Supporting Information

The Effects of Cationic Odd-Even Alkyl Chains on Crystal Structure and Energetic Properties of *Cyclo*-N_5^- Salts

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

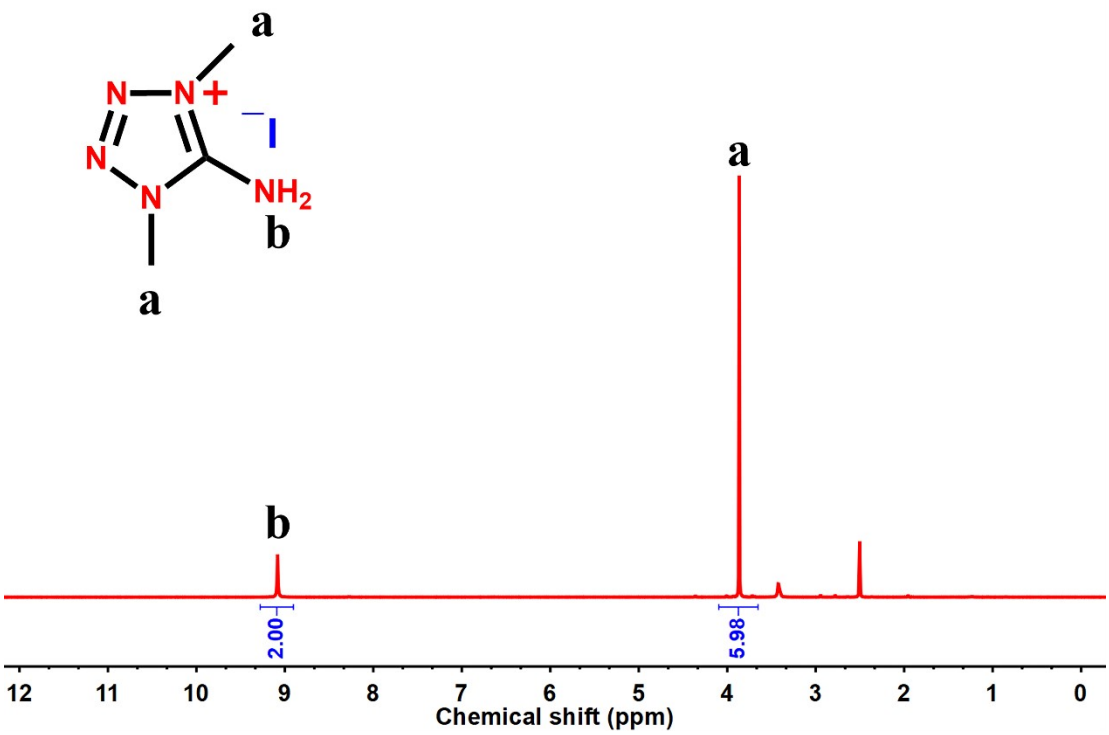


Figure S1. ^{1}H NMR of ADT using DMSO-d_6 as a solvent.

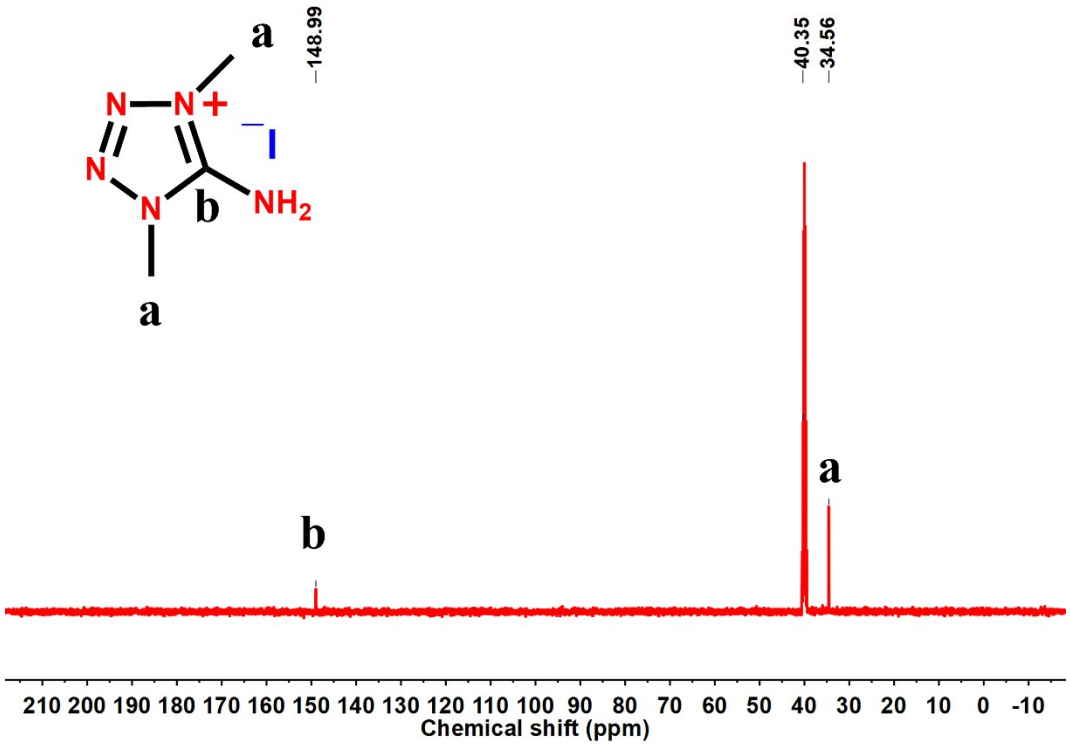


Figure S2. ^{13}C NMR of ADT using DMSO-d_6 as a solvent.

