

## Supplementary Information

### **Illuminating Microemulsions: Ionic Liquid-CdS Quantum Dots Hybrid Materials as Potential White Light Harvesting Systems**

Krishnaiah Damarla,<sup>a</sup> Pankaj Bharmoria,<sup>a</sup> K. Srinivasa Rao,<sup>a</sup> Praveen Singh Gehlot,<sup>a</sup> and Arvind Kumar,<sup>a,b\*</sup>

<b>Contents:</b>	<b>Page No.</b>
<b>1. Experimental section:</b>	<b>.....02</b>
<b>1.0 Materials</b>	<b>.....02</b>
<b>1.1 Synthesis of ILs</b>	<b>.....02</b>
<b>1.2 Microemulsion preparation</b>	<b>.....04</b>
<b>1.3 Synthesis CdS QDs</b>	<b>.....04</b>
<b>2. Methods</b>	<b>.....05</b>
<b>2.0. Isothermal Titration calorimetry (ITC)</b>	<b>.....05</b>
<b>2.1. Dynamic light scattering (DLS)</b>	<b>.....06</b>
<b>2.2. Conductivity</b>	<b>.....06</b>
<b>2.3. Small Angle X-ray Scattering (SAXS)</b>	<b>.....06</b>
<b>2.4. Transmission electron microscopy (HR-TEM)</b>	<b>.....06</b>
<b>2.5. Powder X-ray diffraction (PXRD)</b>	<b>.....10</b>
<b>2.6. UV-Visible and fluorescence spectroscopy</b>	<b>.....11</b>
<b>2.7. Chromaticity diagrams</b>	<b>.....13</b>
<b>2.8. Time Resolved Photoluminescence Spectroscopy</b>	<b>.....14</b>
<b>2.9. Quantum efficiency calculations</b>	<b>.....15</b>
<b>3. Reference</b>	<b>.....15</b>

## 1. Experimental section:

### 1.0 Materials:

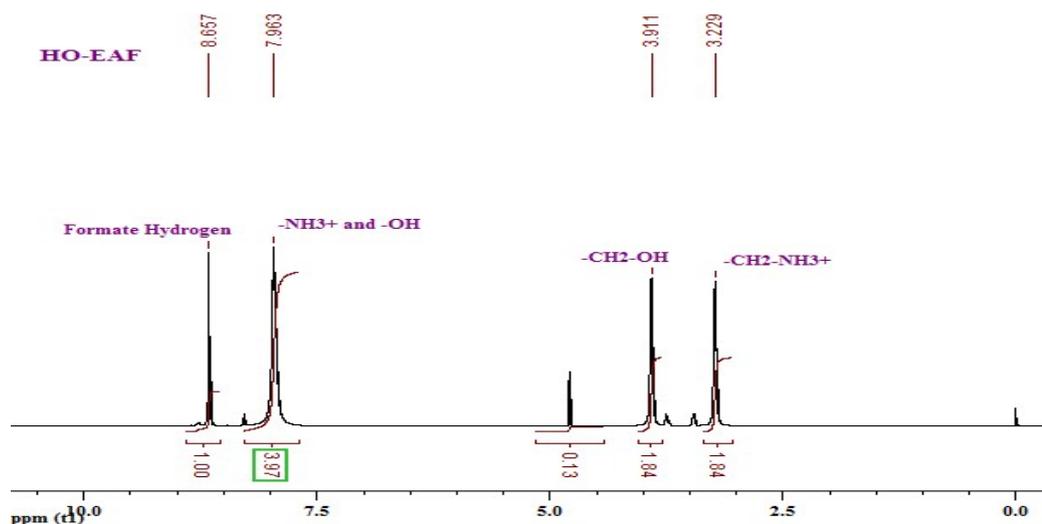
2-Aminoethanol (>99%), formic acid for analysis (98-100%), dioctyl sodium sulfosuccinate (AOT) (>98%), isooctane and L-proline, isopropanol, thionyl chloride, Cd(NO<sub>3</sub>).6H<sub>2</sub>O and sodium sulfide were purchased from TCI Chemical (India) Pvt. Ltd., Merck India, Otto chemicals, SRL India and SD fine chemicals Ltd. India respectively. All the chemicals were of AR grade and were used as received.

### 1.1 Synthesis of Ionic Liquids:

#### I) Hydroxyethylammonium formate (HO-EAF):

Hydroxyethylammonium formate was synthesized by employing simple acid-base reaction following an earlier reported procedure.<sup>1,2</sup> In brief, ethanolamine was taken in a round bottom flask and kept in ice bath. An equimolar amount of formic acid was slowly added to it. The reaction was carried out for 24 h. at room temperature. The viscous liquid obtained was heated at 70°C under high vacuum using rotary evaporator to remove excess ethanolamine and moisture present. The resulted IL was characterized by LC-MS and NMR.

<sup>1</sup>H-NMR: 200MHz ( C<sub>6</sub>D<sub>6</sub> as external solvent ): δH (ppm) 3.169 (t, 2H; -CH<sub>2</sub>-N-), 3.872 (t, 2H; -CH<sub>2</sub>-O-), 7.513 (s, 3H+1H; -NH<sub>3</sub> + OH), 8.642 (s, 1H; -H-COO- ) <sup>13</sup>C{<sup>1</sup>H} NMR (200 MHz, C<sub>6</sub>D<sub>6</sub> as external solvent): δC (ppm)170.225, 59.008, 42.159. ESIMS: (ESI<sup>+</sup>) m/z 62.06 [C<sub>2</sub>H<sub>8</sub>NO]<sup>+</sup> , (ESI<sup>-</sup>) 45.01[CHO<sub>2</sub>]<sup>-</sup>.



**Figure S1.** <sup>1</sup>H NMR spectra of hydroxyethylammonium formate (HO-EAF)

## II) Proliniumisopropylester dioctylsulfosuccinate ([ProC<sub>3</sub>][AOT]):

Synthesis of [ProC<sub>3</sub>][AOT] was done in two steps as reported in our earlier publications<sup>3,4</sup>  
The brief procedure is given below:

- a) *Synthesis of proliniumisopropylester hydrochloride (ProC<sub>3</sub>.HCl).* 0.13 moles of thionyl chloride was added drop wise to isopropanol at 0°C followed by the slow addition of 0.11 moles of proline at room temperature. The reaction mixture was refluxed for 4 h, and the reaction was monitored by TLC. Crude ProC<sub>3</sub>.HCl thus obtained was washed with hexane and dried under vacuum and followed by recrystallization with methanol. The obtained pure hygroscopic ProC<sub>3</sub>.HCl was dried and stored in desiccator.
- b) *Synthesis of [ProC<sub>3</sub>][AOT].* An equimolar mixture of ProC<sub>3</sub>.HCl and dioctyl sodium sulfosuccinate (AOT) were dissolved in dichloromethane (DCM) and stirred for 24 hours at room temperature. The precipitated NaCl was filtered with Whatmann filter paper. The DCM layer was washed with water for several times to completely remove Cl<sup>-</sup> ion present. The washing was performed until the aqueous layer gives clear solution even with the addition of excess 1M AgNO<sub>3</sub>. The DCM layer was then dried over Na<sub>2</sub>SO<sub>4</sub> followed by removal of solvent. Thus obtained IL-surfactant were dried for several hours under vacuum and stored in desiccator prior to use and characterized by LCMS and <sup>1</sup>HNMR techniques.

