Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information

Hydrothermal synthesis of WS_2 quantum dots and their application as a fluorescence sensor for the selective detection of 2,4,6-trinitrophenol

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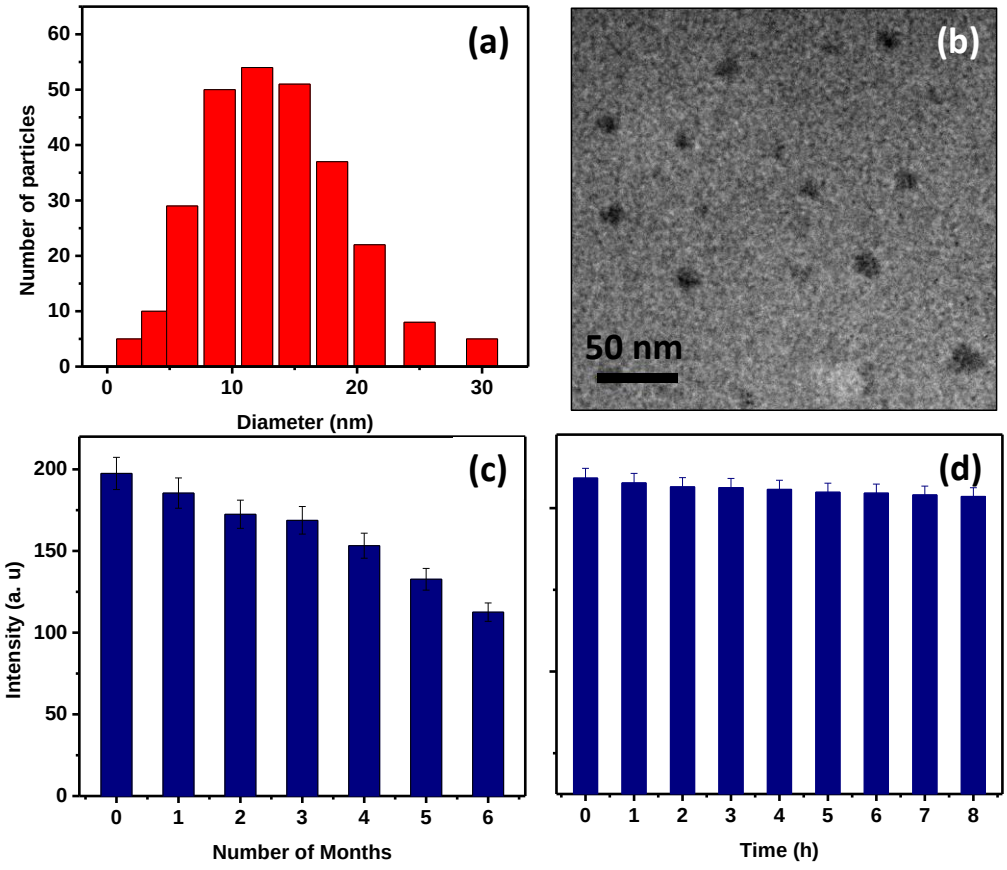


Figure S1: (a) Size distribution histogram obtained from TEM images. The histogram shows a distribution of 8 – 20 nm with an average peak at ~12 nm. (b) TEM image showing the average size of the QDs. (c) Fluorescence intensity of WS_2 QDs showing its temporal stability under room temperature for 6 months (d) Fluorescence intensity of WS_2 QDs under 8 h of continuous UV radiation (Power: 8 W) showing its photostability.

