Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Superior thermally robust energetic materials featuring *Z*-*E* isomeric bis(3,4-diamino-1,2,4-triazol-5-yl)-1H-pyrazole: self-assembly nitrogen-rich tubes and templates with Hofmeister anions capture architecture

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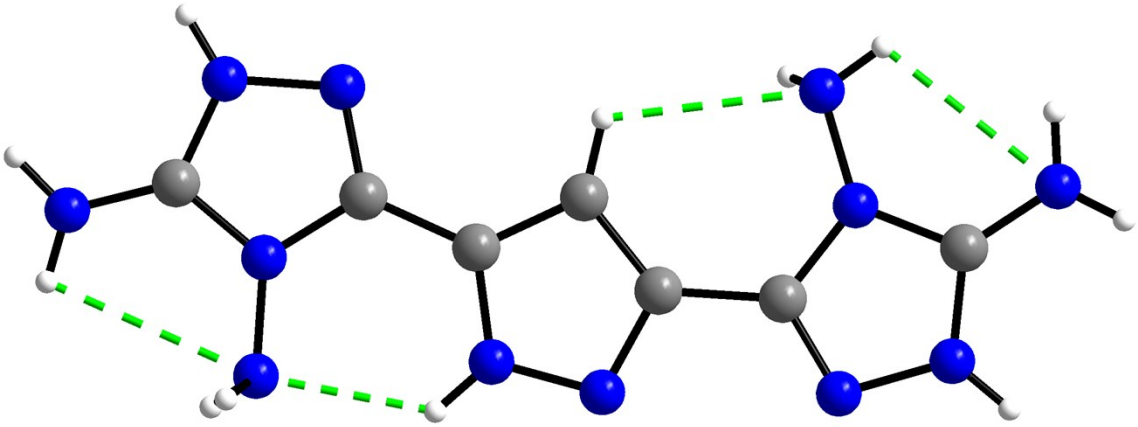
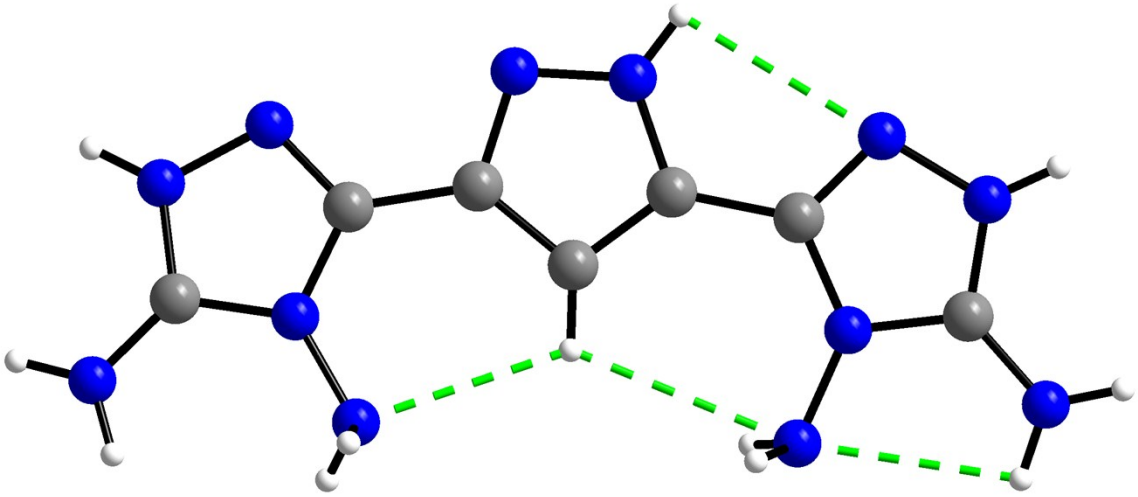


Z-isomer of molecule **3** (green dashed lines denote intramolecular hydrogen bonds)



E-isomer of molecule **3** (green dashed lines denote intramolecular hydrogen bonds)

