Supporting Information

Modulating the 4-*R*-1,5-Diaminotetrazole Pentazolate Salts Properties by Substituent Effects

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

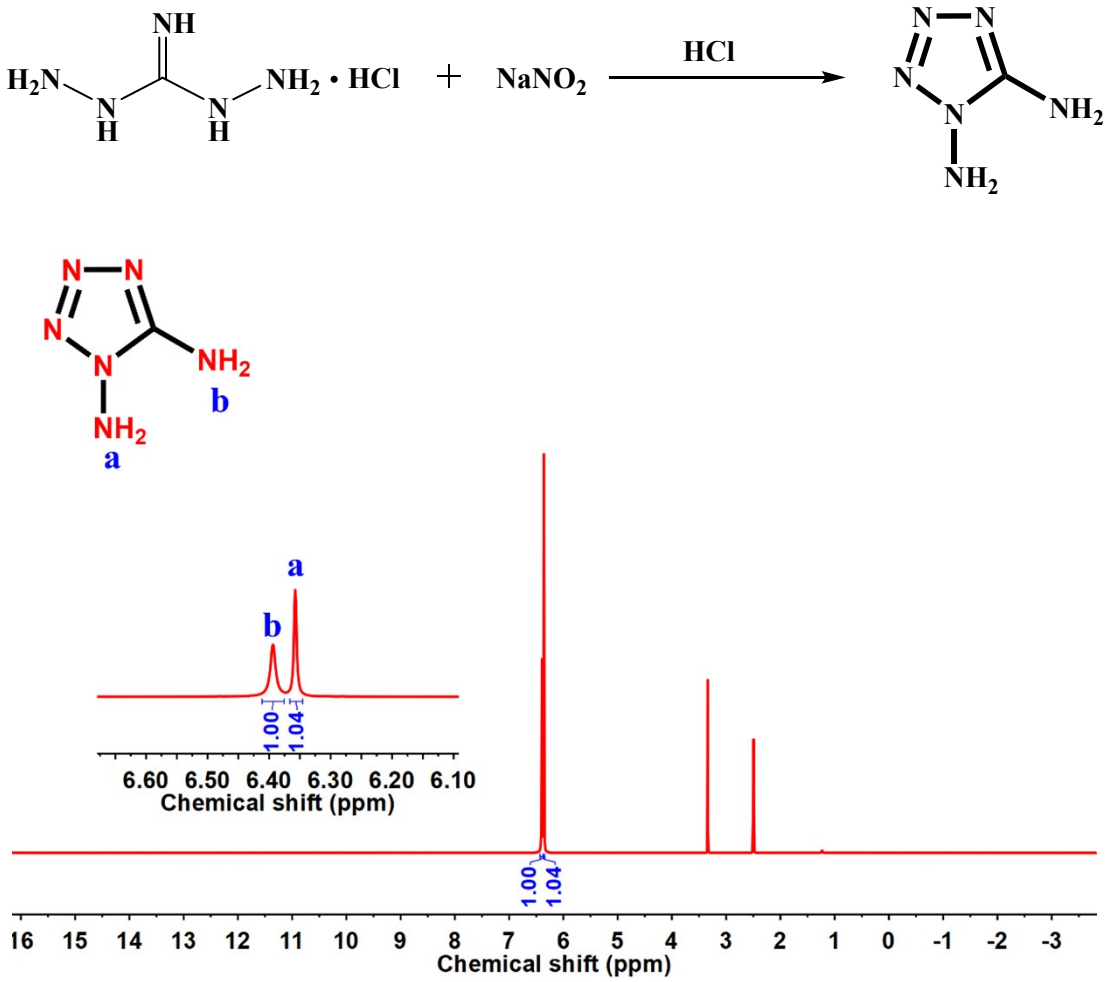


Figure S1. ^{1}H NMR of DAT using DMSO-d_6 as a solvent.

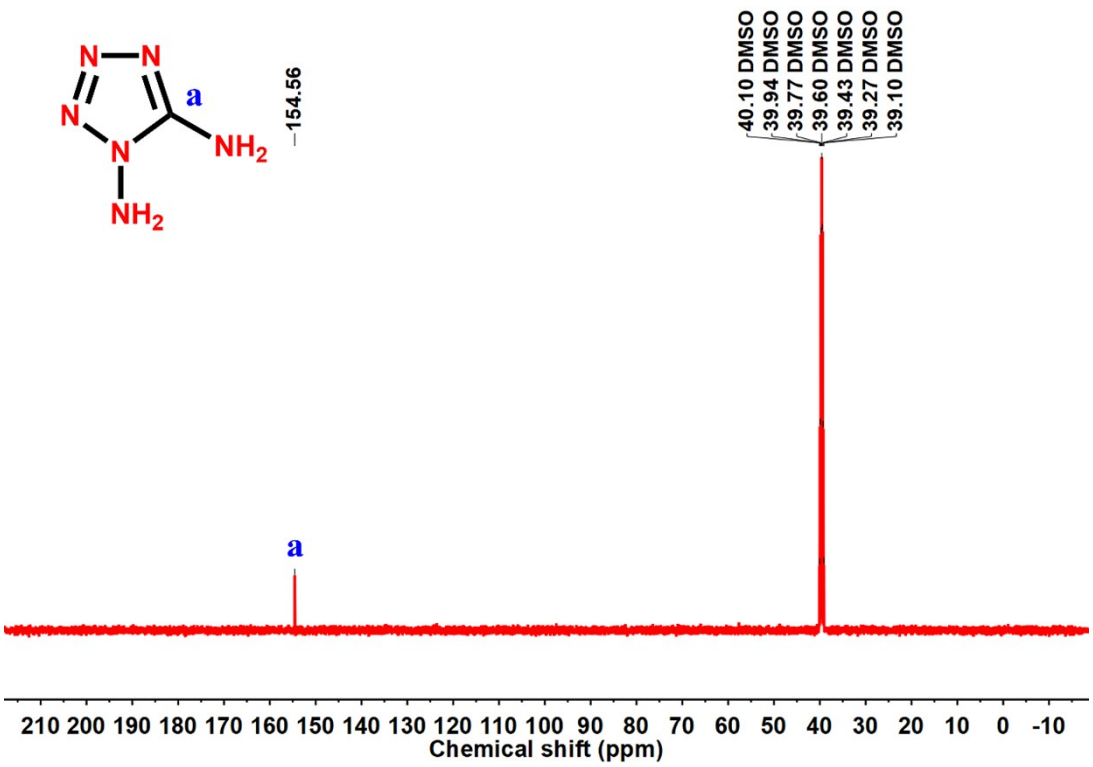


Figure S2. ^{13}C NMR of DAT using DMSO-d_6 as a solvent.

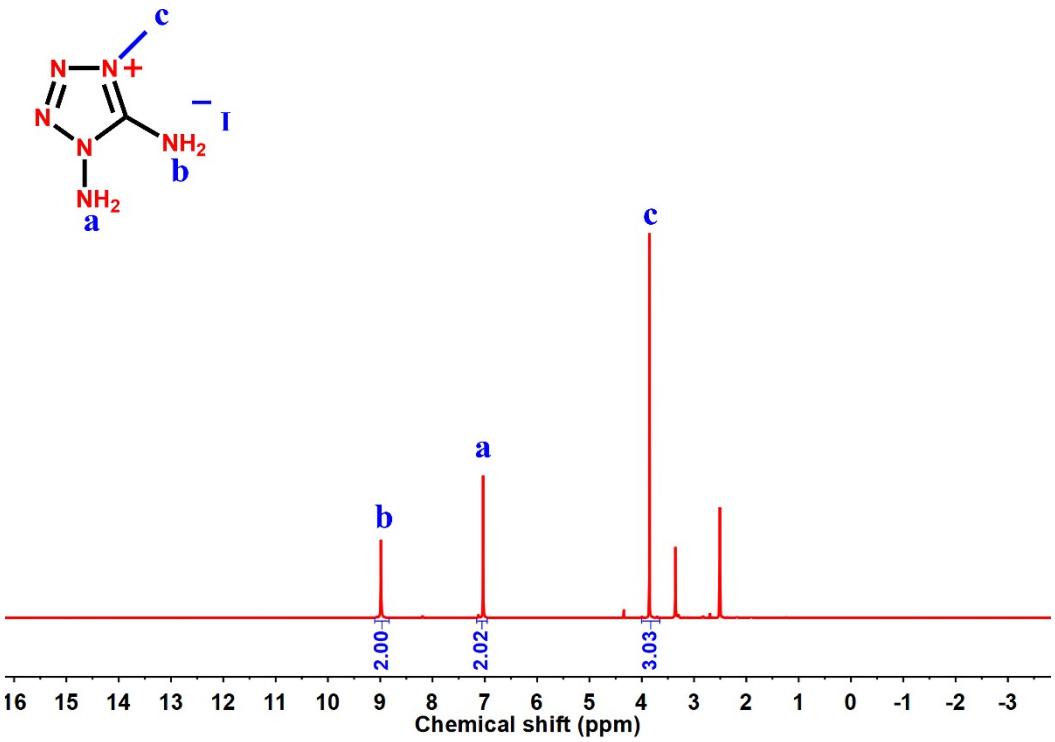


Figure S3. ^{1}H NMR of DMTI using DMSO-d_6 as a solvent.

