Supplementary Information

Experimental section

Materials

Poly(vinylidene Fluoride) (PVDF) (Mw = 53,4000 g/mol), 3,4,9,10-perylenetetracarboxylic dianhydride and tridecan-7-amine were purchased from Alfa Aesar. Aniline, imidazole, dichloromethane, n-hexane, acetone, dimethylformamide (DMF) toluene, methanol, and acetic ether were purchased from Beijing Chemical Works and used without further purification. N-butylamine, dibutylamine, 1-hexamine, cyclohexamine, isooctamine, benzylamine, 4-methylaniline, 4-fluoroaniline, 4-nitroaniline, phenol were purchased from Innochem.

Instruments

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV spectrometer operating at 300 and 75 MHz using deuterated solvents. Relative Molecular Mass was recorded on Bruker ultraflextreme MALDI-TOF. Scanning electron microscopy (SEM) images were collected on S4800 (HITACHI) at 1.5 kV and 1.0 kV. Transmission electron microscopy (TEM) images were collected on JEM-1400 (JEOL) at 100 kV. Samples for TEM measurements were prepared by dropping the solution of PDI@PVDF (the solution was prepared by adding a small amount of PDI@PVDF fibre to 10 ml ethanol with ultrasonic stirring for 20 minutes) onto a copper grid. Fluorescence spectra were measured by fluorescence spectrophotometer (F-7000, HITACHI and ATP 2000, OPTOSKY). UV-vis absorption spectra were recorded on a vertical scan Bruker AXS D8 Advance. Fluorescence decay profiles were recorded on Edinburgh FLS980 spectrometer

Synthesis of compound PDI

3,4,9,10-Perylenetetracarboxylic dianhydride (0.98 g, 2.5 mmol), tridecan-7-amine (1.99 g, 10 mmol), and imidazole (8.00g) were mixed in flask with three necks (100 mL). The solution was stirred at 140°C for 5h under nitrogen protection. Then, ethanol (20mL) was added to it until the solution was cooled to 80°C. Next, the solution added with hydrochloric acid (2 M, 70mL) at room temperature was stirred overnight. Then the solution was filtered , washed to neutral with ethanol and distilled water, and obtained red solid was treated by vacuum drying at 60°C. The residue was purified by column silica gel chromatography with the eluents of dichloromethane/n-hexane (1/3, v/v) to obtain PDI as the red solid. Yield: 90%. ¹H NMR (CDCl₃, 300 MHz, ppm): δ 8.66 (d, *J* = 11.4 Hz, 8H), 5.19 (s, 2H), 2.24 (d, *J* = 11.7 Hz, 4H), 1.86 (s, 4H), 1.49 - 1.02 (m, 32H), 0.81 (d, *J* = 6.5 Hz, 12H). ¹³C NMR (CDCl₃, 400 MHz): 14.10, 22.02, 26.95, 29.25, 31.79, 32.38, 54.78, 123.08, 126.47, 129.62, 131.20, 134.55. MALDI-TOF: calcd. for C₅₀H₆₂N₂O₄ [M]⁺, 754.471; found, 754.223.

Preparation of Electrospun Nanofibers

To prepare a precursor solution for synthesizing the electrospun nanofibers, 100mg of PDI were independently dissolved in 4.0 mL of DMF. In each case, when the solute was completely dissolved, 2.00 g of PVDF as a matrix polymer was added, and the resulting mixture was stirred and loaded into a stainless steel syringe connected to a needle of gauge 19. The distance between the end of the needle and grounded plate was adjusted to be 15 cm before applying 12.00 kV. The precursor solution was ejected to form fine fibers on the surface of a grounded aluminum plate located 15 cm below the tip of the needle. The flow rate was carefully kept at 2.0 ml/h. After collection, the polymer fibers were dried in a 40 °C vacuum oven for 1 d to prevent agglomeration.

Solid-State Fluorescence Sensing Experiments

The PDI@PVDF film was fixed on a special designed scaffold then covered with a quartz cell (Fig. S12). A 365nm LED lamp was used to excite the film, and the fluorescence variation (λ =630nm) in the presence of organic amines was continuously monitored by a spectrometer.

In order to obtain saturated vapor, a small amount of amine is sealed in a sealed sample bottle for overnight to obtain saturated vapor. The diluted vapor of aniline was obtained in a sealed air bag, into which a small volume of the saturated vapor of aniline was injected (using an air-tight glass syringe) to achieve the diluted vapor. For example, injection of 14 mL of saturated aniline vapor (880 ppm) into the 5 L air bag will produce a vapor pressure 714 times diluted (about 1.25 ppm). The lowest vapor pressure of aniline that can be achieved through vapor dilution was about 0.4 ppb, for which two steps of dilution were carried out, i.e., 5 mL of the saturated vapor of aniline was injected into a 5 L air bag, followed by injecting 2 mL of this diluted vapor into other 5 L air bag.



