Fluorescent nonconjugated zwitterionic polymer dot: hydrothermal synthesis and application towards the nano-molar sensing of 2, 4, 6-trinitrophenol

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1.0 Experimental section:

1.1 Materials:

N, N'-Methylene (bis) acrylamide (MBA) 3x cryst, sodium (I) chloride (extrapure AR), and water (HPLC grade) were purchased from SRL. Tris-(2-amino ethyl amine), Deuterium oxide (99.9 atom % D), 2-nitrophenol, 3-nitrophenol, 4-nitrophenol were purchased from Sigma-Aldrich. Also, some other organic analytes such as (2, 4, 6-trinitrophenol, aniline, benzoic acid, nitrobenzene, phenol, 2-aminophenol, isophthalic acid, 5-aminoisopthalic acid, 5-nitroisopthalic acid, terepthalic acid, 5-nitroterepthalic acid, dinitrobenzene, nitrobenzoic acid, toluene, p-toluidine), sodium hydroxide pellets, glacial acetic acid were purchased from Central Drug House (CDH). Ninhydrin was purchased from Merck. Acetone was purchased from Rankem for purification purposes. HPLC-grade water was used to perform all the experiments.

1.2 Synthesis of non-conjugated Zwitterionic polymer dot:

In a suspension of *N*, *N*′-methylene (bis) acrylamide (MBA) (0.25 g, 1.62 mmol) in water (3.0 mL) tris (2-aminoethylamine) (TREN) (0.0787 g, 0.54 mmol) was added under stirring with 1000–1200 rpm at room temperature. After addition, suspension turned clear after 10-15 min of stirring. The clear solution was stirred further till 30 minutes at room temperature. After 30 minutes of stirring, the whole clear solution was kept in an autoclave and put inside the oven for hydrothermal reaction at the temperature of 160°C for 2.5 hours. Thereafter, the autoclave was cooled down to room temperature. A yellowish solution was obtained from the autoclave. The obtained solution was filtered with a 0.22 μm syringe filter. Thereafter, a filtrated solution was precipitated in acetone and washed 3 times with fresh acetone. The obtained yellowish product (polymer dot- PD PAMAM 2.5) was dried on the hot plate at 60°C for 30 min.

The dried non-conjugated zwitterionic polymer dot powder was used for further characterization and different experimental studies.

Similarly, for time dependent studies, hydrothermal reactions were stopped after the said period such as 0.5hours, 1.0 hours, 1.5 hours, 2.0 hours respectively to prepare/isolate the intermediate polymer dot structures – namely PD PAMAM 0.5, PD PAMAM 1.0, PD PAMAM 1.5, PD PAMAM 2.0.

1.3 Instrumentation and Characterization Methods

1.3.1 Nuclear Magnetic Resonance (NMR) Spectroscopy:

Bruker 400-MH_Z spectrometer was used for the ^{1}H-NMR analysis of a tentative 50% converted product and all the polymer dots. D_2O was used as an NMR solvent. The analysis was done by using MestReC software.

^{13}C-NMR spectra of the polymer dots were also obtained to understand the formation of carboxylate ($-COO^-$). The units of measurement for carbon chemical changes are parts per million (δ scale).

1.3.2 FTIR-Spectroscopy:

Fourier transform infrared (FTIR) spectrum of the polymer dot, (PD PAMAM 2.5) was recorded by using a Perkin Elmer spectrum 400 FT-IR spectrophotometer, and the collection was from 500 to 4000 cm^{-1} for 128 scans at 4 cm^{-1}.

Also, to understand the ground state interaction of PD PAMAM 2.5 in the presence and the absence of 2, 4, 6-trinitrophenol (PA). After freeze-drying the polymer dot, PD PAMAM 2.5 in the presence of 2, 4, 6-trinitrophenol (PA), FTIR spectra were obtained.

1.3.3 X-ray photoelectron spectroscopy (XPS):

The 'Omicron ESCA make Oxford instrument Germany' was used to measure the spectra using an Alk alpha monochromatic X-ray source (1486.7 eV).

1.3.4 UV-vis spectroscopy:

Using the Shimadzu UV 2550 Spectrophotometer, UV-vis spectra were acquired.

1.3.5 Thermogravimetric analysis (TGA)

TGA analysis of PD PAMAM 2.5 was done by using "Thermogravimetric Analyzer TGA 8000" from Perkin Elmer.

1.3.6 Powder X-ray diffraction (PXRD):

Using a PANalytical X'PERT PRO diffractometer and CuK radiation (k = 1.542 A; 40 Kv, 20 MA), powder X-ray diffraction (PXRD) data was obtained.

1.3.7 Zeta potential and dynamic light scattering (DLS):

Zeta potential and the hydrodynamic diameter of the polymer dots were observed by using a zeta sizer ultra-particle analyzer from Malvern (Model no: ZSU3305). The solution of the non-conjugated polymer dot (1mg/ml) was prepared by solubilizing in the 10 mM aqueous solution of

NaCl. 2 ml aqueous solution of the polymer dot was taken in 4 winded cuvette having a length of 1 cm and a width of 1cm.

1.3.8 Atomic force microscopy (AFM):

Morphology of the polymer dot, (PD PAMAM 2.5) was observed by atomic force microscope (AFM) topography imaging via noncontact mode with AFM from Agilent Technologies 5500. At the resonance frequency of 289 kHz, silicon cantilever probes were used with a spring constant of 42 N/m. An aqueous solution of the polymer dot, (PD PAMAM 2.5) was prepared with a concentration of 1 mg/ml to study the topography of the non-conjugated Zwitterionic polymer nano-dot. To observe the surface morphology, an aqueous solution of non-conjugated Zwitterionic polymer nano-dot was coated on a silicon wafer and dried on the hot plate at 60°C for 12 hours.

1.3.9 Fluorescence spectrophotometer:

To obtain the fluorescence excitation and emission spectrum of polymer dot (PD PAMAM 2.5) in the presence and absence of different analytes with excitation at 350 nm and slit 1.5, a Fluoro max-4P spectrofluorometer (Horiba Jobin Yvon) was used. A four-winded quartz cuvette was used for the study.

1.3.10 Lifetime measurement:

The weight average lifetime of the non-conjugated zwitterionic polymer dot, PD PAMAM 2.5 was observed in the presence and absence of the 2, 4, 6-trinitrophenol by using time-correlated single photon counting (TCSPC) technique. Fluorescence decay of PD PAMAM 2.5 was observed with excitation at 375 nm by using a diode laser (excitation source). For the fluorescence decay study, a spectrophotometer from the Edinburgh instrument (model: lifeSpec II, U.K) was used. A detector from Hamamatsu MCP PMT (3809U) was used regarding the signal collection. For the fluorescence decay study, 4 winded quartz cuvettes having a path length of 1cm was used. Finally, at the magic angle of 54.7˚C, fluorescence decay emissions were measured and for the data collection, F 900 decay analysis software was used.

The weight-average lifetime of PD PAMAM 2.5 was calculated by using the following equation

$$\langle \tau \rangle = \sum_{i=1}^{N} (C_i \tau_i)$$

$$C_i = B_i / \sum_{i=1}^{N} B_i$$

Where, τ_i = the fluorescence decay time

B_i = the pre-exponential factor

1.3.11 Quenching efficiency:

The % quenching of PD PAMAM 2.5 in the presence of the different analyte was calculated by using the following equation -

$$\% \text{ quenching } = \frac{I_0 - I}{I_0} \times 100$$

Where, ***I*** is the fluorescence intensity of PD PAMAM 2.5 in the presence of an analyte and I_0 is the fluorescence intensity of PD PAMAM 2.5 in the absence of an analyte.

1.3.12 Determination of Quantum Yield:

To obtain the fluorescence quantum yield of PD PAMAM 2.5, quinine sulphate dihydrate in 0.1(M) H_2SO_4 was used as the reference standard.

