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Resonance Raman Investigation of the Interaction Between Aromatic Dithiocarbamate Ligands and CdSe Quantum Dots

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Abstract

Ligand exchange with phenyl dithiocarbamates is known to significantly red-shift the lowest excitonic transition of CdSe quantum dots. Here we show that the resonance Raman spectra of CdSe quantum dots treated with *p*-methoxyphenyldithiocarbamate are nearly identical to those of CdSe quantum dots to which thin CdS shells have been added by standard synthetic methods. We conclude that the dithiocarbamate ligands decompose and react with Cd²⁺ not fully removed following the synthesis to form CdS on the surface of the quantum dots. This red-shifts the absorption spectrum primarily by delocalizing the electron into the CdS shell. These results are consistent with the common use of aliphatic dithiocarbamates as single-source precursors for adding ZnS or CdS shells to CdSe quantum dots, and with the recent demonstration through NMR that phenyldithiocarbamate ligands decompose during nanocrystal ligand exchange.

Introduction

Semiconductor quantum dots (QDs) are structures composed of one or more semiconductor materials having a nearly spherical geometry and diameters typically in the 1-10 nm range. In smaller QDs a significant fraction of the atoms are at the surface and have a smaller coordination number than the atoms in the interior. Typical synthetic routes using solution-phase colloidal methods leave many or most of the surface atoms coordinated to organic or inorganic ligands, typically of more than one type. These “native” ligands may subsequently be either exchanged for others or removed entirely. For most applications, however, some type of ligand coverage is desirable. Ligands serve a number of purposes including passivating surface recombination centers, enhancing solubility in particular solvents, preventing aggregation between QDs, and protecting the QD against chemical reactions.¹

Usually the ligands are assumed to have little effect on the excitonic transitions that dominate the optical spectra of QDs, because the orbital energies are such that transfer of an electron either to or from the ligand is energetically unfavorable. However, the valence band (VB) and conduction band (CB) wavefunctions of the QD may involve some small contribution from ligand orbitals, and it should be possible to increase this contribution by choosing ligands with appropriate orbital energies. If either the CB or the VB wavefunction extends partially into the ligand shell, the effective size of the QD will appear to be larger and the energy of the lowest excitonic transition will shift to lower energy. In addition, such ligands might be used to tune the rates of processes that involve transferring charges to or from the QD.^{2,3}

Recently, Weiss's group⁴⁻⁸ and others^{2,9,10} have shown that exposing CdSe, CdS, or PbS QDs to aromatic dithiocarbamates (DTCs) produces a significant red-shift in the energy of the lowest excitonic transition and that the extent of this shift can be correlated with calculated orbital

energies of the DTCs. It was argued that the DTCs bind as ligands on the surface Cd atoms and their orbitals mix significantly with the semiconductor orbitals making up the VB, thus delocalizing the hole into the ligand shell, decreasing the quantum confinement energy of the hole, and shifting the excitonic transition to lower energy. However, the metal salts of simple alkyl dithiocarbamates are also used as single component precursors in the synthesis of CdS, ZnS, and CdSe/CdS core-shell QDs.¹¹⁻¹⁴ The alkyl dithiocarbamates are more stable than the aromatic analogs and the decomposition reaction used in CdS and ZnS shelling syntheses proceeds quickly only at slightly elevated temperatures (100 – 150°C). It has also recently been shown by NMR that aromatic DTCs decompose at room temperature during ligand exchange with CdSe QDs to form a mixture of products.¹⁵ These observations suggest that the primary role of the aromatic DTCs may be to decompose and react with any surface adsorbed cadmium to form a thin shell of CdS on the surface of the QD. CdS has a larger band gap than CdSe (2.485 eV vs. 1.75 eV¹⁶) with the CdS conduction band being only slightly higher than that of CdSe.¹⁷⁻¹⁹ Most of the difference in the band gaps is in the valence band offset – CdSe/CdS forms a quasi-type-II system.^{12,20,21} The presence of the CdS shell increases the effective radius of the QD and red-shift the electronic spectra, primarily by delocalizing the electron, not the hole, into the shell.

