Electronic Supplementary Information

Improving stability of the hydrazinium pentazolate through cocrystallization

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1. Experimental

Caution: Although no detonations were encountered during the preparation and purification of the *cyclo*-N_5^--containing energetic compounds, all these compounds we prepared are potentially energetic materials. Proper safety practices and equipment were used to prevent an explosion due to friction, heat, static shock, or impact. Caution should be exercised at all times when handling of any of materials.

General methods

Single-crystal X-ray diffraction measurements were conducted on a Bruker D8 QUEST PHOTON 100 diffractometer using Mo-Kα radiation (λ = 0.71073 Å) at 296 K. ^{1}H and ^{13}C spectra were recorded using a 500 MHz (Bruker AVANCE III 500) nuclear magnetic resonance spectrometer operating at 500 and 125.72 MHz, respectively. Chemical shifts in the ^{1}H and ^{13}C spectra are reported relative to Me_4Si as an external standard. IR spectra were recorded on a Thermo Nicolet iS10 spectrometer equipped with a Thermo Scientific Smart iTR diamond ATR accessory. 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 4000-100 cm^{-1}. Powder X-ray diffraction patterns were performed on a Bruker D8 Advance X-ray diffractometer using Cu Kα (λ = 1.5406 Å) radiation. Samples were gently grind with a mortar. The powder patterns were collected by scanning 2θ from 5° to 80° with a step size of 0.02° and a step speed of 0.1 second. DSC plots were acquired on a differential scanning calorimeter (NETZSCH DSC 204 F1 Phoenix) at a scan rate of 5 °C min^{-1} in perforated Al containers under a nitrogen flow of 60 mL min^{-1}. TGA were also performed at a heating rate of 5 °C min^{-1} in flowing high-purity nitrogen on a Mettler Toledo TGA/SDTA851^e instrument. Elemental analyses were carried out on a vario EL III CHNOS elemental analyzer. Impact and friction sensitivity measurements were performed using a standard BAM Fall hammer and BAM friction tester.

Synthesis

$N_2H_5N_5$ and PDO were prepared based on the literature methods.[1,2]

$N_2H_5N_5$/PDO: 0.5 mmol $N_2H_5N_5$ and 0.25 mmol PDO are dissolving in methanol aqueous solution in a 4 mL glass vial. The cocrystal $N_2H_5N_5$/PDO was initially obtained

from methanol/H_2O (1:1 volume ratio) solutions. The solution was allowed to evaporate slowly at 2-8 °C over several days. Alternative solvents reliably producing $N_2H_5N_5$/PDO form include ethanol / H_2O (1:1 volume ratio) and acetonitrile / H_2O (1:1 volume ratio). Yield (86 %). T_d: 101 °C. ^{1}H NMR: δ 8.26 (s, 4H, =CH-CH=), 7.03 (s, 10H, N_2H_5) ppm. ^{13}C NMR: δ 136.59 ppm. IR (ATR): $\tilde{\nu}$ 3311, 2842, 2708, 1588, 1506, 1485, 1448, 1412, 1251, 1218, 1182, 1087, 1052, 1001, 967, 860, 802, 707, 540 cm^{-1}. Elemental analysis for $C_4H_{14}N_{16}O_2$ (318.266): calcd C 15.10, H 4.43, N 70.42 %. Found: C 15.12, H 4.35, N 70.50 %. IS: 35 J. FS: 300 N.

Measurement of hygroscopicity

1. Before the test, the sample shall be dried in a vacuum oven at 50 °C for 2 h.
2. Dryer A is filled with saturated NaCl solution, and dryer B is filled with indicator desiccant. Dryers A and B are placed in a thermostat at 25 °C.
3. Place the weighing bottle in dryer A, cover lid after the mass remains unchanged, and then place it in dryer B for 30 min, and then weigh it for standby.
4. Accurately weigh the sample (about 5 g) and place it in a weighing bottle with known mass.
5. Place the weighing bottle containing the sample in dryer A, remove the weighing bottle lid, and put the lid in dryer A, cover the cap of dryer A, and keep it at constant temperature for 3 h.
6. Close the lid of the weighing bottle, move the weighing bottle into dryer B, and place it for 30 min before weighing.
7. Then put the weighing bottle into dryer A, keep it constant for 3 h, and so on, until the difference between two consecutive weighing is not more than 0.0003 g.
8. The hygroscopicity value is the percentage of water absorbed by the sample in the sample mass.

