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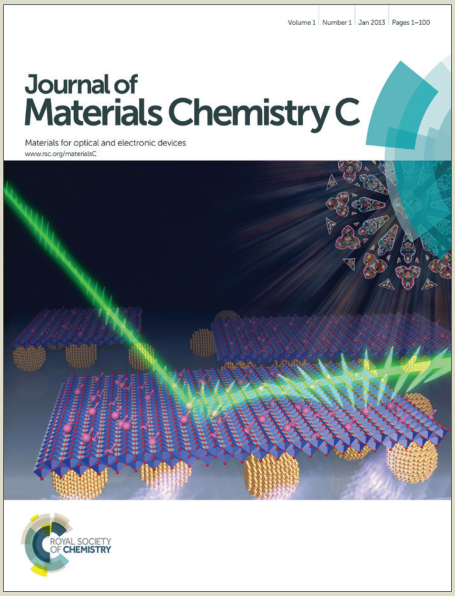

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ARTICLE TYPE

Prolonging the Lifetime of Excited Electrons of QDs by Capping them with π-Conjugated Thiol Ligands

Jie Chang, Hongbo Xia, Suli Wu,* and Shufen Zhang

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Lifetimes of the excited electrons (photoluminescence lifetime) of quantum dots (QDs) have important effect on electron transfer efficiency between QDs and other substances and thus determined their application. Here, a new strategy to prolong the photoluminescence (PL) lifetime of quantum dots (QDs) by using π-conjugated ligands together with thioglycolic acid (TGA) as the QD's ligand shell is reported. 4-mercaptobenzoic acid (4-MBA), 4-Methylbenzeneththiol (4-MBT) or 2-Mercaptobenzothiazole (2-MBTH) was selected as π-conjugated ligand together with thioglycolic acid (TGA) to synthesize aqueous CdTe quantum dots (QDs). The decay curves of TGA-CdTe, 4-MBA-TGA-CdTe, 4-MBT-TGA-CdTe and 2-MBTH-TGA-CdTe (λem=550 nm) were recorded and their average PL lifetimes were calculated. The HOMO and LUMO energy levels of 4-MBA, 4-MBT and 2-MBTH were calculated with Gaussian 09W. By comparing lifetimes of QDs capping by different ligands relating to the HOMO and LUMO energy levels of ligands, we presume that in the QDs/π-conjugated ligand hybrid, electron delocalized field is formed by mixing the LUMO energy levels of π-conjugated ligand with conductive band-edge energy (E_{cb}) of CdTe QDs, which will supply the excited electron with a more stable environment. As a result, the PL lifetime of CdTe QDs is prolonged greatly (from 49 ns to 80 ns) when π-conjugated ligand with appropriate LOMO energy level was used as ligand shell.

Introduction

Quantum dots (QDs) have gained a lot of research interests in the last few decades due to their existing size and shape dependent properties [1] and have been widely studied as luminescence probes and sensors, [2,3] light-emitting devices (LEDs), [4] photogeneration of H_2 in water [5] and solar cell. [6] In particular, CdTe QDs have been intensively studied due to their high fluorescence quantum yield (QY) and narrow bulk band gap of 1.4 eV. In many application processes of QDs, photoinduced electron transfer plays an important role, such as in solar energy conversion, [7] photochemical conversion, and semiconductor-sensitized solar cells. [8] For example, in QDs sensitized solar cell, QDs are excited by sunlight and the electrons in valence band (VB) of QDs are excited to conductive band (CB) of QDs, then the excited electrons in CB of QDs are transferred to semiconductor photoanode.[8] The electron transfer efficiency is one of the most impotant factors which determined the photocurrent and the overall efficiency of QDs sensitized solar cell. Hence, increasing electron transfer efficiency is very important for many applications of QDs, and a great number of studies have focused on electron transfer between semiconductor nanomaterials and other substances. [9] Prolonging the lifetime of the excited electrons stabilized in conductive band (CB) of QDs is one of the effective methods to increase electron transfer efficiency from CB of QDs to other substances. Generally, CdTe QDs have photoluminescence (PL) lifetime about 10~50 ns. [10, 11] The possibility of tailoring the lifetime of the excited electrons in QDs over a wide range, is one of the most significant properties of QDs.

