Electronic Supplementary Information

# $MoS_2$ nanohybrid as a fluorescence sensor for highly selective detection of dopamine

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## Materials and Methods

*Materials and Reagents*: $MoS_2$ powder, Dopamine (DA), Adenine (Ade), Tyrosine (Tyr) were purchased from Sigma-Aldrich, USA. Fructose (Fru), Galactose (Gal), Creatinine (Cre), Thymine (Thy), Uric acid (UA) were purchased from SRL Pvt. Ltd, India. Tryptophan(Try), Tyramine (Tym), Cadmium chloride ($CdCl_2$) were purchased from Alfa Aesar, UK. Lead nitrate ($PbNO_3$) was purchased from Otto Chemicals, India. Glucose (Glu), Glutathione (GSH), Cobalt sulphate ( $CoSO_4$), Ascorbic acid (AA), Tin chloride ($SnCl_2$), Lysin (Lys), glycin (Gly), Sodium carbonate($NaCO_3$), Potassium chloride (KCl), Silver nitrate

($AgNO_3$), Ferrous sulphate ( $FeSO_4$), Ferric chloride ($FeCl_3$), Nickel sulphate ($NiSO_4$), Copper sulphate ($CuSO_4$), Magnesium sulphate ( $MgSO_4$), Calcium carbonate ( $CaCO_3$), Aluminum nitrate $Al_2(NO)_3$, Zinc Sulphate ($ZnSO_4$) Sodium hydroxide (NaOH), Hydrochloric acid (HCl) were from Merck, India. Double distilled water was used throughout the experiments. All reagents purchased were of analytical grade and used without further purification.

*Characterization:* UV-visible experiments were done using a Carry-100 UV-visible spectrophotometer. Fluorescence measurements were carried out using FluoroMax-4C spectrofluorometer (Horiba Instruments, USA), by fixing excitation and emission slit width at 5 nm with an integration time of 0.1 ns. Time resolved fluorescence measurements were executed using time-correlated single-photon counting (TCSPC). For TCSPC measurements, excitation wavelength was fixed at 330 nm and decay profile were collected at 415 nm (laser pulse width <1ns). FTIR spectra were recorded/acquired in a Spectrum 100T Perkin-Elmer FTIR spectrometer in transmission mode by KBr pellet method. pH measurements were conducted using EUTECH instruments' pH meter. Zeta potential measurements were carried out using Zetasizer Nano ZS series; Malvern Instruments, Malvern, UK. Mass spectra was recorded in a Bruker Q-TOF (COMPACT) mass spectrometer. Methanol-water mixture (50:50) was used as the electrospray solvent.

