Supporting Information

Direct and Ultrasensitive Fluorescent Detection of PETN Vapor Based on a Fuorene-

dimer Probe Via a Synergic Backbone and Side-chain Tuning

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Catalogue

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1、Synthesis of the probes



Fig. S1 Structure and synthetic routes for 6TPA-2FT and 6Py-2FT.

Compound 1 was synthesized based on our previous work¹.

1,6-Bis(2,7-dibromo-9-(6- azidohexyl)fluoren-9-yl)hexane (**2**). 1(634.2mg, 0.6 mmol), NaN₃ (78mg, 1.2mmol) were dissolved in 10ml DMSO in a 35-mL glass vial equipped with a small magnetic stirring bar. The vial was tightly sealed with an aluminum/Teflon crimp top. The mixture was then irradiated for 20 min at 60 °C, using an irradiation power of 100W.After completion of the reaction, the vial was cooled to 50 °C by air jet cooling before it was opened. The mixture was poured into 50 ml of water, extracted with ethyl acetate (20ml×3), and the organic layer was washed with water, brine and dried over anhydrous MgSO₄. The ethyl acetate was removed and the residue was purified by silica gel column chromatography to obtain white solid 2. (542mg,92%).¹H NMR (500 MHz, CDCl₃, ppm) δ 7.50 (d, J = 8.1 Hz, 4H), 7.44 (dd, J = 8.0, 2.0 Hz, 4H), 7.37 (d, J = 2.1 Hz, 4H), 3.14 (t, J = 7.0 Hz, 4H), 1.90 – 1.83 (m, 4H), 1.83 – 1.75 (m, 4H), 1.40 (t, J = 7.2 Hz, 4H), 1.18 – 1.01

(m,8H), 0.84 – 0.77 (m, 4H), 0.61 – 0.52 (m, 4H), 0.42 (s, 4H). ¹³C NMR (500 MHz, CDCl3, ppm) δ 152.26, 139.05, 130.27, 126.09, 121.49,121.18, 55.54, 51.36, 39.95, 29.32, 28.69, 26.31, 23.55, 23.50,13.9.

1,6-bis(2,7-dibromo-9-(6-(4-(4-bromophenyl)-1H-1,2,3-triazol-1-yl)hexyl)-9H-fluoren-9-

yl)hexane(**3**).2(196.2mg,0.2mmol),4-Bromophenylacetylene (72.4mg, 0.4mmol), CuSO₄·5H₂O(2 mol %, ca. 1 mg), and sodium ascorbate (0.2 mmol,8 mg) were dissolved in 5ml anhydrous DMF in a 35-mL glass vial equipped with a small magnetic stirring bar. The vial was tightly sealed with an aluminum/Teflon crimp top. The mixture was then irradiated for 10 min at 90 °C, using an irradiation power of 100 W. After completion of the reaction, the vial was cooled to 50 °C by air jet cooling before it was opened. The DMF was removed and finally washed with petroleum ether (200mL) to furnish 3 as a gray solid .(254mg,95%). ¹H NMR (500 MHz, CDCl3, ppm) δ 7.68 (d, J = 8.6 Hz, 4H), 7.64 (s, 2H), 7.56 – 7.52 (m, 4H), 7.49 (d, J = 8.1 Hz,4H), 7.43 (dd, J = 8.1, 4H), 7.35 (d, J = 2.2 Hz, 4H), 4.26 (t, J = 7.2 Hz, 4H), 1.88 – 1.83 (m, 4H), 1.80 – 1.72 (m, 4H), 1.14 – 1.09 (m,8H), 0.79 (s, 4H), 0.54 (s, 4H), 0.40 (s, 4H). ¹³C NMR (500 MHz, CDCl₃, ppm) δ 152.17, 139.04, 131.97, 130.29, 127.22, 126.04, 125.52, 121.49, 121.22, 119.40, 55.51, 50.35, 39.95, 39.87, 30.33, 30.10, 29.13, 26.07, 23.21, 23.36, 22.65, 14.11. MALDI-TOF MS for C₆₀H₅₈Br₆N₆: m/z 1341.98; Anal. Calcd (1341.1).

