

# Electronic Supplementary Information

## Two Target Responsive Reversible Ratiometric pH Nanoprobe:

### A White Light Emitting Quantum Dot Complex

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#### Experimental Section

**Materials:** Manganese acetate tetra-hydrate ( $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , Merck), Zinc acetate di-hydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 99%, Merck), Sodium sulphide ( $\text{Na}_2\text{S}$ , Merck, 57%), 8-Hydroxyquinoline-5-sulphonic acid (Sigma-Aldrich, 99%), Hydrochloric acid (Merck), Sodium hydroxide pellet (Merck), Methanol, Mili-Q water were used to carry out the experiment.

**Synthesis of  $\text{Mn}^{2+}$ -doped ZnS QDs:** The synthesis of  $\text{Mn}^{2+}$ -doped ZnS QDs was carried out in water medium followed by an earlier reported bottom up greener procedure.<sup>11-12</sup> At first, 5.0 mM of  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and 1.0 mM of  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 40.0 ml of Mili-Q grade water under continuous stirring at room temperature. Then 5.0 mM of sodium sulphide was dissolved in 10 ml of Mili-Q water and added to that reaction mixture containing  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  and  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ . The resulting mixture was refluxed at 120° C for 3 hours under continuous stirring. Following this, a white colloidal solution was obtained and subsequently was centrifuged with a speed of 25,000 rpm for 10.0 minutes. Next, the pellet (obtained after centrifugation) was washed and further redispersed with same amount of Mili-Q water and centrifuged again with same condition. This washing cycle was repeated for 2 times and finally the pellet was dispersed in 50.0 ml of Mili-Q water. The so obtained colloidal dispersion was used for UV-vis, fluorescence and transmission electron microscopy (TEM) analysis and their powder form (obtained followed by centrifugation and drying at room temperature) was used powder X-ray diffraction measurements.

**Preparation of HQS solution:** 2.3 mg of pure HQS was dissolved in 10.0 ml of methanol (using sonication for 10 minutes at room temperature) to prepare 1.0 mM HQS solution.

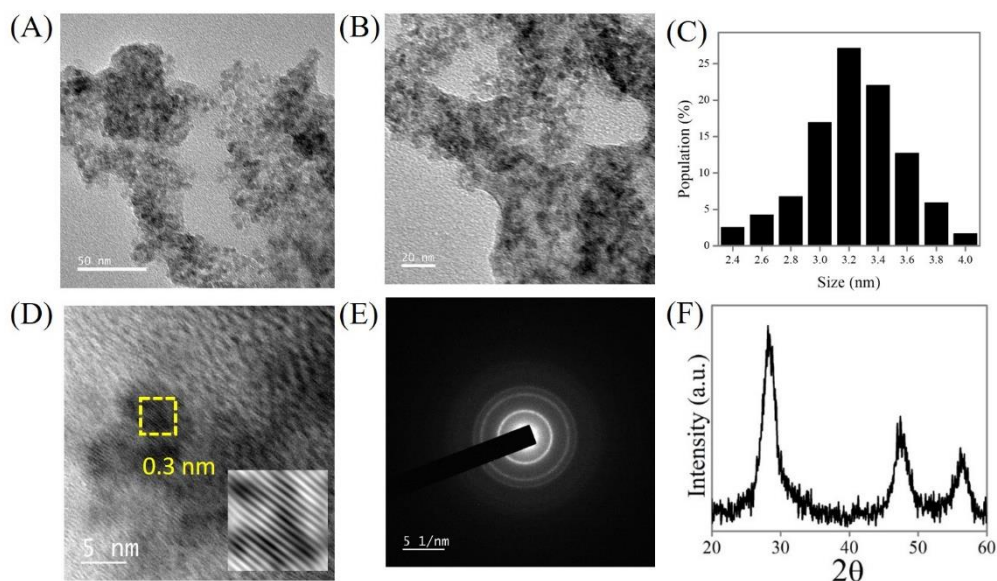
**Synthesis of WLE QDC:** QDC was synthesized by sequential addition of 5.0  $\mu\text{l}$  of 1.0 mM of HQS ligand to the 3.0 mL aqueous dispersion of the as synthesized  $\text{Mn}^{2+}$  doped ZnS QDs (having absorbance of 0.09 at 330 nm). The emission spectrum (at an excitation wavelength of 330 nm) and corresponding chromaticity of the HQS treated  $\text{Mn}^{2+}$  doped ZnS QDs were monitored in order to get optimum amount of HQS for the synthesis of WLE QDC, which

exhibited white light with chromaticity near to the perfect white light sources (0.33, 0.33).<sup>1-2</sup> The optimum amount of the HQS ligand was found 11.5  $\mu\text{M}$ . The resulting dispersion was centrifuged with speed of 25000 rpm for 10 minutes and the pellet was redispersed in equal amount of Mili-Q water to get the purified WLE QDC (with pH -6.5).

**Synthesis of  $\text{Zn}(\text{QS})_2$  complex attached ZnS QDs:** Based on earlier reported methods, firstly ZnS QDs were synthesized and then finally the treatment of HQS to as prepared ZnS QDs resulted the formation of  $\text{Zn}(\text{QS})_2$  complex attached ZnS QDs.<sup>11-12, 21</sup>

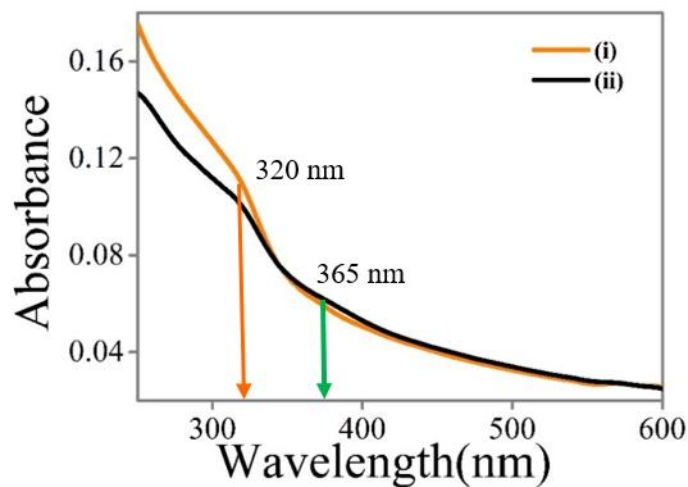
**pH sensing of WLE QDC:** The as prepared aqueous dispersion of the WLE QDC (pH-6.5) was used of pH sensing. The pH sensing of WLE QDC was performed followed by individual sequential addition of 0.1 M NaOH solution and 0.1 M HCl. The changes in the pH and corresponding emission (with color and chromaticity) of the NaOH and HCl added WLE QDC solutions were monitored. The experiments were performed in triplicate.

**Instruments:** Photoluminescence spectra and absorption spectra were recorded using Horiba Fluoromax-4 spectrofluorimeter and Perkin Elmer Lambda 45 UV-Vis Spectrophotometer, respectively. pH of the solutions was measured by using HANNA pH meter . JEOL JEM-2100F transmission electron microscope (maximum accelerating voltage 200 kV) was used to record the particle size of the samples while morphological analysis was carried out using Bruker D2 Advance X-ray diffractometer. CIE-1931 color space of the OSRAM color calculator were used to measure chromaticity of the samples. Hue calculation was performed using Image-J software and following earlier reported method.<sup>4-6</sup>

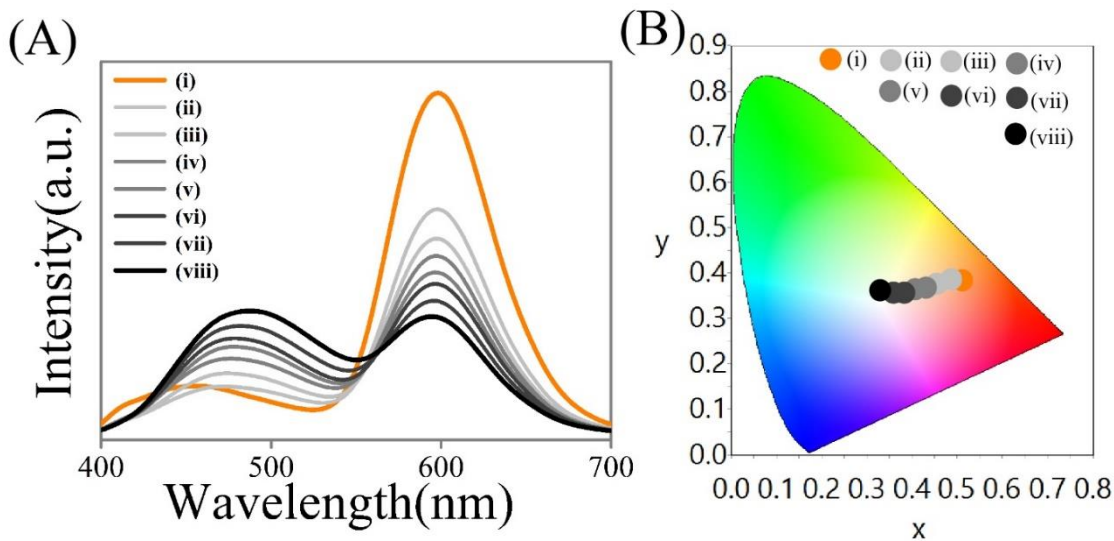


**Fig. S1.** Transmission electron microscopy (TEM) image (A) scale bar-50 nm and (B) scale bar-20 nm, (C) corresponding particle size distribution, (D) high resolution TEM image (scale bar-5 nm) and corresponding inverse fast Fourier transformed image (inset), (E) selected area electron diffraction (SAED) pattern, (F) Powder x-ray diffraction pattern of as-synthesized ligand free  $\text{Mn}^{2+}$  doped ZnS QDs. The particle size distribution was calculated based on the sizes of the

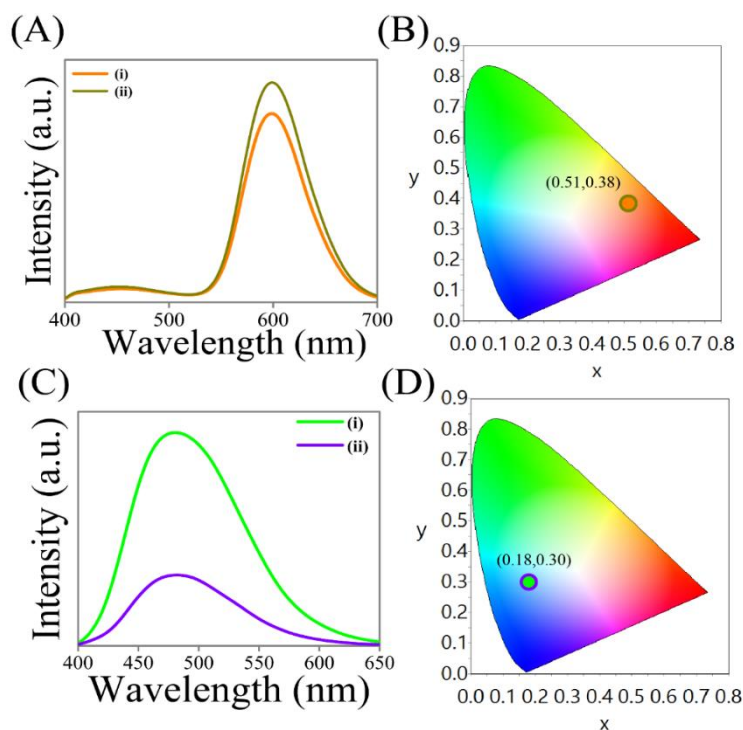
particles in 20 TEM images. The selected area electron diffraction pattern SAED pattern indicated the crystalline nature of the QD.



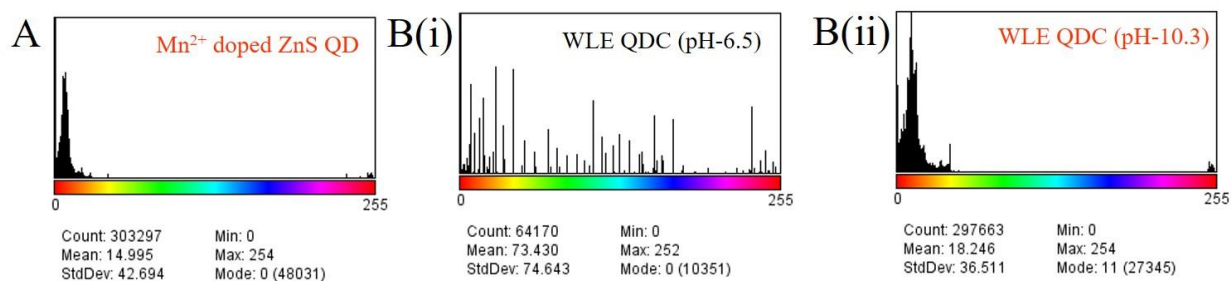
**Fig. S2.** Absorption spectra of (i)  $\text{Mn}^{2+}$  doped ZnS QDs and (ii) HQS treated  $\text{Mn}^{2+}$  doped ZnS QDs.



**Fig. S3.** (A) Emission spectra ( $\lambda_{\text{ex}} = 330 \text{ nm}$ ) and (B) chromaticity color coordinates in CIE diagram of (i) 0.0, (ii) 1.66, (iii) 3.32, (iv) 4.97, (v) 6.62, (vi) 8.26, (vii) 9.90, (viii) 11.53  $\mu\text{M}$  HQS treated  $\text{Mn}^{2+}$  doped ZnS QDs.

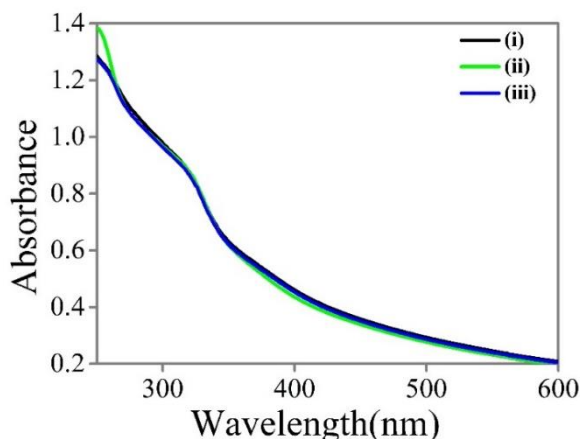


**Fig. S4.** (A) Emission spectra ( $\lambda_{\text{ex}} = 330$  nm) and (B) chromaticity color coordinates of (i) Mn<sup>2+</sup> doped ZnS QDs (pH-6.6) and (ii) upon changing of pH to 10.3. (C) Emission spectra ( $\lambda_{\text{ex}} = 330$  nm) and (D) chromaticity color coordinates of (i) Zn(QS)<sub>2</sub> complex attached ZnS QDs (pH-6.5) and (ii) upon changing pH to 10.3. It is to be mentioned here that since Zn-quinolate complex, being attached to the surface of ZnS QDs via dangling sulphide bonds, has enhanced optical features in comparison to their bare form (as reported by earlier reports),<sup>11-14</sup> hence we have performed control pH experiments with Zn(QS)<sub>2</sub> complex, present on the surface of ZnS QDs – which has similar properties like the Zn(QS)<sub>2</sub> complex attached to the Mn<sup>2+</sup> doped ZnS QDs.

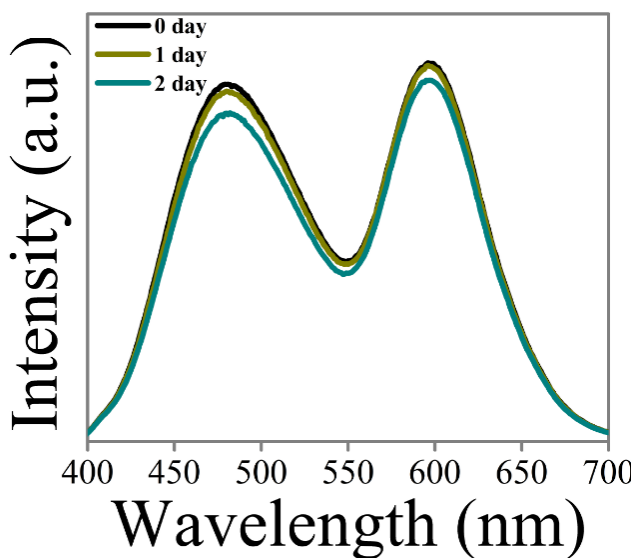


**Figure S5.** Hue histograms of (A) Mn<sup>2+</sup> doped ZnS QD (using the digital photograph of Fig. 1 A (i) of the manuscript) (B) WLE QDC at (i) pH-6.5 (using the digital photograph of Fig. 1 A (ii) of the manuscript) and (ii) pH-10.3 (using the digital photograph of Fig. 1 F (inset) of the manuscript). This results clearly showed that 14.995 Hue value was observed for only Mn<sup>2+</sup>

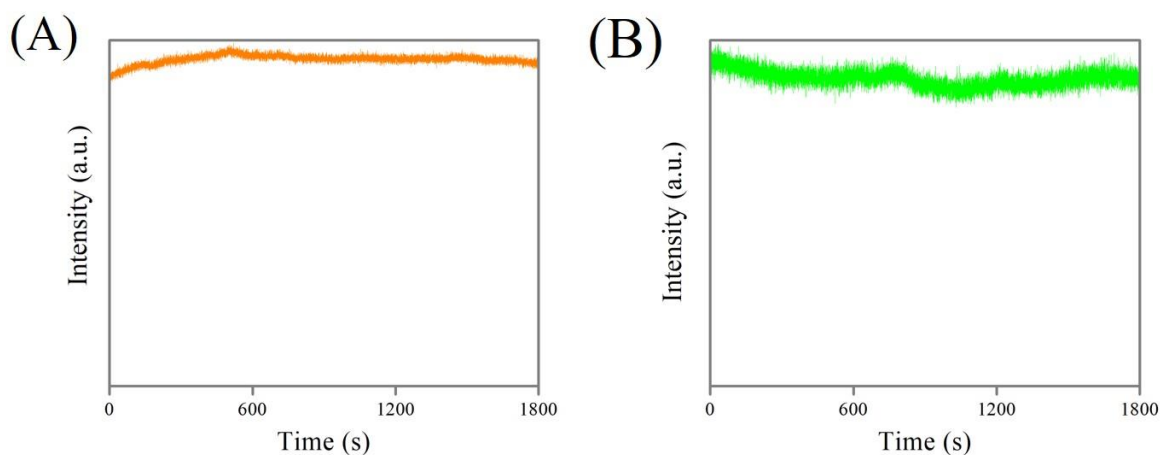
doped ZnS QD while WLE QDC showed the Hue values of 73.430 and 18.246 at pH- 6.5 and 10.3 respectively. The closer Hue value of the WLE QDC at pH-10.3 with that of the only  $Mn^{2+}$  doped ZnS QD further supported their orange emitting nature while restoring pH to 6.5 further changes to white light nature. The calculation of the Hue is completely based on the earlier reported methods and using Image-J software.<sup>18-20</sup>



**Fig. S6.** Absorption spectra of (i) WLE QDC (pH-6.5), (ii) NaOH added WLE QDC (pH-10.3) and (iii) HCl addition to that NaOH added WLE QDC added WLE QDC (pH-6.5).



**Fig. S7. (A)** Luminescence stability ( $\lambda_{ex}$ - 330 nm) at different time intervals of the aqueous dispersion of WLE QDC.




**Figure S8.** Photostability of the aqueous dispersion of WLE QDC monitored with respect to emission maxima at (A) 600 nm and (B) 483 nm

**Table S1.** Chromaticity color coordinates in CIE diagram (with respect to the emission spectra as mentioned in Fig. S3) of different amount HQS treated  $Mn^{2+}$  doped ZnS QDs.

| Sample | Conc. of HQS ( $\mu M$ ) | Chromaticity (x,y) |
|--------|--------------------------|--------------------|
| (a)    | 0.0                      | (0.51,0.38)        |
| (b)    | 1.66                     | (0.48,0.38)        |
| (c)    | 3.32                     | (0.45,0.37)        |
| (d)    | 4.97                     | (0.42,0.36)        |
| (e)    | 6.62                     | (0.40,0.36)        |
| (f)    | 8.26                     | (0.39,0.36)        |
| (g)    | 9.90                     | (0.36,0.35)        |
| (h)    | 11.53                    | (0.33,0.34)        |

**Table S2.** Tabulated form of changes in intensity ratio ( $I_{600}/I_{483}$ ) and chromaticity of WLE QDC followed by altering their pH (in the range of 6.5-10.3). This results are based on three sets of experiments.

