

Colloidal Quantum Dots:

3. Molecular Dynamics Simulation of Quantum Dot Structure

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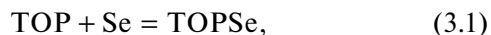
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Abstract—The results of molecular dynamics simulation of the crystal structure of the currently most studied CQDs, based on cadmium selenide nanoparticles, are presented, and issues concerning the structure of the ligand shell of these nanoparticles, primarily made of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) molecules, which act as a medium and as precursors in the chemical reaction that results in the formation of CQDs, are discussed in detail.

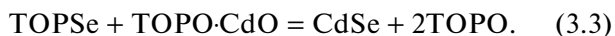
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3.1. TOP and TOPO Ligand Shell

As already detailed in the previous chapter, one of the main methods for the synthesis of semiconductor nanoparticles (NPs) with a narrow size distribution is high-temperature colloidal synthesis [1], which is carried out at temperatures of about 300°C in a special high-boiling solvent that exists in a liquid state at this temperature. For this purpose, C. Murray et al. [1] proposed to use a mixture of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO), which act as a medium and precursors for the chemical reaction that results in the formation of CQDs. Initially, the high-temperature synthesis method was used to produce cadmium chalcogenide (CdS, CdSe, CdTe) nanoparticles, with the TOP molecule forming a compound with a chalcogen molecule, for example, selenium, and TOPO forming a complex with cadmium:



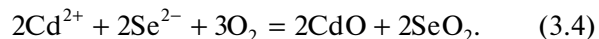
After mixing solutions containing selenium (3.1) and cadmium (3.2), nanoparticles are formed:



The TOP and TOPO molecules also act as stabilizing ligands, coating the particles and preventing their self-coagulation. Such a shell of ligands around NPs is to some extent similar to the densely packed monolayer surfactant shell in reverse micelles, which also prevents the coagulation of NPs synthesized in them [2]. After completion of the synthesis, the mixture is cooled to room temperature, at which the high-boiling solvent used becomes a solid. When storing nanoparticles in the solid phase of a mixture of initial

solvents, their optical properties are preserved quite well for a long time.

As a rule, NPs synthesized in this way are then dissolved in various weakly polar solvents, for example, in chloroform, and the residues of the initial solvent (TOP/TOPO mixture) are washed out by repeated precipitation of the solid phase of quantum dots with methanol, followed by washing with chloroform [3]. Nanoparticles transferred to chloroform are stable in size, but their optical properties gradually deteriorate in the presence of air [4]. The fastest deterioration in properties is observed for CdTe, and it is slightly slower for CdSe. Cadmium sulfide particles are the most stable. The optical properties of the particles do not deteriorate if they are in an inert atmosphere and in the dark. The reason for the deterioration of the NP properties is the interaction of the cadmium cation and chalcogenide anion with atmospheric oxygen [5]:



Oxidation reaction (3.4) leads to a significant decline in the luminescent properties of the nanoparticle. The stabilizing ligand molecule forms the missing bond with an atom located on the surface, thereby increasing its resistance to oxygen. For example, the TOP phosphorus coordinates the selenium atom and the TOPO oxygen coordinates the cadmium atom.

The luminescence quantum yield of NPs in chloroform quickly decreases unless additional measures are taken to stabilize it [4]. The stability of the optical properties of NPs also increases when using a mixture of hexadecylamine and octadecylphosphonic acid instead of TOP and TOPO as the initial solvent and ligand [6].

The quantitative composition of the shell around CdSe NPs was studied already in the first experimental works [3, 7]. Tributylphosphine (TBP) was used instead of TOP in [3], assuming that it would completely give way to TOPO in the shell. It was found that the fraction of surface atoms coordinated by ligands varies from 0.3 to 0.6 depending on the size of the NPs. Cases in which this proportion exceeds 0.5 are explained by the presence of residual amounts of TBP. L. Becerra et al. [7] studied NPs that had a diameter of 3.7 nm and consisted of approximately 1000 atoms directly in the initial TOP/TOPO solvent mixture without washing it. They estimated that about 300 atoms of such NPs are surface atoms and the shell contains 150–170 TOPO ligands, which are coordinated to Cd atoms. Thus, it can be concluded that all Cd atoms on the NP surface are coordinated by TOPO ligands.

The structure of the ligand shell around TOPO-capped CdSe NPs of different sizes without a solvent was also studied through computer simulation in [8–10]. TOPO molecules were supposed to be rigidly bound to Cd atoms, and their shortened analogue trimethylphosphine oxide was used in [10]. Although E. Rabani [9] assumed TOPO to be covalently bound to Cd, he implemented a procedure for preparing NP shell that made it possible to determine the fraction of surface Cd atoms bound to TOPO. This fraction varied from 1.0 for the smallest particles (radius 0.7 nm) to 0.7 for NPs of the maximum size (radius 1.8 nm).

Computer simulation of CdSe NPs, both with and without a shell, was the subject of research in [11, 12]. For example, O. Voznyy [11] studied a shell of acetic acid molecules covalently bound to Cd. Z. Fan et al. [12] studied the structural transformations of CdSe NPs without a ligand shell in vacuum.

In [13], we studied the composition and structure of the mixed ligand shell of TOP/TOPO CdSe NPs, as well as a shell consisting only of TOPO, in solvents of different polarities—chloroform and methanol—by the molecular dynamics method. The case without a solvent was also considered. In contrast to [8–12], the condition of covalent bonding between ligand molecules and NP atoms, which allows ligand molecules to move freely into the solvent during the modeling process, was not used in [13]. Apparently, this approach gives the most complete picture of the qualitative and quantitative composition of the shell and, in addition, makes it possible to find out how the solvent polarity affects the composition and explain the experimentally observed facts described above.

Molecular dynamics calculations in [13] were carried out using the freely available software package NAMD 2.10 [14]. We used the computing power of the “Lomonosov” supercomputer at the Moscow State University [15], the Interdepartmental Supercomputer Center of the Russian Academy of Sciences (<http://www.jscs.ru>), and the Institute for Problems

of Chemical Physics of the Russian Academy of Sciences (<http://www.icp.ac.ru>), with 8 to 32 conventional and up to 8 graphics processors being employed.

A cadmium selenide nanoparticle was modeled as follows. 499 Se atoms and 499 Cd atoms were randomly located at the sites of a $10 \times 10 \times 10$ cubic lattice. The parameters of interatomic interactions—charges and Lennard-Jones potential—were borrowed from [16]. The starting distance between the nearest atoms was 0.4 nm so that the atoms could move freely. The cell volume was kept constant. The temperature was first slowly increased from 0 to 2000 K, held at 2000 K to better mix the atoms, and then slowly cooled to a final value of 298.15 K. The total trajectory length was 1000 ns. As a result, an almost ideal spherical CdSe NP with a radius of about 1.85 nm was formed, which corresponds to the value of the bulk density of the CdSe substance.

A shell of an equal number of TOP and TOPO molecules was created around the prepared CdSe NPs. The total number of ligand molecules was 60, 100, and 150. To create this shell, we used the computer program described in [17]. The program alternately positioned the TOP and TOPO molecules evenly over a sphere of a given radius (2.2 nm) without reference to specific surface Cd or Se atoms. This system was equilibrated for 100 ps.

At the next stage, an environment of solvent molecules—pure chloroform or pure methanol—was built around particles with different amounts of ligands. For this purpose, we also used the program described in [17], replacing hexane molecules with chloroform or methanol and placing them at distances corresponding to the densities. The thickness of the solvent layer was 4 nm, which corresponds to approximately 7000 molecules of chloroform or 13000 molecules of methanol.

Thus, a total of several systems were studied with different amounts of TOP/TOPO ligands in chloroform and methanol and without solvent, as well as another system in which there were 150 TOPO molecules in chloroform. The starting characteristics of all systems are presented in Table 3.1.

For the systems with a solvent, periodic boundary conditions and an isobaric–isothermal NPT ensemble were used. A pressure of 1 atm was maintained using the Berendsen barostat. For the solvent-free systems, spherical boundary conditions were used, with the sphere radius being significantly larger than the size of the modeled object. The temperature was maintained in all cases using a rate override procedure. For rapidly decreasing Lennard-Jones interactions, a cutoff radius of 1.3 nm was used. Integration of classical equations of motion was carried out using the Verlet scheme with speeds in steps of 1 fs. The constructed systems were first equilibrated for 100 ps, and then the calculation itself was carried out for 10–15 ns.

