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The effect of tetraalkylammonium and alkyl sulfate salts on the fluorescence bands of quantum-sized CdS

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Abstract

The effect of alkyl sulfates and tetraalkylammonium salts on fluorescence quantum yield and lifetime of several colloidal Q-CdS particles was studied. The Q-CdS clusters were prepared to emit an isolated fluorescence band, with a maximum fluorescence wavelength at 460 nm, 481 nm or 559 nm. Quaternary ammonium salts and alkyl sulfates bearing alkyl groups with several chain lengths were used: R_4NCl, with $R = C_2H_5$, C_4H_9 or C_6H_{13} and $NaRSO_4$, with $R = CH_3$, C_8H_{17} and as a reference, Na_2SO_4 and/or NaCl. A partial quenching effect of the salts on the Q-CdS clusters fluorescence was observed. For a given alkyl group, the quenching effect increases with the maximum wavelength of the fluorescence band. The influence of the alkyl groups on the quenching of a given fluorescence band was found to be different for the two kinds of salts. We believe that the quenching by tetraalkylammonium salts is due to the adsorption of the cations on the clusters surface. This could lead to ionic pair formation by R_4N^+ with negative either phosphate or surface sites on the Q-CdS clusters, stabilizing electrons in surface traps. The quenching effect increased with the length of the alkyl chain. This may be due to a hydrophobic effect acting to give this trend. In the case of quenching by sodium alkylsulfate salts, the values of K_{SV} are similar for the different substrates and for a given band. This could be explained if the quenching effect is mainly due to Na^+. However, the values of K_{SV} are different for the different bands. Since Cd^{+2} is used to activate the fluorescence when the clusters are prepared, we believe that the quenching process consists in a displacement of Cd^{+2} by Na^+ on the surface of the clusters. Since the several clusters have different surface properties, the effect varies for each of the clusters. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Alkyl sulfates; Q-CdS clusters; Salts

1. Introduction

Semiconductor colloidal particles in the nanometer size range display interesting photochemical and photophysical properties which are different from the bulk and from the molecular substance properties and are currently under intensive research work [1–5]. In particular, the fluorescence characteristics of quantum-confined semiconductor particles, usually named as Q-SC particles, are influenced by the particle size and surface modifications [6–12].

In the semiconductor Q-clusters, the charge carriers electron (e^-) and hole (h^+), generated by the absorption of a photon, are trapped into surface trap states in less than about 1 ps and they can subsequently undergo radiative or non-radiative decay, or transfer to a redox species which is in the solution phase [13,14]. A number of species in the solution phase, which interact in some way with the clusters' surface could modify the extent in which the radiative, non-radiative or chemically reactive route are followed. Therefore, the study of the effects of species in solution on the fluorescence of the clusters, by stationary and time-resolved fluorescence techniques, can provide information on the energetics and dynamics of photogenerated charge carriers. The observed effect depends on the identity and charge of the solute, the pH in the solution phase, and the characteristics of the cluster's surface. The latter are dependent on the preparation method. In particular the surface properties depend strongly on the type and quantities of stabilizers. Chandler and Coffer [15] have studied the influence of the charge of several stabilizers on the fluorescence quenching of Q-CdS particles in inverse micelles and organic solvents. The clusters were prepared using anionic and cationic stabilizers and the quenchers were neutral molecules, positive or negative ions. They observed partial quenching of the excitonic fluorescence, which was dependent of the charge possessed by the quencher, among them the dication methylviologen. We also obtained a partial quenching on the excitonic fluorescence of Q-CdS using this quencher, but we observed complete or

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almost complete quenching of the fluorescence of other Q-CdS clusters prepared under different conditions, with the same quencher [16]. In the absence of stabilizers, i.e., with 'naked' CdS clusters, the fluorescence quenching effect of metal ions like Cu^{+2} has been attributed to the binding of copper ions onto the surface of semiconductor [17].