2. Single-crystal X-ray diffraction analysis of $N_2H_5N_5$/PDO

Table S1. Crystal data, data collection, and refinement for $N_2H_5N_5$/PDO

$C_4H_4N_2O_2 \cdot 2(N_5) \cdot 2(H_5N_2)$	$Z = 1$
$M_r = 318.31$	$F(000) = 166$
Triclinic, $P\bar{1}$	$D_x = 1.608$ Mg m^{-3}
$a = 6.6303$ (4) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.8338$ (5) Å	Cell parameters from 3091 reflections
$c = 7.9449$ (5) Å	$\theta = 3.0$–$27.5°$
$\alpha = 117.137$ (2)°	$\mu = 0.13$ mm^{-1}
$\beta = 93.126$ (2)°	$T = 296$ K
$\gamma = 111.674$ (2)°	Block, colourless
$V = 328.63$ (4) Å^3	0.21 × 0.15 × 0.12 mm
Bruker D8 QUEST PHOTON 100 diffractometer	1265 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	$R_{int} = 0.023$
ϕ and ω scans	$\theta_{max} = 27.6°$, $\theta_{min} = 3.0°$
Absorption correction: multi-scan *SADABS*	$h = -8 \rightarrow 8$
$T_{min} = 0.685$, $T_{max} = 0.746$	$k = -10 \rightarrow 10$
5080 measured reflections	$l = -10 \rightarrow 10$
1519 independent reflections	
Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.050$	H-atom parameters constrained
$wR(F^2) = 0.142$	$w = 1/[\sigma^2(F_o^2) + (0.0755P)^2 + 0.1294P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
1519 reflections	$\Delta\rangle_{max} = 0.46$ e Å^{-3}
100 parameters	$\Delta\rangle_{min} = -0.35$ e Å^{-3}

Data collection: Bruker *APEX3*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: SHELXT 2014/5 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2018*/3 (Sheldrick, 2018); molecular graphics: Bruker *SHELXTL*; software used to prepare material for publication: Bruker *SHELXTL*.

Table S2. Hydrogen bonds (Å, º) for $N_2H_5N_5$/PDO

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

C1—H1···N8^{ii}	0.93	2.67	3.385 (2)	134
C1—H1···N8^{iii}	0.93	2.61	3.138 (2)	117
C2—H2···N4^{ii}	0.93	2.53	3.434 (2)	163
N7—H7*A*···N1^{iii}	0.89	2.16	2.971 (2)	151
N7—H7*A*···N2^{iv}	0.89	2.58	3.056 (2)	114
N7—H7*B*···O1	0.89	1.87	2.7398 (19)	167
N7—H7*C*···N3^{v}	0.89	2.22	3.005 (2)	147
N7—H7*C*···N4^{v}	0.89	2.59	3.111 (2)	118
N8—H8*B*···N4	0.82	2.66	3.446 (2)	161
N8—H8*B*···N5	0.82	1.91	2.722 (2)	170

Symmetry codes: (ii) *x*, *y*, *z*-1; (iii) -*x*+1, -*y*+2, -*z*+1; (iv) *x*+1, *y*+1, *z*+1; (v) -*x*+1, -*y*+1, -*z*+1.

3. Single-crystal X-ray diffraction analysis of PDO

Table S3. Crystal data, data collection, and refinement for PDO

$C_4H_4N_2O_2$	$F(000) = 116$
$M_r = 112.09$	$D_x = 1.597$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 3.7348$ (10) Å	Cell parameters from 710 reflections
$b = 11.013$ (3) Å	$\theta = 5.5$–$27.6°$
$c = 5.7044$ (14) Å	$\mu = 0.13$ mm^{-1}
$\beta = 96.47$ (1)°	$T = 296$ K
$V = 233.13$ (10) Å^3	Plate, yellow
$Z = 2$	0.20 × 0.18 × 0.05 mm
Bruker D8 QUEST PHOTON 100 diffractometer	424 reflections with $I > 2\sigma(I)$
Detector resolution: 10.42 pixels mm^{-1}	$R_{int} = 0.022$
ϕ and ω scans	$\theta_{max} = 27.7°$, $\theta_{min} = 5.5°$
Absorption correction: multi-scan *SADABS*	$h = -3 \rightarrow 4$
$T_{min} = 0.615$, $T_{max} = 0.746$	$k = -14 \rightarrow 14$
1148 measured reflections	$l = -7 \rightarrow 5$
529 independent reflections	
Refinement on F^2	0 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.039$	H-atom parameters constrained
$wR(F^2) = 0.101$	$w = 1/[\sigma^2(F_o^2) + (0.039P)^2 + 0.0785P]$

