

Supporting Information for

**A mild and catalyst-free conversion of solid phase  
benzylidenemalononitrile/benzylidenemalonate to  
N-benzylidene-amine and its application for primary alkyl  
amine vapor fluorescence detection**

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## Experimental Section

### General :

UV-vis absorption and fluorescence analysis conducted on a Jasco V-670 spectrophotometer and a Jasco FP 6500 spectrometer, respectively. The  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were obtained from a Bruker DRX500 instrument, 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. GPC experiments were performed with Waters GPC system using THF as eluent. Cyclic voltammetry experiments were performed with a CH Instruments electrochemical analyzer. The electrochemical behaviors were investigated in a standard three electrode electrochemical cell with 0.1 M tetra-*n*-butylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) in acetonitrile solution, (a glassy carbon working electrode, a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode) and the scanning rate was 100 mV/s under nitrogen at room temperature.

### Preparation of polymer film for SEM measurement

First a solution of P1 and P2 in toluene ( $5 \times 10^{-3}$  M) was prepared, then the film was fabricated onto quartz plate with a size of 10 mm  $\times$  20 mm by spin-coating with a speed of 2500 rpm, then it is vacuum dried to remove the solvent residue and ready for the SEM measurement.

## Synthesis and Characterization

### Diethyl 2-(4-(bis(4-bromophenyl)amino)benzylidene)malonate (M1)

Several drops of piperidine was added to a solution of 4-(bis(4-bromophenyl)amino)benzaldehyde (4.3 g) and diethyl malonate (1.6 g) in 50 mL  $\text{CH}_3\text{CN}$  to initiate the reaction. The solution was stirred at 60°C for 12 h. After the solvent was removed, the residue was purified by column separation with silica-gel to afford yellowish-green solid 5.2 g (yield 91%).

$^1\text{H}$ -NMR(500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.61 (s, 1H) 7.40 (d, 4H, 8.5Hz) 7.32 (d, 2H ,

9.0Hz), 6.97(d, 4H, 8.5Hz), 6.96 (d, 2H, 9.0Hz), 4.34 (q, 2H, 7.0Hz) , 4.29 (q,2H 7.0Hz) , 1.32 (t, 6H 7.0Hz);

<sup>13</sup>C-NMR (500 MHz CDCl<sub>3</sub>): 167.11(1C) 164.44(1C) 149.07(1C) 145.42(2C) 141.18(1C) 132.70(4C) 131.22(2C) 126.75(4C) 126.49(1C) 123.71(1C) 121.76(2C) 117.18(2C) 61.61 (1C) 61.48(1C) 14.15(1C)13.97(1C);

MALDI-TOF MS: 573.0 m/z

### **2-(4-(bis(4-bromophenyl)amino)benzylidene)malononitrile (M2)**

Several drops of piperidine was added to a solution of 4-(bis(4-bromophenyl)amino)benzaldehyde (4.3 g) and malononitrile (0.8 g) in 50 mL CH<sub>3</sub>CN to initiate the reaction. The solution was stirred at 60°C for 12 h. After the solvent was removed, the residue was purified by column separation with silica-gel to afford a red solid 4.3 g (yield 90%).

<sup>1</sup>H-NMR(500 MHz, CDCl<sub>3</sub>, δ): 7.76 (d, 2H, 9.0Hz), 7.55(s, 1H), 7.49(d, 4H, 8.5Hz), 7.04 (d, 4H ,8.5Hz), 6.98(d, 2H, 9.0Hz);

<sup>13</sup>C-NMR (500 MHz CDCl<sub>3</sub>): 157.81(1C), 152.40(1C) , 144.05(2C), 133.18(4C), 132.92(2C), 132.56(1C), 127.84(4C) , 126.01(1C), 123.81(1C) , 119.48(2C), 119.22(2C), 114.77(1C);

MALDI-TOF MS: 479.0 m/z.

