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Laser Ignition of Energetic Complexes: Impact of Metal Ion on Laser Initiation Ability

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1. General methods.

Sulfuric acid and potassium nitrate were purchased from Sinopharm Chemical Reagent. Other reagents were bought from Energy Chemical and used without further purification. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were measured on DSC-Q2000 and SDT-Q600. Impact sensitivities (IS) were measured on a home-made device according to the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria. Single-crystal X-ray diffraction patterns of complexes **1**, **3** **4** and **5** were recorded on a Bruker APEX-II diffractometer with highly oriented graphite crystal monochromated GaKα radiation (λ = 1.34138 nm). Semi-empirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares techniques based on F^2. All the atoms were refined anisotropically. The CCDC numbers of **1**, **3** **4** and **5** are 2036169, 2036170, 2036173 and 2036174.

2. Hydrogen bonds for 1, 3, 4 and 5.

Table S1 Hydrogen bonds present in **1**

D−H···A	d(D−H)/Å	d(H−A)/Å	d(D−A)/Å	D−H−A/°
O10−H10A···O1^{i}	0.806	2.242	2.964	149.38
O10−H10A···O2^{i}	0.806	2.602	3.033	115.16
O9−H9A···N4	0.821	2.022	2.827	166.41
O9−H9B···O4^{ii}	0.851	2.292	3.048	148.02
O10−H10A···O7^{iii}	0.879	2.274	3.078	152.04

Symmetry codes: (i) x, y, z+1; (ii) x+1, y−1, z; (iii) x−1, y+1, z; (iv) x+1, −y+1/2, z−1/2; (v) −x+1, −y+1, −z+1; (vi) −x+1, −y, −z+1; (vii) −x+1/2, y−1/2, z; (viii) x+1/2, −y+3/2, −z+1; (ix) x+1/2, y, −z+1/2; (x) −x+1, y−1/2, −z+1/2; (xi) −x+1, −y+2, −z+1; (xii) x, y+1, z; (xiii) x+1, y, z; (xiv) −x+1, y+1/2, −z+1/2; (xv) x+1, −y+3/2, z−1/2; (xvi) −x+2, −y+1, −z; (xvii) x−1, y, z.

Table S2 Hydrogen bonds present in **3**

D−H···A	d(D−H)/Å	d(H−A)/Å	d(D−A)/Å	D−H−A/°
O6−H6A···O4^{iv}	0.794	2.170	2.957	171.03
O5−H5A···O3^{iv}	0.784	2.471	2.916	117.44
O5−H5A···N2^{v}	0.834	1.963	2.789	170.37
O6−H6B···O1^{vi}	0.759	2.287	3.008	159.09

Symmetry codes: (i) x, y, z+1; (ii) x+1, y−1, z; (iii) x−1, y+1, z; (iv) x+1, −y+1/2, z−1/2; (v) −x+1, −y+1, −z+1; (vi) −x+1, −y, −z+1; (vii) −x+1/2, y−1/2, z; (viii) x+1/2, −y+3/2, −z+1; (ix) x+1/2, y, −z+1/2; (x) −x+1, y−1/2, −z+1/2; (xi) −x+1, −y+2, −z+1; (xii) x, y+1, z; (xiii) x+1, y, z; (xiv) −x+1, y+1/2, −z+1/2; (xv) x+1, −y+3/2, z−1/2; (xvi) −x+2, −y+1, −z; (xvii) x−1, y, z.

Table S3 Hydrogen bonds present in **4**

D−H···A	d(D−H)/Å	d(H−A)/Å	d(D−A)/Å	D−H−A/°

O13−H13A···N2^{vii}	0.906	1.970	2.827	157.09
O13−H13B···O4^{vii}	0.905	2.255	2.964	134.87
O13−H13B···O1	0.905	2.504	3.161	129.85
O14−H14A···O4^{vii}	0.975	2.637	3.525	151.50
O14−H14A···N2^{vii}	0.975	1.898	2.655	132.41
O11−H11A ···O4^{viii}	0.890	2.389	2.885	115.42
O11−H11B···O15	0.889	1.845	2.714	165.19
O10−H10A···O16	0.919	1.855	2.745	162.52
O10−H10B···O8	0.923	2.414	3.103	131.40
O10−H10B···O5^{ix}	0.923	2.250	2.923	129.30
O12−H12B···O8^{x}	0.883	2.449	3.159	137.78
O9−H9A···O2^{xi}	0.946	2.020	2.944	165.00
O9−H9B···O13^{xii}	0.942	1.880	2.744	151.32
O9−H9B···O14^{xii}	0.942	2.053	2.897	148.34

Symmetry codes: (i) x, y, z+1; (ii) x+1, y−1, z; (iii) x−1, y+1, z; (iv) x+1, −y+1/2, z−1/2; (v) −x+1, −y+1, −z+1; (vi) −x+1, −y, −z+1; (vii) −x+1/2, y−1/2, z; (viii) x+1/2, −y+3/2, −z+1; (ix) x+1/2, y, −z+1/2; (x) −x+1, y−1/2, −z+1/2; (xi) −x+1, −y+2, −z+1; (xii) x, y+1, z; (xiii) x+1, y, z; (xiv) −x+1, y+1/2, −z+1/2; (xv) x+1, −y+3/2, z−1/2; (xvi) −x+2, −y+1, −z; (xvii) x−1, y, z.

