Electronic Supplementary Material (ESI) for Chemical Science.

Discovery Strategy Leads to the First Melt-Castable Cocrystal Based on an Energetic Oxidizing Salt

Supplementary Information

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SI 1. Experimental

Caution: Although no unplanned detonations were encountered during this work, ammonium dinitramide is an energetic oxidizing agent. Proper safety practices and equipment was used to prevent an explosion due to friction, heat, static shock, impact, or flame. Be aware that the potential for severe injury exists if these materials are handled improperly. Liquid assisted grinding experiments were conducted while wearing steel-woven Kevlar gloves, a protective face shield, and while standing behind a blast shield.

Ammonium dinitramide (ADN) was received from NAVAIR, Naval Air Warfare Center Weapons Division, China Lake. Acetonitrile (MeCN) was obtained from Fisher Scientific, passed through an activated alumina column, and stored over 4Å molecular sieves prior to use. Diethyl ether was obtained from MilliporeSigma, passed through an activated alumina column, and stored over 4Å molecular sieves prior to use. Urea, Certified A.C.S., was obtained from Fisher Scientific. Ethyl acetate, methylene chloride (DCM), and hexanes were obtained from Fisher Scientific and stored over 4Å molecular sieves prior to use. Ammonium hexafluorophosphate (AH), 99.98 trace metal basis, was obtained from MilliporeSigma. 2-Imidizolidinone (2Im), anhydrous 96%, was obtained from Acros organics and purified via sublimation at 90 °C under reduced pressure prior to use. Pyrazine-1,4-dioxide (PDO) was prepared by the published method.[1] Disposable syringe filters (0.45 μm, polytetrafluoroethylene) were obtained from Macherey-Nagel.

Synthesis

AH-PDO
A co-saturated aqueous solution of PDO and AH was prepared by placing a large excess of both chemicals in a 4 mL vial with 3 mL water. The slurry was placed on an orbital shaker for 24 h at which time 2 mL of the solution was syringe filtered into a fresh 4 mL vial which was sealed and placed in a refrigerator overnight. The resultant crystals were collected via filtration, rinsed with hexanes (2 × 4 mL), and allowed to air dry.

AH-2Im
2Im (10.5 mg, 0.230 mmol) and AH (37.9 mg, 0.230 mmol) were pre-mixed by grinding with a few drops of MeCN. The material was then transferred to a 4 mL vial followed by the addition of 2 mL MeCN. The resulting solution was allowed to evaporate at ambient yielding **AH-2Im**.

ADN-2Im *by melt synthesis*
Inside a laboratory glovebox under N_2 atmosphere, 2Im (6.99 mg, 0.0812 mmol) and freshly dried (high vac., 12 h) ADN (10.1 mg, 0.0812 mmol) were pre-mixed by grinding with a few drops of MeOH. An Aliquot of this material (2.073 mg) was transferred into a DSC pan and subjected to a heat/hold/cool program using a TA Instruments Q20 differential scanning calorimeter as follows: heat 40 °C → 70 °C @ 5 °C/min., hold 3 min., cool 70 °C → 1 °C @ 0.01 °C/min. This material frequently super-cools and rapidly crystallizes resulting in small crystals of poor quality. Different cooling rates were investigated and only rates ≤ 0.1 °C/min provide reasonably large crystals with crystal quality increasing as the rate approaches 0.01 °C/min.

AH-urea
A co-saturated MeCN solution of Urea and AH was prepared by placing a large excess of both chemicals in a 4 mL vial with 2 mL MeCN. The slurry was placed on an orbital shaker for 24 h at which time 2 mL of the solution was syringe filtered into a fresh 4 mL vial which was sealed and placed in a refrigerator overnight. The resultant crystals were collected via filtration, rinsed with 1 mL of a chilled MeCN:hexanes (1:3) mixture followed by 2 mL of anhydrous diethyl ether. The obtained physical mixture containing **AH-urea** was allowed to air dry.

ADN-urea
Urea (19.4 mg, 0.323 mmol) and ADN (20.0 mg, 0.161 mmol) were combined in a 4 mL vial and 2 mL MeCN was added. The solution was allowed to evaporate at ambient yielding **ADN-urea**. Occasionally an oil is obtained which crystallizes upon mechanical disturbance.

Characterization

Single-Crystal X-Ray Structure Determination

Single-crystal X-ray diffraction data were collected using a Rigaku XtaLAB Synergy-S X-ray diffractometer with an α kappa goniometer geometry configuration; an Oxford Cryostream 800 low temperature device is also equipped. The X-ray source is a PhotonJet-S microfocus Cu source (λ = 1.54184 Å) operated at 50 kV and 1 mA. X-ray intensities were measured with a HyPix-6000HE detector held 34 mm from the sample. The data were processed using CrysAlisPro v38.46 (Rigaku Oxford Diffraction) and were corrected for absorption. The structures were determined using OLEX2[2] as well as SHELXT[3] and refined with SHELXL.[4] All non-hydrogen atoms were refined anisotropically with hydrogen atoms located at idealized positions.

Powder X-Ray Diffraction

All powder pattern data were collected using a Panalytical Empyrean system utilizing Cu-Kα radiation (λ = 1.54184 Å) and operating at 45 kV and 40 mA. The system uses a Bragg-Brentano HD X-ray optic and an X'Celerator Scientific detector operating in a continuous 1D scan mode. Scans were conducted according to the following parameters: 2θ = 3° to 50°, step size = 0.008°, and step speed = 20 seconds. The data were plotted using Origin Pro 8.6.

Raman Spectroscopy

Raman spectra were collected using a Renishaw inVia Raman Microscope equipped with a Leica microscope and in the following configurations: 1) a 785 nm laser, 1200 lines/mm gratings, 65 µm slit size, and a RenCam CCD detector; these spectra were collected in extended scan mode with a range of 1500 - 400 cm^{-1} and 3600 - 400 cm^{-1}. 2) a 532 nm laser, 1800 lines/mm gratings, 50 µm slit size, and a RenCam CCD detector; these spectra were collected in static scan mode for the region centered on 3250 cm^{-1} and the region spanning 1700 - 1400 cm^{-1}. Calibration was performed using silicon standards. All spectra were analyzed using the WiRE 3.4 software package (Renishaw) and plotted using Origin Pro 8.6.

Infrared Spectroscopy

Infrared spectra were obtained using a Thermo Scientific Nicolet iS50 FT-IR with diamond ATR. An ATR correction was applied using the algorithm within the OMINC software.

