Electronic Supplementary Information

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1. Experimental Materials and methodology

4-Chlorobenzoic acid, oleum 65% (>98%), fuming nitric acid 100% (>98%), concentrated sulfuric acid 98% (>98%), sodium azide (>98%), chloroform, acetone. All the materials and chemical reagents with analytical grade were bought from the reagents company (Aladdin) and used without further purification. The IR spectra were recorded on a Bruker Equinox 55 infrared spectrometer using KBr pellets from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. ^1H NMR spectra was measured at 400 MHz (Bruker Advance III 400 HD) with DMSO-d_6 as the solvent. ^{13}C NMR spectra were measured at 400 MHz (Bruker Biospin AG) with DMSO-d_6 as the solvent. Elemental analyses (C, H and N) were performed on a Flash EA 1112 fully automatic trace element analyzer. The single crystal X-ray diffraction data collections were carried out on a Rigaku AFC-10/Saturn 724+CCD diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073 Å) using the multi-scan technique. The structures were determined by direct methods using SHELXS-97[1] and refined by full-matrix least-squares procedures on F_2 with SHELXL-97.[2] Thermal stability measurements were performed/tested/analyzed by using differential scanning calorimetry (DSC) on a CDR-4 of Shanghai Precision & Scientific Instrument Co., Ltd. at a heating rate of 5°C/min from 50°C to 500°C.

2. Synthesis

During the syntheses and characterization of these materials, proper protective measures should be used although you are very experienced. Face shield and leather gloves must be worn. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials. Mechanical actions involving scratching or scraping must be avoided.[3]

1,1'-dichloro-2,2',3,3',6,6'-hexanitro-5,5'-dihydroxyazobenzene (1)

For the synthesis of **1** three stages were used, 4-chlorobenzoic acid was nitrated with mixed acid and then reacted with NaN_3 in oleum to obtain 4-chloro-3,5-dinitroaniline.

Concentrated sulfuric acid (230.0 mL) was transferred to a 1000 mL three-necked round-bottomed flask with a mechanical stirrer, and then drop-wise addition of 15 mL fuming nitric acid with occasional swirling in the environment of ice-water bath. Shortly after, 4-chloro-3,5-dinitroaniline(10.00 g, 45.97mmol) was slowly added to this nitrating mixture while maintaining the same temperature. The temperature was slowly raised to 90 °C (takes approximately 1 hour) and maintained for 2.5 h. The reaction mixture was subsequently cooled to ambient temperature and poured into the crushed-ice. A light yellow product was obtained, filtered and washed with distilled water. It was then dried 11.40 g (~90%) and with a DSC exothermic decomposition temperature of 336.0 °C. The yellow crystal of **1** was obtained by slow evaporation of acetone solution at room temperature. IR (KBr):2887, 2667, 2341, 2175, 1575, 1560, 1398, 1336, 1243, 1172cm^{-1}. $C_{12}H_2N_8O_{14}Cl_2$ Calcd: C-26.03, N-20.30, H-0.36%; found: C-23.24, N-21.03, H$<$0.3%, ^1H NMR (400 MHz, DMSO): δ=6.36 (d, 105 H).

8-(2,4,6-triazido-3,5-dinitrophenyl)-8H-[1,2,3]triazolo[4',5':5,6]benzo[1,2-c:3,4-

c']bis([1,2,5]oxadiazole) 1,4-dioxide (2)

In a 100 mL three-necked round-bottomed flask fitted with a reflux condenser and **1** (1.0 g, 1.8 mmol) was pulverized and followed by addition of 20 mL of acetic acid. Then NaN_3 (0.8 g, 12.3 mmol) was slowly added to this solution at ambient temperature. The slurry was stirred slowly for 20 min and then slowly heated to 80 °C. The slurry was stirred for another 1 h to complete the reaction. The aqua compound was filtered and washed with water and dried 0.75 g (~80%). Compound **2** is obtained as a yellow solid. The kelly green crystalline of **2** was obtained by slow evaporation of acetic acid solution at room temperature. IR (KBr):3475, 2345, 2136, 1681, 1587, 1521, 1440, 1355, 1261, 1128, 979, 763 cm^{-1}. $C_{12}N_{18}O_8$ Calcd: C 27.47, N 48.06, H 0%; found: C 27.32, N 48.25%.

3. X-ray crystallography determinations

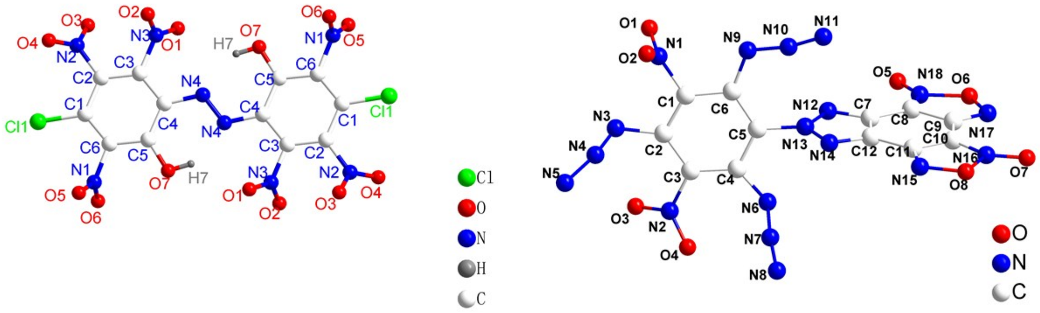


Figure S1. (Left) Molecule structure of compound **1.** (Right) Molecule structure of compound **2**.

X-ray crystallographic files in CIF format for compounds **1** and **2**; structure refinements; selected bond lengths, angles, dihedral angles; hydrogen-bonding details. Meanwhile the experimentally determined densities of **1** and **2** are 1.933 g/cm^3 and 1.877 g/cm^3, which fall in the range designated for new HEDMs (1.8–2.0 g/cm^3).

Table S1. Crystal data and structure refinement details of compounds **1** and **2**.

