Supporting information

A Highly Sensitive Fluorescent Sensor Based on Small Molecule Doped in Electrospun Nanofibers: Detection of Explosives as well as Color Modulation

Wei Xue,[a] Yang Zhang,[a] Juanjuan Duan,[a] Dong Liu,[a] Yawei Ma, [a] Naien Shi, [*a] Linghai Xie, [*a] Shufen Chen,[a] Yan Qian [a] and Wei Huang[*] [a,b]

[a] *Key Laboratory for Organic Electronics and Information Displays & Institute of Advanced Materials(IAM), National Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing University of Posts & Telecommunications, 9 Wenyuan Road, Nanjing 210023, China*

Fax: +86 25 8586 6396; Tel: +86 25 8586 6332

[b] *Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), National Jiangsu Synergistic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, China*

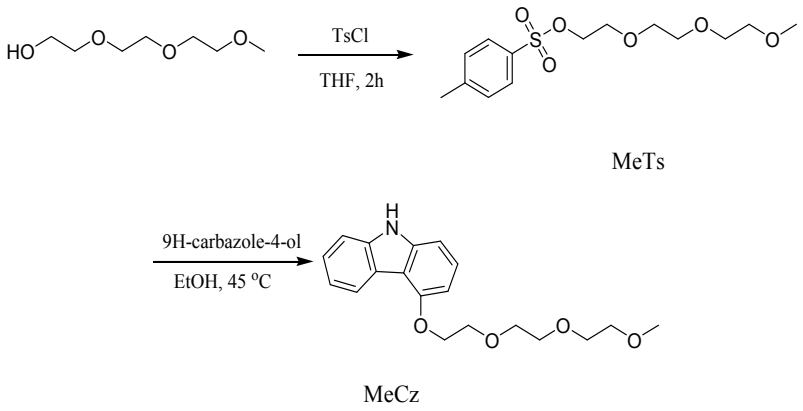
Fax: +86 25 5813 9988; Tel: +86 25 5813 9001.

E-mail: iamneshi@njupt.edu.cn, iamlhxie@njupt.edu.cn, wei-huang@njtech.edu.cn

Contents

A. Experimental Section.

Synthesis of MeTs and MeCz



Scheme S1. The synthesis procedure of 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-9H-carbazole (MeCz).

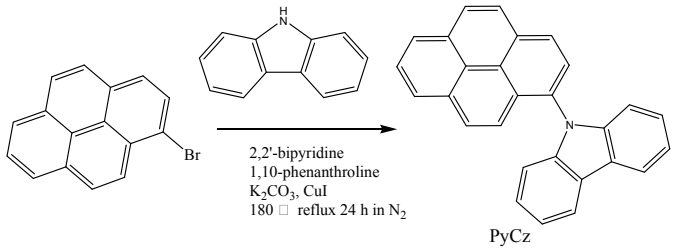
Synthesis of 2-(2-(2-methoxyethoxy)ethoxy)ethyl-4-methylbenzenesulfonate (MeTs, Scheme S1)

2.0 mL aqueous solution of NaOH (1.8 g, 45 mmol) was added to 7.5 mL THF solution of 2-(2-(2-methoxyethoxy)ethoxy)ethanol (5 g, 30 mmol), and the mixture was cooled to 5°C, then 8.0 mL THF solution of 4-methylbenzene-1-sulfonyl chloride (5.72 g, 30 mmol) was added under stirring for 2 h. Then the reaction was quenched by ice water. The organic layer was then dried by $MgSO_4$, filtered, and concentrated in vacuum, and the product of MeTs was obtained as a light yellow oil (8.91 g, 92%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm, Fig. S1) δ 7.74 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.10 (t, J = 4.8 Hz, 2H), 3.63 (t, J = 4.8 Hz, 2H), 3.55 (dd, J = 5.8, 3.4 Hz, 4H), 3.53 (s, 2H), 3.47 (dd, J = 5.8, 3.4 Hz, 2H), 3.31 (s, 3H), 2.35(s, 3H). GC-MS (EI-m/z): Calcd. 318.11, Found 318.15.

Synthesis of 4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)-9H-carbazole (MeCz, Scheme S1)

2.5 mL 10% NaOH aqueous solution and the 2-(2-(2-methoxyethoxy)ethoxy)ethyl- 4-methylbenzenesulfonate (6.01 g, 18.88 mmol) were successively added to a solution of 9H-carbazol-4-ol (3.46 g, 18.88 mmol) in ethanol (57 mL). The resulting mixture was continuously stirred at 45~50°C for 3 days. The reaction mixture was then filtered and the dark reside was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuum. The crude was purified by silica gel chromatography (PE/CH_2Cl_2, 4/1) to furnish MeCz as a brown viscous liquid (4.32 g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm, Fig. S1) δ 8.33 (d, J = 7.8 Hz, 1H), 8.18 (s, 1H), 7.43 – 7.35 (m, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.26– 7.21 (m, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 4.38 (t, J = 5.0 Hz, 2H), 4.05 (t, J = 5.0 Hz, 2H), 3.84 (dd, J = 5.8, 3.8 Hz, 2H), 3.72 (dd, J = 5.8, 3.8 Hz, 2H), 3.67 (dd, J = 5.6, 3.7 Hz, 2H), 3.54 (dd, J = 5.6, 3.7 Hz, 2H), 3.36 (s, 3H). GC-MS (EI-m/z): Calcd. 329.16, Found 329.23.

