Supporting Information

for

Langmuir-Blodgett Film of Perylene Bisimides and Fluorescent Recognition of Diamines

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Contents

1. Synthesis and characterization .................................................................2
2. Fluorescence emission spectra of PEBBO in CHCl₃ at different concentrations ....6
3. Absorption spectra of PEBBO in different solvents ........................................7
4. The change of conformation of PEBBO molecular at the air/water interface ........8
5. The home-made device .............................................................................9
6. The absorption and emission spectra of PEBBO-based fluorescent film ...........10
7. Energy levels of HOMO (π) and LUMO (π*) orbitals of PEBBO .................11
8. The emission spectra of the film in the presence of different concentrations ethylenediamine vapor .................................................................................12
9. The selectivity of the film with a layer thickness of 30 layers. .......................13
10. The sensitivity of the film with a layer thickness of 30 layers. .......................14
11. The reversibility of the film with a layer thickness of 30 layers. ....................15
12. The sensing performance of the film as prepared in a surface pressure of 30.5 mN/m .............................................................................................................16
13. The sensing performance of the film as prepared in a surface pressure of 16.8 mN/m .............................................................................................................17
14. The contact angle images of blank substrate and the LB films based on PEBBO, PEBAO and PEBBA ..............................................................................18
15. The response intensity of PEBAO-based LB film ........................................19
16. The response intensity of PEBBA-based LB film .................................................20
17. Photochemical stability of PEBBO-based LB film .................................................21
18. Plots of $I_0/I$ and $\tau_0/\tau$ of the fluorescence film against ethylenediamine vapor at different concentrations ...............................................................................................22
19. Calculation of static ($K_S$) quenching constant .......................................................23
20. $^1$H NMR and MS spectra of intermediates and target molecules ..........................24
1. Synthesis and characterization

Synthesis of compound PEB

The intermediate PEB was synthesized according to a literature method.[1]

Synthesis of compound TBA

TBA was synthesized according to another literature method.[2]

Synthesis of compound ITD

Triethylene glycol monomethyl ether (0.67 g, 4 mmol) was dissolved in 10 mL of THF and 3 mL of water, then NaOH (0.4 g, 0.01 mol) was added, and the solution was stirred vigorously at 0°C. To the solution p-toluenesulfonyl solution in THF (0.93 g, 4.9 mmol mmol dissolved into 5 mL of THF) was dropwise added with stirring. The system was allowed to react at 0°C for another 3 h. Then, 50 mL water poured into the solution and extracted with 30 mL CH₂Cl₂. The collected organic layer was washed several times with water and dried over anhydrous sodium sulfate, and then the solvent was removed under reduced pressure to get colorless liquid (90%).

The above-mentioned liquid (0.6 g, 0.02 mol, 20 mL) was dissolved in 10 mL of acetone and stirred at room temperature for 0.5 h, and then NaI (3.6 g, 0.024 mol) was added. The system was allowed to react at room temperature for 24 h and filtered. The solvent was removed under reduced pressure to get the white solid. Then the solid was dissolved in ethyl acetate and extracted with water. The collected organic layer was dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel.
using ethyl acetate as eluent to get compound ITD as a colorless liquid (90%). $^1$H NMR (CDCl$_3$/Me$_4$Si, 600 MHz; Fig. S19): δ (ppm), 3.7-3.8 (2H, t, -OCH$_2$-), 3.6-3.7 (6H, t, -CH$_2$-), 3.5-3.6 (2H, t, -OCH$_2$-) 3.3-3.42 (3H, s, -OC$_3$H$_3$-), 3.2-3.3 (2H, t, -CH$_2$-). MS (ESI-MS, m/z): Calcd for [(M+Na)$^+$]: 296.9964, found: 296.9964 (Fig. S20).

**Synthesis of compound TEA**

TEA was synthesized according to a literature method.$^{[2]}$ $^1$H NMR (CDCl$_3$/Me$_4$Si, 600 MHz; Fig. S21): δ (ppm), 7.32-7.35 (2H, s, C$_6$H$_6$), 4.17-4.25 (6H, t, -OCH$_2$-), 3.80-3.88 (6H, t, -CH$_2$-) 3.65-3.70 (9H, s, -OC$_3$H$_3$-), 3.35-3.60 (24H, t, -CH$_2$-). MS (MALDI-TOF, m/z): Calcd for [(M+Na)$^+$]: 631.29, [(M+K)$^+$]: 647.26, found: 631.25, 647.23 (Fig. S22).