4,4',4'',4'''-(hexane-1,6-diylbis(9-(6-(4-(4'-(diphenylamino)-[1,1'-biphenyl]-4-yl)-1H-1,2,3-triazol-1-yl) hexyl)-9H-fluorene-9,7,2-triyl))tetrakis(N,N-diphenylaniline) **6TPA-2FT**. A flask charged with 3 (0.2mg,0.15mmol), 4-(Diphenylamino) phenylboronicacid (390mg, 1.35mmol), potassium carbonate (1.2 g, 8.7mmol), Pd(PPh₃)₄ (9 mg, 0.0075mmol) and 21 mL of toluene/H₂O (2:1, v/v) was degassed for 30 min. The solution was heated to reflux for 36 h, and then poured into 50 ml H₂O and extracted with CHCl₃. The organic layer was washed with brine and then dried over anhydrous MgSO₄. The solvent was removed and the residue was purified by column chromatography on silica gel, and recrystallized in THF/methanol to get slightly green solid 4 (104.8mg, 30%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.81 – 7.76 (m, 4H), 7.62 (d, J = 7.8 Hz, 4H), 7.60 – 7.57 (m, 4H), 7.54(s,2H), 7.48 (dd, J = 8.2, 16H), 7.42 (d, J = 1.7 Hz, 4H), 7.30 – 7.20 (m,24H), 7.12 (dd, J = 8.2, 36H), 7.02 (dt, J = 14.5, 12H), 4.18 (t, J = 7.3 Hz, 4H), 1.97 – 1.90 (m, 4H), 1.90 – 1.82 (m, 4H), 1.68 (p, J = 7.2 Hz, 4H), 1.07 (dd, J = 8.6, 4.9 Hz, 8H), 0.80 (s, 4H), 0.63 (s, 4H), 0.50 (d, J = 8.8 Hz, 4H). ¹³C NMR (500MHz, CDCl₃, ppm) δ 151.23, 147.67, 147.35, 147.09, 140.20, 139.69, 139.36, 135.43, 134.45, 129.31, 127.73, 127.60, 126.91, 126.05, 125.59, 124.47, 124.39, 123.97, 123.89, 123.00, 122.96, 120.71, 119.93, 119.22, 77.23, 76.89, 67.99, 55.08, 50.22, 30.06, 29.71, 29.57, 29.26, 26.06, 25.63, 23.55. MALDI-TOF MS for C₁₆₈H₁₄₂N₁₂: m/z 2328.8; Anal. Calcd (2328.15). Elemental analysis. For C₁₆₈H₁₄₂N₁₂: C, 86.64; H,6.15; N, 7.22. Found: C, 85.62; H, 6.65; N, 6.51;

Melting point: 248.6-250 °C

1,6-bis(2,7-di(pyren-2-yl)-9-(6-(4-(4-(pyren-2-yl) phenyl)-1H-1,2,3-triazol-1-yl)hexyl)-9H-fluoren-9-yl)hexane **6Py- 2FT**.A flask charged with 3(0.2mg,0.15mmol), potassium carbonate (1.2 g, 8.7mmol), 1-pyrenylboronic acid(332.20mg, 1.35mmol), Pd(PPh₃)₄ (9 mg, 0.0075mmol) and 21 mL of toluene/H₂O(2:1, v/v) was degassed for 30 min. The solution was heated to reflux for 36 h, and then poured into 50 ml H₂O and extracted with CHCl₃. The organic layer was washed with brine and then dried over anhydrous MgSO₄. The solvent was removed and the residue was purified by column chromatography on silica gel, and recrystallized in THF/methanol to get slightly green solid. (100mg,32%).¹H NMR (500 MHz, CDCl₃, ppm) δ 8.20 – 8.11 (m, 20H), 8.08 (s, 2H), 8.04 – 7.89 (m, 30H), 7.84 (d, J = 8.0 Hz, 4H), 7.78 (d, J = 7.6 Hz, 4H), 7.58 – 7.51 (m, 14H), 4.19 (t, J = 7.2 Hz, 4H), 2.06 – 2.02(m, 4H), 2.01 – 1.96 (m, 4H), 1.74 (q, J = 7.3 Hz, 4H), 1.11(s, 8H), 0.91 (m, 4 H), 0.83 (m, 4H), 0.73 (s, 4H), 0.6 (d, J=8.8Hz,4H), ¹³CNMR(500MHz,CDCl₃,ppm) δ 150.86, 140.03, 139.97, 138.08, 137.20, 131.49, 130.98, 130.53, 128.53, 127.625, 127.42, 126.03, 125.61, 125.21, 124.99, 124.87, 124.67, 119.83, 119.39, 55.29, 50.26, 40.02, 30.12, 29.79, 29.71, 29.35,2 6.13, 24.06, 23.87. MALDI-TOF MS for C₁₅₆H₁₁₂N₆: m/z 2069.4; Anal. Calcd (2069.90). Elemental analysis. For C₁₅₆H₁₁₂N₆: C, 90.49; H,5.45; N, 4.06.

