



Highly responsive fluorescent sensing of explosives taggant with an organic nanofibril film

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ARTICLE INFO

Article history:

Received 23 June 2007

Received in revised form 24 April 2008

Accepted 1 May 2008

Available online 8 May 2008

Keywords:

Fluorescence quenching

Nanofiber

Film

Sensing

Explosive

ABSTRACT

Efficient sensing of an explosives taggant, 2,3-dimethyl-2,3-dinitrobutane (DMNB), has been performed with an organic nanofibril film through monitoring the fluorescence quenching of the film upon exposure to the DMNB vapor. The nanofibril film was fabricated from an alkoxy-carbonyl-substituted carbazole-cornered conjugate tetracycle molecule, namely ACTC, which possesses a planar, rigid molecular geometry that favors cofacial π - π stacking between the molecules, leading to the formation of nanofibril structures with extended one-dimensional molecular stacking. The nanofibril film thus fabricated demonstrated unprecedented efficiency in detecting DMNB vapor, likely due to the extended one-dimensional molecular packing and the highly porous structure thus formed within the film. The former facilitates the exciton migration along the long-axis of nanofiber, while the latter enhances the adsorption of DMNB vapor and the expedient diffusion of the analyte through the film. The enhanced adsorption and diffusion of DMNB molecules within the matrix of the film also accounts for the improved response time of the film in fluorescence quenching upon exposure to DMNB vapor.

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1. Introduction

Fluorescence-quenching based sensing has gained increasing interest in detection of explosives [1–6]. Various organic molecules and polymers have been fabricated into thin films or porous materials and used in explosives sensing. Particularly, the bulky pentyptcene-substituted phenyleneethynylene polymers, developed in the Swager lab [2], have proven the most efficient in detection of trace explosives vapor through fluorescence quenching. The high efficiency is largely due to an amplified fluorescence quenching that is intrinsic to the efficient exciton migration along the backbone of conjugated polymers. Moreover, the nanocavities generated between the bulky polymer chains facilitate the adsorption and diffusion of the small explosives molecules, e.g., 2,4,6-trinitrotoluene (TNT).

While many fluorescence sensors have demonstrated sufficient sensitivity in detecting TNT related explosives (which possess strong oxidative capability), using these sensors to detect explo-

sives taggants, such as 2,3-dimethyl-2,3-dinitrobutane (DMNB), remains challenging [2,7], mainly due to their low, unfavorable oxidation power (ca. -1.7 V vs. SCE for DMNB [8], compared to that of TNT [9], ca. -0.7 V vs. SCE). DMNB is a required additive in all legally manufactured plastic explosives to allow easy identification of the explosives by either dogs or specialized machines. The high vapor pressure of DMNB (ca. 2.7 ppm at 25 °C [10], compared to ca. 5 ppb of TNT [11]) helps increase the reliability and thus minimize the false positives in explosives identification. However, most conjugated polymers and organic molecules, particularly dyes, used thus far in fluorescence sensing are incapable of producing an excited state that possesses sufficient reducing power to enable efficient fluorescence quenching via photoinduced electron transfer by the weak oxidative VOCs, like DMNB.

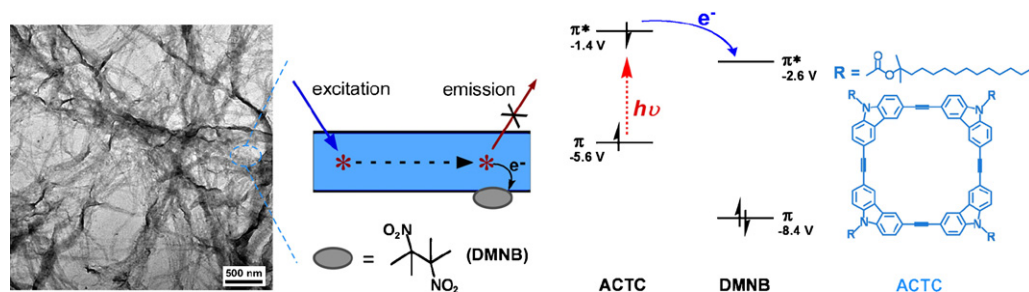
In this work, we report on a fluorescence sensing material that demonstrates unprecedented efficiency in detection of DMNB. The material was fabricated from an alkoxy-carbonyl-substituted carbazole-cornered conjugate tetracycle molecule, namely ACTC, shown in Scheme 1. The incorporation of four carbazole units increased the reducing power of ACTC, as indicative of the high HOMO level, -5.6 V. Moreover, the large electronic transition gap for ACTC (ca. 4.0 eV) [12] adds a large amount of energy to the excited state to make it highly favorable for transferring an electron to the quencher molecule, resulting in an efficient fluorescence quenching. The planar, shape-persistent geometry