We have prepared Q-CdS samples that exhibit an isolated, either excitonic or trapped fluorescence band. This allows to study separately the effect produced by several quenchers on the individual bands and the possibility to obtain new experimental evidences on the characteristics of the surface of the clusters. In a previous paper, we reported the effect of methylviologen, a strongly electron-acceptor dication on the fluorescence of the several Q-CdS clusters [16]. We report in this paper the effect produced by tetraalkylammonium salts (R_4NCl) as analogue of the surfactant CTAC molecules and by alkylsulfate salts ($NaRSO_4$) as analogue of the surfactant SDS molecules, on these individual bands.

2. Experimental details

2.1. Chemicals

Sodium polyphosphate (Merck, extra pure), sodium sulfide (Merck, p.a.), cadmium sulfate (Mallinckrodt, p.a.), tetraethylammonium chloride, tetrabutylammonium chloride, tetrahexylammonium chloride, sodium methyl sulfate, sodium octyl sulfate (Aldrich) were used without further purification.

2.2. Preparation of Q-CdS colloids

Samples with single emission band with maximum wavelength at 460 nm, 481 nm or 559 nm were prepared. An aqueous solution of $CdSO_4$ containing sodium polyphosphate as stabilizer was de-oxygenated by nitrogen bubbling for 30 min. Then a given quantity of $H_2S_{(g)}$ was added while keeping the vessel hermetically closed. In nearly 2 min, the solution became pale yellow and then, after 10 min the excess $H_2S_{(g)}$ was eliminated by nitrogen purging and pH was finally adjusted to its final value of pH = 10.5. These clusters emitted a very weak fluorescence that was greatly enhanced by the addition of excess Cd^{+2}, so in all the cases Cd^{+2} was then added, to activate the fluorescence, until a final ratio $[Cd^{+2}]/[(NaPO_3)_6]$ of 4/1 was reached. By this procedure, the fluorescence was nearly 20-fold increased, in the case of the 559-nm band and 200-fold increased in the 460-nm and 481-nm bands. The fluorescence maximum was shifted by this activation in less than 20 nm in the case of the 559-nm band, less than 10 nm in the case of the 460-nm band and no shift was observed for the 481-nm band. With some samples of each of the bands, this activation process was followed by taking off an aliquot and monitoring the clusters' fluorescence as a function of the excess Cd^{+2} added to the samples with pH = 10.5. The fluorescence increased linearly with the Cd^{+2} concentration in all cases. A similar experiment was carried out on some of the samples but once the pH value was set at 10.5, instead of adding excess Cd^{+2} to activate the fluorescence, Na^+ or tetraethylammonium (TEA) salt was added. Although Na^+ produced a linear increase of the clusters' fluorescence, this was negligible when compared to that observed by the addition of excess Cd^{+2}, while TEA salt produced no effect on the non-activated clusters' fluorescence.

The resulting colloid presents single emission bands with λ_{max} that depend on the initial $CdSO_4$ concentration and pH, and also on the amount of $H_2S_{(g)}$ added. The λ_{max} and experimental conditions are given in Table 1.

2.3. Quenching procedures

The quenching experiments with the several samples showing isolated fluorescence bands were carried out by adding a concentrated tetraalkylammonium chloride or sodium alkyl sulfate in Q-CdS solutions to the corresponding Q-CdS solution. The pH = 10.5 was kept constant during all the experiments of quenching. The $[Cd^{+2}]/[(NaPO_3)_6]$ of 4/1 was maintained, but in the quenching experiments with tetraalkylammonium salts, the Cd^{+2} concentration was 4×10^{-4} M, while in the quenching experiments with sodium salts, the Cd^{+2} concentration was 8×10^{-4} M.

2.4. Apparatus

UV-Visible absorption measurements were performed with a Hewlett Packard HP 8452 A Diode Array Spectrophotometer. Stationary fluorescence experiments were carried out with an Spex Fluoromax spectrofluorometer. Fluorescence lifetime were measured with the time correlated single photon counting technique on an Edinburgh Instruments OB900 equipment.