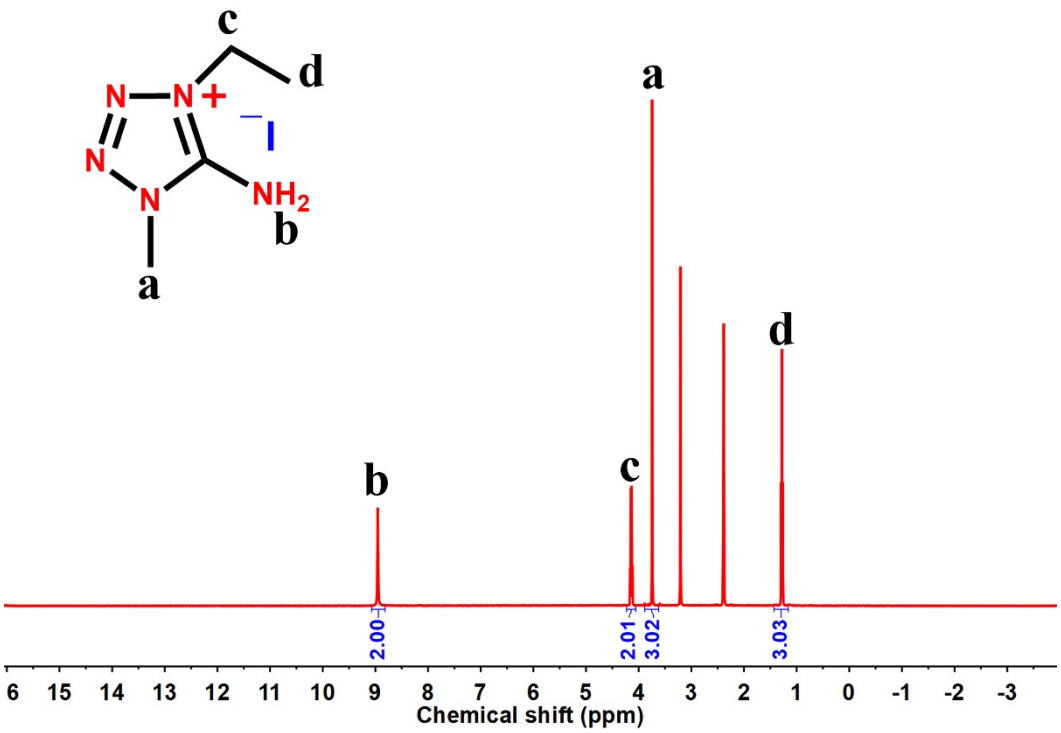


Figure S3. ^{1}H NMR of AEMT using DMSO-d_6 as a solvent.

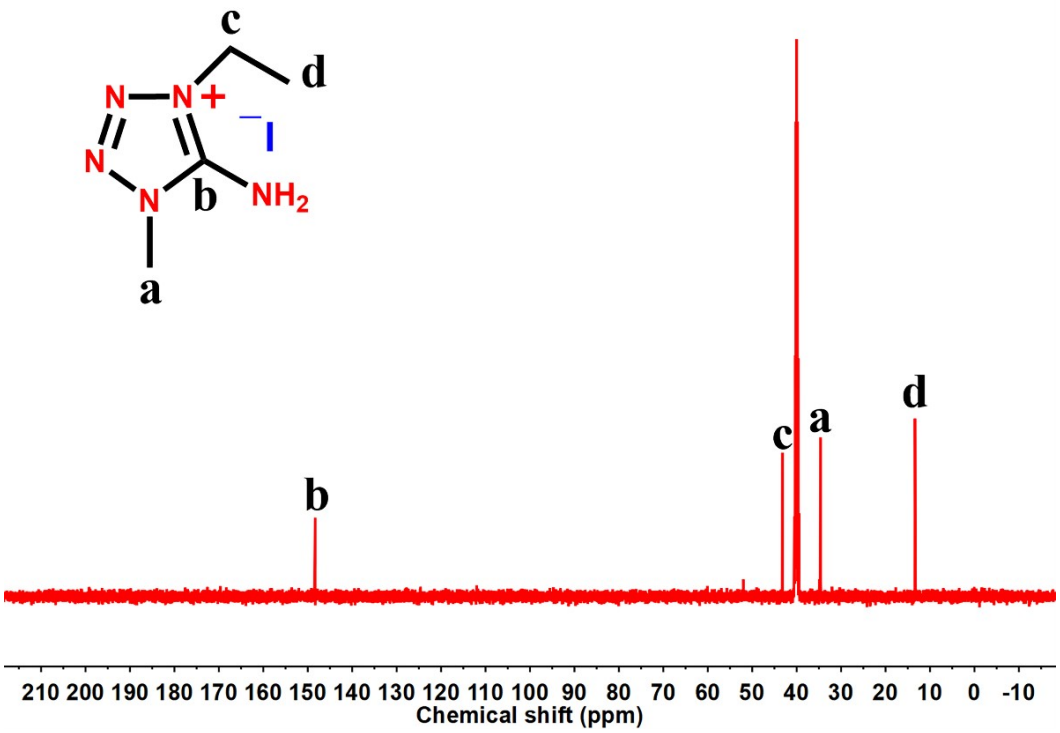


Figure S4. ^{13}C NMR of AEMT using DMSO-d_6 as a solvent.

