

Supporting Information for

Reversible and “fingerprint” fluorescence differentiation of different organic amines vapours using a single conjugated polymer probe

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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. Unless otherwise noted, all the films were prepared from their THF solutions with concentrations as 4mg/mL on (10×20 mm) quartz plates by spin-coating method at 2200 rpm. The films were all 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

4, 4’-(dibromo)triphenylamine (2)

A solution of NBS (3.63 g, 20.4 mmol) in DMF (30 mL) was added dropwise into a solution of triphenylamine (2.5g, 10.2 mmol) in DMF (30mL), and then stirring at 0°C for 4 h. The solvent was removed, and the residue was washed by water (100 mL)

and saturated aqueous NaCl (80mL). After which the organic layer was dried over anhydrous MgSO₄. Then the solvent was removed through rotary evaporation and the residue was purified by silica gel chromatography eluted with petroleum ether to get pellucid liquid (3.6 g, 88%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.31 (m, 4H), 7.24 (m, 2H), 7.05 (m, 3H), 6.91 (m, 4H); MALDI-TOF MS: m/z 401.

4-(bis(4-bromophenyl)amino)benzaldehyde (M3)

To a solution of 4g **2** in 40mL DMF, 20 mL POCl₃ were added. The mixture was stirring at 90°C overnight. After the reaction solution was cooled to room temperature, it was poured into the ice-water mixture and stirred for another hour. Then the solution was extracted with dichloromethane. And the extract was dried over anhydrous MgSO₄. After filtration, the solvent was removed through rotary evaporation and the residue was purified by silica gel chromatography eluted with petroleum ether and dichloromethane to light yellow solid (3.1 g, 72%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 9.84 (s, 1H), 7.70-7.72 (d, 2H, *J* = 8.4 Hz), 7.43-7.45 (d, 4H, *J* = 8.6 Hz), 7.01-7.05 (m, 6H); MALDI-TOF MS: m/z 429

4,4',4''-(tribromo)triphenylamine (4)

A 250 mL three-necked round-bottomed flask charged with triphenylamine (5.0120 g, 20.4 mmol), chloroform (100 mL). A solution of Br₂ (3.25 mL, 0.0634 mol) in chloroform (20 mL) was added dropwise under UV irradiation. The reaction solution turned from purple red to green. The reaction solution was stirring at room temperature for 24 hrs under UV irradiation. Then the mixture was extracted with CHCl₃ (30 mL), and washed with NaOH (2 M aq) and water. The organic layer was separated and dried over anhydrous MgSO₄. The solvent was removed and the residue was pre-purified by column chromatography eluted with chloroform and followed by recrystallization in hexane to get pellucid solid (6.45 g, 66%). ¹H NMR (500 MHz, CDCl₃, ppm) δ 7.34 (m, 6 H), 6.91 (m, 6 H); MALDI-TOF MS: m/z 479.

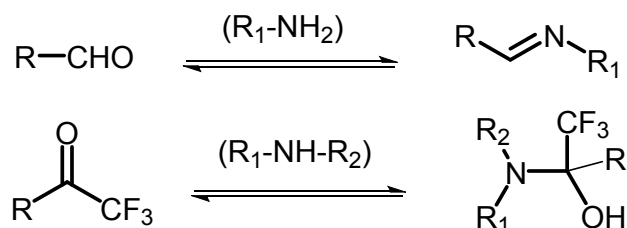
1-(4-(bis(4-bromophenyl)amino)phenyl)-2,2,2-trifluoroethanone (M5)

Under argon atmosphere, a solution of 1.43g (3 mmol) **4**, 4', 4''-(tribromo)triphenylamine in anhydrous THF was cooled to -78°C. After 15 minutes, 2 mL BuLi (1.6mol/L in hexane) was added dropwise to this solution. The solution was

maintained at -78°C for an hour. Then 0.426g (3mmol) ethyltrifluoroacetate in THF (4 mL) is added to this solution. The resulting solution was warmed to room temperature and stirred for another hour. After conventional workup (NaHCO_3 and CH_2Cl_2 extraction), the mixture was purified by flash chromatography to offer **M5** (0.55g, 37%) as the yellow solid. ^1H NMR (500 MHz, CDCl_3 , ppm) δ 7.89-790(d, 2H, $J = 8.5$ Hz), 7.46-7.49(m, 4H), 7.03-7.06 (m, 4H), 6.91-6.99(d, 2H, $J = 9.0$ Hz); HRMS: calcd M^+ for $\text{C}_{20}\text{H}_{12}\text{Br}_2\text{F}_3\text{NO}$ 496.923529; found 496.923224.

