Organic nanofibrils based on linear carbazole trimer for explosive sensing†

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Organic fluorescent nanofibrils were fabricated from a linear carbazole trimer and employed for expedient detection of nitro-aromatic explosives (DNT and TNT) and highly volatile nitro-aliphatic explosives (nitromethane).

Detection of trace explosives is of great concern for homeland security, battlefield protection, and industrial and environmental safety control. Fluorescence quenching based sensing has proven to be one of the most promising approaches for trace explosives detection,[1–3] for which various conjugated polymers, molecular imprinted polymers, dye doped silica and metal–organic frameworks have been fabricated into films and fluorescence quenching upon exposure to the vapor of nitroaromatic explosives (*e.g.*, TNT, DNT) has been explored.[4–8] However, the quenching efficiency of these materials is often limited by short exciton diffusion due to poor molecular organization and/or weak intermolecular electronic interactions as usually observed for polymer based materials.

Recently, our group has reported an alternative approach to increase fluorescence sensing efficiency by fabricating rigid aromatic molecules into nanofibrils.[9] These novel one-dimensional nanostructures possess long range exciton diffusion due to the extended intermolecular $\pi-\pi$ electronic interaction. Upon deposition onto a substrate, the nanofibrils form a nanoporous film in a variable range of porosity through entangled piling of the individual fibrils. The large surface area to volume ratio and porosity thus formed, in combination with the amplified fluorescence quenching relied on the enlarged exciton diffusion, usually enable expedient, effective vapor detection of nitro-aromatic explosives.[9,10] Particularly, for the building-block molecules containing carbazole as the conjugation unit, the nanofibrils fabricated demonstrate not only high sensitivity in vapor sensing, but also strong selectivity towards nitrobased explosives against other common chemical liquids and solids.[11] However, the macrocyclic conjugation structure of these molecules imposes much difficulty to synthesis because it demands special catalysts for making the precursors.[12] To make the nanofibrils more practical in vapor sensing, it is imperative to find alternative building-block molecules that are easier to synthesize but still maintain the chemical properties and features suited for fabrication into nanofibrils and fluorescence sensing of nitrobased explosives.

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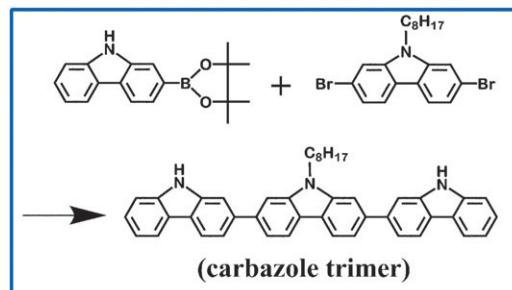
Scheme 1 Synthesis of 2,7-linked carbazole trimer.

Here, we report an easy synthesis of a 2,7-linked carbazole trimer (Scheme 1) and fabrication into nanofibril structures. The nanofibril film thus fabricated demonstrated efficient, fast fluorescent sensing not only for nitroaromatic explosives (*e.g.*, TNT, DNT), but also for nitroaliphatic explosives (*e.g.*, nitromethane), which remain difficult to detect due to their high volatility and low chemical binding to many sensory materials.

