Electronic Supplementary Information

Understanding the effect of an amino group on the selective and ultrafast detection of TNP in water by fluorescent organic probes⁺

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Experimental Section

Caution! TNT and TNP are highly explosive and should be handled carefully and in small amounts. The explosives were handled as dilute solutions with safety measures to avoid explosion.

Materials and methods. All chemicals and solvents used for synthesis were obtained from commercial sources and used as received, without further purification. All reactions were carried out under aerobic conditions.

Physical measurements. ¹H NMR and ¹³C NMR spectra of the sodium salt of the probes were obtained in sodium salt of D₂O at 25 °C on a Bruker ARX-400 spectrometer; chemical shifts are reported relative to the residual solvent signals. FTIR spectra were measured in the 4000-400 cm⁻ ¹ range on a Perkin-Elmer Spectrum I spectrometer with samples prepared as KBr pellets. Melting points were determined by a Büchi M-565 instrument with the heating rate of 10 °C per minutes. UV-Vis spectra of the NAEs in water (a typical concentration of 1 mM) were recorded by Agilent Technologies, Cary 60 UV-Vis spectrophotometer using a quartz cuvette of path length 10 mm. Solid state reflectance spectra were recorded using Agilent Technologies, Cary 5000 series. High Resolution Mass Spectrometry (HRMS) were measured by Thermo Scientific LTQ XL LC-MS instrument for the 50-2000 amu range with ESI ion source. The morphology of the as-prepared samples was examined using field-emission scanning electron microscopy (FE-SEM, JEOL, 8 or 15 kV). Fluorescence spectra were recorded using Horiba Fluorolog3 Fluorescence Spectrophotometer. Time resolved lifetime measurements were performed on Time Correlated Single Photon Counter (Horiba Jobin Yvon) with a 320 nm picosecond diode laser while the acquired data were analyzed by DAS analysis. Fluorescence microscopy imaging was performed using Zeiss instrument of AXIO series, Scope.A1 with an optimos camera.

Density function theory (DFT) calculations were carried out using Gaussian 09 package program. The structure was optimized by hybrid functional, Becke's three parameter exchange and the Lee, Yang, and Parr Correlation Functional (B3LYP) at a split valence basis set 6-31G (d, p). HOMO-LUMO energy of molecular orbitals were obtained using GaussView 5.

Fluorescence study. In a typical experimental setup, 1 mg of finely ground **1**, **2** and **3** were weighed and added to cuvette (path length of 1 cm) containing 2 mL of water under stirring to obtain an uniform suspension for the NAEs detection experiments. The dispersible nature of **1**, **2** and **3** will facilitate vicinal contact between the probe and NAEs. The fluorescence response in 340-500 nm range upon excitation at 285, 300 and 310 nm was measured *in-situ* after incremental addition of freshly prepared aqueous analyte solutions (1 mM) and corresponding fluorescence intensity was monitored at 371, 435 and 380 nm for probes **1**, **2** and **3**, respectively. The solution was stirred at constant rate in fluorescence instrument with stirring attachment during experiment to maintain well dispersion of the solution. All the experiments were performed three times and consistent results were obtained.

Quantum yield measurement. The relative quantum yield was calculated for the compound using 0.1 M quinine sulfate ($\varphi_r = 0.546$) as the reference. For the optical density of both the compound and reference was made close to 0.1 by keeping the slit width equal to one. The emission spectra were also recorded for both the compound and reference at the same slit width with corresponding excitation for compound. The quantum yield of the probes can be determined by using the following equation:

 $\varphi_{\rm s} = \varphi_{\rm r} \left({\rm OD}_{\rm r} / {\rm OD}_{\rm s} \right) \left(I_s / I_r \right) \left(n_s^2 / n_r^2 \right)$

where ϕ_s and ϕ_r are quantum yields of the probe and the reference, respectively, OD is the optical density, *I* is the area under the curve for the emission spectra and *n* is the refractive index of the medium.

Time-resolved emission studies. For calculating emission lifetimes, a picosecond time-correlated single proton counting system (TCSPC, model Horiba Jobin Yvon-IBH) has been used. The probe was excited at 320 nm using pulse diode laser and the repetition rate was fixed at 1 MHz. The lifetime measurement for the compound before and after addition of the TNP was performed at longer time scale keeping the time to amplitude converter (TAC) in the range of 200 ns (0.54 ns per channel). The average lifetime was calculated using DAS 6.3 fluorescence decay analysis software. The decay curve was fitted using a tri-exponential fitting with goodness of fit based on reduced χ^2 (1±0.2) statistics.

