Effects of Aromatic Thiol Capping Agents on the Structural and Electronic Properties of Cd$_n$Te$_n$ (n = 6, 8 and 9) Quantum Dots

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Thiols are efficient capping agents used for the synthesis of semiconductor and metal nanoparticles. Commonly, long-chain thiols are used as passivating agents to provide stabilization to nanoparticles. Theoretical methods rarely reported aromatic thiol ligands’ effects on small-sized CdTe quantum dots’ structural and electronic properties. We have studied and compared the structural and electronic properties of (i) bare and (ii) aromatic thiols (thiophenol, 4-methoxybenzenethiol, 4-mercaptopbenzonitrile, and 4-mercaptopbenzoic acid) capped Cd$_n$Te$_n$ quantum dots (QDs). Aromatic thiols are used as thiol-radical because of the higher tendency of thiol-radicals to bind with Cd atoms. This work provides an understanding of how the capping agents affect specific properties. The results show that all aromatic thiol-radical ligands caused significant structural distortion in the geometries. The aromatic thiol-radical ligands stabilize LUMOs, stabilize or destabilize HOMOs, and decrease HOMO-LUMO gaps for all the capped QDs. The stabilization of LUMOs is more pronounced than the destabilization of HOMOs. We also studied the effect of solvent on structural and electronic properties. TD-DFT calculations were performed to calculate the absorption spectra of bare and capped QDs, and all the capping ligands resulted in the redshift of absorption spectra.

Keywords: CdTe, DFT-density functional theory, capping agent effect, electronic properties, thiols

INTRODUCTION

Semiconductor quantum dots (QDs), or “nanoclusters,” or “nanoparticles” of CdTe and CdSe, are gaining significant attention due to their potential applications in various fields. Optoelectronic devices (Talapin et al., 2010; Kumar and Rao, 2014; Kershaw et al., 2017) (e.g., LEDs (Anikeena et al., 2009; Zou et al., 2017), sensors (Liang et al., 2014; Kanagasubbalakshmi et al., 2018), solar cells (Yaacobi-Gross et al., 2012; Huang et al., 2014; Carey et al., 2015; Bosio et al., 2017; Xiao et al., 2018), photodetectors (Barkhouse et al., 2008; Tu and Lin, 2008; Amelia et al., 2012)) and biomedical devices (Zheng et al., 2007; Yaghini et al., 2009; He and Ma, 2014) use QDs owing to their unique properties: size tunability, changeable surface chemistry (through capping with variety of ligands) (Hines and Kamat, 2013; Hines and Kamat, 2014), photoluminescence and absorption profile (Wuister et al., 2003; Wuister et al., 2004; Weng et al., 2006; Duan et al., 2009). The surface chemistry of semiconductor QDs is important in determining the electronic and structural properties because of their large surface-to-volume ratio.
The synthesis of semiconductor QDs is carried out in various ways, among which aqueous synthesis has considerable advantages in terms of high yield, reproducibility, and selectivity. During the synthesis of QDs, capping ligands tend to cover the surface of newly synthesized QDs and alter the structural and electronic properties of QDs. Ligands-capped CdTe QDs exhibit unique tunable structural, emission, and electronic properties (Akamatsu et al., 2005; Guo et al., 2005; Yaacobi-Gross et al., 2012; Deng et al., 2013; Lin et al., 2014; Amin et al., 2015; Liu et al., 2015; Schnitzenbaumer and Dukovic, 2018).

The presence of ligands on the surface affects the nucleation and growth of QDs considerably. Knowing the ligand effect helps develop a strategy for the synthesis and manipulating the size and properties of the QDs. Experimental characterization of structures and properties during the synthesis process remains challenging due to the minimal size and short lifetime of newly formed particles of QDs. On the other hand, first-principles computational techniques have been a good instrument for investigating the structures and properties of QDs. The cluster models have been used in several theoretical studies to investigate the structural and electronic properties of bare and ligated CdSe/CdTe QDs (Bhattacharya and Kshirsagar, 2007; Bhattacharya and Kshirsagar, 2008; Wang et al., 2009; Xu et al., 2010a; Seal et al., 2010; Haram et al., 2011; Kuznetsov et al., 2012; Lim et al., 2012; Ma et al., 2012; Leubner et al., 2013; Lin et al., 2013; Sriram and Chandiramouli, 2012; Wu et al., 2013; Alnemrat et al., 2014; Kuznetsov and Beratan, 2014; Rajbanshi et al., 2014; Shah and Roy, 2014; Aruda et al., 2016; Kilina et al., 2016; Swenson et al., 2016; Cao et al., 2018). Mainly, these studies were limited to exploring the capping effects of aliphatic ligands on the structural, electronic, and optical properties of CdTe QDs. Most of these computational studies have been conducted on small-sized QDs because of significant challenges associated with the atomistic simulation of large-sized QDs (Bhattacharya and Kshirsagar, 2007; Wang et al., 2009; Seal et al., 2010; Ma et al., 2012). These studies determined the possible lowest energy structures and optical properties of Cd$_n$Te$_n$ (n = 1–16, 19, 20, 24, 28) nanoclusters employing the first-principles calculations.

