Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

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

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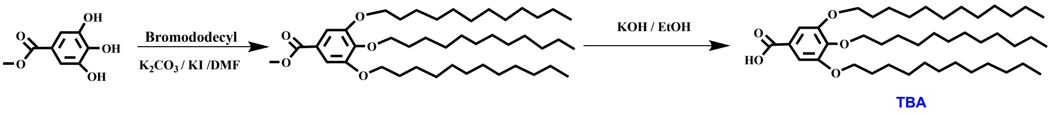
1. Synthesis and characterization

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 CH_2Cl_2. 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_4Si, 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, -OCH_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_4Si, 600 MHz; Fig. S21): δ (ppm), 7.32-7.35 (2H, s, C_6H_6), 4.17-4.25 (6H, t, -OCH_2-), 3.80-3.88 (6H, t, -CH_2-) 3.65-3.70 (9H, s, -OCH_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_4Si, 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_6H_6), 7.27-7.31 (2H, s, C_6H_6), 7.08-

7.12 (2H, s, C_6H_6), 6.64-6.68 (1H, d, perylene), 4.23-4.30 (6H, t, $-OCH_2-$), 4.10-4.21 (6H, t, $-OCH_2-$). 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 $SOCl_2$ (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 $SOCl_2$ (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 $SOCl_2$ (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 ($CDCl_3$ /Me_4Si, 600 MHz; Fig. S25): δ (ppm), 8.22-8.27 (6H, d, perylene), 6.47-6.52 (6H, d, C_6H_6), .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

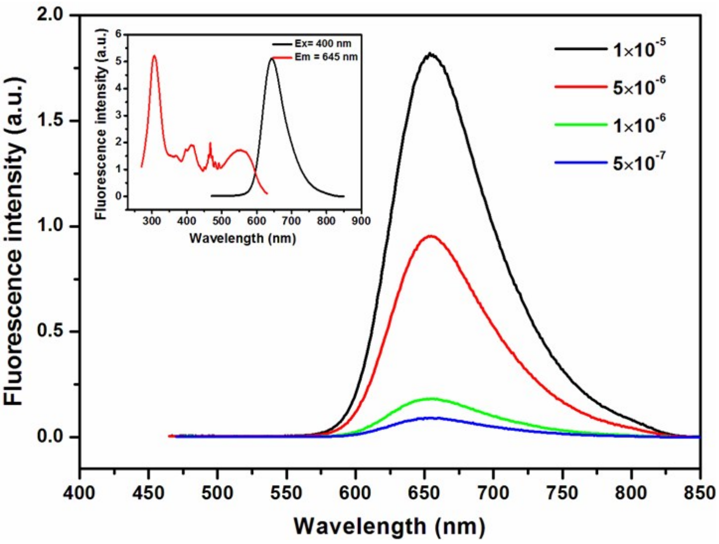


Fig. S1 Fluorescence emission spectra of PEBBO in chloroform at concentrations from 1.0×10^{-5} mol/L to 5.0×10^{-7} mol/L ($\lambda_{ex} = 400$). Inset: the exaction and emission spectra of PEBBO in chloroform at a concentration of 1.0×10^{-6} mol/L at room temperature.

3. Absorption spectra of PEBBO in different solvents

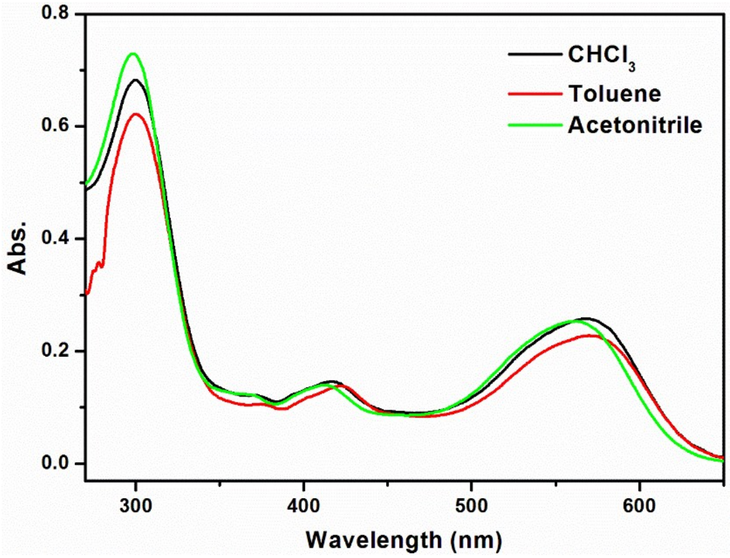


Fig. S2 Absorption spectra of PEBBO in different solvents at a concentration of 1×10^{-5} mol/L.

4. The change of conformation of PEBBO at the air/water interface

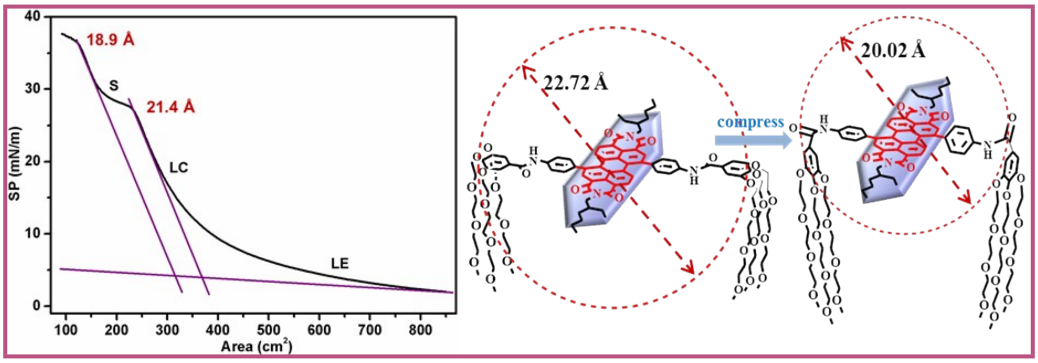


Fig. S3 The change of conformation of PEBBO molecular at the air/water interface.