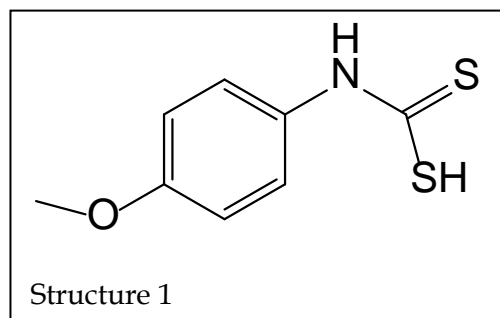
In this paper, we use resonance Raman spectroscopy to elucidate the role of DTCs on CdSe QDs. Resonance Raman (RR) spectroscopy is a powerful technique for probing the orbitals involved in an electronic transition.^{22,23} The vibrational modes that appear with intensity in a RR spectrum correspond to those motions along which there is a change in geometry upon excitation. RR spectroscopy has been widely applied to QDs carrying the usual types of ligands, but such spectra do not show features attributable to ligand vibrations or even to the

semiconductor-ligand bond stretch. This result is not surprising for typical ligands that are not expected to participate significantly in the excitonic transition. However, if aromatic DTCs do red-shift the absorption spectra by delocalizing the hole into the ligand, vibrations of these ligands should show up in the RR spectra, although perhaps with low intensity. If, alternatively, the red-shift is caused by ligand decomposition resulting in the deposition of a CdS shell, the well-known longitudinal optical (LO) phonon of CdS should appear in the spectra. RR spectroscopy thereby provides an excellent way to distinguish between these two mechanisms.

Experimental Methods

CdSe QDs (wurtzite crystal structure, cadmium-rich surface) were synthesized as described previously²⁴ and detailed in the Supporting Information. Their diameter was estimated from the position and width of the first excitonic maximum²⁵ as 3.2 ± 0.3 nm. The standard synthetic method employed typically produces approximately stoichiometric surfaces.²⁶ This was followed by purification and subsequent reaction with a cadmium precursor (cadmium acetate) at 180 °C to ensure a cadmium rich surface.²⁶

These CdSe QDs with a Cd-rich surface were purified, dissolved in chloroform, deposited onto glass coverslips by drop-casting, dried under nitrogen, and then subjected to several different treatments. One batch of these particles was treated with the DTC ligand. The ligand used in this study was *p*-methoxyphenyldithiocarbamate (MPDTC, Structure 1), which was synthesized as its ammonium salt using a slight variation of the methods described in the literature^{5,27} and detailed in the Supporting Information. The MPDTC was dissolved in



dried MeOH at a concentration of about 10 mM and the QD-coated coverslips were soaked in this solution for one to two days in the dark at room temperature (~ 20 °C). Other batches were treated with MPDTC in the same manner but with varying concentrations of cadmium acetate added to provide a source of additional cadmium. As a control, QD-coated slides were also soaked in dried MeOH without ligand for the same period of time.

