Supporting Information

Fluorene Based Fluorometric and Colorimetric Conjugated Polymers for Sensitive Detection of TNP Explosive in Aqueous Medium

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SI-1. Materials and Methods

All chemicals and reagents such as 2,7-dibromo-9H-fluorene, n-octyl bromide, sodium carbonate, potassium carbonate, 1,4-phenyldiboronic acid, 2,5-dibromothiophene, tetrakis(triphenylphosphine)palladium(0), dimethyl sulfoxide, cinnamaldehyde, 4-methoxybenzaldehyde, potassium acetate, ethyl acetate, dichloromethane, potassium-tert-butoxide, methanol, acetone, ethanol, tetrahydrofuran, and nitroaromatic compounds such as 1,3-dinitrobenzene (DNB), picric acid (PA), 4-nitrophenol (NP), 2,4-dinitrotoluene (DNT), and nitroaniline (NA) used throughout research work were of HPLC grade. All chemicals were purchased from Daejung, Korea; Alfa Aesar, Sigma Aldrich, and Oakwood, USA; and used directly without further purification. Mixtures of synthesized compounds were eluted using column containing silica gel of 230–400 mesh size. THF solvent was distilled through still head apparatus by using sodium metal and benzophenone. Desired products were separated by optimized polarity of solvent system based on Rf value. 1H and 13C NMR spectra of all synthesized compounds were performed at a Bruker Avance III HD 400 MHz NMR using CDCl3 as a solvent. The infrared (IR) spectra were recorded in the range of 4000-400 cm⁻¹ using Fourier-transform infrared (FT-IR) spectrometer (Spectrum 2, Perkin Elmer). Fluorescence emission studies were recorded with spectrofluorometer model FluoroMax-Plus-P-C, Horiba Jobin Yvon Technology, USA. Dynamic light scattering (DLS) was performed on Zeta-sizer Nano (model ZSP Malvern Analytical technology, UK), by using software Malvern Zeta-sizer (v7.13). Further, a double beam UV-Vis spectrophotometer (SPECORD 200 PLUS -223E2003C by Analytik Jena, Germany) having a combination of halogen and deuterium lamp with fixed spectral bandwidth was used for UV-Vis analysis.

SI-2. Synthesis and Characterization

SI-2.1. Procedure for Synthesis of 2,7-Dibromo-9-(4-methoxybenzylidene)-9H-fluorene (5)

A solution of fluorene analogue 1 (1.29 g, 4.0 mmol) and potassium-tert-butoxide (0.49 g, 4.4 mmol) in 10 mL of ethanol were refluxed for 1 hour. After an hour of reflux 4-methoxybenzaldehyde 2 was added slowly to reaction mixture under nitrogen atmosphere. Color
of the solution was changed into a yellow solution. The reaction mixture was refluxed for 9 hours. Progress of reaction was monitored by thin layer chromatography. Reaction mixture was slowly cooled down to room temperature. The desired product 5 was extracted with dichloromethane and washed with brine. The organic layer was collected and then dried over anhydrous MgSO4. The solvent of organic layer was removed under reduced pressure. The crude solid material was further chromatographed by silica gel column chromatography using n-hexane/petroleum ether as an eluent. The fluorene analogue 5 was obtained in 85\% yield as yellow powder.

Yield: 85\%; M.P = 133-136 °C; \(R_f = 0.43\) (n-Hexane/EtOAc=98:2); \(^1\)H NMR (400 MHz, CDCl3): \(\delta 7.91\) (dd, 2H, \(J = 8.0, 4.0\) Hz, ArH), 7.67 (s, 1H, olefinic CH), 7.58-7.55 (m, 4H, ArH), 7.50 (d, 1H, \(J = 8.0\) Hz, ArH), 7.46 (d, 1H, \(J = 8.0\) Hz, ArH), 7.05-7.02 (m, 2H, ArH), 3.93 (s, 3H, O-CH\(_3\)).

