Supporting Information

Supramolecular polymer for explosives sensing: role of H-bonding in enhancement of sensitivity in solid state

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Materials and Methods

All the reagents and solvents were purchased from various commercial vendors and were used as received without further purification. Sensors **1–3** were synthesized by employing Sonagashira coupling reactions under a stream of nitrogen atmosphere. Triethylamine was dried over sodium/KOH and distilled freshly under nitrogen atmosphere in prior to the reactions and all solvents used for the photo-physical studies were of spectroscopic grade. All the nitroaromatic compounds (NAC) and other quenchers including benzoic acid (BA), benzoquinone (BQ), 4-methoxybenzoic acid (4-MeOBA) were of analytical grade and used directly without further purification.

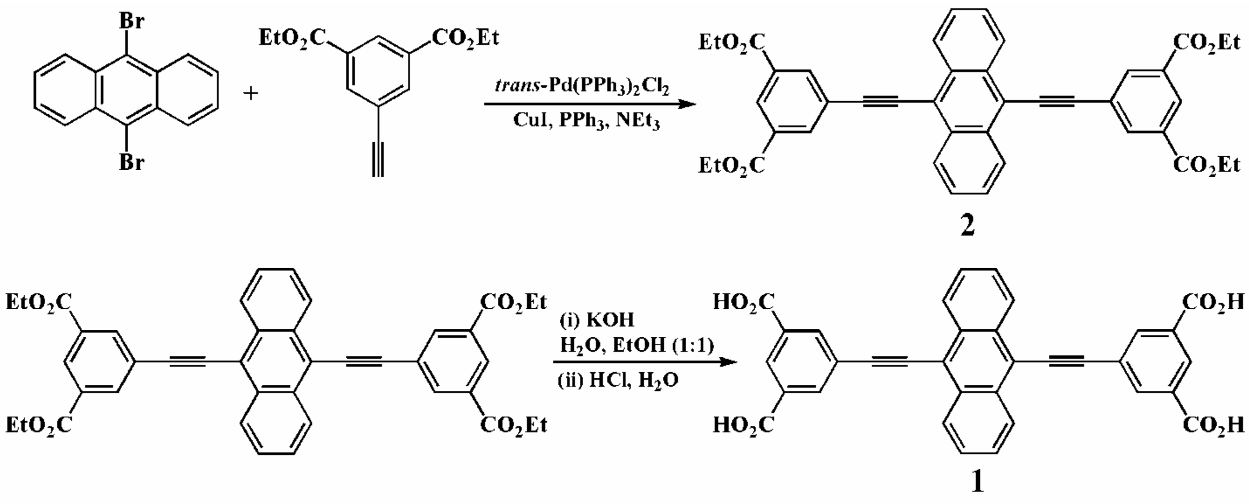
Caution!: TNT and other nitroaromatic compounds used in the present study are highly explosive and should be handled only in small quantity.

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: $CDCl_3$ (7.26) and DMSO-d_6 (2.50).^{13}C NMR were recorded at 75 MHz, and the chemical shifts (δ) are reported in ppm relative to external $CDCl_3$ at 77.8-77.2 ppm. IR spectra were recorded on a Bruker ALPHA FT-IR spectrometer. Electronic absorption spectra were recorded on a Perkin Elmer LAMBDA 750 UV/visible spectrophotometer. Fluorescence emission studies were carried out on HORIBA JOBIN YVON Fluoromax-4 spectrometer.

Synthesis of sensors 1 and 2. In a flame dried 100 mL double-necked round bottom Schlenk flask were dissolved diethyl 5-ethynylbenzene-1,3-dioate (271 mg, 1.1 mmol), 9,10-dibromoanthracene (168 mg, 0.5 mmol), $Pd(PPh_3)_2Cl_2$ (30 mg), PPh_3 (15 mg) and CuI (15 mg) in freshly distilled 30 mL dry triethylamine and then the suspension was refluxed with stirring under nitrogen atmosphere for 48h. During this time the bright orange precipitate was started to form. The volatile solvent was removed under vacuum and the resulting residue was purified by column chromatography (silica gel) using dichloromethane/hexane (4:1) as eluent to obtain the expected 9,10-bis[diethyl-5-ethynylbenzene-1,3-dioate]anthracene **2** as a bright orange solid in 80% yield. Anal. Calcd for $C_{42}H_{34}O_8$: C, 75.66; H, 5.14. Found: C, 75.71; H, 5.20. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.715 (d, 4H), 8.712 (s, 2H), 8.594 (s, 4H), 7.724 (d, 4H), 4.502 (q, 8H), 1.482 (t, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.715, 137.704, 136.895, 132.685, 132.038, 130.823, 127.755, 127.660, 124.759, 118.710, 101.002, 88.539, 62.230, 14.854. IR (KBr): ν = 1718, 1594, 1444, 1313, 1235 cm^{-1}.

