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Bound-Ion Pair X-Type Ligation of Cadmium and Zinc Dithiocarbamates on Cadmium Selenide Quantum Belts

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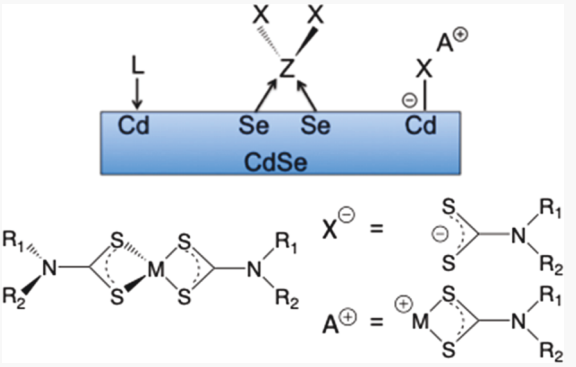
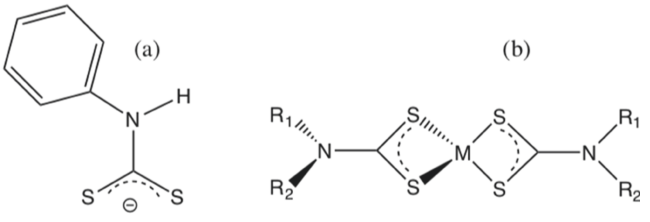
ABSTRACT: Wurtzite CdSe quantum belts with L-type *n*-octylamine, L-type ammonia, or Z-type $Cd(oleate)_2$ ligands are exchanged for several metal-dithiocarbamate ligands $[M(S_2CNR_1R_2)_2]$: $Cd(S_2CNPhMe)_2$, $Cd(S_2CNEt_2)_2$, $Zn(S_2CNPhMe)_2$, and $Zn(S_2CNEt_2)_2$. Successful ligand exchange with all $M(S_2CNR_1R_2)_2$ compounds occurs from $\{CdSe[Cd(oleate)_2]_{0.19}\}$ quantum belts (QBs), which induce similar spectral shifts in the absorption spectra of the ligand-exchanged QBs. Spectroscopic data, experimentally determined lattice strains, and ligand exchanges with $[Na][Et_2NCS_2]$ and $[NH_4][MePhNCS_2]$ establish that the $[M(S_2CNR_1R_2)_2]$ ligands bind as bound-ion-paired X-type ligands with $(S_2CNR_1R_2)^-$ groups ligated directly to the QB surfaces and $[M(S_2CNR_1R_2)]^+$ groups serving as the charge-balancing ion-paired counter-cations. The X-type dithiocarbamate ligands do not impart any special electronic effects to the CdSe QBs.



INTRODUCTION

We describe herein the binding of cadmium and zinc dithiocarbamate compounds to 5-monolayer wurtzite CdSe quantum belts[1] (QBs, or nanoribbons). Dithiocarbamate ligands have been reported to induce charge separation and interesting electronic effects in semiconductor nanocrystals. The phenyldithiocarbamate ($PhHNCS_2^-$) ligand (Figure 1a) has been studied most extensively and reported to relax the quantum confinement in ligated nanocrystals by as much as 1 eV through delocalization of holes into the dithiocarbamate ligands.[2−4] Phenyldithiocarbamate ligands have been reported to increase exciton-migration rates in semiconductor-nanocrystal films.[5,6] Dithiocarbamate ligands have also been reported to increase photoconductivities in nanocrystal films.[7]

Flat (2D) wurtzite CdSe QBs[8−10] and quantum platelets[11] (nanoplatelets) are sensitive reporters of surface ligation, in that their absorption spectra shift by as much as 340 meV upon ligand exchange.[10] Moreover, these nanocrystals exhibit rapid, complete, and reversible interchange of Lewis-basic L-type, Lewis-acidic Z-type, and anionic bound-ion-pair X-type ligation (Figure 2).[10] They are excellent systems for studies of nanocrystal ligand exchange and the effects of ligands on the electronic properties of semiconductor nanocrystals. On the



1 M = Cd, R_1 = Ph, R_2 = H
2 M = Cd, R_1 = Ph, R_2 = Me
3 M = Cd, R_1 = Et, R_2 = Et
4 M = Zn, R_1 = Ph, R_2 = Me
5 M = Zn, R_1 = Et, R_2 = Et

Figure 1. (a) Phenyldithiocarbamate ($PhHNCS_2^-$) ion and (b) metal-dithiocarbamate compounds $M(S_2CNR_1R_2)_2$.

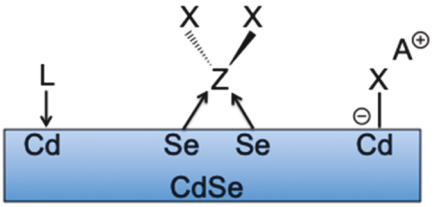


Figure 2. L-type (Lewis basic), Z-type (Lewis acidic), and bound-ion pair X-type (anionic) ligation on a CdSe quantum belt.

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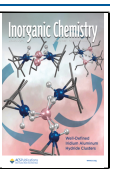

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basis of previous reports,[2−4] we expected that dithiocarbamate ligation should induce very large bathochromic spectral shifts in wurtzite CdSe QBs.

We previously attempted the installation of phenyldithiocarbamates as Z-type ligands via ligand exchange to Cd(S_2CNHPh)$_2$ ligation (compound **1** in Figure 1).[12] The Cd atoms in Z-type CdX_2 ligands occupy normal lattice positions on the surfaces of CdSe QBs, producing strong electronic coupling to the CdSe crystal lattice.[8,9] Unfortunately, the exchange conditions employed in our prior study led to deprotonation of a N-bound proton, triggering the decomposition of compound **1** to form a CdS shell on the CdSe QBs.[12] Thus, our efforts to introduce phenyldithiocarbamate ligands via Z-type ligation were thwarted.

We reasoned that the replacement of the N-bound H atom in **1** with an alkyl substituent would block the decomposition pathway. In compound **2** (Figure 1), N−H is replaced by N−Me: Cd(S_2CNPhMe)$_2$. Compounds **3**, Cd(S_2CNEt$_2$)$_2$, **4**, Zn(S_2CNPhMe)$_2$, and **5**, Zn(S_2CNEt$_2$)$_2$, (Figure 1) are also employed in this study to provide comparisons.

The metal dithiocarbamates M(S_2CNR$_1$R$_2$)$_2$ (**2**−**5**) are installed by the various ligand-exchange pathways described below. As noted above, we expected these compounds to bind as Z-type ligands. Surprisingly, the results exclude both Z- and L-type ligation modes and confirm their binding as bound-ion-pair X-type ligands. Additionally, the spectral data preclude carrier delocalization into the surface-bound dithiocarbamate ligands.

