Supplementing Information

Synthesis Crystal Structure and Properties of 3-Picrylamino-1,2,4-Triazole-Nitric acid Self-assembled Energetic Material

Xiaoyan Zhang,[a] Qisheng Zhang,[b] Yunshu Zhao,[a] Guiying Li,[a] Tiying Jiang,[a] Zhirong Suo, Li Su,*[a]

Shanhu Sun,*[a]

[a]School of Materials and Chemistry, Southwest University of Science and Technology, Mianyang 621010, Sichuan, People's Republic of China

[b]School of Environment and Resource, Southwest University of Science and Technology, Mianyang 621010, Sichuan, People's Republic of China

Table of Contents

SI.1. Preparation and characterization of 3-Picrylamino-1,2,4-Triazole

Synthesis of trinitrophenol (TNP) [1]

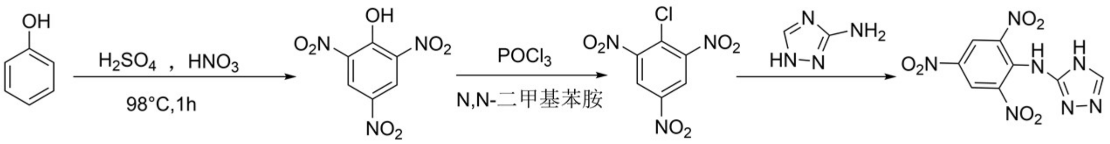
Phenol (5.00g, 53.13mmol) was heated and melted, to which sulfuric acid (98%, 22.5g, 0.25mol) was slowly added dropwise, the temperature was slowly raised to 80°C during the dropwise process, and to 98°C after the dropwise process, the reaction was completed and the phenol sulfonate solution was allowed to cool to room temperature for 1h. Phenol sulfonated solution was slowly added dropwise into nitric acid (68%, 22.5g, 0.22mol), the temperature was slowly increased to 80°C during the dropwise addition, the temperature was increased to 96°C after the dropwise addition, and the reaction was cooled to room temperature after 1h. The solid-liquid mixture was poured into 100mL ice water, stirred for 30min, filtered, washed with slightly acidic water and dried to obtain a light yellow powder.

Synthesis of 2,4,6-trinitrochlorobenzene (PiCl) [2]

Picric acid (2g, 8.73mmol) was weighed and mixed with phosphorus trichloride (20mL), after the solid was completely dissolved, N,N-dimethylaniline (1.2g, 9.93mmol) was added slowly dropwise and the reaction was carried out for 20min at room temperature, then the reaction solution was slowly poured into 400mL of iced water, filtered, and washed with water to obtain a light yellow-green solid.

Synthesis and characterization of PATO [3]

Weighed 3-amino-1,2,4-triazole (0.4218g, 5mmol) was dissolved in DMF (15mL) and placed in an ice-water bath, bitryl chloride (0.4974g, 2mmol) was slowly added to the mixture, and when the solid was completely dissolved, removed from the ice-water bath, and heated the reactants to 100°C, and the reaction was carried out for 5h. After the reaction was completed, it was cooled for 30min, and then poured into the ice water. , filtered and dried to give a yellow solid. FTIR（KBr）：715，738，1096，1173，1205，1308，1432，1530，1616，3141，3251 cm^{-1}；^{1}H NMR (600 MHz, DMSO) ：δ 13.87 (s, 1H), 10.47 (s, 1H), 8.94 (s, 2H), 8.40 (s, 1H)；HPLC-MS (ESI$^-$) : *m/z*: 294.0 [M-H$^-$].



