Dalton Transactions

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Dalton Transactions

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Fluorescent Detection for TNT and 4-Nitrophenol by BSA Au nanoclusters

Xin Yang,[a] Junhai Wang,[a] Dongyue Su,[a] Qingdong Xia,[a] Fang Chai,*[a] Chungang Wang*[b] and Fengyu Qu*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Rapid and sensitive detection of 2, 4, 6-trinitrotoluene (TNT) and 4-Nitrophenol (4-NP) have attracted considerable attention due to their wide applications as nitroaromatic explosive materials. A novel fluorescent method for TNT and 4-NP based on bovine serum albumin functionalized fluorescent gold nanoclusters (BSA Au-NCs) has been developed. The detection probe BSA Au-NCs can be used as fluorescent probe for the sensitive and selective detection of TNT and 4-NP, simultaneity. Good linearity of fluorescence detection using BSA Au-NCs as fluorescent probe were observed for TNT and 4-NP concentrations in the range 10^{-8}-5×10^{-5} M and 10^{-9}-5×10^{-5} M, with detection limit of 10 nM and 1 nM, respectively. The high specificity of TNT and 4-NP with BSA Au-NCs interactions provided the excellent selectivity towards detecting TNT and 4-NP over other relevant nitroaromatic compounds. This system can be applied to test trips to detect TNT and 4-NP with high sensitive and selectivity. The vapour of TNT and 4-NP can be detected by BSA Au-NCs test paper within 1 min with detection limit of 10 pM and 1 pM.

Introduction

Rapid and selective detection of nitroaromatic explosives such as 2,4,6-trinitrotoluene (TNT) and 4-Nitrophenol (4-NP) is an important topic for both potential homeland security threats and environment, because nitroaromatic explosives such as TNT and 4-NP are serious pollution sources of water and potential homeland security threats. It is important to note that TNT is common explosive materials of military and terrorist activities.[1] TNT is also a major source of hazardous water pollution produced through military preparation of landmines, besides one of the most commonly used nitroaromatic explosives.[2] Meanwhile, 4-NP is an aromatic phenolic compound, which is widely used in the manufacturing of the most popular analgesics, pesticides, dyes, and processing of leather. 4-NP is amongst the highly hazardous and toxic phenols which can cause significant damages to the health and the environment.[3, 4] Owing to their significant toxicity to both environment and human, TNT and 4-NP have been included in the Environmental Protection Agency List of Priority Pollutants. So, accurate and ultrasensitive detection of nitroaromatic explosives such as TNT and 4-NP will be of great significance because of their serious pollution and potential security threats.

Recently, different sensors for analyzing explosives, and particularly, nitroaromatic derivatives were reported.[5] For detection of TNT, different analysis methods have been reported.[2, 5-9] Cui and coworkers developed a homogeneous label-free aptasensor for TNT detection based on an assembly strategy of electrochemiluminescent graphene oxide with AuNPs and aptamer.[6] Ray and co-workers reported a highly selective and surface enhanced Raman spectroscopy probe for detecting TNT by cysteine modified gold nanoparticle, the TNT can be detected with 2 pico molar level in aqueous solution.[7] Willner et al developed a series of sensitivity electrochemical sensor for TNT detection based on π-donor–acceptor interactions between TNT and π-donor-modified electrodes or π-donor-cross-linked AuNP-modified electrodes.[5,8] Among them, the colorimetric method has been attention by many researchers due to their observation directly and no sophisticated instruments are required. Mao's group developed a simple method for the colorimetric visualization of TNT at picomolar levels based on cysteamine functionalized gold nanoparticles.[9] Ray and co-workers detected for TNT recognition in 100 picomolar by colorimetric response using para-aminothiophenol modified gold nanoparticle based colorimetric probe.[2] Liu and co-workers exploit a series research about detection for TNT using noble nanoparticles by colorimetric and SERS method with high detection limit of 0.4 pM. [10-12]

Moreover, fluorescence method has individual advantage in many circumstances. The fluorescent probe can be used to detect nitroaromatic with higher sensitivity.[13-24] Zhang and coworkers[19-21] developed a series of fluorescence quenching methods for TNT assay. Wang and co-workers exploited a novel upconversion luminescence enhancement strategy for detecting TNT in aqueous media based on the SPR effect between $NaYF_4$: Yb^{3+}/Er^{3+} upconversion nanoflowers and gold nanoparticles.[22] Cai and co-workers demonstrates a novel method using L-cysteine-capped CdTe quantum dots to assay TNT with detection

limit of 1.1 nM.[23]

For detection of 4-NP, there are few reports compared to TNT. Therefore, environmental monitoring of 4-NP becomes an increasing demand. To meet this goal, a number of highly sensitive and selective 4-NP sensors have been developed recently. [3,25,26] Kubota' group developed a highly sensitive amperometric sensor for 4-NP in nanomolar levels using a modified glassy carbon electrode.[3] Mehdinia and co-workers exploited the detection of 4-NP by using of molecularly imprinted polymer on the surface of magnetic nanoparticles.[22] Zhang's group reported an electrochemical sensor for 4-NP detection based on ZnO /multiwall carbon nanotubes-chitosan nanocomposite with a detection limit at 10^{-9} M.[26] However, a critical drawback of some methods were complicated and time-consuming, therefore, it would desirable design a rapid, simple and intuitionistic sensor to enhance the efficiency of this detection. The fluorescent probe may be the appropriate choice.