Table 1
Fluorescence characteristics of the different clusters according to the preparation procedure

Band	$[CdSO_4]_i$ [a]	$[(NaPO_3)_6]$ [a]	pH_i	$[H_2S]/[Cd^{+2}]_i$	τ_1	τ_2	τ_3	τ_4	$(Rel)_1$ %	$(Rel)_2$ %	$(Rel)_3$ %	$(Rel)_4$ %
460 nm	1×10^{-4}	1×10^{-4}	8.3	1/2	6.4	66	241	553	2	15.6	51.8	30.6
481 nm	1×10^{-4}	1×10^{-4}	8.7	Excess H_2S	8.2	53	170	589	2.7	37.7	45.1	14.5
559 nm	1×10^{-4}	1×10^{-4}	10.5	1/1	4	37	172	765	5	19.8	47.7	27.5

[a] For experiments with sodium salts the concentration was 2×10^{-4} M.

3. Results and discussion

As described in Section 2, we were able to obtain samples that displayed only one fluorescence band. These bands present emission maxima at 460 nm, 481 nm, 559 nm. They are shown in Fig. 1. The corresponding fluorescence decay curves, which have different profiles for each one of the clusters, are shown in Fig. 2. It is clearly seen that the decay does not follow a single exponential decay in all cases. Four exponential terms are needed to fit the experimental data to a decay function. The four decay times and their corresponding weights are given in Table 1.

The 481-nm band is known as the excitonic band and the 559-nm band is a trap band [15], while the 460-nm band has not been reported in literature. Spanhel et al. [6] reported a broad band with a maximum wavelength similar to the excitonic band, but the starting pH to prepare it was 6 and the emission intensity was lower than that from the excitonic band, which was prepared with a starting pH of 8.3. We have prepared the clusters emitting at a maximum wavelength of 460 nm with the similar starting pH and $[Cd^{+2}]/[(NaPO_3)_6]$ ratio than that for the clusters emitting the excitonic band (481 nm). The difference between the preparation conditions for the two bands was the $SH_{2(g)}$ quantity added, as is given in Section 2. According to the excitation onset and the emission spectra, we believe that the clusters corresponding to these two bands present different size and surface traps distribution. The 460-nm band corresponds to smaller clusters, according to its onset, and a wider traps energy distribution than that of the excitonic band, since its emission spectrum is broad. The 559-nm band corresponds to larger particle size and deeper traps than the others. Non-radiative transitions are enhanced for deeper electron traps, because these traps are closer in energy to the hole traps and this makes easier the non-radiative recombination of the electron–hole pair. This is in agreement with the faster initial decay of this band.

From the onset of the excitation spectra we obtained the different band gaps for each of the clusters, 3.1 eV (460-nm band), 2.88 eV (481-nm band) and 2.7 eV (559-nm band). We have studied the effect on these emission bands by tetraalkylammonium and alkyl sulfate salts with alkyl chains of several lengths.

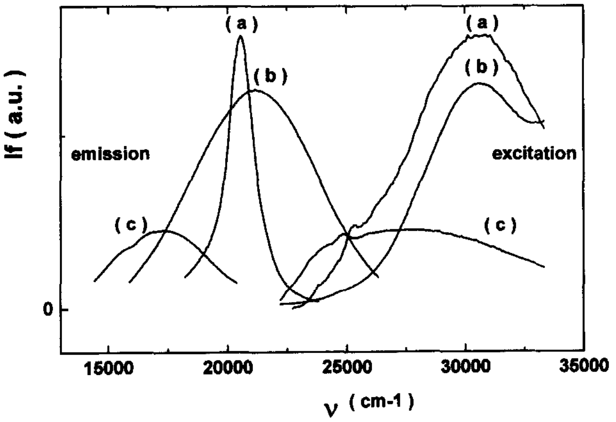

Fig. 1. Fluorescence excitation and emission spectra of the clusters: (a) excitonic band (λ_{max} = 481 nm); (b) broad fluorescence band (λ_{max} = 460 nm) and (c) trapped fluorescence band (λ_{max} = 559 nm).

