Synthesis of cadmium selenide quantum dots modified with thiourea type ligands as fluorescent probes for iodide ions†

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Highly luminescent and stable CdSe quantum dots (QDs) modified with 4-substituted pyridine type ligands containing thiourea groups: 1-(4-fluorobenzoyl)-3-(5-(pyridin-4-yl)-1,3,4-thiadiazol-2-yl) thiourea (PyTU); were prepared through a ligand exchange process, and were characterized by transmission electron microscopy (TEM), fluorescence spectroscopy, UV-vis spectroscopy and FT-IR spectroscopy. The synthesized nanocomposites show higher fluorescence (FL) intensity and are more stable in comparison with original QDs. The PyTU–CdSe QDs allow a highly sensitive determination of iodide *via* significant FL intensity quenching. Under optimal conditions, the relative FL intensity is decreased linearly with increasing iodide concentration in the range 0–50 μM with a detection limit of 1.5×10^{-9} M, while the FL intensity of PyTU–CdSe QDs to other anions including F^-, Cl^-, Br^-, SCN^-, $HCOO^-$, CH_3COO^-, HSO_3^-, and $C_2O_4^{2-}$ is negligible. It is found that the decreased luminescence intensity of the PyTU–CdSe QDs dependent on the concentration of iodide is best described by a Stern–Volmer equation. The possible mechanism is discussed.

Introduction

The selective detection of anions is of importance in environmental monitoring, medicinal diagnostics, and the analysis of biological samples.[1] Among anions, iodide plays an important role in several biological activities such as neurological activity and thyroid function. Hence the iodide content of urine and milk is often required for nutritional, metabolic, and epidemiological studies of thyroid disorder.[2] Some analytical methods have been applied to determine the iodide content, such as ICP-MS,[3] capillary electrophoresis,[4] iodide-selective electrodes[5] *etc*. Nowadays, fluorescent sensors have been extensively developed with high sensitivity and selectivity. Many investigations have been conducted to make fluorescent sensors for anions.[6] However, few reports have been explored for iodide[7] and discrimination between iodide and chemically close anions presents a challenge. The relatively strong hydrogen bonding of urea and thiourea groups has been used in the development of neutral receptors, because the hydrogen bond is directional in character, and correct orientation of the hydrogen bond donors can provide selective anion recognition.[8] It has also been reported that some of these urea or thiourea derivatives could be used in anion sensing based on absorption and fluorescence spectra[9] or ion-selective electrodes.[10] However, there seems to be no report, to our knowledge, of a urea or thiourea group as a part of the framework, modified on the surface of quantum dots and used as fluorescent sensors for the determination of anions.

