

Supporting Information for

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

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Nanocrystal synthesis

Cadmium oxide (CdO, 99.5%), octadecylamine (ODA, 90%), oleylamine (technical grade, 70%), octylamine (99%), *p*-anisidine (*p*-methoxyaniline, >99%), cadmium acetate dihydrate (Cd(Ac)₂·2H₂O), trioctylphosphine (TOP, 97%), trioctylphosphine oxide (TOPO, 90%), octadecene (ODE, 90%), hexane (99.8%), methanol (MeOH, 98%), toluene (99%), and ammonium hydroxide solution (28-30%) were obtained from Aldrich. Selenium (Se, 99%), sulfur (S powder, precipitated, 99.5%), oleic acid (OA, 90%), chloroform (CHCl₃, 99.8%) were obtained from Alfa Aesar. Carbon disulfide (99.9%) was obtained from Fisher Scientific. ODA was recrystallized from toluene before use. TOP and ODE were purified by vacuum distillation. TOPO was purified by repeated recrystallization from acetonitrile. Methanol, chloroform and toluene were purified by distillation from appropriate drying agents. All other chemicals were used as received.

The CdSe quantum dots (wurtzite crystal structure, cadmium-rich surface) were synthesized as described previously.¹ 0.4 mmol of CdO was mixed with 2.4 mmol (0.68 g) of oleic acid and 3.0 ml ODE and heated to 250 °C to get a colorless solution under N₂ flow. After cooling to room temperature, 1.0 g of ODA and 0.3 g of TOPO were added. The mixture was then heated to 285 °C. At this temperature, a solution containing 0.6 mmol of Se, 0.4 mL trioctylphosphine,

and 1.0 ml of ODE was quickly injected under N₂. The reaction was run at 255 °C for about 1 min. When the lowest exciton peak of the CdSe particles reached ~532 nm, the reaction mixture was cooled to room temperature. The raw mixture was extracted by hexane/methanol to get rid of unreacted precursors and dried under vacuum. The purified particles were dissolved in 3.0 mL ODE and heated to 180 °C under N₂ flow. A cadmium precursor solution (0.1 mmol cadmium acetate dihydrate dissolved in 0.2 mL oleylamine and 0.8 mL ODE) was then added dropwise into the reaction mixture. The reaction was quenched when the lowest exciton peak reached ~543 nm. These CdSe QDs with a Cd-rich surface were purified, dissolved in chloroform, deposited onto glass coverslips by drop-casting, and dried under nitrogen.

p-Methoxyphenyldithiocarbamate (MPDTC) was synthesized as its ammonium salt using a slight variation of the methods described in the literature.^{2,3} 2.5 mL of 8 M ammonium hydroxide was added to a solution of 0.6 g of *p*-anisidine (*p*-methoxyaniline) in 1.0 mL acetone, purged with nitrogen, and cooled to 0 °C. 0.6 mL of carbon disulfide was added dropwise over 5 min while stirring and purging with nitrogen at 0 °C. After 15 min, the sample was warmed to room temperature and stirred overnight. The yellowish-white precipitate was centrifuged, washed three times with acetone, and dried overnight under vacuum. 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). As a control, QD-coated slides were also soaked in dried MeOH without ligand for the same period of time.

Further characterization of the *p*-methoxydithiocarbamate ligand and its decomposition

Raman spectra of dithiocarbamates

Figure S1 shows the Raman spectrum of the cadmium salt of diethyldithiocarbamate. Sodium diethyldithiocarbamate trihydrate (Sigma-Aldrich) was dissolved in methanol followed by addition of an equal amount of cadmium acetate (Sigma-Aldrich) to precipitate the cadmium salt. The product was washed with methanol and dried under vacuum. The Raman spectrum of a stationary sample on a microscope slide was acquired using 532 nm excitation. There was no apparent degradation during the experiment and no background has been subtracted from the

spectrum. There are no Raman lines in the 250-300 cm^{-1} range. Bauer *et al.*⁴ assign Cd-S stretching character to a weak line at 306 cm^{-1} , visible as a very weak shoulder in our spectrum, and group of lines from 362-389 cm^{-1} , corresponding to our 375 cm^{-1} peak. The strong lines at 434 and 566 cm^{-1} in our spectrum correspond to their 431 and 564 cm^{-1} lines (CS stretching and SCS bending).

