Electronic Supplementary Information

A series of energetic *cyclo*-pentazolate salts: rapid synthesis, characterization, and promising performance

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1. Single-crystal X-ray diffraction analysis of **2**

Table S1. Crystal data and structure refinement for **2**

	2
CCDC	1885286
Empirical formula	KN_5
Formula weight	109.15
Temperature / K	150
Crystal system	Orthorhombic
Space group	*P*nma
a / Å	7.835(3)
b / Å	6.304(2)
c / Å	7.332(3)
α /°	90.00
β /°	90.00
γ /°	90.00
Volume / Å^3	362.1(2)
Z	4
ρ_{calc} / g cm^{-3}	2.002
μ / mm^{-1}	1.268
F(000)	216.0
Crystal size / mm^3	0.19×0.12×0.08
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	7.612 to 52.55
Index ranges	$-9 \le h \le 9$, $-7 \le k \le 7$, $-8 \le l \le 9$
Reflections collected	2236
Independent reflections	397 [R_{int} = 0.0341, R_{sigma} = 0.0258]
Data / restraints / parameters	397 / 0 / 31
Goodness-of-fit on F^2	1.089
Final *R* indexes [$I >= 2\sigma(I)$]	R_1 = 0.0246, wR_2 = 0.0668
Final *R* indexes [all data]	R_1 = 0.0260, wR_2 = 0.0676
Largest diff. peak / hole / e Å^{-3}	0.31 / -0.43

Table S2. Selected bond lengths for **2**

parameter	bond length (Å)	parameter	bond length (Å)
K1-K1[1]	4.0310(12)	K1-N1	2.8763(14)
K1-K1[2]	4.0310(12)	K1-N1[7]	2.8763(14)
K1-N3[3]	2.9597(19)	K1-N1[8]	2.9735(19)
K1-N3[4]	3.0002(19)	K1-N1[1]	2.9735(19)
K1-N2	3.3106(14)	N3-N2[9]	1.3203(15)
K1-N2[5]	2.9028(14)	N3-N2	1.3203(15)
K1-N2[6]	2.9028(14)	N2-N1	1.3097(19)
K1-N2[7]	3.3106(14)	N1-N1[9]	1.315(2)

[1]1-X,1-Y,2-Z; [2]1-X,2-Y,2-Z; [3]1-X,1-Y,1-Z; [4]1/2-X,1-Y,1/2+Z; [5]1/2+X,3/2-Y,3/2-Z; [6]1/2+X,+Y,3/2-Z; [7]+X,3/2-Y,+Z; [8]1-X,1/2+Y,2-Z; [9]+X,1/2-Y,+Z

Table S3. Selected bond angles for **2**

parameter	bond angle (°)	parameter	bond angle (°)
K1[1]-K1-K1[2]	102.87(3)	N1-K1-N3[4]	72.17(3)
N3[3]-K1-K1[2]	128.531(17)	N1-K1-N3[3]	88.74(4)
N3[3]-K1-K1[1]	128.531(17)	N1[5]-K1-N3[3]	88.74(4)
N3[4]-K1-K1[2]	60.70(2)	N1[6]-K1-N3[4]	68.45(4)
N3[4]-K1-K1[1]	60.70(2)	N1[5]-K1-N3[4]	72.17(3)
N3[3]-K1-N3[4]	139.54(5)	N1[2]-K1-N3[4]	68.45(4)
N3[4]-K1-N2[5]	72.42(4)	N1-K1-N2[5]	99.96(4)
N3[4]-K1-N2	72.41(4)	N1[2]-K1-N2[5]	132.43(3)
N3[3]-K1-N2[5]	76.44(4)	N1-K1-N2	23.10(3)
N3[3]-K1-N2	76.44(4)	N1[5]-K1-N2[8]	162.20(4)
N3[3]-K1-N1[6]	149.97(4)	N1[5]-K1-N2[7]	72.89(4)
N3[3]-K1-N1[2]	149.97(4)	N1[6]-K1-N2[5]	113.33(3)
N2-K1-K1[1]	128.39(3)	N1[5]-K1-N2	99.96(4)
N2-K1-K1[2]	68.64(3)	N1-K1-N2[8]	72.89(4)
N2[7]-K1-K1[1]	64.60(3)	N1[2]-K1-N2	113.33(3)
N2[7]-K1-K1[2]	134.01(3)	N1[6]-K1-N2	132.43(3)
N2[5]-K1-K1[1]	68.64(3)	N1-K1-N2[7]	162.20(4)
N2[8]-K1-K1[1]	134.01(3)	N1[5]-K1-N2[5]	23.10(3)
N2[8]-K1-K1[2]	64.60(3)	N1[5]-K1-N1[6]	92.90(4)
N2[5]-K1-K1[2]	128.39(3)	N1[6]-K1-N1[2]	25.55(4)
N2[7]-K1-N3[4]	125.27(3)	N1-K1-N1[5]	120.27(6)
N2[8]-K1-N3[4]	125.27(3)	N1[5]-K1-N1[2]	115.73(3)
N2[8]-K1-N3[3]	79.18(4)	N1-K1-N1[6]	115.73(3)
N2[7]-K1-N3[3]	79.18(4)	N1-K1-N1[2]	92.90(4)
N2[7]-K1-N2[5]	89.94(4)	K1[3]-N3-K1[9]	88.65(5)
N2[7]-K1-N2	154.75(2)	N2-N3-K1[9]	119.42(9)
N2[8]-K1-N2[5]	154.75(2)	N2-N3-K1[3]	109.78(9)
N2-K1-N2[5]	78.11(5)	N2[10]-N2-K1[9]	119.42(9)
N2[7]-K1-N2[8]	91.87(6)	N2[10]-N3-K1[3]	109.77(9)
N2[8]-K1-N2	89.94(4)	N2[10]-N3-N2	107.68(17)
N2[7]-K1-N1[6]	72.72(3)	K1[11]-N2-K1	83.90(4)
N2[7]-K1-N1[2]	91.19(3)	N3-N2-K1	161.06(10)
N2[8]-K1-N1[2]	72.72(3)	N3-N2-K1[11]	115.04(10)
N2[8]-K1-N1[6]	91.19(3)	N1-N2-K1[11]	118.50(9)
N1-K1-K1[2]	47.45(4)	N1-N2-K1	59.49(7)
N1[6]-K1-K1[2]	69.16(3)	N1-N2-N3	107.99(11)
N1-K1-K1[1]	132.84(4)	K1-N1-K1[2]	87.10(4)
N1[5]-K1-K1[2]	132.84(4)	N2-N1-K1[2]	152.85(10)
N1[5]-K1-K1[1]	47.45(4)	N2-N1-K1	97.41(8)
N1[6]-K1-K1[1]	45.45(2)	N2-N1-N1[10]	108.17(7)
N1[2]-K1-K1[1]	69.16(3)	N1[10]-N1-K1[2]	77.22(2)
N1[2]-K1-K1[2]	45.45(2)	N1[10]-N1-K1	150.13(3)

[1]1-X,2-Y,2-Z; [2]1-X,1-Y,2-Z; [3]1-X,1-Y,1-Z; [4]1/2-X,1-Y,1/2+Z; [5]+X,3/2-Y,+Z; [6]1-X,1/2+Y,2-Z; [7]1/2+X,3/2-Y,3/2-Z; [8]1/2+X,+Y,3/2-Z; [9]1/2-X,1-Y,-1/2+Z; [10]+X,1/2-Y,+Z; [11]-1/2+X,+Y,3/2-Z

2. Single-crystal X-ray diffraction analysis of **3**

Table S4. Crystal data and structure refinement for **3**

	3
CCDC	1887029
Empirical formula	H_4N_6
Formula weight	88.09
Temperature / K	150
Crystal system	Orthorhombic
Space group	*P*cca
a / Å	9.399(4)
b / Å	3.9543(19)
c / Å	10.362(5)
α /°	90.00
β /°	90.00
γ /°	90.00
Volume / Å^3	385.1(3)
Z	4
ρ_{calc} / g cm^{-3}	1.519
μ / mm^{-1}	0.125
F(000)	184.0
Crystal size / mm^3	0.19×0.12×0.08
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	7.866 to 52.56
Index ranges	$-11 \le h \le 10$, $-4 \le k \le 4$, $-12 \le l \le 12$
Reflections collected	1871
Independent reflections	392 [R_{int} = 0.0746, R_{sigma} = 0.0491]
Data / restraints / parameters	392 / 1 / 37
Goodness-of-fit on F^2	1.072
Final *R* indexes [$I >= 2\sigma(I)$]	R_1 = 0.0497, wR_2 = 0.1243
Final *R* indexes [all data]	R_1 = 0.0587, wR_2 = 0.1354
Largest diff. peak / hole / e Å^{-3}	0.34 / -0.22

Table S5. Selected bond lengths for **3**

parameter	bond length (Å)	parameter	bond length (Å)
N3-N3^1	1.316(3)	N2-N1	1.309(2)
N3-N2	1.316(2)		

^{1}1/2-X,1-Y,+Z

Table S6. Selected bond angles for **3**

parameter	bond angle (°)	parameter	bond angle (°)
N3^1-N3-N2	107.83(10)	N2^1-N1-N2	108.2(2)
N1-N2-N3	108.05(15)		

^{1}1/2-X,1-Y,+Z

Table S7. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **3**

Atom	*x*	*y*	*z*	U(eq)
H4A	5630(20)	1780(50)	2110(20)	58(7)
H4B	4560(20)	-700(50)	1930(19)	39(5)

Table S8. Hydrogen bonds for **3**

Donor--H...Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N4--H4A…N3	0.87(2)	2.12(2)	2.960(2)	163.2(19)
N4--H4B…N2	0.874(19)	2.11(2)	2.982(2)	177.4(19)

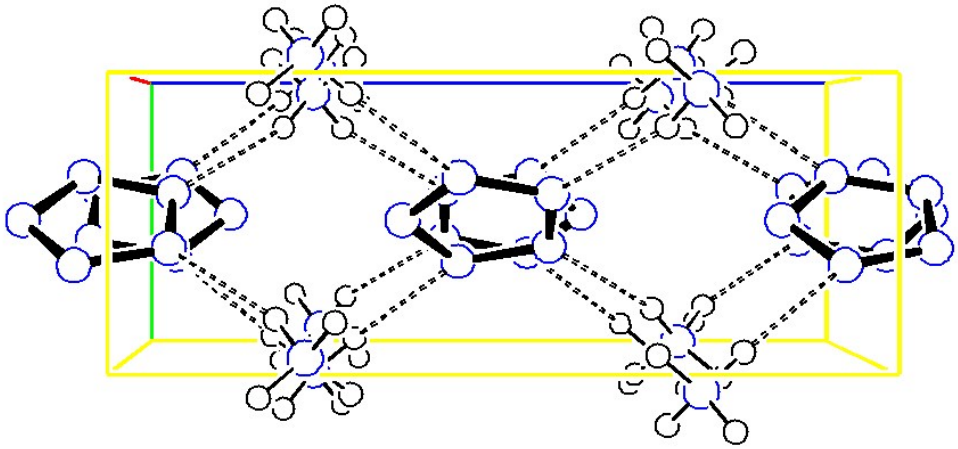


Fig. S1 Ball and stick packing diagram of **3** viewed down the *a* axis. Unit cell indicated and dashed lines indicate strong hydrogen bonding.

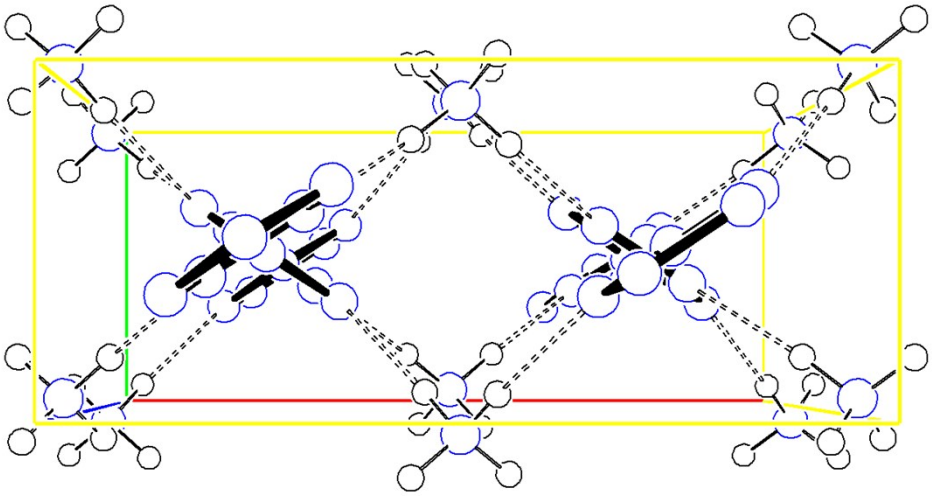


Fig. S2 Ball and stick packing diagram of **3** viewed down the *c* axis. Unit cell indicated and dashed lines indicate strong hydrogen bonding.

