Supporting Information

Synthetic and thermal studies of insensitive energetic materials based on oxidation of melamine structure

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Crystallographic data

The apparatus and conditions of crystal structure determination

A single crystal of MDO·4H_2O suitable for X-ray diffraction analysis was prepared by slow evaporation of H_2O solvent at room temperature. A colorless crystal with dimension of 0.34×0.26×0.15 mm was selected for X-ray single crystal diffraction analysis. The diffraction data were collected on a BRUKER SMART Apex Ⅱ CCD X-ray diffractometer equipped with a Mo *K*α radiation (λ=0.71073 A) using an *ω*-*θ* scan mode at 153(2) K. A total of 10161 reflections were obtained in the range of 3.19≤θ≤25.09◦ , of which 1764 were independent (*R* int =0.0280) were considered to be observed and used for the refinement. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using SHELES-97 and SHELXL-97 programs. A full-matrix least-squares refinement gave the final R_1= 0.0297 and ωR_2= 0.0796(ω=1/[$\sigma^2(F_0^2)$ + (0.0270 P)^2 + 0.0000 P], where P =(F_0^2+2F_c^2)/3). The goodness-of-fit on F^2 is 1.058. The largest difference peak and hole were 0.252 and -0.191 e/Å^3

Table S1. Crystal data and structure refinement parameters for MDO·4H_2O

Compound	MDO·4H_2O
Empirical formula	$C_3H_{14}N_6O_6$
Molar mass (g/mol)	230.20
Temperature (K)	153(2)
Crystal system	Monoclinic
Space group	*P*2(1)/n
Crystal size (mm)	0.34 x 0.26 x 0.15
a (Å)	8.923(2)
b (Å)	6.9505(18)
c (Å)	16.162(4)
α (◦)	114.227(6)
β (◦)	94.259(9)

γ (◦)	107.386(6)
V (Å ^{3})	999.6(4)
Z	4
h	-10<= h <=10
k	-8<= k <=8
l	-19<= l <=19
Dc (g/cm^3)	1.530
λ (Å)	0.71073
μ (Mo K) (mm^{-1})	0.142
F(0 0 0)	488
θ range (◦)	3.19-25.09
Measured reflections	10161
Unique data (Rint)	1764 (0.0280)
R1, wR2 [$I > 2\sigma(I)$]	0.0297,0.0796
R1, wR2 (all data)	0.0313, 0.0810
Goodness-of-fit	1.058
δpmax, δpmin (e/ Å^3)	0.252, -0.191
CCDC number	1947761

Table S2. Selected bond lengths (Å) and bong angles (°) of MDO·4H_2O.

Bond	Dist.	Bond	Dist.
N(1)-C(1)	1.2993(16)	N(1)-H(1A)	0.8800
N(1)-H(1B)	0.8800	N(2)-O(1)	1.3516(13)
N(2)-C(1)	1.3558(16)	N(2)-C(2)	1.3651(16)
N(3)-C(2)	1.3218(16)	N(3)-H(3A)	0.8800
N(3)-H(3B)	0.8800	N(4)-C(2)	1.3343(16)
N(4)-C(3)	1.3414(16)	N(5)-C(3)	1.3120(16)
N(5)-H(5A)	0.8800	N(5)-H(5B)	0.8800
N(6)-C(1)	1.3516(16)	N(6)-O(2)	1.3622(13)
N(6)-C(3)	1.3682(16)	O(3)-H(3C)	0.828(9)
O(3)-H(3D)	0.827(9)	O(4)-H(4C)	0.820(10)
O(4)-H(4D)	0.829(10)	O(5)-H(5C)	0.833(9)
O(5)-H(5D)	0.834(10)	O(6)-H(6C)	0.823(10)

O(6)-H(6D)	0.841(9)		
Angle	(°)	Angle	(°)
C(1)-N(1)-H(1A)	120.0	C(1)-N(1)-H(1B)	120.0
H(1A)-N(1)-H(1B)	120.0	O(1)-N(2)-C(1)	118.36(10)
O(1)-N(2)-C(2)	120.35(10)	C(1)-N(2)-C(2)	121.29(10)
C(2)-N(3)-H(3A)	120.0	C(2)-N(3)-H(3B)	120.0
H(3A)-N(3)-H(3B)	120.0	C(2)-N(4)-C(3)	118.03(10)
C(3)-N(5)-H(5A)	120.0	C(3)-N(5)-H(5B)	120.0
H(5A)-N(5)-H(5B)	120.0	C(1)-N(6)-O(2)	118.44(10)
C(1)-N(6)-C(3)	120.34(10)	O(2)-N(6)-C(3)	121.13(10)
H(3C)-O(3)-H(3D)	107.6(19)	H(4C)-O(4)-H(4D)	108.7(19)
H(5C)-O(5)-H(5D)	102.3(19)	H(6C)-O(6)-H(6D)	107(2)
N(1)-C(1)-N(6)	121.22(11)	N(1)-C(1)-N(2)	121.31(11)
N(6)-C(1)-N(2)	117.47(11)	N(3)-C(2)-N(4)	122.28(11)
N(3)-C(2)-N(2)	116.73(11)	N(4)-C(2)-N(2)	121.00(11)
N(5)-C(3)-N(4)	22.03(11)	N(5)-C(3)-N(6)	116.22(11)
N(4)-C(3)-N(6)	121.74(11)		