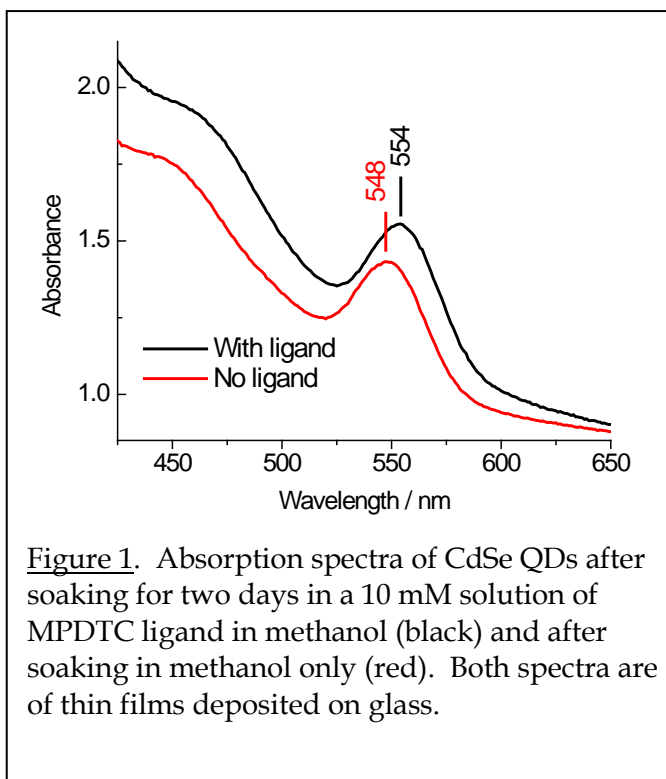
Two other batches of the original Cd-rich CdSe QDs were not exposed to MPDTC but were subjected to other treatments, performed in solution prior to drop-casting the QDs onto coverslips. One was treated with 0.1 mmol sulfur dissolved in 1 mL octadecene (ODE) at 170 °C under N_2 flow in order to add a small amount of sulfur to the existing Cd-rich surface. The reaction was quenched and lowered to room temperature when the lowest exciton peak had shifted to the red by ~ 5 nm. Another was heated to 170 °C under N_2 and treated alternately with the sulfur precursor (0.1 mmol sulfur in 1 mL ODE) and the cadmium precursor (0.1 mmol cadmium acetate in 0.2 mL oleylamine and 0.8 mL ODE) to grow a thin shell of CdS through the traditional SILAR method. The reaction was stopped when the lowest exciton peak of the CdSe/CdS QDs had shifted ~ 13 nm.

Absorption spectra were obtained on a Cary 50 UV-VIS spectrophotometer. Resonance Raman spectra of the QD-coated slides were obtained using 457.9 nm excitation from a Coherent Innova 90C-5 argon-ion laser. The excitation and detection system was a Jobin-Yvon T64000 Raman microscope system consisting of a 0.64-m triple spectrograph coupled to a confocal Raman microprobe with a 10X objective and a UV coated, back illuminated, liquid nitrogen cooled CCD detector. Spectral resolution was about 7 cm^{-1} with the 200 μm slit width employed. The power at the sample was about 0.5 mW, giving an intensity at the focus of about 10^4 W/cm^2 with our 10x objective. The sample was moved continuously under the laser with a

motorized translation stage to prevent local heating or other photoinduced changes. Typically signal was integrated on the detector for 60-120 s before being read out and 5-10 such reads were averaged to give the final spectrum.

Results

Exposure of CdSe QDs to the MPDTC solution consistently produced a small red-shift of the absorption spectrum. The shifts varied somewhat from batch to batch but were typically 5-7 nm for QDs initially absorbing near 550 nm. This shift is considerably smaller than the 20 nm reported for this ligand in ref. 5. Representative absorption spectra are shown in Figure 1.



The resonance Raman spectrum of the MPDTC-treated QDs (Figure 2) shows the expected strong peak from the CdSe longitudinal optical (LO) phonon at 208 cm^{-1} and weaker bands from the first and second overtones of the LO phonon at about 414 cm^{-1} and 620 cm^{-1} , respectively. In addition, the spectrum has well-defined peaks around 273 cm^{-1} and 477 cm^{-1} , corresponding to features previously reported in the Raman spectra of CdSe/CdS core-shell QDs and assigned as the CdS LO phonon and the combination band between the CdSe and CdS LO phonons, respectively.^{28,29} (The LO phonon is characteristically the principal feature observed in the Raman spectra of II-VI semiconductor nanocrystals.) The 273 cm^{-1} peak cannot be the ligand or

the ligand bound to cadmium. We find that the cadmium salt of MPDTC is too unstable for us to obtain its Raman spectrum. However, the Raman spectrum of the more stable cadmium salt of diethyl-DTC (see Supporting Information) shows prominent peaks at 213, 434 and 566 cm^{-1} , and nothing in the 270 cm^{-1} region, in agreement with the literature.³⁰ Similarly, the Raman spectrum of MPDTC (see Supporting Information) shows only a weak, sharp peak at 270 cm^{-1} and much more prominent peaks at 387, 658, 1318, and 1604 cm^{-1} . These characteristic lines are absent in figure 2, with only the CdSe, CdS and combination bands appearing.

