

Computer Simulation of the Adsorption of meso-Tetra(3-Pyridyl)porphyrin Dye on the Surface of Colloidal CdSe Quantum Dots

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Received March 23, 2018

Abstract—A classical all-atom molecular dynamics simulation has been used to study the adsorption of meso-tetra(3-pyridyl)porphyrin dye on colloidal quantum dots of cadmium selenide. The competition between dye molecules and ligands covering the quantum dots has been investigated by the examples of trioctylphosphine, trioctylphosphine oxide, octadecylphosphonic acid, and hexadecylamine. It has been shown that the dye is strongly retained by the surface and is not washed out with a solvent either from a free surface or in the presence of trioctylphosphine in the shell. The strength of the adsorption of the dye is equal to that of trioctylphosphine. At the same time, it gives up its place on the surface to stronger ligands, octadecylphosphonic acid and hexadecylamine.

DOI: 10.1134/S1061933X18050125

1. INTRODUCTION

Colloidal quantum dots (CQDs) make up a new class of luminophores that possess a number of unique advantages over traditional bulk inorganic and molecular organic luminophores [1, 2]. CQDs are substantially more thermo- and photostable than the latter. While the properties of a bulk semiconductor depend only on the substance of which it consists, the properties of CQDs additionally depend on their sizes. The potential of modern high-temperature organometallic synthesis, which was discovered in 1993 [3] and has recently been significantly developed, makes it possible to produce time-stable CQDs with very uniform sizes and excellent optical characteristics [4, 5]. This yields substantially greater possibilities, simply by varying the sizes of quantum dots, to more accurately tune their luminescent properties for wider application in light-emitting devices, lasers, solar batteries, diverse sensors, etc.

The feasibility of additional variations in the optical properties of CQDs by using them for the formation of hybrid nanostructures involving molecules of organic luminophores is of special interest. Due to a large absorption cross section, a quantum dot occurring in such a system plays the role of a light-absorbing antenna, while an organic dye determines the direct function of the system. Hybrid CQD–dye systems are formed via the attachment of dye molecules to quantum dot surfaces. To provide such attachment, dye molecules must have terminal functional atoms

(groups) capable of bonding to the surface. For example, porphyrin devoid of functional groups cannot form hybrid systems, while, e.g., pyridine-substituted porphyrin (Fig. 1, left-hand side) can.

The presence of properly located functional groups in a dye does not ensure the formation of hybrid systems. The reason is a ligand shell, which stabilizes a quantum dot and creates an obstacle through which the dye must “struggle” to the surface. On the one hand, researchers are, at present, trying to reach record characteristics of quantum dots by replacing traditional weak ligands (trioctylphosphine, trioctylphosphine oxide) by stronger ones, such as phosphonic acids, alkylamines, or alkylmercaptans. On the other hand, the use of the strong ligands calls the ability of a dye to penetrate through a ligand shell to the CQD surface into question. Upon the competition of a dye and a ligand for a place on the surface, the former a fortiori occurs in a disadvantageous situation, because the ligand shell is formed directly at the stage of CQD synthesis and densely covers the surface, while the organic dye may be added only after the synthesis completion, because it cannot withstand the synthesis temperature (600 K). Moreover, a dye molecule is, often, much larger than a ligand molecule (Fig. 1). Hence, a dye has to displace several ligand molecules from a CQD surface to get the place for itself, with this circumstance additionally complicating the embedding process. Therefore, it is important to search for ligands that would be rather strongly

