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Novel and remarkable enhanced-fluorescence system based on gold nanoclusters for detection of tetracycline

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ABSTRACT

Tetracycline and Eu^{3+}, while coexisting, usually appear as a complex by chelating. This complex shows low fluorescence intensity, leading to its limitation of analytical goals. Gold nanoclusters (AuNCs), emerging as novel nano-material, are attracting increasing attentions in multiple fields. Herein, gold nanoclusters first function as a fluorescence-enhanced reagent rather than a conventional fluorescent-probe, and a dramatic enhanced-fluorescence system was built based on Eu^{3+}–Tetracycline complex (EuTC) by introducing gold nanoclusters. Simultaneously, three types of gold nanoclusters were employed for exploring various conditions likely affecting the system, which demonstrate that no other gold nanoclusters than DNA-templated gold nanoclusters enormously caused fluorescence-enhancement of EuTC. Moreover, this enhanced-fluorescence system permitted available detection of tetracycline (TC) in a linear range of 0.01–5 μM, with a detection limit of 4 nM at a signal-to-noise ratio of 3. Significantly, the practicality of this method for detection of TC in human urine and milk samples was validated, demonstrating its advantages of simplicity, sensitivity and low cost. Interestingly, this system described here is probably promising for kinds of applications based on its dramatically enhanced-fluorescence.

1. Introduction

Metal-enhanced fluorescence (MEF), usually generated by the interactions of fluorophores with metal [1], has been widely employed as a basic mechanism for medical diagnostics, imaging, and biosensors due to its enhanced-fluorescence signal, decreased lifetime, and improved photostability and sensitivity. To achieve MEF, metallic nanomaterials, especially gold or silver, serve as a critical factor for the fluorescence enhancement of green fluorescent protein, organic fluorophores, quantum dots, upconversion nanocrystals, and lanthanide chelates [2,3]. However, development of enhancing fluorescence by exploring new nanomaterials is still lacking.

Complexes, formed by rare earth metal and organic ligands, typically exhibit superior light absorption, fluorescent characteristic and other advantages including avoiding background interference of organisms and exerting long fluorescence lifetime, large Stokes Shift and narrow emission band [4–6]. As been well known, TC, performing its antibacterial action by interactions with chelate metal [7], functions as one member of antibiotics. In addition, TC and their derivatives have been widely exploited for analytical purposes [8]. As reported in recent years, TC can form complex with the rare metals such as Eu^{3+} through the formation of an organic chelate. In particular, EuTC has served as a sensitive enhanced-fluorescence probe for determining double-stranded and single-stranded DNA [9–12].

Noble metal nanoclusters (NCs), existing in the size of less than 10 nm, usually consist of several to hundred atoms, with properties regulated by their subnanometer dimensions [13–16]. Particularly, gold nanoclusters have been used for different kinds of applications. Up to date, AuNCs are synthesized by two major ways. One way is based on the template-assisted synthesis with polymers [17] and biomolecules (e.g., proteins [18–20] and DNA [21,22] commonly as templates. AuNCs are generally produced by another way of monolayer protection in the presence of molecules with thiol ligands [23–26]. Compared with quantum dots (QDs), AuNCs exist in ultra-small size with low toxicity. As a new type of fluorescent material, unique characteristics of AuNCs have recently attracted growing attentions, potentiating it as a satisfactory candidate for biosensing, catalysis, and imaging [13,16,27,28].

Nanoparticles have been reported to enhance the fluorescence of EuTC by MEF [1], thus we asked whether this complex can be enhanced by nanoclusters, since they are one special type of nanoparticles. In this study, we first developed a novel dramatic enhanced-fluorescence system based on Eu^{3+}-Tetracycline complex by introducing DNA-templated gold nanoclusters. Subsequently, we tested kind of aspects possibly affecting to construct

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an enhanced-fluorescence system by employing three types of AuNCs. Compared with AuNCs@BSA and AuNCs@His, only DNA-templated gold nanoclusters enormously caused fluorescence-enhancement of EuTC, suggesting EuTC with DNA-templated gold nanoclusters may broaden potential ways to design more sensitive assays and fluorescent probes. In addition, this system has been applied to assay TC while Eu^{3+}-AuNCs@DNA_{C12} considered as a base. Importantly, its practicality of this method was validated by detections of TC in human urine and milk samples, and satisfactory results obtained suggested this strategy may broaden avenues for detection of TC.