The carbazole trimer was synthesized from commercial available 2,7-dibromo-9-octyl-9H-carbazole and 9H-carbazole-2-boronic acid pinacol ester in one step by Suzuki-coupling reaction (Scheme 1). The 2,7-substituted carbazoles, compared to 3,6-substituted ones, are ideal building blocks for rigid, rodlike molecules with a longer conjugation distance.[13] Introducing one octyl substituent gives the trimer necessary solubility for solution processing while maintaining minimal sterical hindrance to facilitate the intermolecular arrangement and one-dimensional self-assembly into nanofibrils. Indeed, well-defined nanofibrils could feasibly be fabricated from this molecule through a bisolvent phase transfer process (see ESI†).[9] In comparison, when substituting all the three carbazoles with alkyl chains, the self-assembly through the same process gave only ill-defined big chunks.
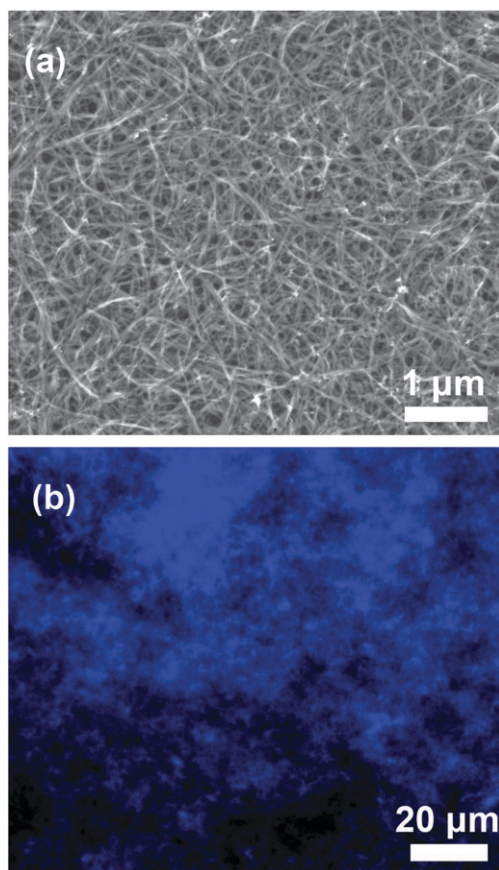
Fig. 1(a) shows a SEM image of the nanofibrils fabricated from the carbazole trimer deposited on a silicon substrate. The nanofibrils feature a high aspect ratio, with diameter of only *ca.* 30 nm and length of several microns. The deposited nanofibrils formed a nanoporous film consisting of entangled fibril networks. The nanofibrils exhibit strong blue fluorescence upon excitation under UV light as shown by fluorescence microscopy imaging (Fig. 1(b)). The maximum wavelength of the fluorescence was measured at 438 nm, 44 nm longer than that measured for the molecules dissolved in solution (Fig. S1, ESI†), which is characteristic of strong intermolecular electronic interaction typically observed in molecular aggregates. Such strong intermolecular interaction is also indicated by the bathochromic shifted absorption peak
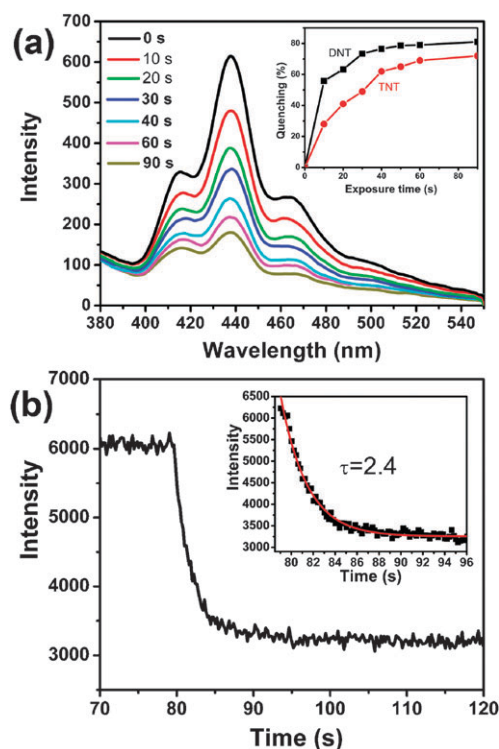
Fig. 1 (a) SEM image of nanofibrils deposited on a silicon substrate. (b) Fluorescence microscopy image of the same nanofibrils deposited on a glass slide.
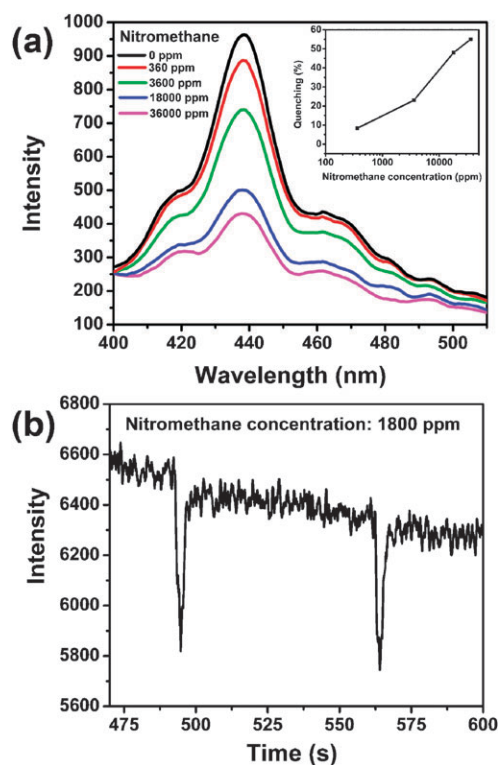

Fig. 2 (a) Fluorescence spectra of the nanofibril film upon exposure to TNT saturated vapor (5 ppb) at various time intervals. The inset shows the time-course of quenching for DNT and TNT vapors. (b) Time course of fluorescence quenching of the nanofibril film upon blowing over with saturated vapor of DNT, indicating a response time of 2.4 s. The intensity was monitored at 438 nm.

(around 400 nm) as measured for the nanofibrils. XRD measurement demonstrates that the nanofibrils are crystalline and the shorter d spacings of 3.8 Å implies to $\pi-\pi$ stacking (Fig. S2, ESI†).

