# Expedient Vapor Probing of Organic Amines Using Fluorescent Nanofibers Fabricated from an n-Type Organic Semiconductor

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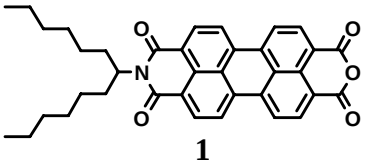
**Supporting Information**

## 1. Synthesis



**1**

N-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxyl-3,4-anhydride-9,10-imide (**1**) was synthesized following the same method previously reported.[1] The only modification is that the hydrolyzed product from N,N'-di(hexylheptyl)-perylene-3,4,9,10-tetracarboxyl-diimide was directly purified by column chromatography (eluent: methylene chloride), yielding 0.35 g (35%) of **1**.

$^1$H-NMR ($CDCl_3$): $\delta$ = 0.83 (t, 6H, $2CH_3$), 1.17-1.42 (m, 16H, $8CH_2$), 1.85 (m, 2H, $CH_2$), 2.24 (m, 2H, $CH_2$), 5.19 (m, 1H, CH), 8.67 (m, 8H, perylene).

## 2. Fabrication of nanofibers

Self-assembly of **1** into nanofibers was performed through a slow solvent-exchange process, which was realized via vapor diffusion within a closed chamber. Briefly, a test tube containing about 0.2 mL $CHCl_3$ solution of **1** (1.7 mM) was placed in a 50 mL jar, which contained about 10 mL of methanol, followed by sealing the jar for slow vapor diffusion between the two solvents (Figure S1). Upon gradual solvent exchange, the solution in the test tube became more dominant with methanol, which is a poor solvent (with low solubility) for molecule **1**, thereby leading to self-assembly of the molecules into nanofibers. Because of the slow crystallization process controlled by the slow vapor diffusion, the nanofibers fabricated via such a process are usually in well-defined shape and sizes as shown in Figure 1. After about 1 day the exchange between the two solvents reached the equilibrium, resulting in complete assembly of the molecules, and precipitating down to the bottom of the test tube. The nanofibers thus obtained were re-dispersed in hexane, producing a suspension well-suited for deposition on a substrate either for microscopy imaging or vapor sensing tests. For each of the sensing tests, the whole amount of the nanofibers thus prepared were deposited on a glass substrate to produce a film that maintained the same surface area (adsorption) for all the sensing tests as presented in Figure 3B.

