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Supporting Information (SI)

Intramolecular assembly of dinitromethyl and bistetrazole: A strategy for constructing advanced and environmentally friendly high-energy density materials.

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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 1,1'-(1*H*,2'*H*-[5,5'-bistetrazole]-1,2'-diyl)bis(propan-2-one) (1) and 1,1'-(2*H*,2'*H*-[5,5'-bistetrazole]-2,2'-diyl)bis(propan-2-one) (2)

H_2BT (1.38 g, 10.0 mmol) was dissolved in an aqueous solution of KOH (1.12 g, 20 mmol, in 30 mL H_2O), to which was added an acetone solution of bromoacetone (2.72 g, 20 mmol, in 10 mL acetone) and stirred at room temperature for 12 h. The mixture was filtered and the filter cake was washed with acetone, and water and dried to give a white powder solid product **2** (0.8 g, 66%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.11 (s), 2.33 (s) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 199.95, 155.68, 62.02, 27.66 ppm. IR (KBr, v/cm^{-1}): v = 1780, 1777, 1424, 1386, 1338, 1276, 1165, 1154, 1107, 1073, 828, 753, 522 cm^{-1}; Elemental analysis calcd (%) for $C_8H_{10}N_8O_2$ (250.09): C: 38.40, H: 4.03, N: 44.78 %; Found (%): C: 38.68, H: 3.96, N: 44.95 %.

The filtrate was concentrated to about 10 mL by spinning under reduced pressure, filtered and washed with water to give a soft, glutinous, rice-white solid product **1** (1.60 g, 33%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 6.14 (s), 5.99 (s), 2.35 (s), 2.33 (s) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 199.99, 199.63, 153.24, 145.77, 62.21, 58.28, 27.66, 27.54 ppm. IR (KBr, v/cm^{-1}): v = 1798, 1784, 1389, 1367, 1358, 1344, 1251, 1167, 1152, 1073, 866, 762, 549 cm^{-1}; Elemental analysis calcd (%) for $C_8H_{10}N_8O_2$ (250.09): C: 38.40, H: 4.03, N: 44.78 %; Found (%): C: 38.20, H: 3.99, N: 44.55 %.

1.3 Synthesis of 2,2'-bis(dinitromethyl)-2*H*,2'*H*-5,5'-bistetrazole (BDNBT)

Compound **2** (1.00 g, 4.0 mmol) was slowly added to 4 mL of nitrosulfuric acid (H_2SO_4: Fuming HNO_3 = 1:1) at -10 °C for 24 h. The reaction was quenched by pouring the reactants into ice, stirred for 2 h, and filtered to give a white solid product **BDNBT** (0.70 g, 50.6 %). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.57 (s) ppm. ^{13}C

NMR (75 MHz, DMSO-d_6): δ = 155.72, 131.03 ppm. IR (KBr, v/cm^{-1}): v = 1814, 1810, 1792, 1789, 1462, 1397, 1337, 1299, 1048, 783, 774, 744 cm^{-1}; Elemental analysis calcd (%) for $C_4H_2N_{12}O_8$ (346.01): C: 13.88, H: 0.58, N: 48.56 %; Found (%): C: 14.03, H: 0.62, N: 48.48 %.

1.4 Synthesis of Sodium (2*H*,2'*H*-[5,5'-bistetrazole]-2,2'-diylbis(dinitromethanide)) (4)

BDNBT (1.00 g, 2.9 mmol) was added to acetonitrile and stirred, to which a few drops of NaOH saturated solution was added dropwise, stirred for 1h, and filtered to give the light green solid **4** (0.90 g, 79.3 %). ^{13}C NMR (75 MHz, DMSO-d_6): δ = 155.72, 131.05 ppm. IR (KBr, v/cm^{-1}): v = 1855, 1786, 1732, 1702, 1625, 1348, 1265, 1244, 1027, 948, 776, 698, 664, 556 cm^{-1}; Elemental analysis calcd (%) for $C_4N_{12}O_8Na_2$ (390.01): C: 12.31, N: 43.08 %; Found (%): C: 12.42, N: 43.27 %.

1.5 Synthesis of Potassium, ammonium, hydrazinium and hydroxylammonium (2*H*,2'*H*-[5,5'-bistetrazole]-2,2'-diylbis(dinitromethanide)) (5-8)

A mixture of 20 mL acetonitrile and 1 g of **BDNBT** (1 equiv., 2.9 mmol) was combined with 2.2 equiv. of the respective base (potassium ammonia, hydrazine hydrate, or hydroxylamine). The resulting suspension was stirred at 50 °C overnight. The solids were subsequently filtered, washed with water and air-dried to obtain the corresponding high-energy salts (**5-8**).

2.5.1 Potassium (2*H*,2'*H*-[5,5'-bistetrazole]-2,2'-diylbis(dinitromethanide)) (5)

White solid. (1.08 g, 88.2 %). ^1H NMR (300 MHz, DMSO-d_6): δ = 7.07 (s) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 155.73, 131.07 ppm. IR (KBr, v/cm^{-1}): v = 1868, 1782, 1733, 1672, 1601, 1438, 1344, 1302, 1216, 1087, 917, 863, 754, 626, 556 cm^{-1}; Elemental analysis calcd (%) for $C_4N_{12}O_8K_2$ (422.12): C: 11.37, N: 39.8 %; Found (%): C: 11.28, N: 39.72 %.

2.5.2 Ammonium (2*H*,2'*H*-[5,5'-bistetrazole]-2,2'-diylbis(dinitromethanide)) (6)

White solid. (1.04 g, 94.3 %). ^1H NMR (300 MHz, DMSO-d_6): δ = 7.07 (s) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 155.73, 131.07 ppm. IR (KBr, v/cm^{-1}): v = 1908, 1836, 1823, 1620, 1536, 1449, 1361, 1235, 1209, 1164, 1079, 929, 843, 719, 676,

518 cm^{-1}; Elemental analysis calcd (%) for $C_4H_8N_{14}O_8$ (380.12): C: 12.63, H: 2.10, N: 44.20 %; Found (%): C: 12.58, H: 2.02, N: 44.52 %.

2.5.3 Hydrazinium (2*H*,2'*H*-[5,5'-bistetrazole]-2,2'-diylbis(dinitromethanide)) (7)

White solid. (1.00 g, 72.4 %). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.58 (s) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 155.72, 131.06 ppm. IR (KBr, v/cm^{-1}): v = 1894, 1848, 1811, 1746, 1741, 1612, 1577, 1466, 1354, 1282, 1094, 911, 876, 716, 681 cm^{-1}; Elemental analysis calcd (%) for $C_4H_{10}N_{16}O_8$ (410.12): C: 11.70, H: 2.44, N: 54.62 %; Found (%): C: 11.58, H: 2.22, N: 54.81 %.

2.5.4Hydroxylammonium (2*H*,2'*H*-[5,5'-bistetrazole]-2,2'-diylbis-(dinitromethanide)) (8)

White solid. (0.90 g, 84.0 %). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 7.67 (s) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 155.72, 131.08 ppm. IR (KBr, v/cm^{-1}): v = 1878, 1802, 1783, 1722, 1648, 1515, 1476, 1328, 1277, 1128, 1013, 955, 856, 751, 622 cm^{-1}; Elemental analysis calcd (%) for $C_4H_8N_{14}O_{10}$ (412.12): C: 11.65, H: 1.94, N: 47.56 %; Found (%): C: 11.78, H: 2.02, N: 47.81 %.

1.6 Synthesis of 3-(Ammoniomethyl)-4,5-diamino-1,2,4-triazol-1-ium 2*H*,2'*H*-[5,5'-bistetrazole]-2,2'-diylbis(dinitromethanide) (9)

To a mixture of 20 mL of deionized water and 1 g of **BDNBT** (1 equiv., 2.9 mmol) was added 1.1 equiv. of the corresponding base (3-(aminomethyl)-4,5-diamino-1,2,4-triazole) and the suspension was stirred at 50 °C overnight. The solid was then collected by filtration and dried in air to get a yellow solid (1.26 g, 92.0 %). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.40 (s, 1H), 5.91 (s, 1H), 4.19 (s, 1H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 155.72, 151.99, 146.81, 131.07, 32.96 ppm. IR (KBr, v/cm^{-1}): v = 2046, 1952, 1833, 1749, 1566, 1402, 1379, 1301, 1033, 885, 824, 762, 514 cm^{-1}; Elemental analysis calcd (%) for $C_7H_{10}N_{18}O_8$ (474.09): C: 17.73, H: 2.13, N: 53.16 %; Found (%): C: 17.58, H: 2.02, N: 53.41 %.

1.7 Synthesis of 2,4,6-triamino-1,3-dihydroxy-1,3,5-triazine-1,3-diium 2*H*,2'*H*-[5,5'-bistetrazole]-2,2'-diylbis(dinitromethanide) (10)

Similar to **9**, to a mixture of 20 mL of deionized water and 1 g of **BDNBT** (1 equiv., 2.9 mmol) was added 1.1 equiv. of the corresponding base (2,4,6-triamino-1,3,5-

triazine-1,3-dioxide) and the suspension was stirred at 50 °C overnight. The solid was then collected by filtration and dried in air to get a white solid (1.37 g, 94.1%). ^{1}H NMR (300 MHz, DMSO-d_6): δ = 9.37 (s, 1H), 9.14 (s, 1H), 8.69 (s, 1H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ = 155.70, 152.60, 151.89, 131.03 ppm. IR (KBr, v/cm^{-1}): v = 2174, 2081, 1966, 1846, 1808, 1711, 1649, 1355, 1142, 1069, 998, 846, 732, 649 cm^{-1}; Elemental analysis calcd (%) for $C_7H_8N_{18}O_{10}$ (504.07): C: 16.67, H: 2.16, N: 50.0 %; Found (%): C: 16.78, H: 2.02, N: 49.81 %.

2. General Methods

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

^{1}H 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 ^{1}H 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 **α-BDNBT** (298K & 193K), **β-BDNBT**, **3**, 0.5 (**4**·2CH_3OH), **5**, **7** (2H_2O), **9** CH_3OH H_2O 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.**

