Detection of nitroaromatic explosives using π- electron rich luminescent polymeric nanocomposites

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Supplementary Information:

Structures

The structures of the nitroaromatic compounds used in this study are given in Chart 1.

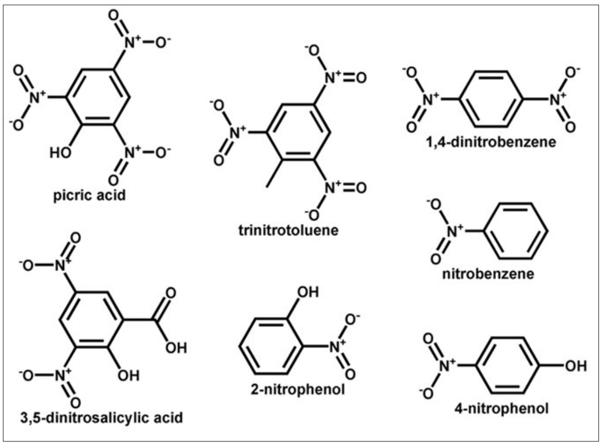


Chart 1: Structures of the nitroaromatic compounds used.

FT-IR spectrum

The FT-IR spectra of the polymers are provided in Fig. S1.

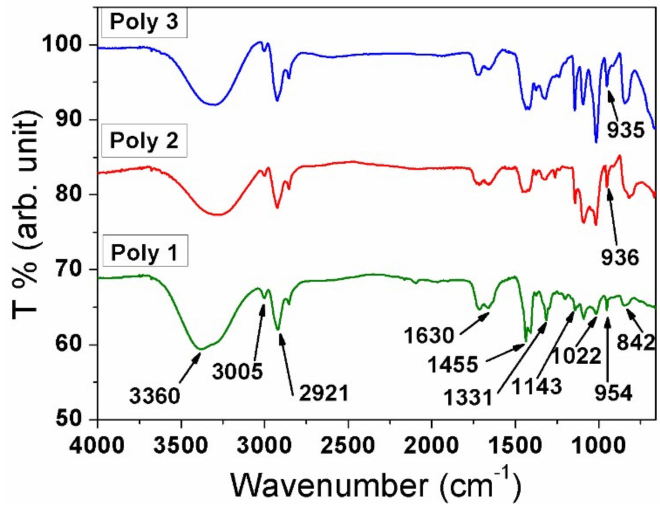


Fig. S1 *FT-IR spectrum of the polymers*

[1]H-NMR spectrum

The [1]H-NMR spectra of the parent polymer, Poly 1, is given in Fig. S2.

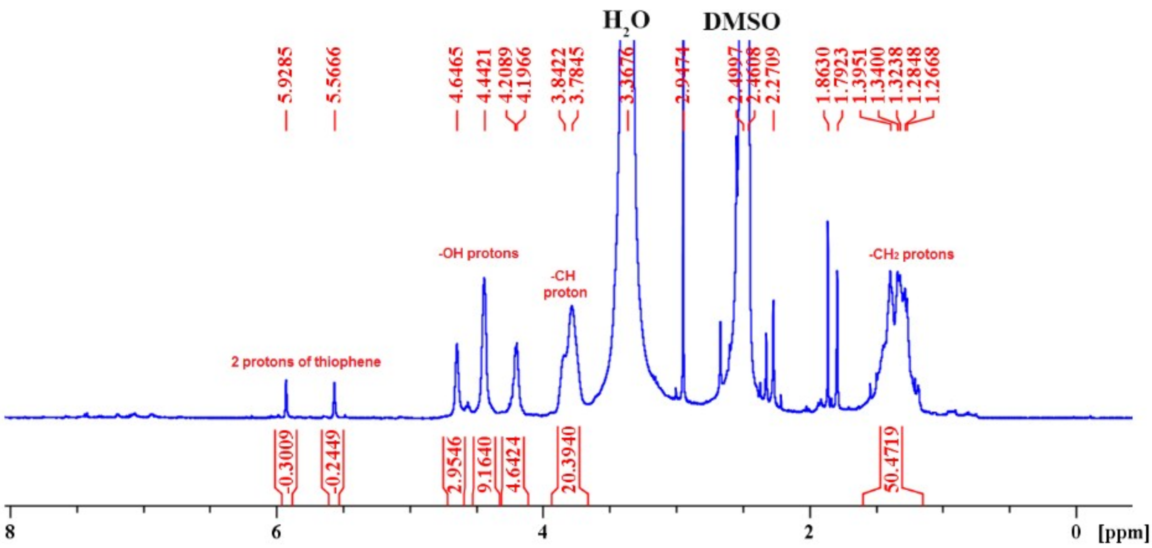
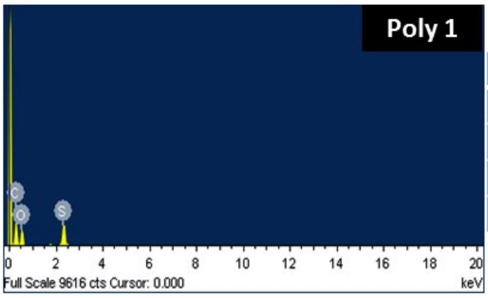


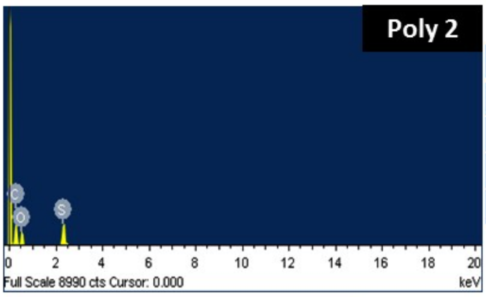
Fig. S2 *[1]H NMR spectrum of PVA-g-polythiophene*

SEM-EDX

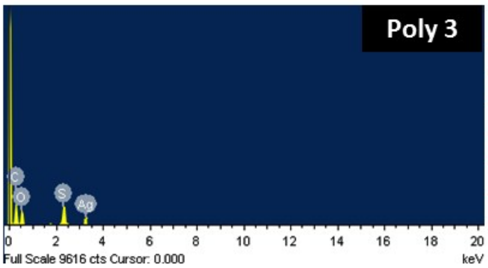
EDX measurements were carried out with the help of Carl Zeiss Σigma VP using EHT 20kV. The elemental composition of all the polymers are also given in Fig. S3.