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Scheme 1. (Left) A TEM image showing the nanofibril structure of a thin film cast on silicon oxide grids from an ACTC solution in THF (1 mM); (middle) a schematic diagram showing the amplified fluorescence quenching of the nanofiber by surface adsorbed DMNB, for which the extended exciton migration along the nanofiber plays a crucial role; (right) energy levels of HOMO (π) and LUMO (π^*) orbitals of ACTC and DMNB showing the large driving force of electron transfer from the photoexcited state of ACTC to DMNB. Geometry optimization and energy calculations were performed with density-functional theory (B3LYP/6-31g*) using Gaussian 03 package.

of the ACTC scaffold enables effective cofacial π - π stacking, leading to formation of extended, one-dimensional self-assembly of the molecule, typically in the morphology of nanofibrils [12]. Indeed, the nanofibril film can be easily fabricated by drop-casting a solution of ACTC onto a flat substrate (e.g., glass), where the evaporation of solvent leads to self-assembly of the molecules into nanofibril structures mainly through the strong π - π stacking. These nanofibril materials are uniquely multifunctional, combining the properties of strong intermolecular electronic coupling, efficient exciton migration and strong interaction with oxidative molecules. This combination of properties is highly desirable for fluorescence sensing of explosives [12].

2. Experimental

2.1. Materials

2,3-Dimethyl-2,3-dinitrobutane (DMNB, 98%) was purchased from Aldrich and used as received. All other molecules and solvents (HPLC or spectroscopic grade) were purchased from Fisher or Aldrich, and used as received. ACTC was synthesized following the methods previously described [12]. A uniform nanofibril film of ACTC was fabricated by spin-casting one drop of the ACTC solution in THF (1 mM) onto a glass cover slip at a speed of 1500 rpm. The thickness of the film thus fabricated was about 90 nm as measured by tapping mode AFM. The rigid, planar geometry of the ACTC molecule (including both core and the side-chains) affords effective cofacial stacking between molecules, leading to formation of one-dimensional, fibril nanostructures as previously characterized by AFM and TEM imaging [12].

2.2. Methods

The fluorescence spectra were measured on a LS 55 fluorometer (PerkinElmer) using either a cuvette or film sample holder. The saturated fluorescence quenching by DMNB was monitored by measuring the fluorescence spectra of the nanofibril film before and after exposure to the saturated vapor of DMNB in a sealed cuvette, where the vapor pressure of DMNB remains constant, at 2.7 ppm. In case of measuring the time course of fluorescence quenching (vide infra, Fig. 3), the measurement was performed following the similar method as previously reported by Yang and Swager [9]. Briefly, the fluorescence spectrum of the nanofibril film was measured immediately after immersing the film for certain amount of time inside a sealed-jar (50 mL) containing small amount of the DMNB powder. The longer the film was kept in the jar, the more the fluorescence was quenched. By measuring the fluorescence intensity of the film after different amounts of time of exposure to the DMNB vapor,