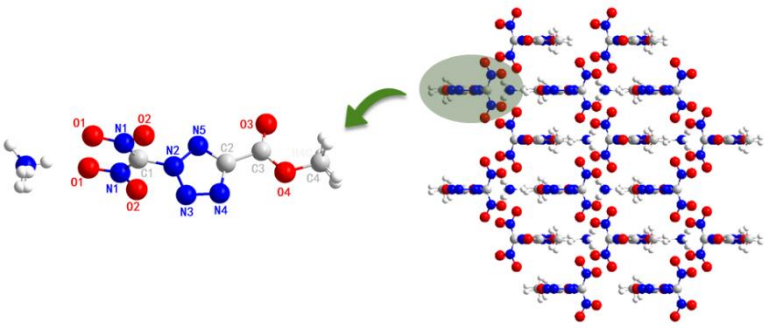


Figure S1 Structures and stacking diagrams of **3**

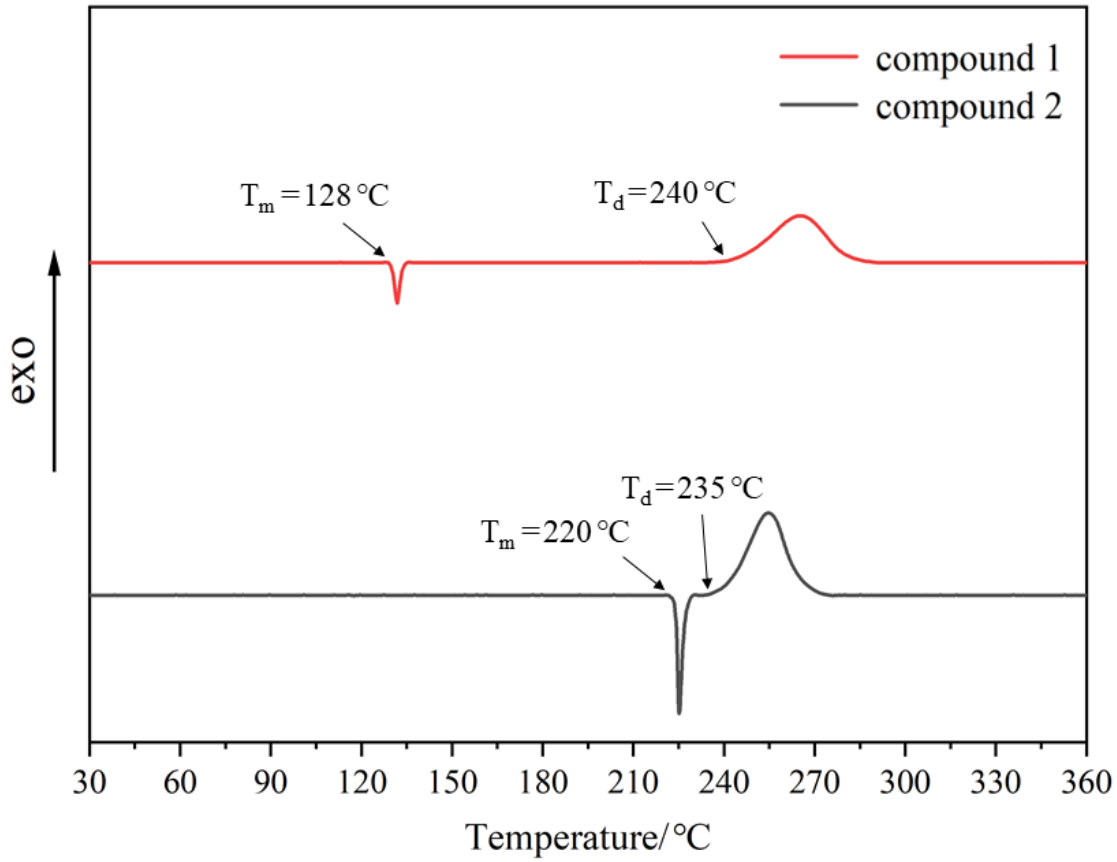


Figure S2 DSC plots of compound **1** and **2**

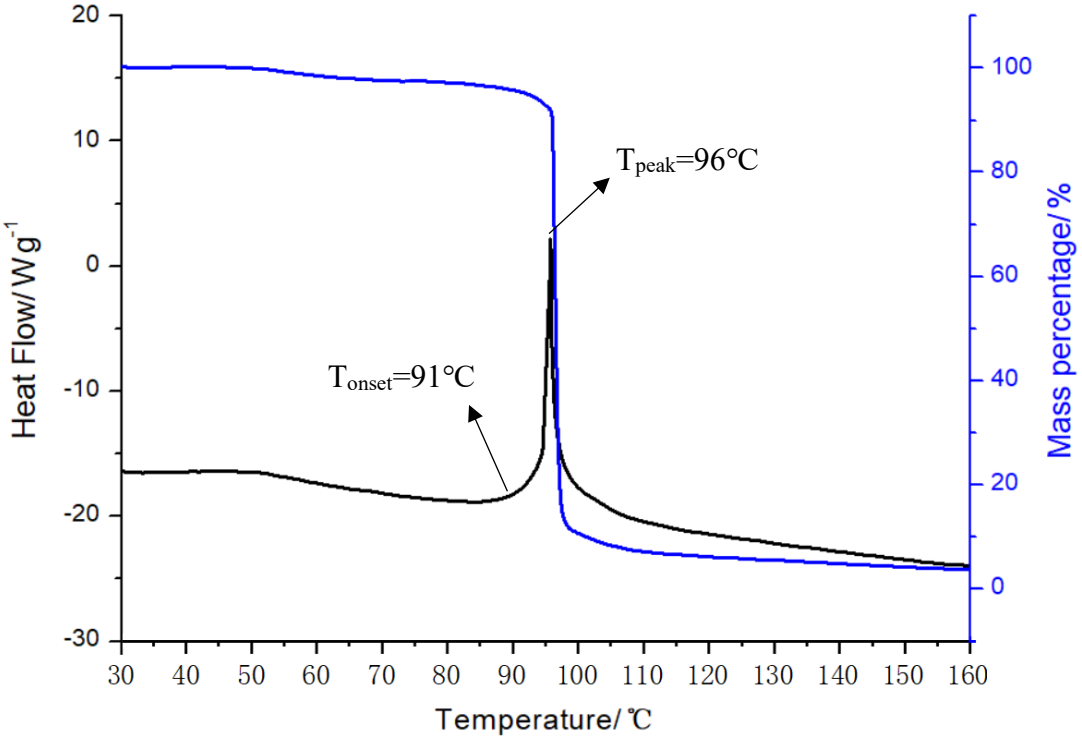


Figure S3 DSC-TG plots of **α-BDNBT**

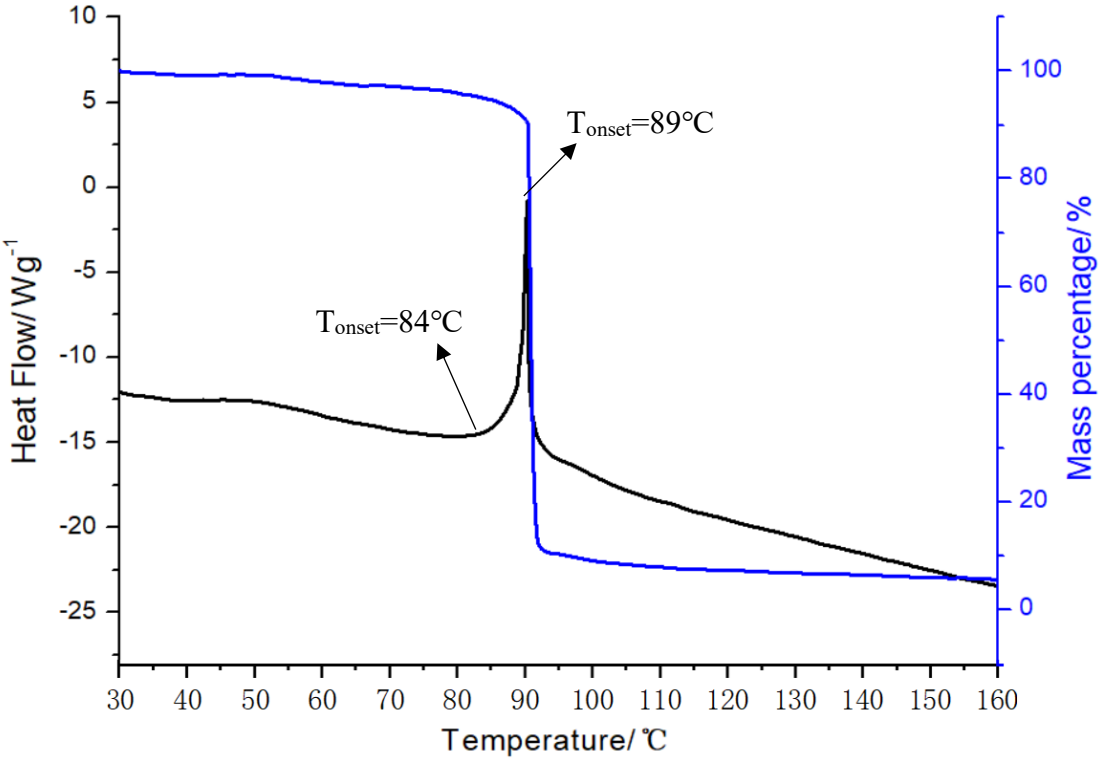


Figure S4 DSC-TG plots of **β-BDNBT**

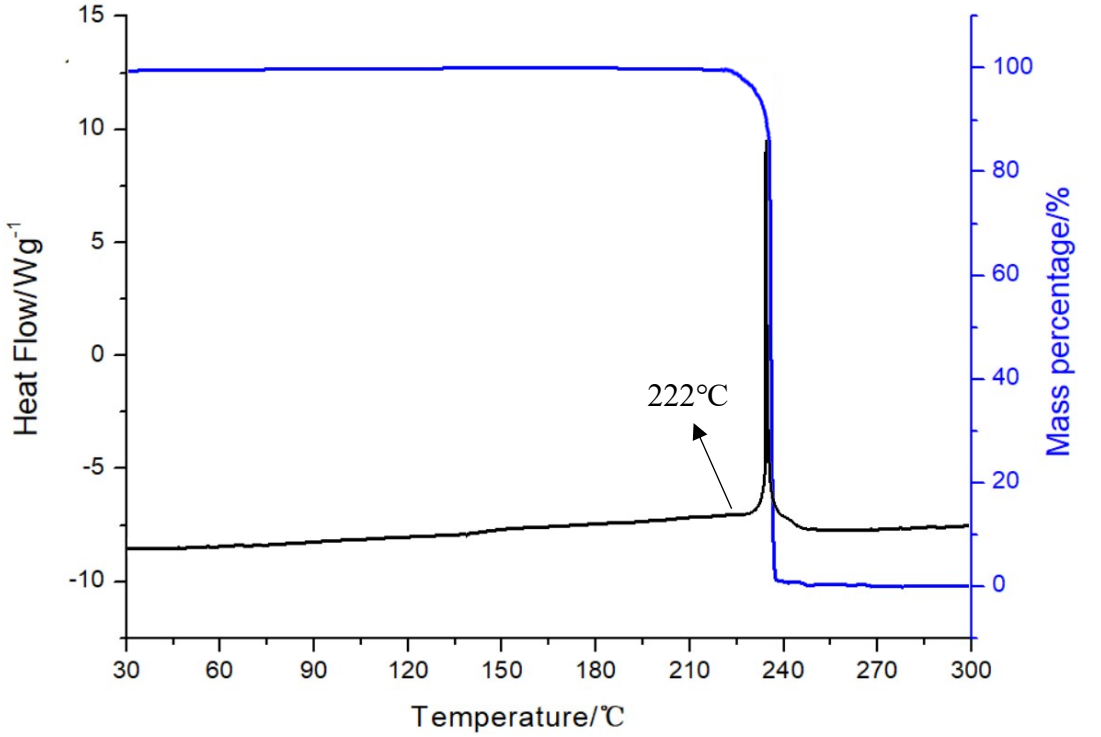


Figure S5 DSC-TG plots of compound **5**

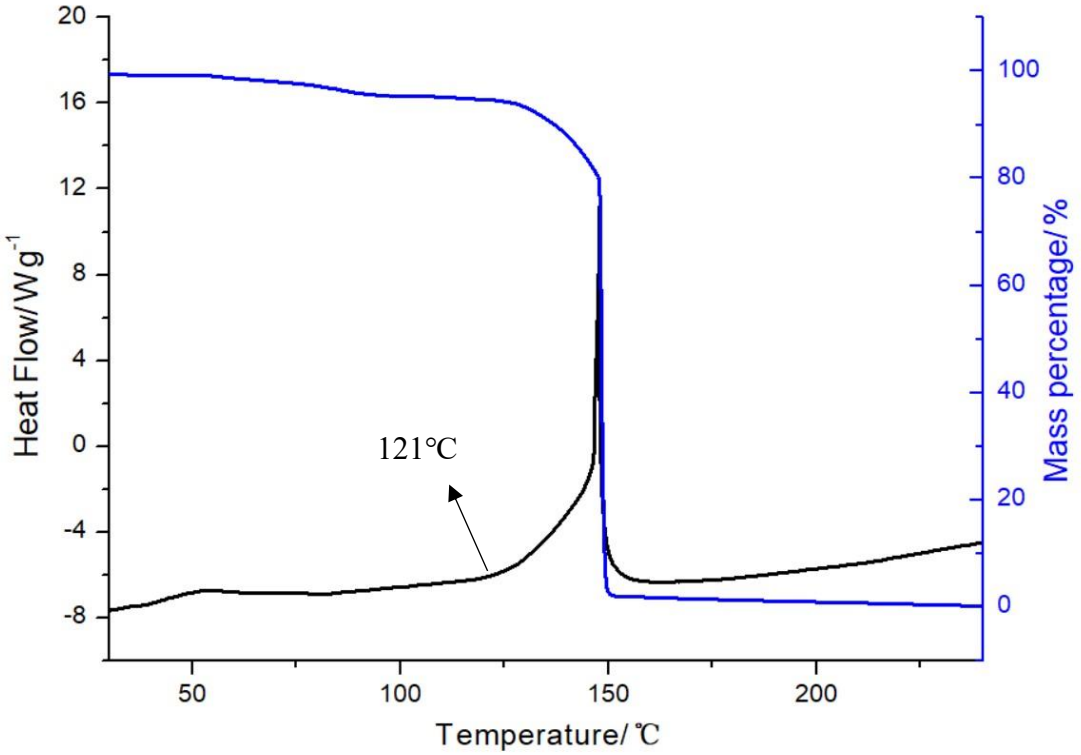


Figure S6 DSC-TG plots of compound **6**

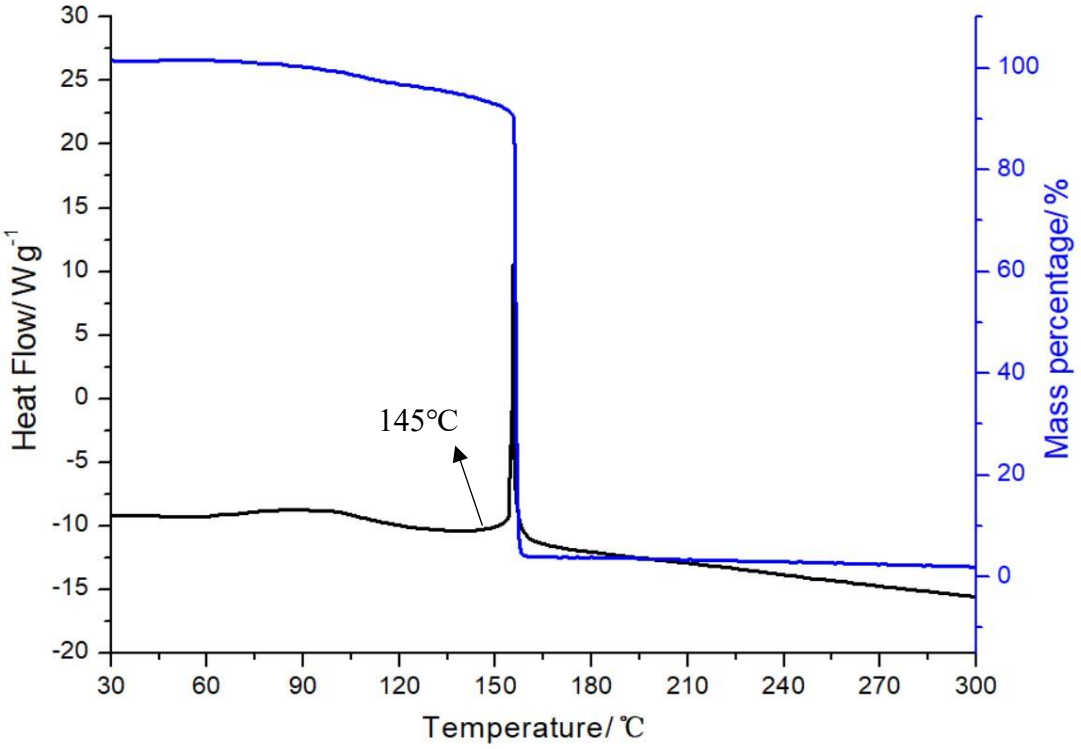


Figure S7 DSC-TG plots of compound **7**

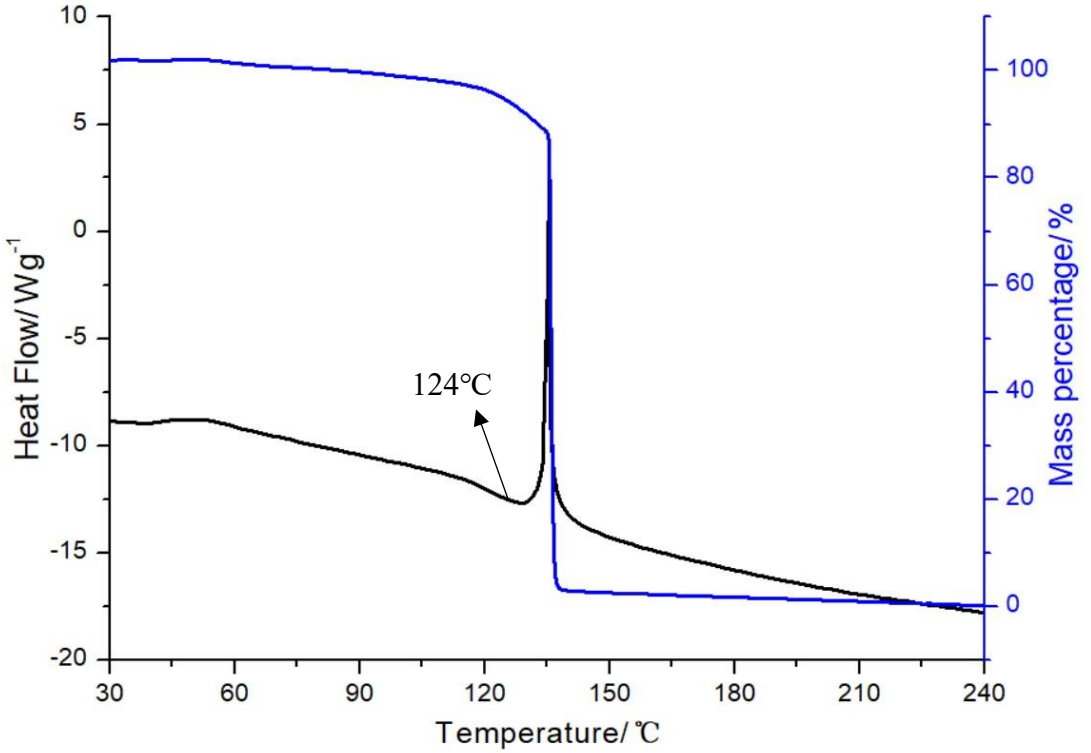


Figure S8 DSC-TG plots of compound **8**

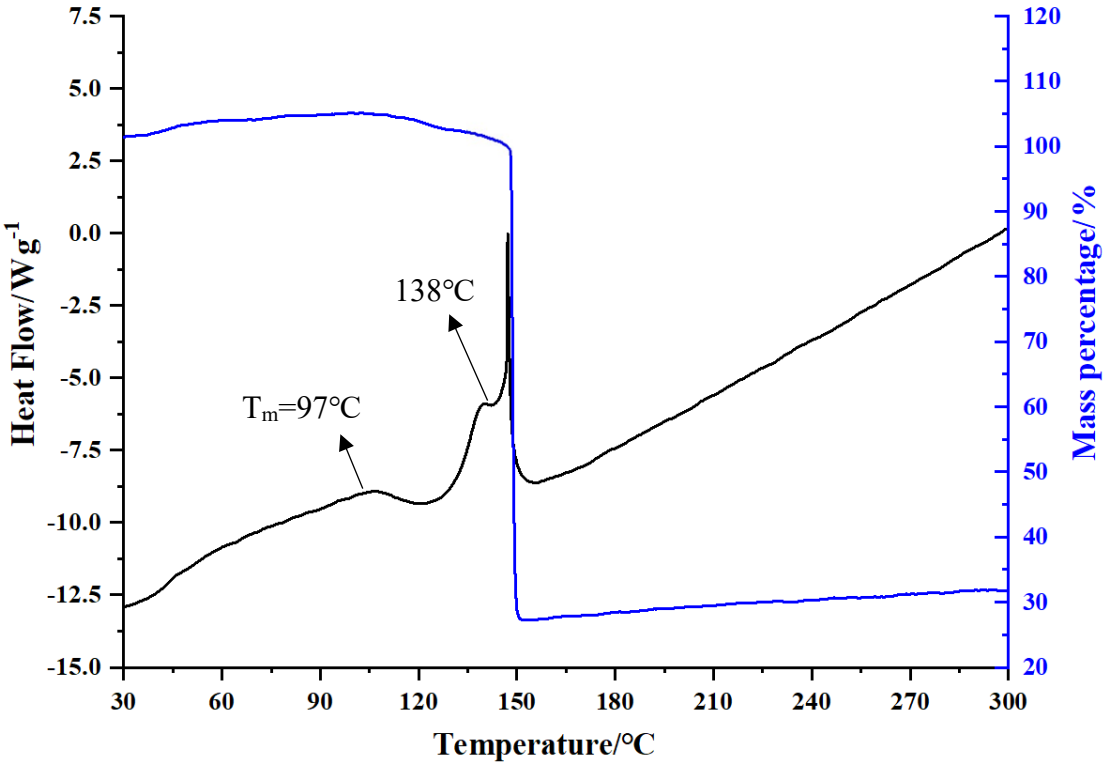


Figure S9 DSC-TG plots of compound **9**

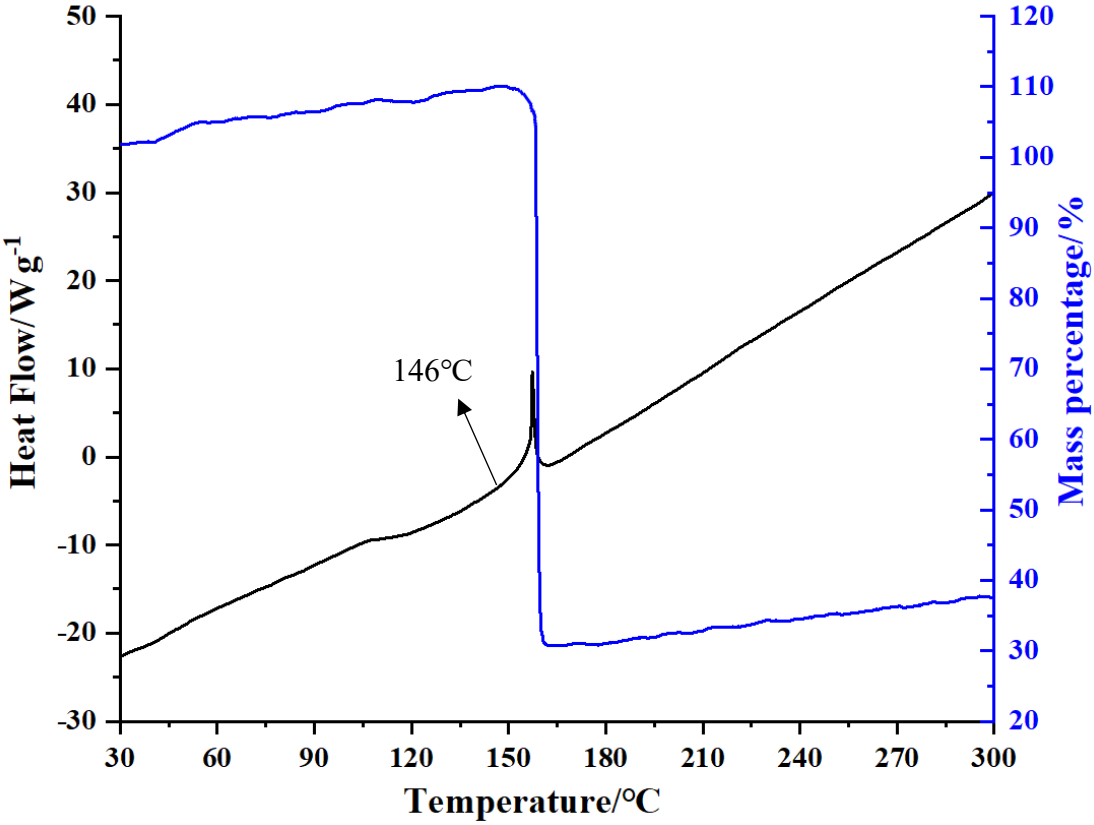


Figure S10 DSC-TG plots of compound **10**

Table S1. Crystal data and structure refinement for **α-BDNBT** (298K & 193K), **β-BDNBT**, **3**, 0.5 (**4**·2CH_3OH), **5**, **7** (2H_2O), **9** CH_3OH H_2O

Crystal	**α-BDNBT**	**α-BDNBT**	**β-BDNBT**
CCDC number	2336254	2336263	2336247
Empirical formula	$C_4H_2N_{12}O_8$	$C_4H_2N_{12}O_8$	$C_4H_2N_{12}O_8$
Formula weight	346.18	346.18	346.18
Temperature/K	298.00	193.00	193.00
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
a [Å]	7.5996(11)	7.5860(6)	9.9607(4)
b [Å]	9.8309(12)	9.7376(7)	13.8634(6)
c [Å]	8.5177(13)	8.4712(7)	8.7688(4)
α [°]	90	90	90
β [°]	106.068(5)	106.588(3)	90.094(3)
γ [°]	90	90	90

Volume	611.50(15)	599.72(8)	1210.87(9)
Z	2	2	4
ρ (g cm^{-3})	1.880	1.917	1.899
μ/mm^{-1}	0.177	0.181	1.608
F(000)	348.0	348.0	696.0
Crystal size (mm^3)	0.13×0.12×0.11	0.13×0.12×0.1	0.13×0.12×0.1
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
Theta range for data collection	6.366 to 54.976	6.366 to 54.972	6.376 to 137.454
Index ranges	-9≤h≤9, -12≤k≤12, -11≤l≤11	-9≤h≤9, -12≤k≤12, -10≤l≤11	-11≤h≤12, -16≤k≤16, -9≤l≤10
Reflections collected	10368	12619	8450
Independent reflections	1399[R_{int} = 0.0671, R_{sigma} = 0.0370]	1365[R_{int} = 0.0767, R_{sigma} = 0.0443]	2215 [R_{int} = 0.0331, R_{sigma} = 0.0312]
Data/restraints/ parameters	1399/0/109	1365/0/109	2215/424/327
Goodness-of-fit on F^2	1.048	1.079	1.020
Final R indices [I>2σ(I)]	R_1 = 0.0392, wR_2 = 0.0950	R_1 = 0.0386, wR_2 = 0.1003	R1 = 0.0838, wR2 = 0.2175
Final R indexes [all data]	R1 = 0.0551, wR2 = 0.1040	R_1 = 0.0418, wR_2 = 0.1037	R1 = 0.1060, wR2 = 0.2407
Largest diff. peak/hole / e Å-3	0.26/-0.19	0.35/-0.27	0.46/-0.41