5. The home-made device

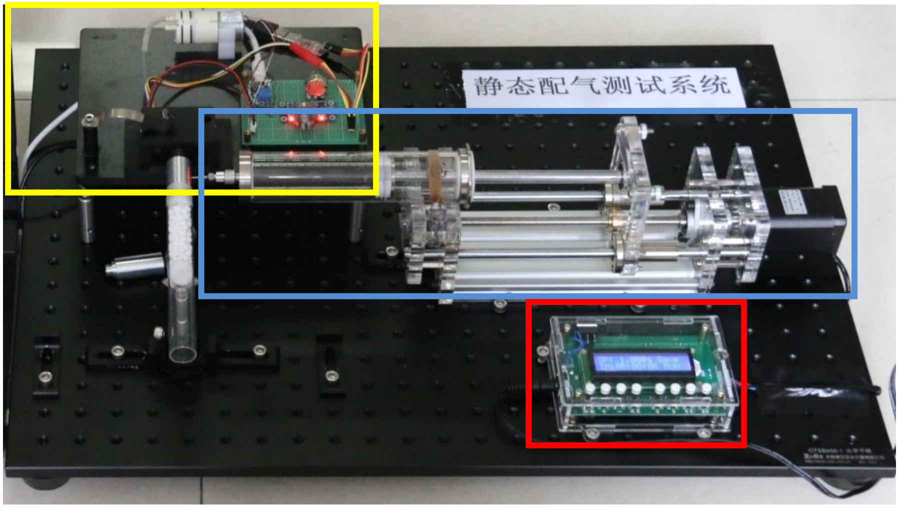


Fig. S4 The home-made device developed for fluorescence detection of organic vapors.

6. The absorption and emission spectra of PEBBO-based fluorescent film

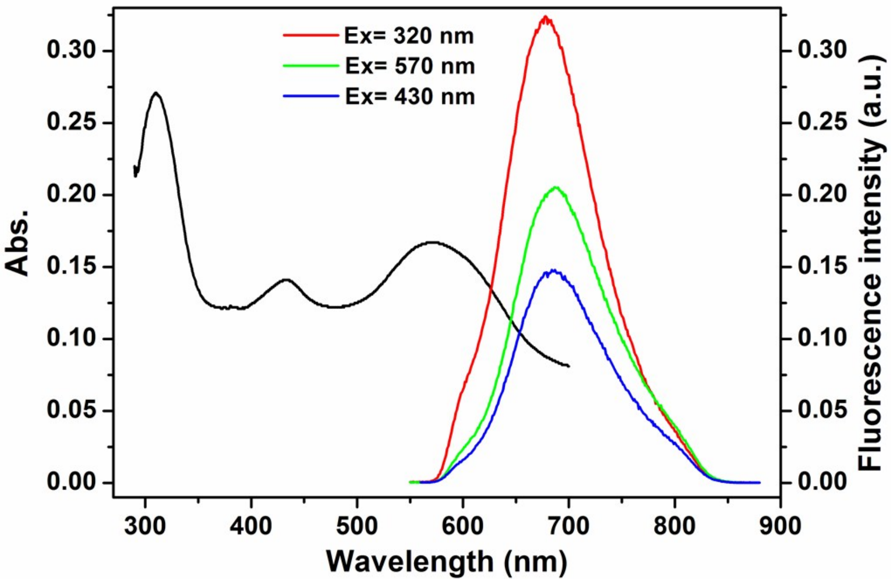


Fig. S5 The absorption and emission spectra of PEBBO-based fluorescent film.

7. Energy levels of HOMO (π) and LUMO (π*) orbitals of PEBBO

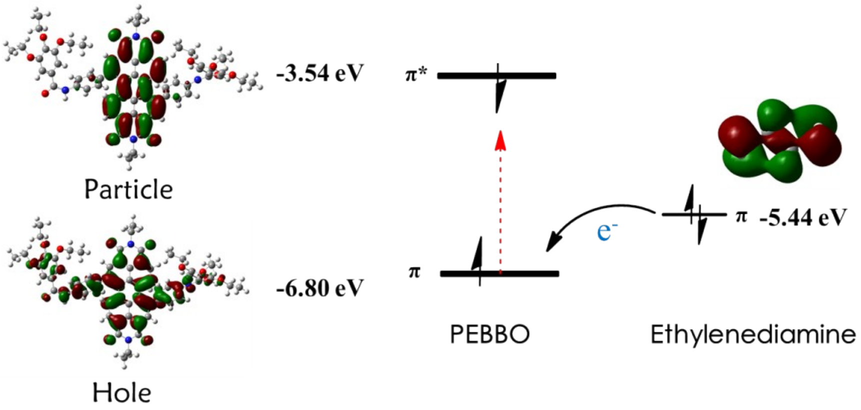


Fig. S6 Energy levels of HOMO (π) and LUMO (π*) orbitals of PEBBO and ethylenediamine showing favorable electron transfer from ethylenediamine to the photo-excited state of PEBBO (Note: the density functional theory (DFT) calculated at theoretical level of TD-cam-b3lyp/6-31g)

8. The emission spectra of the film in the presence of different concentrations ethylenediamine vapor

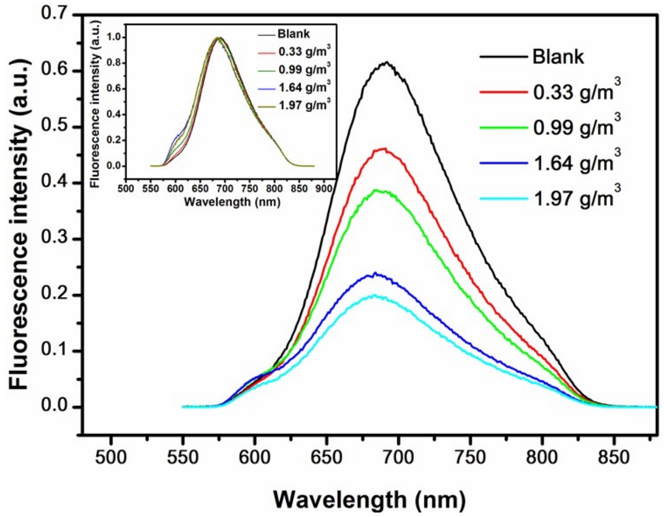


Fig. S7 The emission spectra of the obtained LB film in the presence of different concentrations of ethylenediamine vapor.