	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.04	$(\Delta/\sigma)_{max} < 0.001$
529 reflections	$\Delta\rangle_{max}$ = 0.15 e Å^{-3}
37 parameters	$\Delta\rangle_{min}$ = -0.17 e Å^{-3}

Data collection: Bruker *APEX3*; cell refinement: Bruker *SAINT*; data reduction: Bruker *SAINT*; program(s) used to solve structure: SHELXT 2014/5 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2018*/3 (Sheldrick, 2018); molecular graphics: Bruker *SHELXTL*; software used to prepare material for publication: Bruker *SHELXTL*. Similar to $N_2H_5N_5$/PDO, the PDO molecule in $P2_1/c$ again lies about an inversion centre.

Table S4. Hydrogen bonds (Å, º) for PDO

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1^{ii}	0.93	2.27	3.169 (2)	162
C1—H1···O1^{iii}	0.93	2.30	3.2081 (19)	167

Symmetry codes: (ii) *x*, -*y*+3/2, *z*-1/2; (iii) -*x*+2, -*y*+1, -*z*+2.

4. The noncovalent interactions study

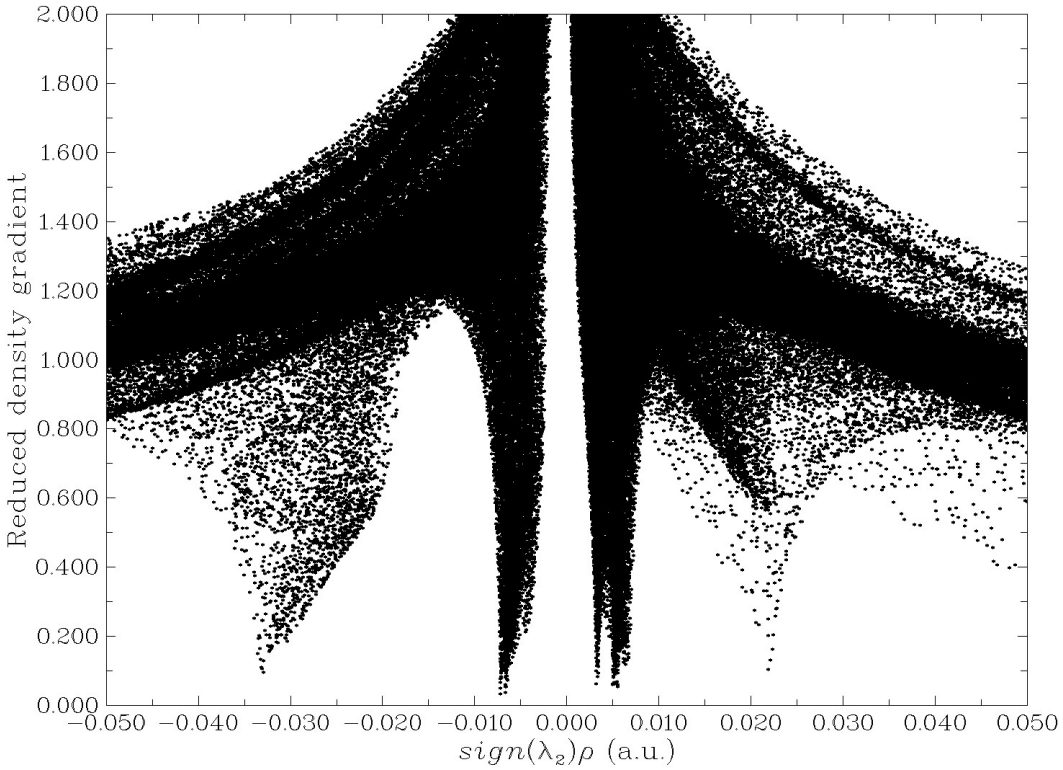


Fig. S1 Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue for $N_2H_5N_5$/PDO.