\(^{13}\)C (100 MHz, CDCl3): \(\delta 160.2\) (C), 141.4 (C), 138.9 (C), 138.1 (C), 136.7 (C), 133.2 (C), 131.3 (C), 131.0 (2 x C), 130.8 (C), 130.2 (C), 127.9 (C), 127.1 (C), 123.5 (2 x C), 121.1 (C), 121.0 (C), 120.9 (C), 120.7 (C), 114.2 (olefinic CH), 55.4 (OCH\(_3\)).

SI-2.2. Procedure for Synthesis of 2,7-Dibromo-9,9-dioctyl-9H-fluorene (6)

2,7-Dibromofluorene (3.0 mmol, 0.97 g) 1 was dissolved in 10.0 mL of DMSO in 100 mL of two neck round bottom flask under inert atmosphere. Temperature of the reaction was maintained at 80 °C. Later on, powdered KOH (17.0 mmol, 0.95 g) was added to reaction mixture at same temperature and continued to stir for 5 minutes. Then KI (0.7 mmol, 0.11 g) was added to the reaction mixture. After 5 minutes of stirring \(n\)-octyl bromide 3 was added to reaction and the mixture was heated at same temperature for 15 hours. Reaction mixture was allowed to cool down to room temperature. Product 6 was extracted from reaction mixture with dichloromethane and washed with brine and water for several times. Extracted organic layer was dried over MgSO4. Solvent from organic layer was removed under reduced pressure. The crude oily liquid was further chromatographed by column chromatography using n-hexane as an eluent. Desired product 6 was obtained in 90\% yield as white pale yellow liquid.

Yield: 90\%; M.P = 65-70 °C; \(R_f = 0.80\) (n-Hexane/EtOAc=99:1); \(^1\)H NMR (400 MHz, CDCl3): \(\delta 7.49\) (d, \(J = 8.0\) Hz, 2H, ArH), 7.44-7.42 (m, 4H, ArH), 1.91-1.87 (m, 4H, aliphatic H), 1.21-1.03 (m, 20H, aliphatic H), 0.81 (t, \(J = 7.0\) Hz 6H, aliphatic H), 0.58-0.54 (m, 4H, aliphatic H); \(^{13}\)C (100 MHz, CDCl3): \(\delta 152.7\) (C), 139.2 (C), 130.2 (3 x C), 126.3 (3 x C), 124.6 (2 x C), 121.6 (2 x C), 121.2 (3 x C), 55.8 (C), 40.3 (C), 31.9 (C), 30.0 (C), 29.3 (C), 23.7 (C), 22.7 (C), 14.2 (C).
SI-2.3. Procedure for Synthesis of 2,7-Dibromo-9-(3-phenylidene)9H-fluorene (7)

A 100 mL two neck round bottom flask along with reflux were flushed with stream of nitrogen. 2,7-Dibromofluorene 1 (0.97 g, 3.0 mmol) was dissolved in 8 mL of ethanol at reflux. Afterward, potassium tertiary butoxide (0.37 g, 3.3 mmol) was added to reaction mixture. After an hour of reflux cinnamaldehyde 4 (0.39 g, 3.0 mmol) was slowly added to reaction mixture under inert atmosphere conditions. The color of the solution was instantly changed into a yellow solution. Reaction timing was optimized through TLC analysis. Resulting reaction mixture was continued for further reflux until the full consumption of corresponding fluorene analogue 1. The desired product 7 was extracted with dichloromethane and washed with brine and distilled with water twice. Extracted organic layer was first dried over anhydrous MgSO4. Solvent of organic layer was removed by using rotary evaporator. The crude solid material was further chromatographed by silica gel column chromatography using n-hexane/petroleum ether as eluent. The desired product 7 was obtained in 70% yield as a yellowish powder.