Table S4 Hydrogen bonds present in **5**

D−H···A	**d(D−H)/Å**	**d(H−A)/Å**	**d(D−A)/Å**	**D−H−A/°**
O10−H10A···O4^{xiii}	0.867	2.603	3.097	117.20
O10−H10A···O3^{xiii}	0.867	2.428	3.279	167.57
O10−H10A···N6^{xiii}	0.867	2.249	2.949	137.73
O10−H10B···O5^{xiv}	0.867	2.135	2.978	163.81
O9−H9A···O8	0.855	2.394	3.097	139.86
O9−H9B···O3 ^{xv}	0.854	2.476	3.066	126.90
O9−H9B···O7^{xvi}	0.854	2.510	3.098	126.79
O11−H11A···O5	0.959	2.583	3.107	114.63
O11−H11A···N3	0.959	1.838	2.782	167.63
O11−H11B···O8^{xvii}	0.575	2.342	2.850	148.90

Symmetry codes: (i) x, y, z+1; (ii) x+1, y−1, z; (iii) x−1, y+1, z; (iv) x+1, −y+1/2, z−1/2; (v) −x+1, −y+1, −z+1; (vi) −x+1, −y, −z+1; (vii) −x+1/2, y−1/2, z; (viii) x+1/2, −y+3/2, −z+1; (ix) x+1/2, y, −z+1/2; (x) −x+1, y−1/2, −z+1/2; (xi) −x+1, −y+2, −z+1; (xii) x, y+1, z; (xiii) x+1, y, z; (xiv) −x+1, y+1/2, −z+1/2; (xv) x+1, −y+3/2, z−1/2; (xvi) −x+2, −y+1, −z; (xvii) x−1, y, z.

3. Bond lengths (Å) and angles (°) for 1, 3, 4 and 5

Table S5 Selected bond lengths (Å) and angles (°) for **1**

Complex1			
O1N5	1.239(3)	N8C6	1.431(3)
O1Na2	2.474(2)	O5N7	1.229(3)
O2N5	1.226(3)	O5Na2^{ii}	2.629(2)
N4C4	1.341(3)	N7C5	1.447(3)
N4C6	1.351(3)	C3C2	1.393(3)
N1C2	1.353(3)	C3N6	1.446(3)
N1C1	1.347(3)	O8Na2^{iii}	2.777(2)
N1Na2	2.626(2)	C4C1	1.465(4)
N5C2	1.431(3)	C5C6	1.394(3)
N2C3	1.335(3)	O3N6	1.220(3)
N2C1	1.356(3)	O3Na1^{iv}	2.574(2)
N2Na1	2.519(2)	N6O4	1.235(3)
N3C4	1.349(3)	O4Na2^{v}	2.564(2)
N3C5	1.347(3)	Na1Na2^{vi}	3.842(2)
N3Na1	2.476(2)	Na1Na2^{v}	3.740(2)
O6N7	1.219(3)	Na1O9^{vi}	2.374(2)
O6Na1^{i}	2.479(2)	Na1O10	2.338(2)
N8O8	1.223(3)	Na2O9	2.343(2)
N8O7	1.212(3)	Na2O10^{v}	2.373(2)
O1N5C2	118.0(2)	O9^{vi}Na1N2	82.17(8)
O2N5O1	123.2(2)	O9^{vi}Na1N3	93.05(8)
O2N5C2	118.8(2)	O9^{vi}Na1O6^{i}	100.92(9)
C3N2C1	102.7(2)	O9^{vi}Na1O3^{iv}	88.95(8)
C3N2Na1	140.85(16)	O9^{vi}Na1Na2^{v}	133.97(7)
C1N2Na1	111.39(15)	O9^{vi}Na1Na2^{vi}	35.19(5)
C4N3Na1	112.90(15)	O10Na1N2	94.22(8)
C5N3C4	102.5(2)	O10Na1N3	103.40(8)
C5N3Na1	141.58(16)	O10Na1O6^{i}	83.42(8)
N7O6Na1^{i}	116.36(16)	O10Na1O3^{iv}	73.21(8)
O8N8C6	118.0(2)	O10Na1Na2^{v}	37.78(6)
O7N8O8	121.8(2)	O10Na1Na2^{vi}	158.18(7)
O7N8C6	120.2(2)	O10Na1O9^{vi}	160.76(9)
N7O5Na2^{ii}	133.59(17)	O1Na2N1	63.52(7)
O6N7O5	124.2(2)	O1Na2O5^{vii}	69.06(7)
O6N7C5	118.6(2)	O1Na2O8^{iii}	144.27(8)
O5N7C5	117.2(2)	O1Na2O4^{v}	137.58(8)
N2C3C2	109.8(2)	O1Na2Na1^{vi}	106.11(6)
N2C3N6	118.6(2)	O1Na2Na1^{v}	76.43(6)
C2C3N6	131.5(2)	N1Na2O5^{vii}	111.11(8)
N8O8Na2^{iii}	136.32(17)	N1Na2O8^{iii}	151.92(8)
N1C2N5	119.9(2)	N1Na2Na1^{v}	104.06(6)
N1C2C3	109.2(2)	N1Na2Na1^{vi}	92.10(5)