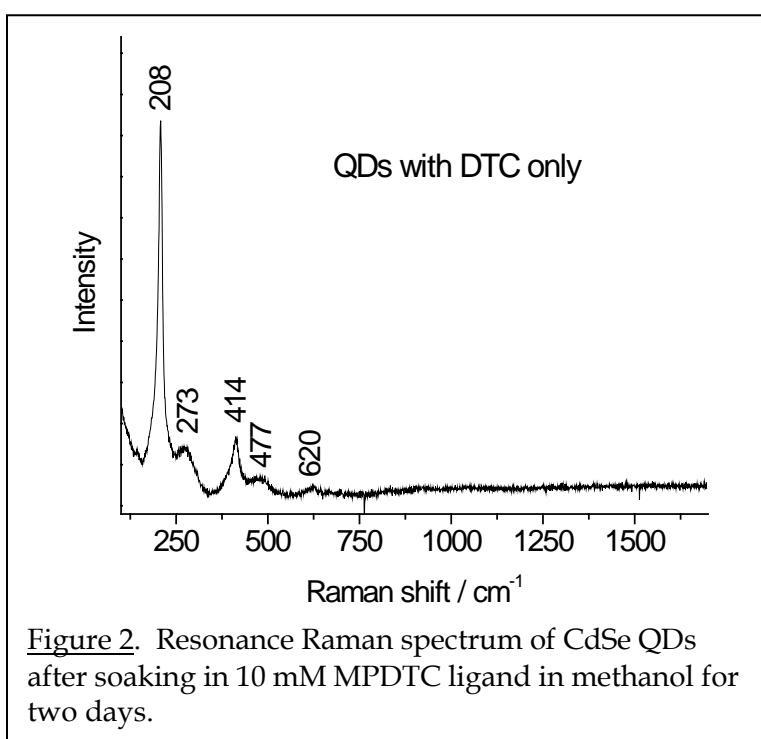
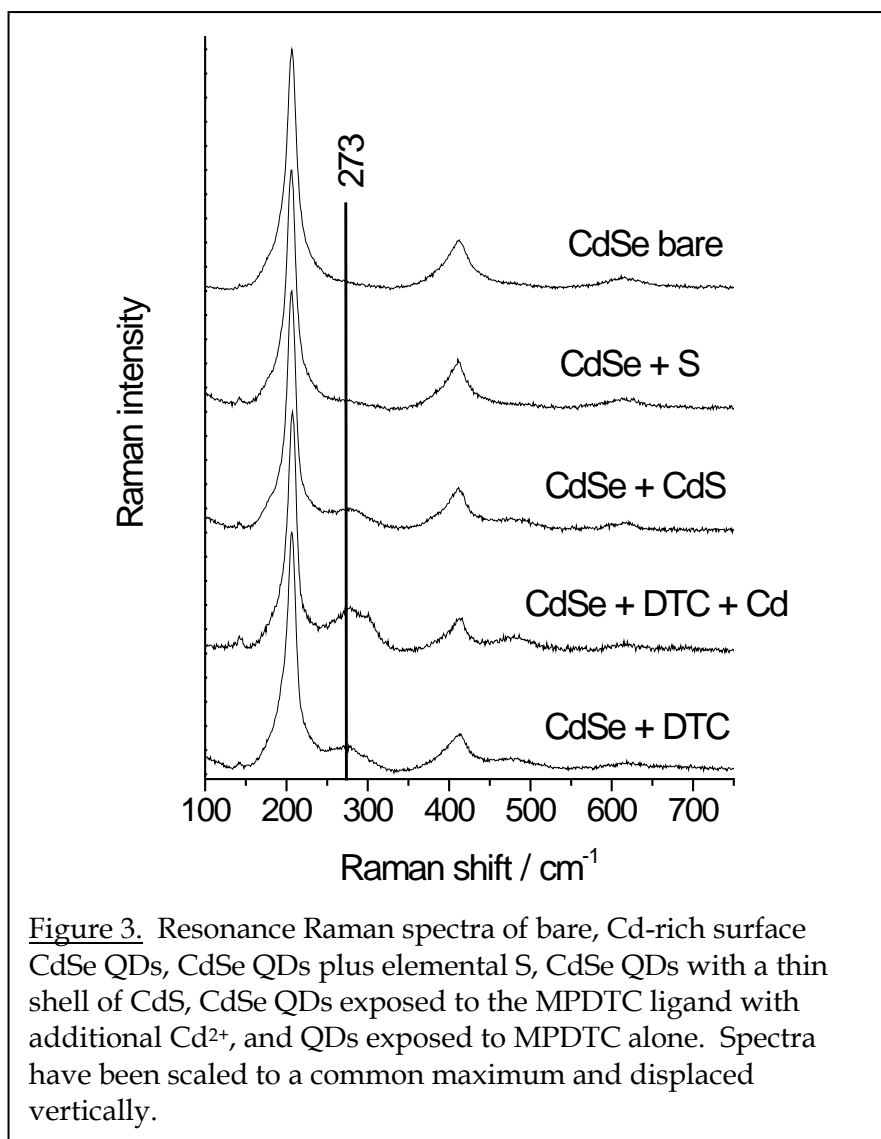


