Supporting Information

Dual Mode Selective Detection and Differentiation of TNT from Other Nitroaromatic Compounds

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1. Experimental

Materials

All chemicals, 9,10-dibromoanthracene, (2-formylphenyl)boronic acid, hexan-1-amine, N1-N¹,N¹-bis(2-aminoethyl)ethane-1,2-(3-aminopropyl)-N1-methylpropane-1,3-diamine, diamine, 1-methyl-2,4-dinitrobenzene, 1-methyl-4-nitrobenzene, 1-methyl-2-nitrobenzene, nitrobenzene, 4-nitrophenol, toluene, picric acid, anthracene-9,10-dione, benzoquinone, benzene-1,2,4,5-tetracarbonitrile, 1,1'-dimethyl-[4,4'-bipyridine]-1,1'-diium, N^1 . N^1 -bis(2aminoethyl)ethane-1,2-diamine, butan-1-amine, butane-1,4-diamine, N¹-(3-aminopropyl)-N¹methylpropane-1,3-diamine, N¹-(3-aminopropyl)propane-1,3-diamine, pentan-1-amine, hexan-1-amine, octan-1-amine, propane-1,3-diamine, 3-aminopropan-1-ol,2-ethylhexan-1amine, benzene-1,2-diamine, benzene-1,3-diamine, benzene-1,4-diamine, 2-phenylethan-1amine, diallylamine, diisopropylamine, 4-aminophenol, aniline, pyren-1-ylmethanamine, 4nitronaphthalen-1-amine, diphenylamine, (E)-N-phenyl-4-(phenyldiazenyl)aniline, Lphenylalanine, naphthalen-1-ylmethanamine and triphenylamine were purchased from commercial suppliers and used as such without further purification. Solvent such as ethanol were purified prior to use according to the standard protocol and stored in molecular sieves. Thin-layer chromatography was carried out using Aluchrosep Silica Gel 60/UV₂₅₄ purchased from Merck Specialities Pvt. Ltd.

General

All the reactions were carried out in oven-dried round bottom flasks under an argon atmosphere unless otherwise mentioned. The ¹H, ¹³C NMR spectra were recorded at Bruker-400 MHz NMR spectrometer instrument. The chemical shift values for ¹H (TMS as internal standard) and ¹³C NMR are recorded in CDCl₃. The value of the coupling constant (*J*) is stated in Hertz (Hz). HR-MS (ESI) was obtained from the Waters QTOF Micro ESI (Time of Flight LC/MS). FT-IR spectra were recorded using Bruker Alpha FT-IR spectrometer and reported in the frequency of absorption (cm⁻¹). UV-Vis absorption spectra were recorded on SHIMADZU UV-3600 plus UV-VIS-NIR spectrophotometer while all emission spectra were performed using PTI Quanta MasterTM Steady State Spectrofluorometer. Fluorescence lifetimes were measured by time-correlated single-photon counting (TCSPC), using a spectrofluorometer (Horiba Scientific) and an LED excitation source is 374 nm. The quality of the fit has been judged by fitting parameters such as χ^2 (<1.2) as well as visual inspection of the residuals. The Powder X-ray diffraction patterns were recorded on a Rigaku, MicroMax-007HF equipped with high-intensity Microfocus rotating anode X-ray generator. The data was collected with the help of Control Win software. A Rigaku, R-axis IV++ detector was used for the wide-angle experiments using Cu K (1.54 Å) radiation outfitted with a Ni filter and Aluminium holder was used as the sample holder. DSC Q 10 differential scanning calorimeter connected to Q Series PCA (TA Instruments, USA) was used to determine the phase transition temperatures of the molecule. TGA data were collected in METTLER TOLEDO, TGA/SDTA851 instrument. Single crystal X-ray intensity data were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (Mo K α = 0.71073 Å) radiation at ambient temperature.

Details of DFT Calculations

All the calculations in this study have been performed with density functional theory (DFT), with the aid of the Turbomole 7.1 suite of programs,^{S1} using the PBE functional.^{S2} The TZVP^{S3} basis set has been employed. The resolution of identity (RI),^{S4} along with the multipole accelerated resolution of identity (marij)^{S5} approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. A solvent correction was incorporated with optimization calculations using the COSMO model,^{S6} with ethanol ($\varepsilon = 24.5$) as the solvent. The values reported are ΔE values Harmonic frequency calculations were performed for all stationary points to confirm them as local minima.