EXPERIMENTAL SECTION

Materials. {CdSe[Cd(oleate)$_2$]$_{0.19}$}[8] and {CdSe[NH$_3$]$_{0.25}$}[11] QBs were prepared from {CdSe[*n*-octylamine]$_{0.53}$}[1] QBs by previous literature methods. A stock solution of Cd(oleate)$_2$ in 1-octadecene was prepared by a previous method.[8] Selenourea (98%), *n*-octylamine (99%), oleylamine (technical grade, 70%), tri-*n*-octylphosphine (TOP, 97%), 1-octadecene (technical grade, 90%), oleic acid (technical grade, 90%), anhydrous carbon disulfide (ACS reagent, 99.9%), zinc diethyldithiocarbamate (98%), *n*-methylaniline (98%), hexane (ACS reagent, ≥98.5%), ammonium hydroxide solution (ACS reagent, 28.0−30.0% NH$_3$ by weight basis), *N*,*N*-dimethylformamide (DMF, ACS reagent, ≥99.8%), methanol (≥99.9%), chloroform (99.9%, with amylenes as stabilizer), dichloromethane (HPLC Plus, for HPLC, GC, and residue analysis, ≥99.9%, contains 50−50 ppm amylene as a stabilizer), and toluene (ACS reagent, ≥99.5%) were purchased from Sigma-Aldrich. Cadmium acetate dihydrate (Cd(OAc)$_2$·2H$_2$O, analytical reagent) was purchased from Mallinckrodt. Zinc acetate dihydrate (Zn(OAc)$_2$·2H$_2$O, ACS reagent, 98%) was purchased from Strem Chemicals. Diethyldithiocarbamic acid diethylammonium salt ([NH$_2$(C$_2$H$_3$)$_2$][(C$_2$H$_3$)$_2$NCS$_2$]) was purchased from TCI America. Ethanol (anhydrous, 200 proof) was purchased from Decon Laboratories, Inc. Transmission electron microscopy (TEM) sample grids (carbon-coated copper) were obtained from Ted Pella, Inc. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. All reagents were used as received without additional purification. All reactions were performed under ambient conditions unless otherwise noted.

Characterization. UV−vis spectra were obtained from an Agilent Cary 60 UV−vis spectrophotometer, and all absorbance spectra maxima were determined by the second derivative. X-ray diffractometer (XRD) patterns were obtained from a Bruker d8 Advance X-ray diffractometer using Cu Kα radiation (1.5418 Å) with a low-background silicon sample holder. TEM images were collected from a JEOL 2000FX microscope with an acceleration voltage of 200 kV. Energy-dispersive X-ray spectroscopy (EDS) measurements were obtained on the same JEOL 2000FX microscope at 200 kV. The error reported for EDS-derived Cd/Se ratios were the standard deviations in measurements from eight different regions of each sample; each measurement included tens of QBs. IR spectra were collected from a Bruker Optics α Fourier transform infrared (FT-IR) system. Dispersions of equal concentrations of QBs were dropped onto the instrument attenuated total reflection (ATR) window and allowed to dry to a thin film. Thus, infrared (IR) analyses were conducted with nearly equal QB quantities. ^{1}H nuclear magnetic resonance (NMR) spectra were collected using a Varian Unity Inova-500 NMR spectrometer. Elemental analyses (C, H, N, and S) were obtained from Galbraith Laboratories, Inc. (Knoxville, TN).

Preparation of [NH$_4$][MePhNCS$_2$]. The synthesis of ammonium *N*-methyl-*N*-phenyldithiocarbamate, [NH$_4$][MePhNCS$_2$], was synthesized by adaption of a literature method.[4] A solution of anhydrous carbon disulfide (6.25 g, 82.1 mmol) in ammonium hydroxide solution (30 mL of a 15 M solution) was kept at 0 °C under N$_2$, while *N*-methylaniline (5.0 mL, 47 mmol) was added dropwise over 15 min. The mixture was constantly stirred vigorously for 1 h to ensure the mixture of the two phases. The solution produced a bright orange supernatant and a light yellow precipitate, which was collected via vacuum filtration on analytical filter paper. The precipitate was washed with 30 mL of 0 °C ethanol and then was allowed to dry in the vacuum filter funnel (approximately 1 h, 3.64 g, 39% yield). ^{1}H NMR (500 MHz, D$_2$O, δ): 7.33 (t, 2*H*, *m*-Hs), 7.24 (t, 1*H*, *p*-H), 7.12 (d, 2*H*, *o*-Hs), 3.59 (s, 3*H*, Me).

Preparation of Metal-Dithiocarbamate Compounds. The syntheses of bis(diethyldithiocarbamato) cadmium(II) (Cd(S_2CNEt$_2$)$_2$),[13] bis(*N*-methyl-*N*-phenyldithiocarbamato) cadmium(II) (Cd(S_2CNPhMe)$_2$),[12,14,15] and bis(*N*-methyl-*N*-phenyldithiocarbamato) zinc(II) (Zn(S_2CNPhMe)$_2$)[12,15,16] were adapted from literature procedures. Generally, a solution of Cd(OAc)$_2$·2H$_2$O (802 mg, 3.01 mmol) or Zn(OAc)$_2$·2H$_2$O (568 mg, 2.59 mmol) in methanol (25 mL) was added dropwise over 30 min to a continuously stirred solution of [NH$_4$][MePhNCS$_2$] (1.0 g, 5.0 mmol) or [NH$_2$(C$_2$H$_3$)$_2$][(C$_2$H$_3$)$_2$NCS$_2$] (1.53 g, 6.88 mmol) in methanol (50 mL) at 0 °C. A white precipitate formed shortly after addition. The solution was stirred for an additional 30 min to an hour at 0 °C and then 30 min at room temperature. Then, the precipitate was collected via vacuum filtration and washed with ice-chilled ethanol (75 mL). The products Cd(S_2CNPhMe)$_2$, Cd(S_2CNEt$_2$)$_2$, and Zn(S_2CNPhMe)$_2$ were dried under vacuum until no residual solvent peaks were detected in the ^{1}H NMR (approximately 3 h).

*Cd(S_2CNPhMe)$_2$ (**2**).*[15] Yield 0.837 g (1.7 mmol, 70%). UV−visible (THF) λ_{max}, nm: 263. IR, cm^{-1}: 1489 ν_s(C=N), 1117 σ(C−N−C), 963 ν_{as}(C−S). ^{1}H NMR (500 MHz, DMSO-d_6, δ): 7.40 (t, 4*H*, *m*-Hs), 7.32 (d, 4*H*, *o*-Hs), 7.28 (t, 2*H*, *p*-Hs), 3.64 (s, 6*H*, Me). ^{13}C {^{1}H} NMR (500 MHz, DMSO-d_6, δ): 208.9, 148.6, 129.6, 126.4, 48.7.

*Cd(S_2CNEt$_2$)$_2$ (**3**).*[17] Yield 1.156 g (2.8 mmol, 94%). UV−visible (THF) λ_{max}, nm: 260. IR, cm^{-1}: 1494 ν_s(C=N), 1144 σ(C−N−C), 986 ν_{as}(C−S). ^{1}H NMR (500 MHz, DMSO-d_6, δ): 3.82 (q, 8*H*, CH_2CH_3), 1.21 (t, 12*H*. CH_2CH_3). ^{13}C {^{1}H} NMR (500 MHz, DMSO-d_6, δ): 203.8, 50.5, 12.4.

