

Effect of benzene derivatives bearing electron-releasing and/or electron-withdrawing groups on the fluorescence of CdS-Q clusters

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Received 28 October 2003; received in revised form 5 June 2004; accepted 8 June 2004
Available online 28 July 2004

Abstract

We present in this paper a study of the effect of benzene derivatives bearing electron-releasing and/or electron-withdrawing groups on the fluorescence intensity and lifetimes of three different fluorescence bands of colloidal CdS-Q, with maximum emission wavelength at 460 nm (broad band), 481 nm (excitonic band) or 559 nm (trapped band), generated by photoexcitation of clusters prepared under different experimental conditions.

Benzene derivatives bearing electron-withdrawing groups produce static quenching of the luminescence from the several clusters, while in the case of benzene derivatives with electron-releasing substituents the quenching effect is essentially dynamic, in both cases occurring through an electron-transfer process.

The several surface traps in the semiconductor clusters give origin to luminescence bands with different efficiency and lifetime and are also surface sites which can have different affinity for the quencher. We have mentioned in a previous work [J. Photochem. Photobiol. A: Chem. 99 (1996) 177] that the excitonic band originates in the radiative recombination of electrons in the conduction band, after some interval of time residing in shallow surface traps, which are in thermal equilibrium with the conduction band. Broad band and trapped band originate, in turn, in the direct radiative recombination of electrons in deep surface traps, which are not in thermal equilibrium with the conduction band. We propose in this paper a mechanistic scheme, which fits our experimental results, based in the consideration of multiple active surface sites.

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Keywords: CdS-Q clusters; Benzene derivatives; Fluorescence

1. Introduction

During the last two decades, there has been an increasing interest in semiconductor structures of different sizes and specifically those with dimensions in the order of a few nanometers, known as nanoparticles (NP). Semiconductor nanoparticles promise to play a major role in several new technologies. The intense interest in this area derives from their unique chemical and electronic properties, which gives rise to their potential use in the fields of non-linear optics, luminescence, electronics, catalysis, solar energy conversion, and optoelectronics, as well as other areas. Preparations of NPs have yielded synthesis methods that are widely used to obtain NP samples for research purposes [1–3]. These preparations have led to detailed examinations of the opto-

electronic properties of nanostructures as they deviate from those of the bulk material. For example, the blue shift in the absorption onset as a function of decreasing NP size can be directly related to quantum confinement of excitons within the NP [4–6].

As particle sizes become smaller, the ratio of surface atoms to those in the interior increase, leading to the surface properties playing an important role in the properties of the material. Semiconductor nanoparticles also exhibit a change in their electronic properties relative to that of the bulk material; as the size of the solid becomes smaller, the band gap becomes larger. This allows chemists and material scientists the unique opportunity to change the electronic and chemical properties of a material simply by controlling its particle size. Research has already led to the fabrication of a number of devices.

The absorption of electromagnetic radiation by nanocrystallite material is relatively straightforward, but luminescent behavior of such particles is more complicated to understand.

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In a keynote paper, Chestnoy et al. [7] explained, on the basis of theoretical and experimental studies, the features expected in the luminescence spectra of quantum confined semiconductors and successfully anticipated the results of many subsequent experiments. However, the understanding of the photophysics of these systems is still far from complete, and further studies are needed.

One way to study the electronic properties in NPs is to observe changes in their luminescence properties in the presence of electron or hole acceptors. Since NPs by nature have a high surface-to-volume ratio, many of their optoelectronic characteristics are related to the nature of the surface. Many studies have examined the fast electron transfer that occurs when electron acceptors or donors are adsorbed on the NP surface. Both steady-state and dynamic fluorescence spectroscopy are useful tools for monitoring electronic changes at the NPs surface [8–13]. Experiences carried out with semiconductor Q clusters to obtain degradation of pollutants show that the presence of organic contaminants can be sensed using the quenching capacity of these compounds on the fluorescence of the colloidal semiconductor particles, which is restored after the destructive oxidation of the pollutants [14].