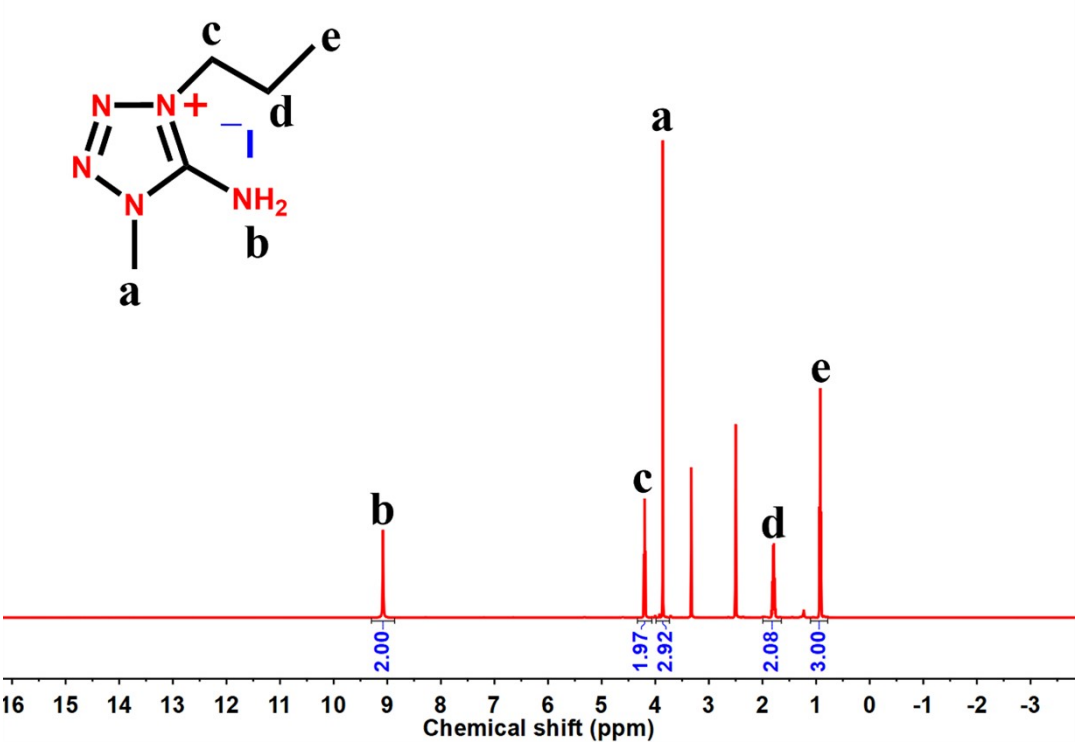


Figure S5. ^{1}H NMR of APMT using DMSO-d_6 as a solvent.

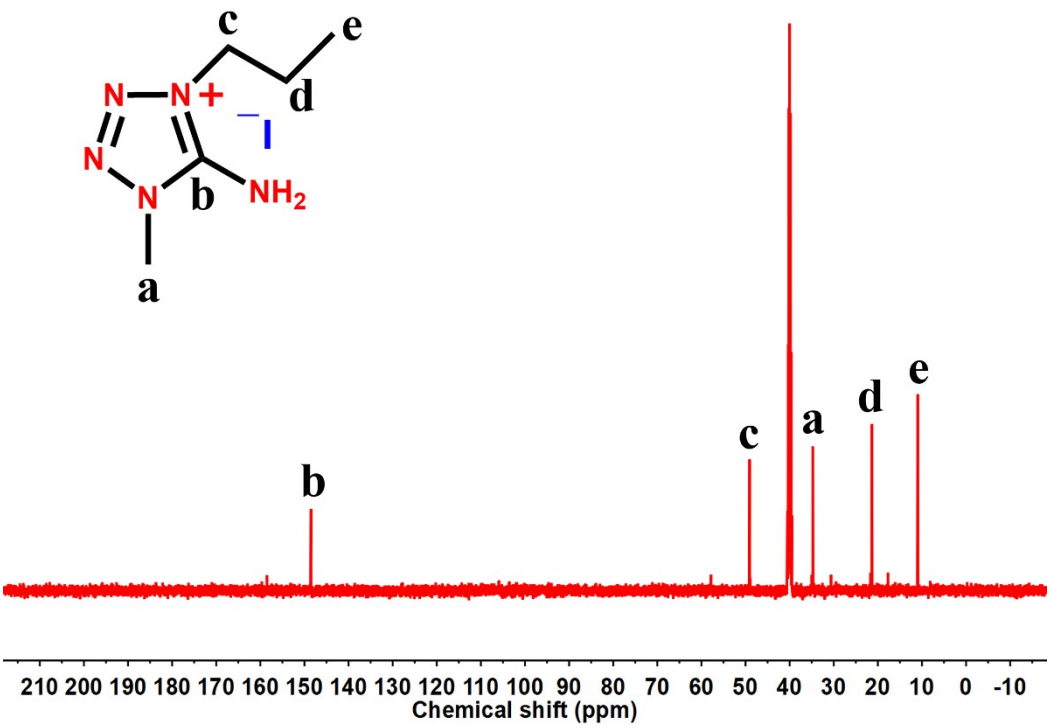


Figure S6. ^{13}C NMR of APMT using DMSO-d_6 as a solvent.

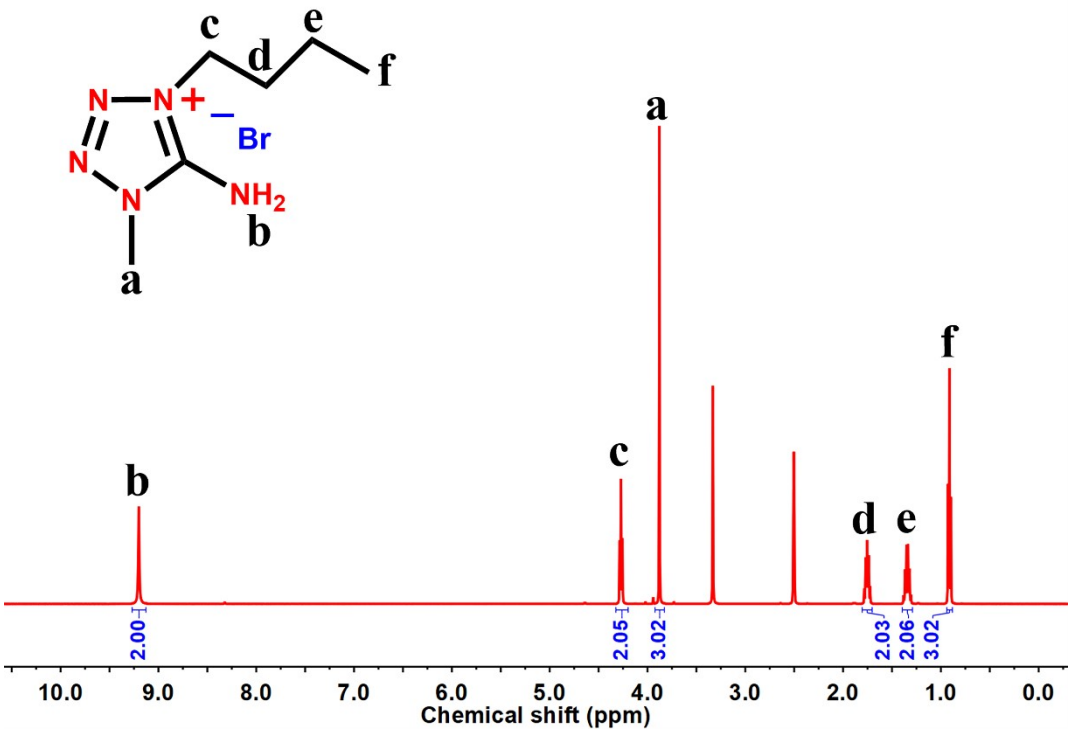


Figure S7. ^{1}H NMR of ABMT using DMSO-d_6 as a solvent.

