Supplementary Information (SI) for CrystEngComm.

Supporting Information

Ionization treatment of pyrazolo[4,3-c]pyrazole derivatives to achieve the low sensitivity of high-energy materials

Lei Shi, Bangxiang Liu, Pengfei Wang, Chao Gao, Chong Zhang, Yang Du, Chengguo Sun* and Bingcheng Hu*

School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu 210094, China.

E-mail: hubc@njust.edu.cn

Contents

1. Experimental section

Caution! The high-energy materials synthesized in the experiment may pose a risk of combustion and explosion. Therefore, protective equipment such as gloves, masks, and goggles should be worn during the experiment. In addition, small-scale experiments should be conducted in a fume hood.

Reagents and instruments. All chemicals used in this study were analytical grade materials purchased from local manufacturers in China and were not further purification. The ^{1}H and ^{13}C NMR spectra were recorded on a 500MHz (Bruker AVANCE III 500) nuclear magnetic resonance spectrometer. The FT-IR spectrum was recorded on the Thermo Nicolet IS10 instrument. Differential scanning calorimetry (DSC) were performed using a differential scanning calorimeter-thermal gravity instrument (TG/DSC, Netzsch STA449 F3) at a heating rate of 5 ℃ min^{-1}.

Synthetic Procedure. According to the previously reported procedure, 6-nitro-pyrazolo[4,3-c]pyrazole-3-carbonic acid[1].

3,6-Dinitropyrazolo[4,3-c]pyrazole (DNPP): 6-Nitro-pyrazolo[4,3-c]pyrazole-3-carbonic acid (1.97 g, 10 mmol) was added in portions to the fuming nitric acid (10 mL) at 0 ℃. The reaction was stirred at 45 ℃ for 20 hours. Then, the solution was poured into ice water (50 mL) with stirring. The formed solid was filtered and washed with water, and dried in vacuum to give yellow solid. Yield: 1.22 g, 61.6%. ^{1}H NMR (500 MHz, DMSO-d6): δ = 15.05 (s, 2H) ppm. ^{13}C NMR (125 MHz, DMSO-d6): δ = 137.89, 131.58 ppm. IR (KBr): ṽ = 3696, 3680, 3592, 3507, 2972, 2921, 2843, 2822, 2746, 1697, 1600, 1506, 1382, 1353, 1241, 1133, 1033, 869, 824, 746, 661, 603 cm^{-1}. Elemental analysis for $C_4H_2N_6O_4$ (198.01): calcd C 24.24, H 1.01, N 42.42; found: C 24.34, H 1.08, N 42.21.

Diammonium 3,6-dinitropyrazolo[4,3-c]pyrazole-1,4-diolate (1): DNPP (0.40 g, 2 mmol) was dissolved in methanol (15 mL) and aqueous ammonia (25% in water, 0.53 mL) was added. The reaction was stirred at room temperature for 1 hours. Then, the solid was filtered off, washed with methanol, and dried in vacuum to give orange solid. Yield: 0.39 g, 84.0%. ^{1}H NMR (500 MHz, DMSO-d6): δ = 6.40 (s, 8H) ppm. ^{13}C NMR (125 MHz, DMSO-d6): δ = 140.16, 138.44 ppm. IR (KBr): ṽ = 3540, 2789, 1692, 1613, 1501, 1439, 1368, 1326, 1179, 1104, 1045, 879, 807, 788, 751, 662 cm^{-1}. Elemental analysis for $C_4H_8N_8O_4$ (232.18): calcd C 20.69, H 3.48, N 48.26; found: C 20.61, H 3.53, N 48.21.

Dihydrazinium 3,6-dinitropyrazolo[4,3-c]pyrazole-1,4-diolate (2): DNPP (0.40 g, 2 mmol) was dissolved in methanol (15 mL) and hydrazine hydrate (85% in water, 0.23 mL) was added. The reaction was stirred at room temperature for 1 hours. Then, the solid was filtered off, washed with methanol, and dried in vacuum to give yellow solid. Yield: 0.46 g, 87.8%. ^{1}H NMR (500 MHz, DMSO-d6): δ = 5.39 (s, 6H) ppm. ^{13}C NMR (125 MHz, DMSO-d6): δ = 140.22, 138.58 ppm. IR (KBr): ṽ = 3348, 3289, 2568, 2167, 1618, 1468, 1436, 1382, 1355, 1295, 1230, 1157, 1096, 1062, 964, 822, 751, 668, 632 cm^{-1}. Elemental analysis for $C_4H_{10}N_{10}O_4$ (262.22): calcd C 18.32, H 3.85, N 53.42; found: C 18.26, H 3.92, N 53.38.

Dihydroxylammonium 3,6-dinitropyrazolo[4,3-c]pyrazole-1,4-diolate (3): DNPP (0.40 g, 2 mmol) was dissolved in methanol (15 mL) and aqueous ammonia (50% in water, 0.20 mL) was added. The reaction was stirred at room temperature for 1 hours. Then, the solid was filtered off, washed with methanol, and dried in vacuum to give yellow solid. Yield: 0.44 g, 83.3%. ^{1}H NMR (500 MHz, DMSO-d6): δ = 8.58 (s, 6H) ppm. ^{13}C NMR (125 MHz, DMSO-d6): δ = 140.02, 137.92 ppm. IR (KBr): ṽ = 3606, 3272, 2972, 2843, 1599, 1514, 1455, 1412, 1380, 1332, 1236, 1109, 1058,

820, 803, 734, 689, 658 cm^{-1}. Elemental analysis for $C_4H_8N_8O_6$ (264.18): calcd C 18.19, H 3.05, N 42.42; found: C 18.26, H 3.09, N 42.35.

Diguanidinium 3,6-Dinitropyrazolo[4,3-c]pyrazole-1,4-diolate (4): DNPP (0.40 g, 2 mmol) was dissolved in methanol (15 mL) and guanidinium carbonate (0.36 g, 2 mmol) was added. The mixture was refluxed for 1 h, and then the mixture was cooled to room temperature. The solid was filtered off, washed with few methanol, and dried in vacuum to give yellow solid. Yield: 0.48 g, 75.9%. ^1H NMR (500 MHz, DMSO-d6): δ = 7.34 (s, 6H) ppm. ^{13}C NMR (125 MHz, DMSO-d6): δ = 158.89 ppm. IR (KBr): ṽ = 3363, 3192, 2829, 1650, 1581, 1537, 1513, 1429, 1339, 1241, 1191, 1124, 1029, 869, 805, 774, 750 cm^{-1}. Elemental analysis for $C_6H_{12}N_{12}O_4$ (316.28): calcd C 22.79, H 3.83, N 53.14; found: C 22.84, H 3.89, N 53.08.

4,5-diamino-3-(6-nitro-1,4-dihydropyrazolo[4,3-c]pyrazol-3-yl)-4H-1,2,4-triazole (5): Phosphorus pentoxide (20.0 g, 0.15 mol) was added to aqueous orthophosphoric acid (85%, 70.0 g, 0.60 mol), and then it was heated to 50 ℃ under stirring for 30 min. A well-stirred mixture of NPPCA (9.85 g, 0.050 mol) and N,N'-diaminoguanidine monohydrochloride (8.16 g, 0.065 mol) was added to the above solution. The mixture was heated to 120 ℃ for another 8 h. Then the mixture was cooled to room temperature, and it was poured into ice water (150 mL). The pH was adjusted to 8 with concentrated sodium hydroxide solution. The solid was filtered off, washed with water, and dried in vacuum to give yellow solid. Yield: 7.76 g, 62.1%. ^1H NMR (500 MHz, DMSO-d6): δ = 13.97 (s, 1H), 6.13 (s, 2H), 5.88 (s, 2H) ppm. ^{13}C NMR (125 MHz, DMSO-d6): δ = 152.15, 143.77, 138.11, 137.55, 130.81 ppm. IR (KBr): ṽ = 3461, 3341, 2971, 1615, 1454, 1382, 1289, 1242, 1136, 1111, 1052, 990, 907, 858, 776, 750, 715 cm^{-1}. Elemental analysis for $C_6H_6N_{10}O_2$ (250.07): calcd C 28.82, H 2.42, N 56.01; found: C 28.89, H 2.37, N 56.07.

4,5-diamino-3-(6-nitro-1,4-dihydropyrazolo[4,3-c]pyrazol-3-yl)-4H-1,2,4-triazolium perchlorate (6): Compound **5** (0.25 g 1.0 mmol) was suspended in distilled water (3 mL) and perchloric acid (2 mL, 70%) was added to it. The mixture was heated to 60 ℃ for 5 h, and then the solution was cooled to room temperature. The solid was filtered off, washed with water and dried in vacuum to obtain the yellow solid. Yield: 0.23 g, 65.7%. ^1H NMR (500 MHz, DMSO-d6): δ = 14.28 (s, 1H), 8.45 (s, 2H), 6.14 (s, 2H) ppm. ^{13}C NMR (125 MHz, DMSO-d6): δ = 152.09, 143.73, 138.06, 137.51, 130.80, 119.71 ppm. IR (KBr): ṽ = 3358, 3248, 3173,1686, 1596, 1525, 1369, 1319, 1284, 1237, 1306, 931, 864, 804, 725, 691, 623, 565 cm^{-1}.

Experimental procedure for measuring hygroscopic ability. The mass of dried salt **3** was accurately weighed by the analytical balance (METTLER TOLEDO: XSR105DU/A), and then the salts were stored under various humidity conditions (40%RH, 60%RH, 80%RH) until an equilibrium has reached (24 h). The salts were weighed again and the exact water content of the salts was determined through calculation.

