Electronic Supplementary Material (ESI) for Dalton Transactions.

Performance enhancement strategy of nitrogen-rich compounds based on nitrogen-boron bonds

Kunkai Wang [a], Kaidi Yang [a], Heng Li [a], Junlin Zhang [a] Minjie Wu [a], Xiangzhi Li [a], Qi Xue [a] , Bozhou Wang [a,b]*, Fuqiang Bi [a,b]*

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1. General information

Reagents and sample preparation

All reagents were purchased from Aladdin Bio-Chem Technology CO., Ltd (Shanghai, China) and were used without further purification unless otherwise indicated. Acetonitrile was purchased from Innochem with extra-dry, molecular sieves (4 A), Water ≤ 50 ppm, in resealable bottle. Mesitylene was distilled with Na under standard procedures. 5-AT was dried in vacuum at 60°C for 6 hours.

Apparatus and measurements

^{1}H, ^{13}C and ^{11}B NMR spectra were measured with AV 500 NMR spectrometer (Bruker, Switzerland). ^{15}N NMR spectra were measured with AV 800 NMR spectrometer (Bruker, Switzerland). Infrared spectra were was measured by an EQUINOX 55 Fourier transform Infrared spectrometer (Bruker, Germany). Elemental analyses were performed with the vario EL cube elemental analyzer (Elmentar, Germany). The thermal analysis experiment and the glass transition temperature (T_g) were performed with a model TG STA 499 F3 instrument (NETZSCH, Germany). The sensitivity towards impact (IS) were determined according to BAM standards. The ignition delay time of fuels could be measured by two methods, including the observation of visible light and the analysis of the radiation signals from the PMT.[1] The density was measured by AccuPyc II 1345 gas displacement pycnometry system (Micromeritics, American). TG-DSC-FTIR-MS technique made by ourselves under a heating rate of 10 ^{o}C/min with Air.

DFT calculations

All quantum chemical calculations were carried out using the program package Gaussian 16. The geometry optimizations of the molecules and frequency analyses were accomplished by using the B3LYP with the 6-31+G** basis set. The ESP analysis of compounds were carried out based upon the B3LYP/6-31+G** method by Gaussian16 with optimized structure, calculated by Multiwfn 3.8 and VMD. The gas-state enthalpies and energies of formation of molecules were calculated using the quantum chemical CBS-4M calculations (H_{CBS-4M}) method in order to obtain accurate values.

2. Experimental procedure

Synthesis of compound Sodium or potassium tetrakis (5-aminotetrazolyl) borates 5a/b

In a 50 mL round-bottom flask, stir bar and condensing tube were added, argon gas was replaced for three times. Sodium or potassium borohydride (189.2 mg for $NaBH_4$, 269.7 mg for KBH_4, 5 mmol) and 10 mL mesitylene were added at room temperature, stirred quickly and slowly added 5-aminotetrazole (1.7014 g, 20 mmol) in portions. Then it was slowly heated (140℃for $NaBH_4$, 145℃ for KBH_4) and stirred for 4 days. The reaction could be monitored by ^{11}B NMR. After all sodium or potassium borohydride was completely consumed, the system was cooled to room temperature, the white solid was filtered and dried in vacuum to obtain potassium tetrakis (5-aminotetrazolyl) borates **5b**1.734 g, yield 90%.

^1H NMR (500 MHz, DMSO) δ 5.89 (s, 8H). ^{13}C NMR (126 MHz, DMSO) δ 158.23. ^{11}B NMR (160 MHz, DMSO) δ 1.58 (s).

Synthesis of compound dihydrobis (5-aminotetrazole) borane 6

In a 25 mL round-bottom flask, stir bar and condensing tube were added, argon gas was replaced for three times. Sodium or potassium borohydride (189.2 mg for $NaBH_4$, 269.7 mg for KBH_4, 5 mmol) and 7mL acetonitrile were added at room temperature, stirred quickly, and slowly added 5-aminotetrazole (850.7 mg, 10 mmol) in portions. Then it was slowly heated to reflux and stirred for 3 days. The reaction could be monitored by ^{11}B NMR. After all sodium or potassium borohydride was completely consumed, the system was cooled to room temperature, the white solid was filtered and dried in vacuum to obtain sodium or potassium dihydrobis (5-aminotetrazolyl) borates **3a/b** 1.0211 g, yield 90%.

^1H NMR (500 MHz, DMSO) δ 5.64 (s, 4H), 3.29 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 159.20. ^{11}B NMR (160 MHz, DMSO) δ -14.51 (s).

Sodium/potassium dihydrobis (5-aminotetrazolyl) borates **3a/b** (1.0211 g, 5 mmol) was added into a 25mL round-bottomed flask, adding the deionized water 3 mL and acetic acid 3 mL, stirred for 30 min, filtration and drying. The product **6** can be filtered in 679.2 mg, yield 75%.

^1H NMR (500 MHz, DMSO) δ 7.12 (b, 4H), 6.46 (s, 1H), 3.29 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 155.50. ^{11}B NMR (160 MHz, DMSO) δ -13.39 (s). The spectrum was consistent with the literature report.[2]

Synthesis of compound 5-aminotetrazolyl borane 7

A 50mL round-bottomed flask was filled with magneton, sealed with a plug, and a balloon was inserted at the top of the plug to balance internal and external pressure. 1M borane tetrahydrofuran solution (10 mL, 10 mmol) and 10 mL THF were added to the round-bottomed flask in an ice water bath. The system temperature was then kept below 5°C, and 5-amino-tetrazole (850.7 mg, 10 mmol) was slowly added. After being stirred for four hours, white solid gradually precipitated. After the reaction was complete, white solid was filtered, washed by ethanol and dried, the product 5-aminotetrazolyl borane **7** was obtained as a white solid (922 mg ; 95% yield).

^1H NMR (500 MHz, DMSO) δ 7.41 (s, 2H), 3.29 (s, 2H). ^{13}C NMR (126 MHz, DMSO) δ 153.99. ^{11}B NMR (160 MHz, DMSO) δ -19.16 (brs). ^{15}N NMR (81 MHz, DMSO) δ -14.33, -157.87, -326.11. IR (KBr, *ν*/cm): 3450, 3356, 3218, 2473, 2445, 2372, 2267, 1650, 1587, 1504, 1488, 1366, 1141, 1087, 1049, 1024,867, 768, 689. Anal. Calcd. for $C_1H_4B_1N_5O_2$ (%):C 12.40, H 4.16, N 72.28. Found C 12.41, H 4.27, N 70.12. HRMS (ESIMS) calcd for $C_1H_4B_1N_5K^+$ $[M + K]^+$ 136.0197, found 136.0191. HRMS (ESIMS) calcd for $C_2H_6B_1N_{10}^-$ $[M]^-$ 181.0875, found 181.0865; calcd for $C_3H_{10}B_2N_{15}^-$ $[M]^-$ 278.1435, found 278.1433; calcd for $C_4H_{14}B_3N_{20}^-$ $[M]^-$ 375.1995, found 375.1993; calcd for $C_5H_{18}B_4N_{25}^-$ $[M]^-$ 472.2555, found 472.2555; calcd for $C_6H_{22}B_5N_{30}^-$ $[M]^-$ 568.3151, found 568.3152; calcd for $C_7H_{26}B_6N_{35}^-$ $[M]^-$ 665.3711, found 665.3714.

