Electronic Supplementary Material (ESI) for

Versatile Surface-Active Ionic Liquid: Construction of Microemulsions and their Applications in Light Harvesting

Krishnaiah Damarla,[a,b] Sanjay Mehra,[a,b] Pratap Bahadur,[c] Debes Ray,[d] V. K. Aswal,[d] and Arvind Kumar,*[a,b]

[a]CSIR-Central Salt and Marine Chemicals Research Institute, G. B. Marg Bhavnagar-364002, Gujarat, India.

[b]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.

[c]Department of Chemistry, V.N. South Gujarat University, Udhana-Magdalla Road, Surat 395 007, Gujarat, India.

[c]Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India.

Corresponding author: arvind@csmcri.res.in; mailme_arvind@yahoo.com

Synthesis of Ionic Liquids

(1) Ehanolammonium nitrate: The reaction was carried out in a methanol solvent where, the nitric acid was slowly added to methanolic solution of ethlyamine in an ice bath and further the reaction mixture was kept for 24 h at room temperature with constant stirring. After that, the methanol solvent was removed and the product was washed with diethyl ether to remove unreacted reactant. After drying, the product was stored in the vacuum desiccator at 70 °C and characterized using ^{1}H NMR and LC-MS techniques

^{1}H NMR (EAN) (200MHz, DMSO-d$_6$, δ$_H$) 1.149 (t, 3 H, CH$_3$- CH$_2$), 2.85 (t, 2H, CH$_2$-N), 7.76 (s, 3H, NH$_3$); ESIMS: (ESI$^+$) m/z 46.09 [C$_2$H$_8$N]$^+$, (ESI$^-$) 62.15 [NO$_3$]$^-$.
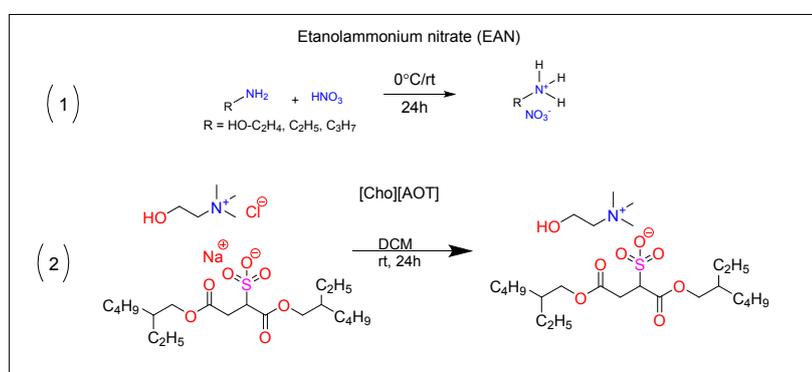

Fig. S1 General synthetic procedure of ILs which are used in this study.

(2) Choline dioctylsulfosuccinate, [Cho][AOT]: Equimolar amounts of choline chloride and aerosol OT were dissolved in water and stirred at room temperature for 24h. The progress of the reaction was monitored by TLC. After completion of the reaction the product was extracted into DCM layer, followed by washing the DCM layer with small amount of water for several times to make the IL chloride free. Washing performed until the aqueous layer gives clear solution even with the addition of excess 1M AgNO$_3$. The chloride free DCM layer was then distilled to obtain [Cho][AOT]. Further, [Cho][AOT] is dried under vacuum for several hours to remove the moisture present and stored in desiccator. The purity of the [Cho] AOT was ensured from ^{1}HNMR, LC-MS techniques

^{1}H-NMR: 600MHz (DMSO-d6): δ$_H$ (ppm) 0.85 (m, 12H), 1.26 (m, 16H), 1.51 (m 2H), 2.80 (m, 2H), 3.10 (m, 4H), 3.41 (s, 9H), 3.66 (m, 1H), 3.90 (m, 5H)

ESI-MS: [C$_5$H$_{14}$NO]$^+$ m/z:104.10, [C$_{20}$H$_{37}$O$_7$S]$^-$ m/z = 421.2.

