Supporting information for:

1,2,3-Triazolyl functionalized thiophene, carbazole and fluorene based A-alt-B type π-conjugated copolymers for sensitive and selective detection of aqueous and vapor phase nitroaromatics (NACs)

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1. Materials and methods

All the air and moisture sensitive reactions and manipulations were carried out under an atmosphere of pre-purified Ar or N₂ by using dual manifold standard Schlenk techniques. Tetrahydrofuran and toluene were dried over Na/benzophenone. Dry DCM, CHCl₃ and 1,2-DCE were obtained by distillation over CaH₂ whereas MeOH and EtOH were dried by Mg cake and stored on 3 Å molecular sieves. Solvents used for all the cross-coupling and polymerization reactions were degassed (three times) via freeze-pump-thaw technique. Unless otherwise mentioned all the chemicals were of analytical grade, obtained from Aldrich, and used without further purification. Silica gel (60-120 mesh) and alumina, used for column chromatography were purchased from SRL, India. Eluting systems for column chromatography purifications were determined by thin layer chromatography (TLC) analysis. TLC plates were visualized under UV light (254 nm) or in iodine chamber.

¹H (600MHz, 400 MHz), ¹³C{¹H} (125 MHz, 100 MHz) NMR spectra were obtained from Bruker Lambda spectrometer using CDCl₃ unless otherwise mentioned. Spectra were internally referenced to residual solvent peaks (δ = 7.26 ppm for proton and δ = 77.2 ppm for carbon (middle peak) for CDCl₃). All coupling constants (J) are given in Hz. The absorption and fluorescence spectra were collected using a Shimadzu spectrophotometer (Model UV-2450) and a Shimadzu spectrofluorimeter (Model RF-6000), respectively. FTIR spectroscopy was recorded in Spectrum-BX (Perkin Elmer). Solid state PL spectra were recorded using Flurolog Horiba (Model FL-1016, Spectracq). Molecular weights and polydispersity indices (PDI = Mₘ/Mₙ) of the polymers were obtained by Malvern tetradevicesector Gel Permeation Chromatography (GPC) using a Viscotek VE 2001 equipped with automatic sampler, pump, injector, inline degasser, column oven (30 °C), styrene/divinylbenzene columns with pore sizes of 500 Å and 100,000 Å, VE 3580 refractometer, four-capillary differential viscometer and 90° angle laser, low angle laser (7°) light scattering detector (VE 3210 & VE270) including UV-vis detector. HPLC grade THF was used as the chromatography eluent, at a flow rate of 1.0 mL/min. Samples were dissolved in the eluent (1 mg/mL) and filtered with a PTFE syringe filter (polytetrafluoroethylene membrane of 0.20 μm pore size) before analysis. Calibration of all four detectors (refractive index, laser light scattering, UV-vis and viscometry) was performed using polystyrene standards (Viscotek). This equipment allows the absolute measurement of homopolymer molecular weights and PDIs. Cyclic voltammetric studies were performed on a BASi Epsilon electrochemical workstation. CV of thin film polymer sample was measured by drop casting of the polymer solution on GC electrode, which was used as a
working electrode. The electrochemical study was conducted in CH$_3$CN with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF$_6$) as the supporting electrolyte. The reference electrode was Ag/AgCl and the auxiliary electrode was a Pt wire. The ferrocene/ferrocenium couple occurs at $E_{1/2} = +0.51 (70) \text{ V versus Ag/AgCl}$ under the same experimental conditions. Thermo gravimetric analysis (TGA) was carried out using a Perkin Elmer Pyris Diamond TG/DTA instrument by measuring their weight losses while heating at a rate of 10 °C/min. MALDI-TOF MS study was performed with DHB (2,5-dihydroxy benzoic acid) matrix by using Bruker UltrafleXtreme instrument. Scanning Electron Microscope (SEM) analysis was carried out with ZEISS MERLIN (GEMINI2) FESEM with Oxford EDS detector.