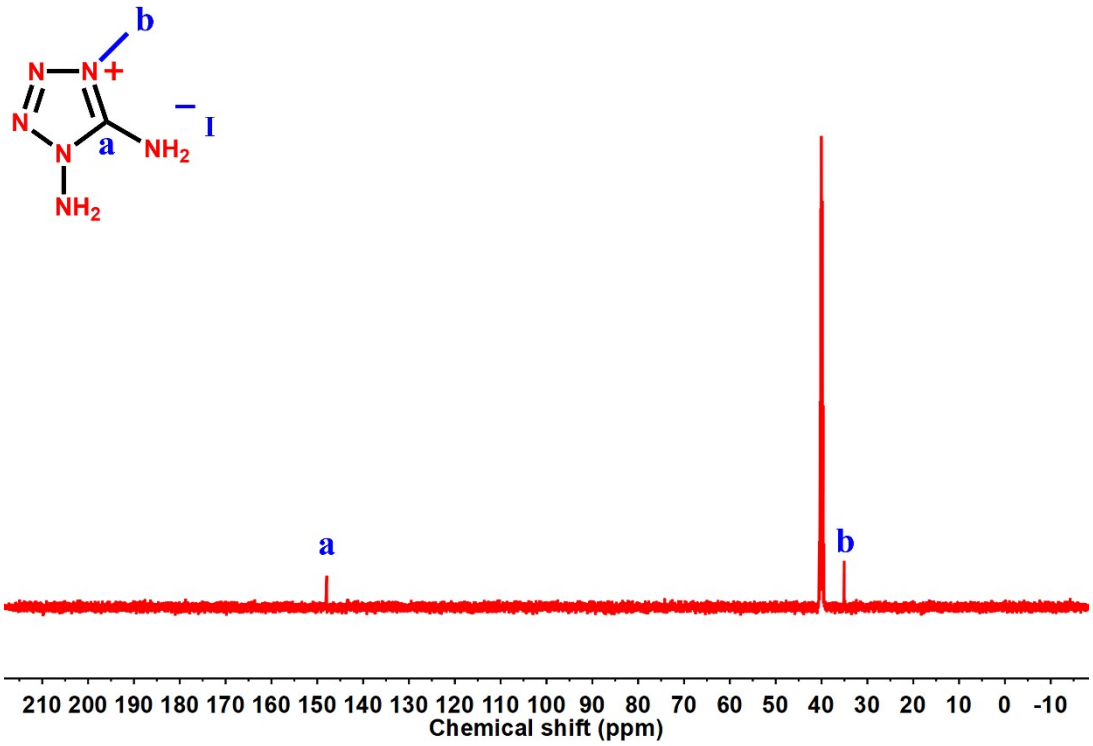


Figure S4. ^{13}C NMR of DMTI using DMSO-d_6 as a solvent.

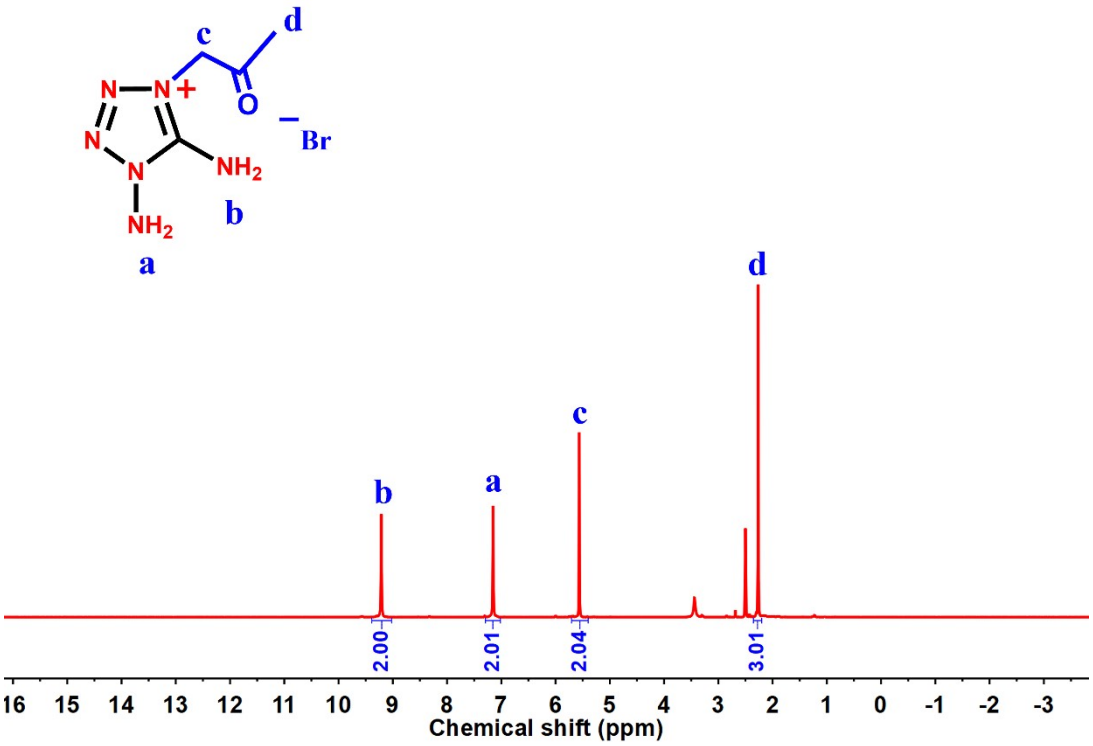


Figure S5. ^{1}H NMR of DOTB using DMSO-d_6 as a solvent.

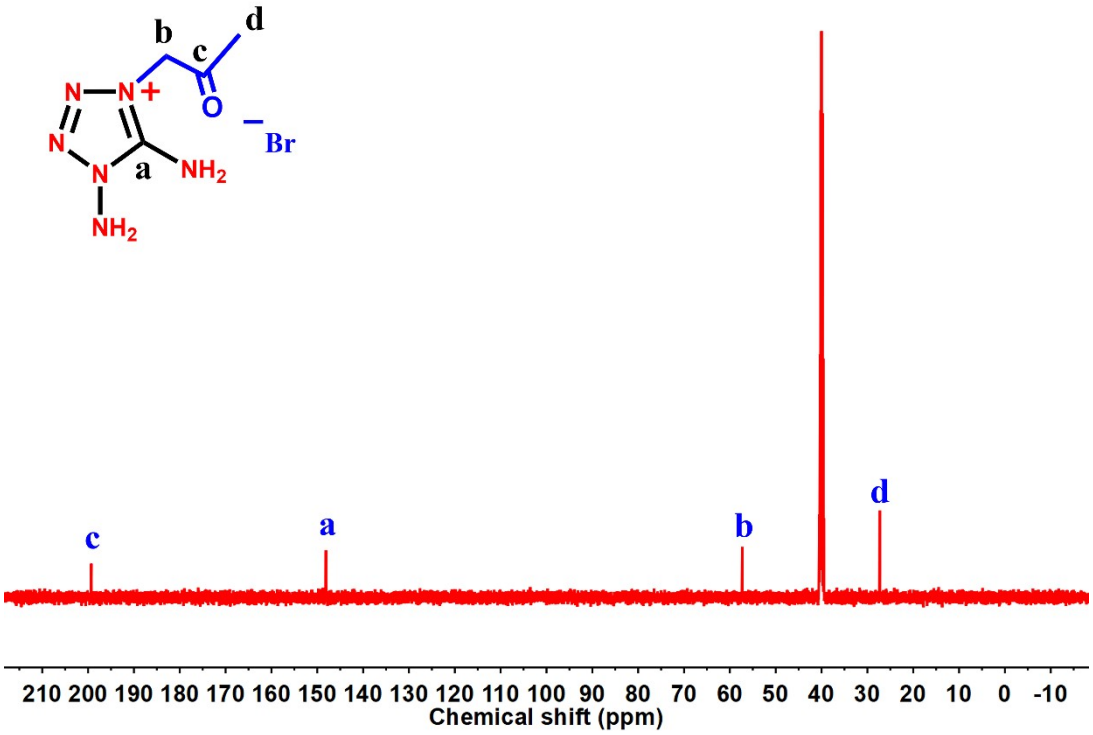


Figure S6. ^{13}C NMR of DOTB using DMSO-d_6 as a solvent.