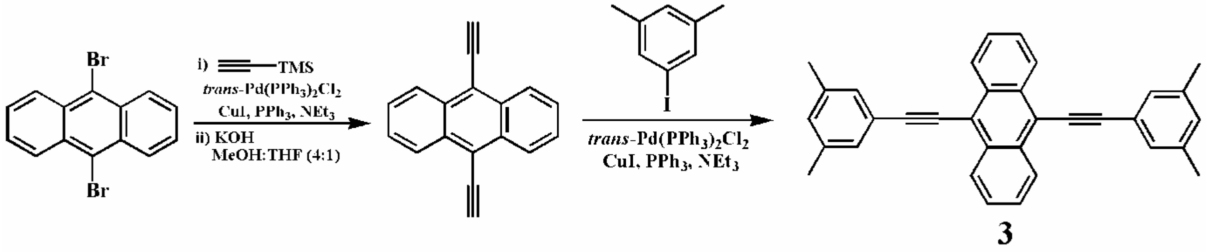
2 (200 mg, 0.3 mmol) was suspended in 50 mL of ethanol and 50 mL of H_2O. To which KOH (160.5 mg, 3 mmol) was added and the mixture was stirred under reflux for overnight. Organic solvent was removed using a rotary evaporator and diluted hydrochloric acid was added to the remaining aqueous solution until it became acidic (pH = ~ 2 to 3). The precipitate was collected by filtration, washed several times with water and dried under vacuum to give 9,10-bis[1,3-dicarboxylicacid-5- ethynylbenzene]anthracene **1** as a dark red solid in 80% yield. Anal. Calcd for $C_{34}H_{18}O_8$: C, 73.65; H, 3.27. Found: C, 73.79; H, 3.53.^{1}H

NMR (400 MHz, DMSO-d_6): δ = 8.715 (d, 4H), 8.533 (s, 4H), 8.515 (s, 2H), 7.842 (d, 4H). IR(KBr): ν = 2922, 1694, 1593, 1437, 1202 cm^{-1}.



Synthesis of 3.

A double-necked 100 mL Schlenk flask was charged with 9,10-diethynylanthracene (79.2 mg, 0.35 mmol), 1-iodo-3,5-dimethylbenzene (324.9 mg, 1.4 mmol), $Pd(PPh_3)_2Cl_2$ (50 mg), PPh_3 (25 mg) and CuI (25 mg) and then flask was pumped under vacuum and refilled with N_2 for three times. To the reaction mixture 20 mL of dried and degassed triethylamine was added and mixture was heated to reflux under nitrogen atmosphere for 36 hours. The organic solvent was removed and the crude product was purified by column chromatography on silica gel with hexane to get sensor **3** as a yellow-orange solid in 75 % yield. Anal. Calcd for $C_{34}H_{26}$: C, 93.97; H, 6.03. Found: C, 94.12; H, 6.27. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.698 (d, 4H), 7.645 (d, 4H), 7.413 (s, 4H), 7.062 (s, 2H), 2.400 (s, 12H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 138.649, 132.560, 131.153, 129.839, 127.785, 127.208, 123.532, 119.000, 103.304, 86.321, 21.715. IR (KBr): ν = 1590 cm^{-1}.



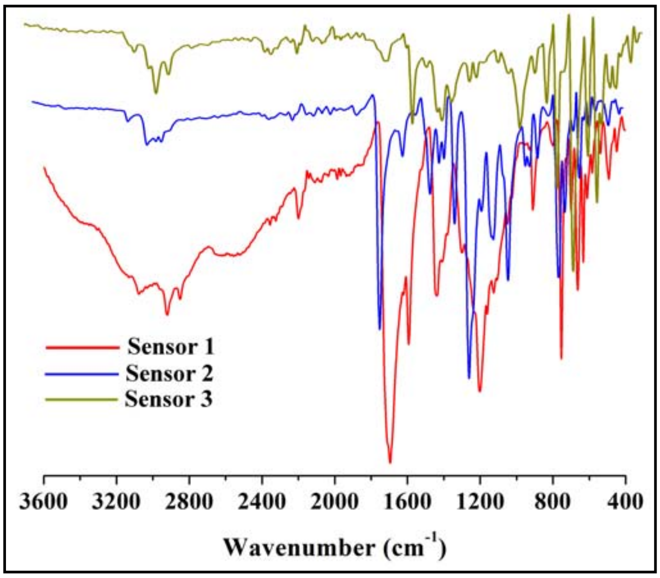


Figure S1. Infra-red spectra of sensors **1-3**.

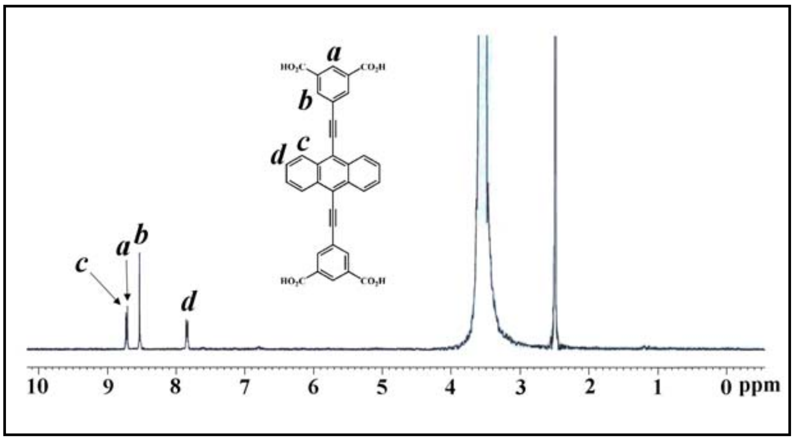


Figure S2. ^{1}H NMR spectrum of sensor **1** recorded in DMSO-d$_6$.