Element	Weight %	Atomic %
C	58.44	67.54
O	33.28	28.87
S	8.28	3.59
Total	100	100



Element	Weight %	Atomic %
C	61.32	69.45
O	31.41	27.81
S	7.27	2.74
Total	100	100



Element	Weight %	Atomic %
C	54.05	63.60
O	34.79	31.87
S	7.56	3.35
Ag	3.6	1.18
Total	100	100

***Fig. S3** EDX spectra of the polymers*

AFM study

The 2D and 3D AFM pictures of the polymers are given in Fig. S4.

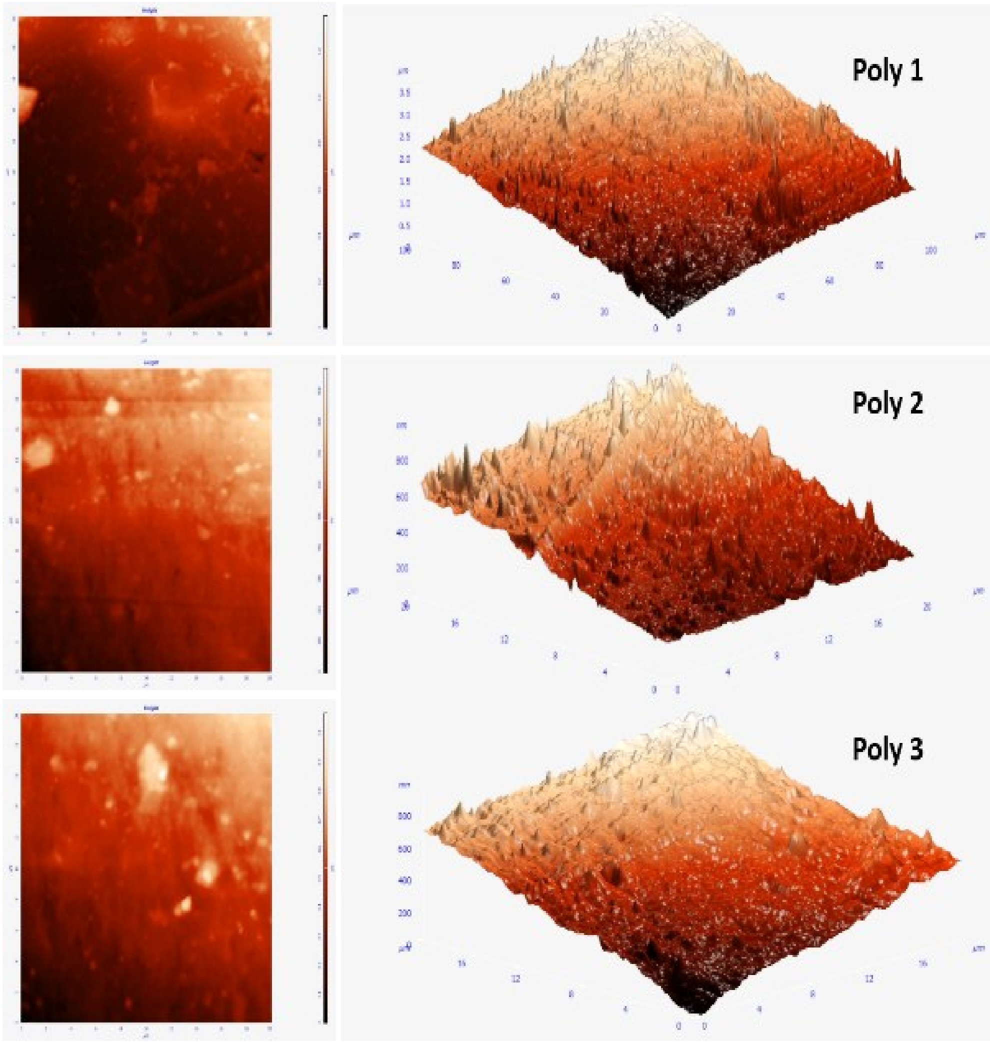


Fig. S4 *2D and 3D AFM images of the polymers*

UV-Vis study

The UV-Vis spectra of the dispersed nanoparticles in ethanol were checked and compared with their respective nanocomposites as shown in Fig. S5.

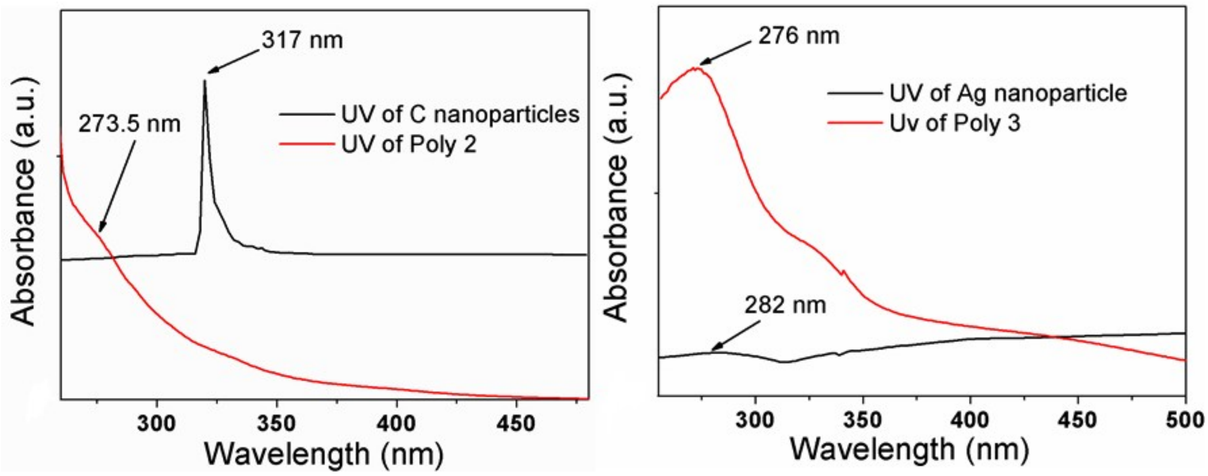


Fig. S5 *UV-vis spectrum of the nanoparticles and the nanocomposites*

Particle size

Particle size of the dispersed carbon and silver nanoparticles in ethanol were carried out in the glass cuvette with square aperture. The particle size of the nanoparticles taken with the help of a Malvern Nano ZS90 are provided in Fig. S6. From the DLS experiments, it was observed that the particle size of the carbon and silver nanoparticles are C = 42 nm and Ag = 50 nm.