*Zn(S_2CNPhMe)$_2$ (**4**).*[15] Yield 0.756 g (1.8 mmol, 71%). UV−visible (THF) λ_{max}, nm: 266. IR, cm^{-1}: 1491 ν_s(C=N), 1117 σ(C−N−C), 964 ν_{as}(C-S). ^{1}H NMR (500 MHz, DMSO-d_6, δ): 7.42 (t, 4*H*, *m*-Hs), 7.32 (m, 6*H*, *p* & *o*-Hs), 3.64 (s, 6*H*, Me). ^{13}C {^{1}H} NMR (500 MHz, DMSO-d_6, δ): 207.5, 147.7, 129.6, 128.1, 126.3, 47.9.

Preparation of {CdSe[NH$_3$]$_{0.25}$} QBs. A dispersion of {CdSe[*n*-octylamine]$_{0.53}$} QBs in *n*-octylamine was prepared by a previous method.[1] An aliquot from this QB dispersion (0.20 mL) was unbundled according to the literature[1] using oleylamine to yield {CdSe[oleylamine]$_x$}. The solution of amine-passivated QBs was centrifuged (3500 rpm, 3 min), and the supernatant was removed.

The QBs were purified by two cycles of resuspension in toluene (2 mL), centrifugation (3500 rpm, 3 min), and removal of the supernatant. The purified {CdSe[oleylamine]$_x$} QBs were dispersed in hexane (1 mL). Then, an aliquot of this dispersion (200 μL) was diluted in hexane (4 mL) and set aside.

An ammonia solution was prepared by adding an aqueous ammonium hydroxide solution (0.10 mL of a 15 M solution) to

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DMF (4.0 mL), creating a 0.38 M solution. The set-aside QB dispersion in hexane was added on top of this solution to create a two-phase mixture. The mixture was shaken to transfer the QBs from the hexane phase to the DMF phase, changing their ligation from oleylamine to ammonia, as described in a previous literature procedure.[11] The upper hexane layer was removed, the lower DMF layer containing the QB dispersion was centrifuged (3500 rpm, 3 min), and the DMF supernatant was removed.

Preparation of {CdSe[Cd(oleate)$_2$]$_{0.19}$} QBs. {CdSe[oleylamine]$_x$} QBs were prepared from {CdSe[*n*-octylamine]$_{0.53}$} QBs as described above. The {CdSe[oleylamine]$_x$} QBs were purified by two cycles of resuspension in toluene (2 mL), centrifugation (3500 rpm, 3 min), and removal of the supernatant. The purified {CdSe[oleylamine]$_x$} QBs were dispersed toluene (1 mL) and resuspended in a solution of 0.11 M Cd(oleate)$_2$ in 1-octadecene to produce {CdSe[Cd(oleate)$_2$]$_{0.19}$} QBs.[8] The {CdSe[Cd(oleate)$_2$]$_{0.19}$} QBs were purified three times by centrifugation (3500 rpm, 3 min) using toluene (2 mL) and methanol (0.3 mL) as flocculants, and the supernatant was removed.

Exchange to [Na][Et$_2$NCS$_2$] or [NH$_4$][MePhNCS$_2$] Using {CdSe[Cd(oleate)$_2$]$_{0.19}$} QBs or {CdSe[*n*-octylamine]$_{0.53}$} QBs. NaEt$_2$(NCS$_2$) was prepared using a previous literature method.[18] Excess NaOH was removed by washing the product with diethyl ether, then precipitating it from acetone with diethyl ether twice, and washing with diethyl ether again. The product was dried under vacuum. The {CdSe[Cd(oleate)$_2$]$_{0.19}$} QBs from the procedure above were suspended in toluene (2 mL) for ligand exchange to [Na][Et$_2$NCS$_2$]. [Na][Et$_2$NCS$_2$] (3 mg) was added to the QB suspensions, which were lightly shaken to dissolve [Na][Et$_2$NCS$_2$]. The resulting dispersion was immediately centrifuged (2000 rpm, 3 min), and the supernatant containing the displaced Cd(oleate)$_2$ and excess NaEt$_2$(NCS$_2$) was removed. The ligand-exchanged {CdSe-{[Na][Et$_2$NCS$_2$]}$_y$} QBs were redispersed in toluene for analysis.

[NH$_4$][MePhNCS$_2$] (5 mg) was added to {CdSe[Cd(oleate)$_2$]$_{0.19}$} QBs or {CdSe[*n*-octylamine]$_{0.53}$} QBs suspended in toluene (2 mL) or CH$_2$Cl$_2$ (2 mL). The QB suspensions were lightly shaken to dissolve the [NH$_4$][MePhNCS$_2$]. The resulting dispersion was immediately centrifuged (2000 rpm, 3 min), and the supernatant containing the displaced Cd(oleate)$_2$ or *n*-octylamine and excess [NH$_4$][MePhNCS$_2$] was removed. The ligand-exchanged {CdSe-{[NH$_4$][MePhNCS$_2$]}$_z$} QBs were redispersed in toluene or CH$_2$Cl$_2$ for analysis.

Exchange to M(S$_2$CNR$_1$R$_2$)$_2$ Ligation Using {CdSe[NH$_3$]$_{0.25}$} QBs. The {CdSe[NH$_3$]$_{0.25}$} QBs from the procedure above were suspended in toluene (2 mL) for ligand exchange to Cd(S$_2$CNEt$_2$)$_2$, or CH$_2$Cl$_2$ (2 mL) for ligand exchange to Cd(S$_2$CNPhMe)$_2$ or Cd(S$_2$CNEt$_2$)$_2$. M(S$_2$CNR$_1$R$_2$)$_2$ powder (5 mg) was added to the QB suspensions, which were lightly shaken to dissolve M(S$_2$CNR$_1$R$_2$)$_2$. The resulting dispersion was immediately centrifuged (2000 rpm, 3 min), and the supernatant containing the displaced NH$_3$ and excess M(S$_2$CNR$_1$R$_2$)$_2$ was removed. The ligand-exchanged QBs were redispersed in toluene or CH$_2$Cl$_2$ for analysis.

Exchange to M(S$_2$CNR$_1$R$_2$)$_2$ Ligation Using {CdSe[Cd(oleate)$_2$]$_{0.19}$} QBs. {CdSe[M(S$_2$CNR$_1$R$_2$)$_2$]$_x$} QBs were prepared from {CdSe[Cd(oleate)$_2$]$_{0.19}$} QBs in the same procedure as described above, starting with {CdSe[NH$_3$]$_{0.25}$} QBs. The ligand exchange to Zn(S$_2$CNPhMe)$_2$, Zn(S$_2$CNEt$_2$)$_2$, or Cd(S$_2$CNEt$_2$)$_2$ took place in toluene (2 mL) or CH$_2$Cl$_2$ (2 mL). The ligand exchange to Cd(S$_2$CNPhMe)$_2$ only occurred in CH$_2$Cl$_2$ (2 mL).

