

[Electronic Supporting Information \(ESI\)](#)

Detection of PETN and RDX Using a FRET- based Fluorescence Sensor System

Manjunatha Ganiga and Jobin Cyriac*

Department of Chemistry, Indian Institute of Space Science and Technology
Thiruvananthapuram – 695 547, INDIA

*Corresponding author: jobincyriac@iist.ac.in

Supporting Information S1

Materials and Methods

Reagents and Materials: 3-Mercaptopropanoic acid (99%) and diphenylamine (99+%) were purchased from Sigma Aldrich. Cadmium chloride monohydrate, thiourea, NaOH, aniline, nitrobenzene, ethylene diamine, phenol and acetic acid were purchased from Merck (India) Ltd. 2,4-Dinitro phenol was obtained from Otto Chemicals. Millimolar concentrations of RDX and PETN were provided by Vikram Sarabhai Space Centre, Thiruvananthapuram, India. All aqueous solutions were prepared using deionized water, and ethanol was purified by distillation before being used.

UV-Visible absorption spectra were recorded using a Cary-100 double beam UV-visible spectrophotometer. Infrared studies were conducted using a Spectrum 100T Perkin-Elmer FT-IR spectrometer. For collecting FTIR spectra, samples were dried in vacuum at room temperature and measured in ATR mode. The hydrodynamic diameter of CdS quantum dots were measured using a particle size analyzer (Zetasizer Nano ZS series, Malvern instruments). All fluorescence measurements were performed using a Fluoro Max-4C Spectrofluorometer (Horiba Scientific, USA). The quantum yield of the DPA was calculated according to the previous report using Rhodamine 6G ($\phi = 0.95$) as a standard.¹⁸ Time-resolved fluorescence measurements were carried out using time-correlated single-photon counting (TCSPC) (pulse width <1 ns).

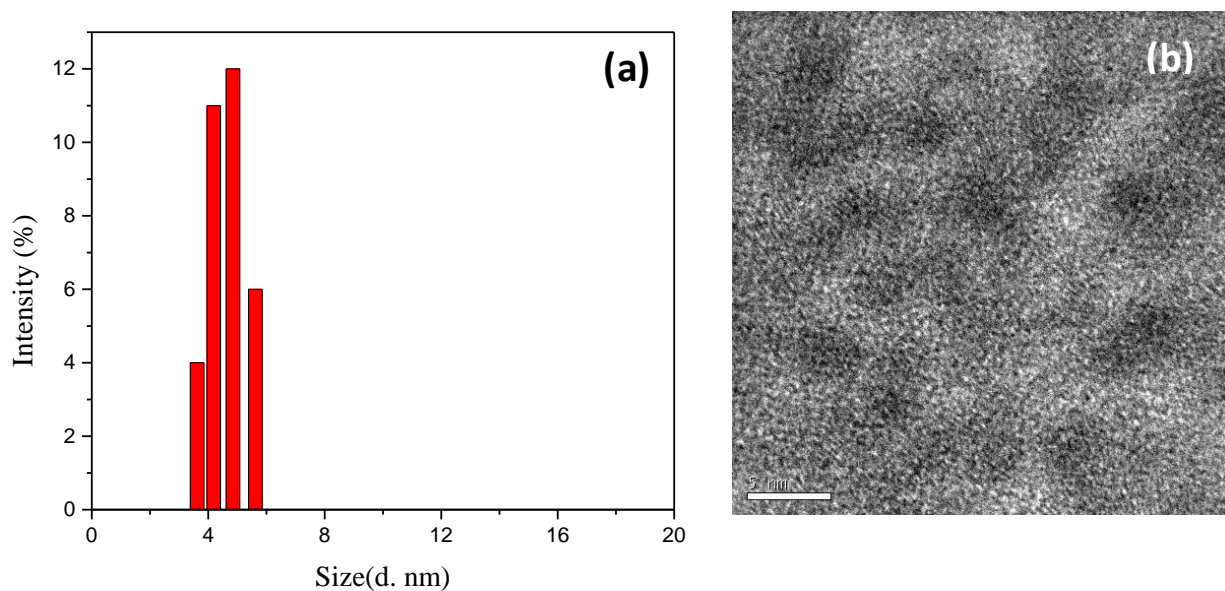


Fig. S2. (a) Hydrodynamic diameter of MPA capped CdS QDs measured using dynamic light scattering (DLS) method. (b) TEM image of the CdS QD.

