

Supporting Information

Multi-fused heat-resistant energetic compound constructed by hydrogen bonds

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1. Materials and experimental processes

Crystals suitable for X-ray diffraction measurement were obtained as described in the Experimental section. Data were collected on a Rigaku AFC-10/Saturn 724⁺ CCD diffractometer. All of the crystals were irradiated with graphite monochromatic Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K in multiscan mode. All of the structures were solved using the direct methods of SHELXS-97 and refined by using full-matrix least-squares procedures on F^2 with SHELXL-97. All nonhydrogen atoms were obtained from the difference Fourier map and refined anisotropically. Hydrogen atoms were generated geometrically, assigned appropriate isotropic thermal parameters, and included in the structure factor calculations.

All reagents purchased commercially were used as received without further purifications (Sigma-Aldrich, TCI, Acros, Aladdin, Energy Chemicals, etc.). ¹³C NMR spectra were recorded on a Bruker AVL300 nuclear magnetic resonance spectrometer. Elemental analysis (C/H/N) was performed on an Elementa Vario El III analyzer. The thermal decomposition behavior was tested using differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) technologies at a heating rate of 5 °C·min⁻¹. The DSC test was determined using a DSC 3 apparatus (METTLER TOLEDO) under a nitrogen atmosphere at a flow rate of 50 mL·min⁻¹ from ambient temperature to 500°C. The TG-DTG experiment was carried out with a TGA/DSC 3+ apparatus (METTLER TOLEDO) under nitrogen gas conditions with a flow rate of 80 mL·min⁻¹. Impact and friction sensitivities were determined on a BFH-10 BAM fall hammer and FSKM-10 BAM friction apparatus, respectively.

Caution! Although we have not encountered any difficulties in the preparation of energetic compounds, we must operate by using the necessary safety precautions. It is strongly recommended to use leather clothing, latex gloves, goggles, earplugs and masks in experimental operations. In the process of processing and storing energetic compounds, the mechanical effects of such energetic materials must also be avoided, including scraping or impinging.

Synthesis of 6-chloropyrimidine-2,4-diamine (CNPA)

4-Chloro-2,6-diaminopyrimidine (14.5 g) solid was slowly fed into the concentrated sulfuric acid system under stirring by adding concentrated sulfuric acid (75 mL) to the flask and placing it in an ice bath. After feeding, the ice bath was removed, and the reaction flask was placed in a water

bath to heat to 35°C. Fuming nitric acid (15 mL) was slowly added to the mixture, and was heated for 30 min. Then, the reaction solution was slowly poured into ice water, and the precipitated yellow solid was filtered, 14.7 g (yield: 78 %). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 160.3, 156.1, 154.0, 110.7 ppm. IR (ν): 629, 655, 674, 708, 737, 850, 912, 1014, 1132, 1181, 1275, 1320, 1423, 1516, 1558, 1653, 3179, 3383, 3522, 3599. Elemental analysis calcd (%) for $\text{C}_4\text{H}_4\text{ClN}_5\text{O}_2$ ($189.56 \text{ g}\cdot\text{mol}^{-1}$): C 25.32, H 2.11, N 36.93; found: C 25.30, H 2.39, N 38.20.

Synthesis of 6,6'-(hydrazine-1,2-diyl)bis(5-nitropyrimidine-2,4-diamine) (PHP)

2,4-Diamino-5-nitro-6-chloropyrimidine (1.9 g) and DMSO (6.0 mL) were added to the round bottom flask. The hydrazine hydrate (0.6 mL, 85 %) was slowly added to the system, and the reaction was continued at room temperature for 2.0 h. After filtration and washing with deionized water, the yellow solid was dried to 1.5 g (yield: 89 %). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$) δ 161.4, 160.4, 155.6, 106.9 ppm. IR (ν): 669, 689, 699, 751, 776, 1003, 1031, 1116, 1174, 1204, 1317, 1392, 1536, 1636, 3397. Elemental analysis calcd (%) for $\text{C}_8\text{H}_{10}\text{N}_{12}\text{O}_4$ ($338.25 \text{ g}\cdot\text{mol}^{-1}$): C 28.38, H 3.54, N 49.66; found: C 28.32, H 3.51, N 49.56.

Synthesis of PHP \cdot 2HClO $_4$

0.5 g of **PHP** was dissolved in a beaker containing 4 mL of perchloric acid, and massive crystals were observed at ambient temperature. After 36 h, light yellow solid 0.61 g was obtained by filtration. IR (ν): 624, 648, 685, 776, 1024, 1057, 1173, 1205, 1309, 1389, 1416, 1520, 1623, 2972, 3282. Elemental analysis calcd (%) for $\text{C}_8\text{H}_{12}\text{Cl}_2\text{N}_{12}\text{O}_{12}$ ($539.25 \text{ g}\cdot\text{mol}^{-1}$): C 17.80, H 2.22, N 31.15; found: C 17.70, H 2.16, N 30.25.