Synthesis of PyCz (Scheme S2)

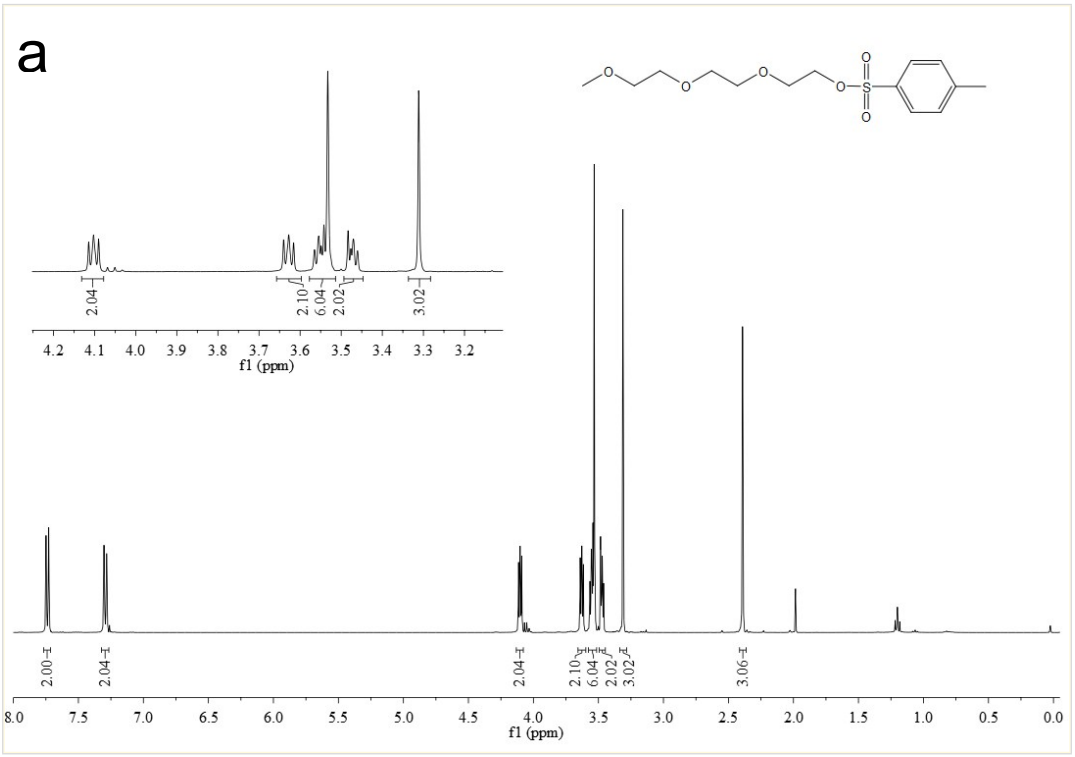


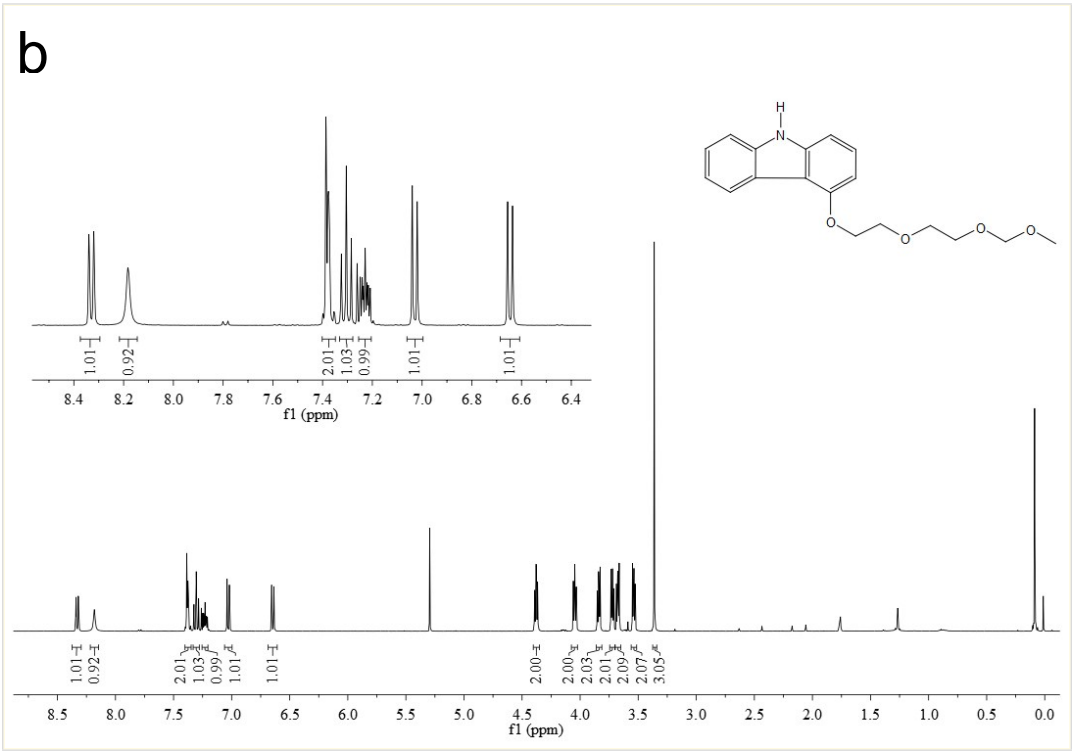
Scheme S2. Synthesis of 9-(pyren-3-yl)-9H-carbazole.

