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Highly Sensitive "Turn-on" Fluorescence Probe for the Detection of Sparfloxacin in Human Serum using Silica-functionalized CdTe Quantum Dots

Dan Li, [*a] *Shaojie Jia,* [a] *Essy Kouadio Fodjo,* [b] *Hu Xu,* [a] *Cong Kong,* [c] *and Yuhong Wang* [a]

[a] Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, P. R. CHINA

[b] Laboratory of Physical Chemistry, University Felix Houphouet Boigny, 22 BP 582 Abidjan 22, Cote d'Ivoire

[c] East China Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences

* Corresponding author phone/fax: +86-21-60873241; E-mail: dany@sit.edu.cn

ABSTRACT In this study, an environment-friendly hydrothermal synthesis of hydrophilic silica-functionalized CdTe quantum dots (SQDs) has been developed by treatment of tetraethyl orthosilicate (TEOS) in the presence of CdTe QDs. The proposed SQDs show favorable photoluminescence (PL) at the peak wavelength of 620 nm with a quantum yield of approximately 32%, and exhibit excellent selectivity and sensitivity toward Sparfloxacin (SPFX) in the range from 0.05×10^{-6} to 200×10^{-6} mol L^{-1}. The detection limit of SPFX is as low as 0.035×10^{-6} mol L^{-1}. The results show that the remarkably enhanced PL intensity of SQDs can be attributed to the hydrogen-bond interactions between the SQDs and SPFX. Furthermore, the amount of SPFX in the human serum samples detected by the present method and HPLC are in good agreement, indicating that the proposed SQDs can be served as a powerful tool for biological analysis.

Keywords Quantum dots • Human serum sample • Fluorescence • Detection • Sparfloxacin

Introduction

Sparfloxacin (SPFX) has been widely used as veterinary and human medicine for the treatment of urinary and digestive infections. It is well known that SPFX can be used for treating Gram-positive and Gram-negative bacteria. [1-3] However, the sensitive and selective detection of SPFX in aqueous phases is of great importance because it can

cause significant impacts on environment and human health. Traditionally, most of the widely used SPFX assays are spectrophotometric methods, [4-8] electrochemistry, [9, 10] High Performance Liquid Chromatography (HPLC) [11-14] and LC-MS [15-17]. However, these methods suffer from intrinsic limitations in terms of complex and time-consuming. Hence, it is desirable to develop low-cost, convenient, highly sensitive and selective detection method for SPFX.

Due to the excellent photophysical properties, the quantum dots (QDs)-based fluorescence probe has attracted increasing attention and has been widely used for pharmaceutical analysis. [18-22] For example, the thioacetamide-capped CdS QDs has been explored as optical sensing nanomaterials for the detection of trace ciprofloxacin. [23] Thiol-capped CdSe QDs was used to determine edaravone based on the fluorescence quenching. [24] However, the common disadvantages among most of QDs are chemical instability and environmental toxicity. [25] Therefore, it is extremely important to develop low/non-toxic PL sensor with a simple process for highly selective and sensitive determination of SPFX in human serum. [26-30]

Herein, we propose a "turn-on" mechanism of silica-functionalized CdTe quantum dots (SQDs) for the determination of SPFX. The fabrication and sensing protocol of the SQDs probe are shown in Scheme 1. It is noteworthy that hydrothermal method enables the proposed SQDs to gain good biocompatibility, which is beneficial for the analysis of SPFX in biological media. For proposed SQDs, the PL intensity is gradually enhanced with the increase of SPFX concentrations. Under the optimal conditions, the detection limit of SPFX is found to be around 0.035×10^{-6} mol L^{-1}, and the detection range was from 0.05×10^{-6} to 200×10^{-6} mol L^{-1} with a correlation coefficient of 0.9967. Moreover, the proposed SQDs have been used to detect SPFX in human serum samples. A series of experiments showed that the PL enhancing of SQDs could be attributed to the hydrogen bond interactions between the SQDs and SPFX. Compared with the current clinical HPLC method, the proposed SQDs-based PL sensor enable highly sensitive and selective analysis of SPFX in biological system.

Scheme 1

Experimental Section

Materials and Instrumentation

Sodium borohydride ($NaBH_4$, 99%), tellurium powder (200 mesh, 99.8%), cadmium chloride hemi (pentahydrate) ($CdCl_2$, 99%), 3-mercaptopropionic acid (MPA, 99%), 3-mercaptopropyl trimethoxysilane (MPS, 95%), tetraethyl orthosilicate (TEOS, 98%), 3-aminopropyl trimethoxysilane (APTES, 97%), diethyl malonate ($C_7H_{12}O_4$, 99%), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, 98.5%) and N-Hydroxysuccinimide

(NHS, 98%) were purchased from Sigma-Aldrich Chemical Co. (USA). Sodium chloride (NaCl, 99%), sodium hydroxide (NaOH, 96%), ammonia solution (NH_4OH, 30 wt%) and Sparfloxacin (SPFX, 99%) were purchased from Shanghai Chemical Reagent Company (Shanghai, China). All the chemicals used in this work were of analytical grade. Milli-Q ultrapure water (Millipore, ≥18 MΩ cm) was used throughout.

PL spectra were recorded on a RF-5301PC FL Spectrophotometer (Tokyo, Japan) equipped with a Xe lamp and a plotter unit and a 1cm quartz cell. UV-vis absorption spectroscopic was obtained on a UV-2100 spectrophotometer (Tokyo, Japan). The transmission electron microscopic (TEM) images of the SQDs were obtained from H-600 transmission electron microscope (Tokyo, Japan). Samples for TEM measurements were prepared by depositing a drop of colloidal solution on a copper grid coated with carbon film and dried at room temperature. All pH measurements were obtained using a pHS-25 pH meter (Shanghai, China). The SPFX in human serum samples were analyzed on HP Agilent 1100 series HPLC.

