Fluorescence and Optical Activity of Chiral CdTe Quantum Dots in Their Interaction with Amino Acids

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ABSTRACT: Ligand-induced chirality in semiconducting nanocrystals has been the subject of extensive study in the past few years and shows potential applications in optics and biology. Yet, the origin of the chiroptical effect in semiconductor nanoparticles is still not fully understood. Here, we examine the effect of the interaction with amino acids on both the fluorescence and the optical activity of chiral semiconductor quantum dots (QDs). A significant fluorescence enhancement is observed for L/D-Cys-CdTe QDs upon interaction with all the tested amino acids, indicating suppression of nonradiative pathways as well as the passivation of surface trap sites brought via the interaction of the amino group with the CdTe QDs’ surface. Heterochiral amino acids are shown to weaken the circular dichroism (CD) signal, which may be attributed to a different binding configuration of cysteine molecules on the QDs’ surface. Furthermore, a red shift of both CD and fluorescence signals in L/D-Cys-CdTe QDs is only observed upon adding cysteine, while other tested amino acids do not exhibit such an effect. We speculate that the thiol group induces orbital hybridization of the highest occupied molecular orbital (HOMOs) of cysteine and the valence band of CdTe QDs, leading to the decrease of the energy band gap and a concomitant red shift of CD and fluorescence spectra. This is further verified by density functional theory calculations. Both the experimental and theoretical findings indicate that the addition of ligands that do not "directly" interact with the valence band (VB) of the QD (noncysteine moieties) changes the QD photophysical properties, as it probably modifies the way cysteine is bound to the surface. Hence, we conclude that it is not only the chemistry of the amino acid ligand that affects both CD and PL but also the exact geometry of binding that modifies these properties. Understanding the relationship between the QD’s surface and chiral amino acid thus provides an additional perspective on the fundamental origin of induced chiroptical effects in semiconductor nanoparticles, potentially enabling us to optimize the design of chiral semiconductor QDs for chiroptic applications.

KEYWORDS: chiral, quantum dots, circular dichroism, fluorescence, thiol group, orbital hybridization

Chiral colloidal quantum dots (QDs) have attracted much attention over the past years. These nanocrystals combine the tunability of artificially prepared quantum materials with unique chiral optical properties. As such, they are a new type of nanomaterials in biological sensing, chiral catalysis, quantum optics, and medicine.1−3 However, only very few types of semiconductor QDs such as cinnabar HgS exhibit intrinsic chirality due to their chiral crystal structure, whereas the vast majority of known QDs are achiral.4 Thanks to the combination of stereospecific chiral ligands and the large surface to volume ratio of QDs, significant electronic/optical chirality was demonstrated in such nanocrystals either synthesized using chiral ligands or upon ligand exchange with chiral molecules. These efforts develop the study in the area of chiral QD research.5−10 Yet, at this point, multiple open questions still exist, especially relating to the microscopic mechanism underlying chirality in these ligand-induced chiral QDs.

Until now, two main theories have been put forward to explain the chiral interaction between QDs and chiral ligands.