Crystal	0.5 (**4**·2CH_3OH)	**5**	**7** ($2H_2O$)
CCDC number	2336255	2339222	2336256
Empirical formula	$C_3H_4N_6NaO_5$	$C_4K_2N_{12}O_8$	$C_{48}H_{160}N_{192}O_{112}$
Formula weight	227.11	422.36	5219.67
Temperature/K	193.00	223.00	193.00

Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/m	$P2_1/c$	C2/c
a [Å]	14.932(5)	7.2374(8)	32.7745(14)
b [Å]	7.5092(19)	8.0107(9)	16.9448(7)
c [Å]	8.709(4)	12.5488(10)	17.7319(7)
α [°]	90	90	90
β [°]	125.26(2)	96.544(4)	91.598(3)
γ [°]	90	90	90
Volume	797.4(5)	722.80(13)	9843.7(7)
Z	4	2	2
ρ(g cm^{-3})	1.892	1.941	1.761
μ/mm^{-1}	0.217	0.731	1.456
F(000)	460.0	420.0	5376.0
Crystal size (mm^3)	0.14×0.13×0.1	0.13×0.11×0.1	0.13×0.12×0.1
Radiation	MoKα (λ=0.71073)	MoKα (λ=0.71073)	CuKα (λ=1.54178)
Theta range for data collection	5.728 to 50.812	5.666 to 54.976	5.394 to 136.872
Index ranges	-18≤h≤17, -6≤k≤9, -10≤l≤10	-9≤h≤9, -10≤k≤10, -16≤l≤16	-39≤h≤39, -20≤k≤19, -19≤l≤21
Reflections collected	2362	17489	41398
Independent reflections	778 [R_{int} = 0.0878, R_{sigma} = 0.0721]	1661[R_{int} =0.0841, R_{sigma} =0.0348]	9031[R_{int} =0.0879, R_{sigma} =0.0531]
Data/restraints/ parameters	778/18/85	1661/0/118	9031/345/963
Goodness-of-fit on F^2	1.052	1.064	1.096
Final R indices [I>2σ(I)]	R_1 = 0.0687, wR_2 = 0.1617	R_1 =0.0307,wR_2 = 0.0741	R_1 =0.0945, wR_2 = 0.2183
Final R indexes [all data]	R_1 = 0.0862, wR_2 = 0.1739	R_1 =0.0440,wR_2 = 0.0824	R_1 =0.1461, wR_2 = 0.2490
Largest diff. peak/hole / e Å-3	0.40/-0.83	0.36/-0.35	0.53/-0.40

Crystal	**9** CH_3OH H_2O	**3**
CCDC number	2339223	2336277
Empirical formula	$C_{15}H_{26}N_{36}O_{18}$	$C_4H_7N_7O_6$
Formula weight	998.72	249.17
Temperature/K	218.00	193.00
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_1/m$
a [Å]	17.3785(17)	7.856(3)
b [Å]	11.5111(12)	8.001(4)
c [Å]	21.222(3)	8.291(4)
α [°]	90	90
β [°]	112.132(5)	103.603(15)
γ [°]	90	90
Volume	3932.5(8)	506.6(4)
Z	4	2
ρ(g cm^{-3})	1.687	1.634
μ/mm^{-1}	1.329	0.151
F(000)	2048.0	256.0
Crystal size (mm^3)	0.15×0.13×0.12	0.13×0.12×0.11
Radiation	CuK α (λ = 1.54178)	MoK α (λ =0.71073)
Theta range for data collection	8.996 to 133.186	5.054 to 54.964
Index ranges	-20⩽h⩽19, -13⩽k⩽13, -25⩽l⩽24	-10⩽h⩽9, 0⩽k⩽10, 0⩽l⩽10
Reflections collected	14734	1222
Independent reflections	3356 [R_{int} = 0.0595, R_{sigma} = 0.0529]	1222
Data/restraints/ parameters	3356/268/393	1222/1/91
Goodness-of-fit on F^2	0.959	0.980
Final R indices [I>2σ(I)]	R_1 = 0.0998, wR_2 = 0.2071	R_1 =0.0671, wR_2 = 0.1560
Final R indexes [all data]	R_1 = 0.1115, wR_2 = 0.2132	R_1 = 0.1219, wR_2 = 0.1844
Largest diff. peak/hole / e	0.56/-0.33	0.29/-0.32

Å-3

Table S2. Selected bond lengths [Å] and angles [°] for **α-BDNBT**

parameter	Å	parameter	Å
O1-N5	1.2132(16)	N2-C1	1.3615(17)
O2-N5	1.2052(16)	N3-N4	1.3401(16)
O3-N6	1.2150(18)	N4-C2	1.4149(17)
O4-N6	1.1989(17)	N5-C2	1.5209(18)
N1-N4	1.3361(15)	N6-C2	1.5311(17)
N1-C1	1.3153(17)	C1-C1_a	1.4525(18)
N2-N3	1.2983(18)	C2-H2	1

parameter	Å	parameter	Å
N4-N1-C1	100.50(10)	O4-N6-C2	118.09(12)
N3-N2-C1	106.15(11)	N1-C1-N2	113.48(12)
N2-N3-N4	105.65(11)	N1-C1-C1_a	123.70(12)
N1-N4-N3	114.22(11)	N2-C1-C1_a	122.81(12)
N1-N4-C2	124.48(10)	N4-C2 -N5	111.62(10)
N3-N4-C2	121.27(10)	N4-C2-N6	109.80(11)
O1-N5-O2	126.43(13)	N5-C2-N6	108.19(10)
O1-N5-C2	117.64(11)	N4-C2-H2	109
O2-N5-C2	115.93(11)	N5-C2-H2	109
O3-N6-O4	127.96(12)	N6-C2-H2	109
O3-N6-C2	113.88(11)		

Table S3. Torsion angles [°] of **α-BDNBT**

parameter	Å	parameter	Å
C1-N1-N4-N3	0.87(14)	O1-N5-C2-N4	-46.83(15)
C1-N1-N4-C2	178.79(12)	O1-N5-C2-N6	74.08(14)

N4-N1-C1-N2	-0.94(14)	O2-N5-C2-N4	132.13(12)
N4-N1-C1-C1_a	178.29(12)	O2-N5-C2-N6	-106.97(13)
C1-N2-N3-N4	-0.12(14)	O3-N6-C2-N4	-41.90(15)
N3-N2-C1-N1	0.71(16)	O3-N6-C2-N5	-163.93(12)
N3-N2-C1-C1_a	-178.52(12)	O4-N6-C2-N4	140.90(12)
N2-N3-N4-N1	-0.49(15)	O4-N6-C2-N5	18.87(16)
N2-N3-N4-C2	-178.49(11)	N1-C1-C1_a-N1_a	180.00(13)
N1-N4-C2-N5	63.46(15)	N1-C1-C1_a-N2_a	0.8(2)
N1-N4-C2-N6	-56.51(15)	N2-C1-C1_a-N1_a	-0.8(2)
N3-N4-C2-N5	-118.76(12)	N2-C1-C1_a-N2_a	180.00(12)
N3-N4-C2-N6	121.28(12)		

Table S4. Hydrogen bonds of **α-BDNBT**

D-H···A	**d(D-H)/Å**	**d(H···A)/ Å**	**d(D···A)/ Å**	**<(DHA)/°**
C2-H2···O3	1	2.59	3.1599(18)	116

Table S5. Selected bond lengths [Å] and angles [°] for **β-BDNBT**

parameter	**Å**	**parameter**	**Å**
O1-N5	1.175(18)	N4-C1	1.355(7)
O1A-N5A	1.18(2)	N5-C2	1.611(12)
O2-N5	1.186(14)	N5A-C2	1.438(15)
O2A-N5A	1.19(2)	N6-C2	1.492(12)
O3-N6	1.146(15)	N6A-C2	1.610(19)
O3A-N6A	1.23(3)	N7-C3	1.296(7)
O4-N6	1.238(18)	N7-N8	1.371(7)
O4A-N6A	1.25(3)	N8-C4	1.433(8)
O5-N11	1.206(14)	N8-N9	1.306(7)
O5A-N11A	1.23(3)	N9-N10	1.319(7)
O6-N11	1.203(17)	N10-C3	1.365(7)
O6A-N11A	1.23(3)	N11-C4	1.591(12)

O7-N12	1.271(16)	N11A-C4	1.529(18)
O7A-N12A	1.26(2)	N12-C4	1.540(12)
O8-N12	1.188(15)	N12A-C4	1.560(16)
O8A-N12A	1.202(19)	C1-C1_a	1.448(8)
N1-N2	1.303(7)	C2-H2A	1
N1-C1	1.332(7)	C2-H2B	1
N2-N3	1.356(8)	C3-C3_b	1.442(8)
N2-C2	1.416(8)	C4-H4A	1
N3-N4	1.289(8)	C4-H4B	1

parameter	**Å**	**parameter**	**Å**
N2-N1-C1	101.8(5)	O6A-N11A-C4	121.9(16)
N1-N2-N3	114.7(5)	O5A-N11A-C4	90.0(17)
N1-N2-C2	125.4(5)	O8-N12-C4	115.3(11)
N3-N2-C2	119.8(5)	O7-N12-C4	95.6(9)
N2-N3-N4	104.1(5)	O7-N12-O8	145.7(12)
N3-N4-C1	108.4(5)	O7A-N12A-O8A	97.7(15)
O1-N5-O2	124.1(12)	O7A-N12A-C4	126.3(12)
O1-N5-C2	112.3(10)	O8A-N12A-C4	129.3(14)
O2-N5-C2	121.2(10)	N1-C1-C1_a	124.7(5)
O1A-N5A-O2A	124.5(17)	N4-C1-C1_a	124.3(5)
O1A-N5A-C2	114.5(15)	N1-C1-N4	111.0(5)
O2A-N5A-C2	120.2(15)	N2-C2-N6	109.6(6)
O3-N6-C2	127.8(13)	N2-C2-N5A	112.6(8)
O3-N6-O4	124.2(16)	N2-C2-N6A	101.6(8)
O4-N6-C2	106.9(11)	N5-C2-N6	102.3(7)
O3A-N6A-O4A	129(2)	N5A-C2-N6A	108.6(11)
O3A-N6A-C2	103.4(18)	N2-C2-N5	110.0(6)
O4A-N6A-C2	124.4(17)	N6A-C2-H2B	111

N8-N7-C3	100.5(4)	N6-C2-H2A	111
N7-N8-C4	123.4(5)	N5A-C2-H2B	111
N7-N8-N9	114.3(5)	N2-C2-H2B	111
N9-N8-C4	122.3(5)	N5-C2-H2A	112
N8-N9-N10	105.6(5)	N2-C2-H2A	111
N9-N10-C3	106.2(5)	N7-C3-C3_b	123.8(5)
O6-N11-C4	113.6(10)	N7-C3-N10	113.4(5)
O5-N11-C4	113.8(9)	N10-C3-C3_b	122.8(5)
O5-N11-O6	132.2(12)	N11A-C4 -N12A	112.7(14)
N8-C4-N12	113.5(6)	N8-C4-H4B	106
N8-C4-N11A	115.8(8)	N11-C4-H4A	110
N8-C4-N12A	109.8(9)	N12-C4-H4A	110
N11-C4-N12	104.2(7)	N11A-C4-H4B	106
N8-C4-H4A	110	N12A-C4-H4B	106

Table S6. Torsion angles [°] of **β-BDNBT**

parameter	**Å**	**parameter**	**Å**
C1-N1-N2-N3	1.7(6)	O1-N5-C2-N6	-142.5(11)
C1-N1-N2-C2	178.4(5)	O2-N5-C2-N2	170.9(10)
N2-N1-C1-N4	-2.2(6)	O2-N5-C2-N6	54.5(13)
N2-N1-C1-C1_a	179.3(5)	O3-N6-C2-N2	-99.1(17)
N1-N2-N3-N4	-0.4(7)	O3-N6-C2-N5	17.6(18)
C2-N2-N3-N4	-177.3(5)	O4-N6-C2-N2	92.9(11)
N1-N2-C2-N5	-74.4(8)	O4-N6-C2-N5	-150.3(10)
N1-N2-C2-N6	37.4(8)	N8-N7-C3-C3_b	178.0(5)
N3-N2-C2-N5	102.1(7)	C3-N7-N8-N9	1.9(6)
N3-N2-C2-N6	-146.1(6)	C3-N7-N8-C4	-177.8(5)
N2-N3-N4-C1	-1.0(6)	N8-N7-C3-N10	-0.7(6)
N3-N4-C1-N1	2.1(7)	N7-N8-N9-N10	-2.4(6)

N3-N4-C1-C1_a	-179.3(5)	C4-N8-N9-N10	177.3(5)
O1-N5-C2-N2	-26.0(13)	N7-N8-C4-N11	79.2(8)
N9-N8-C4-N12	144.4(7)	O7-N12-C4-N8	-74.9(10)
N7-N8-C4-N12	-35.9(9)	O8-N12-C4-N8	89.8(11)
N9-N8-C4-N11	-100.5(7)	O8-N12 -C4-N11	-27.7(13)
N8-N9-N10-C3	1.8(6)	N4-C1-C1_a-N4_a	180.0(6)
N9-N10-C3-C3_b	-179.3(5)	N1-C1-C1_a-N1_a	-180.0(5)
N9-N10-C3-N7	-0.7(7)	N1-C1-C1_a -N4_a	-1.7(9)
O5-N11-C4-N8	-177.8(9)	N4-C1 -C1_a-N1_a	1.7(9)
O5-N11-C4-N12	-56.8(11)	N7-C3-C3_b-N7_b	-180.0(6)
O6-N11-C4-N8	8.4(12)	N7-C3-C3_b-N10_b	1.5(9)
O6-N11-C4-N12	129.5(11)	N10-C3-C3_b-N7_b	-1.5(9)
O7-N12-C4-N11	167.6(9)	N10-C3-C3_b-N10_b	-180.0(5)

Table S7. Hydrogen bonds of **β-BDNBT**

D-H···A	**d(D-H)/Å**	**d(H···A)/ Å**	**d(D···A)/ Å**	**<(DHA)/°**
C2-H2A···N10	1	2.22	3.208(8)	170
C4-H4A···N4	1	2.29	3.276(8)	167

Table S8. Selected bond lengths [Å] and angles [º] for compound 0.5 (**4**·2CH_3OH)

parameter	**Å**	**parameter**	**Å**
Na1-O1	2.738(5)	N1-C1	1.353(7)
Na1-O2	2.530(3)	N2-N3	1.341(8)
Na1-O3	2.287(9)	N3-N4	1.342(7)
Na1-O1_c	2.738(5)	N3-C2	1.402(10)
Na1-O2_c	2.530(3)	N4-C1	1.322(10)
Na1-N1_f	2.533(7)	N5-C2	1.373(5)
Na1-O2_g	2.631(4)	C1-C1_a	1.438(9)
Na1-O2_i	2.631(4)	C3-H3A	0.98
O1-N5	1.242(5)	C3-H3B	0.98

O2-N5	1.248(6)	C3-H3C	0.98
O3-C3	1.390(14)	C3-H3A_c	0.98
O3-H3	0.87(3)	C3-H3B_c	0.98
N1-N2	1.296(9)	C3-H3C_c	0.98

parameter	**Å**	**parameter**	**Å**
O1_c-Na1-O2	48.30(12)	Na1-O1-N5	90.2(3)
O1-Na1-O3	80.2(2)	Na1-O2-N5	100.1(2)
O1-Na1-O1_c	67.86(14)	Na1-O2-Na1_h	107.42(14)
O1-Na1-O2_c	114.31(15)	Na1_h-O2-N5	134.3(2)
O1-Na1-N1_f	114.59(16)	Na1-O3-C3	127.7(8)
O1-Na1-O2_g	164.47(17)	C3-O3-H3	109.2(17)
O1-Na1-O2_i	113.94(10)	Na1-O3-H3	123.1(16)
O2-Na1-O3	100.28(12)	Na1_e-N1-N2	125.4(3)
O1_c-Na1-O2	114.31(15)	N2-N1-C1	106.6(6)
O2-Na1-O2_c	149.49(16)	Na1_e-N1-C1	128.0(5)
O2-Na1-N1_f	83.76(11)	N1-N2-N3	106.2(4)
O2-Na1-O2_g	131.65(15)	N2-N3-C2	122.5(5)
O2-Na1-O2_i	72.58(11)	N4-N3-C2	124.3(5)
O1_c-Na1-O3	80.2(2)	N2-N3-N4	113.2(6)
O2_c-Na1-O3	100.28(12)	N3-N4-C1	101.1(5)
O3-Na1-N1_f	161.7(3)	O1-N5-C2	117.6(5)
O2_g-Na1-O3	84.9(2)	O1-N5-O2	120.7(4)
O2_i-Na1-O3	84.9(2)	O2-N5-C2	121.8(4)
O1_c-Na1-O2_c	48.30(12)	N1-C1-C1_a	123.4(6)
O1_c-Na1-N1_f	114.59(16)	N4-C1-C1_a	123.6(5)
O1_c-Na1-O2_g	113.94(10)	N1-C1-N4	113.0(6)
O1_c-Na1-O2_i	164.47(17)	N5-C2-N5_d	124.4(6)
O2_c-Na1-N1_f	83.76(11)	N3-C2-N5	116.1(3)

O2_c-Na1-O2_g	72.58(11)	N3-C2-N5_d	116.1(3)
O2_c-Na1-O2_i	131.65(15)	O3-C3-H3A	109
O2_g-Na1-N1_f	79.30(15)	O3-C3-H3B	109
O2_i-Na1-N1_f	79.30(15)	O3-C3 -H3C	109
O2_g-Na1-O2_i	59.94(12)	O3-C3-H3A_c	109
O3-C3-H3B_c	109	H3B-C3-H3B_c	140
O3-C3-H3C_c	109	H3B-C3-H3C_c	64
H3A-C3-H3B	110	H3A_c-C3-H3C	140
H3A-C3 -H3C	109	H3B_c-C3-H3C	64
H3A-C3-H3A_c	64	H3C-C3-H3C_c	48
H3A-C3-H3B_c	48	H3A_c-C3-H3B_c	110
H3A-C3-H3C_c	140	H3A_c-C3-H3C_c	109
H3B-C3-H3C	109	H3B_c-C3-H3C_c	109
H3A_c-C3-H3B	48		

Table S9. Torsion angles [º] of 0.5 (**4**·2CH_3OH)

parameter	Å	parameter	Å
O2-Na1-O1-N5	5.0(2)	O1-Na1-O3-C3	145.50(9)
O3-Na1-O1-N5	-108.4(3)	O2-Na1-O3-C3	101.34(12)
O1_c-Na1-O1-N5	168.3(3)	Na1-O1-N5-O2	-8.8(4)
O2_c-Na1-O1-N5	154.7(2)	Na1-O1-N5-C2	172.4(4)
N1_f-Na1-O1-N5	60.4(3)	Na1-O2-N5-O1	9.7(4)
O2_i-Na1-O1-N5	-28.5(3)	Na1-O2-N5-C2	-171.6(4)
O1-Na1-O2-N5	-5.0(2)	Na1_h-O2-N5-O1	136.4(3)
O1-Na1-O2-Na1_h	-148.1(2)	Na1_h-O2-N5-C2	-44.8(5)
O3-Na1-O2-N5	61.8(3)	C1-N1-N2-N3	0.00(2)
O1_c-Na1-O2-N5	-22.0(3)	N2-N1-C1-N4	0.00(2)
O2_c-Na1-O2-N5	-69.8(4)	N1-N2-N3-N4	0.00(2)
N1_f-Na1-O2-N5	-136.2(2)	N1-N2-N3-C2	-180.00(2)