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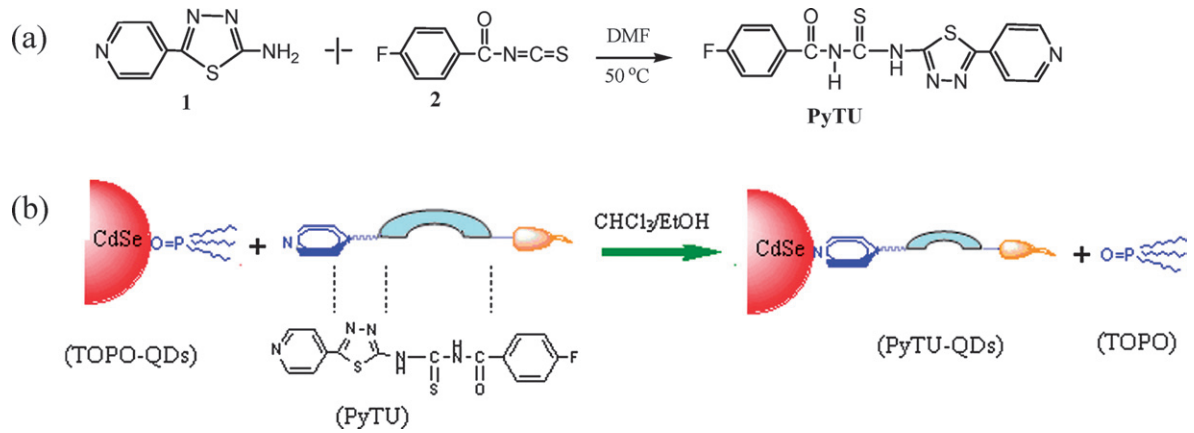
Semiconductor quantum dots (QDs), due to their novel optical, electrical, and catalytic properties, have gained increasing attention during the past decade.[11] Compared with organic fluorophores, QDs have several important advantages including size-selection, narrow emission spectra, resistance to photobleaching, improved brightness, and broad excitation spectra.[11] The uses of QDs have been demonstrated in analytical chemistry as high sensitivity fluorescent sensors recently.[12] Since Chen and Rosenzweig first demonstrated luminescent quantum dot probes for Cu^{2+} and Zn^{2+} ions by utilizing functionalized CdS QDs capped with different organic ligands in aqueous media,[13] the use of QDs or nanoparticles as selective chemosensors for metal ions has been an active research field in recent years. For example, Isarov and Chrysochoos,[14] Gattás-Asfura and Leblanc,[15] and Konishi and Hiratani[16] and coworkers reported CdS QD-based sensors for the determination of Cu^{2+} in the presence of other biological metallic ions. Also, CdSe QDs modified with mercaptoacetic acid and bovine serum albumin (BSA) were assayed for the analysis of Ag^+.[17] More recently, we demonstrated carnitine modified CdSe/ZnS QDs as selective chemosensors for Cd^{2+}.[18] Meanwhile, the employment of QDs or nanocrystals for determination of anions was almost unexplored until 2004, when Sanz-Medel and coworkers reported the synthesis of red photoluminescent CdSe quantum dots, which were modified with *tert*-butyl-*N*-(2-mercaptoethyl)-carbamate (BMC), as a selective fluorescent probe for the determination of free cyanide in methanol.[19] To our knowledge, there are few reports about quantum dots with a selective fluorescence response for iodide ions.[20]

We are interested in constructing a novel quantum dots based chemosensor for iodide ions. To address this goal, semiconductor nanocrystals have to be further modified by appropriate functional groups to allow significantly diverse properties and potential sensor applications. To date, different synthetic



Scheme 1 Synthesis of (a) PyTU and (b) PyTU–CdSe QDs.

strategies have been investigated to modify QDs. One of the most frequently used approaches is the ligand exchange method, which uses organic ligands to replace the original surface ligands, such as thiol (–SH) ligands,[21,22] and other non-thiol organic ligands (4-substituted pyridine, oligomeric phosphine, *etc.*).[23] Skaff and Emrick synthesized water-soluble CdSe QDs modified with 4-substituted pyridine with polyethylene glycol (PEG) chains.[24] This new ligand architecture gives rapid access to modified quantum dots, where neither ionization nor the use of thiols are required.

As part of our ongoing studies on preparing QDs based sensors for iodide recognition, here we present the synthesis and anion binding studies of CdSe QDs modified with 4-substituted pyridine type ligand containing thiourea groups as recognition sites for anions. The strategy for the design of the ligand is based upon three ideas. First, N–H bonds in the thiourea type ligand aligned in parallel may effectively make a complex with an anion. Second, the flexibility of the ligand on the surface of QDs would allow encapsulation of large anions such as iodide. Third, the end pyridine group of ligand affords the binding site for QDs.

In this paper, we report the synthesis of QDs modified with the pyridine derivative 1-(4-fluorobenzoyl)-3-(5-(pyridin-4-yl)-1,3,4-thiadiazol-2-yl)thiourea (PyTU) having a thiourea group (Scheme 1) as fluorescent sensors for iodide.

Experimental

Materials and apparatus

All chemicals used were of analytical grade or of the highest purity available. Cadmium oxide (99.99%), trioctylphosphine oxide (TOPO, 99%), trioctylphosphine (TOP, 90%), and selenium (powder, 99.99%) were purchased from Aldrich (Milwaukee, WI, USA). *n*-Octadecylamine (ODA) was obtained from Alfa Aesar (Karlsruhe, Germany). All anion samples were obtained from Shanghai Chemical Factory, China. All anion samples were potassium salts and prepared with anhydrous ethanol.

UV-vis absorption spectra were acquired on a UV-2501 UV-vis spectrometer (SHIMADZU CORPORATION). Fluorescence spectra were taken on a FluoroMax-P luminescence spectrometer (HORIBA JOBIN YVON INC.). Transmission electron micrographs were recorded by a JEOL-JEM 2010 transmission electron microscope operating at 200 kV. All fluorescence measurements were made with a FluoroMax-P fluorescence spectrophotometer equipped with a 1 cm quartz cell. The IR spectra were detected by a Thermo Nicolet NEXUS IR spectrometer with KBr disks. The ultrasonic bath was a SB120D Supersonic instrument.