It is important to study the effect produced by electron donors and acceptors on the luminescence from semiconductor nanoparticles, since it can be of importance to elucidate the mechanisms acting in the interaction of these substrates with the clusters' surface and in the photochemical processes observed in these systems. For fluorophores with multiple luminescent states, as is thought for semiconductor NPs, multisite quenching models are used to fit experimental data [15]. In this paper, we present a study of the interaction of electron acceptors or donors with CdS NPs and we discuss the fitting of our experimental results using a multisite model.

2. Experimental details

2.1. Chemicals

Cadmium sulfate (Mallinckrodt), sodium polyphosphate (Merck), sodium sulfide (Merck), nitrobenzene (Aldrich), *o*-dinitrobenzene (Sigma), 3-nitrobenzotrile (Aldrich), 4-nitrobenzotrile (Aldrich), 4-nitroaniline (Aldrich), 4-nitroanisole (Aldrich), the dihydrochloride salts of *o*-, *m*-, *p*-phenylenediamine (Aldrich), *N,N*-dimethyl-*p*-phenylenediamine (Aldrich) and *p*-dimethylamino benzylamine (Sigma) were all reagent grade and were used without further purification.

2.2. Preparation of Q-CdS colloids

Colloidal Q-CdS with different sizes and narrow size distributions can be prepared using various synthetic techniques

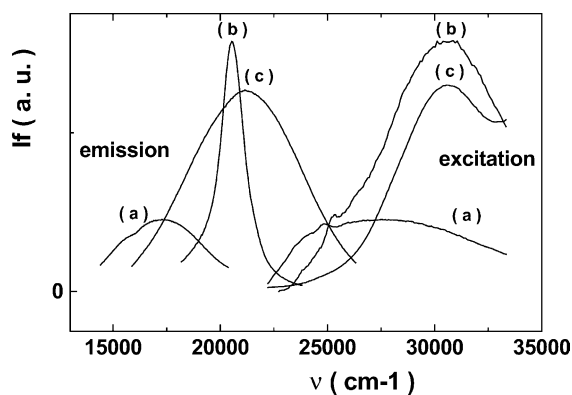


Fig. 1. Fluorescence excitation and emission spectra of the clusters: (a) traps fluorescence band ($\lambda_{\max} = 559$ nm) (b) excitonic band ($\lambda_{\max} = 481$ nm) and (c) broad fluorescence band ($\lambda_{\max} = 460$ nm).

[1–3]. The preparation method that we used is similar to that detailed in reference [3c], as follows.

Samples of colloidal Q-CdS with single emission bands with maximum wavelength at 460 nm (broad band), 481 nm (excitonic band) or 559 nm (traps band) were prepared. Its excitation and emission spectra are shown in Fig. 1. From the onset of the excitation spectra we obtained the different band gaps for each of the clusters, 3.2 eV, 2.88 eV and 2.7 eV, respectively. It is important to note that the positions of the different emission bands do not depend on the excitation wavelength. This may indicate that the size of the particles present in each of the clusters are approximately homogeneous. According to Brus [6b], the estimated size of the clusters are 34 Å, 48 Å and 52 Å, respectively.

An aqueous solution of CdSO₄ containing sodium polyphosphate as stabilizer, which initial concentrations and pH for each cluster are given in Table 1, was de-oxygenated by nitrogen bubbling for 30 min. Then a given quantity of H₂S_(g), depending of the clusters to be prepared (see Table 1), was added while keeping the vessel hermetically closed. In nearly 2 min, the solution became pale yellow and then, after 10 min the excess H₂S_(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.

As mentioned in reference [3c] the fluorescence from these clusters can be greatly enhanced by the addition of excess Cd²⁺. Therefore, excess Cd²⁺ was added to all the clusters, so the fluorescence intensity 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 by this activation procedure. The remarkable increase of fluorescence obtained for these clusters is thought to be produced by the

Table 1
Experimental conditions for the preparation of the several clusters

Band	[CdSO ₄] _i (M)	[(NaPO ₃) ₆](M)	pHi	[H ₂ S]/[Cd ²⁺]
Broad	4 × 10 ⁻⁴	2 × 10 ⁻⁴	8.3	1/2
Excitonic	2 × 10 ⁻⁴	2 × 10 ⁻⁴	8.7	Excess H ₂ S
Trapped	2 × 10 ⁻⁴	2 × 10 ⁻⁴	10.5	1/1

generation of surface defects through S–Cd–OH bonding [16]. The final Cd^{2+} concentration for all the samples was 8×10^{-4} M. (i.e. excess Cd^{2+} added concentration stands for 6×10^{-4} M). The addition of excess Cd^{2+} causes a blue shift fluorescence maximum of 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.