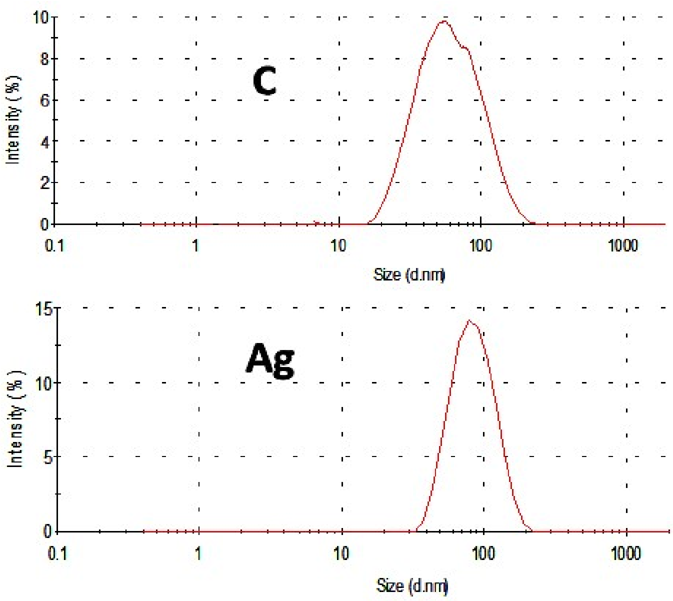
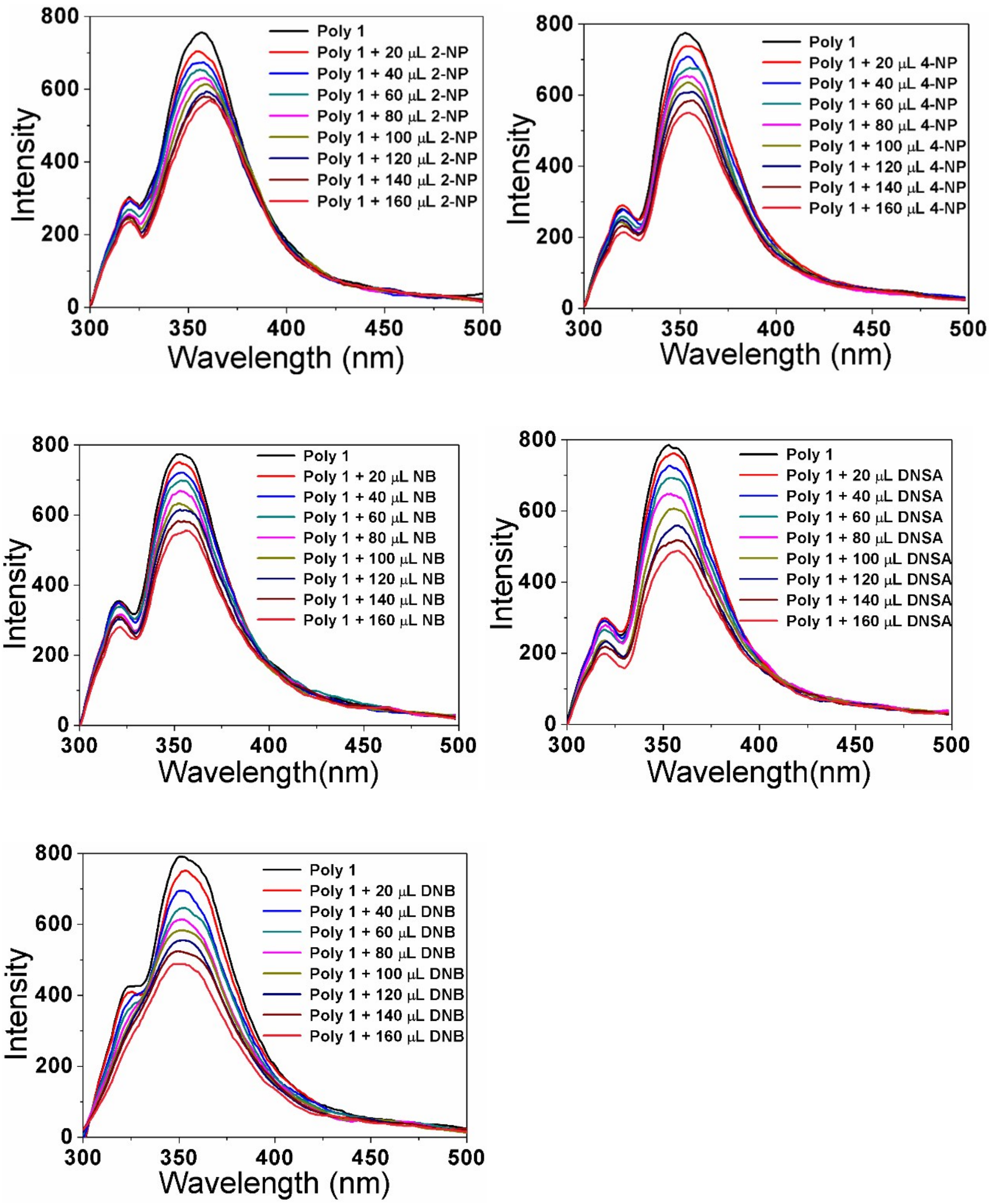
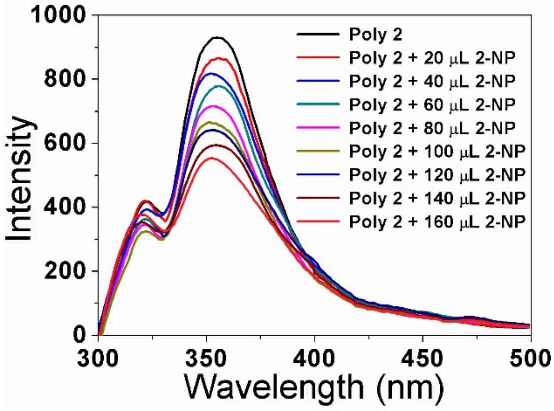