2. Synthesis and characterization

2a. Syntheses

2,5-Dibromo-3-methylthiophene$^1$ (1): To a solution of 3-methylthiophene (5.3 g, 53.9 mmol) in anhydrous THF (60 mL) was added a mixture of N-bromosuccimide (NBS) (24.2 g, 134.9 mmol) in THF (5 ml). The solution was stirred for 12 hours at 28 °C in the dark (by covering the flask with aluminum foil). After the reaction was completed (as monitored by TLC), distilled water was added. The organic phase was extracted from EtOAc (3 x 10 mL), washed with brine, dried over anhydrous MgSO$_4$. After filtration, the filtrate was concentrated under vacuum. The crude compound was purified by silica gel column chromatography (hexanes) to get a colourless oil (12.1 g, 87%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 6.77 (s, 1H, thienyl), 2.15 (s, 3H, -CH$_3$). $^{13}$C{[$^1$H]} NMR (100 MHz, CDCl$_3$): $\delta$ 138.2 (C, thiophene), 132.0 (CH, thiophene), 110.4 (C, thiophene), 108.7 (C, thiophene), 15.3 (-CH$_3$).

2,5-Dibromo-3-(bromomethyl)thiophene$^1$ (2): To a solution of 2,5-dibromo-3-methylthiophene (1) (4 g, 15.6 mmol) in anhydrous CCl$_4$ (40 mL), a mixture of N-bromosuccimide (NBS) (3.6 g, 20.3 mmol) and catalytic amount of AIBN was added. The solution was stirred for 22 hours at 80 °C in the dark (by covering the flask with aluminum foil). After the reaction was completed (as monitored by TLC), distilled water was added. The organic phase was extracted from EtOAc (3 x 10 mL), washed with brine solution, dried over anhydrous MgSO$_4$. It was then filtered, and the filtrate was concentrated under vacuum. The crude compound was purified by silica gel column chromatography (hexanes) to get a colourless oil (3.9 g, 76 %). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.00 (s, 1H, thienyl), 4.36 (s, 2H, -CH$_2$-Br). $^{13}$C{[$^1$H]} NMR (100 MHz, CDCl$_3$): $\delta$ 138.0, 131.1, 112.4, 112.0 (aromatic carbons),

53
25.2 (−CH2-Br). MALDI-TOF (m/z): C5H3Br3S, calculated value 333.748 (M)+, found 333.653 (M)+.

9-heptyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (M1): A solution of n-BuLi (1.6 M in hexanes, 9.3 mL, 14.8 mmol) was added dropwise to a solution of 6 (2.03 g, 4.8 mmol) in THF(50 mL) kept at -78 °C. The obtained mixture was vigorously stirred for 1 h at -78 °C before the addition of 2-isopropoxy-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolan (3.8 g, 15.2 mmol) in one portion. The resulting solution was then allowed to reach room temperature and to react overnight. After removing the solvent under vacuum, CH2Cl2 (50 mL) was added and the obtained solution was washed with water (3 × 50 mL) and dried over anhydrous Na2SO4. The solvent was removed under vacuum and the obtained crude product was purified by flash column chromatography using silica gel (petroleum ether 40 - 60 °C and CH2Cl2, 1:1 v/v) to achieve M1 (1.7 g, 68%) as a white solid. 1H NMR (400 MHz, CDCl3): δ 8.67 (s, 2H, carbazolyl), 7.90 (d, 2H, J = 8 Hz, carbazolyl), 7.39 (d, 2H, J = 8 Hz, carbazolyl), 4.30 (t, 2H, J = 2 Hz, -N-C2H2-), 1.88 - 1.83 (m, 2H, -N-CH2-CH2-), 1.41 - 1.37 (m, 32H, -Me of O-Bpin, -CH2- heptyl), 0.89 - 0.85 (m, 3H, -CH3, heptyl). 13C{1H} NMR (100 MHz, CDCl3): δ 142.7, 132.1, 128.0, 122.8, 108.1 (aromatic carbons), 83.5, 43.0, 31.7, 29.1, 28.9, 27.2, 26.3, 25.4, 24.9, 22.6, 21.0 (−CH2-, heptyl), 14.2 (−CH3, heptyl).

