Supporting Information

Synthesis and characterization of the promising insensitive energetic salts based on 3-amino-5-hydrazinopyrazole

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Section 1. Materials and instrumentations

All the chemical reagents and solvents were purchased from the reagents company of Aladdin and were used as received without further treatment. Elemental analysis was performed with a Flash EA 1112 fully automatic trace element analyzer. Fourier Transform Infrared Spectroscopy (FT-IR) spectra was recorded on an IRPrestige-21 spectrometer using KBr pellets from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

3-amino-5-hydrazinopyrazole dihydrochloride (1) IR (KBr, cm^{-1}) : ν=3419, 3105, 1633, 1528, 1435, 1269, 1089, 920, 796, 705; **MS** (ESI^+): m/z = 114.09 [$C_3H_8N_5^+$]; **MS** (ESI^-): m/z =35.00 [Cl^-]. **$C_3H_9Cl_2N_5$** (186.0): calcd C 19.37, H 4.88, N 37.64; found C 19.33, H 4.91, N 37.68.

3-amino-5-hydrazinopyrazole dinitrate (**2**) **Yield**: 0.39 g, 82%; **IR** (KBr, cm^{-1}) : ν=3428, 1624, 1498, 1384, 1083, 956, 825, 553; MS (ESI^+): m/z = 114.09 [$C_3H_8N_5^+$]; MS (ESI^-): m/z =61.99 [NO_3^-]. **$C_3H_9Cl_2N_5$** (239.1): calcd C 15.07, H 3.79, N 41.00; found C 15.06, H 3.83, N 41.03.

3-amino-5-hydrazinopyrazole dipicrate (**3**) **Yield**: 0.835 g, 73%; **IR** (KBr, cm^{-1}) : ν=3463, 3326, 3140, 2928, 2691, 1605, 1539, 1332, 1168, 1084, 917; MS (ESI^+): m/z = 114.09 [$C_3H_8N_5^+$]; MS (ESI^-): m/z =227.99 [$C_6H_2N_3O_7^-$]. **$C_{15}H_{13}N_{11}O_{14}$** (571.3): calcd C 31.53, H 2.29, N 26.97; found C 31.58, H 2.30, N 26.93.

3-amino-5-hydrazinopyrazole ditrinitroresorcinate (4) Yield: 0.908 g, 75%; **IR** (KBr, cm^{-1}) : ν=3581, 3483, 3384, 3185, 1645, 1541, 1377, 1085, 928, 780, 693; **MS** (ESI^+): m/z = 114.07 [$C_3H_8N_5^+$]; MS (ESI^-): m/z =243.98 [$C_6H_2N_3O_8^-$]. **$C_{15}H_{13}N_{11}O_{16}$** (603.3): calcd C 29.86, H 2.17, N 25.54; found C 29.82, H 2.19, N 25.50.

3-amino-5-hydrazinopyrazole di(5-nitramino-tetrazole) (**5**) Yield: 0.582 g, 78%; **IR** (KBr, cm^{-1}) : ν=3438, 3151, 2953, 2732, 1672, 1616, 1533, 1433, 1335, 989, 744; **MS** (ESI^+): m/z = 114.07 [$C_3H_8N_5^+$]; MS (ESI^-): m/z =129.01 [$CHN_6O_2^-$] **$C_5H_{11}N_{17}O_4$** (373.3): calcd C 16.09, H 2.97, N 63.79; found C 16.09, H 2.93, N 63.84.