By using the following equation, the fluorescence quantum yield (ϕ_f) of PD PAMAM 2.5 was calculated:

$$\Phi_f = \phi_{std} [I_s / I_{std}] \times [A_{std} / A_s] \times [\eta_s / \eta_{std}]^2$$

Where, ϕ_{std} = fluorescence quantum yield of the standard solution (in 0.1 M H_2SO_4, ϕstd is 0.54 for quinine sulphate)

I_s = Integrated emission intensity of the sample

I_{std} = Integrated emission intensity of the standard solution

A_s = Absorbance of the sample

A_{std} = Absorbance of the standard solution

η_s = Refractive index of the sample (and it is 1.33 as the sample was dissolved in water)

η_{std} = Refractive index of the standard solution (and it is 1.33 in 0.1 M H_2SO_4)

In the above equation, all the values of the corresponding parameters were put to obtain the quantum yield. The quantum yield of the polymer dot, PD PAMAM 2.5 was 28%.

1.3.13 Benesi-Hildebrand equation for the determination of association constant, Ka:

Using the Benesi-Hildebrand equation, the association constant was determined using the absorption intensity titration curves as follows: -

$$\frac{1}{A - A_0} = \frac{1}{Ka\,(A_{max} - A_0)\,[C]} + \frac{1}{A_{max} - A_0}$$

Where, A_0 represents the absorbance of PD PAMAM 2.5 in the absence of PA and A represents the absorbance of PD PAMAM 2.5 in the presence of PA, respectively. A_{max} is the saturated absorbance of PD PAMAM 2.5 in the presence of an excess of PA. [C] is the additional concentration (mol/L) of PA.[1]

1.3.14 Determination of the spectral overlap integral, J(λ) and Förster distance, R_0:

The spectral overlap integral, J(λ) between PD PAMAM 2.5 emission spectrum and PA absorption spectrum can be calculated using the following equation.

$$J(\lambda) = \int F_D\,(\lambda).\ \varepsilon_A\,(\lambda).\ \lambda^4\ d\lambda$$

Where, $F_D(\lambda)$ denotes the corrected fluorescence intensity of the PD PAMAM 2.5 in the range of λ to λ + Δλ with the total intensity normalized to unity, and $\varepsilon_A(\lambda)$ is the molar absorptivity of PA with the unit $M^{-1}\ cm^{-1}$ of the PA and λ in nm and the spectral overlap integral J(λ) was calculated by using **a|e – UV-Vis-IR Spectral Software** as established in the literature [2-4] and it was $1.558 \times 10^3\ nm^4\ M^{-1}\ cm^{-1}$ (shown in Figure S14).

Further, the Förster distance, R_0 was also calculated using the following established equation.[5]

$$R_0 = 0.211\ [k^2\,\phi_D\,J(\lambda)/n^4]^{1/6}$$

where, $k^2 = 2/3$ and k^2 is the dipole orientation factor considering randomly oriented transition dipoles, ϕ_D was the quantum yield of donor and n was the refractive index of the solvent, which was used. The calculated value of the Förster distance, R_0 for PD PAMAM 2.5–PA interaction was 0.45 nm. This value ranges outside the limit of classical R_0 ranges ($1nm < R_0 < 10$ nm), which is generally required for significant FRET. Further, considering stochastic interaction between polymer dot and analyte in solution, such low R_0 value indicates absence of significant FRET, in the current system.

1.3.15 Inner Filter Effect (IFE) Correction:

IFE correction for the fluorescence decay of PD PAMAM 2.5 can be calculated by the **Parker equation**.

$$CF = \frac{I_{cor}}{I_{obsd}} = \frac{2.3\ d.A_{ex}}{1 - 10^{-d.Aex}}\ 10^{\,g.Aem}\ \frac{2.3\ s.A_{em}}{1 - 10^{-s.Aem}}$$

Where, CF is the corrected factor, I_{obsd} denotes the measured fluorescence intensity of PD PAMAM 2.5 at 470 nm under excitation of 350 nm, I_{cor} is the corrected fluorescence intensity when IFE is removed from I_{obsd}, A_{ex} and A_{em} are the absorbance of PD PAMAM 2.5 having PA at 350 nm and 470 nm, s, g and d refer respectively to the thickness of the excitation beam (0.1 cm), the distance between the edge of the excitation beam and the edge of the cuvette (0.40 cm) and the width of the cuvette (1.00 cm). The observed and corrected quenching efficiency (E_{obsd} and E_{cor}) are further calculated with the corresponding fluorescence intensity through ($E = 1 - I/I_0$).[6, 7]

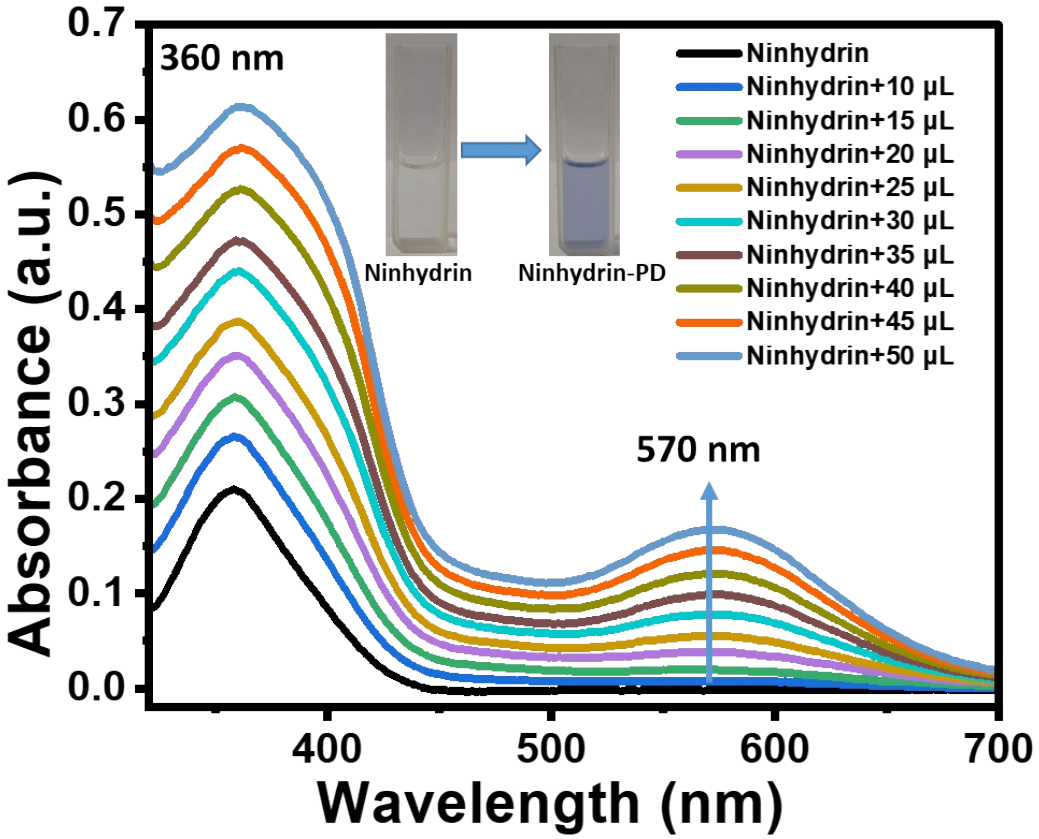


Figure S1: UV-VIS spectra of Ninhydrin with the gradual addition of PD PAMAM 2.5 (0.15 mg/ml) aqueous solution; inset picture showing the blue color of (Ninhydrin-polymer dot) complex.[8]

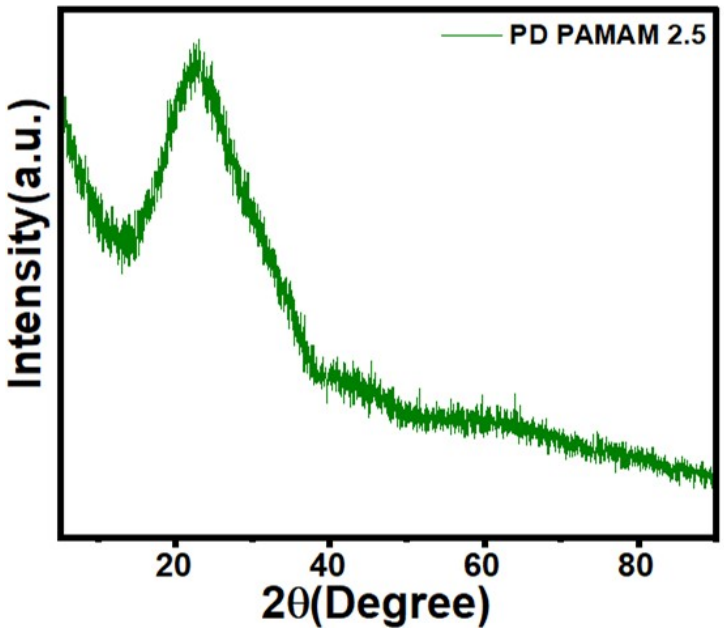


Figure S2: PXRD spectra of PD PAMAM 2.5.