2.3. Electrochemistry

The voltammetric characterizations of the redox processes for benzene substituted with electron-releasing groups were done with a potentiostat–galvanostat Autolab (Electrochemical Instruments), using a Pt disc as working electrode, a saturated calomel electrode as reference, and a large area Pt counter electrode, in a conventional three compartment Pyrex cell. Studies were carried out in ultra pure water (LABCONCO system) at pH 8.4 and NaClO_4 0.1 M as supporting electrolyte. IR drop was corrected using a positive feedback technique. Peak oxidation (half wave) potentials obtained from cyclic voltammetry are reported for electrochemical irreversible (reversible) systems.

2.4. Quenching procedures

The quenching experiments with the several samples showing isolated fluorescence bands were carried out, in the cases in which there were no problems with the solubility of the quencher, by adding a concentrated quencher in Q–CdS solution to the corresponding Q–CdS clusters solution. On the other hand, in cases in which the quencher solubility in water was poor, a concentrated quencher solution in ethanol was used to add the quencher to the Q–CdS clusters solution. Since the addition of nearly 100 μl of ethanol to the Q–CdS clusters solution volume used in the fluorescence cells for our experiments did not alter the fluorescence intensity for any of the clusters, the quencher concentration of the ethanolic mother solution was such that the total volume added during the quenching experiments did not overpass 100 μl . On the other hand, to detect if there is some interaction between the several quenchers and the stabilizer or the cadmium ion, we prepared solutions of the quenchers and polyphosphate or CdSO_4 . We could not detect any effect on the absorbance of the quenchers.

2.5. Apparatus

UV–vis absorption measurements were performed with a Hewlett-Packard HP 8452 A Diode Array Spectrophotome-

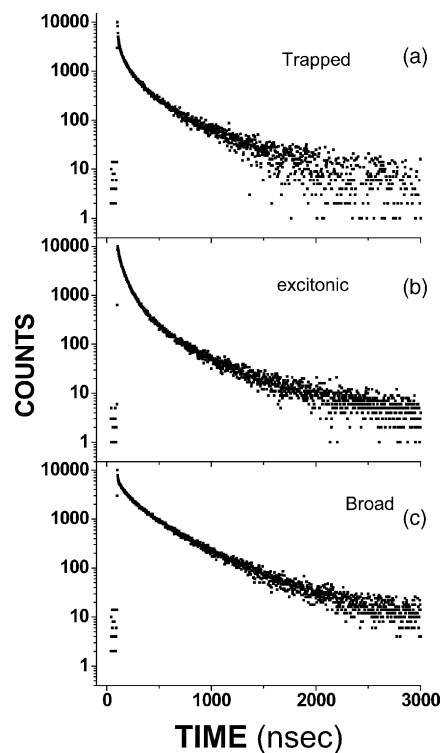


Fig. 2. Fluorescence decay profiles for: (a) traps band (b) excitonic band and (c) broad band.

ter. Stationary fluorescence experiments were carried out with an Spex Fluoromax spectrofluorometer. Fluorescence lifetimes were measured with the time correlated single photon counting technique on an Edinburgh Instruments OB900 equipment, using as excitation source a nF900 ns flashlamp, filled with hydrogen gas, with a FW of 3 ns.

