# Temperature-modulated quenching of quantum dots covalently coupled to chain ends of poly(N-isopropyl acrylamide) brushes on gold

To cite this article: Oya Tagit *et al* 2009 *Nanotechnology* **20** 185501

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**Abstract**
A thermo-responsive polymer/quantum dot platform based on poly($N$-isopropyl acrylamide) (PNIPAM) brushes 'grafted from' a gold substrate and quantum dots (QDs) covalently attached to the PNIPAM layer is presented. The PNIPAM brushes are grafted from the gold surface using an iniferter-initiated controlled radical polymerization. The PNIPAM chain ends are functionalized with amine groups for coupling to water-dispersible COOH-functionalized QDs. Upon increasing the temperature above the lower critical solution temperature (LCST) of PNIPAM the QD luminescence is quenched. The luminescence was observed to recover upon decreasing the temperature below the LCTS. The data obtained are consistent with temperature-modulated thickness changes of the PNIPAM layer and quenching of the QDs by the gold surface via nonradiative energy transfer.

S Supplementary data are available from stacks.iop.org/Nano/20/185501

## 1. Introduction

Optical transduction of stimulus-induced events in polymeric thin film materials is often explored for various sensing applications [1, 2]. In this context, polymer brushes [3, 4] made of polymers undergoing distinct conformational changes [5] in response to changes in pH [1, 6, 7], electric field, solvent composition [8], light absorption, temperature [9, 10] or to biochemical stimulus [11] are conveniently used as responsive layers. Poly($N$-isopropylacrylamide) (PNIPAM) is a temperature-responsive polymer that undergoes a reversible phase transition in water when crossing the polymer lower critical solution temperature (LCST, $\sim$32 °C) [12]. Above the LCST, the PNIPAM chains are hydrophobic and are in a collapsed state while below the LCST the PNIPAM chains are hydrophilic and extend in water. Optical transduction of this temperature-modulated PNIPAM phase transition can be realized by combining nanoparticles with polymer brushes and monitoring their optical properties as a function of temperature. Here, we probe the phase transition of PNIPAM brushes using semiconductor nanocrystals (i.e. quantum dots, QDs).

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QDs have gained much attention as optical transducers due to their unique composition and size-tunable optical properties, broad excitation and narrow emission spectra, and high chemical and photochemical stability [13, 14]. There have been many strategies to immobilize QDs on different types of polymeric surfaces that include adhesion [15], adsorption via electrostatic interactions [16], ligand exchange [17] and covalent attachment [7]. Covalent attachment of QDs to polymer layers offers some advantages. Namely, it reduces the possible problems associated with particle aggregation, weak or reversible bonding and polymer film infiltration [17].

Combining stimulus-responsive surfaces and semiconductor nanoparticles allows one to fabricate robust and cost-effective sensors for various applications. For instance, CdS/polyacrylamide hybrid thin films were prepared on Au electrodes and the solvent-induced, switchable photoelectrochemical functions of the matrices were studied [8]. Ionov *et al* grafted solvent-responsive polymers onto a reflecting surface and immobilized QDs on top of the polymer layer. The fluorescence intensity of the QDs was found to be strongly dependent on the surrounding medium, which influenced the thickness of the polymer layer, and thus the distance of the QDs to the surface [6].

In this contribution, we prepare a hybrid multilayer Au/PNIPAM/QD assembly and probe its optical response to changes of temperature in water. The PNIPAM brushes are grafted from the gold surface using an iniferter-initiated controlled radical polymerization. The PNIPAM chain ends are functionalized with amine groups for covalent coupling to carboxylic acid functionalized QDs. Upon heating and crossing the LCST of PNIPAM, the brushes collapse and QD luminescence intensity decreases. Upon cooling the assembly, the QD luminescence increases again, demonstrating the reversibility of the system. We attribute the decrease and recovery of the luminescence intensity to the nonradiative energy transfer to the gold surface. The data obtained are consistent with temperature-modulated thickness changes of the PNIPAM layer and quenching of the QDs by the proximity of the gold surface.

