Supplementary Information

for

Detection of gaseous amines with a fluorescent film based on a perylene bisimide-functionalized copolymer

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Contents

1. Materials and methods

HEMA and azodi-isobutyronitrile (AIBN) were purchased from TCI Development Co., Ltd. The perylene derivative, *N*-(tricosan-12-yl)-*N′*-(but-ylacrylate)perylene- 3,4,9,10-tetra-carboxyl-bisimide (monomer M1), was synthesized in a stepwise manner according to the published literatures.[1-3] Toluene was freshly distilled from sodium benzophenone ketyl under a nitrogen atmosphere prior to use. Aniline, *o*-toluidine, *tert*-butylamine, ethylamine, methylamine, hydrazine hydrate, 1,6-hexanediamine, spermidine, cadaverine, and putrescine were purchased from J&K (Shanghai) Chemical Ltd., all other reagents and solvents are of the analytical grade and used directly without further purification. Silica gel plates (Φ~15.0 mm) used in the experiment for fabrication of fluorescent films were cut from commercial glass-supported TLC plates.

^{1}H NMR spectra were recorded on a Bruker AV 600 NMR spectrometer in methanol-d_4 using TMS as the internal reference. The molecular weights of the obtained polymers were determined with an Ultimate 3000 DGLC. The UV-vis absorption spectra were measured with a Hitachi U-3900/3900H spectrophotometer and the absorption coefficients of the compounds were calculated based on the Lambert-Beer law. Steady state fluorescence measurements were carried out on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS920) at room temperature with a xenon lamp as the light source.

2. Synthesis details and characterization of poly(HEMA-*co*-PBI)

Monomer M1 (25.0 mg, 0.03 mmol), HEMA (0.50 g, 4.10 mmol) and AIBN (2.0 mg, 0.014 mmol) in 0.2 mL toluene was degassed *via* bubbling of N_2 gas. After being fully dissolved at room temperature, the mixture was stirred at 70 °C for 12 h and then the crude product was dissolved in methanol, poured into 200 mL diethyl ether and filtered to give poly(HEMA-*co*-PBI) as a reddish solid (0.41 g, 82%). ^{1}H NMR (600 MHz, CD_3OD): 0.5~1.2 (m, -CH_3), 1.58~2.06 (br, -C-CH_2-), 3.45~3.90 (s, HO-CH_2-CH_2-), 3.90~4.10 (s, HO-CH_2-CH_2-). $\overline{M}_w \sim 4.44 \times 10^6$ (GPC method, PDI=4.44).

3. Fluorescence quenching experiments

The fluorescence quenching measurements of the films by amine vapors were monitored following the two similar methods as previously developed in our lab.[4,5] Firstly, basic fluorescence measurements were performed at room temperature on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS 920) with a front face method. The fabricated film was inserted into a quartz cell with its surface facing the excitation light source, and fluorescence emission of the film was recorded in the absence and presence of the analyte vapors.[6] Then the continuous fluorescence intensity of the film was monitored on a home-made sensing platform before and after the injection of amine vapors by an air-tight micro-syringe. The generation of dilute analyst vapor was processed by injecting a certain volume of saturated vapors to a 5.0 mL chamber and stand by for 10 min for equilibrium. For example, 5.0 μL saturated aniline vapor (880 ppm) can be gradually diluted into 5.0 mL vapor (880 ppb).[7,8]