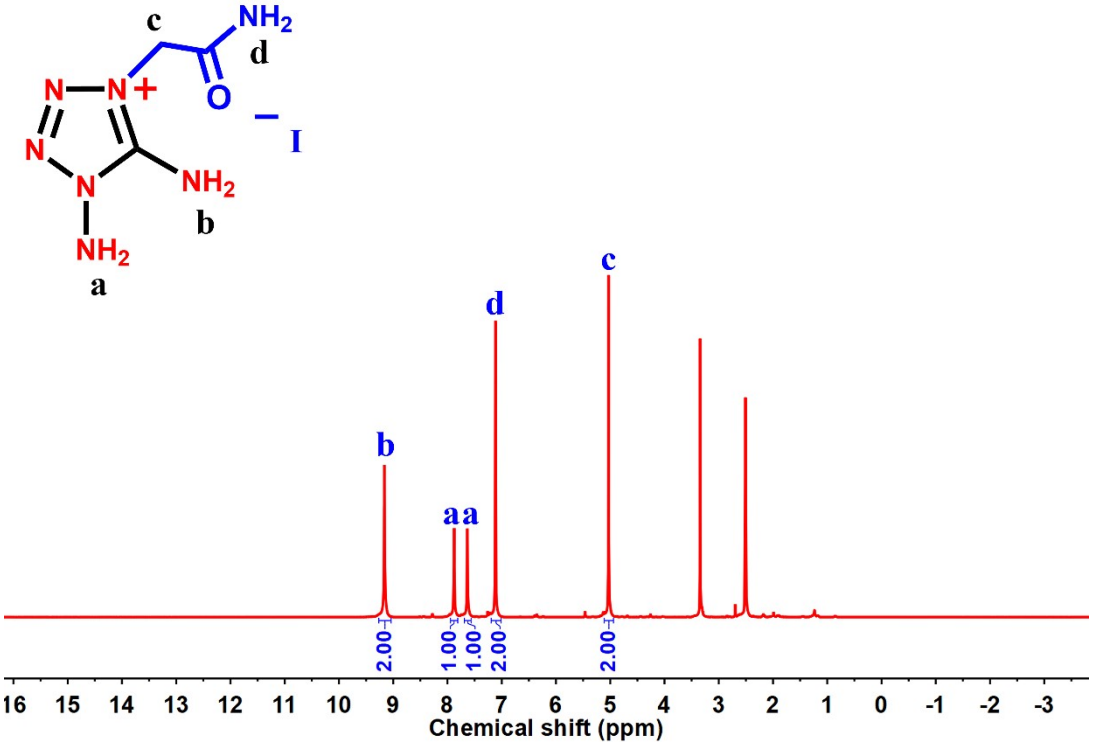


Figure S7. ^{1}H NMR of DAOTI using DMSO-d_6 as a solvent.

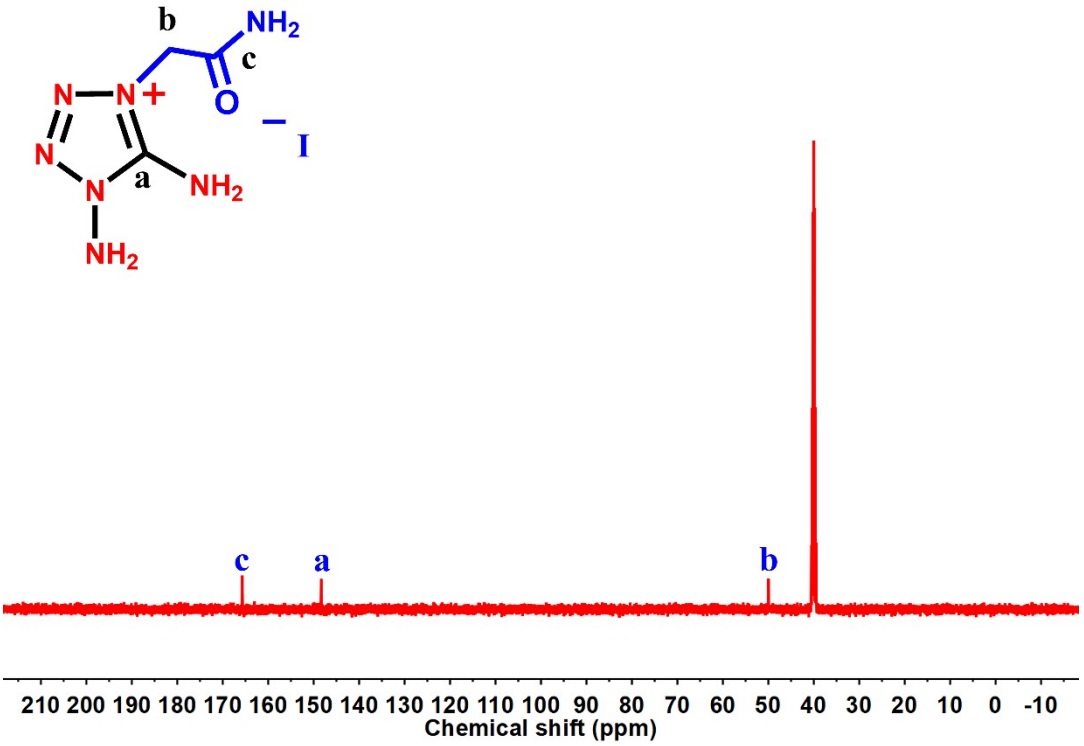


Figure S8. ^{13}C NMR of DAOTI using DMSO-d_6 as a solvent.

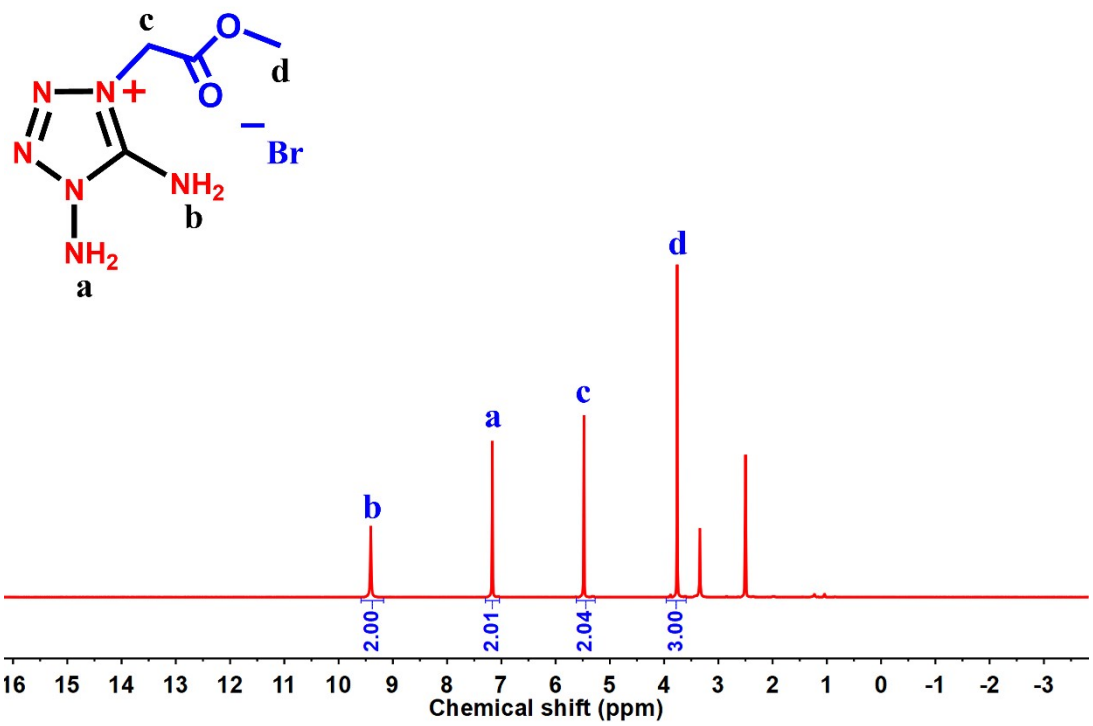


Figure S9. ^{1}H NMR of DMOTB using DMSO-d_6 as a solvent.