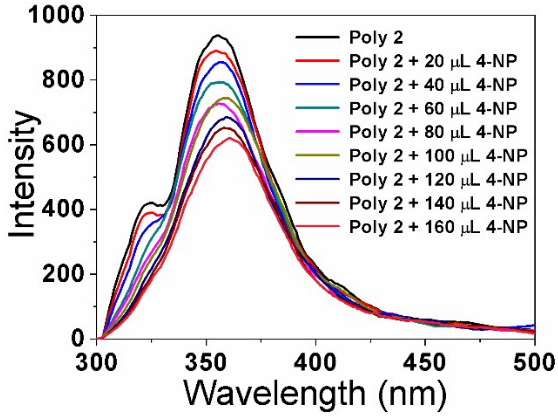
Fig. S6 *Particle size of carbon and silver nanopowders*

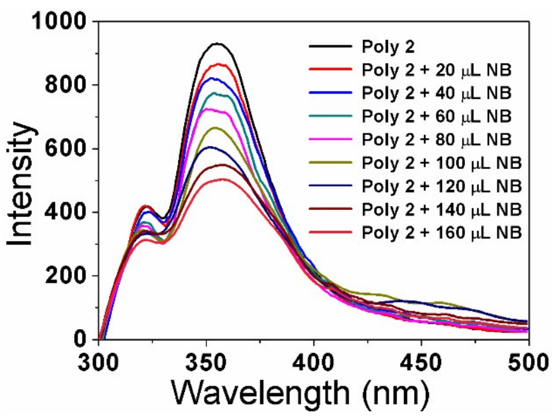
PL plots

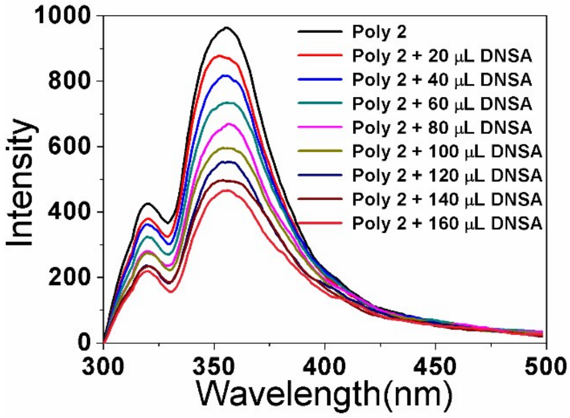
The fluorescence quenching studies of the polymers in presence of 1,4-dinitrobenzene (DNB), nitrobenzene (NB), 3,5-dinitrosalicylic acid (DNSA), 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) is shown in Fig. S7.

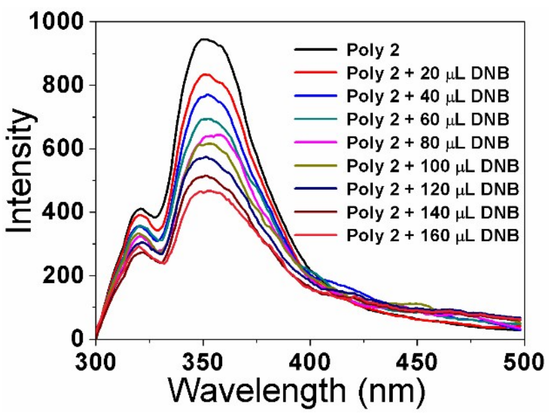


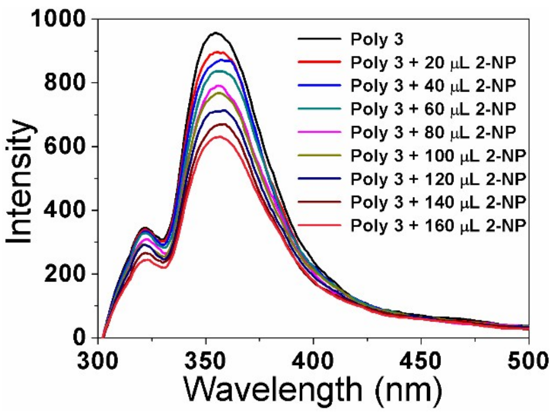

Poly 2
Poly 2 + 20 μL 2-NP
Poly 2 + 40 μL 2-NP
Poly 2 + 60 μL 2-NP
Poly 2 + 80 μL 2-NP
Poly 2 + 100 μL 2-NP
Poly 2 + 120 μL 2-NP
Poly 2 + 140 μL 2-NP
Poly 2 + 160 μL 2-NP
Intensity
Wavelength (nm)

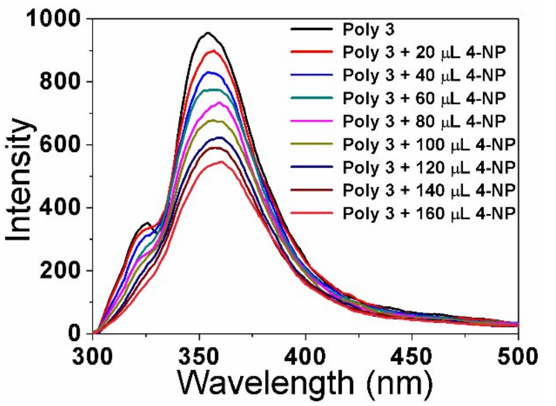

Poly 2
Poly 2 + 20 μL 4-NP
Poly 2 + 40 μL 4-NP
Poly 2 + 60 μL 4-NP
Poly 2 + 80 μL 4-NP
Poly 2 + 100 μL 4-NP
Poly 2 + 120 μL 4-NP
Poly 2 + 140 μL 4-NP
Poly 2 + 160 μL 4-NP
Intensity
Wavelength (nm)


Poly 2
Poly 2 + 20 μL NB
Poly 2 + 40 μL NB
Poly 2 + 60 μL NB
Poly 2 + 80 μL NB
Poly 2 + 100 μL NB
Poly 2 + 120 μL NB
Poly 2 + 140 μL NB
Poly 2 + 160 μL NB
Intensity
Wavelength (nm)


