

Preparation and formation mechanism of strong violet luminescent CdS quantum dots by using a ligand exchange strategy

Tian-Long Zhang, Yun-Sheng Xia, Xue-Lian Diao and Chang-Qing Zhu*

*College of Chemistry and Materials Science, Anhui Key Laboratory of Functional Molecular Solids, Anhui Normal University, Wuhu, 241000, P. R. China; *Author for correspondence (Tel.: +86-553-3937136; Fax: +86-553-3869659; E-mail: zhucq@mail.ahnu.edu.cn)*

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Abstract

A simple and general method has been proposed for preparing strong violet emitting CdS quantum dots, in which a ligand exchange strategy was applied to surface passivation and functionalization with good reproducibility. The resulting quantum dots showed a visible violet luminescence with emission peak centered near 423 nm and photoluminescence quantum yields reached over 30%. Additionally, different mercapto-compounds used as ligands can make different functionalized surfaces, favoring quantum dots dispersion in different media and their further applications. It was observed that the band edge emission has the main contribution to the bright violet luminescence.

Introduction

Semiconductor nanocrystals (NCs), or quantum dots (QDs) have attracted much attention in diverse fields ranging from optoelectronics, photovoltaics to biological sensing due to their unique optical properties (Wendy et al., 2002; Clapp et al., 2004; Fleischhaker & Zentel, 2005). To date, there have been a wide range of very efficiently light-emitting QDs synthesized either in organic media or in aqueous solutions, such as CdSe, CdTe (from green to red region), PbSe, HgTe, and InAs (near-Infrared and infrared region) (Murray et al., 1993; Battaglia & Peng, 2002; Gaponik et al., 2002; Yu et al., 2004; Xu et al., 2006; Piepenbrock et al., 2006). What noteworthy is that the short-wave luminescent QDs also have shown great application potential, such as for fabricating light-emitting devices

(Park et al., 2001) and building up donor-acceptor pair in fluorescence resonance energy transfer (Clapp et al., 2006), etc. However, reports on QDs efficiently emitting in the short wave region are less common. On the one hand, the inherent bulk band gaps for many semiconductors lead to their intrinsic spectral limitation. For instance, CdSe with the small bulk band gap (1.7 eV) can achieve blue luminescence reluctantly through synthesizing extraordinary small particles (Zorman et al., 1995). And ZnSe, due to its large bulk band gap of 2.7 eV, generally exhibits fluorescence of too short wavelength that often could not be observed in visible range (Shavel et al., 2004). On the other hand, short wave emitting often requires obtaining small sized QDs according to quantum confinement effects (Henglein et al., 1989). And small sized QDs need to subtly control their growth via Ostwald ripening process to prepare

(Peng et al., 1998), and often encounter a deep-trap emission that overwhelms the band-edge emission due to inadequate surface passivation (Steckel et al., 2004). Therefore, eliminating the trap emission as well as tuning QDs' energy band gap is of crucial importance to obtain the short-wave luminescent QDs. Recently Jang acquired blue luminescence by introducing CdSeS alloy and interfused CdSe//ZnS nanocrystals (Jang et al., 2003; Jun & Jang, 2005). Also Bawendi obtained blue luminescence through core/shell structure (Bawendi et al., 2004). Blue luminescence seems to be the high point of these QDs, and few of them were obtained strong visible violet luminescence. It should be noted that a two-phase approach and seeding-growth technique can obtain highly violet emitting CdS QDs via carefully adjusting the reaction temperature, time, and the ratio of reactants (Wang et al., 2005). However, this straightforward strategy needs to be carried out in an autoclave in the presence of plentiful myristic acid (MA) and oleic acid (OA), which may hinder the QDs' further surface tailoring with other molecules.

Bulk CdS, with an energy band gap of 2.5 eV, should be a suitable candidate for emitting in the short wave span (Jang et al., 2004). Unfortunately, CdS QDs directly prepared in the presence of thiol stabilizers in aqueous solution often show broad trap emission in long wave with a poor photoluminescence quantum yields (PL QY) (Wuister et al., 2003), and hardly emit strong violet luminescence.