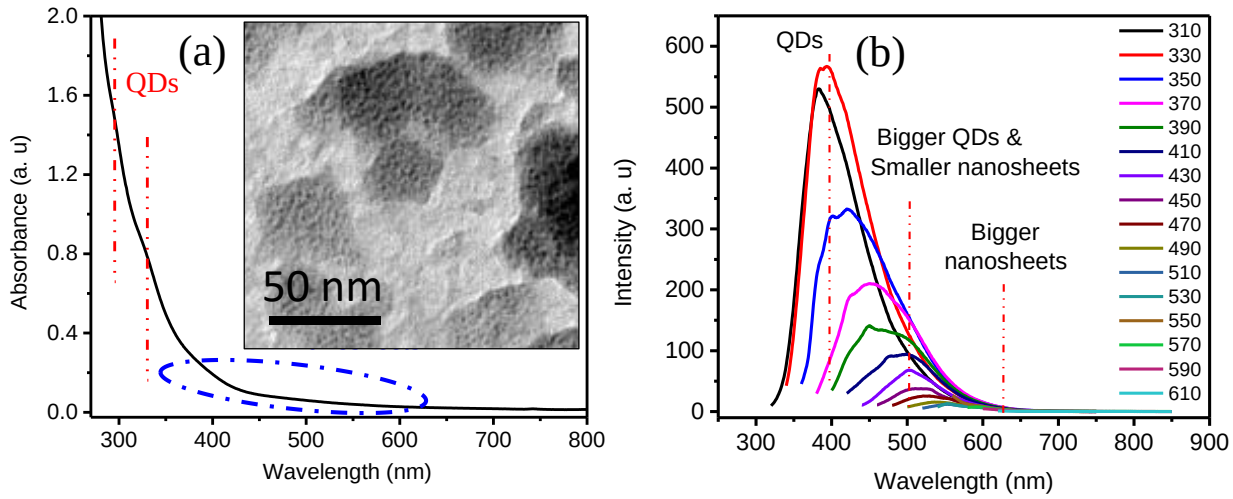



**Fig. S1**. (a) UV-visible absorption spectrum of $MoS_2$ QDNS shows the absorption features for QDs and nanosheets. Inset shows the TEM image of $MoS_2$ QDNS in which nanosheets and QDs are visible (b) Excitation dependent emission spectra of $MoS_2$ QDNS depicts three region of emission that corresponds to QDs, bigger QDs, nanosheets and bigger nanosheets.

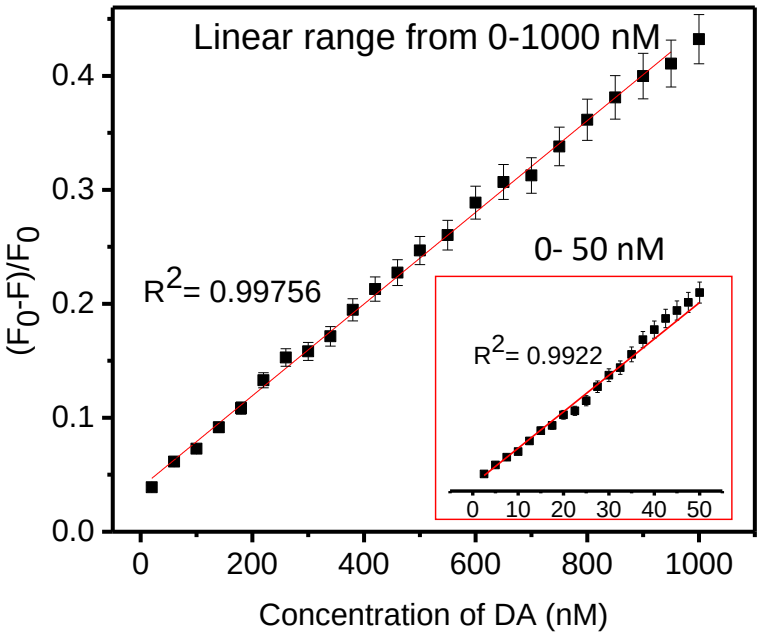



**Fig. S2**. Plot obtained for the quenching of PL intensity of $MoS_2$ QDNS by nanomolar concentrations of DA (20–1000 nM). Inset shows the linear range obtained by addition of 2.5 nM to 50 nM concentration of DA. Deviation from the mean of values obtained from repeated experiments are represented as error bars.