Synthesis of MPA-capped CdTe Quantum Dots (QDs)

The 3-mercaptopropionic acid (MPA)-capped CdTe quantum dots (QDs) was synthesized according to the procedure described previously with some slight modifications and stored at 4°C. [31] In a typical experiment, 0.4 mmol of $CdCl_2$ and 0.68 mmol MPA of solution were dissolved in 50 mL of distilled water. Then, the pH of the solution was adjusted to 11.5 by dropwise addition of 2.0 M NaOH solution under stirring. Afterwards, the solution was placed in a three-necked flask and N_2 was pumped into the system in order to replace air. Subsequently, 0.04 mmol of freshly prepared NaHTe solution was added into the Cd precursor solution under stirring. Then the reaction mixture was heated to 100 °C for 10 min under reflux and atmospheric conditions. The solution was then subject to dialysis utilizing a semi-permeable membrane to remove the impurities. After that, red solution should be obtained, implying the formation of MPA-capped QDs.

Synthesis of Carboxyl-capped CdTe@SiO_2 Quantum Dots (SQDs)

Photoluminescent (PL) SQDs were synthesized by sol-gel process as reported previously with some minor modifications. [32] Typically, 3 mL of 3-aminopropyl trimethoxysilane (APTES) was dissolved in 30 mL of ethanol. Subsequently, 1 mL MPA-capped QDs was added into the 3 mL APTES ethanol (10%) solution under stirring. Then, the solution was adjusted to pH 9.8 by dropwise with 0.5 M NaOH solution, and continuously stirring for 24 h at room temperature. The resultant APTES-capped QDs were separated from the solution by centrifugation (8,000 rpm) and resuspended in 20 mL of ethanol. Afterwards, 10 mL APTES-capped QDs was placed in a three-necked flask,

and then 30 μL ammonia solution and 5 μL TEOS was added successively to the system under continuous stirring. The solution was kept under stirring for 5 h and centrifuged at 6,000 rpm for 5 min. The appearance of pink floccules in the solution indicated that CdTe@SiO_2 QDs were obtained. After that, the APTES molecules on the CdTe@SiO_2 QDs were incubated with diethyl malonate by introducing carboxy groups onto the CdTe@SiO_2 QDs surfaces. In a typical procedure, 0.5 mL APTES-capped QDs was incubated in 3 mL diethyl malonate solution (10%) in presence of 0.20 M EDC/ 0.025M NHS for 2 h. The final obtained solution changed to a milky white color, indicating that carboxyl-capped CdTe@SiO_2 QDs (SQDs) was obtained. The resultant SQDs solution was centrifuged at 6,000 rpm for 5 min and resuspended in 20 mL of ethanol. The quantum yield (QY) of the SQDs was measured using quinine sulfate in a 0.1 M H_2SO_4 solution as standard (see the Electronic Supporting Materials).

Determination of SPFX

All PL measurements were repeated at least three times under the same conditions: The excitation wavelength was excited at 550 nm with both excitation and emission slits set at 5 nm. For the analysis of SPFX, 50 μL carboxyl-capped SQDs suspension in ethanol was added to 2.0 mL of phosphate buffer solution (PBS, 10 mmol L^{-1}, pH=7.5) in a 10×10 mm quartz cell. The PL spectrum was then recorded and the PL intensity was set as F_0. Then, 1 mL of SPFX stock solution with different concentrations was added to the proposed SQDs solution. The corresponding PL spectra were measured at different time intervals. It usually took about 3 min and the PL intensity was set as F. A series of F/F_0 values were obtained by varying the SPFX concentrations.

Determination of SPFX in Human Serum

100 μL of 100-fold diluted human blood serum was spiked with different concentrations of SPFX (10 μL). The spiked samples were then incubated with the carboxyl-capped SQDs for 30 min under atmospheric conditions. Afterward, the PL spectra were recorded. In order to evaluate the performance of the SQDs, the obtained results were compared with those measured by traditional standard HPLC technique.

Results and Discussion

Characterization of Carboxyl-capped CdTe@SiO_2 Quantum Dots (SQDs)

The structure of as-synthesized materials has been investigated using TEM. As displayed in Fig. 1A, TEM image indicates that SQDs are well-dispersed in aqueous solution. The higher magnification TEM image exhibits an egg-yolk structure with a silica shell and multiple QDs as core (Fig. S1A in Supporting Materials). The optical properties of the SQDs were studied using UV-vis absorption and PL spectra (Fig. 1B). The UV-vis absorption and

PL spectra of the QDs and SQDs (Fig. 1B, Fig. S1B in Supporting Materials) show that the typical absorption peak shifts from 545 nm to 550 nm, and the peak of PL emission correspondingly shifts from 606 nm to 620 nm. The redshift of PL spectra for SQDs can be atttibuted to the re-absorption of the high QDs (3.2±0.2 nm, Fig. S2 in Supporting Materials) concentration encapsulated in the silica shell.[32] These excellent photoluminescence (PL) properties indicate that the milky white SQDs solution can emit strong yellow-red fluorescence under excitation at 365 nm with a UV lamp (the inset of Fig. 1B). Consequently, the PL quantum yield of SQDs was calculated to be 32% by utilizing quinine sulfate as the standard (Fig. S3 in Supporting Materials). [33]

Fig. 1

Feasibility of PL SQDs in SPFX Detection

As shown in Fig. 2A, the SQDs could exhibit a strong PL peak at 620 nm without the SPFX. However, the PL intensity of SQDs can be increased nearly 3-fold after the addition of 1 μM SPFX (Fig. 2B), indicating the effective enhancing property of SPFX on the SQDs. This observation is presumably attributed to the intermolecular interactions between SQDs and SPFX. [34] Based on the excellent PL properties, the SQDs are developed as a novel PL probe for the analysis of SPFX in the following experiments.

Fig. 2

Effect of Experimental Parameters on the PL Response Between SQDs and SPFX

To validate the quantification of the ultra-trace amounts of SPFX by the proposed SQDs, it is necessary to optimize the experimental parameters to obtain the maximized PL response toward SPFX. Therefore, the effects of different temperature, pH, incubation time and ionic strength were investigated to obtain the optimum conditions for the analysis of SPFX.

