Electronic Supplementary Information

Coordination polymerization of nitrogen-rich linkers and dicyanamide anions toward energetic coordination polymers with low sensitivities

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1. Experimental details

1.1 Heat of combustion

The constant-volume combustion energies of the compounds were determined by a precise oxygen bomb calorimetry (5E-AC8018, Changsha Kaiyuan Instruments, China). The correct value of the heat exchange was calculated according to the Linio-Pyfengdelel-Wsava equation.[1]

Firstly, we adopt the certified benzoic acid (about 1.0 g, pellet), which has an isothermal heat of combustion of (−26434 ± 3) $J \cdot g^{-1}$ at 298.15 K, by the combustion in an oxygen atmosphere to calibrate the calorimeter. Then, 150 mg of the samples were prepared and mixed with certified benzoic acid, 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 enthalpies of formation ($\Delta_f H$) of the compounds were back calculated by the enthalpy of combustion ($\Delta_c H$). The $\Delta_c H$ values were calculated from $\Delta_c U$ with a gas volume correction: $\Delta_c H = \Delta_c U + \Delta nRT$, where Δn is the change of about molar amount of gases in the reaction process, R = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$ and T = 298.15 K. The constant-volume combustion heat ($\Delta_c U$) **1**, **2**, **3**, and **4** is 13.490, 12.143, 12.695, and 11.308 $kJ \cdot g^{-1}$, respectively, measured by the oxygen bomb calorimetry. The combustion reactions are based on Eqs. 1–4 as follows:

$$CoC_8H_{12}N_{16}O + 11O_2(g) \rightarrow CoO(s) + 8CO_2(g) + 6H_2O(l) + 8N_2(g) \quad (1)$$

$$CuC_6H_5N_{11} + 31/4O_2(g) \rightarrow CuO(s) + 6CO_2(g) + 5/2H_2O(l) + 11/2N_2(g) \quad (2)$$

$$CdC_8H_{10}N_{16} + 11O_2(g) \rightarrow CdO(s) + 8CO_2(g) + 5H_2O(l) + 8N_2(g) \quad (3)$$

$$CdC_8H_{10}N_{16} + 11O_2(g) \rightarrow CdO(s) + 8CO_2(g) + 5H_2O(l) + 8N_2(g) \quad (4)$$

The **1–4** $\Delta_c H$ values are determined to be −13.460, −12.111, −12.667, and −11.280 $kJ \cdot g^{-1}$, respectively. The $\Delta_f H^o$ value of **1–4** was calculated from Hess's law to be 0.935, 1.150, 1.745, and 0.358 $kJ \cdot g^{-1}$, respectively, based on the known enthalpies of CuO (s,

−155.2 kJ·mol^{-1}), CoO (s, −237.9 kJ·mol^{-1}), CdO (s, −258.35 kJ·mol^{-1}), CO_2 (g, −393.51 kJ·mol^{-1}) and H_2O (l, −285.83 kJ·mol^{-1}).

$$\Delta_f H^o[\mathbf{1},s] = \Delta_f H^o[CoO,s] + 8\Delta_f H^o[CO_2,g] + 6\Delta_f H^o[H_2O,l] - \Delta_c H[\mathbf{1},s] \quad (5)$$

$$\Delta_f H^o[\mathbf{2},s] = \Delta_f H^o[CuO,s] + 6\Delta_f H^o[CO_2,g] + 5/2\Delta_f H^o[H_2O,l] - \Delta_c H[\mathbf{2},s] \quad (6)$$

$$\Delta_f H^o[\mathbf{3},s] = \Delta_f H^o[CdO,s] + 8\Delta_f H^o[CO_2,g] + 5\Delta_f H^o[H_2O,l] - \Delta_c H[\mathbf{3},s] \quad (7)$$

$$\Delta_f H^o[\mathbf{4},s] = \Delta_f H^o[CdO,s] + 8\Delta_f H^o[CO_2,g] + 5\Delta_f H^o[H_2O,l] - \Delta_c H[\mathbf{4},s] \quad (8)$$

1.2 Detonation properties

Owing to that the explosion parameter calculation software EXPLO 5 cannot calculate the Cd and Co element, we selected the developed empirical Kamlet formula by Pang[4] to investigate the detonation properties of the metal-based EMs. Detonation performance of the related energetic materials here was evaluated by the developed method based on the empirical Kamlet formula as follows.

$$D = 1.01\ \Phi^{1/2}\ (1 + 1.30\rho) \quad (9)$$

$$P = 1.558\ \Phi\rho^2 \quad (10)$$

$$\Phi = 31.68\ N(MQ)^{1/2} \quad (11)$$

$$Q = -[\Delta H_f(\text{denotation products}) - \Delta H_f(\text{explosive})]/\text{formula weight of explosive} \quad (12)$$

Where D represents detonation velocity (km·s^{-1}) and P is detonation pressure (Gpa), ρ is the density of explosive (g·cm^{-3}). Φ, N, M, and Q are the characteristic parameters of an explosive. N is the moles of detonation gases per gram of explosive, M is the average molecular weight of these gases, and Q is the heat of detonation (kcal·g^{-1}).

