Host-guest energetic materials constructed by incorporating oxidizing gas molecule into organic lattice cavity toward to highenergetic and low-sensitive performance

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SI 1. Experimental

Caution: Although none of the compounds described herein has exploded or detonated in this work, the HNIW is a powerful and dangerous explosive. These materials should be handled extremely carefully by using the proper safety practices and equipment. Nitrous oxide (N_2O) is a compressed liquefied gas, an asphyxiation risk, and a dissociative anaesthetic, which has several recognized ill effects on human health, whether through breathing it in or by contact of the liquid with skin or eyes. This gas must be used in fuming cupboard.

Hexanitrohexaazaisowurtzitane (HNIW) was used as received from Beijing Institute of Technology. Anhydrous solvents include acetone, tetrachloromethane (CCl₄) and ethanol were provided by J&K Scientific Ltd. The N₂O and CO₂ liquefied gas (99.9% purity grade) was supplied by Chengdu Jinkexing Gas Co. Ltd.

Crystallization

Both gas inclusion host-guest energetic materials of $HNIW/N_2O$ and $HNIW/CO_2$ were initially obtained from 1:5 acetone/ CCl₄ solution by persistently saturating the solution with N₂O or CO₂ the gas. The schematic diagram of HNIW and gas inclusion host-guest energetic crystallization device is shown in Figure S1. The gas inclusion host-guest energetic crystal could be scaled up conveniently through the slow addition of anti-solvent CCl₄ to the solution of HNIW. Also, the single crystals of the gas inclusion host-guest energetic materials suitable for X-ray diffraction analysis were grown easily by slow evaporation of acetone/ethanol solution through maintained a slow stream of N₂O or CO₂ gas over the solution surface.

2:1 HNIW/N₂O gas inclusion host-guest energetic crystal

A 250 ml three-necked flask was loaded with 10 g of ϵ -HNIW (0.0228 mol) which was dissolved in 25 ml of anhydrous acetone at room temperature. In fuming cupboard, the N₂O gas was injected into the solution with PTFE tube through gas relief valve, and the outlet gas pressure maintain 1atm. After 5 min aeration, 125 ml dry CCl_4 anti-solvent was added to the HNIW solution with the adding rate of 5 ml/min. The solution was persistent saturated by the N₂O gas in the precipitated process and kept magnetic stirring for 30 min, before the crystals were collected. This solid was determined to be the 2:1 HNIW/N₂O gas inclusion host-guest energetic crystal by both infrared spectroscopy and powder X-ray diffraction.

2:1 HNIW/CO₂ gas inclusion host-guest energetic crystal

Similarly, by replacing the N_2O gas with CO_2 gas to saturate the HNIW solution and using the same crystallization conditions as described above, the host-guest energetic crystal was also precipitated easily. The solid was determined to be the 2:1 gas inclusion host-guest energetic crystal of HNIW/CO₂ by both infrared spectroscopy and powder X-ray diffraction.



Figure S1. Schematic diagram of HNIW and gas host-guest energetic crystallization

device

Fourier Transforms Infrared Spectroscopy (FTIR)

FTIR spectra were carried out by a Nicolet 800 Fourier transforms infrared spectroscopy. The spectra were measured with a resolution of 4 cm⁻¹ in the range of 400~4000 cm⁻¹ using the KBr pellet technique.

Powder X-ray Diffraction (PXRD)

Powder X-ray diffraction patterns were collected on a Bruker D8 Advance using Cu K α radiation (λ =1.54180 Å), equipping with a Vantec-1 detector and operating under the condition of 40 kv and 40 mA. Samples were prepared by finely grinding and packing into the depression of an alloy sample cell. The 20 range measured was 5-50° with steps of 0.02°/0.1s. Compared with the simulated powder patterns form the single X-ray diffraction structures, the experimental powder patterns were found to be in significant agreement with the predicted patterns, respectively.

In situ non-isothermal powder X-ray diffraction (In situ PXRD) was carried out using a temperature programme. A TTK450 temperature chamber was used to precisely control the temperature during the experiment. The first scan data were collected when the temperature was increased from ambient to 30 °C, and then the temperature was raised to 100 °C and the second scan was started after 2min. The next scan was conducted at a 5 °C interval until the temperature up to 185 °C. The heating rate was 0.1 °C/s, and holding 2min before each scan started. The Rietveld refinement method was used to calculate the phase content of the HNIW crystals through the Topas Academy program, which is a standardless X-ray diffraction, quantitative phase analysis method of the complete powder diffraction pattern.