Synthesis of 1-(4-fluorobenzoyl)-3-(5-(pyridin-4-yl)-1,3,4-thiadiazol-2-yl)thiourea (PyTU)

To a solution of 2-amino-5-(pyrid-4-yl)-1,3,4-thiadiazole **1** (9 mmol) in dry DMF (10 mL) was added 4-fluorobenzoyl isothiocyanate **2** (9.9 mmol) at room temperature. After the reaction mixture was stirred and heated at 50 °C for 3 h under an argon atmosphere, the mixture was concentrated and purified by column chromatography on silica gel to give the 1-(4-fluorobenzoyl)-3-(5-(pyridin-4-yl)-1,3,4-thiadiazol-2-yl)thiourea (PyTU) as a pale yellow powder with a yield of 85%. m.p. >300 °C; ^{1}H NMR (400 MHz, DMSO-d6) δ 7.437 (t, 2H, J = 8.8 Hz), 7.959 (d, 2H, J = 4.8 Hz), 8.244 (t, 2H, J = 7.6 Hz), 8.750 (d, 2H, J = 4.8 Hz), 10.871 (s, 1H, NH), 13.391 (s, 1H, NH); IR (KBr) ν: 3266, 3133 (N–H), 1705, 1676 (C=O) cm^{-1}. ESI-MS: m/z = 359 (M^+) Anal. calcd for $C_{15}H_{10}FN_5OS_2$: C 50.13, H 2.80, N 19.49; found C 50.15, H 2.85, N 19.43.

Preparation of CdSe QDs

CdSe quantum dots were synthesized using CdO as a precursor *via* the procedure described by Qu and Peng,[25] although some slight modifications were made here. Briefly, 0.0127 g of CdO (0.1 mmol), 0.1140 g of stearic acid (0.4 mmol), 1.94 g of ODA and 1.94 g of TOPO were mixed whilst heating at 300–320 °C under argon flow for 5 min, and CdO was completely dissolved in ODA and TOPO. The solution of selenium–TOP [0.079 g (2 mL)$^{-1}$] was swiftly injected and a change of solution color to red was observed. After injection, CdSe nanocrystals were left to grow for about 4 min at 250 °C. Then, the mixture was cooled down to room temperature. The precipitate was collected by centrifugation at 12 000 rpm for 5 min followed by washing with methanol several times. Then, the precipitate was re-dispersed in typical nonpolar solvents such as chloroform and toluene.

Finally, the CdSe quantum dot solutions at a concentration of 0.5 mg mL^{-1} were stored.

Synthesis of PyTU–CdSe QDs

PyTU exchanged TOPO to give PyTU–CdSe QDs. Briefly, 2 mL of TOPO–CdSe QDs chloroform solution (0.5 mg mL^{-1}) was added to 2 mL of PyTU ethanol solution (1×10^{-4} M), the mixture was refluxed at 80 °C for 4 h. The PyTU–CdSe QDs were purified by precipitation and centrifugation in anhydrous methanol. The resulting PyTU–CdSe QDs were stored in chloroform and ethanol (v : v = 4 : 1) mixture solution at room temperature for further investigations.

Results and discussion

Synthesis and characterization of PyTU

The synthetic route is depicted in Scheme 1. Reacting 2-amino-5-(pyrid-4-yl)-1,3,4-thiadiazole **1** with 4-fluorobenzoyl isothiocyanate **2** in DMF at 50 °C for 3 h gives the desired compound PyTU with a yield of 85%, which is confirmed by ^{1}H NMR, IR, ESI-MS and elemental analysis.

Characterization of PyTU–CdSe QDs

Fig. 1 shows the emission spectra of PyTU–CdSe QDs in chloroform and ethanol (v : v = 4 : 1) solution obtained by excitation at 450 nm. In comparison with the original QDs in chloroform, the fluorescence (FL) intensity of PyTU–CdSe QD is increased with a blue-shift of 4 nm, which was detected under the same conditions. The absorption spectra of PyTU–CdSe QDs in chloroform and ethanol (v : v = 4 : 1) solution and TOPO–CdSe QDs in chloroform are shown in the inset. As can be seen from the inset, no distinct difference in the positions and peak widths was found, which suggests that the modification process retained the optical properties of the CdSe QDs. The quantum yield (QY) determined by using rhodamine B as a criterion (QY = 89%) is about 23%. The TEM images (Fig. 2) demonstrate that the sizes of the modified QD particles and TOPO QDs are virtually identical, indicating that the modified particles are monodisperse and uniform.