C3C2N5	130.5(2)	O5^{vii}Na2O8^{iii}	84.96(7)
N4C4N3	116.2(2)	O5^{vii}Na2Na1^{v}	110.04(6)
N4C4C1	122.8(2)	O5^{vii}Na2Na1^{vi}	57.07(5)
N3C4C1	121.0(2)	O8^{iii}Na2Na1^{vi}	77.20(6)
N3C5N7	118.8(2)	O8^{iii}Na2Na1^{v}	90.80(6)
N3C5C6	109.4(2)	O4^{v}Na2N1	98.14(8)
C6C5N7	131.7(2)	O4^{v}Na2O5^{vii}	148.72(7)
N1C1N2	115.8(2)	O4^{v}Na2O8^{iii}	63.77(7)
N1C1C4	123.9(2)	O4^{v}Na2Na1^{v}	71.53(6)
N2C1C4	120.3(2)	O4^{v}Na2Na1^{vi}	112.81(6)
N4C6N8	119.4(2)	Na1^{v}Na2Na1^{vi}	162.67(4)
N4C6C5	109.1(2)	O9Na2O1	132.74(8)
C5C6N8	131.3(2)	O9Na2N1	86.41(7)
N6O3Na1^{iv}	124.44(16)	O9Na2O5^{vii}	91.87(8)
O3N6C3	120.0(2)	O9Na2O8^{iii}	69.67(7)
O3N6O4	123.3(2)	O9Na2O4^{v}	78.76(8)
O4N6C3	116.7(2)	O9Na2Na1^{v}	149.53(7)
N6O4Na2^{v}	125.46(15)	O9Na2Na1^{vi}	35.74(6)
N2Na1O3^{iv}	101.68(7)	O9Na2O10^{v}	143.24(9)
N2Na1Na2^{v}	56.50(6)	O10^{v}Na2O1	75.02(8)
N2Na1Na2^{vi}	106.60(6)	O10^{v}Na2N1	130.34(8)
N3Na1N2	69.39(7)	O10^{v}Na2O5^{vii}	75.31(8)
N3Na1O6^{i}	108.57(8)	O10vNa2O8^{iii}	74.91(7)
N3Na1O3^{iv}	170.44(8)	O10^{v}Na2O4^{v}	94.43(9)
N3Na1Na2^{vi}	78.67(6)	O10^{v}Na2Na1^{v}	37.12(6)
N3Na1Na2^{v}	90.50(6)	O10^{v}Na2Na1^{vi}	126.15(7)
O6^{i}Na1N2	176.48(9)	Na2O9Na1^{vi}	109.06(10)
O6^{i}Na1O3iv	80.17(7)	Na1O10Na2^{v}	105.10(9)

(i) 1−x, 2−y, 2−z; (ii) x, y, 1+z; (iii) 1−x, 1−y, 1−z; (iv) −x, 3−y, 1−z; (v) −x, 2−y, 1−z; (vi) 1−x, 2−y, 1−z; (vii) x, y, −1+z

Table S6 Selected bond lengths (Å) and angles (°) for **3**

Complex3			
O3N4	1.230(2)	N2C1	1.352(3)
O3Mg1^{i}	2.6925(18)	N3C2	1.429(3)
O1N3	1.242(2)	C3C2	1.395(3)
O1Mg1	2.5200(18)	C1C1^{ii}	1.455(4)
O4N4	1.230(2)	Mg1Mg1^{iii}	3.4912(2)
O2N3	1.226(2)	Mg1Mg1^{iv}	3.4912(2)
N4C3	1.435(3)	Mg1O5	2.3516(19)
N1C1	1.354(3)	Mg1O5^{iii}	2.3357(19)
N1C2	1.348(3)	Mg1O6	2.4120(19)
N1Mg1	2.614(2)	Mg1O6^{iii}	2.489(2)
N2C3	1.335(3)		

N4O3Mg1[i]	134.01(14)	Mg1[iv]Mg1Mg1[iii]	180
N3O1Mg1	119.48(13)	O5[iii]Mg1O3[v]	70.49(7)
O3N4C3	118.40(18)	O5Mg1O3[v]	71.78(6)
O4N4O3	123.80(19)	O5Mg1O1	127.54(7)
O4N4C3	117.78(18)	O5[iii]Mg1O1	122.18(7)
C1N1Mg1	141.97(15)	O5[iii]Mg1N1	88.83(7)
C2N1C1	102.48(17)	O5Mg1N1	85.61(7)
C2N1Mg1	113.23(14)	O5[iii]Mg1Mg1[iv]	137.97(5)
C3N2C1	103.36(17)	O5Mg1Mg1[iii]	138.32(5)
O1N3C2	117.72(18)	O5[iii]Mg1Mg1[iii]	42.03(5)
O2N3O1	123.14(19)	O5Mg1Mg1[iv]	41.68(5)
O2N3C2	119.11(18)	O5[iii]Mg1O5	96.29(7)
N2C3N4	119.01(19)	O5Mg1O6	79.83(7)
N2C3C2	109.24(18)	O5[iii]Mg1O6	150.49(8)
C2C3N4	131.52(19)	O5Mg1O6[iii]	151.20(8)
N1C1C1[ii]	123.2(2)	O5[iii]Mg1O6[iii]	78.55(6)
N2C1N1	115.34(18)	O6Mg1O3[v]	80.62(6)
N2C1C1[ii]	121.5(2)	O6[iii]Mg1O3[v]	79.87(6)
N1C2N3	120.03(19)	O6[iii]Mg1O1	76.74(7)
N1C2C3	109.56(18)	O6Mg1O1	80.89(7)
C3C2N3	129.9(2)	O6[iii]Mg1N1	122.22(7)
O3[v]Mg1Mg1[iv]	90.73(4)	O6Mg1N1	119.69(7)
O3[v]Mg1Mg1[iii]	89.26(4)	O6Mg1Mg1[iii]	134.52(5)
O1Mg1O3[v]	149.81(6)	O6[iii]Mg1Mg1[iii]	43.69(4)
O1Mg1N1	63.31(6)	O6Mg1Mg1[iv]	45.48(5)
O1Mg1Mg1[iv]	93.10(5)	O6[iii]Mg1Mg1[iv]	136.31(4)
O1Mg1Mg1[iii]	86.90(5)	O6Mg1O6[iii]	90.83(6)
N1Mg1O3[v]	146.83(6)	Mg1[iv]O5Mg1	96.29(7)
N1Mg1Mg1[iv]	87.82(4)	Mg1O6Mg1[iv]	90.83(6)
N1Mg1Mg1[iii]	92.18(4)		

(i) x, 0.5−y, 0.5+z; (ii) 1−x, 1−y, 1−z; (iii) −1+x, y, z; (iv) 1+x, y, z; (v) x, 0.5−y, −0.5+z.

