Electronic Supplementary Material (ESI) for RSC Advances.

1. NMR Spectrum of the salts

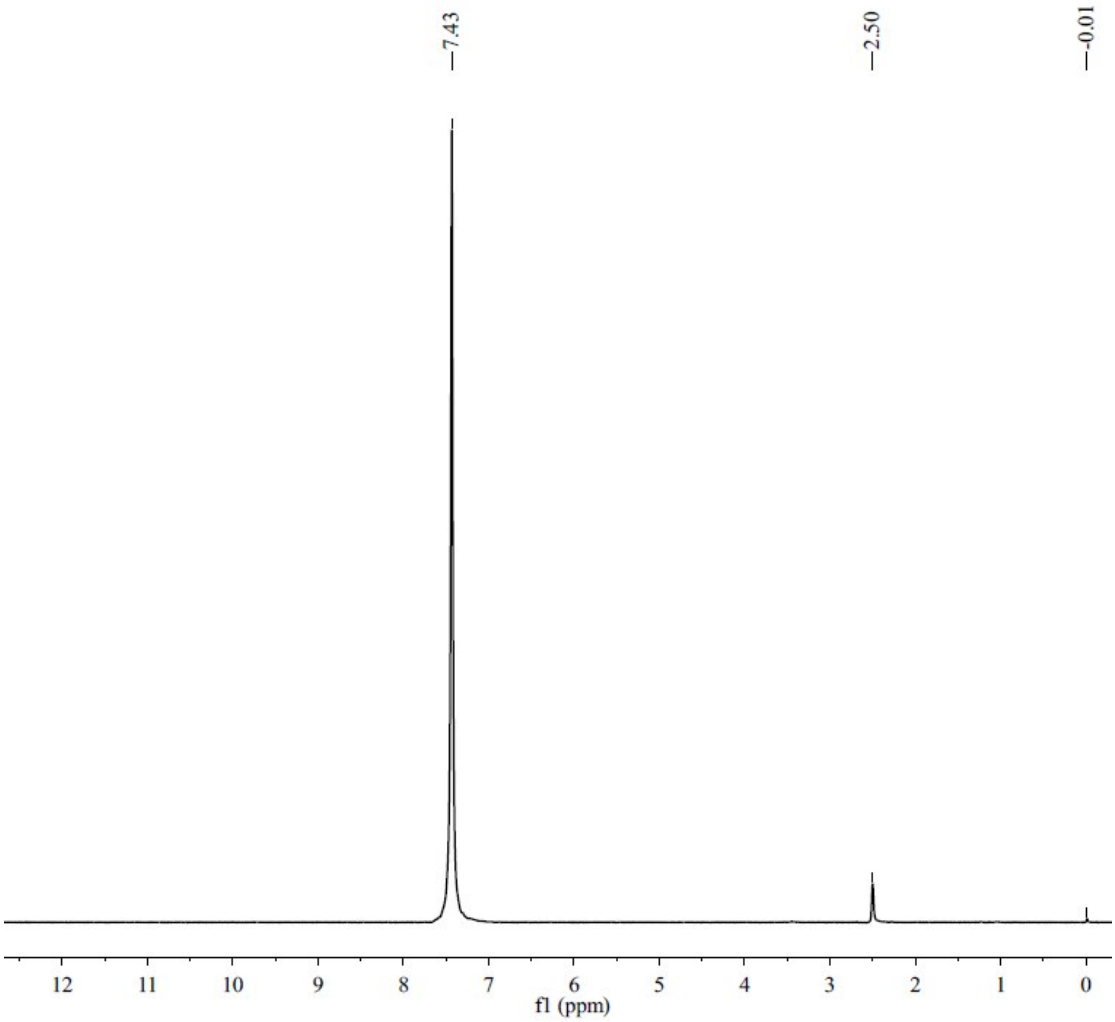


Figure S1. ^{1}H NMR spectrum of diammonium NATF (**2**)

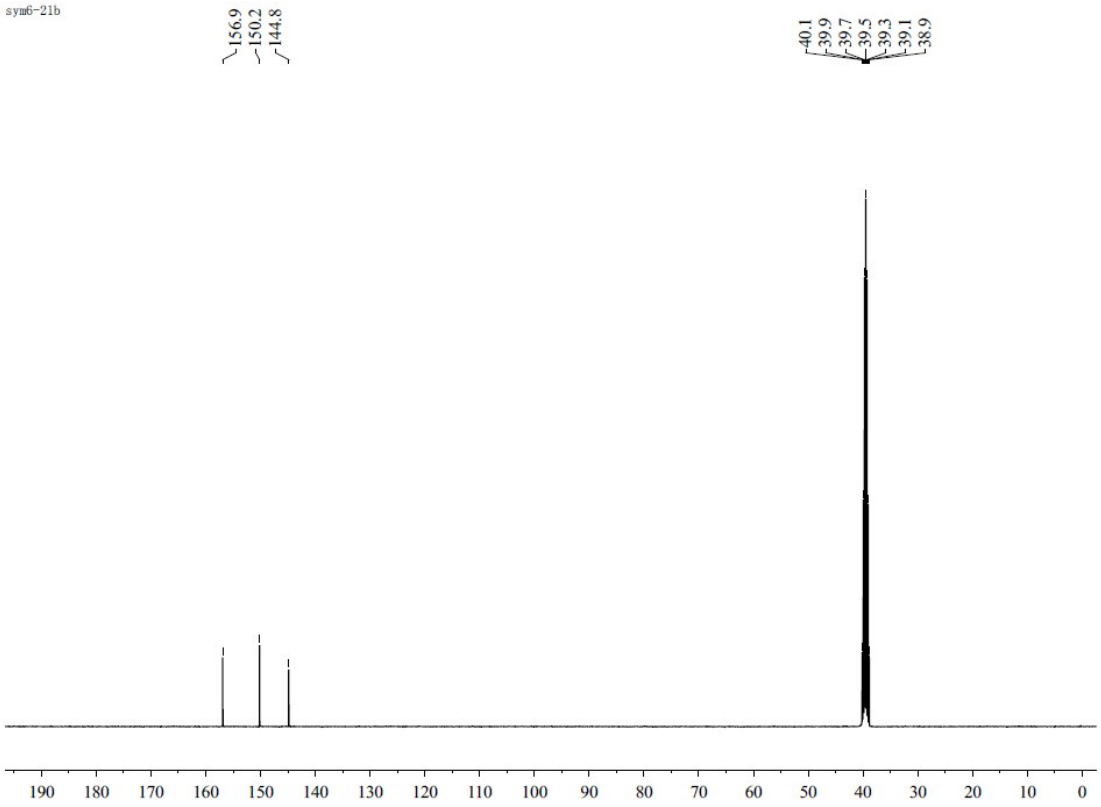


Figure S2. ^{13}C NMR spectrum of diammonium NATF (**2**)