We herein report a novel fluorescent sensor based on bovine serum albumin (BSA) functionalized fluorescent gold nanoclusters (BSA Au-NCs), which was found to be a kind of effective chemosensor for the sensitive and selective detection of both TNT and 4-NP. Besides, this system can be applied to test trips for the highly sensitive and selective detection of TNT and 4-NP.

2. Experimental

2.1 Materials and chemicals

All chemicals used were of analytical grade or of the highest purity available. Chloroauric acid ($HAuCl_4 \cdot 3H_2O$, 99.9%) were obtained from Alfa Aesar (USA) and used as received. BSA (≥98%) was obtained from Genview. 2,4,6-Trinitrotoluene (TNT) (≥98%) and 2,4-dinitrotoluene (DNT) (98%) were supplied by National Security Department of China. 4-Nitrophenol (4-NP) (98%), 2,4,6-Trinitrophenol (TNP) (AR, 98%), 2-Nitrophenol (2-NP) (AR, 98%), 3-Nitrophenol (3-NP) (AR, 98%) were purchased from Aladdin (Shanghai). Nitrobenzene (NB) (AR, 98%), 3-nitrotoluene (3-NT) (98%), toluene (98%) and acetone (AR) were purchased from Beijing Chemical Reagent Company (Beijing, China). All glassware was thoroughly cleaned with freshly prepared 3:1 HCl/HNO_3 (*aqua regia*) and rinsed thoroughly with Mill-Q (18.2 MΩ cm^{-1} resistance) water prior to use. Mill-Q water was used to prepare all the solutions in this study.

2.2 Characterization

The morphology and size of the BSA Au-NCs were characterized by transmission electron microscopy (TEM) using a JEOLFETEM-2100 transmission electron microscope operated at an accelerating voltage of 200 kV. Absorption spectra were recorded on a UV–vis spectroscopy was performed with a UV-2550 spectrophotometer (Shimadzu, Japan) at room temperature. Fluorescence spectra of BSA-Au NCs were recorded by a PerkinElmer LS-55 fluorescence spectrometer.

2.3 Preparation of BSA Au Clusters

BSA Au Clusters was prepared according the literature report.[27] In a typical experiment, aqueous $HAuCl_4$ solution (5 mL, 10 mM, 37 °C) was added to BSA solution (5 mL, 50 mg/mL, 37 °C) under vigorous stirring. Two minutes later, NaOH solution (0.5 mL, 1 M) was introduced, and the mixture was incubated at 37 °C for 12 h. The color of the solution changed from light yellow to light brown, and then to deep brown. The result solution was highly fluorescent BSA Au-NCs with red emission. And the pH value of as prepared BSA Au-NCs was about 10. The deep brown solution of BSA-GNPs emits an intense red fluorescence (Fig. S1(b)). And the TEM of BSA Au-NCs can be observed in Fig.S2. After diluted 10 times, the diluted BSA Au-NCs were used as the fluorescent probe of detection for TNT and 4-NP, respectively.

2.4 Detection for TNT and 4-NP

The different concentrations of fresh solution of TNT and 4-NP in acetone were prepared as used samples in experiments of detection. The as-prepared BSA Au-NCs were diluted to 10 times, the resulting BSA Au-NCs solution was used as detection probe in fluorescent detection for TNT and 4-NP, respectively. The process of detection for TNT and 4-NP was simple and speedy. Typically, 200 μL of BSA Au-NCs probe was mixed with 400 μL different concentrations of TNT in a quartz cuvette, respectively. Fluorescence spectra were recorded immediately after fully mixing the analyte with BSA Au-NCs probe. Meanwhile, the fluorescence responses of BSA Au-NCs to nitroaromatics were also measured by the identical procedure.

2.5 Experiment of detection for nitroaromatics by BSA Au-NCs test papers

The BSA Au-NCs test paper can be prepared simply. Firstly, the filter paper was cut into certain strip shape. Successively, the filter paper strips were soaked in BSA Au-NCs solution for about 1h. After dried in air, the BSA Au-NCs test papers were prepared. The as prepared BSA Au-NCs test papers can be used detecting the vapour of TNT and 4-NP with simple operation. Vapour detection was done with a thin centrifuge tube immediately after removal from the sealed vial, and was fully detection after 1-10 min. The demonstration of detecting process was showed as description of Fig. S2. The sensitivity and selectivity experiment was in accord with above process. The results were obtained by contrasting the fluorescent images of the reacted BSA Au-NCs test papers at UV-lamp.

