Surfactant−Semiconductor Interfaces: Perturbation of the Photoluminescence of Bulk Cadmium Selenide by Adsorption of Tri-*n*-octylphosphine Oxide as a Probe of Solution Aggregation with Relevance to Nanocrystal Stabilization

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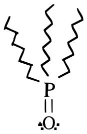
Abstract: The band edge photoluminescence (PL) of bulk single-crystal *n*-CdSe is perturbed by adsorption of tri-*n*-octylphosphine oxide (TOPO) from toluene solution onto the crystal's 0001, $000\bar{1}$, and $11\bar{2}0$ faces. These are three of the crystal faces observed in studies of CdSe nanocrystals, which are commonly capped with TOPO surfactant molecules to control their properties. At low concentration, where monomeric TOPO dominates the toluene solution composition, reversible PL enhancements are observed, indicating that the adsorbate is acting as a labile Lewis base toward the surface. However, above ∼10 mM concentration, there is an abrupt reversal in the PL signature, such that net quenching of PL is observed relative to the PL intensity in the toluene reference ambient. The PL changes at concentrations above 10 mM are not reversible with toluene rinsing, and are associated with a strongly bound species of Lewis acidic character that requires exposure to a strong base such as pyridine for desorption. XPS data are consistent with PL measurements in identifying experimental conditions associated with strong and weak binding of TOPO to CdSe. The PL changes can be fit to a dead-layer model in both the low and high concentration regimes, permitting an estimate for TOPO-induced contractions and expansions of the dead-layer thickness of about 100−300 Å, for the 0001 face, which generally yielded the largest PL changes. Equilibrium binding constants were estimated from the Langmuir adsorption isotherm model as being $\sim10^4$ M^{-1} and at least 10^2 M^{-1} in the low and high concentration regimes, respectively. The concentration at which the PL signature reversal occurs corresponds to incipient aggregate formation in solution based on both ^{31}P NMR and IR spectral changes. MacroModel calculations indicate that TOPO dimer formation is energetically favorable and that a surface adduct formed from the dimer could be stabilized by multiple surface interactions.

Introduction

Semiconductor nanocrystals or quantum dots derived from II−VI compounds have been intensively studied due to their size-dependent physical properties.[1−4] The interaction of amphiphilic surfactant molecules with the semiconductors' surfaces has been critically important in synthesizing these solids: The size of the nanocrystal is controlled by adsorbing long-chain surfactant molecules, capping agents, onto the nanocrystal surface, forming reverse micelle structures. Many capping agents have been used, including thiophenols,[5,6] mercaptoethylamine,[7] and tri-*n*-octylphosphine oxide (TOPO),[8] whose structure is shown below.


TOPO

TOPO-capped CdSe nanocrystals have been particularly well characterized through the use of such methods as NMR and XPS spectroscopies.[9,10] The NMR studies were used to determine the absolute coverage of TOPO ligands and their bonding geometries, and the surface elemental composition was studied by XPS; both studies showed that the TOPO interacts with Cd surface sites. Related studies showed that CdSe nanocrystals have a C_3 axis of symmetry with many exposed surfaces, including the 0001, $000\bar{1}$, $10\bar{1}0$, and $11\bar{2}0$ faces.[11] The

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data from the surface studies described above thus represent an average of the adsorption behavior of these exposed nanocrystal faces.

We have previously demonstrated that the photoluminescence (PL) of bulk, oriented single-crystal CdSe samples can be used to study the adsorption of a variety of analytes from the gas phase and from nonaqueous solution.[12] Many of the systems studied to date fit a dead-layer model, in which the near-surface region of the semiconductor, corresponding to a thickness on the order of the depletion width, is assumed to be nonemissive. The absence of PL from this region is attributed to the electric field therein, which inhibits the recombination of photogenerated electron−hole pairs. The depletion width can result from trapping of electrons in surface states whose energies lie within the band gap. Adsorption of Lewis acids withdraws additional electron density toward the surface, expanding the dead layer and quenching PL intensity; conversely, adsorption of electron-donating Lewis bases shifts surface-trapped electron density back to the bulk, shrinking the dead layer and enhancing the PL intensity.