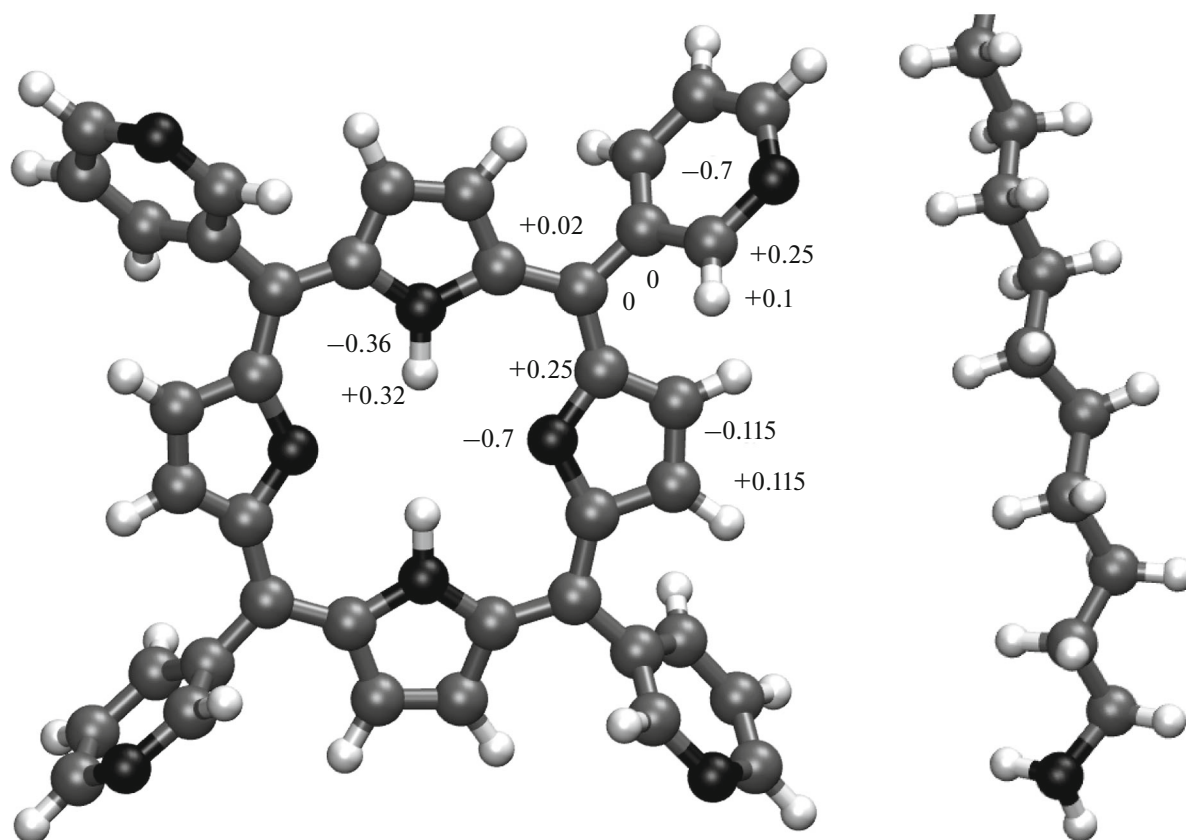


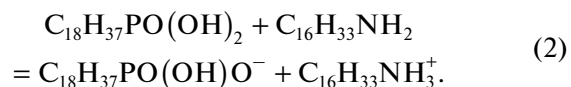
Fig. 1. Structural formulas of porphyrin dye (on the left) and a typical alkylamine (on the right). Nitrogen, carbon, and hydrogen atoms are denoted by black, gray, and white symbols, respectively. The charges used in simulation for nonrepeating dye atoms are shown.

retained by the surface and efficiently protect it from oxidation, which proceeds through the reaction



and, at the same time, could be detached from the surface for embedding a dye into the shell. A large series of experimental works devoted to this problem has been performed Zen'kevich et al. as applied to the adsorption of a dye, meso-tetra-(3-pyridyl)porphyrin (TPyP), on the surface of CdSe quantum dots stabilized with a shell formed from a mixture of ligands, trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO). For example, substantial embedding TPyP into the ligand shell has been shown in [6, 7]. However, TOP and TOPO cannot be desired ligands, because they are rather weakly retained by the CQD surface and pass to a solution under the action of a solvent. This fact has recently been confirmed by computer simulation [8]. There is a recently published work [9] devoted to embedding the dye into an alkylamine-containing shell; however, InP@ZnS quantum dots of indium phosphide with a shell grown of zinc sulfide have been considered in that work. Thus, the question of CdSe CQDs stabilized with amines and phosphonic acids remains open. Previous works [10,

11] devoted to simulating the stability of ligand shells composed of hexadecylamine (HDA) and octadecylphosphonic acid (ODPA) have shown that the stability of the shells depends on the form in which the ligands occur, while the form of a ligand is, in turn, determined by the reagent ratio in the high-temperature synthesis. For example, neutral forms of ODPA are retained by the surface somewhat stronger than TOP and TOPO are and, therewith, can be detached from it. The ionic forms of ODPA carry additional Cd^{2+} cation, which is embedded into the crystal structure of a quantum dot and strongly hinders the detachment of this ligand. The simultaneous use of phosphonic acid and alkylamine in the synthesis leads to the formation of ionic forms free of metal cations according to the following scheme:



These ionic forms have more opportunities for the detachment from the CQD surface than the forms containing Cd^{2+} cation. It is impossible to isolate experimentally a pure desired form of a ligand and study embedding TPyP into a shell composed of only

such ligands; therefore, in this work, a classical molecular dynamics simulation was used, which has already shown its efficiency in studying the stability of ligand shells of CdSe CQDs. Since the experimentally observed process of embedding TPyP into a CQD shell lasts 10^2 – 10^3 s [9], the adsorption of dye molecules from a solvent on a surface protected with a dense ligand shell cannot be simulated directly. Therefore, this problem was solved step-by-step in this work.

Initially, we studied the strength of retaining a dye molecule on a free surface in the presence of a solvent and the absence of the competition with ligands or other due molecules. Then, we investigated the competition of the dye with each of the following ligands: TOP, TOPO, and ODPa in the neutral form, HAD in the neutral form, and a mixture of ODPa and HDA in the ionic forms shown in scheme (2). Then, we studied the dye capability for direct embedding into a dense ligand shell in the absence of a solvent. As in our previous works [8, 10, 11], the all-atom representation was used for all molecules, which has enabled us to study in detail all the processes accompanying the embedding, i.e., the rearrangements of ligands, dyes, and surface atoms. Ligand molecules were not covalently bound to the surface; therefore, they could be detached from it.

2. MOLECULAR MODELS AND SIMULATION DETAILS

The electrostatic repulsion of hydrogen atoms in a TPyP molecule prevents pyridine rings from occurring in the same plane with the central moiety. The barrier for the rotation of a ring through the plane is nearly 30–40 kcal/mol [12], which complicates the observation of this process in molecular dynamics experiments. Because of the presence of nitrogen atoms in the metapositions of the pyridine rings, the calculation leads to four geometrically different isomers of TPyP molecules: isomer I, in which all nitrogen atoms are located on one side of the porphyrin macrocycle plane (denoted as TPyP-I); isomer II, with one nitrogen atom being located on one side of the plane and three other atoms occurring on the other side (TPyP-II); isomer III, in which two neighboring nitrogen atoms are located on one side and two other atoms are on the other side of the molecule plane (TPyP-III); and isomer IV with alternating nitrogen atoms (TPyP-IV). Since the dye is adsorbed via two neighboring pyridine rings, it is sufficient to consider two isomers, namely, TPyP-I and TPyP-IV. In the former and latter, nitrogen atoms are located on one side and on different sides, respectively, irrespective of which side is involved in the adsorption.