4. NMR and MS spectra of the monomer and final copolymer

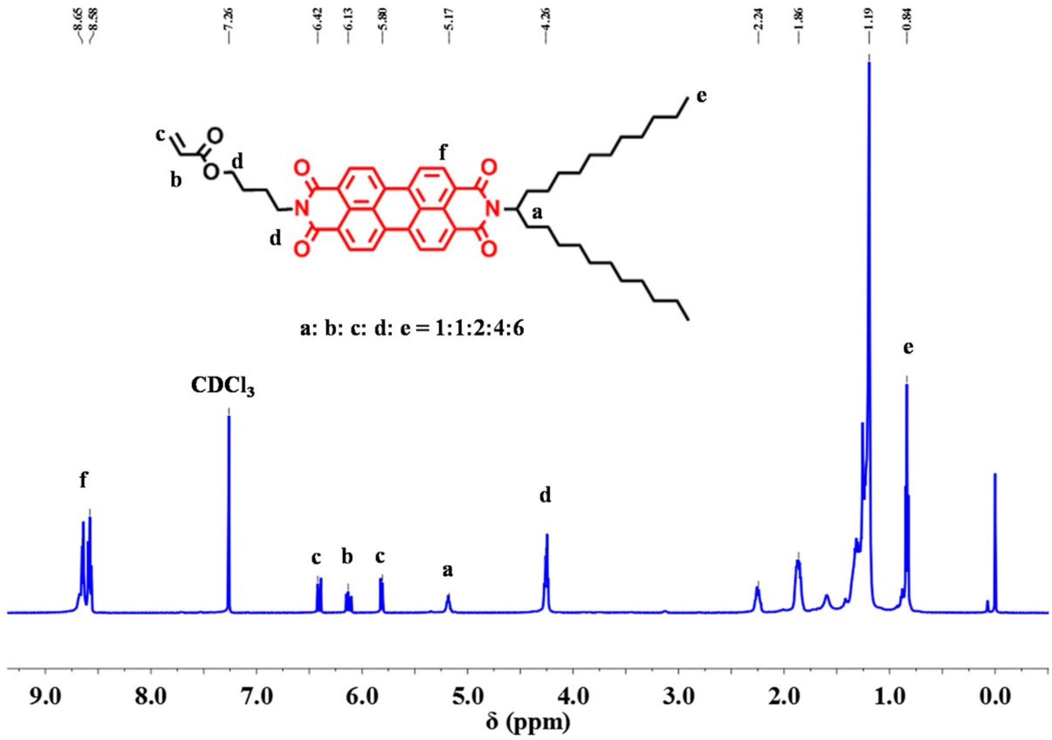

Fig. S1. ^{1}H NMR spectrum of monomer M1 in $CDCl_3$.

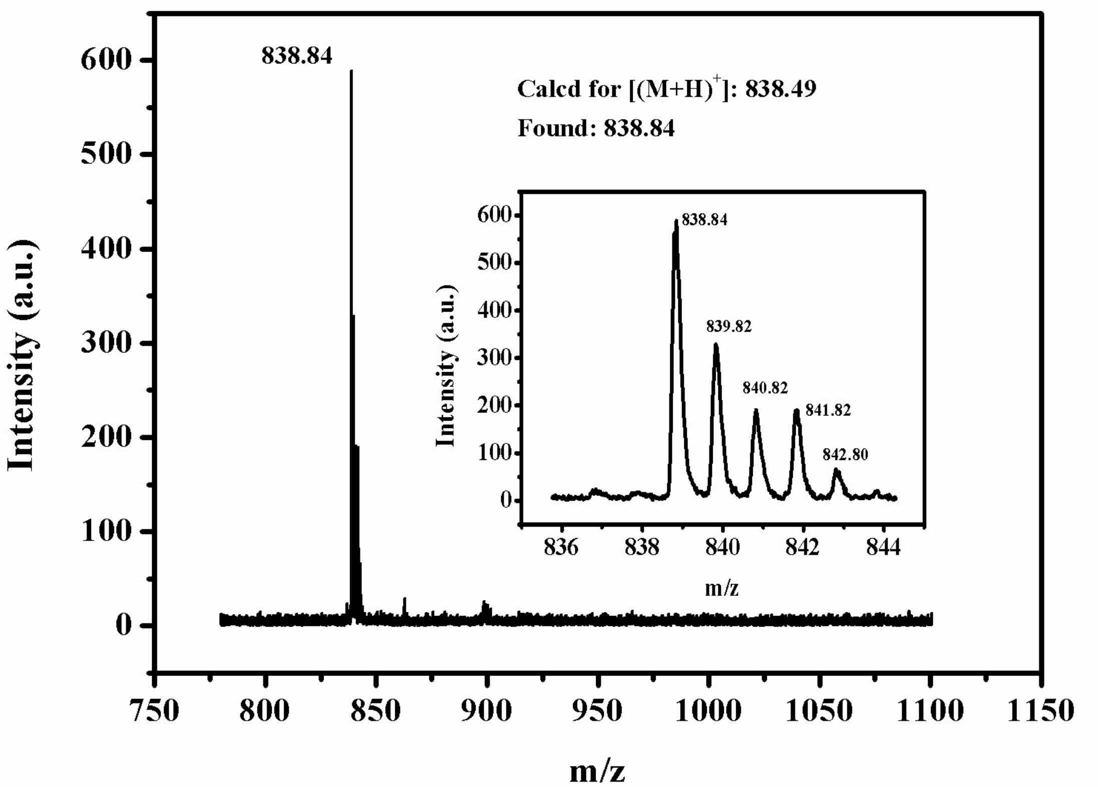

Fig. S2. MALDI-TOF spectrum of monomer M1.

