Supporting Information

Electron rich supramolecular polymers as fluorescent sensors for nitroaromatic explosives

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Experimental section

Methods and materials: All the fluorophores (**1**−**3**) were synthesized following the modified literature method under dry nitrogen atmosphere using standard Schlenk technique.[1] All required solvents were dried and distilled according to the standard literature procedures. Pyrene, 9,10-dibrormoanthracene and 2-methyl-3-butyn-2-ol were purchased from various commercial sources and were used as received without further purification. 1,3,6,8-tetrabromopyrene, 1-bromopyrene were synthesized following the reported procedures.

Caution: TNT and other NACs used in the present investigations are highly explosive and should be handled only in small quantities.

NMR spectra were recorded on a Bruker 400 MHz spectrometer. The chemical shifts (δ) in ^{1}H NMR spectra are reported in ppm relative to tetramethylsilane (Me_4Si) as internal standard (0.0

ppm) or proton resonance resulting from incomplete deuteration of the NMR solvents: DMSO-d_6 (2.55) or $CDCl_3$ (7.26). Electrospray ionization mass spectrometry (ESI-MS) experiments were performed in Bruker Daltonics (Esquire 300 Plus ESI model) using standard spectroscopic grade solvents CH_3CN or CH_3OH. Electronic absorption spectral measurement was done using Perkin Elmer LAMBDA 750 UV/visible spectrophotometer and fluorescence emission studies were carried out on HORIBA JOBIN YVON Fluoromax-4 spectrometer. The life-time analyses were carried out on HORIBA Scientific DAS6 using spectroscopic grade solvents.

Synthesis and characterization of fluorophore 1. In a flame dried 100 mL round bottom Schlenk flask were dissolved 1-bromopyrene (1.0 g, 3.6 mmol) and 0.5 mL (5.4 mmol) 2-methyl-3-butyn-2-ol in freshly distilled 100 mL dry triethylamine. A mixture of 100 mg of $[(PPh_3)_2PdCl_2]$ (0.14 mmol), 50 mg of triphenylphosphine (0.19 mmol) and 50 mg of CuI (0.26 mmol) was added, and the suspension was refluxed with stirring under nitrogen atmosphere for 12 h. The volatile solvent was removed under vacuum and the resulting residue was purified by column chromatography (silica gel) using dichloromethane as eluent to obtain the expected fluorophore **1** as a yellow solid in 82% yield. Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.76; H, 5.76. ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 8.51−8.09 (m, 9H, pyrene-H), 5.76 (s, 1H, OH), 1.64 (s, 6H, $C(CH_3)_2(OH)$). ^{3}C NMR (DMSO-d_6): δ (ppm) = 131.94, 131.66, 131.50, 131.39, 130.24, 129.46, 129.02, 128.12, 127.60, 126.76, 126.70, 125.78, 125.73, 124.53, 124.31, 118.05, 103.00, 80.07, 64.96, 55.80, 32.66. ES-MS: calcd. for $C_{21}H_{16}O$ 284.1; found 285.1 (M+H).

Synthesis and characterization of fluorophore 2. In a flame dried 100 mL round bottom Schlenk flask were dissolved 9,10-dibromoanthracene (1.0 g, 2.97 mmol) and 0.9 mL (8.92 mmol) 2-methyl-3-butyn-2-ol in freshly distilled 100 mL dry triethylamine. A mixture of 100 mg of $[(PPh_3)_2PdCl_2]$ (0.14 mmol), 50 mg of triphenylphosphine (0.19 mmol) and 50 mg of CuI (0.26 mmol) was added, and the suspension was refluxed with stirring under nitrogen atmosphere for 16 h. The volatile solvent was removed under vacuum and the resulting residue was purified by column chromatography (silica gel) using ethyl acetate/hexane (1:3) as eluent to obtain the expected fluorophore **2** as a yellowish-orange solid in 45% yield. Anal. Calcd for $C_{24}H_{22}O_2$: C, 84.18; H, 6.48. Found: C, 84.39; H, 6.66. ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 8.53-8.50 (dd, 4H, anthracene-H), 7.74-7.71 (dd, 4H, anthracene-H), 5.85 (s, 2H, OH), 1.68 (s, 12H, $C(CH3)_2(OH)$). ^{13}C NMR (DMSO-d_6): δ (ppm) = 132.10, 128.29, 127.60, 118.33, 110.33, 77.57, 65.20, 32.59. ES-MS: calcd. for $C_{24}H_{22}O_2$ 342.16; found 343.2 (M+H).

Synthesis and characterization of fluorophore 3. In a flame dried 100 mL round bottom Schlenk flask were dissolved 1,3,6,8-tetrabromopyrene (1.0 g,1.9 mmol) and 1.1 mL (11.6 mmol) 2-methyl-3-butyn-2-ol in freshly distilled 100 mL dry triethylamine. A mixture of 100 mg of $[(PPh_3)_2PdCl_2]$ (0.14 mmol), 50 mg of triphenylphosphine (0.19 mmol) and 50 mg of CuI (0.26 mmol) was added, and the suspension was refluxed with stirring under nitrogen atmosphere for 16 h. The volatile solvent was removed under vacuum and the resulting residue was purified by column chromatography (silica gel) using dichloromethane/methanol (8:2) as eluent to obtain the expected fluorophore **3** as bright-yellow solid in 92% yield. Anal. Calcd for $C_{36}H_{34}O_4$: C, 81.48; H, 6.46. Found: C, 81.78; H, 6.80. ^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 8.49 (s, 4H, pyrene-H_a), 8.09 (s, 2H, pyrene-H_b), 5.76 (s, 4H, OH), 1.65 (s, 24H, C(CH3)$_2$(OH)). ^{13}C NMR (DMSO-d$_6$): δ (ppm) = 133.70, 131.57, 127.26, 123.85, 119.31, 104, 17, 78.99, 64.98, 46.54, 32.53, 9.48. ES-MS: calcd. for $C_{36}H_{34}O_4$ 530.25; found 531.3 (M+H).

