Ligand Effects on Optical Properties of CdSe Nanocrystals

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We report effects of various organic and inorganic ligands on optical properties of CdSe nanocrystals (NCs) by changes in their photoluminescence and absorbance spectra. Surface ligand loss occurring during dilution and purification of solutions of CdSe NCs leads to a decrease of photoluminescence intensity. The complex of trioctylphosphine with Se atoms on the surface of CdSe NCs is found responsible for the trap emission band that is red-shifted relative to the photoluminescence band edge.

Introduction

The size-dependent optical properties of semiconductor nanocrystals (NCs) have been actively studied during the past decade. Their applications, primarily involving CdSe NCs, include photostable luminescent biological labels,[1,2] solar cells,[3−5] and light-emitting devices (LEDs).[6−9] The nature of the ligand capping layer surrounding the NCs and preventing their coagulation strongly affects their luminescent properties.[10] Available through the classic organometallic route[11] and its numerous "greener" modifications,[12−17] the synthesized CdSe NCs are covered with organic ligands containing bulky (C8−C18) alkyl groups. NCs with such hydrophobic capping cannot be used directly in applications that require aqueous solubility or an effective charge transport property. This obstacle is usually eliminated by surface ligand exchange reactions where the appropriate functionality is introduced with a new capping ligand.

For biological labeling applications, CdSe NCs are often overcoated with ZnS, CdS, or ZnSe layers—these improve the fluorescence quantum yield[18] and in the cases of ZnS and ZnSe decrease NC toxicity—using successive surface exchange reactions with hydrophilic molecules (e.g., mercaptoacetic acid[2] or dithiothreitol[19]) or by further embedding into a siloxane shell.[20] For applications involving charge transfer, such as solar cells, the use of a shell of a higher band gap material acting as a potential barrier is not efficient. In this case, to facilitate electron transfer, exchange with a conducting pentathiophene derivative has been reported.[21] Surface exchange reactions of CdSe NCs have also been reported with pyridines,[10,11,22] thiols,[10,12,23,24] amines,[15] and derivatized phosphine oxides.[25]

Despite the importance of surface exchange reactions with organic ligands for functionalization of semiconductor nanoparticles, information on the influence of the organic capping layer on the optical properties of CdSe NCs is fragmented, relative to the large scope of the chemistry involved. Early work by Majetich et al. showed increased photoluminescence (PL) of CdSe NCs capped with butanethiolate, compared to those capped with thio-2-naphtholate.[26] Kuno et al. reported that the surface exchange reaction of CdSe NCs capped with trioctylphosphine oxide (TOPO) and trioctylphosphine selenide (TOPSe), with thiophenol, 4-(trifluoromethyl)thiophenol, pyridine, or 4-methylpyridine, decreased the NC photoluminescence

quantum yield (PL QY) from 10−15% to about 1%. These exchanges also caused small shifts of absorption maxima to lower or higher energies.[10] Guyot-Sionnest et al. used infrared pump−probe spectroscopy to detect different intraband relaxation rates between CdSe NCs capped with TOPO, 4-methylthiophenol, and pyridine, concluding that the photoexcited hole can, depending on the particular surface capping, lie either in a shallow trap, in a deep trap, or as a charge separated complex.[27] Talapin et al. reported blue shifts in UV/vis absorption and PL spectra of CdSe NCs upon exchange of TOPO with amines such as *n*-hexadecylamine, *n*-dodecylamine, and allylamine, producing roughly an order of magnitude increase in PL QY.[15] Exchanges involving *n*-butylamine produced varied effects: for CdSe NCs of 3.2 nm core size no shifts occurred in absorption or PL spectra and PL QY decreased, whereas for 1−2 nm core CdSe NCs displayed a blue-shifted (440 to 414 nm) and increased band edge absorbance.[28−30] Shmelz et al. report that the PL of TOPO capped CdSe and CdSe/ZnS NCs disappears upon exchange with 1,12-diazaperylene,[31] and Yu et al. state that the band edge absorbance coefficients of TOPO, thiol, and pyridine capped CdSe NCs are equal within experimental error.[32] Petruska et al. observed that PL QY increased upon addition of decanoic acid to chloroform solutions of CdSe NCs,[33] and Jang et al. note a 50-fold enhancement of PL QY of CdSe NC solutions treated with sodium borohydride.[34]

The present research systematically examines the consequences of exposure of CdSe NCs to putative surface ligands and other substances, on the optical properties of the NCs. Findings of effects of purification procedures and aging of CdSe NC solutions on their optical properties are also reported. Reversible capping ligand loss is the major process responsible for changes in PL upon purification and upon dilution of more concentrated solutions of CdSe NCs. The chemical species on the surface of CdSe NCs that is responsible for surface state emission is identified; this broad emission band, red-shifted relative to the band edge PL peak and sometimes called "deep trap emission", was reported previously[2,10,18] but its source has been unknown. Since surface state emission and the effects caused by capping ligands are both surface phenomena, in order to enhance them in the present work, we concentrate on small CdSe NCs (average diameter 2.0−2.3 nm) that have a large surface-to-volume ratio.

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Experimental Section

Chemicals. Trioctylphosphine (TOP, 90%), trioctylphosphine oxide (TOPO, either technical purity 90% or 99%), hexadecylamine (HDA), 4-methoxypyridine (4-MeOPy), cadmium oxide (99.99%), cadmium acetate hydrate (99.99%), *n*-tetrabutylammonium hydroxide (Bu$_4$NOH, 40 wt % solution in water), cadmium perchlorate, and Se pellets (99.999%) were purchased from Aldrich. 4-(Dimethylamino)pyridine (DMAP) and *n*-tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$) were purchased from Fluka; methanol, chloroform, pyridine, and ethanol were purchased from Fischer Scientific; octadecylphosphonic acid (ODPA) was purchased from Alfa. All chemicals were used without further purification. S2BN and S22OH (see Figure 6) were a gift from R. Lazar and Prof. A. Shanzer (Weizmann Institute). The synthesis of S2BN was previously reported.[35]

Synthesis of CdSe NCs. TOPO/TOPSe capped CdSe NCs were synthesized by the procedure developed by Peng et al. with minor modifications.[12] Typically, a Se (TOPSe) stock solution was prepared by mixing 0.08 g of Se pellets and 2 g of TOP in a glovebox. Six grams of TOPO and 0.05 g of cadmium acetate hydrate were placed into a 25 mL three-neck round-bottom flask and heated to 100 °C under dry Ar flow. While stirring, the resulting melt was degassed under vacuum at 150−180 °C for about 1 h. Lowering the temperature to ∼100 °C, vacuum was replaced with Ar flow, and the solution in the flask was then heated to 330 °C. Simultaneously with heat removal, a Se solution was quickly injected into the vigorously stirred reaction mixture through a rubber septum. The color change observed within 2−5 s indicated the formation of CdSe NCs. The resulting solution was cooled to 60−90 °C and poured into cold methanol (∼80 mL), and the resulting suspension was stored in the dark. When sedimentation was completed (usually overnight), the colorless solution was decanted, the resulting wet yellow solid was dissolved in 3−5 mL of CHCl$_3$, and the solution was filtered though a 0.2 μm syringe filter. This stock was used as is (corresponds to "zero purification steps" or "unpurified stock solution" in the text) or was subjected to further "purification steps", which involved reprecipitation with methanol, centrifugation, decantation, and redissolving the NCs in CHCl$_3$. (While TOP is not soluble in pure methanol, it is soluble in methanol/CHCl$_3$ mixtures.)

