# Electronic Supplementary Information

## Energetic isostructural metal imidazolate frameworks with bridging dicyanamide linker towards high-performance hypergolic fuels

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# 1. Experimental details

## 1.1 Heat of combustion.

The constant volume combustion of the compounds was determined by a precision oxygen bomb calorimeter (5E-AC8018, Changsha Kaiyuan Instrument Co., Ltd., China) based on the Linio-Pyfengdelel-Wsava equation.[1]

Firstly, we adopted 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 of in an oxygen atmosphere to calibrate the calorimeter. In the second place, 200 mg of the samples was prepared and well mixed with certified benzoic acid (calculated: 800 mg), which was pressed to form a pellet to ensure better combustion. Finally, the pellet was placed in combustion pots, which was subsequently burned in an atmosphere of pure oxygen. The recorded data are the averages of three single measurements.

The constant volume heats of combustion ($\Delta_c U$) were tested by oxygen bomb calorimetry with experimental values of **1** and **2** are −27.98 and −25.91 $kJ \cdot g^{-1}$, respectively. The enthalpy of combustion ($\Delta_c H$) was calculated from $\Delta_c U$ and the gas volume correction: $\Delta_c H = \Delta_c U + \Delta nRT$, where $\Delta n$ is the change of about the number of gas constituents in the reaction process, $R$ = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$ and $T$ = 298.15 K. The combustion reactions are given in eqs **1** and **2** as follows:

$$CuC_{14}H_{12}N_{10}(s) + 35/2O_2(g) \rightarrow CuO(s) + 14CO_2(g) + 6H_2O(l) + 5N_2(g) \quad (1)$$

$$CdC_{14}H_{12}N_{10}(s) + 35/2O_2(g) \rightarrow CdO(s) + 14CO_2(g) + 6H_2O(l) + 5N_2(g) \quad (2)$$

The calculated $\Delta_c H$ values of **1** and **2** are −10735 and −11208 $kJ \cdot mol^{-1}$, respectively. The gravimetric combustion energies densities ($E_g$/$kJ \cdot g^{-1}$) of **1** and **2** are 27.97 and 25.90 $kJ \cdot g^{-1}$, respectively, and the volumetric combustion energy densities ($E_v$/$kJ \cdot cm^{-3}$) of **1** and **2** are 42.91 and 41.98 $kJ \cdot cm^{-3}$, respectively.

## 1.2 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** and **2** were tested on a BAM fall hammer produced by OZM Research Impact sensitivity tests according to STANAG 4489. A 10 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 sensitivities of **1** and **2** were observed to be > 100 J, respectively.[2]

**Friction sensitivity:** The friction sensitivity was determined using a FSKM-10 BAM friction apparatus produced by OZM Research based on STANAG 4487. Friction sensitivities of **1** and **2** both were observed to be >360 N.

## 1.3 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 (*CF*) represents the ratio of actual thrust to isentropic expansion flow. It is calculated by equations $CF = I_{sp} \cdot g \cdot c^{*-1}$, where $g = 9.8\ m \cdot s^{-2}$, $c^*$ is effective velocity calculated by software. In this work, the theoretical specific impulse was 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 ($T_a = 298.15$ K), 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 were also considered. The best thrust of **1** was collected at O/F = 4.0, $A_e/A_t = 4.836$ with $I_{sp}$ =208 s and CF = 1.478. The best thrust of **2** was collected at O/F = 3.0, $A_e/A_t = 4.740$ with $I_{sp}$ =283 s and CF = 1.473.