Dynamic Vapor Sorption (DVS)

DVS experiments were performed using a Q5000 SA Dynamic Vapor Sorption Analyzer. Sample mass was monitored from 10-90% RH at ramp rate of 0.2%/min in salt deliquescence mode starting from initial masses of 8-15 mg.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) thermograms were recorded on TA Instruments Q10 and Q20 DSC instruments. Q10 DSC experiments were carried out at a heating rate of 5 °C/min, covering a temperature range of 25 °C to 300 °C. Samples of ADN were analyzed using a Tzero™ DSC High Pressure Capsule Kit, all other samples were analyzed in Tzero™ hermetic aluminum DSC pans. The instruments were calibrated using an indium standard, all DSC thermograms were analyzed using TA Universal Analysis 2000, V4.5A, build 4.5.0.5 and plotted using Origin Pro 8.6.

Cyclic DSC experiments were carried out on the TA Instruments Q20 as follows:

X = 70 °C in the case of **ADN-urea**, X = 85 °C in the case of **ADN-2Im**

1. 40 °C → X @ 5 °C/min
2. 2 min isothermal hold
3. X → -40 °C @ 1 °C/min
4. -40 °C → X @ 5 °C/min
5. 2 min isothermal hold
6. Steps 3-5 were repeated 6 times

Thermogravimetric Analysis (TGA)
TGA thermograms for each sample were recorded on a TA Instruments Q50 TGA. All experiments were conducted in platinum TGA sample pans under a nitrogen purge of 50 mL/min with a heating rate of 10 °C/min, covering a temperature range of RT to 400 °C. The instrument was calibrated using the Curie points of alumel and nickel standards and all TGA thermograms were analyzed using TA Universal Analysis 2000, V4.5A, build 4.5.0.5 and plotted using Origin Pro 8.6.

Melt Temperature Determination
Melting temperature determination was carried out using an Optimelt Automated Melting Point System from Stanford Research Systems at a ramp rate of 1 °C/min.

SI 2. Crystallographic Data

Table S1. Unit cell constants and other crystallographic data concerning the salt cocrystals and anhydrous 2Im, the anhydrous structure for 2Im was collected for this work as it was absent from the Cambridge Structural Database.

	AH-PDO	2Im	**AH-2Im**	**ADN-2Im**	**AH-urea**	**ADN-urea**	**ADN-urea**
stoichiometry	2:1	N/A	1:1	1:1	1:1	1:2	1:2
space Group	*P2₁/c*	*Fddd*	*P*$\bar{1}$	*C2/c*	*Pbca*	*P2₁/n*	*P2₁/n*
Temp. (K)	100(2)	293(2)	293(2)	273(2)	100.00(10)	293(2)	100(2)
a (Å)	11.4292(5)	9.9700(4)	5.25069(16)	24.7560(5)	7.67243(12)	14.6572(4)	14.7309(5)
b (Å)	5.5925(2)	11.8236(5)	7.8976(3)	4.29000(10)	8.07957(12)	3.71857(12)	3.59237(11)
c (Å)	11.1451(4)	13.3559(5)	11.4023(4)	17.8827(3)	24.2351(4)	20.3958(7)	20.2453(7)
α (°)	90	90	82.781(3)	90	90	90	90
β (°)	92.547(4)	90	79.266(3)	107.988(2)	90	108.778(3)	108.791(4)
γ (°)	90	90	84.108(3)	90	90	90	90
Volume (Å^3)	711.67(5)	1574.40(11)	459.35(3)	1806.37(7)	1502.33(4)	1052.48	1014.25
ρ_{calc} (g cm^{-3})	2.045	1.453	1.801	1.546	1.973	1.541	1.599
formula	$C_2H_6F_6N_2OP$	$C_3H_6N_2O$	$C_3H_{10}F_6N_3OP$	$C_3H_{10}N_6O_5$	$CH_8F_6N_3OP$	$C_2H_{12}N_8O$	$C_2H_{12}N_8O$
fW (g/mol)	219.06	86.10	249.11	210.17	223.07	244.20	244.20
crystal system	monoclinic	orthorhombic	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic
Z	4	16	2	8	8	4	4
$R_{int.}$ (%)	4.03	1.71	4.87	1.68	5.49	3.35	4.18
R_1/R_{w2} (%)	7.32/22.54	5.24/12.85	6.61/20.19	5.87/19.27	3.39/9.64	4.15/12.22	3.96/11.31
deposit #	2175809	2175805	2175806	2175807	2175808	2175810	2175811