In this paper we demonstrate a novel extension of this PL-based methodology to semiconductor−surfactant interfaces by characterizing the adsorption of TOPO from toluene solution onto various faces of single-crystal CdSe. Specifically, we demonstrate that at low concentrations of ≤1 mM, TOPO acts like a labile base, reversibly enhancing the PL intensity upon adsorption. At higher concentrations, stronger binding with Lewis acidic character is observed, represented by quenching of PL intensity that cannot be reversed by toluene rinsing. This abrupt change in PL signature can be correlated with solution aggregate formation, identified through ^{31}P NMR and IR spectral measurements. MacroModel calculations support the formation of a TOPO dimer, whose structure lends itself to strong binding with a variety of faces that are observed in CdSe nanocrystals.

Experimental Section

Materials. Single-crystal *n*-CdSe was etched in concentrated HCl or Br_2/MeOH (1:15 v/v) for 15 s and then rinsed and sonicated in MeOH prior to each experiment. CdSe *c*-plates, cut along the 0001 and $000\bar{1}$ faces, were obtained from several sources, including Atramet, Inc. and Cleveland Crystals, Inc. CdSe *a*-plates, cut along the $11\bar{2}0$ face, were obtained from Cleveland Crystals, Inc. All crystals had a resistivity of approximately 2 Ω·cm. Toluene (Fisher) was distilled over Na/benzophenone before being used to make the tri-*n*-octylphosphine oxide (TOPO) solutions. Cyclohexane (Fisher) was distilled over $CaCl_2$. TOPO (99%), d_8-toluene (99+ atom % D), and tri-*n*-butyl phosphate (99+%) were purchased from Aldrich and used as received.

PL Apparatus. The CdSe sample was placed on a glass rod and held between two Teflon rings in a glass cell, which was continuously kept under flowing N_2.[12] Two sources were used to excite the sample: a Melles-Griot Model 80 HeNe laser (633 nm) and a Coherent Innova 90 Ar^+ laser (458 and 514 nm). The excitation intensity did not exceed 20 mW/cm^2. The resulting 720-nm band-edge PL was collected by an Oriel Instaspec II Si photodiode array and processed by a computer. Because the PL spectral distribution is unaffected by TOPO adsorption from toluene solution at low resolution (0.5 nm), PL intensity is monitored at the band maximum.

XPS. XPS data were collected on a Perkin-Elmer PHI 5400 ESCA system with a Mg X-ray source powered at 300 W. The aperture size was set at 1 mm × 3 mm, and the pass energy was 89.45 eV. Acquisition time for each run was 5 min. Samples were prepared by dipping the CdSe crystal into toluene solutions of varying TOPO concentration and rinsing with toluene. To prepare the neat-TOPO-treated sample, TOPO was heated on a hot plate until melted. The CdSe sample was then placed in the hot liquid, withdrawn, and immediately rinsed with toluene.

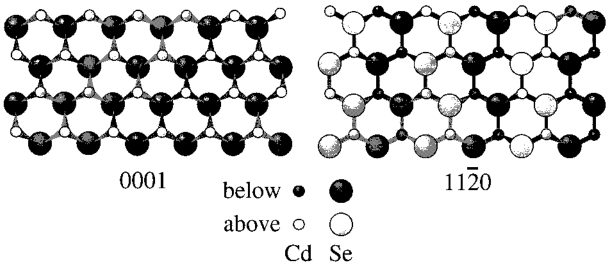

Figure 1. Idealized structures of the polar 0001 and the nonpolar $11\bar{2}0$ CdSe surfaces. The structure of the polar $000\bar{1}$ surface is derived from that shown for the 0001 surface by interchanging the Cd and Se atoms.

NMR Spectroscopy. $^{31}P\{^1H\}$ NMR (121 MHz) spectra of TOPO toluene solutions were obtained with a Bruker AC-300 spectrometer. The samples were run at 21 °C using a 3.6 s acquisition time, and the sweep width was set at 9090 Hz. Data (32 K) were processed using a Lorentzian line broadening of 3 and zero fill. Error in the measurements was ±0.05 ppm. Solutions were made by adding d_8-toluene to freshly distilled toluene in a 1:4 (v/v) ratio. All $^{31}P\{^1H\}$ spectra were referenced to 85% H_3PO_4, which was held in a capillary tube placed inside the 5 mm o.d. NMR tube filled with TOPO solution.