## 2. Tables

**Table S1. Crystal data and structure refinement parameters for 1 and 2.**

| Compound | **1** | **2** |
|---|---|---|
| *CCDC* | 2217909 | 2219269 |
| *Empirical formula* | $C_{14}H_{12}CuN_{10}$ | $C_{14}H_{12}CdN_{10}$ |
| $M_r$ *(g mol$^{-1}$)* | 383.88 | 432.74 |
| *Crystal system* | triclinic | triclinic |
| *Space group* | *P–1* | *P–1* |
| *Z* | 1 | 1 |
| *a/Å* | 6.6425(3) | 6.6598(2) |
| *b/Å* | 7.4782(4) | 7.6512(3) |
| *c/Å* | 8.8833(5) | 9.0619(3) |
| $\alpha$/° | 106.162(5) | 104.038(3) |
| $\beta$/° | 97.561(4) | 95.331(3) |
| $\gamma$/° | 95.007(4) | 94.779(3) |
| *V/Å$^3$* | 416.57(4) | 443.34(3) |
| $D_c$*/g cm$^{-3}$* | 1.530 | 1.621 |
| *Temperature (K)* | 300.04(10) | 296.72(10) |
| *F(000)* | 195.0 | 214.0 |
| GOF *on F$^2$* | 1.039 | 1.030 |
| $R_1(I > 2\sigma(I))^a$ | 0.0388 | 0.0321 |
| $wR_2(I > 2\sigma(I))^b$ | 0.0839 | 0.0570 |
| $R_1$*(all data)*$^a$ | 0.0519 | 0.0352 |
| $wR_2$*(all data)*$^b$ | 0.0900 | 0.0583 |

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

**Table S2. Selected bond distances (Å) and bond angles (°) for 1 and 2.**

| | | | |
|---|---|---|---|
| Compound **1** | | | |
| Cu(1)−N(4) | 2.002(17) | Cu(1)−N(4)#1 | 2.002(17) |
| Cu(1)−N(1) | 2.004(2) | Cu(1)−N(1)#1 | 2.004(2) |
| Cu(1)−N(3)#2 | 2.516(21) | Cu(1)−N(3)#4 | 2.516(21) |
| | | | |
| N(4)#1−Cu(1)−N(1)#1 | 89.81(7) | N(4)#1−Cu(1)−N(3)#4 | 92.71(70) |
| N(4)#1−Cu(1)−N4 | 180.00 | N(4)#1−Cu(1)−N1 | 90.19(7) |
| N(4)#1−Cu(1)−N(3)#2 | 87.29(70) | N(1)#1−Cu(1)−N(3)#4 | 90.12(74) |
| N(1)#1−Cu(1)−N(4) | 90.19(7) | N(1)#1−Cu(1)−N(1) | 180.00 |
| N(1)#1−Cu(1)−N(3)#2 | 89.88(75) | N(3)#4−Cu(1)−N(4) | 87.29(70) |
| N(3)#2−Cu(1)−N(1) | 90.23(86) | N(3)#2−Cu(1)−N(3)#4 | 179.99(65) |
| N(1)−Cu(1)−N(4) | 90.19(7) | N(1)−Cu(1)−N(3)#4 | 89.88(75) |
| N(3)#2−Cu(1)−N4 | 92.71(70) | | |
| | | | |
| Compound **2** | | | |
| Cd(1)−N(3)#2 | 2.407(2) | Cd(1)−N(3)#3 | 2.407(2) |
| Cd(1)−N(1) | 2.357(2) | Cd(1)−N(1)#1 | 2.357(2) |
| Cd(1)−N(4)#1 | 2.282(19) | Cd(1)−N(4) | 2.282(19) |
| | | | |
| N(4)−Cd(1)−N(4)#1 | 180.00(10) | N(4)−Cd(1)−N(1)#1 | 89.02(8) |
| N(4)#1−Cd(1)−N(1)#1 | 90.98(8) | N(4)−Cd(1)−N(1) | 90.98(8) |
| N(3)#2−Cd(1)−N(3)#3 | 180.00(9) | N(4)#1−Cd(1)−N(3)#3 | 87.76(7) |
| N(1)#1−Cd(1)−N(3)#2 | 90.21(8) | N(1)#1−Cd(1)−N(1) | 180.0 |
| N(4)−Cd(1)−N(3)#2 | 87.76(7) | N(1)#1−Cd(1)−N(3)#3 | 89.79(8) |
| N(1)−Cd(1)−N(3)#2 | 89.79(8) | N(4)−Cd(1)−N(3)#3 | 92.24(7) |
| N(4)#1−Cd(1)−N(3)#2 | 92.24(7) | N(1)−Cd(1)−N(3)#3 | 90.21(8) |
| N(4)#1−Cd(1)−N(1) | 89.02(8) | | |