a time course of the fluorescence quenching was obtained. Typically, after about 10 s of exposure the surface adsorption of DMNB reached equilibrium, leading to a saturation of the fluorescence quenching as shown in Fig. 3, where the quenching efficiency (%) is plotted as a function of the total amount of time of exposure to the DMNB vapor. From such a plot, the response time of fluorescence quenching can be estimated for the ACTC nanofibril film. It should be noted that due to the high volatility of DMNB, adsorbed DMNB molecules evaporated from the film during the course of transferring the sample from the DMNB jar to the fluorometer, thus resulting in lower quenching efficiency compared to that obtained in a sealed cuvette (Fig. 3). To prevent direct contact of the film with the explosives analytes, some cotton was used to cover the DMNB powder deposited at the bottom of the jar. Before use the jar was sealed overnight to achieve constant, saturated vapor pressure inside. The presence of cotton also helps maintain a constant vapor pressure.

3. Results and discussion

Fig. 1 shows the fluorescence spectrum of a 90 nm thick nanofibril film spin-cast from a THF solution of ACTC. Upon exposure to the saturated vapor of DMNB (2.7 ppm) [10], the fluorescence was quenched about 73%, nearly four times higher than that obtained for the conjugate polymer films [7]. The higher quenching efficiency is likely due to the stronger reducing power of ACTC, in conjunction with the organized cofacial molecular stacking, which expedites the exciton migration along the nanofibrils [13–15]. As previously observed in our lab [12], the nanofibril film fabricated from ACTC possesses a highly porous structure formed by the entangled mesh

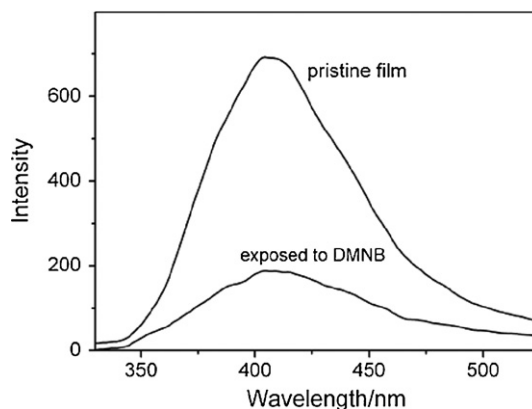


Fig. 1. Fluorescence spectra of a 90 nm thick ACTC nanofibril film before and after exposure to the DMNB vapor (2.7 ppm) for 2 min.

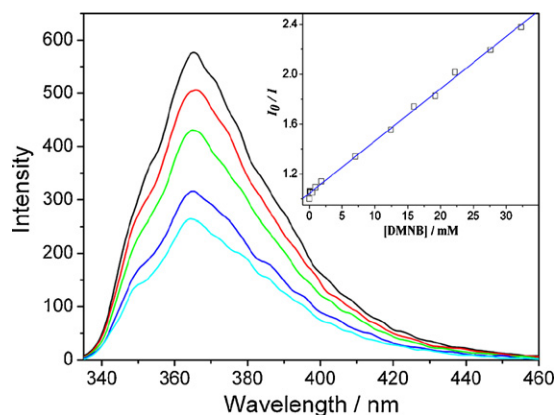


Fig. 2. Fluorescence spectra of a 25 μ M ACTC solution in THF in the presence of different concentrations of DMNB: 0.0, 1.9, 7.0, 19.0 and 28.0 mM. Inset: Stern–Volmer plot of the fluorescence quenching.

of nanofibers. The interconnected interstices thus provide continuous channels for expedient adsorption and diffusion of quencher molecules, which further facilitate the fluorescence quenching.