9. The selectivity of the film with a layer thickness of 30 layers.

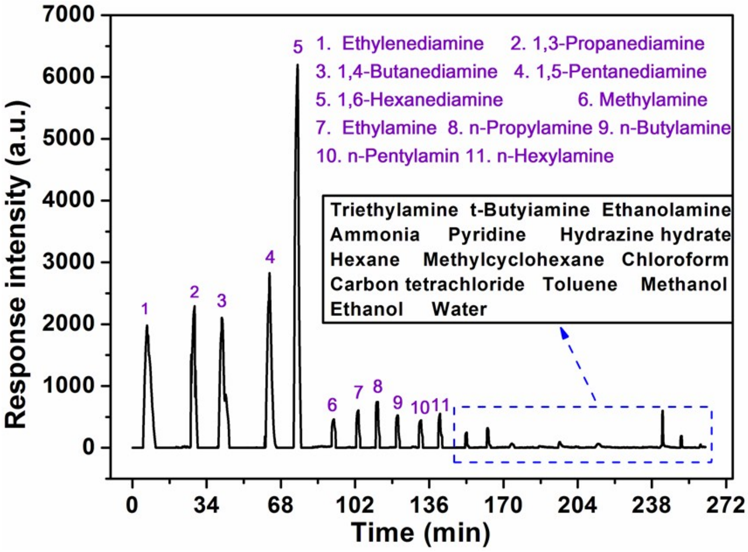


Fig. S8 The selectivity of the film with a layer thickness of 30 layers of the compound.

10. The sensitivity of the film with a layer thickness of 30 layers.

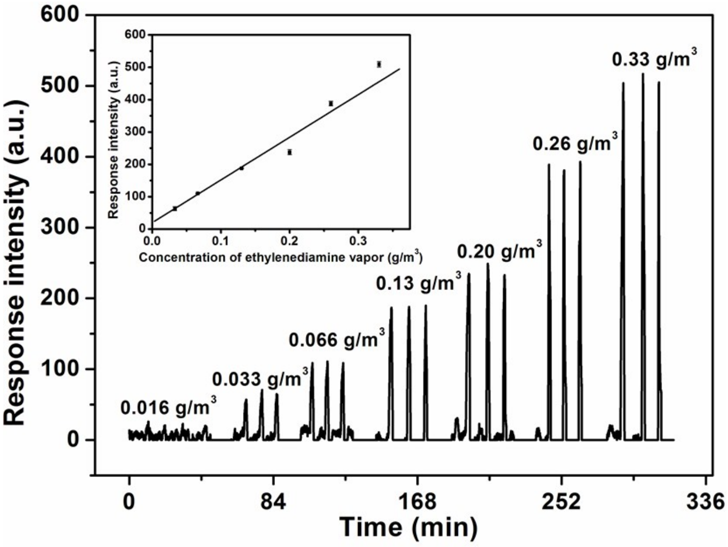


Fig. S9 The sensitivity of the film with a layer thickness of 30 layers of the compound.

11. The reversibility of the film with a layer thickness of 30 layers.

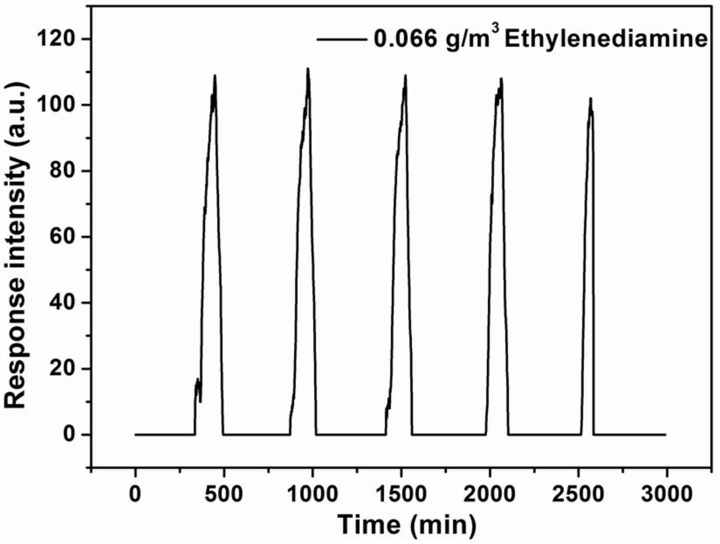


Fig. S10 The reversibility of the film with a layer thickness of 30 layers of the compound.

12. The sensing performance of the film as prepared in a surface pressure of 30.5 mN/m

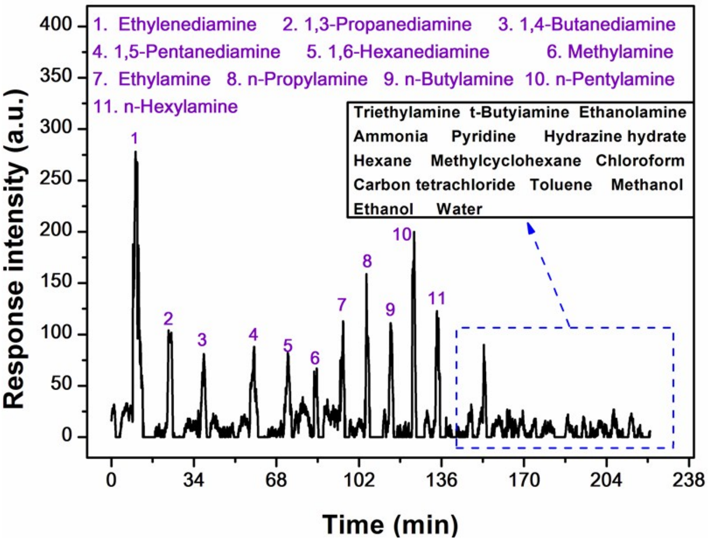


Fig. S11 The sensing performance of the film as prepared in a surface pressure of 30.5 mN/m.