ODPA capped CdSe NCs were synthesized by the procedure developed by Peng et al. with some modifications:[13,14] Typically, 0.0514 g of CdO, 0.2682 g of ODPA, and 3.77 g of TOPO were loaded into a 25 mL three-neck round-bottom flask and heated to 100 °C under dry Ar flow. While stirring, the brown suspension was degassed under vacuum at 150−180 °C for about 1 h. The temperature was lowered to ∼100 °C, vacuum was replaced with Ar flow, and the solution in the flask was heated to 300 °C, producing a colorless solution and indicating reaction of CdO with ODPA. The temperature was next lowered to 270 °C and 2.5 mL of a 0.2 M Se solution in TOP (prepared in the glovebox) was swiftly injected. The heat was immediately removed, and within 4−10 s a color change was observed indicating the formation of CdSe NCs. The purification of these CdSe NCs was carried out as for the TOPO/TOPSe capped nanoparticles (see above).

It should be mentioned that complete dissolution of Se pellets in TOP takes about 5−10 h with heating at ∼50 °C.

Synthesis of TOPSe. To 1.5 mL of TOP (Se:TOP 5:3 molar ratio) 0.531 g of Se pellets were added in the glovebox and stirred for 24 h at 60 °C. The slightly yellow viscous liquid was decanted and used without further purification.

^{31}P (500 MHz, CDCl$_3$): δ 48.8 (s), δ 37.0 (s), δ 37.0 (d, 687 Hz, Se). The integrated intensity of ^{31}P TOPO signal (δ 48.8) is ca. 2% of that for TOPSe (δ 37.0 (s)). No signal for free TOP was detected (δ −30.7).

Spectroscopy. UV−visible spectra were collected with a Shimadzu UV-1601 spectrometer. Photoluminescence (PL) spectra were taken immediately after UV−vis measurements at a standard right angle configuration on an ISA Instruments Jobin Yvon-Spex Fluorolog Model FL3-21 spectrometer, using a 450 W xenon source and Hamamatsu R928 photomultiplier detector. Extinction coefficients for CdSe NC solutions were calculated according to the empirical formulas of Peng et al.[32,36] Between consecutive PL measurements, the solutions of CdSe NCs were kept in the dark. The time resolution in kinetic studies based on PL measurements is about 3 min, the typical acquisition time for a PL spectrum.

NMR Spectra. Solution NMR spectra (^{1}H, proton-decoupled ^{13}C, ^{31}P, and ^{77}Se), were collected in CDCl$_3$ solution using a Bruker AC500 spectrometer. At least 64 scans were taken for each ^{1}H spectrum. All proton-decoupled ^{13}C, ^{31}P, and ^{77}Se NMR spectra for solutions of CdSe NCs were collected for at least 8-h periods, to achieve good spectral signal/noise.

Transmission Electron Microscopy (TEM). TEM samples were prepared by placing a droplet of a ca. 1 mg/mL CdSe NC solution in chloroform on copper grids (400 mesh, Ted Pella, Inc.) coated with a layer of holey carbon (20−30 nm) with an additional ultrathin layer of carbon (3−4 nm) on it. Phase-contrast images of the clusters were obtained with a side-entry Phillips CM12 electron microscope operating at 120 keV. Three typical regions of each sample were obtained at 600K magnification.

Results and Discussion

Effects of NC Purification. To understand the changes in optical properties of CdSe NCs upon purification and aging, one should realize that some of the capping ligands (i.e., a fraction of either TOPO or TOPSe, or both) are reversibly bound to the surface of CdSe NC while others are bound irreversibly. Upon dilution, a solution of dissolved CdSe NCs can dissociate some of the reversibly bound surface ligands and the resulting surface site vacancies are filled with solvent molecules. Previous studies demonstrated that TOPO and a number of amines are reversibly bound to the surfaces of macroscopic n-CdSe single crystals, causing an increase in PL; successive washing of the CdSe single crystal with cyclohexane completely removes these ligands and reverses their effect on PL.[37,38] Of course, the multiple crystallographic facets exposed and defect (vertex, edge) sites on the surfaces of small NCs may produce quite different behavior from macroscopic crystals. From the fact that a number of researchers could not achieve the complete surface exchange of TOPO/TOPSe capping layers with various ligands, we infer that at least some of the ligands are strongly or irreversibly bound to the CdSe NC surfaces.[10,16,24] Donkers et al., analyzing the exchange of phenylethanethiolate ligands attached to gold nanoparticles with other thiolate ligands, suggested that the most labile ligands are bound to nanoparticle surface defect sites such as edges and vertexes.[39] The same argument can be used to understand some of the exchange behavior of CdSe NCs.

We establish below that ligand loss also occurs during purification of CdSe NCs, and in particular in the use of the popular purification method[40−44] of CdSe NCs by their precipitation from CHCl$_3$ by added methanol followed by successive centrifugation and redispersion of the precipitate in CHCl$_3$.

TABLE 1: Quantitative Analysis of TOPO/TOPSe Coverage of CdSe NCs as a Function of the Number of Purification Steps (#PS)[a]

#PS	[CdSe],[b] mM	diameter,[b] nm	A[c]	surf. Cd atoms[c]	[TOPX],[d] mM	B	surf. Cd atoms bound to TOPX, %
1	0.286	2.15_8	96	54	5.44	19	35
2	0.225	2.16_2	97	55	3.57	16	29
5	0.182	2.16_2	97	55	2.20	12	22

[a] *A* and *B* correspond to stoichiometric coefficients in the formula $(CdSe)_A TOPX_B$, where X = O, Se. [b] Size and concentration of CdSe NCs were calculated from UV/vis spectra of CDCl$_3$ solutions using empirical formulas reported by Yu et al.[32] [c] The stoichiometry (*A*) and number of surface Cd atoms were calculated using the spherical model of Kuno et al.[10] In this model, the number of CdSe units on the surface $(CdSe)_{surface}$ was obtained by the following: $(CdSe)_{surface} = (CdSe)_{(diameter=Z)} - (CdSe)_{(diameter-2 \times 0.262)}$, where $(CdSe)_{(diameter=Z)}$ is the number of CdSe units in the NC with diameter Z and 0.262 nm is the CdSe bond length. [d] Methyl proton peaks of the capping ligands were integrated using CH$_2$Cl$_2$ as an internal standard for the estimation of TOPO/TOPSe concentration.
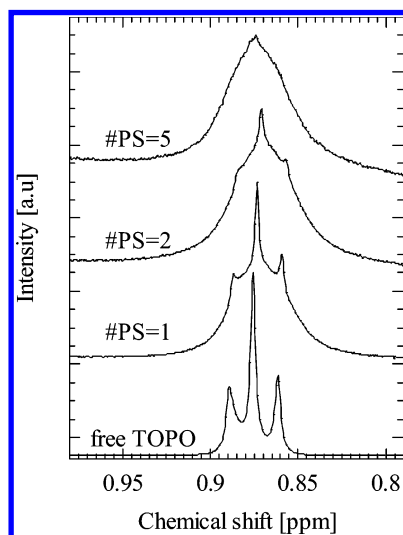
Figure 1. ^{1}H NMR spectra for CH$_3$ protons of free TOPO and solutions of CdSe NCs in CDCl$_3$ as a function of #PS (number in the legend). These spectra were used in Table 1 for the estimation of TOPO/TOPSe coverage.