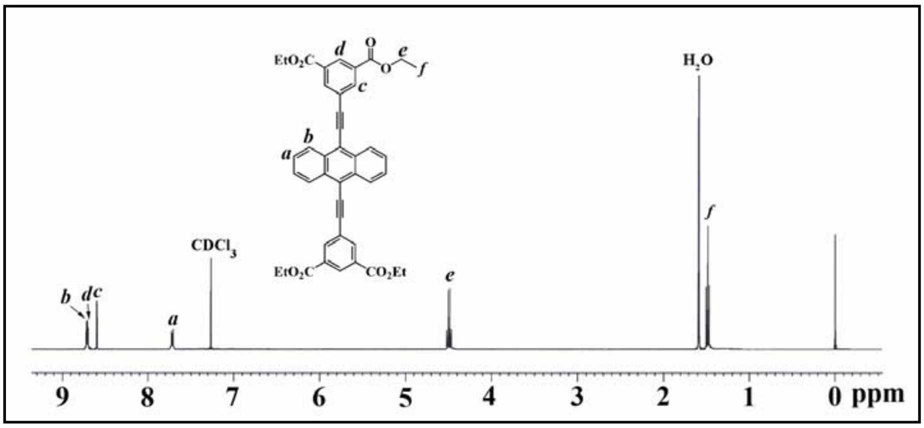


Figure S3. ^{1}H NMR spectrum of sensor **2** recorded in CDCl$_3$.

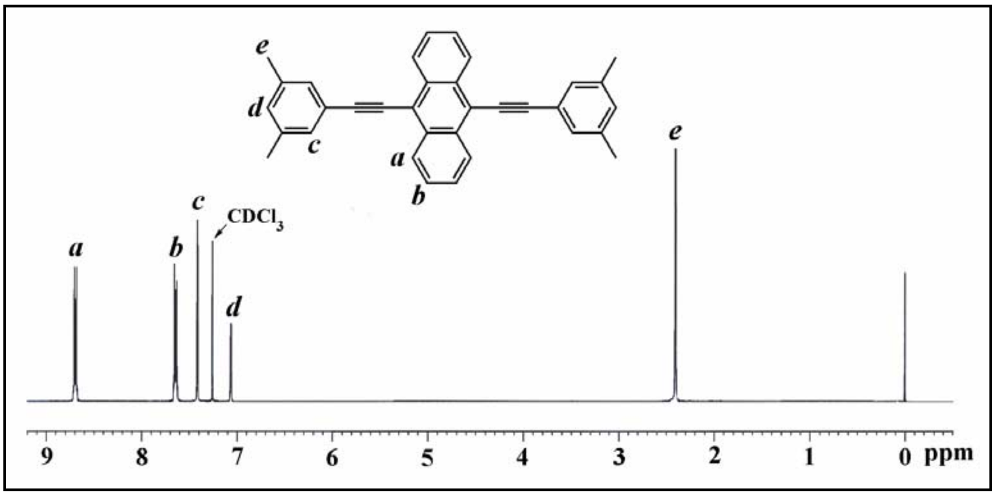


Figure S4. ^{1}H NMR spectrum of sensor **3** recorded in CDCl$_3$.

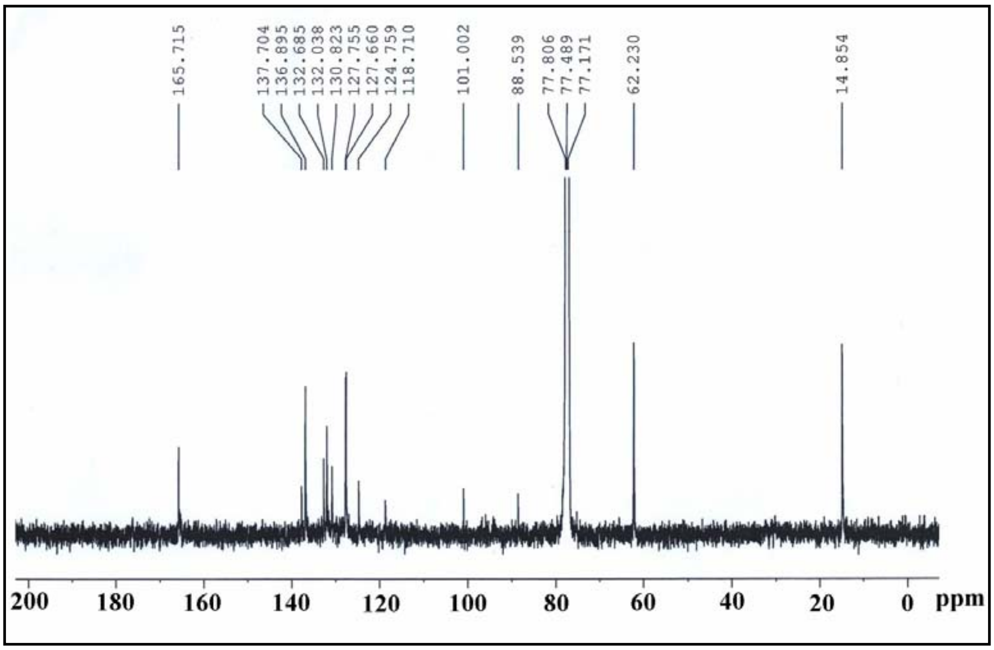


Figure S5. ^{13}C NMR spectrum of the sensor **2** recorded in CDCl$_3$.