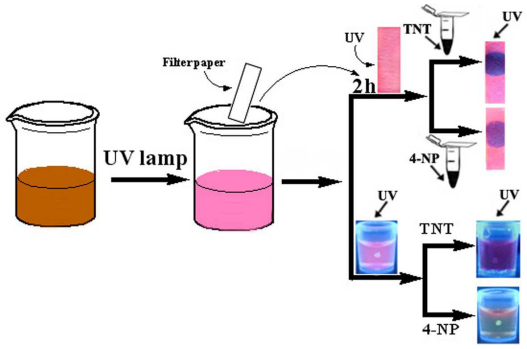
Result and discussion

3.1. Mechanistic Basis for the Sensing System

The overall detection strategy is shown is Scheme 1. As proved by many researchers[6, 9], that as one kind of electron acceptor, TNT can interact with electron donors, typically primary amines, through the strong p-donor (amine)–p-acceptor (TNT) interaction. Amino groups usually donate electrons to electron-deficient molecules, which can readily interact with electron-deficient molecules, for example TNT, to form Meisenheimer complexes (MHCs) [20, 24, 28] The formation of MHCs results in the appearance of new absorption peaks at visible region[29, 30]. BSA is a large globular protein with a good essential amino acid profile, and rich in primary amine groups (cysteine, tryptophan, and tyrosine). There are lots of amino acid residues especially of cysteine on the surfaces of BSA Au-NCs, which ensuring that the BSA Au-NCs have a strong surface affinity to TNT (4-NP) and obvious fluorescence quenching for the ultratrace detection of

TNT (4-NP) qby the donor–acceptor (D–A) interaction between TNT (4-NP) and primary amines.[6, 9, 22]

As illustrate in Scheme 1, the BSA Au-NCs solution was fluorescent sensor of TNT and 4-NP. The fluorescence emission of BSA Au-NCs was quenched by the addition of TNT and 4-NP, which can be detected at the UV lamp. When adding to nitroaromatics (TNT or 4-NP), the primary amines of BSA Au-NCs may be cooperated with nitroaromatics, result in the quenching of fluorescence. The distinguish detection of TNT and 4-NP by BSA Au-NCs can be observed from the different color at daylight (red of TNT and yellow of 4-NP), UV-lamp and corresponding UV-vis spectra and fluorescent spectra. The test paper can be prepared by soaking the filer paper into BSA Au-NCs. The test paper take on red emission under UV-lamp, when met the vapour of TNT and 4-NP, the red emission could be quenched, which resulted in the test paper taking on blue color. Thus, the quantification of TNT and 4-NP can be obtained by fluorescent detection of BSA Au-NCs. In this work, fluorescence emission is acquired to investigate the interaction between nitroaromatics and BSA Au-NCs.



Scheme 1. Schematic of the detection for TNT and 4-NP by BSA Au-NCs

The fluorescence emission and morphologies of the synthesized BSA Au-NCs were examined by fluorescent spectra and TEM. The fluorescence spectra of dilute BSA Au-NCs (1/10) at room temperature are shown in Figure S1. The fluorescence spectra of dilute aqueous BSA Au-NCs show an emission maximum at 358 nm upon excitation at 260 nm and an emission maximum at 640 nm excited at 470 nm. The fluorescence spectra of dilute acetone solution of BSA Au-NCs exhibited emission maximum at about 414 nm (blue) and 640 nm (red), which excited at 260 nm and 470 nm respectively. Due to the influence of solvent, the red emission of BSA Au-NCs decreased obviously. But the blue emission did not affected evidently, so, the fluorescence detecting for nitroaromatics can be investigated the blue emission mainly. From the Fig. S2A, the TEM images of BSA Au-NCs indicated the original dispersed state of nanoparticles with diameter in 3±0.6 nm.