Calculation of Surface tension parameters

The solution (SAIL ([Cho][AOT]) in water) should be prepared 10 times higher than that of *cmc* or *cvc* and left for atleast 15min. Then, the solution was titrated against the pure desired solvent which was taken in standard vessel having diameter 70mm. The data was noted and it is found to be accurate within ±0.1 mN m^{-1}. Thermodynamic parameters of surfactant aggregation and interaction with the solutions are derived using the following equations.

1. Adsorption efficiency (pC_{20}): This parameter indicates the efficiency of surface-active moieties to adsorb at the air-solution interface and can calculated using equation 1.

$$pC_{20} = -\log C_{20} \dots\dots\dots\dots\dots\dots(1)$$

where C_{20} is the concentration required to reduce the surface tension of pure solvent or solution by 20 mN·m^{-1}. A higher pC_{20} value is indicative of a higher adsorption efficiency of the surface-active moieties at the interface and more efficiency in reducing surface tension.

2. Surface pressure at *cmc* (π_{cmc}): This parameter indicates the maximum reduction of surface tension caused by the dissolution of surfactant molecules and hence becomes a measure for the effectiveness of the surfactant to lower the surface tension of either pure solvent or biopolymer solution. It can be calculated using equation 2.[1]

$$\pi_{cmc} = \gamma_o - \gamma_{cmc} \dots\dots\dots(2)$$

where γ_o is the surface tension of pure solvent or solution and γ_{cmc} is the surface tension of the solution at *cmc*.

3. Relative Surface Excess (Γ_{max}): Relative amount of surfactant adsorbed at the interface and can be calculated using Gibb's adsorption equation (3). [1]

$$\Gamma_{max} = \frac{1}{nRT} lt_{[C]\to 0}\left(\frac{\partial \gamma}{\partial lnC}\right)_T \dots\dots\dots\dots(3)$$

Where, *n* = number of species formed per IL molecule in solution upon ionization, R = Universal gas constant, *T* = Absolute temperature and C = Molar concentration of SAIL in the solution.

The value, $(\frac{\delta \gamma}{\delta \ln C})_T$ can be obtained from the slope of γ vs *log*C plot by 2nd order polynomial

4. Area of exclusion per molecule (A_{min}): Minimum area occupied by surfactant monomer at the interface, calculated using equation (4). [1]

$$A \frac{10^{18}}{N_A \Gamma_{max}} min \quad \text{.................4}$$

Where, N_A = Avogadro number and A_{min}= Higher adsorption of monomer at the interface.

5.   Standard Gibb's free energy of Interfacial adsorption (ΔG_{ad}°): Feasibility of surfactant adsorption at the air-solution interface can be calculated using equation (5). [1]

$$\Delta G_{ads}^o = \Delta G_{mic}^o - (\pi_{cmc}/\Gamma_{max}) \quad \text{............5}$$