## 2. Materials and methods

Core/shell CdSe/ZnS quantum dots were obtained as reported in [18]. To render the QD dispersible in water and provide functionality for further chemical reactions, the QDs were dispersed in water using mercaptoacetic acid (MAA, 97%, Aldrich) as reported in [19]. Photopolymerization of NIPAM from the gold substrate was performed using a disulfide-based photo-initiator dithiodiundecane-11,1-diylbis{4[([(diethylamino)carbonothioyl]thioethyl) phenyl]carbamate} (DTCA) synthesized as reported in [20]. 1,2-dioctadecyldisulfane (DDS) was obtained by oxidation of octadecane-1-thiol (ODT, Sigma) in chloroform using an equimolar aqueous solution of iodine and potassium iodide (Merck and Sigma, respectively). To obtain the initiator layer on the gold surface, the gold substrates were incubated overnight in a mixed solution of the initiator DTCA and DDS (1:1 molar ratio). The substrates were then placed in a quartz

flask equipped with a 280 nm cutoff optical filter and containing 5% aqueous solution of NIPAM (Aldrich, recrystallized from hexane before use). The flasks were purged with nitrogen and subsequently irradiated for 10 min by UV-B lamps (280–320 nm range, 15 W G15T8E, Ushio Japan) at a distance of 20 cm. After the photopolymerization, the substrates were extensively rinsed with water and methanol and dried in nitrogen. After grafting the PNIPAM to the gold surface, the substrates were placed in a quartz flask containing 5 ml of a 0.01 M aqueous solution of 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (4-amino-TEMPO) and were irradiated again for 5 min by UV-B lamps. The substrates were subsequently rinsed with methanol and dried in a nitrogen stream. It was previously shown that the height of PNIPAM brushes obtained with this procedure is around 10 nm [20].

To attach MAA-functionalized QDs covalently to the PNIPAM chain ends, 76 mg of (1-ethyl-3-[3-dimethylaminopropyl] carbodiimide) (EDC, Aldrich) and 12 mg of *N*-hydroxysuccinimide (NHS, Aldrich) were separately dissolved in 1 mL PBS buffer (0.01 M, pH 7.4) and then mixed in a quartz flask containing gold substrates with PNIPAM brushes. The reaction was left to proceed for 30 min and after the reaction the physisorbed QDs were removed by rinsing with methanol.

The UV–vis absorption spectra of TOPO-coated CdSe/ZnS QDs in chloroform and MAA-coated QDs in water were obtained using a Varian Cary 300 UV–Vis spectrometer. The concentration of the QD solutions and the diameter of the QDs was estimated based on the absorbance of the first absorption peak following the procedure reported in [21]. Luminescence emission spectra were obtained using an Edinburgh FL 900 spectrofluorometer.

Atomic force microscopy (AFM) was used to characterize the morphology of the gold substrates and the PNIPAM polymer brushes before and after QD immobilization. The imaging was performed using a NanoScope III (Veeco-Digital Instruments, CA, USA) AFM equipped with an EV scanner (15 $\mu$m × 15 $\mu$m scansize). Commercially available triangular silicon nitride cantilevers ($k = 0.3$ N m$^{-1}$, Veeco, CA, USA) were used for all measurements.