Scheme S1. Synthetic route of PATO

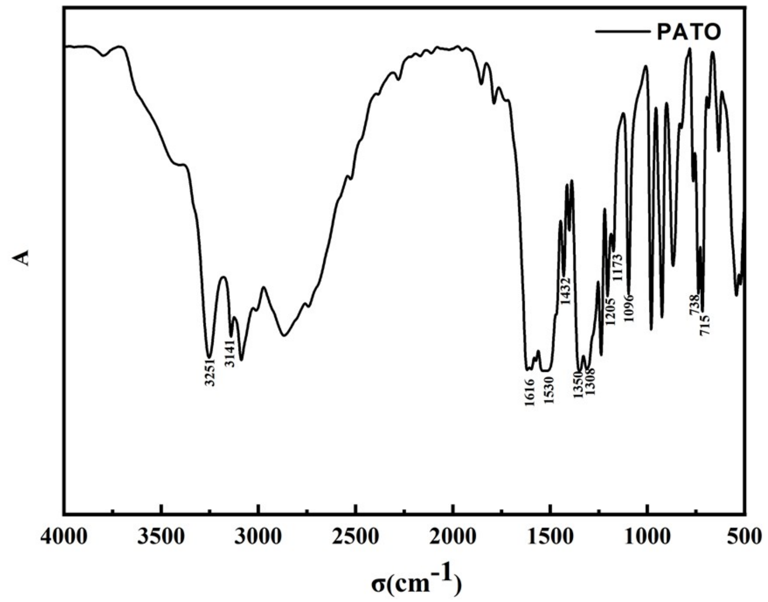


Figure S1. IR spectrum of PATO

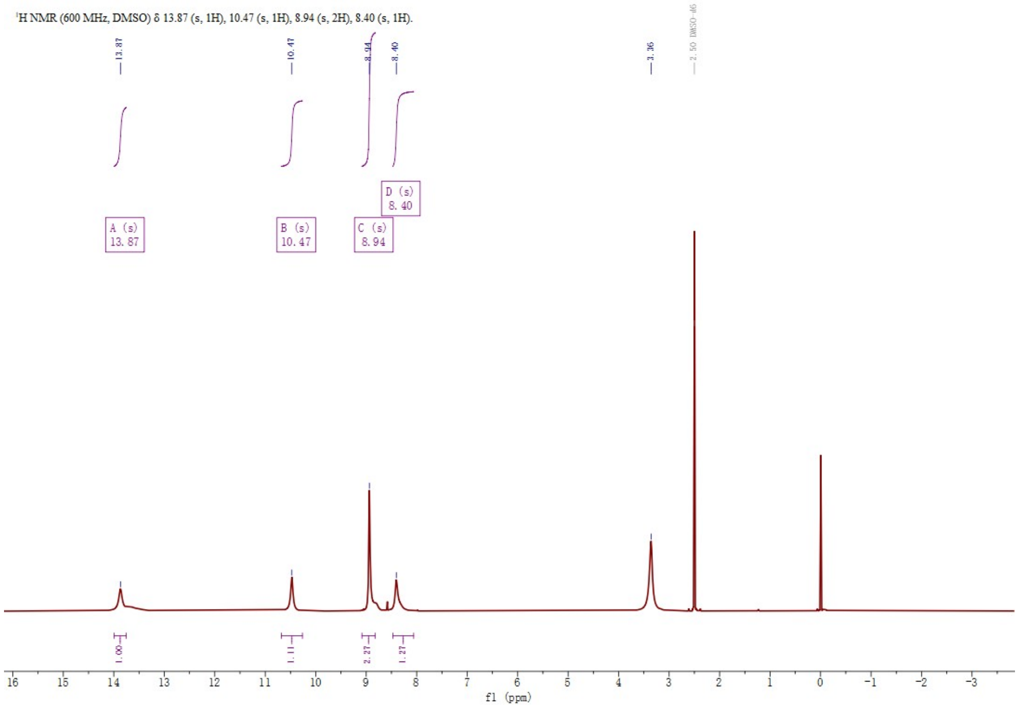


Figure S2. ^{1}H NMR spectrum of PATO