Table S3. Hydrogen bond lengths (Å) and bong angles (°) of MDO·4H_2O

D-H…A	d(D-H) (Å)	d(H…A) (Å)	d(D…A) (Å)	∠DHA(°)
N1-H1A…O5	0.880	1.969	2.792	155.01
N1-H1B…O4	0.880	2.059	2.844	148.17
N3-H3A…O4	0.880	2.085	2.890	151.76
N3-H3B…O3	0.880	2.210	3.043	157.62
N5-H5A…O6	0.880	1.989	2.822	157.42
N5-H5B…O2	0.880	2.076	2.850	146.37
O3-H3C…O2	0.828	1.989	2.815	175.77
O4-H4C…O3	0.820	2.070	2.879	169.22
O5-H5C…O1	0.833	1.775	2.601	170.94
O5-H5C…N2	0.833	2.614	3.410	160.50
O6-H6C…O5	0.823	1.977	2.781	165.43
O3-H3D…O6	0.826	2.010	2.810	163.05
O4-H4D…O2	0.829	1.955	2.779	171.90
O4-H4D…N6	0.829	2.628	3.319	141.72

O5-H5D…N4	0.834	2.196	2.975	155.31
O6-H6D…O1	0.841	1.839	2.675	172.21

X-Ray crystal structure

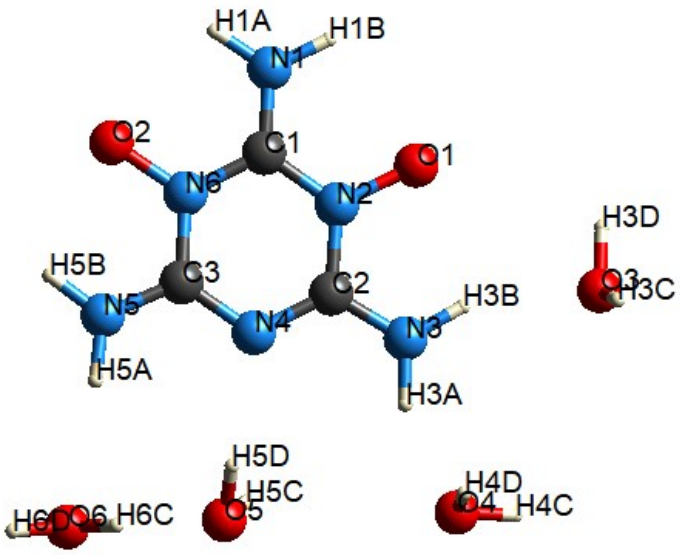

Figure S1. The molecular structure of MDO.

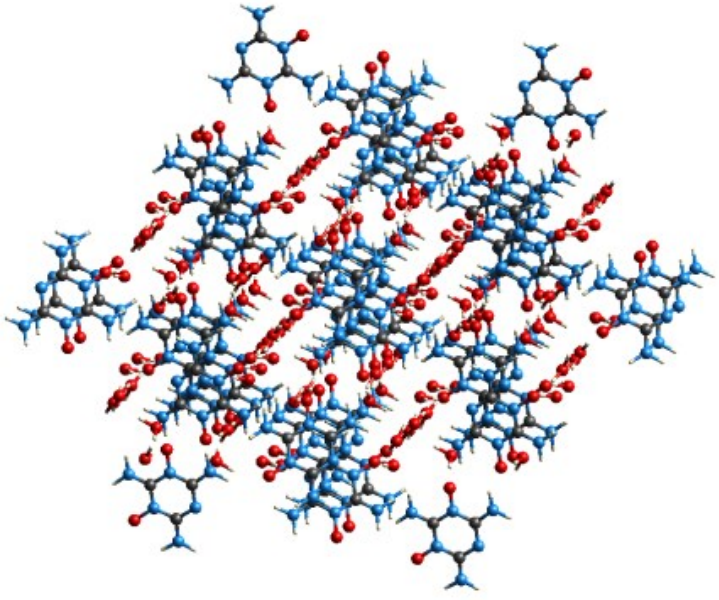

Figure S2. The packing diagram of MDO.