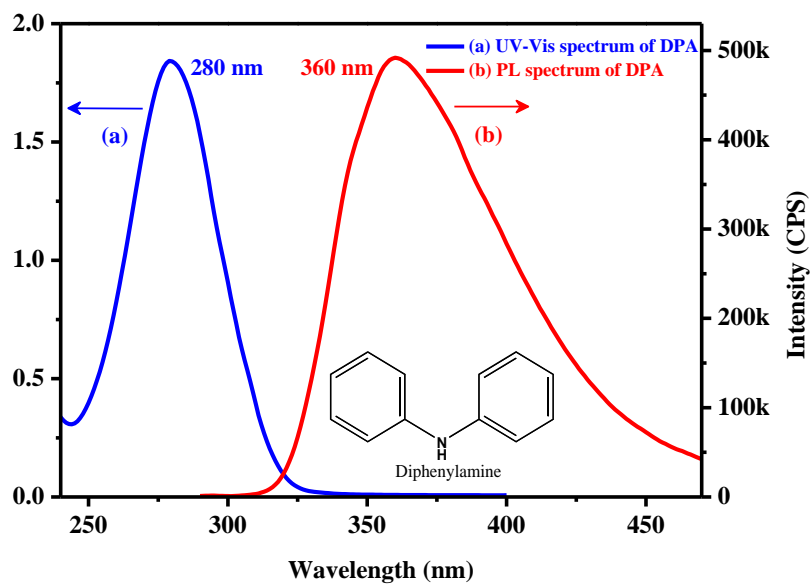


Fig. S3. Absorption (a) and emission (b) spectrum of diphenylamine (DPA); excitation wavelength was fixed at 280 nm.

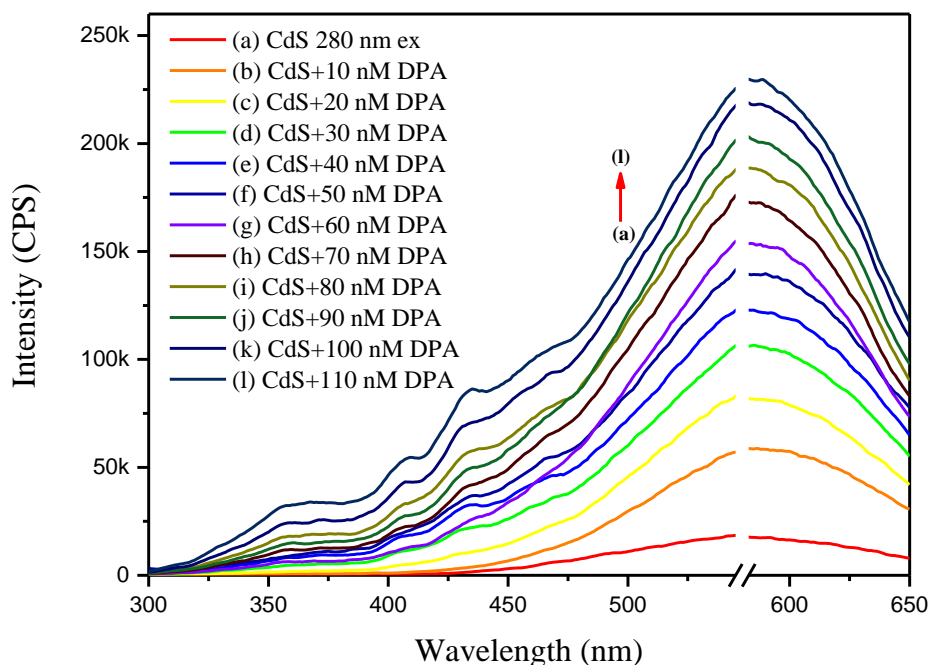


Fig. S4. (a) Fluorescence spectra of CdS QDs solution at 280 nm excitation where no FRET is observed and hence no emission at 585 nm. (b→l) CdS-DPA system at various concentrations of DPA. Emission observed at 585 nm is attributed to FRET process. Spectra were recorded at excitation wavelength of 280 nm and slit width 5 nm. The wavelength region 545 nm - 580 nm (second-order transmission through the emission monochromator) is omitted from the figure for clarity.