When the K-J (Kamlet-Jacbos) equation is employed, the overall calculation process can be described as follows: for the explosives composed of C, H, N, and O elements, all N atoms are converted to N_2; O atoms form H_2O with H atoms first and then form

CO_2 with C atoms; the remaining C atoms are retained in solid state; if there are O atoms left, they will form O_2. To preserve Kamlet's method, the developed theory is employed to determine the detonation products from metal-containing explosives. In most cases, metal atoms are converted to their oxidation states, emitting more heat after detonation. Otherwise, metal atoms can be treated as their reduction states, if the heat of formation (HOF) of metallic oxides is higher than that of H_2O, or there is no O atom in the molecule. Besides, O atoms form H_2O with H atoms first and the remaining ones then form CO_2 with C atoms. However, if the amount of O atoms is not sufficient to oxidize all H atoms, the remaining H atoms can produce NH_3 with N atoms, and the rest of the N atoms are released as N_2 gas. On the other hand, the remaining C atoms are retained in the solid state if they are not completely oxidized by O atoms. If there are redundant O atoms, however, they can be expelled as O_2. The complete detonation reactions are described by Equations 4 and 5. The formation of metal as solid was assumed to be governed by the deficiency of oxygen.

The ΔH_{det} value of **1–4** was calculated to be 1.654, 1.410, 2.091, and 0.704 $kJ \cdot g^{-1}$, respectively. On the basis of Equation 12 with the known $\Delta_f H^o$, Co, Cu, Cd, NH_3 (g, −46 $kJ \cdot mol^{-1}$), H_2O (g, −241.8 $kJ \cdot mol^{-1}$), N_2, C, and the above experimentally determined $\Delta_f H^o$ values of **1–4**.

$$CoC_8H_{12}N_{16}O\ (s) \rightarrow Co(s) + H_2O(g) + 10/3NH_3(g) + 38/3N_2(g) + 8C \quad (13)$$

$$CuC_6H_5N_{11}\ (s) \rightarrow Cu(s) + 5/3NH_3(g) + 28/3N_2(g) + 6C \quad (14)$$

$$CdC_8H_{10}N_{16}(s) \rightarrow Cd(s) + 10/3NH_3(g) + 38/3N_2(g) + 8C \quad (15)$$

$$CdC_8H_{10}N_{16}(s) \rightarrow Cd(s) + 10/3NH_3(g) + 38/3N_2(g) + 8C \quad (16)$$

For **1**

$\rho = 1.668\ g \cdot cm^{-3}$

$Q = \Delta H_{det} = 1.654\ kJ \cdot g^{-1} = 0.397\ kcal \cdot g^{-1}$

$N = 17/407.27 = 0.042\ mol \cdot g^{-1}$

M = (18.015×1+17.03×10/3+28.01×38/3)/17 = 25.39 g·mol^{-1}

P = 1.558×(1.668)^2×[31.68×0.042×(25.39×0.397)$^{1/2}$] = 1.558×(1.668)^2×4.196 = 18.19 GPa

D = 1.01×(4.196)$^{1/2}$×(1+1.30×1.668) = 6.555 km·s^{-1}

For **2**

ρ = 1.811 g·cm^{-3}

Q = ΔH_{det} = 1.410 kJ·g^{-1} = 0.338 kcal·g^{-1}

N = 11/294.75 = 0.037 mol·g^{-1}

M = (17.03×10/3+28.01×38/3)/11 = 29.12 g·mol^{-1}

P = 1.558×(1.811)^2×[31.68×0.037×(29.12×0.338)$^{1/2}$] = 1.558×(1.811)^2×3.710 = 18.96 GPa

D = 1.01×(3.710)$^{1/2}$×(1+1.30×1.811) = 6.526 km·s^{-1}

For **3**

ρ = 1.822 g·cm^{-3}

Q = ΔH_{det} = 2.091 kJ·g^{-1} = 0.501 kcal·g^{-1}

N = 16/442.72 = 0.036 mol·g^{-1}

M = (17.03×10/3+28.01×38/3)/16 = 25.85 g·mol^{-1}

P = 1.558×(1.882)^2×[31.68×0.036×(25.85×0.501)$^{1/2}$] = 1.558×(1.882)^2×4.122 = 21.32 GPa

D = 1.01×(4.122)$^{1/2}$×(1+1.30×1.822) = 6.908 km·s^{-1}

For **4**

ρ = 1.777 g·cm^{-3}

Q = ΔH_{det} = 0.704 kJ·g^{-1} = 0.169 kcal·g^{-1}

N = 16/442.73 = 0.036 mol·g^{-1}

M = (17.03×10/3+28.01×38/3)/16 = 25.85 g·mol^{-1}

P = 1.558×(1.777)^2×[31.68×0.036×(25.85×0.169)$^{1/2}$] = 1.558×(1.777)^2×2.392 = 11.77 GPa

D = 1.01×(2.392)$^{1/2}$×(1+1.30×1.777) = 5.171 km·s^{-1}

1.3 Sensitivity Test

The 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'.