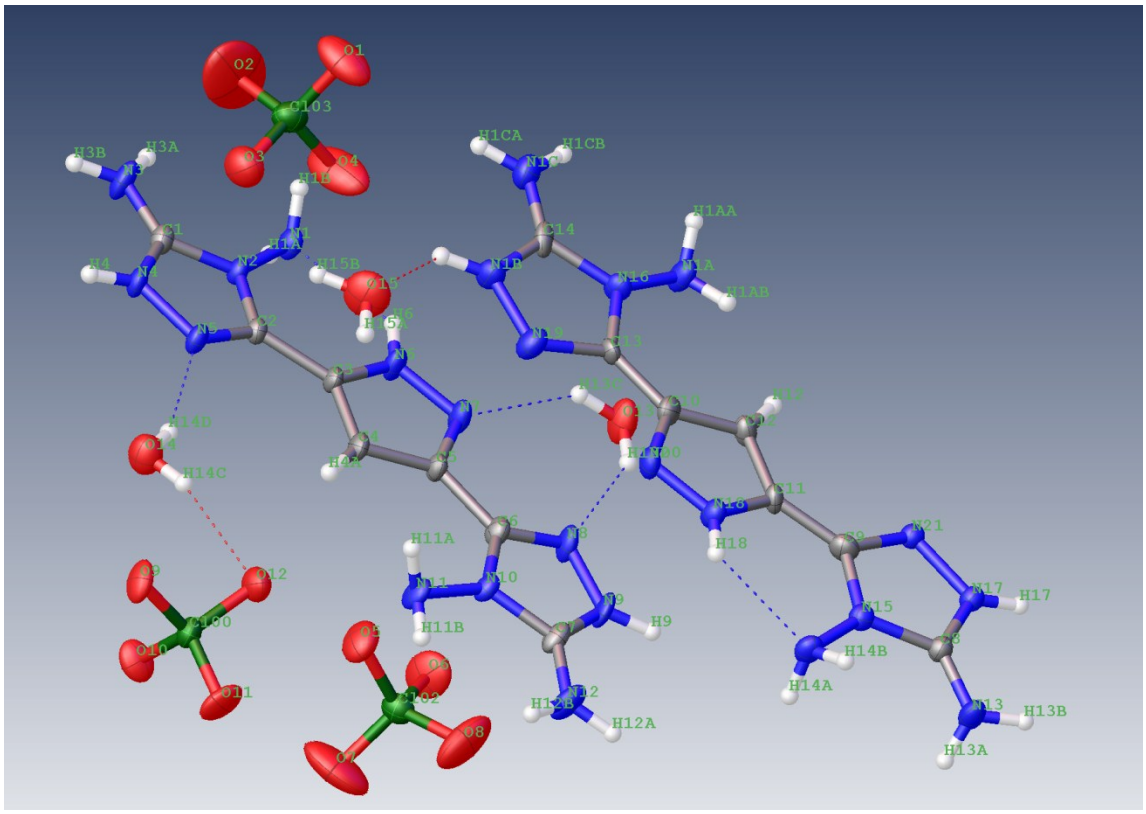


Table S1 Crystal data and structure refinement for 4•2H_2O.

Identification code	CCDC 1886975
Empirical formula	$C_{21}H_{48}Cl_6N_{36}O_{30}$
Formula weight	1497.65
Temperature/K	173
Crystal system	triclinic
Space group	P-1
a/Å	10.876(4)
b/Å	12.218(4)
c/Å	12.367(5)
α/°	66.420(7)
β/°	78.642(7)
γ/°	69.642(7)
Volume/Å^3	1408.9(9)
Z	1
ρ_{calc}g/cm^3	1.765
μ/mm^{-1}	0.427
F(000)	768.0
Crystal size/mm^3	0.19 × 0.15 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.602 to 54.968

Index ranges	$-14 \leq h \leq 13, -15 \leq k \leq 15, -16 \leq l \leq 16$
Reflections collected	12063
Independent reflections	6291 [$R_{int} = 0.0679$, $R_{sigma} = 0.1186$]
Data/restraints/parameters	6291/387/490
Goodness-of-fit on F^2	0.996
Final R indexes [I>=2σ (I)]	$R_1 = 0.0934$, $wR_2 = 0.2572$
Final R indexes [all data]	$R_1 = 0.1531$, $wR_2 = 0.3128$
Largest diff. peak/hole / e $Å^{-3}$	1.01/-0.89

Table S2 Hydrogen Bonds for 4•2H_2O.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1B	H1BA	O4	0.88	2.36	3.0609(12)	137
N1B	H1BA	O15	0.88	2.05	2.6798(11)	128
N1	H1A	O10	0.90	2.58	3.1653(13)	124
N1	H1A	O14	0.90	2.34	3.0423(12)	135
N1	H1B	O1[2]	0.90	2.20	3.0750(12)	165
N1A	H1AA	O7	0.89	2.47	3.2986(13)	154
N1A	H1AB	N20	0.89	2.59	3.4135(14)	153
N3	H3A	O10	0.88	2.29	3.1150(13)	157
N3	H3B	O5[3]	0.88	2.02	2.8579(12)	158
N3	H3B	O11	0.88	2.48	2.9147(12)	111
N4	H4	O13[1]	0.88	1.85	2.6562(11)	152
N1C	H1CA	O2	0.88	2.20	2.8322(11)	129
N1C	H1CA	O4	0.88	2.46	3.1792(13)	140
N1C	H1CB	O7	0.88	2.20	2.9901(12)	149
N1C	H1CB	N14	0.88	2.17	2.5198(10)	103
N6	H6	N1	0.88	2.15	2.7750(11)	128
N6	H6	O6[4]	0.88	2.16	2.7677(11)	126
N9	H9	O9[5]	0.88	2.13	2.8654(12)	141

N9	H9	O14	0.88	2.44	3.0677(12)	129
N11	H11A	O15	0.88	2.38	3.0834(12)	137
N12	H12A	O8	0.88	2.30	2.9844(12)	135
N12	H12A	O9	0.88	2.43	3.1051(13)	134
N12	H12B	O1	0.88	2.37	3.0740(12)	137
N13	H13B	O4	0.88	1.77	2.6489(11)	175
O13	H13C	N7	0.87	2.19	2.9095(12)	141
O13	H13C	O6	0.87	2.53	3.2125(13)	136
O13	H13D	N8	0.87	2.20	2.9624(12)	147
N14	H14A	O7	0.88	2.15	2.7655(11)	126
N14	H14B	O6	0.88	2.51	3.3126(13)	153
N14	H14B	O7	0.88	2.58	3.3620(14)	149
N14	H14B	N1C	0.88	2.18	2.5198(10)	103
O14	H14C	O12	0.85	2.12	2.9465(12)	163
O14	H14D	N5	0.85	2.18	2.9912(12)	159
O15	H15A	N19	0.85	2.08	2.9134(12)	167
O15	H15B	N21	0.85	2.17	2.9553(12)	153
O15	H15B	O3	0.85	2.23	2.9463(12)	142
O15	H15B	N20	0.85	2.13	2.7496(11)	130
N17	H17	O15	0.88	1.80	2.6546(11)	163
N18	H18	O3	0.88	2.16	2.7905(11)	129
N18	H18	N14	0.88	2.16	2.7910(11)	129
N18	H18	N1A	0.88	1.58	2.1432(9)	119
C4	H4A	N11	0.95	2.60	3.0621(12)	110