Synthesis of P7

M3 (215 mg, 0.5 mmol), **M5** (248mg, 0.5mmol) and 9, 9-dioctylfluorene-2, 7-bis (4, 4, 5, 5-tetramethyl-1, 3, 2-dioxaborolane) (654mg, 1.02 mmol) were dissolved in 15 mL of freshly distilled toluene. The tetrakis(triphenylphosphine)-palladium (1 mol %) was added into the mixture in a dry box. 2 M aqueous sodium carbonate (2 mL, 4 mmol) and a drop of phase transfer catalyst, Aliquat 336, were purged in toluene under nitrogen. The reaction mixture was stirred and heated for 60h until the reaction mixture became viscous. An excess of bromobenzene dissolved in 1 mL of anhydrous toluene was added as an end-capper. After further stirring and heating for 12 h, the reaction mixture was cooled to about 50°C and added slowly to a vigorously stirred mixture consisting of 200 mL of methanol. The polymer was collected by filtration and reprecipitation from methanol and acetone. The polymer was purified by a Soxhlet extraction in methanol for 2 days. The final product, a green polymer, was obtained after drying in vacuo at 60°C , with a yield of 82.0%. ^1H -NMR(500MHz, CDCl_3 , 25°C , TMS): 9.88 (s, 1 H), 7.48-7.97(m, 24 H), 7.14-7.38(m, 12H), 2.07(m, 8H), 1.09-1.19(m,40H), 0.75-0.82(m, 20H).The molecular weight was determined by GPC with M_n 6154 and M_w 11170.



Scheme S1. Possible reactions between polymer and amines vapour.

The optical property of the M3, M5 and P7 in THF solution.

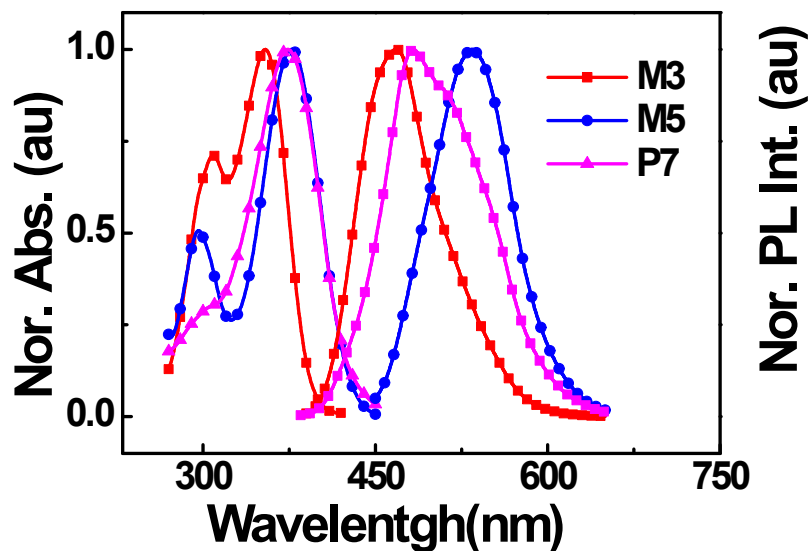


Fig S1 Normalized absorption and fluorescence spectra of M3, M5 and P7 in THF solution.

Calculation of detection limits

Theoretically, it is feasible to detect anylate at dual or multi- wavelength for the probe whose output signal is based on the fluorescent spectra shift. To estimate the detection limit, we measured the changes in fluorescence intensity of P7 films exposed to each amine vapours of at least four different concentrations. And the intensity quenching data ($1 - I/I_0$) or intensity increasing data ($I/I_0 - 1$) are well-fitted to the Langmuir equation with an assumption that the quenching efficiency or increasing efficiency is proportional to the surface adsorption of amine vapour.

