Electronic Supporting Information Contents

A highly sensitive fluorescent nanofiber sensor functionalized with small organic molecules for specific analyte detection

Leqin Cheng,[a] Yunqi Tao,[a] Jie Chen,[b] Xiaohan Zhu,[b] Zhonglin Wei,[c] Ding Zhou,[d] Yuewei Zhang*[a] and Xue Yu*[a]

1. Experimental Section

1.1. Synthesis of compound (1)

The carbazole (0.5 g, 3 mmol), 2-fluorine-5-bromopyridine (0.66 g,3.75 mmol), and cesium carbonate (2.45 g,7.5 mmol) were dissolved in DMSO (4 mL). The reaction mixture was heated to 110 ^{o}C and stirred for 10 h. After the reaction, the mixture was cooled to room temperature and H_2O (10 mL) was added to the mixture to generate a white precipitate. The resulting precipitate was filtered and the filter cake was washed with H_2O, by column chromatography (petroleum ether: ethyl acetate, v:v = 50:1), the desired compound **1** was obtained as light solid (108 mg, 98% yield). The desired compound **2** was obtained as white solid (675 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (d, 1H), 8.11 (d, J = 7.7, 1.0 Hz, 2H), 8.02 (dd, J = 8.6, 2.5 Hz, 1H), 7.82 (d, J = 8.3, 0.9 Hz, 2H), 7.56 (d, J = 8.6, 0.8 Hz, 1H), 7.45 (t, J = 8.4, 7.2, 1.3 Hz, 2H), 7.33 (t, J = 7.5, 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.56, 141.01, 139.32, 126.45, 124.56, 121.37, 120.36, 119.94, 116.92, 111.22. HRMS (ESI): calcd for $C_{17}H_{11}BrN_2$, $[M + H]^+$: 323.0178; found, 323.0180.

1.2. Synthesis of compound (3)

The 4-bromine-1,8-naphthalene diphthalic anhydride (500 mg, 1.8 mmol), and aniline (1.68 mL, 18 mmol) were dissolved in 2-methoxyethanol (10 mL). The reaction mixture was heated to 130 ^{o}C and stirred for 48 hours. After the reaction, the mixture was cooled to room temperature, and a certain amount of n-hexane was added to the reaction mixture, stirred the mixture for 1 hour at room temperature, the precipitate was filtered, the filter cake was washed with n-hexane. By column chromatography (petroleum ether: ethyl acetate, v:v = 50:1), the desired compound **3** was obtained as white solid (260 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, J = 7.3, 1.2 Hz, 1H), 8.64 (d, J = 8.6, 1.2 Hz, 1H), 8.46 (d, J = 7.7 Hz, 1H), 8.08 (d, J = 7.8 Hz, 1H), 7.89 (t, J = 8.5, 7.2 Hz, 1H), 7.60–7.53 (m, 2H), 7.50 (d, 1H), 7.32 (d, J = 7.1, 1.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.81, 133.66, 132.50, 131.64, 131.29, 129.53, 128.94, 128.67, 128.27. HRMS (ESI): calcd for $C_{18}H_{10}BrNO_2$, $[M + H]^+$: 351.9968; found, 351.9955.

1.3. Synthesis of compound PPBD

The compound (2) (100 mg, 0.28 mmol), compound (3) (220 mg, 0.56 mmol), copper(I) chloride (28 mg, 0.28 mmol), cesium carbonate (182 mg, 0.56 mmol), 1,1'-Bis(diphenylphosphino)ferrocene (dppf) (16 mg, 0.028 mmol), and $Pd(OAc)_2$ (4 mg, 0.05 mmol) were dissolved in dry DMF (5 mL). After three cycles of degassing, the reaction mixture was stirred at 100 ^{o}C under a nitrogen atmosphere for 24 hours. By column chromatography (petroleum ether:ethyl acetate, v:v = 30:1), the desired compound **PPBD** was obtained as greenish-yellow solid (40 mg, 32% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (d, J = 2.5 Hz, 1H), 8.78 (d, J = 7.5 Hz, 1H), 8.76 (d, J = 7.4 Hz, 1H), 8.42 (d, J = 8.5 Hz, 1H), 8.17 (d, J = 7.8 Hz, 2H), 8.15-8.11 (m, 1H), 8.04 (d, J = 8.3 Hz, 2H), 7.89 (t, J = 2.6 Hz, 2H), 7.86 (d, 1H), 7.59 (t, J = 8.4, 6.8 Hz, 2H), 7.51 (t, J = 7.5, 1.3 Hz, 2H), 7.40 (s, 1H), 7.39-7.35 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$): δ 164.46, 164.40, 151.88, 149.82, 140.17, 136.59, 135.67, 135.16, 132.12, 131.86, 131.57, 130.40, 130.32, 129.90, 129.38, 128.52, 128.45, 127.29, 124.59, 123.39, 121.76, 121.09, 118.07, 111.95. HRMS (ESI): calcd for $C_{35}H_{21}N_3O_2$, $[M + H]^+$: 516.1707; found, 516.1715.

2. Supplementary Spectra

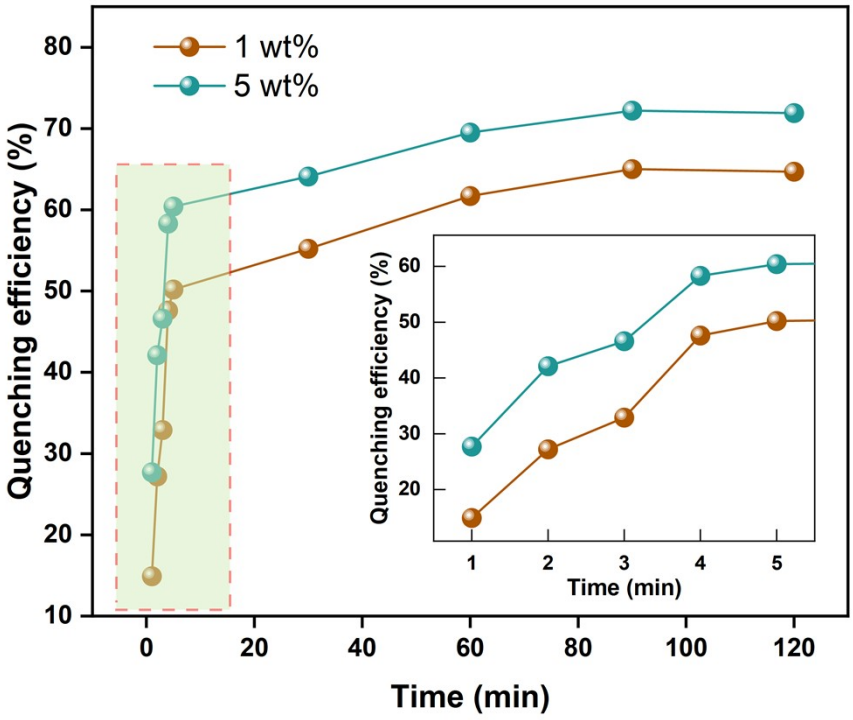


Fig. S1. Plot of the fluorescence quenching efficiency versus time of electrospinning membranes doped with different PPBD contents.