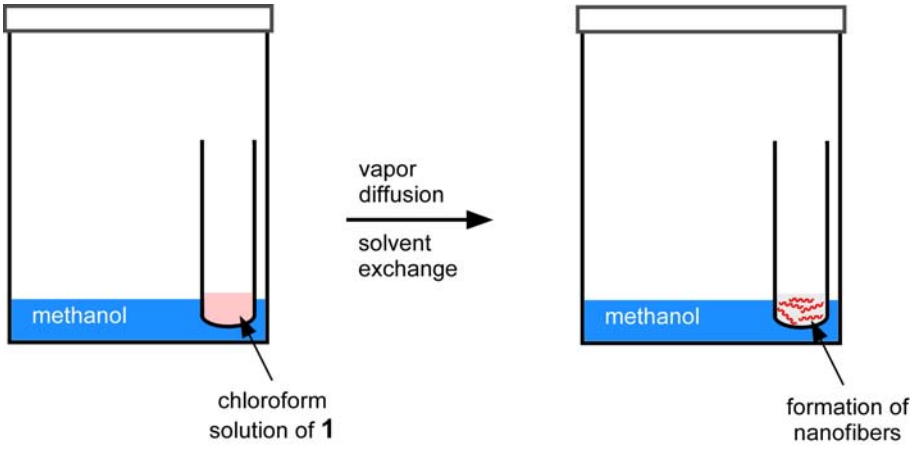



**Figure S1.** A diagram showing the procedure of fabrication of the nanofibers.

### 3. Determination of the fluorescence quantum yield of the nanofibril film

The fluorescence quantum yield ($\phi$) of the nanofibril film was estimated by measuring the absorption and fluorescence intensity in comparison with a thin-film fluorescence standard with $\phi$=100%. The thin-film standard was prepared by sandwiching one drop of a polystyrene/toluene gel between two glass cover slips. Within the gel was dissolved an appropriate concentration of a PTCDI molecule, N,N'-di(hexylheptyl)-perylene-3,4,9,10-tetracarboxyl-diimide (HH-PTCDI). By maintaining molecular dispersion of the molecules within the gel, the fluorescent quantum yield of HH-PTCDI remains 100%, as it is dissolved in a homogeneous solution in toluene or other good organic solvents.[2]

### 4. Materials and microscopy/spectroscopy methods

The organic compounds employed for sensing test include methanol, acetone, acetic acid, THF, acetonitrile, chloroform, toluene, hexane, cyclohexane, nitrobenzene, nitromethane, phenol, cyclohexylamine, bibutylamine, aniline, butylamine, triethylamine, hydrazine, and ammonium hydroxide. All the compounds and/or solvents (HPLC or spectroscopic grade) were purchased from Fisher or Aldrich, and used as received.

UV-vis absorption and fluorescence spectra were measured on a PerkinElmer Lambda 25 spectrophotometer and LS 55 fluorometer, respectively. SEM measurement was performed with a Hitachi S570 microscope (operated at 10 kV). The sample was prepared by casting one drop of the nanofiber suspension in hexane onto a clean glass cover slip, followed by drying in air and then annealing overnight in an oven at 45 $^{o}$C. The dried sample was coated with gold prior to the SEM imaging. The bright-field optical and fluorescence microscopy imaging was carried out with a Leica DMI4000B inverted microscope, using a Rhodamine filter set, which provides excitation in the range of 530-560 nm, and collects emission at > 580 nm.

The fluorescence quenching by amines vapor was monitored following the similar method as previously developed and used for the p-type nanofibril film developed in our lab.[3] Briefly, the fluorescence spectra of the film were measured immediately after immersing inside a sealed-jar (50 mL) containing small amount of the amines. To prevent direct contact of the film with the amines, some cotton was placed above the amines (deposited at the bottom of the jar). Before use the jar was sealed for overnight to achieve saturated vapor inside. The presence of cotton also helps maintain a constant vapor pressure. The fluorescence quenching at the diluted vapor

pressures of amines (e.g., aniline and hydrazine) was performed in a sealed cuvette (5 mL volume), into which a small volume of the saturated vapor of a specific amine was injected (using an air-tight micro-syringe) to achieve the diluted vapor. For example, injection of 5 μL of saturated aniline vapor (880 ppm) into the 5 mL cuvette will produce a vapor pressure $10^3$ times diluted, e.g., 880 ppb. The lowest vapor pressure of aniline that can be achieved through vapor dilution was about 35 ppb, for which two steps of dilution were carried out, i.e., 50 μL of the ambient saturated vapor of aniline was injected into a 5 mL jar immersed in a water bath (ca. 70 ºC, to avoid minimal condensation of the vapor), followed by injecting 20 μL of this diluted vapor into the 5 mL cuvette.

The time-dependent fluorescence quenching profile (shown below in Figure S4) was measured with an Ocean Optics USB4000 fluorometer, which can be switched to the mode to measure the emission intensity at a selected wavelength as a function of time. An open sample holder (Ocean Optics, CUV-ALL-UV) was used to hold the nanofibril film deposited on a glass cover slip, and the fluorescence from the nanofibers was collected at 90º with respect to the excitation beam, which was provided by an $Ar^+$ laser (Melles Griot) tuned at 488 nm. Both the excitation and emission were transported with 0.6 mm premium UV/Vis fibers (Ocean Optics). The fluorescence quenching was carried out by blowing a few mL of saturated aniline vapor (880 ppm) onto the nanofibril film during the course when the emission was continuously recorded by the fluorometer.