### <sup>1</sup>HNMR:

[ProC<sub>3</sub>][AOT], 1H-NMR: 500MHz (DMSO-d<sub>6</sub>): δH (ppm) 9.120 (s, 2H;), 5.132 (q, 1H), 4.47 (t, 1H), 3.980 (t, 4H), 3.730 (dd, 1H), 3.379 (d, 2H), 2.999 (s, 2H), 2.399 (1H), 2,032 (s, 3H), 1.609 (q, 2H), 1.38 (m, 18H;), 0.970 (t, 14H).

ESIMS: (ESI<sup>+</sup>) m/z 157.89 [C<sub>8</sub>H<sub>16</sub>NO<sub>2</sub>]<sup>+</sup>, (ESI<sup>-</sup>) 420.60 [C<sub>20</sub>H<sub>37</sub>O<sub>7</sub>S]<sup>-</sup>.

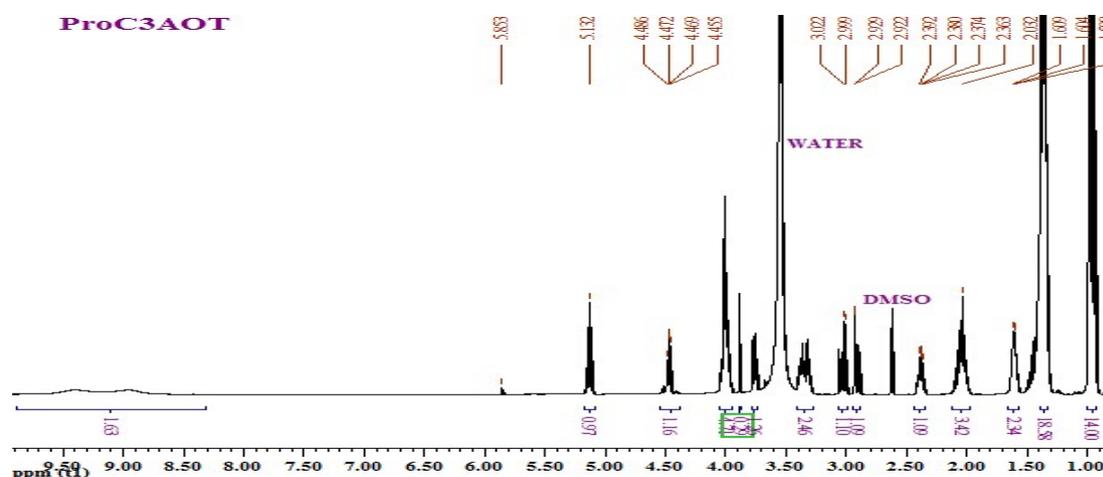
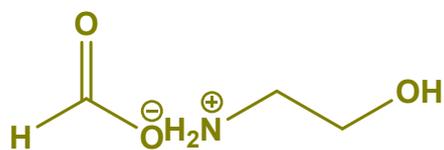
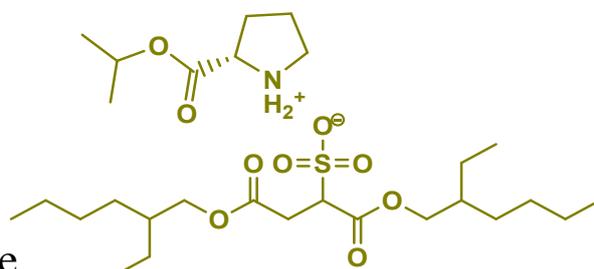


Figure S2.

## Molecular structure of the synthesized compounds



Hydroxyethylammonium formate



[ProC<sub>3</sub>][AOT]

### 1.2 Microemulsions preparation and Phase diagram:

Solutions of different percentage of ProC<sub>3</sub>AOT in isooctane were prepared by weight (5 to 95%) in 2 ml glass vials using the analytical balance (Denver Instrument APX-200) with a precision of 0.0001 g. Ionic liquid, HO-EAF was then added to these clear transparent solutions and stirred on a magnetic stirrer until these turned transparent to turbid. The ternary phase diagram was carried out by identifying the mono and biphasic regions visually.

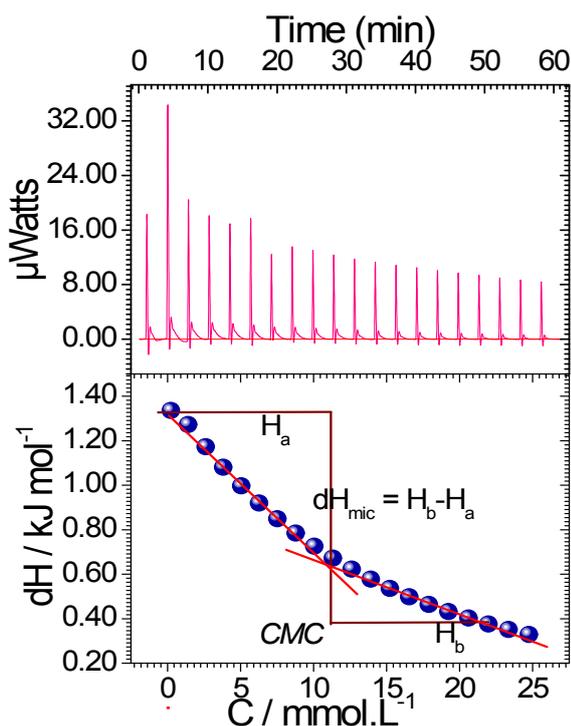
### 1.3 Synthesis and loading of CdS Quantum Dots in MEs:

Reverse micelles (RMs) of microemulsions (MEs); [HO-EAF]/[ProC<sub>3</sub>][AOT]/isooctane at R=1 were taken as a template. In a typical experiment, 2M of Cd (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O and Na<sub>2</sub>S were dissolved in HO-EAF (polar medium) separately by vigorous stirring. Equal amounts of (2M) of Na<sub>2</sub>S and Cd (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O solutions were added to the reverse micelles (1M [ProC<sub>3</sub>][AOT] in isooctane) up to the mole fraction R= 1. Initially Na<sub>2</sub>S was added in slightly warmed MEs with continuous stirring till it formed a uniform transparent solution. Slight warming was done just to ensure homogeneous mixing. Cd (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O solution was then slowly added dropwise to the Na<sub>2</sub>S loaded RMs until to get R=1. Thereafter the reaction was carried out at room temperature for about 12 h. deep yellow coloration of the solution indicated formation of CdS QDs. For characterization of CdS QDs, we methanol was added to the CdS loaded MEs for the demicellization and then the CdS QDs were collected with the help of centrifugation at 10000 rpm for about 15 mins. The collected yellow particles were washed 3 times with methanol, acetone and finally with water to remove traces of NaNO<sub>3</sub>. CdS loaded in MEs were characterized using UV-Vis, fluorescence, and time resolved photoluminescence spectroscopy (TRPL) and CdS QDs collected from MEs were analyzed using HR-TEM and XRD.

## 2. Methods

### 2.0. Isothermal Titration calorimetry (ITC)

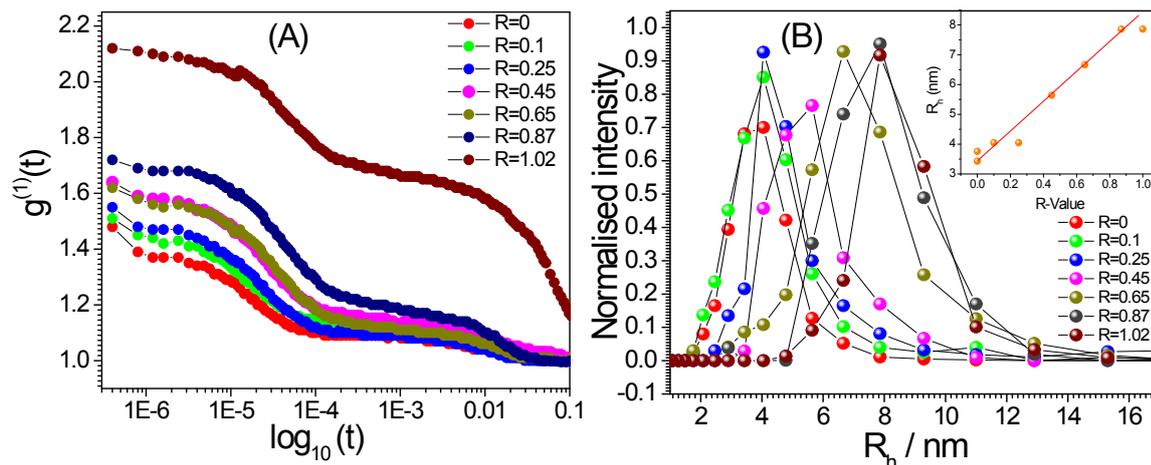
Enthalpy changes ( $\Delta H$ ) due to the aggregation of  $[\text{ProC}_3][\text{AOT}]$  in isooctane and HO-EAF were measured with the aid of MicroCal ITC200 microcalorimeter at 298.15 K. Initially sample and the reference cells were filled with isooctane having 200 $\mu\text{L}$ , then 2  $\mu\text{L}$  aliquots of 120mM  $[\text{ProC}_3][\text{AOT}]$  in isooctane stock solution with an instrument-controlled Hamiltonian syringe having volume capacity of 40  $\mu\text{L}$  were added to the preloaded sample cell with continuous stirring at 500 rpm. Similarly 0.6 $\mu\text{L}$  aliquots of 160 mM of  $\text{ProC}_3\text{AOT}$  in HO-EAF stock solution was added to the sample cell containing EOAF. The parameters such as time of addition and duration between each addition were controlled by the software provided with the instrument. Enthalpy changes at each injection were measured and plotted against the concentration using Origin software provided with the instrument.



**Figure S3.** ITC technique shows the aggregation behavior of  $[\text{ProC}_3][\text{AOT}]$  in Isooctane.

## 2.1. Dynamic light scattering (DLS)

The size of RMs was analyzed at 298.15 K, using a Spectro Size™ 300 (NaBiTec, Germany) light scattering apparatus with a He–Ne laser (660 nm, 4 mW). The apparent hydrodynamic measurements were carried out in a quartz cuvette of 1 cm path length by considering the viscosity and refractive indices of the solutions prepared. Samples prepared at different mole fractions i.e., HO-EAF/[ProC3][AOT] ratio  $R$  from 0 to 1 were analyzed.



**Figure S4.** (A) Intensity autocorrelation function of IL-based reverse micelles at different mole fractions ( $R = [\text{surfactant}] / [\text{Polar Phase}]$ ), (B) Intensity vs. size (inset swelling behavior (size vs R-value) of MEs) distribution plot.

