Electronic Supplementary Material (ESI) for ChemComm.

A Melt Castable Energetic Cocrystal

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SI 1. Experimental

Caution: *Although no unplanned detonations were encountered during this work, DAF and ADNP are both dangerous high explosives. Proper safety practices and equipment were 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.*

3,4-Diaminofurazan (DAF), 97% purity, was used as received from Sigma Aldrich. 4-Amino-3,5-dinitropyrazole (ADNP or LLM-116) was used as received from Lawrence Livermore National Labs.

Crystallization

The cocrystal of DAF (**1**) was initially obtained from acetonitrile solutions, with the stoichiometric ratio of the pure components 1:1, by slow evaporation and then conditions for growth in pure form were determined. 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 or from a melt of the pure components, see below.

*1:1 DAF/ADNP (**1**) from Slurry*

A 4 mL glass vial was loaded with 11.1 mg of DAF (0.111 mmol), 19.3 mg ADNP (0.111 mmol) and 150 µL of dry isopropanol. The vial was sealed and shaken gently for 2 days, during which time the pure components of DAF and ADNP had disappeared and small yellow prisms had appeared. This solid was determined to be the 1:1 DAF/ADNP cocrystal by both Raman spectroscopy and powder X-ray diffraction.

*1:1 DAF/ADNP (**1**) from Melt*

A 4 mL glass vial was loaded with 22.4 mg of DAF (0.223 mmol), 38.6 mg ADNP (0.223 mmol). The open vial was placed in a 180 °C heat block for 5 minutes and then allowed to cool to room temperature. This solid was determined to be the 1:1 DAF/ADNP 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 4000-100 cm^{-1} and analyzed using the WiRE 3.4 software package (Renishaw). Hot stage Raman spectra were collected using a Renishaw inVia Raman Microscope equipped with a Leica microscope, 532 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 3600-2970 cm^{-1} and analyzed using the WiRE 3.4 software package (Renishaw). Calibration was performed using a silicon standard in static mode.

Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction patterns were collected on a Rigaku SmartLab diffractometer using Cu-Kα radiation (λ = 1.54187 Å) and operating at 40 kV and 44 mA. Samples were prepared by finely grinding and packing into the depression of a glass slide and data were collected with a sample rotation rate of 180°/min. The powder patterns were collected by scanning 2θ from 5° to 50° with a step size of 0.02° and a step speed of 1.0 second. The data were processed using Jade 8 XRD Pattern Processing, Identification & Quantification analysis software (Materials Data, Inc.).[1] The powder patterns were all compared to their respective simulated powder patterns from the single crystal X-ray diffraction structures and were found to be in good agreement with the predicted patterns.

Single Crystal Structure Determination

Single crystal X-ray diffraction data for cocrystal **1** was 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 were 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. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in a combination of refined and idealized positions.

Table S1. Crystallographic Data for 1:1 DAF/ADNP (Collected at 85 K)

Material	**DAF/ADNP (1)**
Stoichiometry	1:1
Morphology	Prismatic
Space Group	$P2_1/n$
a (Å)	8.6432(2)
b (Å)	13.5987(3)
c (Å)	9.3093(7)
α (°)	90
β (°)	110.897(8)
γ (°)	90
Volume (Å^3)	1022.21
Z	4
ρ_{calc} (g/cm^3)	1.775
Data/Parameter	1878/201
R_1/wR_2	3.29/8.44
GOF	1.026

Differential Scanning Calorimetry (DSC)

Thermograms for each sample were recorded on a TA Instruments Q10 DSC equipped with air cooling. All experiments were conducted in Tzero™ hermetic aluminum DSC pans under a nitrogen purge with a heating rate of 10 °C/min, while covering the temperature range of 35 °C to 300 °C. Cyclic thermograms of **1** were recorded on a TA Instruments Q20 DSC equipped with a RCS90 chiller. The heat-cool-heat experiment was conducted in Tzero™ hermetic aluminum DSC pans under a nitrogen purge with a heating rate of 10 °C/min, while covering the temperature range of 30 °C to 180 °C. The instrument was calibrated using an indium standard. Thermograms were analyzed using TA Universal Analysis 2000, V 4.5A.

