Electronic Supplementary Information for

Potassium Trinitromethyl Tetrazole (TNMT-K): A New Member of the Primary Explosive Family

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Table S1. Computed Zero-Point Energies (ZPE), Thermal Correction (H_T), Total Energies (E_0), and enthalpy of formation of compound **5.**

Compound	E_0 (a.u)	ZPE (a.u)	H_T (a.u)	$\Delta H_f°$ (g) kJ/mol	ΔH_L kJ/mol	$\Delta H_f°$ (s) kJ/mol
TNMT-K				644.80[a]	497.98[b]	146.82
TNMT-A	-908.641357	0.067357	0.013309	143.71[a]	----	----
MT-A	-296.8592355	0.074564	0.006140	142.81[c]	----	----
CH_4	-40.3796224	0.044793	0.003812	-74.60[c]	----	----
CH_3NO_2	-244.4784821	0.049840	0.005298	-74.30[c]	----	----

[a]Calculated using isodesmic equation as shown in Fig. S1 and Scheme S1. [c]Calculated using equation S2. [c]Obtained at G2 level.

The gas-phase enthalpy of formation $\Delta_fH°(g)$ was predicted using Gaussian 03 program[1] according to isodesmic equation as shown in Figure S1.

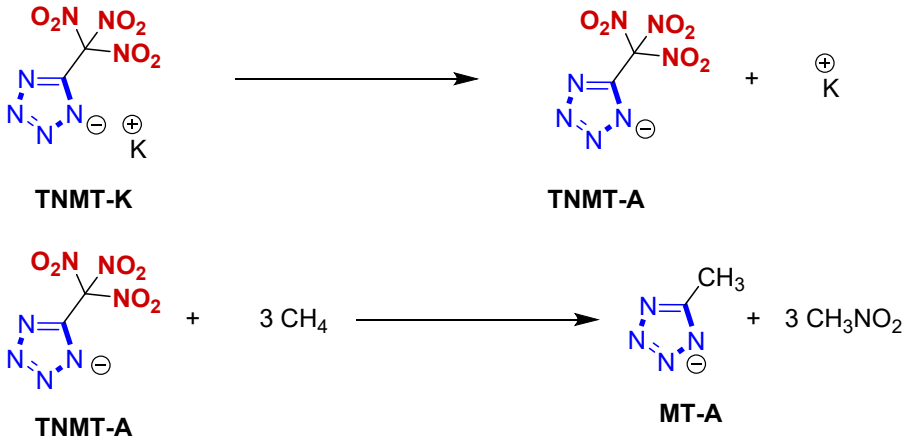
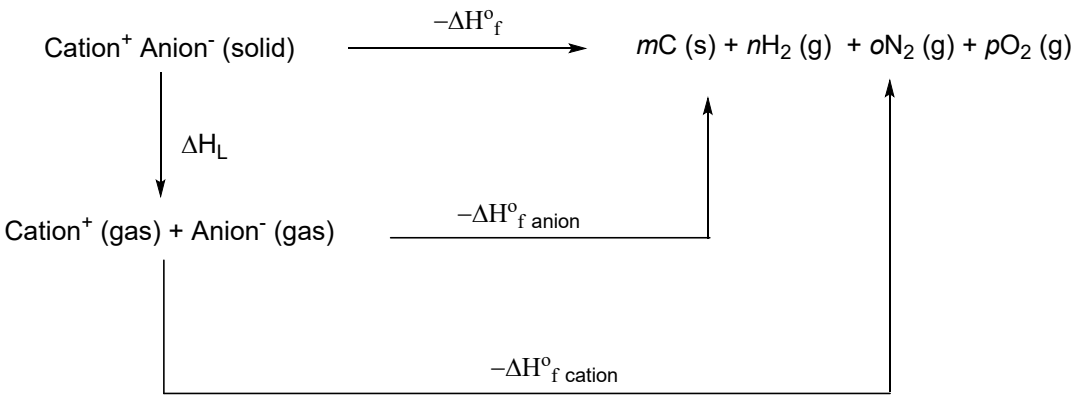


Fig. S1: Isodesmic reaction for TNMT-K.

Then, the solid- phase heat of formation was obtained using a Born-Haber energy cycle.[2-4]



Scheme S1. Born–Haber cycle for the formation of salts.

$\Delta H_f°$ (ionic salt, 298 K) = $\Delta H_f°$ (cation, 298 K) +$\Delta H_f°$ (anion, 298 K) – ΔH_L ...(S1)

$\Delta H_L = U_{POT} + [\rho(nM/2 - 2) + q(nX/2 - 2)]RT$ ...(S2)

$U_{POT} = \gamma(\rho m/Mm) + \delta$ ...(S3)

Where, (U_{POT}), is lattice potential energies, (ΔH_L) is lattice enthalpies, ρ is the density (g/cm^3), nM and nX depend on the nature of the ions Mp+ and Xq–, respectively, and for monoatomic ions are equal to three. Mm is the chemical formula mass of the ionic material (g), and the coefficients γ (in kJmol^{-1}cm) and δ (in kJmol^{-1}) are given in the literature.[2-4] The detonation and propulsive properties were calculated by using the EXPLO5 7.01 program.[5]

EXPERIMENTAL SECTION

General Methods

All reagents and solvents were used as received unless otherwise specified (AKSci, Sigma-Aldrich, Acros Organics, VWR). The densities of the new compounds were obtained at 25 °C with a Micromeritics Accupyc II 1340 gas pycnometer. The thermal stability (melting and decomposition points) was measured by heating individual samples from 30 °C to 400 °C at two heating rates of 5 °C min^{-1} and 10 °C min^{-1} on a Differential Scanning Calorimeter (DSC, TA Instruments Company, Model: Q2000). The FTIR spectra were recorded with KBr plates on a Thermo Nicolet AVATAR 370 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz (Bruker) nuclear magnetic resonance spectrometer operating at 500.19 and 125.77 MHz, respectively, using DMSO-d_6 as the solvent and tetramethylsilane as the external standard locking solvent. Elemental analyses (C, H, N) were performed using a Vario Micro Cube Elemental Analyser. The friction sensitivities (FS) and impact sensitivities (IS) were measured with a standard BAM friction tester and BAM drop hammer. Crystals of TNMT-K were mounted on a nylon loop with Paratone oil on an XtaLAB Synergy, Dualflex, HyPix diffractometer at 100 K. The structures were solved with the ShelXT solution program using dual methods and Olex2.[6] The model was refined with ShelXL using full matrix least squares minimization on F2.[7-9]

Caution!

The compound studied in the present work is potentially a high-energy material. It is strongly recommended that it be synthesized and handled with extreme care, following all standard safety precautions. Compounds **1** and **2** were prepared according to the reported procedure.[10-11].

*[1]H-Tetrazole-5-acetic acid (**1, TAA**).* A mixture of cyanoacetic acid (10.0 g, 117.56 mmol), sodium azide (11.462 g, 176.34 mmol), and $ZnCl_2$ (16.023 g, 117.56 mmol) in isopropanol (150 mL) and water (150 mL) was heated at 90°C for 24 h. After 24 hours, a white precipitate formed in the reaction mixture. Then, it was cooled, and 10% HCl was added drop-wise until the reaction mixture became a clear solution. Subsequently, the reaction mixture was diluted with ethyl acetate (200 mL) and extracted with excess ethyl acetate (4 × 100 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. The crude residue was purified by triturating with chloroform and ethyl acetate to afford pure 2-(2*H*-tetrazol-5-yl)-acetic acid (TAA, **1**). Crystalline, colorless solid; Yield: 10.80 g, 72%, DSC (5 °C min^{-1}): T_m (onset) = 172.97 °C (melting). IR (KBr pellet) ṽ 3013 (m), 2970 (m), 2936 (m), 2705 (m), 2598 (m), 1732 (s), 1560 (m), 1548 (m), 1440 (m), 1423 (m), 1379 (m), 1350 (w), 1311 (m), 1260 (m), 1193 (s), 1097 (m), 1059 (s), 1013 (m), 945 (s), 854 (s), 782 (m), 659 (s) cm^{-1}; ^{1}H NMR (14.99 MHz, DMSO-d_6): δ 4.08 (s, 2H); ^{13}C NMR (60.0 MHz, DMSO-d_6): δ 169.58, 151.07, 30.05.

*5-(Trinitromethyl)-2H-tetrazole (**2, TNMT**).* Compound **1** (5.0 g, 39.04 mmol) was slowly added to a cooled and well-stirred mixture of 98% sulfuric acid (35 mL) and freshly distilled 100% nitric acid (30 mL) at 0 °C. The temperature was slowly elevated to room temperature, and the mixture was then stirred at room temperature for 24 h. Then, the resulting light-yellow solution was carefully poured onto crushed ice (200 g), and the resulting mixture was extracted with dichloromethane (5 × 200 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and the solvent was removed under vacuum at ambient temperature (**caution**: TNMT should be handled with extreme care because it has a low decomposition temperature). Initially, a yellow oil was obtained that solidified with petroleum ether, and 5-(trinitromethyl)-2*H*-tetrazole (**2, TNMT**) was obtained as a pale-yellow solid. Crystalline, pale-yellow solid; Yield: 5.818 g, 68%, DSC (5 °C min^{-1}): T_d (onset) = 88.43°C (decomposition). IR (KBr pellet) ṽ 3037 (m), 2921 (m), 2875 (m), 1599 (s), 1488 (m), 1453 (m), 1435 (m), 1330 (m), 1309 (m), 1276 (s), 1253 (m), 1236 (s), 1188 (s), 1131 (m), 1101 (m), 1041 (m), 1031 (m), 983 (m), 862 (m), 840 (m), 794 (s), 741 (s), 696 (m), 679 (m), 636 (m), 619 (m) cm^{-1}; ^{1}H NMR (60.0 MHz, Acetone-d_6): δ 11.29 (s, 1H); ^{13}C NMR (15.01 MHz, DMSO-d_6): δ 152.47, 121.87.

*Potassium-5-(trinitromethyl)tetrazol-1-ide (**TNMT-K**).* Compound **2** (2.190 g, 10.0 mmol) was dissolved in methanol (20 mL) at 0°C, and then KI (1.910 g, 11.5 mmol, 1.15 equiv.) was added portionwise with extra care and the resulting mixture was stirred for 10 h at room temperature. Then, the reaction mixture was filtered off. The white solid residue was further triturated with n-hexane and dried to give pure TNMT-K in quantitative yield. Crystalline, yellow solid; Yield:

2.54 g, 99%, DSC (5 °C min^{-1}): T_d (onset) = 118 °C (decomposition). IR (KBr pellet) ṽ 1621 (m), 1601 (s), 1580 (s), 1524 (m), 1438 (m), 1366 (m), 1284 (m), 1219 (s), 1185 (s), 1155 (s), 1107 (s), 1033 (s), 1017 (m), 989 (m), 846 (s), 825 (m), 802 (s), 748 (m), 737 (m), 681 (m), 636 (m), 615 (s) cm^{-1}; ^{1}H NMR (60.0 MHz, DMSO-d_6): δ no peaks; ^{13}C NMR (15.01 MHz, DMSO-d_6): δ 150.04, 102.50; Elemental analysis: calcd (%) for $C_2KN_7O_6$ (257.16): C, 9.34, H, 0.00, N, 38.13. Found C, 9.43; H, 0.146; N, 37.92.

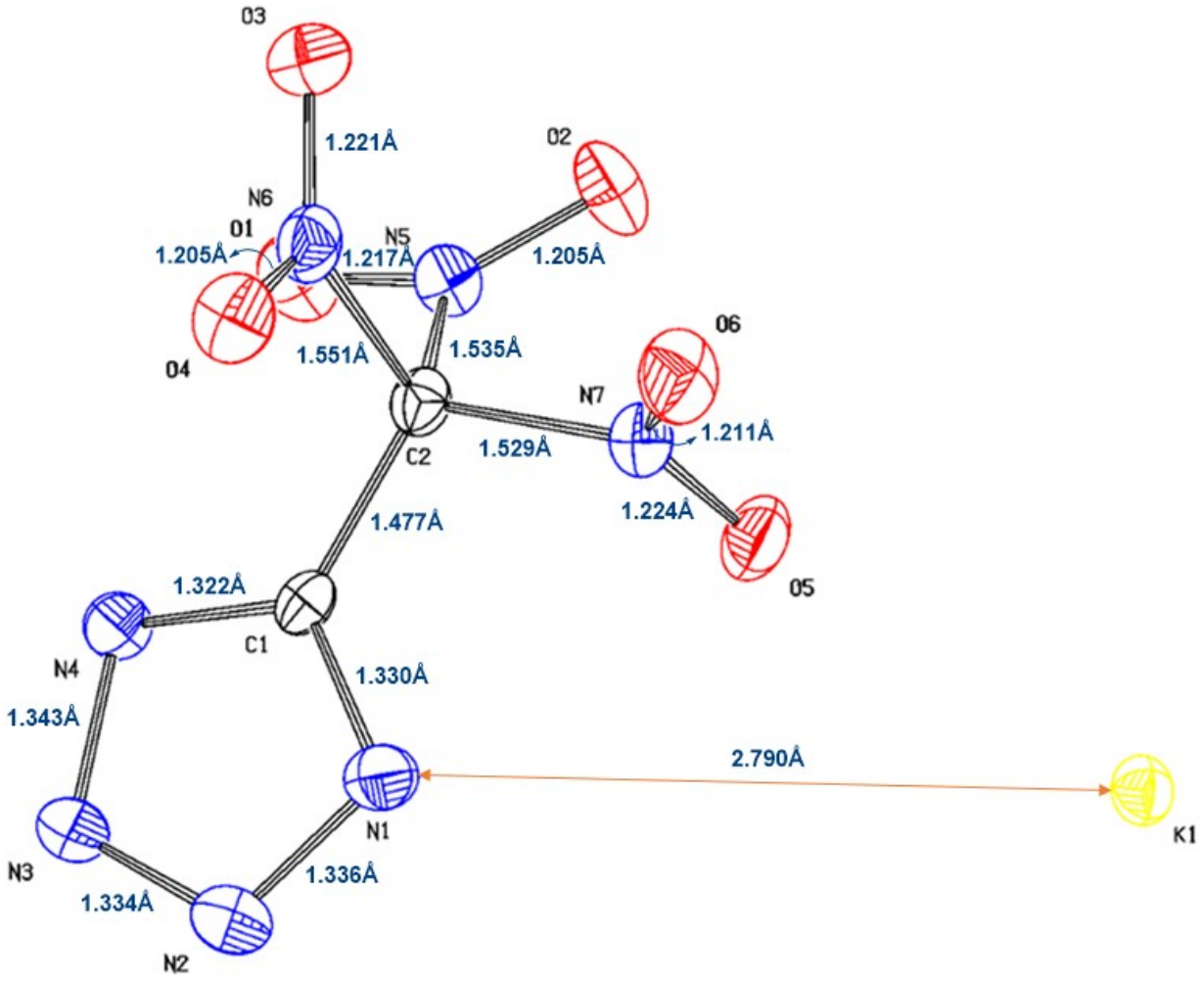
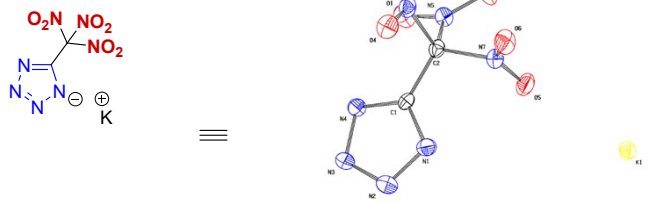


Fig. S2. Molecular unit of TNMT-K (thermal ellipsoid at 50%) (CCDC = 2313279).

