Electronic Supplementary Information

A ratiomeric fluorescent probe for quantitative detection of styrene in air

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Experimental Section

Chemicals and Materials

4-Bromo-1,8-naphthalic anhydride, N-butylamine, 4-aminostyrene, tri(o-tolyl) phosphine, palladium acetate, Di-tert-butyl dicarbonate, sulfuric acid(75%), styrene, methanol, ethanol, dichloromethane, acetonitrile, trimethylamine, ethyl acetate, petroleum ether sodium nitrite, and silica gel are analytical reagents. And the water in this work is double-distilled water.

Synthesis of Compound 1 (N-buty-4-bromine-1,8-naphthalimide).

4-Bromo-1,8-naphthalic anhydride (0.5 g, 1.8 mmol) and butylamine (0.36 mL, 3.6 mmol) were added into ethanol in sequence. Then the mixture was heated to 85^{o}C and kept reflux overnight under nitrogen atmosphere. The mixture was cooled to room temperature, and then extracted by water and dichloromethane, and the organic phase was collected and purified by column chromatography with silica gel (dichloromethane). Finally, Compound 1 was obtained by vacuum drying process as light yellow powder(413 mg, 82%). ^{1}H NMR($CDCl_3$, 600MHz, ppm): 0.99(t, J=12Hz, 3H), 1.47(M, 2H), 1.72(M, 2H), 4.18(t, J=6Hz, 2H), 7.84(t, J=6Hz, 1H), 8.04(d, J=6Hz, 1H), 8.39(d, J=12Hz, 1H), 8.56(d, j=12Hz, 1H), 8.64(d, J=12Hz, 1H). MS(ESI):m/z=353.5[M+Na]$^{+}$.

Synthesis of Compound 2 (4-BOC-aminostyrene).

4-Aminostyrene (360 mg, 3 mmol) and Di-tert-butyl dicarbonate($(BOC)_2O$) (654 mg, 3 mmol) were added into dichloromethane and kept stirring in ice bath. Then 415 μL trimethylamine was added, and 3 mL dichloromethane droplet in 20 min. Then keeping stirring for 7 hours. The mixture was extracted by water and dichloromethane. And the organic phase was collected and purified by chromatography with silica gel (dichloromethane: petroleum ether, 7:1, V/V). Finally, Compound 2 was obtained as white powder (276mg, 77%) by vacuum drying process. ^{1}H NMR($CDCl_3$, 600MHz, ppm): 1.54(s, 9H), 5.17(d, J=18Hz, 1H), 5.68(d, J=18Hz, 1H), 6.70(m, 1H), 7.34(m, 4H). HRMS: m/z= 242.1155[M+Na]$^+$.

Synthesis of Compound 3 (N-buty-4-(BOC-aminostyrene)-1,8-naphthalimide). Compound 1 (330 mg, 1 mmol) was added into the mixture including acetonitrile and trithylamine (1: 3 in V/V) and kept stirring for 5 minutes. Then compound 2 (306 mg, 1.4 mmol), palladium acetate (1.2 mg, 0.0054 mmol) and tri(o-tolyl)phosphine (14.4 mg, 0.036 mmol) were added into the solution. Then the solution was heated to 105 ^{o}C and kept for 48 hours under nitrogen atmosphere. Upon the reaction finished, the mixture was cooled to room temperature and extracted by water and dichloromethane. Then the organic phase was collected and purified by column chromatography on silica gel (dichloromethane: methyl alcohol, 10:1, V/V). The compound 3 (146 mg, 44.2%) obtained by vacuum drying. ^{1}H NMR($CDCl_3$, 600MHz, ppm): 3.21(t, J=12Hz, 3H), 1.46(m, 2H), 1.56(S, 9H), 1.71(m, 2H), 4.21(t, J=12Hz, 2H), 6.71(s, 1H), 7.27(S, 1H), 7.47(d, J=12Hz, 2H), 7.59(d, J=12Hz, 2H), 7.77(t, J=12Hz, 1H), 7.96(d, J=6Hz, 1H), 8.57(d, J=6Hz, 2H), 8.63(d, J=6Hz, 1H). HRMS: m/z=493.2098[M+Na]$^+$

Synthesis of Compound 4 (the probe) (N-buty-4-(aminostyrene)-1,8-naphthalimide).

