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Steady state and time-resolved photophysical study of CdTe quantum dots in water.

Alessandro Iagatti,^{a,b} Luigi Tarpani,^c Eleonora Fiacchi,^c Laura Bussotti,^a Agnese Marcelli,^a Paolo Foggi^{a,b,c} and Loredana Latterini^{c*}*

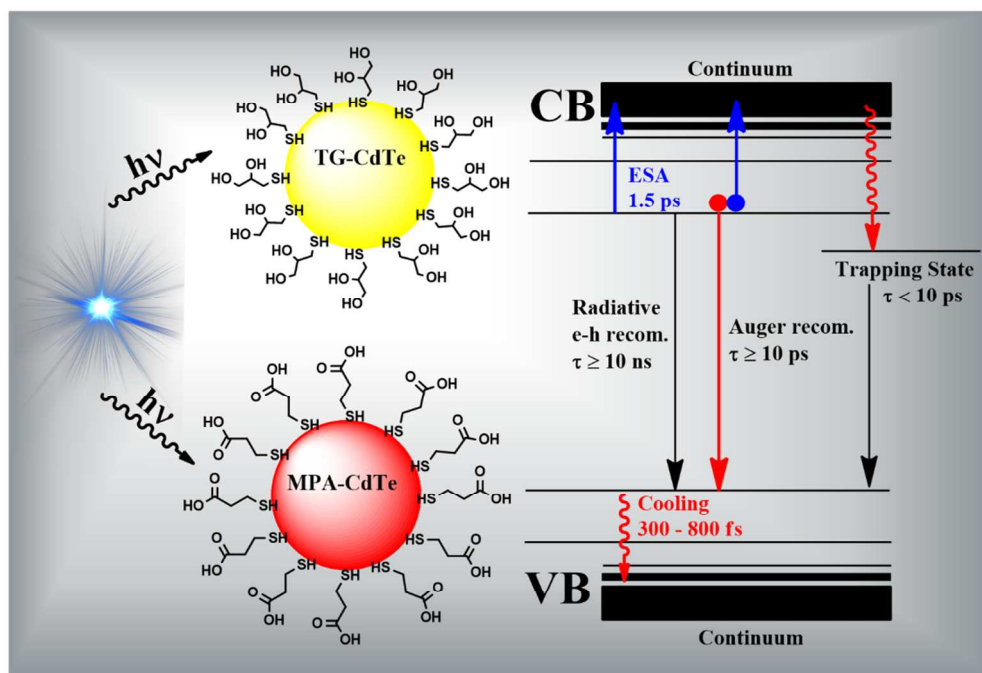
^aEuropean Laboratory for Non Linear Spectroscopy (LENS), Università di Firenze, via Nello Carrara 1, 50019 Sesto Fiorentino, Florence, Italy

^bINO-CNR, Istituto Nazionale di Ottica – Consiglio Nazionale delle Ricerche, Largo Fermi 6, 50125 Florence, Italy

^cDipartimento di Chimica, Biologia e Biotecnologie and Centro Eccellenza Materiali Innovativi Nanostrutturati (CEMIN), Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

E-mail: loredana.latterini@unipg.it; foggi@lens.unifi.it

The non-radiative electron-hole recombination processes are predominant in alkyl-thiol capped CdTe QDs prepared in water due and they are affected by the nature of the capping agent.



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6
7 ^aEuropean Laboratory for Non Linear Spectroscopy (LENS), Università di Firenze, via Nello
8 Carrara 1, 50019 Sesto Fiorentino, Florence, Italy

9 ^bINO-CNR, Istituto Nazionale di Ottica – Consiglio Nazionale delle Ricerche, Largo Fermi 6,
10 50125 Florence, Italy

11 ^cDipartimento di Chimica, Biologia e Biotecnologie and Centro Eccellenza Materiali Innovativi
12 Nanostrutturati (CEMIN), Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

13 E-mail: loredana.latterini@unipg.it ; foggi@lens.unifi.it

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15 Transient Absorption Spectroscopy.

16

17

1 Abstract

2 The exciton generation and recombination dynamics in semiconductor nanocrystals is very
3 sensitive to small variations of dimensions, shape and surface capping. In the present work CdTe
4 quantum dots are synthesized in water using 3-mercaptopropionic acid and 1-thioglycerol as
5 stabilizers. Nanocrystals with an average dimension of 4 ± 1 and 3.7 ± 0.9 nm are obtained, when
6 3-mercaptopropionic acid or 1-thioglycerol, respectively was used as capping agent. The steady-
7 state characterizations show that the two types of colloids have different luminescence behavior.
8 In order to investigate the electronic structure and the dynamics of the exciton state, a combined
9 study in the time domain has been carried out by use of fluorescence time-correlated single
10 photon counting and femtosecond transient absorption techniques.
11 The electron-hole radiative recombination occurs following a non-exponential decay law for
12 both colloids, which results in different average decay time values (on the order of tens of
13 nanoseconds) for the two samples. The data demonstrate that the process is slower for 1-
14 thioglycerol-stabilized colloids.
15 The ultrafast transient absorption measurements are performed at two different excitation
16 wavelengths (at the band gap and at higher energies). The spectra are dominated in both types of
17 samples by the negative band-gap bleaching signals although transient positive absorption bands
18 due to the electrons in the conduction band are observable. The analysis of the signals is affected
19 by the different interactions with the defect states, due to ligand capping capacities. In particular,
20 the data indicate that in 1-thioglycerol-stabilized colloids the non-radiative recombination
21 processes are kinetically more competitive than the radiative recombination. Therefore the
22 comparison of the data obtained for the two samples are interpreted in terms of the effects of the
23 capping agents on the electronic relaxation of the colloids.

1 **Introduction**

2 The design of hybrid nanomaterials based on colloidal semiconductor nanocrystals (or
3 quantum dots, QDs) and organic moieties has attracted prominent attention in the last three
4 decades due to their unique physical and chemical properties. Several different synthetic
5 methods have been developed to obtain such materials. In wet synthetic procedures, the control
6 of the nucleation and growth processes is achieved by using organic capping agents. These
7 species have therefore a crucial role in determining the dimension and the structure properties of
8 the colloidal nanocrystals. The detailed investigations of the effects of the capping agents
9 enabled the development of a wide variety of researches and different applications [1–7]. At the
10 same time a deeper understanding of the influence of stabilizers on the chemical and physical
11 properties of colloids has been achieved [8-13]. It is now clear that ligand molecules affect the
12 lattice properties of the colloids as well as the nanocrystal growth process [14]. So far the
13 influence of the ligand molecules on the photophysical behaviour of QDs and on the dynamics of
14 exciton state has been investigated to a lesser extent. Ligand exchange experiments have
15 demonstrated that the luminescent and photophysical behavior of nanocrystals can be modified
16 by the nature of the organic capping agents [15,16]. In order to produce hybrid nanomaterials
17 based on QDs and organic ligands with defined behavior and functions, the interactions between
18 semiconductor nanocrystals and organic species must be deeply understood.