2. Experimental

2.1. Materials and reagents

Bovine serum albumin (BSA), amino acids and all the DNA sequence were purchased from Shanghai Sangon Biotechnology Co., Ltd. (Shanghai, China). Hydrogen tetrachloroaurate trihydrate ($HAuCl_4$), europium oxide (Eu_2O_3) and all the metal ions were obtained from Sigma-Aldrich (Milwaukee, WI). Sodium tetraborate was purchased from Dingguo Changsheng Biotechnology Co., Ltd. (Beijing, China). Ultrapure water, 18.25 MΩ cm, produced with an Aquapro AWL-0502-P ultrapure water system (Chongqing, China) was employed for all procedures.

2.2. Apparatus

All fluorescence measurements were performed on a Hitachi F-7000 fluorescence spectrophotometer (Tokyo, Japan) with excitation slit set at 5 nm band pass and emission at 5 nm band pass in 1 cm × 1 cm quartz cells. The high-resolution transmission electron microscopy (HRTEM) images were obtained using a TECNAI G2 F20 microscope (FEI, America) at 200 KV. Photographs were taken with an Olympus E-510 digital camera (Tokyo, Japan). A Fangzhong pHS-3C digital pH meter (Chengdu, China) was used to measure pH values of the aqueous solutions and a vortex mixer QL-901 (Haimen, China) was used to blend the solution. The thermostatic water bath (DF-101s) was bought from Gongyi Experimental Instruments Factory (Henan, China).

2.3. Preparation of three kinds of AuNCs

Three types of AuNCs were prepared as follows: the AuNCs@BSA was prepared by a reported method [18]. Briefly, $HAuCl_4$ solution (10 mM, 5 mL) was mixed with BSA solution (50 mg mL^{-1}, 5 mL) under vigorous stirring at 37 °C. Two minutes later, NaOH solution (1.0 M, 0.5 mL) was added, and the mixture was incubated at 37 °C for 12 h. Similarly, the AuNCs@DNA_{C12} were prepared as previously reported [21]. The synthesis reaction was performed by 100 μM $HAuCl_4$, 25 μM DNA_{C12} and 50 mM citrate, and citrate served as not only a buffer (pH=3) but also a reducing agent. The mixture was incubated overnight at room temperature. Furthermore, the AuNCs@His was synthesized by using a biomineralized approach [29]. Typically, an aqueous solution of $HAuCl_4$ (8 mL, 10 mM) was mixed with an aqueous solution of histidine (24 mL, 0.1 M) at room temperature and incubated for 2 h to obtain the desired nanoclusters.

2.4. Construction of the enhanced-fluorescence system

A stock solution of Eu^{3+} was prepared by dissolving Eu_2O_3 with a small amount of nitric acid (0.10 M), and then diluted with ultra water. Then TC was added into diluted Eu^{3+} solution, and the working solution EuTC (2.5×10^{-5} M) was obtained by appropriate dilution. Subsequently, three kinds of AuNCs prepared here were diluted for different times, and further subjected to EuTC respectively to form the enhanced-fluorescence system.

2.5. Detection of TC and interference studies

A stock solution of TC was prepared before use. For detection of TC, 50 μL of buffer solution (sodium tetraborate buffer, pH=9) was mixed with 50 μL Eu^{3+} solution and 10 μL AuNCs@DNA_{C12}, and then 390 μL of different concentration of TC solution was added. After reaction for 5 min at room temperature, the fluorescence intensity of the mixture was measured upon being excited at 375 nm. To investigated the interference of foreign substances, amino acids (Gly, Cys, Ala, Glu, Ser, Val, Lys, Phe, and His), glucose and ascorbic acid were introduced. To evaluated the effects of other metal ions on the fluorescence of EuTC-AuNCs@DNA_{C12}, several metal ions (Na^+, K^+, Ca^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, Cu^{2+}, Co^{2+}, Ba^{2+}, Fe^{3+}, Ni^{2+}, Mg^{2+}, Zn^{2+}, and Hg^{2+}) were added.

2.6. Analysis of TC in urine and milk samples

Human urine sample from one healthy volunteer was collected from Southwest University, Chongqing. For the detection of TC, impurities were precipitated from the urine sample by centrifugation (600 rpm, 10 min). Then, the supernatant was collected into 2 tubes and supplemented with standard TC solutions (2 μM, 4 μM). And the urine samples were filtered through a 0.22 μm membrane and collected in aliquots. Milk samples were collected from Yonghui Supermarket, Chongqing. Briefly, proteins in the milk samples were removed firstly by adding 1% trichloroacetic acid into the milk and sonicating 20 min. After filtering through a 0.22 μm membrane to remove lipids, the supernatant were collected into 3 tubes and spiked with TC solutions (0.5 μM, 3 μM, 6 μM). All the spiked samples described here were further subjected to the detection procedure.