2. Crystallographic data

Table S1 Crystal structure data and refined parameters of PHP·2HClO₄ and PHP·2HClO₄·2H₂O.

Compound	PHP·2HClO ₄	PHP·2HClO ₄ ·2H ₂ O
Formula	C ₈ H ₁₂ Cl ₂ N ₁₂ O ₁₂	C ₈ H ₁₆ Cl ₂ N ₁₂ O ₁₄
weight	539.20	575.23
Temperature [K]	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/c</i>
A [Å]	10.4353(9)	15.3440(13)
B [Å]	17.0537(16)	5.2963(5)
C [Å]	10.9355(9)	14.1981(12)
α [°]	90.00	90.00
β [°]	93.693(2)	116.175(5)
γ [°]	91.691(2)	90.00
V [Å ³]	1942.05(30)	1035.50(16)
Z	4	2
ρ [g·cm ⁻³]	1.844	1.845
F(000)	1096.0	588.0
Crystal size [mm ³]	0.23 × 0.14 × 0.08	0.21 × 0.08 × 0.03
2 θ [°]	3.92 to 50.04	5.74 to 50.04
Reflections collected	9375	4954
Independent reflections	3420	1832
Goodness-of-fit on F ²	1.052	1.092
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.1143, wR ₂ = 0.2997	R ₁ = 0.0735, wR ₂ = 0.1663
Final R indexes [all data]	R ₁ = 0.1884, wR ₂ = 0.3396	R ₁ = 0.1155, wR ₂ = 0.1841
CCDC	2264741	2264743

3. NMR spectra ¹³C NMR Spectra

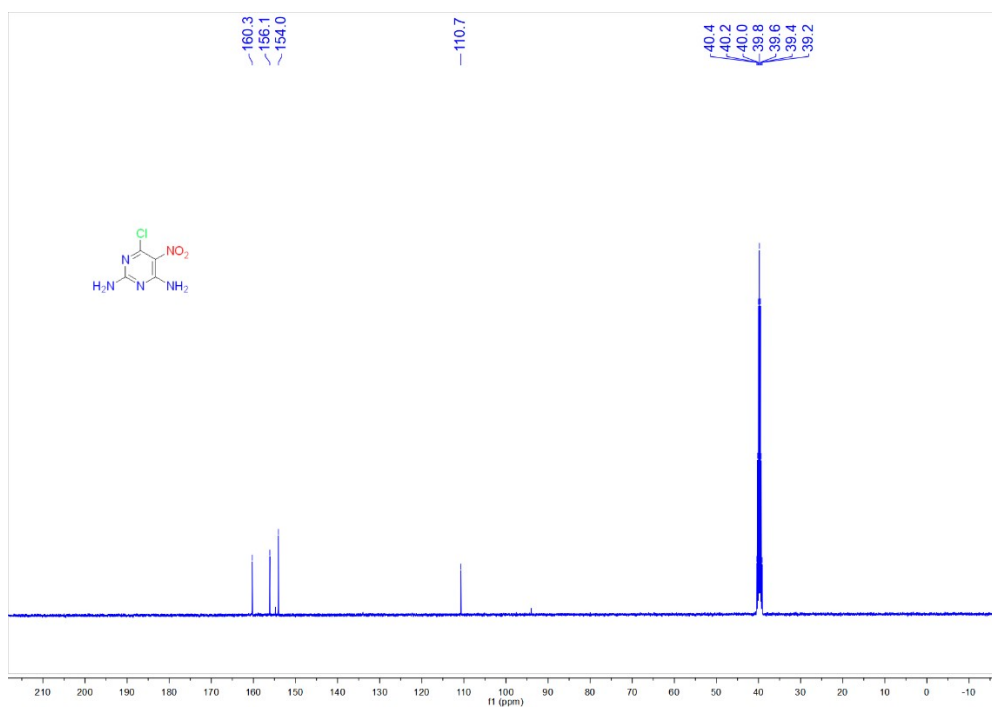


Figure S1. The ¹³C NMR spectra of 2,4-Diamino-5-nitro-6-chloropyrimidine in DMSO.