19 Ultrafast pump-probe transient absorption spectroscopy (TAS) is a powerful tool for studying
20 the relaxation processes of molecules and colloidal nanostructures at early stages after electronic
21 excitation. Yan et al. [17] investigated the transient spectra of CdTe nanocrystals prepared by
22 high temperature thermolysis; multiple bleaching signals dominate TA spectra and the electron
23 cooling rates are reduced when the nanocrystals are capped with a CdS shell. This is due to a

1 reduction of the Auger recombination rates in the core/shell nanostructures, where the electron
2 and hole are spatially separated.

3 In this context the use of TAS to explore the dynamics of CdTe colloids (obtained by mild
4 thermolysis process assisted by organic thiol ligands) appears particularly interesting. Recent
5 studies on CdTe QDs have been reported [18,19] in which the radiative and non-radiative
6 recombination processes were investigated in the presence of 3-mercaptopropionic-acid as
7 stabilizer.

8 In the present work we investigate the photophysics of CdTe QDs synthesized in water using
9 1-thioglycerol (ITG) and 3-mercaptopropionic-acid (MPA) as capping agents. The
10 photophysical properties are investigated with stationary and time-resolved techniques.
11 Stationary photoluminescence studies showed some differences among the samples, in terms of
12 spectral features and efficiency values, which can be compatible with the presence of defect
13 states. The combination of time correlated single photon counting (TCSPC) and UV/Vis TAS
14 allows to characterize the radiative and non-radiative relaxation processes of charge carriers
15 formed upon photoexcitation on a very wide time interval (from 100 fs to 100 ns).

16

17 **Experimental Section**

18 *Materials*

19 Cd(NO₃)₂ *4H₂O, 1-thioglycerol (ITG) and 3-mercaptopropionic-acid (MPA) are from Sigma-
20 Aldrich. MilliQ water is freshly prepared in our laboratory.

21 *Nanocrystal synthesis*

1 CdTe QDs are prepared following literature procedures, with minor modifications [18, 20-22].
2 CdTe nanocrystals were prepared in strongly alkaline aqueous solution (pH=12) to ensure
3 complete deprotonation of the ligands in order to have an higher coordination capacity. Briefly,
4 the solutions of the reactants are freshly prepared as follows: 0.2 mmol of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and
5 0.4 mmol of ITG (or MPA) are added to a 40 ml of milliQ water under vigorous magnetic
6 stirring. When the solution is well mixed, 1 M NaOH is added drop-wise till to obtain a pH value
7 around 12; the solution of Te^{2-} precursor is prepared adding 0.4 mmol of tellurium powder and 1
8 mmol of NaBH_4 in 10 ml of milliQ water; the reduction is carried out at 80 °C under a nitrogen
9 atmosphere.

10 The two stock solutions of the precursors are then mixed with a Cd/Te molar ratio of 1:1 in
11 order to obtain the nanocrystals. The nucleation and the growth stage of the reaction is conducted
12 at 100 °C in an inert atmosphere. The progress of the reaction is spectrophotometrically checked
13 and the samples analyzed for particle dimensions.

14 ***Morphological Characterization***

15 A Philips model 208 Transmission Electron Microscope (operating at 80 kV of beam
16 acceleration) is used to image the nanocrystals and analyze their size distribution. A grain
17 analysis is carried out to determine the height distribution of the particles from the images.

18 ***Photophysical Characterization***

19 UV-VIS absorption spectra are recorded with a Perkin-Elmer Lambda 800 spectrophotometer
20 on air-equilibrated solutions. Photoluminescence spectra, corrected for the instrumental response,
21 are measured with a Fluorolog (Spex F112AI) spectrofluorometer, which are used to determine

1 photoluminescence efficiencies (QY) using quinine sulfate in H_2SO_4 (0.5 M), $\Phi_F = 0.55$ as
2 standard [15].

3 Time Correlated Single Photon Counting (TCSPC) measurements were performed to
4 characterize the radiative electron-hole recombination. The luminescence decay (mean deviation
5 of three independent experiments, ca. 5%) is measured by TCSPC method using an Edinburgh
6 Instrument 199S setup. A 460-nm nanoLED with a 1.3 ns pulse duration was used as excitation
7 source and the signal was acquired by a Hamamatsu R7400U-03 detector.

8 The apparatus used for TAS measurements has been described in detail in previous works [23-
9 26]. Briefly, the fs-laser oscillator is a Ti:sapphire laser (Spectra Physics Tsunami). The short
10 (≤ 70 fs) pulses are stretched and amplified at 1 kHz repetition rate by a regenerative amplifier
11 (BMI Alpha 1000). After compression a total average power of 500 mW and pulse duration of
12 100 fs are obtained. The repetition rate of the output beam is reduced to 100 Hz by a mechanical
13 chopper. Tunable pulses in the UV-Visible interval can be achieved by Second Harmonic
14 Generation (SHG) or by doubling or mixing the output of an optical parametric generator and
15 amplifier (OPG-OPA) based on a BBO crystal (TOPAS by Light Conversion, Vilnius,
16 Lithuania)[27,28]. The probe pulse is generated by focusing a small portion of the 800 nm
17 radiation on a 3 mm thick CaF_2 window mounted on a motorized translation stage. The
18 continuum light is optimized for the 350-750 nm wavelength range. Multichannel detection for
19 transient spectroscopy is achieved by sending the white light continuum, after passing through
20 the sample, to a flat field monochromator coupled to a homemade CCD detector (see technical
21 report at <http://lens.unifi.it/ew/>).

1 TAS measurements are carried out in a 2 mm thick cell under magnetic stirring to avoid the
2 accumulation of long living transient species. To confirm the correct experimental conditions we
3 optimize the stirring speed in order to reproduce results obtained in a flow cell [29-31].