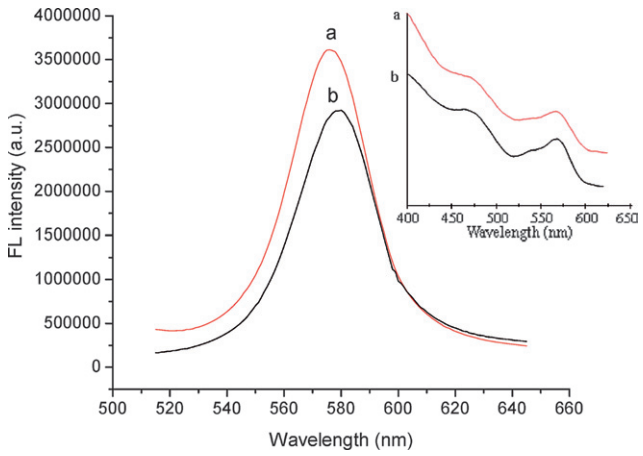


Fig. 1 The fluorescence spectra of (a) PyTU–CdSe QDs in a chloroform and ethanol mixture solution (v : v = 4 : 1) and (b) TOPO-capped CdSe QDs in chloroform (Ex: 450 nm). The inset shows UV-vis spectra of (a) PyTU–CdSe QDs in a chloroform and ethanol mixture solution (v : v = 4 : 1) and (b) TOPO-capped CdSe QDs in chloroform taken under the same conditions.

Fig. 3 depicts typical transmission IR spectra of parent PyTU, the PyTU complex of $CdCl_2$, PyTU-capped CdSe QDs, and TOPO-capped CdSe QDs, respectively. Comparing Fig. 3a with 3c, it is found that the gross resemblance in both spectral

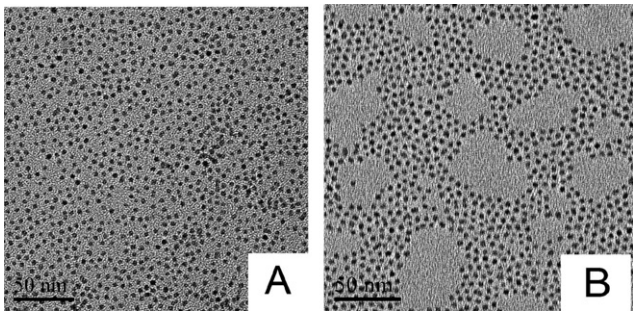


Fig. 2 TEM images of (A) original CdSe QDs in chloroform, and (B) PyTU–CdSe QDs in a chloroform and ethanol mixture solution (v : v = 4 : 1). Scale bars are all 50 nm.

