Surface ligands affect photoinduced modulation of the quantum dots optical performance

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ABSTRACT

Changes of optical properties of the solutions of CdSe/ZnS quantum dots (QDs) covered with the trioctylphosphine oxide (TOPO) ligands under the pulsed ultraviolet (UV) laser irradiation are observed. The fluorescence quantum yield (QY) of QDs decreases by more than an order of magnitude when the radiation dose approaches 2×10^{-15} J per particle. This process is accompanied by a blue shift of both fluorescence and the first excitonic absorption peaks. The fluorescence quenching becomes less pronounced when the overall TOPO content in the solution is increased. When TOPO ligands are replaced with n-hexadecylamine (HDA), QY and spectral properties are not changed at the same irradiation conditions. We assume that the above changes of the optical properties are associated with photooxidation of TOPO ligands by excited QD. Such process is less probable for the HDA ligand due to its different energy structure.

Keywords: quantum dots, surface ligands, laser irradiation, photooxidation

1. INTRODUCTION

Due to the unique fluorescence features semiconductor nanocrystals, also known as quantum dots (QDs)[1-3], are a perspective material for photovoltaics, nanomedicine and biology[4-7]. They have a high photostability[8], and the fluorescence quantum yield (QY) of their fluorescence can reach up to 100%[9]. Quantum confinement effect in such nanocrystals leads to the dependence of their extinction and fluorescence spectra on size[1-3], that allow to control the optical properties of QDs and structures based on them.

Developing new methods of directed modification of radiative properties of QDs could allow to extend the research and development opportunities of nanocrystals-based structures. Yet, there are some reports where QDs fluorescent properties are shown to change upon strong irradiation above the band gap. In particular, under such irradiation photoenhancement[10-16] and photoquenching[14-22] of nanocrystals, as well as a blue shift of the absorption and fluorescence spectra[12-15, 19-23] occur. It has been found that such parameters as: the presence and thickness of the QDs shell[12, 22], type of the solvent of QDs colloidal solutions[12], the presence of oxygen in the atmosphere[18, 19] and the presence of water molecules in the environment[13] affect on the photoinduced changes in QDs properties. In most studies it is assumed that the processes of photoinduced quenching and spectral blue-shift are associated with the photooxidation of the QD surface and, consequently, increasing the number of surface defects and decreasing the size of the nanocrystal[12-23]. These processes, on the one hand, pose the problem of long-term stability of QDs in their operational conditions, and, from the other, create an additional opportunity to control the radiative properties of nanocrystals. A lot of papers are devoted to this topic, but only in a few of them the interference in such processes of organic ligands, which cover the surface of the nanocrystals, is taken into account[13, 15, 18]. The understanding of the role of surface ligands can enhance our ability to control the processes of photoinduced modification of the QDs optical properties.

The purpose of this study is to investigate the influence of surface ligands on the stability of the QDs colloid solutions under strong ultraviolet (UV) laser irradiation at wavelength of 266 nm.

2. EXPERIMENTAL SECTION

2.1 Materials

Cadmium oxide (powder, 99.5%), zinc oxide (powder, 99.99% trace metals basis), 1-octadecene (ODE, technical grade, 90%), oleylamine (OLA, technical grade, 70%), n-hexadecylamine (HDA, technical grade, 90%) selenium (powder, 100 mesh, 99.5%), thiourea (ACS reagent, ≥99.0%) tri-*n*-octylphosphine (TOP, technical grade, 97%), tri-*n*-octylphosphine oxide (TOPO, reagent grade, 99%), 2-ethylhexanoic acid (2-EHA, 99%), tri-*n*-octylamine (TOA, 98%), triethylene glycol dimethyl ether (TEGDME, ReagentPlus, 99%), and anhydrous solvents (chloroform, hexane, methanol and 2-propanol) were purchased from Sigma-Aldrich; *n*-hexadecylphosphonic acid (97%) was purchased from PlasmaChem GmbH. All chemicals were used as received without any purification.