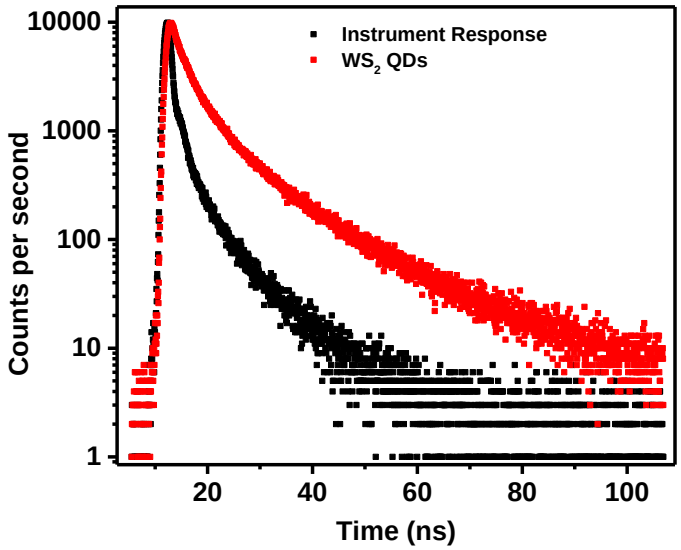


Figure S2: Lifetime spectrum of WS_2 QDs

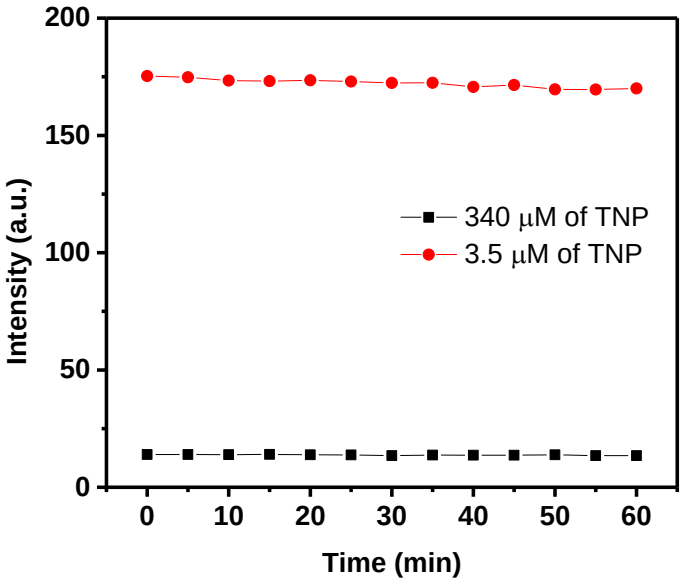


Figure S3: Response time of WS_2 QDs towards detection of TNP. Plot showing the PL intensity of WS_2 QDs as a function of time. No apparent variation in the intensity has been observed.

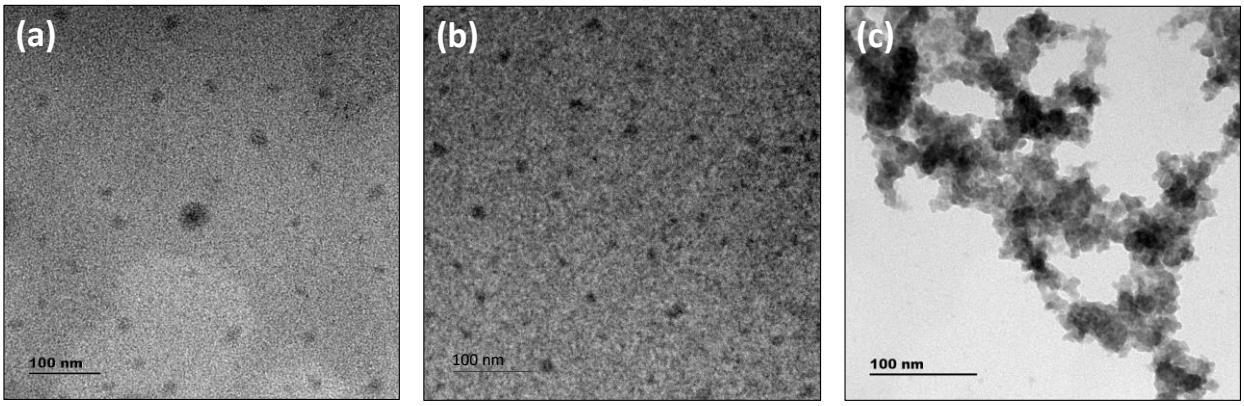
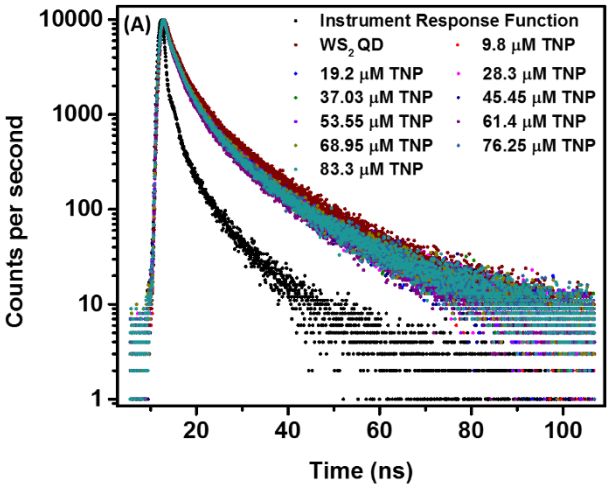