Covering a thin layer of GaAsSb on the InAs QDs was reported to increase the PL lifetime of self-assembled InAs QDs. The GaAsSb covered InAs QDs exhibit much longer decay time than the reference InAs QDs. [12] As to colloidal QDs, covering CdSe or CdS on CdTe to form CdTe/CdSe, CdTe/CdS core-shell quantum dots QDs also lead to prolongation of the lifetime of the CdTe core. [13-15] The charge separation induced by the band offset redshifts the exciton emission and increases the radiative lifetime. However, this method will result in red shift of QDs emission (the VB band-edge energy decreased) and decrease of their quantum yield.

Not only the semiconducting materials can serve as a shell to protect QDs and modulate their fluorescence decay lifetime, organic ligands capping on the surface of QDs are also reported to change the fluorescence decay lifetime of QDs. According to Guyot-Sionnest's report, [16] a dipole model of energy transfer to ligands vibrations accounts for the nonradiative energy relaxation of PbSe. This is to say ligands vibration will decrease the fluorescence efficiency of colloidal QDs and thus decrease the decay lifetime. They replaced oleate ligands by perfluorotetradecanoic acid. As a result, the sample's PL energy stayed the same, whereas the lifetime increased..

This paper describes a new method to control the PL lifetime of QDs by changing the structure of the QD's ligand shell. We propose that capping QDs with π-conjugated ligand with suitable LUMO level will form electron delocalized field by mixing the LUMO energy levels of π-conjugated ligand with conductive band-edge energy (E_{cb}) of CdTe QDs (Figure 1). The electron delocalized field will supply the excited electron of QDs with a more stable environment, and as a result the PL lifetime of CdTe QDs will be prolonged. Here，4-mercaptobenzoic acid (4-MBA), 4-Methylbenzenethiol (4-MBT) or 2-Mercaptobenzothiazole (2-MBTH) was selected as π-conjugated ligand together with thioglycolic acid (TGA) to synthesize aqueous CdTe quantum dots (QDs). As anticipated, the PL lifetime of CdTe QDs is prolonged greatly (from 49 ns to 80 ns) when π-conjugated ligand with appropriate LOMO energy level was used as ligand shell.

Experimental Section

Materials

4-mercaptobenzoic acid (4-MBA, 99%), 4-Methylbenzenethiol (4-MBT, 99%), 4, 4 '- diphenyl sulfide (DPSF, 99%) and 4-Amino-3-hydrazino-5-mercapto-1, 2, 4-triazole (AHMT, 99%) were purchased from Shanghai crystal pure Industrial Company Limited (Shanghai，China). Thiolglycolic acid (TGA, 90%) and $Cd(CH_3COO)_2•2H_2O$ (99.5%) were purchased from TianJin Kermel Chemical Reagent Development Center (Tianjin, China). 2-Mercaptobenzothiazole(2-MBTH,99%), $NaBH_4$ (96%) and potassium tellurite (K_2TeO_3,98%) were purchased from Sinopharm Chemical Reagent Co.(Shanghai, China). The other chemicals were supplied by Shengyang Chemical Reagents Company (Shenyang, China) and used directly without further purification.

Synthesis of CdTe QDs

The CdTe QDs were synthesized according to our previously reported method.[17] The molar ratio of Cd^{2+}/π-conjugated ligands /TGA/TeO_3^{2-} was 5:3:3:1, pH is from 9.0 to 12.5. The concentration of Cd^{2+} was 0.75mmol/L. Typically, 0.075 mmol $Cd(CH_3COO)_2•2H_2O$ was dissolved into 50 ml deionized water in a stand-up flask. Then 0.045 mmol 4-MBA and 0.045 mmol TGA were added successively, and the pH was adjusted with 1 M NaOH solution, and then, 0.015 mmol K_2TeO_3 which was dissolved into 50 ml deionized water was added into the above solution. Then 40 mg of $NaBH_4$ was added into the precursor solution. After the reactions proceeded for another 15 minutes, the crude solution was refluxed at 100℃ in the open-air condition. Through controlling the reaction time, CdTe QDs with desired PL emission spectra can be obtained.