3. Results and discussion

3.1. Characterization of three kinds of AuNCs

To visualize three types of AuNCs, high-resolution transmission electron microscopic (HRTEM) images were obtained. AuNCs@BSA, AuNCs@DNA_{C12} and AuNCs@His displayed different patterns respectively. The majority of AuNCs@BSA are within the size of less than 3 nm (Fig. 1A and D), and AuNCs@DNA_{C12} existing as the size of 1–3 nm were described in Fig. 1B and E, and AuNCs@His is monodispersed with the smallest size (Fig. 1C and F). Additionally, the absorption spectra of these three kinds of AuNCs were recorded (Fig. S1) respectively. Taken together, these data indicated that three kinds of AuNCs have been successfully synthesized [18,21,29].

3.2. Enhanced-fluorescence system built by introducing AuNCs@DNA

Basically, TC coordinates with Eu^{3+} to form a complex under certain conditions, and the fluorescence intensity of this complex could be enhanced by MEF as reported [1]. To broaden its applications, here we tried to pursue another avenue to enhance the fluorescence intensity of EuTC. Subsequently, we tested the possibility to construct an enhanced-fluorescence system by introducing AuNCs to EuTC.

As shown in Fig. 2A, the fluorescence enhanced was about 2-fold of the signal of EuTC while AuNCs@BSA (0.5 mg mL^{-1}) added. Contrastingly, when added into the complex of EuTC, AuNCs@D-NA_{C12} (0.5 mg mL^{-1}) showed a sharp enhanced-fluorescence with

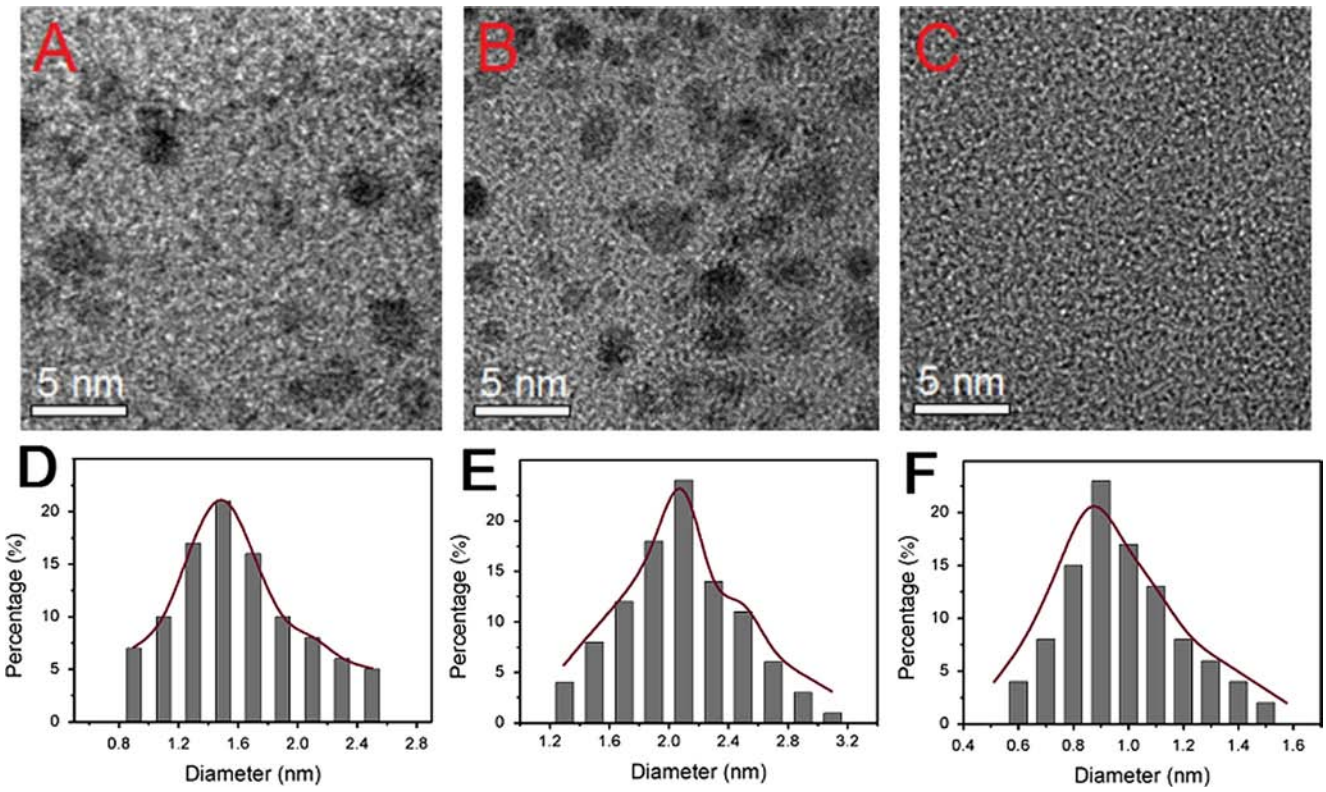

Fig. 1. High-resolution transmission electron microscopy (HR-TEM) images of AuNCs@BSA, AuNCs@DNA_{C12} and AuNCs@His (A, B, C); the size distributions of AuNCs@BSA, AuNCs@DNA_{C12} and AuNCs@His (D, E, F) counted from (A, B, C).

