Electronic Supplementary Information

Surface Ion Engineering for Tuning Dual emission of $Zn_XCd_{1-X}S$ Nanocrystals

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Experimental Section

Materials: Cadmium acetate dihydrate ($Cd(CH_3COO)_2.2H_2O$, 99%), zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$, 99%), sodium sulphide ($Na_2S.9H_2O$, 58%), sodium oleate ($C_{18}H_{33}O_2Na$), amberlite IR-120 cation exchange resin beads (CB), hydrochloric acid, quinine sulphate, sulphuric acid and hexane were of analytical grade and used without further purification. They were purchased from the Merck Limited, Mumbai, India. Mili-Q grade water was used for the synthesis.

Synthesis of $Zn_XCd_{1-X}S$ Nanocrystals: For a typical preparation of $Zn_XCd_{1-X}S$ nanocrystals (NCs), cadmium acetate (5.0 mM) followed by zinc acetate (2.5 mM) were added to the 50 mL Mili-Q grade water under constant stirring and heating. After 5 min, 5.0 mM sodium oleate was added to the mixture upon which the solution became milky white. The milky white solution turned into greenish yellow when sodium sulphide (5.0 mM) was added to it, 5 minutes after sodium oleate addition. Since it is already reported that the distribution, growth kinetics and the composition of Zn and Cd in the resulting $Zn_XCd_{1-X}S$ NCs are sensitive to feed Zn-Cd-S ratios[1], the ratio of Zn, Cd and S was fixed at 1:2:2, for better post synthesis fluorescence tuning of the NCs. The whole mixture was allowed to reflux for 5-6 hours (to avoid discontinuous growth)[2] at 100 ^{0}C with constant stirring. After half an hour, greenish yellow solid particles were found to be floating over the aqueous solution. After 6 hours of reflux, the resulting greenish yellow mixture was centrifuged at 25000 rpm for 15 min and the pellet was thoroughly washed with Mili-Q water. This was followed by ultra-sonication of the redispersion to remove unreacted salts. The mixture was centrifuged again for 15 minutes. The pellet was dried under IR lamp and then kept at room temparature. To monitor the spectroscopic properties of the NCs, dispersions of the NCs were prepared in hexane.[3-4]

Preparation of activated Cation exchange Resin Beads (CB): To activate the polymeric resin beads, 3.0 g of Amberlite IR-120 cation exchange resin beads (sulfonated polystyrene divinylbenzene co-polymer) was first washed with Mili-Q grade water and then added to a 15.0 mL of 3.0 M HCl and was kept for 3 h. After activation, resin beads were washed with copious amount of Mili Q water to remove the excess HCl and washing was continued until the pH of the activated resin beads (CB) medium was 6-7. The beads were then dried under IR lamp for further use.[5]

Sample preparation for Experimental measurements: $Zn_XCd_{1-X}S$ NCs dispersion prepared in hexane (1.0 mg/10mL) was used for (UV-Vis, photoluminescence, FTIR, time-resolved photoluminescence and atomic absorption) spectroscopic as well as TEM measurement. For spectroscopic and TEM measurements, different amounts of CB were added to 10 mL of hexane dispersion of NCs. Solid NCs were used to measure XRD, FTIR. For quantum yield measurement, reference quinine sulphate solution was prepared in 0.1 M H_2SO_4 solution.[6] For preparing atomic absorption spectroscopic (AAS) measurement samples, dispersions of Qdots and different amount of CB treated Qdots (after removing CB) in hexane, were evaporated over hot plate (> 80^0C) untill the mixture was completely dried. After that 30 μL of 12 M HCl was added to each of the dried samples followed by sonication and finally the volume of the each HCl added sample was adjusted to 10 mL with MilliQ water. Then, AAS measurements were performed for the samples using standard solutions of cadmium acetate and zinc acetate salts as the references.