Compound 3 (100 mg, 21.2 mmol) was dissolved in dichloromethane. And the mixture was putted into a apparatus which can generate HCl gas into the mixture. In this apparatus, a constant pressure funnel with 15 mL sulfuric acid was equipped on top of a round-bottom flask with 100 g NaCl for generating HCl gas. And the rest HCl gas was collected by NaOH aqueous solution. Then the mixture was extracted by alkaline aqueous solution (pH=9) and dichloromethane. The organic phase was collected and purified by column chromatography on silica gel (dichloromethane: methyl alcohol, 9:1, V/V). The probe was obtained by vacuum drying as red powder (93 mg, 93%). ^{1}H NMR($CDCl_3$, 600MHz, ppm): 1.00(t, J=12Hz, 3H), 1.47(m, 2H), 2.21(m, J=2H), 4.22(t, J=6Hz, 2H), 6.80(s, 2H), 6.93(d, J=6Hz, 2H), 7.33(d, J=6Hz, 1H), 7.55(d, J=6Hz, 2H), 7.76(d, J=6Hz, 1H), 7.78(t, J=12Hz, 1H), 8.00(d, J=6Hz, 1H), 8.60(d, J=12Hz, 2H), 8.66(d, J=12Hz, 1H). HRMS: m/z=371.1767$[M+H]^+$

Pretreatment (diazotization) of probe

Silica sulfuric acid (0.7 g), probe (20 mg, 53 mmol) and sodium nitrite (138 mg, 2 mmol) were all putted into a mortar. And grounded by a pestle for 15 minutes to obtain the homogeneous mixture. Next, water (1 mL) was added into the mixture with droplet. Then kept grounding the mixture until nitrous acid gas release completely. The aryladiazonium silica sulfate probe was obtained as light yellow powder.