**Synthesis of compound PEBBO**

TEA (1.83 g, 3 mmol) was suspended in an excess of freshly distilled toluene (10 mL) and SOCl$_2$ (400 μL), the solution was refluxed at 80 °C under Ar atmosphere for 6 h. Then (1.138g, 1.43 mmol) PEB was added. The system was allowed to react under Ar atmosphere for another 24 h at room temperature. The solvent was rotary evaporated, and the residue was dissolved in dichloromethane, and then extracted with water (30 mL × 3). The collected organic layer was dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane/acetone (20:1) as eluent to get compound PEBBO as a deep purple solid (75%). $^1$H NMR (CDCl$_3$/Me$_4$Si, 600 MHz; Fig. S23): δ (ppm), 8.58-8.65 (2H, s, perylene), 8.53-8.57 (1H, d, perylene), 8.14-8.18 (1H, d, perylene) 7.54-7.95 (8H, dr, C$_6$H$_6$), 7.27-7.31 (2H, s, C$_6$H$_6$), 7.08-
7.12 (2H, s, C9H6), 6.64-6.68 (1H, d, perylene), 4.23-4.30 (6H, t, -OCH2-), 4.10-4.21 (6H, t, -OCH2-). MS (MALDI-TOF, m/z): Calcd for [(M+Na)+]: 2067.25, [(M+K)+]: 2083.23, found: 2067.95, 2083.99 (Fig. S24).

**Synthesis of compound PEBBA**

TBA (877.5 mg, 1.3 mmol) was suspended in an excess of freshly distilled toluene (10 mL) and SOCl2 (400 μL), the solution was refluxed at 80 °C under Ar atmosphere for 6 h. Then (0.5 g, 0.63 mmol) PEB was added. The system was allowed to react under Ar atmosphere for another 24 h at room temperature. The solvent was rotary evaporated, and the residue was dissolved in dichloromethane, and then extracted with water (30 mL × 3). The collected organic layer was dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane/acetone (20:1) as eluent to get compound PEBBA as a deep purple solid (80%).

**Synthesis of compound PEBAO**

TBA (344.3 mg, 0.51 mmol) was suspended in an excess of freshly distilled toluene (10 mL) and SOCl2 (400 μL), the solution was refluxed at 80 °C under Ar atmosphere for 6 h. Then (0.5 g, 0.63 mmol) PEB was added. The system was allowed to react under Ar atmosphere for another 24 h at room temperature. The solvent was rotary evaporated, and the residue was dissolved in dichloromethane, and then extracted with water (30 mL × 3). The collected organic layer was dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. The
crude product was purified by column chromatography on silica gel using dichloromethane/acetone (20:1) as eluent to get compound 1 as a deep purple solid (30%).

TEA (28 mg, 0.4 mmol) was suspended in an excess of freshly distilled toluene (10 mL) and SOCl₂ (100 μL), the solution was refluxed at 80 °C under Ar atmosphere for 6 h. Then (44 mg, 0.31 mmol) compound 1 was added. The system was allowed to react under Ar atmosphere for another 24 h at room temperature. The solvent was rotary evaporated, and the residue was dissolved in dichloromethane, and then extracted with water (30 mL × 3). The collected organic layer was dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using dichloromethane/acetone (10:1) as eluent to get compound PEBAO as a purple solid (80%). ¹H NMR (CDCl₃ /Me₄Si, 600 MHz; Fig. S25): δ (ppm), 8.22-8.27 (6H, d, perylene), 6.47-6.52 (6H, d, C₆H₆), 1.8-4.3 (84H, dr, alky). MS (MALDI-TOF, m/z): Calcd for [(M+Na)⁺]: 2001.30, found: 2001.31 (Fig. S26).
2. Fluorescence emission spectra of PEBBO in chloroform at different concentrations

Fig. S1 Fluorescence emission spectra of PEBBO in chloroform at concentrations from $1.0 \times 10^{-5}$ mol/L to $5.0 \times 10^{-7}$ mol/L ($\lambda_{ex} = 400$). Inset: the excitation and emission spectra of PEBBO in chloroform at a concentration of $1.0 \times 10^{-6}$ mol/L at room temperature.
3. Absorption spectra of PEBBO in different solvents

![Absorption spectra of PEBBO in different solvents at a concentration of 1×10^{-5} mol/L.](image)

**Fig. S2** Absorption spectra of PEBBO in different solvents at a concentration of 1×10^{-5} mol/L.
4. The change of conformation of PEBBO at the air/water interface

Fig. S3 The change of conformation of PEBBO molecular at the air/water interface.
5. The home-made device

Fig. S4 The home-made device developed for fluorescence detection of organic vapors.
6. The absorption and emission spectra of PEBBO-based fluorescent film.