9*H*-carbazole (0.68 g, 4 mmol), 1-Bromopyrene (1.35 g, 4.8 mmol), K_2CO_3 (1.65 g, 12 mmol), CuI(0.92 g, 4.8 mmol), 2,2'-bipyridine (0.032 g, 0.2 mmol) and 1,10-

phenanthroline (0.036 g, 0.2 mmol) were added in a three-neck flask covered with silver paper. After blowing N_2, 1,2-Dichlorobenzene was added via syringe dropwise at room temperature. The resulting mixture was refluxed for 24 h at 180°C. The mixture was allowed to cool to room temperature and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude was purified by column chromatography (PE) to furnish PyCz as a white solid (1.17 g, 80%). ^{1}H NMR (400Hz, $CDCl_3$, ppm, Fig. S4) δ: 7.03-7.05 (m, 2H), 7.32-7.38 (m, 4H), 7.55-7.58 (d, J=7.6 Hz, 1H), 7.94-7.97 (d, J=8.0 Hz, 1H), 8.05-8.12 (m, 2H), 8.19-8.22 (m, 3H), 8.26-8.30 (m, 3H), 8.36-8.38 (d, J=8.4 Hz, 1H). ^{13}C NMR (100 Hz, $CDCl_3$, ppm, Fig. S4) δ: 110.26, 119.91, 120.39, 122.64, 123.37, 124.63, 125.54, 125.74, 125.81, 125.81, 126.03, 126.50, 126.59, 127.20, 128.26, 128.63, 128.73, 131.00, 131.05, 131.17, 131.44, 142.50. GC-MS (EI-m/z): Calcd. 367.14, Found 367.18.