Item	**1**	**2**
CCDC	1849891	1849892
Empirical formula	$C_{12}H_2N_8O_{14}Cl_2$	$C_{12}N_{18}O_8$
Formula mass	553.12	524.30
Temperature/K	153.15	153.15
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	Pbca
a[Å]	11.430(2)	9.3869(19)
b[Å]	5.4511(11)	15.742(3)
c[Å]	15.427(3)	25.114(5)
β[°]	98.60(3)	90
Volume/Å^3	950.4(3)	3711.1(13)
Z	2	8

Density/g/cm^3	1.933	1.877
μ/1/mm	0.443	0.162
F(000)	552.0	2096.0
Crystal size/mm^3	0.12 × 0.08 × 0.03	0.18 × 0.16 × 0.02
Radiation/Å	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.878 to 54.962	5.306 to 49.996
Index ranges	$-14 \le h \le 14, -7 \le k \le 6, -20 \le l \le 18$	$-11 \le h \le 10, -14 \le k \le 18, -29 \le l \le 20$
Reflections collected	6277	11768
Independent reflections	2129 [R_{int} = 0.0386, R_{sigma} = 0.0439]	3240 [R_{int} = 0.0752, R_{sigma} = 0.0696]
Data/restraints/parameters	2129/0/163	3240/0/343
Goodness-of-fit on F^2	1.197	1.284
Final R indexes [I>=2σ (I)]	R_1 = 0.0978, wR_2 = 0.2058	R_1 = 0.1082, wR_2 = 0.1811
Final R indexes (all data)	R_1 = 0.1100, wR_2 = 0.2146	R_1 = 0.1278, wR_2 = 0.1893
Largest diff. peak/hole/e/Å^3	0.46/-0.46	0.32/-0.41

Table S2 Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2×10^3) of compound **1**

Atom	x	y	z	U(eq)
Cl1	8961.2(11)	896(3)	2629.0(8)	46.3(4)
O1	6876(4)	-5013(8)	5291(3)	57.7(11)
O2	8314(4)	-2719(9)	5888(3)	67.1(13)
O3	9076(3)	-4893(8)	4237(3)	57.0(11)
O4	10188(3)	-1704(9)	4196(3)	64.5(12)
O5	7123(5)	5532(8)	2546(3)	76.7(16)
O6	6012(4)	2830(8)	1849(2)	63.7(13)
N1	6668(4)	3530(7)	2482(3)	38.6(9)
N2	9238(3)	-2685(8)	4166(3)	36.2(9)
N3	7528(3)	-3250(7)	5306(2)	34.9(9)
N4	5477(3)	-607(7)	5061(2)	29.6(8)
O7	5125(3)	3032(7)	3607(3)	50(1)
C1	7980(4)	543(9)	3345(3)	31.7(10)
C2	8176(4)	-1145(8)	4045(3)	30.0(9)
C3	7311(4)	-1493(8)	4569(3)	29.9(9)
C4	6257(4)	-163(8)	4459(3)	28.6(9)

C5	6067(4)	1557(8)	3767(3)	30.5(9)
C6	6929(4)	1817(8)	3230(3)	30.4(9)

Table S3 Anisotropic Displacement Parameters (Å$^2\times10^3$) of compound **1.** The Anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$

Atom	U11	U22	U33	U23	U13	U12
Cl1	49.3(7)	52.7(8)	40.1(7)	0.1(6)	17.2(5)	-1.0(6)
O1	61(3)	45(2)	66(3)	10(2)	7(2)	3(2)
O2	77(3)	69(3)	47(2)	9(2)	-16(2)	-2(2)
O3	51(2)	43(2)	70(3)	-14(2)	-13.2(19)	13.2(18)
O4	36(2)	79(3)	82(3)	23(3)	20.6(19)	8(2)
O5	100(4)	49(3)	69(3)	24(2)	-28(3)	-31(2)
O6	91(3)	52(3)	38(2)	2.7(19)	-24(2)	-7(2)
N1	43(2)	31(2)	40(2)	5.2(18)	0.5(17)	-0.1(17)
N2	30(2)	42(2)	35(2)	0.3(18)	1.1(15)	6.4(17)
N3	37(2)	32(2)	36(2)	1.7(17)	5.2(16)	6.8(17)
N4	25.7(16)	32(2)	30.0(18)	-1.3(15)	0.6(14)	1.7(14)
O7	41(2)	46(2)	63(2)	15.5(19)	9.0(17)	5.8(16)
C1	34(2)	33(2)	28(2)	-6.6(18)	4.8(17)	-2.6(18)
C2	28(2)	33(2)	28(2)	-3.5(18)	1.6(16)	4.1(17)
C3	33(2)	29(2)	27(2)	0.0(17)	0.8(16)	5.1(17)
C4	28(2)	30(2)	27(2)	-1.3(17)	0.8(15)	-1.0(17)
C5	29(2)	26(2)	35(2)	-0.3(18)	-2.2(17)	3.4(16)
C6	36(2)	26(2)	27(2)	3.7(17)	-1.0(17)	-0.7(18)

Table S4 Bond Lengths of compound **1**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C1	1.699(5)	N4	N41	1.266(7)
O1	N3	1.215(6)	N4	C4	1.402(6)
O2	N3	1.207(5)	O7	C5	1.337(5)
O3	N2	1.225(6)	C1	C2	1.411(6)
O4	N2	1.204(5)	C1	C6	1.375(6)
O5	N1	1.206(6)	C2	C3	1.381(6)
O6	N1	1.201(5)	C3	C4	1.395(6)
N1	C6	1.479(6)	C4	C5	1.412(6)
N2	C2	1.465(5)	C5	C6	1.386(6)

N3	C3	1.478(6)

Table S5 Bond Angles of compound **1**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O5	N1	C6	118.3(4)	C3	C2	N2	120.0(4)
O6	N1	O5	124.2(4)	C3	C2	C1	119.4(4)
O6	N1	C6	117.5(4)	C2	C3	N3	119.1(4)
O3	N2	C2	116.1(4)	C2	C3	C4	122.5(4)
O4	N2	O3	125.5(4)	C4	C3	N3	118.3(4)
O4	N2	C2	118.4(4)	N4	C4	C5	125.1(4)
O1	N3	C3	117.8(4)	C3	C4	N4	116.9(4)
O2	N3	O1	126.2(4)	C3	C4	C5	118.0(4)
O2	N3	C3	115.9(4)	O7	C5	C4	124.6(4)
N41	N4	C4	115.4(5)	O7	C5	C6	116.9(4)
C2	C1	Cl1	121.7(3)	C6	C5	C4	118.5(4)
C6	C1	Cl1	120.5(4)	C1	C6	N1	119.3(4)
C6	C1	C2	117.7(4)	C1	C6	C5	123.7(4)
C1	C2	N2	120.4(4)	C5	C6	N1	116.9(4)