Figure S4: TEM image of (a) WS_2 QDs alone and in the presence of (b) 100 µM and (c) 250 µM concentrations of TNP.



(B)	τ_1 (ns)	α_1	τ_2 (ns)	α_2	$\langle\tau\rangle$ (ns)	χ^2
WS_2 QD	4.42	33.54	14.70	66.46	13.34	1.05
9.8 µM TNP	4.35	33.86	14.56	66.14	13.20	1.11
19.2 µM TNP	3.66	39.93	13.64	60.07	12.12	1.21
28.3 µM TNP	3.59	43.25	13.45	56.75	11.78	1.19
37.03 µM TNP	3.57	43.52	13.26	56.48	11.59	1.04
45.45 µM TNP	3.49	43.52	13.11	56.48	11.47	1.31
53.55 µM TNP	3.47	42.89	12.82	57.11	11.24	1.17
61.4 µM TNP	3.34	43.21	12.75	56.79	11.18	1.18
68.95 µM TNP	3.16	43.43	11.93	56.57	10.44	1.16
76.25 µM TNP	3.12	43.01	11.78	56.99	10.33	1.13
83.3 µM TNP	2.91	47.43	11.12	52.57	9.55	1.19

Figure S5: (A) Lifetime analysis of WS_2 NP at different concentrations of TNP. (B) Table showing the corresponding lifetime components along with average lifetime values. The small decrease in the lifetime components and average lifetime with respect to the concentration of TNP marks the complexity of the quenching mechanism involved.