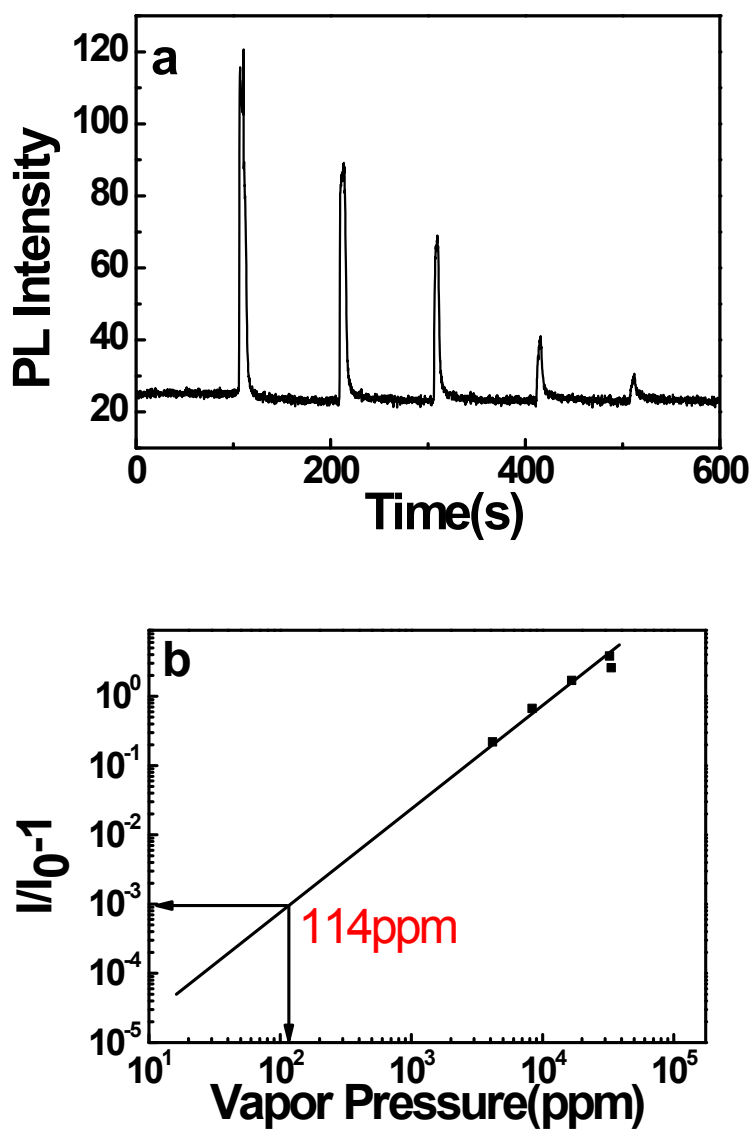


Fig S2 (a) Changes in fluorescence intensity of **P7** films exposed to *n*-propylamine vapour with different concentrations; (b) Fluorescence increasing efficiency (I/I_0-1) as a function of the vapour pressure of *n*-propylamine at 435 nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

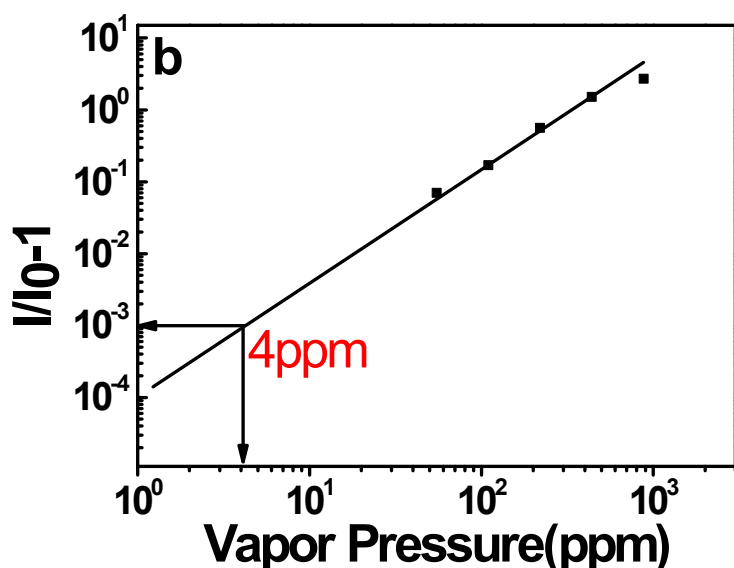
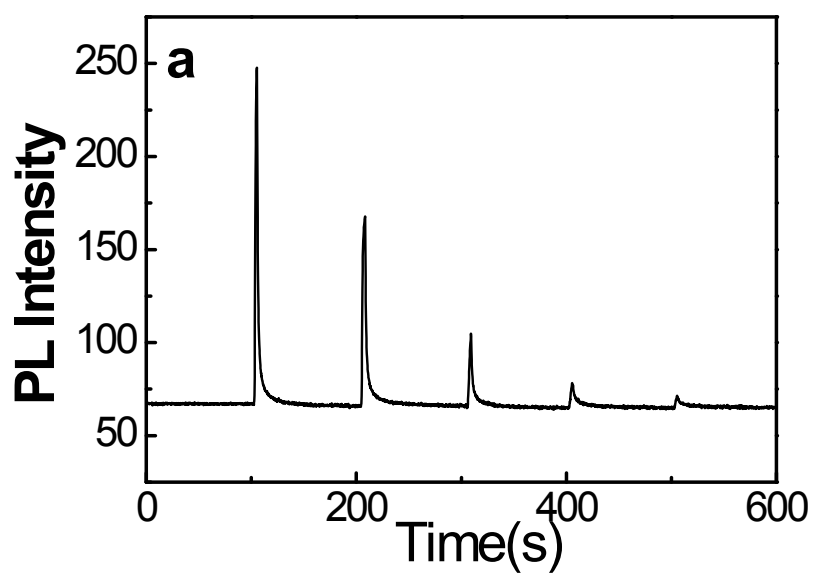


