Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information (SI)

A Novel N-N Bond Cleavage in 1,5-Diaminotetrazole: Synthesis and Characterization of 5-Picrylamino-1,2,3,4-tetrazole (PAT)

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Experimental Section

Caution: Proper safety precautions should be taken when handling these compounds. Laboratories and personnel should be properly grounded, and safety equipment such as Kevlar gloves, leather coats, face shields, and ear plugs are recommended.

General methods: All chemical reagents and solvents (analytical grade) were used as supplied unless otherwise stated. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Avance III 500MHz Digital NMR Spectrometer operating at 500, 126 MHz. ^{15}N NMR spectrum was recorded on a Bruker Avance 300 instrument (^{15}N : 30 MHz). FT-IR spectra were recorded on a BOMEM MB Series 154S FTIR spectrometer. Mass spectra were recorded on Finnigan TSQ Quantum ultra instrument using electro spray ionization (ESI) method. Elemental analysis was performed by on a Vario EL III recorder. The decomposition point was recorded on a DSC823^e at a heating rate of 5 ^{o}C·min^{-1} in closed Al containers with a nitrogen flow of 30 mL·min^{-1}. Sensitivity data were determined using a HGZ-1 drophammer and a BAM friction tester. The electrostatic sensitivity test was carried out using an Electric Spark Tester ESD JGY-50 III.

Preparation of PAT (3)

A solution of picryl chloride (0.988 g, 4 mmol), DAT (0.200 g, 2 mmol), solid K_2CO_3 (0.276 g, 2 mmol) in 10 mL ethanol was stirred at 80 ^{o}C for 12 hours. The reaction was filtrated to remove solid and the filtrate was concentrated to be chromatographed on silica with PE: EA to afford 0.26 g of **3**, dark red solid (yield 44%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ 14.44 ppm (br, 2H), 8.48 ppm (s, 2H), 6.43 ppm (s, 3H) ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ 158.6, 156.1, 144.6, 140.5, 126.8, 123.3 ppm. IR: 3607 (w), 3536(w), 3090 (w), 1631 (m), 1558 (m), 1490 (w), 1426 (w), 1371 (vw), 1332 (m), 1069 (vs), 932 (vw), 908 (w), 788 (m), 708 (w) cm^{-1}. ESI-MS: *m/z* 294.92 [M-H]$^-$. Elemental analysis for $2C_7H_4N_8O_6 \cdot 5H_2O$ (682.44): calcd C 21.77, H 3.65, N 29.01 %; found: C 21.19, H 3.42, N 29.74 %. Electrostatic discharge sensitivity (ESD): 1.0 J.

0.065 g of 2,4,6-trinitroaniline was obtained as a,yellow solid (yield 14.3%). ESI-MS: *m/z* 227.01 [M-H]$^-$. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ 9.17 (s, 2H), 9.05 (d, 2H) ppm. ^{13}C NMR (500 MHz, [D$_6$]DMSO): δ 143.0, 133.7, 132.1, 127.5 ppm.

Reaction of 4-nitrochlorobenzene and DAT

A solution of 4-nitro-chlorobenzene (0.628 g, 4 mmol), DAT (0.2 g, 2 mmol), solid K_2CO_3 (0.276

g, 2 mmol) in 10 mL DMSO was stirred at 100 °C for 12 hours. The mother liquor was evaporated in vacuum to dryness and the remaining black oil was dry-column flash chromatographed.

4-Nitroaniline: 0.13 g of yellowish powder was obtained (yield 47 %). ESI-MS: *m/z* 161.00 $[M+23]^+$, fragment: 122.12, 92.09; ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ 7.95 (m, 2H), 6.72 (s, 2H), 6.59 (m, 2H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ 155.2, 135.1, 125.9, 111.8 ppm.

Bis(4-nitrophenyl)amine: 0.084 g (yield 16 %) of yellow powder was obtained. ESI-MS: *m/z* 257.89 $[M-1]^-$, fragment: 212.00, 179.94; ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ 9.99 (s, 1H), 8.20 (d, 4H), 7.38 (m, 4H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ 147.1, 140.1, 125.1, 116.4 ppm.