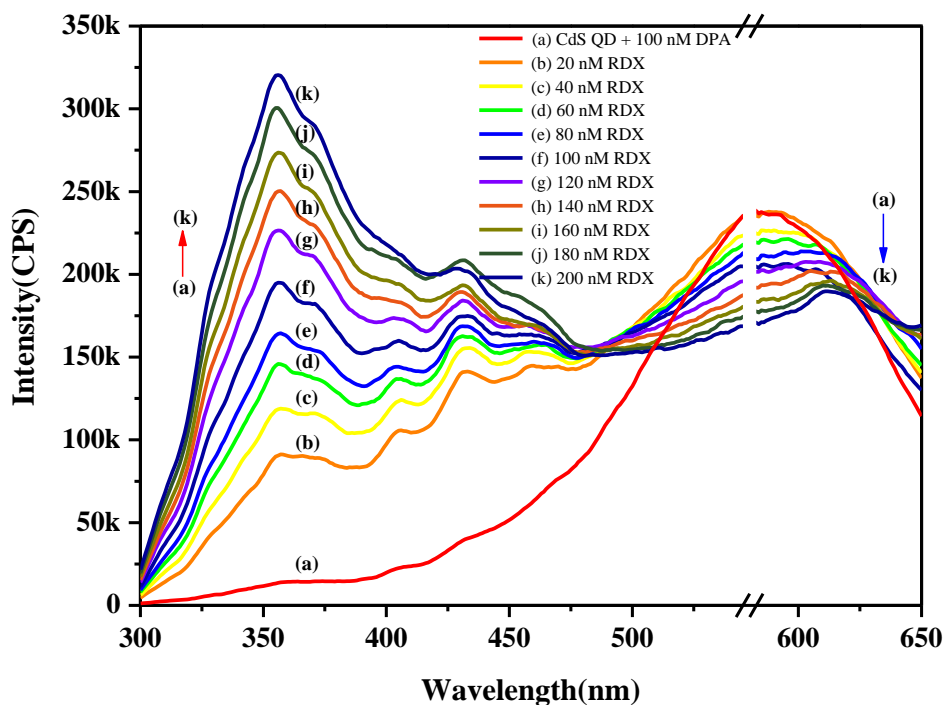


Fig. S5. Detection of RDX: Various concentrations (traces b-k) of RDX were added to the CdS QD-DPA system. Trace (a) represents the fluorescence spectrum of the CdS QD-DPA system. An increase in the emission at 355 nm and decrease in the FRET emission at 585 nm are observed. The wavelength region 545 nm -580 nm, where the second-order transmission through the emission monochromator occurs, is omitted for clarity.