The efficient fluorescence quenching was also observed for ACTC in solution as shown in Fig. 2, where the fluorescence spectra of an ACTC solution (25 μ M in THF) were measured in the presence of varying concentrations of DMNB. Upon addition of about 25 mM DMNB, the fluorescence of ACTC was quenched more than 50%. The Stern–Volmer plot (inset of Fig. 2) of the quenching demonstrates a linear dependence on the DMNB concentration, implying a single mechanism (static or dynamic) for the fluorescence quenching. Considering the strong electron–donor–acceptor interaction between ACTC and DMNB, a static quenching mechanism is assumed for the observation shown in Fig. 2. A binding constant of $41 \pm 0.6 \text{ M}^{-1}$ is thus deduced from the slope of the Stern–Volmer plot. It is reasonable to assume that in the case of ACTC nanofibrils the surface binding (adsorption) with DMNB would be significantly increased, mainly due to the higher density of ACTC molecules. The increased surface binding, in conjunction with the effective exciton migration along the nanofiber, enables amplified fluorescence quenching for the nanofibril films as evidenced in Fig. 1.

The highly porous structure of the nanofibril film also produces a fast response to quencher molecules, mainly due to the expedient diffusion within the nanofibril interstices. Indeed, within only about 10 s of exposure to DMNB vapor, the fluorescence quenching became saturated, reaching the adsorption equilibrium (Fig. 3). Fast quenching response is conducive for expedient, onsite explo-

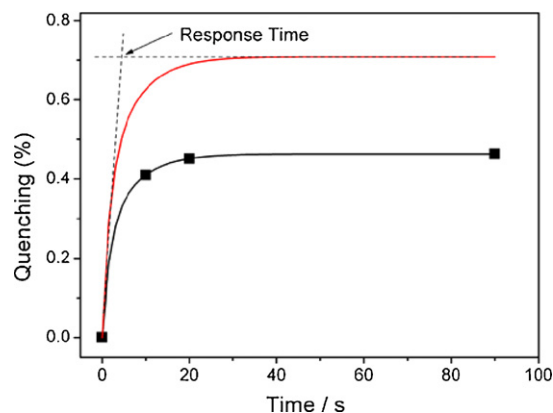


Fig. 3. Fluorescence quenching (%) of a 90 nm thick ACTC nanofibril film as a function of the time of exposure to DMNB vapor (2.7 ppm): black points and line represent the experimental data and the exponential fitting, respectively; red line represents the corrected time-course with consideration of the evaporation of DMNB during the transfer of the film from the DMNB jar to the fluorometer, for which the saturated quenching (%) at the adsorption equilibrium was set as 73%, the value obtained from the static quenching performed in the sealed cuvette as shown in Fig. 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

res detection. Compared to the quenching performed in a sealed cuvette as shown in Fig. 1, the saturated quenching efficiency obtained in Fig. 3 is about 30% lower, which is likely due to the evaporation of pre-adsorbed DMNB molecules from the film during the course of transferring the sample from the DMNB jar to the fluorometer. If the time-dependent quenching could be performed *in situ* in a sealed system (where the DMNB vapor remains constant), the time-course curve shown in Fig. 3 would have shifted up by 30% (as depicted by the red line shown in Fig. 3) to reach a saturated quenching efficiency of 73%, the value obtained from the static quenching in a sealed cuvette as shown in Fig. 1.

The effective fluorescence quenching observed above is solely due to the electron transfer from the excited state of ACTC to DMNB as depicted in Scheme 1. There is no possibility for excited state energy transfer, since the emission wavelength of ACTC is far above the absorption edge of DMNB. The 'photo-damaged' ACTC (mainly due to the photooxidation) can be repaired by a strong reducing reagent like hydrazine, leading to recovery of the fluorescence. Indeed, the fluorescence of the nanofibril film after photoquenched by DMNB was recovered close to 100% after immersing the film in the saturated vapor of hydrazine for 1–2 h. The recovered film demonstrated similar quenching efficiency when re-exposed to the DMNB vapor. Fig. 4 shows six continuous cycles of fluorescence

