Electronic Supplementary Information

for

1,2-Bis(5-(trinitromethyl)-1,2,4-oxadiazol-3-yl)diazene: A Water Stable, High-Performing Green Oxidizer

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1. Experimental Section

Caution! Although no explosions or detonations occurred during the preparation or handling of these nitrogen-rich compounds, appropriate safety precautions (protective gloves and coats, face shield and explosion-proof baffle) must be followed to ensure safety.

General Information

Reagents were purchased from Aldrich and Acros Organics and were used as received. ^{1}H, ^{13}C and ^{15}N NMR spectra were recorded on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 500, 125, and 50.69 MHz, respectively, by using DMSO-d_6 or acetone-d_6 or chloroform-d or acetonitrile-d_3 as the solvent and locking solvent. Tetramethyl silane, and nitromethane are used as references for ^{1}H, ^{13}C, and ^{15}N, respectively, NMR spectra. The melting and decomposition (onset) points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q2000) at a scan rate of 5 °C min^{-1}. IR spectra were recorded using KBr pellets for solids on a Nicolet Thermo-model AVATAR 370-spectrometer. Density was measured at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses (C, H, N) were determined using a Vario Micro-cube Elementar Analyser. The sensitivities to impact (IS) and friction (FS) were determined according to BAM standards.

Synthesis of Compound 14: Compound **13**[1] (430 mg, 1.05 mmol) was dissolved in concentrated H_2SO_4 (3.0 mL) and cooled to -5 ℃. To this fuming HNO_3 (1.5 mL) was added dropwise over 30 minutes. The temperature of this reaction was kept below 0 ℃ during this addition. After that, the reaction mixture was stirred at ice temperature for 1 hour and at room temperature for 2 hours. A yellow precipitate formed, and the reaction mixture was poured into ice-cold water. The precipitate was collected by filtration and washed with cold water (2.0 mL) and dried at room temperature to give a pure yellow solid compound **5** (455 mg, 93%). T_{dec} (5 °C min^{-1}): 125 °C (onset); ^{13}C NMR (125 MHz, acetone-d_6): δ 175.9, 164.4, 118.9; ^{15}N NMR (50.66 MHz, acetone-d_6): δ +143.6, +4.0, -40.4, -130.6; IR (KBr): ν 3429, 2888, 1614 (C=N), 1495 (NO_2), 1334 (C-N), 1275 (C-O), 1092, 1020, 961, 938, 840, 797, 767, 725, 662 cm^{-1}. Anal. Calcd for $C_6N_{12}O_{14}$ (436.96): C, 15.53; H, 0.00; N, 36.21; found: C, 15.50; H, 0.214; N, 35.83.

2. Theoretical Calculations

Heats of formation for compounds **14**, was calculated based on isodesmic reactions (Scheme S1). The calculations were carried out using Gaussian 03 (Revision D.01) suite of programs.[2] The geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-31+G** level. The gas phase enthalpy of formation was calculated, and the enthalpy of reaction was obtained by combining the MP2/6- 311++G** energy difference for the reactions, the scaled zero-point energies (ZPE), values of thermal correction (HT), and other thermal factors.

Isodesmic Reactions

Scheme S1.

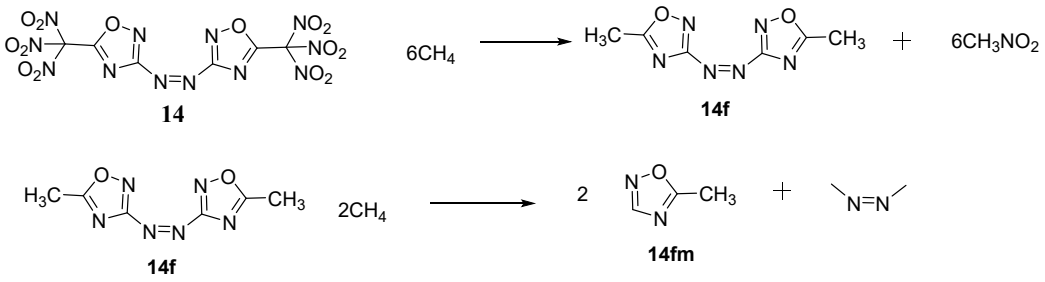

Table S1 Calculated zero point energy (ZPE), values of the correction (Hr), total energy (E0) and gas-state heats of formation (HOF).[a]

Compound	ZPE [Hartree /Particle]	HT [Hartree /Particle]	E0 [kJ mol^{-1}]	HOF (gas) [kJ mol^{-1}]
14	0.148746	0.177314	-1933.9127816	461.414
14f	0.137505	0.150788	-709.3940216	295.552
14fm	0.074089	0.080182	-300.6855029	17.0516

[a] The enthalpy of sublimation was calculated by using Trouton's rule. Solid-state heats of formation of the resulting compounds were calculated with Equation (1) in which T_m is the melting temperature.

$$\Delta Hf = \Delta Hf(g) - \Delta Hsub = \Delta Hf(g) - 188[J\ mol^{-1}\ K^{-1}] \times T_m \qquad (1)$$

References

1. Y. Tang, C. He, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Chem. Eur. J.* 2017, **23**, 16401–16407.

2. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03 (Revision E.01), Gaussian, Inc., Wallingford CT, 2004.