[1]1+X,+Y,+Z; [2]2-X,2-Y,-1-Z; [3]2-X,2-Y,-Z; [4]1-X,2-Y,-Z; [5]-1+X,+Y,+Z

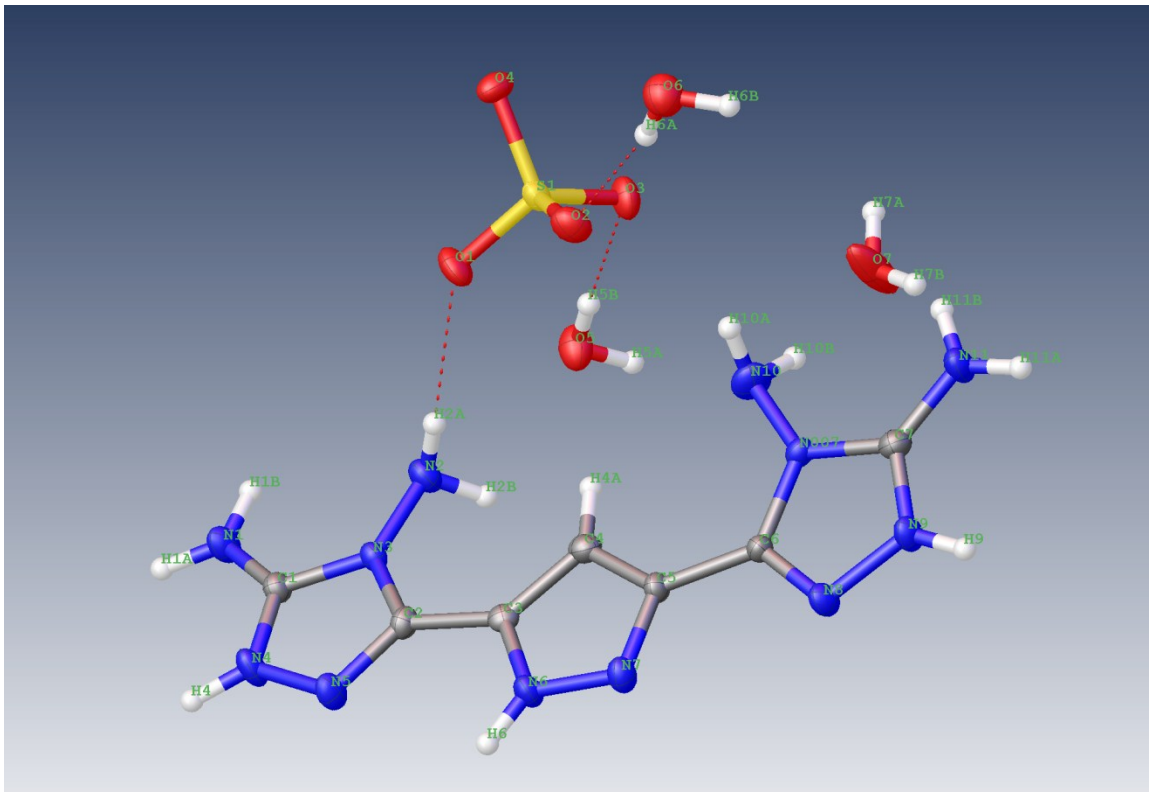


Table S3 Crystal data and structure refinement for 5•3H_2O.

Identification code	CCDC1886976
Empirical formula	$C_7H_{18}N_{12}O_7S$
Formula weight	414.39
Temperature/K	173
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.6062(7)
b/Å	10.0221(11)
c/Å	24.619(3)
α/°	90
β/°	95.193(4)
γ/°	90
Volume/Å^3	1623.3(3)
Z	4
ρ_{calc}g/cm^3	1.696
μ/mm^{-1}	0.268
F(000)	864.0
Crystal size/mm^3	0.15 × 0.08 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.322 to 52.79

Index ranges	$-7 \le h \le 7, -12 \le k \le 12, -15 \le l \le 30$
Reflections collected	9494
Independent reflections	3227 [$R_{int} = 0.0870$, $R_{sigma} = 0.1042$]
Data/restraints/parameters	3227/2/263
Goodness-of-fit on F^2	0.999
Final R indexes [I>=2σ (I)]	$R_1 = 0.0574$, $wR_2 = 0.1298$
Final R indexes [all data]	$R_1 = 0.1197$, $wR_2 = 0.1587$
Largest diff. peak/hole / e $Å^{-3}$	0.40/-0.41

Table S4 Hydrogen Bonds for 5•3H_2O.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1A	O1[4]	0.88	2.06	2.8717(3)	152
N1	H1B	N2	0.88	2.53	2.8203(3)	100
N1	H1B	N8	0.88	2.18	3.0572(4)	171
N2	H2A	O1	0.87	2.15	2.9794(4)	161
N2	H2B	O5	0.87	2.40	2.7956(3)	108
N4	H4	O7[3]	0.88	1.76	2.5996(3)	159
O5	H5A	O4[1]	0.85	1.96	2.7789(3)	162
O5	H5B	O1	0.85	2.54	3.0695(4)	121
O5	H5B	O3	0.85	1.98	2.8233(3)	176
N6	H6	O2[3]	0.88	1.92	2.7846(3)	167
O6	H6A	O2[2]	0.85	1.98	2.8091(3)	166
O6	H6B	O3	0.85	2.07	2.8884(4)	161
O6	H7A	O3	0.85	1.89	2.7361(3)	172
O6	H7A	O3	0.84	1.86	2.7018(3)	177
O7	H5B	O3	0.85	1.89	2.7360(4)	172
O7	H7B	O4[5]	0.84	1.86	2,7020(5)	177
N9	H9	O5[5]	0.88	1.85	2.7238(3)	171
N10	H10A	O2	0.87	2.43	3.1228(4)	137

