Supplementing Information

Hunting for Advanced High-Energy-Density Materials with Well-Balanced Energy and Safety through Energetic Host–Guest Inclusion Strategy

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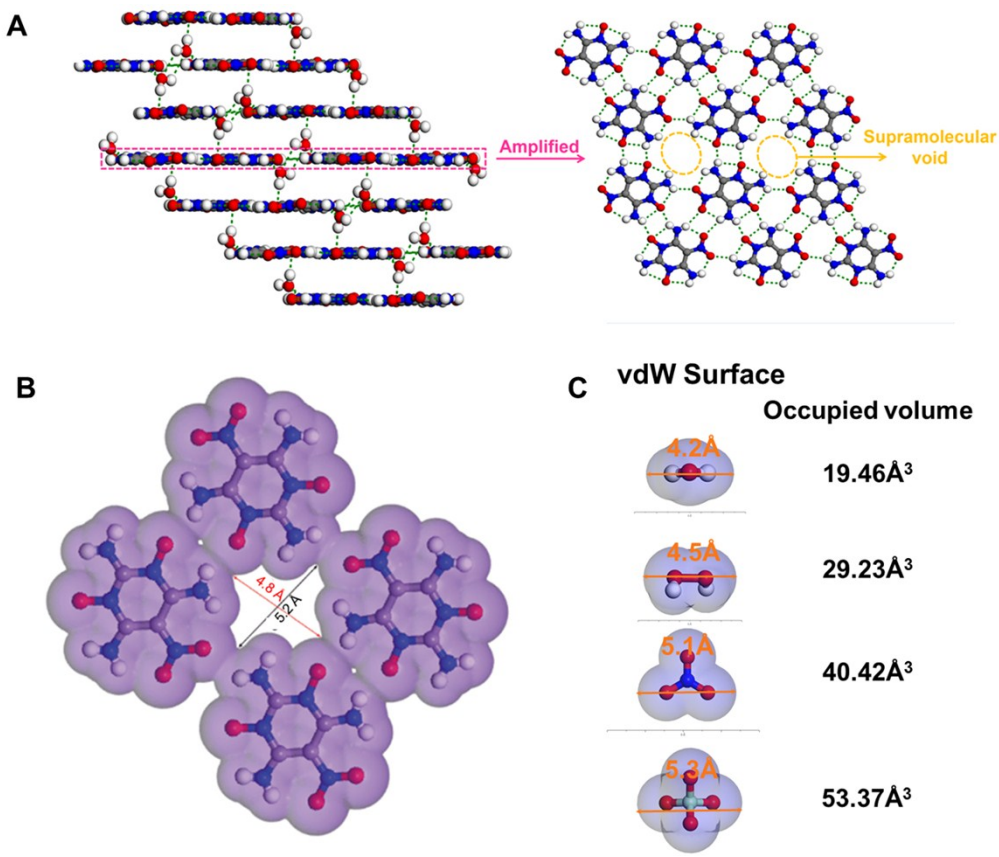


Fig. S1. Crystal structural analysis on ICM-102 monohydrate. (A) 3D crystal structure of ICM-102 monohydrate (left) and 2D molecular sheet of ICM-102 monohydrate in crystal (right), (B) the size of supramolecular void fabricated by four ICM-102 molecules, (C) the sizes of water (H_2O), hydrogen peroxide (H_2O_2), nitrate anion (NO_3^-) and perchloric acid anion (ClO_4^-).

Table S1. Crystallographic data for HGI-1. Single crystal X-ray diffraction data was collected on an Oxford Xcalibur diffratometer with Mo-K_α monochromated radiation (λ =0.71073 Å). The crystal structures were solved by direct methods.[1] The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL script package. All non-hydrogen atoms were refined anisotropoically.

