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Supporting Information (SI)

A novel synthesis method for nitrogen-rich energetic frameworks containing bistetrazoles: assembling an advanced high-energy density material with high nitrogen content and good oxygen balance

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Content

1.Experimental

1.1 Safety precautions

Warning! All new compounds involved are potential explosives with a risk of explosion. Avoid mechanical impacts and electrostatic friction during experiments. The use of full protective equipment by laboratory staff is strongly recommended.

1.2 Synthesis of sodium [5,2':5',5''-tertetrazole]-1,1''-diide (Na_2TT)

1.38 g (10.0 mmol) of **H_2BT** was dissolved in an aqueous NaOH solution (0.80 g of NaOH in 20 ml of H_2O). Subsequently, 100 ml of freshly prepared NCN_3 was added, and the reaction was conducted at 10 ℃ for 24 hours. After the reaction was completed, the mixture was filtered and washed with acetonitrile, resulting in a white powder weighing 1.82 g, achieving a yield of 72.8%. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 157.71, 154.40, 152.15 ppm. IR (KBr, v/cm^{-1}): v = 1428, 1386, 1384, 1351, 1334, 1320, 1304, 1205, 1186, 1174, 961, 918, 666 cm^{-1}; Elemental analysis calcd (%) for $C_3N_{12}Na_2$ (250.02): C: 14.41, N: 67.21 %; Found (%): C: 14.82, N: 67.53 %.

Synthesis of freshly prepared NCN_3: 3.18 g (30.0 mmol) of BrCN was dissolved in 100 ml of acetonitrile and cooled to 0 °C. Then, NaN_3 (7.80 g, 120.0 mmol) was added and the reaction was carried out at 0 °C for 6 hours. The filtrate was filtered to remove insoluble inorganic salts, and the filtrate was stored at low temperature to obtain the freshly prepared NCN_3.

1.3 Synthesis of 1H,1''H-5,2':5',5''-tertetrazole (H_2TT)

1.00 g (4 mmol) of **Na_2TT** was dissolved in deionized water and stirred at room temperature. 37 % concentrated hydrochloric acid was added drop by drop until

reaching a pH of 2~3. The mixture was then filtered, washed with ice water, resulting in 0.75 g of white powder with an 91% yield. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 155.53, 155.07, 154.75 ppm. IR (KBr, v/cm^{-1}): v = 1559, 1438, 1417, 1290, 1223, 1154, 1125, 1092, 1078, 1038, 1012, 985, 706, 682 cm^{-1}; Elemental analysis calcd (%) for $C_3H_2N_{12}$ (206.13): C: 17.48, H: 0.98, N: 81.54 %; Found (%): C: 17.13, H: 1.06, N: 81.81 %.

1.4 Synthesis of magnesium [5,2':5',5''-tertetrazole]-1,1''-diide (MgTT)

1.00 g (4.9 mmol) of **H_2TT** and 0.69 g of $Mg_2(OH)_2CO_3$ were put into deionised water and stirred at room temperature. The mixture was heated to reflux for 6 h. At the end of the reaction, the mixture was filtered and washed with ice water to give 0.88 g of white powder in 79% yield. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 159.90, 157.97, 152.16 ppm. IR (KBr, v/cm^{-1}): v = 1469, 1423, 1341, 1322, 1274, 1239, 1202, 1176, 1131, 1064, 973, 876, 649 cm^{-1}; Elemental analysis calcd (%) for C_3MgN_{12} (228.42): C: 15.77, N: 73.58 %; Found (%): C: 16.02, N: 73.94 %.

1.5 Synthesis of 1,1'-(2H,2''H-[5,2':5',5''-tertetrazole]-2,2''-diyl) bis(propan-2-one) (1)

Na_2TT (1.00 g, 4.0 mmol) was dissolved in 50 ml of water. Then 2 ml (23.8 mmol) of acetone bromide was added and the reaction was carried out at 70 °C for 18 hours. The reaction mixture was filtered, followed by sequential washings with water and acetone. The obtained solid was then dried to yield a white powder weighing 1.12 g, resulting in a yield of 88%. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.22 (s, 2H), 6.12 (s, 2H), 2.36 (s, 3H), 2.33(s, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ =

199.92, 199.62, 158.37, 156.61, 155.67, 62.87, 62.19, 27.67 ppm. IR (KBr, v/cm^{-1}): v = 1800, 1790, 1557, 1436,1429, 1345, 1258, 1152, 1074, 1068, 1047, 991, 833, 677 cm^{-1}; Elemental analysis calcd (%) for $C_9H_{10}N_{12}O_2$ (318.10): C: 33.97, H: 3.17, N: 52.81 %; Found (%): C: 34.13, H: 3.62, N: 51.48 %.

1.6 Synthesis of 2,2''-bis(dinitromethyl)-2H,2''H-5,2':5',5''-tertetrazole (BDNTT)

Compound **1** (0.50 g, 1.2 mmol) was dissolved in 3 ml of H_2SO_4 at a temperature of -5°C. Then, 3 ml of Fuming HNO_3 was slowly added dropwise while maintaining the reaction temperature at -10°C for a duration of 2 days. The reaction mixture was subsequently poured into ice water to quench the reaction. The resulting mixture was filtered, washed with water and dried, yielding a white powder weighing 0.47 g with a yield of 72%. ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.26 (s, 2H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 158.58, 156.31, 155.50, 131.06 ppm. IR (KBr, v/cm^{-1}): v = 1695, 1687, 1673, 1438, 1260, 1252, 1249, 1233, 1144, 966, 938, 770 cm^{-1}; Elemental analysis calcd (%) for $C_5H_2N_{16}O_8$ (414.02): C: 14.50, H: 0.49, N: 54.11 %; Found (%): C: 14.32, H: 0.39, N: 53.69 %.

1.7 Synthesis of sodium [5,5'-bitetrazole]-1,1'-diide (Na_2BT)

A solution was prepared by dissolving 1.98 g (10.0 mmol) of 2,3-dicyano-5,6-dichloropyrazine in 15 mL of DMF. Slowly, 2.64 g (40.0 mmol) of NaN_3 was added to the solution, and the mixture was stirred at room temperature for 0.5 hours. The reaction mixture was then heated to 95 °C and allowed to react for 6 hours. After cooling back to room temperature, the resulting solid was filtered to obtain light yellow powder weighing 0.88 g, with a yield of 48%. IR (KBr, v/cm^{-1}): v = 734, 1015, 1049, 1148, 1182, 1308,1345 cm^{-1}.[1]

1.8 Synthesis of sodium 1H-[5,5'-bitetrazol]-2'-ide (NaHBT)

A solution was prepared by dissolving 1.98 g (10.0 mmol) of 2,3-dicyano-5,6-dichloropyrazine in 15 mL of acetone. Slowly, 2.64 g (40.0 mmol) of NaN_3 was added to the solution. The temperature was then raised to 55 ℃ and the reaction proceeded for 6 hours. After cooling back to room temperature, the resulting mixture was filtered to obtain light yellow powder weighing 0.83 g, with a yield of 52%. ^{13}C NMR (75 MHz, D_2O): δ = 149.76 ppm. IR (KBr, v/cm^{-1}): v = 3424, 1425, 1353, 1325, 1303, 1290, 1195, 1137, 1084, 709 cm^{-1}; Elemental analysis calcd (%) for C_2HN_8Na (160.08): C: 15.01, H: 0.63, N: 70.00 %; Found (%): C: 14.92, H: 0.72, N: 69.69 %.

1.9 Synthesis of potassium [5,5'-bitetrazole]-1,1'-diide (K_2BT)

A solution was prepared by dissolving 1.98 g (10.0 mmol) of 2,3-dicyano-5,6-dichloropyrazine in 15 mL of DMF. Slowly, 3.20 g (40.0 mmol) of KN_3 was added to the solution. The temperature was then raised to 95 ℃ and the reaction proceeded for 6 hours. After cooling back to room temperature, the resulting mixture was filtered to obtain a white solid weighing 1.18 g, with a yield of 52%. IR (KBr, v/cm^{-1}): v = 732, 1009, 1042, 1140, 1170, 1302, 1334 cm^{-1}.[2]

1.10 Synthesis of 1H,1'H-5,5'-bitetrazole (H_2BT)

Method 1: 1.00 g (5.5 mmol) of **Na_2BT** was dissolved in deionized water and stirred. 37% concentrated hydrochloric acid was added drop by drop until reaching a pH of 2~3. The mixture was then filtered, washed with ice water, resulting in 0.65 g of white powder with an 86% yield.

Method 2: 1.00 g (5.5 mmol) of **Na_2BT** was added to acetone and stirred. 37% concentrated hydrochloric acid was then added dropwise until reaching a pH of 2~3. The mixture was stirred for 0.5 hours, filtered and the filtrate was obtained as 0.7g of white powder after centrifugation under reduced pressure, with a yield of 91%. IR (KBr, v/cm^{-1}): 3177, 3014, 2803, 2692, 2657, 2513, 1626, 1529, 1500, 685 cm^{-1}.[24]

H_2BT can be prepared equally well using **NaHBT** and **K_2BT** and the procedure is the same as the two methods described above.

