

Interaction of CdSe Quantum Dots with some aliphatic and aromatic diamines

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ABSTRACT

Recent advances in the chemistry of semiconductor nanocrystal show that CdSe quantum dots have set the latest trends in the era of reduced dimensionality. The interactions of these CdSe quantum dots with organic molecules have led to new materials showing fascinating physical properties of potential technological importance. It is very to explore the interactions of quantum dots with various molecules for which they can be used as effective sensors with wide range of applications. In order to develop sensors for the detection of amines, several investigations have already been carried out. Earlier studies have already revealed that the direct interaction between the CdSe surface and amine functional groups passivates the surface and blocks the trapping of electrons at the defect sites. The latest research in the field of applications of quantum dots suffers huge drawbacks because of inadequate results available for the systematic study of structural and electronic properties of quantum dots as a sensor. This work provides an overview of efforts made to interact CdSe quantum dots with various aliphatic (Ethylene diamine, Hexamethylenediamine) and aromatic diamines (Orthophenylenediamine, Metaphenylenediamine and Paraphenylenediamine). There are tremendous structural transformations in the structures of the molecular systems. Significant changes in the electronic properties were also marked after interactions between the diamines and CdSe quantum dots.

Keywords: Diamines, "quantum dots", sensors

INTRODUCTION

Among different nanoscale materials, semiconductor quantum dots are interesting because of their structure, unique physical properties and emerging applications in different fields. Semiconductor quantum dots present considerable advantages over bulk single crystal semiconductors.¹⁻³ Quantum dots and nanomaterials have been used amazingly to act as sensors for various inorganic, organic and biomaterials.⁴⁻⁵ Amongst the II-VI quantum dots, the size, shape and surface passivation of semiconductor CdSe nanocrystals have been topics of great interest in both theoretical and experimental investigations.⁶ Owing to their unique optical and electronic properties, CdSe nanocrystals are the ideal candidates for biological applications,⁷⁻⁸ laser media,⁹ light emitting diodes,¹⁰⁻¹¹

nonlinear optics,¹²⁻¹³ and photovoltaics.¹⁴ CdSe quantum dots have size-dependent fluorescence, tunable across the visible spectrum and so have become the most extensively investigated quantum dots.¹⁵

In the present era, it is essential to study the interactions of quantum dots with various molecules for which they can be used as effective sensors with wide range of applications. In order to develop sensors for the detection of amines, several investigations have already been carried out. Studies revealed that the direct interaction between the CdSe surface and amine functional groups passivates the surface and blocks the trapping of electrons at the defect sites. The photo-induced charge transfer between CdSe quantum dots and *p*-phenylenediamine has also been studied, wherein a surface bound complexation equilibrium model has been proposed to explain the interactions¹⁶. The same model was used to explain the quenching phenomenon effective for CdSe quantum dots emission in studying the interactions between different diamines with CdSe QDs.¹⁷ The interactions between monoamines or diamines and CdSe quantum dots (of varied sizes) have been reported by many scientists.¹⁷⁻¹⁸ It was found that band edge photoluminescence intensity was enhanced for a single crystal of CdSe by interaction with ethylene diamine.¹⁸ In certain cases, the emission properties and lifetime values of CdSe quantum dots were found to be dependent on the oxidation potential of the amines and the crystallite sizes. Smaller CdSe quantum dots ensure better surface coverage

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of amines and, hence, higher quenching efficiency of amines could be realized as compared to larger CdSe quantum dots¹⁹. We have picked up the diamines used by Liang *et al.* (2005) to carry out the theoretical investigations in order to have a better understanding of the interactions. We have analyzed the HOMO-LUMO gaps, the Fermi energies, the binding energies and the structural properties of CdSe quantum dots of diameter ~ 12 Å, and the alterations in their properties on interaction with various diamines considered, viz. ethylene diamine (EDA), hexamethylene diamine (HDA), orthophenylene diamine (OPD), metaphenylene diamine (MPD) and paraphenylene diamine (PPD).