Drop Weight Impact Sensitivity Analysis

For the analysis of the sensitivity to impact, approximately 2 mg (± 10%) of material for each sample is contained within nonhermetic DSC pans and then struck by a freefalling 5 lb drop weight. A reproducible Dh_{50}, height of the 50% probability of detonation, is obtained by utilizing the Bruceton Analysis (up-and-down method) with varying drop heights. This system is a nonstandard impact sensitivity apparatus and the Dh_{50} values obtained are only used for relative comparison to materials tested with this device; for reference the Dh_{50} of ε-CL-20 and β-HMX are 29 and 55 cm, respectively.[4]

SI 2. Raman Spectroscopy of ADNP Cocrystal

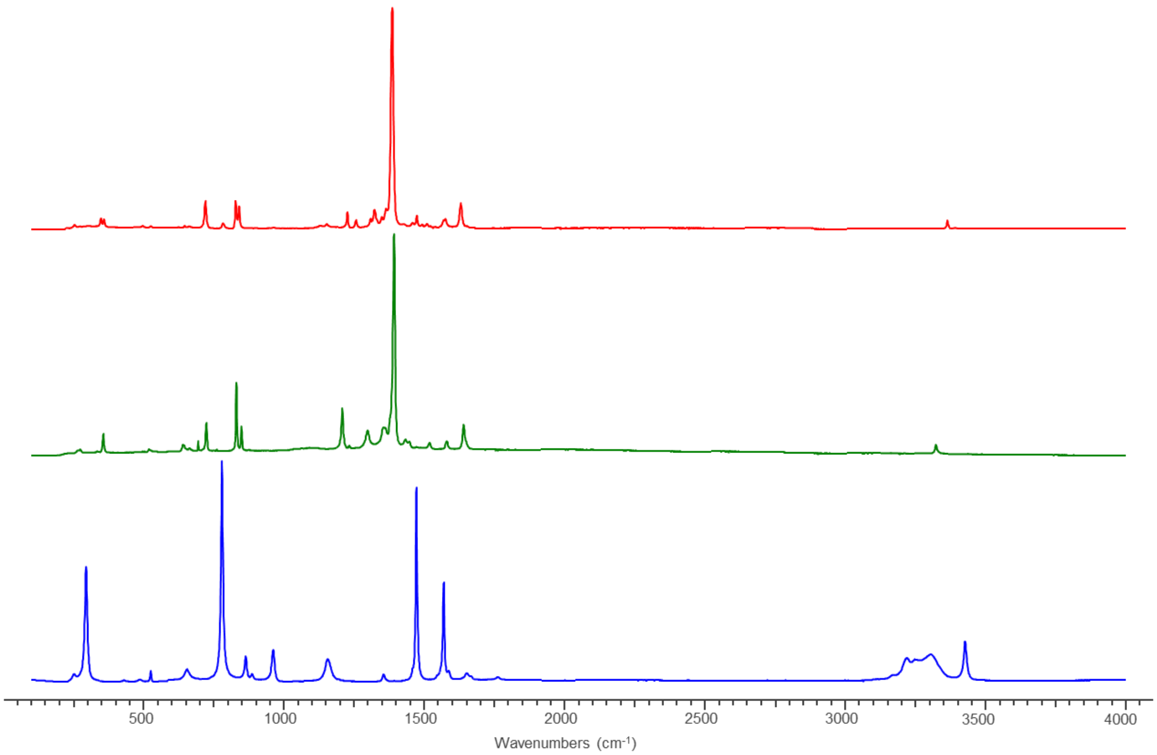

Figure S1. Raman spectra of **1**, ADNP, and DAF (from top to bottom).

