

Luminescent ‘On-Off’ CdSe/ZnS Quantum Dot Chemodosimeter for Hydroxide Based on Photoinduced Electron Transfer from a Carboxylate Moiety

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Abstract A CdSe-ZnS quantum dot (QD) has been surface functionalised by a place exchange reaction with *p*-mercaptomethyl benzoate synthesized by a three-step procedure. The resulting lumophore-spacer-receptor QD-conjugate was characterized by IR, UV-visible and fluorescence spectroscopy. The emission profile of the QD reveals a narrow emission peak centred at 542 nm. Addition of hydroxide to the solution containing the QD-conjugate results in quenching of the original fluorescence, which is attributed to a photoinduced electron transfer reaction from the electron-rich benzoate moiety to the QD valence band. This is the first reported example of fluorescent quenching of a CdSe-ZnS QD luminescence by an aryl carboxylate moiety.

Keywords Quantum dot · Luminescence · Photoinduced electron transfer · Chemodosimeter

Introduction

Colloidal quantum dot (QD) nanocrystals have been demonstrated to be a complementary alternative to organic dyes for luminescent sensing applications [1, 2]. The most popular QDs used for biological imaging and sensing purposes are those composed of a CdSe core surrounded by a coating of ZnS [3–6]. A distinct advantageous property of these inorganic-organic hybrid particles over organic fluorophores, from a synthetic point of view, is the ability to tailor the emission

properties across the visible electromagnetic spectrum simply by tuning the CdSe core size, which typically ranges between 1.5 nm to 5.0 nm in diameter [7]. Other notable properties of QDs include the ability to excite at variable wavelengths due to a continuous absorption spectrum, a high resistance to photobleaching and a narrow, symmetrical emission band [8–10].

Perhaps the most common luminescent sensing mechanism utilized to date with QD systems is based on Forster resonance energy transfer [1, 11–15]. An alternative mechanism growing in popularity is that based on photoinduced electron transfer (PET) [16–20]. The rational design of chemosensors based on PET requires knowledge of the redox potentials and the photophysical parameters of the lumophore [21]. Furthermore, another requirement is the strategic engineering of the sensing system based on a lumophore-spacer-receptor design [22, 23]. Although the scientific literature is rich with a plethora of examples based on all organic-based fluorophore-spacer-receptor PET models [24, 25], the same cannot be said of lumophore-spacer-receptor systems based on semiconductor quantum dots as only recently have systematic studies on the redox properties of QDs been reported [26–28]. These studies have provided insight into their physico-chemical properties and demonstrated that the redox potentials of QDs are dependent on the luminescent core diameter, the protective shell thickness and the nature of the passivating ligands. The determination of the thermodynamic feasibility for PET reaction is rather simple once accurate standard potentials are known. Common PET receptor units that have thus far been demonstrated with QDs include receptors for protons, such as amines [16] and phenolates [13], crown ethers [18] for sodium and potassium ions, and thioureas [19, 20] for anions. A classic pH-sensitive receptor that is yet to be demonstrated with QDs is the carboxylate moiety [29].

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In this work, we report the synthesis of a thiol pendant organic ligand, its attachment on the quantum dot and characterization of the photophysical properties of the resulting QD-spacer-receptor conjugate by UV-visible and steady-state fluorescence spectroscopy. The ligand consists of an aromatic carboxylate moiety with a short methylene spacer anchored to the QD surface via a pendant thiol ligand according to a lumophore-spacer-receptor architecture. A single carbon-atom spacer is purposely incorporated into the ligand design in order to minimize the distance between the ZnS layer and the organic receptor, thus maximizing the rate of PET and the fluorescence switching factor. Based on prior knowledge of the redox potentials of both the QD and the carboxylate donor, and the fluorescence properties of a QD, we successfully demonstrate for the first time, a CdSe/ZnS QD nano-sized sensor as an ‘on-off’ chemodosimeter for hydroxide based on a PET quenching mechanism.

Experimental

Chemicals

All chemicals were purchased from commercial sources and used as received: *p*-toluic acid (Acros Organics), *N*-bromosuccinimide (GPR), chlorobenzene (BDH), benzyl peroxide (FLUKA), hexanes (Sigma Aldrich), ethyl acetate (Sigma Aldrich), potassium thioacetate (Acros Organics), methanol (Sigma Aldrich), hydrochloric acid (Sigma Aldrich), potassium carbonate (Analar), sodium sulfate (Sigma Aldrich), acetone (Sigma Aldrich), DMSO- d_6 (Sigma Aldrich), $CDCl_3$ (Sigma Aldrich), CdSe/ZnS core quantum dot with 2.4 nm core diameter and 8.0 nm total diameter (Evident Technologies), chloroform (FLUKA), tetrabutylammonium hydroxide (0.1 M in 2-propanol/methanol 10:1 (v/v)) (FLUKA), chloroform (Fischer Chemical).