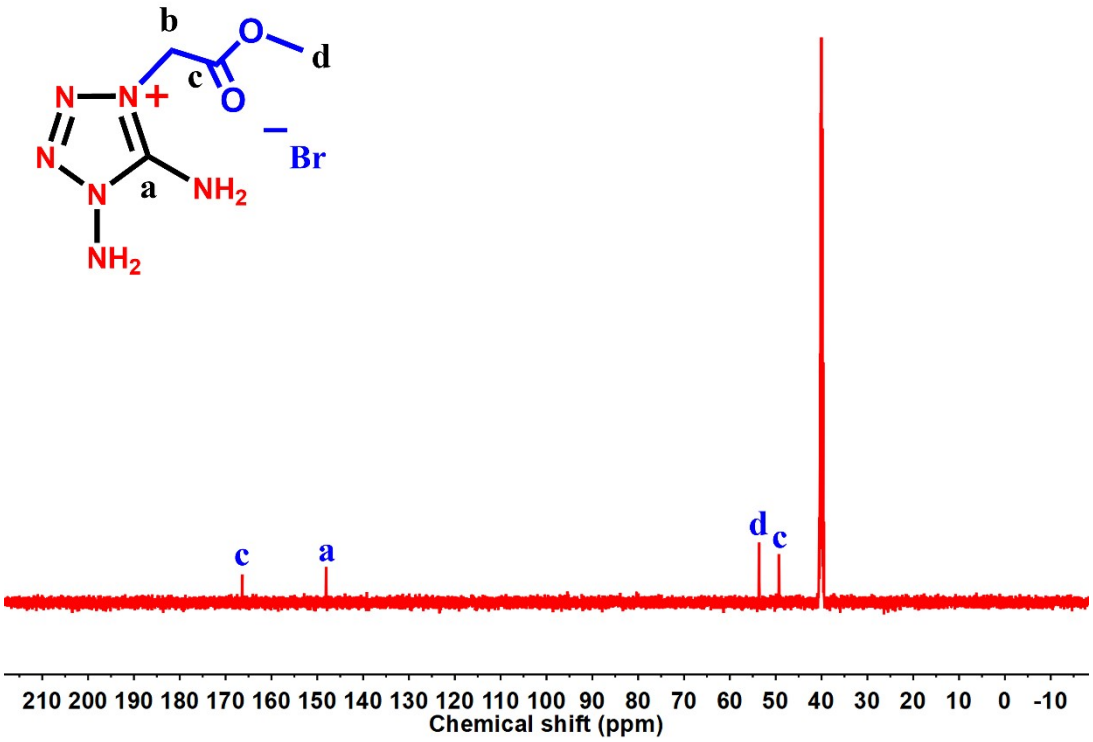


Figure S10. ^{13}C NMR of DMOTB using DMSO-d_6 as a solvent.

2. FT-IR spectra

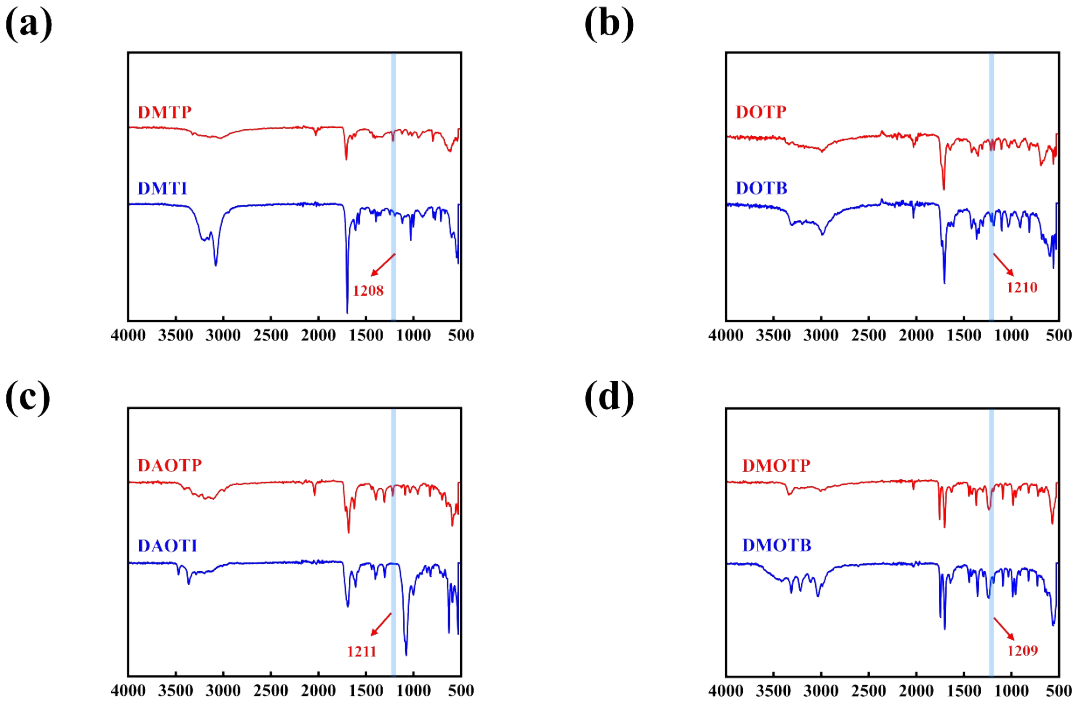


Figure S11. The IR spectra of (a) DMTI and DMTP, (b) DOTB and DOTP, (c) DAOTI and DAOTP, (d) DMOTB and DMOTP.

3. Optical photographs

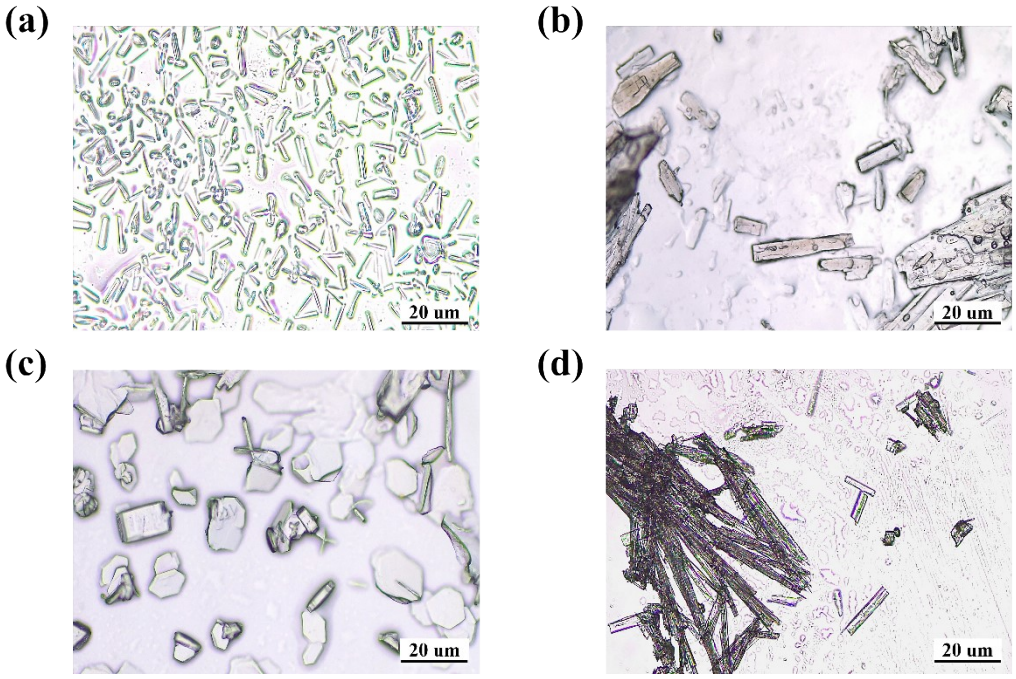


Figure S12. Optical photographs of the (a) DMTP, (b) DOTP, (c) DAOTP, and (d) DMOTP.

4. Crystal structure data

Table S1. Crystal data and structure refinement details for DMTP, DOTP.