Table S2. Single crystal X-ray data and structure refinement for TNMT-K.



TNMT-K CCDC No 2313279

Compound	TNMT-K
Formula	$C_2KN_7O_6$
$D_{calc.}$/ g cm^{-3}	1.981
m/mm^{-1}	5.850
Formula Weight	257.19
Colour	yellow
Shape	block-shaped
Size/mm^3	0.07×0.05×0.01
T/K	100.00(10)
Crystal System	orthorhombic
Flack Parameter	-0.011(16)
Hooft Parameter	-0.008(16)
Space Group	$P2_12_12_1$
a/Å	8.6205(5)
b/Å	9.5989(7)
c/Å	10.4231(6)
α/°	90
β°	90
γ/°	90
V/Å^3	862.48(9)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K$_a$
Q_{min}/°	6.268
Q_{max}/°	77.961
Measured Refl's.	3224
Indep't Refl's	1607
Refl's I≥2 s(I)	1400
R_{int}	0.0512
Parameters	145
Restraints	0
Largest Peak	0.392
Deepest Hole	-0.483
GooF	1.083
wR_2 (all data)	0.0991
wR_2	0.0956
R_1 (all data)	0.0516
R_1	0.0414

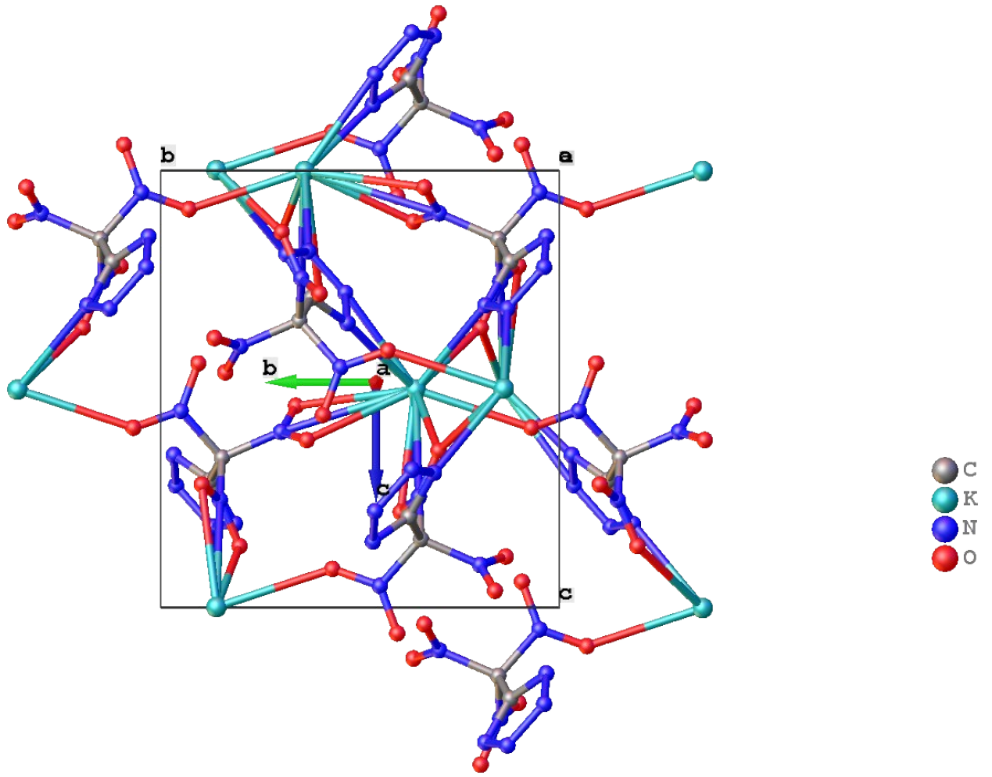


Fig. 3. Packing diagram of TNMT-K viewed along the **a** axis

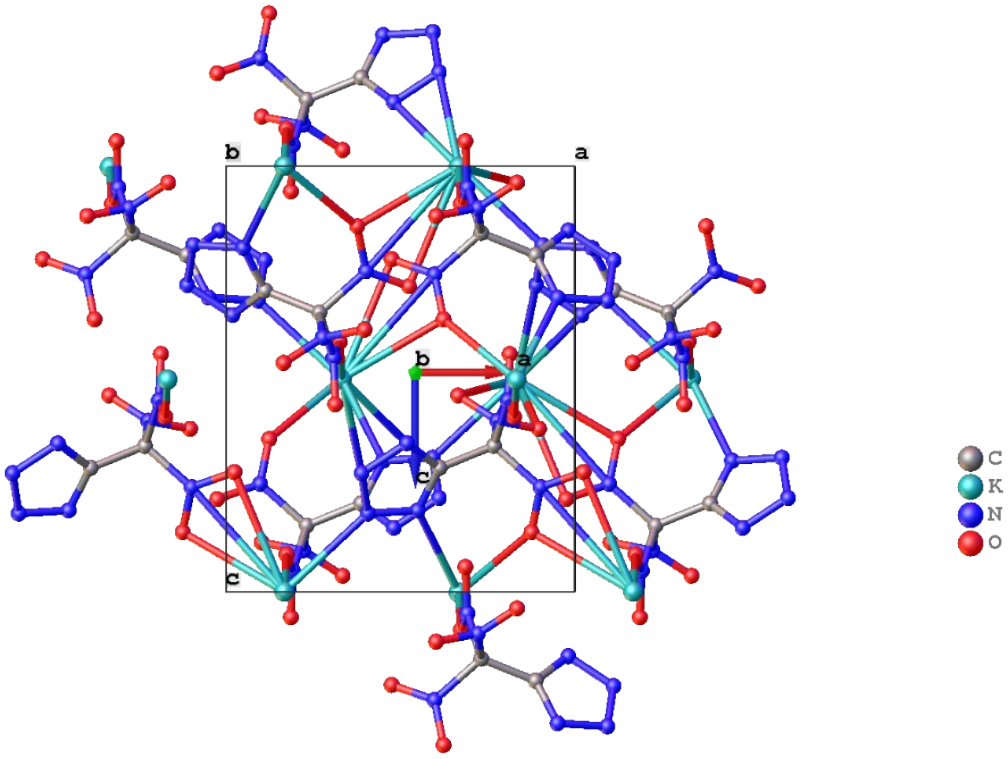


Fig. 4. Packing diagram of TNMT-K viewed along the **b** axis

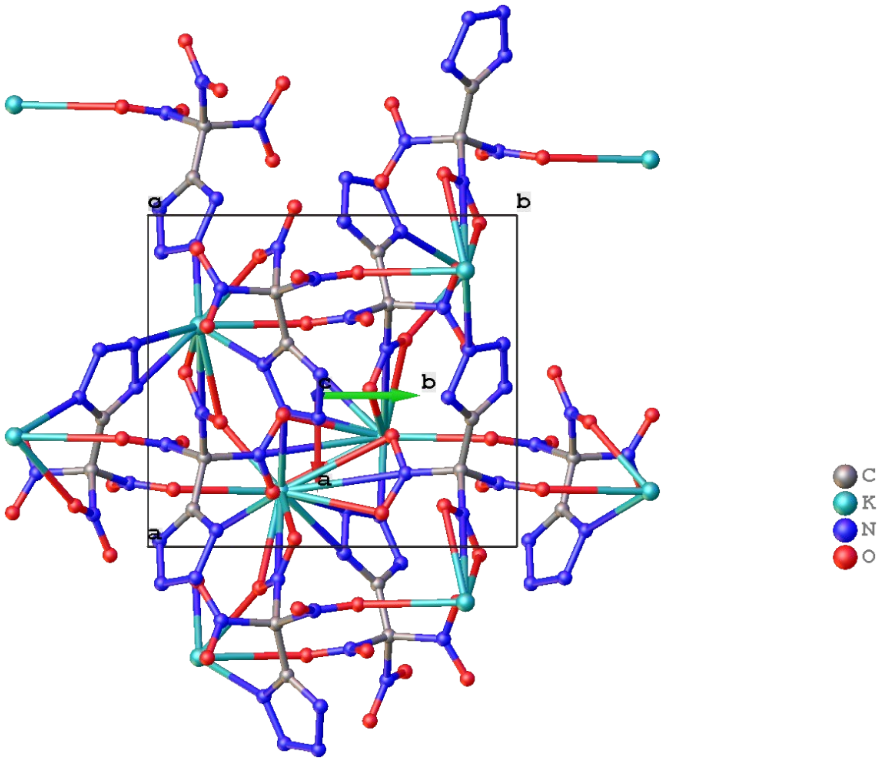


Fig. 5. Packing diagram of TNMT-K viewed along the **c** axis

Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for TNMT-K.

Atom	x	y	z	U_{eq}
K1	3327.4(11)	1392.6(10)	4988.1(12)	19.0(3)
O1	3762(4)	6970(5)	1407(4)	27.6(9)
O2	5247(4)	6019(5)	2817(4)	30.2(10)
O3	3975(4)	8659(4)	3834(4)	28.3(9)
O4	1655(5)	8387(4)	4617(4)	27.0(9)
O5	3265(5)	4302(4)	4117(4)	28.3(9)
O6	3135(5)	5933(4)	5590(4)	31.2(10)
N1	188(5)	5319(5)	3492(5)	23.3(10)
N2	-1109(5)	5376(5)	2792(5)	26.6(11)
N3	-932(5)	6296(5)	1844(4)	22.8(10)
N4	493(5)	6855(5)	1916(4)	18.7(10)
N5	4018(5)	6477(5)	2462(4)	22.1(9)
N6	2778(5)	8011(5)	4020(5)	22.2(10)
N7	3080(5)	5495(5)	4502(5)	22.3(10)
C1	1124(6)	6226(6)	2916(5)	16.4(10)
C2	2683(6)	6529(5)	3434(5)	17.4(11)

Table S4. Anisotropic Displacement Parameters (×10^4) for TNMT-K.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K1	20.7(4)	17.1(5)	19.0(4)	-1.6(6)	-3.4(6)	2.4(4)
O1	21.5(19)	40(2)	21(2)	5.9(18)	3.5(15)	1.7(17)
O2	20.4(18)	42(3)	28(2)	3(2)	-4.5(16)	8.8(18)
O3	28.0(18)	24.9(19)	32(2)	1(2)	-1.5(18)	-5.0(19)
O4	31.0(18)	25(2)	25(2)	-5.2(15)	6.1(17)	5.4(18)
O5	36(2)	17.3(18)	32(2)	3.0(17)	-4(2)	2.2(18)
O6	43(2)	33(2)	17(2)	1.6(19)	-9(2)	1(2)
N1	23(2)	23(2)	24(2)	3(2)	-2.6(19)	-5(2)
N2	18.7(19)	29(3)	32(3)	1(2)	-1(2)	-3(2)
N3	19.9(19)	23(2)	25(2)	0(2)	-5.4(19)	-3(2)
N4	18.3(19)	23(2)	15(2)	3.9(19)	2.2(17)	-1.7(18)
N5	20.4(18)	22(2)	24(2)	1(2)	-2.8(18)	1(2)
N6	27(2)	21(2)	19(2)	4(2)	-3(2)	1(2)
N7	23(2)	21(2)	23(2)	4(2)	-3.2(19)	1(2)
C1	20(2)	14(2)	15(2)	3(2)	1.9(19)	-1(2)
C2	22(2)	15(3)	15(3)	0(2)	-1.9(19)	1(2)

Table S5. Bond Lengths in Å for TNMT-K.

Atom	Atom	Length/Å
K1	O1[1]	2.811(4)
K1	O1[2]	2.953(4)
K1	O2[2]	3.192(4)
K1	O3[3]	2.940(4)
K1	O4[3]	3.248(4)
K1	O5	2.937(4)
K1	N1[4]	2.790(5)
K1	N2[4]	2.911(5)
K1	N3[5]	2.814(4)
K1	N4[1]	2.811(4)
K1	N5[2]	3.430(5)
K1	N6[3]	3.432(5)
O1	N5	1.217(6)
O2	N5	1.205(6)
O3	N6	1.221(6)
O4	N6	1.205(6)
O5	N7	1.224(6)
O6	N7	1.211(6)
N1	N2	1.336(6)
N1	C1	1.330(7)
N2	N3	1.334(7)
N3	N4	1.343(6)
N4	C1	1.322(7)
N5	C2	1.535(7)
N6	C2	1.551(7)
N7	C2	1.529(7)
C1	C2	1.477(7)

[1]1/2-x,1-y,1/2+z; [2]1-x,-1/2+y,1/2-z; [3]+x,-1+y,+z; [4]1/2+x,1/2-y,1-z; [5]-x,-1/2+y,1/2-z

Table S6. Torsion Angles in ° for TNMT-K.

Atom	Atom	Atom	Atom	Angle/°
K1[1]	O1	N5	K1[2]	-170.7(6)
K1[1]	O1	N5	O2	-163.9(4)
K1[2]	O1	N5	O2	6.9(6)
K1[1]	O1	N5	C2	12.4(8)
K1[2]	O1	N5	C2	-176.9(4)
K1[2]	O2	N5	O1	-6.2(6)
K1[2]	O2	N5	C2	177.6(4)
K1[3]	O3	N6	O4	-4.7(6)
K1[3]	O3	N6	C2	175.8(3)
K1[3]	O4	N6	O3	4.2(5)
K1[3]	O4	N6	C2	-176.3(4)
K1	O5	N7	O6	17.0(10)
K1	O5	N7	C2	-161.1(4)
K1[4]	N1	N2	N3	173.5(4)
K1[5]	N3	N4	K1[1]	1.6(6)
K1[5]	N3	N4	C1	-169.9(4)
K1[1]	N4	C1	N1	-170.8(4)
K1[1]	N4	C1	C2	12.8(8)
O1	N5	C2	N6	-83.2(5)
O1	N5	C2	N7	163.3(4)
O1	N5	C2	C1	40.3(7)
O2	N5	C2	N6	93.4(5)
O2	N5	C2	N7	-20.2(6)
O2	N5	C2	C1	-143.1(5)
O3	N6	C2	N5	-15.0(6)
O3	N6	C2	N7	98.3(5)
O3	N6	C2	C1	-141.0(5)
O4	N6	C2	N5	165.5(4)
O4	N6	C2	N7	-81.2(5)
O4	N6	C2	C1	39.5(6)
O5	N7	C2	N5	-58.4(5)
O5	N7	C2	N6	-170.0(4)
O5	N7	C2	C1	68.1(6)
O6	N7	C2	N5	123.3(5)
O6	N7	C2	N6	11.7(6)
O6	N7	C2	C1	-110.2(5)
N1	N2	N3	K1[5]	172.2(3)
N1	N2	N3	N4	-0.1(6)
N1	C1	C2	N5	131.1(5)
N1	C1	C2	N6	-109.3(6)
N1	C1	C2	N7	9.8(7)
N2	N1	C1	N4	0.7(6)
N2	N1	C1	C2	177.2(5)
N2	N3	N4	K1[1]	172.0(3)
N2	N3	N4	C1	0.5(6)
N3	N4	C1	N1	-0.7(6)
N3	N4	C1	C2	-177.1(5)
N4	C1	C2	N5	-52.8(7)
N4	C1	C2	N6	66.8(7)

Atom	Atom	Atom	Atom	Angle/°
N4	C1	C2	N7	-174.1(5)
C1	N1	N2	K1[4]	-173.8(4)
C1	N1	N2	N3	-0.4(6)

[1]1/2-x,1-y,-1/2+z; [2]1-x,1/2+y,1/2-z; [3]+x,1+y,+z; [4]-1/2+x,1/2-y,1-z; [5]-x,1/2+y,1/2-z

Table S7. Bond Angles in ° for TNMT-K.

