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Highly sensitive detection of 2,4,6-trinitrophenol (TNP) based on the lysozyme capped CdS quantum dots

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Abstract

This work presented a novel method for nitroaromatic compounds detection by using lysozyme-capped CdS quantum dots (Lys-CdS QDs). Cd^{2+} could react with S^{2-} to generate fluorescent CdS QDs in the presence of lysozyme. The Lys-CdS QDs could bind 2,4,6-trinitrophenol (TNP) in water via the acid-base pairing interaction between electron-rich amino ligands and electron-deficient aromatic rings. Electrons of the QDs transfer to the TNP molecules lead to the fluorescence quenching. The fluorescence decreases with the increase of TNP concentration and the fluorescence intensity is negatively proportional to the TNP concentration in the range from 0.5 μmol/L to 15 μmol/L with the detection limit of 0.1 μmol/L. The newly-developed fluorescence probe shows an excellent resistant to interference of metal ions such as Cu^{2+}, Fe^{3+}, and Pb^{2+} when compared with other fluorescence probes. The present method was cost-effective, convenient, and does not require any complicated synthetic procedures.

Key words: Nitroaromatic compounds; 2,4,6-trinitrophenol; fluorescence detection; CdS quantum dots

1. Introduction

Nitroaromatic compounds are produced in large scale in the chemical industry. They are used in the manufacture of pesticides, dyes, pharmaceuticals and raw materials in explosives preparations. They present a high toxicity and have been proved to be potential carcinogens or mutagens.[1,2] Among different nitroaromatic compounds, 2,4,6-trinitrophenol (TNP) is the most common and powerful explosive, as well as being capable of explosion without any triggers.[3] Due to its higher water solubility, it contaminates groundwater and causes irritants in the skin, eyes and respiratory system.[4,5] Due to its contamination on environment and the risk of human health, selective and ultra-sensitive detection of TNP has attracted increasing attentions.

A wide variety of materials and strategies for detecting nitroaromatic compounds have been developed. Among them, fluorescence-quenching of materials is an effective and intriguing method for the determination of nitroaromatic compounds. To date, considerable effort has been devoted to the development of fluorescence-sensing materials to detect nitroaromatic compounds. The most popular fluorescence-sensing materials are conjugated polymers and luminescent dyes, such as fluoranthene,[6] poly(acrylic acid)-poly(pyrene methanol) (PAA-PM)[7] and poly(*p*-phenyleneethynylene)s (PPEs),[8] which could sense the electron deficient nitroaromatics in solution via directional bonding. Venkatramaiah et al. have prepared a novel fluoranthene based fluorescent chemosensor for the detection of picric acid.[6] Niamnont et al. have successfully prepared a series of triphenylamine-based fluorophores, which show variable fluorescence quenching sensitivity toward nitroaromatic compounds and are useful for identifying different nitroaromatic compounds.[9] Olley et al. have investigated a series of branched fluorescent chromophores for the detection of nitroaromatic compounds in solution via a collisional process.[10] The sensitivity of this method based on these materials is satisfying. However, these materials rely mainly on complicated synthesis and usually are hydrophobic, which make the assay procedure time-consuming and complex.

Recently, quantum dots has been widely used as fluorescent materials for the analysis of biological molecules and environmental contaminants, because of their novel optical properties and sensitive response to these analytes. Liu et al. designed a near-infrared fluorescence probe for the determination of TNP based on bovine serum albumin (BSA) coated $CuInS_2$ QDs.[11] Wang et al. prepared MoS_2 QDs by using cysteine as precursors to detect TNP based on fluorescence

quenching of MoS_2 QDs.[12] Chen et al reported a sensitive method for TNT detection by using water-soluble L-cysteine-capped CdTe QDs as the fluorescence probe via forming Meisenheimer complexes between TNT and cysteine. Cysteine is used both as the stabilizer of the QDs and the primary amine provider.[13] However, most QDs involved are pre-synthesized QDs, which need to be synthesized ahead of time and complicated synthetic procedure. The assay systems are frequently limited by high background signals caused by nonspecific adsorption of decorated QDs on surfaces or poor quenching of donor couples.[14]

The operating mechanism of our assay system was represented in Scheme 1. In this work, the fluorescent CdS QDs could be generated in the presence of Cd^{2+} and S^{2-} with lysozyme as stabilizers. The lysozyme was employed to render the CdS QDs stable against aggregation and water-soluble. As well-known that, the fluorescence properties of QDs had a close connection to the composition of surface capped layers. Abundant amino groups existed on lysozyme and could effectively bind TNP via forming Meisenheimer complexes between electron-rich amino groups of lysome and electron-deficient nitroaromatic rings.[15,16] TNP bound to the surface of lysozyme can lead to the fluorescence quenching through the electron transfer from the conductive band of CdS QDs to the lowest unoccupied molecular orbital of TNP.[17,18] The new generation of CdS QDs in situ could avoid some drawbacks of presynthesized QDs in relevant analytical systems by decreasing the background signal. Thus, we develop a novel fluorescence probe for rapid and highly sensitive detection of explosive TNP molecules.