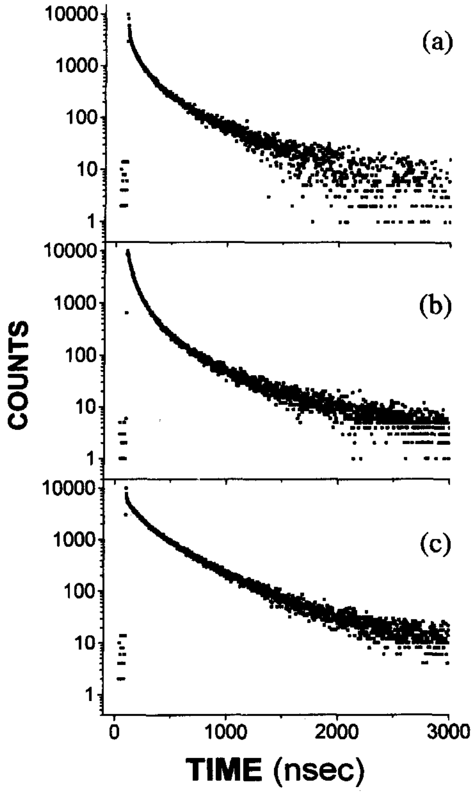

Fig. 2. Fluorescence decay profiles for clusters: (a) trapped fluorescence band (λ_{max} = 559 nm), (b) excitonic band (λ_{max} = 481 nm) and (c) broad fluorescence band (λ_{max} = 460 nm).

3.1. Effect of tetraalkyl ammonium salts

We have studied the effect of tetraalkylammonium chlorides, bearing ethyl (TEACl), butyl (TBACl) and hexyl groups (THACl), on the fluorescence from these clusters. Partial quenching effect that increases with the length of the alkyl chain was observed, as shown in Fig. 3 and for a given tetraalkylammonium salt, the quenching effect increased with the maximum wavelength of the fluorescence band (Fig. 4).

Since quaternary ammonium salts are stable to oxidation and reduction and have no low-lying excited states, the quenching effect observed may be due to electrostatic interaction of the alkylammonium cations with surface traps, through its adsorption, either assisted or not by polyphosphate.

The dependence of the quenching effect on the chain length of the alkyl groups may be explained through a hydrophobic effect acting in the adsorption of the alkylammonium cations on the clusters' surface. Our experimental results, i.e., quenching by THA > TBA > TEA, is equivalent to the trend found for the adsorption of tetraalkylammonium cations on

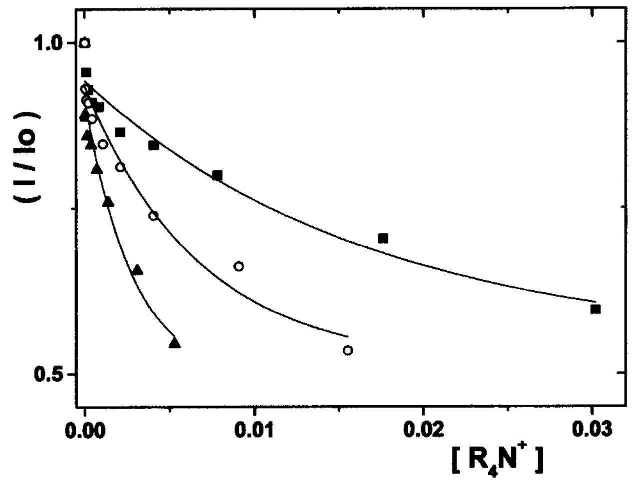

Fig. 3. Relative fluorescence emission intensity, (I/I_0), for samples emitting trapped fluorescence band ($\lambda_{\max}=559$ nm), as a function of the added tetraalkylammonium chlorides concentration: [TEACl] (■), [TBACl] (○) and [THACl] (▲).

electrodes, which increases with the length of the carbon chain [18].