3.2. Sensitivity

3.2.2. Fluorescence Responses of BSA Au-NCs to TNT and 4-NP.

The maximum fluorescence emission of the BSA Au-NCs was shown in Fig. 1a, the maximum emission wavelengths was at 414 nm excited at 260 nm. The fluorescence emission of BSA Au-NCs was readily quenched in the presence of TNT and 4-NP. As illustrated in Fig. 1a, after diluted 10 times the emission of BSA Au-NCs solution was still strong with bright pink fluorescence emission under a UV lamp (Fig. 1b). When in presence of different concentrations of TNT, the fluorescence emission of BSA Au-NCs was quenched immediately. The fluorescence emission intensity was sensitive and proportionately decreased with an increasing concentration of TNT (Fig. 1a). Accompany the increase of concentration of TNT, the max fluorescence emission of BSA Au-NCs decreased intensely and blue shifted from 414 nm to 398 nm. Fig. 1a revealed a gradual shift in the proton resonances for the methyl groups of amine and the methylene group to a lower field, along with the downfield shift of the aromatic proton resonance of TNT, [31-34] confirming the interaction of BSA with the TNT. When the concentration of TNT reached 10^{-3} M, the fluorescence had decayed to less than half of its original intensity. The fluorescence intensity of BSA Au-NCs toward TNT decreased linearly. Detection limit is one of the main parameters to evaluate an analytical method or system. As described in the inset of Fig. 1a, a linear relation (range was 10^{-8} to 5×10^{-5} M) with R^2 of 0.9727 could be described by the equation, I=0.9339-2.1096C, where I and C denote the fluorescent intensity at 414 nm and concentration of TNT, respectively. Under the current experimental condition, the lowest TNT concentration that could be detected was 10 nM. Moreover, corresponding photograph (Fig. 1b) exhibits a very obvious fluorescence quenching with TNT analyte under UV-lamp. From Fig. 1b, the strong pink emissions of BSA Au-NCs were decreased gradually with the addition concentrations of TNT (from 10^{-9} to 10^{-3} M) under UV light.

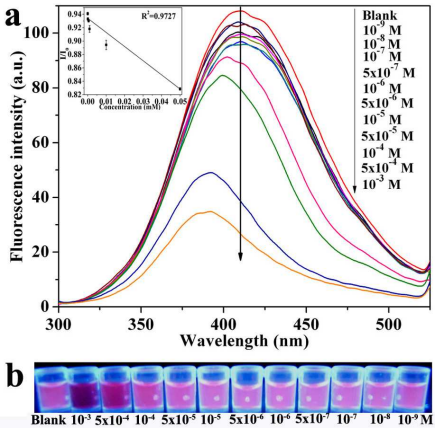


Fig. 1. (a) Fluorescence emission spectra of BSA Au-NCs in presence of varying concentrations of TNT, the inset shows the linear relationship between fluorescence emission with concentration of TNT (10^{-8}-5×10^{-5} M). (b) Corresponding photograph of detection for TNT under UV light.

Part a of Figure 2 showed the fluorescence responses of BSA Au-NCs to 4-NP analyte in solution. The fluorescence intensities decreased with increasing successive of 4-NP concentrations in BSA Au-NCs probes. With the addition of 4-NP, further aggregation of the BSA Au-NCs occurred based on the charge transfer interaction between 4-NP and amine groups of BSA Au-NCs.[9] When the addition of 4-NP was more than 10^{-5} M, with the decrease of intensity, the fluorescence emission of BSA Au-NCs has split two peaks (394 nm and 421 nm) completely. The fluorescence emission at 394 nm was blue shift to about 366 nm and almost quenched by 4-NP with concentration of 10^{-3} M. The related photograph in Fig. 2b illustrated the quenching of BSA

Au-NCs clearly.

Concerning the three electron-withdrawing nitro groups of TNT molecule, the negative charge could be dispersed throughout the entire molecular, leading to a strongly reduced electron density of the aromatic ring. Though the phenolic group was a weak electron donating group, the electron-withdrawing nitro group of 4-NP play a definitive role to make the whole molecule became electron-deficient one in this detection. Amino groups of BSA molecules usually donate electrons to electron-deficient molecules, which can readily interact with electron-deficient TNT or 4-NP. The fluorescence emission of BSA Au-NCs was quenched substantially which indicated that interaction between amino groups of BSA with nitroaromatic. Therefore, TNT and 4-NP detection could be easily realized via monitoring the fluorescence quenching of the BSA Au-NCs under the UV light. There exists a linear relationship of fluorescence intensity of detection between 10^{-9} and 5×10^{-5} M. As shown in the inset of Fig. 2a, the fluorescence intensity of BSA Au-NCs toward 4-NP decreased linearly over the TNT concentration range of from 10^{-9} to 10^{-5} M. From the linear regression equation: I=0.9334–9.37338C, the correlation coefficient was calculated to be 0.9687. Thus, we suggest that BSA Au-NCs can be used for detecting 4-NP with the minimum detectable concentration at 1 nM. These observations clearly indicate that the amine ligands of BSA were very stable and highly productive, ensuring that the nanoclusters have a strong surface affinity to TNT and 4-NP and prominent fluorescence quenching for the ultratrace detection of TNT and 4-NP.