Impact sensitivity: The impact sensitivities of **1**–**4** were tested on a BAM fall hammer produced by OZM Research Impact sensitivity tests according to STANAG 4489. A 5 kg weight was dropped from a set height onto a 10 mg sample placed on a copper cap. The test results showed that the explosion happened with approximate 50% initiation probability. Impact sensitivity of **1**–**4** were observed to be > 40, 25, > 40, and > 40 J, respectively.[2]

Friction sensitivity: The friction sensitivity was determined using a FSKM-10 BAM friction apparatus produced by OZM Research on the basis of STANAG 4487. Friction sensitivity of **1-4** were observed to be > 360, > 360, > 360, and 360 N, respectively.[2]

1.4 Specific impulse and thrust coefficient

Specific impulse and thrust coefficient are crucial parameters to access propellant performance. Specific impulse represents the duration of per unit propellant producing the same thrust and thrust coefficient (C_F) represents the ratio of actual thrust to

isentropic expansion flow. It is calculated by equations $C_F = I_{sp} \cdot g \cdot c^{*-1}$, where g = 9.8 $m \cdot s^{-2}$, c^* is effective velocity calculated by software.

In this work, the theoretical specific impulse is calculated by chemical equilibrium application (CEA) codes and reported by NASA researchers.[3] In the entire calculation, the chemical formula of fuels and oxidizer (HNO_3), heat of formation ($\Delta_f H^o$ = 339 $kJ \cdot mol^{-1}$), ambient temperature (T_a = 298.15K), fuel-to-oxidizer ratio (O/F = 1.0–4.0), chamber pressure (P_c = 25 atm), ambient pressure (P_e = 1 atm), expansion ratio (exit-to-throat area ratio, A_e/A_t = 2–5), freezing flow conditions during expansion also considered. The best thrust is collected at O/F = 4.0, A_e/A_t = 4.836 with I_{sp} = 217 s and C_F = 1.478.

2. Tables

Table S1. Selected bond distances (Å) and bond angles (°).

Compound **1**			
Co(1)−N(14)	2.126(2)	Co(1)−N(11)#2	2.088(2)
Co(1)−N(26)	2.142(2)	Co(1)−N(13)	2.109(2)
Co(1)−N(16)#1	2.148(2)	Co(1)−N(21)	2.139(2)
N(14)−Co(1)−N(26)	91.59(7)	N(11)#2−Co(1)−N(21)	92.60(8)
N(14)−Co(1)−N(16)#1	90.41(8)	N(13)−Co(1)−N(14)	177.85(8)
N(14)−Co(1)−N(21)	87.54(7)	N(13)−Co(1)−N(26)	90.27(8)
N(26)−Co(1)−N(16)#1	85.56(8)	N(13)−Co(1)−N(16)#1	88.65(8)
N(11)#2−Co(1)−N(14)	89.04(8)	N(13)−Co(1)−N(21)	90.47(8)
N(11)#2−Co(1)−N(26)	95.46(8)	N(21)−Co(1)−N(26)	171.88(8)
N(11)#2−Co(1)−N(16)#1	178.85(8)	N(21)−Co(1)−N(16)#1	86.37(8)
Compound **2**			
Cu(1)−N(21)	2.221(3)	Cu(1)−N(13)	1.997(3)
Cu(1)−N(16)#1	1.981(3)	Cu(1)−N(14)	1.962(2)
Cu(1)−N(11)#2	1.995(3)		
N(16)#1−Cu(1)−N(21)	98.83(10)	N(14)−Cu(1)−N(21)	93.19(12)
N(16)#1−Cu(1)−N(11)#2	161.52(11)	N(14)−Cu(1)−N(16)#1	91.48(10)
N(13)−Cu(1)−N(21)	94.84(11)	N(14)−Cu(1)−N(13)	171.71(13)
N(13)−Cu(1)−N(16)#1	89.35(10)	N(14)−Cu(1)−N(11)#2	89.29(11)
N(13)−Cu(1)−N(11)#2	87.33(10)	N(11)#2−Cu(1)−N(21)	99.56(10)
Compound **3**			
Cd(1)−N(21)#1	2.3288(16)	Cd(1)−N(13)	2.3527(18)
Cd(1)−N(21)	2.3288(16)	Cd(1)−N(11)#2	2.346(2)
Cd(1)−N(13)#1	2.3527(18)	Cd(1)−N(11)#3	2.346(2)

N(21)#1−Cd(1)−N(21)	180.0	N(21)−Cd(1)−N(11)#3	89.22(7)
N(21)#1−Cd(1)−N(13)	86.42(6)	N(13)−Cd(1)−N(13)#1	180.0
N(21)#1−Cd(1)−N(13)#1	93.58(6)	N(11)#3−Cd(1)−N(13)#1	94.54(7)
N(21)−Cd(1)−N(13)#1	86.42(6)	N(11)#3−Cd(1)−N(13)	85.46(7)
N(21)−Cd(1)−N(13)	93.58(6)	N(11)#2−Cd(1)−N(13)	94.54(7)
N(21)#1−Cd(1)−N(11)#2	89.22(7)	N(11)#2−Cd(1)−N(13)#1	85.46(7)
N(21)−Cd(1)−N(11)#2	90.78(7)	N(11)#2−Cd(1)−N(11)#3	180.0
N(21)#1−Cd(1)−N(11)#3	90.78(7)		

Compound **4**

Cd(2)−N(21)	2.355(2)	Cd(1)−N(11)#4	2.365(2)
Cd(2)−N(21)#1	2.355(2)	Cd(1)−N(11)	2.365(2)
Cd(2)−N(43)#2	2.320(2)	Cd(1)−N(33)#5	2.338(2)
Cd(2)−N(43)#3	2.320(2)	Cd(1)−N(33)#6	2.338(2)
Cd(2)−N(41)	2.312(2)	Cd(1)−N(31)#4	2.314(2)
Cd(2)−N(41)#1	2.312(2)	Cd(1)−N(31)	2.314(2)