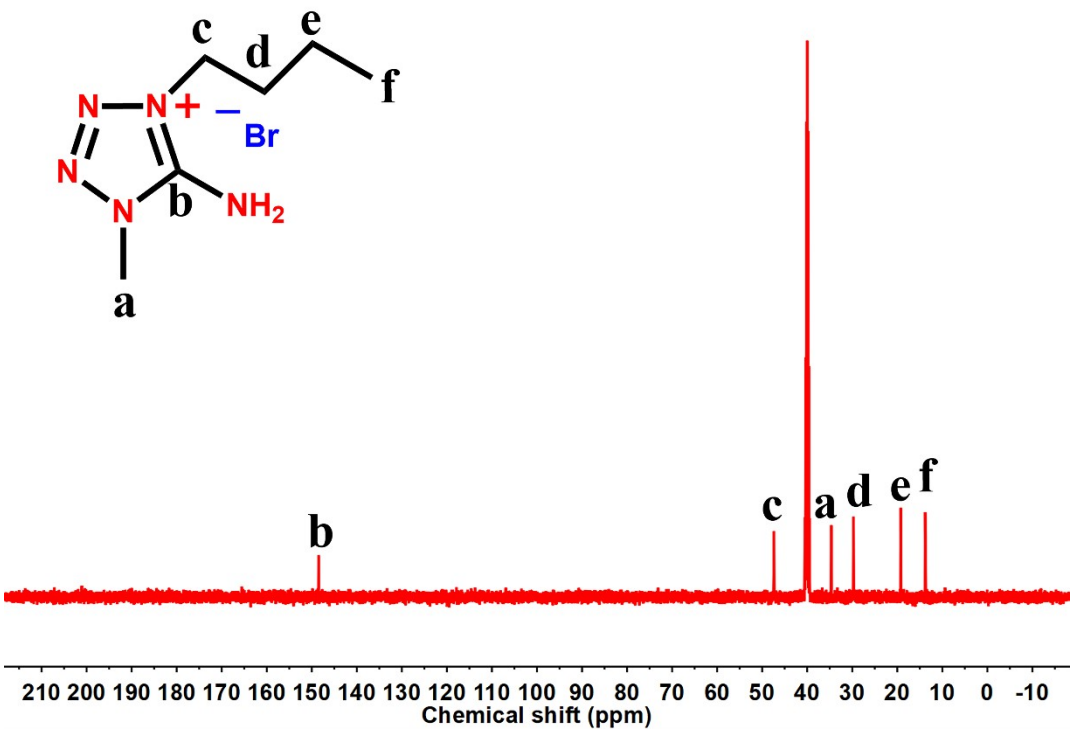


Figure S8. ^{13}C NMR of ABMT using DMSO-d_6 as a solvent.

2. FT-IR spectra

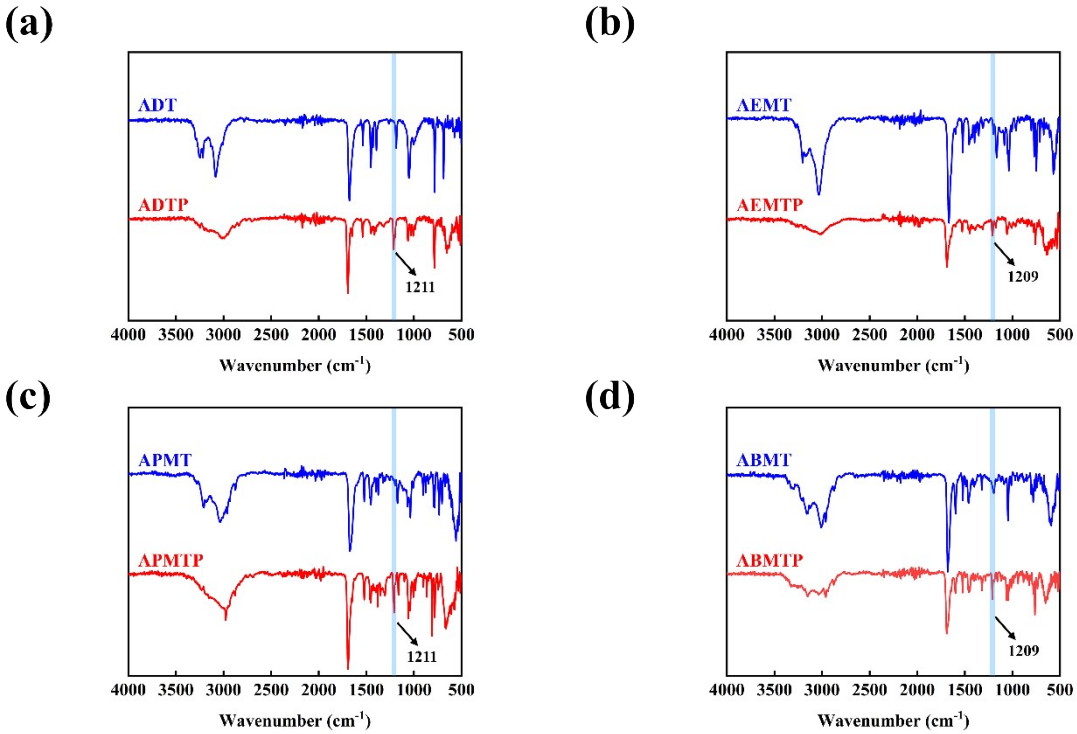


Figure S9. The IR spectra of (a) ADT and ADTTP, (b) AEMT and AEMTP, (c) APMT and APMTP, (d) ABMT and ABMTP.

