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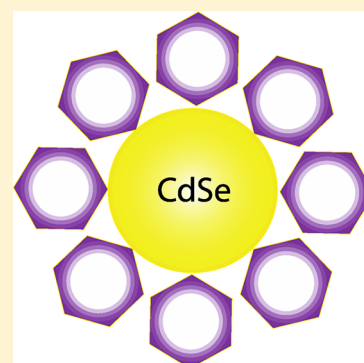
Controlling the Electronic Coupling between CdSe Quantum Dots and Thiol Capping Ligands via pH and Ligand Selection

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S Supporting Information

ABSTRACT: Comparison of the UV–vis absorption spectra of CdSe quantum dots (QDs) capped with various mercaptocarboxylic acid capping ligands reveals that only 4-mercaptobenzoic acid (MBzA) capping ligands lower the apparent optical band gap. We propose that the delocalization of the excitons in the CdSe QDs is extended onto the ligands via electronic coupling to the π system of the 4-mercaptobenzoic acid molecules through the Cd–S bond. Furthermore, we demonstrate that the electronic coupling between the QDs and the (MBzA) thiol ligands is influenced by the strength of the Cd–S bond that can be changed by protonating the S atom.



INTRODUCTION

Many applications of quantum dots (QDs) involve electron transport into, out of, or between the QDs. The delocalization of the quantum confined excitons (bound electron–hole pairs) strongly influences the electron transport to and from QDs and is critical for efficient collection of photoexcited electrons in energy conversion devices.¹ The delocalization of excitons by structural engineering was recently proposed to increase the electrochemical stability of QDs during oxidation/reduction cycles.² One effective way to tailor the exciton delocalization for QDs is through adjusting the electronic coupling between the QDs and the usually organic capping ligands.³

The surfaces of QDs synthesized from the hot-injection method⁴ are typically covered with surfactant molecules. The surfactant molecules play a crucial role in controlling the size and monodispersity of QDs during the synthesis procedure.⁵ Replacing the long-chain surfactants for shorter molecules can influence both the processability and electronic properties of QDs, and ligand exchange is necessary for many QD applications. While the surface ligands can alter the fluorescence properties of the QDs by introducing or passivating surface states,⁶ the question of whether surface capping ligands influence the energy of the first excitonic transition in the UV–vis absorption spectra of QDs is still open.^{2,7} While it is well-documented that inorganic shells in core–shell QDs can delocalize the excitons into the QDs shell when there is a type II band alignment between the core and the shell,⁸ the delocalization of excitons has only rarely been observed for organic ligands capped QDs such as CdSe/ZnS core–shell QDs modified with amphiphilic calixarene derivatives⁹ and CdSe QDs modified with a tetramer of aniline grafted with a carbodithiolate group.¹⁰ The electronic coupling between QDs and the ligands can be inferred from the exciton

delocalization. Here, by using the conjugated molecule, 4-mercaptobenzoic acid (MBzA), as the capping ligand for CdSe QDs, an obvious red-shift of the first exciton peak in the UV–vis absorption spectrum is observed that is not seen with aliphatic thiol capping ligands. This shows the exciton can be delocalized onto the molecular ligands through the anchoring group of thiol for CdSe QDs. We further show that the absorption energy of the first exciton peak for MBzA capped CdSe QDs dispersed in aqueous solution can be tuned by changing the pH of the solution.