N(31)#4−Cd(1)−N(11)	86.24(9)	N(31)−Cd(1)−N(33)#6	94.61(9)
N(31)−Cd(1)−N(11)#4	86.23(9)	N(31)#4−Cd(1)−N(33)#5	94.61(9)
N(31)−Cd(1)−N(11)	93.77(9)	N(31)#4−Cd(1)−N(31)	180.0
N(31)#4−Cd(1)−N(11)#4	93.76(9)	N(31)#4−Cd(1)−N(11)	86.24(9)
N(31)#4−Cd(1)−N(33)#6	85.39(9)	N(31)−Cd(1)−N(11)#4	86.23(9)
N(31)−Cd(1)−N(33)#5	85.39(10)	N(31)−Cd(1)−N(11)	93.77(9)
N(31)−Cd(1)−N(33)#6	94.61(9)	N(31)#4−Cd(1)−N(11)	86.24(9)
N(31)#4−Cd(1)−N(33)#5	94.61(9)	N(31)−Cd(1)−N(11)#4	86.23(9)
N(31)#4−Cd(1)−N(31)	180.0	N(31)−Cd(1)−N(11)	93.77(9)
N(31)#4−Cd(1)−N(11)	86.24(9)	N(31)#4−Cd(1)−N(11)#4	93.76(9)
N(31)−Cd(1)−N(11)#4	86.23(9)	N(31)#4−Cd(1)−N(33)#6	85.39(9)
N(31)−Cd(1)−N(11)	93.77(9)	N(31)−Cd(1)−N(33)#5	85.39(10)
N(31)#4−Cd(1)−N(11)#4	93.76(9)	N(31)−Cd(1)−N(33)#6	94.61(9)
N(31)#4−Cd(1)−N(33)#6	85.39(9)	N(31)#4−Cd(1)−N(33)#5	94.61(9)
N(31)−Cd(1)−N(33)#5	85.39(10)	N(31)#4−Cd(1)−N(31)	180.0

Symmetry codes for the compounds **1**, **2**, **3** and **4**. For **1**, #1 −1 + *x*, *y*, *z*.; #2 1 + *x*, *y*, *z*. For **2**, #1 *x*, 3/2 − *y*, −1/2 + *z*; #2 − *x*, − *y*, 1 − *z*; #3 *x*, 3/2 − *y*, 1/2 + *z*. For **3**, #1 2 − *x*,1 − *y*,1 – *z*.; #2 *x*, 3/2 − *y*, 1/2 + *z*.; #3 2 − *x*, -1/2 + *y*, 1/2 – *z*.; #4 2 − *x*, 1/2 + *y*, 1/2 – *z*. For **4**, #1 1 − *x*, 2 − *y*, −*z*.; #2 − *x*, 2 − *y*, −*z*.; #3 1 + *x*, *y*, *z*.; #4 1 − *x*, −*y*, 1 – *z*.; #5 2 − *x*, − *y*, 1 – *z*.; #6 −1 + *x*, *y*, *z*.

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

Donor–H···Acceptor	**d(D–H)**	**d(H···A)**	**d(D···A)**	**∠D---H···A**
Compound **1**				
O(1W)–H(1WA)···N(15)#4	0.71(5)	2.23(5)	2.929(3)	169
O(1W)–H(1WB)···N(27)#2	0.82(4)	2.14(4)	2.918(3)	159
N(25)–H(25A)···N(11)#2	0.88	2.80	3.440(3)	130
N(30)–H(30B)···N(22)#6	0.88	2.14	2.982(3)	160
Compound **2**				
N(25)–H(25A)···N(22)#9	0.86	2.17	3.005(4)	164
Compound **3**				
N(25)–H(25A)···N(11)#1	0.86	2.29	3.059(3)	150
N(25)–H(25B)···N(13)#2	0.86	2.45	3.135(3)	138
Compound **4**				
N(15)–H(15A)···N(33)#7	0.86	2.39	3.218(4)	162
N(15)–H(15B)···N(22)#6	0.86	2.41	3.255(3)	168
N(25)–H(25A)···N(14)	0.86	2.33	3.217(4)	154
N(25)–H(25B)···N(43)#8	0.86	2.53	3.330(4)	154

Symmetry codes: #1 *x*, 3/2 − *y*, 1/2 + *z*; #2 1 − *x*, 1 − *y*,1 – *z*; #3 *x*, 3/2 − *y*, 1/2 + *z*; #4 –1/2 + *x*, 3/2 − *y*, 1/2 + *z*.; #5 2 − *x*,1 − *y*, −*z*; #6 1 − *x*, 1 − *y*, – *z*.; #7 2 − *x*,1 − *y*, 1 −*z*; #8 1 + *x*, *y*, *z*.; #9 *x*, 1/2 − *y*, − 1/2 + *z*.