The compositions of the simulated systems are presented in Table 1. A TPyP molecule was constructed using the WebLabViewer Pro software and optimized with respect to energy using the NAMD 2.12 software [13]. The parameters of TPyP molecule were taken

from works [14, 15] devoted to the simulation of porphyrin and pyridine and from standard aromatic-nitrogen-containing amino acids of the CHARMM27 force field. The charges unique atoms of TPyP are shown in Fig. 1. The parameters of the atoms of CdSe and the molecules of ligands were taken from [16] and [11], respectively. The solvent (chloroform) was described using an all-atom model, although the criteria formulated in [17] allowed us to use a simplified single-atom model. These criteria follow from the fact that chloroform molecules are not components of the structure of the studied object, but rather play the role of an environment, and that solvent molecules make up almost 80% of their total number. The use of the simplified model would enable us to increase substantially the rate of the calculations. However, the absence of reliable parameters for the single-atom model of chloroform as a solvent forced us to use the all-atom model, the parameters of which were taken from [18].

An initial quantum dot with a composition of $\text{Cd}_{499}\text{Se}_{499}$ and a radius of 1.9 nm obtained by the self-assembly of individual Cd and Se atoms as described in [8] was covered with a shell composed of molecules of the ligands and the dye. The shell was created using the computer software designed for constructing water-containing reverse micelles and modified as applied to molecules of the ligands and the dye. This model has been described in detail elsewhere [19]. The creation of a shell surrounding a CQD encounters the same problem as that in the case of reverse micelles, i.e., the selection of the number of molecules in the shell, because the simulation results are sensitive to initial conditions [20]. The amounts of molecules were chosen so as to provide a small excess of them in the shell. In the absence of this excess, all molecules will remain in the shell and the aim will not be attained. If the excess is too large, the quantum dot itself may be strongly deformed and the simulation results may become unreliable. In C10–C12 systems, the shell contained ligands alone, while the dye was located outside of the shell. Previously, this approach was successfully used for simulating the possibility of embedding thiocarbocyanine dye into reverse micelles [21].

The energy of the constructed systems was thoroughly optimized to exclude abrupt changes in the coordinates of atoms at the onset of the simulation. Initially, a shell with a frozen core and, then, the entire system were optimized. In the case of systems containing chloroform, it was added after this step, and these systems were optimized together with it. The total time of the energy minimization was 1–2 ns. Then, the molecular dynamics calculations themselves were performed. The calculations were carried out using the freely distributed NAMD 2.12 molecular dynamics package. The integration step was equal to 1 fs, and the coordinates of the system were recorded in a special time-scale file every 10^5 steps. For solvent-containing

Table 1. Initial parameters of simulated systems

No.	System composition	CHCl ₃	<i>t</i> , ns
C1	TPyP-I	–	2100
C2	CQD + TPyP-I + TPyP-IV	–	430
C3	CQD + TPyP-I + TPyP-IV	+	71
C4	CQD + 10 TPyP-I + 10 TPyP-IV	+	70
C5	CQD + 10 TPyP-I + 10 TPyP-IV + 98 TOP	–	169
C6	CQD + 10 TPyP-I + 10 TPyP-IV + 100 TOPO	–	217
C7	CQD + 10 TPyP-I + 10 TPyP-IV + 200 ODPA	–	137
C8	CQD + 10 TPyP-I + 10 TPyP-IV + 200 HDA	–	155
C9	CQD + 10 TPyP-I + 10 TPyP-IV + 99 ODPA [–] + 99 HDA ⁺	–	114
C10	CQD + 28 TPyP-I* + 110 TOPO	+	100
C11	CQD + 20 TPyP-I* + 20 TPyP-IV* + 200 ODPA	–	109
C12	CQD + 20 TPyP-I* + 20 TPyP-IV* + 50 TOP + 50 TOPO	–	160

* TPyP molecules are located outside of the ligand shell.

systems, the isobaric–isothermal *NPT* ensemble and periodic boundary conditions were used, while other systems were simulated under spherical boundary conditions. A pressure of 1 atm (for solvent-containing systems) and a temperature of 298.15 K were maintained with the use of the Berendsen barostat and the procedure of velocity rescaling. The simulation results were analyzed using the VMD software [22] and our own programs.

This work was carried out using the equipment of the Center for Collective Use of Giant-Powered Computational Resources, Moscow State University [23]. The time of each calculation was 72 h when using 8 (for the C1 system) or 64 (for C2–C12) CPU kernels with the involvement of graphic accelerators by the CUDA technique.

3. RESULTS AND DISCUSSION

3.1. Porphyrin Molecule

In the C1 system, a dye molecule was monitored for 2100 ns, with saving of instantaneous coordinates of atoms every 0.1 ns (in all, 2×10^4 configurations). Analysis of the obtained trajectory has shown that the shape of the central (porphyrin) moiety of TPyP is almost planar. The torsion angle passing through the four porphyrin carbon atoms bonded to pyridine rings fluctuated within a range of 180° – 166° . These values agree with the quantum-mechanical calculation and X-ray spectroscopy data on a molecule of unsubstituted porphyrin [14].