Table S6 Torsion Angles of compound **1**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C1	C2	N2	-0.9(6)	N3	C3	C4	C5	178.5(4)
Cl1	C1	C2	C3	-175.2(3)	N41	N4	C4	C3	-179.3(5)
Cl1	C1	C6	N1	-0.9(6)	N41	N4	C4	C5	2.3(7)
Cl1	C1	C6	C5	177.5(4)	N4	C4	C5	O7	1.5(7)
O1	N3	C3	C2	-117.9(5)	N4	C4	C5	C6	179.1(4)
O1	N3	C3	C4	65.1(6)	O7	C5	C6	N1	-5.7(6)
O2	N3	C3	C2	65.2(6)	O7	C5	C6	C1	175.9(4)
O2	N3	C3	C4	-111.7(5)	C1	C2	C3	N3	-179.5(4)
O3	N2	C2	C1	-128.1(5)	C1	C2	C3	C4	-2.7(7)
O3	N2	C2	C3	46.1(6)	C2	C1	C6	N1	-177.5(4)
O4	N2	C2	C1	52.6(6)	C2	C1	C6	C5	0.9(7)
O4	N2	C2	C3	-133.1(5)	C2	C3	C4	N4	-177.0(4)

O5	N1	C6	C1	-79.3(6)	C2	C3	C4	C5	1.6(7)
O5	N1	C6	C5	102.2(6)	C3	C4	C5	O7	-176.9(4)
O6	N1	C6	C1	100.9(5)	C3	C4	C5	C6	0.6(6)
O6	N1	C6	C5	-77.7(6)	C4	C5	C6	N1	176.6(4)
N2	C2	C3	N3	6.2(6)	C4	C5	C6	C1	-1.9(7)
N2	C2	C3	C4	-176.9(4)	C6	C1	C2	N2	175.6(4)
N3	C3	C4	N4	-0.1(6)	C6	C1	C2	C3	1.4(6)

Table S7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) of compound **1**

Atom	x	y	z	U(eq)
H7	4661	2504	3938	60

Table S8 Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for compound **2**

Atom	x	y	z	U(eq)
O1	12682(4)	6059(3)	5499.0(18)	41.4(11)
O2	12204(4)	7351(3)	5275.5(18)	41.5(11)
O3	9209(5)	5107(3)	3817.1(17)	45.0(12)
O4	7123(5)	5667(3)	3886.2(17)	44.8(11)
O5	5709(4)	3856(3)	6986.6(19)	44.1(11)
O6	3712(5)	4347(3)	7440.7(18)	46.0(12)
O7	1050(4)	6838(3)	7401.6(18)	49.9(12)
O8	2195(5)	7722(3)	6806.5(17)	46.4(12)
N1	11872(5)	6609(3)	5336.2(19)	30.4(11)
N2	8312(5)	5527(3)	4056.9(19)	32.3(11)
N3	11344(5)	6048(3)	4355(2)	32.4(12)
N4	11254(5)	6181(4)	3962(3)	42.1(15)
N5	11374(7)	6367(4)	3476(3)	67.3(19)
N6	6207(5)	5631(3)	4920(2)	37.8(13)
N7	5389(6)	6071(4)	4640(2)	40.9(13)
N8	4525(6)	6403(4)	4408(3)	62.4(18)
N9	9902(5)	6714(3)	6102.3(19)	31.9(11)
N10	9015(5)	6863(3)	6463(2)	33.7(12)

N11	8413(6)	7044(4)	6832(2)	51.3(15)
N12	6722(5)	5461(3)	6195.7(17)	26.1(10)
N13	6924(4)	6151(3)	5888.1(17)	23.9(10)
N14	6011(5)	6796(3)	5948.8(18)	27.2(11)
N15	3377(5)	7676(3)	6482(2)	39.1(13)
N16	2066(5)	6922(3)	7103.0(19)	35.3(12)
N17	2921(5)	5087(3)	7448(2)	40.9(13)
N18	4906(5)	4454(3)	7057(2)	35.6(12)
C1	10406(5)	6357(3)	5208(2)	26.0(12)
C2	10105(6)	6089(3)	4694(2)	27.0(12)
C3	8682(5)	5866(3)	4581(2)	22.9(12)
C4	7630(6)	5909(3)	4973(2)	24.1(12)
C5	8006(5)	6159(3)	5487(2)	24.2(12)
C6	9397(6)	6402(3)	5617(2)	27.2(13)
C7	5588(5)	5693(3)	6478(2)	22.3(11)
C8	4797(6)	5237(4)	6878(2)	29.9(13)
C9	3562(6)	5601(4)	7114(2)	31.6(14)
C10	3169(5)	6448(4)	6958(2)	30.6(13)
C11	3933(6)	6916(4)	6574(2)	31.1(13)
C12	5159(5)	6512(3)	6330(2)	23.5(12)

Table S9 Anisotropic Displacement Parameters (Å^2×10^3) of compound **2.** The Anisotropic displacement factor exponent takes the form: -2π^2 [h2a*2U11+2hka*b*U12+…]

Atom	U11	U22	U33	U23	U13	U12
O1	23(2)	40(2)	61(3)	2(2)	-3(2)	-1.0(19)
O2	32(2)	33(2)	60(3)	7(2)	-1(2)	-9.2(19)
O3	48(3)	45(3)	42(3)	-11(2)	16(2)	2(2)
O4	36(3)	61(3)	38(3)	-6(2)	-5(2)	-5(2)
O5	40(3)	30(2)	62(3)	5(2)	12(2)	2(2)
O6	43(3)	45(2)	49(3)	11(2)	18(2)	-11(2)
O7	30(2)	73(3)	47(3)	1(3)	6(2)	3(2)
O8	41(3)	52(3)	46(3)	-1(2)	0(2)	13(2)