Fluorescence images of the QD/PNIPAM brush layers were obtained using a custom-built microscope based on an inverted Olympus IX71 microscope incorporating spectroscopic capabilities and equipped with suitable filters and dichroic mirrors. Fluorescence images were obtained using a mercury lamp (Olympus, Japan) as the excitation light source, a 40× objective and a sensitive colour camera (AxioCam HRC, Zeiss, Germany). Fluorescence spectra were obtained by 469 nm laser excitation and confocal detection of the emitted light via a prism spectrometer by a cooled CCD camera (Newton EMCCD, Andor, Northern Ireland). The size of the excitation spot was ∼3 $\mu$m. For measurement in an aqueous environment, a drop of Milli Q (Millipore, 18.2 MΩ) water was placed on top of the sample. A PDMS seal was used to avoid water spillage. A custom-made heating stage was used to perform the above-described photoluminescence imaging at 25 °C(±1 °C) and 50 °C(±2 °C).
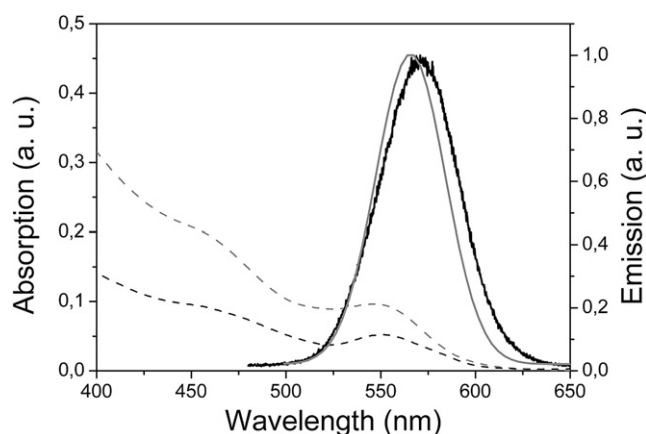
**Figure 1.** Absorption (dashed line) and normalized emission (solid line) spectra of QDs (excitation at 460 nm) in chloroform (grey) and in water (black).

## 3. Results and discussion

CdSe/ZnS core–shell quantum dots are commonly synthesized by pyrolysis of organometallic precursors in the presence of organic coordinating solvents [18]. Among the methods used to render the QDs dispersible in water, a ligand exchange reaction with bifunctional ligands is commonly performed [19, 22, 23]. This type of ligand has a functional group which is able to bind to the surface of the QDs and a hydrophilic part (usually COOH or OH) which makes the QDs dispersible in an aqueous medium. We have replaced the TOPO ligands on the QD surface with MAA (see the experimental section). MAA-coated QDs were dispersible in water with no obvious signs of nanoparticle aggregation. We present the absorption and emission (excited at 460 nm) spectra of QDs before and after MAA coating in figure 1, which was chosen among the ligand exchange reactions we performed for QDs of different sizes.

The lowest energy absorption bands of the spectra of both compounds (dispersed in chloroform and water) peak at a similar wavelength ∼550 nm, although the spectrum of the MAA-coated QDs is slightly broader. The emission peak of the MAA-coated QDs (∼570 nm) is slightly shifted with respect to that observed for the TOPO-coated QDs (∼565 nm). It is known that exchanging the TOPO ligands on the surface of QDs with thiols (or other types of ligands) may cause changes in the absorption and emission profiles [24]. Nevertheless, the slight differences observed here could be related simply to the changes in the dielectric environment of the QDs (different solvents) or to the presence of charges on the QD surface. The size of the CdSe core calculated from the first absorption peak is ∼3 nm [21] and is similar to the QD diameter obtained from the TEM images (see figure S1 in supporting information available at stacks.iop.org/Nano/20/185501). The quantum yield of the QDs in water is 46% as calculated using Rhodamine 110 as the reference. The PNIPAM polymer films were obtained by an 'iniferter-type' controlled radical polymerization. Iniferters are initiators of radical polymerization that also act as propagation and termination agents [20]. We synthesized a disulfide-based initiator, DTCA,

to graft the polymer chains to the gold substrate [20]. (The structure of the initiator is shown in figure 2(a).) In the context of the present work there are three attractive features which such a type of polymerization may provide. First, the initiator was shown to bind effectively to the gold surface, while retaining its polymerization initiating functions [20]. This feature allows us to grow polymeric chains directly from the gold substrate.