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First, the QDs' chirality was speculated to be induced by a structural chiral deformation of the outer shell layer, which could be caused by chiral distortion of the surface atoms or by a chiral arrangement of the ligand shell. For example, Gun'ko and co-workers reported the chiral induction effect of L- and D-penicillamine on the originally achiral CdS QDs, and through density functional calculation they showed that the spatial arrangement of surface Cd atoms was significantly distorted by chiral penicillamine ligands, leading to a chiral structure in the surface layers.\(^1\) A second alternative relates the chiral properties to the electronic interaction between the chiral binding molecules and the semiconductor QDs (rather than physical distortion), which can in turn lead to CD or circularly polarized luminescence (CPL). In plasmonic metal nanosystems this interaction likely originates from a dipolar interaction, as reported by Govorov et al.\(^2\) Yet, for QDs, the dipolar interaction is expected to be much weaker due to the difference in dielectric constant, and it is thus believed that the interaction originates from the hybridization of the molecular orbital between the ligand and QDs.\(^3\) Kotov and co-workers reported the chiral interaction between the L/D-cysteine and graphene quantum dots (GQDs), whereby the molecular orbital of chiral edge-ligands likely introduces a symmetry-breaking perturbation to the electronic states of GQDs.\(^4\) Markovich and co-workers reported that all the features of CD response can be accounted for as a sum of the chiral responses of individual excitonic states.\(^5\) Balaz et al. studying postsynthesis ligand-exchanged colloidal CdSe QDs, concluded that the induced chiroptical activity originated from the hybridization of the HOMO level of the ligand molecular orbital and valence band (VB) level of CdSe QDs.\(^6\) However, despite these advances, the understanding of the origin of the induced chiroptical effect in QDs is still lacking. This is partly since almost all past reports focus on the interaction between originally achiral QDs and their chiral ligands, whereas only a few reports until now study the interaction between the surface of already chiral semiconductor QDs and other chiral moieties (such as amino acids). These latter experiments offer an attractive alternative platform for further promoting the understanding of the fundamental mechanism underlying chiral induction in semiconductor QDs.

Amino acids, such as cysteine and its derivatives, are the most commonly used chiral capping molecules.\(^7\) Although almost all of them bind with the QD surface via an anionic thiolate functional group, they actually often induce different chiroptical responses, which reveals the significance of the detailed interaction between the QDs and the amino acids.\(^8\) At the same time, coating an emitting QD core with short chiral amino acid ligands can result in lower fluorescence intensity, which is mainly due to the enhanced surface-defect states and photogenerated hole trapping in thiol ligands.\(^9\) The latter is believed to be intimately linked with the ligand-induced CD, as the wave function hybridization coupling occurs more readily between the HOMO of the thiol ligand and the highest valence band hole state.\(^10\) Therefore, we believe that fluorescence and chirality are inseparable, and both are closely related properties of chiral QDs. Li and co-workers, for example, have synthesized soluble \(\beta\)-cyclodextrin and \(\alpha\)-cyclodextrin-capped core/shell CdSe/ZnS QDs and shown that within a certain range of parameters fluorescence could be enhanced by one enantiomer of an amino acid.\(^11\) Simonet and co-workers studied the interaction between chiral L-Cys-capped CdSe/ZnS QDs and L/D-carnitine.\(^12\) Their results revealed that the fluorescence intensity of L-Cys-capped CdSe/ZnS QDs decayed following the addition of D-carnitine but remained unaffected by the addition of L-carnitine. In contrast, fluorescence of D-Cys-capped QDs was only suppressed by the presence of L-carnitine. This suppression was attributed to a breaking of a chemical bond between the QDs’ surface and the carbonyl group of cysteine. The research verified the “preferential interaction” model, which demonstrates that the heterochiral interactions between amino acids are generally stronger than homochiral ones. However, both of these studies mostly focused on the variation of fluorescence intensity, while

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**Figure 1.** (a) X-ray Diffraction pattern, (b) Fourier transform infrared spectra, (c, d, e) X-ray photoelectron spectra, (f) UV−vis absorption spectrum and fluorescence emission spectrum (excited at 358 nm) of L-Cys-CdTe QDs.
the chiroptical properties such as CD spectrum or intensity change were seldom involved. Hence, the influence of the interaction with amino acids on the fluorescence and optical activity of chiral QDs is still unclear and calls for further study.