Recent computational and experimental studies have confirmed the utilization of aromatic capping ligands in synthesis and the capping exchange process of CdSe/CdTe QDs (Bloom et al., 2013; Lin et al., 2013; Kumar et al., 2015; Aruda et al., 2016; Swenson et al., 2016). However, significant and systematic studies that would have investigated the effect of aromatic ligands on the structural, electronic, and optical properties of CdTe QDs are rare. Hence, the present study aims to fill that knowledge gap and provide a systematic computational analysis of the structural, electronic, and optical properties of aromatic thiol capped CdTe QDs.

In one of our previous studies, we had performed an extensive search for the lowest energy geometries of Cd$_n$Te$_n$ QDs (n = 1–17) using particle swarm optimization (PSO) algorithms and density functional theory (DFT) approaches and explored structural and electronic properties (Imran et al., 2019). The present study presents structural and electronic properties of bare and capped small-sized Cd$_n$Te$_n$ (n = 6,8 and 9) QDs. We have used four aromatic thiol ligands for capping: thiophenol (TP), 4-methoxybenzenethiol (MBT), 4-mercaptobenzonitrile (MBN), and 4-mercaptobenzoic acid (MBA) (see Figure 1).

**Computational Methods**

All the calculations described here were performed using the Gaussian 09W package (Frisch et al., 2013). Recent studies have used the simulated annealing technique to find CdTe clusters’ lowest energy structures (Wang et al., 2009; Ma et al., 2012). Our previous study performed an extensive structural search for CdTe clusters using PSO algorithms as implemented in CALYPSO, evaluated the candidate clusters by DFT and MP2 theory levels. We re-used the lowest energy CdTe structures from our previous work for the sake of the present work (Imran et al., 2019). All the...
symmetric structures of bare and capped QDs were optimized without symmetry constraints. Vibrational frequency analysis indicated that optimized QD structures are actual minimum energy structures.

All the calculations were performed using hybrid functional B3LYP (Becke, 1993) with basis sets of Los Alamos double-$\zeta$ effective core potential (Lanl2dz) (Hay and Wadt, 1985a; Hay and Wadt, 1985b; Wadt et al., 1985) in the gas phase as implemented in the Gaussian 09W package. Earlier studies had found the B3LYP/Lanl2dz level of theory to be a practical approach in terms of accuracy and efficiency when used to study CdTe and CdSe bare and capped QDs (Kuznetsov et al., 2012; Lim et al., 2012; Kuznetsov and Beratan, 2014). However, utilizing the B3LYP functional may underestimate the HOMO-LUMO gaps and excited-state energy, which may be corrected by using range-separated functionals, as shown in previous studies (Salzner and Aydin, 2011; Kurban et al., 2019; Muz and Kurban, 2020). In small-sized QDs, all the cadmium atoms are exposed to the surface and potentially coordinated with ligands. We also varied the number of ligands attached to QDs to explore the effect of ligand density on the structural and electronic properties of QDs. Theoretical studies were simulated in toluene solvent (dielectric constant $\varepsilon = 2.2706$). The ligand-binding energies (BE) were calculated with the help of the following equation:

$$BE = |E(Cd_{n}Te_{n}L_{n}) - (E(Cd_{n}Te_{n}) + nE(L))|/n$$

Where $E(Cd_{n}Te_{n}L_{n})$ is the energy of capped QD, $E(Cd_{n}Te_{n})$ is the energy of bare QD, and $E(L)$ is the energy of the capping agent. Time-dependent DFT calculations were performed using the B3LYP/Lanl2dz approach both in the gas and implicit solvent to study the electronic transitions of both bare and capped QDs. Calculated spectra were plotted with the help of Gabedit 2.5.0 (Allouche, 2011) to determine $\lambda_{\text{max}}E_{\text{max}}$ from plots. Molecular structures and orbitals were visualized using Molden 5.8 (Schaafenaar and Noordik, 2000) and GaussView, respectively.