N1	22(2)	31(3)	38(3)	-1(2)	-2(2)	-3(2)
N2	28(3)	37(3)	32(3)	2(2)	2(2)	-3(2)
N3	13(2)	30(3)	54(4)	6(3)	7(3)	1(2)
N4	14(3)	38(3)	74(5)	-26(4)	6(3)	1(2)
N5	62(4)	74(5)	65(5)	-7(4)	15(4)	-3(4)
N6	25(3)	42(3)	46(3)	1(3)	-5(2)	-3(2)
N7	28(3)	50(3)	45(3)	-2(3)	0(3)	-16(3)
N8	34(3)	78(5)	75(5)	16(4)	-13(3)	-3(3)
N9	24(3)	36(3)	36(3)	-11(2)	0(2)	-4(2)
N10	28(3)	41(3)	32(3)	-2(2)	-5(2)	-5(2)
N11	39(3)	78(4)	38(3)	-9(3)	0(3)	-6(3)
N12	24(2)	28(2)	25(2)	-1(2)	1(2)	-3(2)
N13	19(2)	26(2)	27(2)	-2(2)	2.8(19)	1.6(19)
N14	23(2)	27(2)	31(3)	-3(2)	-3(2)	6(2)
N15	26(3)	51(3)	40(3)	-8(3)	13(2)	12(2)
N16	18(2)	58(3)	30(3)	-6(3)	0(2)	1(2)
N17	39(3)	40(3)	44(3)	0(3)	8(3)	0(3)
N18	34(3)	35(3)	38(3)	1(2)	7(2)	-10(2)
C1	14(3)	29(3)	34(3)	-2(3)	-2(2)	-2(2)
C2	23(3)	20(3)	38(3)	4(3)	3(2)	3(2)
C3	22(3)	21(3)	25(3)	1(2)	1(2)	0(2)
C4	26(3)	17(2)	30(3)	3(2)	0(2)	-3(2)
C5	21(3)	21(3)	31(3)	-3(2)	5(2)	0(2)
C6	25(3)	18(3)	39(3)	0(2)	0(3)	-1(2)
C7	14(3)	30(3)	23(3)	-1(2)	1(2)	-5(2)
C8	26(3)	29(3)	35(3)	-2(3)	-5(3)	-6(2)
C9	24(3)	43(3)	27(3)	1(3)	4(2)	-8(3)
C10	12(3)	46(3)	34(3)	-9(3)	-5(2)	1(2)
C11	24(3)	40(3)	29(3)	-5(3)	0(3)	-1(3)
C12	13(3)	34(3)	24(3)	0(2)	-1(2)	-4(2)

Table S10 Bond Lengths of compound **2**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.222(6)	N12	N13	1.347(6)
O2	N1	1.219(6)	N12	C7	1.329(6)
O3	N2	1.229(6)	N13	N14	1.337(6)
O4	N2	1.216(6)	N13	C5	1.430(6)
O5	N18	1.220(6)	N14	C12	1.326(7)

O6	N17	1.381(6)	N15	C11	1.325(8)
O6	N18	1.487(6)	N16	C10	1.328(7)
O7	N16	1.220(6)	N17	C9	1.311(7)
O8	N15	1.378(6)	N18	C8	1.316(7)
O8	N16	1.468(7)	C1	C2	1.387(7)
N1	C1	1.468(7)	C1	C6	1.399(7)
N2	C3	1.463(7)	C2	C3	1.410(7)
N3	N4	1.012(7)	C3	C4	1.395(7)
N3	C2	1.442(7)	C4	C5	1.397(7)
N4	N5	1.261(9)	C5	C6	1.399(7)
N6	N7	1.251(7)	C7	C8	1.441(7)
N6	C4	1.412(7)	C7	C12	1.401(7)
N7	N8	1.126(8)	C8	C9	1.422(8)
N9	N10	1.253(7)	C9	C10	1.438(8)
N9	C6	1.397(7)	C10	C11	1.410(8)
N10	N11	1.121(7)	C11	C12	1.450(7)

Table S11 Bond Angles of compound **2**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N17	O6	N18	108.5(4)	C3	C2	N3	129.3(5)
N15	O8	N16	108.7(4)	C2	C3	N2	119.8(5)
O1	N1	C1	117.8(5)	C4	C3	N2	118.9(5)
O2	N1	O1	124.2(5)	C4	C3	C2	121.1(5)
O2	N1	C1	118.1(5)	C3	C4	N6	126.1(5)
O3	N2	C3	118.3(5)	C3	C4	C5	119.1(5)
O4	N2	O3	123.6(5)	C5	C4	N6	114.4(5)
O4	N2	C3	118.0(5)	C4	C5	N13	118.0(5)
N4	N3	C2	119.9(6)	C4	C5	C6	121.8(5)
N3	N4	N5	170.0(7)	C6	C5	N13	120.1(5)
N7	N6	C4	117.5(5)	N9	C6	C1	115.4(5)
N8	N7	N6	171.6(6)	N9	C6	C5	128.0(5)
N10	N9	C6	118.2(5)	C1	C6	C5	116.6(5)
N11	N10	N9	168.4(6)	N12	C7	C8	130.3(5)
C7	N12	N13	101.3(4)	N12	C7	C12	110.1(5)
N12	N13	C5	120.7(4)	C12	C7	C8	119.6(5)
N14	N13	N12	117.2(4)	N18	C8	C7	131.7(5)
N14	N13	C5	121.9(4)	N18	C8	C9	107.2(5)
C12	N14	N13	102.3(4)	C9	C8	C7	120.7(5)

C11	N15	O8	105.2(5)	N17	C9	C8	113.1(5)
O7	N16	O8	118.0(5)	N17	C9	C10	128.9(5)
O7	N16	C10	135.8(6)	C8	C9	C10	117.9(5)
C10	N16	O8	106.2(4)	N16	C10	C9	130.3(6)
C9	N17	O6	105.3(5)	N16	C10	C11	106.9(5)
O5	N18	O6	118.2(4)	C11	C10	C9	122.8(5)
O5	N18	C8	136.1(5)	N15	C11	C10	113.0(5)
C8	N18	O6	105.7(5)	N15	C11	C12	129.5(5)
C2	C1	N1	118.5(5)	C10	C11	C12	117.5(5)
C2	C1	C6	124.1(5)	N14	C12	C7	109.1(5)
C6	C1	N1	117.4(5)	N14	C12	C11	129.5(5)
C1	C2	N3	113.5(5)	C7	C12	C11	121.4(5)
C1	C2	C3	117.1(5)				