2.2 Synthesis of core-shell CdSe/ZnS quantum dots

Core CdSe quantum dots were prepared using a modified procedure[24]. Briefly, 1 mmol of cadmium oxide, 0.5 mmol of *n*-hexadecylphosphonic acid, 2 mmol of 2-ethylhexanoic acid, 2 ml of try-*n*-octylamine, and 8 ml of ODE were placed into a 25 ml three-necked reaction flask. The flask was heated to 120°C and evacuated at 10 mbar for 10 minutes. Then, under argon atmosphere, the cadmium oxide was dissolved at 220°C. After complete dissolution of CdO, the reaction mixture was cooled down to 120°C and evacuated again to remove residual water. The selenium precursor was prepared by dissolution of 2 mmol of Se powder in 2 ml of TOP and 0.5 ml of ODE under an argon flow without external heating. Selenium solution was swiftly injected into the cadmium precursor solution at 240°C, kept in argon atmosphere under vigorous stirring. The reaction was monitored by UV-Vis spectroscopy and was stopped after 5 minutes by intensely cooling with an air flow. The obtained QDs were isolated from the crude solution by precipitation with 2-propanol, and then were purified by two successive dissolution/precipitation cycles using chloroform/methanol as a solvent/coagulant combination, respectively.

Precursor stock solutions for the coating of a ZnS shell over the CdSe cores were made according to the following procedures. Zinc stock solution was prepared by dissolving 25 mmol of ZnO in 52 mmol of 2-EHA diluted with 20 ml of TEGDME. Oxide dissolution was conducted at 220°C under vigorous stirring until clear solution was obtained. The sulfur stock solution was prepared by dissolving 34 mmol of thiourea in 40 ml of TEGDME under sonication. All solutions were leveled with TEGDME to obtain final precursor concentrations of 0.85 M.

Shell coating was done in the following way. Purified CdSe cores were dissolved in hexane, and a portion containing 400 nmol of them was transferred into a mixture of 6 ml ODE and 6 ml OLA. Hexane was further removed by mild heating under a reduced pressure, and, finally, the mixture was degassed at 90°C during 20 minutes. Under argon atmosphere, 1 mmol of TOP was injected into the flask, and the core solution was allowed to settle for 15 minutes prior to the beginning of shell growth. Then the mixture was heated to 170 °C, and the injection of shell precursors was started with a syringe pump at a flow rate of 5 ml/h. The total amount of injected shell precursors was calculated to yield three ZnS monolayers over CdSe cores. The growth of the shell was monitored using UV-Vis spectrophotometry and fluorescence measurements.

After completion of shell growth, the resulting QDs were isolated from the crude solution by precipitation with 2-propanol, and then were purified in two successive dissolution/precipitation cycles using chloroform and methanol as the solvent and coagulant, respectively. Finally, the product was dissolved in chloroform, and 1 mmol of TOPO or HDA was added to this solution to change surface ligands from oleylamine to TOPO/HDA for further processing.

2.3 Laser irradiation of core-shell CdSe/ZnS quantum dots

We used colloidal solutions of previously prepared CdSe/ZnS QDs in chloroform with a fluorescence spectral maximum at 573 nm. Samples of QDs coated either with trioctylphosphine oxide (TOPO) or n-hexadecylamine (HDA) with various QDs/excess ligand ratio at a constant amount of QDs were prepared and their description is given in Table 1. Estimated molar concentration of QDs in all samples was 1.5×10^{-6} M[25].

Directional modification of QDs properties was performed by UV-laser irradiating of 1 ml of each sample with various doses of irradiation. For irradiation we used the fourth harmonic of YAG:Nd[3+] pulsed laser with a wavelength of 266 nm, and pulse energy of 1 mJ, pulse duration of 8 ns and pulse repetition frequency of 10 Hz. Homogeneity of exposure was

achieved by stirring the solution continuously. Registration of QY, fluorescence decay kinetics, fluorescence and absorption spectra was performed after irradiating.

Table 1. Samples used in the experiment.

Sample name	Type of ligand	Excess ligand concentration, mg/ml
TOPO-0.1	trioctylphosphine oxide	0.1
TOPO-0.7	trioctylphosphine oxide	0.7
TOPO-5	trioctylphosphine oxide	5
HDA-0.1	hexadecylamine	0.1

Measurements of extinction spectra and fluorescence spectra were performed on the Cary 60 UV-Vis (Agilent Technologies) and Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) respectively. Fluorescence excitation for measuring of decay kinetics was performed by YAG:Nd^{3+} pulsed laser with a wavelength of 266 nm, pulse energy of 120 μJ, pulse duration of 350 ps, and pulse repetition frequency of 50 Hz. Recording of fluorescence decay kinetics was carried out on the setup which includes monochromator M266 (Solar Laser Systems), the photomultiplier (Hamamatsu) and the digital oscilloscope Tektronix DPO 3054.