**RESULTS AND DISCUSSION**

**Bare Cd$_n$Te$_n$ (n = 6, 8 and 9) Quantum Dots**

Figure 2 shows the minimum energy structures of bare Cd$_6$Te$_6$, Cd$_8$Te$_8$, and Cd$_9$Te$_9$ QDs in the gas phase and their Frontier
molecular orbitals. Table 2 shows calculated HOMO/LUMO energies, HOMO-LUMO gaps, $E_{\text{max}}$, and $\lambda_{\text{max}}$.

Cd$_6$Te$_6$ ($C_{3v}$ symmetry) structure shows that it consists of stacks of Cd$_3$Te$_3$ rings of hexagonal shape with a Cd-Te bond distance of 2.87 Å inside the hexagonal rings Cd-Te bond distance between the two layers is 3.045 Å.

Cd-Te bond lengths in Cd$_8$Te$_8$ ($S_4$ symmetry) are calculated to be 2.856–3.002 Å in distorted six Cd$_2$Te$_2$ rhombi and four Cd$_3$Te$_3$ hexagonal rings.

Cd$_9$Te$_9$ ($D_{3h}$ symmetry) consists of three interconnected Cd$_3$Te$_3$ hexagonal rings, and Cd-Te bond lengths in upper and lower hexagonal layers are 2.85 Å, while in the middle layer, Cd-Te bond lengths expand to 2.994 Å. The interlayer Cd-Te bond lengths are calculated to be 3.163 Å which is greater than the interlayer bond length of Cd$_6$Te$_6$ QD.

Geometry optimization with implicit solvent (toluene) and gas-phase gave similar geometries for all QDs. However, the amount of NBO charges on Cd and Te atoms increased by adding implicit solvent (toluene) during calculations.

In the gas phase, HOMO-LUMO gaps of Cd$_6$Te$_6$, Cd$_8$Te$_8$, and Cd$_9$Te$_9$ QDs revealed that all the QDs were semiconductor-like (Table 1). The calculated HOMO-LUMO gaps are 3.05, 3.09, and 2.76 eV for Cd$_6$Te$_6$, Cd$_8$Te$_8$, and Cd$_9$Te$_9$ QDs. Generally, an increase in the size of QDs decreases HOMO-LUMO gaps, but in the present study, HOMO-LUMO gaps of Cd$_9$Te$_9$ QD are less than Cd$_6$Te$_6$ QD while Cd$_8$Te$_8$ QD shows a higher HOMO-LUMO gap than the other two species. We attribute this observation to different structural motifs of each size of QD. Cd$_6$Te$_6$ and Cd$_9$Te$_9$ are similar to wurtzite structures with six atoms in a ring, whereas Cd$_8$Te$_8$ QD shows a higher HOMO-LUMO gap than the other two species. Probably this structural difference is the reason behind the unexpected higher bandgap of Cd$_8$Te$_8$.

Table 2 presents TD-DFT calculations of excitation energies ($E_{\text{max}}$) and absorption wavelengths ($\lambda_{\text{max}}$) of excited states with maximum oscillator strength. The calculated excitation energies ($E_{\text{max}}$) of bare QDs in the gas phase are close to the HOMO-LUMO gaps of the same QDs and consistent with the previous computational report.
The inclusion of toluene solvent in calculations slightly increased the excitation energies. A blue shift in the absorption maxima caused by the solvent is an interesting observation. One may find few previously published studies on solvents’ effect on the absorption spectrum of CdSe clusters reporting a blue shift occurrence (Xu et al., 2010a; Xu et al., 2010b; Lim et al., 2012). In our research, we have observed a similar blue shift occurrence in the case of CdTe clusters.

IP, and EA, values are considered to be an index of stability of QDs. It is energetically not favorable for QDs with large IP, and EA, values to be activated toward a chemical reaction. Hence, QDs with large IP, and EA, values can be considered more stable. Calculated IP/IP, and EA, values are given in Table 3. It is observed that IP/IP, values decrease with an increase in the size of bare QDs, while EA/EA, values increase gradually with an increase in the size of bare QDs.