2.General Methods

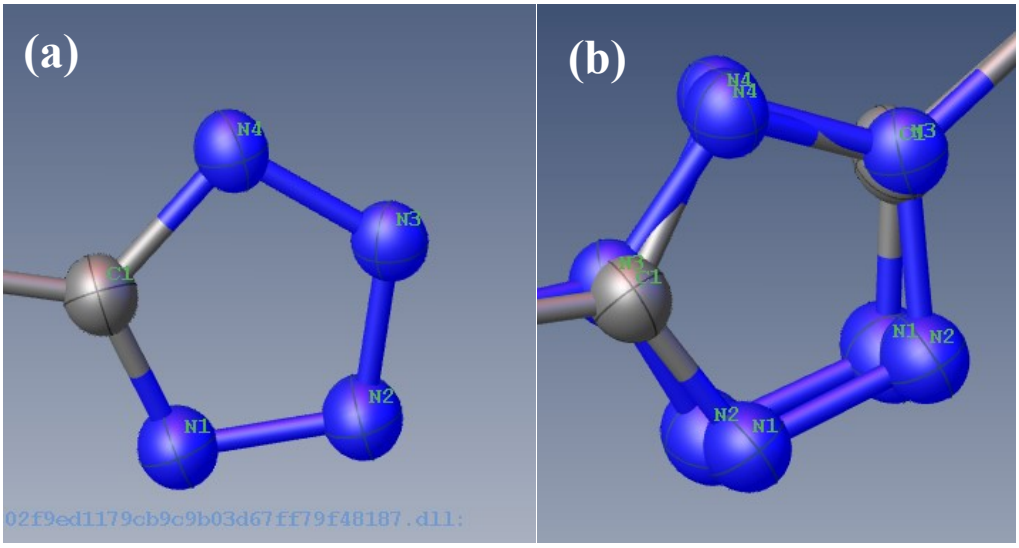
^1H and ^{13}C NMR spectra

^1H and ^{13}C NMR spectra were recorded on 300 MHz (Bruker AVANCE 300) clear magnetic resonance spectrometers operating at 300 and 75 MHz, respectively, by using either DMSO-d_6 as the solvent and locking solvent unless otherwise stated. Chemical shifts in ^1H and ^{13}C NMR spectra are reported relative to DMSO. DSC was performed at a heating rate of 10 °C min^{-1} in closed Al containers with a nitrogen flow of 30 mL min^{-1} on an STD-Q600 instrument. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR equipped with an ATR unit at 25 °C. Impact sensitivity, friction sensitivity and electrostatic discharge sensitivity of samples are measured by using the standard BAM methods.

X-ray Crystallography

The crystal of **MgTT** and **BDNTT** were performed on a Bruker Smart Apex II diffractometer with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å), respectively. Integration and scaling of intensity data were accomplished using the SAINT program2. The structures were solved by intrinsic using SHELXT2014 and refinement was carried out by a full- matrix least-squares technique using SHELXT2014. The hydrogen atoms were refined isotropically, and the heavy atoms

were refined anisotropically. N-H and O-H hydrogens were located from different electron density maps, and C-H hydrogens were placed in calculated positions and refined with a riding model. Data were corrected for the effects of absorption using SADABS4 Relevant crystal data and refinement results are summarized in **Table S1.** **BDNTT** appears to be stacking phenomenon is overlapping of molecules in two opposite directions. They are sterically equivalent and do not affect the validity of the connectivity. The details of the model are shown below. Fig. (a) is a plot of the smallest asymmetric unit and Fig. (b) is a plot after growth. The structure in Fig. (a) is half of that in Fig. (b).



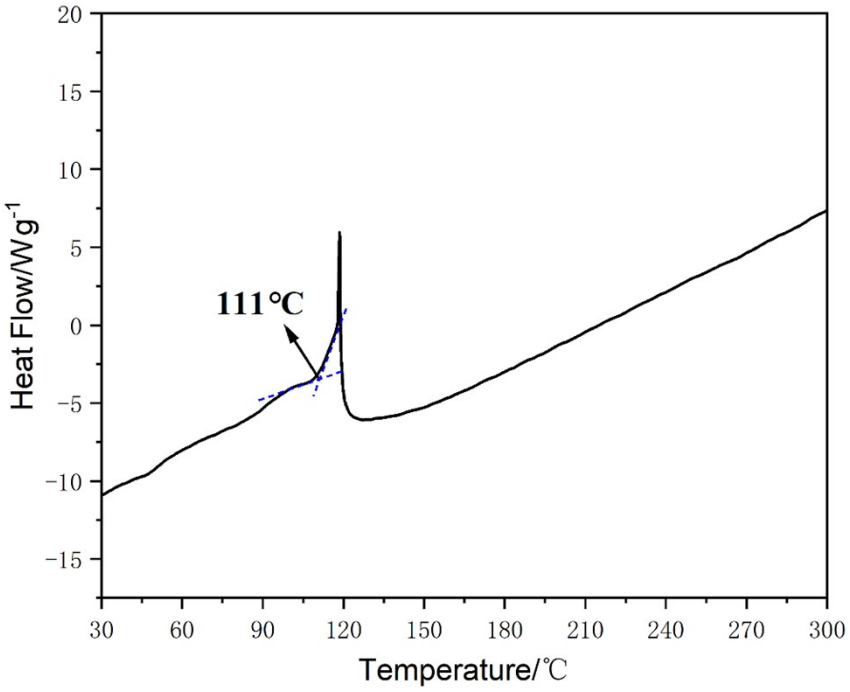


Figure S1 DSC plots of **BDNTT**

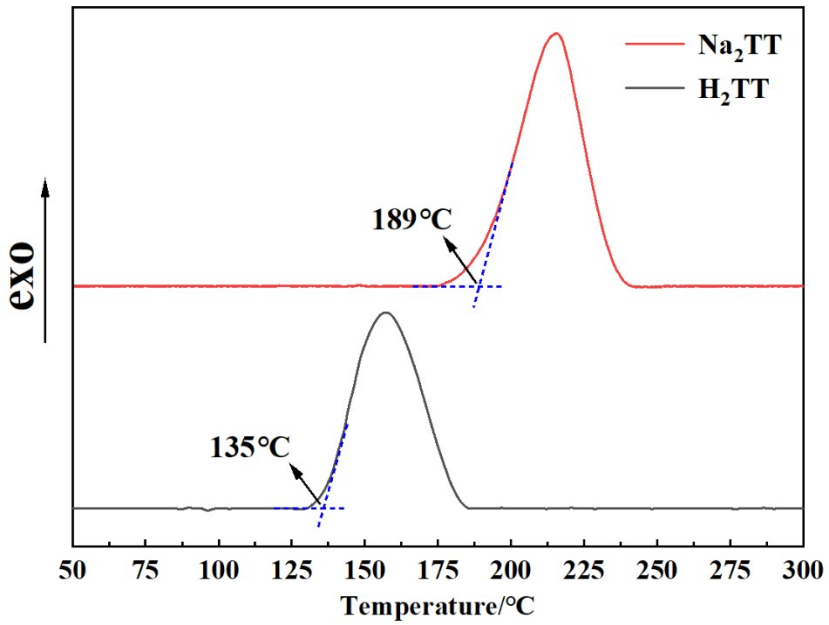


Figure S2 DSC plots of **Na_2TT** and **H_2TT**

Table S1. Crystal data and structure refinement for **Mg_2TT**·7H_2O, **BDNTT** (298K & 193K), **Na_2BT**•5H_2O, **K_2BT**, **H_2BT**.