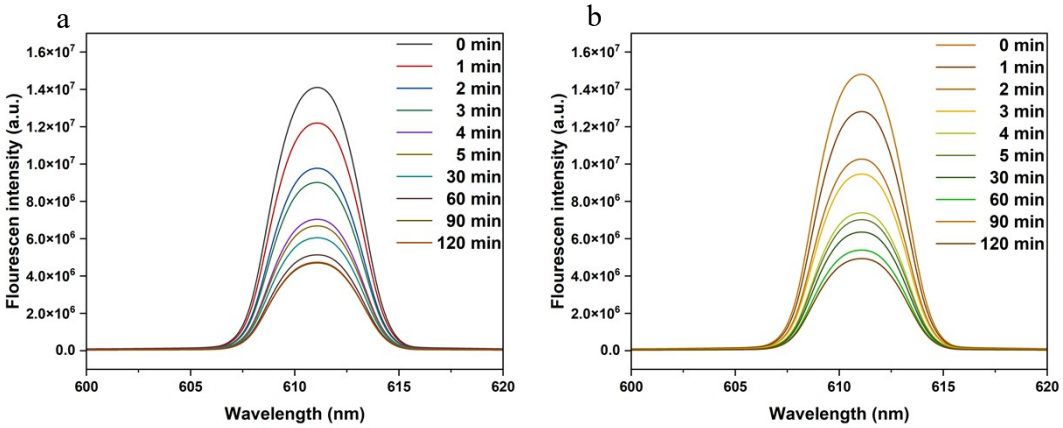


Fig. S2. Fluorescence spectra of the second batch (a) and the third batch. (b) in response to PETN.

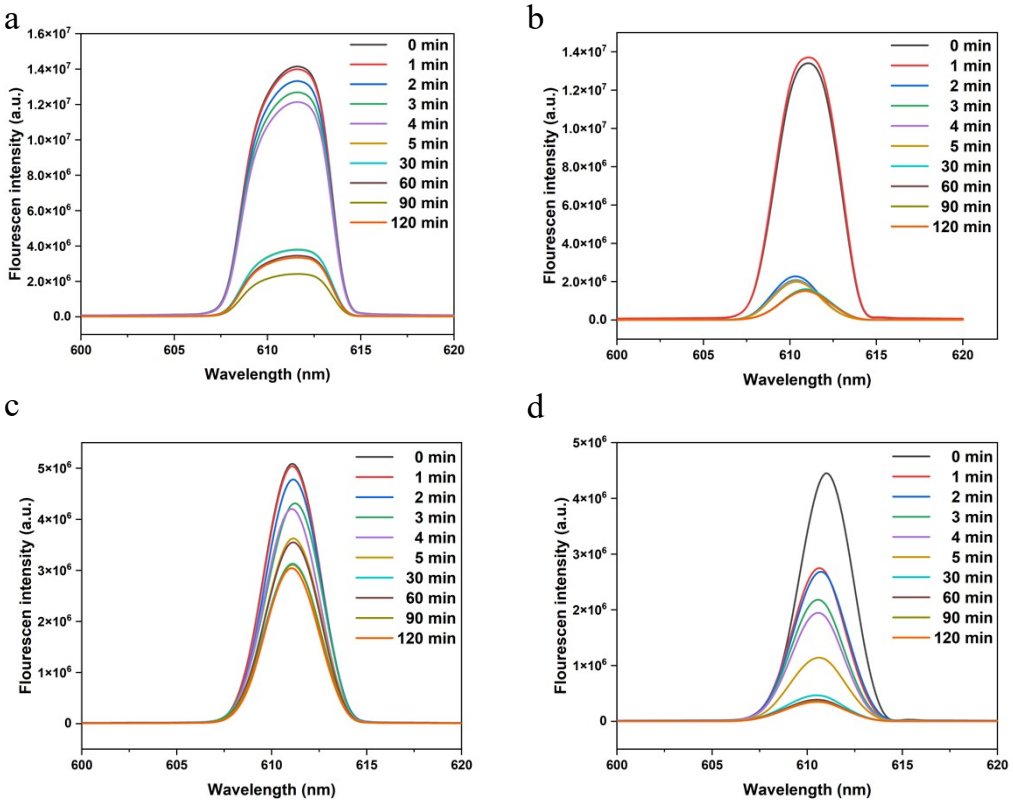


Fig. S3. Fluorescence spectrum (a) fluorescence spectrum of PPBD/PEO fiber film in RDX vapor. (b) fluorescence spectrum of PPBD/PEO fiber film in TNT vapor. (c) fluorescence spectrum of PPBD/PEO fiber film in 2,6-dimethylnitrobenzene vapor. (d) fluorescence spectrum of PPBD/PEO fiber film in HMX vapor.