3. X-ray crystallographic data

Table S2. Selected crystal parameters of **14**	**14**
CCDC	**2106963**
Empirical formula	$C_6N_{12}O_{14}$
Formula mass	464.18
Crystal System	triclinic
Space Group	*P*-1
Z	2
a/Å	5.92194(16)
b/Å	11.2781(3)
c/Å	12.7041(4)
α/°	106.137(2)
β/°	92.992(2)
γ/°	92.277(2)
V/Å^3	812.64(4)
$D_{calc.}$/ g cm^{-3}	1.897
T/K	100(10)
F(000)	464.0
h, k, l	7,14,15
μ (mm^{-1})	1.691
R1 [I > 2σ(I)]	0.0660
Completeness to theta full	0.951
*w*R2 (all data)	0.1903
S on F2	1.057

Compound 14

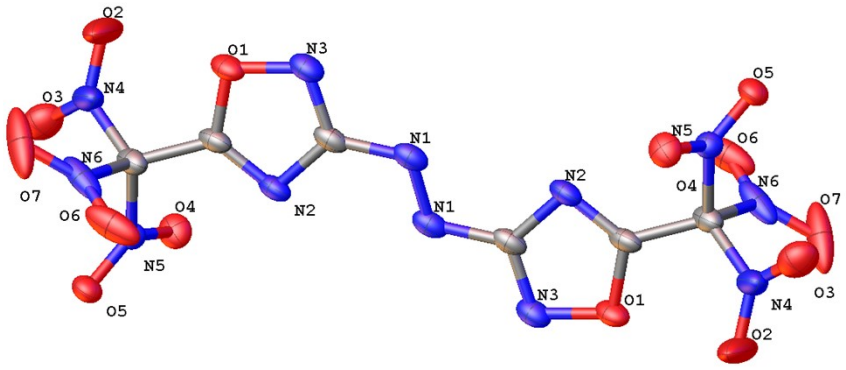

Figure S1: Molecular structure of **14**

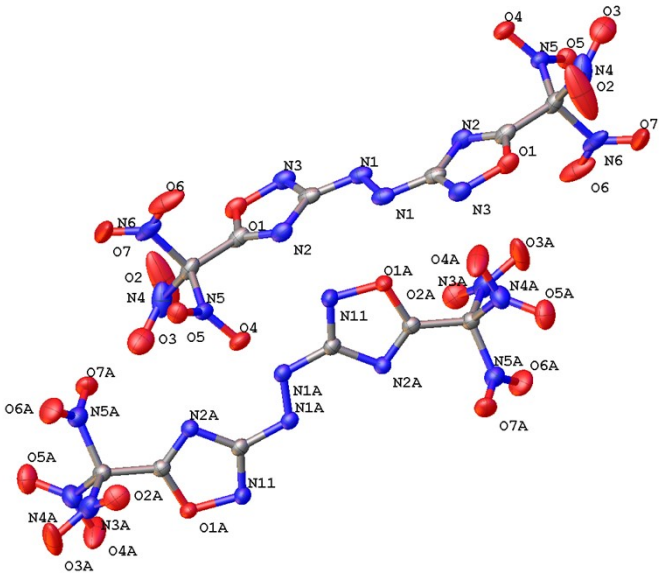

Figure S2: Single-crystal X-ray structure of **14**

Table S3: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **14**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O1	-1903(4)	2395(2)	6231.9(18)	29.3(5)
O2	-564(10)	653(4)	7108(3)	108(2)
O3	2306(5)	1020(2)	8264(3)	46.1(7)
O4	4450(4)	2989(2)	7537(2)	31.5(5)
O5	3422(4)	3848(2)	9190.8(18)	28.3(5)
O6	-1208(5)	4318(4)	8904(2)	57.9(9)
O7	-1653(5)	2516(4)	9217(3)	75.1(13)
N1	-832(4)	4619(2)	4901(2)	27.2(6)
N2	658(4)	3962(3)	6513(2)	26.8(6)
N3	-2378(4)	2977(3)	5419(2)	29.6(6)
N4	836(7)	1320(3)	7725(3)	45.9(9)
N5	3094(4)	3261(2)	8241(2)	23.0(5)
N6	-890(5)	3229(4)	8761(2)	45.0(9)
C1	-819(5)	3874(3)	5619(2)	25.8(6)
C2	-93(5)	3041(3)	6829(2)	25.9(7)
C3	702(5)	2711(3)	7844(3)	27.8(7)
O1A	2531(3)	2500(2)	3813.3(18)	25.3(5)
O2A	2211(4)	666(2)	1199(2)	38.9(6)
O3A	2118(5)	2404(4)	731(3)	68.7(11)
O4A	3531(6)	4300(3)	2913(3)	61.0(10)
O5A	6152(5)	4021(2)	1734(2)	42.1(6)
O6A	6859(5)	1151(3)	822(2)	43.7(7)
O7A	8484(4)	2205(2)	2435(2)	36.1(6)
N1A	4185(4)	340(2)	5120(2)	21.1(5)
N2A	5064(4)	1064(2)	3489(2)	21.1(5)
N3A	2769(5)	1722(3)	1264(2)	37.4(7)
N4A	4822(5)	3685(3)	2303(3)	36.1(7)
N5A	6893(5)	1807(3)	1757(2)	31.2(6)