Diamines have a wide array of applications. Aliphatic diamines are used as crosslinking agents for preparation of environmental friendly coatings based on natural shellac.²⁰ Both aliphatic and aromatic diamines are used as monomers for copolymers like nylons, polyesters and polyurethanes because of their characteristic properties.²¹

Ethylene diamine (EDA) is a colourless to yellowish liquid, with an ammonia-like odour. It is relatively basic and is completely miscible with polar solvents such as water and ethanol. It is widely used as a building block for polymers and as a ligand for coordination compounds. EDA is used as a solvent for proteins like albumin or casein, as a part of electroplating baths, as a lubricant for textiles, as stabilizer in latex emulsions, and in polyamide adhesives and also as a corrosion inhibitor in paints and coolants. It is also a renowned chelating agent. Hexamethylene diamine (HDA) is a diamine with a hexamethylene hydrocarbon chain and amine functional groups at each end. It has a strong amine odour, similar to piperidine. HDA is used as a raw material in the production of nylon polymers and hexamethylene diisocyanate (HDI) (for use as monomer feedstock in polyurethane production). It is also used as a cross-linking agent in epoxy resins. Orthophenylene diamine (OPD) belongs to the aromatic amine family. De Nys and Terwinghe²⁴ (1990) reported the successful employment of OPD to enhance the mass transfer of reactant species in the leaching of sphalerite under low pulp density conditions in a plug flow reactor, resulting in an increase in the extent of zinc extraction. It has also been reported that fast zinc dissolution rates were obtained in the presence of OPD or metaphenylene diamine (MPD) in a low pulp density leach study. Paraphenylene diamine (PPD) is used as a component of engineering polymers and composites, aramid fibres, hair dyes, rubber chemicals, textile dyes and pigments. PPD is selected because of its high temperature stability, high strength and chemical and electrical resistance.

The knowledge of interactions between the above-mentioned diamines and CdSe nanoclusters is potentially of great importance as it will help in better fabrication of light emitters, where quenching is to be avoided and also to develop sensors for the detection of diamines based on their interactions with quantum dots.

COMPUTATIONAL DETAILS

Our calculations employ numerical basis sets of double zeta quality. The geometries of various diamines, CdSe

quantum dot of size ~ 1.2 nm and the combination of the two (in order to study their interactions) were fully optimized without restrictions. The results thus obtained are presented in the following section.

RESULT AND DISCUSSION

ISOLATED SYSTEMS

Table 1 lists some of the calculated electronic properties of the systems investigated in this chapter. Of the three isomeric phenylene diamines, the meta isomer appears to be the most stable. It also has the largest HOMO-LUMO gap, having the lowest energy HOMO and the highest energy LUMO. It can also be seen that the HOMO is stabilized and the LUMO destabilized in the case of the aliphatic diamines, leading to larger separations between the two energy levels. The HOMO-LUMO plots shown in Figure 1 clearly indicate that the two MOs are respectively the π and π^* orbitals for the aromatic diamines. For the aliphatic diamines, particularly in the case of HDA, the HOMOs are centered on the amine nitrogens, while the LUMO is delocalized over the entire molecule. In EDA, there is some delocalization of the nitrogen lone pairs with the ethylene double bond.

Table 1 Calculated electronic properties (eV) for the various diamines

Diamine	E (HOMO)	E(LUMO)	HOMO-LUMO gap	Binding energy
EDA	-5.09	1.62	6.71	-46.20
HDA	-5.10	1.72	6.81	-98.53
OPD	-3.79	-0.03	3.77	-77.12
MPD	-3.96	0.02	3.98	-77.33
PPD	-3.45	-0.30	3.15	-77.18

It can be said here that there might be a possibility that in electronic applications, these compounds can also operate as rectifiers if they have a donor electron rich part and an acceptor electron poor part. From the contour plots (Figure 1) of aliphatic diamines, the HOMO is centred around the electron rich site i.e. around the amino groups as well as around the small bridging hydrocarbon chain and the LUMO is also centred around the electron rich site and partly on the intermediate ethylene group. Another observation that is evident from these plots is that the molecular orbital contours (both HOMO and LUMO isosurfaces) in case of aromatic diamines are more symmetrical than in the case of aliphatic diamines.

