

Supporting Information for

Highly efficient single fluorescent probe for multiplicate amines vapours via reaction between amine and aldehyde/-dioxaborolane

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and Jiangong Cheng^{*a}

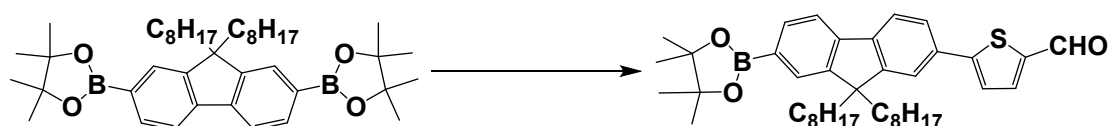
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General: UV-vis absorption and fluorescence analysis were conducted on a Jasco V-670 spectrophotometer and a Jasco FP 6500 spectrometer, respectively. The NMR spectra were obtained from a Bruker DRX500 instrument, and tetramethylsilane (TMS) was used as an internal standard. Mass spectra were recorded on BIFLEX III MALDI-TOF (Bruker Daltonics Inc.) and GCT-MS Micromass UK mass spectrometers. All the films on (10×20 mm) quartz plates were spin-coated at 2500 rpm from their 1×10⁻² M THF solutions, and placed in vacuum for 1 hour before use. The fluorescence responses of films to various analytes were progressed by inserting the films into sealed vials (3.8 mL) containing cotton and analytes at room temperature, which prevents direct film analyte contact and helps to maintain a constant vapour pressure. The fluorescence time-course responses were recorded immediately after exposing the films to analytes by front-face (30°) detection.

Materials: All solvents and reagents were obtained from commercial sources and used as received.

Synthesis and Characterization



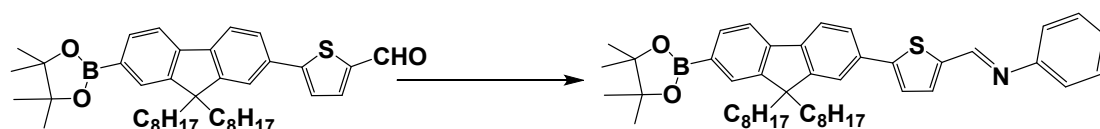
To a 1:1.5 mixture of 9,9-dioctylfluorene-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) and 5-bromo-2-formylthiophene, tetra(triphenylphosphine)-palladium

[Pd(PPh₃)₄] (1.0 Mol %) in degassed THF and a drop of 2 M potassium carbonate aqueous solution were added. The mixture was stirred at 70 °C for 72 h under the protection of argon. Then the solvent was evaporated and the residue was purified by column chromatography on silica gel using hexane and dichloromethane as eluent to afford pale yellow product (yield 67%). ¹H-NMR(500MHz, CDCl₃, 25 °C, TMS): δ=9.90 (s, 1H), 7.83 (d, 1H, *J*= 7.6 Hz), 7.80-7.75 (m, 3H), 7.71 (d, 1H, *J*= 7.55 Hz), 7.68-7.66 (m, 1H), 7.62 (s, 1H), 7.47 (d, 1H, *J*= 3.95 Hz), 2.04-1.98 (m, 4H), 1.39 (s, 12H), 1.19-1.15 (m, 4H), 1.10-1.03 (m, 16H), 0.80-0.77 (t, 6H), 0.60-0.59(m, 4H) ¹³C NMR (125MHz, CDCl₃) δ182.56, 155.05, 152.38, 150.24, 142.94, 142.51, 142.02, 137.34, 133.88, 132.06, 128.88, 125.38, 123.83, 120.71, 120.64, 119.31, 83.74, 83.64, 55.29, 40.07, 31.69, 29.82, 29.09, 29.06, 24.88, 23.62, 22.51, 13.98 HRMS: calcd M⁺ for C₄₀H₅₅BO₃S 626.3965; found 626.3972.

Supporting results and discussion:

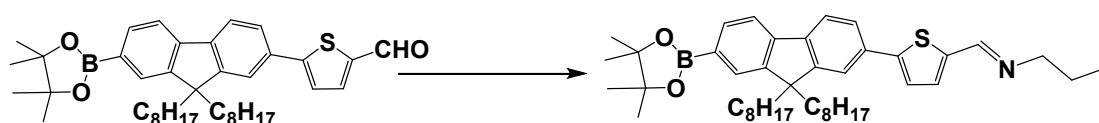
Characterization of the products upon exposure in different amines.

(1) Initially, we tried to separate the main products from the reaction between BFTA and the primary amines after reacting in the solutions by column chromatography separation methods but failed. It is because that the Schiff base reaction is usually reversible in the solution and the Schiff base easily decomposed to foremost raw material using column chromatography separation methods. To promote positive reactions, we put the drop-casted film into the atmosphere of different primary amine vapour for 5 minutes, respectively. Then the excess amine vapours were removed by vacuum cleaner and the residue on the films was characterized by ¹H NMR spectra and HRMS (high resolution mass spectrum). Because the amount of the remainder on the films was limited, the ¹³C NMR spectra could not be provided clearly.