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

| | **1** | **2** | **Cu-MIX** | **Cd-MIX** |
|---|---|---|---|---|
| ***ID*(ms)** | 28(1) | 40(1) | 209(1) | 328(1) |
| | 30(2) | 36(2) | 186(2) | 353(2) |
| | 28(3) | 37(3) | 172(3) | 320(3) |
| | 32(4) | 39(4) | 180(4) | 316(4) |
| | 30(5) | 39(5) | 174(5) | 343(5) |
| **Flame duration(ms)** | 1231(1) | 693(1) | 323(1) | 420(1) |
| | 1235(2) | 684(2) | 295(2) | 431(2) |
| | 1269(3) | 680(3) | 305(3) | 442(3) |
| | 1278(4) | 666(4) | 318(4) | 430(4) |
| | 1253(5) | 675(5) | 317(5) | 416(5) |
| **Flame hight(cm)** (approximate values) | 8(1) | 7(1) | 8(1) | 4(1) |
| | 7(2) | 7(2) | 8(2) | 4(2) |
| | 8(3) | 6(3) | 10(3) | 6(3) |
| | 8(4) | 6(4) | 10(4) | 5(4) |
| | 7(5) | 6(5) | 9(5) | 4(5) |

## 3. Graphics

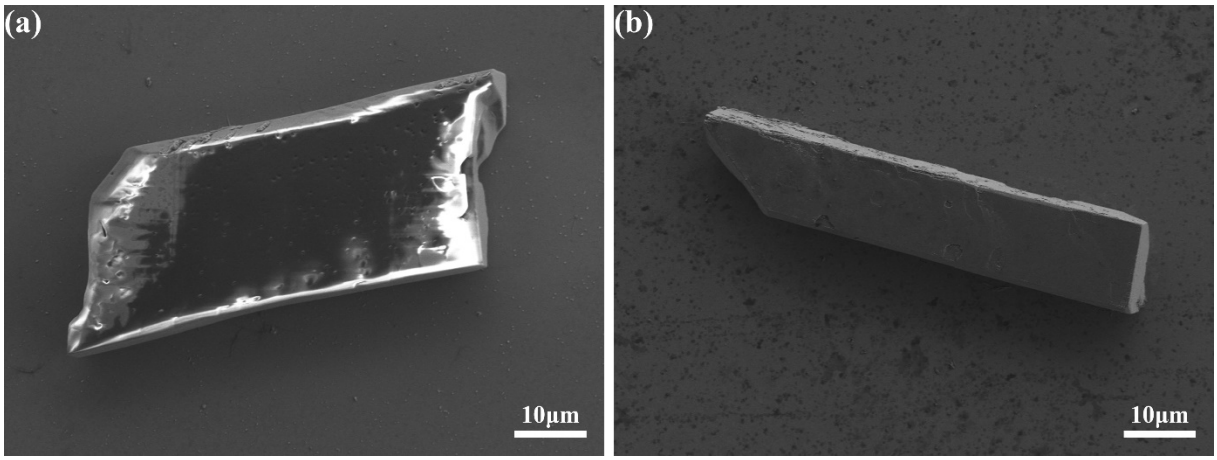


**Fig. S1** (a) The morphology of **1** recorded by FE-SEM. (b) The morphology of **2** recorded by FE-SEM.

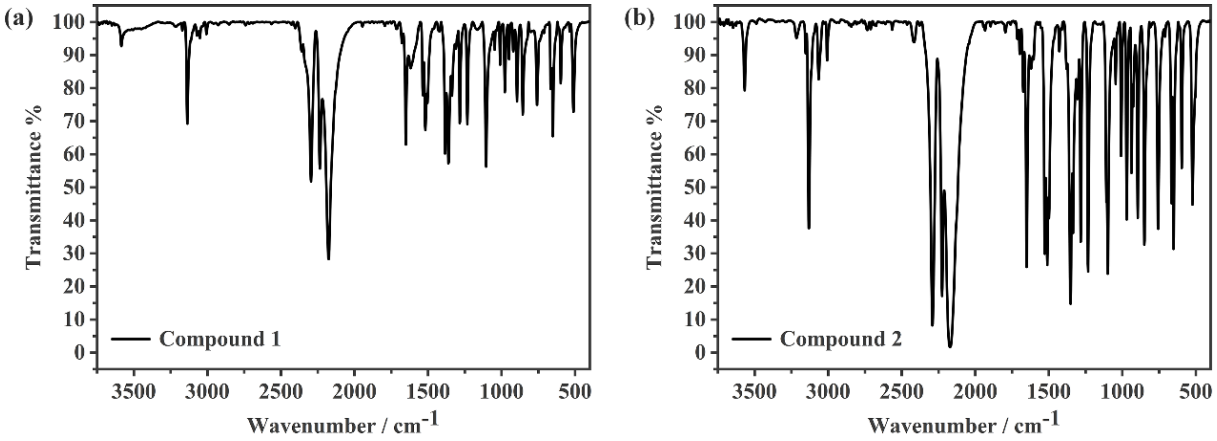


**Fig. S2** The IR spectra of **1** (a) and **2** (b).

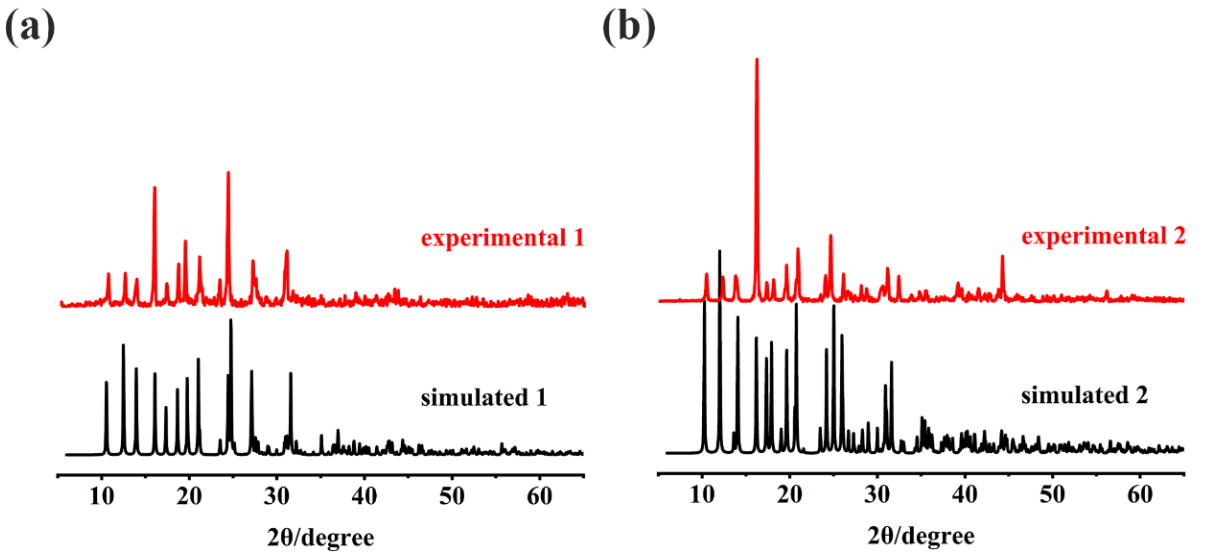


**Fig. S3** Powdered X-ray diffraction (PXRD) patterns of **1** (a) and **2** (b).

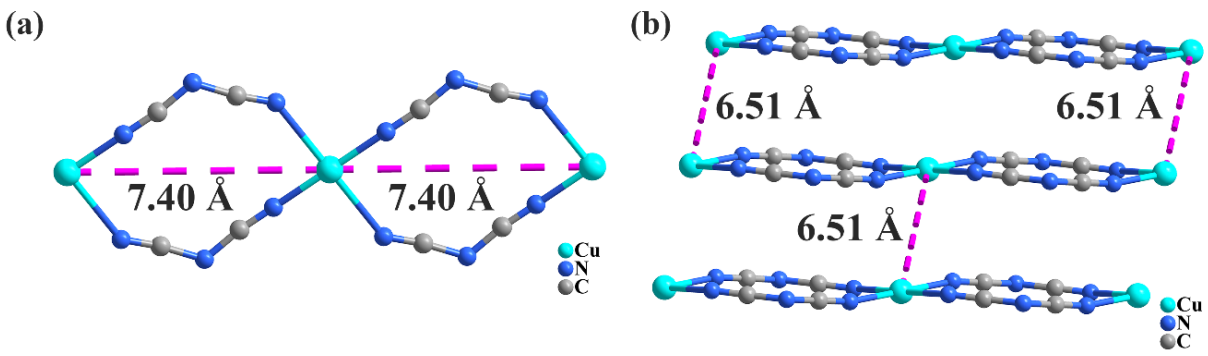


**Fig. S4** The distances of Cu(II) atoms in the 1D chain and between 1D chains of **1** (indicated by the pink dashed line).