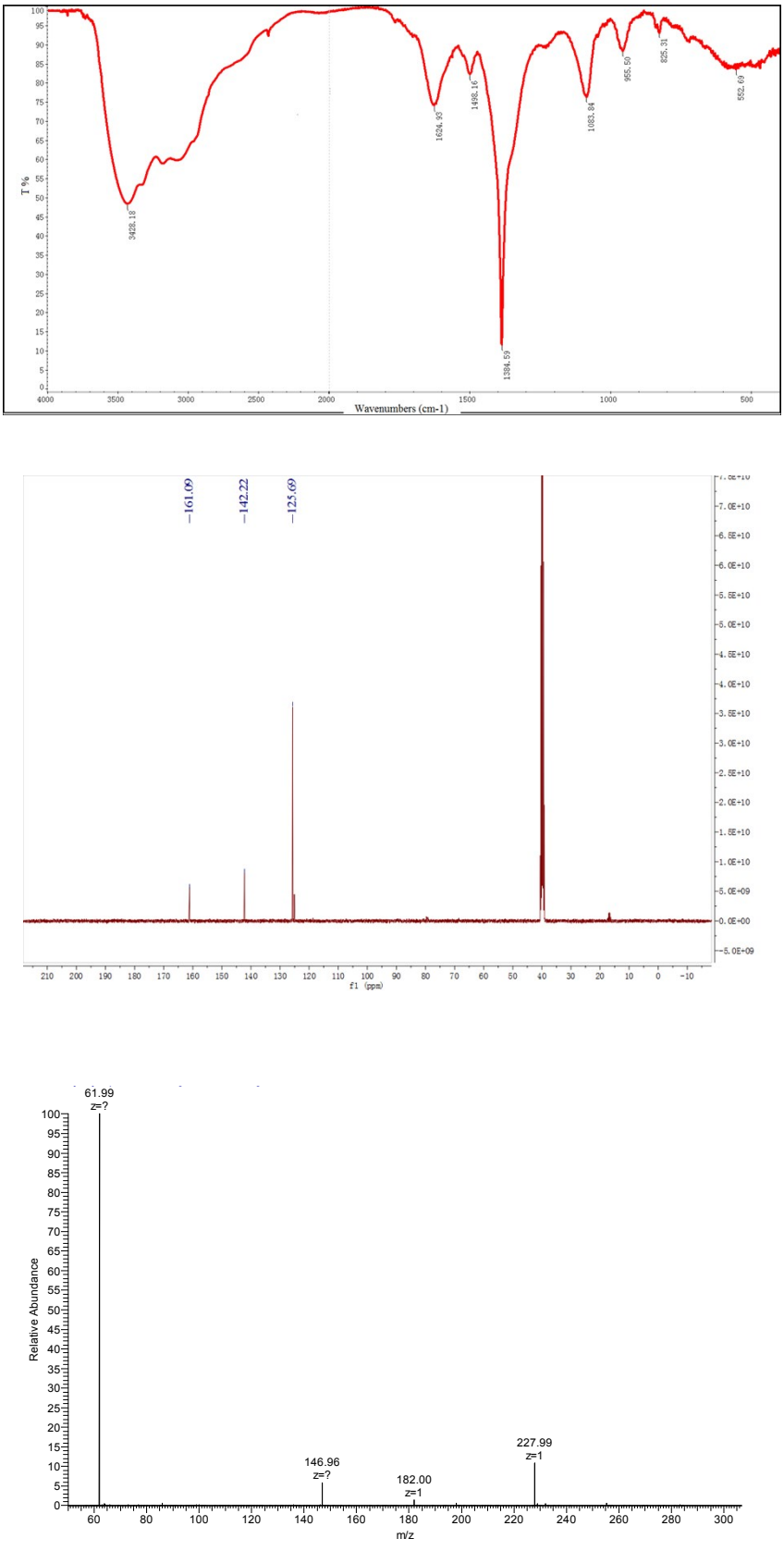
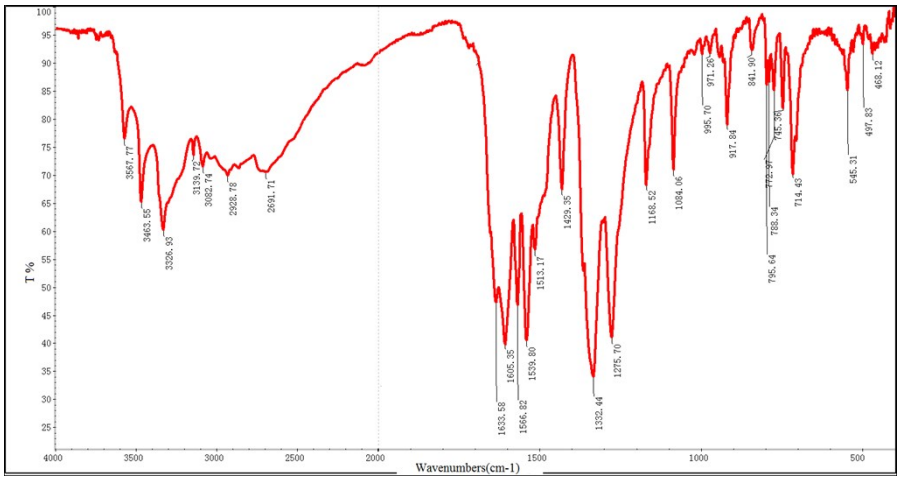
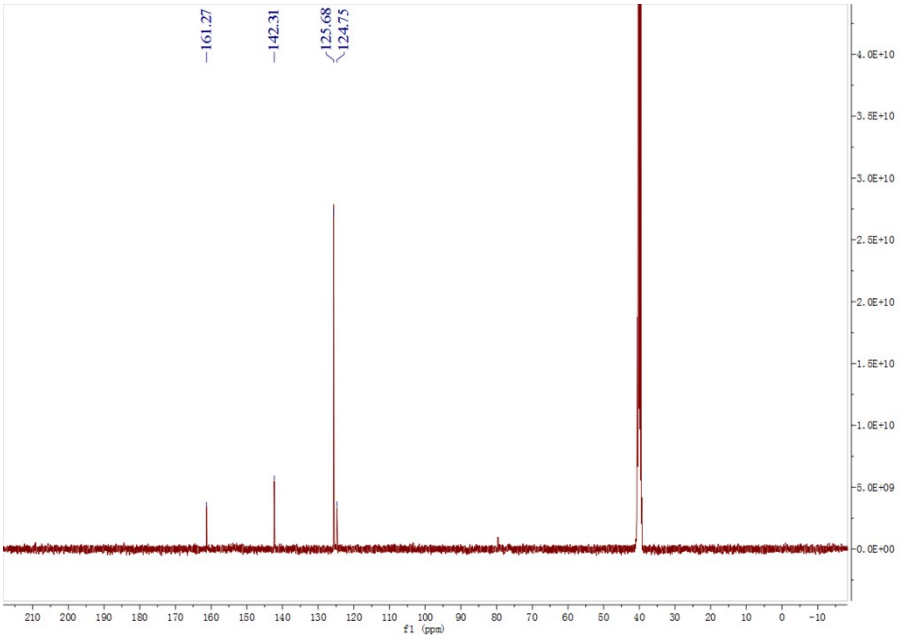