N10 H10B O6	0.87	2.12	2.9408(4)	157
N11 H11A O6[2]	0.88	2.01	2.8384(3)	156
N11 H11B O4[2]	0.88	2.06	2.8178(3)	144

[1]-1+X,+Y,+Z; [2]1-X,-1/2+Y,1/2-Z; [3]1-X,1-Y,1-Z; [4]1-X,2-Y,1-Z; [5]+X,-1+Y,+Z

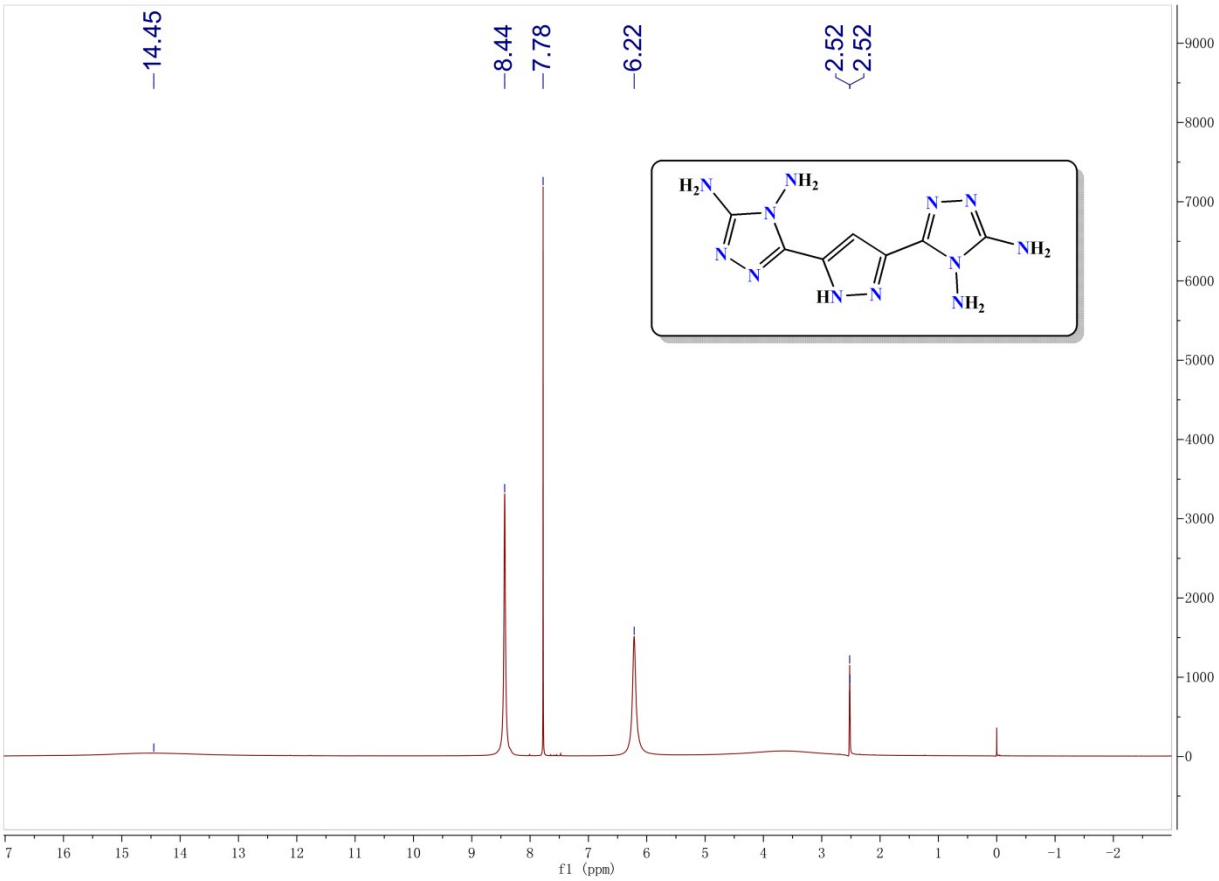


Figure S1. [1]H NMR of energetic material **3**

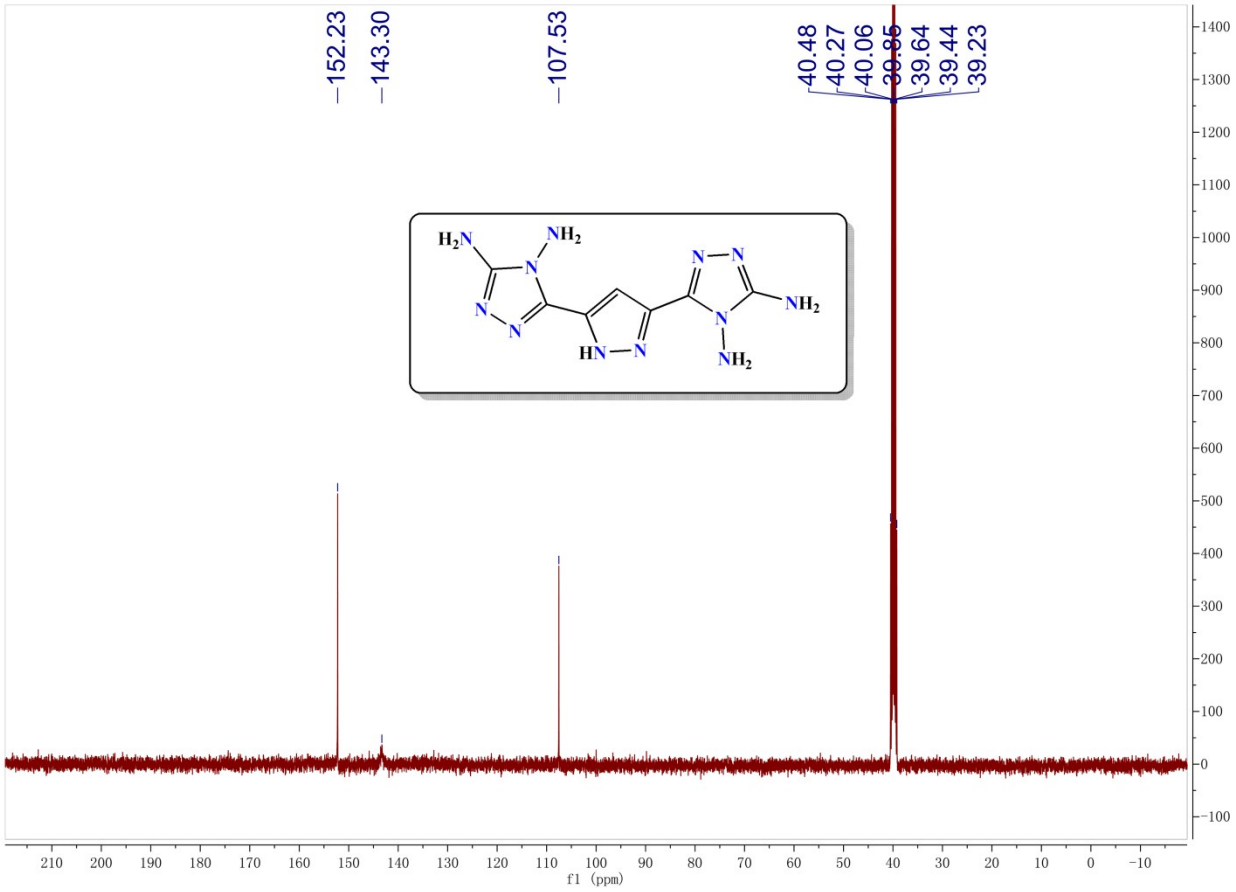


Figure S2. ^{13}C NMR of energetic material **3**

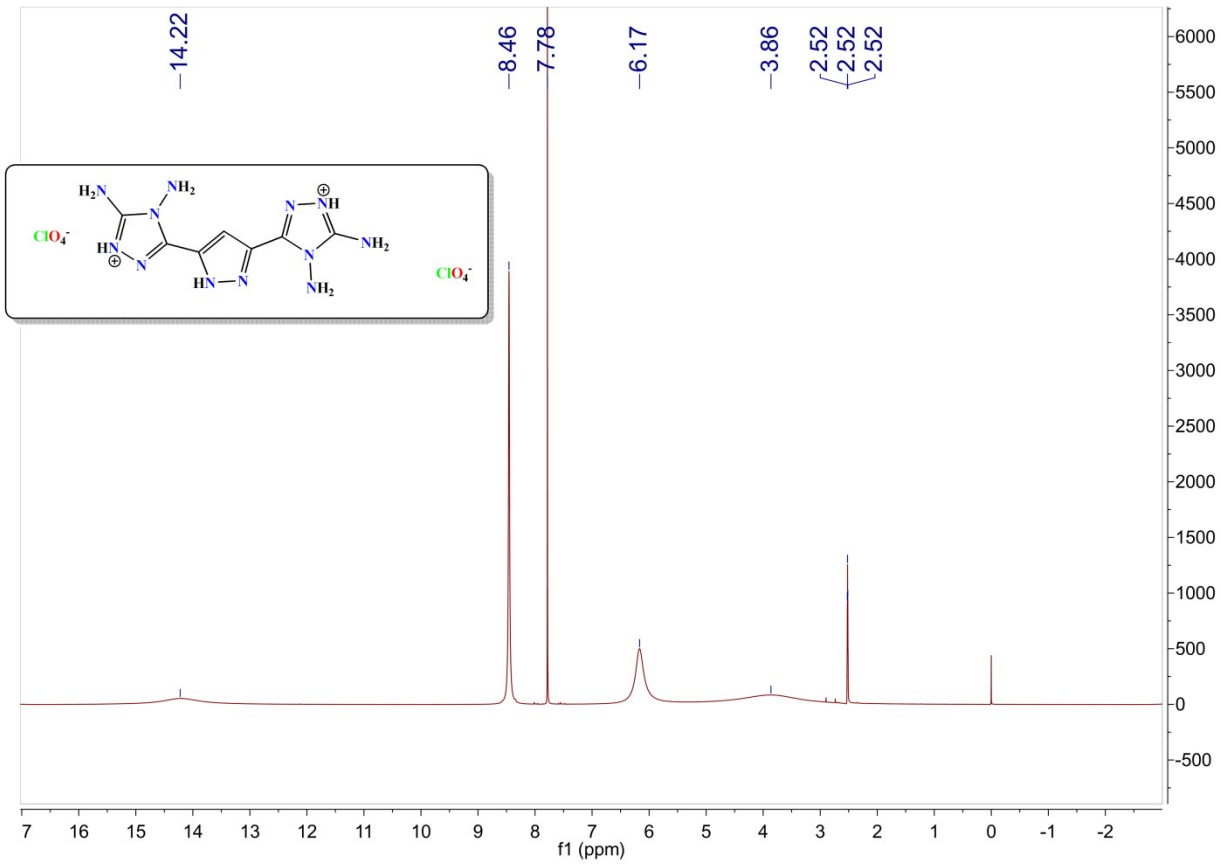