IR Spectroscopy. IR spectra of TOPO−cyclohexane solutions were collected on a Nicolet 740 FT-IR spectrometer. Sixteen scans were recorded in the range of 1400−1000 cm^{-1}. The IR cell was designed such that there was a 5-mm path length between the two salt plates. Nicolet Advantage software was used to analyze the data. TOPO solutions were prepared from freshly distilled cyclohexane and stored in a N_2 glovebox before use.

Computer Modeling. Computer simulations were performed using MacroModel Version 4.5 molecular modeling software. Energy minimizations were performed with an MM2 force field. TOPO dimers were formed by placing two monomers, whose energies had previously been minimized, initially at ∼6 Å from each other. Calculations were done using several different initial monomer positions, and each yielded a similar dimer once minimized.

Results and Discussion

Adsorption of TOPO onto several bulk single-crystal CdSe faces was studied. Figure 1 presents idealized views of these surfaces. The polar 0001 and $000\bar{1}$ surfaces have exposed planes of Cd and Se atoms, respectively; in contrast, the nonpolar $11\bar{2}0$ face consists of chains of alternating Cd and Se atoms.[13−15] It should be kept in mind that the etched surfaces employed in our studies are handled in such a way that traces of water and oxide phases, e.g., may also be present on the surface. All of these samples exhibit band-edge PL ($\lambda_{max} \approx$ 720 nm; $E_g \approx 1.7$ eV)[16] when excited with ultraband gap light.

In sections below we describe the dependence of CdSe PL intensity on crystal face and TOPO concentration and use these measurements to estimate TOPO-induced changes in dead-layer thickness and, in conjunction with XPS measurements, the binding affinity of TOPO for the CdSe surface. Solution ^{31}P NMR and IR spectra, along with MacroModel calculations, are used to correlate the PL data with solution aggregate formation and to identify plausible aggregate and adsorbate structures.

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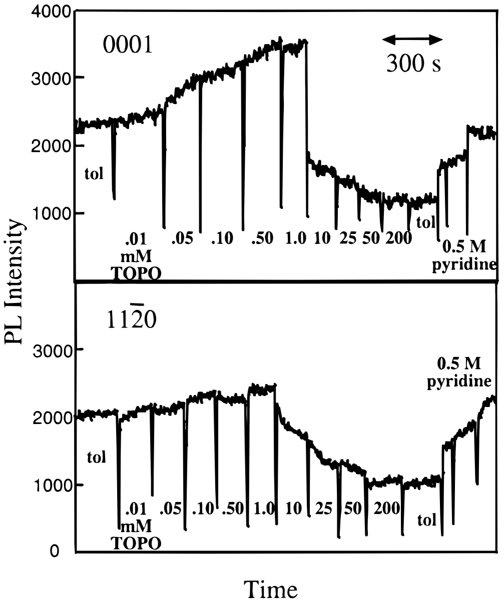

Figure 2. Changes in PL intensity, monitored at 720 nm, due to the adsorption of TOPO onto the 0001 (top panel) and $11\bar{2}0$ (bottom panel) faces of CdSe from toluene solution. Repeated rinses with a 0.5 M pyridine solution in toluene were used at the end of each run to restore the original toluene reference baseline. The samples were excited with 458 nm light. Neat toluene is denoted "tol".

Adsorption Experiments. (a) PL Traces. Typical PL traces for the adsorption of TOPO onto the CdSe surfaces are shown in Figure 2. For all surfaces examined, TOPO begins to elicit a PL intensity enhancement at ~0.01 mM and gives a concentration-dependent increase in PL up to approximately 1 mM. At concentrations of ~10 mM, the PL signature abruptly reverses: the CdSe PL is quenched relative to the toluene reference PL level, with this response saturating near 50 mM. This reversal in PL signature consistently occurs at ~10 mM independent of the crystal face and etchant employed in the experiment, suggesting an origin in solution composition that we attribute to aggregate formation (vide infra).