3. Optical photographs

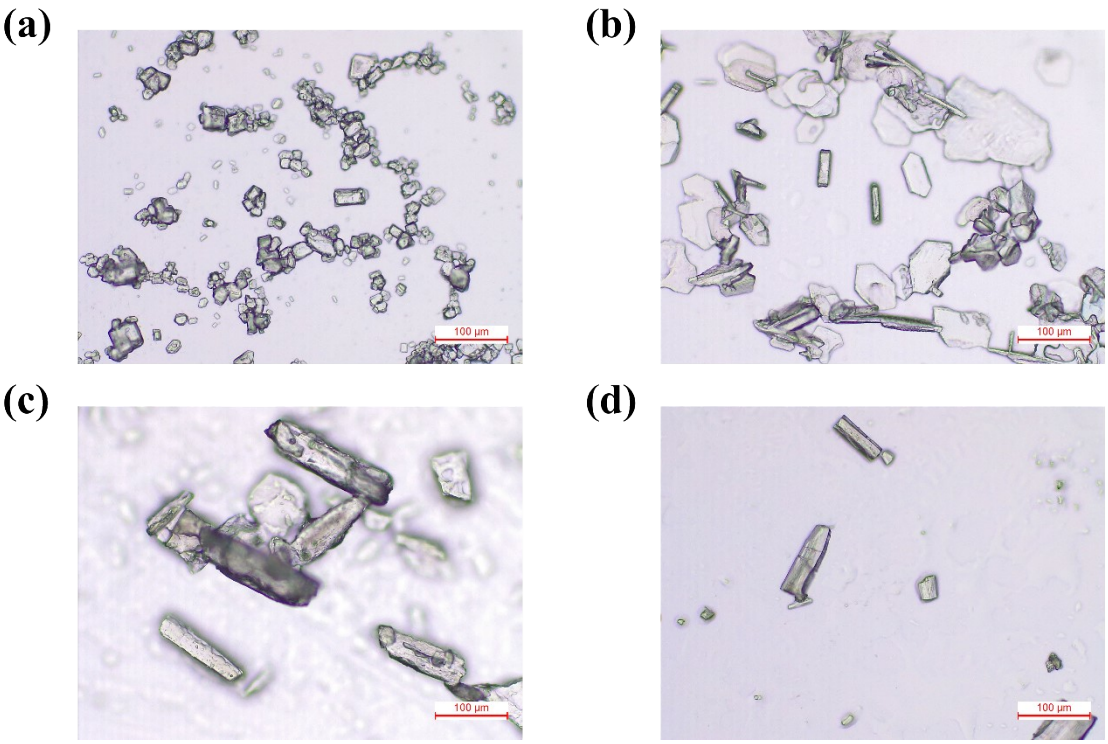


Figure S10. Optical photographs of the (a) ADTP, (b) AEMTP, (c) APMTP, and (d) ABMTP.

4. Thermal analysis

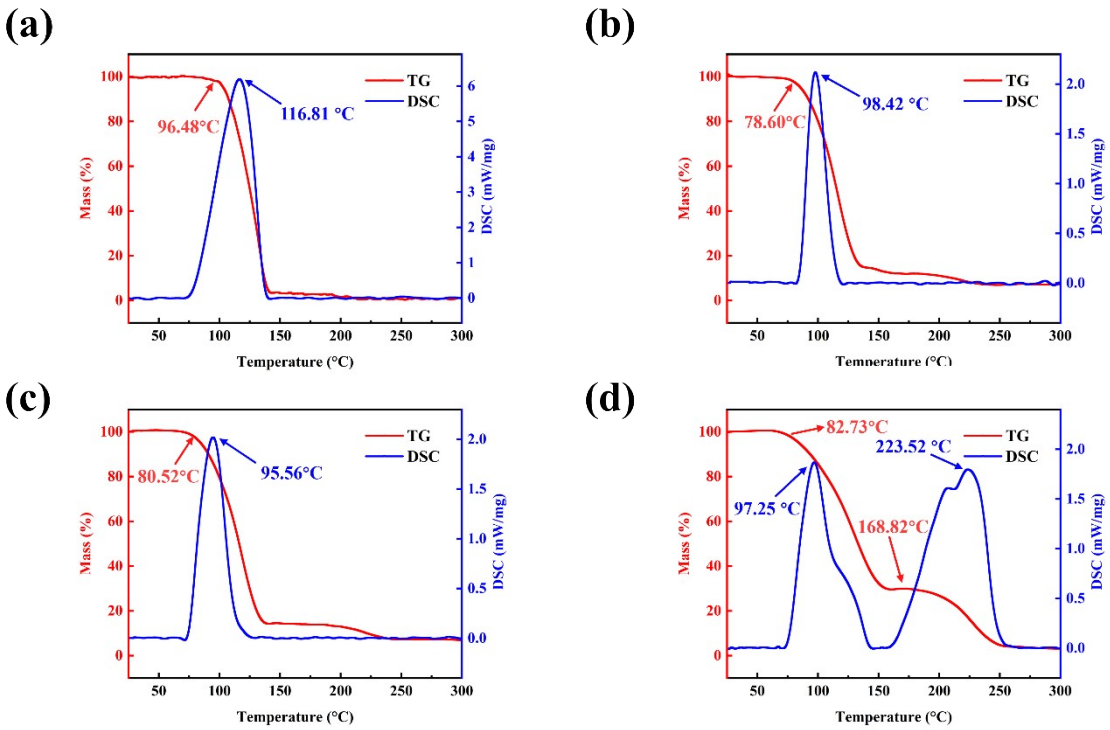


Figure S11. DSC and TG plots for the (a) ADTP, (b) AEMTP, (c) APMTP, and (d) ABMTP.