As shown in Fig. 3A, the SQDs PL response towards SPFX (F/F_0) was almost the same from 10°C to 60°C. This may indicate that the temperature has no obvious effect on the PL response (F/F_0). Moreover, the effect of pH on the PL response (F/F_0) was also investigated as displayed in Fig. 3B. Under strongly acidic (pH<4) or alkaline (pH>10) conditions, the PL response (F/F_0) is found to decrease, whereas the PL response (F/F_0) hit the climax at pH=7.5 and remained stable in the range from 7.0 to 8.0 which corresponds to the physiological pH environment. These results indicate that the SQDs with excellent PL properties can be regarded as good candidate for potential application in biological system. In addition, the effect of buffer system on the PL response (F/F_0) is negligible (Fig. S4 in Supporting Materials). Thus, a Tris-HCl buffer (pH=7.5) was used in all subsequent detection. As displayed in Fig.

3C, the PL enhancement effect can be completed within 3 min of incubation. The relatively short incubation time proves the fast reaction kinetics between SQDs and SPFX. Furthermore, the influence of ionic strength on the PL response (F/F_0) is shown in Fig. 3D. It can be clearly seen that there was no obvious change in PL response (F/F_0) even in an aqueous solution with high ionic strength (1.2 M NaCl). All the above results revealed that the reaction between SQDs and SPFX is extremely stable under high temperature (60^{o}C), weak acidic or alkaline conditions, and high ionic strength, which further confirms the feasibility for practical biological detection.

Fig. 3

Selectivity of SQDs probe for SPFX

To further evaluate the selectivity of the proposed SQDs probe, the effects of potential interfering substances on the PL response (F/F_0) of SQDs-SPFX system were studied (Fig. 4). The potential interfering substances (including HSA, glucose and typical metal ions and some anions, etc.) exhibited little influence on the PL response towards SPFX (F/F_0) even at concentrations 1000 times higher than that of SPFX. However, the slight influence on the detection of SPFX observed upon addition of norfloxacin, lomefloxacin and ciprofloxacin may result from the weaker hydrogen-bond interactions. [34] These results clearly demonstrate that the SQDs can serve as a novel PL sensor for highly selective and sensitive SPFX detection.

Fig. 4

Quantitative Analysis of SPFX in Human Serum Using PL SQDs

The PL response as function of SPFX concentration has been investigated. As shown in Fig. 5, the relationship between the ratio F/F_0 and the logarithmic concentration of SPFX fits well into a Boltzmann sigmoidal curve under the optimized conditions. The limit of detection (LOD) for SPFX was 0.035×10^{-6} mol L^{-1} (3 times the standard deviation of the blank), and the detection range was from 0.05×10^{-6} mol L^{-1} to 200×10^{-6} mol L^{-1} with a correlation coefficient of 0.9967. Meanwhile, the LOD value obtained for SPFX using the SQDs probe is comparable with previously reported methods, and the detection range is much wider than those of recently reported methods (Table S1). The lower LOD and the wide detection of SQDs probe validate the feasibility for the determination of SPFX in biological system with the advantages of sensitivity and selectivity.

To further confirm the accuracy and stability of the proposed method, a comparison experiment between the proposed SQDs-based method and HPLC method was conducted. The reference samples 1-3 in Table 1 with different concentrations of SPFX were detected using HPLC under the same conditions. As exhibited in Table 1, the

results obtained from SQDs-based method are closed to the certified value of reference samples with a little error, which demonstrates that the SQDs-based PL sensor could be applied for detecting SPFX in real samples.

To evaluate the performance of SQDs for SPFX detection in real biological samples, the detection of the amount of SPFX in human serum samples are performed. However, the concentrations of each sample have been determined with SQDs-based PL sensor and HPLC method. The experimental results are summarized in Table 2. As shown in Table 2, the results obtained from SQDs-based PL sensor match well with those of obtained with HPLC, indicating therefore the feasibility of SQDs PL probe for SPFX in biological samples.

Fig. 5

Table 1

Table 2

PL Enhanced Mechanism Between SQDs and SPFX

For the PL enhancing of SQDs-SPFX system, we excluded the energy transfer process between SPFX and SQDs because of no spectral overlap between the absorption spectra of SPFX and the SQDs PL spectrum (Fig. S5 in Supporting Materials). [35] The PL enhancement mechanism could be attributed to the charge separation or electron transfer mechanism. As shown in Fig. 6A, the surface of the SQDs is modified by hydrophilic groups (carboxylic and hydroxyl groups). In addition, there are many COOH, C-F and C=O groups on the surface of SPFX. When the SPFX is added into the SQDs, strong intermolecular hydrogen-bond interactions will be formed. Therefore, the existence of strong intermolecular hydrogen-bonds may lead to significant PL enhancement of SQDs.

To confirm the intermolecular hydrogen-bonds mechanism, we collected the FTIR spectrum of SQDs and SQDs-SPFX. The result shows that, the C–OH vibrations of SQDs-SPFX at about 3445 cm^{-1} (Fig. 6B, red line), is red-shifted by 48 cm^{-1} with respect to that of the initial SQDs (3493 cm^{-1}, Fig. 6B, black line). This red shift may indicate that the hydrogen bonding exists between SPFX and SQDs. In addition, the PL intensity of the SQDs is enhanced when the SQDs are mixed with substances containing hydrogen-bonds group (including COOH, C-F, C-OH and C-N) (Table S2). However, a decrease in F/F_0 was appeared with decrease in the concentrations of hydrogen-bonds group (Fig. S6 in Supporting Materials), which may be attributed to the existence of hydroxyl-group-free SQDs. Moreover, to exclude the possibility that the PL enhancement was caused by SPFX itself, a control experiment was conducted. As shown in Fig. S7 (Supporting Materials), the PL intensity of the SQDs-SPFX system was much higher than that of SQDs and SPFX. Thus, the PL enhancement of SQDs-SPFX

system was not caused by SPFX itself. Thus, it is evident that the intermolecular hydrogen-bonds interactions led to the enhanced PL intensity of SQDs. It can be therefore assumed that the PL enhancement of SQDs-SPFX system is mainly due to the intermolecular hydrogen-bonds interactions between the SQDs and SPFX.