Capped Cd₈Te₈ (n = 6, 8 and 9) Quantum Dots

We capped CdTe QDs with aromatic thiol-radical ligands: TP (C₆H₅S⁻), MBT (CH₃OC₆H₄S⁻), MBN (CNC₆H₄S⁻), and MBA (COOHC₆H₄S⁻). The aromatic ligands were coordinated to the QDs via sulfur, which significantly changed the geometries of bare QDs after geometry relaxation. We explored different numbers of capping ligands and different modes of ligands’ coordination with QD. Capped Cd₈Te₈L₆ and Cd₈Te₈L₄ (L = TP, MBT, MBN, and MBA) species gave stable and physically acceptable geometry after geometry relaxation. For both Cd₈Te₈L₆ and Cd₈Te₈L₄ species, different geometries arose from bare QD because of Cd-Te bond breakage and Cd-S-Te bridge formation in the form of a 5-membered ring. However, the overall structural motif remained intact, containing interconnected two hexagonal (6-membered rings) layers (see Figure 3 and Supplementary Figure S1).
Closed structural configurations were observed after optimization of $\text{Cd}_6\text{Te}_6\text{L}_6$ and $\text{Cd}_6\text{Te}_6\text{L}_4$ species, and these results are different from previous works of Kuznetsov et al. (2012), Lim et al. (2012), and Kuznetsov et al. (2012) where they had capped $\text{Cd}_6\text{Te}_6$ with small-sized ligands and observed open structures after geometry relaxation. The capping of $\text{Cd}_9\text{Te}_9$ QDs (with $S_4$ point group) by all four aromatic ligands led to a slight opening of the bare QD structure due to Cd-Te bond breakage, Cd-S-Cd bridge formation with 4-membered rings, Cd-S-Te bridge formation with 5-membered rings, and formation of one 8-membered ring. We explored the geometries of two $\text{Cd}_9\text{Te}_9\text{L}_8$ and $\text{Cd}_9\text{Te}_9\text{L}_4$ species and found that ligands caused a slight opening of the bare QD structure in both cases. On a relative scale, the coordination of eight ligands caused a larger opening than four ligands (see Figure 4 and Supplementary Figure S2).

Similarly, $\text{Cd}_9\text{Te}_9$ QD (with $D_{3h}$ point group) was also capped with the aromatic thiol-radical ligands, which led to significant changes in QD’s structure compared to its bare lowest energy structure (see Figure 5 and Supplementary Figure S3). Optimized structures of $\text{Cd}_9\text{Te}_9\text{L}_9$ species showed open structures after capping with aromatic ligands, which is different from previous works where they had capped $\text{Cd}_6\text{Te}_6$ with small-sized ligands and observed open structures after geometry relaxation.

**TABLE 4** | Ligand's total net charge change and net charge change per ligand (in e unit) for capped $\text{Cd}_n\text{Te}_n\text{L}_n$ (where $L =$ TP, MBT, MBN, and MBA) calculated with B3LYP/Lanl2dz approach in the gas phase.

| Ligands | Capped-QDs | $\text{Cd}_6\text{Te}_6$ | $\text{Cd}_8\text{Te}_8$ | $\text{Cd}_9\text{Te}_9$ |
|---------|------------|----------------|----------------|----------------|
| TP      | total      | −2.111 | −2.596 | −3.106 |
|         | per ligand | −0.351 | −0.324 | −0.345 |
| MBT     | total      | −1.733 | −2.388 | −2.863 |
|         | per ligand | −0.288 | −0.298 | −0.318 |
| MBN     | total      | −2.187 | −2.716 | −3.245 |
|         | per ligand | −0.364 | −0.339 | −0.361 |
| MBA     | total      | −2.242 | −2.932 | −3.493 |
|         | per ligand | −0.373 | −0.366 | −0.388 |