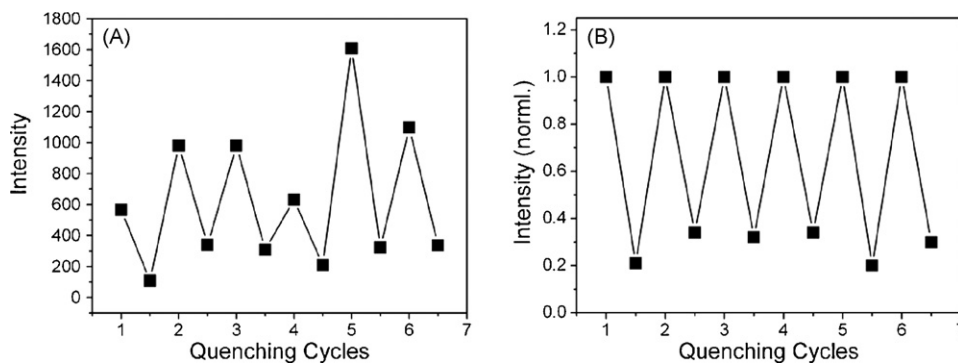


Fig. 4. Six continuous cycles of quenching–recovery test of a drop-cast ACTC film: (A) plotted with the originally measured intensities; (B) plotted with the normalized intensities. The quenching was measured after exposing the film to the saturated vapor of DMNB for 5 min in a sealed cuvette. After each cycle of quenching, the fluorescence of the film was recovered by immersing it in the saturated vapor of hydrazine for 1 h, except for cycles 4 and 5, for which the film was healed in the hydrazine vapor for less and longer than 1 h, respectively, to examine (as demonstrated in B) to what extent the fluorescence quenching efficiency is dependent on the healing time.

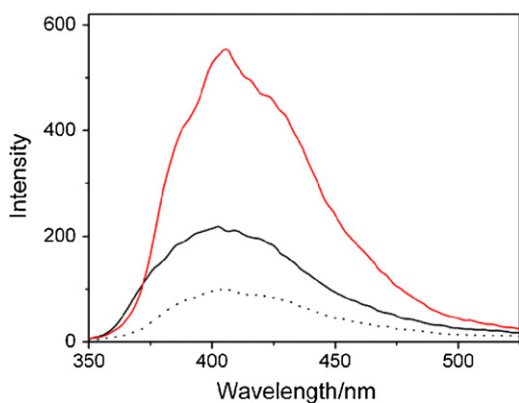


Fig. 5. Fluorescence spectra of a drop-cast ACTC film before (black-solid) and after immersing in a saturated hydrazine vapor for 2 h (red-solid). The spectrum of the hydrazine-healed film after exposing to the DMNB vapor (2.7 ppm) for 5 min is also shown (black-dotted). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

quenching-recovery tested with the saturated vapor of DMNB. Efficient quenching was obtained for the film over repeated use, implying high stability and sustainability of the film against permanent photobleaching, a problem that is usually detrimental to organic sensors for their practical application.

The ability of hydrazine for reducing the oxidized defects was also observed for conjugated polymer films, for which the fluorescence of the film pre-oxidized by iodine was completely recovered upon immersing the film in the saturated hydrazine vapor [16]. In this study, even for the pristine nanofibril film, which is intrinsically intercalated with small number of oxygen molecules or the analogous oxidized trap sites, the fluorescence of the film was dramatically enhanced upon immersing it in a hydrazine vapor for extended time. Fig. 5 shows the fluorescence spectra of an ACTC film drop-cast from a 1 mM THF solution before and after immersed in a saturated hydrazine vapor for 2 h (followed by blowing of nitrogen to remove the hydrazine condensation). About two times increase in fluorescence intensity was obtained after 'healing' the film with hydrazine. Exposing the film to hydrazine for longer times (up to 6 h) did not result in further enhancement in fluorescence, implying an expedient repair of the oxidized defects by hydrazine. Compared to the fluorescence spectrum of the pristine film, the spectrum obtained after exposure to hydrazine became narrower and shifted to longer wavelength, characteristic of enhanced, more organized molecular stacking as observed for other planar aromatic molecules [17,18]. The enhanced molecular stacking thus observed might be due to the removal of the intercalated oxygen or the oxidized defects [16]. As depicted in Scheme 1, the fluorescence quenching efficiency is primarily determined by the exciton migration along the nanofibers, which in turn is dependent on the extent of molecular stacking and organization. The enhanced molecular stacking obtained for the hydrazine-healed film should demonstrate increased fluorescence quenching by DMNB. Indeed, upon exposing the 'healed' film to DMNB vapor (2.7 ppm), the fluorescence was quenched by 83%, significantly more effective than that observed for the pristine film as shown in Fig. 1 (where 73% quenching was observed). The degree of quenching (if defined as I_0/I , as usually used in Stern–Volmer equation) of the former, 5.9, is about 60% higher than that obtained for the latter, 3.7.