Characterization: UV-Vis and PL spectra (using λ_{ex} = 369 nm) were recorded on a Perkin Elmer Lambda 45 UV-Vis spectrophotometer and Horiba Fluoromax-4 spectrofluorometer respectively. Time-resolved photoluminescence (TRPL) intensity decays of the Qdots both in absence and presence of CB were recorded using a Life Spec II spectrofluorometer (Edinburgh Instrument). The sample was excited by Pico Quant 375 nm LED source. The decay curves were analyzed by FAST software, provided by Edinburgh Instrument along with the fluorescence instrument. The XRD patterns for the powder NCs were recorded by a Brucker D2 Phaser X-ray diffractometer (having CuKα radiation $1.5418A^0$). A JEOL JEM 2100 transmission electron microscope (operated at a maximum accelerating voltage of 200 kV) was used to analyze size and structure of alloyed NCs deposited on Formvar carbon-coated copper grids. FTIR spectra of NC samples were recorded in a Perkin-Elmer (Model: Spectrum One) spectrophotometer. Elemental analysis was carried out using a fast sequential absorption spectrophotometer (Varian AA240FS model).

Results

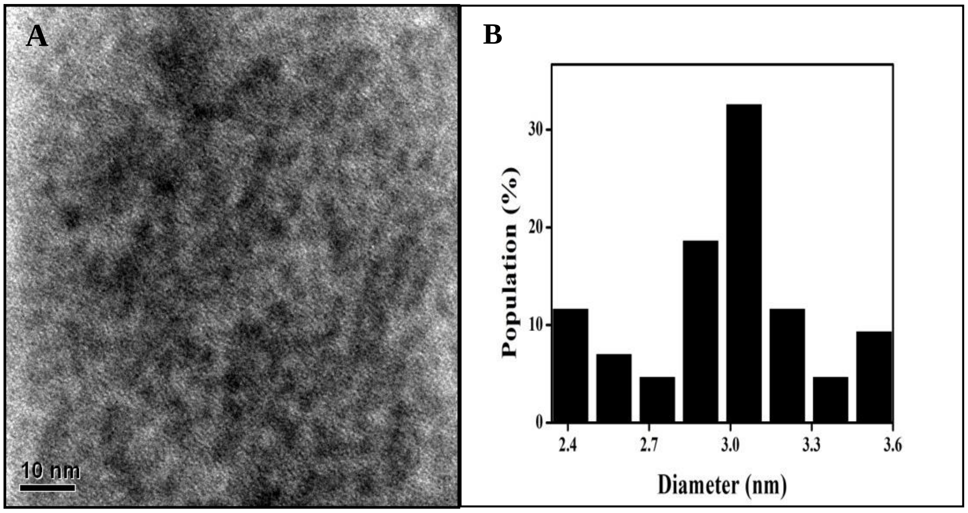

Figure S1. (**A**) TEM image and (**B**) corresponding particle size distribution of as-synthesized oleate capped $Zn_XCd_{1-X}S$ NCs.