Yield: 70%; M.P = 212-214 °C; Rf = 0.45 (n-Hexane/EtOAc=80:20); 1H NMR (400 MHz, CDCl3): δ H 8.02 (s, 1H, ArH), 7.72 (s, 1H, ArH), 7.53-7.47 (m, 3H, ArH), 7.44-7.34 (m, 5H, ArH), 7.30 (d, 1H, J=8.0 Hz, ArH), 7.21-7.18 (m, 2H, olefinic CH), 6.97 (d, J= 16.0 Hz, olefinic CH) ; 13C (100 MHz, CDCl3): δ 141.2 (CH), 138.7 (C), 136.7 (C), 132.6 (C), 129.6 (C), 129.2 (C), 129.0 (C), 128.0 (C), 127.4 (C), 123.8 (C), 123.4 (C), 121.2 (C), 120.0 (C).

SI-2.4. Procedure for Synthesis of Fluorene-based Polymer (CP 1)

A two neck round bottom flask of 100 mL provided with a magnetic stirrer was flushed with nitrogen stream and degassed for several times. 2,7-dibromo-9-(4-methoxybenzylidene)-9H-fluorene 5 (0.536 mmol, 1.7 g) and 2,7-dibromo-9,9-dioctyl-9H-fluorene 6 (0.166 mmol, 1.8 g) were dissolved in 24 mL of THF at a temperature of 85 °C. Afterwards, Pd(PPh3)4 (0.03 mmol, 0.04 g) was added to reaction mixture under inert atmosphere conditions followed by the addition of 8 mL of concentrated aqueous solution of potassium carbonate (2.0 M) and 1,4-phenylenediboronic acid 8 (1.2 mmol, 0.66 g). Subsequently, whole of this reaction mixture was stirred for 48 hours at 85 °C. After cooled down to room temperature crude was filtered off and the resulting solid was precipitated three times in methanol to afford the polymer as a greenish solid with 89% yield.
Yield: 89%; M.P = 80-85 °C; Rf = 0.80 (n-Hexane/EtOAc=99:1); \( ^1 \)H NMR (400 MHz, CDC\(_3\)) \( \delta \)
8.12-8.01 (m, 1H, ArH), 7.80-7.68 (m, 6H, ArH), 7.66-7.57 (m, 9H, ArH), 7.55-7.45 (m, 4H, ArH),
7.03-6.99 (m, 1H, ArH), 3.74 (s, 1H, O-CH\(_3\)), 2.08-2.00 (m, 3H, aliphatic H), 1.29-0.77 (m, 34H,
aliphatic H).

FT-IR (KBr, cm\(^{-1}\)): 3028, 2922, 2850, 1601, 1508, 1459, 1247, 1172, 1133, 811, 757,
695. Anal. Calcd for C\(_{56}\)H\(_{60}\)O: C, 89.79; H, 8.07; O, 2.14. Found: C, 89.00; H, 8.00.

\( M_n \) via GPC in tetrahydrofuran: 8100, \( M_w = 26900 \), PDI: 3.32.

**SI-2.5. Procedure for Synthesis of Fluorene-Based Polymer (CP 2)**

2,5-Dibromothiophene 9 (0.536 mmol, 1.7 g) and 2,7-dibromo-9,9-dioctyl 9H-fluorene 6 (0.166 mmol, 1.8 g) were dissolved in 20 mL of THF at a temperature of 66 °C. Afterward, Pd(PPh\(_3\))\(_4\) (0.03 mmol, 0.04 g) was added to the reaction mixture under inert atmosphere conditions followed by the addition of 8 mL of concentrated aqueous solution of potassium carbonate (2.0 M) and 1,4-phenylenediboronic acid 8 (1.2 mmol, 0.66 g). Subsequently, the reaction mixture was stirred for 72 hours at 66 °C. After cooling down to room temperature crude was filtered off and the resulting solid was re-precipitated three times in methanol to afford the polymer CP 2 as brown solid with 86% yield.