FIGURE 5 | Optimized gas-phase structures of bare and capped $\text{Cd}_9\text{Te}_9$ QDs: $\text{Cd}_9\text{Te}_9\text{(TP)}_9$ (A), $\text{Cd}_9\text{Te}_9\text{(MBT)}_9$ (B), $\text{Cd}_9\text{Te}_9\text{(MBN)}_9$ (C), and $\text{Cd}_9\text{Te}_9\text{(MBA)}_9$ (D). Atoms are represented as follows: Cd by dark yellow spheres, Te by dark gray spheres, C brown spheres, H light gray sphere, O red spheres, S sapphire spheres, and N blue spheres.
structures with a hexagonal ring at the center while above and lower layer opened up to stabilize the structure. It resulted in Cd-Te bond breaking, Cd-S-Cd bridge formation with 4-membered rings, and Cd-S-Te bridge formation with 5-membered rings. However, in the case of Cd₈Te₈L₈ species with a smaller number of capping ligands attached to QDs, the closed-shell configuration of Cd₈Te₈ QDs remained intact with the slight opening of the QDs structures. These changes in the structure of capped Cd₈Te₈ QDs also arise from the formation of multiple Cd-S-Te bridges in 5-membered ring configuration and breakage of Cd-Te bonds. These findings are consistent with the previous works of Kuznetsov et al. (2012), Lim et al. (2012).

We performed NBO charge analysis to explore the distribution of charges on QDs after capping with aromatic ligands. Cd atoms in all Cd₆Te₆L₆ species displayed positive charges that range from 0.71e to 0.85e. While positive charges on Cd atoms in bare Cd₆Te₆ QDs were 0.76e. There was an increase in the positive charge on Cd atoms in ligated Cd₈Te₈L₈ species varied from 0.64e to 0.71e. Cd atoms in Cd₉Te₉L₉ species varied from 0.74e to 0.91e. The positive charges on the Te atom in ligated Cd₉Te₉L₉ species varied from 0.308e to 0.363e. This could be another reason for higher ligand binding energies of Cd₉Te₉(MBA)₉ for each value of n.

Calculated ligand binding energies are given in Table 5. The ligand-binding energies of all ligated QDs decrease in the following order: Cd₅Te₅(MBA)₅ > Cd₅Te₅(MBN)₅ > Cd₅Te₅(TP)₅ > Cd₅Te₅(MBT)₅ for each value of n. A possible explanation of this sequence of ligand binding energies can be the HOMOs, and LUMOs stabilization, and higher IP, and EA, values depicted by MBA and MBN capped QDs (see Table 1, 2, and 5). On the other hand, Cd₉Te₉(MBT)₉ and Cd₉Te₉(TP)₉ present lower ligand binding energy due to their HOMOs destabilization and low IP, and EA, values. These results are also reflected in NBO charge analysis, where MBA exhibits the biggest charge change by withdrawing electron density from the QDs. Charge analysis also reveals that oxygens of -COOH groups in Cd₉Te₉(MBA)₉ possess greater charges about (−0.598−0.787) e compared to the nitrogen of -CN groups in Cd₉Te₉(MBN)₉ that shows charges about (−0.308−0.363) e. This could be another reason for higher ligand binding energies of Cd₉Te₉(MBA)₉.

Our calculated ligand binding energies values are close to the previous findings of Lim and co-workers (Lim et al., 2012), who calculated binding energies with the B3LYP/Lanl2dz approach in the gas phase for Cd₅Se₅/Cd₅Te₅ QDs (n = 3, 4, 6, and 9) capped with SCH₂COOH−, SCH₂CH₂CO₂H−, and SCH₂CH₂NH₂.

### Table 5

| Species (symmetry, spin state) | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) | Gap, (eV) | BE/L, kcal/mol |
|-------------------------------|-------------------------|-------------------------|-----------|---------------|
| Cd₅Te₅(TP)₅ (C₁⁻)             | −5.97                   | −3.97                   | 2.02      | −19.3         |
| Cd₅Te₅(MBT)₅ (C₁⁻)            | −5.28                   | −4.71                   | 0.57      | −16.6         |
| Cd₅Te₅(MBN)₅ (C₁⁻)            | −6.60                   | −5.44                   | 1.16      | −21.3         |
| Cd₅Te₅(MBA)₅ (C₁⁻)            | −6.22                   | −5.41                   | 0.81      | −17.7         |
| Cd₉Te₉(TP)₉ (C₁⁻)             | −6.76                   | −5.14                   | 1.62      | −30.6         |
| Cd₉Te₉(MBN)₉ (C₁⁻)            | −6.53                   | −5.57                   | 0.96      | −29.2         |
| Cd₉Te₉(MBA)₉ (C₁⁻)            | −6.17                   | −5.10                   | 1.07      | −38.8         |
| Cd₉Te₉(MBT)₉ (C₁⁻)            | −6.17                   | −5.10                   | 1.07      | −38.8         |

