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Instant Visual Detection of Trinitrotoluene Particulates on Various Surfaces by Ratiometric Fluorescence of Dual-Emission Quantum Dots Hybrid

Kui Zhang,[†,‡] Haibo Zhou,[†,‡] Qingsong Mei,[†,‡] Suhua Wang,*[,†,‡] Guijian Guan,[†] Renyong Liu,[†] Jian Zhang,[†,‡] and Zhongping Zhang*[,†,‡]

[†]Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei, Anhui 230031, China

[‡]Department of Chemistry, University of Science & Technology of China, Hefei, Anhui 230026, China

Supporting Information

ABSTRACT: To detect trace trinitrotoluene (TNT) explosives deposited on various surfaces instantly and on-site still remains a challenge for homeland security needs against terrorism. This work demonstrates a new concept and its utility for visual detection of TNT particulates on various package materials. The concept takes advantages of the superior fluorescent properties of quantum dots (QDs) for visual signal output via ratiometric fluorescence, the feasibility of surface grafting of QDs for chemical recognition of TNT, and the ease of operation of the fingerprint lifting technique. Two differently sized CdTe QDs emitting red and green fluorescences, respectively, have been hybridized by embedding the red-emitting one in silica nanoparticles and covalently linking the green-emitting one to the silica surface, respectively, to form a dual-emissive fluorescent hybrid nanoparticle. The fluorescence of red QDs in the silica nanoparticles stays constant, whereas the green QDs functionalized with polyamine can selectively bind TNT by the formation of Meisenheimer complex, leading to the green fluorescence quenching due to resonance energy transfer. The variations of the two fluorescence intensity ratios display continuous color changes from yellow-green to red upon exposure to different amounts of TNT. By immobilization of the probes on a piece of filter paper, a fingerprint lifting technique has been innovated to visualize trace TNT particulates on various surfaces by the appearance of a different color against a yellow-green background under a UV lamp. This method shows high selectivity and sensitivity with a detection limit as low as 5 ng/mm^2 on a manila envelope and the attribute of being seen with the naked eye.

Here we report a ratiometric fluorescence probe comprising dual-emission quantum dots (QDs) and the establishment of its utility for instant, on-site, and visual identification of 2,4,6-trinitrotoluene (TNT) particulates deposited on various package surfaces such as manila envelopes, synthetic fabric bags, and rubber materials. Instant on-site identification of trace TNT deposited on various surfaces are in high demand for homeland security needs in a wide variety of scenarios,[1,2] such as mail sorting centers, airports and luggage, transit centers, and other civilian situations. The current methods of detection of TNT residue on solid surfaces are commonly performed off-site and involve complex instrumentation such as ion mobility spectrometry, gas/liquid chromatography, mass spectrometry, and surface acoustic wave method,[3] which require frequent instrument calibration, sophisticated vapor sampling, and preconcentration procedures. These costly instrument-based techniques are not applicable for most of the on-site identification of TNT. Thus, a detection strategy has trended toward portable, visual, and operating ease of sensitive techniques such as chemosensors and biosensors.[4−7] Due to its low vapor pressure and strong adhesion to solid surface, however, the rapid on-site identification of TNT particulates on the surface of suspicious objects is still a challenging task. The ratiometric fluorescence probe reported herein is promising to meet the challenge, which employs functional dual-emission quantum dots hybrid as the recognition element specific for TNT and ratiometric fluorescence as visual signal output for the indication of TNT presence.

Ratiometric fluorescence technique[8] possesses advantages in terms of sensitive visual detection for trace TNT because of its independence of the probe concentration and the ability of quantitative analysis. However, the development of ratiometric fluorescence methods is limited by the design of new dual-emission organic fluorophores which should be specific and sensitive to TNT. Fluorescent quantum dots are superior in this regard[9] because they not only afford the single-excitation/multiple-emissions for signal transduction but also have the feasibility of surface grafting for chemical recognition of TNT, which is central to ratiometric fluorescence detection. In this report, the ratiometric fluorescent probe comprises two differently sized QDs as illustrated in Figure 1, in which the red fluorescence of the larger QDs encapsulated in the silica nanoparticle is inert to TNT and the green fluorescence of the smaller QDs attached to the surface of the silica nanoparticle is specifically sensitive to TNT. A ratiometric fluorescence response is therefore realized upon the quenching of the green fluorescence by TNT while the red fluorescence intensity stays constant. A small variation in the ratio of the two intensities leads to a clear change in the fluorescence color of the probe, which can be easily observed with the naked eye under a UV lamp. We further demonstrate the utility of the ratiometric fluorescent probe for the visualization of