CCDC	1831628
Formula	$C_4H_6N_6O_4 \cdot 0.5H_2O_2$
Mr	219.16
Crystal system	monoclinic
Space group	C 2/c
a [Å]	14.128(7)
b [Å]	14.696(8)
c [Å]	7.415(4)
α [°]	90
β [°]	98.866(6)
γ [°]	90
V [Å^3]	1521.1(14)
Z	8
T(K)	100
ρ[g cm^{-3}]	1.914
Mu [mm^{-1}]	0.174
F(000)	904
θ [°]	2.012 to 27.480
index range	$-18 \leq h \leq 18$
	$-18 \leq k \leq 18$
	$-9 \leq l \leq 9$
reflections collected	4861
independent reflections	1714 [R_{int} = 0.0339, R_{sigma} = 0.0436]
data/restraints/parameters	1714/14/157
GOF on F^2	1.121
*R*1 [I>2σ(I)]	0.0535
*wR*2 [I>2σ(I)]	0.1555
*R*1(all data)	0.0718
*wR*2(all data)	0.1903
largest diff. peak and hole [e Å^{-3}]	0.51/-0.33

Table S2. Crystallographic data for HGI-2. Single crystal X-ray diffraction data was collected on an Oxford Xcalibur diffratometer with Mo-K_α monochromated radiation (λ =0.71073 Å). The crystal structures were solved by direct methods.[1] The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL script package. All non-hydrogen atoms were refined anisotropoically.

CCDC	1887848
Formula	$C_4H_6N_6O_4{\bullet}HNO_3$
Mr	265.17
Crystal system	orthorhombic
Space group	Pbca
a [Å]	11.239(3)
b [Å]	11.869(3)
c [Å]	13.511(3)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	1802.2(7)
Z	8
T(K)	173
ρ[g cm^{-3}]	1.955
Mu [mm^{-1}]	0.184
F(000)	1088
θ [°]	3.015 to 25.123
index range	-13≤ h ≤ 13
	-14≤ k ≤ 13
	-16≤ l ≤ 13
reflections collected	12301
independent reflections	1577 [R_{int} =0.0801, R_{sigma} = 0.0507]
data/restraints/parameters	1577/21/191
GOF on F^2	1.042
*R*1 [I>2σ(I)]	0.0447
*wR*2 [I>2σ(I)]	0.1137
*R*1(all data)	0.0625
*wR*2(all data)	0.1268
largest diff. peak and hole [e Å^{-3}]	0.492/-0.295

Table S3. Crystallographic data for HGI-3. Single crystal X-ray diffraction data was collected on an Oxford Xcalibur diffratometer with Mo-K_α monochromated radiation (λ =0.71073 Å). The crystal structures were solved by direct methods.[1] The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL script package. All non-hydrogen atoms were refined anisotropoically.

CCDC	1887847
Formula	$C_4H_6N_6O_4{\cdot}HClO_4$
Mr	302.61
Crystal system	orthorhombic
Space group	Pbca
a [Å]	12.410(2)
b [Å]	9.9590(19)
c [Å]	16.305(3)
α [°]	90
β [°]	90
γ [°]	90
V [Å^3]	2015.2(7)
Z	8
T(K)	173
ρ[g cm^{-3}]	1.995
Mu [mm^{-1}]	0.439
F(000)	1232
θ [°]	2.99 to 22.48
index range	$-14 \leq h \leq 15$
	$-12 \leq k \leq 12$
	$-20 \leq l \leq 12$
reflections collected	9864
independent reflections	2146 [R_{int} =0.0800, R_{sigma} = 0.0600]
data/restraints/parameters	2146/1/176
GOF on F^2	1.045
*R*1 [I>2σ(I)]	0.0456
*wR*2 [I>2σ(I)]	0.1001
*R*1(all data)	0.0685
*wR*2(all data)	0.1124
largest diff. peak and hole [e Å^{-3}]	0.405/-0.467

Table S4. The specific parameters of hydrogen bonds of HGI-1.