Both TOPO and TOPSe are soluble in methanol while TOPO/TOPSe capped CdSe NCs are not, and in every purification step a fraction of the reversibly bound ligands is lost and discarded in the methanol supernatant.

To measure the quantity of TOPO/TOPSe on the surfaces of CdSe NCs during purification, quantitative ^{1}H NMR was performed and its results were compared to the concentrations of NCs obtained through their UV/vis spectra. Table 1 shows that the amount of surface-bound TOPO/TOPSe ligands decreases incrementally with successive purifications. The surface coverage for the sample having experienced five purification steps (#PS = 5), 22% of the estimated number of surface Cd atoms bearing ligands, is reasonably close to the 30% result reported by Kuno et al.,[10] based on thermogravimetric analysis of NCs also treated (for size fractionation) with multiple precipitations with CH$_3$OH. From the methyl proton NMR peak shapes of TOPO/TOPSe for the samples with #PS = 1 and 2 (Figure 1; note the evidently superimposed broad and sharp resonances), we infer that the broad peak corresponds to strongly bound ligands and the sharp peak to loosely bound TOPO/TOPSe ligands. After #PS = 5, the latter ligands have been largely removed, as seen by the substantial absence of sharp resonances (Figure 1).

The apparent motional freedom (sharp resonances in Figure 1) of the loosely bound TOPO/TOPSe ligands reflects either a rapid dynamic equilibrium that fully dissociates a very minor fraction of them at any one time, or a local binding−unbinding or dynamic site−site exchange. We do not believe that the sharp TOPO/TOPSe peaks in Figure 1 represent a large population of ligands that are fully dissociated from the NCs. If this were

the case, considering the relative volumes of the supernatant and of the precipitate layer, the supernatant that is discarded following precipitation and centrifugation should, on each purification step, carry away >90% of the loosely bound ligand. Clearly the loss of loosely bound ligand with successive purification steps (Table 1) is more gradual than that. Additional evidence comes from ^{31}P NMR spectra (Figure S-1) of CdSe NCs, where after two purification steps (#PS = 2), the integrated intensities of free TOPO and TOPSe− identifiable from their chemical shifts−amount to only ca. 0.24% compared to the resonances of the bound ligands.[45] This percentage is far too small to be consistent with the loss of ligand in Table 1 from #PS = 2 to #PS = 5, considering that the latter is now largely free of loosely bound TOPO/TOPSe. There is also precedent for reasonably sharp ^{1}H resonances from the well-solvated terminal methyls of alkanethiolate-protected Au NCs.[46]

Both the number of purification steps and the aging of freshly prepared solutions have strong effects on the CdSe NC PL efficiencies. Figure 2a,b and Table 2 (solution I column) show the changes observed in optical properties of freshly prepared, dilute CdSe NC solutions in CHCl$_3$ as a function of the number of purification steps.[47] The highest[48] PL intensity (note scaling factors in Figure 2a) is observed for unpurified NCs and substantially decreases (by about 90%) for the purified NCs. An analogous drop in PL with purification was mentioned by Petruska et al.[42] Also, as purification proceeds, the band edge absorption and PL maxima shift slightly (ca. 6 nm for PL and ca. 3 nm for UV/vis spectra) to lower energy and the relative surface trap emission at ca. 700 nm increases (see also Table S-2). Figure 2c shows that, upon preparation of a fresh, dilute NC solution from the concentrated stock solution, the PL intensity gradually falls with time, over hours, as the diluted NC solution is aged. The PL intensity is restored and the trap band emission is suppressed upon addition of hexadecylamine ligand (HDA, Figure 2c).[49] While Figure 2c is for unpurified NCs, the temporal changes for NC with #PS = 1, 2, 5 are similar to that shown in Figure 2c. Numerical values for PL intensities are given in Table 2 for #PS = 0, 1, 2, and 5, for freshly prepared dilute solutions (solution I), those aged for >10^3 min (solution II) but before HDA ligand was added, and finally to times where the effect of HDA ligand addition reached roughly steady state (solution III).

The results in Table 2 support the gradual loss of ligand during purification steps concluded above from Table 1, as well as during aging of a dilute solution. The aging effect on PL intensity is less for more-purified NCs; thus, the PL intensity in solution II for unpurified NCs is 52% of that in solution I, whereas for the most purified NCs (#PS = 5) the PL intensity in solution II has decayed less, remaining 76% of that in solution I. The difference in aging is consistent with the more-purified NCs having already lost some of their surface ligands during purification, before preparation of the diluted solution. The large

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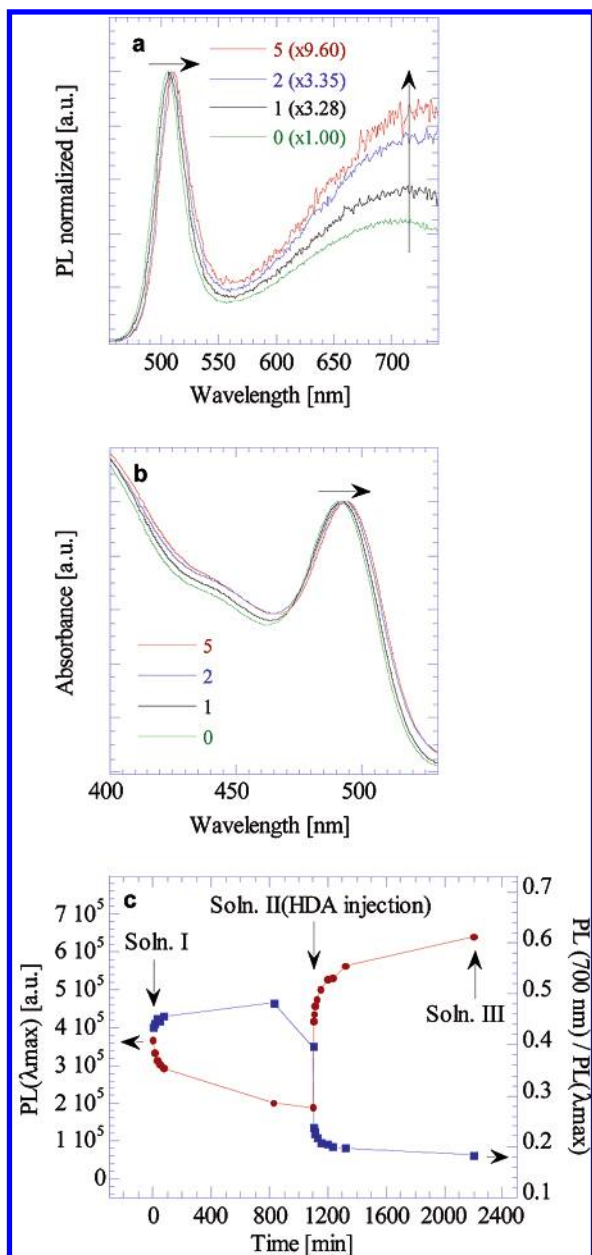
Figure 2. Optical properties of CdSe NCs as a function of purification step number (#PS). (a) PL spectra normalized according to the absorbance at the excitation wavelength (380 nm), taken from corresponding UV/vis spectra. The number in parentheses indicates the multiplier necessary to bring the spectra to the same intensity scale. (b) Fragment of normalized UV/vis spectra. The arrows in (a) and (b) indicate the direction of spectral changes that accompany purification steps. (c) Changes in the main PL band intensity (red curve) and in the relative trap band intensity (blue curve) over time for a solution of unpurified CdSe NCs in CHCl₃ (#PS = 0). "Soln. I" corresponds to intensities in the first PL spectrum taken after solution preparation, "Soln. II" is for the PL immediately before 1.0 mM HDA is added to the solution, and "Soln. III" is from the last spectrum taken. See Table 2 and Table S-2 for numerical data.

increase in PL intensity following addition of HDA is interpreted as reflecting elimination of nonemissive surface states or nonradiative decay pathways produced by ligand loss. The increase in PL intensity upon addition of HDA is largest for the sample with #PS = 5, which had experienced the largest prior loss of ligands (see solution III column in Table 2). Both solution aging and effects caused by added ligands will be discussed in further detail in later sections.

