

## Supporting information

### **Bio-inspired enol-degradation for multipurpose oxygen sensing**

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#### **2. Characterization and Procedures of Synthesis**

**3. <sup>1</sup>H NMR and <sup>13</sup>C NMR**

# 1. Experimental details

## 1.1 Materials

Fluorene, and 2-(4-nitrophenyl)acetic acid were purchased from Aldrich. 2-bromohexane, tetrabutylammonium iodide (TBAI), 4-iodoaniline, benzyl bromide, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, CuI, trimethyl silyl acetylene (TMSA), were purchased from Aladdin.

## 1.2 Instrument characterization

UV-Vis absorption spectra were measured using a Shimadzu UV-2550 PC double-beam spectrophotometer.

Fluorescence spectra were obtained with a Shimadzu spectrofluorimeter RF-5301PC.

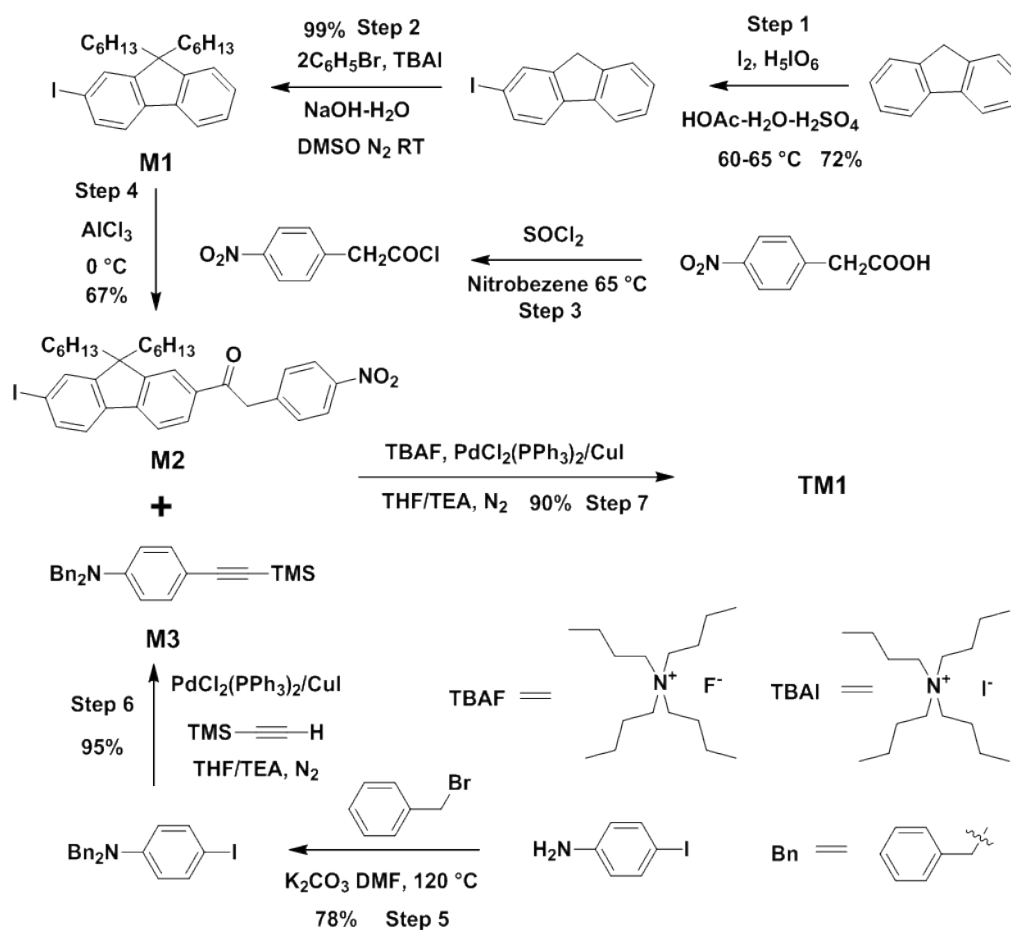
ESI-HRMS analysis was performed on an Agilent 1290-microTOF-Q II mass spectrometer. Accurate masses were reported for the molecular ion [M+H]<sup>+</sup> or [M]<sup>+</sup>.

Nuclear magnetic resonance spectra (<sup>1</sup>H NMR and <sup>13</sup>C NMR) were recorded with Varian Mercury (300 MHz). For CDCl<sub>3</sub> and CD<sub>3</sub>CN solutions, the chemical shifts were reported as parts per million (ppm) referred to the residual protium or carbon of the solvents; H in CDCl<sub>3</sub> (δ=7.26 ppm) and C in CDCl<sub>3</sub> (δ=77.0 ppm) or H in CD<sub>3</sub>CN (δ=1.94 ppm). Coupling constants are reported in Hertz (Hz).

The melting points were determined using a SGW X-4B microscopy melting point apparatus (Shanghai) and were uncorrected.