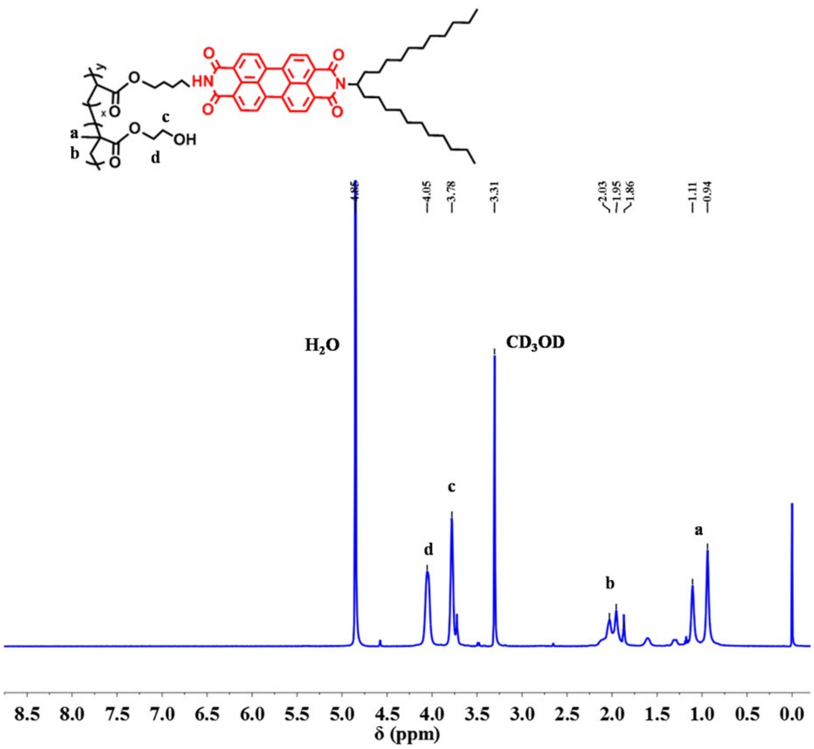

Fig. S3. [1]H NMR spectrum of poly(HEMA-*co*-PBI) in CD_3OD.