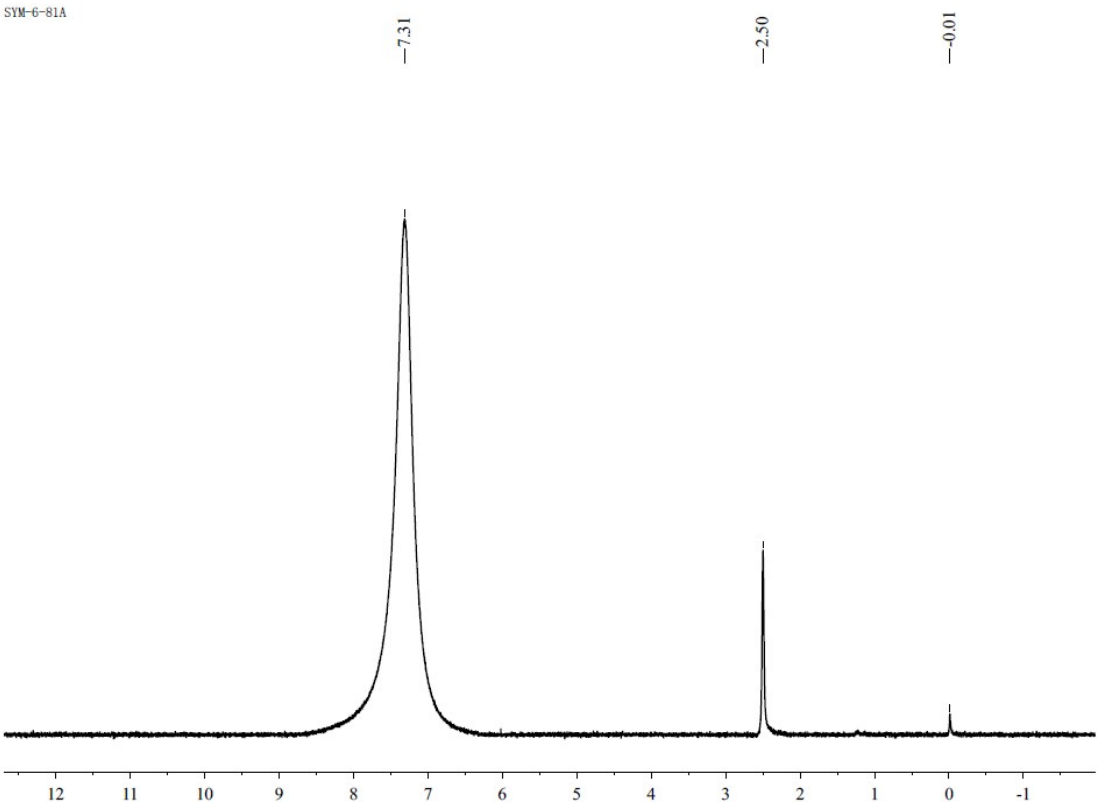


Figure S3. ^{1}H NMR spectrum of dihydrazinium NATF (**4**)

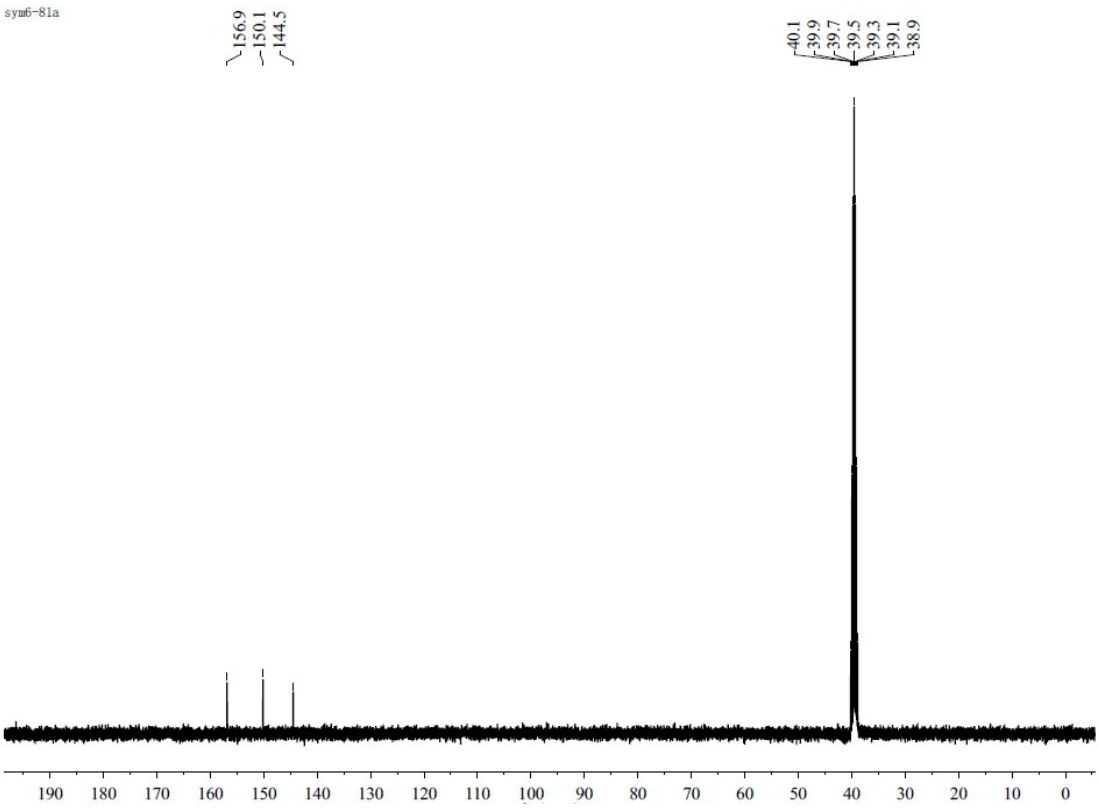


Figure S4. ^{13}C NMR spectrum of dihydrazinium NATF (**4**)

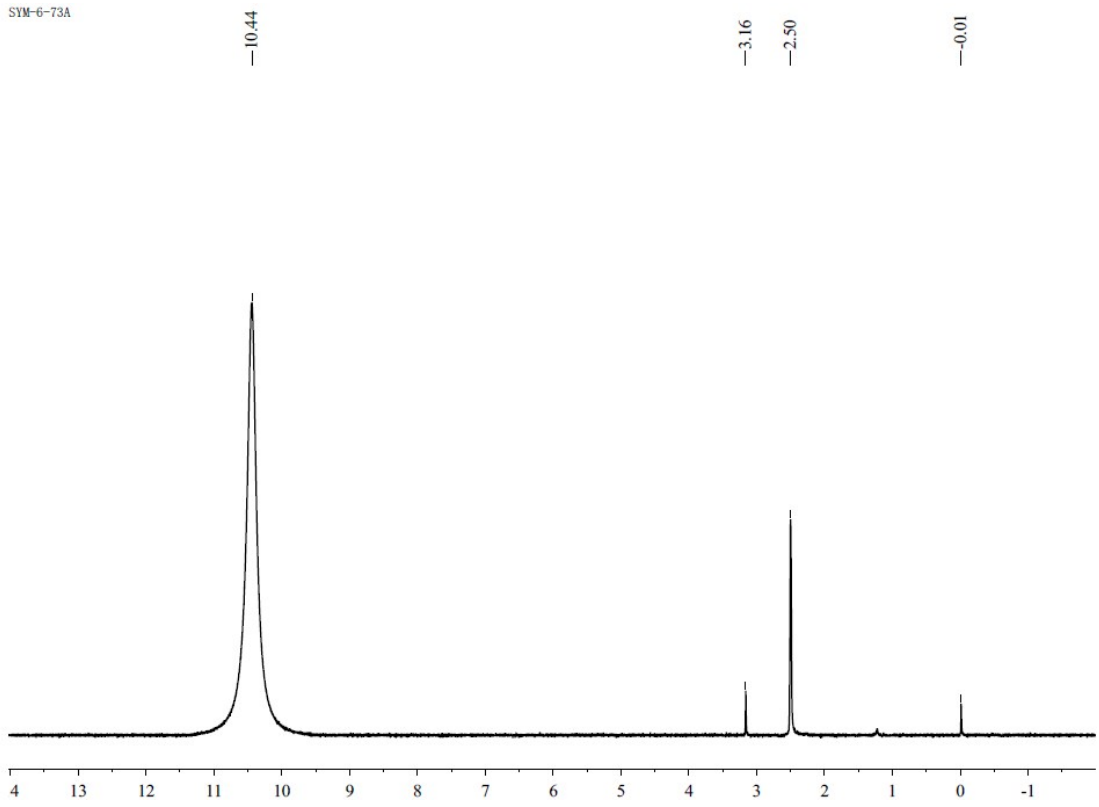


Figure S5. ^{1}H NMR spectrum of dihydroxylammonium NATF (**5**)