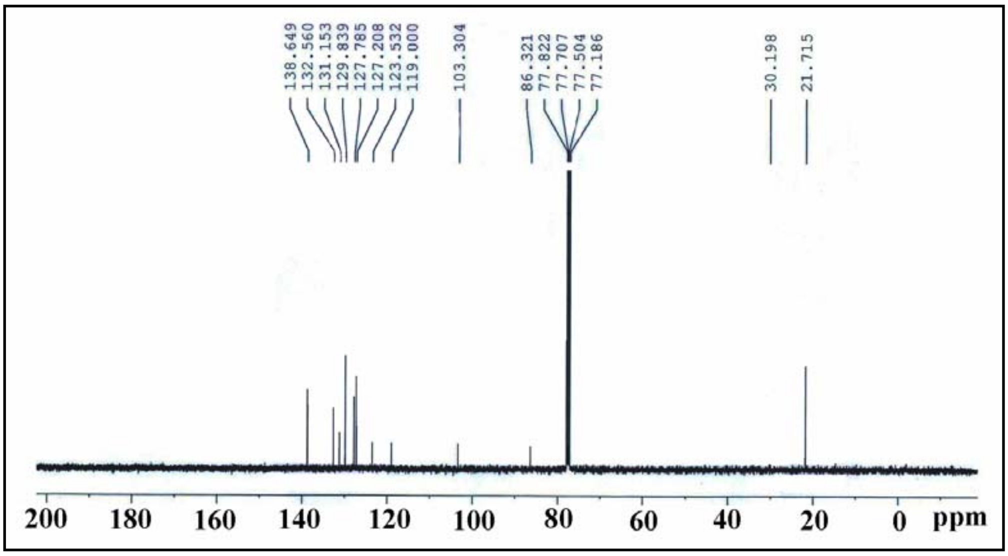


Figure S6. ^{13}C NMR spectrum of sensor **3** recorded in $CDCl_3$.

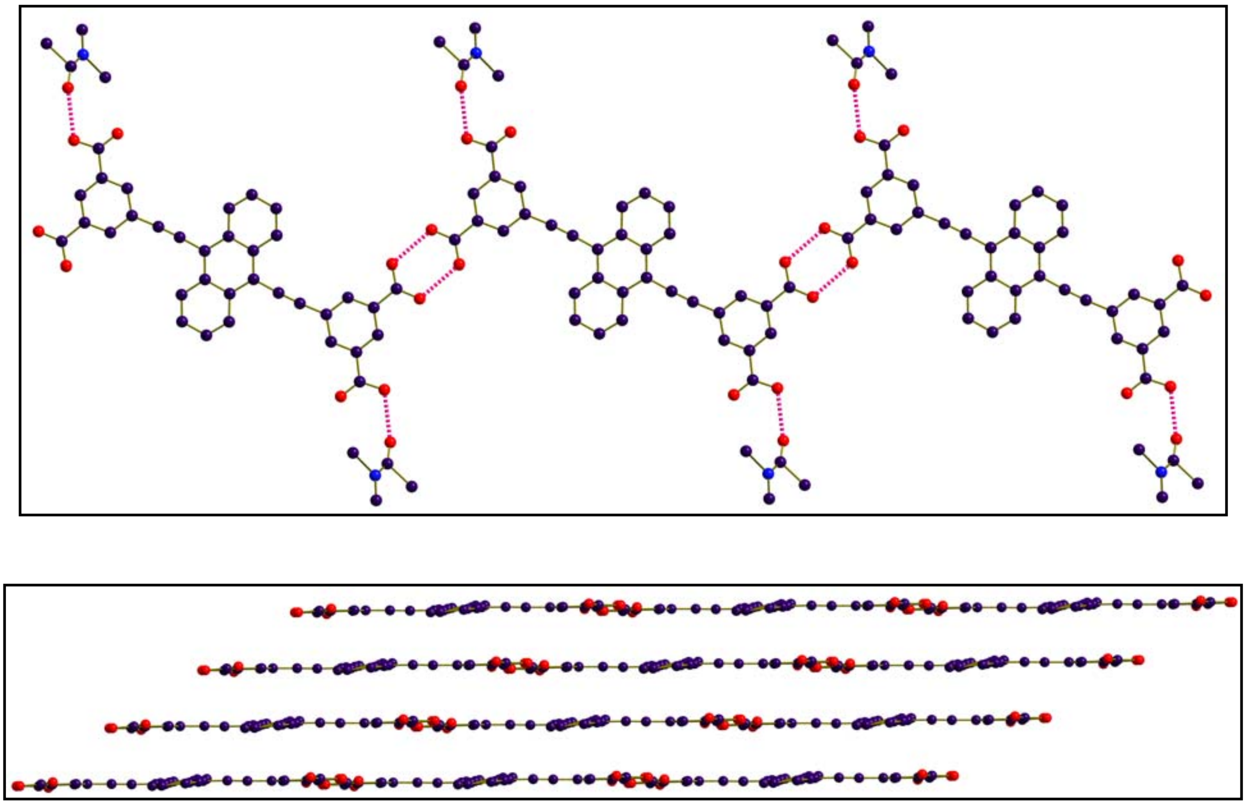


Figure S7. Solid-state packing structure of **1** top view (above) and side-view (below). (Color codes; Purple = carbon, red = oxygen, blue = nitrogen and magenta = hydrogen)