Figure S1. IR (top), ^{13}C NMR, and MS (bottom) Spectrum of **2**.





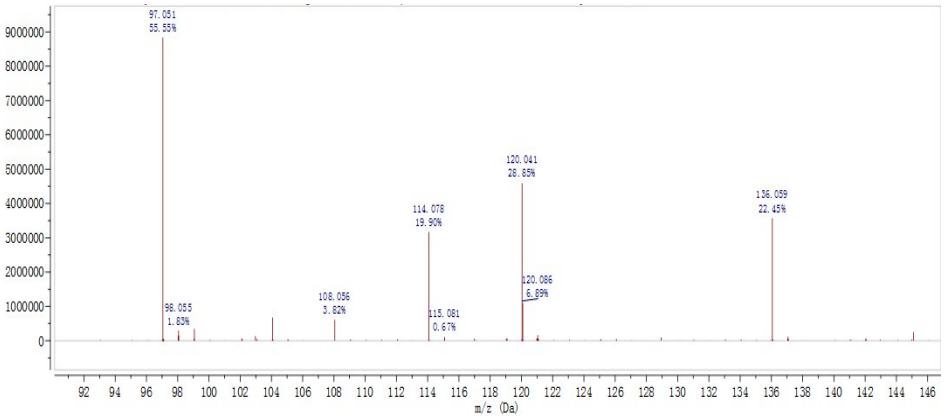


Figure S2. IR (top), ^{13}C NMR, and MS (bottom) Spectrum of **3**.