Here, we present a comprehensive investigation aimed at understanding the interaction between the surface of chiral semiconductor QDs and amino acid molecules by characterizing the induced changes to chiral optical absorption and to fluorescence. We show that a significant fluorescence enhancement is observed for \(L/D\)-Cys-CdTe QDs after interacting with all the tested amino acids, and reduced CD signals are shown only when heterochiral amino acids are added. It is further demonstrated that a red shift of CD and fluorescence signals in \(L/D\)-Cys-CdTe QDs can only be observed upon adding cysteine, while other tested amino acids do not have such an effect. In addition, we use density functional theory (DFT) models to highlight the importance of thiol groups on the orbital hybridization between QDs and chiral ligands. All in all, we believe these investigations of the interaction between QDs’ surface and chiral amino acids will further advance the fundamental understanding of induced chirality in semiconductor nanoparticles as well as the design of advanced optically active nanostructures.

RESULTS AND DISCUSSION

First, CdTe QDs capped with \(L\)- or \(D\)-cysteine were synthesized in an aqueous solution following a literature method with some modifications.\(^{11}\) The X-ray diffraction pattern of \(L\)-Cys-CdTe QDs can be seen in Figure 1(a). The three peaks at 23.8\(^{\circ}\), 39.6\(^{\circ}\), and 46.8\(^{\circ}\) are assigned to the (111), (220), and (311) planes of crystalline CdTe. Transmission electron microscopy (TEM) images are displayed in Figure S1, with an average diameter of about 3.2 nm, and the interplanar distance between adjacent lattice planes is determined as \(d = 0.37\ \text{nm}\), matching the \(d\) (111) value of CdTe. The Fourier transform infrared (FT-IR) spectra of the free \(L\)-Cys and \(L\)-Cys-CdTe QDs are illustrated in Figure 1(b). The signal peaked at 2500 cm\(^{-1}\) (S–H) disappears upon binding of the free \(L\)-cysteine molecules on the surface of CdTe QDs, indicating strong bonding between the thiol group of cysteine molecules and surface cadmium atoms. The broad absorption band at 3430 cm\(^{-1}\) of \(L\)-Cys-CdTe QDs is likely due to the formation of a partial hydrogen bond between the amino groups and carboxylate groups of surface-bound cysteine molecules.\(^{21}\) The symmetric and asymmetric stretching modes of the carboxylate (COO–) group at 1400 and 1580 cm\(^{-1}\) can also be observed in \(L\)-Cys-CdTe QDs. Because the \(L\)-Cys-CdTe QDs were prepared in high pH medium (pH = 11), carboxyl groups undergo deprotonation, providing the electrostatic repulsion to keep the CdTe QDs well dispersed in solution.\(^{21}\)

The surface composition and elemental analysis results for \(L\)-Cys-CdTe QDs are characterized via XPS. Figure 1(c) shows the original XPS spectrum with all the elements. The double peaks at 411 and 405 eV as well as 582.5 and 572 eV can be attributed to Cd\(_{3d5}\) and Te\(_{3d5}\).\(^{22}\) In the Te 3d spectral region, two symmetric peaks can be clearly seen, corresponding to the 3d\(_{3/2}\) and 3d\(_{5/2}\) splitting caused by the spin–orbit interaction (Figure 1(d)).\(^{23}\) The S 2p spectral signal (Figure 1(e)) exhibited two symmetric peaks at 161.5 eV (S 2p\(_{3/2}\)/2) and 162.7 eV (S 2p\(_{1/2}\)/2), which again, can be attributed to spin–orbit-induced splitting, confirming that Cd–S bonds are formed on the QDs’ surface.\(^{24}\) The XPS results thus provide additional evidence for the binding properties of thiol group in \(L\)-cysteine to the CdTe QDs’ surface.\(^{25}\) UV–vis absorption and fluorescence spectra of \(L\)-Cys-CdTe QDs are illustrated in Figure 1(f). Upon illumination at 358 nm, we observe an emission band centered at 562 nm, having a FWHM of 50 nm, which confirms a reasonably narrow size distribution. The clear excitonic absorption band at 548 nm observed in the absorption spectrum of \(L\)-Cys-CdTe QDs corresponds to a band gap energy of 2.26 eV. This spectral position of this peak is evidently blue-shifted relative to the CdTe bulk band gap (1.5 eV; 827 nm), indicating a substantial contribution of quantum confinement. The diameter of the synthesized QD particle can be calculated from the absorption maximum.\(^{26}\)