To describe the Cd^{2+} and Se^{2-} ions, we used the model from [16], in which the absolute value of charges for these ions is 1.18. The absolute values of charges for the O and P atoms in the TOP and TOPO molecules were also 1.18. This charge on P in TOPO is slightly higher than the value +1.13 obtained in [18], in which the structure of trimethylphosphine oxide near CdSe NPs was optimized using DFT, or the value +1.031 used in MD simulation of phosphine oxide with phenyl substituents [19]. The oxygen charge is significantly greater in absolute value than the values from the same works (-0.81 , -0.803 , respectively). The greater negative charge on the O atom may cause stronger binding of the TOPO molecule to the NP surface. The charge on the phosphorus atom in TOP also significantly exceeds the charge of +0.75 used in MD calculations of the trimethylphosphine molecule [20]. This may also be the reason for the stronger interaction of the TOP molecule with the CdSe surface. The difficulty in choosing charges for phosphorus and oxygen is due to the lack of works in which the TOP and TOPO ligands would not be attached to the NP surface, leaving the particle itself nonrigid. The charges for the carbon and hydrogen atoms were borrowed from the CHARMM27 force field, while the positive charge of phosphorus in the TOP molecule was compensated by additional negative charges for the carbon atoms near phosphorus. Models for chloroform and methanol molecules were borrowed from [21, 22].

In this simulation, the radius of a particle consisting of 499 molecules resulting from self-assembly of individual cadmium and selenium ions was approximately 1.8–1.9 nm. Each Se atom was surrounded by four Cd atoms, and each Cd atom, by four Se atoms. At the same time, the structure of the particle is not perfectly ordered: it has defects, both on the surface and in the bulk (Fig. 3.1). Of 998 atoms in the particle, there were 198 selenium atoms and the same number of cadmium atoms on its surface.

This result differs significantly from the theoretical estimate of ~ 300 surface atoms obtained in [7] for CdSe NPs with the same size and the same number of atoms. Let us estimate the number of atoms that should be on the surface of a CdSe particle composed of 998 atoms and having an average calculated radius of 1.867 nm. If we assume that the Cd and Se atoms are located on the surface in a smooth monolayer, then its thickness should be 0.185 nm; this is the average diameter of one atom, calculated based on the average atomic volume. The volume of a spherical layer of this thickness is 27% of the volume of the entire ball. Therefore, under the assumption made, there should really be about 30% of surface atoms as in [7]. However, in reality, the surface atoms do not form a smooth monolayer: some atoms are slightly displaced relative to their neighbors. As a result, the thickness of the surface layer is approximately 1.5 times greater and its volume fraction is 39%. This agrees well with the man-

Table 3.1. Characteristics of the simulated systems: initial (subscript 1) and final (subscript 2) quantities of TOP and TOPO molecules

No.	$N_{\text{TOP},1}$	$N_{\text{TOPO},1}$	Solvent	$N_{\text{TOP},2}$	$N_{\text{TOPO},2}$
C1	30	30	—	30	30
C2	30	30	Chloroform	24	30
C3	30	30	Methanol	16	30
C4	50	50	—	49	50
C5	50	50	Chloroform	42	50
C6	50	50	Methanol	31	50
C7	75	75	—	37	68
C8	75	75	Chloroform	38	63
C9	75	75	Methanol	34	69
C10	—	150	Chloroform	—	126

ually calculated number of atoms on the surface. Subsequently, the number 396 was used to calculate the fraction of surface atoms bound to ligands.

The surface area formed by CdSe NPs is approximately 44 nm². According to quantum chemical calculations of a trimethylphosphine oxide molecule with a CdSe particle [18], the wide part of the ligand molecule is located at a distance of 0.4 nm from the surface of the solid CdSe particle (the sum of the Cd–O distance and the O–P bond length). If we take into account thermal motion, then this distance can be taken as 0.5 nm. As a result, the area of the sphere on which the wide parts of the TOP and TOPO molecules are located is about 70 nm². The number of ligand molecules can be calculated based on the area covered by 1 molecule, but this value is not known. For an initial rough estimate, we can assume that it is 0.75 nm² [17]. Then, around 94 ligand molecules, for

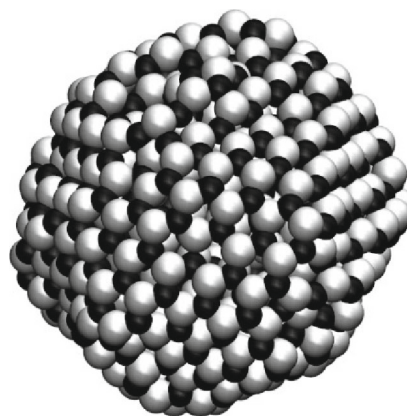


Fig. 3.1. A CdSe nanoparticle obtained as a result of self-assembly from ions after 1000 ns simulation; cadmium atoms are represented by black balls, and selenium atoms are given in white.

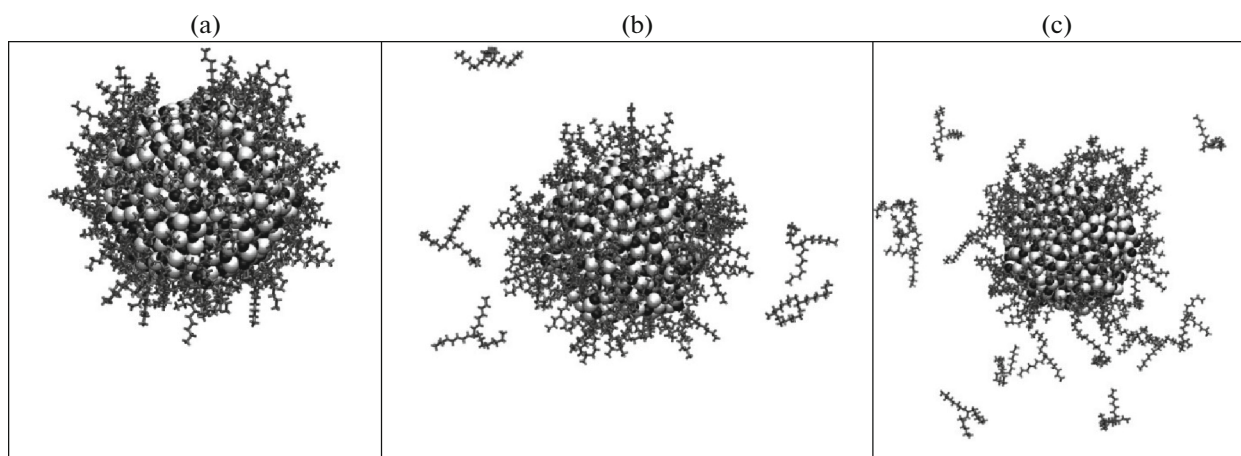


Fig. 3.2. Systems (a) 1, (b) 2, and (c) after 15 ns of simulation. Cadmium atoms are represented by black balls, selenium atoms are in white, and TOP and TOPO molecules are in gray (solvent not shown).

example, 47 TOP and 47 TOPO, can optimally be placed around the existing CdSe particle.

In [13], we selected three different numbers of ligand molecules. The first number is 100, which is presumably the optimal one. The second number is 60. Ligands taken in this quantity will be able to freely fit on the NP surface and will not displace each other from the surface. In this way it will be possible to assess how tightly TOP and TOPO are connected in the absence of competition between themselves. The third number of ligands is 150 molecules. This is obviously an excessive number; as a result, there will be competition between ligands for space on the surface. As a result, a dense coat of ligand molecules will remain on the surface.

In systems C1–C3, 30 TOP and 30 TOPO molecules were uniformly distributed on the surface of CdSe NPs at the beginning of the simulation. In system C1, there was no solvent around the particle; it was chloroform in system C2 and methanol in system C3.