2.4 Experimental results and discussion

According to the purpose of this study - to investigate the influence of surface ligands on the stability of the QDs colloid solutions under strong UV irradiation - we have prepared three samples of QDs coated by TOPO and one sample of QDs coated by HDA. Description of samples is given in section 2.3. Then we irradiated the samples, gradually increasing the dose to trace the changes in the process of the QDs spectral properties modification induced by irradiation. Simultaneously we changed both the total amount of TOPO, and type of surface ligand (TOPO by HDA).

As a result of irradiation of QDs samples covered by TOPO, we observed a number of effects such as: decrease in the magnitude and blue shift of the fluorescence peak and the first exciton absorption peak, as well as reduction in QY. Changing the fluorescence and absorption spectra of sample TOPO-0.1 is shown in fig. 1a and fig. 2a, respectively, and it is typical for TOPO-coated samples. Dependences the blue shifts of the first excitonic absorption and fluorescence peaks from irradiation dose for all TOPO-coated samples are shown in fig. 1b and fig. 2b. They are monotonically and at the dose of 7 x 10^{-17} J per particle for all TOPO-coated samples no changes were observed in fluorescence and absorption spectra. Table 2 shows the optical properties changing of all samples at irradiation dose equal to 6 x 10^{-15} J per particle. At this dose, it is best to see the difference in changing the optical properties of the samples with different amounts of TOPO in solution. It should be noted that with increasing radiation dose to 1.2 x 10^{-14} J per particle and above we observed almost complete bleaching of all solutions.

Table 2. Optical properties of the samples irradiated with a dose of 6 x 10^{-15} J per particle.

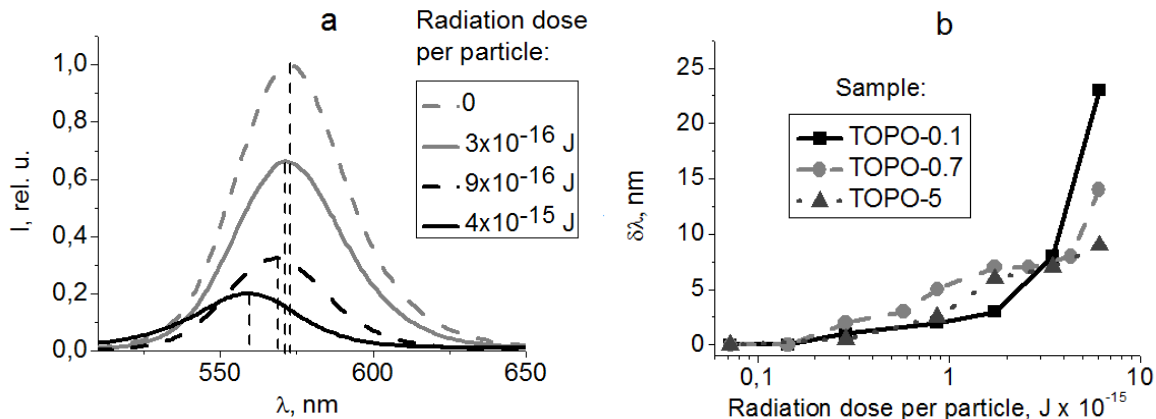| Sample	Fluorescence peak blue shift, nm	First excitonic absorption peak blue shift, nm	The ratio of the QY after irradiation to the initial	The ratio of the fluorescence decay time after irradiation to the initial
TOPO-0.1	23	35	Too low fluorescence signal	Too low fluorescence signal
TOPO-0.7	14	20	0.1	0.22
TOPO-5	9	15	0.7	0.57
HDA-0.1	3	0	1	1