Compound	DMTP	DOTP
CCDC No.	2405859	2474835
Empirical formula	$C_2H_7N_{11}$	$C_4H_9N_{11}O$
Formula weight	185.19	227.22
Temperature (K)	223.00	193.00
Wavelength (Å)	1.54178	1.54178
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$C2/m$
a (Å)	5.6423(2)	20.246(4)
b (Å)	10.7594(3)	5.1030(12)
c (Å)	13.1479(5)	11.589(2)
α (°)	90	90
β (°)	90	123.767(11)
γ (°)	90	90
Volume (Å^3)	798.18(5)	995.4(4)
Z	4	4
Density (g cm^{-3})	1.541	1.516
μ (mm^{-1})	1.046	1.034
F (000)	384	472
Crystal size (mm^3)	0.11×0.12×0.13	0.11×0.12×0.13
Theta range for data collection	10.624 to 136.762	9.18 to 137.53
Index ranges	$-6 \le h \le 6$ $-12 \le k \le 10$ $-15 \le l \le 15$	$-24 \le h \le 20$ $0 \le k \le 6$ $0 \le l \le 13$
Reflections collected	5900	1008
Independent reflections	1458 (R_{int}= 0.0351, R_{sigma}= 0.0280)	1008 (R_{sigma}= 0.0669)
Data/restraints/parameters	1458/0/120	1008/205/149
Goodness-of-fit on F^2	1.072	1.051
Final R indices (I>2sigma(I))	R_1 = 0.0301 wR_2 = 0.0768	R_1 = 0.0883 wR_2 = 0.2184
R indices (all data)	R1 = 0.0331 wR_2 = 0.0794	R1 = 0.1165 wR_2 = 0.2376
Largest diff. peak and hole (e. Å^{-3})	0.14 and -0.19	0.40 and -0.41

Table S2. Crystal data and structure refinement details for DAOTP, DMOTP.

Compound	DAOTP	DMOTP
CCDC No.	2468095	2503243
Empirical formula	$C_3H_8N_{12}O$	$C_4H_{10.2}N_{11}O_{2.3}$
Formula weight	228.21	249.23
Temperature (K)	193.00	193.00
Wavelength (Å)	0.71073	1.54178
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pnma*
a (Å)	9.9792(7)	8.1617(8)
b (Å)	10.7261(7)	6.6935(10)
c (Å)	10.1674(8)	20.236(3)
α (°)	90	90
β (°)	113.243(2)	90
γ (°)	90	90
Volume (Å^3)	999.97(12)	1105.5(3)
Z	4	4
Density (g cm^{-3})	1.516	1.497
μ (mm^{-1})	0.123	1.074
F (000)	472.0	518.0
Crystal size (mm^3)	0.12 × 0.12 × 0.11	0.15 × 0.14 × 0.12
Theta range for data collection	4.442 to 55.034	8.74 to 136.792
Index ranges	$-12 \le h \le 12$ $-13 \le k \le 12$ $-13 \le l \le 12$	$0 \le h \le 9$ $0 \le k \le 8$ $0 \le l \le 24$
Reflections collected	11626	1106
Independent reflections	2287 (R_{int}= 0.0524, R_{sigma}= 0.0376)	1106 (R_{sigma}= 0.0640)
Data/restraints/parameters	2287/0/154	1106/242/183
Goodness-of-fit on F^2	1.038	1.003
Final R indices (I>2sigma(I))	R_1 = 0.0453 wR_2 = 0.0971	R_1 = 0.0831 wR_2 = 0.2263
R indices (all data)	R_1 = 0.0819 wR_2 = 0.1152	R_1 = 0.1028 wR_2 = 0.2451
Largest diff. peak and hole (e. Å^{-3})	0.48 and -0.21	0.44 and -0.28

Table S3. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for DMTP. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U_{eq}
C1	2478(4)	4656.0(19)	4032.2(15)	27.2(5)
C2	-54(5)	3140(2)	3082(2)	40.4(6)
N1	2199(3)	5871.6(16)	4211.0(13)	28.4(4)
N2	144(4)	6283.7(17)	3788.5(15)	34.7(5)
N3	-833(4)	5363.6(18)	3344.7(15)	34.8(5)
N4	567(3)	4348.1(16)	3495.0(13)	28.5(4)
N5	4221(3)	3942.3(17)	4348.0(15)	33.6(4)
N6	3790(4)	6621.0(17)	4746.8(17)	38.8(5)
N7	4519(4)	1278.5(19)	3827.4(18)	42.7(5)
N8	6099(4)	754(2)	3223.7(18)	51.5(6)
N9	5749(4)	-458(2)	3266.9(17)	47.0(5)
N10	4000(4)	-672.1(19)	3876.2(16)	43.3(5)
N11	3224(4)	400.3(19)	4230.3(15)	39.9(5)

Table S4. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for DOTP. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U_{eq}
O1	5973(4)	220(120)	5529(6)	43(5)
N1	4888(4)	510(20)	8604(8)	40(3)
N2	5111(4)	1899(15)	7838(7)	36.8(16)
N3	4681(4)	3896(17)	6974(8)	43.7(18)
N4	5074(4)	4800(70)	6517(7)	42(3)
N5	5765(4)	3469(15)	7091(7)	34.7(15)
N6	6352(4)	-290(40)	8685(7)	30(3)
C1	5801(5)	1579(17)	7941(8)	31.3(17)
C2	6355(5)	4107(18)	6776(9)	35.6(18)
C3	6388(5)	1973(19)	5871(9)	38.0(19)
C4	6932(6)	2590(20)	5434(11)	50(3)
N7	6553(5)	5868(17)	10622(8)	49(2)
N8	6050(4)	5270(50)	10941(8)	50(3)
N9	6404(5)	3096(18)	11839(9)	48(2)
N10	7090(5)	2722(19)	12046(9)	52(2)
N11	7180(4)	4446(18)	11273(8)	46(2)

Table S5. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for DAOTP. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U_{eq}
C1	7542(2)	6716.6(16)	3911(2)	31.7(4)
C2	7280(2)	7309.0(18)	5145(2)	33.9(4)
C3	4845.6(19)	8342.1(16)	4064(2)	28.4(4)
N1	8932(2)	6553.9(19)	4154(2)	45.2(5)
N2	5740.6(17)	7442.1(14)	4809.1(17)	32.0(4)
N3	4984(2)	6580.4(15)	5242(2)	42.4(4)
N4	3662.8(19)	6930.8(16)	4803(2)	43.3(4)
N5	3548.2(16)	8026.1(15)	4063.9(18)	33.8(4)
N6	2294.5(17)	8727.3(16)	3430(2)	42.1(4)
N7	5151.1(17)	9333.2(15)	3486.2(18)	35.3(4)
O1	6518.4(15)	6429.9(13)	2801.7(16)	42.3(4)
N8	10999(2)	4667.2(18)	2243(2)	51.6(5)
N9	10311.5(19)	5722.8(18)	2142(2)	45.6(5)
N10	10805.5(19)	6521.8(17)	1466(2)	46.3(5)
N11	11812(2)	5956.8(19)	1157(2)	51.2(5)
N12	11933(2)	4810.4(17)	1628(2)	46.4(5)

Table S6. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for DMOTP. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U_{eq}
O1	9454(5)	2500	4072(2)	93.1(15)
O2	7632(5)	2500	3246(2)	82.3(13)
C2	6567(7)	2500	4302(3)	85.6(19)
C3	8076(7)	2500	3868(3)	71.8(15)
C4	8982(11)	2500	2765(5)	115(3)
N1	7052(7)	3026(8)	4987(4)	69(2)
N2	7069(10)	4850(13)	5304(5)	73(2)
N3	7575(8)	4618(10)	5879(4)	77.0(18)
N4	7976(6)	2630(40)	5952(3)	67(2)
N5	8464(7)	1728(10)	6528(3)	73.2(19)
N6	7855(10)	-296(15)	5297(6)	78(3)
C1	7638(9)	1661(12)	5394(4)	60.0(17)
N7	7976(14)	-2500	3434(7)	86(2)
N8	7209(11)	-2500	3991(5)	111(3)
N9	5616(10)	-2500	3866(5)	106(3)
N10	5436(12)	-2500	3221(5)	88(2)
N11	6912(16)	-2500	2966(5)	85(3)

N(7A)	7870(50)	-2600(110)	3470(30)	91(4)
N(8A)	7180(40)	-3540(70)	3980(20)	85(4)
N(9A)	5560(40)	-3570(70)	3880(20)	89(4)
N(10A)	5250(60)	-2600(120)	3320(20)	92(4)
N(11A)	6690(80)	-2130(110)	3040(20)	94(4)
O(3)	8520(20)	2500	2196(11)	139(10)

Table S7. Bond lengths for DMTP.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
C1–N1	1.338(3)	N9–N10	1.292(3)
C1–N4	1.331(3)	N2–N3	1.275(3)
C1–N5	1.315(3)	N3–N4	1.363(3)
C2–N4	1.451(3)	N1–N6	1.397(3)
N1–N2	1.360(3)	N7–N8	1.320(3)
N7–N11	1.306(3)	N10–N11	1.319(3)
N8–N9	1.320(3)		

Table S8. Bond angles for DMTP.