Single Crystal Structure Determination

Single crystal X-ray diffraction data of HNIW/N₂O and HNIW/CO₂ were collected on a Bruker APEX-II CCD diffractometer with graphite-monochromated Mo K α radiation (λ =0.71073 Å). Data were collected in ω -scans in twelve setting of 2 θ . The crystal was kept at 293 K during data collection. The structures were solved by Intrinsic Phasing with the ShelXT structure solution program and refined using Least Squares minimization with the ShelXL refinement package^[1,2]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in a combination of refined and idealized positions. The crystal and refinement data are given in Table S1.

CCDC 1585914 and 1585915 contain the supplementary crystallographic data for this work. These data are provided free of charge by the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures/.

Table S1. Crystallographic Data for HNIW/CO₂ and HNIW/N₂O Crystals (Collected at 293 K)

host-guest energetic crystal	HNIW/CO ₂	HNIW/N ₂ O		
Empirical formula	C6.5H6N12O13	C6H6N13O12.5		
Formula weight	460.23	460.24		
Stoichiometry	2:1	2:1		
Temperature /K	293	293		
Crystal system	orthorhombic	orthorhombic		
Space group	Pbca	Pbca		
a /Å	9.6731(10)	9.5768(17)		
b /Å	13.2031(12)	13.256(2)		
c /Å	23.553(2)	23.625(4)		
α /°	90	90		
β /°	90	90		
γ /°	90	90		
Volume /Å ³	3008.0(5)	2999.3(9)		
Z	8	8		
Density (calculated) /g.cm ⁻³	2.033	2.038		
Crystal size /mm ³	0.2×0.17×0.13	0.12×0.08×0.05		
2θ range for data collection /°	2.725 to 51.578	3.488 to 61.512		

Inday ranges	$-11 \le h \le 8, -14 \le k \le 15, -28 \le$	$-13 \le h \le 13, -16 \le k \le 19, -33$		
index ranges	$l \leq 28$	$\leq 1 \leq 33$		
Reflections collected	16082	28734		
Data/restraints/param	2793/0/286	4660/6/286		
eters	2190101200			
Goodness of fit on F2	1.036	1.017		
Final R indexes	$R_1 = 0.037 \text{ w}R_2 = 0.091$	R1 = 0.0601, wR2 = 0.1752		
[I>=2σ (I)]	1 0.057, W12 0.051			
Final R indexes [all	R1 = 0.0417 wR2 = 0.0947	R1 = 0.01245 wR2 = 0.2262		
data]				

Differential Scanning Calorimetry-Thermogravimetry (DSC-TG)

Differential Scanning Calorimetry-Thermogravimetry (DSC-TG) technology were carried out on NETZSCH STA 449F3, with sample mass of 1-2 mg in an open aluminum sample cell. All experiments were run under a nitrogen purge with a heating rate of 10 °C/min, while covering the temperature range of 50 °C to 450 °C.

Thermogravimetry-Infrared Spectroscopy (TG-IR)

Thermogravimetry-Infrared Spectroscopy (TG-IR) was employed to analyze the gas products of phase transition and decomposition processes. Thermograms for each sample was recorded on a TA Instruments TGA 2050 and all experiments were run in platinum TGA sample pans without cover under a nitrogen purge. The temperature programme was set from 30 °C to 500 °C at the heating rate of 10 °C/min. The gas release form the TG analysis was injected into a Nicolet 710 infrared spectroscopy synchronously through a connected heated gas line. The temperature of infrared gas cell is maintained at 200 °C. The spectra were measured with a resolution of 5cm⁻¹ in the range of 600-4000 cm⁻¹ and then analyzed using the OMNIC 8.2 software package with OMNIC Series module.

Powder Pattern Simulations

The simulated diffraction patterns are calculated by mercury software using the

settings of wavelength of 1.54056Å, step of 0.02° and FWHM peak shape of 0.1°. No absorption is simulated. Fixed slit widths are assumed. No background is included. Experimental displacement parameters, either isotropic or anisotropic, are taken into account in the calculation based on the crystal structure has been read in from a .cif or .res file.

Lattice Cavity Volume Calculations

The crystal structure of α -HNIW with the guest H₂O molecules removed was used to calculate the void volume in the crystal unit cells. By using a probe radius of 0.7 Å and grid spacing of 0.2 Å, the Mercury software (CCDC INC.) was employed for cavity volumes calculation (*i. e.* bounded by contact surfaces). Voids were calculated by using Contact Surface maps, which provides the volume that can be occupied by the full probe (including its radius) and thus gives an estimate of the volume that could be filled by solvent or guest molecules. The empty spaces (voids) in the anhydrate α -HNIW are 194.9 Å³, which approximately occupy 6.7% of unit cell volume in the unit cell was also calculated with the same probe parameters. The voids' volume of ε -HNIW is 43.2 Å³, which approximately occupy 3.0% of unit cell volume.