O2_g-Na1-O2 -N5	154.1(2)	N2-N3-N4-C1	0.00(2)
O2_i-Na1-O2-N5	143.1(2)	C2-N3-N4-C1	180.00(2)
N2-N3-C2-N5	-80.2(4)	O1-N5-C2-N5_d	-168.4(5)
N4-N3-C2-N5	99.8(4)	O2-N5-C2-N3	171.4(4)
N3-N4-C1-N1	0.00(2)	O2-N5-C2-N5_d	12.8(8)
O1-N5-C2-N3	-9.8(6)		

Table S10. Hydrogen bonds of 0.5 (**4**·2CH_3OH)

D-H···A	d(D-H)/Å	d(H···A)/ Å	d(D···A)/ Å	<(DHA)/°
O3-H3···O1	0.87(3)	2.39(2)	3.008(9)	129.0(11)
C3-H3A···O1	0.98	2.57	3.224(14)	124

Table S11. Selected bond lengths [Å] and angles [º] for compound **5**

parameter	Å	parameter	Å
O1-N6	1.241(2)	N2-C2	1.401(2)
O2-N6	1.242(2)	N3-N4	1.306(2)
O3-N5	1.239(2)	N4-C1	1.353(2)
O4-N5	1.232(2)	N5-C2	1.383(2)
N1-N2	1.334(2)	N6-C2	1.371(2)
N1-C1	1.322(2)	C1-C1_a	1.455(2)
N2-N3	1.335(2)		

parameter	Å	parameter	Å
N2-N1 -C1	100.99(13)	O1 -N6 -O2	121.34(14)
N1 -N2 -N3	113.82(14)	O1 -N6 -C2	117.33(14)
N1 -N2 -C2	123.98(14)	O2 -N6 -C2	121.33(14)
N3 -N2 -C2	122.01(14)	N1 -C1 -N4	113.08(14)
N2 -N3 -N4	105.90(14)	N1 -C1 -C1_a	123.87(15)
N3 -N4 -C1	106.21(14)	N4 -C1 -C1_a	123.05(14)

O3 -N5 -O4	121.72(16)	N2 -C2 -N5	116.71(14)
O3 -N5 -C2	116.86(14)	N2 -C2 -N6	117.38(14)
O4 -N5 -C2	121.40(15)	N5 -C2 -N6	125.84(14)

Table S12. Torsion angles [°] of **5**

parameter	Å	parameter	Å
C1 -N1 -N2 -N3	0.02(18)	O3 -N5 -C2 -N2	-0.5(2)
C1 -N1 -N2 -C2	-175.10(15)	O3 -N5 -C2 -N6	176.41(17)
N2 -N1 -C1 -N4	0.0(2)	O4 -N5 -C2 -N2	178.10(19)
N2 -N1 -C1 -C1_a	179.40(15)	O4 -N5 -C2 -N6	-5.0(3)
N1 -N2 -N3 -N4	-0.04(19)	O1 -N6 -C2 -N2	-1.7(2)
C2 -N2 -N3 -N4	175.18(15)	O1 -N6 -C2 -N5	-178.63(17)
N1 -N2 -C2 -N5	94.44(19)	O2 -N6 -C2 -N2	177.67(16)
N1 -N2 -C2 -N6	-82.8(2)	O2 -N6 -C2 -N5	0.7(3)
N3 -N2 -C2 -N5	-80.3(2)	N1 -C1 -C1_a -N1_a	180.00(15)
N3 -N2 -C2 -N6	102.50(19)	N1 -C1 -C1_a -N4_a	0.7(3)
N2 -N3 -N4 -C1	0.04(18)	N4 -C1 -C1_a -N1_a	-0.7(3)
N3 -N4 -C1 -N1	0.0(2)	N4 -C1 -C1_a -N4_a	180.00(16)
N3 -N4 -C1 -C1_a	-179.43(15)		

Table S13. Selected bond lengths [Å] and angles [°] for compound (**7**·2H_2O)

parameter	Å	parameter	Å
O4A-N1A	1.31(2)	O27-O27A	1.37(3)
O7A-N1A	1.254(17)	O27-O27A_b	1.37(3)
O9-N13	1.242(6)	O27-H27B_b	0.87
O10-N13	1.249(6)	O27-H27B	0.87
O11-N14	1.243(6)	O27-H27A_b	0.87
O12-N14	1.241(7)	O27-H27A	0.87
O13-N44	1.245(17)	O27A-H27D	0.88
O14-N23	1.283(14)	O27A-H27C	0.92

O15-N24	1.29(2)	O27A-H27A	0.77
O16-N24	1.24(2)	O25-O25_a	1.464(9)
O30-N44	1.30(3)	O25-H25A	0.87
O31-N23	1.277(19)	O25-H25B	0.87
O1-N1	1.240(7)	N1A-C9A	1.36(2)
O2-N1	1.244(7)	N13-C5	1.357(7)
O3-N2	1.235(6)	N14-C5	1.399(7)
O4-N2	1.250(7)	N15-N17	1.343(7)
O5-N11	1.247(7)	N15-N16	1.345(7)
O6-N11	1.242(7)	N15-C5	1.410(7)
O7-N12	1.247(8)	N16-C6	1.339(7)
O8-N12	1.226(8)	N17-N18	1.303(7)
O17-N25	1.246(6)	N18-C6	1.350(7)
O18-N25	1.262(7)	N19-C7	1.266(8)
O19-N26	1.221(5)	N19-N20	1.319(8)
O20-N26	1.251(7)	N20-N21	1.316(9)
O21-N35	1.242(6)	N20-C8	1.394(12)
O22-N35	1.234(5)	N20-C9A	1.463(16)
O23-N36	1.249(7)	N21-N22	1.316(8)
O24-N36	1.239(7)	N22-C7	1.392(8)
N23-C8	1.337(15)	N29-C10	1.357(6)
N24-C8	1.37(2)	N30-C10	1.314(6)
O26-O26A	1.59(2)	N31-N32	1.335(5)
N44-C9A	1.376(19)	N31-C11	1.326(6)
O26-H26B	0.85	N32-N33	1.346(6)
O26-H26A	0.8	N32-C12	1.383(6)
N1-C1	1.363(7)	N33-N34	1.308(5)
N2-C1	1.383(7)	N34-C11	1.362(6)
N3-N4	1.344(6)	N35-C12	1.383(7)

N3-N6	1.348(5)	N36-C12	1.369(7)
N3-C1	1.381(6)	C6-C7	1.424(8)
N4-N5	1.309(5)	C2-C3	1.453(7)
N5-C2	1.356(6)	N37-N38	1.445(7)
N6-C2	1.309(6)	N37-H37B	0.99
N7-C3	1.311(6)	N37-H37A	0.88
N7-N8	1.333(5)	N38-H38C	0.91
N8-N9	1.336(6)	N38-H38A	0.91
N8-C4	1.385(6)	N38-H38B	0.91
N9-N10	1.306(5)	C10-C11	1.450(7)
N10-C3	1.358(6)	N39-N40	1.427(7)
N11-C4	1.363(7)	N39-H39A	0.91
N12-C4	1.384(8)	N39-H39B	0.91
N25-C9	1.371(7)	N39-H39C	0.91
N26-C9	1.382(7)	N40-H40A	0.88
N27-N28	1.330(6)	N40-H40B	0.88
N27-N30	1.341(5)	N41-N42	1.394(8)
N27-C9	1.395(6)	N41-H41A	0.88
N28-N29	1.301(5)	N41-H41B	0.88
N23-C8	1.337(15)	N29-C10	1.357(6)
N24-C8	1.37(2)	N30-C10	1.314(6)
O26-O26A	1.59(2)	N31-N32	1.335(5)
N44-C9A	1.376(19)	N31-C11	1.326(6)
O26-H26B	0.85	N32-N33	1.346(6)
O26-H26A	0.8	N32-C12	1.383(6)
N1-C1	1.363(7)	N33-N34	1.308(5)
N2-C1	1.383(7)	N34-C11	1.362(6)
N3-N4	1.344(6)	N35-C12	1.383(7)
N3-N6	1.348(5)	N36-C12	1.369(7)

N3-C1	1.381(6)	C6-C7	1.424(8)
N4-N5	1.309(5)	C2-C3	1.453(7)
N5-C2	1.356(6)	N37-N38	1.445(7)
N6-C2	1.309(6)	N37-H37B	0.99
N7-C3	1.311(6)	N37-H37A	0.88
N7-N8	1.333(5)	N38-H38C	0.91
N8-N9	1.336(6)	N38-H38A	0.91
N8-C4	1.385(6)	N38-H38B	0.91
N9-N10	1.306(5)	C10-C11	1.450(7)
N10-C3	1.358(6)	N39-N40	1.427(7)
N11-C4	1.363(7)	N39-H39A	0.91
N12-C4	1.384(8)	N39-H39B	0.91
N25-C9	1.371(7)	N39-H39C	0.91
N26-C9	1.382(7)	N40-H40A	0.88
N27-N28	1.330(6)	N40-H40B	0.88
N27-N30	1.341(5)	N41-N42	1.394(8)
N27-C9	1.395(6)	N41-H41A	0.88
N28-N29	1.301(5)	N41-H41B	0.88

parameter	**Å**	**parameter**	**Å**
O27A_b-O27-H27B	92	O12-N14-C5	117.0(5)
O27A-O27-H27A_b	149	O11-N14-O12	122.6(5)
O27A-O27-H27B_b	92	N16-N15-C5	123.7(5)
H27A_b-O27-H27B_b	105	N17-N15-C5	122.3(5)
O27A_b-O27-H27A_b	31	N16-N15-N17	113.8(5)
O27A_b-O27-H27B_b	88	N15-N16-C6	100.4(4)
H27A-O27-H27B_b	75	N15-N17-N18	105.9(5)
O27A_b-O27-H27A	149	N17-N18-C6	106.9(5)
O27A-O27-H27B	88	N20-N19-C7	104.0(6)

H27A_b-O27-H27B	75	N21-N20-C8	121.5(7)
H27A-O27-H27B	105	N19-N20-C8	122.1(7)
O27A-O27-H27A	31	N19-N20-C9A	126.7(9)
H27A-O27-H27A_b	180	N19-N20-N21	113.1(5)
H27B-O27-H27B_b	180	N21-N20-C9A	115.9(8)
O27-O27A-H27A	36	N20-N21-N22	106.4(5)
H27A-O27A-H27D	162	N21-N22-C7	104.4(5)
H27C-O27A-H27D	104	O14-N23-C8	120.3(10)
H27A-O27A-H27C	77	O31-N23-C8	123.2(11)
H25A-O25-H25B	104	O14-N23-O31	116.4(11)
O25_a-O25-H25A	116	O15-N24-C8	114.6(17)
O25_a-O25-H25B	110	O15-N24-O16	122.3(18)
O4A-N1A-C9A	114.2(13)	O16-N24-C8	122.6(19)
O4A-N1A-O7A	118.5(17)	O30-N44-C9A	111.1(16)
O7A-N1A-C9A	127.3(17)	O13-N44-C9A	127.0(14)
O9-N13-O10	120.8(5)	O13-N44-O30	122.0(17)
O10-N13-C5	121.1(5)	H26A-O26-H26B	112
O9-N13-C5	118.2(5)	O2-N1-C1	121.8(5)
O11-N14-C5	120.4(5)	O1-N1-C1	116.9(5)
O1-N1-O2	121.3(5)	N30-N27-C9	123.5(4)
O4-N2-C1	116.2(5)	N28-N27-C9	122.7(4)
O3-N2-C1	121.9(5)	N28-N27-N30	113.7(4)
O3-N2-O4	121.9(5)	N27-N28-N29	105.9(4)
N4-N3-N6	113.1(3)	N28-N29-C10	106.5(4)
N6-N3-C1	124.0(4)	N27-N30-C10	101.1(4)
N4-N3-C1	122.6(4)	N32-N31-C11	101.4(4)
N3-N4-N5	106.1(3)	N33-N32-C12	122.6(4)
N4-N5-C2	105.8(4)	N31-N32-N33	113.6(3)
N3-N6-C2	101.0(4)	N31-N32-C12	123.8(4)

N8-N7-C3	101.5(4)	N32-N33-N34	105.9(3)
N7-N8-N9	113.1(3)	N33-N34-C11	106.4(4)
N7-N8-C4	123.0(4)	O22-N35-C12	121.6(4)
N9-N8-C4	123.8(4)	O21-N35-C12	116.5(4)
N8-N9-N10	106.5(3)	O21-N35-O22	121.8(5)
N9-N10-C3	105.5(4)	O23-N36-C12	116.8(5)
O6-N11-C4	120.9(5)	O23-N36-O24	121.8(5)
O5-N11-O6	122.3(5)	O24-N36-C12	121.4(5)
O5-N11-C4	116.8(5)	N14-C5-N15	115.0(5)
O7-N12-O8	123.7(6)	N13-C5-N14	126.6(5)
O7-N12-C4	115.3(5)	N13-C5-N15	116.9(5)
O8 -N12-C4	121.0(6)	N16-C6-C7	123.6(5)
O17-N25-O18	120.5(5)	N18-C6-C7	123.4(5)
O17-N25-C9	121.8(5)	N16-C6-N18	113.0(5)
O18-N25-C9	117.7(5)	N19-C7-N22	112.1(5)
O20-N26-C9	115.6(4)	N19-C7-C6	125.4(5)
O19-N26-O20	122.1(5)	N22-C7-C6	122.4(5)
O19-N26-C9	122.3(5)	N20-C8-N24	127.4(12)
N23-C8-N24	124.5(13)	N26-C9-N27	117.1(4)
N20-C8-N23	104.3(9)	N29-C10-N30	112.8(4)
N1A-C9A-N44	116.9(14)	N29-C10-C11	123.8(4)
N1A-C9A-N20	131.9(13)	N30-C10-C11	123.3(4)
N20-C9A-N44	110.7(12)	N31-C11-N34	112.7(4)
N1-C1-N3	117.5(5)	N31-C11-C10	124.3(4)
N2-C1-N3	117.2(5)	N34-C11-C10	122.9(4)
N1-C1-N2	125.1(5)	N32-C12-N35	116.9(4)
N5-C2-N6	114.0(4)	N32-C12-N36	118.6(5)
N5-C2-C3	122.4(4)	N35-C12-N36	124.4(5)
N6-C2-C3	123.6(4)	N40-N39-H39A	110

N7-C3-N10	113.4(4)	N40-N39-H39B	109
N7-C3-C2	123.8(4)	N40-N39-H39C	109
N10-C3-C2	122.8(4)	H39A-N39-H39B	110
N11-C4-N12	123.9(5)	H39A-N39-H39C	110
N8-C4-N12	117.5(5)	H39B-N39-H39C	109
N8-C4-N11	118.3(5)	N39-N40-H40A	109
N38-N37-H37A	109	N39-N40-H40B	109
N38-N37-H37B	89	H40A-N40-H40B	109
H37A-N37-H37B	90	N42-N41-H41A	110
H38A-N38-H38C	110	N42-N41-H41B	108
H38B-N38-H38C	109	H41A-N41-H41B	109
H38A-N38-H38B	109	N41-N42-H42A	110
N37-N38-H38A	109	N41-N42-H42B	110
N37-N38-H38B	109	N41-N42-H42C	110
N37-N38-H38C	109	H42A-N42-H42B	109
N25-C9-N26	124.4(5)	H42A-N42-H42C	109
N25-C9-N27	118.2(5)	H42B-N42-H42C	109
N46-N45-H45A	110	N49-N50-H50B	110
N46-N45-H45B	110	H29A_c-O29-H29B	119
H45A-N45-H45B	108	H29A-O29-H29B_c	119
N45-N46-H46A	109	H29A-O29-H29B	107
N45-N46-H46B	109	H29B-O29-H29B_c	132
N45-N46-H46C	109	H29A_c-O29-H29B_c	107
H46A-N46-H46B	110	H29A-O29-H29A_c	32
H46A-N46-H46C	109	H43A-N43-H43C	109
H46B-N46-H46C	110	N51-N43-H43A	110
H28A-O28-H28B	105	N51-N43-H43B	110
N48-N47-H47B	110	N51-N43-H43C	110
N48-N47-H47C	110	H43B-N43-H43C	109

H47A-N47-H47B	109	H43A-N43-H43B	109
H47A-N47-H47C	109	N43-N51-H51B	110
H47B-N47-H47C	109	H51A-N51-H51B	108
N48-N47-H47A	109	N43-N51-H51A	111
N47-N48-H48A	111	N48A-N47A-H47E	109
H48A-N48-H48B	109	N48A-N47A-H47F	109
N47-N48-H48B	110	N48A-N47A-H47D	110
H28C-O28A-H28D	105	H47D-N47A-H47E	110
N50-N49-H49B	109	H47D-N47A-H47F	109
N50-N49-H49A	110	H47E-N47A-H47F	109
H49A-N49-H49C	110	N47A-N48A-H48C	110
N50-N49-H49C	110	N47A-N48A-H48D	110
H49A-N49-H49B	109	H48C-N48A-H48D	109
H49B-N49-H49C	109	N50A-N49A-H49D	109
H50A-N50-H50B	108	N50A-N49A-H49F	109
N49-N50-H50A	109	H49D-N49A-H49E	110
H49D-N49A-H49F	110	N49A-N50A-H50D	119
H49E-N49A-H49F	110	H50C-N50A-H50D	103
N50A-N49A-H49E	109	N49A-N50A-H50C	112

Table S14. Torsion angles [º] of **7**·2H_2O

parameter	Å	parameter	Å
O9-N13-C5-N14	-167.6(5)	N7-N8-C4-N11	74.5(7)
O10-N13-C5-N14	13.9(9)	N9-N8-C4-N11	-106.4(6)
O9-N13-C5-N15	-2.2(7)	N7-N8-C4-N12	-100.0(6)
O10-N13-C5-N15	179.3(5)	C4-N8-N9-N10	-179.4(5)
O11-N14-C5-N15	-167.3(5)	N8-N9-N10-C3	-0.4(6)
O12-N14-C5-N15	11.1(7)	N9-N10-C3-C2	-176.8(5)
O12-N14-C5-N13	176.7(5)	N9-N10-C3-N7	1.1(6)