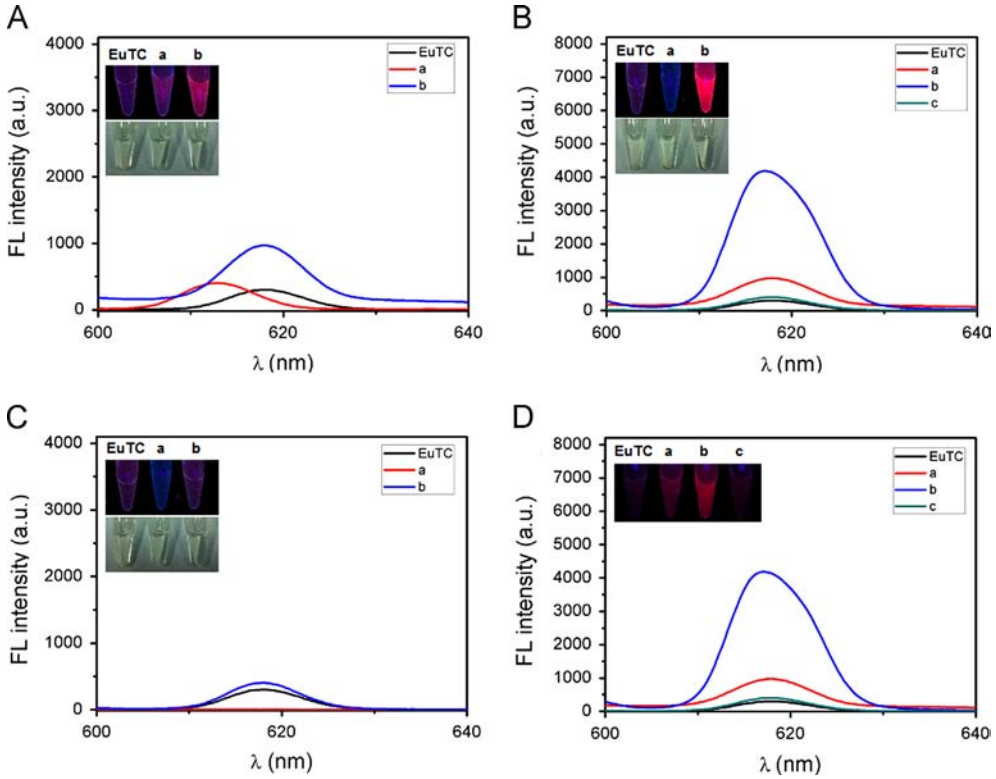

Fig. 2. (A) Fluorescence emission spectra of EuTC, AuNCs@BSA (a) and the mixture of EuTC with AuNCs@BSA (b); (B) Fluorescence emission spectra of EuTC, AuNCs@$DNAC_{12}$ (a) and the mixture of EuTC with AuNCs@$DNAC_{12}$ (b); (C) Fluorescence emission spectra of EuTC, AuNCs@His (a) and the mixture of EuTC with AuNCs@His (b); (D) Fluorescence emission spectra of EuTC, the mixture of EuTC with AuNCs@BSA (a), the mixture of EuTC with AuNCs@DNA_{C12} (b), and the mixture of EuTC with AuNCs@His (c). Inset: The photographs were under 365 nm UV light (top) and daylight (bottom).

13-fold of that of EuTC alone (Fig. 2B). Followed by introducing AuNCs@His (0.5 mg mL^{-1}) into the complex of EuTC, there is no obvious enhanced-fluorescence observed as incated in Fig. 2C. Taken together, the fluorescence intensity of EuTC was enhanced strikingly in the presence of AuNCs@DNA_{C12} compared with that of EuTC, and the enhanced-signal in the presence of AuNCs@BSA was not as remarkable as AuNCs@DNA_{C12}, and AuNCs@His clearly implied no enhanced-effect on EuTC (Fig. 2D). All these data demonstrated EuTC with completely different fluorescence signals were observed by adding different kinds of AuNCs. Importantly, the fluorescence intensity of EuTC was only dramatically enhanced by AuNCs@DNA_{C12} prepared rather than AuNCs@BSA and AuNCs @His, suggesting only AuNCs synthesized with DNA can be applied to build a highly enhanced-fluorescence system.