The average lifetime was evaluated using the following equation:

$$\tau_{(avg)} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2 + \alpha_3 \tau_3^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2 + \alpha_3 \tau_3}$$

where, τ is the average lifetime and α is the pre-exponential factor with subscripts 1, 2 and 3 representing various species. The compound was well suspended in water and the fluorescence decay curves for the probe before and after addition of TNP were collected at different concentration.

Detection limit calculation. For calculating detection limit, NAEs (stock solution) were added to the probe (guest-free) (1 mg in 2 mL water) and fluorescence intensities were recorded. By plotting the fluorescence intensity with increasing concentration of NAEs, slope (*m*) was calculated from the graph. Standard deviation (σ) was calculated from four blank measurements of probe. Detection limit was calculated based on the formula: ($3\sigma/m$).



Fig. S1 ¹H NMR (top) and ¹³C NMR (bottom) spectra of sodium salt of 1 in D_2O .



Fig. S2 ¹H NMR (top) and ¹³C NMR (bottom) spectra of sodium salt of 2 in D_2O .



Fig. S3 ¹H NMR (top) and ¹³C NMR (bottom) spectra of sodium salt of 3 in D_2O .



Fig. S4 HRMS spectrum of 1.



Fig. S5 HRMS spectrum of 2.

Fig S6 HRMS spectrum of 3.

Fig. S7 FTIR spectrum of 1.

Fig. S8 FTIR spectrum of 2.

Fig. S9 FTIR spectrum of 3.

Fig. S10 Solid state reflectance spectrum of 1.

Fig. S11 Solid state reflectance spectrum of 2.

Fig. S12 Solid state reflectance spectrum of 3.

Fluorescence quenching performance of 1 with different nitro aromatic explosives:

Fig. S13 Percentage of fluorescence quenching obtained for different analytes at room temperature.

Fig. S14 Emission spectra of 1 dispersed in water upon incremental addition of TNT solution (1 mM) followed by 30 μ L TNP in water.

Fig. 15 Emission spectra of 1 dispersed in water upon incremental addition of 2,4-DNT solution (1 mM) followed by 30 μ L TNP in water.

Fig. S16 Emission spectra of 1 dispersed in water upon incremental addition of 2,6-DNT solution (1 mM) followed by 30 μ L TNP in water.

Fig. S17 Emission spectra of 1 dispersed in water upon incremental addition of 4-NT solution (1 mM) followed by 30 μ L TNP in water.

Fig. S18 Emission spectra of 1 dispersed in water upon incremental addition of 2-NT solution (1 mM) followed by 30 μ L TNP in water.

Fig. S19 Emission spectra of **1** dispersed in water upon incremental addition of DNB solution (1 mM) followed by 30 μL TNP in water.

Fig. S20 Emission spectra of 1 dispersed in water upon incremental addition of NB solution (1 mM) followed by 30 μ L TNP in water.

Fig. S21 Emission spectra of 1 dispersed in water upon incremental addition of NM solution (1 mM) followed by 30 μ L TNP in water.

Fig. S22 Emission spectra of **1** dispersed in water upon incremental addition of 4-NP solution (1 mM).

Fig. S23 Emission spectra of **1** dispersed in water upon incremental addition of 2-NP solution (1 mM).

Fig. S24 Emission spectra of **1** dispersed in water upon incremental consecutive addition of 2,4-DNP solution (1 mM).

Fluorescence quenching performance of 2 with different nitro aromatic explosives:

Fig. S25 Percentage of fluorescence quenching obtained for different analytes at room temperature.

Fig. S26 Emission spectra of 2 dispersed in water upon incremental addition of TNT solution (1 mM) followed by 30 μ L TNP.

Fig. S27 Emission spectra of 2 dispersed in water upon incremental addition of 2,4-DNT solution (1 mM) followed by 30 μ L TNP.

Fig. S28 Emission spectra of 2 dispersed in water upon incremental addition of 2,6-DNT solution (1 mM) followed by 30 μ L TNP.