## 2.2. Conductivity

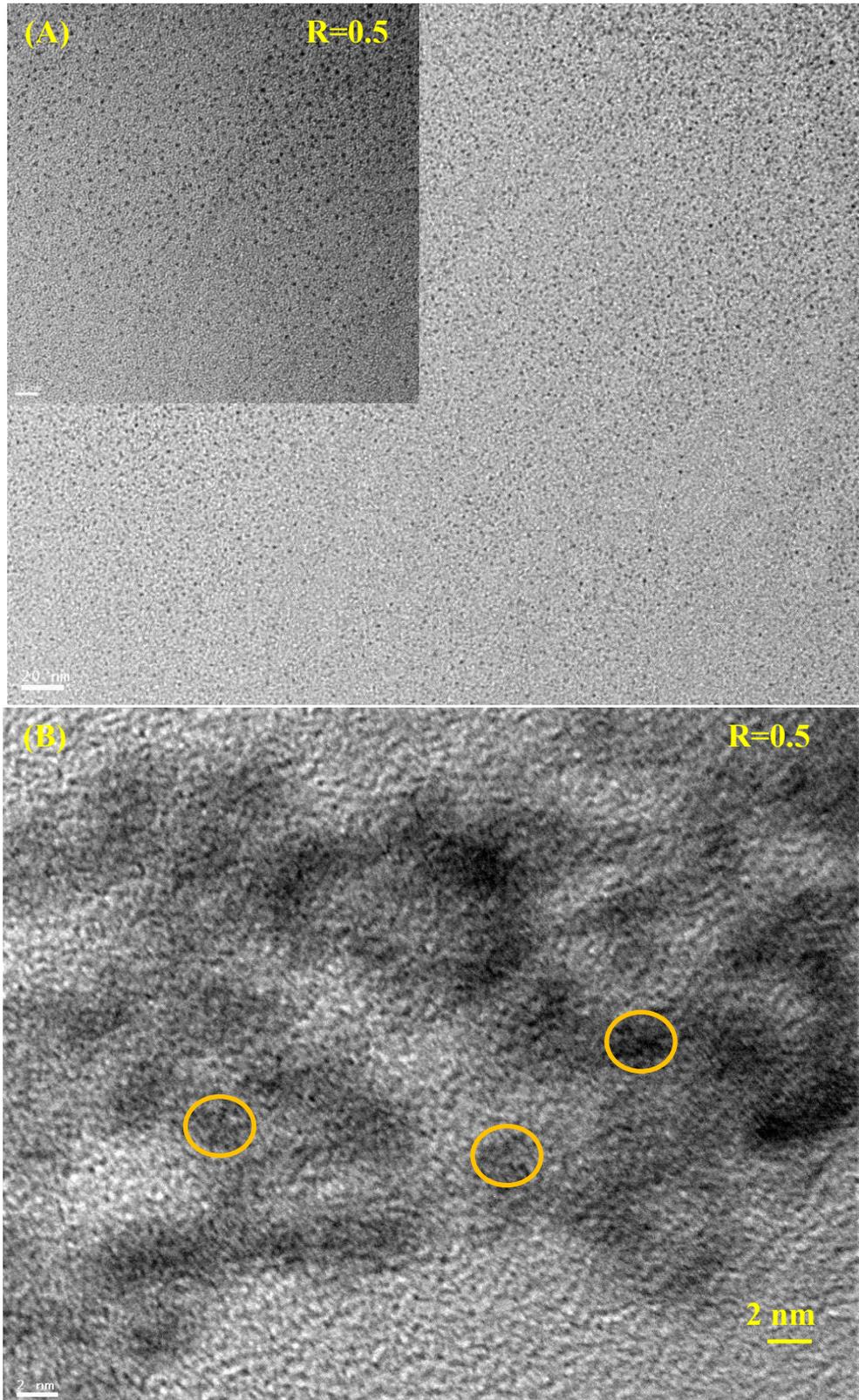
Detection of micro regions (IL/O, O/IL and bicontinuous) of MEs was carried out using conductivity measurements were performed using a Keithley 2635A source meter unit (SMU). The micelles of [ProC<sub>3</sub>][AOT] in HO-EAF having the mole fraction equal to one ( $R=1$ ) were subjected to titrate with isooctane at ambient conditions and the conductivities were noted for the micelles at every addition (each addition having 0.6g isooctane) until the solution became turbid.

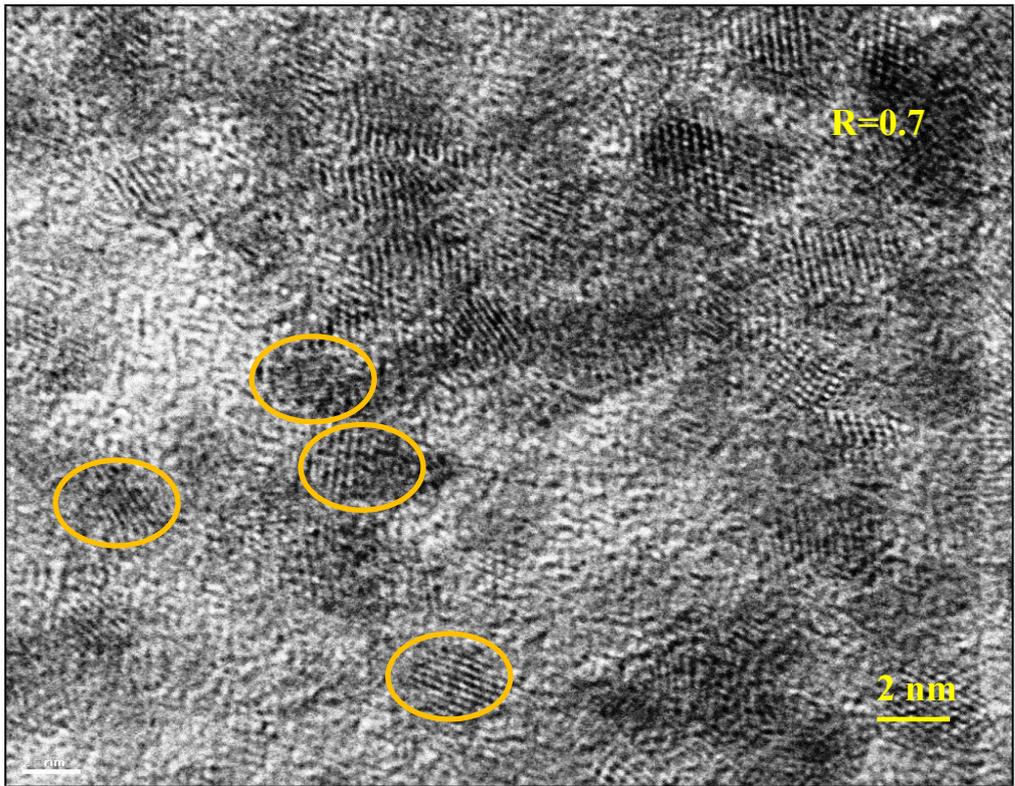
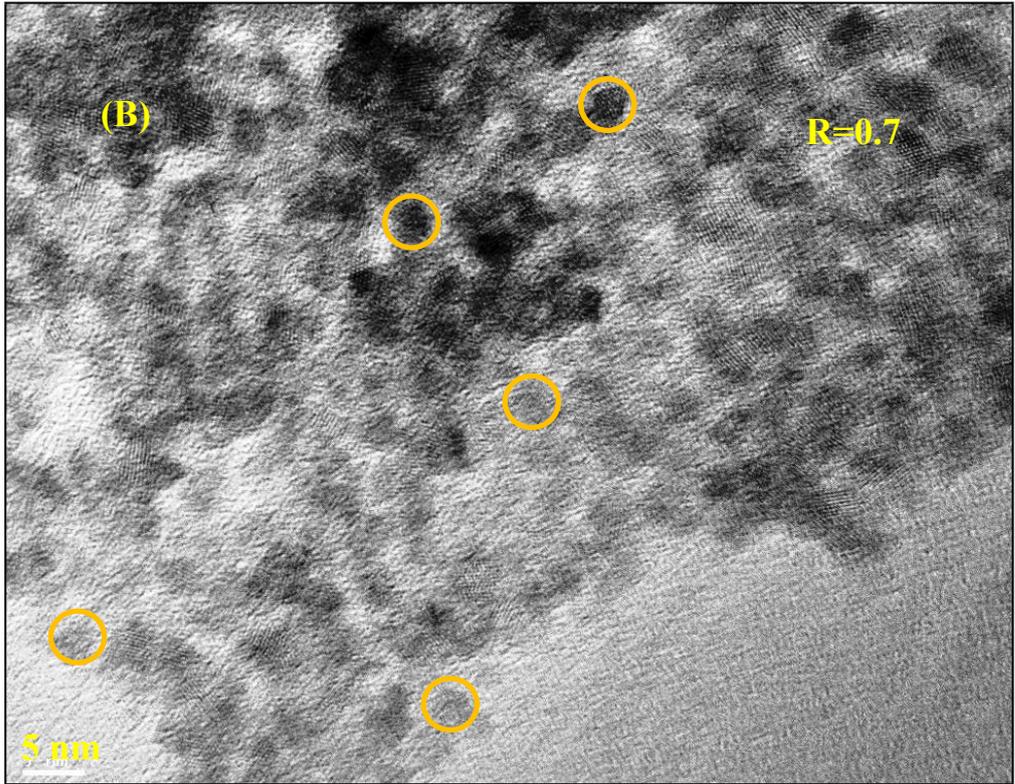
## 2.3. Small Angle X-ray Scattering (SAXS)