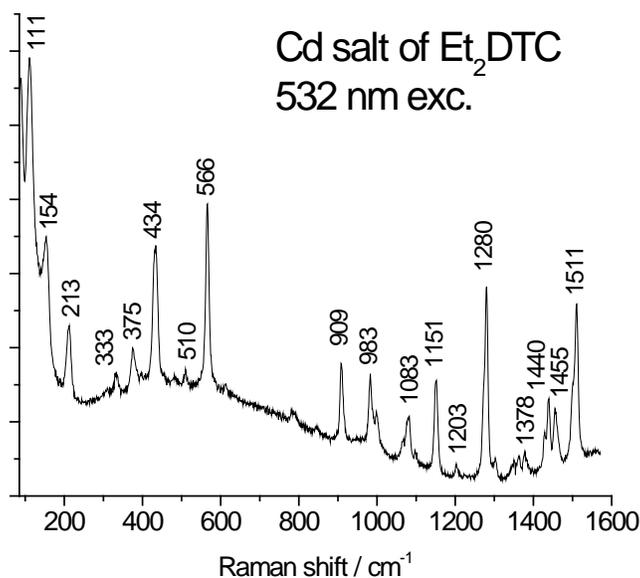


Figure S1. Nonresonant Raman spectrum of the cadmium salt of diethyldithiocarbamate.

The Raman spectrum of the as-synthesized *p*-methoxyphenyldithiocarbamate (ammonium salt) is shown in Figure S2. The solid sample was contained in a fused silica capillary and a longer excitation wavelength (561 nm, obtained from a Coherent OBIS diode-pumped solid-state laser) was employed because of the significant background from these samples, presumably a result of decomposition to fluorescent products. As a result, these background subtracted spectra have more baseline noise than the diethyl-DTC spectra above. The weak line at 270 cm^{-1} probably corresponds to the phenyl group mode at 260 cm^{-1} in anisole.⁵ The cadmium salt of *p*-methoxyphenyldithiocarbamate had even more background fluorescence, probably attributable to decomposition products, and only a few of the strongest Raman lines could be observed.

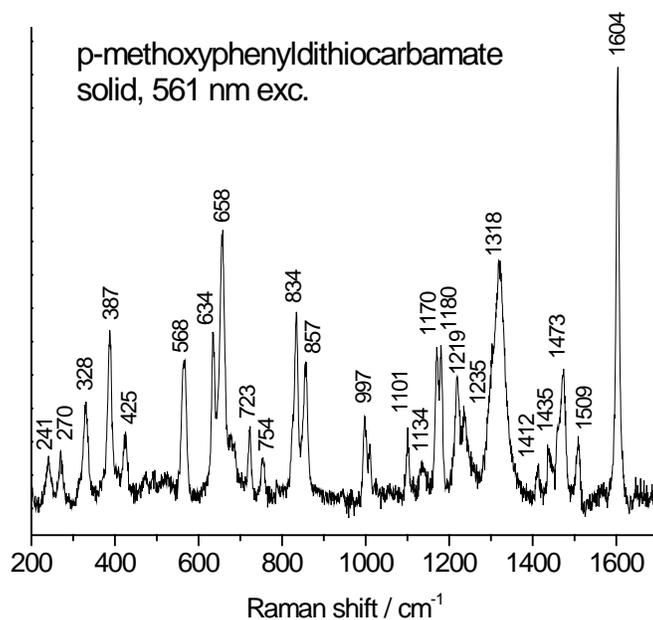


Figure S2. Nonresonant Raman spectrum of solid *p*-methoxyphenyldithiocarbamate (ammonium salt).

NMR spectra

The ¹³C NMR spectrum of *p*-methoxyphenyldithiocarbamate in methanol is shown in Figure S3. It agrees well with the spectrum published by the Weiss group.² Resonances labeled with an asterisk are assigned to the principal decomposition products, *p*-anisidine and carbon disulfide.

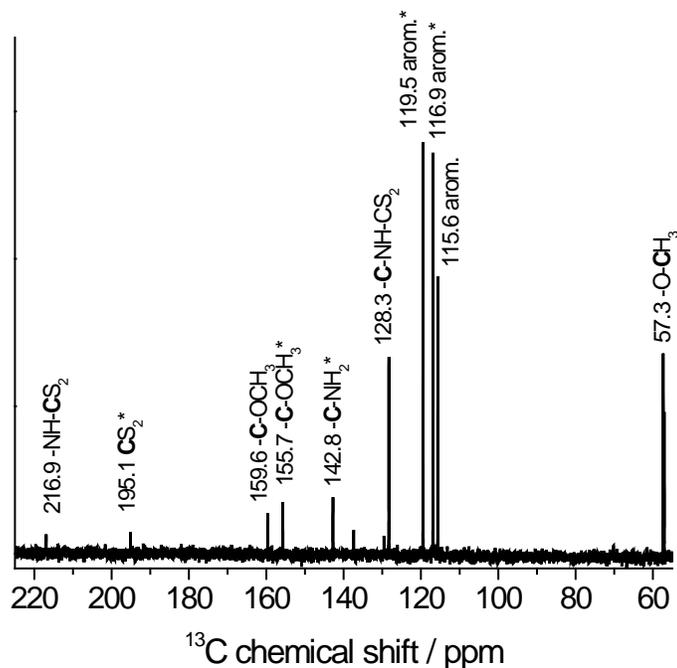


Figure S3. ¹³C NMR spectrum of *p*-methoxyphenyldithiocarbamate in methanol.

The proton NMR spectrum of *p*-methoxyphenyldithiocarbamate in methanol is shown in Figure S4 at “0 hours” (shortly after its isolation from the reaction mixture) and after sitting in the NMR tube for 16 hours. The 0 hour spectrum shows predominantly features assignable to MPDTC and the parent substituted aniline, *p*-anisidine. The *p*-anisidine contribution evidently arises from decomposition of the MPDTC rather than unreacted starting material because it is nearly absent from spectra measured in DMSO. The spectrum after 16 hours shows a reduction in the concentration of MPDTC and an increase in *p*-anisidine, and it also shows new resonances demonstrating the presence of two other products, both of which contain methoxyphenyl groups in slightly different chemical environments. Asterisks mark resonances from residual protons in the solvent. Spectra of *p*-anisidine itself in methanol show no degradation over a period of 48 hours.

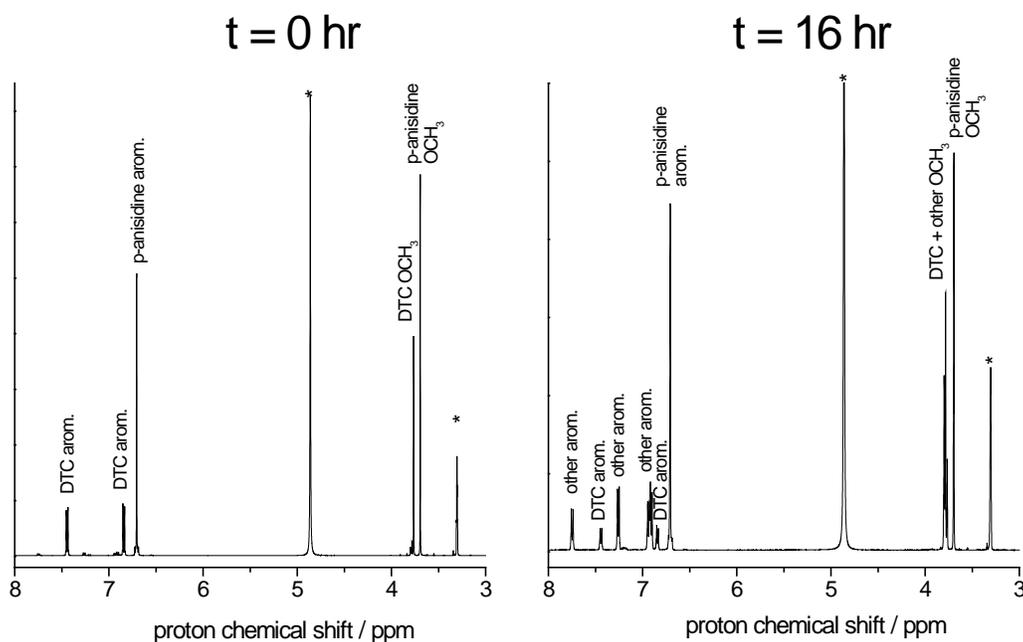


Figure S4. Proton NMR spectra of *p*-methoxyphenyldithiocarbamate in methanol, shortly after its isolation from the reaction mixture and after sitting in the NMR tube for 16 hours.