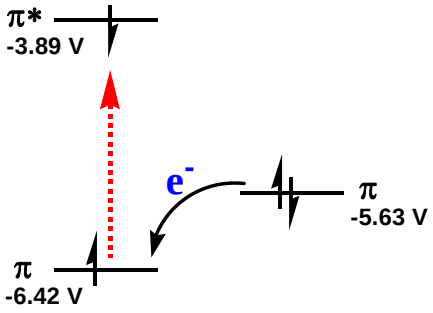



**Figure S2.** Energy levels of HOMO (π) and LUMO (π*) orbitals of **1** and aniline showing the favorable electron transfer from amine to the photoexcited state of **1**. The same diagram applies to the other amines, while the reducing power (or the π-orbital level) would be different from that of aniline (see Table S1, *vide infra*). Geometry optimization and energy calculation were performed with density-functional theory (B3LYP/6-311g**// B3LYP/6-31g*) using Gaussian 03 package.

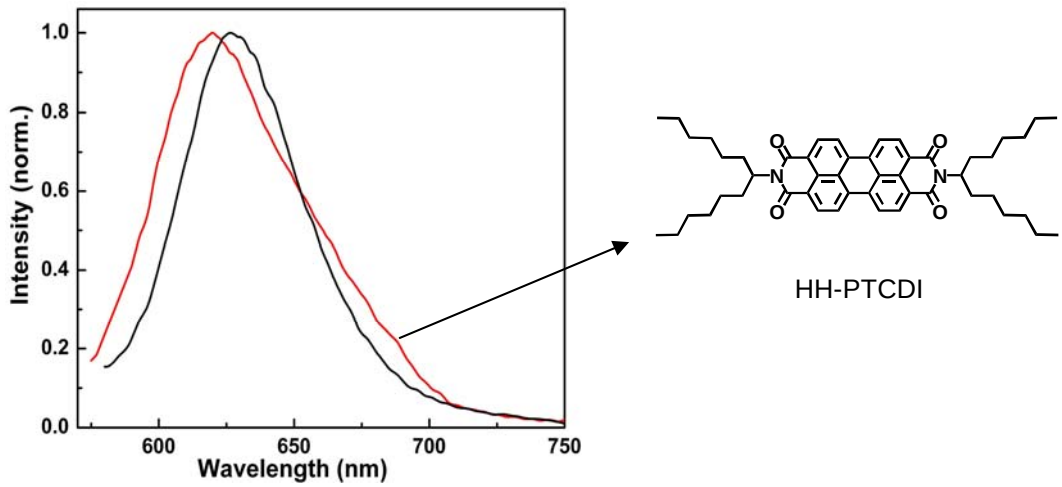
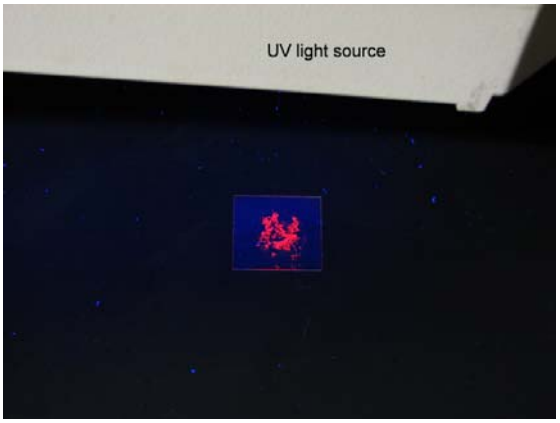



**Figure S3.** Comparison between the fluorescence spectra of the nanofibril film of **1** (black) and a thin film (red) drop-cast from the THF solutions of a PTCDI molecule modified by two bulky, branched side-chains, N,N'-di(hexylheptyl)-perylene-3,4,9,10-tetracarboxyl-diimide (HH-PTCDI), which forms ill-shaped aggregates, mainly due to the significant steric hindrance caused by the large side-chains.