SI 3. Thermal Ellipsoid plots

AH-PDO

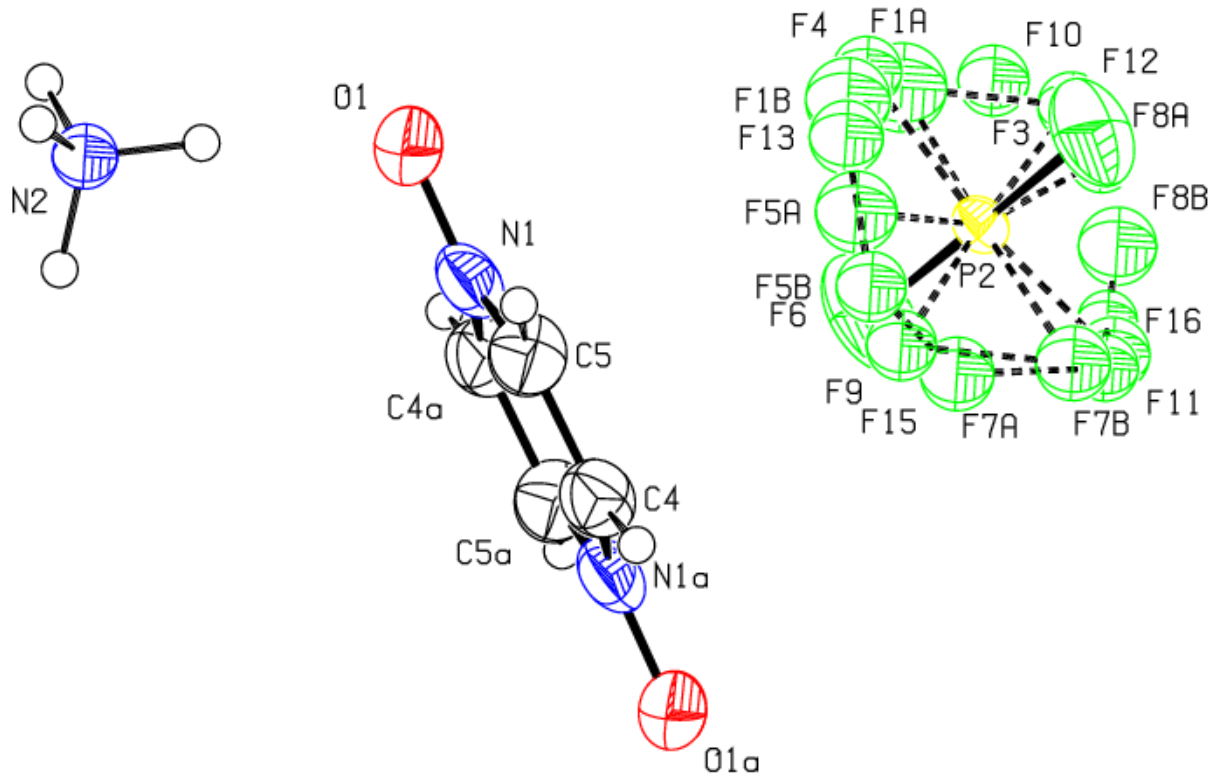


Figure S1. Thermal ellipsoid plot for **AH-PDO** at 100(2) K

2Im

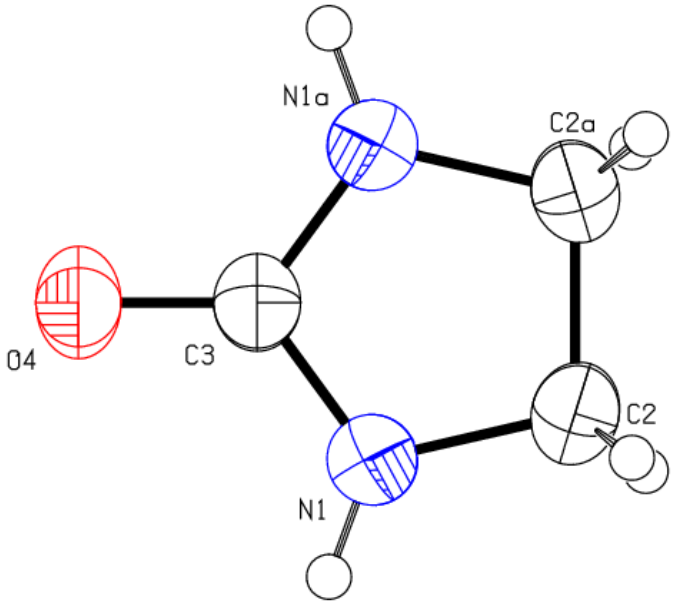


Figure S2. Thermal ellipsoid plot for 2Im at 293(2) K

AH-2Im

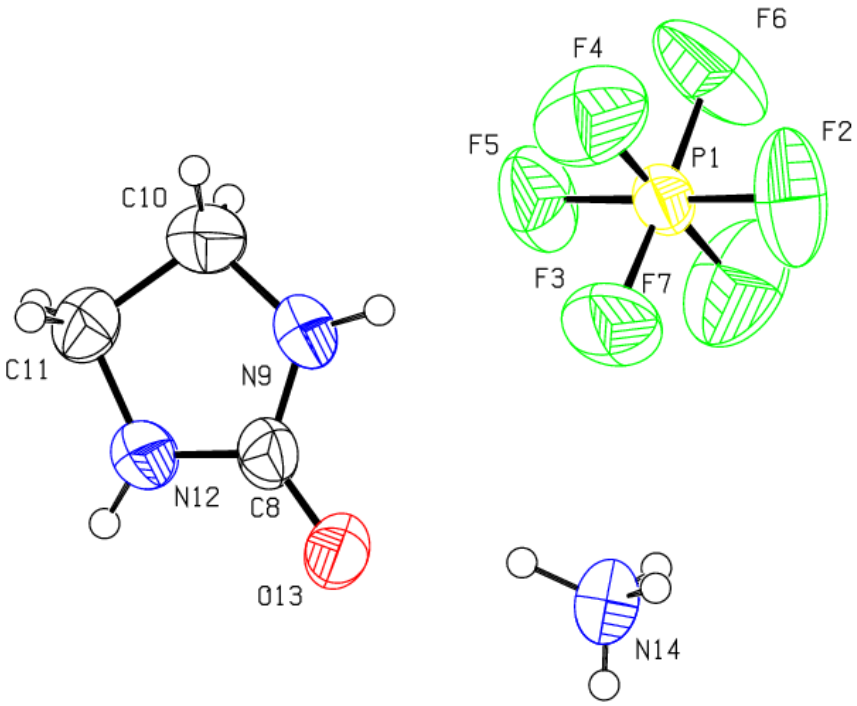


Figure S3. Thermal ellipsoid plot for **AH-2Im** at 293(2) K

ADN-2Im

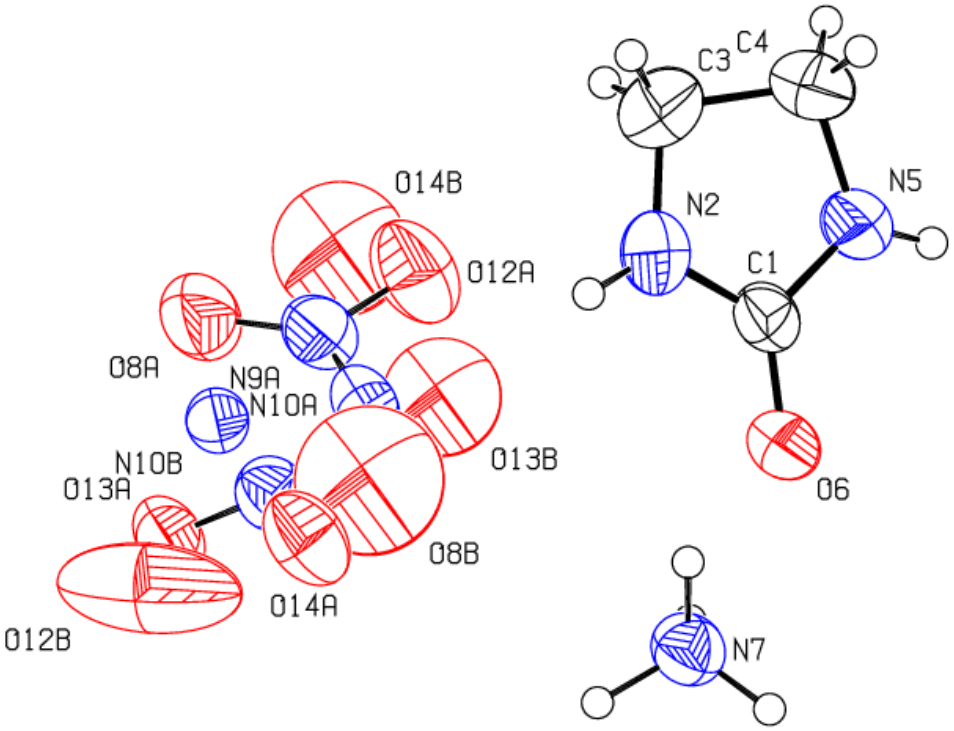