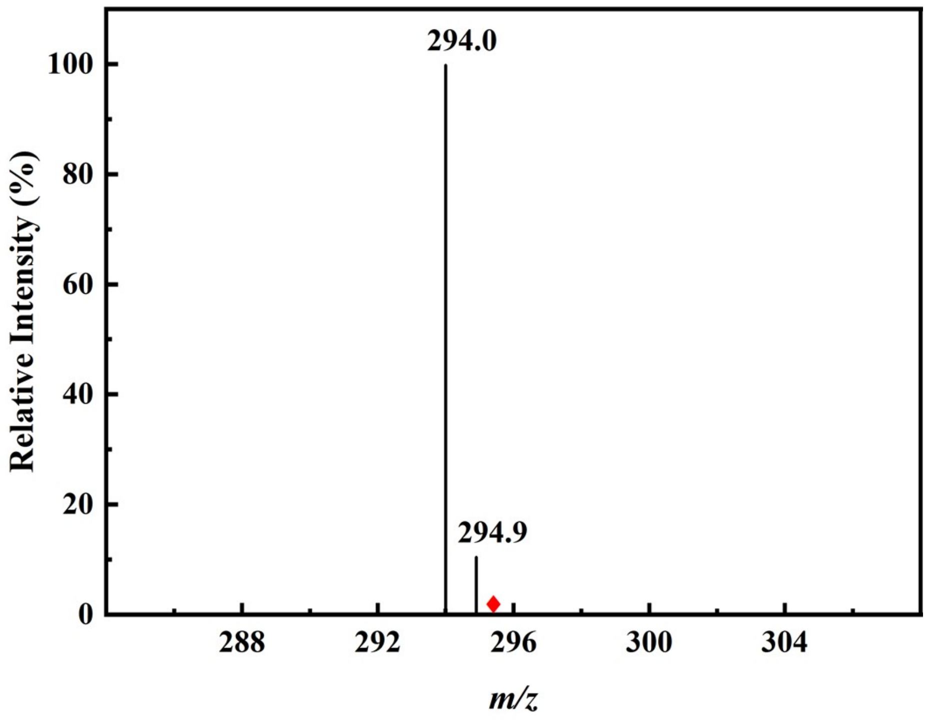


Figure S3 . Mass Spectrometry of PATO

SI 2. Characterization and Crystallographic information of 3-Picrylamino-1,2,4-Triazole-Nitric acid self-assembled energetic material (PATO-N)