EXPERIMENTAL SECTION

Chemicals. CdO (99.998%, Alfa-Aesar), oleic acid (OA, 90%, Alfa-Aesar), 1-octadecene (ODE, 90%, Acros), Se (99.999%, Alfa-Aesar), tri-*n*-octylphosphine (TOP, 90%, Alfa-Aesar), toluene (HPLC 99.9%, Fischer), hexane (>97.9%, EMD) 1-butanol (ACS bulk, 99%, Alfa-Aesar), ethanol (absolute purity, Pharmco-Aaper), methanol (99.9%, Fisher scientific), tetramethylammonium hydroxide pentahydrate (TMAOH.SH₂O, 98%, Alfa-Aesar), pyridine (99.9%, Fischer), and ethyl acetate (99.98%, EMD) were used without further purification. 3-Mercaptopropionic acid (MPA, 99+%, Aldrich), 4-mercaptobenzoic acid (MBzA, 90%, Aldrich), and 11-mercaptopundecanoic acid (MUA, 95%, Aldrich) were used as the ligands to replace the oleic acid molecules on the CdSe QDs. MXA will be used as a generic abbreviation for these ligands in the following text.

Synthesis and Purification of the CdSe QDs. Oleic acid capped QDs were synthesized by following a standard hot-injection procedure with minor modifications. In a typical reaction, 0.256 g of CdO (2.0 mmol) was mixed with 1.6 mL of oleic acid (5.0 mmol) and 8.0 mL of ODE in a three-neck flask. A clear solution was obtained after heating up to 190 °C for 2 h under a N₂ atmosphere. The Se precursor was

Received: March 23, 2012

Revised: June 15, 2012

Published: June 27, 2012

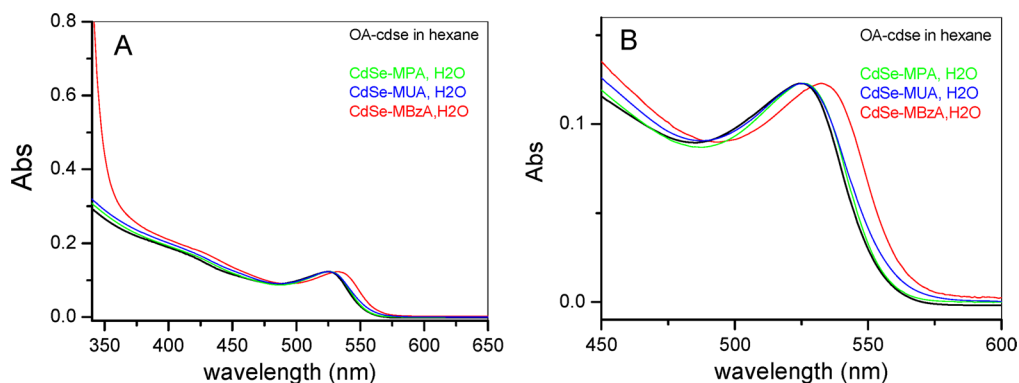


Figure 1. Effects of MXA molecules on the UV–vis absorption spectra of CdSe QDs: comparison between MXA molecules and oleic acid capped QDs. The full spectra are shown in (A), and the absorption in the exciton region is expanded and shown in (B). Compared with oleic acid capped QDs, no shifts or slight blue shifts of <5 meV are observed for both MPA and MUA ligand capped CdSe QDs. In contrast, a 30 meV red-shift is observed for MBzA capped CdSe QDs. The sharp increase at <370 nm for MBzA capped quantum dots is due to the absorption from the MBzA ligands on the surface.

made by heating 0.145 g of Se (1.8 mmol) in a mixture of 1.22 g of TOP (2.7 mmol) and 4.0 mL of ODE at $\sim 100^\circ\text{C}$ for ~ 10 min. After being cooled to room temperature, the Se precursor solution was quickly injected into the Cd precursor solution. After 3 min, the flask was removed from the heating bath, and the reaction was quenched by adding 20 mL of toluene. CdSe QDs with the exciton absorption peak ranging from 530 to 550 nm were obtained.

The QDs were then purified by precipitation/redispersion cycles (to get rid of the excess ligands and narrow the size distribution). Typically, 4.0 mL of the toluene-quenched reactants was taken, and 20 mL of butanol and 20 mL of methanol were added to flocculate the dispersion. After 3 h, 13 mL of the suspension was centrifuged, and the upper solution was decanted. After being washed with methanol the precipitated QDs were then redissolved in 1.5 mL of hexane. 6 mL of butanol and 6 mL of methanol were then added to reprecipitate the QDs. The purification was repeated for another cycle with the hexane/butanol/methanol mixture. The purified QDs were finally dissolved in hexane and stored in the dark.