Atom	x	y	z	U_{eq}
N11	2361(4)	1897(2)	4631(2)	25.3(6)
C1A	3899(5)	1081(3)	4400(2)	20.1(6)
C2A	4158(5)	1940(3)	3188(2)	21.1(6)
C3A	4636(5)	2311(3)	2177(2)	22.9(6)

Table S4: Anisotropic Displacement Parameters ($\times 10^4$) for **14**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	19.3(10)	38.7(12)	24.2(11)	1.1(9)	-0.5(8)	-6.1(9)
O2	169(5)	75(2)	80(3)	51(2)	-81(3)	-89(3)
O3	50.6(17)	33.2(13)	52.0(17)	6.2(12)	11.9(14)	3.4(12)
O4	20.9(10)	41.6(13)	32.5(12)	10.0(10)	8.1(9)	4.5(9)
O5	25.5(11)	33.9(12)	23.1(11)	5.7(9)	-3.9(8)	-3.8(9)
O6	26.7(13)	89(2)	34.6(15)	-22.3(15)	4.6(11)	6.3(14)
O7	30.6(14)	171(4)	54(2)	76(2)	19.8(13)	30.4(19)
N1	20.1(11)	31.9(13)	22.8(13)	-3.6(10)	0.0(9)	4.4(9)
N2	21.0(12)	34.8(14)	18.6(12)	-1.4(10)	-1.2(10)	-1.6(10)
N3	20.7(12)	38.6(15)	23.9(13)	0.3(11)	-0.9(10)	0.3(11)
N4	66(2)	41.4(18)	23.7(15)	3.9(13)	-0.7(15)	-28.1(17)
N5	18.5(12)	24.8(12)	25.0(13)	6.2(10)	1.7(10)	0.3(9)
N6	15.2(13)	95(3)	18.2(14)	4.9(16)	0.8(10)	4.5(15)
C1	18.3(13)	31.8(16)	20.1(14)	-4.4(12)	0.3(11)	3.7(12)
C2	19.5(13)	32.3(16)	19.0(14)	-4.0(12)	2.5(11)	-3.8(12)
C3	22.4(14)	36.5(17)	20.1(15)	1.4(12)	3.8(12)	-6.7(12)
O1A	21.8(10)	33.0(11)	24.6(11)	12.3(9)	6.4(8)	8.4(8)
O2A	38.7(14)	36.5(14)	32.7(13)	-2.2(10)	-5.5(10)	-6.6(11)
O3A	43.8(16)	124(3)	60(2)	69(2)	-22.3(15)	-25.3(18)
O4A	95(3)	35.6(14)	65(2)	23.2(14)	52.1(19)	31.0(15)
O5A	53.8(16)	37.4(14)	36.8(14)	14.4(11)	4.2(12)	-9.5(12)
O6A	49.4(16)	49.0(15)	29.5(13)	2.6(11)	14.2(11)	11.1(12)
O7A	19.7(11)	53.3(15)	38.4(14)	19.1(12)	-2.4(10)	-0.5(10)
N1A	19.0(11)	22.8(12)	19.8(12)	3.2(9)	1.6(9)	-0.8(9)
N2A	21.2(12)	23.6(12)	17.7(12)	4.1(9)	1.6(9)	2.5(9)
N3A	28.9(14)	60(2)	24.4(14)	13.3(14)	0.1(11)	-0.6(13)
N4A	43.5(17)	36.0(16)	32.2(15)	14.1(13)	4.3(13)	7.0(13)
N5A	28.9(14)	35.4(15)	30.6(15)	10.4(12)	5.4(11)	3.8(11)
N11	23.4(12)	30.5(13)	24.9(13)	11.4(11)	5.4(10)	3.7(10)
C1A	17.1(12)	21.4(13)	19.8(13)	2.8(11)	1.2(10)	-1.8(10)
C2A	18.8(13)	23.2(14)	18.7(14)	2.2(11)	-0.3(10)	0.0(11)
C3A	21.0(14)	27.7(15)	18.8(14)	4.4(11)	0.4(11)	2.2(11)

Table S5: Bond Lengths in Å for **14**.