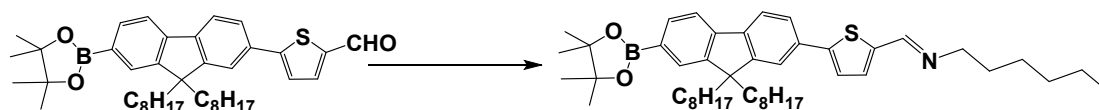


The drop-casted film of 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctyl-9H-fluoren-7-yl) thiophene-2-carbaldehyde (BFTA) was put aside in an atmosphere of aniline vapour. After 5 minutes, the exposed film was taken out and

dried in vacuum oven to remove the volatile remainder. Then the species on the film were dissolved in CDCl_3 and the $^1\text{H-NMR}$ spectrum was recorded. The high resolution mass spectrum (HR-MS) and the $^1\text{H-NMR}$ spectroscopies exhibit that the structure of the final product was consistent with the expected Schiff's base structure. $^1\text{H-NMR}$ (500MHz, CDCl_3 , 25 °C, TMS): δ =8.55 (s, 1H), 7.83-7.82 (d, 1H, J =3.2 Hz), 7.76-7.74 (m, 4H), 7.63-7.60(m, 2H), 7.58-7.56(m, 1H), 7.47-7.38(m, 5H), 6.81 (s, 1H), 2.03-1.92 (m, 4H), 1.39 (s, 12H), 1.18-1.15 (m, 4H), 1.09-1.02 (m, 16H), 0.79-0.77 (t, 6H), 0.60(m, 4H). HRMS: calcd M^+ for $\text{C}_{46}\text{H}_{61}\text{BNO}_2\text{S}$ 701.4547; found 701.4563.

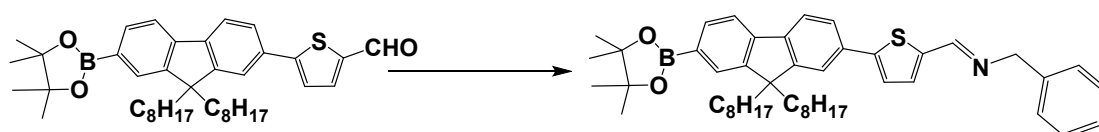


The drop-casted film of 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctyl-9H-fluoren-7-yl) thiophene-2-carbaldehyde (BFTA) was put aside in an atmosphere of *n*-propylamine vapour. After 5 minutes, the exposed film was taken out and dried by vacuum oven to remove the volatile remainder. Then the species on the film were dissolved with CDCl_3 and the $^1\text{H-NMR}$ spectrum was recorded. The high resolution mass spectrum (HR-MS) and the NMR spectroscopies exhibit that the structure of the final product was consistent with the expected Schiff's base structure. $^1\text{H-NMR}$ (500MHz, CDCl_3 , 25 °C, TMS): δ =8.33 (s, 1H), 7.81 (d, 1H, J = 7.5 Hz), 7.74-7.67 (m, 4H), 7.64-7.60(m, 2H), 7.34-7.33 (d, 1H, J =3.5 Hz), 3.58-3.55(m, 2H), 2.02-1.94 (m, 4H), 1.76-1.72(m, 2H), 1.39 (s, 12H), 1.25(s, 2H), 1.19-1.15 (m, 4H), 1.17-1.02 (m, 16H), 0.97-0.96(m, 3H), 0.80-0.78 (t, 6H), 0.61(m, 4H). HRMS: calcd M^+ for $\text{C}_{43}\text{H}_{63}\text{BNO}_2\text{S}$ 668.4674; found 668.4659.



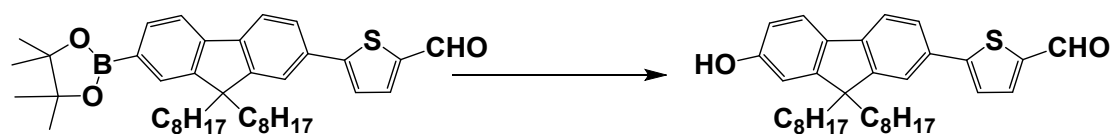
The drop-casted film of 5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctyl-9H-fluoren-7-yl) thiophene-2-carbaldehyde (BFTA) was put aside in an atmosphere of *n*-hexylamine vapour. After 5 minutes, the exposed film was taken out and dried in vacuum oven to remove the volatile remainder. Then the species on the film were dissolved with CDCl_3 and the $^1\text{H-NMR}$ spectrum was recorded. The high

resolution mass spectrum (HR-MS) and the NMR spectroscopies exhibit that the structure of the final product was consistent with the expected Schiff's base structure. $^1\text{H-NMR}$ (500MHz, CDCl_3 , 25 °C, TMS): δ =8.33 (s, 1H), 7.81-7.80 (d, 1H, J =7.5 Hz), 7.74-7.68 (m, 4H), 7.63-7.60(m, 2H), 7.34-7.33 (d, 1H, J =3.5 Hz), 3.60-3.58(m, 2H), 2.00-1.97 (m, 4H), 1.70-1.68(m, 3H), 1.39 (s, 12H), 1.33-1.26(m, 4H), 1.18-1.15 (m, 4H), 1.10-1.02 (m, 16H), 0.90(t, 4H), 0.80-0.78 (t, 6H), 0.61(m, 4H) HRMS: calcd M^+ for $\text{C}_{46}\text{H}_{69}\text{BNO}_2\text{S}$ 710.5144; found 710.5133.