The repulsion between hydrogen atoms brings pyridine rings out of the plane of the porphyrin moiety of the molecule. However, the resulting angle does not reach 90° . The deviation from the perpendicular orientation is shown in Fig. 2a (black). The distribution maxima of the angles correspond to 56° and 124°

($124^\circ = 180^\circ - 56^\circ$), while the width at the half-height is 14° for both peaks. Some difference in the intensities of the peaks is of statistical rather than systematic character. This was shown by considering the TPyP molecule in a time interval of 0.2 ns, while saving the configurations at each integration step (in all, 2×10^5 configurations, Fig. 2b). Analysis of this figure has shown that the passage through the perpendicular position has an energy barrier. This barrier is low in accordance with the data of [12]; therefore, each passage may occur within time periods of 0.1 ns and shorter. For this reason, when the passage through the barrier is fixed every 0.1 ns (Fig. 2a), the barrier may be overcome twice between the reference points, so that, at consecutive reference points, the system occurs on the same side of the barrier. In addition, Fig. 2a indicates that the passage through 0° has a much higher energy barrier, which cannot be detected in the molecular dynamics calculation within a time interval of nearly 2000 ns. Since the trajectory length for the C2–C10 systems is much shorter, the passage of pyridine rings through the plane of TPyP is even less possible; therefore, the use of individual isomers is necessitated.

3.2. Adsorption of Porphyrin Molecule on the Free Surface of CdSe CQD

In the C2 system, a CdSe CQD was considered with TPyP-I and TPyP-IV isomers attached to it in a perpendicular position at the initial time moment. In the C3 system, the same configuration was observed in the presence of chloroform. Different positions of the nitrogen atoms of pyridine rings relative to the dye plane in these isomers may lead to different tilts of TPyP to the CQD surface. A computer program was written for calculating the tilt of the TPyP plane to the

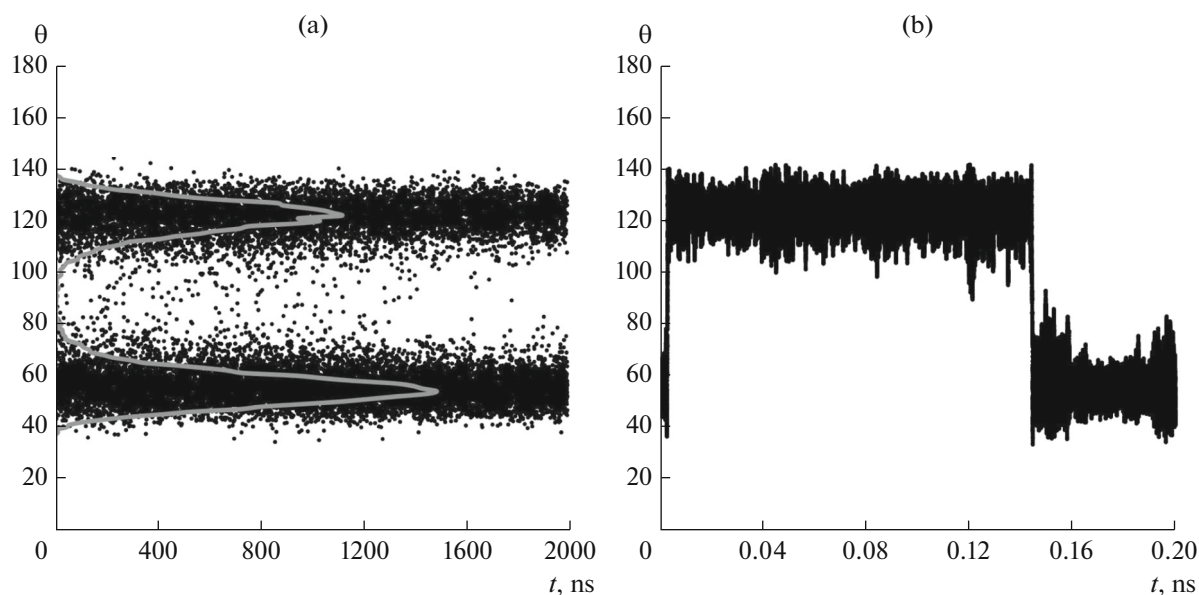


Fig. 2. Time variations in the tilt of pyridine ring to the plane of TPyP molecule within intervals of (a) 2000 and (b) 0.2 ns. Distribution over angles is shown by the gray line in panel (a).