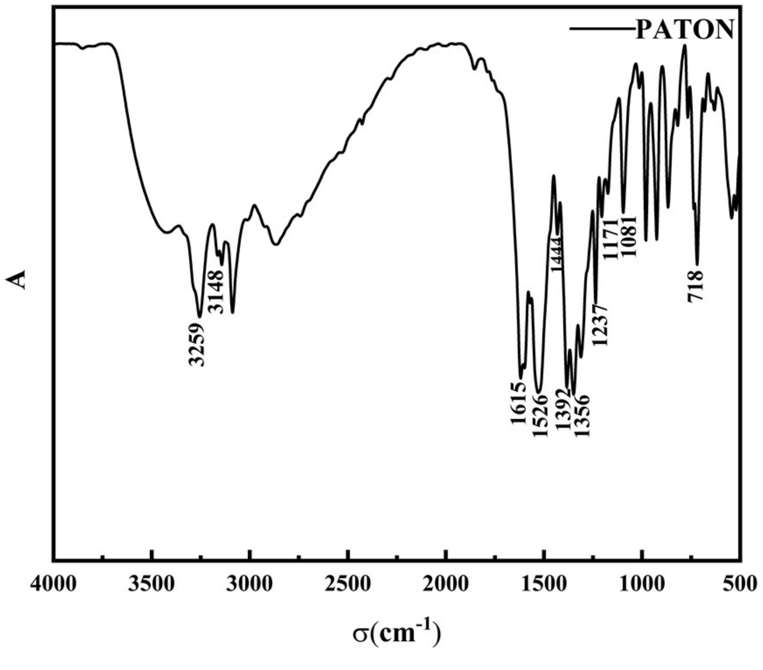


Figure S4. IR spectrum of PATO-N

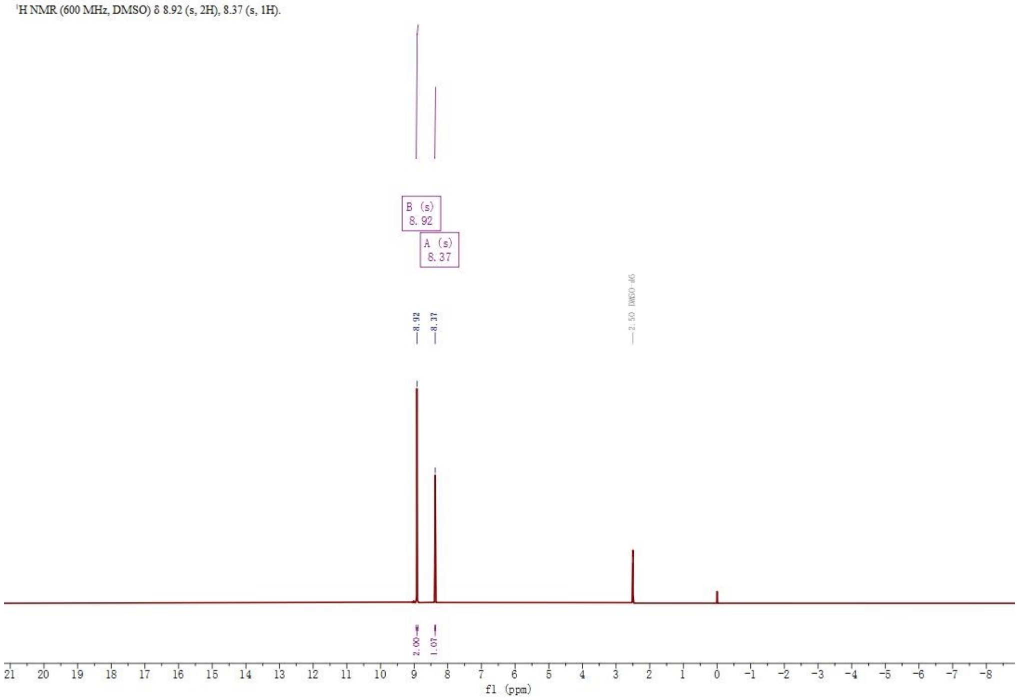


Figure S5. ^{1}H NMR spectrum of PATO-N

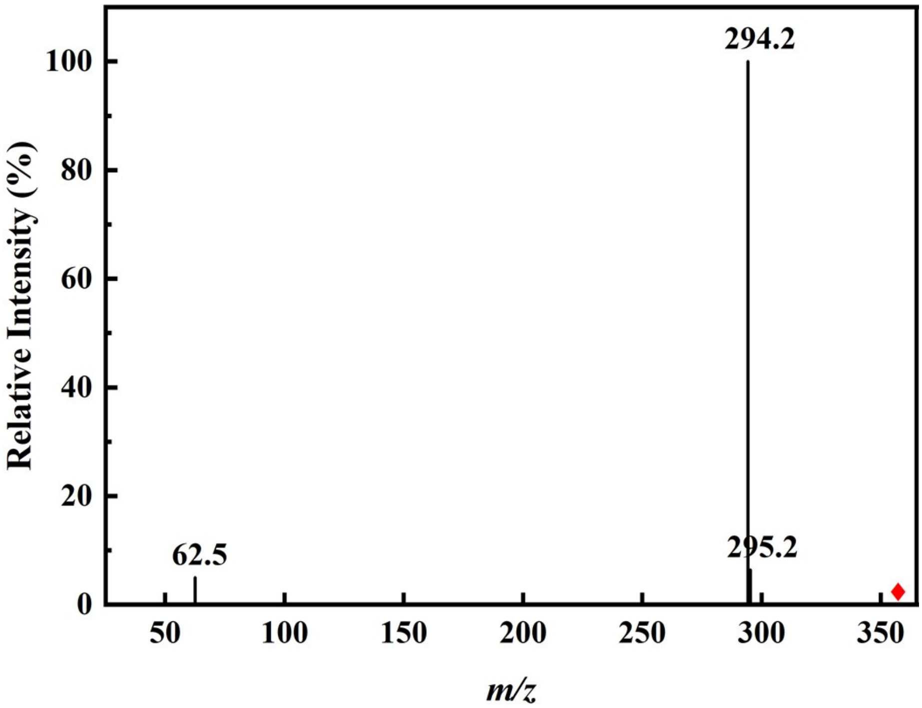


Figure S6. Mass Spectrometry of PATO-N

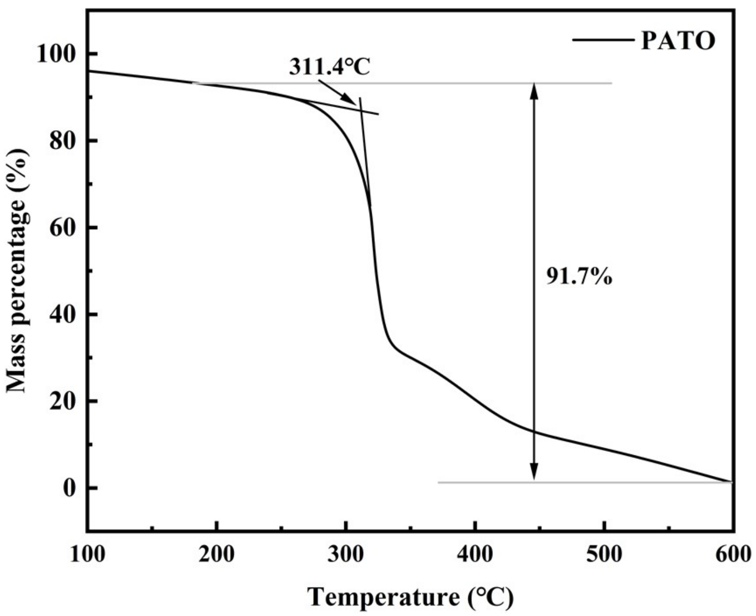