Exchange to M(S$_2$CNR$_1$R$_2$)$_2$ Ligation Using {CdSe[*n*-octylamine]$_{0.53}$} QBs. A dispersion of {CdSe[*n*-octylamine]$_{0.53}$} QBs in *n*-octylamine was prepared by a previous method.[1] An aliquot from this QB dispersion (0.20 mL) was purified by two cycles of resuspension in toluene (2 mL), centrifugation (3500 rpm, 3 min), and removal of the supernatant. The purified {CdSe[*n*-octylamine]$_{0.53}$} QBs were dispersed in toluene (1 mL) or CH$_2$Cl$_2$ (1 mL). An aliquot (100 μL) of the {CdSe[*n*-octylamine]$_{0.53}$} QB suspension was diluted with toluene (2 mL) or CH$_2$Cl$_2$ (2 mL) accordingly. M(S$_2$CNR$_1$R$_2$)$_2$ powder (5 mg) was added to the QB suspensions, which were lightly shaken to dissolve the M(S$_2$CNR$_1$R$_2$)$_2$. The resulting dispersion was immediately centrifuged (2000 rpm, 3 min), and the supernatant containing the displaced *n*-octylamine and excess M(S$_2$CNR$_1$R$_2$)$_2$ was removed. The ligand-exchanged QBs were redispersed in toluene or CH$_2$Cl$_2$ for analysis. The ligand exchange to Zn(S$_2$CNPhMe)$_2$, Zn(S$_2$CNEt$_2$)$_2$, or Cd(S$_2$CNEt$_2$)$_2$ took place in toluene (2 mL), while the ligand exchange to Cd(S$_2$CNPhMe)$_2$ occurred in CH$_2$Cl$_2$ (2 mL).

RESULTS

Ligand Exchanges with Metal Dithiocarbamates. A CH$_2$Cl$_2$ dispersion of {CdSe[*n*-octylamine]$_{0.53}$} QBs was combined with a 10-fold excess of solid Cd(S$_2$CNPhMe)$_2$. (Exchanges conducted with smaller excesses were incomplete.) Ligand exchange occurred within a minute. The lowest-energy feature in the absorption spectrum was observed to shift from 449 to 466 nm, consistent with the exchange of the *n*-octylamine ligation by Cd(S$_2$CNPhMe)$_2$ ligation (Figure 3a,b). Similar exchanges were conducted with toluene dispersions of {CdSe[*n*-octylamine]$_{0.53}$} QBs and Cd(S$_2$CNEt$_2$)$_2$, Zn(S$_2$CNPhMe)$_2$, and Zn(S$_2$CNEt$_2$)$_2$, within the same 1 min time scale. These exchanges produced similar spectral shifts, although that induced by Zn(S$_2$CNEt$_2$)$_2$ was smaller than the others (Figure 3c–e). Exchange reactions of Cd(S$_2$CNPhMe)$_2$ and {CdSe[*n*-octylamine]$_{0.53}$} QBs conducted in toluene dispersions also produced smaller spectral shifts, all of which we interpreted to indicate incomplete ligand exchange.

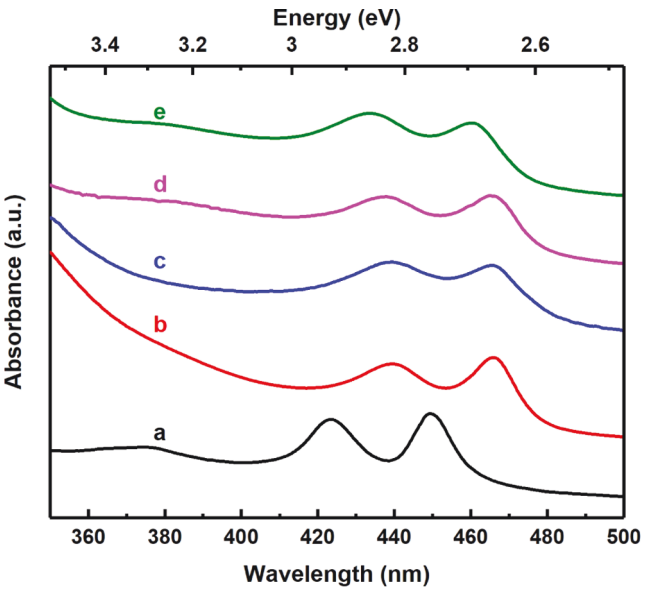

Figure 3. Absorption spectra of five monolayer wurtzite CdSe QBs ligated with (a) octylamine and after ligand exchange to: (b) Cd(S$_2$CNPhMe)$_2$, (c) Cd(S$_2$CNEt$_2$)$_2$, (d) Zn(S$_2$CNPhMe)$_2$, and partial ligand exchange to (e) Zn(S$_2$CNEt$_2$)$_2$.

IR spectra of the ligand-exchanged QBs gave evidence for retention of residual *n*-octylamine (Figure S1). The results suggested that the exchange of the metal-dithiocarbamate ligands was substantial, but that some amounts of ligated *n*-octylamine remained. We have previously observed such incomplete exchanges with {CdSe[*n*-octylamine]$_{0.53}$} QBs.[11]

We thus investigated ligand-exchange reactions of the metal dithiocarbamates with CdSe QBs having other initial ligation to achieve complete exchanges. Dispersions of {CdSe-[NH$_3$]$_{0.25}$} QBs[11] were combined with Cd(S$_2$CNPhMe)$_2$ (in CH$_2$Cl$_2$) or Cd(S$_2$CNEt$_2$)$_2$ (in toluene), producing immediate

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spectral shifts (Figure 4b,c) consistent with those achieved starting with the {CdSe[*n*-octylamine]$_{0.53}$} QBs. However, no

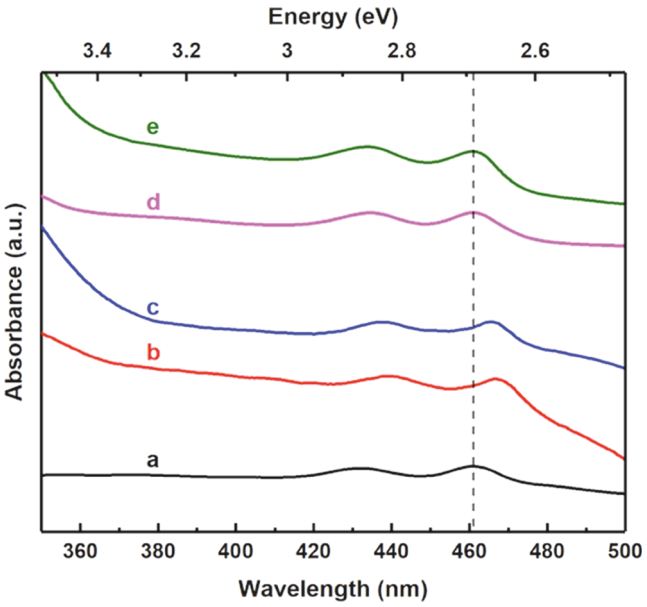

Figure 4. Absorption spectra of CdSe QBs ligated with (a) ammonia and after ligand exchange to: (b) $Cd(S_2CNPhMe)_2$ and (c) $Cd(S_2CNEt_2)_2$; failed ligand exchange to (d) $Zn(S_2CNPhMe)_2$ and (e) $Zn(S_2CNEt_2)_2$. The dashed line emphasizes the lack of spectral shifting in (d) and (e).

reaction was observed with {CdSe[NH_3]$_{0.25}$} QBs and either $Zn(S_2CNPhMe)_2$ (Figure 4d) or $Zn(S_2CNEt_2)_2$ (Figure 4e). IR spectra of the cadmium-dithiocarbamate-exchanged QBs were consistent with the complete replacement of the initial NH_3 ligation (Figure S2).