O11-N14-C5-N13	-1.7(9)	O5-N11-C4-N12	178.5(5)
N17-N15-N16-C6	-1.4(6)	O6-N11-C4-N8	-172.7(5)
C5-N15-N16-C6	-177.2(5)	O6-N11-C4-N12	1.5(8)
C5-N15-N17-N18	177.9(5)	O5-N11-C4-N8	4.4(7)
N17-N15-C5-N13	82.1(7)	O8-N12-C4-N11	10.1(9)
N16-N15-C5-N14	64.6(7)	O7-N12-C4-N8	4.5(7)
N17-N15-C5-N14	-110.8(6)	O7-N12-C4-N11	-169.7(5)
N16-N15-N17-N18	2.0(6)	O8-N12-C4-N8	-175.8(5)
N16-N15-C5-N13	-102.4(6)	O17-N25-C9-N27	-179.6(4)
N15-N16-C6-N18	0.3(6)	O17-N25-C9-N26	6.2(8)
N15-N16-C6-C7	-179.3(5)	O18-N25-C9-N27	1.7(7)
N15-N17-N18-C6	-1.6(6)	O18-N25-C9-N26	-172.5(5)
N17-N18-C6-N16	0.9(6)	O20-N26-C9-N27	-1.9(6)
N17-N18-C6-C7	-179.5(5)	O20-N26-C9-N25	172.3(5)
C7-N19-N20-N21	-0.8(8)	O19-N26-C9-N27	178.7(4)
C7-N19-N20-C8	159.0(8)	O19-N26-C9-N25	-7.1(7)
N20-N19-C7-N22	1.1(7)	N30-N27-N28-N29	0.3(6)
N20-N19-C7-C6	178.5(6)	N28-N27-C9-N26	-87.4(6)
N19-N20-N21-N22	0.2(8)	N30-N27-C9-N26	87.6(6)
N19-N20-C8-N24	-48(2)	N30-N27-C9-N25	-87.0(7)
N19-N20-C8-N23	110.4(9)	N28-N27-C9-N25	98.0(6)
N21-N20-C8-N23	-91.6(10)	N28-N27-N30-C10	-0.5(6)
C8-N20-N21-N22	-159.7(7)	C9-N27-N28-N29	175.8(5)
N21-N20-C8-N24	110.1(17)	C9-N27-N30-C10	-176.0(5)
N20-N21-N22-C7	0.5(7)	N27-N28-N29-C10	0.0(6)
N21-N22-C7-C6	-178.5(5)	N28-N29-C10-N30	-0.4(6)
N21-N22-C7-N19	-1.0(7)	N28-N29-C10-C11	178.6(5)
O31-N23-C8-N24	165.9(17)	N27-N30-C10-N29	0.6(6)
O14-N23-C8-N20	-178.6(9)	N27-N30-C10-C11	-178.4(5)

O31-N23-C8-N20	6.7(16)	N32-N31-C11-N34	-1.0(6)
O14-N23-C8-N24	-19(2)	N32-N31-C11-C10	-176.9(5)
O16-N24-C8-N20	166.7(16)	C11-N31-N32-N33	1.8(6)
O15-N24-C8-N23	-176.4(14)	C11-N31-N32-C12	179.2(5)
O15-N24-C8-N20	-22(3)	N33-N32-C12-N35	-103.4(6)
O16-N24-C8-N23	12(3)	N33-N32-C12-N36	78.5(7)
O2-N1-C1-N2	-9.6(9)	N31-N32-N33-N34	-1.9(6)
O2-N1-C1-N3	175.0(5)	N31-N32-C12-N35	79.5(7)
O1-N1-C1-N3	-4.3(7)	C12-N32-N33-N34	-179.4(5)
O1-N1-C1-N2	171.2(5)	N31-N32-C12-N36	-98.6(6)
O3-N2-C1-N1	1.8(8)	N32-N33-N34-C11	1.1(6)
O3-N2-C1-N3	177.2(5)	N33-N34-C11-C10	175.9(5)
O4-N2-C1-N3	-1.5(7)	N33-N34-C11-N31	0.0(6)
O4-N2-C1-N1	-176.9(5)	O21-N35-C12-N36	177.6(5)
N6-N3-C1-N1	100.2(6)	O22-N35-C12-N36	-0.6(7)
N4-N3-C1-N2	110.3(6)	O21-N35-C12-N32	-0.4(6)
N6-N3-C1-N2	-75.6(7)	O22-N35-C12-N32	-178.5(4)
C1-N3-N6-C2	-175.4(5)	O23-N36-C12-N32	2.2(7)
N6-N3-N4-N5	0.7(6)	O24-N36-C12-N32	-179.3(5)
C1-N3-N4-N5	175.4(5)	O24-N36-C12-N35	2.8(8)
N4-N3-C1-N1	-73.9(7)	O23-N36-C12-N35	-175.7(5)
N4-N3-N6-C2	-0.8(6)	N16-C6-C7-N19	-177.2(6)
N3-N4-N5-C2	-0.3(6)	N18-C6-C7-N22	-179.7(5)
N4-N5-C2-N6	-0.3(7)	N16-C6-C7-N22	0.0(8)
N4-N5-C2-C3	-179.4(5)	N18-C6-C7-N19	3.2(9)
N3-N6-C2-N5	0.7(6)	N5-C2-C3-N7	5.2(8)
N3-N6-C2-C3	179.8(5)	N5-C2-C3-N10	-177.1(5)
C3-N7-N8-N9	0.9(6)	N6-C2-C3-N10	3.9(8)
C3-N7-N8-C4	-180.0(5)	N6-C2-C3-N7	-173.8(5)

N8-N7-C3-N10	-1.2(6)	N29-C10-C11-N31	-4.9(8)
N8-N7-C3-C2	176.7(5)	N30-C10-C11-N31	174.0(5)
N7-N8-N9-N10	-0.3(6)	N30-C10-C11-N34	-1.5(8)
N9-N8-C4-N12	79.1(7)	N29-C10-C11-N34	179.6(5)

Table S15. Hydrogen bonds of **7**·2H_2O

D-H···A	**d(D-H)/Å**	**d(H···A)/ Å**	**d(D···A)/ Å**	**<(DHA)/°**
O25-H25A···O15	0.87	2.19	2.722(11)	119
O25-H25A···N34	0.87	2.33	3.103(7)	148
O26-H26A···N42	0.8	2.27	2.80(2)	123
O28-H28A···O29	0.87	1.84	2.683(19)	164
O28-H28B···N10	0.87	2.21	3.053(11)	164
O28A-H28D···O2	0.87	2.19	2.689(16)	116
O28A-H28D···O3	0.87	2.42	3.164(16)	143
O29-H29A···O28	0.86	1.92	2.683(19)	147
N37-H37A···O22	0.88	2.37	2.923(6)	121
N38-H38A···N29	0.91	2.39	3.204(7)	149
N38-H38C···N46	0.91	2.41	3.155(12)	139
N40-H40B···N37	0.88	2.09	2.803(7)	137
N41-H41A···O14	0.88	2.53	3.090(11)	122
N41-H41A···O23	0.88	2.56	3.280(7)	140
N42-H42A···O14	0.91	2.52	2.983(11)	112
N42-H42A···O26	0.91	1.91	2.80(2)	163
N42-H42C···O7	0.91	2.53	3.292(9)	142
N45-H45A···N39	0.89	2.31	2.954(16)	128
N45-H45B···O22	0.89	2.1	2.946(16)	159
N46-H46A···O5	0.91	2.27	3.053(12)	143
N46-H46B···N38	0.91	2.49	3.155(12)	130
N47-H47A···O29	0.91	1.68	2.570(12)	167

N47-H47B···N19	0.91	2.45	3.301(12)	155
N48-H48A···N50	0.88	2.29	3.13(2)	160
N48-H48B···O3	0.88	2.28	3.046(14)	145
N49-H49B···O25	0.91	1.83	2.724(12)	165
N50-H50B···N48	0.89	2.28	3.13(2)	161

Table S16. Selected bond lengths [Å] and angles [^{o}] for **9**

parameter	**Å**	**parameter**	**Å**
O5 -N17	1.255(15)	N18A -C7A	1.37(3)
O5A-N17A	1.27(3)	N1 -C1	1.302(7)
O6 -N17	1.250(13)	N1 -N2	1.337(6)
O6A-N17A	1.25(2)	N2 -C2	1.395(8)
O7 -N18	1.257(17)	N2 -N3	1.350(6)
O7A-N18A	1.24(3)	N3 -N4	1.299(7)
O8 -N18	1.261(11)	N4 -C1	1.364(6)
O8A-N18A	1.24(3)	N5 -C2	1.372(7)
O1 -N5	1.265(6)	N6 -C2	1.374(8)
O2 -N5	1.251(7)	N7 -C3	1.295(8)
O3 -N6	1.233(6)	N8 -N9	1.389(8)
O4 -N6	1.255(7)	N8 -C3	1.335(8)
O10-C8	1.216(19)	N9 -C4	1.275(7)
O10-H10	0.83	N10-N11	1.391(6)
O9 -H9B_c	0.86	N10-C4	1.366(7)
O9 -H9B	0.86	N10-C3	1.352(7)
O9 -H9A	0.86	N12-C5	1.478(8)
O9 -H9A_c	0.86	N7 -H7A	0.87
N13-N14	1.357(8)	N7 -H7B	0.87
N13-C6	1.311(6)	N8 -H8	0.87
N14-N15	1.323(6)	N11-H11A	0.87

N14-C7A	1.41(3)	N11-H11B	0.87
N14-C7	1.435(14)	N12-H12B	0.9
N15-N16	1.308(7)	N12-H12A	0.9
N16-C6	1.353(7)	N12-H12C	0.9
N17-C7	1.378(18)	C6 -C6_b	1.457(7)
N17A -C7A	1.38(3)	C1 -C1_a	1.471(7)
N18-C7	1.374(17)	C4 -C5	1.489(8)
C5 -H5B	0.98	C8 -H8C	0.97
C5 -H5A	0.98	C8 -H8A	0.97
C8 -H8B	0.97		

parameter	**Å**	**parameter**	**Å**
C8 -O10-H10	110	N1 -N2 -C2	122.9(5)
H9A-O9 -H9A_c	75	N3 -N2 -C2	123.4(5)
H9A-O9 -H9B_c	135	N1 -N2 -N3	113.6(5)
H9A_c-O9 -H9B	135	N2 -N3 -N4	105.3(4)
H9B-O9 -H9B_c	106	N3 -N4 -C1	106.4(4)
H9A_c-O9-H9B_c	104	O1 -N5 -C2	116.8(5)
H9A-O9 -H9B	104	O2 -N5 -C2	121.5(5)
N14-N13-C6	100.1(4)	O1 -N5 -O2	121.6(4)
N13-N14-C7	120.6(7)	O3 -N6 -O4	122.2(5)
N15-N14-C7A	115.2(12)	O4 -N6 -C2	120.6(5)
N13-N14-C7A	129.5(12)	O3 -N6 -C2	117.2(5)
N15-N14-C7	123.4(7)	N9 -N8 -C3	113.0(5)
N13-N14-N15	114.0(4)	N8 -N9 -C4	102.4(5)
N14-N15-N16	105.9(5)	N11-N10-C4	124.1(4)
N15-N16-C6	106.0(4)	C3 -N10-C4	107.0(4)
O5 -N17-C7	115.2(11)	N11-N10-C3	128.8(5)
O5 -N17-O6	121.7(12)	C3 -N7 -H7A	120

O6 -N17-C7	123.2(11)	H7A-N7 -H7B	120
O5A-N17A -C7A	120.9(19)	C3 -N7 -H7B	120
O5A-N17A -O6A	121(2)	C3 -N8 -H8	124
O6A-N17A -C7A	118(2)	N9 -N8 -H8	123
O8 -N18-C7	120.7(11)	N10-N11-H11A	109
O7 -N18-C7	116.0(10)	N10-N11-H11B	110
O7 -N18-O8	123.3(11)	H11A -N11-H11B	109
O7A-N18A -O8A	126(2)	C5 -N12-H12B	109
O8A-N18A -C7A	119(2)	H12B -N12-H12C	109
O7A-N18A -C7A	112(2)	H12A -N12-H12B	109
N2 -N1 -C1	101.3(4)	H12A-N12-H12C	109
C5 -N12-H12A	109	N8 -C3 -N10	104.2(5)
C5 -N12-H12C	110	N7 -C3 -N10	126.1(6)
N16-C6 -C6_b	122.6(4)	N9 -C4 -C5	125.0(5)
N13-C6 -C6_b	123.4(5)	N10-C4 -C5	121.6(5)
N13-C6 -N16	114.0(5)	N9 -C4 -N10	113.4(5)
N17-C7 -N18	125.2(12)	N12-C5 -C4	109.4(5)
N14-C7 -N17	120.4(11)	H5A-C5 -H5B	108
N14-C7 -N18	114.2(10)	N12-C5 -H5A	110
N17A -C7A-N18A	128(2)	C4 -C5 -H5B	110
N14-C7A-N17A	103.5(17)	C4 -C5 -H5A	110
N14-C7A-N18A	128(2)	N12-C5 -H5B	110
N4 -C1 -C1_a	122.4(5)	H8B-C8 -H8C	109
N1 -C1 -N4	113.4(5)	O10-C8 -H8A	109
N1 -C1 -C1_a	124.1(4)	O10-C8 -H8B	110
N5 -C2 -N6	126.2(5)	O10-C8 -H8C	109
N2 -C2 -N6	116.6(5)	H8A-C8 -H8B	110
N2 -C2 -N5	116.5(5)	H8A-C8 -H8C	109
N7 -C3 -N8	129.7(6)		

Table S17. Torsion angles [º] of **9**

parameter	Å	parameter	Å
C6 -N13-N14-N15	-0.8(6)	N3 -N4 -C1 -C1_a	178.0(4)
C6 -N13-N14-C7	-165.2(7)	O2 -N5 -C2 -N2	-176.2(5)
N14-N13-C6 -N16	0.4(6)	O1 -N5 -C2 -N6	174.5(5)
N14-N13-C6 -C6_b	178.1(5)	O1 -N5 -C2 -N2	4.9(7)
N15-N14-C7 -N17	-89.0(13)	O2 -N5 -C2 -N6	-6.6(8)
N13-N14-N15-N16	0.9(7)	O4 -N6 -C2 -N5	0.4(8)
C7 -N14-N15-N16	164.8(8)	O3 -N6 -C2 -N5	-179.9(5)
N13-N14-C7 -N17	73.9(13)	O4 -N6 -C2 -N2	170.1(5)
N13-N14-C7 -N18	-110.6(10)	O3 -N6 -C2 -N2	-10.2(7)
N15-N14-C7 -N18	86.6(12)	C3 -N8 -N9 -C4	-1.6(6)
N14-N15-N16-C6	-0.5(6)	N9 -N8 -C3 -N7	-178.3(6)
N15-N16-C6 -N13	0.1(6)	N9 -N8 -C3 -N10	1.5(7)
N15-N16-C6 -C6_b	-177.6(5)	N8 -N9 -C4 -N10	1.1(6)
O5 -N17-C7 -N14	-6.2(17)	N8 -N9 -C4 -C5	179.9(5)
O6 -N17-C7 -N14	175.4(10)	N11-N10-C3 -N8	177.1(5)
O5 -N17-C7 -N18	178.7(12)	C4 -N10-C3 -N8	-0.7(6)
O6 -N17-C7 -N18	0(2)	N11-N10-C4 -N9	-178.2(5)
O8 -N18-C7 -N17	-1.1(18)	N11-N10-C3 -N7	-3.1(10)
O7 -N18-C7 -N14	5.7(15)	C4 -N10-C3 -N7	179.1(6)
O8 -N18-C7 -N14	-176.4(8)	C3 -N10-C4 -C5	-179.1(5)
O7 -N18-C7 -N17	-179.0(12)	C3 -N10-C4 -N9	-0.3(6)
C1 -N1 -N2 -C2	179.6(5)	N11-N10-C4 -C5	2.9(8)
C1 -N1 -N2 -N3	0.4(6)	N16-C6 -C6_b -N13_b	-2.6(7)
N2 -N1 -C1 -C1_a	-178.7(5)	N13-C6 -C6_b -N13_b	-180.0(5)
N2 -N1 -C1 -N4	0.6(6)	N16-C6 -C6_b -N16_b	180.0(5)
N1 -N2 -N3 -N4	-1.2(6)	N13-C6 -C6_b -N16_b	2.6(7)
N3 -N2 -C2 -N6	102.3(6)	N1 -C1 -C1_a -N1_a	-180.0(5)

N3 -N2 -C2 -N5	-87.0(7)	N1 -C1 -C1_a -N4_a	-0.8(8)
C2 -N2 -N3 -N4	179.6(5)	N4 -C1 -C1_a -N1_a	0.8(8)
N1 -N2 -C2 -N5	93.8(6)	N4 -C1 -C1_a -N4_a	-180.0(5)
N1 -N2 -C2 -N6	-76.9(7)	N9 -C4 -C5 -N12	-7.3(8)
N2 -N3 -N4 -C1	1.4(5)	N10-C4 -C5 -N12	171.4(5)
N3 -N4 -C1 -N1	-1.4(6)		

Table S18. Hydrogen bonds of **9**

D-H···A	**d(D-H)/Å**	**d(H···A)/ Å**	**d(D···A)/ Å**	**<(DHA)/°**
N7-H7A···O6	0.87	1.98	2.831(10)	166
N7-H7B···O2	0.87	2.15	2.996(7)	163
N8-H8···O1	0.87	2.31	3.013(6)	138
N8-H8···O8	0.87	2.28	2.926(9)	131
O9-H9A···N12	0.86	2.3	2.826(7)	120
O9-H9B···O10	0.86	2.33	3.120(12)	152
N11-H11A···O3	0.87	2.38	3.174(7)	152
N11-H11B···O1	0.87	2.22	3.094(6)	175
N12-H12A···O9	0.9	1.97	2.826(7)	158
N12-H12B···O2	0.9	2.27	3.011(7)	139
N12-H12B···O4	0.9	2.27	2.938(7)	131
N12-H12C···O5	0.9	2.34	2.811(11)	112
N12-H12C···N4	0.9	2.28	3.067(7)	145
C5-H5A···N15	0.98	2.51	3.396(8)	150
C5-H5B···O4	0.98	2.55	2.958(7)	105
C8-H8A···O9	0.97	1.51	2.460(16)	167
C8-H8B···O4	0.97	2.57	3.470(14)	155
C8-H8B···N6	0.97	2.28	3.207(14)	159

Theoretical calculations were performed by using the Gaussian 09 (Revision E.01)

suite of programs.[错误！未找到引用源。] 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.[1] 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 $\Delta(PV)$ value in eq (2) is the PV work term. It equals $\Delta(nRT)$ for the reactions of ideal gas. For the isodesmic reaction, $\Delta n = 0$, so $\Delta(PV) = 0$. 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):

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

Where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [3] [Eq. (2)]

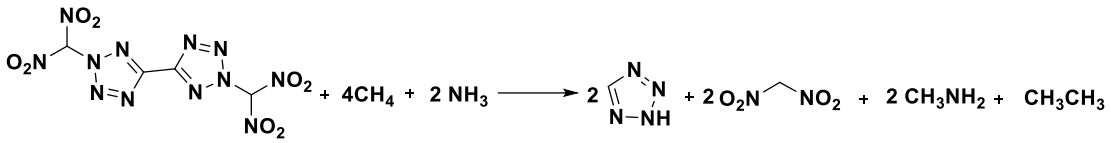
$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (2)$$

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

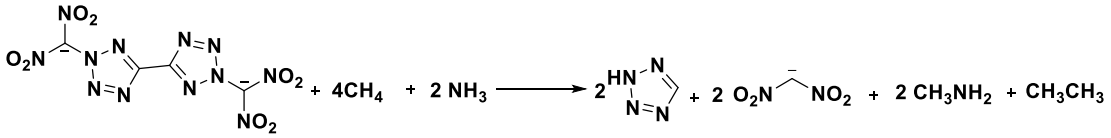
equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

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

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.[4,5]

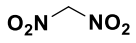
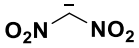
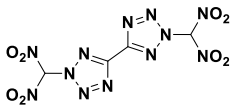
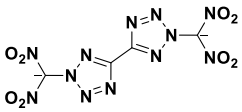


Scheme S1. Isodesmic reactions of neutral compounds.