X-ray data collection and structure refinements. The diffraction data of fluorophores **1** and **3** was collected on a Bruker SMART APEX CCD diffractometer using the SMART/SAINT software and.[2] Intensity data were collected using graphite-monochromatic Mo-Kα radiation (0.7107 Å) at 295 K on a crystal as obtained after several attempts. The structure was solved by direct methods using the SHELX-97[3] incorporated in WinGX.[4-6] Empirical absorption corrections were applied with SADABS.[7] All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were assigned isotropic displacement coefficients, U(H) = 1.2U(C) or 1.5U (C-methyl), and their coordinates were allowed to ride on their respective carbons.

Fluorescence quenching titrations in solution. A 2 mL stock solution (5.0×10^{-6} M) of the fluorophore (**1−3**) was placed in a quartz cell of 1 cm width and analyte solution (1.0×10^{-3} M) was added in an incremental fashion. Their corresponding fluorescence emission spectra were recorded at 298 K. Each titration was repeated at least two times to get concordant value. For all measurement excitation wavelength (λ_{ex}) 363 nm for **1**, 270 nm for **2**, 310 nm for **3** and the corresponding emission wavelength (λ_{em}) was monitored from 380 nm for **1**, 280 nm for **2**, 320 nm for **3**. Both excitation and emission slit width were kept at 1 nm for all measurements. Relative fluorescence intensities were measured for solution of fluorophores **1−3** in chloroform and the various analytes was used as quencher in chloroform. There was no change in shape of the emission spectra except gradual quenching of the initial fluorescence emission intensity upon titration with electron deficient nitroaromatic quenchers. Analysis of the normalized fluorescence emission intensity (I_0/I) as a function of increasing quenchers concentration ([Q]) was well described by the Stern-Volmer equation $I_0/I = 1 + K_{SV}[G]$. The Stern-Volmer binding constant was calculated from the slope of the Stern-Volmer plot.

Solid-state fluorescence quenching study. The fluorescence quenching of the fluorophores **1−3** with 2,4-dinitrotoluene in solid state was performed by inserting the freshly prepared thin film in to the beaker containing solid 2,4-dinitrotoluene and cotton quaze, which prevents the direct contact of the film with 2,4-dinitrotoluene and maintain the vapor pressure of the quencher during measurements. After a certain period of exposure, film was placed in the sample holder immediately and checked for the fluorescence quenching of the initial film intensity. For all measurement the excitation wavelength λ_{ex} = 364 nm for **1**; 410 nm for **2**; 427 nm for **3** and their corresponding emission was monitored from λ = 370−700 nm for **1**; 420−700 nm for **2**; 450−700 nm for **3**. For all the measurements excitation and emission slit width were kept at 2 nm. The observed fluorescence quenching was calculated using following equation

$$\boldsymbol{\eta = (I_0\text{-}I/I_0) \times 100\ \%}$$

Where, I_0 is the initial fluorescence intensity of the fluorophore and I is the fluorescence intensity after a period of exposure time.

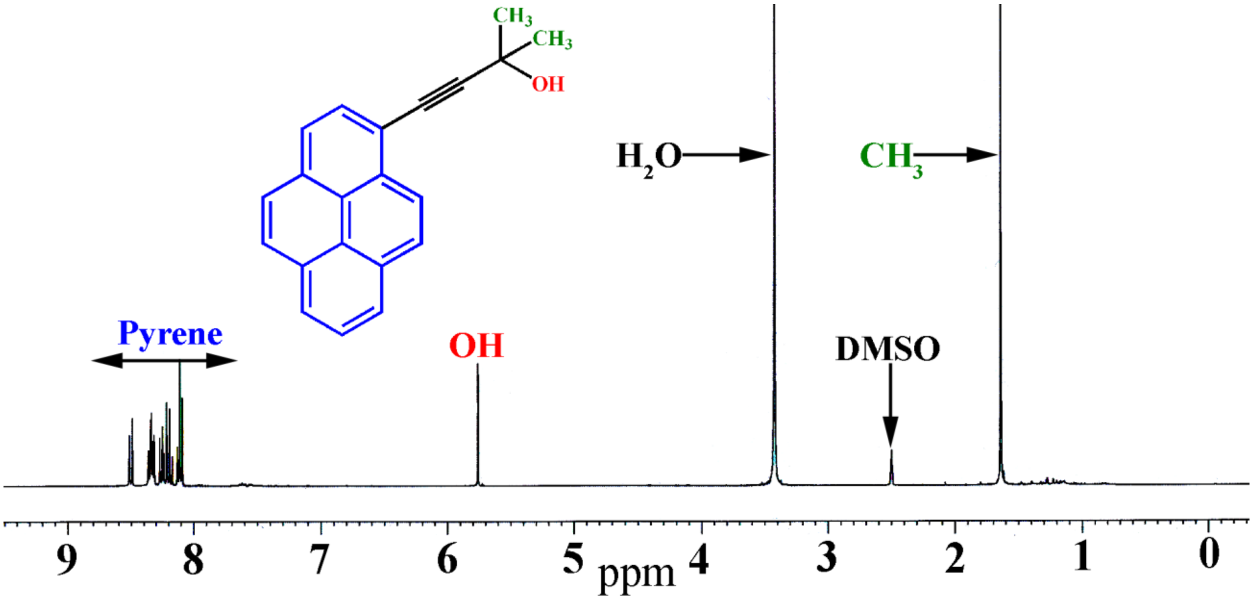

Fig. S1. ^{1}H NMR spectrum of fluorophore **1** recorded in DMSO-d$_6$.