### Table 1, 2, and 5

Effects of Capping Agents on CdTe

Calculated ligand binding energies are given in Table 5. The ligand-binding energies of all ligated QDs decrease in the following order: Cd₅Te₅(MBA)₅ > Cd₅Te₅(MBN)₅ > Cd₅Te₅(TP)₅ > Cd₅Te₅(MBT)₅ for each value of n. A possible explanation of this sequence of ligand binding energies can be the HOMOs, and LUMOs stabilization, and higher IP, and EA, values depicted by MBA and MBN capped QDs (see Table 1, 2, and 5). On the other hand, Cd₉Te₉(MBT)₉ and Cd₉Te₉(TP)₉ present lower ligand binding energy due to their HOMOs destabilization and low IP, and EA, values. These results are also reflected in NBO charge analysis, where MBA exhibits the biggest charge change by withdrawing electron density from the QDs. Charge analysis also reveals that oxygens of -COOH groups in Cd₉Te₉(MBA)₉ possess greater charges about (−0.598−0.787) e compared to the nitrogen of -CN groups in Cd₉Te₉(MBN)₉ that shows charges about (−0.308−0.363) e. This could be another reason for higher ligand binding energies of Cd₉Te₉(MBA)₉.

Our calculated ligand binding energies values are close to the previous findings of Lim and co-workers (Lim et al., 2012), who calculated binding energies with the B3LYP/Lanl2dz approach in the gas phase for Cd₅Se₅/Cd₅Te₅ QDs (n = 3, 4, 6, and 9) capped with SCH₂COOH−, SCH₂CH₂CO₂H−, and SCH₂CH₂NH₂.
ligands. Our calculated values also agree with the work of Kuznetsov and co-workers (Kuznetsov et al., 2012), who studied Cd\text{6}Te\text{6}/Cd\text{6}Te\text{6} QDs (n = 6,9) capped with NH\text{3}, SCH\text{3}, and OPH\text{3} ligands in the gas phase using B3LYP/Lanl2dz approach.

Figure 6 presents the interaction of S containing ligands with Cd\text{6}Te\text{6} QD frontier orbitals. The partial density of states (PDOS) plots (see Figure 7) shows the dominant contributions of sulfur 3\text{p} orbitals of the aromatic thiol-radical ligands in the HOMOs of capped Cd\text{6}Te\text{6} QDs with minor contributions from QD atoms. On the other hand, the LUMOs of the capped Cd\text{6}Te\text{6} QD show high contributions from both QD atoms and ligand groups: with slightly higher contributions from Te atoms (see Figure 7). The S containing ligands tend to use their lone pair and their unpaired electrons to interact with Cd and Te atoms. An unpaired electron is present in the sulfur 3\text{p} orbital of thiol-radical ligands. Seemingly, the singly occupied \( \beta \)-LUMOs of thiol-radical ligands favorably interact with the doubly occupied HOMO of
FIGURE 7 | The partial density of states (PDOS) plots (stacked) near the HOMO/LUMO gaps for the capped Cd₆Te₆(TP)₆ (A), Cd₆Te₆(MBT)₆ (B), Cd₆Te₆(MBN)₆ (C) and Cd₆Te₆(MBA)₆ (D) QDs calculated with B3LYP/Lanl2DZ approach.

FIGURE 8 | HOMO-LUMO gap [eV] for bare and capped Cd₆Te₆Lnₖ (n = 6, 8, and 9) QDs.
the QD, which possesses some d-character from Cd atoms. This interaction destabilizes the HOMO of the capped QDs, as depicted in Figures 7A, B. The interaction of the LUMOs of QD with the α-LUMOs and β-LUMOs of thiol-radical ligands highly stabilizes the LUMOs of the capped QDs.

Capping with all four aromatic thiol-radical ligands stabilize the LUMOs of all QDs, while HOMOs are either stabilize or destabilize (see Tables 2 and 5). Both TP and MBT ligands destabilize HOMOS in all capped QDs. The effect is much prominent for HOMOs of MBT capped QDs: MBT destabilizes the HOMO by 8.72 eV for Cd₆Te₆, 8.68 eV for Cd₈Te₈, and 8.44 eV for Cd₉Te₉.