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
NH_3	-56.58	86.27	10.05	-45.9
CH_3NH_2	-95.89	160.78	11.64	-22.5
CH_3CH_3	-79.86	187.31	11.79	-84
	-258.32	117.69	11.84	334.3
	-449.61	132.90	14.71	-25.61
	-449.08	100.12	18.42	-232.98
	-1412.23	350.61	55.15	838.79
	-1411.16	286.52	53.52	437.86

[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});

3.References

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[2] Hariharan, P. C.; Pople, J. A.; Influence of Polarization Functions On MO Hydrogenation Energies. Theor. Chim. Acta. 1973, 28, 213-222.

[3] Ochterski, J. W.; Petersson, G. A.; A Complete Basis Set Model Chemistry. V. Extensions to Six or More Heavy Atoms. Montgomery JA, J. Chem. Phys. 1996, 104, 2598-2619.

[4] Jenkins, H. D.; Tudeal, D.; Glasser, L. Lattice Potential Energy Estimation for Complex Ionic Salts from Density Measurements. Inorg. Chem. 2002, 41, 2364-2367.

[5] Jenkins, H. D.; Roobottom, H. K.; Passmore J, Glasser L. Relationships among Ionic Lattice Energies, Molecular (Formula Unit) Volumes, And Thermochemical Radii. Inorg. Chem. 1999, 38, 3609-3620.

4. ^{1}H and ^{13}C NMR Spectra of BDNBT and Compounds 1-10

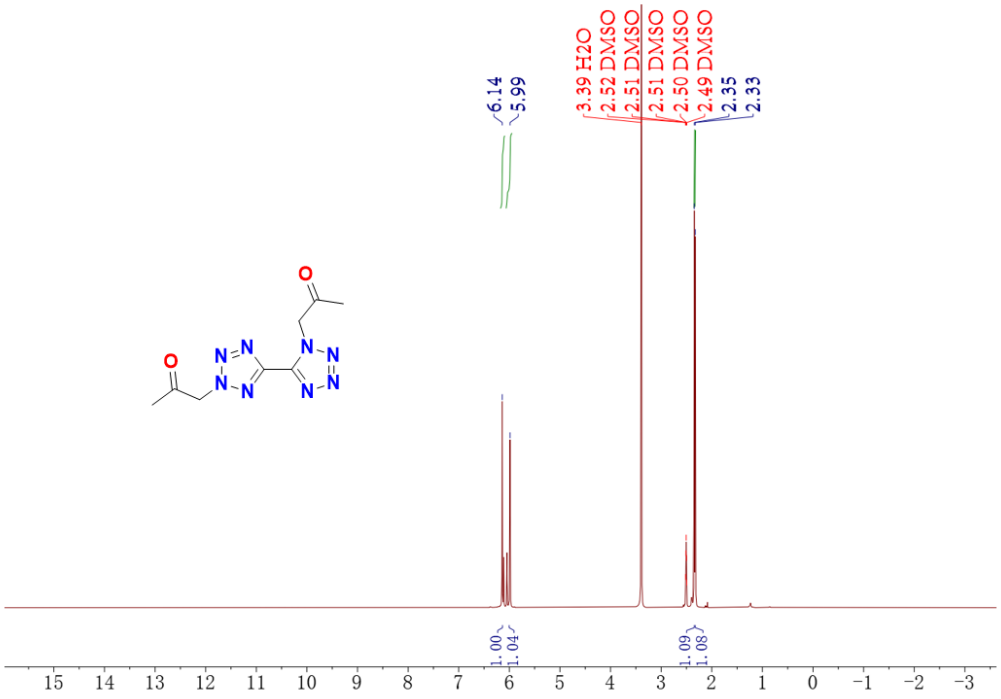

Figure S11 ^{1}H NMR spectra (300 MHz) of **1** in [D_6] DMSO at 25 °C.

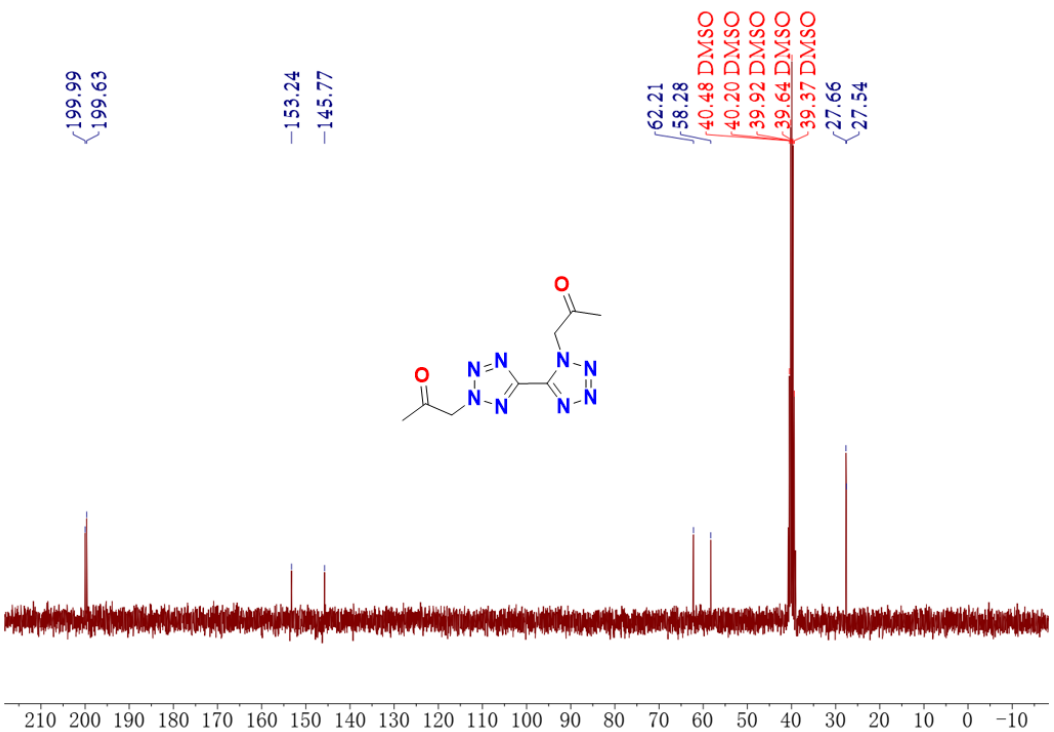

Figure S12 ^{13}C NMR spectra (75 MHz) of **1** in [D_6] DMSO at 25 °C.

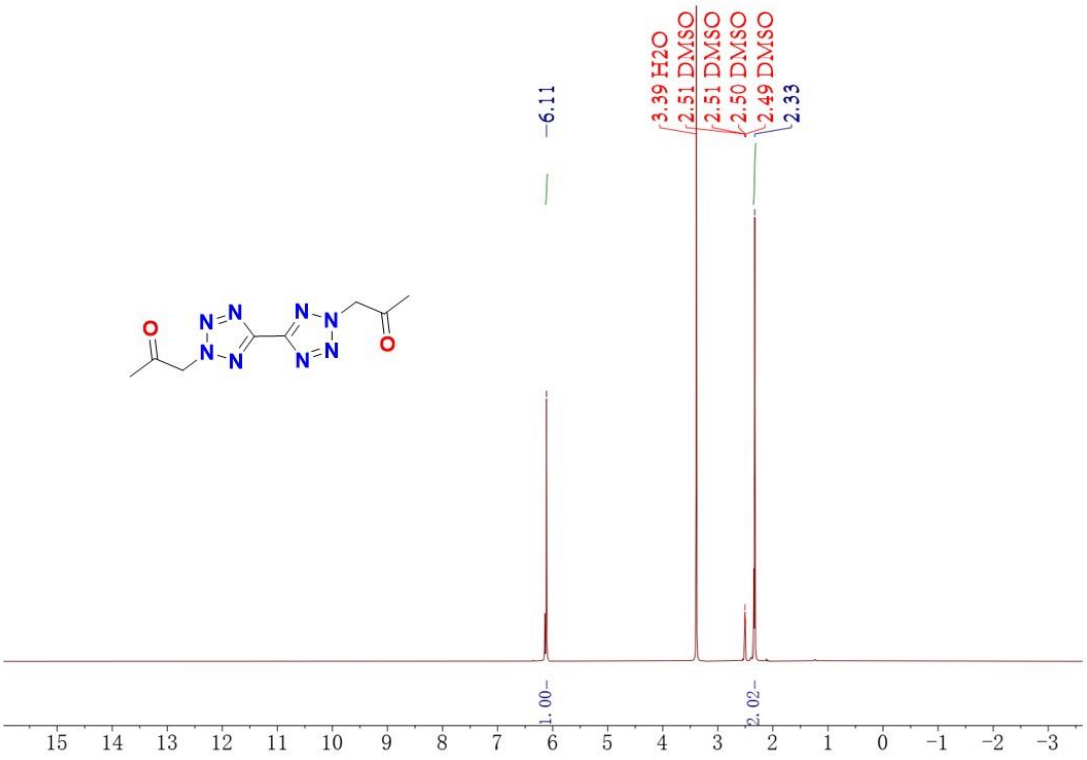

Figure S13 ^{1}H NMR spectra (300 MHz) of **2** in [D_6] DMSO at 25 °C.

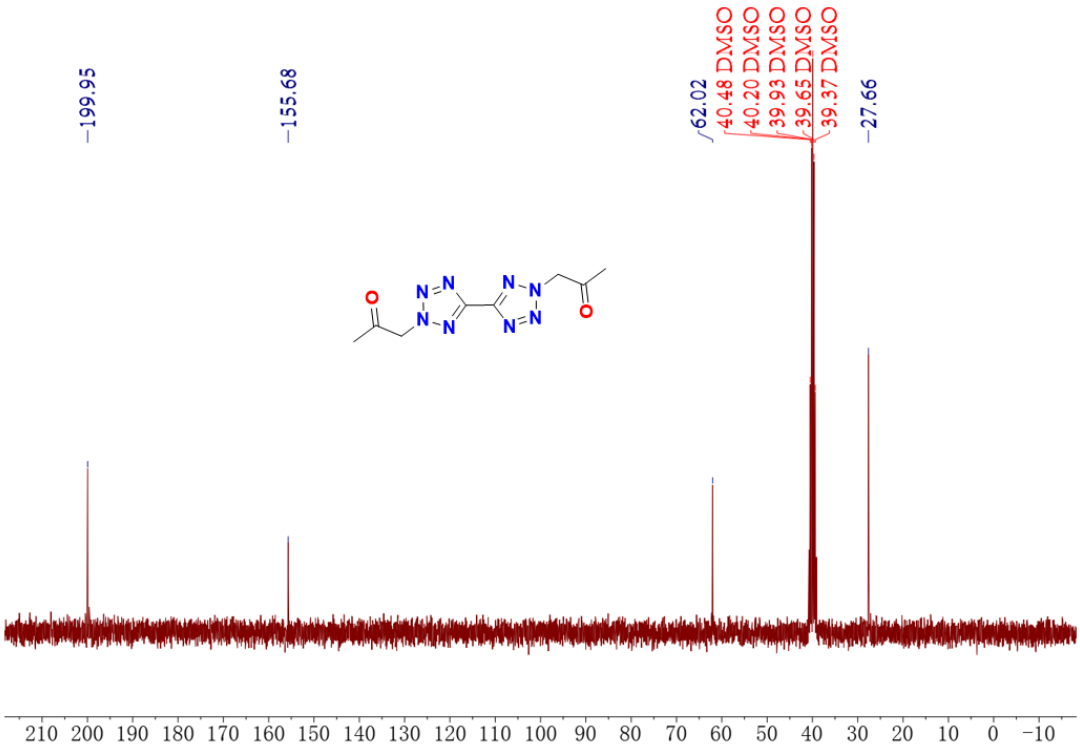

Figure S14 ^{13}C NMR spectra (75 MHz) of **2** in [D_6] DMSO at 25 °C.

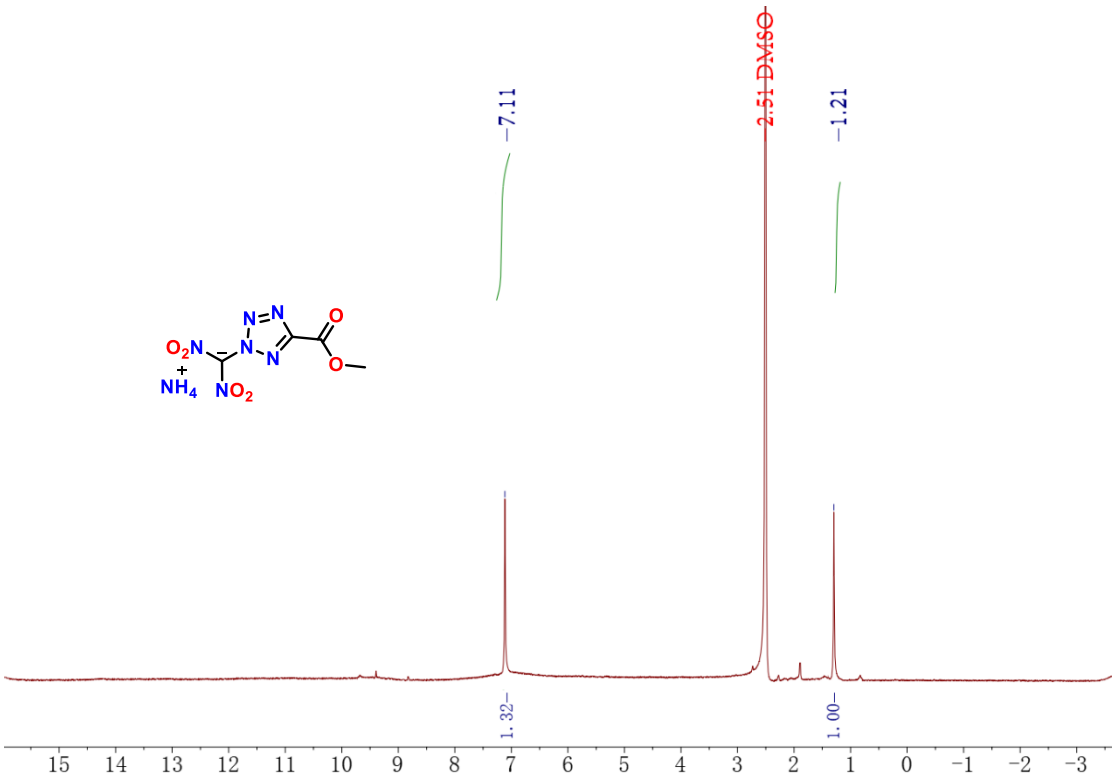

Figure S15 ^{1}H NMR spectra (300 MHz) of **3** in [D_6] DMSO at 25 °C.

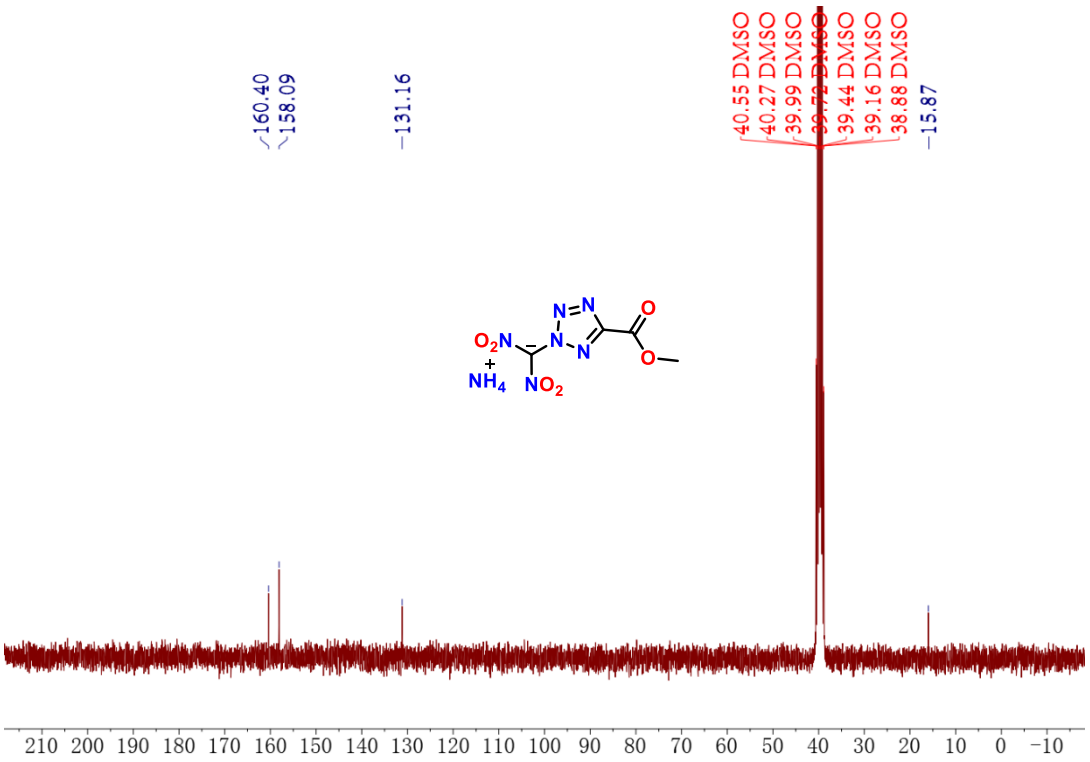

Figure S16 ^{13}C NMR spectra (75 MHz) of **3** in [D_6] DMSO at 25 °C.