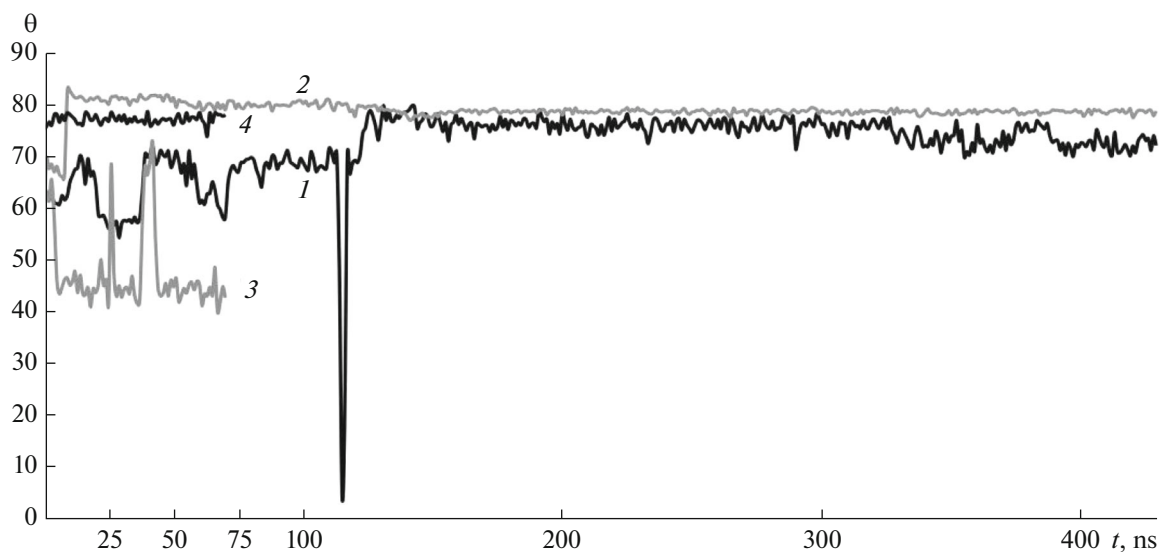


Fig. 3. Averaged tilt of TPyP plane to CQD surface in the absence of chloroform in the C2 system ((1) TPyP-I, (2) TPyP-IV) and in its presence in the C3 system ((3) TPyP-I, and (4) TPyP-IV).

CQD surface. The analysis of the obtained angles shows that isomer TPyP-IV is always oriented almost perpendicularly to the CQD surface, while the tilt of isomer TPyP-I may vary within a range of 0° – 90° , with the orientation of molecules of both isomers being in fact unaffected by the presence or absence of chloroform (Fig. 3).

In addition, the tilt of pyridine rings to the plane of the central moiety of the TPyP molecule was monitored in the C2 and C3 systems (Fig. 4). The pyridine ring bonded to the CQD surface exhibits actually no

rotation through the perpendicular position (Fig. 4a). The presence of chloroform has no effect on the rotation. In the absence of chloroform, the pyridine ring located at a distance from the surface shows that the rotation character coincides with the rotation of pyridine in a free TPyP molecule (Fig. 2), while, in the presence of chloroform, the rotation is strongly hindered (although it is observed) (Fig. 4b). The presence of chloroform slows down the overcoming of the energy barrier relevant to the passage of the pyridine ring through the perpendicular position by one or two

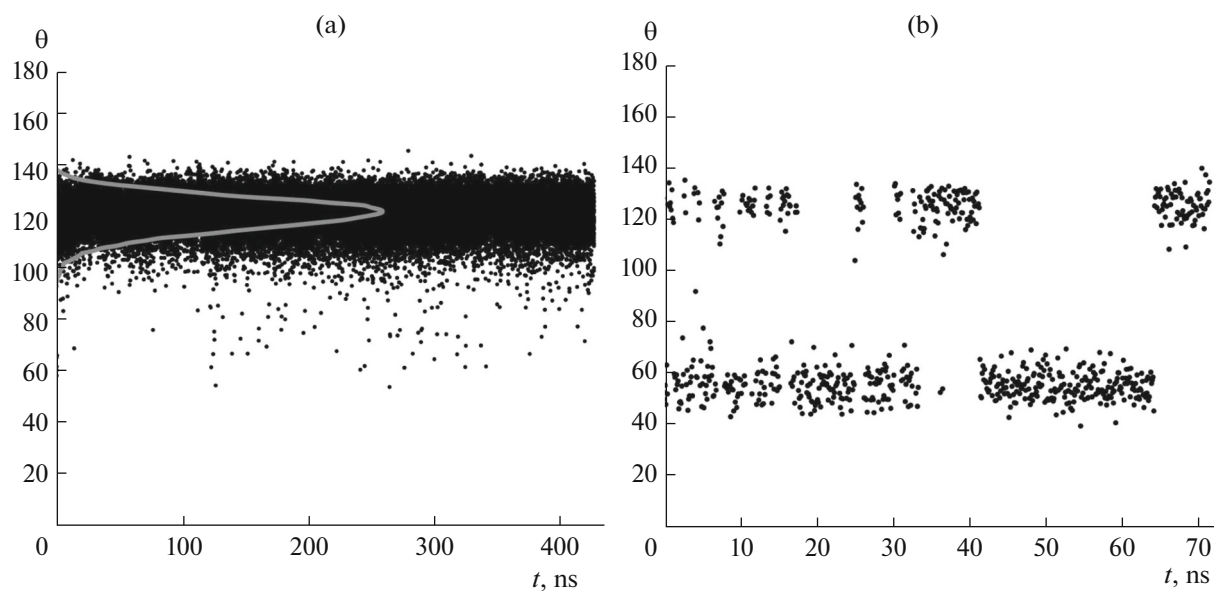


Fig. 4. Variations in the tilt of pyridine ring to the plane of dye molecule adsorbed on the surface of CdSe CQD: (a) for a ring bonded to CQD in the C2 system (gray line shows the distribution over angles) and (b) for a ring unbonded to CQD in the C3 system.

orders of magnitude. The monitoring of nitrogen atoms involved in the adsorption has shown that they do not change the cadmium atoms, to which they are bonded. The interatomic distance in an N–Cd pair varies within a range of 0.21–0.26 nm and does not depend on the presence of chloroform.