Reaction of 1-chloro-2,4-dinitrobenzene and DAT at 80 °C

1-chloro-2,4-dinitrobenzene (0.505 g, 2.5 mmol) was added to the stirred reaction mixture of potassium carbonate (0.276 g, 2 mmol) and DAT (0.200 g, 2 mmol) in ethanol (15 mL) at room temperature. The reaction mixture was heated and kept refluxing for 6 h. The solid in reaction mixture was filtered off and washed with ethanol. The combined filtrate was concentrated and purified on a silica gel column chromatography employed by a solvent mixture of petroleum ether: dichloromethane: ethyl acetate = 1:1:1 to afford **8** as pure yellowish solid (0.248 g, 0.933 mmol, 46% yield). Melt point: 171-172 °C; IR: 3275(vw), 3118(vw), 3080(vw), 1647(s), 1622(s), 1522(s), 1500(s), 1428(s), 1357(s), 1282(s), 1157(s), 1087(m), 973(m), 927(m), 838(m), 765(vw), 742(m) cm^{-1}; ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ 11.33 (s, 1H), 8.93 (d, J = 2.2 Hz, 1H), 8.39 (dd, J = 9.3, 2.2 Hz, 1H), 7.24 (s, 2H), 6.50 (d, J = 9.4 Hz, 1H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ 153.6, 144.9, 132.1, 130.1, 122.1, 114.4 ppm. ESI-MS: *m/z* = 264.87 $(M-H)^-$. Elemental Analysis for $C_7H_6N_8O_4$ (266.05): calcd C 31.59, H 2.27, N 42.10 %; found C 31.63, H 2.22, N 42.00 %.

Reaction of 1-chloro-2,4-dinitrobenzene and DAT at 100 °C

A solution of 1-chloro-2,4-dinitrobenzene (0.505 g, 2.5 mmol), DAT (0.2 g, 2 mmol), solid K_2CO_3 (0.276 g, 2 mmol) in 10 mL DMSO was stirred at 100 °C for 12 hours. The mother liquor was evaporated in vacuum to dryness and the remaining black oil was dry-column flash chromatographed.

2,4-Dinitroaniline: 0.150 g of yellow powder was obtained (yield 41 %). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ 8.69 (d, J = 2.6, 1H), 8.31 (s, 2H), 8.06 (dd, J = 9.4, 2.6, 1H), 7.04 (d, J = 9.4, 1H) ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ 150.1, 135.4, 129.4, 128.9, 123.6, 120.1 ppm.

Bis(2,4-dinitrophenyl)amine: 0.154 g of yellow powder was obtained (yield 22 %). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ 11.13 (s, 1H), 8.92 (d, J = 2.5, 2H), 8.48 (dd, J = 9.2, 2.5, 2H), 7.83 (d, J = 9.2, 2H). ppm. ^{13}C NMR (126 MHz, [D$_6$]DMSO): δ 147.0, 140.5, 138.2, 132.5, 131.7, 121.8 ppm.