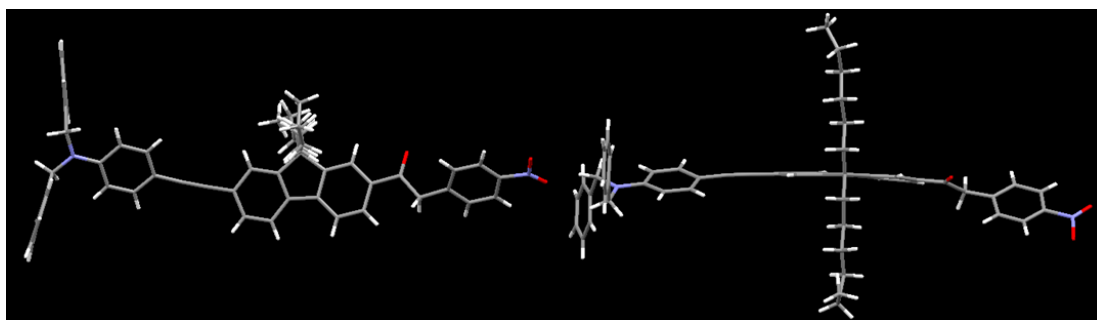
### 1.3 Synthetic route and crystal data of TM1

#### Synthetic route of TM1

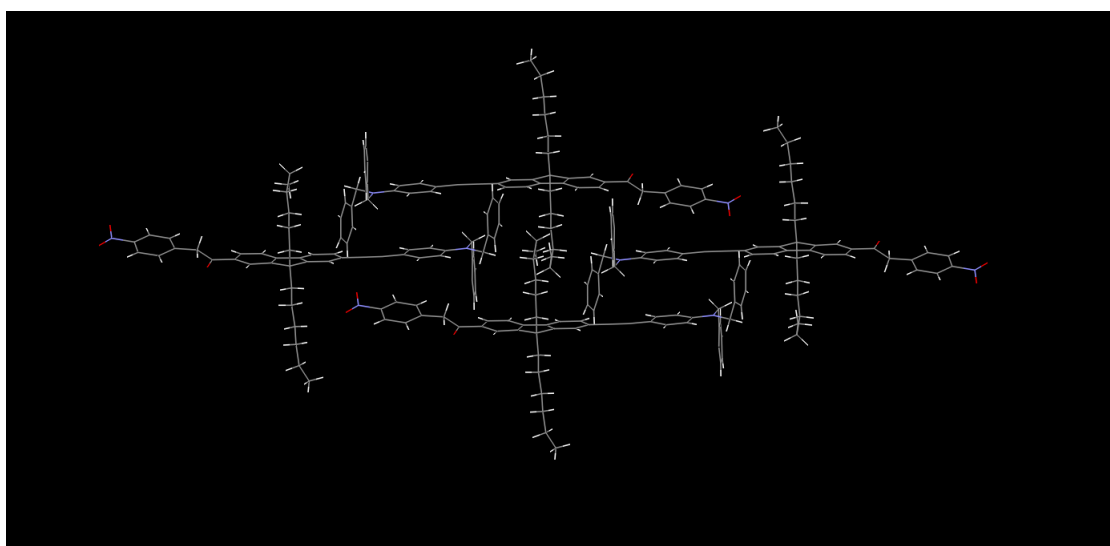


**Table S1.** Summary of crystal data and intensity collection parameters for **TM1**

<b>Compound</b>	<b>TM1</b>
Formula	C <sub>55</sub> H <sub>56</sub> N <sub>2</sub> O <sub>3</sub>
Formula mass	793.02
Space group	triclinic, P-1
a/Å	10.881(8)
b/Å	14.131(7)
c/Å	16.395(9)
α/°	69.740(17)
β/°	77.21(2)
γ/°	71.67(2)
V/ Å <sup>3</sup>	2227(2)
Z/mg.m <sup>-3</sup>	2, 1.183
F <sub>000</sub>	848
Theta range/°	3.05 to 27.48
No. of collected reflns	19109 / 9096
No. of unique reflns.(R <sub>int</sub> )	0.1007
Data/restrains/parameters	9096 / 6 / 543
R <sub>1</sub> ,wR <sub>2</sub> [obs I>2σ(I)]	R1 = 0.1624, wR2 = 0.3530
R <sub>1</sub> ,wR <sub>2</sub> (all data)	R1 = 0.3491, wR2 = 0.4566
Residual peak/hole e. Å <sup>-3</sup>	0.483 and -0.343
CCDC number	987215

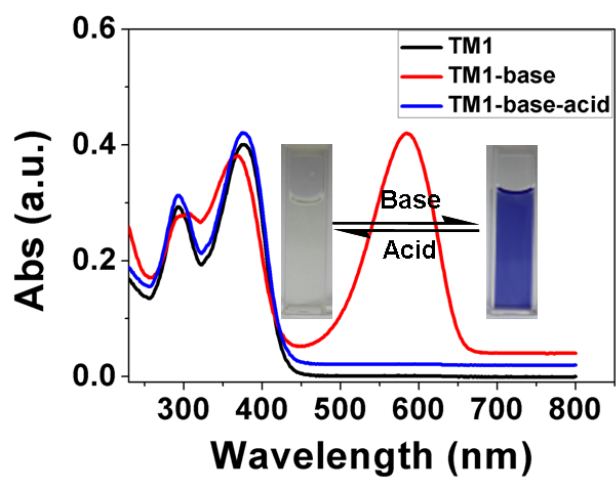


Crystal structure of **TM1**



The crystal packing of **TM1**

#### 1.4 The basochromic property of TM1



**Figure S1** (a) Absorption spectra of **TM1** ( $1.0 \times 10^{-5}$  M, black curve) in acetonitrile, treated with t-BuOK (20eq, red curve), and then neutralized with  $\text{CH}_3\text{COOH}$  (50eq, blue curve).