3. Results and discussion

The 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 2. We believe that the multiexponential decay of the fluorescence from Q–CdS clusters is originated in surface traps generated by the addition of excess Cd^{2+} . These surface traps correspond to different energy sublevels in which the electrons, excited by the absorption of a photon, reside

Table 2
Fluorescence characteristics for the several clusters

Band	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_4 (ns)	(Rel) ₁ %	(Rel) ₂ %	(Rel) ₃ %	(Rel) ₄ %
Broad	6.4	66	241	553	2	15.6	51.8	30.6
Excitonic	8.2	53	170	589	2.7	37.7	45.1	14.5
Trapped	4	37	172	765	5	19.8	47.7	27.5

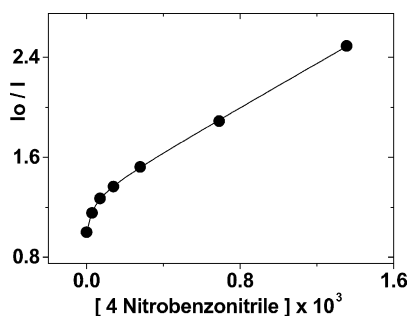


Fig. 3. Stern–Volmer plot for the quenching of the fluorescence of the traps band by 4-NBZN.

temporarily until they can interact with trapped holes to produce radiative deactivation. These processes are assumed by many researchers working with semiconductors NPs and can observe multiexponential decay of fluorescence [15].

We have studied the effect produced by benzene derivatives bearing electron-withdrawing and/or electron-releasing groups on the fluorescence bands of Q-CdS. The results are different depending on the substituents, so we consider three separate groups, namely electron-withdrawing substituents, electron-releasing substituents and both, one electron-withdrawing and one electron-releasing substituent. The quenchers used were: as acceptors, nitrobenzene (NB), *o*-dinitrobenzene (*o*-diNB), 3-nitrobenzonitrile (3-NBZN), and 4-nitrobenzonitrile (4-NBZN); as donor-acceptor, 4-nitroaniline (4-NA) and 4-nitroanisole (4-NAN) and as donors, *o*-phenylenediamine (*o*-PDA), *m*-phenylenediamine (*m*-PDA), *p*-phenylenediamine (*p*-PDA), *N,N*-dimethyl-*p*-phenylenediamine (D-*p*-PDA) and *p*-dimethylamino benzylamine (*p*-DBA).

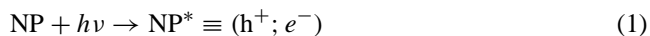
3.1. Effect of benzene substituted with electron-withdrawing groups: NB, *o*-diNB, 3-NBZN and 4-NBZN

The Stern–Volmer plots for the Q-CdS fluorescence quenching by benzene substituted with several electron-withdrawing groups exhibit downward curvature, as shown in Fig. 3, which corresponds to the quenching of the trapped-fluorescence band by 4-NBZN. The fluorescence decay curves were determined at several quencher concentrations. They did not evidence changes, so we can conclude that the quenching effect is static.

A Stern–Volmer plot that exhibits downward curvature is an indication that there are multiple fluorescence pathways [15], some of which are more/less susceptible to quenching. The non-linear quenching and the multiexponential fluorescence decay of Q-CdS shown in Fig. 2 support such a multiple path fluorescence model. Although the fluorescence decay curves (Fig. 2) can be fitted with four lifetimes, the fact that only two quenching zones are observed in the Stern–Volmer plots suggests that the simplest case, with two active surface sites each one with its own affinity for the quencher, can be applicable. For this particular case, a mech-

anistic scheme which accounts for our experimental results would be as follows:

The first step corresponds to the excitation of Q-CdS nanoparticles (NP)



The radiative recombination can be effected in two different sites



Two non-radiative pathways can also be considered



The affinity for the quencher is different for both sites, so the two static quenching processes must be written as:



where the binding complexes NP₁-Q and NP₂-Q are non-fluorescent when they are excited by the absorption of a photon.

Since the fluorescence is emitted by the two sites, we have:

$$\Phi_F^0 = \Phi_{F1}^0 + \Phi_{F2}^0 = f_1 \Gamma_F^0 + f_2 \Phi_F^0$$

(without quencher present)

and

$$\Phi_F = \Phi_{F1} + \Phi_{F2} \quad (\text{in the presence of quencher})$$

where f_i is the relative fractional contribution to the observed fluorescence from the i th emitting state in the absence of quencher.