An analogous state of affairs was observed in the C4, in which ten molecules of isomer I and ten molecules of isomer IV were located in the CQD shell in the chloroform medium. Each nitrogen molecule was permanently bonded to the surface via the same cadmium atom. Rotation of pyridine rings involved in the adsorption was actually absent, while the rotation of other rings was hindered. The tilt of TPyP molecules remained almost unchanged. All of the aforementioned indicates rather strong bonding of TPyP molecules to the surface in the absence of competition with other ligands. Now, let us consider the changes caused by a deficiency of a free surface in the system.

3.3. Competition between Dye Molecules and Ligands

Each of the C5–C9 systems contained ten molecules of TPyP-I isomer, ten molecules of TPyP-IV isomer, and a certain number of molecules of a main ligand (TOP, TOPO, ODPA, or HDA). The latter amount was selected so as, together with 20 molecules of TPyP, to provide a small deficiency of the CQD surface area accessible for adsorption. The simulation was carried out in the absence of chloroform in order to study only the competition between dye molecules and ligand molecules, rather than the resistance to the action of a solvent. Moreover, as has been shown

above, chloroform hinders the rotation of pyridine rings and complicates the calculations.

In the course of simulation, the most weakly bonded molecules were detached from the surface and gave their places to molecules stronger interacting with it. The number of molecules located in the shell at each time moment was calculated using the computer program described in [10] as updated to apply to dye molecules. In the case of the dye, a molecule was considered to be bonded to the surface, provided that one of the pyridine nitrogens was located at a distance of no more than 0.26 nm from any atom of the surface. Figure 5 shows the fraction of molecules that have remained in the shell by the end of the simulation relative to their initial number.

In the C5 system, 19 dye molecules of the initial 20 molecules have remained in the shell; i.e., the dye fraction is 0.95, while only 26 TOP molecules (fraction equal to 0.26) of initial 100 molecules have remained in the shell, and unoccupied regions have been formed on the CQD surface. TOP molecules are very easily detached from the surface, thereby making the shell discontinuous and, at the same time, multi-layered. The detachment of TOP from the free CQD surface cannot be due to the competition with the dye. The ligand itself is bonded to the surface very weakly and detaches from it even in the absence of the competition. Hence, TPyP is retained in the shell much stronger than TOP is.

In the shell of the C6 system, 15 TPyP molecules and 74 TOPO molecules have remained, thereby cor-

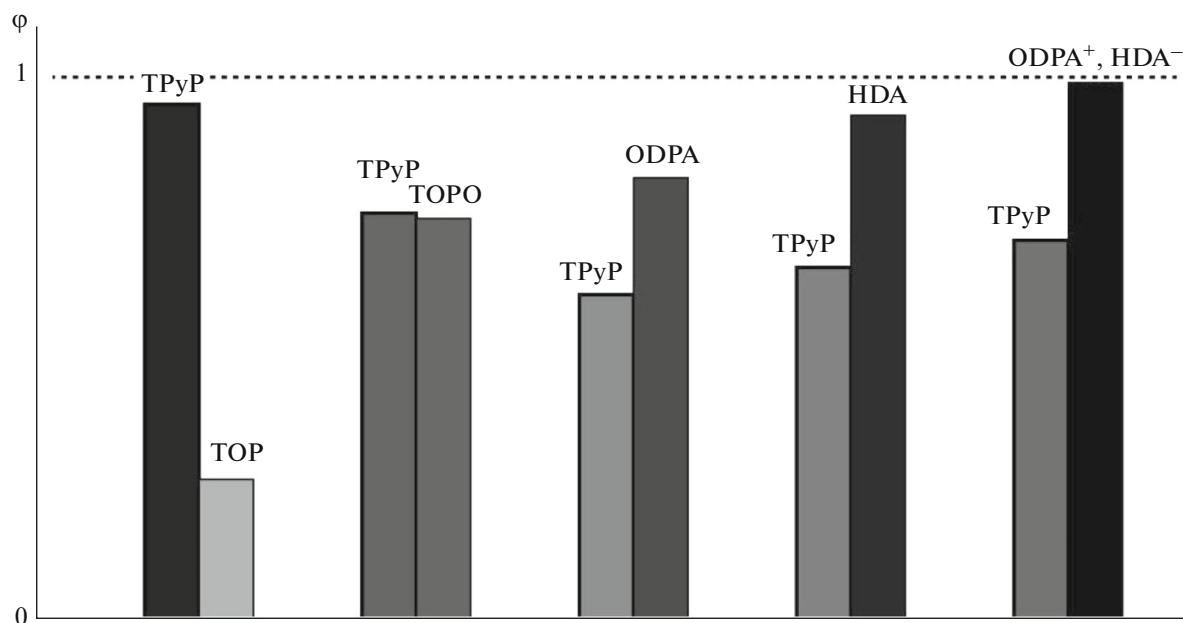


Fig. 5. Fractions of molecules remaining in the shell for the C5–C9 systems (from the left to the right).

responding to nearly equal fractions (0.75 and 0.74) of these molecules relative to their initial amounts. The CQD surface has remained densely covered; i.e., the dye and TOPO strongly interact with it and compete for the sites of adsorption indeed. The equal fractions of the TPyP and TOPO molecules that have escaped from the shell indicate the equal strengths of their bonding to the surface. In the absence of TPyP, the first 100 TOPO molecules form a dense shell on the CQD with a radius of 1.9 nm [8]. Therefore, 26 ligand molecules released from it correspond to 15 embedded dye molecules; i.e., the ratio between them is nearly 2 : 1.