Atom	Atom	Length/Å
O1	N3	1.392(4)
O1	C2	1.342(4)
O2	N4	1.193(5)
O3	N4	1.196(5)
O4	N5	1.217(3)

Atom	Atom	Length/Å
O5	N5	1.205(3)
O6	N6	1.213(5)
O7	N6	1.202(5)
N1	N1[1]	1.249(5)
N1	C1	1.401(4)
N2	C1	1.375(4)
N2	C2	1.285(4)
N3	C1	1.303(4)
N4	C3	1.539(5)
N5	C3	1.526(4)
N6	C3	1.539(4)
C2	C3	1.497(5)
O1A	N11	1.396(3)
O1A	C2A	1.344(3)
O2A	N3A	1.202(4)
O3A	N3A	1.219(4)
O4A	N4A	1.213(4)
O5A	N4A	1.214(4)
O6A	N5A	1.210(4)
O7A	N5A	1.224(4)
N1A	N1A[2]	1.254(5)
N1A	C1A	1.409(4)
N2A	C1A	1.374(4)
N2A	C2A	1.281(4)
N3A	C3A	1.546(4)
N4A	C3A	1.512(4)
N5A	C3A	1.537(4)
N11	C1A	1.307(4)
C2A	C3A	1.494(4)

---- [1]-x,1-y,1-z; [2]1-x,-y,1-z

Table S6: Bond Angles in ° for **14**.

Atom	Atom	Atom	Angle/°
C2	O1	N3	105.1(2)
N1[1]	N1	C1	112.2(3)
C2	N2	C1	100.6(3)
C1	N3	O1	103.6(2)
O2	N4	O3	126.8(4)
O2	N4	C3	116.1(4)
O3	N4	C3	117.1(3)
O4	N5	C3	113.3(2)
O5	N5	O4	128.8(3)
O5	N5	C3	117.8(2)
O6	N6	C3	113.7(3)
O7	N6	O6	129.5(4)
O7	N6	C3	116.8(4)
N2	C1	N1	128.0(3)
N3	C1	N1	116.7(3)
N3	C1	N2	115.3(3)
O1	C2	C3	117.9(3)
N2	C2	O1	115.4(3)
N2	C2	C3	126.4(3)
N5	C3	N4	104.7(3)

Atom	Atom	Atom	Angle/°
N5	C3	N6	108.3(2)
N6	C3	N4	107.4(3)
C2	C3	N4	115.8(3)
C2	C3	N5	111.0(2)
C2	C3	N6	109.3(3)
C2A	O1A	N11	105.3(2)
N1A[2]	N1A	C1A	111.3(3)
C2A	N2A	C1A	100.6(2)
O2A	N3A	O3A	131.0(3)
O2A	N3A	C3A	114.4(3)
O3A	N3A	C3A	114.6(3)
O4A	N4A	O5A	128.3(3)
O4A	N4A	C3A	115.7(3)
O5A	N4A	C3A	115.8(3)
O6A	N5A	O7A	130.4(3)
O6A	N5A	C3A	117.3(3)
O7A	N5A	C3A	112.2(3)
C1A	N11	O1A	103.0(2)
N2A	C1A	N1A	127.9(3)
N11	C1A	N1A	116.3(3)
N11	C1A	N2A	115.7(3)
O1A	C2A	C3A	118.7(2)
N2A	C2A	O1A	115.4(3)
N2A	C2A	C3A	125.7(3)
N4A	C3A	N3A	108.0(3)
N4A	C3A	N5A	106.3(2)
N5A	C3A	N3A	107.2(2)
C2A	C3A	N3A	109.4(2)
C2A	C3A	N4A	116.1(2)
C2A	C3A	N5A	109.5(2)

---- [1]-x,1-y,1-z; [2]1-x,-y,1-z

Table S7: Torsion Angles in ° for **14**.

Atom	Atom	Atom	Atom	Angle/°
O1	N3	C1	N1	178.5(2)
O1	N3	C1	N2	-1.0(3)
O1	C2	C3	N4	45.0(4)
O1	C2	C3	N5	164.2(2)
O1	C2	C3	N6	-76.4(3)
O2	N4	C3	N5	-156.6(4)
O2	N4	C3	N6	88.4(4)
O2	N4	C3	C2	-34.0(5)
O3	N4	C3	N5	24.2(4)
O3	N4	C3	N6	-90.8(4)
O3	N4	C3	C2	146.7(3)
O4	N5	C3	N4	71.5(3)
O4	N5	C3	N6	-174.1(3)
O4	N5	C3	C2	-54.1(3)
O5	N5	C3	N4	-105.5(3)
O5	N5	C3	N6	8.9(4)
O5	N5	C3	C2	128.9(3)
O6	N6	C3	N4	-177.2(3)

