

Dissociative CdSe/ZnS quantum dot-molecule complex for luminescent sensing of metal ions in aqueous solutions

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The optical properties of dissociative luminescent sensors based on a complex consisting of highly luminescent hydrophobic core/shell CdSe/ZnS quantum dots (QDs) and 1-(2-pyridilazo)-2-naphthol (PAN) molecules in organic solutions and a polymer film are reported. It is demonstrated, using Ni²⁺ and Co²⁺ ions as an illustrative example, that the QD/PAN sensor may have applications in the quantitative luminescent sensing of metal ions in aqueous solutions. © 2010 American Institute of Physics. [doi:10.1063/1.3490218]

I. INTRODUCTION

Luminescent sensors based on complexes consisting of a semiconductor nanocrystal (quantum dot, QD) with organic dye molecules bound to its surface are highly sensitive detectors of various species, including metal ions, and have applications in biology, medicine, and ecology.¹ Using a QD as a sensor luminophor offers considerable advantages over conventional organic and protein based fluorophores.² QDs have absorption and photoluminescence (PL) excitation bands over a broad spectral range. The molar extinction coefficients of QDs are an order of magnitude larger than those of conventional dyes. QDs also have a narrow and symmetric PL band, with quantum yields (QY) of up to 80%, together with a high resistance to both photobleaching and chemical degradation. Finally, because of quantum-confinement effects, PL emission of QDs can be tuned across a broad spectral range simply by changing the size of the nanocrystals.

QD luminescence in these QD/molecule sensors is initially quenched by fluorescence resonant energy transfer (FRET) from the QD to the dye molecule. A large value of the overlapping integral can be obtained by optimizing the QD size. One type of these sensors utilizes the fact that the absorption spectrum of the dye molecule is modified in the presence of an analyte, resulting in a decrease in the overlapping integral value and an increase in the QD PL intensity.³ A variety of these organic dye molecules are used as indicators in quantitative colorimetric analysis of metal ions in water solutions.⁴ Alternatively, the presence of an analyte may result in the dissociation of the QD/molecule complex and a resultant increase in the QD PL intensity.⁵ In either case, the PL intensity is a function of the analyte concentration, and so can be used for analytical purposes.

In this paper, we report the optical properties of disso-

ciative luminescent sensors for Ni²⁺ and Co²⁺ ions, based on a complex consisting of highly luminescent hydrophobic core/shell CdSe/ZnS quantum dots and 1-(2-pyridilazo)-2-naphthol (PAN) molecules bound to the QD surface. The azo-dye PAN is a well-known metallochromic indicator for the colorimetric determination of a variety of metal ions, including Ni²⁺ and Co²⁺ (Refs. 6 and 7 and references therein). When immobilized in a polymer membrane⁷ or resin,⁸ PAN is able to extract and concentrate metal ions from aqueous solutions, allowing a more sensitive determination of analytes. The advantage of our approach is that measurement of the changes in the PL response of the QD/PAN sensor induced by the presence of analyte is at least an order of magnitude more sensitive than colorimetric measurements.

II. EXPERIMENTAL

A. Materials and apparatus

The PAN and organic solvents used in this study were purchased from Fluka and used as received. All metal salts [NiSO₄, Co(NO₃)₂·6H₂O, and Zn(CCl₃COO)₂·2H₂O] were of analytical reagent grade and dissolved in bidistilled water. The two-component polyurethane adhesive Novacote[®] NC-250-A (resin)+CA-350 (hardener) (Ref. 9) used for the preparation of the polymer films were purchased from Coim UK, Ltd.

CdSe/ZnS core/shell quantum dots were synthesized according to a protocol adapted from Ref. 10 and described in detail elsewhere.¹¹ The QDs have a CdSe core of the desired diameter and an epitaxially grown ZnS shell approximately two monolayers thick. The QDs exhibit strong band-edge PL with a QY of nearly 50% in a toluene solution. The quantum dot surface is covered in trioctylphosphine oxide (TOPO) molecules coupled with the shell Zn ions by coordination bonds.