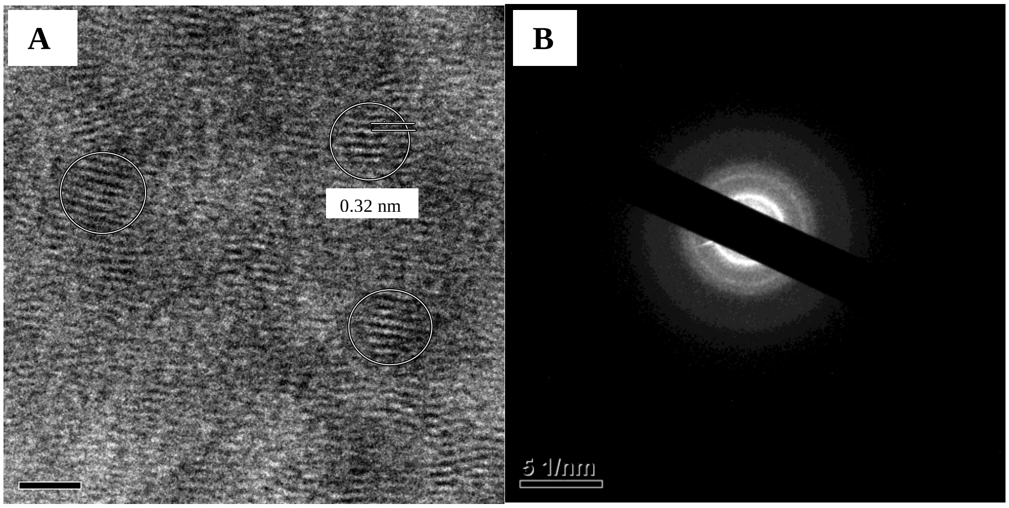

Figure S2. (**A**) High Resolution TEM (HRTEM : Scale bar 2 nm) image and (**B**) SAED pattern of as-synthesized oleate capped $Zn_XCd_{1-X}S$ NCs.

Table S1

Interplanar distances of as prepared $Zn_XCd_{1-X}S$ NCs measures from HRTEM image (reported)[7] and observed

Planes	$d_{spacing}$ (nm)					
	[X]Wurzite CdS	$Zn_XCd_{1-X}S$			[Y]Wurzite ZnS	**Observed**
		x =0.0	x = 0.5	x = 1.0		
(002)	0.3367	0.335	0.326	0.312	0.3128	**0.32**
(110)	0.2068	0.207	0.193	-	0.1911	
(112)	-	-	-	-	-	

[X] JCPDS Card No. 06-0314.[Y]JCPDS Card No. 05-0492.

Quantum Yield calculation with respect to quinine sulphate (QS) in 0.1 M H_2SO_4:

We have calculated Quantum yield with respect to quinine sulphate using the formula:

$$Q_s = Q_R \times \frac{I_s}{I_R} \times \frac{A_R}{A_S} \times \frac{\eta_S^2}{\eta_R^2} \qquad (1)$$

where,

Q_S = quantum yield of sample; Q_R = quantum yield of reference; I_S = area under PL curve of sample; I_R = area under PL curve of reference; A_R = absorbance of the reference; A_S = absorbance of the sample; η_S = refractive index of sample; η_R = refractive index of reference.

Q.Y. of quinine sulphate = 0.54

Refractive Index: hexane = 1.38; water = 1.33

(The concentration of all samples and the reference quinine sulphate were adjusted so that the optical densities of all samples were 0.1 ± 0.01 at the excitation wavelength (369 nm)).[8-9]

Table S2

Variation of Quantum Yield with the amount of CB

Amount of CB added (mg)	Quantum Yield (%)
0	12.0
10	10.4
20	10.2
30	9.2
40	7.5
50	7.3
60	6.3
70	6.1
80	5.6
90	4.7
100	4.5
110	4.3
120	3.1
130	2.5
140	2.4
150	1.7
160	1.5