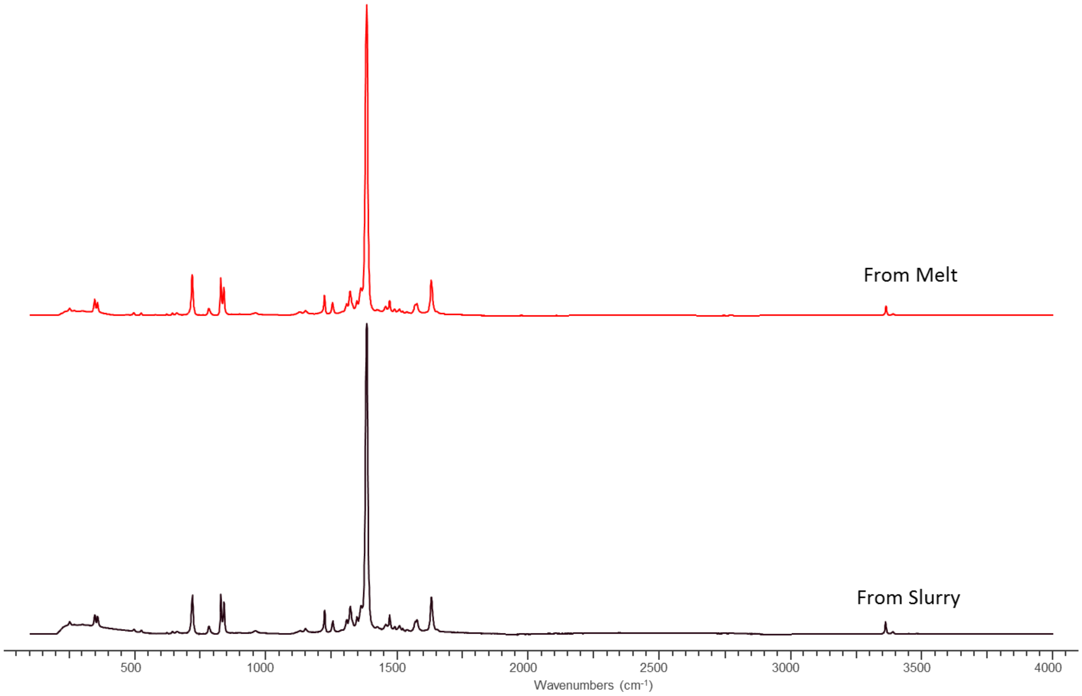

Figure S2. Raman spectra of **1** from both the melt and slurry of the pure components ADNP and DAF (from top to bottom).