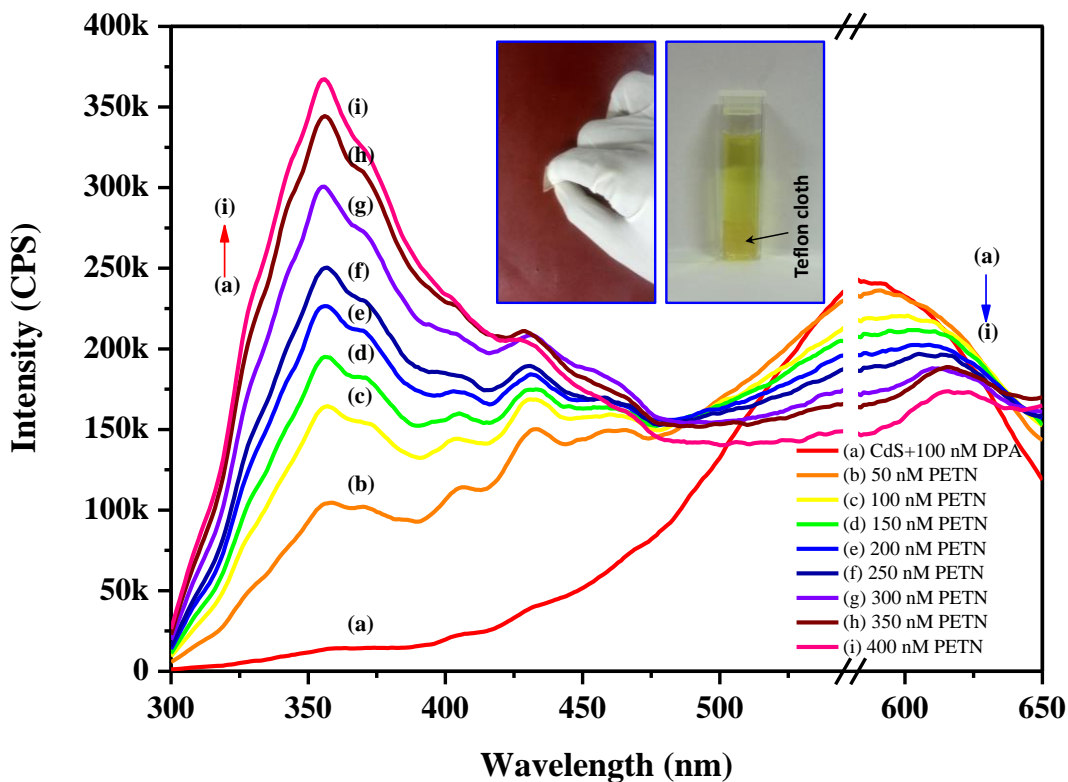


Fig. S6. . In situ sampling of PETN using a Teflon cloth. Fluorescence spectra collected after sampling from a leather surface. The teflon cloth was directly placed in the cuvette for collecting the spectra. Details of the sampling method are given in the text. Inset shows the photographs of sampling by wiping the substrate with Teflon and the cuvette containing the swabbed substrate.

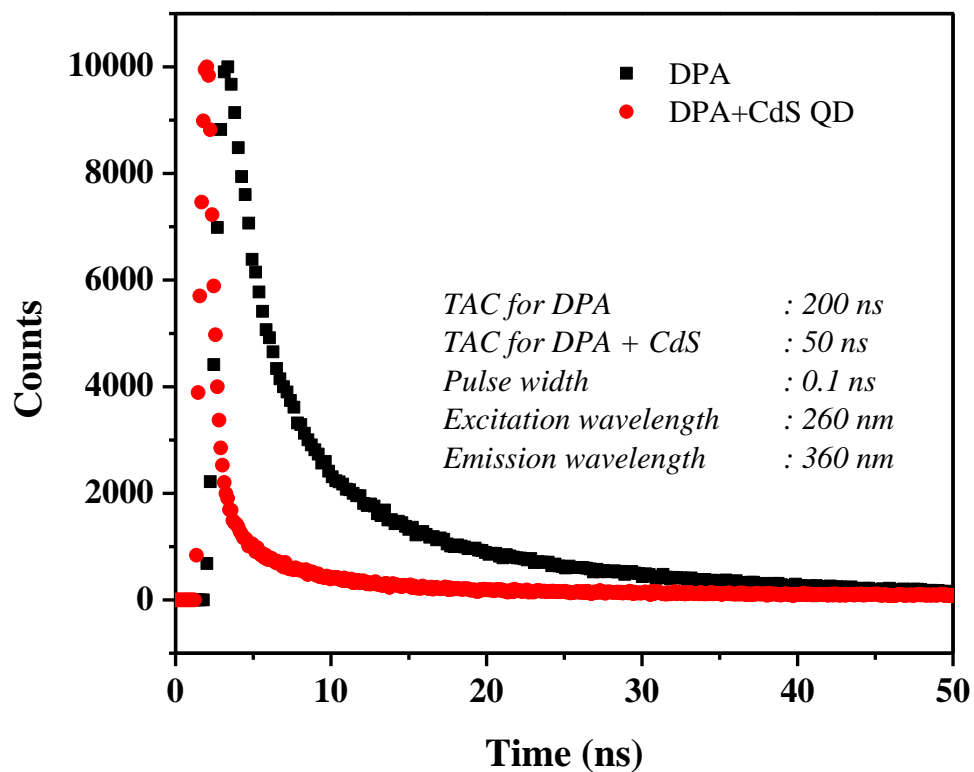


Fig. S7. Decay curves of diphenylamine (DPA) (black trace) and diphenylamine in the presence of the acceptor, CdS QDs (red trace).