Table S7 Selected bond lengths (Å) and angles (°) for **4**

Complex4			
Ca1O13	2.477(6)	N4C4	1.347(5)
Ca1O14	2.445(15)	N4C6	1.342(5)
Ca1O11	2.367(3)	N3C4	1.350(5)
Ca1O10	2.391(3)	N3C5	1.352(5)
Ca1O12	2.401(3)	N2C1	1.342(5)
Ca1O9	2.361(3)	N2C3	1.353(4)
Ca1N4	2.525(3)	N1C1	1.349(5)
Ca1N1	2.584(3)	N1C2	1.341(4)
O8N8	1.228(4)	N8C6	1.442(5)
O7N8	1.224(4)	N7C5	1.438(5)

O6N7	1.227(4)	N6C3	1.431(5)
O5N7	1.231(4)	N5C2	1.435(5)
O4N6	1.234(4)	C4C1	1.458(5)
O3N6	1.230(4)	C6C5	1.383(5)
O2N5	1.237(4)	C3C2	1.391(5)
O1N5	1.227(4)		
O13Ca1N4	105.1(2)	C2N1Ca1	137.3(3)
O13Ca1N1	72.12(14)	C2N1C1	103.4(3)
O14Ca1N4	89.3(8)	O8N8C6	118.1(3)
O14Ca1N1	75.2(4)	O7N8O8	123.0(4)
O11Ca1O13	70.8(3)	O7N8C6	118.9(4)
O11Ca1O14	87.8(8)	O6N7O5	123.9(3)
O11Ca1O10	75.16(10)	O6N7C5	118.6(4)
O11Ca1O12	104.99(11)	O5N7C5	117.5(3)
O11Ca1N4	173.59(10)	O4N6C3	117.8(3)
O11Ca1N1	109.38(10)	O3N6O4	124.0(3)
O10Ca1O13	127.26(14)	O3N6C3	118.2(4)
O10Ca1O14	125.6(5)	O2N5C2	117.9(4)
O10Ca1O12	76.44(11)	O1N5O2	123.9(3)
O10Ca1N4	111.14(10)	O1N5C2	118.2(3)
O10Ca1N1	159.24(10)	N4C4C1	117.4(4)
O12Ca1O13	75.0(3)	N3C4N4	116.2(3)
O12Ca1O14	58.6(9)	N3C4C1	126.3(4)
O12Ca1N4	78.24(11)	N4C6N8	118.1(4)
O12Ca1N1	120.00(11)	N4C6C5	109.2(3)
O9Ca1O13	133.8(3)	C5C6N8	132.7(4)
O9Ca1O14	149.8(8)	N3C5N7	119.7(4)
O9Ca1O11	86.43(11)	N3C5C6	110.2(3)
O9Ca1O10	81.19(10)	C6C5N7	130.1(3)
O9Ca1O12	151.09(12)	N2C1N1	115.6(3)
O9Ca1N4	93.26(11)	N2C1C4	126.1(4)
O9Ca1N1	78.94(10)	N1C1C4	118.4(4)
N4Ca1N1	64.32(10)	N2C3N6	119.3(4)
C4N4Ca1	118.2(2)	N2C3C2	109.5(3)
C6N4Ca1	134.3(3)	C2C3N6	130.8(4)
C6N4C4	102.8(3)	N1C2N5	118.9(4)
C4N3C5	101.6(3)	N1C2C3	108.9(3)
C1N2C3	102.6(3)	C3C2N5	132.1(4)
C1N1Ca1	116.0(2)		

Table S8 Selected bond lengths (Å) and angles (°) for **5**

Complex5			
Ba1O1	3.062(3)	O8N8	1.235(5)
Ba1O11^{ii}	2.813(4)	O3N6	1.219(5)

Ba1O11^{iii}	2.839(4)	O5N7	1.240(5)
Ba1O2^{iv}	3.029(3)	O7N8	1.223(5)
Ba1O4^{iii}	3.010(3)	N3C4	1.346(5)
Ba1N1	2.815(3)	N3C5	1.348(6)
Ba1O10	2.748(3)	N6C3	1.429(6)
Ba1O9	2.740(3)	N7C5	1.425(6)
Ba1N2^{iii}	3.141(3)	N8C6	1.425(5)
Ba1N4	3.061(4)	N5C2	1.439(5)
O1N5	1.240(4)	N2C3	1.343(5)
O2N5	1.217(5)	N2C1	1.339(5)
O4N6	1.255(5)	N4C6	1.354(5)
O6N7	1.221(5)	N4C4	1.341(5)
N1C2	1.337(5)	C3C2	1.403(6)
N1C1	1.346(5)	C6C5	1.399(6)
C4C1	1.457(6)		
O1Ba1N2^{iii}	102.70(8)	O9Ba1N4	90.03(10)
O11^{ii}Ba1O1	80.08(10)	N4Ba1O1	108.89(9)
O11^{iii}Ba1O1	144.06(10)	N4Ba1N2^{iii}	145.25(9)
O11^{ii}Ba1O11^{iii}	64.88(13)	N5O1Ba1	124.7(2)
O11^{iii}Ba1O2^{iv}	130.70(11)	N5O2Ba1^{vi}	123.7(2)
O11^{ii}Ba1O2^{iv}	129.97(10)	N6O4Ba1^{v}	113.5(2)
O11^{ii}Ba1O4^{iii}	68.03(11)	C2N1Ba1	130.1(3)
O11^{iii}Ba1O4^{iii}	101.73(11)	C2N1C1	103.7(3)
O11iiBa1N1	69.89(11)	C1N1Ba1	126.1(3)
O11^{iii}Ba1N2^{iii}	72.73(11)	C4N3C5	103.2(4)
O11^{ii}Ba1N2^{iii}	92.85(11)	O4N6C3	116.6(4)
O11^{ii}Ba1N4	78.95(11)	O3N6O4	123.7(4)
O11^{iii}Ba1N4	73.23(11)	O3N6C3	119.7(4)
O2^{iv}Ba1Ba1^{i}	140.08(6)	O6N7O5	123.1(4)
O2^{iv}Ba1O1	78.01(9)	O6N7C5	119.1(4)
O2^{iv}Ba1N2^{iii}	135.65(9)	O5N7C5	117.5(4)
O2^{iv}Ba1N4	66.83(9)	O8N8C6	118.7(4)
O4^{iii}Ba1Ba1^{i}	84.28(6)	O7N8O8	122.4(4)
O4^{iii}Ba1O1	55.12(8)	O7N8C6	118.9(4)
O4^{iii}Ba1O2^{iv}	127.56(9)	O1N5C2	116.0(3)
O4^{iii}Ba1N2^{iii}	51.45(9)	O2N5O1	123.2(4)
O4^{iii}Ba1N4	144.92(9)	O2N5C2	120.8(4)
N1Ba1Ba1^{i}	93.93(8)	C3N2Ba1^{v}	111.1(3)
N1Ba1O1	52.10(9)	C1N2Ba1^{v}	140.3(3)
N1Ba1O11^{iii}	117.12(11)	C1N2C3	102.8(3)
N1Ba1O2^{iv}	61.11(9)	C6N4Ba1	139.6(3)
N1Ba1O4^{iii}	99.23(9)	C4N4Ba1	116.0(3)
N1Ba1N2^{iii}	150.54(9)	C4N4C6	103.1(3)
N1Ba1N4	56.84(10)	N2C3N6	119.4(4)