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A Shimadzu UV Probe 3600 spectrophotometer and a Varian Fluorescence, Cary Eclipse spectrophotometer were used for recording the absorption and PL spectra. The Raman spectra of the Zn/PAN and QD/PAN complexes excited by a 457.9 nm Ar-ion laser light were recorded in the back scattering geometry using an “inVia” Renishaw micro-Raman spectrometer with 50 \times objective and ~ 3 cm $^{-1}$ spectral resolution. A MicroTime100, PicoQuant time-resolved fluorescence microscope was used for the PL decay time measurements. pH values were determined using a Hanna Instruments HI98108 pH Meter.

B. Sample preparation

QD/PAN complexes in organic solutions (chloroform, carbon tetrachloride, hexane and toluene) were prepared by adding PAN solutions with various concentrations (C_{PAN}) to a QD solution with a concentration (C_{QD}) of about 5×10^{-7} M in such a way that the $C_{\text{QD}}:C_{\text{PAN}}$ ratio (R) varied from 3:1 to 1:10. Reference solutions of PAN chelates with Zn^{2+} , Co^{2+} , and Ni^{2+} ions were prepared by adding PAN solution to aqueous solutions of metal salts and stirring.¹² Powders of the PAN/ Zn^{2+} and QD/PAN complexes for the Raman analysis were obtained by drying of their toluene solutions.

The polymeric films with embedded QD/PAN complexes were fabricated as follows. First, toluene solutions of CdSe/ZnS QDs ($C_{\text{QD}} \sim 1.3 \times 10^{-4}$ M) and PAN with C_{PAN} in the range $0.4\text{--}13 \times 10^{-4}$ M were prepared. Next, 1.5 ml of the QD solution and 1.5 ml PAN solution were added to 1 ml of Novacote[®] NC-250-A+CA-350 adhesive with a component ratio of 1:20. The mixture was stirred for 5 min and then placed in an ultrasonic bath for 10 min. Finally, the mixture was deposited on a 12 μm thick, polyethylene-terephthalate substrate and dried, in accordance with the adhesive specification, at $T \sim 100$ °C for 15 min, followed by a room temperature drying step for ~ 20 hours. Thin polymer films of 1–3 μm thickness with embedded QD/PAN complexes were obtained as a result of this procedure. Taking into account the 1.6 times solidification shrinkage of the films, the concentration of the components was calculated to be $C_{\text{QD}} = 4 \times 10^{-4}$ M and $C_{\text{PAN}} \approx (1.2\text{--}40) \times 10^{-4}$ M, resulting in an R value that varied from 3:1 to 1:10. We also prepared reference samples of polymeric films, containing either QDs or PAN with the same molar concentrations. Polymeric films containing PAN chelates with Zn^{2+} , Co^{2+} , and Ni^{2+} ions were prepared by immersion of the film containing PAN in an aqueous solution of the corresponding metal salt.

III. RESULTS AND DISCUSSION

A. QD/PAN complex formation in organic solutions

Our initial investigations focused on a study of the formation of QD/PAN complexes in chloroform, carbon tetrachloride, hexane and toluene using PL and absorption spectroscopy. In order to carry out reliable spectroscopy measurements, diluted solutions of the reagents, with C_{QD} of approximately 5×10^{-7} M, and C_{PAN} in the range $(0.17\text{--}5) \times 10^{-6}$ M were used. In this, and in subsequent