Found: C, 89.54; H, 5.56; N, 3.95. Melting point: 259-261 °C.

$2 \, {}_{\sim} \,$ Comparison of representative fluorescent probes for PETN detection

No	Molecular structure	detection method	limit of detection
12	CdS-S CdS-S	solution	3200pg
2 ³		solution	
34		Detection	320ng
	N N	decomposition	520pg
4 ⁵		solution	0.8nM
56	Sit SiPh	surface detection	1pg/cm ²

Table S1 Comparison of representative fluorescent probes for PETN detection

67		Detection decomposition	0.2ng
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3、PETN crystal



Fig S2 crystal structure of PETN

Crystal growth experiment(Solvent evaporation method): Weigh a 10mg PETN powder into the vial, and dissolve it with THF, and standing until the solvent evaporates.

4、Geometric structure of 6TPA-2FT and 6Py-2FT



Fig. S3 Geometric structure of 6TPA-2FT(left) and 6Py-2FT(right)



5、Optical and Electrochemical Figures







Fig. S4 (a)UV–vis absorption and emission spectra of 6TPA-2FT in THF and Film;(b)UV–vis absorption and emission spectra of 6Py-2FT in THF and Film;(c) The molar absorption coefficient results of 6TPA-2FT and 6Py-2FT were measured at the absorption maxima (λ max) in THF (concentration, 10⁻¹⁰ M); (d) UV-vs the absorption spectra of PETN and emission spectra of 6TPA-2FT and 6Py-2FT in Film.

6 . Testing procedures for the sensing properties of the material.

First, we take a small quantity of PETN (4 mg) and put into the bottom of the cuvette. The fluorescence responses of films to PETN vapor were progressed by inserting the films into hermetically sealed vials (3.8 mL) containing cotton and analyte at room temperature, which could prevent direct contact between the probe and analyte as well as help to maintain a constant vapor pressure. The fluorescence time-course responses were recorded immediately after exposing the films to analytes by front-face (30°) detection.

The sensing properties of the probes were systematically investigated covering stability, sensitivity, and selectivity as follows. The specific parameters are shown in the following table S1

	0			
	Excitation(nm)	Emission(nm)	slit	Time(s)
6TPA-2FT	380	430	2	300
6Py-2FT	388	461	2	300

Table S2 Test parameter settings of HORIBA FluoroMax

7、 The change of fluorescence after contacting with nitrate ester explosives



1、PETN



2、NG



3、 MN



5、TEGDN

Fig. S5 left: Intermolecular interactions before contacting with 6TPA-2FT and nitrate ester explosives (1,PETN; 2,NG; 3,MN; 4,EGDN; 5,TEGDN.) simulated with Materials Studio 8; right: Intermolecular interactions after contacting with 6TPA-2FT and nitrate ester explosives simulated with Materials Studio 8; insert: the amplified schematic diagram of the intermolecular interaction between 6TPA-2FT and nitrate ester explosives.



Fig. S6 Intermolecular interactions 6Py-2FT (left) before and (right) after with PETN simulated with Materials Studio 8 (the inset is the amplified schematic diagram of the intermolecular interaction between probe and analyte).

8、Infrared spectra (film)



Fig. S7 Infrared spectra (film) of 6TPA-2FT and 6Py-2FT before and after exposed PETN vapor

9、Lifetime decay of 6TPA-2FT and 6Py-2FT



Fig. S8 Lifetime decay of 6TPA-2FT and 6Py-2FT before and after exposed PETN vapor

	$ au_1$ (ns)	a ₁ (%)	$ au_2$ (ns)	a ₂	τ ₃ (ns)	a 3	τ ₄ (ns)	a 4	x ²	τ _{avg} (ns)
6TPA-2FT	0.01	77.26	0.09	21.59	0.57	1.15			0.963	0.156
6TPA-2FT +PETN	0.01	70.22	0.06	28.63	0.36	1.14			0.871	0.173
6Py-2FT	0.04	30.77	0.14	33.02	1.31	9.39	0.45	26.82	1.06	0.95
6Py-2FT +PETN	0.05	29.12	0.16	35.53	1.35	9.25	0.46	26.09	1.16	1.12

Table S3 Fluorescence lifetime decay of each component and their fractions.

$10\,{\scriptstyle \smallsetminus}\,$ Selectivity to solvents and nitrate explosives



Fig. S9 (a)6TPA-2FT filters excited by UV lamp 365 nm after 5 min exposure in 1, air; 2, PETN; 3, TEGDN; 4, NG; 5, MN; 6, EGDN;(b)6TPA-2FT filters excited by UV lamp 365 nm after 5 min exposure in 1,Toluene; 2, Acetone; 3, H₂O; 4, THF; 5,CH₂Cl₂



Fig. S10 sensing quenching responses upon different aromatic explosive vapors

11、 Hidden PETN Detection Experiment.