3. Single-crystal X-ray diffraction analysis of **4**·2H_2O

Table S9. Crystal data and structure refinement for **4**·2H_2O

	4·2H_2O
CCDC	1881964
Empirical formula	$H_8N_6O_3$
Formula weight	140.12
Temperature / K	173
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	3.685(3)
b / Å	14.638(10)
c / Å	11.575(8)
α /°	90.00
β /°	90.32(5)
γ /°	90.00
Volume / Å^3	624.4(8)
Z	4
ρ_{calc} / g cm^{-3}	1.491
μ / mm^{-1}	0.141
F(000)	296.0
Crystal size / mm^3	0.40×0.16×0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.486 to 55.316
Index ranges	$-4 \le h \le 4$, $-18 \le k \le 19$, $-14 \le l \le 15$
Reflections collected	4450
Independent reflections	1395 [R_{int} = 0.0598, R_{sigma} = 0.0600]
Data / restraints / parameters	1395 / 3 / 99
Goodness-of-fit on F^2	1.009
Final R indexes [$I >= 2\sigma(I)$]	R_1 = 0.0452, wR_2 = 0.1065
Final R indexes [all data]	R_1 = 0.0779, wR_2 = 0.1228
Largest diff. peak / hole / e Å^{-3}	0.31 / -0.28

Table S10. Selected bond lengths for **4**·2H_2O

parameter	bond length (Å)	parameter	bond length (Å)
O1-N6	1.410(2)	N2-N3	1.312(2)
N1-N2	1.314(2)	N3-N4	1.318(2)
N1-N5	1.316(2)	N4-N5	1.316(3)

Table S11. Selected bond angles for **4**·2H_2O

parameter	bond angle (°)	parameter	bond angle (°)
N2-N1-N5	108.61(16)	N5-N4-N3	107.97(16)
N3-N2-N1	107.58(16)	N1-N5-N4	107.54(16)
N2-N3-N4	108.30(16)		

Table S12. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **4**·2H_2O

Atom	*x*	*y*	*z*	U(eq)
H3A	10645	6739	-163	46
H3B	8299	6528	-1063	46
H1	709	6073	4451	52
H6A	3270	5255	3141	28
H6B	642	5554	2341	28
H6C	3120(70)	6218(14)	2770(20)	48(8)
H2A	7570(70)	4745(19)	1030(20)	42(8)
H2B	7480(80)	5590(20)	690(30)	54(9)

Table S13. Hydrogen bonds for **4**·2H_2O

Donor--H...Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O1--H1…N3	0.84	1.90	2.736(3)	177
O2--H2A…O3	0.86(3)	1.95(3)	2.786(3)	164(2)
O2--H2B…O3	0.84(3)	1.93(3)	2.765(3)	170(3)
O3--H3A…N4	0.85	2.03	2.867(3)	170
O3--H3B…N1	0.85	2.06	2.880(3)	164
N6--H6A…N2	0.87	2.12	2.947(3)	158
N6--H6B…O2	0.87	1.89	2.732(3)	165
N6--H6C…N5	0.91(2)	2.10(2)	2.969(3)	161(2)

4. Single-crystal X-ray diffraction analysis of **5**

Table S14. Crystal data and structure refinement for **5**

	5
CCDC	1883083
Empirical formula	H_5N_7
Formula weight	103.11
Temperature / K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	6.4527(16)
b / Å	12.247(3)
c / Å	5.4073(14)
α /°	90.00
β /°	97.766(6)
γ /°	90.00
Volume / Å^3	423.40(19)
Z	4
ρ_{calc} / g cm^{-3}	1.618
μ / mm^{-1}	0.133
F(000)	216.0
Crystal size / mm^3	0.19×0.12×0.08
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.372 to 53.338
Index ranges	$-8 \le h \le 8$, $-15 \le k \le 15$, $-6 \le l \le 6$
Reflections collected	3281
Independent reflections	890 [R_{int} = 0.0444, R_{sigma} = 0.0428]
Data / restraints / parameters	890 / 0 / 73
Goodness-of-fit on F^2	1.116
Final R indexes [$I >= 2\sigma(I)$]	R_1 = 0.0406, wR_2 = 0.0971
Final R indexes [all data]	R_1 = 0.0490, wR_2 = 0.1008
Largest diff. peak / hole / e Å^{-3}	0.21 / -0.28

Table S15. Selected bond lengths for **5**

parameter	bond length (Å)	parameter	bond length (Å)
N2-N1	1.4494(17)	N4-N5	1.3261(18)
N3-N4	1.3240(18)	N7-N6	1.3277(19)
N3-N7	1.3150(17)	N6-N5	1.3206(19)

Table S16. Selected bond angles for **5**

parameter	bond angle (°)	parameter	bond angle (°)
N7-N3-N4	108.44(12)	N5-N6-N7	108.10(12)
N3-N4-N5	107.73(12)	N6-N5-N4	107.91(13)
N3-N7-N6	107.81(12)		

Table S17. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **5**

Atom	*x*	*y*	*z*	U(eq)
H1A	2058	7021	-1891	18
H1B	1978	5816	-1582	18
H1C	3646	6462	-78	18
H2A	1100(30)	5992(17)	2070(40)	30(5)
H2B	-280(30)	6603(14)	420(40)	28(5)

Table S18. Hydrogen bonds for **5**

Donor--H...Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N1--H1A…N2	0.91	2.07	2.959(2)	165
N1--H1B…N6	0.91	2.58	3.049(2)	113
N1--H1B…N7	0.91	2.13	2.9788(19)	155
N1--H1C…N3	0.91	2.14	2.9048(18)	141
N1--H1C…N4	0.91	2.61	3.0914(19)	114
N2--H2A…N6	0.89(2)	2.39(2)	3.269(2)	170.5(18)
N2--H2B…N5	0.84(2)	2.35(2)	3.143(2)	157.8(19)

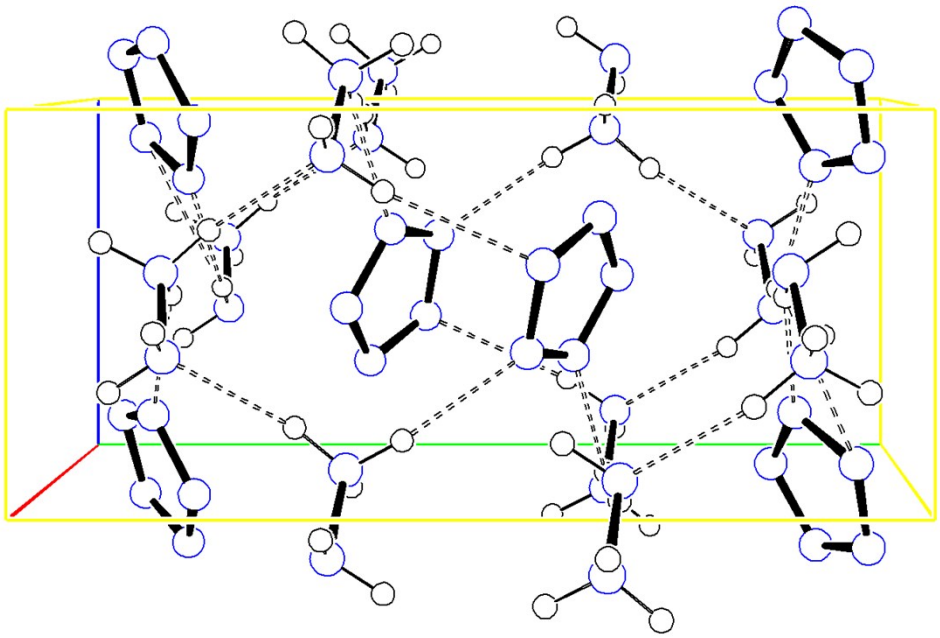


Fig. S3 Ball and stick packing diagram of **5** viewed down the *a* axis. Unit cell indicated and dashed lines indicate strong hydrogen bonding.

5. Single-crystal X-ray diffraction analysis of **6**

Table S19. Crystal data and structure refinement for **6**

	6
CCDC	1885299
Empirical formula	CH_7N_9
Formula weight	145.16
Temperature / K	150
Crystal system	monoclinic
Space group	$P2_1/n$
a / Å	8.429(5)
b / Å	6.861(5)
c / Å	11.434(8)
α /°	90.00
β /°	98.964(12)
γ /°	90.00
Volume / Å^3	653.2(8)
Z	4
ρ_{calc} / g cm^{-3}	1.476
μ / mm^{-1}	0.118
F(000)	304.0
Crystal size / mm^3	0.16×0.05×0.03
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.608 to 56.144
Index ranges	$-11 \le h \le 10$, $-8 \le k \le 8$, $-14 \le l \le 14$
Reflections collected	3913
Independent reflections	1520 [R_{int} = 0.0818, R_{sigma} = 0.0918]
Data / restraints / parameters	1520 / 1 / 96
Goodness-of-fit on F^2	1.055
Final R indexes [$I >= 2\sigma(I)$]	R_1 = 0.0674, wR_2 = 0.1831
Final R indexes [all data]	R_1 = 0.1129, wR_2 = 0.2283
Largest diff. peak / hole / e Å^{-3}	0.29 / -0.41

Table S20. Selected bond lengths for **6**

parameter	bond length (Å)	parameter	bond length (Å)
N8-N9	1.408(4)	N4-N3	1.319(4)
N8-C1	1.324(4)	N1-N5	1.318(4)
N7-C1	1.316(4)	N1-N2	1.320(4)
N6-C1	1.310(4)	N3-N2	1.304(4)
N4-N5	1.314(4)		

Table S21. Selected bond angles for **6**

parameter	bond angle (°)	parameter	bond angle (°)
C1-N8-N9	120.0(3)	N2-N1-N5	107.8(2)
N7-C1-N8	118.7(3)	N4-N5-N1	107.5(2)
N6-C1-N8	120.4(3)	N2-N3-N4	107.7(3)

N6-C1-N7	120.9(3)	N3-N2-N1	108.5(3)
N5-N4-N3	108.5(3)		

Table S22. Selected torsion angles for **6**

parameter	torsion angle (°)	parameter	torsion angle (°)
N9-N8-C1-N7	178.6(3)	N5-N1-N2-N3	-0.2(4)
N9-N8-C1-N6	-1.5(4)	N3-N4-N5-N1	0.2(4)
N4-N3-N2-N1	0.3(4)	N2-N1-N5-N4	0.0(4)
N5-N4-N3-N2	-0.3(3)		

Table S23. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **6**

Atom	*x*	*y*	*z*	U(eq)
H8	7700.1	3360.93	-298.15	30
H7A	6355.12	6688.59	1388.67	33
H7B	7301.69	6378.52	371.66	33
H6A	5346.74	4035.09	2257.63	33
H6B	5633.52	1992.7	1809.48	33
H9A	6539.43	352.51	-368.85	36
H9B	8080(30)	410(80)	380(50)	98(19)

Table S24. Hydrogen bonds for **6**

Donor--H...Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N6--H6A…N3	0.88	2.40	3.268(5)	169
N6--H6A…N4	0.88	2.58	3.288(5)	139
N6--H6B…N9	0.88	2.35	2.692(4)	103
N6--H6B…N5	0.88	2.28	3.048(4)	146
N7--H7A…N4	0.88	2.07	2.911(4)	160
N7--H7B…N1	0.88	2.57	3.316(5)	143
N7--H7B…N2	0.88	2.14	3.016(4)	174
N8--H8…N1	0.88	2.15	2.997(4)	162
N9--H9B…N3	0.93(3)	2.52(4)	3.207(5)	132(4)

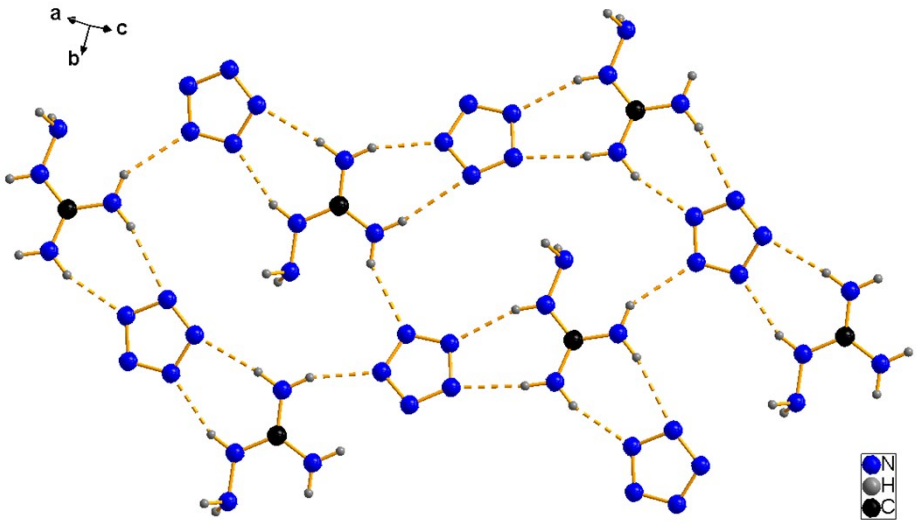


Fig. S4 A 2D layer formed by aminoguanidinium cations and *cyclo*-N_5^- anions in the crystal structure of **6**. Dashed lines indicate strong hydrogen bonding.