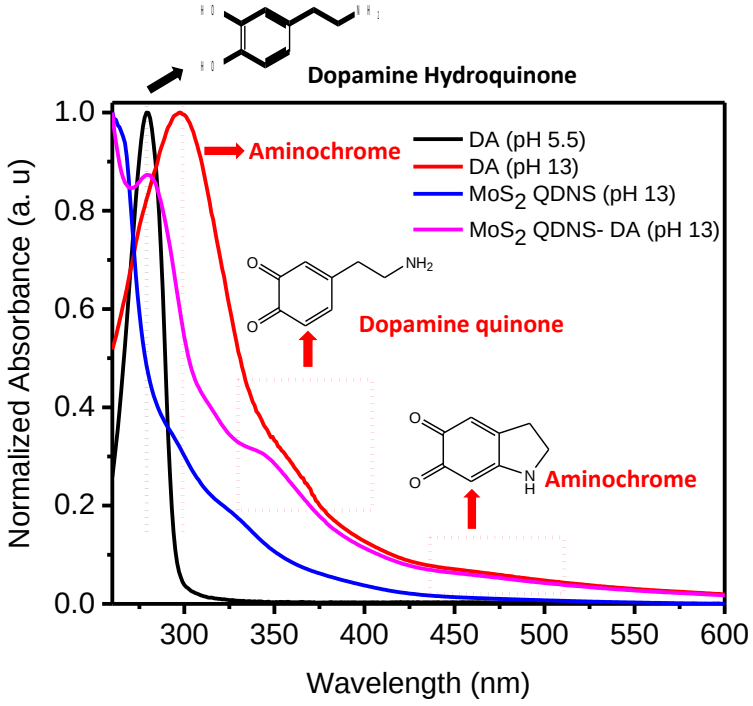



**Fig. S3.** Absorption spectra of DA as such, DA at pH 13, $MoS_2$ QDNS and $MoS_2$ QDNS- DA solutions.

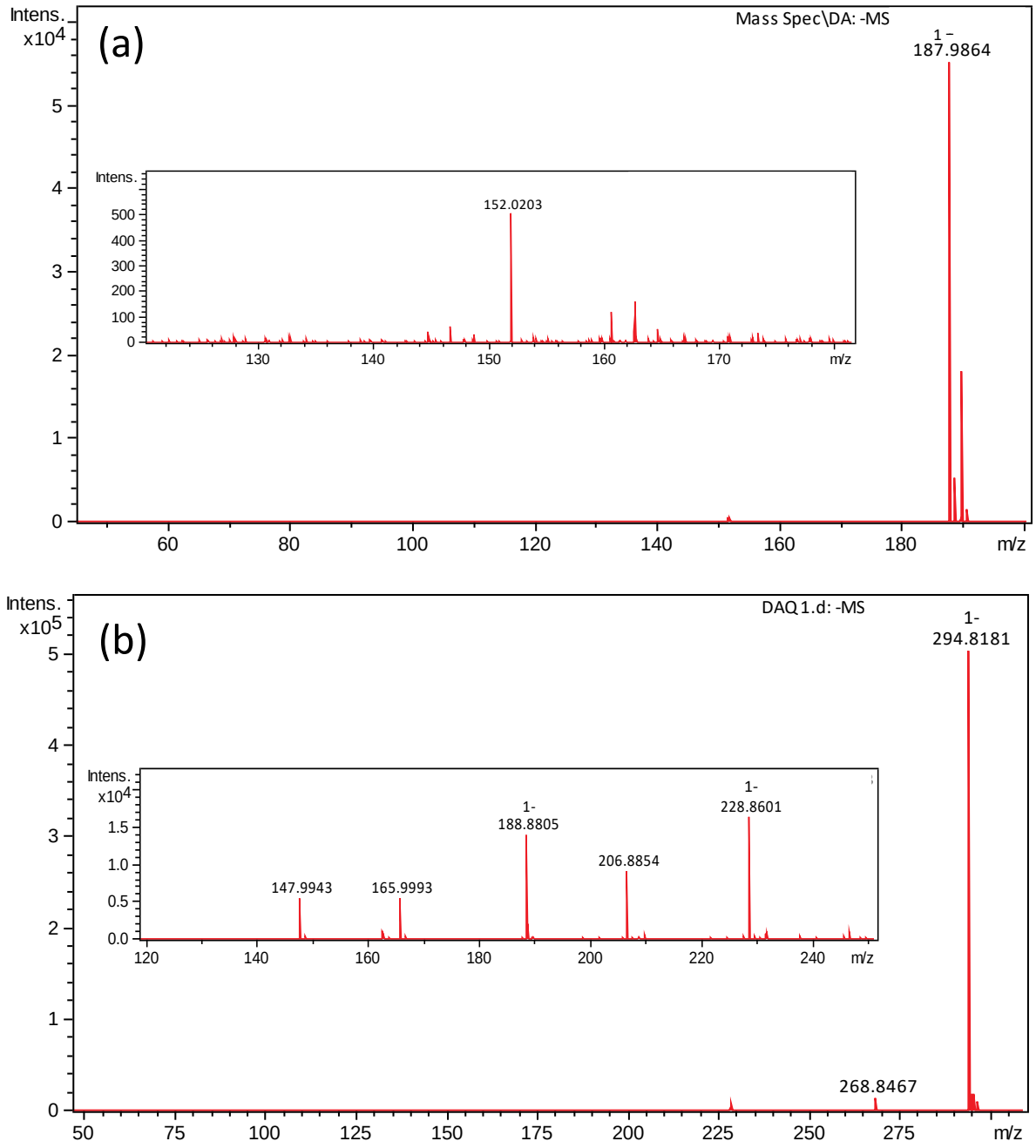



**Fig. S4**: Mass spectra of (a) DA in acidic media (pH 5.5) showing $(M–H)^-$ peak for dopamine hydrochloride (m/z 188) and that of dopamine (m/z 152) and (b) dopamine in alkaline media (pH 13) showing peaks for oxidized forms of DA such as aminochrome (m/z 148) and its dimer form (m/z 295). All MS spectra were collected in negative ion mode.