Experimental procedure for measuring mechanical sensitivity. All compounds are dried in vacuum for 24 h. The experiment was measured at 20 ℃ and 55%RH. The impact sensitivity and friction sensitivity were measured with a standard BAM Fall Hammer and a BAM Friction Test Apparatus to measure, respectively. The sample was weighed 10 mg for each time, and the experiment was measured 3 times for each sample.

2. ^{1}H and ^{13}C NMR spectra

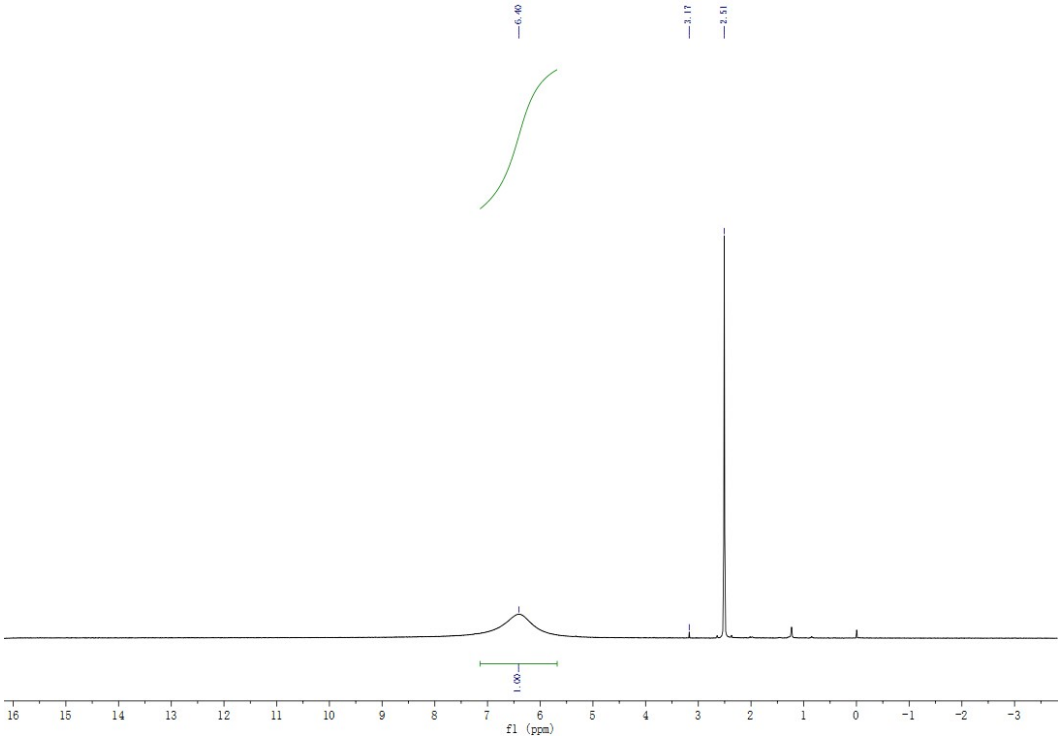


Figure S1. ^{1}H NMR of **1**

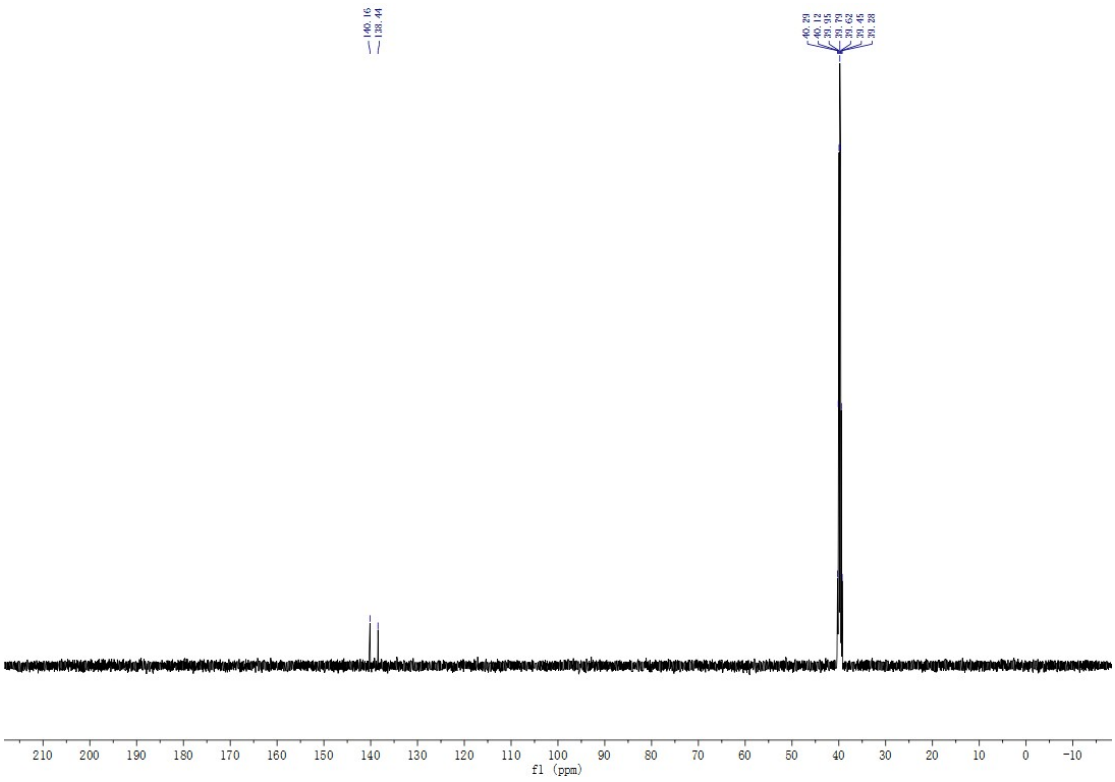


Figure S2. ^{13}C NMR of **1**

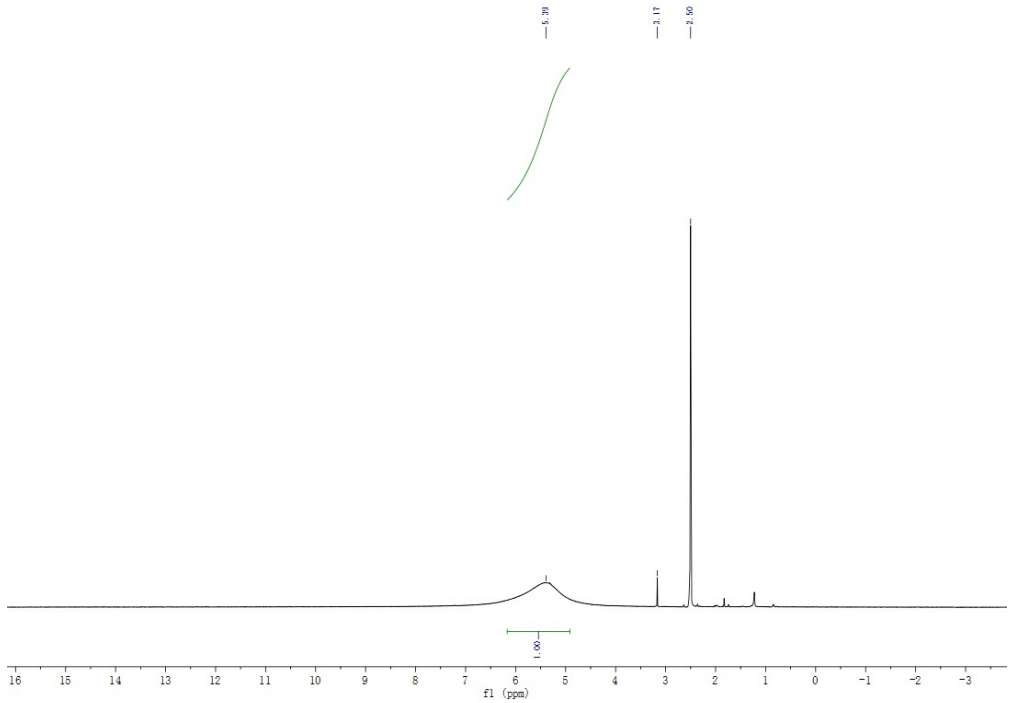


Figure S3. ^{1}H NMR of **2**

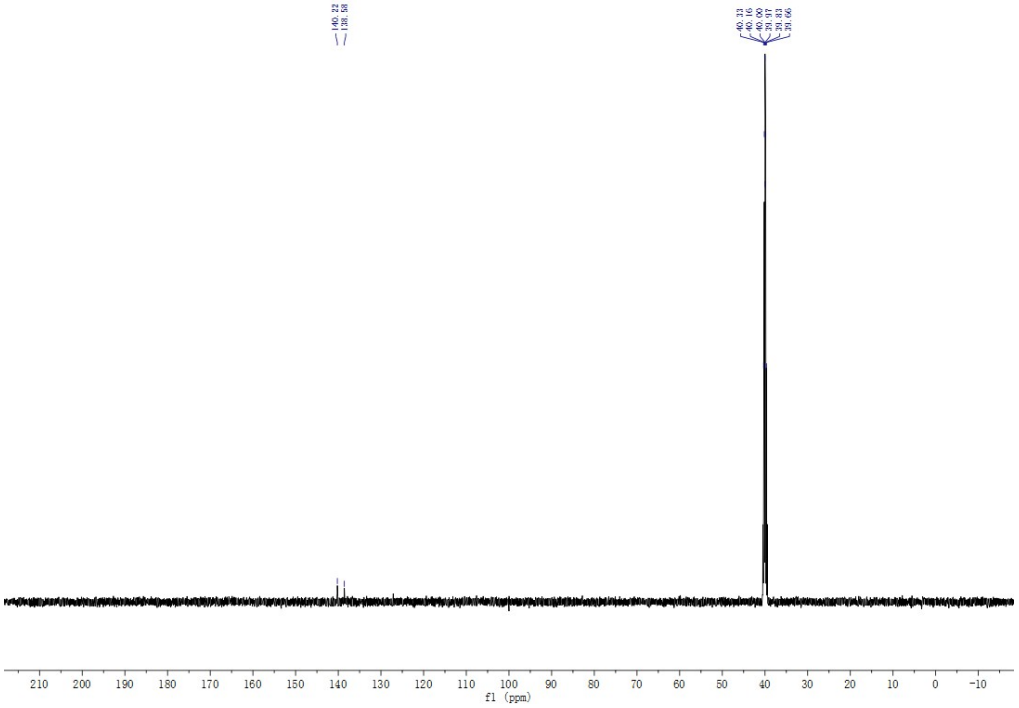


Figure S4. ^{13}C NMR of **2**

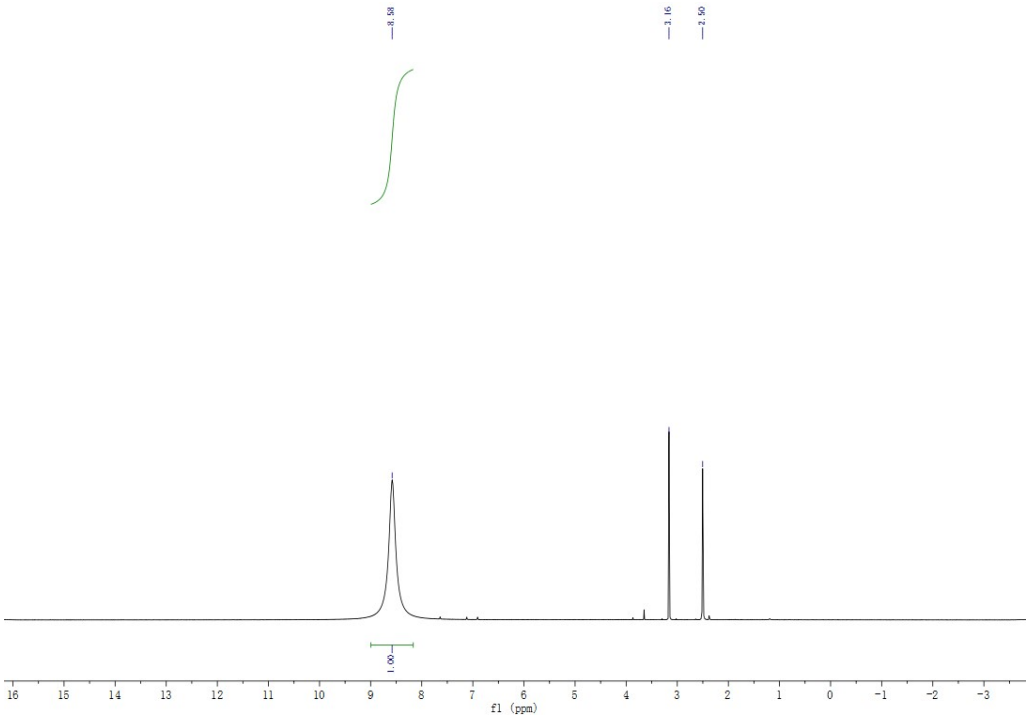


Figure S5. ^{1}H NMR of **3**

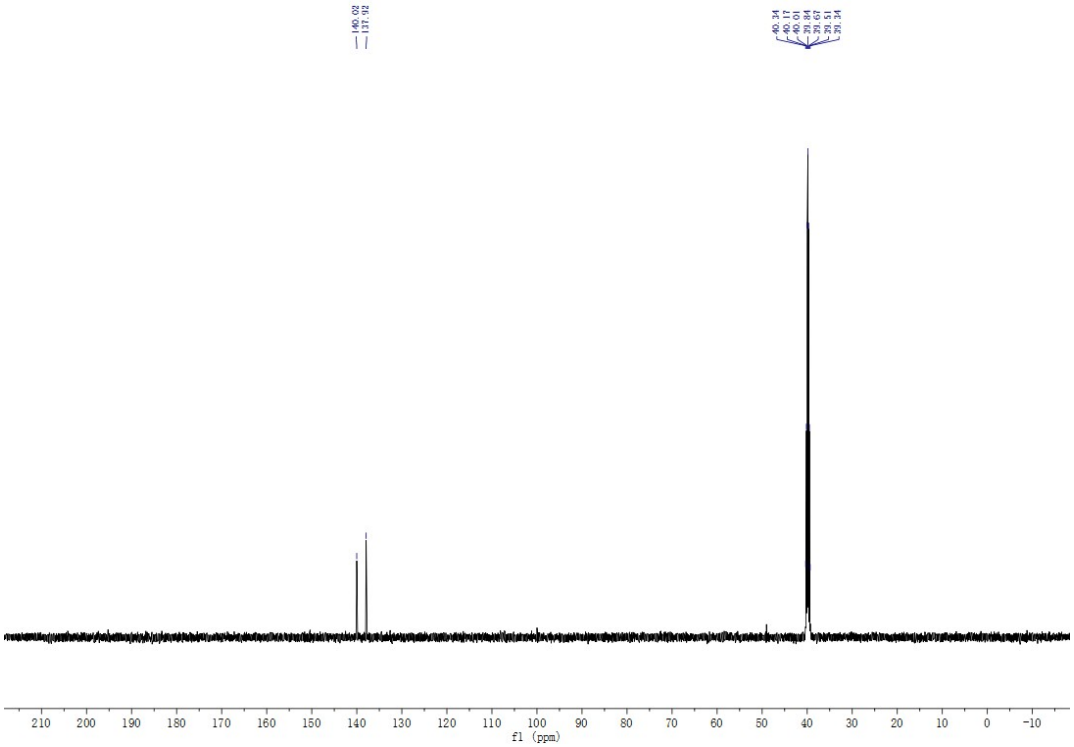


Figure S6. ^{13}C NMR of **3**

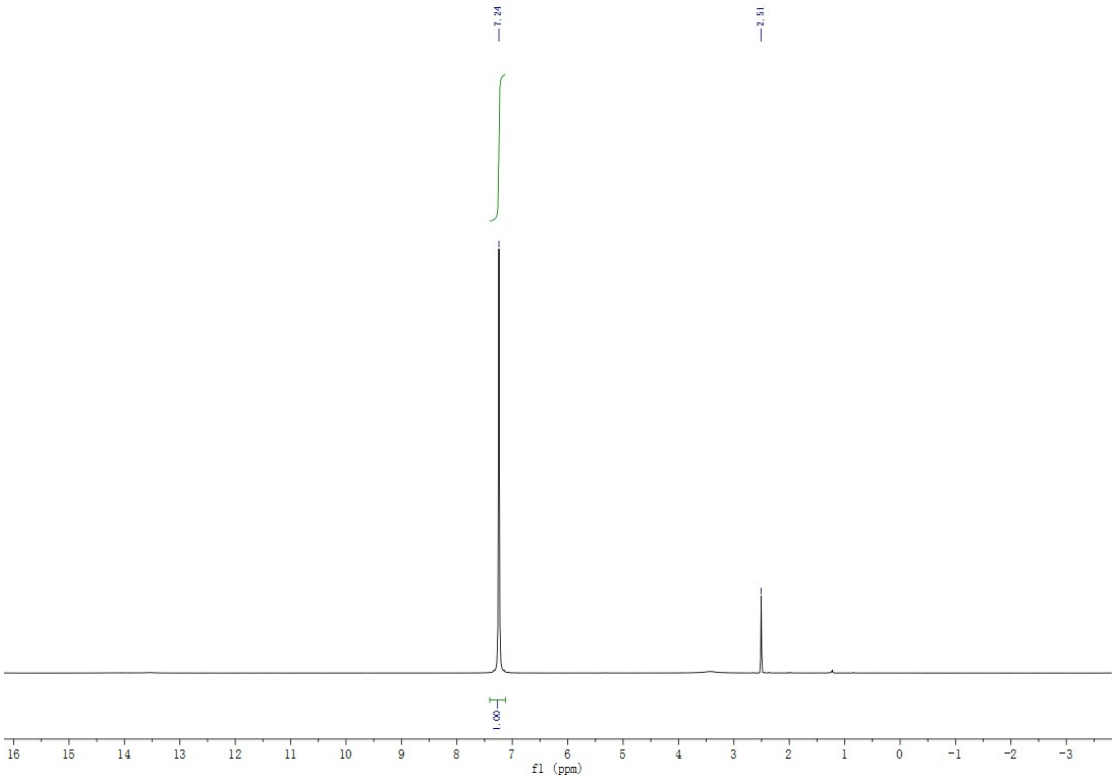


Figure S7. ^{1}H NMR of **4**

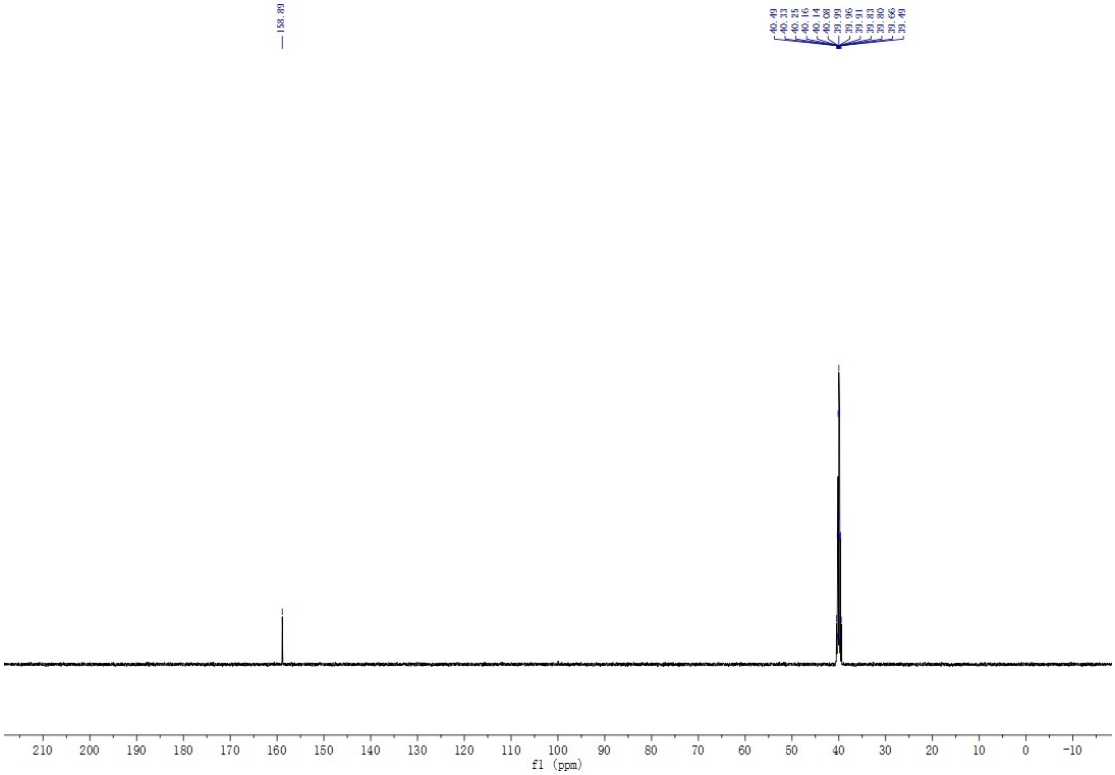


Figure S8. ^{13}C NMR of **4**

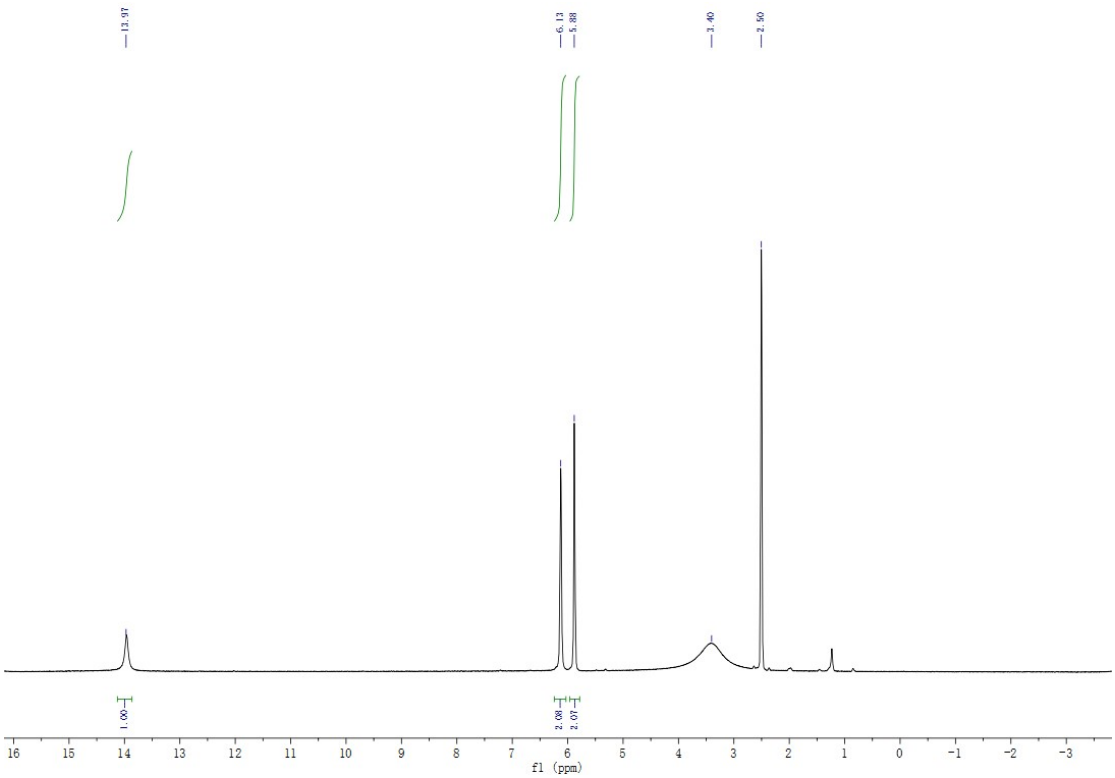


Figure S9. ^{1}H NMR of **5**

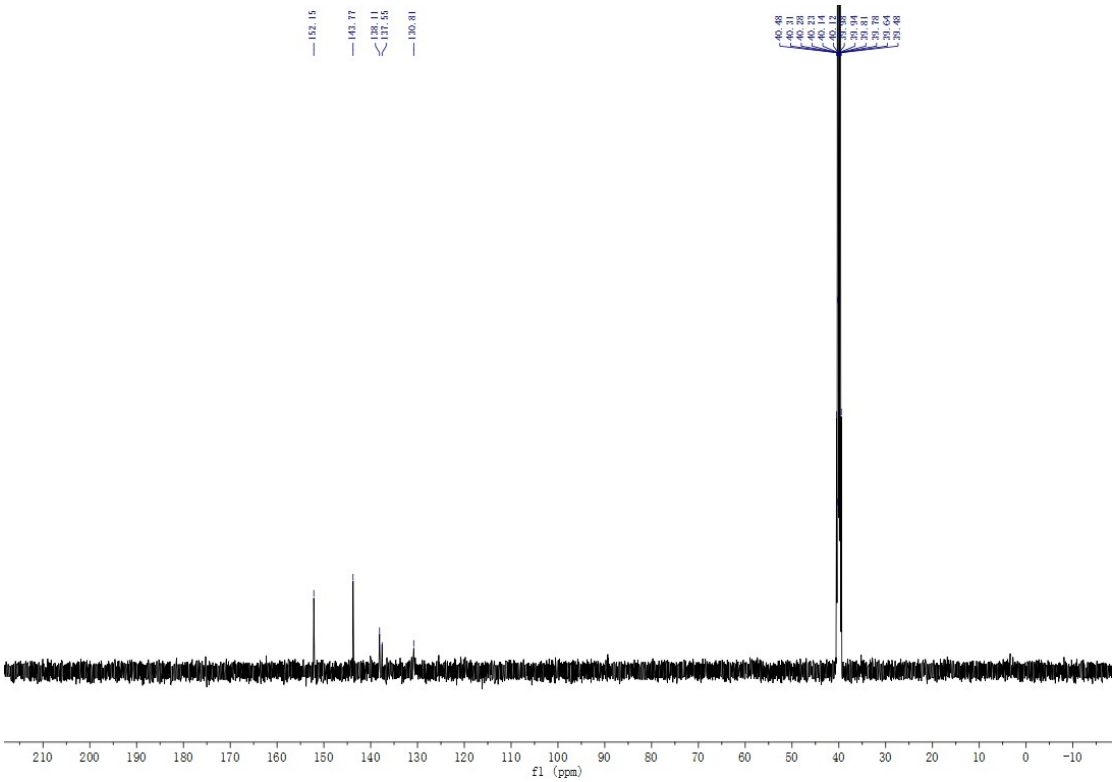


Figure S10. ^{13}C NMR of **5**