Figure 1. a – the fluorescence spectra of sample TOPO-0.7 at different irradiation doses, b - the dependence of the blue shift of the fluorescence spectra on irradiation dose per particle of the TOPO-coated samples.
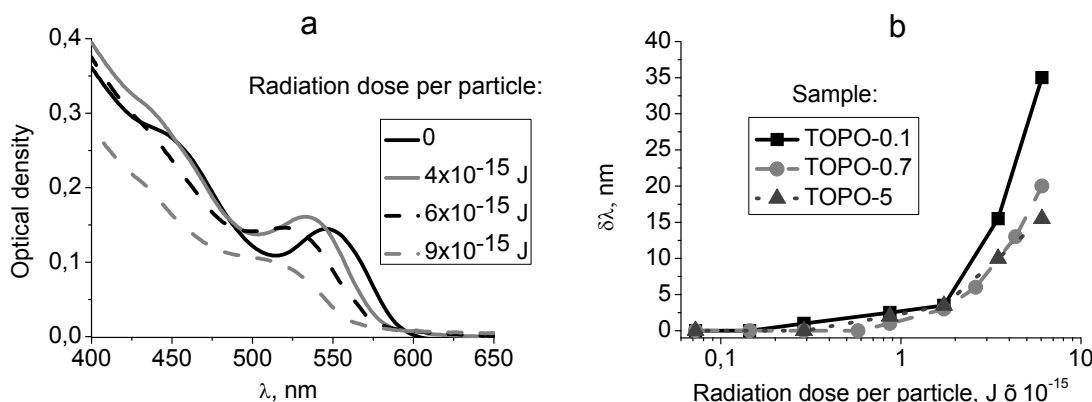

Figure 2. a - the extinction spectra of the sample TOPO-0.7 at different irradiation doses; b - the dependence of the first exciton absorption peak blue shift of TOPO-coated samples on the irradiation dose per particle.

Fluorescence QY of all TOPO-coated samples decreases monotonically up to a dose equal to 1.7×10^{-15} J per particle. Fig. 3a shows the dependence from irradiation dose per particle of the QY of TOPO-coated samples. Interestingly, with increasing concentration of TOPO in solution the rate of QY drop is decreased, and for the sample TOPO-5 at the value of dose of irradiation 6×10^{-15} J the quantum yield began to grow. The ratio of the QY after irradiation to the initial for the samples irradiated with a dose of 6×10^{-15} J per particle can be found in Table 2.

Studying the kinetics of fluorescence confirm the fact that the sample's QY depends on the TOPO content, because rate of average fluorescence decay time (τ) drop changes in a similar way with increasing concentration of TOPO. At the value of irradiation dose 6×10^{-15} J per particle the τ of sample TOPO-5 began to grow as well as the QY. Fig. 3b shows the dependence from the irradiation dose per particle of the τ of TOPO-coated samples. The ratio of the τ after irradiation to the initial for the samples irradiated with a dose of 6×10^{-16} J per particle is given in Table 2.

After observing the changes in the optical properties of the TOPO-coated samples, we tested the other ligand for comparison. The choice fell on HDA as the most popular, used for the synthesis and storage of QDs. The fluorescence spectrum of sample HDA-0.1 at the dose of 6×10^{-15} J per particle undergoes a slight blue shift by 3 nm and then at twice the dose is shifted to the red by 5 nm relative to the non-irradiated sample. It should be noted that, until the radiation dose of 6×10^{-15} J per particle when fluorescence spectra underwent a blue shift of the maximum, the shift of the absorption spectra of the sample HDA-0.1 was not observed. This doesn't allow us to correlate the fluorescence blue

shift with structural changes in QDs. With further increase of radiation dose in the extinction spectra the scattering component increased sharply, indicating the coalescence of nanocrystals with each other. This explains the red shift of the fluorescence spectra.
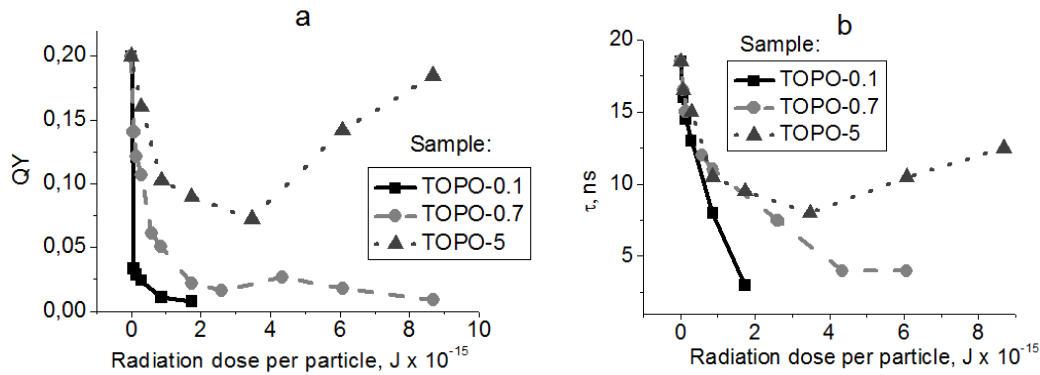

Figure 3. a - the dependence of the fluorescence QY on irradiation dose per particle of TOPO-coated samples; b - the dependence of the average fluorescence decay time on the irradiation dose per particle of the TOPO-coated samples.