Herein we report a simple method for preparing short-wave emitting CdS QDs, in which ligand exchange strategy was employed for surface passivation and functionalization (Figure 1). The resulting QDs shows clear visible violet luminescence with emission peak centered near 423 nm and PL QY reaches over 30% (quinine sulfate as a reference). In addition, the different mercapto-compounds investigated can be introduced easily, in favor of their further applications. Moreover, the evolution of the PL spectra in the ligand exchange process was recorded, indicating the formation mechanism of violet emission. To our best knowledge, little research has been conducted in applying the evolution of the PL spectra to elucidate the ligand exchange process before. And this research could also provide important information on the interaction between the organic ligands and the NCs surface in the ligand exchange reaction.

Experimental

Reagents

Octadecene (ODE, 90%), oil acid (OA, 90%), cadmium oxide (CdO, 99.5%), 3, 6-Dioxa-1, 8-octane-dithiol (DODT, 95%), 1-dodecanethiol (DDT, 98%+), 3-mercaptopropionic acid (MPA, 99%), were purchased from Alfa Aesar. Sulfur (99.5%+, powder), methanol, anhydrous tetrahydrofuran (THF) and other routine reagents were

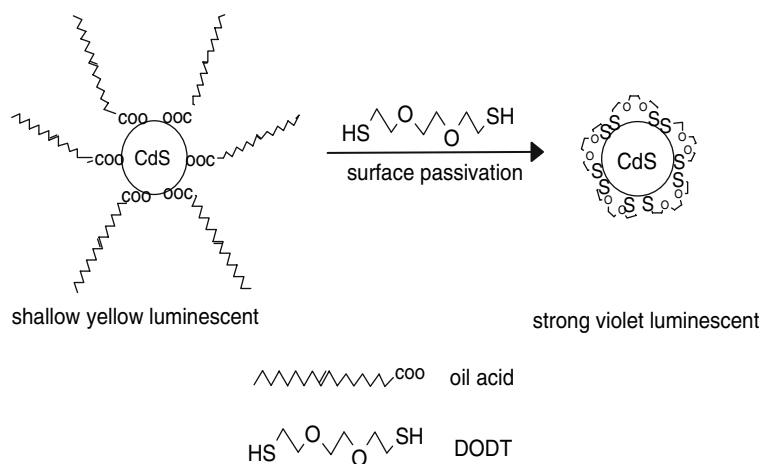


Figure 1. Schematic process for preparing violet luminescent CdS QDs via ligand exchange strategy.

purchased from Shanghai Reagent Company (Shanghai, China). Reagents without special indications were of analytical grade and used as received without further purification.

Preparation of CdS QDs capped by OA

CdS QDs were synthesized in ODE following the method of Yu and Peng with minor modifications (Yu & Peng, 2002). Typically, a mixture of 0.2 mmol CdO, 0.35 mmol OA and 4 g ODE was heated to 300°C. A solution of 0.15 mmol sulfur dissolved in ODE was swiftly injected into the reaction system, and the mixture was cooled down to 250°C for CdS QDs growth. The size of CdS QDs was monitored by UV–Vis absorbance spectroscopy and photoluminescence spectroscopy (Yu et al., 2003). The reaction mixture for the synthesis of CdS NCs in ODE after a given reaction time was separated to two fractions by extraction with chloroform and methanol (1:1, v/v). After the extracting process was applied twice, the NCs were precipitated by adding a mixture of methanol and acetone (1:2, v/v) and isolated by centrifugation and decantation. The resulting wet precipitate was stored for future use. As can be easily understood, CdS QDs of large sizes cannot emit violet color due to the size-dependent optical properties of the QDs (Alivisatos, 1996), reaction time should be controlled to obtain CdS NCs of appropriate sizes. In this work, reaction time was fixed for 15 minutes to obtain CdS QDs of 2.6 nm with band-edge emission centering at about 401 nm. OA used here has been proven to be a good ligand for obtaining highly luminescent small CdS QDs (Yu & Peng, 2002). And it can be easily replaced by the following mercapto-compounds, due to the binding ability of Cd-carboxyl weaker than that of Cd-thiol (Aldana et al. 2005; Liu et al., 2006). Different from other methods (Jang et al., 2004; Wang et al., 2005), a smaller quantity of OA was used here. Overmuch OA would make ligand exchange difficult to perform according to our observation.

