Electronic Supplementary Material (ESI) for Analyst.

# Supporting Information

# A renewable test strip combined with solid-state ratiometric fluorescence emission spectra for highly selective and fast determination of hydrazine gas

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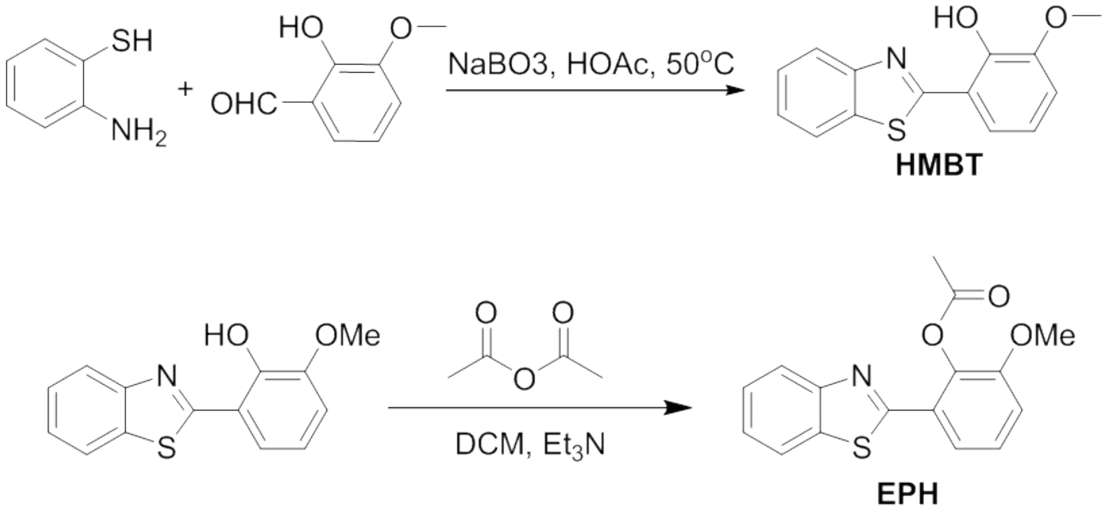
# 1. Synthetic experiment

### Materials and methods

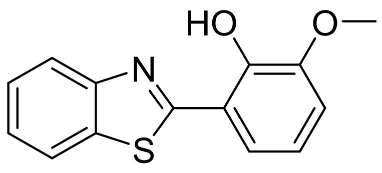
All chemical reagents were commercially available and used directly without any further purified procedures in our experiments. Column chromatography was performed by using silica gel (Haiyang, Qingdao) 300-400 mesh. Thin-layer chromatography (TLC) was performed on silica gel plates and visualized by handheld ultraviolet (UV)-lamp. UV absorption spectra was obtained with Hitachi U-3900 UV/vis spectrophotometer in quartz cuvette $(1cm \times 1cm)$. Fluorescence spectrum was recorded with Hitachi F-7000 fluorescence spectrometer. Excitation and emission slit widths were modified to adjust the fluorescence intensity to suitable range. Bruker AM-400 spectrometer was employed for $^{1}H$ and $^{13}C$ NMR (in deuterochloroform, $Me_4Si$ as internal standard). Measurement of the mass spectra was performed by using HP 1100 LC-MS spectrometer. The pH of solution was monitored by PHB-4 (INESA Scientific Instrument Co., Ltd.).

### Synthetic method



**Scheme S1.** Synthetic procedure for preparation of target probe **EPH**.

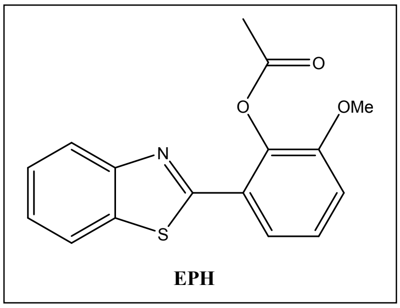
### Synthesis of HMBT (Benzothiazole Derivatives)



**HMBT**

**HMBT** was synthesized according to the similar procedures.[1] O-Aminothiophenol (1.25 g, 10 mmol), 3-methoxy salicylaldehyde (1.672 g, 11 mmol), sodium borate (1.636 g, 20 mmol) and glacial acetic acid (50 mL) were added to a 100 mL single-necked flask in sequence, then the reaction mixture was heated to 50 °C and maintained this temperature for 5 hours. After that reaction time, the solution was neutralized with 30% NaOH solution after being poured into ice water when it was still hot. A large amount of light gray solid was precipitated in this process. Filtering and washing with water to provide a light brown solid **HMBT** in a yield of 56%.$^1$H-NMR (DMSO-$d_6$, 400 MHz) δ 11.22 (s, 1H), 8.15 (d, *J*=8.0 Hz, 1H), 8.07 (d, *J*= 8.0 Hz, 1H), 7.74 (d, *J*= 8.0 Hz, 1H), 7.55 (t, *J*= 7.6 Hz, 1H ), 7.46 (t, *J*= 7.6 Hz 1H ), 7.16 (d, *J*= 7.2 Hz, 1H), 6.98 (t, *J*= 8.0 Hz， 1H), 3.88 (s, 3H); $^{13}$C-NMR (DMSO-$d_6$, 100 MHz) δ 165.96, 151.82, 149.01, 146.82, 134.64, 126.98, 125.64, 122.58, 122.50, 120.29, 119.94, 118.93, 114.68, 56.55.