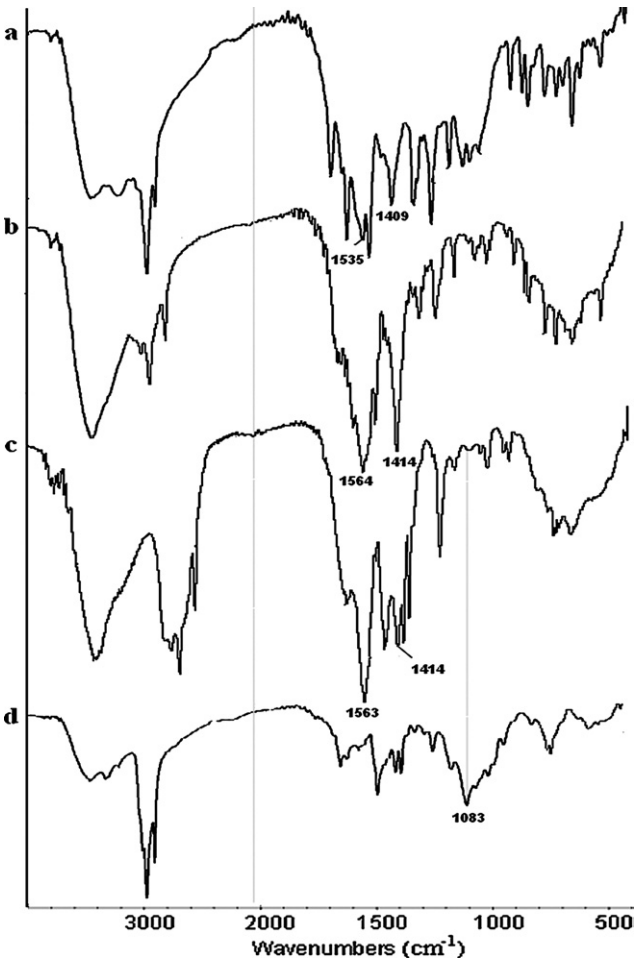


Fig. 3 IR spectra of (a) pure PyTU, (b) the complex of PyTU and $CdCl_2$, (c) a PyTU–CdSe QDs sample, and (d) TOPO-capped CdSe QDs.

features and peak positions for several vibrational modes guarantees a successful attachment of PyTU onto CdSe QDs. The characteristic peaks of pyridine located at 1535 and 1409 cm^{-1} are attributed to the symmetric and asymmetric ring breathing and the C–C and C–N stretching modes, respectively. Pyridine is a good electron donor due to the presence of a pair of isolated nitrogen electrons. CdSe quantum dots show a good electron affinity, meaning that the nitrogen readily coordinates with them to form a stable complex. As a consequence, the characteristic bands of pyridine were shifted to 1564 and 1414 cm^{-1} for the PyTU QD complexes. And the IR spectrum of the PyTU–Cd^{2+} complex (Fig. 3b) further proved PyTU was bound onto the surface of the QDs. The characteristic band associated with P=O at 1083 cm^{-1} for TOPO nearly disappears in the PyTU–CdSe QD spectra, suggesting that PyTU-capped particles have very few adsorbed TOPO ligands remaining.

^{31}P NMR measurements of the QDs in $CDCl_3$ provide more information about the fate of the TOPO ligand on the particle surface when the particles were exposed to the PyTU. According to literature,[26] high-resolution ^{31}P NMR measurements of TOPO-capped CdSe quantum dots in solution usually exhibit several broad signals associated with the bound TOPO ligand. The complexity of the NMR signal suggests that a variety of phosphorus chemical environments are available to TOPO ligands bound to the QD surface, which may include bound dimers of TOPO.[27] In the experiments on QDs in a $CDCl_3$ solution (*ca.* 5 mg mL^{-1}) in the absence of PyTU, no ^{31}P signals was observed, presumably because of the low concentration of the nanoparticles. However, after PyTU (40 mg) was added with ultrasonic irradiation for 5 min, a sharp ^{31}P signal appeared at 47.5 ppm, which corresponds to free TOPO ligand in $CDCl_3$.[26] This result emphasizes the fact that ligand replacement occurred.

Detection of iodide

The FL emission of PyTU–CdSe QDs turned out to be highly sensitive to the presence of iodide ions. The changes in FL intensity of PyTU–CdSe QDs upon addition of a particular anion are shown in Fig. 4, and the fluorescence ratio $(I_0 - I)/I_0$ is displayed in Fig. 5. As can be seen from Fig. 4 and 5, it is clear that there was marked quenching upon addition of iodide, and no significant effect was observed in presence of F^-, Cl^-, Br^-, I^-, SCN^-, $HCOO^-$, CH_3COO^-, HSO_3^-, and $C_2O_4^{2-}$.

Fig. 6 shows the effect of increasing concentration of iodide on the FL emission of PyTU–CdSe QDs. As can be seen, the QDs fluorescence emission was progressively quenched by addition of iodide. Also, a slight blue-shift could be observed. Results found here could also suggest some possible quenching mechanisms of the luminescence of QDs by iodide: first, the interaction of the iodide with the functional groups of the QDs modified surface would bring about a disruption by iodide of the hydrogen bonds between the PyTU groups of the surface-modified CdSe QDs. This would result in a destabilisation of the QDs in solution, with a modification of their luminescence. Also, as a result of the very high surface-to-volume ratio of these nanoparticles, iodide adsorption on this large surface could be expected. The similar phenomena that the adsorption of negatively charged cyanide on the surface of films of CdSe quantum dots resulted in an increased electron localization due to compression of the electron