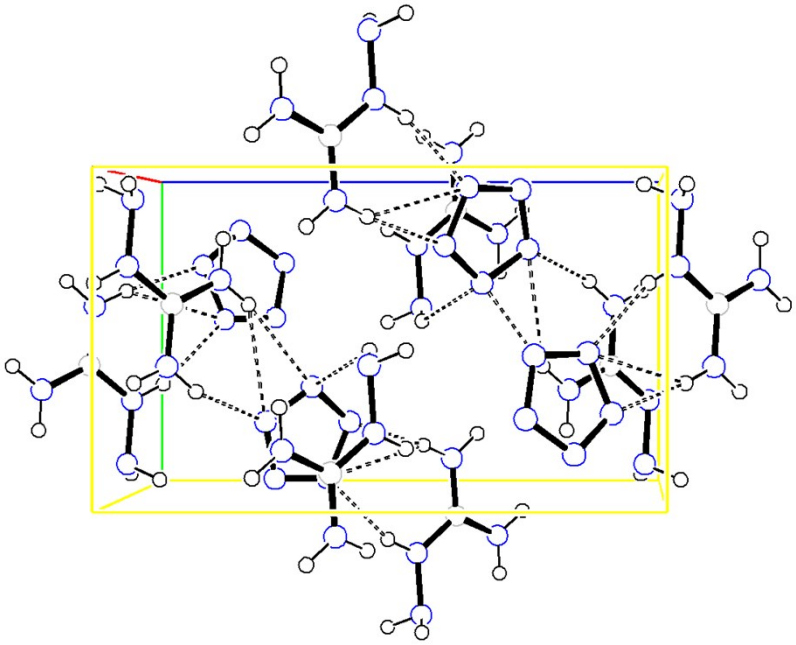


Fig. S5 Ball and stick packing diagram of **6** viewed down the *a* axis. Unit cell indicated and dashed lines indicate strong hydrogen bonding.

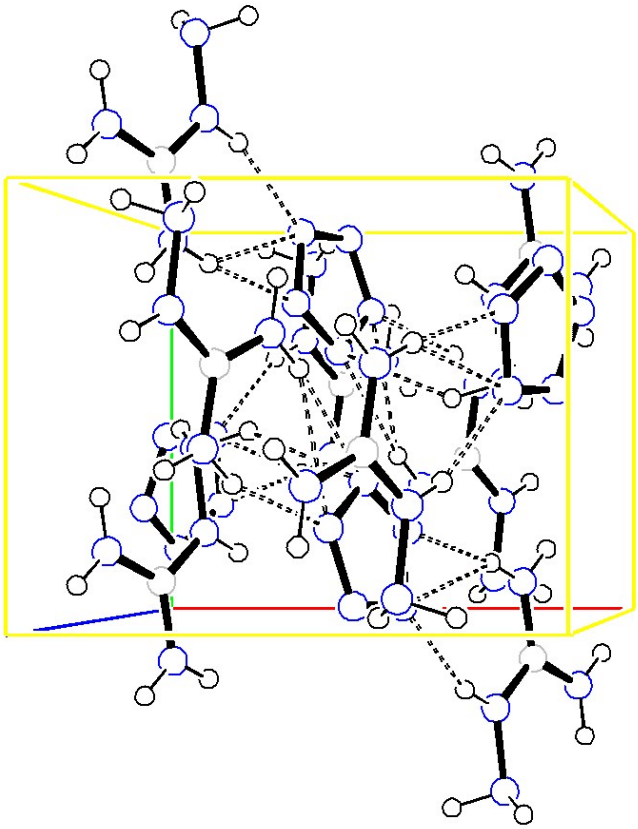


Fig. S6 Ball and stick packing diagram of **6** viewed down the *c* axis. Unit cell indicated and dashed lines indicate strong hydrogen bonding.

6. Single-crystal X-ray diffraction analysis of **7**

Table S25. Crystal data and structure refinement for **7**

	7
CCDC	1883605
Empirical formula	CH_8N_{10}
Formula weight	160.17
Temperature / K	173
Crystal system	triclinic
Space group	*P*-1
a / Å	6.2136(13)
b / Å	7.7039(16)
c / Å	8.5102(17)
α /°	71.562(4)
β /°	87.896(4)
γ /°	70.411(4)
Volume / Å^3	363.00(13)
Z	2
ρ_{calc} / g cm^{-3}	1.465
μ / mm^{-1}	0.117
F(000)	168.0

Crystal size / mm^3	0.19×0.12×0.05
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.06 to 53.198
Index ranges	$-6 \le h \le 7$, $-9 \le k \le 9$, $-10 \le l \le 10$
Reflections collected	3058
Independent reflections	1481 [R_{int} = 0.0229, R_{sigma} = 0.0339]
Data / restraints / parameters	1481 / 1 / 111
Goodness-of-fit on F^2	1.139
Final R indexes [$I >= 2\sigma(I)$]	R_1 = 0.0388, wR_2 = 0.1151
Final R indexes [all data]	R_1 = 0.0444, wR_2 = 0.1211
Largest diff. peak / hole / e $Å^{-3}$	0.26 / -0.28

Table S26. Selected bond lengths for **7**

parameter	bond length (Å)	parameter	bond length (Å)
N8-N9	1.4094(17)	N5-N4	1.3072(18)
N8-C1	1.3303(17)	N1-N5	1.3123(19)
N6-N7	1.4137(17)	N3-N4	1.3153(18)
N6-C1	1.3350(19)	N3-N2	1.314(2)
N10-C1	1.3236(19)	N1-N2	1.3168(18)

Table S27. Selected bond angles for **7**

parameter	bond angle (°)	parameter	bond angle (°)
C1-N8-N9	117.91(12)	N2-N1-N5	107.71(12)
C1-N6-N7	118.75(11)	N3-N2-N1	107.69(12)
N4-N5-N1	108.69(12)	N8-C1-N6	119.82(13)
N2-N3-N4	108.36(12)	N10-C1-N8	119.94(13)
N5-N4-N3	107.54(13)	N10-C1-N6	120.22(12)

Table S28. Hydrogen atom coordinates ($Å \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **7**

Atom	x	y	z	U(eq)
H8	1593	8934	4391	30
H7A	1278	8196	7831	32
H7B	1606	10043	7509	32
H10A	7133	6433	4412	38
H10B	7849	6328	6144	38
H9A	3450(30)	9010(30)	1980(20)	34
H9B	2960(30)	7300(30)	2580(20)	34
H6	5120(30)	7580(30)	7750(20)	40(5)

Table S29. Hydrogen bonds for **7**

Donor--H...Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N6--H6…N5	0.881(18)	2.037(17)	2.9001(18)	166(2)
N7--H7A…N4	0.89	2.32	3.047(2)	139
N7--H7B…N2	0.89	2.36	3.244(2)	176

N8--H8…N7	0.88	2.28	3.021(2)	142
N9--H9A…N1	0.870(19)	2.268(19)	3.130(2)	171.1(18)
N9--H9B…N2	0.83(2)	2.59(2)	3.324(2)	147.9(19)
N10--H10A…N3	0.88	2.41	3.2667(19)	164
N10--H10A…N9	0.88	2.31	2.6536(19)	103
N10--H10B…N3	0.88	2.16	3.0018(19)	159

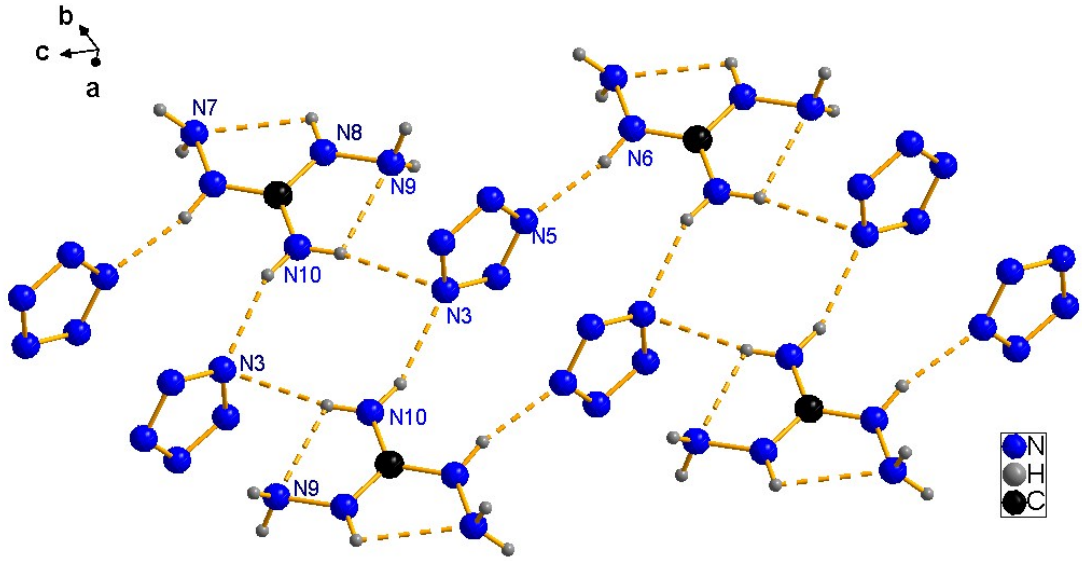


Fig. S7 A layer-like structure formed by diaminoguanidinium cations and *cyclo*-N_5^- anions in the crystal structure of **7**. Dashed lines indicate strong hydrogen bonding.

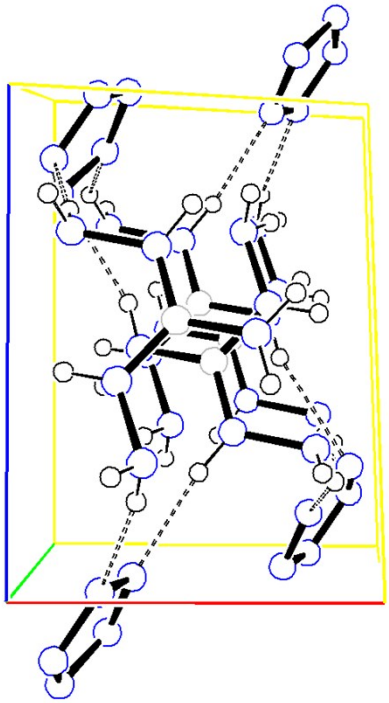


Fig. S8 Ball and stick packing diagram of **7** viewed down the *b* axis. Unit cell indicated

and dashed lines indicate strong hydrogen bonding.