Ligand exchanges starting with {CdSe[Cd(oleate)$_2$]$_{0.19}$} QBs were successful with all of the cadmium and zinc dithiocarbamates **2**–**5** (Figure 1) and required less than a minute to complete. Exchange with $Cd(S_2CNPhMe)_2$ was conducted in CH_2Cl_2, and the other exchanges were conducted in toluene. The spectral shifts (Figure 5) were consistent with those obtained starting from {CdSe[*n*-octylamine]$_{0.53}$} QBs, except with $Zn(S_2CNEt_2)_2$, for which exchange was incomplete with {CdSe[*n*-octylamine]$_{0.53}$}. The spectral shifts (Figure 5) were also consistent with those for the cadmium dithiocarbamates obtained starting from {CdSe[NH_3]$_{0.25}$} QBs. The IR spectra of the ligand-exchanged QBs (Figures 6 and 7) showed no remaining Cd(oleate)$_2$, as indicated by the absence of the characteristically broad CO_2 stretches at 1536 and 1412 cm^{-1},[8] consistent with complete ligand exchanges.

Characterization of the Metal-Dithiocarbamate-Ligated QBs. Figures 6 and 7 compare the IR spectra of the pure metal-dithiocarbamate ligands to the correspondingly ligated CdSe QBs. As expected, they were closely similar and exhibited the rich structure associated with dithiocarbamate ligands.[19] TEM images of the ligand-exchanged QBs showed retention of the initial QB morphologies, with the QBs highly agglomerated due to the comparatively poor dispersibilities of the metal-dithiocarbamate-ligated QBs (Figure 8). XRD patterns of the exchanged QBs indexed to the wurtzite lattice structure and indicated low compressive strains (1.1–2.1%, Figure S3).

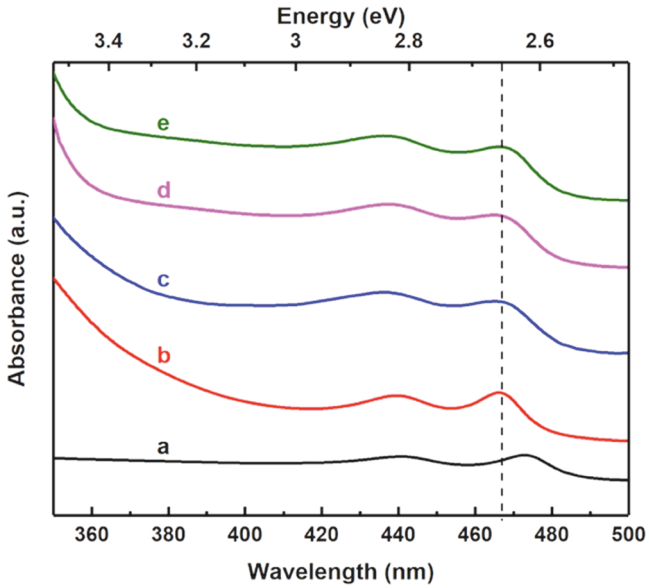

Figure 5. Absorption spectra of CdSe QBs ligated with (a) Cd(oleate)$_2$ and after ligand exchange to: (b) $Cd(S_2CNPhMe)_2$, (c) $Cd(S_2CNEt_2)_2$, (d) $Zn(S_2CNPhMe)_2$, and (e) $Zn(S_2CNEt_2)_2$. The dashed line emphasizes the similarity of the spectral shifts in (b–e).

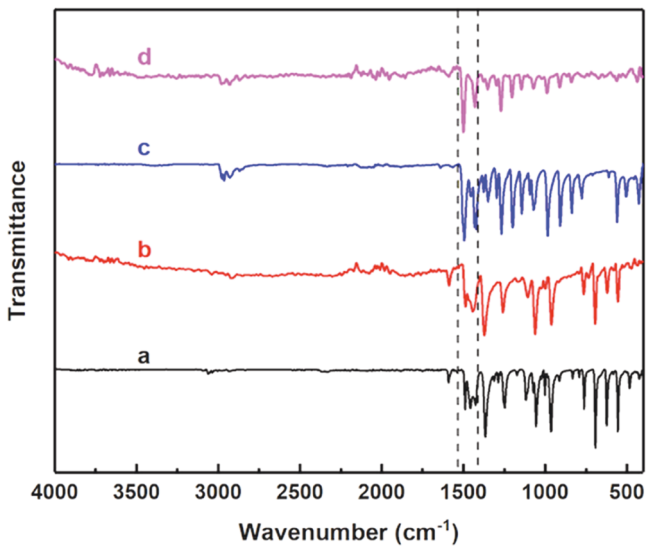

Figure 6. IR spectra of (a) $Cd(S_2CNPhMe)_2$, (b) CdSe QBs ligated with $Cd(S_2CNPhMe)_2$ after a ligand exchange from Cd(oleate)$_2$ ligation, (c) $Cd(S_2CNEt_2)_2$, and (d) CdSe QBs ligated with $Cd(S_2CNEt_2)_2$ after a ligand exchange from Cd(oleate)$_2$ ligation. The dashed lines indicate the locations of the prominent IR features for {CdSe[Cd(oleate)$_2$]$_{0.19}$} QBs at 1536 and 1412 cm^{-1}.

The compositions of the ligand-exchanged QBs were determined by energy-dispersive X-ray spectroscopy in the TEM and by combustion-based elemental analysis. The ligation stoichiometries determined by the two methods (Table 1) were in good agreement and consistent with expectation, as further described in the Discussion section.