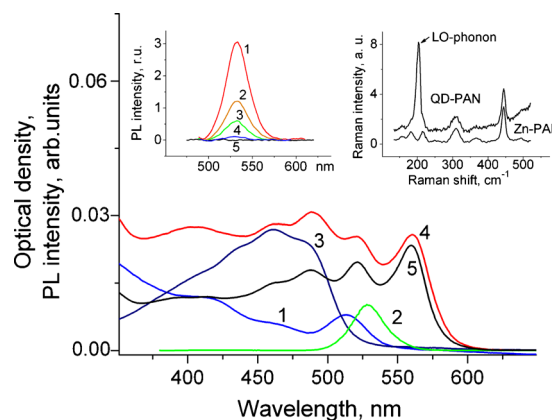


FIG. 1. (Color online) Absorption (1) and PL (2) spectra of CdSe/ZnS QDs in toluene. $C_{\text{QD}} = 5 \times 10^{-7}$ M. $\lambda_{\text{exc}} = 360$ nm. (3) absorption spectrum of neutral PAN in toluene ($C_{\text{PAN}} = 10^{-6}$ M). (4) absorption spectrum of a mixture of QDs and PAN in toluene ($C_{\text{QD}} = 5 \times 10^{-7}$ M and $C_{\text{PAN}} = 10^{-6}$ M) that coincides with the characteristic absorption spectrum of the PAN/ Zn^{2+} complexes (5). Left inset: PL spectra of QD and PAN mixture at different $C_{\text{QD}}:C_{\text{PAN}}$ ratios (R) 1—1:0, 2—3:1, 3—2:1, 4—1:1, and 5—1:10. $C_{\text{QD}} = 5 \times 10^{-7}$ M. $\lambda_{\text{exc}} = 360$ nm. Right inset: Raman spectra of Zn/PAN and QD/PAN complexes in a metal-ligand vibration region. A LO-phonon band of CdSe QDs is marked.

experiments, CdSe/ZnS QDs with diameters of 2.5 nm and 530 nm PL bands were mainly used. Figure 1 (curves 1 and 2) shows the absorption and PL spectra of the 2.5 nm QDs in toluene. Figure 1 (curve 3) illustrates the absorption spectra of neutral PAN in a toluene solution at a concentration of 10^{-6} M.

The addition of PAN to the QD solutions results in a dramatic change in the absorption spectrum of the mixture. This change is illustrated in Fig. 1 (curve 4) for a toluene solution. The characteristic absorption spectrum of the PAN/ Zn^{2+} complexes in toluene with a 560 nm band¹³ appears in the spectrum of the mixture. An absorption spectrum of PAN/ Zn^{2+} complexes in toluene is shown for comparison in Fig. 1 (curve 5). The appearance of the characteristic PAN/ Zn^{2+} absorption spectrum indicates the formation of chelate compounds between the PAN molecules and the surface Zn ions of the QD shell, i.e., QD/PAN complexes. The presence of PAN coupled to Zn ions on the nanocrystal surface is supported by the Raman spectrum of the QD/PAN powder that well matches the spectrum of the PAN/ Zn^{2+} powder whose band positions are consistent with previous reports on PAN/ Zn^{2+} complex.¹⁴ That is illustrated in the right inset in Fig. 1 where Raman spectra of QD/PAN and PAN/ Zn^{2+} in the important region of the metal-ligand vibration below 500 cm $^{-1}$ are compared. This is unsurprising, since PAN can form a nonluminescent, colored chelate complex with Zn^{2+} ions.¹³ The characteristic time required for this process decreases with an increase in the reagent concentrations that are expected for bimolecular reactions. For a $C_{\text{QD}} = 5 \times 10^{-7}$ M and $C_{\text{PAN}} = 10^{-6}$ M, the increase in the intensity of the characteristic 560 nm absorption band saturates approximately 3 h after the addition of the PAN at room temperature (curve 4 in Fig. 1). This long characteristic time for QD/PAN formation may be due to the slow substitution of the surface TOPO molecules by PAN.

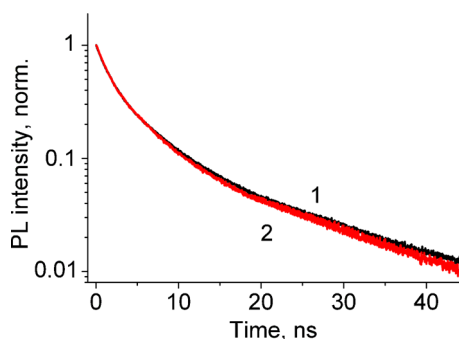


FIG. 2. (Color online) PL decay curves of free QD (1) and QD/PAN mixture (2) in toluene at R of 2:1. $\lambda_{\text{EXC}}=405$ nm, $\lambda_{\text{EM}}=530$ nm.