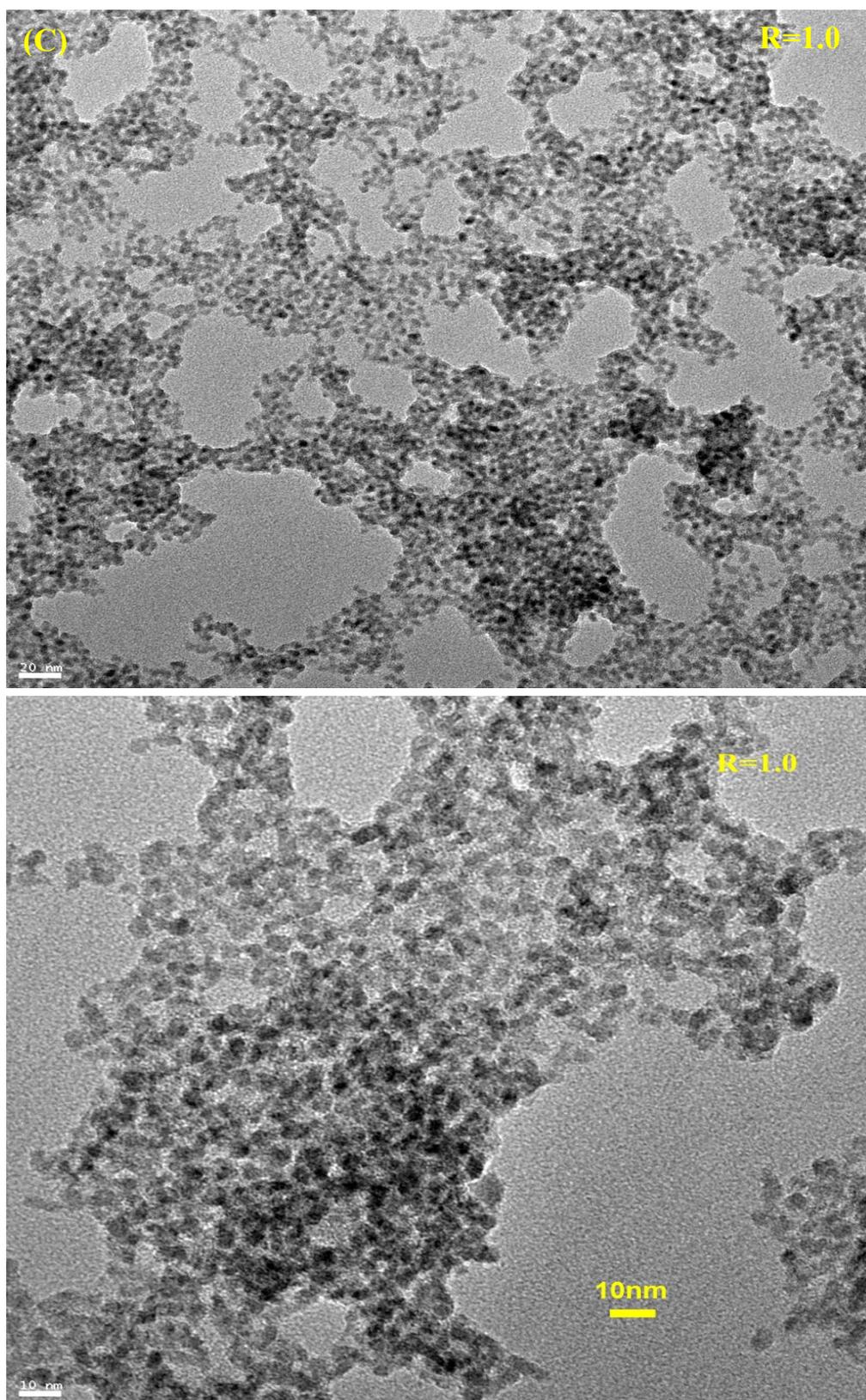
Small-angle X-ray scattering (SAXS) measurements were performed as reported in literature.<sup>5</sup> The measurements were performed using SAXSess mc<sup>2</sup>, a modular nanostructure analyzer from Anton Paar GmbH, Graz, Austria, equipped with a sealed copper tube (operated at 40 kV/50 mA and using a monochromatic Cu K $\alpha$  radiation with  $\lambda = 1.54 \text{ \AA}$ ) line collimated X-ray source and charge coupled device (CCD) detector. The sample was sealed in 1 mm quartz capillary and was placed at 309 mm from the detector to record the resulting scattering intensities as a function of  $q$  (within the range 0.1–6 nm).

#### 2.4. High Resolution - Transmission electron microscopy (HR-TEM)

Transmission electronic microscope (TEM) images were recorded using a JEOL JEM 2100 microscope. The samples were prepared by mounting acetone dispersion on lacey carbon formvar coated Cu grids. TEM images reveals that all the shapes are constituent of very small nanoparticles with average particle depending upon R values of RMs.