Parameter	bond angle (°)	Parameter	bond angle (°)
N4–C1–N1	103.95(19)	C1–N4–C2	128.1(2)
N5–C1–N1	127.1(2)	C1–N4–N3	110.31(18)
N5–C1–N4	128.9(2)	N3–N4–C2	121.60(18)
C1–N1–N2	110.33(18)	N11–N7–N8	108.19(19)
C1–N1–N6	125.23(19)	N9–N8–N7	107.20(2)
N2–N1–N6	124.44(17)	N10–N9–N8	108.50(2)
N3–N2–N1	107.62(17)	N9–N10–N11	108.45(19)
N2–N3–N4	107.79(17)	N7–N11–N10	107.70(19)

Table S9. Torsion angles for DMTP.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C1–N1–N2–N3	−0.8(2)	N5–C1–N1–N6	2.5(3)
N1–C1–N4–C2	179.3(2)	N5–C1–N4–C2	−2.5(4)
N1–C1–N4–N3	0.5(2)	N5–C1–N4–N3	178.7(2)
N1–N2–N3–N4	1.1(2)	N6–N1–N2–N3	178.69(19)
N2–N3–N4–C1	−1.0(2)	N7–N8–N9–N10	0.2(3)
N2–N3–N4–C2	−179.94(19)	N8–N7–N11–N10	0.0(3)
N4–C1–N1–N2	0.2(2)	N8–N9–N10–N11	−0.2(3)
N4–C1–N1–N6	−179.33(19)	N9–N10–N11–N7	0.2(3)
N5–C1–N1–N2	−178.1(2)	N11–N7–N8–N9	−0.1(3)

Table S10. Hydrogen bonds for DMTP.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
C2-H2B···N2	0.970	2.652	3.169(3)	113.72
C2-H2A···N8	0.970	2.850	3.367(3)	114.10
C2-H2B···N7	0.970	2.930	3.410(3)	111.5
C2-H2B···N9	0.970	2.780	3.365(3)	119.2
N5-H5A···N7	0.870	2.084	2.952(3)	174.7
N5-H5B···N3	0.870	3.020	3.445(3)	112.1
N5-H5B···N11	0.870	2.170	3.016(3)	165.3
N6-H6A···N6	0.920	3.040	3.461(2)	109.4
N6-H6A···N9	0.920	2.670	3.366(3)	132.8
N6-H6A···N10	0.920	2.850	3.409(3)	120.8
N6-H6B···N6	0.870	3.200	3.461(2)	100.1
N6-H6B···N10	0.870	2.260	3.132(3)	174.7
N6-H6A···N2	0.920	2.570	3.062(3)	113.8

Table S11. Bond lengths for DOTP.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1–C3	1.13(5)	N6–C1	1.352(10)
N1–N2	1.393(10)	C2–C3	1.539(13)
N2–N3	1.353(11)	C3–C4	1.478(12)
N2–C1	1.343(10)	N7–N8	1.298(11)
N3–N4	1.263(17)	N7–N11	1.282(10)
N4–N5	1.350(2)	N8–N9	1.410(2)
N5–C1	1.352(11)	N9–N10	1.285(11)
N5–C2	1.466(10)	N10–N11	1.338(12)

Table S12. Bond angles for DOTP.

Parameter	bond angle (°)	Parameter	bond angle (°)
N3–N2–N1	123.5(7)	N6–C1–N5	131.1(8)
C1–N2–N1	124.8(7)	N5–C2–C3	111.3(7)
C1–N2–N3	111.5(7)	O1–C3–C2	119.3(14)
N4–N3–N2	106.9(13)	O1–C3–C4	126.5(13)
N3–N4–N5	109(2)	C4–C3–C2	113.9(8)
N4–N5–C2	121.9(12)	N11–N7–N8	112.1(11)
C1–N5–N4	109.8(11)	N7–N8–N9	103.7(10)
C1–N5–C2	128.3(7)	N10–N9–N8	107.9(8)
N2–C1–N5	102.5(7)	N9–N10–N11	108.2(8)
N2–C1–N6	126.3(7)	N7–N11–N10	107.9(7)

Table S13. Torsion angles for DOTP.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
N1–N2–N3–N4	176.2(14)	N5–C2–C3–O1	1(2)
N1–N2–C1–N5	−175.4(8)	N5–C2–C3–C4	175.9(7)
N1–N2–C1–N6	7.0(15)	C1–N2–N3–N4	1.0(15)
N2–N3–N4–N5	−1(2)	C1–N5–C2–C3	71.0(11)
N3–N2–C1–N5	−0.3(9)	C2–N5–C1–N2	179.7(8)
N3–N2–C1–N6	−177.9(10)	C2–N5–C1–N6	−2.9(16)
N3–N4–N5–C1	1(2)	N7–N8–N9–N10	4.4(15)
N3–N4–N5–C2	−179.0(12)	N8–N7–N11–N10	2.2(14)
N4–N5–C1–N2	−0.5(14)	N8–N9–N10–N11	−3.3(13)
N4–N5–C1–N6	177.0(15)	N9–N10–N11–N7	0.9(11)
N4–N5–C2–C3	−108.8(15)	N11–N7–N8–N9	−4.0(16)

Table S14. Hydrogen bonds for DOTP.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
N1-H1A···N6	0.8800	2.5300	2.941(4)	109.10
N1-H1B···N8	0.8800	2.8400	3.42(2)	125.30
N6-H6B···N11	0.8800	2.9800	3.471(16)	117.50

Table S15. Bond lengths for DAOTP.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
C1–C2	1.519(3)	N3–N4	1.270(2)
C1–N1	1.321(3)	N4–N5	1.375(2)
C1–O1	1.225(2)	N5–N6	1.382(2)
C2–N2	1.443(2)	N8–N9	1.307(2)
C3–N2	1.330(2)	N8–N12	1.321(2)
C3–N5	1.338(2)	N9–N10	1.310(2)
C3–N7	1.308(2)	N10–N11	1.313(2)
N2–N3	1.371(2)	N11–N12	1.308(3)

Table S16. Bond angles DAOTP.

Parameter	bond angle (°)	Parameter	bond angle (°)
N1–C1–C2	114.28(18)	N4–N3–N2	108.32(16)
O1–C1–C2	120.86(17)	N3–N4–N5	107.21(15)
O1–C1–N1	124.9(2)	C3–N5–N4	110.15(15)
N2–C2–C1	111.10(16)	C3–N5–N6	124.06(16)
N2–C3–N5	104.38(15)	N4–N5–N6	125.78(15)
N7–C3–N2	128.51(16)	N9–N8–N12	107.98(17)
N7–C3–N5	127.09(17)	N8–N9–N10	108.28(16)
C3–N2–C2	128.27(16)	N9–N10–N11	107.77(17)

C3–N2–N3	109.93(15)	N12–N11–N10	108.36(17)
N3–N2–C2	121.79(16)	N11–N12–N8	107.60(17)

Table S17. Torsion angles for DAOTP.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C1–C2–N2–C3	−82.6(2)	N5–C3–N2–N3	0.7(2)
C1–C2–N2–N3	96.5(2)	N7–C3–N2–C2	−1.7(3)
C2–N2–N3–N4	179.94(17)	N7–C3–N2–N3	179.13(19)
C3–N2–N3–N4	−0.8(2)	N7–C3–N5–N4	−178.84(19)
N1–C1–C2–N2	−179.27(17)	N7–C3–N5–N6	0.0(3)
N2–C3–N5–N4	−0.4(2)	O1–C1–C2–N2	0.8(3)
N2–C3–N5–N6	178.43(17)	N8–N9–N10–N11	−0.4(2)
N2–N3–N4–N5	0.5(2)	N9–N8–N12–N11	0.1(2)
N3–N4–N5–C3	−0.1(2)	N9–N10–N11–N12	0.5(2)
N3–N4–N5–N6	−178.88(18)	N10–N11–N12–N8	−0.4(2)
N5–C3–N2–C2	179.89(17)	N12–N8–N9–N10	0.2(2)

Table S18. Hydrogen bonds for DAOTP.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
C2-H2A···N8	0.990	2.330	3.301(3)	167.90
C2-H2B···N10	0.990	2.830	3.468(3)	123.20
C2-H2B···N12	0.990	2.810	3.490(3)	126.70
N6-H6A···N10	0.880	2.260	3.074(3)	153.70
N6-H6B···N8	0.880	2.830	3.242(2)	110.30
N6-H6B···N9	0.880	2.850	3.239(2)	108.50
N6-H6B···N11	0.880	2.180	3.014(3)	159.00
N7-H7A···N11	0.880	2.590	3.388(2)	151.30
N7-H7A···N12	0.880	2.130	3.001(2)	170.00
N7-H7B···O1	0.880	1.950	2.798(2)	160.50
N1-H1A···N10	0.890	2.290	3.312(3)	157.00
N1-H1B···N9	0.870	2.170	3.016(3)	164.00