Crystal	**Mg_2TT**·7 H_2O	**BDNTT** (298K)

CCDC number	2349953	2336294
Empirical formula	$C_3H_{14}MgN_{12}O_7$	$C_5H_2N_{16}O_8$
Formula weight	354.57	414.23
Temperature/K	223.00	298.00
Crystal system	triclinic	monoclinic
Space group	P-1	C2/c
a [Å]	6.5363(3)	19.0737(14)
b [Å]	9.9124(3)	8.8138(6)
c [Å]	12.1756(4)	8.6876(5)
α [°]	100.358(2)	90
β [°]	99.193(3)	90.350(3)
γ [°]	108.096(2)	90
Volume	717.75(5)	1460.46(17)
Z	2	4
ρ(g cm^{-3})	1.641	1.884
μ/mm^{-1}	1.698	0.173
F(000)	368.0	832.0
Crystal size (mm^3)	0.13 × 0.11 × 0.1	0.13×0.11×0.1
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
Theta range for data collection	7.586 to 136.732	4.272 to 54.954
Index ranges	-7≤h≤7, -11≤k≤11, -14≤l≤14	-24≤h≤24, -11≤k≤11, -9≤l≤11
Reflections collected	8869	8207
Independent reflections	2608 [R_{int} = 0.0453, R_{sigma} = 0.0396]	1679 [R_{int} = 0.0487, R_{sigma} = 0.0327]
Data/restraints/ parameters	2608/2/235	1679/69/145
Goodness-of-fit on F^2	1.026	1.075
Final R indices [I>2σ(I)]	R_1 = 0.0533, wR_2 = 0.1501	R_1 = 0.0434, wR_2 = 0.1068
Final R indexes [all data]	R_1 = 0.0632, wR_2 = 0.1598	R_1 = 0.0661, wR_2 = 0.1292
Largest diff.peak/hole/e Å-3	0.55/-0.37	0.23/-0.22

Crystal	**BDNTT** (193K)	**Na_2BT**·5H_2O
CCDC number	2336281	2336291
Empirical formula	$C_5H_2N_{16}O_8$	$C_4H_{20}N_{16}Na_4O_{10}$
Formula weight	414.23	544.32
Temperature/K	193.00	193.00
Crystal system	monoclinic	triclinic
Space group	C2/c	P-1
a [Å]	18.922(2)	7.1884(8)
b [Å]	8.7592(9)	7.5195(7)
c [Å]	8.6734(8)	21.1688(19)
α [°]	90	94.666(4)
β [°]	90.310(7)	92.681(4)
γ [°]	90	112.464(4)
Volume	1437.6(2)	1050.14(18)
Z	4	2
ρ(g cm^{-3})	1.914	1.721
μ/mm^{-1}	0.176	0.221
F(000)	832.0	560.0
Crystal size (mm^3)	0.12×0.11×0.1	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
Theta range for data collection	4.306 to 54.928	5.814 to 55.03
Index ranges	-24≤h≤21, -11≤k≤11, -11≤l≤11	-9≤h≤9, -9≤k≤9, -27≤l≤27
Reflections collected	7805	16269
Independent reflections	1648 [R_{int} = 0.0626, R_{sigma} = 0.0486]	4774[R_{int} =0.0573, R_{sigma} = 0.0540]
Data/restraints/ parameters	1648/69/136	4774/1/384
Goodness-of-fit on F^2	1.041	1.104
Final R indices [I>2σ(I)]	R_1 = 0.0424, wR_2 = 0.0977	R_1 =0.0427,wR_2 = 0.1075
Final R indexes [all data]	R_1 = 0.0627, wR_2 = 0.1166	R_1 =0.0492, wR_2 =0.1135
Largest diff. peak/hole / e Å-3	0.28/-0.26	0.41/-0.38

Crystal	**NaHBT**·3 H_2O	**K_2BT**
CCDC number	2336298	2336292
Empirical formula	$C_2H_7N_8NaO_3$	$C_2K_2N_8$
Formula weight	214.15	214.30
Temperature/K	193.00	193.00
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12$	C2/m
a [Å]	22.6230(16)	10.4558(9)
b [Å]	32.769(2)	8.9261(6)
c [Å]	3.5078(3)	3.5674(3)
α [°]	90	90
β [°]	90	93.355(3)
γ [°]	90	90
Volume	2600.5(3)	332.37(5)
Z	12	2
ρ(g cm^{-3})	1.641	2.141
μ/mm^{-1}	1.671	1.372
F(000)	1320.0	212.0
Crystal size (mm^3)	0.13 × 0.12 × 0.11	0.12 × 0.09 × 0.08
Radiation	CuKα (λ = 1.54178)	MoKα (λ = 0.71073)
Theta range for data collection	4.746 to 137.278	6.006 to 54.914
Index ranges	-23≤h≤27, -38≤k≤39, -3≤l≤4	-13≤h≤13, -11≤k≤11, -4≤l≤4
Reflections collected	13631	7030
Independent reflections	4706 [R_{int} = 0.0917, R_{sigma} = 0.0906]	406[R_{int} =0.0626, R_{sigma} = 0.0184]
Data/restraints/ parameters	4706/3/397	406/0/30
Goodness-of-fit on F^2	1.050	1.149
Final R indices [I>2σ(I)]	R_1 = 0.0714, wR_2 = 0.1852	R_1 =0.0258, wR_2 = 0.0654
Final R indexes [all data]	R_1 = 0.1034, wR_2 = 0.2043	R_1 =0.0278, wR_2 = 0.0672
Largest diff. peak/hole /e Å-3	0.43/-0.40	0.42/-0.30

Crystal	**H_2BT**
CCDC number	2336252
Empirical formula	$C_2H_2N_8$
Formula weight	138.12
Temperature/K	193.00
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	4.9542(5)
b [Å]	6.3958(6)
c [Å]	8.5251(8)
α [°]	90
β [°]	98.967(7)
γ [°]	90
Volume	266.83(4)
Z	2
ρ(g cm^{-3})	1.719
μ/mm^{-1}	1.173
F(000)	140.0
Crystal size (mm^3)	0.13 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54178)
Theta range for data collection	17.41 to 136.372
Index ranges	-5≤h≤5, 0≤k≤7, 0≤l≤10
Reflections collected	468
Independent reflections	468 [R_{int} = ?, R_{sigma} = 0.0431]
Data/restraints/ parameters	468 [R_{int} = ?, R_{sigma} = 0.0431]
Goodness-of-fit on F^2	0.971
Final R indices [I>2σ(I)]	R_1 = 0.0791, wR_2 = 0.1826
Final R indexes [all data]	R_1 = 0.0887, wR_2 = 0.1871
Largest diff. peak/hole / e Å-3	0.56/-0.41

Table S2. Selected bond lengths [Å] and angles [°] for **Mg_2TT**·7 H_2O

parameter	Å	parameter	Å
Mg1-O7	2.0274(19)	O2-H2B	0.86
Mg1-O4	2.061(2)	N1-N2	1.346(3)
Mg1-O1	2.053(2)	N1-C1	1.335(3)
Mg1-O3	2.122(2)	N2-N3	1.309(3)
Mg1-O5	2.068(2)	N3-N4	1.338(3)
Mg1-O6	2.0435(19)	N4-C1	1.317(3)
O1-H1A	0.85(5)	N5-C1	1.418(3)
O1-H1B	0.78(5)	N5-N6	1.336(3)
O3-H3A	0.85(4)	N5-N7	1.333(3)
O3-H3B	0.81(5)	N6-C2	1.335(3)
O4-H4B	0.86	N7-N8	1.315(3)
O4-H4A	0.86	N8-C2	1.350(3)
O5-H5A	0.86	N9-N10	1.342(3)
O5-H5B	0.86	N9-C3	1.333(3)
O6-H6B	0.86	N10-N11	1.314(3)
O6-H6A	0.86	N11-N12	1.350(3)
O7-H7A	0.86	N12-C3	1.333(3)
O7-H7B	0.86	C2-C3	1.442(3)
O2-H2A	0.86		

parameter	Å	parameter	Å
O3-Mg1-O7	86.34(8)	H6A-O6-H6B	104
O4-Mg1-O5	86.74(8)	Mg1-O6-H6B	127
O4-Mg1-O6	90.37(8)	Mg1-O7-H7A	127
O4-Mg1-O7	88.60(8)	Mg1-O7-H7B	128
O5-Mg1-O6	92.85(8)	H7A-O7-H7B	104
O5-Mg1-O7	92.02(8)	H2A-O2-H2B	105

O6-Mg1-O7	174.96(9)	N2-N1-C1	102.84(18)
O3-Mg1-O5	174.91(9)	N1-N2-N3	109.78(19)
O1-Mg1-O3	92.19(9)	N2-N3-N4	109.99(19)
O1-Mg1-O4	177.39(9)	N3-N4-C1	103.57(18)
O1-Mg1-O5	92.60(8)	N6-N5-N7	114.10(19)
O1-Mg1-O6	92.19(8)	N6-N5-C1	123.19(18)
O1-Mg1-O7	88.91(8)	N7-N5-C1	122.70(19)
O3-Mg1-O4	88.41(8)	N5-N6-C2	100.95(18)
O3-Mg1-O6	88.70(8)	N5-N7-N8	105.70(18)
Mg1-O1-H1A	122(3)	N7-N8-C2	106.55(19)
Mg1-O1-H1B	126(3)	N10-N9-C3	104.22(19)
H1A-O1-H1B	106(5)	N9-N10-N11	109.74(18)
Mg1-O3-H3A	117(3)	N10-N11-N12	109.50(19)
Mg1-O3-H3B	119(4)	N11-N12-C3	103.96(18)
H3A-O3-H3B	104(5)	N1-C1-N4	113.8(2)
Mg1-O4-H4A	109	N1-C1-N5	122.26(19)
Mg1-O4-H4B	110	N4-C1-N5	123.90(19)
H4A-O4-H4B	104	N8-C2-C3	124.2(2)
Mg1-O5-H5B	109	N6-C2-N8	112.69(19)
H5A-O5-H5B	104	N6-C2-C3	123.15(19)
Mg1-O5-H5A	110	N9-C3-N12	112.6(2)
Mg1-O6-H6A	128	N9-C3-C2	122.9(2)