Fig. 6

Conclusions

We have developed a SQDs-based "turn-on" PL probe for highly sensitive and selective detection of SPFX in human serum samples. The low cost, low-toxic and unique PL properties of the SQDs allow one to use the SQDs for the detection of SPFX in biological system. The PL intensity of the SQDs was obviously enhanced with the increase in the concentration of SPFX because of the formation of intermolecular hydrogen bonding interactions. Under optimal conditions, a good linear relationship between the PL response and SPFX concentration in the range from 0.05×10^{-6} to 200×10^{-6} mol L^{-1} was obtained. The LOD was 0.035×10^{-6} mol L^{-1} for SPFX. Moreover, the SQDs probe showed a high selectivity for SPFX in the presence of other interfering substances. These results indicate that the SQDs-based probe offers great potential for the practical applications in biological analysis.

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References

[1] E. Kłosińska-Szmurło, F. A. Pluciński, M. Grudzień, K. Betlejewska-Kielak, J. Biernacka and A. P. Mazurek, *J. Biol. Phys*., 2014, **40**: 335-345.

[2] E. Rodriguez, M. C. Moreno-Bondi and M. D. Marazuela, *Food Chem.*, 2011, **127**: 1354-1360.

[3] N. Sultana, M. S. Arayne, S. Gul and S. Shamim, *J. Mol. Struct.*, 2010, **975**: 285-291.

[4] M. R. Jan, J. Shah and Inayatullah, *J. Appl. Spectrosc.*, 2010, **77**: 400-405.

[5] C. Y. Sun, H. Ping, M. W. Zhang, H. K. Li and F. R. Guan, *Spectrochim Acta Part A*, 2011, **82**: 375-382.

[6] M. Hou, X. Y. Yan and L. Xiong, *J. Lumin.*, 2015, **157**: 58-62.

[7] A. M. El-Didamony, *Luminescence*, 2011, **26**: 112-117.

[8] M. Kaczmarek and S. Lis, *Analyst*, 2011, **136**: 2592-2597.

[9] A. E. Radi, T. Wahdan, Z. Anwar and H. Mostafa, *Electroanalysis*, 2010, **22**: 2665-2671.

[10] K. G. Kumar, P. Augustine, R. Poduval and S. John, *Pharmazie*, 2006, **61**: 291-292.

[11] N. Cavazos-Rocha, I. Carmona-Alvarado, L. Vera-Cabrera, N. Waksman-de-Torres and M. Salazar-Cavazos, *J. Chromatogr. Sci.*, 2014, **52**:1281-1287.

[12] M. Ramos-Payan, M. Villar-Navarro, R. Fernandez-Torres, M. Callejon-Mochon and M. Á. Bello-Lopez, *Anal. Bioanal. Chem.*, 2013, **405**: 2575-2584.

[13] A. V. Herrera-Herrera, J. Hernández-Borges, T. M. Borges-Miquel and M. Á. Rodríguez-Delgado, *J. Pharmaceut. Biomed.*, 2013, **75**: 130-137.

[14] M. Seifrtova, L. Novakova, C. Lino, A. Pena and P. Solich, *Anal. Chim. Acta*, 2009, **649**: 158-179.

[15] K. Noh, K. Kwon, T. C. Jeong and W. K. Kang, *Biomed. Chromatogr.*, 2010, **24**: 1199-1202.

[16] L. G. Chen, X. P. Zhang, Y. Xu, X. B. Du, X. Sun, L. Sun, H. Wang, Q. Zhao, A. M. Yu, H. Q. Zhang and L. Ding, *Anal. Chim. Acta*, 2010, **662**: 31-38.

[17] Y. Xiao, H. Chang, A. Jia and J. Y. Hu, *J. Chromatogr. A*, 2008, **1214**: 100-108.

[18] Q. Ma and X. G. Su, *Analyst*, 2011, **136**: 4883-4893.

[19] Q. Wang, X. Liu, L. C. Zhang and Y. Lv, *Analyst*, 2012, **137**: 5392-5397.

[20] H. T. Li, Z. H. Kang, Y. Liu and S. T. Lee, *J. Mater. Chem.*, 2012, **22**: 24230-24253.

[21] K. V. Joshi, B. K. Joshi, A. Pandya, P. G. Sutariya and S. K. Menon, *Analyst*, 2012, **137**: 4647-4650.

[22] Z. B. Qu, X. G. Zhou, L. Gu, R. M. Lan, D. D. Sun, D. J. Yu and G. Y. Shi, *Chem. Commun.*, 2013, **49**: 9830-9832.

[23] D. Li, Z. Y. Yan and W. Q. Cheng, *Spectrochim. Acta Part A*, 2008, **71**: 1204-1211.

[24] P. Liao, Z. Y. Yan, Z. J. Xu and X. Sun, *Spectrochim. Acta Part A*, 2009, **72**:1066-1070.

[25] A. M. Derfus, W. C. W. Chan and S. N. Bhatia, *Nano Lett.*, 2004, **4**: 11-18.

[26] M. Bottrill and M. Green, *Chem. Commun.*, 2011, **47**: 7039–7050.

[27] X. Y. Cheng, S. B. Lowe, P. J. Reece and J. J. Gooding, *Chem. Soc. Rev.*, 2014, **43**: 2680-2700.

[28] L. Li, Y. Cheng, Y. P. Ding, S. Q. Gu, F. F. Zhang and W. J. Yu, *Eur. J. Inorg. Chem.*, 2013, **14**: 2564-2570.

[29] Y. H. Yi, J. H. Deng, Y. Y. Zhang, H. T. Li and S. Z.Yao, *Chem. Commun.*, 2013, **49**: 612-614.

[30] R. J. Gui, A. J. Wan and H. Jin, *Analyst*, 2013, **138**: 5956-5964.