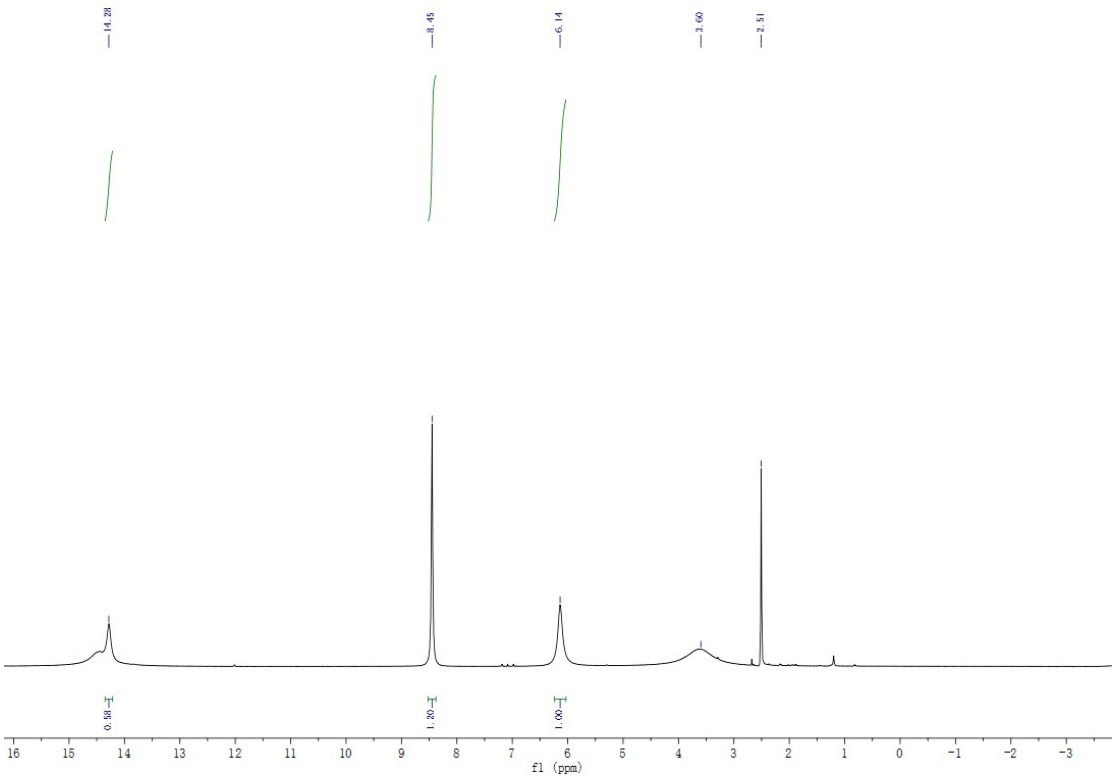


Figure S11. ^{1}H NMR of **6**

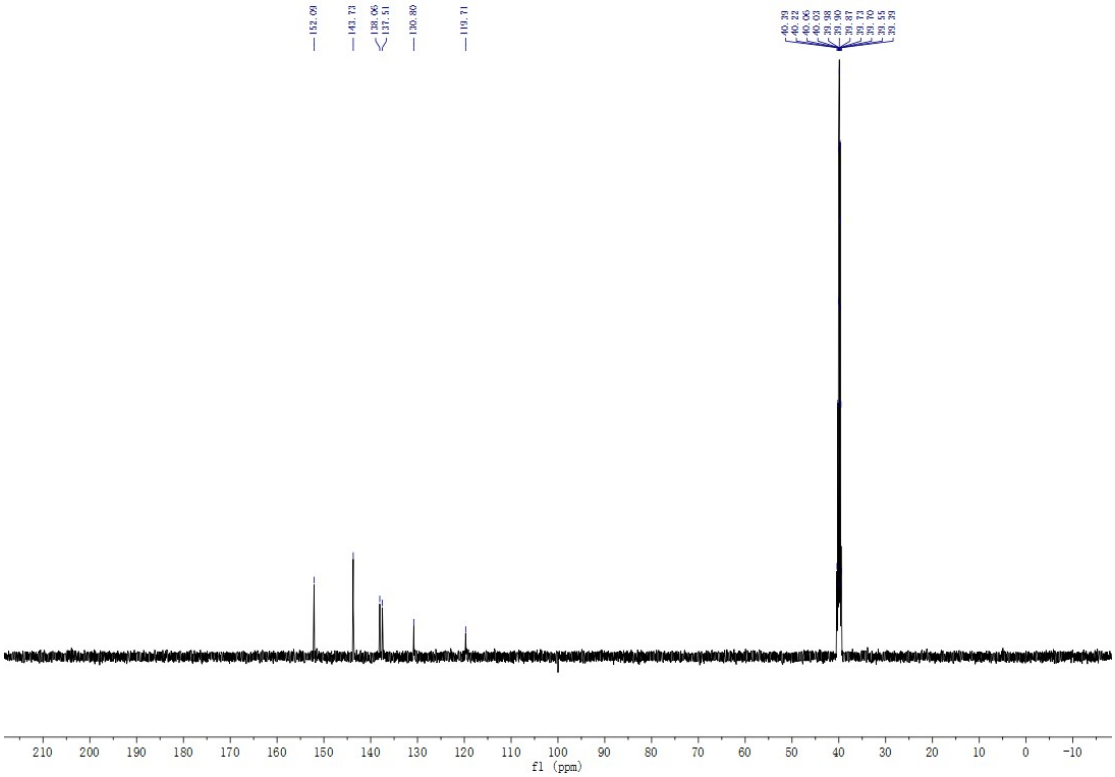


Figure S12. ^{13}C NMR of **6**

3. Crystal structure data

Table S1. Crystal data and structure refinement details for **1**-**3**.

Compound	**1**	**2**	**3**
CCDC No.	2327960	2404240	2404241
Empirical formula	$C_4H_8N_8O_4$	$C_4H_{10}N_{10}O_4$	$C_4H_8N_8O_6$
Formula weight	232.18	262.22	264.18
Temperature (K)	193	233	233
Wavelength (Å)	1.54178	1.54178	0.71073
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P12_1/c1$	P-1	$P12_1/c1$
a (Å)	3.4551(3)	3.6169(18)	3.6899(7)
b (Å)	14.0564(9)	7.881(3)	13.747(3)
c (Å)	9.0385(6)	9.865(5)	9.3323(13)
α (°)	90	109.743(19)	90
β (°)	93.842(6)	97.40(2)	95.909(10)
γ (°)	90	101.86(2)	90
Volume ($Å^3$)	437.98(6)	252.9(2)	470.88(14)
Z	2	1	2
Density ($g\ cm^{-3}$)	1.761	1.721	1.863
μ (mm^{-1})	1.354	1.309	0.171
F(000)	240	136	272
Crystal size (mm^3)	0.13 × 0.1 × 0.07	0.12 × 0.11 × 0.1	0.12 × 0.11 × 0.10
Theta range for data collection	5.83 to 68.236	6.181 to 67.516	2.963 to 27.225
Index ranges	$-4 \le h \le 4$ $-16 \le k \le 16$ $-10 \le l \le 10$	$-4 \le h \le 4$ $-10 \le k \le 10$ $-12 \le l \le 10$	$-4 \le h \le 4$ $-17 \le k \le 17$ $-11 \le l \le 12$