Fluorescence Quenching Titrations in Solution. A 2 mL stock solution (1.0×10^{-6} M) of the sensors (**1-3**) was placed in a quartz cell of 1 cm width and quenchers (1.0×10^{-3}M) solution was added gradually in an incremental fashion. Their corresponding fluorescence emission spectra were recorded at 298 K. Each titration was repeated at least three times to get concordant value. For all measurement, sensors (**1-3**) were excited at λ_{ex} = 440 nm and their corresponding emission wavelength was monitored from λ_{em} = 450 nm. Both excitation and emission slit width were 1 nm for all the measurement. Relative fluorescence intensities were measured for solution of sensors **1-3** in DCM/DMA and various analytes were used as quenchers in methanol. 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 study of the sensors **1** and **2** with nitrobenzene in solid state was performed by inserting the film (freshly prepared thin film on glass surface) in to a beaker containing nitrobenzene and cotton gauze, which prevents the direct contact of the film with nitrobenzene and also maintain the vapor pressure of the quencher during measurements. After a period of exposure, film was placed immediately in the sample holder and checked for the fluorescence quenching of the initial film intensity. For all measurement the excitation wavelength λ_{ex} = 440 nm and corresponding emission was monitored at λ_{em} = 450 nm onwards. The excitation and emission slit width were at 2 nm. The observed fluorescence quenching was calculated using following equation

$$\eta = (I_0 - I)/I_0 \times 100\ \%$$

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

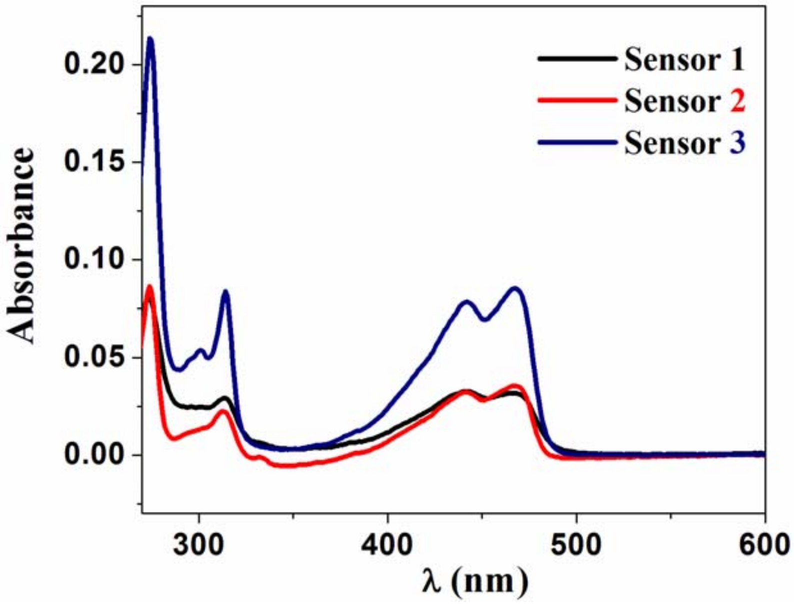


Figure S8. Electronic absorption spectra of sensors (**1**-**3**) recorded in DCM or DMA.

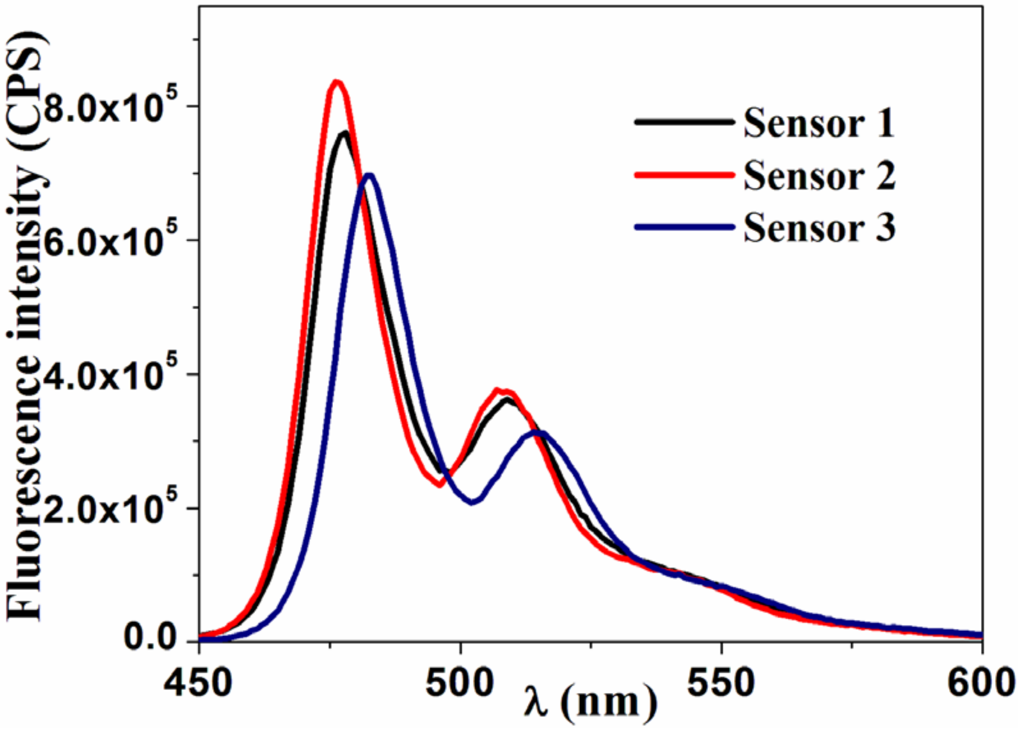


Figure S9. Emission spectra of sensors (**1**-**3**) recorded in DCM or DMA.