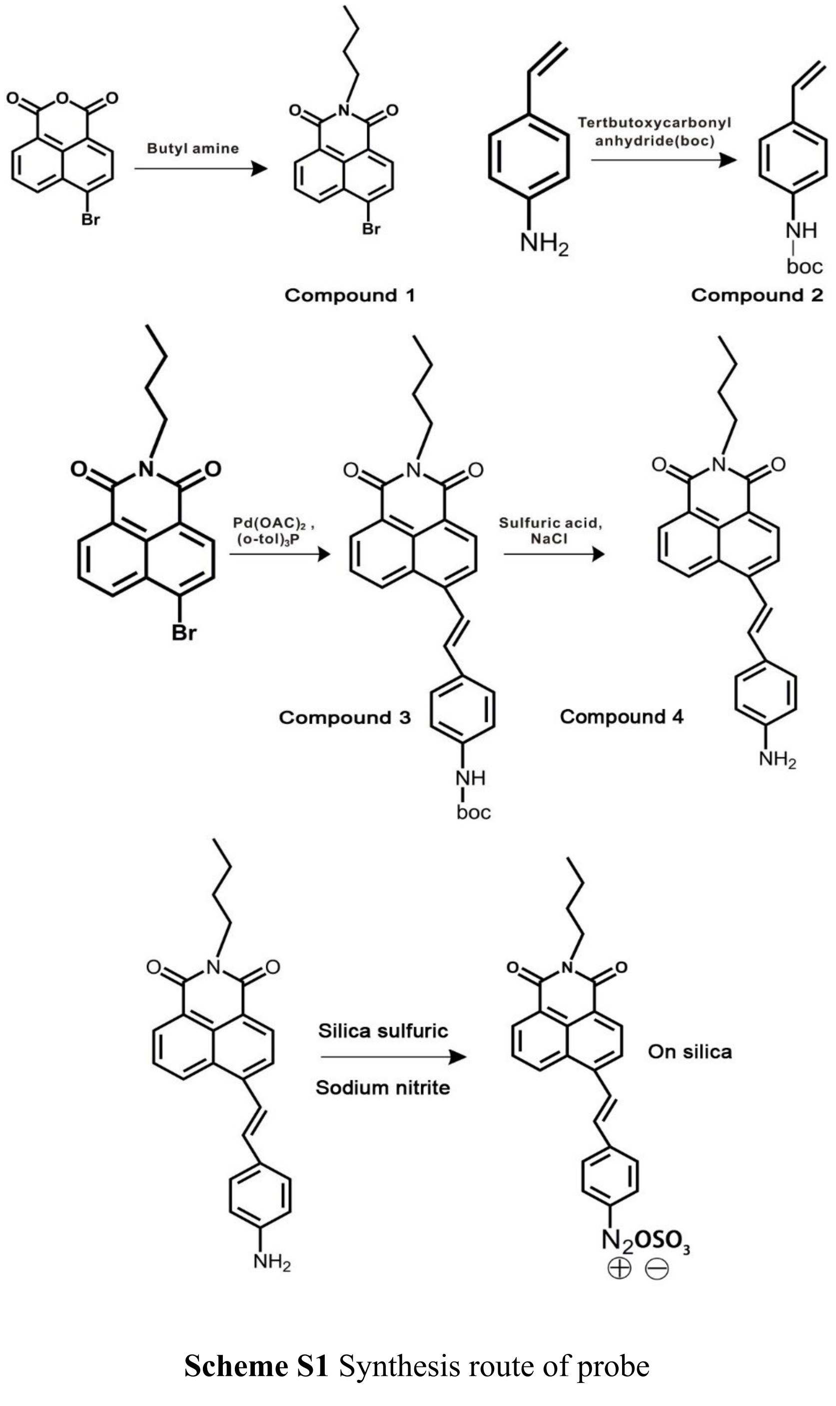
Measurements

The fluorescence spectra were measured on a Hitachi F-7000 fluorometer. And the Evolution 220 UV-vis spectrophotometer was used for recording UV-vis spectra. The Spectrum 100 spectrometer (PerkinElmer, America) was used for recording FTIR spectroscopy. 1H NMR spectra were measured on an AV600 nuclear magnetic resonance spectromete (Bruker, Switzerland). Mass spectra were obtained through a Bruker Esquire HCT Plus mass spectrometer. HPLC data were acquired from an Agilent 600 Infinity liquid chromatograph (Diode Array Detector).

Fluorescence method for quantitative detection of gaseous styrene

To achieve the quantitative determination of styrene in air, a gas-liquid mixing collecting system was designed to absorb gaseous isocyanates efficiently. And the schematic diagram of this system was showed in Fig. S17.

To build a working curve between fluorescence emission ratio values and amounts of styrene, fluorescence spectra of probe solution (2 μM) containing different weight of styrene were measured respectively. Fluorescence emission ratio I_{550}/I_{483} values were calculated according to fluorescence spectra. The working curve was obtained by plotting I_{550}/I_{483} values versus weights of styrene. To execute the quantitative detection, samples were made by volatilizing certain content styrene into gas sampling bags. The sample flow through porous plate absorption tubes with rate at 0.5 L/min for 60 min. Finally, the concentration of gaseous EI samples can be calculated according to the linear equation and the total volume of tested gas.



