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**Supporting information for article:**

# A novel energetic cocrystal of DATNBI/TNT with low sensitivity and an unexpected polymorphic transition

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**Caution!**

Although we have encountered no difficulties during preparation and handling of these compounds, they are potentially explosive energetic materials. Manipulations must be carried out by using appropriate standard safety precautions.

## S1. Instruments and characterizations

### S1.1 Single-crystal X-ray diffraction

The cocrystal-1 crystal was mounted on a Mite Gen Micro Mesh using a small amount of cargille immersion oil. Data were collected using a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryoflex low-temperature device was used to keep the crystals at 296 K during data collection. Data were collected, and the unit cell was refined using APEX2.

### S1.2 Powder X-ray diffraction (PXRD)

The powder X-ray diffraction patterns were recorded on a Bruker D8 X-ray diffraction instrument equipped with a Cu Kα radiation source ($\lambda$=1.54180 Å, 40 kV, 40 mA). The scanning rate was set to 0.02°, and data were collected at a 2θ range from 5° to 60°.

### S1.3 Thermal analysis

Differential scanning calorimetry (DSC) was performed using a NETZSCH STA 449F3. DSC curves were measured at a temperature range of 30-500 °C with a dynamic atmosphere of $N_2$ at a flow rate of 30 mL·min$^{-1}$. The heating rate is 10 K·min$^{-1}$. 2 mg of samples were obtained using a $Al_2O_3$ crucible.

### S1.4 In-situ X-ray diffraction

The polymorphic transition processes of samples (cocrystal-1) under thermal stimulation were detected using in-situ XRD, which was conducted with a Bruker D8 XRD instrument through a heating

stage, in which a program that can control the temperature rise was involved. A series of XRD patterns were obtained at intervals of 5 °C between 30 and 125 °C.

**S1.5 Infrared (IR)**

Infrared spectroscopy was performed using a Nicolet 800 Fourier transform infrared spectroscope (FTIR). The spectrum was collected at a range of 4000–400 cm$^{-1}$ using pressed KBr pellets, and the interval was 4 cm$^{-1}$.

**S1.6 Ultra-high performance liquid chromatography (HPLC)**

The thermal stimulation of the samples (cocrystal-1 and cocrystal-2) was conducted using the ultra-high performance liquid chromatography technique (HPLC, Shimadzu, LC-20AT).

**S1.7 Hot-stage microscopy (HSM)**

Hot-stage microscopy was performed on cocrystal-1 using a Linkam LTS420 heating stage. The crystal was mounted on the hot stage and observed using a Scope.A1 optical microscope manufactured by ZEISS Germany.

**S1.8 Mechanical sensitivity**

The impact sensitivity was tested using the characteristic drop height ($H_{50}$) method. According to the GJB-772A-97 601.2 method, a single sample of about 35 mg was tested using a 5 kg drop hammer. The friction sensitivity was measured using a standard BAM friction tester.

## S2. Single crystal structure data

**Table S1.** Crystallographic data for the DATNBI/TNT cocrystal-1.

```
Bond precision:   C-C = 0.0072 A            Wavelength=0.71073

Cell:           a=4.9325(12)      b=6.8773(16)      c=22.462(5)
                alpha=84.728(4)   beta=84.780(4)    gamma=86.014(4)
Temperature:    296 K

                Calculated                Reported
Volume          754.2(3)                  754.1(3)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C6 H4 N10 O8, 2(C7 H5 N3  2(C7 H5 N3 O6), C6 H4 N10
                O6)                       O8
Sum formula     C20 H14 N16 O20           C20 H14 N16 O20
Mr              798.47                    798.47
Dx,g cm-3       1.758                     1.758
Z               1                         1
Mu (mm-1)       0.159                     0.159
F000            406.0                     406.0
F000'           406.26
h,k,lmax        5,8,26                    5,8,26
Nref            2648                      2584
Tmin,Tmax       0.987,0.992               0.616,0.746
Tmin'           0.987

Correction method= # Reported T Limits: Tmin=0.616 Tmax=0.746
AbsCorr = NONE

Data completeness= 0.976          Theta(max)= 25.008

R(reflections)= 0.0782( 1421)     wR2(reflections)= 0.2874( 2584)

S = 0.950                Npar= 255
```
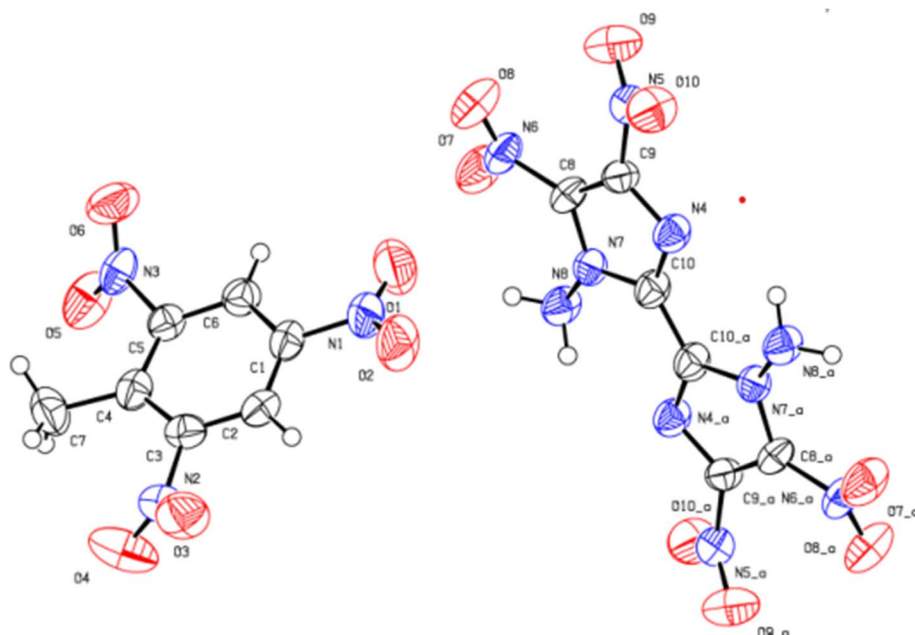
### S3. Detonation property evaluations