Donor-H···Acceptor	D-H (Å)	H···A (Å)	D···A (Å)	∠D-H···A (°)
N(1)-H(1A)···O(2)	0.88	2.26	2.594(3)	103
N(1)-H(1A)···O(4)	0.88	2.11	2.822(3)	137
N(1)-H(1B)···O(1)	0.88	2.29	2.625(3)	102
N(1)-H(1B)···O(5)	0.88	2.02	2.834(5)	152
N(2)-H(2A)···O(1)	0.88	2.24	2.610(3)	105
N(2)-H(2A)···O(2)	0.88	1.92	2.716(3)	149
N(2)-H(2B)···O(3)	0.88	2.01	2.618(3)	125
N(2)-H(2B)···O(3)	0.88	2.30	3.133(3)	158
N(4)-H(4A)···O(4)	0.85(3)	2.03(3)	2.609(3)	125(2)
N(4)-H(4A)···O(5)	0.85(3)	2.43(3)	3.119(5)	140(2)
N(4)-H(4B)···O(2)	0.90(3)	2.21(3)	2.593(3)	105(2)
N(4)- H(4B)···O(1)	0.90(3)	1.94(3)	2.757(3)	150(3)

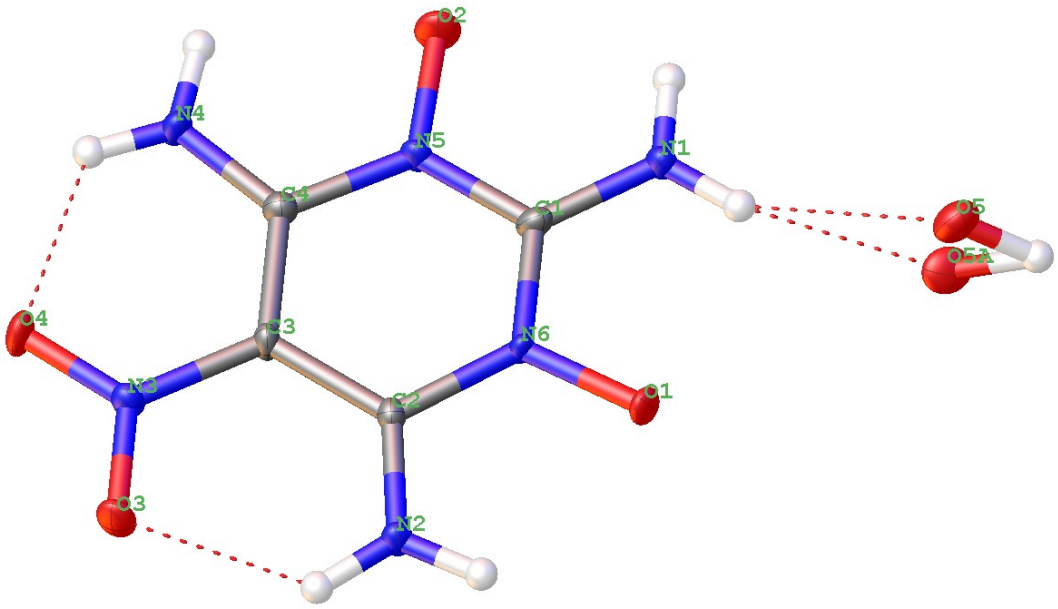


Table S5. The specific parameters of hydrogen bonds of HGI-2.

Donor-H···Acceptor	D-H (Å)	H···A (Å)	D···A (Å)	∠D-H···A (°)
N(2)-H(2A)···O(3)	0.88(4)	2.20(3)	2.582(3)	106(3)
N(2)-H(2A) ···O(1)	0.88(4)	2.59(3)	3.198(3)	127(3)
N(2)-H(2A)···O(2)	0.88(4)	2.59(4)	3.461(3)	169(2)
N(2)-H(2B)···O(2)	0.90(4)	1.94(4)	2.618(3)	130(3)
N(2)-H(2B)···O(6)	0.90(4)	2.57(3)	3.212(3)	129(3)
N(2)-H(2B)···O(7)	0.90(4)	2.43(4)	3.149(3)	137(3)
N(2)-H(2B)···N(1)	0.90(4)	2.57(4)	2.924(3)	104(2)
O(4)-H(4)···O(5)	0.84(4)	1.77(4)	2.601(3)	169(4)
N(4)-H(4A)···O(4)	0.87(2)	2.39(4)	2.681(3)	100(3)
N(4)-H(4A)···N(6)	0.87(2)	2.39(4)	2.843(3)	113(4)
N(4)-H(4B)···O(3)	0.86(2)	2.35(4)	2.654(3)	101(2)
N(6)-H(6A)···O(4)	0.82(2)	2.20(3)	2.552(3)	106(3)
N(6)-H(6A)···N(4)	0.82(2)	2.14(3)	2.843(3)	143(3)
N(6)-H(6B)···O(1)	0.90(4)	1.94(3)	2.597(3)	129(3)
N(6)-H(6B)···N(1)	0.90(4)	2.59(3)	2.907(3)	102(2)
N(6)-H(6B)···O(5)	0.90(4)	2.28(3)	3.041(3)	142(3)