Table S19. Bond lengths for DMOTP.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1–C3	1.197(7)	N8–N8A	0.700(5)
O2–C3	1.311(7)	N8–N7A	1.190(6)
O2–C4	1.470(8)	N8–N9A	1.550(4)
C2–C3	1.512(8)	N9–N10	1.313(10)
C2–N1	1.484(10)	N9–N8A	1.470(4)
N1–N2	1.379(10)	N9–N9A	0.720(5)
N1–C1	1.320(9)	N9–N10A	1.150(5)
N2–N3	1.244(12)	N10–N11	1.312(8)

N3–N4	1.38(2)	N10–N9A	1.510(4)
N4–N5	1.372(14)	N10–N11A	1.110(6)
N4–C1	1.333(15)	N11–N7A	1.280(7)
N6–C1	1.337(12)	N11–N10A	1.540(6)
N7–N8	1.290(10)	N7A–N8A	1.337(14)
N7–N11	1.286(9)	N7A–N11A	1.337(14)
N7–N8A	1.46(5)	N8A–N9A	1.338(13)
N7–N11A	1.35(7)	N9A–N10A	1.333(14)
N8–N9	1.325(8)	N10A–N11A	1.340(14)

Table S20. Bond angles for DMOTP.

Parameter	bond angle (°)	Parameter	bond angle (°)
C3–O2–C4	115.4(6)	N10A–N9–N10	9(3)
N1–C2–C3	109.0(5)	N10A–N9–N8A	110(3)
O1–C3–O2	126.2(6)	N9–N10–N9A	28.4(19)
O1–C3–C2	124.4(6)	N11–N10–N9	106.8(7)
O2–C3–C2	109.4(5)	N11–N10–N9A	106.7(14)
N2–N1–C2	130.4(7)	N11A–N10–N9	103(3)
C1–N1–C2	121.0(5)	N11A–N10–N11	13(4)
C1–N1–N2	108.5(8)	N11A–N10–N9A	110(3)
N3–N2–N1	109.2(9)	N7–N11–N10	109.2(7)
N2–N3–N4	107.5(7)	N7–N11–N10A	104.8(19)
N5–N4–N3	126.0(13)	N10–N11–N10A	5.0(16)
C1–N4–N3	109.3(10)	N7A–N11–N7	5.8(18)
C1–N4–N5	124(2)	N7A–N11–N10	104(2)
N1–C1–N4	105.5(12)	N7A–N11–N10A	100(3)
N1–C1–N6	129.4(8)	N8–N7A–N11	115(4)
N4–C1–N6	125.1(13)	N8–N7A–N8A	31(2)
N8–N7–N8A	29(2)	N8–N7A–N11A	104(3)
N8–N7–N11A	98(2)	N11–N7A–N8A	112(3)
N11–N7–N8	108.5(7)	N11–N7A–N11A	15(3)
N11–N7–N8A	104.8(16)	N8A–N7A–N11A	108.0(6)
N11–N7–N11A	15(3)	N7–N8A–N9	93(3)
N11A–N7–N8A	101(3)	N8–N8A–N7	62(3)
N7–N8–N9	108.0(7)	N8–N8A–N9	64(3)
N7–N8–N9A	107.1(18)	N8–N8A–N7A	63(5)
N9–N8–N9A	27.7(18)	N8–N8A–N9A	93(4)
N7A–N8–N7	4(3)	N7A–N8A–N7	2(3)
N7A–N8–N9	106(3)	N7A–N8A–N9	91.4(19)
N7A–N8–N9A	104(3)	N7A–N8A–N9A	107.9(6)
N8A–N8–N7	89(4)	N9A–N8A–N7	110(3)
N8A–N8–N9	87(3)	N9A–N8A–N9	29(2)

N8A–N8–N7A	86(5)	N9–N9A–N8	59(3)
N8A–N8–N9A	60(3)	N9–N9A–N10	60(3)
N8–N9–N8A	28.3(18)	N9–N9A–N8A	85(4)
N10–N9–N8	107.5(7)	N9–N9A–N10A	60(4)
N10–N9–N8A	104.6(19)	N10–N9A–N8	88(2)
N9A–N9–N8	93(3)	N8A–N9A–N8	27(2)
N9A–N9–N10	91(4)	N8A–N9A–N10	101(2)
N9A–N9–N8A	65(3)	N10A–N9A–N8	94(2)
N9A–N9–N10A	88(5)	N10A–N9A–N10	7(2)
N10A–N9–N8	116(3)	N10A–N9A–N8A	108.0(6)
N9–N10A–N11	102(4)	N11A–N10A–N11	11(3)
N9–N10A–N9A	33(2)	N10–N11A–N7	119(3)
N9–N10A–N11A	99(3)	N10–N11A–N7A	113(2)
N9A–N10A–N11	104(2)	N10–N11A–N10A	6(2)
N9A–N10A–N11A	107.9(7)	N7A–N11A–N7	5.5(18)
N10A–N11A–N7	113.0(19)	N7A–N11A–N10A	107.7(6)

Table S21. Torsion angles for DMOTP.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C2–N1–N2–N3	−179.6(6)	N7–N11–N7A–N8	143(39)
C2–N1–C1–N4	178.6(6)	N7–N11–N7A–N8A	178(37)
C2–N1–C1–N6	−2.1(12)	N7–N11–N7A–N11A	102(34)
C3–C2–N1–N2	94.1(7)	N7–N11–N10A–N9	4(5)
C3–C2–N1–C1	−82.9(6)	N7–N11–N10A–N9A	−29(5)
C4–O2–C3–O1	0.000(1)	N7–N11–N10A–N11A	81(13)
C4–O2–C3–C2	180.000(1)	N7–N8A–N9A–N8	−62(3)
N1–C2–C3–O1	14.5(2)	N7–N8A–N9A–N9	−57(5)
N1–C2–C3–O2	−165.5(2)	N7–N8A–N9A–N10	1(4)
N1–N2–N3–N4	2.5(10)	N7–N8A–N9A–N10A	−1(4)
N2–N1–C1–N4	1.1(8)	N8–N7–N11–N10	0.000(3)
N2–N1–C1–N6	−179.6(9)	N8–N7–N11–N7A	−32(34)
N2–N3–N4–N5	−174.7(8)	N8–N7–N11–N10A	−3(3)
N2–N3–N4–C1	−1.9(9)	N8–N7–N8A–N9	59(3)
N3–N4–C1–N1	0.4(8)	N8–N7–N8A–N7A	108(100)
N3–N4–C1–N6	−179.0(8)	N8–N7–N8A–N9A	83(4)
N5–N4–C1–N1	173.4(6)	N8–N7–N11A–N10	−23(7)
N5–N4–C1–N6	−6.0(12)	N8–N7–N11A–N7A	−36(35)
C1–N1–N2–N3	−2.4(10)	N8–N7–N11A–N10A	−21(5)
N7–N8–N9–N10	0.000(2)	N8–N9–N10–N11	0.000(2)

N7–N8–N9–N8A	88(4)	N8–N9–N10–N9A	94(3)
N7–N8–N9–N9A	93(4)	N8–N9–N10–N11A	−13(4)
N7–N8–N9–N10A	4(4)	N8–N9–N8A–N7	−57(3)
N7–N8–N7A–N11	−118(51)	N8–N9–N8A–N7A	−59(5)
N7–N8–N7A–N8A	150(47)	N8–N9–N8A–N9A	175(5)
N7–N8–N7A–N11A	−108(50)	N8–N9–N9A–N10	−107.6(8)
N7–N8–N8A–N9	−108.1(8)	N8–N9–N9A–N8A	−2(2)
N7–N8–N8A–N7A	−2(3)	N8–N9–N9A–N10A	−116(3)
N7–N8–N8A–N9A	−110(2)	N8–N9–N10A–N11	−5(6)
N7–N8–N9A–N9	−96(3)	N8–N9–N10A–N9A	93(4)
N7–N8–N9A–N10	−41(2)	N8–N9–N10A–N11A	−16(6)
N7–N8–N9A–N8A	79(4)	N8–N7A–N8A–N7	−71(99)
N7–N8–N9A–N10A	−45(3)	N8–N7A–N8A–N9	60(3)
N8–N7A–N8A–N9A	85(4)	N8–N9A–N10A–N9	−50(3)
N8–N7A–N11A–N7	140(39)	N8–N9A–N10A–N11	40(4)
N8–N7A–N11A–N10	−28(6)	N8–N9A–N10A–N11A	29(4)
N8–N7A–N11A–N10A	−26(5)	N9–N8–N7A–N11	6(6)
N8–N8A–N9A–N9	4(4)	N9–N8–N7A–N8A	−86(3)
N8–N8A–N9A–N10	63(5)	N9–N8–N7A–N11A	16(4)
N8–N8A–N9A–N10A	60(5)		

Table S22. Hydrogen bonds for DMOTP.