Both sites are independently quenched, so it can be supposed that each one of them is quenched following a Stern–Volmer law:

$$\frac{\Phi_{F1}^0}{\Phi_{F1}} = 1 + K_1[Q] = f_1 \frac{\Phi_F^0}{\Phi_{F1}} \quad (8)$$

$$\frac{\Phi_{F2}^0}{\Phi_{F2}} = 1 + K_2[Q] = f_2 \frac{\Phi_F^0}{\Phi_{F2}} \quad (9)$$

where K_i represent in this case the adsorption equilibrium constant of the quencher to the i th site. The global quenching effect is then given by:

$$\frac{\Phi_F^0}{\Phi_F} = \frac{\Phi_F^0}{(\Phi_{F1} + \Phi_{F2})}$$

Replacing in this equation the expressions of Φ_{F1} y Φ_{F2} given by Eqs. (8) and (9), respectively and reordering, we have:

$$\frac{\Phi_0}{\Phi_F} = \frac{1}{(f_1/1 + K_1[Q]) + (f_2/1 + K_2[Q])} \quad (10)$$

Using Eq. (10), a non-linear regression analysis was performed on our quenching data like those shown in Fig. 3. This yielded values for the relative fractional contribution to the fluorescence in the absence of quencher f_i and the adsorption equilibrium constant K_i , which are given in Table 3. The solid line in Fig. 3 is the fitted curve, which closely matches the quenching data.

According to the values of redox potential measured for CdS: valence band (VB) 1.25 V versus SCE and conduction band (CB) -1.25 V versus SCE [17], the electron donors which oxidation potential ($E_{1/2}$; D/D⁺) is lower than 1.25 V could release an electron to the valence band holes (h⁺) and the electron acceptors which reduction potential ($E_{1/2}$; A/A⁻) is higher than -1.25 V could take an electron from the conduction band of CdS. In both cases a luminescence quenching due to the charge transfer process could be observed, but if the corresponding potential is outside the range (-1.25 V to 1.25 V versus SCE), the electron-transfer quenching would not be detectable.

According to literature half-wave potentials for the A/A⁻ couple, which are given in Table 5, all the nitro compound studied can remove one electron from the conduction band of Q-CdS and undergo a redox process, so we believe that the quenching process is a charge-transfer one.

On the other side, benzonitrile ($E_{1/2} = -2.35$ V [18]) is unable to remove electrons from the conduction band of Q-CdS and quench the clusters' fluorescence. This was confirmed by us, since we could not detect fluorescence quenching when benzonitrile was added to any of the clusters solutions.

The K_i values (adsorption equilibrium constants) given in Table 3 for nitrobenzene and the nitrobenzonitriles are similar. The values of $E_{1/2}$ (A/A⁻), for these compounds, which are shown in Table 5, show little differences, but

they do not follow the same tendency of the K_i values. This is indicative that the electron-transfer from the conduction band of Q-CdS to these electron-acceptors is a fast process and so it is not affected by the small differences between the values of $E_{1/2}$ (A/A⁻) for the several nitro compounds. We believe that nitro group is responsible for the quenching action for all the clusters. The addition to the benzenic ring of a second nitro group (*o*-diNB) renders higher K_i values with respect to those for nitrobenzenes. Although the $E_{1/2}$ value of *o*-diNB is less negative than the other nitro compounds and so its K_i value must be higher, the difference is higher than that to be expected, we therefore believe that this could be due to the presence of two nitro groups instead of one, rendering an enhanced quenching effect for all the clusters.

On the other side, the f_i values for both the broad band and the trapped band are similar ($f_1 \approx 0.25$ and $f_2 \approx 0.75$), which indicates that both clusters show similar active sites for quenching. Excitonic band, in its turn, undergoes quenching mainly in only one type of active surface sites, although in some cases quenching is observed in a second site which accounts nearly 2–4% of the quenching effect. This is indicative that these clusters are emitting mainly through the radiative recombination of electrons in the conduction band and also (in minor extension) radiative recombination of electrons in shallow surface traps which are in dynamic equilibrium with the conduction band.