2. Experimental

2.1 Materials

All reagents were of at least analytical grade. The water used in all experiments had a resistivity higher than 18 MΩ cm^{-1}. Cadmium (II) chloride ($CdCl_2$), sodium hydroxide (NaOH), Sodiumsulfide nonahydrate ($Na_2S•9H_2O$), trihydroxymethyl aminomethane (Tris) and hydrochloric acid were purchased from Shanghai Qingxi Technology Co., Ltd. Phenol, TNP, dinitrotoluene (DNT), 4-nitrophenol (4-NP) and 2-nitrophenol (2-NP) were purchased from Sigma-Aldrich Corporation. Lysozyme was purchased from Dingguo Corporation. The 0.1 mol/L Tris-HCl buffered solution (pH 9.0) was used as the medium for detection process.

2.2 Apparatus

The fluorescence spectra were obtained by using a Shimadzu RF-5301 PC spectrofluorophotometer equipped with a xenon lamp using right-angle geometry. UV-vis absorption spectra were obtained by a Varian GBC Cintra 10e UV-vis spectrometer. In both experiments, a 1 cm path-length quartz cuvette was used. FT-IR spectra were recorded with a Bruker IFS66V FT-IR spectrometer equipped with a DGTS detector. All pH measurements were made with a PHS-3C pH meter (Tuopu Co., Hangzhou, China). Transmission electron microscopy (TEM) experiments were performed on a Philips Tecnai F20 TEM operating at 200 KV acceleration voltage. The fluorescence lifetime and the quantum yield were obtained using FLS 920 Fluorescence spectrometer.

2.3 Preparation of Lys-CdS QDs

Lys-CdS QDs were synthesized in aqueous solution. 300 μL 5 mmol/L lysozyme solution, 120 μL 50 mmol/L $CdCl_2$ solution and 150 μL 0.1 mol/L Tris-HCl buffer (pH 9.0) were added into 2 mL calibrated test tube, and shaken thoroughly for 10 minutes. After that, 90 μL 30 mmol/L Na_2S solution was added into the test tube and diluted to 1500 μL with deionized water followed by the thoroughly shaking and equilibrated for 20 minutes. 100μL Lys-CdS QDs was diluted to 1500 μL with deionized water. The fluorescence spectra were recorded from 405 nm to 650 nm with the excitation wavelength of 340 nm. The slit widths of excitation and emission were both 10 nm.

2.4 The detection process

The Lys-CdS QDs solution (100 μL), 0.1mol/L Tris-HCl buffer (pH 9.0, 150μL), and different amount of TNP or other aromatic compounds (DNT, 4-NP, 2-NP) and phenol were successively added into a 2.0 mL calibrated test tube. Then, the solution was diluted to 1500 μL with deionized water followed by the thoroughly shaking and equilibrated for 3 min until the solution was fully mixed. The fluorescence spectra were recorded from 405 nm to 650 nm with the excitation wavelength of 340 nm. The slit widths of excitation and emission were both 10 nm. The fluorescence (FL) intensity of the maximum emission peak was used for the quantitative analysis of the target molecules.

3. Results and discussions

3.1.Spectral characterization of Lys-CdS QDs

As shown in Fig. 1, there was an increased absorption below 400 nm and a shoulder around 365 nm that was the result of $1S_h$–$1S_e$ excitonic transition characteristic of CdS QDs.[19] The fluorescence emission spectra of the Lys-CdS QDs showed a fluorescent peak with maximum emission wavelength of 533 nm which arised from excitonic emission of CdS QDs.[20,21] Furthermore, the size and shape of the synthesized Lys-CdS QDs was studied by TEM and shown in Fig. 2. It could be seen that the synthesized particles are nearly spherical and the average size of the Lys-CdS QDs varies from 4 to 7 nm.[22,23,24]

The interaction between CdS QDs and lysozyme molecules are mainly through interaction between surface Cd^{2+} ions and lysozyme. If there is no lysozyme molecule as stabilizers in the assay system, Cd^{2+} and S^{2-} would generate some yellow precipitation, and a fluorescence signal of CdS QDs is hardly observed. The FT-IR spectra of the CdS crystals with and without lysozyme as stabilizers were compared to confirm the coordination of the lysozyme on the surface of the CdS QDs. As shown in the Fig. S1 curve b, the majority of lysozyme functional groups could be clearly found through the stretching vibration of N-H (3330cm^{-1}), the amide I band (1660cm^{-1}), amide II (1530cm^{-1}) band and amide III (1400-1200cm^{-1}) for –CONH group.[22] which were the characteristic peak of lysozyme of Lys-CdS QDs.[25] And these characteristic peaks were not observed in the FT-IR spectra of uncapped CdS crystals (Fig.S1 curve a) which indicated the successful capping of lysozyme on the surface of the CdS QDs.