**Synthesis of 2- (benzothiazole) -6- methoxy phenoxy acetate (EPH)**



**EPH**

**EPH** was synthesized according to the following method. **HMBT** (1.285 g, 5 mmol) was dissolved in dichloromethane in a 25 mL single-necked flask, where triethylamine (1.01 g, 10 mmol) was added and the reaction was stirred under ambient temperature. Then, acetic anhydride (0.561 g, 5.5 mmol) was added dropwise until the TLC indicates the starting materials **HMBT** disappeared. The reaction mixture was dried by rotary evaporator to provide the crude products, which was further purified by column chromatography with eluent of PE/EA (v/v = 20/1). The pure product **EPH** was 0.897 g (60%yield).$^1$H-NMR (CDCl$_3$, 400 MHz) δ 8.10 (d, *J*=8.0 Hz, 1H), 7.92 (d, *J*= 8.0 Hz, 1H), 7.50 (t, *J*= 7.2 Hz, 1H), 7.40 (t, *J*= 7.2 Hz, 1H ), 7.34 (t, *J*= 8.0 Hz, 1H ), 7.10 (t, *J*= 7.6Hz， 1H), 3.89(s, 3H), 2.48（s, 3H）；$^{13}$C-NMR (CDCl$_3$, 100 MHz) δ 168.41, 162.28, 152.84, 152.00, 138.20, 135.50, 127.40, 126.70, 126.28, 125.35, 123.42, 121.39, 121.31, 114.12, 56.30, 21.21; HRMS (ES$^+$): calc. for $C_{16}H_{13}NO_3S$ $[M+Na]^+$ 322.3440, found 322.0518.

## 2. Preparation of EPH-coated test strips [2,3]

A total of 5.967 mg (2 mM) of **EPH** was dissolved in acetonitrile. A filter paper was cut into a slip of paper with the size of 1 x 4 cm, which was immersed into the solution for 30 min to ensure all **EPH** was coated onto the surface of this slip of paper. After dried in air, the test strips could be used for $N_2H_4$ gas detection.

## 3. Solid-state fluorescence emission test by using EPH-coated test strips

Solid-state fluorescence emission measurements were determined on a Hitachi Fluorescence Spectrophotometer F-7000. Accessories include a solid sample cuvette (powder box, quartz plate) and working stage. Solid-state fluorescence emission spectra were obtained using excitation wavelength $\lambda_{ex}$=310 nm; scan from 335 nm to 600 nm; slit width (ex / em):5 nm /5 nm; PMT voltage: 350 V. software: FL Solutions, test method for solid samples is the similar as the approach for liquid samples.

## 4. pH titration for EPH

Stock solution of **EPH** (1.0 mM) was prepared in DMSO. The solution for spectroscopic measurement was obtained by diluting the stock solution to 10 μM in water (include 1 mM CTAB) medium. In the pH titration experiments using a 1 cm×1 cm optical path length cell（3 mL volume）, and slight pH variations of the solution were adjusted with minimum volumes of HCl (1 M) and NaOH (1 M) solution from 3.6 to 10.2. All spectroscopic experiments were carried out at room temperature (approximate 28 $^{o}$C).

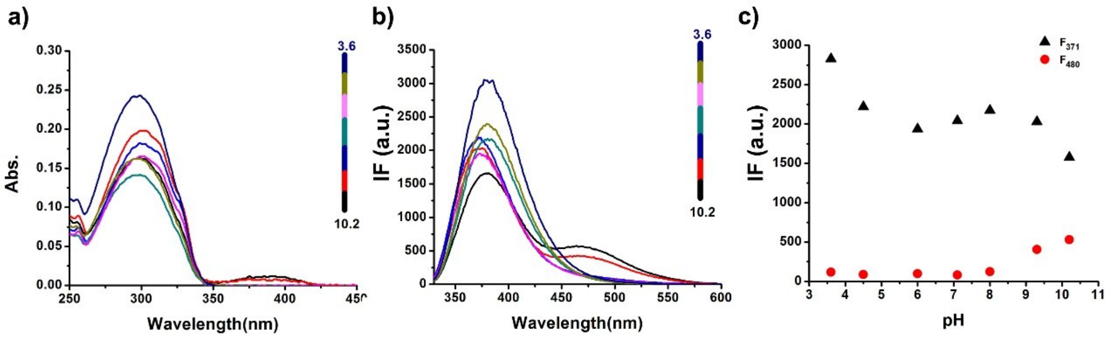


**Figure S1.** (a) pH effect on the absorption of **EPH** (10 μM). (b) pH effect on the fluorescence intensity of **EPH**, emission signal was collected from 330 nm to 600 nm. (c) pH effect on the fluorescence intensity of **EPH** at 371 nm (in black) and 480 nm (in red) in water. $\lambda_{ex}$=330 nm.

## 5.1 $^1$H-NMR spectra of EPH, EPH treated with $N_2H_4$, EPH treated with $NH_3$, and HMBT in 0.5 mL DMSO-$d_6$.

$^1$H-NMR titration was conducted in DMSO-$d_6$ solution of **EPH**. Initially, **EPH** was dissolved in DMSO-$d_6$ and the $^1$H-NMR spectrum was recorded. Then a drop of $N_2H_4{\cdot}H_2O$ (80%) and $NH_3{\cdot}H_2O$ was added to the DMSO-$d_6$ solution of **EPH**, respectively. Herein, the incubation time of $N_2H_4{\cdot}H_2O$ (80%) and $NH_3{\cdot}H_2O$ with **EPH** in DMSO-$d_6$ is nearly to 90 min. And the $^1$H-NMR spectra were also recorded. Finally, **HMBT** was dissolved in DMSO-$d_6$ and the $^1$H-NMR spectrum was recorded.