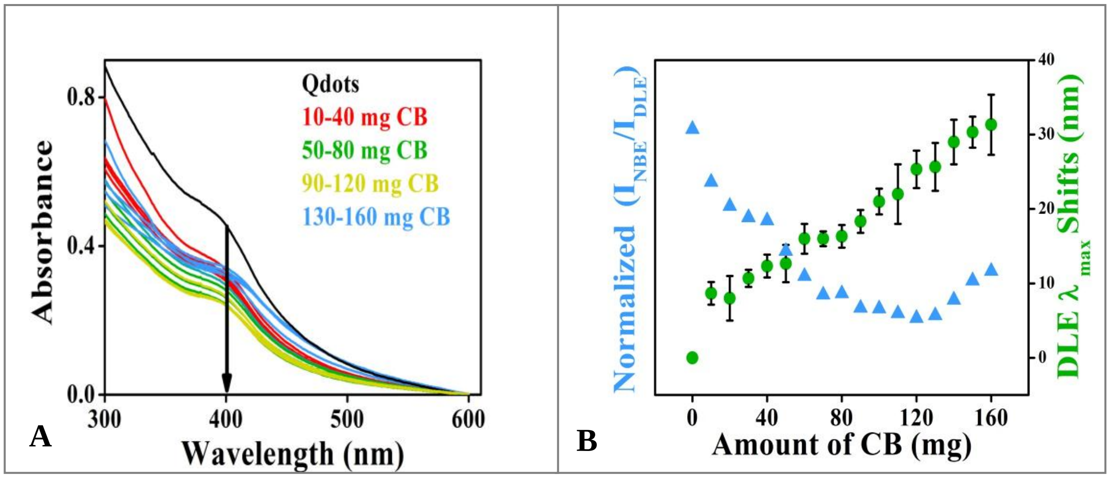

Figure S3. (A) Room temperature UV-Vis spectra of 10-160 mg CB added $Zn_XCd_{1-X}S$ NCs in hexane and (**B**) Dependence of wavelength shifts and NBE/DLE intensity ratio on the amount of CB added (recorded at 3 h after addition).

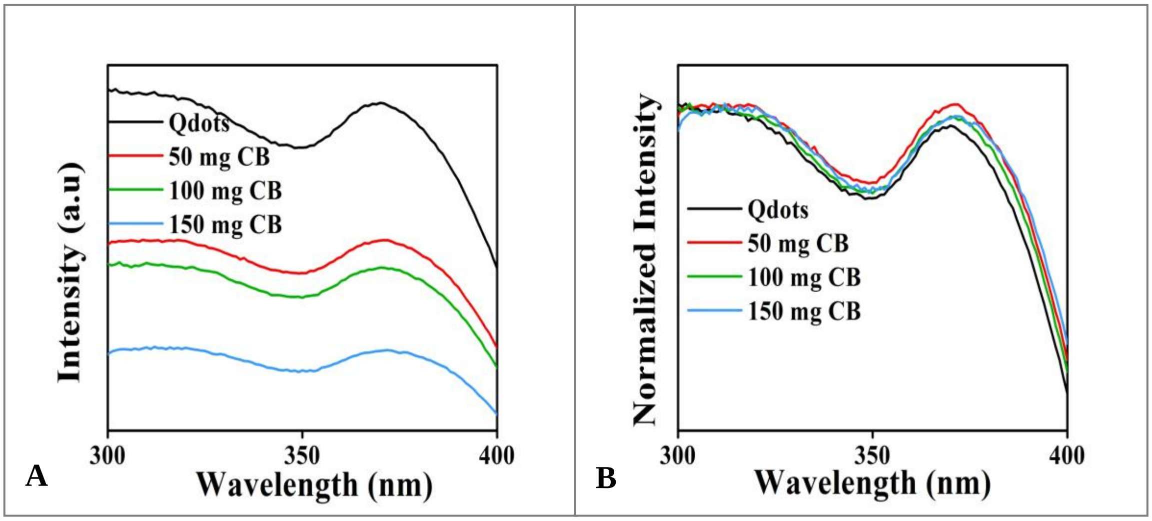

Figure S4. (A) Room temperature Excitation spectra (λ_{em} = 539 nm) of different amount CB added $Zn_XCd_{1-X}S$ NCs in hexane and (**B**) corresponding normalized excitation spectra.

