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 $^1$H and $^{13}$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 (Bu$_4$NPF$_6$) in acetonitrile solution, (a glassycarbon 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 CH$_3$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%).

$^1$H-NMR (500 MHz, CDCl$_3$, $\delta$): 7.61 (s, 1H) 7.40 (d, 4H, 8.5 Hz) 7.32 (d, 2H, 8.5 Hz)
9.0 Hz), 6.97 (d, 4H, 8.5 Hz), 6.96 (d, 2H, 9.0 Hz), 4.34 (q, 2H, 7.0 Hz), 4.29 (q, 2H, 7.0 Hz), 1.32 (t, 6H, 7.0 Hz);

$^{13}$C-NMR (500 MHz CDCl$_3$): 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$_3$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%).

$^1$H-NMR(500 MHz, CDCl$_3$, δ): 7.76 (d, 2H, 9.0 Hz), 7.55 (s, 1H), 7.49 (d, 4H, 8.5 Hz), 7.04 (d, 4H, 8.5 Hz), 6.98 (d, 2H, 9.0 Hz);

$^{13}$C-NMR (500 MHz CDCl$_3$): 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$^{-3}$ 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%.

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

$^{13}$C-NMR(500 MHz 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 C$_{22}$H$_{20}$N$_2$Br$_2$, 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 × 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%.

\(^1\)H-NMR(500 MHz CDCl\textsubscript{3}, 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);

\(^{13}\)CNMR (500 MHz CDCl\textsubscript{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 C\textsubscript{22} H\textsubscript{20} N\textsubscript{2} Br\textsubscript{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 Pd(PPh\textsubscript{3})\textsubscript{4} (34 mg, 0.03 mmol) was added 6 mL freshly distilled and degassed toluene and 2 mL K\textsubscript{2}CO\textsubscript{3} aqueous solution(2mol/L) by injection, then kept stirring at 90\(^\circ\)C for 48 h. Cooled to room temperature, the reaction mixture was extracted with CH\textsubscript{2}Cl\textsubscript{2}, washed with brine and dried over MgSO\textsubscript{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.

\(^1\)H-NMR(500 MHz, CDCl\textsubscript{3}, δ): 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).

Mn = 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(PPh₃)₄ (34 mg, 0.03 mmol) was added 6 mL freshly distillled and degassed toluene and 2 mL K₂CO₃ aqueous solution(2mol/L) by injection, then kept stirring at 90°C for 48 h. The reaction mixture was extracted with CH₂Cl₂, and dried over MgSO₄. 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.

¹H-NMR(500 MHz, CDCl₃, 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

<table>
<thead>
<tr>
<th></th>
<th>λ_{max Abs} (nm)</th>
<th>λ_{max PL} (nm)</th>
<th>E_{ox} (eV)</th>
<th>E_g (eV)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>378</td>
<td>430</td>
<td>0.91</td>
<td>2.95</td>
<td>-5.65 ev</td>
<td>-2.70</td>
</tr>
<tr>
<td>P1</td>
<td>380</td>
<td>531</td>
<td>0.94</td>
<td>2.71</td>
<td>-5.68 ev</td>
<td>-2.97</td>
</tr>
<tr>
<td>P2</td>
<td>376</td>
<td>573</td>
<td>1.09</td>
<td>2.36</td>
<td>-5.83 ev</td>
<td>-3.47</td>
</tr>
</tbody>
</table>

E_{HOMO} = e(E_{ox} + 4.741) (eV), \hspace{1cm} E_{LUMO} = E_g + E_{HOMO}

Table S2. Reaction selectivity

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amine</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-Propylamine</td>
<td>100%</td>
</tr>
<tr>
<td>2</td>
<td>n-Hexamine</td>
<td>100%</td>
</tr>
<tr>
<td>3</td>
<td>Benzylamine</td>
<td>100%</td>
</tr>
<tr>
<td>4</td>
<td>Aniline</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>Diisopropylamine</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Diethylamine</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Triethylamine</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>N,N-Dimethylbenzylamine</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>Cyclohexylamine</td>
<td>0</td>
</tr>
</tbody>
</table>

All samples were treated by exposed in amine vapors for 5mins then vacuumed and tested by $^1$H-NMR with CDCl3.
**Figure S2** Proposed mechanism of M1 and M2 with primary alkyl amine

**Figure S3** $^{13}$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 \( \quad Y: \) amine \( \quad Z: \) 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.