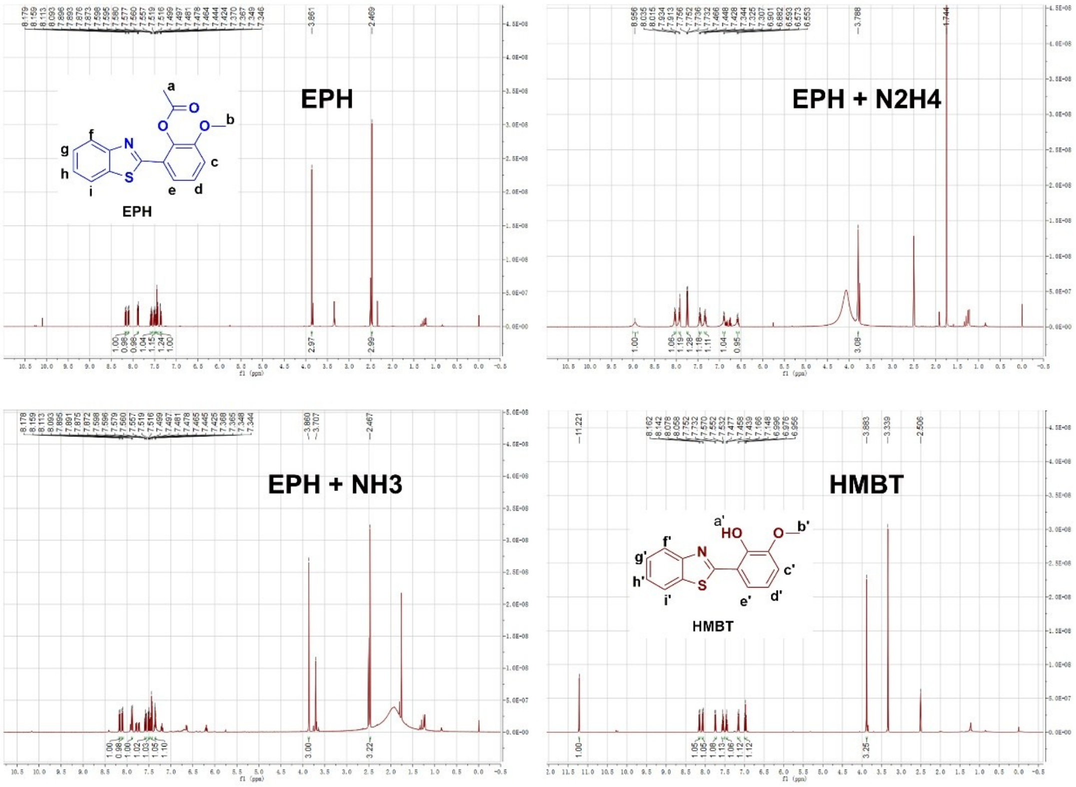


**Figure S2**. $^1$H-NMR spectra of **EPH**, **EPH** treated $N_2H_4$, **EPH** treated with $NH_3$, and **HMBT** in 0.5 mL DMSO-$d_6$.

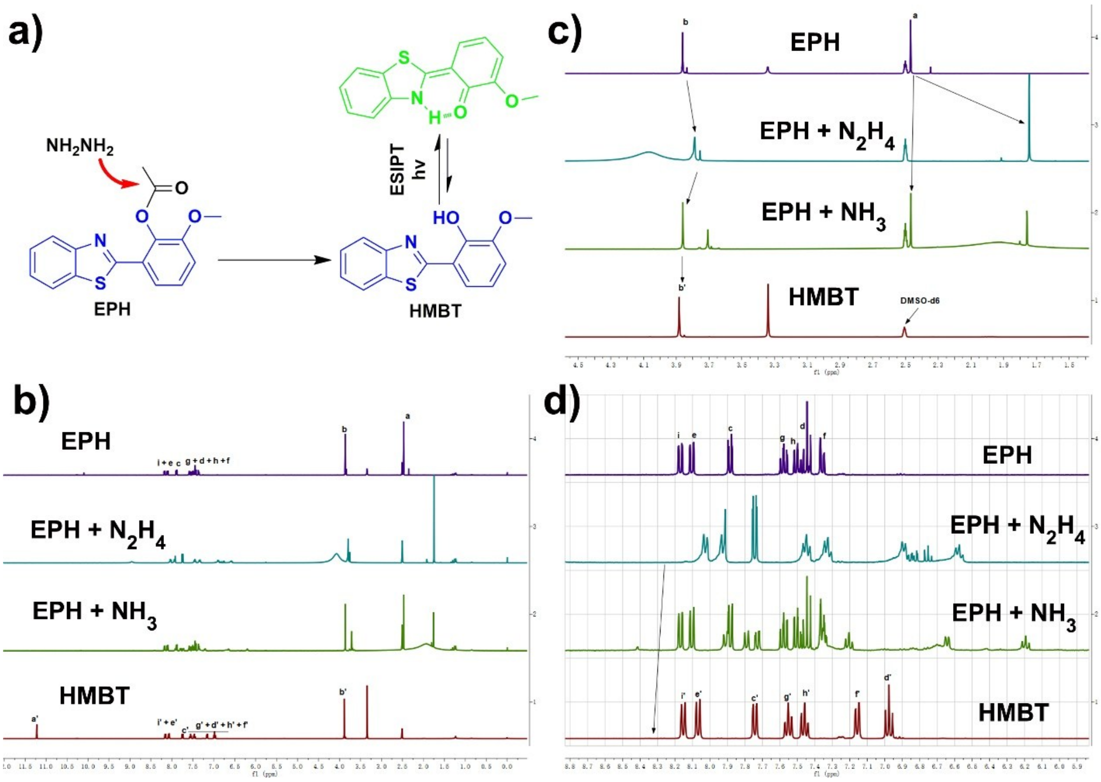


**Figure S3**. (a) Deduced mechanism of **EPH** for selective detection of N2H4. (b) $^1$H-NMR spectra of **EPH**, **EPH** treated $N_2H_4$, **EPH** treated with $NH_3$, and **HMBT** in 0.5 mL DMSO-$d_6$. (c) The enlarged $^1$H-NMR spectra from 1.5-4.5 ppm. (d) The enlarged $^1$H-NMR spectra from 5.9-8.8 ppm.