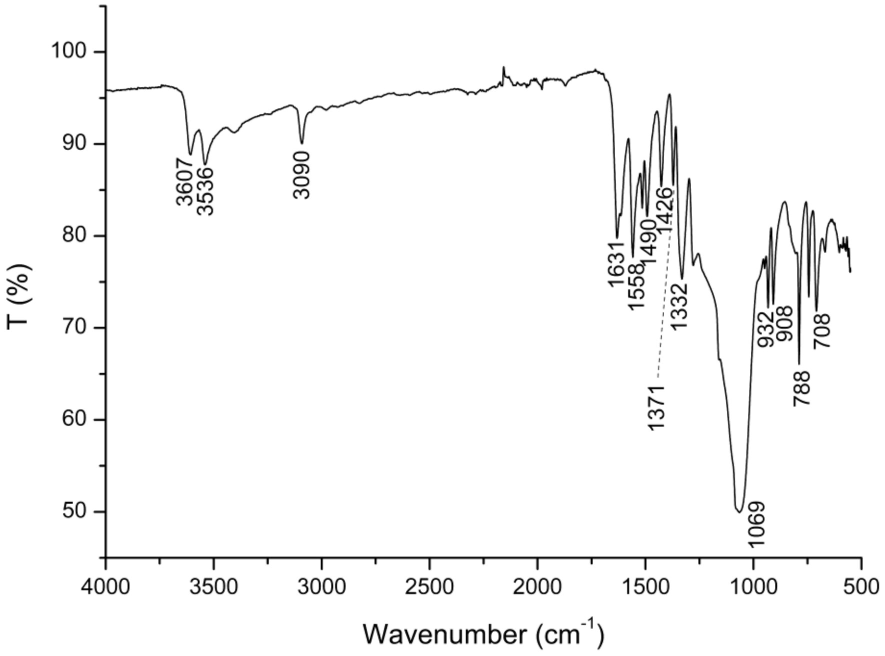


Figure S1. Infra-red spectrum of **3**

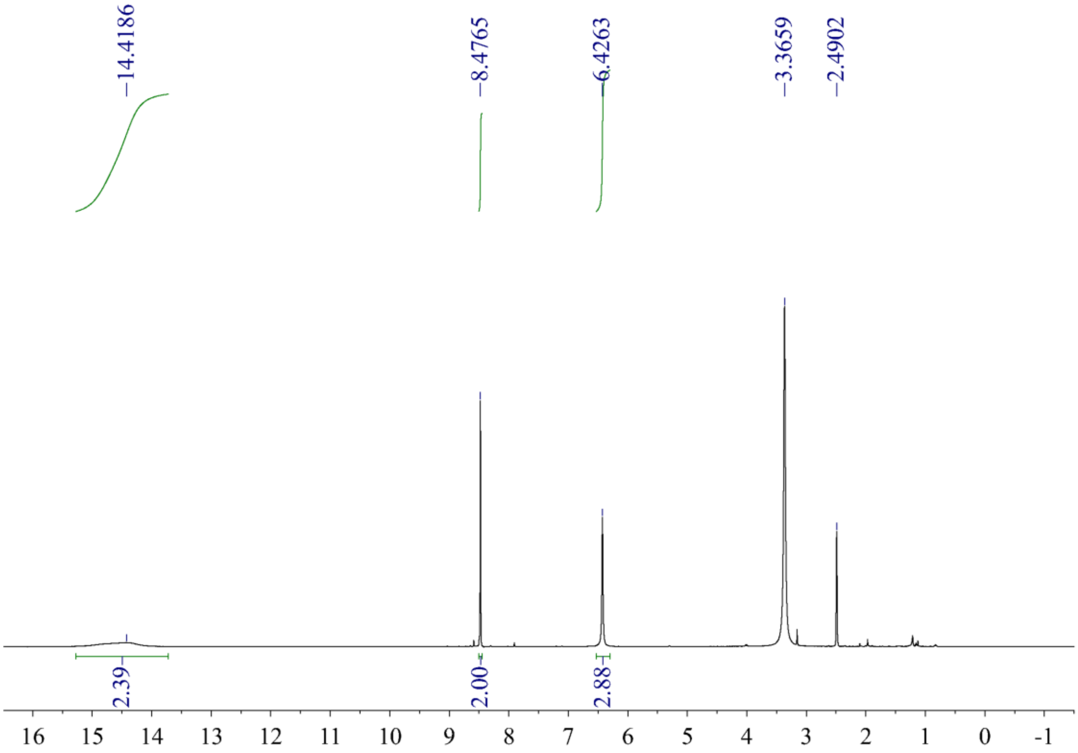


Figure S2. ^{1}H NMR spectrum (500 MHz) of **3** in DMSO at 25 °C

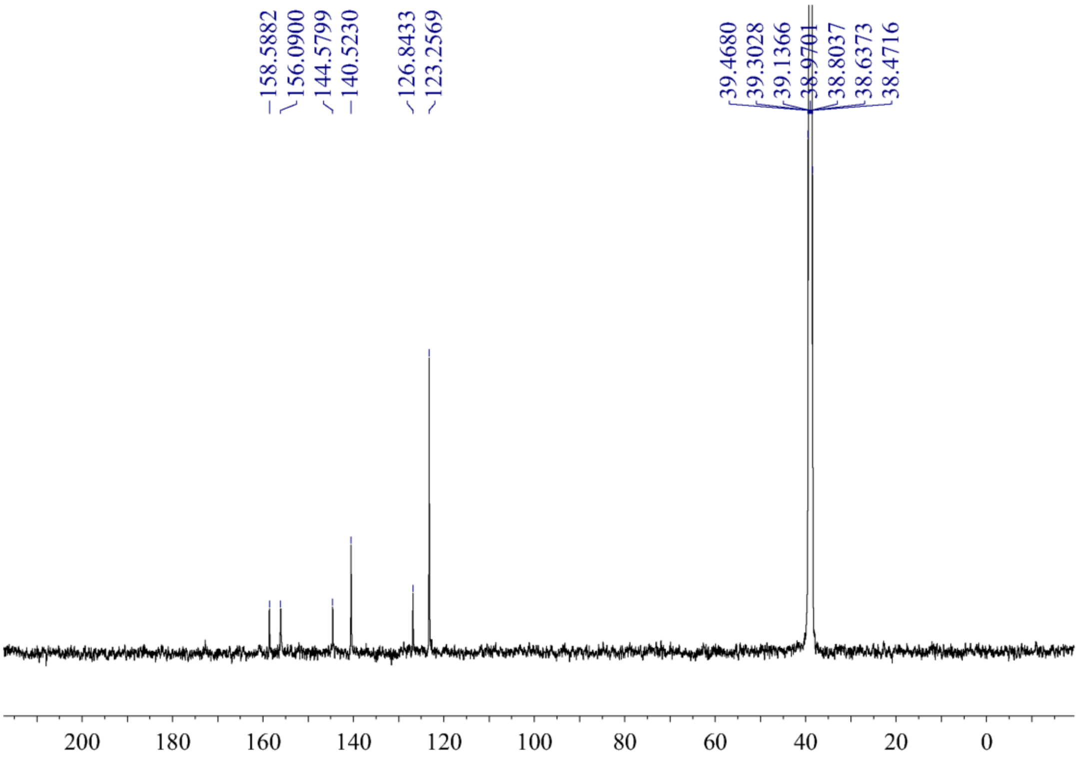


Figure S3. ^{13}C NMR spectrum (126 MHz) of **3** in DMSO at 25 °C