Table S3. Torsion angles [°] of **Mg_2TT**·7 H_2O

parameter	Å	parameter	Å
C1-N1-N2-N3	-0.4(3)	N7-N5-C1-N4	-172.5(3)
N2-N1-C1-N4	0.2(3)	N5-N6-C2-N8	0.0(3)
N2-N1-C1-N5	-178.4(2)	N5-N6-C2-C3	-180.0(2)
N1-N2-N3-N4	0.4(3)	N5-N7-N8-C2	-0.7(3)

N2-N3-N4-C1	-0.3(3)	N7-N8-C2-N6	0.5(3)
N3-N4-C1-N1	0.0(3)	N7-N8-C2-C3	-179.6(3)
N3-N4-C1-N5	178.6(2)	C3-N9-N10-N11	0.1(3)
N7-N5-N6-C2	-0.4(3)	N10-N9-C3-N12	-0.1(3)
C1-N5-N6-C2	-179.1(2)	N10-N9-C3-C2	-179.3(3)
N6-N5-N7-N8	0.7(3)	N9-N10-N11-N12	0.0(3)
C1-N5-N7-N8	179.4(2)	N10-N11-N12-C3	0.0(3)
N6-N5-C1-N1	-175.4(2)	N11-N12-C3-N9	0.1(3)
N6-N5-C1-N4	6.1(4)	N11-N12-C3-C2	179.3(3)
N7-N5-C1-N1	6.0(4)	N6-C2-C3-N9	-5.5(4)
N6-C2-C3-N12	175.3(3)	N8-C2-C3-N12	-4.7(5)
N8-C2-C3-N9	174.5(3)		

Table S2. Selected bond lengths [Å] and angles [°] for **BDNTT**

parameter	**Å**	**parameter**	**Å**
O1-N10	1.196(3)	N5-N6	1.300(2)
O2-N10	1.205(2)	N5-C2	1.354(3)
O3-N9	1.198(3)	N6-N7	1.330(2)
O4-N9	1.216(2)	N7-N8	1.333(2)
N1-N2	1.30(2)	N7-C3	1.415(2)
N1-C1	1.34(3)	N8-C2	1.312(2)
N2-N3	1.36(2)	N9-C3	1.510(3)
N3-N4	1.3132	N10-C3	1.524(3)
N3-C2_a	1.403(18)	C1-C2	1.44(3)
N4-C1	1.3679	C3-H3	0.98

parameter	**Å**	**parameter**	**Å**
N2-N1-C1	107.2(15)	O2-N10-C3	118.51(17)

N1-N2-N3	105.0(13)	N1-C1-N4	112.47
N2-N3-N4	115	N1-C1-C2	126(2)
N2-N3-C2_a	120.2(14)	N4-C1-C2	121.19
N4-N3-C2_a	124.13	N5-C2-N8	113.72(17)
N3-N4-C1	99.57	N5-C2-C1	124.9(11)
N6-N5-C2	106.14(16)	N3_a-C2-N5	121.9(7)
N5-N6-N7	105.31(16)	N8-C2-C1	121.3(11)
N6-N7-N8	114.76(15)	N3_a-C2-N8	124.3(7)
N6-N7-C3	121.95(15)	N3_a-C2-C1	6.6(13)
N8-N7-C3	123.28(15)	N7-C3-N9	112.83(17)
N7-N8-C2	100.06(15)	N7-C3-N10	108.20(14)
O3-N9-O4	128.2(2)	N9-C3-N10	107.98(14)
O3-N9-C3	117.65(17)	N7-C3-H3	109
O4-N9-C3	114.10(19)	N9-C3-H3	109
O1-N10-O2	126.7(2)	N10-C3-H3	109
O1-N10-C3	114.78(19)		

Table S3. Torsion angles [°] of **BDNTT**

parameter	**Å**	**parameter**	**Å**
C1-N1-N2-N3	-2(2)	C3-N7-N8-C2	-178.88(17)
N2-N1-C1-N4	6.76	N6-N7-C3-N9	-102.0(2)
N2-N1-C1-C2	-179.9(19)	N6-N7-C3-N10	138.60(17)
N1-N2-N3-N4	-4	N8-N7-C3-N9	76.8(2)
N1-N2-N3-C2_a	-175.1(15)	N8-N7-C3-N10	-42.6(2)
N2-N3-N4-C1	7.52	N7-N8-C2-N5	0.1(2)
C2_a-N3-N4-C1	178.21	N7-N8-C2-C1	175.7(12)
N2-N3-C2_a-N5_a	-167.6(12)	N7-N8-C2-N3_a	-177.3(10)
N2-N3-C2_a-N8_a	10(2)	O3-N9-C3-N7	-12.0(2)
N2-N3-C2_a-C1_a	74(11)	O3-N9-C3-N10	107.5(2)

N4-N3-C2_a-N5_a	22.17	O4-N9-C3-N7	166.20(17)
N4-N3-C2_a-N8_a	-160.58	O4-N9-C3-N10	-74.3(2)
N4-N3-C2_a-C1_a	-96.13	O1-N10-C3-N7	-60.3(2)
N3-N4-C1-N1	-8.5	O1-N10-C3-N9	177.31(17)
N3-N4-C1-C2	177.8	O2-N10-C3-N7	118.90(19)
C2-N5-N6-N7	0.2(2)	O2-N10-C3-N9	-3.5(2)
N6-N5-C2-N8	-0.2(2)	N1-C1-C2-N5	-176.2(16)
N6-N5-C2-C1	-175.6(13)	N1-C1-C2-N8	9(3)
N6-N5-C2-N3_a	177.3(10)	N1-C1-C2-N3_a	-111(12)
N5-N6-N7-N8	-0.1(2)	N4-C1-C2-N5	-3.38
N5-N6-N7-C3	178.79(17)	N4-C1-C2-N8	-178.44
N6-N7-N8-C2	0.0(2)	N4-C1-C2-N3_a	62.23

Table S4. Hydrogen bonds of **BDNTT**

D-H···A	**d(D-H)/Å**	**d(H···A)/ Å**	**d(D···A)/ Å**	**<(DHA)/°**
C3-H3..O1	0.98	2.59	3.479(3)	150
C3-H3..O2	0.98	2.55	3.324(3)	136

Table S5. Selected bond lengths [Å] and angles [°] for **Na_2BT•5H_2O**

parameter	**Å**	**parameter**	**Å**
Na1-O1	2.3542(14)	O3-H3A	0.84(3)
Na1-O2	2.3908(15)	O3-H3B	0.78(3)
Na1-O3	2.4465(16)	O4-H4A	0.90(3)
Na1-N14	2.4249(14)	O4-H4B	0.87(3)
Na1-O1_a	2.3709(15)	O5-H5A	0.82(2)
Na1-N9_a	2.4586(14)	O5-H5B	0.81(3)
Na2-O2	2.3205(16)	O6-H6B	0.85(3)
Na2-O3	2.4460(15)	O6-H6A	0.79(3)
Na2-O4	2.6157(16)	O7-H7A	0.87

Na2-O5	2.4264(16)	O7-H7B	0.84(3)
Na2-O6	2.3344(16)	O8-H8B	0.79(3)
Na2-N10_a	2.5568(15)	O8-H8A	0.85(3)
Na3-O4	2.3613(16)	O9-H9B	0.84(3)
Na3-O6	2.4944(14)	O9-H9A	0.80(3)
Na3-O7	2.3164(15)	O10-H10A	0.87(3)
Na3-O8	2.4505(16)	O10-H10B	0.81(3)
Na3-O9	2.3730(16)	N1-N2	1.3467(18)
Na3-N2_b	2.6123(15)	N1-C1	1.3309(19)
Na4-O8	2.4829(16)	N2-N3	1.3101(19)
Na4-O9	2.3744(15)	N3-N4	1.3486(18)
Na4-O10	2.3456(16)	N4-C1	1.3358(19)
Na4-N5	2.4257(15)	N5-N8	1.3451(18)
Na4-O10_b	2.3854(15)	N5-C2	1.331(2)
Na4-N1_b	2.4190(15)	N6-C2	1.3360(19)
O1-H1A	0.83(2)	N6-N7	1.3447(18)
O1-H1B	0.81(3)	N7-N8	1.313(2)
O2-H2A	0.84(3)	N9-N10	1.3430(18)
O2-H2B	0.82(3)	N9-C4	1.3333(19)
N10-N11	1.3090(19)	N14-N15	1.3410(18)
N11-N12	1.3459(18)	N14-C3	1.3406(19)
N12-C4	1.3381(19)	N15-N16	1.3149(19)
N13-C3	1.3352(19)	C1-C2	1.465(2)
N13-N16	1.3482(18)	C3-C4	1.465(2)

parameter	**Å**	**parameter**	**Å**
Na4_b-O10-H10A	119.4(17)	Na2_a-N10-N9	120.62(9)
Na4_b-O10-H10B	113.7(19)	N10-N11-N12	109.84(12)
Na4_b-N1-C1	143.39(10)	N11-N12-C4	104.14(12)