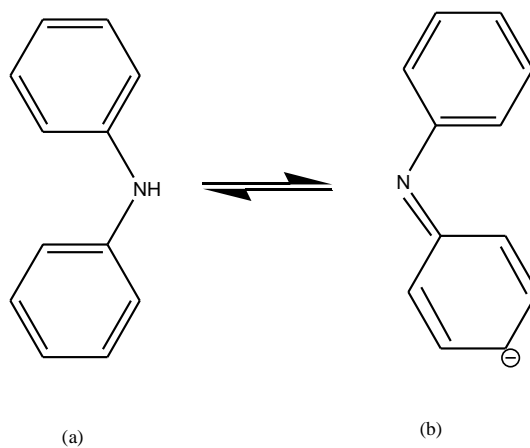


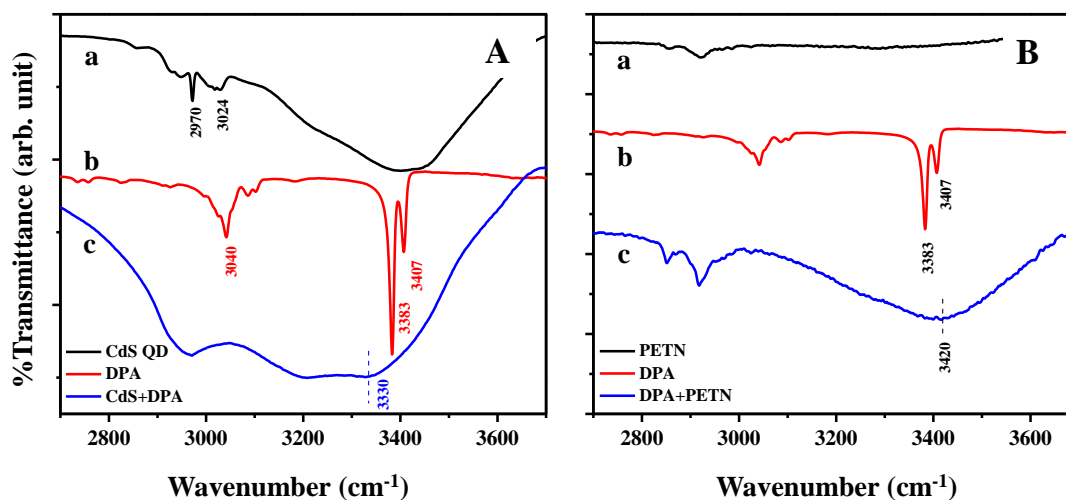
Fig. S8: Scheme showing two possible molecular structures of DPA.

Supporting Information S9

Infrared Spectral Analysis (Figure 5B)

PETN (Figure 5B (a)) shows a doublet at 1284 cm^{-1} and 1273 cm^{-1} that is due to the symmetric stretching of the NO_2 group and O-NO_2 bending, respectively.^{Ref.} Other prominent peaks include 1645 cm^{-1} , which is due to the asymmetric stretching of NO_2 , and 1386 and 1473 cm^{-1} , which are due to the bending vibrations of CH_2 . In the case of the DPA-PETN pair (Figure 5B, trace (c)), the O-NO_2 bending frequency at 1273 cm^{-1} red shifted to 1268 cm^{-1} , whereas the NO_2 stretching frequency, 1284 cm^{-1} , was unaffected. It should be noted that the C-O and -O-N stretching frequencies of PETN that appear at 1002 cm^{-1} and 853 cm^{-1} , respectively, are at 998 cm^{-1} and 843 cm^{-1} for the case of the DPA-PETN pair. Additionally, the NH_{wag} vibration for pure DPA shown at 741 cm^{-1} is blue shifted to 746 cm^{-1} for the DPA-PETN pair. From this infrared spectroscopy evidence, we suggest that in the DPA-PETN pair, (i) the O-NO_2 bending vibration is weakened, (ii) the NO_2 bond strength is unaffected, (iii) the C-O and -O-N stretching are weakened and (iv) the NH_{wag} (bending) becomes stronger. This could result only from the interaction between the positively charged N of PETN and the lone pair of the N from DPA. If the interaction is via the H of $>\text{NH}$ group (of DPA) and the negatively charged O atoms of PETN, then one should expect a difference in the NO_2 stretching vibrations and an unaffected C-O and O-N bond in PETN.

