Two Novel TNB Energetic Cocrystals with Low Melting Point: A Potential Strategy to Construct Melt Cast Explosive Carriers

Shen Qiao,[a,b] Jianhua Wang,[b] Yanwu Yu,[b] Yucun Liu,[b] Zongwei Yang,*[a] Hongzhen Li,*[a]

[a] *Institute of Chemical Materials, China Academy of Engineering Physics (CAEP), Mianyang 621999, China.*

[b] *College of Environment and Safety Engineering, North University of China, Taiyuan 030051, China.*

Supporting Information (SI)

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SI 1. Experimental

SI 1.1 Materials

1,3,5-Trinitrobenzene (TNB) was supplied by the Institute of Chemical Materials, Chinese Academy of Engineering Physics (CAEP). 1,4-dinitroimidazole (1,4-DNI) and 1-methyl-3,5-dinitro-1,2,4-triazole (DNMT) were obtained from North University of China. The other chemicals and reagents used in this work were purchased from trade without further purification.

Caution: *Although there are no explosions and detonations in the course of this work. TNB, 1,4-DNI and DNMT are all dangerous energetic materials with a potential risk. These materials should be handled carefully with proper safety practices and special protective devices.*

SI 1.2 Crystallization

1:1 TNB/1,4-DNI (1): TNB (149 mg, 0.7 mmol) and 1,4-DNI (110 mg, 0.7 mmol) were mingled with ethanol (10 mL) and heated at 40 ℃. The mixed solution was stirred until all the solids were fully dissolved. The solution was filtered into a glass bottle sealed with a perforated seal film. Subsequently, the solvent was evaporated at room temperature. After some days, 1:1 TNB/1,4-DNI cocrystal was obtained.

1:1 TNB/DNMT (2): TNB (149 mg, 0.7 mmol) and DNMT (121 mg, 0.7 mmol) were mingled with ethanol (10 mL) and heated at 40 ℃. The mixed solution was stirred until all the solids were fully dissolved. The solution was filtered into a glass bottle sealed with a perforated seal film. Subsequently, the solvent was evaporated at room temperature. After some days, 1:1 TNB/DNMT cocrystal was obtained.

SI 2. Powder X-ray Diffraction (PXRD)

Powder X-ray Diffraction (PXRD, D8 Advance, Bruker) patterns were recorded with the Cu-Kα radiation (λ = 1.54056 Å). The current and voltage were set at 30 mA and 40 kV, respectively. The materials were scanned over the range from 5° to 50° with a step size of 0.03°and a step of 0.2 seconds. Meanwhile, the PXRD patterns of the cocrystals were simulated from the crystal structure according to Crystallographic Information Files (CIFs).

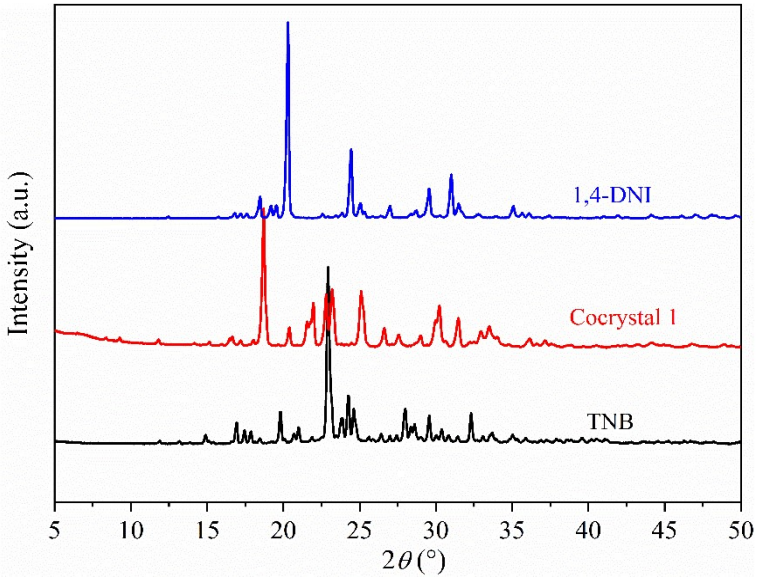

Fig. S1 PXRD patterns for cocrystal **1** and raw materials.