Reflections collected	5248	2850	9659
Independent reflections	808[R(int)=0.058]	1032[R(int)=0.075]	1076[R(int)=0.079]
Data/restraints/parameters	808/4/84	1032/0/89	1076/2/86
Goodness-of-fit on F^2	1.030	0.944	1.097
Final R indices [I>2sigma(I)]	R1 = 0.0436 wR2 = 0.1114	R1 = 0.0486 wR2 = 0.1188	R1 = 0.0689 wR2 = 0.1864
R indices (all data)	R1 = 0.0522 wR2 = 0.1182	R1 = 0.1036 wR2 = 0.1469	R1 = 0.0799 wR2 = 0.1925
Largest diff. peak and hole (e. $Å^{-3}$)	0.402 and -0.301	0.294 and -0.446	0.321 and -0.599

Table S2. Crystal data and structure refinement details for **4**-**6**.

Compound	**4**	**5**·2H_2O	**6**·2H_2O
CCDC No.	2327959	2404239	2404238
Empirical formula	$C_6H_{12}N_{12}O_4$	$C_6H_{10}N_{10}O_4$	$C_6H_{11}N_{10}O_8Cl$
Formula weight	316.28	286.24	386.70
Temperature (K)	193	213	223
Wavelength (Å)	1.54178	1.54184	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P12_1/c1$	$P12_1/n1$	$P12_1/n1$
a (Å)	3.55870(10)	3.9810(2)	10.4988(4)
b (Å)	17.1844(6)	26.2212(13)	13.0416(5)
c (Å)	10.0828(4)	11.0929(5)	11.0271(5)
α (°)	90	90	90
β (°)	94.393(3)	98.702(3)	103.205(2)
γ (°)	90	90	90
Volume (Å^3)	614.79(4)	1144.62(10)	1469.92(10)
Z	2	4	4
Density (g cm^{-3})	1.709	1.661	1.747