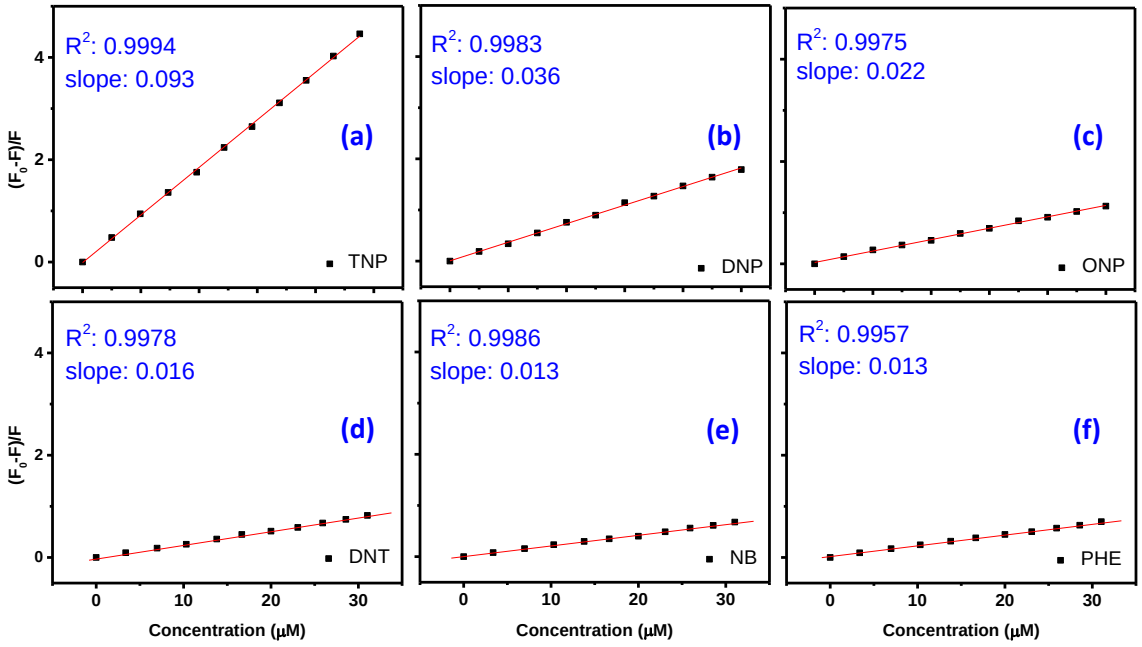


Figure S6: K_{sv} plots of TNP (a), DNP (b), ONP (c), DNT (d), NB (e) and PHE (f)

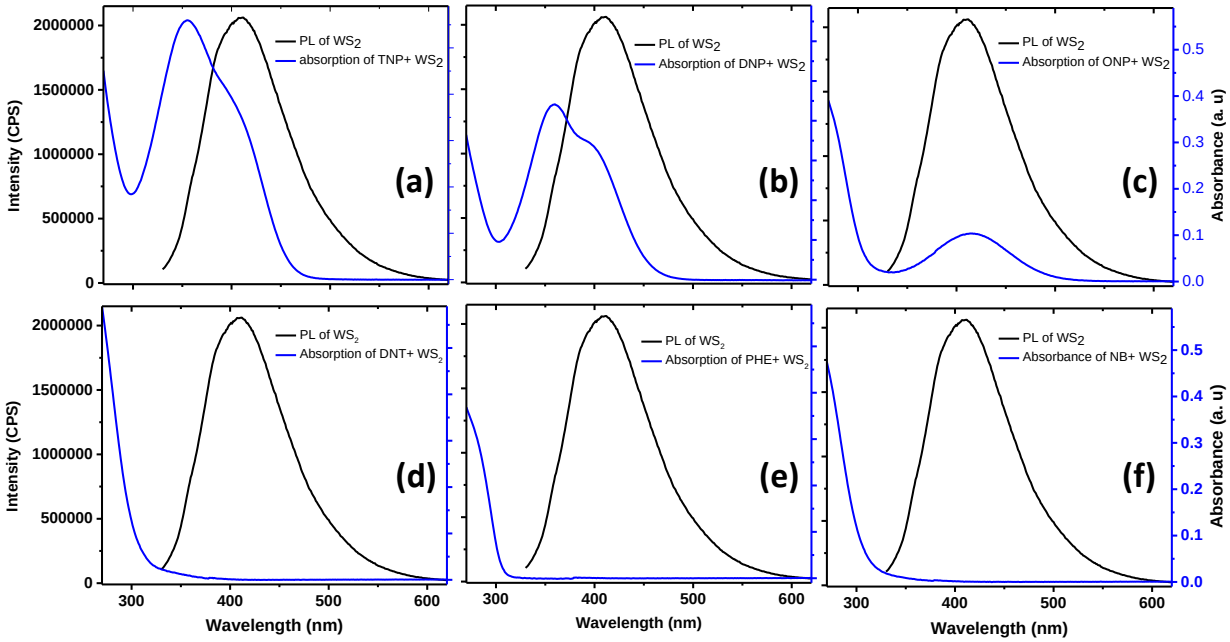


Figure S7: Spectral overlap of PL emission spectra of WS_2 with the absorption spectra of WS_2 along with TNP (A), DNP (B), ONP (C), DNT (D), NB (E) and PHE (F).