3.3. Influence of concentration variations of AuNCs to this system

Additionally, to validate the influence of concentration variations of AuNCs added, three types of AuNCs were diluted for different times (0.5–0.05 mg mL^{-1}) and further supplemented into EuTC. Fig. S2A showed that the flourescence intensities of EuTC were all substantially enhanced in the presences of varied concentrations of AuNCs@DNA_{C12}. However, different results of enhanced-intensity of EuTC at a certain extent were obtained in the presences of different diluted AuNCs@BSA (Fig. S2B). In contrast, altering the concentrations of AuNCs@His implied no effect on the fluorescence signals of EuTC (Fig. S2C). Taken together, these data illustrated that similarly dramatic enhanced-fluorescence were obtained by additions of diluted AuNCs@DNA_{C12} (0.5–0.05 mg mL^{-1}) to EuTC. Nevertheless, the similarly less enhanced-fluorescence by AuNCs@BSA and no obvious enhanced-fluorescence by AuNCs@His were observed. These results demonstrated that the dramatic Enhanced-fluorescence of EuTC was mainly caused by AuNCs@DNA_{C12} but not necessarily related to varied dilutions of AuNCs@DNA_{C12} in a certain range.

3.4. Fluorescence of EuTC maximally enhanced by AuNCs templated with DNAs of cytosine

Considering the novel enhanced-fluorescence of EuTC was induced by introducing AuNCs@DNA_{C12}, a series of AuNCs as an attempt were synthesized by 15 other DNA sequences (Fig. 3A) with the same method, and followed by supplementing into EuTC. However, we successfully synthesized AuNCs with DNA sequences of 1–8, and failed to prepare the AuNCs with DNA sequences of 9–16 (Fig. 3A). Hence, we applied the successful synthesized AuNCs to enhance the fluorescence of EuTC. As shown in Fig. 3B, all the AuNCs prepared with DNA sequences only including cytosine but different length significantly enhanced the fluorescence signals of EuTC, indicating the length of DNA consisting of cytosine did not play a critical role for this phenomenon of enhancement. In contrast, the AuNCs prepared with DNA sequences including adenine did not as dramatically enhanced the fluorescence intensity of EuTC as the AuNCs with DNAs of cytosine (Fig. 3B). Taken together, the templated DNA sequences of AuNCs were critical for enhancing fluorescence of EuTC, and the sequences consisting of cytosine were the optimal choices. In addition, to address whether the AuNCs@DNA or DNA enhanced the fluorescence signal of EuTC, DNAs sequenced with 1–4 of Fig. 3A directly added into EuTC were further explored. As shown in Fig. 3B, no enhanced-fluorescence were observed, suggesting that the remarkably enhanced-fluorescence of EuTC was resulted from DNA-templated AuNCs rather than DNAs alone.

3.5. Optimization of detection conditions

In view of its satisfactory fluorescence signal, we next employed the system of EuTC-AuNCs@DNA_{C12} built here to detect TC. As shown in Fig. S3, the excitation and emission wavelengths of EuTC and EuTC-AuNCs@DNA_{C12} were 375 and 618 nm respectively.

To investigate the effect of pH value for detecting TC, a pH titration of EuTC-AuNCs@DNA_{C12} was firstly performed. The Fluorescence intensity of Eu^{3+}-AuNCs@DNA_{C12} greatly increased and reached the maximum at pH=9.0 in the presence of TC (Fig. 4A). As shown in Fig. 4B, the fluorescence intensity of EuTC complex increased enormously by more than 10 μL AuNCs@DNA_{C12}. Thus, 10 μL AuNCs@DNA_{C12} with the total volume of 500 μL were used as the working concentration for the following experiments owing to cost saving. Considering the concentration of Eu^{3+} may show an influence for detecting TC, different concentrations of Eu^{3+} were subjected to experiments. The fluorescence intensity increased at the beginning and then decreased in accord with the increase of the concentration of Eu^{3+} (Fig. 4C), and reached the maximum at 25 μM of Eu^{3+}. Hence, conditions (pH=9.0, 10 μL AuNCs@DNA_{C12} and 25 μM of Eu^{3+}) were selected as the optimum to obtain a satisfactory signal.

Additionally, the fluorescence intensity reached an appropriate value instantly at room temperature due to its fast reaction, and 5 min and room temperature was finally selected as optimized conditions.