In system C1, not a single ligand molecule left the NP surface throughout the entire molecular dynamics time trajectory (15 ns) (Fig. 3.2a). In this case, the particle was not completely covered; there were large free areas on it. One of them is clearly visible in the same figure. In systems C2 and C3, some ligand molecules gradually moved into the bulk solvent during the first nanoseconds of the calculation (Figs. 3.2b, 3.2c). In this case, only TOP molecules moved, whereas TOPO remained entirely on the surface.

In the case of chloroform, there were 6 TOP molecules released versus 14 in the case of methanol (Table 3.1). It should be noted that the numbers of molecules moved into the solvent are different in these systems, so such movement cannot be attributed to a poor starting location of the molecules. The transfer of

TOP molecules to chloroform can be explained by the solubility of a nonpolar molecule in a nonpolar solvent. Even the increased interaction energy of TOP with the surface does not prevent such a transition. Methanol is much more polar than chloroform, so it would be logical to expect fewer or no TOP molecules in its volume. The larger number of TOP in methanol can be explained by the fact that methanol, as a polar liquid, interacts well with Cd^{2+} and Se^{2-} ions and therefore displaces TOP from the CdSe surface. If we used lower energy of TOP binding to the surface, then the amount of released TOP molecules would possibly become greater. However, what is important to us at this stage is the very fact of such a transition from the free surface in the presence of a solvent.

In systems C4–C6, 50 TOP and TOPO molecules were located on the surface at the initial point of time. There was no solvent in C4, but there were chloroform in C5 and methanol in C6.

In the C4 system, only 1 ligand molecule (TOP) left the nanoparticle surface. At the same time, almost no open areas were observed on the surface. Deformation of the particle itself, for example, as happens with the core of a reverse micelle when an excess amount of surfactant molecules is present on its surface [17, 23], also did not occur. The Cd^{2+} and Se^{2-} ions interact with each other only through Coulomb and van der Waals interactions, so the core can be freely rearranged if necessary. Since this does not happen, the considered amount of the ligand (about 100) can be placed on the NP surface. Although the packing of molecules is very dense, we cannot confidently say that it will be impossible to accommodate more molecules. In systems C5 and C6, 8 and 19 TOP molecules gradually moved, respectively, while all of the TOPO remained on the surface. As a result, small ligand-free areas were observed on the surface of the particle. Therefore, the observed TOP transfer is due to the

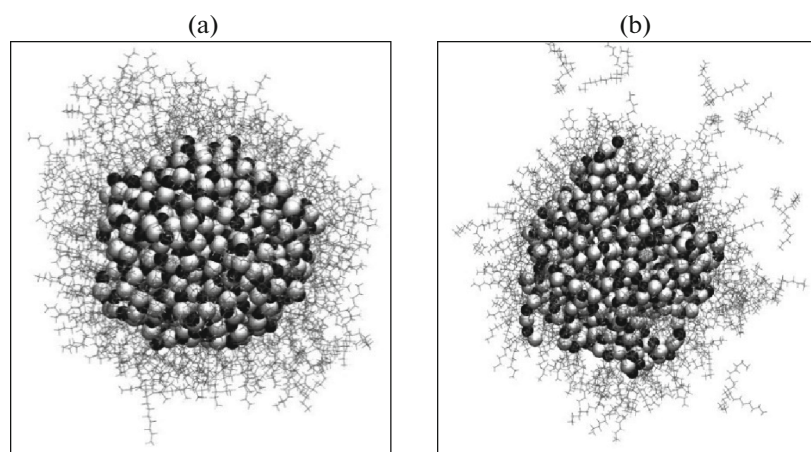


Fig. 3.3. A CdSe nanoparticle in systems (a) 7 and (b) 10 after 10 ns.

presence of solvent in the system, not to an excess number of ligand molecules or their unfavorable starting location. To check how many ligand molecules can maximally fit on the surface of the CdSe particle in question, systems were considered in which the ligand was obviously in an excess amount.

In systems C7–C9, at the beginning of the simulation, 75 TOP and TOPO molecules were placed on the surface. The particle was without a solvent in system C7, and it was surrounded by chloroform in system C8 and methanol in system C9.

In all systems of this series, a mass departure of ligand molecules was observed already at the very beginning of the simulation. In each case, a little more than 100 ligand molecules remained on the surface (Table 3.1), that is, approximately the same as in the C4 system. From 80 to 90% of escaped molecules are TOP. At the same time, the particle itself did not undergo deformation (Fig. 3.3a), thereby indicating that there is enough space on the surface of the particle in question for at least 105 ligand molecules.

Thus, the fact that 105 molecules remained in the solvent-free system gives reason to believe that this particular amount of the ligand is the optimal quantity capable of closely packing around CdSe NPs with a radius of 1.86 nm. This number is consistent with the results reported in [3], according to which the ratio of the numbers of P and Cd atoms for CdSe NPs with a radius of about 1.8 nm is 0.21. The same value also obtained in the given case as well: $105/499 = 0.21$. Since about 396 atoms of this particle are surface atoms out of 998 atoms and each atom coordinates no more than one ligand molecule, the proportion of passivated surface atoms is 27%. This quantity is also consistent with the published result [3], according to which this proportion for particles of large radii is 30%. However, the value of this fraction obtained in this calculation differs significantly from the results reported by L. Becerra et al. [7], who studied a particle

of the same size. In [7], this proportion was almost 55%. This value was obtained in [7] by dividing 160 (the number of ligands) by 300 (the number of surface atoms). In this calculation, it was possible to manually count the number of atoms on the surface. Regarding the number 160, which was also obtained in [7] by interpreting the results of experiments using mathematical models, one can reason as follows. In systems C7–C9, 150 ligand molecules were initially introduced, of which only slightly more than 100 remained on the surface, despite the fact that overestimated values of the interaction energies of ligands with NP atoms were used (Table 3.1). Since TOP molecules tend to leave the surface in the presence of a solvent even if there is free space on the surface, we prepared a C10 system in which 150 TOPO molecules were placed on a CdSe particle in the presence of chloroform. In this system, 126 TOPO molecules remained on the surface and the rest went into chloroform. In this case, the particle was strongly deformed (Fig. 3.3b), indicating an excess amount of the ligand. Due to excessively strong binding to the surface, these excess TOPO molecules do not leave the surface. If a smaller absolute charge on the oxygen atom is used, the binding is not so strong; as a result, more molecules escape from the surface and the particle is not deformed. Thus, only no more than 126 TOPO molecules, which strongly interact with the particle surface, can be accommodated on the surface, but not 160 molecules.

For NPs of all systems (Table 3.1), pair correlation functions of the Cd^{2+} ion and the O atom of TOPO molecules were constructed. Their analysis shows that these oxygen atoms are located at a distance of about 0.19 nm from the cadmium atoms (Fig. 3.4), which is slightly less than the corresponding distance obtained in [18].

It can be assumed that as a result of synthesis, the CdSe nanoparticle is covered with a dense layer of

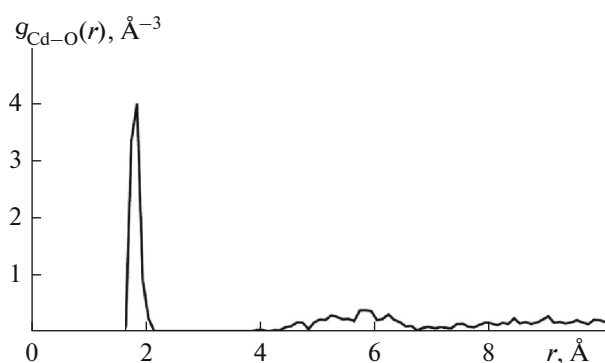


Fig. 3.4. Pair correlation function for $\text{Cd}^{2+}-\text{O}$ (TOPO) in the C4 system.

TOP and TOPO ligands. Since the TOP molecule is bound weaker than the TOPO molecule, it leaves the surface more easily. While the particle is in the initial TOP/TOPO solvent, another molecule takes the place of the departed one; as a result, an equilibrium ratio of the amounts of TOP/TOPO ligands is established and, most importantly, a dense shell of ligands around the particle is preserved, protecting it from oxidation. After replacing the original solvent with another (chloroform or methanol), the ligand (TOP) molecules also continue to gradually pass into the solvent, resulting in the appearance of uncovered areas on the particle surface, which are available for oxidation. This is consistent with the results of [4].