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

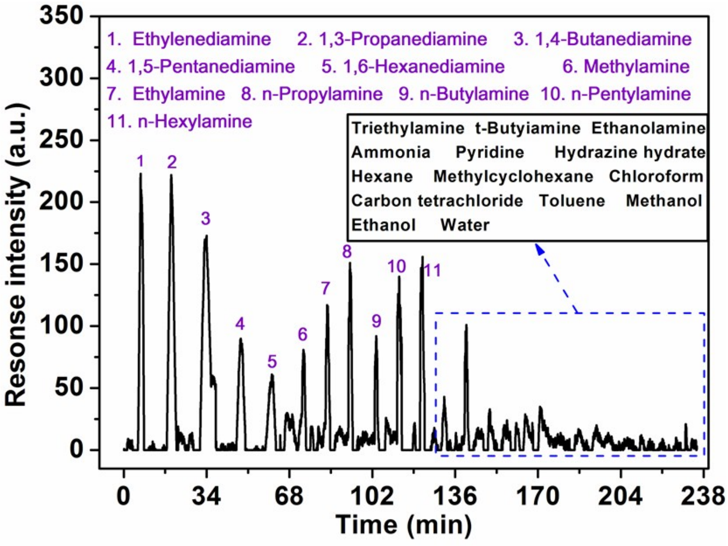


Fig. S12 The sensing performance of the film as prepared in a surface pressure of 16.8 mN/m.

14. The contact angle images of blank substrate and PEBBO, PEBAO and PEBBA LB films

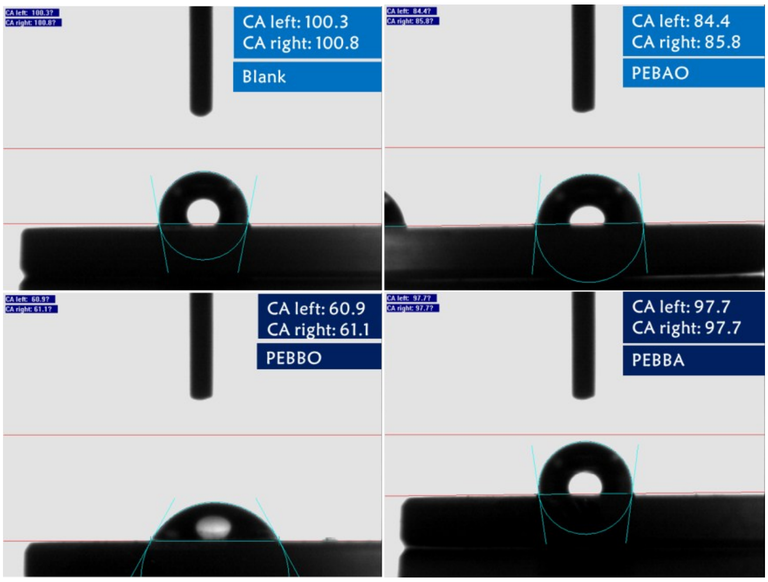


Fig. S13 The contact angle images of blank substrate and the LB films based on PEBBO, PEBAO or PEBBA.

15. The response intensity of the PEBAO LB film

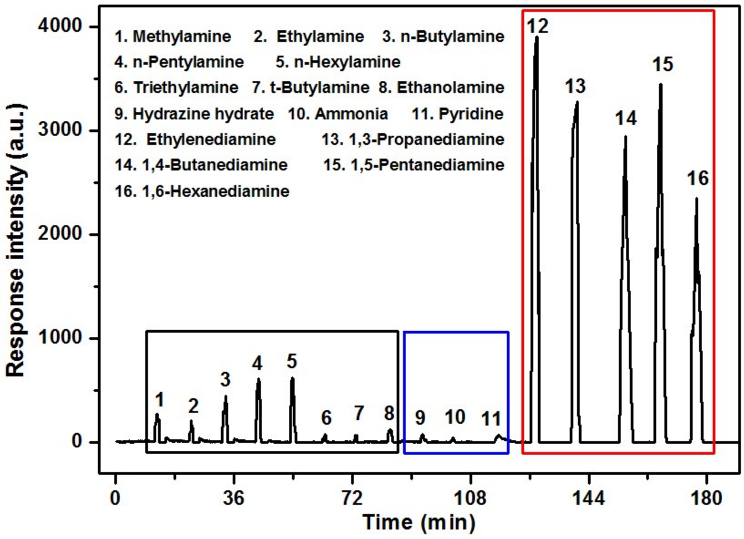


Fig. S14 The response intensity of PEBAO-based LB film to the vapor of diamines, monoiamines and other organic amines measured on the home-made device.

16. The response intensity of the PEBBA LB film

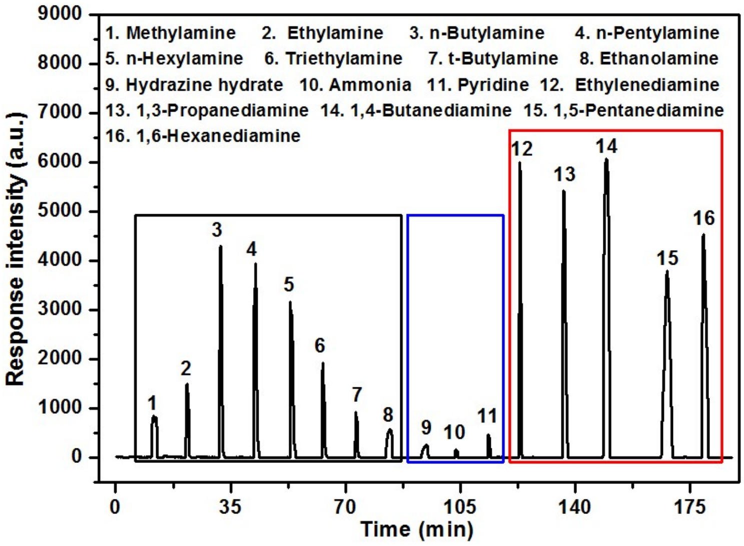


Fig. S15 The response intensity of the PEBBA-based LB film to the vapor of diamines, mono-amines and other organic amines measured on the home-made device.