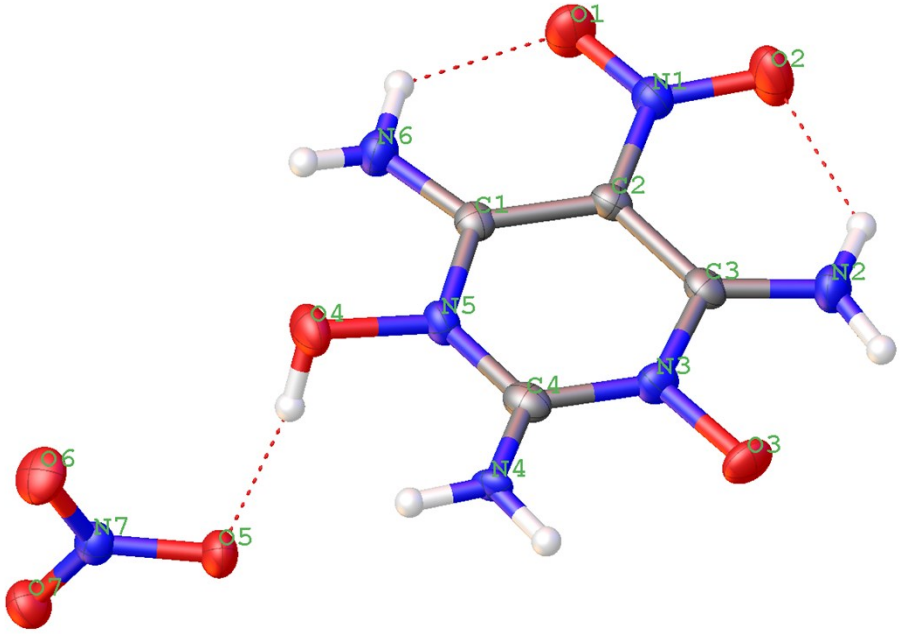
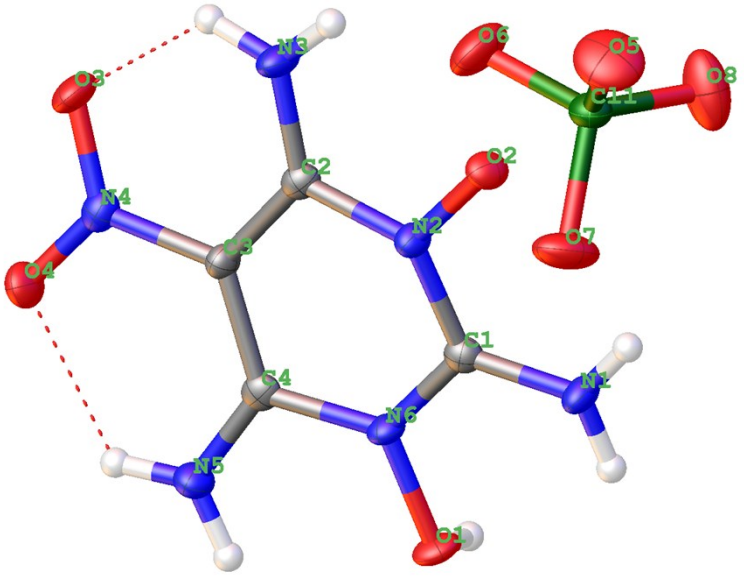


Table S6. The specific parameters of hydrogen bonds of HGI-3.

