Supporting Information

Synthesis and Characteristics of a Novel, High-Nitrogen, Heat-Resistant, Insensitive Material (NOG_2Tz)

Zhanda Fu,[†] Cheng He[†], and Fu-Xue Chen[†]*
fuxue.chen@bit.edu.cn

General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm relative to TMS. The solvent is [D_6]dimethyl sulphoxide (DMSO-d_6) unless otherwise specified. The melting, decomposition points and TG are recorded with the peak value on a METTLER TOLEDO differential scanning calorimeter at a scan rate of 10 ^{o}C min^{-1}. IR spectra were recorded on an IR-408 using KBr pellets. ESI-MS were recorded and analysed on an Aglient 500-MS, a Bruker Apex IV FTMS and a Bruker Compass Data Analysis 4.0. NOG and BT were prepared according to reported methods.[1] Other materials were purchased from Alfa Aesar.

Caution! When handling these energetic materials, small scale and good safety practices (leather gloves, face shield) are strongly encouraged.

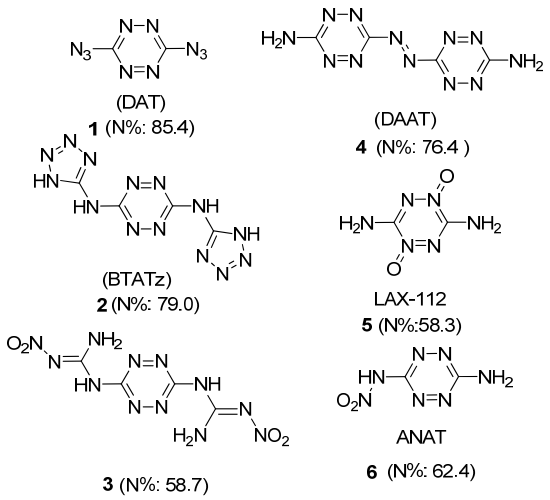


Figure S1 High-nitrogen *s*-tetrazine derivatives for energetic material applications

3-methoxy-5-methoxy-1,2,4-oxadiazole (**7**)

NOG (344 mg, 2 mmol) was added to a solution of methanol (8 mL) and sodium methoxide (30% solution in methanol, 720 mg, 4 mmol). The mixture was stirred with an overhead stirrer at 70 °C, then BT (270 mg, 1 mmol) was added in portions over 3-5 min. The reaction was maintained at 70 °C for 2 h. The reaction was then poured into ice water (10 mL) and acidified by adding 3N HCl, until the pH was equal to 1. The pink-orange precipitate was filtered, washed thoroughly with water and air dried to give **7** (280 mg, 89.2%). $T_{dec.}$: 260 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 7.01 (bs, 4H, NH_2), 3.83 (s, 3H, CH_3) ppm. ^{13}C NMR (100 MHz DMSO-d_6): δ_C 56.2, 159.4, 172.4, 174.2 ppm. IR (KBr) ν_{max}: 3439, 3367, 3192, 3121, 2957, 2759, 1670, 1645, 1586, 1562, 1524, 1465, 1385, 1282, 1100, 1005, 1003, 976, 771, 514 cm^{-1}. ESI-MS (157): *m/z* positive mode, 158[*M*+H]$^+$; 180[*M*+23]$^+$.

3,6-bi(3-nitro-1,2,4-oxadiazole-5-guanyl)-1,2,4,5-tetrazine (8)

