Supporting Information for the Design and Synthesis of a Series of Nitrogen-rich Energetic Cocrystals of 5,5'-dinitro-2H,2H'-3,3'-bi-1,2,4-triazole (DNBT)

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SI 1. Experimental

Caution: *Although no unplanned detonations were encountered during this work, DNBT, α-ANTA, DNPP and 3,4-DNP are all dangerous high explosives. Proper safety practices and equipment was used to prevent an explosion due to friction, heat, static shock, or impact. Be aware that the potential for severe injury exists if these materials are handled improperly.*

5,5'-Dinitro-2H,2H'-3,3'-bi-1,2,4-triazole (DNBT), 5-amino-3-nitro-1H-1,2,4-triazole (ANTA), 1H,4H-3,6-dinitropyrazolo[4,3-c]pyrazole (DNPP) and 3,4-dinitropyrazole (3,4-DNP) were received from Lawrence Livermore National Labs.

Crystallization

All cocrystals of DNBT (**1-3**) were initially obtained from acetonitrile solutions, with the stoichiometric ratio of the pure components (2:1, 1:1 and 2:1 respectively), by slow evaporation and then conditions for their pure growth was determined, see below.

*2:1 ANTA/DNBT (**1**)*

A glass vial was loaded with 7.63 mg of DNBT (0.0338 mmol) and 8.72 mg ANTA (0.0675 mmol), which were subsequently dissolved with 2.3 mL of dry acetonitrile and 0.2 mL of dry acetone. Sonication was used to ensure dissolution, before the solution was filtered through a 0.45 μm PTFE filter into a 4 mL glass vial. The cap on the vial was left loose to allow for slow evaporation of the solvent. After six days at room temperature colorless plates formed on the bottom and side of the vial and were determined to be the 2:1 ANTA:DNBT cocrystal by both Raman spectroscopy and powder X-ray diffraction.

*1:1 DNPP/DNBT (**2**)*

A glass vial was loaded with 7.63 mg of DNBT (0.0338 mmol) and 6.69 mg DNPP (0.0338 mmol), which were subsequently dissolved with 1.4 mL of dry acetonitrile. Sonication was used to ensure dissolution, before the solution was filtered through a 0.45 μm PTFE filter into a 4 mL glass vial. The cap on the vial was left loose to allow for slow evaporation of the solvent. After five days at room temperature colorless plates formed on the bottom of the vial and were

determined to be the 1:1 DNPP/DNBT cocrystal by both Raman spectroscopy and powder X-ray diffraction.

*2:1 3,4-DNP/DNBT (**3**)*

A glass vial was loaded with 22.6 mg of DNBT (0.100 mmol) and 31.6 mg 3,4-DNP (0.200 mmol), which were subsequently dissolved with 0.25 mL of dry isopropanol. Sonication was used to ensure dissolution, before the solution was filtered through a 0.45 μm PTFE filter into a 4 mL glass vial. The cap on the vial was left loose to allow for slow evaporation of the solvent. After one day at room temperature colorless plates formed on the bottom of the vial and were determined to be the 2:1 3,4-DNP:DNBT cocrystal by both Raman spectroscopy and powder X-ray diffraction.

The cocrystal synthesis could be scaled up conveniently with the use of solvent mediated transformation in a slurry of the pure components at room temperature. For example, the cocrystal **2** was obtained by loading a glass vial with 11.31 mg of DNBT (0.050 mmol), 9.91 mg DNPP (0.050 mmol) and 0.2 mL of dry isopropanol. The vial was sealed and shaken gently for 2 days, during which time the pure components of DNBT and DNPP had disappeared and a white powder had appeared. This solid was determined to be the 1:1 DNBT:DNPP cocrystal by both Raman spectroscopy and powder X-ray diffraction.

Raman Spectroscopy

Raman spectra were collected using a Renishaw inVia Raman Microscope equipped with a Leica microscope, 633 nm laser, 1800 lines/mm grating, 50 μm slit and a RenCam CCD detector. Spectra were collected in extended scan mode with a range of 100-4000 cm^{-1} and then analyzed using the WiRE 3.4 software package (Renishaw). Calibration was performed using a silicon standard.

Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction patterns were collected on a Bruker D8 Advance diffractometer using Cu-Kα radiation (λ = 1.54187 Å) and operating at 40 kV and 40 mA. Samples were prepared by finely grinding and packing into the depression of a glass slide. The spectrum was collected by scanning 2θ from 4° to 70° with a step size of 0.02° and a step speed of 0.5 seconds. Powder

patterns were processed using Jade 8 XRD Pattern Processing, Identification & Quantification analysis software (Materials Data, Inc.).[1] All powder patterns were compared to their respective simulated powder patterns from the single crystal X-ray diffraction structures and were found to be in substantial agreement with the predicted patterns.

Single Crystal Structure Determination

Single crystal X-ray diffraction data for cocrystals **1-3** were collected using a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode (λ = 1.54187 Å) operated at 1.2 kW power (40 kV, 30 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. The data was processed with CrystalClear 2.0 (Rigaku)[2] and corrected for absorption. The structures were solved and refined with the Bruker SHELXTL (version 2008/4)[3] software package using direct methods.[4] All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of refined and idealized positions.

Differential Scanning Calorimetry (DSC)

Thermograms of each sample were recorded on a TA Instruments Q20 DSC. All experiments were run in Tzero™ hermetic aluminum DSC pans and studied under a nitrogen purge with a heating rate of 10 °C/min, while covering the temperature range of 35 °C to 350 °C. Calibration of the instrument was performed using an indium standard. Thermograms were analyzed using TA Universal Analysis 2000, V 4.5A.

SI 2. Raman Spectroscopy of DNBT Cocrystals

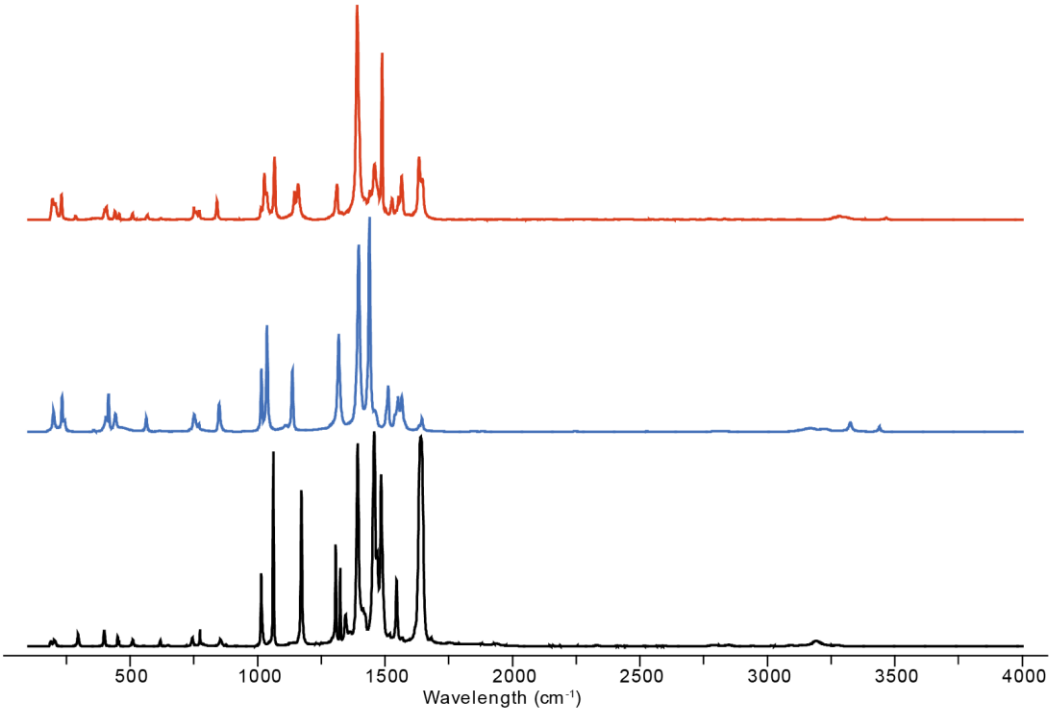

Figure S1. Raman spectra of **1**, α-ANTA and DNBT (from top to bottom).