Poly 2
Poly 2 + 20 μL DNSA
Poly 2 + 40 μL DNSA
Poly 2 + 60 μL DNSA
Poly 2 + 80 μL DNSA
Poly 2 + 100 μL DNSA
Poly 2 + 120 μL DNSA
Poly 2 + 140 μL DNSA
Poly 2 + 160 μL DNSA
Intensity
Wavelength(nm)


Poly 2
Poly 2 + 20 μL DNB
Poly 2 + 40 μL DNB
Poly 2 + 60 μL DNB
Poly 2 + 80 μL DNB
Poly 2 + 100 μL DNB
Poly 2 + 120 μL DNB
Poly 2 + 140 μL DNB
Poly 2 + 160 μL DNB
Intensity
Wavelength (nm)


Poly 3
Poly 3 + 20 μL 2-NP
Poly 3 + 40 μL 2-NP
Poly 3 + 60 μL 2-NP
Poly 3 + 80 μL 2-NP
Poly 3 + 100 μL 2-NP
Poly 3 + 120 μL 2-NP
Poly 3 + 140 μL 2-NP
Poly 3 + 160 μL 2-NP
Intensity
Wavelength (nm)


Poly 3
Poly 3 + 20 μL 4-NP
Poly 3 + 40 μL 4-NP
Poly 3 + 60 μL 4-NP
Poly 3 + 80 μL 4-NP
Poly 3 + 100 μL 4-NP
Poly 3 + 120 μL 4-NP
Poly 3 + 140 μL 4-NP
Poly 3 + 160 μL 4-NP
Intensity
Wavelength (nm)

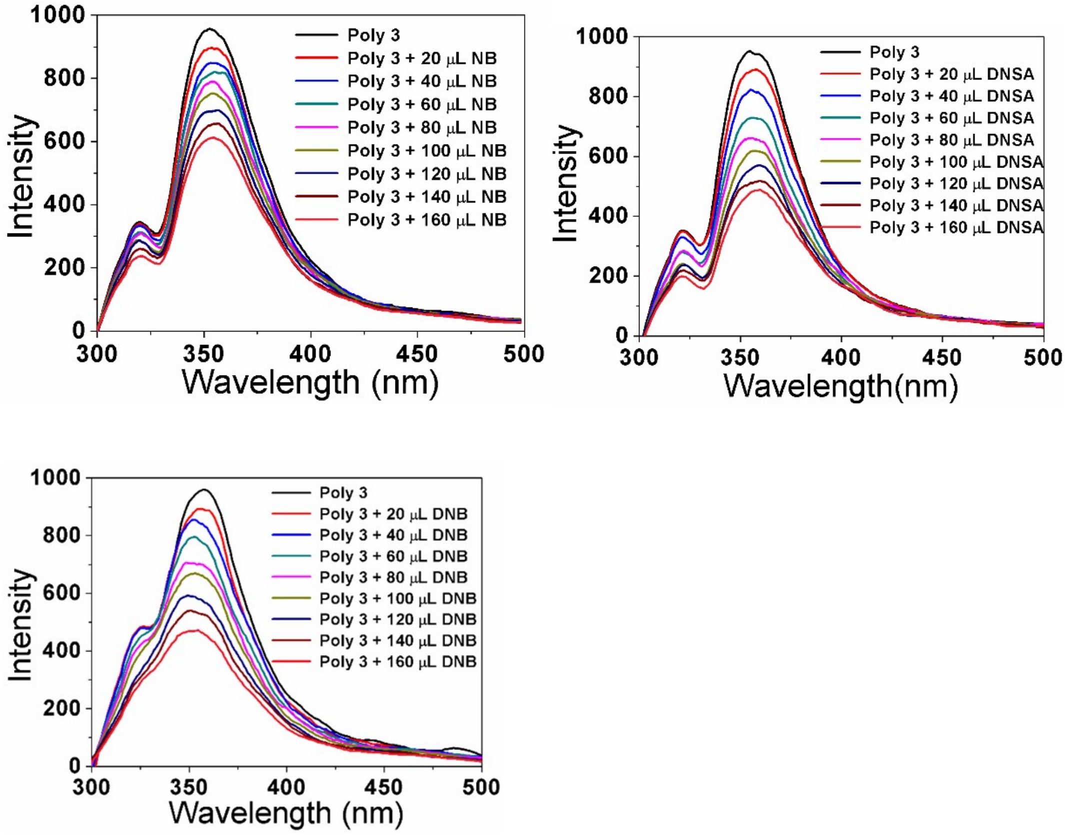


Fig. S7 *PL spectra of the polymers in presence of other nitroaromatic compounds.*

Interference study

The interference of some common organic solvents (DMSO, ethanol, acetone), compounds with electron withdrawing groups (chloroform, iso-propanol, acrylonitrile, benzoic acid) nitroaromatic compounds (nitrobenzene and nitrophenols) and other organic analytes in the PL quenching of the polymers with PA and TNT was monitored. The results as shown in Fig. S8 A and B clearly shows that the interference of all these compounds in the PL quenching studies is negligible.