5. Crystal structure data

Table S1. Crystal data and structure refinement details for ADTP, AEMTP.

Compound	ADTP	AEMTP
CCDC No.	2405862	2405860
Empirical formula	$C_3H_8N_{10}$	$C_4H_{10}N_{10}$
Formula weight	184.19	198.22
Temperature (K)	223.00	223.00
Wavelength (Å)	0.71073	1.54178
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/c$
a (Å)	5.7099(5)	6.5378(8)
b (Å)	11.4189(12)	12.7108(11)
c (Å)	12.7418(12)	11.4681(10)
α (°)	90	90
β (°)	90	91.954(7)
γ (°)	90	90
Volume (Å^3)	830.78(14)	952.45(17)
Z	4	4
Density (g cm^{-3})	1.473	1.382
μ (mm^{-1})	0.113	0.880
F(000)	384.0	416.0
Crystal size (mm^3)	0.11 × 0.12 × 0.13	0.12 × 0.13 × 0.15
Theta range for data collection	4.79 to 55.114	10.392 to 136.556
Index ranges	$-7 \le h \le 7$ $-14 \le k \le 14$ $-16 \le l \le 16$	$-7 \le h \le 6$ $-15 \le k \le 14$ $-13 \le l \le 13$
Reflections collected	9214	6275
Independent reflections	1910 (R(int)= 0.0743)	1736 (R(int)= 0.0638)
Data/restraints/parameters	1910/0/120	1736/9/160
Goodness-of-fit on F^2	1.073	1.002
Final R indices (I>2sigma(I))	R1 = 0.0439 wR_2 = 0.0892	R1 = 0.0689 wR_2 = 0.1972
R indices (all data)	R1 = 0.0649 wR_2 = 0.1037	R1 = 0.1151 wR_2 = 0.2594
Largest diff. peak and hole (e. Å^{-3})	0.20 and -0.20	0.17 and -0.17

Table S2. Crystal data and structure refinement details for APMTP, ABMTP.

Compound	APMTP	ABMTP
CCDC No.	2405863	2405864
Empirical formula	$C_5H_{12}N_{10}$	$C_6H_{14}N_{10}$
Formula weight	212.25	226.27
Temperature (K)	223.00	223.00
Wavelength (Å)	1.54178	1.54184
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	P-1
a (Å)	13.3794(5)	5.8120(2)
b (Å)	5.9025(2)	7.1091(2)
c (Å)	13.0926(6)	14.9725(6)
α (°)	90	81.638(3)
β (°)	95.010(3)	85.154(3)
γ (°)	90	70.130(2)
Volume (Å^3)	1030.00(7)	575.21(4)
Z	4	2
Density (g cm^{-3})	1.369	1.306
μ (mm^{-1})	0.849	0.792
F(000)	448.0	240.0
Crystal size (mm^3)	0.11 × 0.12 × 0.13	0.10 × 0.12 × 0.15
Theta range for data collection	6.632 to 136.632	5.97 to 136.772
Index ranges	$-16 \le h \le 15$ $-5 \le k \le 7$ $-15 \le l \le 13$	$-7 \le h \le 6$ $-8 \le k \le 8$ $-18 \le l \le 17$
Reflections collected	7676	7549
Independent reflections	1879 (R(int)= 0.0586)	2092 (R(int)= 0.0499)
Data/restraints/parameters	1879/0/138	2092/13/159
Goodness-of-fit on F^2	1.060	1.046
Final R indices (I>2sigma(I))	R1 = 0.0430 wR_2 = 0.1085	R1 = 0.0462 wR_2 = 0.1226
R indices (all data)	R1 = 0.0627 wR_2 = 0.1195	R1 = 0.0635 wR_2 = 0.1394
Largest diff. peak and hole (e. Å^{-3})	0.35 and -0.25	0.28 and -0.13

Table S3. Bond lengths for ADTP.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
C1-N7	1.448(4)	N9-N10	1.356(3)
C2-N6	1.309(4)	N1-N2	1.303(4)
C2-N7	1.338(3)	N1-N5	1.312(4)
C2-N10	1.333(3)	N2-N3	1.315(3)
C3-N10	1.459(4)	N3-N4	1.302(4)
N7-N8	1.360(3)	N4-N5	1.316(4)

Table S4. Bond angles for ADTP.

Parameter	bond angle (°)	Parameter	bond angle (°)
N6-C2-N7	127.9(3)	C2-N10-C3	128.5(3)
N6-C2-N10	127.8(3)	C2-N10-N9	109.8(2)
N10-C2-N7	104.3(2)	N9-N10-C3	121.6(2)
C2-N7-C1	127.9(3)	N2-N1-N5	108.3(3)
C2-N7-N8	109.8(2)	N1-N2-N3	108.1(2)
N8-N7-C1	122.2(2)	N4-N3-N2	107.8(3)
N9-N8-N7	107.8(2)	N3-N4-N5	108.4(3)
N8-N9-N10	108.3(2)	N1-N5-N4	107.4(3)

Table S5. Torsion angles for ADTP.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C1-N7-N8-N9	178.0(3)	N8-N9-N10-C2	0.1(3)
C2-N7-N8-N9	0.7(3)	N8-N9-N10-C3	-177.4(3)
N6-C2-N7-C1	118.3(4)	N10-C2-N7-C1	-177.7(3)
N6-C2-N7-N8	-179.1(3)	N10-C2-N7-N8	-0.6(3)
N6-C2-N10-C3	-4.0(5)	N1-N2-N3-N4	-0.4(3)
N6-C2-N10-N9	178.8(3)	N2-N1-N5-N4	0.9(4)
N7-C2-N10-C3	177.6(3)	N2-N3-N4-N5	1.0(4)
N7-C2-N10-N9	0.3(3)	N3-N4-N5-N1	-1.1(4)
N7-N8-N9-N10	-0.5(3)	N5-N1-N2-N3	-0.3(4)

Table S6. Hydrogen bonds for ADTP.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N6-H6A···N2	0.8700	2.0900	2.946(4)	169.00
N6-H6B···N1	0.8700	2.0610	2.924(3)	171.00
C3-H3C···N3	0.9700	2.6100	3.559(4)	165.00

Table S7. Bond lengths for AEMTP.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
N6-C2	1.322(5)	N7-C1A	1.607(19)
N1-N2	1.298(4)	N8-N9	1.282(5)
N1-N5	1.312(5)	N9-N10	1.354(4)
N2-N3	1.305(5)	N10-C2	1.325(6)
N3-N4	1.310(4)	N10-C3A	1.600(13)
N4-N5	1.307(4)	N10-C1	1.29(2)
N7-N8	1.355(5)	C4-C3	1.50(2)
N7-C3	1.296(18)	C4A-C1	1.466(19)
N6-C2	1.334(4)		

Table S8. Bond angles for AEMTP.