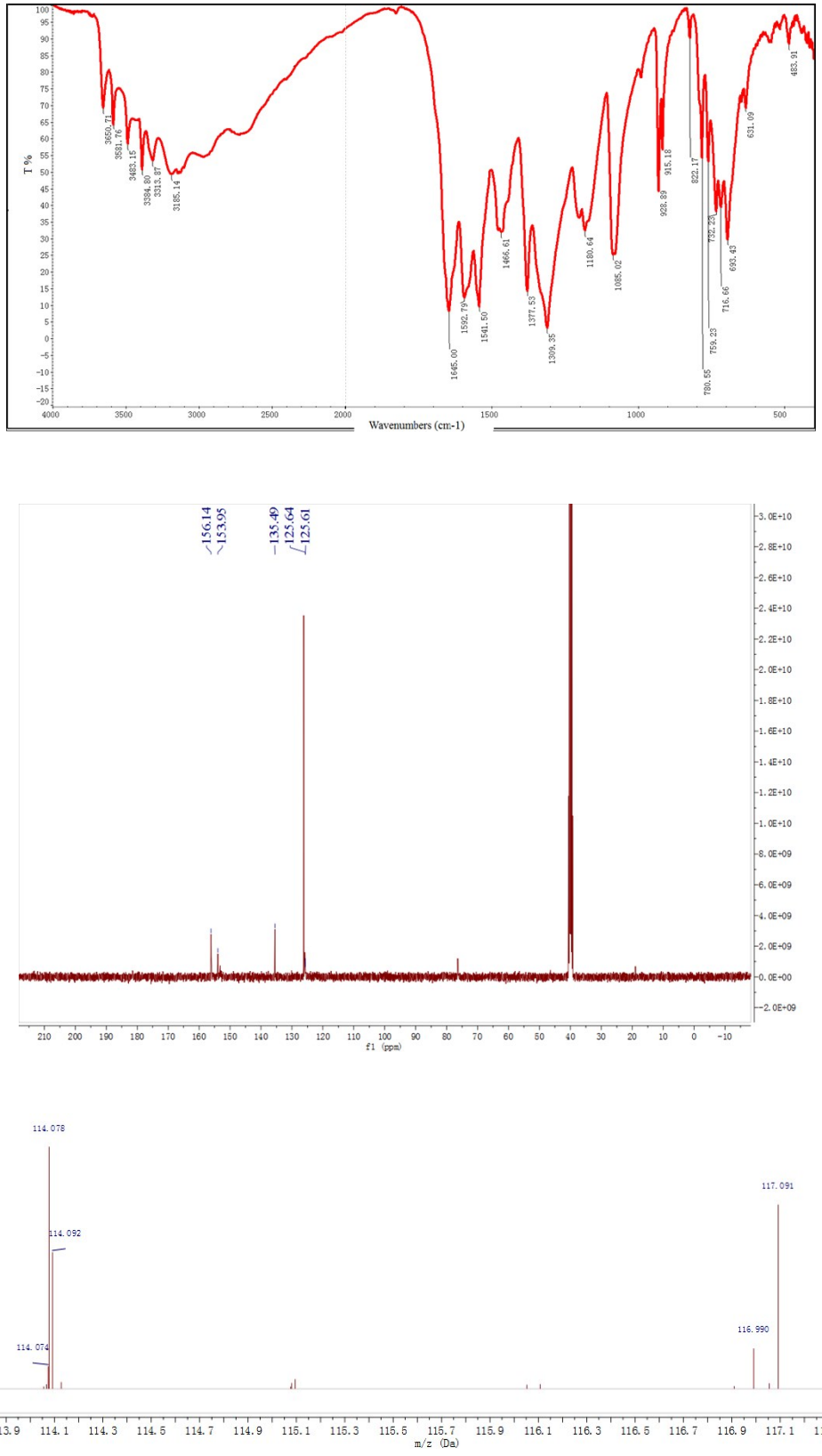


Figure S3. IR (top), ^{13}C NMR, and MS (bottom) Spectrum of **4**.