The drop-casted film of 5-(2-(4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolan-2-yl)-9, 9-dioctyl-9H-fluoren-7-yl) thiophene-2-carbaldehyde (BFTA) was put aside in an atmosphere of benzylamine vapour. After 5 minutes, the exposed film was taken out and dried in vacuum oven to remove the volatile remainder. Then the species on the film were dissolved with CDCl_3 and the $^1\text{H-NMR}$ spectrum was recorded. The high resolution mass spectrum (HR-MS) and the NMR spectroscopies exhibit that the structure of the final product was consistent with the expected Schiff's base structure. $^1\text{H-NMR}$ (500MHz, CDCl_3 , 25°C, TMS): δ =8.42 (s, 1H), 7.81-7.80 (d, 1H, J =7.5 Hz), 7.74-7.68 (m, 4H), 7.63-7.60(m, 2H), 7.35-7.34(m, 5H), 7.31-7.30 (d, 1H, J =3.5 Hz), 4.82(s, 2H), 2.00-1.95 (m, 4H), 1.39 (s, 12H), 1.26-1.25 (m, 2H), 1.18-1.15 (m, 4H), 1.10-1.02 (m, 16H), 0.80-0.78 (t, 6H), 0.61(m, 4H). HRMS: calcd M^+ for $\text{C}_{47}\text{H}_{63}\text{BNO}_2\text{S}$ 716.4675; found 716.4667.

(2) The reactions between BFTA and the secondary amines in the solutions were investigated and the main product was characterized by $^1\text{H-NMR}$ spectra, $^{13}\text{C-NMR}$ spectra and HRMS (high resolution mass spectrum).



Excess secondary amine (diethylamine or diisopropylamine, 4-20equiv.) was added to a solution of reactant in common solvents. The solution was stirred at room temperature for half an hour. Then the solvent was evaporated and the residue was purified by column chromatography on silica gel using CH_2Cl_2 as eluent to afford 5-(2-hydroxy-9, -dioctyl-9H-fluoren-7-yl) thiophene-2-carbaldehyde with the yield of ~70%. $^1\text{H-NMR}$ (500MHz, CDCl_3 , 25°C, TMS): δ = 9.89 (s, 1H), 7.77 (d, 1H, J = 3.95 Hz), 7.64 (m, 2H), 7.57 (m, 2H), 7.45 (d, 1H, J = 3.95 Hz), 6.84 (m, 2H), 5.28 (s, 1H), 1.96-1.94 (m, 4H), 1.20-1.17 (m, 4H), 1.11-1.05 (m, 16H), 0.81-0.78 (t, 6H), 0.64(m, 4H). ^{13}C NMR (125MHz, CDCl_3) δ =182.96, 156.33, 155.95, 153.60, 151.27, 142.93, 141.48, 137.87, 133.07, 130.46, 125.53, 123.56, 121.11, 120.47, 119.35, 114.39, 110.26, 55.22, 40.42, 31.75, 29.96, 29.69, 19.19, 23.72, 22.56, 14.03. HRMS: calcd M^+ for $\text{C}_{34}\text{H}_{44}\text{O}_2\text{S}$ 516.3062; found 516.3071.

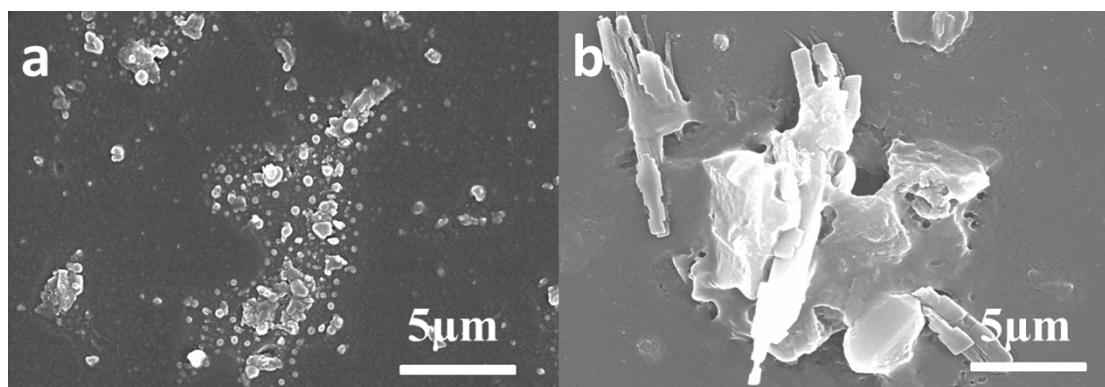


Fig S1 SEM images of BFTA films by spin-coating its THF solution $1 \times 10^{-3}\text{M}$ (a) and $1 \times 10^{-1}\text{M}$ (b).