Instrumentation

1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker AM 250 NMR spectrometer equipped with a $^1H/^{13}C$ 5 mm dual probe at 250.1 and 62.9 MHz, respectively. Spectra are reported in ppm versus tetramethylsilane ($\delta=0.00$) for 1H NMR and $CDCl_3$ ($\delta=77.00$) for ^{13}C NMR. 1H NMR spectra were recorded in 0.8 ml of a 1:1 solution of $CDCl_3/DMSO-d_6$. ^{13}C NMR samples of thioacetic acid *S*-(4-carboxybenzyl) ester were recorded in $DMSO-d_6$. Infrared (IR) spectra were recorded on a Shimadzu IR-Affinity 1 spectrometer. Bromomethylbenzoic acid and thioacetic acid *S*-(4-carboxybenzyl) ester were recorded by attenuated total reflectance (ATR) as solid samples. The IR spectra of the QD and QD-spacer-receptor were recorded as a thin film on sodium chloride windows. GC-MS was performed on a Thermo

Finnigan Trace DSQ spectrometer using a BP1 bonded phase (polysiloxane) column. Samples were injected as solutions in 1:1 diethyl ether/acetone. Melting points were recorded on a Griffin melting point apparatus and are uncorrected. UV-visible absorption and fluorescence spectra were recorded on a Jasco V-650 spectrophotometer and Jasco FP-8300 fluorescence spectrometer, respectively. Fluorescence experiments were performed in emission mode with excitation slit width at 2.5 nm and the emission slit width at 5.0 nm, unless stated otherwise. All fluorescent measurements performed in chloroform. The excitation wavelength was set at 370 nm.

Synthesis

4-Bromomethylbenzoic Acid (**2**)

A solution of *p*-toluic acid (**1**) (3.0 g, 22 mmol), *N*-bromosuccinimide (4.1 g, 23 mmol), benzoyl peroxide (0.25 g, 1.0 mmol) and chlorobenzene (30 ml) were refluxed for 1 h. After cooling to ambient temperature, the product was filtered by suction filtration and the resulting mixture was extracted with hexanes (3×10 ml), collected by suction filtration, washed with deionised water (2×15 ml) and hexanes (2×15 ml). The solid was recrystallized from 10 ml of ethyl acetate to yield white-beige crystals (1.7 g, 40 %). m.p. 214–216 °C; ν_{max} (cm^{-1}) 2812, 1672, 1608, 1421, 1284, 1224; 1H NMR (250 MHz, $CDCl_3/DMSO-d_6$): δ 4.70 (2H, s), 7.55(2H, d, $J=8.3$ Hz), 7.95(2H, d, $J=8.3$ Hz); m/z (EI): 216(M^+ ,6), 214(M^+ , 7), 135(13), 134(100).

Thioacetic Acid *S*-(4-Carboxybenzyl) Ester (**3**)

p-Bromomethylbenzoic acid (1.5 g, 7.0 mmol) and potassium thioacetate (0.81 g, 7.1 mmol) were dissolved in 100 ml of methanol and stirred for 48 h. The product was identified by TLC (R_f of 0.47) in 1:1 ethyl acetate/hexanes solution. The solvent was removed under reduced pressure and the product collected by suction filtration in a sintered funnel. The white crystals were washed with water to remove the excess potassium thioacetate (0.69 g, 50 %). m.p. 153–156 °C (lit. 154–155 °C) [30]; ν_{max} (cm^{-1}) 2630, 2364, 1676, 1608, 1419, 1282, 1126; 1H NMR (250 MHz, $CDCl_3$): δ 2.37 (3H, s), 4.16 (2H, s), 7.40(2H, d, $J=8.1$ Hz), 8.04(2H, d, $J=8.1$ Hz); ^{13}C NMR (250 MHz, $DMSO-d_6$) δ 30.5, 32.5, 129.0, 129.7, 143.0, 167.3, 194.7; m/z (EI): 210 (M^+ , 8), 150(100), 135(4), 134(28).