Ligand exchange with DODT

Ligand exchange was performed as shown in Figure 1. The precipitated CdS QDs were dispersed in 30 ml anhydrous THF to which 0.2 ml DODT was added. The resulting solution was then allowed to reflux at 50°C for a certain

time under N₂ flow. The PL spectra were recorded at various time intervals. Several other solvents such as acetone, N, N-dimethylformamide, and ethyl acetate as well as other two mercapto-compounds, DDT and MPA were also investigated in the ligand.

Characterization

UV–Vis absorption spectra and PL spectra were recorded using a Hitachi U-3010 spectrophotometer (Tokyo, Japan) and a Hitachi F-4500 fluorometer (Tokyo, Japan), respectively. All optical measurements were performed at room temperature. PL QY of CdS QDs were calculated by comparison with quinine sulfate in 0.1M H₂SO₄ assuming its PL QY as 57.7% (Eastman, 1967). High-resolution transmission electron microscopy (HRTEM) was performed on a JEOL-2010 transmission electron microscopy using an acceleration voltage of 200 kV. Fluorescence lifetimes were measured with the time correlated single photo counting technique on the Combined Steady State and Lifetime Spectrometer (Edinburgh Analytical Instruments F900). FT-Infrared (FT-IR200) spectra were recorded in KBr medium in the range 400–4000 cm⁻¹.

Results and discussion

Characterization of OA capped CdS NCs

Figure 2 shows the typical UV–Vis and PL spectra of CdS NCs capped by OA recorded before post-preparative treatments. The UV–Vis spectrum presents a main sharp peak at 374 nm, ascribed to the first optically allowed transition between quantum confined state in conduction and valence band, and less intense but well-defined features at higher energies. The sharpness of the first absorption peak and the luminescence linewidth (full width at half maximum, fwhm ~26 nm) indicate a narrow size distribution of the synthesized NCs. The luminescence of the CdS NCs is dominated by strong band-edge emission ascribed to the exciton radiative recombination, and exhibits a relative weak, broad band contribution on the low energy side. This broad emission band peaked at $\lambda = 540$ nm is attributed to recombination via surface localized states (Comparelli et al., 2003).

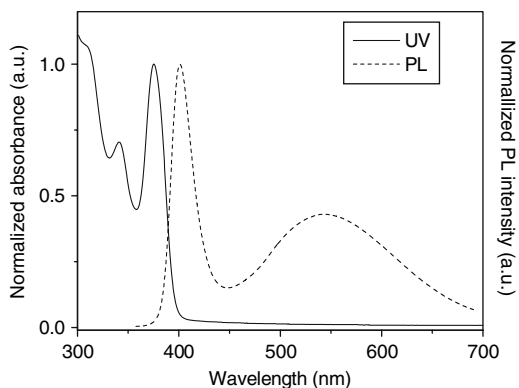


Figure 2. Normalized UV-Vis absorption and PL spectra ($\lambda_{\text{ex}} = 330$ nm) of OA capped CdS NCs dispersed in chloroform before post-preparative treatments.

The Stokes shift between absorption and the band-edge emission could be attributed to the optically forbidden transition of the ground exciton (“dark exciton”), separated from the first optically active state by the e-h exchange interaction (Norris & Bawendi, 1995; Talapin et al., 2001). A typical high-resolution TEM (HRTEM) image of CdS NCs capped by OA was shown in Figure 3. The image confirms that the CdS NCs were obtained for 2.6 nm in diameter which well conforms to the calculations from absorption spectra with a uniform size distribution and regular shape. Moreover, the