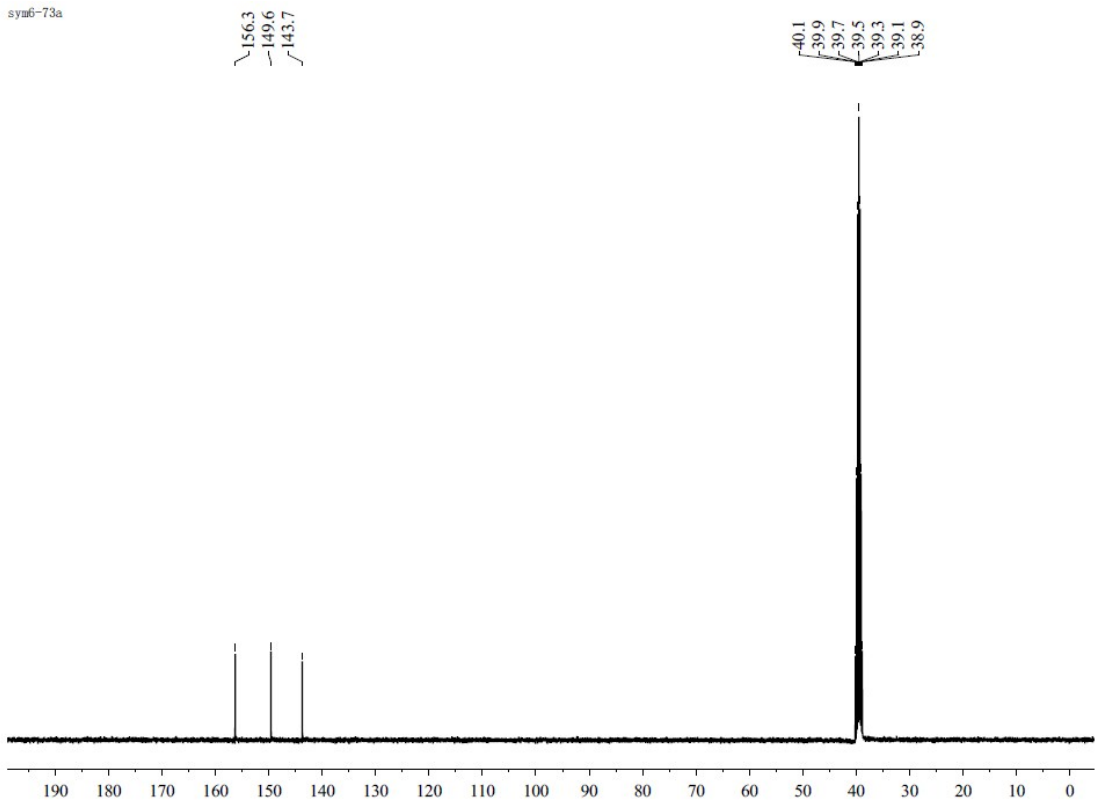


Figure S6. ^{13}C NMR spectrum of dihydroxylammonium NATF (**5**)

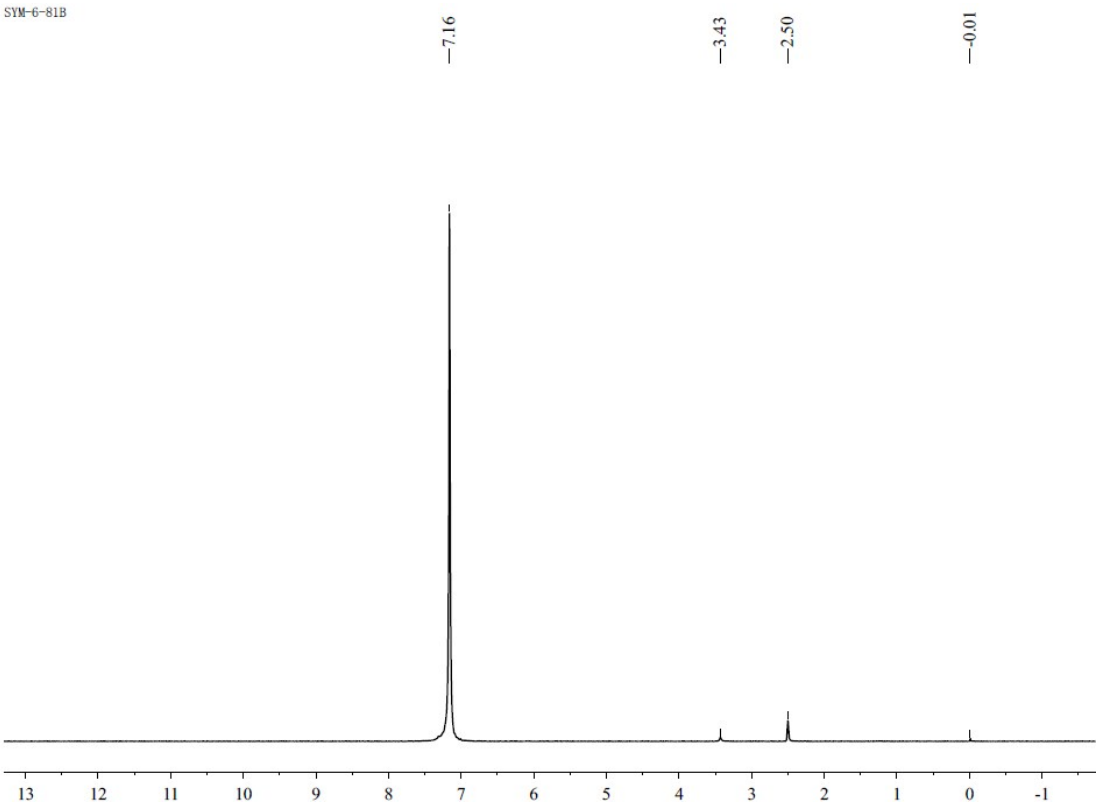


Figure S7. ^{1}H NMR spectrum of bis(guanidinium) NATF (**6**)