3.2 The effect of pH value and incubation time

To optimize the TNP detection conditions, pH value and reaction time were further examined. We systematically investigated the influence of pH value on the fluorescence intensity of Lys-CdS QDs and TNP-Lys-CdS system. As shown in Fig. 3, It could be seen that when the pH value changed from 6.6 to 9.0, the fluorescence intensity of Lys-CdS QDs solution and TNP-Lys-CdS system both increased gradually, and the fluorescence intensity ratio F_0/F (F_0 and F were the fluorescence intensity of Lys-CdS QDs in the absence and presence of 10 μmol/L TNP) at pH 9.0 reached the maximum value. The effect of incubation time was also studied, Fig. S2 showed the temporal evolution of the fluorescence intensity of Lys-CdS QDs solution after the addition of 2.5 μmol/L TNP. It could be seen that the fluorescence intensity of Lys-CdS QDs rapidly decreased after the addition of TNP, and reached equilibrium in 3 minutes. Therefore, pH 9.0 and reaction time of 3 minutes were selected for the further detection process.

3.3 The interactions between TNP and Lys-CdS QDs

A linear Stern-Volmer relationship may be observed if either a static or dynamic quenching process is dominant. The fluorescence lifetime measurements could help us to distinguish between static and dynamic process. With static quenching, the fluorescence decay lifetime of a material will remain unchanged as the concentration of analyte is increased. However, dynamic quenching provides an additional relaxation pathway for the excited molecules and therefore results in a decrease in the average fluorescence lifetime.[26, 27] Fig. 4 showed the fluorescence decay curves of Lys-CdS QDs in the absence and presence of TNP and the related data was given in table 1. The decay curves of Lys-CdS QDs with and without TNP fitted well to triexponential function.[28, 29] The average lifetime of Lys-CdS QDs was 72.41 ns. After the introducing of TNP to the Lys-CdS QDs, the average lifetime reduced from 72.41 to 57.75, indicating the dynamic quenching process was dominant for the quenching mechanism. TNP is a typically electron-deficient compound due to the strong electron-withdrawing effect of the three nitro groups.[30] The organic amino ligands modified nanocrystals utilized as the receptors of nitroaromatic compounds have been mentioned in some previous reports.[12,17,31] In the case of Lys-CdS QDs, the electron-rich lysozyme can absorb the electron-deficient TNP to the surface of Lys-CdS QDs through formation of TNP-Lysozyme Meisenheimer complexes. And the electron transfer from amino groups of Lys-CdS QDs to TNP leads to the dynamic fluorescence quenching of Lys-CdS QDs.[32] The fluorescence quantum yield of Lys-CdS QDs was 28.98%.

Fig. 5 showed the evolution of fluorescence spectra of Lys-CdS QDs with increasing TNP concentration. It could be seen that the fluorescence intensity of Lys-CdS QDs obviously decreased with TNP concentration increasing from 0 to 30 μmol/L. Furthermore, inset in Fig. 5 showed that there was a good linear relationship between the fluorescence intensity ratio F_0/F (F_0 and F were the fluorescence intensity of Lys-CdS QDs before and after the addition of TNP) and the TNP concentration in the range from 0.5 μmol/L to 15 μmol/L. The regression equation was

$$F_0/F=0.91222+0.32996[TNP],\ \mu mol/L$$

The correlation coefficient were $R^2=0.999$, and the detection limit for TNP was 0.1 μmol/L, calculated following the 3σ IUPAC criteria. A comparison between the proposed method and some other techniques for TNP detection in LOD and linear range were summed up in Table S1.[33,34,12,35,36] Compared with conventional methods, our present method offered a

comparable detection limit and linear range. We established a novel method for TNP detection based on dynamic quenching of the Lys-CdS QDs. Our method could significantly reduce time and costs related with TNP assay.

3.4 The interactions between TNP, DNT, 4-NP, 2-NP or phenol and Lys-CdS QDs

To check the selectivity of Lys-CdS QDs toward TNP, we had also performed this fluorescence quenching experiment with other compounds such as DNT, 4-NP, 2-NP and phenol. The structure, full name and abbreviation of the analytes were shown in Fig. S3. Compared to the fluorescence intensity of blank (F_0), four nitroaromatic explosives and phenol showed obviously different quenching behaviors for Lys-CdS QDs. As shown in Fig. 6A, the fluorescence quenching was in the order of TNP > DNT > 4-NP > 2-NP> Phenol, that was related to the number of nitro groups in the corresponding aromatic ring and whether or not existing the intarmolecular hydrogen bond. Both 4-NP and 2-NP molecules had two nitro groups. However, 4-NP had stronger quenching ability to Lys-CdS QDs than 2-NP. 2-NP was prone to form the intarmolecular hydrogen bond between the hydroxyl and nitro group, which would weaken the electron-withdrawing ability of nitro group.