17. Photochemical stability of PEBBO LB film

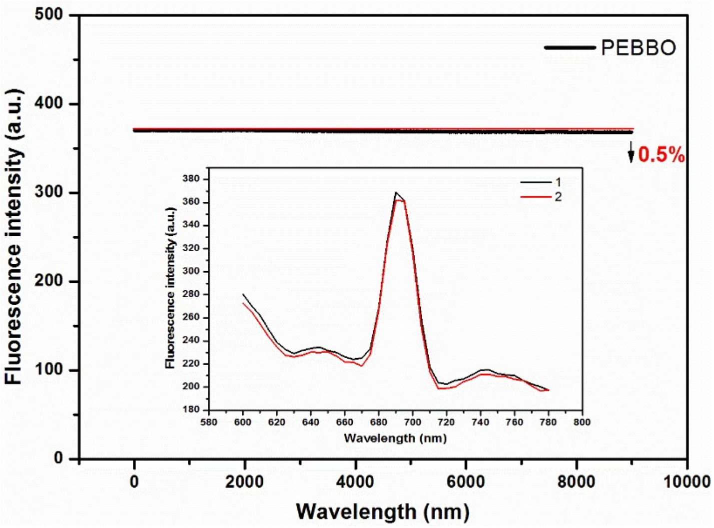


Fig. S16 Fluorescence emission intensities of PEBBO-based LB film recorded at the wavelength of 690 nm (λ_{ex} = 460 nm, 150W, Xe Lamp).

18. Plots of I_0/I and τ_0/τ of the fluorescence film against ethylenediamine vapor at different concentrations

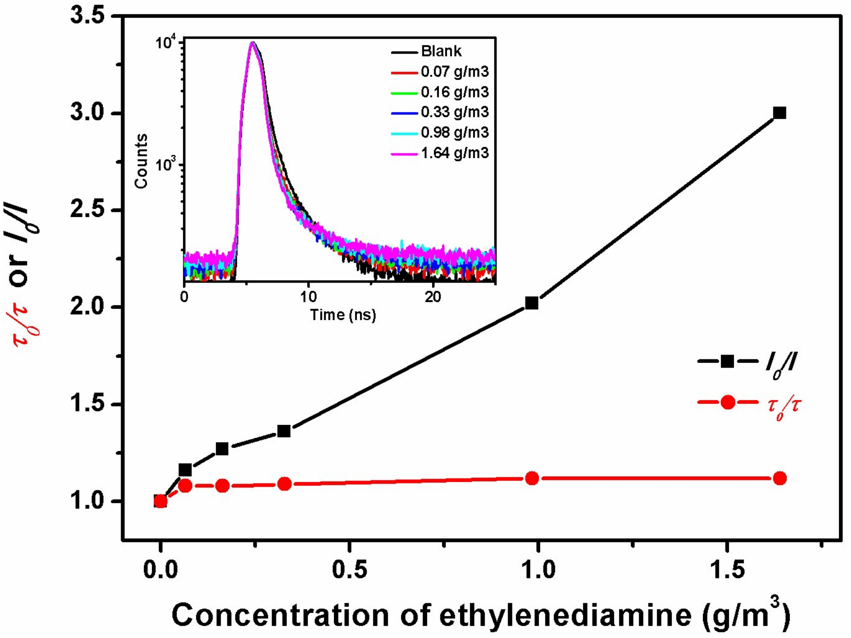


Fig. S17 Plots of I_0/I and τ_0/τ of the fluorescence film against the pressure of ethylenediamine vapor from 0.07 g/m^3 to 1.64 g/m^3.

19. Calculation of static (K_S) quenching constant

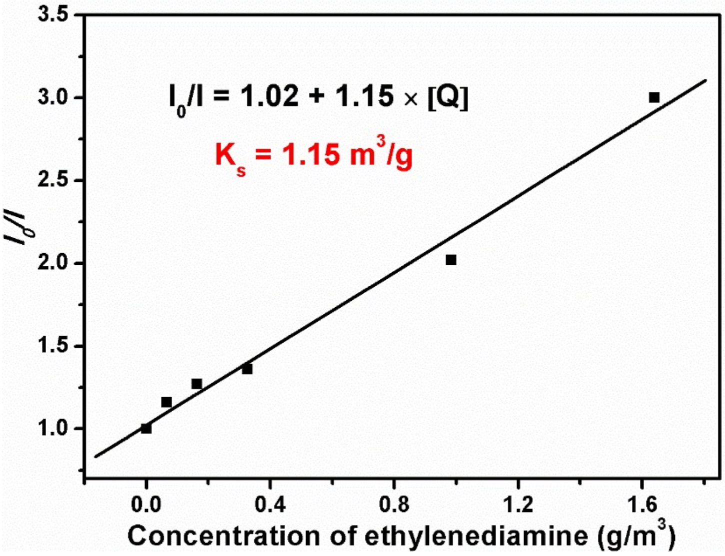


Fig. S18 Calculation of static (K_S) quenching constant.

$$I_0 / I = 1 + K_S[Q] \qquad (1)$$

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 $m^3 \cdot g^{-1}$.