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (M2): In a 100 ml oven dried Schlenk flask purged with argon, compound 8 (1.64 g, 3.1 mmol) was dissolved in 25 mL of dry THF and it was brought to -78 °C. At this temperature n-BuLi (4.6 mL of 1.6 M in n-hexane, 7.5 mmol) was added slowly through syringe over 15 min. It was stirred at this temperature for another 30 min. Then 2-isopropoxy-4,4,5,5- tetramethyl-1,3,2-dioxaborolan (2.06 g, 7.8 mmol) was added slowly through syringe over 10 min and stirred at -78°C for another 90 min. The reaction mixture was allowed to come 28 °C slowly and stirred for another 24h. Then the reaction was quenched by 3 mL of water. The compound was extracted from DCM and the organic layer was washed with brine solution followed by water, and dried over anhydrous MgSO4. The product was recrystallized from hexanes to obtain white crystalline solid. Yield: 1.5 g (78%); 1H NMR (400 MHz, CDCl3) δ 7.81-7.70 (m, 6H, fluorene), 2.01-1.97 (m, 4H, octyl protons), 1.38 (s, 24 H, -Me of O-Bpin), 1.19-1.00 (m, 20H, octyl), 0.80-0.78 (m, 4H, octyl), 0.56-0.53 (m, 6H, -Me octyl); 13C{1H} NMR (100 MHz, CDCl3) δ 150.7, 144.1, 133.9, 129.1, 119.6 (aromatic carbons), 83.9,55.4, 40.3, 32.0, 30.1, 29.4, 25.2, 22.8 (−CH2-, octyl), 14.1 (−CH3, octyl).
2,2’-(3-Hexylthiophene-2,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (M3): In a 100 ml oven dried Schlenk flask purged with argon, compound 10 (1.1 g, 3.3 mmol) was dissolved in 25 mL of dry THF and it was brought to -78 °C. At this temperature nBuLi (4.6 mL of 1.6 M in n-hexane, 7.5 mmol) was added slowly through syringe over 15 min. It was stirred at this temperature for another 30 min. Then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.2 g, 8.6 mmol) was added slowly through syringe over 10 min and stirred at -78 °C for another 90 min. The reaction mixture was allowed to come room temperature (28 °C) slowly and stirred for another 24h. Then the reaction was quenched by 3 mL of water. The compound was extracted in DCM and the organic layer was washed with brine solution followed by water, and dried over anhydrous MgSO₄. The product was obtained after concentration of the DCM solution, as light yellow oil. Yield: 1.0 g (78%); ¹H NMR (400 MHz, CDCl₃) δ 7.50 (s, 1H, thiényl), 2.86 (t, 2H, hexyl protons), 1.61-1.56 (m, 8H, hexyl protons), 1.39-1.31 (s, 24 H, -Me of -O-Bpin), 0.90-0.86 (m, 3H, hexyl). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 145.7, 141.1, 127.0, 125.8, 108.1 (aromatic carbons), 55.6, 43.0, 31.7, 25.4, 24.9, 22.6, 21.0 (-CH₂-, hexyl), 14.3 (-CH₃, hexyl).

Hydroxyapatite [HAP, Ca₁₀(PO₄)₆(OH)₂]: Ca(NO₃)₂. 4H₂O (15.0 g, 0.066 mol) dissolved in water (60 mL) was brought to pH 11-12 with concentrated NH₄OH and thereafter diluted to 120 mL. A solution of (NH₄)₂HPO₄ (5.28 g, 0.04 mol) in 100 mL water was brought to pH 11-12 with concentrated NH₄OH and thereafter diluted to 160 mL. The calcium solution was vigorously stirred at room temperature, and the phosphate solution was added drop wise over a period of 30 min to produce a milky and gelatinous precipitate which was then stirred and boiled for 10 min. The precipitate was filtered, washed, dried at 80 °C overnight and calcined at 500 °C for 3 h. All the synthetic steps were carried out using doubly distilled water.

Preparation of Copper(II)-hydroxyapatite (Cu-HAP): A calcium hydroxapatite (2.0 mmol) sample of Ca/P = 1.67 [Ca₁₀(PO₄)₆(OH)₂] (HAP) was stirred with Cu(NO₃)₂ (0.20 mmol) in H₂O (150 mL) at 70 °C for 24 h. The obtained slurry was filtered, washed with deionized water, and dried overnight at 110 °C to afford a Cu(II)-exchanged hydroxyapatite (CuHAP, Cu content: 0.10 mmol g⁻¹) as a blue powder. No Cu(II) was detected in the filtrate or in the washing water. Thus, the Cu content can be estimated to be the same molar amount as that of Cu(NO₃)₂ used.
Scheme S1: Synthesis of 2,5-dibromo-3-bromomethyl thiophene from 3-methylthiophene.

Scheme S2: Synthetic scheme for the key precursors and the monomers M1, M2 and M3.
2b. NMR Spectra

**Figure S1a:** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 3.

**Figure S1b:** $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of 3.
Figure S2a: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 4.

Figure 2b: $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of 4.
Figure S2c: DEPT-135 (100 MHz, CDCl$_3$) spectrum of 4.