Figure S3. ^{1}H NMR of energetic material **4**

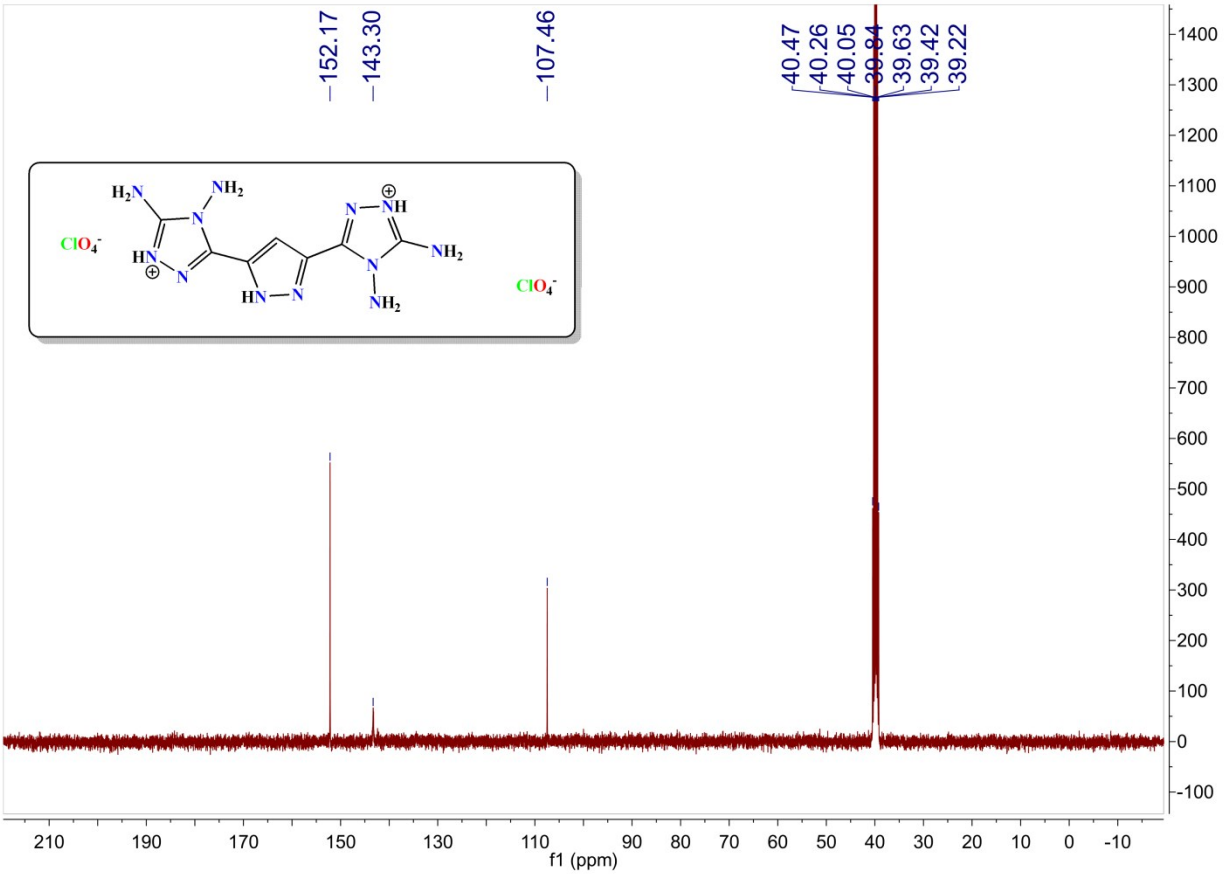


Figure S4. ^{13}C NMR of energetic material **4**

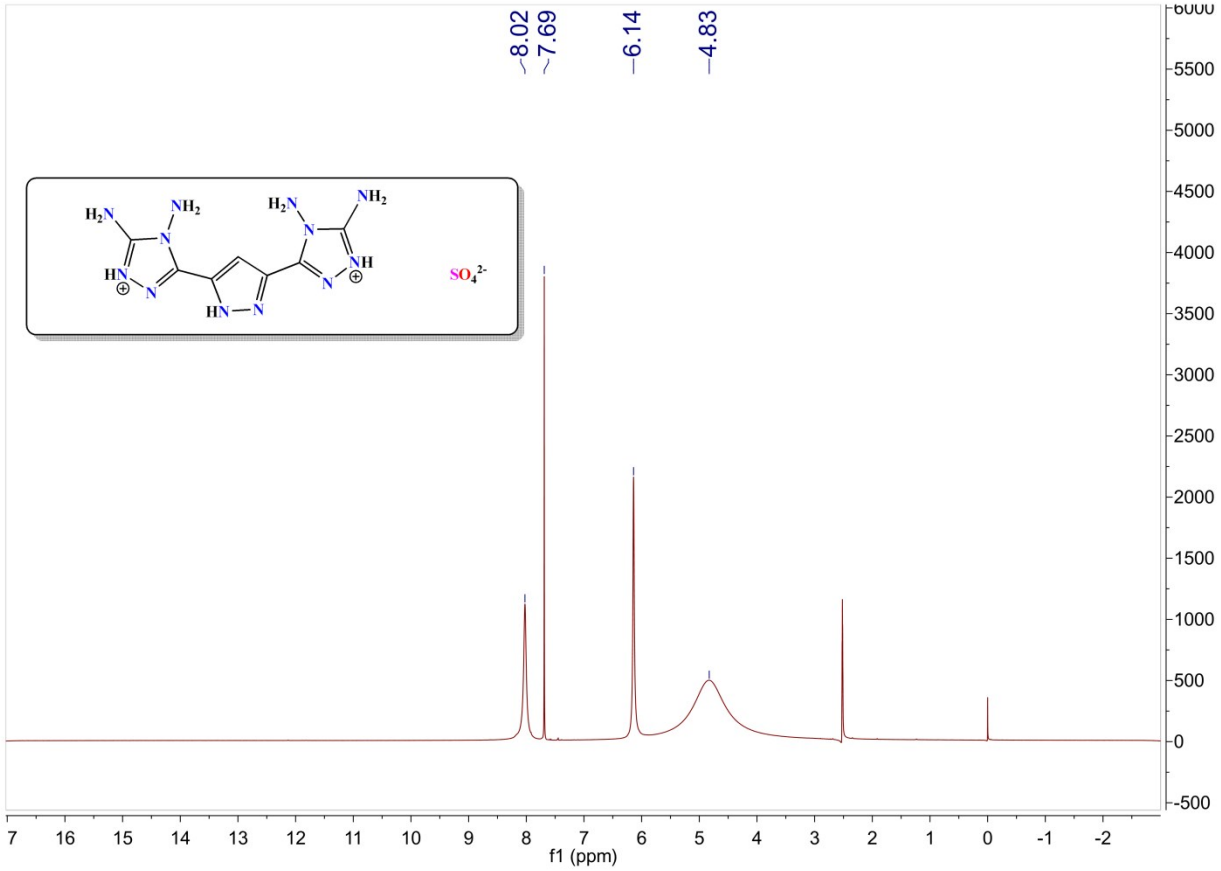