### **N-(4-(bis(4-bromophenyl)amino)benzylidene)-propylamine from Diethyl 2-(4-(bis(4-bromophenyl)amino)benzylidene)malonate**

A solution of Diethyl 2-(4-(bis(4-bromophenyl)amino)benzylidene)malonate (1.4 × 10<sup>-3</sup> M) was spincoated onto quartz, then it is dried under vacuum to afford the sensing film. The sensing film was put inside an atmosphere of *n*-propylamine for 5 min, then it is dried under vacuum to afford the target compound in a yield of 100%.

<sup>1</sup>H-NMR(500MHz CDCl<sub>3</sub>, δ): 8.19 (s, 1H), 7.59 (d, 2H, 8.5Hz), 7.37 (d,4H, 8.5Hz), 7.03(d,2H , 8.5Hz), 6.96 (d, 4H, 8.5Hz), 3.55 (t, 2H), 1.71(dt, 2H), 0.95(t, 3H);

<sup>13</sup>C-NMR(500 MHz CDCl<sub>3</sub>): 159.85(1C), 148.85(1C), 145.95(2C), 132.51(4C), 131.12(1C), 129.19(2C), 126.14(4C,) 122.98(2C), 116.35(2C), 63.49(1C), 24.10(1C) , 11.82(1C) .

HR-MS: calcd 469.9993 for C<sub>22</sub> H<sub>20</sub> N<sub>2</sub> Br<sub>2</sub>, found 469.9995.

**N-(4-(bis(4-bromophenyl)amino)benzylidene)-propylamine** **from**  
**2-(4-(bis(4-bromophenyl)amino)benzylidene)malononitrile**

A solution of 2-(4-(bis(4-bromophenyl)amino)benzylidene)malononitrile ( $1.4 \times 10^{-3}$  M) was spincoated onto quartz, then it is dried under vacuum to obtain the sensing film. The sensing film was put inside an atmosphere of *n*-propylamine for 5 min, then it is dried under vacuum to afford the target compound in a yield of 100%.

$^1\text{H-NMR}$ (500 MHz  $\text{CDCl}_3$ ,  $\delta$ ): 8.19 (s, 1H), 7.59 (d,2H, 8.5Hz), 7.37 (d,4H, 8.5Hz), 7.03(d,2H , 8.5Hz), 6.96 (d, 4H, 8.5Hz), 3.55 (t, 2H, ), 1.71(dt, 2H), 0.95(t, 3H);

$^{13}\text{CNMR}$  (500 MHz  $\text{CDCl}_3$ ): 159.85(1C), 148.85(1C), 145.95(2C), 132.51(4C),131.12(1C), 129.19(2C), 126.14(4C), 122.98(2C), 116.35 (2C), 63.49(1C), 24.10(1C) , 11.82(1C).

HR-MS: calcd 469.9993 for  $\text{C}_{22}\text{H}_{20}\text{N}_2\text{Br}_2$ , found 469.9995

### Synthesis of P1

Under Ar atmosphere protection, to a mixture of 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (240 mg), diethyl 2-(4-(bis(4-bromophenyl)amino)benzylidene)malonate (176 mg), aliquat 336 (20 mg), and  $\text{Pd}(\text{PPh}_3)_4$  (34 mg, 0.03 mmol) was added 6 mL freshly distilled and degassed toluene and 2 mL  $\text{K}_2\text{CO}_3$  aqueous solution(2mol/L) by injection, then kept stirring at  $90^\circ\text{C}$  for 48 h. Cooled to room temperature, the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , washed with brine and dried over  $\text{MgSO}_4$ . Then it is reprecipitated in MeOH for three times and extracted with acetone for 24 h to remove the oligomer and the catalyst. After dried under vacuum 160 mg (yield 49.5%) deep green solid was obtained.

$^1\text{H-NMR}$ (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.85-7.75(2H), 7.70-7.62(4H), 7.62-7.55(4H), 7.52-7.45(s,1H) 7.41-7.32(d,2H) 7.15-7.07(d,2H), 4.39-4.32(2H), 4.32-4.25(2H), 2.11-1.97(4H), 1.40-1.27(6H), 1.17-1.07(22H), 0.85-0.67(10H).