NMR spectra

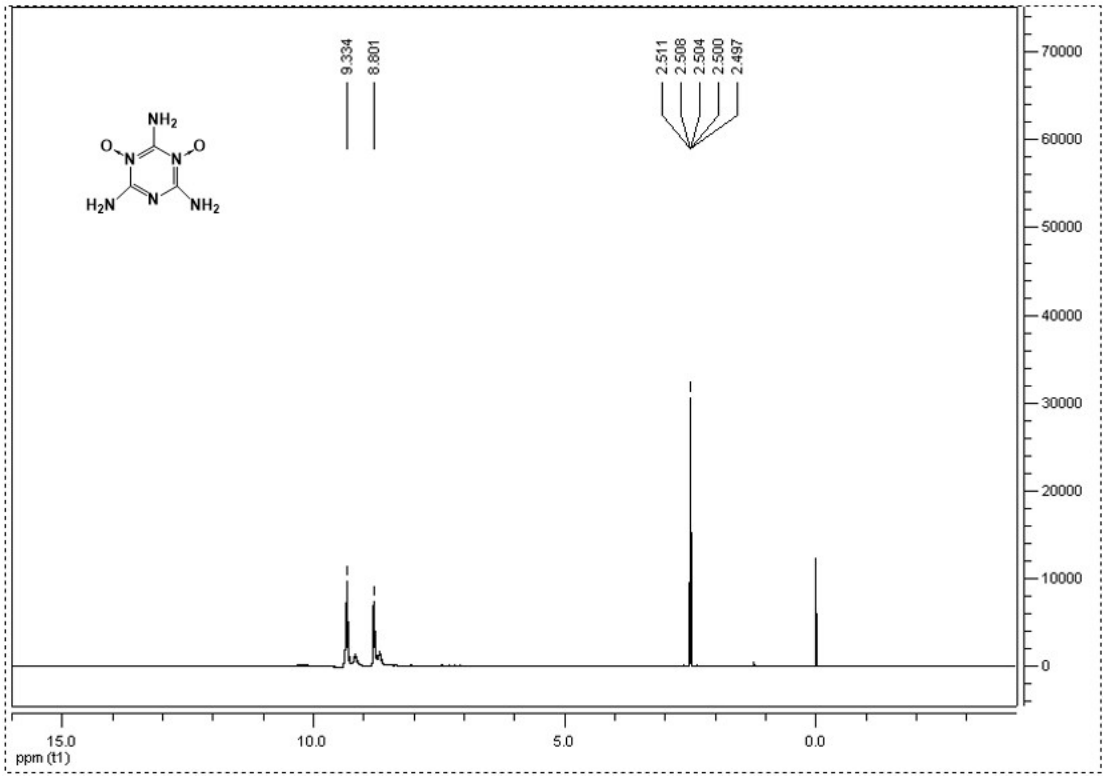

Figure S3. ^{1}H NMR spectrum of MDO.

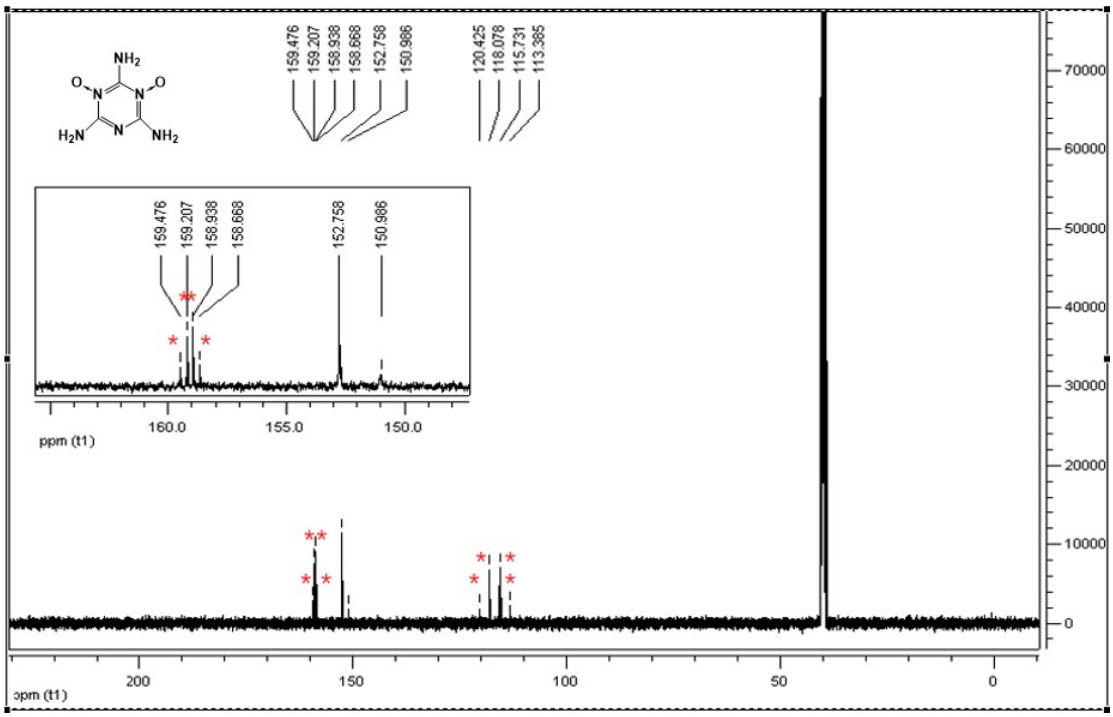

Figure S4. ^{13}C NMR spectrum of MDO (* is residual trifluoroacetic acid solvent peak).