Electrostatic Potential Surface Density Map Calculations

Electrostatic potential surfaces of HNIW, CO_2 and N_2O were performed using the B3LYP functional with 6-311++g(d,p) basis set available in the Gaussian 03 suite of programs. All surfaces were normalized between -13 and 26 kJ/mol.

Packing Coefficient Calculations

Packing coefficient (C_k) provides a convenient method for comparing structures of different composition. The C_k of each sample was calculated with the equation: $C_k=Z*V_m/V_c$, where Z is the number of molecules presenting in the unit cell, V_m is the volume which is occupied by the molecule and V_c is the volume of the unit cell. Z and V_c were determined by single crystal X-ray diffraction. Molecular volumes (V_m)

were calculated with the Material Studio 6.0 Connolly surface module, which employs vdw factor of 1.0, Connolly radius of 1.0 Å, and Grid interval of 0.15 Å.

Oxygen Balance Calculations

Oxygen balance (OB) is an expression that is used to indicate the degree to which an energetic material (molecular formula is $C_aH_bN_cO_d$) can be complete conversion into neutral molecular components such as CO₂, H₂O, N₂, etc. upon detonation. The OB is calculated with the equation: OB%=-1600(2a+0.5b-d)/M_W, where a, b, d are the numbers of carbon, hydrogen, and oxygen atoms in the molecule, respectively, and M_W is the molecular weight.

Heat of Formation Calculations

The complex properties are calculated by treating them as a formulation of the two components in molar ratios. The heat of formation of a solid host-guest energetic crystal is the summing its lattice energy and the heat of formation of gaseous state molecules. The gas-phase heat of formation of the molecules are obtained by using the atomization method with PM6 calculations^[3]. The lattice energy is calculated by using COMPASS field with the field assigned charges, Ewald and atom-based summation methods for electrostatic and van de Waals interactions, respectively^[4]. Therefore, the solid-state heat of formation of ε -HNIW, HNIW/CO₂ and HNIW/N₂O are 365.4 kJ.mol⁻¹, 168.5 kJ.mol⁻¹ and 407.4 kJ.mol⁻¹, respectively.

Drop Weight Impact Sensitivity Tests

The impact sensitivity was determined with a WL-1 type impact sensitivity instrument. Approximately 30 mg of material for each sample was placed in steel anvils and then struck by a freefalling 2 kg drop weight. Samples were tested for a 50% probability to detonate (H_{50}) when impact from a specified height by using the up and down method. And a series of 25-30 trials is performed.

Friction Sensitivity Tests

The friction sensitivity was measured on a WM-1 pendulum friction apparatus. Approximately 30 mg of material for each sample was placed between steel anvils and hit by a 1.5 kg pendulum hammer fixed on a tilt angle of 90°. The gauge pressure was 3.92 MPa. The detonation probability (P) was used as an indication of friction sensitivity.

Electrostatic Spark Sensitivity Tests

For the analysis of sensitivity to electrostatic spark, approximately 20 mg of material for each sample is tested per time. The test energy (E) was taken to be the energy stored on the charged capacitor, as given by the formula $E=0.5CV^2$, where C is the capacitance of the capacitor (30000 pF), V is charge voltage. The electrostatic spark sensitivity E_{50} and V_{50} were the 50% probability of required ignition energy and voltage, respectively, which were obtained by utilizing the up and down method to test a series of 25-30 samples with varying charge voltage.

Shock Sensitivity Tests

Shock sensitivity is measured with polymer bonded explosives (PBX), usually by the card gap tests (CGT). The principle of this test is to subject the explosive under test to the action of a shock wave of known pressure generated by means of a calibrated donor charge and a shock wave pressure attenuator. In the CGT, the pressed HMX/binder (95/5) pellet was used as a donor explosive with a diameter of Φ 10mm*10mm, and a loading density of 1.860 g.cm⁻³. An acceptor explosive in a cylinder was a pressed HNIW-based PBX pellet sample with a diameter of Φ10mm*10mm. The sample was ε-HNIW/Estane (97/3)pellet and HNIW/N₂O/Estane (97/3) pellet with a loading density of 1.921 g.cm⁻³ and 1.879 g.cm⁻³, respectively. The shock sensitivity has been measured by this method as a thickness of aluminum cards corresponding to 50% explosion, L_{50} . The higher L_{50} , the more sensitive to shock. The results show that the shock sensitivity of ε -HNIW/Estane (97/3) and HNIW/N₂O/Estane (97/3) are 10.2 mm and 10.5 mm, respectively.