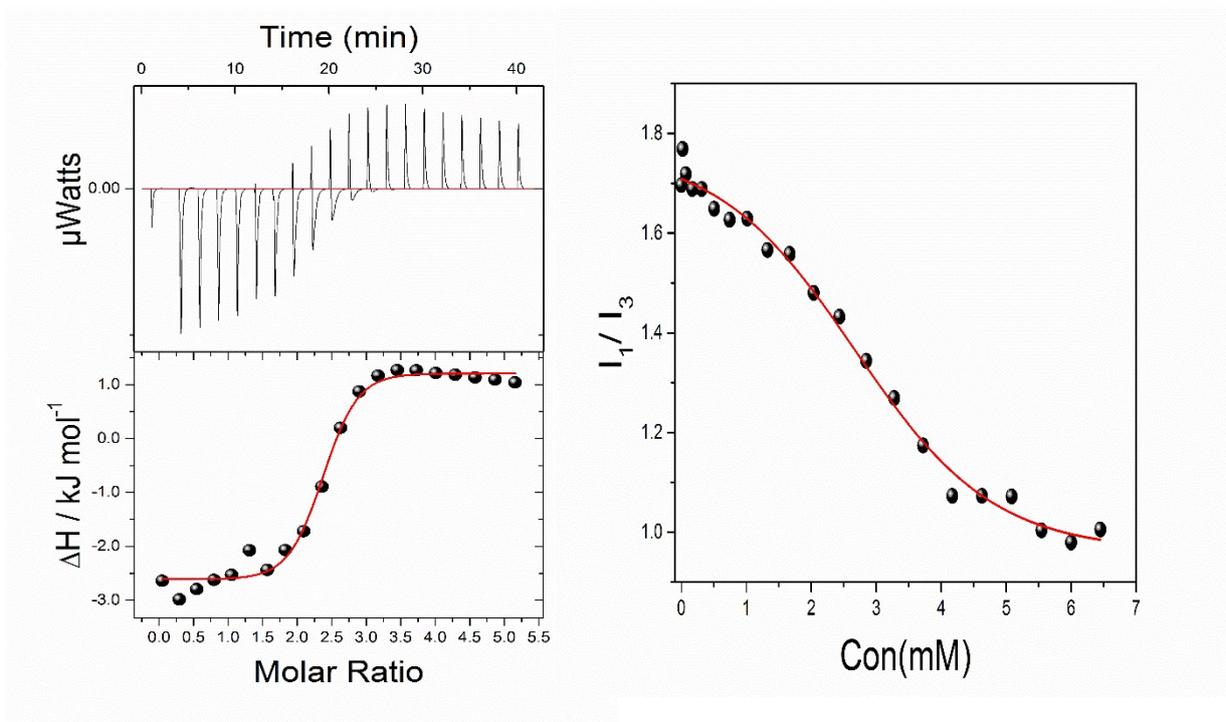Where, ΔG_m^o is the standard Gibb's free energy of micellization.

Fig. S2 ITC and Pyrene fluorescence showing the aggregation behavior of [Cho][AOT] in water).

Table S1. Surface parameters of [Cho][AOT] in various solvents.

Medium	CVC (mM)	γ_{cvc} (mNm^{-1})	π_{cvc} (mNm^{-1})	pC$_{20}$	Γ_{max} ($\mu mol\ m^{-2}$)	A$_{min}$ (A^o)	P
water	2.38	29.45	41.32	4.12	1.45	114.5	0.183
EG	3.65	38.15	11.15	------	-------	-------	--------
EAN	18.1	29.48	18.11	1.70	0.54	304.003	0.138
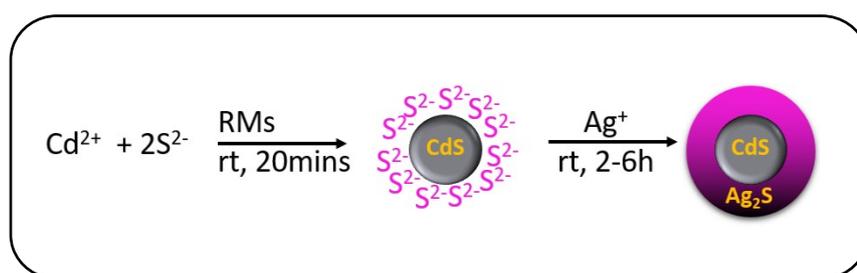
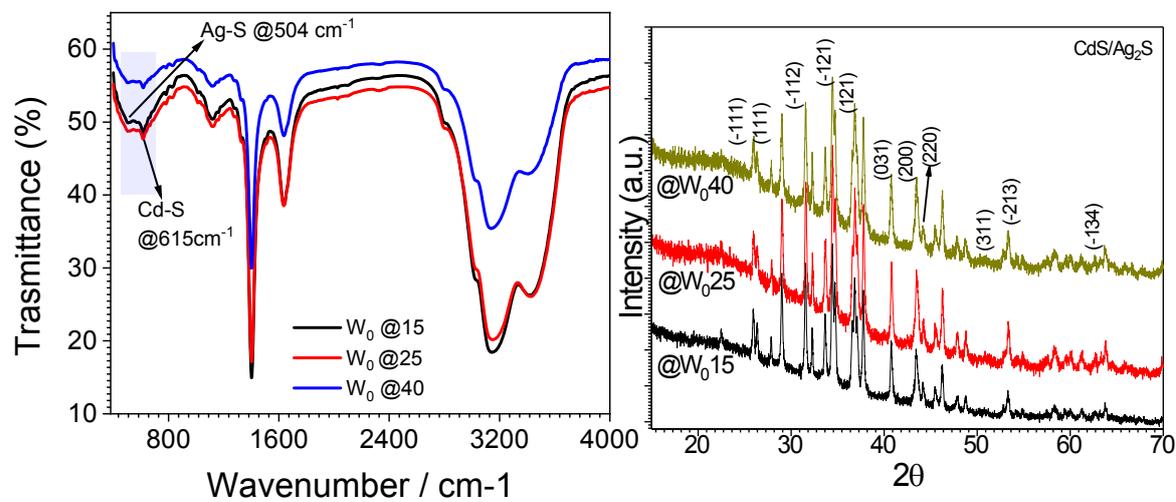**Fig. S3** Reaction procedure of core/shell QDs.