Figure S3a: $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 5.
Figure S3b: $^{13}$C{$^1$H} NMR (100 MHz, DMSO-D$_6$) spectrum of 5.

Figure S4a: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 6.
Figure S4b: $^{13}$C-$^1$H NMR (100 MHz, CDCl$_3$) spectrum of 6.

Figure S4c: DEPT-135 (100 MHz, CDCl$_3$) spectrum of 6.
Figure S5a: $^1$H NMR (400 MHz, CDCl$_3$) spectrum of M1.

Figure S5b: $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of M1.
Figure S5c: DEPT-135 (100 MHz, CDCl₃) spectrum of M1.

Figure S6a: ¹H NMR (400 MHz, CDCl₃) spectrum of 7.
Figure S6b: $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl$_3$) spectrum of 7.

Figure S7a: $^1\text{H}$ NMR (400 MHz, CDCl$_3$) spectrum of 8.
Figure S7b: $^{13}$C$\{^1$H$\}$ NMR (100 MHz, CDCl$_3$) spectrum of 8.

Figure S8a: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of M2.
Figure S9a: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of M3.

Figure S10a: $^1$H NMR (600 MHz, CDCl$_3$) spectrum of P1.
**Figure S10b:** $^{13}$C-$^{1}$H NMR (100 MHz, CDCl$_3$) spectrum of P1.

**Figure S11a:** $^1$H NMR (600 MHz, CDCl$_3$) spectrum of P2.
Figure S11b: $^{13}\text{C}^{1}{\text{H}}$ NMR (100 MHz, CDCl$_3$) spectrum of P2.

Figure S11c: DEPT-135 (100 MHz, CDCl$_3$) spectrum of P2.
Figure S12a: $^1$H NMR (600 MHz, CDCl$_3$) spectrum of P3.

Figure S12b: $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) spectrum of P3.
2c. Mass spectrometry

Figure S13: MALDI-TOF MS of 3

Figure S14: HRMS of 4.
Figure S15: MALDI-TOF MS of 6

2d. FT-IR spectrum (measured as KBr pellets)

Figure S16a: FT-IR spectrum of P1.
Figure S16b: FT-IR spectrum of P2.

Figure S16c: FT-IR spectrum of P3.
2e. Thermal studies

![TGA thermograms of the polymers (P1-P3) recorded at a rate of 10 °C/min under N₂.]

Figure S17: TGA thermograms of the polymers (P1-P3) recorded at a rate of 10 °C/min under N₂.

3. Photophysical and Sensing studies

3a. Determination of quantum yield

All the UV–Vis absorption and fluorescence emission spectra were collected using a Shimadzu (model UV 2450) UV–Vis spectrophotometer and a Spex Fluorolog-3 (model FL3–11) spectrofluorimeter, respectively. Throughout all the measurements, the concentration was maintained at ~1 × 10⁻⁵ M. Fluorescence quantum yields were measured with respect to a secondary standard quinine sulphate (λₘₐₓ=350 nm) in 0.1 M H₂SO₄ (Φ = 0.54) at 298 K³. The following equation was used to calculate the quantum yields:

\[
\frac{\Phi_S}{\Phi_R} = \frac{A_S}{A_R} \times \frac{(Abs)_R}{(Abs)_S} \times \frac{\eta_S^2}{\eta_R^2}
\]

Here Φ represents the quantum yield, (Abs) represents the absorbance, A represents the area under the fluorescence curve, and η is the refractive index of the medium. \(\eta_{CHCl_3}\) was calculated using Arago-biot (AB) equation.³ The subscript S and R denotes the corresponding parameters for the sample and reference, respectively.

3b. Experimental details and determination of time resolved fluorescence spectra

The time-resolved emission decays were recorded using a Time-Correlated Single Photon Counting (TCSPC) picoseconds spectrophotometer. The fluorescence decay response of P1, P2 and P3, and with incremental addition of picric acid was investigated in CHCl₃. The solution of picric acid was prepared in CHCl₃ and was added to the stock solution of P1, P2
and P3, which were prepared in CHCl3. All the samples were excited using a picosecond diode laser at 400 nm (IBH, UK, Nanoled), and the signals were recorded at magic angle (54.71) using a Hamamatsu micro channel plate photomultiplier tube (3809U). The typical instrument response function in our setup is 100 ps. The instrument response function of our setup is ~800 ps. Time-resolved fluorescence decays were analyzed using IBH DAS-6 decay analysis software.