Donor-H···Acceptor	D-H (Å)	H···A (Å)	D···A (Å)	∠D-H···A (°)
O(1)-H(1)···O(2)	0.87(3)	1.59(3)	2.465(3)	175(3)
O(1)-H(1)···N(2)	0.87(3)	2.44(3)	3.180(3)	144(3)
N(1)-H(1A)···O(2)	0.86	2.33	2.653(3)	102
N(1)-H(1A)···O(7)	0.86	2.09	2.952(3)	175
N(1)-H(1B)···O(1)	0.86	2.32	2.642(3)	103
N(1)-H(1B)···O(6)	0.86	2.10	2.905(3)	155
N(3)-H(3A)···O(2)	0.86	2.21	2.591(3)	106
N(3)-H(3A)···O(2)	0.86	2.18	2.824(3)	131
N(3)-H(3A)···O(5)	0.86	2.46	3.160(3)	138
N(3)-H(3B)···O(3)	0.86	2.01	2.598(3)	125
N(3)-H(3B)···O(7)	0.86	2.48	3.057(3)	125
N(5)-H(5A)···O(1)	0.86	2.27	2.636(3)	106
N(5)-H(5A)···O(8)	0.86	2.57	3.036(3)	115
N(5)-H(5A)···O(3)	0.86	2.26	2.842(3)	125
N(5)-H(5B)···O(4)	0.86	2.02	2.616(3)	126