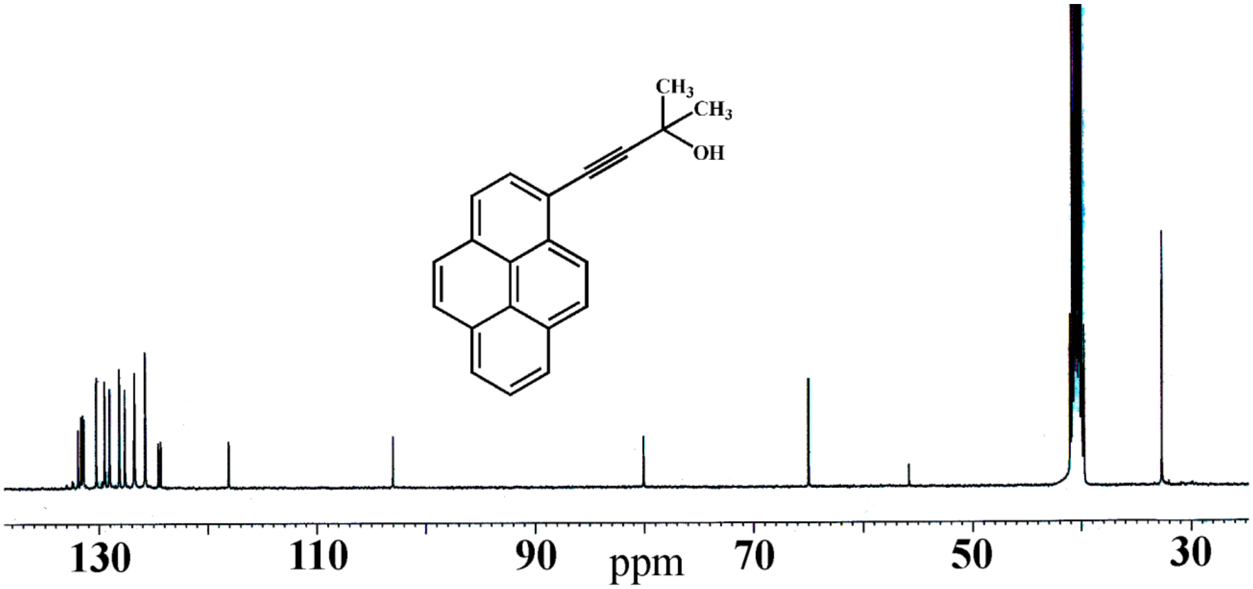

Fig. S2. ^{13}C NMR spectrum of fluorophore **1** recorded in DMSO-d$_6$.

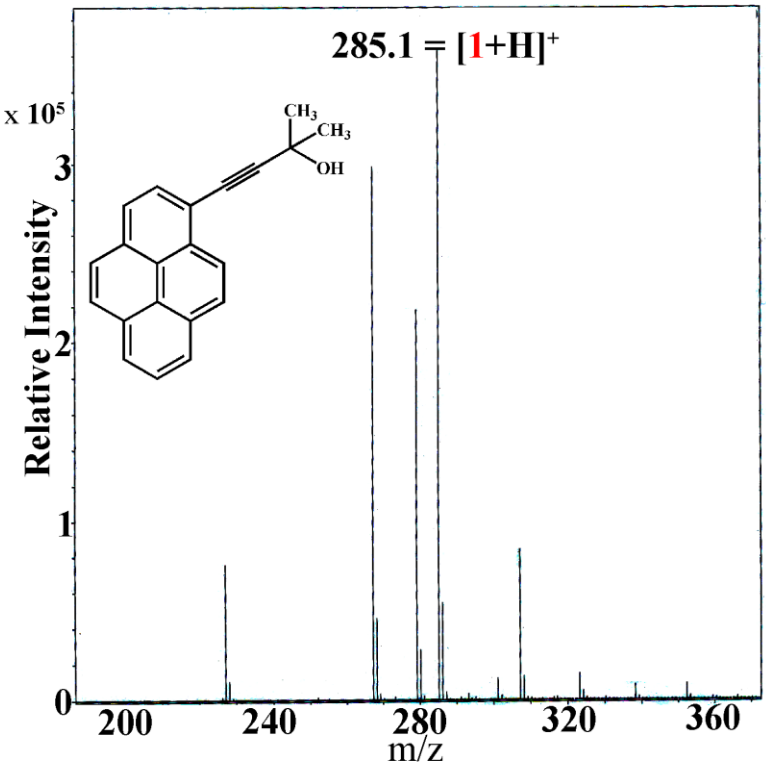

Fig. S3. ESI-MS spectrum of fluorophore **1** recorded in acetonitrile.