Thus, to increase the stability of NPs to oxidation, it is necessary to use a ligand that interacts better with the CdSe surface. In addition, it is possible to increase the proportion of passivated atoms, for example, by using ligands with unbranched nonpolar moieties. As follows from the results discussed above [13], the presence of even one oxygen atom significantly increases the strength of binding to the particle. Therefore, instead of TOP and TOPO, it is better to use alkylphosphonic (general formula $\text{RPO}(\text{OH})_2$) and alkylcarboxylic (RCOOH) acids. According to some studies [6], alkylamines (RNH_2) and alkylmercaptans (RSH) also bind well to the surface.

3.2. TOP, TOPO, ODP, and HDA Ligand Shell

For more effective passivation of surface centers during the synthesis of CQDs or during their postpreparative processing, various phosphonic acids, amines, and other substances are used, in particular octadecylphosphonic acid (ODPA), hexadecylamine (HDA), and their analogs [6]. Molecules of these compounds can be incorporated into the ligand shell of CQDs and, replacing the TOP and TOPO molecules in it, significantly improve the luminescent properties of CQDs [24, 25]. ODP and HDA molecules have only one hydrocarbon chain in their structure, which allows more molecules of these ligands to

be packed into the shell. In addition, ODP and HDA may interact more strongly with Cd than TOPO.

Following [26], we consider the issue of the stability of mixed ligand shells of CdSe CQDs from TOP, TOPO, ODP, and HDA molecules in various ratios, with the simulation being carried out both in vacuum and in chloroform or methanol. The all-atom approximation of all molecules allows one to calculate the proportion of passivated surface atoms and evaluate the relative strength of binding of ligands to the CQD surface. To conduct a computer experiment, CdSe nanoparticles with radii of 1.9 and 4.5 nm were used, which made it possible to reveal the role of surface curvature in the structure of the ligand shell.

The construction of a CdSe nanoparticle with a radius of 4.5 nm was carried out in the same way as described in detail above for a particle of 1.9 nm. For this purpose, 6911 Se atoms and the same number of Cd atoms were randomly located at the sites of a $24 \times 24 \times 24$ cubic lattice. The starting distance between the nearest atoms was 0.4 nm, so that the atoms could move freely. The cell volume was kept constant. The temperature was first slowly increased from 0 to 2000 K, held at 2000 K to better mix the atoms, and then slowly cooled to a final value of 298.15 K. The total trajectory length was more than 300 ns. As a result, an almost ideal spherical CdSe CQD with a radius of about 4.5 nm was formed, which corresponds to the bulk density value of the CdSe substance.

To count the number of surface atoms, a computer program was developed that according to a given criterion, sorted all atoms of a CdSe nanoparticle, classifying them as either bulk or surface. This criterion was formulated in such a way that the number of surface atoms for a CQD with a radius of 1.9 nm coincided with the number calculated manually in [13]. As a result of applying this program, it was found that among 13822 CdSe CQD atoms with a radius of 4.5 nm, the surface atoms made approximately 2400 or 17%. A geometric estimate based on the density of bulk CdSe and the surface layer thickness described in [13] also leads to the same value, which will be used further for calculations.

The starting compositions of all systems are presented in Table 3.2. The quantities of ligand molecules were selected based both on the results regarding the total number of TOP and TOPO molecules densely covering the surface of CQDs with a radius of 1.9 nm, which were obtained in [13], and on the experimental procedure for the actual synthesis of these CQDs using the ligands TOP, TOPO, and ODP [24].

Some ligand-coated nanoparticles were simulated without solvent (in vacuum). Such calculations make it possible to determine the number of molecules in a densely packed shell. The use of a solvent (chloroform, methanol) allows one to determine how strongly a particular ligand binds in various solvents. Explicit consideration of the solvent significantly increases the

Table 3.2. Starting (in parentheses) and final amounts of TOP, TOPO, ODPa, and HDA molecules

No.	<i>R</i> , nm	Solvent	ODPA	TOPO	TOP
C0	1.9	—	—	68 (75)	37 (75)
C1	4.5	—	—	299 (303)	126 (303)
C2	1.9	—	24 (30)	49 (53)	30 (53)
C2	1.9	Chloroform	21 (30)	49 (53)	23 (53)
C2	1.9	Methanol	21 (30)	48 (53)	28 (53)
C3	1.9	—	130 (160)	26 (30)	11 (30)
C3	1.9	Chloroform	115 (160)	25 (30)	11 (30)
C3	1.9	Methanol	75 (160)	19 (30)	3 (30)
			HDA	TOPO	TOP
C4	1.9	Chloroform	30 (30)	53 (53)	12 (53)
C5	1.9	Chloroform	150 (160)	30 (30)	11 (30)

Table 3.3. Effective charges of underlined atoms

Atom	<i>q</i> , e^-	Atom	<i>q</i> , e^-	Atom	<i>q</i> , e^-
<u>Cd</u> Se	+1.18	C ₁₆ H ₃₃ <u>NH</u> ₂	-0.8	<u>CH</u> Cl ₃	+0.082
Cd <u>Se</u>	-1.18	C ₁₆ H ₃₃ <u>NH</u> ₂	+0.4	<u>CH</u> Cl ₃	-0.087
C ₁₈ H ₃₇ <u>P</u> O(OH) ₂	+1.5	(C ₈ H ₁₇) ₃ <u>P</u> O	+0.78	<u>CH</u> ₃ OH	+0.228
C ₁₈ H ₃₇ <u>P</u> O(OH) ₂	-0.78	(C ₈ H ₁₇) ₃ <u>P</u> O	-0.78	<u>CH</u> ₃ OH	0
C ₁₈ H ₃₇ P <u>O</u> (H) ₂	-0.57	(C ₈ H ₁₇) ₃ <u>P</u>	+0.78	<u>CH</u> ₃ <u>O</u> H	-0.66
C ₁₈ H ₃₇ P <u>O</u> (H) ₂	+0.21	<u>CH</u> Cl ₃	+0.179	<u>CH</u> ₃ <u>O</u> H	+0.432

computational complexity of the problem, while the use of a single-atom model, as was proposed for hexane molecules when modeling reverse micelles in [27], is not justified due to the small number of atoms in the chloroform and methanol molecules compared to hexane.

The effective charges of the most important atoms are presented in Table 3.3. To describe the Cd and Se atoms, we used the model from [16]. The molecular models of TOP and TOPO were taken from [13] with slightly lower charges on P and O in absolute value. The charges for oxygen and phosphorus in ODPa were borrowed from the CHARMM27 force field for phosphate residues in protein molecules, and the amino acids arginine and lysine (neutral form) were taken for charges of the atoms of the HDA amino group. The charges for the carbon and hydrogen atoms are also borrowed from CHARMM27, with the positive charge of phosphorus in the TOP molecule being compensated by additional negative charges on the carbon atoms near phosphorus. Models for chloroform and methanol molecules were taken from [21, 22].

Around a CdSe nanoparticle with a radius of 4.5 nm at the beginning of the simulation, 303 TOP and TOPO molecules were uniformly located. Since the behavior of TOP and TOPO molecules in the pres-

ence of solvents has already been studied in [13], the main interest was aimed at studying the number of ligands in a close-packed layer covering the surface of such a radius. Therefore, there was no solvent around the particle. After 10 ns of computation, the number of molecules remaining in the shell was counted. In [13], for a nanoparticle with a radius of 1.9 nm, this calculation was carried out directly, visually assessing the distance of each molecule from the surface.

It is unreasonable to perform calculation of this kind around a large particle, so a computer program was written that estimated the distance of the phosphorus atom in TOP and the oxygen atom in TOPO from the nearest Se and Cd atoms, respectively. If this distance is greater than a certain value, then the molecule was considered to be outside the nanoparticle shell. This distance was 0.8 nm for TOP and 0.6 nm for TOPO. As a result of applying the program to a CQD with a radius of 4.5 nm, the numbers of TOP and TOPO molecules remaining in the shell are 126 and 299, respectively (System C1). Taking into account the total number of surface atoms, the proportion of passivated atoms is 18%. For the particle with a radius of 1.9 nm, this fraction was found to be 26% (System C0) [13].