Atom	Atom	Atom	Angle/°
O1[1]	K1	O1[2]	134.32(6)
O1[1]	K1	O2[2]	142.32(12)
O1[2]	K1	O2[2]	40.78(10)
O1[1]	K1	O3[3]	146.73(12)
O1[2]	K1	O4[3]	119.02(11)
O1[1]	K1	O4[3]	105.97(11)
O1[1]	K1	O5	67.61(12)
O1[1]	K1	N2[4]	90.85(13)
O1[1]	K1	N3[5]	84.57(12)
O1[2]	K1	N5[2]	20.27(10)
O1[1]	K1	N5[2]	143.70(12)
O1[1]	K1	N6[3]	126.52(12)
O1[2]	K1	N6[3]	98.63(12)
O2[2]	K1	O4[3]	87.82(10)
O2[2]	K1	N5[2]	20.57(10)
O2[2]	K1	N6[3]	71.20(11)
O3[3]	K1	O1[2]	78.72(11)
O3[3]	K1	O2[2]	56.75(12)
O3[3]	K1	O4[3]	40.79(10)
O3[3]	K1	N5[2]	65.78(11)
O3[3]	K1	N6[3]	20.26(10)
O4[3]	K1	N5[2]	103.21(11)
O4[3]	K1	N6[3]	20.55(9)
O5	K1	O1[2]	71.63(12)
O5	K1	O2[2]	80.26(12)
O5	K1	O3[3]	136.52(12)
O5	K1	O4[3]	143.10(11)
O5	K1	N5[2]	76.09(12)
O5	K1	N6[3]	143.70(12)
N1[4]	K1	O1[2]	84.35(12)
N1[4]	K1	O1[1]	113.50(13)
N1[4]	K1	O2[2]	103.46(13)
N1[4]	K1	O3[3]	66.28(13)
N1[4]	K1	O4[3]	78.44(12)
N1[4]	K1	O5	138.25(13)
N1[4]	K1	N2[4]	27.01(13)
N1[4]	K1	N3[5]	142.00(15)
N1[4]	K1	N4[1]	74.82(14)
N1[4]	K1	N5[2]	93.06(12)
N1[4]	K1	N6[3]	71.90(13)
N2[4]	K1	O1[2]	111.05(12)
N2[4]	K1	O2[2]	126.76(12)
N2[4]	K1	O3[3]	76.88(13)
N2[4]	K1	O4[3]	69.54(12)
N2[4]	K1	O5	143.46(14)
N2[4]	K1	N5[2]	119.63(12)
N2[4]	K1	N6[3]	72.84(13)

Atom	Atom	Atom	Angle/°
N3[5]	K1	O1[2]	107.18(13)
N3[5]	K1	O2[2]	69.94(12)
N3[5]	K1	O3[3]	80.35(13)
N3[5]	K1	O4[3]	64.19(13)
N3[5]	K1	O5	78.93(13)
N3[5]	K1	N2[4]	130.00(14)
N3[5]	K1	N5[2]	89.13(12)
N3[5]	K1	N6[3]	70.62(13)
N4[1]	K1	O1[2]	86.13(12)
N4[1]	K1	O1[1]	61.38(12)
N4[1]	K1	O2[2]	125.66(12)
N4[1]	K1	O3[3]	139.27(12)
N4[1]	K1	O4[3]	140.99(12)
N4[1]	K1	O5	70.04(13)
N4[1]	K1	N2[4]	73.76(14)
N4[1]	K1	N3[5]	140.38(14)
N4[1]	K1	N5[2]	106.07(12)
N4[1]	K1	N6[3]	145.69(13)
N5[2]	K1	N6[3]	84.01(12)
K1[6]	O1	K1[7]	112.97(13)
N5	O1	K1[7]	102.6(3)
N5	O1	K1[6]	144.0(3)
N5	O2	K1[7]	90.9(3)
N6	O3	K1[8]	103.2(3)
N6	O4	K1[8]	88.3(3)
N7	O5	K1	142.3(4)
N2	N1	K1[9]	81.5(3)
C1	N1	K1[9]	172.1(4)
C1	N1	N2	103.6(4)
N1	N2	K1[9]	71.5(3)
N3	N2	K1[9]	173.7(4)
N3	N2	N1	109.6(4)
N2	N3	K1[10]	116.1(3)
N2	N3	N4	109.1(4)
N4	N3	K1[10]	134.1(3)
N3	N4	K1[6]	122.0(3)
C1	N4	K1[6]	133.5(3)
C1	N4	N3	103.8(4)
O1	N5	K1[7]	57.2(3)
O1	N5	C2	116.6(4)
O2	N5	K1[7]	68.5(3)
O2	N5	O1	125.4(5)
O2	N5	C2	117.9(4)
C2	N5	K1[7]	173.2(3)
O3	N6	K1[8]	56.5(3)
O3	N6	C2	116.7(4)
O4	N6	K1[8]	71.1(3)
O4	N6	O3	127.5(5)
O4	N6	C2	115.8(4)

Atom	Atom	Atom	Angle/°
C2	N6	K1[8]	172.3(3)
O5	N7	C2	113.5(5)
O6	N7	O5	128.8(5)
O6	N7	C2	117.7(4)
N1	C1	C2	121.0(5)
N4	C1	N1	113.9(4)
N4	C1	C2	125.0(5)
N5	C2	N6	104.5(4)
N7	C2	N5	107.0(4)
N7	C2	N6	107.3(4)
C1	C2	N5	115.8(4)
C1	C2	N6	111.8(4)
C1	C2	N7	110.0(4)

[1]1/2-x,1-y,1/2+z; [2]1-x,-1/2+y,1/2-z; [3]+x,-1+y,+z; [4]1/2+x,1/2-y,1-z; [5]-x,-1/2+y,1/2-z; [6]1/2-x,1-y,-1/2+z; [7]1-x,1/2+y,1/2-z; [8]+x,1+y,+z; [9]-1/2+x,1/2-y,1-z; [10]-x,1/2+y,1/2-z

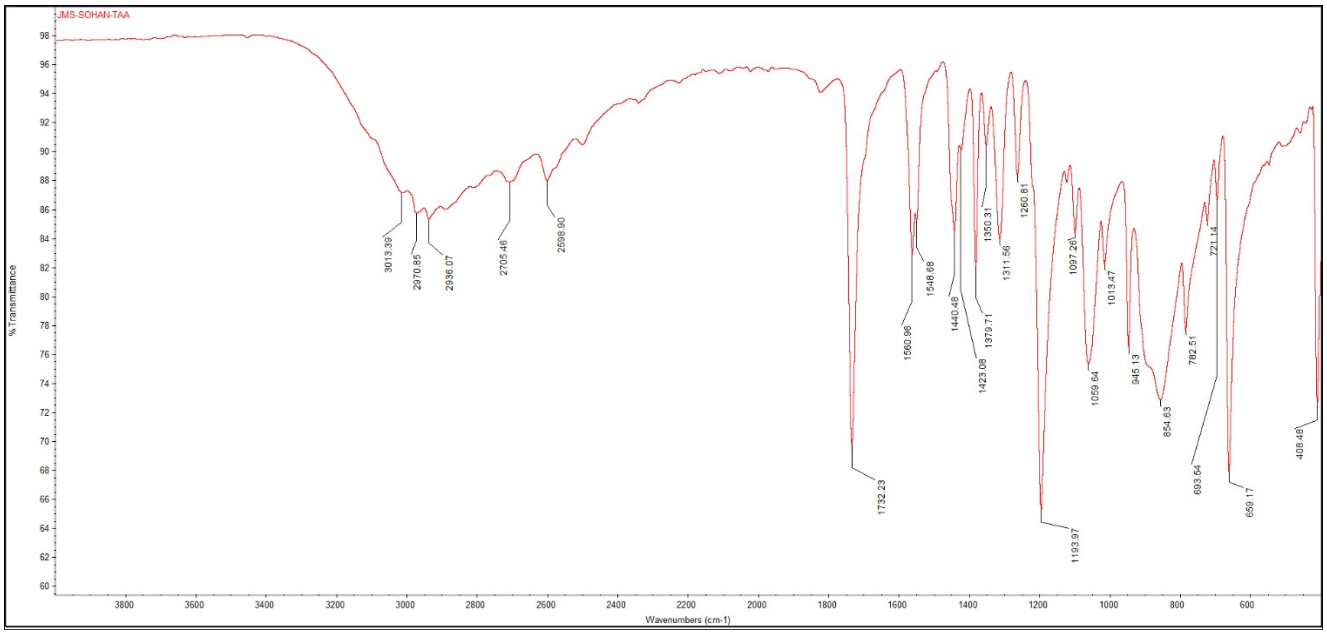


Fig. S6. FTIR-Spectrum of TAA (1)**.**

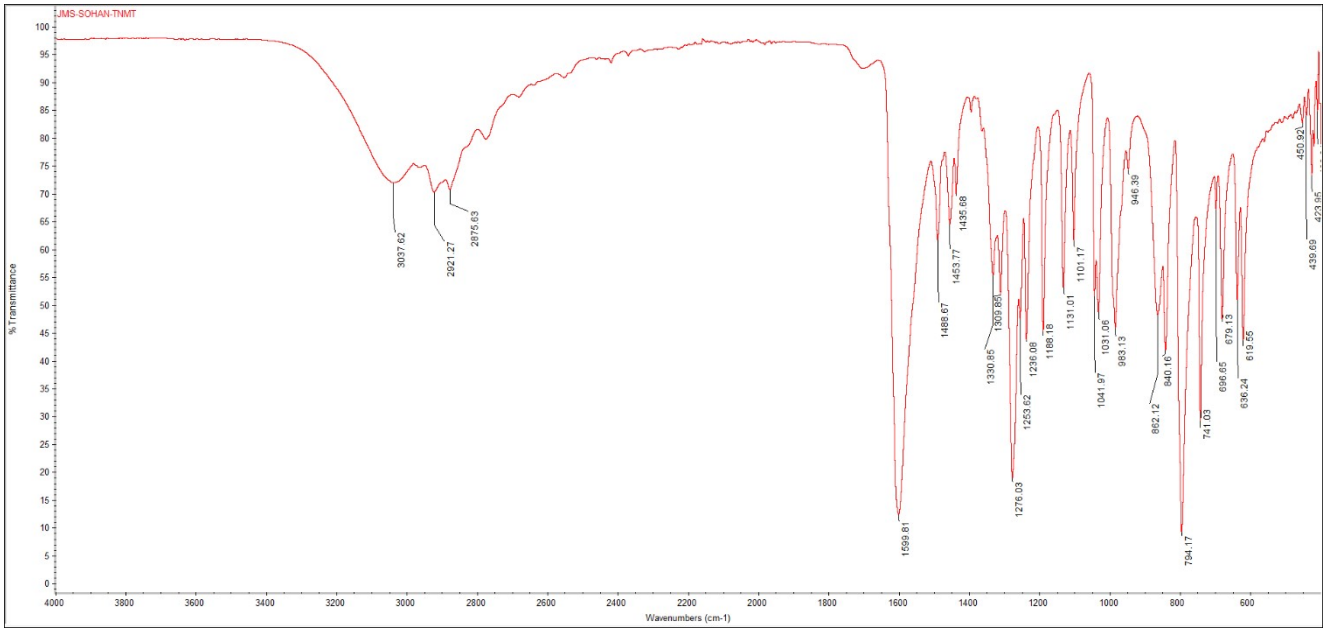


Fig. S7. FTIR-Spectrum of TNMT (2)**.**

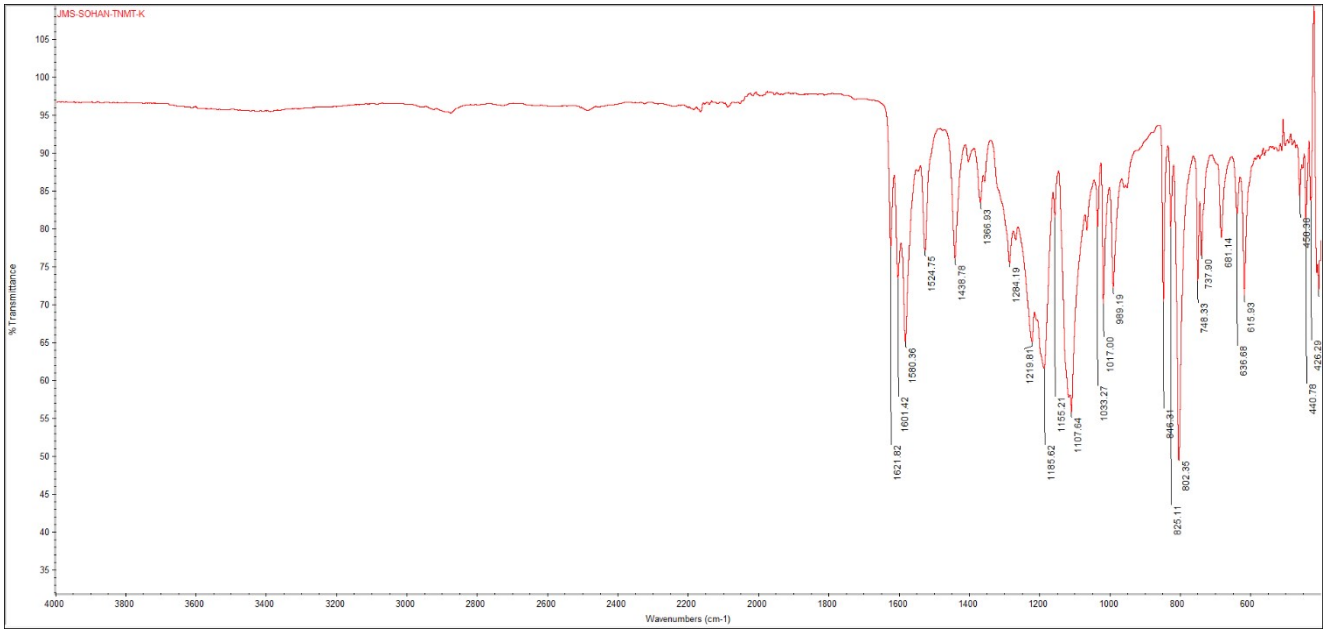


Fig. S8. FTIR-Spectrum of TNMT-K**.**

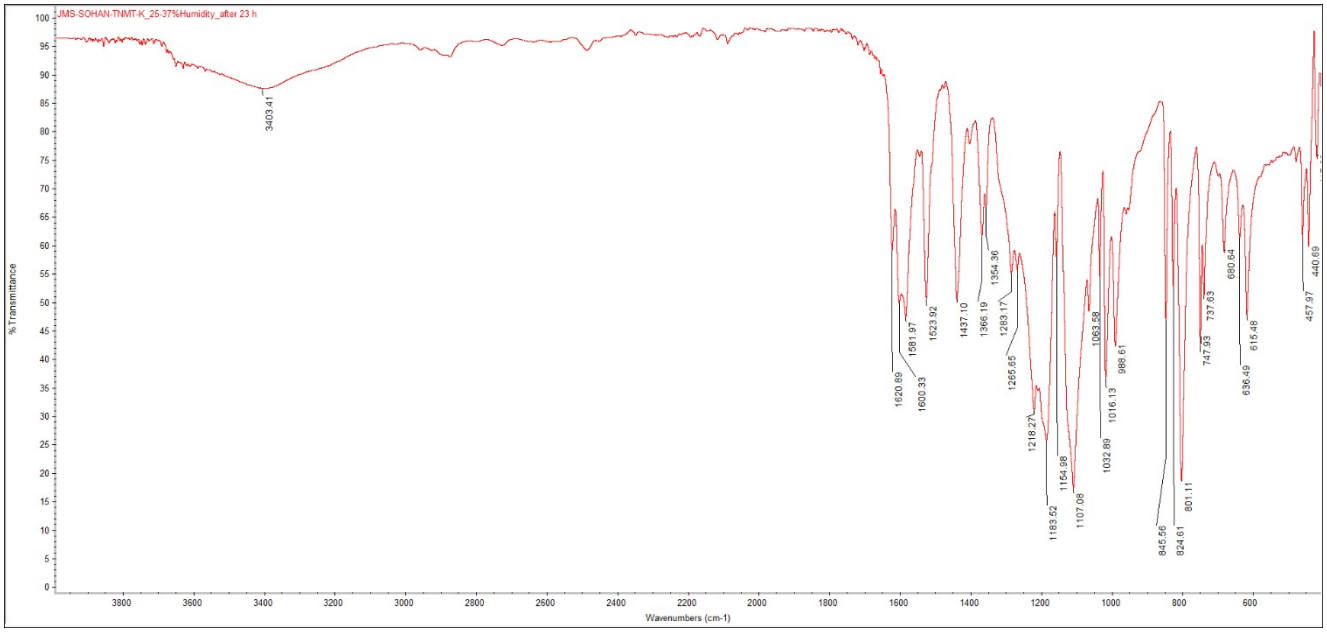


Fig. S9. FTIR-Spectrum of TNMT-K sample stored at 23-37% humidity after 23 hours.