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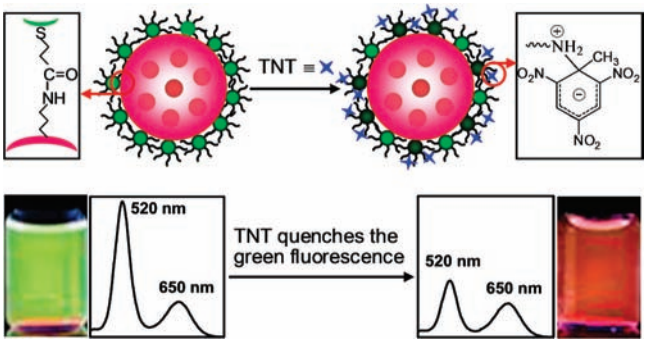

Figure 1. Schematic illustration of the structure of the ratiometric fluorescent probe and the working principle for the visual detection of TNT. The red QDs are stabilized within the silica nanoparticle and inert to TNT. The green QDs are covalently linked to the silica nanoparticle through amide bonding and functionalized with polyallylamine-bearing amino groups reactive to TNT to form the Meisenheimer complex. The bottom panel shows the fluorescence changes of the hybrid probe using a single wavelength excitation upon exposure to a certain amount of TNT and the corresponding digital photos of the probe solution recorded under a UV lamp.

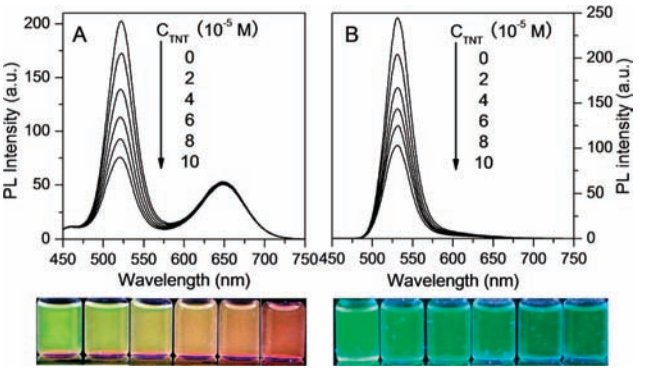

Figure 2. Dependence of the fluorescence spectra (λ_{ex} = 365 nm) of (A) the ratiometric probe and (B) the pure green QDs modified with polyallylamine upon the exposure to different amount of TNT. (Bottom panel) Comparison between the fluorescence colors of the ratiometric probe solutions (left) and the pure green QDs solutions (right) after exposure to TNT. The concentrations of TNT from left to right are 0, 2×10^{-5}, 4×10^{-5}, 6×10^{-5}, 8×10^{-5}, and 10×10^{-5} mol/L, respectively. All the photos were taken under a 365 nm UV lamp.

TNT particulates deposited on various surfaces by the fluorescence color change.

Figure 1 illustrates the architecture of the hybrid ratiometric probe and the detecting principle for TNT. The probe was fabricated by the hybridization of red fluorescent QD-doped silica nanoparticles and green fluorescent QDs through covalent bonding to the silica surface. The hybrid probe shows unique, well-resolved dual emission bands under a single wavelength excitation (Figure 1). The green QDs functionalized with polyallylamine (PAA) are very reactive to TNT. As shown in our previous work,[10] the electron-withdrawing analyte, TNT, readily reacts with electron-donating primary amino groups to form the Meisenheimer complex, which often has a strong absorption in the visible range. The absorption spectrum of the complex overlaps with the emission spectrum of the green QDs (Figure S3, Supporting Information [SI]), leading to the Förster resonance energy transfer (FRET). Therefore, the amino groups of the PAA chains chemically recognize TNT molecules by the formation of the Meisenheimer complex and subsequently reduce the green fluorescence intensity due to the effective FRET from the excited green QDs to the complex. The decrease of the green emission of the ratiometric probe results in the color change of the emission, facilitating the visual detection of TNT.