Fig S3 (a) Changes in fluorescence intensity of **P7** films exposed to *n*-hexylamine vapour with different concentrations; (b) Fluorescence increasing efficiency (I/I_0-1) as a function of the vapour pressure of *n*-hexylamine at 435 nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

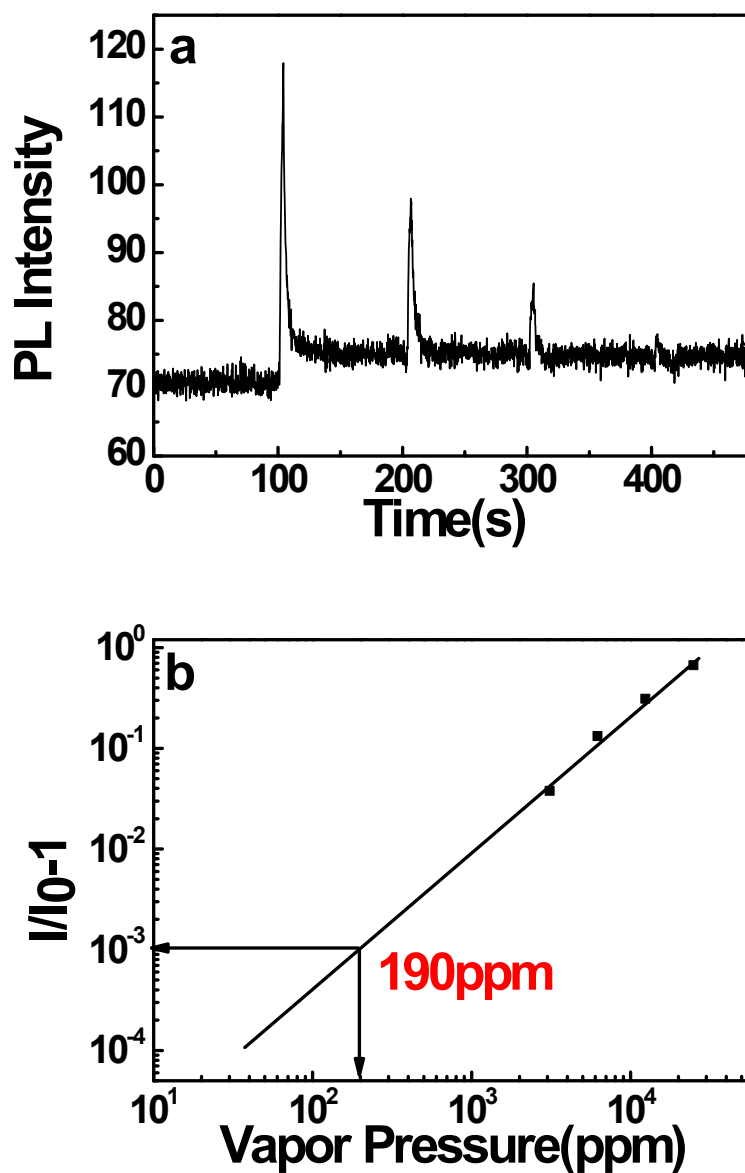


Fig S4 (a) Changes in fluorescence intensity of P7 films exposed to diethylamine vapour with different concentrations; (b) Fluorescence increasing efficiency ($I/I_0 - 1$) as a function of the vapour pressure of diethylamine at 475 nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