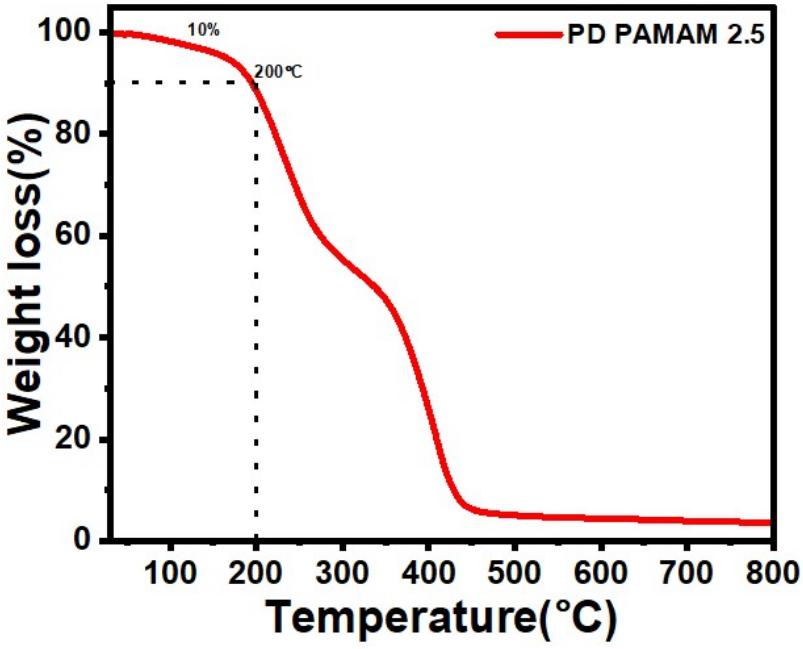


Figure S3: TGA of PD PAMAM 2.5.

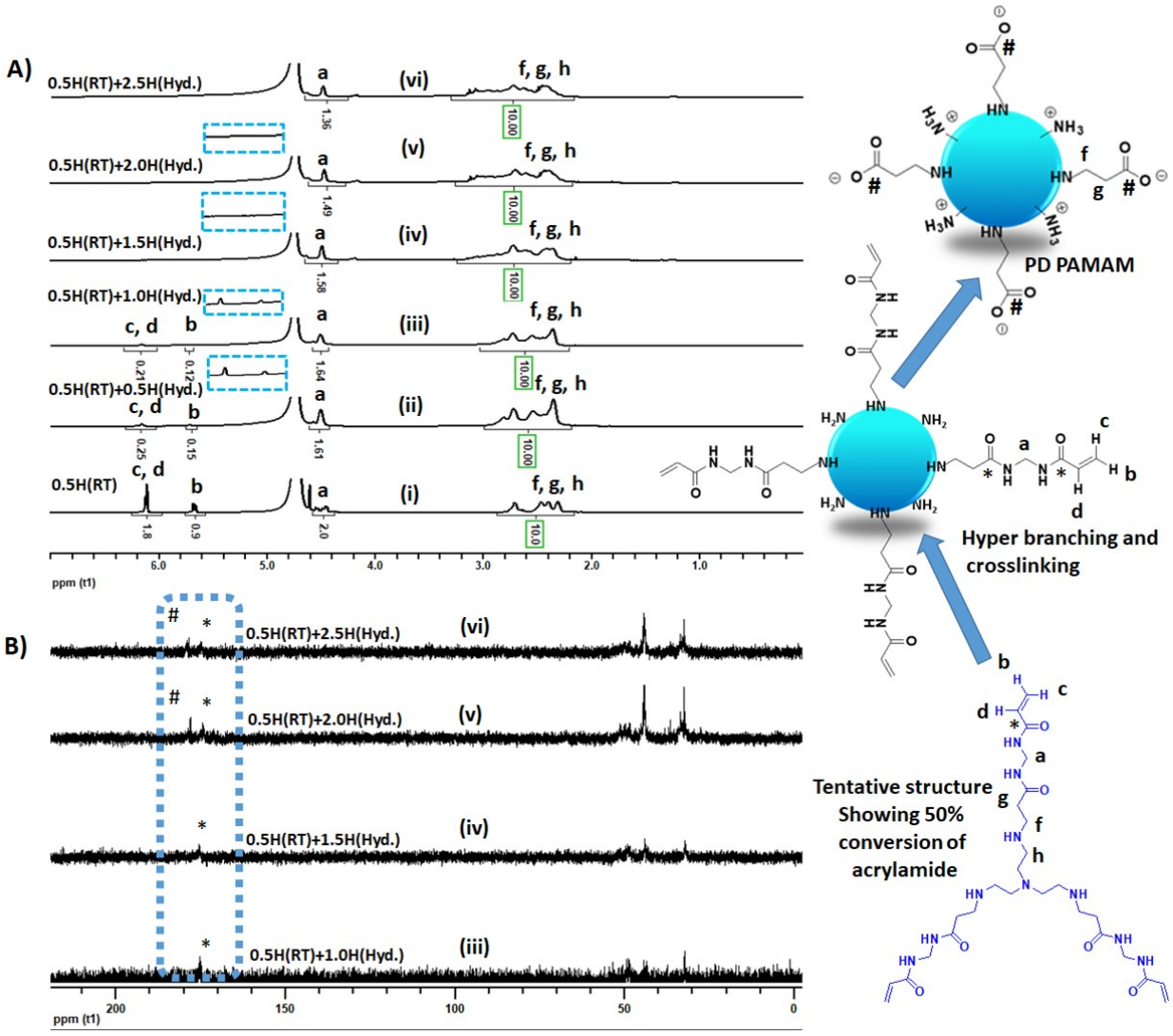


Figure S4: A) ^{1}HNMR spectra of (i) 50% acrylamide converted structure (after step 1), (ii) PD PAMAM 0.5, (iii) PD PAMAM 1.0, (iv) PD PAMAM 1.5, (v) PD PAMAM 2.0, and (vi) PD PAMAM 2.5, B) 13C-NMR spectra of (iii) PD PAMAM 1.0, (iv) PD PAMAM 1.5, (v) PD PAMAM 2.0, and (vi) PD PAMAM 2.5.

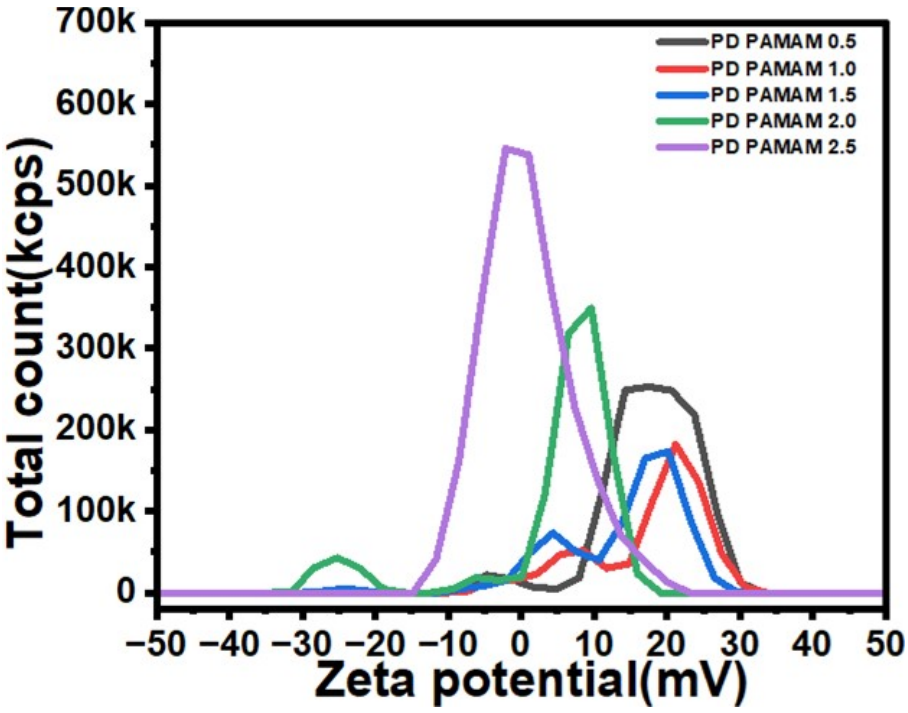


Figure S5: Zeta potential curve of PD PAMAM 0.5, PD PAMAM 1.0, PD PAMAM 1.5, PD PAMAM 2.0, PD PAMAM 2.5 in water at pH~7.