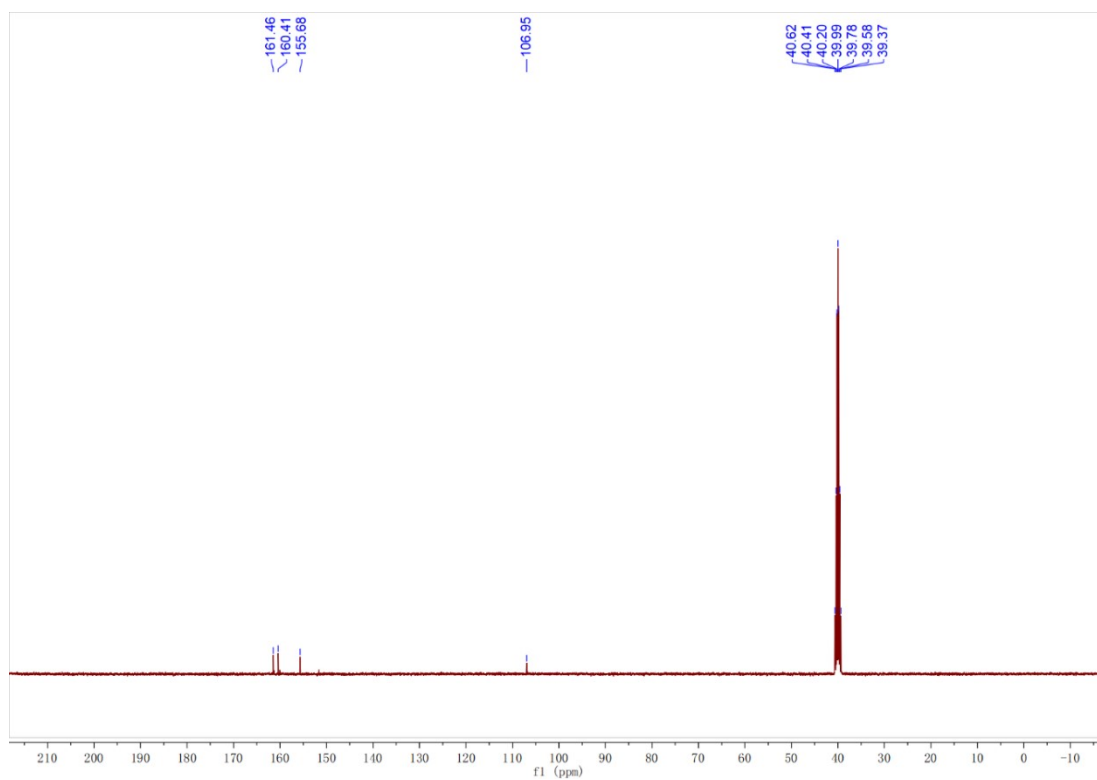


Figure S2. The ¹³C NMR spectra of PHP in DMSO.

4. DSC curves

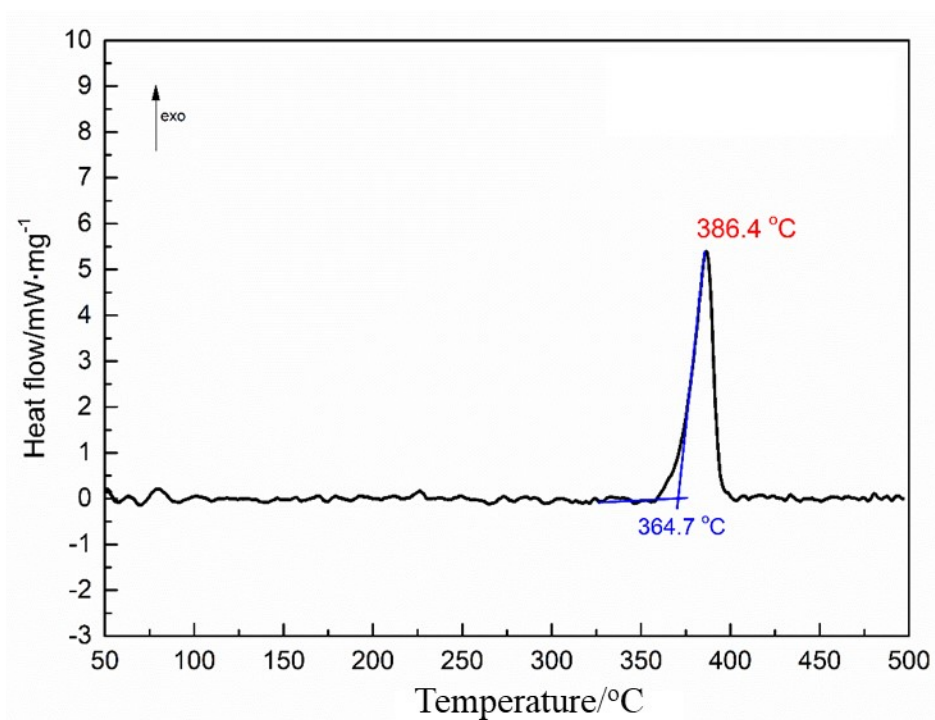


Figure S3. DSC spectra of PHP.