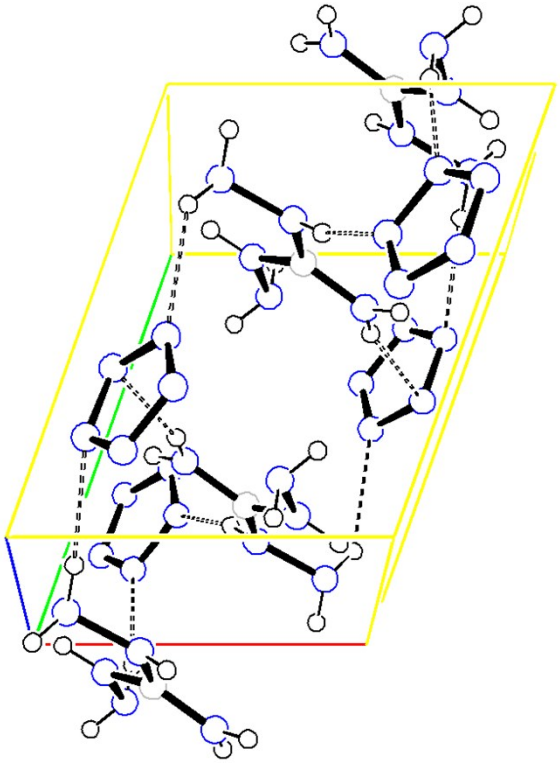


Fig. S9 Ball and stick packing diagram of **7** viewed down the *c* axis. Unit cell indicated and dashed lines indicate strong hydrogen bonding.

7. Single-crystal X-ray diffraction analysis of **8**

Table S30. Crystal data and structure refinement for **8**

	8
CCDC	1885298
Empirical formula	$C_2H_8N_{10}$
Formula weight	172.18
Temperature / K	150
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	3.6171(11)
b / Å	20.792(6)
c / Å	10.069(3)
α /°	90.00
β /°	97.773(6)
γ /°	90.00
Volume / Å^3	750.3(4)
Z	4
ρ_{calc} / g cm^{-3}	1.524
μ / mm^{-1}	0.119
F(000)	360.0

Crystal size / mm^3	0.19×0.12×0.08
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.918 to 52.742
Index ranges	$-4 \le h \le 4$, $-25 \le k \le 25$, $-12 \le l \le 12$
Reflections collected	4400
Independent reflections	1527 [R_{int} = 0.0517, R_{sigma} = 0.0626]
Data / restraints / parameters	1527 / 1 / 116
Goodness-of-fit on F^2	0.985
Final R indexes [$I >= 2\sigma(I)$]	R_1 = 0.0432, wR_2 = 0.0954
Final R indexes [all data]	R_1 = 0.0729, wR_2 = 0.1096
Largest diff. peak / hole / e Å^{-3}	0.20 / -0.22

Table S31. Selected bond lengths for **8**

parameter	bond length (Å)	parameter	bond length (Å)
N8-C1	1.335(3)	N3-N2	1.316(2)
N8-C2	1.345(3)	N4-N5	1.314(2)
N6-C2	1.320(2)	N7-C2	1.333(3)
N9-C1	1.333(3)	N1-N2	1.319(2)
N10-C1	1.332(3)	N1-N5	1.316(2)
N3-N4	1.318(2)		

Table S32. Selected bond angles for **8**

parameter	bond angle (°)	parameter	bond angle (°)
C1-N8-C2	124.29(17)	N9-C1-N8	115.80(18)
N2-N3-N4	108.00(16)	N10-C1-N8	126.80(18)
N5-N4-N3	107.88(16)	N10-C1-N9	117.38(18)
N5-N1-N2	107.79(16)	N6-C2-N8	116.32(18)
N3-N2-N1	108.04(16)	N6-C2-N7	118.66(18)
N4-N5-N1	108.28(17)	N7-C2-N8	125.00(18)

Table S33. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **8**

Atom	x	y	z	U(eq)
H6A	4720.26	7012.26	5073.27	25
H6B	4696.62	6378.53	5833.01	25
H9A	239.04	4379.67	2699.96	24
H9B	-303.19	4594.55	4107.93	24
H10A	2492.74	5051.4	1270.35	24
H10B	3546.24	5741.8	1665.8	24
H7A	2410(60)	7102(9)	2900(20)	25
H7B	190(70)	6505(12)	2180(20)	50(8)

Table S34. Hydrogen bonds for **8**

Donor--H...Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N6--H6A…N1	0.88	2.61	3.363(3)	144

N6--H6A…N5	0.88	2.13	3.001(3)	173
N6--H6B…N2	0.88	2.31	3.081(3)	147
N7--H7A…N1	0.942(19)	2.146(19)	3.057(3)	162.6(17)
N7--H7B…N10	0.92(2)	2.57(3)	2.893(3)	100.8(18)
N7--H7B…N4	0.92(2)	2.19(2)	3.077(3)	162(2)
N9--H9A…N2	0.88	2.54	3.185(3)	130
N9--H9A…N3	0.88	2.53	3.268(3)	142
N9--H9B…N8	0.88	2.06	2.939(3)	175
N10--H10A…N3	0.88	2.35	3.124(3)	147
N10--H10B…N7	0.88	2.36	2.893(3)	119
N10--H10B…N4	0.88	2.37	3.164(3)	150

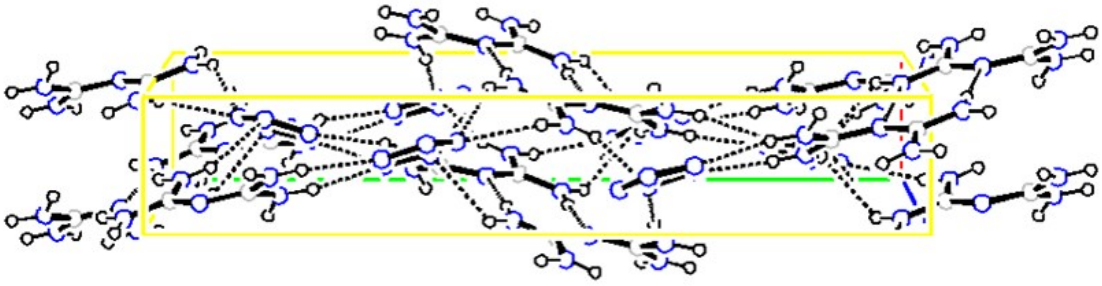


Fig. S10 Ball and stick packing diagram of **8** viewed down the *c* axis. Unit cell indicated and dashed lines indicate strong hydrogen bonding.

8. Single-crystal X-ray diffraction analysis of **9**

Table S35. Crystal data and structure refinement for **9**

	9
CCDC	1883082
Empirical formula	$C_2H_6N_{10}$
Formula weight	170.17
Temperature / K	150
Crystal system	triclinic
Space group	*P*-1
a / Å	5.298(2)
b / Å	7.156(3)
c / Å	10.106(4)
α /°	100.047(8)
β /°	104.076(7)
γ /°	104.089(7)
Volume / Å^3	349.2(2)
Z	2
ρ_{calc} / g cm^{-3}	1.618
μ / mm^{-1}	0.128
F(000)	176.0

Crystal size / mm^3	0.19×0.05×0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.29 to 50.996
Index ranges	$-6 \le h \le 5$, $-8 \le k \le 8$, $-12 \le l \le 12$
Reflections collected	2529
Independent reflections	1271 [R_{int} = 0.0366, R_{sigma} = 0.0591]
Data / restraints / parameters	1271 / 2 / 117
Goodness-of-fit on F^2	1.015
Final R indexes [$I >= 2\sigma(I)$]	R_1 = 0.0448, wR_2 = 0.1237
Final R indexes [all data]	R_1 = 0.0704, wR_2 = 0.1319
Largest diff. peak / hole / e Å^{-3}	0.24 / -0.25

Table S36. Selected bond lengths for **9**

parameter	bond length (Å)	parameter	bond length (Å)
N6-N7	1.386(3)	N7-C2	1.288(3)
N6-C1	1.329(3)	N5-N1	1.313(3)
N10-C1	1.312(3)	N5-N4	1.323(3)
N8-N9	1.405(3)	N1-N2	1.320(3)
N8-C1	1.351(3)	N2-N3	1.323(3)
N8-C2	1.376(3)	N4-N3	1.319(3)

Table S37. Selected bond angles for **9**

parameter	bond angle (°)	parameter	bond angle (°)
C1-N6-N7	111.76(19)	N1-N2-N3	108.1(2)
C1-N8-N9	121.1(2)	N3-N4-N5	107.89(19)
C1-N8-C2	107.11(19)	N4-N3-N2	107.8(2)
C2-N8-N9	131.8(2)	N6-C1-N8	105.5(2)
C2-N7-N6	104.16(19)	N10-C1-N6	129.3(2)
N1-N5-N4	108.2(2)	N10-C1-N8	125.2(2)
N5-N1-N2	108.0(2)	N7-C2-N8	111.5(2)

Table S38. Hydrogen atom coordinates (Å×10^4) and isotropic displacement parameters (Å^2×10^3) for **9**

Atom	x	y	z	U(eq)
H6	2783	6398	4885	26
H10A	7753	8660	5490	30
H10B	9463	9107	7022	30
H2	2712	5470	8519	26
H9A	7760(70)	8540(40)	9810(30)	53(10)
H9B	8670(60)	6950(30)	9380(30)	44(9)

Table S39. Hydrogen bonds for **9**

Donor--H...Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N6--H6…N4	0.88	2.16	2.956(3)	151
N6--H6…N7	0.88	2.36	2.902(3)	120

N9--H9A…N2	0.89(3)	2.59(4)	3.320(3)	140(3)
N9--H9B…N3	0.89(3)	2.58(2)	3.272(4)	136(2)
N10--H10A…N5	0.88	2.11	2.958(3)	160
N10--H10B…N9	0.88	2.55	2.837(3)	100
N10--H10B…N1	0.88	2.18	2.990(3)	152

9. Single-crystal X-ray diffraction analysis of **10**

Table S40. Crystal data and structure refinement for **10**

	10
CCDC	1884809
Empirical formula	$C_3H_7N_{13}$
Formula weight	225.22
Temperature / K	173
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å	8.083(3)
b / Å	7.141(2)
c / Å	16.094(5)
α /°	90.00
β /°	101.864(7)
γ /°	90.00
Volume / Å^3	909.2(5)
Z	4
ρ_{calc} / g cm^{-3}	1.645
μ / mm^{-1}	0.129
F(000)	464.0
Crystal size / mm^3	0.12×0.06×0.03
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.15 to 54.374
Index ranges	$-10 \le h \le 10$, $-8 \le k \le 9$, $-19 \le l \le 20$
Reflections collected	6113
Independent reflections	1976 [R_{int} = 0.0690, R_{sigma} = 0.0700]
Data / restraints / parameters	1976 / 1 / 154
Goodness-of-fit on F^2	0.984
Final R indexes [$I >= 2\sigma(I)$]	R_1 = 0.0573, wR_2 = 0.1297
Final R indexes [all data]	R_1 = 0.1046, wR_2 = 0.1515
Largest diff. peak / hole / e Å^{-3}	0.23 / -0.25

Table S41. Selected bond lengths for **10**

parameter	bond length (Å)	parameter	bond length (Å)
N9-N10	1.402(3)	N7-C1	1.344(3)
N9-C2	1.344(3)	N13-C3	1.326(3)
N9-C1	1.341(3)	N1-N2	1.301(3)
N11-N12	1.400(3)	N1-N5	1.314(3)
N11-C2	1.353(3)	N4-N3	1.309(3)
N11-C3	1.394(3)	N4-N5	1.313(3)

N8-N7	1.408(3)	N3-N2	1.312(3)
N8-C2	1.309(3)	N6-C1	1.307(3)
N10-C3	1.315(3)		