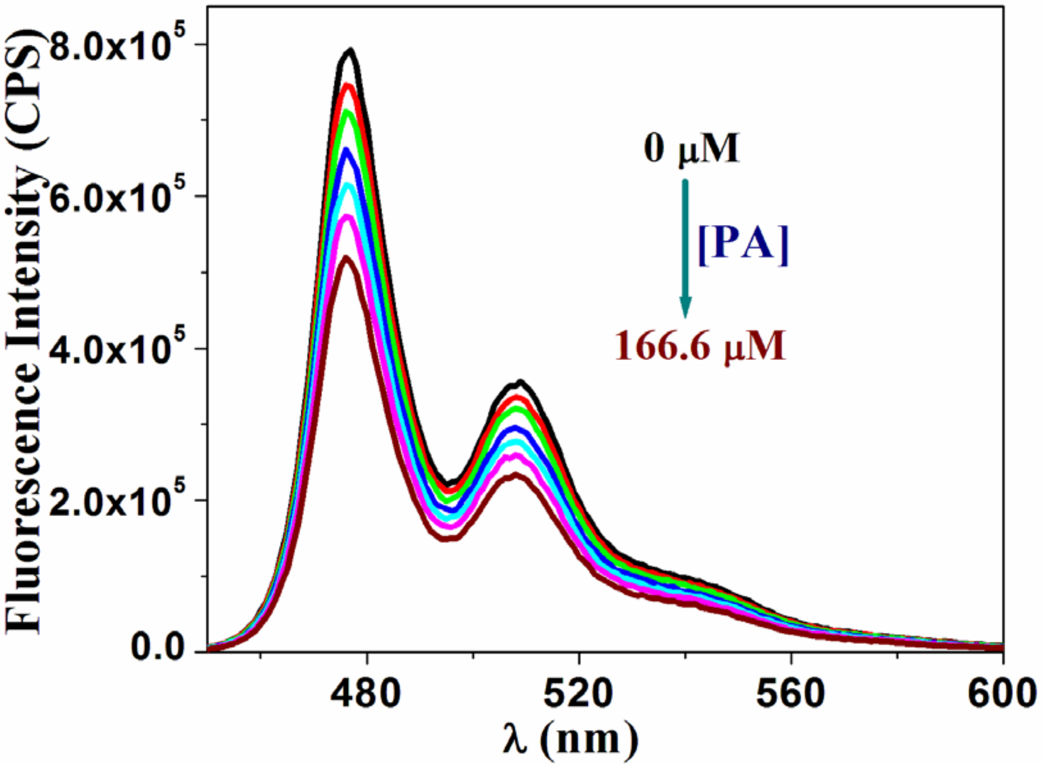


Figure S10. Reduction in the emission intensity of sensor **3** upon gradual addition of PA at room temperature.

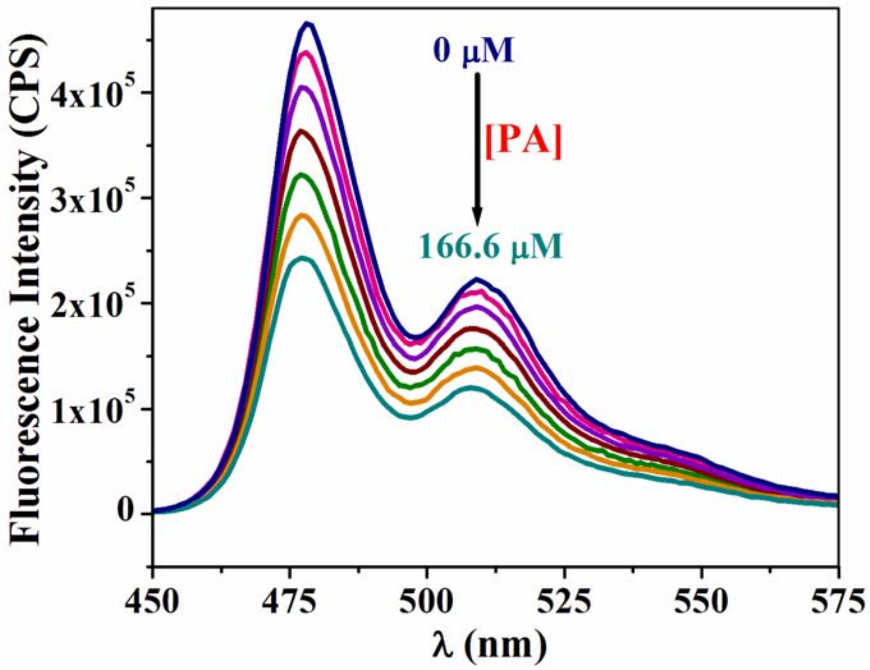


Figure S11. Reduction in the emission intensity of sensor **2** upon gradual addition of PA at room temperature.