Figure S7. TG curves of PATO

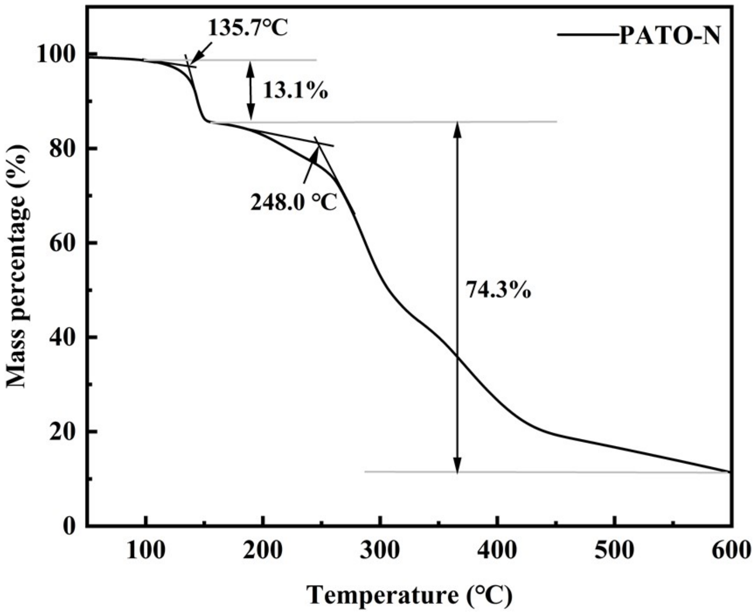


Figure S8. TG curves of PATO-N

Table S1 International hydrogen bond distance and angle for PATO/HNO_3 crystal

X-H···Y	d（Å）	D（Å）	（deg）
N_4-H_4···O_7	2.227	3.008	147.78
N_5-H_5···O_9	1.840	2.707	167.95