Fig. S29 Emission spectra of 2 dispersed in water upon incremental addition of 4-NT solution (1 mM) followed by 30 μ L TNP.

Fig. S30 Emission spectra of **2** dispersed in water upon incremental addition of 2-NT solution (1 mM) followed by 30 μL TNP.

Fig. S31 Emission spectra of 2 dispersed in water upon incremental addition of DNB solution (1 mM) followed by 30 μ L TNP.

Fig. S32 Emission spectra of 2 dispersed in water upon incremental addition of NB solution (1 mM) followed by 30 μ L TNP.

Fig. S33 Emission spectra of 2 dispersed in water upon incremental consecutive addition of 2,4-DNP solution (1 mM) followed by 30 μ L TNP.

Fig. S34 Emission spectra of 2 dispersed in water upon incremental consecutive addition of 4-NP solution (1 mM) followed by 30 μ L TNP.

Fig. S35 Emission spectra of 2 dispersed in water upon incremental consecutive addition of 2-NP solution (1 mM) followed by 30 μ L TNP.

Fluorescence quenching performance of 3 with different nitro aromatic explosives:

Fig. S36 Percentage of fluorescence quenching obtained for different analytes at room temperature.

Fig. S37 Emission spectra of 3 dispersed in water upon incremental addition of TNT solution (1 mM) followed by $30 \ \mu L$ TNP.

Fig. S38 Emission spectra of 3 dispersed in water upon incremental addition of 2,4-DNT solution (1 mM) followed by 30 μ L TNP.

Fig. S39 Emission spectra of 3 dispersed in water upon incremental addition of 2,6-DNT solution (1 mM) followed by 30 μ L TNP.

Fig. S40 Emission spectra of 3 dispersed in water upon incremental addition of 4-NT solution (1 mM) followed by 30 μ L TNP.

Fig. S41 Emission spectra of 3 dispersed in water upon incremental addition of 2-NT solution (1 mM) followed by 30 μ L TNP.

Fig. S42 Emission spectra of 3 dispersed in water upon incremental addition of DNB solution (1 mM) followed by $30 \ \mu L$ TNP.

Fig. S43 Emission spectra of 3 dispersed in water upon incremental addition of NB solution (1 mM) followed by $30 \ \mu L$ TNP.

Figure S44. Emission spectra of **3** dispersed in water upon incremental consecutive addition of 2,4-DNP solution (1 mM) followed by 30 μ L TNP.

Fig. S45 Emission spectra of 3 dispersed in water upon incremental consecutive addition of 4-NP solution (1 mM) followed by $30 \ \mu L$ TNP.

Fig. S46 Emission spectra of 3 dispersed in water upon incremental consecutive addition of 2-NP solution (1 mM) followed by 30 μ L TNP.

Fig. S47 Stern-Volmer plots for different nitro-analytes in case of 1.

Fig. S48 Stern-Volmer plot for TNP in case of **1**. The relative fluorescence intensity is linear with TNP concentration in the range of $0-25 \ \mu\text{M}$, $I_0/I = 1 + 1.759 \ x \ 10^5 \ ([TNP]) \ (R^2 = 0.924)$.

Fig. S49 Stern-Volmer plot for TNT in case of **1**. The relative fluorescence intensity is linear with TNT concentration in the range of 0–25 μ M, I₀/I = 1 + 993.21 ([TNT]) (R² = 0.966).

Fig. S50 Stern-Volmer plot for 2,4-DNT in case of **1**. The relative fluorescence intensity is linear with 2,4-DNT concentration in the range of 5–35 μ M, I₀/I = 1 + 3300.43 ([2,4-DNT]) (R² = 0.905).

Fig. S51 Stern-Volmer plot for 2,6-DNT in case of **1**. The relative fluorescence intensity is linear with 2,6-DNT concentration in the range of $5-30 \mu$ M, $I_0/I = 1 + 1778.87 ([2,6-DNT]) (R^2 = 0.899)$.

Fig. S52 Stern-Volmer plot for 4-NT in case of 1. The relative fluorescence intensity is linear with 4-NT concentration in the range of 5–30 μ M, I₀/I = 1 + 5119.88 ([4-NT]) (R² = 0.949).