Table S12 Torsion Angles of compound **2**

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	N1	C1	C2	-90.0(7)	N13	C5	C6	N9	-5.0(8)
O1	N1	C1	C6	89.8(6)	N13	C5	C6	C1	177.3(5)
O2	N1	C1	C2	90.2(6)	N14	N13	C5	C4	-83.0(6)
O2	N1	C1	C6	-90.0(7)	N14	N13	C5	C6	97.7(6)
O3	N2	C3	C2	31.2(7)	N15	O8	N16	O7	-178.0(5)
O3	N2	C3	C4	-144.5(5)	N15	O8	N16	C10	1.5(6)
O4	N2	C3	C2	-149.8(5)	N15	C11	C12	N14	-1.4(10)
O4	N2	C3	C4	34.5(7)	N15	C11	C12	C7	-179.5(6)
O5	N18	C8	C7	4.8(12)	N16	O8	N15	C11	-0.5(6)
O5	N18	C8	C9	178.2(7)	N16	C10	C11	N15	1.6(7)
O6	N17	C9	C8	-0.8(7)	N16	C10	C11	C12	-176.9(5)
O6	N17	C9	C10	178.2(6)	N17	O6	N18	O5	-178.4(5)
O6	N18	C8	C7	-175.9(5)	N17	O6	N18	C8	2.1(6)
O6	N18	C8	C9	-2.5(6)	N17	C9	C10	N16	-0.8(10)
O7	N16	C10	C9	0.6(11)	N17	C9	C10	C11	-177.3(6)
O7	N16	C10	C11	177.5(6)	N18	O6	N17	C9	-0.8(6)
O8	N15	C11	C10	-0.7(6)	N18	C8	C9	N17	2.2(7)
O8	N15	C11	C12	177.7(5)	N18	C8	C9	C10	-176.9(5)
O8	N16	C10	C9	-178.7(5)	C1	C2	C3	N2	-176.1(5)
O8	N16	C10	C11	-1.8(6)	C1	C2	C3	C4	-0.5(8)
N1	C1	C2	N3	3.5(7)	C2	N3	N4	N5	161(4)
N1	C1	C2	C3	-178.9(5)	C2	C1	C6	N9	-178.1(5)

N1	C1	C6	N9	2.1(7)	C2	C1	C6	C5	-0.1(8)
N1	C1	C6	C5	-179.9(5)	C2	C3	C4	N6	-173.8(5)
N2	C3	C4	N6	1.8(8)	C2	C3	C4	C5	-1.5(8)
N2	C3	C4	C5	174.2(5)	C3	C4	C5	N13	-176.5(5)
N3	C2	C3	N2	1.0(9)	C3	C4	C5	C6	2.7(8)
N3	C2	C3	C4	176.6(5)	C4	C5	C6	N9	175.7(5)
N4	N3	C2	C1	-146.4(7)	C4	C5	C6	C1	-2.0(8)
N4	N3	C2	C3	36.4(10)	C5	N13	N14	C12	176.3(5)
N6	C4	C5	N13	-3.3(7)	C6	N9	N10	N11	-176(3)
N6	C4	C5	C6	176.0(5)	C6	C1	C2	N3	-176.3(5)
N7	N6	C4	C3	-73.3(7)	C6	C1	C2	C3	1.3(8)
N7	N6	C4	C5	114.0(6)	C7	N12	N13	N14	-0.4(6)
N10	N9	C6	C1	171.7(5)	C7	N12	N13	C5	-175.8(4)
N10	N9	C6	C5	-6.0(9)	C7	C8	C9	N17	176.5(5)
N12	N13	N14	C12	0.9(6)	C7	C8	C9	C10	-2.6(8)
N12	N13	C5	C4	92.1(6)	C8	C7	C12	N14	-178.2(5)
N12	N13	C5	C6	-87.1(6)	C8	C7	C12	C11	0.2(8)
N12	C7	C8	N18	-4.5(10)	C8	C9	C10	N16	178.1(6)
N12	C7	C8	C9	-177.1(5)	C8	C9	C10	C11	1.6(8)
N12	C7	C12	N14	0.9(6)	C9	C10	C11	N15	178.9(5)
N12	C7	C12	C11	179.3(5)	C9	C10	C11	C12	0.3(8)
N13	N12	C7	C8	178.7(5)	C10	C11	C12	N14	176.9(5)
N13	N12	C7	C12	-0.3(5)	C10	C11	C12	C7	-1.2(8)
N13	N14	C12	C7	-1.0(5)	C12	C7	C8	N18	174.4(6)
N13	N14	C12	C11	-179.3(5)	C12	C7	C8	C9	1.8(8)

4. FT-IR spectra

FT-IR spectra of 4-Chloro-3,5-dinitroaniline and compounds **1** and **2**.