4 The resulting kinetic traces are fitted by a multi-exponential decay function. For the short time
5 scale the data are fitted by a decay function convoluted with a Gaussian-shaped instrument
6 function (FWHM = 100 fs). To better evaluate the weight of the single components we first
7 analyze the data by using a tail fitting procedure.

8 **Results and Discussion**

9 To investigate the photophysical behavior of CdTe nanocrystals (or quantum dots, QDs) in
10 water, sample are prepared following the literature procedures [18, 20-22] using a [Cd]/[Te]
11 molar ratio of 1, while the ratio between Cd and stabilizers has been fixed to 2. TEM images
12 (inset Figure 1) show the formation of spherical nanocrystals, having an average size of 4 ± 1 nm
13 for 3-mercaptopropionic acid capped CdTe (MPA-CdTe) and 3.7 ± 0.9 nm 1-thioglycerol was
14 used as capping agent (TG-CdTe).

15 In Figure 1, the absorption and photoluminescence spectra of MPA and TG capped CdTe are
16 shown. Both colloids present the band-gap absorption. However TG-CdTe samples show a
17 better-defined band.

18 The lowest absorption bands of the samples are at 565 and 520 nm for MPA-CdTe and TG-
19 CdTe, respectively. In addition both systems present the characteristic absorption due to the
20 continuum. Following the model proposed by Donegá and Koole [32], the QDs extinction
21 coefficient at 400 nm can be determined by the following equation:

$$22 \quad \varepsilon_{400} = \left[\mu_{400} N_A z \frac{V_{QD}}{V_{UC}} \right] (2303)^{-1} \quad (1)$$

1 where μ_{400} is the absorption cross section per unit ion pair at 400 nm, N_A is the Avogadro's
2 number, z is the number of unit ion pairs per unit cell, V_{QD} and V_{UC} are volumes (cm^3) of the QD
3 and unit cell. Another method to determine the extinction coefficient ε of CdTe nanocrystals at
4 the band gap has been developed by Peng et al. [33] and is given by the following empirical
5 function:

$$6 \quad \varepsilon = 3450\Delta E(D)^{2.4} \quad (2)$$

7 where ΔE is the energy gap and D is the diameter of the nanoparticles. The absorption
8 coefficient values calculated with the two methods are reported in Table 1 along with the QDs
9 molar concentrations, determined using the Lambert-Beer law.

10 Since for both samples the concentration values are the same at the two wavelengths, within
11 the experimental error, we conclude that the accuracy of the methods for the absorption
12 coefficient determination is rather good. The comparison of the coefficients for the MPA- and
13 TG-capped samples indicates that the nature of the capping agent has a moderate influence on
14 the probabilities of the electronic transitions in the colloids, thus suggesting that the electronic
15 structure of the nanocrystals is not altered by the presence of stabilizers of different nature.

16 The photoluminescence spectrum of the CdTe-MPA QDs obtained exciting the sample at the
17 BG (565 nm) presents an emission band centered at 595 nm with a clear shoulder on the red edge
18 (Figure 1A). The appearance of this component is generally ascribed to the contribution of trap
19 states [15,16,34]. The occurrence of dissipative or trapping processes has been confirmed by the
20 quite low luminescence efficiency measured (17%) for the CdTe-MPA suspension (Table 2). In
21 addition we need to consider that a contribution to the red-edge component of the QDs
22 luminescence due to the broad size distribution of these nanocrystals has to be taken into

1 account. The photoluminescence behavior of the TG capped QDs (Figure 1B), upon excitation of
2 the nanocrystals at 520 nm, shows a single symmetric emission band centered at 560 nm. TG-
3 CdTe QDs have an higher Stokes shift and a lower luminescence QY (10%) compared to MPA-
4 capped samples. This is a proof that the luminescent properties of TG capped QDs are strongly
5 affected by the presence of defects.

6 TCSPC measurements, carried out exciting the samples at 460 nm and collecting the photons
7 at 620 nm, show a nonexponential behaviour of the luminescence decay curves, as previously
8 observed for other colloidal samples [16,18,35-37]. The photoluminescence decays could be
9 reproduced for both colloids by bi-exponential functions having decay time components in the ns
10 range (7.1-51.0 ns, Table 3), which is a consequence of the distribution of radiative decay times
11 related to excitonic populations [16,36,38].

12 The photoluminescence decay times, as well as the quantum yield, show some differences for
13 the two samples under investigation. This suggests that the interactions with the organic ligands
14 alters the dynamics of the exciton relaxation. In particular, longer decay times are measured for
15 TG-CdTe, for which the presence of a larger amount of surface defects reducing the
16 luminescence quantum efficiency (QY) has been expected on the basis of spectral features.
17 Assuming that no other interactions occur within the excited states and considering the average
18 decay times $\langle\tau_L\rangle$ (Table 3) and the luminescence efficiencies, the average radiative (k_r)
19 recombination rate constants can be determined for the two samples. For MPA- and TG-CdTe k_r
20 values of 7.0 and $2.5 \times 10^6 \text{ s}^{-1}$, respectively have been determined; on the other hand the average
21 non-radiative rate constants (k_{nr}) operative for the excitonic state, determined considering $\langle\tau_L\rangle$
22 and k_r , are in the order of 3.3 and $2.2 \times 10^7 \text{ s}^{-1}$ for MPA- and TG-capped colloids, respectively.
23 The average data indicate that the non-radiative recombination pathway dominates the exciton

1 relaxation and a negligible effect has been observed on the non-radiative rates to account for the
2 differences in the luminescence behavior. The lack of decay associated spectra prevents a more
3 accurate analysis of the radiative and non-radiative rate constants; but it could be argued, on the
4 basis of luminescence decay times values (Table 2), that for MPA-CdTe the radiative
5 recombination is more competitive than for TG-CdTe since a faster luminescence component has
6 been determined (7.1 ns).

7 To investigate in deeper details the dynamics of exciton states at short times, transient
8 absorption measurements with fs-resolution have been carried out.