20. ^{1}H NMR and MS spectra of intermediates and target molecule

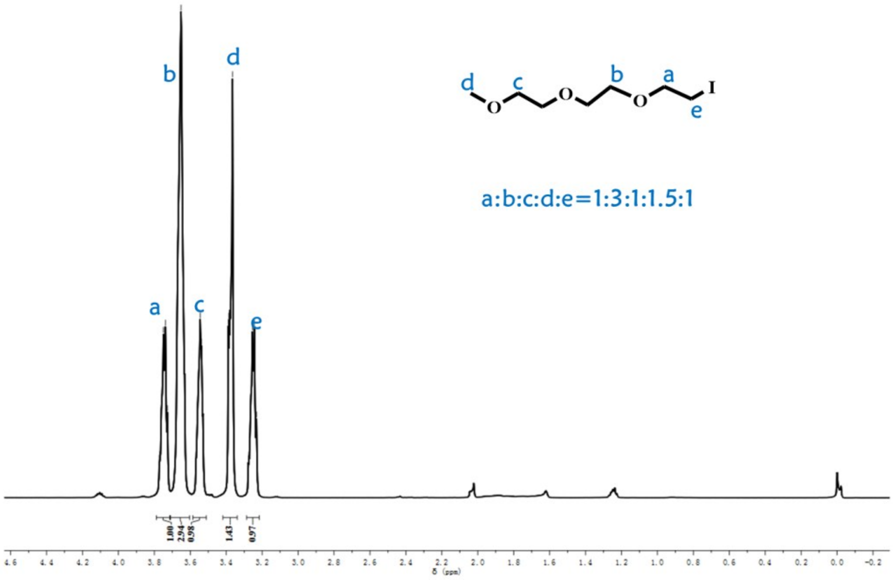


Fig. S19 ^{1}H NMR spectrum of ITD in $CDCl_3$.

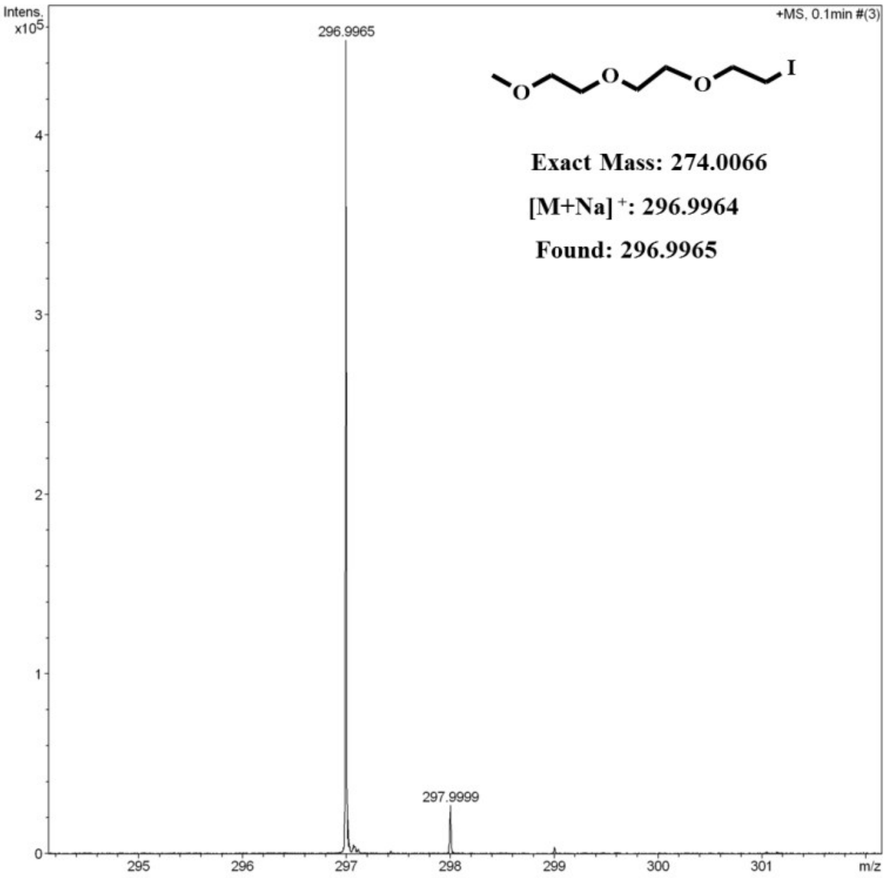


Fig. S20 ESI-MS spectrum of ITD.

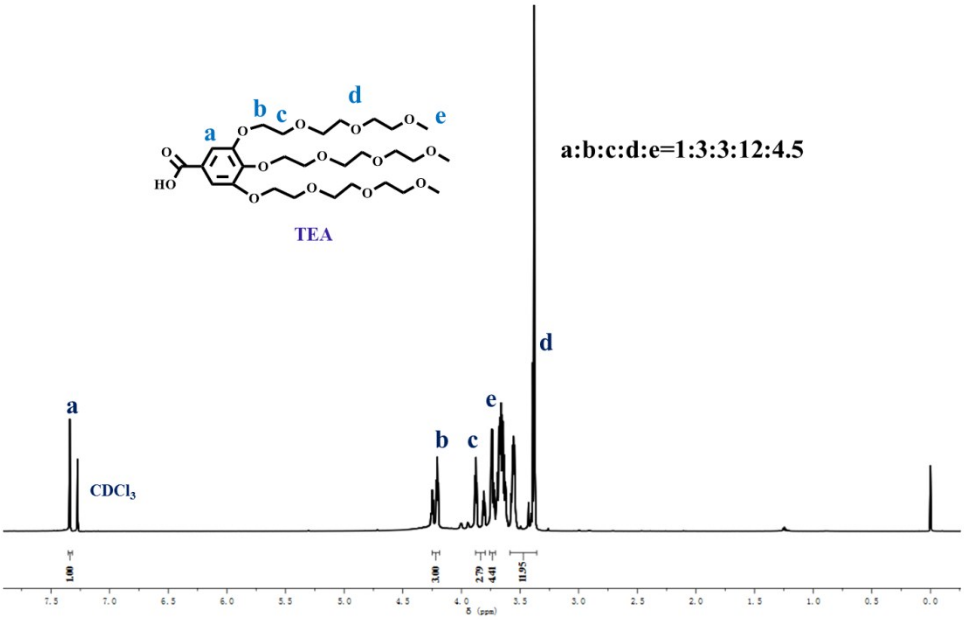


Fig. S21 ^{1}H NMR spectrum of TEA in $CDCl_3$.