5. Calculation of the content of PBI units

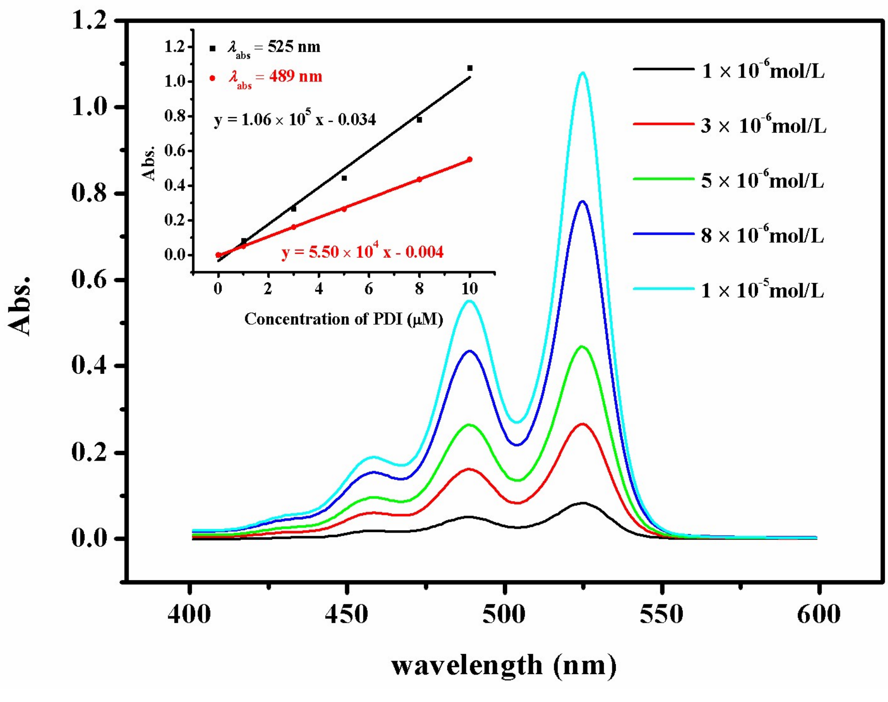

Fig. S4. The standard working curve for absorption of M1 in MeOH.

6. Photochemical stability of the fluorescent film

The photochemical stability of the film as produced was tested by continuously monitoring its fluorescence emission at the maximum excitation and emission wavelengths ($\lambda_{ex}/\lambda_{em}$ = 490/540 nm) for about 2 h. It is seen that the emission intensity of the film is stable and the emission didn't show any decrease over 2 h continuous illumination, suggesting the superior photo-chemical stability of the film. Fig. S5 depicts a typical result from the tests.

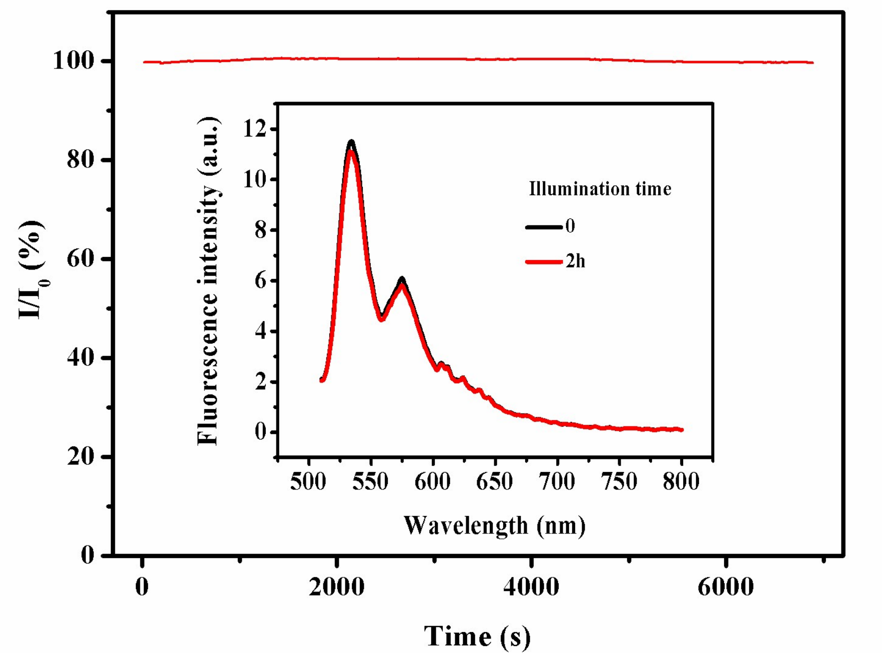

Fig. S5 Variation of fluorescence emission intensities of polymer in film state recorded at the wavelength of 540 nm (λ_{ex} = 490 nm, 150 W, Xe Lamp).

7. Determination of detection limit of the film to aniline

The detection limit (*DL*) of the sensing film has been determined according to the following equations:

$$S_b = \sqrt{\frac{\sum_{i=1}^{n} X_i - \bar{X}}{n-1}} \quad (1)$$

$$S = \frac{\Delta I}{\Delta C} \quad (2)$$

$$DL = \frac{3S_b}{S} \quad (3)$$

The standard deviation (S_b) was calculated as follow: Firstly, the response intensity of the film in air was recorded (x_i) for more than 10 times and the corresponding average intensity ($\bar{x}$) was calculated. By fitting the intensity data and the average intensity as obtained into eq. 1, the value of the standard deviation (S_b) was acquired. Then, the film was exposed in aniline vapor of different concentrations, and the response intensity (Fig. 3b) was recorded. Corresponding variations of the intensity (ΔI) and vapor concentration (Δc) data were fitted into eq. 2, then S value for the present system was obtained. Finally, the DL for the present system was calculated according to eq. 3.

8. References

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