Thus, the proportion of passivated centers depends on the curvature radius of the nanoparticle surface.

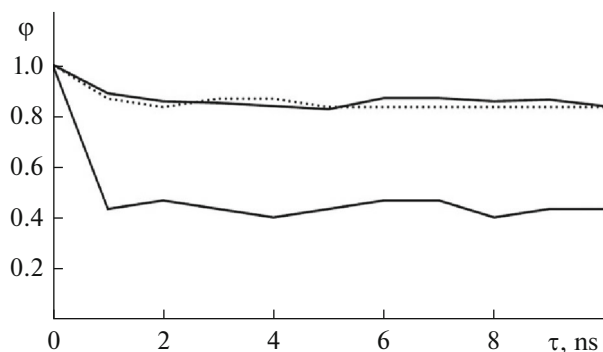


Fig. 3.5. The proportion of ligand molecules (ϕ) in the CdSe CQD shell relative to the initial value at different times ($\tau = 0\text{--}10$ ns) in the C3–vacuum system. The dotted, upper solid, and lower solid curves refer to ODPA, TOPO, and TOP, respectively.

This can be explained by the fact that the TOP and TOPO molecules have a compact polar group consisting of only one or two atoms and the wide nonpolar moiety of three octyl chains, the effective transverse size of which determines the maximum density of the ligand shell. Based on the above data, it is possible to calculate the cross-sectional area of the TOP and TOPO molecules, which determines the maximum density of their packing in the ligand shell, using the formula:

$$\sigma_{\text{TOP}} = 4\pi(R+h)^2/N_{\text{TOP}}, \quad (3.5)$$

where N_{TOP} is the total number of TOP and TOPO molecules in the ligand shell; R is the nanoparticle radius; and h is the distance from the nanoparticle surface, which determines the densest packing of the ligand shell. Assuming that the area σ_{TOP} does not depend on R at a distance h from the CQD surface, we can calculate these h and σ_{TOP} values. Taking into account that $R_1 = 1.9$ nm, $N_{\text{TOP}}^{(1)} = 105$, $R_2 = 4.5$ nm, and $N_{\text{TOP}}^{(2)} = 425$, we obtain from the equation

$$\frac{(R_1+h)^2}{N_{\text{TOP}}^{(1)}} = \frac{(R_2+h)^2}{N_{\text{TOP}}^{(2)}}, \quad (3.6)$$

the value $h = 0.67$ nm. Substituting the value of h found from Eq. (3.6) into Eq. (3.5), we find $\sigma_{\text{TOP}} = 0.79$ nm².

From the above modeling data for CdSe nanoparticles with a radius of 1.9 or 4.5 nm, we can calculate the effective area per conventional CdSe molecule on the nanoparticle surface:

$$\sigma_{\text{CdSe}} = 4\pi R^2/N_{\text{CdSe}} \approx 0.22 \text{ nm}^2, \quad (3.7)$$

where N_{CdSe} is half of the total number of atoms on the surface of a CQD with radius R . The calculated values of σ_{CdSe} for CQDs of radii 1.9 and 4.5 nm approximately coincide.

Combining Eqs. (3.5) and (3.7), we then obtain a formula that determines the degree of passivation (η) of surface centers by the TOP and TOPO ligand shell depending on the nanoparticle radius:

$$\begin{aligned} \eta &= 0.5N_{\text{TOP}}/N_{\text{CdSe}} \\ &= 0.5(\sigma_{\text{CdSe}}/\sigma_{\text{TOP}})(1+h/R)^2. \end{aligned} \quad (3.8)$$

For the limiting case of a flat surface, Eq. (3.8) gives the value $\eta_{\infty} = 14\%$; for nanoparticles with a radius of 4.5 or 1.9 nm, η is 18 or 25%, respectively; and for nanoparticles of the smallest physically significant radius of ~ 1 nm, η approaches 40%.

Mixed ODPA, TOP, and TOPO ligand shells were considered. Around the particle with a radius of 1.9 nm at the beginning of the simulation, two sets of ligands ODPA, TOP, and TOPO were deposited: (1) 30, 53, and 53 (System C2) and (2) 160, 30, and 30 (System C3), respectively. In each case, the particle was either without a solvent or in chloroform or methanol (Table 3.2).

At the end of the computation, the number of molecules remaining in the shell was calculated. For TOP and TOPO, the computer program described above was used with the same settings. For ODPA, counting was done either manually (for some systems) or through a program. The program screened out ODPA molecules for which the distance from the phosphorus atom to the nearest cadmium or selenium atom exceeded 0.6 nm. The value of 0.6 nm was chosen so that the number of ODPA molecules calculated by different methods was almost the same. This distance of 0.6 nm coincides with the cutoff distance for rejection of TOPO molecules.

The process of transfer of ligand molecules from the CQD shell to the environment may take some time and may not be completed in 10 ns. To study this issue, the program was used for one of the systems (C3–vacuum) to calculate how many ligand molecules are retained in the shell at different times (Fig. 3.5). Figure 3.5 clearly demonstrates that the release of the main number of ligand molecules from the shell occurs within the first 1–2 ns of the computation; subsequently, some fluctuations in the number of molecules are observed. Therefore, a trajectory length of 10 ns is sufficient for the release of all necessary molecules.

As a result of the calculations, it was found that first, ODPA molecules are retained in the shell in approximately the same way as TOPO (Fig. 3.5) and, second, they also gradually leave the shell in the presence of the solvent (Table 3.2). This finding is slightly inconsistent with the results of experimental studies, according to which the binding strength of ODPA should be stronger than that of TOPO [25]. The result of this discrepancy may be that ODPA in the shell is in one of the ionic forms, not in the neutral form. This

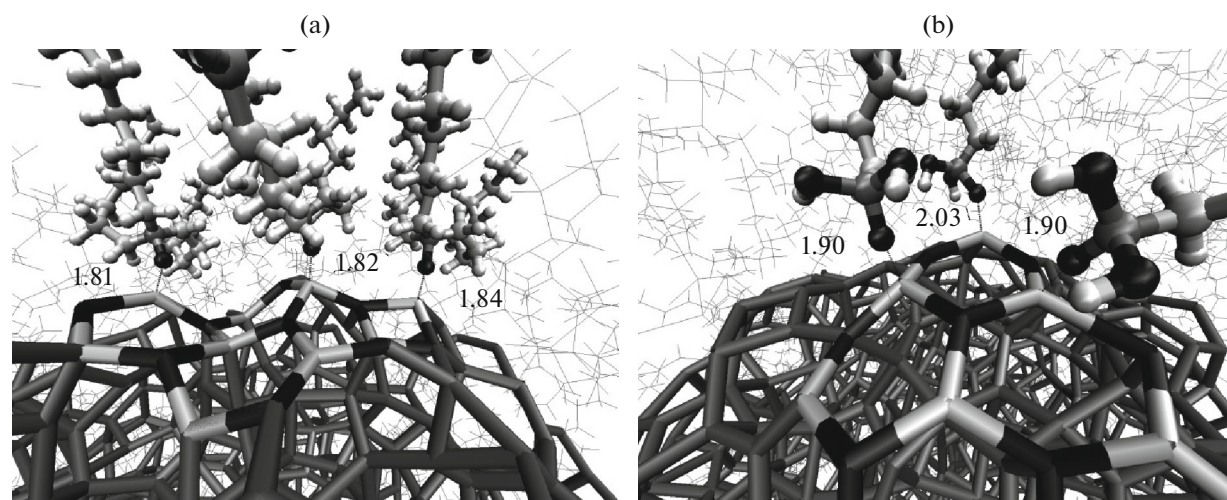


Fig. 3.6. (a) TOPO and (b) ODPa molecules coordinating Cd atoms on the surface of CQDs in the C0 and C2–methanol systems, according to the simulation results. The oxygen of the ligands is shown in black; the hydrogen, in white; the selenium of nanoparticle, in black; and the cadmium, in light gray. The numbers show the distances (in Å) between oxygen and the nearest Cd atom.

issue will be discussed in more detail in the next section.