For a given tetraalkylammonium cation, the quenching effect increases with the fluorescence maximum wavelength from the cluster. A non-linear behaviour of Stern–Volmer plots was observed in all cases. They are shown in Fig. 5, which is similar to those obtained with all the samples of Q-CdS clusters and all alkylammonium salts. On this plot it is evident that the response of the system is different in the concentration range which is below (Zone I) and above (Zone II) the stabilizer polyphosphate concentration used in the experiment. According to this facts, we believe that there are two distinct effects on the fluorescence of the several clusters. One is due to the adsorption of tetraalkylammonium salts on the Q-CdS clusters surface, assisted by negatively charged polyphosphate (Zone I) and the other is due to the adsorption of the salt to the clusters surface, not assisted by polyphosphate (Zone II). At the same time, we have carried out quenching experiments with clusters prepared using several polyphosphate concentrations, with the same initial [Cd^{+2}] (2×10^{-4} M) and final [Cd^{+2}] (8×10^{-4} M) in all the cases. A nearly proportional increase of the slope in Zone I with polyphosphate concentration was observed, while the slope in Zone II was nearly constant, supporting the assumption of assistance of polyphosphate in Zone I.

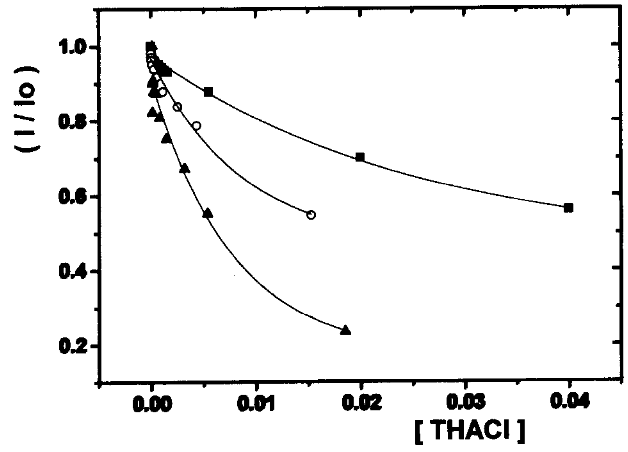

Fig. 4. Relative fluorescence emission intensity, (I/I_0), as a function of the added THACl concentration for clusters emitting at maximum wavelengths of 460 nm (■), 481 nm (○) and 559 nm (▲).

We have also determined the fluorescence decay profiles at several alkylammonium concentrations. No significant difference is observed between the decay curves, therefore no influence of alkylammonium concentration on the fluorescence lifetime could be evidenced. These experimental observations can be explained through a mechanistic scheme with a first step that represents the absorption of the tetraalkylammonium cation to the Q-CdS particles, assisted by polyphosphate (PP), that renders the static quenching observed in Zone I, Fig. 5:

$$\mathrm{RN}_4^+ + (\mathrm{CdS})_{\mathrm{ACT}}(\mathrm{PP}) \overset{K_\mathrm{I}}{\leftrightarrow} ((\mathrm{CdS})_{\mathrm{ACT}}(\mathrm{PP})-\mathrm{RN}_4^+)) \qquad (1)$$

A second step represents the excitation of activated Q-CdS $(\mathrm{CdS})_{\mathrm{ACT}}$.

$$(\mathrm{CdS})_{\mathrm{ACT}} + h\nu \xrightarrow{I_a} (\mathrm{h}^+,\mathrm{e}^-) \qquad (2)$$

A non-radiative process:

$$(\mathrm{h}^+,\mathrm{e}^-) \xrightarrow{K_d} (\mathrm{CdS})_{\mathrm{ACT}} \qquad (3)$$

A radiative process:

$$(\mathrm{h}^+,\mathrm{e}^-) \xrightarrow{k_f} (\mathrm{CdS})_{\mathrm{ACT}} + h\nu' \qquad (4)$$