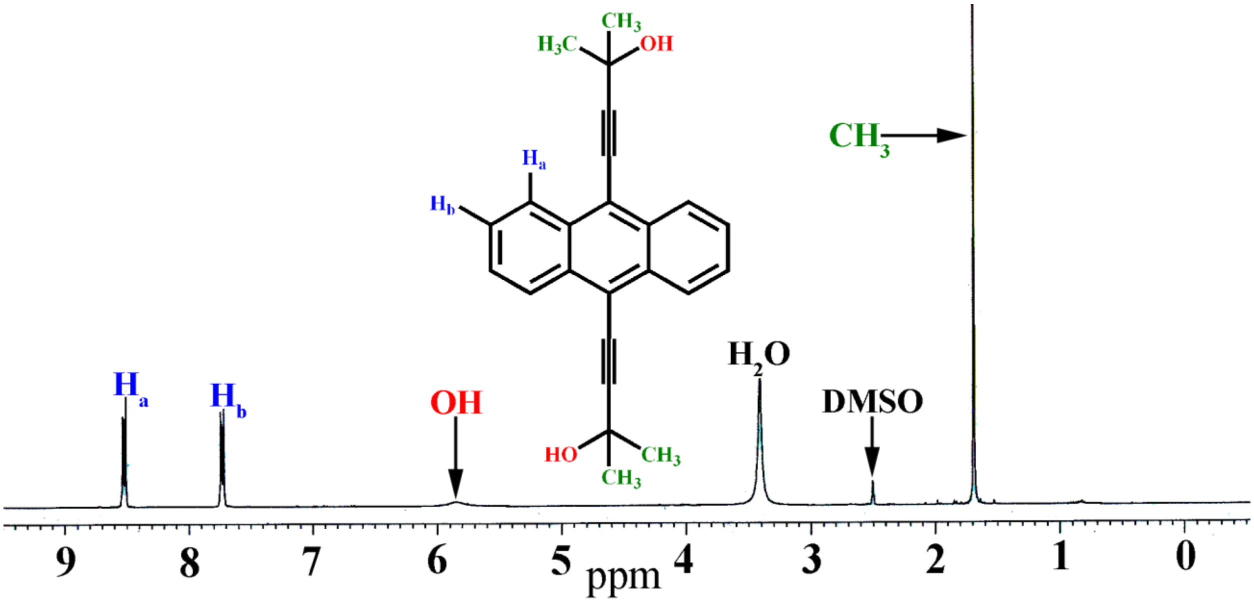

Fig. S4. ^{1}H NMR spectrum of fluorophore **2** recorded in DMSO-d$_6$.

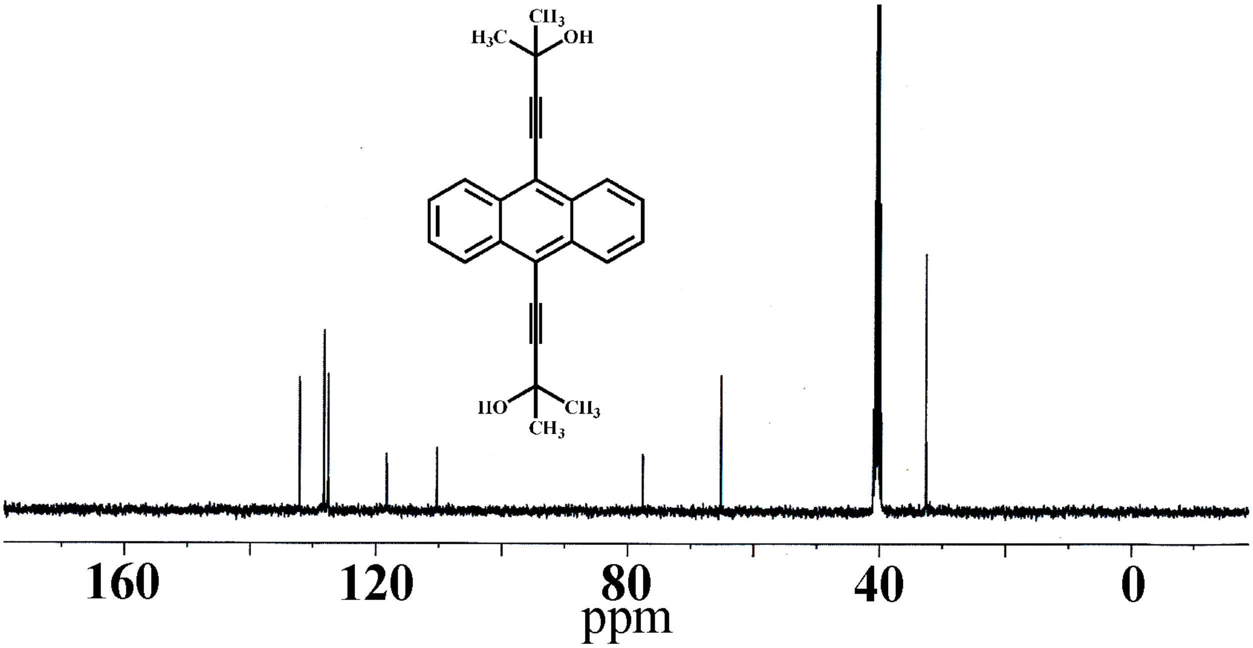

Fig. S5. ^{13}C NMR spectrum of fluorophore **2** recorded in DMSO-d$_6$.