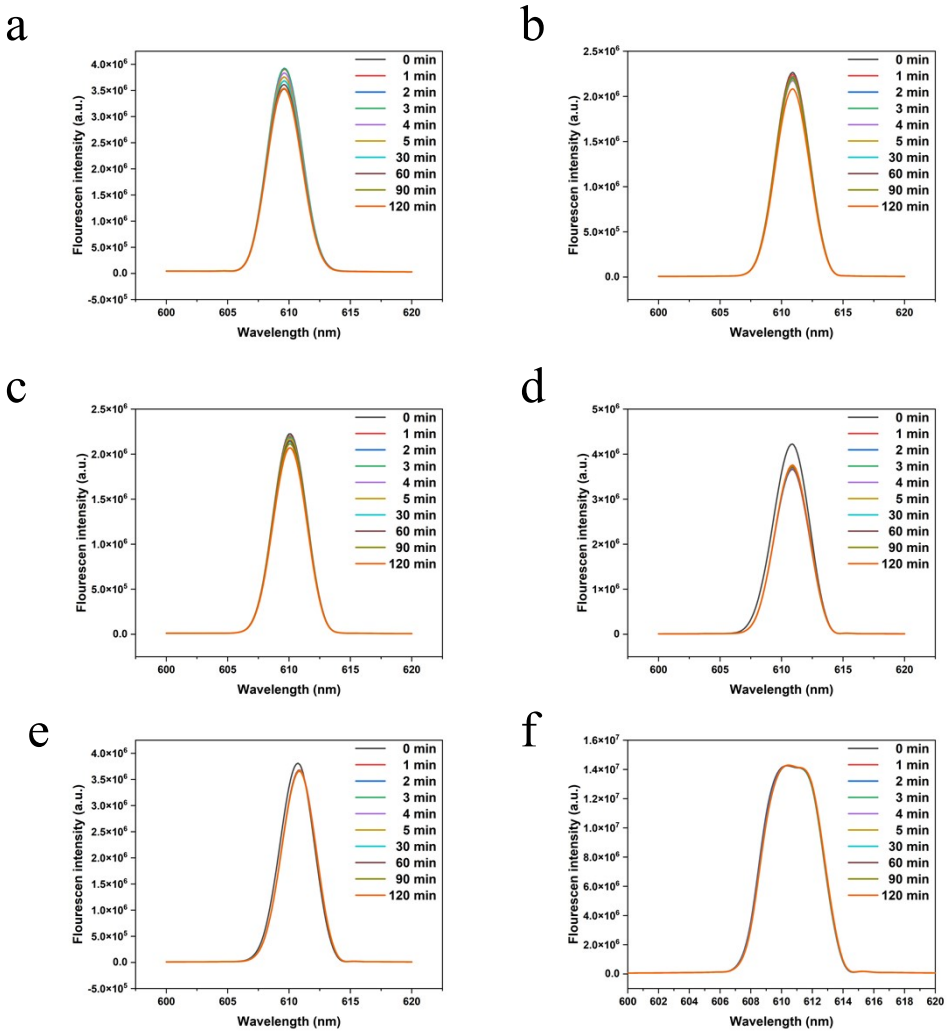
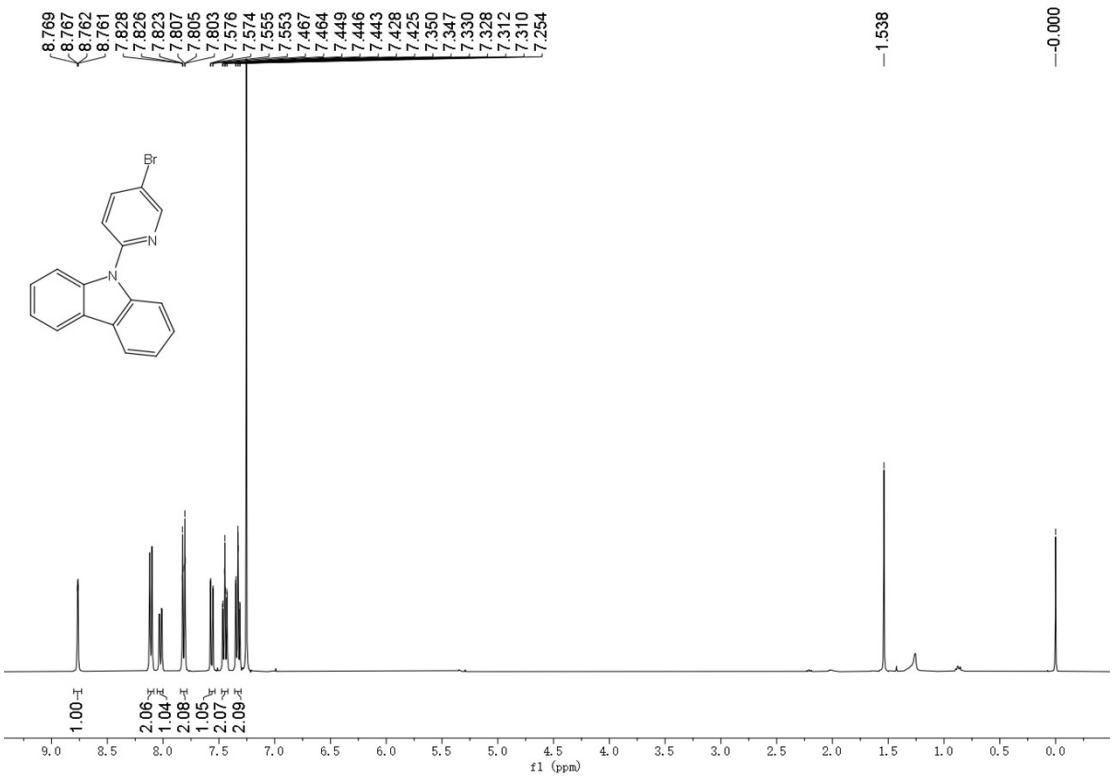
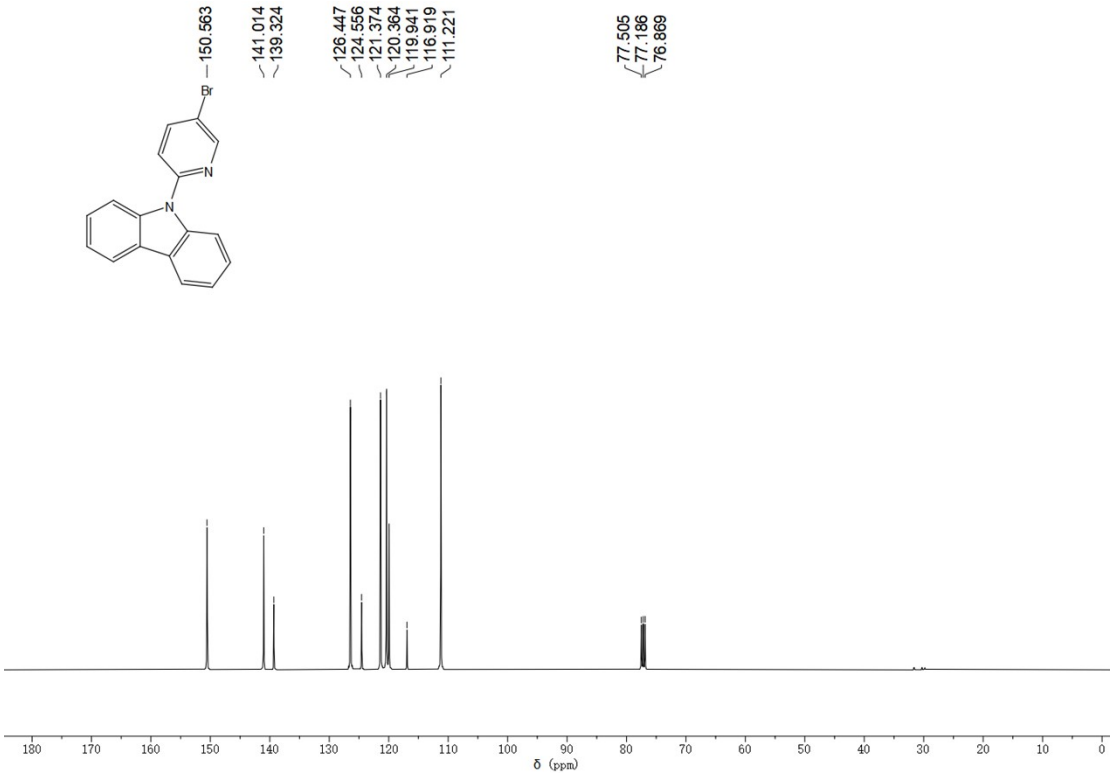