Ligand Exchange for CdSe QDs. Following a reported procedure,¹¹ oleic acid molecules on QDs were exchanged for thiol-terminated MXA ligands. 1.0 g of TMAOH \cdot 5H₂O (0.092 M) was dissolved in 60 mL of CH₃OH with a suitable amount of MXA molecules added (i.e., 0.070 g for MBzA, 7.6 mM). 0.8 mL of QDs dissolved in hexane (optical density, OD ~ 40) was added under continuous stirring. The mixed solution was refluxed for more than 6 h under a N₂ atmosphere. The final clear methanol solution of QDs was precipitated with excess ethyl acetate (volume ratio 1:10). The dispersion was centrifuged, and the solid precipitate was collected after decanting the upper solution. The red solid was dried and readily dissolved in H₂O. Buffered aqueous solutions of 10 mM citrate (pH = 4.8), phosphate (pH = 6.0 and 7.0), and borate (pH = 9.2, 11.0, and 12.5) were used to dissolve the MXA capped QDs.

To obtain pyridine capped CdSe QDs, the oleic acid capped QDs dispersed hexane was dried up in a 20 mL vial. Pure pyridine was then added, and the QDs were redispersed into pyridine by sitting in a sealed vial (in the air) for 20 min.¹²

UV–vis Characterization. A Perkin-Elmer Lambda 950 was used to measure the UV–vis absorption spectra for the QDs dispersed in various solutions.

RESULTS AND DISCUSSION

Electronic coupling between the CdSe QDs and the capping ligands can extend the excitonic wave function from the inorganic core out onto the ligand molecules. As a result, a red-shift is expected in the UV–vis absorption spectra. Because of the instability of the uncapped CdSe QDs to both aggregation and ripening, the UV–vis absorption spectra of naked QDs

have not been measured in solution. Pyridine capped CdSe QDs should be a good approximation to uncapped CdSe QDs due to a relatively weak interaction between the N lone pair electrons and the Cd surface sites.¹³ However, pyridine capped QDs are labile and thus susceptible to oxidation and Ostwald ripening. In contrast, oleic acid molecules effectively passivate the CdSe QDs and offer some stability. Because of the very large energy gap of insulating molecules, akin to a type I band alignment,¹⁴ the electronic coupling between the oleic acid ligands and CdSe QDs is weak.¹⁵ So the oleic acid capped CdSe QDs are selected as the reference system in this study.

Figure 1 shows that no obvious shifts for the first exciton transition in the UV–vis spectra are observed for MPA and MUA capped CdSe QDs when compared with oleic acid capped QDs. In contrast, an obvious shift from 525 to 532 nm is observed for MBzA capped QDs. The red-shift corresponds to an increase of 0.10 nm in diameter for the QDs, when using the polynomial fitting equation that relates exciton diameter with optical absorption at the excitonic peak:¹⁶

$$D = (1.6122 \times 10^{-9})\lambda^4 - (2.6575 \times 10^{-6})\lambda^3 + (1.6242 \times 10^{-3})\lambda^2 - (0.4277)\lambda + 41.57$$

where D is the apparent diameter of the CdSe QDs and λ is the wavelength in nm of the exciton peak.