The absorption spectra of the exchanged QBs exhibited the expected profiles, with two peaks corresponding to the n = 1 light-hole and heavy-hole quantum-well transitions.[20] Remarkably, the four $M(S_2CNR_1R_2)_2$ ligands (**2**–**5**) produced nearly identical shifts (Figure 5). The positions of the lowest-energy

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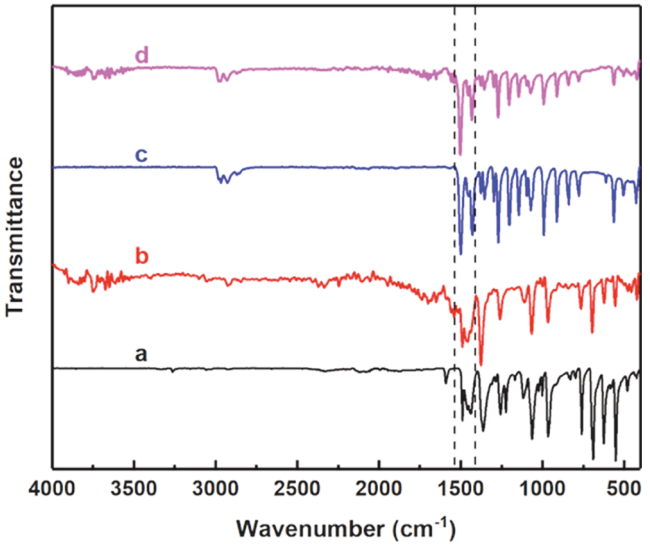

Figure 7. IR spectra of (a) $Zn(S_2CNPhMe)_2$ and (b) CdSe QBs ligated with $Zn(S_2CNPhMe)_2$ after a ligand exchange from Cd(oleate)$_2$ ligation; (c) $Zn(S_2CNEt_2)_2$ and (d) CdSe QBs ligated with $Zn(S_2CNEt_2)_2$ after a ligand exchange from Cd(oleate)$_2$ ligation. The dashed lines indicate the locations of the prominent IR features for $\{CdSe[Cd(oleate)_2]_{0.19}\}$ QBs at 1536 and 1412 cm^{-1}.

Table 1. Composition of CdSe QBs with Metal-Dithiocarbamate Ligation Determined by Combustion-Based Elemental Analysis (EA) and Energy-Dispersive X-ray Spectroscopy (EDS) in the TEM

CdSe QB specimen	x by EA	x by EDS
$CdSe[Cd(S_2CNPhMe)_2]_x$	0.20 ± 0.05	0.21 ± 0.05
$CdSe[Cd(S_2CNEt_2)_2]_x$	0.19 ± 0.05	0.20 ± 0.04
$CdSe[Zn(S_2CNPhMe)_2]_x$	0.24 ± 0.05	0.26 ± 0.03
$CdSe[Zn(S_2CNEt_2)_2]_x$	0.23 ± 0.05	0.25 ± 0.02

features in the four cases fell in a very narrow range of 466–467 nm. As explained in the Discussion section, the spectral similarity of the zinc- and cadmium-dithiocarbamate-ligated QBs ruled out Z-type ligation, which was surprising to us. Although one could imagine the metal-dithiocarbamates binding through S atoms in an L-type manner, the spectral shifts observed were out of the expected range for L-type ligation. They did, however, fall in the range expected for bound-ion-pair X-type ligation. The following experiments were conducted to test that possibility.

Ligand Exchanges with Ammonium and Sodium Dithiocarbamates. The binding of dithiocarbamate ions as anionic X-type ligands would seemingly require dissociation of the metal-dithiocarbamate compounds $M(S_2CNR_1R_2)_2$ to the salts $[M(S_2CNR_1R_2)][R_1R_2NCS_2]$, with the $[R_1R_2NCS_2]^-$ fragment bound to the QB surface and the $[M(S_2CNR_1R_2)]^+$

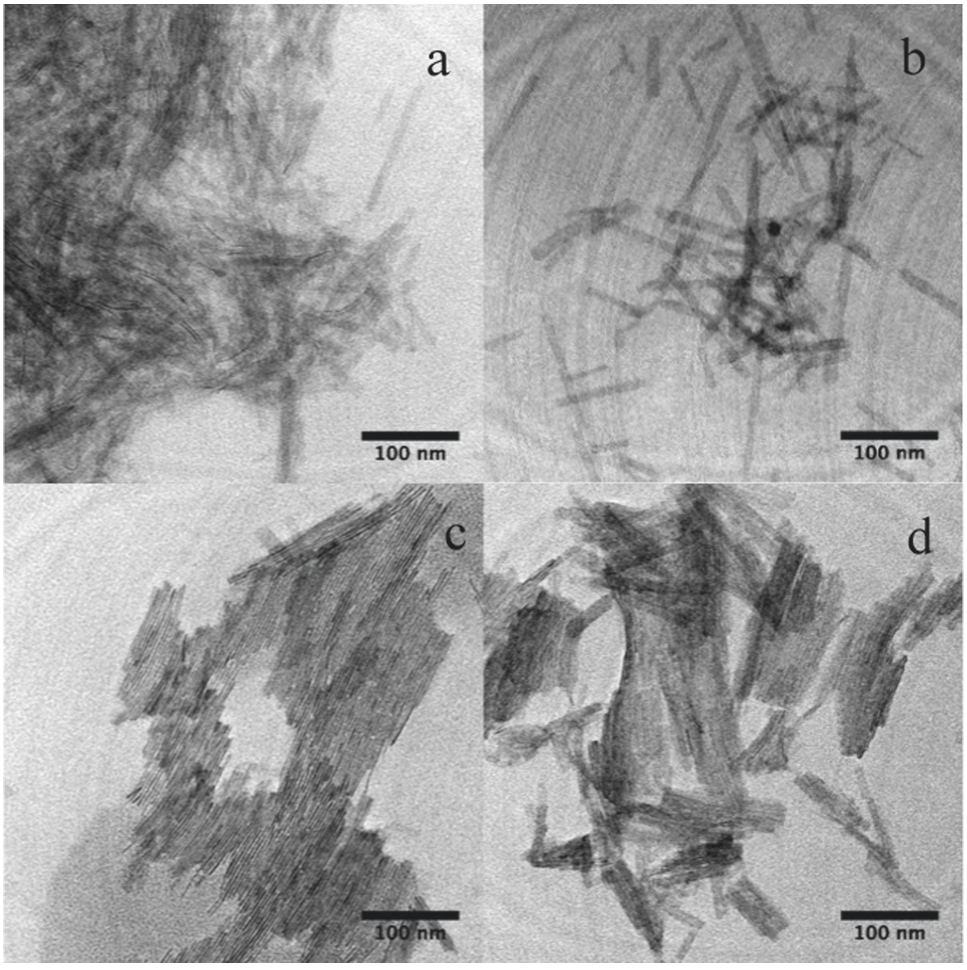

Figure 8. TEM images of CdSe QBs ligated with: (a) $Zn(S_2CNPhMe)_2$, (b) $Zn(S_2CNEt_2)_2$, (c) $Cd(S_2CNPhMe)_2$, and (d) $Cd(S_2CNEt_2)_2$.

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fragment serving as an ion-paired countercation (Figure 2).[10] If so, we reasoned that the complex $[M(S_2CNR_1R_2)]^+$ countercation should be replaceable by simpler countercations, such as $[NH_4]^+$ or Na^+.