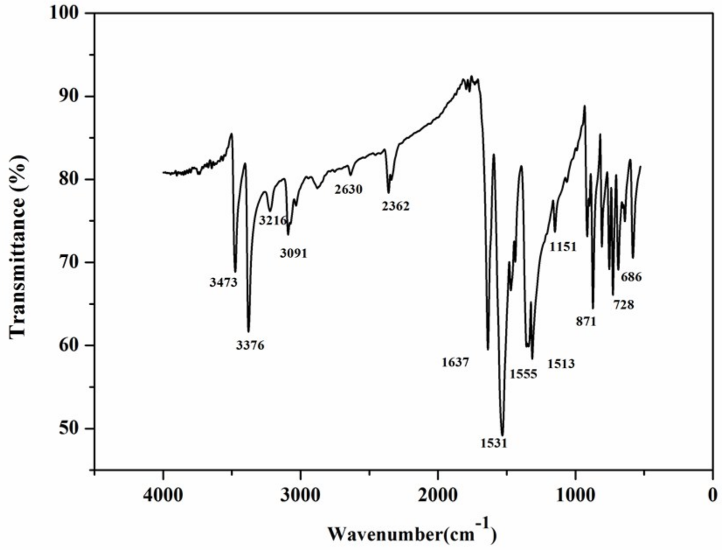


Figure S2. The IR spectrum of 4-Chloro-3,5-dinitroaniline

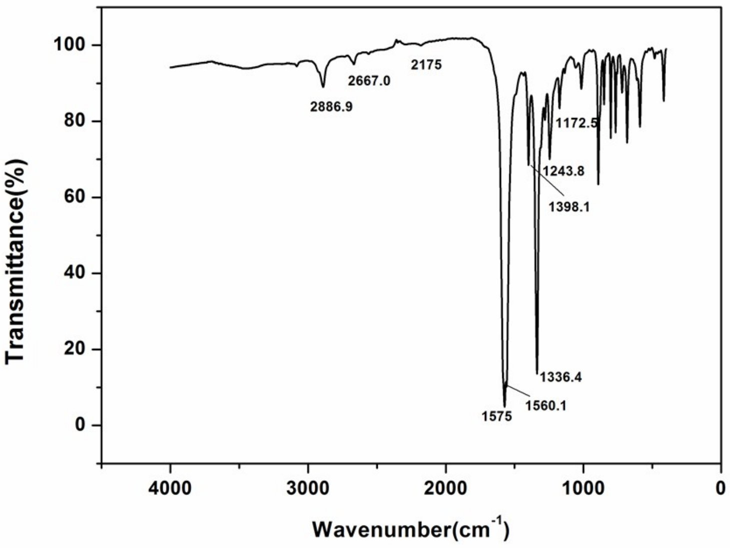


Figure S3. The IR spectrum of **1**

The FT-IR spectrum characteristic absorption bands of compound **1** range from 2100 cm^{-1} to 2300 cm^{-1} are attributed to the azo bond. The other intense absorption bands at 3000~3450 cm^{-1} that are assigned to N−H bond of 4-chloro-3,5-dinitroaniline have disappeared (see Fig. S2† and S3†).

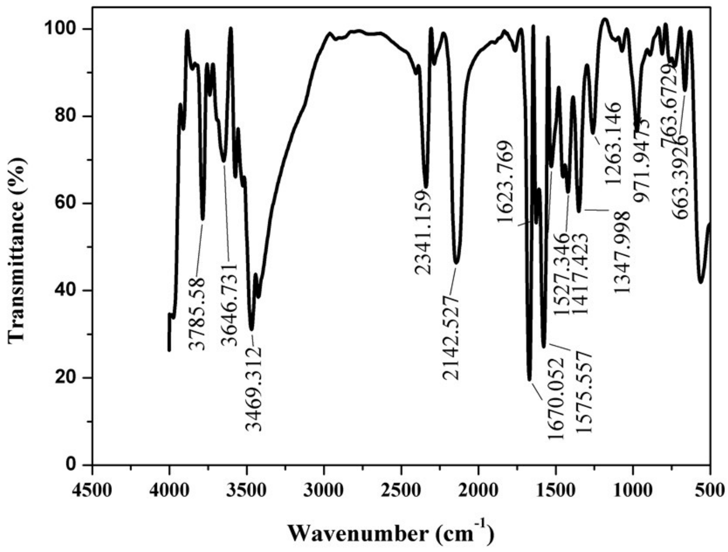


Figure S4. The IR spectrum of **2**

The FT-IR spectrum of compound **2** contains strong Ar–NO_2 symmetric stretching bands at 1575 and 1348 cm^{-1}. The other strong stretching bands appear in 2341 and 2142, and 1670 and 1623 cm^{-1} are attributed to the –N_3 bond (Fig. S4†).

5. ^{1}H NMR spectrum of **1**

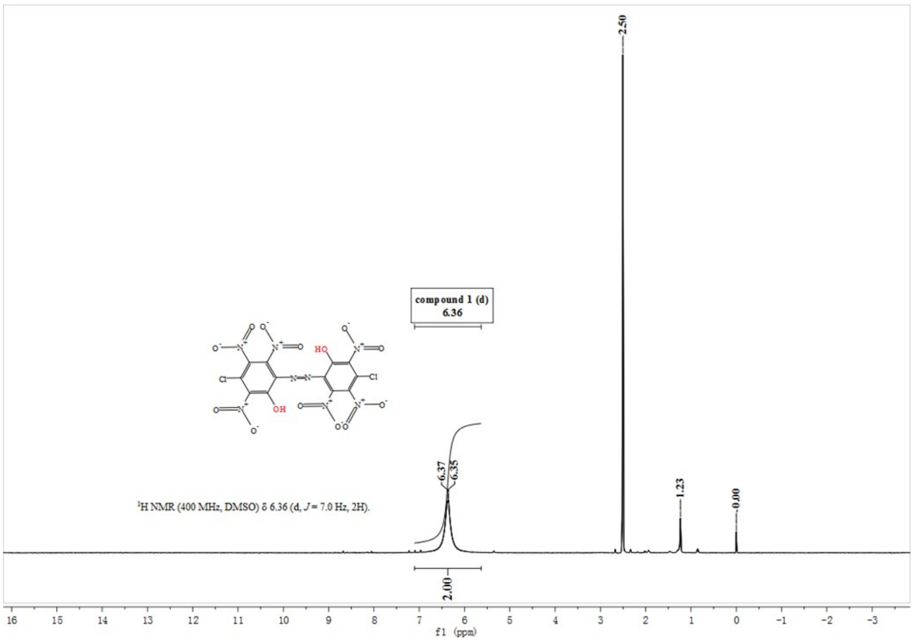


Figure S5 ^{1}H NMR spectra of **1**

The ^{1}H NMR spectrum of compound **1** shows the single resonance peak at δ=6.36 ppm is assigned to the Ar–OH group. The other signals can be assigned to the peak of TMSO solvent among DMSO at δ= 0 ppm and the peak of DMSO solvent at δ=2.50 ppm. The peak at δ=1.23 ppm may be attributed to H^+ or impurity. Because the peak of H_2O in DMSO-d_6 appears at 3.33 ppm and the raw material Ar-NH_2 peak usually appears at 2.5~5.0 ppm. The ^{1}H NMR spectra is showed in Figure S5.