The Stern–Volmer plot was used to evaluate the relative affinities of Lys-CdS QDs to nitroaromatic compounds and Phenol [4]. F_0 and F are fluorescence intensity before and after addition of nitroaromatic compounds or phenol. *K*sv is the Stern-Volmer constant (M^{-1}) and [A] is the molar concentration of analytes added.[10, 37]

$$(F_0/F) - 1 = Ksv\,[A]$$

As shown in Fig. 6B, the linear Stern–Volmer relationships were observed for TNP, DNT, 4-NP, 2-NP and Phenol in concentration range of 0.5–15 μM, respectively. The *K*sv value for Lys-CdS QDs fluorescence quenching with TNP, DNT, 4-NP, 2-NP and phenol are 32880, 12320, 5000, 1980 and 158 M^{-1}, respectively. The affinity between Lys-CdS QDs and the nitroaromatic compounds corresponding to K_{SV} follows the order of TNP > DNT > 4-NP > 2-NP > Phenol. It is observed that K_{SV} values for TNP are quite larger than those for other nitroaromatic compounds and phenol, suggesting very predominant selectivity of TNP from others. The fluorescence dynamic quenching process mainly results in photoinduced electron transfer (PET) mechanisms. During the PET mechanism, electrons are first excited from the HOMO energy levels of Lys-CdS QDs to its LUMO energy levels and then transferred to the LUMO energy levels of electron-deficient nitroaromatic compounds causing fluorescence quenching. The energy gap between the LUMOs of donor fluorophore

(Lys-CdS QDs) and acceptor nitroaromatic compounds is the main driving force for this transition.[38,39] TNP has the lowest LUMO energy level,[4] which make the high selectivity of Lys-CdS QDs toward TNP.

3.5 Interference study

In this work, we studied the effect of a series of foreign metal ions and organic molecules on the fluorescence of Lys-CdS QDs before and after adding 2.5 μM TNP. From Fig. 7, it could be seen that the fluorescence intensity of Lys-CdS QDs and TNP-Lys-CdS QDs system both showed the high tolerance to most common metal ions and organic molecules. The fluorescence intensity of Lys-CdS QDs decreased dramatically with 2.5 μM TNP and kept stable even in the presence of 25 μmol/L heavy metal ions such as Cu^{2+}, Fe^{3+}, Pb^{2+}. These results indicated that the lysozyme layers prevented these metal ions being adsorbed on the surface of CdS QDs. And other common organic molecules such as hydroquinon, tartaric acid, pyridine also could not induce the fluorescence quenching of Lys-CdS QDs under the same conditions. Therefore, this method has high selectivity and excellent resistance to interferences.

3.6 Analytical applications

To further investigate the potential practical applications of this method, the detection of TNP in tap and spring water samples were carried out. The water samples were filtered several times through qualitative filter paper. The results showed that TNP was not detected in the above samples, so the results obtained by standard addition method were listed in Table 1. From Table 2, we could see that the RSD was lower than 3.8%, and the average recoveries of TNP in the real samples was in the range of 98–110%, indicating that this method has potential in environmental applications for TNP detection.

4. Conclusion

In summary, we have successfully utilized the lysozyme as the stabilizer to prepare the Lys-CdS QDs for the detection of TNP. The fluorescence of Lys-CdS QDs was quenched by TNP through the dynamic quenching mechanism. This method is highly sensitive to detect TNP down to 0.1μM, and selective to TNP over other nitroaromatic compounds (TNP, DNT, 4-NP and 2-NP), which is dependent on their electron-accepting ability. The proposed method was simple, convenient and had more resistant to the interference of heavy metal ions and other organic molecules. The one-pot synthesized aptamer-functionalized CdS QDs have been developed as a new class of fluorophores that could be applied for the detection

of various analytes based on different signal-transducing mechanisms.

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Captions:

Scheme 1 The schematic illustration of the novel Lys-CdS QDs probe for the detection of TNP

Fig. 1 The UV-Vis absorption (Dash line) and fluorescence emission spectra (Solid line) of the Lys-CdS QDs

Fig. 2 TEM image of Lys-CdS QDs (0.29 mg/L)

Fig. 3 Fluorescence intensity of Lys-CdS QDs (1.45 mg/L) assay system without TNP (curve a) and with 10 μmol/L TNP (curve b) in different pH environments (pH 6.6-9.0).

Fig. 4 Black curves were fluorescence decay curve of (1) Lys-CdS QDs and (2) Lys-CdS QDs after the addition of TNP, respectively. The excitation wavelength was tuned to 360 nm. Fluorescence emission was collected at 535 nm. Green curves were the Decay fit of (1) Lys-CdS QDs and (2) Lys-CdS QDs after the addition of TNP, respectively. The concentration of Lys-CdS QDs and TNP were 1.45 mg/L and 1 μmol/L, respectively.