Second, controlled living radical polymerization allows us to set the molar mass of the polymer, and therefore the resulting film thickness. Finally, the reactive diethyldithiocarbamyl group remaining at the end of the growing PNIPAM chain can be exchanged for another chemical group to introduce functionality for further coupling with QDs [25]. A more detailed description and characterization of the PNIPAM brushes can be found in [20]. In order to couple the QDs to the PNIPAM chain ends we exchanged the radical chain ends of PNIPAM with 4-amino-TEMPO groups. EDC-assisted coupling between carboxylic acids and primary amines permits linking the functionalized PNIPAM chain ends to the MAA-coated QDs, resulting in an amide bond formation [26]. Addition of NHS improves the efficiency of the reaction by increased stability of the NHS ester intermediate. The general experimental scheme is presented in figure 2(b).

Fluorescence imaging of a sample with a removed initiator layer (by scratching it from the glass surface) showed that, after washing the substrate, emission originated only from the areas where the brush has been grown and the quantum dots were covalently attached to the chain ends (see figure S2, supporting information available at stacks.iop.org/Nano/20/185501).

The surface of the QD/PNIPAM layer was investigated by AFM. Figure 3 shows AFM height images of the PNIPAM brushes obtained before and after the attachment of QDs. Upon attachment of the QDs the surface roughness and variations in height increase significantly, indicating the presence of the nanoparticles on top of the PNIPAM brushes. The root-mean-square (rms) roughness of the surface calculated before (0.8 nm) and after (2.3 nm) QD attachment is in good agreement with the results obtained by Gupta *et al*, where the rms values for PAA brushes without immobilized QDs was 0.7, and 2.2 nm after QD attachment [7]. AFM results suggest that the amino end functionalized PNIPAM brushes can serve as efficient layers for covalent immobilization of carboxy-terminated QDs.

The central analysis of the hybrid polymer/QD platform was via temperature variation. The PNIPAM brushes were shown previously to display LCST behaviour similar to that of linear polymers or polymer networks [25, 27, 28]. Upon increasing the temperature and crossing the LCST, the polymer chains collapse, reducing the thickness of the polymer layer on the substrate. Upon decreasing the temperature below the LCST, the brush layer swells in water to restore the original thickness. This behaviour suggests that, in the present study, in which a layer of QDs sits on top of the brush layer, it should therefore be possible to modulate the distance of the nanoparticles to the gold substrate. The temperature-induced collapse and swelling will result in a modulation of the distance between the QDs and gold substrate, which will be reflected in
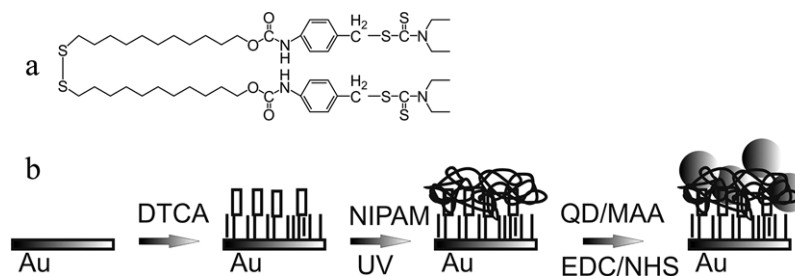
**Figure 2.** (a) The chemical structure of the iniferter DTCA, (b) scheme of the gold surface functionalization with PNIPAM and QDs. The polymer chains are grown directly from the Au surface by UV-initiated controlled radical polymerization. The radical chain ends are transformed to amines for coupling to COOH-modified QDs.
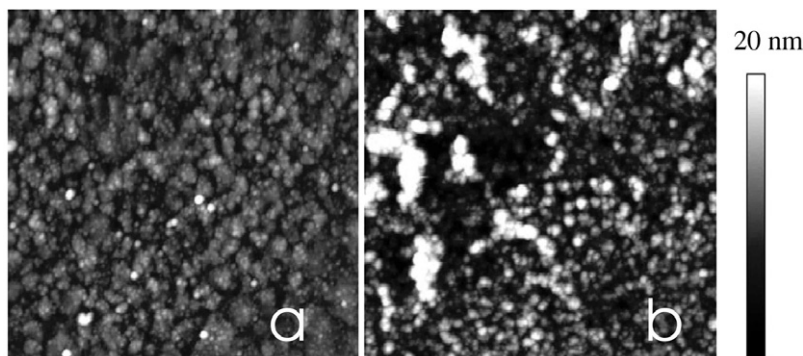