The response of the dual-wavelength fluorescence of the probe to TNT has been monitored to prove the working principle, as shown in Figure 2. The hybrid ratiometric probe exhibits two well-resolved emission peaks at 520 and 650 nm, which are emitted from the green QDs on the surface and the red QDs embedded in the silica nanoparticles, respectively, under a single wavelength excitation. The intensity of the green emission from the reactive small QDs is gradually decreased by the addition of TNT, whereas the intensity of the red emission from the encapsulated large QDs still remains constant (Figure 2A). The changes in the intensity ratio of the two emission wavelengths result in a continuous fluorescence color evolution (Figure 2, bottom panel). Clearly, even a slight decrease of the green emission intensity leads to an obviously distinguishable color from the original background with the naked eye. The advantages of the ratiometric fluorescence for visual detection can be confirmed by the comparison with the single fluorescence quenching experiment which are employed in most of the current fluorometry for TNT detection (Figure 2B).[10,11] It can be seen that, unlike the ratiometric probe, the fluorescence images of the pure green QDs are hard to distinguish among the other images by the naked eye. The comparison clearly shows that the ratiometric fluorescence method is more sensitive and reliable for visual detection of TNT than a single fluorescence quenching method, although the intensity of the green emission decreases at the same level.

The ratiometric probe also possesses the ability to react with TNT in a dose−response manner, which can be utilized for quantitation of the analyte. The intensity ratios of the two fluorescences at 520 and 650 nm gradually decrease with the increasing amount of TNT. The signal ratios versus the TNT concentrations can be fitted to a linear regression equation with a correlation coefficient of 0.998 (Figure S4 [SI]). Moreover, the ratiometric probe also exhibits high selectivity for TNT over other explosives including 2,4-dinitrotoluene (DNT), nitrobenzene (NB), and cyclotrimethylenetrinitramine (RDX) (Figures S5 and S6 [SI]). These nitro-containing compounds show little effect on the intensity ratio of the two fluorescences of the probe even after exposure to a high concentration of these compounds, and thus featured selectivity can greatly reduce the potential for false positives. The high selectivity facilitates the identification of the explosive structures, and the determination of explosives is crucial for the evaluation of the threat and for choosing the appropriate disposal procedures.

It is well documented that explosives such as TNT can contaminate and remain adhering to the package surfaces even with extremely cautious handling. Thus, instant on-site visual detection of the trace TNT deposited on various packages is very crucial for security-screening needs. For this purpose, an approach resembling the fingerprint lifting technique has been innovated as illustrated in the top panel of Figure 3. TNT residues deposited on surfaces are captured by the formation of Meisenheimer complexes and lifted from the surface to a TNT-indicating paper. Due to the FRET process between the green QDs and the complexes, these ratiometric probes bonded with TNT particulates emit different colors from the background,

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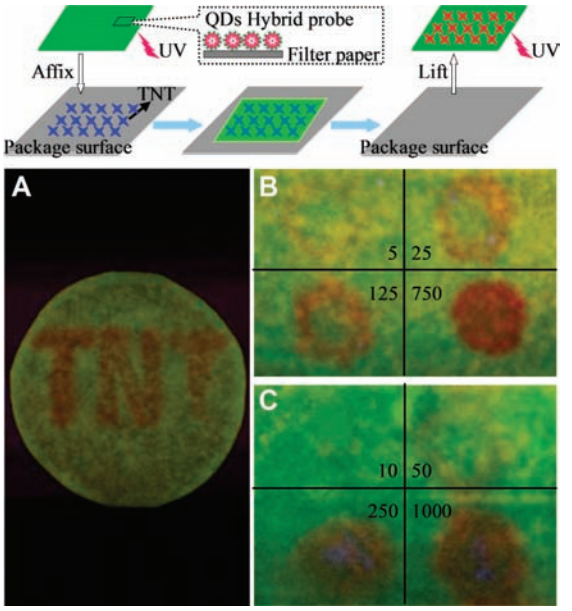