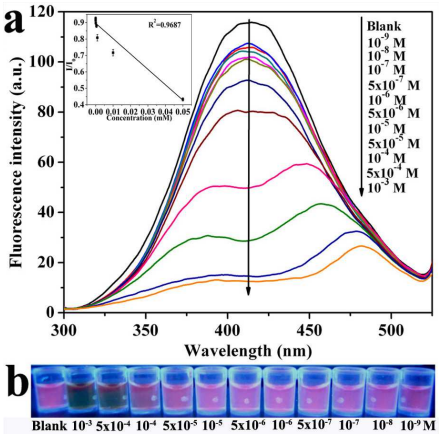


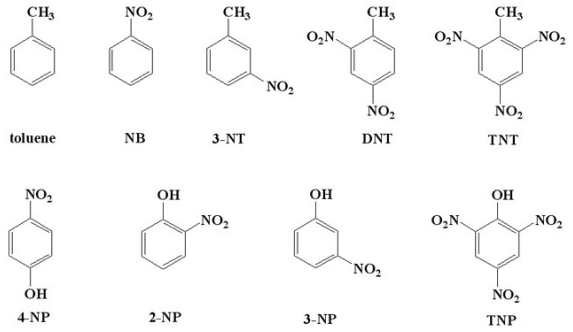
Fig. 2. (a) Fluorescence emission spectra of BSA Au-NCs in presence of varying concentrations of 4-NP, the inset was the linear relationship between fluorescence emission with concentration of 4-NP (10^{-9}-5×10^{-5} M). (b) Corresponding photograph of detection for 4-NP under UV light.

3.3 Effect of pH values

To further demonstrate mechanism of detection in this method, the effect of detection by BSA Au-NCs at different pH values (pH=5.5, 7 and 10) were investigated respectively. As seen in the Fig. S4 and S5, the detection for TNT and 4-NP with different concentrations at different pH values were performed respectively. The fluorescent detection of TNT at pH=5.5 and pH=7 have not regular variety, though the most of fluorescent intensity of BSA Au-NCs were reduced by TNT. Though the intensity of fluorescence emission at pH=5.5 and pH=7 were reduced accompany the addition of concentration of TNT, but they did not decrease with gradually linear ship. However, the detection for TNT by BSA Au-NCs at pH=10 was feasible. The most possible reason was TNT reacted with NaOH product alkali metal salt, the interaction of alkali metal salt with the BSA Au-NCs result in the quenching of fluorescence emission beside the D–A interaction from TNT and amines. The corresponding absorbance of detection at different pH values were recorded in Fig. S6, which indicated that the absorbance of mix solution was affect by pH values especially to TNT. Compared with TNT, the detections for 4-NP were not affected by different pH values. As depict in Fig. S5, the fluorescent intensity decreased gradually with the addition of concentration of 4-NP at pH= 5.5, 7 and 10, respectively, which indicated the good applicability of BSA Au-NCs for 4-NP. Though the effect of pH values can be neglect, the optimized condition was at pH=10, which probably due to the interaction between 4-nitrophenolate and BSA Au-NCs.

3.4. Selectivity of the sensing system

To further ascertain the recognition selectivity of the BSA Au-NCs, we investigated the fluorescence response of this approach for TNT and 4-NP over other nitroaromatic under the same conditions. We compared the detection of other structurally similar nitroaromatic compounds (10^{-3} M in acetone) (point out at scheme 2), such as toluene, nitrobenzene (NB), 3-nitrotoluene (3-NT), 2, 4, 6-Trinitrophenol (TNP), 2-Nitrophenol (2-NP), 3-Nitrophenol (3-NP) and 2, 4-dinitrotoluene (DNT).



Scheme 2. The structure of nitroaromatics used in the present study

The selectivity by fluorescence detection was also investigated in detail. Fig. 3a shows that the fluorescence of BSA Au-NCs was not fully quenched by any nitroaromatic except 4-NP, which explain the specific of 4-NP. Compare with others, the intensity of fluorescence emission with 2-NP has quenched evidently in the same concentrations, which can be seen from the Fig. 3a. In order to prove the selectivity of BSA Au-NCs further, the reaction between BSA Au-NCs and 10^{-4} M of 4-NP, 2-NP and 3-NP at was tested through fluorescence spectra. When in presence of 10^{-4} M of 4-NP, the intensity of fluorescence of BSA Au-NCs at 414 nm almost quenched completely (Fig. S7). However, the intensity of fluorescence emission of BSA Au-NCs with 2-NP and 3-NP were much higher than 4-NP, which indicated though the possible effect could be occurred in presence of the high concentration (10^{-3} M) of 2-NP and 3-NP, there is good selectivity existed in detection for 4-NP by BSA Au-NCs. The main reason of good selectivity of 4-NP over 2-NP and 3-NP was the stronger D–A interaction, otherwise the interaction between BSA and 4-nitrophenolate is not be neglected. Theoretically, the nitro in 4-NP is an electron withdrawing group. The acidity of 4-