Figure 3 compares the low-frequency Raman spectra of the original CdSe QDs, the sample treated with the MPDTC ligand, and three other samples. The original CdSe QDs show no Raman activity in the 250-300 cm^{-1} region, as expected. CdSe QDs on which a very thin CdS shell has been grown using standard techniques show an absorption red-shift of about 13 nm and broad but clearly defined Raman bands at $\sim 280 \text{ cm}^{-1}$ and $\sim 482 \text{ cm}^{-1}$. As discussed above, the CdSe QDs treated with DTC have an absorption maximum shifted 5-7 nm to the red and exhibit

additional broad but well-defined Raman peaks at about 273 cm^{-1} and 477 cm^{-1} . The spectra of the MPDTC-treated QDs and the spectra of the thin-shell CdSe/CdS QDs are extremely similar. QDs treated with the MPDTC ligand plus varying concentrations of cadmium acetate show variable absorption red-shifts, up to about 16 nm, and in the samples showing the largest red-shift the CdS-like Raman peak becomes slightly stronger develops a shoulder at higher frequency. Treating the CdSe QDs with elemental S alone also red-shifts the absorption maximum by about 5 nm but produces only barely discernible additional intensity in the 250-300 cm^{-1} region of the Raman spectrum. Results from a similar experiment starting with larger QDs are shown in the Supporting Information.



Discussion

The results in figures 2 and 3 can be understood in terms of thin layers of CdS being deposited on the CdSe QDs. CdSe QDs exposed to a methanol solution of *p*-methoxyphenyl-DTC for two days at room temperature show absorption spectral shifts and resonance Raman spectra that are nearly identical to that of CdSe QDs on which a very thin (< 1 monolayer) layer of CdS has been grown through standard SILAR techniques, using cadmium acetate and elemental sulfur. These results are consistent with reactivity studies of phenyldithiocarbamates,