5. IR spectrum

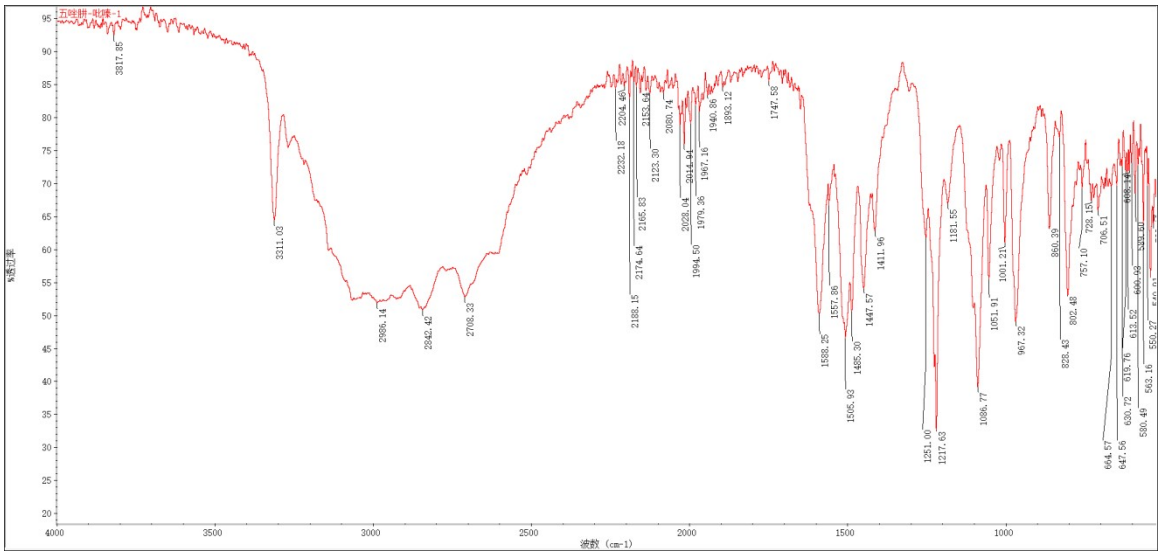


Fig. S2 The IR spectrum of $N_2H_5N_5$/PDO.