Finally, the absorption of the alkylammonium cation to the clusters' surface, at quencher concentration higher than polyphosphate concentration (Zone II), rendering the static quenching observed in this concentration zone:

$$(\mathrm{CdS})_{\mathrm{ACT}} + (\mathrm{R}_4\mathrm{N}^+)_{\mathrm{eq}} \overset{K_{\mathrm{II}}}{\leftrightarrow} (\mathrm{CdS})_{\mathrm{ACT}} - (\mathrm{R}_4\mathrm{N}^+) \qquad (5)$$

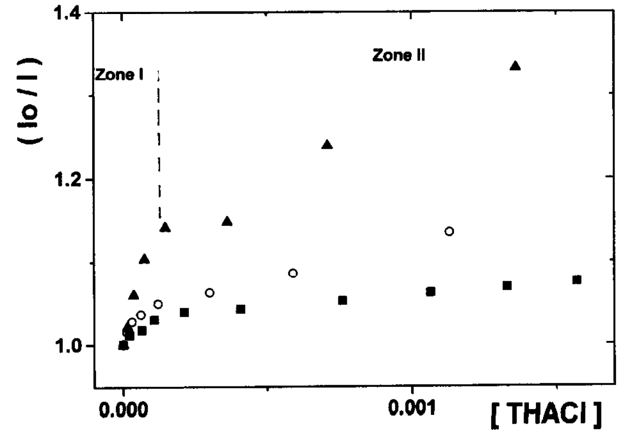

Fig. 5. Stern–Volmer plot for the quenching by THACl of clusters emitting at maximum wavelengths of 460 nm (■), 481 nm (○) and 559 nm (▲).

Where K_I and K_{II} represents the equilibrium constant for the association of the tetraalkylammonium cation to the clusters, with or without the assistance of polyphosphate, respectively. $[R_4N^+]_{eq}$ represents the free alkylammonium cation concentration, from step (1).

The dependence of the fluorescence intensity upon quencher concentration is easily derived by consideration of the constants K_I or K_{II}, assuming that step (5) occurs under conditions in which step (1) reaches a saturation. The ratio of fluorescence intensities in the absence and the presence of quencher is then given, for both concentration zones, by the Stern–Volmer expression for static quenching:

$$(I^0/I)=1+K[R_4N^+] \qquad (6)$$

Where K represents K_I or K_{II}. The values of these constants can be obtained from the slopes corresponding to Zone I and Zone II, respectively, in plots like the presented in Fig. 5. The values for all the cases studied are given in Table 2.

3.2. *Effect of sodium alkyl sulfates*

We have studied the effect of sodium alkyl sulfates, bearing methyl (MeS), octhyl (OctS) groups, using NaCl and Na_2SO_4 as reference salts, on the fluorescence from the several Q-CdS clusters. For a given emission, we found similar effect for all the sodium salts, with an increase of the quenching effect when the fluorescence maximum wavelength increased.

Furthermore, the several sodium salts did not alter the decay profiles of the clusters. This is indicative that the quenching process is static and the experimental results can be explained through a mechanistic scheme similar to the presented above for the case of alkylammonium salts, by replacing Na^+ by R_4N^+.The fluorescence quenching step is now:

$$(CdS)_{ACT}+Na^+ \overset{K_S}{\leftrightarrow} (CdS)_{ACT}-Na^+ \qquad (7)$$

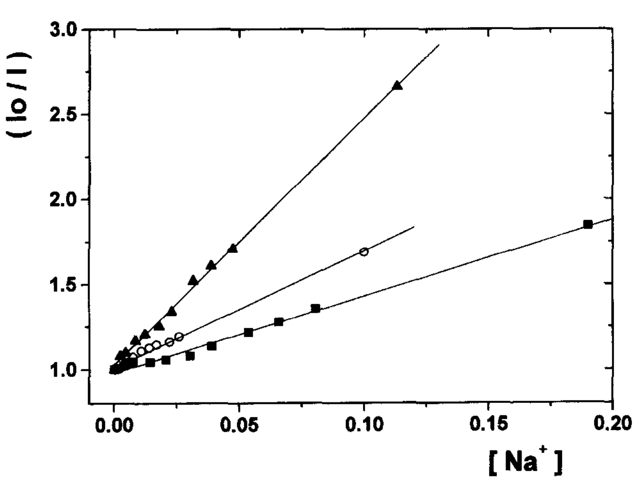

Fig. 6. Stern–Volmer plot for the quenching by Na^+ of clusters emitting at maximum wavelengths of 460 nm (■), 481 nm (○) and 559 nm (▲).

Table 2
Stern–Volmer constants for the several bands and quenchers

Band	TEACl		TBACl		THACl		NaCl	MeS	OctS
	K_I	K_{II}	K_I	K_{II}	K_I	K_{II}	K_S	K_S	K_S
460 nm	1.8	98	3.1	126	18.5	257	4.5	2.9	3.7
481 nm	10	148	14.2	318	50	572	6.9	6.4	7.4
559 nm	19.3	473	48.3	831	126	1426	14.5	14.5	14.5

The Stern–Volmer plots obtained for the quenching processes were linear, as it is shown in Fig. 6 for the several bands. The values of the constants (K_S) are given in Table 2. It can be observed there that they are independent of the sodium source, so these constants represent the equilibrium constants for the association of sodium cation to the several clusters.

4. Conclusions

We believe that the quenching by tetraalkylammonium salts is due to the adsorption of the cations on the clusters surface, which could be due to ionic pair formation by R_4N^+ with negative either phosphate or surface sites on the Q-CdS clusters, stabilizing electrons in surface traps. The presence of the adsorbed tetraalkylammonium cation could enhance the non-radiative recombination with deep-traps, less mobile holes and lower the radiative electron–hole recombinations. This enhancement may be due to an electrostatic effect due to the presence of the positive charge.

Although we do not have enough experimental data to distinguish between the interaction with the polyphosphate or the Q-CdS clusters, we believe that this effect is due to interaction of R_4N^+ with sites of the clusters surface, because some experimental data obtained by our group indicate that the quenching of Q-CdS fluorescence by CTAC is dynamic. The quenching by R_4N^+ is more effective when the salt concentration is lower than the polyphosphate concentration (Zone I) and this is indicative that polyphosphate is assisting the electrostatic interaction Q-CdS–R_4N^+.

According to the experimental results, the adsorption of the several cations R_4N^+ enhances by increasing the number of carbon atoms in the alkyl chains. This denotes that a hydrophobic effect could be acting to give this trend.

With respect to the increase of the quenching effect with the fluorescence maximum wavelength from the cluster, it is possible that non-radiative transitions are enhanced for deeper electron traps, because these traps are closer in energy to the hole traps and this makes easier the non-radiative recombination of the electron–hole pair. Our results indicate that the clusters emitting the excitonic band have deeper electron traps than those corresponding to the 460-nm band.

In the case of quenching of the Q-CdS clusters fluorescence by sodium alkylsulfate salts, since the values of K_{SV} are similar for the different substrates and for a given band, the quenching effect is mainly due to Na^+. The values of K_{SV}

are different for the different bands. Since Cd^{+2} is used to activate the fluorescence when the clusters are prepared, we believe that the quenching process consists in a displacement of Cd^{+2} by Na^{+} on the clusters' surface. Since the several clusters have different surface properties, the effect varies for each of the clusters. Besides, since the fluorescence decay profiles are not affected by the concentration of the salts, we believe that the quenching process is a static one.

According to the results presented in this paper, as well as other experimental results obtained by our group, the effect of quenchers on the fluorescence bands from the several clusters is strongly dependent of the preparation of the clusters. Therefore, it is important to optimize the preparation techniques to obtain a diversity of particles and so perform more detailed studies about their characteristics.

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