B. **^{1}H NMR (400 MHz, $CDCl_3$, ppm), ^{13}C NMR (100 MHz, $CDCl_3$, ppm), and MS of the synthesized compounds.**





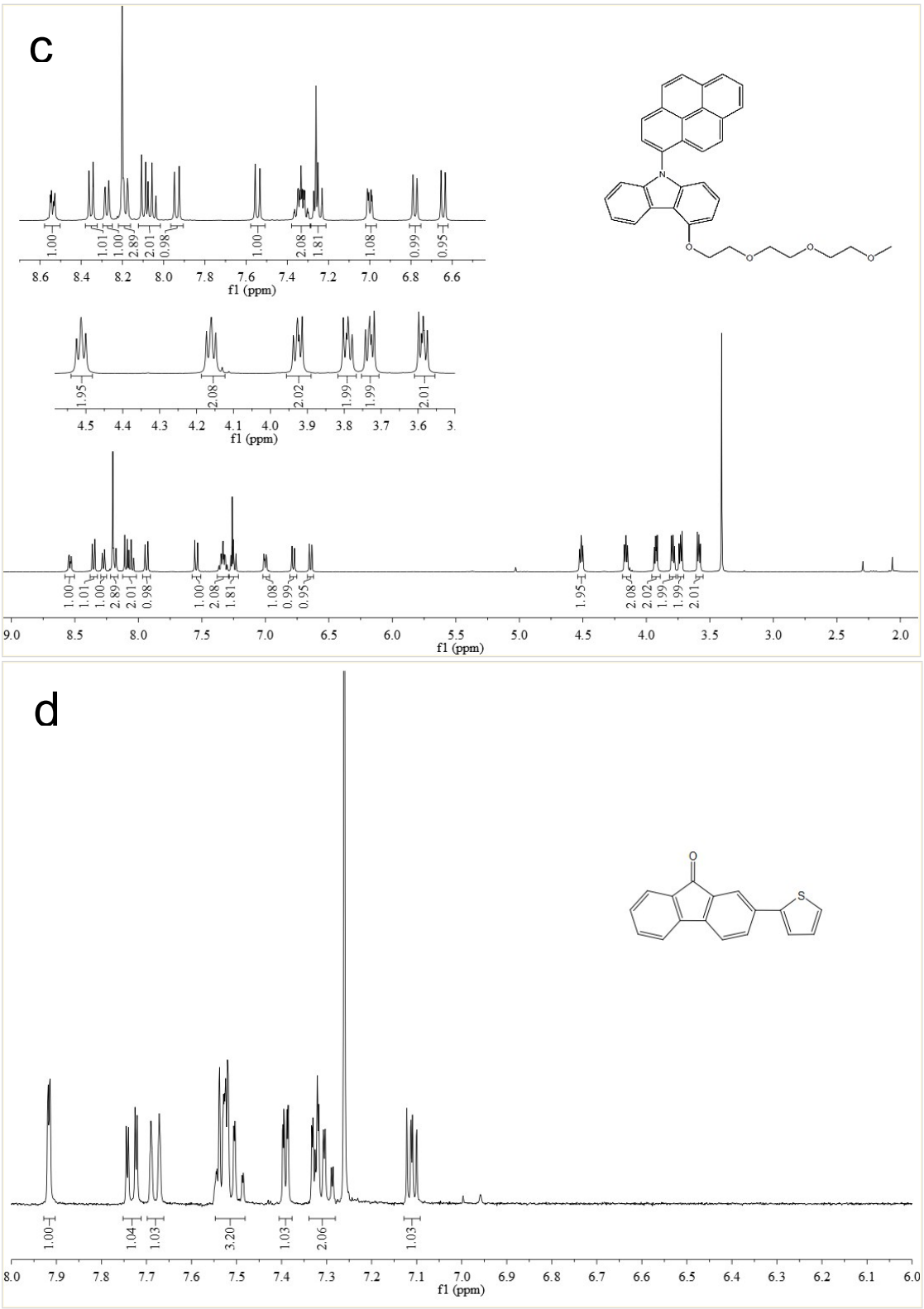


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$, ppm) of (a) MeTs, (b) MeCz, (c) MePyCz and (d) ThFO

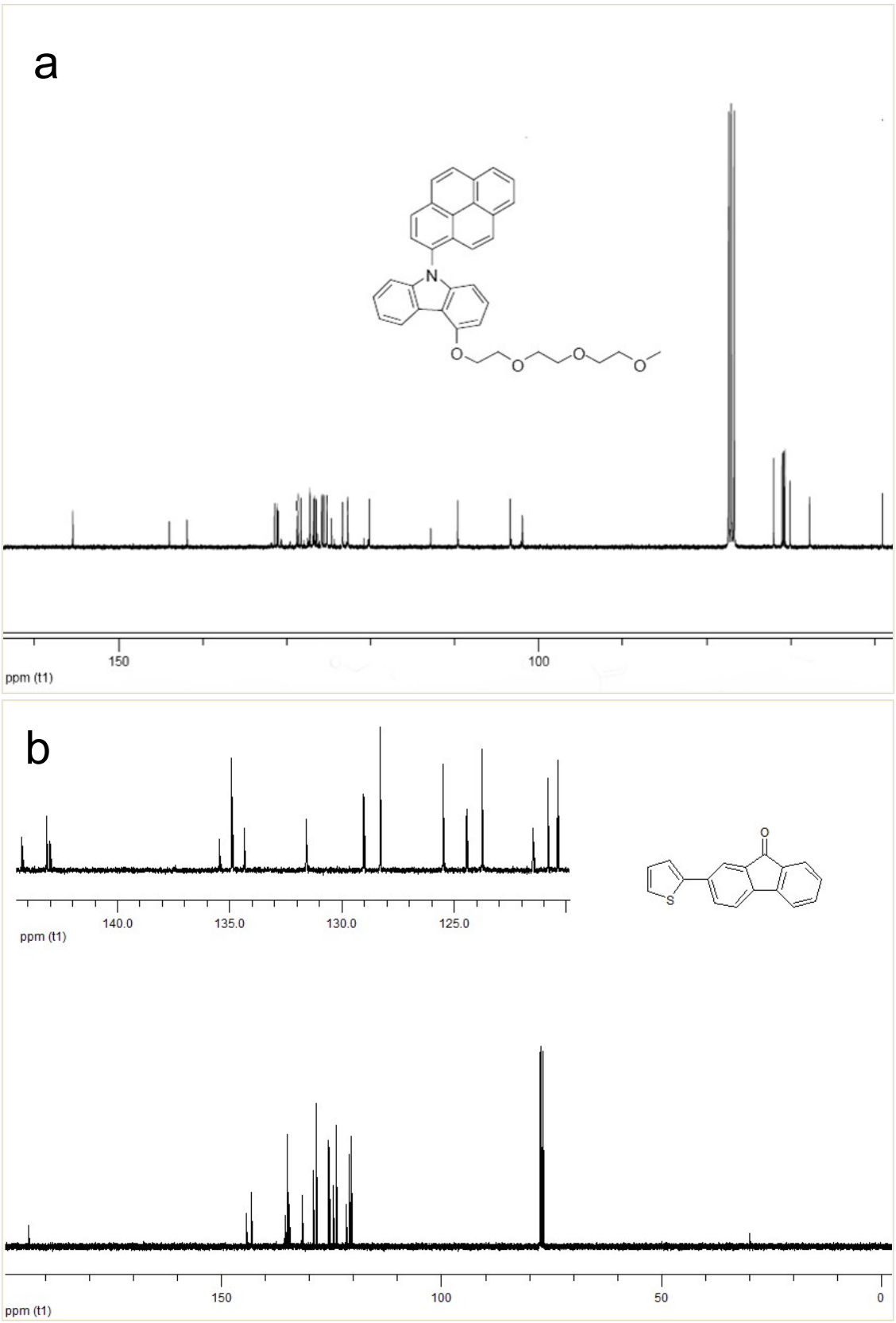


Fig. S2 ^{13}C NMR spectrum (100 MHz, $CDCl_3$, ppm) of (a) MePyCz and (b) ThFO.