Fig. S4. Fluorescence spectrum (a) fluorescence spectrum of PPBD/PEO fiber film in water vapor. (b) fluorescence spectrum of PPBD/PEO fiber film in benzene vapor. (c) fluorescence spectrum of PPBD/PEO fiber film in phenol vapor. (d) fluorescence spectrum of PPBD/PEO fiber film in fragrance vapor. (e) fluorescence spectrum of PPBD/PEO fiber film in urea vapor. (f) fluorescence spectrum of PPBD/PEO fiber film in $NaNO_2$ vapor.

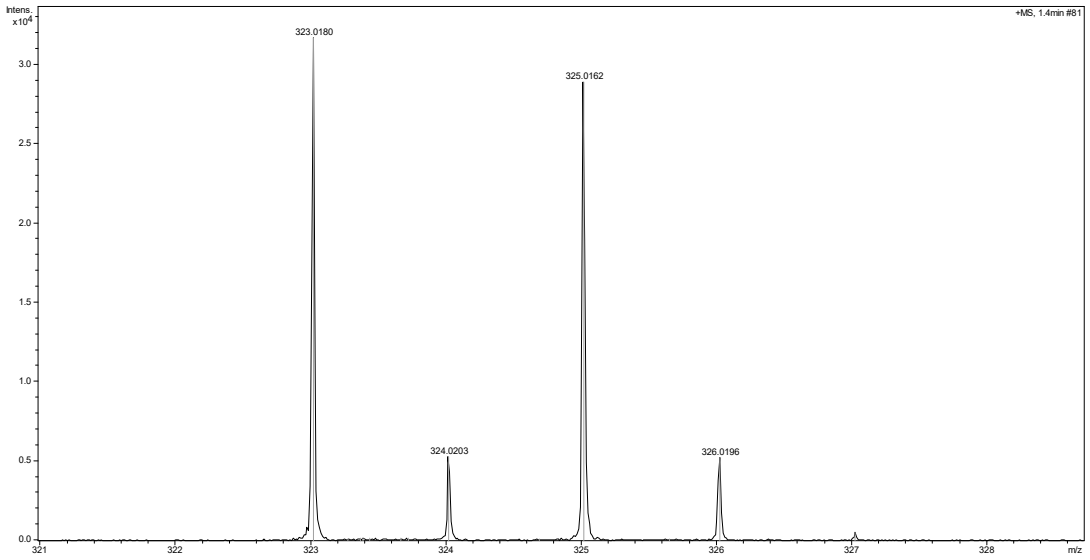
3. Characterization data for Compounds



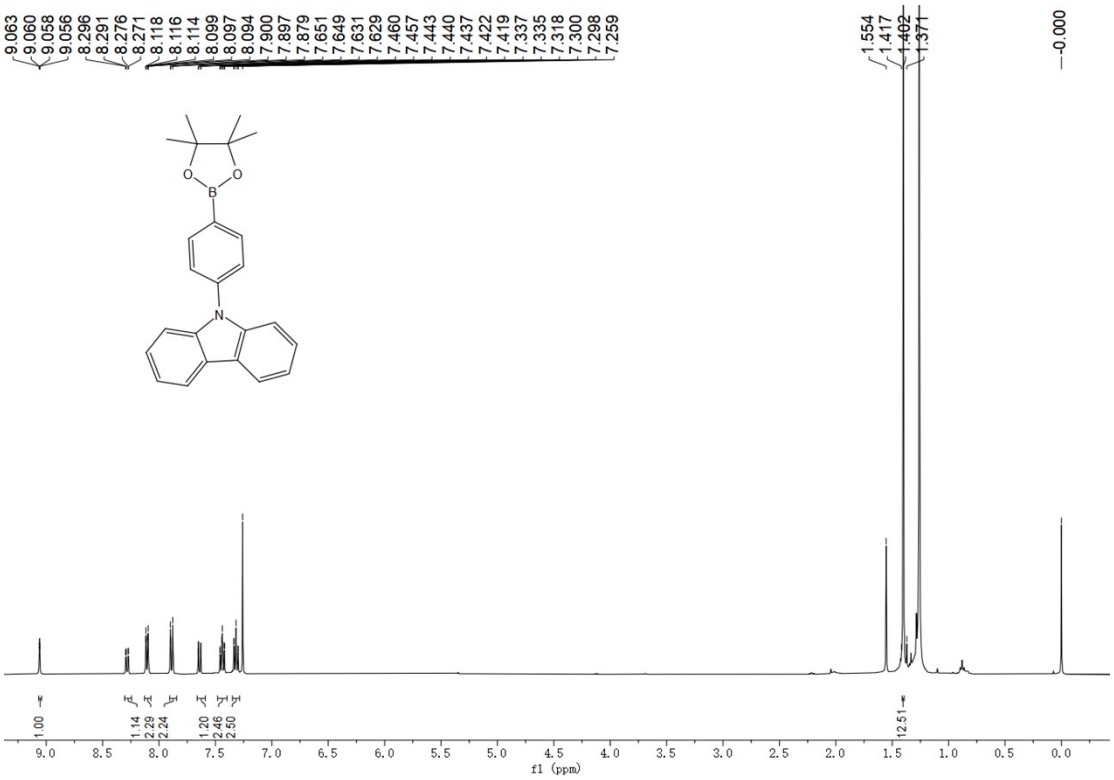
^{1}H NMR of **compound (1)**