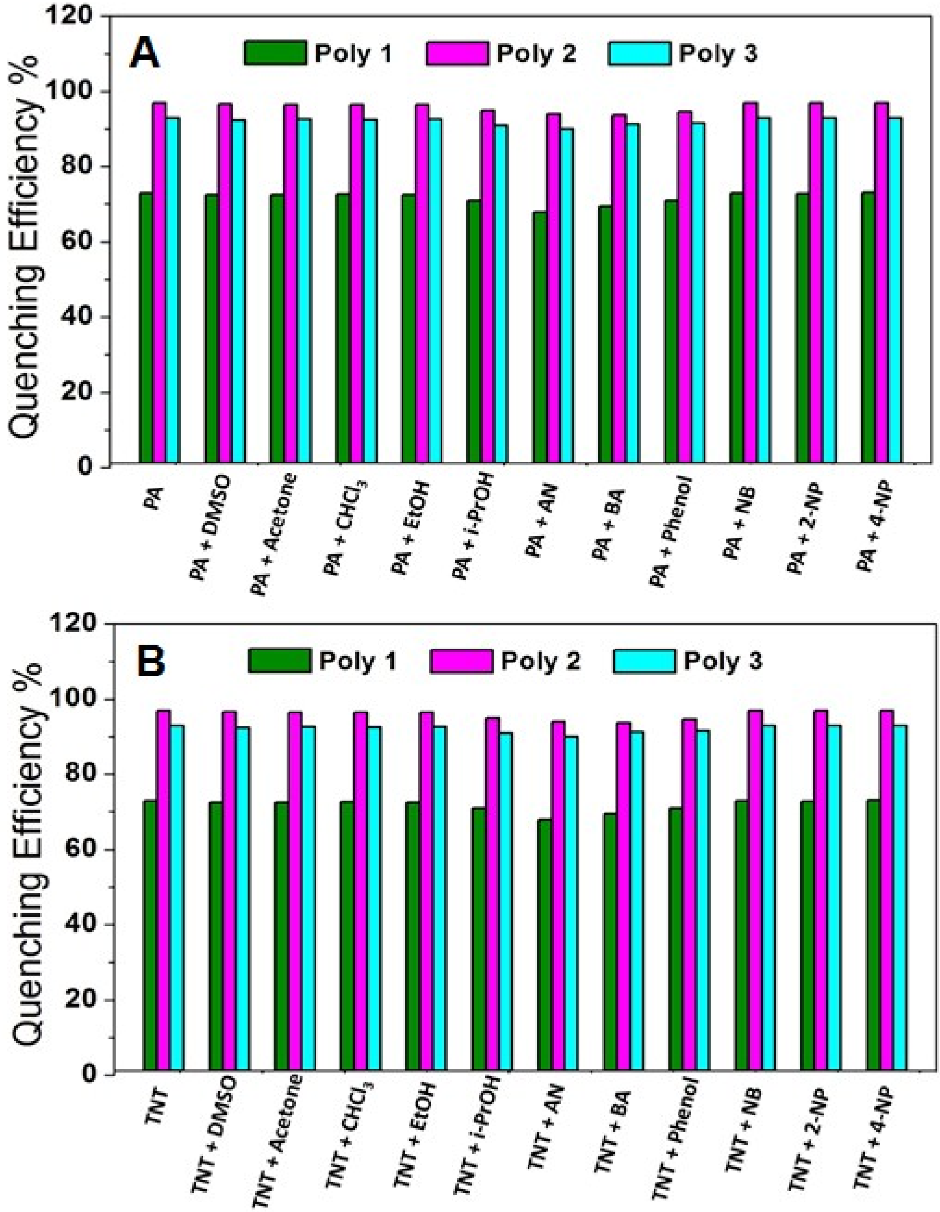


Fig. S8 *Interference study of the polymers in presence of (A) PA and (B) TNT.*

Fig. S9 shows the PL quenching rates of the polymers in presence of different analytes. For Poly 2 and Poly 3, the PL quenching rates are significantly faster for PA and TNT compared to other nitroaromatics.

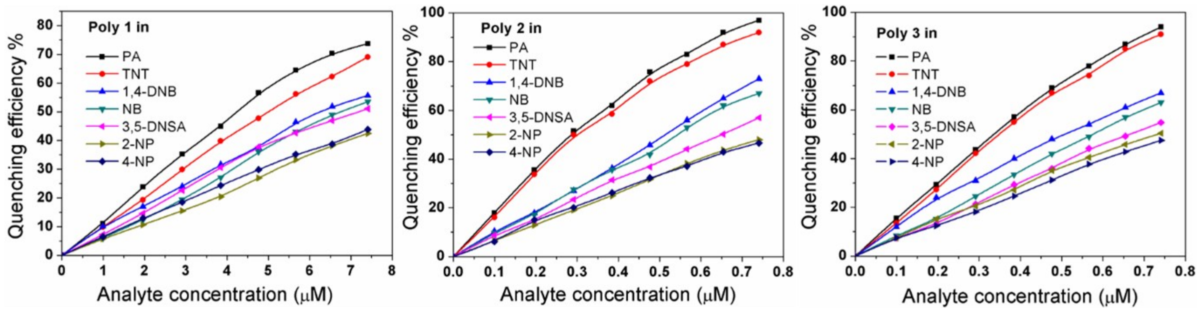


Fig. S9 *Quenching efficiency vs analyte concentration.*

TRPL study:

The time-resolved photoluminescence quenching of the polymers in presence of PA and TNT are given in Fig. S10.