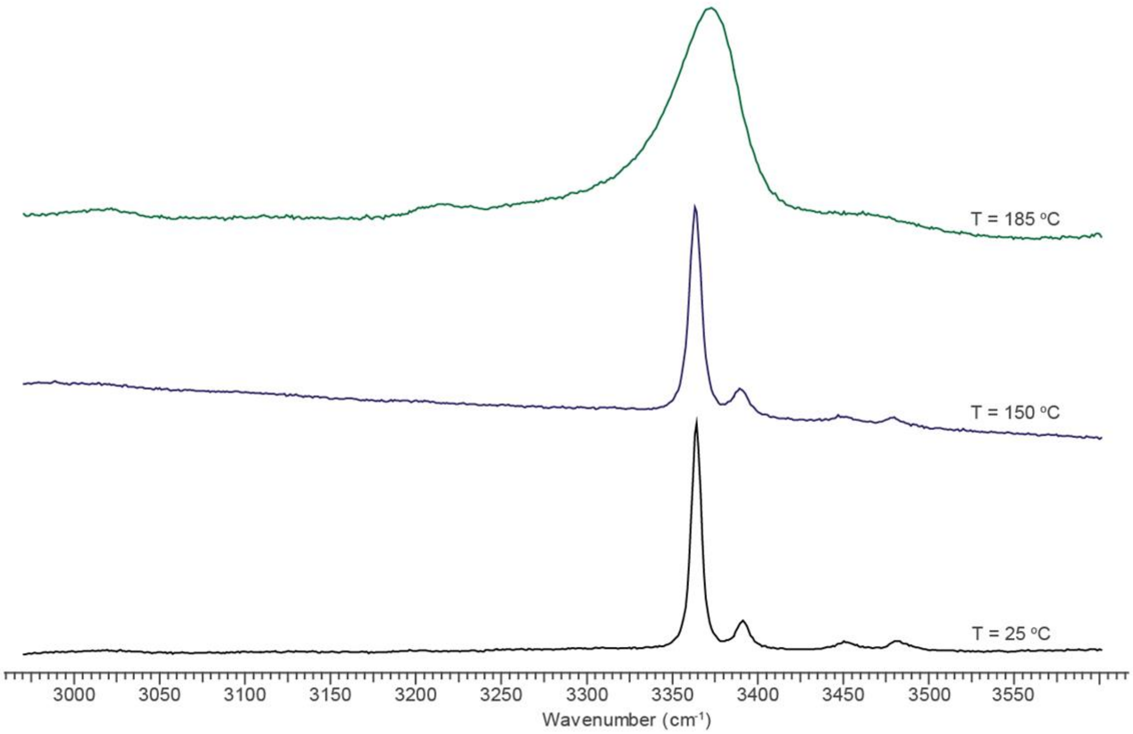

Figure S3. Hot stage Raman spectra of **1** at 20, 150 and 180 °C (past the melting point).

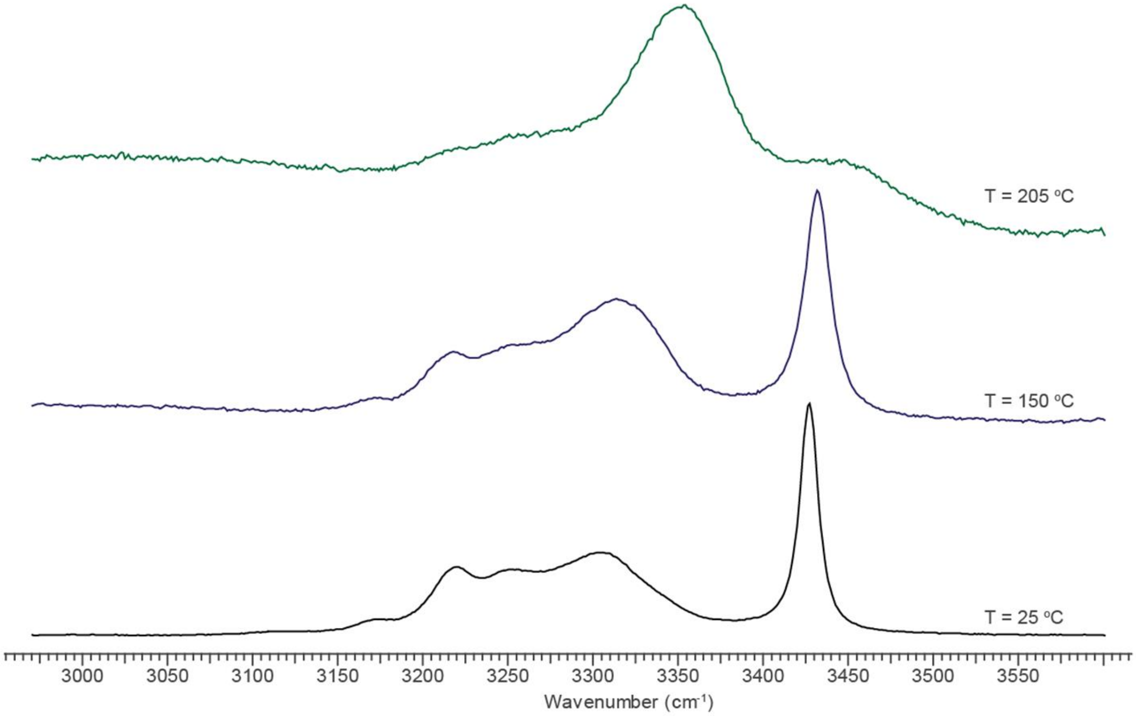

Figure S4. Hot stage Raman spectra of DAF at 20, 150 and 205 °C (past the melting point).