C_8-$H_8\cdots O_6$	2.241	3.187	174.43
N_6-$H_6\cdots O_8$	1.829	2.704	172.74

Table S2 Bonding length information of PATO/HNO_3 crystal

Bond	Length/Å	Bond	Length/Å	Bond	Length/Å
O(8)-N(8)	1.257(7)	O(9 -N(8)	1.264(6)	O(1)- N(1)	1.208(7)
O(7)- N(8)	1.244(7)	O(6)-N(3)	1.217(7)	O(5) -N(3)	1.232(7)
O(2)- N(1)	1.227(7)	N(3)- C(5)	1.472(8)	N(1)- C(1)	1.476(8)
O(3)- N(2)	1.227(8)	N(6)- N(7)	1.362(7)	N(6)-C(8)	1.307(9)
O(4)- N(2)	1.219(8)	N(4)- C(7)	1.385(7)	N(4)-C(6)	1.378(8)
N(7)- C(7)	1.304(8)	N(5)- C(7)	1.362(8)	N(5) -C(8)	1.339(8)
N(2)- C(3)	1.468(8)	C(6)-C(5)	1.422(9)	C(6)- C(1)	1.416(8)
C(4) -C(5)	1.379(8)	C(4)-C(3)	1.394(9)	C(2)-C(1)	1.377(9)
C(2) -C(3)	1.369(9)				

Table S3 Angle information of PATO/HNO_3 crystal

Bond	Angle/(°)	Bond	Angle/(°)	Bond	Angle/(°)
O(6) -N(3)- O(5)	125.1(5)	O(1)- N(1) -C(1)	118.9(5)	O(4)- N(2)- O(3)	125.6(6)
O(6)-N(3)-C(5)	117.9(6)	O(2)- N(1)- C(1)	116.5(6)	O(4)- N(2)- C(3)	118.0(6)
O(5)- N(3)- C(5)	117.0(5)	C(8) -N(6)- N(7)	112.4(5)	N(7) -C(7) -N(4)	124.9(5)
O(8)-N(8)- O(9)	119.3(5)	C(6)- N(4)- C(7)	121.2(5)	N(7) -C(7)-N(5)	112.6(5)
O(7) -N(8)-O(8)	120.5(5)	C(7)- N(7)- N(6)	102.7(5)	N(5) -C(7) -N(4)	122.5(6)
O(7)- N(8) -O(9)	120.2(5)	C(8) -N(5)- C(7)	105.3(5)	N(4)- C(6)- C(5)	122.2(5)
O(1)- N(1) -O(2)	124.5(6)	O(3)-N(2)- C(3)	116.3(6)	N(4) -C(6)- C(1)	122.9(6)
C(1)- C(6) -C(5)	114.9(5)	C(5)- C(4) -C(3)	118.0(6)	C(6)- C(5)- N(3)	120.5(5)
C(4)-C(5)- N(3)	116.5(5)	C(4) -C(5) -C(6)	123.0(5)	N(6) -C(8)- N(5)	107.0(5)
C(3) -C(2)- C(1)	118.9(6)	C(6)- C(1)- N(1)	121.0(5)	C(2)- C(1)-N(1)	116.2(5)
C(2)- C(1)- C(6)	122.8(6)	C(4)-C(3)-N(2)	117.9(6)	C(2) -C(3)- N(2)	120.1(6)
C(2)- C(3)- C(4)	122.0(6)				

SI 3. The effect of humidity and temperature of the PATO-N

Experimental section

A specified amount of the PATO-N sample was weighed into a glass petri dish, whic hwas then placed in a climate chamber. The sample was subjected to controlled conditions of 60°C and 50% relative humidity (RH) for one week. Subsequently, it was removed and analyzed by X-ray diffraction.