Figure S5. ^{1}H NMR of energetic material **5**

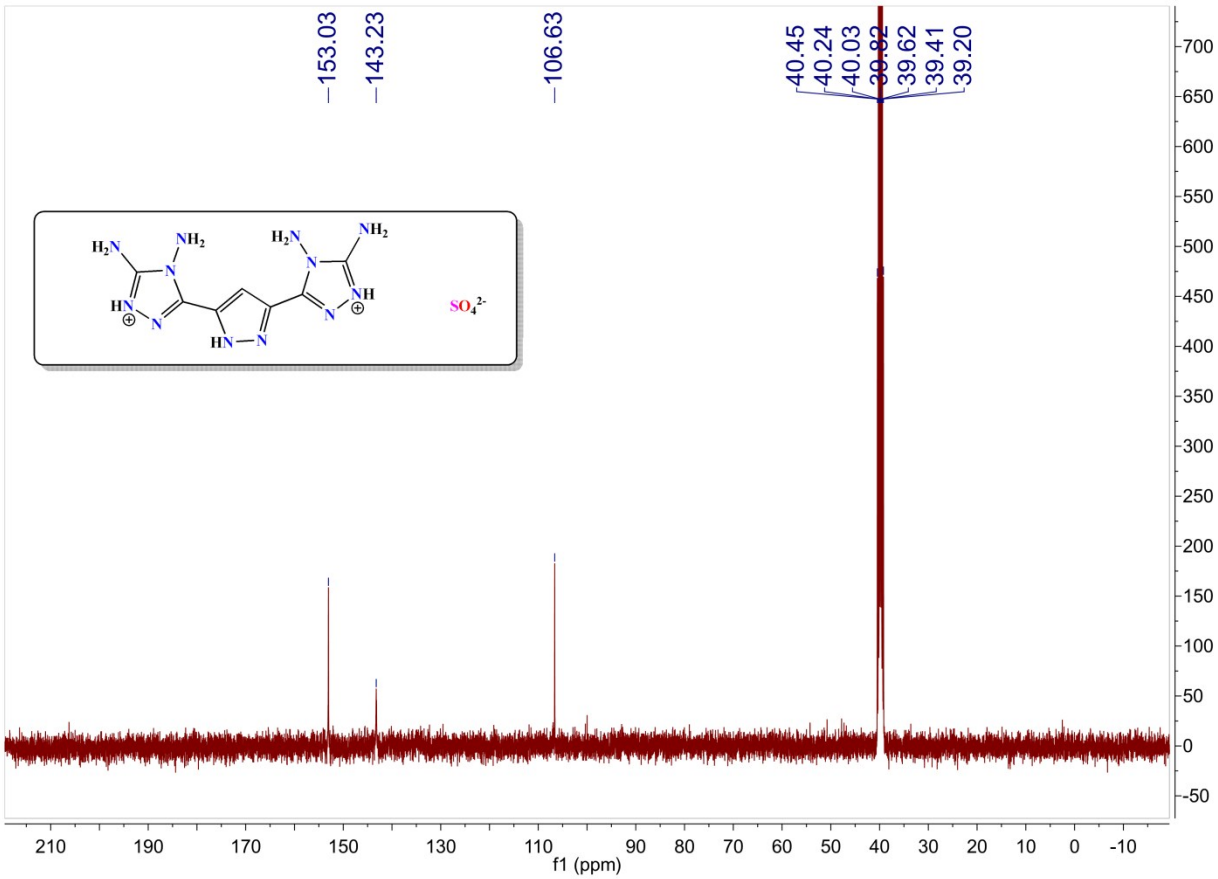


Figure S6. ^{13}C NMR of energetic material **5**

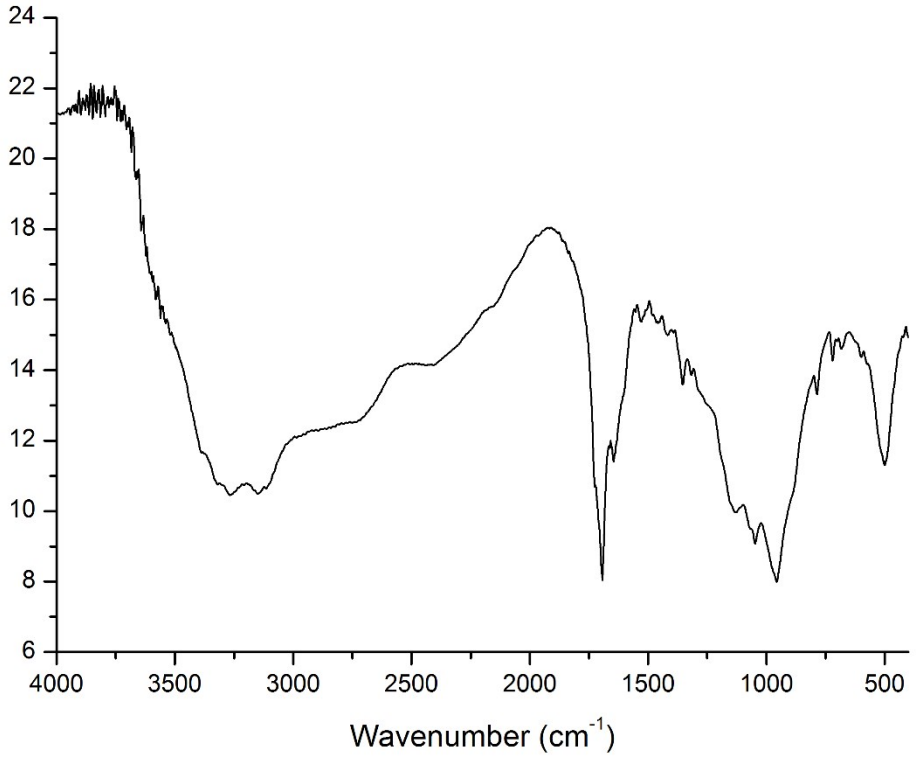


Figure S7. IR spectra of energetic material **3**