SI 3. Powder X-ray Diffraction Patterns of ADNP Cocrystal

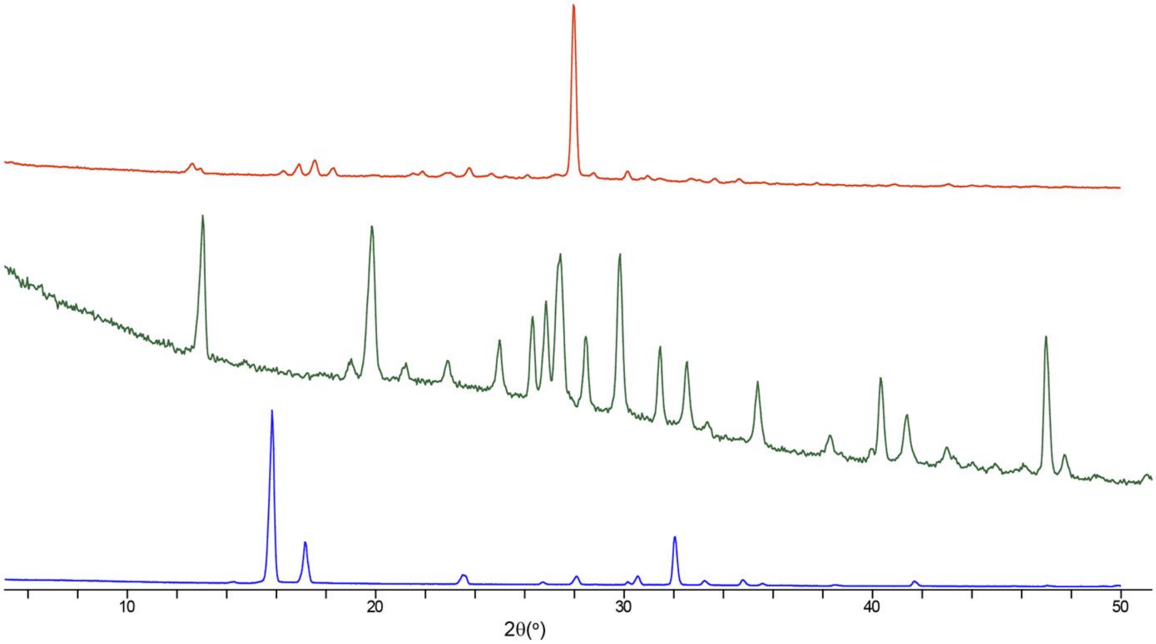

Figure S5. PXRD patterns of **1**, ADNP, and DAF (from top to bottom).