9 In TAS measurements, the excitation has been carried out at two wavelengths in order to have
10 information on the relaxation processes in the manifold of the conduction band (CB). In
11 particular, taking into account the steady-state absorption spectra of the CdTe colloids, the
12 samples have been excited near the BG and at energies about 0.72 eV (5800 cm^{-1}) above the
13 band gap (pump wavelength were set at 520 and 400 nm and 476 and 374 nm, for MPA- and
14 TG-CdTe, respectively). It is important to notice that the pump power was kept below 100 nJ,
15 with the aim to reduce multiexciton generation, whose dynamics would complicate the relaxation
16 processes at least in the picosecond time window. The transient data of MPA-CdTe QDs
17 recorded upon excitation at 520 and 400 nm are shown in Figure 2 and 3, respectively; the
18 spectra of TG-CdTe are reported in Figures 4 and 5.

19 In general all the recorded transient spectra are dominated by the band gap bleaching signals
20 but a broad excited state absorption (ESA) signal is also observed after the laser excitation pulse.
21 In order to make easier the comparison in Figures 2-5A, the steady state absorption spectra of the
22 samples are reported together with the transient spectra recorded 3 ps after the laser pulse.

1 Differently from what previously observed [17], the transient bleaching signals are broad and the
2 contribution of selected electronic transitions could not be resolved.

3 The kinetic analysis has been carried out on the transient signals at different wavelengths. The
4 ESA band is detected on the red-edge of the transient spectra (above 650 nm) and it forms
5 instantaneously with excitation pulse. Data from the literature support the assignment of this
6 ESA signal to the intraband transitions in CB [29]. The decay of the ESA signal can be
7 satisfactorily reproduced by a double exponential function (Table 4) with a short component in
8 the ps interval and a very long component (in the order of nanoseconds), which resemble the
9 radiative decay times. This observation suggests that this signal can be assigned to the absorption
10 of the electron in the conduction states which relax through the radiative process [19, 29].

11 More importantly, the bleaching signal generated upon CdTe excitation is due to charge carrier
12 formation, thus its kinetic analysis gives more pieces of information on the dynamics of these
13 species. It has to be noted that due to the difference between the masses of electron and holes, the
14 dynamics is dominated by the electron relaxation. The bleaching analysis has been carried out at
15 different wavelengths (Figure 2-5B) and the traces could be reproduced by multi-exponential
16 functions, similarly to what previously observed for CdTe and CdSe QDs [11, 17, 19, 29, 39].
17 The traces evidenced a fast rise component, whose contribution (in amplitude and time) changed
18 with the probe wavelength, and a quite complex decay, which was fitted by a triexponential
19 function at all the probed wavelengths.

20 The rise component in the signal was reproduced by an exponential growth with a time
21 constant τ_1 varying from 300 to 800 fs going from the blue to the red edge. This relaxation time
22 is consistent with the electron cooling process into the VB. This assignment is supported by the
23 red-shift of the maximum of the bleaching band in the first ps for both the particle types (Figure

1 6); a further proof of the assignment is the higher contribution (relative weight) of this
2 component when the nanocrystals are excited at energies higher than the band gap.

3 Usually in QDs the fast non-radiative electron-hole recombination is dominated by surface
4 trapping and/or Auger recombination [40-42]. Thus, in the present cases, the decay times τ_2 and
5 τ_3 could be assigned to either to Auger recombination or to non-radiative recombination
6 processes induced by the presence of defect states [10,18,40,43]. Increasing the pump power the
7 decay time τ_2 remains constant, while the third component τ_3 shortens upon an increase of the
8 laser power. These observations support the assignment of τ_2 to recombination assisted by the
9 trap states and τ_3 to Auger recombination process [44]. These processes occur in both types of
10 nanoparticles and a general scheme of the electronic transitions and relaxation processes can be
11 drawn as reported in Figure 7.

12 The excitation of the samples with an excess of energy (400 nm for MPA and 374 nm for TG)
13 compared to the BG transition originates similar transient spectral features, although some
14 differences can be noticed in the fitting parameters obtained from the kinetic analysis. In
15 particular, the decay time τ_2 shortens for both the colloids when the excitation wavelengths are
16 set at higher energies. This decay behaviour, ascribed to the effect of trapping sites, is explained
17 by the higher kinetic energy of the electrons into the conduction manifold when promoted with
18 extra-energy. The τ_3 component becomes five times faster in MPA-CdTe increasing the
19 excitation energy, but it does not change for the TG-CdTe; this behavior can be related to the
20 higher absorption coefficients of MPA-CdTe at 400 nm which makes probable multi-exciton
21 formation. However the contribution of a cooling process mediated by the ligand (non-adiabatic
22 cooling) cannot be excluded at this stage. Indeed the τ_2 and τ_3 decay times are in general longer
23 for MPA- than TG-CdTe. Thus, we can conclude that the presence of TG as capping agent, for

1 which a higher contribution of defect states is deduced from the luminescent behaviour,
2 significantly reduces the two ps-components, suggesting that in this sample the non-radiative
3 recombination processes are kinetically more competitive than the radiative recombination.

4

5 **Conclusions**

6 CdTe-QDs were prepared in water using two different alkyl-thiols as stabilizers, namely 3-
7 mercaptopropionic acid (MPA) and 1-thioglycerol (TG). The optical properties of the two
8 samples show significant differences, despite the similar dimensions. Indeed higher absorption
9 coefficients and higher luminescent quantum efficiency have been determined for the MPA-
10 CdTe while a larger stock-shift was measured for TG-QDs. These data suggest that luminescent
11 behavior of TG-CdTe colloids is affected by the presence of defect states.

12 In order to explore if defects influence the electronic structure of the colloids or the dynamics
13 of the exciton states, time resolved measurements have been carried out. The Time Correlated
14 Single Photon Counting measurements indicate that the radiative electron-hole recombination
15 occurs in the ns-time region with a bi-exponential behavior; the data analysis pointed out that
16 exciton relaxation is kinetically determined by non-radiative cooling process.

17 The exciton dynamics was further studied with ultrafast Transient Absorption Spectroscopy
18 monitoring the bleaching signal. The kinetic analysis of TAS signals at different probe
19 wavelengths evidences a multiexponential recombination. At all analyzed wavelengths a rise
20 time, in the order of hundreds of fs, was detected and assigned to the electron cooling in the VB.
21 A decay component of few ps (τ_2) was ascribed to the trapping states, while the intermediate
22 decay time (τ_3) was attributed to Auger recombination; the latter component presents the biggest

1 differences between the two samples. The identification of these processes is supported by pump
2 fluence dependent measurements. In particular, the τ_3 component is almost one order of
3 magnitude longer for MPA-CdTe.