Preparation of DPAP Thin Film on filter paper

Whatman filter paper (7.62 \times 3.00 cm size, pore size 2.5 µm) was dipped in an ethanol solution of **AIP** (before heating the solution for 90 °C for 3h) for 5 min and allowed drying it for 25-30 min. The dried filter paper with **AIP** polymer is heated to 90 °C for 3h. Thus obtained **AIP**-coated filter papers were then cut into pieces (5 cm \times 1 cm) to get the test strips and used for the detection of explosives.

Procedure for explosive sensing using AIP

Solutions of various explosive samples in various concentrations (1 mM, 1 μ M, 1 nM) in acetone were prepared. The explosive solutions were spotted onto the **AIP** test strips at the desired concentration level using a glass microsyringe. In order to ensure consistent analysis, 20 μ L volume of each solution was drop-casted on 0.5 cm² area of **AIP** coated strip and allowed to dry for 3-5 min. The visible color change is identified by bare eyes and the

corresponding fluorescence change is monitored under UV-light (365 nm). A solvent blank was spotted near to the spot of each explosive. The detection limit of **AIP** was calculated from the lowest concentration of the explosive that enabled an independent observer to detect the quenching visually.

Detection of TNT in water using AIP-coated strips.

A solution was prepared by dissolving TNT (1.5 mg) in water (10 mL) by overnight stirring at room temperature. The TNT sample (20 μ L) was spotted on the test strips using a glass syringe. The visible color change is identified by bare eyes and the fluorescence quenching was monitored under 365 nm illumination by an independent observer. The minimum detection level of TNT was qualitatively judged by the naked eye detectable fluorescence quenching on the test strip and quantitatively determined by measuring the fluorescence quenching (%) using the front face technique.

Detection and distinction of nitroaromatic compounds by various amines

The process of detection and distinction of nitroaromatic explosive compounds comprises of drop-casting 20 μ L of free amine samples in acetone/methanol on glass slide (glass substrates to be cleaned with acetone and IPA for 15 min each in an ultrasonic bath and blow-dried with a hot-air gun before use) and place 1 mg of nitroaromatic compounds on the amine solution. The immediate color change is identified by bare eyes.

Void percentage calculation

The void space in the unit cell is calculated by keeping the probe radius of 0.4 Å and approximate grid spacing of 0.4 Å, and **M1** showed a void space of 29.5 %.

2. Synthesis



Scheme S1. Synthesis of molecule 3.



Scheme S2. Synthesis of model derivative M1.

Procedure for synthesis of 3 (2,2'-(anthracene-9,10-iyl)dibenzaldehyde).^{S7}



In a 100 mL two-necked round bottom flask, the (2-formylphenyl)boronic acid (2) (558 mg, 2.5 equiv., 7.35 mmol), 9,10-dibromoanthracene (1) (500 mg, 1 equiv., 2.94 mmol) and K_2CO_3 (380 mg, 23 mmol) were dissolved in toluene (15 mL), ethanol (2 mL) and water (4 mL). Argon was bubbled vigorously through the solution for 5 min followed by the addition of tetrakis(triphenylphosphine)palladium (110 mg, 0.1 mmol), after which argon was bubbled again through the solution for another 5 min. The solution was then heated at reflux for 24 h. After cooling to room temperature, the crude product was extracted with dichloromethane and the collected organic crude phase was dried over sodium sulphate and concentrated on a rotary evaporator. Crude product was purified by silica column

chromatography using petether:ethylacetate (1:0.2) as the eluent, affording the product **3** as light yellow solid (408.27 mg, Yield: 71 %).

¹**H** NMR (400 MHz, CDCl₃), $\delta = 9.44$ (s, -CHO, 1H) 9.43 (s, -CHO, 1H), 8.30 (d, J = 5.02, 2H), 7.87 (m, 2H), 7.75 (t, J = 8.57, 2H), 7.53 (m, 6H), 7.40 (m, 4H).