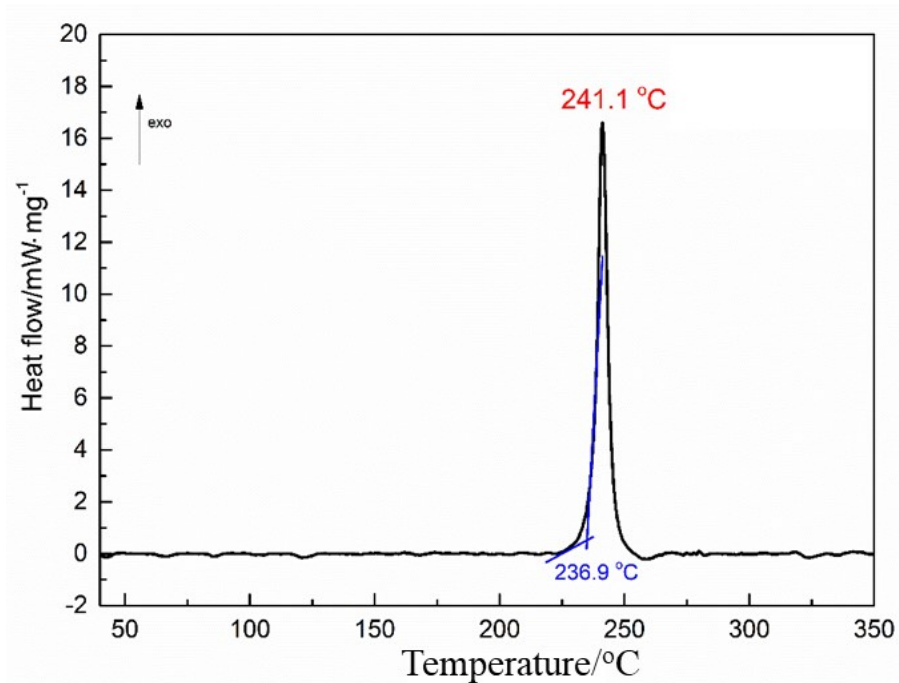


Figure S4. DSC spectra of PHP·2HClO₄.

5. Heats of formation

The the equation were provided in the supporting materials. Firstly, the enthalpy of formation of neutral molecule is required. The molecular formula of PHP is $C_8H_{10}N_{12}O_4$. According to the definition of enthalpy of formation, the enthalpy of formation of PHP is equal to its enthalpy minus the enthalpy of the most stable element. The calculation formula is as follows:

$$\Delta_f H_m^\theta(M) = H(M) - 8H(C(g)) - 5H(H_2) - 6H(N_2) - 2H(O_2) + 8(C(s))$$

The above enthalpy values are calculated quantitatively. All structures were optimized under B3PW91/6-31G (d, p), and then calculated under PWPB95D3/def2-QZVPP with high precision single point energy. After zero point energy correction, their enthalpy values were obtained respectively. Because the steady state of carbon in the standard state is the solid phase, the enthalpy of the gas phase is quantified, so the standard molar enthalpy of sublimation of the carbon needs to be added. Then, according to the enthalpy of formation of the neutral molecule, the enthalpy of formation of its cation M^+ can be calculated, and the calculation formula is as follows:

$$\Delta_f H_m^\theta(M^+) = \Delta_f H_m^\theta(M) - \Delta_f H_m^\theta(H^+) - H(M) + H(H^+) + H(M^+)$$

Then, according to the empirical formula, the lattice energy of the ionic salt ΔH_L was calculated:

$$U_{POT}/KJ \text{ mol}^{-1} = \gamma(\rho_m/M_m)^{1/3} + \sigma$$

$$\Delta H_L = U_{POT} + [p(\eta_M/2-2) + q(\eta_X/2-2)]/RT$$

Finally, according to the Born-Haber cycle, the enthalpy of formation of ionic salts can be calculated as follows:

$$\Delta_f H_m^\theta(salt) = \Delta_f H_m^\theta(cation) + \Delta_f H_m^\theta(anion) - \Delta H_L$$

The anions in the calculation of $PHP \cdot 2HClO_4$ is perchlorate, and was calculated using the G4 thermodynamic combination method in a process similar to the calculation of cation formation enthalpies. The enthalpy of formation of protons is derived from the National Institute of Standards and Technology (NIST).