Table S42. Selected bond angles for **10**

parameter	bond angle (°)	parameter	bond angle (°)
C2-N9-N10	113.8(2)	N1-N2-N3	107.8(2)
C1-N9-N10	137.9(2)	N4-N5-N1	107.5(2)
C1-N9-C2	108.2(2)	N9-C2-N11	105.4(2)
C2-N11-N12	129.8(2)	N8-C2-N9	114.4(2)
C2-N11-C3	106.1(2)	N8-C2-N11	140.2(2)
C3-N11-N12	124.0(2)	N10-C3-N11	113.8(2)
C2-N8-N7	99.9(2)	N10-C3-N13	124.9(2)
C3-N10-N9	100.92(19)	N13-C3-N11	121.4(2)
C1-N7-N8	113.8(2)	N9-C1-N7	103.7(2)
N2-N1-N5	108.6(2)	N6-C1-N9	127.4(2)
N3-N4-N5	108.0(2)	N6-C1-N7	128.9(3)
N4-N3-N2	108.2(2)		

Table S43. Hydrogen atom coordinates ($Å \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **10**

Atom	*x*	*y*	*z*	U(eq)
H13A	9099.1	2769.65	8368	44
H13B	10383.01	4006.92	8944.74	44
H6A	4563.02	6710.14	6169.31	44
H6B	4144.99	8759.47	5959.13	44
H12A	11530.27	8229.89	8762.68	47
H7	6140(30)	11310(40)	6782(18)	38(8)
H12B	10670(40)	8210(40)	9444(17)	67(12)

Table S44. Hydrogen bonds for **10**

Donor--H...Acceptor	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N6--H6A…N1	0.88	1.99	2.851(3)	165
N6--H6B…N3	0.88	2.04	2.880(3)	158
N7--H7…N2	1.00(3)	1.98(3)	2.893(3)	151(2)
N12--H12B…N5	0.89(3)	2.54(3)	3.123(4)	124(2)
N13--H13A…N8	0.88	2.18	3.048(3)	170
N13--H13B…N12	0.88	2.56	2.870(3)	102
N13--H13B…N4	0.88	2.13	2.925(4)	150

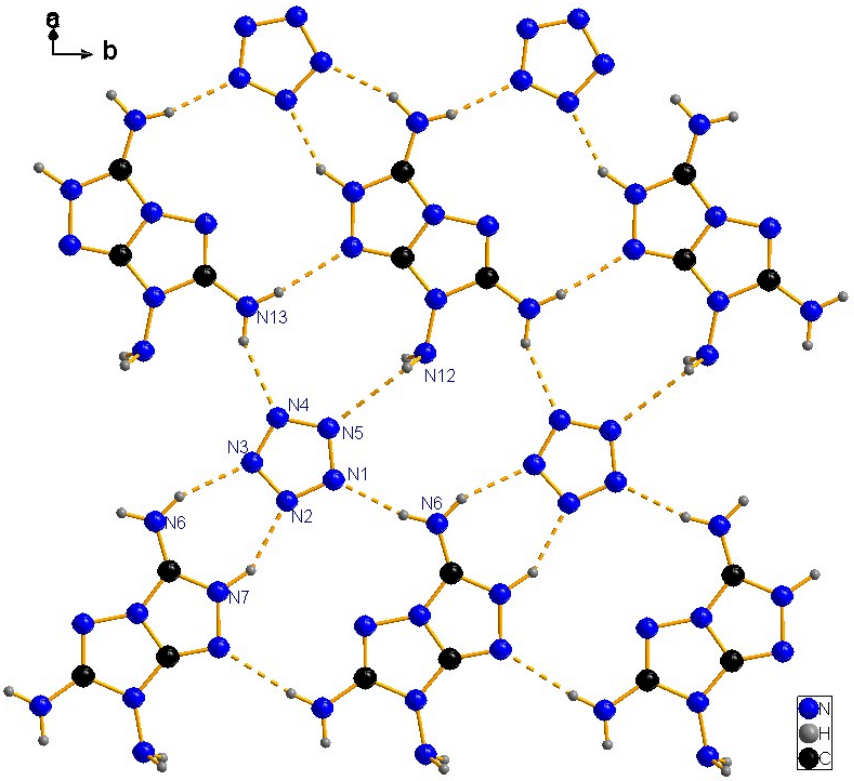


Fig. S11 A 2D layer formed by fuesd cations and *cyclo*-N_5^- anions in the crystal structure of **10**. Dashed lines indicate strong hydrogen bonding.

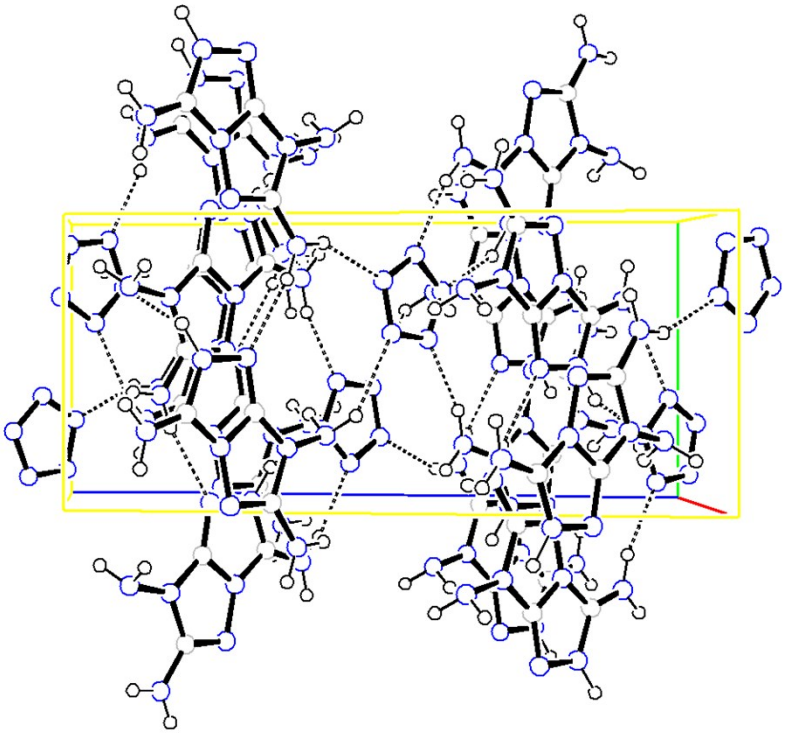


Fig. S12 Ball and stick packing diagram of **10** viewed down the *a* axis. Unit cell indicated and dashed lines indicate strong hydrogen bonding.

10. The noncovalent interactions study[1]

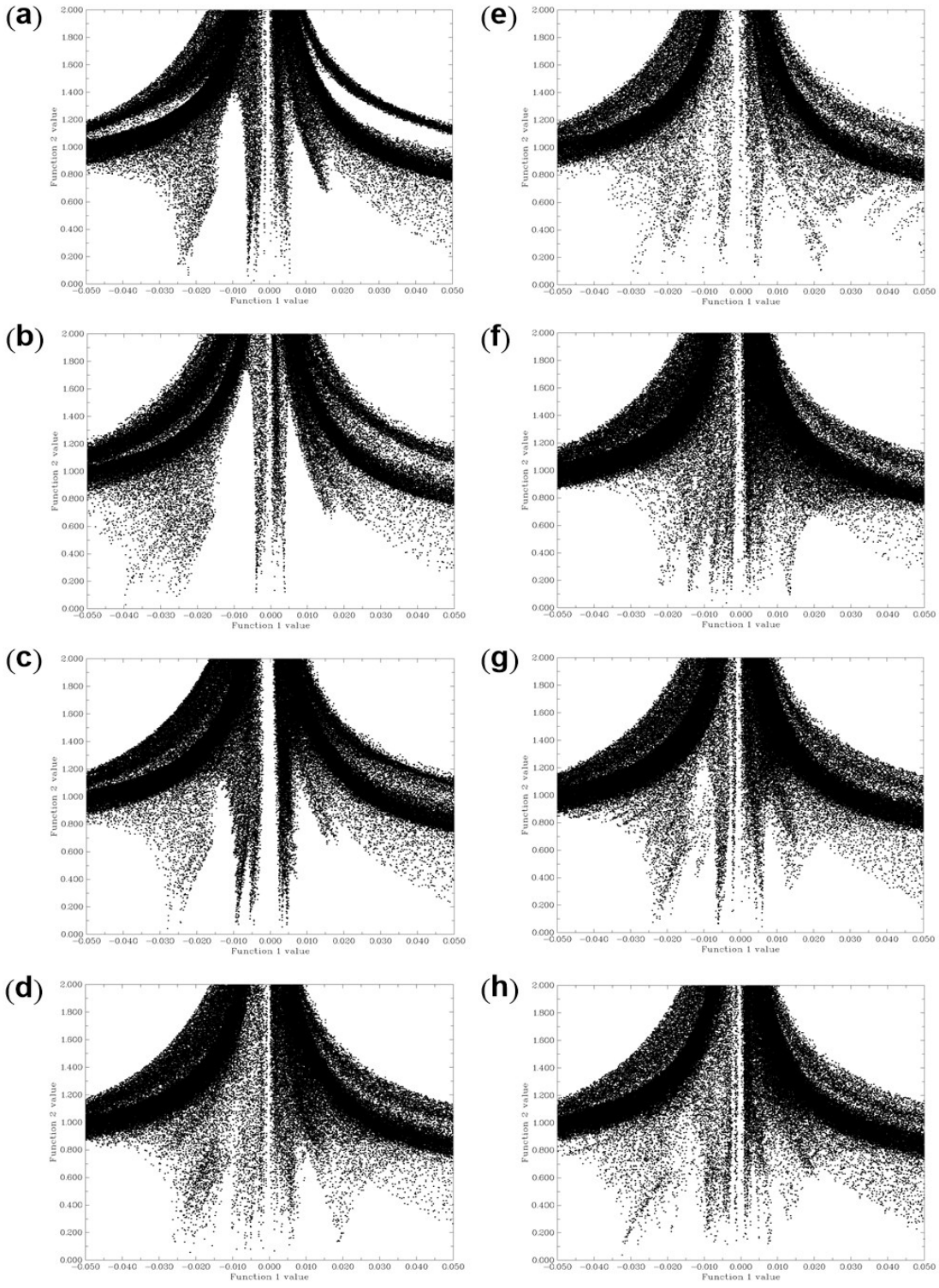


Fig. S13 (a-h) Plots of the reduced density gradient versus the electron density multiplied by the sign of the second Hessian eigenvalue for **3**-**10** (**4** is dihydrate). Strong hydrogen bonds: -0.05 < Function 1 value < -0.03; moderate hydrogen bonds: -0.03 < Function 1 value < -0.02; weak hydrogen bonds: -0.02 < Function 1 value < -0.01.

11. ^{1}H and ^{13}C NMR spectra

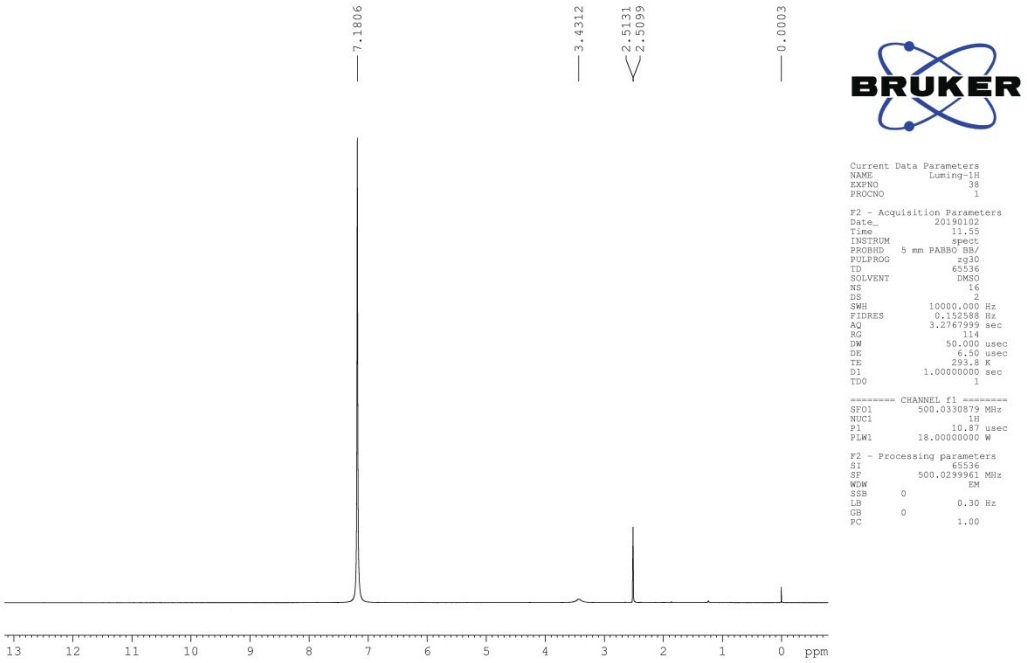


Fig. S14 ^{1}H NMR spectrum of **3** in d_6-DMSO.