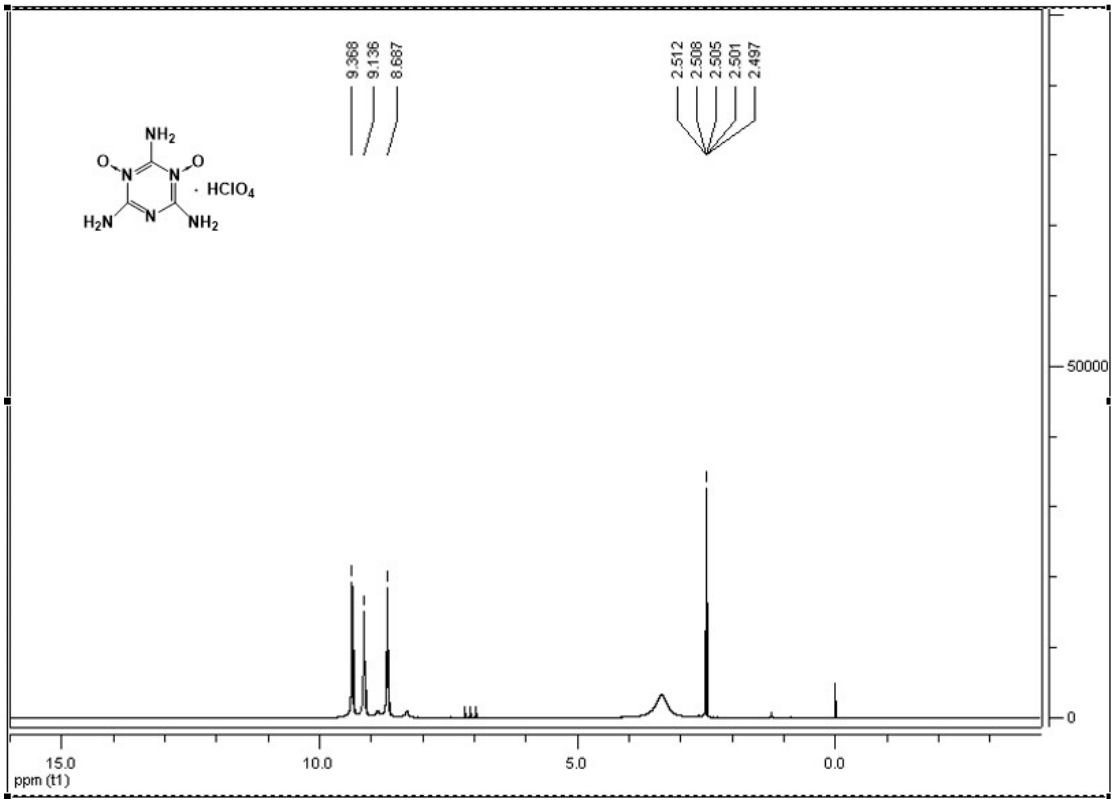

Figure S5. ^{1}H NMR spectrum of MDOP.

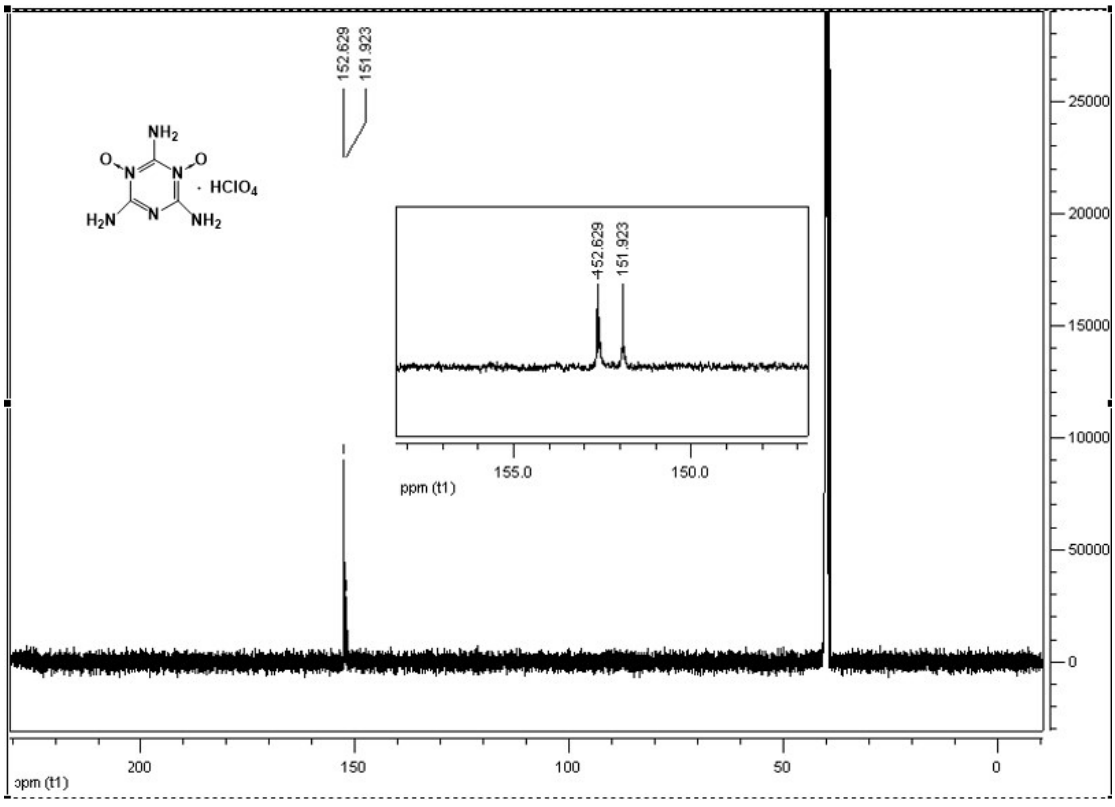

Figure S6. ^{13}C NMR spectrum of MDOP.