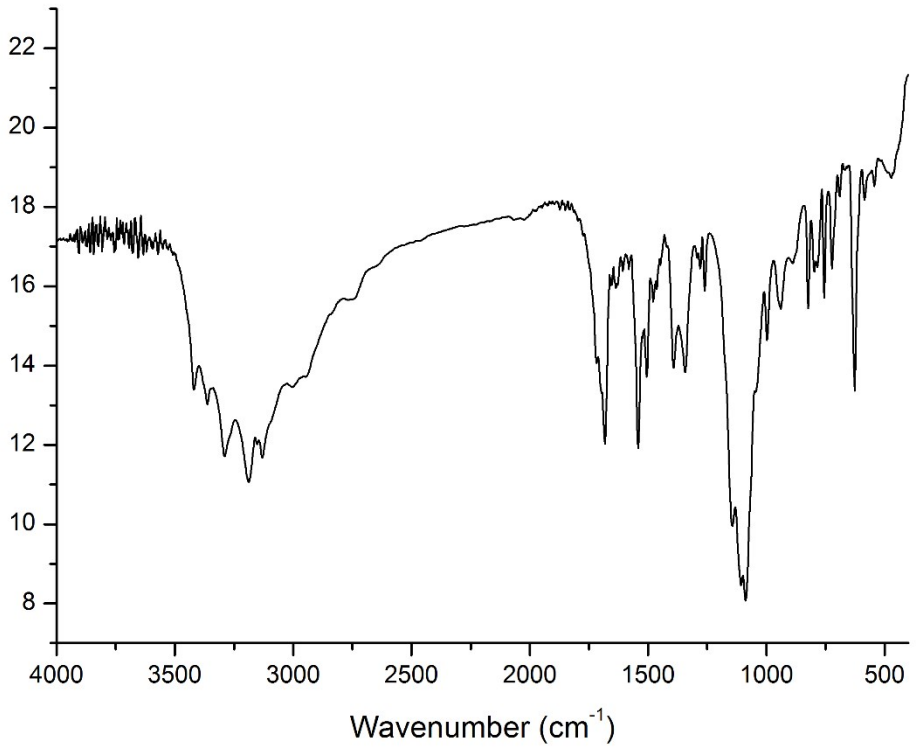


Figure S8. IR spectra of energetic material **4**

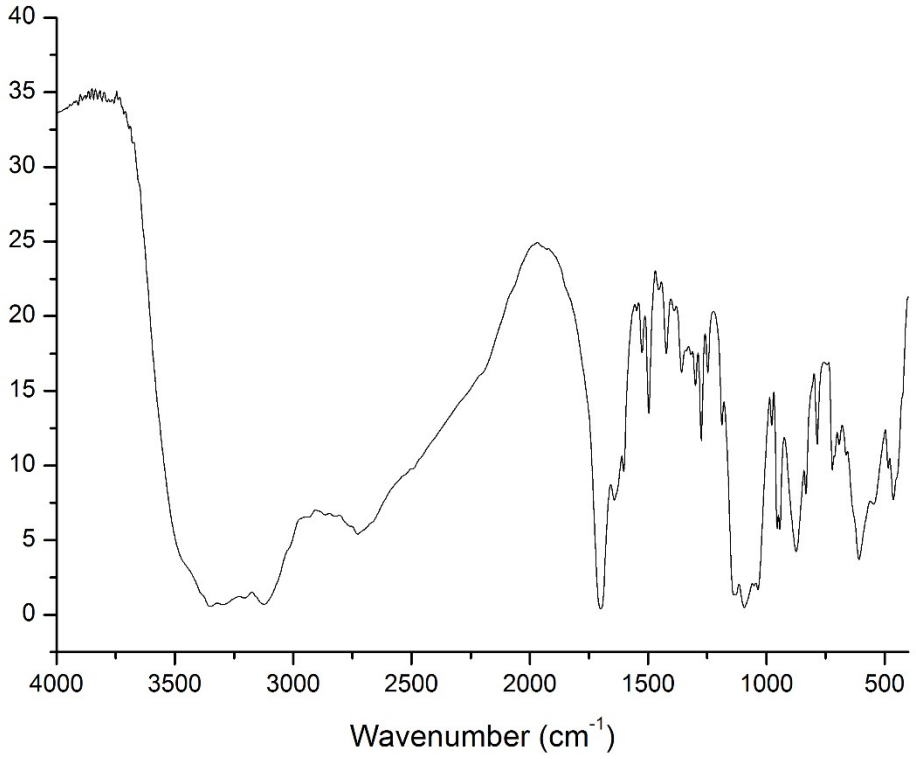


Figure S9. IR spectra of energetic material **5**