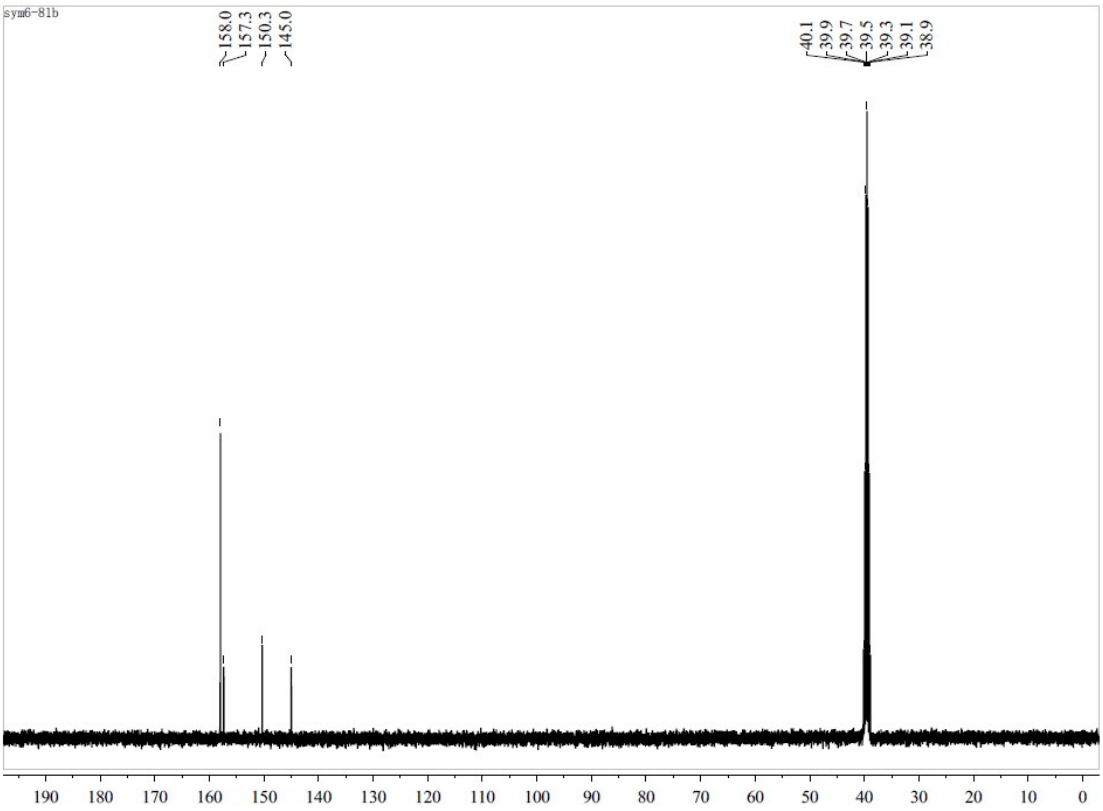


Figure S8. ^{13}C NMR spectrum of bis(guanidinium) NATF (**6**)

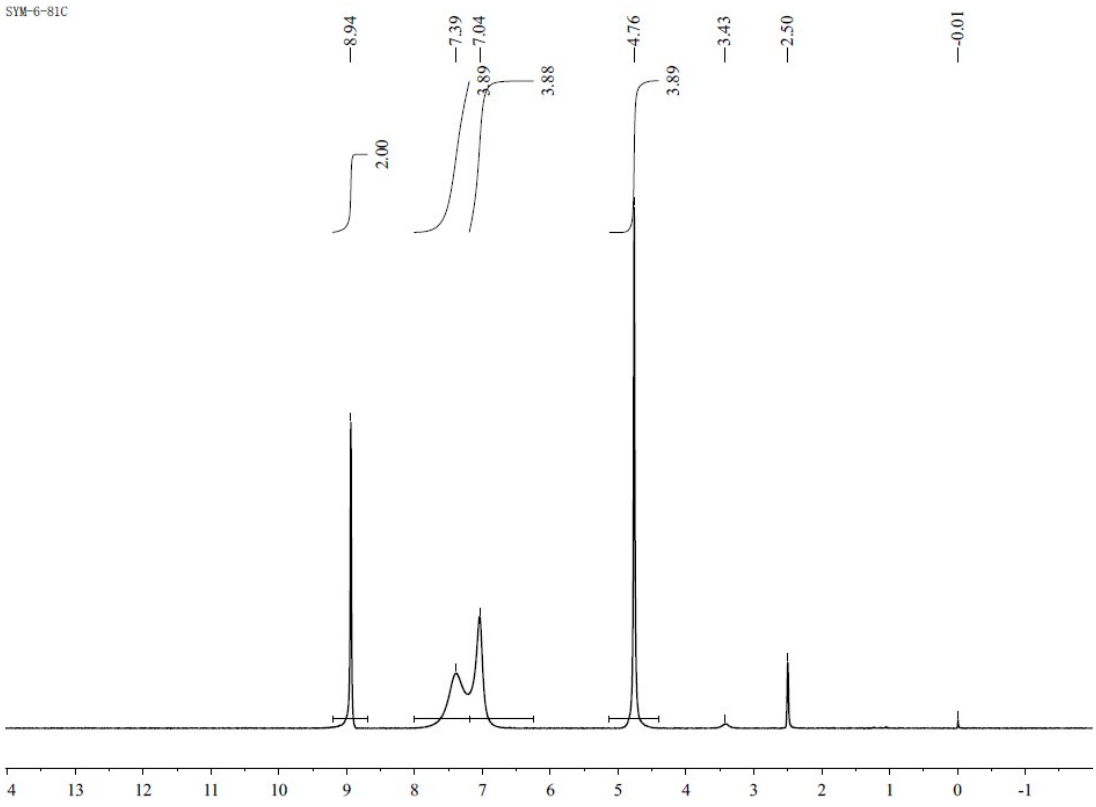


Figure S9. ^{1}H NMR spectrum of bis(aminoguanidinium) NATF (**7**)

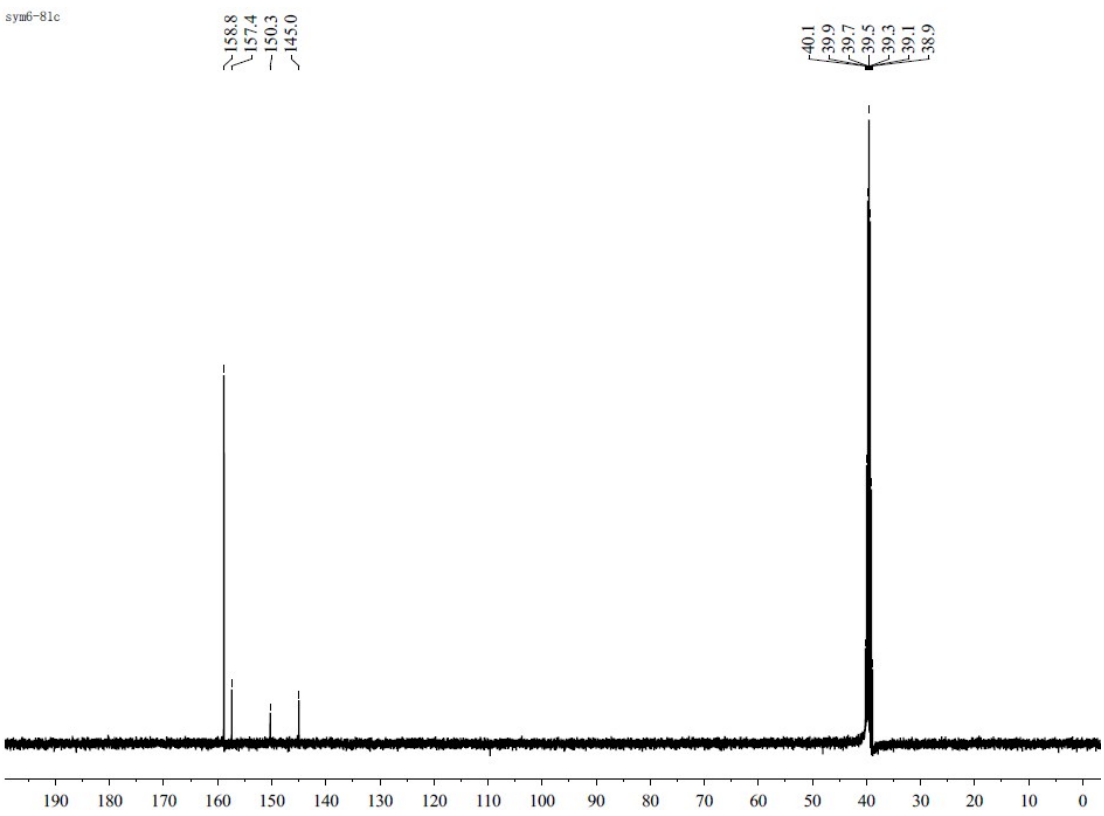


Figure S10. ^{13}C NMR spectrum of bis(aminoguanidinium) NATF (**7**)