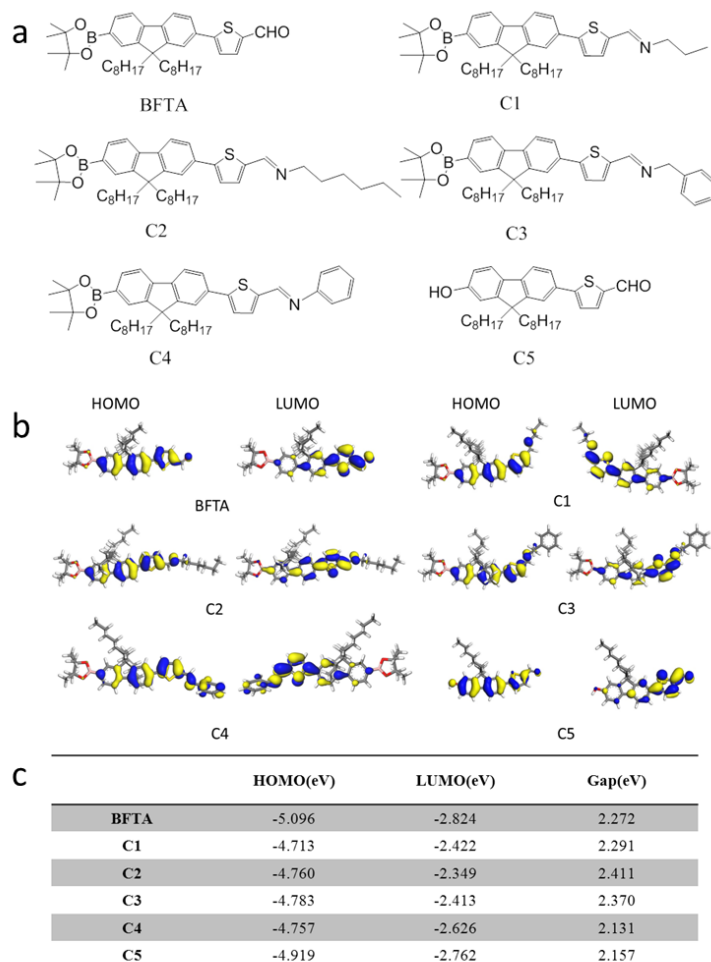


Fig S2 Structures (a), electron distributions of the HOMO and LUMO energy levels (b) and the band gap of BFTA and C1-C5 (c).

Fluorescence intensity change at dual wavelength and Detection limits

Theoretically, it is feasible to detect anlyate at dual or multi- wavelength for the probe whose output signal is based on the fluorescent spectra shift (including redshift or blueshift). In fact, the fluorescence intensity changes at different wavelength were recorded by the fluorescence spectrometer in the vapours of different amines except for aniline vapour in which the fluorescence change is merely based on fluorescence quenching. To estimate the detection limit, we measured the changes in fluorescence intensity of BFTA films exposed to each amine vapours of at least four different concentrations (1, 10, 25, 50 and 100 times diluted from the saturated vapour). And the intensity quenching data ($1 - I/I_0$) are well-fitted to the Langmuir equation with an assumption that the quenching efficiency is proportional to the surface adsorption of

amine vapour. If the signal to noise ratio of the fluorescence detection device was considered as 1 %, the detection limits of BFTA can be estimated to be ppm~ppt level (Scheme S1). Experiments confirmed that the detection limits measured at 470 nm are more sensitive for these amines compared with detection at other wavelength.

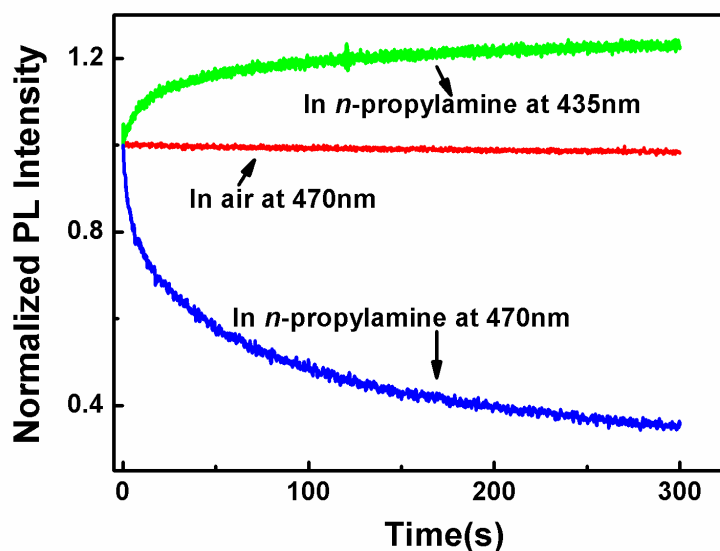


Fig S3 Changes in fluorescence intensity of BFTA films exposed to air and the saturated *n*-propylamine vapour at different wavelength for 300 s at 20 °C.