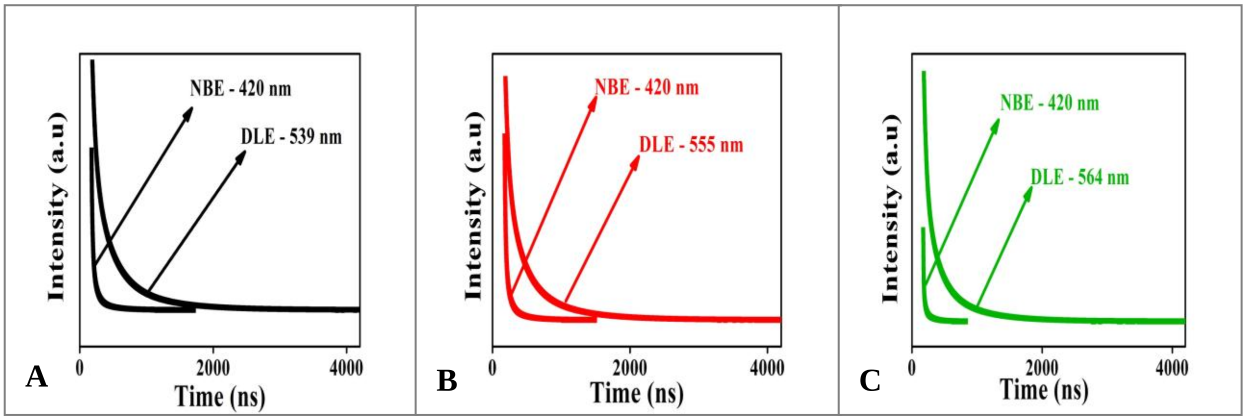

Figure S5. Photoluminescence decay curves of (**A**) $Zn_XCd_{1-X}S$ NCs; (**B**) 50 mg CB added NCs and (**C**) 150 mg of CB added NCs.

Table S3

(A) Decay parameters of $Zn_XCd_{1-X}S$ NCs and CB added NCs: Near Band Edge Emission (monitored at 420 nm).

Amount of CB added (mg)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τ_{av} (ns)	χ^2
0	20.7%	14.7	41.4%	58.0	37.9%	235.0	192.6	0.993
50	19.6%	13.5	39.5%	55.3	40.9%	211.8	176.3	0.998
150	11.7%	5.0	31.8%	23.9	56.5%	113.8	103.5	0.999

(B) Decay parameters of $Zn_XCd_{1-X}S$ NCs and CB added NCs: Deep Level Emission (monitored at 539 nm (as synthesized), 555 nm (50 mg CB added) and 564 nm (150 mg CB added).

Amount of CB added (mg)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	τ_3 (ns)	τ_{av} (ns)	χ^2
0	8.7%	53.1	46.5%	248.4	44.8%	711.8	583.0	1.044
50	7.7%	46.8	40.5%	209.4	51.8%	635.2	543.6	1.065
150	12.6%	40.8	39.4%	188.2	48.0%	589.8	499.8	0.999

Decay profiles were fitted to a multi-exponential model:

$$I(t) = \sum_i \alpha_i \exp\left({}^{-t}\!/_{\tau_i}\right) \qquad (2)$$

Where, three exponentials were used to fit near band edge emission (NBE) as well as deep level emission (DLE), with obtaining χ^2 close to 1.0; for all fit. We also report intensity-average life times (**τ_{av}**) in Table S3, determined from the results of three exponential models using

$$\tau_{av} = \frac{\sum_i \alpha_i \tau_i^2}{\sum_i \alpha_i \tau_i} \qquad (3)$$

Where, α_i and τ_i are the pre-exponential factors and excited-state luminescence decay time associated with the *i*-th component, respectively.