**Table S1:** Time resolved fluorescence data of P1, P2 and P3

<table>
<thead>
<tr>
<th>Polymer</th>
<th>τ1 (ns)</th>
<th>τ2 (ns)</th>
<th>α1</th>
<th>α2</th>
<th>τav (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>0.32</td>
<td>0.53</td>
<td>0.72</td>
<td>0.28</td>
<td>0.38</td>
</tr>
<tr>
<td>P2</td>
<td>0.23</td>
<td>0.42</td>
<td>0.36</td>
<td>0.64</td>
<td>0.30</td>
</tr>
<tr>
<td>P3</td>
<td>0.28</td>
<td>0.62</td>
<td>0.32</td>
<td>0.68</td>
<td>0.36</td>
</tr>
</tbody>
</table>

**Figure S18:** Fluorescence life time decay of (a) free P1 and P1 in presence of picric acid (10 and 20 eqv.), (b) free P3 and P3 in presence of picric acid (10 and 20 eqv.).

**3c. Concentration dependent fluorescence study**

Polymer concentrations were calculated as per the molecular weight of the repeating unit (monomole). To determine the optimum concentration in which self-aggregation of the sensing probe in solution is less, the concentration dependent emission spectra (1 × 10⁻³ M to 1 × 10⁻⁵ M) was recorded in CHCl3. All the π-conjugated polymers displayed less aggregation behavior with concentration 10⁻⁵ M as evidenced from concentration-dependent fluorescence study.
Figure S19: Concentration dependent fluorescence spectra of (a) P1 (b) P2 and (c) P3 in CHCl$_3$ at 28 °C.

Figure S20: Concentration dependent DLS spectra of (a) P1 (b) P2 and (c) P3 in CHCl$_3$ solution at 28 °C. It should be noted that, D$_H$ is derived from a hard sphere model, thus the values obtained for the rigid π-conjugated polymers may not be absolutely correct. However, it is reliable enough for relative comparison between unimers and aggregates.$^4$

3d. Fluorescence titration studies of the sensing probes towards NACs

The fluorescence spectroscopic titrations were performed with a continuous variation of concentrations (~1 × 10$^{-5}$ M to ~1 × 10$^{-3}$ M) of NACs in CHCl$_3$ with respect to monomole concentration of the polymer probes.

The percentage of emission quenching of the polymer probes P1–P3 towards different nitroaromatics compounds have been calculated by considering the intensity value of PL spectrum profile of polymer probes towards different nitroaromatics. The details of the calculation are as follows: At first, the value of the emission intensity of the free polymer and polymer-analyte have been estimated at $\lambda_{em}$ position from the emission quenching experiments. Then, the percentage of quenching has been calculated as:

\[
\text{Percentage of quenching} = \left(\frac{\text{PL Intensity of probe} - \text{PL intensity of probe-analyte}}{\text{PL intensity of probe}}\right) \times 100 \%
\]
**Figure S21:** Emission quenching of the polymer P1 towards different nitroaromatics and non-nitroaromatics in CHCl₃ solution. Analyte concentration: ~$10^{-5}$ M, polymer: ~$1 \times 10^{-5}$ M in CHCl₃.

**Figure S22:** Fluorescence quenching behavior of P1 ((~$1 \times 10^{-5}$ M in CHCl₃) upon incremental addition of (a) picric acid, (b) 2,6-dinitrotoluene, (c) 2,4-dinitrophenol, (d) 4-nitrobenzoic acid, (e) 4-nitrophenol, (f) nitrotoluene, (g) nitrobenzene with concentration range of NACs: ~$1.1 \times 10^{-5}$ M to ~$1.2 \times 10^{-4}$ M).
Figure S23: Fluorescence quenching behavior of P2 ((~1 x 10^{-5} M in CHCl₃) upon incremental addition of (a) picric acid, (b) 2,6-dinitrotoluene, (c) 2,4-dinitrophenol, (d) 4-nitrobenzoic acid, (e) 4-nitrophenol, (f) nitrotoluene, (g) nitrobenzene with concentration range of NACs: ~1.1 × 10^{-5} M to ~1.2 × 10^{-4} M).