Figure S4. Thermal ellipsoid plot for **ADN-2Im** at 293(2) K

AH-urea

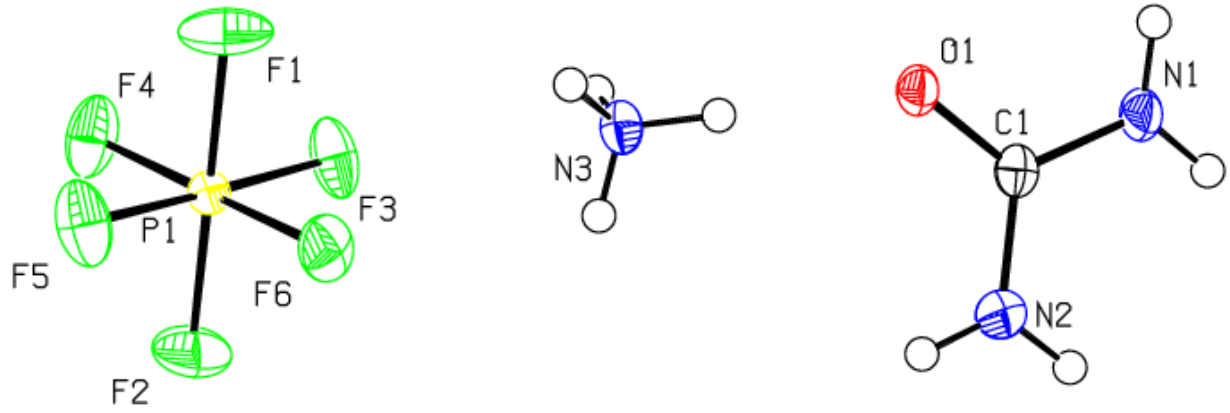


Figure S5. Thermal ellipsoid plot for **AH-urea** at 100(2) K

ADN-urea

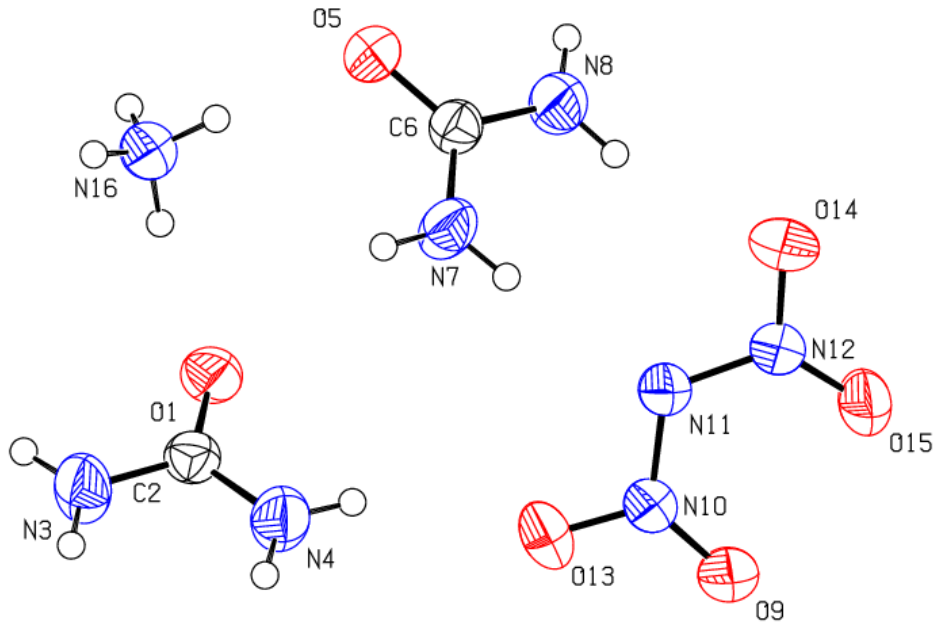


Figure S6. Thermal ellipsoid plot for **ADN-urea** at 293(2) K

ADN-urea

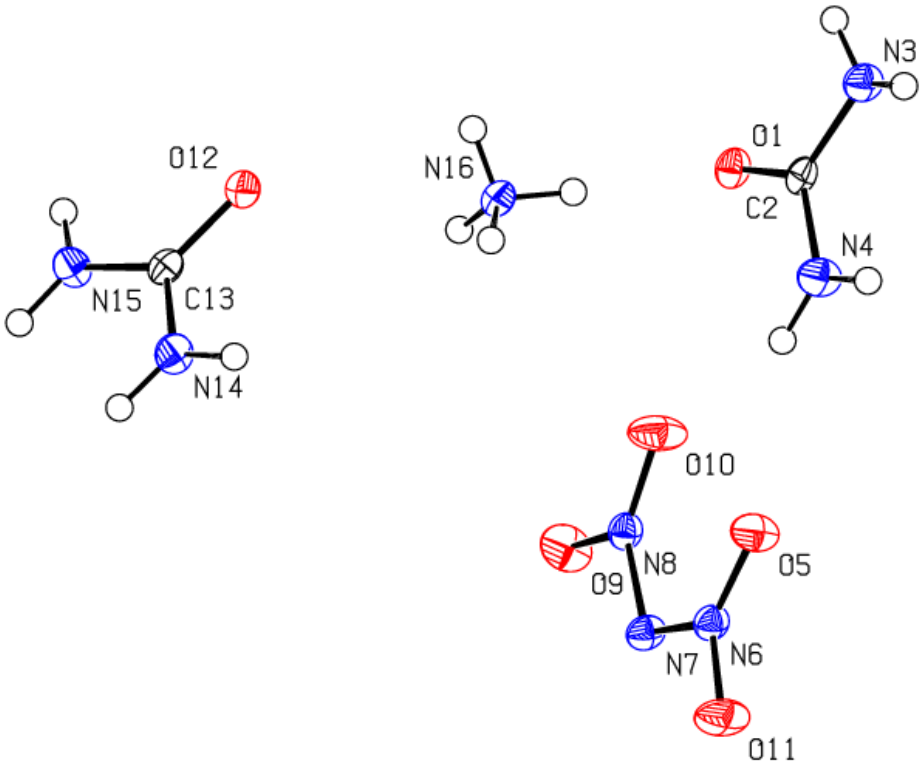


Figure S7. Thermal ellipsoid plot for **ADN-urea** at 100.00(10) K

SI 4. Raman Spectra

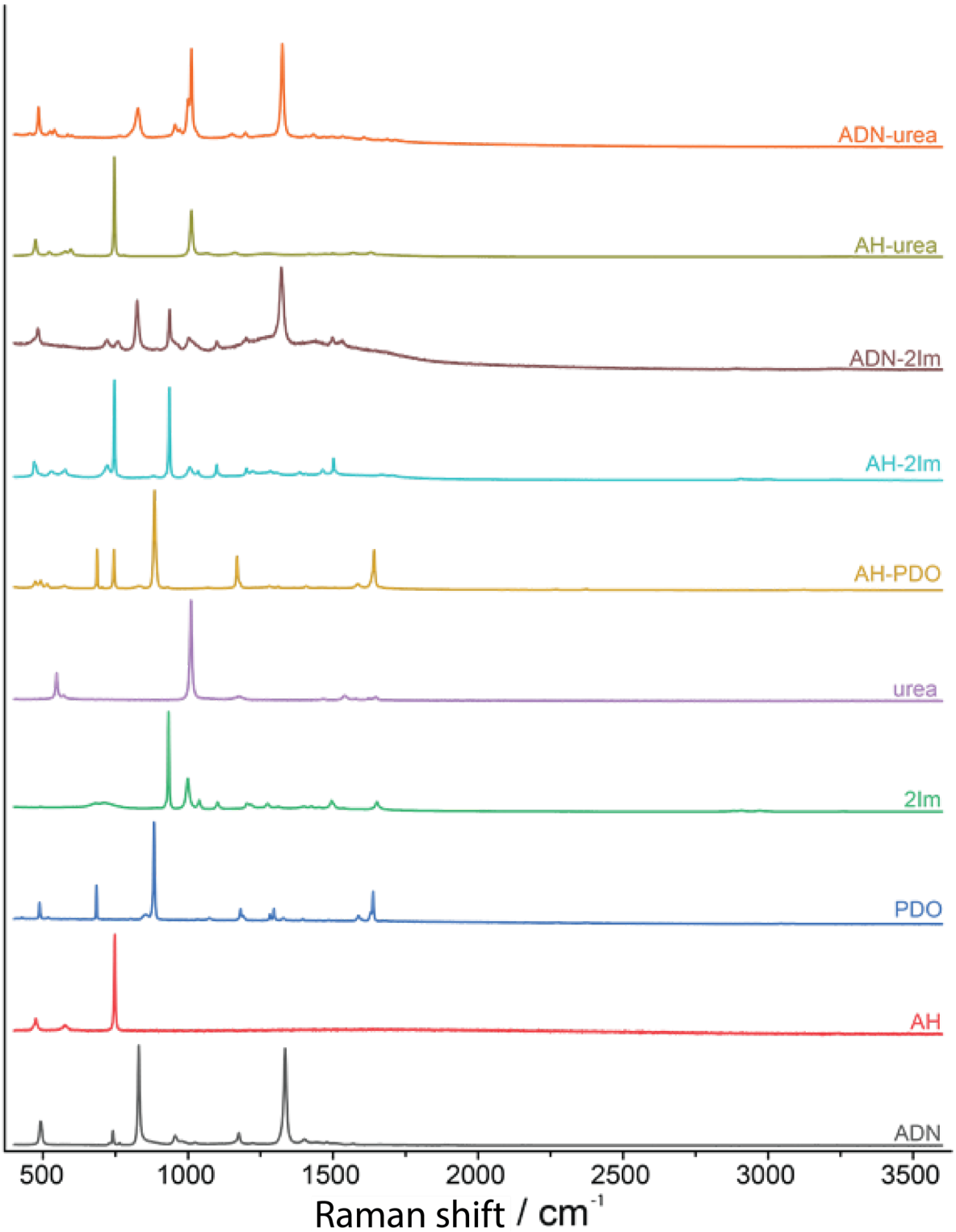