The $11\bar{2}0$ and $000\bar{1}$ surfaces give similar PL signatures upon adsorption of TOPO, with the principal difference compared to the 0001 surface being that the fractional PL change is significantly smaller in the low concentration regime and slightly smaller in the high concentration regime. These results were observed both by comparisons among several crystals and by use of an individual crystal, performing the PL experiment on the front 0001 face, back $000\bar{1}$ face, and edge $11\bar{2}0$ face of a single CdSe *c*-plate. The larger response of the 0001 face is intriguing and may arise because, relative to the $000\bar{1}$ and $11\bar{2}0$ faces, the 0001 surface of CdSe is Cd rich; i.e., this face has the largest surface density of Cd atoms available for binding TOPO.[13-15] However, our data do not permit us to determine whether the differences in relative PL intensity changes arise from different absolute coverages, different binding sites, different forms of ligation, or some combination thereof.

Although not shown in Figure 2, at low concentrations of ≤1 mM, the TOPO can be removed from the surface with repeated toluene rinses, and the PL drops to the original toluene baseline level, suggesting that the adsorbate is labile. At higher concentrations, beginning at ~10 mM, the TOPO PL response is not reversible by rinsing with toluene alone. At these higher concentrations, however, as shown in Figure 2, removal of TOPO from the CdSe surfaces could be achieved by rinsing with a toluene solution of pyridine. In studies of TOPO-capped nanocrystals, washing with neat pyridine displaced almost all of the adsorbed TOPO.[8b,10]

Two related systems were briefly examined to explore the generality of these effects. PL data of TOPO adsorbed onto the 0001 CdSe surface from cyclohexane solution give a similar signature, but the reversal from enhancement to quenching occurred at a lower concentration of ~1 mM. This result is consistent with aggregate formation at lower concentration in the more nonpolar cyclohexane solvent. Use of tri-*n*-butyl phosphate [$(n\text{-}C_4H_9O)_3P{=}O$] as the adsorbate in toluene solution caused an abrupt PL signature enhancement near the reported critical association concentration (CAC) of 0.7 mM at which aggregates begin to form in solution.[17]

(b) Dead-Layer Model. As noted in the Introduction, the direction of the PL changes is consistent with the TOPO adsorbate acting as a Lewis base at low concentrations and as a Lewis acid at higher concentrations, with 1−10 mM representing the transition region. Evidence will be presented below suggesting that TOPO monomers adsorb at low concentration and that dimers and/or higher oligomers adsorb at higher concentrations.

We find that the PL changes caused by TOPO adsorption in both concentration regimes can quantitatively be analyzed using the dead-layer model, eq 1,[18,19] where PL_{ref} is the reference PL

$$PL_{ref}/PL_x = \exp(-\alpha'\Delta D) \qquad (1)$$

intensity in toluene solvent, PL_x is the intensity of PL upon exposure to the analyte, $\alpha' = \alpha + \beta$ is the sum of the semiconductor absorptivities for exciting and emitted light, and $\Delta D = (D_{ref} - D_x)$ is the change in dead-layer thickness upon adsorption of the chalcogenide species. This model assumes that the surface recombination velocity, S, is either very large or unaffected by adsorption of the analyte species onto the surface ($S \gg L/\tau$ and $S \gg \alpha L^2/\tau$, where L and τ are the minority carrier diffusion length and lifetime, respectively).

Use of different excitation wavelengths should provide different PL ratios (eq 1), but a constant value for ΔD, which is assumed to be a rough measure of the change in depletion width. Representative fits to the dead-layer model are shown in Figure 3 for saturated enhancements at ~1 mM (low concentration regime) and for saturated PL quenchings at ~50 mM (high concentration regime) elicited by TOPO adsorption onto the 0001 and $11\bar{2}0$ surfaces. Good fits within experimental error were obtained in all cases with contractions in ΔD of ~130 Å for the 0001 face in the low concentration regime and expansions in ΔD of ~200 Å for the 0001 face and ~150 Å for the $11\bar{2}0$ face in the high concentration regime. For all of the samples examined, typical values for ΔD ranged from 100 to 300 Å.