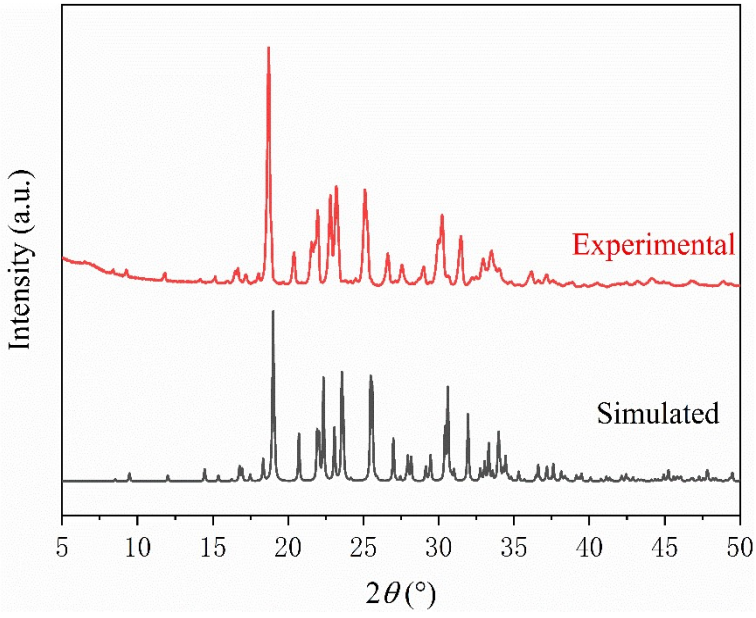

Fig. S2 Comparison of experimental and simulated PXRD patterns for cocrystal **1**.

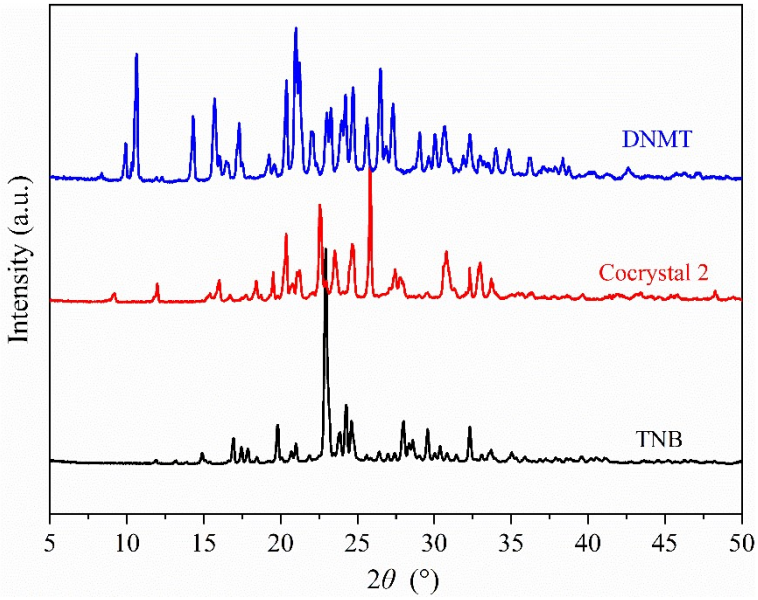

Fig. S3 PXRD patterns for cocrystal **2** and raw materials.