\[
d = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + 1.0064\lambda - 194.84 \text{ (nm)}
\]

where \(\lambda\) is the wavelength of the excitonic absorption peak. The diameter of \(L\)-Cys-CdTe QDs calculated from eq 1 is 3.2 nm, consistent with the particle size observed in the corresponding HRTEM image (Figure S1(b)).

To study the chiral origin of \(L\)-Cys-CdTe, we performed CD measurements. Figure 2(a) shows the CD spectra of both \(L\)-Cys- and \(D\)-Cys- CdTe QDs, exhibiting (as expected) mirror-image CD spectra. The CD spectra of free \(L\)-cysteine and \(L\)-Cys-CdTe QDs are compared in Figure 2(b). As can be seen, the CD signal at about 210 nm is assigned to the free \(L\)-cysteine. After combining with CdTe QDs, this CD signal is no longer seen, and a new peak at about 215 nm is found. In addition, new CD peaks are detected at 248, 300, and 320 nm (Figure 2(a)), indicating that the free cysteine was consumed to form a new Cd–Cys complex in the reaction process.\(^{22}\) To further prove the origin of chirality is indeed binding to cysteine, TGA (an achiral organic-ligand)-capped CdTe QDs were prepared, and the corresponding CD spectra are shown in Figure 2(c). As expected, no CD signal was observed for TGA-

![Figure 2. CD spectra of (a) \(L\)-Cys/\(D\)-Cys-CdTe QDs, (b) free cysteine and \(L\)-Cys-CdTe QDs, and (c) TGA-capped CdTe QDs.](https://dx.doi.org/10.1021/acsnano.9b09101)
capped CdTe QDs. One must note here that we focus on the UV spectral range since CdTe exhibits a much weaker CD response close to the band edge, especially as compared with CdS and CdSe QDs. This difference, already noted by Kotov et al., is beyond the scope of this work and may arise from the different physicochemical properties of CdTe, such as the detailed surface chemistry, the exciton Bohr radius, crystal structure, and so on. Since all these evidently affect the alignment of the QD valence band relative to the molecular HOMO level, this can have a significant effect on the magnitude of induced dichroism at the band edge. This can explain why CdS and CdSe exhibit substantially stronger excitonic CD signals near the band edge, relative to the weaker effect in CdTe. Notably, however, CD signatures well above the noise level are still observed well into the visible range where cysteine does not absorb.

To explore the influence of chiral amino acids on induced CD, we characterized the CD spectra of L-Cys-CdTe QDs upon addition of different concentrations of L- and D-cysteine. The concentration of QDs in all the measurement was kept at 1 mM. As illustrated in Figure 3(a–d), the intensity of CD signals of L-Cys-CdTe QDs at 248 nm decreases almost 10 times with the addition of D-cysteine. Additionally, the CD signals of L-Cys-CdTe QDs red-shifted from 248 to 260 nm as the concentration of D-cysteine increased to 1.8 mM. When more D-cysteine is added (4.1 mM), the peak position remains almost unchanged. As can be seen in Figure 3(e), the UV–vis absorption intensity of the peak at about 248 nm increases with D-cysteine addition. The CD and absorption spectra of interaction between L-Cys-CdTe QDs and L-cysteine are shown in Figure 3(f–j). Upon adding L-cysteine, the CD signal red-shifted from 248 to 252 nm in L-Cys-CdTe QDs (Figure 3(f–i)). Notably, the shift is smaller than that observed upon addition of D-cysteine. As is shown in Figure 3(j), the UV–vis absorption spectrum at about 248 nm does not change significantly with the addition of L-cysteine.