The emission from surface traps, giving the broad PL band around 700 nm, increases with purification relative to the 500 nm emission (Figure 2a), and substantially decreases on addition of HDA (Table 2, right-hand solution III column). These trap states are some chemical species on the NC surface (whose nature is discussed at the end of the paper), and the rise in their PL emission intensity (relative to the 500 nm PL maximum) shows that they are more resistive to loss during purification steps than the original, desired TOPO ligand. After the addition of HDA, the extent of trap emission decreases substantially, but never disappears completely.

The small, lower energy shift in the maxima of PL and UV/vis spectra associated with successive purification steps (Figure 2a,b, Table S-2) may have two sources, which at present cannot be distinguished. In one, the ligand loss (and its presumed replacement by solvent molecules) is analogous to ligand exchange reactions known to cause energy shifts.[10,15] The other source may be gradual loss of the smallest NC particles during purification steps. The UV/vis absorbance spectra of the methanol fraction that is discarded after the centrifugation step during purification indicate the presence of small amounts of CdSe NCs. The purification procedure potentially acts as a size-selective precipitation.[11] Talapin et al. reported that PL QY may change nonmonotonically for various fractions (up to 3-fold) of CdSe NCs obtained through size-selective precipitation.[50] In the present work the possible size difference between samples with #PS = 5 and #PS = 0 is minor, as judged from the small ca. 5 nm PL spectral shift compared to the large ca. 50 nm shift reported for size-selected fractions.[50] This minor effect will not be discussed further.

The loss of surface ligand may not be the sole process causing a decrease in PL efficiency during NC purification. Table 2 shows that, although the PL restorative effect of adding HDA is maximal for the sample with #PS = 5, its restored "steady state" PL intensity (solution III % times solution I) is still ca. 4-fold lower than the initial emission intensity (solution I) of diluted solutions of unpurified NCs (#PS = 0). This suggests that some irreversible process or processes occur on NC surfaces during purification steps that effect an irreversible decline in PL intensity. This may be related to the binding of CH₃OH to vacancies on CdSe surfaces exposed by ligand loss (or displacement). First, we noticed that concentrated (>10 μM) chloroform solutions of extensively purified (i.e., #PS = 5) CdSe NCs can exhibit spontaneous precipitation, while the analogous solutions with #PS = 0−2 remain soluble and retain their original spectra over comparable times. The precipitate and the solution have the same yellow color, and the former is completely redissolved by addition of a drop of methanol. Second, the effect of methanol is illustrated in Figure 3, where its addition to a chloroform solution of CdSe NCs causes a noticeable decline in PL. This supports the hypothesis that methanol binding to the NC surface is associated both with precipitation effects and with the decline in PL during the purification steps. A drop in PL quantum yield of CdSe NC solutions, from 70% in hexane to 30−35% in ethanol or propanol, was also reported by Petruska et al.[42]

Further Information on NC Solution Aging. Descriptions of changes in optical properties of dilute solutions of CdSe NCs with time are scarce and somewhat contradictory. Hines et al. mention a loss over time in the PL quantum yield of CdSe NC solutions in chloroform, and suggest oxidative formation of a surface layer of CdO—a semiconductor with small indirect band gap.[18] Contrarily, Myung et al. report a >6-fold increase in PL intensity of dilute chloroform solutions of CdSe NCs, an increase

TABLE 2: Changes in Optical Properties of CdSe NCs as a Function of Purification Step Number (#PS)

| #PS | PL intensity at λ_{max}, ca. 500 nm, a.u.[a] | | | PL(700 nm)/PL(λ_{max}),[a] % | | |
	soln I,[b] au	soln II (rel to I),[b] %	soln III (rel to I),[b] %	soln I[b]	soln II[b]	soln III[b]
0	3.0×10^6	52	176	43	40	18
1	9.2×10^5	62	161	55	45	23
2	9.0×10^5	68	168	74	68	30
5	3.1×10^5	76	250	84	74	34

[a] PL intensity of the ca. 500 nm peak, PL(λ_{max}), is normalized by the UV/vis absorbance of the solution at the excitation wavelength (380 nm). (See Table S-2 for PL and UV/vis spectral data.) [b] As in the legend for Figure 2c, PL intensities for solution I are from the first PL spectrum taken after solution preparation; those in solution II are taken immediately before addition of 1.0 mM HDA; intensities of solution III are those in the last spectrum taken.
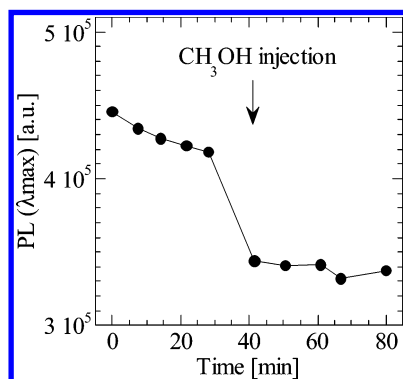

Figure 3. Change in PL intensity at ca. 500 nm over time for a solution of CdSe NCs (#PS = 2) in CHCl$_3$. Arrow indicates when CH$_3$OH is added, to a concentration of 0.08 M.

also observed on bubbling oxygen through the solution and that was larger than observed in hexane solutions. The suggested

explanation was passivation of surface states by chemisorbed oxygen, resulting in PL enhancement.[44] Mekis et al. observed a similar quantum yield improvement for toluene solutions of CdSe NCs, both in air and in a glovebox, ruling out surface oxidation. A slow surface reconstruction was suggested.[43]