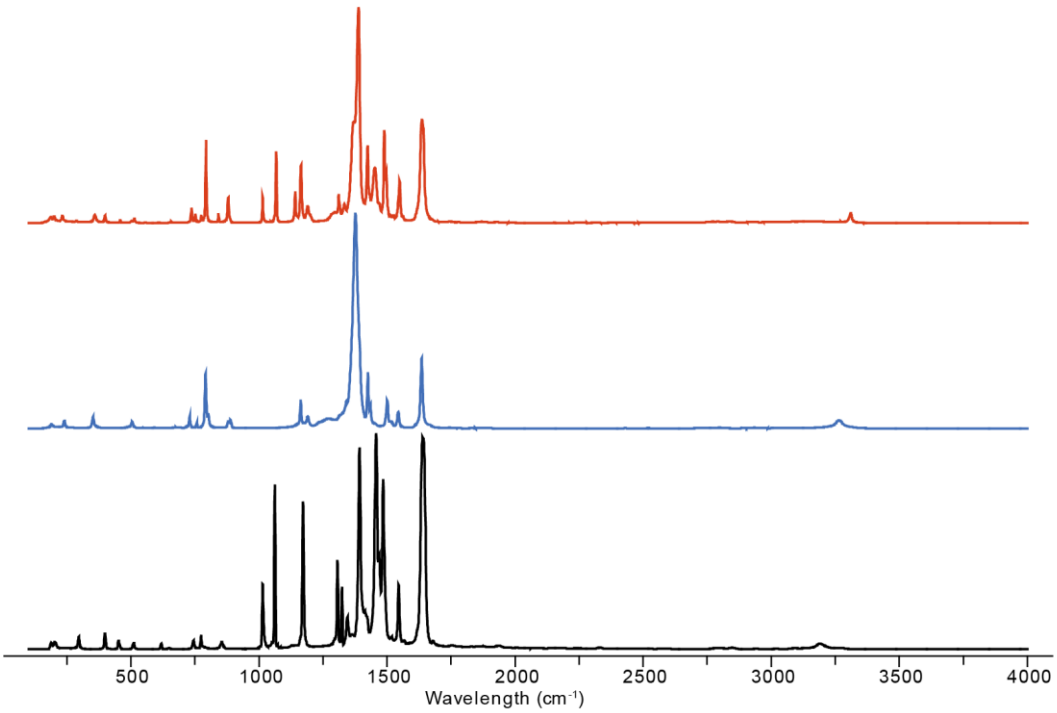

Figure S2. Raman spectra of **2**, DNPP and DNBT (from top to bottom).