Yield: 86%; M.P = 90-95 °C; Rf = 0.80 (n-Hexane/EtOAc=99:1); \( ^1 \)H NMR (400 MHz, CDC\(_3\)) \( \delta \)
7.78-7.52 (m, 4H, ArH), 7.46-7.24 (m, 4H, ArH), 7.17-7.09 (m, 2H, ArH), 7.09-6.89 (m, 1H, ArH),
2.27-0.51 (m, 34H, aliphatic H). FT-IR (KBr, cm\(^{-1}\)): 2922, 2851, 1491, 1429, 978, 829, 790, 754,
688. Anal. Calcd for C\(_{41}\)H\(_{52}\)S: C, 85.36; H, 9.09; S, 5.56. Found: C, 84.87; H, 9.00; S, 5.36. \( M_n \) via GPC in tetrahydrofuran: 8400, \( M_w = 23800 \), PDI: 2.83.

**SI-2.6. Procedure for Synthesis of Fluorene-Based Polymer (CP 3)**

2,7-Dibromo-9-(3-phenylidene)9H-fluorene 7 (1.0 mmol, 1.7 g) was dissolved in 16 mL of THF at a temperature of 50 °C under inert conditions. Afterward, Pd(PPh\(_3\))\(_4\) (0.03 mmol, 0.04 g) was added to reaction mixture followed by the addition of 8 mL of aqueous potassium carbonate (2.0 M) and 1,4-phenylenediboronic acid 8 (2.2 mmol, 0.36 g). Subsequently, whole of this reaction mixture was stirred for 36 hours at 85 °C. After this reaction mixture was cooled down to room temperature and diluted with 100 mL of chloroform. The collected organic layer was dried over anhydrous MgSO\(_4\) and solvent was removed by rotary evaporator. The crude was dissolved in 1 mL of chloroform and poured in 100 mL of methanol. Subsequently, precipitates were filtered off.
The crude product was dissolved in 1.0 mL of chloroform and precipitated in methanol twice to obtain a brown solid with 81% yield. Yield: 81%; M.P = 90-93 °C; FT-IR (KBr, cm⁻¹): 3021, 1457, 954, 807, 747, 687. Anal. Calcd for C₃₀H₂₄: C, 93.71; H, 6.29. Found: C, 93.22; H, 6.00. Mₐ via GPC in tetrahydrofuran: 8700, Mₘ = 20300, PDI: 2.33.

SI-3. Fluorescence Spectral Acquisition

Fluorescence based sensing evaluations were carried out for various nitroaromatic compounds (NACs). For this purpose, 100 µM stock solutions of CP 1, CP 2, and CP 3 were prepared in H₂O/THF (3:2, v/v). The stock solutions of all conjugated polymers (CPs) were diluted from 500 nM to 50 µM to find the maximum emission intensity. Next, 10 µM stock solution of each NACs was prepared in H₂O/THF (3:2, v/v). For titration experiments, fluorescence emission spectra of CPs were recorded by substantial incremental addition of TNP (0–50 pM) and other nitroaromatic compounds (0–100 nM) in the final 1400 µL solution. Cuvette (path length 10x10 mm) containing specific solution was covered with a PTFE stopper and placed into the sample holder of the spectrofluorometer. All the titration experiments were accomplished at room temperature after a regular interval of ~1 minute and were repeated three time. Fluorescence emission spectra of CP 1, CP 2, and CP 3 were recorded at an excitation wavelength (λₑₓ) of 400 nm and at slit width of 2/2 nm.

SI-4. Determination of Association Constant (kₐ)

Binding efficiency confirms the strong association between conjugated polymer and analyte. This binding efficiency was calculated using the following Benesi–Hildebrand equation 1.¹

\[ F_{\text{lim}} - F_{0}/F_{X} - F_{0} = 1 + (1/K[C])^{n} \]  

Where Fₓ, Fₘ, and F₀ represent the emission intensity of a CP at a medium concentration of nitroaromatic compounds, fluorescence intensity at the maximum association between CP and an analyte, and intensity of fluorescent compound, respectively. While C is the analyte concentration, n is the number of analytes being sensed by the sensor (here, n=1) and K is the binding or association constant (kₐ).

SI-5. Determination of Limit of Detection

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Limit of detection (LOD) was estimated through the following equation 2.

\[
\text{LOD} = \frac{3 \sigma}{S} \quad \text{------------------ (2)}
\]

Where \( \sigma \) represents the standard deviation while \( S \) is the slope of the Stern-Volmer plot.