p-Mercaptomethylbenzoate (**4**)

Thioacetic acid *S*-(4-carboxybenzyl) ester (100 mg, 0.48 mmol) was dissolved in 8 mL of methanol and drops of 6 M HCl were added. The solution was refluxed and stirred under a nitrogen atmosphere for 4 h. The reaction was monitored by TLC in 1:9

ethyl acetate/ hexanes (R_f of 0.28). The reaction was worked-up with potassium carbonate solution, extracted with dichloromethane (3×10 ml), washed with 10 ml deionised water and dried with sodium sulphate. The solvent was removed under reduced pressure by rotary evaporator to yield a pale yellow oil (67 mg, 77 %). $^1\text{H NMR}$ (250 MHz, CDCl_3): δ 1.79 (1H, br t), 3.73(2H, s), 3.89 (3H, s), 7.37 (2H, d, $J=8.0$ Hz), 7.97 (2H, d, $J=8.0$ Hz). The thiol peak was confirmed by deuterium exchange with D_2O .

Ligand Exchange Reaction: QD with *p*-Mercaptomethylbenzoate

A solution of CdSe/ZnS core shell quantum dot (0.6 ml, 6 mg) in toluene and *p*-mercaptomethylbenzoate in chloroform (10 ml) were refluxed for 40 h. After cooling to ambient temperature, the solvent was removed under reduced pressure using a rotary evaporator. The residue was suspended in 5 ml of acetone and centrifuged for 5 min. The supernatant was decanted and the procedure repeated five more times. The residue was washed by suspending in 3 ml acetone and centrifuged for 3 min. The supernatant solution was decanted and the solid washed twice with acetone. The product was vacuum dried yielding a bright orange powder (18 mg).

Results

The multi-step synthesis of the designed ligand is shown in Scheme 1. The ligand was synthesized in three steps beginning with the bromination of *p*-toluic acid (**1**) with bromosuccinimide (NBS) in 37 % yield. Treatment of 4-bromomethylbenzoic acid (**2**) with potassium thioacetate in methanol resulted in the formation of thioacetic acid *S*-(4-carboxybenzyl ester) (**3**) in 50 % yield. The carboxylic acid was then reacted with dilute hydrochloric acid in methanol resulting in the simultaneous deprotection of the thioester to the thiol, and conversion of the carboxylic acid moiety to the ester (**4**). Formation of the thiol was confirmed by a deuterium exchange with deuterium oxide (D_2O), which results in the disappearance of the broad resonance at 1.79 ppm. Deprotection of the thiol was subsequently done in situ (to prevent oxidation of the thiol to the disulfide). The place exchange reaction of the trioctylphosphine oxide (TOPO) ligands on the CdSe/ZnS QD surface was accomplished by

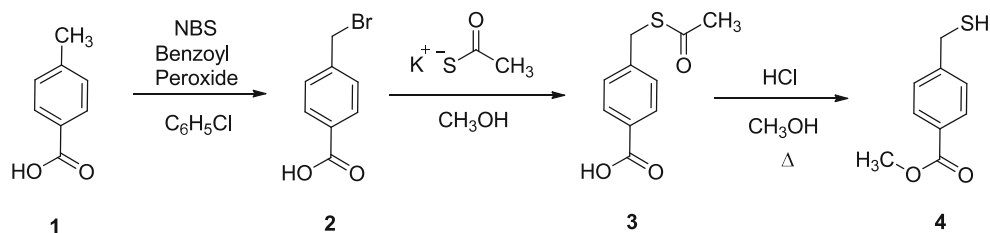
refluxing the mixture in chloroform for 40 h. The resulting QD-spacer-receptor conjugate was isolated after reiterative sequences of precipitation from acetone and centrifugation to yield an orange solid. The conversion of the carboxylic acid to the ester was purposely incorporated into the synthetic scheme as esters are easier to characterize by $^1\text{H NMR}$ and IR than carboxylic acids (since they are not as hygroscopic). Furthermore, the ester functionality can serve as a platform for future covalent modification with other functional molecules.

The $^1\text{H NMR}$ of the original QD has broad peaks at 0.8 and 1.2 ppm due to the methyl and methylene protons of the TOPO ligands, which is a strongly co-ordinating ligand used to passivate the QD surface. Trace resonances were observed at 2.00, 2.80, 5.00, and 5.80 ppm, which are attributed to octadecene, a non-coordinating high boiling solvent used in the synthesis of the QD. Attempts to confirm the place exchange by comparison of the $^1\text{H NMR}$ spectrum of the QD with the QD-conjugate were not successful. The QD-conjugate was found to have low solubility in deuterated chloroform and in a 1:1 ratio of $\text{CDCl}_3/\text{DMSO}-d_6$ even when heated.