3. NMR spectra of new compounds

Fig. S1 ^1H NMR (500 MHz, DMSO) of **5b:**

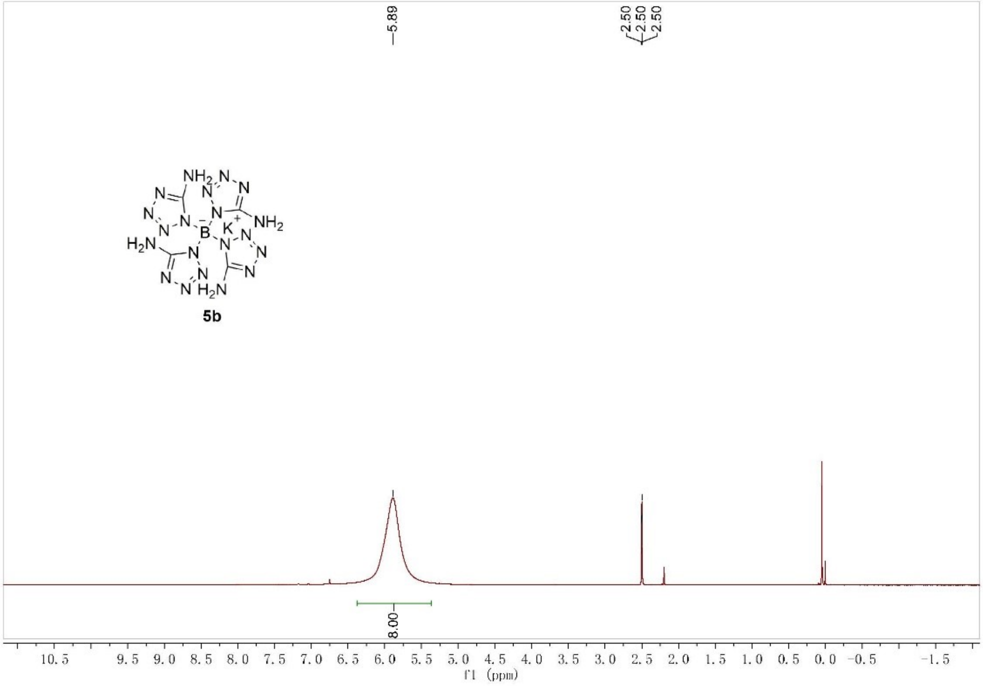


Fig. S2 ^{13}C NMR (126 MHz, DMSO) of **5b:**

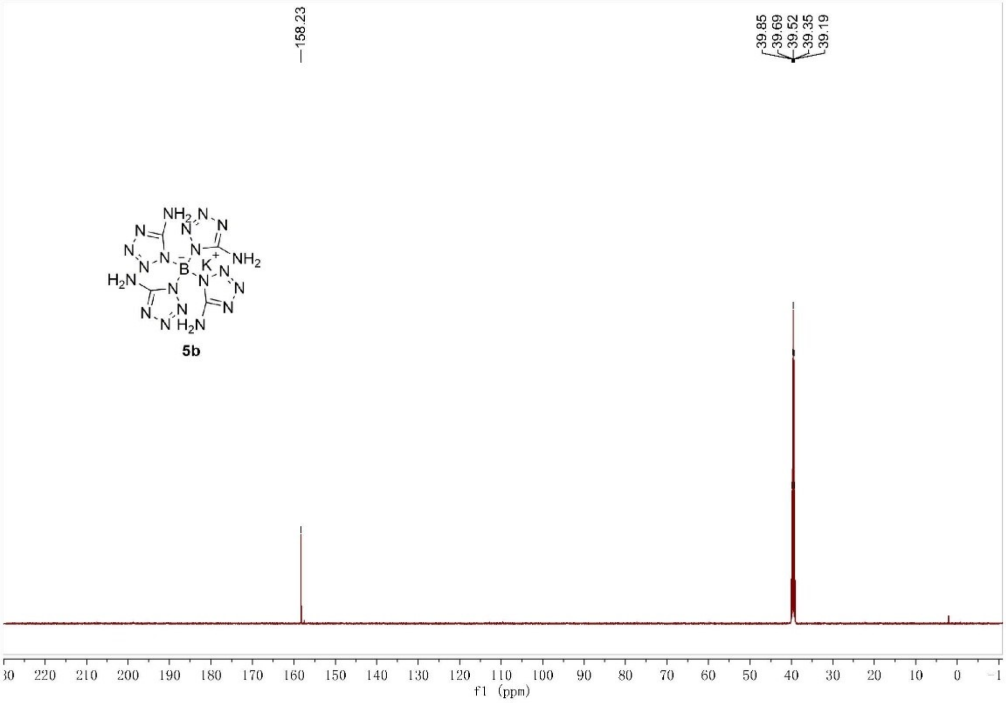


Fig. S3 ^{11}B NMR (160 MHz, DMSO) of **5b**:

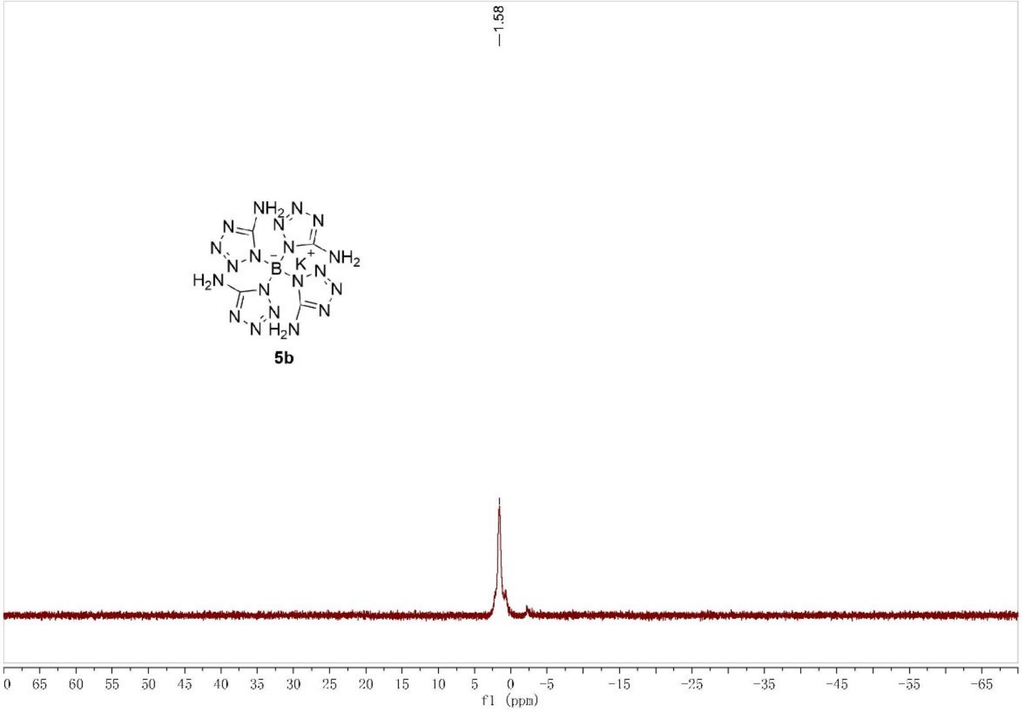


Fig. S4 ^{1}H NMR (500 MHz, DMSO) of **7:**

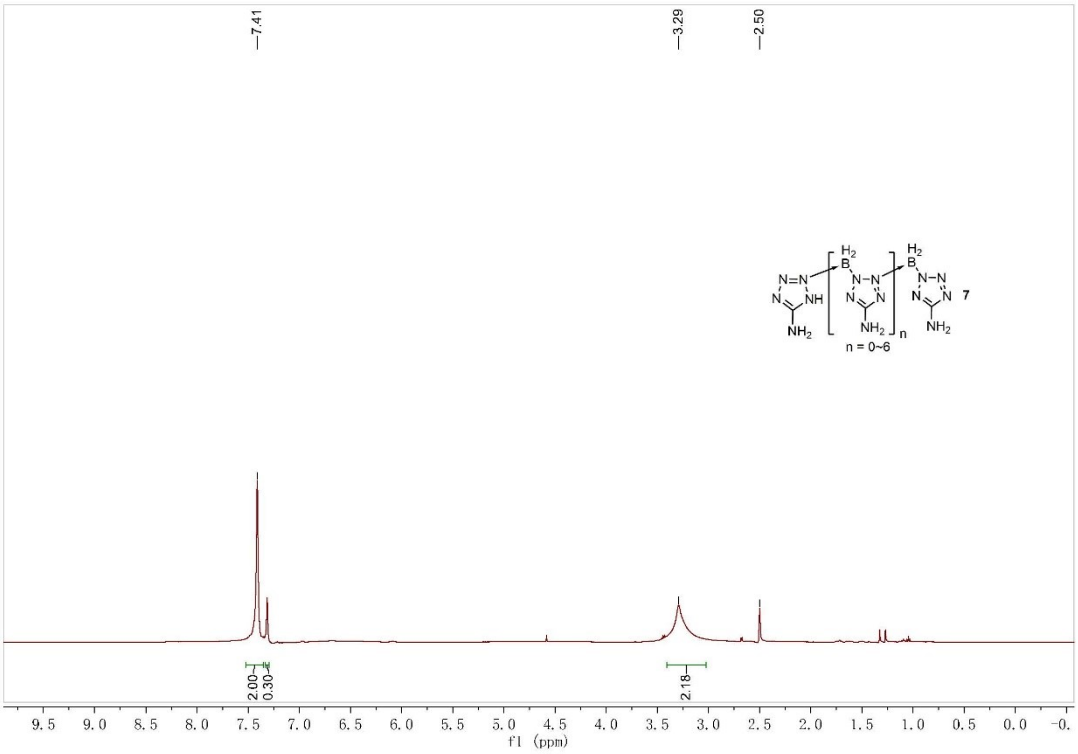


Fig. S5^{13}C NMR (126 MHz, DMSO) of **7:**

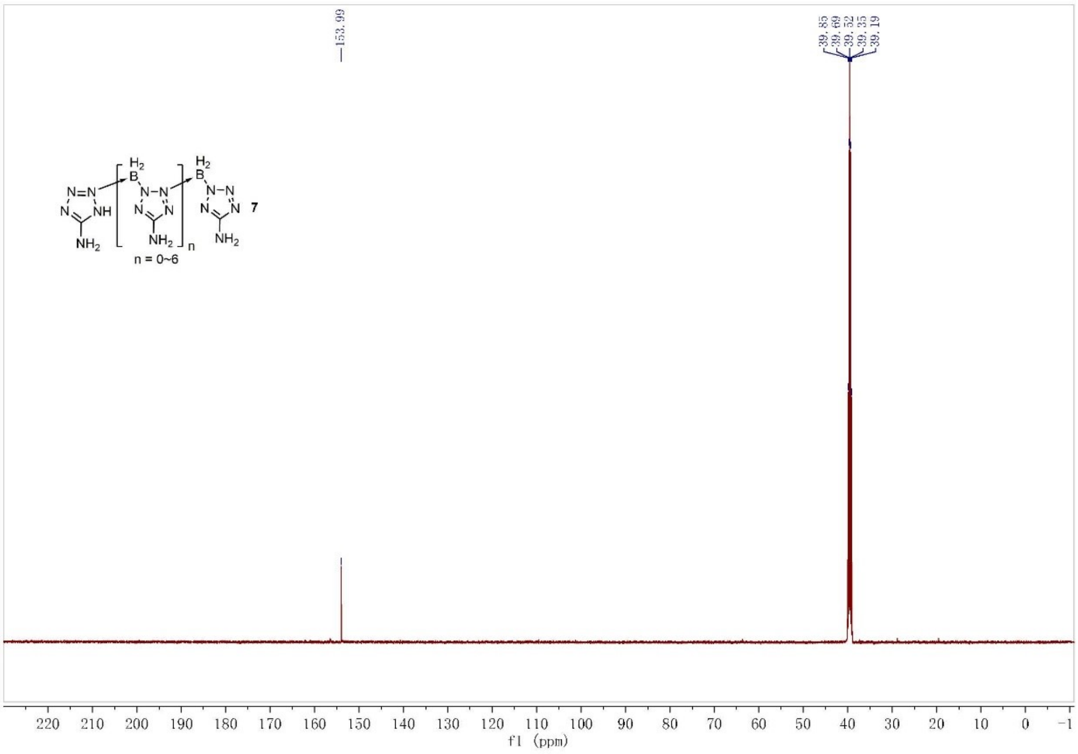


Fig. S6 ^{11}B NMR (160 MHz, DMSO) of **7**:

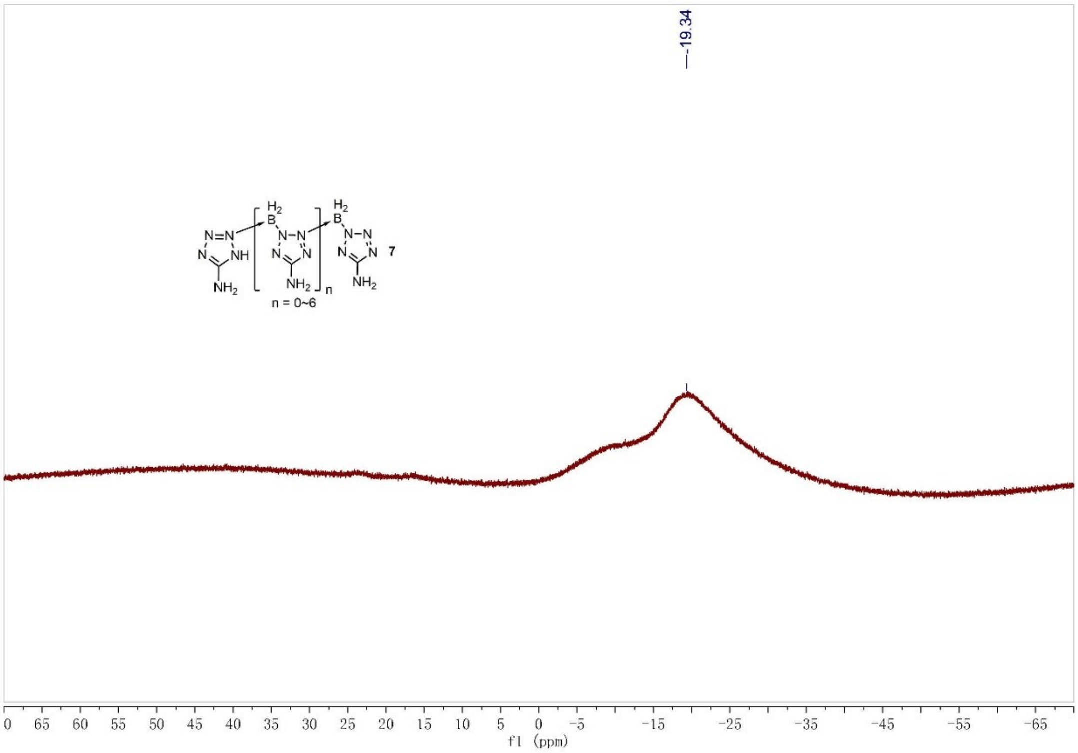
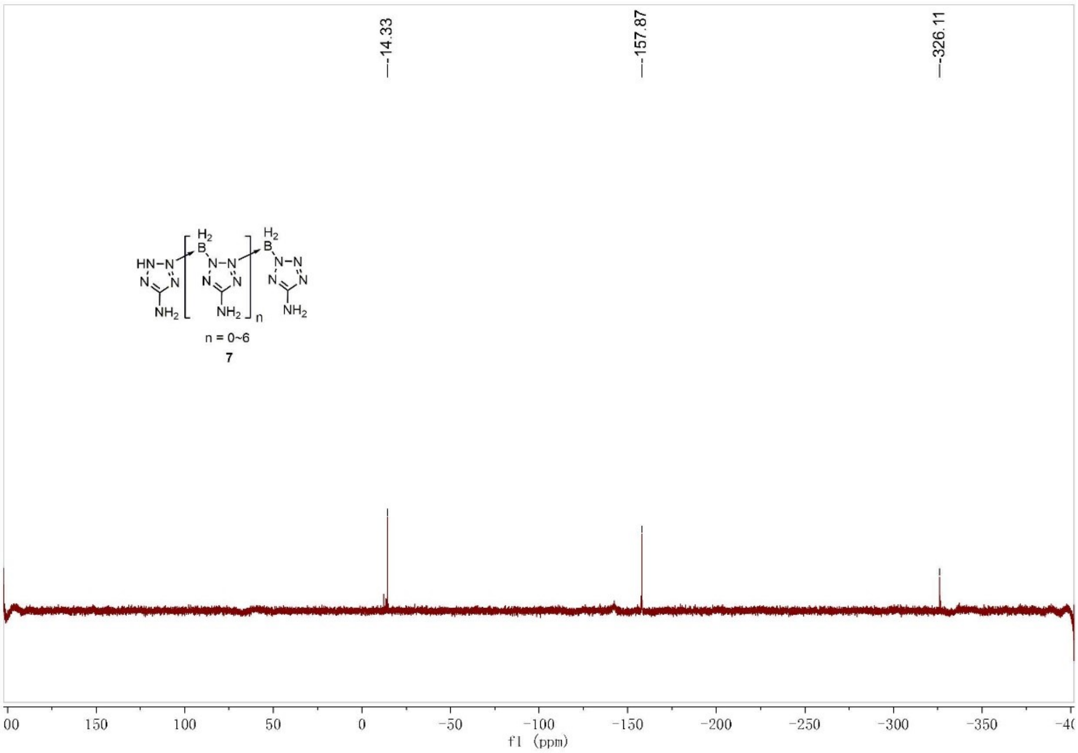


Fig. S7 ^{15}N NMR (81 MHz, DMSO) of **7** (NH$_3$ was selected as the NMR external references)