***Table S1.*** Physical properties and the quenching results of various amines and phenol.

| Analyte | Oxidation potential[4] $E_{1/2}$ value(V) vs SCE | Driving force[a] $\Delta G$ ($-e$V) | Vapor pressure[b] ppm at 25°C | Quenching efficiency (10 s of exposure) (%) |
|---|---|---|---|---|
| Butylamine | 1.52 | 0.62 | 120400 | 96 |
| Pentylamine | 1.69[c] | 0.45 | 39480 | 95 |
| Hexylamine | 1.72[d] | 0.42 | 8580 | 95 |
| Octylamine | - | - | 1280 | 94 |
| Dibutylamine | 1.20 | 0.94 | 3360 | 91 |
| Triethylamine | 0.99 | 1.15 | 75990 | 85 |
| Cyclohexylamine | 1.72[d] | 0.42 | 11840 | 94 |
| Cyclopentylamine | - | - | - | 94 |
| Aniline | 0.86 | 1.28 | 880 | 95 |
| Hydrazine | 0.43 | 1.71 | 5920 | 98 |
| Phenol | 1.37 | 0.77 | 340 | 54 |

[a] The driving force for the fluorescence quenching, i.e., photoinduced electron transfer from the analyte to **1** was calculated using the Rehm-Weller equation: $\Delta G = -e(E^o_{red}-E^o_{ox}) - \Delta E_{oo}$, where $E^o_{red}$ and $E^o_{ox}$ are the reduction potential of electron acceptor and the oxidation potential of electron donor, respectively, and $\Delta E_{oo}$ is the singlet excitation energy. [b] The vapor pressure data are cited from CRC handbook of Chemistry and Physics, 85th Edition, CRC Press, 2004, p15-16 to 25. [c] The oxidation potential of pentylamine (determined as the peak potential) is cited from ref. 5.[5] [d] The oxidation potentials of hexylamine and cyclohexylamine are cited from ref. 6.[6] *The relatively lower quenching efficiency observed for the tertiary amines might be due to the weaker chemical binding with the anhydride, with which the binding of a tertiary amine is primarily through the donor-acceptor interaction, but lack of hydrogen bonding.*




**A movie clip:**

Under UV (366 nm) irradiation, the nanofibril film of **1** deposited on a glass cover slip exhibits strong red emission as shown in this image captured by a Canon digital camera (PowerShot S3IS). Upon blowing over with saturated vapor of aniline (880 ppm), the red emission was completely quenched, resulting in a dark-red, non-fluorescent film, as shown in this movie clip captured by the same camera:
http://www.chem.siu.edu/zang/image/gas-sensor.wmv