## 1.5 Synthetic route of TM2

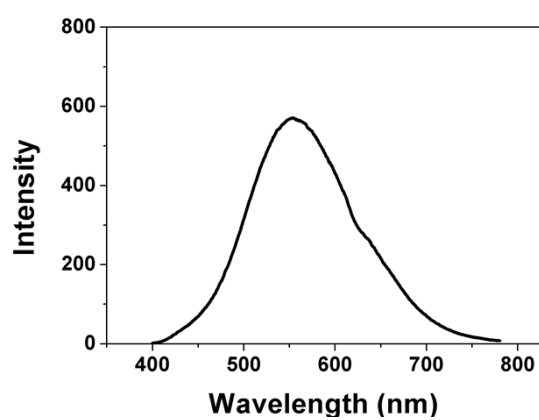
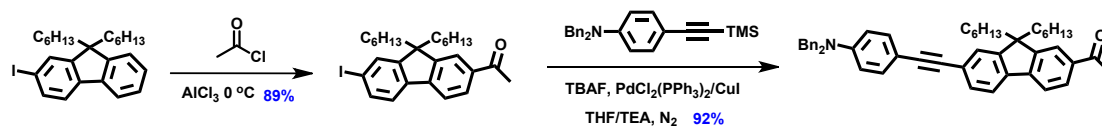


Figure S2 Fluorescence spectra of TM2 ( $1.0 \times 10^{-5}$  M) in acetonitrile.

## 1.6 Procedures of the testing solid paper for oxygen sensing

2.5 cm x 0.8 cm paper stripes were cut from filter paper, and then were immersed in acetonitrile solution of **TMI** ( $10^{-4}$  M) over night. The methyl ketone absorbed paper stripes were obtained when the solvent was evaporated at 40 °C.

Detection of oxygen with methyl ketone absorbed paper stripes in glove box:

The solution of t-BuOK in t-butanol was added dropwise to the paper stripes in glove box at 15 °C.

Detection of oxygen with methyl ketone absorbed paper stripes in air:

The solution of t-BuOK in t-butanol was added dropwise to the paper stripes in air at 15 °C.

Note:

1. Before adding the solution of t-BuOK, the methyl ketone absorbed paper stripes can be stored in any condition and are not sensitive to oxygen.
2. The solid paper stripes were obtained, due to that the melting point of t-butanol is higher than room temperature. In order to obtain the solid paper, the addition of the solution of t-BuOK to paper stripes should be at less than 25 °C. If the temperature is at more than 25 °C when the solution of t-BuOK was added dropwise to the paper stripes, the solution of t-butanol would flow out of stripes, and the paper stripes could not be used. Although this method is limited by temperature, this method is simple, rapid and accurate to achieve the solid testing paper. This method is good choice, when we should test the feasibility of our new sample used in paper.



## 1.7 Apparatus and procedure of degradation

Under oxygen atmosphere, 2-(4-nitrophenyl)-1-phenylethanone (**TM3**) (0.24g, 1 mmol) was dissolved in 20 ml acetonitrile solution containing t-BuOK (2.2 g, 40 mmol). After 4h, the reaction mixture was quenched with hydrochloric acid and extracted with EtOAc at 40 °C. Separated organic phase was dried over MgSO<sub>4</sub> and evaporation of the solution gave crude product which was purified by column chromatography (Hexane/EtOAc/CH<sub>3</sub>COOH=10:1:0.1~10:2:0.1) to afforded two white solid. The first production (less polar) is benzoic acid (0.07 g, 60%) and the second production (a large polar) is 4-nitro benzoic acid (0.12 g, 70%), whose structure are characterized by <sup>1</sup>H-NMR and MS.

