

Enhanced fluorescence sensing of amine vapor based on ultrathin nanofibers

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The fluorescence sensing of amine vapor was largely enhanced upon using ultrathin nanofibers, which were fabricated from *N*-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide by a new self-assembly approach.

Volatile amines have been widely used in various areas including chemical, pharmaceutical, and food industries.¹ Some of the amines have even been used in the military, *e.g.* hydrazine as fuel additives in rocket and fighter jet propulsion systems.² In addition, some biogenic amines are found to be released from certain diseases like uremia and lung cancer.^{3,4} Therefore, detecting these amines at the trace vapor level is very crucial for environmental pollution monitoring and control, food safety, and even medical diagnosis. Fluorescent sensing or probing represents one simple, expedient, and effective detection technique as compared to other techniques and has been extensively applied to the detection of amines in solutions.⁵ However, the same technique still remains challenging for the vapor detection of amines, mainly because there are not so many organic materials available that can meet the requirements for vapor detection, including sufficient emission in the solid state, rapid response, and a high sensitivity and selectivity.⁶ Especially, the availability of *n*-type organic materials (*i.e.*, electron accepting, and suited for sensing reductive reagents like amines) is much more limited compared to the *p*-type counterparts.⁷

In our group, one *n*-type organic molecule has recently been fabricated into well-defined fibril structures with efficient fluorescent emission; these fibril materials have successfully been employed in the vapor detection of amines with high selectivity.⁸ The detection mechanism is primarily based on the fluorescence quenching of the nanofibril film in the presence of amine vapor. However, the reported sensing system still lacks of sufficient sensitivity (or low detection limit) to meet the practical requirement, particularly in the case when the under-detection amine exists at extremely low concentrations (pressure). Therefore, it is critical to largely improve the sensing sensitivity to meet the practical requirement for trace vapor detection of amines in real cases.

In this work, we report the fabrication of ultrathin nanofibers only 30–50 nm in diameter from a perylene based molecule, *N*-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide, which was previously fabricated into fibril structures in our lab and successfully employed in fluorescent sensing of amine vapor.⁸ The ultrathin nanofibers hereby

fabricated, in comparison with the much larger fibers previously reported,⁸ enables great enhancement in fluorescence quenching efficiency, mainly due to the increased surface area offered by the ultrathin nanofibers, which in turn allows for increased vapor exposure to amines. Moreover, films formed from thinner fibers possess increase porosity, facilitating the expedient cross-film diffusion of gaseous species and thus enhancing the collection and accumulation of the trace vapor analytes, combination of which leads to unprecedented sensing sensitivity.

The ultrathin nanofibers were prepared by directly injecting 0.3 mL chloroform solution (3.4 mM) of the perylene monoimide into 1.2 mL of hexane in a small test tube, followed by 30 min of aging. Fig. 1A shows a SEM image of the nanofibers measured by a FEI NanoNova microscope, demonstrating relatively uniform size and shape with diameter ranging from 30 to 50 nm. The nanofibers exhibit the same UV absorption

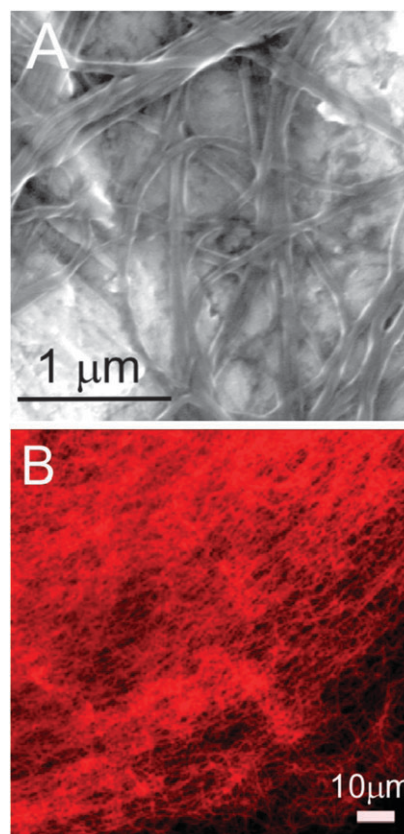


Fig. 1 (A) SEM image of the nanofibers deposited on a glass slide. (B) Fluorescence optical microscopy image of a nanofibril film deposited on a glass slide.

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and fluorescence emission spectra as that of the larger fibers (350 nm in diameter), which was fabricated through a vapor-diffusion process, *i.e.* about 0.2 mL CHCl_3 solution of the perylene monoimide (1.7 mM) was exposed to a methanol vapor in a closed chamber for 1 day.⁸ The same spectral property (and thus electronic structure) are indicative of the same intermolecular organization for these two sizes of fibril structures despite of the different fabrication methods. This simplifies the comparative study when employing the two sizes of fibers for the vapor sensing of amines, for which the fiber size will be the only major factor determining the sensing sensitivity, rather than the molecular stacking mode. The same intermolecular stacking structure of the ultrathin nanofiber also yields the same fluorescence quantum yield as that of the larger fibers (*ca.* 15%), which facilitates the application in fluorescence sensing. Fig. 1B shows a fluorescence microscopy image of a nanofibril film deposited on a glass substrate, where strong red fluorescence emission of the nanofibers can easily be observed even by naked eyes.