¹³**C** NMR (100 MHz, CDCl₃), $\delta = 191.78$, 191.45, 142.60, 142.52, 135.74, 134.22, 134.12, 132.67, 132.51, 130.48, 128.81, 127.56, 126.60, 126.25, 126.21.

FT-IR (v_{max} in cm⁻¹): 3367.23, 3246.72, 1691.41(aldehyde), 1593.58, 1518.44, 1504.26, 1437.63, 1405.02, 1379.50, 1290.50, 1290.18, 1262.08, 1199.44, 1159.74, 1134.22, 1086.02, 1026.47, 941.40, 869.10, 822.31, 754.26, 640.83, 608.22

HR-MS: calcd for $C_{28}H_{19}O_2 [M+H]^+$ 387.1306, found 387.1380.

Procedure for Synthesis of M1 ((1E,1'E)-1,1'-(anthracene-9,10-diylbis(2,1-phenylene))bis(N-hexylmethanimine))



In a 50 mL two-necked round bottom flask, the 2,2'-(anthracene-9,10-iyl)dibenzaldehyde (**3**) (100 mg, 1 equiv., 0.287 mmol) and n-hexylamine (**A7**) (57.61 mg, 2.2 equiv., 0.569 mmol) were dissolved in DMF (6 mL). Argon was bubbled vigorously through the solution for 10 min. The solution was then heated at 100 °C for 6 h. After cooling to room temperature, the crude product was extracted with dichloromethane and the collected organic crude phase was dried over sodium sulphate and concentrated on a rotary evaporator. The crude product was purified by recrystallization method by using ethanol and dichloromethane (4:1) affording the product as light yellow crystals and the crystals were further washed multiple times with pentane and dried under reduced pressure (78.19 mg, Yield: 79 %).

¹**H** NMR (400 MHz, CDCl₃), $\delta = 8.35$ (t, J = 7.39, 2H), 7.62 (m, 8H), 7.57 (m, 6H), 3.18 (t, 4H), 1.48 (t, 4H), 1.09 (m, 12 H), 0.78 (t, 6H)

¹³**C** NMR (100 MHz, CDCl₃), $\delta = 159.11$, 139.29, 136.27, 134.45, 131.97, 130.17, 128.39, 126.91, 126.58, 125.63, 61.32, 31.42, 30.50, 26.58, 22.44, 14.01.

FT-IR (v_{max} in cm⁻¹): 2958.91, 2922.05, 2853.99, 1638.95 (imine peak), 1595.00, 1558.14, 1539.71, 1518.44, 1456.06, 1436.21, 1368.16, 1349.73, 1308.61, 1271.75, 1207.95, 1185.26, 1156.91, 1145.56, 1091.69, 1023.64, 964.09, 942.82, 775.52, 759.93, 728.74, 670.61, 643.67, 630.91, 609.64

HR-MS: calcd for $C_{40}H_{44}N_2$ [M]⁺ 553.3582, found 553.3577.



¹H (top) and ¹³C (bottom) NMR spectra of 2,2'-(anthracene-9,10-iyl)dibenzaldehyde **3**.



¹H (top) and ¹³C (bottom) NMR spectra of ((1E,1'E)-1,1'-(anthracene-9,10-diylbis(2,1-phenylene))bis(N-hexylmethanimine)**M1**.

Synthesis of anthracene based imine-linked polymer, AIP^{S8}

AIP was synthesized by mixing molecule **3** (200 mg; 5.96 mmol), tris(2-aminoethyl)amine (**A1**) (101 mg; 2.78 mmol) and N1-(3-aminopropyl)-N1-methylpropane-1,3-diamine (**A2**) (46 mg; 1.79 mmol) in ethanol. The solution was vigorously stirred and poured into a petri dish (or taking solution on filter paper) followed by evaporation of solvent in a fume hood for 2-3 hours at room temperature and after that heated to 90°C for 3 hour in oven.

Characterization of AIP

FT-IR (*v*_{max} in cm⁻¹): 3279.33, 3065.24, 2951.82, 2882.35, 1643.21(imine peak), 1515.61, 1434.21, 1385.17, 1362.49, 1302.94, 1243.39, 1171.08, 1103.03, 1067.59, 1243.39, 1171.08, 1103.03, 1067.59, 1033.56, 975.43, 941.40, 918.72



MALDI-TOF spectra of oligomers formed in ethanol.