[31] L. Zou, Z. Y. Gu, N. Zhang, Y. L. Zhang, Z. Fang, W. H. Zhu and X. H. Zhong, *J. Mater. Chem.*, 2008, **18**: 2807-2815.

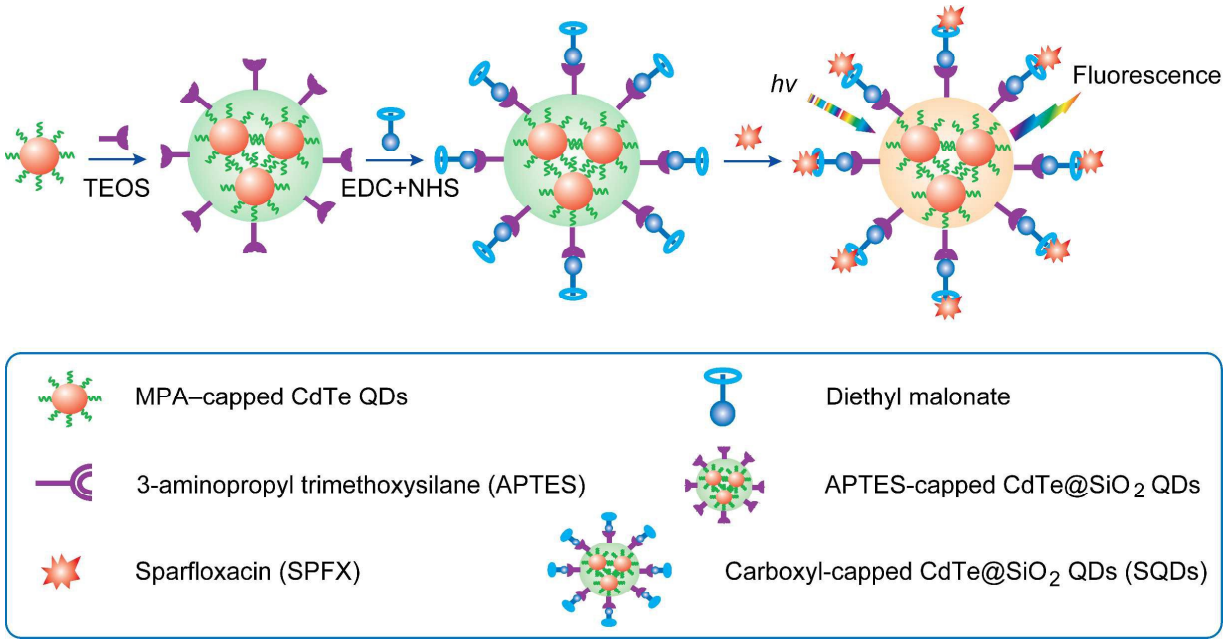
[32] P. Yang and N. Murase, *ChemPhysChem*, 2010, **11**: 815-821.

[33] A. Jaiswal, S. S. Ghosh and A. Chattopadhyay, *Chem. Commun.*, 2012, **48**:407-409.

[34] M. M. Yang, H. Li, J. Liu, W. Q. Kong, S. Y. Zhao, C. X. Li, H. Huang, Y. Liu and Z. H. Kang, *J. Mater. Chem. B*, 2014, **2**: 7964-7970.

[35] H. Li, J. Liu, M. M. Yang, W. Q. Kong, H. Huang and Y. Liu, *RSC Adv.*, 2014, **4**: 46437-46443.

Captions



Scheme 1. Schematic illustration of the proposed carboxyl-capped CdTe@SiO_2 quantum dots (SQDs) for the detection of Sparfloxacin (SPFX). Initially, the MPA–capped CdTe QDs were obtained using hydrothermal approach. Then the CdTe@SiO_2 QDs were prepared by deposition of silica shells, followed by modification with APTES, then the APTES-capped CdTe@SiO_2 QDs were incubated with diethyl malonate introducing carboxyl group onto the QDs surfaces. The resulting SQDs can be used for label-free detection of SPFX.

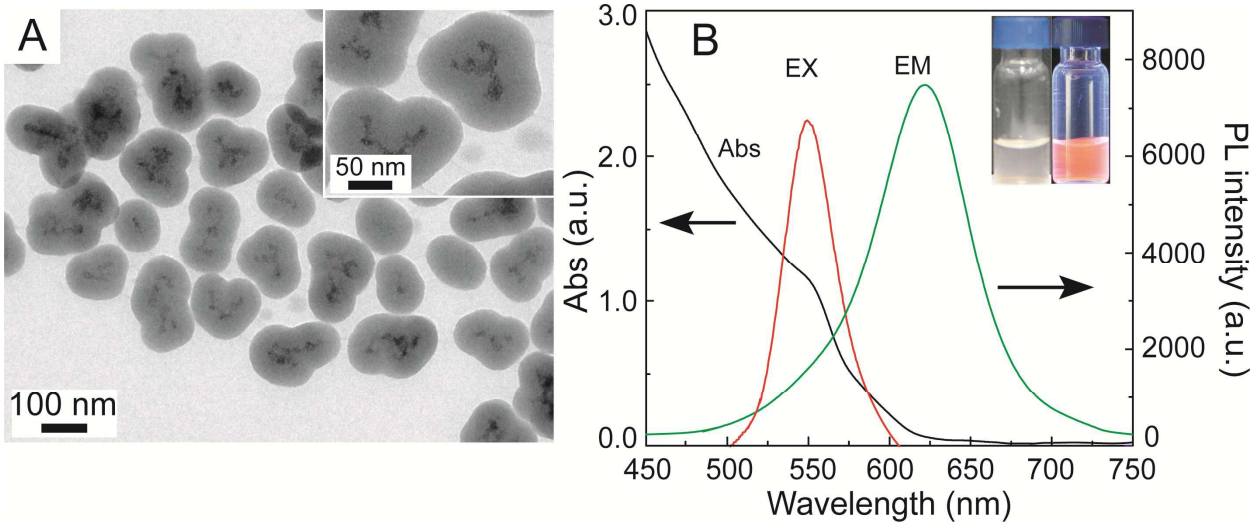


Fig. 1 (A) TEM image of photoluminescent SQDs. Inset: the high-resolution TEM image of SQDs. (B) UV and fluorescence spectra of SQDs. Inset: photographs of photoluminescent SQDs under daylight (left) and 365 nm UV light (right).