μ (mm^{-1})	1.249	1.220	0.329
F(000)	328	592	792
Crystal size (mm^3)	0.13 × 0.12 × 0.1	0.13 × 0.11 × 0.1	0.15 × 0.13 × 0.12
Theta range for data collection	5.097 to 68.195	4.370 to 68.490	2.458 to 24.541
Index ranges	$-4 \le h \le 4$ $-20 \le k \le 20$ $-12 \le l \le 11$	$-4 \le h \le 3$ $-31 \le k \le 31$ $-13 \le l \le 13$	$-13 \le h \le 12$ $-16 \le k \le 16$ $-14 \le l \le 14$
Reflections collected	6855	8674	26099
Independent reflections	1132[R(int)=0.044]	2066[R(int)=0.0618]	3381[R(int)=0.0729]
Data/restraints/parameters	1132/0/101	2066/1/217	3381/0/233
Goodness-of-fit on F^2	1.123	1.027	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0383 wR2 = 0.0970	R1 = 0.0409 wR2 = 0.1045	R1 = 0.0453 wR2 = 0.1353
R indices (all data)	R1 = 0.0477 wR2 = 0.1018	R1 = 0.0590 wR2 = 0.1155	R1 = 0.0631 wR2 = 0.1846
Largest diff. peak and hole (e. Å^{-3})	0.234 and -0.201	0.155 and -0.247	0.481 and -0.461

Table S3. Bond lengths for **1**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N4	1.232(2)	C1-C2_a	1.400(3)
O2-N4	1.239(2)	C2-C2_a	1.388(3)
N2-N3	1.346(2)	N1-H1A	0.8700
N2-C2	1.370(3)	N1-H1B	0.8700
N3-C1	1.344(3)	N1-H1C	0.83(3)
N4-C1	1.413(3)	N1-H1D	0.89(2)

Table S4. Bond angles for **1**.