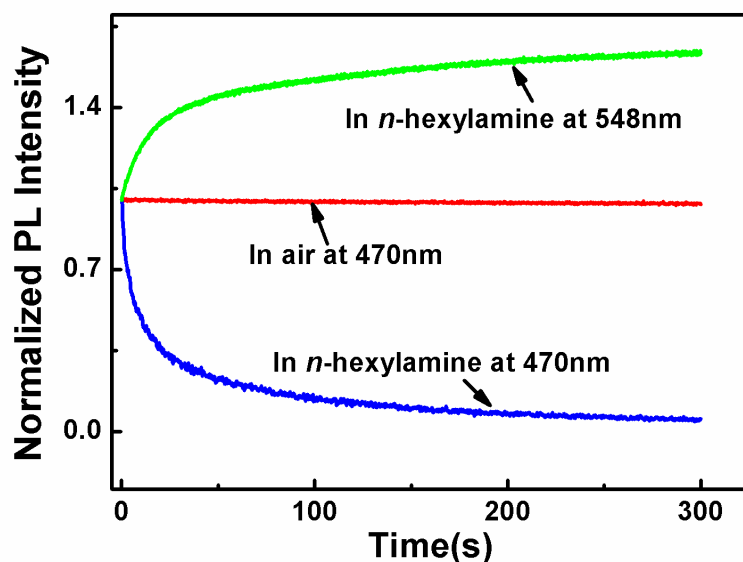


Fig S4 Changes in fluorescence intensity of BFTA films exposed to air and the saturated *n*-hexylamine vapour at different wavelength for 300 s at 20 °C.

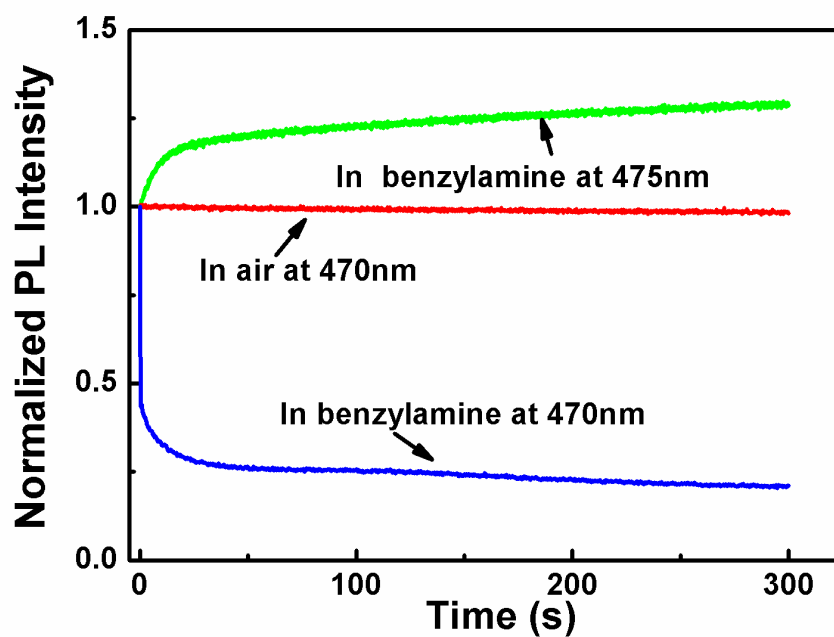


Fig S5 Changes in fluorescence intensity of **BFTA** films exposed to air and the saturated bezylamine vapour at different wavelength for 300 s at 20 °C.

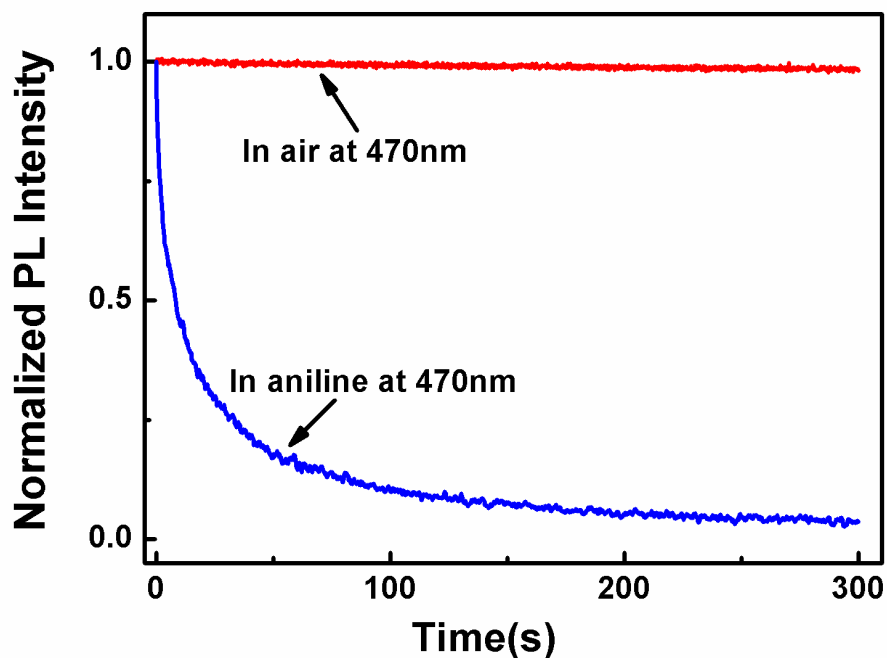
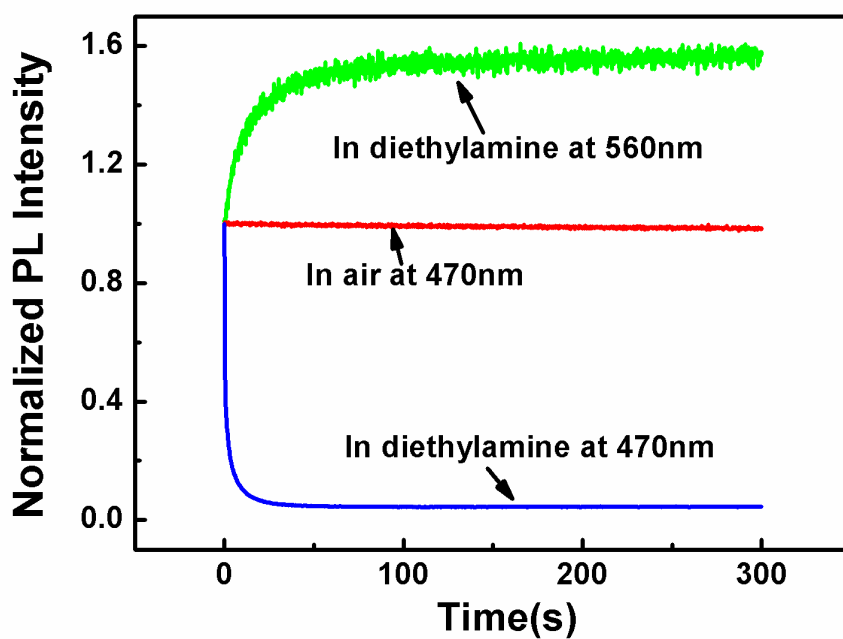