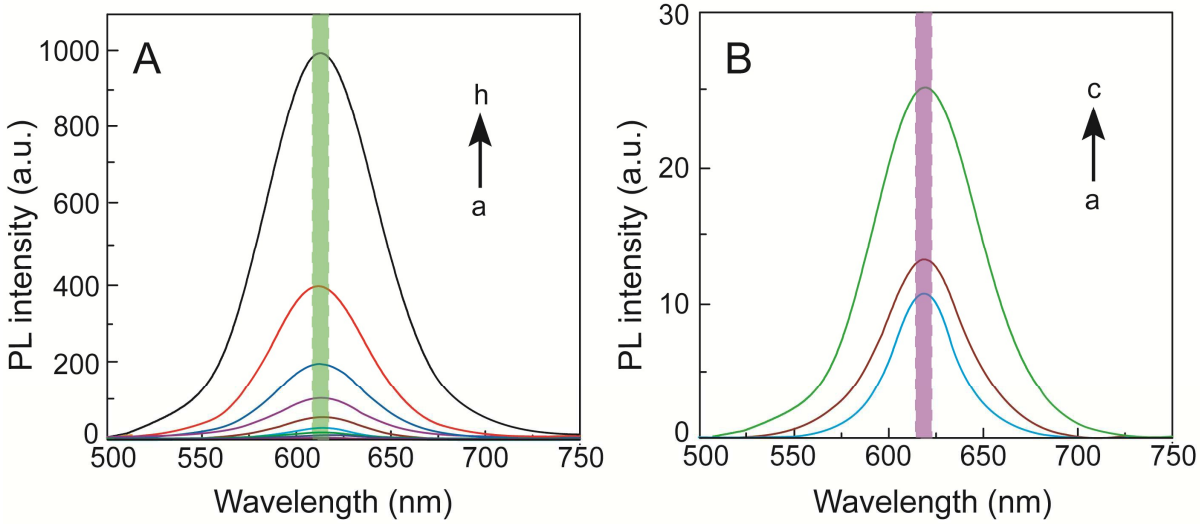


Fig. 2 (A)The PL emission spectra of SQDs in the presence of increasing concentrations of SPFX (a–h: 0, 0.50, 1.00, 2.00, 5, 10, 20 and 200 μM). (B) The enlarged curve in the low concentration range (a–c: 0, 0.50 and 1.00 μM).

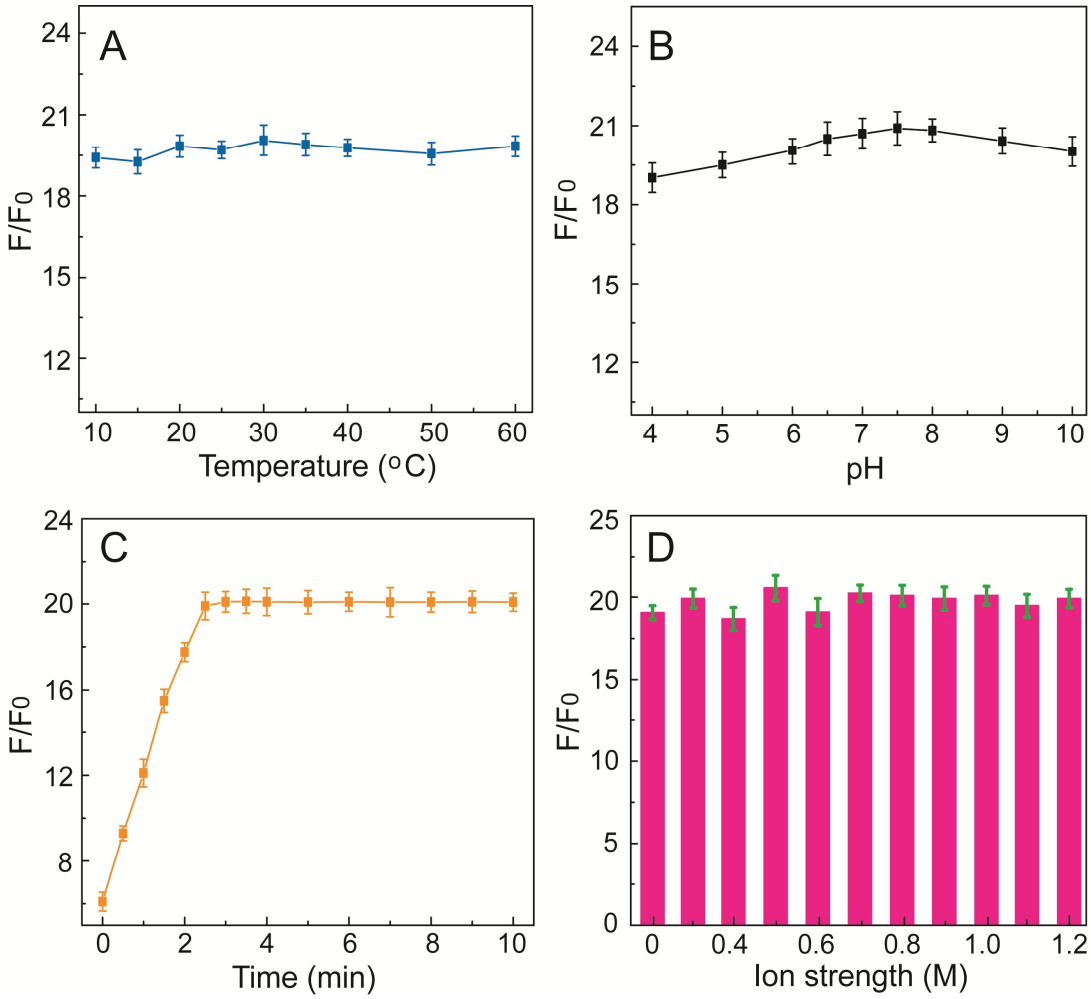


Fig. 3 The effects of different temperature (A), pH (B), incubation time (C) and ionic strength in NaCl aqueous solution (D) on the PL response F/F0 of SQDs toward SPFX (5 μM) in Tris-HCl solution.