Proposed chemical structure of the **oligomers formed in ethanol** based on MALDI-TOF analysis.





Figure S1. Comparison of the FT-IR spectra of 3, A1, A2 and AIP.

Figure S2. Comparison of the PXRD profiles of molecules M1 and AIP.

Figure S3. a) Absorption and b) steady state emission spectra of **AIP** and **M1** in dichloromethane ($C = 10^{-5}$ M, l = s1 mm, $\lambda_{ex} = 345$ nm).

In order to understand the photophysical properties, absorption and emission spectra of **AIP** in dichloromethane (1 x 10⁻⁵ M) were recorded. It can be seen that **AIP** exhibits strong absorption characteristics in the UV region ($\lambda_{max} = 377 \text{ nm}$), and blue emission from 400 to 550 nm with λ_{max} of 430 nm ($\lambda_{ex} = 377 \text{ nm}$). Both **M1** and **AIP** exhibited almost similar absorption features in solution (320-420 nm). Model derivative **M1** exhibited a blue emission, which is nearly same as **AIP**.

Figure S4. Emission lifetime of **AIP** and **M1** in dichloromethane ($C = 10^{-5}$ M, l = 1 mm, $\lambda_{ex} = 374$ nm).

Figure S5. Emission lifetime of **AIP** and **M1** in thin films on strips ($\lambda_{ex} = 374$ nm).

Figure S6. Wavelength dependent emission lifetime of a) **M1** and b) **AIP** in thin films on strips ($\lambda_{ex} = 374$ nm).

Figure S7. Absorption spectral changes of AIP coated strip on contact with different acceptors (1 mM).

Figure S8. a) Steady state emission spectral changes and b) variation of fluorescence quenching of **AIP** coated strip with different acceptors (1 mM) ($\lambda_{ex} = 379$ nm, error bar = 3%).

Figure S9. a) Absorption and b) steady-state emission spectral changes of **M1** coated strip with varying concentration of TNT ($\lambda_{ex} = 379$ nm).

Figure S10. Emission lifetime decay profile of **M1** coated strip with varying concentration of TNT ($\lambda_{ex} = 374 \text{ nm}, \lambda_{mon} = 441 \text{ nm}$).

Figure S11. Crystal structure of M1 showing single molecule.

Figure S12. The unit cell of M1 showing the packing of molecules using intermolecular interactions.

Figure S13. a) Absorption and b) steady-state emission spectral changes of **M1** in dichloromethane (C = 1 mM, l = 1 cm, $\lambda_{ex} = 377 \text{ nm}$) with varying concentration of TNT ($\lambda_{ex} = 377 \text{ nm}$).

Figure S14. a) Absorption and b) steady-state emission spectral changes of **AIP** in dichloromethane (C = 1 mM, l = 1 cm, $\lambda_{ex} = 377 \text{ nm}$) with varying concentration of TNT ($\lambda_{ex} = 377 \text{ nm}$).

Figure S15. Photographs of **AIP** coated strip showing visible (left) and fluorescence (right) color changes with different acceptors such as benzoquinone, anthraquinone and tetracyanobenzene under visible (left) and under UV light (365 nm) excitation (right).

Figure S16. a) Steady-state emission spectral changes and b) variation of fluorescence quenching of **AIP** coated strip with different acceptors) such as benzoquinone, anthraquinone and tetracyanobenzene (1 mM) ($\lambda_{ex} = 379$ nm, error bar = 3%).

Figure S17. Absorption spectral changes of **AIP** coated strip with different acceptors such as benzoquinone, anthraquinone and tetracyanobenzene (1 mM).

Figure S18. Photographs of **AIP** coated strip showing visible color (left) and fluorescence (right) changes with different nitro explosives (1 mM) and TNT in water.

Figure S19. a) Steady-state emission spectral changes and b) variation of fluorescence quenching of **AIP** coated strip with different nitro aliphatic acceptors (1 mM) and TNT in water ($\lambda_{ex} = 379$ nm, error bar = 3%).

Figure S20. Absorption spectral changes of **AIP** coated strip with different nitro acceptors (1 mM) and TNT in water.