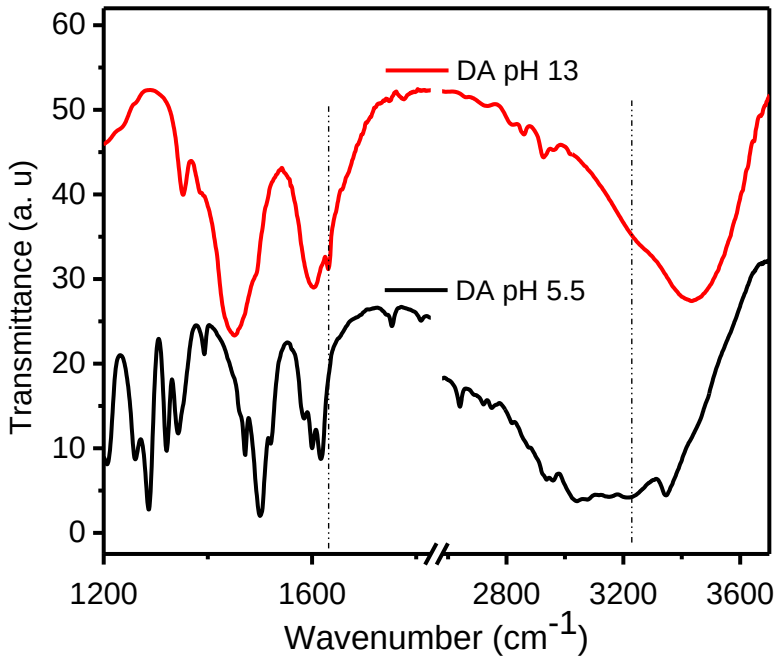



**Fig. S5**: Comparative IR spectra of DA at pH 13 and DA as such (pH 5.5).

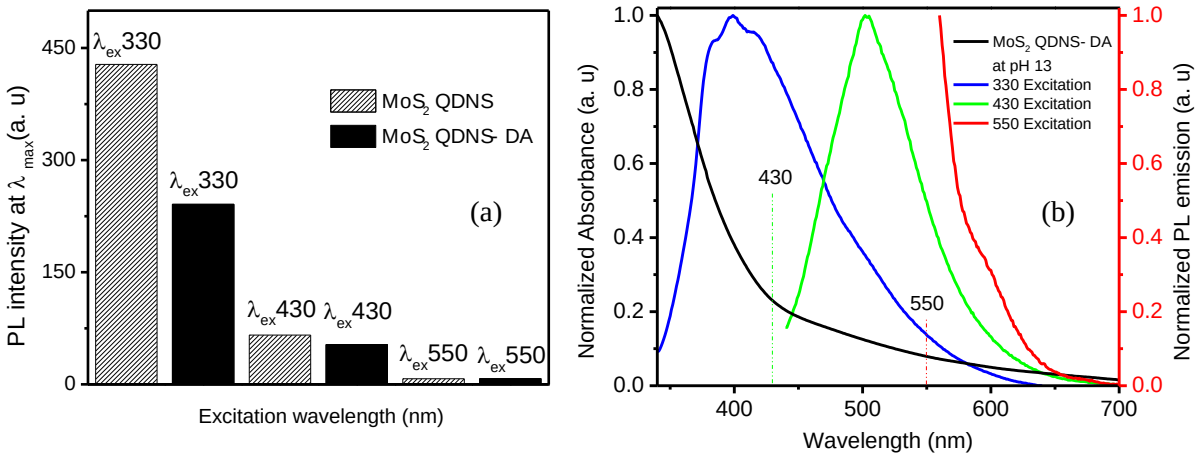



**Fig. S6 (a)** Comparison of PL intensity of $MoS_2$ QDNS and $MoS_2$ QDNS–DA complex at different excitation wavelength. (**b)** Spectral overlap of absorption spectra of $MoS_2$ QDNS-DA solution (black) to that of PL spectra of $MoS_2$ QDNS excited at different wavelength (330, 430 and 550 nm).

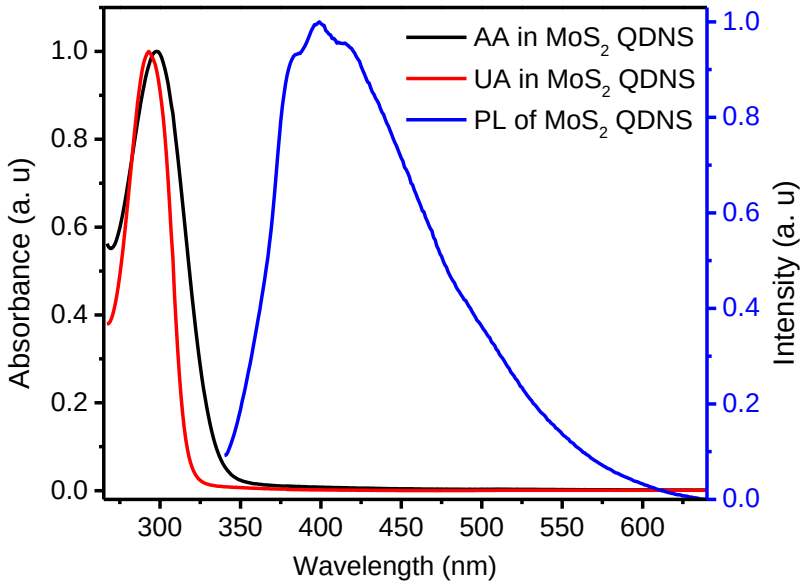



**Fig. S7**. Absorption spectra of AA and UA in $MoS_2$ QDNS along with the PL spectra of $MoS_2$ QDNS at pH 13 showing zero overlap.