NOG (860 mg, 5 mmol) was placed in an oven-dried, round-bottomed flask (50 mL) with a stirbar and dissolved in anhydrous dimethylformamide (20 mL). The solution was cooled to 0 °C and NaH (60% dispersion in oil, 280 mg, 7 mmol,) was added in portions over 5 min. The reaction was stirred for 30 min at 0 °C and BT (540 mg, 2 mmol) was added in one portion. The reaction was stirred at 0 °C for 1 h and then allowed to warm to room temperature and stirred for an additional 4 h. The reaction was then poured into ice water (20 mL) and acidified by the addition of 3 N HCl until the pH was equal to 1. The orange precipitate was filtered, washed thoroughly with water and dried to give **8** (800 mg, 94.7%). $T_{dec.}$: 329 °C, ^{1}H NMR (400 MHz, DMSO-d_6): δ_H 12.36 (bs, NH), 9.27 (bs, 2H), 8.74(bs, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 155.8, 159.2, 169.0, 175.3 ppm. IR (KBr) ν_{max}: 3365, 3264, 3216, 1633, 1568, 1538, 1477, 1405, 1386, 1302, 1052, 1026, 980, 955, 828, 787, 755, 695, 599 cm^{-1}. HRMS (421.0584): *m/z* negative mode, 421.05796 [*M*–H]$^-$. The crystal density was calculated by a patented method.[2]

X-ray analysis data of **7** and **8**·2DMSO

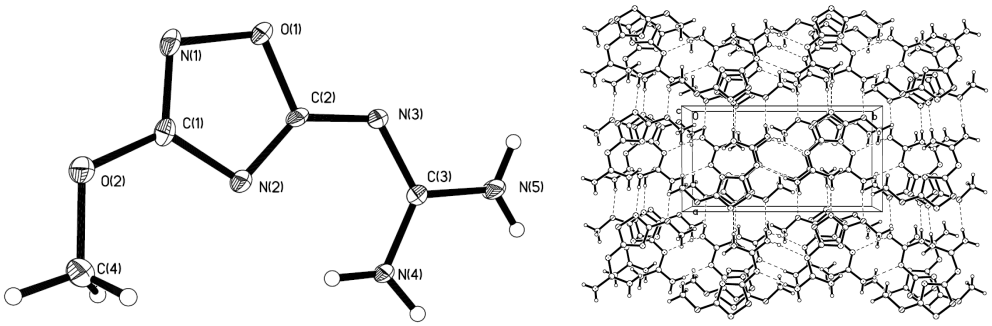
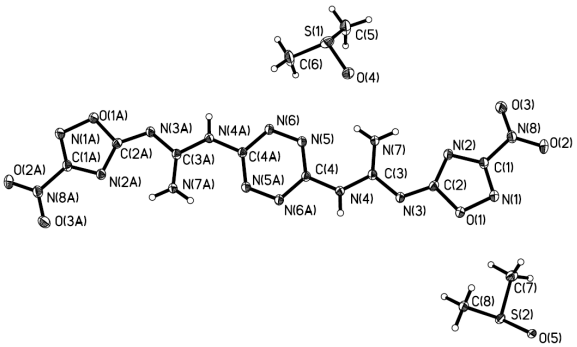
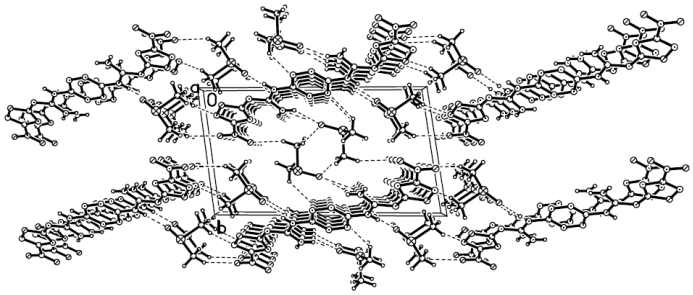


Figure S1 Displacement ellipsoid plot (30%) and ball-and-stick packing diagram of **7.**



(a)



(b)

Figure S2 Displacement ellipsoid plot (30%) (a) and ball-and-stick packing diagram (b) of **8**·2DMSO