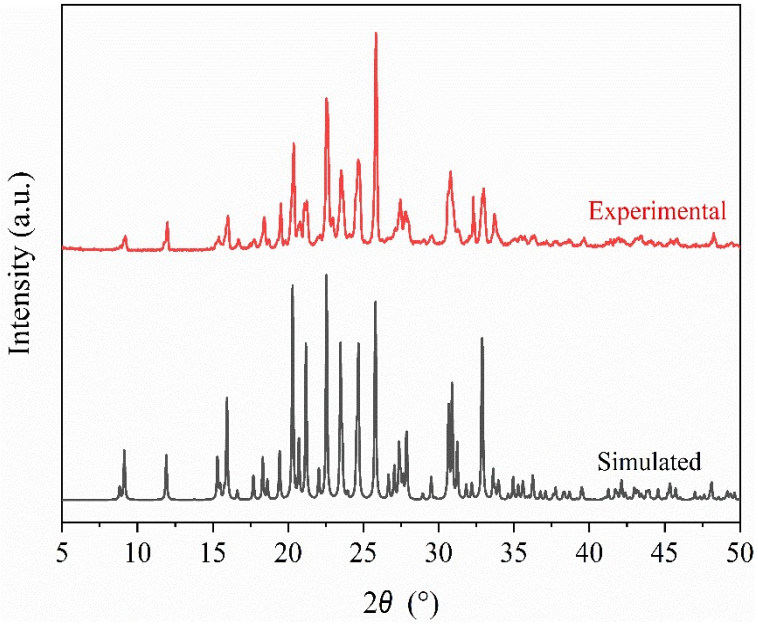

Fig. S4 Comparison of experimental and simulated PXRD patterns for cocrystal **2**.

SI 3. Single Crystal X-ray Diffraction (SXRD)

Single crystal X-ray diffraction data for the cocrystals were collected using a Bruker APEX-II-CCD diffractometer with graphite-monochromated Mo−Kα radiation (λ = 0.71073 Å). The crystals were kept at 296 K during data collection. The

data were processed using Olex2 software. The structures were solved and refined with SHELXL.