O10Ba1O1	58.98(9)	C2C3N6	130.9(4)
O10Ba1O11^{ii}	129.64(10)	N4C6N8	121.6(4)
O10Ba1O11^{iii}	141.59(11)	N4C6C5	108.9(4)
O10Ba1O2^{iv}	71.81(9)	C5C6N8	129.0(4)
O10Ba1O4^{iii}	64.88(9)	N1C2N5	117.0(4)
O10Ba1N1	100.9(1)	N1C2C3	108.3(4)
O10Ba1N2^{iii}	71.28(9)	C3C2N5	134.6(4)
O10Ba1N4	138.59(9)	N3C4C1	123.1(4)
O9Ba1Ba1i	105.63(7)	N4C4N3	115.8(4)
O9Ba1O1	140.94(9)	N4C4C1	121.2(4)
O9Ba1O11ii	138.23(10)	N3C5N7	120.1(4)
O9Ba1O11^{iii}	73.36(10)	N3C5C6	109.0(4)
O9Ba1O2^{iv}	78.84(9)	C6C5N7	130.8(4)
O9Ba1O4^{iii}	122.47(10)	N1C1C4	119.0(4)
O9Ba1N1	134.91(10)	N2C1N1	115.7(4)
O9Ba1O10	84.03(10)	N2C1C4	125.4(4)
O9Ba1N2^{iii}	73.71(10)		

(i) 2−x, 1−y, 1−z; (ii) 1−x, 1−y, 1−z; (iii) 1+x, y, z; (iv) x, 1.5−y, −0.5+z; (v) −1+x, y, z; (vi) x, 1.5−y, 0.5+z.

4. Composition of detonation products of complexes 1, 3, 4 and 5

Table S9. Composition of detonation products of complex **1**

Products	mol/mol	mol/kg	Mol %
N_2	3.99E+00	1.01E+01	34.9533
CO_2	2.00E+00	5.07E+00	17.4928
C(d)	1.96E+00	4.98E+00	17.1638
H_2O	1.41E+00	3.58E+00	12.3389
Na_2CO_3(s)	1.00E+00	2.54E+00	8.753
CH_2O_2	5.57E−01	1.41E+00	4.8762
CO	4.79E−01	1.22E+00	4.1941
NH_3	1.15E−02	2.93E−02	0.101
H_2	1.03E−02	2.61E−02	0.0901
CH_4	2.08E−03	5.29E−03	0.0182
HCN	1.89E−03	4.79E−03	0.0165
C_2H_6	9.78E−05	2.48E−04	0.0009
C_2H_4	8.79E−05	2.23E−04	0.0008
CH_3OH	2.83E−05	7.17E−05	0.0002
NO	5.75E−06	1.46E−05	0.0001
N_2H_4	3.41E−06	8.66E−06	0
H	2.42E−06	6.13E−06	0
NH_2	2.34E−06	5.95E−06	0
CH_2O	9.25E−07	2.35E−06	0
OH	6.57E−07	1.67E−06	0
CHNO	5.11E−07	1.30E−06	0

CNO	5.11E−07	1.30E−06	0
O_2	2.02E−07	5.12E−07	0
O	1.02E−07	2.58E−07	0
NO_2	9.34E−09	2.37E−08	0
N_2O	8.36E−09	2.12E−08	0
N	7.47E−09	1.90E−08	0
C(gr)	2.75E−10	6.98E−10	0
Na_2CO_3(l)	7.37E−11	1.87E−10	0
NaOH(l)	8.75E−12	2.22E−11	0
Na	7.13E−12	1.81E−11	0
NaOH(s)	4.25E−12	1.08E−11	0
NaOH	1.74E−17	4.41E−17	0
Na_2O(l)	5.14E−18	1.30E−17	0
Na(s)	3.73E−18	9.47E−18	0
Na(l)	3.59E−18	9.11E−18	0
NaO	9.41E−19	2.39E−18	0
Na_2O(s)	7.85E−19	1.99E−18	0