In this study, aniline was chosen as the target vapor analyte, mainly due to its relatively lower saturated vapor pressure (880 ppm) compared to other organic amines, which makes it easy to dilute the vapor down to a pressure level that matches the detection limit for the new nanofibril sensing system as described below. For example, 35 ppb of aniline vapor can be simply generated by injecting 0.2 μL saturated aniline vapor into a 5 mL cuvette. This value represents the lowest vapor pressure we can make in the lab so far, and has been used in the test of the fluorescence quenching sensitivity of the ultrathin nanofibers. The fluorescence quenching experiments were performed by injecting the saturated aniline vapor (into a sealed optical cell (5 mL) with the nanofibers deposited on one inner surface. The fluorescence spectra of such a nanofibril film (0.35 mg totally deposited) in the presence of different pressures of aniline vapor are shown in Fig. 2A.

Dramatic fluorescence quenching (13%) was observed for the nanofibril film after 60 s of exposure to only 35 ppb aniline vapor. As calculated, considering both the molecular amount of the nanofibers and aniline vapor, one aniline molecule can quench the fluorescence emission corresponding to seven building-block molecules within a nanofiber, *i.e.*, the fluorescence quenching is amplified due to the one-dimensional enhancement of exciton diffusion along the long axis of nanofiber.¹⁰ Under the same measurement condition, only *ca.* 4% quenching (Fig. 3A) was observed with the larger nanofibers (350 nm in diameter), *i.e.* one aniline molecule can only quench two building-block molecules emission. The decreased quenching efficiency is likely due to the enlarged cross-section size of the fibers, for which the exciton diffusion is more bulk dispersed, not as confined along the long axis as expected for the ultrathin nanofibers. One-dimensional confined exciton diffusion is usually conducive to enhancement of fluorescence quenching if the intermolecular energy transfer is dominant along the long axis of nanofibers.¹⁰ This implies an effective way to improve the quenching (sensing) efficiency simply by decreasing the size of the nanofibers, which in turn increase the surface area of the nanofibril film thus deposited. It should be noted that the real sensitivity of the nanofibril film shown in Fig. 2 should be much higher than the measured

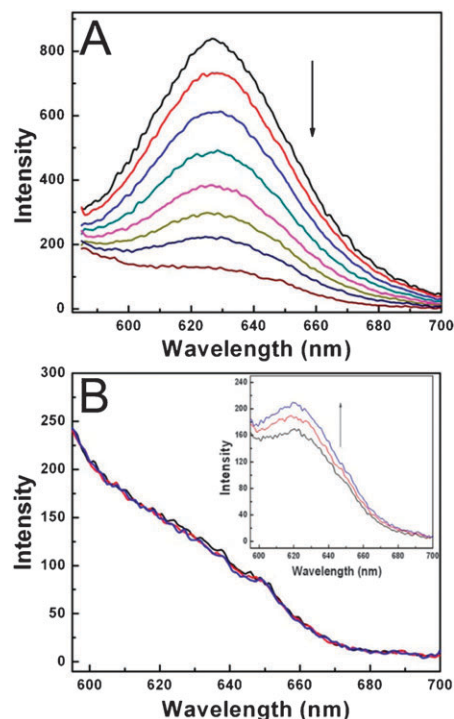


Fig. 2 (A) Fluorescence spectra of a nanofibril film after 60 s of exposure to aniline vapor at 35, 70, 175, 350, 525, 875, 1750 ppb. (B) Fluorescence spectra of a nanofibril film measured 15 min (red) and 30 min (blue) after the complete quenching (shown in black) in the presence of 1750 ppb aniline vapor. No spectral change with time indicates irreversibility of the quenching process. The same test was also performed with the larger fibers (350 nm in diameter) as shown in the inset, where significant recovery of the fluorescence emission was observed.

value if taking into account the technical fact that the small volume (0.2 μL) of aniline vapor can't be released completely into the cuvette due to the significant absorption in the syringe. Moreover, the smaller size of nanofibers are conducive to enhancing the porosity of the film thus deposited, *i.e.*, producing a smaller pore structure but with a more bulky inter-pore connection. This enhanced porosity, along with the increased surface area, not only facilitates the adsorption of amine vapor, but also strengthen the accumulation of the amine species thus collected from the gaseous phase. Indeed, once the aniline molecules were adsorbed into the nanofibril film, they usually remain condensed within the solid phase, no release back to the gaseous atmosphere. This is consistent with the results presented in Fig. 2B, where the quenched fluorescence remained unchanged even 30 min after the film was exposed to 1750 ppb of aniline vapor. In contrast, for the film deposited from the larger fibers (diameter of 350 nm) the fluorescence intensity turned to gradually increase after exposure to the same vapor pressure of aniline, indicating significant release of aniline molecules back to the gaseous phase (inset, Fig. 2B). The sustainable accumulation of gaseous analytes within the film matrix is crucial for enabling trace vapor sensing, for which expedient and effective collection of analyte molecules from the atmosphere environment is often a defining factor for the sensing system.