Table S1: Zeta potential value of non-conjugated zwitterionic polymer dot, PD PAMAM 0.5, PD PAMAM 1.0, PD PAMAM 1.5, PD PAMAM 2.0, PD PAMAM 2.5.

Sample	Zeta potential (mV)
PD PAMAM 0.5	17.72
PD PAMAM 1.0	17.37
PD PAMAM 1.5	13.93
PD PAMAM 2.0	4.64
PD PAMAM 2.5	3.73

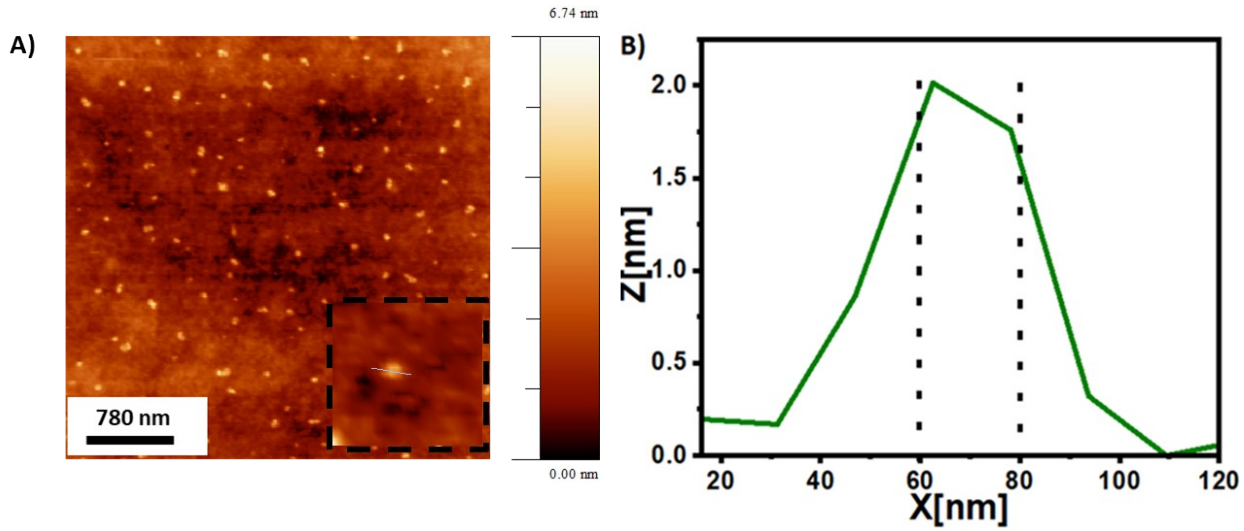


Figure S6: A) AFM microgram of PD PAMAM 2.5; inset picture displays zoomed out pic. of single polymer dot, B) Height profile graph of PD PAMAM 2.5.

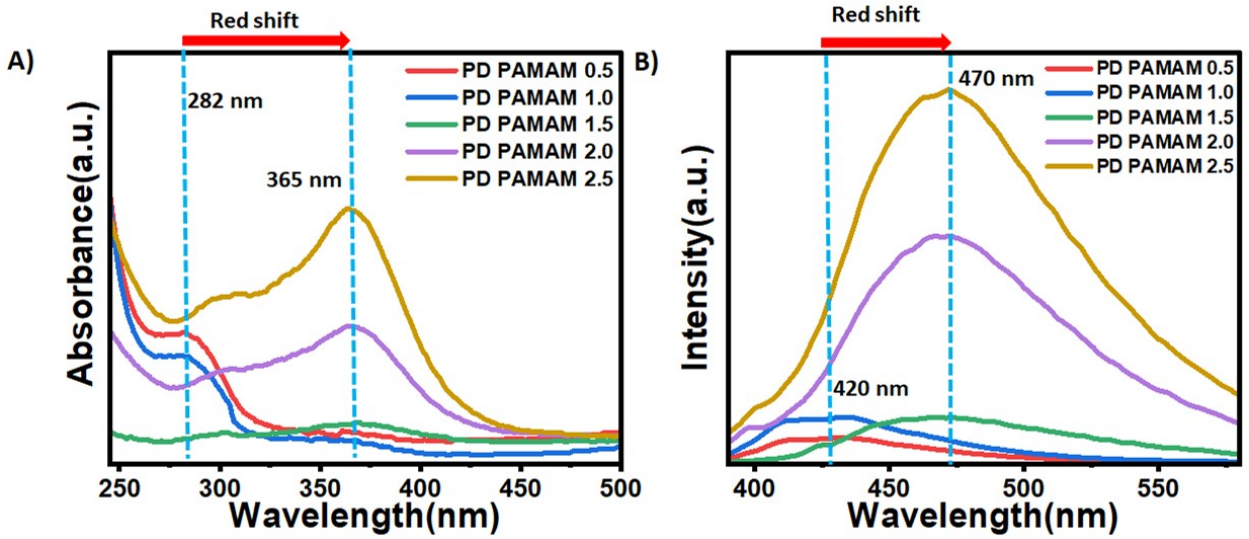


Figure S7: A) UV-VIS absorption spectra of PD PAMAM 0.5, PD PAMAM 1.0, PD PAMAM 1.5, PD PAMAM 2.0, PD PAMAM 2.5. B) Fluorescence emission spectra of, PD PAMAM 0.5, PD PAMAM 1.0, PD PAMAM 1.5, PD PAMAM 2.0, PD PAMAM 2.5 with excitation at 350 nm.

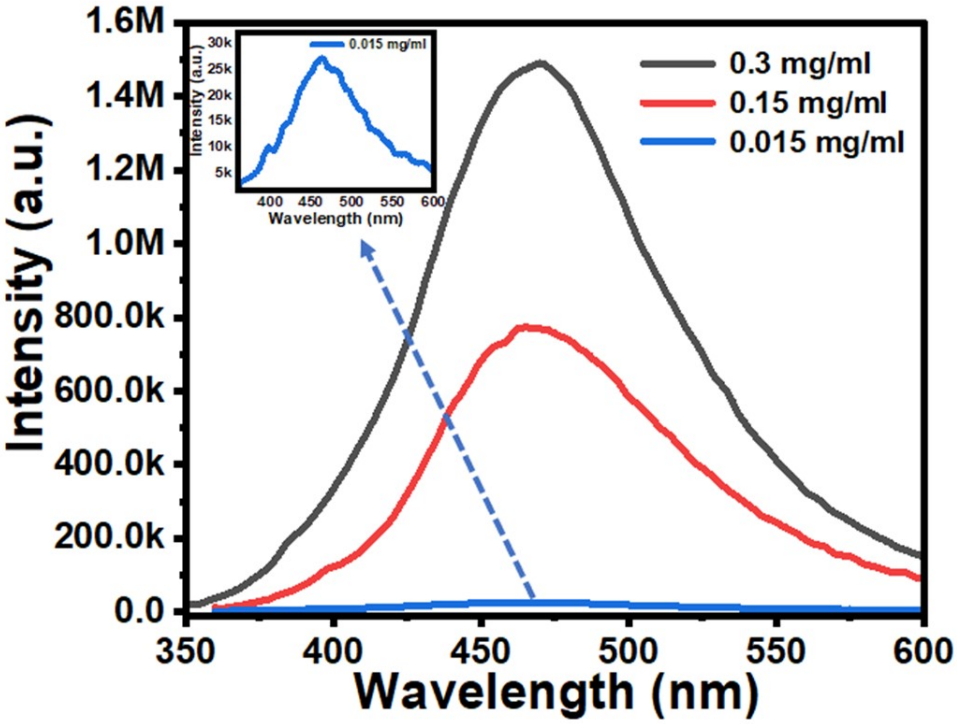


Figure S8: Concentration-dependent fluorescence emission spectra of PD PAMAM 2.5 at pH 7.