Vacuum stability tests

The dried and accurately weighed samples of HNIW (5.0 g) were placed in the heating tubes followed by its assembly and evacuation. Then immersing the heating tubes in a constant temperature bath at 100 °C for a period of 48 h. After that the volume of evolved gases were recorded. Three measurements were performed for each energetic material. Then the average value is taken as the final result. The results show that the released gases of ϵ -HNIW, HNIW/N₂O and HNIW/CO₂ after 100 °C /48 h vacuum stability experiment are 0.04, 0.72 and 1.08 ml/g/100°C/48h, respectively. Although the volume of evolved gases of host-guest energetic materials are higher than ϵ -HNIW, it still within the acceptable range.

Heat of explosion measurements

Calorimetric measurements of the heat of explosion of HNIW was performed with the adiabatic bomb calorimetry. The spherical bomb, has a volume of 10.1L, is placed in a polished steel calorimeter vessel containing distilled water. The calorimeter is surrounded by constant temperature jacket. The ϵ -HNIW/Estane (97/3) pellet and HNIW/N₂O/Estane (97/3) pellet with a diameter of Φ 25mm*30mm were used. And two measurements were performed for each explosive. Finally, the heat of explosion ϵ -HNIW/Estane (97/3) and HNIW/N₂O/Estane (97/3) are 6269 J.g⁻¹ and 6647 J.g⁻¹, respectively.

Detonation pressure measurements

The detonation pressure of HNIW was determined by manganin pressure gauges. The constant current is inputted to the manganin pressure gauges. The pressure gauge is a H-type miniature manganin component. The initial voltage and the voltage charge of the pressure gauge under the action of detonation wave are measured by an oscilloscope based on the piezoresistive effect, and then the detonation pressure is obtained. Five pressed pellets of ε -HNIW/Estane (97/3) and HNIW/N₂O/Estane (97/3) with a diameter of Φ 20mm*20mm were used to measure the detonation pressure. As shown in Table 2, the detonation pressure of HNIW/N₂O (35.1 GPa) is superior to ε -

HNIW (32.8 GPa). It should be pointed out that the experimental value of HNIW is obvious lower than calculated owing to the effect of HNIW-based formulation and low pressed pellet density.

Sample	ρ (g.cm ⁻³)	V ₀ /V	$\Delta V/V$	$\Delta V/V_0$	P (GPa)
ε-HNIW/Estane (97/3)	1.8910	0.081	0.063	0.778	32.8
HNIW/N ₂ O/Estane (97/3)	1.8601	0.077	0.064	0.826	35.1

Table S2. Detonation pressure of ε -HNIW and HNIW/N₂O

Notes: D represent the density of pressed pellet; V_0 represent the initial electric pressure of the manometer measured by oscilloscope when constant current through manganin pressure gauges; V represent the electric pressure of the manometer measured by oscilloscope under the action of detonation wave; ΔV represent the change of voltage under the action of detonation wave measured by manganin pressure gauges; P represent the detonation pressure.

Combustion tests

For combustion experiments, weigh 50 mg of sample and place it on glass sheet. The combustion rate of ε -HNIW and HNIW/N₂O were captured by high-speed video recording (HSVR, Photron, FASTCAM-APX RS2) after ignition. The different in burning speed can be acquired by comparing the burning time. The combustion flame of HNIW/N₂O is stronger than ε -HNIW after ignition. And the average combustion rate of HNIW/N₂O (54.3 mg.s⁻¹) is slightly faster than ε -HNIW (47.1 mg.s⁻¹), indicating better combustion properties of HNIW with incorporating N₂O than raw ε -HNIW.



SI 2. Morphology of gas inclusion host-guest energetic materials of HNIW

Figure S2. Typical habit morphology of HNIW/CO₂: (a) Slow evaporate crystallization; (b) Solvent/anti-solvent crystallization.



Figure S3. Typical habit morphology of HNIW/N₂O: (a) Slow evaporate crystallization; (b) Solvent/anti-solvent crystallization.