Characterization

Fluorescence measurements were carried out using JascoFP6500 luminescence spectrometer at room temperature. The room temperature fluorescence quantum yields of sample were measured with an excitation wavelength of 490 nm, by using 1,3,5,7-tetramethyl-8-phenyl-4-bora-3a,4a-diaza-s-indacene (BODIPY, λexc = 485 nm, ΦFR = 0.72 in tetrahydrofuran) as a reference. The quantum yields of sample were finally decided by comparing the integrated emission of sample to that of BODIPY at an identical optical density of 0.05–0.1. UV/Vis absorption spectra were recorded on a HP8453spectrophotometer. Power X-ray diffraction (XRD) measurements were performed on Rigaku D/max 2400 x-ray diffractometer For the XRD characterization, acetone was used to precipitate and purify the CdTe QDs. The free TGA was removed by centrifugation and separation. Fluorescence decay traces of QD with different capping ligands were recorded in the Time Correlated Single Photon Counting (TCSPC) mode using the FLS920 Spectrofluorometre (Edinburgh Instruments, UK). Briefly, the samples were excited by a 472.6-nm pulsed laser (EPL-470 Edinburgh Instruments, UK.) with a 10 MHz repetition rate. The full width at half maximum of the laser pulse was ~88.2ps. The fluorescence was collected after crossing through a polarizer. The bandwidth monochromator for excitation wavelengthand emission wavelength is different, respectively are 0.1 nm and 1 nm. In the peak channel the counts reached 5000.

Methods of analysis

Time resolved fluorescence decay traces were deconvoluted from the signal and fitted using FluoFit 4.4 package (Picoquant GmbH). The experimental decay traces were fitted to multi-exponential functions via a Levenberg-Marquard algorithm-based nonlinear least-squares error minimization deconvolution method. Usually, up to four different exponential terms were used to fit the experimental decay traces. The quality of fittings was judged by the reduced chi-squared method, χ2, the weighted residuals and the correlation functions.

Results and discussion

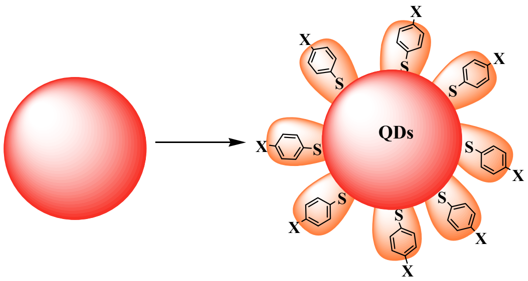
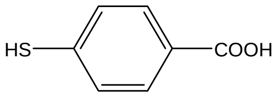
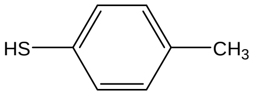


Fig.1 Diagrammatic sketch of electron delocalized field in π-conjugated ligand capped QDs.

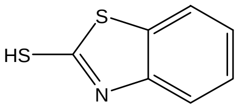
4-mercaptobenzoic acid (4-MBA), 4-Methylbenzenethiol (4-MBT) or 2-Mercaptobenzothiazole (2-MBTH) (their structures were shown in Chart 1) was selected as π-conjugated ligand together with thioglycolic acid (TGA) to synthesize aqueous CdTe quantum dots (QDs). Through controlling the reaction time, CdTe QDs with desired PL emission spectra can be obtained.



4-MBA



4-MBT



2-MBTH

Chart 1. Structures of 4-MBA, 4-MBT and 2-MBTH

The fluorescence spectra and quantum yields (QYs) of CdTe QDs capped with TGA (TGA-CdTe), 4-MBA together with TGA (4-MBA-TGA-CdTe), 4-MBT together with TGA (4-MBT-TGA-CdTe) and 2-MBTH together with TGA (2-MBTH-TGA-CdTe) (supporting information Figure S1-S3) indicated that the addition of π-conjugated ligand did not affect the growing process of CdTe QDs and high quality CdTe QDs were prepared.

The decay curves of TGA-CdTe, 4-MBA-TGA-CdTe, 4-MBT-TGA-CdTe and 2-MBTH-TGA-CdTe (λem=550 nm) were recorded and shown in Figure 2. The average lifetimes (τ_{av}), using a nanosecond diode excitation source at 405nm, were calculated according to previous reports. [18] The calculated results were summarized in Table 1. Excitingly, the fluorescence lifetime of CdTe QDs capped with π-conjugated ligands was greatly increased. The fluorescence lifetime of CdTe QDs capped with commonly used TGA was 49 ns, while the PL lifetime of 2-MBTH-TGA-CdTe, 4-MBT-TGA-CdTe and 4-MBA-TGA-CdTe were prolonged to 58 ns, 71 ns and 80 ns, respectively. The results suggested that π-conjugated ligand indeed provide the excited electrons of CdTe nanocrystal with a more stable environment.