6. NMR spectra

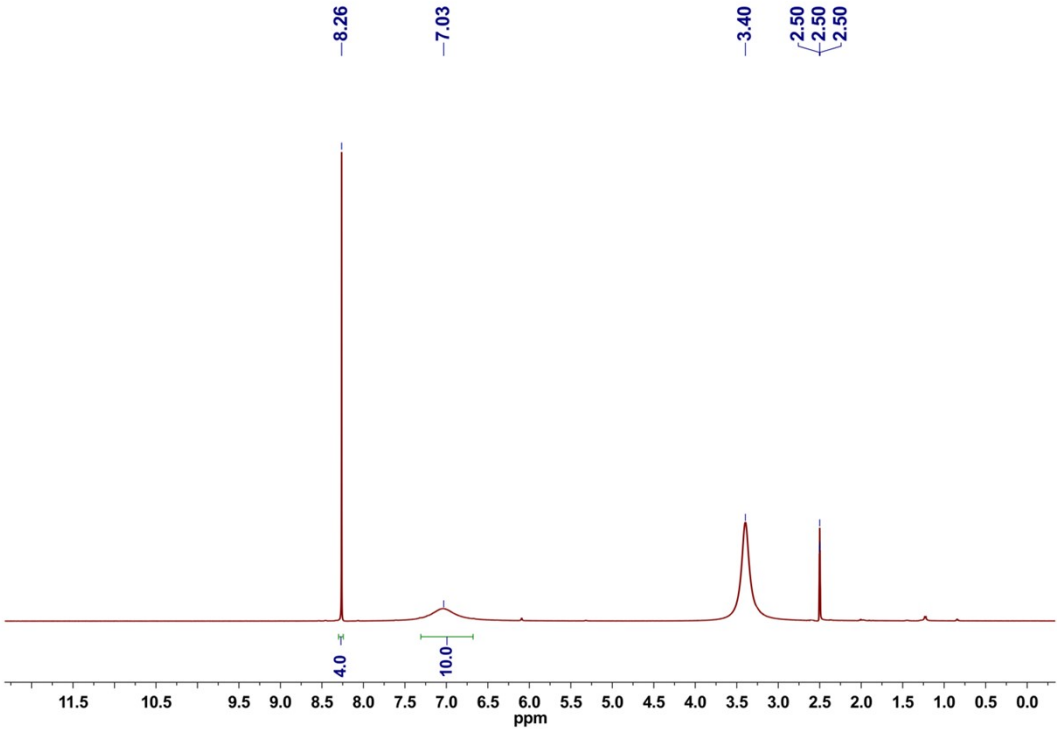


Fig. S3 ^{1}H NMR spectrum of $N_2H_5N_5$/PDO in d_6-DMSO.

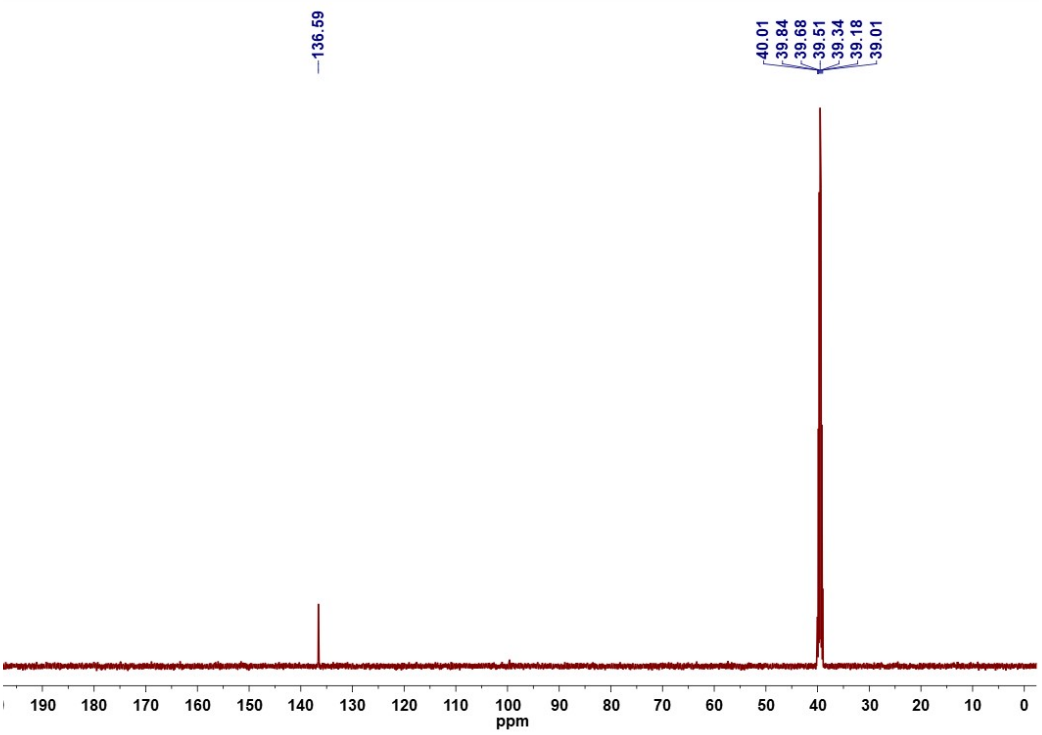


Fig. S4 ^{13}C NMR spectrum of $N_2H_5N_5$/PDO in d_6-DMSO.