Table S10. Composition of detonation products of complex **3**

Products	mol/mol	mol/kg	Mol %
N_2	1.99E+00	9.20E+00	26.2485
H_2O	1.57E+00	7.23E+00	20.6305
CO_2	1.22E+00	5.63E+00	16.0594
C(d)	1.15E+00	5.32E+00	15.1834
MgO(s)	1.00E+00	4.62E+00	13.1812
CH_2O_2	3.78E−01	1.75E+00	4.9846
CO	2.42E−01	1.12E+00	3.1866
NH_3	1.65E−02	7.63E−02	0.2176
H_2	1.43E−02	6.59E−02	0.1879
CH_4	7.62E−03	3.52E−02	0.1005
HCN	7.46E−04	3.45E−03	0.0098
C_2H_6	5.48E−04	2.53E−03	0.0072
C_2H_4	1.53E−04	7.06E−04	0.002
CH_3OH	4.86E−05	2.24E−04	0.0006
N_2H_4	1.57E−06	7.25E−06	0
CH_2O	7.63E−07	3.53E−06	0
NH_2	7.15E−07	3.30E−06	0
H	6.67E−07	3.08E−06	0
NO	4.79E−07	2.21E−06	0
CHNO	2.30E−07	1.06E−06	0
OH	1.36E−07	6.28E−07	0
CNO	3.00E−08	1.39E−07	0
O_2	8.46E−09	3.91E−08	0
O	3.88E−09	1.79E−08	0

N_2O	5.30E−10	2.45E−09	0
C(gr)	3.71E−10	1.71E−09	0
N	2.30E−10	1.06E−09	0
NO_2	2.24E−10	1.04E−09	0
$Mg(OH)_2$(s)	3.12E−11	1.44E−10	0
Mg	4.41E−15	2.04E−14	0
MgOH	6.49E−19	3.00E−18	0
MgO	4.89E−20	2.26E−19	0
Mg(s)	1.77E−20	8.18E−20	0
Mg(l)	5.18E−21	2.39E−20	0
MgO(l)	1.13E−21	5.21E−21	0

Table S11. Composition of detonation products of complex **4**

Products	mol/mol	mol/kg	Mol %
H_2O	6.06E+00	1.26E+01	35.4285
N_2	3.97E+00	8.26E+00	23.21
CO_2	2.23E+00	4.64E+00	13.0326
C(d)	1.94E+00	4.04E+00	11.3531
CH_2O_2	1.72E+00	3.57E+00	10.0398
CaO(l)	1.00E+00	2.08E+00	5.8487
NH_3	6.32E−02	1.31E−01	0.3694
CO	5.27E−02	1.10E−01	0.3083
CH_4	4.85E−02	1.01E−01	0.2838
H_2	1.51E−02	3.14E−02	0.0883
C_2H_6	6.26E−03	1.30E−02	0.0366
C_2H_4	7.57E−05	1.58E−04	0.0004
CH_3OH	5.54E−05	1.15E−04	0.0003
HCN	5.21E−05	1.08E−04	0.0003
CaO(s)	6.62E−06	1.38E−05	0
N_2H_4	1.22E−06	2.54E−06	0
NH_2	2.25E−08	4.68E−08	0
CH_2O	1.96E−08	4.08E−08	0
H	7.43E−09	1.55E−08	0
NO	2.94E−09	6.12E−09	0
CHNO	2.18E−09	4.54E−09	0
OH	8.88E−10	1.85E−09	0
C(gr)	1.32E−10	2.74E−10	0
CNO	3.89E−11	8.11E−11	0
O_2	2.44E−11	5.09E−11	0
O	3.63E−12	7.55E−12	0
N_2O	1.37E−12	2.85E−12	0
NO_2	3.83E−13	7.98E−13	0
N	9.20E−14	1.91E−13	0
Ca	7.96E−20	1.66E−19	0

Table S12. Composition of detonation products of complex **5**

Products	mol/mol	mol/kg	Mol %
N_2	4.00E+00	7.94E+00	28.5701
H_2O	2.99E+00	5.93E+00	21.3212
CO_2	2.97E+00	5.89E+00	21.1797
C(d)	1.95E+00	3.87E+00	13.9325
CO	1.08E+00	2.15E+00	7.7443
BaO(s)	1.00E+00	1.99E+00	7.1428
H_2	1.49E−02	2.97E−02	0.1067
NO	2.19E−04	4.36E−04	0.0016
O_2	4.88E−05	9.69E−05	0.0003
H	3.86E−05	7.67E−05	0.0003
O	3.55E−05	7.05E−05	0.0003
NH_2	2.65E−05	5.26E−05	0.0002
OH	1.35E−05	2.67E−05	0.0001
NO_2	3.24E−06	6.43E−06	0
N	2.31E−06	4.59E−06	0
N_2O	2.47E−07	4.91E−07	0
Ba	2.80E−10	5.56E−10	0
BaO(l)	1.85E−10	3.68E−10	0

5. Snap shots of laser initiation experiments

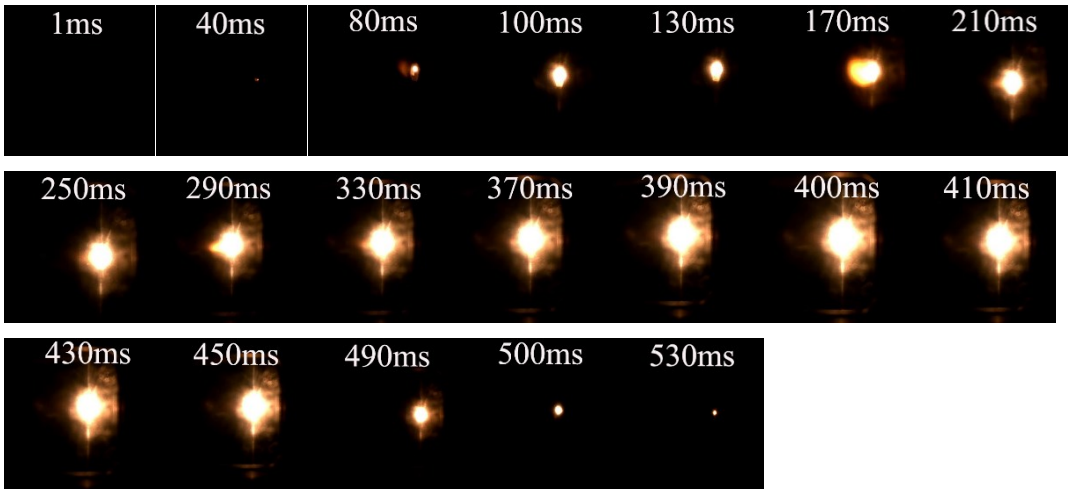
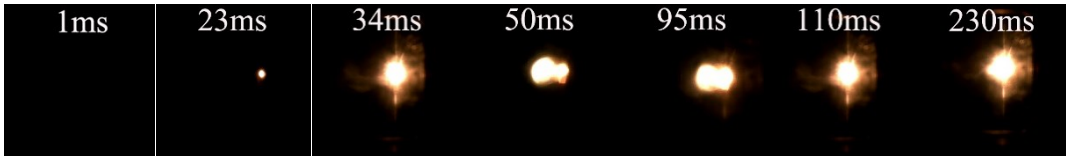