Result and discussion

To evaluate the impact of storage conditions on the phase composition of PATO-N, XRD tests were performed on samples stored at 50 RH, 60℃ for one week and samples stored at room temperature sealed conditions. The corresponding XRD patterns are presented in the Figure S9. As shown in the figure, the characteristic diffraction peaks of PATO-N stored at 50% relative humidity and 60° C are located at 14.8° , 18.0° , 20.2° ， 22° , 23.5° , 25.2° , 26.2° , and 28° , while those of PATON stored under sealed conditions at room temperature are located at 22.1° , 23.3° , 26.2° , and 28.5° . The diffraction peak of PATO is wider and the peak intensity is lower, owing to the low crystallinity; the main characteristic diffraction peaks are located at 15°, 18°, 20.3°, 23.3°, 26.2°, and 28.8°. The characteristic peak positions in the XRD patterns of samples placed in 50% relative humidity at 60° C partially overlap with those of PATO and PATO-N (stored at room temperature in sealed containers).This indicates the sample is a mixture of two substances, and under these storage conditions, part of the sample reverted to its raw material state due to the removal of nitric acid. Therefore the storage conditions have a certain impact on PATO-N.

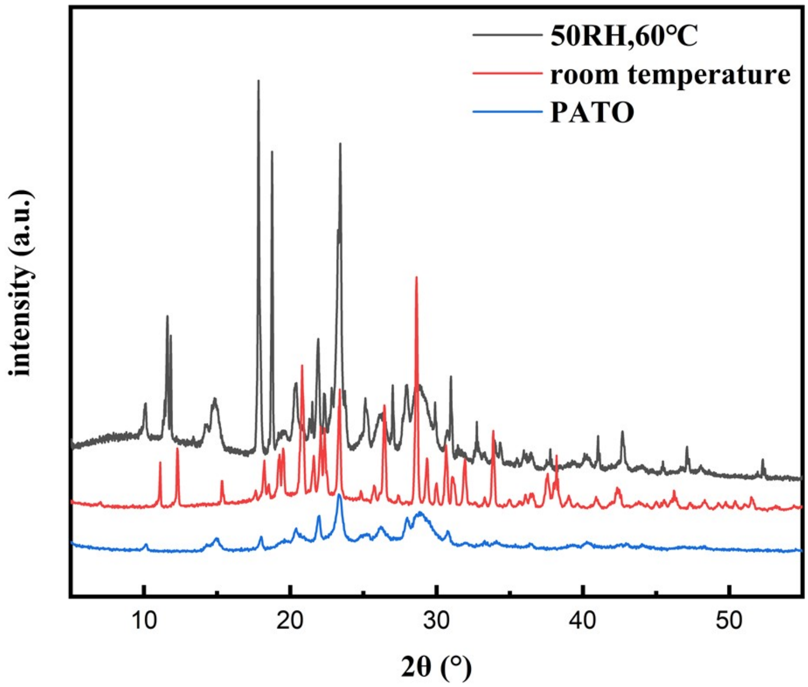


Figure S9. X-ray diffraction patterns of PATO-N stored at 50 RH,60 ℃, PATO-N stored at at room temperature, and PATO.

SI 4. The compatibility of PATO-N and CL-20

Experimental section

PATON and CL-20 were first dried in an oven at 60°C for one hour. Subsequently, the two materials were mixed in a 1:1 mass ratio and gently ground in an agate mortar. Finally, the resulting mixture was subjected to simultaneous thermogravimetric-differential scanning calorimetry testing.