Figure S24: Emission quenching of the polymer P3 towards different nitroaromatics and non-nitroaromatics in CHCl₃ solution. Analyte concentration: ~10^{-5} M, polymer: ~1 × 10^{-5} M in CHCl₃.
Figure S25: Fluorescence quenching behavior of P3 (\(\sim1 \times 10^{-5}\) M in CHCl\(_3\)) upon incremental addition of (a) picric acid, (b) 2,6-dinitrotoluene, (c) 2,4-dinitrophenol, (d) 4-nitrobenzoic acid, (e) 4-nitrophenol, (f) nitrotoluene, (g) nitrobenzene with concentration range of NACs: \(\sim1.1 \times 10^{-5}\) M to \(\sim1.2 \times 10^{-4}\) M.

Figure S26: Percentage of emission quenching of P1–P3 towards different nitroaromatics and non-nitro aromatic compounds in CHCl\(_3\). Toluene: TOL, 1,2-dichlorobenzene: DCB, Nitrobenzene: NB, Nitrotoluene: NT, Nitrobenzoic acid: NBA, p-Hydroxy nitrobenzene: HNB, 2,4-Dinitrophenol: DNP, 2,6-Dinitrobenzene: DNT, Picric acid: PA.
3e. Calculation of Stern-Volmer constants

The sensitivity of the sensing probes (P1, P2, P3) towards the nitroaromatics was estimated from their Stern-Volmer constants, $K_{sv}$ as determined from the equation:

$$\frac{I_o}{I} = 1 + K_{sv} [Q]$$

$I_o$ and $I$ are the fluorescence intensities in the absence and presence of nitroaromatics respectively, and the Stern-Volmer plots were plotted as a function of the nitroaromatic concentration, $[Q]$. The Stern-Volmer constants, $K_{sv}$ can be calculated from the slope of the Stern-Volmer plots.

![Stern-Volmer plot for P1](image)

**Figure S27**: The Stern-Volmer plot for the P1 towards the different nitroaromatics. 1: NB, 2: NT, NBA, 4: HNB, 5: DNP, 6: DNT, 7: PA.

![Stern-Volmer plot for P3](image)

**Figure S28**: The Stern-Volmer plot for the P3 towards the different nitroaromatics. 1: NB, 2: NT, NBA, 4: HNB, 5: DNP, 6: DNT, 7: PA.
Table S2: Association constant of P1, P2 and P3 towards different nitroaromatics.

<table>
<thead>
<tr>
<th>Nitroaromatics</th>
<th>P1 (M⁻¹)</th>
<th>P2 (M⁻¹)</th>
<th>P3 (M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrobenzene (NB)</td>
<td>2.58 × 10³</td>
<td>4.40 × 10³</td>
<td>3.10 × 10³</td>
</tr>
<tr>
<td>Nitrotoluene (NT)</td>
<td>2.21 × 10³</td>
<td>2.11 × 10³</td>
<td>2.03 × 10³</td>
</tr>
<tr>
<td>Nitrobenzoic acid (NBA)</td>
<td>1.16 × 10⁴</td>
<td>1.23 × 10⁴</td>
<td>1.15 × 10⁴</td>
</tr>
<tr>
<td>p-Hydroxy nitrobenzene (HNB)</td>
<td>1.45 × 10⁴</td>
<td>1.42 × 10⁴</td>
<td>1.33 × 10⁴</td>
</tr>
<tr>
<td>2,4-Dinitrophenol (DNP)</td>
<td>1.71 × 10⁴</td>
<td>2.45 × 10⁴</td>
<td>2.01 × 10⁴</td>
</tr>
<tr>
<td>2,6-Dinitrotoluene(DNT)</td>
<td>1.91 × 10⁴</td>
<td>2.66 × 10⁴</td>
<td>2.21 × 10⁴</td>
</tr>
<tr>
<td>Picric acid (PA)</td>
<td>2.84 × 10⁴</td>
<td>6.40 × 10⁴</td>
<td>3.10 × 10⁴</td>
</tr>
</tbody>
</table>

3f. Calculation of the limit of detection (LOD)

The limit of detection (LOD) of the sensing probes (P1, P2 and P3) towards nitroaromatics has been determined from emission spectra using the following equation:

\[
\text{LOD} = 3\sigma/S
\]

Here, \(\sigma\) is standard deviation for the blank measurement, and \(S\) is the slope of the calibration curve (fluorescence intensity vs NAC concentration). The value of \(\sigma\) has been estimated from emission spectra of the free polymer sample without nitroaromatic analytes for an appropriate numbers (8 to 10 times). The get the slope (S), change in fluorescence intensity data at \(\lambda_{\text{em}}\) of 458 nm, 464 nm and 551 nm (for P1, P2 and P3 respectively) was plotted against the concentration of NACs. Emission spectra was recorded by treating NAC solution with varying concentration (ca. \(10^{-5}\) M to \(10^{-6}\) M in CHCl₃) to the polymer probe of ca. 1 x \(10^{-5}\) M in CHCl₃. There was a good linear relationship between fluorescent intensity data and concentrations of NACs at micromolar concentration, indicating quantitative detection.
Figure S29: Plot for evaluation of LOD for P1 towards PA. Change in intensity at $\lambda_{em}$ of 458 nm with varying concentration of PA was plotted.