**SI-6. Job Plot Measurement**

Binding stoichiometry of a conjugated polymer and nitroaromatic compounds was estimated by continuous variation method that is regarded as Job’s plot. To obtain Job’s plot measurement (continuous variation measurement), 10 \( \mu \)M of CP 1, CP 2, and CP 3 was taken and the mole fraction of respective analyte was gradually added to it in aqueous media \( \text{H}_2\text{O}/\text{THF} \) (3:2, v/v). Relative fluorescence intensity \( (I-I_0) \) was plotted against mole fractions of analyte to obtain Job’s plot.

**SI-7. Determination of Percent Quenching Efficiency**

The percent quenching efficiency was calculated from gradual decrease in emission intensity of conjugated polymer by increasing the concentration of nitroaromatic compounds. The following equation was applied to calculate the percent quenching efficiency of conjugated polymer.

\[
\% \text{ quenching efficiency} = \left( \frac{I-I_0}{I} \right) \times 100 \quad \text{------------------ (3)}
\]

Where, \( I \) is emission intensity of sensor with maximum concentration of an analyte and \( I_0 \) represents the emission intensity of pure conjugated polymer without any analyte.

**SI-8. Computational methods**

Theoretical studies via density functional theory (DFT) were executed by the Gaussian 09 program and their graphical results were assessed by using GaussView 5.0 program. The most stable geometries were obtained through optimization and frequency calculations at B3LYP/6-31G(d) method, which is considered as a suitable choice to investigate the geometric, thermodynamic, and electronic properties. Interaction potential between CP 1, CP 2, and CP 3 and various analytes were calculated through equation 4. Interaction mechanisms between conjugated polymer and analytes were visualized through HOMO and LUMO analysis, performed at same level of DFT.
Changes in HOMO-LUMO energy gap (H–L gap) provided deeper insight into their interactions which can be calculated through equation 5.

\[ E_{\text{Interaction}} = E_{\text{complex}} - (E_{\text{sensor}} + E_{\text{analyte}}) \]  (4)

\[ H-L_{\text{gap}} = E_{\text{LUMO}} - E_{\text{HOMO}} \]  (5)

Isosurfaces of HOMO and LUMO orbitals were drawn through Gnuplot 4.6.5.5

**SI-9. Colorimetric Sensing**

To perform colorimetric (under UV and daylight) experiments, 50 μM stock solution of conjugated polymers along with 1 μM stock solution of each nitroaromatic compounds were prepared H2O/THF (3:2, v/v). The visual sensing experiments were carried out by mixing 10 μM of each conjugated polymer to 500 nM of each nitroaromatic compound. Significant color changes were noticed upon mixing the solutions of sensors and analytes under both UV irradiations and daylight.

**SI.10. Detection of Explosives in Industrial Effluents**

Industrial wastewater samples were collected from Pakistan Ordinance Factory (POF), Havelian, Abbottabad, KPK, Pakistan. Impurities like dust and other small particles were removed through filtration using Whatman filter paper. The water samples were spiked with TNP (10 and 50 PM) to test determination and recovery of these nitroaromatic explosives. Same experimental parameters were employed for the fluorescence detection of TNP in real samples.

**SI-11. Preparation of Sensors’ Coated Test Strips**

The TLC plates (thickness: 250 μm) were utilized for the construction of explosive responsive sensors’ coated test strips. The TLC plates were immersed in 10 μM solution of CP 1, CP 2, and CP 3 in THF. Immersed paper strips were used for direct sensing after drying in an oven at 30 °C for 1 hour. TNP (10 nM) were applied onto the dry TLC strips adsorbed with respective conjugated polymer.

**SI-12. Selection of Solvent and Optimization of Concentration for Maximum Emission**
Figure S1. (a) Emission spectrum of CP 1 (10 µM) in different solvents and (b) emission profile of CP 1, CP 2, and CP 3 in the presence of different water fractions (0-99%).
**Figure S2.** Optimization of fluorescence emission intensity of CP 1 (a), CP 2 (b), and CP 3 (c) with concentration range from 500 nM to 50 μM in H2O/THF (3:2, v/v); (d) and (e) represent solid state fluorescence emission and excitation of CPs.