Fig. S53 Stern-Volmer plot for 2-NT in case of 1. The relative fluorescence intensity is linear with 2-NT concentration in the range of 5–20 μ M, I₀/I = 1 + 2192.66 ([2-NT]) (R² = 0.948).

Fig. S54 Stern-Volmer plot for DNB in case of **1**. The relative fluorescence intensity is linear with DNB concentration in the range of 5–20 μ M, I₀/I = 1 + 1892.44 ([DNB]) (R² = 0.996).

Fig. S55 Stern-Volmer plot for NB in case of **1**. The relative fluorescence intensity is linear with NB concentration in the range of 5–30 μ M, I₀/I = 1 + 2375.67 ([NB]) (R² = 0.887).

Fig. S56 Stern-Volmer plot for different nitrophenols.

Fig. S57 Stern-Volmer plots for different nitro-analytes in case of 2.

Fig. S58 Stern-Volmer plot for TNP in case of **2**. The relative fluorescence intensity is linear with TNP concentration in the range of 0–25 μ M, I₀/I = 1 + 9.87 x 10⁴ ([TNP]) (R² = 0.951).

Fig. S59 Stern-Volmer plot for TNT in case of **2**. The relative fluorescence intensity is linear with TNT concentration in the range of 0–25 μ M, I₀/I = 1 + 7.855 x 10³ ([TNT]) (R² = 0.999).

Fig. S60 Stern-Volmer plot for 2,4-DNT in case of **2**. The relative fluorescence intensity is linear with 2,4-DNT concentration in the range of 0–25 μ M, I₀/I = 1 + 1.92 x 10³ ([2,4-DNT]) (R² = 0.877).

Fig. S61 Stern-Volmer plot for 2,6-DNT in case of **2**. The relative fluorescence intensity is linear with 2,6-DNT concentration in the range of 0–30 μ M, I₀/I = 1 + 3.071 x 10³ ([2,6-DNT]) (R² = 0.944).

Fig. S62 Stern-Volmer plot for 4-NT in case of **2**. The relative fluorescence intensity is linear with 4-NT concentration in the range of 0–30 μ M, I₀/I = 1 + 3.937 x 10³ ([4-NT]) (R² = 0.967).

Fig. S63 Stern-Volmer plot for 4-NT in case of **2**. The relative fluorescence intensity is linear with 4-NT concentration in the range of 0–30 μ M, $I_0/I = 1 + 2.653 \times 10^3$ ([4-NT]) (R² = 0.910).

Fig. S64 Stern-Volmer plot for DNB in case of **2**. The relative fluorescence intensity is linear with DNB concentration in the range of 0–30 μ M, I₀/I = 1 + 5.112 x 10³ ([DNB]) (R² = 0.883).

Fig. S65 Stern-Volmer plot for NB in case of **2**. The relative fluorescence intensity is linear with NB concentration in the range of 0–30 μ M, I₀/I = 1 + 2.112 x 10³ ([NB]) (R² = 0.967).

Fig. S66 Stern-Volmer plot for different nitro-phenols in case of 2.

Fig. S67 Stern-Volmer plots for different nitro-analytes in case of 3.

Fig. S68 Stern-Volmer plot for TNP in case of **3**. The relative fluorescence intensity is linear with TNP concentration in the range of $0-15 \ \mu\text{M}$, $I_0/I = 1 + 1.646 \ x \ 10^4 ([TNP]) (R^2 = 0.985)$.

Fig. S69 Stern-Volmer plot for TNT in case of **3**. The relative fluorescence intensity is linear with TNT concentration in the range of 0–15 μ M, I₀/I = 1 + 8.619 x 10³ ([TNT]) (R² = 0.99).

Fig. S70 Stern-Volmer plot for 2,4-DNT in case of **3**. The relative fluorescence intensity is linear with 2,4-DNT concentration in the range of 0–25 μ M, I₀/I = 1 + 1.09 x 10³ ([2,4-DNT]) (R² = 0.982).

Fig. S71 Stern-Volmer plot for 2,6-DNT in case of **3**. The relative fluorescence intensity is linear with 2,6-DNT concentration in the range of 0–30 μ M, I₀/I = 1 + 2.498 x 10³ ([2,6-DNT]).