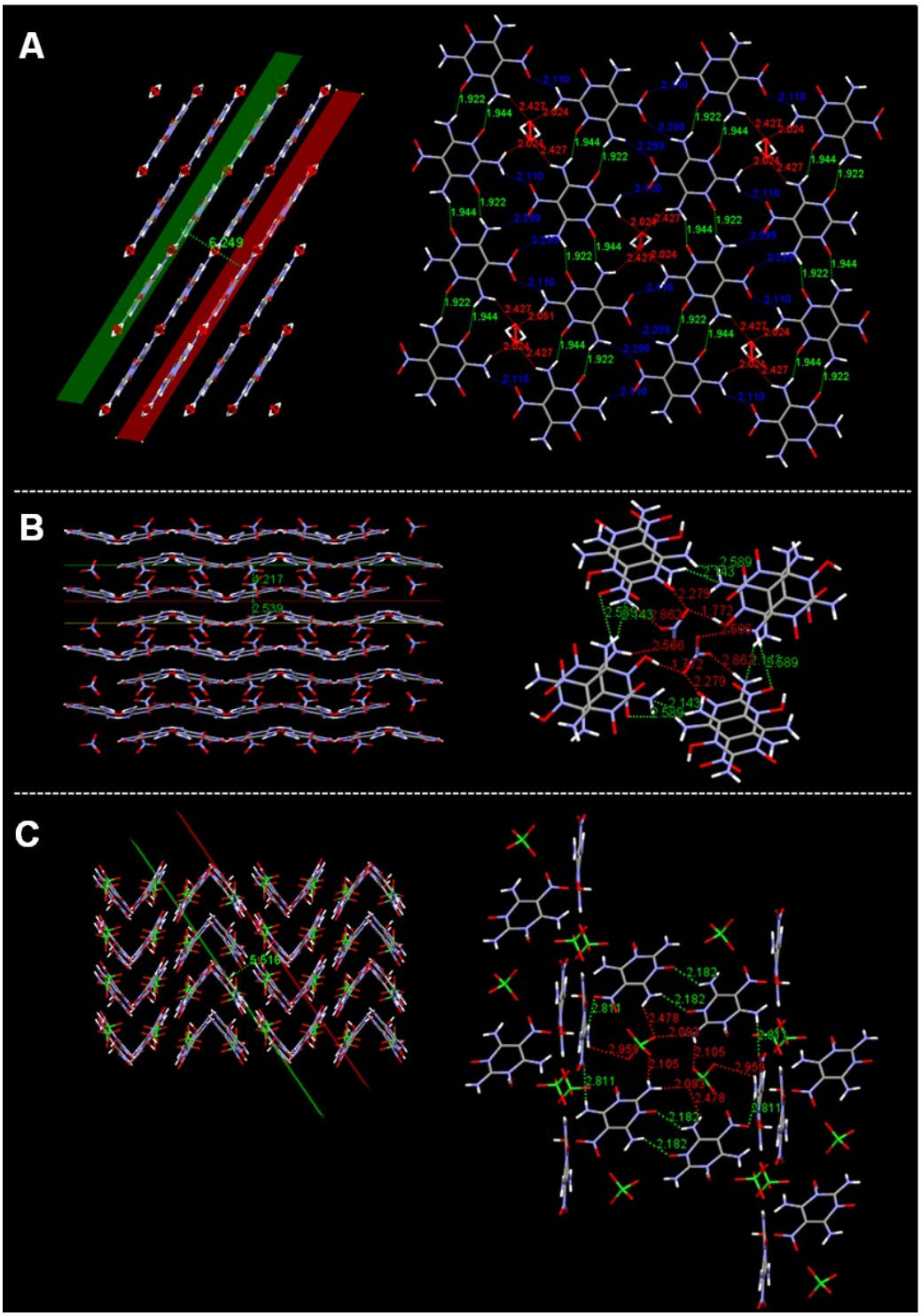


Figure S2. Crystal structural analysis on HGI-1, HGI-2 and HGI-3. (A) Interlamellar spacing and hydrogen bonds in the 2D molecular sheet in HGI-1 crystal. (B) Interlamellar spacing and hydrogen bonds in the 2D molecular sheet in HGI-2 crystal. (C) Interlamellar spacing and hydrogen bonds in the 2D molecular sheet in HGI-3 crystal.

Table S7. Physical properties of HGI-1, HGI-2, HGI-3 and the comparison with FOX-7, RDX, HMX and ε-CL-20.

	T_d[a] (°C)	ρ[b] (g cm^{-3})	$\Delta_f H_m$[c] (kJ mol^{-1})	P[d] (GPa)	v_D[e] (m s^{-1})	IS[f] (J)	FS[g] (N)	OB[h] (%)
HGI-1	186	1.915[i]	-40.3	34.8	9124	24	>360	-47.5
HGI-2	177	1.955[j]	-56.15	39.1	9251	8	168	-27.2
HGI-3	233	1.995[j]	1.24	42.5	9495	14	216	-15.9
FOX-7	220	1.88	-118.9	35.9	9000	24.7	>360	-21.6
RDX	210	1.80	86.3	34.9	8795	7.5	120	-21.6
HMX	279	1.90	116.1	39.2	9144	7.5	120	-21.7
ε-CL-20	215	2.04	365.4	46.7	9445	4	48	-11.0

[a)] Onset decomposition temperature; [b)] Measured density by using a gas pycnometer at 298 K; [c)] Heat of formation; [d)] Detonation pressure calculated by using EXPLO5/6.02; [e)] Detonation velocity calculated by using EXPLO5/6.02; [f)] Impact sensitivity evaluated by a standard BAM fall-hammer method; [g)] Friction sensitivity evaluated by a BAM friction tester; [h)] Oxygen balance based on CO_2 for $C_aH_bN_cO_dCl_e$: OB (%) =1600×(d-a-(b-e)/2)/*Mw*. [i)] Crystal density at 100 K; [j)] Crystal density at 173 K.

The theoretical calculations on the solid-state heat of formation of HGI-1, HGI-2 and HGI-3. Because these three host-guest inclusion materials all contain two components (ICM-102 and the corresponding oxidant molecules) in their crystals, we consider them as a whole system to calculated their solid heat of formations ($\Delta_f H$). Detailed calculation processes are presented by the following example of HGI-1.