**SI-13. Fluorescence Emission Studies of Conjugated Polymers in the Presence of NACs**
Figure S3. Change in fluorescence emission behavior of CP 1 (10 µM) in aqueous solution (H₂O/THF (3:2, v/v) upon addition of different concentrations (0–100 nM) of TNT (a), DNT (b), DNB (c), NB (d), NT (e), NP (f), and NA (g).
Figure S4. Change in fluorescence emission behavior of CP 2 (10 µM) in aqueous solution (H₂O/THF (3:2, v/v) upon addition of different concentrations (0–100 nM) of TNT (a), DNT (b), DNB (c), NB (d), NT (e), NP (f), and NA (g).
Figure S5. Change in fluorescence emission behavior of CP 3 (10 μM) in aqueous solution (H2O/THF 3:2, v/v) upon addition of different concentrations (0–100 nM) of TNT (a), DNT (b), DNB (c), NB (d), NT (e), NP (f), and NA (g).

Table S1. Calculated Ksv rate constants and LOD of CP 1 for nitroaromatics

| Sr. No | Nitroaromatics | K_a (M⁻¹) | LOD      |
|--------|----------------|-----------|----------|
| 1      | TNP            | 4.27 × 10⁶ | 3.2 pM   |
| 2      | TNT            | 1.6 × 10³  | 27 nM    |
| 3      | DNT            | 7.2 × 10²  | 51 nM    |
| 4      | DNB            | 47.3       | 91 nM    |
| 5      | NB             | Insignificant (-) | - |
| 6      | NT             | -          | -        |
| 7      | NP             | -          | -        |
| 8      | NA             | -          | -        |

Table S2. Calculated Ksv rate constants and LOD of CP 2 for nitroaromatics

| Sr. No | Nitroaromatics | K_a (M⁻¹) | LOD      |
|--------|----------------|-----------|----------|
| 1      | TNP            | 3.71 × 10⁶ | 5.7 pM   |
| 2      | TNT            | 1.4 × 10³  | 48 nM    |
| 3      | DNT            | 7.2 × 10²  | 56 nM    |
| 4      | DNB            | 47.3       | 78 nM    |
Table S3. Calculated $K_{sv}$ rate constants and LOD of CP 3 for nitroaromatics

| Sr. No | Nitroaromatics | $K_a$ (M$^{-1}$) | LOD   |
|--------|----------------|-----------------|-------|
| 1      | TNP            | $2.13 \times 10^6$ | 6.1 pM |
| 2      | TNT            | $2.13 \times 10^2$ | 53 nM  |
| 3      | DNT            | $7.7 \times 10^1$ | 87.2 nM |
| 4      | DNB            | -               | -     |
| 5      | NB             | -               | -     |
| 6      | NT             | -               | -     |
| 7      | NP             | -               | -     |
| 8      | NA             | -               | -     |

SI-14. Changes in the Stern-Volmer (SV) Plot of CP 1, CP 2 and CP 3 Due to NACs
Figure S6. Changes in the Stern-Volmer (SV) plot of CP 1 (a), CP 2 (b), and CP 3 (c) treated with different concentrations of nitroaromatic compounds (0–50 pM).

Figure S7. Job’s plot explaining 1:2 stoichiometric associations of CP 3 with TNP explosive.
Figure S8. The Benesi-Hildebrand graphs for binding association between CP 1 (a) and CP 2 (b) and TNP.
SI-17. Optimized Complexes of Conjugated Polymers with NACs

**Figure S9.** Optimized complexes of CP 1 with TNP, TNT, DNT, DNB, NB, NT, NP, and NA. (obtained through calculations at Gaussian 09 program using B3LYP/6-31G(d) methodology).