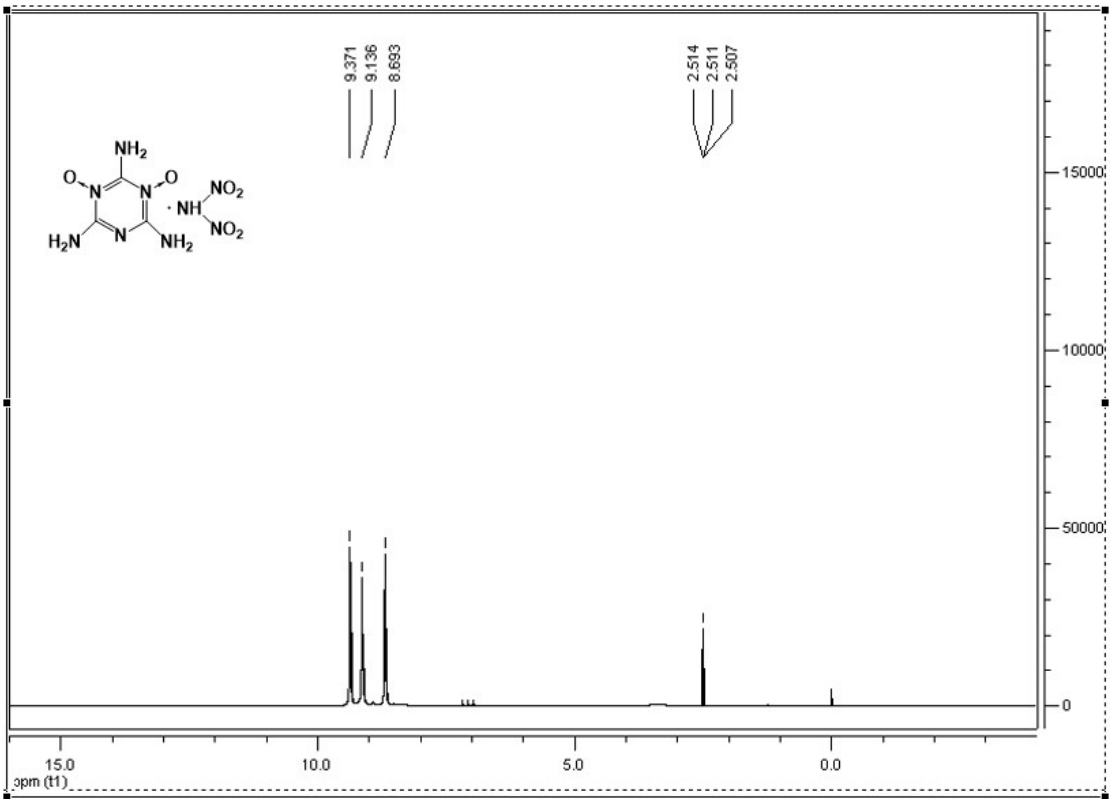

Figure S7. ^{1}H NMR spectrum of MDODA.

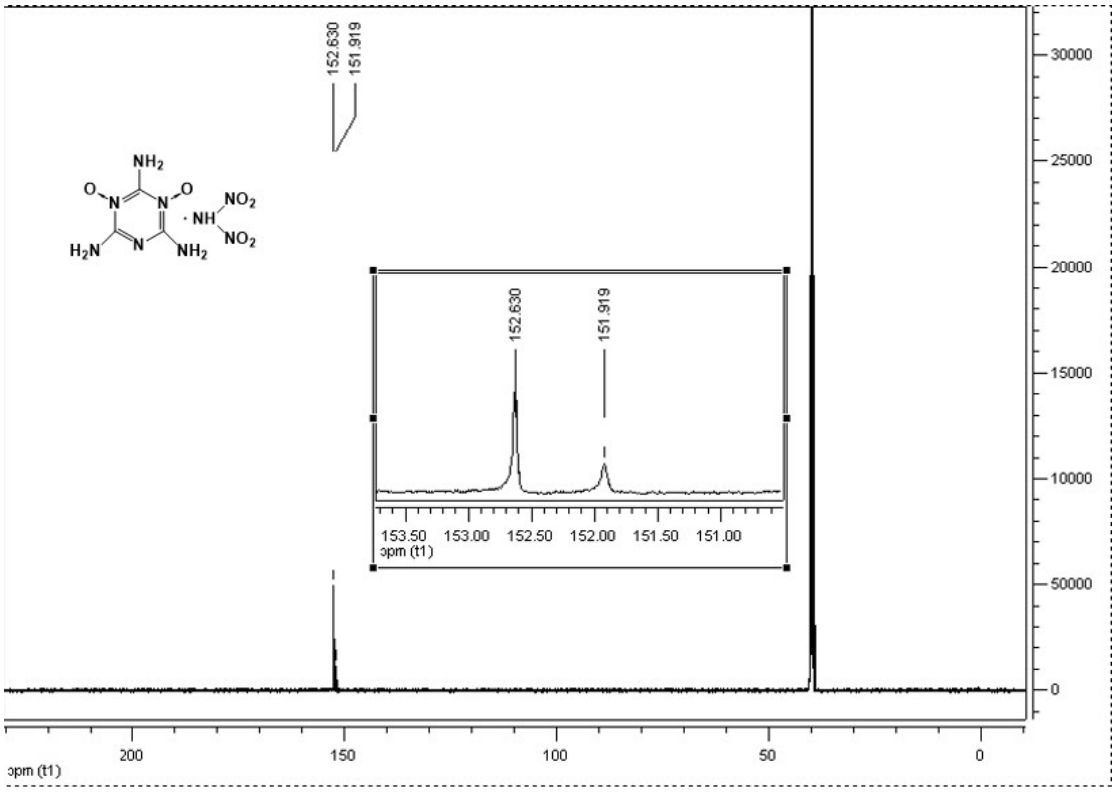

Figure S8. ^{13}C NMR spectrum of MDODA.