NP is stronger than that of 2-NP and 3-NP due to the effect of electron withdrawing and the electron withdrawing effect of conjugation. So the product 4-nitrophenolate was more than 2-NP and 3-NP and corresponding function between BSA was more stable. Moreover, other nitroaromatics including TNP have no influence on the detection (Fig. 3b), indicating that this novel sensor has excellent selectivity for TNT. The reason is that TNP, DNT, 3-NT and NB are much weaker Lewis acids or electronic acceptors compared to TNT, and they cannot likely form the effective Meisenheimer complex with amine groups like TNT.[18] The photograph of selectivity illustrated the quenching of BSA Au-NCs fluorescence by TNT and 4-NP. The fluorescence emission of 2-NP turned to red emission, which could be visualized with the naked eye. However, other nitroaromatic could not quench the fluorescence of BSA Au-NCs completely at the same conditions. Importantly, from the Fig. 3b, the photo images of fluorescence of the BSA Au-NCs was quenched in the presence of TNT and 4-NP, while apparent fluorescence quenching was not completely observed in the presence of 10^{-3} M of other nitroaromatic.

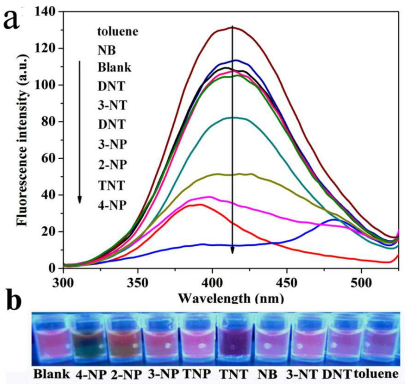


Fig. 3. (a) Fluorescence emission of BSA Au-NCs in presence of different nitroaromatic compounds. (b) Photograph of the different explosives under visible light (concentrations of all analytes were 10^{-3} M).

To further illustrate the selectivity of this BSA Au-NCs-based detection system, we used the quenching constants to express the intensity ratio of decrease. The quenching constant was 1- I/I_0 (value of fluorescent intensity of analyte/intensity of control). And corresponding value of quenching constant was 1- I/I_0. As listed in Fig. 4, the quenching constants in presence of all of nitroaromatics at 414 nm can be observed clearly. By comparison, the quenching constants of BSA Au-NCs with TNT and 4-NP are much larger than those with 2-NP, 3-NP, 3-NT, TNP, DNT, toluene, NB, respectively. 4-NP quenched the fluorescence emission almost completely. It can be deduced that highest fluorescence quenching of BSA Au-NCs with TNT and 4-NP are closely related to the formation of amine complexes at the surface of BSA. Though the quenching constant of 2-NP, 3-NP and TNP were much higher than other nitroaromatics, moreover the weak interactions may lie between amine ligands and NB, 3-NT molecules and so on, the detection of TNT and 4-NP cannot be influenced. So, the selectivity of detection distinguish from other nitroaromatic can be deduced by fluorescent probe, especially fluorescent imaging.

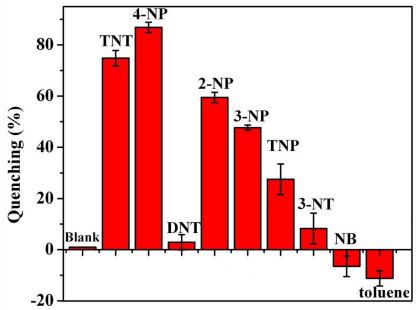


Fig. 4. The fluorescence emission quenching constants of nitroaromatic at 414 nm, concentrations of all analytes were 10-3 M, (The error bars represent standard deviations based on three independent measurements.)

3.4 Detection of vapour.

To evaluate the potential application of this assay, BSA Au-NCs were attempted to disperse on a filter paper strip. Although most of the work was performed in solution, the feasibility of solid state detection of nitroaromatic vapours were demonstrated by BSA Au-NCs test paper. BSA Au-NCs were kept in reserve by filter paper in the process of absorption. Meanwhile, there has been considerable interest in the detection of nitroaromatic vapours.

The investigation of vapour detection such as the condition of preparation of test paper and reaction time were discussed in detail. From Fig. 5a and 5b, the different concentrations of TNT and 4-NP quenched the red fluorescence emission of BSA Au-NCs test paper, resulted in the BSA Au-NCs test paper was blue in colour (which was the background colour of filter pater) under UV lamp. The blue colour of test papers was deepened gradually with the addition of concentrations and reaction time. It can be observed, when the concentrations of TNT exceed 10^{-11} M, the vapour of TNT can quench the fluorescence emission of BSA-GNPs test paper within 1 min. The detection limit of TNT by test paper can be determined at 10 pM. However, the test paper can be quenched by 10^{-12} M of 4-NP within 1min, which indicated the detection limit was 1 pM. The BSA Au-NCs test paper can strongly adsorb TNT or 4-NP vapour from atmospheric phase by the specific interactions of TNT (4-NP) with amine ligands and exhibit an amplifying quenching response.