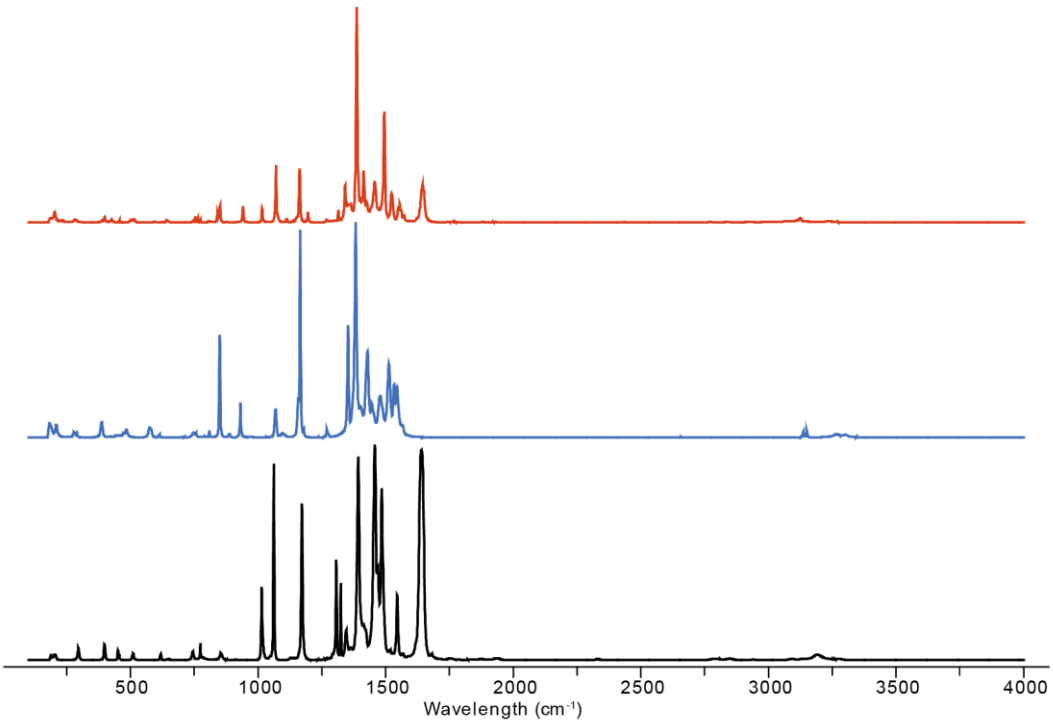

Figure S3. Raman spectra of **3**, 3,4-DNP and DNBT (from top to bottom).

SI 3. Powder X-ray Diffraction of DNBT Cocrystals

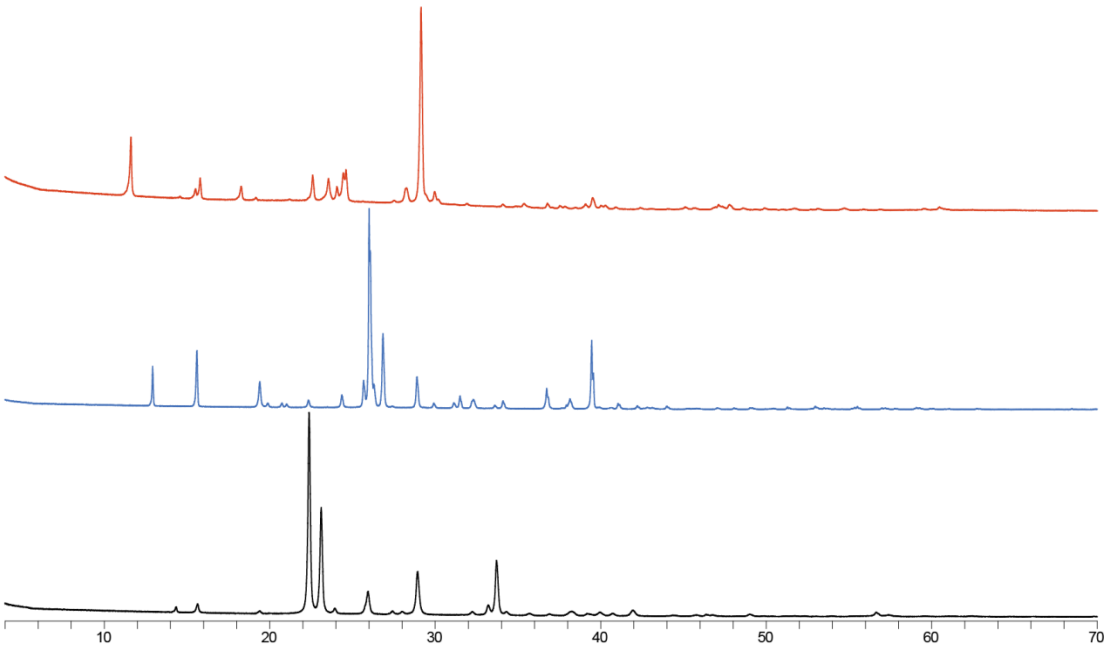

Figure S4. PXRD patterns of **1**, α-ANTA and DNBT (from top to bottom).