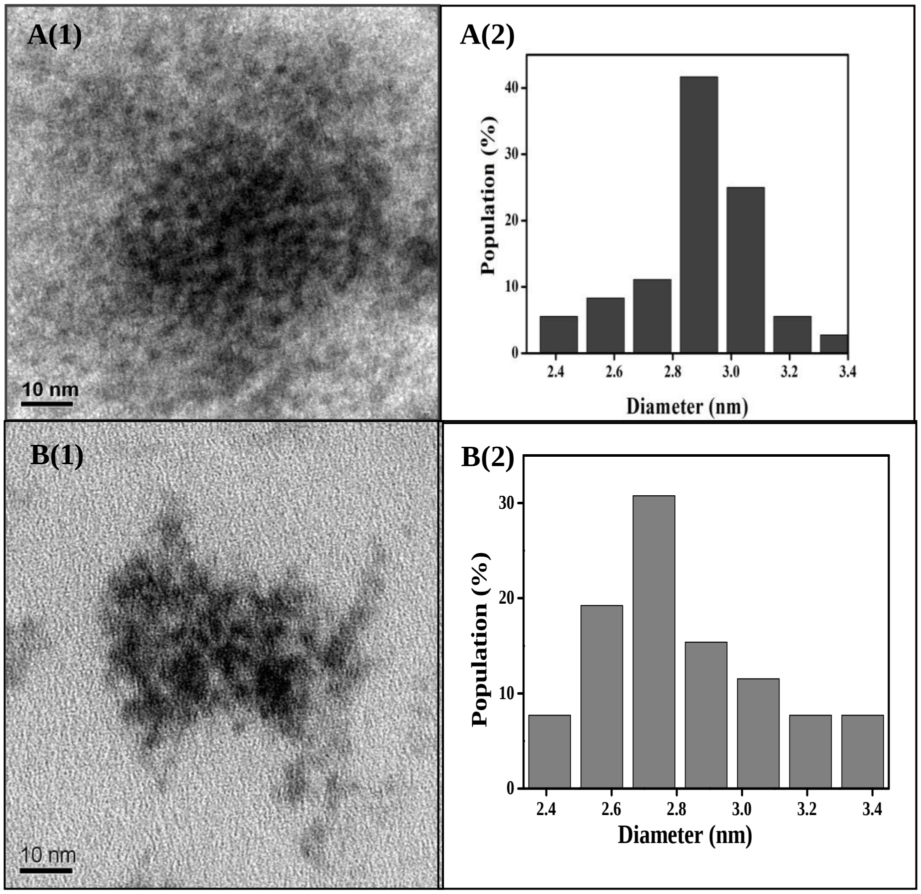

Figure S6. TEM image and corresponding particle size distribution of (**A**) 50 mg of CB treated NCs and (**B**) 150 mg of CB treated NCs.

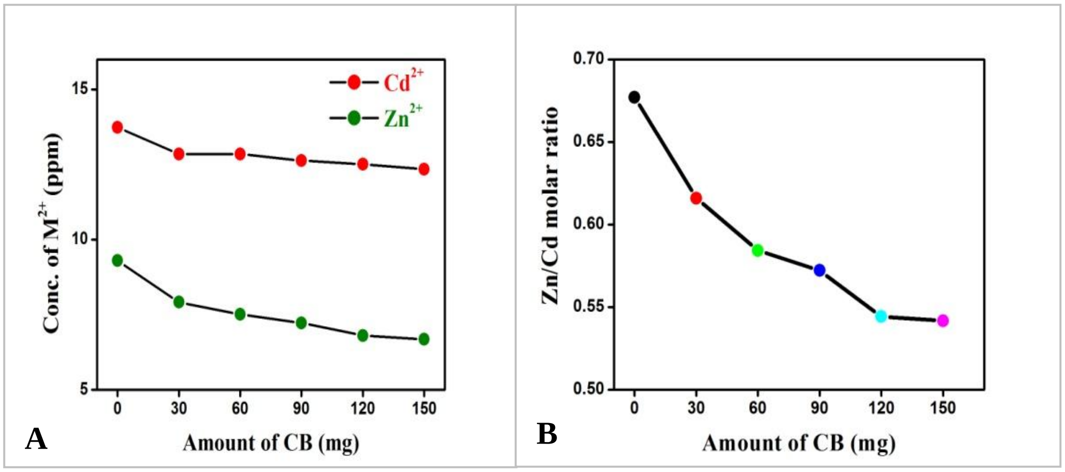

Figure S7. Variation of (**A**) individual metal ion (Zn^{2+} and Cd^{2+}) concentration and (**B**) their molar ratio with respect to the amount of CB added to $Zn_XCd_{1-X}S$ NC dispersion.