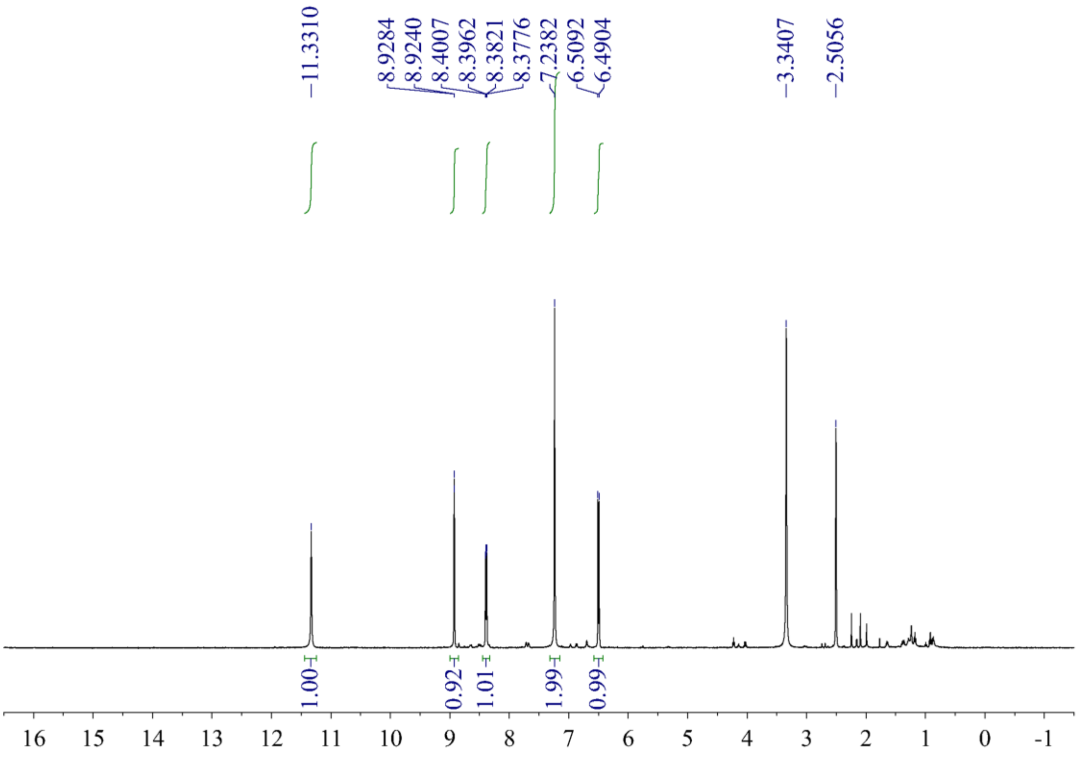


Figure S4. ^{1}H NMR spectrum (500 MHz) of **8** in DMSO at 25 ^{o}C

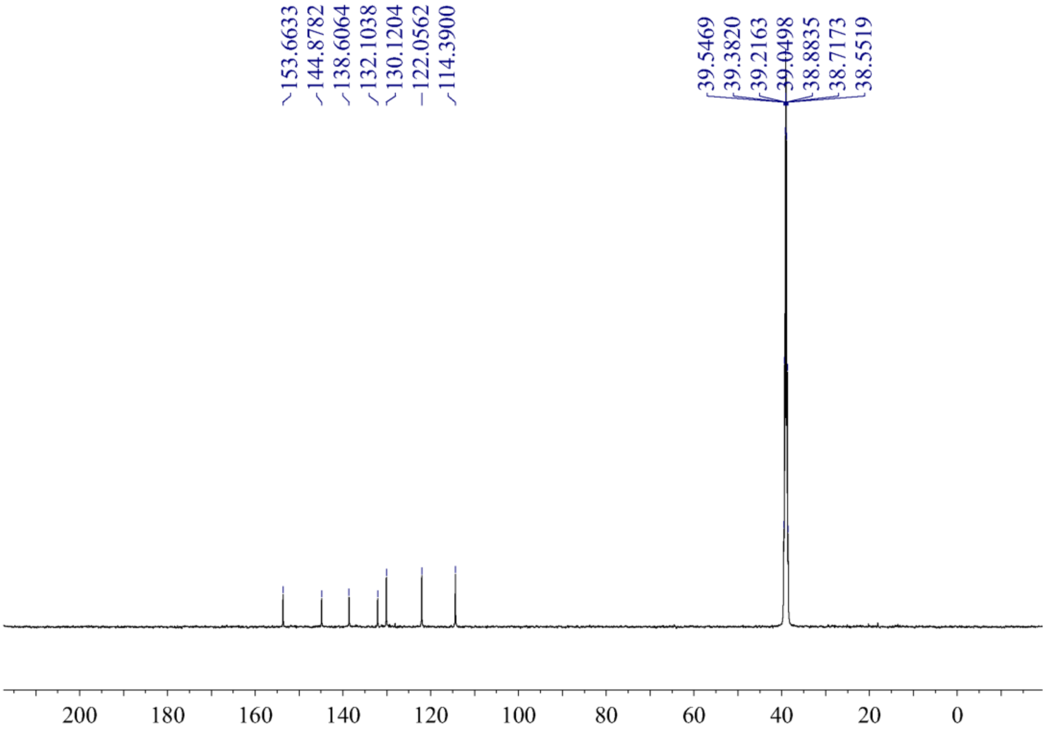


Figure S5. ^{13}C NMR spectrum (126 MHz) of **8** in DMSO at 25 ^{o}C

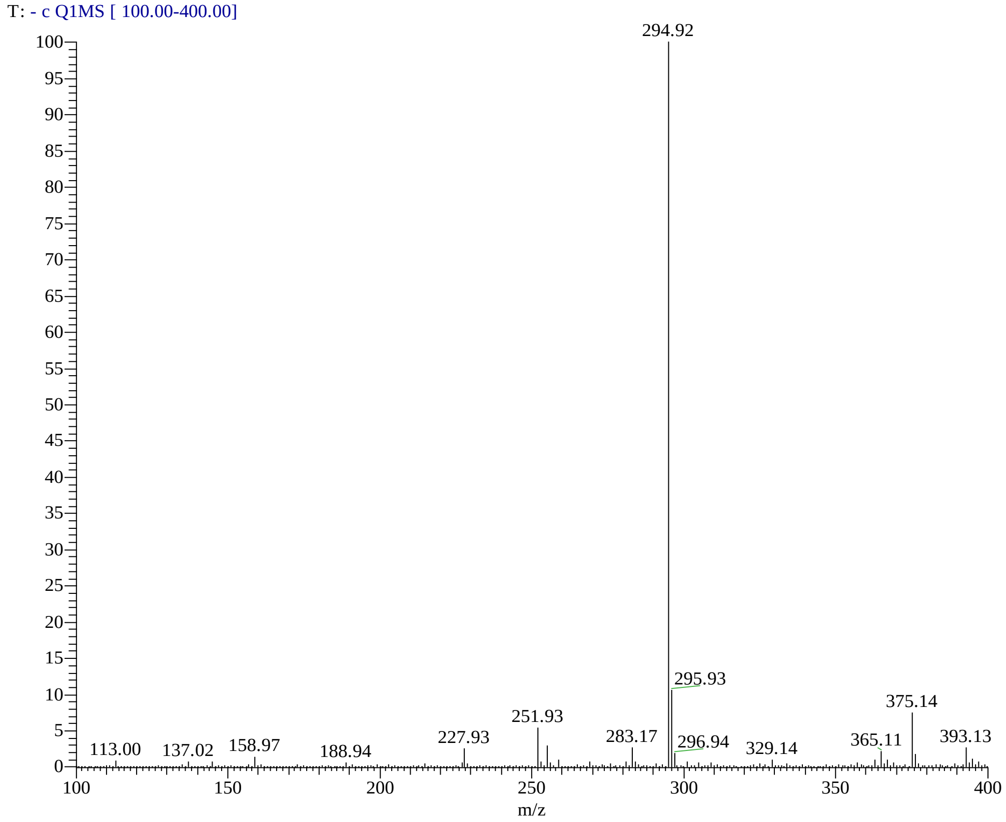


Figure S6. Mass spectrum of **3**