Fig. S72 Stern-Volmer plot for 4-NT in case of **3**. The relative fluorescence intensity is linear with 4-NT concentration in the range of 0–30 μ M, I₀/I = 1 + 1.118 x 10⁴ ([4-NT]) (R² = 0.972).

Fig. S73 Stern-Volmer plot for 2-NT in case of **3**. The relative fluorescence intensity is linear with 2-NT concentration in the range of 5–30 μ M, I₀/I = 1 + 3.22 x 10² ([2-NT]) (R² = 0.873).

Fig. S74 Stern-Volmer plot for DNB in case of 3. The relative fluorescence intensity is linear with DNB concentration in the range of 0–15 μ M, I₀/I = 1 + 6.01 x 10² ([DNB]) (R² = 1).

Fig. S75 Stern-Volmer plot for NB in case of **3**. The relative fluorescence intensity is linear with NB concentration in the range of 0–15 μ M, I₀/I = 1 + 3.22 x 10² ([NB]) (R² = 0.873).

Fig. S76 Stern-Volmer plot for different nitro-phenols in case of 3.

Calculation of detection limit of TNP for 1:

Fig. S77 Linear region of fluorescence intensity of probe **1** upon incremental addition of TNP (1 – 50 μ L, 1 mM stock solution) at $\lambda_{em} = 371$ nm (upon $\lambda_{ex} = 285$ nm) (R² = 0.97117).

Calculation of standard deviation:

Blank Readings (1)	FL Intensity
Reading 1	4.06E+07
Reading 2	4.11E+07
Reading 3	4.12E+07
Reading 4	4.09E+07
Standard Deviation (σ)	2.6E+05

Detection Limit calculation:

Slope from Graph (m)	1.4E+12 M ⁻¹
Detection limit($3\sigma/m$)	5.57E-7 M (120 ppb)

Calculation of Detection limit of TNP for 2:

Fig. S78 Linear region of fluorescence intensity of probe **2** upon incremental addition of TNP (1 – 50 μ L, 1 mM stock solution) at $\lambda_{em} = 300$ nm (upon $\lambda_{ex} = 435$ nm) (R² = 0.97099).

Calculation of standard deviation:

Blank Readings (2)	FL Intensity
Reading 1	4.025E+07
Reading 2	3.97E+07
Reading 3	3.75E+07
Reading 4	3.76E+07
Standard Deviation (σ)	1.405E+06

Detection Limit calculation:

Slope from Graph (m)	1.123E+12 M ⁻¹
Detection limit($3\sigma/m$)	3.7E-6 M (0.8 ppm)

Calculation of Detection limit of TNP for 3:

Fig. S79 Linear region of fluorescence intensity of probe **3** upon incremental addition of TNP (1 – 50 μ L, 1 mM stock solution) at $\lambda_{em} = 310$ nm (upon $\lambda_{ex} = 380$ nm) (R² = 0.97418).

Calculation of standard deviation:

Blank Readings (3)	FL Intensity
Reading 1	3.25E+07
Reading 2	3.22E+07
Reading 3	3.38E+07
Reading 4	3.39E+07
Standard Deviation (σ)	8.756E+05

Detection Limit calculation:

Slope from Graph (m)	4.934E+11 M ⁻¹
Detection limit($3\sigma/m$)	5.32 E-6 M (1.2 ppm)

Fig. S80 Spectral overlap of absorption spectra of different nitro-analytes and emission spectrum of 1.

Fig. S81 Spectral overlap of absorption spectra of different nitro-analytes and emission spectrum of 2.

Fig. S82 Spectral overlap of absorption spectra of different nitro-analytes and emission spectrum of 3.

(c)

Fig. 83 Quenching and recyclability test for 1 (a), 2 (b) and 3 (c) after TNP addition for five cycles, respectively.

Fig. S84 FTIR spectrum of probe 1 and after 5 recycles of probe 1.

Fig. S85 FTIR spectrum of probe 2 and after 5 recycles of probe 2.

Fig. S86 FTIR spectrum of probe 3 and after 5 recycles of probe 3.

Fig. S87 Optimized structure of **3** in presence of TNP (top) and the corresponding HOMO-LUMO energy diagram where TNP interacts with the COOH group (bottom).

Fig. S88 Comparison of HOMO-LUMO energy diagram of 1 and 3 in presence of TNP.