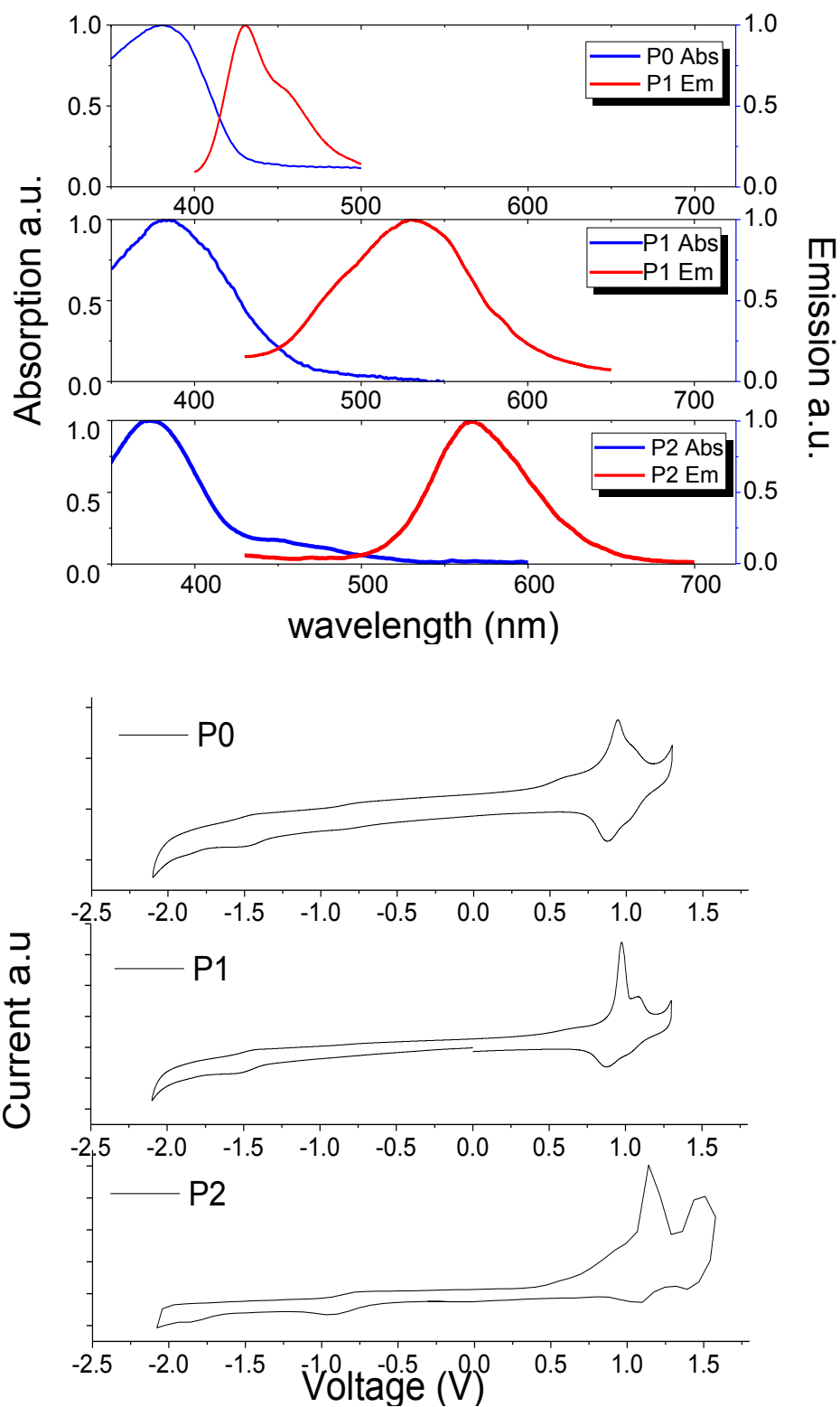
$M_n = 7555$  Da PDI=1.90

## Synthesis of P2

Under Ar atmosphere protection, to a mixture of 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (214 mg), 2-(4-(bis(4-bromophenyl)amino)benzylidene)malononitrile (150 mg), aliquat 336 (20 mg), and Pd(PPh<sub>3</sub>)<sub>4</sub> (34 mg, 0.03 mmol) was added 6 mL freshly distilled and degassed toluene and 2 mL K<sub>2</sub>CO<sub>3</sub> aqueous solution (2 mol/L) by injection, then kept stirring at 90°C for 48 h. The reaction mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and dried over MgSO<sub>4</sub>. It is precipitated in MeOH for three times, then extracted with acetone to remove the oligomer and the catalyst. After dried under vacuum, 150 mg (yield 56.2%) deep-red solid could be obtained.