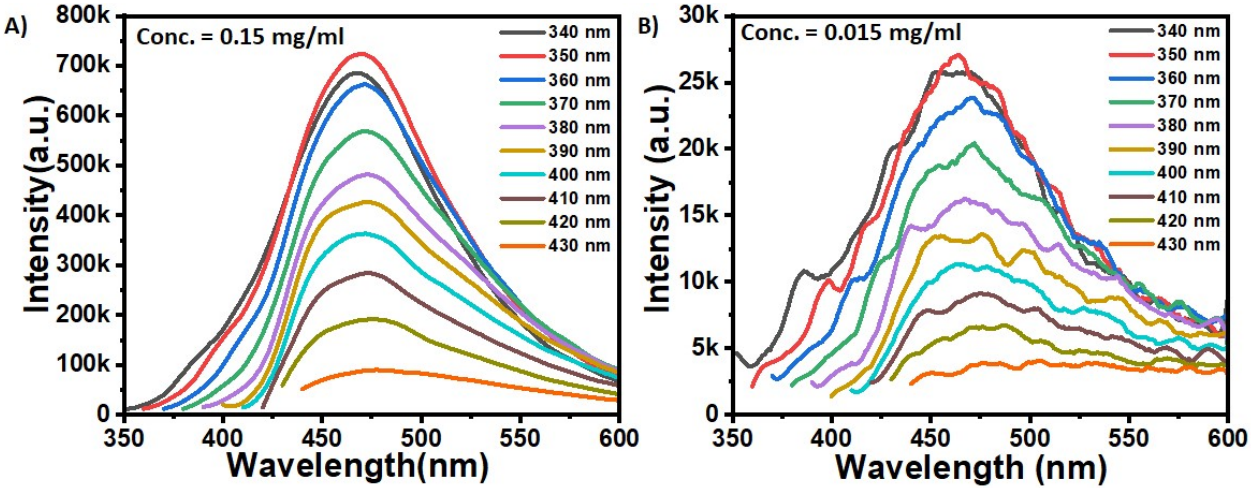


Figure S9: A) Fluorescent emission spectra of PD PAMAM 2.5 (0.15 mg/ml) with varying excitation wavelength from 340 nm to 430 nm at pH 7 and slit 1.5. B) Fluorescent emission spectra of PD PAMAM 2.5 (0.015 mg/ml) with varying excitation wavelength from 340 nm to 430 nm at pH 7 and slit 1.5.

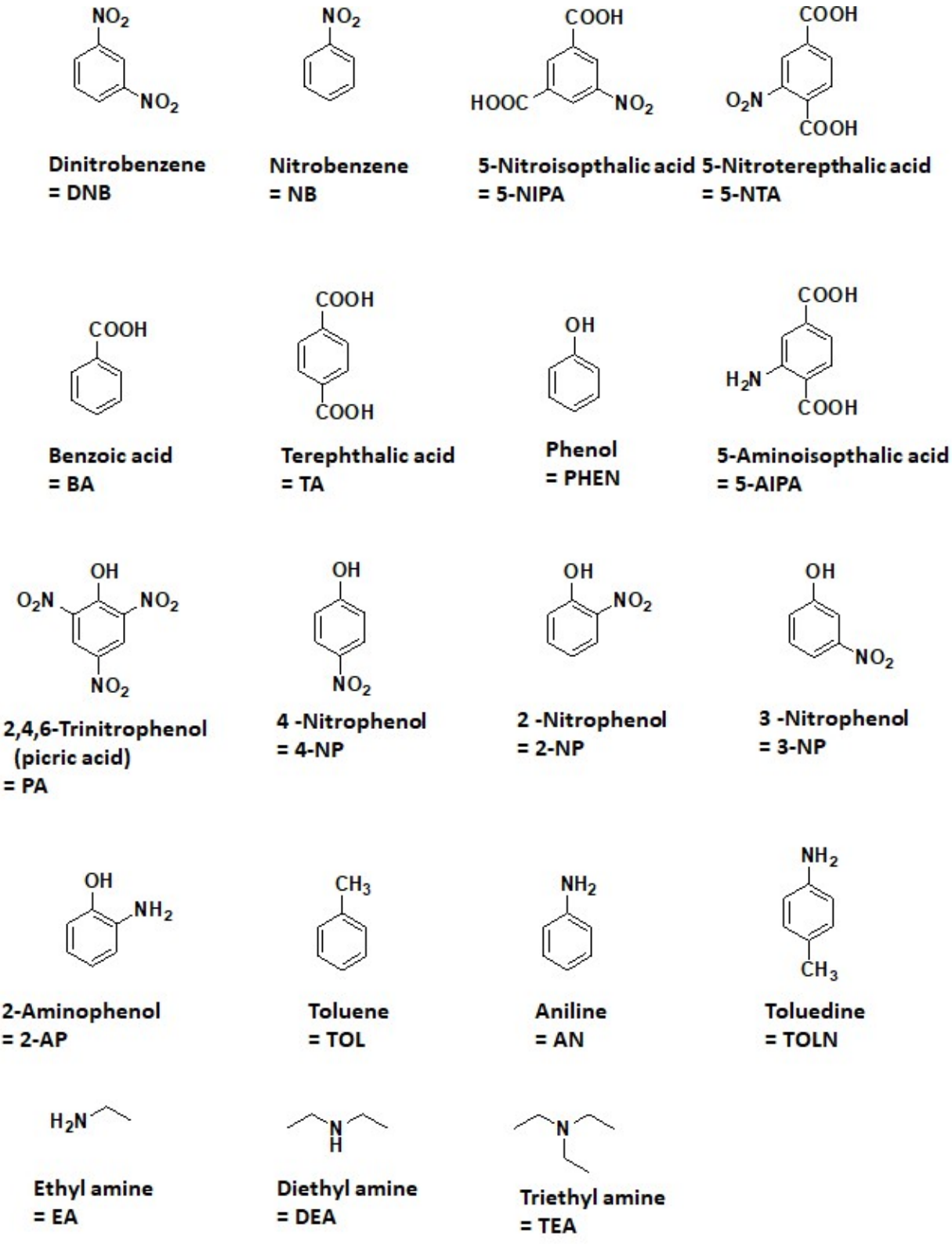
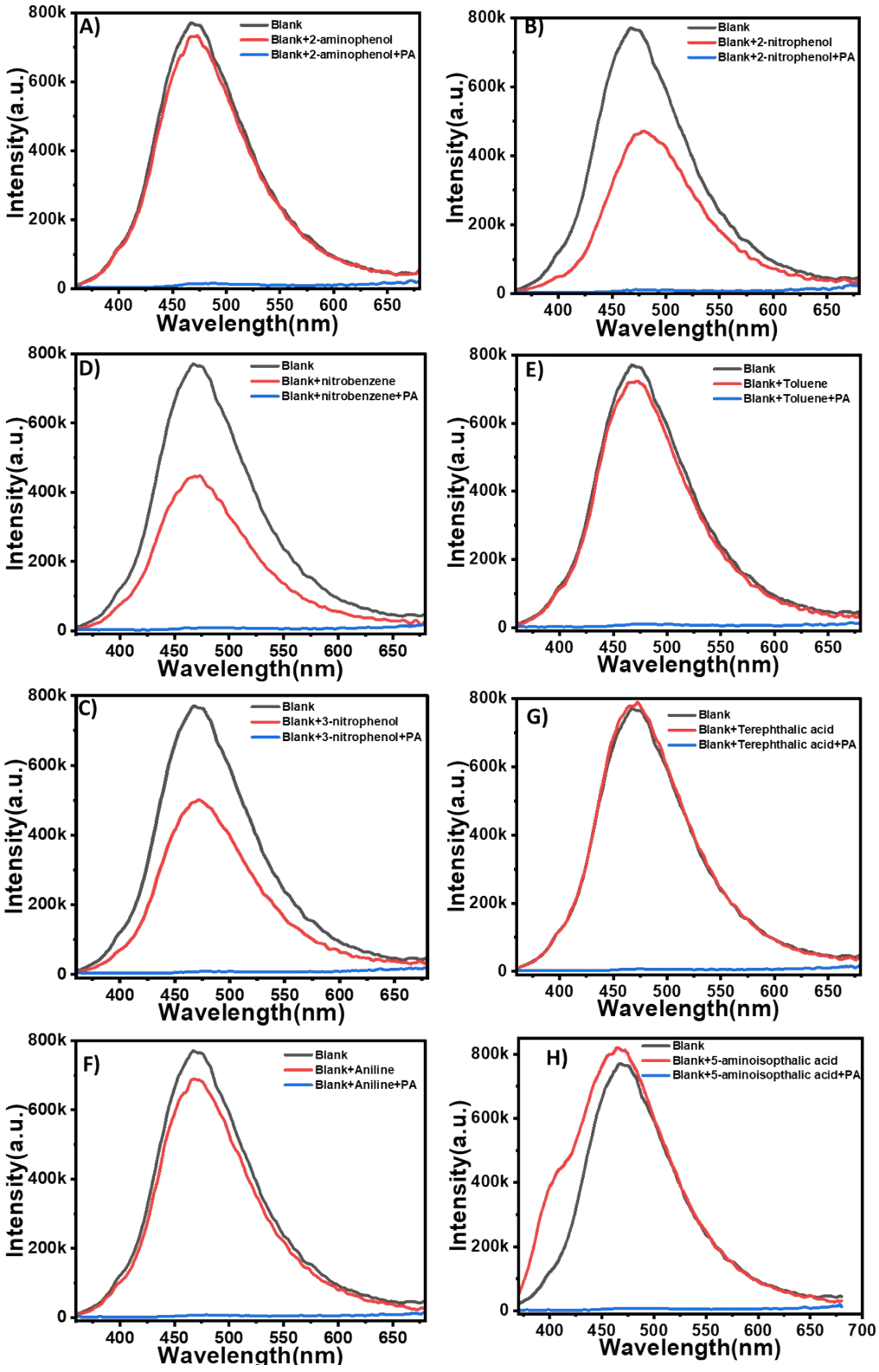
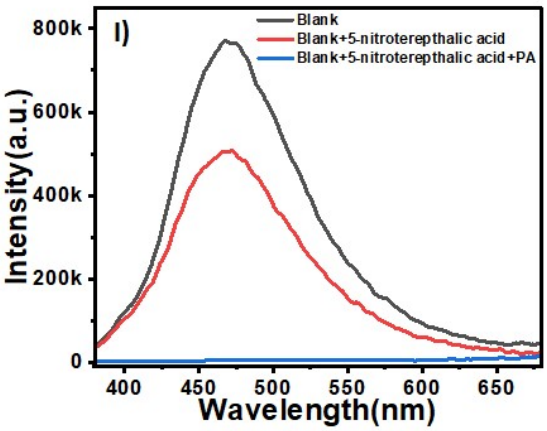
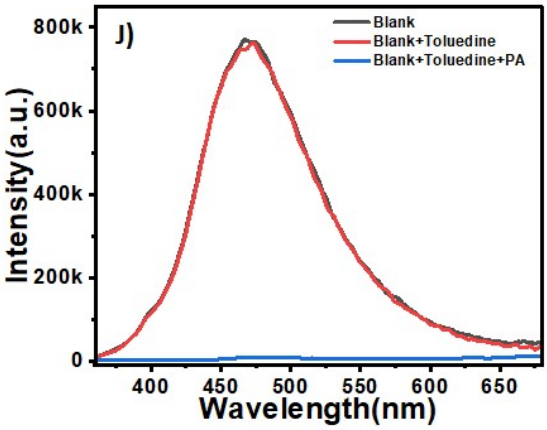
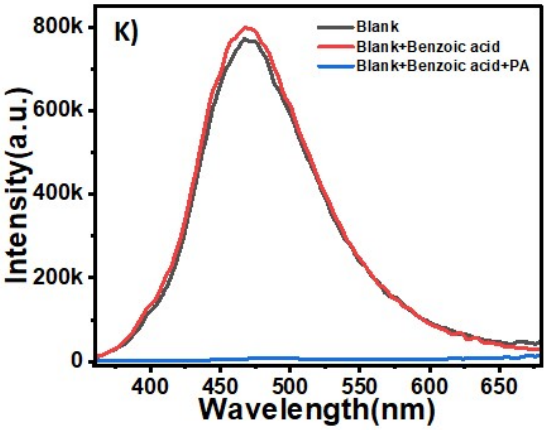