Our results show that *both* decreases and increases in PL intensity can occur, depending on circumstances. Thus, the data uniformly show (such as Figure 2c) that the PL intensity gradually decays for freshly diluted CdSe NC solutions ($\sim 10^{-7} - 10^{-6}$ M) in chloroform prepared from an unpurified stock solution ($\sim 10^{-4} - 10^{-3}$ M; see Experimental Section). On the other hand, the PL intensity of a freshly synthesized, unpurified stock solution of CdSe NCs typically gradually increases over 1 week, to an approximately steady state. Figure 4a shows, for example, PL spectra of CdSe NC solutions in CHCl$_3$ (freshly diluted from the unpurified stock solution that had been stored for the indicated time); the PL intensity increases by ca. 2.5-fold and then remains approximately
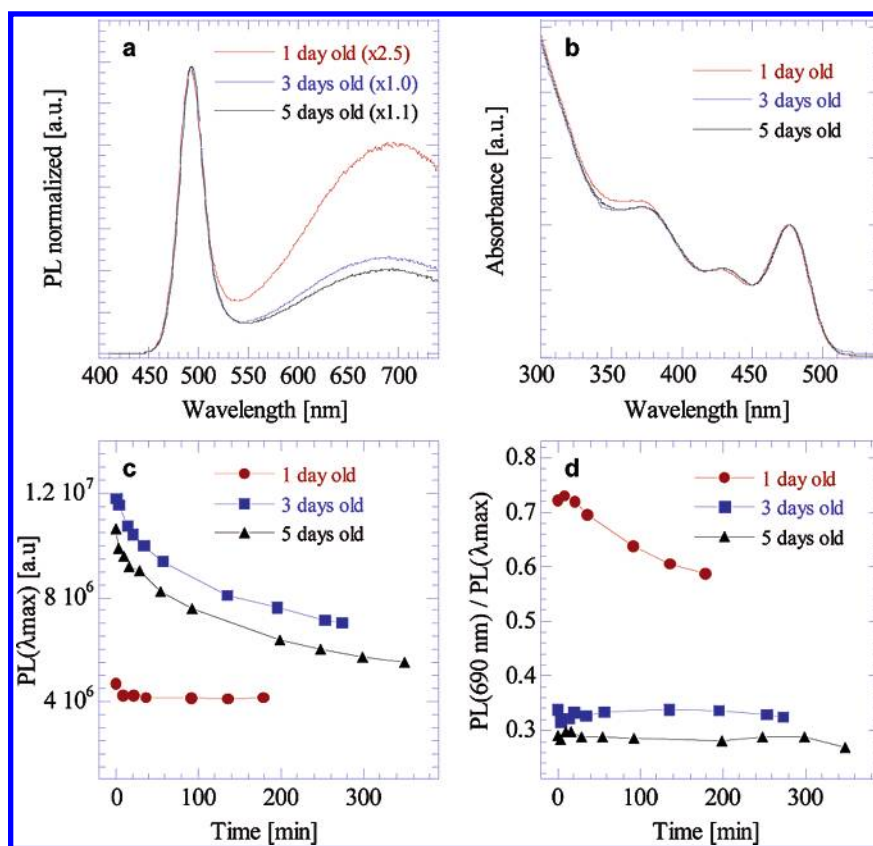
Figure 4. Optical properties of CdSe NCs solutions in CHCl$_3$ prepared by dilution of the unpurified stock solution on the first, third, and fifth days following the date of synthesis. (a) PL spectra normalized by the absorption at the excitation wavelength (380 nm) taken from corresponding UV/vis spectra. The number in parentheses indicates the multiplier necessary to bring the spectra to the same intensity scale. (b) Normalized UV/vis absorbance spectra. (c) Changes in PL maximum intensity over time after dilution. (d) Changes in the ratio of the surface trap emission (PL at 690 nm) to the PL peak intensity over time. The spectra in (a) correspond to the points at 0 min in (c) and (d). Between PL measurements, the NCs solutions were kept in the dark.

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constant. The band edge energy and peak width do not change (Figure 4a), but the relative intensity of the surface trap emission (broad peak around 690 nm) noticeably decreases with aging of the stock solution (Figure 4d). The NC absorbance spectra of the Figure 4a solutions show only a small change at 340−380 nm (Figure 4b) after 1 day. All solutions freshly prepared from the stock solutions exhibit PL intensity decay over several hours (Figure 4c, Table S-2); the decay is steeper for solutions prepared from more aged stock solutions. (Their absorbance spectra are unchanged.) The relative (to the band edge maximum) trap emission intensity decays in a solution freshly diluted from 1 day old stock solution, but remains quite stable when a dilute solution is prepared from more aged stock solutions (Figure 4d). The PL changes over time for aged (for weeks) solutions of purified CdSe NCs on dilution exhibit no consistent trend: PL may slightly (±30% of its initial value) decrease, increase, or remain stable. The reason for such varied trends of behavior is not clear, but we believe that various equilibria between ligands or/and quenchers at the NC surface and in the solution determine the PL intensities observed.

Against the variety of PL intensity changes, in both band edge and trap emissions, described in Figures 2c and 4, the association of intensity changes with ligand loss as documented in Tables 1 and 2, and further evidence on ligand changes to be presented below, it seems clear that aging processes that yield or restore nonluminescent NC surface states can *originate* in loss of or changes in surface ligands to a degree sufficient to accommodate the degree of PL intensity alterations experienced. Similar to previous studies of macroscopic n-CdSe single crystals,[37,38] PL intensity can be directly correlated to the amount of the bound TOPO/TOPSe in the way that the maximal observed PL corresponds to the highest surface coverage. While it is unclear what processes occur on the NC surface after ligand loss—whether reconstructive[43] or oxidative[51,52]—we propose that ligation changes provide the primary gateways for occurrences of those processes.

Effects of Ligand Changes. The typical literature strategy for ligand exchange reactions has been to introduce a large excess of the desired ligand into CdSe NC solutions (sometimes with refluxing) followed by isolation and purifications based on changes in solubility in certain solvents between the original TOPO/TOPSe-covered NCs and those coated with the new ligand.[1,10−12,15,19,22,25,31] Our present experience that purification by repetitive precipitation with a polar solvent has a significant impact on both ligand composition and optical properties of CdSe NCs (Tables 1 and 2) suggests that real effects of ligand exchange reactions may be convoluted with the consequences of ligand changes during purification.

Accordingly, we adopt here an alternative procedure in which an excess of the desired ligand is added to a dilute (10^{-6}−10^{-7} M) solution of purified CdSe NCs in a spectrophotometric cuvette, taking NC PL and UV/vis spectra successively before and after the ligand addition. The changes in spectra and intensities are recorded as a function of time, allowing information on both the ligand's effect on the spectra and the dynamics of the spectral changes. This procedure was used above, where the amine ligand HDA was added to solutions of CdSe NCs that had been subjected to various numbers of purification steps (Table 2, Figure 2c). One must realize that if there have been previous ligand losses (as in purification steps), changes observed upon addition of a new ligand can be a combination of ligand binding to vacant (solvated) surface sites on the CdSe NCs and of ligand exchange itself, and these processes may have quite differing kinetics. For instance, in Figure 2c after

TABLE 3: Effects of Adding Ligands and Other Substances on Optical Properties of Purified (#PS = 1) CdSe NCs in Chloroform Solutions

substance	PL intensity change at λ_{max}, %		PL(700 nm)/ PL(λ_{max}),[a] %
HDA	126		29/17
DMAP	−39		31/43
4-MeOPy	54		32/27
4-HOPy		NCs dissolved[b]	
pyridine	32		30/30
PhSH	−96		21/1130
HDT	−66		20/144
S2BN[c]	64		47/113
S22OH		NCs coagulated[b]	
TOPO	34		22/21
TOPSe	−61		23/56
TOP(50 mM)	454[b]		54/111[b]
TOP(10 mM)	119 (256)[d]		20/296 (162)[d]
TOP(2 mM)	134 (233)[d]		28/113 (108)[d]
HAc	95		10/21
CdAc$_2$[c]	919		43/23
Cd(ClO$_4$)$_2$[c]	−12		42/44
ZnAc$_2$[c]	437		39/44
PbAc$_2$[c]	149		37/36
HgAc$_2$[c]		PL disappeared, color changed	
AgNO$_3$[c]		PL disappeared, color changed	
Bu$_4$NPF$_6$	3		39/43
Bu$_4$NOH[c]	−27		40/29
blank	−2		28/27