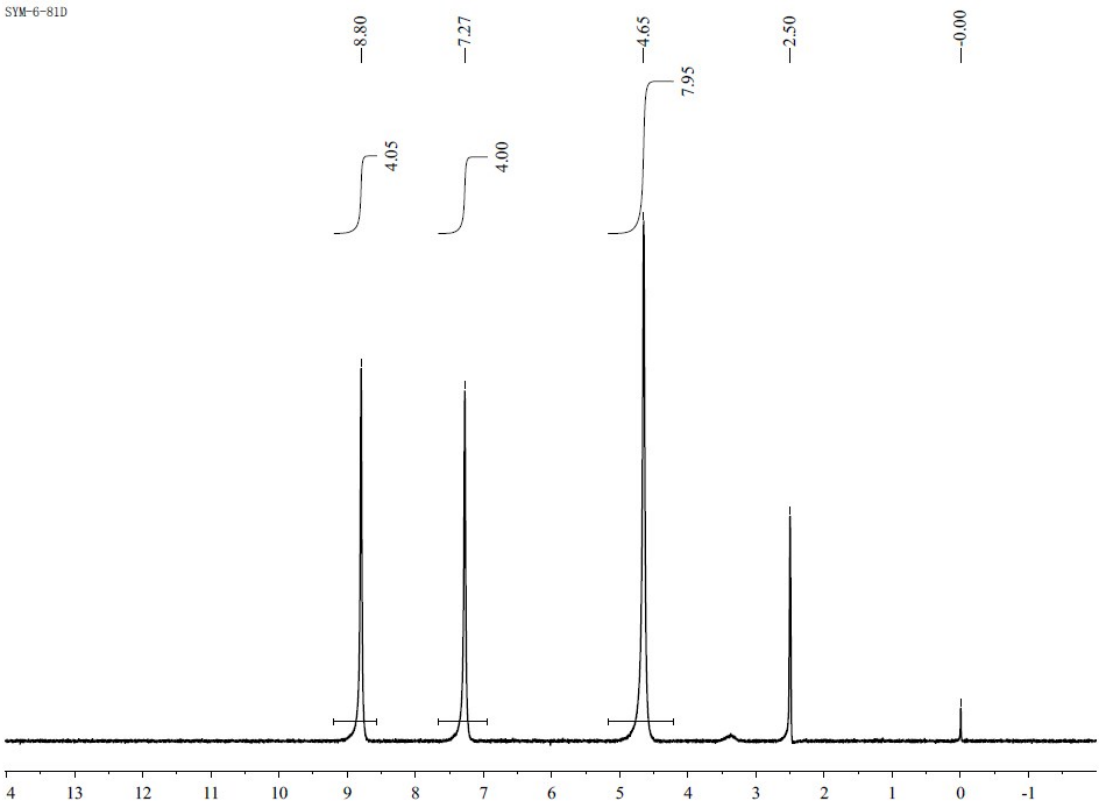


Figure S11. ^{1}H NMR spectrum of bis(diaminoguanidinium) NATF (**8**)

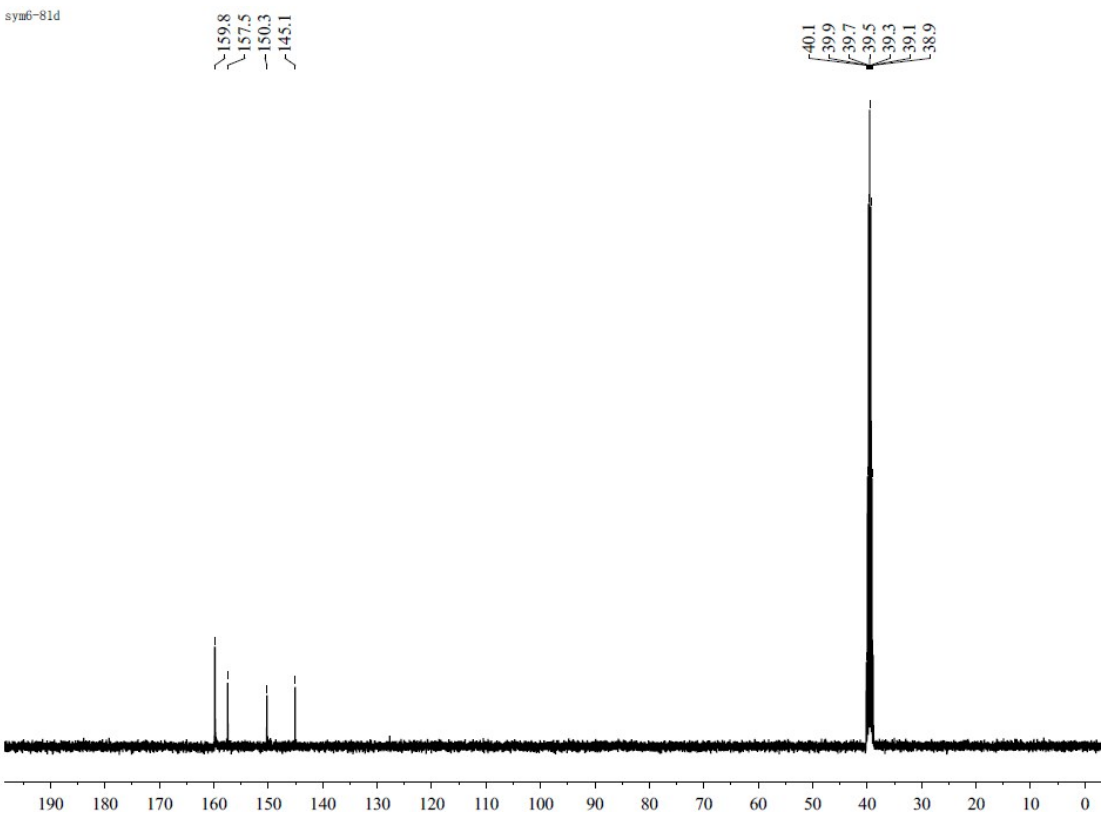


Figure S12. ^{13}C NMR spectrum of bis(diaminoguanidinium) NATF (**8**)