4. Conclusion

Through a fluorescence quenching mechanism, nanofibril film fabricated from a planar conjugate tetracycle molecule, namely

ACTC, has proven effective in sensing DMNB at the trace vapor level, typical of the concentrations of the taggant in explosives. The quenching efficiency obtained for the nanofibril film is about one order of magnitude higher than the conjugate polymer based sensory films (when fabricated at the same thickness of ca. 100 nm). Such improved fluorescence quenching is largely due to the highly organized molecular stacking within the nanofiber, and the highly porous structure of the film that consists of an entangled mesh of a large number of nanofibers. The former facilitates the exciton migration along the long-axis of nanofiber, while the latter enhances the adsorption of DMNB vapor and the expedient diffusion of DMNB molecules through the film. The enhanced adsorption and diffusion of DMNB molecules within the matrix of the film also accounts for the improved time response upon exposure to DMNB vapor. The combination of efficient and fast fluorescence quenching will provide the sensory film with wide options to be employed in explosives taggant detection, which remains challenging for the current organic based sensors. Future studies will be directed towards designing new building block molecules with functional side-chains that will improve the surface binding affinity and selectivity of the nanofiber for DMNB and other explosives taggants.

Acknowledgement

This work was supported by NSF (CAREER CHE 0641353, CBET 730667 and CHE 0642413), ACS PRF (45732-G10).

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Biographies

Tammene Naddo was born in Ethiopia in 1961. He completed his BS studies in Chemistry in 1982 at Addis Ababa University, Ethiopia. In 1985 he rejoined the same University and graduated with MS degree in Chemistry in 1987. Currently, Tammene is pursuing his Ph.D. under the supervision of Ling Zang at the Department of Chemistry and Biochemistry of Southern Illinois University at Carbondale. His major research interest centers on fluorescence sensory detection of explosives using organic nanofibril films.

Xiaomei Yang was born in China in 1968. She received her BS in 1991 and Ph.D. in 1996, both in chemistry from Tsinghua University. She is currently working in the Department of Chemistry, Southern Illinois University, on the computational optimization of molecular structure and the intermolecular interaction and stacking.

Jeffrey Moore was born near Joliet, IL in 1962. He received his BS in chemistry (1984) from the University of Illinois, and his Ph.D. in Materials Science and Engineering with Samuel Stupp (1989). After a NSF position at Caltech with Robert Grubbs, he began his independent career at the University of Michigan in Ann Arbor. He returned in 1993 to the University of Illinois, where he is currently the Murchison-Mallory Professor of Chemistry and Materials Science and Engineering. His research focuses on molecular self-assembly, structure-controlled macromolecules and foldamers, stimuli-responsive materials, and self-healing polymers.

Ling Zang was born in China in 1968, where he received his B.S. in 1991 from Tsinghua University and his Ph.D. in 1995 from the Chinese Academy of Sciences. After about 2 years stay in Germany as an Alexander von Humboldt Fellow, he moved to the US in 1998 to continue his research, first at Bowling Green State University and then at Columbia University. In 2003, he joined the chemistry faculty at Southern Illinois University, where he was promoted to Associate Professor in 2008. In the fall of 2008, he will move to University of Utah to join the faculty of the Department of Materials Science and Engineering, where he will be a USTAR endowed associate professor. His current research interest centers on the manipulation of functional nanostructures, nanomaterials and molecular devices, and the characterization at single-molecule and nanometer scales.