Parameter	bond angle (°)	Parameter	bond angle (°)
N3-N2-C2	108.19(15)	N2-C2-C2_a	109.78(17)
N2-N3-C1	107.92(16)	C1_a-C2-C2_a	103.30(17)
O1-N4-O2	122.92(17)	H1A-N1-H1B	105.00
O1-N4-C1	119.84(17)	H1A-N1-H1C	129.00
O2-N4-C1	117.24(17)	H1A-N1-H1D	106.00
N3-C1-N4	120.35(18)	H1B-N1-H1C	116.00
N3-C1-C2_a	110.81(16)	H1B-N1-H1D	117.00
N4-C1-C2_a	128.78(18)	H1C-N1-H1D	83(5)
N2-C2-C1_a	146.92(18)		

Table S5. Torsion angles for **1**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C2-N2-N3-C1	0.1(2)	O2-N4-C1-C2_a	-2.2(3)
N3-N2-C2-C1_a	180.0(3)	N3-C1-C2_a-C2	0.0(2)
N3-N2-C2-C2_a	-0.1(2)	N3-C1-C2_a-N2_a	-179.9(3)
N2-N3-C1-N4	-177.72(17)	N4-C1-C2_a-C2	177.4(2)
N2-N3-C1-C2_a	0.0(2)	N4-C1-C2_a-N2_a	-2.5(5)
O1-N4-C1-N3	-4.6(3)	N2-C2-C2_a-C1	0.0(2)
O1-N4-C1-C2_a	178.2(2)	N2-C2-C2_a-N2_a	-180.00(15)
O2-N4-C1-N3	175.01(18)	C1_a-C2-C2_a-C1	-179.98(17)

Table S6. Hydrogen bonds for **1**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N1-H1A···N2	0.8700	1.9500	2.786(3)	161.00
N1-H1B···N3	0.8700	2.0900	2.958(3)	176.00
N1-H1C···O2	0.83(3)	2.24(3)	3.049(2)	163(3)
N1-H1D···N1	0.89(2)	2.57(2)	3.455(4)	175(7)

Table S7. Bond lengths for **2**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.237(4)	C1-C2_a	1.405(4)
O2-N1	1.247(4)	N4-N5	1.437(4)
N1-C2	1.401(4)	N4-H4A	0.85(4)
N2-N3	1.341(4)	N4-H4B	0.96(4)
N2-C2	1.339(4)	N5-H5A	0.9000
N3-C1	1.375(4)	N5-H5B	0.9000
C1-C1_a	1.384(4)	N5-H5C	0.9000

Table S8. Bond angles for **2**.

Parameter	bond angle (°)	Parameter	bond angle (°)
O1-N1-O2	122.0(3)	N2-C2-C1_a	110.2(2)
O1-N1-C2	118.4(3)	N5-N4-H4A	108(2)
O2-N1-C2	119.6(3)	N5-N4-H4B	111(2)
N3-N2-C2	109.7(2)	H4A-N4-H4B	103(4)
N2-N3-C1	106.2(2)	N4-N5-H5A	109.00
N3-C1-C1_a	111.3(2)	N4-N5-H5B	109.00
N3-C1-C2_a	146.1(3)	N4-N5-H5C	109.00
C1_a-C1-C2_a	102.6(2)	H5A-N5-H5B	109.00
N1-C2-N2	121.2(2)	H5A-N5-H5C	109.00
N1-C2-C1_a	128.6(2)	H5B-N5-H5C	110.00

Table S9. Torsion angles for **2**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
O1-N1-C2-N2	177.2(2)	N2-N3-C1-C1_a	0.4(3)
O1-N1-C2-C1_a	-3.6(4)	N2-N3-C1-C2_a	179.5(4)
O2-N1-C2-N2	-3.2(4)	N3-C1-C1_a-C2	-0.5(3)
O2-N1-C2-C1_a	176.0(3)	N3-C1-C1_a-N3_a	-180.0(2)
C2-N2-N3-C1	0.0(3)	C2_a-C1-C1_a-C2	-180.0(2)
N3-N2-C2-N1	179.0(2)	N3-C1-C2_a-N1_a	-0.4(6)
N3-N2-C2-C1_a	-0.3(3)	N3-C1-C2_a-N2_a	-179.6(3)

Table S10. Hydrogen bonds for **2**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N4-H4A···O1	0.85(4)	2.51(4)	3.200(4)	139(3)
N4-H4B···O2	0.96(4)	2.56(4)	3.090(4)	115(3)
N4-H4B···O2	0.96(4)	2.24(4)	3.133(4)	155(3)
N5-H5A···N3	0.9000	1.8900	2.781(4)	171.00
N5-H5B···N2	0.9000	2.0300	2.870(4)	155.00
N5-H5C···N4	0.9000	1.9900	2.887(4)	172.00

Table S11. Bond lengths for **3**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O2-N1	1.228(4)	C1-C2_a	1.403(4)
O3-N1	1.243(4)	O1-N4	1.298(4)
N1-C2	1.414(4)	O1-H1	0.910(18)
N2-N3	1.350(4)	N4-H4A	0.9500
N2-C2	1.345(4)	N4-H4B	1.0000
N3-C1	1.366(4)	N4-H4C	1.0300
C1-C1_a	1.385(4)		

Table S12. Bond angles for **3**.

Parameter	bond angle (°)	Parameter	bond angle (°)
O2-N1-O3	122.9(3)	N1-C2-C1_a	128.6(3)
O2-N1-C2	120.4(3)	N2-C2-C1_a	111.0(3)
O3-N1-C2	116.8(2)	N4-O1-H1	114.7(12)
N3-N2-C2	107.8(2)	O1-N4-H4A	103.00
N2-N3-C1	107.9(2)	O1-N4-H4B	109.00
N3-C1-C1_a	110.5(2)	O1-N4-H4C	112.00
N3-C1-C2_a	146.6(3)	H4A-N4-H4B	115.00
C1_a-C1-C2_a	102.9(2)	H4A-N4-H4C	109.00
N1-C2-N2	120.4(3)	H4B-N4-H4C	109.00

Table S13. Torsion angles for **3**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
O2-N1-C2-N2	-4.2(4)	N2-N3-C1-C1_a	1.0(3)
O2-N1-C2-C1_a	177.0(3)	N2-N3-C1-C2_a	179.4(4)
O3-N1-C2-N2	175.5(3)	N3-C1-C1_a-C2	-0.9(3)
O3-N1-C2-C1_a	-3.3(5)	N3-C1-C1_a-N3_a	-180.0(2)
C2-N2-N3-C1	-0.7(3)	C2_a-C1-C1_a-C2	180.0(2)
N3-N2-C2-N1	-178.9(3)	N3-C1-C2_a-N1_a	2.2(7)
N3-N2-C2-C1_a	0.1(3)	N3-C1-C2_a-N2_a	-178.9(4)

Table S14. Hydrogen bonds for **3**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
O1-H1-N2	0.910(18)	2.608(14)	3.516(4)	175(5)
O1-H1-N3	0.910(18)	1.76(4)	2.582(4)	150(5)
N4-H4A-O3	0.9500	2.0400	2.987(4)	175.00
N4-H4B-N2	1.0000	1.8500	2.830(4)	164.00.
N4-H4C-O1	1.0300	1.9100	2.862(5)	152.00
N4-H4C-O3	1.0300	2.6000	3.012(4)	104.00

Table S15. Bond lengths for **4**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.2508(19)	N5-C5	1.330(2)
O2-N1	1.2509(18)	N6-C5	1.325(2)
N1-C3	1.393(2)	N4-H4A	0.8800
N2-N3	1.340(2)	N4-H4B	0.8800
N2-C3	1.360(2)	N5-H5A	0.8800
N3-C4	1.373(2)	N5-H5B	0.8800
C3-C4_a	1.409(2)	N6-H6A	0.8800
C4-C4_a	1.386(2)	N6-H6B	0.8800
N4-C5	1.325(2)		

Table S16. Bond angles for **4**.

Parameter	bond angle (°)	Parameter	bond angle (°)
O1-N1-O2	121.20(14)	C5-N4-H4B	120.00
O1-N1-C3	118.28(13)	H4A-N4-H4B	120.00
O2-N1-C3	120.52(14)	N4-C5-N5	120.29(16)
N3-N2-C3	109.55(13)	N4-C5-N6	119.78(16)
N2-N3-C4	106.44(13)	N5-C5-N6	119.92(16)
N1-C3-N2	121.25(14)	C5-N5-H5A	120.00
N1-C3-C4_a	129.05(14)	C5-N5-H5B	120.00
N2-C3-C4_a	109.61(14)	H5A-N5-H5B	120.00
N3-C4-C3_a	145.60(15)	C5-N6-H6A	120.00
N3-C4-C4_a	111.61(14)	C5-N6-H6B	120.00
C3_a-C4-C4_a	102.79(13)	H6A-N6-H6B	120.00
C5-N4-H4A	120.00		

Table S17. Torsion angles for **4**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
O1-N1-C3-N2	-178.05(14)	N2-N3-C4-C4_a	0.06(18)
O1-N1-C3-C4_a	-2.0(2)	N1-C3-C4_a-C4	-176.37(15)
O2-N1-C3-N2	1.0(2)	N1-C3-C4_a-N3_a	3.5(3)
O2-N1-C3-C4_a	177.10(15)	N2-C3-C4_a-C4	0.08(16)
C3-N2-N3-C4	0.00(17)	N2-C3-C4_a-N3_a	179.9(2)
N3-N2-C3-N1	176.72(14)	N3-C4-C4_a-C3	-0.08(17)
N3-N2-C3-C4_a	-0.05(18)	N3-C4-C4_a-N3_a	-179.98(15)
N2-N3-C4-C3_a	179.9(2)	C3_a-C4-C4_a-C3	180.00(12)