Experiments with larger quantum dots

The effects on the absorption and Raman spectra of the MPDTC ligand were also examined using larger CdSe quantum dots ($r \approx 4.7$ nm based on the lowest excitonic absorption maximum of 601 nm), also synthesized with a Cd-rich surface. The plots in Figure S5 show the absorption and resonance Raman spectra of these larger QDs deposited on a microscope slide and soaked in methanol for 2 days (QDs alone), soaked in methanol plus 0.33 mM added cadmium acetate (QDs+Cd), soaked in 10 mM MPDTC (QDs+DTC), and soaked in 10 mM MPDTC plus 0.33 mM cadmium acetate (QDs+DTC+Cd). The MPDTC alone red-shifts the absorption spectrum by about 2 nm, while the DTC+Cd red-shifts it by about 6 nm. These are smaller than the shifts observed with the smaller QDs, but consistent with the observation that a given thickness of CdS shell produces a smaller red-shift in larger QDs; according to ref. 6, adding a 0.3 nm thick shell of CdS (about 1 monolayer) to a CdSe core red-shifts the absorption of QDs originally absorbing at 550 and 600 nm by about 24 and 11 nm, respectively. The QDs alone and QDs+Cd show no Raman intensity in the 275 cm^{-1} region, while both of the samples with MPDTC do, indicative of

the formation of CdS. The CdS peak is somewhat stronger in the presence of added Cd, which, together with the larger absorption red-shift, implies that more CdS is formed on the surface when additional Cd²⁺ is available.

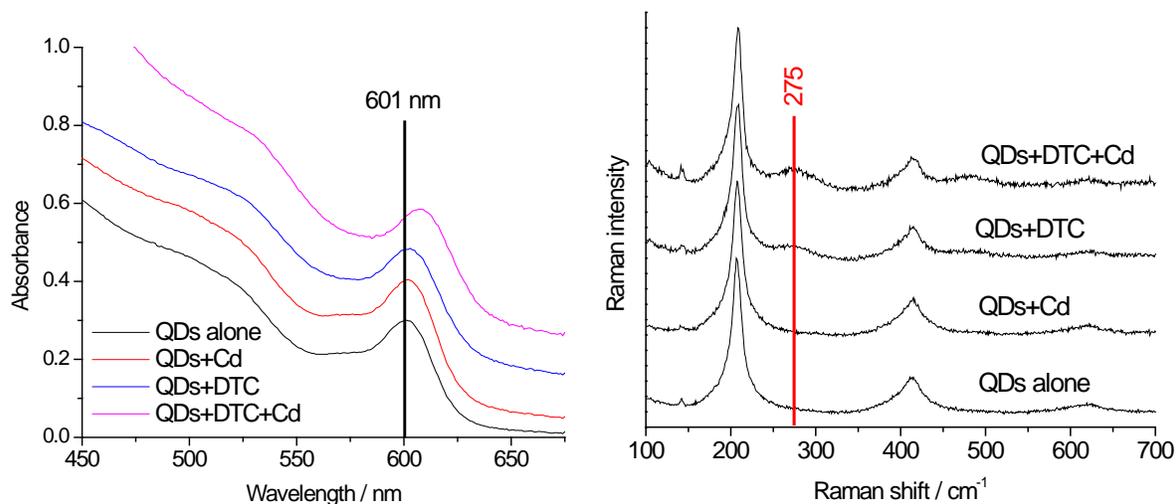


Figure S5. Absorption (left) and resonance Raman (right) spectra of larger CdSe QDs with and without exposure to additional Cd²⁺ and/or MPDTC.