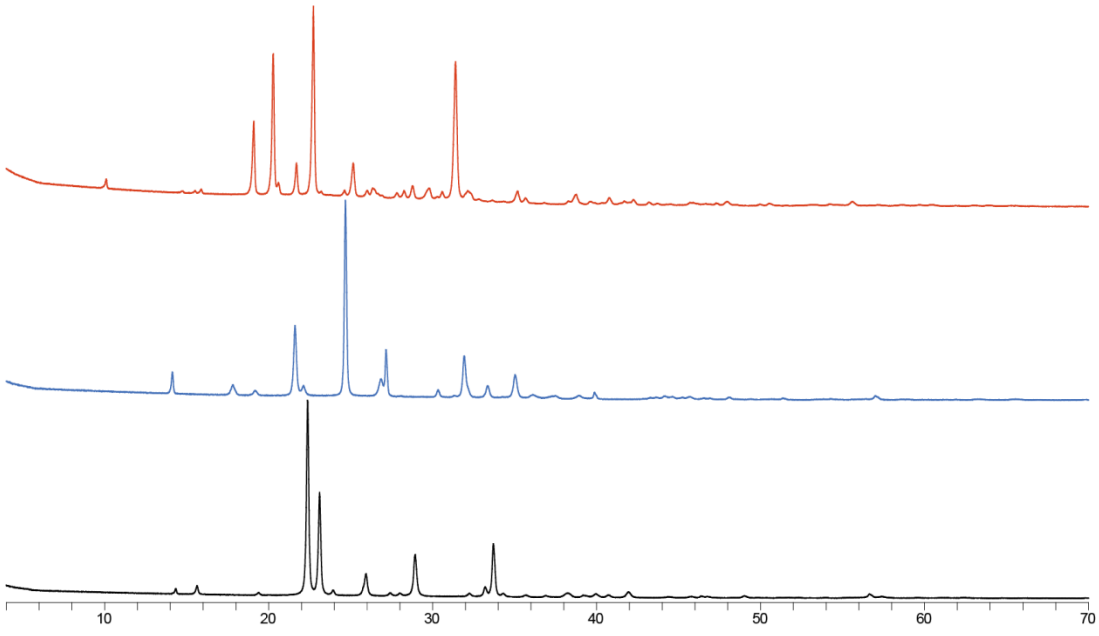

Figure S5. PXRD patterns of **2**, DNPP and DNBT (from top to bottom).

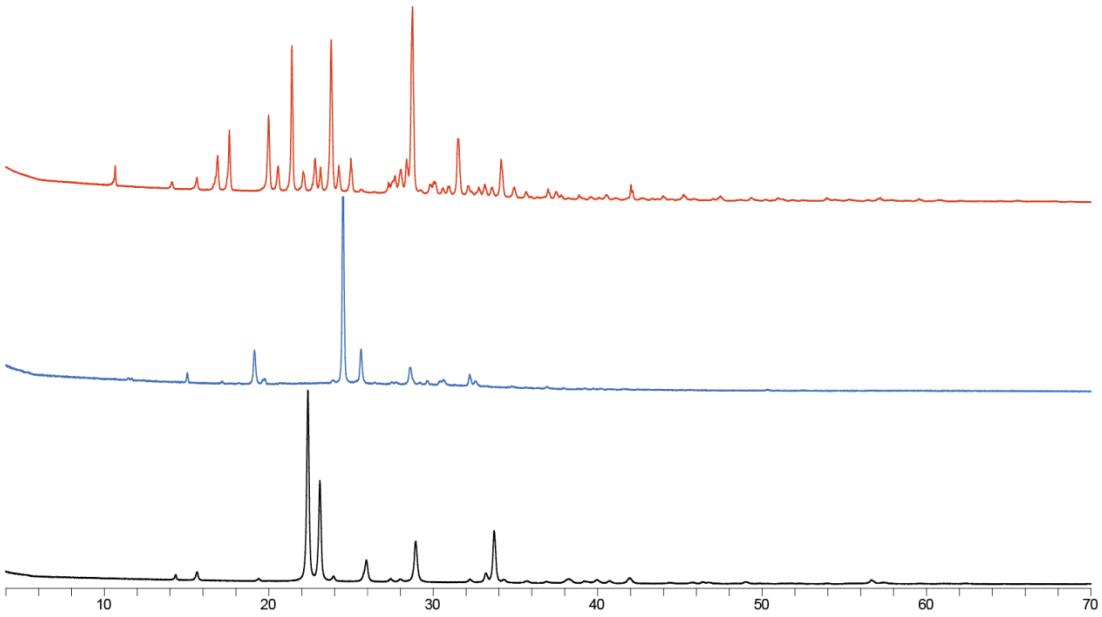

Figure S6. PXRD patterns of **3**, 3,4-DNP and DNBT (from top to bottom).