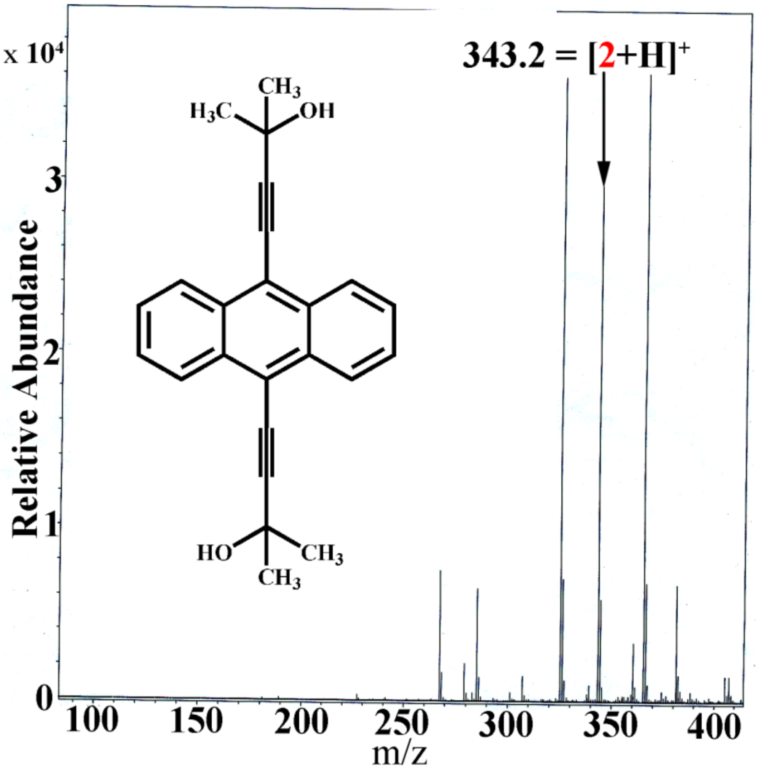

Fig. S6. ESI-MS spectrum of fluorophore **2** recorded in acetonitrile.

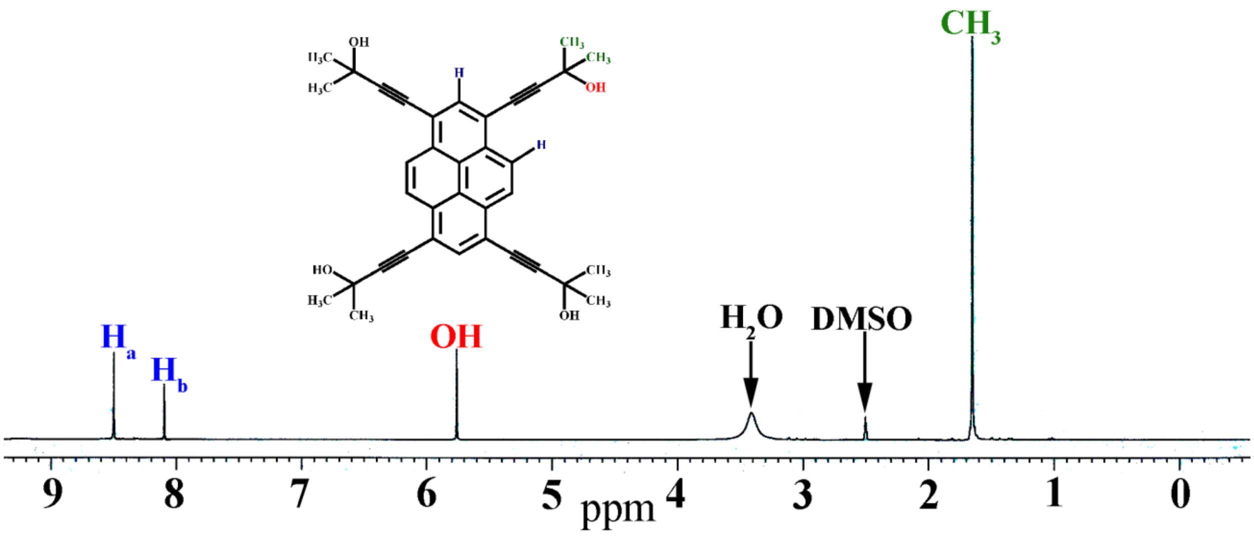

Fig. S7. ^{1}H NMR spectrum of fluorophore **3** recorded in DMSO-d$_6$.