Table S18. Hydrogen bonds for **4**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N4-H4A···N3	0.8800	2.0400	2.919(2)	174.00
N4-H4B···O2	0.8800	2.1000	2.936(2)	159.00
N5-H5A···O2	0.8800	2.2100	3.073(2)	167.00
N5-H5B···N2	0.8800	2.2400	3.073(2)	158.00
N6-H6A···O1	0.8800	2.2300	2.943(2)	137.00
N6-H6B···O1	0.8800	2.1300	2.996(2)	166.00

Table S19. Bond lengths for **5**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.233(2)	C1-C2	1.401(3)
O2-N1	1.215(3)	C2-C3	1.383(3)
N1-C1	1.420(3)	C3-C4	1.423(3)
N2-N3	1.339(3)	N3-H3	0.8700
N2-C1	1.330(3)	C4-C5	1.447(3)
N3-C3	1.378(2)	N4-H4	0.87(3)
N4-N5	1.352(3)	N9-H9A	0.94(3)
N4-C2	1.345(3)	N9-H9B	0.83(3)
N5-C4	1.343(2)	N10-H10A	0.8700
N6-N7	1.396(2)	N10-H10B	0.84(2)
N6-C5	1.306(2)	O3-H3A	0.8600
N7-C6	1.316(2)	O3-H3B	0.8600
N8-N9	1.398(2)	O4A-H4AA	0.8600
N8-C5	1.366(2)	O4A-H4AB	0.8600
N8-C6	1.367(2)	O04-H04A	0.8600
N10-C6	1.354(3)	O04-H04B	0.8600

Table S20. Bond angles for **5**.

Parameter	bond angle (°)	Parameter	bond angle (°)
O1-N1-O2	123.8(2)	N2-N3-H3	124.00
O1-N1-C1	115.88(18)	N5-C4-C5	118.30(16)
O2-N1-C1	120.33(18)	N5-C4-C3	108.58(16)
N3-N2-C1	106.01(16)	N5-N4-H4	118(2)
N2-N3-C3	111.34(15)	C2-N4-H4	131(2)
N5-N4-C2	110.34(16)	C3-C4-C5	133.12(16)
N4-N5-C4	107.74(15)	N6-C5-N8	109.60(16)
N7-N6-C5	107.80(15)	N6-C5-C4	126.05(16)
N6-N7-C6	107.10(16)	N8-C5-C4	124.34(16)
N9-N8-C5	123.22(16)	N7-C6-N10	127.13(18)
N9-N8-C6	130.69(16)	N8-C6-N10	123.17(16)
C5-N8-C6	105.99(14)	N7-C6-N8	109.51(16)
N1-C1-N2	122.36(19)	N8-N9-H9A	107.7(15)
N1-C1-C2	126.21(18)	N8-N9-H9B	108.7(18)
N2-C1-C2	111.39(18)	H9A-N9-H9B	105(2)
N4-C2-C1	146.92(19)	C6-N10-H10A	110.00
N4-C2-C3	108.16(17)	C6-N10-H10B	117.2(17)
C1-C2-C3	104.92(16)	H10A-N10-H10B	127.00
N3-C3-C2	106.35(16)	H3A-O3-H3B	104.00
N3-C3-C4	148.47(18)	H4AA-O4A-H4AB	104.00
C2-C3-C4	105.19(16)	H04A-O04-H04B	105.00
C3-N3-H3	124.00		

Table S21. Torsion angles for **5**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
O1-N1-C1-N2	177.6(2)	N7-N6-C5-N8	-0.3(2)
O2-N1-C1-N2	-1.3(3)	C5-N6-N7-C6	-0.1(2)
O1-N1-C1-C2	0.2(3)	N7-N6-C5-C4	178.73(19)
O2-N1-C1-C2	-178.7(2)	N6-N7-C6-N8	0.4(2)
N3-N2-C1-C2	-0.2(2)	N6-N7-C6-N10	175.3(2)
C1-N2-N3-C3	0.1(2)	N9-N8-C5-N6	177.13(18)
N3-N2-C1-N1	-177.9(2)	C5-N8-C6-N10	-175.72(19)
N2-N3-C3-C2	0.0(2)	C6-N8-C5-C4	-178.53(18)
N2-N3-C3-C4	179.4(3)	N9-N8-C6-N10	8.0(3)
C2-N4-N5-C4	-0.1(2)	C5-N8-C6-N7	-0.5(2)
N5-N4-C2-C3	-0.2(2)	N9-N8-C6-N7	-176.8(2)
N5-N4-C2-C1	-179.9(3)	N9-N8-C5-C4	-1.9(3)
N4-N5-C4-C3	0.4(2)	C6-N8-C5-N6	0.5(2)
N4-N5-C4-C5	-179.18(18)	N2-C1-C2-C3	0.2(3)
N2-C1-C2-N4	179.9(3)	C1-C2-C3-N3	-0.1(2)
N1-C1-C2-C3	177.8(2)	N4-C2-C3-C4	0.4(2)
N1-C1-C2-N4	-2.5(5)	C1-C2-C3-C4	-179.77(17)
N4-C2-C3-N3	-179.93(17)	N3-C3-C4-C5	-0.4(5)

Table S22. Hydrogen bonds for **5**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N3-H3···N9	0.8700	2.4100	2.937(3)	120.00
N3-H3···N7	0.8700	2.0400	2.853(2)	154.00
O3-H3A···N2	0.8600	2.3800	3.231(2)	173.00
O3-H3B···O2	0.86000	2.3200	3.166(3)	169.00
N4-H4···O4A	0.87(3)	2.01(3)	2.882(4)	175(3)
N9-H9A···N10	0.94(3)	2.59(3)	3.364(3)	140.3(18)
N9-H9A···N6	0.94(3)	2.37(3)	2.836(3)	110.4(19)
N9-H9B···N6	0.83(3)	2.11(3)	2.946(3)	177(2)
N10-H10A···O3	0.8700	2.2300	3.100(3)	175.00
N10-H10B···N5	0.84(2)	2.33(2)	3.168(2)	176(2)

Table S23. Bond lengths for **6**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
Cl1-O6	1.421(2)	N9-N10	1.397(3)
Cl1-O5	1.421(3)	N9-C5	1.376(3)
Cl1-O3	1.426(2)	C1-C2	1.400(3)
Cl1-O4	1.431(2)	C2-C3	1.384(3)
O1-N1	1.234(3)	C3-C4	1.412(3)
O2-N1	1.221(3)	N3-H3	0.8700
N1-C1	1.424(3)	C4-C5	1.453(3)
N2-N3	1.341(3)	N4-H4	0.8700
N2-C1	1.329(3)	N7-H7	0.8700
N3-C3	1.357(3)	N8-H8B	0.8700

N4-N5	1.348(3)	N8-H8A	0.8700
N4-C2	1.356(3)	N10-H10A	0.7800
N5-C4	1.341(3)	N10-H10B	0.8700
N6-C5	1.300(3)	O7-H7A	0.8600
N6-N7	1.381(3)	O7-H7B	0.8600
N7-C6	1.323(3)	O8-H8C	0.8600
N8-C6	1.316(3)	O8-H8D	0.8600
N9-C6	1.363(3)		

Table S24. Bond angles for **6**.

Parameter	bond angle (°)	Parameter	bond angle (°)
O4-Cl1-O6	109.61(14)	N3-C3-C2	107.12(19)
O5-Cl1-O6	111.02(17)	C3-N3-H3	124.00
O3-Cl1-O5	108.16(16)	C2-C3-C4	105.29(18)
O3-Cl1-O6	109.66(15)	N2-N3-H3	124.00
O3-Cl1-O4	109.45(13)	C2-N4-H4	125.00
O4-Cl1-O5	108.90(15)	C3-C4-C5	131.40(19)
O2-N1-C1	119.94(19)	N5-C4-C3	109.33(18)
O1-N1-C1	115.55(19)	N5-C4-C5	119.23(18)
O1-N1-O2	124.5(2)	N5-N4-H4	125.00
N3-N2-C1	105.88(18)	N9-C5-C4	124.16(19)
N2-N3-C3	111.35(18)	N6-C5-N9	110.58(18)
N5-N4-C2	110.42(17)	N6-C5-C4	125.21(19)
N4-N5-C4	107.39(17)	N8-C6-N9	125.3(2)
N7-N6-C5	105.07(17)	N7-C6-N8	128.9(2)
N6-N7-C6	111.45(18)	N7-C6-N9	105.83(18)
N10-N9-C6	127.27(17)	N6-N7-H7	124.00
N10-N9-C5	125.62(17)	C6-N7-H7	124.00
C5-N9-C6	107.06(17)	C6-N8-H8B	120.00
N1-C1-N2	120.17(19)	C6-N8-H8A	120.00
N1-C1-C2	128.5(2)	H8A-N8-H8B	120.00
N2-C1-C2	111.37(19)	H10A-N10-H10B	110.00
N4-C2-C3	107.57(19)	N9-N10-H10A	101.00
C1-C2-C3	104.28(19)	N9-N10-H10B	109.00
N4-C2-C1	148.2(2)	H7A-O7-H7B	105.00
N3-C3-C4	147.6(2)	H8C-O8-H8D	105.00

Table S25. Torsion angles for **6**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
O1-N1-C1-N2	-173.1(2)	N7-N6-C5-N9	-0.7(3)
O2-N1-C1-N2	6.2(3)	C5-N6-N7-C6	1.1(3)
O1-N1-C1-C2	7.2(3)	N7-N6-C5-C4	-178.1(2)
O2-N1-C1-C2	-173.5(2)	N6-N7-C6-N8	178.8(2)
N3-N2-C1-C2	-0.8(3)	N6-N7-C6-N9	-1.1(3)
C1-N2-N3-C3	0.4(3)	N10-N9-C5-N6	177.4(2)
N3-N2-C1-N1	179.5(2)	C5-N9-C6-N8	-179.2(2)