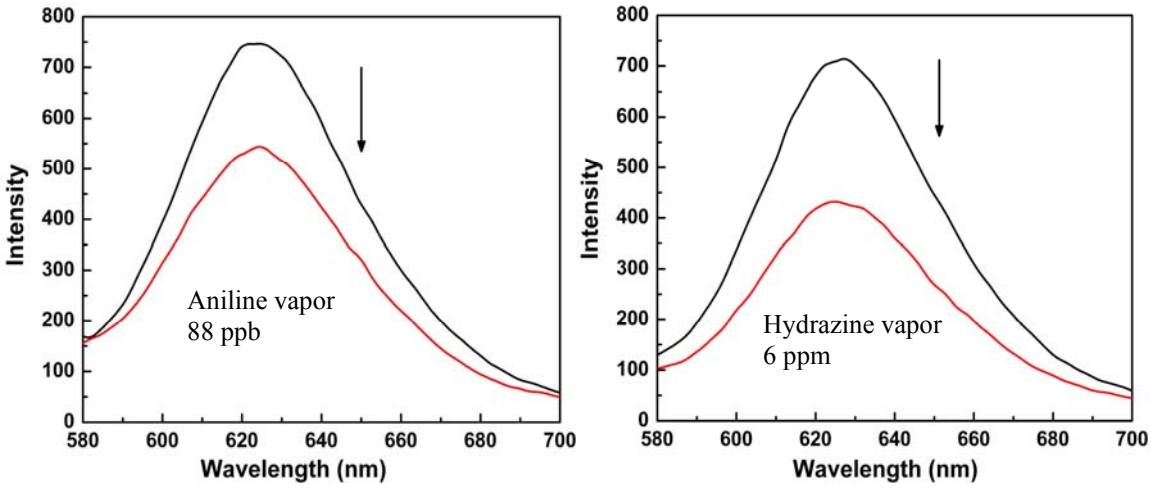



**Figure S4.** Fluorescence spectra of a nanofibril film before (black) and after (red) exposure to diluted vapor of aniline and hydrazine.

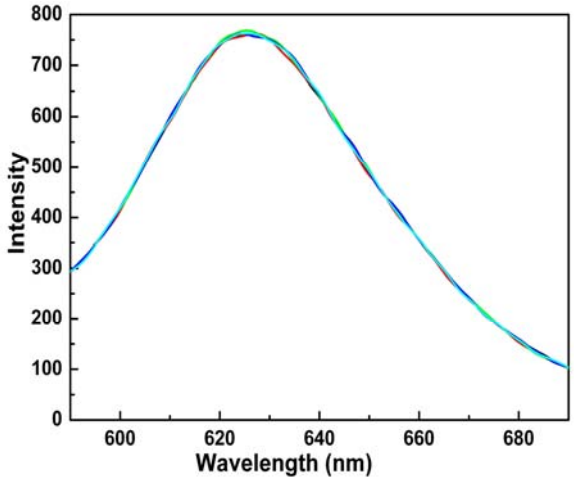



**Figure S5.** Fluorescence spectra of a nanofibril film after continuous irradiation at 550 nm for 0, 10, 20, 30, 60 min. The film was held in the LS55 fluorometer with a constant excitation slit of 5 nm and a pulsed Xenon discharge lamp (7.3 W) as the light source. The unchanged fluorescence indicates the robust photostability of the film.

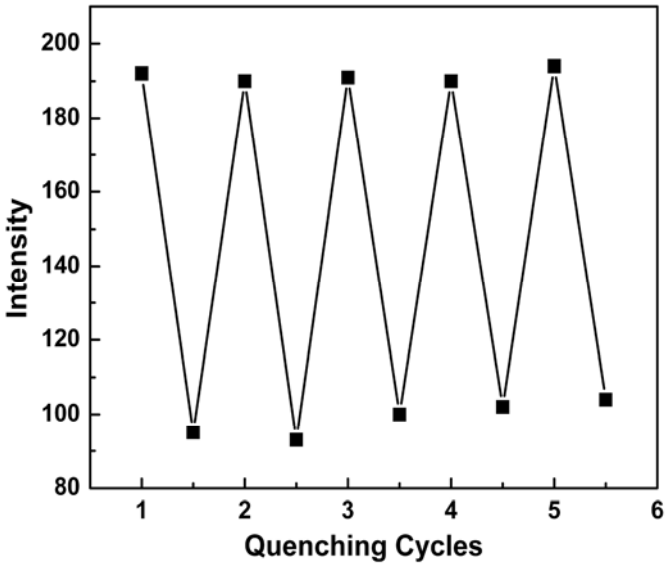



**Figure S6.** Five continuous cycles of quenching-recovery were tested for a nanofibril film upon exposure to the saturated vapor of phenol (335 ppm). The quenching was performed by exposing the film to the phenol vapor for 15 s. After each cycle of quenching, the fluorescence of the film was recovered by exposing the film to an open air for 60 min or at an elevated temperature (60 ºC) for 5 min.

**References:**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