We then considered the interactions of these diamines with CdSe quantum dots. It becomes important to mention here that our calculations employed uncapped CdSe quantum dot, which were made to interact with diamines, first without assignment of charge and then with assignment of -6 charge. The charge has been assigned on the basis of the non-stoichiometry in the structure of the Cd₁₃Se₁₆ quantum dot. The purpose of non-assignment of charge was to primarily study the charge transfer in case of neutral

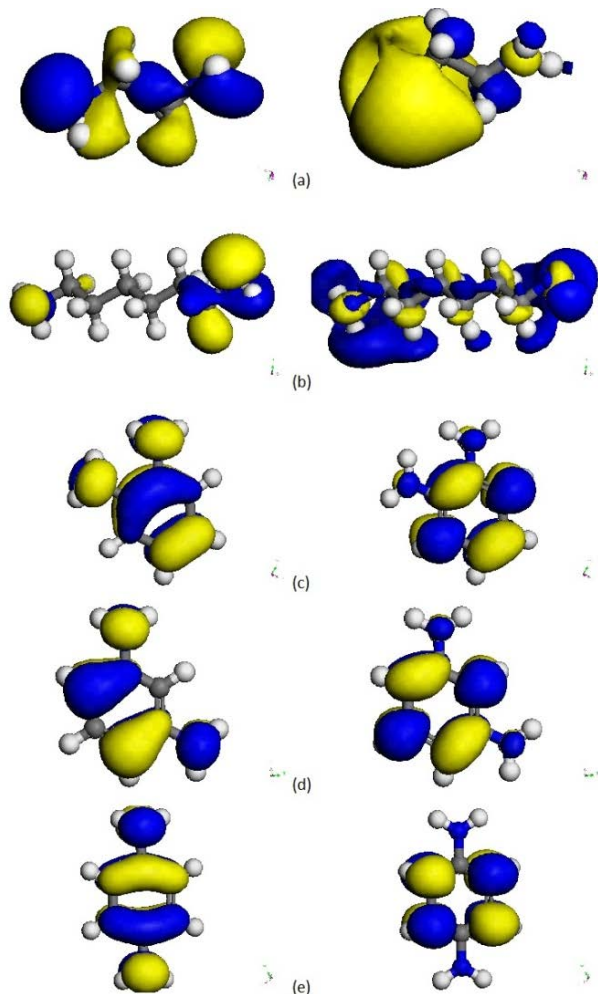


Figure 1. HOMO (left) and LUMO (right) plots of (a) EDA (b) HAD (c) OPD (d) MPO (e) PPO

molecules and then incorporation of hexaanionic charge was done to gauge the significance of interactions of a negatively charged CdSe quantum dot with various diamines. The band gap energies of the CdSe quantum dots, thus optimized, are 1.58 and 0.42 eV, respectively, for the neutral and charged CdSe quantum dot. Though the HOMO energies for the uncharged and charged quantum dots are very different (-4.24 and 11.13 eV, respectively), the HOMO contours for the two are similar, being localized at the surface Se atoms. The LUMO energies (-3.34 and 11.55 eV) are also very different, and the LUMO shifts from the central metal atom to the peripheral selenium atoms (Figure 2).

COMBINED SYSTEM

With neutral CdSe quantum dot

The various optimized structures of the diamines considered were made to interact with the optimized Cd₁₃Se₁₆ quantum dot cluster (Chapter 3). The combined system of the two was then further put to geometry optimization to obtain the most stable structure and to know if there is any complexation or increase in coordination at the surface of the latter. For convenience, we have chosen one molecule of diamine in each of the cases in order to avoid steric interactions between the molecules on the

surface of the quantum dot. Table 2 lists the HOMO and LUMO energies of the various systems studied. On comparison with the corresponding values for the neutral CdSe quantum dot, we find that the HOMO (-4.24 eV) moves lower in all cases, except for HDA. The LUMO (-3.34 eV), however, moves up in all cases.

From the calculated bandgap values in Table 2, it becomes important to note that the bandgap of the combined systems of CdSe-diamines is higher than that of the isolated CdSe quantum dots for all the cases. The adsorbed species with aliphatic diamines, particularly EDA, have lower bandgap values. It is apparent that the HOMO energy moves up for the CdSe-HDA system because of transfer of electron density to the quantum dot from the diamine.