Fig. 5 The fluorescence spectra of Lys-CdS QDs (1.45 mg/L) upon the addition of different concentrations of TNP in the range from 0 to 30 μmol/L (0, 0.5, 1.0, 2.0, 5.0, 7.5, 10, 15, 20 and 30 μmol/L). Inset: Stern–Volmer plots of Lys-CdS QDs at 533nm in the present of TNP. 10 mmol/L pH 9.0 Tris-HCl buffer solution incubation for 3 minutes.

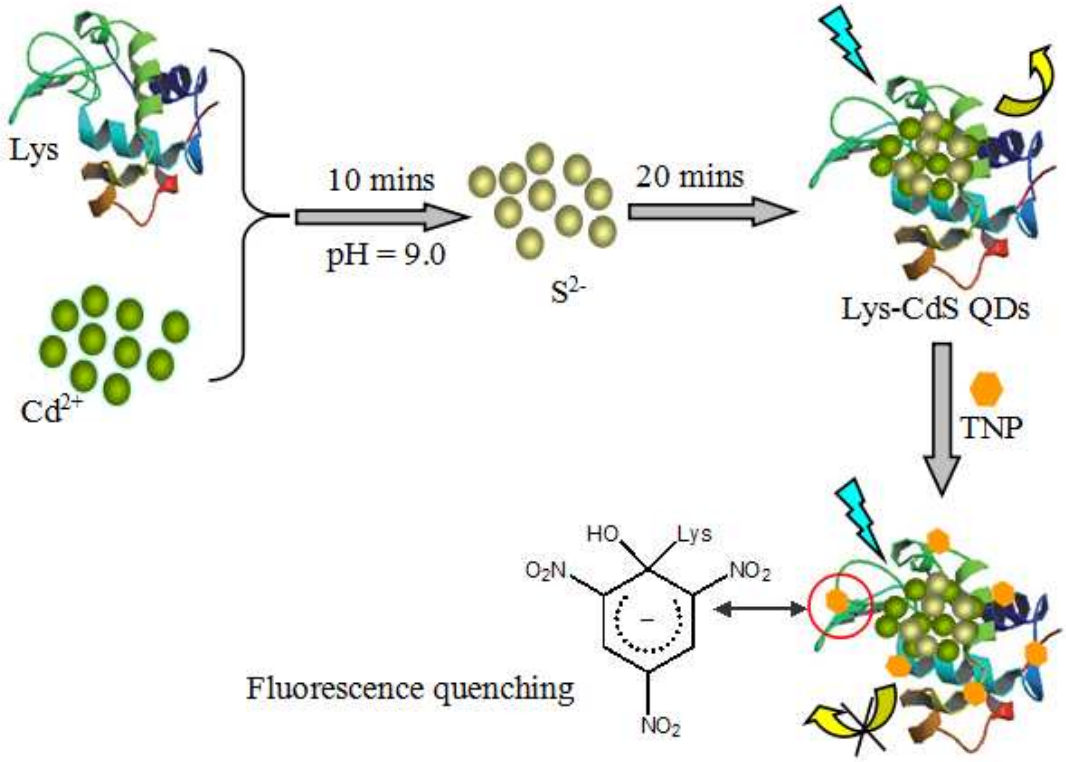
Fig. 6A The fluorescence quenching ratios F/F_0 of Lys-CdS QDs (1.45 mg/L) after the addition of 12.5 μmol/L TNP, DNT, 4-NP, 2-NP and phenol. F_0 and F were the fluorescence intensity of Lys-CdS QDs before and after the addition of 12.5μmol/L nitroaromatic compounds and phenol, respectively. **Fig. 6B** Stern-Volmer plots of Lys-capped CdS QDs with the increasing concentration of TNP, DNT, 4-NP, 2-NP and phenol. 10 mmol/L Tris-HCl buffer solution incubation for 3 minutes.