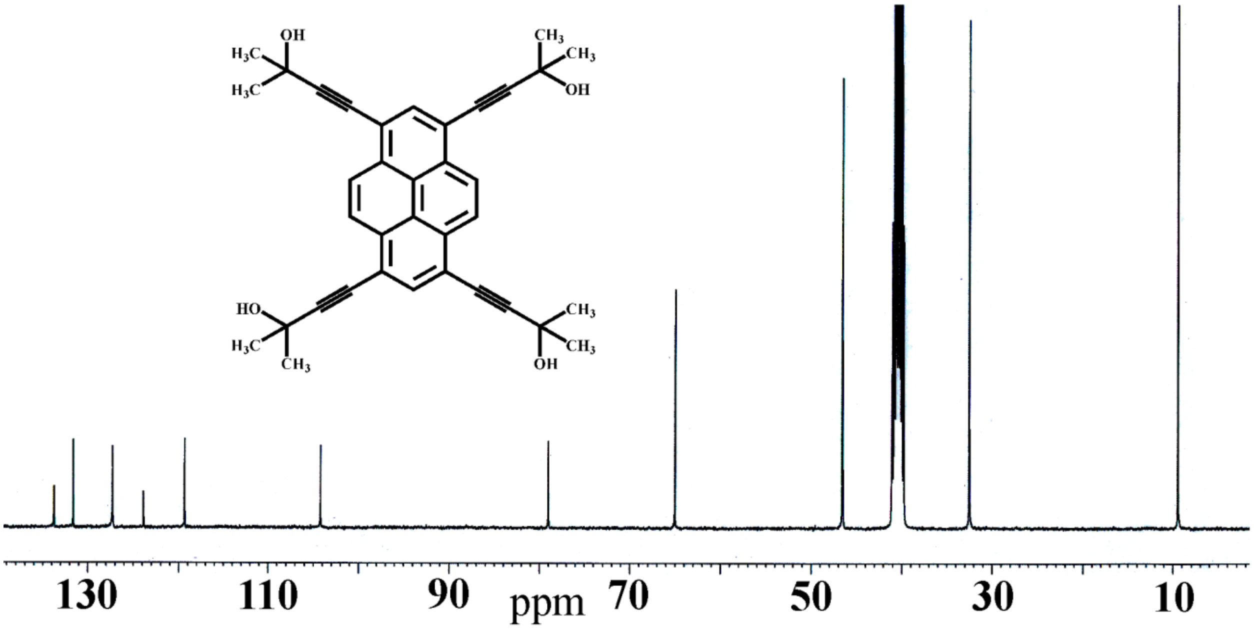

Fig. S8. ^{13}C NMR spectrum of fluorophore **3** recorded in DMSO-d$_6$.

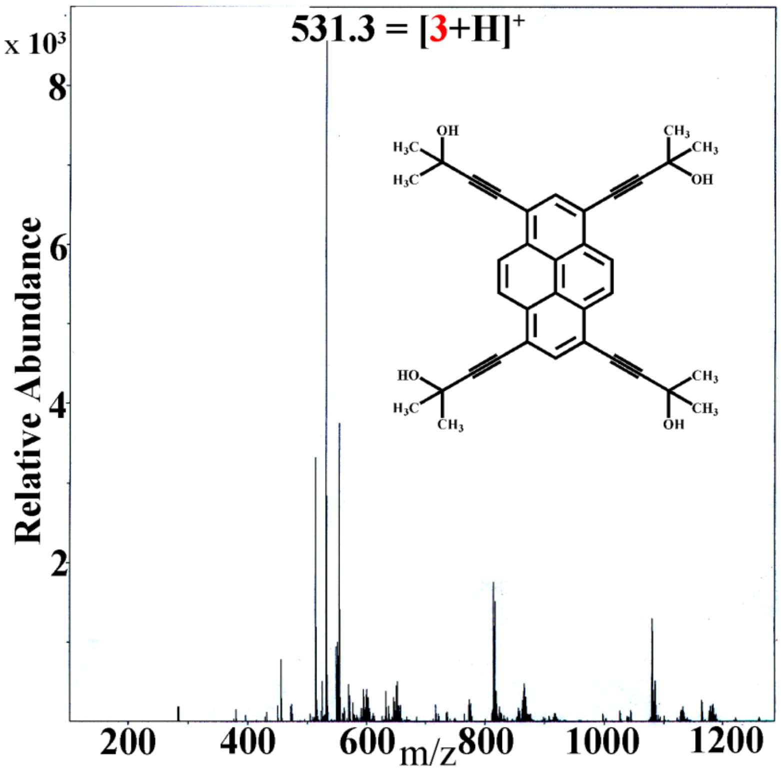

Fig. S9. ESI-MS spectrum of fluorophore **3** recorded in acetonitrile.

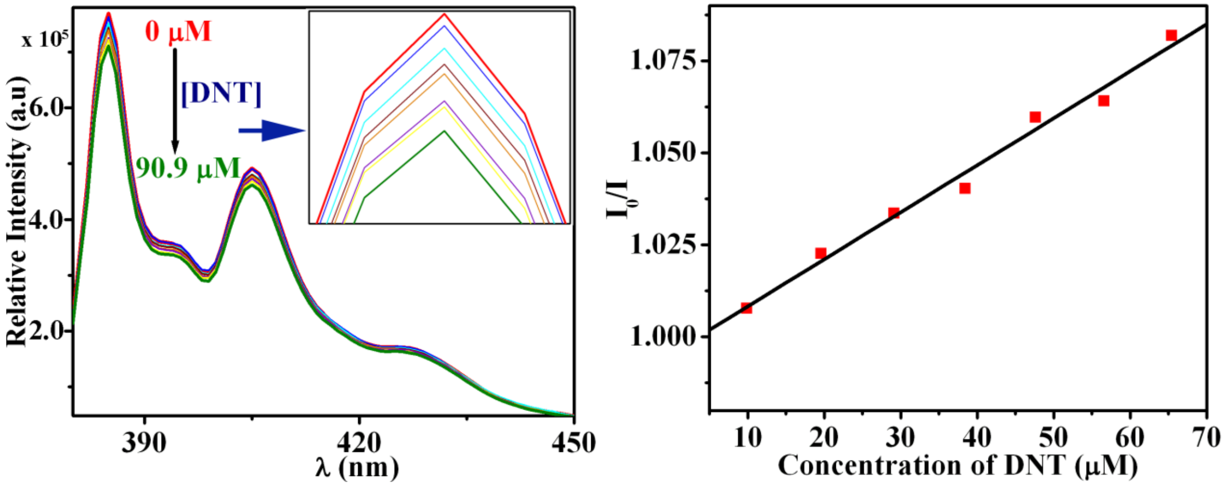

Fig. S10. Fluorescence quenching (left) of the fluorophore **1** (5.0 μM) with DNT in chloroform solution and its corresponding Stern-Volmer plot (right).