Figure S21. Photograph showing the visible color changes of 3, A1, A2, 3+A1 and 3+A2 in the presence of TNT (1 mM).

Figure S22. Reflectance spectra of a) A1, b) A4, c) A10 and d) A14 with TNT (1 mM).

Figure S23. Reflectance spectra of a) A1, b) A4 and c) A14 with DNT (1 mM).

Figure S24. Reflectance spectra of a) A1 and b) A14 with NB (1 mM).

Figure S25. FT-IR spectra of A1 with TNT, DNT, and NB (1 mM).

Figure S26. FT-IR spectra of A4 with TNT and DNT (1 mM).

Figure S27. FT-IR spectra of A10 with TNT (1 mM).

Figure S28. FT-IR spectra of molecule A14 with TNT, DNT, and NB (1 mM).

Figure S29. Photograph of the visible color differentiation of TNT, DNT and NB using various amines.

Figure S30. Photograph of the well plate showing the complexes formed by TNT, DNT and NB with various amines.

Figure S31. Photograph of the concentration depedent visible color differentiation of TNT using various amines.

Figure S32. Photograph of the concentration depedent visible color differentiation of DNT using various amines.

Figure S33. Photograph of the concentration depedent visible color differentiation of NB using various amines.

Figure S34. Photograph of the explosive detection kit developed using AIP and amines A1, A4, A10 and A14.

4. Tables

Table S1.	Emission	lifetime o	f AIP	and M1 in	n dichloro	methane ($(C = 10^{-5})$	M, <i>l</i> = 1	mm, /	$l_{ex} =$
374 nm).										

Sl. No	Compounds	Wavelength monitored	Lifetime
1	M1	432 nm	$\tau_1 = 0.008 \text{ ns} (4.49\%)$ $\tau_2 = 1.91 \text{ ns} (95.51\%)$
2	AIP	430 nm	$\tau_1 = 0.07 \text{ ns} (41.86\%)$ $\tau_2 = 3.62 \text{ ns} (58.14\%)$

Table S2. Emission lifetime of **AIP** and **M1** coated strips ($\lambda_{ex} = 374 \text{ nm}$).

Sl. No	Compounds	Wavelength monitored	Lifetime
1	M1	441 nm	$\tau_1 = 0.007 \text{ ns} (0.02 \%)$ $\tau_2 = 5.27 \text{ ns} (98.98 \%)$
2	AIP	474 nm	$\tau_1 = 4.2 \text{ ns} (69.01\%)$ $\tau_2 = 1.13 \text{ ns} (33.99\%)$

Table S3. Wavelength dependent emission lifetime of **AIP** coated strip ($\lambda_{ex} = 374$ nm).

Sl. No	Conc. of TNT	Life time
1	420 nm	$\tau_1 = 0.06 \text{ ns} (10.95 \%)$ $\tau_2 = 4.48 \text{ ns} (89.05 \%)$
2	440 nm	$\tau_1 = 0.07 \text{ ns} (17.62 \%)$ $\tau_2 = 3.57 \text{ ns} (82.38 \%)$
3	460 nm	$\tau_1 = 0.08 \text{ ns} (32.13 \%)$ $\tau_2 = 3.92 \text{ ns} (67.87 \%)$
4	480 nm	$\tau_1 = 0.09 \text{ ns} (39.71 \%)$ $\tau_2 = 4.26 \text{ ns} (60.29 \%)$
5	500 nm	$\tau_1 = 0.09 \text{ ns} (47.72 \%)$ $\tau_2 = 4.60 \text{ ns} (52.28 \%)$
6	520 nm	$\tau_1 = 0.08 \text{ ns} (39.86 \%)$ $\tau_2 = 5.22 \text{ ns} (60.14 \%)$
7	540 nm	$\tau_1 = 0.04 \text{ ns} (45.07 \%)$ $\tau_2 = 5.60 \text{ ns} (54.93 \%)$