4. Laser ignition experiments

Lazer ignition experiment of **5-AT:**

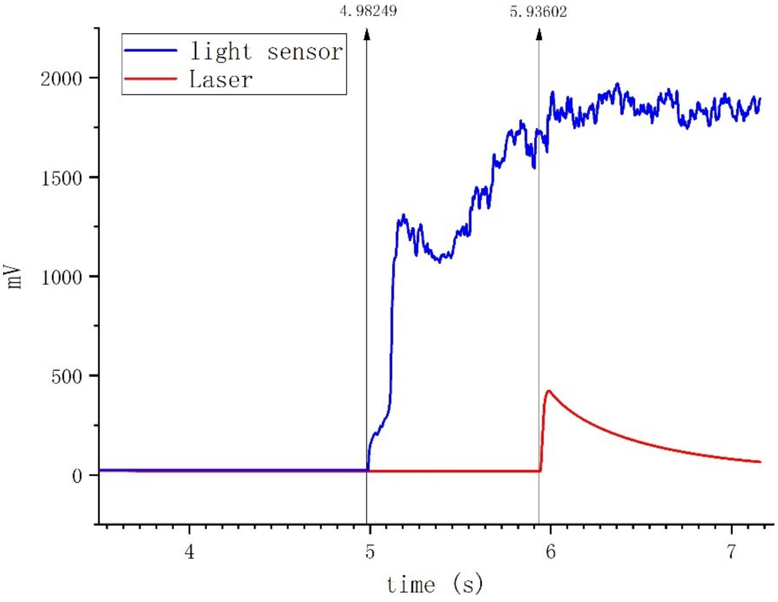


Fig. S8 Laser ignition experiment of **5-AT** at 40w

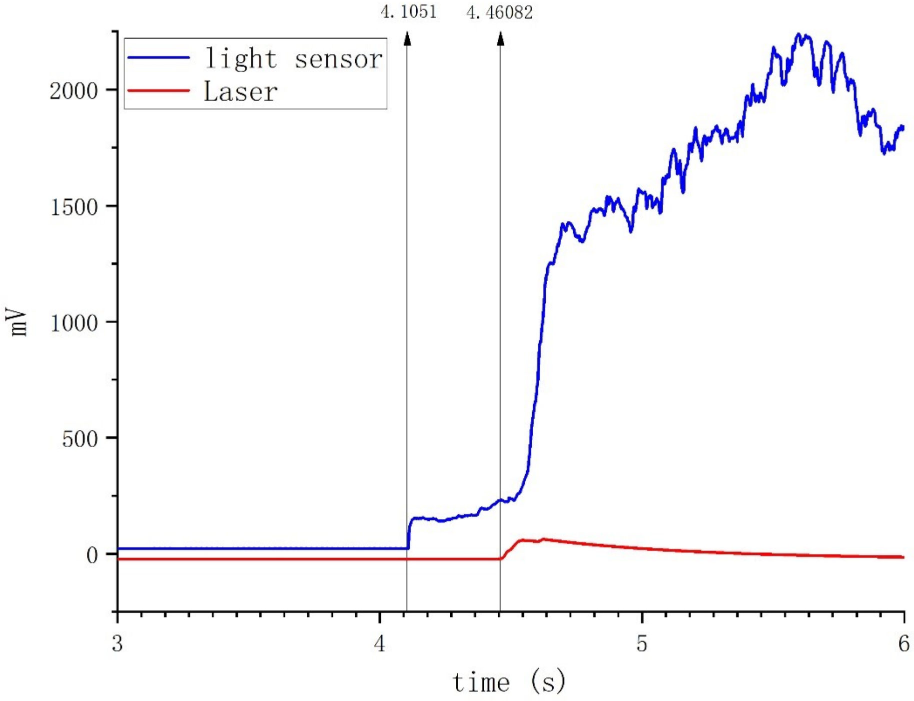


Fig. S9 Laser ignition experiment of **5-AT** at 67w

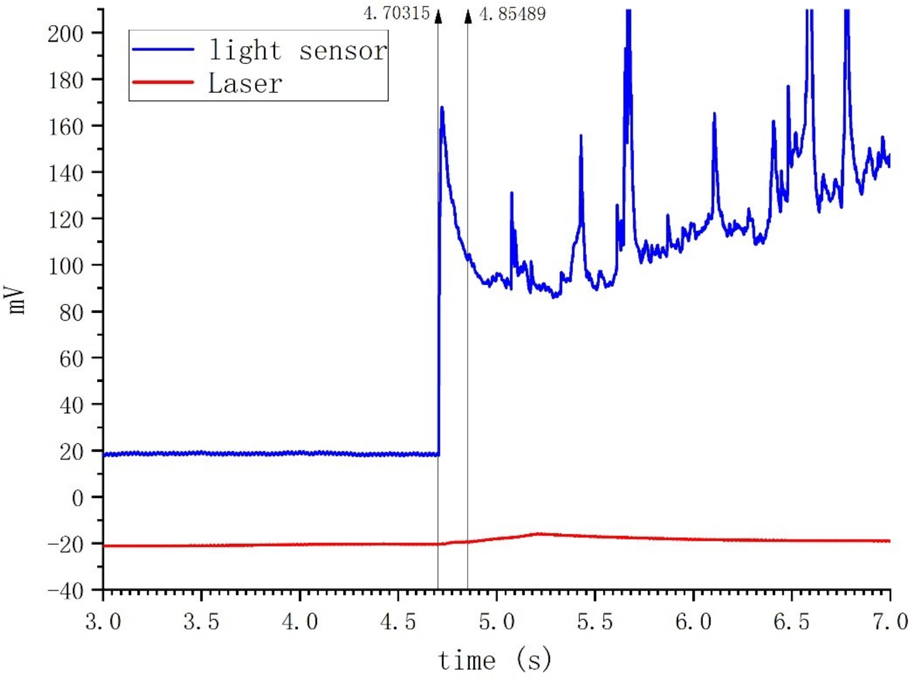


Fig. S10 Laser ignition experiment of **5-AT** at 94w

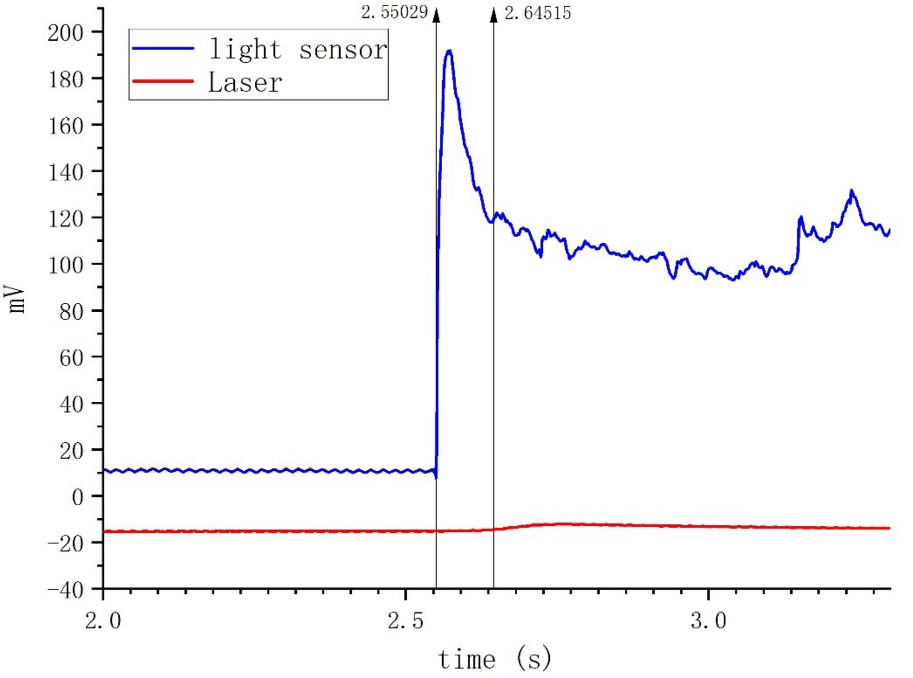


Fig. S11 Laser ignition experiment of **5-AT** at 121w

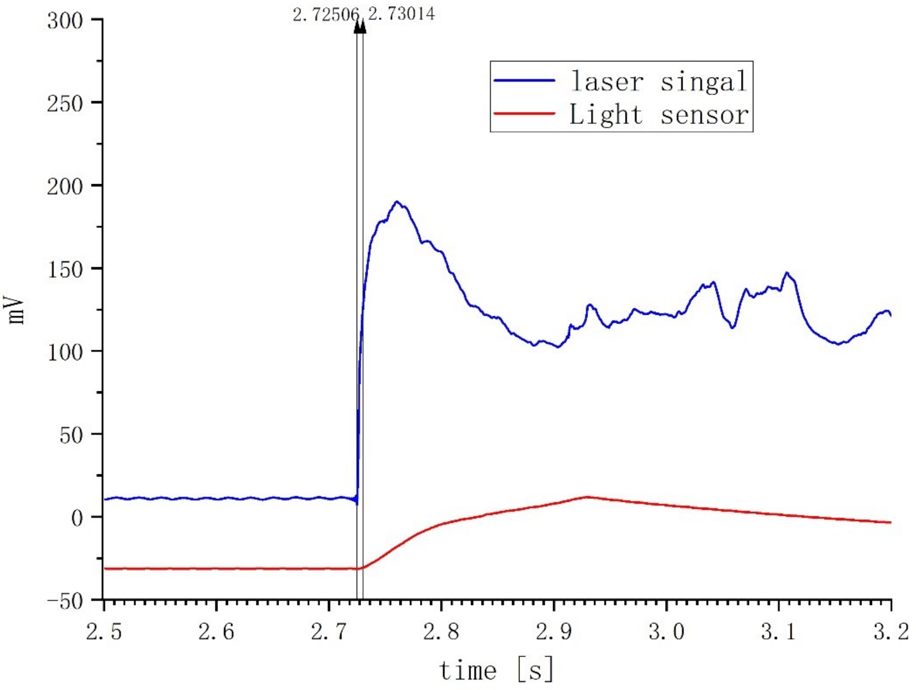


Fig. S12 Laser ignition experiment of **5-AT** at 175w

Laser ignition experiments of **7**

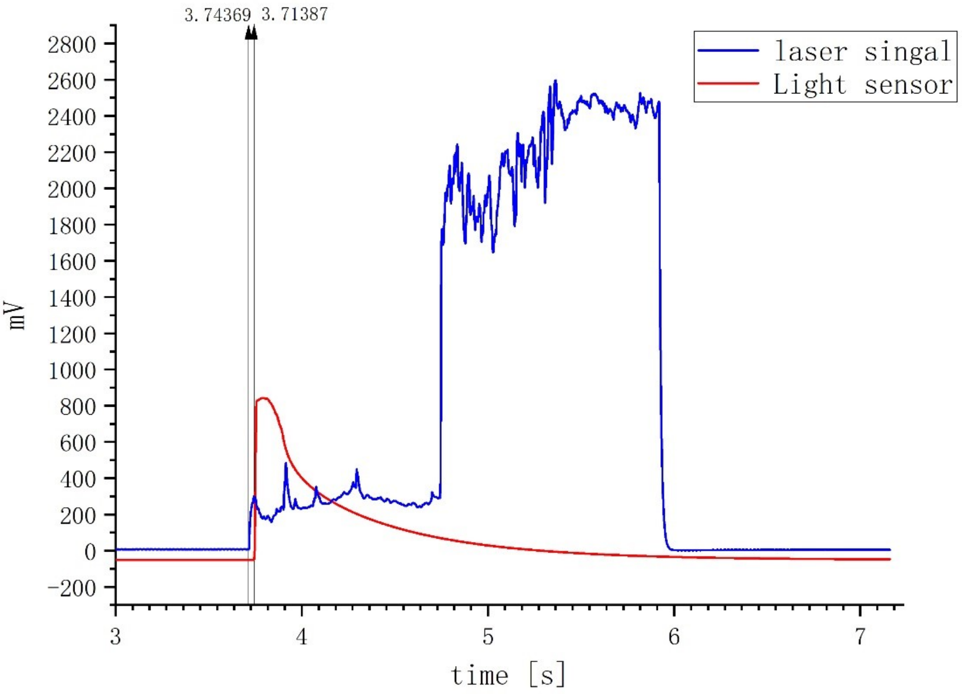