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of scripts[2]. The geometric optimization and frequency analyses were completed by using the B3LYP functional with the 6-31+G** basis set. Single energy points were calculated at the MP2/6-311++G** level of theory. For all of the compounds, the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The isodesmic reaction was carried out to obtain the gas-phase heat of formation of molecule ICM-102 (Fig. S3A). The gas-phase enthalpies of the building-block molecules were obtained by using the atomization method with the G2 ab initio calculations. For HGI-1, the solid-state heat of formation (HOF, $\Delta_f H°$) was calculated based on a Born–Haber energy cycle[3] (Fig. S3B) with following simplified calculation Equation:

$$\Delta_f H° \text{ (HGI-1, 298K)} = \Delta_f H°\text{(HGI-1, 298K)} + 0.5\Delta_f H°(H_2O_2, 298K) - \Delta H_{sub}$$

The heat of sublimation can be estimated using the DFT method with the GGA-RPBE (revised Perdew-Burke-Ernzerhof) exchange-correlation functional in Dmol3 program[4-5].

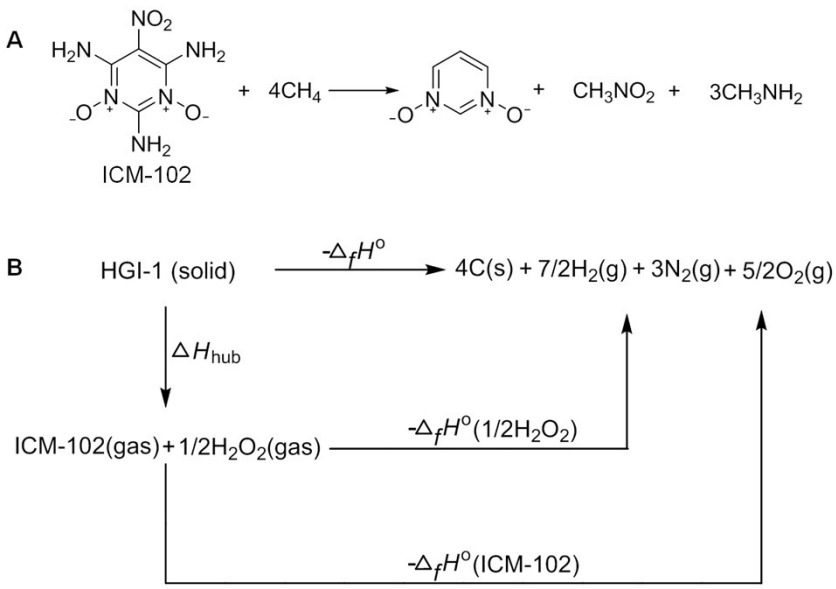


Fig. S3. **Theoretical calculations on the solid-state heat of formation of HGI-1.** (A) Isodesmic reaction of molecule ICM-102. (B) Born–Haber cycle for the formation of HGI-1.