Simultaneously, a reduction in the QD PL intensity by two orders of magnitude was observed, indicating that practically all of the QDs bind to form nonluminescent QD/PAN complexes. The inset in Fig. 1 demonstrates the reduction in the QD PL intensity measured 3 h after the addition of the PAN for various R values. We found that the mean PL decay times of around 9 ns are practically identical for QDs and QD/PAN solutions with various R . Figure 2 illustrates representative PL decay curves $F(t)$ for pure QDs and for QD/PAN mixtures in toluene. These curves are well fitted by a sum of two exponentials $F(t)=\sum \alpha_i \exp(-t/\tau_i)$, where α_i and τ_i are the amplitude and decay time of the i th component, respectively. The mean time for the multiexponential PL decays is $\langle \tau \rangle = \sum \alpha_i \tau_i^2 / \sum \alpha_i \tau_i$, where $\alpha_i \tau_i$ are the weights of the i th component in the PL emission. The same mean decay time $\langle \tau \rangle$ for solutions of free QDs and the QD/PAN mixture suggests that the emission from QDs in the QD/PAN mixture principally originates from unbound nanocrystals present in the mixture. Therefore, static quenching of the QD PL takes place and the reduction in the PL intensity observed with increasing PAN concentration reflects the formation of nonluminescent QD/PAN complexes. Analysis of the PL intensity dependence on PAN concentration in terms of the theory of static quenching¹⁵ showed that complexes consisting of one QD and one PAN molecule dominate at R values lower than 1:2. We believe that the QD PL quenching in the QD/PAN complexes is most likely due to FRET from the 2.5 nm QDs to the PAN/ Zn^{2+} compound due to the large value of the overlapping integral between the QD PL band and the absorption band of the PAN/ Zn^{2+} compound (Fig. 1). Identifying FRET as the mechanism responsible for quenching is supported by the fact that no significant decrease in PL was observed in an experiment with QDs of 5.3 nm diameter and a PL band located at 630 nm when the spectral overlap of the PAN/ Zn^{2+} absorption and the QD PL bands is negligible.

Similar changes in the absorption and PL spectra of a mixture of QD and PAN solutions have been observed for other hydrophobic solvents, such as chloroform, carbon tetrachloride, and hexane, supporting the conclusion that formation of nonradiating QD/PAN complexes is occurring, where PAN molecules are bound to QD shell Zn ions.

The QD/PAN complexes prepared demonstrated remarkable PL behavior. When mixing the QD/PAN organic solution with water containing Co^{2+} or Ni^{2+} ions, an increase in the QD PL with ion concentration was observed. This raises

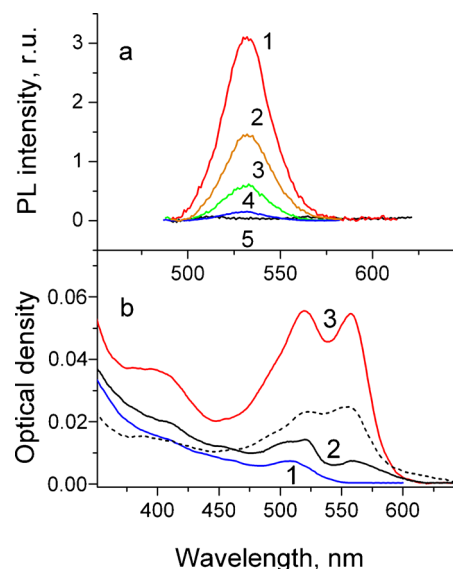


FIG. 3. (Color online) PL (a) and absorption (b) spectra of 2 μm thick polymeric films containing free QDs, QD/PAN and PAN/ Zn^{2+} . $C_{\text{QD}}=4 \times 10^{-4}$ M. (a): 1—free QDs; 2–5—QDs/PAN at R of 3:1, 2:1, 1:1, and 1:10, respectively. $\lambda_{\text{EXC}}=360$ nm. (b): 1—free QDs; 2–3—QDs/PAN at R of 1:1 and 1:10, respectively; dashed line is the film with PAN/ Zn^{2+} chelate compound, $C_{\text{PAN}}=3 \times 10^{-3}$ M.

the possibility that QD/PAN complexes could be used for luminescence sensing of Co^{2+} or Ni^{2+} ions in solution. However, in practice, the use of a QD/PAN PL sensor in solution form has obvious limitations, necessitating a redirection of our efforts to an examination of the sensing properties of QD/PAN complexes in polymer films.