In the case of the C7 system, 12 TPyP molecules of the initial 20 molecules (fraction of 0.6) and 163 ODPA molecules of the initial 200 molecules (fraction of 0.82) have remained in the dense shell. Assuming that, in the absence of the dye, 200 ODPA molecules are densely packed, 12 dye molecules replace 37 molecules of this ligand released from the shell; i.e., their ratio is, in this case, equal to 3 : 1. Although it was concluded in [10] that the neutral form of ODPA is retained equivalent to that of TOPO, the results of simulating the C6 and C7 systems correct this estimate toward a stronger retention of the neutral form of ODPA as compared with TOPO and TPyP. Since some experimental works [24] and simulations [11] indicate that ODPA occurs in the cadmium-containing ionic forms, the detachment of which is substantially more hindered than that of its neutral form,

the competition of this ligand with the dye will be still more in favor of the ligand.

In the C8 system, 186 and 13 molecules of the 200 initial HDA molecules and 20 initial TPyP molecules, respectively, have remained in the dense shell. It is obvious that 14 ligand molecules detached from the shell cannot provide a place for 13 dye molecules. Hence, 200 HDA molecules do not form a dense shell. The deficiency of the surface area is smaller in this system than in the previous ones. At the same time, there is a deficiency and, hence, competition for the adsorption sites occurs, as a result of which one-third of dye molecules and only 7% of ligand molecules are detached from the surface. Hence, the dye is retained substantially weaker than HDA.

In the C9 system, an analogous situation is observed with a smaller deficiency of the surface; two detached ligand molecules correspond to 14 dye molecules. The situation that was observed for the C8 and C9 systems may result from the denser packing of HDA than that of ODPA, as well as the ionic forms of these molecules compared with the neutral forms. The latter effect seems to be due to the attraction between oppositely charged active groups of phosphate anions and alkylammonium cations.

Thus, it has been found that, if TPyP dye has, in advance, been incorporated into a shell having a small deficiency of the area accessible for adsorption, TPyP is superior to TOP, appears to be equivalent to TOPO, and is inferior ODPA and HDA. However, the dye is, initially, outside of the ligand shell; therefore, the pos-

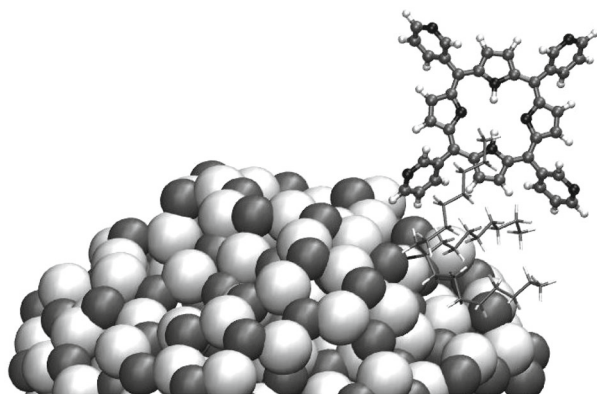


Fig. 6. Competition between dye molecules (thick lines, spheres) and ligand (thin lines) for adsorption site on the surface of a CdSe CQD (spheres) in the C10 system. Se and H atoms are denoted by white symbols; Cd, C, and P atoms are shown by gray symbols; and N and O atoms are depicted by black symbols. Chloroform is not shown for clarity.

sibility of forming a hybrid CQD–dye structure depends on not only the relative strengths of bonding the ligands and the dye to the CQD surface, but also the ability of the dye to penetrate through the ligand shell to the surface.

3.4. Dye Molecule Embedding into the Shell

Commonly, CQD solutions in chloroform, which are used to obtain hybrid CQD–dye structures, have concentrations on the order of 10^{-6} M [9]. The ratio between the amounts of CQDs and a dye is nearly equal to 1 : 1. This corresponds to an average distance between two CQDs in a solution of 100 nm and the average distance between a dye molecule and a CQD of 50 nm. The characteristic time of diffusion of one dye molecule to a CQD shell estimated by Eq. (5) as presented in [25] is on the order of 10^{-5} s. Since chloroform is a rather good solvent for the dye and the quantum dots, each approach of a dye molecule to the shell does not necessarily lead to its subsequent penetration into the shell. This process may occupy several orders of magnitude in the time scale, thereby approaching the characteristic time to 10^{-2} – 10^{-1} s. These slow processes may be excluded from simulation by placing the dye in advance at the boundary with the CQD shell and removing the solvent from the system.

In the C10–C12 systems, several tens of dye molecules were placed at the external boundary of a CQD, with the solvent being present in the C10 system and absent in the C11 and C12 systems. In the first of these systems, almost all dye molecules were not bonded to the quantum dot and passed into the solvent bulk. Only one molecule was embedded into the CQD shell, thereby supporting the hypothesis that the collisions

between the dye molecules and CQDs are very inefficient. TPyP-I was adsorbed via one pyridine ring, while the attachment of the second ring was hindered by the alkyl chain of TOPO ligand (Fig. 6).

In the C10 system, the dye appeared to be embedded into the shell already within the initial 10 ns of simulation, while the hindrance of the TOPO alkyl chains could not be overcome during subsequent 90 ns. Obviously, the second ring will be not be attached until the hindering alkyl chain of the ligand is removed from under the dye molecule. Therewith, the three alkyl chains of TOPO may limit the mobility of each other.