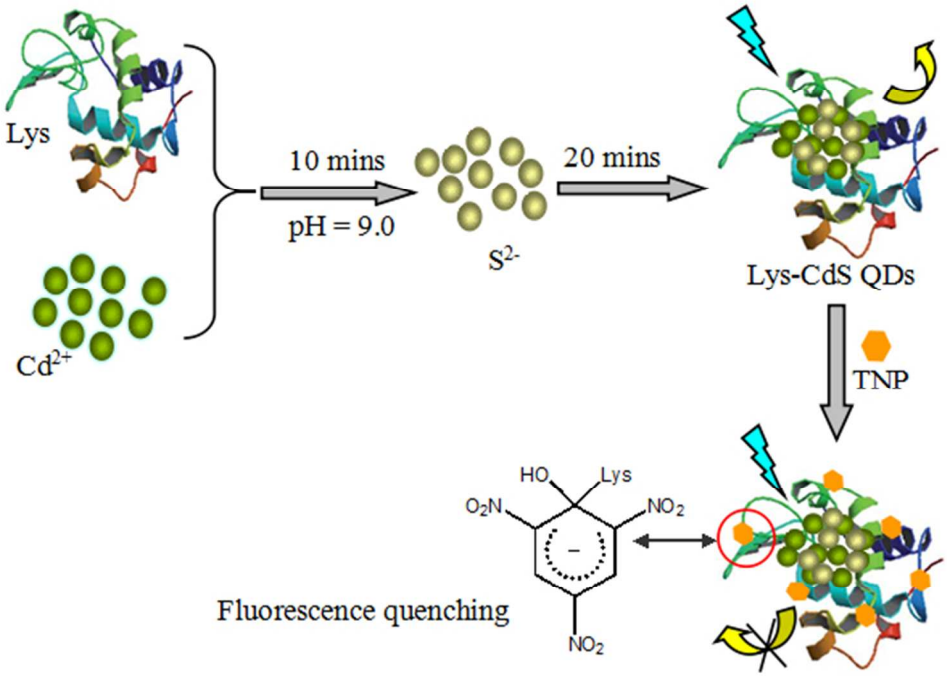
Fig. 7 The fluorescence intensity of Lys-CdS QDs (1.45 mg/L) before and after adding 2.5 μmol/L TNP in the presence of 25 μmol/L metal cations and other organic molecules. (1)blank (2)K^+ (3)Ca^{2+} (4)Na^+ (5)Mg^{2+} (6)Ba^{2+} (7)Fe^{3+} (8)Zn^{2+} (9)Cu^{2+} (10)Pb^{2+} (11)sodiumcitrate (12) tartaric acid (13) resorcinol (14) hydroquinone (15) dimethylformamide (16) acetonitrile (17) pyridine (18) furan and (19) acetic acid. 10 mmol/L pH 9.0 Tris-HCl buffer solution incubation for 3 minutes.

Table1 Fitting Parameters of the Lys-CdS QDs and Lys-CdS QDs/TNP

Table2 Results of TNP determination in real water samples

Graphic Abstract





Scheme 1
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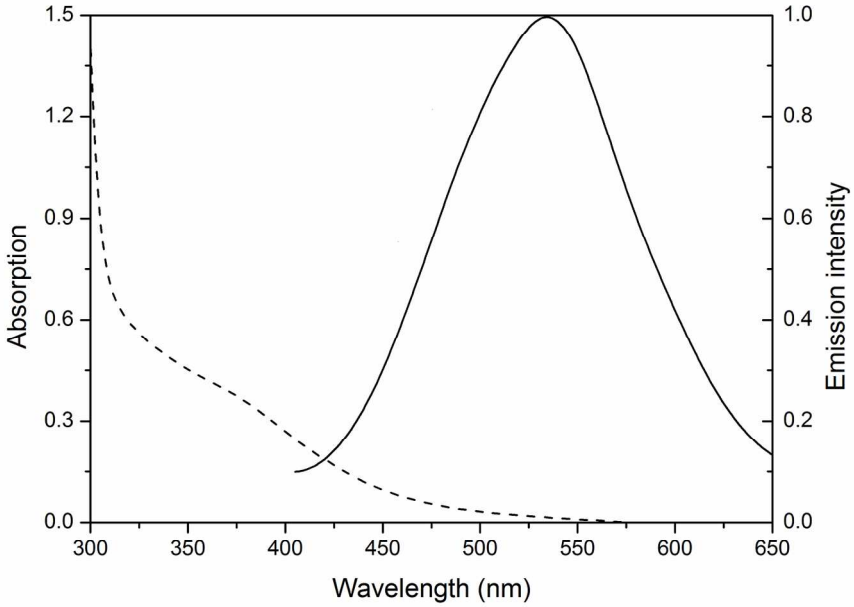

Fig. 1
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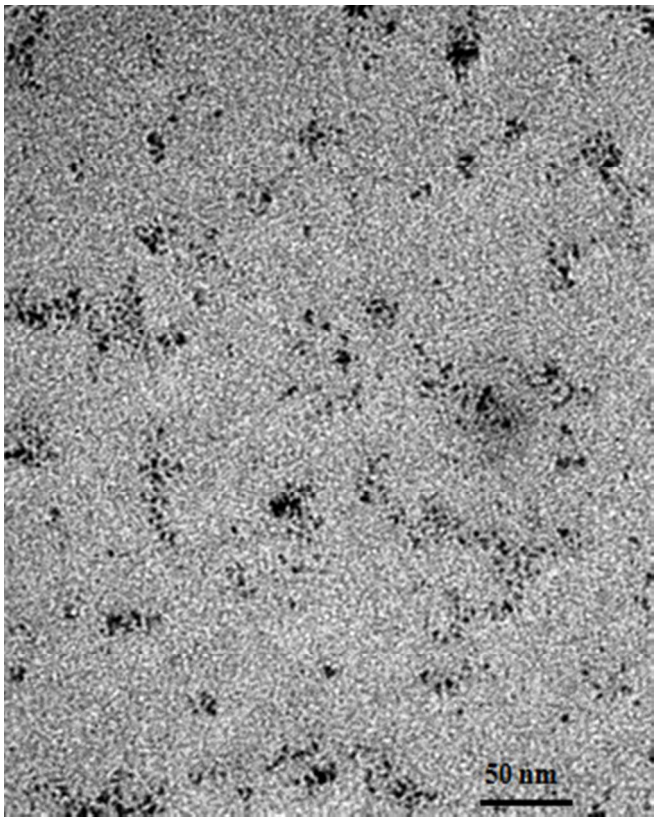