Parameter	bond angle (°)	Parameter	bond angle (°)
N2-N1-N5	108.2(4)	N8-N9-N10	108.1(4)
N1-N2-N3	108.2(4)	N9-N10-C3A	115.0(6)
N5-N4-N3	108.0(4)	C2-N10-N9	109.8(3)
N2-N3-N4	107.9(3)	C2-N10-C3A	135.1(6)
N4-N5-N1	107.7(3)	C1-N10-N9	134.1(9)
N8-N7-C1A	121.3(9)	C2-N10-C2	116.0(9)
C3-N7-N8	121.3(7)	N7-C3-C4	104.5(14)
C2-N7-N8	110.0(4)	N6-C2-N7	126.9(5)
C3-N7-C2	128.7(8)	N6-C2-N10	128.4(4)
C2-N7-C1A	128.0(9)	N10-C2-N7	104.7(4)
N9-N8-N7	107.3(3)	N10-C1-C4A	106.2(16)

Table S9. Torsion angles for AEMTP.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N1-N2-N3-N4	0.3(5)	N9-N10-C1-C4A	-12(2)
N2-N1-N5-N4	-0.9(4)	C3-N7-N8-N9	-178.8(12)
N2-N3-N4-N5	-0.8(5)	C3-N7-C2-N6	-0.6(14)
N3-N4-N5-N1	1.1(4)	C3-N7-C2-N10	179.2(13)
N5-N1-N2-N3	0.4(5)	C2-N7-N8-N9	-0.2(4)
N7-N8-N9-N10	-0.4(4)	C2-N7-C3-C4	85.2(14)
N8-N7-C3-C4	-96.6(10)	C2-N10-C1-C4A	166.9(10)
N8-N7-C2-N6	-179.0(3)	C3A-N10-C2-N6	-3.7(12)
N8-N7-C2-N10	0.8(4)	C3A-N10-C2-N7	176.5(10)
N8-N9-N10-C2	1.0(4)	C1-N10-C2-N6	-0.4(13)
N8-N9-N10-C3A	-177.2(8)	C1-N10-C2-N7	179.7(12)
N8-N9-N10-C1	180.0(16)	C1A-N7-N8-N9	170.5(10)
N9-N10-C2-N6	178.8(2)	C1A-N7-C2-N6	11.1(12)
N9-N10-C2-N7	-1.1(4)	C1A-N7-C2-N10	-169.1(11)

Table S10. Hydrogen bonds for AEMTP.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N6-H6B···N5	0.8700	2.0750	2.929(4)	167.00
N6-H6A···N4	0.8700	2.1300	2.986(5)	167.00
C3A-H3AC···N8	0.9700	2.5600	3.310(15)	134.00
C3-H3A···N3	0.9800	2.5500	3.38(2)	143.00

Table S11. Bond lengths for APMTP.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
C1-N6	1.308(2)	N8-N9	1.269(2)
C1-N7	1.340(2)	N9-N10	1.362(2)
C1-N10	1.339(2)	N1-N2	1.317(3)
C2-N10	1.456(2)	N1-N5	1.294(2)
C3-C4	1.512(3)	N2-C3	1.296(3)
C3-N7	1.466(2)	N3-N4	1.316(3)
C4-C5	1.511(3)	N4-N5	1.308(2)
N7-N8	1.365(2)		

Table S12. Bond angles for APMTP.

Parameter	bond angle (°)	Parameter	bond angle (°)
N6-C1-N7	128.19(16)	N8-N9-N10	107.95(15)
N6-C1-N10	127.13(17)	C1-N10-C2	128.46(16)
N10-C1-N7	104.68(15)	C1-N10-N9	109.72(15)
N7-C3-C4	112.97(15)	N9-N10-C2	121.79(16)
C5-C4-C3	113.47(18)	N5-N1-N2	107.92(17)
C1-N7-C3	128.90(15)	N3-N2-N1	107.86(17)
C1-N7-N8	109.22(15)	N2-N3-N4	108.34(17)
N8-N7-C3	121.87(15)	N5-N4-N3	107.23(17)
N9-N8-N7	108.42(15)	N1-N5-N4	108.64(17)

Table S13. Torsion angles for APMTP.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C1-N7-N8-N9	-1.12(19)	N7-N8-N9-N10	1.0(2)
C3-N7-N8-N9	179.84(16)	N8-N9-N10-C1	-0.5(2)
C4-C3-N7-C1	-87.2(2)	N8-N9-N10-C2	-178.47(16)
C4-C3-N7-N8	91.7(2)	N10-C1-N7-C3	179.74(16)
N6-C1-N7-C3	-0.5(3)	N10-C1-N7-N8	0.79(17)
N6-C1-N7-N8	-179.43(17)	N1-N2-N3-N4	-0.9(2)
N6-C1-N10-C2	-2.2(3)	N2-N1-N5-N4	-0.4(2)
N6-C1-N10-N9	180.00(16)	N2-N3-N4-N5	0.6(2)
N7-C1-N10-C2	117.61(16)	N3-N4-N5-N1	-0.1(2)
N7-C1-N10-N9	-0.12(18)	N5-N1-N2-N3	0.8(2)
N7-C3-C4-C5	-67.1(2)		

Table S14. Hydrogen bonds for APMTP.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N6-H6A···N1	0.8700	2.0600	2.906(2)	163.00
N6-H6B···N5	0.8700	2.0677	2.910(2)	163.00
C2-H2A···N2	0.9700	2.5300	3.407(3)	150.00

Table S15. Bond lengths for ABMTP.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
N10-C5	1.312(3)	N2-N3	1.320(3)
N9-C5	1.328(3)	N7-N8	1.267(3)
N9-N8	1.367(2)	N1-N5	1.314(2)
N9-C4	1.465(3)	N4-N5	1.297(3)
N6-N7	1.359(3)	N4-N3	1.308(3)
N6-C5	1.348(2)	C3-C2	1.509(3)
N6-C6	1.444(9)	C3-C4	1.516(3)
N6-C6A	1.470(12)	C2-C1	1.514(3)
N2-N1	1.293(3)		

Table S16. Bond angles for ABMTP.