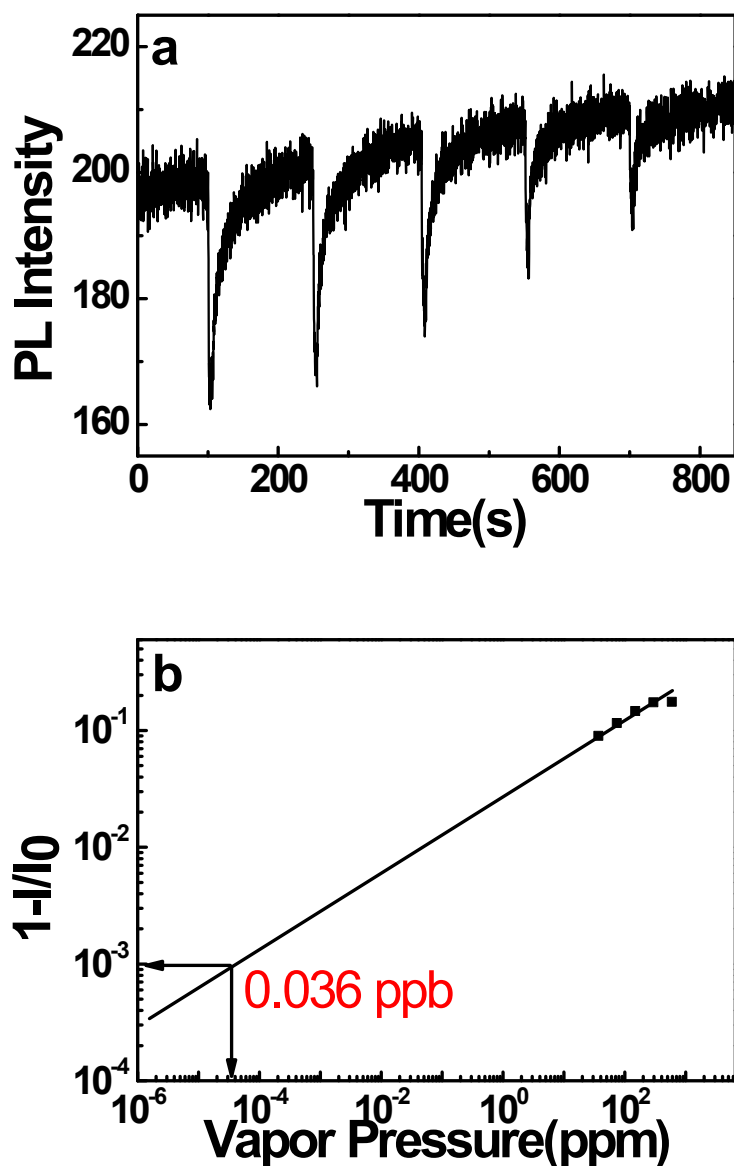


Fig S5 (a) Changes in fluorescence intensity of P7 films exposed to dipropylamine vapour with different concentrations; (b) Fluorescence increasing efficiency (I/I_0-1) as a function of the vapour pressure of dipropylamine at 525 nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