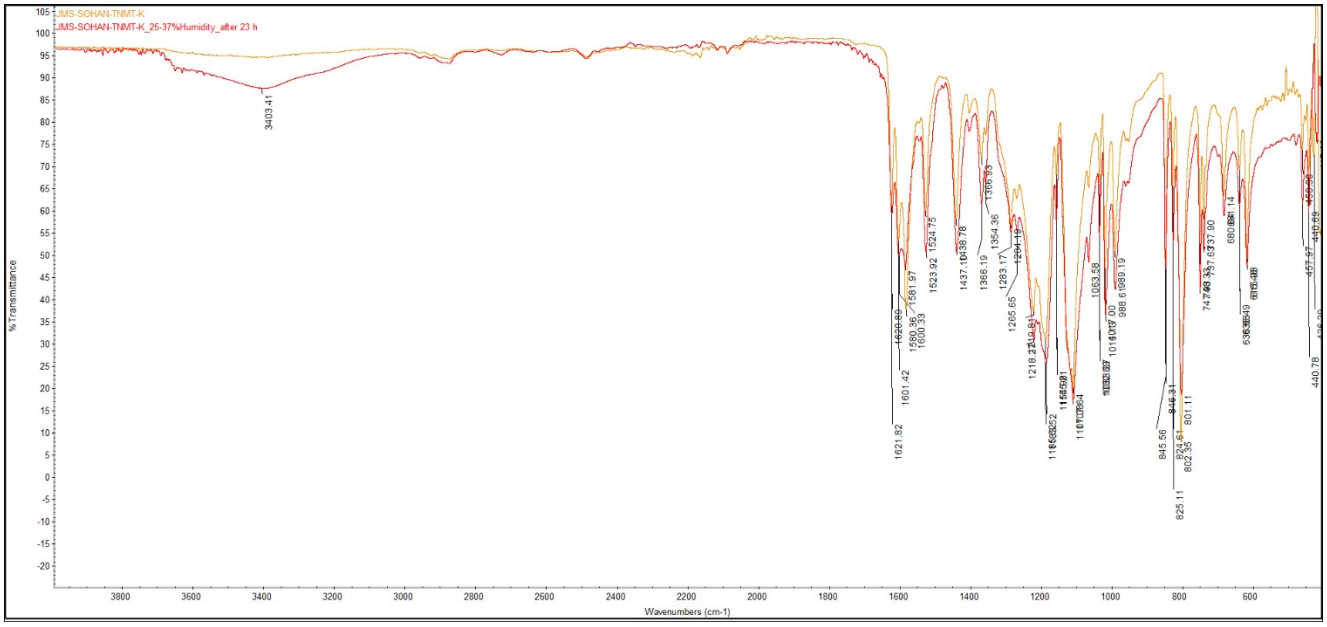


Fig. S10. Comparison of FTIR-Spectrum of TNMT-K and a TNMT-K sample stored at 23-37% humidity after 23 hours.

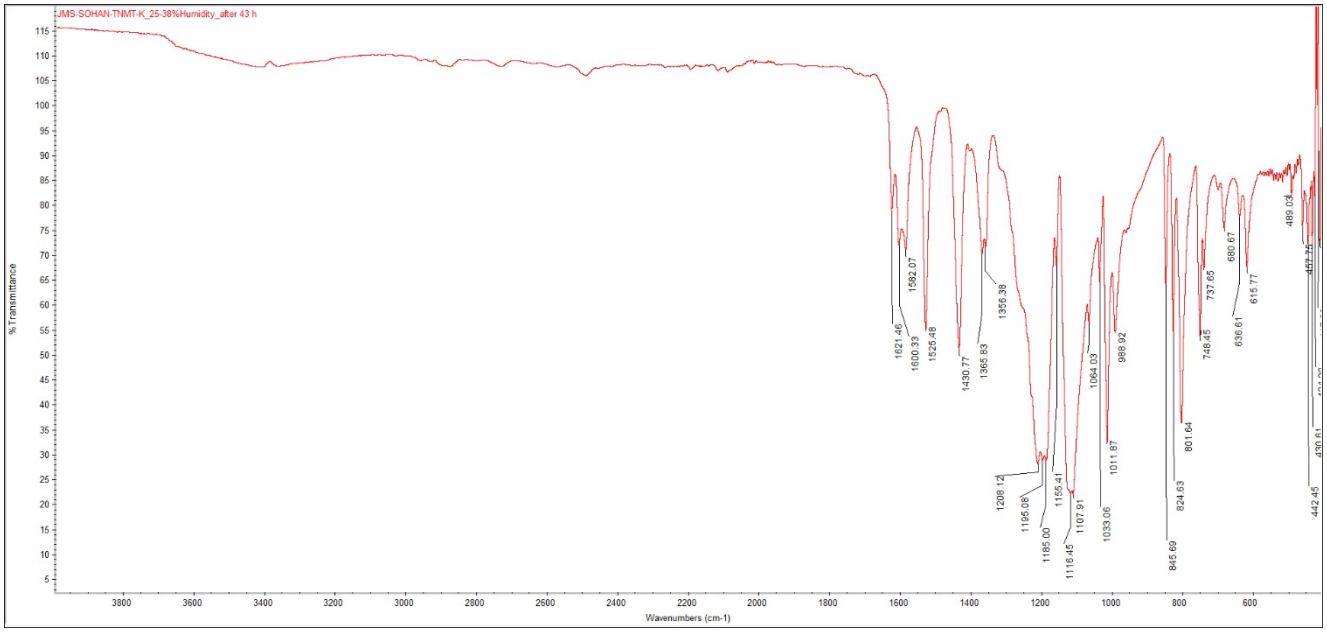


Fig. S11. FTIR-Spectrum of TNMT-K sample stored at 25-38% humidity after 43 hours.

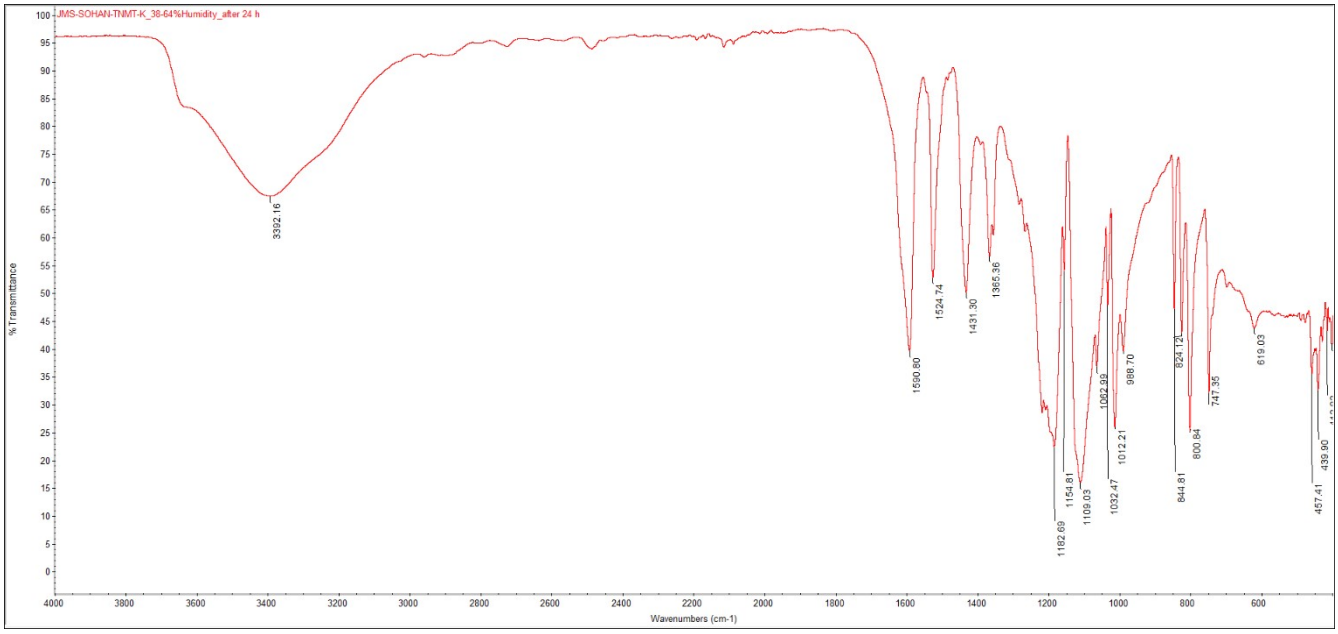


Fig. S12. FTIR-Spectrum of TNMT-K sample stored at 38-64% humidity after 24 hours.

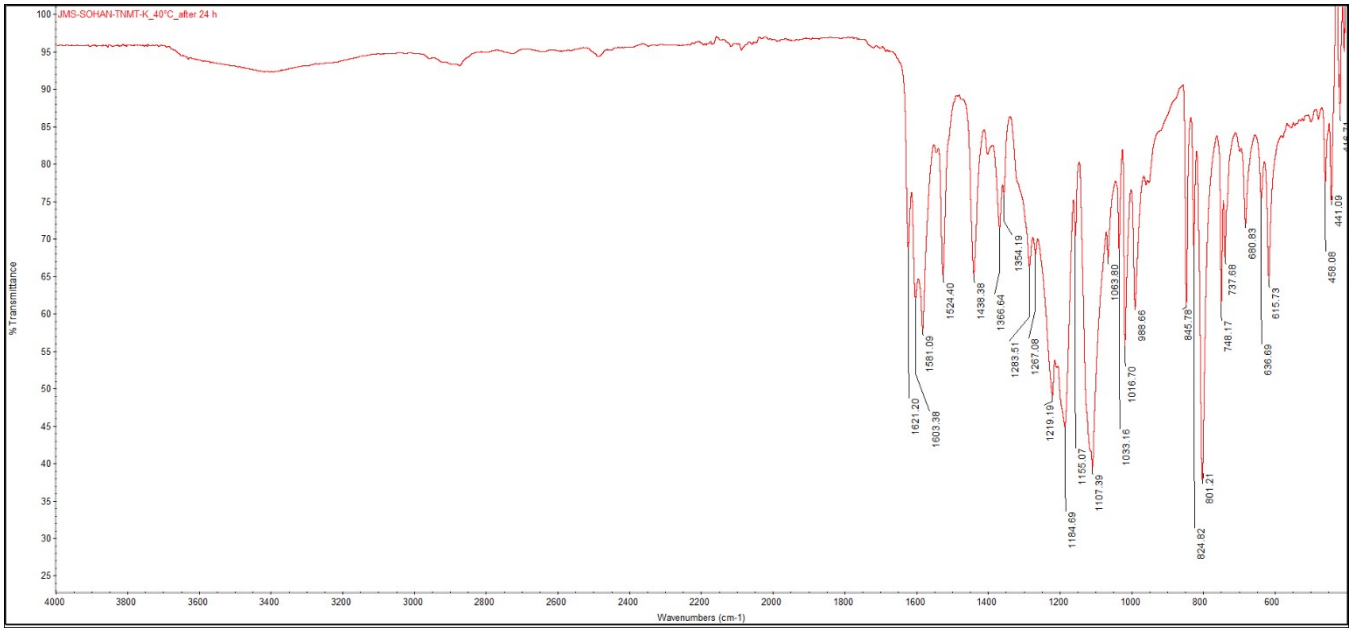


Fig. S13. FTIR-Spectrum of TNMT-K sample stored at 40 °C for 24 hours.

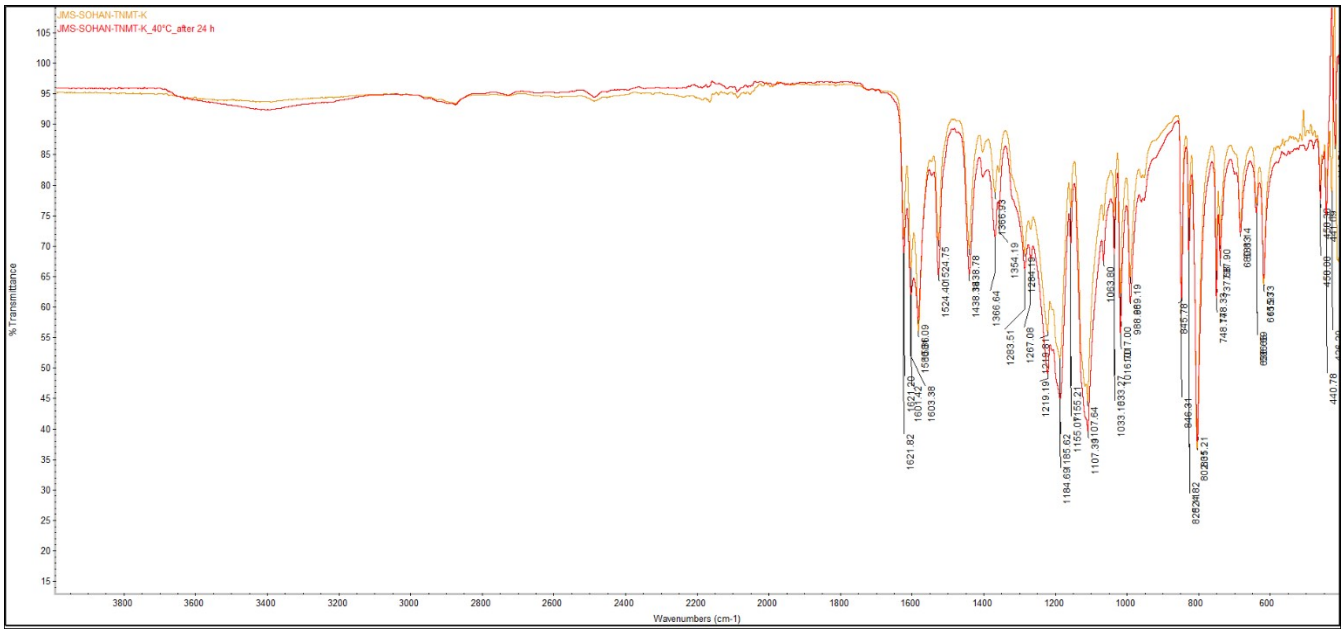


Fig. S14. Comparison of the FTIR spectra of TNMT-K and a TNMT-K sample stored at 40 °C for 24 hours.