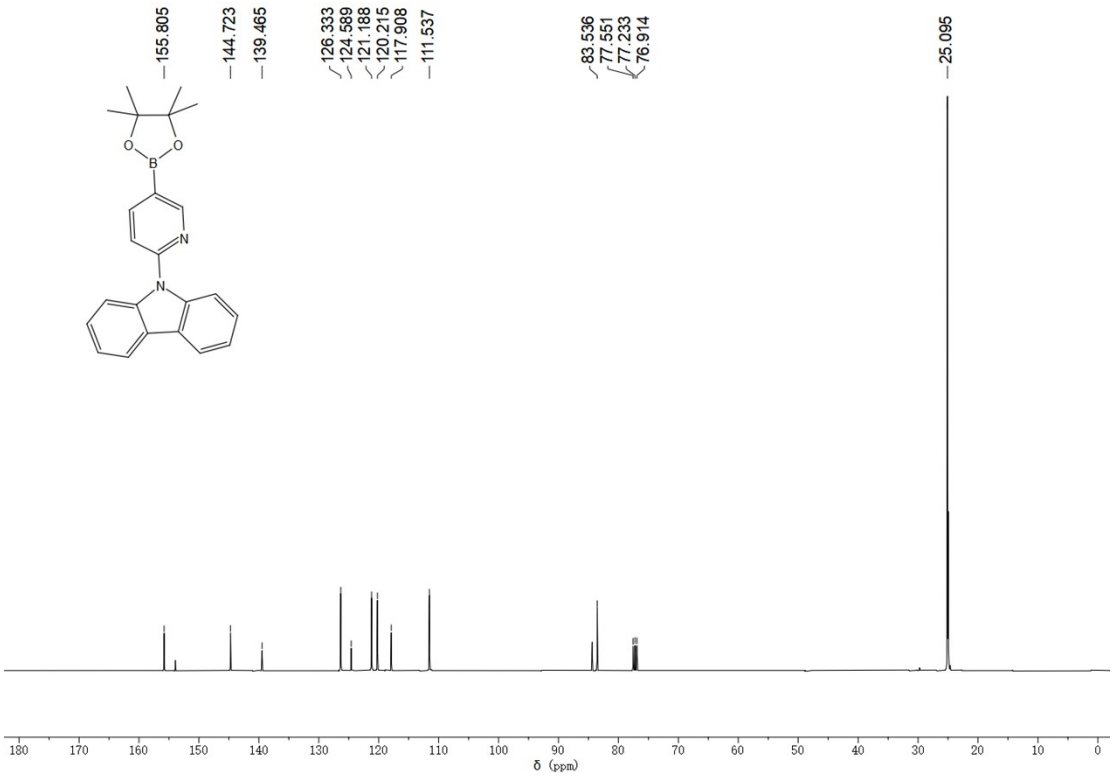
^{13}C NMR of **compound (1)**



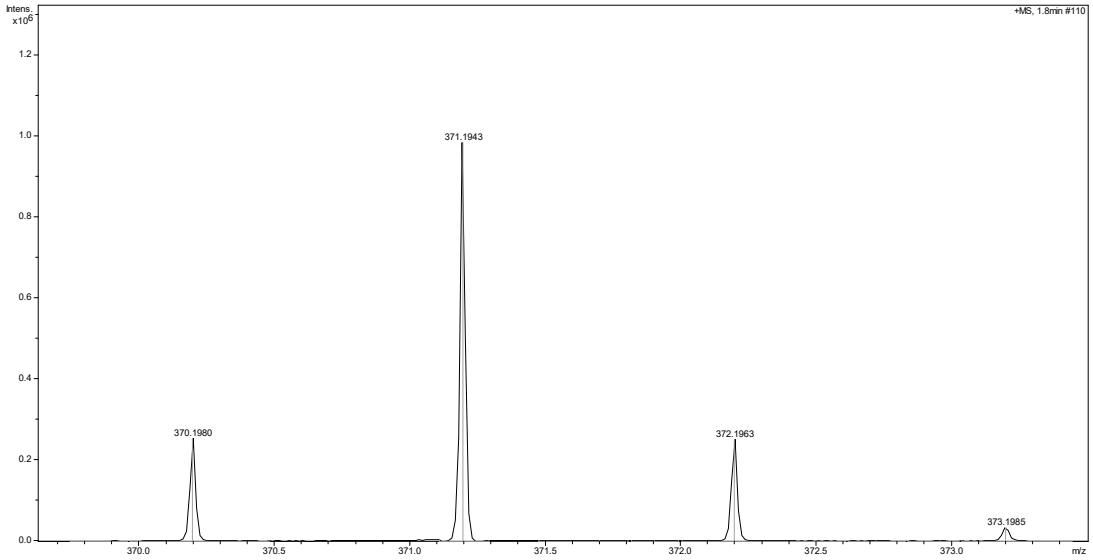
HRMS of **compound (1)**



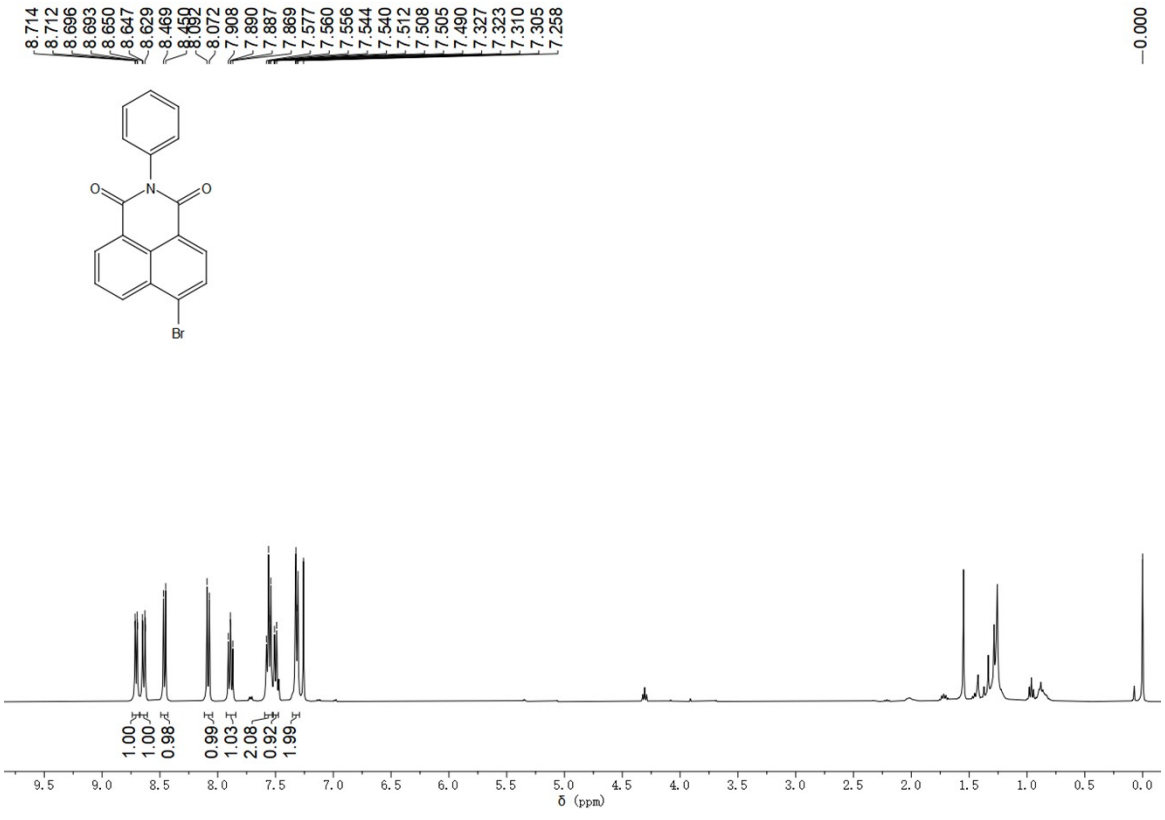
^{1}H NMR of **compound (2)**



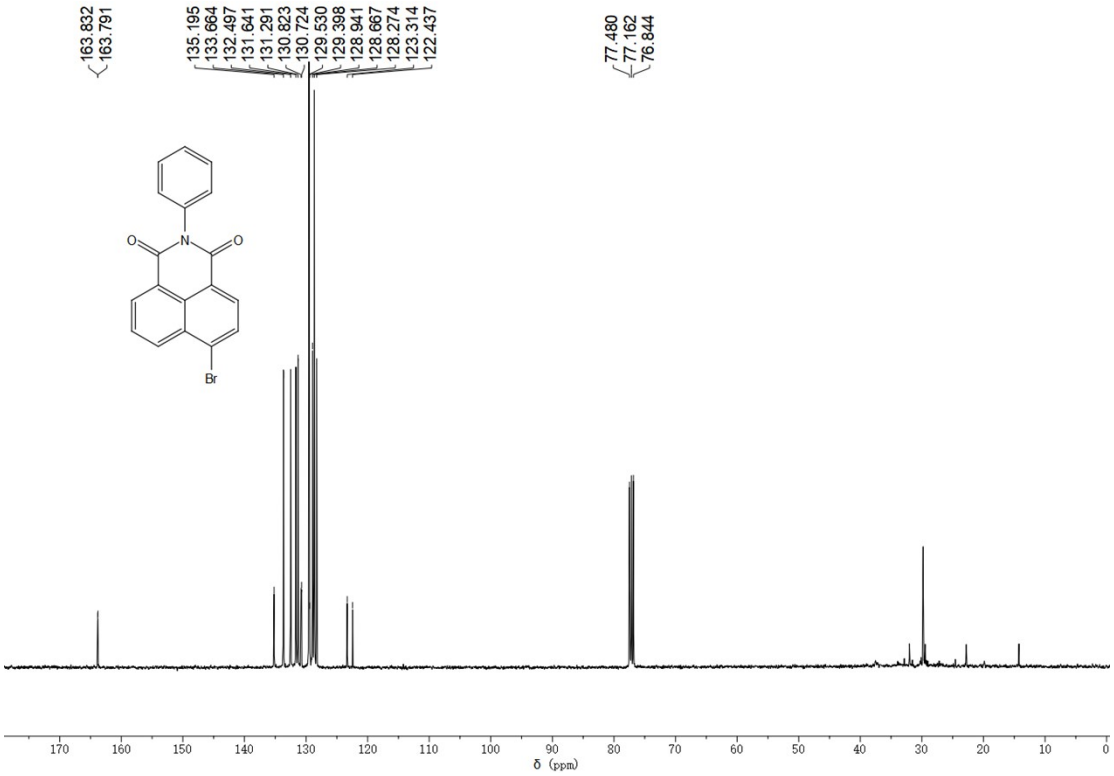
^{13}C NMR of **compound (2)**



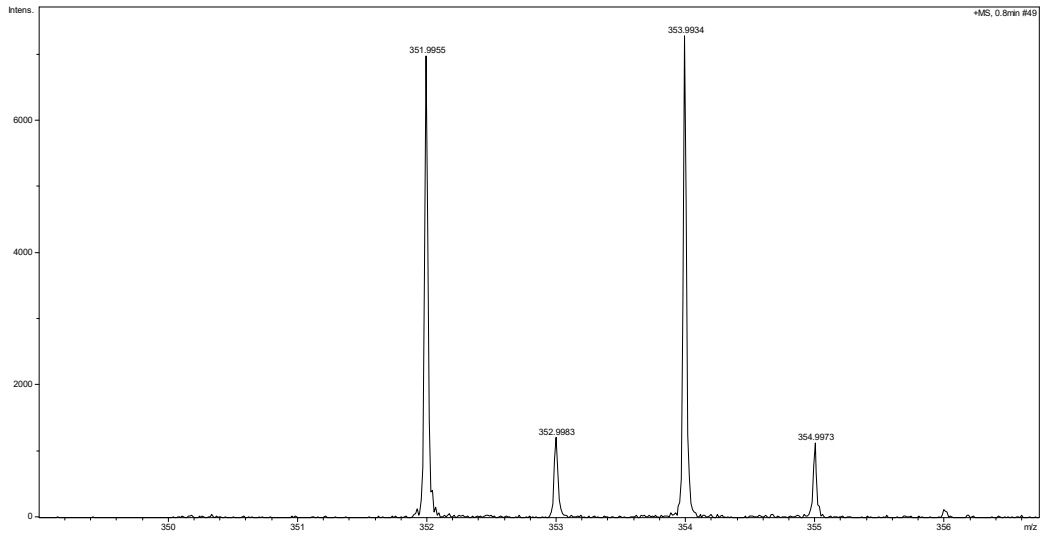
HRMS of **compound (2)**



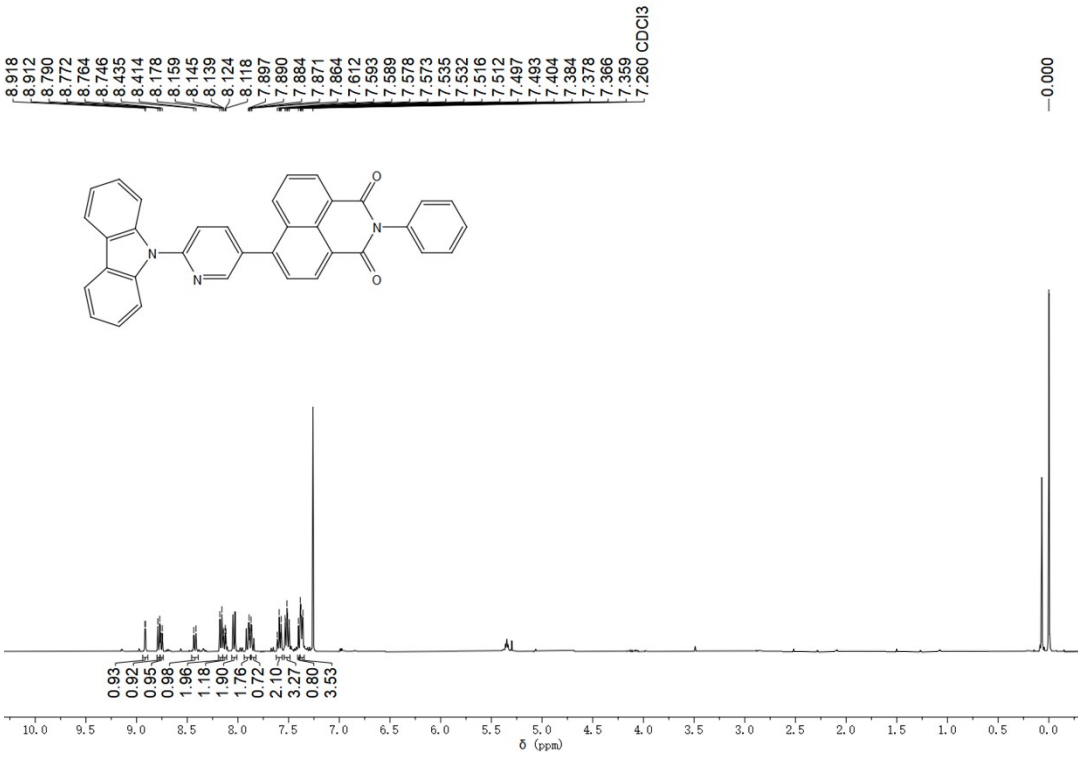
^{1}H NMR of **compound (3)**



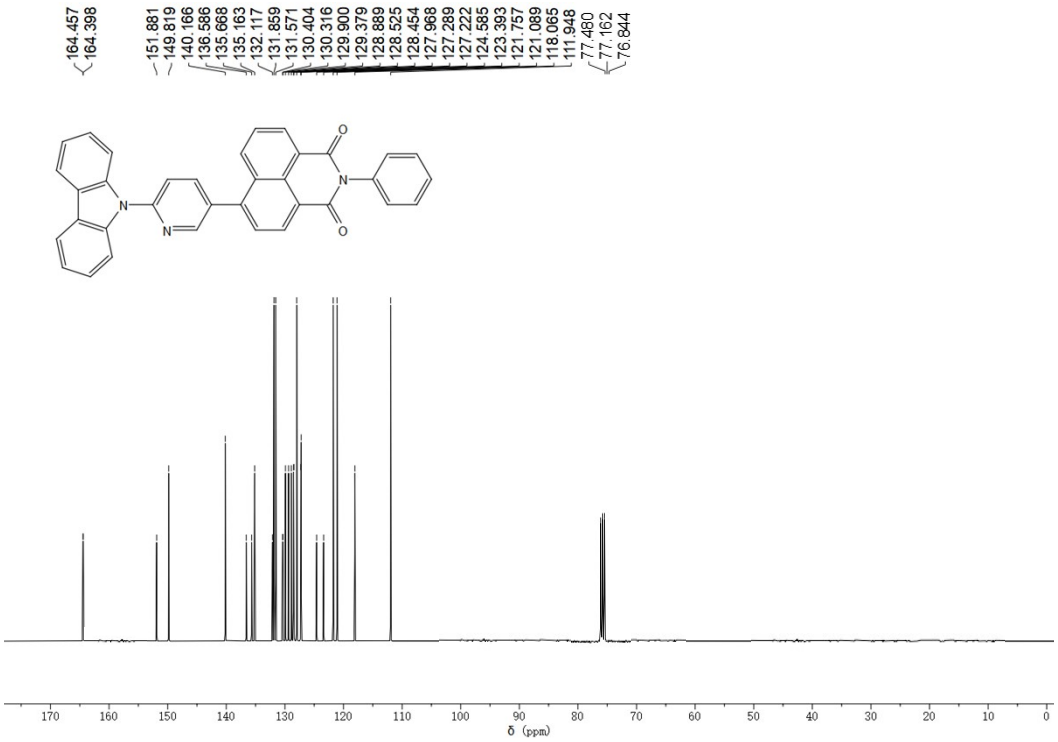
^{13}C NMR of **compound (3)**



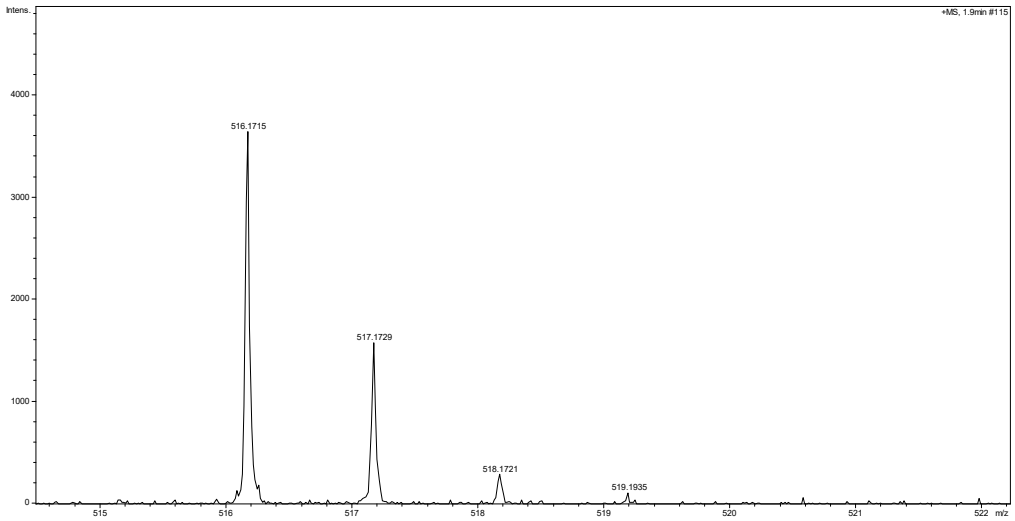
HRMS of **compound (3)**



^{1}H NMR of **PPBD**