**Figure S10.** Optimized complexes of CP 2 with TNP, TNT, DNT, DNB, NB, NT, NP, and NA. (obtained through calculations at Gaussian 09 program using B3LYP/6-31G(d) methodology).
Figure S11. Optimized complexes of CP 3 with TNP, TNT, DNT, DNB, NB, NT, NP, and NA. (obtained through calculations at Gaussian 09 program using B3LYP/6-31G(d) methodology).

SI-18. Reproducibility of fluorescence sensing response
Figure S12. Repeated fluorescence quenching response of CP 1 (a), CP 2 (b), and CP 3 (c) against TNP (0–50 pM) and selectivity of CP 1 (d), CP 2 (e), and CP 3 (f) for TNP.

SI-19. Fluorescence response time
Figure S13. Fluorescence quenching efficiency of CP 1 (a), 2 (b), and 3 (c) for TNP within time frame of 0–30 sec.

SI-20. Fluorescence Response of CPs Towards TNP in the Presence of Interferences
Figure S14. Measurement of fluorescence quenching response of CP 2 (a) and CP 3 (b) (10 μM) towards TNP explosive (20 nM) in the presence of potential interferences.

SI-21. Effect of pH

Figure S15. Effect of pH on the sensing efficiency of CP 1 (a), 2 (b), and 3 (c) for TNP explosive.
SI-22. Colorimetric Analysis

**Figure S16.** Color changes of CP 3 (10 μM) with addition of 500 nM of TNP explosive under UV (365 nm).
Figure S17. Color changes of CP 1, CP 2, and CP 3 (10 µM) with addition of 500 nM of TNP and other nitroaromatic compounds under daylight.

SI-23. Test Strip Experiment

Figure S18. Test strips of CP 3 (10 µM) and its response to TNP and other nitroaromatics solutions (10 nM in THF) under UV radiations (365 nm).
Figure S19. Digital image of test strip; dried test strips of CP 1 (a), and CP 1 treated with alternate addition of TNP explosive (b, d, and f) and ethanol (c and e).

SI-24. Fluorescence Response of CPs Towards TNP in Industrial Wastewaters
Figure S20. Fluorescence results of CP 1 (a), CP 2 (b), and CP 3 (c) towards TNP explosive in industrial wastewater.

SI-25. REFERENCES

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Figure S21. Compound 5 (1H NMR, CDCl3, 400 MHz)
Compound 5 (1H NMR, CDCl3, 400 MHz)
Compound 5 (1H NMR, CDCl3, 400 MHz)
Compound 5 (1H NMR, CDCl₃, 400 MHz)
Compound 5 (1H NMR, CDCl3, 400 MHz)
Compound 5 (13C NMR, CDCl3, 100 MHz)

Figure S22. Compound 5 (13C NMR, CDCl3, 100 MHz)
Compound 5 (13C NMR, CDCl3, 100 MHz)
Compound 5 (13C NMR, CDCl3, 100 MHz)
Compound 5 (13C NMR, CDCl3, 100 MHz)
Compound 5 (13C NMR, CDCl₃, 100 MHz)
Compound 5 (13C NMR, CDCl3, 100 MHz)
Figure S23. Compound 6 (1H NMR, CDCl3, 400 MHz)
Compound 6 (1H NMR, CDCl₃, 400 MHz)
Compound 6 (1H NMR, CDCl₃, 400 MHz)
Compound 6 (1H NMR, CDCl$_3$, 400 MHz)
Compound 6 (1H NMR, CDCl₃, 400 MHz)
Compound 6 (13C NMR, CDCl3, 100 MHz)

Figure S24. Compound 6 (13C NMR, CDCl3, 100 MHz)

Current Data Parameters
NAME            NMR FID
EXPNO               112
PROCNO                1

F2 - Acquisition Parameters
Date_          20201231
Time               1.55 h
INSTRUM           spect
PROBHD   Z116098_0621 (zpgp30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                   4
SWH           22058.824 Hz
FIDRES         0.673182 Hz
AQ            1.4854827 sec
DW                22.667 usec
RG               6.50 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6238359 MHz
NUC1                13C
P1                10.00 usec
PLW1        72.56700134 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2         90.00 usec
PLW2        16.68099976 W
PLW12        0.20593999 W
PLW13        0.10342000 W