Table 2 Calculated electronic parameters (eV) for the optimized structures of CdSe quantum dots with various diamines

CdSe-Diamine	E(HOMO)	E(LUMO)	Bandgap	Binding Energy	Fermi Energy
CdSe-EDA	-4.31	-2.93	1.39	-113.13	-3.35
CdSe-HDA	-3.95	-2.50	1.45	-164.51	-2.95
CdSe-OPD	-5.00	-3.20	1.81	-142.56	-4.83
CdSe-MPD	-5.05	-3.22	1.83	-142.36	-4.90
CdSe-PPD	-4.92	-3.14	1.78	-142.09	-4.75

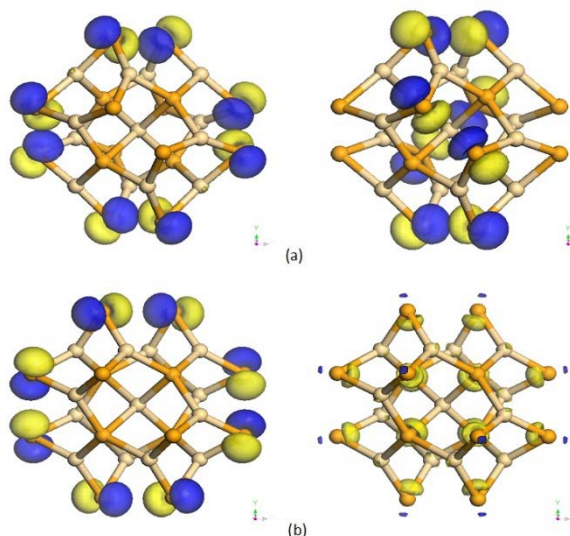


Figure 2. HOMO (left) and LUMO (right) plots of (a) neutral quantum dot (b) hexaanionically charged CdSe quantum dot

Amongst the aromatic diamines, the smallest bandgap and, hence, largest conductivity is observed for the para isomer. It has already been proved that on using 1,4-phenylenediamine linker (for CdSe quantum dot and other biomolecules or organic compounds), a 1000 fold

improvement in conductivity is observed²²⁻²³. Better supporting theoretical evidence is obtained from the HOMO-LUMO plots in Figure 5.3, where a clear difference is seen in the PPD (e) case, there being a presence of the PPD MOs in the HOMO, unlike the cases of the other diamines.

The adsorption energies are given in Table 3. It is immediately apparent that the binding of the aliphatic diamines is stronger and the adsorption process is highly exothermic. The reason is clear from the HOMO-LUMO energies given in Table 5.1. The aliphatic amines have HOMOs that are lower in energy than that of the CdSe quantum dot, while the aromatic amines have higher HOMOs. EDA is adsorbed more strongly than HDA on the surface of the quantum dot. Amongst the aromatic systems, the adsorption energy follows the reverse order of the relative stabilities, i.e. the least stable ortho isomer binds most strongly.

Table 3 Calculations of adsorption energies (eV)

CdSe- DA	Binding Energies			Adsorption Energy
	CdSe- DA*	DA	CdSe+DA	
CdSe- EDA	-113.13	-	-108.44	-4.69
CdSe- HDA	-164.51	-	-160.48	-4.03
CdSe- OPD	-142.56	-	-139.29	-3.27
CdSe- MPD	-142.36	-	-139.49	-2.87
CdSe-PPD	-142.09	-	-139.34	-2.75

*DA: Diamine, Binding energy of CdSe: -62.42 eV

On interaction with the amines, the overall Mulliken charges on the CdSe quantum dots are -0.229, -0.549, -0.295, -0.259 and -0.377e, respectively, for interaction with EDA, HDA, OPD, MPD and PPD. Thus, the quantum dot gains an overall negative charge on interacting with various aliphatic as well as aromatic diamines. Interestingly, there seems to be no correlation between the charge transfer and the adsorption energy, although the most strongly adsorbed diamine transfers the least amount of charge to the quantum dot.

The diamine molecules may be playing a role in stabilizing the energies of orbitals corresponding to the unfilled orbitals of the quantum dot cluster. In both the aliphatic as well as aromatic diamine cases with CdSe quantum dot, the magnitude of the adsorption energy decreases as the distance between the two amino groups increases.