Exchange reactions of $[NH_4][PhMeNCS_2]$ and $\{CdSe[n\text{-octylamine}]_{0.53}\}$ or $\{CdSe[Cd(oleate)_2]_{0.19}\}$ QBs were conducted under the conditions described above. In both cases, immediate spectral shifts were observed, with the lowest-energy features shifted to 467 nm (Figure 9), consistent with

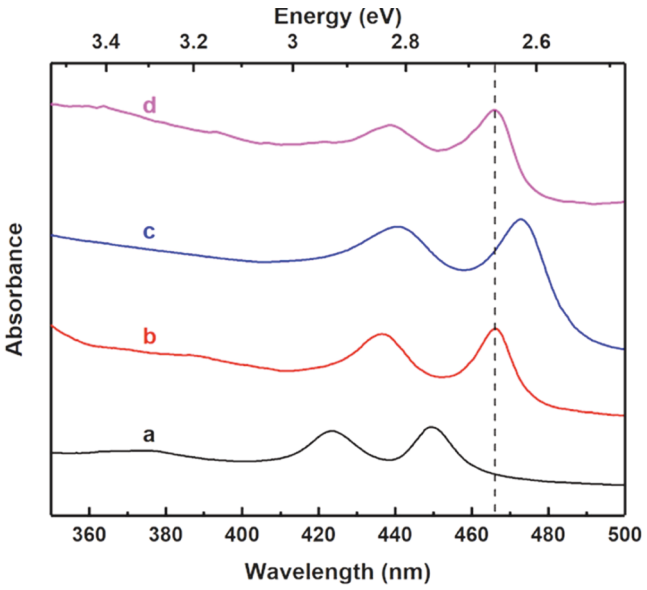

Figure 9. Absorption spectra of CdSe QBs ligated with: (a) *n*-octylamine, (b) $[NH_4][PhMeNCS_2]$ after ligand exchange from *n*-octylamine ligation, (c) $Cd(oleate)_2$, and (d) $[NH_4][PhMeNCS_2]$ after ligand exchange from $Cd(oleate)_2$ ligation. The dashed line shows the peaks for (b) and (d) both shifted to 466 nm.

the ligand exchanges described above employing $Cd(S_2CNPhMe)_2$ and $Zn(S_2CNPhMe)_2$ (Figure 5). The IR spectra were also consistent with the exchange of the initial ligands by $[NH_4][PhMeNCS_2]$ (Figure S4).

The corresponding exchange reaction was conducted with $[Na][Et_2NCS_2]$ and $\{CdSe[Cd(oleate)_2]_{0.19}\}$ QBs. An immediate spectral shift was again observed, with the lowest-energy feature appearing at 466 nm (Figure 10). The results were again consistent with those obtained with $Cd(S_2CNEt_2)_2$ and $Zn(S_2CNEt_2)_2$ (Figure 5). The IR spectrum confirmed the replacement of $Cd(oleate)_2$ ligands by $[Et_2NCS_2]^-$ ligands (Figure S5). These experiments supported bound-ion-pair X-type ligation of dithiocarbamate ligands in all cases, as described in more detail below.

DISCUSSION

Z-Type vs L-Type vs X-Type Ligation. Z-type ligation on wurtzite CdSe QBs is distinguished by comparing the spectral shifts induced by corresponding cadmium and zinc Lewis acids, such as $Cd(oleate)_2$ and $Zn(oleate)_2$.[8] The metal atoms in these Z-type ligands adopt normal lattice sites on the surfaces of the QBs. The Cd atom in $Cd(oleate)_2$ thus extends the CdSe lattice, increasing the effective thickness of the QB, and decreasing the quantum confinement in the thickness dimension.[8] In contrast, $Zn(oleate)_2$ binding initiates a nascent type-I shell formation[21] and does not extend the CdSe crystal

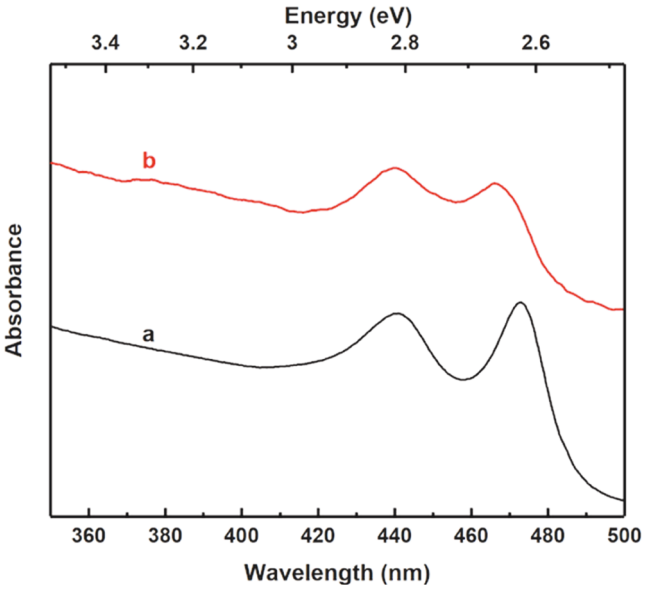

Figure 10. Absorption spectra of CdSe QBs ligated with: (a) $Cd(oleate)_2$ and (b) $[Na][Et_2NCS_2]$ after ligand exchange from $Cd(oleate)_2$ ligation.

lattice. Thus, the binding of $Zn(oleate)_2$ does not relax the quantum confinement.

Consequently, the lowest-energy absorption feature for $\{CdSe[Cd(oleate)_2]_{0.19}\}$ QBs is at 473 nm, whereas that for $\{CdSe[Zn(oleate)_2]_z\}$ QBs is at 454 nm, a difference of 110 meV (Table 2).[8] Similar differences are also observed in comparisons of the Z-type ligands CdX_2 and ZnX_2 (X = Cl, Br, and I).[9] Cd- and Zn-centered Z-type ligands on CdSe QBs induce significantly different spectral shifts.

In the present study, we compare the spectral shifts induced by $Cd(S_2CNPhMe)_2$ vs $Zn(S_2CNPhMe)_2$ ligation and $Cd(S_2CNEt_2)_2$ vs $Zn(S_2CNEt_2)_2$ ligation on CdSe QBs. Surprisingly, there is no discernible difference (Table 2). These results rule out the binding of cadmium and zinc dithiocarbamates as Z-type ligands, through their Lewis-acidic metal atoms. Thus, they must either be bound as L-type or bound-ion-pair X-type ligands.