F2 - Processing parameters
SI                32768
SF          100.6127547 MHz
WDW                  EM
SSB                  0
LB                 1.00 Hz
PC                 1.40

Figure S24. Compound 6 (13C NMR, CDCl3, 100 MHz)  S45
Compound 6 (13C NMR, CDCl3, 100 MHz)
Compound 6 (13C NMR, CDCl₃, 100 MHz)
Compound 6 (13C NMR, CDCl3, 100 MHz)
Compound 7 (1H NMR, CDCl₃, 400 MHz)

Figure S25. Compound 7 (1H NMR, CDCl₃, 400 MHz)  S49
Compound 7 (1H NMR, CDCl3, 400 MHz)
Compound 7 (1H NMR, CDCl3, 400 MHz)
Compound 7 (1H NMR, CDCl3, 400 MHz)
Compound 7 (1H NMR, CDCl₃, 400 MHz)
Compound 7 (13C NMR, CDCl3, 100 MHz)

Figure S26. Compound 7 (13C NMR, CDCl3, 100 MHz)
Compound 7 (13C NMR, CDCl3, 100 MHz)
Compound 7 (13C NMR, CDCl₃, 100 MHz)
Compound 7 (13C NMR, CDCl3, 100 MHz)
Compound 7 (13C NMR, CDCl₃, 100 MHz)
Compound 7 (13C NMR, CDCl3, 100 MHz)
Figure S27. Compound CP 1 (1H NMR, CDCl3, 400 MHz)
Compound CP 1 (1H NMR, CDCl3, 400 MHz)
Compound CP 1 (1H NMR, CDCl3, 400 MHz)
Compound CP 1 (1H NMR, CDCl3, 400 MHz)
### Compound CP 2 (1H NMR, CDCl₃, 400 MHz)

![structure of Compound CP 2](image)

### Current Data Parameters

| NAME            | NMR FID |
|-----------------|---------|
| EXPNO           | 124     |
| PROCNO          | 1       |

**F2 - Acquisition Parameters**

- Date: 20210113
- Time: 17.00 h
- INSTRUM: spect
- PROBHD: Z116098_0621
- PULPROG: zg30
- TD: 65536
- SOLVENT: CDCl₃
- NS: 16
- DS: 2
- SWH: 8012.820 Hz
- FIDRES: 0.244532 Hz
- AQ: 4.0894465 sec
- RG: 98.53
- DW: 62.400 usec
- DE: 6.50 usec
- TE: 298.0 K
- D1: 1.00000000 sec
- TD0: 1
- SFO1: 400.1324708 MHz
- NUC1: 1H
- P1: 10.00 usec
- PLW1: 16.68099976 W

**F2 - Processing parameters**

- SI: 65536
- SF: 400.1300172 MHz
- WDW: RM
- SSB: 0
- LB: 0.30 Hz
- GB: 0
- PC: 1.00

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Figure S28. Compound CP 2 (1H NMR, CDCl₃, 400 MHz)  S65
Compound CP 2 (1H NMR, CDCl3, 400 MHz)
Compound CP 2 (1H NMR, CDCl3, 400 MHz)
Compound CP 2 (1H NMR, CDCl₃, 400 MHz)
Figure S29. FT-IR spectra of CP 1
Sample ID: Naeem_DZAK_CP2
Method Name: UAF Data
Sample Scans: 40
User: Chemistry Department
Background Scans: 40
Date/Time: 11/05/2021 4:39:02 PM
Resolution: 4
Range: 4000 - 650
System Status: Good
Apodization: Happ-Genzel
File Location: C:\Users\Public\Documents\Agilent\MicroLab\Results\Data\Naeem_DZAK_CP2_2021-11-05T16-39-02.a2r

Figure S30. FT-IR spectra of CP 2
Figure S31. FT-IR spectra of CP 3