Figure S1. Snap shots of the laser initiation process of **TNBI**.



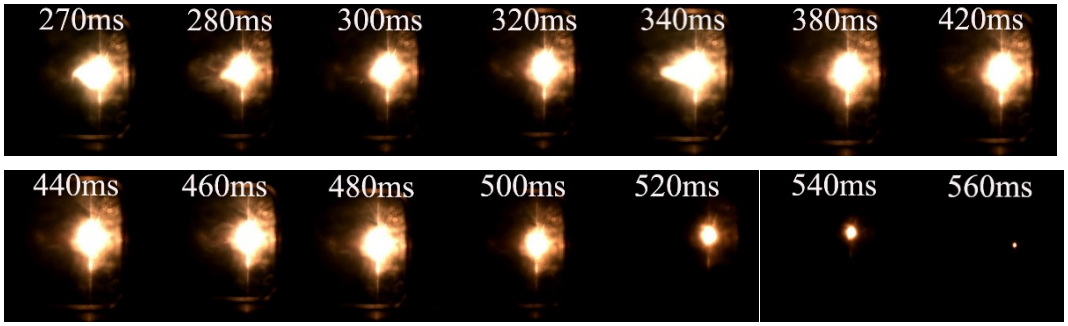


Figure S2. Snap shots of the laser initiation process of complex **2**.

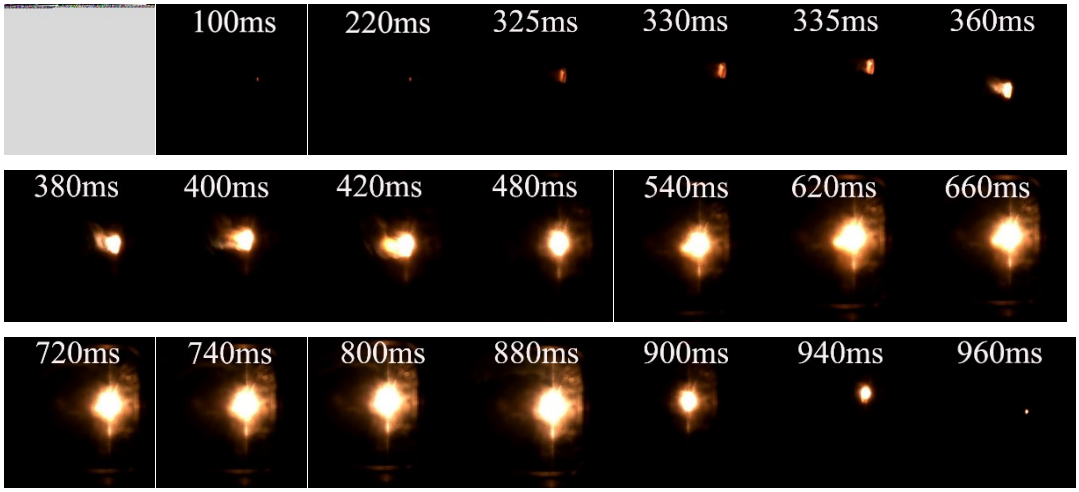


Figure S3. Snap shots of the laser initiation process of complex **3**.

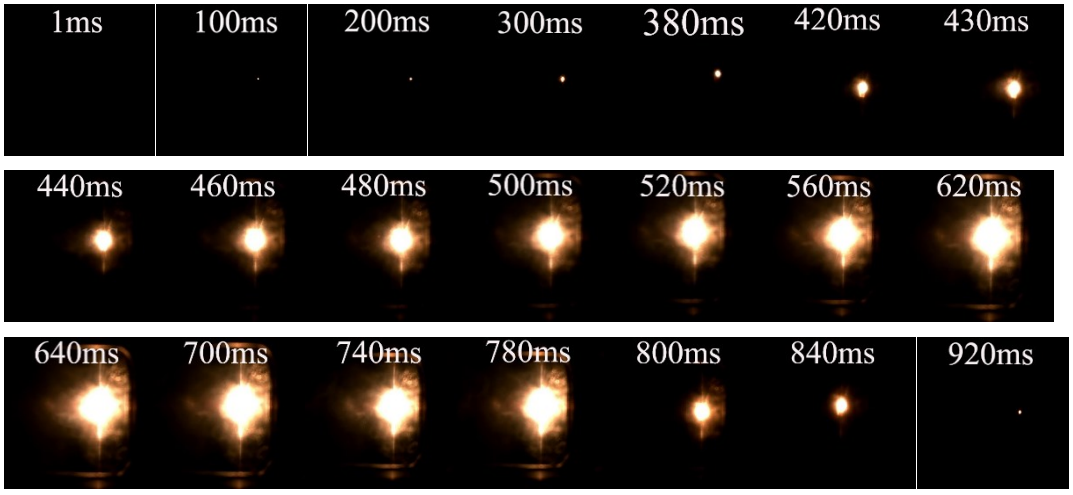


Figure S4. Snap shots of the laser initiation process of complex **4**.