The HOMO-LUMO plots of the neutral CdSe-diamine systems are given in Figure 3. They clearly show that the atomic orbitals of the surface selenium atoms with unsatisfied valencies are the ones which mainly play a role in the highest occupied and lowest unoccupied orbitals for

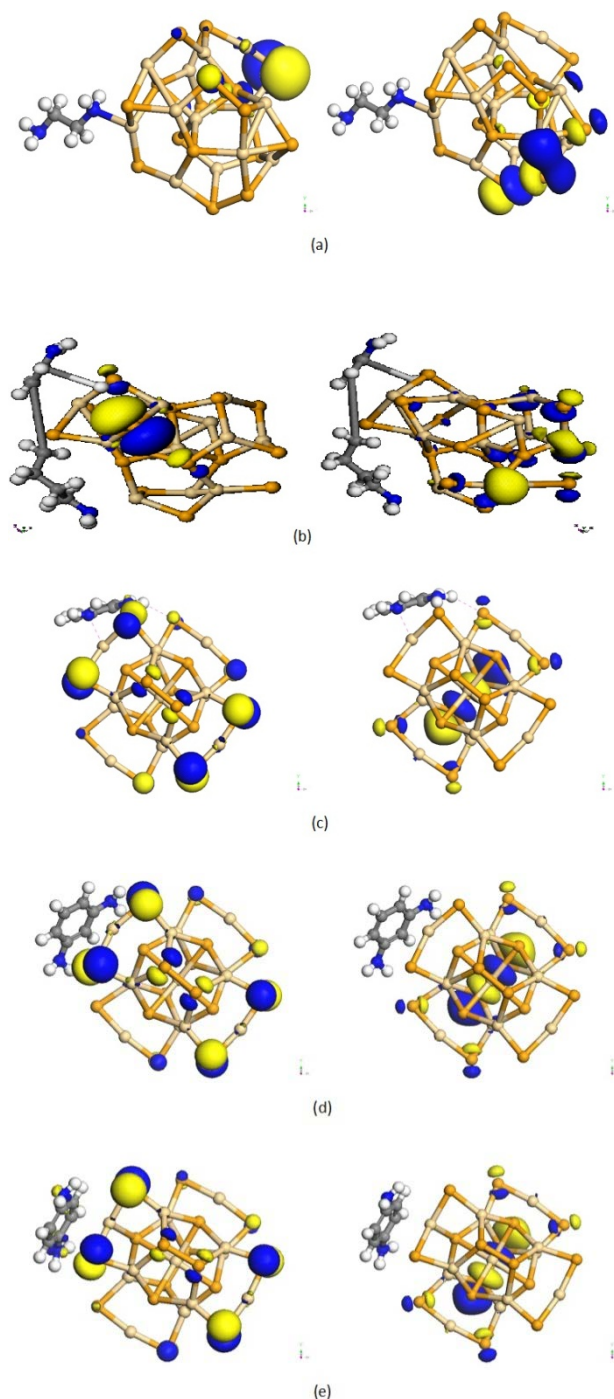


Figure 3. Homo (left) and LUMO (right) plots of neutral systems (a) CdSe-EDA (b) CdSe-HAD (c) CdSe-OPD (d) CdSe-MPD (e) CdSe-PPD

deciding the conducting properties, and that is the precise reason behind the small band gap of these compound systems. Both the HOMO and the LUMO densities are centred on the CdSe nanocluster, which makes the latter eligible to act both as an electron donor as well as an electron acceptor. In the case of aliphatic diamines, the nucleophilicity is transferred from the diamines to the CdSe quantum dot, the charge transfer being more in the case of HDA. Similarly in case of aromatic diamines also, the electron density is shifted from the aromatic diamines to the

CdSe quantum dot in the order of MPD < OPD < PPD, just in the order of the nucleophilicity. The HOMO for CdSe-PPD also has some contribution from the diamine. In PPD, the structure is highly stable due to symmetry, and the charge density is uniformly spread over the entire phenyl ring whereas the uniformity in the charge density cloud reduces in the other cases.