Table S1 Crystallographic data for **7** and **8**·2DMSO

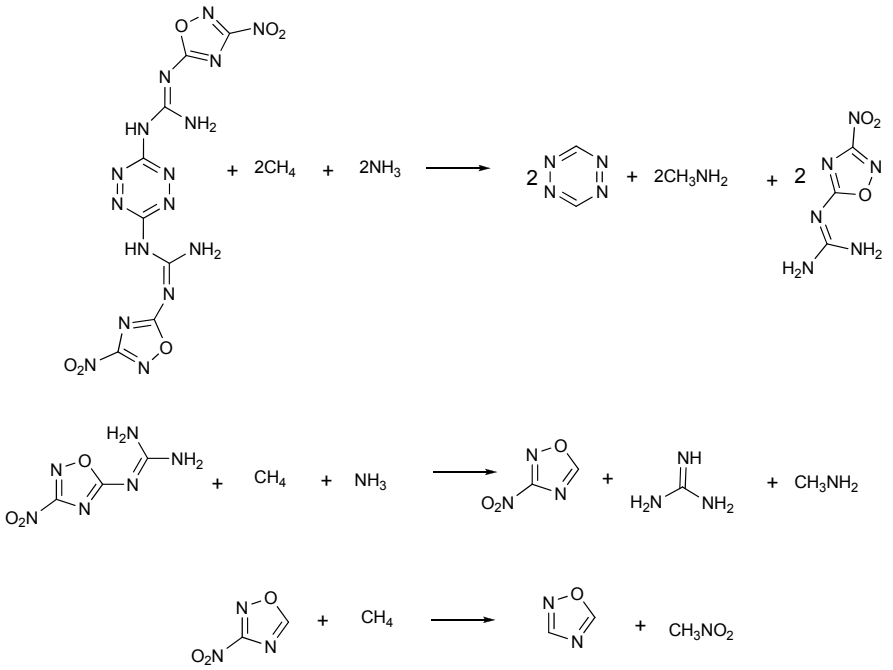
Compound	**7**	**8**·2DMSO
Empirical formula	C4H7N5O2	C12 H18 N16 O8 S2
Formula weight	157.15	578.09
Temperature	153(2) K	153(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space	Monoclinic, P2(1)/c	Triclinic, P-1

group		
Unit cell dimensions	a= 7.129(3) Å α=90° b= 13.514(5) Å β= 91.715(5)° c= 6.915(3) Å γ=90°	a=5.750(2) Å α=80.614(11)° b=8.875(3) Å β=80.732(10)° c =15.739(6) Å γ=81.456(10)°
Volume	665.9(5) $Å^3$	775.9(5) $Å^3$
Z, Calculated density	4, 1.567 g cm^{-3}	1, 1.573 g cm^{-3}
Absorption coefficient	0.128 mm^{-1}	0.383 mm^{-1}
F(000)	328	382
Crystal size	0.32 × 0.28 × 0.11 mm	0.61 × 0.21 × 0.07 mm
Theta range for data collection	2.86° to 29.10°	2.34° to 29.09°
Limiting indices	–7<=h<=9, –18<=k<=18, –9<=l<=9	–7<=h<=7, –10<=k<=12, –21<=l<=21
Reflections collected/unique	5660/1753 [R(int)= 0.0387]	8329/4037 [R(int)=0.0305]
Completeness to theta=27.48	98.2%	97.0%
Absorption correction	None	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1753/0/177	4037/19/279
Goodness-of-fit on F^2	1.002	1.002
Final R indices	R_1=0.0492, wR_2=0.1355	R_1=0.0511, wR_2=0.1117

[I>2sigma(I)]		
R indices (all data)	R_1=0.0784, wR_2=0.1470	R_1=0.0858, wR_2=0.1271
Largest diff. peak and hole	0.287 and -0.235 e. Å^{-3}	0.595 and -0.346 e. Å^{-3}

Calculated total energy (E0), zero-point energy (ZPE), enthalpy of formation (HOF) of compound 8

Isodesmic reactions for compound **8**



All the calculations are done at the semi-empirical level using the PM6 method[3] implemented in the MOPAC package.[4] The heat of formation is obtained at room temperature (298.15K) throughout the atomisation reaction.