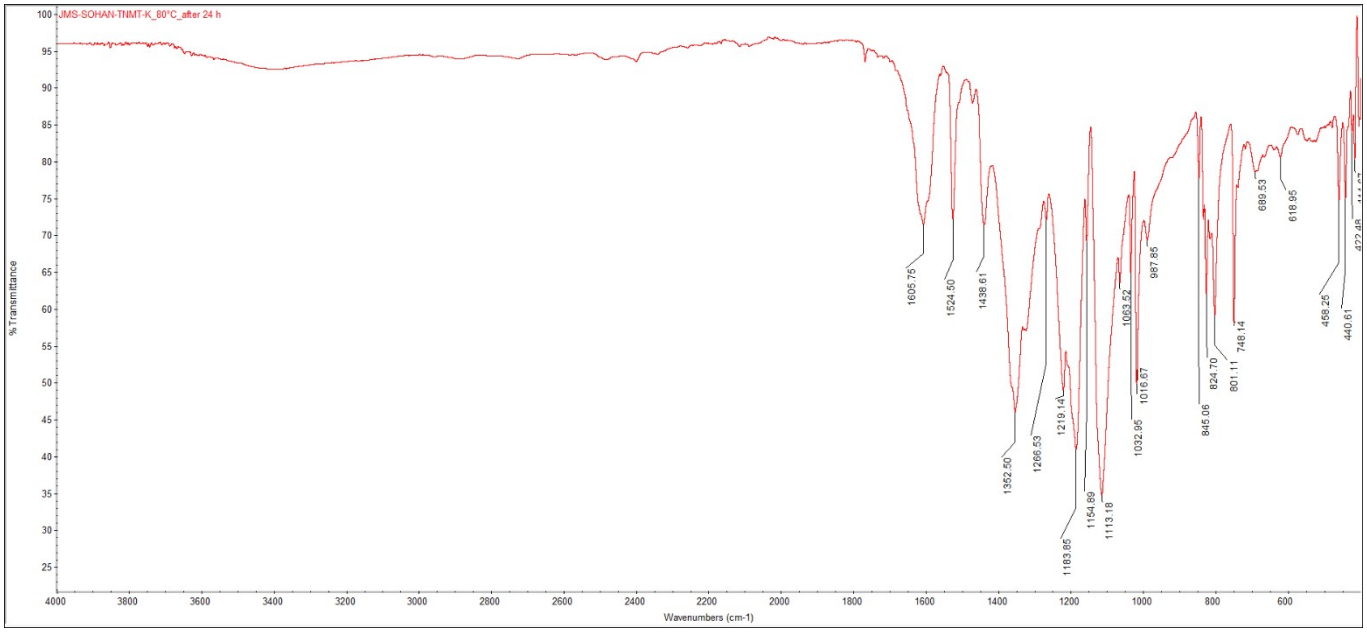


Fig. S15. FTIR-Spectrum of TNMT-K sample stored at 80 °C for 24 hours.

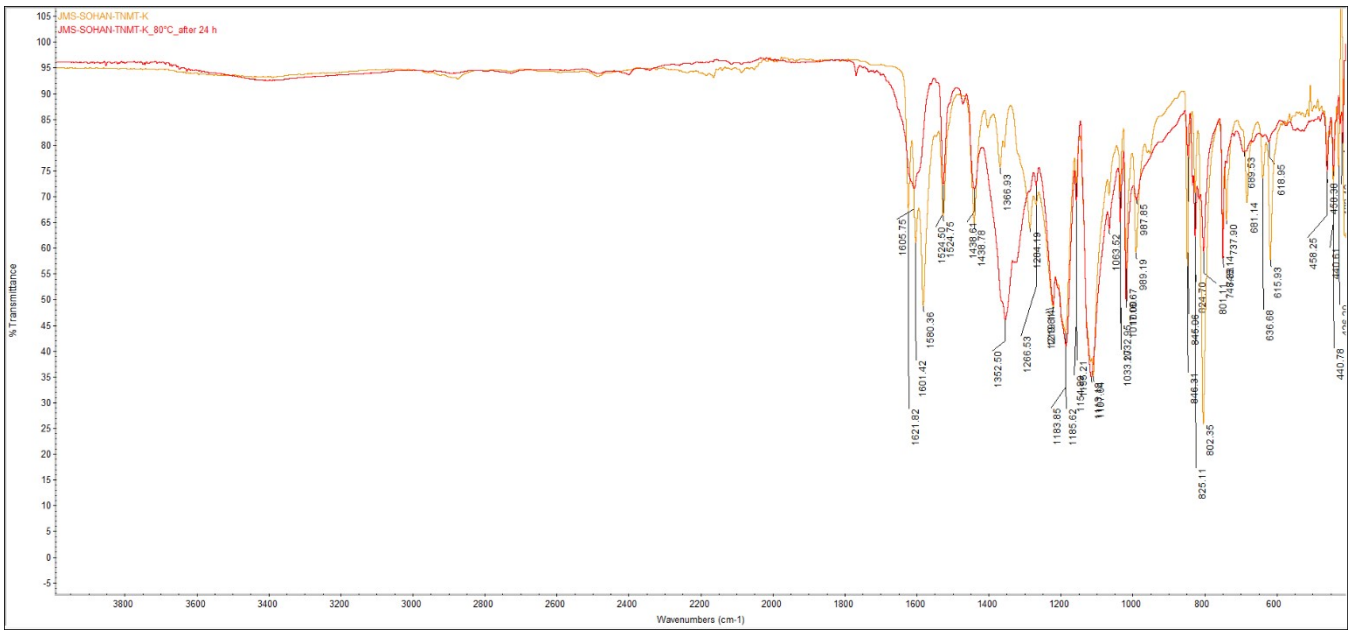


Fig. S16. Comparison of the FTIR spectra of TNMT-K and a TNMT-K sample stored at 80 °C for 24 hours.

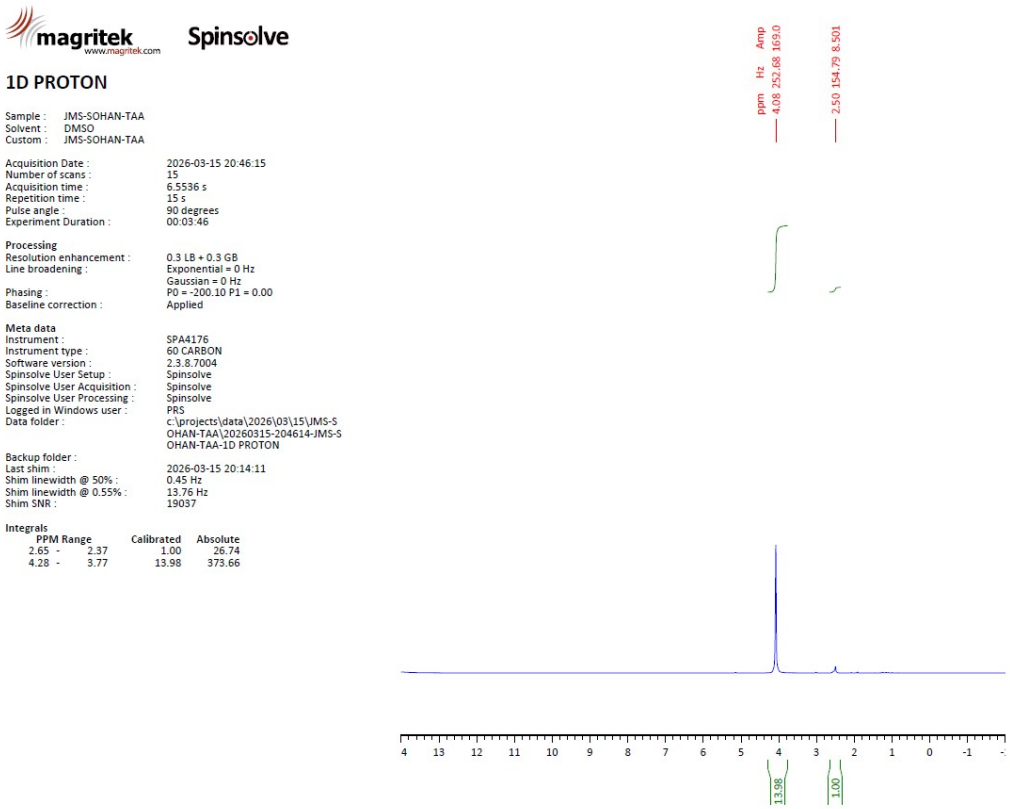


Fig. S17. ^{1}H NMR Spectrum of TAA (1)

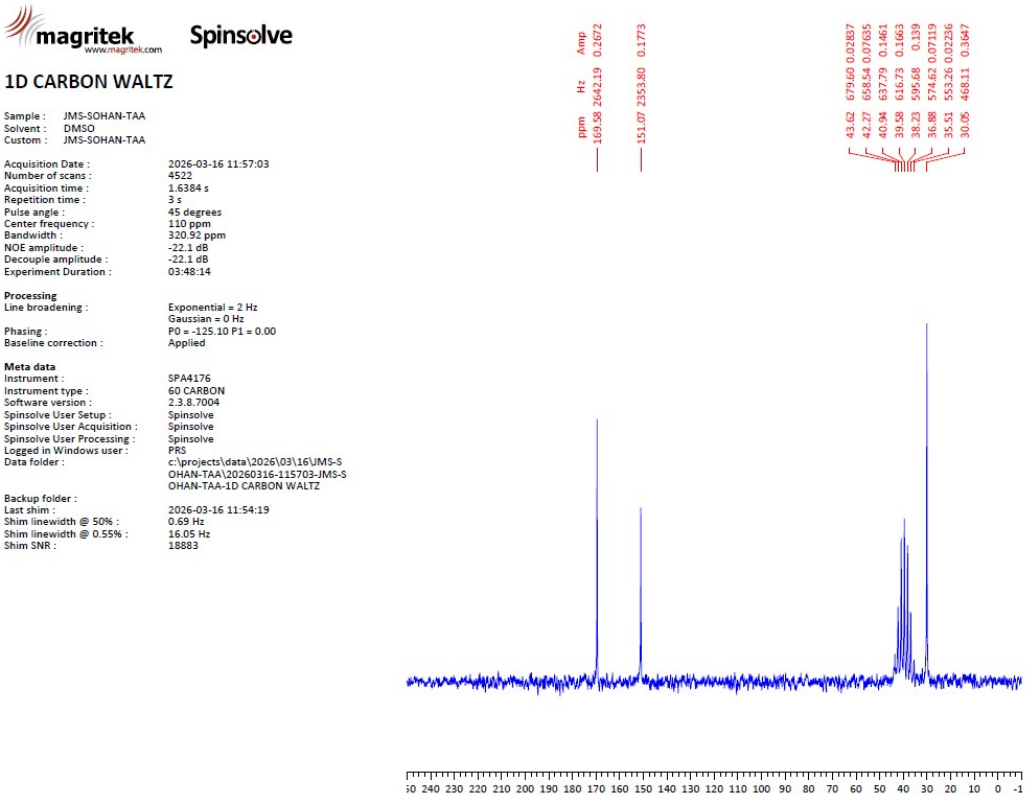


Fig. S18. ^{13}C NMR Spectrum of TAA (1)

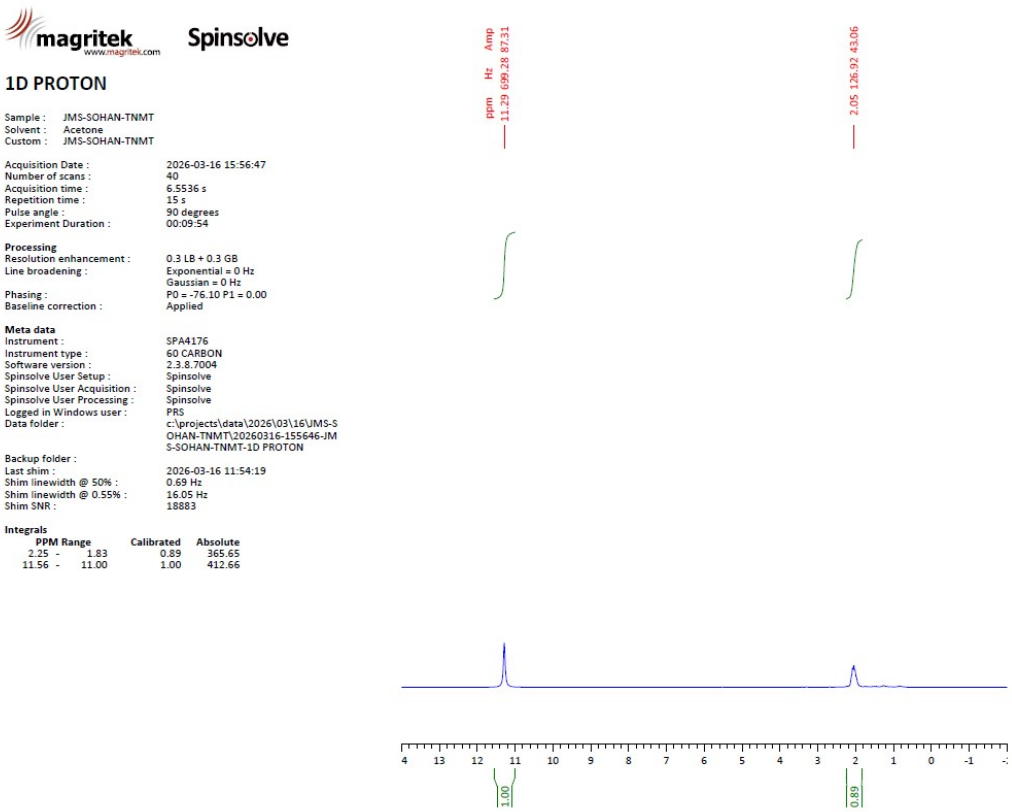


Fig. S19. ^{1}H NMR Spectrum of TNMT (2).

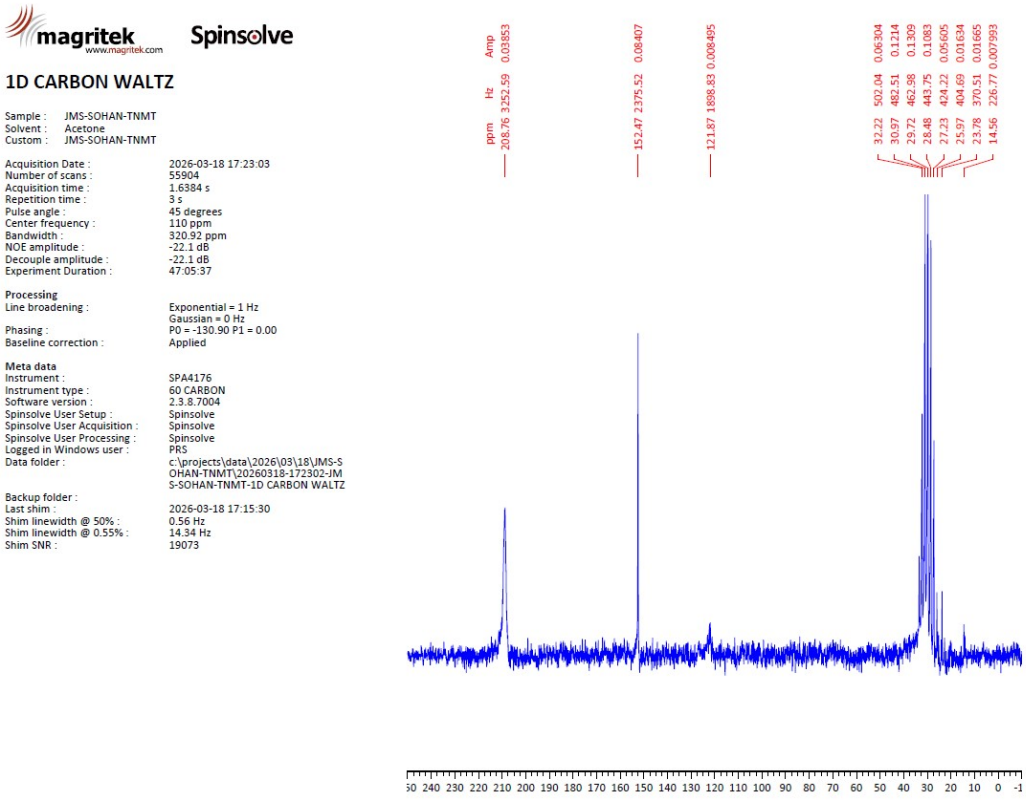


Fig. S20. ^{13}C NMR Spectrum of TNMT (2).