The fact that there is no correlation between the charge transfer and the adsorption energy indicates that the structural deformation caused by the adsorption may contribute to reducing the adsorption energy, as part of the energy would be used up for deformation of the cluster. Large structural deformations of both species, particularly in the case of the aliphatic diamines, are apparent. In the case of the aromatic diamines, the cluster retains its spherical shape, although some internal bond rearrangement occurs. Apart from causing structural changes in the CdSe nanocluster, the diamines themselves also undergo structural transformations to form new products with different properties. It is already established that the surface selenium atoms are not likely to be passivated, and it appears that surface passivation first and foremost occurs via ligand coordination to the surface metal atoms.²⁴ Similar observations have been observed in the present case. During geometry optimization, EDA oriented in such a fashion such that the nitrogen of one of the amine groups forms a bond with the positive centre on the neutral quantum dot i.e. the surface cadmium atom. This clearly indicates that the capping with diamines is feasible to enhance the interacting properties of the quantum dots. HDA gets dissociated to form CH₂=CH-NH₂ (i.e. ethenamine) and the rest of the molecule appears to be similar to n-butylamine where the nitrogen end gets tetrahedrally coordinated, with the fourth coordinate bond getting formed with a surface cadmium atom and the other end of the butylamine chain showing bonding of the terminal -CH₂ with a surface selenium atom (Figure 3).

Table 4 lists the deformation energies for the CdSe quantum dot and the diamine in each case. These were calculated as the difference in single-point energies of each component at the optimized geometry of the combined system, and the optimized geometry of each isolated system. An interesting observation is the stabilization of the CdSe quantum dot as a result of the adsorption of the diamine. This stabilization is largest for the aliphatic diamine, but quite high for the aromatic diamines too. The adsorbed molecule gets stabilized, the largest change being for OPD. The aliphatic diamine and the meta isomer suffer the least distortion. The stabilization of the quantum dot structure through a reorganization of the internal bonds, triggered by an adsorbent, is not a new phenomenon. Earlier, we had observed this for the case of MgO nanoclusters, which reconstructed into nanotubes on adsorption of carbonyls²⁶⁻²⁷. In that case, too, the new structure was found to be much more stable than the parent structure. The aromatic diamines after interaction with the CdSe quantum dot tend to lose planarity in their structure, making them non-aromatic in nature. This is clearly evident from the dihedral angles recorded for the phenyl ring after interaction, which very clearly deviate from the zero value requirements for the aromaticity.

Table 4 Deformation energy (eV) of the quantum dot and the diamine in each adsorbed system

System	Deformation energy	
	CdSe	Diamine
CdSe-EDA	-6.45	0.02
CdSe-OPD	-4.41	0.18
CdSe-MPD	-4.41	0.05
CdSe-PPD	-4.42	0.11

Interestingly, in all the cases of interaction between aromatic diamines and the cadmium selenide neutral quantum dot, the phenyl ring tilts towards the face of the quantum dot in order to interact with it. The dihedral angles for the same indicate that the π cloud on the aromatic ring interacts mainly with the quantum dot to alter the structural properties and enhance the electronic properties of the system.

With charged quantum dots

Much experimental evidence seems to indicate that the semiconductor nanoclusters might possess positive or negative surface charges depending upon the synthetic techniques used. The explanations of results based on various experimental research of these quantum dots therefore lacks one of the most important concepts, i.e. charge, which needs to be taken into consideration. There is a possibility that the quantum dot is positively/negatively charged due to the presence of extra atoms (either Cd or Se). In fact, most of the negatively/positively charged quantum dots are talked about only after they are capped with some electrophilic or nucleophilic species. Basic studies on the effects of charge on conductivity have had a profound impact on the discovery and design of new conducting materials²⁸⁻²⁹. Therefore, in order to gain an insight into the difference between neutral and surface-charged quantum dots, we have performed calculations on hexa-anionic complexes, i.e. Cd₁₃Se₁₆⁶⁻-diamine complexes.

Negative charge on the CdSe quantum dots leads to a decrease in binding energies of the CdSe-diamines systems. The bandgap for the EDA case enlarges, but declines for HDA on addition of charge on the CdSe quantum dot system. Consequently, the trend for the two aliphatic diamine systems reverses, with the former having a greater HOMO-LUMO gap. In the case of aromatic diamines, the CdSe-OPD charged system has the lowest bandgap and should exhibit superior conducting properties. This trend is opposite to that observed for the neutral systems. A clear difference is discernible in the behaviours of the three aromatic diamines. For OPD and PPD, the HOMO density is concentrated on the surface Se atoms and the LUMO density plot involves the orbitals of the diamine rings, which would easily accept the electron density from the electron rich centres of the quantum dot, and, hence, enhance the conducting properties on acting as a linker.

