

Detection of Explosives with a Fluorescent Nanofibril Film

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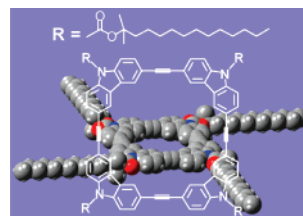
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Fluorescence-quenching-based chemical detection represents one of the most sensitive and convenient methods that have been widely employed in explosives identification.^{1–6} Aromatic molecules and conjugated polymers (when fabricated as films) are proven effective in sensing explosives vapor via fluorescence quenching. Although porous films of conjugated polymers have typically been utilized, the quenching efficiency of these materials is often limited by the short exciton diffusion because of the poor molecular organization and/or weak intermolecular electronic interactions.^{2,4} Consequently, very thin films are needed to achieve desirable amplification of signal transduction, whereas a sufficiently thick film is usually required to produce a measurable fluorescence intensity and to minimize the interference of photobleaching. Because of these limitations, there is a need to develop new sensing materials that enable long-range exciton migration and thus produce sensing systems independent of film thickness and with more flexibility for device fabrication.

Herein we report an efficient sensing film fabricated from the alkoxy carbonyl-substituted, carbazole-cornered, arylene-ethynylene tetracycle (ACTC), shown in Scheme 1. The incorporation of carbazole enhances the electron donating power of the molecule and thus increases the efficiency of fluorescence quenching by oxidative explosives. The large-area planar molecular surface of ACTC enables effective long-range π - π stacking between the molecules.⁷ Nanofibers in length of micrometers can be easily fabricated via surface casting (see Supporting Information). It has been demonstrated that one-dimensional π - π stacking is highly favorable for exciton migration via cofacial intermolecular electronic coupling.⁸⁻¹⁰ Thereby, long-range exciton diffusion would be expected within the film cast from ACTC. Moreover, the shape-persistent molecular structure of ACTC,^{11,12} in combination with the networks formed by interdigitated nanofibers, produces multiscale porosity, making it an ideal sensing material for probing oxidative gaseous molecules. Indeed, efficient fluorescence quenching is observed when the ACTC film is exposed to explosives vapor, leading to potential applications in explosives sensing.

This investigation was primarily focused on two explosives compounds, 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT), which both exist in commercial explosive products and have been widely exploited for the purpose of evaluating explosive sensing devices. The ACTC film was fabricated by spin-casting a THF solution (0.2–1.0 mM) onto a glass substrate, followed by annealing in vacuum at 60 °C for 3 h to remove the enclathrated solvent. The film thus fabricated is quite fluorescent, with a quantum

Scheme 1. Molecular Structure of ACTC. The Planar Geometry and Shape-Persistent Core Favors Effective π - π Stacking between Molecules



yield of ca. 0.19. Upon exposure to saturated vapor of DNT or TNT, the fluorescence of the ACTC film was dramatically quenched (Figure 1A). Since the emission wavelength of ACTC is far above the absorption range of the two explosives (Figures S5–S6, Supporting Information), and thus there is no possibility for excited-state energy transfer, the observed fluorescence quenching must explicitly be due to the photoinduced electron transfer from the excited ACTC to the quencher. Such a photoinduced electron transfer is highly favored by the large driving forces (2.4 and 1.9 eV for TNT and DNT, respectively, Figure S7).

As shown in the inset of Figure 1, the quenching response to DNT is faster than that to TNT, likely because of the higher vapor concentration of DNT (ca. 100 ppb, compared to ca. 5 ppb of TNT). The fluorescence quenching eventually saturated for both explosives upon reaching the adsorption equilibrium. It is remarkable to note that at adsorption equilibrium (after ca. 60 s of exposure) the quenching efficiency of TNT (83%) was comparable to that of DNT (90%), although the latter provides about 20 times higher vapor concentration. The relatively strong quenching thus observed for TNT is likely due to its higher partition into the film. Generally, the partition coefficient (between a solid adsorbent and air) of a volatile organic compound tends to scale inversely with its saturated vapor pressure, as indeed observed for polymer materials, therefore the partition coefficient of TNT is about 1 order of magnitude higher than that of DNT. The quenching response observed for the ACTC film is significantly faster than that previously observed for other organic materials,^{1,13,14} consistent with the fibril porous structure of the film, which facilitates both gaseous adsorption and exciton migration across the film. The quenching efficiency obtained for ACTC films is higher than those previously reported for other explosive sensing materials at the same thickness.^{2,4}

The porous film morphology (inset of Figure 2) and the extended one-dimensional π - π stacking facilitate the access of quencher molecules to the excited states (Supporting Information, part X), thereby resulting in effective fluorescence quenching, which should be little dependent on the film thickness as is indeed evidenced by the observations shown in Figures 2 and S11. This behavior is in