B. Dissociative luminescent sensor for Co^{2+} , Ni^{2+} , and H^+ ions

Thin polymer films with thicknesses of 1–3 μm containing QD/PAN complexes were prepared, as described in Sec. II. Thin polymer films allow precise absorption and luminescence measurements at QD and PAN concentrations in films of about 10^{-4} M, that is, three orders of magnitude higher than those in organic solutions. It is expected that polymeric films may work as preconcentrators of the ions being sensed, increasing the sensitivity of the sensor.

Preliminary examinations of polymeric films with QD/PAN complexes exhibit PL behavior similar to QD/PAN in solution: QD PL quenching with increased C_{PAN} concentration [Fig. 3(a)] and a mean QD PL decay time independent of the PAN molar ratio. In parallel with the decrease in QD PL intensity, a characteristic PAN/ Zn^{2+} absorption spectrum emerges, totally dominating the film absorption at $R=1:10$. This is illustrated in Fig. 3(b), where a comparison of the absorption spectra of polymeric films containing free QDs (1), QD/PAN complexes (2 and 3), and PAN/ Zn^{2+} chelate compounds (dashed line) are presented. The reference polymeric film with PAN/ Zn^{2+} chelates was prepared by submerging a film with PAN in an aqueous solution of 10^{-3} M $\text{Zn}(\text{CCl}_3\text{COO})_2$ for 3 h at room temperature.

For the experiments on Co^{2+} sensing, a number of QD/PAN films with R equal to 1:10 and 1:1 were prepared and submerged in aqueous solutions with a pH of 6.5 containing

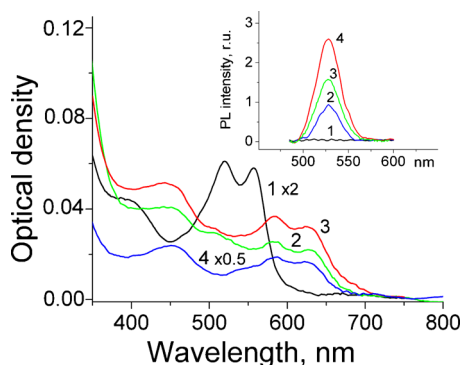


FIG. 4. (Color online) Absorption spectra of polymeric films with QD/PAN complexes ($C_{\text{QD}}=4 \times 10^{-4}$ M, $R=1:10$) 1—as prepared; 2 and 3—after submersion in 5×10^{-6} M and 10^{-5} M cobalt nitrate solution, respectively. 4—the film with PAN after immersion in a cobalt nitrate solution with a concentration of 6×10^{-6} M. The multiplication factors are shown. Inset: PL spectra of polymeric films with QD/PAN complexes. 1—as prepared; 2–4—after submersion in a cobalt nitrate solution with concentrations of 10^{-6} M, 5×10^{-6} M and 10^{-5} M, respectively. $\lambda_{\text{EXC}}=360$ nm.

Co^{2+} ions at various C_{Co} concentrations, and kept submerged for 5 h at room temperature. The diffusion of Co^{2+} ions into the film results in changes in the film absorption spectra and an increase in the QD PL intensity. Figure 4 illustrates changes in the absorption spectra of QD/PAN films with R equal to 1:10 after treatment in cobalt nitrate solutions. This treatment leads to a damping of the PAN/ Zn^{2+} absorption bands (1) and to the appearance of new absorption bands at 585 nm and 630 nm (2 and 3). These bands are characteristic of the PAN/ Co^{2+} chelate compound, as can be seen by comparison with the absorption spectrum of a film containing PAN after immersion in the cobalt nitrate solution (4). In Fig. 4 (inset), the increase in QD PL intensity with cobalt ion concentration is illustrated. Significantly, a mean luminescence decay time of ~ 10 ns was measured for these samples. This decay time, as well as the spectral position and linewidth of the PL band, is very similar to those from CdSe/ZnS quantum dots embedded in the polymer film. This allows us to assign this PL band to the band-edge luminescence of free QDs.