3.2. Effect of benzene substituted with nitro group with an electron-releasing group amino or methoxy: 4-NA and 4-NAN

In these cases, the Stern–Volmer plots for the quenching of the excitonic band were linear for both quenchers, while for broad and trapped bands, a slight curvature is observed at high quencher concentrations, as it is shown in Fig. 4 for the quenching of the luminiscence from the three bands by 4-nitroaniline. The corresponding values of K_i obtained from the slopes in Fig. 4 at low quencher concentrations and, between parentheses, the values obtained by fitting of our data to Eq. (10) are given in Table 3.

Table 3

Adsorption equilibrium constant of the quenchers to the *i*th site (K_i) and Stern–Volmer constants (K_{SV}) for the quenching of the fluorescence from the clusters by the several quenchers

Uencher	f_1^a	Broad				Excitonic				Trapped		
		K_1	f_2^a	K_2	f_1^a	K_1	f_2^a	K_2	f_1^a	K_1	f_2^a	K_2
NB	27	16020	73	227		100	978	26	40697	74	995	
<i>o</i> -diNB	24	40537	76	1770		100	869	20	259419	80	1527	
3-NBZN	29	14175	71	168	3	15947	97	147	24	16769	76	378
4-NBZN	28	19678	72	222	4	20910	96	305	24	36427	76	666
4-NA		1180 ^b				1326 ^b				1240 ^b		
	64 ^c	2260 ^c	36 ^c	(129) ^c					47 ^c	3196 ^c	53 ^c	116 ^c
4-NAN		1110 ^b				660 ^b				360 ^b		
	52 ^c	2468 ^c	48 ^c	(318) ^c					26 ^c	1786 ^c	74 ^c	32 ^c

^a The fractional contribution of the two surface active sites considered for the model, expressed as percentages.

^b Values of K_i obtained from the slopes of the Stern–Volmer plots, as shown in Fig. 4, at low quencher concentrations.

^c Values of K_i and f_i obtained by fitting of our data to Eq. (10).

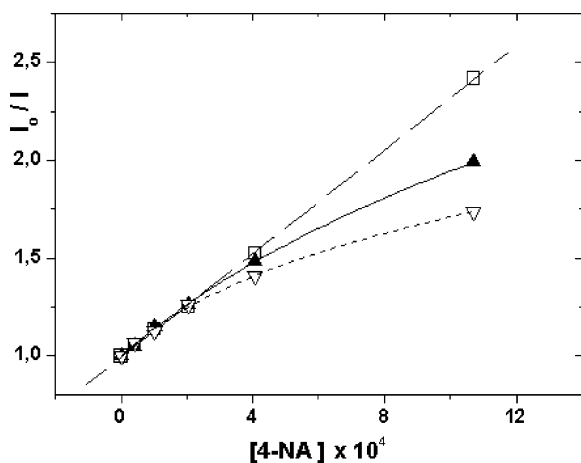


Fig. 4. Stern–Volmer plots for the quenching of the three fluorescence bands: (□) excitonic band (▲) broad band and (▽) traps band by 4-NA.

From the reduction half-wave potentials ($E_{1/2}$; A/A^-) for these compounds given in Table 5, it can be deduced that they can remove an electron from the conduction band of CdS and undergo a redox process, as it is the case for the nitro benzene derivatives. The presence of electron-donors as amino or methoxy could be then lowering the quenching effect of the nitro group, so as instead of zone II observed with nitrobenzenes, only a slight curvature at high quencher concentrations is observed in these cases. Consequently, the quenching mechanism could be similar to the above given, but step (7) is only evidenced at high quencher concentrations.

The fluorescence decay curves were also determined for both quenchers at several quencher concentrations and we could not detect differences for any of the CdS-Q clusters. As well as in the case of benzene substituted with electron-withdrawing groups, we conclude that the quenching effect is static, although less efficient. This is indicative that the nitro group can be responsible for the quenching effect and not the amino or methoxy groups, since we could not detect changes in the fluorescence decay times, as is to be expected for the quenching by electron-donors groups.

3.3. Effect of benzene substituted with electron-releasing groups: *o*-PDA, *m*-PDA, *p*-PDA, *D*-*p*-PDA and *p*-DBA

The Stern–Volmer plots were linear for all the quenchers, with all the clusters used in the experiments, as it is shown in Fig. 5 for the case of excitonic band and the compound *p*-DBA. The values of K_{SV} obtained from the plots are given in Table 4.