To corroborate the dead-layer results in the high concentration regime, Kelvin probe contact potential difference (CPD) and time-resolved photoluminescence (TRPL) measurements[20,21] were performed on TOPO-treated 0001 CdSe surfaces, which were prepared by dipping the crystal in 10 mM TOPO−toluene solutions and rinsing the sample with toluene. Results from both experiments were consistent with TOPO-induced changes in depletion width. An increase in depletion width thickness

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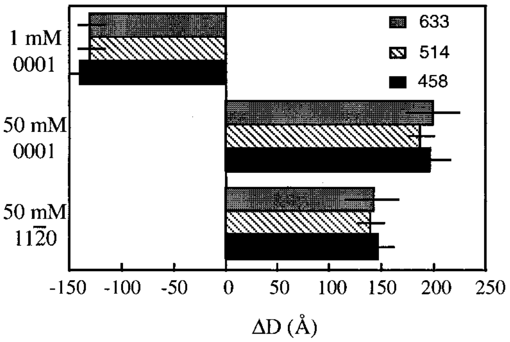

Figure 3. Dead-layer model fits for adsorption of TOPO from 1 mM toluene solution onto the 0001 surface of CdSe and from 50 mM toluene solutions onto the 11$\bar{2}$0 and 0001 surfaces of CdSe. The ΔD values shown correspond to the 1 mM saturated contraction and 50 mM saturated expansions of the dead-layer thickness, calculated using eq 1 and measured PL intensity ratios. The horizontal lines indicate the error calculated assuming a ±50 count uncertainty in the PL measurements; PL intensities ranged from 1200 to 3500 counts. Values for the absorptivities used in eq 1 for faces perpendicular (0001) and parallel (11$\bar{2}$0) to the *c* axis can be found in ref 16.

upon TOPO adsorption was deduced from photosaturation CPD measurements.[21] TRPL measurements show only a slight reduction in the PL decay time after TOPO adsorption, compared to freshly etched CdSe samples, indicating that the kinetics of electron−hole pair recombination are not significantly affected by TOPO adsorption.

(c) Binding Constants. The concentration dependence of the PL changes was analyzed using the Langmuir adsorption isotherm model, which permits an estimation of the equilibrium binding constant of TOPO to these crystal surfaces. This model has the form

$$\Theta = KC/(1 + KC) \quad \text{or} \quad 1/\Theta = 1 + 1/KC \tag{2}$$

where Θ is the fractional surface coverage, K is the equilibrium binding constant, and C is the analyte concentration. A double reciprocal plot of Θ^{-1} vs C^{-1} should be linear with a slope of K^{-1}. In our experiments, we assume that the maximum PL change and ΔD value correspond to all surface sites being filled, i.e., $\Theta = 1$. At intermediate concentrations Θ is calculated as the fractional dead-layer change using eq 3, assuming an unpinned surface, where PL_{sat} is the saturated PL intensity.

$$\Theta = \ln[(PL_{ref}/PL_x)]/\ln[(PL_{ref}/PL_{sat})] \tag{3}$$

Representative fits to this model for TOPO adsorption onto the 0001 CdSe surface at low and high concentrations are shown in Figure 4 and are of good quality. Values of K for the TOPO species in the low concentration regime are typically $\sim 10^4$ M^{-1} for all crystal faces examined. This similarity suggests that a comparable kind of interaction characterizes the binding of TOPO to all three crystal faces. Our data do not permit us to say whether these surfaces have intrinsically similar TOPO binding capabilities because of the uncertain role of adventitious impurities that may be present.

In the high concentration regime, all of the CdSe surfaces examined give apparent values of K of $\sim 10^2$ M^{-1}. This number is a lower limit, however, since the total concentration is used in constructing plots such as that shown in Figure 4B. If aggregates are binding to the surface, their concentrations in solution are smaller and values of K are consequently larger. The irreversibility of the PL changes in this concentration regime upon exposure to toluene (Figure 2) is consistent with the presence of strongly bound TOPO aggregates.