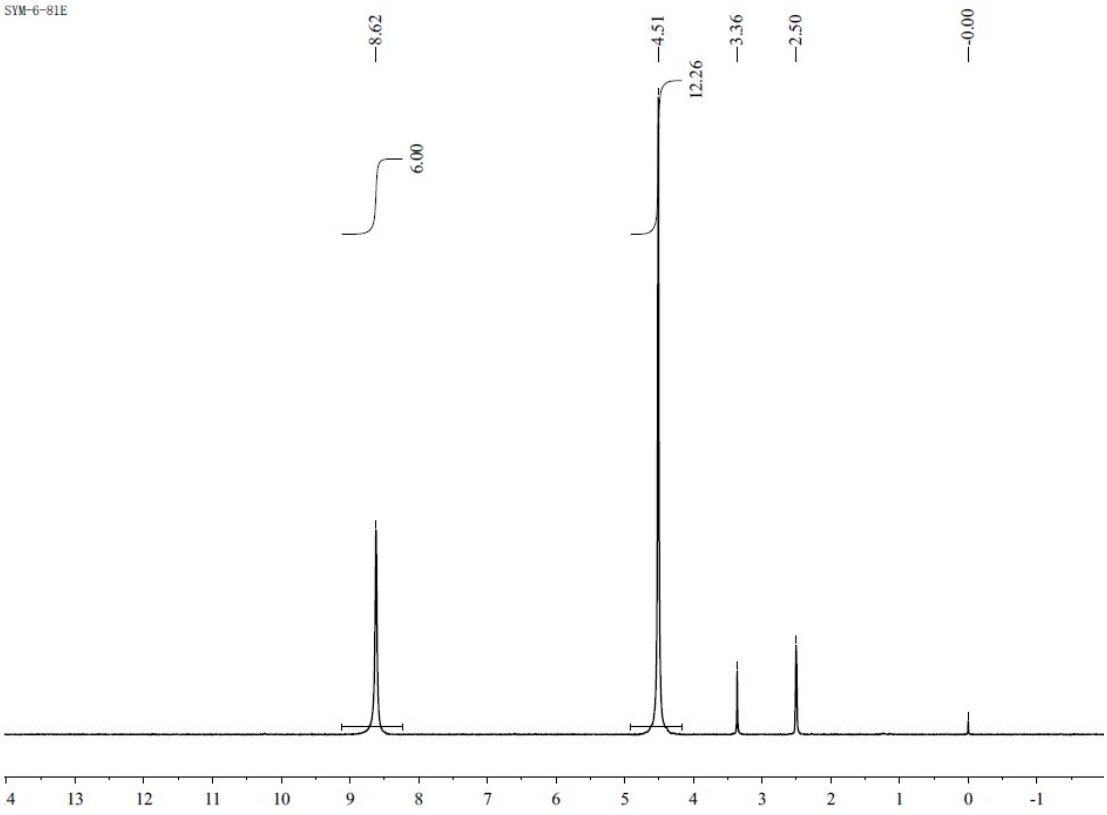


Figure S13. ^{1}H NMR spectrum of bis(triaminoguanidinium) NATF (**9**)

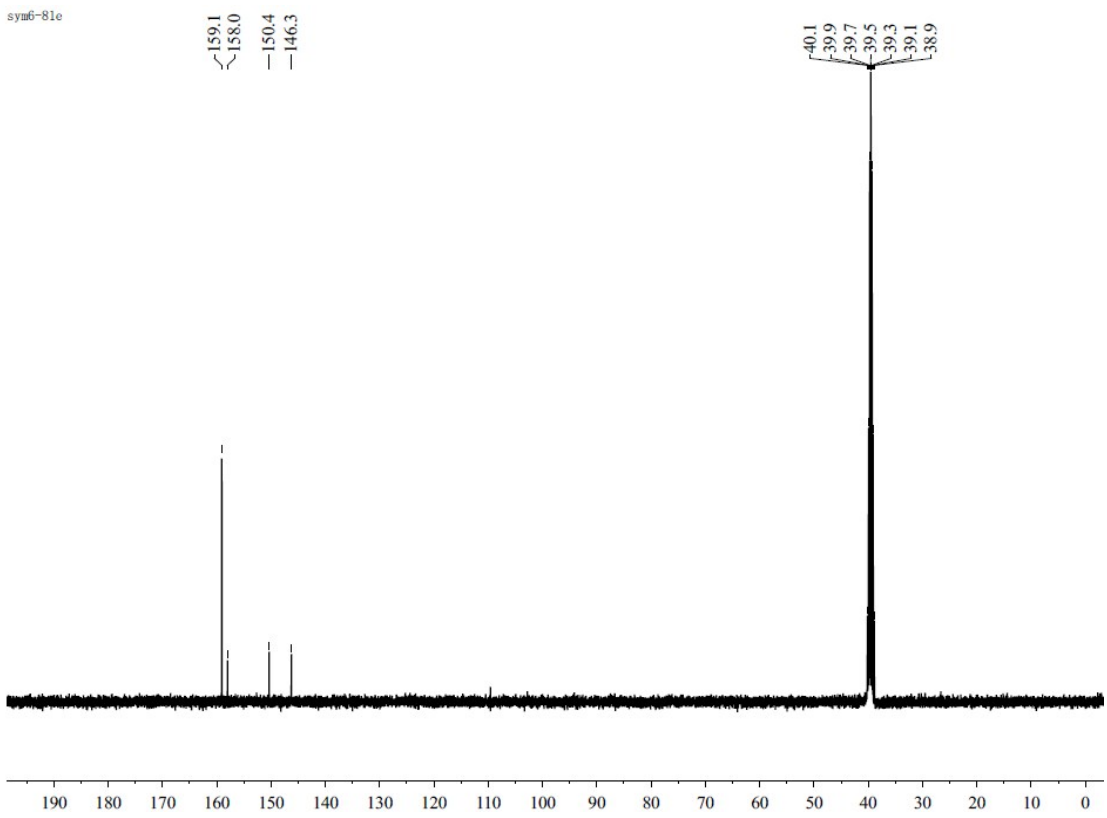


Figure S14. ^{13}C NMR spectrum of bis(triaminoguanidinium) NATF (**9**)

2. Crystallographic data

Table S1 Crystallographic data and structure refinement parameters for **5** [a].

	5
CCDC number	1476973
Empirical formula	$C_3H_8N_{10}O_5$
Mw	264.19
Crystal system	Triclinic
Space group	P -1
a[Å]	7.2173(13)
b[Å]	8.1190(14)
c[Å]	9.0665(16)
α[°]	84.202(3)
β[°]	71.566(3)
γ[°]	73.613(3)
V[Å^3]	483.50(15)
Z	2
T[K]	293(2)
λ[Å]	0.71073
Density[mg m^{-3}]	1.815
μ[mm^{-1}]	0.17
F(000)	272
Crystal size[mm^{-3}]	0.21×0.17×0.11
θ range[°]	2.368-25.999
Index ranges	-4≤h≤8
	-9≤k≤9
	-10≤l≤11
Reflections collected	2890
Independent reflections	1885 [R(int)=0.0152]

Data/retraints/parameters	1885/0/196
GOF	1.057
$R[F^2 > 2\sigma(F^2)]$	0.0339
$wR(F^2)$[b]	0.0886

[a] These data can be obtained free of charge from The Cambridge Cry-tallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[b] $w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 0.3662P]$,where $P = (F_o^2 + 2F_c^2)/3$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for salt **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	1186(2)	-625(2)	6396(1)	25(1)
N(2)	2211(2)	151(2)	5226(1)	27(1)
N(3)	884(2)	2901(2)	6571(2)	31(1)
N(4)	2673(2)	4375(2)	4639(2)	32(1)
N(5)	5469(2)	3293(2)	1694(1)	29(1)
N(6)	6651(2)	2318(2)	468(2)	32(1)
N(7)	6401(2)	769(2)	718(2)	33(1)
N(8)	5051(2)	686(2)	2115(1)	31(1)
N(9)	6268(2)	2481(2)	7234(2)	29(1)
N(10)	824(2)	2594(2)	-54(2)	32(1)
O(1)	1297(2)	4475(1)	6089(1)	35(1)
O(2)	1421(2)	-2203(1)	6195(1)	35(1)
O(3)	46(2)	62(1)	7648(1)	36(1)
O(4)	4342(2)	3559(2)	7872(2)	43(1)
O(5)	410(2)	3670(2)	1186(1)	43(1)
C(1)	1996(2)	1865(2)	5413(2)	24(1)
C(2)	3109(2)	2804(2)	4202(2)	24(1)
C(3)	4517(2)	2253(2)	2683(2)	24(1)

Table S3. Bond lengths [Å] and angles [°] for salt **5**.