Fig S11fluorescence intensity of 6TPA-2FT before and after detection hidden PETN (a) 0℃, (b) 30℃, (c) 40℃.



Fig S12 fluorescence intensity of 6TPA-2FT before and after standing 1h(left); fluorescence intensity of 6TPA-2FT before and after detection hidden PETN (right).

12、NMR、 mass spectrum and Elemental analysis



Fig. S14 ¹³CNMR spectrum of 2 in CDCl₃.



Fig. S15 ¹H NMR spectrum of 3 in CDCl₃.



Fig. S16 $^{\rm 13}C$ NMR spectrum of 3 in CDCl_3.



Fig. S18 ¹H NMR spectrum of 6TPA-2FT in CDCl₃.



Fig. S19 ¹³C NMR spectrum of 6TPA-2FT in CDCl3.



Fig. S20 Mass spectra of 6TPA-2FT.



Fig. S22 ¹³C NMR spectrum of 6Py-2FT in CDCl3.



Fig. S23 Mass spectra of 6Py-2FT.

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送检人	刘骜	送检日期	2018年1月31日	联系电话				
样品名称	6TPA-2F	T		登记编号	508			
检测项目	CHN							
		检测	则结果					
样品	质量	2.185 毫克	2.185	毫克	毫克			
百	N	653 9	650	%	%			
分含	C	85.60 9	85.63	%	%			
量	Н	6.70 9	6 6.76	%	%			
附 注: 方法简述: 际准: JY/ □/仪器型	F 017-1996 号: Eleme	元素分析仪方法通则 ntar 公司 Vario EL III	型全自动元素分析	F仪				
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送检人	刘骜	送检日期	2018年1月31日	联系电话	
样品名称	6PY-2FT			登记编号	509
检测项目	CHN				
		检测	则结果		
样品质	量	2、138 毫克	2.133	毫克	毫克
T		2.05 %	3, P4	%	9
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Fig S24 Elemental analysis data of 6TPA-2FT and 6Py-2FT.

12、Parameter settings of Materials Studio 8

Parameter settings of Materials Studio 8 Table S2. Parameter settings of Materials Studio 8.0 The frontier molecular orbitals:

Step1. For cite Anneal:	Step2. DMol3 Geometry Optimization
Annealing cycles: 10;QuInitial temperature: 300KEnMid-cycle temperature: 1000KMailHeating ramps per cycle: 7MailDynamics steps per ramp: 1000MailEnsemble: NVTMailOptimize after each cycleFuQuality: Ultra-fineUsForce field: DeridingIntCharges: Use currentSCQuality: Ultra-fineCcSummation method: Electrostatic: atomBailbased; Van der Waals: atom basedOrPrintCh <td>Quality Fine Energy 1.0e-5 Max. force 0.002 Ha/Å Max. displacement 0.05 Å Max. iterations: 50 Max. step size: 0.3 Å Functional: GGA-BLYP Jse symmetry Integration accuracy: Fine SCF tolerance Fine Core treatment All Electron Basis set DNP+ 4.4 Drbital cutoff quality Fine Properties: Optics; Orbitals Charge:1 (Nitrate explosives) 0 (6TPA-2FT or 6Py-2FT) Spin unrestricted(Nitrate explosives)</td>	Quality Fine Energy 1.0e-5 Max. force 0.002 Ha/Å Max. displacement 0.05 Å Max. iterations: 50 Max. step size: 0.3 Å Functional: GGA-BLYP Jse symmetry Integration accuracy: Fine SCF tolerance Fine Core treatment All Electron Basis set DNP+ 4.4 Drbital cutoff quality Fine Properties: Optics; Orbitals Charge:1 (Nitrate explosives) 0 (6TPA-2FT or 6Py-2FT) Spin unrestricted(Nitrate explosives)

Dynamics simulation:

Step 1.Forcite Geometry Optimization	Step 2.Forcite Dynamics
Ensemble: NVE	Ensemble: NVE
Quality: Ultra-fine	Total simulation time: 500ps
Force field: COMPASS II	Quality: Ultra-fine
Charges: Force field assigned	Force field: COMPASS II
Quality: Ultra-fine	Charges: Force field assigned
Summation method: Electrostatic: atom	Quality: Ultra-fine Summation method:
based; Van der Waals: atom based	Electrostatic: atom based; Van der Waals:
	atom based

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