**Figure 3.** AFM height images of PNIPAM brush layer on gold before (a) and after (b) attachment of the QDs. (Scan size: 1 $\mu$m × 1 $\mu$m.)
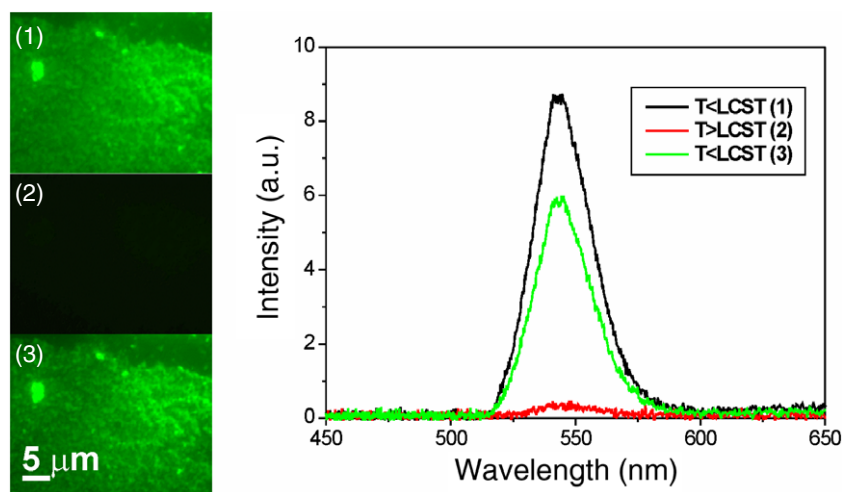


**Figure 4.** Left: luminescence images of Au/PNIPAM/QD assembly obtained at 25 °C (1), after heating to 50 °C (2), and after cooling back to 25 °C (3). Right: spectra measured at below the LCST (1, 3) and above the LCST (2), showing the quenching and recovery behaviour. (This figure is in colour only in the electronic version)

the emission properties as a loss of luminescence intensity due to energy transfer from the QDs to the gold surface.

The temperature response of the QD/PNIPAM luminescence upon heating and cooling the system in an aqueous environment is shown in figure 4 (left). The temperature was varied from 25 to 50 °C. During heating, a decrease in the luminescence intensity was observed. Upon crossing the LCST and reaching 50 °C, almost no luminescence (94% less intensity than initially as calculated from the spectra) could be observed from the sample (figure 4(2)). Subsequently, the heating was

switched off and the luminescence intensity could be observed to recover (68% of the initial intensity) (figure 4(3)).

Corresponding spectral measurements obtained for temperatures below and above the LCST are shown in figure 4 (right). The emission peak upon excitation of the sample with a 469 nm laser line is centred around 547 nm and no apparent shift is observed compared to the emission peak of MAA-coated QDs in water. The incomplete recovery of the fluorescence upon cooling the sample below its LCST could be explained by the hysteresis in the swelling/deswelling processes,

which are usually observed in PNIPAM-related systems due to intra- and inter-chain interactions formed in the collapsed state at $T >$ LCST [27]. Such hysteresis in the first cycle was reported to increase for thin hydrogel films due to the constraint imposed by the crosslink points [27]. In our system, the immobilized QDs might act as additional surface crosslink points influencing the hysteresis.

The hybrid polymer/QD system shows a remarkable on/off switching and good recovery of the emission spectra. In order to elucidate the mechanism of switching, we consider a number of possible scenarios. There is a possibility that the QDs could be incorporated into the polymer layer by swelling and hydrogen bond formation with PNIPAM. However, at $T >$ LCST, PNIPAM becomes hydrophobic and would expel the noncovalently attached QDs. The good recovery of the fluorescence intensity after each heating/cooling cycle indicates that only the emission originating from the covalently bound QDs is observed. Additionally Snaith *et al* [17] reported that QDs with diameters larger than 3 nm form bilayer structures on polymer brushes rather than infiltrate the brush interior due to unfavourable entropic penalties. Hence, we can conclude that the observed intensity changes are related to changes in the Au/PNIPAM/QD assembly that originate from the temperature-induced thickness variations of the PNIPAM layer.