N(1)-O(3)	1.2468(16)
N(1)-O(2)	1.2683(16)
N(1)-N(2)	1.3039(17)
N(2)-C(1)	1.3776(18)
N(3)-C(1)	1.3110(18)
N(3)-O(1)	1.3902(17)
N(4)-C(2)	1.2962(19)
N(4)-O(1)	1.3683(17)
N(5)-C(3)	1.3316(19)
N(5)-N(6)	1.3367(17)
N(6)-N(7)	1.3077(18)
N(7)-N(8)	1.3408(18)
N(8)-C(3)	1.3274(18)
N(9)-O(4)	1.3934(17)
N(9)-H(9A)	0.93(2)
N(9)-H(9B)	0.86(2)
N(9)-H(9C)	0.89(2)
N(10)-O(5)	1.3990(17)
N(10)-H(10A)	0.91(2)
N(10)-H(10B)	0.90(3)
N(10)-H(10C)	0.94(2)
O(4)-H(4)	0.83(3)
O(5)-H(5)	0.87(3)
C(1)-C(2)	1.432(2)
C(2)-C(3)	1.454(2)
O(3)-N(1)-O(2)	119.80(12)
O(3)-N(1)-N(2)	125.18(12)
O(2)-N(1)-N(2)	115.03(11)
N(1)-N(2)-C(1)	116.42(12)
C(1)-N(3)-O(1)	104.85(11)
C(2)-N(4)-O(1)	106.00(12)
C(3)-N(5)-N(6)	104.91(12)
N(7)-N(6)-N(5)	109.19(12)
N(6)-N(7)-N(8)	109.74(12)
C(3)-N(8)-N(7)	104.50(12)

O(4)-N(9)-H(9A)	106.9(12)
O(4)-N(9)-H(9B)	111.3(15)
H(9A)-N(9)-H(9B)	114(2)
O(4)-N(9)-H(9C)	105.2(13)
H(9A)-N(9)-H(9C)	107.3(18)
H(9B)-N(9)-H(9C)	112(2)
O(5)-N(10)-H(10A)	113.0(14)
O(5)-N(10)-H(10B)	107.7(16)
H(10A)-N(10)-H(10B)	108(2)
O(5)-N(10)-H(10C)	107.2(13)
H(10A)-N(10)-H(10C)	109.4(19)
H(10B)-N(10)-H(10C)	111(2)
N(4)-O(1)-N(3)	111.30(10)
N(9)-O(4)-H(4)	104.8(16)
N(10)-O(5)-H(5)	102.7(16)
N(3)-C(1)-N(2)	131.13(13)
N(3)-C(1)-C(2)	108.78(12)
N(2)-C(1)-C(2)	120.09(12)
N(4)-C(2)-C(1)	109.07(13)
N(4)-C(2)-C(3)	120.67(13)
C(1)-C(2)-C(3)	130.26(13)
N(8)-C(3)-N(5)	111.66(13)
N(8)-C(3)-C(2)	125.60(13)
N(5)-C(3)-C(2)	122.73(13)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for salt **5**.

The anisotropicdisplacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	30(1)	22(1)	21(1)	1(1)	-5(1)	-8(1)
N(2)	35(1)	22(1)	21(1)	-1(1)	0(1)	-11(1)
N(3)	40(1)	24(1)	24(1)	-3(1)	0(1)	-12(1)
N(4)	40(1)	24(1)	25(1)	-4(1)	1(1)	-11(1)
N(5)	32(1)	25(1)	26(1)	-2(1)	1(1)	-10(1)
N(6)	34(1)	31(1)	26(1)	-2(1)	1(1)	-10(1)
N(7)	37(1)	30(1)	26(1)	-6(1)	2(1)	-11(1)
N(8)	36(1)	26(1)	25(1)	-4(1)	1(1)	-11(1)
N(9)	31(1)	25(1)	27(1)	-1(1)	-2(1)	-8(1)
N(10)	38(1)	27(1)	25(1)	-2(1)	1(1)	-11(1)
O(1)	49(1)	23(1)	26(1)	-7(1)	3(1)	-12(1)
O(2)	51(1)	21(1)	30(1)	0(1)	-3(1)	-14(1)
O(3)	42(1)	31(1)	24(1)	-3(1)	6(1)	-10(1)
O(4)	29(1)	25(1)	65(1)	-9(1)	4(1)	-9(1)
O(5)	71(1)	33(1)	24(1)	-2(1)	-2(1)	-24(1)
C(1)	27(1)	23(1)	20(1)	-2(1)	-4(1)	-8(1)
C(2)	28(1)	23(1)	23(1)	-1(1)	-6(1)	-8(1)
C(3)	27(1)	23(1)	21(1)	-1(1)	-5(1)	-9(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for salt **5**.

	x	y	z	U(eq)
H(4)	4540(30)	4510(30)	7950(30)	59(6)
H(5)	-120(40)	3090(30)	1990(30)	64(7)
H(9A)	7000(30)	2450(30)	7920(20)	49(6)
H(10A)	1530(30)	1500(30)	90(30)	56(6)
H(9B)	6830(30)	2810(30)	6310(30)	59(6)
H(10B)	1560(40)	3040(30)	-910(30)	79(8)
H(9C)	6080(30)	1440(30)	7250(20)	49(6)
H(10C)	-430(40)	2580(30)	-150(30)	59(6)

Table S6. Torsion angles [°] for salt **5**.

O(3)-N(1)-N(2)-C(1)	0.0(2)
O(2)-N(1)-N(2)-C(1)	-179.62(12)
C(3)-N(5)-N(6)-N(7)	0.28(16)
N(5)-N(6)-N(7)-N(8)	-0.07(17)
N(6)-N(7)-N(8)-C(3)	-0.17(16)
C(2)-N(4)-O(1)-N(3)	0.65(16)
C(1)-N(3)-O(1)-N(4)	-0.44(16)
O(1)-N(3)-C(1)-N(2)	-179.91(14)
O(1)-N(3)-C(1)-C(2)	0.07(16)
N(1)-N(2)-C(1)-N(3)	-1.7(2)
N(1)-N(2)-C(1)-C(2)	178.34(12)
O(1)-N(4)-C(2)-C(1)	-0.59(16)
O(1)-N(4)-C(2)-C(3)	178.82(12)
N(3)-C(1)-C(2)-N(4)	0.34(18)
N(2)-C(1)-C(2)-N(4)	-179.69(13)
N(3)-C(1)-C(2)-C(3)	-178.99(14)
N(2)-C(1)-C(2)-C(3)	1.0(2)
N(7)-N(8)-C(3)-N(5)	0.35(17)
N(7)-N(8)-C(3)-C(2)	-178.34(13)
N(6)-N(5)-C(3)-N(8)	-0.40(17)
N(6)-N(5)-C(3)-C(2)	178.34(13)
N(4)-C(2)-C(3)-N(8)	-179.27(14)
C(1)-C(2)-C(3)-N(8)	0.0(2)
N(4)-C(2)-C(3)-N(5)	2.2(2)
C(1)-C(2)-C(3)-N(5)	-178.56(14)

Table S7. Hydrogen bonds for salt **5** [Å and °].