[a] The first number is the relative PL(700 nm)/PL(λ_{max}) intensity immediately prior to adding the substance; the second is taken after ca. 15 h following addition. Reproducibility is ca. 10% for PL intensity and ca. 25% for PL(700 nm)/PL(λ_{max}). PL(λ_{max}) is the PL value at the band edge maximum, which is at 491−501 nm (see Table S-3 for details). [b] CdSe NCs from different batches were used. [c] 50 μL of CH$_3$OH was added ([CH$_3$OH]= 0.4 M) to provide solubility of the metal salts. [d] The numbers in parentheses correspond to the moment when the PL change was maximal (see text).
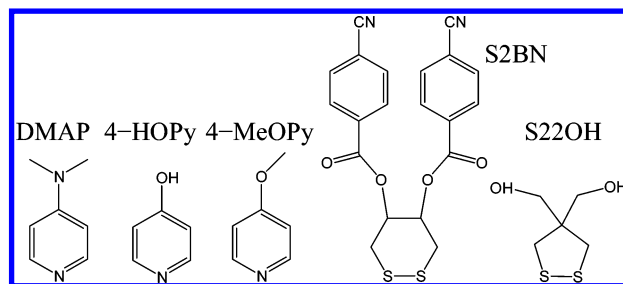

Figure 5. Structures of molecules abbreviated in Table 3.

adding HDA there is an immediate increase in PL to a value close to the original intensity (before the dilute solution was allowed to age), followed by a slower one (which can be well fitted as exponential with time). We interpret this behavior as a fast coordination of HDA to sites from which ligand had been lost during aging, followed by a slower, first-order ligand exchange reaction with TOPO/TOPSe. Accordingly, in the following experiments, the stock solution of CdSe NCs employed had been subjected to only one purification step to minimize previous ligand loss.

Table 3 summarizes the effects of adding various ligands and substances to CdSe NC solutions. Table S-3 gives further data on the relatively minor changes seen in PL and UV/vis spectra, and Figure 5 gives structures for some of the ligand abbreviations in the tables. For most of the measurements, the once-purified CdSe NCs used were from the same batch. Their 1−3 μM chloroform solutions were aged so that the initial rapid
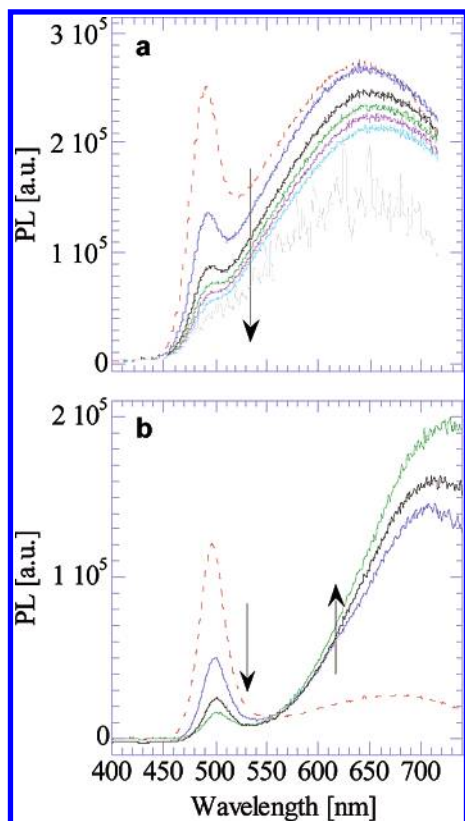
Figure 6. (a) Time dependency of PL spectra of CdSe NCs in chloroform after addition of 10 mM S22OH (Figure 5). The original PL spectrum (multiplied by 0.33 to fit the scale) is shown by the dashed line; the arrow shows the direction of changes in the spectra. (b) Time dependency (times are indicated) of PL spectra of CdSe NCs in chloroform after addition of 10 mM PhSH. The original PL spectrum is shown by the dashed line; the arrow shows the direction of changes in the spectra.

changes in PL intensities upon dilution (e.g., Figure 2) have passed; this allows a better recognition of the effect of the added substance. Spectra were taken immediately before adding the substance (at 10 mM, unless specified otherwise, and at 1 mM for inorganic salts and Bu$_4$NOH), and again after ca. 15 h. The blank experiment was identical, except that no substance was added.

The addition of HDA caused an increase in PL that was already presented in Table 2 and Figure 2c, and which agrees with a previous report on the effect of amines on PL of CdSe NCs.[15] The effect of added pyridine ligands is varied: 4-MeOPy and pyridine produce an increase in PL, DMAP causes a decrease, and 4-HOPy provokes dissolution of the NCs (loss of characteristic absorbance). The intensity increases contradict other reports[10,18] of a substantial loss of PL quantum yield of CdSe NCs following ligand exchange with pyridine and 4-methylpyridine. Our experiments differ, however, in that we did not isolate and purify the exchanged NCs, which as shown above can cause a considerable decrease in PL intensity. It appears, from the minor amount of free TOPO ligand[53] seen in the ^{31}P NMR spectrum of the 4-MeOPy/CdSe exchange solution, that the PL intensity increase in that case was due more to filling of vacant surface sites than actual exchange of TOPO by 4-MeOPy ligands (see Figure S-1).

Addition of HDT and PhSH thiols caused substantial decreases in the band edge PL and a substantial relative increase of the 700 nm trap emission band (Table 3 and Figure 6b, for PhSH). The PL intensity of the band edge peak drops ca. 8-fold within 1 min (suggesting rapid coordination to vacant surface

sites) and decreases more gradually during the next 15 h. The intensity of the trap emission (measured at 625 nm) relative to the band edge PL peak (ca. 500 nm) changes from 7% to 170%; most of the change is due to loss in the band edge emission, since the absolute intensity of the trap emission only doubles (in relation to that before PhSH addition). One concludes that PhSH is a potent quencher of the band edge luminescence.

The dithiols produce different behaviors: dithiol S2BN causes an increase in both band edge and trap emission PL intensity, whereas the dithiol S22OH causes a rather rapid (over 50 min) precipitation of CdSe NCs. Observing the CdSe NC spectra during the precipitation (Figure 6a), there is a much more substantial loss in the band edge peak at ca. 486 nm than in the trap band emission. In fact, the longest time spectrum in Figure 6a, where the concentration of NCs has fallen to a very low value, retains only a hint of the 486 nm PL. This behavior suggests that the chemical species causing the trap emission are resistant toward exchange with S22OH. The difference in the position and the relative (to the λ_{max} at 486 nm) intensity of the surface trap emission is due to the smaller size of CdSe NCs used in this experiment (see below).

The effects of added TOPO, TOPSe, and TOP on the optical properties of CdSe NCs are important since these ligands are all present in the synthesis and some of them remain after purification. Addition of TOPO produces a modest increase in PL (34%), TOPSe causes a substantial PL drop of 61%, and TOP provokes a large PL intensity enhancement (~130%). This diversity of behavior may account for the diversity of reported[10,11,43] PL quantum yields for TOPO/TOPSe CdSe NCs, since the relative numbers of these ligands on the NC surface may vary depending on aging and purification method effects. The different effects of TOPO, TOPSe, and TOP on the PL of CdSe NCs will be central in our analysis of the chemical nature of the trap states, discussed later.