Surprisingly, the QY of sample HDA-0.1 did not have changes until the irradiation dose approached 6×10^{-15} J per particle. This is a very interesting fact, since surface ligand exchange has improved the radiation resistance of quantum dots. This allow to select the surface ligands to improve stability of the colloidal solution of quantum dots in storage and operation. Dependence from irradiation dose per particle of the sample HDA-0.1 QY is shown in Fig. 4a.

The average fluorescence decay time of sample HDA-0.1 is not changed until the radiation dose of 6×10^{-15} J per particle, it is in full compliance with the immutability of QY. With further increase of radiation dose the τ decreases, indicating a decrease in QY. However, this decrease in QY, probably due to the sticking of nanoparticles, as evidenced by the red shift of the fluorescence and extinction spectra. Dependence from the radiation dose per particle of the τ is shown in Fig. 4b.
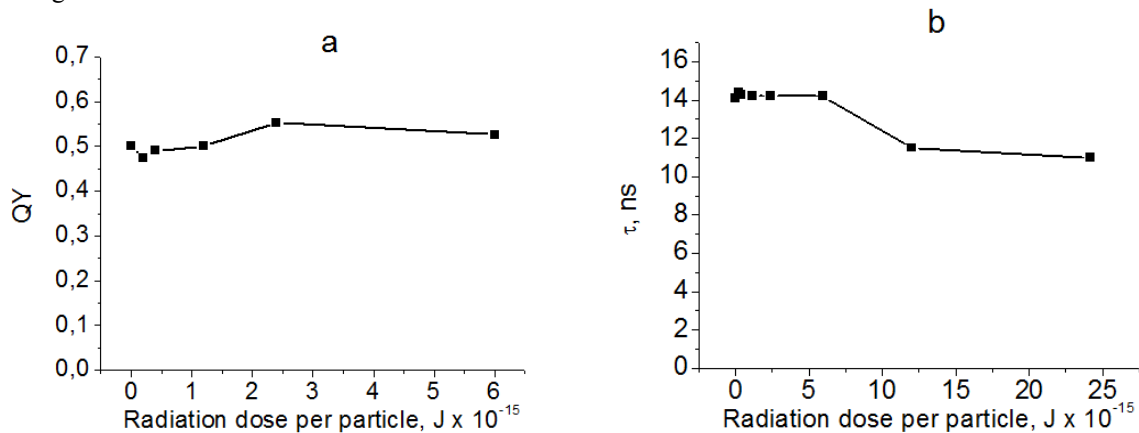

Figure 4. a – the dependence of fluorescence QY from irradiation dose per particle of the sample HDA-0.1; b - the dependence of average fluorescence decay time on the radiation dose per particle of the sample HDA-0.1.
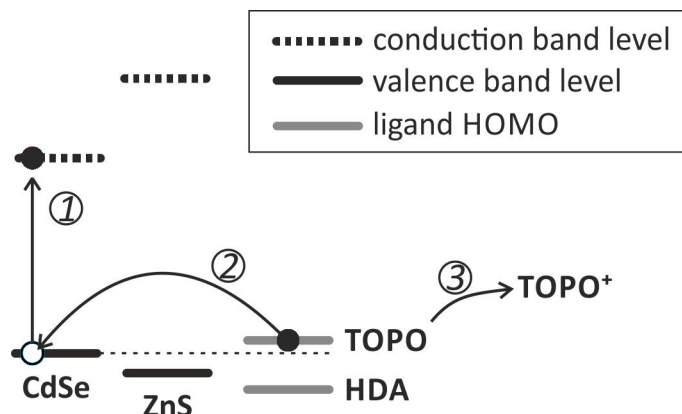
Figure 5. Shematic representation of the ligand photooxidation process which occur upon laser irradiation of QDs. 1 - electron from valence band of CdSe moves to the first excited state; 2 - electron from highest occupied molecular orbital of TOPO migrate to the vacant position in the VB of CdSe core via rapid tunneling through ZnS shell; 3 - TOPO$^+$ desorb from the surface of QDs.