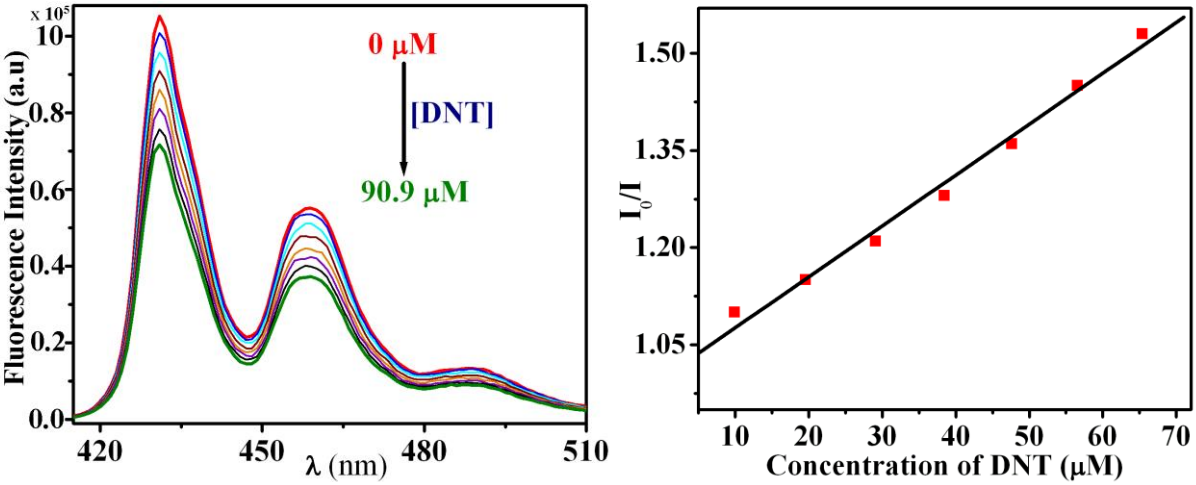

Fig. S11. Fluorescence quenching (left) of the fluorophore **3** (5.0 μM) with DNT in chloroform solution and its corresponding Stern-Volmer plot (right).

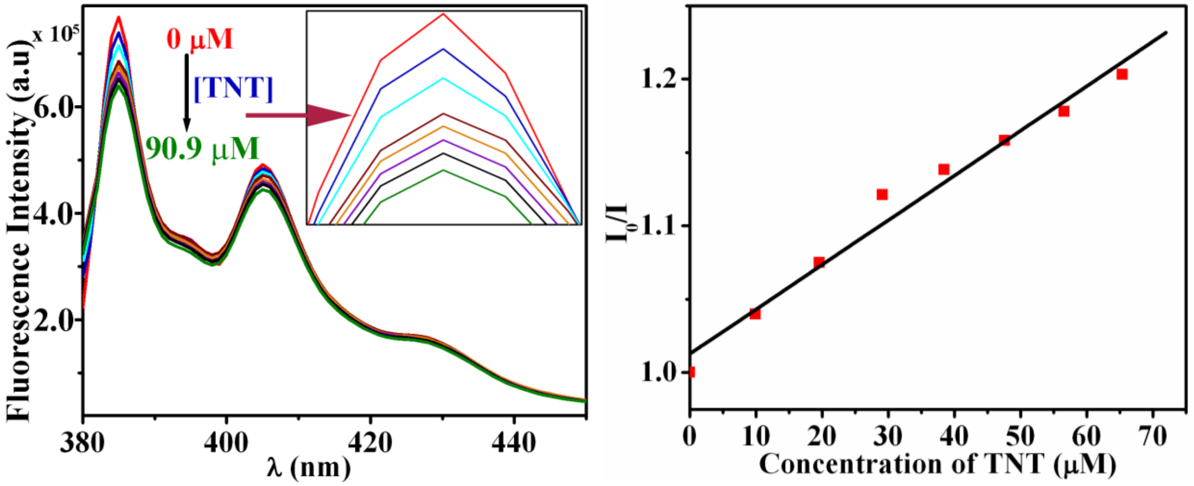

Fig. S12. Fluorescence quenching (left) of the fluorophore **1** (5.0 μM) with TNT in chloroform solution and its corresponding Stern-Volmer plot (right).

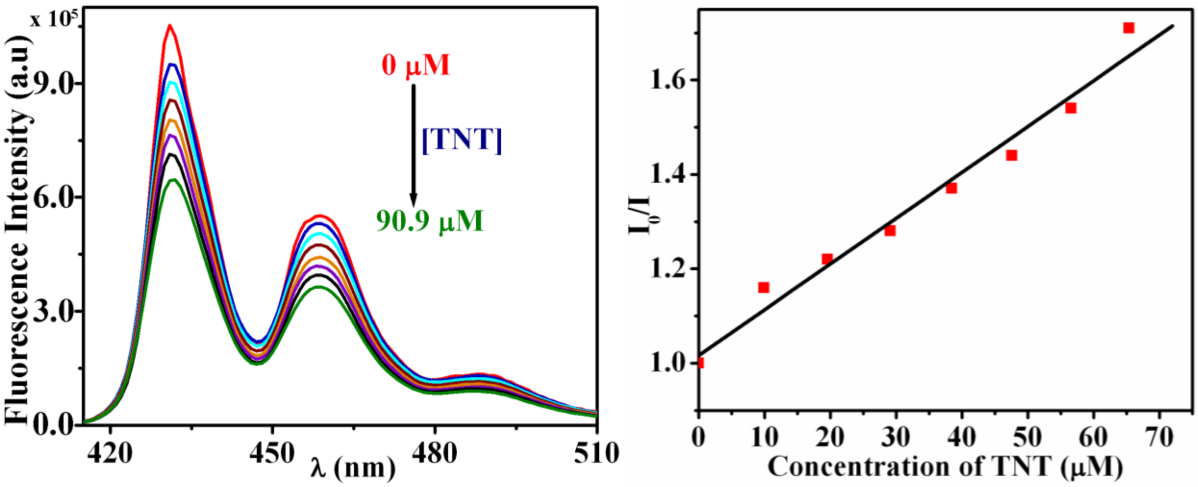

Fig. S13. Fluorescence quenching (left) of the fluorophore **3** (5.0 μM) with TNT in chloroform solution and its corresponding Stern-Volmer plot (right).