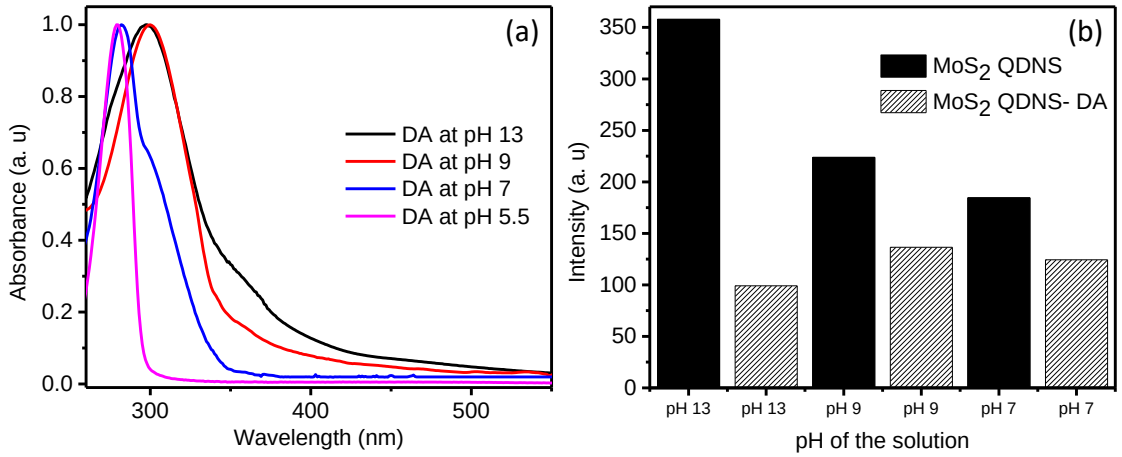
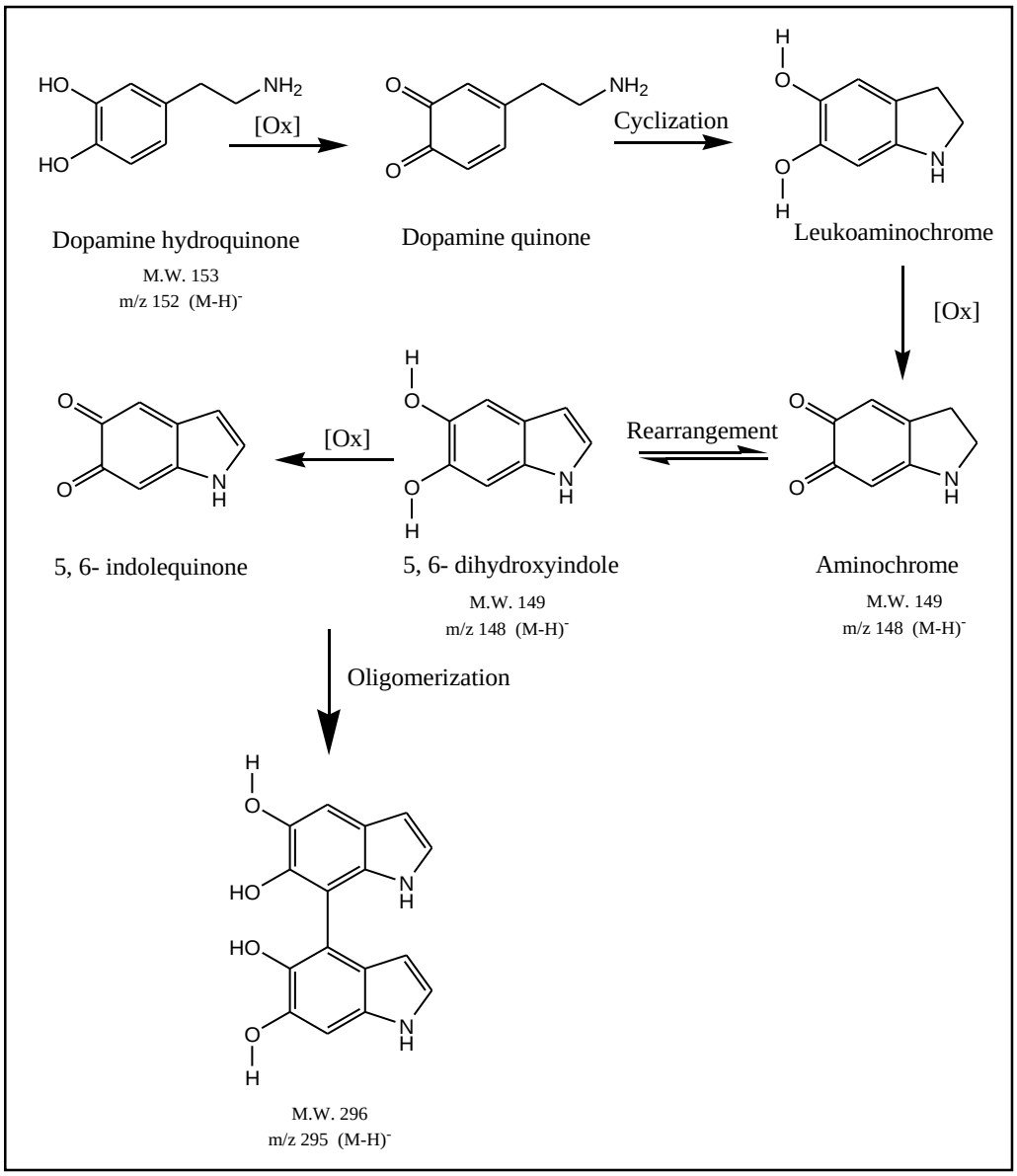



**Fig. S8**: **a)** UV- Vis absorption spectra of DA at different pH, showing a shift in peak position, as DA changes from hydroquinone form (acidic pH) to different oxidized form (neutral and basic pH). **b)** The response of DA towards PL emission of $MoS_2$ QDNS at pH 13, 9, and 7.