The increase of the apparent size for MBzA capped CdSe QDs is not due to the ripening of the QDs during ligand exchange since we do not see an obvious change in the fwhm of the exciton peak after ligand exchange (Figure 1B). Instead, we propose that the size increase is due to the stronger electronic coupling between CdSe QDs and the MBzA ligands than for the nonconjugated aliphatic MUA or MPA molecules. This exciton delocalization is qualitatively different from the exciton delocalization caused by the type II band alignment between the core and the shell for QDs (i.e., CdSe–CdS core–shell QDs),⁸ for which delocalization across the complete shell layer thickness is expected. For the MBzA capped CdSe QDs, the apparent size increase of the exciton (0.10 nm) is significantly less than the molecular length of MBzA (0.65 nm \times 2) and even less than the Cd–S bond length (0.25 nm \times 2).¹⁷

The relatively small increase of the expected apparent size might be due to a partial coverage of the ligand capping layer instead of being close-packed on the QD surfaces. Quantitative studies of the surface chemistry and surface structure of QDs

are providing a more detailed understanding of their interfacial chemistry.^{18,19} Determining the number of surface bound ligands on the QDs and estimating their binding strength are the first steps. Therefore, a series of experiments to quantify the surface coverage of MBzA molecules on the QD surfaces are presented below.

The coverage of MBzA molecules on CdSe QDs was estimated by measuring the ratio of the number of surface Cd atoms to the number of MBzA molecules. To quantify the number of Cd atoms on the QDs surfaces, the UV-vis spectrum of MBzA capped CdSe QDs in aqueous solution was first collected and is shown as spectrum 1 in Figure 2. The

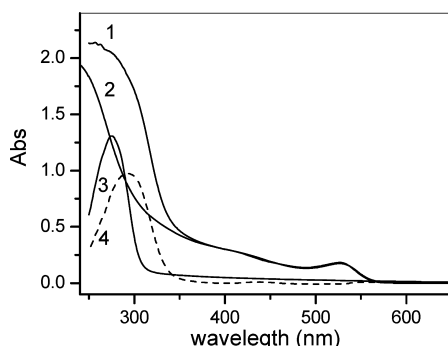


Figure 2. Quantifying the coverage of MBzA molecules on CdSe QDs using UV-vis absorption spectroscopy. The absorption spectrum of MBzA capped CdSe QDs in H₂O is shown as spectrum 1. The normalized absorption spectrum of OA capped CdSe QDs in hexane is shown as spectrum 2. The normalization is carried out by linear scaling the absorption intensity for the first exciton peak in spectrum 2 to be the same as that for spectrum 1. The phenomenological absorption spectrum of the adsorbed MBzA molecules on QDs is obtained by direct subtraction of spectrum 2 from spectrum 1, and it is shown as spectrum 4 (dashed line). The absorption spectrum of the free MBzA molecules desorbed from the QDs is shown as spectrum 3, for which the CdSe QDs were digested with 6 M HCl.

concentration and the size of the CdSe QDs were calculated from the absorbance and the absorption energy of the first exciton peak, respectively.¹⁶ The number of surface Cd atoms was then estimated from a spherical model for the QDs.²⁰ To quantify the number of the MBzA molecules adsorbed on the CdSe QDs, the concentration of MBzA was measured by the absorbance at its absorption maximum at 275 nm (spectrum 3,

Figure 2) that was calibrated with standards of known concentrations of MBzA. To avoid any interferences from the UV-vis absorption of CdSe QDs at 275 nm, the MBzA capped CdSe QDs were digested by reaction with excess 6 M HCl. The ratio between MBzA molecules and surface Cd atoms of the QDs was then calculated. It is worth noting that the assumption of the spherical model for QDs²¹ is an approximation since the actual faceted QD geometry is not known. Also, since we neglect the dynamic equilibrium between the surface-bound ligands and free ligands in solution,²² our calculation represents an upper limit of the surface coverage. The above calculation provides an estimate of the $45 \pm 5\%$ coverage of MBzA molecules on CdSe QDs which agrees with a previous reported value of 52%.²² Using pyridine as an intermediate capping ligand¹³ to replace the initially bound oleic acid ligands does not increase the determined coverage of MBzA molecules on CdSe QDs. As the estimated coverage of MBzA on CdSe QDs is less than 100%, it suggests additional Cd surface sites might be blocked by MBzA molecules or some oleic acid (oleate) ligands might still remain on the surface even after the ligand exchange procedures.