Based on the simulation results, it was found that the ODPa molecule in the neutral form can interact with 1–3 cadmium atoms through oxygen and also with 1 to 2 selenium atoms through hydrogen atoms. ODPa molecules are capable of passivating neighboring Cd atoms on the surface, whereas TOPO usually combines with atoms located one Cd atom apart and, sometimes, with neighboring ones (Fig. 3.6). The average number of surface atoms passivated by one ODPa molecule is approximately 2. Thus, the proportion of passivated surface atoms is 32% in the C2–vacuum system and 74% in the C3–vacuum system. The disadvantage is that ODPa molecules in neutral form can be gradually washed out of the shell by the action of chloroform or another solvent (Table 3.2).

Now consider the mixed ligand shells HDA, TOP, and TOPO. Around the particle with a radius of 1.9 nm, the same number of HDA, TOP, and TOPO ligand molecules were deposited as in the previous case: 30, 53, and 53 (System C4) or 160, 30, and 30 (System C5) molecules, respectively. A shell of chloroform molecules was created around the particles to immediately study whether the HDA molecules would go into the solvent.

The number of molecules remaining in the shell was also calculated manually for HDA molecules and using a computer program for TOP and TOPO. The calculated number of molecules is presented in Table 3.2. As a result, it was found that almost all HDA molecules are retained in the shell. This indicates very good strength of binding the HDA molecule to the surface. Even the presence of a solvent has almost no effect on the escape of molecules from the shell. This

is consistent with known experimental data on the relative strength of binding of ligands to the surface of CdSe CQDs.

The nitrogen atom in the HDA molecule has a lone electron pair, which it donates to the cadmium cation. This bond is stronger than with the lone pair of oxygen in TOPO or ODPa molecules. The nitrogen atom in the cationic form of HDA does not have a lone electron pair, so it cannot form such a strong bond. All that would remain is the electrostatic interaction of the positively charged ammonium group with the negatively charged selenium. The strength of this interaction is much weaker than that of cadmium with the amino group. As a result of the simulation, it was discovered that the hydrogen atoms of the amino group are capable of entering into electrostatic interaction with selenium atoms. Therefore, each HDA molecule is capable of passivating more than one surface atom. In the C4–chloroform system, too many TOP molecules have been washed away by the solvent, so open spots appear on the nanoparticle surface. But even in this system, the proportion of passivated atoms was 31%, which is higher than for CdSe CQDs of the same radius coated with a mixture of only TOP and TOPO. In the C5–chloroform system, there were initially few TOP molecules, so the surface remained much more protected by ligands: the degree of passivation was 67%.

Thus, as a result of computer simulation, it was established that the number of surface atoms of a CdSe nanoparticle with a radius of 4.5 nm, containing 6911 CdSe molecules, is 17% of their total number. Optimally, about 425 molecules of a mixture of stabilizing ligands TOP and TOPO can be placed on the surface of this CQD with the formation of coordination bonds with 18% of surface atoms. The proportion of surface

atoms associated with the TOP and TOPO ligands depends on the surface curvature radius: it is minimal 14% for an infinitely large radius (flat surface) and reaches almost 40% for a particle of the smallest possible radius of 1 nm.

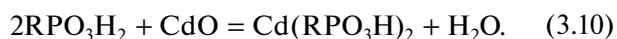
It was shown that if the ODPA molecule were in a neutral form in the shell, it would be retained approximately in the same way as the TOPO molecule, not stronger as observed in experimental studies. Partial replacement of the TOP and TOPO ligands in the shell with ODPA makes it possible to more than double the proportion of passivated surface ions of CdSe CQDs. The presence of neutral HDA molecules in the ligand shell of such a CQD can also double the proportion of protected surface ions; however, they are not washed out from the surface unlike the neutral form of ODPA.

3.3. Role of Various Chemical Forms of ODPA in Stabilization of CdSe CQDs

As discussed above, the stability of the optical properties of CdSe CQDs can be improved by carrying out the synthesis with additional ligands, such as phosphonic acids, amines, and thiols. When CdSe QDs synthesized in the presence of TOPO and ODPA are kept in chloroform, their quantum yield not only does not decrease, but increases [28].

However, using modeling in [26], we could not explain the experimentally observed better stabilizing effect of ODPA compared to TOP and TOPO. It turned out that ODPA molecules are able to be washed out of the shell by the action of a solvent, like TOP and TOPO. This means that the ODPA molecule binds to the surface no stronger than the TOPO molecule, despite the presence of two additional oxygen atoms. A more compact structure allows ODPA molecules to pack more tightly into the shell, coordinating neighboring cadmium atoms. On the other hand, TOPO is capable of coordinating at best no more than half of the surface cadmium atoms, but this is clearly not enough to explain the stabilizing effect of ODPA and, even more so, the improvement of the properties of CQDs over time.

Experimental studies have shown that ODPA can be present in the shell in different ionic forms. This is commonsense because when basic cadmium oxide is dissolved in the dibasic acid ODPA at high temperature, the following reactions can occur:



The ratio of the salts produced in reactions (3.9) and (3.10) depends on the ratio $x = [\text{ODPA}]/[\text{CdO}]$. If $x < 1$, then there will be a purely normal salt. If $1 < x < 2$, there will be a mixture of normal and acid salts. At $x = 2$, there will only be an acid salt. At $x > 2$, there will be a mixture of the acid salt and the neutral acid ODPA. Further interaction of cadmium compounds

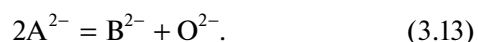
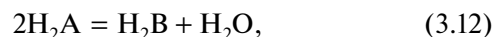
with the TOPSe complex will lead to the formation of more complex compounds in the solution. Let us look at this in detail below. For now, it is important to note the obvious: the qualitative and quantitative composition of the ligand shells of these mixtures must depend on the initial ratios of ODPA to cadmium and selenium. Therefore, when experimenters establish that ODPA in the ligand shell is in *form 1* and *form 2* in a certain ratio, it should be understood that this is true only for their particular synthesis. If the initial proportions change, the ODPA forms themselves and their ratio will be different. Consider what stabilizing effect will be caused by various forms of ODPA. As will be shown below, by chemical reactions in the initial mixtures, ODPA can be converted into normal salts (3.9) and (3.10), the anhydride, and its acid cadmium salt. The formation of the normal anhydride salt remains questionable, so we will not take it into account.

If ODPA stabilizes CdSe CQDs so well, then it seems tempting to abandon TOPO entirely. However, particles are not formed in this case [28]. Obviously, this is due to specific forms of ODPA, which are produced in a system with a large excess of ODPA relative to CdO. Therefore, by examining in detail the interactions of ODPA with cadmium and selenium, it will be possible to answer this question. In addition, it should also be explained why the addition of a neutral component to TOPO-free ODPA, such as octadecene, leads to the formation of nanoparticles and good stabilization of their properties. The possible effect of amines in combination with ODPA should also be considered, since they can interact with each other at different stages of the synthesis. For example, if an amine reacts with an acid at the very beginning:

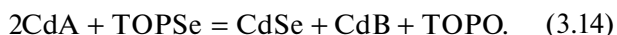


this will inevitably affect the products of the acid reaction with cadmium.

So, the products that can be formed as a result of the interaction of ODPA with cadmium oxide and amines at the first stage of the synthesis (3.9–3.11) have been discussed above. Now consider what ligands can be formed further upon the addition of selenium and what effect they have on the nanoparticle. For simplicity, let us denote the anionic residue of ODPA by A and the anionic residue of its anhydride by B. Then the acid and anhydride will take the formulas H_2A and H_2B , respectively. Composing equations that simultaneously contain derivatives of the acid and its anhydride, we will take into account the formal relations:



Normal salt of octadecylphosphonic acid. If only the normal salt CdA is formed in the system (at $x < 1$), its possible reaction with TOPSe can be written taking into account Eq. (3.13) as follows:



For each CdSe molecule, one CdB ligand is formed, containing one excess cadmium atom. Immediately after formation, the nanoparticle will be coated with the ligands CdB, TOPO, and possibly CdA and TOP. In this case, the number of CdB molecules is equal to the number of CdSe molecules in the nanoparticle. It is important to find out whether CdB molecules can detach from the surface of a nanoparticle under synthesis conditions at 300°C in a mixture of high-boiling solvents. Computer simulation of a system in which a chemical reaction occurs must be carried out using quantum chemistry methods. However, this seems problematic for such a complex system. Therefore, it will be difficult to fully answer this question. To begin with, we can consider a simpler system and find an answer to the question of whether a ligand molecule containing a cadmium cation is capable of detaching from the surface of a nanoparticle at room temperature in a chloroform environment. The ligand molecule can be either CdA or CdB because their behavior is likely to be the same.