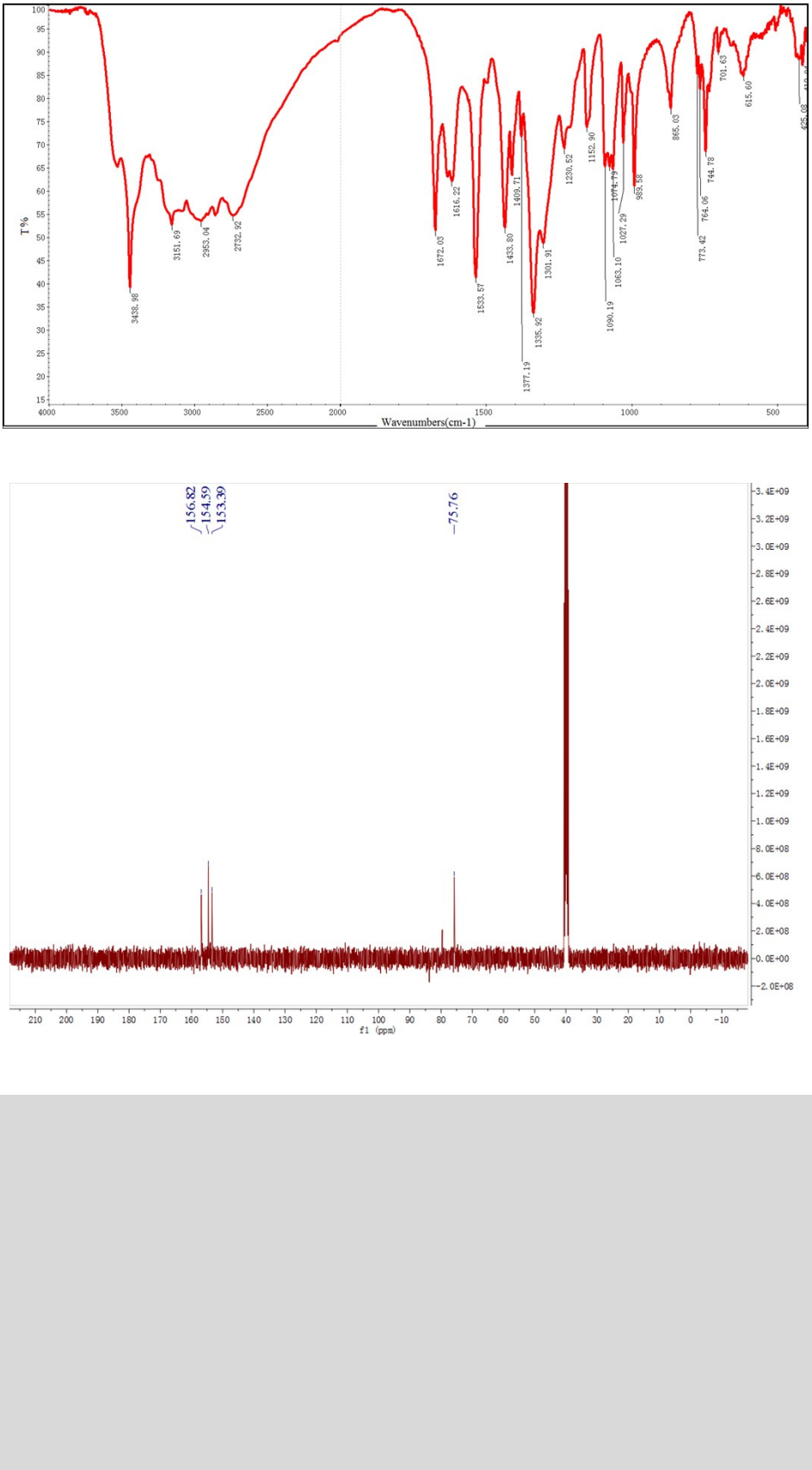


Figure S4. IR (top), ^{13}C NMR, and MS (bottom) Spectrum of **5**

Section 2. X-ray crystallography

The obtained signal crystal of five 3-amino-5-hydrazinopyrazole derivatives were used in the X-ray diffraction study. Crystallographic data and experimental details for structure analyses are outlined in **Table S1** to **Table S11**.

Table S1. Crystallographic data for compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_3H_9Cl_2N_5$	$C_3H_9N_7O_6$	$C_{15}H_{15}N_{11}O_{15}$	$C_{15}H_{23}N_{11}O_{21}$	$C_5H_{15}N_{17}O_6$
FW(g·mol^{-1})	186.05	239.17	589.38	693.44	409.34
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Orthorhombic
Space group	*P-1*	$P2_1/c$	*P-1*	*P-1*	*Pbca*
Crystalsize(mm)	0.13 × 0.12 × 0.08	0.23 × 0.21 × 0.2	0.13 × 0.12 × 0.1	0.13 × 0.12 × 0.1	0.15 × 0.12 × 0.1
a(Å)	5.1549(10)	6.6631(13)	7.8469(16)	9.4180(19)	9.5665(19)
b (Å)	6.9133(14)	9.3281(19)	12.050(2)	10.361(2)	6.7226(13)
c (Å)	11.867(2)	14.077(3)	12.748(3)	13.935(3)	50.601(10)
α (°)	74.96(3)	90.00	73.00(3)	100.85(3)	90.00
β (°)	80.75(3)	93.39(3)	83.11(3)	90.30(3)	90.00
γ (°)	88.14(3)	90.00	76.27(3)	92.25(3)	90.00
V (Å^3)	403.10(15)	873.4(3)	1118.1(5)	1334.3(5)	3254.2(11)
Z	2	4	2	2	8
ρ (g·cm^{-3})	1.533	1.819	1.751	1.726	1.671
μ (mm^{-1})	0.741	0.171	0.158	0.163	0.146
F(000)	192.0	496.0	604.0	716.0	1696.0
Refl. coll.	3564	1498	15502	12404	11169
Indep. reflns.	1803	1498	5127	6042	3556
Params.	91	146	370	428	261
S	1.105	1.161	1.117	1.105	1.212
$R_1(I > 2\sigma(I))^a$	0.0344	0.0544	0.0477	0.0758	0.0924
R_1 (all data)	0.0371	0.0573	0.0516	0.0974	0.1103
w$R_2(I > 2\sigma(I))^a$	0.0841	0.1338	0.1104	0.1717	0.1753
wR_2 (all data)	0.0874	0.1355	0.1131	0.1903	0.1848
CCDC No.	2005504	2005505	2005506	2005507	2005508

Table S2. Selected bond lengths for salt **1**

Bond length (Å)							
N1-N2	1.399(2)	N2-H2	0.8500	N-C1	1.353(3)	N3-H3	0.8500
N2-C3	1.358(3)	N4-H4A	0.8500	N3-N4	1.432(2)	N4-H4B	0.8500
N3-C3	1.371(3)	N4-H4C	0.8500	N5-C1	1.332(3)	N5-H5A	0.8500
C1-C2	1.404(3)	N5-H5B	0.8500	C2-H2A	0.9500	C2-C3	1.381(3)