Figure 3. (Top panel) General strategy resembles the fingerprint lifting technique for performing visual detection of TNT particulates on the surfaces using the ratiometric hybrid probe immobilized on a piece of filter paper. The TNT particulates are first captured by the primary amino groups on the probe and then lifted from the surfaces. The lifted TNT particulates are visualized as differently colored spots in the yellow-green background under UV illumination. (Bottom panel, A−C) Color images of trace TNT particulates captured and lifted from various substrates including (A) a rubber surface, (B) a manila envelope with amounts of 5 ng, 25 ng, 125 ng, and 750 ng, respectively, and (C) a synthetic fabric bag with amounts of 10 ng, 50 ng, 250 ng, and 1000 ng, respectively. All the images were taken under the illumination of a 365 nm UV lamp.

suggesting the presence of the explosive residues. In order to establish its utility, the ratiometric fluorescence probe has been immobilized onto filter papers to make TNT-indicating papers. The immobilization has been accomplished by immersion of a piece of filter paper in the ratiometric probe solution and the subsequent adsorption of the hybrid probes into the filter paper due to the hydrophilic and hydrogen-bonding interactions. The piece of filter paper is then removed and kept in the dark for 10 min before performing the detection tests. The as-prepared indicating paper displays yellow-green fluorescence under a 365 nm UV lamp. Trace TNT particulates on various surfaces are simulated by depositing TNT acetonitrile solution on a manila envelope, a rubber stamp, and a synthetic fabric bag and then by drying in air. The amount of TNT deposited on the surfaces is estimated on the bases of concentration, volume applied, and size of the spot formed after drying. It can be seen that the trace TNT particulates are clearly revealed as differently colored spots against the clear yellow-green background under the illumination of the UV lamp. Clearly, the patterns of the color spots are consistent with the corresponding areas with the TNT residues. As can be seen in Figure 3B, when the contaminated spot containing 25 ng/mm^2 of TNT was applied on the manila envelope, a deep red spot appeared and was very pronounced in the yellow-green background. Trace TNT particulates deposited on other substrates such as the synthetic fabric bag and the rubber stamp were also clearly visualized using the same procedure. The detection limit is defined as the least amount of TNT on the surface capable of producing a differently colored fluorescence spot that can be noted by the independent observers. The currently unoptimized detection limits for TNT are thus found to be 5 ng/mm^2 on the manila envelope and 50 ng/mm^2 on synthetic fabric bag. The difference in the sensitivity could be due to the different smoothness of the surfaces of the envelope and the synthetic fabrics.

In conclusion, a dual-emission quantum dots probe has been constructed by hybridization of two differently sized quantum dots, and its utility has been established for visual detection of TNT particulates on various surfaces using an approach resembling the fingerprint lifting technique. The presence of TNT particulates on the surfaces can be revealed by the fluorescence color change of the probe. The probe can also be used to quantitate TNT in solutions on the basis of the measurement of ratiometric fluorescence. The method shows high selectivity and sensitivity for TNT particulates on an envelope with the naked eye. The sensitivity could be further improved by judiciously selecting an initial fluorescence color more sensitive to the naked eye, which can be optimized by tuning the ratios of the differently sized quantum dots. This concept reported herein could be significant and could be extended to the visual detection of a wide range of organic and biological molecules through properly functionalizing the green quantum dots on the silica surfaces.

■ ASSOCIATED CONTENT

Supporting Information. Experimental section, and supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
zpzhang@iim.ac.cn; shwang@iim.ac.cn