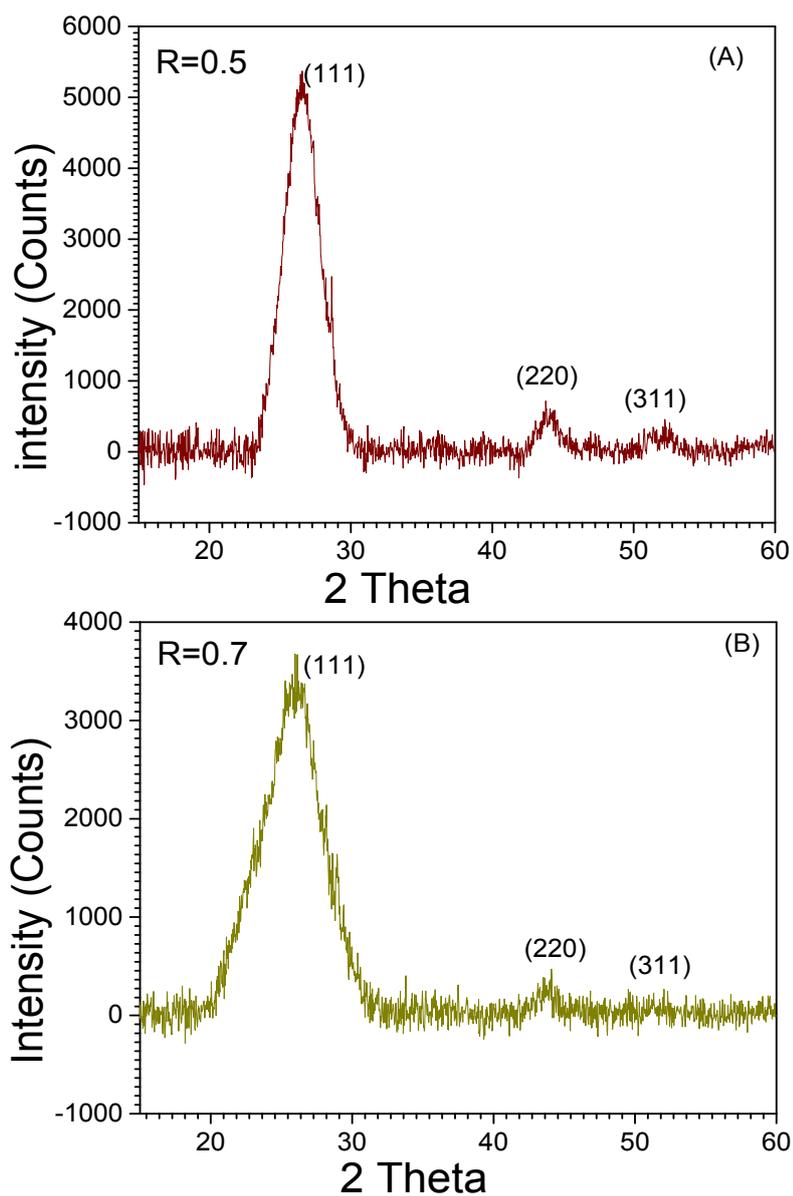




**Figure S5.** TEM and HR-TEM images of CdS QDs synthesized at different R values (A) R=0.5 (B) R=0.7 and (C) R= 1.0

## 2.5. Powder X-ray diffraction (PXRD)

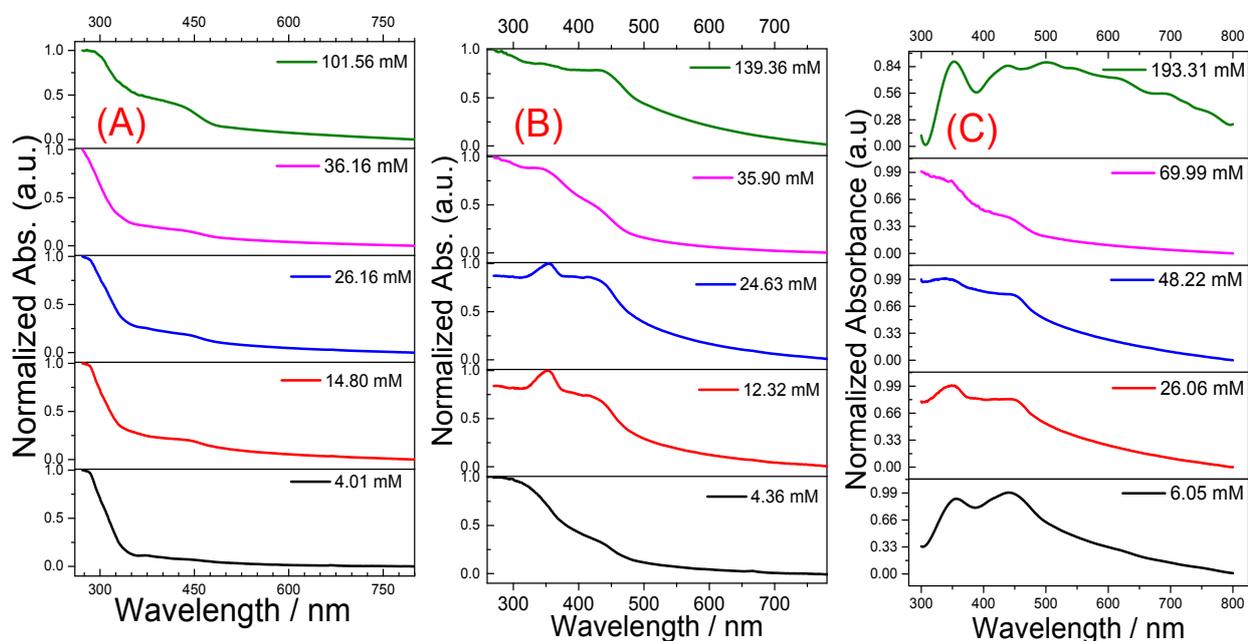
X-ray measurements were performed using a PANalytical Empyrean (PIXcel 3D detector) system with  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). All synthesized samples exhibit XRD peaks and well resolved diffraction peaks can be indexed to the (111), (220), and (311) planes of a zinc blende structured CdS.



**Figure S6.** XRD spectra of CdS QDs synthesized at (A) R=0.5, (B) 0.7.

## 2.6. UV-Visible and fluorescence spectroscopy

UV-vis spectra and Fluorescence spectra were recorded using UV 3600 Shimadzu UV-vis-NIR spectrophotometer and Fluorolog Horiba Jobin Yvon spectrophotometer respectively at 298.15k for the absorbance and emission spectra of CdS QDs.



**Figure S7.** UV-Vis spectra of (A) R=0.5, (B) 0.7 and (C) R=1.0 at variable concentration of CdS QDs dispersed in reverse micelles.