4 Increasing the excitation energy a reduction of the τ_2 and τ_3 decay times was noticed for both
5 the samples due to the increased mobility of the electrons in the conduction manifold. The
6 increase is more evident for MPA-CdTe.

7 The comparison of the results obtained in QDs with two different stabilizers shows important
8 differences in the non-radiative decay component and the contribution of a cooling process
9 mediated by the ligand can be supposed.

10

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- 6

1 **Table 1.** Molar extinction coefficient of CdTe QDs in water at different wavelengths.

MPA-CdTe		TG-CdTe	
$\epsilon_{400} = 748000$	$[QDs] = 3.4 \times 10^{-6}$	$\epsilon_{400} = 545000$	$[QDs] = 5.3 \times 10^{-6}$
$\epsilon_{565} = 198000$	$[QDs] = 3.6 \times 10^{-6}$	$\epsilon_{520} = 215000$	$[QDs] = 5.5 \times 10^{-6}$

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4 **Table 2.** Band gap position, FWHM of the luminescence band, Stokes shift and luminescence
5 QY of CdTe as a function of the capping agent.

Sample	BG (nm) [eV]	FWHM (cm ⁻¹)	Stokes shift (cm ⁻¹)	QY (%)
MPA-CdTe	565 [2.19]	1840	890	17
TG-CdTe	518 [2.39]	1820	1420	10

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9 **Table 3.** Luminescence decay parameters for CdTe QDs in water obtained from TCSPC
10 measurements.

Sample	τ_{1L} (ns)	A ₁ (%)	τ_{2L} (ns)	A ₁ (%)	$\langle \tau_L \rangle$ (ns)	χ_{sq}
MPA-CdTe	7.1	49.0	30.1	51.0	25.8	0.98
TG-CdTe	20.8	58.9	51.6	41.1	40.3	1.03

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1
2
3 **Table 4.** Fitting parameters (decay time and relative weight) of transient absorption decay traces
4 at selected probe wavelengths recorded for CdTe QDs in water using different pump
5 wavelengths.

MPA-CdTe										
λ_{pump} (nm)	λ_{probe} (nm)	A ₁ (%)	τ_1 (ps) ±S.D.	A ₂ (%)	τ_2 (ps) ±S.D.	A ₃ (%)	τ_3 (ps) ±S.D.	A ₄ (%)	τ_4 (ns)	τ_{ESA}^{660} (ps) ± S. D.
400	460	0	0	87	1.6±0.2	3	30 ±3	10	25.8	1.4±0.1
	520	-44	0.41±0.05	26	1.8±0.1	12	16±1.8	18		
	565	-47	0.61±0.02	34	0.9±0.07	8	20±1	10		
	600	-72	0.80±0.09	6	1.0±0.1	9	25±2	13		
520	565	-14	0.32±0.06	33	6.7 ±0.8	12	129±10	41	25.8	1.5 ±0.3
	600	-31	0.33±0.07	28	12 ±1.3	11	140±14	30		
TG-CdTe										
λ_{pump} (nm)	λ_{probe} (nm)	A ₁ (%)	τ_1 (ps) ±S.D.	A ₂ (%)	τ_2 (ps) ±S.D.	A ₃ (%)	τ_3 (ps) ±S.D.	A ₄ (%)	τ_4 (ns)	τ_{ESA}^{660} (ps) ± S. D.
374	480	-50	0.58±0.09	49	0.6±0.1	0.5	9.0±1.5	0.8	40.3	3.2±0.7
	520	-50	0.47±0.06	26	1.1±0.13	10	12±1.3	15		
	540	-51	0.70±0.08	35	1.1±0.12	7	16±1.8	8		
476	520	-6	0.33±0.07	28	2.0±0.3	21	14±2.5	45	40.3	low signal
	540	-12	0.36±0.06	32	2.7±0.3	18	15±2	38		
	560	-21	0.40±0.09	41	5.8±0.7	6	16±4	32		

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1

2 **Figure Captions**

3 **Figure 1:** Absorption (black line) and luminescence spectra (red line) of MPA-CdTe (A, $\lambda_{\text{exc}} =$
4 565 nm) and TG-CdTe (B, $\lambda_{\text{exc}} = 520$ nm) QDs in water; inset TEM images of the samples (scale
5 bar corresponds to 30 nm)

6 **Figure 2:** (A) Transient absorption spectrum (red line) of MPA-CdTe recorded 3 ps after the
7 excitation pulse ($\lambda_{\text{pump}} = 520$ nm) compared to the stationary absorption spectrum (blue line); (B)
8 signal decay traces at selected probe wavelengths.

9 **Figure 3:** (A) Transient absorption spectrum (red line) of MPA-CdTe recorded 3 ps after the
10 excitation pulse ($\lambda_{\text{pump}} = 400$ nm) compared to the stationary absorption spectrum (blue line); (B)
11 signal decay traces at selected probe wavelengths.

12 **Figure 4:** (A) Transient absorption spectrum (red line) of TG-CdTe recorded 3 ps after the
13 excitation pulse ($\lambda_{\text{pump}} = 476$ nm) compared to the stationary absorption spectrum (blue line); (B)
14 signal decay traces at selected probe wavelengths.