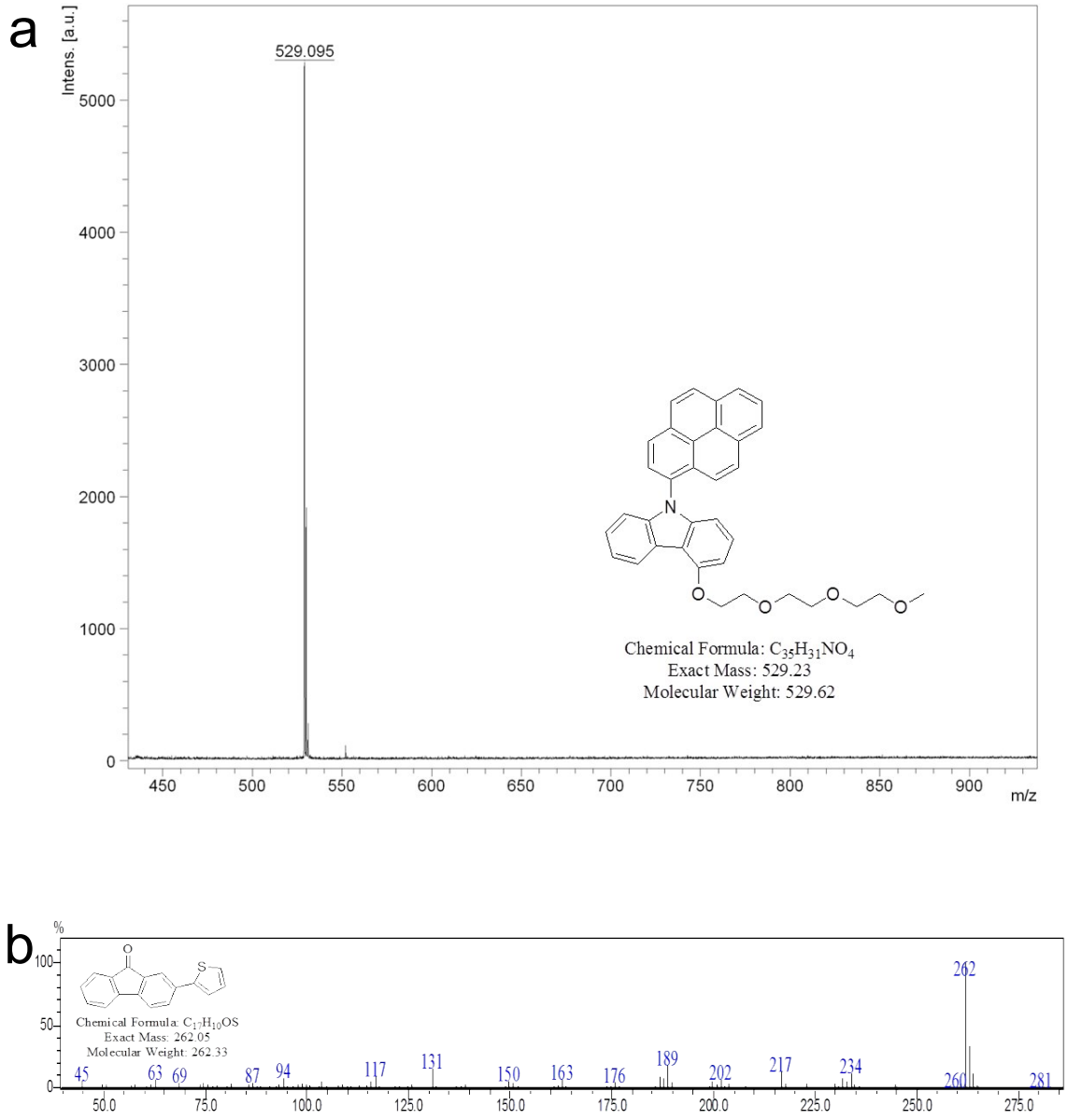


Fig. S3 (a) MALDI-TOF MS of MePyCz (b) GC-MS of ThFO.