### 5.2. Deduced mechanism of EPH for detection of $N_2H_4$ by ESI-MS

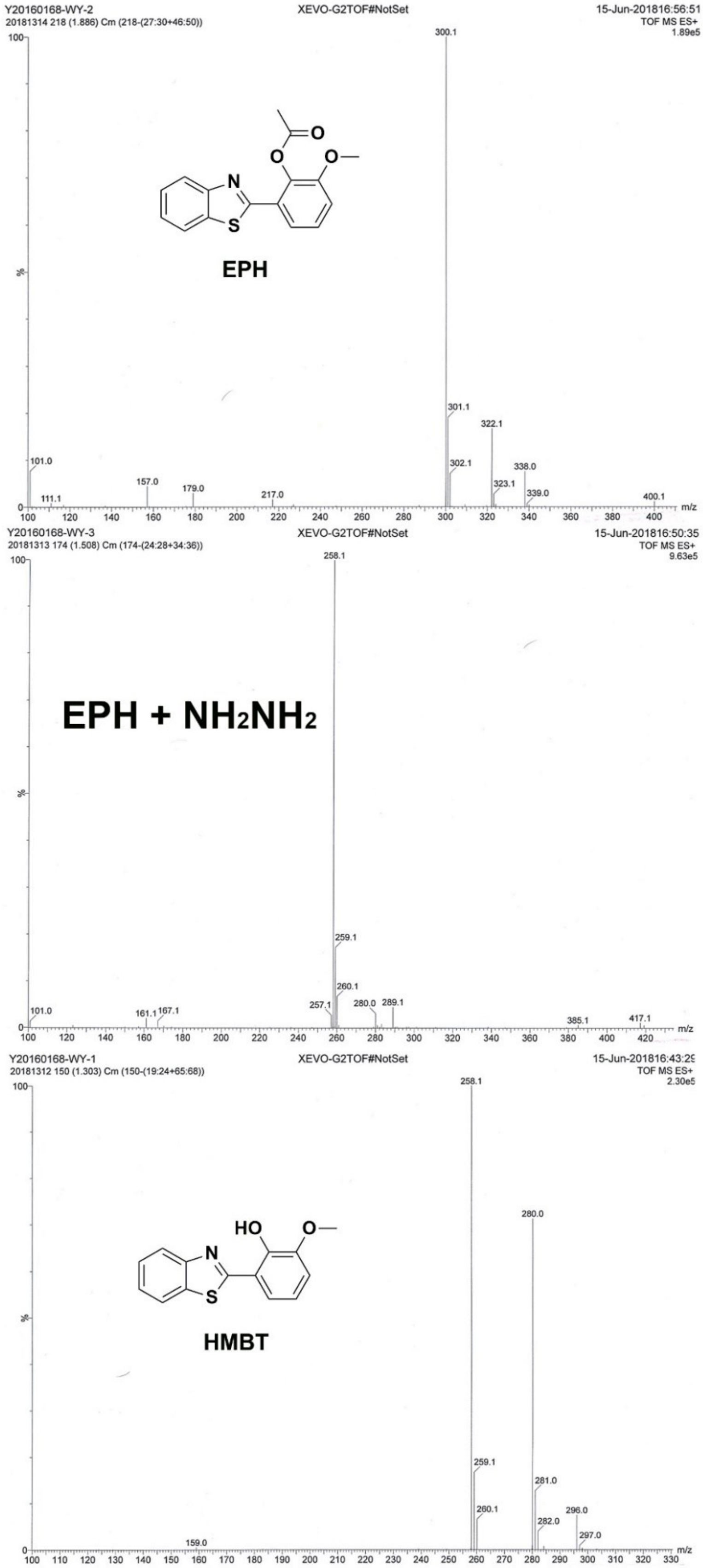


**Figure S4**. Deduced mechanism of **EPH** for detection of $N_2H_4$ by ESI-MS.

## 6. Detection of $N_2H_4$ gas with test strips

The **EPH**-coated tests were covered on the top of the screw bottles (10 mL) containing different concentrations of hydrazine aqueous solution (1 mL, concentrations: blank, 0.1%, 0.5%, 1%, 5%, 10%, 20%, 30%, 40% and 50%) for 30min at room temperature. Fluorescence color changes of the test strips can be observed under the a 365nm handheld UV lamp irradiation. The solid-state fluorescence spectra were obtained using the reflect fluorescence from scanning the test strips on a Hitachi Fluorescence Spectrophotometer F-7000. Accessories include a solid sample cuvette (powder box, quartz plate) and working stage.

For the time dependent assay with test strips, the **EPH**-coated tests were covered on the top of the screw bottles (10 mL) containing 80% of hydrazine aqueous solution (1 mL) for increasing time at room temperature. Then, the fluorescence color changes of the test strips can be observed under the a 365nm handheld UV lamp irradiation. The solid-state fluorescence spectra were obtained using the reflect fluorescence from scanning the test strips on a Hitachi Fluorescence Spectrophotometer F-7000. Accessories include a solid sample cuvette (powder box, quartz plate) and working stage.