Fig S6 Changes in fluorescence intensity of **BFTA** films exposed to air and the saturated aniline vapour for 300 s at 20 °C.



Fig

S7 Changes in fluorescence intensity of **BFTA** films exposed to air and the saturated diethylamine vapour at different wavelength for 300 s at 20 °C.

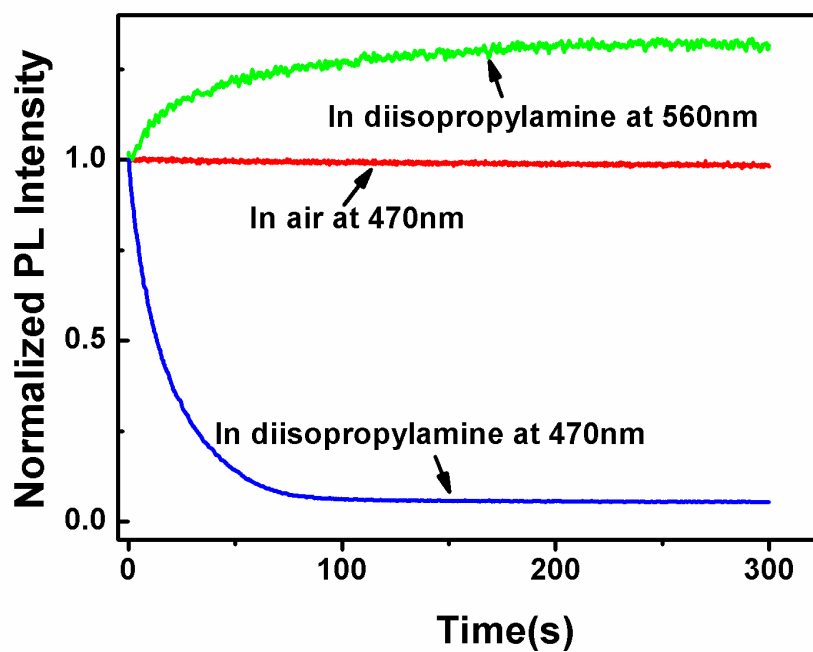


Fig S8 Changes in fluorescence intensity of **BFTA** films exposed to air and the saturated diisopropylamine vapour at different wavelength for 300 s at 20 °C.

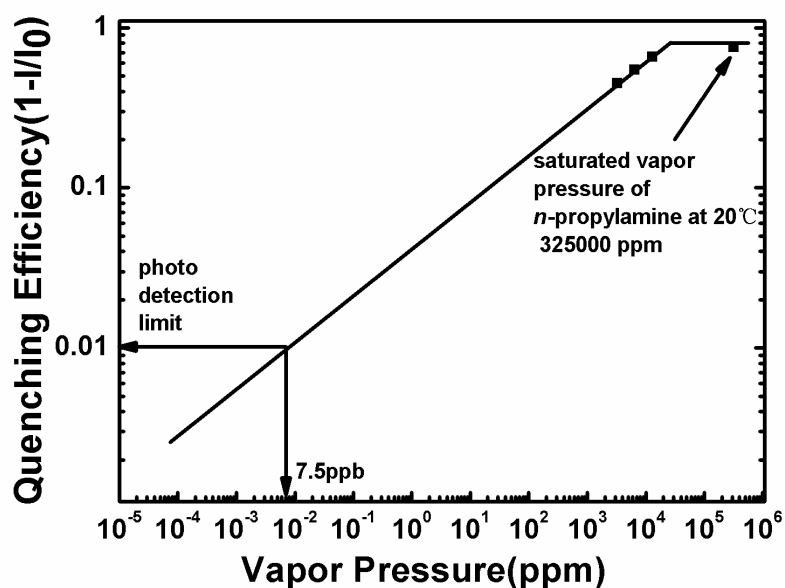


Fig S9 Fluorescence quenching efficiency ($1-I/I_0$) as a function of the vapour pressure of *n*-propylamine at 470 nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