^{13}C NMR of **PPBD**



HRMS of **compound PPBD**

4. Table

Table S1 Variables affecting the electrospinning

Variable	**Injection pump feed rate (mm/min)**	**Orthovoltage (kV)**	**Negative voltage (kV)**	**Relative humidity (%)**	**Temperature (℃)**	**Distance of the nozzle to the receiver (cm)**
1	0.100	10.0	-1.00	5	25	15
2	0.125	10.5	-1.25	10	26	16
3	0.150	11.0	-1.50	15	27	17
4	0.175	11.5	-1.75	20	29	18
5	0.200	12.0	-2.00	25	30	19
6	0.225	12.5	-2.25	30	31	20
7	0.250	13.0	-2.50	35	32	21
8	0.275	13.5	-2.75	40	33	22
9	0.300	14.0	-3.00	45	34	23
10	0.325	14.5	——	——	35	24
11	0.350	15.0	——	——	——	25

Table S2 The original fluorescence spectrum

	PETN	HMX	RDX	TNT	2,6-

					dimethylnitrobenzene
I_0	15122401	4452490	14037300	13403500	5077050
I	5088540	330960	3314800	1502030	3042080
K_{SV} (M^{-1})	1.8×10^3	327	3.95×10^3	1.08×10^3	95

Table S3. PPBD and its optimal conformation with the explosives

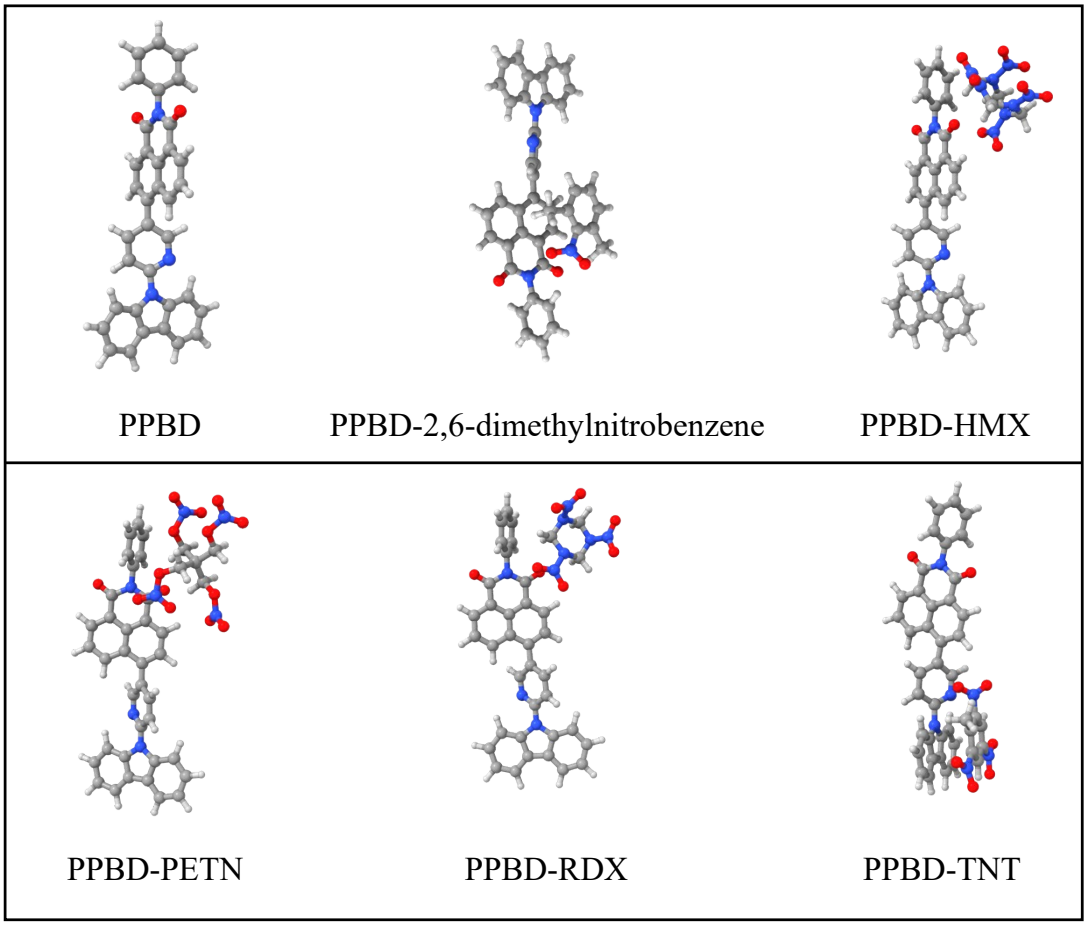


Table S4. Weak interaction map of the PPBD and its optimal conformation with the explosive charge

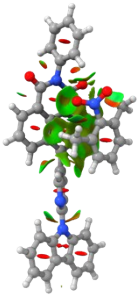
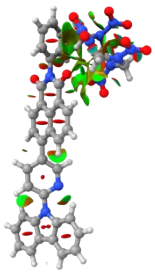
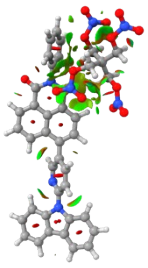