Atom	Atom	Atom	Atom	Angle/°
O6	N6	C3	N5	70.2(3)
O6	N6	C3	C2	-50.8(4)
O7	N6	C3	N4	1.9(4)
O7	N6	C3	N5	-110.7(3)
O7	N6	C3	C2	128.3(3)
N1[1]	N1	C1	N2	5.2(5)
N1[1]	N1	C1	N3	-174.1(3)
N2	C2	C3	N4	-141.7(3)
N2	C2	C3	N5	-22.5(4)
N2	C2	C3	N6	96.9(4)
N3	O1	C2	N2	0.2(3)
N3	O1	C2	C3	174.3(3)
C1	N2	C2	O1	-0.8(3)
C1	N2	C2	C3	-174.2(3)
C2	O1	N3	C1	0.4(3)
C2	N2	C1	N1	-178.3(3)
C2	N2	C1	N3	1.1(3)
O1A	N11	C1A	N1A	178.0(2)
O1A	N11	C1A	N2A	-1.0(3)
O1A	C2A	C3A	N3A	-76.8(3)
O1A	C2A	C3A	N4A	45.7(4)
O1A	C2A	C3A	N5A	166.1(2)
O2A	N3A	C3A	N4A	-169.1(3)
O2A	N3A	C3A	N5A	76.8(3)
O2A	N3A	C3A	C2A	-41.8(4)
O3A	N3A	C3A	N4A	11.1(4)
O3A	N3A	C3A	N5A	-103.0(3)
O3A	N3A	C3A	C2A	138.3(3)
O4A	N4A	C3A	N3A	86.0(4)
O4A	N4A	C3A	N5A	-159.3(3)
O4A	N4A	C3A	C2A	-37.2(4)
O5A	N4A	C3A	N3A	-89.9(3)
O5A	N4A	C3A	N5A	24.8(4)
O5A	N4A	C3A	C2A	146.9(3)
O6A	N5A	C3A	N3A	4.7(4)
O6A	N5A	C3A	N4A	-110.5(3)
O6A	N5A	C3A	C2A	123.3(3)
O7A	N5A	C3A	N3A	-178.7(3)
O7A	N5A	C3A	N4A	66.0(3)
O7A	N5A	C3A	C2A	-60.2(3)
N1A[2]	N1A	C1A	N2A	4.3(5)
N1A[2]	N1A	C1A	N11	-174.6(3)
N2A	C2A	C3A	N3A	98.3(3)
N2A	C2A	C3A	N4A	-139.2(3)
N2A	C2A	C3A	N5A	-18.8(4)
N11	O1A	C2A	N2A	-0.1(3)
N11	O1A	C2A	C3A	175.4(2)
C1A	N2A	C2A	O1A	-0.4(3)
C1A	N2A	C2A	C3A	-175.7(3)
C2A	O1A	N11	C1A	0.7(3)
C2A	N2A	C1A	N1A	-178.0(3)
C2A	N2A	C1A	N11	1.0(3)