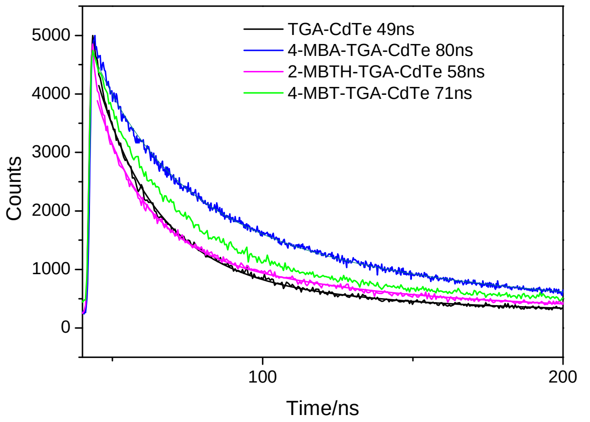


Fig.2 Fluorescence decay curves of QDs in the absence and presence of π-conjugated ligands. λem=550 nm, λex=405 nm.

Table 1. Parameters of multi-exponential fits with Equation 1 to the observed luminescence decay of QDs

	τ_1 [ns]	α_1 [%]	τ_2 [ns]	α_2 [%]	τ_{av} [ns]	χ^2
4-MBA-TGA-QDs	24	40.6	119	59.4	80	1.098
4-MBT-TGA-QDs	25	50.7	119	49.3	71	1.055
2-MBTH-TGA-CdTe	21	40.1	82	59.9	58	1.167
TGA-CdTe	22	47.6	74	52.4	49	1.173

π-Conjugated ligands have been reported to act as an ideal candidate for enhancing fluorescence intensity of nanocrystal. [19] A reasonable explanation is the photoinduced electron transfers from π-conjugated ligand to nanocrystals due to its high degree of electronic delocalization in π-conjugated system. [20] Moreover, exchange of the non-conjugated ligands of the QD for π-conjugated phenyldithiocarbamate (PTC) ligands decreased Eg of the QD through mixing of the states in the valence band (VB) of the semiconductor with the highest occupied molecular orbitals (HOMOs) of PTC. [21] But mixing appropriate LUMO energy level of π-conjugated ligands with E_{cb} of QDs to form electron delocalized field has not been reported up to now.

In order to prove that the PL lifetime prolongation was induced by mixing of E_{cb} of CdTe QDs with LUMO energy level of π-conjugated ligand, the E_{cb} of CdTe QDs, LUMO and HOMO energy levels of ligands were calculated. It is well established that QDs have size-dependent properties. The QDs with different sizes have different E_{cb} and E_{vb}. The corresponding valence and conduction band-edge energies of QDs with different sizes were calculated (the calculation is detailed in supporting information) and listed in Table 2.

The HOMO and LUMO energy levels of 4-MBA, 4-MBT and 2-MBTH were calculated with Gaussian 09W and the results were also summarized in Table 2. Figure S4 provides straightforward representations of the electron density distribution for 4-MBA, 4-MBT and 2-MBTH. Orbital analysis exhibits that they all have planar structure.

The calculated results showed that the E_{cb} of the CdTe QDs is about -1.8 ev, and the energy difference (△E) from the LUMO energy of 4-MBA, 4-MBT and 2-MBTH to E_{cb} is 1.39 ev, 1.34 ev and 0.79 ev, respectively. The △E is small enough for the possibility that the LUMO energy of π-conjugated ligands can mix with the E_{cb} of QDs and form shared electron delocalization area which is larger than that of QDs capped with only TGA (Figure 3). The electron delocalized field will supply the excited electron with a more stable environment, and as a result the PL lifetime of CdTe QDs was prolonged. Thus, the LUMO energy levels of π-conjugated ligand could perform as a medium for the delay of the electrons and are beneficial to obtain long lifetime fluorescence. Comparing the fluorescence lifetime of CdTe QDs

Table 2. Energy level of π-conjugated ligands and CdTe QDs with different emission wavelengths

	LUMO/E_{cb}	HOMO/E_{vb}	E_g
4-MBA	-0.41 ev	-6.33 ev	5.92 ev
2-MBTH	-1.01 ev	-6.22 ev	5.21 ev
4-MBT	-0.46 ev	-6.61ev	6.15 ev
CdTe 550 nm	-1.8 ev	-5.09 ev	3.29 ev
CdTe 525 nm	-0.7 ev	-5.28 ev	4.58 ev
CdTe 575 nm	-2.13 ev	-5.02 ev	2.89 ev