A shell composed of ODPa molecules having one alkyl radical was considered to clarify the effect of ligand branching on the dye adsorption in the C11 system. The solvent was absent in this system. Its absence had to ensure that all molecules located near the surface are embedded into the shell and no molecule moves away from the CQD. In this system, the dye was indeed efficiently embedded into the shell composed of ODPa molecules by displacing some ligand molecules. Already after 109-ns simulation, around ten dye molecules were embedded into the shell, having displaced 25 ligand molecules. However, the dye was also adsorbed via one pyridine ring, while the attachment of the second ring was hindered with octadecyl radicals of the ligands. Hence, the mobility of alkyl radicals of a ligand is independent of the degree of its branching and the ligand must be detached from the surface to provide the complete adsorption of the dye. For this purpose, TOP is the most suitable ligand, capable of being detached from the surface even in the absence of the competition and a solvent.

In the C12 system, almost 40% of all dye molecules were embedded into the shell (Fig. 7). Therewith, many molecules were adsorbed via two pyridine rings, while the majority of TOP was desorbed, leaving the CQD surface open. Thus, only ligand detachment allows TPyP molecules to be attached to the surface via two pyridine rings.

4. CONCLUSIONS

The following main stages may be distinguished in meso-tetra(3-pyridyl)porphyrin dye adsorption on the surface of CdSe CQDs in chloroform. The first stage is the diffusion of dye molecules in a solvent to the external surface of the ligand shell of a quantum dot. At the concentrations used in the experiments, the characteristic time required for one molecule to approach the surface is 10^{-5} s. If a dye molecule lingers at the ligand shell, which takes place for every hundredth (or more seldom) approach, it may be embedded into the shell. Embedding begins from the adsorption of a TPyP molecule via one pyridine ring. In this case, the molecule stands on the vertex, as can be seen in Fig. 6. The embedding of the dye in this way is pos-

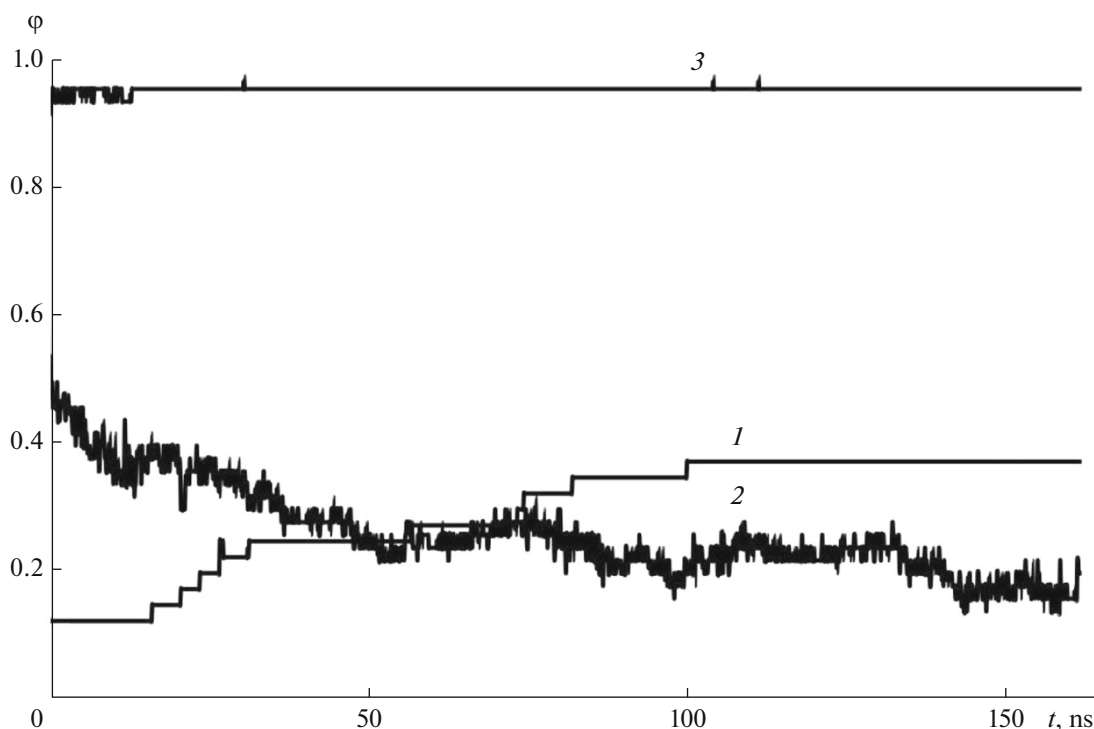


Fig. 7. Embedding of dye molecules into a shell and displacement of ligands in the C12 system, i.e., fraction ϕ of molecules in the shell of the total amount of molecules of a corresponding type: (1) TPyP, (2) TOP, and (3) TOPO.

sible for any ligands, even those strongly retained by the CQD surface, such as ionic forms of ODPA and HDA. However, the subsequent bonding of the dye via the second pyridine ring is strongly hindered when a ligand is incapable of being detached from the CQD surface. TOP is detached most easily; therefore, when it is present in the shell, dye molecules may be adsorbed “edgewise.” Nevertheless, even for ligands that are much more strongly bonded to the surface (TOPO, ODPA, and HDA), complete adsorption, i.e., bonding of a dye molecule with the CQD surface via both pyridine rings, is possible.

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation, project no. 14-13-01426.

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Translated by A. Kirilin