Reference: Gruzdkov, Y. A.; Gupta, Y. M. *J. Phys. Chem. A* **2001**, *105*, 6197.



(A) show the $2800\text{-}3700\text{ cm}^{-1}$ region of infrared spectra of CdS QDs (trace a), DPA (trace b) and the CdS QD-DPA sensor system (trace c). (B) show the infrared spectra of PETN (trace a), DPA (trace b) and the DPA-PETN mixture (trace c).

Supporting information S10

1. Calculation of quantum yield

Quantum yield of the donor (diphenylamine (DPA)) in the absence and the presence of the acceptor is calculated by using

$$\varphi_c = \varphi_o \times \frac{I_c}{I_o} \times \frac{A_o}{A_c} \times \frac{\eta_c^2}{\eta_o^2}$$

Where,

Φ_o and Φ_c are the photoluminescence quantum yield of the standard (Rhodamine 6G) and sample (DPA), respectively

I_o and I_c are the integrated emission intensity of the standard and sample, respectively

A_o and A_c are the absorbance of the standard and sample, respectively

η_o and η_c are the refractive index of the reference and sample solutions, respectively

(a) **In the absence of the acceptor:**

$$\varphi_c = 0.2326$$

(b) **In the presence of the acceptor:**

$$\varphi_c = 0.1274$$

2. Calculation of FRET efficiency

FRET efficiency (E) has been calculated using steady state fluorescence data by,

$$E = 1 - \frac{\varphi_{DA}}{\varphi_D}$$

φ_D = Donor (DPA) alone quantum yield

φ_{DA} = Donor quantum yield in the presence of acceptor (CdS QDs)

$$E = 1 - \frac{0.1274}{0.2326}$$

$$E = 0.4522$$

3. Calculation of spectral overlap (J_{DA})

The degree of the spectral overlap between donor emission and the acceptor absorption is expressed in terms of spectral overlap (J_{DA}) given by,

$$J_{DA} = \int_0^{\infty} I_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda$$

$I_D(\lambda)$ = Donor normalized fluorescence emission

$\varepsilon_A(\lambda)$ = Acceptor's absorption spectrum in molar absorptivity

λ = wavelength

Spectral integral has been calculated using a/e-UV-Vis-IR-Spectral analysis software

$$J_{DA} = 1.086e+14 \text{ nm}^4/(\text{M} \cdot \text{cm})$$

4. Calculation of Förster distance (Ro) and distance between the donor and the acceptor

(r)

Forster distance (Ro) is given by,¹

$$R_o = [9 \times 10^3 \times \kappa^2 \times \eta^{-4} \times \varphi_D \times J_{DA}]^{1/6} \text{ (in } \text{Å}^6)$$

Where,

κ^2 = Orientation factor, 2/3 for randomly oriented dipoles

φ_D = Quantum yield of donor in the absence of the acceptor

J_{DA} = Integral of the spectral overlap between the donor emission and the acceptor absorption

n = Refractive index of the medium

N_A = Avogadro's number

$$R_o = 32.28 \text{ Å}$$

Distance between the donor and the acceptor, r is calculated using,

$$r = \frac{R_o [n - En]^{1/6}}{E}$$

Where, n is the number of acceptor to donor ratio (taken as 0.1).²

E = FRET efficiency

R_o = Förster distance

r = distance between the donor and the acceptor

$$r = 43.99 \text{ Å}^0$$

References

1. Y. Xia, L. Song and C. Zhu, *Anal. Chem.*, 2011, **83**, 1401-1407.
2. E. R. Goldman, I. L. Medintz, J. L. Whitley, A. Hayhurst, A. R. Clapp, H. T. Uyeda, J. R. Deschamps, M. E. Lassman and H. Mattoussi, *J. Am. Chem. Soc.*, 2005, **127**, 6744-6751.