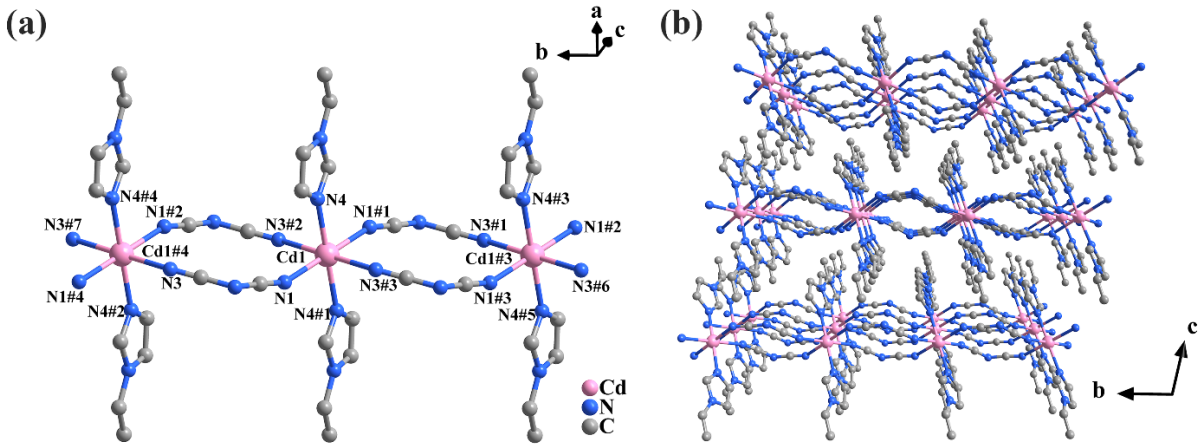


**Fig. S5** The structure of **2**. (a) Coordination environments of one Cd(II) ion, 1-VIM ligands and $N(CN)_2^-$. (b) The 3D supramolecular structures of **2**. Symmetry codes: #1 1 – *x*, –*y*, –*z*. #2 1 – *x*, 1 – *y*, –*z*. #3 *x*, –1 + *y*, *z*. #4 *x*, 1 + *y*, *z*. #5 1 – *x*, –1 – *y*, –*z*. #6 *x*, –2 + *y*, *z*. #7 1 – *x*, 2 – *y*, –*z*.

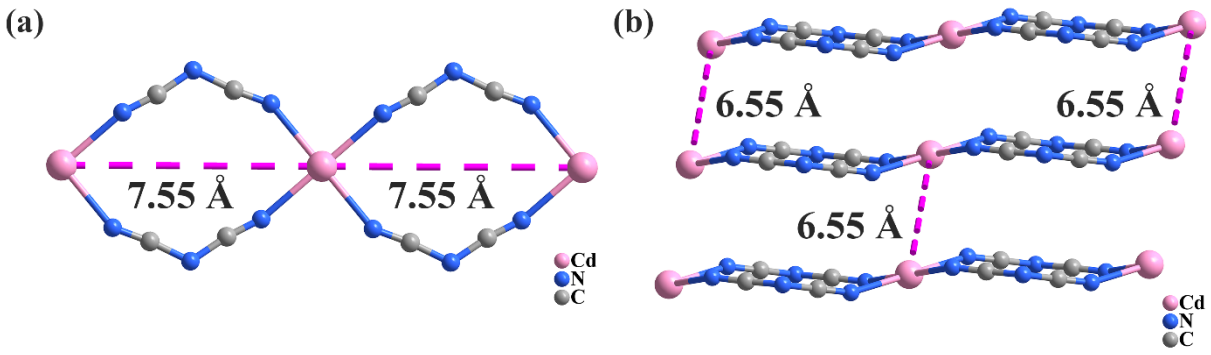


**Fig. S6** The distances of Cd(II) atoms in the 1D chain and between 1D chains of **2** (indicated by the pink dashed line).