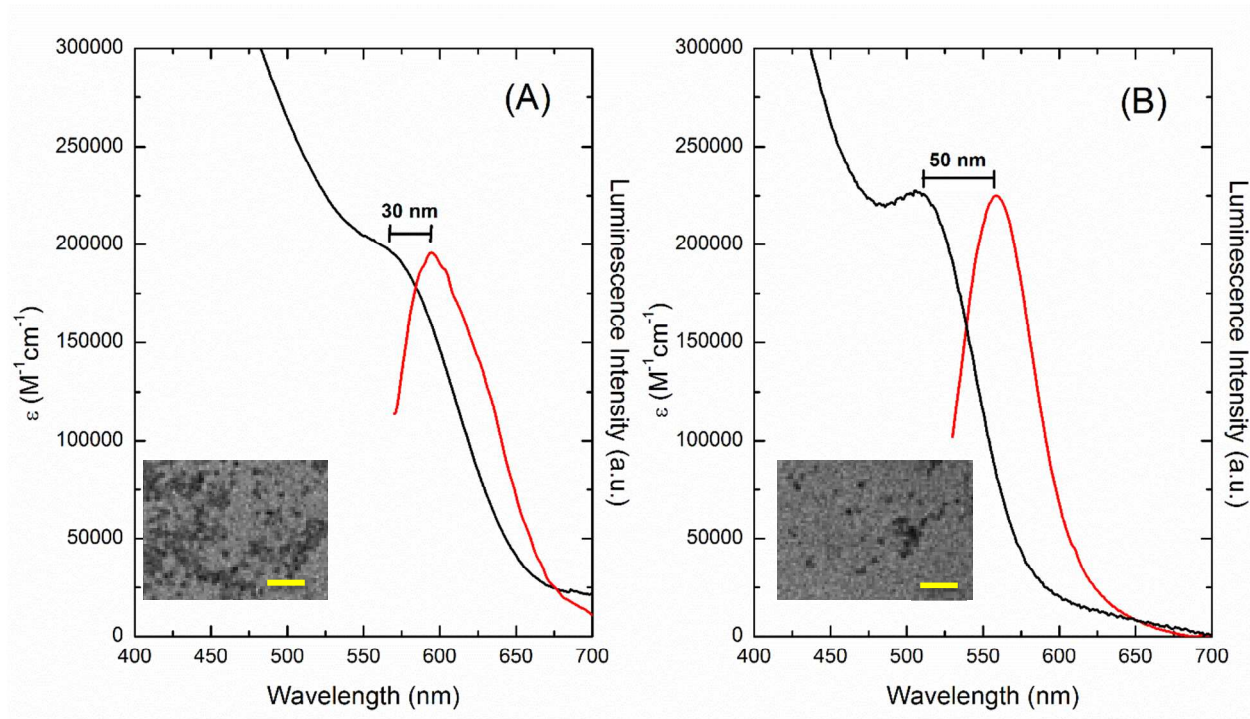
15 **Figure 5:** (A) Transient absorption spectrum (red line) of TG-CdTe recorded 3 ps after the
16 excitation pulse ($\lambda_{\text{pump}} = 374$ nm) compared to the stationary absorption spectrum (blue line); (B)
17 signal decay traces at selected probe wavelengths.

18 **Figure 6:** Transient spectra of (A) MPA-CdTe ($\lambda_{\text{pump}} = 400$ nm) and (B) TG-CdTe ($\lambda_{\text{pump}} = 374$
19 nm) nanocrystals at different delays

20 **Figure 7:** Scheme of the electronic transition and recombination processes occurring in TG- and
21 MPA-CdTe QDs

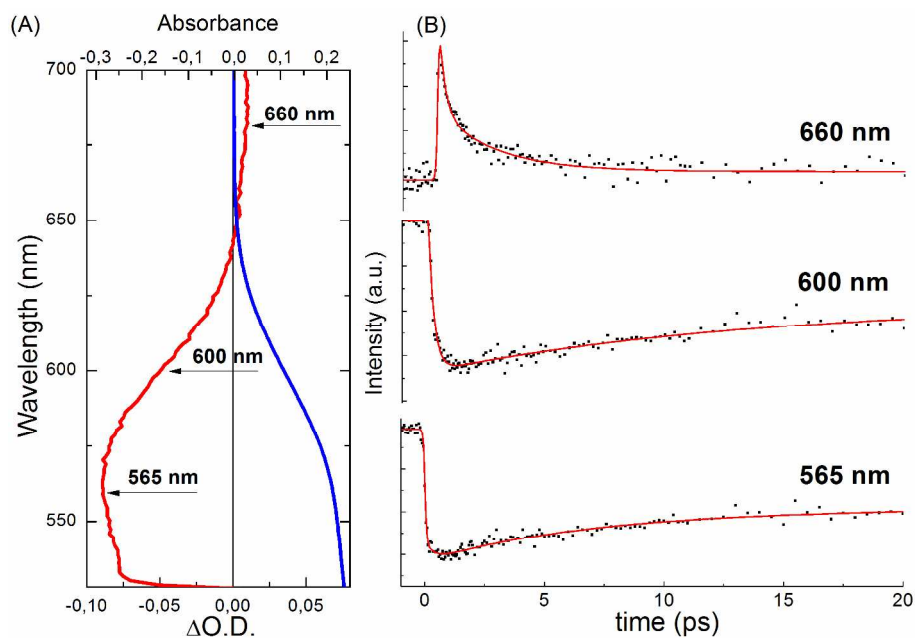
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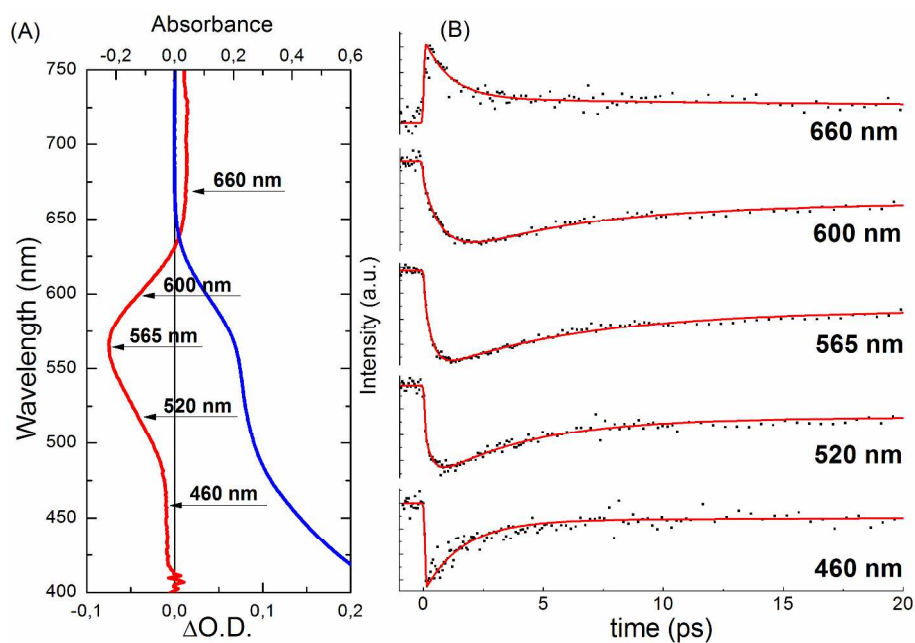


1
2 **Figure 1:** Absorption (black line) and luminescence spectra (red line) of MPA-CdTe (A, $\lambda_{exc} =$
3 565 nm) and TG-CdTe (B, $\lambda_{exc} = 520$ nm) QDs in water; inset TEM images of the samples (scale
4 bar corresponds to 30 nm)