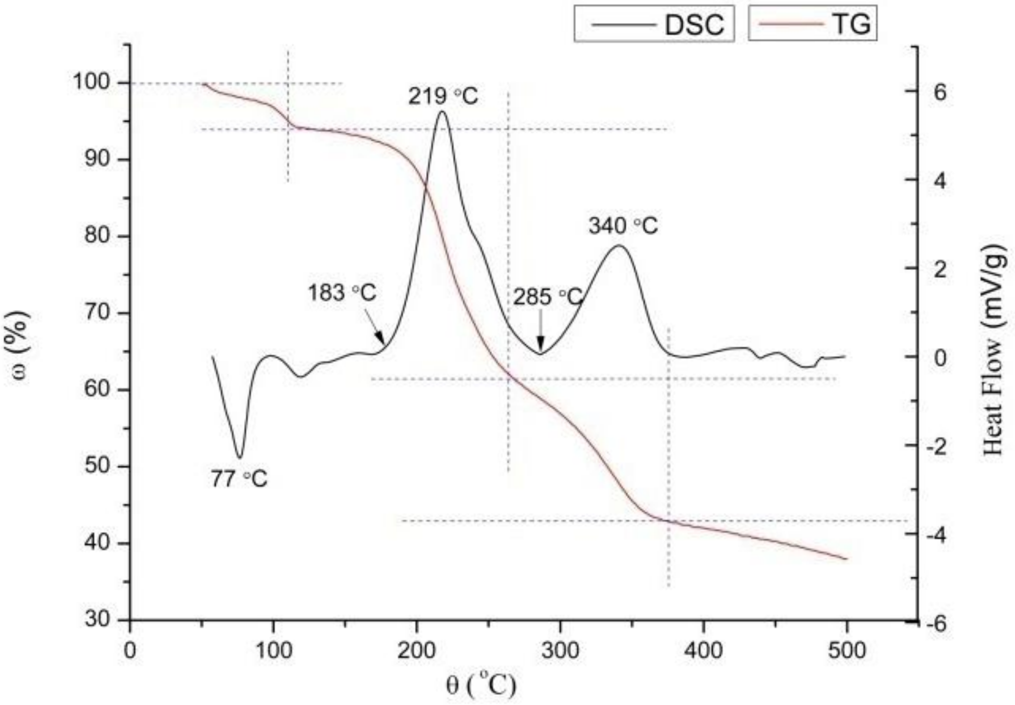


Figure S7. TG-DSC plot of the compound **3**

X-ray Structural Analysis of 3

Single crystals of **3** suitable for X-ray crystallographic analysis were obtained by slowly evaporation from isopropanol at room temperature.

The X-ray diffraction measurements for **3** were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at 291 K by using graphite-monochromated Mo Kα radiation (λ = 0.71075 Å). Data were collected by ω scan technique. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined. Please see its CIF files. Relevant data are given in Table S1.