The continuous porous structure formed within the nanofibril film as depicted in Fig. 1 enables easy penetration and diffusion for gaseous molecules. This, in conjunction with the large surface area to volume ratio intrinsic to the small size of the nanofibrils, is expected to result in expedient sample collection and thus enhanced vapor sensing. Indeed, fast and efficient fluorescence quenching was observed for the nanofibril film when exposed to TNT and DNT vapors (Fig. 2(a) and Fig. S3, ESI†). The fluorescence quenching reached 50% and 70% after 30 and 60 s (respectively) of exposure to the saturated vapor of TNT (ca. 5 ppb). The same fluorescence quenching became much faster when exposed to the saturated vapor of DNT (Fig. 2(a) inset), for which 50% quenching took only 10 s. The faster response thus observed for DNT is likely due to its 20 times higher vapor pressure (ca. 100 ppb) compared to that of TNT.[14]

To further explore the sensing response time, we measured the fluorescence intensity of the nanofibril film as a function of time before and after blowing saturated vapor of DNT over the film (Fig. 2(b)). Fitting the intensity decay into a single exponential kinetics deduces a quick response time (defined as the decay lifetime) of 2.4 s for the quenching process

(Fig. 2(b) inset). The fast response is conducive to practical application for onsite monitoring of explosive vapors. Moreover, the sensory materials thus reported are fully reversible. After tested with the explosives, the quenched fluorescence can be recovered simply by heating the film at 50 °C in a vacuum oven for 10 min. As shown in Fig. S4 (ESI†), over several repeated uses, the quenching efficiency remained nearly unchanged under the same testing conditions, implying high photostability of the film, which is usually critical for organic sensors when considered for practical application.

Following the initial success of sensing of nitroaromatic explosives, we explored the sensing capability of the nanofibril film over the nitroaliphatic explosives, specifically, nitromethane, which represents one of the highly volatile explosives (vapor pressure 36 000 ppm), and still remains challenging for detection by current sensing techniques. To the best of our knowledge, there has been no report on fluorescence-quenching based vapor detection of nitromethane under ambient conditions. This is likely due to the weak oxidizing power (i.e., low electron affinity) of nitromethane, particularly in comparison with the nitroaromatic compounds. The high volatility of nitromethane brings additional difficulty to vapor detection, for which strong interfacial binding (surface condensation) and sufficiently large surface area are usually demanded to achieve efficient sensing.

Because of its high volatility, the fluorescence quenching experiments of nitromethane were carried out in a sealed cell so as to maintain constant vapor pressure. Using this setup,

Fig. 3 (a) Fluorescence spectra of the nanofibril film upon exposure to various concentrations of nitromethane vapor. The inset shows the vapor concentration dependent quenching. (b) Time course of the fluorescence quenching upon blowing over with 1800 ppm nitromethane vapor.

the local vapor concentration could be continuously adjusted by injecting different amount of nitromethane vapor into the cell. The lowest vapor pressure we could reach in this case is about 1% dilution of the saturated vapor, corresponding to 360 ppm, at which about 8% fluorescence quenching was observed for the nanofibril film. With increasing the vapor pressure of nitromethane, the fluorescence quenching increases, reaching 55% under the saturated vapor of 36 000 ppm (Fig. 3(a)).

To explore the vapor sensing of nitromethane in open air, the nanofibril film was blown over with nitromethane vapor in different concentrations. Upon blowing at 1800 ppm (5% dilution from the saturated pressure), a significant fluorescence quenching (11%) was observed (Fig. 3(b)). Remarkably, the response was very fast and reversible. Fitting the intensity decay into a single exponential kinetics gives a response time of 0.63 s (Fig. S5, ESI†). The fast response is highly favorable for the onsite security monitoring. The effective vapor sensing obtained for nitromethane is largely due to the porous structure and large surface area to volume ratio of the nanofibril film, the combination of which enables efficient collection and accumulation of volatile molecules.

The fluorescence quenching observed above can be attributed to the photoinduced electron transfer from the excited carbazole trimer (within the nanofibril) to the surface adsorbed explosive molecule (Fig. S6, ESI†). Such an electron transfer is highly favored by the large driving force for TNT and DNT (2.1 eV and 1.6 eV, respectively). The driving force for nitromethane (0.4 eV) is significantly smaller, though still sufficient for affording an efficient electron transfer as indeed observed. The strong electron-donor–acceptor interaction between the carbazole trimer and the nitro-explosive molecules was also characterized by the steady state fluorescence quenching in solutions (Fig. S7, ESI†), for which fairly large static quenching constants were obtained for DNT and nitromethane (720 M^{-1} and 27 M^{-1}, respectively). Considering the intense effect of solvent, the quenching constant in gas phase should be significantly higher.

In summary, we have fabricated fluorescent nanofibrils from a 2,7-linked carbazole trimer. The film deposited from these nanofibrils demonstrated efficient vapor sensing for nitrobased explosives including TNT, DNT, and highly volatile nitromethane. The sensing mechanism relies primarily on the photoinduced electron transfer between the carbazole trimer and explosives, which is thermodynamically favorable by large driving force. The tunable porosity and large surface area to volume ratio intrinsic to the nanofibril film imply potential applications in sensor devices for on-site explosives monitoring.

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