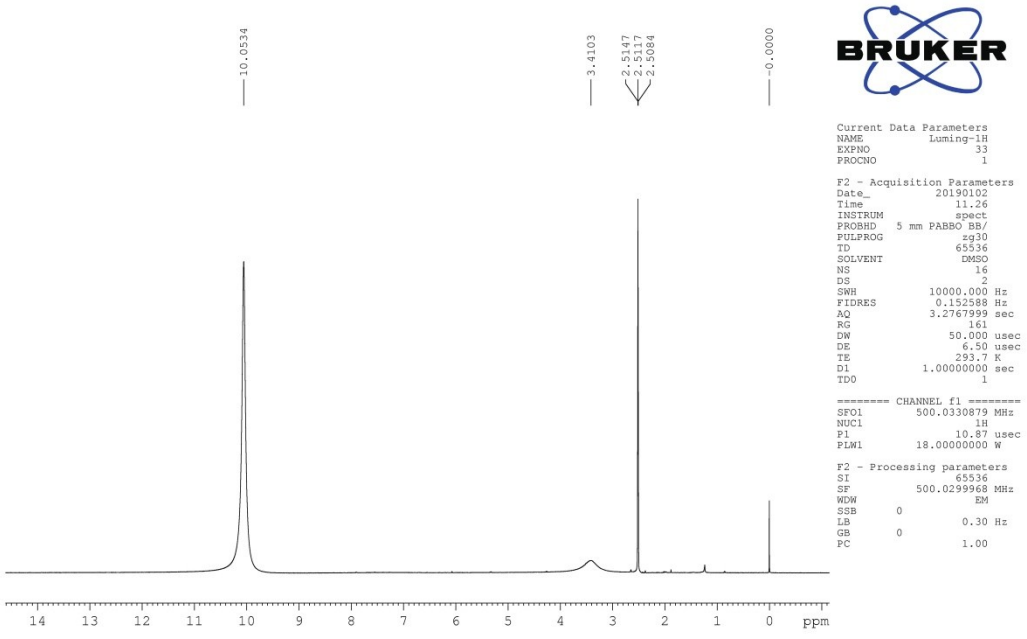


Fig. S15 ^{1}H NMR spectrum of **4** in d_6-DMSO.

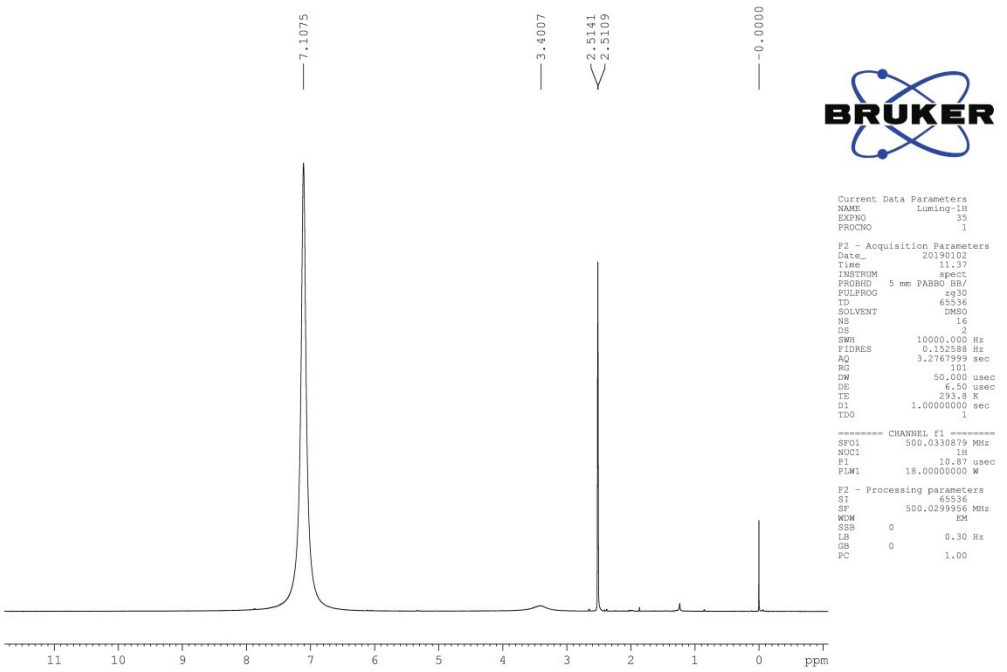


Fig. S16 ^{1}H NMR spectrum of **5** in d_6-DMSO.

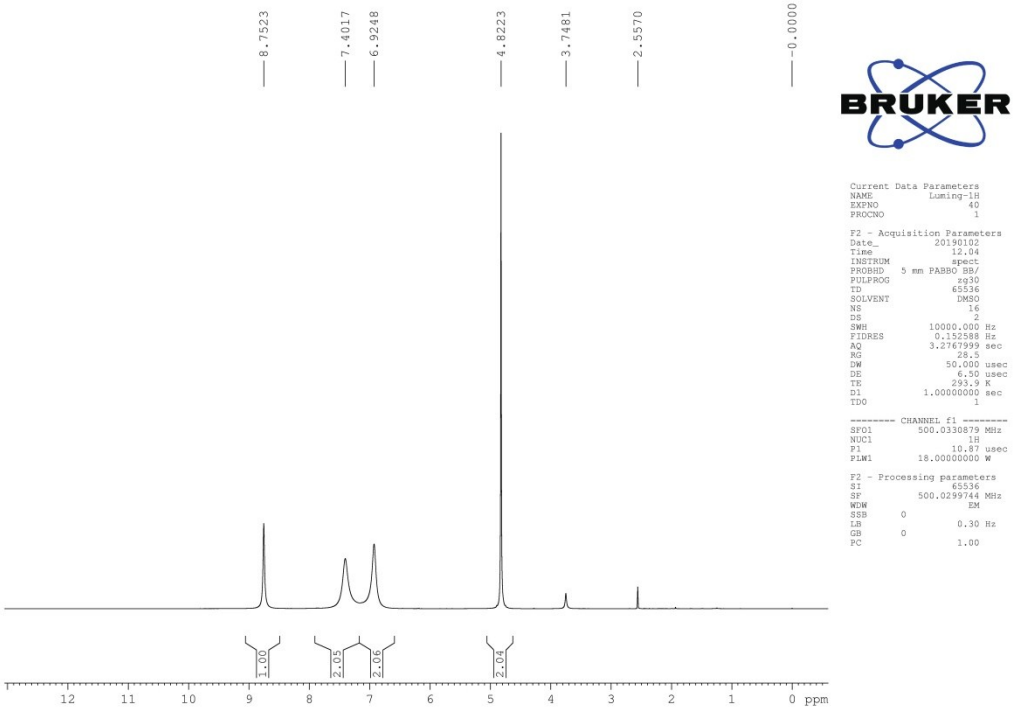


Fig. S17 ^{1}H NMR spectrum of **6** in d_6-DMSO.

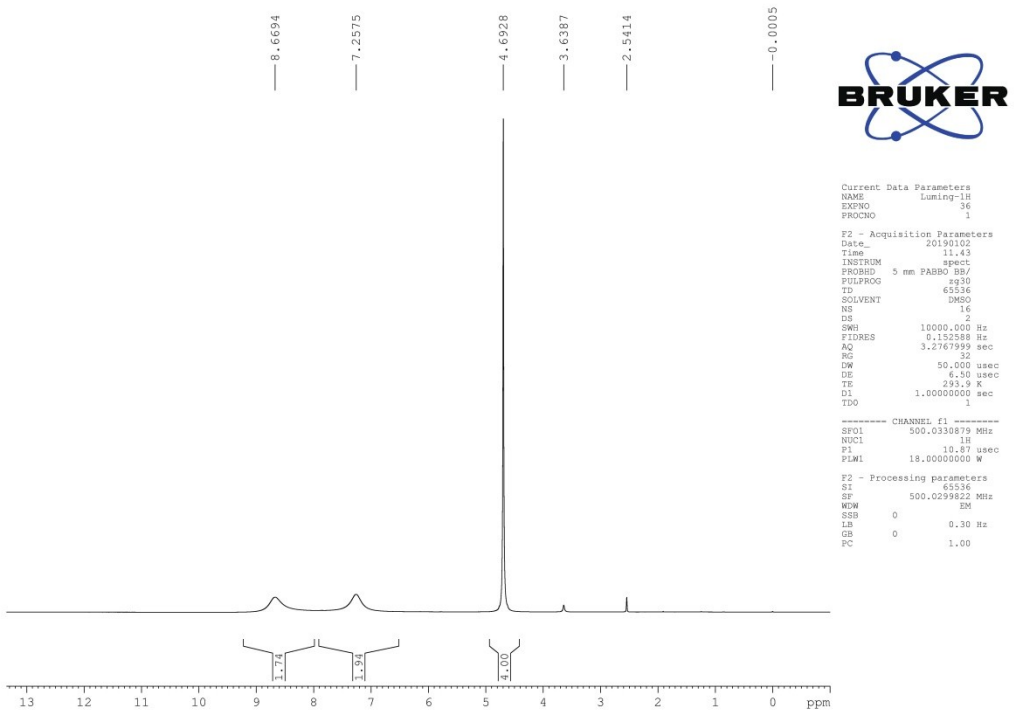


Fig. S18 ^{1}H NMR spectrum of **7** in d_6-DMSO.

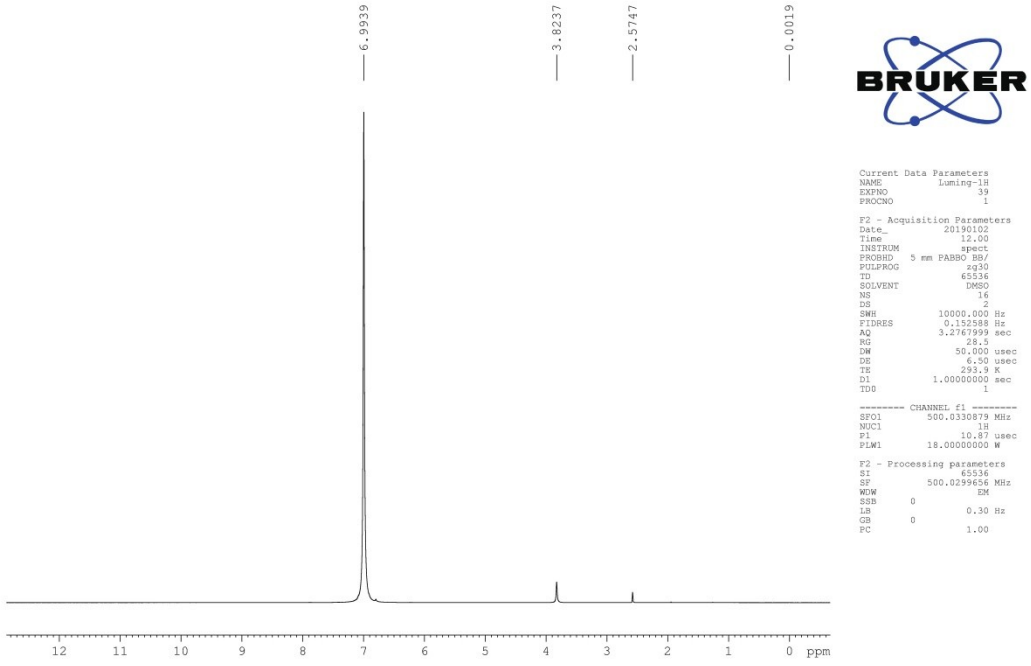


Fig. S19 ^{1}H NMR spectrum of **8** in d_6-DMSO.