The effect of quencher concentration on the fluorescence decay profiles is shown in Fig. 6 for the case of excitonic band and the compound *p*-DBA. Fluorescence lifetimes (only τ_2 and τ_3) are shortened when quencher concentration is increased, suggesting that these quenching processes are, at least in part, dynamic.

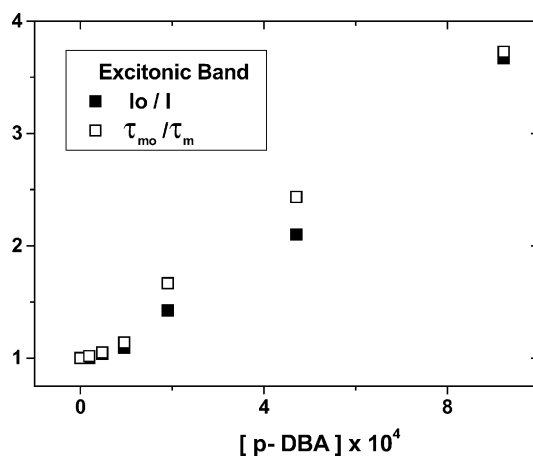


Fig. 5. Stern–Volmer plots for the quenching by *p*-DBA of the excitonic fluorescence band: (■) (I_0/I) and (□) (τ_{mo}/τ_m).

Table 4
Stern–Volmer constants (K_{SV}) for the quenching of the fluorescence from the clusters by the several quenchers

Quencher	Broad	Excitonic	Trapped
<i>o</i> -PDA	193	278	509
<i>m</i> -PDA	166	347	465
<i>p</i> -PDA	147	464	267
<i>D</i> - <i>p</i> -PDA	200	516	483
<i>p</i> -DBA	426	1900	1085

For microheterogeneous systems, where non-single exponential lifetimes are often observed, a comparison of steady-state fluorescence quenching data with transient fluorescence quenching data using a preexponential weighted mean lifetime:

$$\tau_m = \frac{\sum_i \alpha_i \tau_i}{\sum_i \alpha_i} \quad (11)$$

where α_i is the pre-exponential factor for each decay component, allows to estimate the contribution of dynamic and

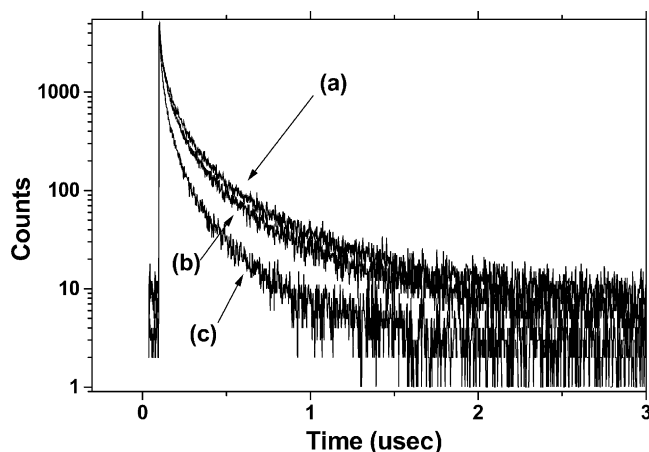


Fig. 6. Fluorescence decay profiles for clusters of the excitonic band at several *p*-DBA concentrations. [*p*-DBA] = (a) 0 M (b) 1.9×10^{-4} M and (c) 9.2×10^{-4} M.

Table 5
Reduction and oxidation half-wave potentials of the quenchers

Quencher	Acceptors						Donors				
	NB	<i>o</i> -diNB	3-NBZN	4-NBZN	4-NA	4-NAN	<i>o</i> -PDA	<i>m</i> -PDA	<i>p</i> -PDA	D- <i>p</i> -PDA	<i>p</i> -DBA
$-E_{1/2}(A/A^-)^a$	1.15 ^b	0.81 ^b	0.94 ^b	0.87 ^b	1.07 ^c	1.25 ^b					
$E_{1/2}(D/D^+)^d$							0.1	0.32	-0.12	-0.1	-0.06

^a $E_{1/2}(A/A^-)$, in Volts, vs. SCE in acetonitrile.