––––[1]-x,1-y,1-z; [2]1-x,-y,1-z

4. NMR and FTIR Spectroscopy

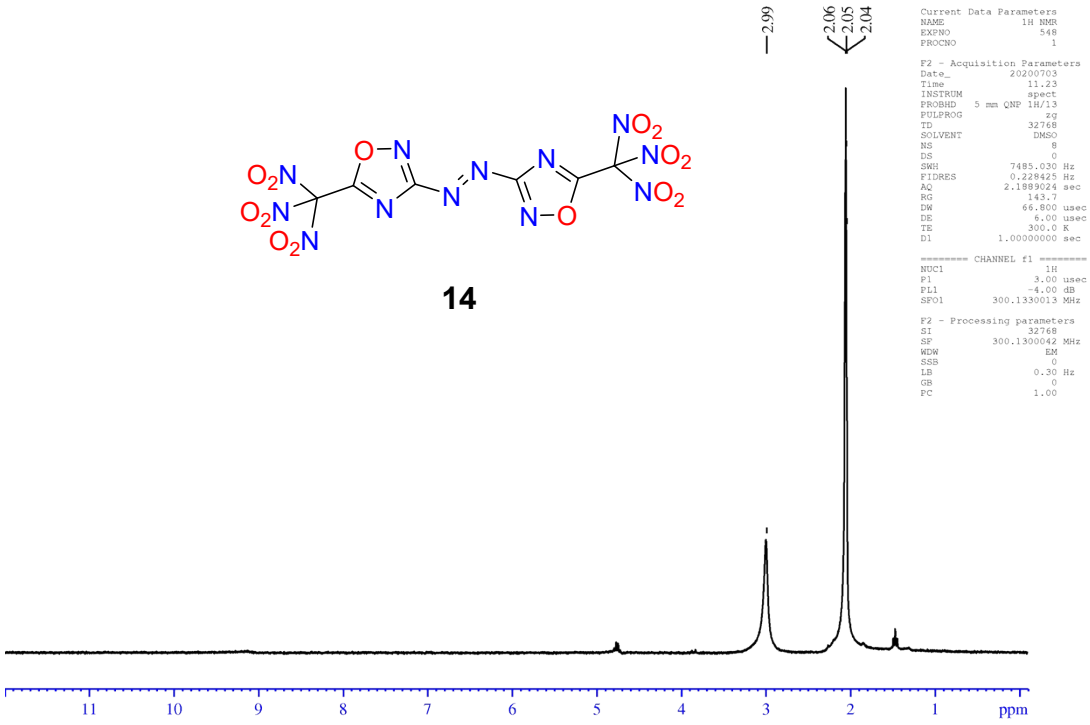

Figure S3. ^{1}H NMR spectrum of **14** in acetone-d_6

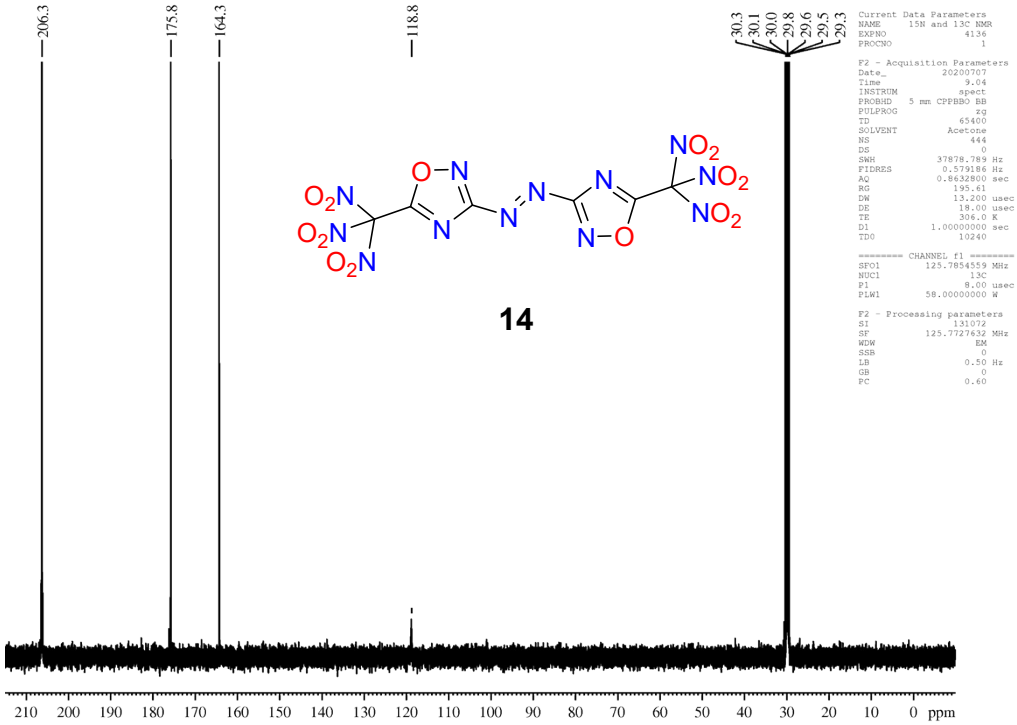

Figure S4. ^{13}C NMR spectrum of **14** in acetone-d_6

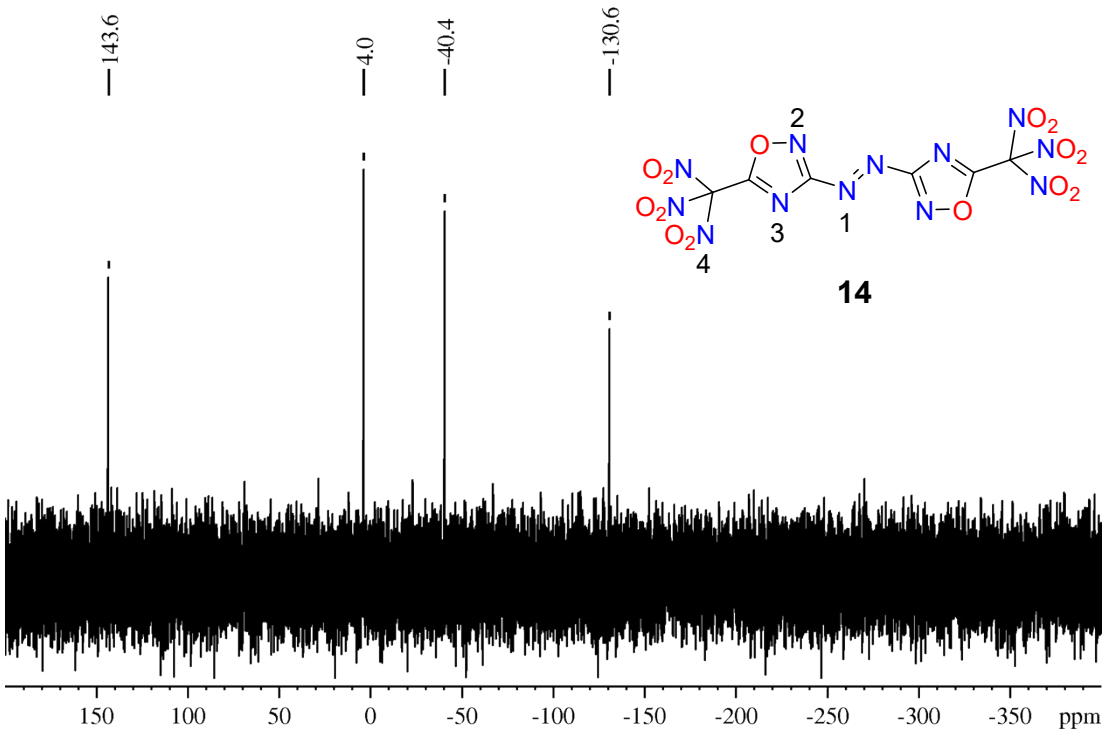

Figure S5. ^{15}N NMR spectrum of **14** in acetone-d_6

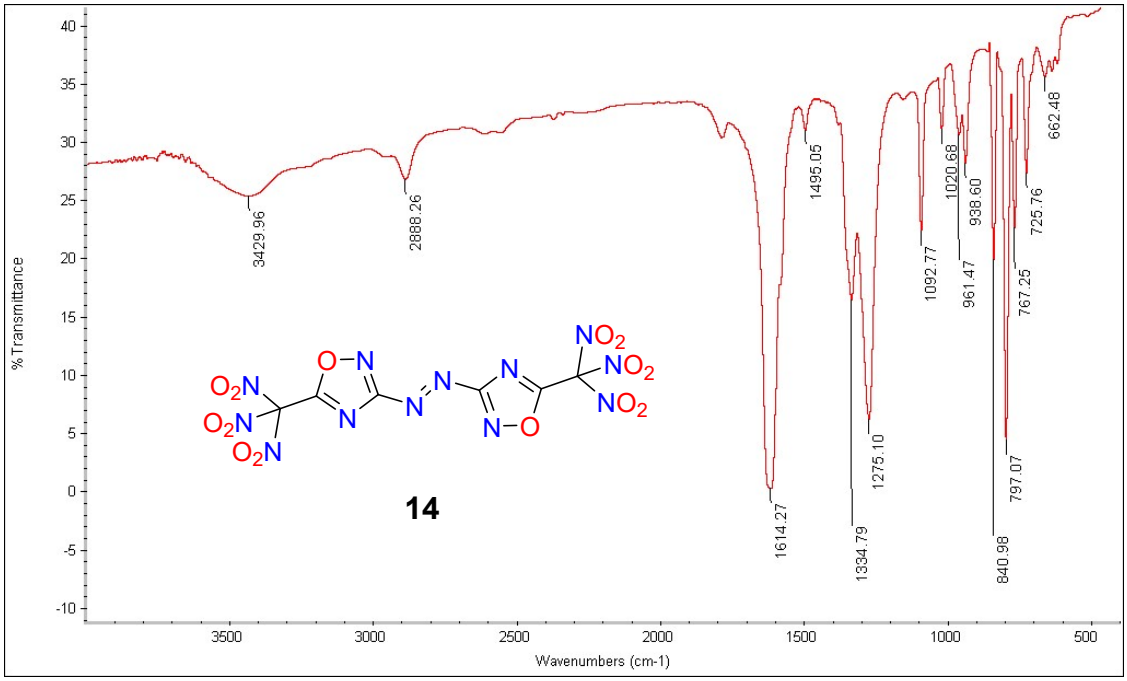

Figure S6. FTIR spectra of **14**

5. DSC Plots

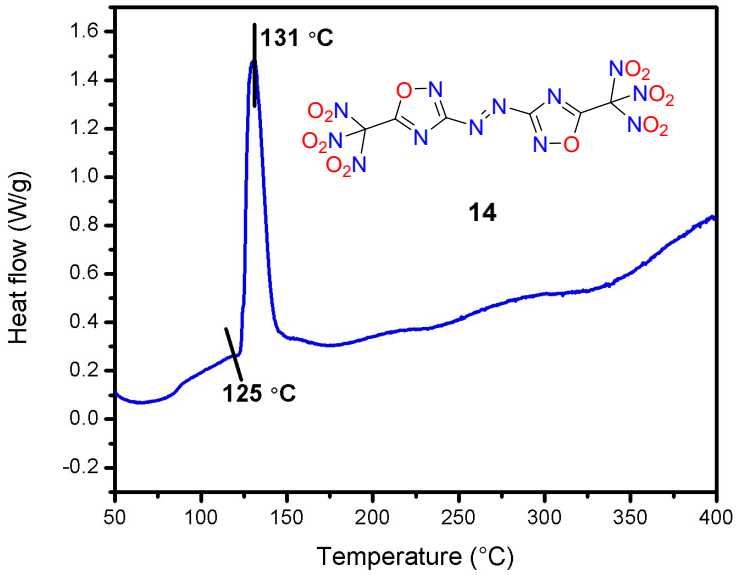

Figure S7. DSC thermogram of **14** at 5 °C per minute

Hydrolytic Stability of compound 14 in water. The stability of compound **14** in water was determined and the results are shown in the Figures S8-S10. Compound **14** (50 mg) was added to water (2.0 mL) and kept at room temperature until the water evaporated. Since compound **14** is insoluble in water, it doesn't hydrolyze to the carbonyl compound **14·Oxo**·or any other side products. After the evaporation of water, a yellow solid product was collected and its thermostability was determined using DSC at the heating rate of 10 °C per minute. The DSC thermograms of pure compound **14** (Figure S9) and that of the yellow solid **14** from water (Figure S10) are almost identical.