(d) XPS Measurements. Another technique we employed to characterize the affinity of TOPO for CdSe surfaces under our different experimental conditions was XPS. TOPO-capped CdSe nanocrystals were studied by XPS, and the P_{2p} peak was used to determine whether adsorption had occurred.[10] XPS measurements of the 0001 face of CdSe samples dipped in 0.05 and 50 mM TOPO−toluene solutions, followed by a toluene rinse, were made and compared with data obtained on a freshly etched but untreated sample. The P_{2p} peak was present only on the 50 mM TOPO-treated sample, consistent with the irreversible PL response seen from this concentrated solution. However, when a 50 mM TOPO-treated sample was rinsed with a 0.5 M toluene solution of pyridine prior to obtaining XPS data, no P_{2p} peak was evident. This result supports the displacement of surface-confined TOPO by pyridine inferred from PL data (Figure 2). XPS experiments on a 11$\bar{2}$0 surface treated with 50 mM TOPO were also conducted to see if the relative amount of phosphorus on the surface differed from that observed using the 0001 face. Similar peak sizes were found with both the 0001 and 11$\bar{2}$0 faces, indicating that similar amounts of P are on both surfaces.

To better relate these data to nanocrystal surfaces, which are prepared in neat TOPO, the 0001 surface of a CdSe crystal was dipped in neat, hot TOPO and rinsed with toluene. Its XPS P_{2p} signal was similar to that of the 50 mM TOPO-treated samples, indicating similar degrees of adsorption from these two liquids on 0001 bulk CdSe surfaces. As seen with bulk CdSe in this study, washing the TOPO-capped CdSe nanocrystals with pyridine was reported to result in the loss of the P_{2p} peak in XPS measurements.[10] It is noteworthy that ^{31}P NMR data of TOPO-capped CdSe nanocrystals reveal that a small amount of TOPO remains after the pyridine exchange reaction, evidencing the presence of more strongly bound adsorbates.[8b]

Evidence for Aggregate Formation. TOPO has been reported to form reverse micelles in toluene solution with a critical micelle concentration (CMC) of ∼170 mM, determined by studying the concentration dependence of the dielectric properties of the solutions.[17] However, we would not anticipate large TOPO reverse micelles having a strong electronic interaction with any of the CdSe surfaces, as we would expect that exposed alkyl chains would have little affinity for the surface. From prior studies, we would expect that the monomeric TOPO species that should dominate the solution composition at low concentration would bind to Cd sites of Lewis acidity through the surfactant's basic oxygen atom.[22,23] On the other hand, small oligomeric structures such as dimers present at higher concentrations could afford new binding modes that might account for the dramatic reversal from Lewis basic to Lewis acidic binding character observed in the PL measurements. Evidence for aggregates of TOPO species was thus sought from ^{31}P NMR and IR spectral data and from MacroModel calculations.

NMR Spectroscopy. ^{31}P NMR has been used in previous studies to ascertain if micelles are present in solution and to determine the CMC.[24−27] The reversal of the PL response near

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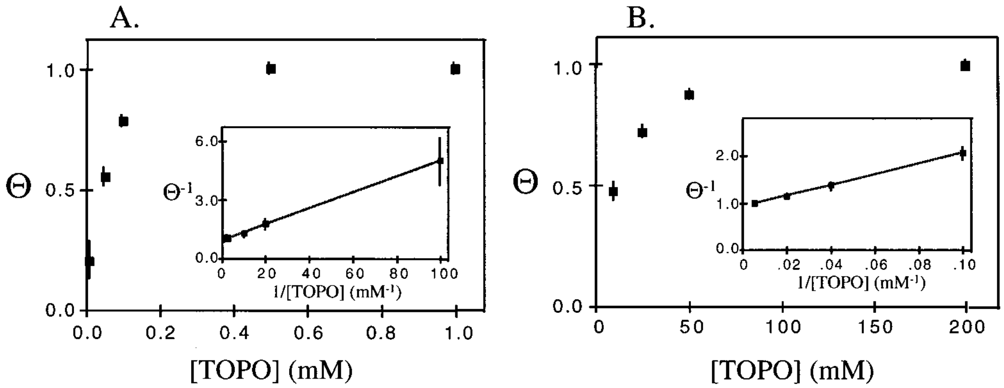

Figure 4. Fractional surface coverage, Θ, determined using eq 3, vs concentration of TOPO in toluene solution for adsorption onto the 0001 face of CdSe in the low (left-hand panel) and high (right-hand panel) concentration regimes; data are those shown in the top panel of Figure 2. Insets show the double reciprocal plot of the same data, eq 2, yielding an equilibrium binding constant of $(2.4 \pm 1.0) \times 10^4$ M^{-1} in the low concentration regime and $(1.0 \pm 0.1) \times 10^2$ M^{-1} in the high concentration regime. Error was calculated assuming a ± 50 count error in the PL measurements; PL intensities ranged from 1200 to 3500 counts.