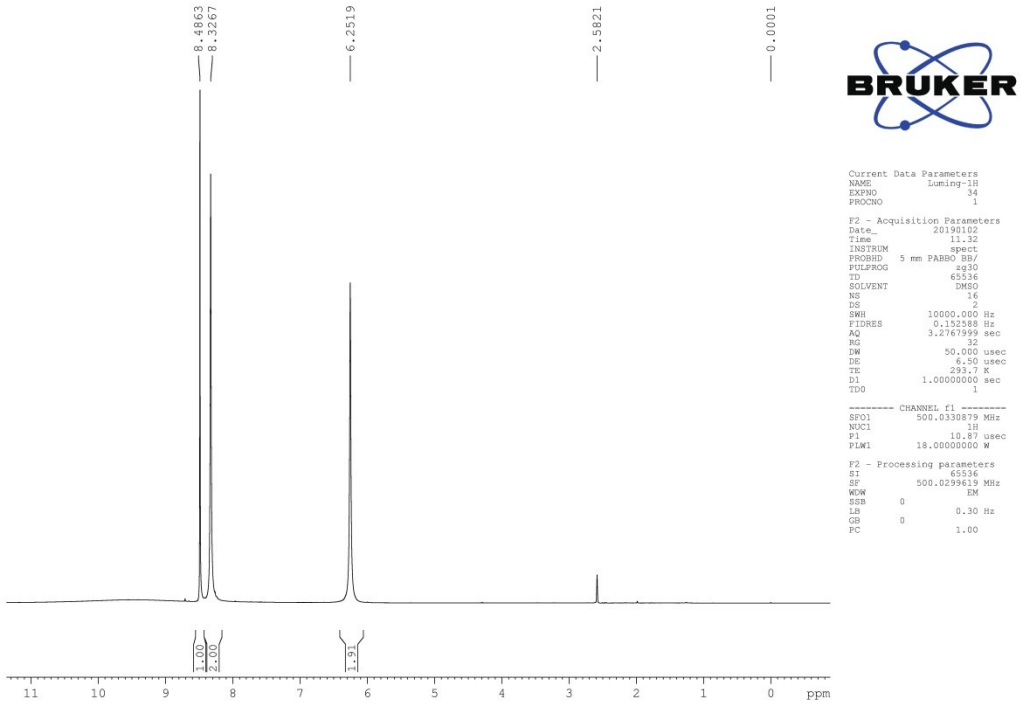


Fig. S20 ^{1}H NMR spectrum of **9** in d_6-DMSO.

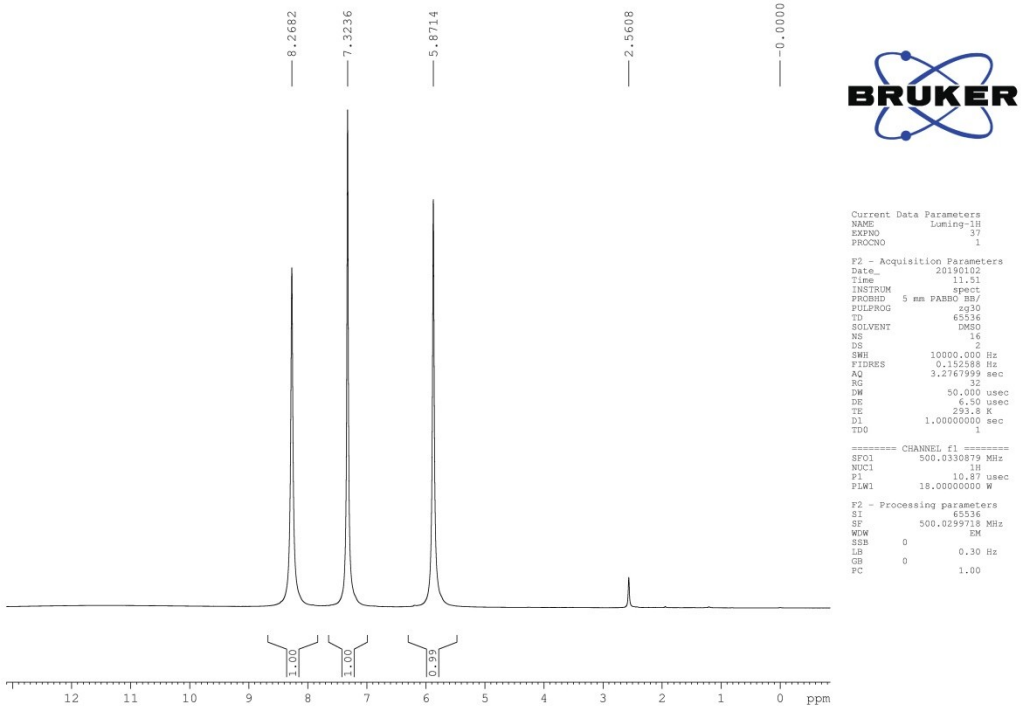


Fig. S21 ^{1}H NMR spectrum of **10** in d_6-DMSO.

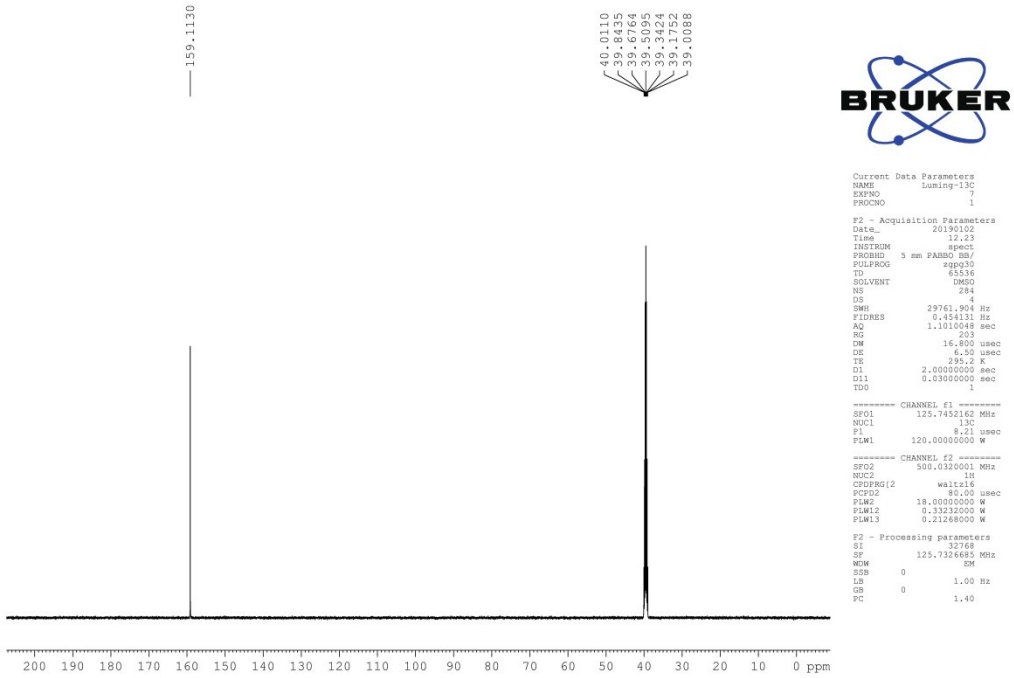


Fig. S22 ^{13}C NMR spectrum of **6** in d_6-DMSO.

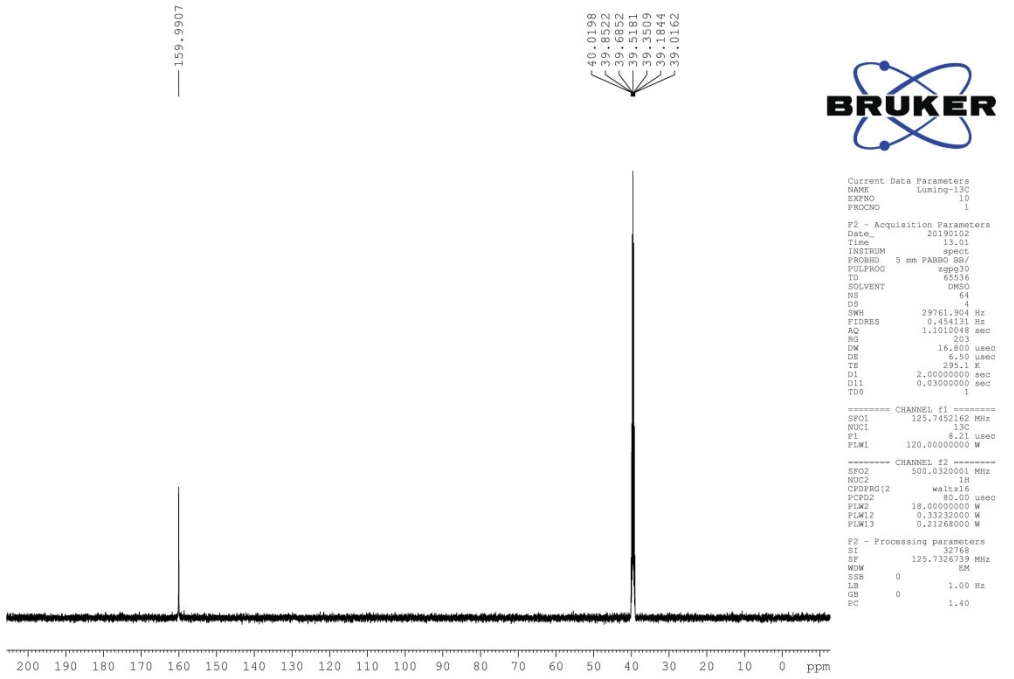


Fig. S23 ^{13}C NMR spectrum of **7** in d_6-DMSO.

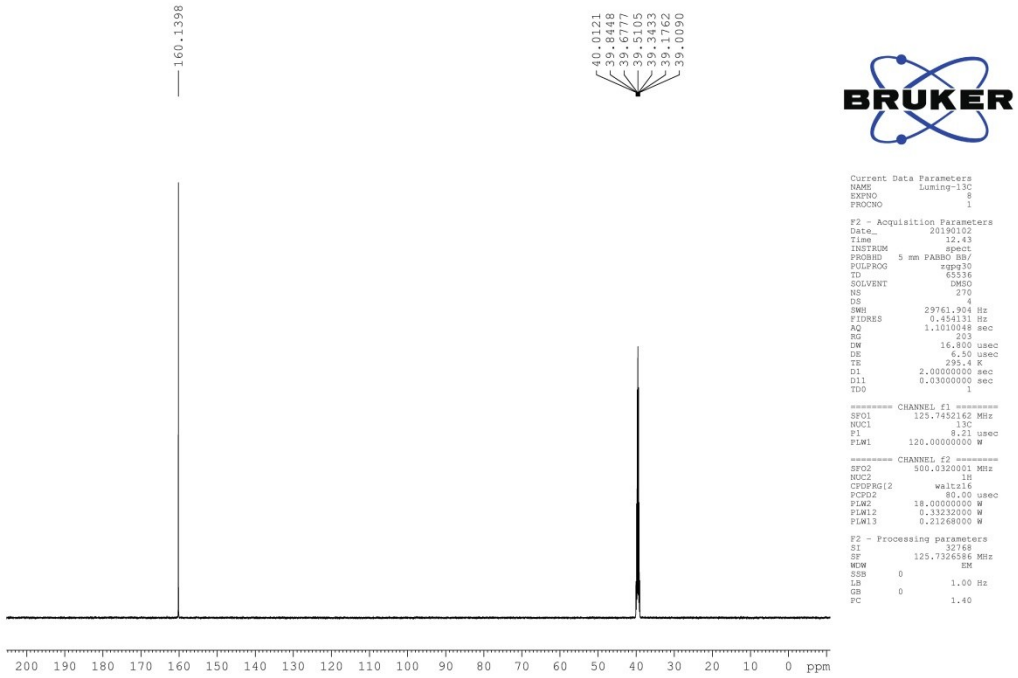


Fig. S24 ^{13}C NMR spectrum of **8** in d_6-DMSO.