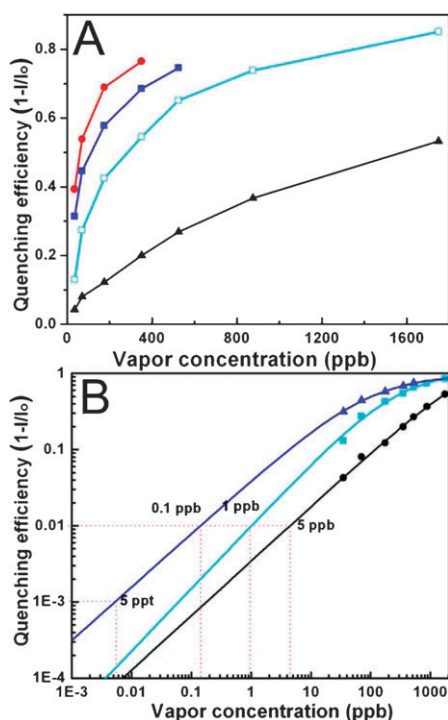


Fig. 3 (A) Fluorescence quenching efficiency ($1 - I/I_0$) as a function of the vapor concentration aniline, measured for the nanofibril films deposited from both the ultrathin nanofibers (30–50 nm) and large fibers (350 nm); comparative investigation was performed on three different films fabricated from the ultrathin nanofibers using various amount of fibril materials (cyan: 0.35 mg; blue: 0.15 mg; red: 0.1 mg) as well as a film fabricated from the large fibers (black: 0.35 mg). (B) Fitting the three sets of data in (A) with the Langmuir equation aiming to predict the detection limit based on the common photon detection threshold of PMT. All data are with an error of $\pm 3\%$.

Technically, as small as 0.1% (or below) change in fluorescence emission intensity can be detected by a well-calibrated photodetector (*e.g.*, PMT).⁹ Based on such a photon detection threshold, one way to further improve the vapor sensing sensitivity (or detection limit) is to increase the signal-to-noise ratio. Generally, the less the nanofibers are employed, the less the quencher molecules are needed for the same percentage of fluorescence quenching, thereby leading to enhanced sensitivity to the trace vapor analyte. However, to maintain the sufficient adsorption and accumulation for the trace vapor, the film deposited from a smaller amount of fibers must maintain a sufficiently high surface area and porosity. To this end, ultrathin nanofibers are ideally suited for fabrication as thin films (potentially using much less materials), while still maintain high surface area and porosity. Fig. 3A shows the fluorescence quenching in response to the vapor of aniline measured for the nanofibril films deposited from different amount of fibril materials. Under the same vapor pressure, larger quenching percentage was observed for the film fabricated with less amount of nanofibers. For example, under the vapor pressure

of 35 ppb, 31% of fluorescence quenching was observed for the film deposited from 0.15 mg nanofibers, whereas only 13% of fluorescence quenching was obtained for the film deposited from 0.35 mg nanofibers. When decreasing the amount of nanofibers down to 0.1 mg, the quenching efficiency was further increased to 39% under the same condition. The increased quenching efficiency implies direct improvement of the detection limit. Fig. 3B shows the fluorescence quenching data fitted with the Langmuir equation. Taking a fluorescence intensity change as 1%, the detection level for the 0.35 mg film is predicted at *ca.* 1 ppb, whereas for the 0.15 mg film the value could be as low as 0.1 ppb. In contrast, for the film deposited from 0.35 mg large fibers (350 nm diameter) the detection level is up to 5 ppb. The lower sensitivity thus observed for the large fibers is mainly due to the intrinsic smaller surface area and lower porosity. If assuming as small as 0.1% (or below) fluorescence quenching can be measured by a well-calibrated photodetector (*e.g.*, PMT), the detection limit for the 0.15 mg film could even be as low as *ca.* 5 ppt.

In conclusion, the fluorescence sensing sensitivity of perylene based nanofibril films for amine vapor was largely enhanced by decreasing the size of the nanofibers, which were fabricated through a new solution-based self-assembly processing. The enhanced fluorescence sensing is mainly due to the increased surface area and the enhanced exciton diffusion along the long axis of nanofiber, along with the increased porosity intrinsic to the film deposited from the ultrathin nanofibers. The sensing efficiency (or detection limit) can further be enhanced by reducing the amount of the nanofibers employed in the film. The unprecedented sensitivity obtained hereby may provide the sensing system broad applications in the practical trace vapor detection of amines.

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