Scheme S1. Synthetic route of PDI



Fig. S1. ¹H NMR (a), ¹³C NMR (b) and MALDI-TOF (c) spectra of PDI (solvent in NMR: CDCl₃).



Fig. S2. (a) Concentration-dependent UV-Vis spectra of 1 from 4.42×10^{-6} M to $3.76.3 \times 10^{-5}$ M in CHCl₃ (λ_{ex} = 405 nm); (b) Normalized concentration-dependent fluorescence spectra of 1 from 1.4×10^{-6} M to 2.3×10^{-2} M in CHCl₃ (λ ex= 365nm)



Fig. S3. UV-Vis spectra and fluorescence spectra of PDI in CHCl₃ (1.4×10⁻⁶ M, λ_{ex} = 405 nm).



Fig. S4. Concentration-dependent fluorescence spectra of PDI from 1.4×10^{-6} M to 2.3×10^{-2} M in CHCl₃ (λ_{ex} = 405 nm).Inset: Concentration-dependent color change of PDI from 1.4×10^{-6} M to 2.3×10^{-2} M in CHCl₃ (λ_{ex} = 365 nm)



Fig. S5. SEM images of PDI. The solvent was evaporated in vacuum



Fig. S6. SEM images of PDI. The solvent was naturally evaporated in 3 hours.



Fig. S7. SEM images of PDI. The solvent was slowly evaporated in several days.



Fig. S8. XRD spectra of PDI (the solvent was slowly evaporated in several days)



Fig. S9. XRD spectra of PDI@PVDF



Fig. S10. PDI agglomerates under cross-polarized microscope



Fig. S11. (a) picture of a PDI \subset PVDF ; (b) picture of a PDI \subset PVDF under ultraviolet excitation (λ_{ex} =365nm); (c) picture of PDI molecular lamellae; (d) picture of PDI molecular lamellae under ultraviolet excitation (λ ex=365nm); (e) picture of electrospinning PDI@PVDF film; (f) picture of electrospinning PDI@PVDF film under ultraviolet excitation (λ ex=365nm)



Fig. S12. Gas sensor detection device



Fig S13. The pressure-dependent fluorescence response (λ_{em} =630nm) of the PDI@PVDF film exposed to aniline vapor.



Fig S14. Fluorescence response of the PDI@PVDF film to the saturated vapor of various organic reagents; 1, n-butylamine; 2, dibutylamine; 3, 1-hexamine; 4, cyclohexamine; 5, isooctamine; 6, benzylamine; 7, phenol; 8, aniline; 9, 4-fluoroaniline; 10, 4-methylaniline; 11, 4-nitroaniline, 12, n-hexane, 13, dichloromethane, 14, chloroform, 15, toluene, 16, methanol, 17, acetone, 18, acetic ether. Error bar: standard deviation.



Fig. S15 a) Fluorescence spectra of PDI in dichloromethane (0.01mM) upon gradual addition of aniline (0~50mM); b) Fluorescence spectra of PDI in dichloromethane (0.1mM) upon gradual addition of aniline (0~50mM) c) Fluorescence spectra of PDI in dichloromethane (1mM) upon gradual addition of aniline (0~50mM); d) Fluorescence quenching efficiency of PDI solutions with different concentrations upon gradual addition of aniline (0~50mM) (λ_{ex} =365nm).



Fig. S16 a) Fluorescence decay profiles of PDI at 0.01mM, 0.1mM, 1mM (monitored at 536 nm), b) Fluorescence decay profiles of PDI at 0.01mM, 0.1mM, 1mM (monitored at 574 nm), c) Fluorescence decay profiles of PDI at 0.1mM (monitored at 536 nm) upon gradual addition of aniline (0~50mM), d) Fluorescence decay profiles of PDI at 0.1mM (monitored at 574 nm) upon gradual addition of aniline (0~50mM) e) Concentration-dependent fluorescence lifetime of PDI solution (monitored at 536 nm, 574nm), f) Fluorescence lifetime of PDI solution at 0.1mM upon gradual addition of aniline (monitored at 536 nm, 574nm).



Fig. S17. Plots of τ_0/τ and I_0/I of the PDI (0.1mM) against the concentration of aniline.



Fig. S18. Time-resolved fluorescence intensity of PDI⊂PVDF (a) and PDI molecular lamellae (b) upon consecutive exposures to 250 ppb aniline vapor