N2-N1-C1	104.83(12)	N16-N13-C3	104.64(12)
Na4_b-N1-N2	110.50(9)	Na1-N14-C3	142.12(11)
Na3_b-N2-N3	134.91(10)	Na1-N14-N15	111.08(9)
N1-N2-N3	109.34(12)	N15-N14-C3	104.68(12)
Na3_b-N2-N1	114.81(9)	N14-N15-N16	109.66(12)
N2-N3-N4	109.58(12)	N13-N16-N15	109.39(12)
N3-N4-C1	104.45(12)	N1-C1-N4	111.80(13)
Na4-N5-C2	147.05(11)	N1-C1-C2	124.21(13)
N8-N5-C2	104.76(12)	N4-C1-C2	124.00(13)
Na4-N5-N8	104.28(9)	N5-C2-N6	111.97(13)
N7-N6-C2	104.30(12)	N5-C2-C1	123.79(13)
N6-N7-N8	109.76(12)	N6-C2-C1	124.23(13)
N5-N8-N7	109.21(12)	N13-C3-N14	111.63(13)
N10-N9-C4	104.63(12)	N13-C3-C4	123.89(13)
Na1_a-N9-C4	147.79(10)	N14-C3-C4	124.48(13)
Na1_a-N9-N10	105.31(9)	N9-C4-N12	111.91(13)
N9-N10-N11	109.48(12)	N9-C4-C3	124.14(13)
Na2_a-N10-N11	129.67(10)	N12-C4-C3	123.95(13)

Table S6. Torsion angles [°] of **Na_2BT•5H_2O**

parameter	Å	parameter	Å
C1-N1-N2-N3	-0.09(18)	C4-N9-N10-Na2_a	-174.99(10)
C1-N1-N2-Na3_b	170.47(10)	N10-N9-C4-C3	-179.67(15)
Na4_b-N1-N2-N3	-170.33(11)	N10-N9-C4-N12	-0.13(18)
Na4_b-N1-N2-Na3_b	0.22(13)	Na1_a-N9-C4-N12	-158.04(17)
N2-N1-C1-N4	0.0(2)	N9-N10-N11-N12	0.18(19)
Na4_b-N1-C1-N4	164.57(15)	Na2_a-N10-N11-N12	174.55(11)
N2-N1-C1-C2	179.44(15)	N10-N11-N12-C4	-0.25(18)
Na4_b-N1-C1-C2	-16.0(3)	N11-N12-C4-C3	179.77(15)

Na3_b-N2-N3-N4	-167.72(12)	N11-N12-C4-N9	0.24(18)
N1-N2-N3-N4	0.14(19)	N16-N13-C3-C4	-179.38(15)
N2-N3-N4-C1	-0.13(19)	N16-N13-C3-N14	0.35(18)
N3-N4-C1-N1	0.08(19)	C3-N13-N16-N15	-0.39(18)
N3-N4-C1-C2	-179.36(15)	Na1-N14-N15-N16	-167.34(11)
N8-N5-C2-C1	-179.91(15)	C3-N14-N15-N16	-0.08(18)
Na4-N5-C2-N6	-151.31(17)	N15-N14-C3-C4	179.56(15)
Na4-N5-N8-N7	164.53(11)	Na1-N14-C3-N13	160.24(14)
C2-N5-N8-N7	0.26(18)	N15-N14-C3-N13	-0.18(18)
N8-N5-C2-N6	-0.20(19)	Na1-N14-C3-C4	-20.0(3)
Na4-N5-C2-C1	29.0(3)	N14-N15-N16-N13	0.30(19)
N7-N6-C2-N5	0.07(19)	N4-C1-C2-N5	175.38(16)
N7-N6-C2-C1	179.77(15)	N1-C1-C2-N5	-4.0(3)
C2-N6-N7-N8	0.10(19)	N4-C1-C2-N6	-4.3(3)
N6-N7-N8-N5	-0.23(19)	N1-C1-C2-N6	176.33(16)
Na1_a-N9-N10-N11	167.97(11)	N14-C3-C4-N12	179.32(16)
Na1_a-N9-N10-Na2_a	-6.99(13)	N13-C3-C4-N9	178.51(16)
Na1_a-N9-C4-C3	22.4(3)	N13-C3-C4-N12	-1.0(3)
C4-N9-N10-N11	-0.03(19)	N14-C3-C4-N9	-1.2(3)

Table S8. Selected bond lengths [Å] and angles [°] for **K_2BT**

parameter	Å	parameter	Å
N1-N2	1.347(2)	N2-N2_a	1.321(2)
N1-C1	1.334(2)	C1-C1_b	1.453(4)

parameter	Å	parameter	Å
N2-N1-C1	104.10(15)	N1-C1-C1_b	123.64(12)
N1-N2-N2_a	109.54(14)	N1_a-C1-C1_b	123.64(12)
N1-C1-N1_a	112.7(2)		

Table S9. Torsion angles [º] of **K_2BT**

parameter	Å	parameter	Å
C1-N1-N2-N2_a	0.1(2)	N2-N1-C1-C1_b	179.97(9)
N2-N1-C1-N1_a	-0.03(17)	N1-N2-N2_a-N1_a	-0.1(2)

Table S11. Selected bond lengths [Å] and angles [º] for **H_2BT**

parameter	Å	parameter	Å
N1-N2	1.356(6)	N4-C1	1.3297
N1-C1	1.315(6)	N4-H4	0.97
N2-N3	1.283(7)	C1-C1_a	1.443(6)
N3-N4	1.3709		

parameter	Å	parameter	Å
N2-N1-C1	108.5(4)	C1-N4-H4	154
N1-N2-N3	106.7(4)	N4-C1-C1_a	125.5
N2-N3-N4	110.71	N1-C1-N4	109.21
N3-N4-C1	104.91	N1-C1-C1_a	125.3(4)
N3-N4-H4	101		

Table S12. Torsion angles [º] of **H_2BT**

parameter	Å	parameter	Å
C1-N1-N2-N3	0.3(5)	N3-N4-C1-C1_a	-177.86
N2-N1-C1-C1_a	178.0(4)	N1-C1-C1_a-N1_a	180.0(5)
N2-N1-C1-N4	-0.86	N1-C1-C1_a-N4_a	1.32
N1-N2-N3-N4	0.3	N4-C1-C1_a-N1_a	-1.32
N2-N3-N4-C1	-0.81	N4-C1-C1_a-N4_a	-180
N3-N4-C1-N1	1		

Table S7. Hydrogen bonds of **H_2BT**

D-H···A	d(D-H)/Å	d(H···A)/ Å	d(D···A)/ Å	<(DHA)/°
N4-H4..N1	0.97	1.86	2.8162	168

Table S13. Selected bond lengths [Å] and angles [°] for **NaHBT•**$3H_2O$

parameter	Å	parameter	Å
Na1-O1	2.399(7)	N1-N2	1.300(10)
Na1-O2	2.411(7)	N1-N4	1.343(9)
Na1-O3	2.348(7)	N2-N3	1.342(9)
Na1-N2	2.675(7)	N3-C1	1.342(9)
Na1-O1_b	2.407(7)	N4-C1	1.326(10)
Na1-O3_b	2.371(7)	N5-N6	1.333(9)
Na2-O4_c	2.393(6)	N5-C2	1.343(10)
Na2-O6_d	2.412(6)	N6-N7	1.309(10)
Na2-O6	2.391(6)	N7-N8	1.327(9)
Na2-O4	2.340(6)	N8-C2	1.344(9)
Na2-O5	2.439(7)	N5-H5	0.88
Na2-N15	2.704(7)	N9-N10	1.341(9)
Na3-O7_f	2.455(7)	N9-C3	1.345(10)
Na3-O9_e	2.378(6)	N10-N11	1.304(10)
Na3-O7	2.384(7)	N11-N12	1.334(9)
Na3-O8	2.409(7)	N12-C3	1.330(9)
Na3-O9	2.384(6)	N13-C4	1.334(10)
Na3-N24	2.686(7)	N13-N14	1.360(9)
N16-C4	1.334(9)	N14-N15	1.306(10)
N9-H9	0.88	N15-N16	1.346(9)
N17-C5	1.336(9)	N21-N24	1.357(9)
N17-N18	1.351(9)	N22-C6	1.321(10)