Table S1. Summary of quenching constant (K_{sv}) of probe **1** for different nitro-explosive analytes at room temperature.

Nitro Analytes	Stern-Volmer Constant (K _{sv}) M ⁻¹	Adjusted R ²	K _{sv} of TNP higher than other NACs	Quenching rate constant (K _q) M ⁻¹ ns ⁻¹
TNP	1.759 x 10 ⁵	0.924		3.03 X 10 ⁴
TNT	993.21	0.966	177 times	181.2
2,4-DNT	3.3×10^4	0.905	53 times	6.02×10^3
2,6-DNT	1.778 x 10 ³	0.899	99 times	324.45
4-NT	5.119 x 10 ³	0.949	35 times	934.12
2-NT	2.192×10^3	0.948	81 times	400
DNB	1.892×10^3	0.996	93 times	345.25
NB	2.375 x 10 ³	0.887	74 times	433.39

Table S2. Summary of quenching constant (K_{sv}) of probe **2** for different nitro-explosive analytes at room temperature.

Nitro Analytes	Stern-Volmer Constant (K _{sv}) M ⁻¹	Adjusted R ²	K _{sv} of TNP higher than other NACs	Quenching rate constant (K _q) M ⁻¹ ns ⁻¹
TNP	9.873 x 10 ⁴	0.951		$1.32 \text{ X}10^4$
TNT	7.855×10^3	0.999	12 times	$1.05 \text{ X } 10^3$
2,4-DNT	1.921×10^3	0.877	51 times	257.14
2,6-DNT	3.071 x 10 ³	0.944	32 times	411.11
DNB	5.112 x 10 ³	0.883	19 times	684.33
NB	2.112×10^3	0.967	46 times	282.83
2-NT	2.653×10^3	0.910	36 times	355.15
4-NT	3.937 x 10 ⁴	0.967	24 times	5270.41

Nitro Analytes	Stern-Volmer Constant (K _{sv}) M ⁻¹	Adjusted R ²	K _{sv} of TNP higher than other NACs	Quenching rate constant (Kq) M ⁻¹ ns ⁻¹
TNP	1.646 x 10 ⁴	0.985		5185.5
TNT	8.619 x 10 ³	0.999	2 times	2715.5
2,4-DNT	$1.09 \ge 10^3$	0.982	15 times	343.4
2,6-DNT	2.498 x 10 ³	0.855	6 times	787.01
DNB	$6.01 \ge 10^2$	1	27 times	189.35
NB	$3.22 \ge 10^2$	0.874	50 times	101.44
2-NT	5.392×10^3	0.976	3 times	1698.8
4-NT	$1.118 \ge 10^4$	0.972	14 times	3522.36

Table S3. Summary of quenching constant (K_{sv}) of probe **3** for different nitro-explosive analytes at room temperature.

Table S4. K_{sv} and K_q values of different nitro-phenols.

	Probe 1				
Nitro phenols	$K_{sv}(M^{-1})$	$K_q (M^{-1}s^{-1})$			
TNP	1.76 x 10 ⁵	3.21 X 10 ¹³			
2,4-DNP	5.65 x 10 ⁴	1.02 X 10 ¹³			
4-NP	4.54 x 10 ⁴	8.28 X 10 ¹²			
2-NP	1.25 x 10 ⁴	2.28 X 10 ¹²			
	Probe 2				
TNP	9.87 x 10 ⁴	1.32 X 10 ¹³			
2,4-DNP	1.96 x 10 ⁴	2.62 X 10 ¹²			
4-NP	1.60 x 10 ⁴	2.14 X 10 ¹²			
2-NP	1.17 x 10 ⁴	1.56 X 10 ¹²			
	Probe 3				
TNP	1.64 x 10 ⁴	5.17 X 10 ¹²			
2,4-DNP	1.36 x 10 ⁴	4.29 X 10 ¹²			
4-NP	8.97 x 10 ³	2.83 X 10 ¹²			
2-NP	3.80 x 10 ³	1.19 X 10 ¹²			