Fig. S13 Laser ignition experiment of **7** at 40w

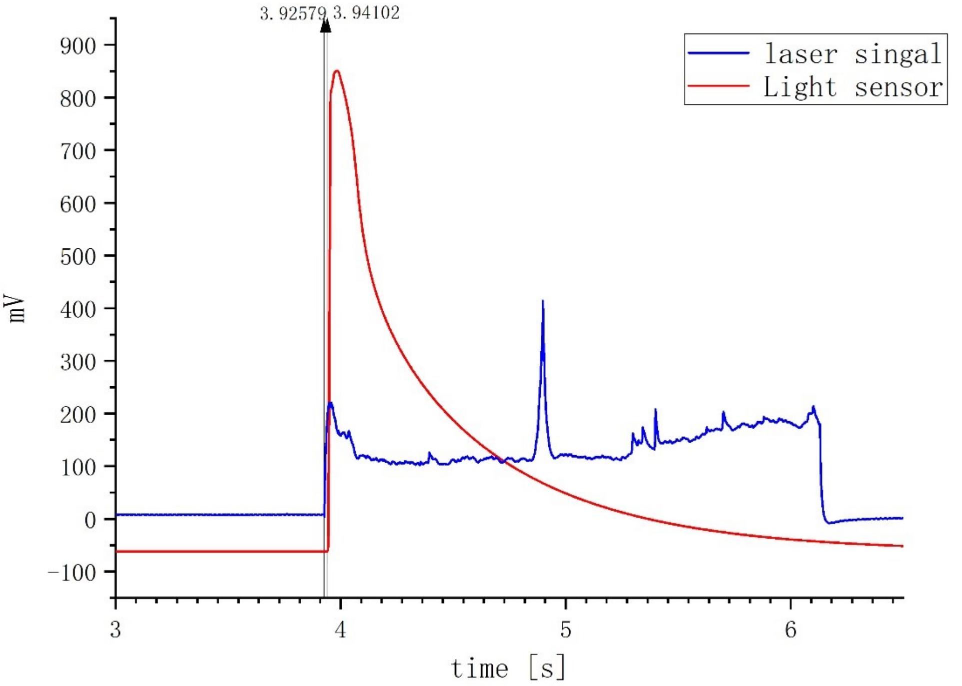


Fig. S14 Laser ignition experiment of **7** at 67w

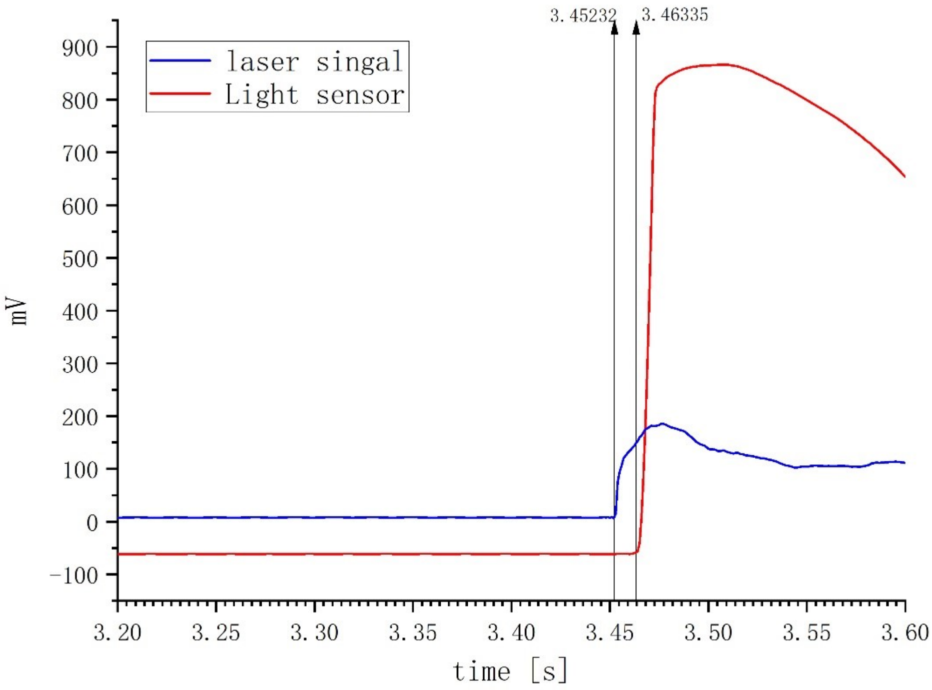


Fig. S15 Laser ignition experiment of **7** at 94w

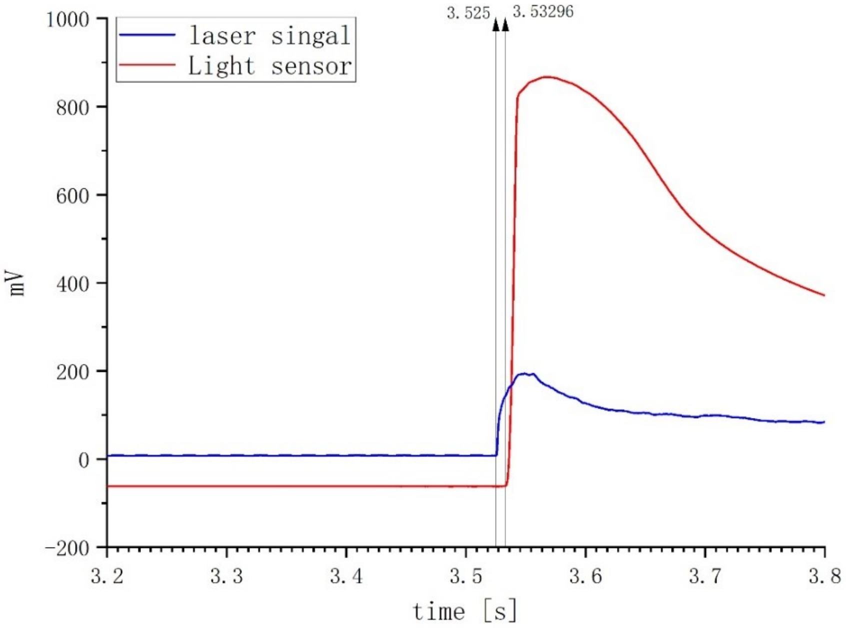


Fig. S16 Laser ignition experiment of **7** at 121w

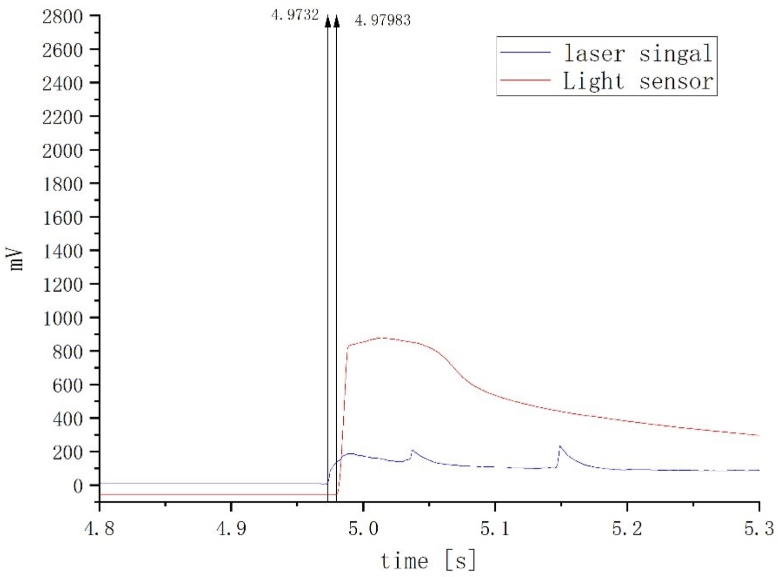


Fig. S17 Laser ignition experiment of **7** at 175w

5. Gas phase decomposition products of 7 by TG-DSC-FTIR-MS

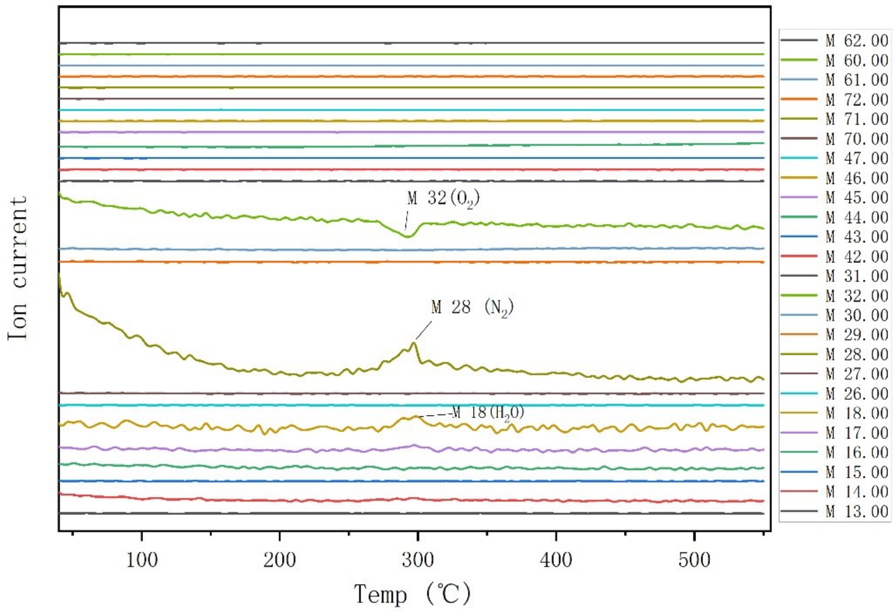


Fig. S18 The Mass spectrum signal of **7** gas phase decomposition products

6. Detonation product simulation by Explo 5

Table S1 The detonation products simulation **of C_1BN_5 7** by Explo 5

Products	Mol %
N_2	42.89
BN(s)	24.31
NH_3	10.52
CH_4	6.2
C	5.4736
C_2H_6	4.5
H_2	3.76
C_2H_4	1.34
HCN	0.9127
N_2H_4	0.0216
NH_2	0.0068

Table S2 Input orientation of monomer **7**:

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	7	0	-6.364175	0.365101	-0.313042
2	7	0	-7.325575	-0.706299	0.111058
3	6	0	-8.534975	-0.169999	0.327558
4	7	0	-8.481175	1.246001	0.075758
5	7	0	-7.238575	1.584601	-0.296342
6	7	0	-9.563746	-0.809264	0.695969
7	5	0	-4.913976	0.248106	-0.661253
8	1	0	-10.472222	-0.303236	0.841247
9	1	0	-9.508515	-1.845489	0.856245
10	1	0	-4.214926	1.347214	-1.02346
11	1	0	-4.302419	-0.956736	-0.61374