^{13}C NMR spectrum of compounds 1 and 2

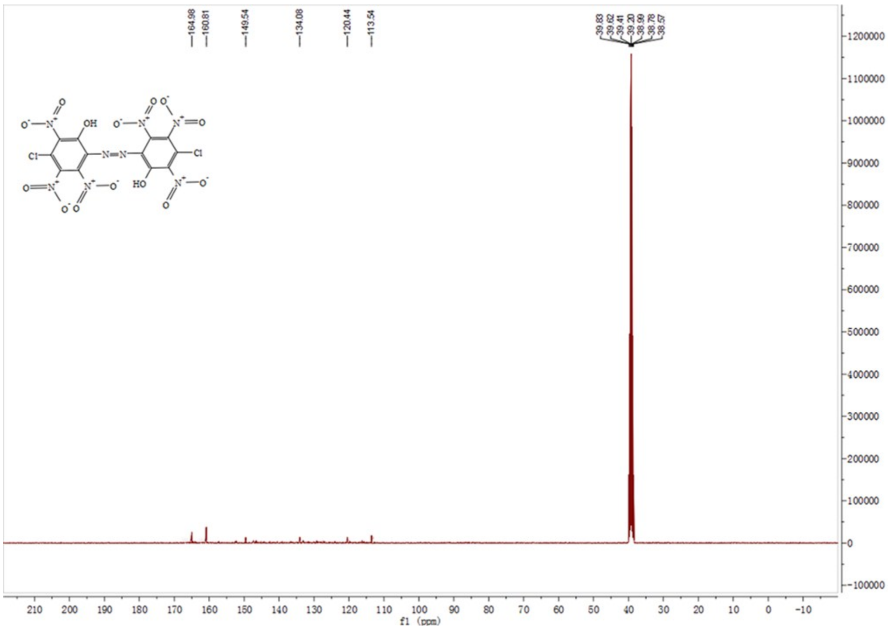


Figure S6 ^{13}C NMR spectra of **1**

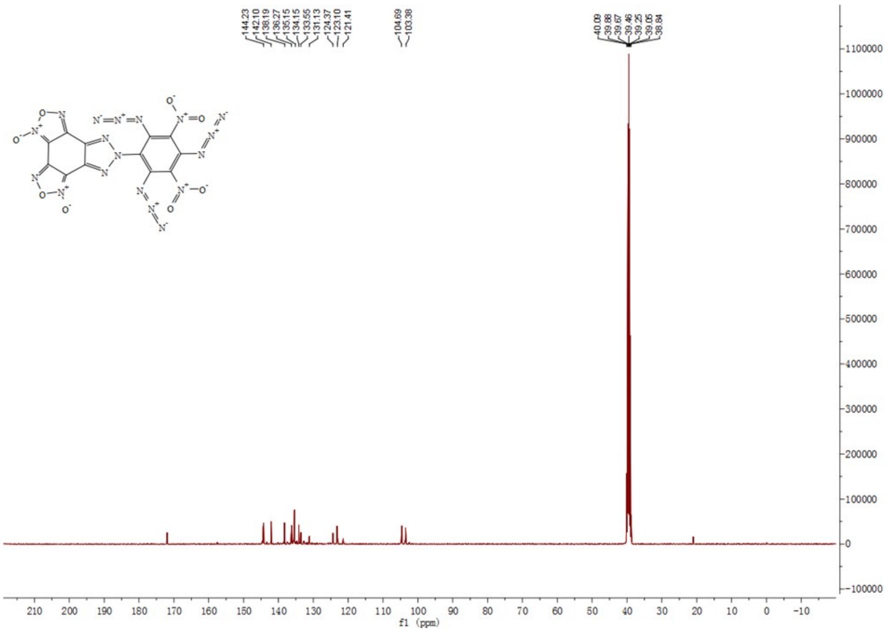
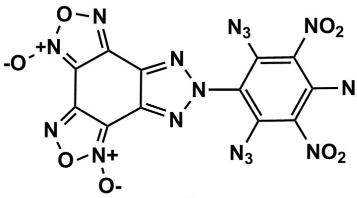
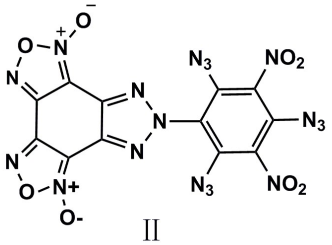


Figure S7 ^{13}C NMR spectra of **2**

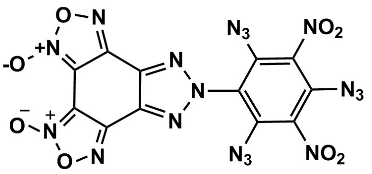
The spectroscopic data for the new compounds **1** and **2** were measured and the ^{13}C NMR spectra are shown in Figure S6 and S7. The value of solvent peaks are too large, resulting in the carbon absorption peaks is not obvious. Though we want get better results by increasing concentration and extending test time, the data are not satisfactory. In the ^{13}C NMR spectrum of compound **1**, the six signals associated with the benzene ring (d ≈ 164.98, 160.81, 149.54, 134.08, 120.44 and 113.54 ppm). In the ^{13}C NMR spectrum of compound **2**, there are thirteen absorption peaks among 100~150 ppm. All of this indicates that there may be a symmetric isomer. The position of the N-oxide also can appear on another N in furazan ring. The isomer may be caused by the furazan-N-oxide rings opening to the dinitroso compound and reclosure to the alternative N-oxide. The possible isomers are shown as I and II. III



I



II



III

Moreover, it is still possible to exist another isomer III. While the structure of III has an electrostatic repulsion of the negative N-oxide, making the structure unstable.

6. Thermal stability measurement (DSC)

To investigate the thermal behavior of compounds **1** and **2**, DSC of two compounds are tested with a linear heating rate of 5°C/min. The curves are shown in figure S2 and S3.