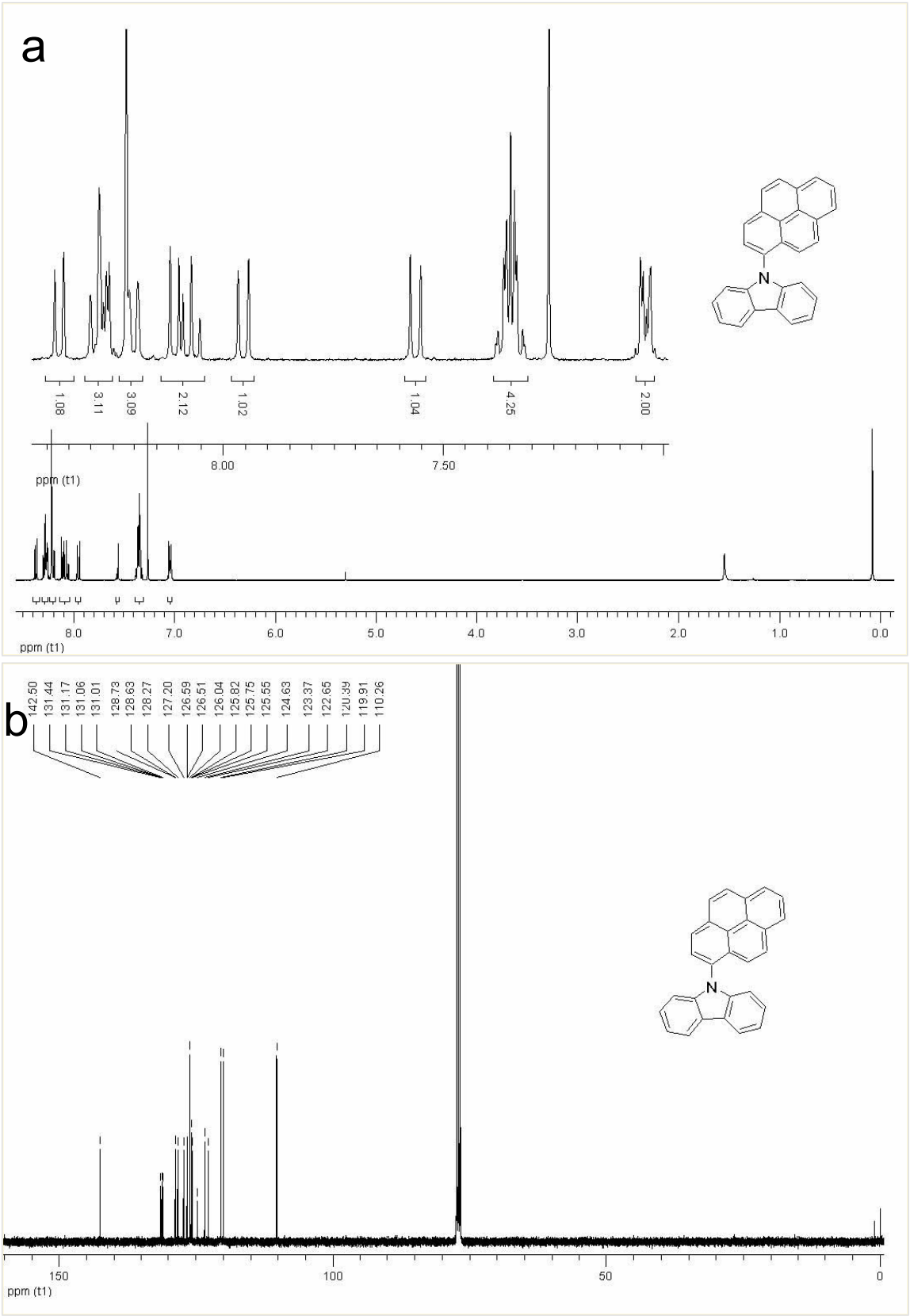


Fig. S4 (a) ^{1}H NMR (400 MHz, $CDCl_3$, ppm) and (b) ^{13}C NMR spectrum (100 MHz, $CDCl_3$, ppm) of PyCz.

C. **The diameter distribution of the PEO/MePyCz fibers.**

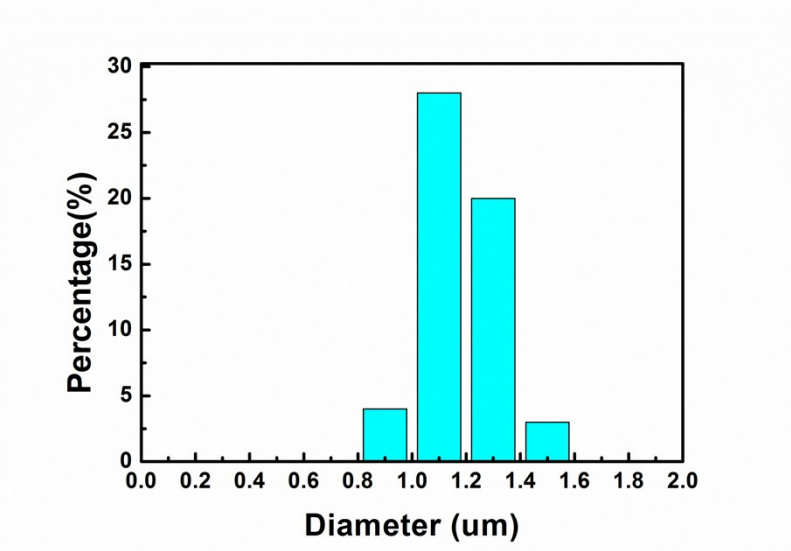


Fig. S5 The diameter distribution of the PEO/MePyCz fibers.