Table S3 Standard orientation of monomer **7**:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	7	0	-1.226488	-0.12017	-0.00001
2	7	0	0.029966	-0.940762	-0.000066
3	6	0	1.099222	-0.132164	-0.000006
4	7	0	0.660926	1.238693	0.000004
5	7	0	-0.679107	1.277116	-0.000019
6	7	0	2.306055	-0.514671	0.000034
7	5	0	-2.651436	-0.575735	0.000041
8	1	0	3.08126	0.193534	0.000079
9	1	0	2.531776	-1.540123	0.000022
10	1	0	-3.651884	0.333664	0.000088
11	1	0	-2.938774	-1.896849	0.000041

Table S4 Combustion time comparison of **5-AT** and **7**

Laser	**5-AT**	**7**
40w	0.67S	1.28s
67w	0.27S	1.64s
94w	weak[a]	1.63
121w	weak[a]	1.64
175w	0.68s	1.68

[a]Combustion is too weak to observe

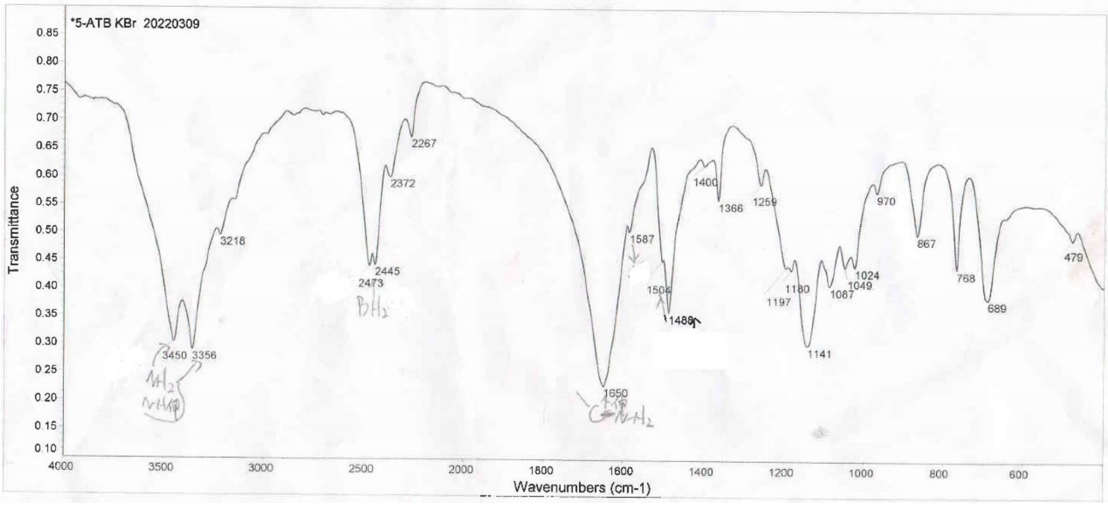


Fig. S19 The IR spectrum signal of **7**

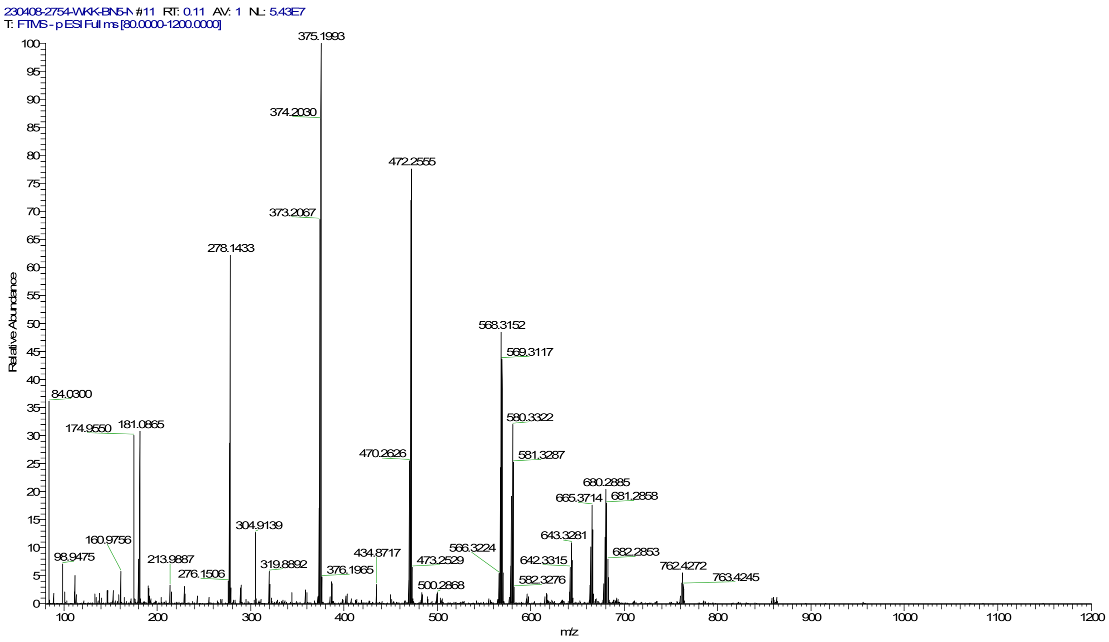


Fig. S20 The negative ion HRMS signal of oligomer **7**

Table S5 Enthalpy of formation of oligomer 7

Compound	$C_2H_7N_{10}B$	$C_3H_{11}N_{15}B_2$	$C_4H_{15}N_{20}B_3$	$C_5H_{19}N_{25}B_4$	$C_6H_{23}N_{30}B_5$	Monomer **7**
Enthalpy of formation (kJ/mol)	144.06	200.45	315.33	397.69	467.3	184.07

Table S6 Heat of detonation and detonation velocity of oligomer 7

Compound	5-AT	$C_2H_7N_{10}B$	$C_3H_{11}N_{15}B$ 2	$C_4H_{15}N_{20}B_3$	$C_5H_{19}N_{25}B_4$	$C_6H_{23}N_{30}B_5$	Monomer **7**
Heat of detonation (kJ/mol)	3289	2495	2860	4223	4280	4208	6016
Detonation velocity (m/s)	8212	6933	7446	8197	7944	8141	7462

Notes and references

1. a) X.F. Huang, M.Q. Zhang, C.Y. Lin, Y.H Yang, S.J. Li, H. Li, Y.J. Yang, Z. Qin, F.Q. Zhao, *Chemical Engineering Journal*, 2022, **450**, 138133. b) S. Li, X. Pan, Y. Jiang, S. Chang, X. Jin, Y. Yang, X. Huang, Y. Guo, *Propellants Explos. Pyrotech.* 2019, **44**, 1319–1326.
2. T. J. Groshens, *Journal of Coordination Chemistry*, 2010, **63**, 1882-1892.