**Scheme S1:** Oxidation pathway of dopamine[1-6].

| System | $\tau_1$ (ns) | $\alpha_1$ (%) | $\tau_2$ (ns) | $\alpha_2$ (%) | $\tau_3$ (ns) | $\alpha 3$ (%) | $\langle\tau\rangle$ (ns) | $\chi^2$ |
|---|---|---|---|---|---|---|---|---|
| $MoS_2$ QDNS | 1.05 | 29.67 | 5.55 | 38.66 | 29.18 | 31.67 | 32.89 | 1.2 |
| 0.2 μM of DA | 0.83 | 31.91 | 5.06 | 36.40 | 28.27 | 31.87 | 32.62 | 1.2 |
| 0.4 μM | 0.60 | 37.98 | 4.52 | 32.44 | 27.44 | 29.58 | 30.20 | 1.2 |
| 0.6 μM | 0.56 | 42.83 | 4.32 | 28.85 | 26.46 | 28.32 | 28.78 | 1.2 |
| 0.8 μM | 0.54 | 45.20 | 4.16 | 27.35 | 25.78 | 27.45 | 27.94 | 1.2 |
| 1.0 μM | 0.51 | 48.53 | 3.98 | 24.74 | 24.33 | 26.73 | 27.17 | 1.1 |
| 1.2 μM | 0.50 | 51.77 | 3.87 | 22.99 | 23.84 | 25.23 | 25.91 | 1.1 |
| 1.4 μM | 0.50 | 54.45 | 3.88 | 21.31 | 22.48 | 24.25 | 25.13 | 1.09 |
| 1.6 μM | 0.48 | 56.28 | 3.62 | 20.09 | 21.74 | 23.62 | 24.64 | 1.1 |
| 1.8 μM | 0.45 | 58.89 | 3.21 | 18.47 | 19.80 | 22.65 | 23.98 | 1.1 |
| 2.0 μM | 0.45 | 61.00 | 3.14 | 16.85 | 18.82 | 22.15 | 23.73 | 1.02 |

**Table S1**. The lifetime components of $MoS_2$ QDNS and $MoS_2$ QDNS-DA, showing concentration dependent lifetime values. All decay profiles are fitted into tri-exponential functions. Decrease in all the components and average lifetime values of $MoS_2$ QDNS-DA complex implies to the interaction of excited state $MoS_2$ QDNS with DA. (Excitation was at 344 nm and the emission was collected at 415 nm).

| Method | Sensor System | LOD | Reference |
|---|---|---|---|
| Colorimetry | 40-aminobenzo-18-crown-6 (ABCE) and 4-mercaptophenyl boronic acid (MPBA) modified Au nanoparticles. | 46 nM | [7] |
| Electrochemistry | Thin layer of poly(tetrafluoroethylene) (PTFE) with nanoparticle arrays and an aluminum film | 0.5 μM<br>10 μM–1nM (S/N=3) | [8] |
| Electrochemistry | GS-$Au_{25}$ modified sol–gel electrode | 0.30 μM | [9] |
| Electrochemistry (Enzyme catalyzed) | Glassy carbon electrodes were modified by laccase. | 10 nM | [10] |
| Electrochemistry (Enzyme catalyzed) | carbon fiber microelectrode modified with tyrosinase immobilized in chitosan and ceria-based metal oxides | 1 nM | [11] |
| Fluorimetry | Mono-6-amino-β-cyclodextrin (NH2-β-CD) functionalised gold nanoclusters (β-CD-AuNC) | 2 nM<br>5–1000 nM (S/N=3) | [12] |
| Fluorimetry | Water-soluble silicon nanoparticles (SiNPs) | 0.3 nM<br>0.005 to 10.0 μM | [13] |
| Fluorimetry | Hierarchical CdS Spherical Aggregates | 10 nM | [14] |
| Fluorimetry | Polydopamine | 40 nM | [15] |
| Fluorimetry | $MoS_2$ QDNS | 0.9 nM,<br>2.5 nM- 6 μM | Present study |

**Table S2**. Comparison of various dopamine detection methods.

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