N18-N19	1.311(10)	N22-N23	1.345(9)
N19-N20	1.334(9)	N23-N24	1.286(10)
N20-C5	1.328(10)	N20-H20	0.88
N21-C6	1.330(9)	C1-C2	1.435(9)
C5-C6	1.472(9)	C3-C4	1.444(9)

parameter	**Å**	**parameter**	**Å**
N2-N1-N4	111.2(6)	N6-N5-H5	127
N1-N2-N3	106.6(6)	N10-N9-C3	104.6(6)
Na1-N2-N1	106.6(5)	N9-N10-N11	109.4(6)
Na1-N2-N3	144.6(5)	N10-N11-N12	109.9(6)
N2-N3-C1	107.9(6)	N11-N12-C3	105.2(6)
N1-N4-C1	105.6(6)	N14-N13-C4	105.3(6)
N6-N5-C2	105.8(6)	N13-N14-N15	110.9(6)
N5-N6-N7	108.4(6)	Na2-N15-N16	145.3(5)
N6-N7-N8	111.0(6)	Na2-N15-N14	106.6(5)
N7-N8-C2	104.4(6)	N14-N15-N16	106.2(6)
C2-N5-H5	127	N15-N16-C4	108.9(6)
C3-N9-H9	128	N3-C1-N4	108.8(6)
N10-N9-H9	128	N8-C2-C1	124.9(6)
N18-N17-C5	103.8(6)	N5-C2-C1	124.8(6)
N17-N18-N19	109.9(6)	N5-C2-N8	110.4(6)
N18-N19-N20	109.2(6)	N9-C3-C4	123.6(6)
N19-N20-C5	105.2(6)	N12-C3-C4	125.5(6)
N24-N21-C6	107.2(6)	N9-C3-N12	110.9(6)
N23-N22-C6	105.0(6)	N16-C4-C3	126.3(6)
N22-N23-N24	111.7(6)	N13-C4-N16	108.7(6)
Na3-N24-N21	145.3(5)	N13-C4-C3	125.1(6)
N21-N24-N23	106.5(6)	N17-C5-N20	112.0(6)

Na3-N24-N23	106.2(5)	N17-C5-C6	124.2(6)
N19-N20-H20	127	N20-C5-C6	123.8(6)
C5-N20-H20	127	N21-C6-N22	109.7(6)
N3-C1-C2	124.2(6)	N21-C6-C5	124.3(6)
N4-C1-C2	127.0(6)	N22-C6-C5	126.0(6)

Table S14. Torsion angles [°] of **NaHBT**•$3H_2O$

parameter	Å	parameter	Å
N2-N1-N4-C1	-1.4(8)	N15-N16-C4-C3	-179.0(7)
N4-N1-N2-Na1	-166.0(5)	N15-N16-C4-N13	1.1(8)
N4-N1-N2-N3	1.5(8)	N18-N17-C5-C6	179.6(7)
Na1-N2-N3-C1	158.0(7)	C5-N17-N18-N19	-0.2(8)
N1-N2-N3-C1	-1.0(8)	N18-N17-C5-N20	0.8(8)
N2-N3-C1-N4	0.2(8)	N17-N18-N19-N20	-0.5(9)
N2-N3-C1-C2	-176.3(7)	N18-N19-N20-C5	1.0(8)
N1-N4-C1-C2	177.1(7)	N19-N20-C5-C6	-179.9(7)
N1-N4-C1-N3	0.7(8)	N19-N20-C5-N17	-1.1(8)
N6-N5-C2-N8	0.1(8)	N24-N21-C6-N22	1.6(8)
C2-N5-N6-N7	0.0(8)	C6-N21-N24-N23	-0.9(8)
N6-N5-C2-C1	179.2(7)	C6-N21-N24-Na3	-160.8(7)
N5-N6-N7-N8	-0.1(9)	N24-N21-C6-C5	179.3(6)
N6-N7-N8-C2	0.1(8)	N23-N22-C6-N21	-1.7(8)
N7-N8-C2-N5	-0.1(8)	C6-N22-N23-N24	1.1(8)
N7-N8-C2-C1	-179.2(7)	N23-N22-C6-C5	-179.3(7)
N10-N9-C3-C4	179.4(7)	N22-N23-N24-N21	-0.2(8)
N10-N9-C3-N12	-0.1(8)	N22-N23-N24-Na3	168.1(5)
C3-N9-N10-N11	-0.7(8)	N3-C1-C2-N5	-12.0(12)
N9-N10-N11-N12	1.2(9)	N4-C1-C2-N8	-8.9(12)
N10-N11-N12-C3	-1.2(8)	N3-C1-C2-N8	167.0(7)

N11-N12-C3-C4	-178.7(7)	N4-C1-C2-N5	172.1(7)
N11-N12-C3-N9	0.8(8)	N9-C3-C4-N13	171.3(7)
C4-N13-N14-N15	0.4(8)	N12-C3-C4-N16	170.9(7)
N14-N13-C4-N16	-0.9(8)	N9-C3-C4-N16	-8.6(12)
N14-N13-C4-C3	179.2(7)	N12-C3-C4-N13	-9.3(12)
N13-N14-N15-N16	0.3(8)	N17-C5-C6-N21	-165.8(7)
N13-N14-N15-Na2	-168.2(5)	N17-C5-C6-N22	11.5(12)
Na2-N15-N16-C4	159.6(7)	N20-C5-C6-N21	12.8(11)
N14-N15-N16-C4	-0.9(8)	N20-C5-C6-N22	-169.9(7)

Table S15. Hydrogen bonds of **NaHBT•**$3H_2O$

D-H···A	**d(D-H)/Å**	**d(H···A)/ Å**	**d(D···A)/ Å**	**<(DHA)/°**
N5--H5..N16	0.88	1.97	2.733(10)	144
N9--H9..N3	0.88	2	2.771(9)	146
N20--H20..N21	0.88	1.97	2.741(9)	146

Theoretical calculations were performed by using the Gaussian 09 (Revision E.01) suite of programs.[3] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP) functional with the 6-311+G** basis set.[4] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M. All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

The predictions of heat of formation (HOF) adopt the hybrid DFT-B3LYP methods with 6-311+G** basis set via designed isodesmic reactions. The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of the title compounds are in Scheme S1. The change of enthalpy for the reactions at 298 K can be expressed as

$$\Delta H_{298} = \sum \Delta_f H_P - \sum \Delta_f H_R \qquad (1)$$

Where $\sum \Delta_f H_P$ and $\sum \Delta_f H_R$ are the HOF of reactants and products at 298 K, respectively, and ΔH_{298} can be calculated using the following expression:

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \qquad (2)$$

Where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔHT is thermal correction from 0 to 298 K. The Δ(PV) value in eq (2) is the PV work term. It equals Δ(nRT) for the reactions of ideal gas. For the isodesmic reaction, Δn = 0, so Δ(PV) = 0. On the left side of Eq. (1), apart from target compound, all the others are called reference compounds. The HOF of reference compounds is available from the experiments.

For energetic salts, the solid-phase heats of formation are calculated based on a Born-Haber energy cycle. The heat of formation of a salt can be simplified by the formula given in Equation (1):

$$\Delta H_f^0(\text{salt},298\ \text{K}) = \Delta H_f^0(\text{cation},298\ \text{K}) + \Delta H_f^0(\text{anion},298\ \text{K}) - \Delta H_L \quad (1)$$

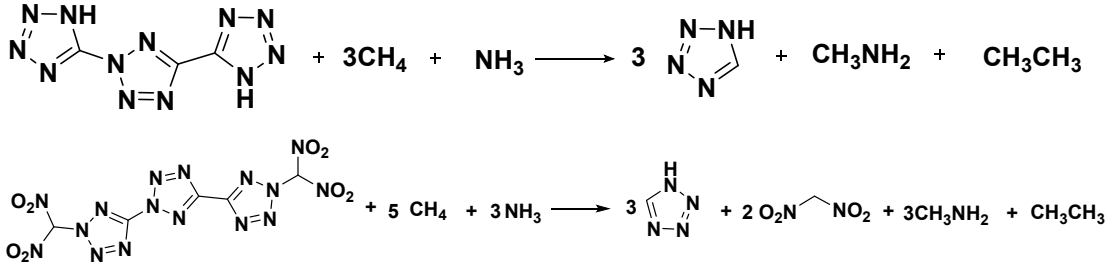
Where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [5] [Eq. (2)]

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

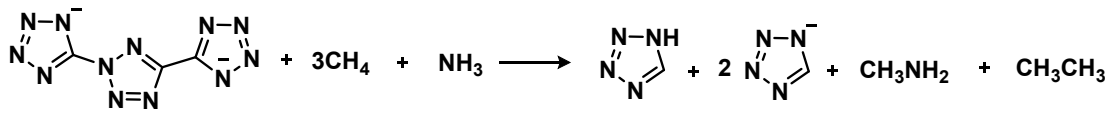
where n_M and n_X depend on the nature of the ions, Mp^+ and Xq^-, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions.The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

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

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.[6,7]

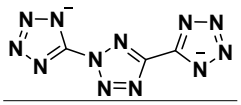
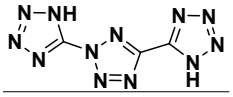
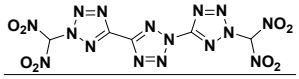


Scheme S1. Isodesmic reactions of neutral compounds.



Scheme S2. Isodesmic reactions of ionic compounds.