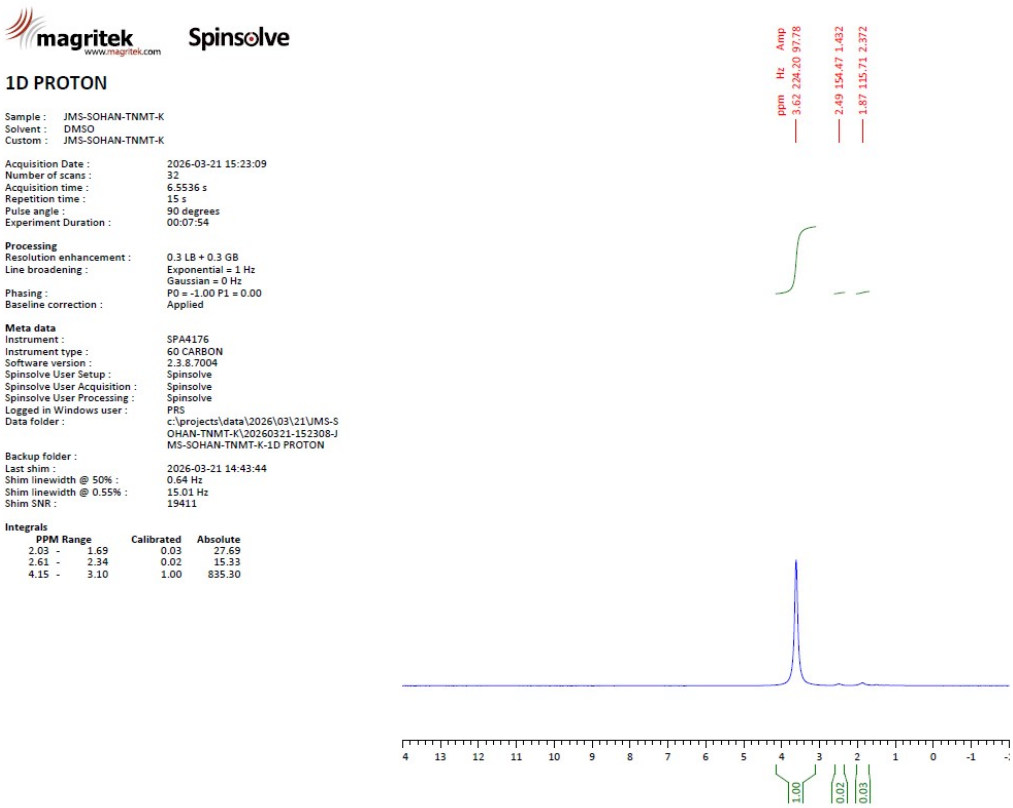


Fig. S21. ^{1}H NMR Spectrum of TNMT-K

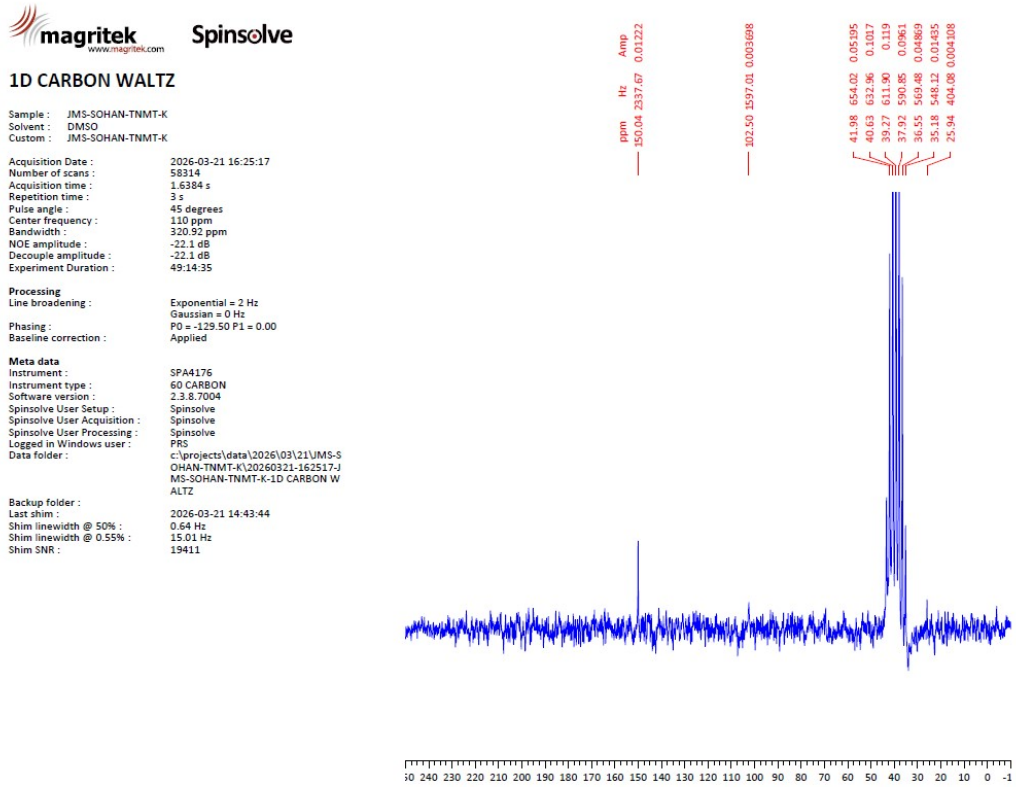


Fig. S22. ^{13}C NMR Spectrum of TNMT-K

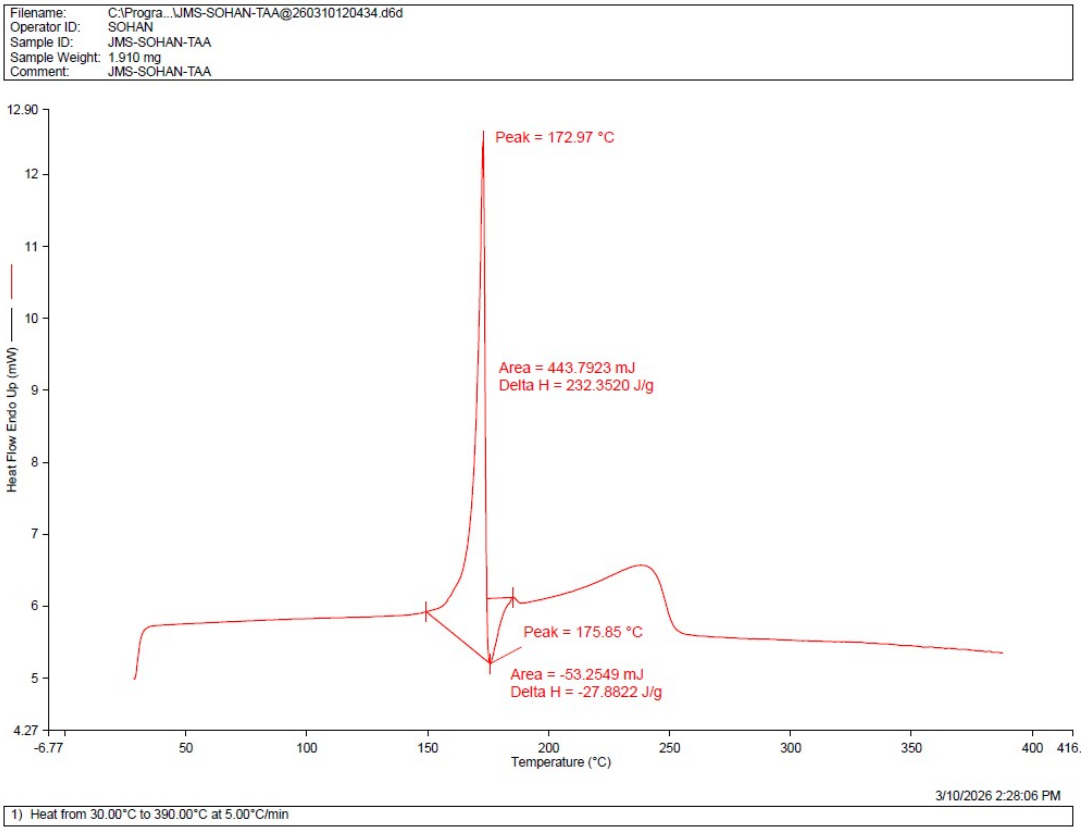


Fig. S23. DSC plot of TAA (a) at 5 °C min^{-1}

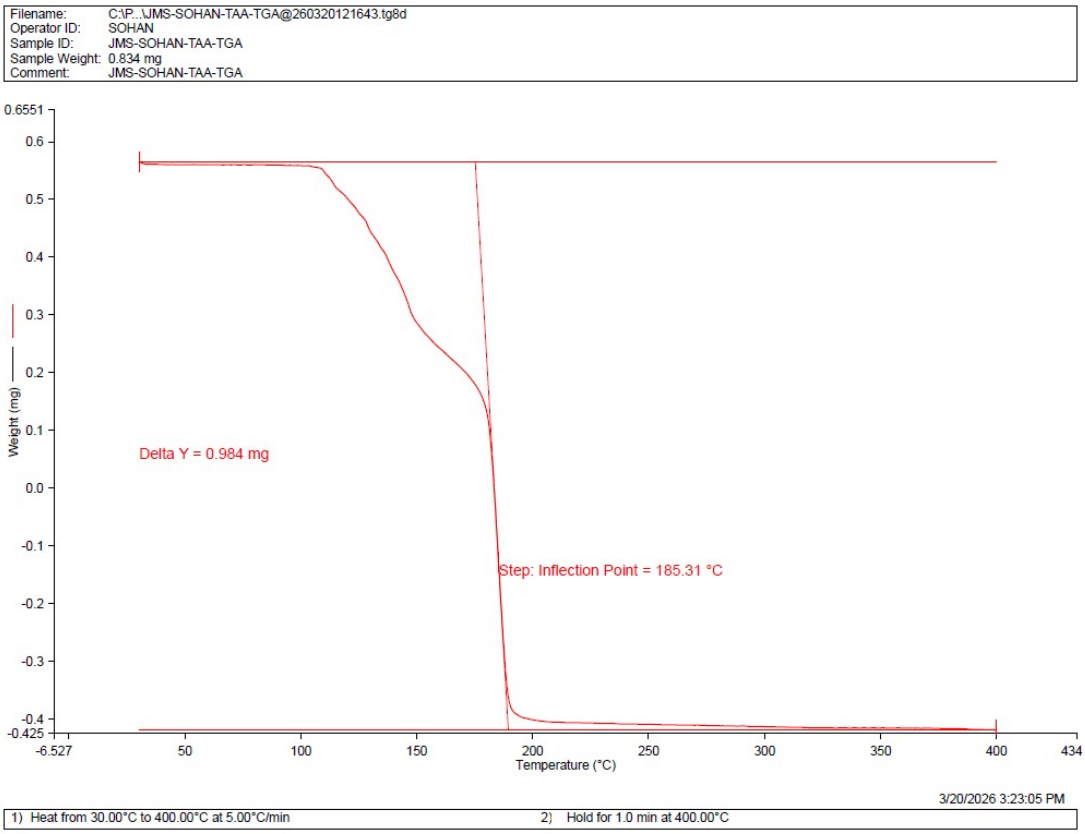


Fig. S24. TGA plot of TAA (1) at 5 °C min^{-1}

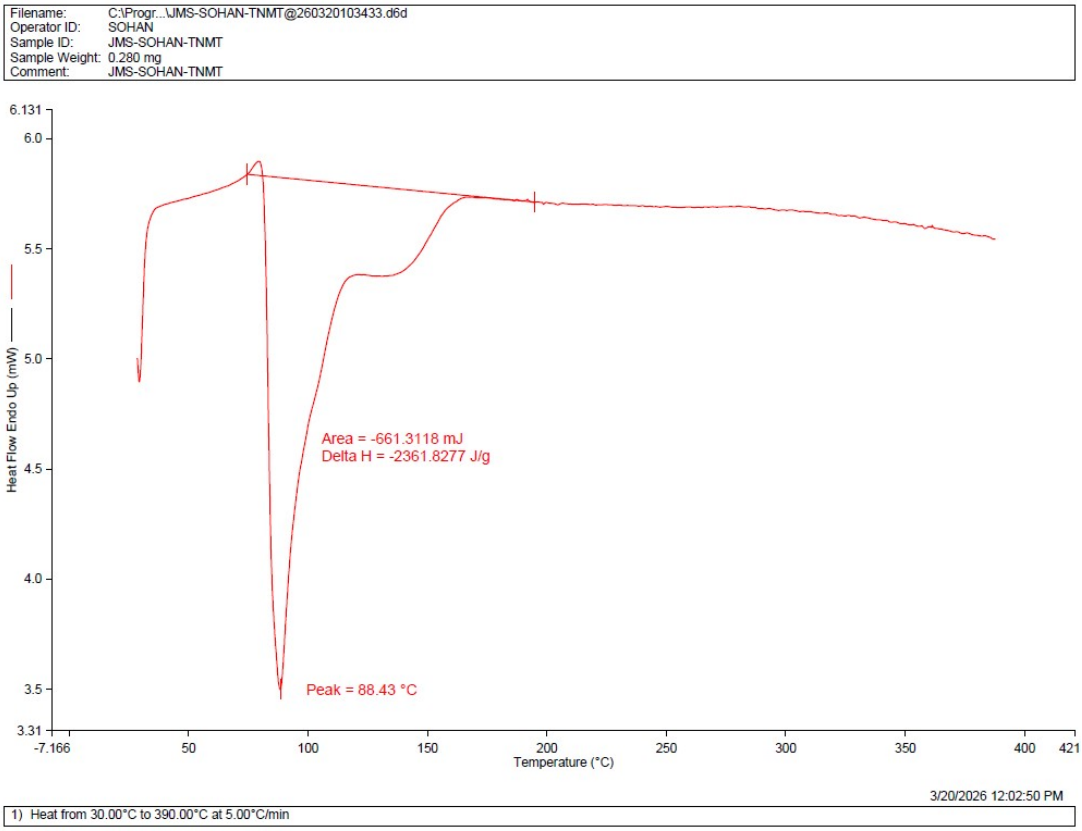


Fig. S25. DSC plot of TNMT (2) at 5 °C min^{-1}

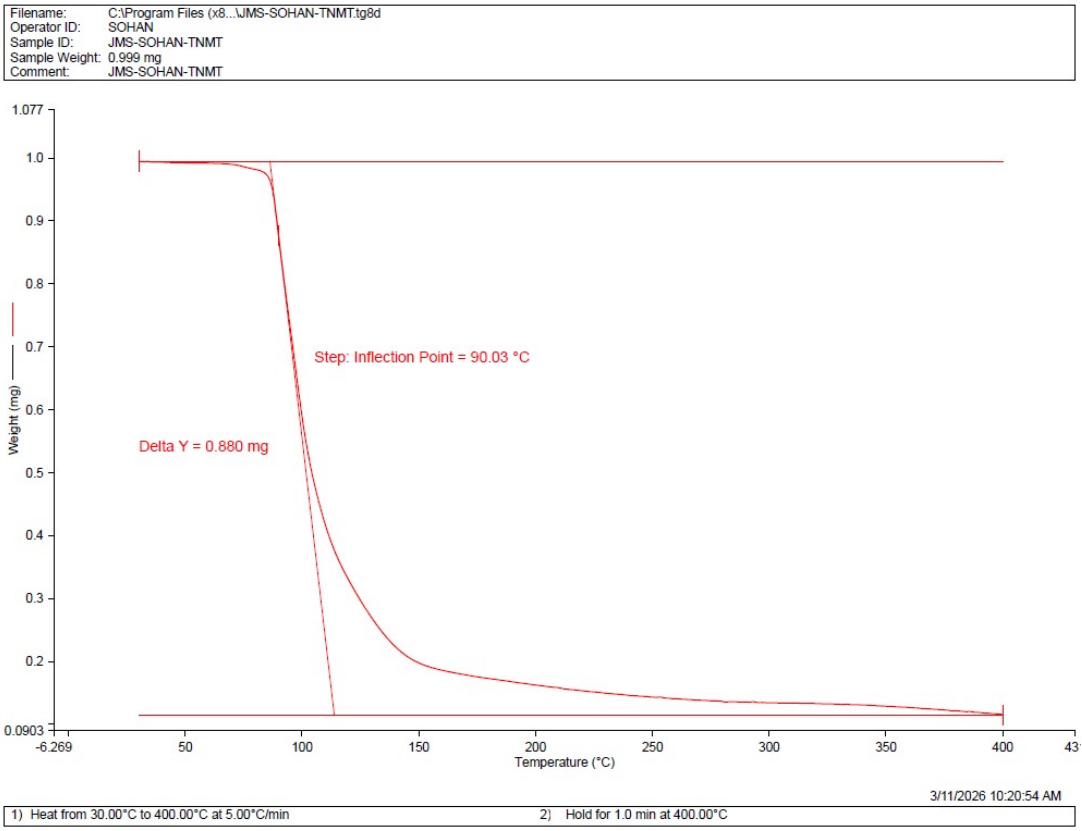


Fig. S26. TGA plot of TNMT (2) at 5 °C min^{-1}

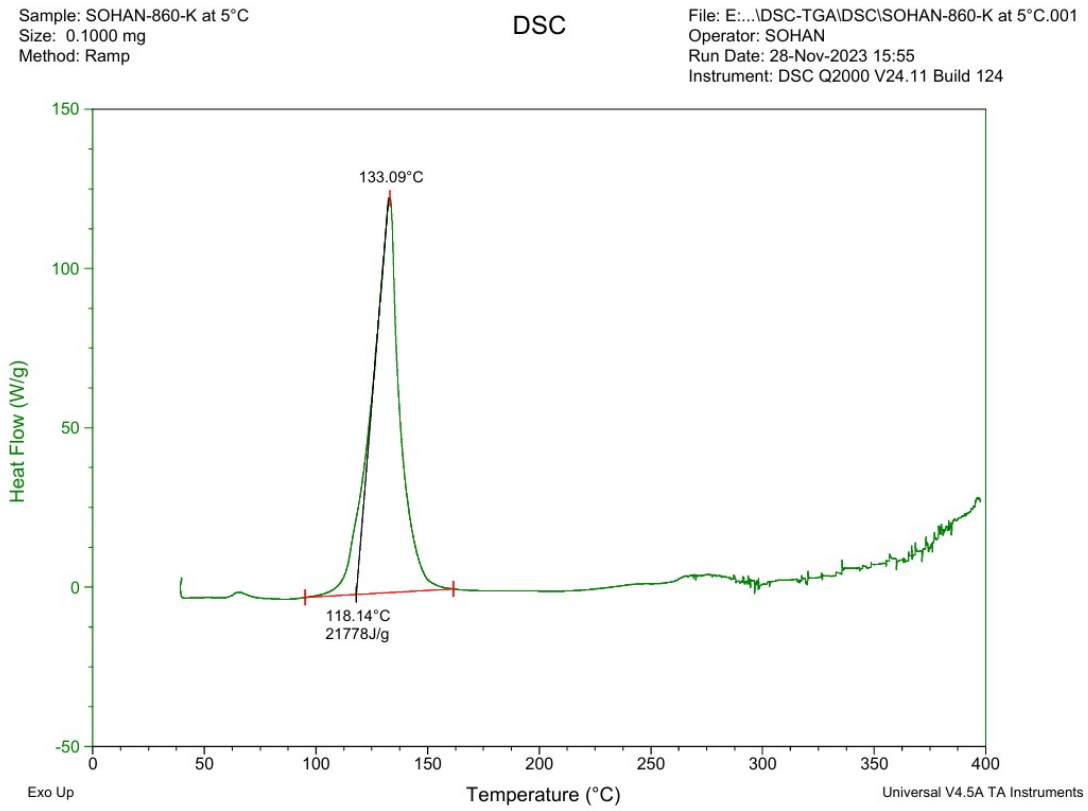


Fig. S27. DSC plot of TNMT-K at 5 °C min^{-1}

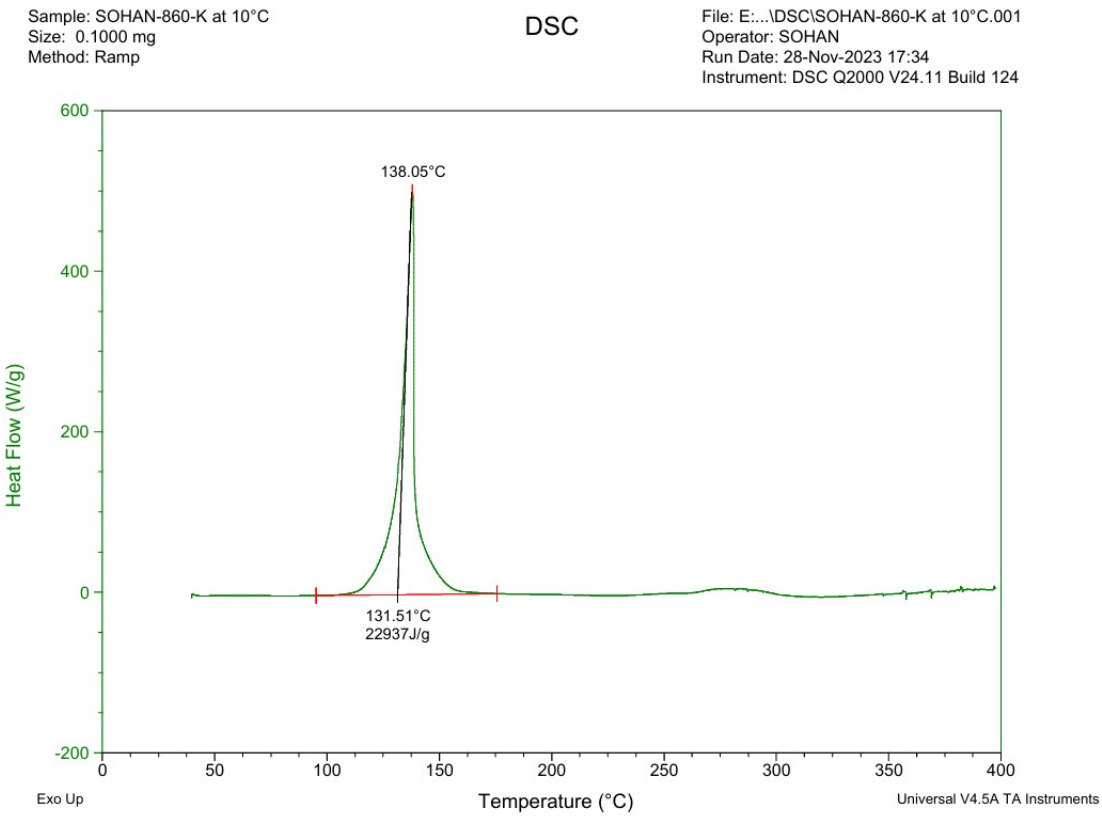


Fig. S28. DSC plot of TNMT-K at 10 °C min^{-1}