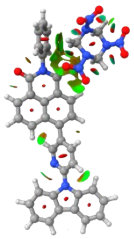
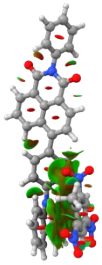
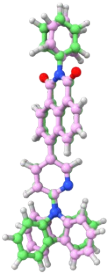
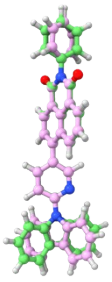
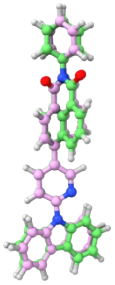
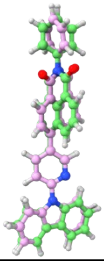
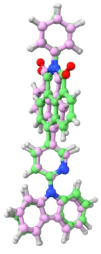
		
PPBD-2,6-dimethylnitrobenzene	PPBD-HMX	PPBD-PETN
		
PPBD-RDX	PPBD-TNT	

Table S5. The acking of the PPBD with its explosives in the optimal conformation and the corresponding RMSD values

		
PPBD-2,6-dimethylnitrobenzene	PPBD-HMX	PPBD-PETN
1.9433 A	1.9645 A	2.2650 A
		
PPBD-RDX	PPBD-TNT	
2.2871 A	2.6256 A	