SI 4. ORTEP Diagrams of DNBT Cocrystals

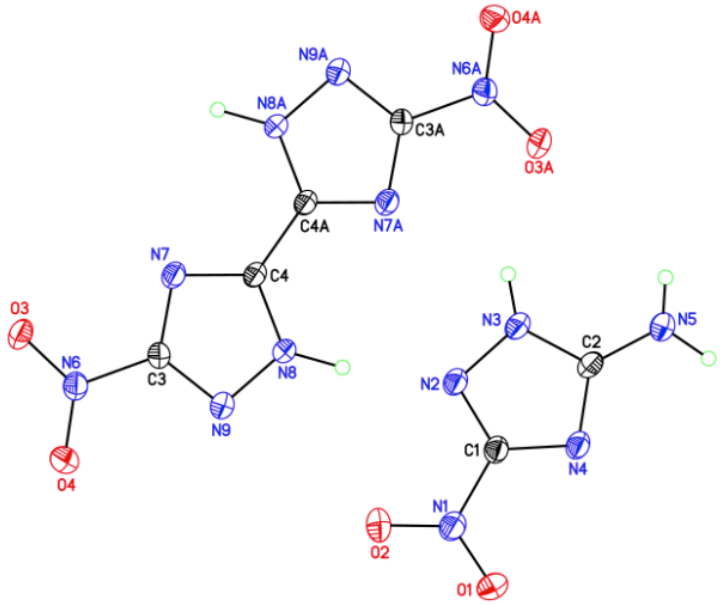

Figure S7. ORTEP diagram for **1** collected at 85 K with thermal ellipsoids of 50% probability.

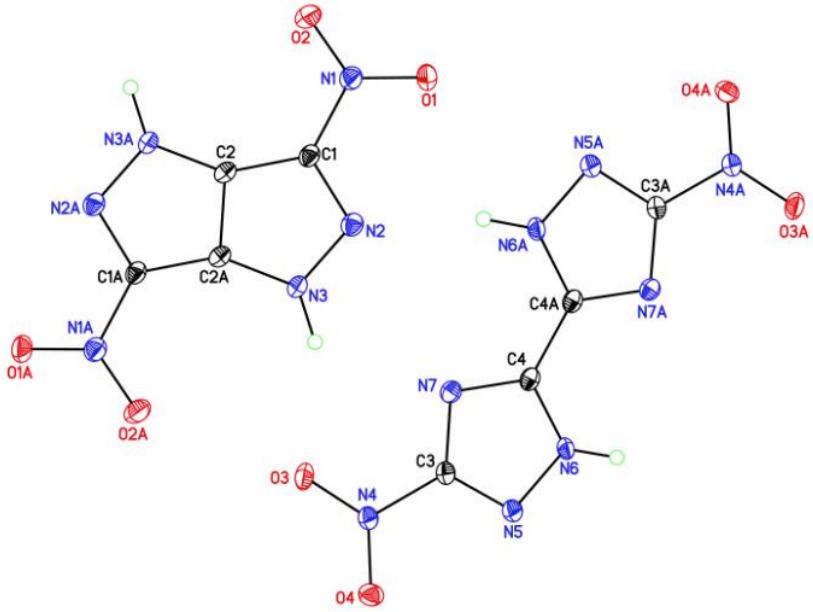

Figure S8. ORTEP diagram for **2** collected at 85 K with thermal ellipsoids of 50% probability.