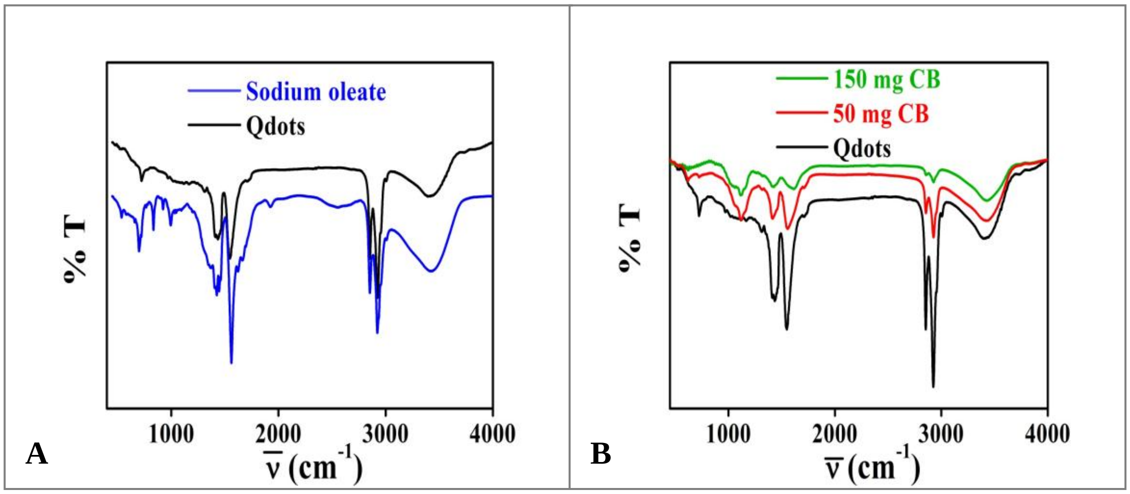

Figure S8. FTIR spectra of (**A**) sodium oleate and oleate capped $Zn_XCd_{1-X}S$; (**B**) different amounts (50 mg and 150 mg) of CB added NCs.

Table S4.[10]

FTIR Peak positions of various functional groups observed with samples as in Figure 7.

Peak position (Wave number, cm^{-1})	Functional groups
3430	-O-H stretching
2930	-C-H asymmetric stretching
2845	-C-H symmetric stretching
1560	$-COO^-$ asymmetric stretching
1440	-C-H bending
1123	-C-O stretching

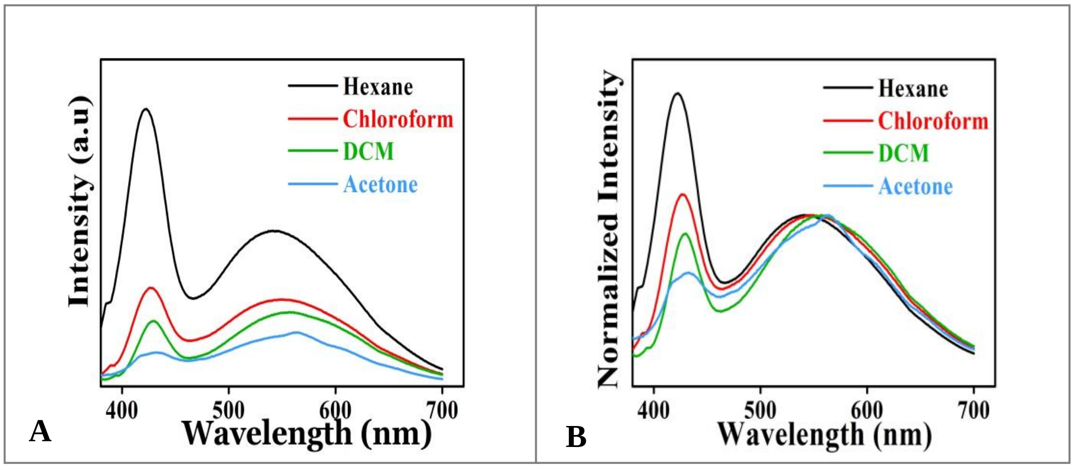

Figure S9. (A) Emission spectra (λ_{ex} = 369 nm) of $Zn_XCd_{1-X}S$ NCs in different organic solvents and (**B**) corresponding normalized (to DLE maximum) emission spectra.