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, δ): 7.78-7.72(5H), 7.72-7.62(4H), 7.62-7.53(6H), 7.37-7.30(4H), 7.23-7.15(2H), 2.15-2.00(4H), 1.17-1.07(22H), 0.87-0.65(10H).

Mn = 8934 Da PDI=4.40



**Figure S1** UV-vis absorption, emission and CV spectra of P0, P1 and P2 in film state.

**Table S1.** Optical, Electrochemical Properties and energy level of P0, P1 and P2

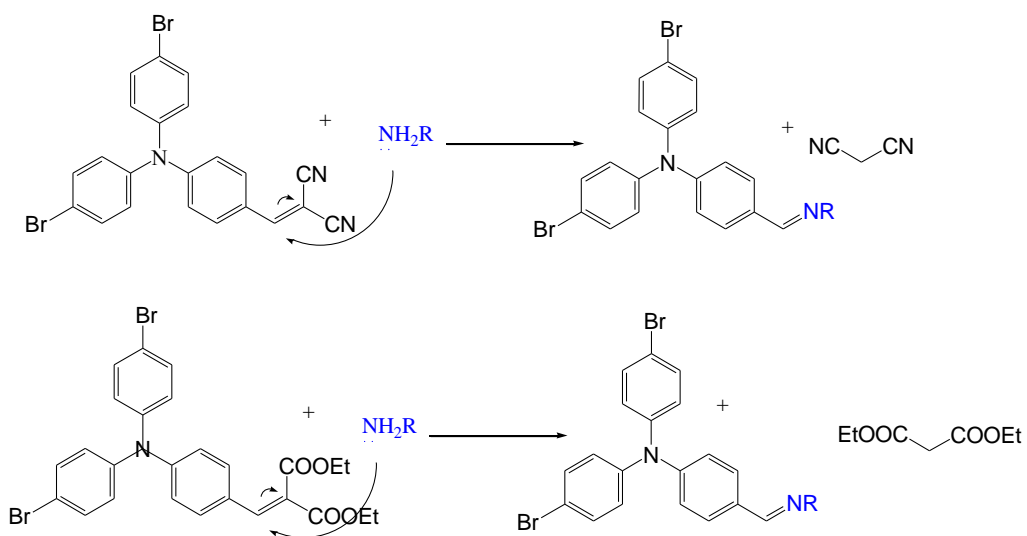
	$\lambda_{\max}$ Abs (nm)	$\lambda_{\max}$ PL (nm)	$E_{ox}$ (eV)	$E_g$ (eV)	HOMO (eV)	LUMO (eV)
P0	378	430	0.91	2.95	-5.65ev	-2.70
P1	380	531	0.94	2.71	-5.68ev	-2.97
P2	376	573	1.09	2.36	-5.83ev	-3.47

$$E_{\text{HOMO}} = -e(E_{\text{OX}} + 4.741) \text{ (eV)}, \quad E_{\text{LUMO}} = E_g + E_{\text{HOMO}}$$