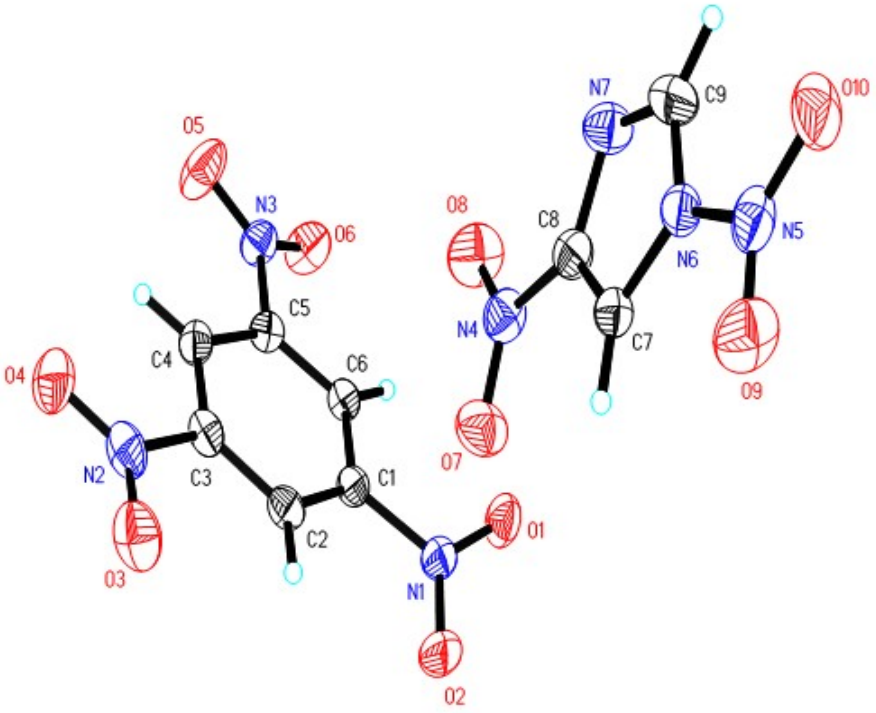

Fig. S5 OPTEP diagram for cocrystal **1** with 50% probability ellipsoids

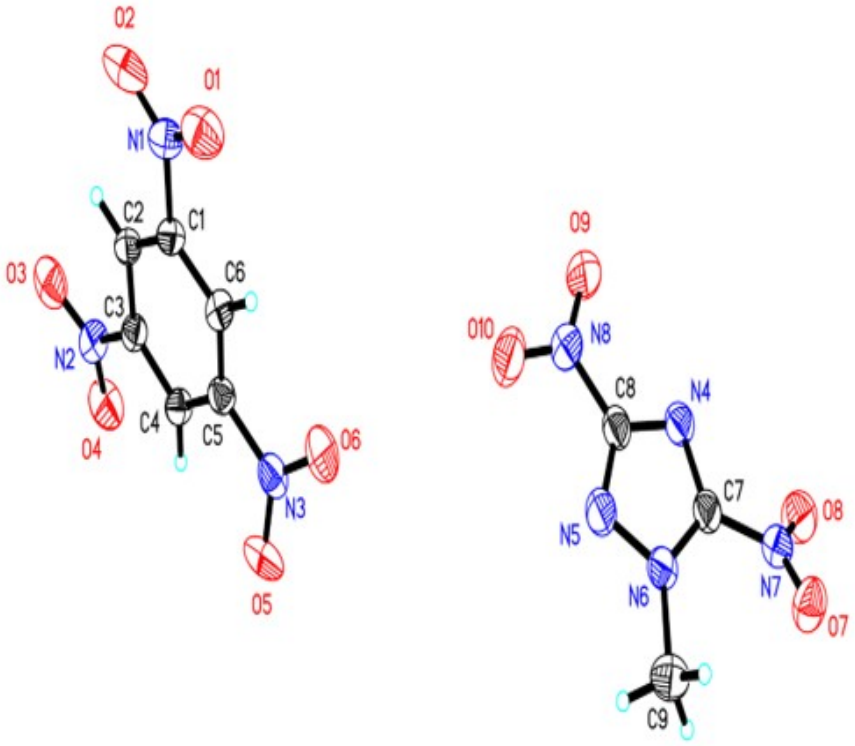

Fig. S6 OPTEP diagram for cocrystal **2** with 50% probability ellipsoids

Table S1. Crystallographic Data for cocrystal **1** and **2** (collected at 296 K)

Material	**1**	**2**
Formula	$C_9H_5N_7O_{10}$	$C_9H_6N_8O_{10}$
CCDC	2125442	2125443
Stoichiometry	1:1	1:1
Crystal System	Orthorhombic	Orthorhombic
Space Group	$P2_12_12_1$	$P2_12_12_1$
a (Å)	6.4839(5)	6.7852(17)
b (Å)	10.5895(8)	11.054(3)
c (Å)	20.8436(15)	20.043(5)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Cell Volum (Å^3)	1431.15(19)	1503.4(6)
Z	4	4
ρ_{calc}(g/cm^3)	1.723	1.706
No. of reflections measured	10415	10367
No. of independent reflections	2793	2796
R_{int}	0.0198	0.0513
R_1 (I > 2σ(I))	0.0275	0.0399
w$R(F^2)$ (I > 2σ(I))	0.0703	0.0921
R_1 (all reflections)	0.0301	0.0838
$wR(F^2)$ (all reflections)	0.0722	0.1144
Goodness of fit on F^2	1.035	1.037

SI 4. Differential Scanning Calorimetry (DSC)

Thermal analyses of all samples were performed on a TA Q100 differential scanning calorimetry. 0.3 mg of samples were placed in aluminum pans and the

thermal behavior of the samples were studied under nitrogen purge (60.0 mL/min) at a heating rate of 10 ℃/min over a range from 50 ℃ to 350 ℃, the result is shown in **Fig. S7** and **Fig. S8**. Cyclic thermograms of cocrystal were recorded on a PerkinElmer DSC8500. The heat-cool-heat experiment was in non-hermetic aluminum DSC pans under a nitrogen purge with a heating rate of 10 ℃/min and a cooling rate of 1 ℃/min, while covering the temperature range of -30 ℃ to 110 ℃, the result is shown in **Fig. S9**.