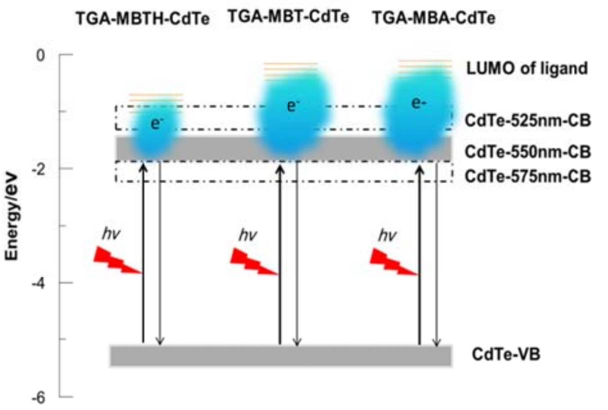


Fig.3 Energy level diagram of CdTe QDs, π-conjugated ligand and the electron delocalized field.

capped with different π-conjugated ligands, the fluorescence lifetime of 4-MBA-TGA-CdTe was longer than that of 4-MBT-TGA-CdTe and 2-MBTH-TGA-CdTe. As Figure 3 illustrates, the LUMO energy of 4-MBA is higher than that of 4-MBT and 2-MBTH, which will result in larger electron delocalization field in 4-MBA ligands capped CdTe QDs than that in 4-MBT-TGA-CdTe and 2-MBTH-TGA-CdTe. Larger electron delocalization field means that the excited electrons have more space to randomly populate. As a result, the larger electron delocalization field will supply more stable environment for the exited electron of QDs and the lifetime of 4-MBA-TGA-CdTe is longer than that of 4-MBT-TGA-CdTe and 2-MBTH-TGA-CdTe.

To gain more insight about the interaction between QDs and π-conjugated ligands, the PL lifetime were measured for CdTe QDs with different emission wavelengths (different E_{cb} as listed in Table 2 and Figure 3) capped with 4-MBA, 4-MBT and 2-MBTH. As shown in Figure 4, the PL lifetime of different QDs with emissions at 525 nm, 550 nm, and 575 nm were compared. The PL lifetime of QDs with emission at 550 nm was greatly prolonged by capped with π-conjugated ligands. But for the QDs with emission at 525 nm, their PL lifetime was prolonged slightly by capped with π-conjugated ligands because the E_{cb} (-0.7 ev) was too close to LUMO energy level of 4-MBA (△E=0.56 ev) and 2-MBTH (△E =0.31 ev). As for the QDs with emission at 575 nm capped with 4-MBA, the PL lifetime prolongation was lower than that of QDs with emission at 550 nm because the E_{cb} (-2.13ev) was too far (△E=1.72 ev) from the LUMO energy level of 4-MBA (-0.41ev) and the possibility of forming electron delocalization field is relatively lower.

4, 4 '- diphenyl sulfide (DPSF) and 4-Amino-3-hydrazino-5-mercapto-1, 2, 4-triazole (AHMT) were also selected as ligands to cap CdTe QDs with emission wavelength of 550 nm. The PL lifetimes of DPSF-TGA-CdTe and AHMT-TGA-CdTe (λ_{em}=550 nm) were also recorded and the result (Figure 5) illustrated that the presence of DPSF and AHMT did not increased the PL lifetime of CdTe QDs. As Table 3 showed, the LUMO energy level (0.46 ev) of AHMT was too far (△E=2.26 ev) from E_{cb} of CdTe QDs with emission at 550 nm to form an electron delocalized area. As for the AHMT, although the LUMO energy level (-0.665 ev) was suitable for mixing with E_{cb} of CdTe QDs,

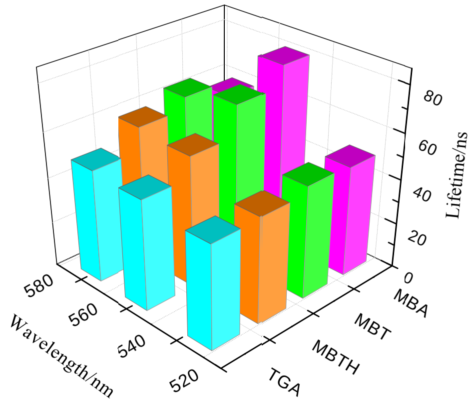


Fig.4 PL lifetime of QDs with different emission wavelengthes capped with different ligands.