We also compared the infra-red spectra of the QD and the QD-conjugate. The CdSe/ZnS QD exhibit intense bands about $2,900\text{ cm}^{-1}$ from the alkyl chains of the TOPO ligands. These peaks were barely visible in the IR spectrum of the QD-conjugate suggesting most of the TOPO ligands were replaced with *p*-mercaptomethyl benzoate. The spectrum of the QD-conjugate exhibits broad, intense peaks at $1,100\text{ cm}^{-1}$ and $1,650\text{ cm}^{-1}$, which are attributed to the C–O and C=O stretching, respectively. No such peaks were observed in the IR of the QD, thus providing supporting evidence that the ligand place exchange reaction was successful.

The absorption spectra of the CdSe/ZnS core-shell QD in chloroform is shown before and after treatment with the *p*-mercaptomethylbenzoate Fig. 1. The QD-spacer-receptor conjugate displays a noticeable different UV-visible spectrum with a peak at 245 nm, a shoulder emerging at 275 nm and a tailing of the absorbance past 370 nm. This absorption profile resembles that of the model ligand and corresponds to the π to π^* transition due to the aromatic chromophore and the tailing due to the n to π^* transition of the carbonyl. As reported elsewhere, the exciton peak at 521 nm is relatively unchanged [13, 14]. Titration with 15 mM tetrabutylammonium hydroxide (Bu_4NOH) solution results in no change at the excitation

Scheme 1 The synthesis of the *p*-mercaptomethylbenzoate ligand



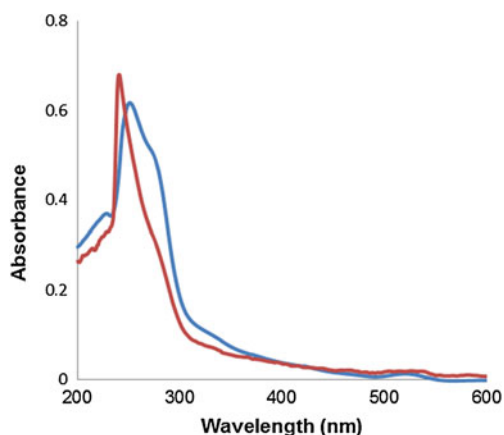


Fig. 1 Normalized absorption spectra of the CdSe/ZnS core-shell QDs in chloroform before (red line) and after (blue line) the place exchange reaction with *p*-mercaptomethylbenzoate refluxed for 40 h

wavelength of 370 nm. The exciton peak was observed to shift ever slightly to 523 nm while the absorbance remained constant.

The emission spectrum of the QD shows a narrow and symmetrical band centred at 545 nm. Little change is observed between the initial QD and QD-spacer receptor conjugate when excited at 370 nm [19]. Addition of excess Bu_4NOH results in the quenching of the fluorescence and a concomitant bathochromic shift of 5 nm without the formation of any new bands, as shown in Fig. 2, which is attributed to a change in solvent polarity on addition of the 2-propanol/methanol Bu_4NOH solution. The fluorescence response upon addition of Bu_4NOH is discernible to the naked eye. Figure 3 highlights the dramatic change in the fluorescence before and after the addition of Bu_4NOH as the QD is switched from ‘on’ to ‘off’ from emitting a green glow to becoming a clear, colourless solution. Addition