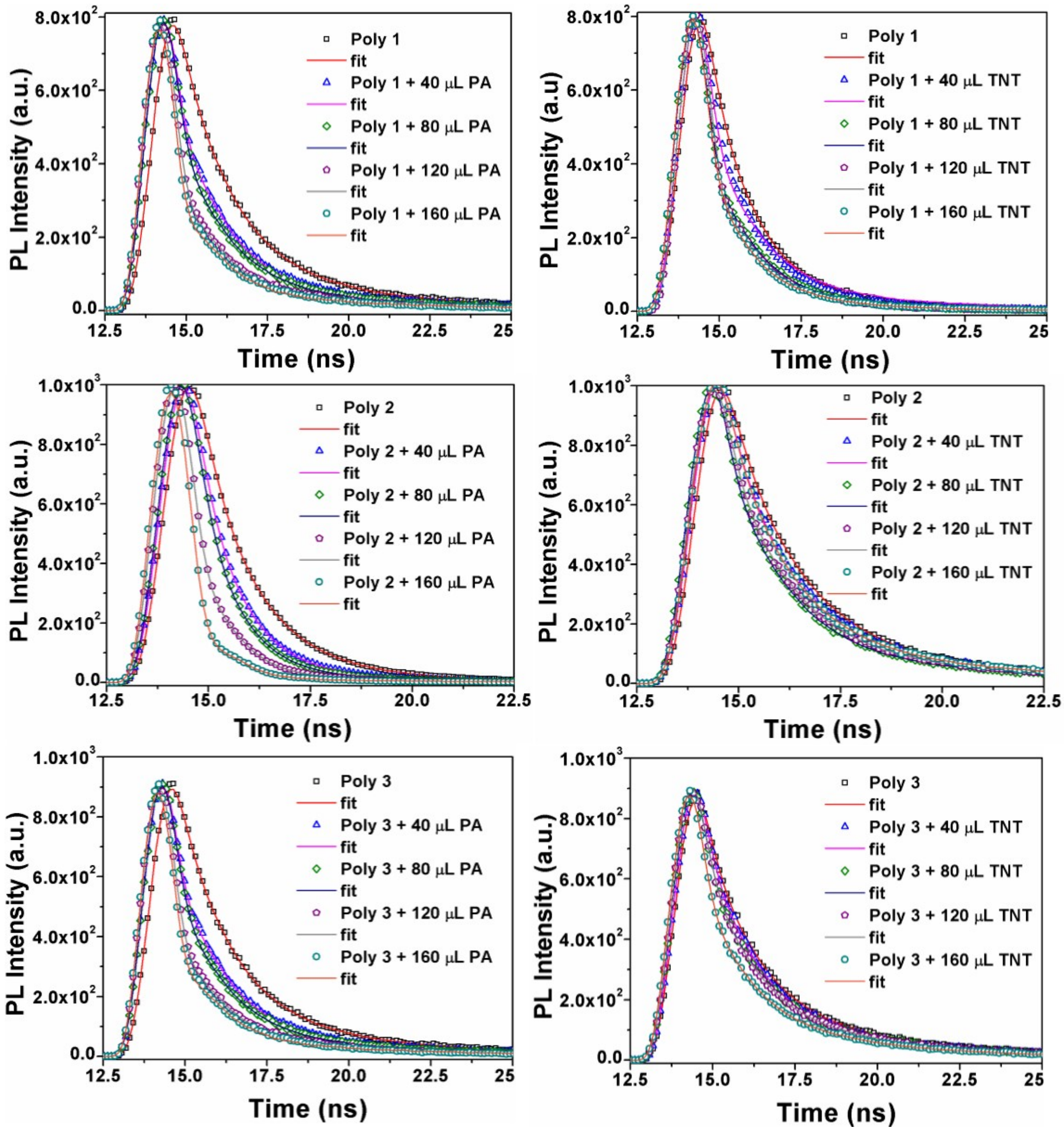


Fig S10 *Time resolved fluorescence plots of the polymers in presence of PA and TNT.*

Cyclic Voltammetry plots

CV plots of the polymers and that of the polymers in presence of PA are shown in Fig. S11.

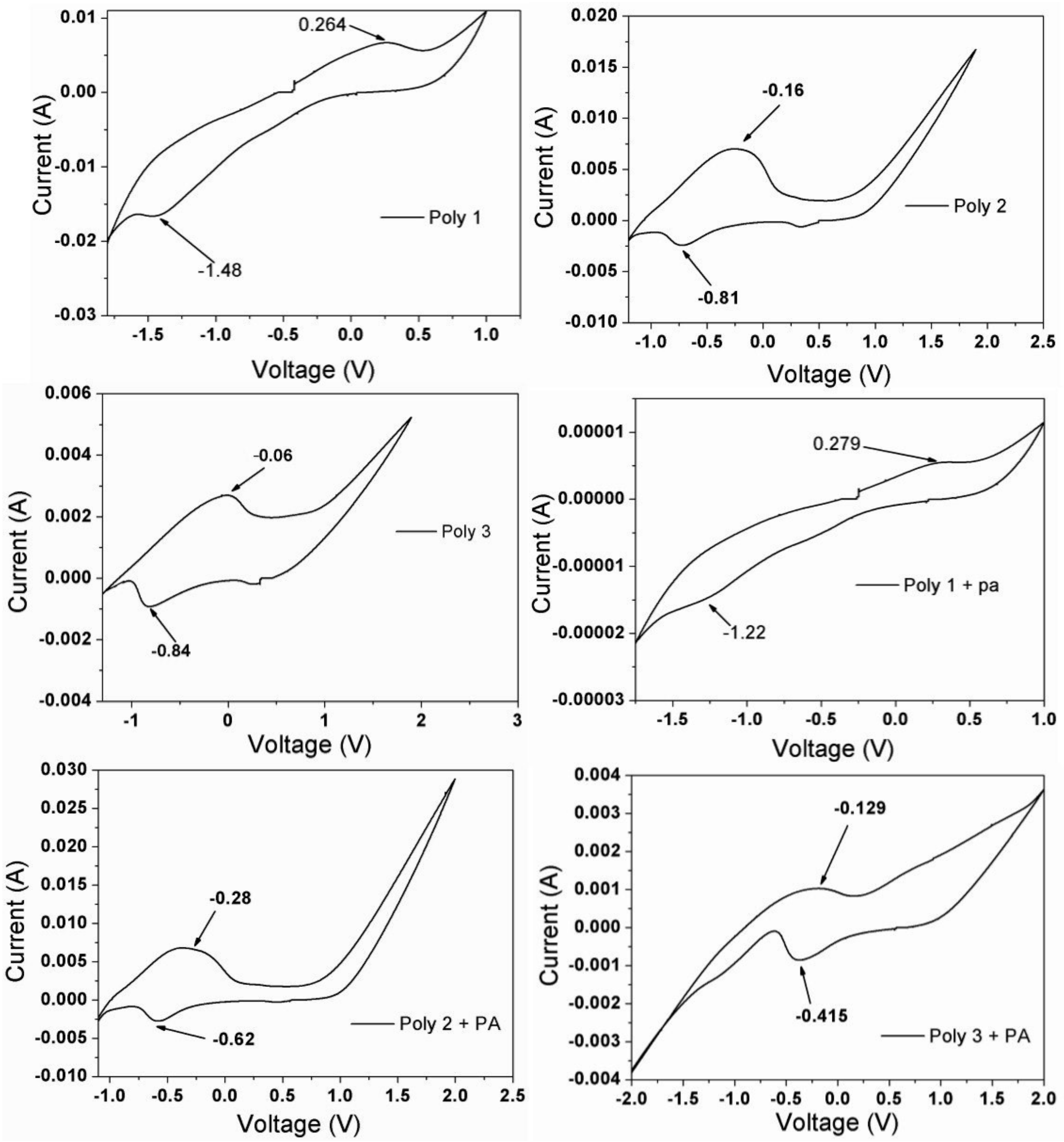


Fig S11 *CV plots of the polymers in absence and in presence of PA*

Zeta Potential plots

Zeta potential plots of the polymers in absence and in presence of PA are given in Fig. S12 below.