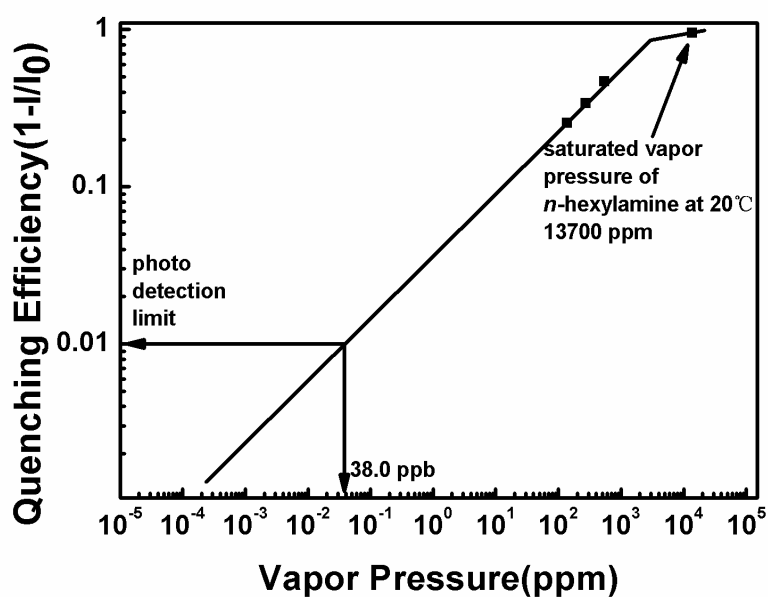


Fig S10 Fluorescence quenching efficiency ($1-I/I_0$) as a function of the vapour pressure of *n*-hexylamine at 470 nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

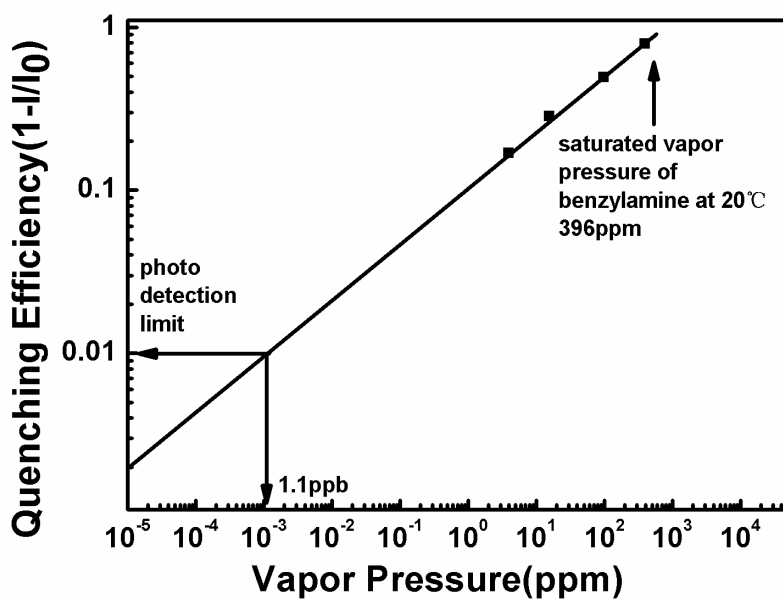


Fig S11 Fluorescence quenching efficiency ($1-I/I_0$) as a function of the vapour pressure of benzylamine at 470 nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

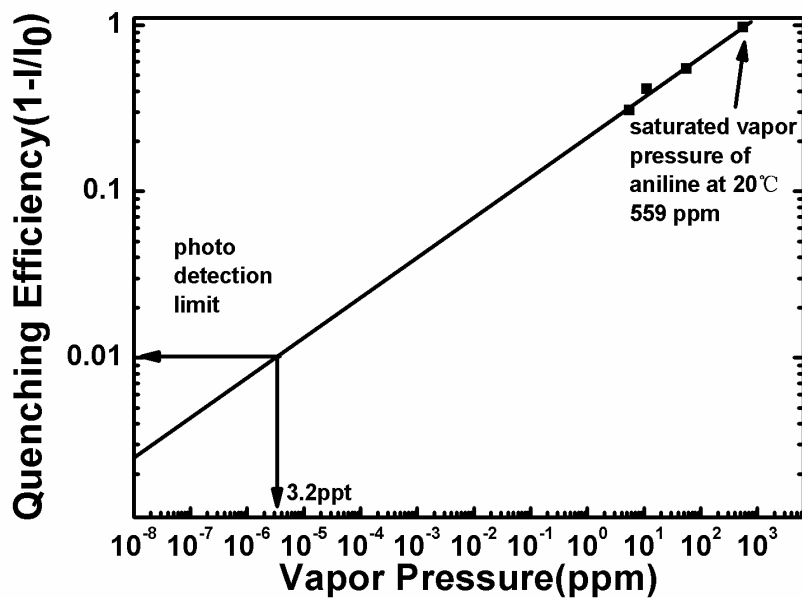


Fig S12 Fluorescence quenching efficiency ($1-I/I_0$) as a function of the vapour pressure of aniline at 470 nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