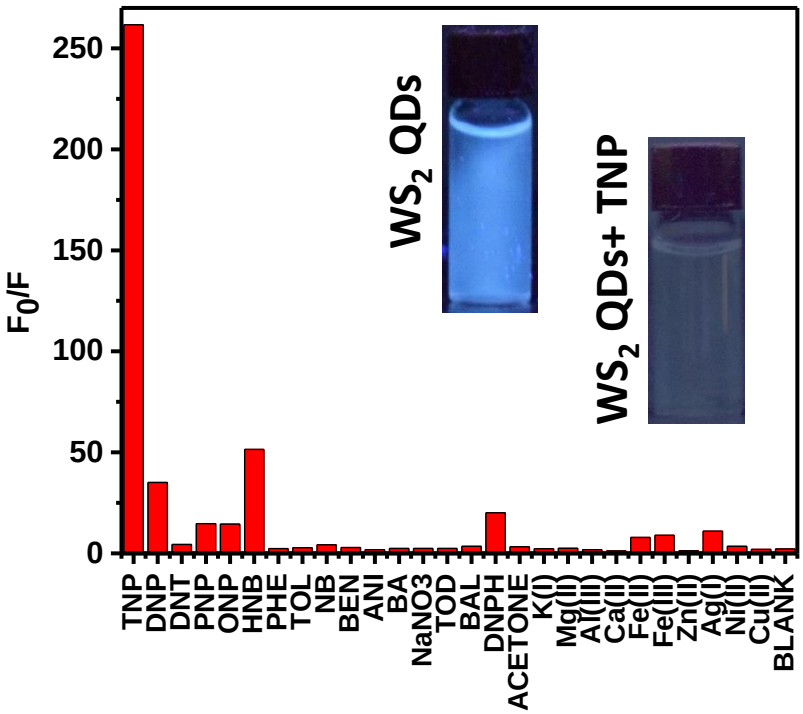


Figure S8: Selectivity study; only TNP could quench the PL emission of WS_2 QDs.

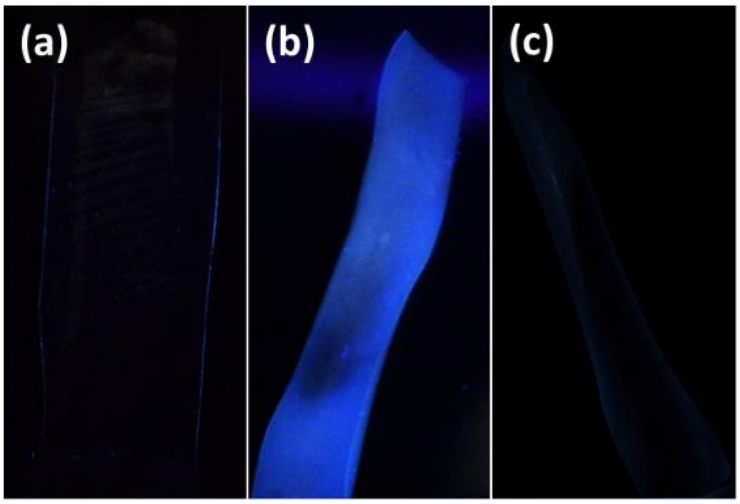


Figure S9: Photographs of (a) a PVA film (b) WS_2 QDs incorporated in the PVA film (c) WS_2 QDs -PVA film after keeping in a desiccator containing 100 mg of TNP for one day.