Figure S8. Raman spectra of ADN, AH, PDO, 2Im, urea (tetragonal), **AH-PDO**, **AH-2Im**, **ADN-2Im**, **AH-urea**, and **ADN-urea**. Collected using an excitation wavelength of 785 nm.

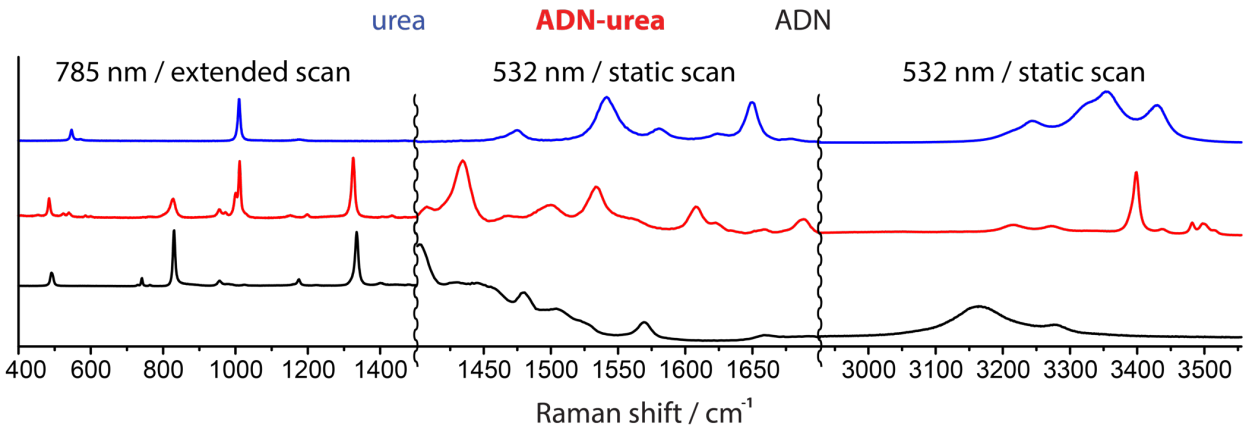


Figure S9. Raman spectra of ADN, urea, and **ADN-urea**. Left) Collected using an excitation wavelength of 785 nm. Middle and right) collected using an excitation wavelength of 532 nm.