Probe	Ksv, M ⁻¹	Kq, M ⁻¹ s ⁻¹	Detection Limit	Medium	Reference
Probe 1	1.76 x 10 ⁵	3.03 x 10 ¹³	5.5 x 10 ⁻⁷ M (120 ppb)		
Probe 2	9.87 x 10 ⁴	1.32 x 10 ¹³	3.7 x 10 ⁻⁶ M (800 ppb)	H ₂ O	This work
Probe 3	1.65 x 10 ⁴	5.19 x 10 ¹²	5.3 x 10 ⁻⁶ M (1.2 ppm)		
		-	Organic Probe		
F1 F2	3.94×10^4	NA	$5.7 \times 10^{-7} \text{ M} (131 \text{ ppb})$	H ₂ O	<i>Chem. Commun.</i> , 2017, 53 , 10524
F2	2.1 X 10 ⁻	NA NA	$9.5 \times 10^{-7} \text{ M} (213 \text{ ppb})$	H ₂ U DME	10524
L	NA	INA	4.5 x 10 ° M (98 ppb)	DMF	4505-4507
DNSA-SQ	NA	NA	7 x 10 ⁻⁸ M	CH ₃ CN:H ₂ O (9:1)	<i>Chem. Commun.</i> , 2013, 49 , 4764-4766
Compound 1	3.43 x 10 ³	NA	15.2 x 10 ⁻⁶ M (3.48 ppm)	H ₂ O	<i>Cryst. Growth Des.</i> , 2015, 15 , 3493-3497
Cage 4	2.2 x 10 ⁵	NA	6.4 ppb	DCM	<i>Chem. Commun.</i> , 2014, 50 , 15788-15791
Nph-An	7 x 10 ⁴	NA	4.7 x 10 ⁻⁷ M (108 ppb)	THF:H ₂ O (1:9)	<i>Sensors and Actuators B,</i> 2016, 230 , 746-752
PA	1.77×10^4	NA	NA	H ₂ O	Sensors and Actuators B,
PF	3.9 X 10 ⁴	NA	NA NA		2014, 203, 612-620
$[7_{7}(\mathbf{I}),(4_{7}(\mathbf{k}))]$	2 40 x 104	Metal C	Drganic Framework	DMA	Cham. Commun. 2015 51
(MOF-1)	2.40 x 10 ³ and	INA	NA	DMA	8300 Chem. Commun., 2015, 51 ,
[Zn(L)(dipb)](H ₂ O) ₂ (MOF-2)	2.46 x 10 ⁴	NA	NA		
$[Cd_3(TPT)_2(DMF)_2] \\ \cdot 0.5H_2O]_n$	6.56 x 10 ⁴	NA	NA	EtOH	<i>Dalton Trans.</i> , 2015, 44 , 230-236.
[Tb(1,3,5-BTC)] _n	3.4 x 10 ⁴	NA	8.1 x 10 ⁻⁸ M	EtOH	<i>J. Mater. Chem. A</i> , 2013, 1 , 8745-8752
Zr ₆ O ₄ (OH) ₄ (L) ₆	2.9 x 10 ⁴	NA	2.6 x 10 ⁻⁶ M	H ₂ O	<i>Chem. Commun.</i> , 2014, 50 , 8915-8918
{[Cd(BIDPT)(oba)]	2.33 x 10 ⁴	NA	NA	DMF	Inorganic Chemistry
$\{[Zn(BIDPT)(4,4'-sdb)] \\ \cdot 2.25H_2O\}_n (2)$	2.78×10^4	NA	NA		66 , 51-54
[Zr ₆ O ₄ (OH) ₆ (L) ₆] _n	5.8 x 10 ⁴	NA	0.4 ppm	H ₂ O	Dalton Trans., 2015, 44 , 15175-15180
[Cd(NDC) _{0.5} (PCA)] _n	3.5 x 10 ⁴	NA	NA	MeCN	Angew. Chem. Int. Ed., 2013, 52 , 2881-2885
$[Zn_8(ad)_4(BPDC)_6$ (0.2Me ₂ NH ₂)]·G	4.6 x 10 ⁴	NA	12.9 x 10 ⁻⁶ M	H ₂ O	<i>Chem. Eur. J.</i> , 2015, 21 , 965
[Zn ₂ (NDC) ₂ (bpy)] Gx	0.4 x 10 ⁴	NA	NA	EtOH	J. Mater. Chem. C, 2014, 2, 10073
$\{ [Cd_5Cl_6(L)(HL)_2] \\ \cdot 7H_2O\}_n$	4.05 x 10 ⁴	NA	1.87 x 10 ⁻⁷ M (42.84 ppb)	EtOH	<i>Cryst. Growth Des.</i> , 2016, 16 , 842-851
BUT-12 BUT-13	3.1x10 ⁵ 5.1x10 ⁵	NA	23 ppb and 10 ppb	H ₂ O	J. Am. Chem. Soc., 2016, 138, 6204-6216
${[CuL(I)] \cdot DMF \cdot H_2O}_n$	1.51 x 10 ⁵	NA	215 ppb	CH ₃ CN	<i>ChemistrySelect</i> , 2017, 2 , 3200-3206
[La(TPT)(DMSO) ₂]·H ₂ O (La-MOF (1))	9.89 x 10 ⁴	NA	NA	EtOH	Dalton Trans., 2015, 44 , 13340-13346
Covalent Organic Framework					
Py-Azine COF	7.8 x 10 ⁴	9.8 x 10 ¹³	NA	CH ₃ CN	<i>J. Am. Chem. Soc.</i> , 2013, 135 , 17310-17313
3D-Py-COF	3.1 x 10 ⁴	NA	NA	DMF	<i>J. Am. Chem. Soc.</i> , 2016, 138 , 3302-3305
TfpBDH-COF	2.6 x 10 ⁴	NA	NA	IPA	<i>Chem. Sci.</i> , 2015, 6 , 3931- 3939