Scheme S1 Synthesis route of probe

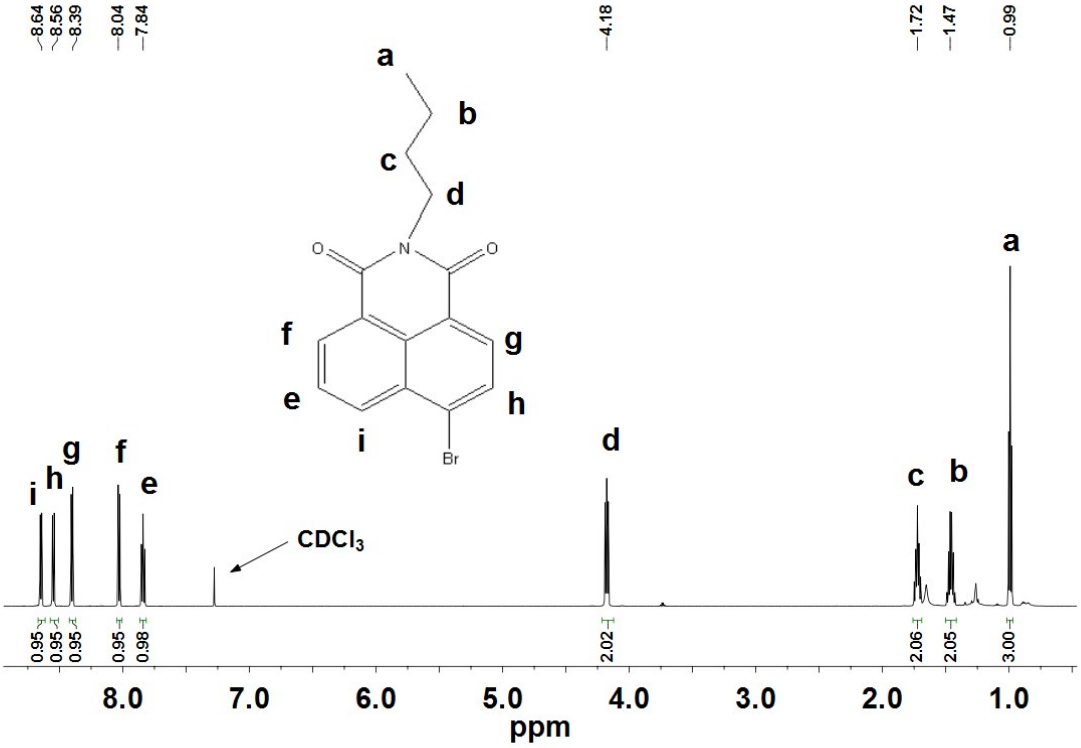


Fig. S1 ^{1}H NMR spectrum of Compound 1.

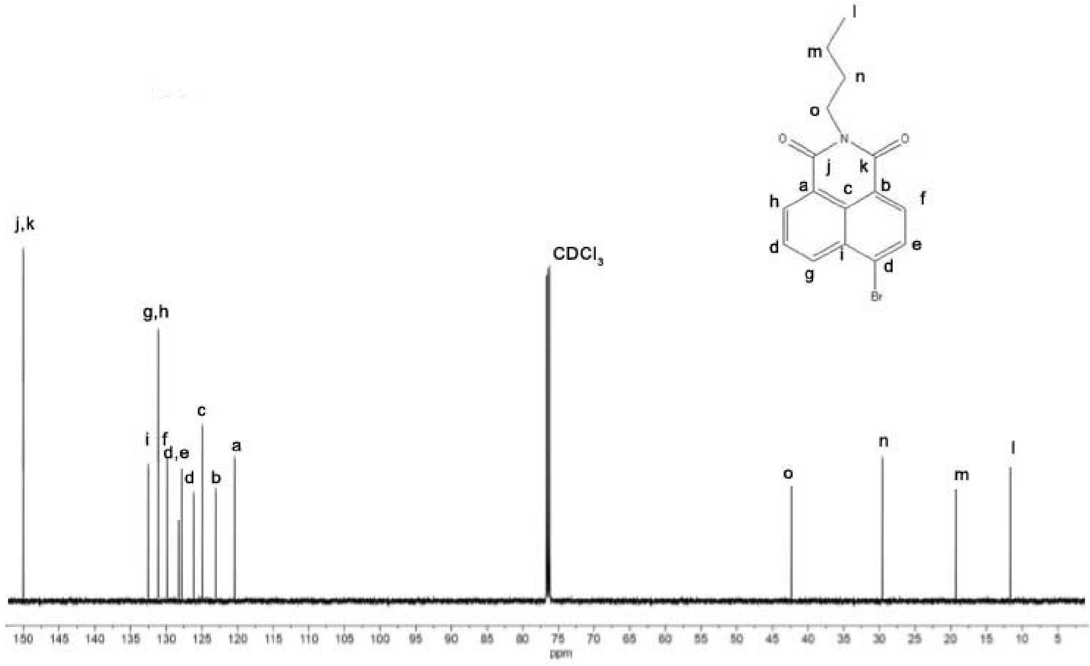


Fig. S2 ^{13}C NMR spectrum of Compound 1.