As noted above, the metal-dithiocarbamate compounds contain Lewis-basic S atoms, which potentially may coordinate with the QB surface Cd atoms in an L-type fashion. However, the spectral shifts of the lowest-energy absorption features in prior examples of L-type ligation range from 447 to 460 nm (Table 2). These shifts to higher energies are due in part to higher compressive strains induced by L-type ligation, as verified by low-angle XRD.[23] These strains are manifested in the thickness dimension of the QBs, producing contractions of the lattice parameter *a* in the wurtzite structure.[8,9] L-type ligation induces contractions in *a* of 3.4%,[8] whereas those induced by bound-ion-pair X-type ligation are generally in the range of 1.2−2.3%.[10] The lattice contractions in *a* measured by XRD here for the dithiocarbamate-ligated QBs are in the range of 1.1−2.1% (Table S1), very consistent with bound-ion-pair X-type ligation.[10] Thus, the spectral shifts and lattice contractions we observed for the metal-dithiocarbamate-ligated QBs fall outside of the ranges for L-type ligation but near to (Table 2) and within the ranges (Table S1) for bound-ion-pair X-type ligation.[8,10]

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Table 2. Lowest-Energy λ_{max} Values for Variously Passivated Wurtzite CdSe QBs or Nanoplatelets

CdSe QBs	λ_{max} (nm)	λ_{max} (eV)	ΔE (meV)
dithiocarbamates			
$Cd(S_2CNPhMe)_2$	467	2.655	107
$Zn(S_2CNPhMe)_2$	467	2.655	107
$Cd(S_2CNEt_2)_2$	466	2.661	101
$Zn(S_2CNEt_2)_2$	466	2.661	101
$[NH_4][PhMeNCS_2]$	467	2.655	107
$[Na][Et_2NCS_2]$	466	2.661	101
L-type ligation			
n-octylamine	449–452[a]	2.762	0
oleylamine	449–450[a]	2.756	6
NH_3	461	2.690	72
n-dodecanethiol	456[b]	2.719	43
NMF	447[c]	2.774	−12
bound-ion-pair X-type ligation			
n-dodecanethiolate	463[b]	2.678	84
halide	459–462[d]	2.702	60
NO_3^-	462[d]	2.684	78
Acetate	461[d]	2.690	72
benzoate	460[d]	2.696	66
Z-type ligation			
$Cd(oleate)_2$	473[e]	2.622	140
$Zn(oleate)_2$	454[e]	2.731	31
$CdCl_2$	474[f]	2.616	146
$ZnCl_2$	455[g]	2.725	37
6-monolayer wurtzite *n*-octylamine-ligated CdSe QBs	517[e]	2.398	364

[a]These data were taken from ref 1. [b]These data were taken from ref 22. [c]This datum is unpublished. [d]These data were taken from ref 10. [e]These data were taken from ref 8. [f]This datum was taken from ref 11. [g]This datum was taken from ref 9.

In cases of bound-ion-pair X-type ligation, the spectral shifts observed are somewhat dependent on the X-type anionic ligand but essentially independent of the ion-paired counter-cation.[10] Thus, the spectral shifts induced by dithiocarbamate salts with other (non Zn^{2+} or Cd^{2+}) cations should be very nearly the same as those induced by cadmium and zinc dithiocarbamates, if the dithiocarbamates are binding as anionic X-type ligands. The results of the exchange reactions with $[NH_4][PhMeNCS_2]$ and $[Na][Et_2NCS_2]$ are therefore very informative. They induce the same spectral shifts as the metal-dithiocarbamate compounds. The results strongly support the binding of the anions $[PhMeNCS_2]^-$ and $[Et_2NCS_2]^-$ as X-type ligands in all cases studied herein.

$M(S_2CNR_1R_2)_2$ Ligation Stoichiometry in CdSe QBs. The ligand-binding stoichiometries for L-type, Z-type, and bound-ion-pair X-type ligation on wurtzite CdSe QBs have been described in several prior publications.[8,10,23] In short, half of the surface Cd and Se atoms on the majority facets of the QBs are nominally three-coordinate and available for ligand binding.[8] The binding of one X-type ligand per three-coordinate surface Cd atom produces the idealized stoichiometry $\{CdSe[M(S_2CNR_1R_2)_2]_{0.26}\}$.[10] A previous study of bound-ion-pair X-type ligation on wurtzite CdSe QBs found the experimental compositions to fall into two groups, one close to $\{CdSe[X]_{0.26}[A]_{0.26}\}$ and another close to $\{CdSe[X]_{0.52}[A]_{0.52}\}$, corresponding to one and two X-type ligands per three-coordinate surface Cd atom.[10] However, there was considerable scatter in the analytical data, and the compositions were found to be quite sensitive to washing steps.[10,23] The compositions close to $\{CdSe[X]_{0.52}[A]_{0.52}\}$ were found to revert to those close to $\{CdSe[X]_{0.26}[A]_{0.26}\}$ upon washing.[10]

In contrast, the ligation stoichiometries of the $\{CdSe[M(S_2CNR_1R_2)_2]_x\}$ investigated here fell uniformly in the range of $x = 0.19–0.26$, whether analyzed by combustion-based elemental analysis or EDS in the TEM (see Table 1). These stoichiometries are near ideal for the binding of one anionic dithiocarbamate ligand ($[R_1R_2NCS_2]^-$) per three-coordinate surface Cd atom. Each of these bound anionic ligands is associated with an ion-paired cation of type $[M(S_2CNR_1R_2)]^+$ to balance surface charge. Several binding geometries are possible for the surface-bound dithiocarbamate ligands. We have no experimental data to distinguish among the possibilities.

Lack of Extraordinary Electronic Effects of Dithiocarbamate Ligands. As noted in the Introduction section, special electronic effects have been ascribed to the phenyldithiocarbamate ligand, a primary dithiocarbamate (due to the N–H; see Figure 1a and compound **1** in Figure 1b). These special effects include significant bathochromic shifts of quantum-dot absorption spectra due to hole delocalization.[2−4] However, we do not observe such bathochromic shifts induced by the binding of analogous secondary dithiocarbamate anions (lacking a N–H) as bound-ion-pair X-type ligation on CdSe QBs. Bound-ion-pair X-type ligation produces spectral shifts that fall within a narrow range (Table 2),[10] and the shifts induced by $[PhMeNCS_2]^-$ and $[Et_2NCS_2]^-$ ligation are near to that expected range. The nearly identical spectral shifts produced by the $[PhMeNCS_2]^-$ and $[Et_2NCS_2]^-$ ligands show that the aromatic ring does not increase the conjugating, delocalizing ability of the secondary dithiocarbamate units. Our failure to observe such delocalization is consistent with the inherent instability of primary dithiocarbamate ligands,[12,24−27] and the likelihood that the unusual electronic properties previously attributed to them (see the Introduction section) actually result from their decomposition to metal-sulfide shells or matrices, as has been recently demonstrated.[24]

CONCLUSIONS

Dithiocarbamate ligands from metal-dithiocarbamate compounds $M(S_2CNR_1R_2)_2$ (M = Cd or Zn), or the salts $[NH_4][(PhMeNCS_2)]$ and $[Na][Et_2NCS_2]$, bind to CdSe QBs as bound-ion-pair X-type ligands. The intact, secondary dithiocarbamate ligands are not found to impart any unusual electronic effects or carrier delocalization to the CdSe QBs. We speculate that Z-type ligation of $M(S_2CNR_1R_2)_2$ may be disfavored by steric effects around the tetrahedrally coordinated metal centers in the putative $M(S_2CNR_1R_2)_2$ ligands, and that L-type ligation of $M(S_2CNR_1R_2)_2$ may be disfavored by steric effects or low Lewis basicities of dithiocarbamate sulfur atoms in the nondissociated $M(S_2CNR_1R_2)_2$ compounds.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c00226.

Additional IR spectra, XRD data, a table of compressive strains, and elemental analysis data and analyses (PDF)

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Notes

The authors declare no competing financial interest.

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