Subsequently, a study of the chiral interaction between L-Cys-CdTe QDs with other amino acids was carried out. As illustrated in Figure 4(a), the CD spectra of L-Cys-CdTe QDs are almost unchanged with the addition of L-leucine. When we added D-glutamic acid, the CD signals from L-Cys-CdTe QDs gradually decreased for both 215 and 248 nm, while no shift in CD signals can be observed (Figure 4(c)). Both L-leucine and D-glutamic acid do not seem to alter the UV–vis absorption spectra of L-Cys-CdTe QDs (Figure 4(b) and (d)). In order to further examine the interaction more comprehensively, experiments of interactions between D-Cys-CdTe QDs and other tested amino acids were also performed (Figures S2–S3). The chiral QDs demonstrate similar properties in absorption and CD spectra. The results of experiments on the chiral interactions between L-Cys-CdTe QDs and other amino acids are summarized as follows.

(a) The red shift of CD signals at about 248 nm in L-Cys-CdTe QDs can be observed only with the addition of cysteine. The mechanism underlying the red shift is discussed below. It is notable that the shift is smaller upon addition of L-cysteine than upon addition of D-cysteine, which indicates that the packing density is higher for heterochiral pairs. This is in agreement with the observation that homochiral interaction between amino acids (L-Cys-CdTe QDs with addition of L-cysteine, Figures 3, S2, and S3) is weaker than heterochiral interactions (L-Cys-CdTe QDs with addition of D-cysteine,

(b) D-cysteine, D-glutamic acid, and other D-amino acids may weaken the chiral signal of L-Cys-CdTe QDs, while L-cysteine, L-leucine, and other L-amino acids do not have such an effect. This is also the case for the interaction between D-Cys-CdTe QDs and other amino acids (shown in Figures S10–S12). A possible explanation for this phenomenon is an induced change in the binding configuration of cysteine molecules on the QD surface caused by heterochiral amino acids. Indeed, a very recent study has demonstrated that cysteine can be bound to the QD surface in two configurations, via the S– and NH2 group (bidentate mode), or via all three functional groups S–, NH2, COO– (tridentate mode), which have opposite CD signals. Upon addition of heterochiral amino acids, which have stronger interaction with chiral ligands, the binding configurations of the chiral cysteine ligands may be modified from the tridentate mode to bidentate mode, which will result in a shift of the CD signal.
in a reduced CD signal due to the opposite contributions to the CD response of those two binding configurations.

To further explore the interaction between L-Cys-CdTe QDs and chiral amino acids, we perform fluorescence measurements. As shown in Figure 5(a), all the samples show an emission band centered at 562 nm under 358 nm excitation, which is attributed to the band gap emission of CdTe QDs. Upon adding D-cysteine, the fluorescence spectra illustrate a gradual red shift from 562 nm to 574 nm (Figure 5(b)). The fluorescence intensity varies among the samples (Figure 5(c)). The fluorescence intensity initially increases, reaching a maximum when the dosage of D-cysteine is 1.8 mM, and then drastically decreases upon further addition of D-cysteine to the L-Cys-CdTe QDs.

Figure 5 shows the fluorescence spectra of L-Cys-CdTe QDs upon adding L-cysteine. The fluorescence intensity fluctuates slightly: increases with 0.5 mM L-Cys, then it decreases with higher concentration of L-cysteine (Figure 5(d)). The addition of L-cysteine leads to 7 nm red shift of emission peak from 562 to 569 nm (shown in Figure 5(e)), which is smaller compared with that of D-cysteine.

As can be seen in Figure 5, the emission of L-Cys-CdTe QDs exhibits a red shift upon addition of cysteine. Notably, the shift upon addition of L-cysteine is smaller than that upon addition of D-cysteine. These results are in agreement with the “preferential interaction” model, indicating that the homochiral interaction between amino acids is usually weaker than heterochiral interactions. This means the favorable chemical interactions can take place among the heterochiral materials. The mechanism of red shift for fluorescence spectra is discussed below, and we believe that it is the “preferential interaction” mechanism that determines the smaller shift of L-Cys-CdTe QDs’ emission behavior with addition of L-cysteine.