Table S1. Crystallographic details of **3**

	Compound **3**
formula	$2(C_7H_4N_8O_6), 5(H_2O)$
formula weight[g·mol^{-1}]	682.44
temperature	291
crystal system	Monoclinic
space group	P21/c
cell parameters	a=18.6978(11) Å b=12.23850(13) Å c=13.6407(12) Å β =110.702(3)°
cell volume	2919.9(3) Å^3
formula Z	4
calc. density [g/cm^3]	1.552
Absorption correction	multi-scan
Theta range for data collection[◦]	2.3-26.0
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R_1=0.0564,wR_2=0.1416
R indices (all data)	R_1= 0.0692,wR_2= 0.1466
Largest diff. peak and hole	0.189 and -0.174 e.Å^{-3}
CCDC	896931

Table S2. Selected bond distances

parameter	bond length(Å)	parameter	bond length(Å)
O1-N1	1.221(3)	O3-N2	1.199(3)
O2-N1	1.232(3)	O5-N3	1.222(3)
O4-N2	1.249(3)	N2-C4	1.455(3)
O6-N3	1.223(3)	N4-C7	1.403(4)
N3-C6	1.433(4)	N5-N6	1.366(3)
N4-C1	1.355(3)	N6-N7	1.290(3)
N5-C7	1.322(3)	N8-C7	1.311(3)
N7-N8	1.352(4)		

Table S3. Selected bond angles (^{o})

parameter	bond angle (^{o})	parameter	bond angle (^{o})
N4-C7-N8	125.8(2)	N4-C7-N5	123.0(2)
N12-C8-C13	127.1(2)	N12-C8-C9	120.8(3)
N12-C14-N16	124.9(2)	N12-C14-N13	123.5(3)
C1-N4-C7	123.8(2)	N4-C1-C2	122.1(2)
N4-C1-C6	124.4(2)		

Table S4. Selected torsion angles (^{o})

parameter	bond angle (^{o})	parameter	bond angle (^{o})
C1-N4-C7-N8	-16.4(4)	C14-N12-C8-C13	-24.5(4)
C7-N4-C1-C2	146.2(3)	C14-N12-C8-C9	151.2(3)
C1-N4-C7-N5	160.3(3)	C8-N12-C14-N16	-26.3(4)
C7-N4-C1-C6	-32.5(4)	C8-N12-C14-N13	157.5(3)
N6-N5-C7-N4	179.1(2)	N14-N13-C14-N12	175.0(2)
N7-N8-C7-N4	-177.0(2)	N15-N16-C14-N12	-176.8(2)
N4-C1-C6-N3	-9.6(4)	N12-C8-C13-C12	169.7(3)
N4-C1-C6-C5	170.8(3)	N12-C8-C13-N11	-18.6(4)
N4-C1-C2-C3	-171.6(3)	N12-C8-C9-C10	-171.5(2)
N4-C1-C2-N1	-0.8(4)	N12-C8-C9-N9	7.2(4)

Table S5. Hydrogen bonds

D—H • • • A	D—H	H • • • A	D—H • • • A	Symmetry Code

O1W—H1X•••N6	0.8800	2.4500	3.332(3)	1-x,1/2+y,1/2-z
O1W— H1Y•••N7	0.7900	2.6100	3.292(3)	1+x,y,z
O2W— H2X•••N16	0.8500	2.0300	2.877(3)	
O2W— H2Y•••N14	0.8500	2.0700	2.900(3)	x,3/2-y,1/2+z
O3W— H3X•••N15	0.8500	2.5200	2.869(3)	
O3W—H3X•••O4W	0.8500	2.5200	2.822(3)	-x,1-y,-z
O3W—H3X•••O5W	0.8500	2.5800	2.918(3)	x,3/2-y,-1/2+z
O3W—H3Y•••O4W	0.8500	2.3500	2.822(3)	-x,1-y,-z
N4—H4•••O1	0.8600	2.0300	2.593(3)	
N4—H4•••O10	0.8600	2.4900	3.274(3)	x,-1+y,z
O4W—H4X•••O1W	0.8500	2.2400	2.885(3)	-1+x,y,z
O4W—H4Y•••O11	0.8500	2.5400	3.284(3)	x,-1+y,z
O5W— H5X•••N7	0.8500	2.5000	3.245(3)	
O5W—H5X…N8	0.8500	2.0200	2.872(3)	
O5W—H5Y•••O1W	0.8500	2.5000	3.160(3)	-1+x,y,z
N12— H12A•••O7	0.8600	1.9300	2.508(3)	
N12—H12A•••N9	0.8600	2.5600	2.856(3)	
N13—H13•••N2	0.8600	2.2900	3.139(3)	x,3/2-y,-1/2+z
C3—H3•••O3	0.9300	2.3600	2.677(3)	
C10—H10•••O8	0.9300	2.3200	2.653(4)	
C10—H10•••O2	0.9300	2.5400	3.465(3)	1-x,1/2+y,3/2-z

Computational Details

Calculations were carried out by using the Gaussian09 suite of programs. The geometry optimization and the frequency analysis were performed at the level of Becke three Lee-Yan-Parr (B3LYP) Functionals[1] with 6-311+G** basis set.[2] All of the optimized structures were characterized to be local minima on the potential surface without any imaginary frequencies.