N2-N3-C3-C2	0.1(3)	C6-N9-C5-C4	177.5(2)
N2-N3-C3-C4	-178.6(3)	N10-N9-C6-N8	3.5(4)
C2-N4-N5-C4	-0.4(3)	C5-N9-C6-N7	0.7(2)
N5-N4-C2-C3	0.7(3)	N10-N9-C6-N7	-176.7(2)
N5-N4-C2-C1	-178.2(3)	N10-N9-C5-C4	-5.1(3)
N4-N5-C4-C3	0.0(3)	C6-N9-C5-N6	0.0(3)
N4-N5-C4-C5	177.88(19)	N2-C1-C2-C3	0.9(3)
N2-C1-C2-N4	179.8(3)	N3-C3-C4-N5	179.2(3)
N1-C1-C2-C3	-179.4(2)	C2-C3-C4-C5	-177.1(2)
N1-C1-C2-N4	-0.5(5)	C2-C3-C4-N5	0.5(2)
N4-C2-C3-N3	-179.98(19)	C3-C4-C5-N6	178.6(2)
C1-C2-C3-N3	-0.6(2)	C3-C4-C5-N9	1.4(4)
N4-C2-C3-C4	-0.7(2)	N5-C4-C5-N9	-176.0(2)
C1-C2-C3-C4	178.69(18)	N5-C4-C5-N6	1.2(3)
N3-C3-C4-C5	1.6(5)		

Table S26. Hydrogen bonds for **6**.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N3-H3···N10	0.8700	2.3300	2.893(3)	154.00
N3-H3···O1	0.8700	2.1400	2.837(3)	173.00
N4-H4···O8	0.8700	1.9400	2.801(3)	169.00
N7-H7···O7	0.8700	1.9300	2.694(3)	175(3)
O7-H7A···N6	0.8600	2.0000	2.850(3)	140.3(18)
O7-H7B···N5	0.8600	2.5300	3.063(3)	110.4(19)
O7-H7B···O4	0.8600	2.2300	2.898(3)	177(2)
N8-H8A···O3	0.8700	2.1400	2.986(3)	175.00
N8-H8B···O6	0.8700	2.2600	3.050(3)	176(2)
N10-H10A···O7	0.7800	2.3000	3.039(3)	158.00
N10-H10B···O8	0.8700	2.2000	2.966(3)	146.00

4. ESP analysis

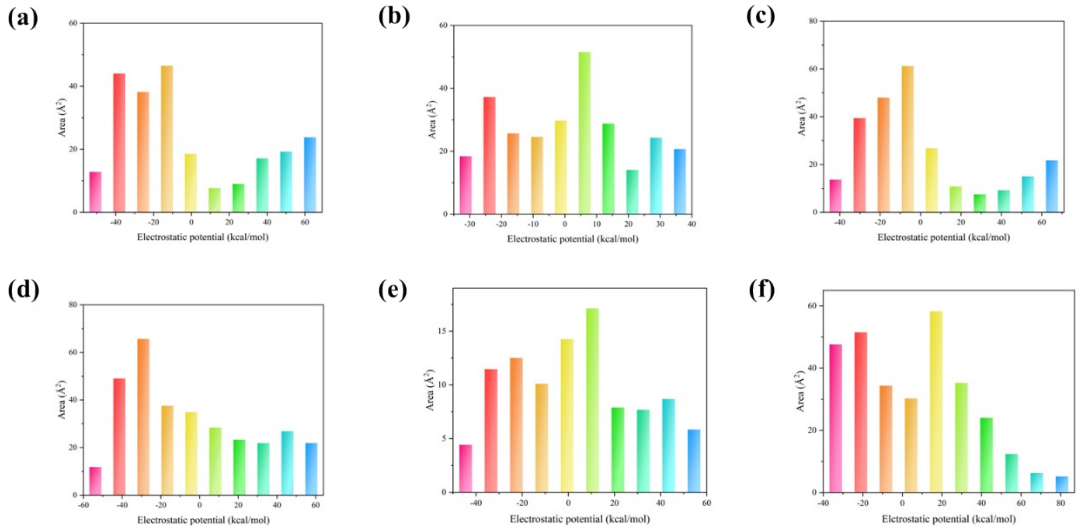


Figure S13. Quantitative distribution of ESP in **1**(a), **2**(b), **3**(c), **4**(d), **5**(e) and **6**(f)

5. Hygroscopic ability

Table S27 The hygroscopic ability of salt **3**.

Salt	Humidity/%RH	m_1/mg [a]	m_2/mg [b]	m_3/mg [c]	Hygroscopicity/%
3	40	200.05	200.05	-	-
	60	200.17	200.17	-	-
	80	200.11	201.69	1.58	0.79

[a] The mass of dried salts.

[b] The mass of salts that reaches equilibrium under the humidity conditions.

[c] The mass of water.

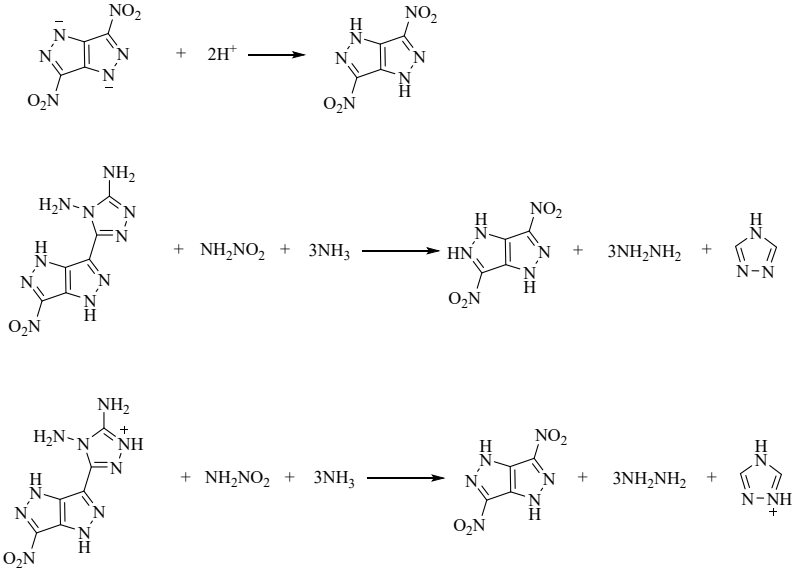
6. Heats of formation

The enthalpy of formation is an important parameter in chemical thermodynamics calculation, and is a crucial basis for evaluating the detonation velocity and detonation pressure of energetic compounds. The enthalpy of formation of **1-6** was theoretically calculated with the Gaussian 09 program[2]. At the B3LYP/6-311+G** level[3-6], geometric optimization and frequency analysis were carried out for cations in all compounds, and the stable structures at the local energy minimum on the potential energy surface were obtained without imaginary frequencies. The enthalpy of formation of the compound was calculated based on the designed isodesmic reaction. The enthalpy of formation of ammonium, hydrazinium, hydroxylammonium, guanidinium and perchlorate has been reported in relevant literature, and this work will cite directly.

At 298 K, the standard heat of formation of cations can be calculated by the following equation:

$$\Delta H(\text{cation, 298K}) = \Delta E(\text{cation, 298K}) + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT$$

where ΔE_0 is the difference in total energies between the products and reactants at 0 K, ΔZPE is the difference in zero energy between the product and reactant at 0 K, and ΔHT is the temperature correction factor. As shown in **Scheme S1.**, the following is the isodesmic reactions for all the calculated compounds. The heat of formation of DNPP and small molecules can be found in the literature or calculated with G4.



Scheme S1. Isodesmic reactions for all the calculated cations.

At 298 K, the standard enthalpy of formation of ionic compound can be calculated by the following equation:

$$\Delta H_f\,(\text{salt, 298K}) = \Delta H_f\,(\text{cation, 298K}) + \Delta H_f(\text{anion, 298K}) - \Delta H_L$$

where ΔH_L is the lattice energy of the salts, which could be obtained with the following formula proposed by Jenkins et al[7].

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

where n_M and n_X depend on the nature of the ions, M^{p+} and X^{q-}, and are equal to three for monatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The following is the equation for lattice potential energy U_{POT}:

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

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material. The value of coefficient γ and δ are acquired from relevant literature[8].

7. References

1. Y. Li, T. Tang, P. Lian, Y. Luo, W. Yang, Y. Wang, H. Li, Z. Zhang and B. Wang, *Chin. J. Org. Chem.*, 2012, **32**, 580-588.

2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. A. Petersson, *Gaussian 09 (Revision D.01)*. Gaussian. Inc.: Wallingford CT 2009.

3. P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem. C*, 1994, **98**, 11623-11627.

4. K. Raghavachari, *Theor. Chem. Acc.*, 2000, **103**, 361-363.

5. J. A. Pople, J. S. Binkley and R. Seeger, *Int. J. Chem.*, 1976, **10**, 1-19.

6. P. C. Hariharan and J. A. Pople, *Theor. Chem. Acc.*, 1973, **28**, 213-222.

7. H. D. B. Jenkins, H. K. Roobottom, J. Passmore and L. Glasser, *Inorg. Chem.*, 1999, **38**, 3609-3620.

8. H. D. B. Jenkins, D. Tudela and L. Glasser, *Inorg. Chem.*, 2002, **41**, 2364-2367.