3. Graphics

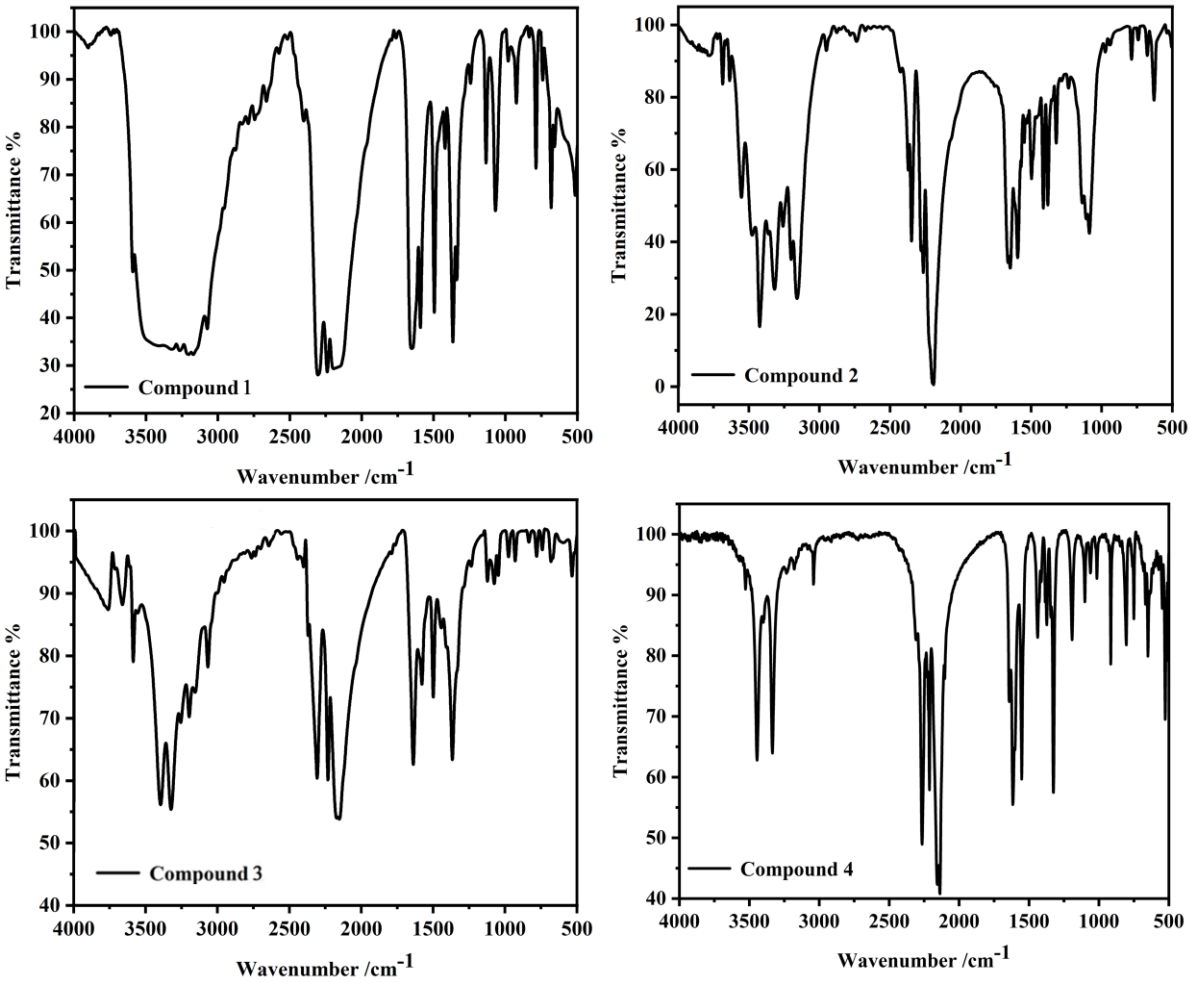

Fig. S1 Fourier transform infrared (FT-IR) spectra of the compounds **1**–**4**.