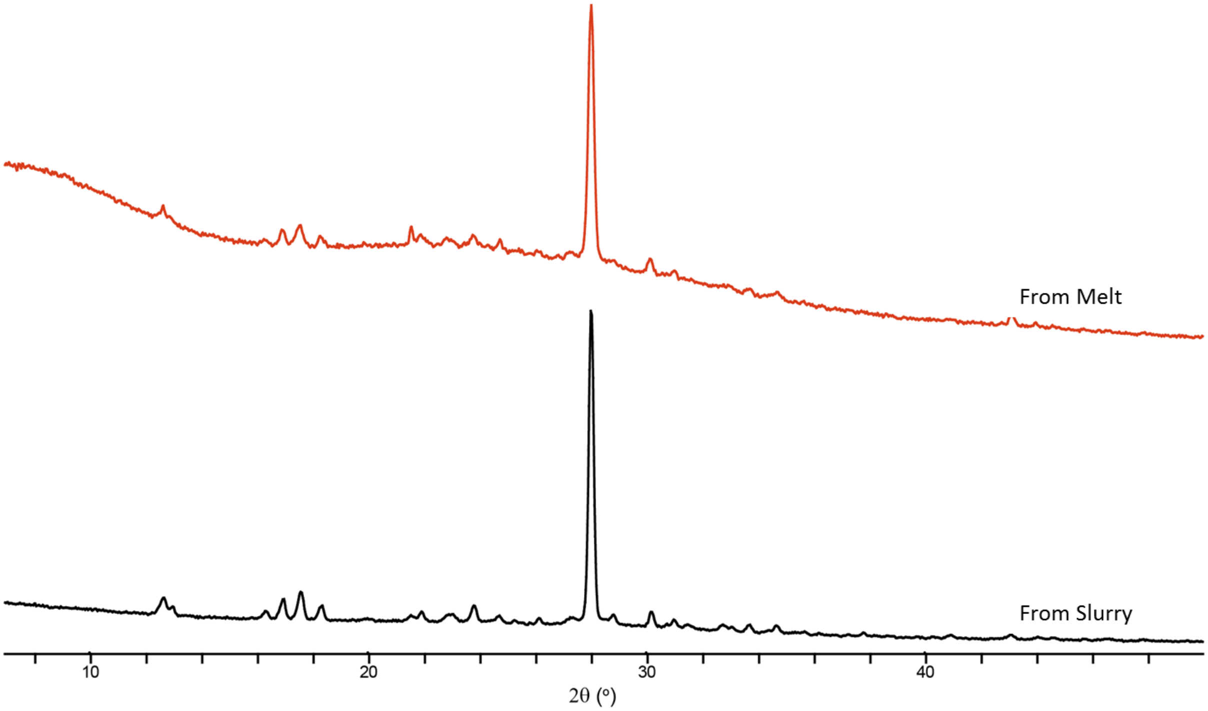

Figure S6. PXRD patterns of **1** from both the melt and slurry of the pure components ADNP and DAF (from top to bottom).

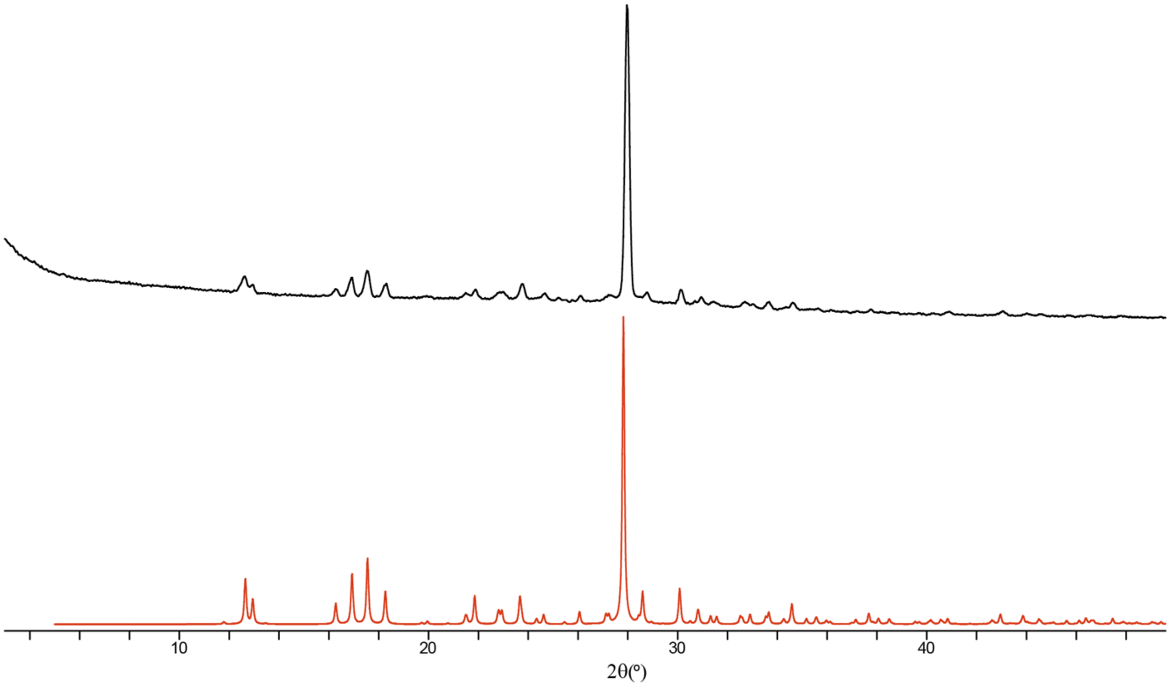

Figure S7. PXRD patterns of **1** and the simulated structure of **1** from the CIF (from top to bottom).