Fig. 2
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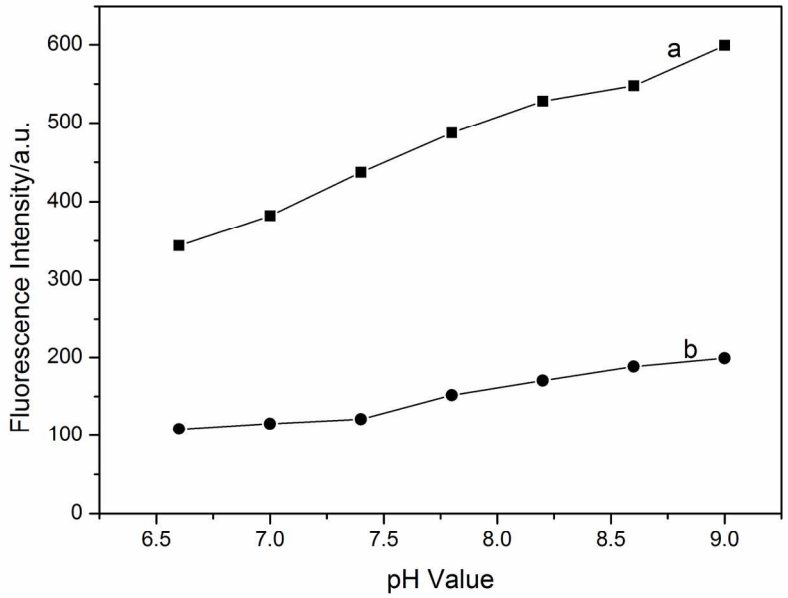

Fig. 3
148x104mm (300 x 300 DPI)

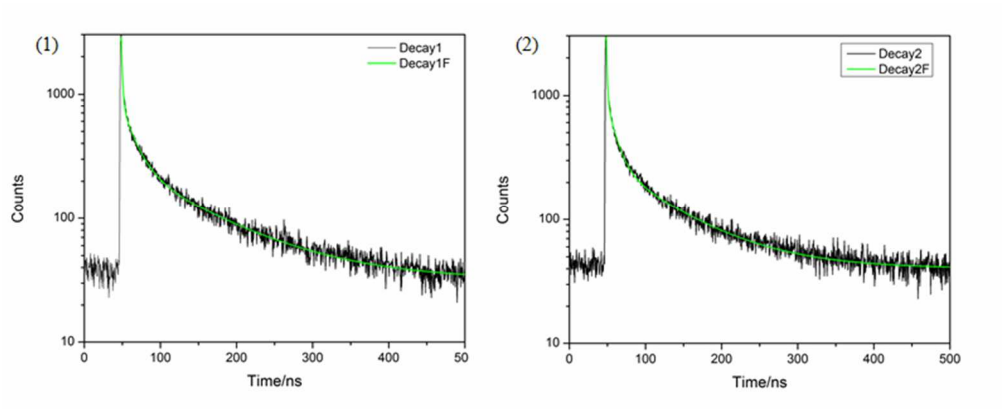

Fig. 4
210x85mm (96 x 96 DPI)