Parameter	bond angle (°)	Parameter	bond angle (°)
C5-N8-N9	109.70(18)	N5-N4-N3	108.03(17)
C5-N9-C4	128.85(17)	N10-C5-N9	128.56(17)
N8-N9-C4	121.4(2)	N10-C5-N6	126.6(2)
N7-N6-C6	118.3(9)	N9-C5-N6	104.81(18)
N7-N6-C6A	127.5(13)	N4-N5-N1	108.09(17)
C5-N6-N7	108.99(18)	N7-N8-N9	107.9(2)
C5-N6-C6	132.5(9)	N4-N3-N2	107.83(19)
C5-N6-C6A	123.5(13)	C2-C3-C4	114.60(17)
N1-N2-N3	107.71(17)	C3-C2-C1	112.41(19)
N8-N7-N6	108.62(18)	N9-C4-C3	112.65(17)
N2-N1-N5	108.32(18)		

Table S17. Torsion angles for ABMTP.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N6-N7-N8-N9	-0.3(2)	N3-N4-N5-N1	-0.7(3)
N2-N1-N5-N4	0.2(3)	C2-C3-C4-N9	66.6(2)
N7-N6-C5-N10	-179.66(18)	C4-N9-C5-N10	0.9(3)
N7-N6-C5-N9	0.00(2)	C4-N9-C5-N6	-178.80(17)
N1-N2-N3-N4	-0.8(3)	C4-N9-N8-N7	179.04(17)
C5-N9-N8-N7	0.3(2)	C4-C3-C2-C1	178.8(2)
C5-N9-C4-C3	88.3(2)	C6-N6-N7-N8	176.6(9)
C5-N6-N7-N8	0.2(2)	C6-N6-C5-N10	4.7(11)
N5-N4-N3-N2	0.9(3)	C6-N6-C5-N9	-175.6(10)
N8-N9-C5-N10	179.47(18)	C6A-N6-N7-N8	-177.5(13)
N8-N9-C5-N6	-0.2(2)	C6A-N6-C5-N10	-1.8(13)
N8-N9-C4-C3	-90.1(2)	C6A-N6-C5-N9	177.9(12)
N3-N2-N1-N5	0.3(3)		

Table S18. Hydrogen bonds for ABMTP.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N10-H10A···N2	0.8700	2.0800	2.941(3)	168.00
N10-H10B···N1	0.8700	2.0890	2.945(3)	168.00
C6-H6C···N4	0.9700	2.6000	3.554(19)	166.00
C6-H6C···N5	0.9700	2.5300	3.366(19)	145.00

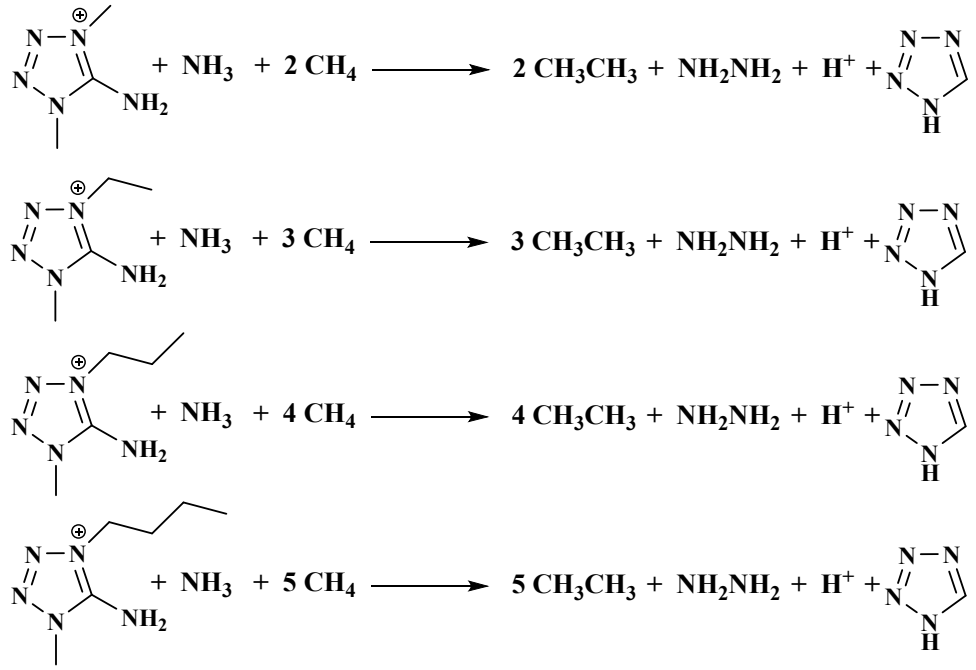
6. Heats of formation

The enthalpy of formation is an important parameter in chemical thermodynamics calculation, which is a crucial basis for evaluating the detonation velocity and detonation pressure of energetic compounds. The formation of ADTP, AEMTP, APMTP, and ABMTP was theoretically calculated with the Gaussian 09 program.[1] At the B3LYP/6-311+G** level,[2-5] 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 cation section was calculated based on the designed isodesmic reaction. The enthalpy of formation of *cyclo*-N_5^- has been reported in relevant literature,[6] and this work will cite directly.

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

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

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 cations. The heat of formation of small molecules can be found in 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:

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

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-} 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}:

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

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

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