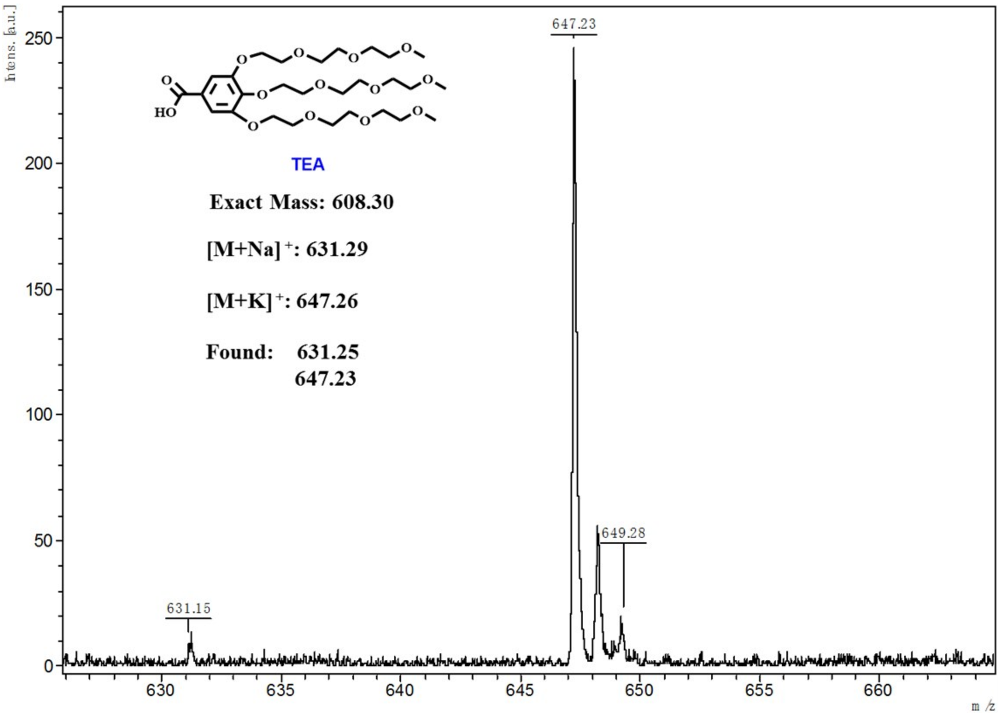


Fig. S22 MALDI-TOF spectrum of TEA.

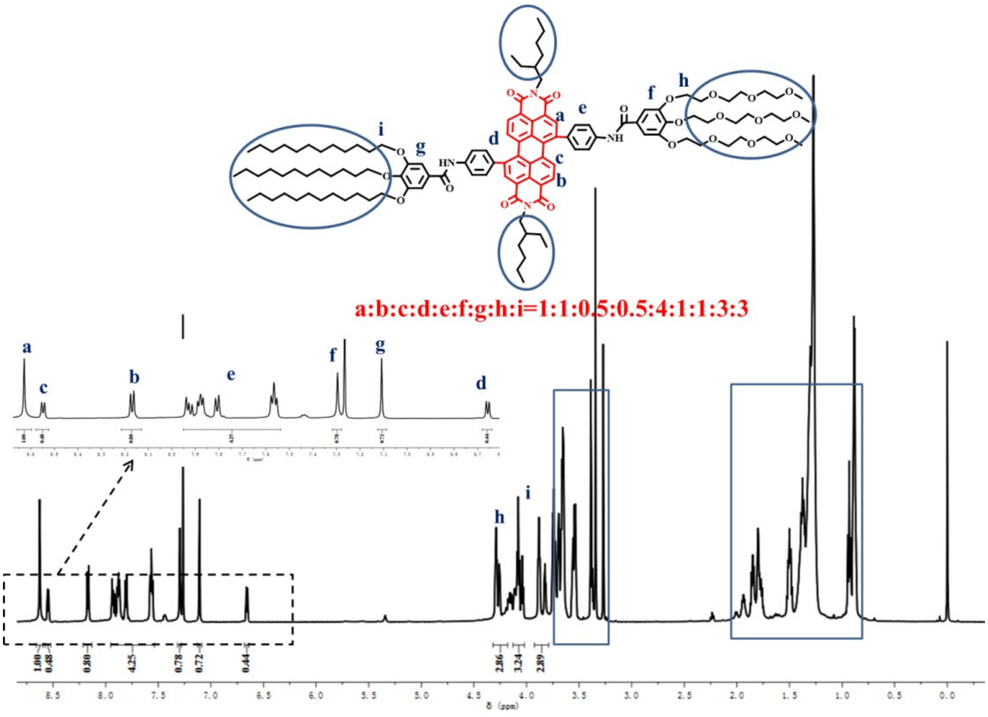


Fig. S23 ^{1}H NMR spectrum of PEBAO in $CDCl_3$.