SI 4. ORTEP Diagrams of ADNP Cocrystal

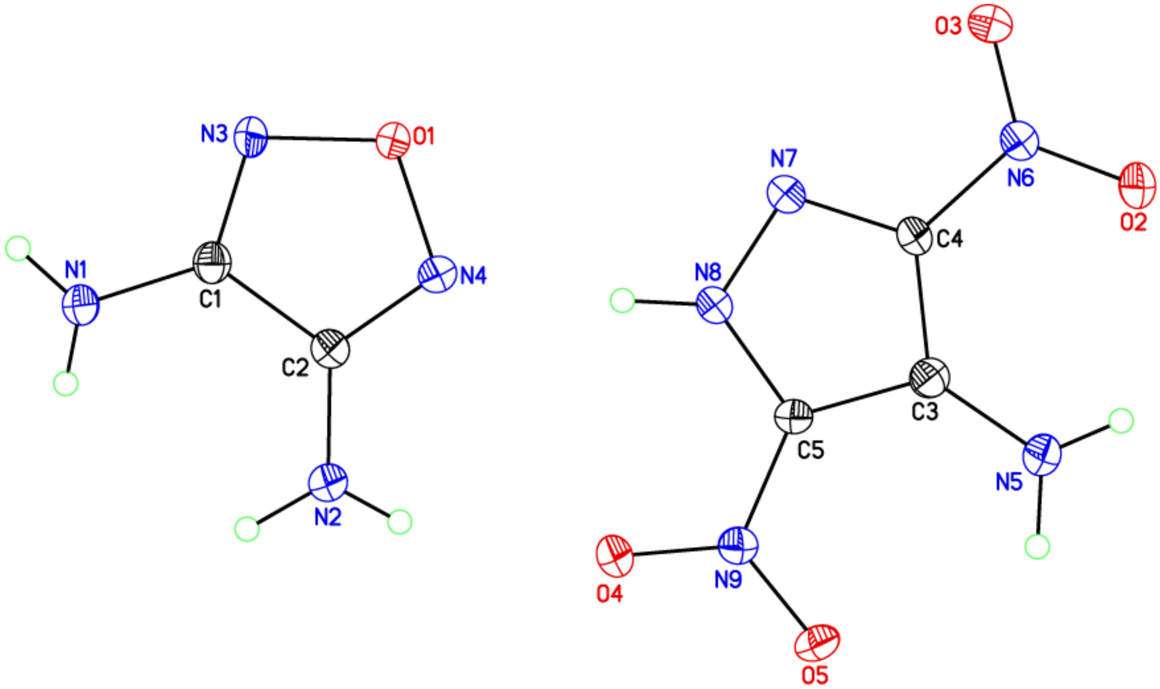

Figure S8. ORTEP diagram for **1** collected at 85 K with thermal ellipsoids of 50% probability.

SI 5. Differential Scanning Calorimetry of ADNP Cocrystal

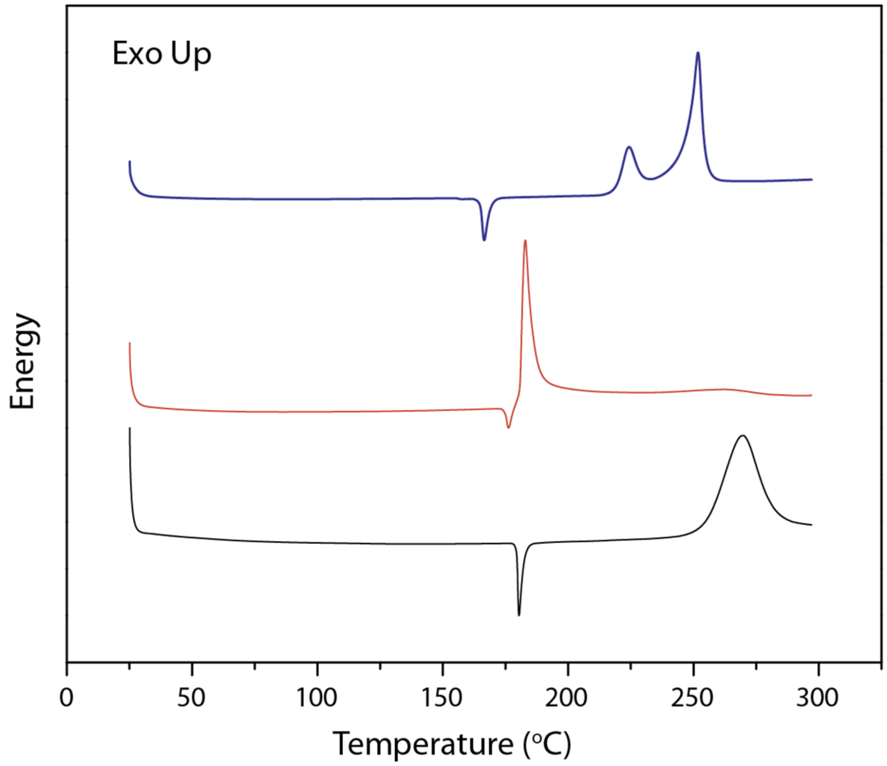

Figure S9. Typical DSC traces of **1**, ADNP, and DAF (from top to bottom).