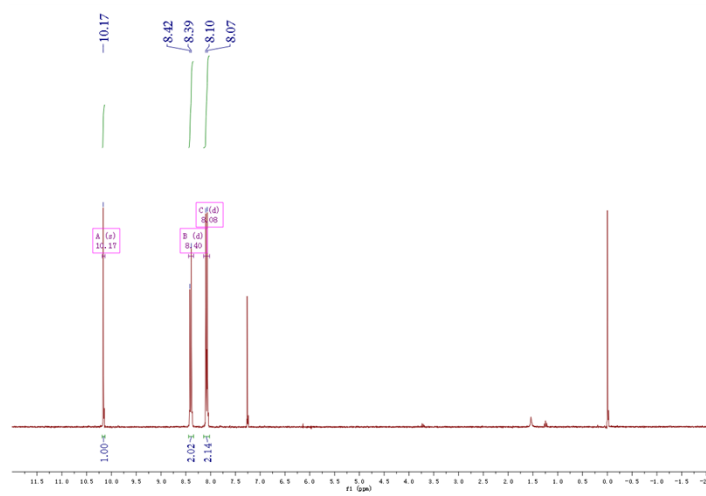
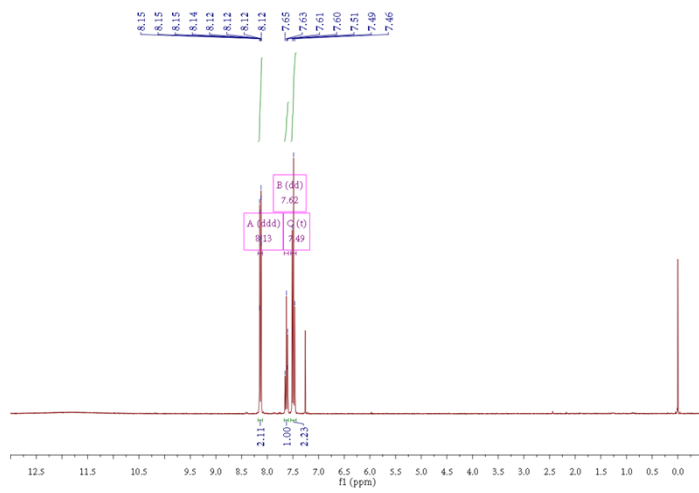
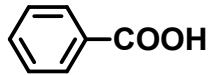
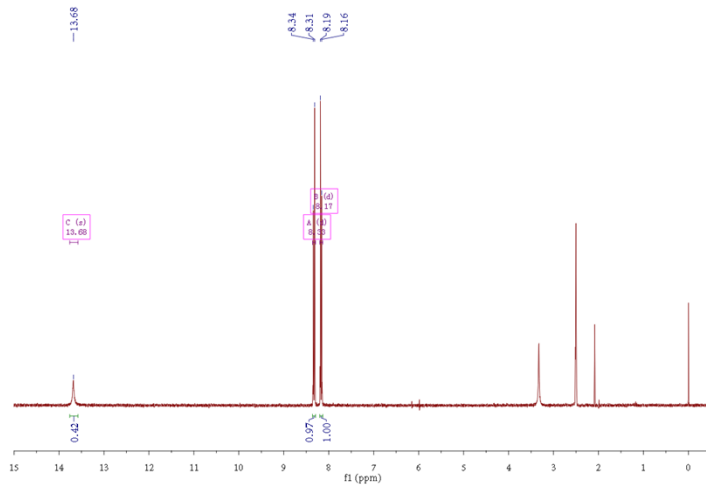
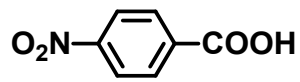
4-Nitrobenzaldehyde was obtained using the same procedure, after 5 min.

In glove box, 2-(4-nitrophenyl)-1-phenylethanone (**TM3**) (0.24g, 1 mmol) was dissolved in 20 ml acetonitrile solution containing t-BuOK (2.2 g, 40 mmol) at 25 °C, 40 °C and 80 °C. After 24h, no new product was observed.

Benzoic acid: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.13 (m, 2H), 7.62 (m, 1H), 7.49 (t, *J* = 7.8 Hz, 2H). LC-HRMS: *m/z* calc. [M-H]<sup>-</sup> for C<sub>7</sub>H<sub>5</sub>O<sub>2</sub> 121.0290, found 121.0289.

4-Nitro Benzoic acid: <sup>1</sup>H NMR (300 MHz, DMSO) δ 13.68 (s, 1H), 8.33 (d, *J* = 8.9 Hz, 2H), 8.17 (d, *J* = 8.9 Hz, 2H). LC-HRMS: *m/z* calc. [M-H]<sup>-</sup> for C<sub>7</sub>H<sub>4</sub>NO<sub>4</sub> 166.0140, found 166.0149.

4-Nitrobenzaldehyde: <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 10.17 (s, 1H), 8.40 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 8.9 Hz, 2H).



## 1.8 The enol-degradation mechanism of TM1

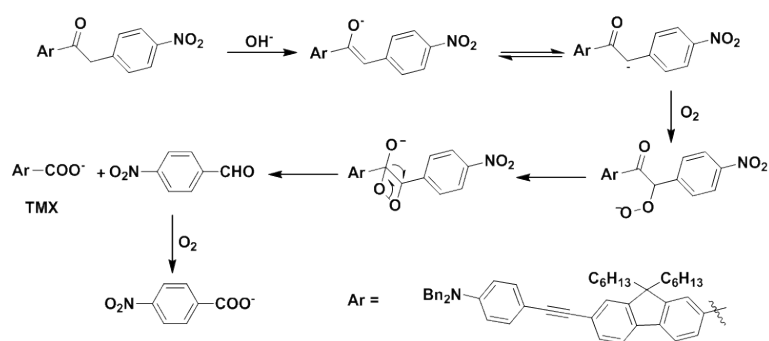


Figure S3. The enol-degradation mechanism of TM1.