Because of the coupling between the MBzA ligands and the CdSe QDs, the UV-vis absorption of MBzA molecules on the surfaces of CdSe QDs will differ from the free MBzA molecules in the solution. To show this effect, a phenomenological absorption spectrum of MBzA molecules on QDs is obtained by subtraction of spectrum 1 with spectrum 2 and is shown as spectrum 4 in Figure 2. Comparison between spectrum 4 and spectrum 3, which is the absorption spectrum for free MBzA molecules in aqueous solution, shows that the absorption maximum of MBzA shifts from ~ 275 to ~ 300 nm upon binding to the CdSe QDs. This significant ~ 0.4 eV red-shift provides additional evidence for the relatively strong electronic coupling between the MBzA ligands and the CdSe QDs.²³

Figure 3A shows the effect of pH on the absorption spectra of CdSe QDs capped with different MXA molecules. A red-shift of 48 meV in energy (from 529 to 540 nm in wavelength) is observed for MBzA capped CdSe QDs when the pH changes from 6.0 to 12.5, corresponding to a shift of -7.5 meV per pH unit (Figure 3B). As the pH increases from 6.0 to 12.5, the apparent diameter for the MBzA capped CdSe QDs increases from 2.68 to 2.85 nm, suggesting that the electronic coupling, and consequently the exciton delocalization, between the MBzA ligands and the CdSe QDs becomes larger. The first exciton peak wavelengths were also measured at different pHs

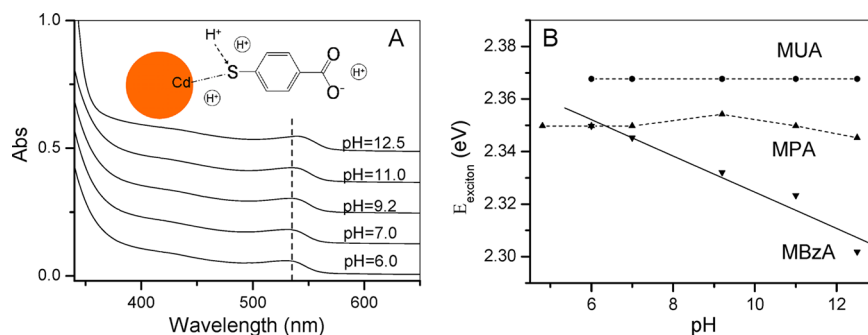


Figure 3. (A) UV-vis spectra of MBzA capped CdSe QDs in aqueous solution at different pH values. The spectra are offset for clarity, and a dashed line is used to show the shift of the exciton peak. Inset: scheme for the protonation of S atoms at the interface, which weakens the bonding between Cd and S. (B) Exciton peak energies for CdSe QDs capped with MBzA, MPA, and MUA as a function of pH changes from 6.0 to 12.5. Different batches of QDs were used for the three series of experiments. As a result, the positions of the exciton peaks are slightly different for MUA, MPA, and MBzA capped QDs.

for MPA and MUA capped QDs for comparison (Figure S1). Figure 3B shows no obvious wavelength changes for MPA or MUA were measured. Even though the apparent sizes for the CdSe QDs vary slightly with the different capping ligands, a reproducible trend shows that the MUA and MPA ligands do not shift the UV-vis spectra, while the MBzA ligand always shifts the UV-vis spectra in the red direction. Since the pK_a of the carboxylic acid group of MPA²⁴ and MUA²⁵ is close to that of MBzA²² (5.2 and 5.7 compared with 4.8), the ionization state of the COOH group of the ligands on the QDs are similar for MPA, MUA, and MBzA. On the other hand, it is known that the pK_a of SH group for MPA²⁶ and MUA is significantly larger than for MBzA²⁷ (10.2 compared with 5.8). The low pK_a for SH group in MBzA indicates that the SH group between CdSe and MBzA is ionized (thiolated) in the tested pH range (from 6.0 to 12.5). However, such an increase in coupling strength due to pH increase does not have obvious effects on the UV-vis absorption in the region for the MBzA ligands (Figure S2).