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

The equation of detonation velocity and pressure are as follow:

$$D = \frac{100}{M}(695 + 1150\rho)(1.00X_{N_2} + 0.64X_{H_2O} + 1.34X_{CO_2} + 0.72X_{CO} + 0.18X_{H_2} + 0.50X_{O_2} + 0.12X_C) \qquad (1)$$

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

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, DATNBI, TNT were also calculated by the same method.

**Table S2.** Predicted detonation performances of cocrystals and raw materials.

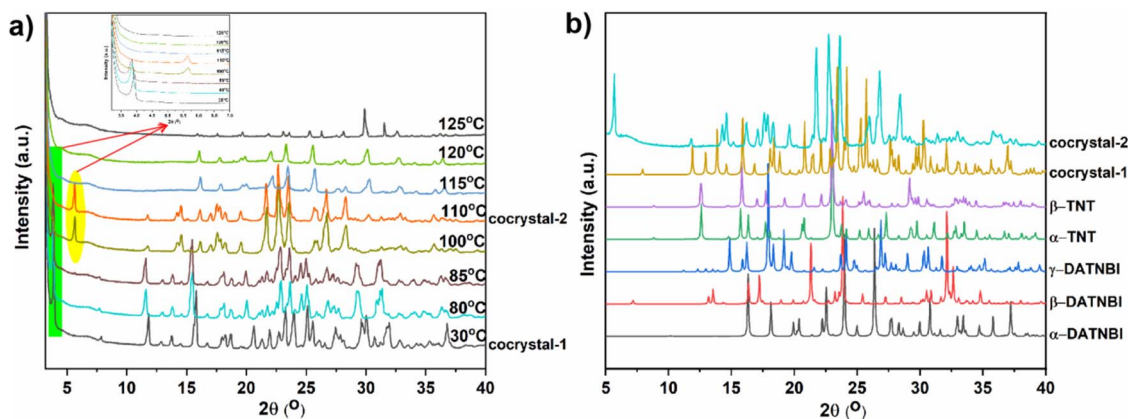| Sample | $\rho(g \cdot cm^{-3})$ | $D_v(m \cdot s^{-1})$ | P(Gpa) |
|---|---|---|---|
| DATNBI | 1.95 | 9104. | 38 |
| TNT/DATNBI | 1.76 | 7747 | 26 |
| TNT | 1.64 | 6910 | 20 |

## S4. Experimental



**Figure S1** (a) In-situ XRD patterns of cocrystal-1. (b) XRD patterns for raw materials (α-DATNBI, β-DATNBI, γ-DATNBI, α-TNT and β-TNT), cocrystal-1 and cocrystal-2.
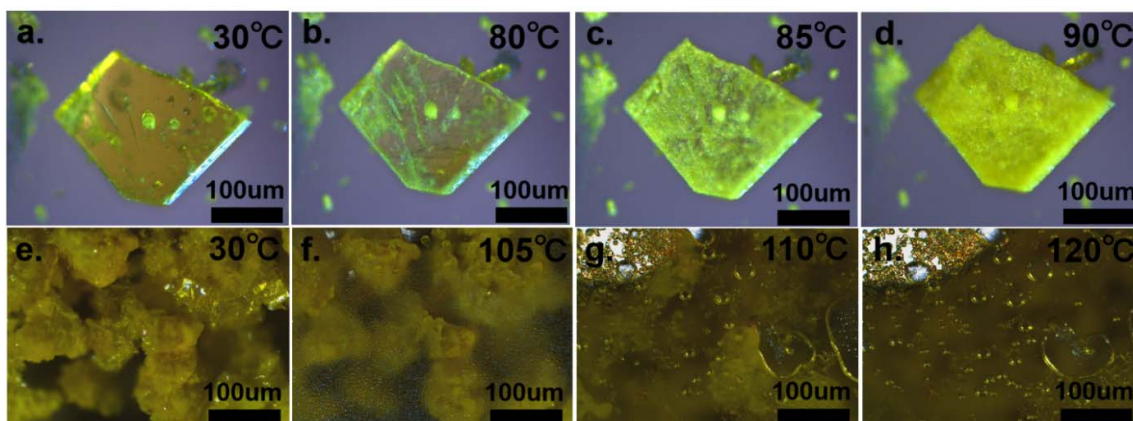


**Figure S2** In-situ hot-stage microscope of cocrystal-1. (a)-(d)Polymorphic transition process of cocrystal-1 single crystal. (e)-(f)Cocrystal-1 powder undergoes two-phase separation and TNT melting under thermal stimulation. (g)-(h)Melting process of DATNBI.