## 1.9 High resolution mass spectrometry

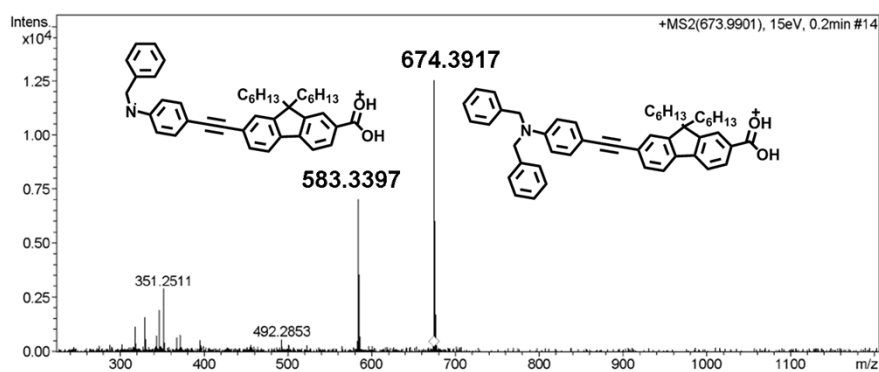
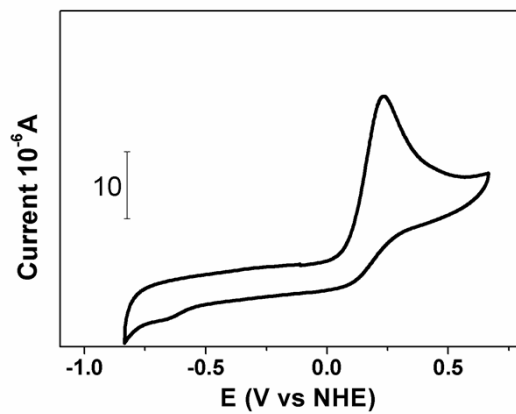


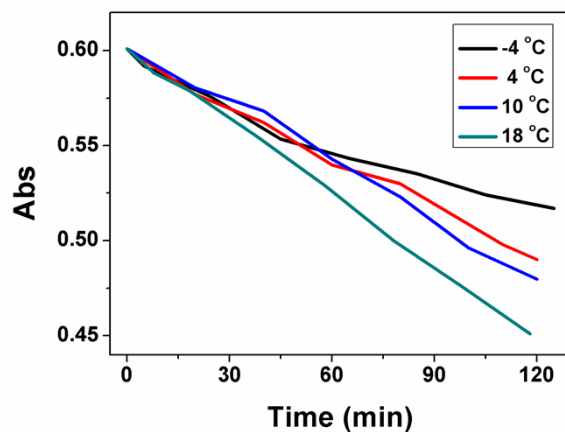
Figure S4. High resolution mass spectrometry of TM1 ( $1.0 \times 10^{-5}$  M) after treated with 30 eq *t*-BuOK in acetonitrile and then exposed to oxygen (100%) for 3h.

### 1.10 Cyclic voltammogram of TM1-enolate

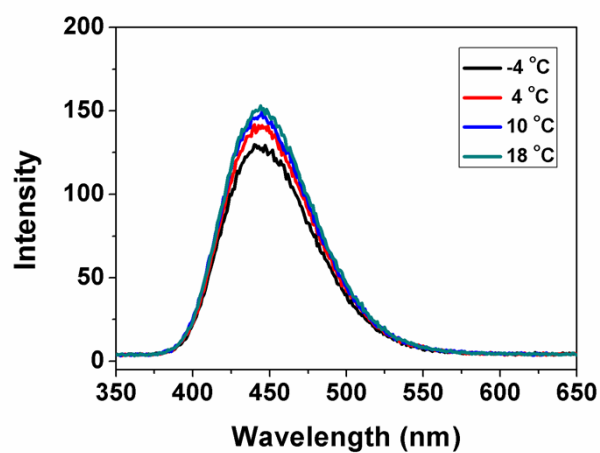


**Figure S5.** Cyclic voltammograms (CV) of **TM1-enolate** (TM1,  $1.0 \times 10^{-3}$  M, 30 eq t-BuOK, 25 °C) in acetonitrile. Scan rate: 100 mV/s.

## 1.11 The change of absorption and fluorescence at different temperature



**Figure S6a**, Absorbance (at 585 nm) changes of **TM1** ( $1.0 \times 10^{-5}$  M, acetonitrile solution, 30 eq t-BuOK, 21% O<sub>2</sub>) at four different temperatures (-4 °C, 4 °C, 10 °C, 18 °C).



**Figure S6b**. Fluorescence spectra of **TM1-enolate** solution ( $1.0 \times 10^{-5}$  M, acetonitrile solution, 30 eq t-BuOK) after exposed to oxygen for 1 min at four different temperatures (-4 °C, 4 °C, 10 °C, 18 °C).

## 1.12 The relationship between the oxygen concentration and the color disappearing time of TM1-enolate solution

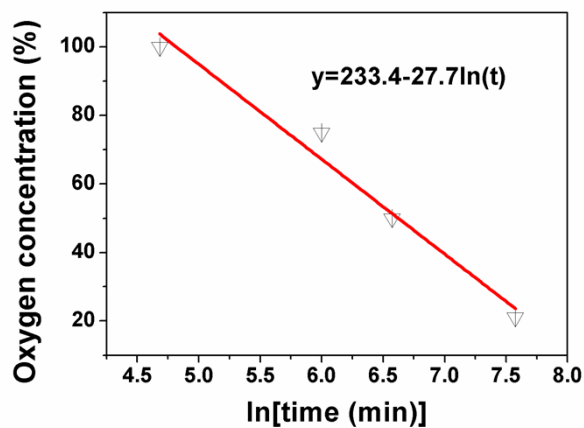


Figure S7, Linear plot of oxygen concentration versus the natural logarithm of the colour disappearing time of TM1-enolate solution ( $1.0 \times 10^{-5}$  M, acetonitrile solution, 30 eq t-BuOK).