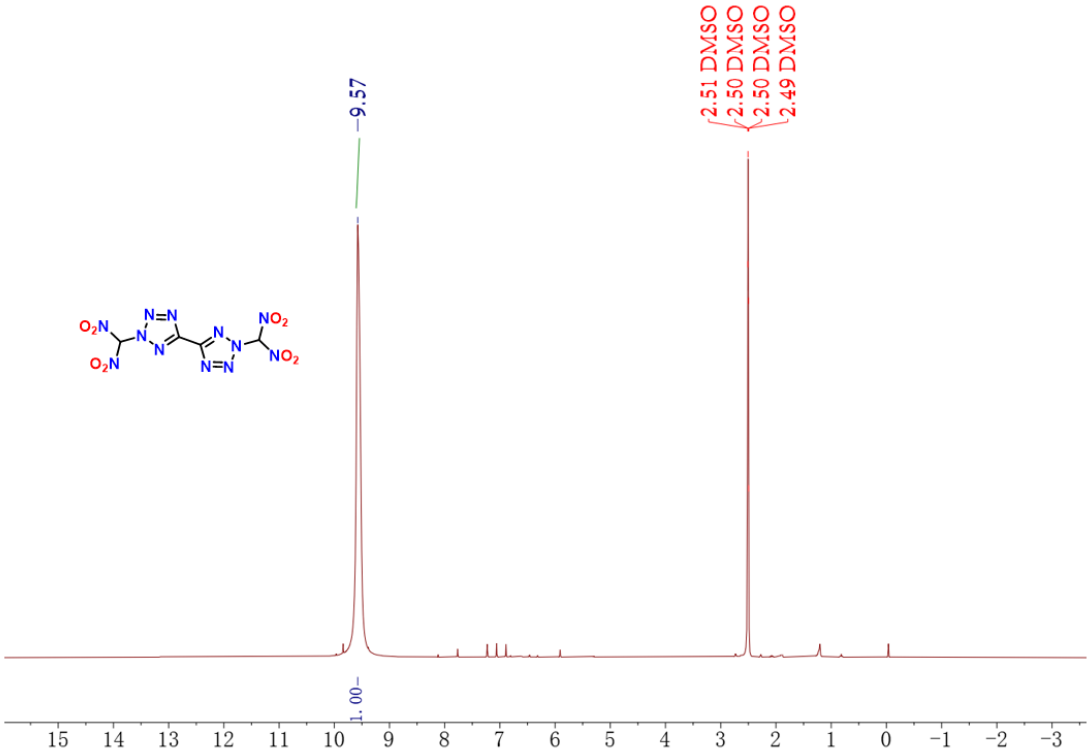

Figure S17 ^{1}H NMR spectra (300 MHz) of **BDNBT** in [D_6] DMSO at 25 °C.

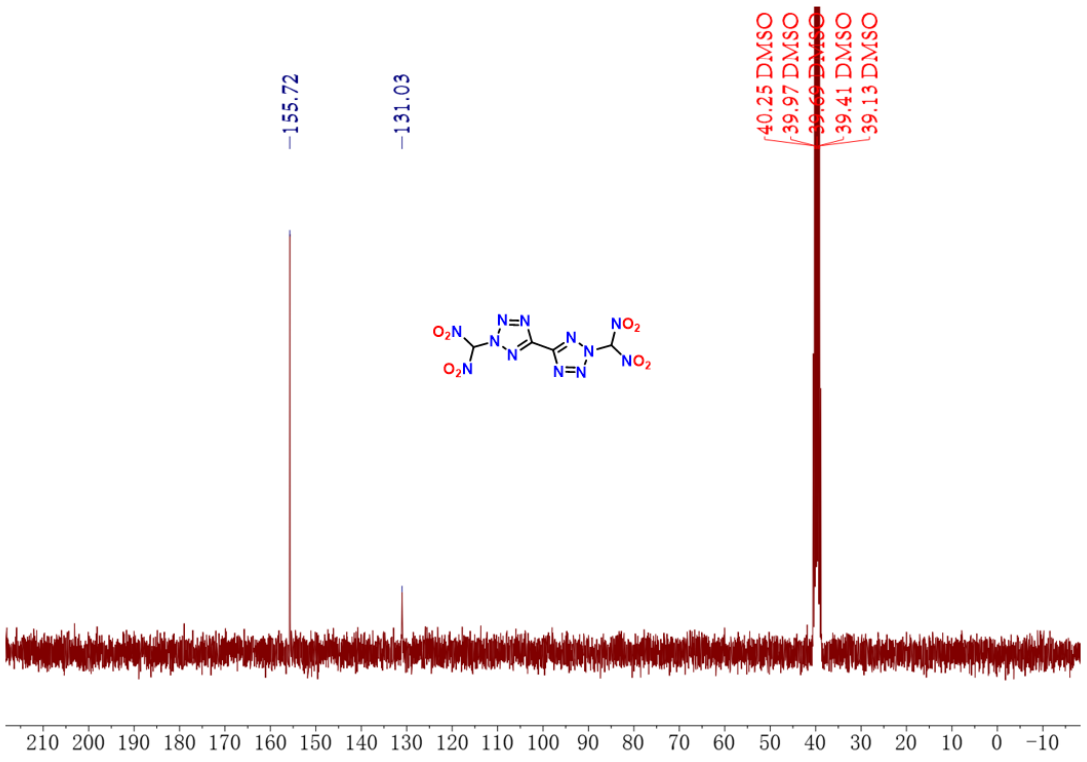

Figure S18 ^{13}C NMR spectra (75 MHz) of **BDNBT** in [D_6] DMSO at 25 °C.

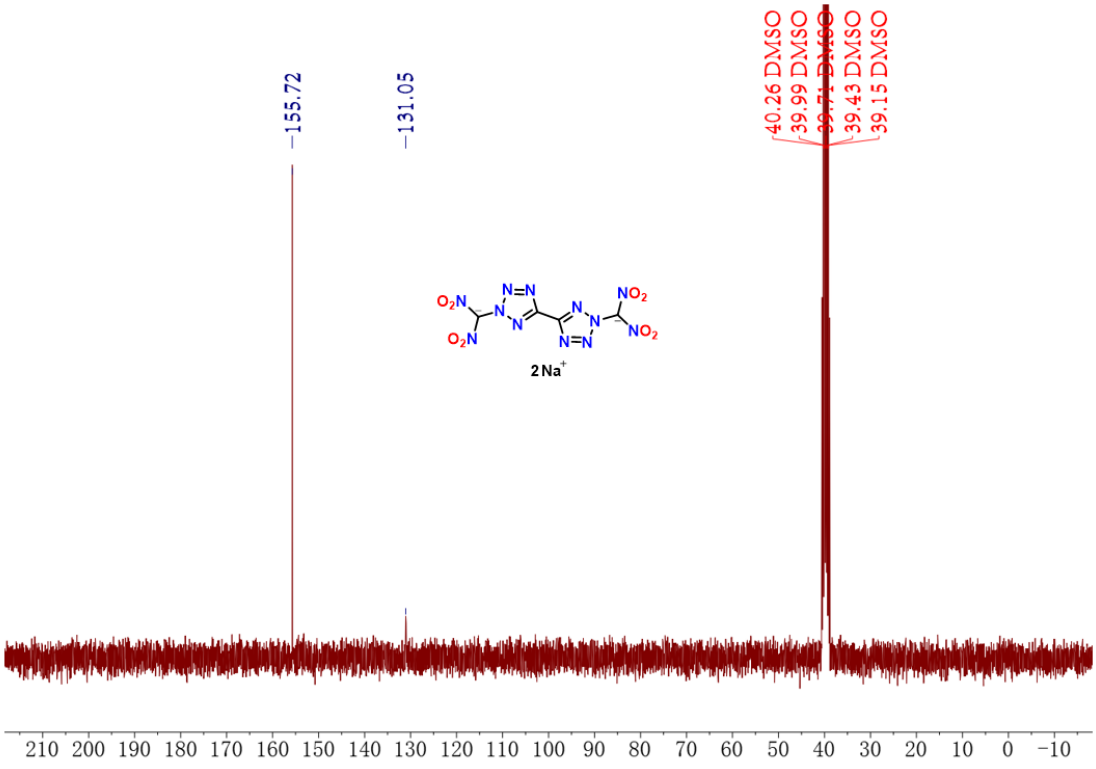

Figure S19 ^{13}C NMR spectra (75 MHz) of **4** in [D_6] DMSO at 25 ºC.

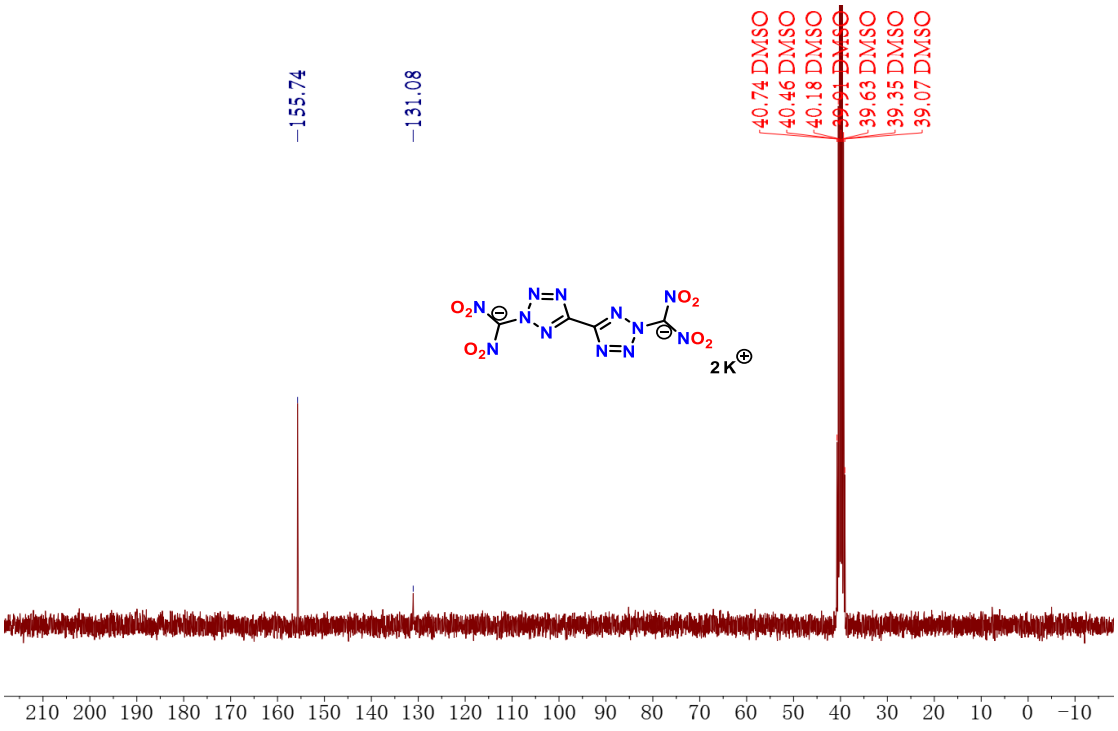

Figure S20 ^{13}C NMR spectra (75 MHz) of **5** in [D_6] DMSO at 25 ºC.

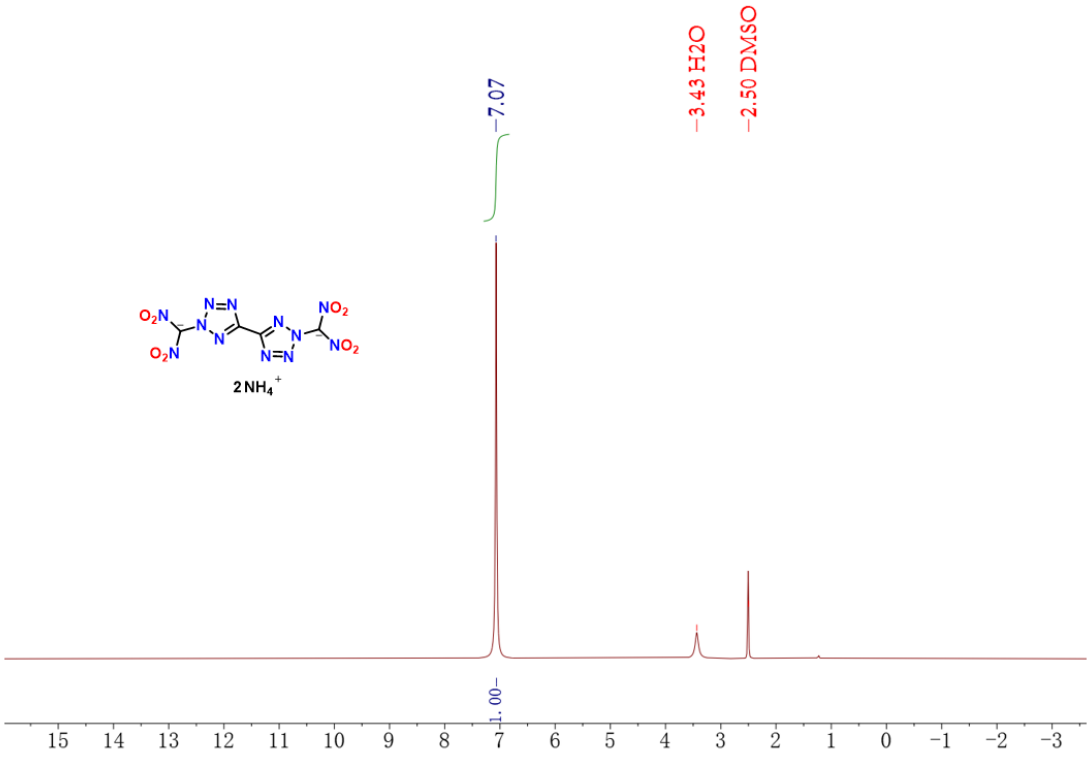

Figure S21 ^{1}H NMR spectra (300 MHz) of **6** in [D_6] DMSO at 25 °C.

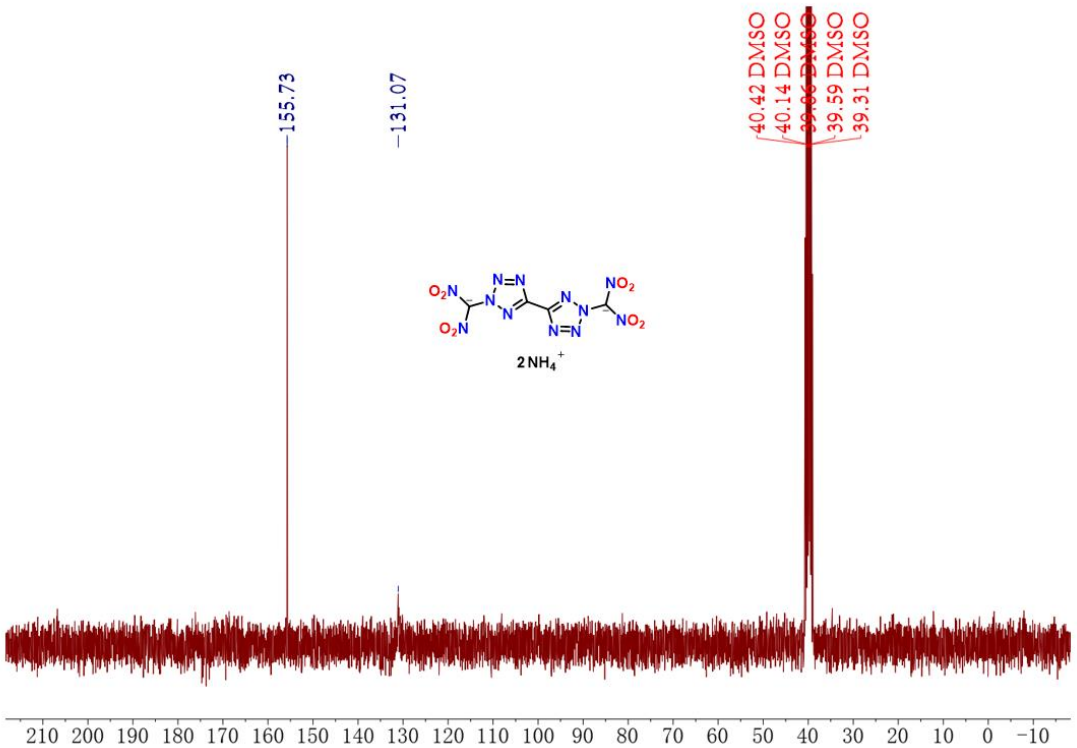

Figure S22 ^{13}C NMR spectra (75 MHz) of **6** in [D_6] DMSO at 25 °C.

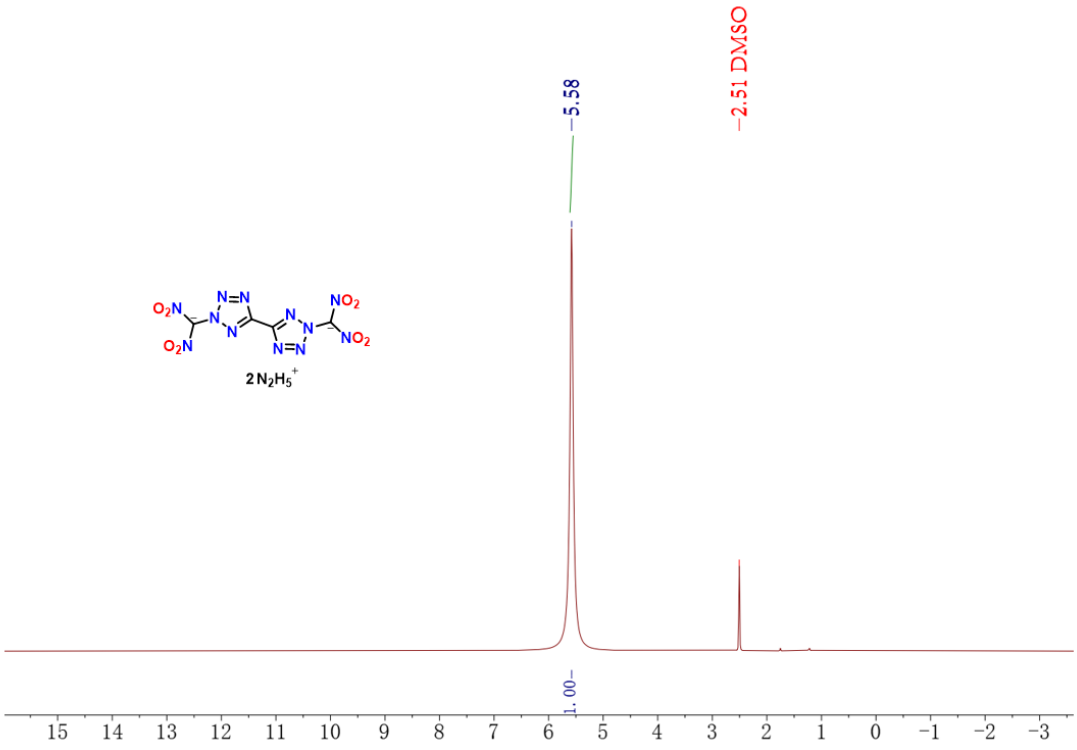

Figure S23 ^{1}H NMR spectra (300 MHz) of **7** in [D_6] DMSO at 25 °C.