Fig. S4 FTIR and PXRD images of the core/shell QDs CdS/Ag$_2$S at different R (W$_o$) values (W$_o$ @15, W$_o$ @25 and W$_o$ @40).
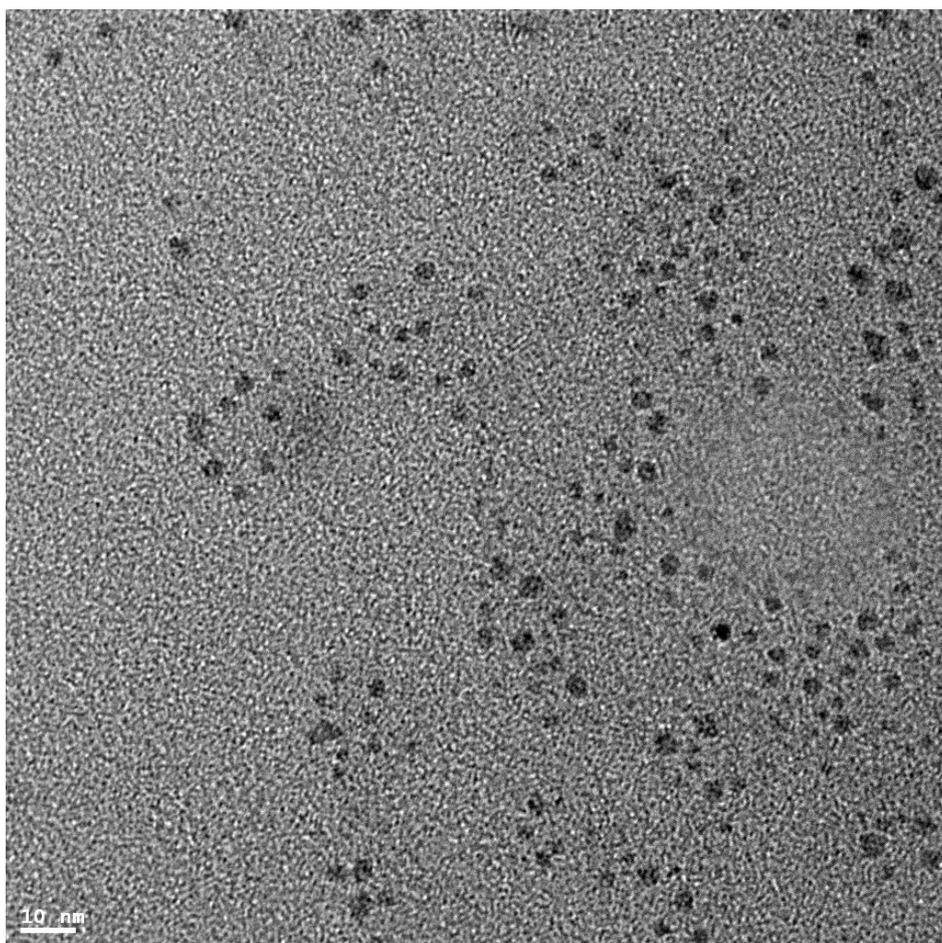
Fig. S5 TEM images of the core/shell QDs CdS/Ag$_2$S at W$_o$ @25
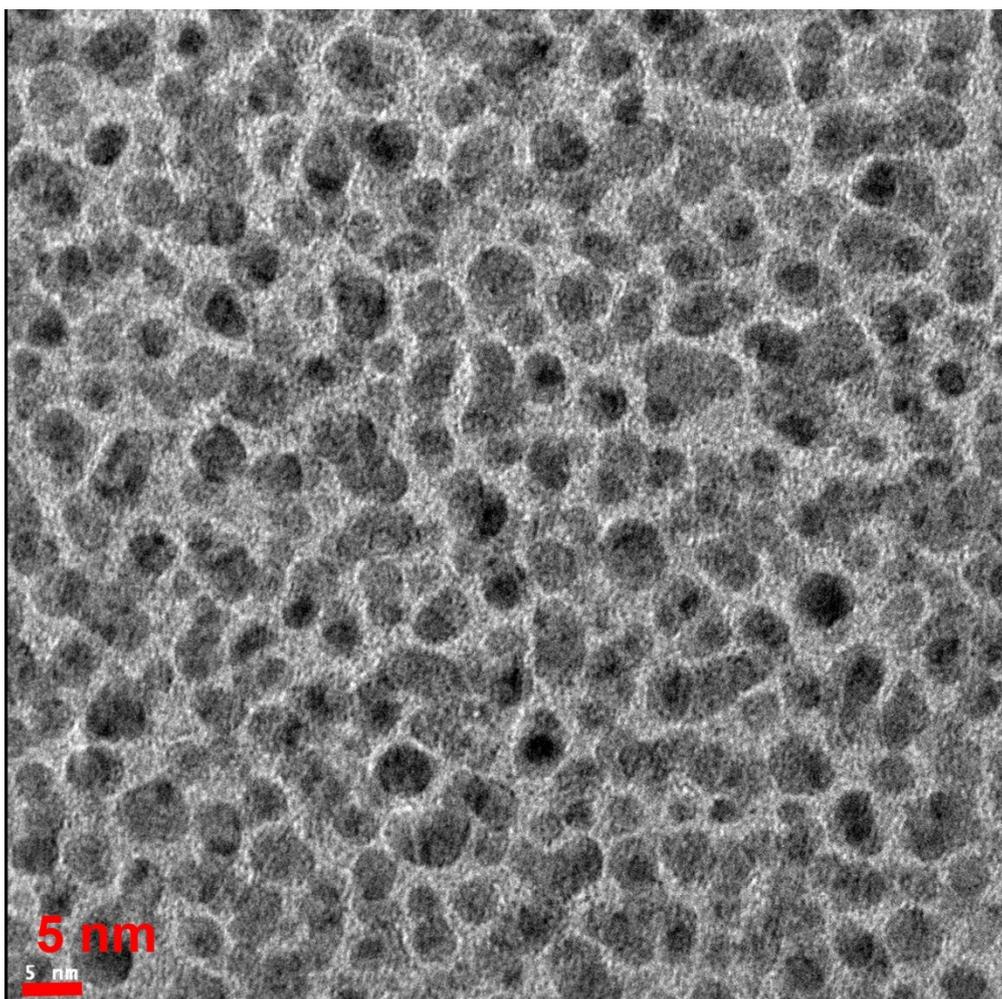
Fig. S6 TEM images of the core/shell QDs CdS/Ag$_2$S at W$_o$ @40).

References

1. Drach, M.; Rudziå„Ski, W. A.; Warszyå„Ski, P.; Narkiewicz-Michaå„Ek, J. Adsorption of Surfactants at Air/Solution Interfaces: Theoretical Description of Adsorption Equilibrium Based on a Model of Clustering of the Surfactant Molecules at the Air/Solution Interface. *Phys. Chem. Chem. Phys.* **2001**, *3*(22), 5035–5042.