SI 5. Infrared Spectra for ADN, urea, and ADN-urea

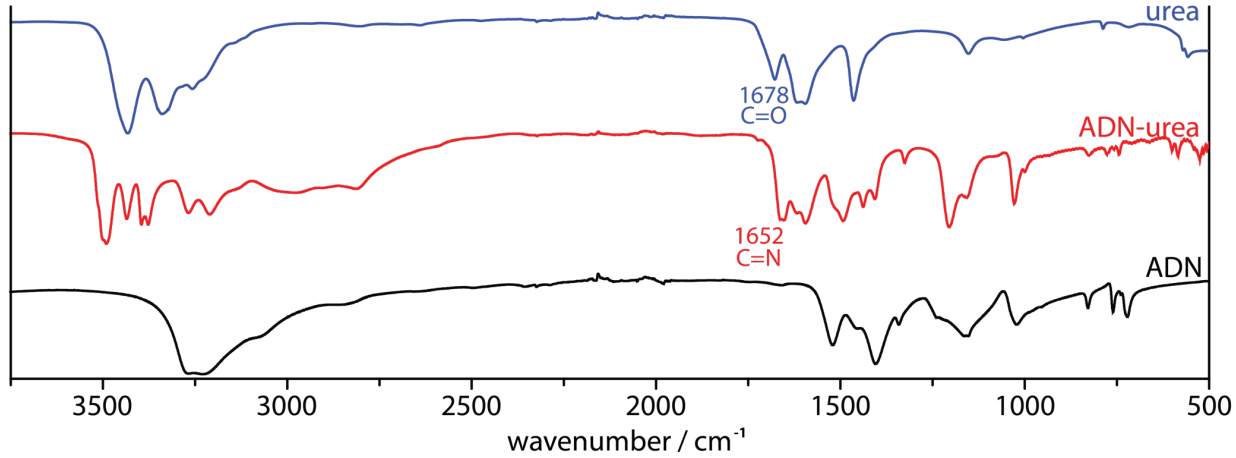


Figure S10. ATF-FTIR spectra of ADN, urea, and **ADN-urea**.

SI 6. PXRD data

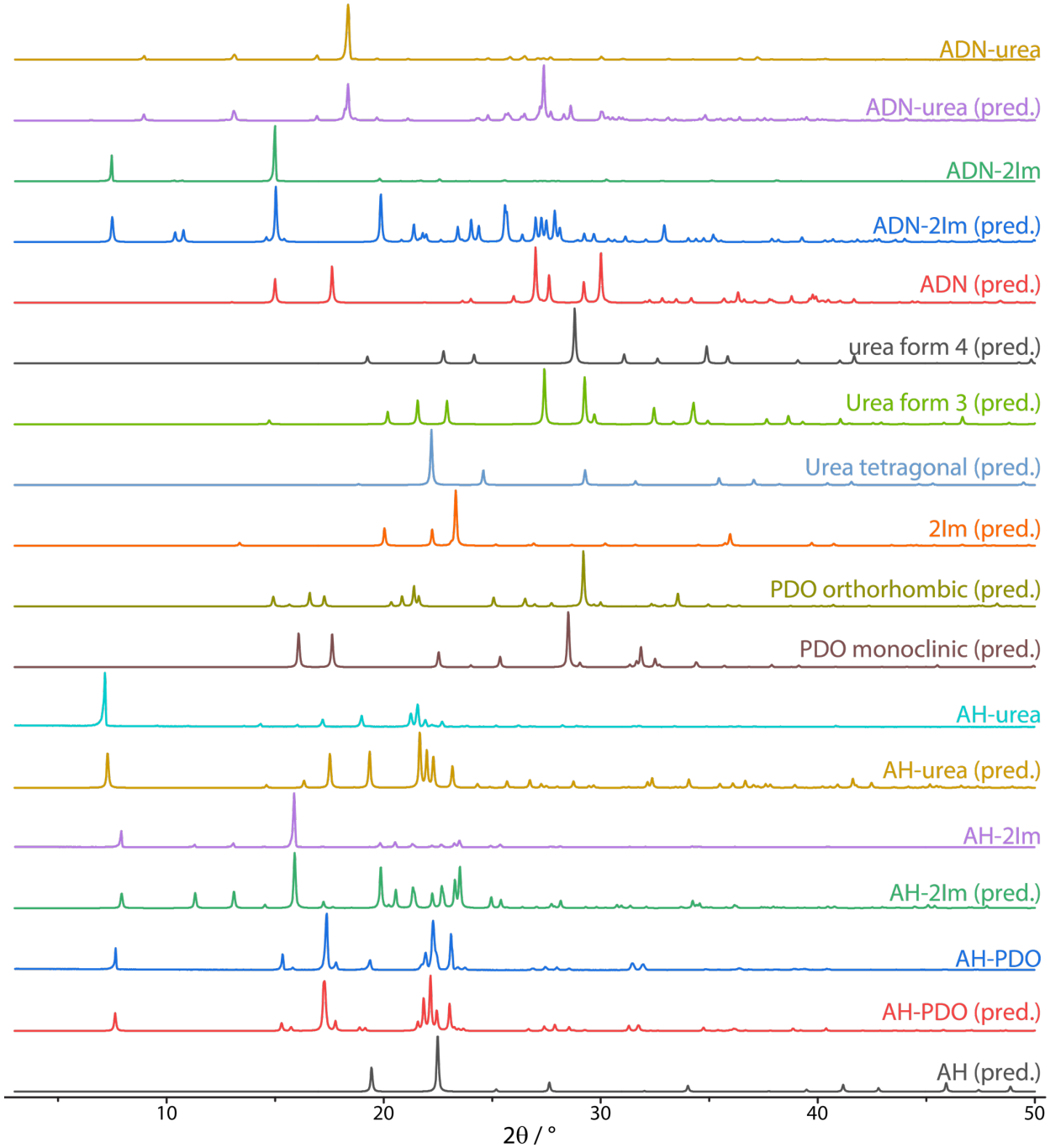


Figure S11. Predicted (pred.) and experimental PXRD data for the AH and ADN salt cocrystals and coformers. Note that the structures for **AH-PDO** and **AH-urea** were obtained at 100 K while the structure for **ADN-2Im** was obtained at 273K, thus the simulated PXRD patterns exhibit a uniform, and minor, 2θ shift relative to the experimental diffractogram collected at RT. In the **AH-urea** PXRD pattern there is a peak at around 21° 2θ which appears absent in the predicted PXRD pattern; the prediction does in fact calculate a peak at that 2θ value (h,k,l = 0,1,5) but having an approximately 0 intensity.

SI 7. Thermal analysis and post-cyclic DSC characterization of the ADN salt cocrystals