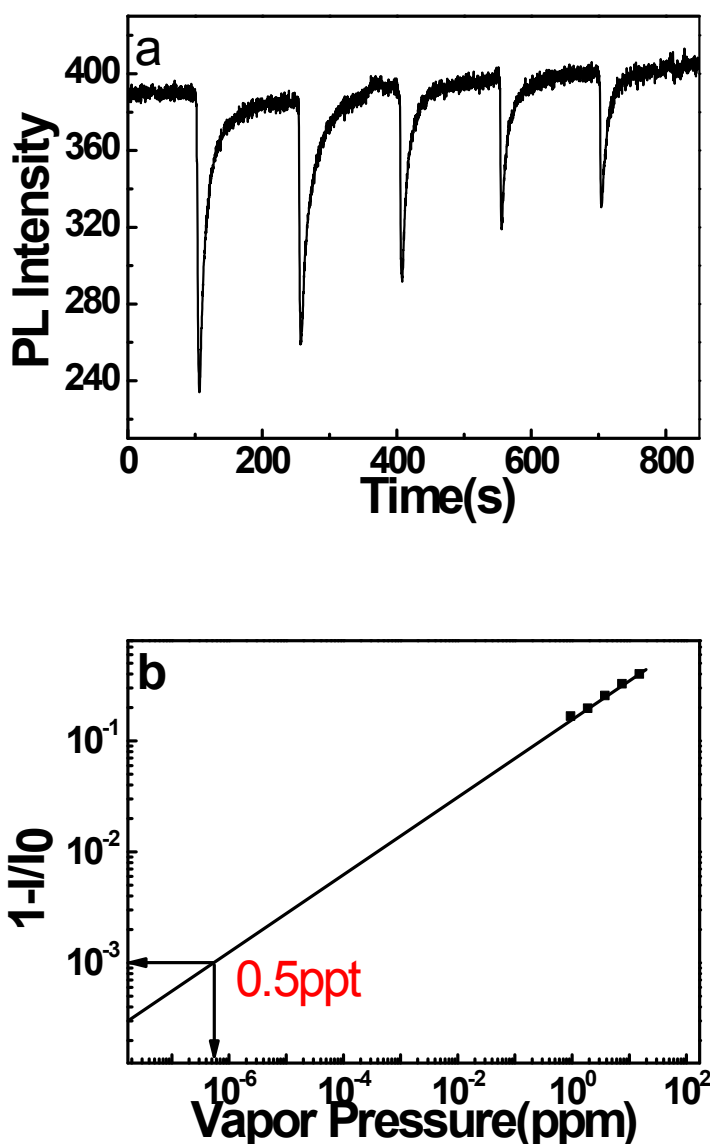


Fig S6 (a) Changes in fluorescence intensity of **P7** films exposed to o-toluidine vapour with different concentrations; (b) Fluorescence quenching efficiency ($1-I/I_0$) as a function of the vapour pressure of o-toluidine at 525nm: data (error $\pm 5\%$) fitted with the Langmuir equation.

The selectivity of the P7 films towards tertiary amines.

It reported that trifluoroacetyl group can bind tertiary amine to form the zwitterions in solution. For tertiary amine such as triethylamine, the fluorescence color of this probe shows almost no change in presence of it observed by naked eyes. The maximum emission peak of the fluorescence spectra keeps almost unchanged with slightly wider spectra. In this situation, zwitterion is hardly formed without solvent.

Thus we deduce the tiny change is caused by the solvent effect.

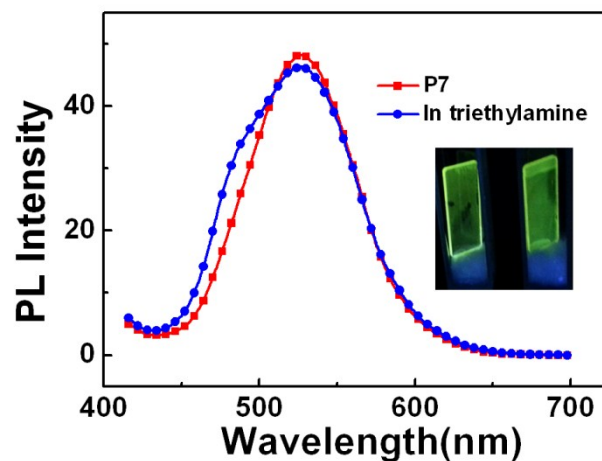


Fig S7 The fluorescence spectra of **P7** films before and after exposure in trimethylamine vapour. Inset: fluorescence change before (left) and after (right) exposure to trimethylamine vapour.

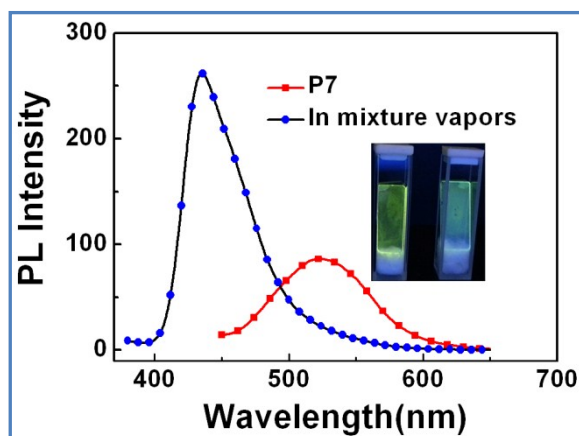


Fig. S8. The fluorescence spectra of **P7** films before and after exposure in the mixture vapour of six amines. Inset: fluorescence change before (left) and after (right) exposure to mixture amines vapour.