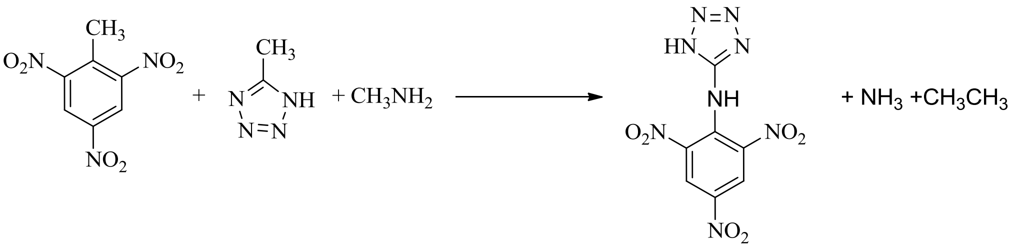
The predictions of heats of formation (HOF) adopt the hybrid DFT-B3LYP methods with 6-311+G** basis set via designed isodesmic reactions. The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. 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 $\Delta_f H_R$ and $\Delta_f H_P$ 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; ΔH_T 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 are available either from the experiments or from the high level computing like CBS-4M.



Scheme S1. Isodesmic reaction for compound **3**

Table S6. The theoretic calculation of heat of formation (HOF) for compound **3**

Compd.	E_0 (a.u)	ZPE(kJ/mol) [a]	H_T (kJ/mol)	HOF (kJ/mol)
3	-1158.4628311	379.11	48.14	452.23
NH_3	-56.5826354	86.26	10.05	-46.11[b]
CH_3-CH_3	-79.8565484	187.35	11.77	-84.00 [b]
TNT	-901.3734241	311.25	38.18	2.77
5-methyl-1*H*-tetrazole	-297.6593033	187.22	16.49	280.70 [c]
CH_3NH_2	-95.8938391	160.75	11.64	-22.97 [b]

[a] Scale factor for ZPE and vibrational frequencies is 0.96.[4]

[b] D. R. Lide, *CRC Handbook of Chemistry and Physics, 88th Edition (*2008*),* CRC Press/Taylor and Francis, Boca Raton, FL.

[c] A. A. Kozyro, V. V. Simirskii, A. P. Krasulin, V. M. Sevruk, G. Ya. Kabo, M. L. Frenkel, P. N. Gaponik, Y. V. Grigor'ev, Thermodynamic properties of tetrazole derivatives in different aggregation states, Russ. J. Phys. Chem. (Engl. Transl.), 1990, **64**, 348-350.

Detonation Parameters

Detonation velocity (*D*) and detonation pressure (*P*) were evaluated by the semi-empirical Kamlet & Jacobs formula[5] as

$$P = 1.558\rho^2\Phi \qquad (1)$$

$$D = 1.01\Phi^{1/2}\,(1+1.30\rho_0) \qquad (2)$$

$$\Phi = 0.4889\ \mathrm{N}\ (\mathrm{MQ})^{\ 1/2} \qquad (3)$$

where *D* is the predicted detonation velocity (km/s) and *P* is the detonation pressure (GPa), ρ is the density of a compound (cm^3/mol). Φ, N, M and Q are characteristic parameters of an explosive, Q is chemical energy of detonation (kJ/g). The experiment densities and the calculated heats of formation were used in computing the D and P values.

References

1 (*a*) A. D. Becke, *J. Phys. Chem.*, 1993, **98**, 5648-5652; (*b*) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627.

2 P. C. Hariharan and J. A. Pople, *Theoretica Chimica Acta.*, 1973, **28**, 213-222.

3 F. C. B. Edward and M. R. Betsy. *J. Phys. Chem. A*, 2006, **110**, 1005-1013.

4 A. P. Scott and L. Radom. *J. Phys. Chem.* 1996, **100**, 16502-16513

5 M. J. Kamlet and S. J. Jacobs, *J. Chem. Phys.*, 1968, **48**, 23-35.