Table S3. Selected dihedral angles for salt **1**

Dihedral angle (º)							
C1-N1-N2-C3	9.0(2)	N2-N1-C1-N5	172.92(17)	N2-N1-C1-C2	-7.3(2)	N1-N2-C3-N3	167.99(16)
N1-N2-C3-C2	-7.5(2)	N4-N3-C3-N2	166.24(16)	N4-N3-C3-C2	-19.4(3)	N1-C1-C2-C3	2.7(2)
N5-C1-C2-C3	-177.5(2)	C1-C2-C3-N2	3.1(2)	C1-C2-C3-N3	-171.6(2)		

Table S4. Selected bond lengths for salt **2**

Bond length (Å)							
N1-C1	1.362(4)	N2-H2A	0.8500	N2-N3	1.368(4)	O3-N6	1.276(3)
N2-C1	1.332(4)	N3-C3	1.338(4)	N4-N5	1.423(4)	N4-C3	1.380(4)
C1-C2	1.394(4)	O1-N6	1.238(4)	C2-H2	0.9500	O4-N7	1.269(4)
O5-N7	1.238(4)	C2-C3	1.387(4)	O6-N7			

Table S5. Selected dihedral angles for salt **2**

Dihedral angle (º)							
C1-N2-N3-C3	5.1(3)	N3-N2-C1-N1	179.8(3)	N3-N2-C1-C2	-3.5(4)	N2-N3-C3-N4	-179.8(3)
N2-N3-C3-C2	-4.8(4)	N5-N4-C3-N3	-167.5(3)	N5-N4-C3-C2	18.8(5)	N1-C1-C2-C3	176.9(3)
N2-C1-C2-C3	0.5(4)	C1-C2-C3-N3	2.7(4)	C1-C2-C3-N4	177.0(3)		

Table S6. Selected bond lengths for salt **3**

Bond length (Å)							
O1-N6	1.233(2)	C10-C11	1.441(2)	C10-C15	1.380(2)	O3-N7	1.225(2)
C11-C12	1.443(2)	O4-N7	1.234(2)	C12-C13	1.369(2)	N6-C4	1.452(2)
N2-C1	1.376(2)	N7-C6	1.442(2)	N3-N4	1.376(2)	N8-C8	1.460(2)
N3-C1	1.337(2)	C4-C5	1.376(2)	N4-C3	1.343(2)	N5-C3	1.342(2)
O8-N9	1.214(2)	N1-H1A	0.8500	O9-N9	1.213(2)	O10-C11	1.260(2)
O11-N10	1.228(2)	O12-N10	1.228(2)	N3-H3	0.8500	O13-N11	1.229(2)
C5-H5	0.9500	N9-C10	1.457(2)	N10-C12	1.456(2)		

Table S7. Selected dihedral angles for salt **3**

Dihedral angle (º)							
O1-N6-C4-C5	-153.24(16)	O1-N6-C4-C9	29.4(2)	O3-N7-C6-C7	174.18(17)	O4-N7-C6-C5	172.63(16)
O4-N7-C6-C7	-7.3(2)	O5-N8-C8-C9	-148.81(16)	O6-N8-C8-C7	-148.07(16)	N6-C4-C5-C6	-177.12(15)
C9-C4-C5-C6	0.1(3)	N6-C4-C9-O7	-10.0(3)	C5-C4-C9-C8	-6.4(2)	C4-C5-C6-C7	4.4(3)
N7-C6-C7-C8	178.15(16)	C5-C6-C7-C8	-1.8(3)	C6-C7-C8-N8	175.74(15)	C6-C7-C8-C9	-5.6(3)

Table S8. Selected bond lengths for salt **4**

Bond length (Å)							
O1-N6	1.228(2)	N10-C12	1.433(2)	O2-N6	1.223(2)	N11-C14	1.468(3)
O4-N7	1.253(2)	C10-C15	1.445(3)	O5-N7	1.231(2)	C10-C11	1.377(3)
O6-N8	1.226(2)	C11-C12	1.381(3)	O7-N8	1.216(2)	C12-C13	1.419(3)
O8-C9	1.259(2)	C13-C14	1.371(3)	O3-H3	0.8400	C14-C15	1.438(3)
N6-C4	1.464(3)	N1-N2	1.441(2)	N7-C6	1.426(2)	N2-C1	1.380(3)
N8-C8	1.446(3)	N3-N4	1.373(2)	C4-C9	1.436(3)	N3-C1	1.333(2)
N4-C3	1.345(3)	N5-C3	1.362(3)	O9-N9	1.232(2)	O10-N9	1.229(2)
O11-N10	1.229(2)	C2-C3	1.390(3)	O12-N10	1.246(2)	O14-N11	1.203(3)
O15-N11	1.213(2)	O16-C15	1.255(2)	N9-C10	1.447(2)		