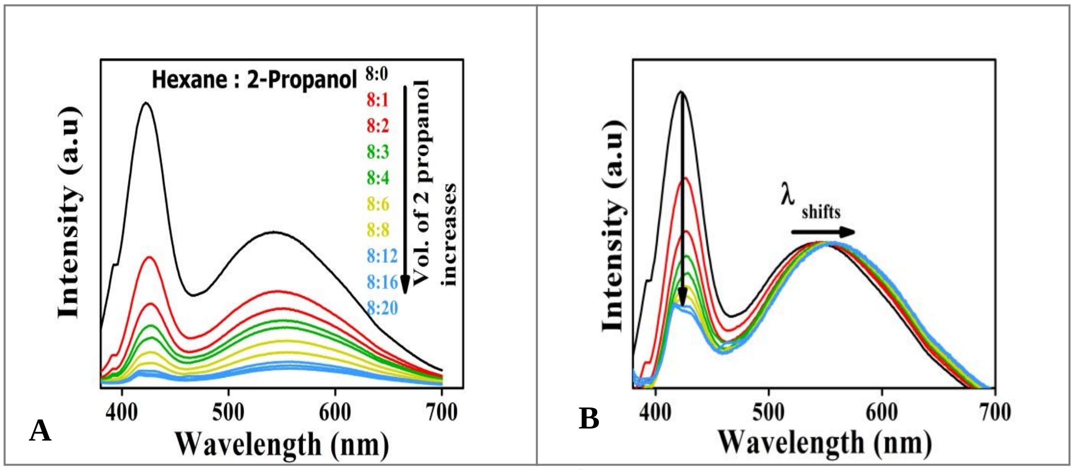

Figure S10. (**A**) Emission spectra (λ_{ex} = 369 nm) of $Zn_XCd_{1-X}S$ NCs in hexane at different volume of 2-propanol (V/V) and (**B**) corresponding normalized (to DLE maximum) emission spectra.

References:

1) J. Ouyang, C. I. Ratcliffe, D. Kingston, B. Wilkinson, J. Kuijper, X. Wu, J. A. Ripmeester and K. Yu, *J. Phys. Chem. C*, 2008, **112**, 4908-4919.

2) M. Zanella, A. Z. Abbasi, A. K. Schaper and W. J. Parak, *J. Phys. Chem. C*, 2010, 114, 6205-6215.

3) R. C. Weast, M. J. Astle, W. H. Beyer, *Hand book of Chemistry and Physics*, 64th ed, CRC Press, Inc., Boca Ratan, Fl, 1983, p E 50-51.

4) U. Resch, A. Eychmuller, M. Haase and H. Weller, *Langmuir*, 1992, **8**, 2215-2218.

5) K. K. Dey, B. R. Panda, A. Paul and A. Chattopadhyay, *J. Colloid Interface Sci.*, 2010, **348**, 335-341.

6) W. H. Melhuis, *J. Phys. Chem.*, 1961, 65, 229-235.

7) M.R. Kim, S. Park and D. Jang, *J. Phys. Chem. C*, 2010, **114**, 6452-6457.

8) Q. Zhang, Y, Gao, S. Zhang, J. Wu, H. Zhou, J. Yang, X. Tao and Y.Tian, *Dalton Trans.*, 2012, **41**, 7067-7072.

9) J. E. Murphy, M. C. Beard, A. G. Norman, S. P. Ahrenkiel, J. C. Johnson, P. Yu, O. I. Micic, R. J. Ellingson, A. J. Nozik, J. Am. Chem. Sci, 2006, 128, 3241-3247.

10) T. V. V. Kumar, S. Prabhakar and G. B. Raju, *J. Colloid Interface Sci.*, 2002, **247**, 275–281.