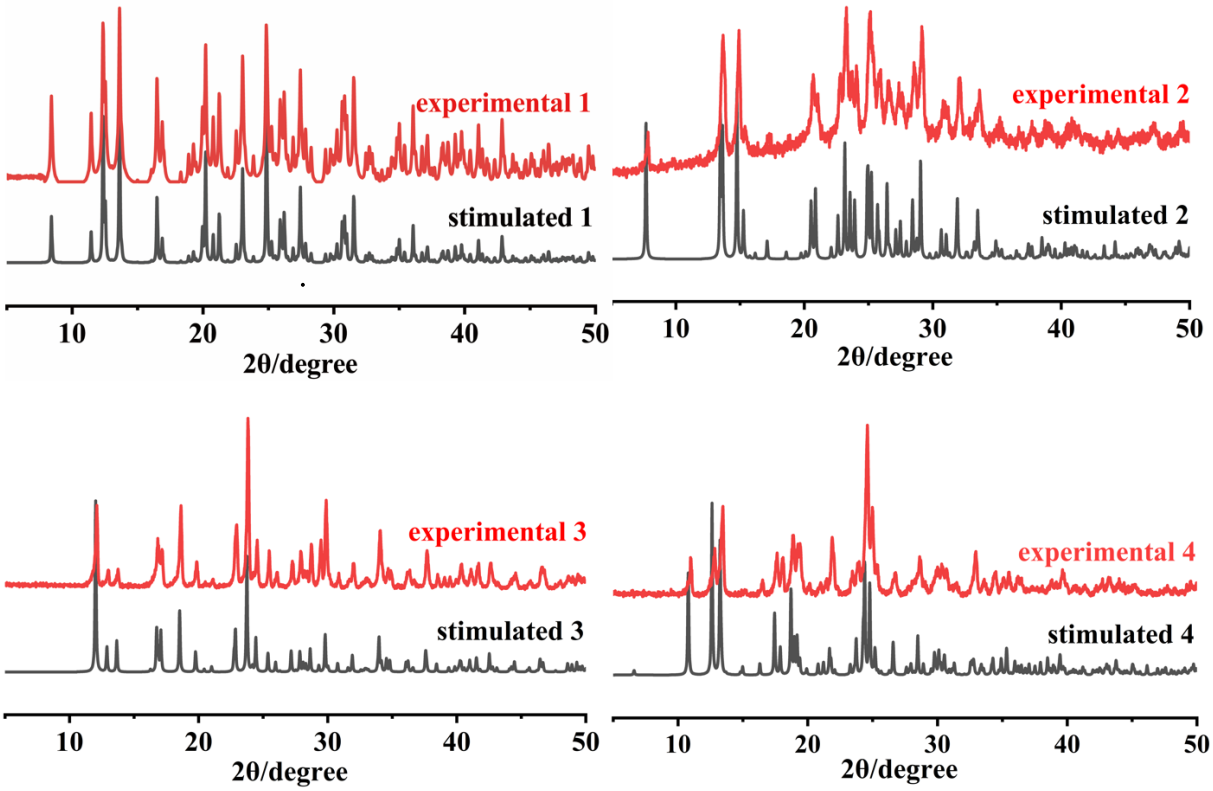

Fig. S2 Powdered *X*-ray diffraction (PXRD) patterns of the compounds **1–4.**

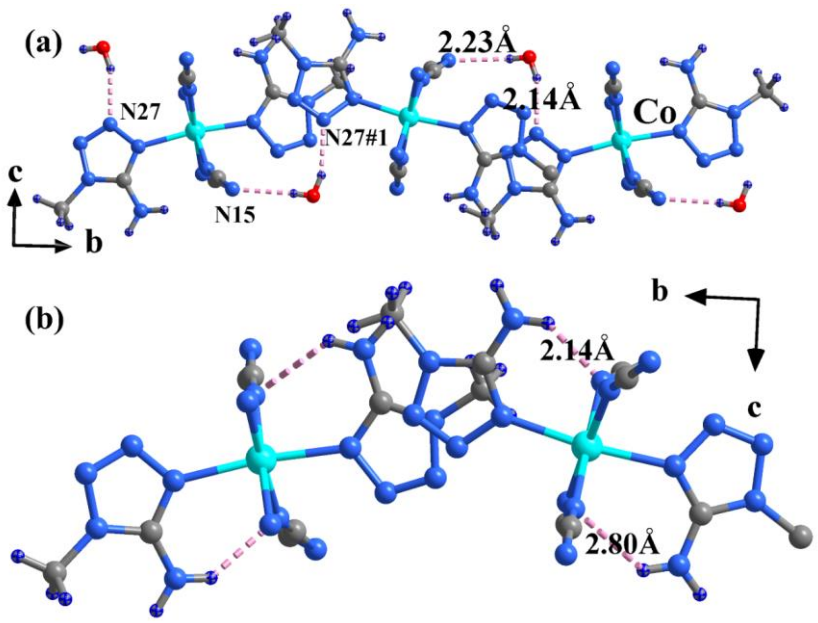

Fig. S3 Hydrogen bonds of the compound **1** generated by (a) water molecules and (b) adjacent nitrogen atoms.

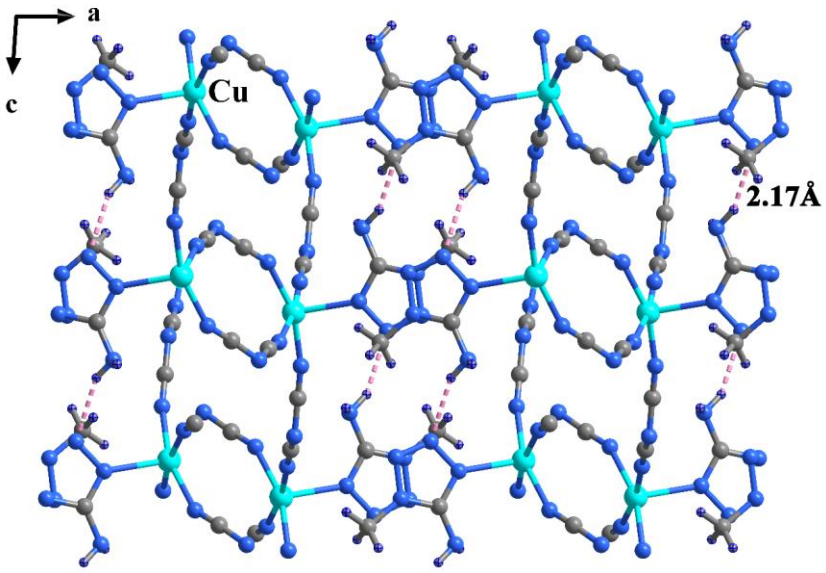

Fig. S4 Hydrogen bonds of the compound **2** running along *c* direction.