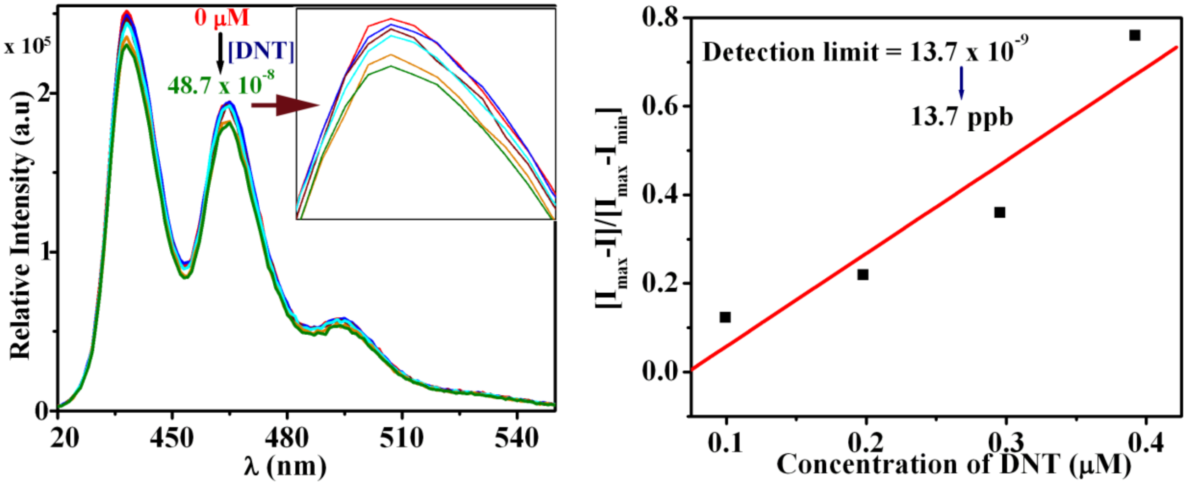

Fig. S14. Changes in initial fluorescence intensity of the fluorophore **2** upon gradual addition of DNT (0−48.7 × 10^{-8} M in chloroform) and its corresponding detection limit plot.

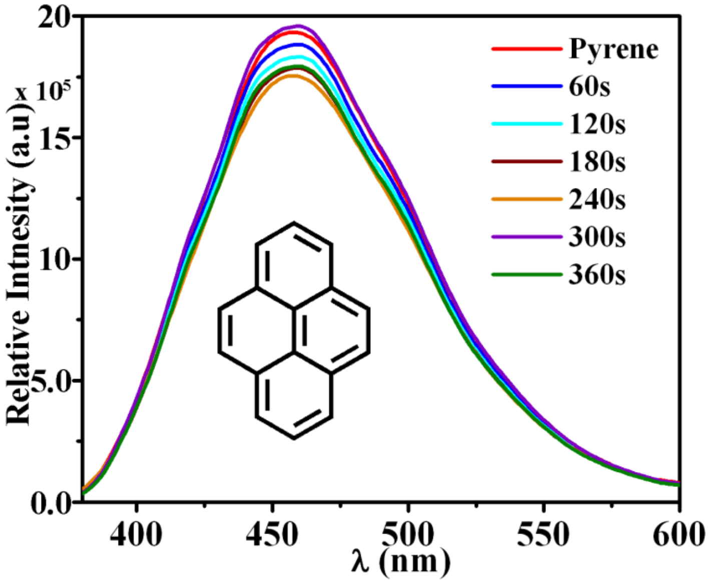

Fig. S15. Fluorescence spectra (left) of thin film of pyrene upon exposure to the saturated vapor of DNT at different time interval.

Table S1. Crystallographic Data and Refinement Parameters of **1** and **3**.

	1	**3**
empirical formula	$C_{21}H_{16}O$	$C_{36}H_{34}O_4$
formula weight	284.34	530.63
crystal system	monoclinic	Orthorhombic
space group	*P* -2yc	-*P* 2n 2ab
T, K	295	296
λ (Mo Kα), Å	0.71073	0.71073
a, Å	23.955(4)	16.8215(8)
b, Å	7.5099(12)	24.9185(14)
c, Å	8.5462(14)	7.4008(4)
α, °	90	90

β, °	95.195(3)	90
γ, °	90	90
V, Å^3	1531.1(4)	3102.2(3)
Z	4	4
ρ_{calcd}, g cm^{-1}	1.234	1.136
μ, mm^{-1}	0.074	0.073
GOF[a]	1.069	0.936
R1[b] $[I > 2\sigma(I)]$	0.0695(3580)	0.0840(1156)
wR2[c] $[I > 2\sigma(I)]$	0.0893(5662)	0.2771(2734)

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[a] GOF = $\{\Sigma [\, w(F_0^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n and p denotes the number of data points and the number of parameters, respectively. [b] R1 = $(\Sigma \,||F_0| - |F_c||)/\Sigma |F_0|$; [c] wR2 = $\{ \Sigma [\, w(F_0^2 - F_c^2)^2]/\Sigma[\, w(F_0^2)^2]\}^{1/2}$, where $w = 1/ [\, \sigma^2(F_0^2) + (aP)^2 + (bP)]$ and $P = [\, \max (0,F_0^2) + 2F_c^2]/3$.

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