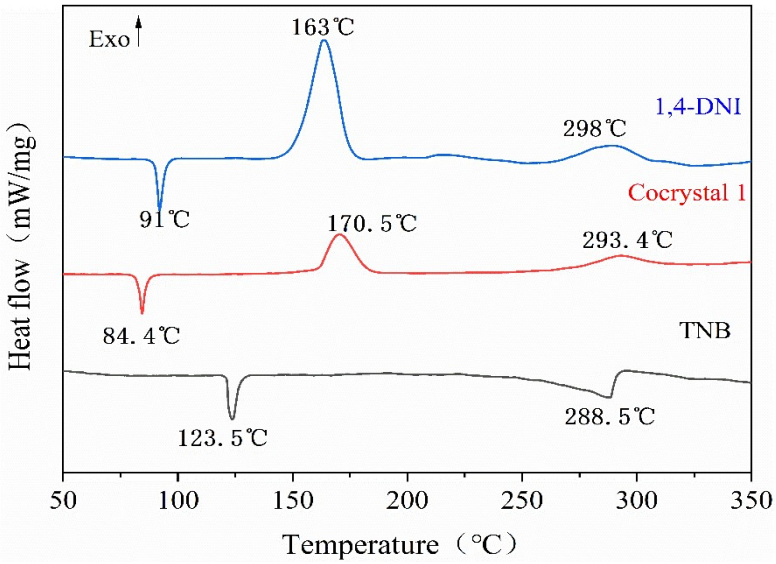

Fig. S7 The DSC curves of cocrystal **1** and raw materials. (Note: the second endothermic peak of TNB may be attributed to the fact that the absorbed heat of the sublimation is greater than that of the heat release of the decomposition. As a result, the TNB displays an endothermic peak during slow decomposition process.)

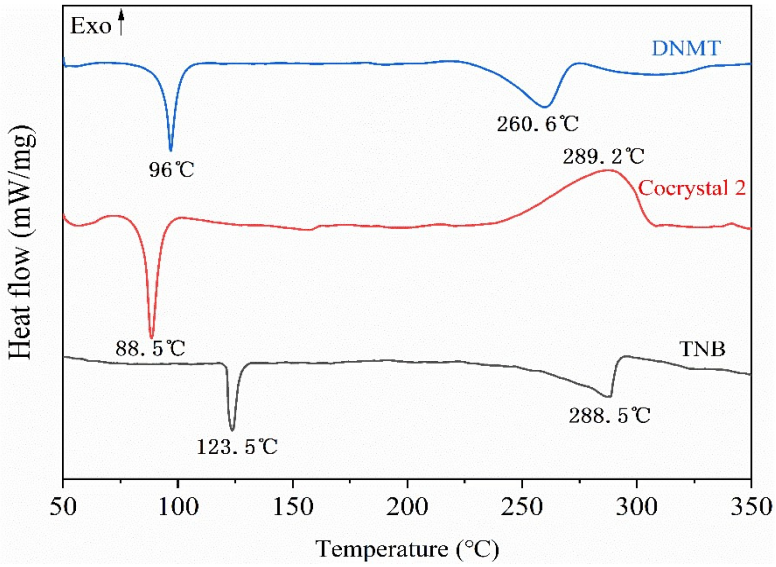

Fig. S8 The DSC curves of cocrystal **2** and raw materials. (Note: the second endothermic peak of DNMT may be attributed to the fact that the absorbed heat of the sublimation is greater than that of the heat release of the decomposition. As a result, the DNMT displays an endothermic peak during slow decomposition process.)