Significant differences in the binding constants of the alkanethiol molecules to CdSe QDs, ranging from 10^3 to 10^9 M^{-1} , have been reported.¹⁸ The oxidation of adjacent thiols to form disulfides, which have a 10–100 times weaker binding strength to Cd atoms,^{28,29} can account for some of the reported variations; however, the state of protonation of the thiol appears to be the major reason for such variations. There is ample precedent in the literature showing that the strength of thiol ligand binding to transition metal centers is reduced by protonation of the bound thiol.^{30,31} It has also been reported that the binding energy for thiolate to Cd is ~ 40 times higher than the binding energy for the thiol group to Cd (1283 kJ/mol compared to 34.7 kJ/mol³²), and the protonation of S atoms significantly decreases the Cd–S bond strength.^{33,34} The MXA molecules might also dissociate from the QDs due to the reduction of the binding strength when the thiolate is protonated at low pH.¹¹ We also found that MUA capped QDs, buffered at pH = 4.8 with 10 mM aqueous citrate buffer, will crash out of solution within 30 min even when sitting in the dark. At high pH in aqueous solutions, the binding moiety of Cd–S (H) tends to be a thiolate rather than a thiol for MBzA capped CdSe QDs. As a result, the electronic coupling between the MBzA ligands and the QDs tends to be stronger at higher pH. The stronger coupling will result in more exciton delocalization and a red-shift of the excitonic absorption peak.³⁵ However, it is not clear whether conformational change of the bound MBzA molecule on QDs is involved or not.³⁶

The solution pH affects the ionization of both the COOH and SH groups of the MBzA ligands. It was reported that ionization of the carboxyl group of MPA ligands red-shifts the luminescence peak of CdSe QDs from 2.42 to 2.39 eV when the pH is raised from pH 7.4 to pH 14.³⁷ Though the ionization of COOH might contribute to the red-shift of the first exciton peak in the UV-vis absorption maximum at high pH (Figure 3A), the lack of pH dependence for MPA and MUA shown in Figure 3B excludes this possibility.

The protonation or hydroxylation of Se or Cd atoms at the QD surface shifts the conduction band and valence band positions.³⁸ Effects associated with the protonation of surface atoms with MPA, MUA, and MBzA capped CdSe QDs could also account for the trends shown in Figure 3B. MUA would tend to form a more compact capping layer than MBzA or MPA due to the dispersion forces between the longer aliphatic chains that might prevent protons from approaching the QD

surface. Two facts enable us to exclude this possibility. The first is that MPA, which is the shortest of the three ligands, shows a similar behavior to MUA. Second, it is known that the aliphatic thiols do not effectively protect the QDs from oxidation by O_2 that apparently can still approach the surface of the capped CdSe QDs.³⁹ As the proton is much smaller and more mobile than the O_2 molecule, protons should be able to protonate the Se atoms when the aqueous solutions of capped QDs are equilibrated for >20 min. Therefore, it is unlikely that protonation of the surface Se atoms contributes to the exciton absorption shift for the MBzA capped QDs.

One reviewer referred us a recent paper⁴⁰ that points out the possibility that a significant increase (from 50 μM to 10 mM) for the free ligands of MPA present in the CdSe QDs solution in acetonitrile might introduce small shifts in the band-edge absorption spectra. We believe this is not the case during our experiments. While the total concentration of the MXA ligands are as small as 50 μM , free MXA ligands in the aqueous solution will be less as they only come off the QDs due to the dynamic equilibrium. Furthermore, exactly the same solution of QDs for each MXA ligand are split into solutions buffered at different pH to show the pH effect shown in Figure 3. So the variation of the ligand concentration, if exist, is minimize during our experiments.