D. **Time-dependent fluorescence quenching process of PEO/MePyCz fibrous film with the MePyCz content of 5.0 wt%.**

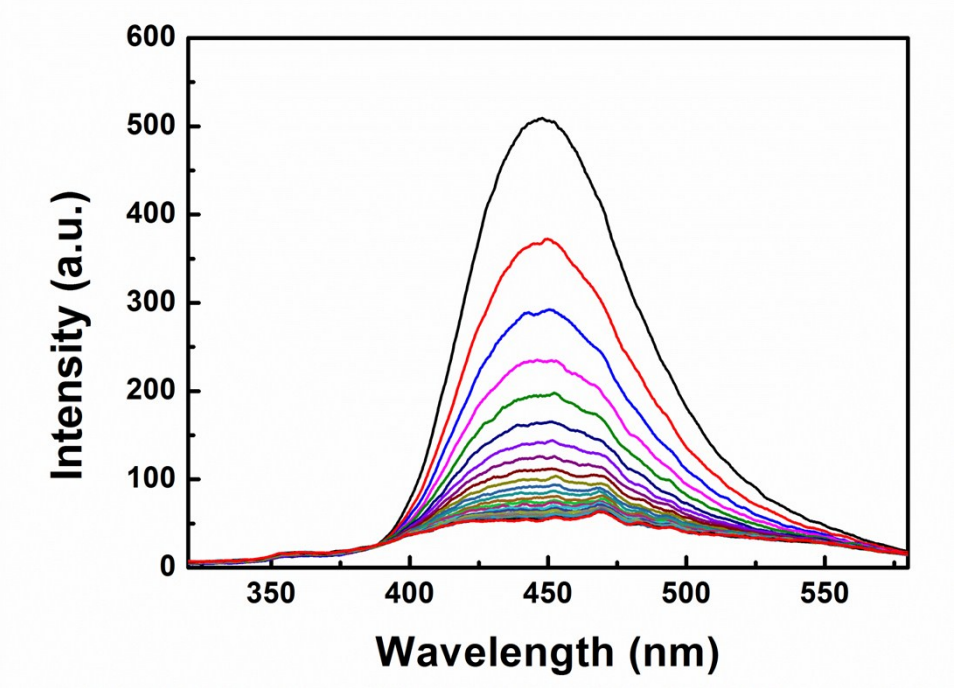


Fig. S6 Time-dependent fluorescence quenching process of PEO/MePyCz fibrous film with the MePyCz content of 5.0 wt%.

E. **Energy levels of HOMO and LUMO orbitals of MePyCz, PyCz and the target explosives.**

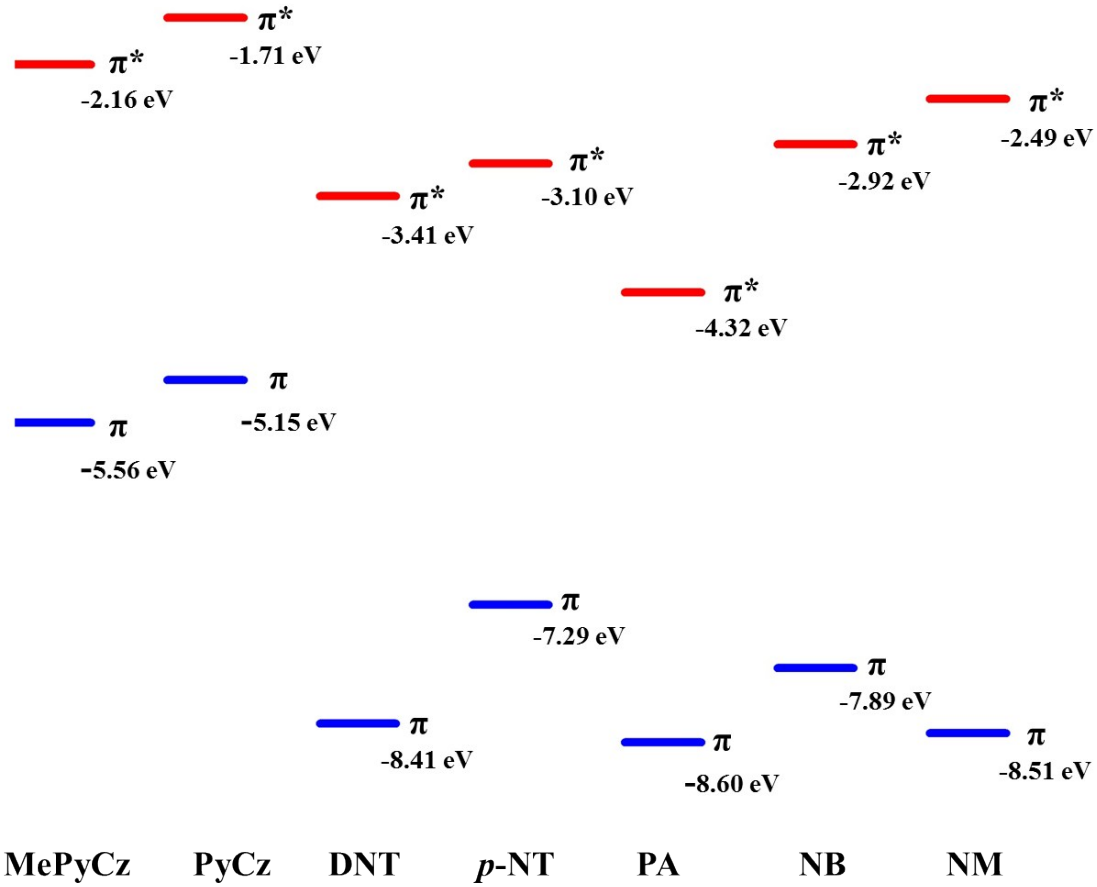


Fig. S7 Energy levels of HOMO and LUMO orbitals of MePyCz, PyCz and the target explosives. Geometry optimization and energy calculation were performed with density-functional theory (B3LYP/6-31g*) using Gaussian 09 package.