Result and discussion

To investigate the expected compatibility between PATON and CL-20, TG-DSC analysis was performed on their mixture. The results are shown in the figure below. Figure S8 presents the DSC curves for CL-20, PATO-N, and CL-20/PATO-N, while Table S4 lists the maximum exothermic peaks. The pure CL-20 system exhibits a single exothermic peak with a peak temperature of 234.6 °C. The pure PATO-N system displays two exothermic peaks, the first peak corresponds to release of nitric acid, with a peak temperature of 147.3 ℃, the second peak corresponds to its decomposition. Compared to the two pure components, the exothermic peak temperature of the mixture is closer to that of CL-20, as CL-20 dominates the thermal decomposition in the mixed system due to its poor thermal stability. As shown in

Table S4, the peak temperature difference between the mixed component and the single component is 8.3 ℃.According to the standards established by STANAG 4147[4], they are considered borderline compatible.The compatible might actually be due to the acidic effects of PATO-N.

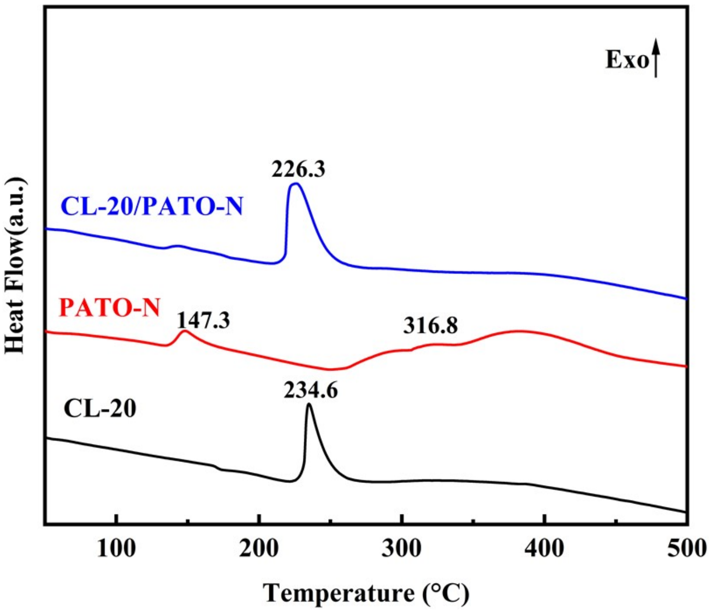


Figure S10. DSC curves of PATO-N, CL-20, and CL-20/PATO-N.

Table S4 1:1-CL-20/PATON-N materail system obtained by pressure DSC

system		Peak temperature		
Mixture system	Single system	$^{a}T_{P2}$/℃	$^{b}T_{p1}$/℃	$^{c}\Delta T_{p}$/℃
1:1-CL-20/PATO-N	CL-20	226.3	234.6	8.3

a:The maximum exothermic peak temperature of mixture system. b: The maximum exothermic peak temperature of single system. c:$\Delta T_{p=}T_{p1}$-$T_{P2.}$

SI 5. References.

1. X. H. Zhang, L. X. Ding, G. J. Zhu, *Explosive laboratory preparation method,* The Publishing House of Ordnance Industry, Beijing, 1997.

2. M. Pietrzak, J. P. Wehling, S. S. Kong, P. M. Tolstoy, L. G. Shenderovich, C. López, R. M. Claramunt, J. Elguero, G. S. Denisov, H. H. Limbach, *Chemistry A European Journal*, 2010, 16, 1679.

3. P. Leonard, P. Bowden, M.Shorty, M. Schmitt, *Propellants Explosives Pyrotechnics* 2019, 44, 203.

4. J. S. Li, J. J. Chen, C. C. Hwang, K. T. Lu, T. F. Yeh, *Propellants, Explosives, Pyrotechnics,* 2019, 44, 1270.