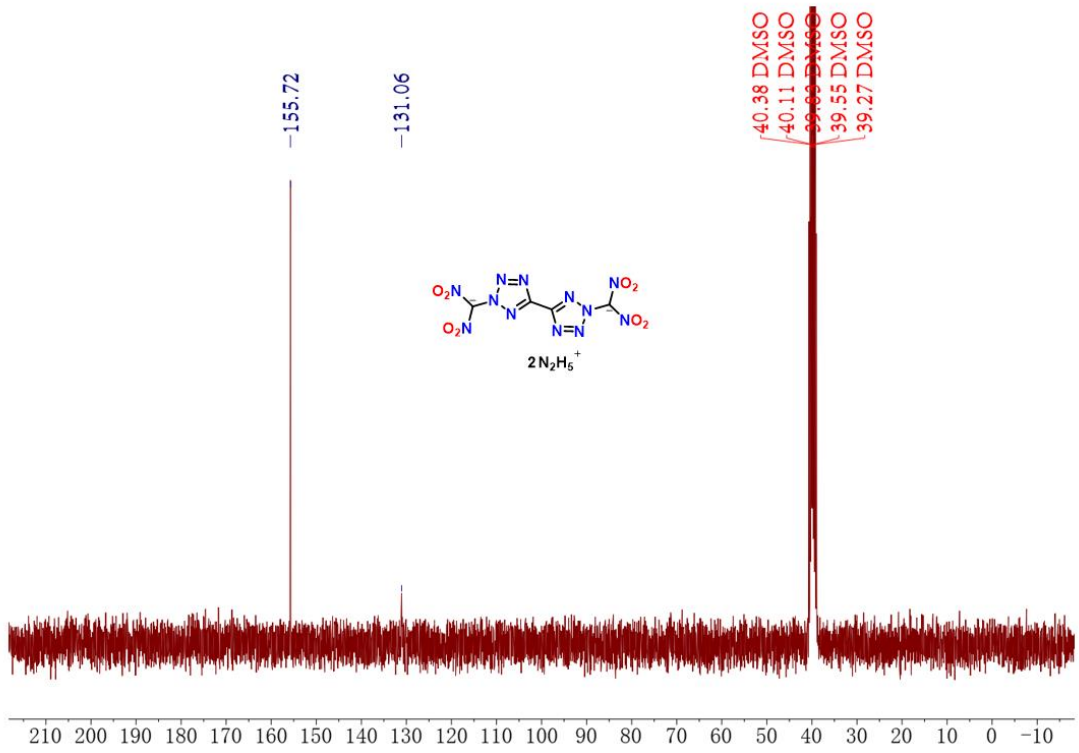

Figure S24 ^{13}C NMR spectra (75 MHz) of **7** in [D_6] DMSO at 25 °C.

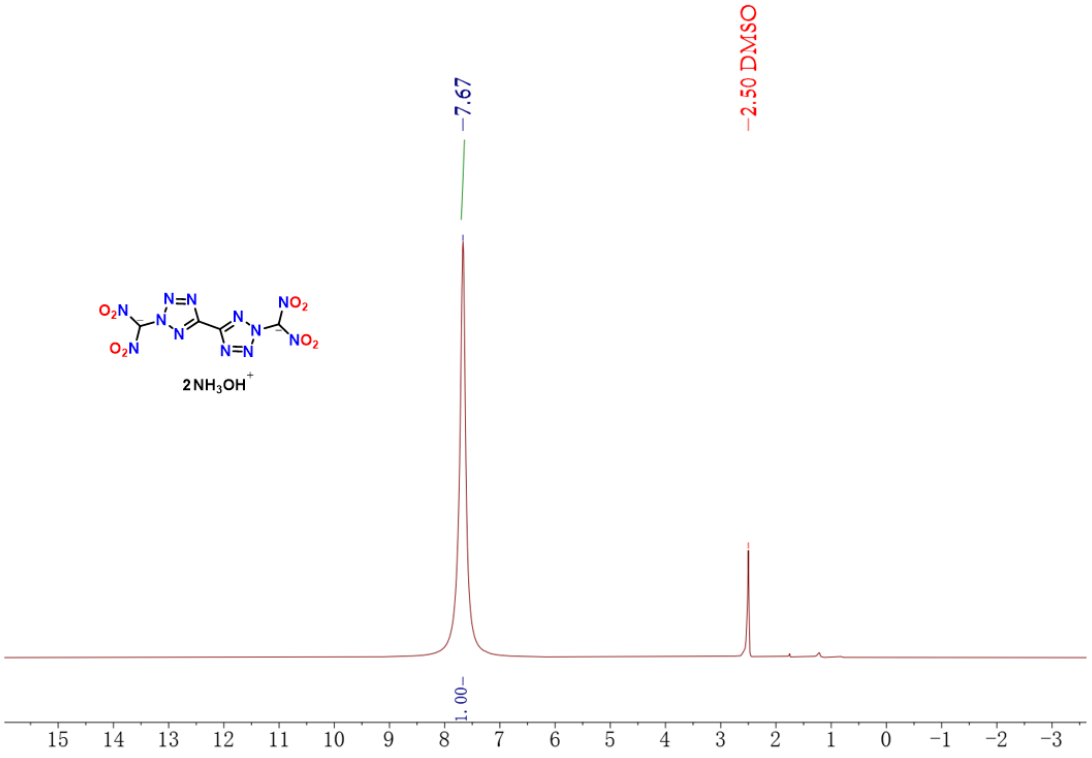

Figure S25 ^{1}H NMR spectra (300 MHz) of **8** in [D_6] DMSO at 25 °C.

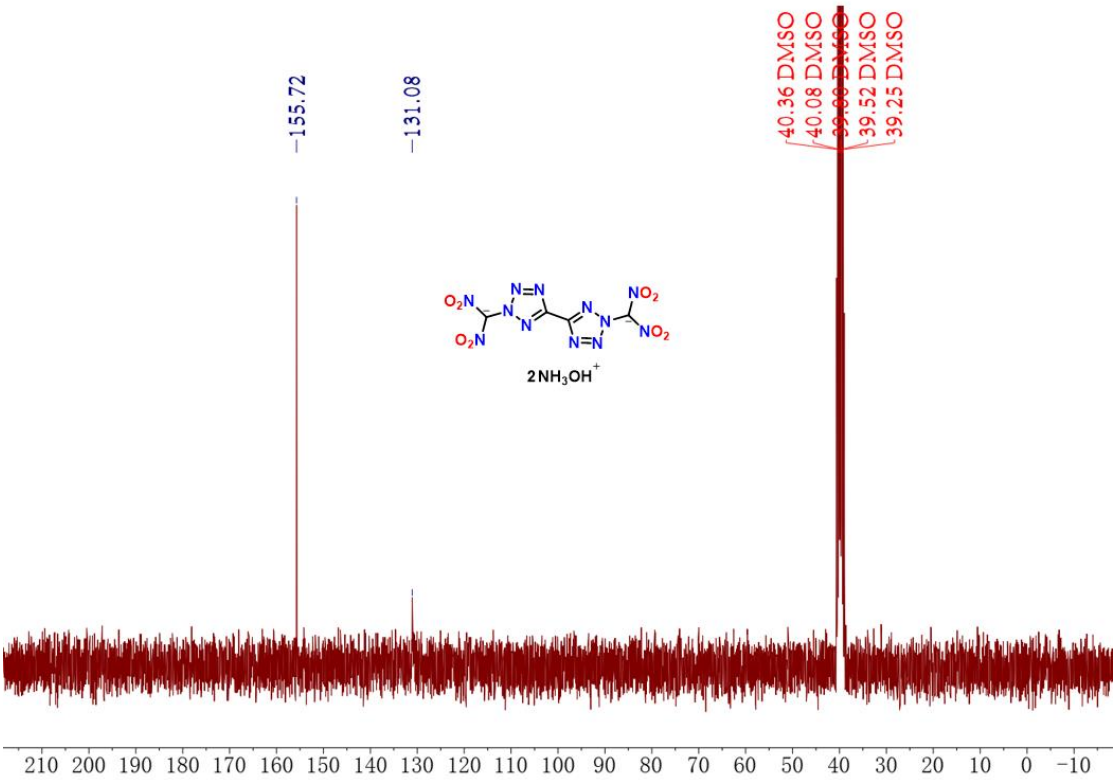

Figure S26 ^{13}C NMR spectra (75 MHz) of **8** in [D_6] DMSO at 25 °C.

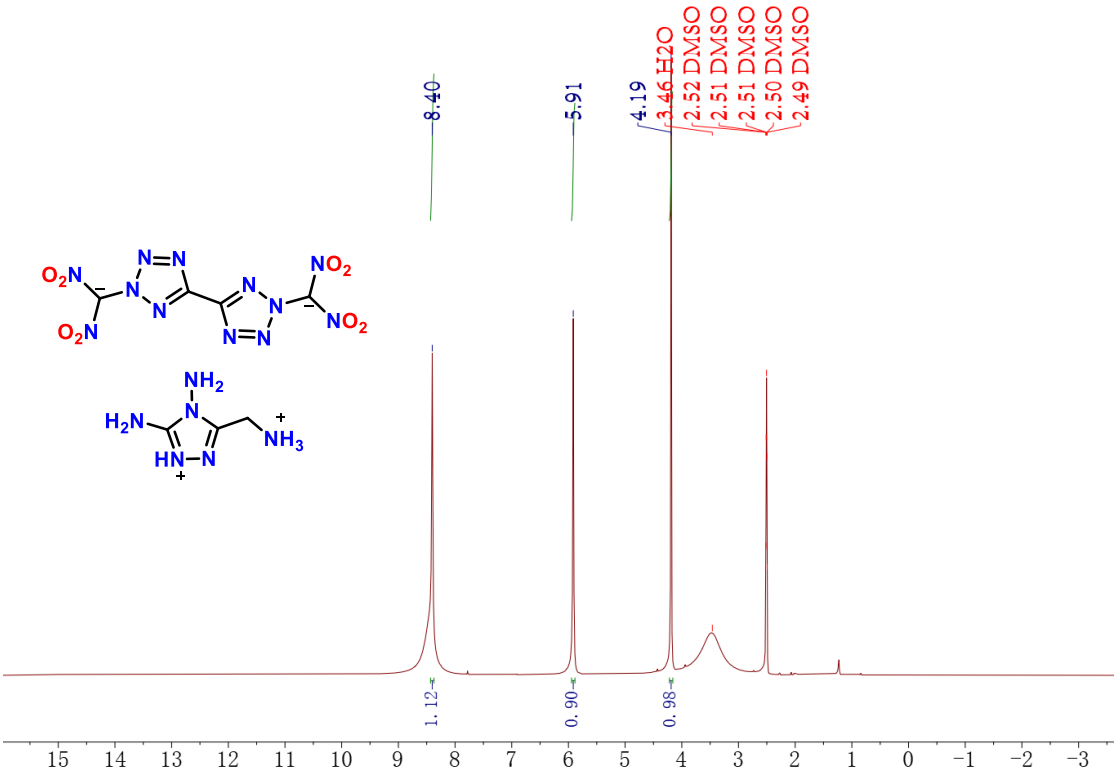

Figure S27 ^{1}H NMR spectra (300 MHz) of **9** in [D_6] DMSO at 25 °C.

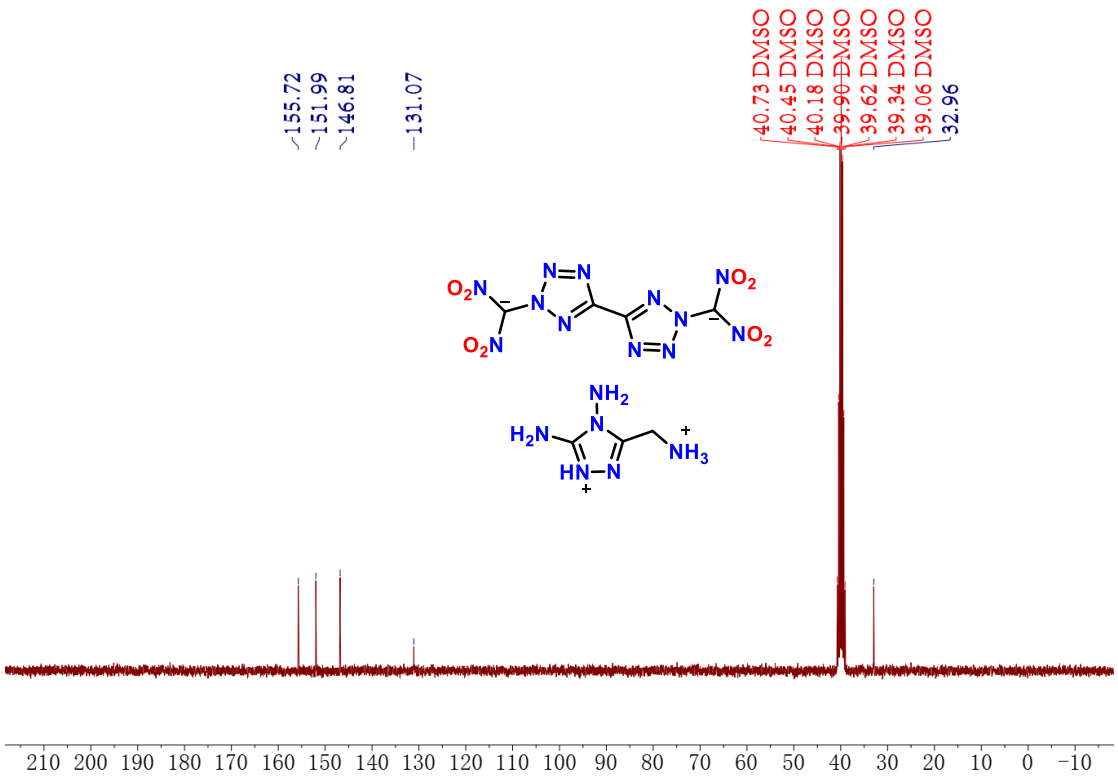

Figure S28 ^{13}C NMR spectra (75 MHz) of **9** in [D_6] DMSO at 25 °C.

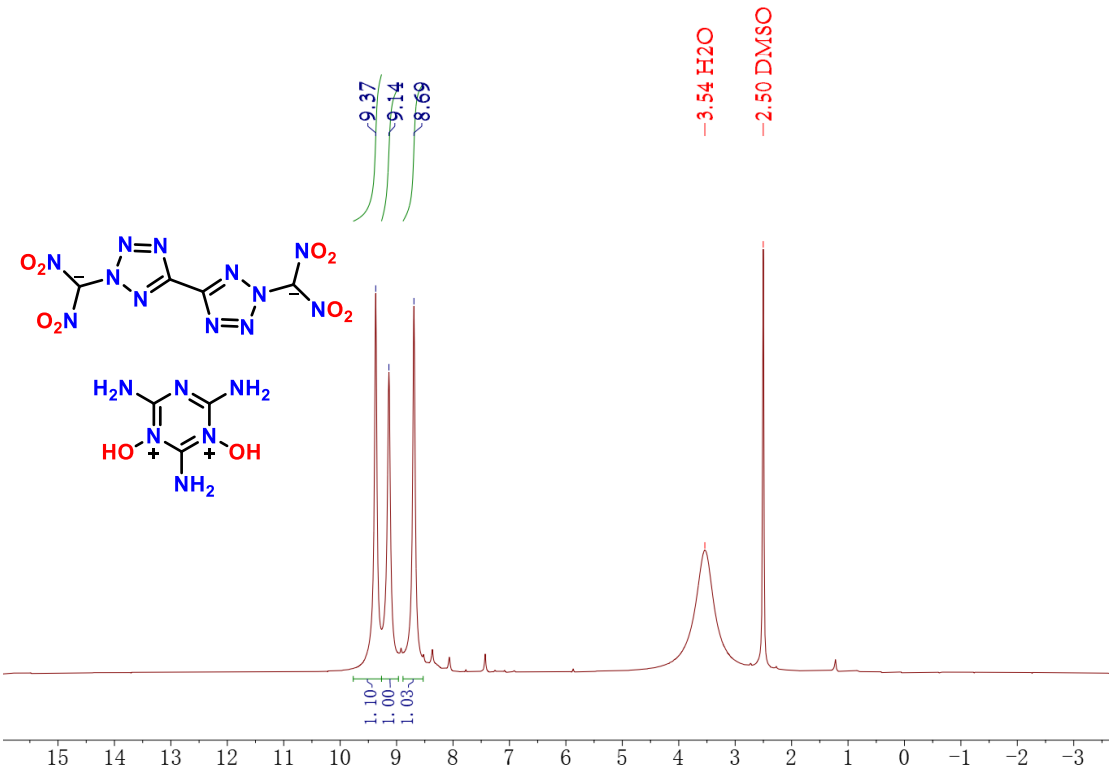

Figure S29 ^{1}H NMR spectra (300 MHz) of **10** in [D_6] DMSO at 25 °C.

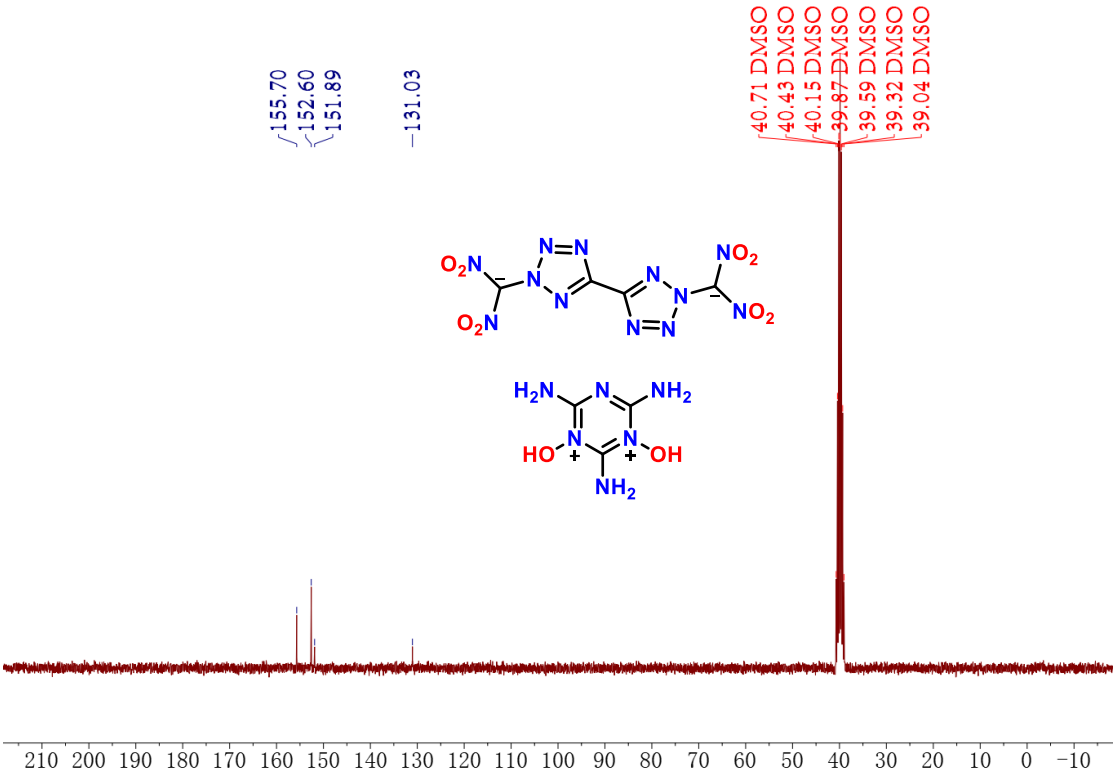

Figure S30 ^{13}C NMR spectra (75 MHz) of **10** in [D_6] DMSO at 25 °C.