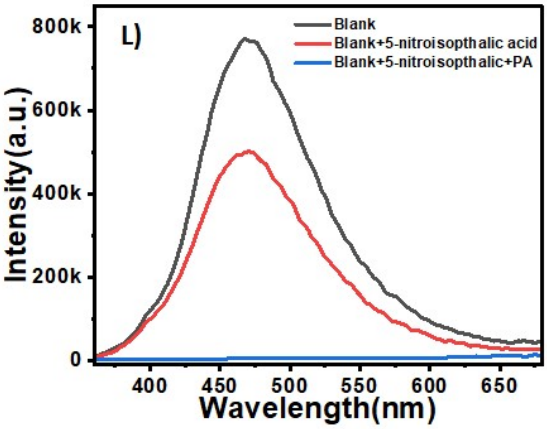
Figure S10: Structure of different organic analytes.

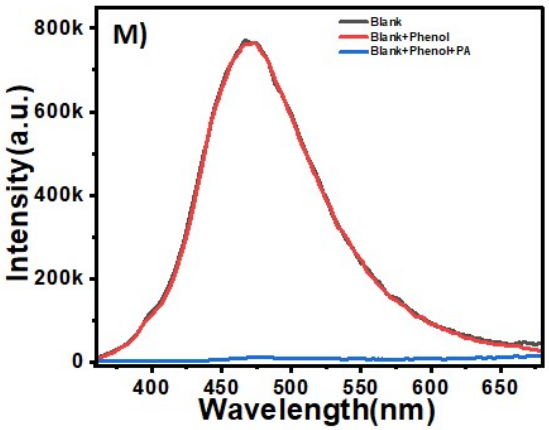

A)
Blank
Blank+2-aminophenol
Blank+2-aminophenol+PA
B)
Blank
Blank+2-nitrophenol
Blank+2-nitrophenol+PA
D)
Blank
Blank+nitrobenzene
Blank+nitrobenzene+PA
E)
Blank
Blank+Toluene
Blank+Toluene+PA
C)
Blank
Blank+3-nitrophenol
Blank+3-nitrophenol+PA
G)
Blank
Blank+Terephthalic acid
Blank+Terephthalic acid+PA
F)
Blank
Blank+Aniline
Blank+Aniline+PA
H)
Blank
Blank+5-aminoisopthalic acid
Blank+5-aminoisopthalic acid+PA
Intensity(a.u.)
Wavelength(nm)
0
200k
400k
600k
800k
400
450
500
550
600
650
700

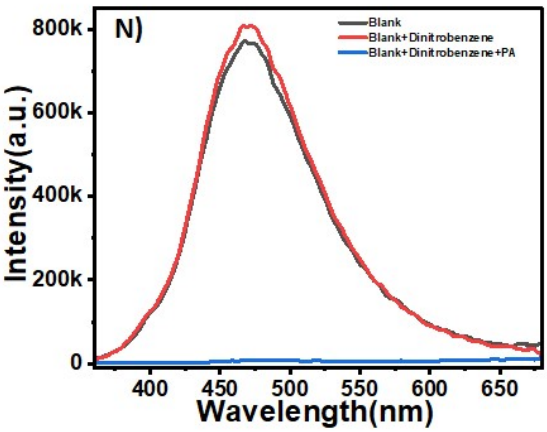

I)
Blank
Blank+5-nitroterepthalic acid
Blank+5-nitroterepthalic acid+PA
Intensity(a.u.)
Wavelength(nm)