TOP addition differs from the other substances in two aspects: first, it causes increases in both the main PL peak and the trap emission intensities, and second, the band edge PL intensity over time may increase to a stable roughly steady-state emission (as in Figure 7c), or it may thereafter slowly decline (as in Figure S-4).[54] In all experiments a blue shift is observed upon addition of TOP, both in PL (Figure 7a,b) and in UV/vis spectra (Table S-3). The trap emission rises quite rapidly upon TOP addition, more rapidly than the increasing band edge peak at ca. 500 nm, so that the relative PL(700 nm)/PL(λ_{max}) intensities rapidly reach a maximum and then decline, reaching a steady state of nearly equal intensities (Figure 7c).
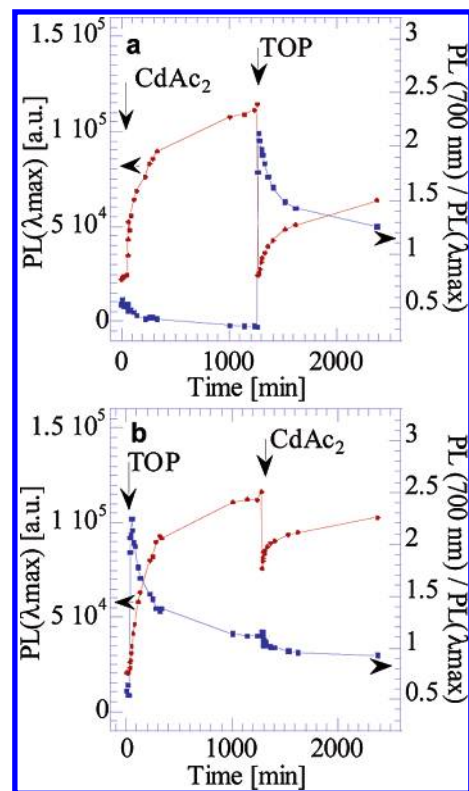
The largest enhancements in the main band PL of CdSe NCs were produced by addition of the acetate salts CdAc$_2$ and ZnAc$_2$. These salts did not cause significant shifts in PL and UV/vis spectral energies; a small blue shift was observed for PbAc$_2$ (Table S-3). ZnAc$_2$ and HgAc$_2$ belong to the same metals subgroup as Cd, and CdAc$_2$ is potentially present as an impurity, being used in the synthesis of CdSe NCs. The mercury and silver salts supposedly might effect the replacement of Cd atoms in the CdSe NCs core with the different metal; their additions were accompanied by a strong red shift in the UV/vis spectra and nearly complete quenching of the NC PL. The mercury and silver results (possibly caused by replacement of Cd^{2+} in CdSe NCs with Hg^{2+} or Ag$^+$) will be reported elsewhere.[55]

The strong effect of the CdAc$_2$ and ZnAc$_2$ acetates on enhancing PL of CdSe NCs cannot be explained solely by vacant site filling or ligand exchange with acetate anion, since the PL increase caused by acetic acid (HAc) is considerably smaller. The effect also cannot be interpreted as one of the metal cation

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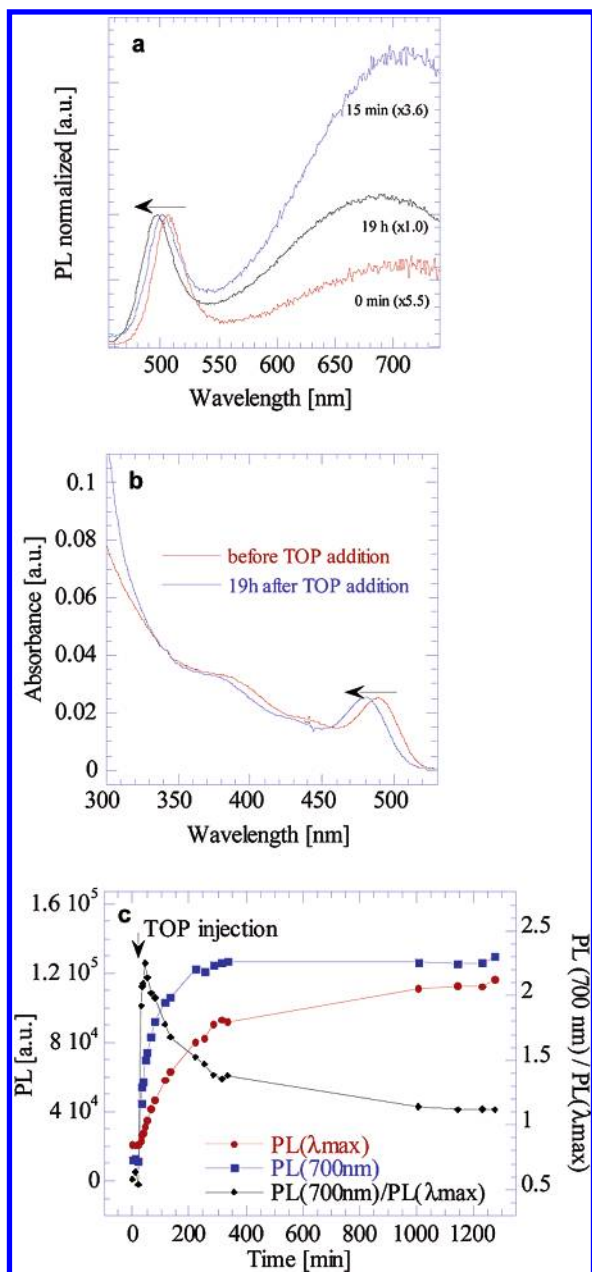
Figure 7. Time evolution of (a) PL and (b) UV/vis spectra of CdSe NCs in chloroform, upon addition of TOP. (Horizontal arrows indicate the direction of spectral change.) (c) Changes in actual and relative 500 and 700 nm PL intensities over time. 0.05 M TOP and 5×10^{-7} M CdSe NCs.

Figure 8. Changes in band edge (ca. 500 nm) PL intensity over time for solutions of CdSe NCs in CHCl$_3$ upon sequential additions of (a) CdAc$_2$ followed by TOP and (b) TOP followed by CdAc$_2$, as indicated by the vertical arrows. 5×10^{-7} M CdSe NCs, 0.2 mM CdAc$_2$, and 0.05 M TOP.

(at least for Cd^{2+}), since adding Cd(ClO$_4$)$_2$ produced a small decrease in PL intensity (Table 3). Spanhel et al.[56] have reported an enhancement in PL for CdS NCs, caused by successive additions of base (NaOH, to a pH of 10.5) and Cd(ClO$_4$)$_2$ solutions to phosphate-stabilized CdS NCs dissolved in water. They suggest[56] that deprotonation of thiol terminations on the colloidal particle surfaces leads to binding of the excess Cd^{2+} ions, with the inherent assumption being made that the uncoordinated thiol terminations are responsible for nonradiative PL decay. The analogy to the present case would be deprotonation of selenol group terminations on the CdSe NC surfaces by the more basic CdAc$_2$ solution, with subsequent Cd^{2+} coordination. Prompted by a reviewer's suggestion, to test whether basicity plays a role here, Bu$_4$N$^+$OH$^-$ was added, causing a moderate decrease in PL for CdS NCs (Table 3); thus

basicity was excluded as a source of the strong PL enhancement caused by CdAc$_2$ and ZnAc$_2$.