Table S2 Calculated heats of formation by MOPAC

Compd.	E_0/ev	ZPE/ev	HOF/(KJ mol^{-1})
NOG	-2367.64277	2.60549941449	235.07941
8	-5667.81698	5.60450188663	957.34882

References

1. (*a*)Z. Fu, R. Su, Y. Wang, Y-F. Wang, W. Zeng, N. Xiao, Y. Wu, Z. Zhou, J. Chen and F-X. Chen, *Angew. Chem., Int. Ed.*, submitted, DOI: 10.1002/anie.201105870; (*b*) Y. Li, A. Asadi and D. M. Perrin, *J. Fluorine Chem.*, 2009, **130**, 377-382
2. Y.-K. Wu, D.-Y. Chen, H.-S. Dong, *Chinese Patent*, 2011, CN101957300A.
3. J. J. P. Stewart, *J. Mol. Modeling,* 2007, **13**, 1173-1213.
4. MOPAC2009, J. J. P. Stewart, *Stewart Computational Chemistry*, Colorado Springs: CO, USA, HTTP://OpenMOPAC. net (2008).

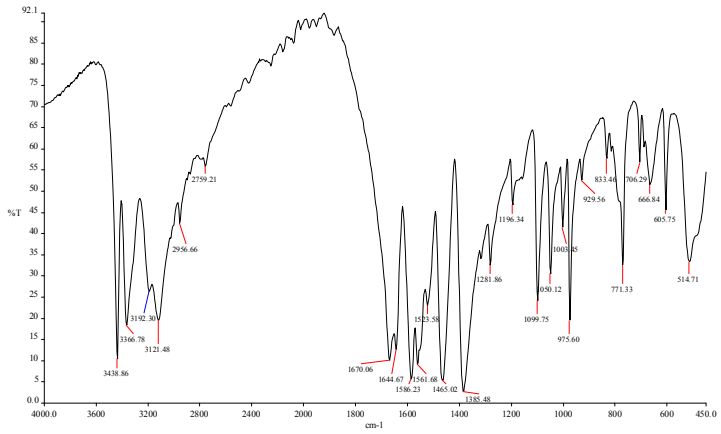


Figure S1 IR spectra of of **7**

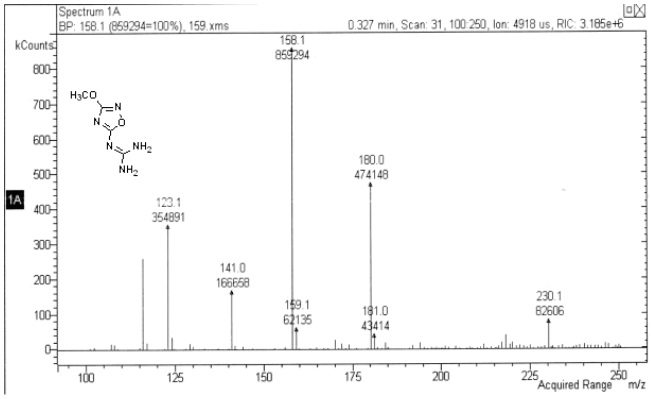


Figure S2 ESI of **7**

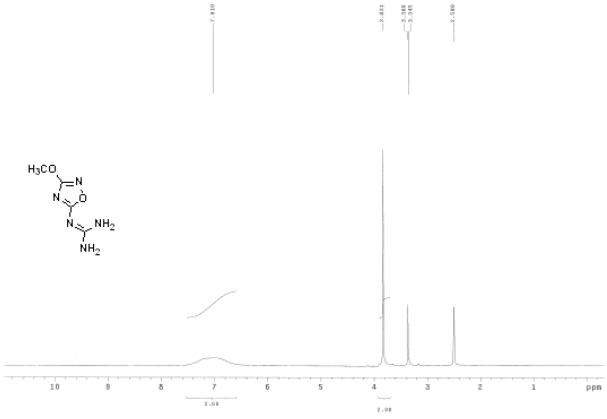


Figure S3 ^{1}H NMR of **7**

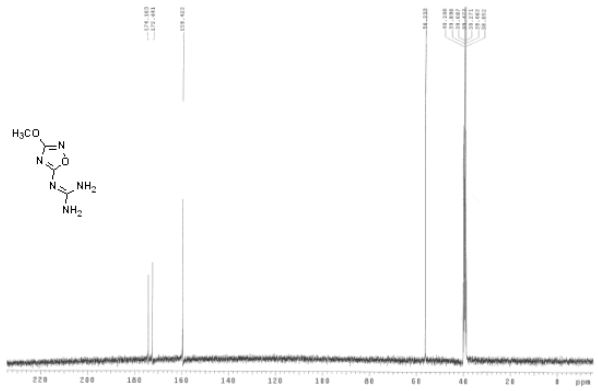


Figure S4 ^{13}C NMR of **7**