Figure S30: Plot for evaluation of LOD for P3 towards PA. Change in intensity at $\lambda_{em}$ of 551 nm with varying concentration of PA was plotted.

Table S3: Limit of detection of P1, P2 and P3 towards picric acid.

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>P2</th>
<th>P3</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOD (in M)</td>
<td>$9.51 \times 10^{-7}$</td>
<td>$5.25 \times 10^{-7}$</td>
<td>$6.21 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

3g. Preparation of thin film of the polymer probes for the sensing studies

The quartz substrates (17 $\times$ 15 $\times$ 1 mm$^3$) were cleaned in a fresh piranha solution (7:3 mixture of 98% H$_2$SO$_4$ / 30% H$_2$O$_2$) followed by ultra-sonication in alkaline isopropanol, 0.1 N aqueous HCl and Milli-Q water for 1 h each. A solution of polymers in chlorobenzene ($\sim 3 \times 10^{-4}$ M) was spin casted on quartz plate at 1000 rpm for 60 second. PL data of the polymer film was measured. After that the film was dipped in different concentration of aqueous picric acid
solution for 10 min followed by repetitive and extensive washing (at least 20 times) by Milli-Q water to remove any unbound (free) picric acid. After drying in air, PL response was recorded.

For the vapor phase study, the thin film of the polymers was exposed to the vapor of the picric acid at room temperature for different time. The PL spectra were recorded with different time interval, after exposing the polymer thin film to the vapor of picric acid in glass chamber. For the film repeatability measurement the polymer film was exposed to the vapor of picric acid for 300 sec and the emission spectrum was recorded. After each measurement, the film was washed with ethanol:water mixture to remove the picric acid and dried under hot air. The emission spectra were recorded and the whole process was repeated for the reputability test.

**Figure S31:** Experimental setup for demonstrating sensing vapor phase detection of PA at ambient condition.

**3h. Detection of aqueous PA sample by polymer thin film probes:**

![Emission spectra](image)

**Figure S32:** (a) Emission spectra of P1 (as thin film) after exposing to aqueous PA solution by varying the concentrations. (b) Emission spectra of P1 (as thin film) after exposing with PA vapour for different time.
**Figure S33:** (a) Emission spectra of P3 (as thin film) after exposing to aqueous PA solution by varying the concentrations. (b) Emission spectra of P3 (as thin film) after exposing with PA vapour for different time.

**Figure S34:** Emission spectra of P2 (as thin film) after exposing to aqueous PA solution by varying the concentrations.

3i. Repeatability studies

**Figure S35:** The quenching efficiency of P1 as a function of reproducibility of sensing ability of polymer thin film to the saturated vapor of PA.
3j. Contact mode detection

For contact mode sensing, Whatman 42 filter paper was cut into small pieces and dipped into concentrated DCM solution of the sensing probes and subsequently dried in air. PA solution of different concentration (10⁻³ – 10⁻⁹ M) were prepared and 10 µL of each solution was drop-casted on each fresh filter paper strip. When the strips were illuminated under UV at 365 nm, dark spots were observed for PA. The spots were prominent for concentrated samples and slowly faded upon dilution which can be detected by naked eye (under UV illumination at 365 nm). The size of each test strip is 1 cm².

Figure S37: Visual appearance of P1 coated on filter paper before and after the drop casting of different concentrations of PA by contact mode method under illumination at 365nm light.
**Figure S38:** Visual appearance of P3 coated on filter paper before and after the drop casting of different concentrations of PA by contact mode method under illumination at 365nm.

**Figure S39:** Visual appearance of P1 before and after the addition of PA under (a) illumination at 365 nm light. (b) under ambient light.

**Figure S40:** Visual appearance of P2 before and after the addition of PA under (a) illumination at 365 nm light. (b) under ambient light.

**Figure S41:** Visual appearance of P3 before and after the addition of PA under (a) illumination at 365 nm. (b) under ambient light.
4. $^1$H NMR titration response of the probes towards PA

To investigate the mode of supramolecular interaction between the monomer and NACs, $^1$H NMR spectroscopic titration studies were carried out with incremental addition of picric acid (PA).