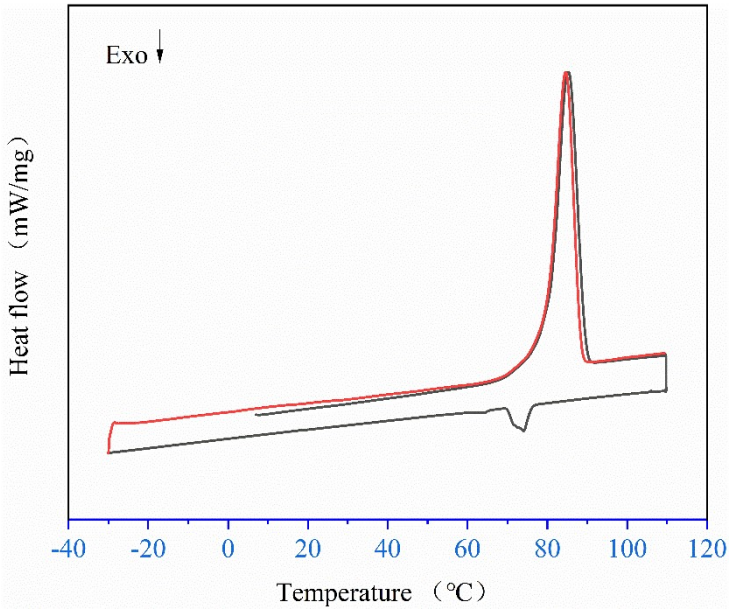

Fig. S9 Cyclic DSC past the melting of cocrystal **1**, two cycles of heat-cool-heat. (first cycle is black, endothermic peaks corresponding to melting process during heat cycle, the exothermic peak corresponding to solidification process during cool cycle.)

SI 5. Hot stage microscopy (HSM)

Hot stage microscopy (HSM) of cocrystals were performed using a Linkam LTS420 Heating and Cooling Stage. The cocrystals were mounted on the hot stage and observed using a Scope.A1 optical microscope by ZEISS. Samples were heated from 30 to 95 °C at a heating rate of 2 °C per minute. After this the temperature was decreased to 30 °C.

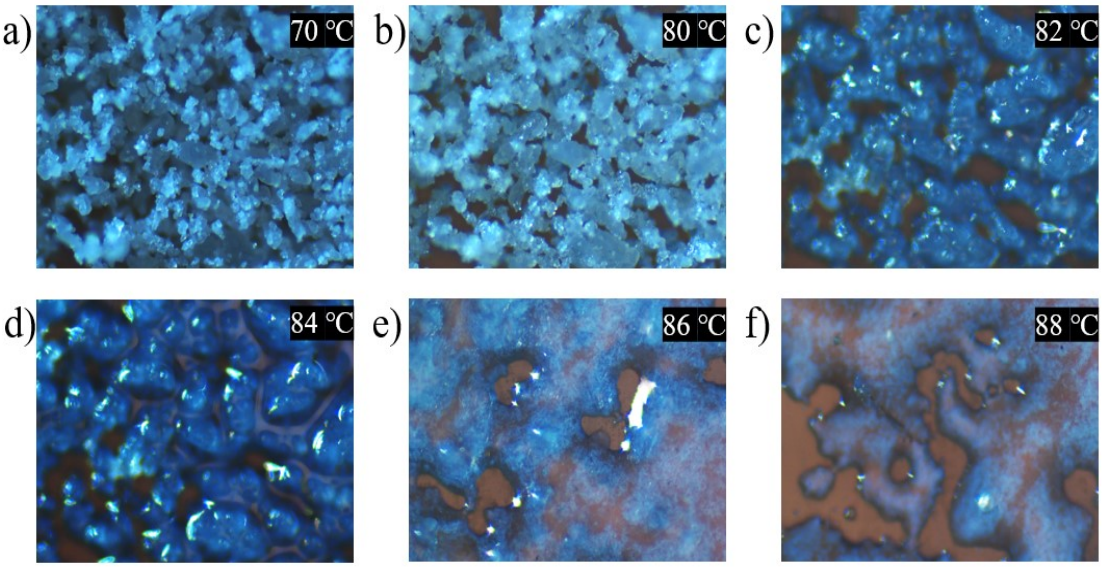

Fig. S10 Hot stage microscopy images of cocrystal 1 at a) 70 °C, b) 80 °C, c) 82 °C, d) 84 °C, e) 86 °C, and f) 88 °C.