## 1. 13 Colour disappearing time of the paper test strip with the different vacuity.

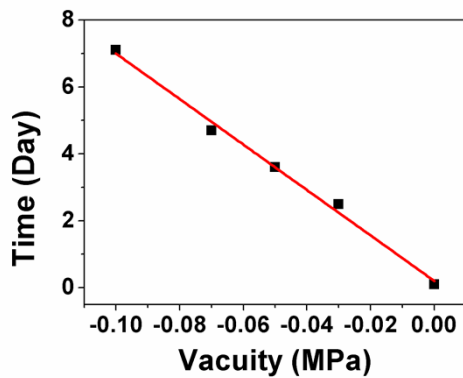
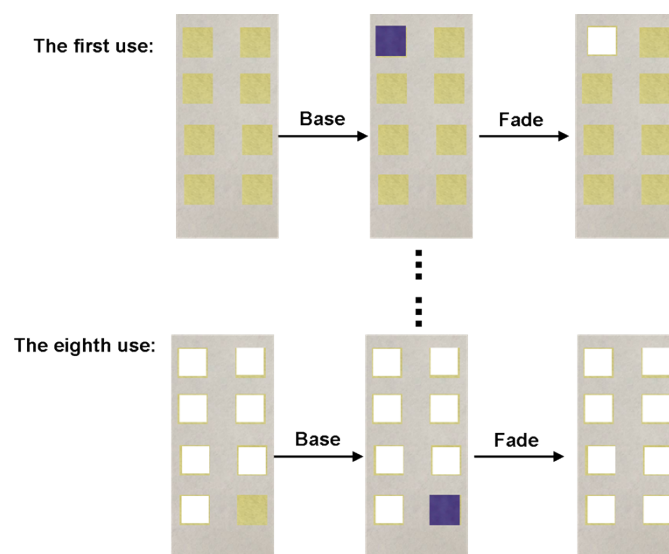


Figure S8. Linear plot of colour disappearing time of the paper test versus the vacuity.

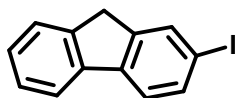
## 1.14 The structure of the reusable paper stripe



**Figure S9**, Illustration of a multiple-used sensor strip. Eight individually sealed independent sensing regions in this strip is for illustration only, and actual number of sensing units in the strip dependent on needs. The yellow color represents a valid region, and the white color represents a invalid region.

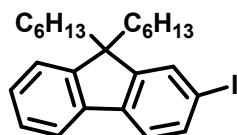
## 2. Characterization and Procedures of Synthesis

### 2-Iodofluorene (1)



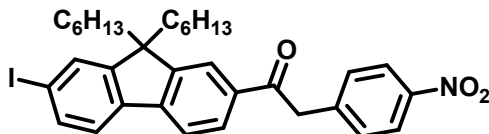
**Fluorene** (6.65 g, 40 mmol) was dissolved in a mixture of water (11.0 mL), acetic acid (54.5 mL), and sulfuric acid (1.6 mL) at 98°C, followed by cooling to 65°C. Then, iodine (3.38 g, 13 mmol) and periodic acid (1.52 g, 6.7 mmol) were added and stirred for 4 h. The precipitate was collected by filtration and washed with 2M NaHCO<sub>3</sub> aqueous solution and water. The crude product was recrystallized from hexane to give a white solid (7.04 g, 72%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.89 (s, 1H), 7.82 – 7.73 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.51 (dd, *J* = 10.6, 8.0 Hz, 2H), 7.44 – 7.28 (m, 2H), 3.87 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ = 145.37, 142.58, 141.21, 140.66, 135.64, 134.05, 127.23, 126.85, 124.92, 121.41, 119.92, 91.80, 36.55. LC-HRMS: *m/z* calc. for C<sub>13</sub>H<sub>10</sub>I 292.9822, found 292.9812. m.p.: 117.5-118.4°C.

### 2-Iodo-9,9-dihexylfluorene (2)



Under nitrogen atmosphere, **2-bromohexane** (1.87 mL, 13.2 mmol) was added dropwise to 20 mL of DMSO solution containing **2-iodofluorene** (1, 1.47 g, 5.05 mmol) and tetrabutylammonium iodide (0.055 g), after 2.2 mL of 50% aqueous NaOH was added. The reaction mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with ethyl acetate and quenched with diluted HCl, then was washed with dilute HCl and H<sub>2</sub>O (3 times). Separated organic phase was dried over MgSO<sub>4</sub> and evaporation of the solution gave crude product (2.0 g), which was prepared as next step reaction material.