![NMR Spectra](image)

**Figure S42:** Change in chemical shift of the protons in P1 during $^1$H NMR titration in CDCl$_3$ on incremental addition of PA (* = residual CHCl$_3$).
Figure S43. Change in chemical shift of the protons in P3 during $^1$H NMR titration in CDCl$_3$ on incremental addition of PA (* = residual CHCl$_3$).

5. Electrochemical characterization

**Determination of HOMO and LUMO from CV studies:** Cyclic voltammetric analysis was conducted in acetonitrile using Bu$_4$NPF$_6$ (0.1 M) as supporting electrolytes, Pt wire counter electrode and Ag/AgCl reference electrode. The solution of P1, P2 and P3 were drop casted onto the glossy carbon disc electrode from their DCM solutions. The HOMO energy levels for polymer probes were estimated by conventional electrochemical studies. The HOMO energy level ($E_{\text{HOMO}}$) was calculated from the onset oxidation potential ($E_{\text{ox onset}}$) using the following equation: $E_{\text{HOMO}}$ (eV) = [$E_{\text{ox onset}}$ - $E_{\text{ox(ferrocene)}}$] - 4.80, where the energy level was calibrated against the Ag/AgCl couple. The LUMO energy level ($E_{\text{LUMO}}$) was calculated from the $E_{\text{HOMO}}$ energy level and its optical band gap following the equation: $E_{\text{LUMO}}$ = ($E_{\text{HOMO}}$ + $E_{\text{g opt}}$) eV, as there is no prominent reduction process for the polymer probes.
**Figure S44:** Cyclic voltammogram of (a) acetonitrile (blank run), (b) P1 polymer film in acetonitrile, (c) P2 polymer film in acetonitrile and (d) P3 polymer film in acetonitrile using TBAPF$_6$ as supporting electrolyte, Pt disc working electrode, and Ag/AgCl reference electrode. Scan rate at 100 mV/s.

6. **FESEM analysis**

**Preparation of sample for FESEM analysis:** The sample for FESEM analysis was prepared on a clean 1 cm $\times$ 1.5 cm aluminium plate. A solution of the probe in chloroform ($\sim 5 \times 10^{-4}$ M) was dropped on the alumina plate and it was dried under a closed chamber for 2 h. The surface morphology was analyzed. The film was dipped in aqueous solution of picric acid derivative (2,4,6-trinitrophenyl 3-bromobenzoate) for 5 min followed by repetitive and extensive washing by Milli-Q water to remove the unbound (free) analyte. After that surface morphology was analyzed.
Figure S45: FESEM images of the sensing probes left: P1, right: P1 in presence of picric acid derivative (2,4,6-trinitrophenyl 3-bromobenzoate).

Figure S46: FESEM images of the sensing probes left: P2, right: P2in presence of picric acid derivative (2,4,6-trinitrophenyl 3-bromobenzoate).
Figure S47: FESEM images of the sensing probes left: P3, right: P3 in presence of picric acid derivative (2,4,6-trinitrophenyl 3-bromobenzoate).

7. Computational studies

Figure S48: Model probes (MP1, MP2 and MP3) for theoretical studies.

The Density functional theory (DFT) calculation was performed using the Gaussian 09 program based on Becke’s three-parameter set with Lee-Yang-Parr correlation functional (B3LYP) and the 6-31G(d,p) basis set for all the model complexes (MP1, MP2, MP3). The energy levels of the HOMO/LUMO calculations were executed at the B3LYP structures using the same basis set as those used in the ground-state DFT calculations.\(^5\)
Figure S49: DFT computed optimized structure of model probes (a) MP1, (b) MP2 and (c) MP3.

Figure S50a: Calculated HOMO (red) and LUMO (blue) energy level diagram for model complex MP1 and NACs by DFT, frontier orbital theory using B3LYP functional and polarized 6–31 G/ basis set.
Figure S50b: Calculated HOMO (red) and LUMO (blue) energy level diagram for model complex MP2 and NACs by DFT, frontier orbital theory using B3LYP functional and polarized 6–31 G' basis set.
Figure S50c: Calculated HOMO (red) and LUMO (blue) energy level diagram for model complex MP3 and NACs by DFT, frontier orbital theory using B3LYP functional and polarized 6–31 G⁄ basis set.

8. References:


