Calixarene capped ZnS quantum dots as an optical nanoprobe for detection and determination of menadione (VK_3)

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Materials and methods:

All chemicals used are of analytical grade or of the highest purity available. All solutions were prepared with double-distilled, deionised water. Zinc acetate tetra hydrate, sodium sulfide (Na_2S) and polyvinylpyrrolidone (PVP) and were purchased from Aldrich with high purity. Working standard solutions were prepared daily in deionised water. UV–Vis absorption spectra were acquired on a Jasco V-570 UV–Vis. spectrometer. Fluorescence spectra were recorded on a model Fluorolog Horiba Jobin Yvon spectrofluorimeter at room temperature. IR spectra were measured with a Bruker Tensor-27 FT-IR spectrometer. Transmission electron micrograph (TEM) was recorded by JEOL, JEM-2100(200 kV). DLS measurements were performed using Nanotrac instrument. pH measurement were made by using model EQ-664 (Equip-tronics).

Synthesis of ZnS Quantum Dots

The synthesized ZnSQDs by a soft chemical method as reported by M. Chatterjee and co workers[1] with some modification. In this method, PVP was used as a capping agent. The reaction was carried out in aqueous medium. Calculated amount of PVP was dissolved in 50 ml of water and stirred for 20 minutes followed by the addition of 10 ml 0.1 M aqueous solution of zinc acetate tetrahydrate, with constant stirring. The pH of the solution was adjusted to 8.0 by 0.1 N NaOH. Then 20 ml of 0.1 M freshly prepared aqueous of Na_2S was added drop wise to get transparent colorless aqueous solution of ZnSQDs. Stirred this solution for 20 min.

Reflux it with water condenser for 8 h. Particles were collected by centrifugation at 8000 rpm. To remove unreacted sulfide and excess PVP, the particles were washed trice with water. The purified ZnSQD were dried under vaccum.

Preparing p-Sulfonato calix [4]arene coated ZnSQD:

pSC[4]A coated ZnSQDs were prepared following procedure describe earlier with some modification[2]. 1 mg of ZnSQD was dispersed in 1 ml THF and 25 mg of pSC[4]A was added. The mixture was sonicated in bath type sonicator of 100 W for 5 minutes. Then 5 ml of DMSO was added and left it for overnight in dark. Then resulting complex, pSC[4]A coated ZnSQD was obtained by centrifugation. The supernant was discarded and surface modified QDs were dispersed in 2 ml water and stored in a dark at room temperature (25± 2°C).

Preparation of pharmaceutical sample solution:

Tablets: Twenty tablets were accurately weighed and finely powdered. Accurately weighed portions of the powder equivalent to 0.1 mg of VK3 was transferred to a 100 ml volumetric flask and added about 80 ml of buffer solution (phosphate buffer pH-7.4). The mixture was shaken well and brought to volume with buffer solution and filtered through 0.45 micron nylon filter paper. This solution was diluted further as and when required.

Injections: Tow vials of VK_3 injection were transferred in to a 100 ml volumetric flask and added about 80 ml of buffer solution (phosphate buffer pH-7.4) were added. The mixture was shaken well and brought to volume with buffer solution. This solution was diluted further as and when required.

Then 5 ml aliquot of the above prepared sample solution was added in to the 10 ml (15×10^{-6}M) pSC [4] A –ZnSQD solution. Furthermore, 5 ml (0.5×10^{-6}M) solution of VK_3 was added. After incubation of 10 min, fluorescence intensity was determined.

Figure S1

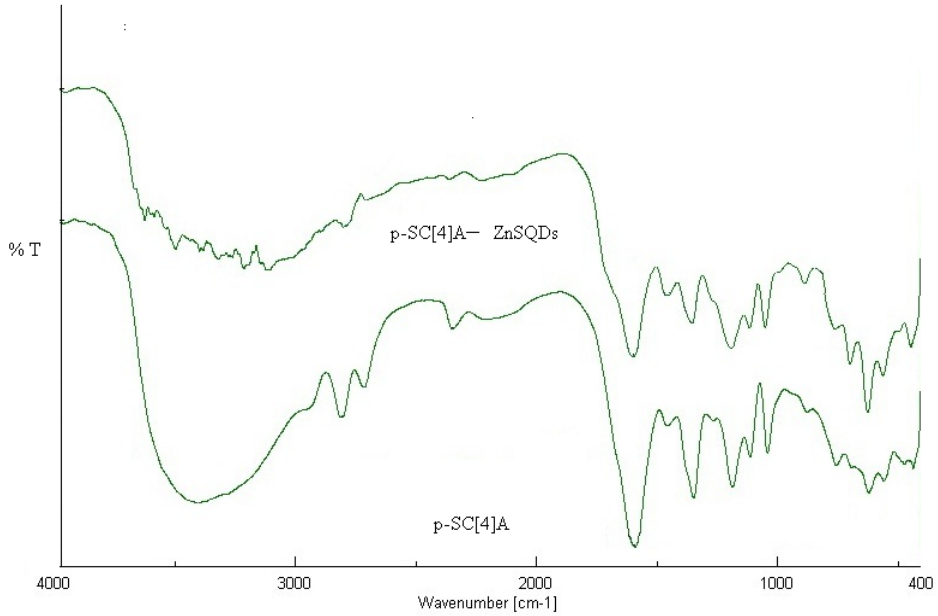

Fig. S1 FT-IR Spectra of p-SC[4]A and p-SC[4]A-ZnSQDs

Figure S 2

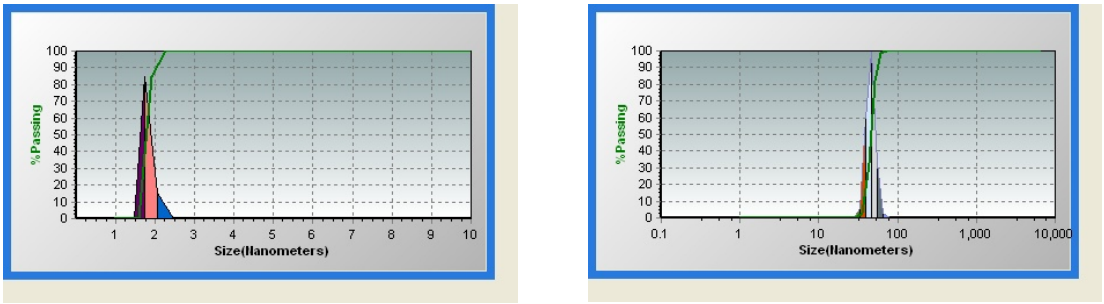

Fig. S2 DLS plot of ZnS QD and p-SC [4] A

Figure S 3

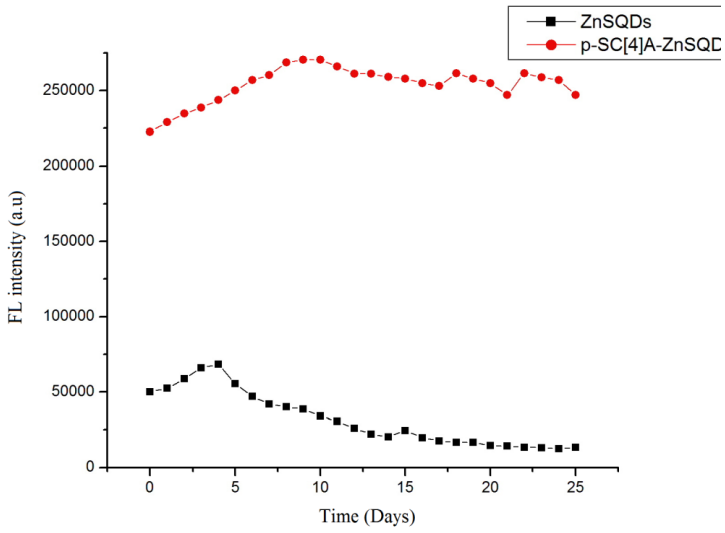

Fig. S3 : Photostability of ZnSQDs and pSC[4]A-ZnSQDs

Figure S 4

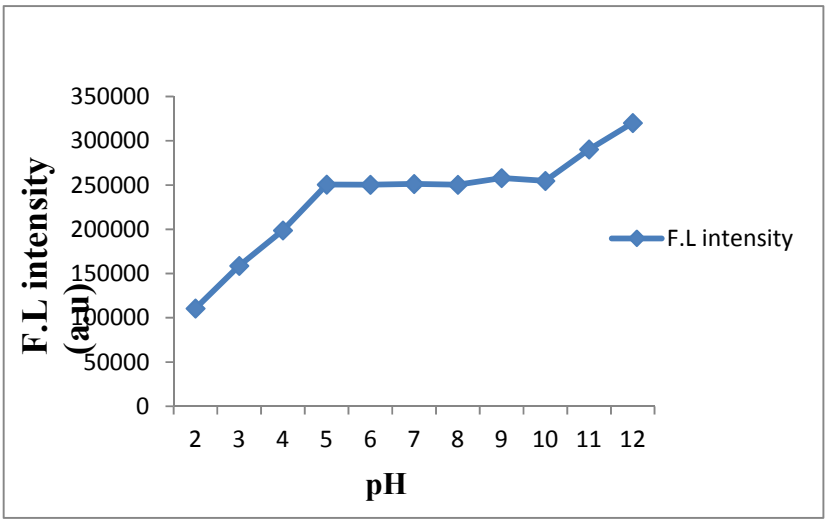

Fig. S4: The effect of pH on the luminescence of p-SC [4] A- ZnSQDs**.**

Figure S 5

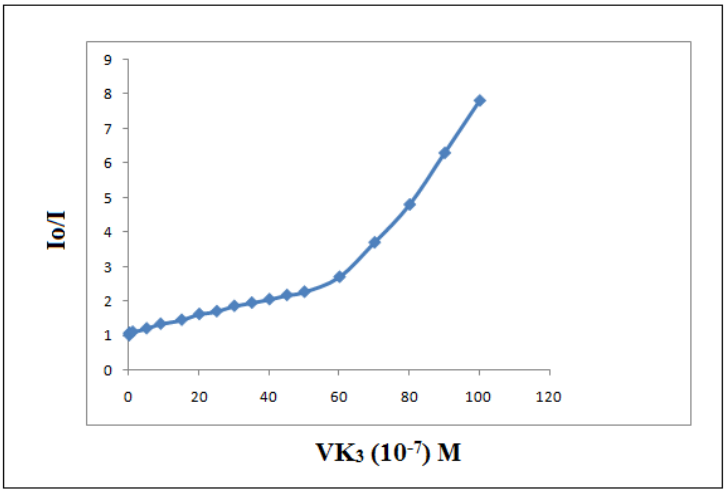

Fig. S5: Stern-Volmer plot for VK_3 quenching of pSC[4]A-ZnSQDs fluorescence.

Figure S 6

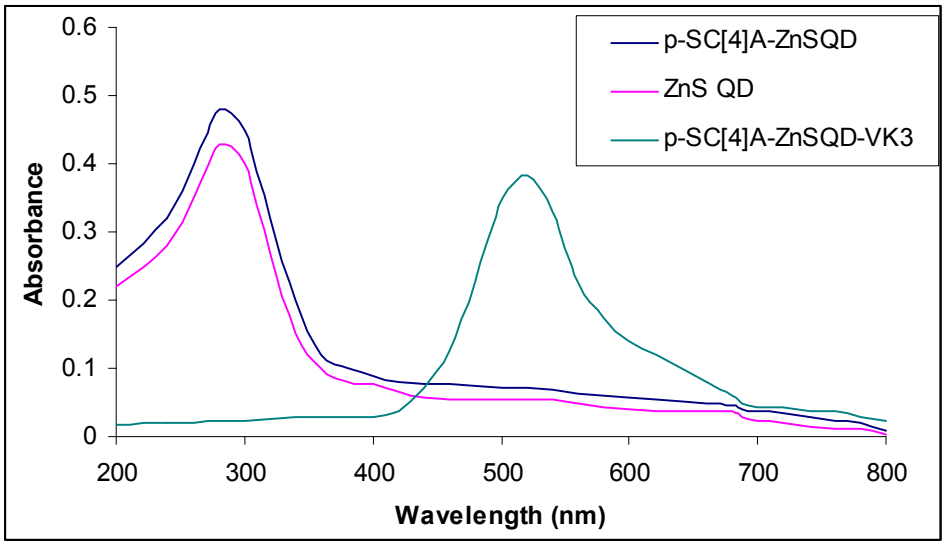

Fig. S6: UV-visible spectra of ZnSQD, p-SC[4]A-ZnSQD and p-SC[4]A-ZnSQD-VK3

Table S1

Methods	Linear range	Detection limit	References
Spectrofluorimetric	5.0×10^{-7} – 3.0×10^{-5} M	2.0×10^{-7} M	14b
Spectrofluorimetric	0.1×10^{-3} –2.0×10^{-3} M	0.022×10^{-3} M	23a
Spectrofluorimetric	3.50×10^{-7} to 1.05×10^{-5} M	7.50×10^{-8} M	23b
Polarographic	5×10^{-7} to 3×10^{-5} M	1.5×10^{-7} M	23c
Potentiometric	10^{-1} to 10^{-5} M	2×10^{-5} M	23d
Flow-Injection	0.5×10^{-3} - 10×10^{-3} M	2.6×10^{-3} M	23e
Spectrofluorimetric	5×10^{-9} to 1×10^{-6} M	8×10^{-9} M	This work

Table S1 Comparison of proposed sensor with previously reported VK3 sensors

Table S2

Pharmaceutical Samples	Sample content (µg/ml)	VK_3 added (µg/ml)	VK_3 found (µg/ml)	% Recovery + S.D. (n=3)
Kenadion (injection)	0.01	0.5	0.499	98.0 $\pm$ 1.6
Kenadion (tablets)	0.02	0.5	0.532	102.3 $\pm$0.7
Klot	0.05	0.5	0.570	103.7 $\pm$1.2
Vitadion	0.08	0.5	0.592	102.1 $\pm$1.1
Vitaencil C.K.P	0.10	0.5	0.599	99.8 $\pm$0.9

Table S2: Results obtained by the proposed sensor for pharmaceutical samples

References:

1. A.G.Ghosh, M.K.Naskar, A.Patra and M.Chatterjee, *Optical Materials,* 2006, **28**,1047

2. T. Jin, F.Fujii, H.Sakata, M. Tamura and M.Kinjo, *Chem. Commun.*, 2005, 4300