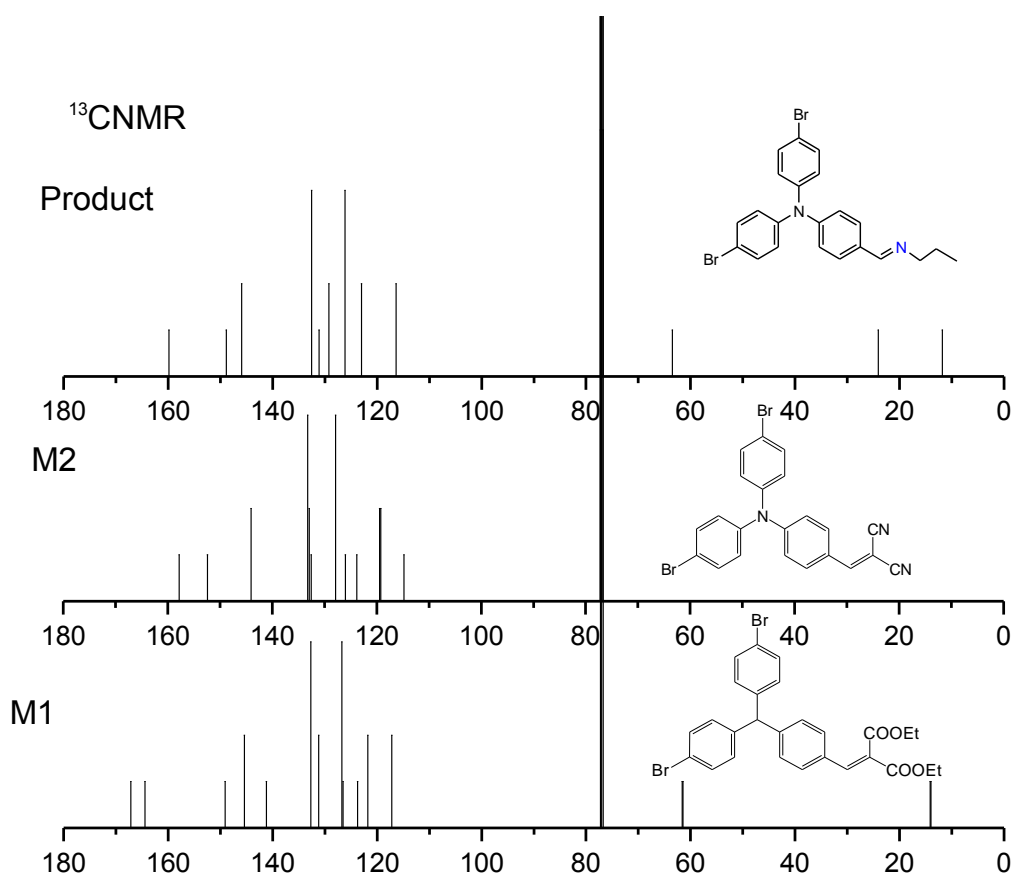
**Table S2.** Reaction selectivity

Entry	Amine	yield
1	<i>n</i> -Propylamine	100%
2	<i>n</i> -Hexamine	100%
3	Benzylamine	100%
4	Aniline	0
5	Diisopropylamine	0
6	Diethylamine	0
7	Triethylamine	0
8	N,N-Dimethylbenzylamine	0
9	cyclohexylamine	0

All samples were treated by exposed in amine vapors for 5mins then vacuumed and tested by  $^1\text{H-NMR}$  with  $\text{CDCl}_3$ .