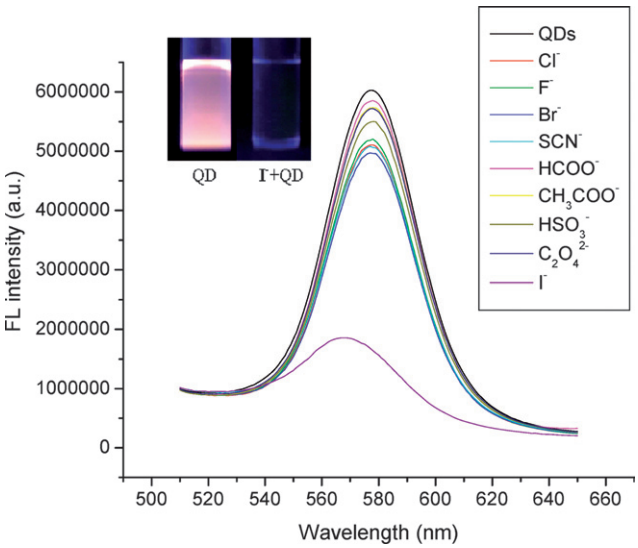


Fig. 4 Fluorescence spectra change of PyTU QDs upon addition of potassium salts (5×10^{-5} M) with excitation at 450 nm. The inset shows the fluorescence image of PyTU QDs, and PyTU QDs with iodide, which were taken under the illumination of a UV light (365 nm). Typically, 2 mL of various potassium salt–ethanol solutions were added to 0.5 mL of PyTU QDs solution (chloroform and ethanol, v : v = 4 : 1), and then the solution was mixed well for 10 min and tested.

wave function in the dots and therefore an increase of the size quantization (size-dependent increase in band gap) of the QDs was reported.[28] This is a possible mechanism to account for the observed quenching of luminescence emission by iodide. It was found that iodide quenches the fluorescence of PyTU–CdSe QDs with a concentration dependence that is best described by a Stern–Volmer type equation:

$$I_0/I = 1 + K_{SV}[S]$$

The dependence of I_0/I on $[S]$, where $[S]$ is the iodide concentration and I is the FL intensity of PyTU–CdSe QDs at given iodide concentrations, is shown in Fig. 6, inset. A good linear relationship ($R = 0.9982$) was found between the relative FL

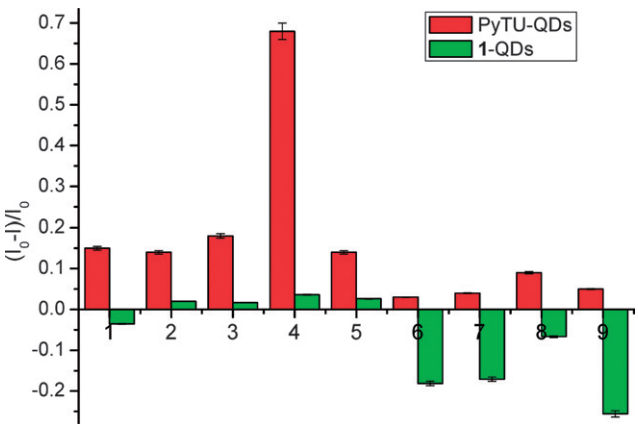


Fig. 5 Fluorescence ratio $(I_0 - I)/I_0$ of PyTU–CdSe QDs and **1**-modified CdSe QDs upon addition of 5×10^{-5} M relevant anions (from 1 to 9: F^-, Cl^-, Br^-, I^-, SCN^-, $HCOO^-$, CH_3COO^-, HSO_3^-, $C_2O_4^{2-}$).