Similar absorption/luminescence changes were observed for polymeric film containing QD/PAN treated in a 6.5 pH aqueous solution of Ni^{2+} ions (Fig. 5). In this case, the characteristic absorption bands of a PAN/ Ni^{2+} chelate at 530 nm and 570 nm appear in the film spectrum (curves 2 and 3) with a simultaneous reduction in the PAN/ Ni^{2+} absorption bands (1). The appearance of these bands was accompanied by an increase in the QD PL signal, with an intensity which is proportional to the Ni^{2+} ion concentration (Inset in Fig. 5). As a result, we conclude that dissociation of QD/PAN complexes occurs in the presence of cobalt or nickel ions, followed by the formation of the stable, nonluminescent chelate compounds PAN/ Co^{2+} or PAN/ Ni^{2+} , leaving highly luminescent free QDs. The dissociation of the QD/PAN complexes by Co or Ni ions may be explained by the relatively weak binding of the PAN molecule to the QD shell Zn ions. Indeed, in the absence of the metal ions, a dynamic equilibrium is established between the competing processes of association and dissociation of the PAN and QDs, in which

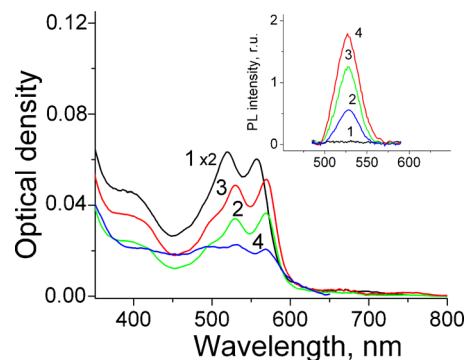


FIG. 5. (Color online) Absorption spectra of polymeric films with QD/PAN complexes ($C_{\text{QD}}=4 \times 10^{-4}$ M, $R=1:10$) 1—as prepared; 2 and 3—after submersion in 10^{-5} M and 2×10^{-5} M nickel sulfate solutions, respectively. 4—the film with PAN after submersion in 10^{-5} M nickel sulfate solution. The multiplication factor is shown. Inset: PL spectra of polymeric films with QD/PAN complexes: 1—as prepared; 2–4—after submersion in 10^{-6} M, 5×10^{-6} M and 10^{-5} M nickel sulfate solutions, respectively. $\lambda_{\text{EXC}}=360$ nm.

only a small fraction of the QDs and PAN molecules are free. In the presence of metal ions, a competing process of the formation of PAN/Co or PAN/Ni compounds occurs. When the association constant of this reaction is much greater than that for QD/PAN complexes, the reaction may be considered practically irreversible, leading to a permanent decrease in the number of PAN molecules capable of binding with Zn ions on the surface of the QD shell. Furthermore, we can reasonably assume that the PAN/ion complex formed is unable to bind to the QDs, since the main metal binding site on the PAN molecule is already occupied by a metal ion. We conclude that the dissociation of a majority of the QD/PAN complexes is expected. This qualitative model is consistent with a much lower value of the overall formation constant ($\lg \beta$) of the complex of PAN with Zn^{2+} ions of 21.7 (Ref. 16) than those with Co^{2+} of 25.8 (Ref. 17) and Ni^{2+} of 27.9.¹⁸ From this point of view it becomes clear why no changes in the QD/PAN luminescence have been observed in our experiments with the Cd^{2+} and Mn^{2+} ions which have $\lg \beta$ of 8.7,¹⁹ and <16.4 ,¹⁶ respectively.