The fluorescence spectra of L-Cys-CdTe QDs with the addition of L-leucine and D-glutamic acid are illustrated in Figure 6(a) and (b). With the addition of L-leucine and D-glutamic acid dosage, the fluorescence intensity of L-Cys-CdTe QDs increases, reaching a maximal value at a concentration of 0.5 mM for both L-leucine and D-glutamic acid. Upon further addition, the fluorescence intensity shows a decrease at higher concentrations of L-leucine and D-glutamic acid from 0.5 mM to 1 mM. The fluorescence spectra of D-Cys-CdTe QDs in the presence of other amino acids exhibit a similar trend (Figures S18–S23).

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Notably, the fluorescence increase upon the addition of a low concentration of amino acids is observed for all samples (Figures 5 and 6). Several researchers have studied the fluorescence properties of QDs interacting with amino acids. McLendon and co-workers found that the fluorescence of CdS QDs was enhanced after addition of a very low concentration (1 mM) of triethylamine. They assigned this increase to the attachment of amino groups on the surface defect sites, leading to improved passivation. Similarly, Chatterjee and co-workers observed an enhanced fluorescence intensity of cysteine-capped CdS QDs upon addition of adenine. The fluorescence enhancement is likely due to a similar passivation of the surface of CdS QDs by amine-bound adenine molecules.

In fact, the impact of amino acids on the photophysical properties of QDs is quite complicated and often indeterminate. Due to the large surface to volume ratio, the properties of QDs is quite complicated and often indeterminate. Several mechanisms have been previously proposed including dipole–dipole interactions, size-dependent effects, and delocalization of the excitons.

Dipolar Coulomb interaction is commonly regarded as one of the most important mechanisms that generate a CD signal in metallic nanoparticles. When replacing plasmons with excitons, this theory can be extended to semiconductor nanoparticles. In our experiments, however, the coupling between excitons and molecular transition via dipole–dipole interactions should be very weak due to the comparatively large dielectric constant of a CdTe QD nanoparticle.

Another possible explanation is the generation of QD aggregation, as CD and fluorescence properties of QDs are highly dependent on their extent of aggregation. Yet, in our experiments, we believe that the red shift of CD and fluorescence spectra is not caused by aggregation for the following reasons: (1) The QD solutions after addition of cysteine are optically clear, and the precipitation of QDs cannot be observed. (2) As is shown in Figure 5, the FWHM of the fluorescence peak decreases after adding d-cysteine to the l-Cys-CdTe QDs from 1.8 mM to 5 mM. The decreased FWHM of the fluorescence spectra as well as the fluorescence intensity indicates that addition of d-cysteine to the l-cysteine-capped CdTe QDs induces neither the aggregation of QDs nor the Ostwald ripening process. In addition, aggregation may also lead to a “double size effect” of luminescence because of the predominance of nonradiative recombination of excitons, which is not observed in our experiments. (3) DLS experiments were performed, and the results, shown in Figure S25, indicate that the diameter distribution of l-Cys-CdTe QDs with addition of d-cysteine was between 2.9 to 3.4 nm. No obvious diameter increase was observed, which means the addition of d-cysteine may not lead to aggregation. Based on the analysis above, aggregation can be excluded as the cause of the red shift.