Comparison of alkylthiol and aromatic dithiocarbamate reactivity on quantum dots

The effects on the absorption and Raman spectra of *p*-methoxyphenyldithiocarbamate were compared with those of a simple alkylthiol, 1-hexadecanethiol (Sigma-Aldrich, >95%). Cd-rich CdSe QDs were deposited on microscope slides and soaked for 2 days in methanol containing no added ligands, 10 mM MPDTC, or 10 mM thiol. A duplicate of each sample was prepared with 0.33 mM additional cadmium acetate. The absorption and resonance Raman spectra, scaled and vertically offset, are shown in Figure S6.

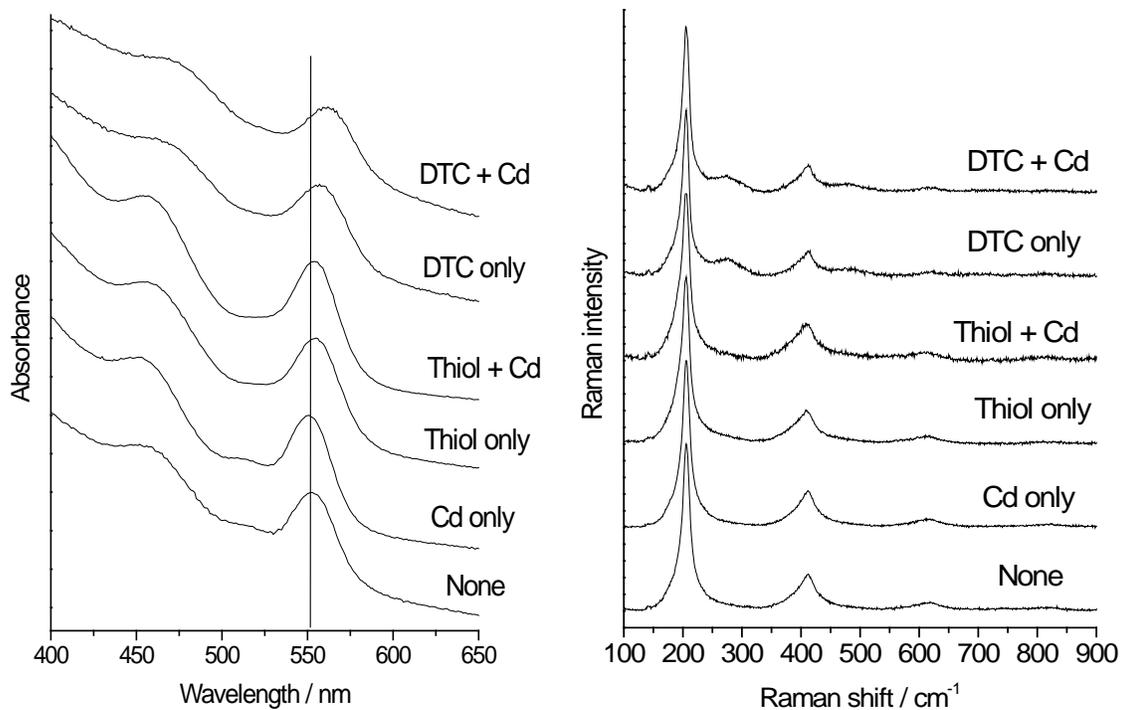


Figure S6. Absorption (left) and resonance Raman (right) spectra of CdSe QDs treated as indicated with Cd^{2+} , 1-hexadecanethiol, and/or MPDTC.

Relative to MeOH only, the thiol shifted the absorption spectrum 3 nm to the red and MPDTC shifted it 4 nm. Adding Cd^{2+} shifted the MeOH only and thiol samples each 1 nm to the blue, while it shifted the DTC spectrum 3 nm farther to the red. The DTC only and DTC+Cd resonance Raman spectra show CdS peaks at nearly the same frequency ($\sim 275 \text{ cm}^{-1}$) and about the same intensity. The thiol liganded spectra show no CdS peak. These results are consistent with slight expansion of the hole wavefunction onto the alkylthiol ligand without decomposition to form CdS.

References

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