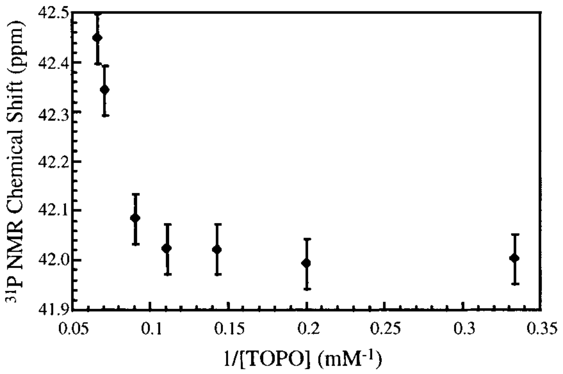

Figure 5. ^{31}P NMR chemical shift vs inverse concentration of TOPO. Data were obtained at 21 °C.

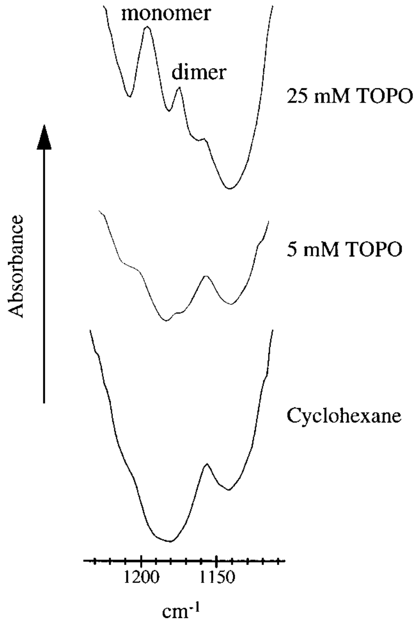

Figure 6. IR spectra in the P=O stretching region for cyclohexane and 5 and 25 mM TOPO solutions in cyclohexane.

10 mM leads us to believe that there may be a variety of species in solution at these higher concentrations. NMR data were used to seek evidence for aggregate formation in toluene in this concentration regime. A plot of ^{31}P NMR chemical shift vs reciprocal TOPO concentration is given in Figure 5. The change in slope near 10 mM suggests that aggregates form above this concentration, which also corresponds to the PL signature change from enhancement to quenching.

The variation of the ^{31}P chemical shift begins to occur at a much lower concentration than the reported CMC of ~170 mM. We believe that at this lower concentration smaller aggregates (dimers, trimers, e.g.) are formed and that this value may correspond to the critical association concentration (CAC) of TOPO in toluene solution. We tried to fit the chemical shift data to a simple model representing a monomer−dimer equilibrium,[28,29] but the poor fit obtained suggests that other species, presumably higher oligomers, are present as well.

(b) IR Spectroscopy. Shorter chain phosphine oxides ($Me_3P{=}O$, $Et_3P{=}O$) are known to form dimers in many solvents from IR measurements. Typically, the P=O stretching frequency shifts to lower energy with increasing concentration.[30] We conducted IR experiments with TOPO in cyclohexane solution, which provides a more transparent window in the P=O stretching region than toluene. At concentrations <3 mM, only a shoulder at 1195 cm^{-1} is observed in this spectral region, which we attribute to the monomer. Above 3 mM the TOPO solutions exhibit a second peak at 1177 cm^{-1} (Figure 6), consistent with aggregate formation. This peak continues to grow up to ~25 mM. The onset of association at 3 mM is at a lower concentration than was seen by ^{31}P NMR in toluene. However, it parallels the PL data, which displayed the characteristic enhancement-to-quenching transition at this lower concentration. The difference in the two solvents is reasonable given that oligomers would be expected to form at lower concentration in the more nonpolar cyclohexane solvent.