Figure 8, by adding CdAc$_2$ and TOP in different orders, shows that the effects of sequential additions of TOP and CdAc$_2$ are not cumulative. Figure 8a shows that when the PL intensity increase at 500 nm starts to level off following an addition of CdAc$_2$, a subsequent injection of TOP into this solution leads to an immediate drop of PL intensity to its original value (before the addition of CdAc$_2$), and then PL starts to rise (Figure 8a). Reversing of the order of addition leads again (Figure 8b) to a PL intensity decrease upon addition of CdAc$_2$, although the decrease is much less than in Figure 8a. The smaller decrease may reflect the much smaller concentration of added CdAc$_2$ (relative to the TOP concentration), and/or the weaker binding of the metal cation relative to TOP. However, one must note that, in both experiments, the final PL intensity is smaller than after addition of either ligand alone, so it is not a matter simply of one ligand completely displacing the other, but rather a "mixed" ligand environment persists or some other, irreversible change in the NC surface has occurred.

The Nature of Trapped Emission States on CdSe NCs. The broad emission near 700 nm, strongly red-shifted from the band edge PL peak, has been previously attributed to unknown surface states,[2,10,18] and we have referred to it as from trap states. The idea that this emission is surface related follows from its increase, relative to the PL band edge maximum intensity, as the NC size is decreased. Additionally, the trap emission disappears upon capping the NCs with some higher band gap semiconductor material.[10,18] Figure 9 shows how the trap emission blue shifts and increases with the decrease of the NC size. Figure 9 also shows that, for ODPA capped CdSe NCs, the trap emission is very weak even at a core size that is very
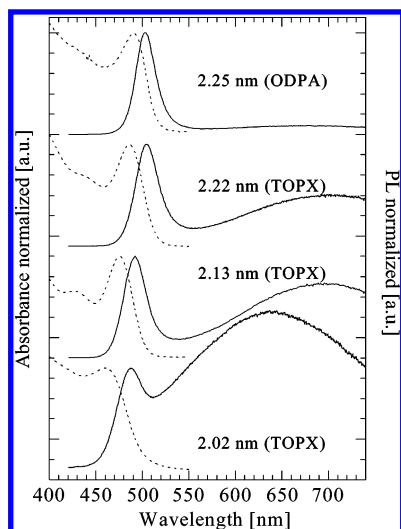
Figure 9. UV/vis (dashed line) and PL (solid line) spectra of CdSe NCs of various sizes (indicated). The capping ligand is shown in parentheses (TOPX= TOPO/TOPSe).

close to the TOPO/TOPSe CdSe NCs that display a significant trap emission peak.

The concurrent increase of the relative trap emission intensity (PL(700 nm)/PL(λ_{max})) and decrease of the band edge PL intensity observed for ligands such as DMAP, thiols, S22OH, and TOPSe may signify that the surface-related chemical states responsible for the trap emission are resistive toward ligand exchange (Table 3, Figure 6). That the absolute trap emission intensity remains either unchanged or increases in these cases implies that the amounts of the surface states can remain unchanged while ligand exchange, occurring at other sites, opens up pathways for nonradiative relaxations that lead to the decrease in the band edge PL. The same explanation can be applied to the increase in relative trap emission while the band edge PL declines during purification of CdSe NCs (Table 1, Figure 2).

We propose that the chemical state responsible for the trap emission is associated with TOP-bound Se atoms at the surface of a CdSe NC. The following support this hypothesis: (i) Both absolute and relative (to band edge PL peak) trap emission intensities are greatly increased (>10-fold) only in the case of addition of TOP (Table 3 and Figure 7). (ii) The synthetic procedure for ODPA capped CdSe NCs uses a TOPSe:Cd ratio of 1:1, while that of TOPO/TOPSe capped CdSe NCs relies on a much larger TOPSe:Cd ratio, 10:1. ODPA capped CdSe NCs exhibit substantially weaker trap emission than TOPO/TOPSe capped CdSe NCs of the similar size. (iii) The double covalent bond between Se and P in TOPSe is expected to be stronger than the coordination bonds between Cd^{2+} at the NC surface and most of the studied ligands. Although Se atoms on the NC surface are also bound to Cd atoms, the higher strength of the Se−P bond can be responsible for the greater stability of surface-bound TOPSe molecules, which is reflected by stability of the trap emission toward purification and ligand exchange. (iv) Aging of CdSe solutions leads to decrease of both absolute and relative intensity of the trap emission (Figure 4). Since all the Se in the synthesis of CdSe NCs exists as TOPSe, it seems highly possible that it is immediately after the synthesis that the amount of the surface Se atoms bound to TOP is maximal. The observed decrease in the trap emission intensity during aging of CdSe NCs could then occur through removal of the TOP bound to surface Se by oxidation of the Se−P bond.

Conclusions

We presented the first systematic study of effects of purification, aging, and ligand exchange on the optical properties of CdSe NCs. Basically, PL of CdSe NCs increases upon addition of HDA, TOP, pyridines, and a number of acetates ($CdAc_2$, $ZnAc_2$, $PbAc_2$) and decreases upon addition of thiols. PL decline observed during purification or dilution of solutions of CdSe NCs is due to occurring surface ligand loss. Following changes in PL intensity of CdSe NC solutions over time was found a simple and efficient tool of monitoring processes occurring on the NC surface. The complex of TOP with Se atoms on the surface of CdSe is a suggested chemical state causing trap emission strongly red-shifted relative to the band edge PL peak.

Supporting Information Available: ^{31}P NMR spectrum of CdSe NCs (Figure S-1), Tables S-2 and S-3 (full versions of Tables 2 and 3, respectively), and augmented version of Figure 8 (Figure S-4). This material is available free of charge via the Internet at http://pubs.acs.org.

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(47) The purification was done 3 weeks after the synthesis, and all optical measurements were carried out immediately after the purification to minimize the effect of aging.

(48) For all the data in Table 2 and Figure 2a,b, the PL intensities were normalized by the UV/vis spectral absorbance at the excitation wavelength (380 nm). The data shown in Figure 2c are not normalized.

(49) TOPO also could be used for this experiment. HDA was chosen because of its stronger effect on PL of CdSe NC solutions (see Table 3 for comparison of effects of TOPO and HDA).

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(53) The ratio of free TOPO signal to the signal of bound either TOPO or TOPSe changed from 0.24% for ca. 1 mM solution of CdSe NCs in CDCl$_3$ to 0.34% after 1 day following the addition of a large excess of 4-MeOPy. This implies that for concentrated solutions of CdSe NCs the ligand exchange reaction with 4-MeOPy is either very slow or thermodynamically not viable.

(54) We were not able to ascertain what conditions are responsible for the difference in behavior (either PL increases and reaches a steady state of PL after addition of TOP, or it passes through a maximum and slowly declines). Purification and aging conditions as well as the initial capping of CdSe NCs (TOPO/TOPSe or ODPA) and concentration of TOP were varied but no reproducible tendency was found, except that for a particular synthesized batch of NCs the observed behavior is reproducible.

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