On the basis of our previous analysis, we believe that fluorescence and CD properties caused by the interaction among amino acids should be closely related with the configuration of the amino acid type. As shown in Figure 8, the configuration difference of cysteine, leucine, and glutamic acid lies in the thiol group. We speculate that the thiol-group-induced hybridization of the HOMO level of cysteine with the valence band of CdTe QDs may be responsible for the red shift of the CD and fluorescence.
spectrum (see the scheme of induced hybridization in Figure 9), which is a mechanism analogous to that of phenyl-dithiocarbamate.43

To verify our speculation and further understand the role of the thiol group, DFT calculations were performed using the Dmol3 package.44 The hybrid B3LYP functional in combination with van der Waals correction (standard DFT computations with empirical pair potentials, DFT-D) was used.45 A double numerical basis set including polarization functions (DND) was used to describe the valence electrons, and the core electrons were dealt with using the all-electron method. We used the spin-polarized scheme throughout the calculations. The L-Cys-(CdTe)13 complex served as the QD model. We note that this complex is actually much smaller compared with the synthesized QDs, but its use is necessary to keep the computation tractable. The geometries of the capped QDs were optimized starting with C1 symmetry structures without any symmetry constraints. The conductor-like screening model (COSMO) was employed to characterize the surrounding water, with a macroscopic dielectric constant (ε) of 78.54.46 The self-consistent field procedure was used with a convergence criterion of 1.0 × 10⁻⁵ hartree on the electron density (1 hartree = 27.21 eV). The convergence tolerance was 2.0 × 10⁻⁵ hartree for energy. We determined the ground state structure using minimal energies and further corroborated the results by having no imaginary frequency in their harmonic frequency calculation.

As shown in Figure 10, cysteine and (CdTe)13 orbital hybridization is evident in the HOMO. In general, the occupied molecular orbitals, such as the HOMO, are delocalized over both the (CdTe)13 nanocluster and the ligand. On the contrary, the unoccupied orbitals (LUMO, LUMO+1, LUMO+2) remain localized in QDs. Besides, in order to verify the sulfur role on the orbital hybridization, we examined the calculated molecular orbital (HOMO) in the interaction between CdTe QDs and amino acids through nitrogen and oxygen attachment on the QDs’ surface (shown in Supporting Information Figure S26(a) and (b)). As is shown, nitrogen and oxygen attachment cannot lead to the orbital hybridization in the HOMO.

Therefore, we can conclude that the hybridization of the CdTe energy level and the HOMO levels of the cysteine molecules should be the main source of the induced chirality of (CdTe)13 nanoclusters. It is believed that sulfur 3p-orbitals play an important role in the HOMO levels of thiol-binding (cysteine) QDs compared to the contributions only from Te for the LUMOs of the capped QD group.50 Sulfur has an unpaired electron in its 3p-orbital in thiol groups, which means it has the ability to react with Te and Cd atoms. Consequently, this interaction may somewhat destabilize the HOMO and stabilize the LUMO of the capped QDs.51 This is probably the reason that the fluorescence spectra red shift was only shown with the addition of cysteine. Compared with CdSe or CdS QDs, the chiral induction on excitonic transitions of CdTe QDs is much weaker and decays very rapidly with size, so chiral induction on the surface states is more significant.23,50 The thiol group of cysteine may cause the chiral distortion of QD surface atoms and then induce the chirality of CdTe. In addition, the thiol group may also induce the orbital hybridization, leading to the red shift of both fluorescence and CD signals. These findings illustrate the decisive role of the thiol group on the chiral origin and the interaction mechanism among amino acids. When no thiolated amino acids are involved, the interaction between cysteine ligands and other amino acids only influences the intensity of the CD signals. In this case, the transformation of binding configuration of chiral cysteine molecules may be responsible for the decrease in CD activity. This advances our understanding that the chiral origin and chiral interaction among amino acids are not only the result of the electronic related activity but also related with the amino acids’ configuration. We hope this research will have important applications in biotechnology recognition, biomarkers, and related fields.