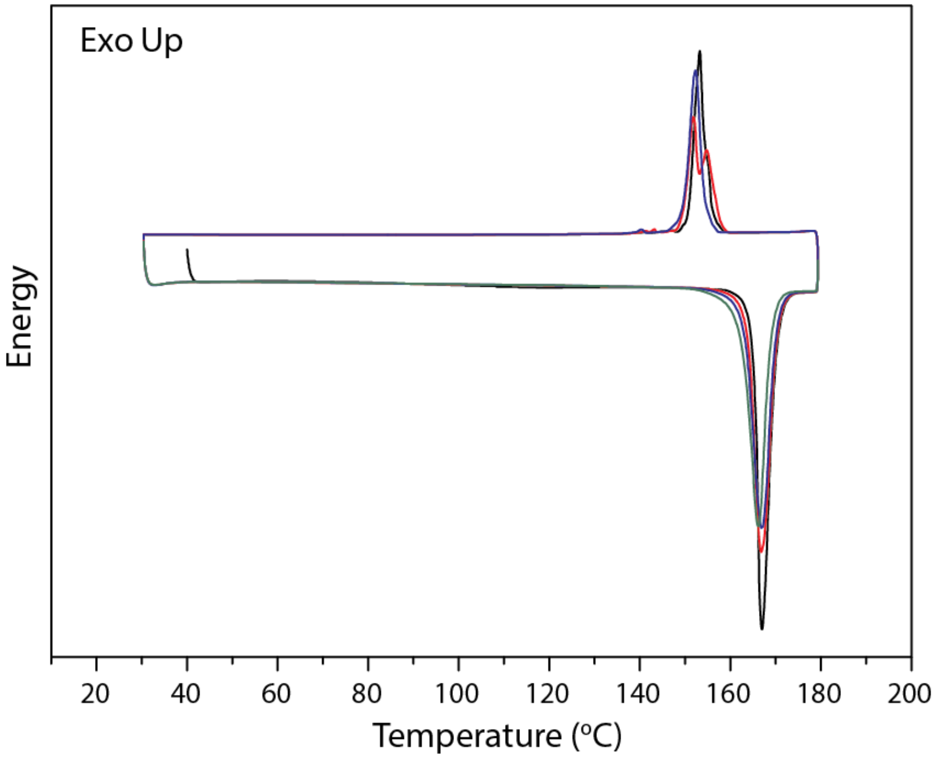

Figure S10. Cyclic DSC past the melting of **1**, three cycles of heat-cool-heat (first cycle is black).

SI 6. Morphology of ADNP Cocrystal

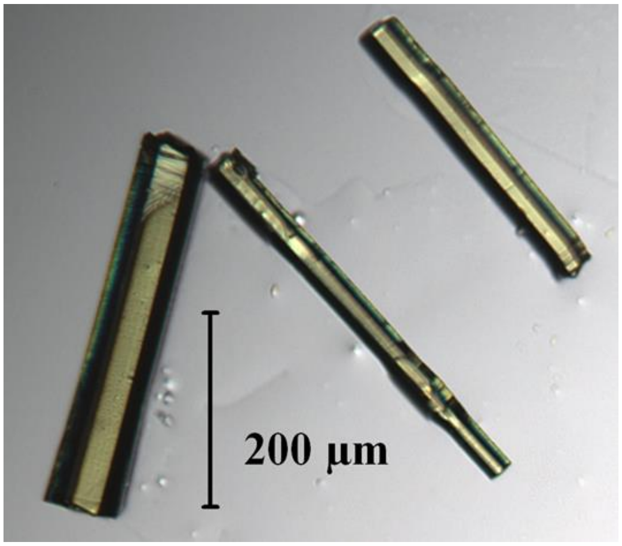

Figure S11. Typical rod morphology of the 1:1 DAF/ADNP cocrystal.

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.

(4) Bennion, J. C.; McBain, A.; Son, S. F.; Matzger, A. J. *Cryst. Growth Des.* **2015**, *15*, 2545.