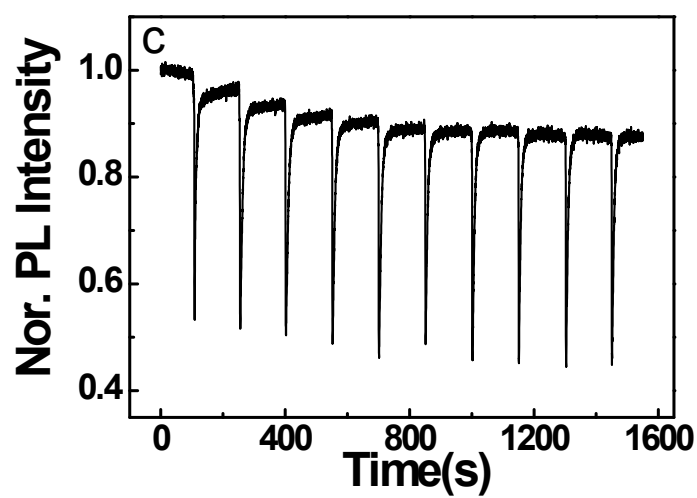
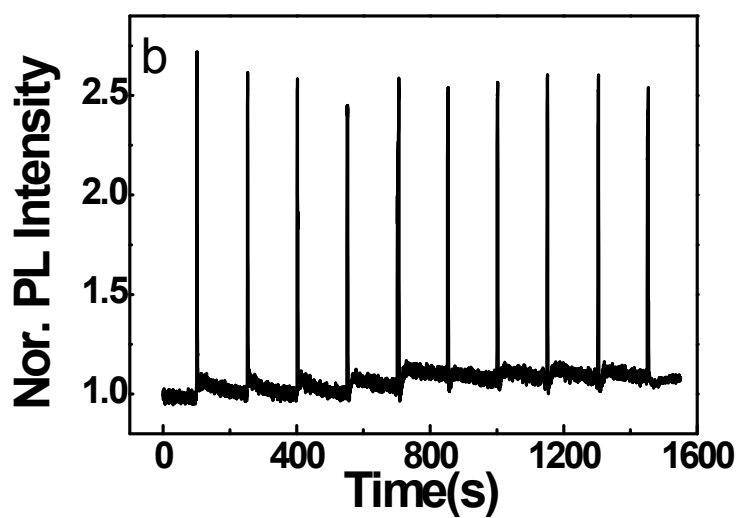
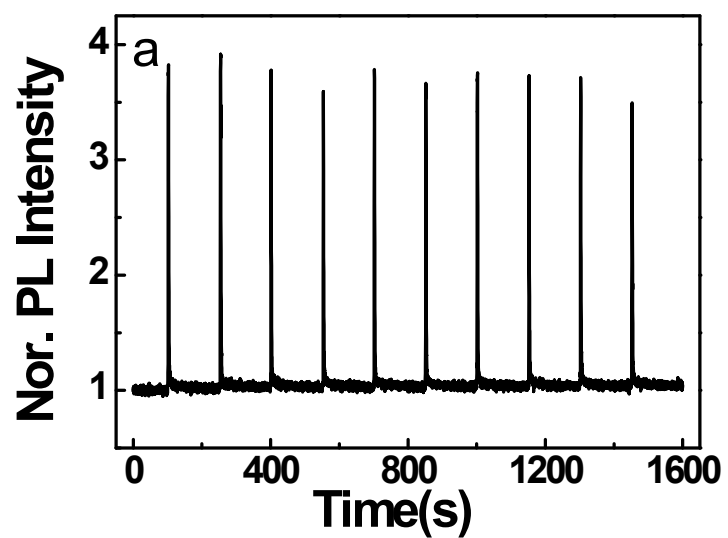


Fig S9 Time resolved fluorescence intensity of P7 film at 435nm(a) , 475nm (b) and

525nm (c), respectively, upon consecutive exposure to a mixture amines of n-propylamine, n-hexylamine, diethylamine, dipropylamine, aniline and o-toluidine.