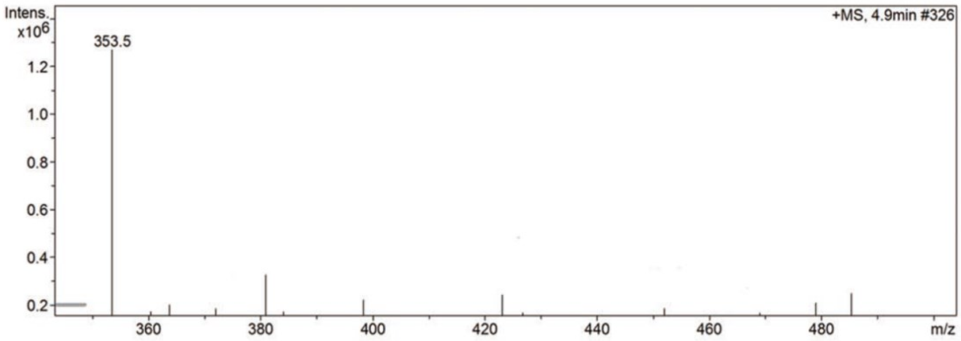


Fig. S3 ESI-MASS spectrum of Compound 1.

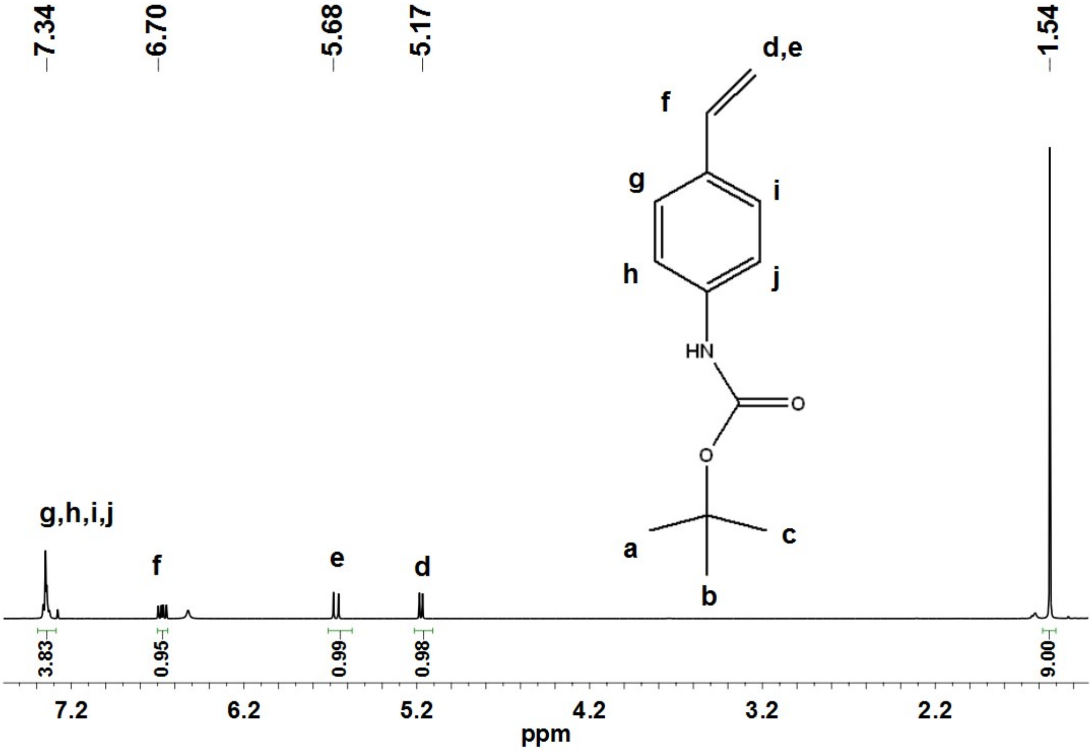


Fig. S4 ^{1}H NMR spectrum of Compound 2.