7. PXRD patterns

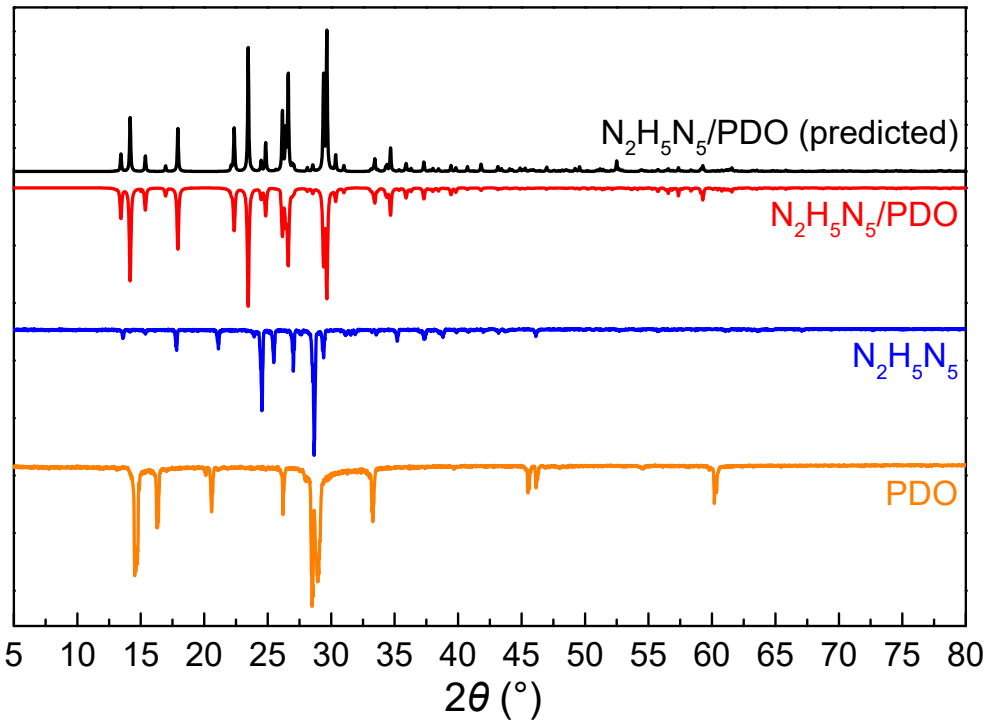


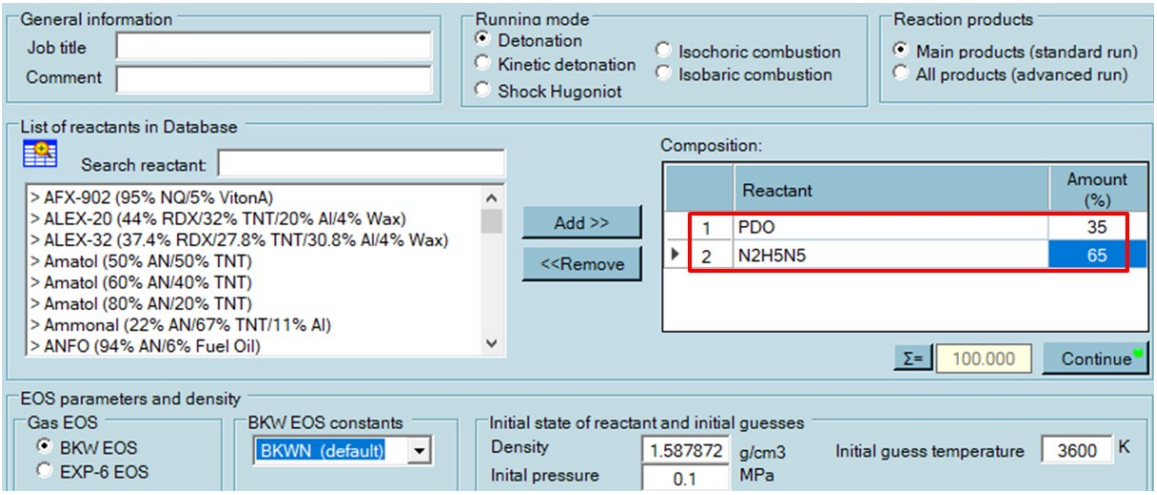
Fig. S5 The PXRD pattern of $N_2H_5N_5$/PDO, $N_2H_5N_5$, and PDO and the predicted $N_2H_5N_5$/PDO pattern from single-crystal structure.