SI 3. IR spectra of gas inclusion host-guest energetic materials

Figure S4. Full range (500-4000 cm⁻¹) IR spectra of ϵ -HNIW, α -HNIW, HNIW/CO₂ and HNIW/N₂O (from bottom to top)



Figure S5. Zoomed in (2200-2400 cm⁻¹) IR spectra of ϵ -HNIW, α - HNIW, HNIW/CO₂ and HNIW/N₂O (from bottom to top)



Figure S6. Zoomed in (500-1750 cm⁻¹) IR spectra of ϵ -HNIW, α -HNIW, HNIW/CO₂ and HNIW/N₂O (from bottom to top)



Figure S7. Zoomed in (2975-3100 cm⁻¹) IR spectra of ϵ -HNIW, α -HNIW, HNIW/CO₂ and HNIW/N₂O (from bottom to top)



Figure S8. Zoomed in (1520-1700 cm⁻¹) IR spectra of ϵ -HNIW, α -HNIW, HNIW/CO₂ and HNIW/N₂O (from bottom to top)



SI 4. Powder X-ray diffraction of gas inclusion host-guest energetic materials

Figure S9. Powder patterns of HNIW/CO₂ and simulated structure of HNIW/CO₂ from the CIF (from bottom to top)



Figure S10. Powder patterns of HNIW/N₂O and simulated structure of HNIW/N₂O from the CIF (from bottom to top)



Figure S11. Powder patterns of simulated structure of α -, β -, γ -, ϵ -HNIW from CIF (00-052-2431, 00-052-2342, CCDC 117779, 00-050-2045, respectively)



SI 5. ORTEP diagram of gas inclusion host-guest energetic materials of HNIW

Figure S12. ORTEP diagram for HNIW/CO₂ collected at 298 K with thermal ellipsoids of 50% probability.



Figure S13. ORTEP diagram for HNIW/N₂O collected at 298 K with thermal ellipsoids of 50% probability.

SI 6. The hydrogen bonding interaction of gas inclusion host-guest energetic materials

Table S3. Hydrogen bond lengths (Å) and bond angles (°) for HNIW/N₂O and HNIW/CO₂

		d(D–H),	$d(H \cdots A),$	$d(D \cdots A),$	Angle(D–H····A),
	<i>D</i> –п…А	Å	Å	Å	0
HNIW/CO ₂	С3-Н3…О13	0.980	2.725	3.219	116.88
	C4–H4…O13	0.981	2.547	3.116	111.76
HNIW/N ₂ O	С3-Н3…О13	0.980	2.699	3.185	115.63
	C4–H4…O13	0.980	2.533	3.086	111.02
	C3–H3…N14	0.980	2.699	3.185	115.63
	C4–H4…N14	0.980	2.533	3.086	111.02



Figure S14. The Hydrogen bonding interaction of HNIW/CO₂ (a) and HNIW/ N_2O (b)

SI 7. Differential scanning calorimetry-thermogravimetry of gas inclusion hostguest energetic materials of HNIW



Figure S15. Typical DSC-TG traces of ε -HNIW (The blue line represents the weight loss percent and the black line represents heat flow)



Figure S16. Typical DSC-TG traces of α -HNIW (The blue line represents the weight loss percent and the black line represents heat flow)



Figure S17. Typical DSC-TG traces of HNIW/CO₂ (The blue line represents the weight loss percent and the black line represents heat flow)



Figure S18. Typical DSC-TG traces of $HNIW/N_2O$ (The blue line represents the weight loss percent and the black line represents heat flow)

SI 8. In situ Powder X-ray diffraction of ε-HNIW and gas inclusion host-guest energetic materials of HNIW



Figure S19. In-situ PXRD patterns of ε -HNIW (a) and HNIW/N₂O (b) with increasing temperature form 30 °C to 185 °C (from bottom to top, D-30 °C represent the temperature back to 30 °C)



Figure S20. Thermally induced solid-state phase transition of ε -HNIW and HNIW/N₂O to γ -HNIW as a function of temperature. The phase transition of HNIW/N₂O needs higher initial temperature and much slower than ε -HNIW.

SI 9. Thermogravimetry-infrared spectroscopy of gas inclusion host-guest energetic materials of HNIW



Figure S21. The IR signal spectrum of ε -HNIW, HNIW/CO₂ and HNIW/N₂O (from bottom to top)







Figure S22. The three-dimensional IR spectra of gas inclusion host-guest energetic crystal thermal decomposition gas products, (a) ϵ -HNIW, (b) HNIW/CO₂ and (c) HNIW/N₂O.

SI 10. Combustion experiments of ε-HNIW and gas inclusion host-guest energetic materials of HNIW



Figure S23. Selected frames from high-speed video of ϵ -HNIW combustion test



Figure S24. Selected frames from high-speed video of HNIW/N₂O combustion test

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