Table S9. Selected dihedral angles for salt **4**

Dihedral angle (º)							
O1-N6-C4-C5	-121.83(19)	O1-N6-C4-C9	58.2(2)	O2-N6-C4-C9	-121.32(19)	O4-N7-C6-C5	6.2(3)
O4-N7-C6-C7	-172.16(18)	O5-N7-C6-C5	-174.84(18)	O5-N7-C6-C7	6.8(3)	O6-N8-C8-C9	172.59(18)
N6-C4-C5-O3	1.7(3)	N6-C4-C5-C6	-179.17(17)	C9-C4-C5-O3	-178.39(18)	C9-C4-C5-C6	0.8(3)
N6-C4-C9-O8	0.2(3)	N6-C4-C9-C8	178.23(16)	C5-C4-C9-O8	-179.76(19)	C5-C4-C9-C8	-1.7(3)
O3-C5-C6-N7	2.0(3)	O3-C5-C6-C7	-179.68(18)	C4-C5-C6-N7	-177.14(18)	C4-C5-C6-C7	1.2(3)
N7-C6-C7-C8	176.34(18)	C5-C6-C7-C8	-2.0(3)	C6-C7-C8-N8	-178.19(18)	C6-C7-C8-C9	1.0(3)

Table S10. Selected bond lengths for salt **5**

Bond length (Å)							
O1-N16	1.303(4)	N12-N13	1.389(4)	O2-N16	1.258(4)	N12-C3	1.355(5)

N1-N16	1.307(4)	N13-C5	1.351(5)	N1-C1	1.396(5)	N14-N15	1.437(4)
N2-N3	1.363(4)	N14-C5	1.399(5)	N2-C1	1.353(5)	C3-C4	1.411(5)
N3-N4	1.307(4)	C4-C5	1.387(5)	N4-N5	1.356(4)	N5-C1	1.347(5)
O3-N17	1.283(4)	O4-N17	1.254(4)	N6-N17	1.322(4)	N6-C2	1.381(5)
N7-N8	1.362(4)	N7-C2	1.345(5)	N8-N9	1.307(4)	N9-N10	1.357(4)
N10-C2	1.357(5)	N11-C3	1.343(5)				

Table S11. Selected dihedral angles for salt **5**

Dihedral angle (°)							
C1-N1-N16-O1	-179.4(3)	C1-N1-N16-O2	0.1(5)	N16-N1-C1-N5	179.6(3)	C1-N2-N3-N4	-0.1(4)
N3-N2-C1-N1	-178.6(4)	N3-N2-C1-N5	-0.2(4)	N2-N3-N4-N5	0.3(4)	N3-N4-N5-C1	-0.5(4)
N4-N5-C1-N1	179.1(3)	N4-N5-C1-N2	0.4(4)	C2-N6-N17-O3	176.3(3)	N17-N6-C2-N7	-175.9(3)
N17-N6-C2-N10	1.4(6)	C2-N7-N8-N9	-0.6(4)	N8-N7-C2-N6	178.3(3)	N8-N7-C2-N10	0.3(4)
N7-N8-N9-N10	0.6(4)	N8-N9-N10-C2	-0.4(4)	N9-N10-C2-N6	-177.5(4)	N9-N10-C2-N7	0.0(4)
C3-N12-N13-C5	0.8(4)	N13-N12-C3-N11	179.7(3)	N13-N12-C3-C4	-0.3(4)	N12-N13-C5-C4	-1.0(4)

Section 3. Non-isothermal kinetics and hygroscopic property analysis

The kinetic parameters of the energetic salts **2-5**, including the pre-exponential factor (A_k), apparent activation energy (E_a) and the linear coefficient (R) have been calculated using various heating modes of Kissinger's method and Ozawa-Doyle's method. The non-isothermal kinetic parameters of the salts were listed in Table S13.

Table S12. Peak temperatures of the first exothermic stage determined by DSC curves at different heating rates of salts **2-5**.

β(°C·min^{-1})	5	10	15	20
2	171.5	178.4	183.7	187.4
3	149.8	156.4	161.8	166.1
4	158.5	164.8	170.4	174.0
5	186.3	192.4	197.5	201.8

Table S13. The Non-Isothermal kinetic parameters of salts **2-5**.