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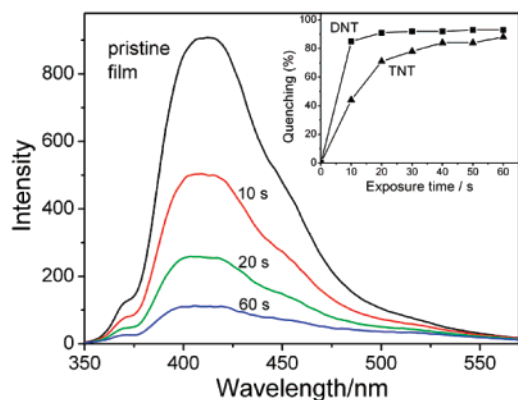


Figure 1. Fluorescence spectra of a 90 nm thick ACTC film upon exposure to saturated vapor of TNT (5 ppb) at different times. Related quenching behavior obtained with DNT (100 ppb) is shown in Figure S10. The inset shows the time-course of quenching for TNT and DNT.

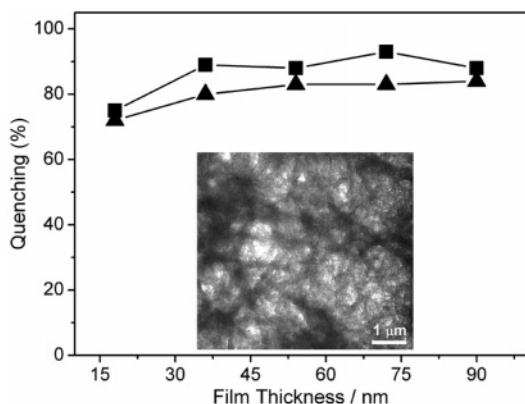


Figure 2. Thickness dependence of fluorescence quenching efficiency of ACTC films. The quenching was tested upon exposing the film to saturated vapor of TNT (▲) and DNT (■) for 60 s. The inset is a TEM image of a thin film of ACTC cast on silicon oxide from 2 mM THF solution.

contrast to what was usually observed for other organic film sensors, for which the emission quenching efficiency was inversely proportional to the film thickness owing to the diffusion limit of the exciton and the gaseous adsorbates.^{2,4} For example, for the conducting polymer reported by Swager et al.,¹³ the quenching efficiency by TNT decreases about four times when increasing the film thickness from 2.5 to 20 nm. The unusual, slightly lower quenching efficiency obtained with the thinnest film shown in Figure 2 might be due to the evaporation of quencher molecules from the film during the course of transferring the sample from the explosives jar to the fluorometer. In general, thin porous films are not expected to hold the gaseous adsorbates as effectively as the thick films. The thickness-independent film fabricated in this study opens unprecedented opportunities for developing new types of sensors that can tolerate thick films. A thick film normally provides devices with improved reproducibility and sustainability.

After exposure to explosives vapor, the film's fluorescence is slowly recovered by exposure to air for a few days or quickly recovered by exposure to the vapor of hydrazine, a strong reducing reagent capable of reducing the oxidized defects within the film. For example, after immersing in the saturated vapor of hydrazine (ca. 140 ppm) for about 1 h, the fluorescence of ACTC film returns close to 90% (Figure S12). The recovered film showed similar quenching efficiency when re-exposed to the explosives. Figure 3 shows five continuous cycles of fluorescence quenching–recovery tested with DNT. Efficient quenching was obtained for the film over repeated use, implying high stability of the film against

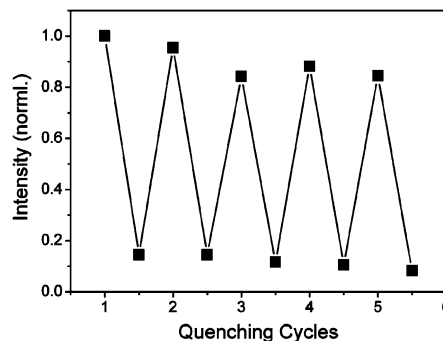


Figure 3. Five continuous cycles of quenching–recovery test of a 90 nm ACTC film. The quenching was performed by exposing the film to a saturated vapor of DNT for 30 s. After each cycle of quenching, the fluorescence of the film was recovered by immersing it in a saturated vapor of hydrazine (ca. 140 ppm). All emission intensities are normalized to the intensity of the pristine film before exposure to DNT.

photobleaching, a problem that is detrimental to organic sensors for their practical application.

In summary, a new type of fluorescence sensory material has been developed from an arylene–ethynylene macrocycle. Films fabricated from such materials have demonstrated compelling efficiency in detection of explosive vapor, probably due to the extended 1D molecular stacking between the component molecules and intrinsic nanoporous morphology formed within the film. The former facilitates bulky exciton migration, while the latter favors adsorption and diffusion of gaseous adsorbates within the film. A combination of these two characteristics enables efficient fluorescence quenching of the film by gaseous quenchers.

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Supporting Information Available: Synthesis of ACTC, film preparation and characterization, fluorescence quenching measurement. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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