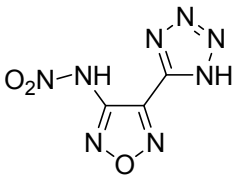
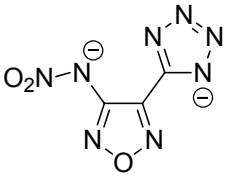
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(10)-H(10C)...N(6)#1	0.94(2)	2.07(2)	2.967(2)	159.2(19)
N(9)-H(9C)...N(8)#2	0.89(2)	2.07(2)	2.930(2)	162.7(19)
N(9)-H(9C)...N(2)#2	0.89(2)	2.48(2)	2.9724(18)	115.2(16)
N(10)-H(10B)...O(4)#3	0.90(3)	2.10(3)	2.8986(19)	148(2)
N(10)-H(10B)...N(3)#3	0.90(3)	2.50(2)	3.032(2)	118(2)
N(9)-H(9B)...O(2)#2	0.86(2)	2.24(2)	3.0238(18)	150(2)
N(9)-H(9B)...N(4)#4	0.86(2)	2.44(2)	3.0638(19)	129.6(19)
N(10)-H(10A)...O(3)#5	0.91(2)	2.44(2)	2.9576(19)	116.7(17)
N(10)-H(10A)...N(7)#6	0.91(2)	2.05(2)	2.883(2)	152(2)
N(9)-H(9A)...O(3)#7	0.93(2)	2.45(2)	2.9847(19)	116.4(15)
N(9)-H(9A)...N(6)#8	0.93(2)	2.24(2)	3.018(2)	141.0(17)
O(5)-H(5)...O(3)#5	0.87(3)	2.53(3)	3.1783(17)	131.9(19)
O(5)-H(5)...O(2)#5	0.87(3)	1.81(3)	2.6715(16)	171(2)
O(5)-H(5)...N(1)#5	0.87(3)	2.51(3)	3.3407(17)	160(2)
O(4)-H(4)...N(5)#4	0.83(3)	1.85(3)	2.6721(18)	171(2)
O(4)-H(4)...N(5)#4	0.83(3)	1.85(3)	2.6721(18)	171(2)
O(5)-H(5)...N(1)#5	0.87(3)	2.51(3)	3.3407(17)	160(2)
O(5)-H(5)...O(2)#5	0.87(3)	1.81(3)	2.6715(16)	171(2)
O(5)-H(5)...O(3)#5	0.87(3)	2.53(3)	3.1783(17)	131.9(19)
N(9)-H(9A)...N(6)#8	0.93(2)	2.24(2)	3.018(2)	141.0(17)
N(9)-H(9A)...O(3)#7	0.93(2)	2.45(2)	2.9847(19)	116.4(15)
N(10)-H(10A)...N(7)#6	0.91(2)	2.05(2)	2.883(2)	152(2)
N(10)-H(10A)...O(3)#5	0.91(2)	2.44(2)	2.9576(19)	116.7(17)
N(9)-H(9B)...N(4)#4	0.86(2)	2.44(2)	3.0638(19)	129.6(19)
N(9)-H(9B)...O(2)#2	0.86(2)	2.24(2)	3.0238(18)	150(2)
N(10)-H(10B)...N(3)#3	0.90(3)	2.50(2)	3.032(2)	118(2)
N(10)-H(10B)...O(4)#3	0.90(3)	2.10(3)	2.8986(19)	148(2)
N(9)-H(9C)...N(2)#2	0.89(2)	2.48(2)	2.9724(18)	115.2(16)
N(9)-H(9C)...N(8)#2	0.89(2)	2.07(2)	2.930(2)	162.7(19)
N(10)-H(10C)...N(6)#1	0.94(2)	2.07(2)	2.967(2)	159.2(19)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+1,-y,-z+1 #3 x,y,z-1 #4 -x+1,-y+1,-z+1
#5 -x,-y,-z+1 #6 -x+1,-y,-z #7 x+1,y,z #8 x,y,z+1

3. Ab Initio computational data

Table S8 Ab Initio computational data

Compounds	E_0 (Hartree)	ZPE (Hartree)	H_T (Hartree)	HOF (kJ/mol)
	-261.532452	0.045697	0.004418	196.75[i]
CH_4	-40.3984857	0.044793	0.003812	-74.6[ii]
NH_3	-56.4341763	0.034372	0.003818	-45.9[2]
CH_3NH_2	-95.6318759	0.064032	0.004369	-23.0[2]
NH_2NO_2	-260.5478787	0.039257	0.003356	-6.1[iii]
Tetrazole	-257.7256749	0.046855	0.00443	333.2[iv]
	-777.48901	0.092337	0.011604	635.04
	-776.3585889	0.065737	0.011197	472.1

[a] Total energy (E_0) calculated by B3LYP/6-31+G**/MP2/6-311++G** method (Hartree/Particle); [b] Zero-point correction (ZPE) (Hartree/Particle); [c] Values of thermal correction (H_T) (Hartree/Particle); [d] Heat of formation (HOT) (kJ/mol).

Calculations were carried out by using the Gaussian 09 (Revision E.01) suite of programs.[4] The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G**basis set, and single-point energies were calculated at the MP2(full)/6-311++G**level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

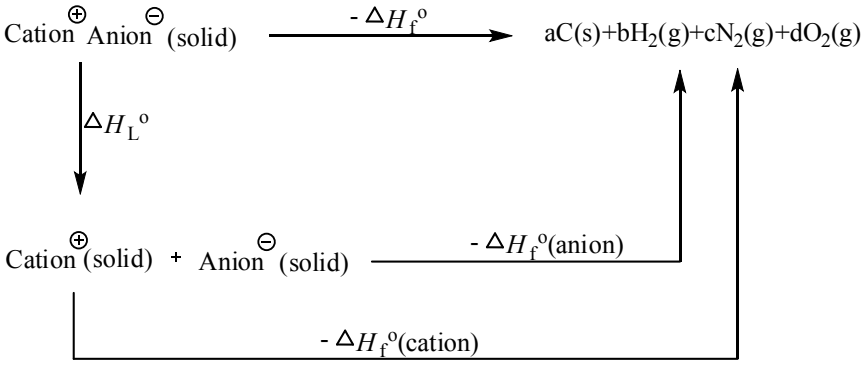


Figure S15. Born-Haber cycle for the formation for energetic salts

Based on the Born-Haber energy cycle (Figure 5), the heat of formation of a salt can be simplified according to Equation (1), where ΔH_L is the lattice energy of the salt.

ΔH_f^o(ionic salt, 298K) = ΔH_f^o(cation, 298K)＋ ΔH_f^o(anion, 298K)－ΔH_L (1)

The ΔH_L value could be predicted by the formula suggested by Jenkins et al [Eq. (2)], [5] where

U_{POT} is the lattice potential energy and nM and nX depend on the nature of the ions $M^{p+}$and X^{q-}, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

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

The equation for the lattice potential energy, U_{POT}, takes the form of Equation (3), where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ ($kJ^{-1}mol^{-1}cm$) and δ ($kJ^{-1}mol^{-1}$) are assigned literature values. [5]

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

4. Detonation performances calculation

Detonation pressure (P) and detonation velocity (D) were calculation according to the Kamlet-Jacobs equations[v].

$$D = 1.01(N\overline{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (4)$$

$$P = 1.558\rho^2\overline{M}^{1/2}Q^{1/2} \quad (5)$$

where each term in eqs 4 and 5 is defined as follows: D, the detonation velocity (km s^{-1}); P, the detonation pressure (GPa); N, the moles of detonation gases per gram explosive; $\overline{M}$, the average molecular weight of these gases (g mol^{-1}); Q, the heat of detonation (J g^{-1}); and ρ, the loaded density of explosives (g cm^{-3}). The measured density was used for the calculation here.

Ref:

i Wang R, Guo Y, Zeng Z, et al. Chem. Eur. J., 2009, 15, 2625-2634.
ii Eur. J. Inorg. Chem., 2008, 2560-2568.
iii Wang K, Parrish D A, Shreeve J M. Chem. Eur. J., 2011, 17, 14485-14492.
iv W. Zhu, C. Zhang, T. Wei, H. Xiao, Struct. Chem., 2011, 22, 149-159.
v (a) M. J. Kamlet, S. J. Jacobs, *J. Chem. Phys*. **1968**, *48*, 23-35; (b) M. J. Kamlet, J. E. Ablard, *J. Chem. Phys*. **1968**, *48*, 36-42; (c) M. J. Kamlet , C. Dicknison, *J. Chem. Phys*. **1968**, *48*, 43-49. (d) H. Gao, C. Ye, C. Piekarski, J. M. Shreeve, J. Phys. Chem. C **2007**, 111, 10718-10731.