Table S5. Detection of TNP by Organic, MOF and COF probes.

Compound	HOMO (eV)	LUMO (eV)	Band Gap (eV)
1	-5.9977	-1.5866	4.4111
2	-6.4695	-2.1328	4.3367
3	-6.5462	-2.1069	4.4393
TNP	-8.2374	-3.8978	4.3396
TNT	-8.4592	-3.4926	4.9666
2,4-DNT	-7.7645	-3.2174	4.5471
2,6-DNT	-7.6448	-3.2877	4.3571
4-NT	-7.6542	-2.7924	4.8619
2-NT	-7.5546	-2.7467	4.8079
DNB	-7.9855	-3.4311	4.5544
NB	-7.5912	-2.4283	5.1629

Table S6. HOMO and LUMO energies calculation for probes 1, 2 and 3 and nitro-explosive analytes using B3LYP/6-31G* level.

Table S7. Average lifetime calculated for probe 1 before and after incremental addition of TNP and χ^2 value.

	Probe 1	Probe $1 + 20 \ \mu L \ TNP$	Probe $1 + 50 \mu L$ TNP	
α1	0.296	0.669	0.26	
τ_1	0.81	0.106	0.81	
α2	0.057	0.269	0.05	
$ au_2$	8.71	0.074	8.03	
α3	0.64	0.06	0.68	
τ3	0.142	7.06	0.145	
Average Lifetime	5.48	5.82	4.78	
(τ_{avg}) (ns)				
χ^2 value	1.2	0.97	1.08	

	Probe 2	Probe 2 + 10 μL TNP	Probe 2 + 20 μL TNP	Probe 2 + 50 μL TNP
α1	0.52	0.209	0.53	0.487
τ_1	2.645	0.354	2.6	2.41
α2	0.18	0.5109	0.17	0.111
τ2	0.417	2.55	0.413	0.34
α3	0.292	0.28	0.29	0.28
τ3	9.94	10.2	10.2	9.81
Average Lifetime $(\tau_{avg}) (ns)$	7.47	7.67	7.66	7.71
χ^2 value	1.11	1.18	1.17	1.03

Table S8. Average lifetime calculated for probe 2 before and after incremental addition of TNP and χ^2 value.

Table S9. Average lifetime calculated for probe 3 before and after incremental addition of TNP and χ^2 value.

	Probe 3	Probe 3 + 10 μL TNP	Probe 3 + 20 μL TNP	Probe 3 + 50 μL TNP
α1	0.5049	0.36	0.35	0.35
τ1	0.34	0.27	0.26	0.27
α2	0.406	0.49	0.49	0.47
τ2	1.68	1.5	1.43	1.47
α3	0.093	0.15	0.16	0.17
τ3	5.91	4.8	4.77	4.7
Average Lifetime (τ_{avg}) (ns)	3.174	2.95	3.001	3.02
χ^2 value	1.16	1.22	1.15	1.15