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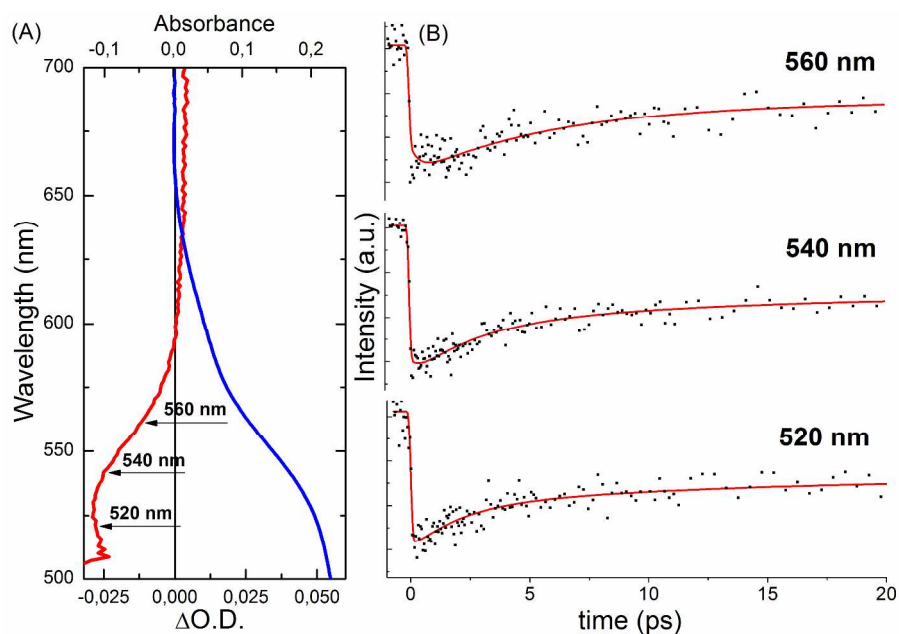


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2 **Figure 2:** (A) Transient absorption spectrum (red line) of MPA-CdTe recorded 3 ps after the
3 excitation pulse ($\lambda_{\text{pump}} = 520$ nm) compared to the stationary absorption spectrum (blue line); (B)
4 signal decay traces at selected probe wavelengths.



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8 **Figure 3:** (A) Transient absorption spectrum (red line) of MPA-CdTe recorded 3 ps after the
9 excitation pulse ($\lambda_{\text{pump}} = 400$ nm) compared to the stationary absorption spectrum (blue line); (B)
10 signal decay traces at selected probe wavelengths.

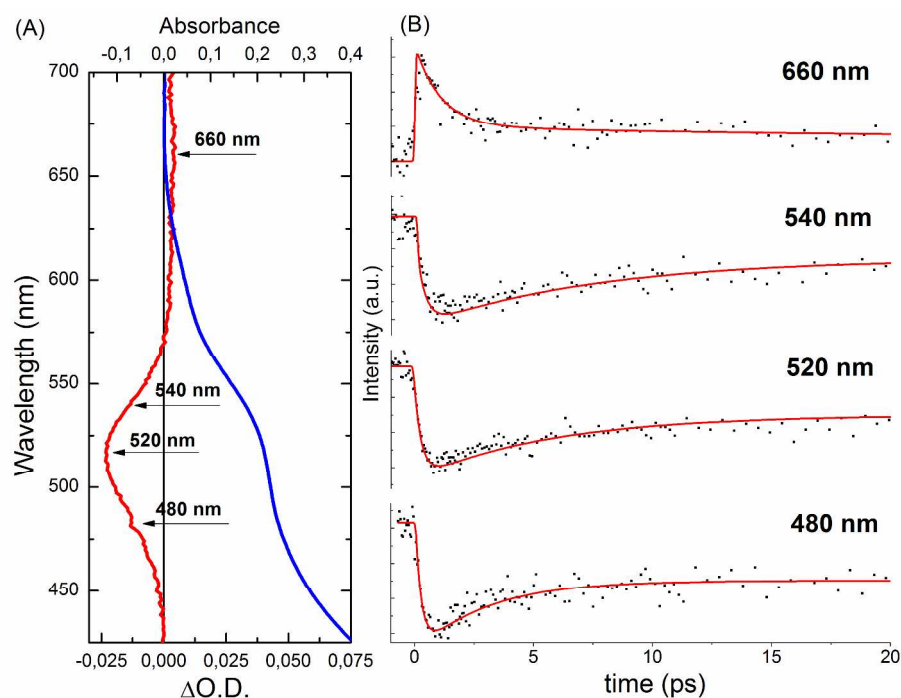
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3 **Figure 4:** (A) Transient absorption spectrum (red line) of TG-CdTe recorded 3 ps after the
 4 excitation pulse ($\lambda_{\text{pump}} = 476$ nm) compared to the stationary absorption spectrum (blue line); (B)
 5 signal decay traces at selected probe wavelengths.

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7 **Figure 5:** (A) Transient absorption spectrum (red line) of TG-CdTe recorded 3 ps after the
 8 excitation pulse ($\lambda_{\text{pump}} = 374$ nm) compared to the stationary absorption spectrum (blue line); (B)
 9 signal decay traces at selected probe wavelengths.