(a) Computer Modeling. MacroModel calculations were performed to determine whether the proposed TOPO dimer was a reasonable structure. To form the dimer, two monomers were placed within 6 Å of each other and the energy was minimized. Regardless of the initial monomer placement, a "head-to-tail" TOPO dimer formed with approximately the same bond angles and distances between the interacting P and O atoms, Figure 7. The relative stability of the dimer was determined by comparing its energy (119 kJ/mol) to that of two monomers (86 kJ/mol × 2 = 172 kJ/mol).[31] The interaction of alternating P and O atoms, as shown in Figure 7, seems to stabilize the molecules

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[28] Chen, J.-S.; Shiau, J.-C.; Fang, C.-Y. *J. Chin. Chem. Soc.* **1995**, *42*, 499.

[29] Chen, J.-S.; Fang, C.-Y.; Baird, J. K. *Z. Phys. Chem.* **1997**, *199*, 49.

[30] Mayer, U.; Hoffman, H.; Kellner, R. *Monatsh. Chem.* **1988**, *119*, 1207.

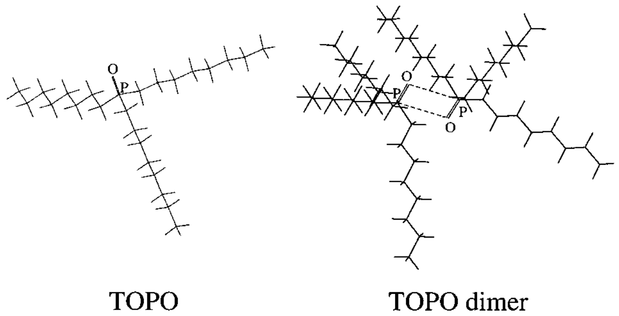

Figure 7. TOPO monomer and proposed TOPO dimer, as calculated by MacroModel. The planar parallelogram created by the alternating P and O interactions results in a O−P−O bond angle of 85° with the P−O−P angle opened to 95°. The distances between opposite P atoms, between opposite O atoms, and between adjacent P and O atoms are 4.6, 4.3, and 4.2 Å, respectively. The P═O bond distance is 1.5 Å.

according to these energy minimizations. This structure, with the two opposing O atoms and two opposing P atoms 4.3 and 4.6 Å from one another, respectively, may account for the irreversibility of the TOPO adsorption in the high concentration regime: The lattice constant for the CdSe wurtzite structure is 4.3 Å; therefore, if the TOPO dimer lies roughly parallel to the surface, it can interact with multiple Cd and Se surface sites, strengthening the binding to the surface, Figure 8. The more similar PL responses of the 0001 and $11\bar{2}0$ faces in the high concentration regime relative to the low concentration regime (vide supra) are consistent with a mode of multisite ligation that is less sensitive to the surfaces' structural differences.

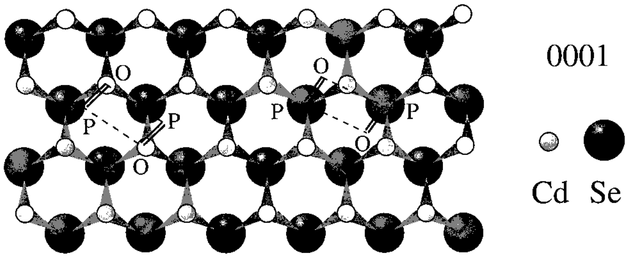

Figure 8. Proposed TOPO dimer structure superimposed onto the idealized 0001 CdSe surface. The alkyl groups are omitted for clarity.

Conclusions

Collectively, our data demonstrate that the PL of semiconductor surfaces can be used to monitor surfactant aggregation phenomena when the monomer and its oligomers have sufficiently different interactions with the semiconductor surface. Because surfactants are often used as capping agents in the synthesis of semiconductor nanocrystals, PL responses of bulk, oriented single crystals to the adsorption of surfactants may provide a general tool for characterizing these important interfaces. We are currently exploring related systems in our laboratories.

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(31) A corresponding B3LYP/6-31G* calculation for H_3PO yielded a stabilization energy of ∼38 kJ/mol for the dimer relative to a pair of monomers. The direction of the calculated IR and NMR peak shifts for dimer formation is consistent with our experimental data. For a general reference about the B3LYP/6-31G* calculation see: Foresman, J. B.; Frisch, A. *Exploring Chemistry with Electronic Structure Methods*, 2nd ed.; Gaussian, Inc.: Pittsburgh, 1996. We thank Professor Frank Weinhold for performing this calculation.