which have been shown by NMR to decompose to a mixture of products under the conditions of ligand exchange with CdSe QDs.¹⁵ Consistent with these results, our NMR spectra of the MPDTC ligand in methanol (Supporting Information) also show that the ligand decomposes within one day to form both the starting materials (carbon disulfide and *p*-anisidine) and other products. We also note that cadmium salts of alkyl dithiocarbamates are increasingly used as a single-source precursor in synthetic methods for CdS. The alkyl groups are much less electron donating than the methoxyphenyl group and as such, the diethyl-DTC is more stable than the *p*-methoxyphenyl-DTC. As a result, the synthetic methods using metal diethyldithiocarbamate salts also use the higher temperatures (100 – 150°C) that are required to make these more stable DTC ligands decompose.^{12-14,31} These pieces of evidence indicate that some or all of the *p*-methoxyphenyl-DTC ligand is decomposing at room temperature to leave S atoms on the Cd-rich surface, effectively producing a thin shell of CdS on the CdSe QDs. Adding a small amount of Cd²⁺ to the MPDTC increases the intensity of the CdS-like peaks in the Raman spectrum and increases the absorption red-shift to a value close to that reported in refs. 5-7. We note that cadmium stearate was used as the cadmium source in the synthesis in refs. 5-7 and the synthesis reaction was run under cadmium-rich conditions. It is notoriously difficult to remove cadmium stearate completely from QD preparations synthesized in this way,³² and this is particularly true when the purification is done by precipitation by the addition of methanol, as was done in refs. 5-7. Ref. 32 shows that the stearates tend to precipitate with the CdSe QDs and that five cycles of this purification removes less than 20% of the excess cadmium stearate. We therefore suggest that under the conditions of those experiments a small amount of unreacted cadmium stearate was still present when the DTC ligand was added, allowing the deposition of a small amount of additional cadmium as well as sulfur onto the CdSe surface. We also note that the exact

frequency of the CdS “LO phonon” in CdSe/CdS core-shell structures varies by as much as 25 cm^{-1} from very thin to very thick shells, and also depends on excitation wavelength.^{28,29,33} The rather low frequencies we observe, 273-280 cm^{-1} , indicate a thin CdS shell.

We carried out the experiment multiple times with different batches of QDs and always obtained qualitatively the same results, although the magnitude of the absorption red-shift and the intensity of the CdS Raman peak varied slightly from batch to batch. Because of the difficulty of removing excess cadmium stearate precursor, the CdSe QDs used in these experiments were synthesized using cadmium oleate and cadmium acetate as the precursors (see Supporting Information). Oleates are more easily removed in the purification process. Under these conditions, the small variations in the intensity of the CdS Raman peak are due to variations in the extent to which excess cadmium remains on the QD surface following purification. We also carried out the same experiment using larger QDs ($\lambda_{\text{max}} = 601 \text{ nm}$, $r \sim 4.7 \text{ nm}$; see Supporting Information) and obtained a smaller absorption red-shift as expected, but the Raman spectrum showed a comparable CdS LO phonon.

CdSe/CdS is a “type 1 1/2” or “quasi-type II” heterostructure: the hole is largely localized to the CdSe core, but the electron is delocalized over both core and shell because of the very small offset between the conduction band energies of the two materials. Growing a thin shell of CdS onto a CdSe core thus has very little effect on the hole wavefunction, but slightly increases the effective radius of the electron wavefunction, decreasing its quantum confinement and shifting the exciton to a lower energy. Since the electron has a much smaller effective mass than the hole, its quantum confinement energy in the original CdSe core is much greater than that of the hole and a much smaller increase in the effective radius of the electron is required to achieve a given shift in the energy of the lowest excitonic transition. The exciton wavelength maps in refs.

12 and 34 show that adding a CdS shell of average thickness 0.1 nm shifts the first excitonic absorption of a 3.2 nm diameter CdSe QD from 550 to 560 nm, while a 0.2 nm shell shifts it to 567 nm. Both of these maps show that it takes very little added CdS (less than half a monolayer, on average) to produce the observed spectral shifts. The present results show that this amount of CdS is readily observable in the Raman spectrum.