On the other hand, both MBN and MBA ligands tend to stabilize HOMOS of all capped QDs. MBN capped QDs show a more pronounced effect with HOMOs stabilization by 4.52 eV for Cd₆Te₆, 4.19 eV for Cd₈Te₈, and 5.82 eV for Cd₉Te₉. All the aromatic thiol-radical ligands decrease the HOMO-LUMO gap of all the capped QDs (see Tables 2 and 5) due to the interaction of frontier orbitals of ligands with frontier orbitals of QDs, as shown in Figure 8. These observations are due to the stronger stabilization of LUMOs as compared to HOMOs. A drastic decrease in the HOMO-LUMO gap is observed for capped Cd₂₆Te₆(TP)₆, Cd₂₆Te₆(MBT)₆, Cd₂₆Te₆(MBN)₆, and Cd₂₆Te₆(MBA)₆. While all the other capped QDs show a less pronounced decrease in the HOMO-LUMO gap. This effect of thiol-radical capping ligands is in line with the previous report, where SCH₂COOH, SCH₂CH₂CO₂H, and SCH₂CH₂NH₂ capped CdₙTeₙ/CdₙTe₁₆ species (n = 3, 4, 6, and 9) were studied by Lim et al. (2012).

We further explore the effect of aromatic thiol-radical ligands on vertical and adiabatic IPs and EAs of QDs in the gas phase (see Table 1 and Figure 9). Analysis of IP/EA values for bare, and capped QDs reveals that both IP/IPₐ values show a decrease after capping with all aromatic thiol-radical ligands. However, Cd₆Te₆(MBA)₆, Cd₈Te₈(MBN)₈, and Cd₉Te₉(MBA)₉ species exhibited an increase in IP/EA values as compared to bare QDs. EA/EAₐ values increase after capping with all aromatic thiol-radical ligands as compared to bare QDs. It is worth noticing that the capping of QDs with MBT ligand causes the highest decrease in IP values. Generally, IP, and EA values are considered to be an index of stability of capped-QDs. It is energetically not favorable for QDs with large IP, and EA values to be activated toward a chemical reaction. Hence QDs with large IP and EA values can be more stable toward a chemical reaction. It is observed that IP and EA values of capped-QDs decrease in the order MBA > MBN > TP > MBT, so the large IP and EA values of MBA capped QDs are associated with their higher stability.

The density of states (DOS) plots of thiol-radical ligands revealed the presence of midgap states which were not present in the parent thiol ligands. The conversion of thiol into thiol-radical by dehydrogenation generates one singly occupied 3p orbital of the sulfur, which appears as midgap states between the HOMO and LUMO states (see Supplementary Figures S5, S6). The PDOS plots of Cd₆Te₆L₆ species are presented in Figure 8 as a representative, while DOS plots of the rest of ligands and QDs (both bare and capped species) are given in the supporting information. As indicated in Figure 7, the Frontier orbitals of the capped Cd₆Te₆ QDs are mainly composed of ligands’ orbitals, which affect the electronic properties of capped QDs, especially the HOMOs and LUMOs energies of the QDs.

To probe the effect of capping on electronic transitions of QDs, we also performed a TD-DFT study. TDDB3LYP/Lanl2dz calculations for bare and capped QDs are given in Tables 3 and 6. We computed excitation energies (Eₘₐₓ), and maximum absorption wavelengths (λₘₐₓ) for maximum intensity excited states in the gas phase and with implicit solvent (toluene).

All ligated QDs displayed a decrease in excitation energies compared to the excitation energies of their respective bare
QDs. For capped QDs species, all the thiol-radical ligands altered the absorption spectra of bare Cd\textsubscript{6}Te\textsubscript{6} and Cd\textsubscript{8}Te\textsubscript{8} QDs by shifting the absorption peaks towards lower energy (redshift) because of the midgap states generated by 3p orbitals of sulfur, as shown in Figure 10. Aromatic ligands are known to influence the electronic and optical properties of QDs by stabilizing the LUMOs and reducing the bandgap. The delocalization of the exciton across the ligand shell is attributed to a significant redshift in the absorption spectra of capped CdTe QDs compared to bare QDs. The ligands’ Frontier orbitals coincide with the bandgap of CdTe QDs. Such a resonance situation might generate interfacial QD-ligand states, which would improve the optical properties of the QDs and perhaps open up new relaxation routes for photoexcited charge carriers, hence cause a redshift of the absorption peaks in capped QDs.