### Size of CdS QDs calculated from Peng's equation at different wavelengths (Figure 3A):

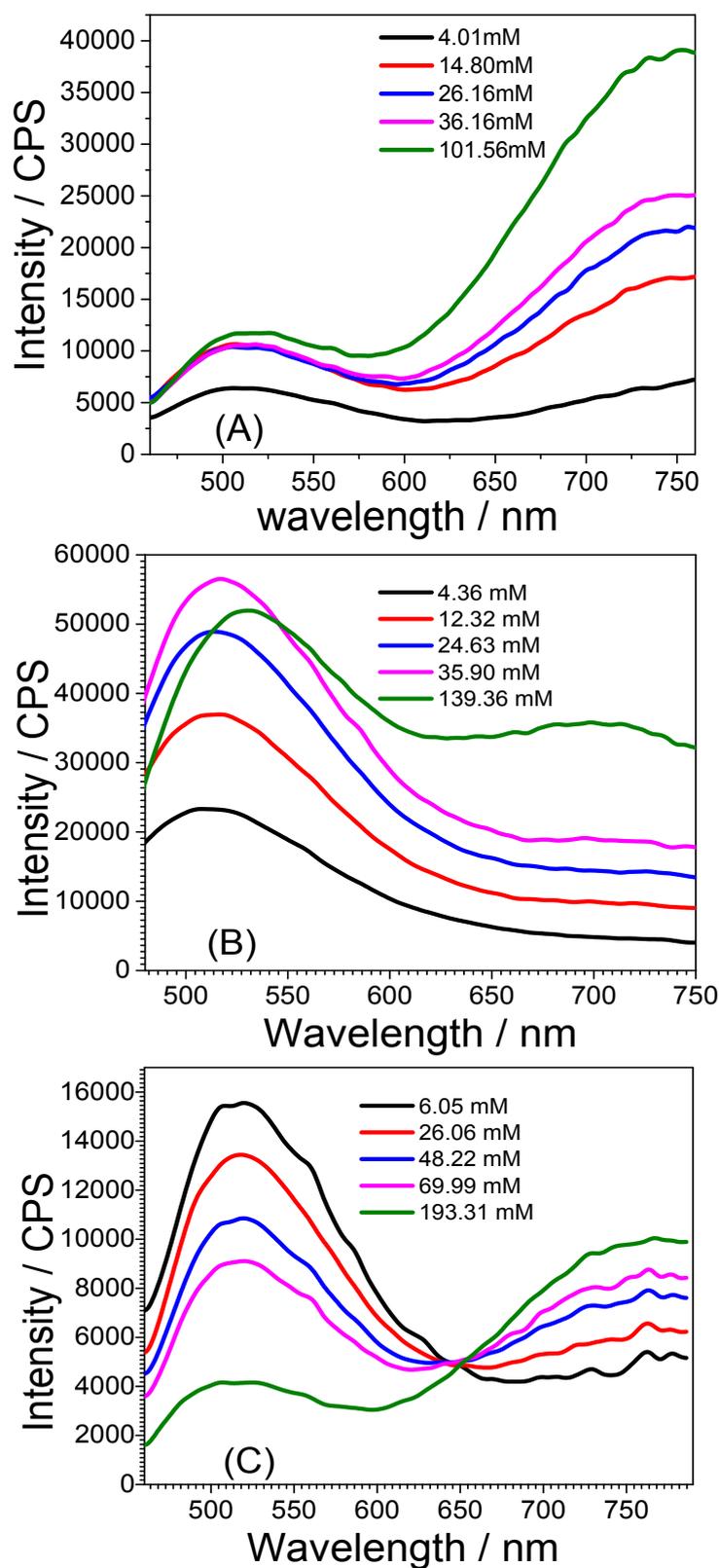
$$D = (-6.6521 \times 10^{-8})\lambda^3 + (1.9557 \times 10^{-4})\lambda^2 - (9.2352 \times 10^{-2})\lambda + 13.29$$

Where D is the size (nm),  $\lambda$  is the wavelength

Wavelength ( $\lambda$ )	Size
353 nm	2.133 nm
452 nm	4.680 nm
520 nm	8.790 nm

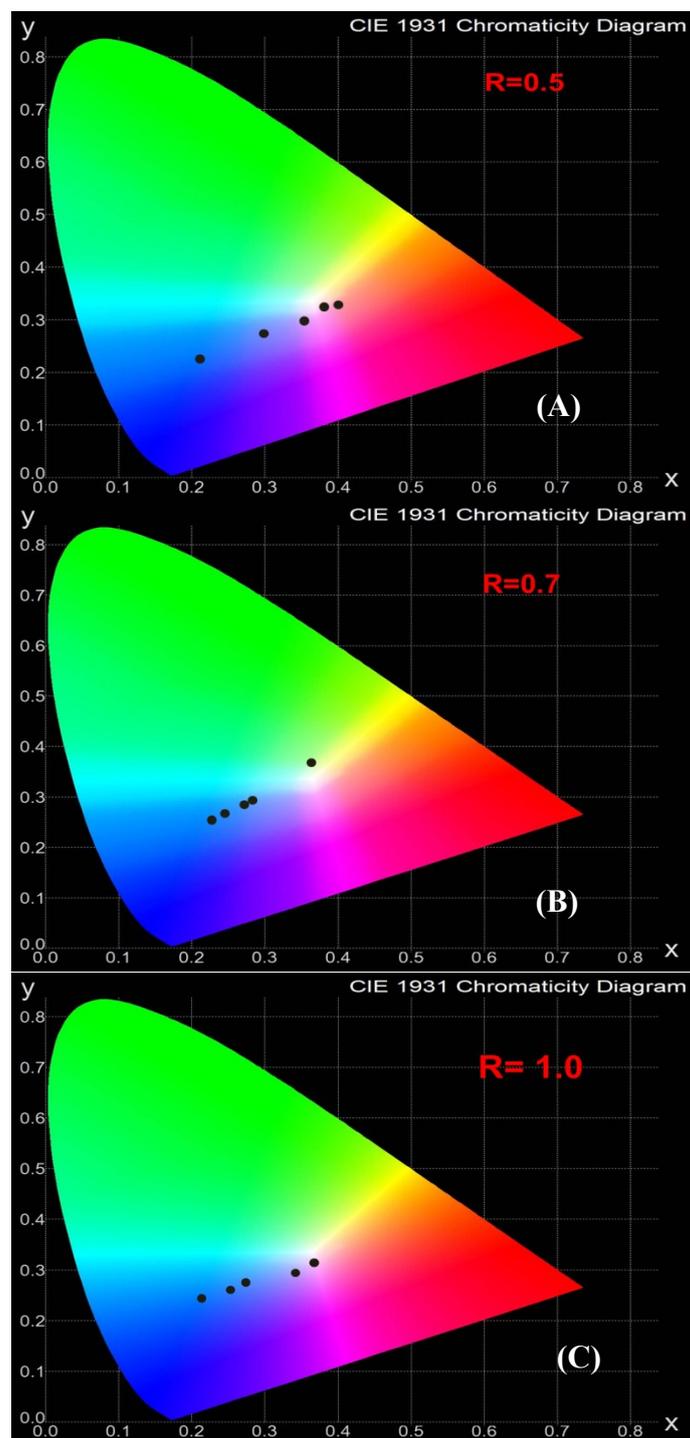
The spectra with wavelength at 452 nm have been considered.