| Sample/Color  | pH        | $I_{600}/I_{483}$ | Chromaticity (x,y) |
|---|-----------|-------------------|--------------------|
| Orange QDC  | 10.3±0.05 | 10.64±0.14        | (0.54,0.40)        |
|  | 10.2±0.06 | 8.19±0.12         | (0.53,0.40)        |
|   | 10.0±0.06 | 6.72±0.13         | (0.52,0.39)        |
|   | 9.3±0.09  | 5.06±0.12         | (0.49,0.39)        |
|   | 8.6±0.06  | 3.66±0.02         | (0.45,0.38)        |
|   | 7.6±0.03  | 2.08±0.01         | (0.38, 0.37)       |
|   | 7.0±0.09  | 1.41±0.01         | (0.37, 0.36)       |
|   | 6.7±0.06  | 1.15±0.03         | (0.35,0.35)        |
| White QDC   | 6.5±0.05  | 0.98±0.01         | (0.33,0.34)        |

**Table S3.** Quantum yields (QY; using quinine sulphate as standard) of (a)  $Mn^{2+}$  doped ZnS QDs (b) WLE QDC and (c) Zn-quinolate complex present in WLE QDC (this has been calculated followed by deconvoluting the emission spectra of WLE QDC at 483 nm).

| Sample                                     | QY (%) |
|--|--------|
| (a) WLE QDC                                | 4.4    |
| (b) $Mn^{2+}$ doped ZnS QDs                | 4.7    |
| (c) Zn-Quinolate complex in WLE QDC        | 2.3    |
| (d) Only Zn-Quinolate complex <sup>3</sup> | 0.9    |

**Table S4.** Zeta potential of WLE QDC at (a) pH-6.5 and (b) pH-10.3. Zeta potential of WLE QDC followed by addition of (c)  $Na^+$  (3.33  $\mu M$ ), (d)  $K^+$  (3.33  $\mu M$ ), (e)  $Mg^{2+}$  (3.33  $\mu M$ ) and (f)  $Ca^{2+}$  (3.33  $\mu M$ ) ions.

| Sample                  | pH   | Zeta Potential (mV) |
|-------------------------|------|---------------------|
| (a) WLE QDC             | 6.5  | +19.6               |
| (b) WLE QDC             | 10.3 | -36.6               |
| (b) WLE QDC + $Na^+$    | 6.5  | +19.2               |
| (c) WLE QDC + $K^+$     | 6.5  | +20.0               |
| (d) WLE QDC + $Mg^{2+}$ | 6.5  | +16.0               |
| (e) WLE QDC + $Ca^{2+}$ | 6.5  | +19.1               |

**Table S5.** Tabulated form of the comparison of different ratiometric pH optical nanoprobe.

| <b>Ref. No.</b>  | <b>Used Optical Nanoprobe</b>   | <b>pH Range</b> | <b>Advantages</b>  | <b>Disadvantages</b>  |
|------------------|---|-----------------|--|---|
| <b>This Work</b> | White light emitting quantum dot complex (Zn(QS) <sub>2</sub> complexed Mn <sup>2+</sup> doped ZnS QDs) | 6.5-10.3        | Nontoxic, Reversible Ratiometric (I <sub>600 nm</sub> /I <sub>483 nm</sub> )<br>Luminescence Color, Chromaticity based detection of pH | -----   |
| <b>3</b>         | FITC conjugated CdSe/CdZnS nanocrystals   | 6-8             | Ratiometric (I <sub>600 nm</sub> /I <sub>515 nm</sub> ) detection  | Toxicity & environmental sustainability                       |
| <b>4</b>         | BSA-Ce/Au NCs.  | 6-9             | Ratiometric (I <sub>400 nm</sub> /I <sub>650 nm</sub> ) detection  | Costly fabrication procedure<br>Non-radiative energy transfer |
| <b>5</b>         | (PyMMP-b-P2VP) diblock copolymer coated CdSe/ZnS QDs  | 1-4             | Ratiometric (I <sub>630 nm</sub> /I <sub>470 nm</sub> ) detection  | Toxicity & environmental sustainability                       |
| <b>6</b>         | CdSe/CdZnS NC SNARF conjugate   | 6-9             | Ratiometric & Color changes  | Toxicity & environmental sustainability                       |
| <b>10</b>        | D-penicillamine decorated Mn <sup>2+</sup> doped CdSSe/ZnS QD   | 4.5-8.5         | Ratiometric (I <sub>510 nm</sub> /I <sub>610 nm</sub> ) detection  | Toxicity & environmental sustainability                       |