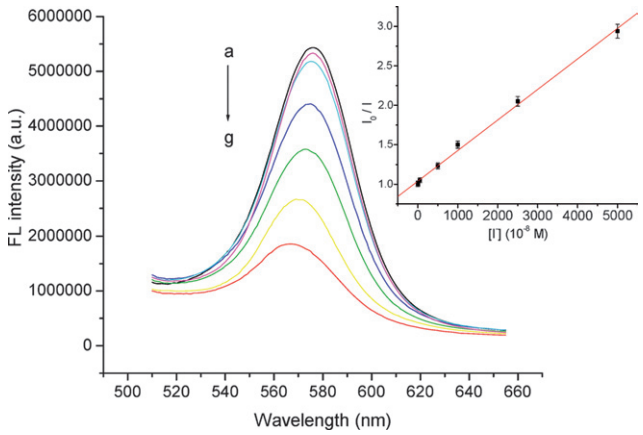
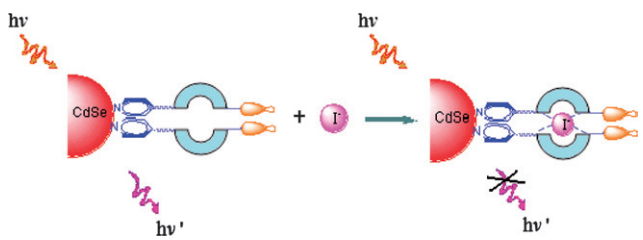


Fig. 6 The effect of increasing concentrations of iodide on the FL intensity of PyTU–CdSe QDs (from a to g: 0, 5×10^{-8}, 5×10^{-7}, 5×10^{-6}, 1×10^{-5}, 2.5×10^{-5}, 5×10^{-5} M). The inset shows a Stern–Volmer plot of the iodide concentration dependence of the FL intensity of PyTU–CdSe QDs with a 0.9982 correlation coefficient. Typically, 2 mL of various concentrations of iodide–ethanol was added to 0.5 mL of PyTU–CdSe QDs solution (chloroform and ethanol, v : v = 4 : 1), and then the solution was mixed well for 10 min and tested.

intensity and the concentration of iodide in the range 0–50 μM. The quenching constant K_{SV} is found to be 3.9×10^4 M^{-1}. The detection limit, calculated following the 3σ IUPAC criteria, is lowered to 1.5×10^{-9} M (0.19 μg L^{-1}).

The preference for iodide suggests that the cavity formed by C═O···H–N and C═S···H–N of PyTUs on the surface of QDs is more complementary to the sizes of the iodide ion than to the size of other anions. In general, halide anions tend to associate with receptors according to their basicity[29] (*i.e.*, in the order $F^- > Cl^- > Br^- > I^-$). However, many examples of size discrimination of halides due to the size of receptor binding site have been reported.[30] As anions have diverse geometries, complementarity between the receptor and anion is crucial in determining selectivity.[31] The complementarity between the receptor and halides is mostly achieved by the size of the receptor binding site due to the spherical shape of halides. We propose that the cavity in a PyTU–CdSe QD fits well with the size of an iodide ion, thus, iodide has a greater effect on the fluorescence emission of PyTU–CdSe QDs (Scheme 2).

To further elucidate the roles of the binding sites of PyTU in iodide recognition, we have carried out control experiments, which applied compound **1**-modified QD systems for anion recognition studies (the detailed synthetic procedure and characterization of **1**-modified QDs is given in the ESI†). No significant changes in the fluorescence intensity were observed in the typical experiment (shown in Fig. 5), indicating that there is little interaction between **1**-modified CdSe QDs and iodide. The result clearly indicates that the thiourea group and carbonyl group of PyTU play important roles for iodide recognition.



Scheme 2 Schematic diagram of the binding interaction between PyTU–CdSe QDs and iodide ions.

Conclusions

Studies to obtain functionalized nanoparticles of CdSe semiconductor QDs have been carried out. The novel PyTU ligand was designed and synthesized. PyTU and CdSe quantum dots have been successfully combined to develop a novel and highly sensitive luminescence nanoprobe for optical recognition of iodide. Quenching of the luminescence emitted by the synthesized nanoparticles allows the detection of iodide concentrations as low as 1.5×10^{-9} M, thus affording a very sensitive detection system for this chemical species. A disadvantage of the synthesized QDs, however, is that they are insoluble in water, a clear limitation for environmental applications. However, the possibility of modifying the chemistry of the core–shell system in the QDs, by adding different water-soluble organic ligands, is already in progress in our laboratory. In any case, the synthesized surface-functionalized nanoparticles have considerable potential as optical nanoprobes and are opening new applications as colorimetric probes, which allows a rapid quantitative assay of iodide. Such optosensing strategies are in progress in our laboratory and could eventually allow the development of highly sensitive and selective optosensors for other analyte determinations based either on fluorescence intensity or on colorimetric shift induced by the analyte on the surface-modified QDs.

Acknowledgements

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