Although many pathways of QD optical properties modification are given in literature[10-22], here we try to give specific explanation to the observed drastic difference in resistance to photodegradation of TOPO- and HDA-coated QD colloids. We assume that the underlying reason for that is in the energetic structure of corresponding QDs. Using data on the QDs energy bands[26] and the values of highest occupied molecular orbital (HOMO) energies[27] (the respective value of *n*-octadecylamine is used as an approximation here) we can plot an energy diagram for TOPO and HDA coated CdSe/ZnS QDs (Fig. 5). One can see that the HOMO of TOPO lies slightly above than the valence band (VB) of CdSe core while the HOMO of HDA lies slightly below. According to this diagram we can propose the following ligand photooxidation mechanism. First, upon excitation above the band gap, the electron from VB of CdSe moves to the first excited state (1 in Fig. 5). Although the radiative recombination of the photoexcited electron-hole couple is the major relaxation pathway in this situation, there is a possibility that the electron from HOMO of TOPO can migrate to the vacant position in the VB of CdSe core via rapid tunneling through ZnS shell (2 in Fig. 5). Upon oxidation, TOPO$^+$ can either desorb from the surface of QDs (3 in Fig. 5), or decompose with release of oxygen. In case of TOPO desorption it would likely simplify the photoinduced oxidation of QDs by oxygen molecules from environment. Thus, in any case the active oxygen species, that appearing on the surface of the nanocrystal, creates additional surface defects reducing QY and reduces the effective size of the nanocrystal, resulting in a blue shift. When the total amount of TOPO in the solution is increased we can expect the lower probability of TOPO desorption from QD surface and the higher probability of re-sorption of TOPO molecules from solution, preventing interaction of the oxygen from environment with a surface of the nanocrystal. This is in good agreement with the observed increase of colloid photostability when the amount of loaded TOPO rises.

When TOPO ligands are changed to hexadecylamine, the processes 2 and 3 are less probable due to unfavorable transition of the electron from lower-lying HOMO of HDA to higher lying VB of CdSe (Fig. 5). We believe, that this is the reason for the observed stability of HDA-coated CdSe/ZnS QDs to photodegradation.

3. CONCLUSION

This work demonstrates the possibility of controllable modification of spectral properties of the air saturated colloidal solutions CdSe/ZnS QDs covered with the trioctylphosphine oxide (TOPO) ligands by nanosecond pulsed λ=266 nm laser irradiation. It has been shown that under the influence of the laser irradiation the fluorescence quantum yield of QDs covered with TOPO is constantly decreasing. QY value drops by more than an order of magnitude when the radiation dose is close to 2×10^{-15} J per particle. Besides, when the radiation dose rises, the fluorescence decay kinetics change and its average decay time decreases. The observed decrease of QDs QY is accompanied by a blue shift of both the fluorescence spectrum maximum and the first excitonic absorption peak. With the increase of irradiation dose up to 6×10^{-15} J per particle, these shifts exceed 35 nm. The increase of total amount of TOPO in the solution leads to slowdown of decline of QY and fluorescence decay time. Surprisingly, when TOPO ligands are replaced with n-hexadecylamine (HDA), no changes in the sample QY at the dose lower than 6×10^{-15} J are observed. At much higher doses up to 2.4×10^{-14} J we observe only a 5 nm red spectral shift of fluorescence and a decrease of decay time from 14 to 11 ns, which is

most likely associated with slight aggregation of nanoparticles. This suggestion is supported by the increase of the scattering component in the extinction spectrum.

We assume that the above changes of the optical properties are associated with oxidation of TOPO ligands by excited QD. This is possible due to specific HOMO energy of TOPO which is slightly above the VB of CdSe cores. Upon oxidation, $TOPO^+$ can either desorb from the surface of QDs, or decompose with release of oxygen. The oxygen, that appearing on the surface of the nanocrystal from environment or from TOPO creates additional surface defects reducing QY. It also reduces the effective size of the nanocrystal, resulting in a blue shift. Increasing free TOPO content in solution reduces the probability of TOPO desorption from QD surface and increases the probability of re-sorption of TOPO molecules. This is prevents the interaction of the oxygen from environment with a surface of the nanocrystal. Such processes are less probable for the HDA ligand due to its different energy of HOMO, which is lower than the VB of CdSe core of QDs.

We believe that such influence of surface ligands allow to increase the stability of QDs during storage and operation, as well as create an additional opportunity to control the photoinduced spectral modification of nanocrystals.

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