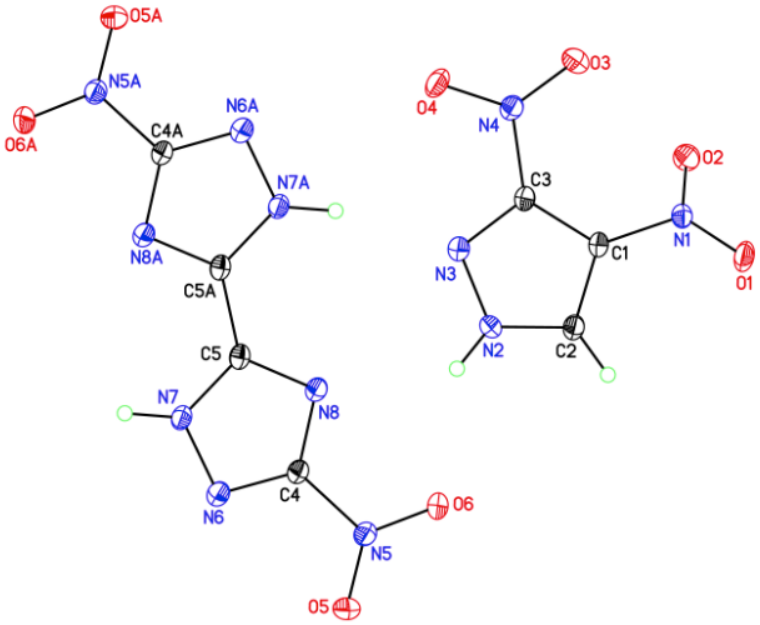

Figure S7. ORTEP diagram for **3** collected at 85 K with thermal ellipsoids of 50% probability.

SI 5. Differential Scanning Calorimetry of DNBT Cocrystals

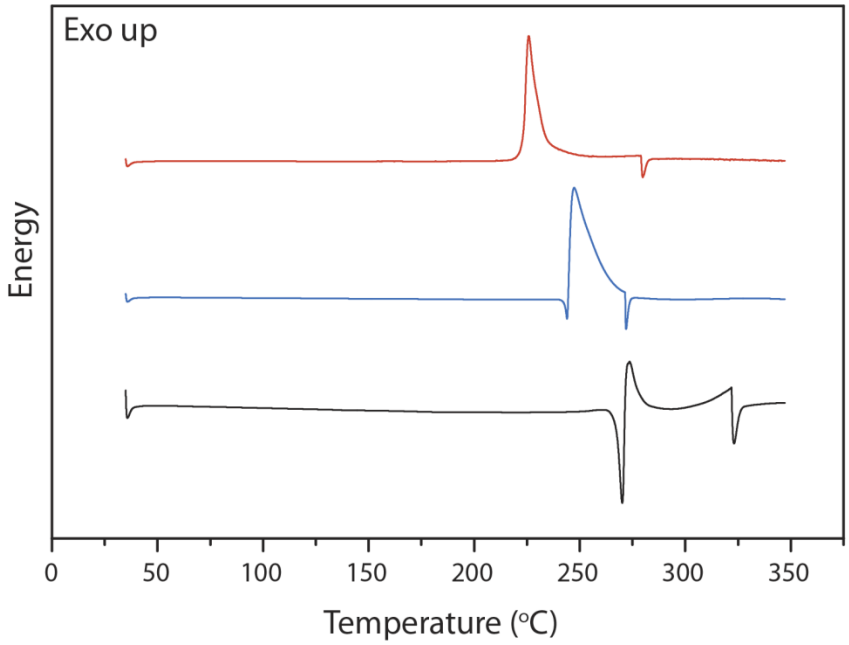

Figure S10. Typical DSC traces of **1**, ANTA and DNBT (from top to bottom).