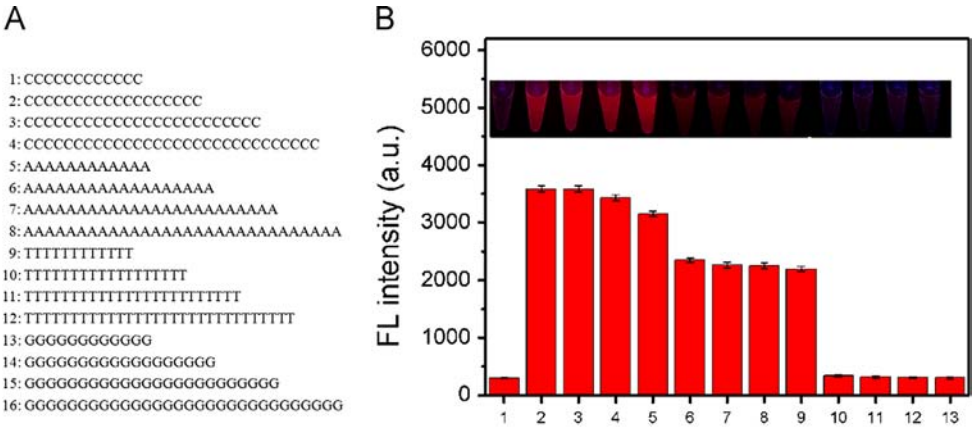

Fig. 3. (A) Different sequences of DNA; (B) Fluorescence bar plots of EuTC alone (1), the mixture of EuTC with AuNCs@DNA_{C12} (2), AuNCs@DNA_{C18} (3), AuNCs@DNA_{C24} (4), AuNCs@DNA_{C30} (5), AuNCs@DNA_{A12} (6), AuNCs@DNA_{A18} (7), AuNCs@DNA_{A24} (8), AuNCs@DNA_{A30} (9), DNA_{C12} (10), DNA_{C18} (11), DNA_{C24} (12), DNA_{C30} (13), respectively. Inset: Visual observation.

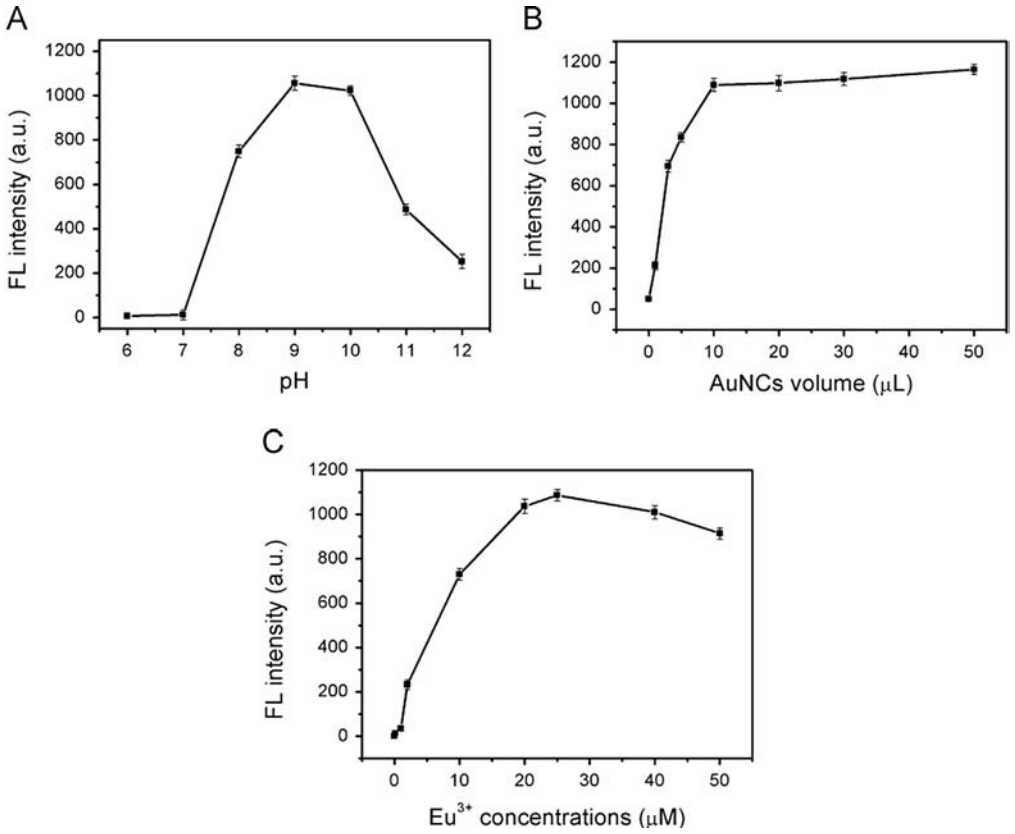

Fig. 4. Influence of pH (A), amounts of AuNCs@DNA_{C12} (B) and concentrations of Eu^{3+} (C) on the fluorescence intensity of Eu-AuNCs@DNA_{C12} in the presence of TC (10 μM).