J)
Blank
Blank+Toluedine
Blank+Toluedine+PA
Intensity(a.u.)
Wavelength(nm)


K)
Blank
Blank+Benzoic acid
Blank+Benzoic acid+PA
Intensity(a.u.)
Wavelength(nm)


L)
Blank
Blank+5-nitroisopthalic acid
Blank+5-nitroisopthalic+PA
Intensity(a.u.)
Wavelength(nm)


M)
Blank
Blank+Phenol
Blank+Phenol+PA
Intensity(a.u.)
Wavelength(nm)


N)
Blank
Blank+Dinitrobenzene
Blank+Dinitrobenzene+PA
Intensity(a.u.)
Wavelength(nm)

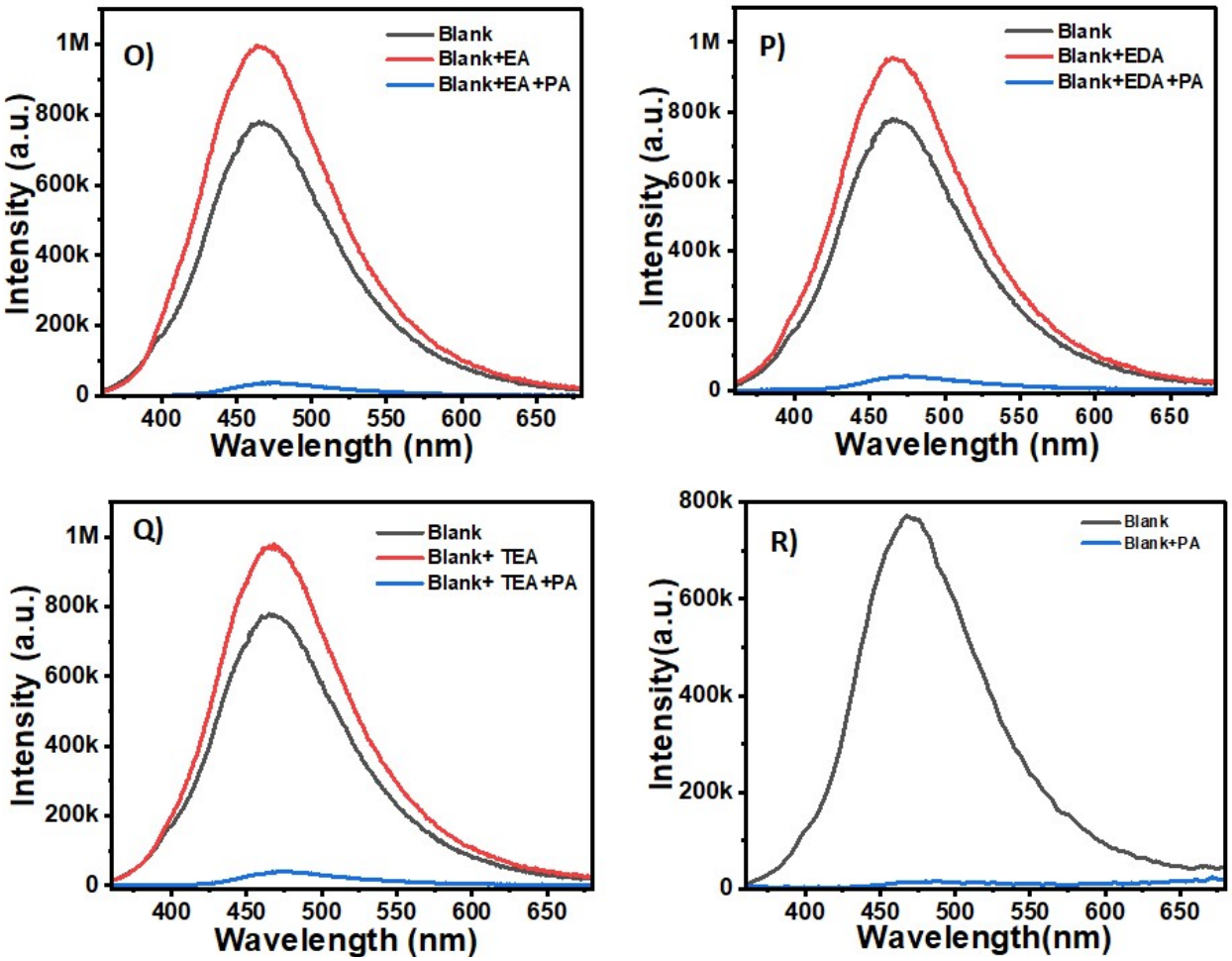


Figure S11: 2, 4, 6-trinitrophenol (PA) sensing by PD PAMAM 2.5 (0.15 mg/ml) in the presence of other interfering organic analyte (0.24 mM) A) 2-aminophenol, B) 2-nitrophenol, C) nitrobenzene, D) toluene, E) 3-nitrophenol, F) terepthalic acid, G) aniline, H) 5-aminoisopthalic acid, I) 5-nitroterepthalic acid J) toluedine, K) benzoic acid, L) 5-nitroisopthalic acid, M) phenol, N) dinitrobenzene, O) ethyl amine (EA), P) diethyl amine (EDA), Q) triethyl amine with excitation at 350 nm. R) In the absence of other interfering organic analyte 2, 4, 6-trinitrophenol (PA) sensing by PD PAMAM 2.5 (0.15 mg/ml) with excitation at 350 nm and slit 1.5.

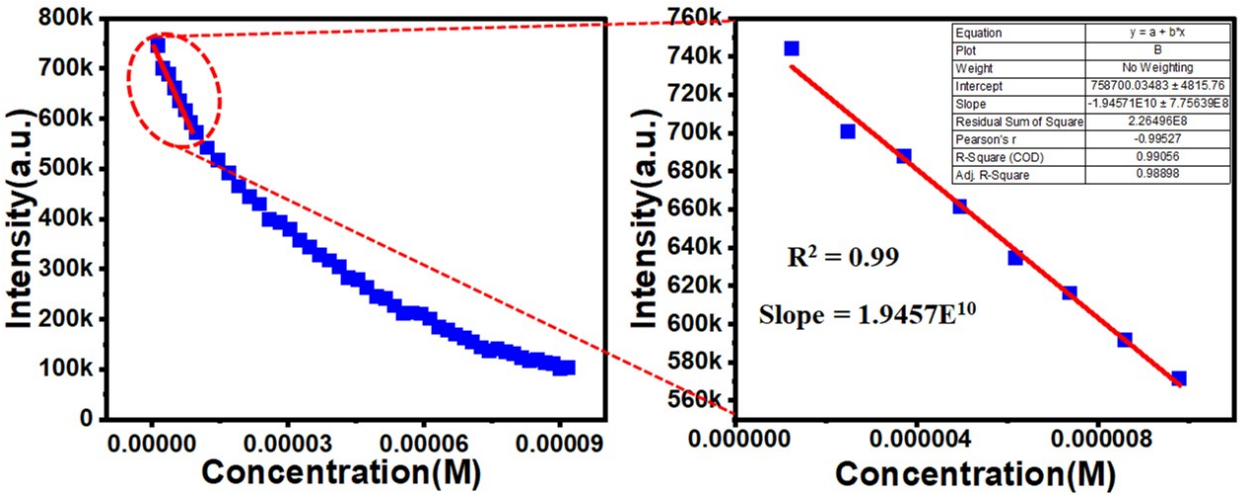


Figure S12: LOD plot for the detection of 2, 4, 6-trinitrophenol (PA) by PD PAMAM 2.5.