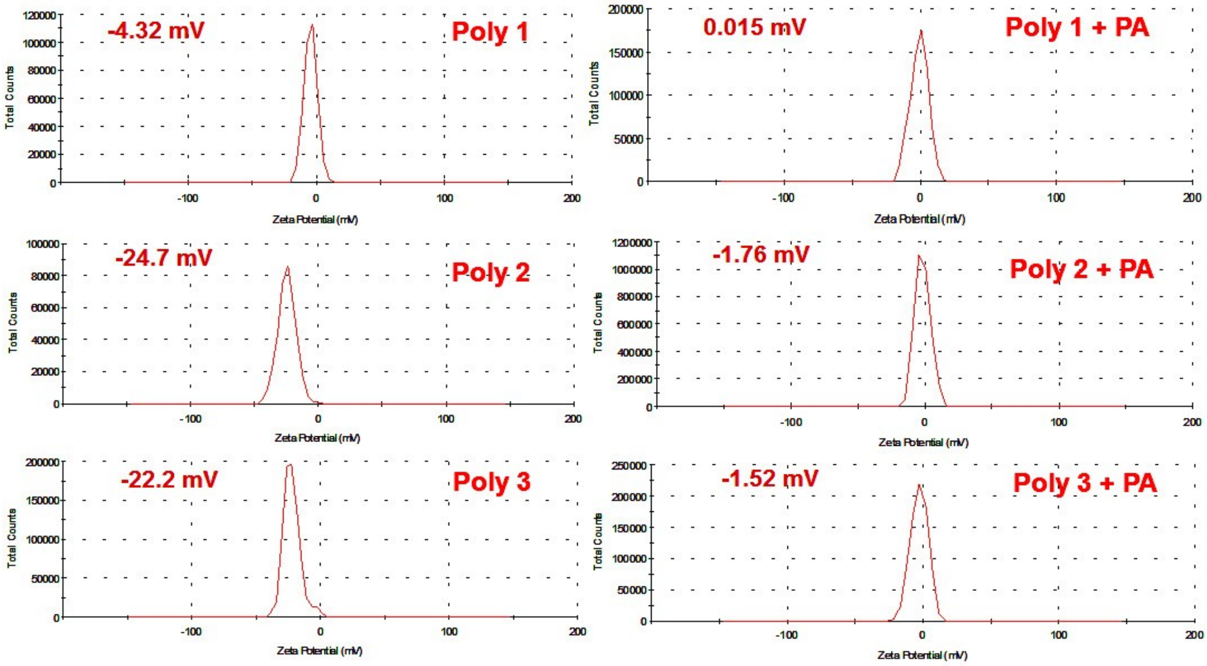


Fig S12 *Zeta potential plots of the polymers in absence and in presence of PA*

Comparative analysis of our work with earlier reported works

Table S1: Comparative values of LODs of Poly 2 and Poly 3 with previous reported sensors:

Sl. no.	Sensor systems	LOD for PA	LOD for TNT	Ref.
1.	Cationic bispyrene fluorophore, Py-dilM-Py	1×10^{-6} M	-	2
2.	Eu(III) based metal organic frameworks	1×10^{-7} M	-	3
3.	Self-assembled pentacenequinone derivative	3.5×10^{-7} M	-	4
4.	Conjugated polymer grafted silica nanoparticles	-	1×10^{-6} M	5
5.	Fluorescent labelled molecularly imprinted polymer (MIP)	-	4×10^{-7} M	6
6.	Sodium dodecyl sulfate (SDS)	1 µM	-	7
7.	Functionalized reduced graphene oxide	125 ppb	-	8
8.	DNSA-SQ	70 nM	-	9
9.	N- rich carbon nanodots	-	1 nM	10

10.	BSA Au nanoclusters	-	10 nM	11
11.	Isobenzotriazolophanes	19 ppm	-	12
12.	Tripyrenyltruxene	0.15 ppm	-	13
13.	Phosphole Oxide	2.03 mM	-	14
14.	**PVA-g-PTh-C nanocomposite**	**4.6 nM**	**5.8 nM**	**(Our system)**
15.	**PVA-g-PTh-Ag nanocomposite**	**6.5 nM**	**7.35 nM**	**(Our system)**

Table S2: t-test results of the polymers with PA

A. For Poly 1 with 5 µM PA

Independent t-test on col (B) and col (C)

Data	N	Mean	Standard Deviation
B	199	145.36	106.67
C	199	145.37	106.67

t = 0.109 and p = 0.913

At the 0.05 level, the two means are NOT significantly different.

Independent t-test on col (C) and col (D)

Data	N	Mean	Standard Deviation
C	199	145.37	106.67
D	199	145.36	106.68

t = 0.429 and p = 0.668

At the 0.05 level, the two means are NOT significantly different.

Independent t-test on col (B) and col (D)

Data	N	Mean	Standard Deviation
B	199	145.37	106.67
C	199	145.38	106.68

t = 0.59 and p = 0.56

At the 0.05 level, the two means are NOT significantly different.

B. For Poly 2 with 0.5 µM PA

Independent t-test on col (B) and col (C)

Data	N	Mean	Standard Deviation
B	199	91.57	66.46
C	199	91.56	66.46

t = 0.162 and p = 0.87

At the 0.05 level, the two means are NOT significantly different.

Independent t-test on col (C) and col (D)

Data	N	Mean	Standard Deviation
C	199	91.57	66.45
D	199	91.56	66.46

t = 0.147 and p = 0.88

At the 0.05 level, the two means are NOT significantly different.

Independent t-test on col (B) and col (D)

Data	N	Mean	Standard Deviation
B	199	91.57	66.46
C	199	91.56	66.45

t = 0.38 and p = 0.71

At the 0.05 level, the two means are NOT significantly different.

C. For Poly 3 with 0.5 µM PA

Independent t-test on col (B) and col (C)

Data	N	Mean	Standard Deviation
B	200	114.68	83.24
C	200	114.67	83.25

t = 0.34 and p = 0.73

At the 0.05 level, the two means are NOT significantly different.

Independent t-test on col (C) and col (D)

Data	N	Mean	Standard Deviation
C	200	114.68	83.24
D	200	114.67	83.25

t = 0.41 and p = 0.68

At the 0.05 level, the two means are NOT significantly different.

Independent t-test on col (B) and col (D)

Data	N	Mean	Standard Deviation
B	200	114.68	83.24
C	200	114.67	83.23

t = 0.58 and p = 0.61

At the 0.05 level, the two means are NOT significantly different.

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