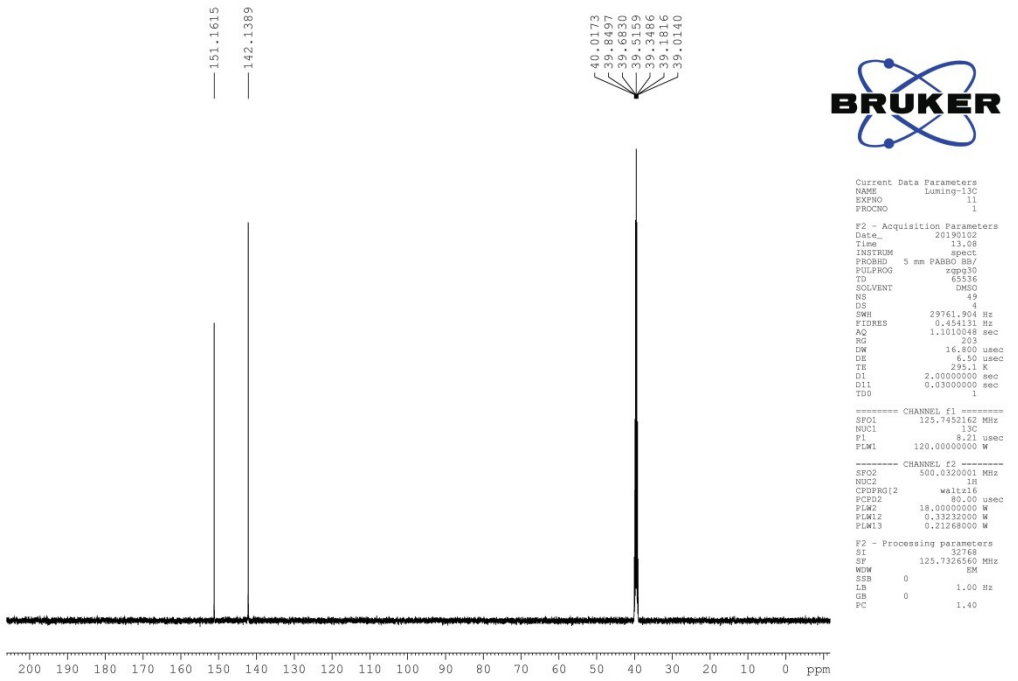


Fig. S25 ^{13}C NMR spectrum of **9** in d_6-DMSO.

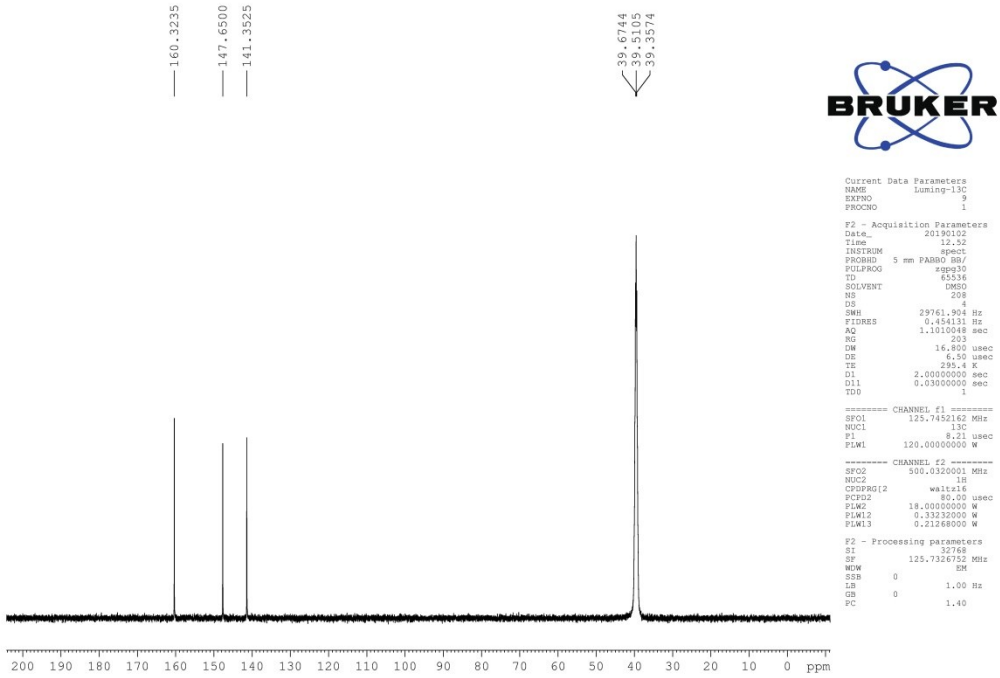


Fig. S26 ^{13}C NMR spectrum of **10** in d_6-DMSO.

12. Powder X-ray diffraction (PXRD) pattern of AgN5 (**1**)

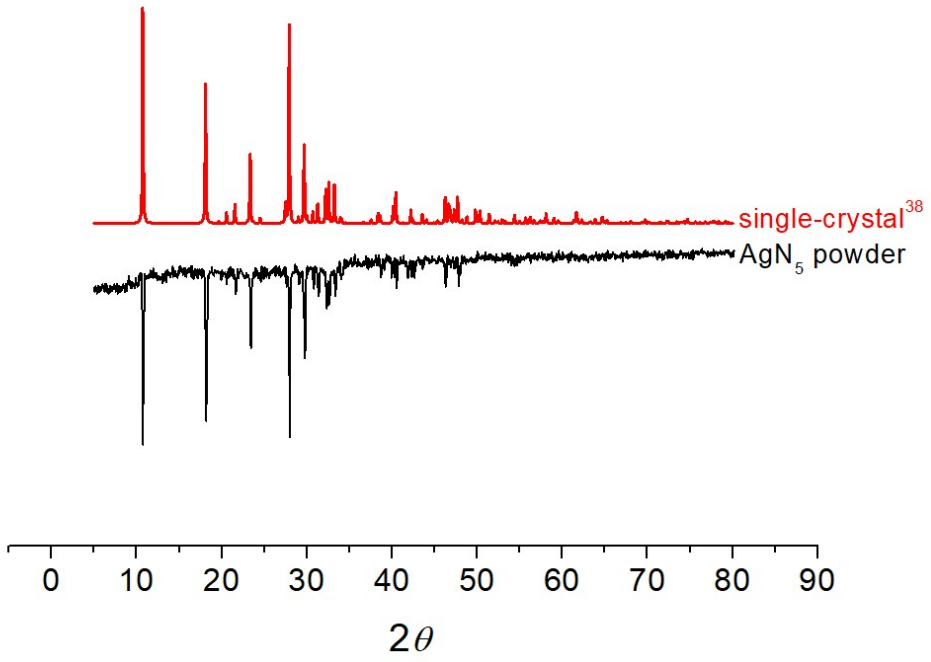


Fig. S27 The PXRD pattern of AgN_5 and the calculated pattern from its single-crystal structure.

13. Topology for **2**

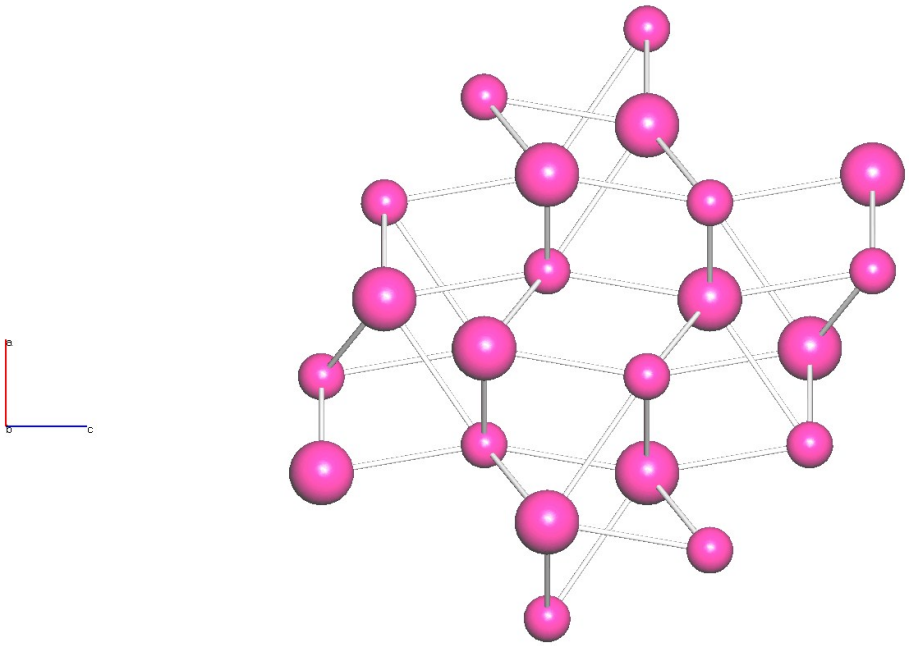


Fig. S28 Topology for **2** (topological type: $\{4^{15}.6^{6}\}\{4^{17}.6^{4}\}$). The *cyclo*-$N_5^-$ ligands are represented by small spheres and the K ions are represented by larger spheres.

14. TG and DSC curves of **4**·$2H_2O$

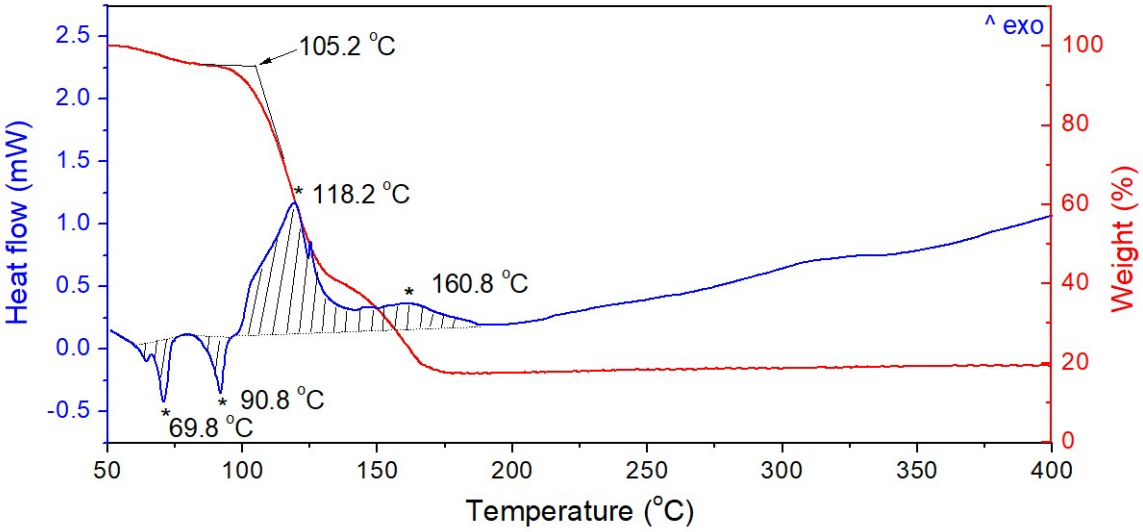


Fig. S29 TG and DSC curves of **4**·$2H_2O$ under nitrogen with a heating rate of 5 °C min^{-1}.

15. Calculation of heats of formation

For energetic salts, the solid-phase heats of formation are calculated on the basis of a Born-Haber energy cycle (Scheme S1).

Based on a Born-Haber energy cycle, the heat of formation of a salt can be simplified by the formula given in Equation (1):

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

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al.[2] [Eq. (2)]

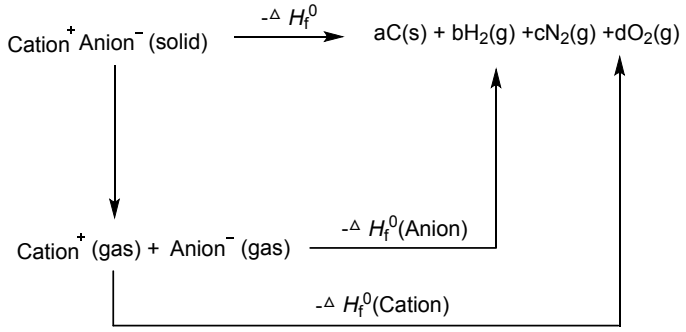
$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (2)

where n_M and n_X depend on the nature of the ions, M_p^+ and X_q^-, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.

The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

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

Where ρ_m/g cm^{-3} is the density, M_m is the chemical formula mass of the ionic material, and values for the coefficients γ/ kJ mol^{-1} cm and δ/kJ mol^{-1} are taken from the literature[3].



Scheme S1. Born-Haber cycle for the formation of energetic salts

References

1 E. R. Johnson and S. Keinan, *J. Am. Chem. Soc.*, 2010, **132**, 6498-6506.

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

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