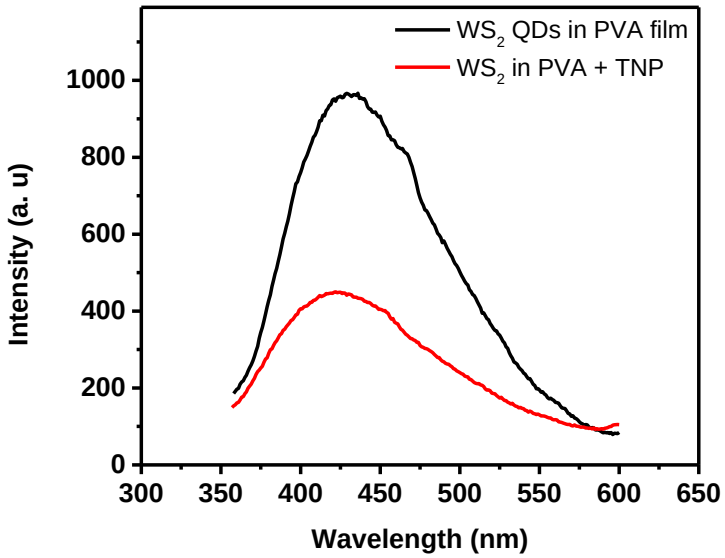


Figure S10: The PL emission spectra of (a) WS_2 QDs incorporated in the PVA film (b) the same PVA film after keeping in a desiccator containing 100 mg of TNP for one day.

Table S1: Table showing the size distribution from dynamic light scattering (DLS) measurements and zeta potential values of sensor material with and without the presence of the analyte. The reduction in zeta potential indicates the destabilizing action of TNP which in turn leads to the aggregation sensor materials.

	Size (nm)	Zeta
WS_2	37.84	- 21.1
WS_2 +TNP (125 µM)	92.60, 436.5	- 10.5
TNP	-	- 0.91

Table S2: Lifetime analysis of WS_2 QDs with different analytes showing a decrease in the lifetime component.

	τ_1 (ns)	α_1	τ_2 (ns)	α_2	$<\tau>$ (ns)	χ^2
WS_2	4.42	33.54	14.70	66.46	13.3	1.11
TNP	3.49	43.52	13.11	56.48	9.5	1.31
DNP	4.16	41.81	14.25	58.19	12.5	1.07
ONP	4.11	39.62	14.39	60.38	12.7	1.05
DNT	4.13	37.07	14.3	62.93	12.8	1.09
PHE	4.12	43.97	14.63	56.03	12.7	1.08
NB	4.20	33.21	14.21	66.79	12.9	1.08

FRET Efficiency Calculations

FRET Efficiency (E) has been calculated using two methods

- **Method I**: Using steady-state fluorescence data by using equation [1]

$$E= 1-(F_{DA}/F_D)$$

Where,

F_{DA} is the fluorescence intensity of *Donor* in the presence of *Acceptor*

F_D is the fluorescence intensity of *Donor* alone

FRET efficiency, E= 56.3 %.

- **Method II**: Using time-resolved fluorescence data, FRET efficiency was calculated using the equation[2, 3]

$$E= 1-(\tau_{DA}/\tau_{D)}$$

Where,

τ_{DA} is the fluorescence lifetime of *Donor* in the presence of *Acceptor*

τ_D is the fluorescence lifetime of *Donor* alone

FRET efficiency, E= 28.5 %

Inner Filter Effect Correction

To eliminate inner filter effect, fluorescence intensity

$$F_{corr(\lambda ex)} = F_{obs(\lambda ex)} /W$$

Where, W is correction factor, which can be obtained from the equation

$$W = (1–10^{- A_{FL}}) / A_{FL}$$

$F_{corr(\lambda ex)}$ is the corrected fluorescence in the absence of inner- filter effects, $F_{obs(\lambda ex)}$ is the measured fluorescence intensity, and A_{FL} is the absorbances of the fluorescent component, respectively.

References:

1. J. R. Lakowicz, Principles of fluorescence spectroscopy, Springer Science & Business Media, 2013.
2. K. K. Haldar, T. Sen and A. Patra, *The Journal of Physical Chemistry C*, 2010, 114, 4869-4874.
3. J. H. Han, S. Yamamoto, S. Park and H. Sugiyama, *Chemistry–A European Journal*, 2017, 23, 7607-7613.
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