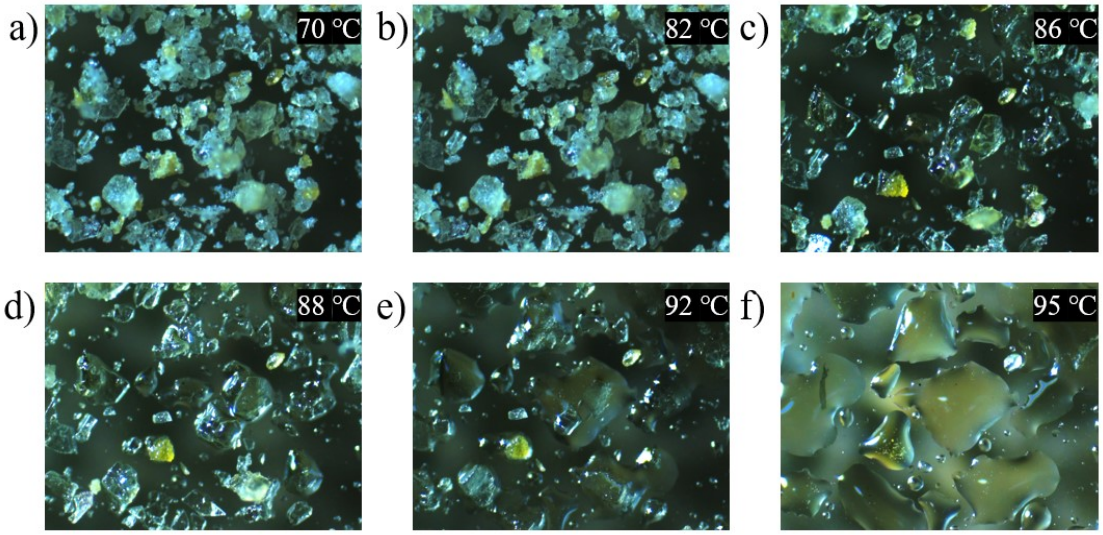

Fig. S11 Hot stage microscopy images of cocrystal 2 at a) 70 °C, b) 82 °C, c) 86 °C, d) 88 °C, e) 92 °C, and f) 95 °C.

SI 6. Impact Sensitivity Tests

Impact sensitivities of the cocrystals and the raw materials were conducted with a standard BAM Fall hammer. The sample was enclosed in a still jacket of 40 mm^3 and then impacted with a drop about 2 or 5 kg. The impact sensitivity of the sample was expressed by the impact energy of 50% explosion probability ($E_{50\%}$). In this work, TNT acted as the reference.

Table S2. Impact sensitivity of samples

Samples	TNB	1,4-DNI	DNMT	**1**	**2**	TNT
$E_{50\%}$(J)	26	14	20	18	22	15

SI 7. Detonation property evaluations

The detonation velocity and pressure of the cocrystal were calculated according to the calculation method of the empirical nitrogen equivalent equations[1].

The equation of detonation velocity and pressure are as follow:

$$D = \frac{100}{M}(695 + 1150\rho)(1.00x_{N_2} + 0.64x_{H_2O} + 1.34x_{CO_2} + 0.72x_{CO} + 0.18x_{H_2} + 0.50x_{O_2} + x_C) \quad (1)$$

$$P = 1.060\left[\rho\frac{100}{M}(1.00x_{N_2} + 0.64x_{H_2O} + 1.34x_{CO_2} + 0.72x_{CO} + 0.18x_{H_2} + 0.50x_{O_2} + 0.12x_C)\right]^2 - 0.619 \quad (2)$$

695, 1150, 1.060 and 0.619 are constants. 1.00, 0.64, 1.34, 0.72, 0.18, 0.50, 0.12 are the nitrogen equivalent coefficient of gaseous detonation products N_2, H_2O, CO_2, CO, H_2, O_2, C of explosive.

For comparisons, TNB, 1,4-DNI, DNMT, and TNT were also calculated by the same method.

Table S3. Predicted detonation performances of cocrystals, raw materials and references

Samples	Density (g/cm^3)	Detonation velocity (m/s)	Detonation pressure (GPa)
TNB	1.688	7277	22.40
1,4-DNI	1.751	8228	29.38
1	1.723	7704	26.08
DNMT	1.666	8028	27.20
2	1.706	7709	25.35
TNT	1.64	6910	19.91

SI 8. References

1. R. Hu, E. Yao, H. Ma, H. Zhang, H. Gao, L. Han, F. Zhao, Y. Luo, H. Zhao, *Chin. J. Energy Mater.*, 2015, **23**, 1243-1244.