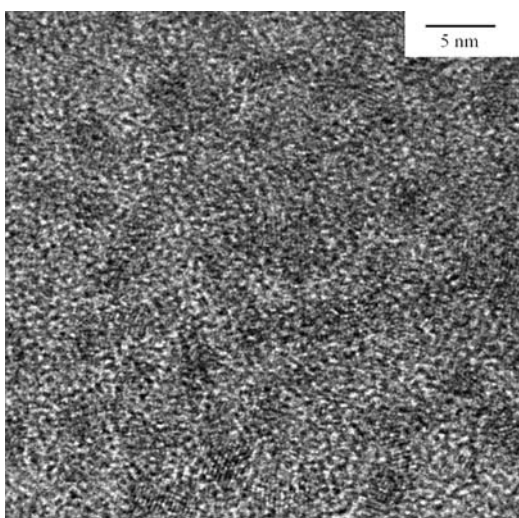


Figure 3. HRTEM image of CdS QDs dispersed in THF after post-preparative treatments, scale bar is 5 nm.

clear lattice fringes in the HRTEM indicate the fine crystalline nature of the NCs.

Influence of post-preparative treatments

To facilitate the ligand exchange reaction and obtain highly reproducible results, post-preparative treatments as extraction of OA excess and un-reacted precursors, precipitation in methanol and acetone and re-dispersion in chloroform were performed twice before the ligand exchange. The obtained mud-like precipitate, consisting of CdS NCs partially capped with OA, was collected and re-dissolved again in THF, yielding an optically clear solution. As shown in Figure 4, after post-preparative treatments, the intensity of the broad band increases, as previously reported in reference (Zezza et al., 2003).

The reaction media and the amount of DODT

Ligand exchange, as a well-established method to tailor the NCs surface, which has been mostly reported performing at the interface between two phases (Murray et al., 1993; Chan & Nie, 1998), tends to be insufficient. THF with moderate polarity is compatible with plenty of organic molecules, thus opted as the reaction media for the ligand exchange. Compared with several other solvents investigated, it can provide a homogeneous phase reaction condition to ensure the facile ligand

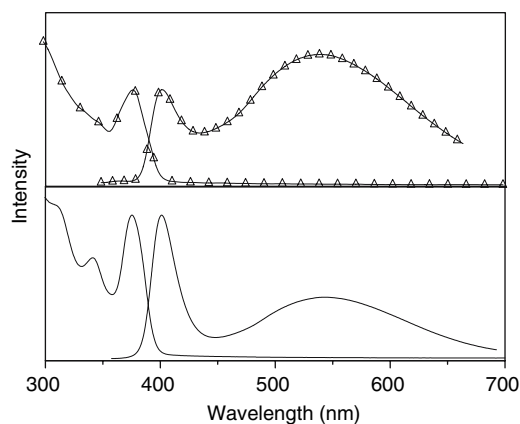


Figure 4. Normalized UV-Vis absorption and PL spectra of CdS QDs in solution as prepared (solid line) and after post-preparative treatments (triangles) at RT. Excitation at $\lambda = 330$ nm.

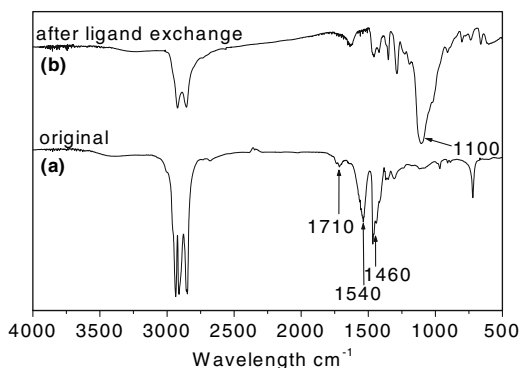


Figure 5. FTIR spectra of the CdS QDs. (a) OA capped CdS QDs. (b) After ligand replacement with DODT.

replacement and efficient surface passivation. It should be emphasized that adding excessive amount of DODT in a lump would induce nanocrystal aggregation, causing a sharp loss in quantity of CdS QDs. Therefore, carefully adding appropriate quantity of DODT is strongly recommended taking the passivation efficiency into account.