The addition of the solvent shifted the redshift toward higher wavelengths for all capped QDs except for Cd\textsubscript{6}Te\textsubscript{6}(TP)\textsubscript{6} and Cd\textsubscript{6}Te\textsubscript{6}(MBN)\textsubscript{6} QDs. It was observed that the redshift in the gas phase for capped-Cd\textsubscript{6}Te\textsubscript{6} QDs decreased in the following order: TP > MBT > MBA > MBN. For capped-Cd\textsubscript{8}Te\textsubscript{8} QDs, it decreased in the order: MBT ≈ MBN > MBA > TP. These results align with previous studies of similar QDs, which suggested that aromatic thiol ligands cause a redshift of the spectrum (Tan et al., 2012; Nadler and Sanz, 2015; Plata et al., 2017).

| Species (symmetry, spin state) | \( E_{\text{HOMO}} \) (eV) (gas phase; toluene) | \( E_{\text{LUMO}} \) (eV) (gas phase; toluene) | Gap, (eV) | \( E_{\text{max}} \) (eV) | \( \lambda_{\text{max}} \) (nm) |
|-------------------------------|-----------------------------------------------|-----------------------------------------------|----------|-----------------|-----------------|
| Cd\textsubscript{6}Te\textsubscript{6}(TP)\textsubscript{6} (C\textsubscript{1}A) | -5.57 | -3.97 | 1.6 | 2.59 | 455 |
| Cd\textsubscript{6}Te\textsubscript{6}(MBT)\textsubscript{6} (C\textsubscript{1}A) | -5.70 | -3.85 | 1.85 | 2.88 | 429 |
| Cd\textsubscript{6}Te\textsubscript{6}(MBN)\textsubscript{6} (C\textsubscript{1}A) | -5.74 | -3.98 | 2.16 | 2.90 | 495 |
| Cd\textsubscript{6}Te\textsubscript{6}(MBA)\textsubscript{6} (C\textsubscript{1}A) | -5.93 | -4.14 | 2.41 | 2.87 | 483 |
| Cd\textsubscript{8}Te\textsubscript{8}(TP)\textsubscript{8} (C\textsubscript{1}A) | -5.53 | -3.88 | 1.89 | 2.94 | 538 |
| Cd\textsubscript{8}Te\textsubscript{8}(MBT)\textsubscript{8} (C\textsubscript{1}A) | -5.45 | -3.92 | 2.09 | 2.89 | 438 |
| Cd\textsubscript{8}Te\textsubscript{8}(MBN)\textsubscript{8} (C\textsubscript{1}A) | -6.62 | -4.48 | 2.17 | 2.45 | 483 |
| Cd\textsubscript{8}Te\textsubscript{8}(MBA)\textsubscript{8} (C\textsubscript{1}A) | -6.47 | -4.20 | 2.20 | 2.30 | 538 |

**CONCLUSION**

The effects of aromatic thiol-radical ligands on the structural and electronic properties of Cd\textsubscript{n}Te\textsubscript{n} quantum dots (\( n = 6,8,9 \)) were investigated by a systematic DFT study using B3LYP/Lanl2dz
theory level. We chose thiophenol (TP), 4-methoxybenzene-thiol (MBT), 4-mercaptobenzoitrile (MBN), and 4-mercaptobenzoic acid (MBA) as model capping ligands (see Figure 1). All the four ligands coordinated to the Cd₆Te₆ QDs successfully and formed stable ligand-QD species when subjected to geometry optimization. Generally, the ligands slightly opened up the Cd₆Te₆ and Cd₈Te₈ QDs, but the overall structural motif remained intact. While in the case of Cd₉Te₉, QDs capping with ligands caused the complete opening of the closed structure of bare QDs. Each QDs ligands-QD complexes showed a steady increase in ligand binding energies in the order: MBT < TP < MBN < MBA. The capping of aromatic thiol-radical ligands causes a slight increase in Cd atoms' positive charges due to their electron-withdrawing ability. Adsorption of the ligands decreases the HOMO-LUMO gap due to the stabilization of the LUMOs of QDs. Finally, the TD-DFT study revealed that all the ligands shifted the absorption spectra to redshift in the gas phase and with implicit solvent (toluene).

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DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

The research idea belongs to MJS. MI performed major computational work. TF and JI have significantly contributed to the discussion and write-up.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmats.2021.755332/full#supplementary-material

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