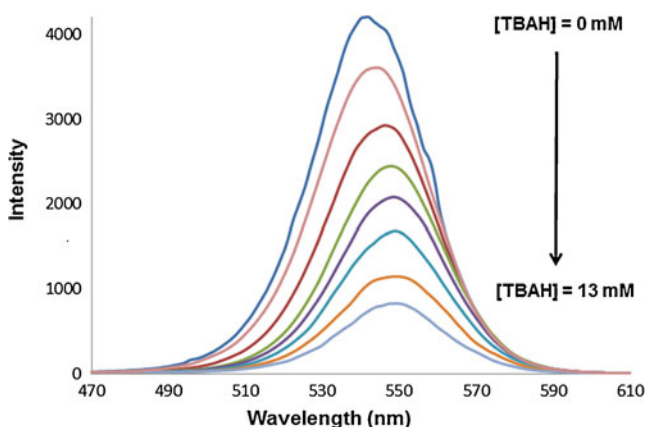


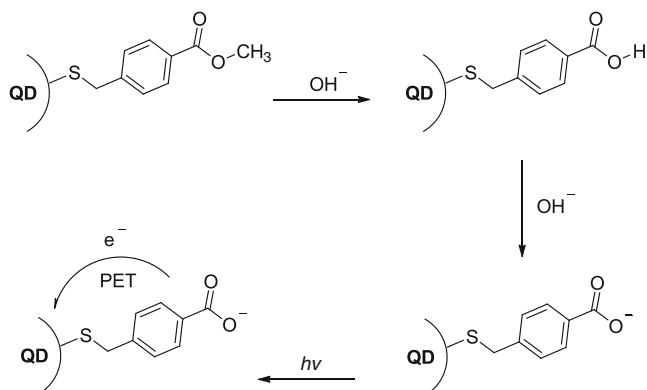
Fig. 2 Fluorescence spectra of QD-conjugate in chloroform upon addition of increasing amounts of tetrabutylammonium hydroxide in 10:1 (v/v) 2-propanol/methanol solution



Fig. 3 Irradiation of the QD-conjugate with 365 nm UV light in chloroform in the absence (left) and presence (right) of excess tetrabutylammonium hydroxide solution

of the same amount of Bu_4NOH to an identical concentration of QD solution does not result in switching ‘off’ the green fluorescence.

Scheme 2 illustrates the postulated mechanism responsible for quenching the fluorescence. Addition of hydroxide results in hydrolysis of the ester to the carboxylic acid, which subsequently reacts with another equivalent of hydroxide by an acid-base reaction. The resulting electron-rich carboxylate facilitates an efficient PET reaction on irradiation of the QD core that readily quenches the fluorescence. The carboxylate reacts as an electron donor that is less positive than the valence band of the QD. In a separate experiment, addition of Bu_4NOH to the QD with TOPO ligands resulted in essentially no loss of fluorescence. Hence, this is convincing evidence that the source of fluorescence quenching is the carboxylate ligand and not the hydroxide ions. Attempts to revive the fluorescence of the QD-conjugate with the addition of trifluoroacetic acid proved unsuccessful. It is quite conceivable that at low pH the thiol ligand is unstable and deabsorbs from the QD surface [18].



Scheme 2 The reactivity of the QD-conjugate with hydroxide resulting in quenching of the fluorescence emission by photoinduced electron transfer

The driving force for PET reactions (in kcal mol^{-1}) was predicted using the Weller equation as given in Eq. 1,

$$\Delta G_{\text{PET}} = 23.06(E_{\text{ox}} - E_{\text{red}} - \Delta E_s - q^2/\epsilon r) \quad (1)$$

which requires knowledge of the redox potentials of the donor E_{ox} and the acceptor (quantum dot) E_{red} , the optical band gap of the quantum dot ΔE_s and the Coulombic term $q^2/\epsilon r$ (where q is the elementary charge, ϵ is the dielectric constant and r is the distance between the donor and acceptor). The oxidation potential of the carboxylate is 1.22 V [31] versus SCE and the reduction potential of the QD is -0.96 V [27] versus SCE and the band gap is ca. 2.4 V [27]. The total radius of the QD is 4.0 nm. Since the core radius is 1.2 nm, the ZnS layer is estimated to be 2.8 nm in thickness. Given the dielectric constant of chloroform is 4.8, the Coulombic term provides a negligible contribution to the overall free energy on the order of less than 0.1 V. Hence, the estimated driving force for PET is ~ -0.2 V or -5 kcal mol^{-1} .

Conclusions

In this study, a CdSe/ZnS QD was surface functionalized with *p*-mercaptomethylbenzoate according to a lumophore-spacer-receptor format. The QD-conjugate exhibits modularity as the absorbed ligands retain their chemical properties. Addition of increasing amount of tetrabutylammonium hydroxide results in efficient quenching of the fluorescence due to hydrolysis of the ester via a carboxylic acid intermediate to the aryl carboxylate, and subsequently to photoinduced electron transfer from the electron-rich carboxylate to the QD lumophore core. Attempts to restore the fluorescence upon addition of acid were unsuccessful. A remedy in the future might be to use bidentate dithiolane [32] or carbodithioate ligands [33], which have greater stability in acidic media.

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