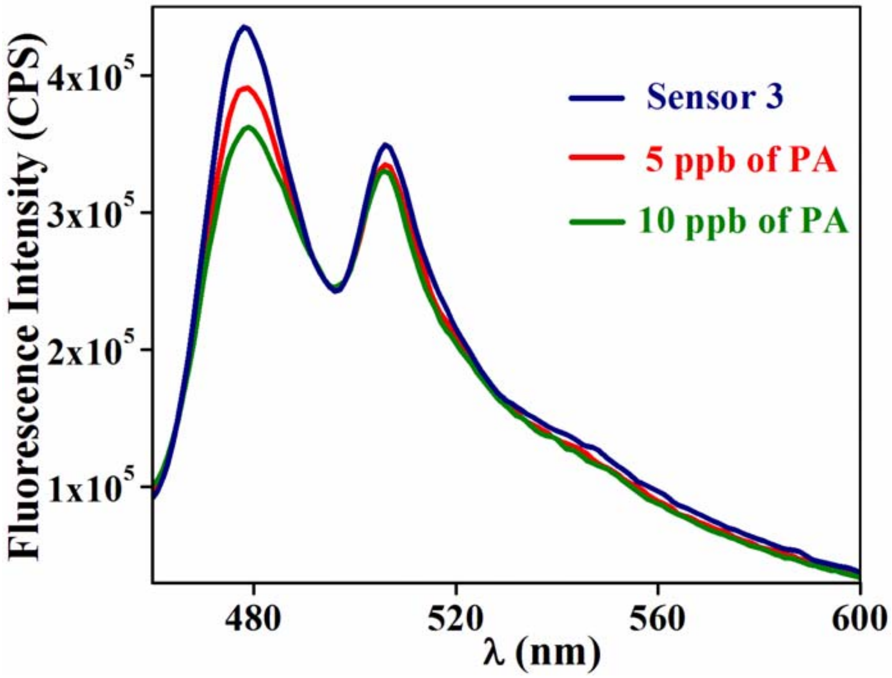


Figure S12. Reduction in the emission intensity of sensor **1** (0.005 μM in DMA) upon gradual addition of PA (5-10 ppb in methanol) at room temperature.

8. Preparation of thin layers and solid state fluorescence study:

For making the thin layers of the sample on quartz slide, a saturated solution of sensor **1** in dimethyl acetamide (DMA) was prepared. 5μL saturated solution was placed on the middle of a cleaned air dried quartz slide. The slide kept inside a desiccator and dried by applying vacuum for 2 hrs. This glass was then used for the fluorescence study of the sample. The thin layer of sensor **2** was made in similar way as mentioned above instead of using DMA, chloroform used as a solvent following the known procedure.[1]

Nitrobenzene (3 mL) was placed in small (25 mL) glass beakers and that was covered by aluminium foil for several days to ensure that the equilibrated vapour pressure of analytes reached. The original fluorescence spectrum of the thin layer was recorded before keeping the glass slide into the beakers containing the analytes. After specified exposure time, the slide was taken out and without any further delay mounted to the sample holder of the fluorescence spectrophotometer and the emission spectrum was recorded.

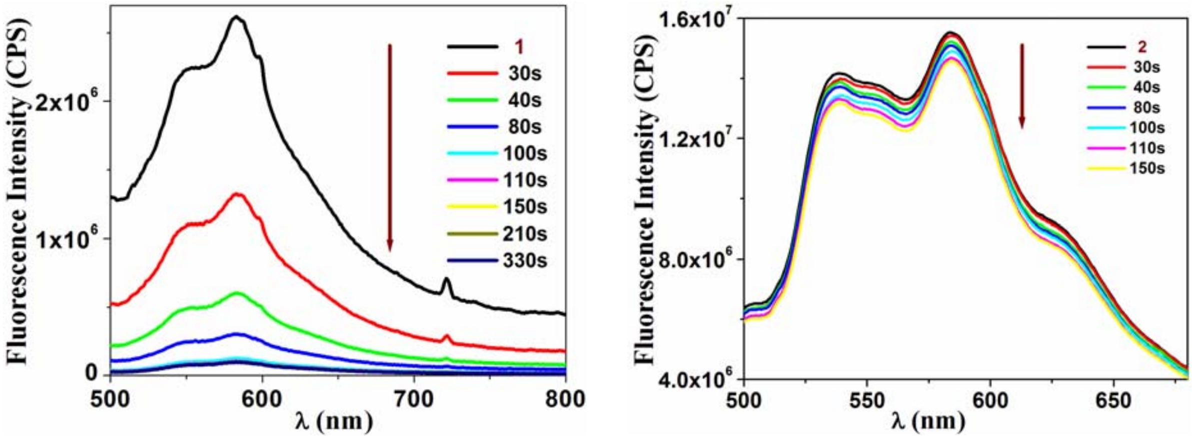


Figure S13. Reduction in the emission intensity of thin layer of sensor **1** and **2** upon gradual exposure to the nitrobenzene vapor at room temperature upon specified time (left side).

IR spectra of sensor 1

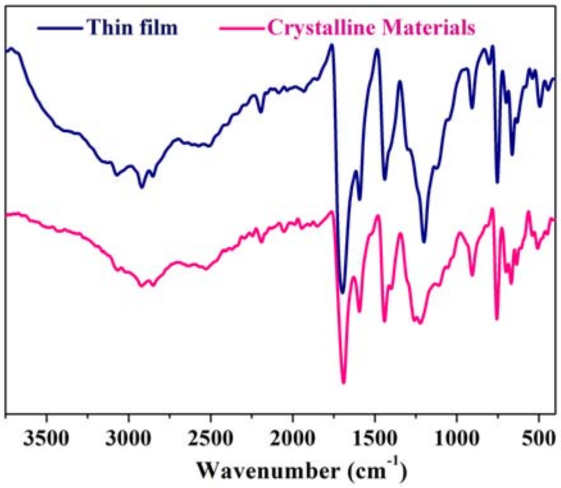


Figure S14. The comparative IR spectra of the sensor **1** in the crystalline form (pink) and its thin film (blue). The broad peak in the region 3200-2700 cm^{-1} in the both form of the compound indicates the presence of the H- bonding.