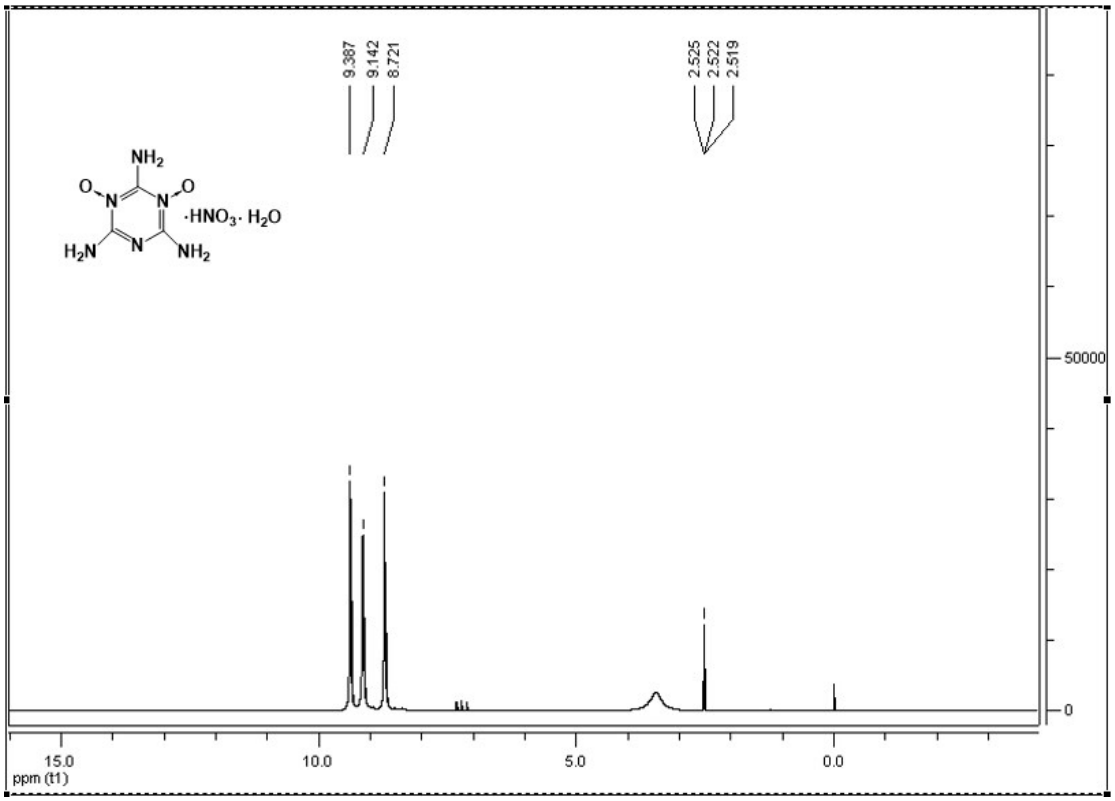

Figure S9. ^{1}H NMR spectrum of MDOMN.

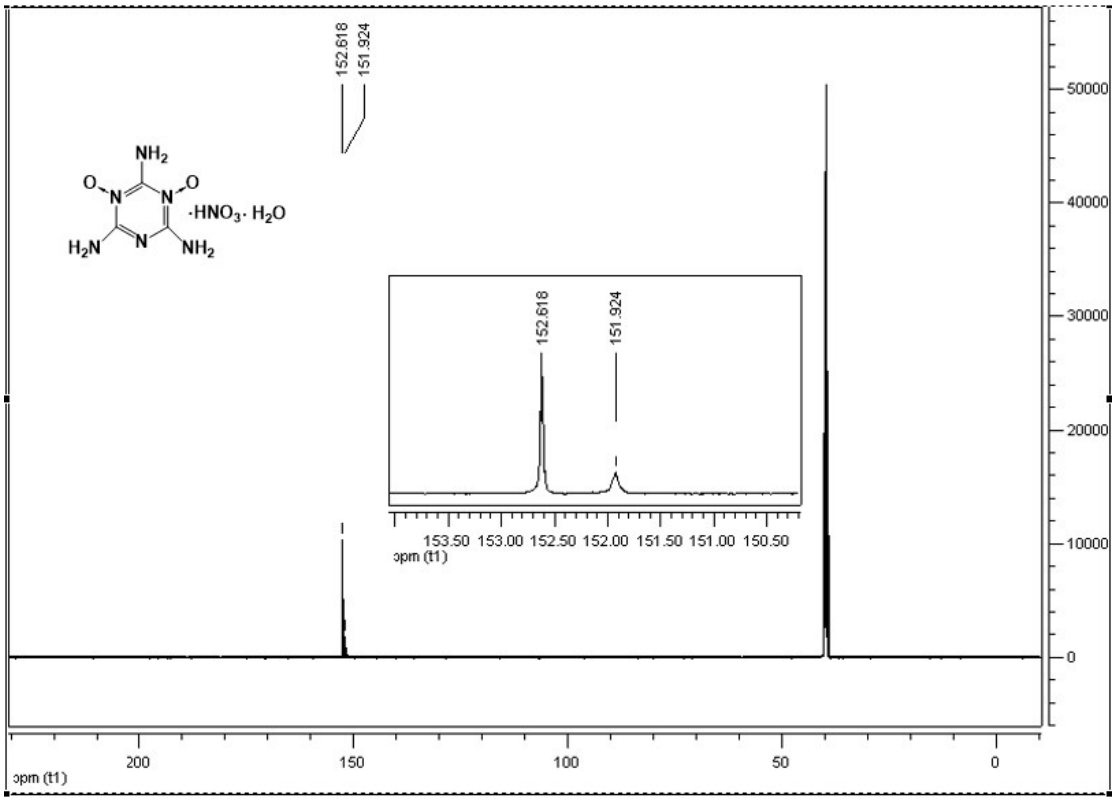

Figure S10. ^{13}C NMR spectrum of MDOMN.