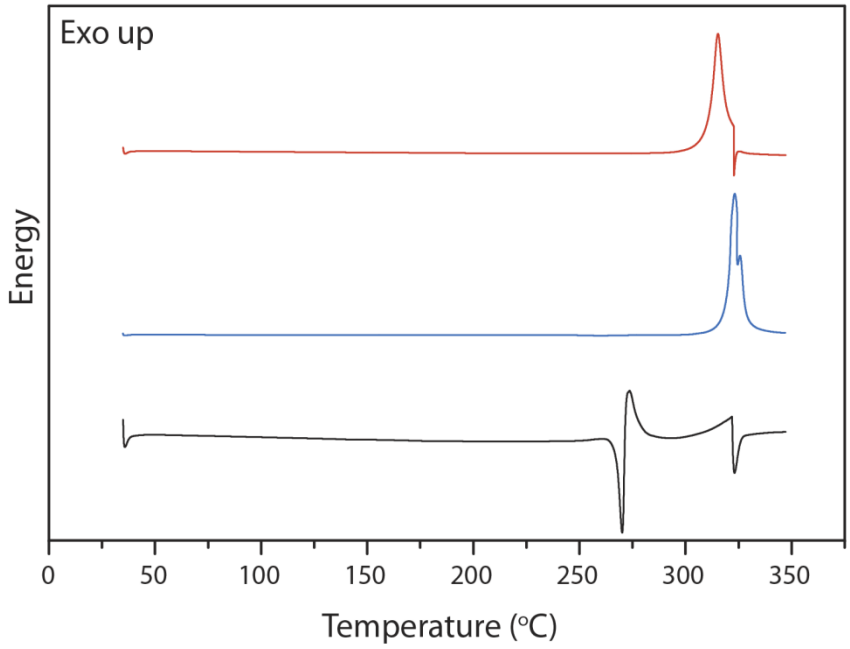

Figure S11. Typical DSC traces of **2**, DNPP and DNBT (from top to bottom).

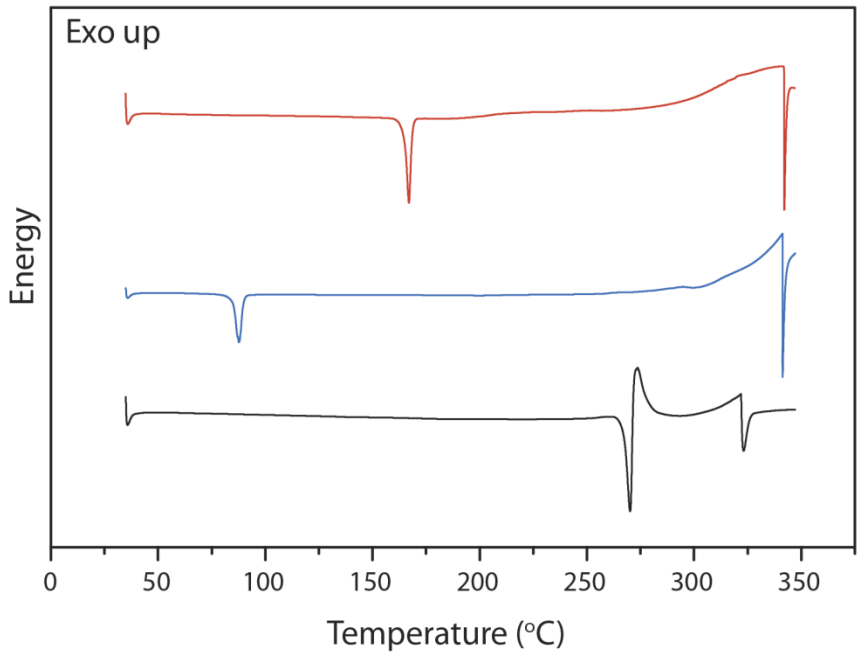

Figure S12. Typical DSC traces of **3**, 3,4-DNP and DNBT (from top to bottom).

SI 6. Morphology of DNBT Cocrystals

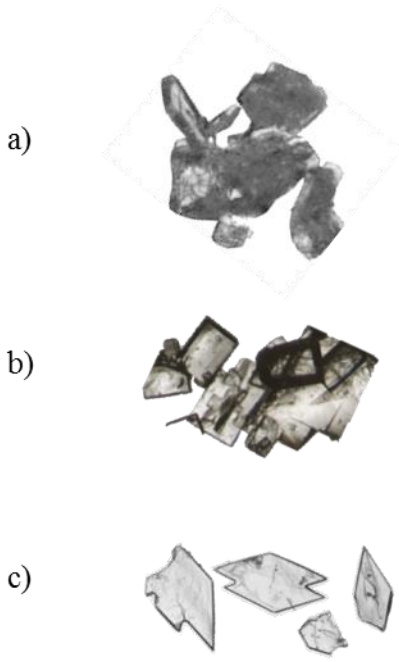

Figure S13. Typical plate habit morphology of the three DNBT cocrystals (**1**-**3**): (a) 2:1 ANTA/DNBT cocrystal (**1**); (b) 1:1 DNPP/DNBT cocrystal (**2**); (c) 2:1 3,4-DNP/DNBT cocrystal (**3**).

SI 7. References

(1) Jade Plus 8.2 ed.; Materials Data, Inc. 1995-2007.

(2) CrystalClear Expert 2.0 r12, Rigaku Americas and Rigaku Corporation (2011), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

(3) Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.