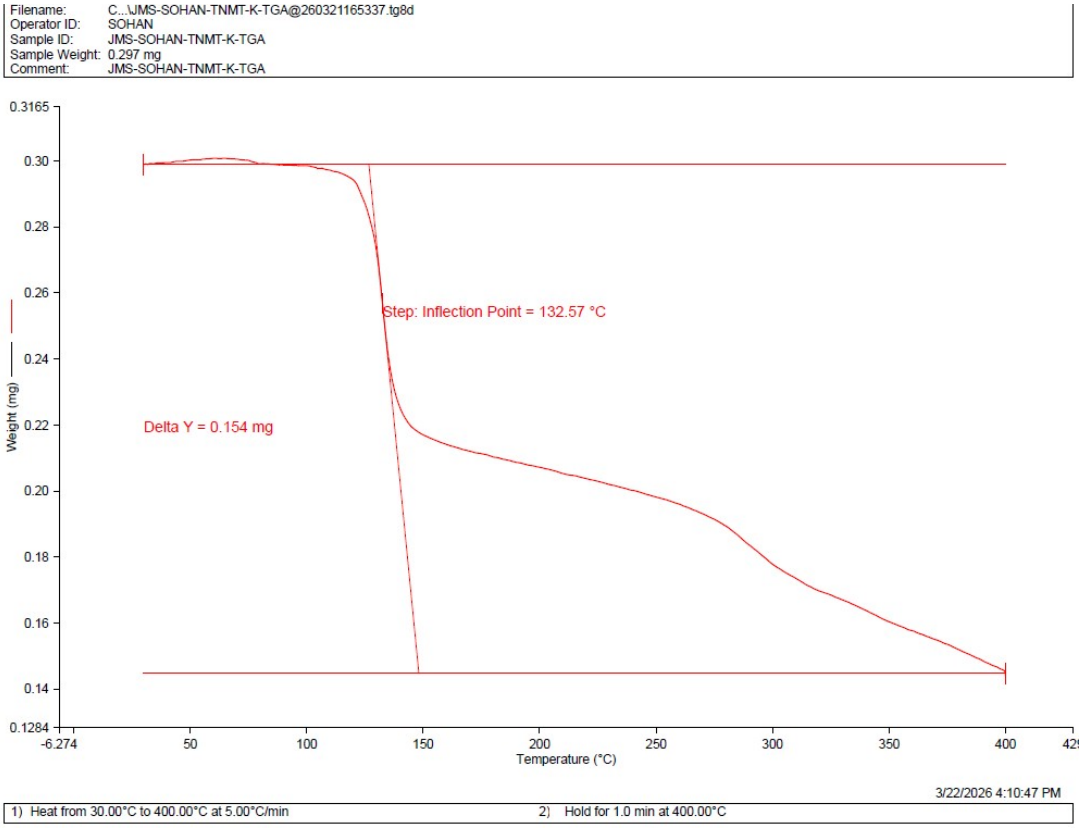


Fig. S29. DSC plot of TNMT-K at 5 °C min^{-1}

Fig. S30. **Stability test**: TNMT-K sample stored at 38-64% humidity for 24 hours (see FTIR, **Fig. S12).**

Fig. S31. **Stability test** (i) TNMT-K sample stored at 80 °C and (ii) TNMT-K sample stored at 40 °C (see FTIR, **Figs. S13-S16).**

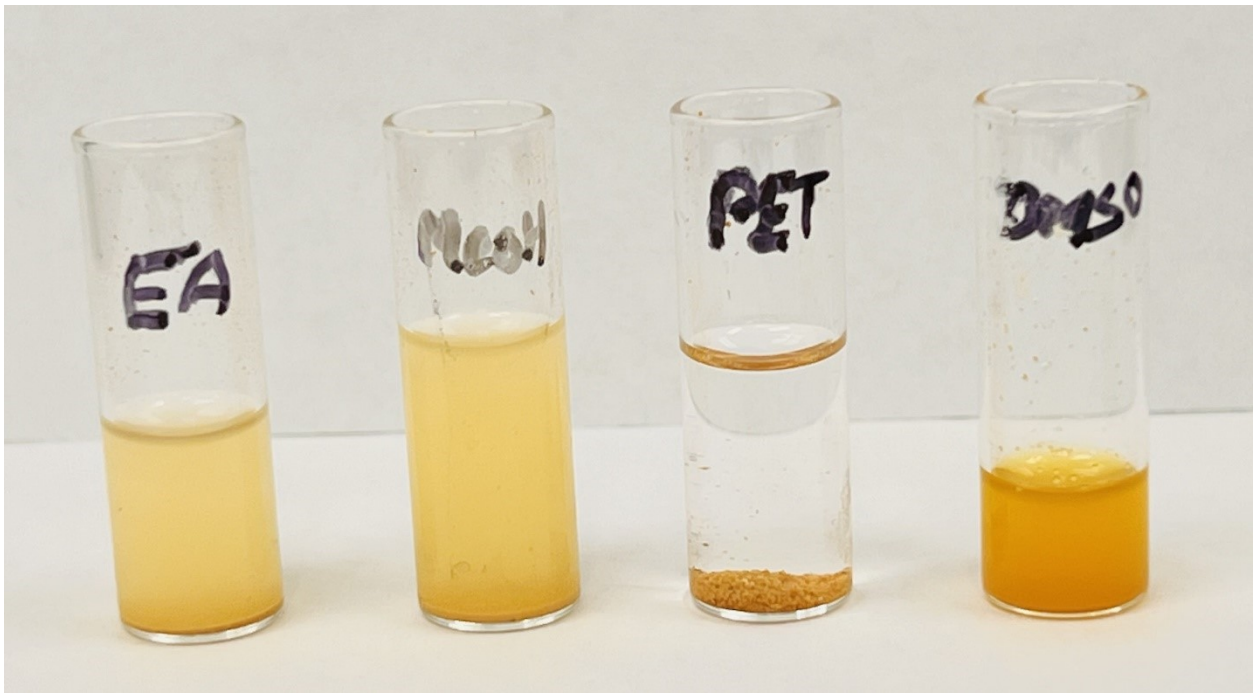


Fig. S32. TNMT-K sample stored in different solvents for 24 hours: (i) ethyl acetate, (ii) methanol, (iii) petroleum ether, and (iv) dimethyl sulfoxide at room temperature (stable in all solvents).

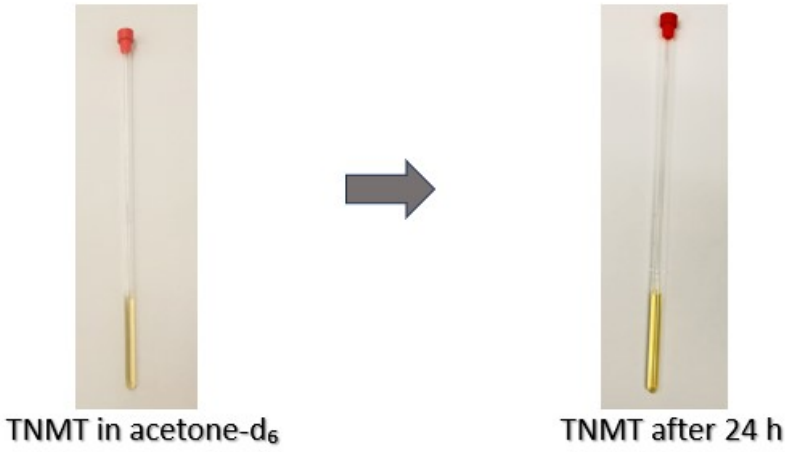


Fig. S33. Stability test: TNMT (2) sample dissolved in acetone-d_6 and stored for 24 hours at room temperature (stable).