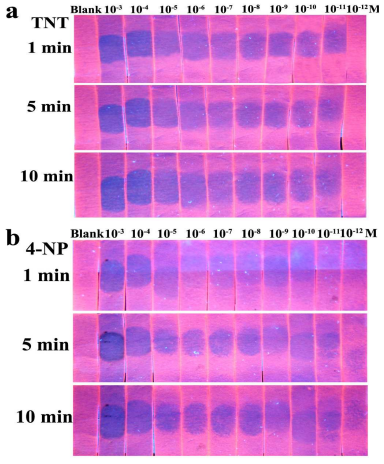


Fig. 5. Detection Photographs of the test strips with BSA Au-NCs under UV light, results of sensitivity of a. TNT, b. 4-NP with different reaction time.

The selectivity of BSA Au-NCs test paper was attempted to detect other nitroaromatics at same conditions. As depicted in Fig. 6, the photo images of the test strips reacting with different nitroaromatics (10^{-4} M) presented clear contrast, which can be determined the specific of test strips for TNT and 4-NP. The BSA Au-NCs can be used to detect 4-NP over 2-NP, 3-NP with good selectivity, which can also be proved by the vapour detection.

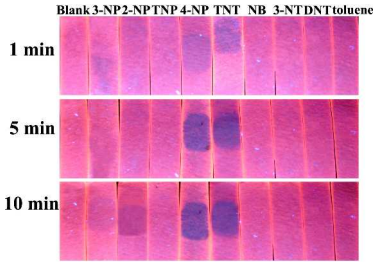


Fig.6. The vapour detection of a. TNT and b. 4-NP within 1-10 min by the BSA Au-NCs test paper (concentrations of all analytes were 10^{-4} M).

All these results indicate that the BSA Au-NCs provide an effective fluorescent platform for TNT and 4-NP detection with high sensitivity and selectivity.

Conclusions

In conclusion, we have demonstrated a novel fluorescent method to detect TNT and 4-NP, simultaneity. The present sensor utilizes a BSA Au-NCs detecting for TNT and 4-NP though exceptional fluorescent method with the limit of 10 nM and 1 nM, respectively. The BSA Au-NCs detecting probe can detect TNT and 4-NP over other nitroaromatic simultaneously. Especially, the proposed method allows us to detect TNT and 4-NP through fluorescent test paper conveniently. The fluorescent test paper can detect the vapour of TNT and 4-NP with limit of 10 pM and 1 pM, respectively, which appears to great potential practicality for the detection of TNT and 4-NP in real samples.

Acknowledgements

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (Project No. 21205024, 634166684), the National Science Foundation for Post-doctoral Scientists of China (Grant No. 2012M520659, 2013T60307), Program for Scientific and Technological Innovation Team Construction in Universities of Heilongjiang (No. 2011TD010).