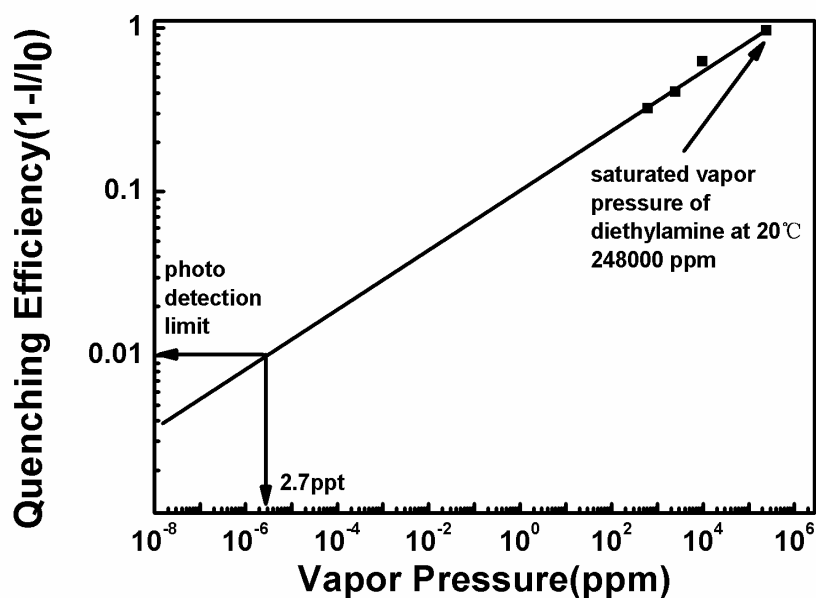


Fig S13 Fluorescence quenching efficiency ($1-I/I_0$) as a function of the vapour pressure of diethylamine at 470 nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

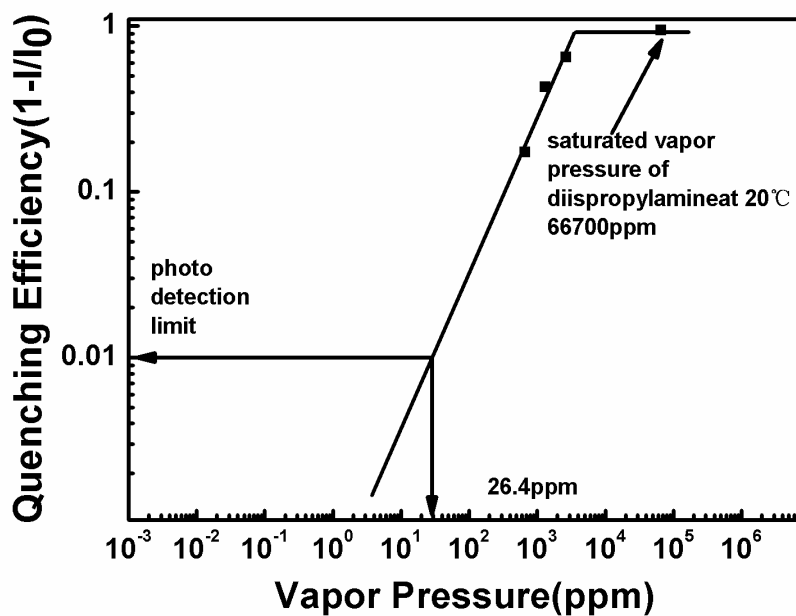


Fig S14 Fluorescence quenching efficiency ($1-I/I_0$) as a function of the vapour pressure of diisopropylamine at 470 nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

Table S1. Saturated vapour pressure of different amines at 20 °C (KPa) and the photo detection limits of BFTA for these amines

	1 ^[d]	2 ^[e]	3 ^[f]	4 ^[g]	5 ^[h]	6 ^[i]
SP ^[a]	33.0 ^[j]	0.89 ^[k]	0.059 ^[l]	0.056 ^[k]	25.11 ^[l]	6.67 ^[i]
]	
DL ^[b]	7.5ppb	37.1ppb	1.3ppb	3.2ppt	2.7ppt	26.4ppm
IDLH ^[c]	-	-	-	100	200	200

[a] saturated vapour pressure at 20 °C/KPa [b] photo detection limit [c] IDLH/ppm [d] *n*-propylamine [e] *n*-hexylamine [f] benzylamine [g] aniline [h] diethylamine [i] diisopropylamine [j] From Wikipedia, the free encyclopedia [k] Calculated through Antoine equation according to the data from the Lange's Hand book of Chemistry [l] Calculated through Antoine equation according to the data from the CRC Handbook

Effects of common organic solvents on sensing performance.

To further demonstrate the selectivity of this probe, several common organic solvents including dichloromethane, tetrahydrofuran, acetone, ethanol and ethyl acetate were selected as interference reagents and the interaction of the probe with these solvents were investigated. No obvious fluorescence intensity change (less than 2 %) of the films was observed upon exposure to these vapours indicating the sensing film possessed excellent selectivity towards organic amines.

The selectivity of the BFTA films towards tertiary amines and quaternary ammonium.

At present, the quaternary ammonium could not be detected by our probe for their poor volatility. As for tertiary amine such as triethylamine, our research shows that the fluorescence color of this probe change from blue to yellow in presence of it. Further study indicates this change is not caused by chemical reaction but by the solvent effect.

The influence of a mixture of more than one amine on the sensitivity.

When the fluorescent films were exposed to the mixture of more than one amine, Schiff base reaction and the photooxidation of arylboronate reaction may occur simultaneously leading to the complex product remaining on the film.