The interpretation put forward in ref. 5 is that the aromatic DTC ligands bind intact to surface Cd atoms and cause the red-shift by delocalizing the hole wavefunction into the conjugated system of the ligand. Several other aspects of the spectroscopy are inconsistent with this interpretation, but are consistent with there being a thin CdS shell formed by DTC addition. A shift of the magnitude reported there (20 nm) would be very difficult to achieve by delocalizing the hole alone. The original QDs used in that study absorb at 542 nm, 0.55 eV above the bulk band gap. Since the ratio of electron to hole effective masses is roughly 1:4, the hole accounts for only about 20% of this confinement energy, or about 0.11 eV. The measured spectral shift caused by adding the ligand is 20 nm or 0.08 eV, implying that adding the ligand has reduced the hole quantum confinement energy by nearly a factor of four. This means that the effective radius of the hole would have to increase by a factor of about 1.9 ($E \sim 1/r^2$), or by about 15 Å. This is larger than the maximum extent of the aromatic DTC ligands (see structure 1), which makes this assignment untenable. The electron, on the other hand, starts out with about 0.44 eV of confinement energy, so the observed red-shift would require a reduction in its confinement energy by only about 20%. This corresponds to an increase in the radius of about 10%, or somewhat less than half of a CdS monolayer.

A second difficulty with the attribution of the red-shift to hole delocalization is the nearly constant separation between the two lowest-energy excitonic transitions as the spectrum shifts.

The first two excitonic transitions are assigned as $1S_e1S_{3/2}$ and $1S_e2S_{3/2}$, respectively; they involve the same electron state but different hole states.³⁵ Their energy separation decreases as the overall size of a CdSe QD increases, and should also decrease if the effective radius for the hole wavefunction is increased by another mechanism, *e.g.* delocalization into the ligands. This energy difference is observed to remain essentially constant in the spectra in ref. 12 and in many other papers on CdSe/CdS core/shell QDs. The $1S_e2S_{3/2}$ transition is weak and not well resolved in our optical spectra or those of ref. 5, but it is clearly resolved in Fig. 1B of ref. 8, in which the ligand is the unsubstituted phenyl-DTC. Addition of phenyl-DTC causes the strong $1S_e1S_{3/2}$ and weaker $1S_e2S_{3/2}$ transitions shift to the red by essentially identical amounts. This shows that it is primarily the electron energies, not the hole energies, that are changed by adding the DTC. The increased absorbance below 400 nm in the solution phase spectra in Fig. 1 of ref. 7 is also consistent with the growth of a CdS shell on the CdSe QDs.

FTIR spectra of CdSe QDs treated with aromatic DTC ligands show vibrational lines attributable to aromatic groups.⁹ That result is not inconsistent with our conclusion, nor with the result of Munro *et al.* that the aniline decomposition product binds to the QD surface.¹⁵ Resonance Raman spectroscopy is uniquely sensitive to only those groups that undergo a change in charge density upon absorption of light at the resonant wavelength.^{22,23} Ligands on QDs are normally not observed in resonance Raman spectra because they do not couple to the excitonic transitions and their ordinary, unenhanced Raman spectra are many orders of magnitude weaker than the resonance enhanced spectra of the QDs. The aromatic DTCs and/or their decomposition products evidently fall into this category. We cannot determine whether intact DTC ligands or their organic decomposition products remain on the surface, but if they do, their aromatic groups do not substantially participate in the excitonic transition. We conclude that the spectral red-shift

may be assigned to increased delocalization of the electron into a very thin, and necessarily irregular, layer of CdS on the surface.

Conclusions

Aromatic dithiocarbamates, under conditions used for room-temperature ligand exchange with CdSe QDs, decompose to form a thin layer of CdS on the surface of the QD. The thickness of the shell varies with the amount of Cd²⁺ on the particle surfaces and free Cd²⁺ not fully removed following the CdSe QD synthesis. The observed red-shift of the lowest excitonic absorption following treatment of CdSe QDs with aromatic DTCs results primarily from delocalization of the electron into the CdS shell, rather than delocalization of the hole into intact DTC ligands on the surface.

Supporting Information Available. Synthetic methods, experimental details, Raman and NMR characterization of the MPDTC ligand and its decomposition, and several control experiments are given in the Supporting Information. This information is available free of charge via the Internet at <http://pubs.acs.org>.

Acknowledgments

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TOC graphic