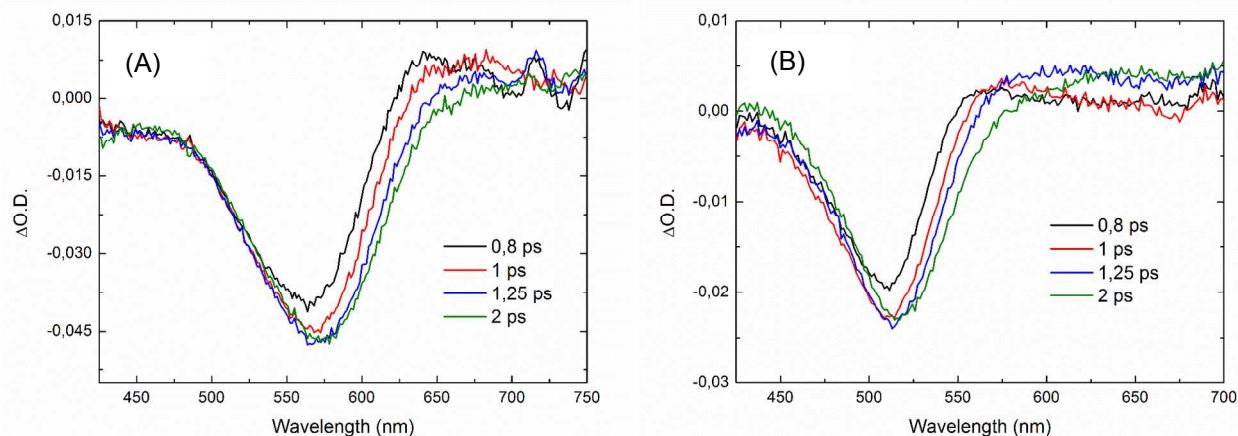
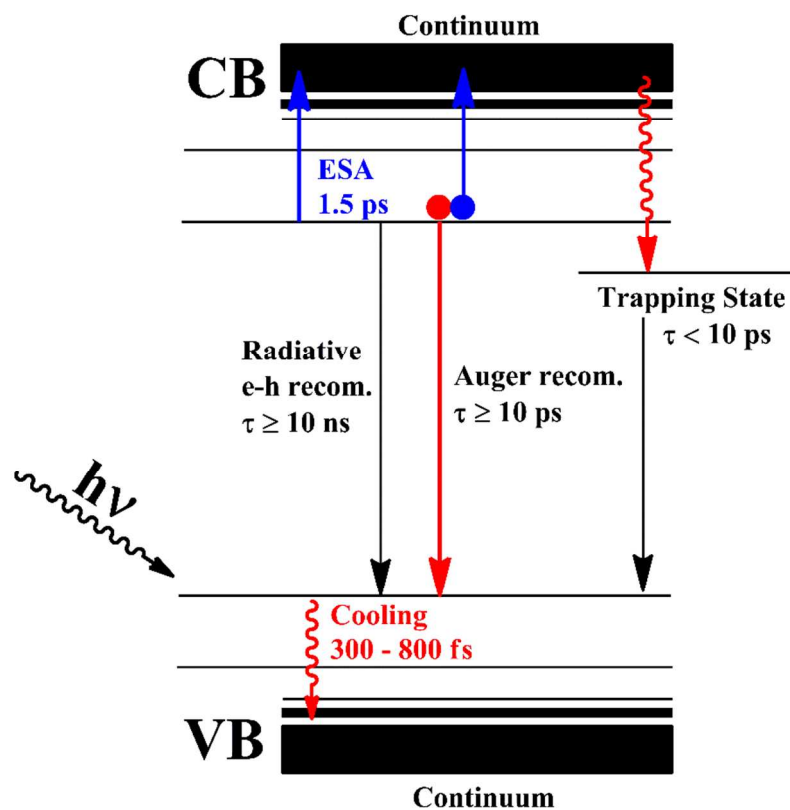
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Figure 6: Transient spectra of (A) MPA-CdTe ($\lambda_{\text{pump}} = 400$ nm) and (B) TG-CdTe ($\lambda_{\text{pump}} = 374$ nm) nanocrystals at different delays



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9 **Figure 7:** Scheme of the electronic transition and recombination processes occurring in TG- and
10 MPA-CdTe QDs

1 Steady state and time-resolved photophysical study of CdTe quantum dots in
2 water.

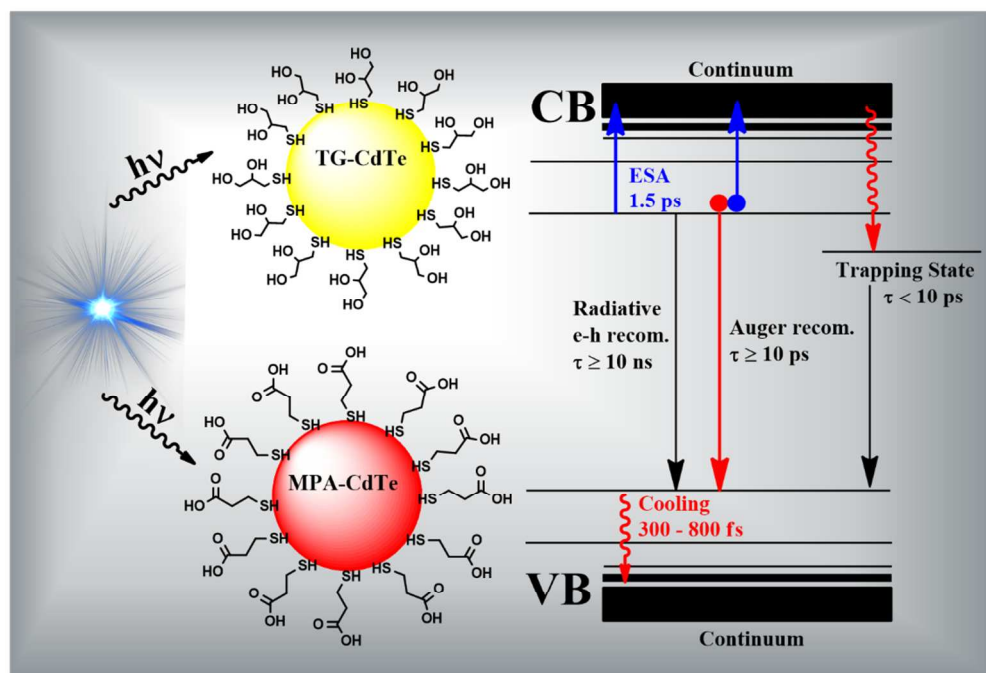
3 *Alessandro Iagatti,^{a,b} Luigi Tarpani,^c Eleonora Fiacchi,^c Laura Bussotti,^a Agnese Marcelli,^a*
4 *Paolo Foggi^{a,b;c*} and Loredana Latterini^{c*}*

5
6 ^aEuropean Laboratory for Non Linear Spectroscopy (LENS), Università di Firenze, via Nello
7 Carrara 1, 50019 Sesto Fiorentino, Florence, Italy

8 ^bINO-CNR, Istituto Nazionale di Ottica – Consiglio Nazionale delle Ricerche, Largo Fermi 6,
9 50125 Florence, Italy

10 ^cDipartimento di Chimica, Biologia e Biotecnologie and Centro Eccellenza Materiali Innovativi
11 Nanostrutturati (CEMIN), Università di Perugia, Via Elce di Sotto 8, 06123 Perugia, Italy

12 E-mail: loredana.latterini@unipg.it ; foggi@lens.unifi.it



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