Sl. No	Conc. of TNT	Life time
1	420 nm	$\tau_1 = 0.05 \text{ ns} (9.17 \%)$ $\tau_2 = 1.99 \text{ ns} (90.83 \%)$
2	440 nm	$\tau_1 = 0.05 \text{ ns} (12.72 \%)$ $\tau_2 = 2.07 \text{ ns} (90.83 \%)$
3	460 nm	$\tau_1 = 0.04 \text{ ns} (19.56 \%)$ $\tau_2 = 2.95 \text{ ns} (80.44 \%)$
4	480 nm	$\tau_1 = 0.03 \text{ ns} (21.55 \%)$ $\tau_2 = 3.69 \text{ ns} (78.45 \%)$
5	500 nm	$\tau_1 = 0.02 \text{ ns} (21.53 \%)$ $\tau_2 = 4.35 \text{ ns} (78.47 \%)$
6	520 nm	$\tau_1 = 0.01 \text{ ns} (23.84 \%)$ $\tau_2 = 4.78 \text{ ns} (77.16 \%)$
7	540 nm	$\tau_1 = 0.01 \text{ ns} (24.10 \%)$ $\tau_2 = 5.76 \text{ ns} (75.90 \%)$

Table S4. Wavelength dependent emission lifetime of **M1** coated strip ($\lambda_{ex} = 374 \text{ nm}$).

Table S5. Variation of the emission lifetime of **AIP** coated strip with increasing TNT concentration ($\lambda_{ex} = 374 \text{ nm}$, $\lambda_{mon} = 474 \text{ nm}$).

Sl. No	Conc. of TNT	Lifetime
1	0	$\tau_1 = 4.2 \text{ ns} (69.01\%)$ $\tau_2 = 1.13 \text{ ns} (33.99\%)$
2	10 ⁻¹² M	$\tau_1 = 3.92 \text{ ns} (60.04\%)$ $\tau_2 = 0.81 \text{ ns} (39.96\%)$
3	10 ⁻⁰⁹ M	$\tau_1 = 1.74 \text{ ns} (94.94\%)$ $\tau_2 = 0.008 \text{ ns} (5.06\%)$
4	10 ⁻⁰⁶ M	$\tau_1 = 1.56 \text{ ns} (75.22\%)$ $\tau_2 = 0.05 \text{ ns} (24.78\%)$
5	10 ⁻⁰³ M	$\tau_1 = 1.33 \text{ ns} (65.00\%)$ $\tau_2 = 0.003 \text{ ns} (35.00\%)$

Sl. No	Conc. of TNT	Life time
1	0	$\tau_1 = 0.007 \text{ ns} (0.02 \%)$ $\tau_2 = 5.27 \text{ ns} (98.98 \%)$
2	10 ⁻¹² M	$\tau_1 = 0.001 \text{ ns} (19.21 \%)$ $\tau_2 = 4.62 \text{ ns} (80.79 \%)$
3	10 ⁻⁰⁹ M	$\tau_1 = 0.004 \text{ ns} (16.66 \%)$ $\tau_2 = 3.64 \text{ ns} (83.34 \%)$
4	10 ⁻⁰⁶ M	$\tau_1 = 0.005 \text{ ns} (13.33 \%)$ $\tau_2 = 3.03 \text{ ns} (86.67 \%)$
5	10 ⁻⁰³ M	$\tau_1 = 0.005 \text{ ns} (8.09 \%)$ $\tau_2 = 2.81 \text{ ns} (91.91 \%)$

Table S6. Variation of the emission lifetime of **M1** coated strip with increasing TNT concentration ($\lambda_{ex} = 374 \text{ nm}$, $\lambda_{mon} = 441 \text{ nm}$).

Table S7. Variation of the emission lifetime of **AIP** in dichloromethane ($C = 10^{-3}$ M, l = 1 mm) with increasing TNT concentration ($\lambda_{ex} = 374$ nm, $\lambda_{mon} = 430$ nm).