Table S19. Ab initio computational values of small molecules used in isodesmic and tautomeric reactions.

Compound	E_0[a]	ZPE[b]	H_T[c]	HOF[d]
CH_4	-40.53	112.26	10.04	-74.6[e]
NH_3	-56.58	86.27	10.05	-45.9[e]
CH_3NH_2	-95.89	160.78	11.64	-22.5[e]
CH_3CH_3	-79.86	187.31	11.79	-84[e]
	-258.32	117.69	11.84	334.3
	-257.79	84.91	11.26	175.75
	-771.407	189.3662	26.57794	999.666
	-772.544	255.31	30.62	1140.313
	-1669.33	417.9107	64.79997	1260.852

[a]Total energy calculated by B3LYP/6-311+G**method (a.u);

[b]Zero-point correction (kJ mol^{-1});

[c]Thermal correction to enthalpy (kJ mol^{-1});

[d]Heat of formation (kJ mol^{-1});

[e]Data are from Ref. [D. R. Lide, ed., CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, FL.]

3.References

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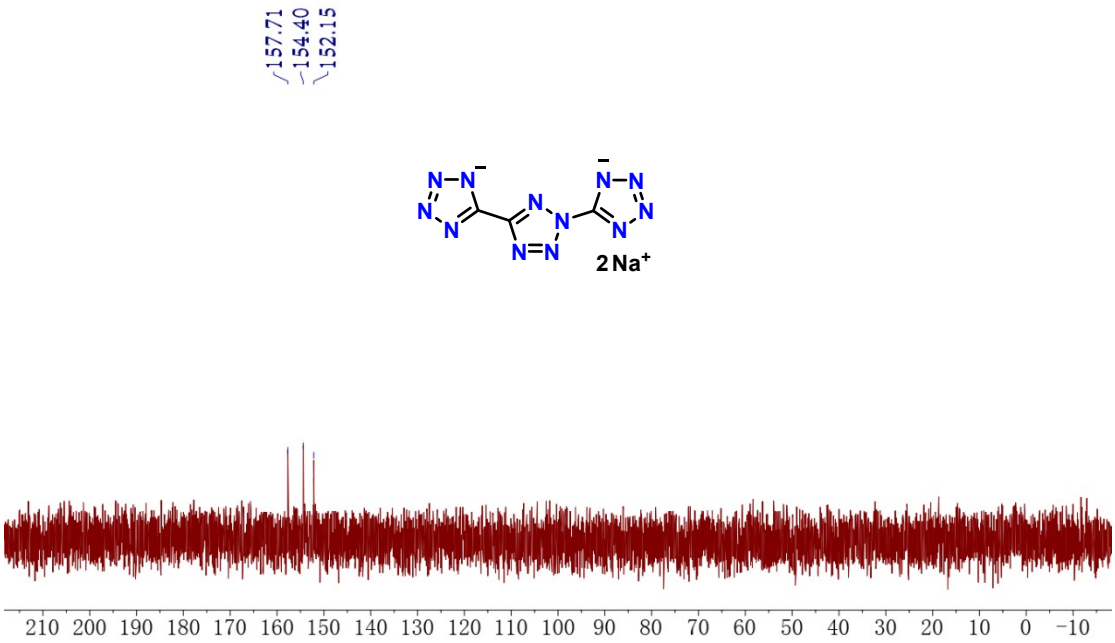

4.^{1}H & ^{13}C NMR Spectra of Na_2TT, H_2TT, BDNTT and compound 1

Figure S3 ^{13}C NMR spectra (300 MHz) of **Na_2TT** in [D_6] H_2O at 25 ^{o}C.

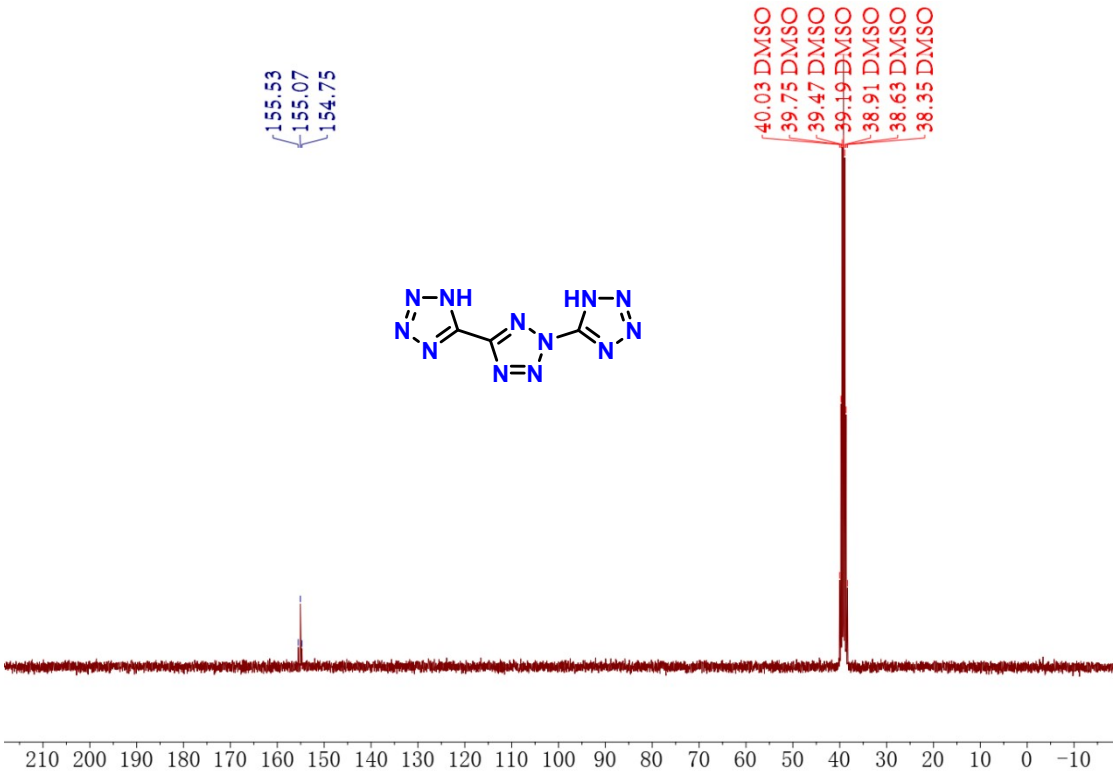

Figure S4 ^{13}C NMR spectra (300 MHz) of **H_2TT** in [D_6] DMSO at 25 °C.

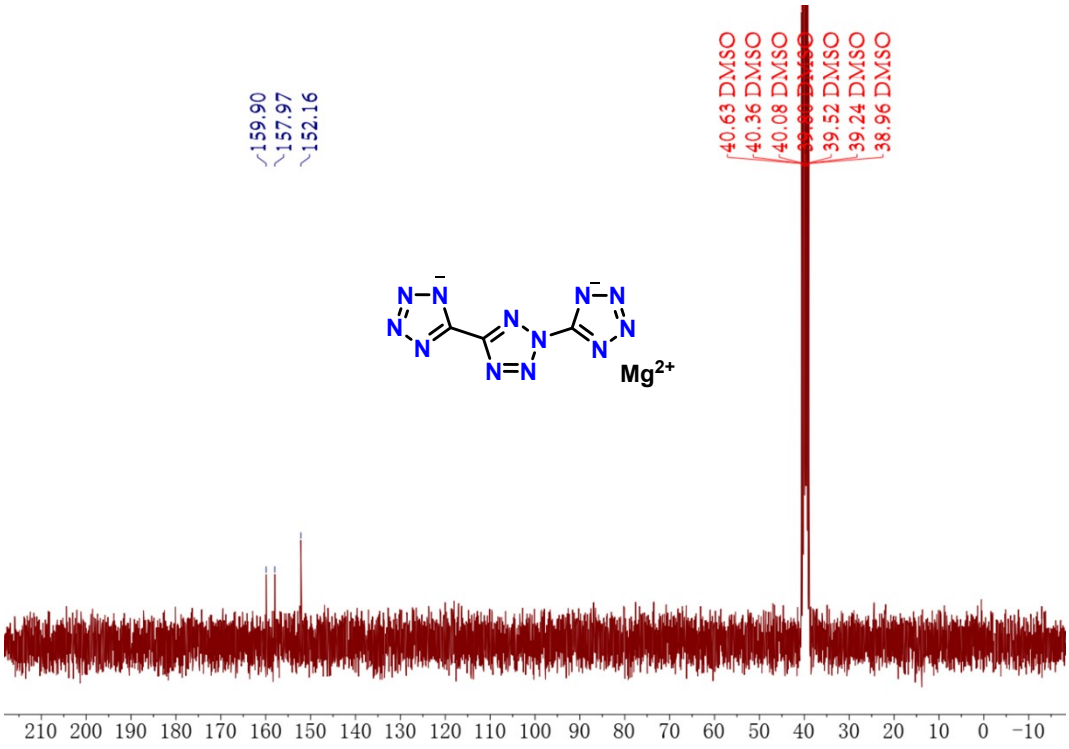

Figure S5 ^{13}C NMR spectra (300 MHz) of **MgTT** in [D_6] DMSO at 25 °C.