### 1-(9,9-dihexyl-7-iodo-9H-fluoren-2-yl)-2-(4-nitrophenyl)ethanone (4)

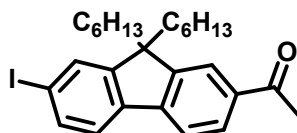


A solution of **2-(4-nitrophenyl)acetic acid** (1.81 g, 10 mmol) in nitrobenzene (30 mL) was added SOCl<sub>2</sub> (3 mL) at 65°C and stirred over night. Excess SOCl<sub>2</sub> was stripped off under vacuum at room temperature. The resulting solution was added **2-Iodo-9,9-dihexylfluorene** (2, 4.8 g) with ice bath under nitrogen atmosphere, then added AlCl<sub>3</sub> (2.05 g). After 4h, the reaction mixture was then poured onto ice, and washed with brine. The organic layer was distilled off nitrobenzene, after added 150 mL water. The resulting solid was dissolved by water and CH<sub>2</sub>Cl<sub>2</sub>. Separated organic phase was dried over MgSO<sub>4</sub> and evaporation of the solution gave crude product which was purified by column chromatography to afforded a pale yellow solid (4.17 g, 67%). <sup>1</sup>H NMR



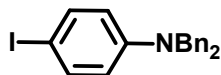
(300 MHz, CDCl<sub>3</sub>)  $\delta$  8.30 – 8.16 (m, 2H), 8.08 – 7.94 (m, 2H), 7.82 – 7.67 (m, 3H), 7.49 (dd,  $J$  = 10.2, 8.6 Hz, 3H), 4.47 (s, 2H), 2.11 – 1.84 (m, 4H), 1.21 – 0.93 (m, 12H), 0.76 (t,  $J$  = 7.0 Hz, 6H), 0.68 – 0.43 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  = 195.59, 154.12, 150.61, 146.85, 145.46, 142.26, 138.99, 136.17, 135.09, 132.24, 130.55, 128.13, 123.56, 122.59, 122.32, 119.79, 94.70, 55.48, 45.03, 39.90, 31.31, 29.40, 23.59, 22.41, 13.88. LC-HRMS:  $m/z$  calc. for C<sub>33</sub>H<sub>39</sub>INO<sub>3</sub> 624.1975, found 624.1977. m.p.: 77.0-77.5°C.

#### 1-(9,9-dihexyl-7-iodo-9H-fluoren-2-yl)ethanone (6)



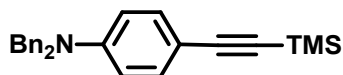
**2-Iodo-9,9-dihexylfluorene** (2, 0.515 g) was added dropwise to the solution of 6 ml dry dichloromethane, containing **Acetyl chloride** (0.1 ml) and AlCl<sub>3</sub> (0.2 g), in an ice bath under a nitrogen atmosphere. After stirring overnight the reaction mixture was quenched with hydrochloric acid on ice and extracted with dichloromethane. Separated organic phase was dried over MgSO<sub>4</sub> and evaporation of the solution gave crude product which was purified by column chromatography to afford a pale yellow oil (0.5g, 89%).

#### N,N-dibenzyl-4-iodobenzenamine (7)



To a vigorously stirred solution of **4-iodoaniline** (10.95 g, 50 mmol) and BnBr (13 ml, 110 mmol) in DMF (50 ml) was added K<sub>2</sub>CO<sub>3</sub> (12.5 g). The reaction was stirred for 18h at 120 °C. CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added and the reaction mixture was washed with H<sub>2</sub>O (3 times), the organic layer was dried and concentrated under reduced pressure. The crude residue was recrystallized from EtOH to yield the title compound as colorless needles (78%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (ddd,  $J$  = 31.4, 19.5, 8.3 Hz, 12H), 6.51 (d,  $J$  = 8.8 Hz, 2H), 4.62 (s, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  148.55, 137.85, 137.69, 128.70, 127.03, 126.45, 114.73, 90.08, 54.22. LC-HRMS:  $m/z$  calc. for C<sub>20</sub>H<sub>19</sub>IN 400.0562, found 400.0557. m.p.: 119.5-120.0°C.

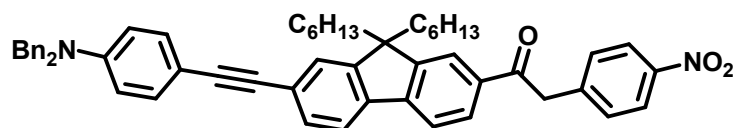
#### N,N-dibenzyl-4-(2-(trimethylsilyl)ethynyl)benzenamine (8)



To a stirred solution of **N,N-dibenzyl-4-iodobenzenamine** (7, 0.4 g), Pd[PPh<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub> (30 mg), CuI (20 mg), THF 5ml and Et<sub>3</sub>N 5 ml was added TMSA by syringe under nitrogen atmosphere. The mixture was stirred at room temperature over night. The residue was washed with sat. NH<sub>4</sub>Cl (aq.) and H<sub>2</sub>O, the organic layer was dried and concentrated under reduced pressure. The crude residue was recrystallized from EtOH to yield the title compound as brown needles (95%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.39 – 7.15 (m, 12H), 6.63 (d,  $J$  = 8.9 Hz, 2H), 4.65 (s, 4H), 0.21 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  149.34, 138.11, 133.53, 128.96, 127.31, 126.78, 112.18, 110.79, 106.50, 91.67, 54.23,

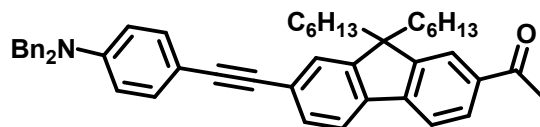
0.44. LC-HRMS: m/z calc. for C<sub>25</sub>H<sub>28</sub>NSi 370.1986, found 370.1980. m.p.: 128.5-128.8°C.