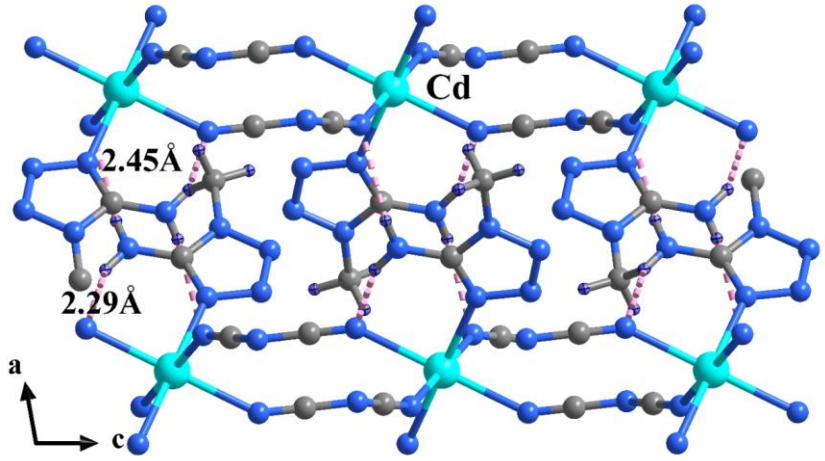

Fig. S5 Hydrogen bonds of the compound **3** running along *c* direction。

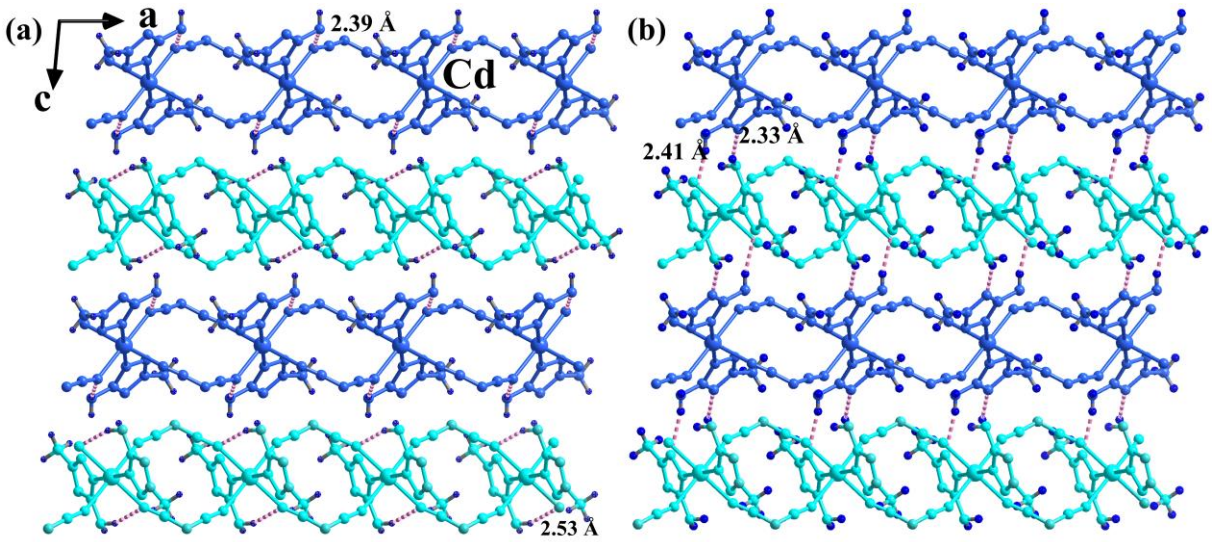

Fig. S6 Hydrogen bonds of the compound **4** (a) between single-chain ending-on DCA^{-} anions and the amine group of 2-MAT ligand and (b) interleaved chains.