	E_k(kJ·mol^{-1})	ln[A_k(s^{1-})]	R_k	E_o(kJ·mol^{-1})	R_o
2	140.3	14.35	-0.9978	140.6	-0.9981
3	124.0	13.18	-0.9948	124.7	-0.9953
4	134.5	14.15	-0.9952	134.8	-0.9957
5	154.4	15.45	-0.9930	154.2	-0.9936

The Arrhenius equations of salts **2-5** were expressed as follows:

$\ln k = 14.35\text{-}140.5\times10^3/(RT)$ (**2**)

$\ln k = 13.18\text{-}124.4\times10^3/(RT)$ (**3**)

$\ln k = 14.15\text{-}134.7\times10^3/(RT)$ (**4**)

$\ln k = 15.45\text{-}154.3\times10^3/(RT)$ (**5**)

The hygroscopic property of salt **2** was tested and the test process was given in the supporting information. The salt **2** sample was put in the drying oven and dried at 60 °C for 2 hours to make the sample dry thoroughly. The testing sample (about 3g) was put into the weighing bottle and the

bottle was put into drying vessel with saturated solution of potassium nitrate at the bottom. The temperature of the test environment is 25 °C and the relative humidity is 50%.The weighing bottle was weighed every 24 hours until the weight difference between the two the weighing bottle is no more than 0.0002g. The hygroscopic property for salt **2** was calculated according to following equation. The curve of hygroscopicity with time is given in Figure S5. The hygroscopicity for salt **2** is 0.1018%, which is acceptable.

$$\omega = \frac{W_t - W_0}{W_0} \times 100\%$$

In which, ω is the mass change fraction,%; W_t is the weight of sample after hygroscopic test, g; W_0 is the weight of the dried sample, g.

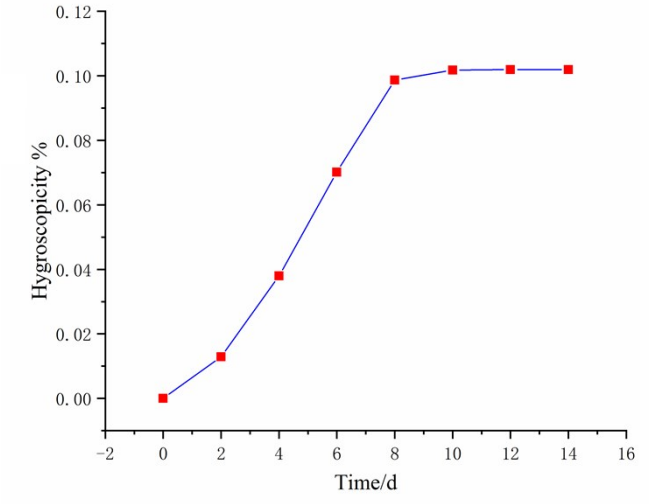


Figure S5 Change curve of hygroscopicity

Section 4. Measurement of energy of constant volume combustion

The combustion heat was measured by a Parr-6200 bomb calorimeter (static jacket) with a 6510 water handling system. The calorimeter was calibrated by the combustion of certified benzoic acid in an oxygen atmosphere at a pressure of 3.05 MPa. The constant-volume heat of combustion (Q_v =-2456.75 kJ·mol^{-1}) of salt **2** was averaged after three independent experiments. The constant-pressure heat of combustion (Q_p= -2450.56 kJ·mol^{-1}) was calculated by the formula $Q_p = Q_v + \Delta nRT$. The heat of formation ($\Delta_f H$ = -16.2 kJ·mol^{-1}) for salt **2** were calculated according to the Hess thermochemical cycle and the combustion reactions (**6**), which was given in the supporting information.

$$C_3H_9N_7O_6\ (s) + 2.25O_2(g) \rightarrow 3CO_2(g) + 4.5H_2O(l) + 3.5N_2(g) \qquad (6)$$

Section 5. Computational structural considerations

Electrostatic potential (ESP) and natural bond orbitals (NBO) and of HAP were calculated using the density functional theory with B3LYP/6-311++G** method. The optimized geometry of HAP is given in Figure S6. The calculated NBO charges for HAP are displayed in Table S14.

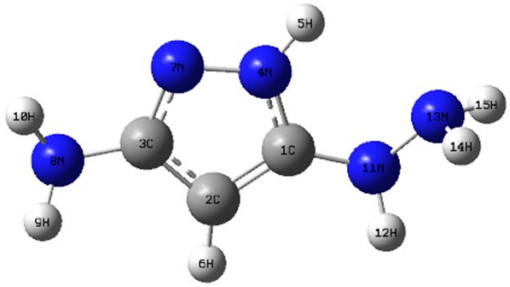


Figure S6 Optimized geometry of HAP

Table S14. Natural Population Analysis for HAP

Charge(a.u.)							
C1	0.358	H9	0.366	C2	-0.420	H10	0.377
C3	0.341	N11	-0.466	N4	-0.375	H12	0.354
H5	0.412	N13	-0.662	H6	0.216	H14	0.341
N7	-0.393	H15	0.359	N8	-0.808		