(11)–C(13)	105.21(15)
N(21)#1–Zn(1)–N(11)#1	88.97(6)	C(13)–N(11)–Zn(1)	130.43(12)
N(21)–Zn(1)–N(11)	88.97(6)	C(22)–N(21)–Zn(1)	170.7(2)
N(21)–Zn(1)–N(11)#3	88.97(6)	N(11)–C(11)–N(12)	111.56(14)
N(21)–Zn(1)–N(11)#1	91.03(6)	N(12)#4–C(14)–N(12)	111.6(2)
N(21)#1–Zn(1)–N(11)	91.03(6)	N(21)–C(22)–B(21)	179.2(4)
N(21)#1–Zn(1)–N(11)#2	88.97(6)	C(13)–C(12)–N(12)	105.81(16)
N(21)–Zn(1)–N(11)#2	91.03(6)	C(12)–C(13)–N(11)	110.34(17)
N(21)#1–Zn(1)–N(11)#3	91.03(6)		

Symmetry codes for compounds **1**, **2** and **3**. For **1**, #1 1 – *x,* 1 – *y,* 1 – *z*. #2 1 – *x, y, z*. #3 *x,* 1 – *y,* 1 – *z*. #4 2 – *x, y, z*. #5 1 + *x, y, z*. For **2**, #1 – *x,* 1 – *y,* 1 – *z*. #2 *x,* 1 – *y,* 1 – *z*. #3 – *x, y, z*. #4 1 – *x, y, z*. #5 1 + *x, y, z*. For **3**, #1 2 – *x,* 1 – *y,* 1 – *z*. #2 *x,* 1 – *y,* 1 – *z*. #3 2 – *x, y, z*. #4 1 – *x, y, z*. #5 –1 + *x, y, z*.

Table S3 The values of *ID* time, flame duration and flame height from droplet tests for 5 times (numbers in parentheses represent the order of experiments).

	Experiment times	1	2	3
***ID* (ms)**	1	15	16	31
	2	15	19	27
	3	14	14	30
	4	12	13	29
	5	16	18	27
Flame duration (ms)	1	319	322	412
	2	450	481	215
	3	400	313	334
	4	279	327	418
	5	233	278	533
Flame hight (cm) (approximate values)	1	>10	8	9
	2	>10	>10	>10
	3	>10	>10	>10
	4	>10	8	>10
	5	>10	>10	7

Table S4 Comparison of density, energy density and thermal decomposition temperature of selected cyanide hydride spontaneous combustion compounds.

Explosive	ρ^a ($g \cdot cm^{-3}$)	E_v^b ($kJ \cdot cm^{-3}$)	$T_{dec}{}^c$ (℃)	**Refs**
1	1.47	37.53	268	This work
2	1.32	37.99	317	This work
3	1.40	36.73	248	This work
Cu-MIm-CBH	1.30	35.03	182	*Chem. Eng. J.* **2021**, 426: 131866
Cu-EIm-CBH	1.20	33.47	193	*Chem. Eng. J.* **2021**, 426: 131866
Cu-AIm-CBH	1.25	36.67	178	*Chem. Eng. J.* **2021**, 426: 131866
Cu-VIm-CBH	1.28	34.68	163	*Chem. Eng. J.* **2021**, 426: 131866
Ni-AIm-CBH	1.22	−	165	*Inorg. Chem.* **2021**, 60(22): 17033-17039
Mn-AIm-CBH	1.18	−	248	*Inorg. Chem.* **2021**, 60(22): 17033-17039

[a] density. [b] volume energy density. [c] thermal decomposition temperature. Cu-MIm-CBH = $CuCBH_2MIm_2$; CBH = $NaBH_3CN$; MIm = 1-methylimidazole; Cu-EIm-CBH = $CuCBH_2EIm_2$; EIm = 1-ethylimidazole; Cu-AIm-CBH = $CuCBH_2EIm_2$; AIm = 1-allylimidazole; Cu-VIm-CBH = $CuCBH_2EIm_2$; VIm = 1-vinylimidazole; Ni-AIm-CBH = $NiCBH_2EIm_2$; Mn-AIm-CBH = $MnCBH_2EIm_2$.