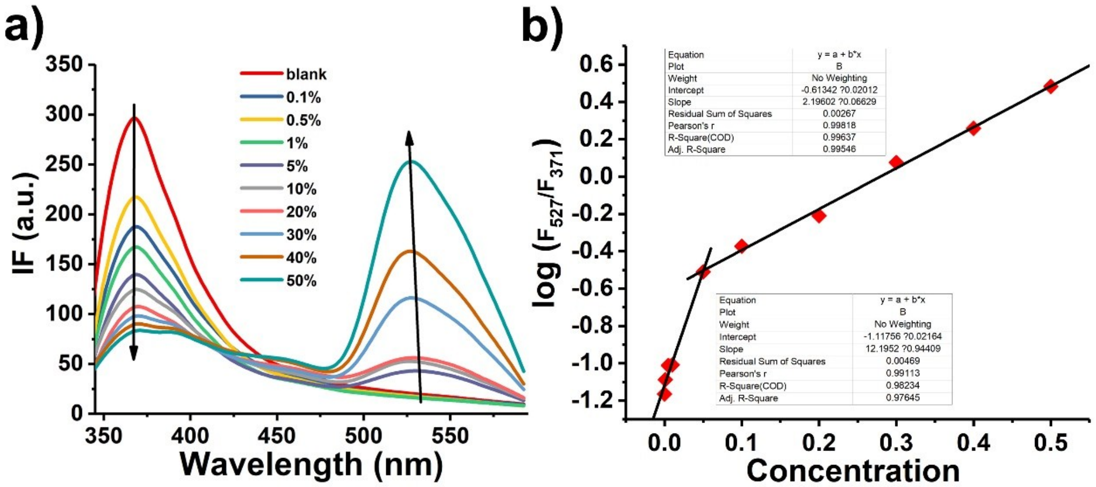


**Figure S5.** (a) The solid-state fluorescence spectra change of **EPH**-coated test strips after exposure to different concentration of $N_2H_4$ gas. The solid-state fluorescence spectra were obtained using the reflect fluorescence for the solid test strips. $\lambda_{ex}$= 310 nm. (b) The linear relationship between the concentration of $N_2H_4$ gas and solid-state fluorescence intensity ratio changes by using the linear fitting in origin software. The solid-state fluorescence intensity ratio changes were based on the peak heights of the maxima solid-state fluorescence emission intensity of the spectra at 371 and 527 nm, respectively, against the increasing concentration of $N_2H_4$ gas. Note: Herein the percentage of $N_2H_4$ gas is the aqueous hydrazine concentration, which is taken as the resource of $N_2H_4$ gas. The values of the solid-state fluorescence intensity ratio were treated with $\log_{10}(x)$, which functions as log ($F_{527}/F_{371}$).

## 7. Selective detection of N2H4 gas over other interference gases with test strips

In this assay, $CO_2$ was commercially available; $NO_2$ was obtained through the reaction between concentrated (about 65 percent) nitric acid and copper at room temperature; $SO_2$ was obtained through the reaction between concentrated sulfuric acid and sodium sulfite at room temperature; $NH_3$ was obtained through heating the $NH_3{\cdot}H_2O$ (ammonia solution 28-30%) and 80% of hydrazine aqueous solution (80% $N_2H_4{\cdot}H_2O$) was taken as the source of the $N_2H_4$ gas. All the gas should be collected in airtight jars, respectively. Then, the test strips were placed in airtight jars for 30mins at room temperature under the atmosphere of different kinds of gas. Fluorescence color response of the test strips can be observed under the 365nm handheld UV lamp irradiation, and the solid-state fluorescence spectra were obtained using the reflect fluorescence from scanning the test strips on a Hitachi Fluorescence Spectrophotometer F-7000. Accessories include a solid sample cuvette (powder box, quartz plate) and working stage. After this process, these test strips were exposed to the $N_2H_4$ gas for another 30mins at room temperature. Finally, the fluorescence color changes were also observed under the 365nm handheld UV lamp irradiation, and the solid-state fluorescence spectra were obtained using the reflect fluorescence from scanning the test strips on a Hitachi Fluorescence Spectrophotometer F-7000. Accessories include a solid sample cuvette (powder box, quartz plate) and working stage.