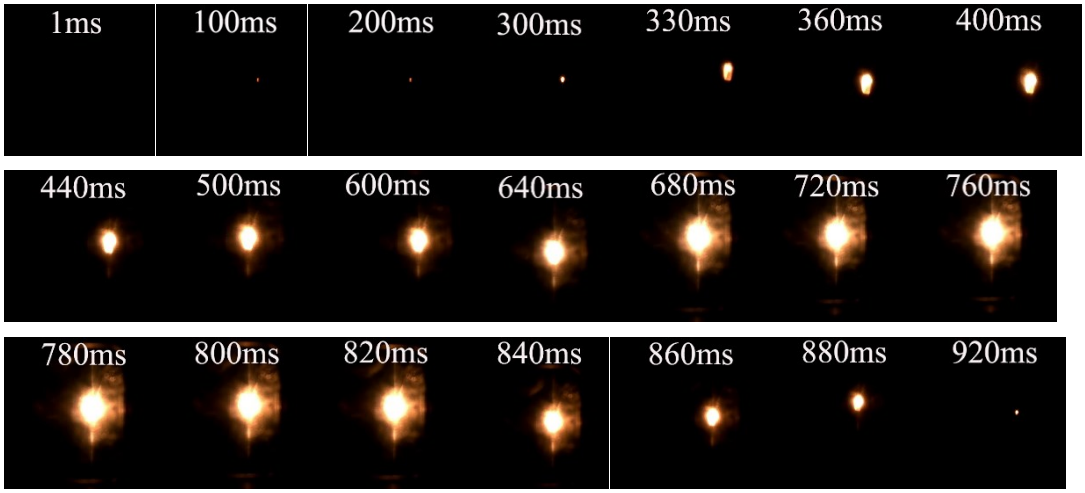


Figure S5. Snap shots of the laser initiation process of complex **5**.

6. Detailed calculation of enthalpies of formation.

Table S13. Detailed calculation of enthalpies of formation of complexes **1**, **3**, **4**, and **5**

	Calc. Density (g/cm^3)	Formula sum	Q_v (kJ/mol)
Complex **1**	1.972	C6 H4 N8 Na2 O10	2296.636
Complex **3**	1.890	C3 H4 Mg N4 O6	1345.988
Complex **4**	1.814	C6 H16 Ca N8 O15	2547.710
Complex **5**	2.411	C6 H6 Ba N8 O11	3241.980
	n_s-n_0	$\Delta_c H$ （kJ/mol）	$\Delta_f H$
$Na_2C_6H_4N_8O_{10} + 2.5O_2 =$ $2H_2O + 6CO_2 + 4N_2 + 1Na_2O$	7.5	2315.218232	383.207
$MgC_3H_4N_4O_6 + 1.5O_2 =$ $2H_2O + 3CO_2 + 2N_2 + MgO$	3.5	1354.660389	-149.831
$CaC_6H_{16}N_8O_{15} + 3O_2 =$ $8H_2O + 6CO_2 + 4N_2 + CaO$	7	2565.053456	-1019.89
$BaC_6H_6N_8O_{11} + 2.5O_2 =$ $3H_2O + 6CO_2 + 4N_2 + BaO$	7.5	3260.562421	908.813

$\Delta_f H(C_6H_4N_8Na_2O_{10},s) =$
$1\Delta_f H(Na_2O,s)+2\Delta_f H(H_2O,l)+5\Delta_f H(CO,g)+1\Delta_f H(CO_2,g)+4\Delta_f H(N_2,g) - \Delta_c H(C_6H_4N_8Na_2O_{10})$

$\Delta_f H(C_3H_4MgN_4O_6,s) =$
$\Delta_f H(MgO,s)+2\Delta_f H(H_2O,l)+3\Delta_f H(CO,g)+2\Delta_f H(N_2,g) -\Delta_c H(C_3H_4MgN_4O_6)$

$\Delta_f H(C_6H_{16}CaN_8O_{15},s) =$
$\Delta_f H(CaO,s)+8\Delta_f H(H_2O,l)+6\Delta_f H(CO,g)+4\Delta_f H(N_2,g) -\Delta_c H(C_6H_{16}CaN_8O_{15})$

$\Delta_f H(C_6 H_6 Ba N_8 O_{11},s)$ =
$\Delta_f H(BaO,s)+3\Delta_f H(H_2O,l)+5\Delta_f H(CO,g)+1\Delta_f H(CO_2,g)+4\Delta_f H(N_2,g)$ $-\Delta_c H(C_6 H_6 Ba N_8 O_{11})$

7. References.

(1) T. W. Myers, J. A. Bjorgaard, K. E. Brown, D. E. Chavez, S. K. Hanson, R. J. Scharff, S. Tretiak, and J. M. Veauthier, Energetic Chromophores: Low−Energy Laser Initiation in Explosive Fe(II) Tetrazine Complexes. *J. Am. Chem. Soc*. 2016, **138**, 4685−4692.

(2) T. W. Myers, K. E. Brown, D. E. Chavez, R. J. Scharff, and J. M. Veauthier, Laser Initiation of Fe(II) Complexes of 4−Nitropyrazolyl Substituted Tetrazine Ligands. *Inorg. Chem*. 2017, **56**, 2297−2303.

(3) J. Evers, I. Gospodinov, M. Joas, T. M. Klapötke, and J. Stierstorfer, Cocrystallization of Photosensitive Energetic Copper(II) Perchlorate Complexes with the Nitrogen−rich Ligand 1,2−Di(1Htetrazol−5−yl)ethane. *Inorg. Chem.* 2014, **53**, 11749−11756.

(4) M. Joas, T. M. Klapötke, and N. Szimhardt, *Chem. Eur. J.* 2013, **19**, 9995−10003.

(6) G. Steinhauser, and T. M. Klapötke, *Angew. Chem. Int. Ed.* 2008, **47**, 3330−3347.