**Fig. S5** The absorption and emission spectra of PEBBO-based fluorescent film.
7. Energy levels of HOMO (\(\pi\)) and LUMO (\(\pi^*\)) orbitals of PEBBO

![Diagram showing energy levels of HOMO (\(\pi\)) and LUMO (\(\pi^*\)) orbitals of PEBBO and ethylenediamine. The diagram illustrates favorable electron transfer from ethylenediamine to the photo-excited state of PEBBO. (Note: the density functional theory (DFT) calculated at theoretical level of TD-cam-b3lyp/6-31g)](image)

**Fig. S6** Energy levels of HOMO (\(\pi\)) and LUMO (\(\pi^*\)) orbitals of PEBBO and ethylenediamine showing favorable electron transfer from ethylenediamine to the photo-excited state of PEBBO (Note: the density functional theory (DFT) calculated at theoretical level of TD-cam-b3lyp/6-31g)
8. The emission spectra of the film in the presence of different concentrations ethylenediamine vapor

![Emission Spectra](image)

**Fig. S7** The emission spectra of the obtained LB film in the presence of different concentrations of ethylenediamine vapor.
9. The selectivity of the film with a layer thickness of 30 layers.

**Fig. S8** The selectivity of the film with a layer thickness of 30 layers of the compound.
10. The sensitivity of the film with a layer thickness of 30 layers.

Fig. S9 The sensitivity of the film with a layer thickness of 30 layers of the compound.
11. The reversibility of the film with a layer thickness of 30 layers.

**Fig. S10** The reversibility of the film with a layer thickness of 30 layers of the compound.
12. The sensing performance of the film as prepared in a surface pressure of 30.5 mN/m.

Fig. S11 The sensing performance of the film as prepared in a surface pressure of 30.5 mN/m.
13. The sensing performance of the film as prepared in a surface pressure of 16.8 mN/m

**Fig. S12** The sensing performance of the film as prepared in a surface pressure of 16.8 mN/m.
14. The contact angle images of blank substrate and PEBBO, PEBAO and PEBBA LB films

**Fig. S13** The contact angle images of blank substrate and the LB films based on PEBBO, PEBAO or PEBBA.
15. The response intensity of the PEBAO LB film

**Fig. S14** The response intensity of PEBAO-based LB film to the vapor of diamines, monoamines and other organic amines measured on the home-made device.
16. The response intensity of the PEBBA LB film

**Fig. S15** The response intensity of the PEBBA-based LB film to the vapor of diamines, monoamines and other organic amines measured on the home-made device.
17. Photochemical stability of PEBBO LB film

Fig. S16 Fluorescence emission intensities of PEBBO-based LB film recorded at the wavelength of 690 nm ($\lambda_{\text{ex}} = 460$ nm, 150W, Xe Lamp).
18. Plots of $I_0/I$ and $\tau_0/\tau$ of the fluorescence film against ethylenediamine vapor at different concentrations

![Graph showing plots of $I_0/I$ and $\tau_0/\tau$ against concentration of ethylenediamine vapor](image)

**Fig. S17** Plots of $I_0/I$ and $\tau_0/\tau$ of the fluorescence film against the pressure of ethylenediamine vapor from 0.07 g/m$^3$ to 1.64 g/m$^3$. 
19. Calculation of static ($K_S$) quenching constant

For a pure static quenching process, it can be ideally fitted by the well-known equation (Eq. 1). Accordingly, the static quenching constant, $K_S$, was calculated, and it is found to be $1.15 \text{ m}^3/\text{g}$. 

$$I_0 / I = 1 + K_S [Q] \quad (1)$$
20. $^1$H NMR and MS spectra of intermediates and target molecule

Fig. S19 $^1$H NMR spectrum of ITD in CDCl$_3$. 
Fig. S20 ESI-MS spectrum of ITD.

Exact Mass: 274.0066

$[\text{M+Na}]^+: 296.9964$

Found: 296.9965
Fig. S21 $^1$H NMR spectrum of TEA in CDCl$_3$. 

Fig. S22 MALDI-TOF spectrum of TEA.

Exact Mass: 608.30

[M+Na]^+: 631.29

[M+K]^+: 647.26

Found: 631.25
       647.23
Fig. S23 $^1$H NMR spectrum of PEBAO in CDCl$_3$.
**Fig. S24** MALDI-TOF spectrum of PEBAO.

Exact Mass: 2044.26
[M+Na]+: 2067.25
[M+K]+: 2083.23
Found: 2067.95
2083.99
Fig. S25 $^1$H NMR spectrum of PEBAO in CDCl$_3$. 

$a:b = 2:7$
Fig. S26 MALDI-TOF spectrum of PEBBO.

Exact Mass: 1978.30
Found: 2001.31
References