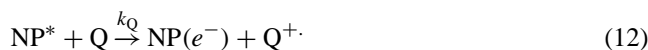
^b Reference [20].

^c Reference [21].

^d $E_{1/2}(D/D^+)$, in Volts vs. SCE, estimated in our laboratory in pH 8.4 aqueous media.

static quenching to the global quenching process. For a dynamic quenching process, a plot of (τ_{m0}/τ_m) should yield a similar relationship as a plot of (I_0/I) [19]. When the ratio (τ_{m0}/τ_m) is plotted as a function of the quencher concentration, using the data obtained for the clusters to calculate τ_{m0} and the corresponding data in the presence of the quencher to calculate τ_m with Eq. (11), the points follow the same linear trend as the (I_0/I) data, as it is shown in Fig. 5 for the case of excitonic band and the compound *p*-DBA. These experimental results are indicative that the quenching by electron donors is essentially dynamic.

Our experimental results can be accounted by a mechanistic scheme which is similar to that given for benzenes substituted with electron-withdrawing groups, except that benzenes bearing electron-releasing groups interact with surface-trapped positive charge carriers (h^+). Since Stern–Volmer plots, as shown in Fig. 5 are linear, we believe that only one class of hole trap is present on the clusters' surface and then, instead of steps (6) and (7) in the above mechanistic scheme we place one slow step, which represents the interaction of the quencher with that hole trap, followed by other(s) fast step(s), which in turn represent the interaction of the quencher radical cation (Q^+) with electrons that are leaving the several surface traps to produce emission:



The consideration of this mechanism renders the usual Stern–Volmer equation. The values of K_{SV} obtained from the slopes in the Stern–Volmer plots for the different quenchers and the three clusters are given in Table 4.

The values of oxidation $E_{1/2}$ for the several electron-donors were determined by us in alkaline aqueous solutions and they are given in Table 5. All these values are lower than 1.25 V, which indicates that the quenching process could be a charge transfer one. Some correlation seems to exist between the values of K_{SV} for the case of excitonic band (Table 4) and the values of oxidation potentials given in Table 4. This is not the case, however, for the other fluorescence bands, so we believe that the electron-transfer process from the electron-donor to the valence band in the Q-CdS is a fast process (although slower than other subsequent steps), which is independent from the small differences between the half-wave potentials of the several quenchers. Further-

more, only two of the four components needed to fit the decay curves were affected by the quencher action, which can be indicative that in the clusters' surface there are only two kinds of sites that can be quenched. This was also observed in the case of electron-acceptors.

4. Conclusions

For fluorophores with multiple luminescent states, as is thought for semiconductor NPs, multisite quenching models are used to fit experimental data. We suggest, for the case of quenching of CdS NPs fluorescence by benzenes substituted with electron-withdrawing groups, a multisite model with two active sites, which accounts for our experimental results. It is interesting to note that the number of active sites used to fit the quenching results has not to be necessarily the same as the number of lifetime components used to fit the fluorescence decay profiles. As an example, even though four lifetime components are at least necessary to fit the decay curves for the excitonic band, this is known to be generated from electrons in the conduction band. Our quenching results are coincident with the last mentioned. These facts are indicative that not every electron surface trap is susceptible to quenching.

Since the Stern–Volmer plots were linear in all the quenching experiments with electron-donors, we can conclude that there is only one class of hole (h^+) trap on the surface of all the CdS clusters that were used in our experiences. As well as in the cases of the quenching by electron-acceptors, not every electron traps are susceptible to quenching, since only two of the four lifetime components were affected by the addition of quenchers. In summary; on the surface of the CdS NPs there exist at least four class of traps for electrons that were excited from the VB to the CB, but only two of them are accessible to quenchers. On the other hand, only one class of hole trap can be detected.

Acknowledgements

Thanks are due to Universidad Nacional de Río Cuarto and CONICET (Argentina) for financial support. We wish to express our thanks to Dr. C.M. Previtali for valuable dis-

cussions and also to Dr. L. Otero for his collaboration in the electrochemical measurements.

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