Sl. No	Conc. of TNT	Lifetime
1	0	$\tau_1 = 0.71 \text{ ns} (69.01\%)$ $\tau_2 = 3.62 \text{ ns} (33.99\%)$
2	10 ⁻⁰³ M	$\tau_1 = 0.68 \text{ ns} (65.00\%)$ $\tau_2 = 3.46 \text{ ns} (35.00\%)$
3	10 ⁻⁰⁴ M	$\tau_1 = 0.65 \text{ ns} (75.22\%)$ $\tau_2 = 3.51 \text{ ns} (24.78\%)$
4	10 ⁻⁰⁵ M	$\tau_1 = 0.71 \text{ ns} (94.94\%)$ $\tau_2 = 3.67 \text{ ns} (5.06\%)$
5	10 ⁻⁶ M	$\tau_1 = 0.78 \text{ ns} (60.04\%)$ $\tau_2 = 4.04 \text{ ns} (39.96\%)$

Sl. No	Conc. of TNT	Lifetime
1	0	$\tau_1 = 0.08 \text{ ns} (69.01\%)$ $\tau_2 = 1.91 \text{ ns} (33.99\%)$
2	10 ⁻⁶ M	$\tau_1 = 0.40 \text{ ns} (60.04\%)$ $\tau_2 = 1.95 \text{ ns} (39.96\%)$
3	10 ⁻⁰⁵ M	$\tau_1 = 0.55 \text{ ns} (94.94\%)$ $\tau_2 = 1.99 \text{ ns} (5.06\%)$
4	10 ⁻⁰⁴ M	$\tau_1 = 0.23 \text{ ns} (75.22\%)$ $\tau_2 = 1.91 \text{ ns} (24.78\%)$
5	10 ⁻⁰³ M	$\tau_1 = 0.06 \text{ ns} (65.00\%)$ $\tau_2 = 1.89 \text{ ns} (35.00\%)$

Table S8. Variation of the emission lifetime of **M1** in dichloromethane ($C = 10^{-3}$ M, l = 1 mm) with increasing TNT concentration ($\lambda_{ex} = 374$ nm, $\lambda_{mon} = 432$ nm).

Table S9. Binding energy calculation, HOMO-LUMO gap and π - π stacking interaction of AIP and different nitroaromatic acceptors.

Complex	$\Delta \mathbf{E}$ (kcal/mol)	HOMO-LUMO gap	π - π stacking distance
		(eV)	(Å)
AIP+TNT	-21.1	0.86	4.2
AIP+DNT	-5.2	1.26	5.2
AIP+ONT	-9.8	1.52	4.5
AIP+PNT	-9.8	1.48	4.4
AIP+RDX	-3.2	1.67	-

Chemical structure	TNT	DNT	NB
H_2N NH_2 H_2N NH_2 A1	~	 Image: A second s	~
$H_2N \longrightarrow N H_2$ I A2	>	 Image: A second s	~
$H_2N \xrightarrow{N} NH_2$ H_3	~	~	~
$H_2N \xrightarrow{NH_2} A4$	~	~	~
H ₂ N A5	~	~	~
H ₂ N A6	~	×	×
H ₂ N A7	~	×	×
H ₂ N A8	~	×	×
H ₂ N A9	~	×	×
H ₂ N A10	~	×	×
H ₂ N OH A11	\checkmark	×	×

Table S10. Chemical structure of various amines used and its response towards different nitroaromatic compounds.

NO ₂ NH ₂ A23	×	×	×
	×	×	×
	×	×	×
	×	×	×
A27	×	×	×
	×	×	×

5. References

- S1. Ahlrichs, R.; Bar, M.; Haäser, M.; Horn, H.; Kölmel, C. Chem. Phys. Lett. 1989, 162, 165-169.
- S2. Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865.
- S3. Ansgar, S.; Christian, H.; Reinhart, A. J. Chem. Phys. 1994, 100, 5829-5835.
- S4. Eichkorn, K.; Treutler, O.; Öhm, H.; Haser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, 240, 283–289.
- S5. Sierka, M.; Hogekamp, A.; Ahlrichs, R. J. Chem. Phys. 2003, 118, 9136-9148.
- S6. Klamt, A.; Schuurmann, G. J. Chem. Soc., Perkin Trans. 2 1993, 799-805.
- S7. D. Zehm, W. Fudicka, M. Hans, U. Schilde, A. Kelling, T. Linker, *Chem. Eur. J.* 2008, 14, 11429.
- S8. Taynton, P.; Ni, H; Zhu, C.; Yu, K.; Loob, S.; Jin, Y.; Qi, H. J.; Zhang W. Adv. Mater. 2016, 28, 2904-2909.