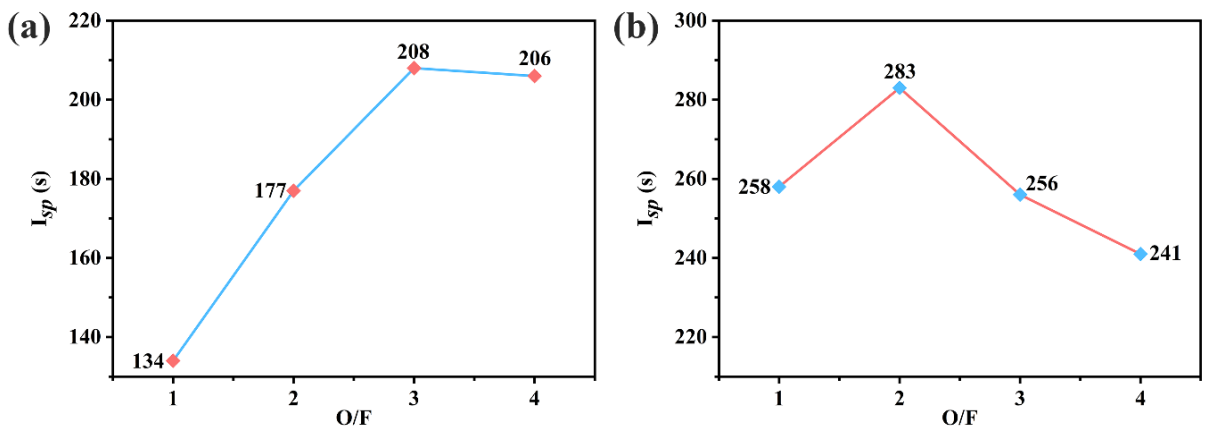


**Fig. S7** Specific impulse curves of WFNA/ECPs **1** (a) and **2** (b).

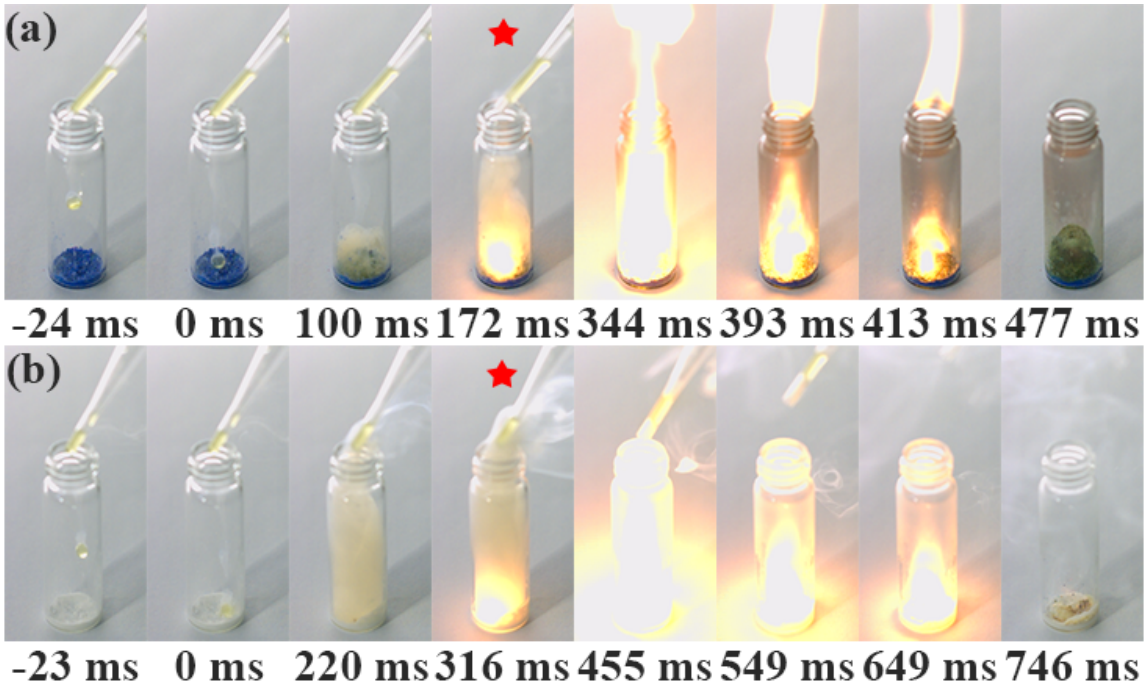


**Fig. S8** High-speed camera captures the moments of physical mixture of $M(NO_3)_2$, 1-VIM and NaDCA for ignition delay experiment with WFNA. (a) M = Cu; (b) M = Cd.

## 4. References

[1] M. M. Popov, 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.