Notes and references

1 M. N. Germain, R. L. Arechederra and S. D. Minteer, *J. Am. Chem. Soc.*, 2008, **130**, 15272–15273.
2 S. S. R. Dasary, D. Senapati, A. K. Singh, Y. Anjaneyulu, H. T. Yu and C. R. Paresh, *ACS Appl. Mater. Interfaces.*, 2010, **2**, 3455–3460.
3 R. L. Phabyanno, W. J. R. Santos, O. F. G. Marìlia, A. A. Tanaka, S. M. C. N. Tanaka and L. T. Kubota, *Electroanal*. 2008, **20**, 2333 – 2339.
4 J. Tang, D. P. Tang, B. L. Su, J. X. Huang, B. Qiu and G. N. Chen, *Biosens. Bioelectron*., 2011, **26**, 3219–3226.
5 M. Riskin, R. Tel-Vered, O. Lioubashevski and I. Willner, *J. Am. Chem. Soc.*, 2009, **131**, 7368–7378.
6 Y. Q. Yu, Q. Cao, M. Zhou and H. Cui, *Biosens. Bioelectron*., 2009, **43**, 137–142.
7 S. S. R. Dasary, A. K. Singh, D. Senapati, H. T. Yu and C. R. Paresh, *J. Am. Chem. Soc.*, 2009, **38**, 13806–13812.
8 M. Riskin, R. Tel-Vered, T. Bourenko, E. Granot and I. Willner, *J. Am. Chem. Soc.*, 2008, **30**, 9726–9733.
9 Y. Jiang, H. Zhao, N. N. Zhu, Y. Q. Lin, P. Yu and L. Q. Mao, *Angew. Chem. Int. Ed.,* 2008, **47**, 8601–8604.
10 H. L. Liu, Y. D. Sun, Z. Jin, L. B. Yang and J. H. Liu, *Chem. Sci.,* 2013, **4**, 3490-3496.
11 H. L. Liu, D. Y. Lin, Y. D. Sun, L. B. Yang and J. H. Liu, *Chem. Eur. J.*, 2013, **19**, 8789-8796.
12 D. Y. Lin, H. L. Liu, K. Qian, X. Zhou, L. B. Yang and J. H. Liu, *Anal Chim Acta.*, 2012, **744**, 92-98.
13 Y. X. Ma, H. Li, S. Peng and L. Y. Wang, *Anal. Chem.*, 2012, **84**, 8415–8421.
14 B. Balan, C. Vijayakumar, M. Tsuji, A. Saeki and S. Seki, *J. Phys. Chem. B.*, 2012, **116**, 10371–10378.
15 Y. K. Che, D. E. Gross, H. L. Huang, D. J. Yang, X. M. Yang, E. Discekici, Z. Xue, H. J. Zhao, J. S. Moore and L. Zang, *J. Am. Chem. Soc.*, 2012, **134**, 4978–4982.
16 B. Gole, A. K. Bar and P. S. Mukherjee, *Chem. Commun.*, 2011, **47**, 12137–12139.
17 K. K. Kartha, S. S. Babu, S. Srinivasan and A. Ajayaghosh, *J. Am. Chem. Soc.*, 2012, **134**, 4834–4841.
18 R. C. Stringer, S. Gangopadhyay and S. A. Grant, *Anal. Chem.*, 2010, **82**, 4015–4019.
19 C. G. Xie, B. H. Liu, Z. Y. Wang, D. M. Gao, G. J. Guan and Z. P. Zhang, *Anal Chem*., 2008, **80**, 437–443.
20 R. Y. Tu, B. H. Liu, Z. Y. Wang, D. Gao, F. Wang, Q. Fang and Z. P. Zhang, *Anal Chem*., 2008, **80**, 3458–3465.
21 D. M. Gao, Z. Y. Wang, B. H. Liu, L. Ni, M. H. Wu and Z. P. Zhang, *Anal. Chem*., 2008, **80**, 8545–8553.
22 N. N. Tu and L. Y. Wang, *Chem. Commun*., 2013, **49**, 6319–6321.
23 Y. F. Chen, Z. Chen, Y. J. He, H. L. Lin, P. T. Sheng, C. B. Liu, S. L. Luo and Q. Y. Cai, *Nanotechnology*, 2010, **21**, 125502 (5pp).
24 W. S. Zou, Y. Q. Wang, F. Wang, Q. Shao, J. Zhang and J. Liu, *Anal Bioanal Chem*., 2013, **405**, 4905–4912.
25 A. Mehdinia, T. B. Kayyal, A. Jabbari, M. O. Aziz-Zanjani and E. Ziaei, *J. Chromatography A*, 2013, **1283**, 82-88.
26 Y. F. Hu, Z. H. Zhang, H. B. Zhang, L. J. Luo and S. Z. Yao, *Thin Solid Films*, 2012, **520**, 5314–5321.
27 J. P. Xie, Y. G. Zheng and J. Y. Ying, *J. Am. Chem. Soc.*, 2009, **131**, 888–889.
28 Y. Q. Wang, W. S. Zou, *Talanta*, 2011, **85**, 469–475.
29 W. S. Zou, J. Q. Qiao, X. Hu, X. Ge and H. Z. Lian, *Anal. Chim. Acta.*, 2011, **708**, 134–140.
30 W. S. Zou, J. Yang, T. T. Yang, X. Hu and H. Z. Lian, *J. Mater. Chem.*, 2012, **22**, 4720–4727.
31 H. Kong, J. Sinha, J. Sun, H. E. Katz, *Adv. Funct. Mater.*, 2013, **23**, 91-99.
32 K. S. Bejoymohandas, T. M. George, S. Bhattacharya, S. Natarajan, M. L. P. Reddy, *J. Mater. Chem. C*., 2014, **2**, 515–523.
33 J. L. Pablos, M. T. López, F. Serna, F. C. García and J. García, *Chem. Comm.*, 2014. **50**, 2484–2487.
34 Y. H. Lee, H. Liu, J. Y. Lee, S. H. Kim, S. K. Kim, J. L. Sessler, Y. Kim and J. S. Kim, *Chem. Eur. J*., 2010, **16**, 5895–5894.

[a] *Key Laboratory of Design and Synthesis of Functional Materials and Green Catalysis, Colleges of Heilongjiang Province, Harbin Normal University, 150025, P.R. China. E-mail: fangchai@gmail.com, 13654558066@163.com*
[b] *Faculty of Chemistry, Northeast Normal University, Changchun, 130024, P.R. China. E-mail: wangcg925@nenu.edu.cn*

† Electronic Supplementary Information (ESI) available: [Fig. S1-S7]. See DOI: 10.1039/b000000x/

Graphic Abstract