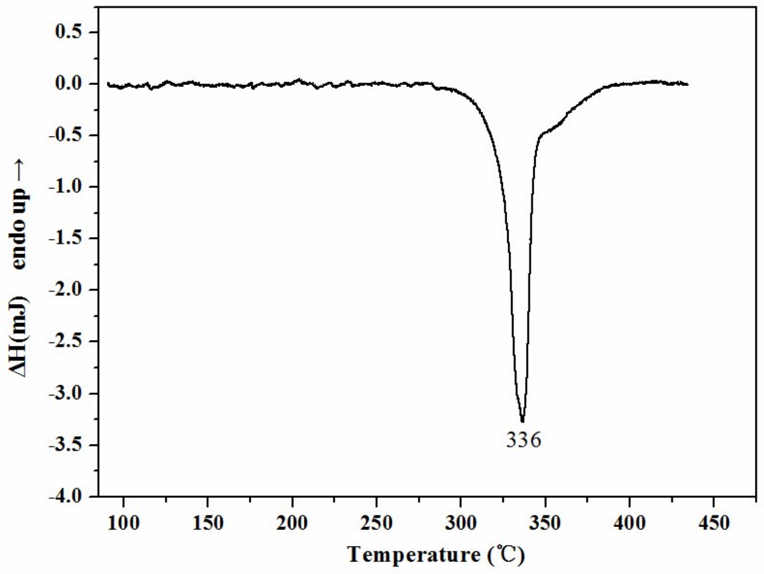


Figure S8. DSC curve of compound **1**.

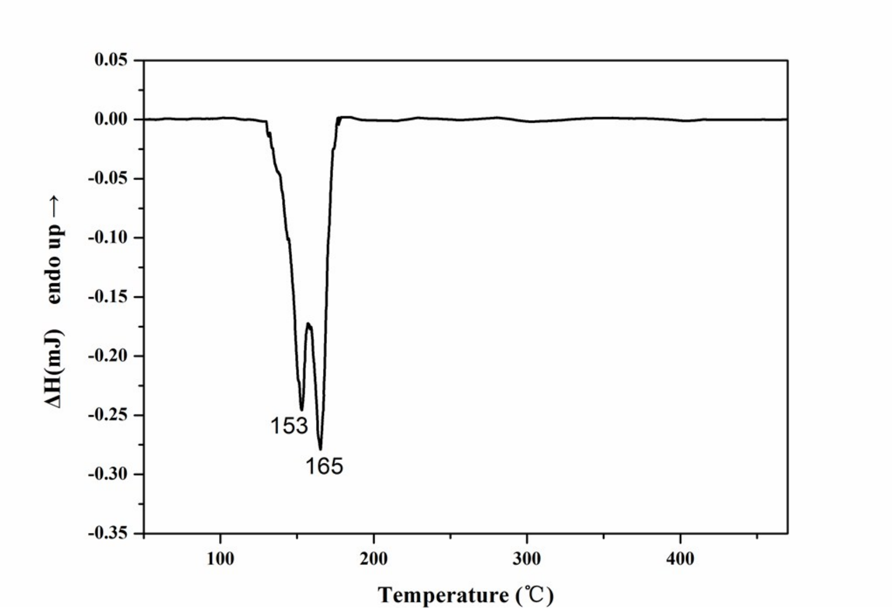


Figure S9 DSC curve of compound **2**.

7. Non-isothermal kinetics analysis

Kinetics parameters, including apparent activation energy (Ea) and the pre-exponential factor (A), were calculated by using Kissinger's method[4] (Eq. (1)) and Ozawa-Doyle's method[5] (Eq. (2)) according to the peak temperatures of first decomposition processes shown in the DSC curves.

$$\ln\frac{\beta}{T_p^2} = \ln\left(\frac{AR}{Ea}\right) - \frac{E_a}{RT_p} \qquad (1)$$

$$\ln\beta + 0.4567\frac{E_a}{RT_p} = C \qquad (2)$$

Where Tp is the peak temperature (K) of first reaction process, A is the pre-exponential factor (1/s), Ea is the apparent activation energy (kJ/mol), R is the gas constant (J/mol K), β is the heating rate (K/min) and C is a constant. The results are listed in table S13. The symbol "S" stands for the standard deviation. Ea is equal to the average of E_k and E_o.

Table S13. Peak temperatures and kinetics parameters of **1** and **2**.

β (K/min)	Peaks temperatures Tp (K)	
	1	**2**
5	609.2	426.2
10	619.2	433.3
15	634.7	438.0
20	640.2	438.2
Kissinger's method		
E_k (kJ/mol)	124.2	155.8
Log A (1/s)	8.217	17.03
Linear correlation coefficient (R_k)	-0.9773	-0.9807

S	0.1445	0.138
Ozawa-Doyle's method		
E_o (kJ/mol)	128.0	155.0
Linear correlation coefficient (R_k)	-0.9806	-0.9823
S	6.267e-002	5.993e-002
Ea (kJ/mol)	126.1	155.4

8. Experimental energies of combustion

As a well-established experimental technique, Bomb calorimetry was used to measure energies of combustion and calculated the heat of formation. Therefore, the energy of combustion of **2** was also determined by an oxygen bomb calorimetry, and the measured constant volume combustion energies was 11.16 kJ/g (-5844 kJ/mol). On the basis of the calculated constant volume combustion enthalpy and the Hess's law, the standard formation enthalpy of compound **2** was back-calculated to 1090 kJ/mol. Due to the unavoidable heat exchange between the calorimeter and its surroundings, this value is slightly lower than the calculated value (1161 kJ/mol). The oxygen balance, which is the index of the deficiency or excess of oxygen in a compound required to convert carbon to carbon, for compound **1** is 2.89% and compound **2** is -12.2% according to the formula of 1600 (c–a–b/2)/Mw (CaHbOcNd, Mw = molecular mass).

sample mass(g)	constant volume combustion energies (kJ/g)	constant volume combustion energies (kJ/mol)	constant pressure combustion (kJ/mol)	formation enthalpy (kJ/mol)
0.0842	-11.16	-5844	-5812	1090

9. Sensitivities

For initial safety testing, impact sensitivity (IS) and friction sensitivity (FS) values of compounds **1** and **2** measured by using a BAM fall hammer apparatus and a BAM friction tester according to the corresponding standard methods

10. Calculation method of HOMO, LUMO and ESP

To obtain a better understanding and analysis of compounds **1** and **2**, first we used the calculations that based upon the B3LYP (Becke three-parameter Lee–Yang–Parr)/6-311++g(d, p) method gain optimized structure using Gaussian 09. The HOMO, LUMO, ESP of the energetic compounds **1** and **2** was computed at the optimized structure.

11. References

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