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
C6-H2A···N8	0.9900	2.9500	3.445(3)	112.00
C6-H2A···N8A	0.9900	2.3200	2.770(5)	106.70
C6-H2A···N9A	0.9900	2.0400	2.890(5)	141.50

C2-H2B···N8	0.9900	2.7000	3.445(3)	132.40
C2-H2B···N8A	0.9900	2.0800	2.770(5)	125.30
C2-H2B···N9A	0.9900	1.9700	2.890(5)	152.70
N6-H6B···O1	0.8900	3.0700	3.369(11)	102.40
N6-H6B···N8A	0.8900	2.7100	3.480(5)	145.90
O3-H3A···O2	0.8700	2.8300	3.473(19)	132.20

5. Calculated Bader charge

Table S23. The Bader charge data of DMTP.

Atom	Charge (e)	Atom	Charge (e)
C1	1.480791	H5A	0.542075
C2	0.210513	H5B	0.432267
H2A	0.193799	N6	-0.60201
H2B	0.080914	H6A	0.396377
H2C	0.098166	H6B	0.395736
N1	-0.44192	N7	-0.28302
N2	-0.02731	N8	-0.13522
N3	-0.00688	N9	-0.12544
N4	-0.74555	N10	-0.12533
N15	-1.13418	N11	-0.2038

Table S24. The Bader charge data of DOTP.

Atom	Charge (e)	Atom	Charge (e)
O1	-1.10401	H4C	0.071199
N1	-0.60655	N6	-1.08647
H1A	0.380602	H6A	0.466966
H1B	0.44782	H6B	0.459865
N2	-0.40696	N8	-0.17274
N3	0.024728	N10	-0.17526
N4	-0.01746	N11	-0.13925
N5	-0.76142	N9	-0.21849
C1	1.455912	N7	-0.18567
C3	0.994159	C2	0.228055
C4	-0.09335	H2A	0.110438
H4A	0.070969	H2B	0.174345
H4B	0.082568		

Table S25. The Bader charge data of DAOTP.

Atom	Charge (e)	Atom	Charge (e)
C1	1.444814	H6A	0.389218
C2	0.274703	N7	-1.07573

H2A	0.101771	H7A	0.484064
H2B	0.09627	H7B	0.442956
C3	1.496677	O1	-1.14266
N1	-1.0959	H1B	0.394386
N2	-0.76256	H1A	0.463547
N3	-0.01565	N8	-0.23099
N4	-0.00063	N9	-0.19207
N5	-0.43378	N10	-0.11779
N6	-0.64167	N11	-0.11849
H6B	0.469392	N12	-0.2299

Table S26. The Bader charge data of DMOTP.

Atom	Charge (e)	Atom	Charge (e)
O1	-1.13803	N2	-0.43932
O2	-1.05286	N7	-0.13603
C3	1.591063	N8	-0.28679
N5	-0.75053	N9	-0.1725
N4	-0.00604	N10	-0.11534
N3	-0.0269	N11	-0.12644
N1	-0.60186	C2	0.268452
H1A	0.393222	H2A	0.117604
H1B	0.394439	H2B	0.17122
N6	-1.12931	C4	0.348966
H6B	0.424486	H4B	0.078201
H6A	0.537413	H4A	0.062016
C1	1.492225	H4C	0.10263

6. The calculated method of ESP and HOMO/LUMO

The theoretical calculations including geometry optimization, electrostatic potential (ESP) and electronic structure analysis were carried out using the Dmol3 module in the Materials Studio 2020 software package. The GGA-BLYP functional was employed with the DNP 3.5 basis set. The convergence criteria of energy, force and displacement were set to 1.0×10^{-5} Ha, 0.002 Ha·Å^{-1} and 0.005 Å, respectively. The electrostatic potential was mapped on the electron density isosurface to visually reveal the charge distribution and reactive sites. The electronic structure parameters including the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the HOMO–LUMO energy gap were obtained to evaluate the molecular stability and electron transfer properties.

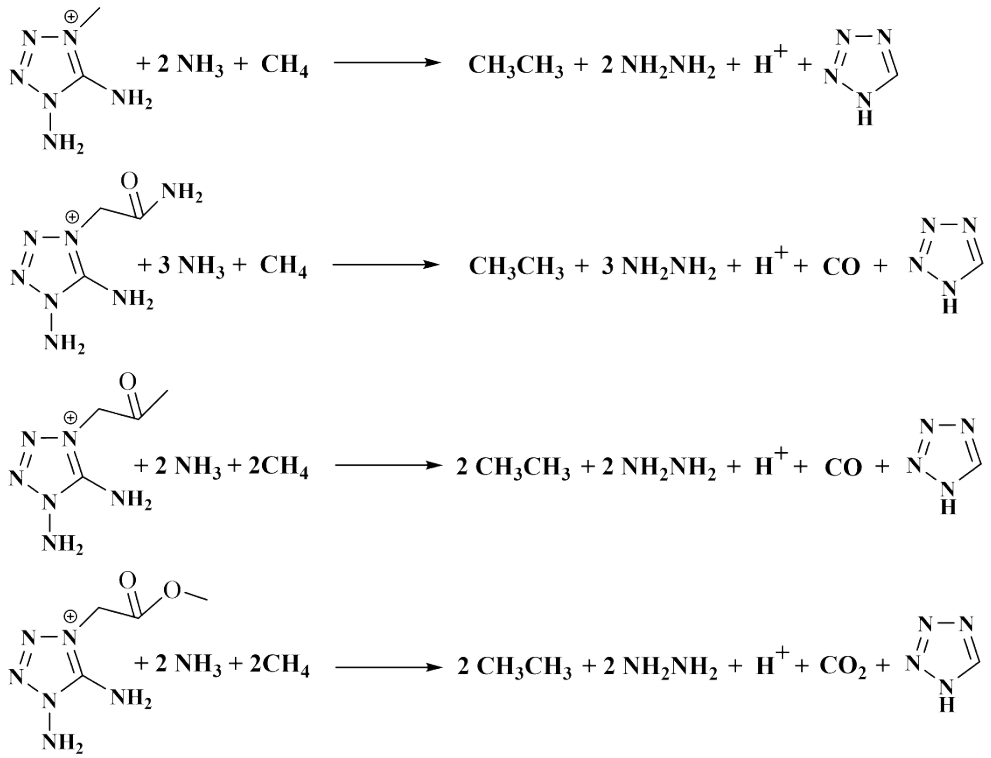
7. Heats of formation

The enthalpy of formation is an important parameter in chemical thermodynamics calculation, which is a crucial basis for evaluating the detonation velocity and detonation pressure of energetic compounds. The formation of DMTP, DOTP, DAOTP, and DMOTP was theoretically calculated with the Gaussian 09 program.[1] At the B3LYP/6-311+G** level,[2-5] geometric optimization and frequency analysis were carried out for cations in all compounds, and the stable structures at the local energy minimum on the potential energy surface were obtained without imaginary frequencies. The enthalpy of formation of the cation section was calculated based on the designed isodesmic reaction. The enthalpy of formation of *cyclo*-N_5^- has been reported in relevant literature,[6] and this work will cite directly.

At 298 K, the standard heat of formation of cations can be calculated by the following equation:

ΔH (cation, 298 K) = ΔE (cation, 298 K) + Δ (PV) = ΔE_0 + ΔZPE + ΔH_T + ΔnRT

where ΔE_0 is the difference in total energies between the products and reactants at 0 K, ΔZPE is the difference in zero energy between the product and reactant at 0 K, and ΔHT is the temperature correction factor. As shown in **Scheme S1.**, the following are the isoseismic reactions for all the calculated cations. The heat of formation of small molecules can be found in literature or calculated with G4.



Scheme S1. Isodesmic reactions for all the calculated cations.

At 298 K, the standard enthalpy of formation of ionic compound can be calculated by the following equation:

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

where ΔH_L is the lattice energy of the salts, which could be obtained with the following formula proposed by Jenkins *et al*. [7]

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

where n_M and n_X depend on the nature of the ions, M^{p+} and X^{q-} are equal to three for monatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The following is the equation for lattice potential energy U_{POT}:

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

where ρ_m (g cm^{-3}) is the density of the salt, M_m is the chemical formula mass of the ionic material. The value of coefficient γ and δ are acquired from relevant literature.[8]

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