Characterization of DODT capped CdS NCs

FTIR spectrometry was used to confirm the ligand replacement. As shown in Figure 5, the observed band at 1710 cm^{-1} is assigned to the C=O stretch

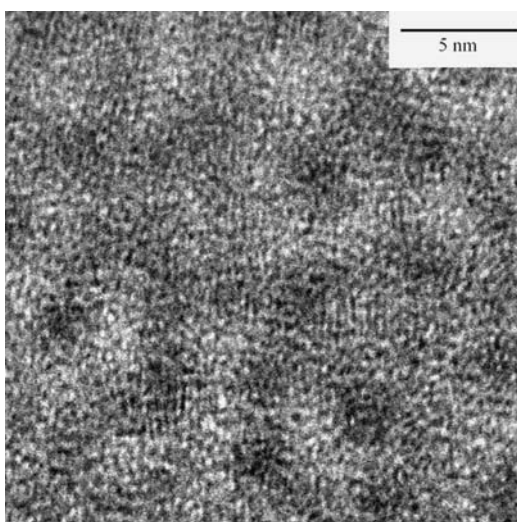


Figure 6. HRTEM image of CdS QDs after ligand exchange with DODT in THF, scale bar is 5 nm.

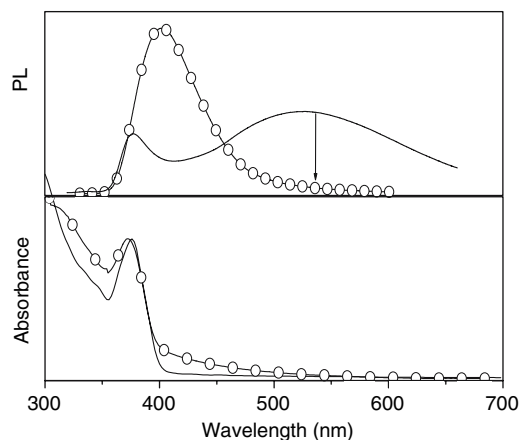


Figure 7. Absorption and PL spectra of CdS QDs before (solid line) and after ligand exchange (circles) at RT. Excitation at $\lambda = 330\text{ nm}$.

of the carboxyl group (Lee & Harris, 2006). Another two bands at 1540 and 1460 cm^{-1} are characteristic of the asymmetric $\gamma_{\text{as}}(\text{COO}^-)$ and the symmetric $\gamma_{\text{s}}(\text{COO}^-)$ stretch respectively, suggesting that OA is chemisorbed as a carboxylate onto the CdS NCs (Wu et al., 2004). After ligand exchange, the FTIR spectrum shows a new band at 1100 cm^{-1} attributed to C–O bond stretching of DODT, indicating a successful surface ligand replacement with DODT. The shape and the crystallinity of the CdS NCs after the ligand exchange were observed using HRTEM. In Figure 6, the NCs maintained their original shapes without deformation or growth, confirmed by the UV absorption spectrum. In Figure 7, the first absorption peak after ligand exchange also appeared at 374 nm , showing no obvious shift compared to the initial. After ligand exchange, the trap emission completely disappeared through the ligand exchange treatment (Figure 7). Consequently, a clear luminescence color change from

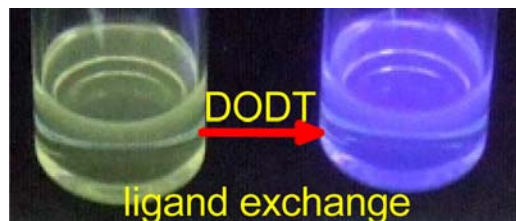


Figure 8. Photo of OA capped CdS (left) and DODT capped CdS taken under a 365 nm UV lamp.

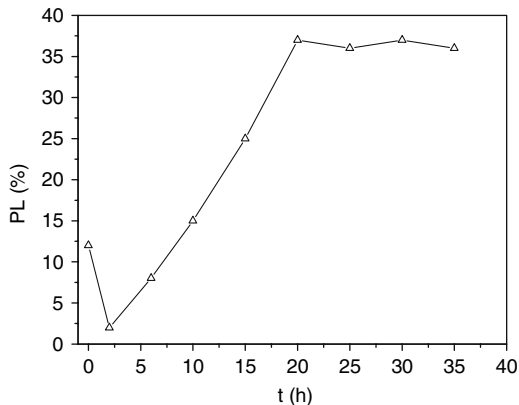


Figure 9. PL QY of the CdS QDs in the ligand exchange process.

shallow yellow to fresh violet was observed (Figure 8), suggesting an effective passivation for the surface trapping states. Apart from the color change, the PL QY also enhanced greatly compared to the initial (Figure 9).