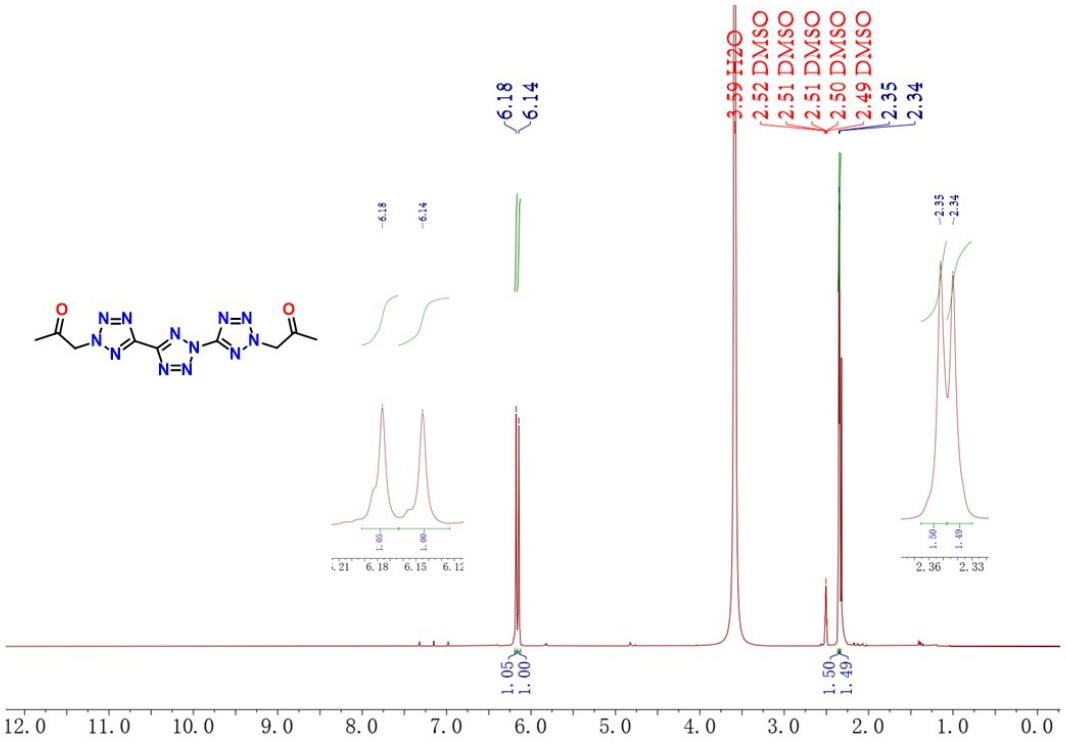

Figure S6 ^{1}H NMR spectra (300 MHz) of **1** in [D_6] DMSO at 25 °C.

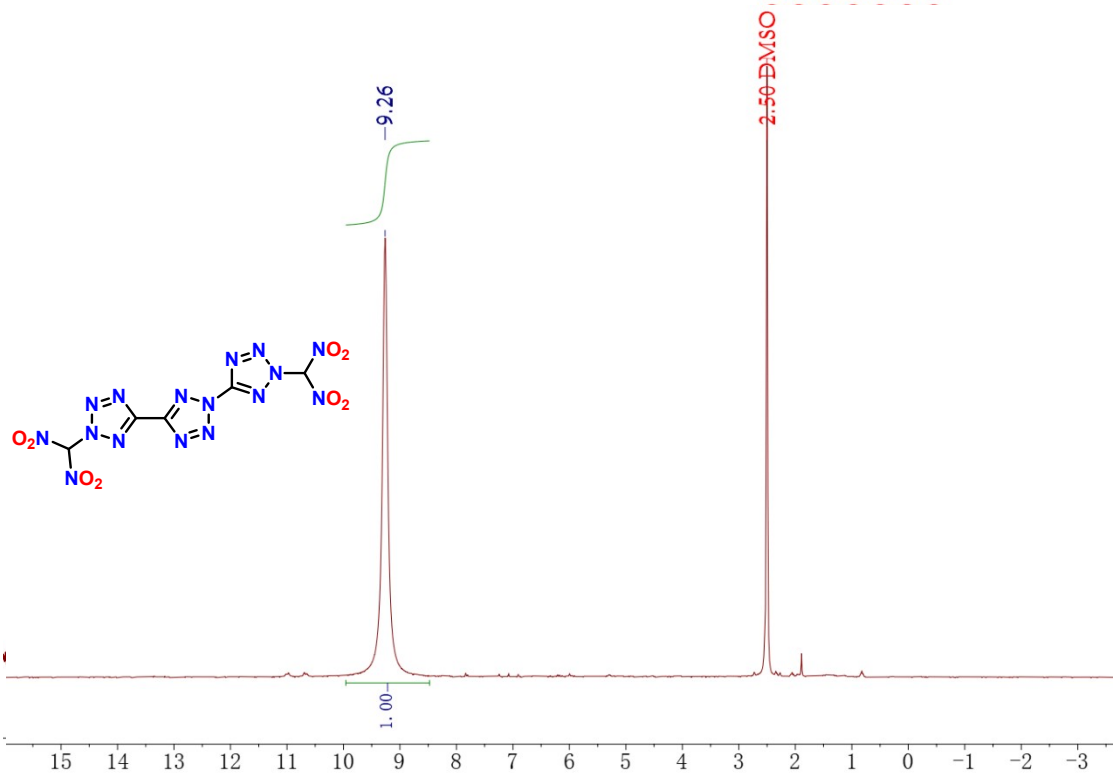

Figure S7 ^{13}C NMR spectra (75 MHz) of **1** in [D_6] DMSO at 25 °C.

Figure S8 ^{1}H NMR spectra (300 MHz) of **BDNTT** in [D_6] DMSO at 25 °C.

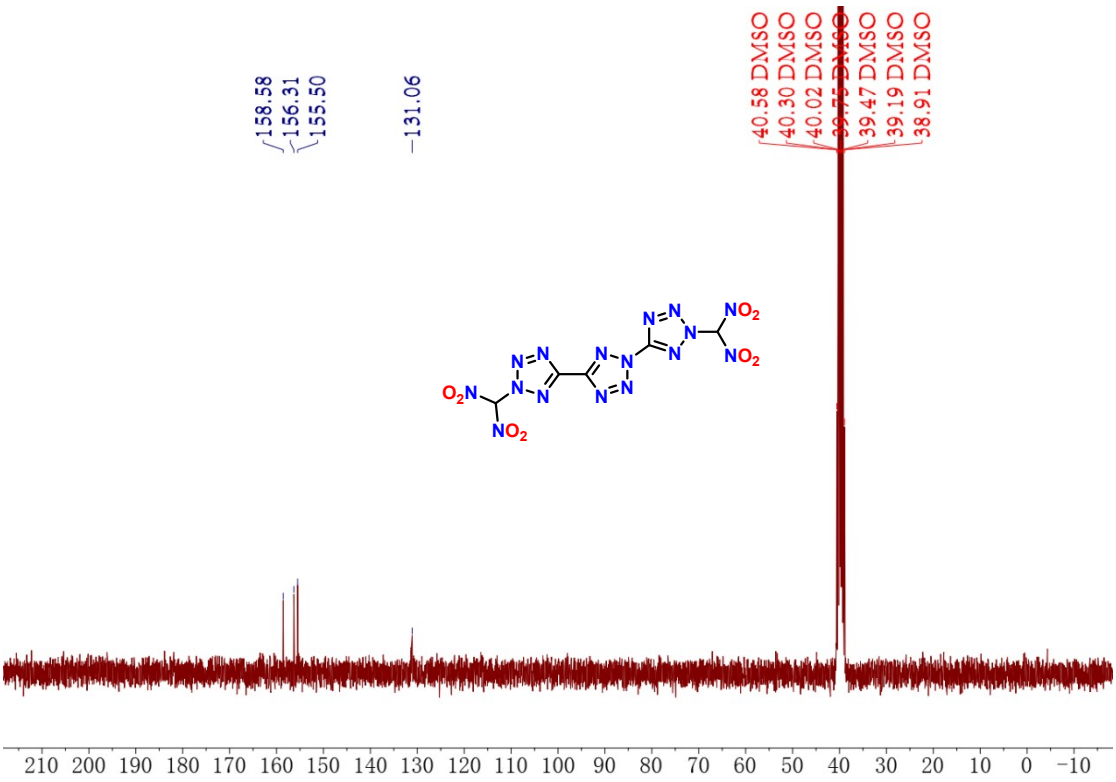

Figure S9 ^{13}C NMR spectra (75 MHz) of **BDNTT** in [D_6] DMSO at 25 °C.