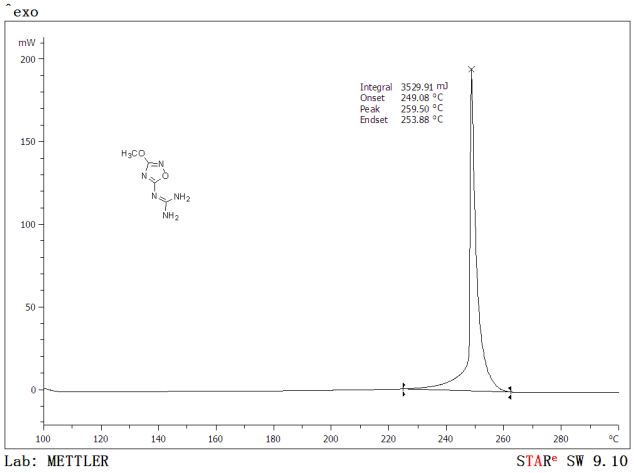


Figure S5 DSC of **7**

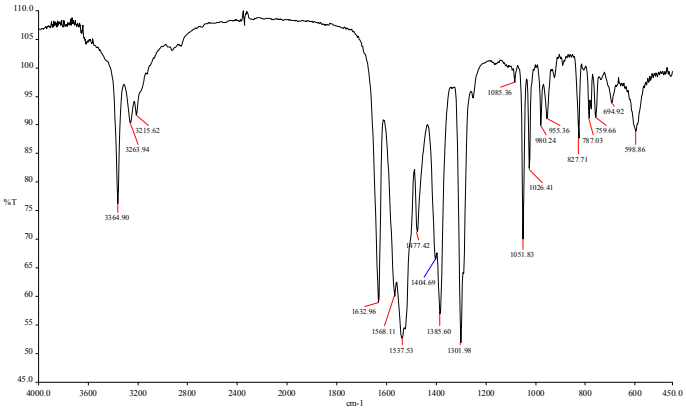


Figure S6 IR of of **8**

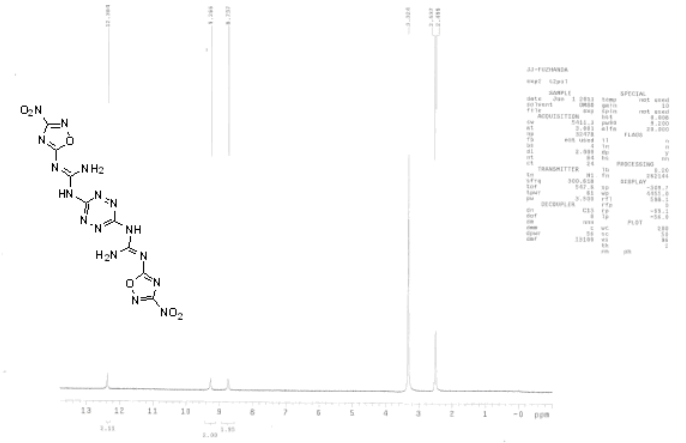


Figure S7 ^{1}H NMR of **8**

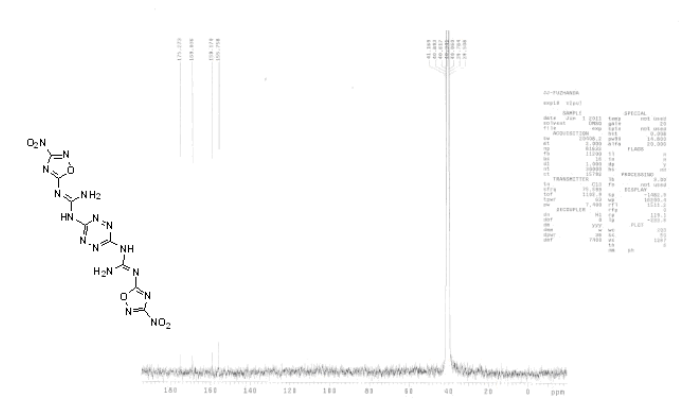


Figure S8 ^{13}C NMR of **8**

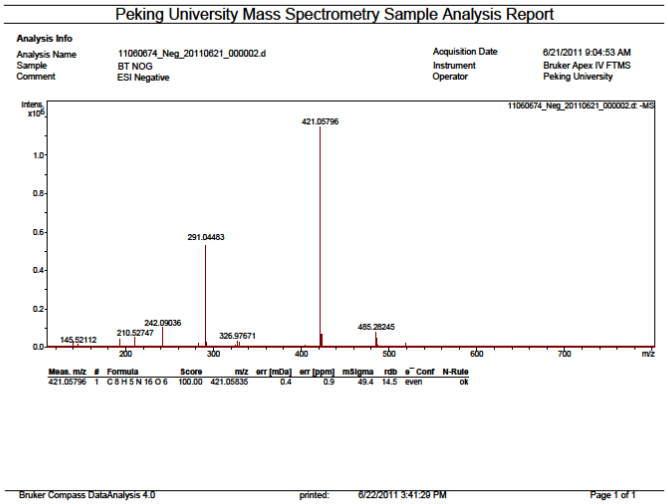


Figure S9 HRMS of **8**

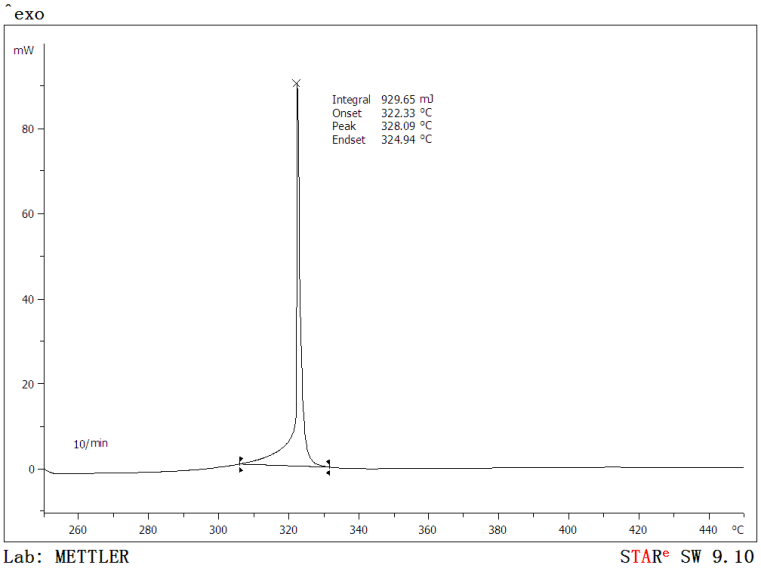


Figure S10 DSC of **8**

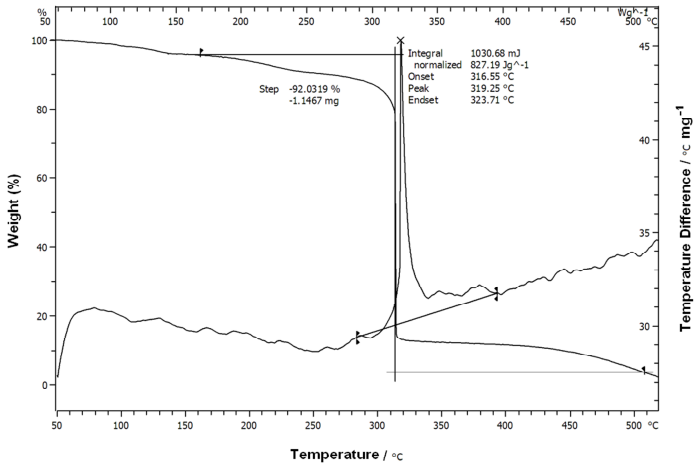


Figure S11 TGA of **8**