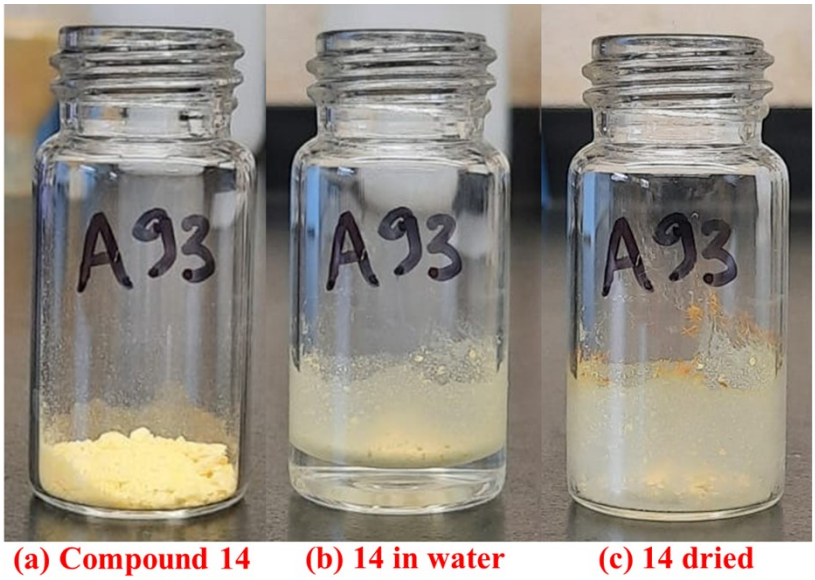

Figure S8. Stability test in water (a) Pure compound **14**; (b) Compound **14** in water; (c) Compound **14** after evaporation of water.

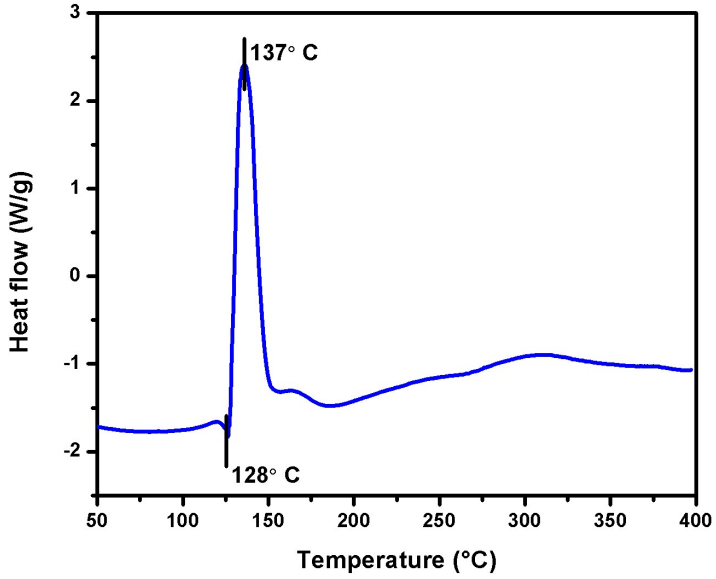

Figure S9. DSC thermogram of pure compound **14**·at 10 °C per minute

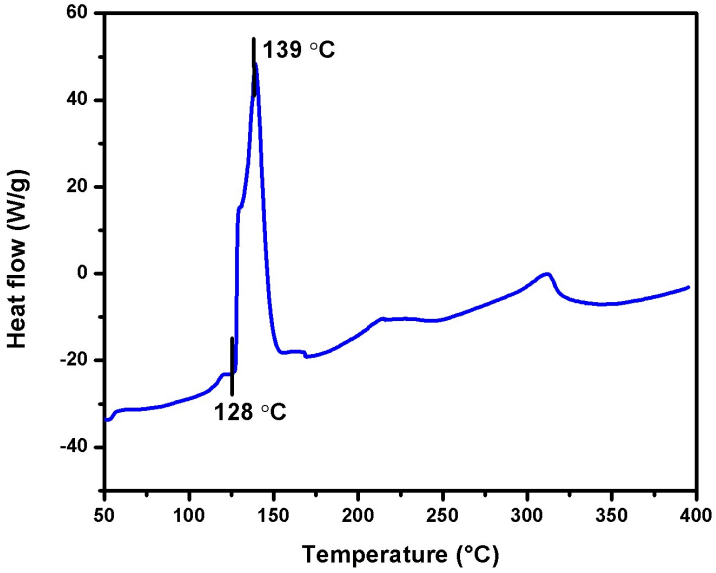

Figure S10. DSC thermogram of **14**·(after drying from water) at 10 °C per minute