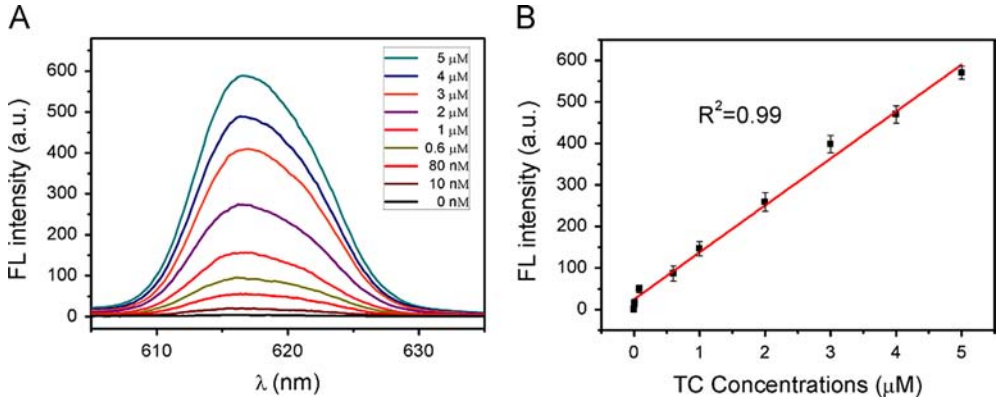

Fig. 5. (A) Fluorescence emission spectra of Eu^{3+}-AuNCs@DNA_{C12} in the presence of various concentrations of TC, (B) the linear relationship between the fluorescent intensity and the concentrations of TC.

3.6. Detection of TC

As shown in Fig. 5A, the fluorescence intensity of Eu^{3+}-AuNCs@DNA_{C12} increased in accord with the amount of TC added. Meanwhile, the fluorescent intensity increased versus the concentration of TC displayed a linear range from 10 nM to 5 μM (R^2=0.99) with the detection limit of 4 nM at a signal-to-noise ratio of 3 (Fig. 5B).

3.7. Interference experiments

To the best of our knowledge, various samples contain substances including biological compounds, amino acids, glucose, vitamins and common metal ions and so on. To address the question whether foreign coexisting substances show effect on the measurement of TC or not, further interference experiments were performed.

To validate the influence of biological compounds towards the fluorescence of EuTC-AuNCs@DNA_{C12}, bilirubin, bile acid, heparin sodium, ibuprofen and H_2O_2 were separately introduced into that complex. As Fig. 6A indicated, these biological compounds showed little effect on the fluorescence intensity of the complex under the current experimental condition.

As indicated in Fig. 6B, only TC increased the fluorescence of Eu^{3+}-AuNCs@DNA_{C12}, and no remarkable fluorescence responses were observed upon the addition of the amino acids (Gly, Cys, Ala, Glu, Ser, Val, Lys, Phe, and His), glucose, and ascorbic acid. Furthermore, in order to investigate the influence of other metal