F. **Time-dependent fluorescence quenching process of PEO/MePyCz spin-coating film with the MePyCz content of 0. 5 wt%.**

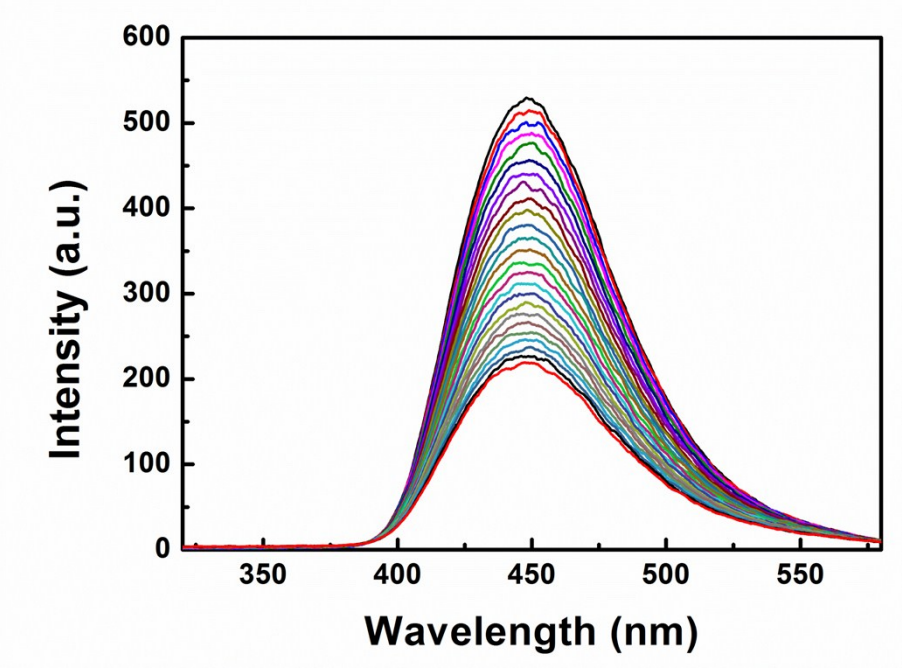


Fig. S8 Time-dependent fluorescence quenching process of PEO/MePyCz spin-coating film with the MePyCz content of 0.5 wt%.

G. **FESEM images of PEO/ThFO fibers and PEO/MePyCz/ThFO hybrid fibers.**

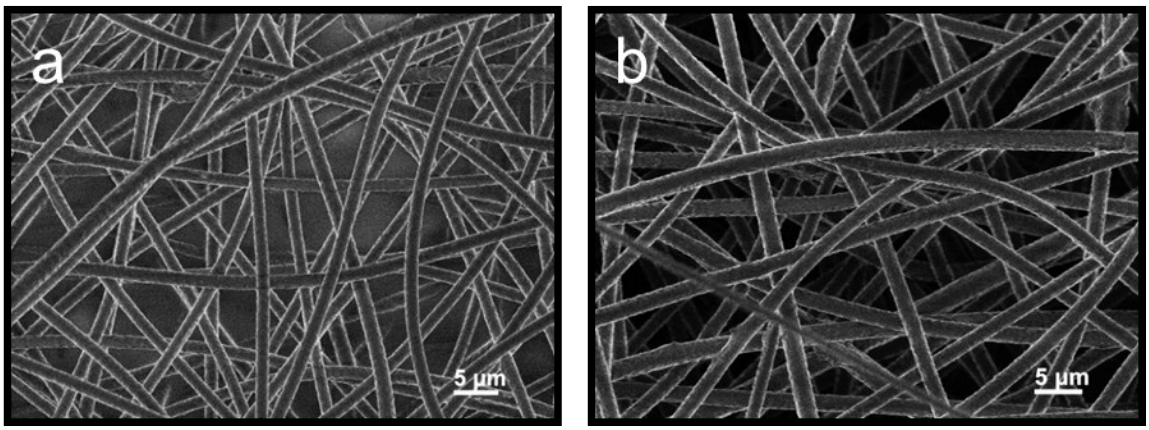


Fig. S9 FESEM images of (a) PEO/ThFO fibers and (b) PEO/MePyCz/ThFO (v_{MePyCz}:v_{ThFO}= 4:1) hybrid fibers.

H. **Fluorescence decay profiles of PEO/MePyCz/ThFO hybrid nanofibers.**

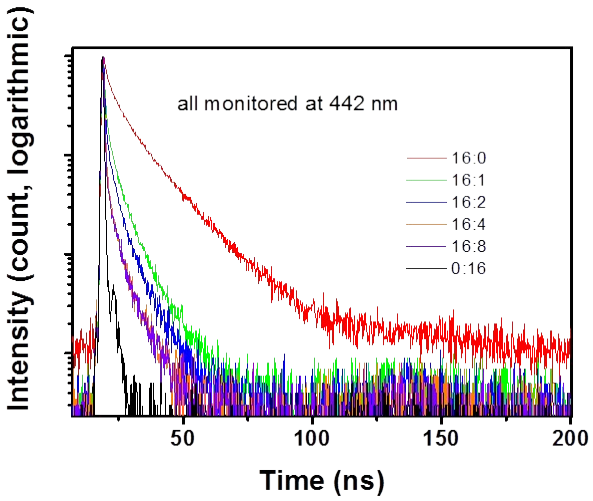


Fig. S10 Fluorescence decay profiles of PEO/MePyCz/ThFO hybrid nanofibers at different volume ratio of MePyCz and ThFO chloroform solution (v_{MePyCz}:v_{ThFO}= 16:0, 16:1, 16:2, 16:4, 16:8, 0:16) monitored at 442 nm.