8. Computational details

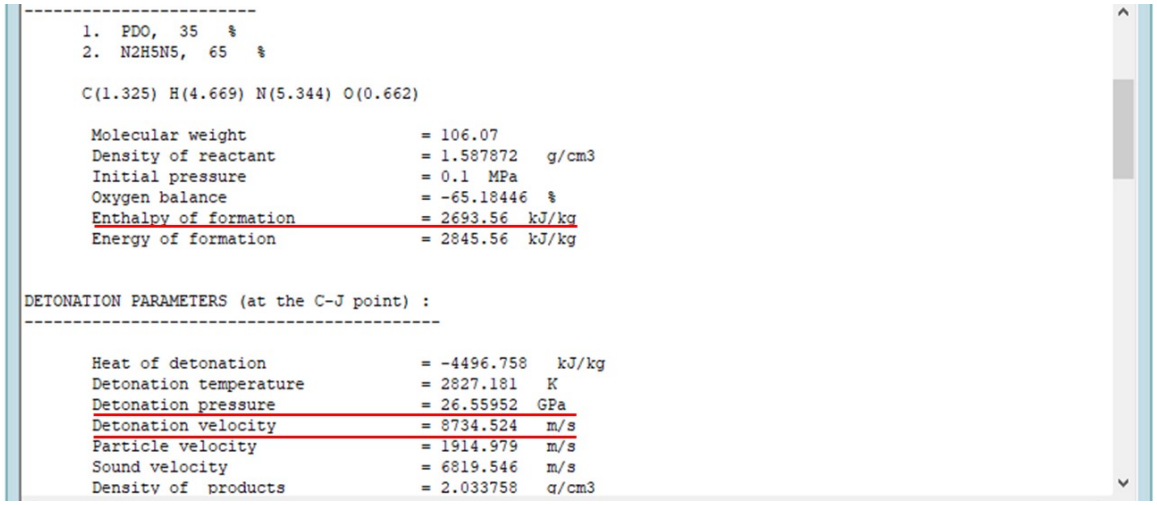
1. Input the densities, heats of formation and molecular formulas of $N_2H_5N_5$ and PDO into EXPLO5 software. The relevant data of $N_2H_5N_5$ is from Ref. 1. The density of PDO is from its crystal density, and its heat of formation is from Ref. 3.

Compound	Formula	TMD, g/	Hf, kJ/mol	C	H	N	O
N2H5N5	H5N7	1.583	429.6	0	5	7	0
PDO	C4H4N2O2	1.597	-4.8	4	4	2	2

2. According to the molar ratio (2:1) of $N_2H_5N_5$ and PDO in cocrystal, its mass ratio is 64.78% : 35.22%. Because only integers can be entered in EXPLO5 software, it takes 65% and 35%.



3. After the software calculation is completed, the heat of formation, detonation velocity and detonation pressure of cocrystal are read from the output results.



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      1.  PDO,  35   %
      2.  N2H5N5,  65   %

      C(1.325) H(4.669) N(5.344) O(0.662)

       Molecular weight                = 106.07
       Density of reactant             = 1.587872   g/cm3
       Initial pressure                = 0.1  MPa
       Oxygen balance                  = -65.18446  %
       Enthalpy of formation           = 2693.56  kJ/kg
       Energy of formation             = 2845.56  kJ/kg


DETONATION PARAMETERS (at the C-J point) :
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       Heat of detonation              = -4496.758   kJ/kg
       Detonation temperature          = 2827.181   K
       Detonation pressure             = 26.55952  GPa
       Detonation velocity             = 8734.524   m/s
       Particle velocity               = 1914.979   m/s
       Sound velocity                  = 6819.546   m/s
       Density of  products            = 2.033758   g/cm3
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9. References

1 Y. Xu, L. Tian, D. Li, P. Wang and M. Lu, *J. Mater. Chem. A*, 2019, **7**, 12468-12479.

2 V. N. Yadav and C. H. Gorbitz, *Acta*. *Crystallogr*. *C*. *Struct*. *Chem*., 2014, **70**, 43-5.

3 W. E. Acree, Joyce R. Powell, Sheryl A. Tucker, Maria D. M. C. Ribeiro da Silva, M. Agostinha R. Matos, J. M. Gonçalves, L. M. N. B. F. Santos, V. M. F. Morais and G. Pilcher, *J. Org. Chem.*, 1997, **62**, 3722-3726.