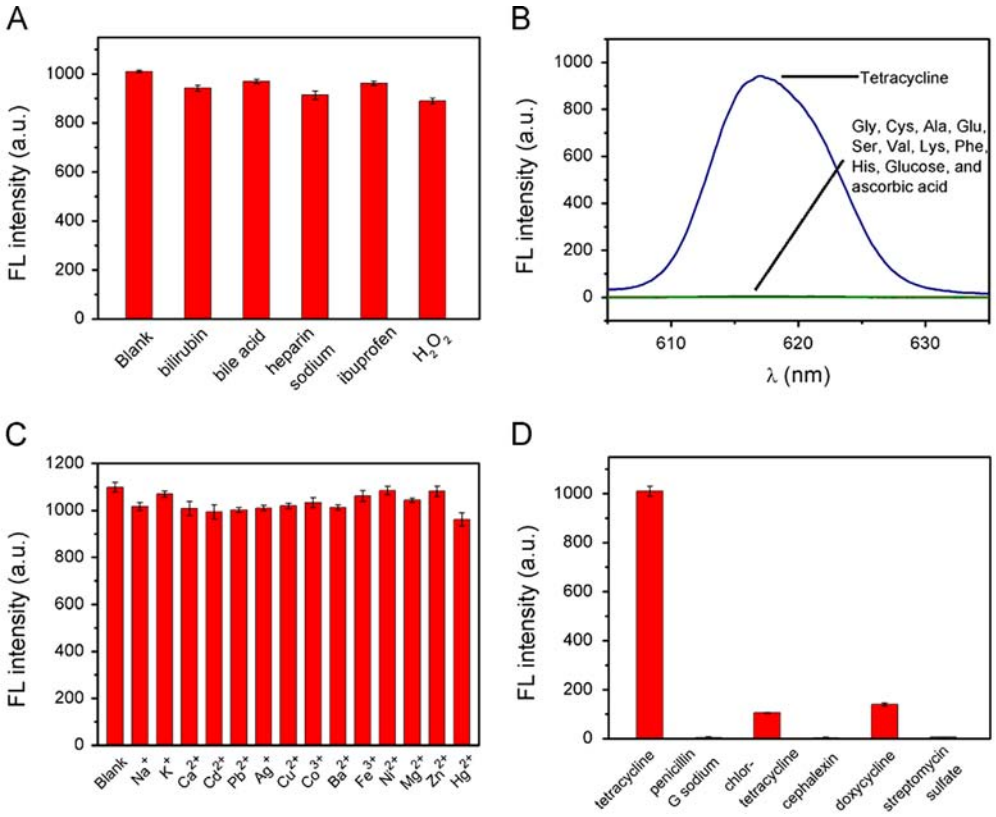

Fig. 6. (A) Influence of biological compounds (10 μM) on the fluorescence of EuTC-AuNCs@DNA_{C12} by introducing bilirubin, bile acid, heparin sodium, ibuprofen, H_2O_2 respectively; (B) Emission spectra of Eu^{3+}-AuNCs@DNA_{C12} in the presence of TC (10 μM), amino acids including (100 μM), glucose (100 μM) and ascorbic acid (100 μM); (C) influence of coexisting metal ions (100 μM) on the fluorescence intensity of EuTC-AuNCs@DNA_{C12}; (D) comparison of the fluorescence enhancement of Eu-AuNCs@DNA_{C12} by introducing tetracycline, penicillin G sodium, chlortetracycline, cephalexin, doxycycline, streptomycin sulfate, and each concentration was 10 μM.

Table 1
The recovery of TC in human urine and milk samples detected by the current method.

Samples	TC spiked (μM)	TC measured (μM)	Recovery (%)	RSD (%, $n=3$)
Human urine	2.00	1.88	94.0	2.3
	4.00	4.09	102.0	2.8
Milk	0.50	0.55	110.0	3.5
	3.00	2.87	95.7	3.1
	6.00	6.17	103.0	3.2

ions on the interaction between Eu^{3+} and TC, competitive experiments were further carried out in the presence of Eu^{3+} (25 μM) together with Na^+, K^+, Ca^{2+}, Cd^{2+}, Pb^{2+}, Ag^+, Cu^{2+}, Co^{2+}, Ba^{2+}, Fe^{3+}, Ni^{2+}, Mg^{2+}, Zn^{2+} and Hg^{2+}. As shown in Fig. 6C, all of the metal ions described here showed little effect on the fluorescence of EuTC-AuNCs@DNA_{C12}. All these results demonstrated that there was no obvious effect from coexisting substances during the procedure of assaying TC.

Next, the selectivity of this analytical strategy was evaluated by testing the response to other antibiotics (each 10 μM) under optimum conditions for the case of 10 μM tetracycline. Fig. 6D revealed that the additions of penicillin G sodium, chlortetracycline, cephalexin, doxycycline, and streptomycin sulfate respectively to this complex showed little effect. These data suggested that tetracycline specifically caused enhancement of the fluorescence intensity, supporting that this complex may serve as a potential fluorescence probe for assaying tetracycline.

3.8. Analysis of urine and milk samples

To evaluate its applicability, the described method was applied to the analysis of TC in one human urine sample and milk samples. Briefly, the urine and milk samples were directly supplemented with various amounts of TC. The TC content detected in all samples was derived from standard curves and regression equations. Importantly, as listed in Table 1, the average recovery in samples performed by the standard addition method and the RSD were generally satisfactory. Therefore, the present method has potential for practical applications of detecting TC in actual samples.

4. Conclusion

In summary, this is the first report on remarkably enhancing the fluorescence intensity of EuTC by introducing DNA-templated AuNCs, while this complex was employed as a base of fluorescent system. The novel proposed system was created by adding AuNCs@DNA rather than AuNCs@BSA and AuNCs@His, and the sequences of DNA for synthesizing AuNCs played a crucial role during the fluorescence-enhancing process, whereas the lengths of DNA were not as vital as the sequences. Additionally, we have successfully utilized this enhanced-fluorescence method for simple, sensitive and cost-effective quantification of TC while Eu^{3+}-AuNCs@DNA_{C12} serving as a base. The detection of TC is in a linear range from 10 nM to 10 μM, with a detection limit of 4 nM. Significantly, this strategy may broaden potential ways to detect TC in actual samples.

Acknowledgments

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2013.12.008.

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