3. Graphics

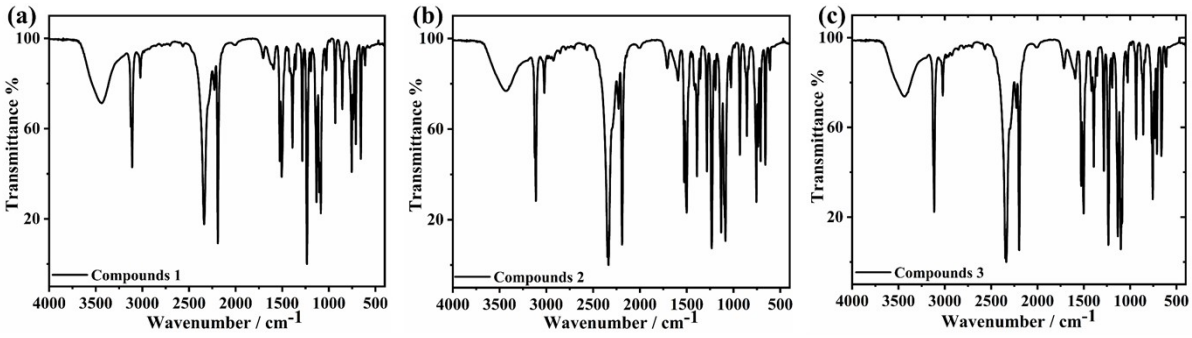

Fig. S1 The IR spectra of **1** (a), **2** (b) and **3** (c).

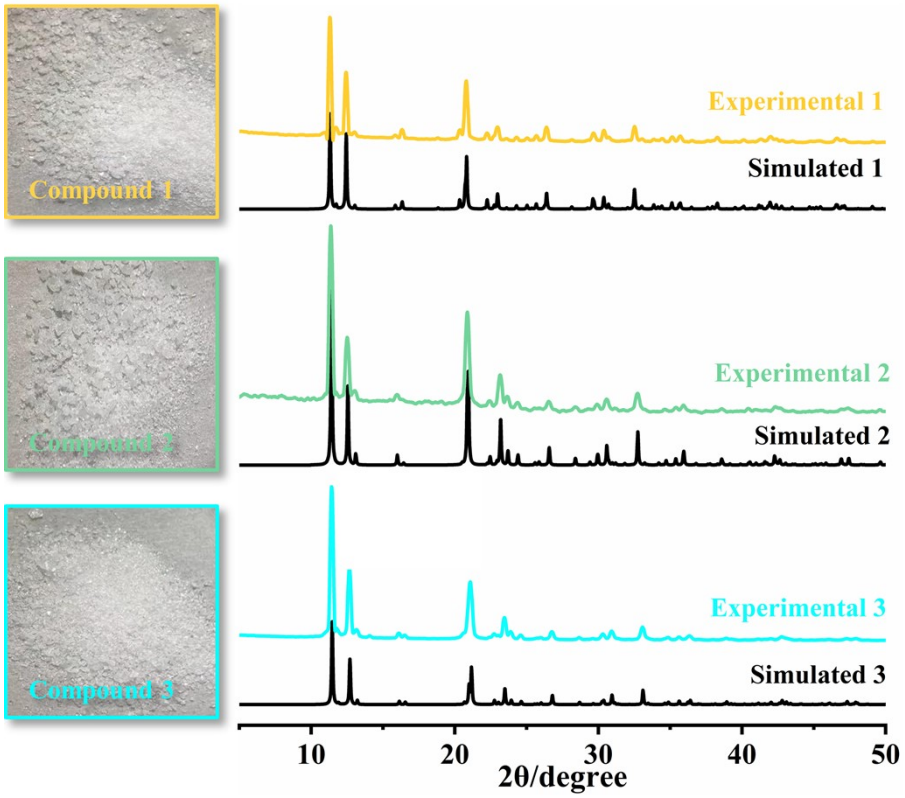

Fig. S2 The PXRD spectra of **1**, **2** and **3**.