Table 5 Calculated electronic properties (eV) for the optimized structures of charged CdSe quantum dots with various diamines

CdSe-Diamine	E(HOMO)	E(LUMO)	Band gap	Binding Energy	Fermi energy
CdSe-EDA	8.51	10.48	1.97	-99.477	10.07
CdSe-HDA	9.56	10.44	0.88	-145.643	9.75
CdSe-OPD	8.72	10.41	1.69	-127.414	9.72
CdSe-MPD	8.39	10.27	1.88	-127.641	9.49
CdSe-PPD	8.45	10.43	1.99	-129.203	9.96

Table 6 Calculations of adsorption energies (eV) for charged CdSe quantum dots + Diamine systems

CdSe-Diamine	Binding energy			Adsorption Energy
	CdSe-DA	DA	(CdSe+DA)	
CdSe-EDA	-99.48	-46.03	-92.19	-7.29
CdSe-HDA	-145.64	-98.07	-144.23	-1.41
CdSe-OPD	-127.41	-76.87	-123.03	-4.38
CdSe-MPD	-127.64	-77.08	-123.24	-4.40
CdSe-PPD	-129.20	-76.92	-123.08	-6.12

*Binding energy of CdSe is -46.16 eV

The quantum dot efficiently acts as a donor in these cases due to its nucleophilicity, which is attributed to the hexanionic charge on it. In the case of the meta isomer, the LUMO is a d orbital on the central metal atom. In case of all aromatic diamines, it is noted that the phenyl ring tries to align itself in a direction parallel to the nearest surface bond of the CdSe quantum dot. The adsorption energies, given in Table 6, show that the reactions are more strongly exothermic than in the neutral cases, except for HDA. As shown in Figure 4, HDA undergoes destructive adsorption. The strongest adsorptions are found for EDA and PPD.

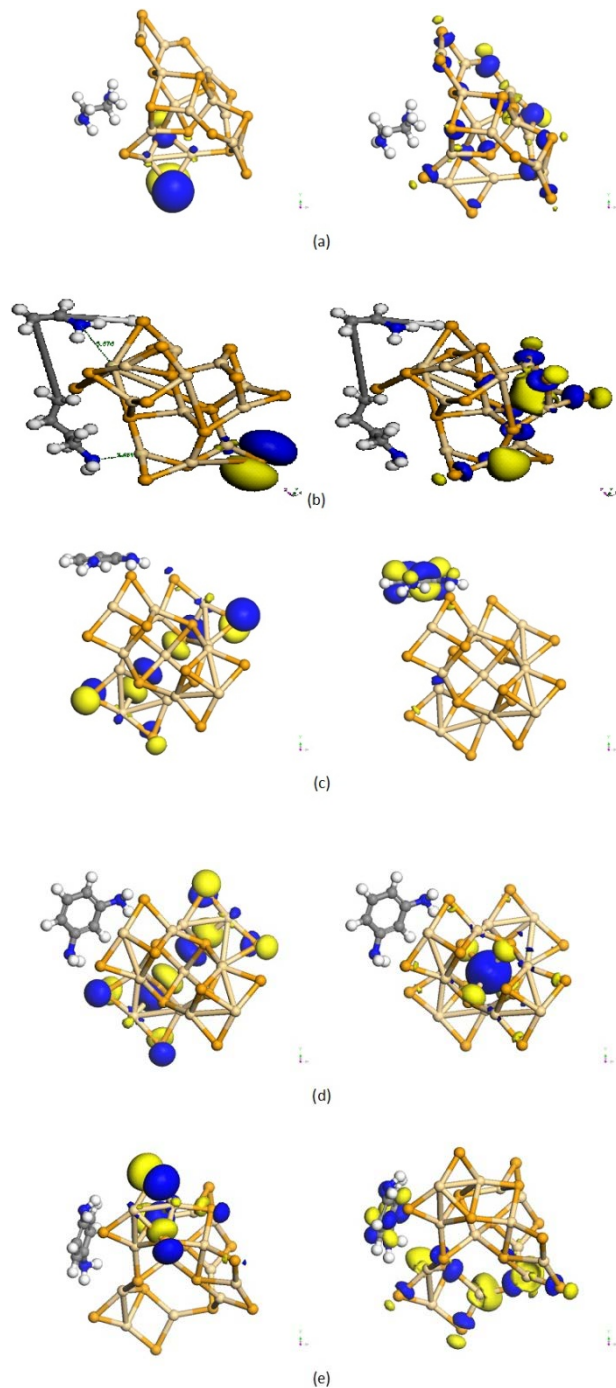


Figure 4. HOMO (left) and LUMO (right) plots of hexanionically charged (a) CdSe-EDA (b) CdSe-HDA (c) CdSe-OPD (d) CdSe-MPD (e) CdSe-PPD.