Consider system C1, in which the shell consists of a mixture of ligands TOP, TOPO, and CdA (Table 3.4). In this and subsequent systems, a slightly excess amount of ligands is intentionally incorporated so that there is a need to remove them from the surface. As a result of observing the C1 system for 20 ns, the following was discovered. All CdA molecules remained in the shell, and some TOP and TOPO molecules went into the solvent. All excess cadmium cations were incorporated into the structure of the nanoparticle. Let us determine where they have been built-in. We consider the radial atom–atom distribution function of pairs of Cd–Se and Cd–Cd in the C1 system (Fig. 3.7a).

For comparison, we will construct the same graph for the starting CdSe nanoparticle without excess cadmium cations (Fig. 3.7b). Note the small peak of the Cd–Cd function at $r = 2.7 \text{ \AA}$, which is absent in the

Table 3.4. Starting amounts of ligand molecules

	ODPA/HDA	TOP	TOPO	ODPA	HDA
C1	CdA	53	53	30	–
C2	Cd(HA) ₂	53	53	20	–
C3	H ₂ B	53	53	20	–
C4	Cd(HB) ₂	53	53	10	–
C5	RPO ₃ H [–] , RNH ₃ ⁺	53	53	20	20

second figure. Excess cadmium cations are incorporated at a short distance from other cadmium cations. An examination of these short Cd–Cd bonds shows that they are all located near the surface of the nanoparticle; the number of these short bonds is approximately equal to the number of excess cadmium atoms.

Consequently, excess cadmium cations are located only on the surface and cannot be incorporated into the bulk of the nanoparticle. Thus, we can draw an important conclusion that the maximum number of CdA ligand molecules is equal to the maximum number of excess cadmium cations that can be located on the nanoparticle surface. For the latter quantity, we can roughly estimate the number of surface atoms of cadmium and selenium. The fraction of surface atoms is known to decrease with increasing nanoparticle size. Therefore, if the CdA and CdB molecules are strongly bound to the surface under synthesis conditions, the nanoparticles will not be able to grow.

Acid salt of octadecylphosphonic acid. Now consider another extreme case when the initial ratio is $x = 2$. In this case, dissolution of cadmium in ODPA leads to the formation of its acid salt Cd(HA)₂. This substance can react with the TOPSe complex according to the following equation:

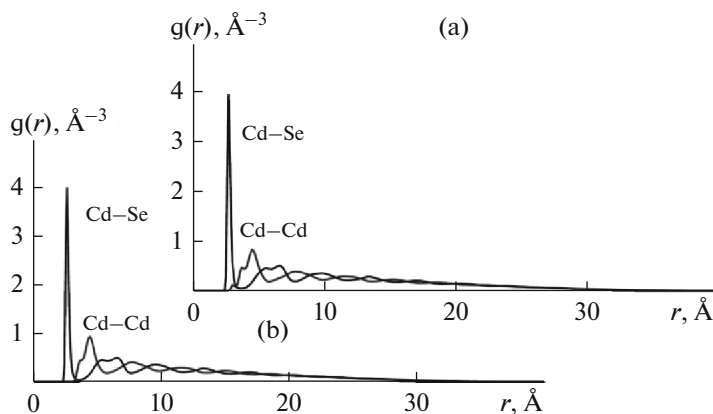
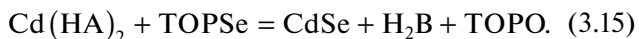


Fig. 3.7. Atom–atom correlation functions.

In this reaction, one molecule of ODPa and TOPO anhydride each is produced per CdSe molecule. In addition to these ligands, the shell may contain excess TOP and unreacted Cd(HA)₂. However, as the reaction proceeds, the proportion of the latter should decrease. Just as in the previous case, let us find out whether the H₂B and Cd(HA)₂ ligands can be detached from the surface under the influence of an external solvent.

System C2 contains ligands Cd(HA)₂, TOP, and TOPO, and system C3 contains ligands H₂B, TOP, and TOPO. Under conditions of insufficient surface area, excess ligands should tend to leave the shell. This is what happened with TOP, TOPO, and H₂B molecules. The Cd(HA)₂ molecules remain entirely in the shell. The acid salt of ODPa contains one excess cadmium atom. A similar analysis of the distribution of excess cadmium cations showed that they are also incorporated into the structure of the nanoparticle and located on its surface. However, unlike the normal salt, the acid salt has two anionic ODPa residues per excess cadmium atom. In addition, the acid salt is gradually consumed in the system, so the number of excess cadmium atoms gradually decreases and the growth of nanoparticles becomes possible. With a sufficient amount of TOPSe, all the acid salt will be consumed and the ligand shell will retain the ligands H₂B, TOP, and TOPO—all are quite easy to wash out with chloroform. Therefore, the luminescent properties of such nanoparticles should gradually decrease, as happens in the case of synthesis in a mixture of TOP and TOPO. If there is a lack of selenium, part of the Cd(HA)₂ will remain in the ligand shell of the nanoparticle and protect it.

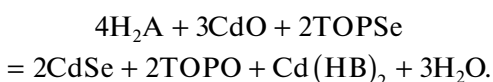
A mixture of normal and acid salts of octadecylphosphonic acid. Typically, the x ratio in the range from 1 to 2 is used for synthesis. Under these conditions, a mixture of CdA and Cd(HA)₂ salts is formed when cadmium oxide is dissolved in ODPa. The larger the x , the greater the proportion of the acidic salt. The ratio $x = 4 : 3$ is interesting. In this case, the ratio of normal and acid salts is 2 : 1:



Adding Eq. (3.16) to (3.14) and (3.15), we get a total equation in which the reaction products include CdB and H₂B in a 1 : 1 ratio. As is known, dibasic acids can react with their normal salts to form an acid salt:

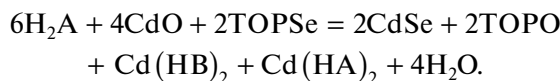


Taking into account Eq. (3.17), the overall equation for the formation of nanoparticles can be written as follows:



At the ratio of $x = 4 : 3$, the only ligand Cd(HB)₂ is formed in the system. If $1 < x < 4 : 3$, then there will be CdB in the mixture; at $2 > x > 4 : 3$, there will be H₂B in the mixture. As in the previous case, this reasoning is valid if there is a sufficient amount of selenium, that is, if the Cd : Se ratio does not exceed 3 : 2.

If Cd : Se > 3 : 2, the system at $1 < x < 2$ will always contain a mixture of ODPa derivatives. The qualitative and quantitative composition of this mixture is very diverse, and a complete analysis is beyond the scope of our consideration. Omitting the details of the calculations, we present one interesting variant of a mixture of ligands, when Cd : Se = 2 and $x = 3 : 2$



In the case of Cd : Se = 2 and $2 > x > 3 : 2$, either ODPa itself or its anhydride will be present in the mixture with acid salts of ODPa and anhydride.

As can be seen, at any [Cd/Se] and [ODPa/CdO] ratio, Cd(HB)₂ is always present among the ligands. This molecule contains one cadmium atom per four octadecane chains. Therefore, it is likely that such a molecule will be weaker bound to the nanoparticle surface and will be able to detach from it under the influence of solvents. To test this assumption, consider the C4 system, which has the ligands Cd(HB)₂, TOP, and TOPO. Observation of this system showed that all Cd(HB)₂ molecules remain in the shell and the TOP and TOPO molecules are gradually washed out of it. In the C4 system, all excess cadmium cations are also located on the surface. Due to the fact that the amount is four times less than in the case of CdA per octadecane chain, these ligands should hinder the growth of nanoparticles less than CdA. At the same time, the presence of the cadmium cation allows the Cd(HB)₂ molecule to resist the leaching effect of the solvent and protect the surface of the nanoparticle from oxidation.