CONCLUSION

In this work, the fluorescence and optical activity of chiral CdTe quantum dots in their interaction with amino acids have
been investigated. Experimentally, fluorescence enhancement is observed for L/D-Cys-CdTe QDs interacting with all the tested amino acids, indicating a suppression of nonradiative path as well as the passivation of surface defect sites brought by amino group on CdTe QDs’ surface. It is notable that only the Cys-capped CdTe QDs with addition of cysteine exhibited a red shift for both fluorescence and CD spectra, while the shift for homochiral cysteine is smaller than that of heterochiral cysteine, which is consistent with the “preferential interaction” model. The addition of other amino acids (leucine, glutamicacid, etc.) resulted in no shift of the fluorescence and CD spectra. We believe that due to the presence of sulfur in the thiol group, the HOMO of cysteine hybridizes with the valence band of CdTe QDs and is thus responsible for the fluorescence and CD spectra red shift. This is supported both by experiments and by DFT calculations. Overall, this combined experimental and theoretical work demonstrates that it is not only the chemistry of the amino acid ligand that affects, in a sense, both CD and PL. Rather, it is also the exact geometry of binding that modifies these properties. We see that addition of ligands that do not “directly” interact with the VB of the QD (non-cysteine moieties) changes their photophysical properties, as it probably changes the way cysteine is bound to the surface.

METHODS
Preparation. CdCl₂·2.5H₂O (580 mg) was added in 50 mL of water in a 100 mL three-necked vessel and stirred for 30 min to ensure complete dissolution. Then, L-Cys/d-Cys was added under stirring in a N₂ atmosphere. Then, pH adjustment to an appropriate value was done by dropwise addition of a 1 M solution of NaOH. A 2 mL amount of freshly prepared NaHTe solution was injected into the Cd²⁺ precursorsolution using a syringe under vigorous stirring in a nitrogen atmosphere. The mixture of NaHTe and the Cd²⁺ precursor solution was heated to 100 °C and refluxed for 2 h in an oil bath. After the solution was cooled to room temperature, dimethyl carbinol was added to precipitate the sample solution by centrifugation at 10 000 rpm. Then, vacuum drying was applied to get the solid samples, which were stored in the dark under an Ar environment. The next interaction procedure was as follows: Different concentrations of amino acid were added to the functional CdTe QD solution (1 mM) and intensely stirred. Finally, deionized water was added to dilute the solution to the final volume of 10.0 mL.
Characterization. Fluorescence spectroscopy was performed using an RF-S3020PC fluorescence spectrophotometer (Shimadzu, Japan). FT-IR spectra were recorded on a Nicolet iS5 spectrometer (Thermo Electron Corporation). Powder XRD patterns of the prepared QDs were obtained on a BDX330 X-ray diffractometer using Cu K radiation. XPS measurements were performed by using an AMICUS surface analysis spectrometer. TEM images of the nanoparticles were carried out with a Hitachi H-600 transmission electron microscope. UV/vis absorption spectra were obtained by a Hitachi U-3010 spectrophotometer. CD spectra were performed using a Jasco J-810 spectropolarimeter using samples in aqueous solution; Hitachi U-3010 spectrophotometer. UV/vis absorption spectra were obtained by a nanomanipulation system. TEM images of the CdTe QDs were carried out with a Hitachi H-600 transmission electron microscope. TEM images of the CdTe QDs were performed using an RF-5301PC fluorescence spectrophotometer (Shimadzu, Japan).

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Notes
The authors declare no competing financial interest.

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ASSOCIATED CONTENT
Supporting Information
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STEM, HRTEM image, schematic structure of L-Cys-CdTe QDs; CD spectra, CD signal position, and absorption spectra of interaction between L-cysteine-capped CdTe QDs and D-cysteine, D-glutamic, L-cysteine, L-phenylalanine, L-alanine, and L-valine; fluorescence properties of D-Cys-capped CdTe QDs with addition of D-cysteine, D-glutamic, L-cysteine, L-phenylalanine, L-alanine, and L-valine; calculated HOMO in the interaction between L-Cys-CdTe QDs and amino acids (PDF)
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