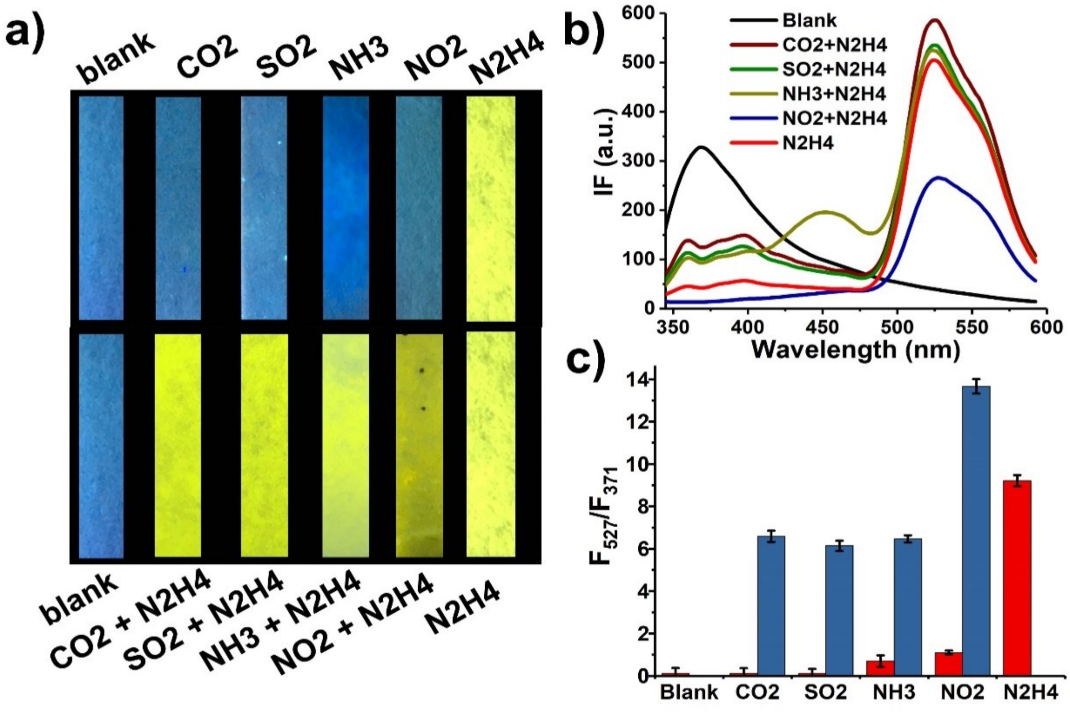


**Figure S6.** (a) up: The fluorescence color changes of **EPH**-coated test strips after exposure to different gases including $CO_2$, $SO_2$, $NH_3$, $NO_2$ and $N_2H_4$, respectively, under a hand-held UV lamp irradiation (365 nm). bottom: The fluorescence color changes of **EPH**-coated test strips exposure to different gases and then further treated with $N_2H_4$ gas (bottom). (b) Solid-state fluorescence changes of **EPH-coated** test strips after first exposure to different gases and then these test strips were further treated with $N_2H_4$ gas. The fluorescence spectra were obtained using the reflect fluorescence for the solid test strips. $\lambda_{ex}$= 310 nm. (c) The solid-state fluorescence intensity ratio changes with respect to different gases.