IR spectra

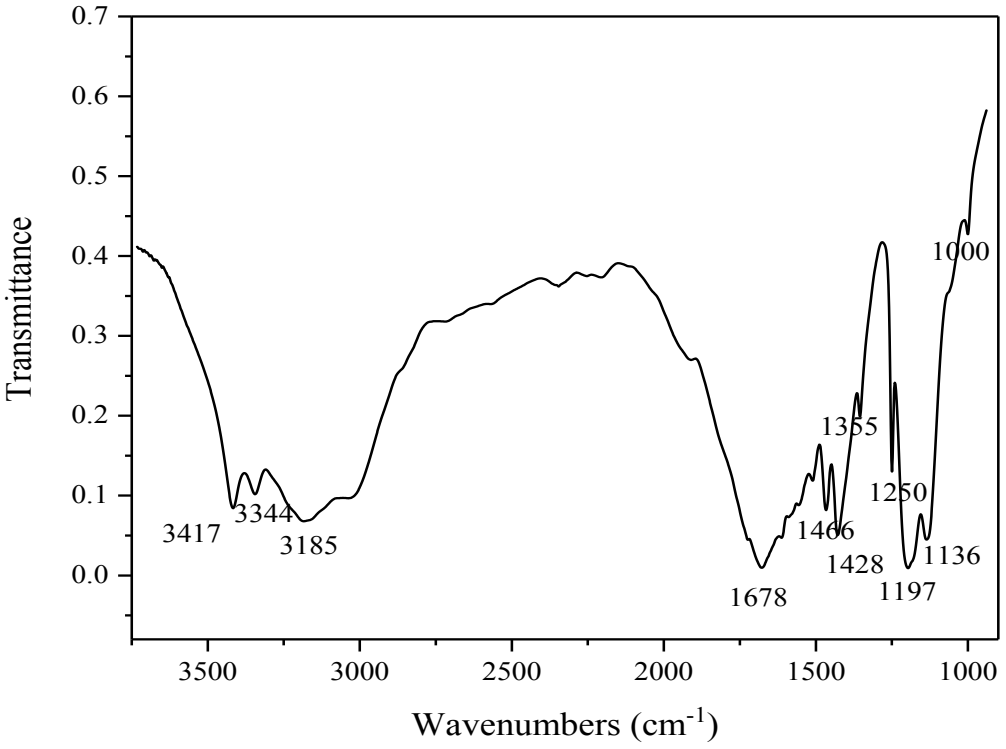

Figure S11. IR spectrum of MDO.

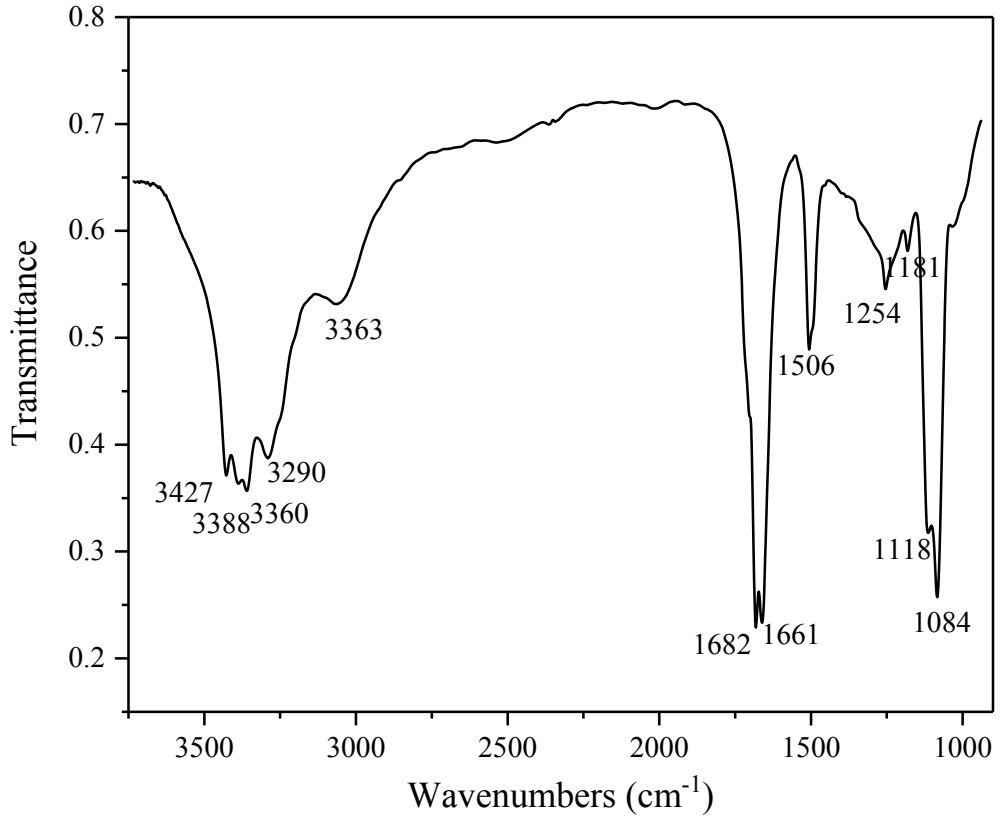

Figure S12. IR spectrum of MDOP.