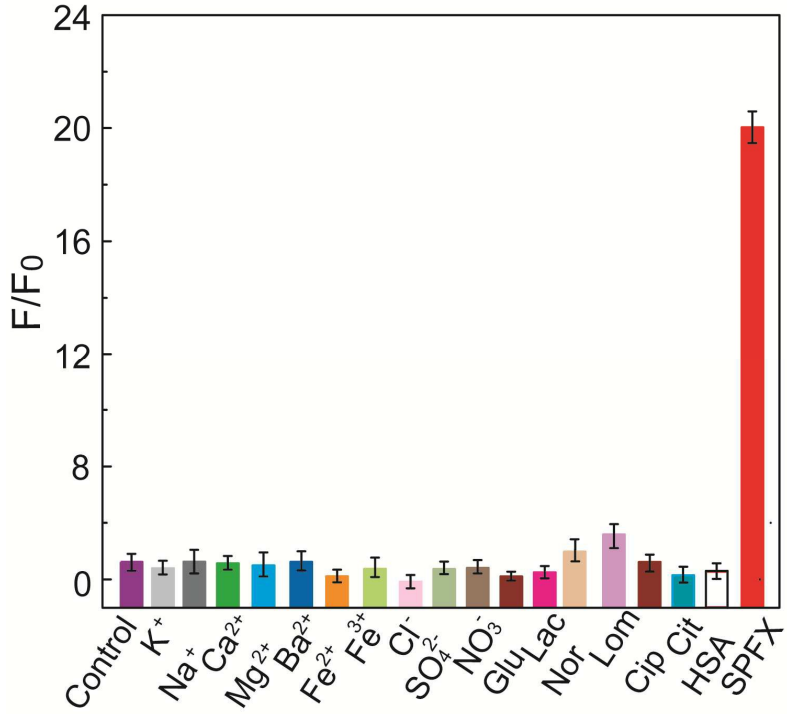


Fig. 4 Effect of potential interfering substances (Glu=Glucose, Lac=Lactose, Nor=Norfloxacin, Lom=Lomefloxacin, Cip=Ciprofloxacin, Cit=Citric acid, HSA= Human serum albumin) on the PL response F/F_0 of SQDs toward SPFX (5 μM) at pH 7.5 (Tris-HCl, 0.1 M) Each concentration of analytes is 5 mM. Each point is an average of three successive measurements.

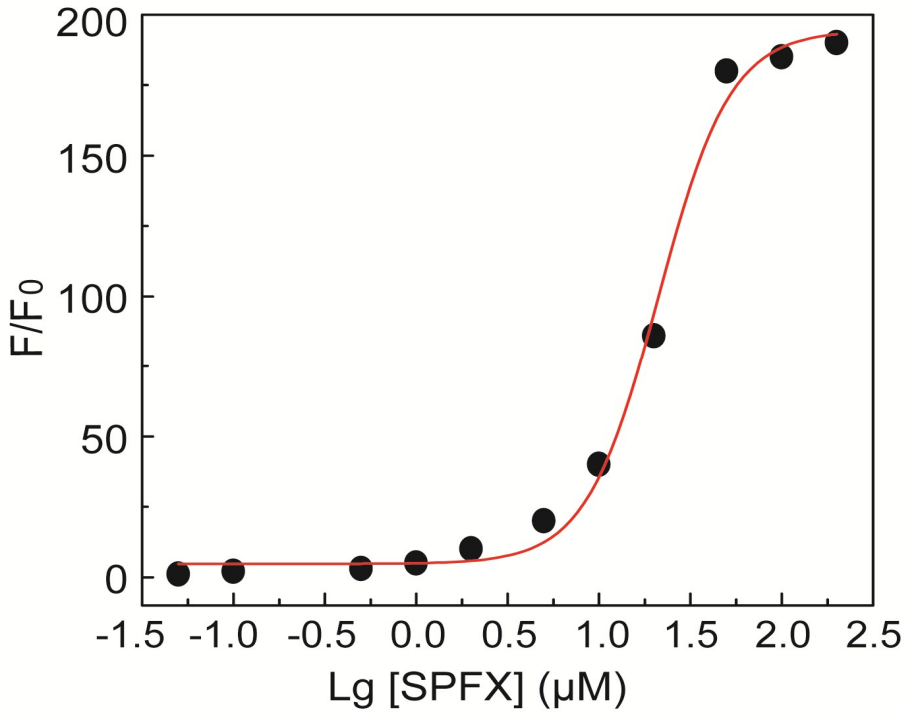


Fig. 5 The relationship between F/F_0 and the logarithmic concentration of SPFX. F_0 and F are the PL intensities without and with SPFX, respectively. The Boltzmann fitting curve describes the relationship between the PL response (F/F_0) of SQDs and the concentration of SPFX (0-200 μM).

Table 1 Application of SQDs probe for detecting SPFX in reference samples

Reference sample	Amount labeled (μM)	Amount determinated by the proposed method (μM) [a]	Amount determinated by HPLC method (μM) [a]
1	1.00	0.92±0.18	1.05±0.12
2	5.00	4.85±0.51	5.13±0.23
3	20.0	20.8±0.65	21.5±0.35

[a] All values are the average of three determination ± standard deviation.