The photoluminescence of QDs embedded in various matrices (also polymers) was found to be temperature-dependent and to decrease linearly by $1.3\%/\,^\circ$C with increasing temperature [29]. Given the temperature range investigated here, this effect would correspond to around 30% of the decrease in intensity, which is far below the quenching observed in our study. We have additionally investigated the effects of the temperature on the emission of the bare QDs in solution by repeatedly heating and cooling the sample for 10 cycles. The apparent variation in the luminescence intensity was less than 15%, much below the decrease observed for our system, where the QDs are coupled to the PNIPAM brushes grown from the gold substrate (figure S3, supporting information available at stacks.iop.org/Nano/20/185501). Therefore, the quenching of the luminescence is not a property of the QDs alone, but rather of the QD/PNIPAM/Au system.

The most plausible explanation for the observed emission changes is quenching of the luminescence of the QDs by the Au substrate (figure 5). In general, the interaction between QDs and metals may result in enhanced photoluminescence [30, 31] or in increased nonradiative decay rates due to energy transfer via electromagnetic interaction [31, 32]. Photoluminescence enhancement is not expected to be pronounced in our study as we excited the QDs at frequencies far from the gold surface plasmon resonance. Quenching of the luminescence by energy transfer to metals is a short-distance (in the 10 nm range) effect, which is modulated by the spectral overlap and distance between the energy donor and acceptor, and which is sensitive to surface roughness and to the local environment. In our system the distance between the QDs and gold is modulated via temperature-induced swelling and deswelling of the PNIPAM layer. This in turn influences the decay rates and results in
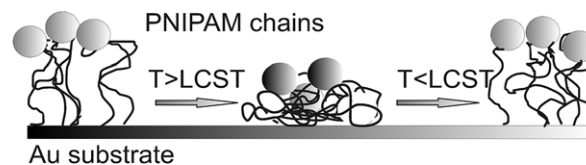


**Figure 5.** Proposed structure and temperature-dependent behaviour of the Au/PNIPAM/QD assembly. At T<LCST the polymer brushes are hydrophilic and are in the extended configuration. The quenching of the emission by the gold substrate is limited. At T>LCST the PNIPAM chains collapse, reducing the brush film thickness and bringing the QDs closer to the gold surface where pronounced quenching takes place. The transition is reversible and, upon cooling, the PNIPAM brushes swell in water and the luminescence is recovered.

luminescence quenching. The photoluminescence decay rate is a sum of the internal decay rates (radiative and nonradiative) of the QD and the energy transfer rate from the QD to the metal. To elucidate the exact mechanism for the quenching a more detailed study including lifetime measurements shall be performed in the future.

## 4. Conclusion

We have demonstrated a thermo-responsive metal/polymer/ quantum dot platform based on PNIPAM brushes grafted from a gold substrate using an iniferter-type polymerization and QDs covalently attached to the PNIPAM chain ends. The EDC/NHS chemistry was shown to be efficient in coupling COOH-functionalized QDs to amine-terminated PNIPAM brushes. Luminescence imaging and luminescence spectra measurements showed that, upon increasing the temperature above the LCST of PNIPAM, the QD emission is quenched. When decreasing the temperature below the LCTS, recovery of the luminescence can be observed. The results obtained are consistent with temperature-modulated thickness of the PNIPAM brushes and quenching of the nanoparticles luminescence by the gold substrate. The Au/PNIPAM/QD system reported here may be explored in sensing and surface thermometry. The iniferter-type polymerization would also allow one to control the film thickness and improve the sensitivity and time response of the system.

## Acknowledgments

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