Formation mechanism

To elucidate the formation mechanism, we recorded the integrated PL spectra evolution in the ligand exchange process. As shown in Figures 9 and 10, in the beginning, excess DODT resulted in the detachment of OA from the surface, inducing many dangling bonds of the surface atoms. Surface trapping states ensue from the abundant dangling bonds, leading to the reduction of PL QY. Intensely broadened PL features were found in the temporal evolution of the PL spectra, suggesting a surface structure/reconstruction at the NCs surface (Qu & Peng, 2002). With the ligand exchange going on, DODT would be adsorbed onto the surface, removing most of the surface trapping states and passivating the NCs surface. Due to a favorable surface structure/reconstruction that was growing, the PL profile was narrowing and the PL QY was improving. Best

Table 1. The fluorescence lifetime of CdS QDs before and after ligand exchange for different λ_{em}

λ_{em}	τ/ns
401 nm	5.02
540 nm	13.23
423 nm	7.74

results were acquired after 20 h surface exchange treatment. Longer treatments, up to 35 h, do not improve the optical properties, indicating an optimal surface structure/reconstruction has grown. Moreover, according to Figure 9, it is quite evident that the strong violet emission was derived from the band-edge emission and the trap emission of the initial CdS QDs. This can be further confirmed by time-resolved PL spectroscopy (Zhelev et al. 2006). In Figure 11 and Table 1, two main contributions are present in the data, a fast decay (characteristic of CdS QDs capped by OA recorded at $\lambda_{em} = 401$ nm corresponding to the band edge emission in the PL spectrum) and a slow decay (characteristic of trap emission of CdS QDs at $\lambda_{em} = 540$ nm corresponding to the broad part of the PL spectrum). After ligand exchange, the fluorescence half-life of CdS QDs capped by DODT was 7.74 ns, which was commensurate with the fluorescence half-life of band-edge emission (5.02 ns). The data obtained from the time-resolved spectroscopy proposed that the band-edge emission of the CdS QDs contributed most to the achieved violet emission. This can also explain why the achieved PL QY is much higher than that of the CdS QDs prepared via direct modification with mercapto-compounds. As mentioned above, preparation directly in the presence of thiol stabilizers often presents weak trap emission.

Surface exchange with other two mercapto-compounds

In order to tailor the surface functionality, other two mercapto-compounds, DDT and MPA, were

Table 2. Main properties of CdS QDs passivated by three different mercapto-compounds

λ_{em} (nm, OA capped CdS QDs)	Surface modified molecule	λ_{em} (nm, after ligand exchange)	PL QY [%]	Dispersion media
401	DODT	423 (violet)	37	CHCl ₃
401	DDT	423 (violet)	36	CHCl ₃
401	MPA	422 (violet)	34	PBS buffer