## 8. NMR spectrum and HRMS

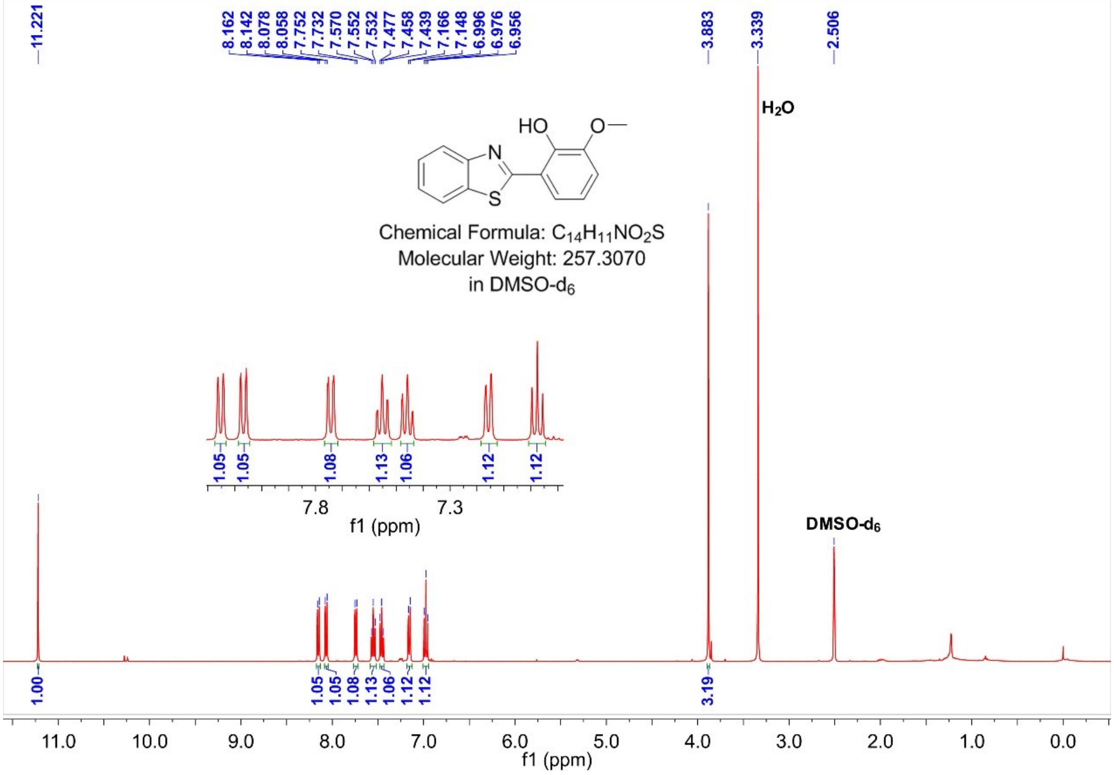


**Figure S7.** $^{1}$H NMR spectrum of probe **HMBT**.

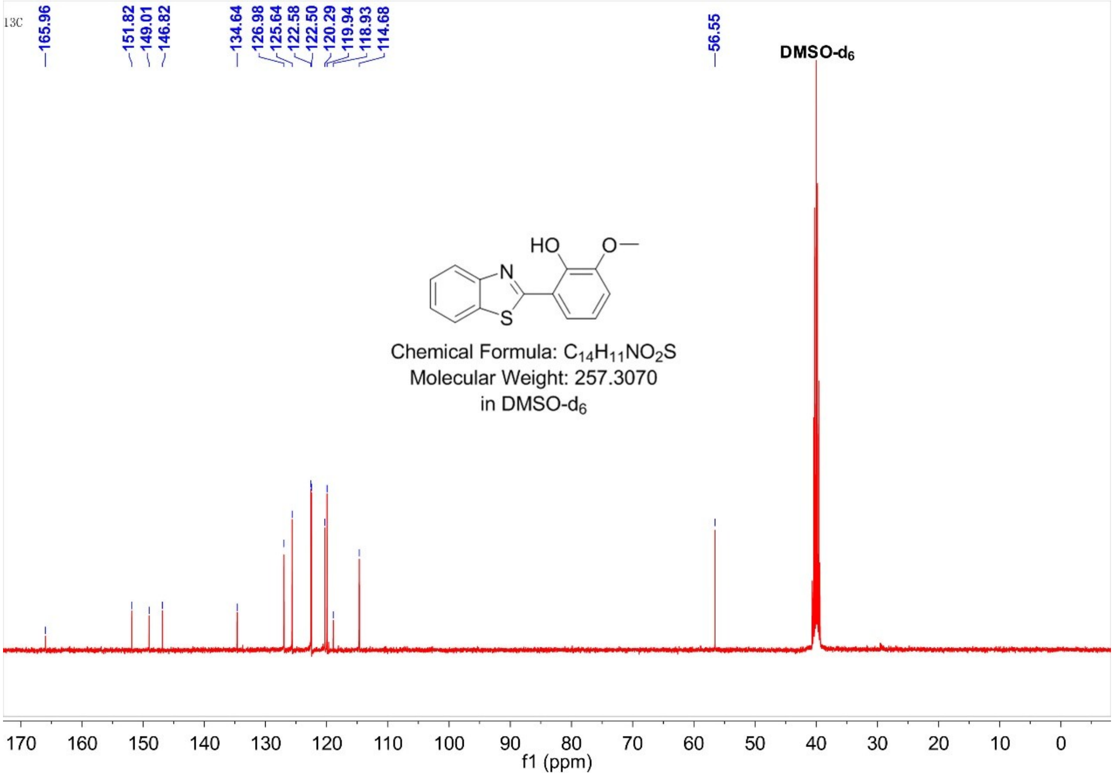


**Figure S8.** $^{13}$C NMR spectrum of probe **HMBT**.

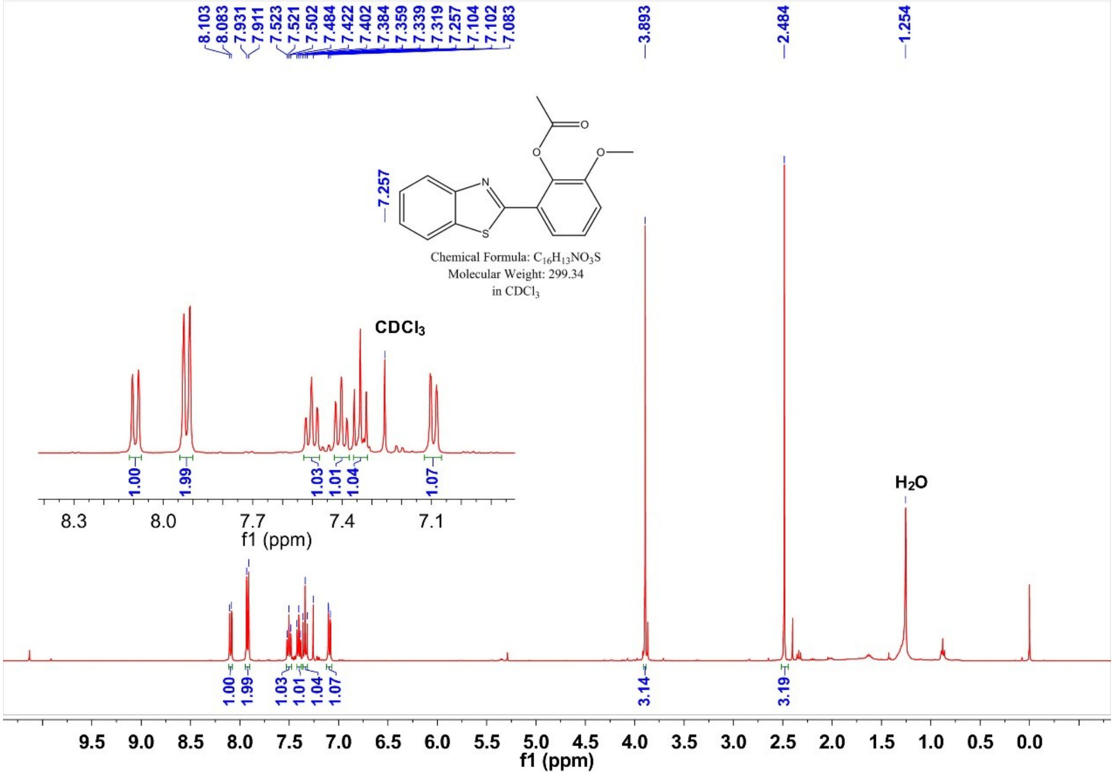


**Figure S9.** $^1$H NMR spectrum of probe **EPH**.

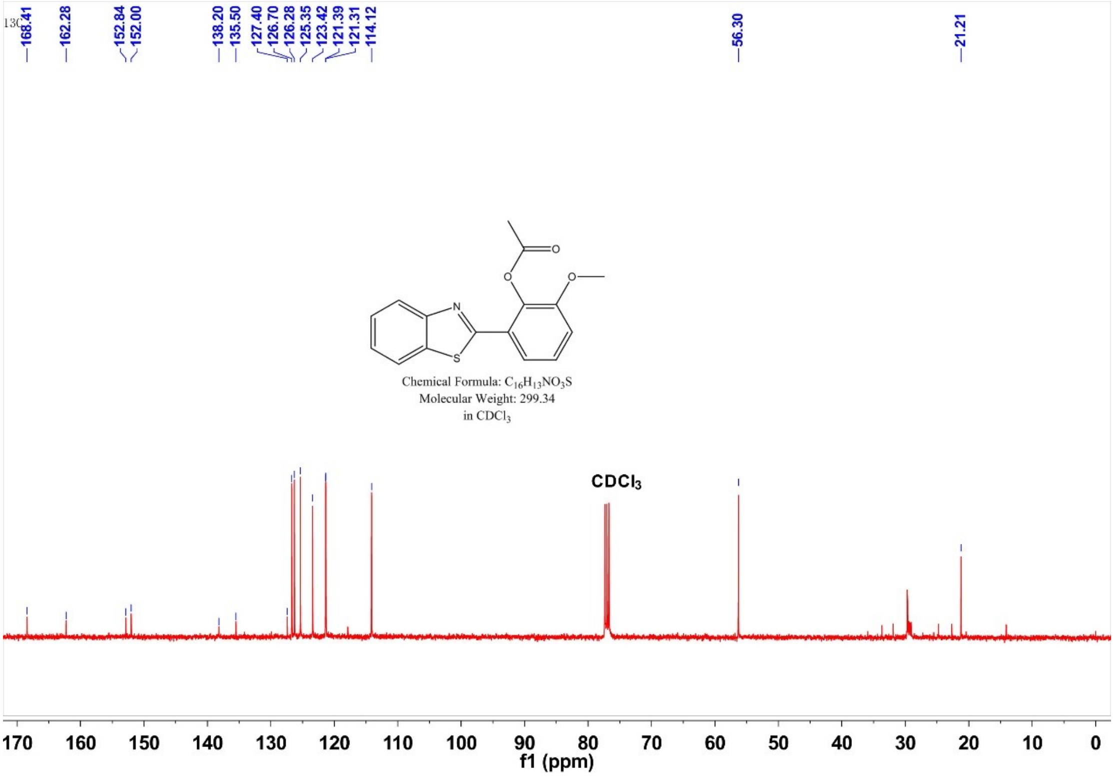
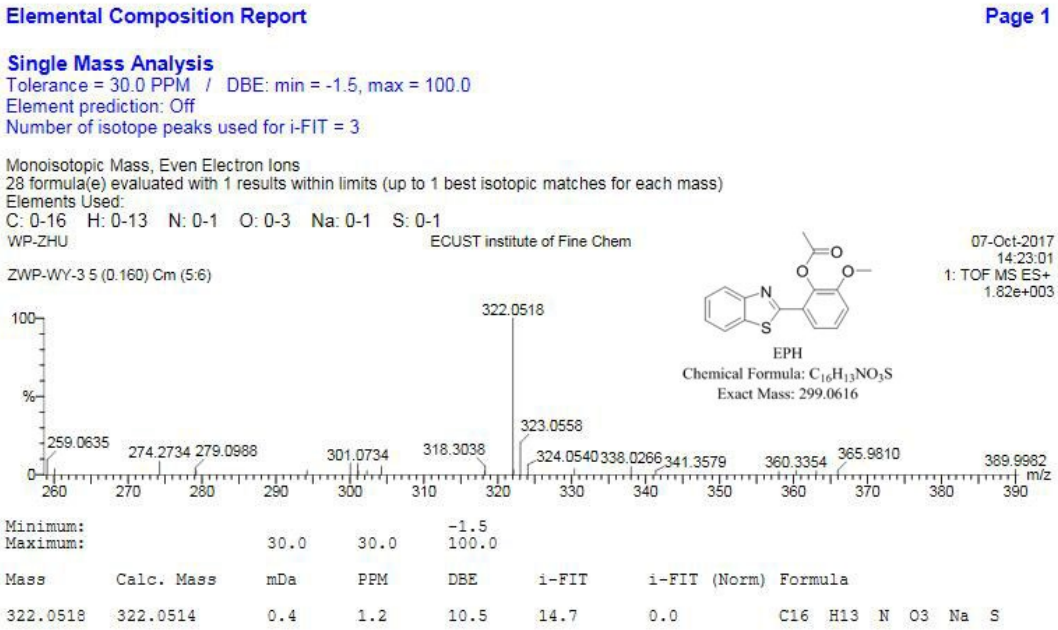


**Figure S10.** $^{13}$C NMR spectrum of probe **EPH**.



**Elemental Composition Report** Page 1

**Single Mass Analysis**
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
28 formula(e) evaluated with 1 results within limits (up to 1 best isotopic matches for each mass)
Elements Used:
C: 0-16 H: 0-13 N: 0-1 O: 0-3 Na: 0-1 S: 0-1

WP-ZHU
ECUST institute of Fine Chem
07-Oct-2017
14:23:01
ZWP-WY-3 5 (0.160) Cm (5:6)
1: TOF MS ES+
1.82e+003

EPH
Chemical Formula: $C_{16}H_{13}NO_3S$
Exact Mass: 299.0616

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Minimum:                                  -1.5
Maximum:                 30.0      30.0   100.0

Mass      Calc. Mass     mDa       PPM    DBE       i-FIT      i-FIT (Norm) Formula

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```

**Figure S11.** HRMS spectrum of probe **EPH**.

## 9. References

*1.* Z. Xu, L. Xu, J. Zhou, Y. Xu, W. Zhu, X. Qian, *Chem. Commun.,* 2012, 48, 10871-10873.

2. L. Chen, D.Wu, J. Kim, J. Yoon, *Anal. Chem.,* 2017, 89, 12596-2601.

3. X. Zhou, Y. Zeng, L. Chen, X. Wu, J. Yoon, *Angew.Chem. Int.Ed.,* 2016, 55 ,4729-4733.