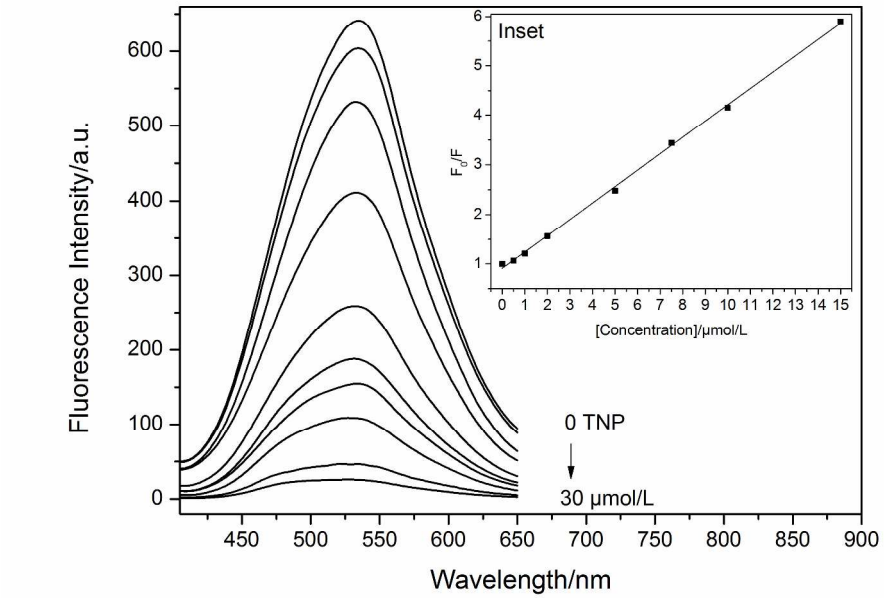

Fig. 5
296x209mm (300 x 300 DPI)

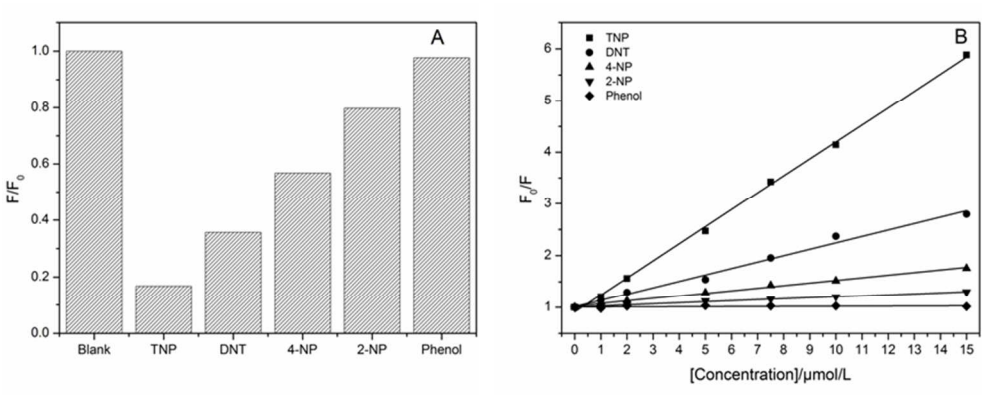

Fig. 6
230x90mm (96 x 96 DPI)

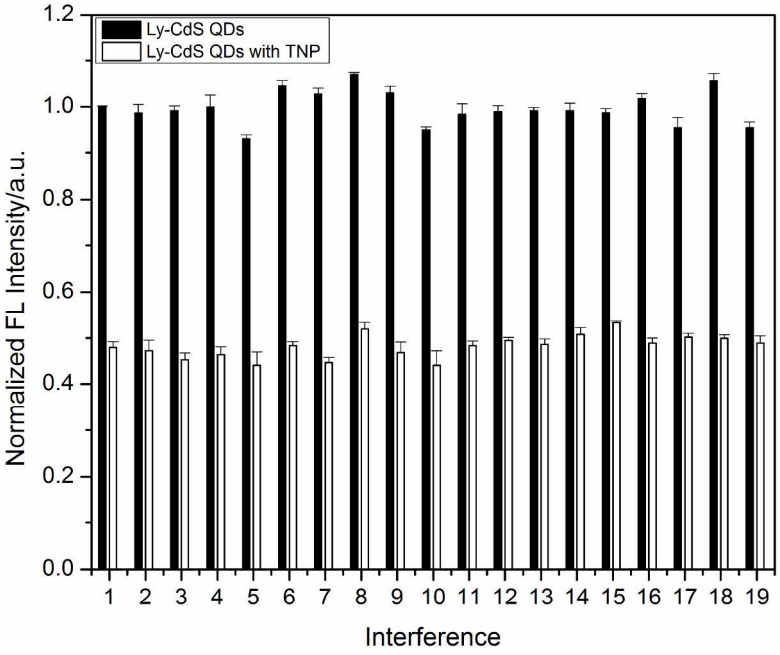

Fig. 7
279x215mm (300 x 300 DPI)

Table 1

Samples	α_1	α_2	α_3	τ_1	τ_2	τ_3	τ_{AV}
Lyz-CdS QDs	10.85	24.75	64.40	1.59	16.86	105.69	72.41
Lyz-CdS QDs/TNP	11.11	24.08	64.81	1.21	11.53	84.62	57.75

τ = lifetime in nanoseconds

τ_{av} = Average lifetime in nanoseconds

α= amplitude

Table 2

Samples	Added (μmol/L)	Founded (μmol/L)	Recovery (%)	RSD (n=3) (%)
Tap water	0.5	0.52	104	3.3
	2	2.20	110	3.8
Spring water	0.5	0.49	98	2.7
	2	2.01	101	2.6