Octadecylphosphonic acid and hexadecylamine. When using octadecylphosphonic acid in a mixture of TOP and TOPO, two extreme cases are possible. If the x ratio is small, the ligand shell contains many CdB molecules, which interfere with the growth of nanoparticles. If x is large, the shell contains molecules that are gradually washed out by the solvent during storage of the nanoparticles. Therefore, there is a need to select some optimal value of x and the corresponding Cd : Se ratio, at which a balance would be maintained between comfortable growth of nanoparticles and their good postsynthetic stabilization. Another approach to stabilize the surface of nanoparticles is the use of additional ligands other than TOP and TOPO, e.g., hexadecylamine. The key difference is the reaction of the amine with the acid, which results in the formation of the ionic forms RPO₃H⁻ and R^{*}NH₃⁺. The ionic form of ODPa, which can be

Table 3.5. Dipole moments of systems

	ODPA/HDA	TOP	TOPO	ODPA	HDA	μ , a.u.
C1	CdA	27	51	30	—	185
C2	Cd(HA) ₂	14	52	20	—	80
C3	H ₂ B	26	52	15	—	41
C4	Cd(HB) ₂	12	50	10	—	50
C5	RPO ₃ H ⁻ /RNH ₃ ⁺	18	50	20	20	145
D1	—	—	—	—	—	21
D2	—	37	68	—	—	33
D3	H ₂ A	23	49	21	—	41
D4	RNH ₂	12	53	—	30	70

written HA⁻ in our previous notation, does not contain cadmium as a cation. Instead of cadmium, the shell will contain the cationic form of the amine. Therefore, the number of such ligands is limited only by the packing density. Let us check whether the ionic forms of ODPA and HDA are well retained in the shell under the action of a solvent.

System C5 contained ODPA and HDA molecules in ionic forms, as well as TOP and TOPO molecules. TOP and TOPO are used to create an excess of ligands. Observation of this system showed that ODPA and HDA molecules do not leave the shell, but TOP and TOPO do. A detailed study of the nanoparticle structure revealed that it almost coincides with the structure of the nanoparticle coated with a mixture of TOP and TOPO. The peak corresponding to short Cd–Cd distances is absent in the graph of the radial distribution function. There are no other Cd atoms near the Cd atoms. Consequently, the number of such ionic forms in the shell can reach 100%.

Dipole moment of a nanoparticle. The observations of systems C1–C5 revealed that the ligands CdA,

Cd(HA)₂, Cd(HB)₂, HA⁻, and R^{*}NH₃⁺ are not washed out of the shell by chloroform. This means strong binding to the nanoparticle surface. However, this does not allow us to judge the relative strength of binding of these ligands to the surface. The presence of ligands around a nanoparticle affects its dipole moment. Indeed, if there are no ligands around a small nanoparticle, the ions are weakly ordered in it and, as a consequence, the dipole moment is small. The ligand shell can be considered to create an electric field around the nanoparticle. Then the stronger the field, the more ordered the ions in the nanoparticle should be and the larger its dipole moment.

For comparison, the dipole moments of CdSe nanoparticles were calculated in systems C1–C5 and in the following four systems: System D1, which is an initial CdSe nanoparticle containing 499 Cd and Se atoms each; System D2, which is a nanoparticle with a shell of 37 TOP and 68 TOPO molecules; System D3, a nanoparticle with a shell of 30 TOP, 49 TOPO, and 24 H₂A molecules; and System D4, a nanoparticle with a shell of 12 TOP, 53 TOPO, and 30 neutral HDA molecules.

The calculation was carried out using the standard formula:

$$\mu = \left\langle \left| \sum q_i r_i \right| \right\rangle,$$

with averaging over 1000 instantaneous configurations. The calculated dipole moments are presented in Table 3.5, and the charge values used are given in Table 3.6.

Based on the calculation results, we can conclude that the presence of ligands does affect the nanoparticle structure. A nanoparticle without a ligand environment is weakly ordered and its dipole moment is minimal. In the TOP and TOPO environment, the atoms of the nanoparticle are slightly ordered and its dipole moment increases, but not much. If some of the molecules are replaced with ODPA or its anhydride, the dipole moment will increase slightly. This means that

Table 3.6. Charges of atoms in different groups

Atom	q, e^-	Atom	q, e^-	Atom	q, e^-
Cd	+1.18	O in X–O–Y	–0.57	P in TOP, TOPO	+0.78
Se	–1.18	O in X=O, X–O ⁻	–0.78	$\Sigma(\text{RNH}_3^+)$	+0.59
H in H–O	+0.21	P in RPO ₃ H ₂	+1.5	$\Sigma(\text{RPO}_3\text{H}^-)$	–0.59
H in RNH ₂	+0.4	P in RPO ₃ H ⁻	+1.33	$\Sigma(\text{HAnh}^-)$	–0.59
H in RNH ₃ ⁺	+0.3	P in RPO ₃ ²⁻	+1.16	$\Sigma(\text{RPO}_3^{2-})$	–1.18
N in RNH ₂	–0.8	P in H ₂ B	+1.425	C in CHCl ₃	+0.179
N in RNH ₃ ⁺	–0.31	P in HB ⁻	+1.34	H in CHCl ₃	+0.082
				Cl in CHCl ₃	–0.087

the latter two ligands interact with the nanoparticle more strongly than TOP and TOPO. Similar reasoning can be applied to the remaining ligands. Of course, it is not entirely correct to directly talk about comparing the binding strength of ligands due to the fact that there are different numbers of ligand molecules in the shell in each system. However, the general trend is becoming quite clear.

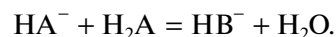
Among the various ODPAs derivatives, the CdA ligand binds most strongly, and H₂A and H₂B form the weakest bonds. Excessive amounts of CdA can block the growth of nanoparticles. If the shell consists only of the ligands TOP, TOPO, H₂A, and H₂B, the protection of the nanoparticle is weak due to the gradual leaching of the ligands by the solvent. Therefore, it is necessary to search for the optimal balance of the starting ODPAs : Cd and Cd : Se ratios, on which the final forms of ODPAs in the ligand shell depend. From Table 3.5 it follows that the binding strength of the RPO₃H⁻/RNH₃⁺ ligands is comparable to that of CdA. Unlike CdA, they do not introduce excess cadmium cations into the nanoparticle. Therefore, their content can reach 100%. For the same reason, they do not block the growth of nanoparticles during the synthesis process. Therefore, further use of such mixtures of ligands is promising.

Octadecylphosphonic acid without additives or with neutral additives. It was experimentally established that nanoparticles are not formed in the presence of ODPAs alone. At the same time, the addition of octadecene molecules, which does not contain functional groups, to ODPAs promotes the formation of nanoparticles. Both of these experimental facts seem like a real mystery at first glance. However, they can be explained by involving the results obtained from the systems discussed above.

As already noted, dissolution of CdO in octadecylphosphonic acid results in normal CdA and acidic Cd(HA)₂ salts. The cadmium cation has a coordination number of 4 or 6. This means that in addition to the anionic ODPAs residues, there are neutral molecules in its coordination sphere. If synthesis occurs in the presence of TOPO, then these will be TOPO molecules. In the case of octadecene, these will be octadecene molecules. Although the latter lacks functional groups, it will simply fill the remaining space around the cadmium cation. TOPO and, especially, octadecene ligand molecules are easily detached from the nanoparticle surface. It is reasonable to assume that they will just as easily depart from the single cadmium cation. The TOPSe complex can fit into the vacated space, and the reaction to give CdSe will be possible.

If there are no additional ligands besides ODPAs, the acid salt Cd(HA)₂ is formed by dissolving CdO. In this case, the cadmium cation is surrounded by H₂A molecules in addition to two anionic residues. At high

temperatures, the interaction of two HA⁻ anions with two H₂A molecules can be assumed:



In this case, the cadmium cation will be surrounded by two anionic HB⁻ residues; there are no other molecules in the environment. As was established for the C4 system, the HB⁻ anion is quite strongly retained by the surface. It can be assumed that it is also strongly retained near the cadmium cation. Since there are no other molecules in the environment of the cadmium cation and HB⁻ is not detachable, the TOPSe complex does not have the opportunity to approach Cd; hence, nanoparticles do not grow.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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