We propose that polymer films with embedded QD/PAN complexes can be used for optical sensing of Co^{2+} and Ni^{2+} ions in aqueous solutions. Practically nonluminescent films with $C_{\text{QD}}=4 \times 10^{-4}$ M and R of 1:1 have been used for the titration experiments. The integrated intensities of the QD PL band were measured after submerging the films for 5 h in Co^{2+} and Ni^{2+} solutions of various concentrations at room temperature. These conditions were chosen to allow completion of the complex dissociation process. Figure 6 demonstrates the ion concentration dependencies of the PL intensity for Co^{2+} (a) and Ni^{2+} (b). We found that concentrations of 10^{-8} M Co^{2+} and 10^{-8} M Ni^{2+} in water solutions can be determined within experimental errors of $\sim 15\%$, even without optimization of the sensor parameters. These values are more than an order of magnitude lower than the detection limit of 6.7 ng ml^{-1} for Co(II) and 3.2 ng ml^{-1} for Ni(II) obtained by colorimetric measurements with PAN as a complexing reagent in the aqueous phase using the nonionic surfactant Tween 80.²⁰

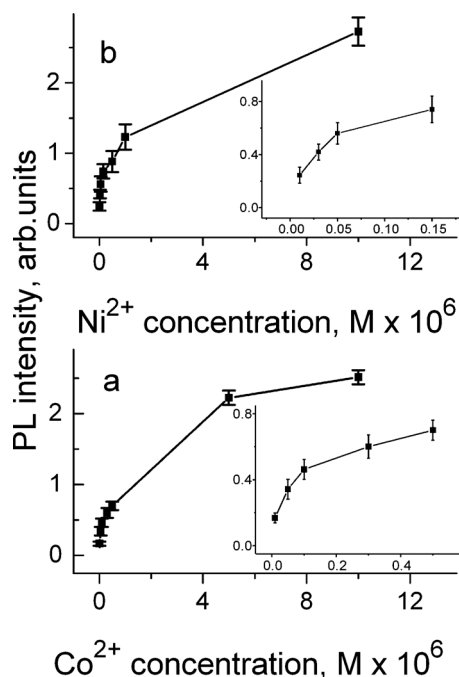


FIG. 6. PL intensity of QD/PAN films ($C_{QD} = 4 \times 10^{-4}$ M, $R = 1:1$) as a function of concentration of (a) Co^{2+} and (b) Ni^{2+} in aqueous solutions. Insets show the regions of low ion concentration. $\lambda_{exc} = 360$ nm.

The polymer films with QD/PAN complexes do not exhibit any changes in the PL intensity when they are kept in water at pH values in the range 6–13. This is why the experiments described here were carried out at a pH=6.5. However, we found that the PL from films appears and grows in intensity at pH levels below 5. This can be explained by PAN/ Zn^{2+} complex instability in an acid environment.¹³ This fact may be exploited when using these polymeric films for optical pH sensing.

IV. CONCLUSION

In conclusion, we have investigated the optical properties of complexes consisting of luminescent, hydrophobic core/shell CdSe/ZnS quantum dots and PAN molecules, which are a colorimetric indicator of Co and Ni ions. Using absorption-luminescence analysis, we showed that, in both organic solutions and when embedded in polymer films, the QDs and PAN form a complex where the PAN binds to surface Zn ions in the ZnS QD shells. Due to the strong spectral overlap between the QDs PL and PAN/ Zn^{2+} absorption bands, the QD luminescence is quenched via efficient FRET. We found that the presence of Co^{2+} and Ni^{2+} ions, both in organic solution or polymeric film, results in the dissociation of the QD/PAN complex due to the formation of stable PAN/Co and PAN/Ni chelates. Significantly, dissociation of QD/PAN complexes is followed by the appearance of QD luminescence, whose intensity increases with the concentra-

tion of the metal ions in the water solution, allowing quantitative PL sensing of the relevant metal ion. Incorporation of QD/PAN sensors in hydrophobic polymer films, allowing metal ion diffusion and concentration, together with the utilization of the luminescent response from highly luminescent, hydrophobic QDs, offers considerable promise for the fabrication of highly sensitive, analytical indicators of transition metal ions in aqueous solutions for biological and ecological applications. We expect that this approach will have application to the selective detection of a variety of metal ions, depending on the QD and molecule-indicator pairs chosen.

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