With the purpose to show the exciton delocalization for QDs due to the presence of surface ligands, the research here focused on the static shift of the first exciton peak in the UV-vis spectra without deliberately considering the kinetics of ligands adsorption. Different buffer systems were chosen to tune the pH from 4.6 to 12.5 for the purpose to offer the buffering stability (citrate for pH 4.8, phosphate for pH 6.0 and 7.0, borate for pH 9.2, 11.0, and 12.5). Since the UV-vis absorption spectra were typically collected >5 min later after splitting a master solution of the QDs solution (in H_2O) into different pH buffers, the adsorption/desorption equilibrium is assumed for the ligands on QDs. However, as anonymously pointed out by a reviewer, it might be interesting for future research to investigate the reversibility of the shift in exciton peak by continuous changing the pH through titration of the QDs solutions with either NaOH or HCl.

Various bifunctional thiols that contain another functional group are often bound to CdSe QDs via the thiol group for applications of QDs to such as specific binding or sensing.⁴¹ However, the fact that the capping ligand bonds themselves can respond to the environment has been largely neglected. In contrast, the Au–S bond, associated with SAMs on Au surfaces is insensitive to the environment and the S–H bond is dissociated upon adsorption of thiols to Au surfaces.^{42,43} Our results show that the strength of the Cd–S–R bond on CdSe QDs is sensitive to the environmental pH, and one should be cognizant of this when investigating processes such as pH-dependent fluorescence quantum yields,⁴⁴ fluorescence lifetimes,⁴⁵ and electron injection rates into semiconductor substrates.⁴⁶ Alkyl dithiols have been used to couple quantum dots in multilayer QD solar cells, and our results suggest that aromatic dithiols may also be effective QD coupling ligands.

A large range of electronic structures and adsorption chemistries might be provided by different organic capping ligands that could influence the photo physics of QDs.⁴⁷ While the ligand of phenyldithiocarbamate was already shown to have the correct orbital energies and symmetry to cause exciton delocalization,^{2,47} the demonstration of the exciton delocalization and the ability of tuning it with a different ligand of MBzA

clearly provides more ligand choices for investigations. The comparison between the two molecules also implies that the conjugation close to the anchoring group inside the ligands might be an important factor to delocalize the excitons.

It worth to note that fluorescence emission and time-resolved exciton relaxation are sensitive to the presence of ligands on QDs, and extra insights into exciton delocalization might be provided by these luminescence-based characterization techniques.^{40,47} However, since the deep trap states from QDs will severely decrease the absolute intensity and even completely quench the exciton luminescence, the fluorescence spectra of MBzA capped CdSe QDs were not systematically studied here. We also want to point out an effort on fluorescence spectra of mercaptocarboxylic acids capped CdSe QDs for which a shift in the opposite direction due to pH change is observed if exciton delocalization is not taken into account.³⁷ Photoluminescence data of MBzA capped CdSe QDs together with time-resolved relaxation data are needed to clarify the roles of the MBzA ligands in future studies.

CONCLUSION

Significant electronic coupling is found between CdSe QDs and MBzA surface capping molecules through the Cd–S bond that is not present in alkyl thiol capping ligands. Adjusting the pH, and thus the extent of protonation of sulfur atoms in the Cd–S(H) bond, changes the coupling between the MBzA ligands and the CdSe QDs. The ability to extend the electronic coupling into capping ligands will allow study and optimization of carrier transport in, out, and through QDs in various device configurations.

ASSOCIATED CONTENT

Supporting Information

UV–vis absorption spectra of the QDs capped with MUA and MPA molecules, the full UV–vis spectra of the QDs capped with MBzA molecules, and detailed explanations on the spectra shown in Figure 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was funded by NASA EPSCoR (Award NNX10AR90A). The authors thank Dr. John Rowley and Professor Mark Mehn for helpful comments and discussions.

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