Table 2 Statistical data obtained in the analysis of blood samples using the SQDs-based PL method and HPLC

Sample number	Amount added (μM)	The proposed method		HPLC method	
		Amount found (μM)	Recovery(%)±RSD(%) (n=3)	Amount found (μM)	Recovery(%)±RSD(%) (n=3)
1	0.25	0.21±0.03	84.0±5.38	0.20±0.01	80.0±5.38
2	0.50	0.43±0.05	86.0±3.86	0.54±0.02	108±3.86
3	1.50	1.37±0.12	91.3±2.14	1.55±0.09	103±2.14
4	5.00	4.78±0.35	95.6±1.25	4.85±0.28	97.0±1.25

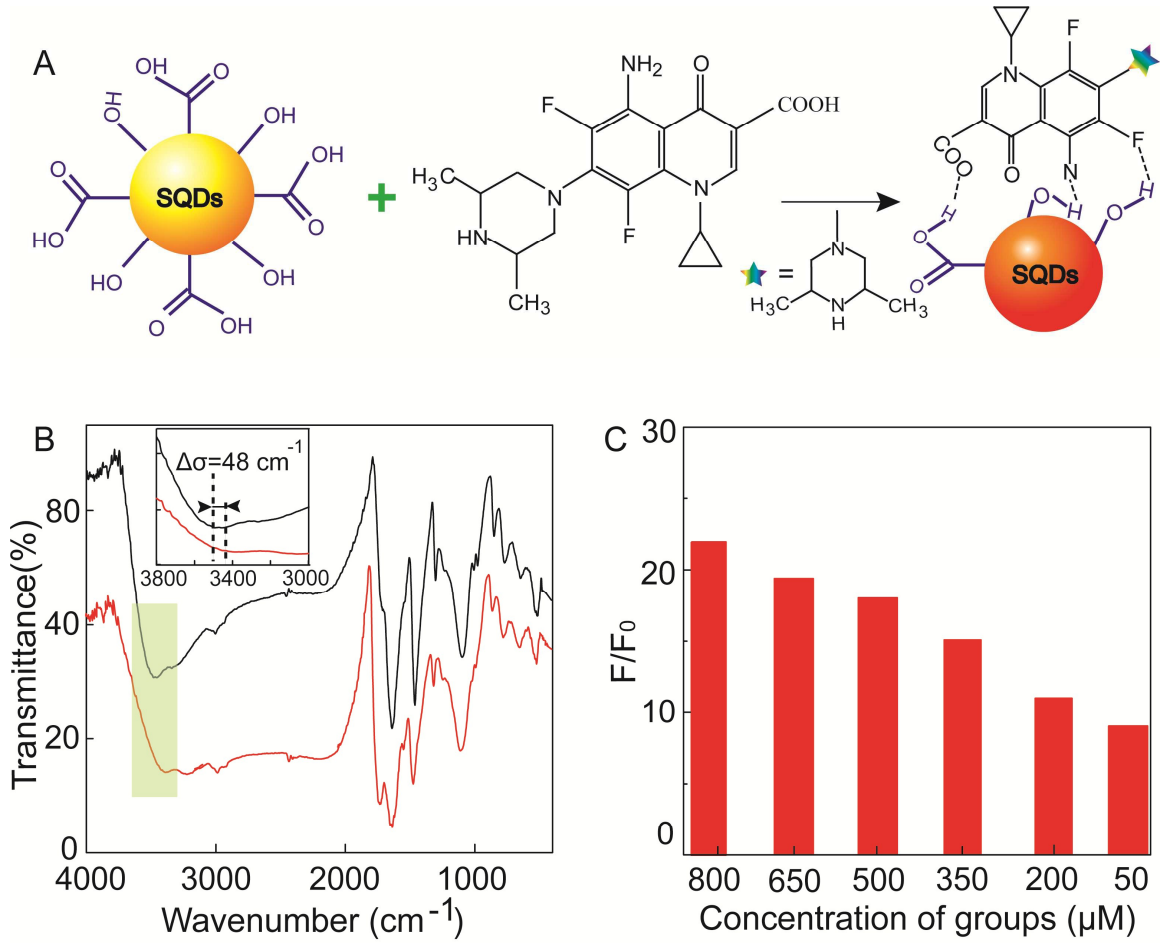
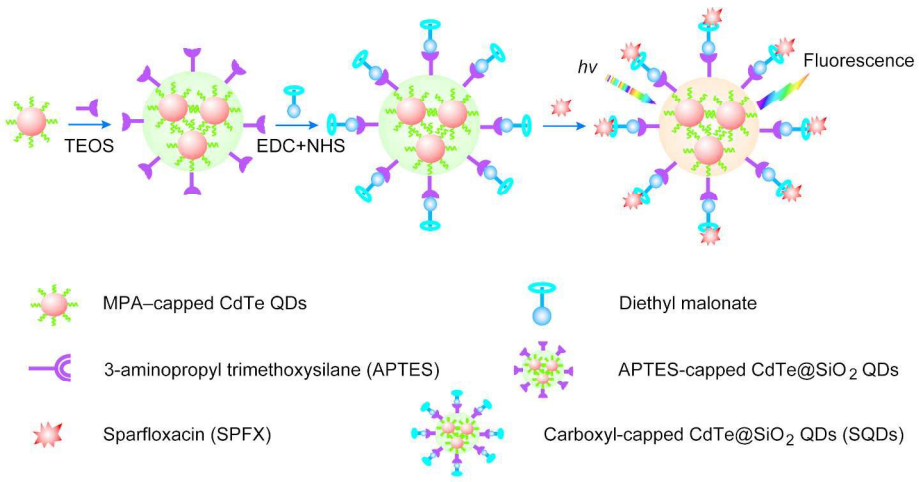


Fig. 6 (A) The schematic illustration of hydrogen-bonds interactions between SPFX and SQDs. (B) FTIR spectra of the SQDs (black line) and SQDs-SPFX system (red line), and the inset is the enlarged spectral region from 3800 cm^{-1} to 3000 cm^{-1}. (C) F/F_0 with the concentration of hydrogen-bonds groups: 850 μM, 650 μM, 500 μM, 350 μM, 200 μM, and 50 μM (at 25 ^{o}C, pH= 7.5).



The hydrophilic carboxyl-capped CdTe@SiO2 quantum dots (SQDs) can served as a “turn-on” photoluminescence (PL) probe for highly sensitive and selective detection of Sparfloxacin in human serum.

456x255mm (150 x 150 DPI)