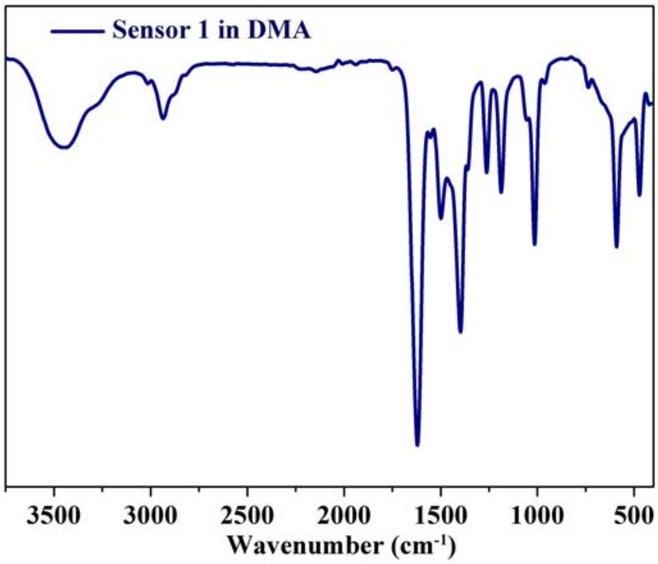


Figure S15. The IR spectra of the sensor **1** in dimethylacetamide (micromolar concentration).

STM Studies

All experiments were performed at room temperature using a NT-MDT (*Molecular Devices and Tools for Nano Technology*) instrument equipped with a narrow scanner. Platinum/iridium STM tips (Pt/Ir, 80%/20%, diameter = 0.2 mm) were prepared by mechanically cutting with a wire cutter. The sensor **1** dissolved in dimethylacetamide (DMA) to make a saturated solution (as prepared for the solid state fluorescence sensing). For a typical experiment, the freshly cleaved surface of highly oriented pyrolytic graphite (HOPG) (Structure Probe, Inc., SPI-1 grade) was first imaged to determine the quality of the Pt/Ir tip and the smoothness of the graphite surface. Once this was determined, a droplet (~ 1 μL) of the saturated solution of sensor **1** in DMA was applied. The slide kept inside desiccator and the solvent was dried by applying vacuum for 2 hrs.The resulting thin layer was imaged by scanning tunnelling microscopy (STM) in the constant-height mode. STM imaging was performed by changing the tunneling parameters (voltage applied to the tip and the average tunneling current). Raw STM images were processed using a NOVA software package.

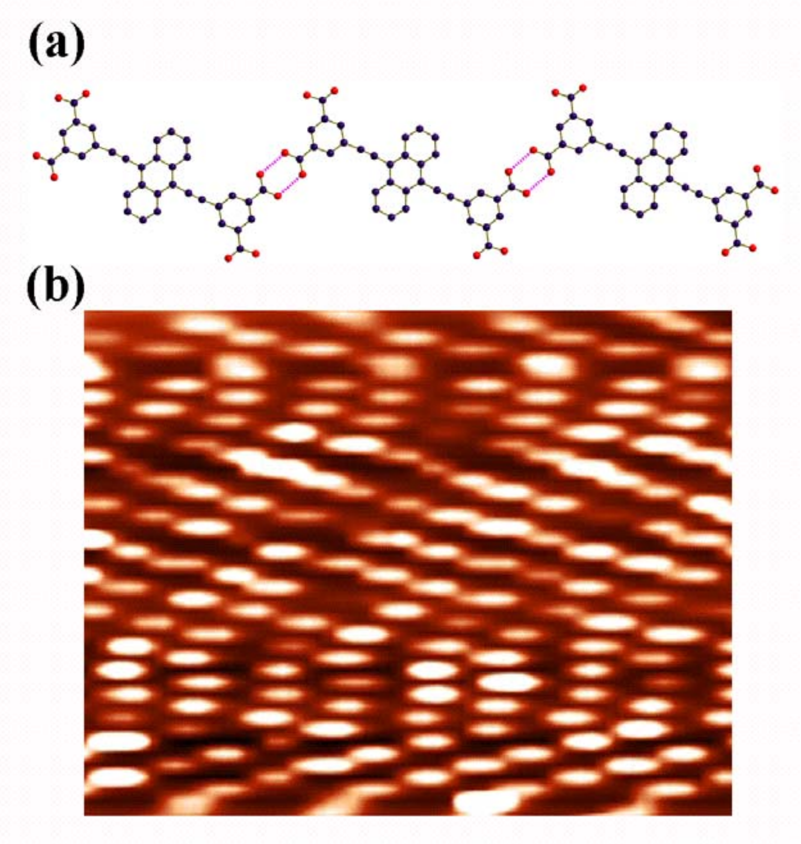


Figure S16. (a) One-dimensional polymeric nature through H-bonding of sensor **1** as obtained from the X-single crystal diffraction. (b) The STM image of the sensor **1** on HOPG (deposition from dimethylacetamide, with V_{bias} = -1.5 V and I_{set} = 50 pA) surface produce highly ordered pattern.

The STM picture of the film of **1** as given in Figure 16(b) reveals the formation of a polymeric network in which the sensor **1** associate by H-bonding. This interpretation is reinforced by the observation of 3D crystal structure of sensor **1** as obtained from the X-ray single crystal diffraction study and the earlier study of similar kind of system.[2-3]

References:

1) S. Shanmugaraju, S. A. Joshi and P. S. Mukherjee, *J. Mater. Chem.* 2011, 9130 and references therein.

2) H. Zhou, H. Dang, J.-H, Yi, A. Nanci, A. Rochefort and J. D. Wuest, *J. Am. Chem. Soc.*, 2007, **129**, 13774.

3) H. W. Kim, J. Jung, M. Han, S. Lim, K.Tamada, M. Hara, M. Kawai, Y. Kim and Y. Kuk, *J. Am. Chem. Soc.*, 2011, **133**, 9236.