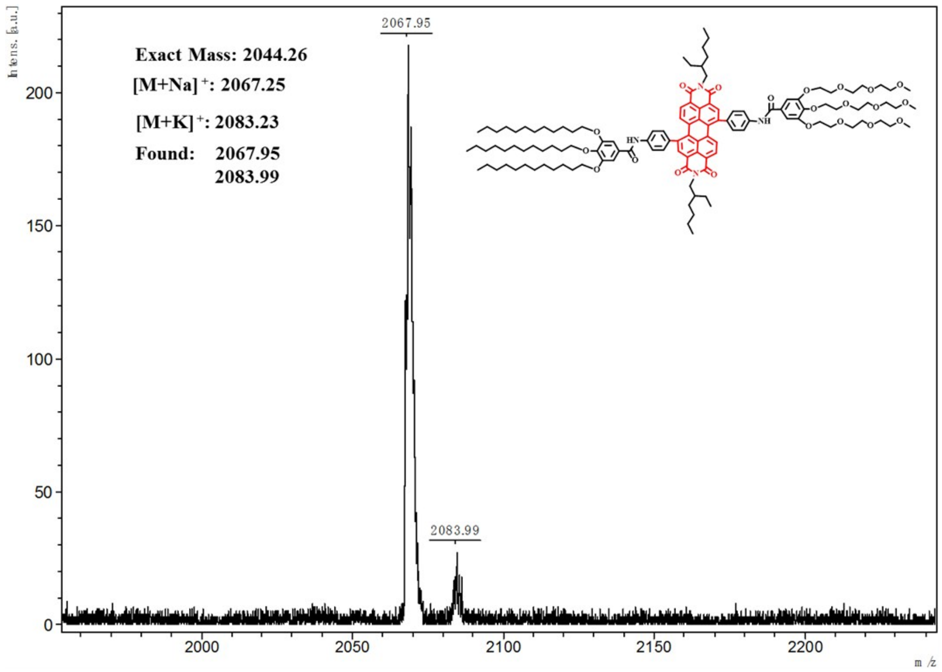


Fig. S24 MALDI-TOF spectrum of PEBAO.

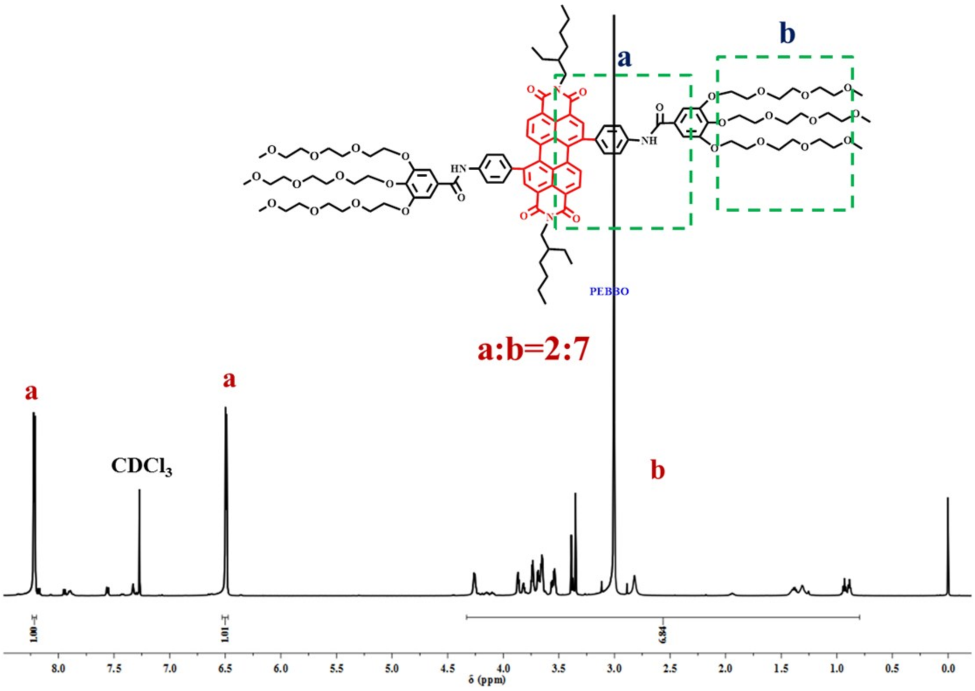


Fig. S25 ^{1}H NMR spectrum of PEBAO in CDCl$_3$.

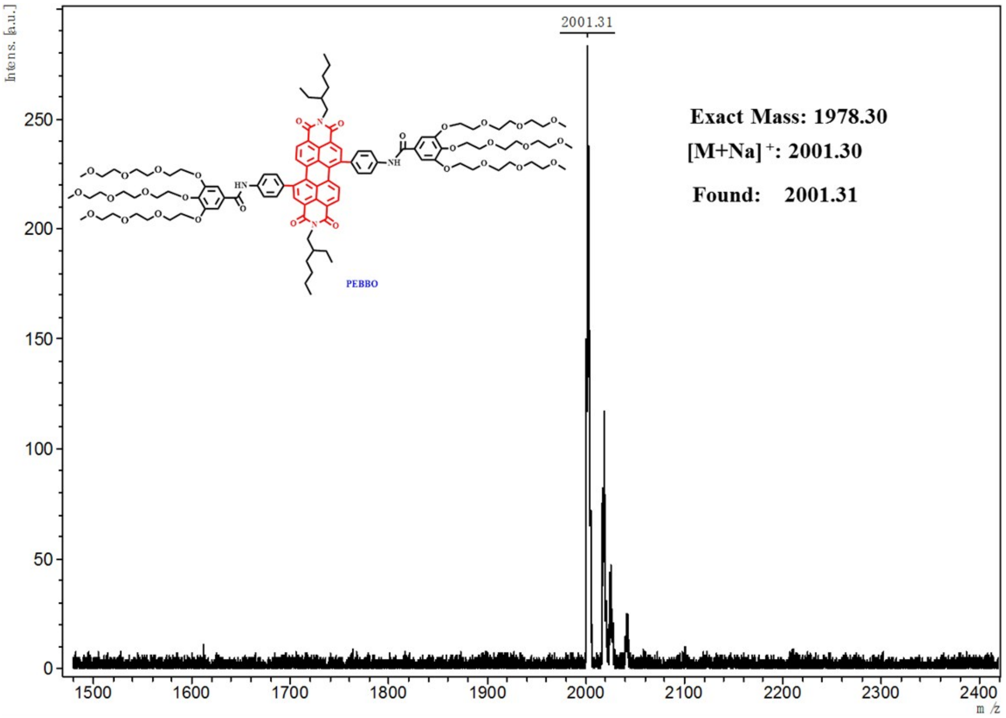


Fig. S26 MALDI-TOF spectrum of PEBBO.

References

[S1] C. Shang, G. Wang, M. He, X. Chang, J. Fan, K. Liu, H. Peng and Y. Fang, *Sens. Actuators B*, 2017, **241**, 1316-1323.

[S2] J. Fan, X. Chang, M. He, C. Shang, G. Wang, S. Yin, H. Peng and Y. Fang, *ACS Appl. Mater. Interfaces*, 2016, **8**, 18584-18592.