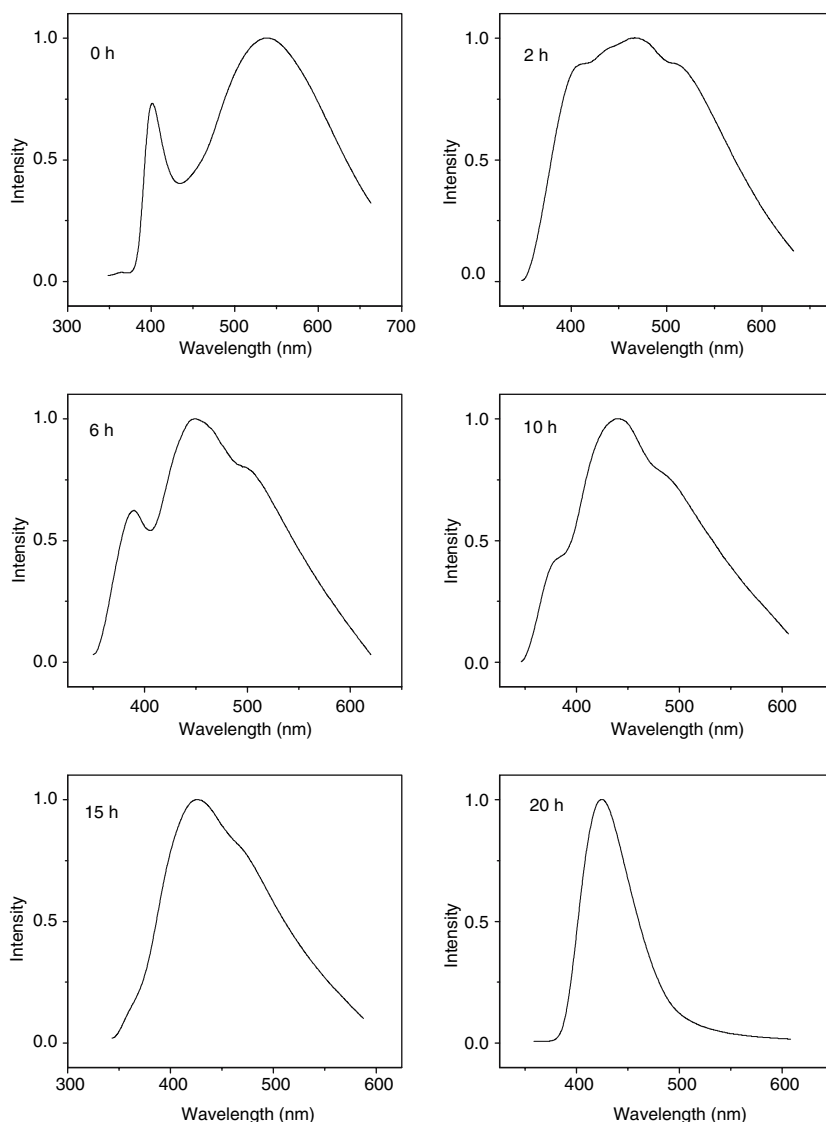


Figure 10. Temporal evolution of the PL spectra of CdS QDs in the ligand exchange reaction (all the spectra were normalized).

also investigated for ligand exchange in a similar way. Likewise, strong violet luminescence can be obtained with an almost identical violet emission with the PL QY evidently enhanced (Table 2). It is worth noting that the resulting QDs can be precipitated as a powder and re-dispersed in different solvents (Table 2), or incorporated in polymer matrix, thus considerably increasing their application possibility as violet-emitting optoelectronics.

Conclusion

A ligand exchange method has been employed to obtain strong violet luminescent CdS QDs with different functionalized surface. Formation mechanism was investigated, proposing that the band-edge emission contributed significantly to the obtained strong violet luminescence. This work not only develops a new method to obtain highly violet CdS QDs, but also provides new insight into

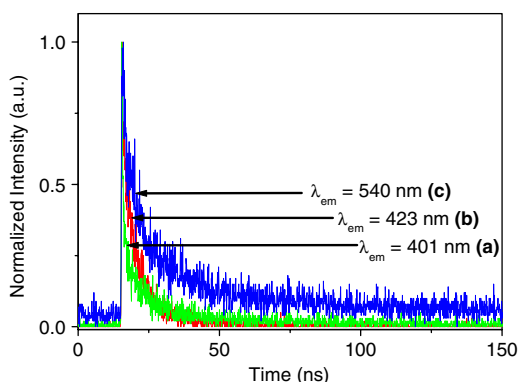


Figure 11. Time-resolved PL lifetime spectra of CdS QDs before and after ligand exchange. (a), (c): the CdS QDs capped by OA dispersed in THF; (b): CdS QDs capped by DODT dispersed in THF. All data were recorded at $\lambda_{\text{ex}} = 371$ nm.

the comprehension on the interaction between the ligands and the NCs surface.

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