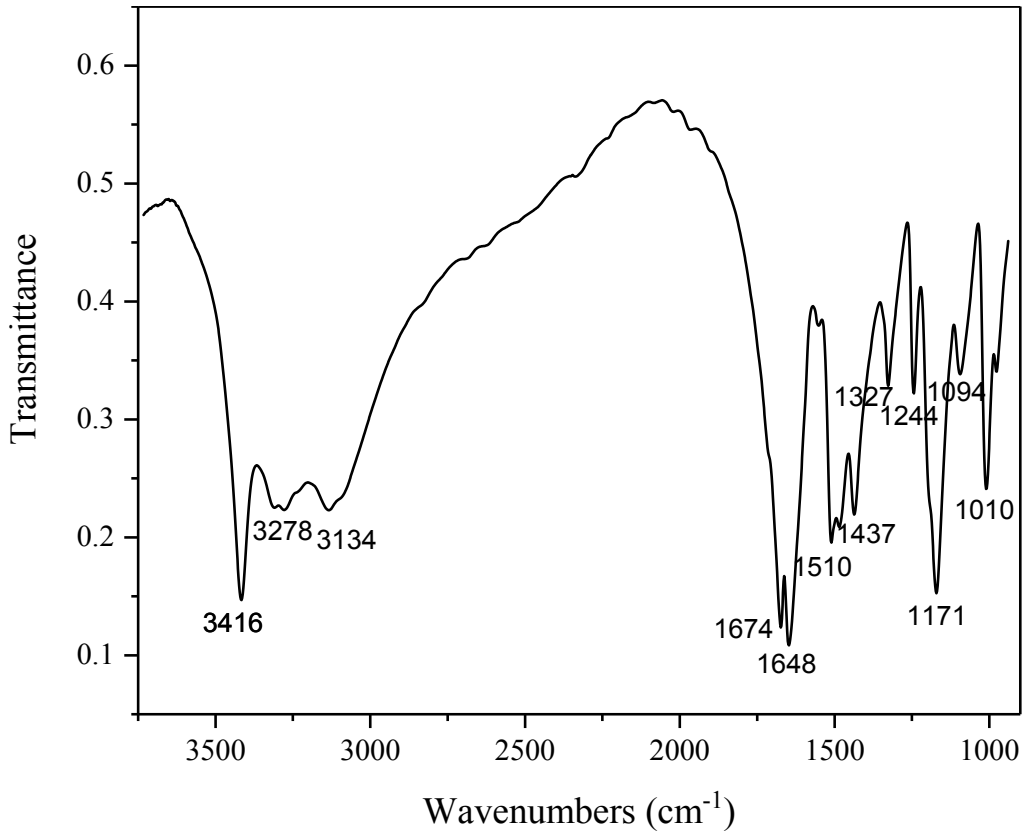

Figure S13. IR spectrum of MDODA.

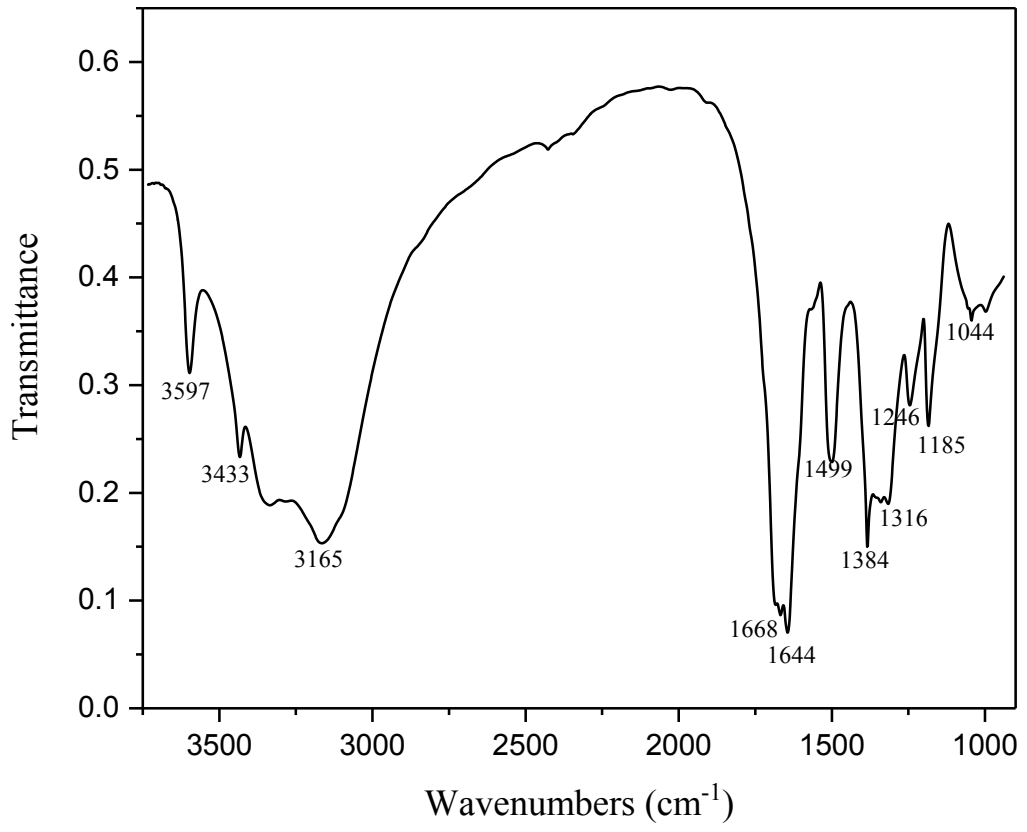

Figure S14. IR spectrum of MDOMN.

Samples images

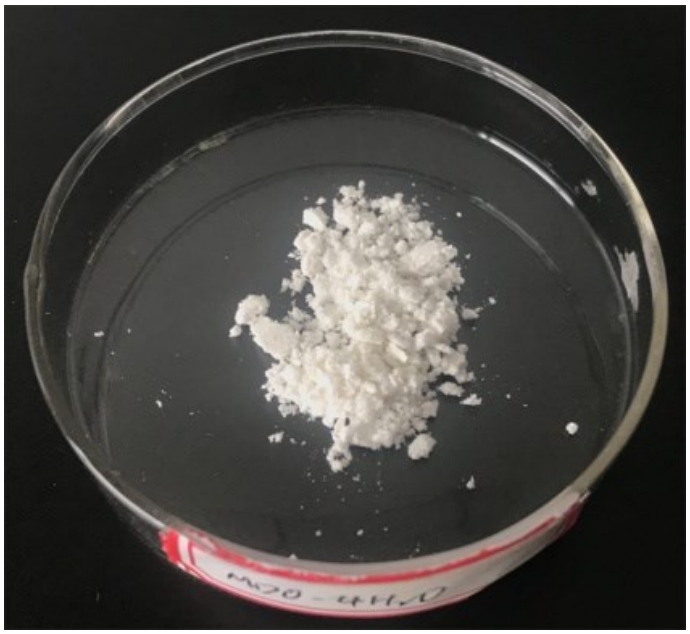

Figure S15. MDO sample.

Figure S16. MDO crystal sample.