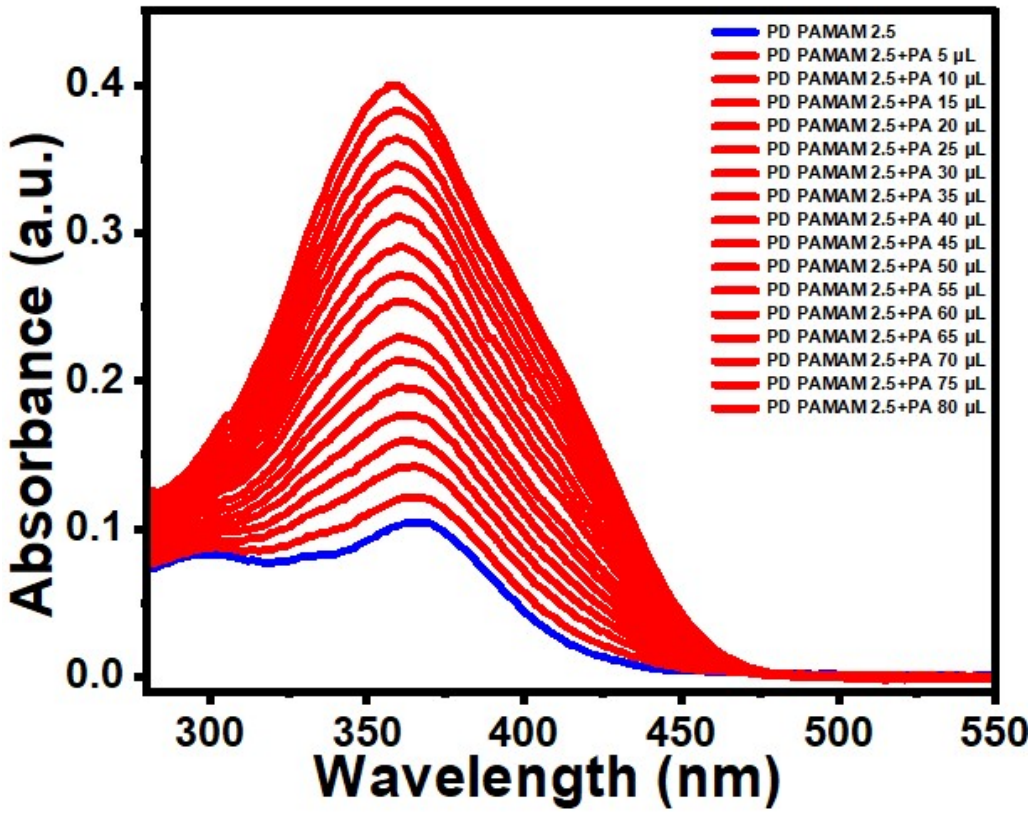


Figure S13: UV-VIS spectra of PD PAMAM 2.5 in the absence of PA (Blue line) and in the presence of PA (red line).[1] (Used for Benesi-Hildebrand plot)

Table S2: Comparison table for **PD PAMAM 2.5** with the other reported fluorophore for the detection of 2, 4, 6-trinitrophenol (PA).

S.L NO	Probe	Solvent	LOD	Quantum yield (ϕ_f)	Ksv (M^{-1})	λex (nm)	λem (nm)	Ref.
1.	Tetraphenylpyrazine-Based Manganese Metal−Organic Framework	water	0.2 μM	_____	1.18×10^5	340	410	[9]
2.	Yellow-Green Carbon Dot	water	2 μM	13.2%	2.31×10^4	427	536	[10]
3.	Multifunctional carbon dot	Britton–Robinson (BR) buffer solution	4.4 nM	25.0%	5.47×10^3	365	420	[11]
4.	Carbon Dot	water	0.75 μM	23.6%	2.6×10^4	365	426	[12]
5.	Molybdenum Disulfide Quantum Dot	water	95 nM	23.6%	4.3×10^4	365	400-480	[13]
6.	Boron Nitride Quantum Dot	water	0.14 μM	2.6%	2.017×10^4	305	395	[14]
7.	Covalent-organic polymers	methanol	4.63 nM	4.1%	2.6×10^5	365	456	[15]
8.	**Non-conjugated Zwitterionic polymer nano-dot**	**water**	**0.77 nM 0.00077 μM**	**28.0%**	**3.51×10^4**	**350**	**470**	**This work**

Table S3: Fluorescence decay parameter used for the detection of the weight average lifetime of PD PAMAM 2.5 in the absence and the presence of 2, 4, 6-trinitrophenol (PA).

Sample	a_1	a_2	a_3	t_1	t_2	t_3	χ^2	Average lifetime (ns)
PD PAMAM 2.5	6.17	35.76	58.07	0.4877	3.3251	7.3355	1.259	6.48
PD PAMAM 2.5+25µM PA	5.81	31.97	62.22	0.4423	3.0781	7.2197	1.121	6.44
PD PAMAM 2.5 +100µM PA	6.81	31.35	61.84	0.5058	3.1265	7.1571	1.177	6.38

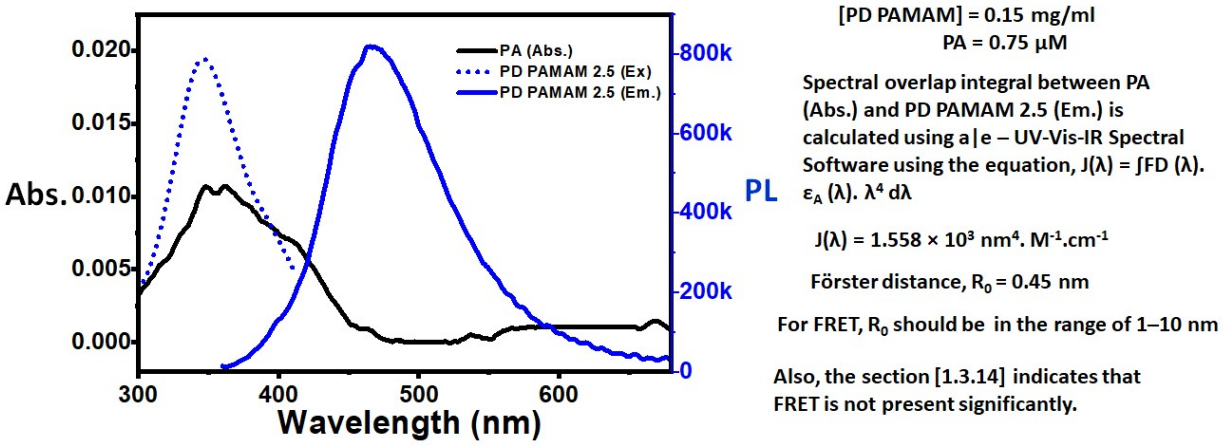


Figure S14: Absorption spectra of PA, and the fluorescence excitation/emission spectra of PD PAMAM 2.5 respectively. A significantly less J(λ) value and extremely low R_0 value, signifies no significant FRET, especially considering stochastic interaction between polymer dot and analyte in solution.

Table S4: IFE correction parameters for PD PAMAM 2.5 in the presence of PA. (calculated following a similar process as reported earlier[5,6])

Concentration of PA (μM)	A_{ex}	A_{em}	I_{obsd}	I_{corr}	I_{cor} / I_{obsd}	E_{obsd} (%)	E_{cor} (%)	Quenching by IFE (%) (E_{obsd} - E_{cor})
0	0.092	0.003	766647	851447.71	1.11	0	0	0
1.24	0.109	0.003	744278	842306.57	1.13	2.91	1.07	1.84
2.48	0.13	0.003	700555	811327.74	1.15	8.62	4.71	3.91
3.72	0.146	0.003	687671	810423.15	1.17	10.3	4.82	5.48
4.95	0.165	0.003	661287	795527.89	1.20	13.74	6.57	7.17
6.17	0.182	0.003	634293	777125.01	1.22	17.26	8.73	8.53
7.38	0.201	0.004	616080	771067.09	1.25	19.64	9.44	10.2
8.59	0.217	0.005	591491	753726.88	1.27	22.85	11.48	11.37
9.8	0.241	0.005	571412	746733.27	1.30	25.47	12.3	13.17
12.19	0.276	0.005	541342	733604.57	1.35	29.39	13.84	15.55
14.5	0.315	0.006	516307	728876.44	1.41	32.65	14.39	18.26
16.9	0.349	0.007	491193	718295.17	1.46	35.93	15.64	20.29
19.2	0.385	0.009	464344	705155.95	1.51	39.43	17.18	22.25

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