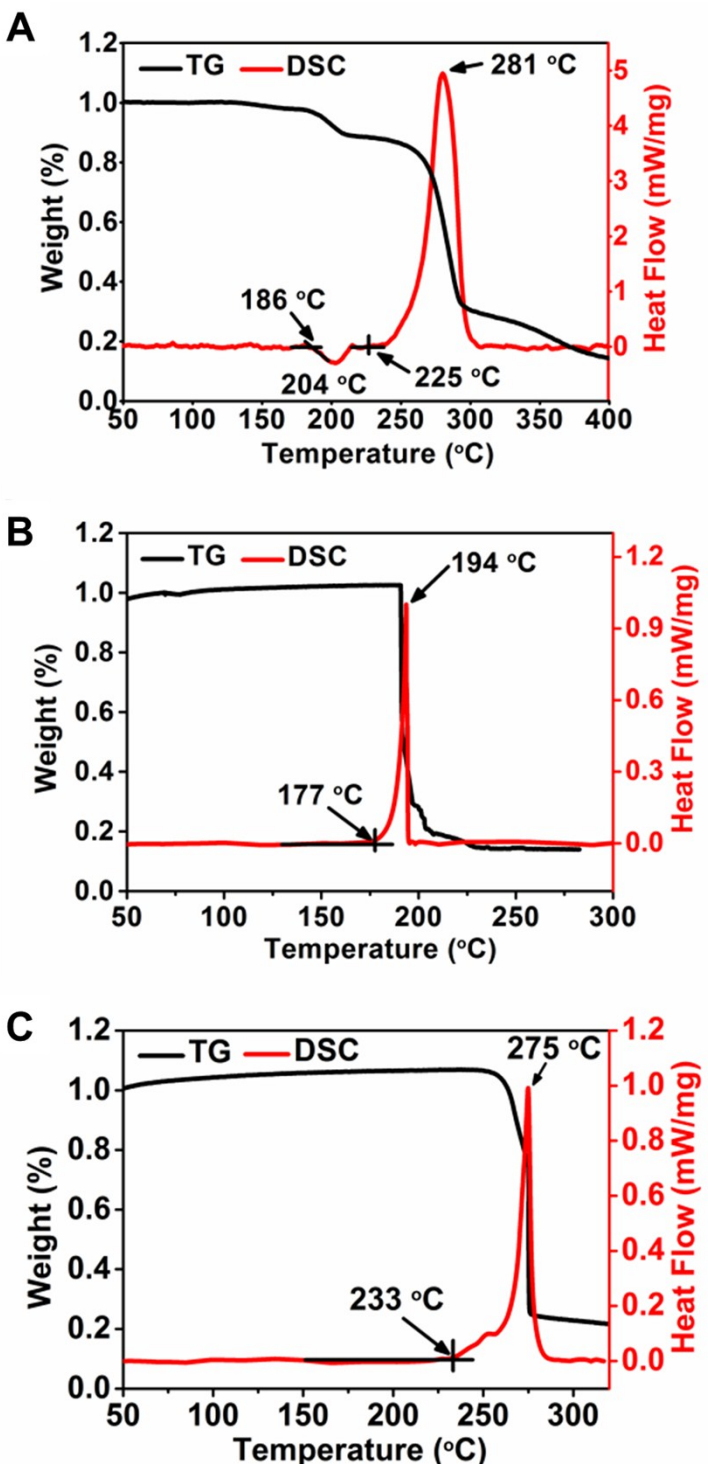


Fig. S4. Thermogravimetry (TG) and differential scanning calorimetry (DSC) curves of HGI-1, HGI-2 and HGI-3. (A) Thermogravimetry (TG) and differential scanning calorimetry (DSC) curves of HGI-1. (B) Thermogravimetry (TG) and differential scanning calorimetry (DSC) curves of HGI-2. (C) Thermogravimetry (TG) and differential scanning calorimetry (DSC) curves of HGI-3.

Table S8. Effect of replacing ammonium perchlorate (AP) with HGI-3 on the energy characteristics of GAP (GAP 10 % / Al 5 % / AP 60 % / RDX 25 %) propellant[6].

GAP (%)	Al (%)	AP (%)	RDX (%)	HGI-3 (%)	I_{sp}/(N s kg^{-1})	C*/(m s^{-1})	T_c/K	M_c
10	5	60	25	0	2568.35	1477.7	3359.9	25.88
10	5	55	25	5	2583.45	1491.3	3389.4	25.68
10	5	50	25	10	2593.06	1504.8	3410.8	25.47
10	5	45	25	15	2599.24	1517.1	3425.2	25.25
10	5	40	25	20	2602.77	1528.1	3432.9	25.01
10	5	35	25	25	2604.34	1537.7	3434.6	24.76
10	5	30	25	30	2604.24	1546.0	3430.7	24.51
10	5	25	25	35	2602.77	1553.1	3421.5	24.25
10	5	20	25	40	2600.22	1558.9	3407.8	23.98
10	5	15	25	45	2596.49	1563.6	3389.5	23.72

References

1. Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*, Hemisphere Publishing Corp, New York, **1989**.

2. Frisch, M. J. *et al.* Gaussian 09, Revision A.01; Gaussian, Inc.: Wallingford, CT, **2009**.

3. Cox, J. D.; Wagman, D. D.; Medvedev, V. A. *CODATA Key Values for Thermodynamics*, Hemisphere Publishing Corp, New York, **1989**.

4. B. Delley, *J. Chem. Phys.* 1990, **92**, 508-517.

5. B. Delley, *J. Chem. Phys.* 2000, **113**, 7756-7764.

6. M. Li, F. -Q. Zhao, Y. Luo, S. -Y. Xu and E. -G. Yao, *Chin. J. Energy Mater.,* 2014, **22**, 286-290.