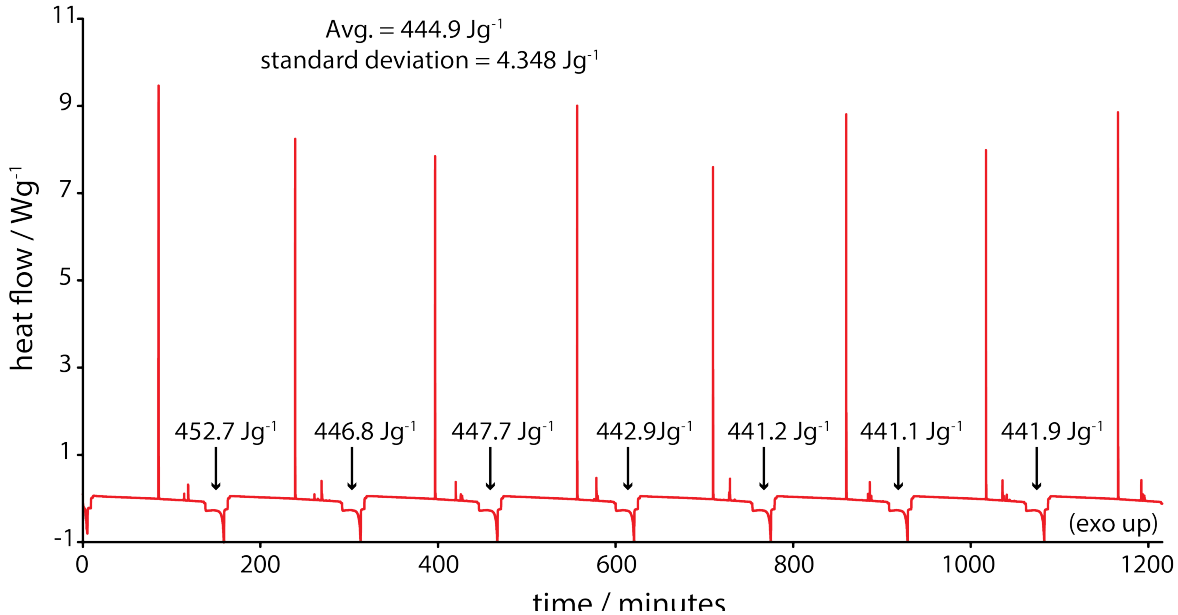


Figure S12 Cyclic DSC thermogram for **ADN-2Im** with heat of fusion values.

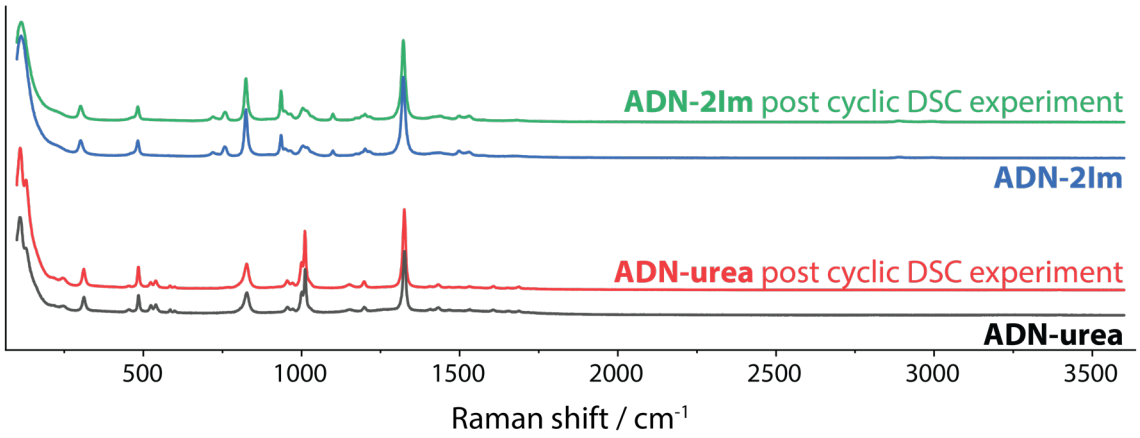


Figure S13 Raman spectra for the ADN salt cocrystals before and after cyclic DSC experiments.

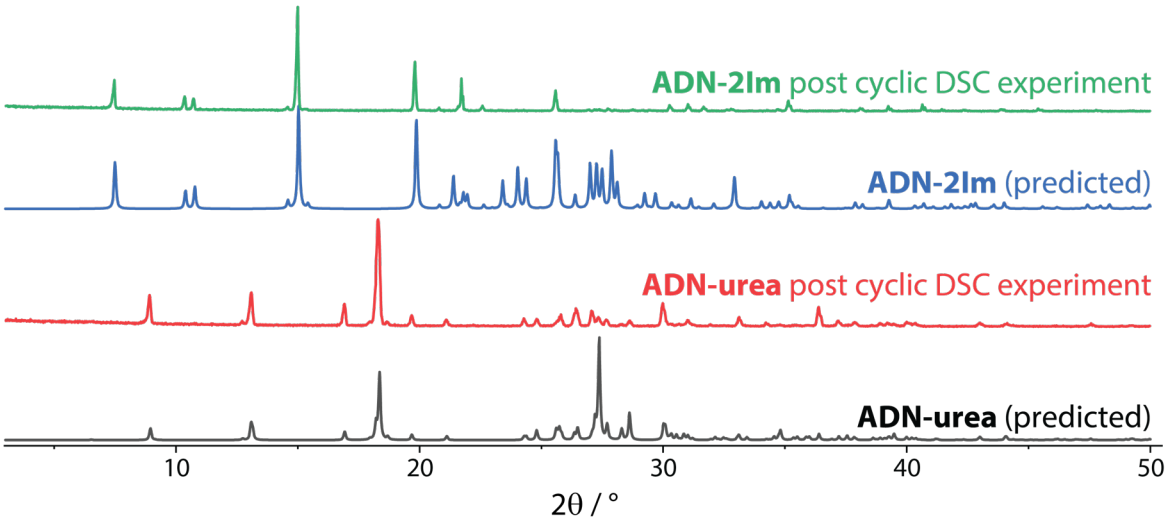


Figure S14 PXRD data for the ADN salt cocrystals before and after cyclic DSC experiments with predicted diffractograms for ADN-urea and ADN-2Im; note that the structure for **ADN-2Im** was obtained at 273K, thus the simulated PXRD patterns exhibit a uniform, and minor, 2θ shift relative to the experimental diffractogram collected at RT.