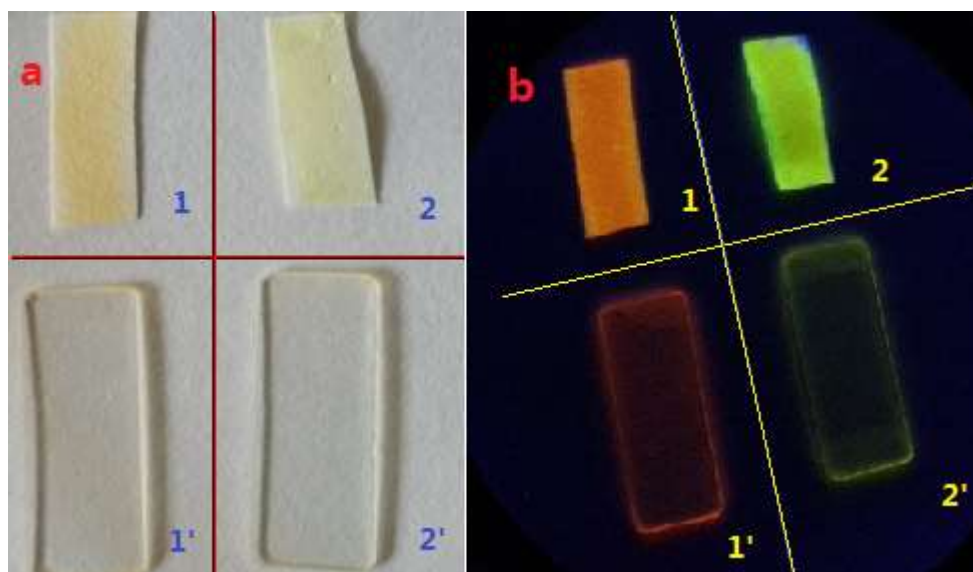


**Figure S2** Proposed mechanism of M1 and M2 with primary alkyl amine

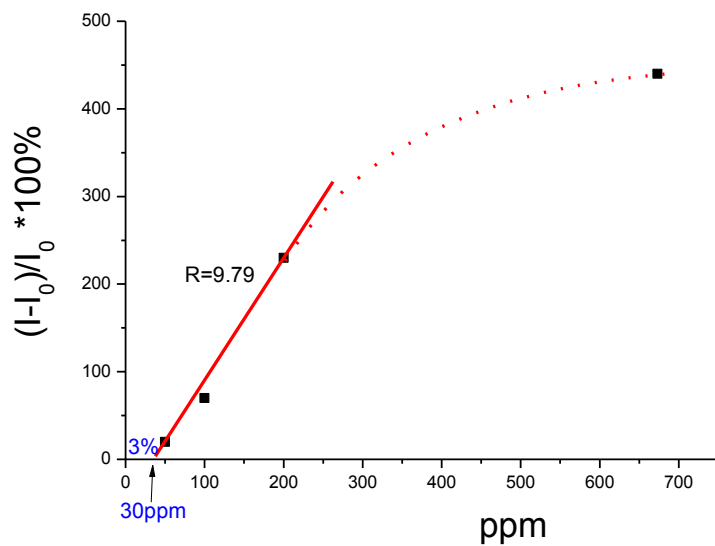


**Figure S3** <sup>13</sup>C-NMR of M1, M2 and the Schiff base product

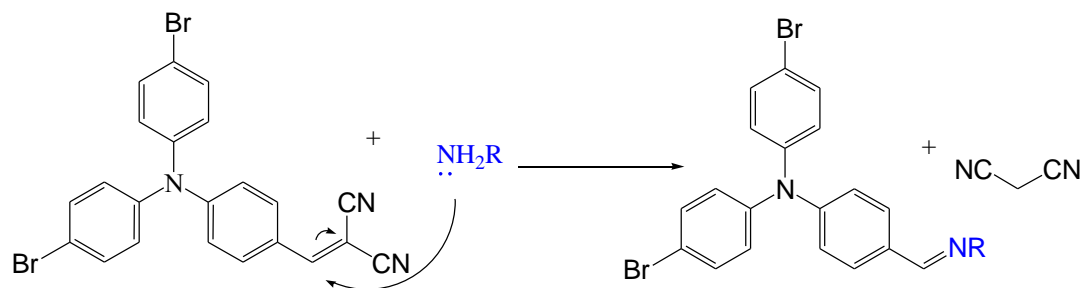




**Figure S4** Visible color (a) and fluorescence (b) of P2 1: P2 on filter paper stripe. 1': P2 on quartz chip. 2: P2 on filter paper stripe after exposed to saturated benzylamine vapor for 300 s. 2': P2 on quartz chip after exposed to saturated benzylamine vapor for 300 s.



**Figure S5** Detection limit for Benzylamine (BZA), 30 ppm calculated



We supposed the reaction between P2 and primary alkyl amine follows a first order reaction.

Namely,  $X + Y \rightarrow Z$

Among them, X: C=C structure    Y: amine    Z: C=N structure

Chemical equilibrium:  $[Z] = k [X][Y]$

[X] was regarded as constant at low concentration of Y, so that [Z] was regarded as linear to [Y].

Intensity of Z regarded as linear to concentration of Y and the limitation of detection could be calculated from the extension of linear fitting.

Since the value of  $(I-I_0)/I_0$  is 20% , 70% and 230% fluorescent enhancement under 50, 100 and 200 ppm benzylamine, respectively, the detection limit could be calculated to be 30 ppm.