**1-(7-(2-(4-(dibutylamino)phenyl)ethynyl)-9,9-dihexyl-9H-fluoren-2-yl)-2-(4-nitrophenyl)ethanone (9)**



To a stirred solution of **N,N-dibenzyl-4-(2-(trimethylsilyl)ethynyl)benzenamine (8)**, 0.37 g) Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (30 mg), CuI (20 mg), THF (15 mL) and Et<sub>3</sub>N (15 mL) at room temperature was added TBAF solution (1M in THF, 3.0 ml) and the reaction was stirred for 1h. Then, the mixture was added **1-(9,9-dihexyl-7-iodo-9H-fluoren-2-yl)-2-(4-nitrophenyl)ethanone (4)**, 0.84 g) and stirred over night. The residue was washed with sat. NH<sub>4</sub>Cl (aq.) and H<sub>2</sub>O. Separated organic phase was dried over MgSO<sub>4</sub> and evaporation of the solution gave crude product which was purified by column chromatography to afforded a pale yellow solid ( 0.71 g, 90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 8.7 Hz, 2H), 8.07 – 7.91 (m, 2H), 7.72 (dd, *J* = 15.4, 8.1 Hz, 2H), 7.48 (dd, *J* = 8.2, 5.1 Hz, 4H), 7.43 – 7.17 (m, 12H), 6.71 (d, *J* = 8.8 Hz, 2H), 4.70 (s, 4H), 4.47 (s, 2H), 1.99 (t, *J* = 8.7 Hz, 4H), 1.22 – 0.90 (m, 12H), 0.75 (t, *J* = 7.0 Hz, 6H), 0.69 – 0.41 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 196.01, 152.27, 151.81, 149.40, 147.26, 146.42, 142.70, 139.09, 138.09, 134.97, 133.20, 130.91, 130.84, 129.02, 128.47, 127.37, 126.79, 126.03, 124.53, 123.97, 122.93, 120.99, 120.11, 112.44, 110.71, 91.90, 88.55, 55.65, 54.30, 45.43, 40.47, 31.76, 29.88, 24.00, 22.83, 14.25. LC-HRMS: m/z calc. for C<sub>55</sub>H<sub>57</sub>N<sub>2</sub>O<sub>3</sub> 793.4364, found 793.4357. m.p.: 135.3-136.0°C.

**1-(7-((4-(dibenzylamino)phenyl)ethynyl)-9,9-dihexyl-9H-fluoren-2-yl)ethanone (10)**



To a solution of **N,N-dibenzyl-4-(2-(trimethylsilyl)ethynyl)benzenamine (8)** (0.37 g) in THF at room temperature was added TBAF solution (1M in THF, 3.0 ml) and the reaction was stirred for 1h. The mixture was diluted with sat. NH<sub>4</sub>Cl (aq. 10 mL), and extracted with EtOAc. Separated organic phase was dried over MgSO<sub>4</sub> and evaporation of the solution gave a yellow solid, which was dissolved in a mixture of Pd[PPh<sub>3</sub>]<sub>2</sub>Cl<sub>2</sub> (30 mg), CuI (20 mg), THF (15 mL) and Et<sub>3</sub>N (15 mL) at room temperature. The mixture was added **1-(9,9-dihexyl-7-iodo-9H-fluoren-2-yl)ethanone (6)**, 0.5 g) and stirred over night. The residue was washed with sat. NH<sub>4</sub>Cl (aq.) and H<sub>2</sub>O. Separated organic phase was dried over MgSO<sub>4</sub> and evaporation of the solution gave crude product which was purified by column chromatography to afforded a pale yellow solid (0.62 g, 92%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 8.08 – 7.91 (m, 2H), 7.83 – 7.65 (m, 2H), 7.64 – 7.46 (m, 2H), 7.46 – 7.23 (m, 10H), 6.71 (d, *J* = 8.9 Hz, 2H), 4.69 (s, 4H), 2.66 (s, 3H), 2.14 – 1.88 (m, 4H), 1.19 – 0.92 (m, 12H), 0.75 (t, *J* = 7.0 Hz, 6H), 0.57 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 197.76, 151.92, 151.24, 149.08, 145.41, 139.11, 137.84, 135.93, 132.85, 130.44, 128.65, 128.13, 127.02, 126.54, 125.72, 123.92, 122.33, 120.45, 119.48, 112.24, 110.67, 91.30, 88.32, 55.29, 54.05, 40.12, 31.38, 29.52, 26.64, 23.66, 22.44, 13.84. LC-HRMS: m/z calc. for C<sub>33</sub>H<sub>54</sub>NO<sub>3</sub> 671.4127, found 671.4119. m.p.: 137.0-137.8°C.

### 3. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR