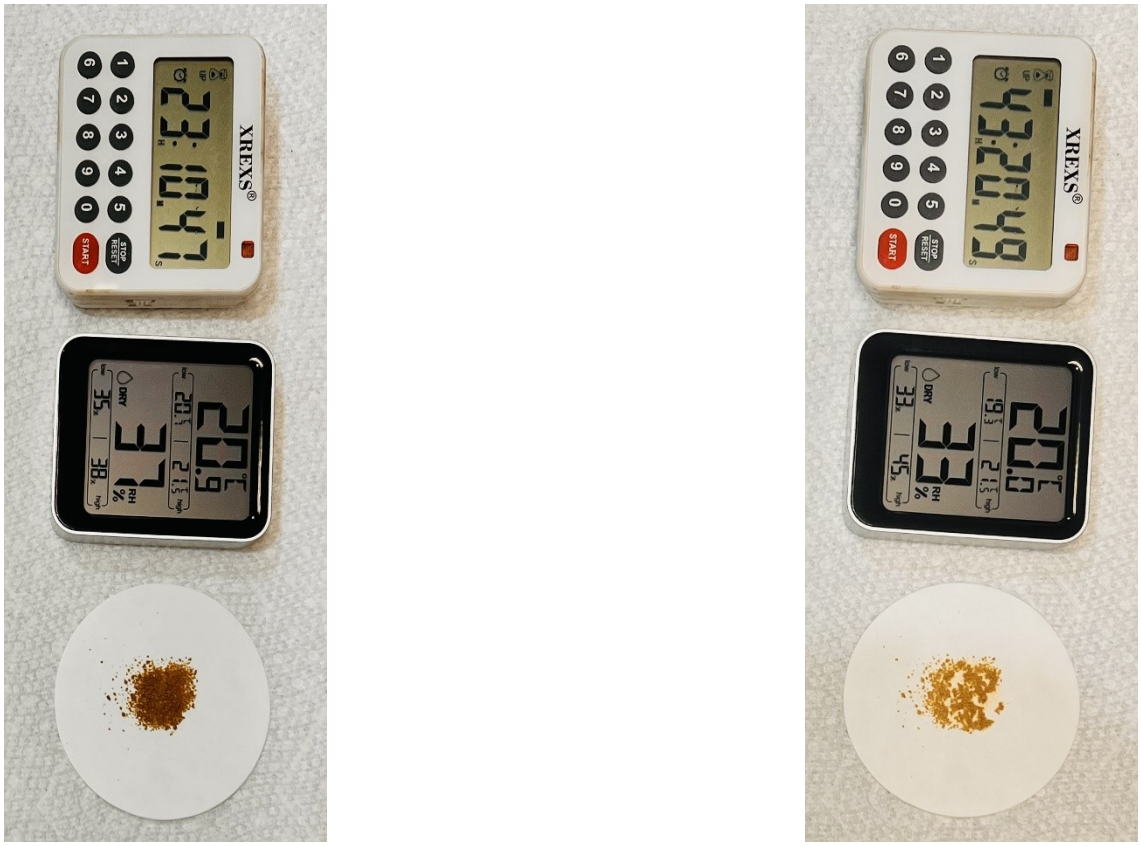


Fig. S34. **Stability test:** TNMT-K sample stored at room temperature under 25-38% humidity (i) TNMT-K after 23 hours and (ii) TNMT-K after 43 hours (see FTIR, **Figs S9-S11).**

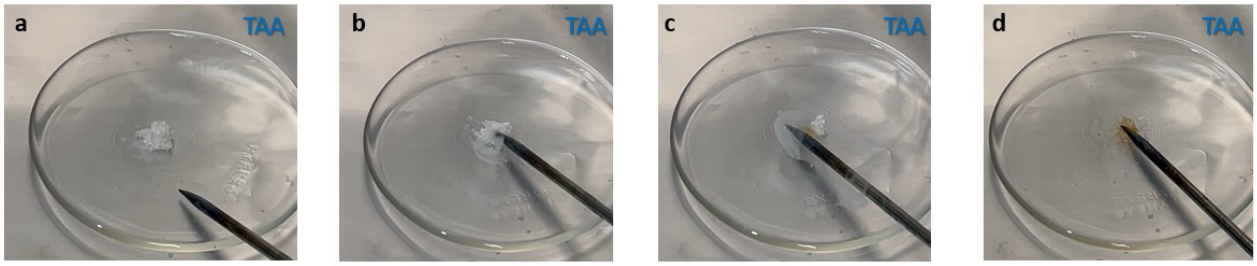


Fig. S35. Hot-needle test for TAA (1): White fume

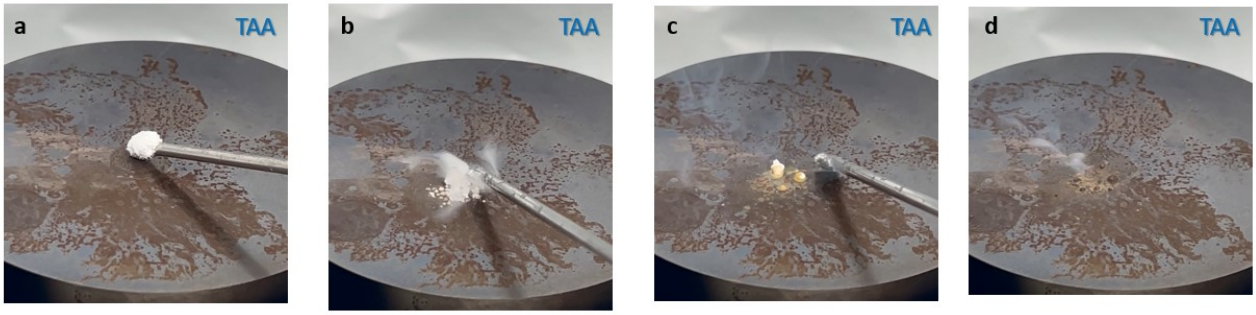


Fig. S36. Hot-plate test for TAA (1): White fume

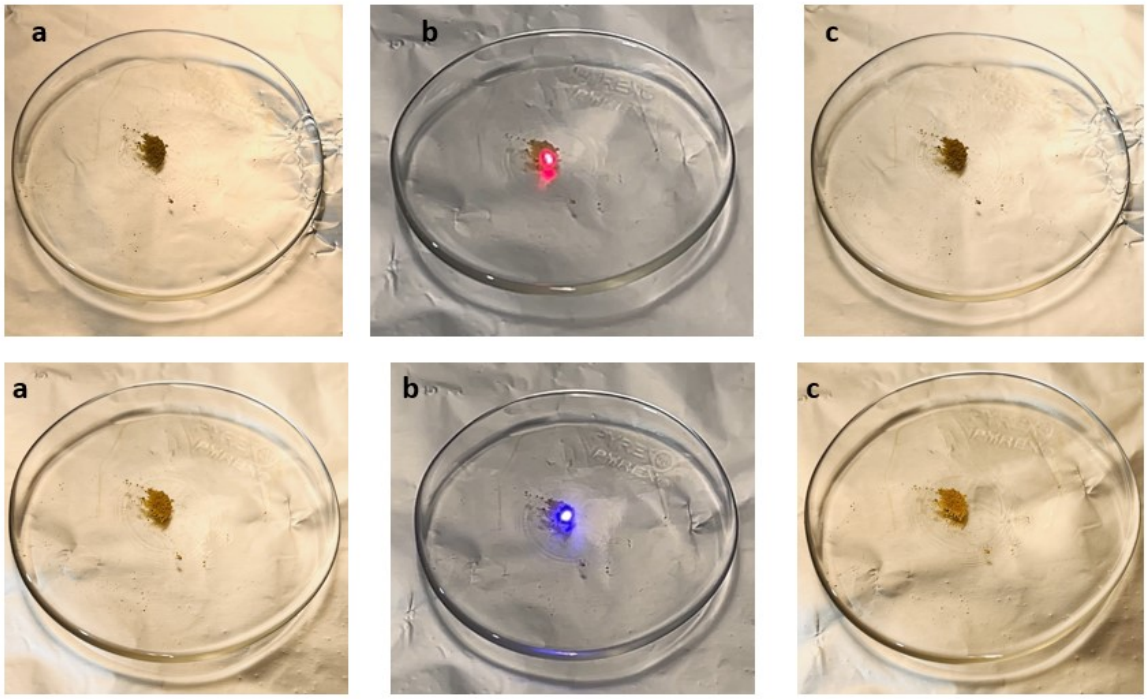


Fig. S37. Laser irradiation test: TNMT-K was exposed to laser light (red 650 nm) and blue (450 nm)-(a) beginning, (b) laser irradiation, (c) after.

Table S8. Detonation parameters of TNMT-K

Heat of detonation	=	-5039.4 kJ/kg
Detonation temperature	=	3828.576 K
Detonation pressure	=	26.27235 GPa
Detonation velocity	=	7862.806 m/s
Particle velocity	=	1713.504 m/s
Sound velocity	=	6149.303 m/s
Exponent 'Gamma'	=	3.588717
Density of all products	=	2.493368 g/cm^3
Density of gaseous products	=	2.288313 g/cm^3
Specific volume of all products	=	0.401064 cm^3/g
Specific volume of gaseous prod.	=	0.4370032 cm^3/g
Volume of gas at STP	=	497.889 dm^3/kg
Moles of gaseous products	=	22.213 mol/kg

Moles of condensed products	=	1.944 mol/kg
Mean molecular mass of gas. prod.	=	32.92023 g/mol
Mean molecular mass of cond. prod.	=	138.025 g/mol
Mean molecular mass of all prod.	=	41.37924 g/mol
Entropy of products	=	5.6867 kJ/kg K
Internal energy of products	=	6507.458 kJ/kg, i.e. 2.68954 kJ/cm^3
Compression energy	=	1468.058 kJ/kg, i.e. 2.862714 kJ/cm^3
TNT equivalent from Qd	=	115.52 %
TNT equivalent from pCJ	=	141.56 %

Table S9. Concentration of detonation products of TNMT-K

PRODUCT		mol/mol exp.	mol/kg expl.	Mol %	Mass %
N_2	=	3.333448E+00	1.296204E+01	53.6563	36.3106
CO_2	=	1.491089E+00	5.798066E+00	24.0011	25.5173
O_2	=	5.436759E-01	2.114072E+00	8.7512	6.7648
K_2CO_3(s)	=	5.000000E-01	1.944239E+00	8.0482	26.8354
NO	=	2.604502E-01	1.012755E+00	4.1923	3.0389
NO_2	=	5.824693E-02	2.264919E-01	0.9376	1.0420
NO_3	=	1.392327E-02	5.414035E-02	0.2241	0.3357
CO	=	8.910457E-03	3.464812E-02	0.1434	0.0970
O	=	2.606202E-03	1.013416E-02	0.0420	0.0162
N_2O	=	2.392372E-04	9.302687E-04	0.0039	0.0041
N	=	3.842376E-06	1.494100E-05	0.0001	0.0000
CNO	=	7.365906E-07	2.864217E-06	0.0000	0.0000
KO	=	2.468737E-11	9.599630E-11	0.0000	0.0000
KO_2(l)	=	5.254700E-22	2.043279E-21	0.0000	0.0000
K_2CO_3(l)	=	4.531573E-22	1.762092E-21	0.0000	0.0000
KO_2(s)	=	2.171050E-22	8.442083E-22	0.0000	0.0000

Table S10. Thermodynamic properties of combustion products of TNMT-K

PARAMETER		CHAMBER	THROAT	EXIT (Pc/Pe)
Pressure (MPa)	=	7.000	3.887	0.1000
Pressure ratio (Pc/P)	=	1.000	1.801	70.000
Temperature (K)	=	3086.0	2905.6	2114.0
Enthalpy (kJ/kg)	=	567.5	172.5	-1747.7
Internal energy (kJ/kg)	=	-134.1	-481.5	-2191.7
Entropy (kJ/K kg)	=	7.495	7.495	7.495
Qp (kJ/kg)	=	-3201.8	-3358.2	-4460.6
Mol gas (mol/kg expl.)	=	27.135	26.832	24.047
Mol tot. (mol/kg expl.)	=	27.344	27.075	25.261
V (dm3/kg expl.)	=	608.2	601.4	539.0
Mass gas (g/kg expl.)	=	971.15	966.35	832.20

Mass cond. (g/kg expl.)	=	28.79	33.58	167.55
Mw mean (g)	=	36.569	36.931	39.577
Density, all prod. (kg/m^3)	=	10.052	5.996	0.237
Density, gas prod. (kg/m^3)	=	9.764	5.795	0.197
R (J/kg K)	=	225.60	223.08	199.93
Cp (J/kgK)	=	1258.7	1231.3	1276.8
Cv (J/kgK)	=	1033.1	1008.2	1076.9
Cp/Cv	=	1.218	1.221	1.186
Sonic velocity (m/s)	=	921.0	889.7	718.5
Mach number (m/s)	=		0.999	2.995
Flow velocity (m/s)	=		888.8	2151.8
Mass flux (kg/m^{2}s)	=		5328.99	508.99

Table S11. Performance parameters of TNMT-K

PARAMETER		THROAT	EXIT (Pc/Pe)
Pressure ratio (Pc/P)	=	1.801	70.000
Area ratio (Ae/At)	=	1.000	10.470
Characteristic vel. (m/s)	=	1313.6	1313.6
Exhaust velocity (m/s)	=	888.8	2151.8
Thrust coefficient	=	0.677	1.638
Specific impulse, Isp (s)	=	90.64	219.43
Vacuum spec. impulse (s)	=	163.58	239.07
Isp * rho (g/cm^3 s)	=	176.74	427.88
Ivacuum * rho (g/cm^3 s)	=	318.98	466.19

NOTE: Specific impulse at Pc=7.0 MPa, and Pc/Pe=70.00 equals 219.426 (s)

Table S12. Concentration of combustion products (mol/kg of explosive) of TNMT-K.

PRODUCT		CHAMBER	THROAT	EXIT (Pc/Pe)
CN_2	=	4.65629E-12	5.97624E-13	7.29711E-19
CNO	=	2.74838E-07	7.54423E-08	1.29059E-11
CO	=	1.24228E+00	9.04533E-01	7.12133E-02
CO_2	=	6.32608E+00	6.62911E+00	6.49181E+00
K_2	=	1.80624E-01	1.65500E-01	2.69391E-02
K_2CO_3(l)	=	1.38529E-03	2.43308E-01	1.21393E+00
K_2CO_3(s)	=	2.07186E-01	2.21057E-19	6.90008E-06
K_2O	=	4.78396E-01	5.33477E-01	3.42742E-01
K_2O(l)	=	0.00000E+00	0.00000E+00	0.00000E+00
K_2O(s)	=	0.00000E+00	0.00000E+00	1.00051E-22
K_2O_2	=	1.18713E-02	1.25756E-02	7.09320E-03

K_2O_2(l)	=	0.00000E+00	0.00000E+00	0.00000E+00
K_2O_2(s)	=	0.00000E+00	0.00000E+00	0.00000E+00
KCN	=	2.05816E-05	7.75559E-06	4.90457E-09
KO	=	2.12953E+00	1.97875E+00	7.07056E-01
KO_2(l)	=	3.00014E-20	1.57183E-20	2.88790E-22
KO_2(s)	=	5.12560E-21	3.09398E-21	2.11408E-22
N	=	5.23267E-05	2.17774E-05	7.48215E-08
N_2	=	1.32667E+01	1.33360E+01	1.35406E+01
NO	=	6.84195E-01	5.46316E-01	1.38070E-01
NO_2	=	1.60572E-03	1.09196E-03	1.15323E-04
O	=	1.36423E-01	9.68575E-02	1.09693E-02
O_2	=	2.67760E+00	2.62773E+00	2.71049E+00

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