the electron density distribution (Figure S5) indicates that the electrons were not in a planar form. The non-planar structure doesn't favor electron delocalization. All these results combined together suggest that the energy difference between LUMO energy level of π-conjugated ligands and E_{cb} of CdTe QDs (△E) plays an important role in providing the excited electron with a stable environment. Furthermore, the planar structure of the π-conjugated ligands is necessary to form an electron delocalized field and provide the excited electrons with stable environment.

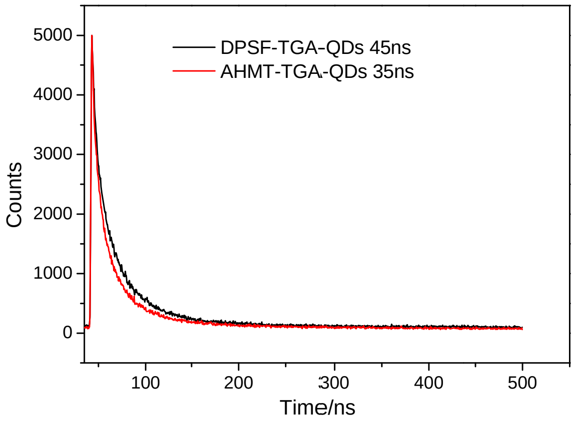


Fig.5 Fluorescence decay curves of QDs in the presence of DPSF (a) and AHMT (b). λem=550 nm, λex=405 nm.

Table 3. Energy level of π-conjugated ligand and CdTe QDs with different emission wavelengths

	LUMO/E_{cb}	HOMO/E_{vb}	△E
CdTe 550 nm	-1.8ev	-5.09ev	3.29ev
DPSF	-0.665ev	-5.53ev	4.86ev
AHMT	0.46ev	-6.91ev	7.37ev

Conclusions

In summary, we achieved control of the PL lifetime of CdTe QDs by using π-conjugated ligand with appropriate LUMO energy level as capping shell of CdTe QDs. The LUMO energy of π-conjugated ligands can mix with the E_{cb} of QDs and form shared electron delocalization area which is larger than that of QDs capped with commonly used ligand-TGA. The electron delocalized field will supply the excited electron with a more stable environment, and thus prolong the PL lifetime of CdTe QDs. The results show a difference in PL lifetimes between the QDs with different E_{cb} capped with the same ligand and the QDs with the same E_{cb} capped with ligands having different LUMO energy levels. Such difference indicates that the energy difference between LUMO energy level of π-conjugated ligands and E_{cb} of CdTe QDs ($\triangle E$) plays an important role in providing the excited electron with a stable environment. Furthermore, the planar structure of the π-conjugated ligands is necessary to form electron delocalized field and provide the excited electrons with a stable environment.

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Notes and references

[a] *E-432 West Campus, No.2 Linggong Road, High-Tech Zone, Dalian, China. Fax: 86 0411 84986264; Tel: 86 0411 84986264; E-mail: wusuli@dlut.edu.cn*

† Electronic Supplementary Information (ESI) available: [The fluorescence spectra and quantum yields (QYs) of CdTe QDs capped with TGA (TGA-CdTe), 4-MBA together with TGA (4-MBA-TGA-CdTe), 4-MBT together with TGA (4-MBT-TGA-CdTe) and 2-MBTH together with TGA (2-MBTH-TGA-CdTe), TEM of CdTe, representations of the electron density distribution for 4-MBA, 4-MBT, 2-MBTH, DPSF and AHMT]. See DOI: 10.1039/b000000x/

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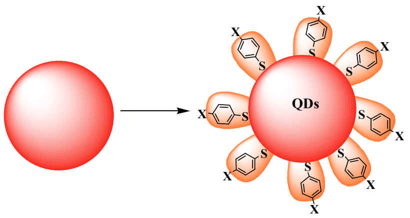

A new strategy is reported here to stabilize the excited electrons within QDs using -conjugated ligand. Electron delocalized field is formed by mixing the LUMO energy levels of π-conjugated ligand with conductive band-edge energy(E_{cb}) of CdTe QDs, which will supply the excited electron with a more stable environment.