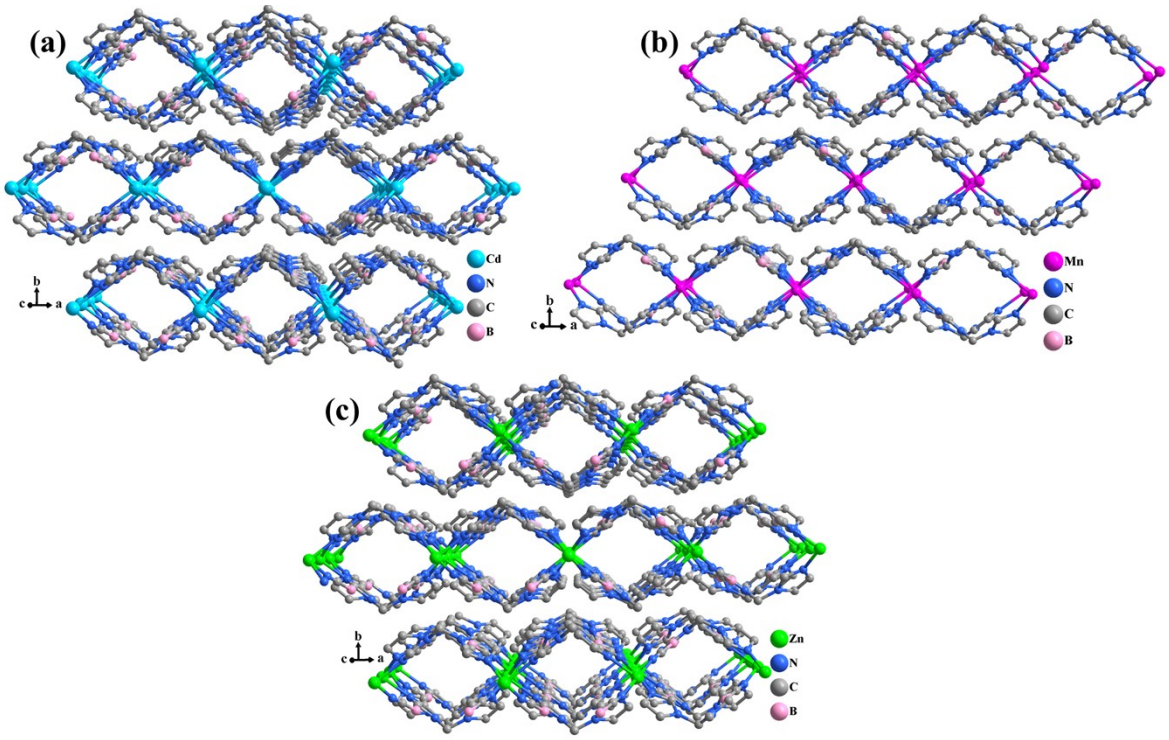

Fig. S3 The three-dimensional supramolecular structures of **1** (a), **2** (b) and **3** (c).

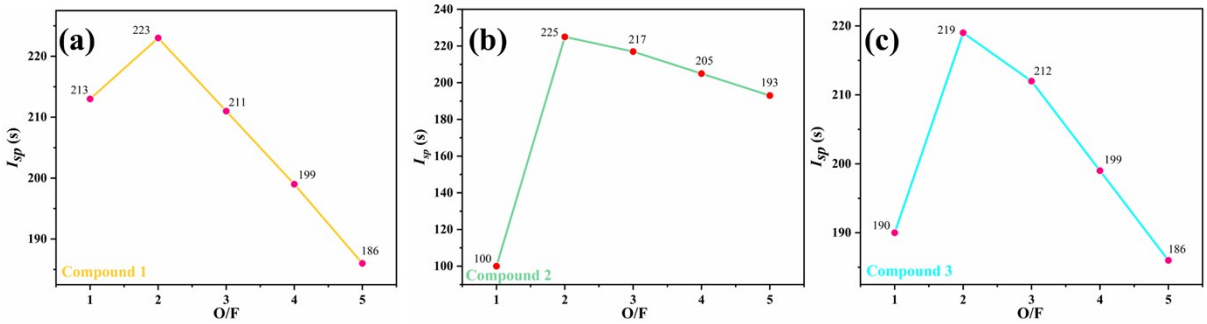

Fig. S4 The specific impulse curves of WFNA/ **1** (a), **2** (b) and **3** (c).

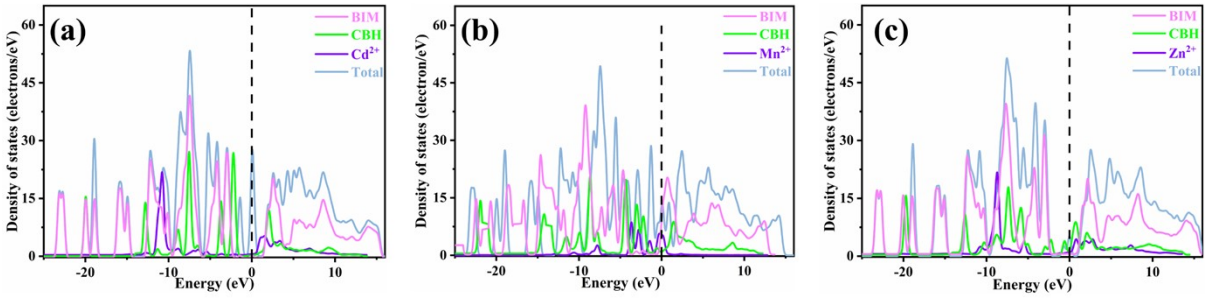

Fig. S5 The state densities and partial wave state densities of **1** (a), **2** (b) and **3** (c).

4. References

[1] Impact: insensitive > 40 J, less sensitive ≥ 35 J, sensitive ≥ 4 J, very sensitive ≤ 3 J; Friction: insensitive > 360 N, less sensitive = 360 N, 80 N < sensitive < 360 N, very sensitive ≤ 80 N, extremely sensitive ≤ 10 N.

[2] R. Sunil, A. Virkar, M. Vignesh Kumar, I. Krishnamoorthy, V. Malhotra, IOP Conf. Ser.: Mater. Sci. Eng. 912 (2020) 042023.

[3] Qin Wang: *CSD Communication*, 2025, DOI: 10.5517/ccdc.csd.cc2j63xs.