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■ REFERENCES

(1) Steinfeld, J. I.; Wormhoudt, J. *Annu. Rev. Phys. Chem.* **1998**, *49*, 203–232.
(2) Yinon, J. *Trends Anal. Chem.* **2002**, *21*, 292–301.
(3) (a) Moore, D. S. *Rev. Sci. Instrum.* **2004**, *75*, 2499–2512. (b) Singh, S. *J. Hazard. Mater.* **2007**, *144*, 15–28.
(4) (a) Rose, A.; Zhu, Z. G.; Madigan, C. F.; Swager, T. M.; Bulovic, V. *Nature* **2005**, *434*, 876–879. (b) Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864–11873. (c) Zahn, S.; Swager, T. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4225–4230.
(5) (a) Toal, S. J.; Sanchez, J. C.; Dugan, R. E.; Trogler, W. C. *J. Forensic Sci.* **2007**, *52*, 79–83. (b) Sohn, H.; Calhoun, R. M.; Sailor, M. J.; Trogler, W. C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2104–2105.
(6) (a) Forzani, E. S.; Lu, D. L.; Leright, M. J.; Aguilar, A. D.; Tsow, F.; Iglesias, R. A.; Zhang, Q.; Lu, J.; Li, J. H.; Tao, N. J. *J. Am. Chem. Soc.* **2009**, *131*, 1390–1391. (b) Dasary, S. S. R.; Singh, A. K.; Senapati, D.; Yu, H. T.; Ray, P. C. *J. Am. Chem. Soc.* **2009**, *131*, 13806–13812. (c) Jiang, Y.; Zhao, H.;

Zhu, N. N.; Lin, Y. Q.; Yu, P.; Mao, L. Q. *Angew. Chem., Int. Ed.* **2008**, *47*, 8601–8604.

(7) (a) Smith, R. G.; D'Souza, N.; Nicklin, S. *Analyst* **2008**, *133*, 571–584. (b) Germain, M. E.; Knapp, M. J. *Chem. Soc. Rev.* **2009**, *38*, 2543–2555. (c) Goldman, E. R.; Medintz, I. L.; Whitley, J. L.; Hayhurst, A.; Clapp, A. R.; Uyeda, H. T.; Deschamps, J. R.; Lassman, M. E.; Mattoussi, H. *J. Am. Chem. Soc.* **2005**, *127*, 6744–6751.

(8) (a) Kubo, Y.; Yamamoto, M.; Ikeda, M.; Takeuchi, M.; Shinkai, S.; Yamaguchi, S.; Tamao, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2036–2040. (b) Peng, X. J.; Wu, Y. K.; Fan, J. L.; Tian, M. Z.; Han, K. L. *J. Org. Chem.* **2005**, *70*, 10524–10531. (c) Haidekker, M. A.; Brady, T. P.; Lichlyter, D.; Theodorakis, E. A. *J. Am. Chem. Soc.* **2006**, *128*, 398–399. (d) Shynkar, V. V.; Klymchenko, A. S.; Kunzelmann, C.; Duportail, G.; Muller, C. D.; Demchenko, A. P.; Freyssinet, J. M.; Mely, Y. *J. Am. Chem. Soc.* **2007**, *129*, 2187–2193. (e) Wang, Z.; Palacios, M. A.; Zyryanov, G. *Chem.— Eur. J.* **2008**, *14*, 8540–8546. (f) Wu, C. F.; Bull, B.; Christensen, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 2741–2745. (g) Domaille, D. W.; Zeng, L.; Chang, C. J. *J. Am. Chem. Soc.* **2010**, *132*, 1194–1195.

(9) (a) Han, M. Y.; Gao, X. H.; Su, J. Z.; Nie, S. *Nat. Biotechnol.* **2001**, *19*, 631–635. (b) Alivisatos, A. P. *Science* **1996**, *271*, 933–937.

(10) (a) Tu, R. Y.; Liu, B. H.; Wang, Z. Y.; Gao, D. M.; Wang, F.; Fang, Q. L.; Zhang, Z. P. *Anal. Chem.* **2008**, *80*, 3458–3465. (b) Gao, D. M.; Wang, Z. Y.; Liu, B. H.; Ni, L.; Wu, M. H.; Zhang, Z. P. *Anal. Chem.* **2008**, *80*, 8545–8553.

(11) (a) Shi, G. H.; Shang, Z. B.; Wang, Y.; Jin, W. J.; Zhang, T. C. *Spectrochim. Acta, Part A* **2008**, *70*, 247–252. (b) Stringer, R. C.; Gangopadhyay, S.; Grant, S. A. *Anal. Chem.* **2010**, *82*, 4015–4019.