Figure 4 shows that considerable distortion occurs in all cases, particularly in the case of the aliphatic amines. On comparison of the structures, it is observed that there are drastic changes in the structure of the charged CdSe quantum dot as well. Certain bond distances increase to the extent of dissociation. It can also be clearly seen that due to the assignment of negative charge, the nucleophilic centres of the diamines move farther away from the quantum dot. Consequently, unlike the earlier cases discussed, the bond between nitrogen and cadmium in the case of EDA, and nitrogen and cadmium in the HDA case does not get formed.

The n-butylamine type analogue formed after dissociation from HDA remains attached to Se, but a Se-Cd bond gets cleaved. A hydrogen of the hydrocarbon chain gets cleaved from the HDA chain and gets attached to a selenium atom on the surface of the CdSe quantum dot. In almost all the considered cases, the CdSe cluster gets opened up in three-dimensional space in order to take care of the steric interactions due to the approach of the diamine towards the former.

From the Mulliken population analysis, it is found that the negative charge on the quantum dot decreases from an initial charge of $-6e$ to -5.948 , -5.851 , -5.694 , -5.761 and $-5.804e$, respectively, for interaction with EDA, HDA, OPD, MPD and PPD, indicating a small amount of charge transfer from the quantum dot to the diamine in each case. The effective charge on cadmium atoms does not change significantly compared to the neutral case, whereas the negative charge on Se increases slightly to $-0.2e$. The nucleophilicity on the Se changes in accordance with the type of diamine, the quantum dot is made to interact with. Apparently, addition of negative charge increases the electron density on the selenium atom, thereby increasing the bonding interactions of selenium with the incoming electrophiles. The reversal of the charge transfer effect is also one of the most important consequences of interaction with a negatively charged quantum dot.

CONCLUSIONS

It is very rightly put that as the particles' size becomes smaller, the ratio of surface atoms to those in the interior increases, leading to the surface properties playing an important role in the properties of the material. The understanding of the surface chemistry and structural properties of these combined systems is still far from complete and further studies are needed.

There are tremendous structural transformations in the structures of the molecular systems considered in this chapter. The symmetry of the aliphatic diamines (C_{2h}) and aromatic diamines (OPD (C_{2v}), MPD (C_{2v}), PPD (D_{2h})) gets distorted on interaction with CdSe to C_1 point group. The latter also become completely non-symmetrical (C_1) from tetrahedral (T_d) symmetry, in both the charged and neutral cases. It is clearly evident from the present studies that the uncharged quantum dot tends to undergo surface bound complexation with the diamine, but on the assignment of a negative charge, the nucleophilic centres tend to move away due to increased nucleophilicity of the quantum dot. OPD, MPD and PPD all can be treated as hole acceptors since their oxidation potential is lower than the valence band edge of CdSe. The charge transfer process occurs between the diamines (aliphatic and aromatic) and the quantum dot (anionic or neutral). As mentioned earlier, there is not much change in the charge on cadmium atoms but the nucleophilicity of the selenium atoms is enhanced on assignment of negative charge and so, the charge gets transferred from the CdSe quantum dot to the diamines in the charged CdSe case, but the trend in charge transfer is just the opposite when an uncharged CdSe quantum dot is considered.

The aliphatic diamine with a shorter methylene chain gets adsorbed better than the one with a longer hydrocarbon chain. The interaction tendencies of aromatic diamines remain more or less similar with the neutral quantum dot, but PPD shows maximum interaction. These interacting properties can be further explored on making these molecules also to interact with cationic quantum dots and then, the enhancement in the electronic properties can be achieved accordingly.

Surface bound aliphatic and aromatic diamine molecules play an important role in dictating the electronic and physical properties of the quantum dot. The internal structure of the quantum dot (as has been proved in the previous chapter) resembles the bulk to a certain extent. Even though the quantum dot considered in our case is too small, we believe the cluster used and the observations made after interaction with various aliphatic and aromatic diamines considered are sufficient for benchmark purposes of various theoretical methodologies.

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