SI 8. Dynamic Vapor Sorption

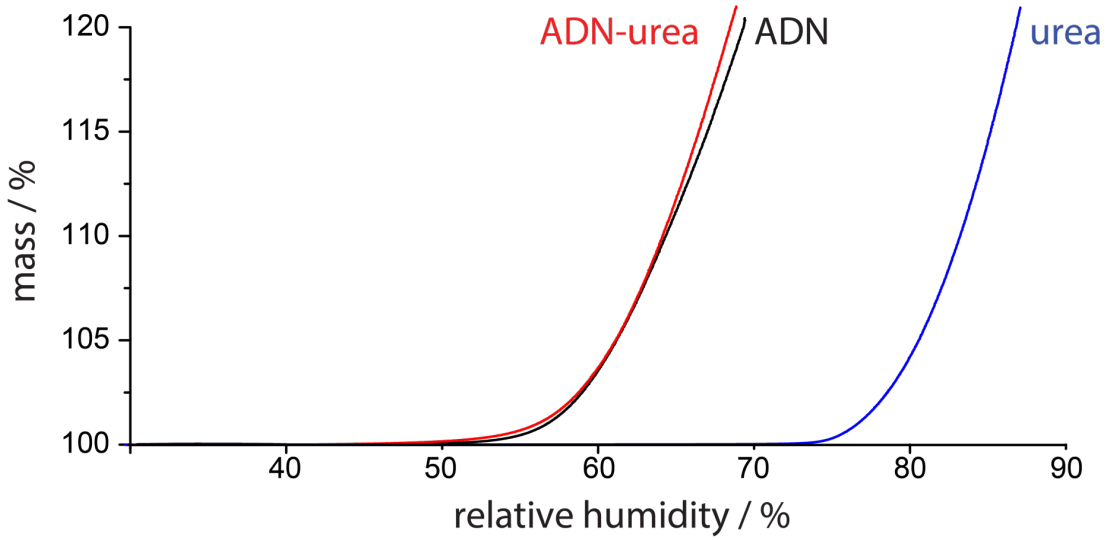


Figure S15. Dynamic vapor sorption traces for ADN, **ADN-urea**, and urea.

SI 9. Energetic Performance

Table S2. Melt Castable Formulations and Their Compositions as used for CHEETAH calculations; CHEETAH is a thermodynamic code published by Lawrence Livermore National Laboratory for the purpose of calculating relevant performance criteria for energetic materials and their formulations.[6]

Formulation	Composition in weight percent
Comp. B	40% TNT or **ADN-urea**, 60% RDX
Amatol	50% DNAN or **ADN-urea**, 35% Ammonium Nitrate, 15% RDX
ARX-4027	40% DNAN or **ADN-urea**, 60% RDX

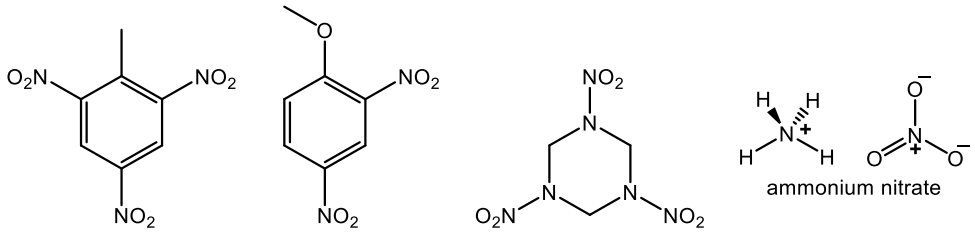


Figure S14. Structures of energetic materials used in melt castable formulations listed in table S2.

SI 10. Sensitivity

Sensitivity to mechanical stimuli

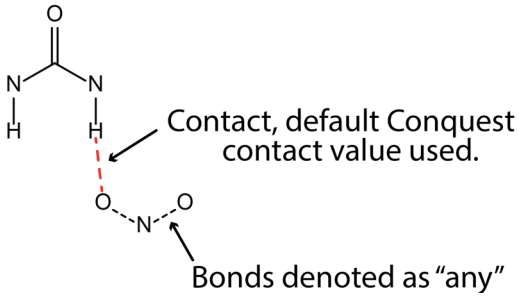
The impact sensitivity of both ADN and **ADN-urea** were investigated using an in-house apparatus [5] whereby a 2.380 kg stainless-steel impactor impinges samples of 2 mg ± 10% inside aluminum DSC pans resting on an anvil from varying heights. Twenty samples of each material were tested with D_{h50} measured as the dropping height at which there was a 50% probability of detonation. The D_{h50} value was found to be 35 cm for ADN whereas **ADN-urea** did not detonate at the limiting height of our apparatus (145 cm).

SI 11. CSD search

Urea-nitro synthon

Search conducted using ConQuest.2020.1[5.41] on Oct. 12, 2021. The search was conducted with the following requirements:

1)



2) 3D coordinates determined

3) Only single crystal structures

4) only organics

Functional group interactions with ammonium ions in salt cocrystals deposited with the CSD
The initial search was not conducted as part of this report; details concerning the search parameters can be found within the ESI corresponding to that publication.[7] The CSD ref codes corresponding to that search are provided below (table S3) for convenience.

Table S3. CSD ref codes corresponding to ammonium salt cocrystals compiled in reference 6

AMPCPL	DAJZOD	FOHFOY	KECDAY	OYAGUS02	QOBJAS	SEDDUD	URAMCL01	XIGNIL
BEGVUF	DUTWOF	HMTAAB	MINRUY	OYAHAZ02	QUSBUD	TEBCEI	VIQVOJ	YABJES
BOVPOR	FADCAP	HORWET	NIDDIN	OYAVER02	QUSDEP	TPHCUR	VIQVUP	ZUCQUM01
CACGOE	FENZUT	JEBLOS	NOCYOV	POPATC10	RADGOU	UDOXUH	VUBCEA01	
CUKTUX	FEYTIO	JULHUT	NOGNAZ	QIDTOP	RAXJAB	UFOHOM	XIGNEH	

SI 12. References

[1] McKay, S. E.; Sooter, J. A.; Bodige, S. G.; S.C. Blackstock, S. C., "Oxidation Methods for Aromatic Diazines: Substituted Pyrazine-*N*-Oxides, Pyrazine-*N*,*N*'-Dioxides, and 2,2':6,2''-Terpyridine-1,1'-Dioxide." *Heterocycl. Commun.*, **2001**, 7, 307.

[2] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., "A Complete Structure Solution, Refinement and Analysis Program." *Appl. Cryst*., **2015**, *42*, 339.

[3] Sheldrick, G. M., "SHELXT - Integrated Space-Group and Crystal-Structure Determination." *Acta Cryst.* **2015**, *A71*, 3.

[4] Sheldrick, G. M., "Crystal structure refinement with SHELXL." *Acta Cryst*. **2015**, *C71*, 3.

[5] Bennion, J. C.; Chowdhury, N.; Kampf, J. W.; Matzger, A. J., "Hydrogen Peroxide Solvates of 2, 4, 6, 8, 10, 12 Hexanitro-2, 4, 6, 8, 10, 12-hexaazaisowurtzitane." *Angew. Chemie Int. Ed.*, **2016**, 13312.

[6] Bastea, S.; Fried, L.E.; Glaesman, K. R.; Howard, W. M.; Kuo, I. F. W.; Souers, P. C.; Vitello, P.A., *Cheetah 7.0 Thermochemical Code*; Energetic Materials Center, Lawrence Livermore National Laboratory: Livermore, CA, **2012**.

[7] Bellas, M. K.; MacKenzie, L. V.; Matzger, A. J., "Lamellar Architecture Affords Salt Cocrystals with Tunable Stoichiometry." *Cryst. Growth Des.* **2021**, 21, 3540.