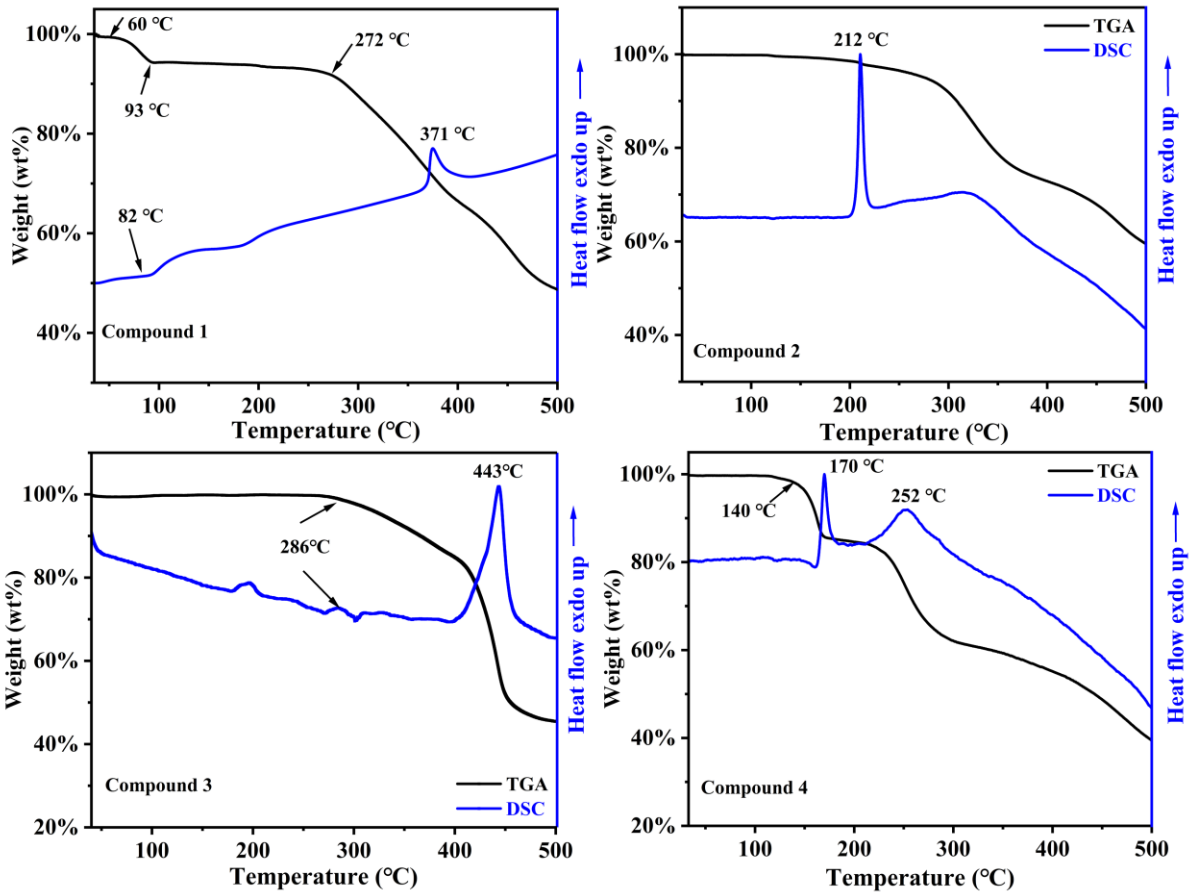

Fig. S7 DSC-TGA curves of **1-4**.

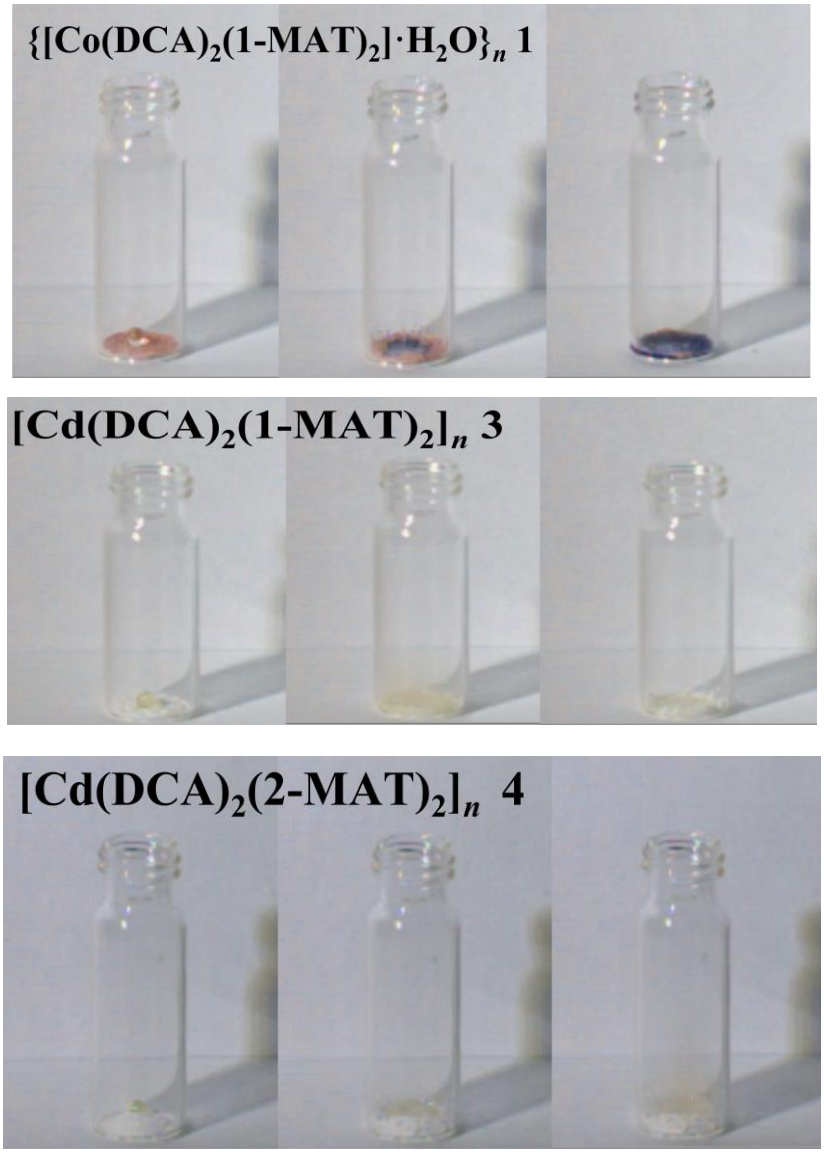

Fig. S8 Hypergolicity drop tests of the compounds **1**, **3** and **4.**

4. References

[1] Popov, M. M. Thermometry and Calorimetry; Moscow University Publishing House: Moscow. **1954**, 382.

[2] 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.

[3] G.S. Mcbride BJ, Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications II. Users Manual and Program Description, NASA Ref. Publ. 1311, NASA Lewis Research Center Cleveland, Ohio 44135; 1996.

[4] Y. Wang, J.-C. Zhang, H. Su, S.-H. Li, S.-W. Zhang, and S.-P. Pang, *J. Phys. Chem. A*, 2014, **118**, 4575-4581.