### Emission spectra:



**Figure S8.** Emission spectra of (A) R=0.5, (B) 0.7 and (C) R=1.0 at variable concentration of CdS QDs dispersed in reverse micelles.

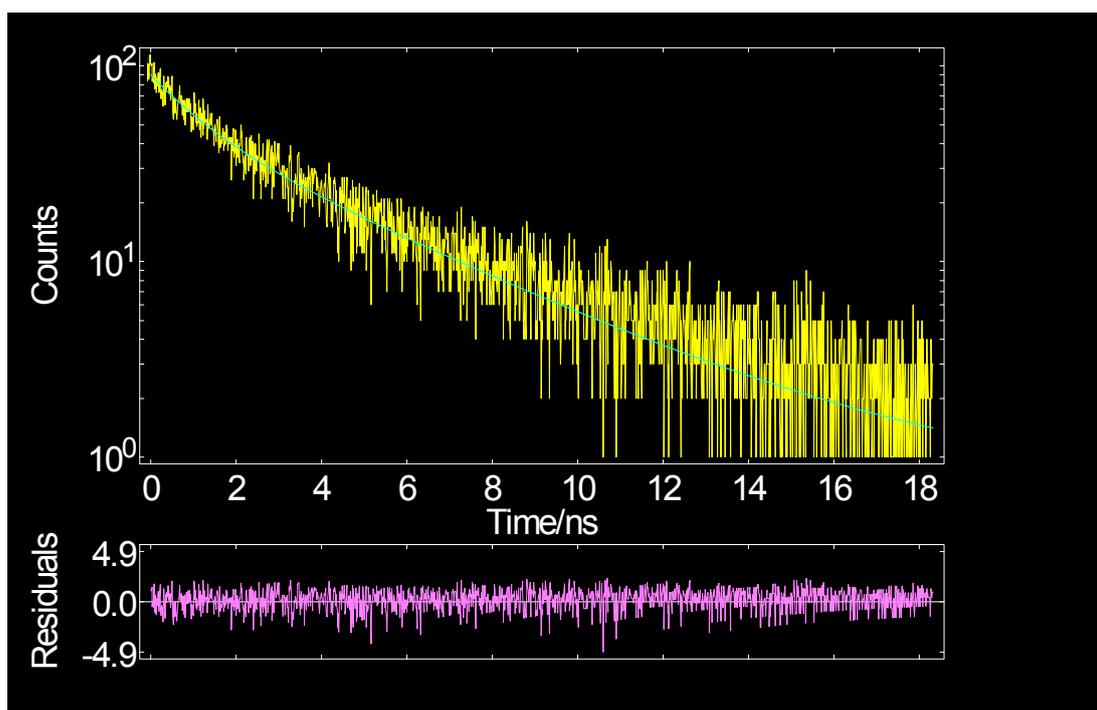
## 2.7. Chromaticity diagrams:



**Figure S9.** CIE Chromaticity diagram of CdS loaded microemulsions having variable CdS concentrations (similar as provided in Figure S6) at different R values (A) R=0.5 (B) R=0.7 and (C) R=1.

## 2.8. Time Resolved Photoluminescence Spectroscopy.

Fluorescence decay profiles were measured using a time-correlated single-photon counting spectrometer i.e., Edinburgh instruments OB 920 fluorescence spectrophotometer using a pulsed diode laser (Laser - EPLED-405 nm; emission: 500 nm) as an excitation source. Fluorescence lifetimes were measured by plotting fluorescence decay curves as a function of time (t).



EDINBURGH  
INSTRUMENTS  
F900 8/4/2011

### Fit Results

Fit :  $A+B1\exp(-t/\tau_1)+B2\exp(-t/\tau_2)$

Decay Scan : **Fit Result500nm 200sec**  
 File location : C:\Documents and Settings\instrument\Desktop\krishna-smc\Fit Result exponential f  
 Range (ch) : 0 to 4095  
 Peak Count : 101 in channel 2593  
 Total Count : 26336

Time Calibration : 0.012 ns/ch  
 Total Experiment Time : 199.98 s

Fit Range (ch) : 2594 to 4095

Parameter	Value	Std. Dev.	Rel %
$\tau_1$	1.102E-009 s	1.5241E-010 s	
$\tau_2$	4.256E-009 s	2.3110E-010 s	
B1	39.162	3.7843	16.72
B2	50.493	4.0271	83.28
A	0.729		
$\chi^2$	1.062		

Figure S10. Time resolved photoluminescence spectra of CdS QDs loaded at R=1.

## 2.9. Quantum efficiency calculations:

Using quinine sulphate as standard quantum efficiency was calculated with following formula.

2M quinine sulphate was taken in sulphuric acid having the quantum yield is 0.577.

$$\phi = \phi_R \times \frac{I}{I_R} \times \frac{A_R}{A} \times \frac{\eta^2}{\eta_R^2}$$

Where,

$\phi, \phi_R$  = Quantum yield of sample and reference,

$I, I_R$  = Emission of the sample and reference,

$A, A_R$  = optical density of the sample and reference,

$\eta^2, \eta_R^2$  = refractive index of the sample and reference respectively.

## 3. References

1. J. P. Belieres and C. A. Angell, , Protic Ionic Liquids: Preparation, Characterization, and Proton Free Energy Level Representation. *J. Phys. Chem. B* **2007**, *111*, 4926-4937.
2. K. S. Rao, S. So, and A. Kumar, Vesicles and reverse vesicles of an ionic liquid in ionic liquids. *Chem. Commun.* **2013**, *49*, 8111-8113.
3. T. J. Trivedi, K. S. Rao, T. Singh, S. K. Mandal, N. Sutradhar, A. B. Panda and A. Kumar, Task-Specific, Biodegradable Amino Acid Ionic Liquid Surfactants. *ChemSusChem.* **4** (2011) 604-608.
4. K. S. Rao, P. S. Gehlot, T. J. Trivedi and A. Kumar, Self-assembly of new surface active ionic liquids based on Aerosol-OT in aqueous media; *Journal of Colloid and Interface Science*, **2014**, *428*, 267–275.
5. R. Rai and S. Pandey, Evidence of Water-in-Ionic Liquid Microemulsion Formation by Nonionic Surfactant Brij-35, *Langmuir*, **2014**, *30*, 10156–10160.
6. W. W. Yu, L. Qu, W. Guo, X. Peng, Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals, *Chem. Mater.* **2003**, *15*, 2854-2860.