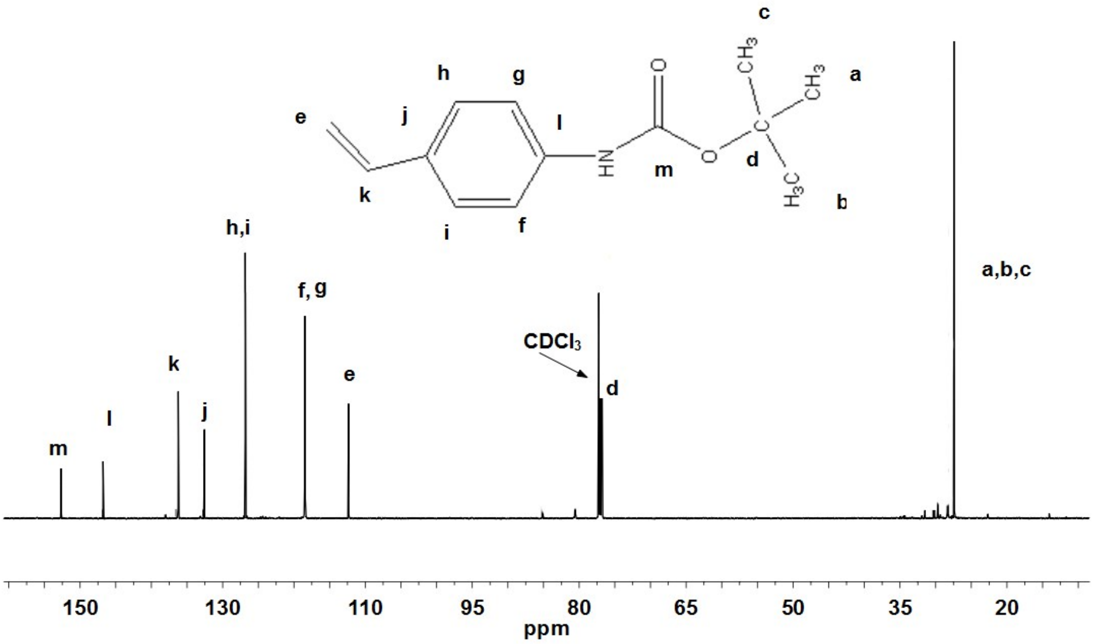


Fig. S5 ^{13}C NMR spectrum of Compound 2.

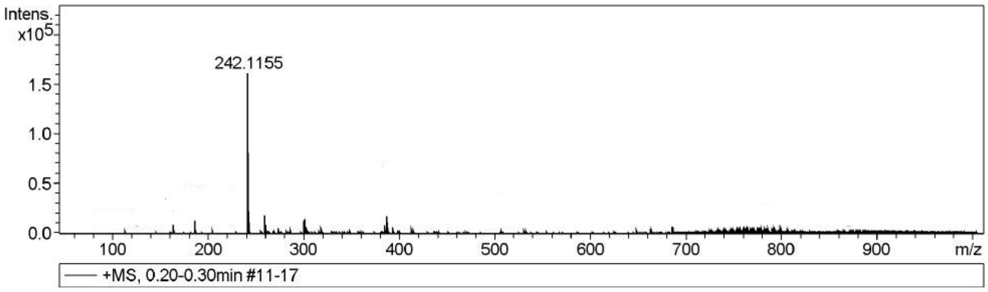


Fig. S6 HRMS spectrum of Compound 2.

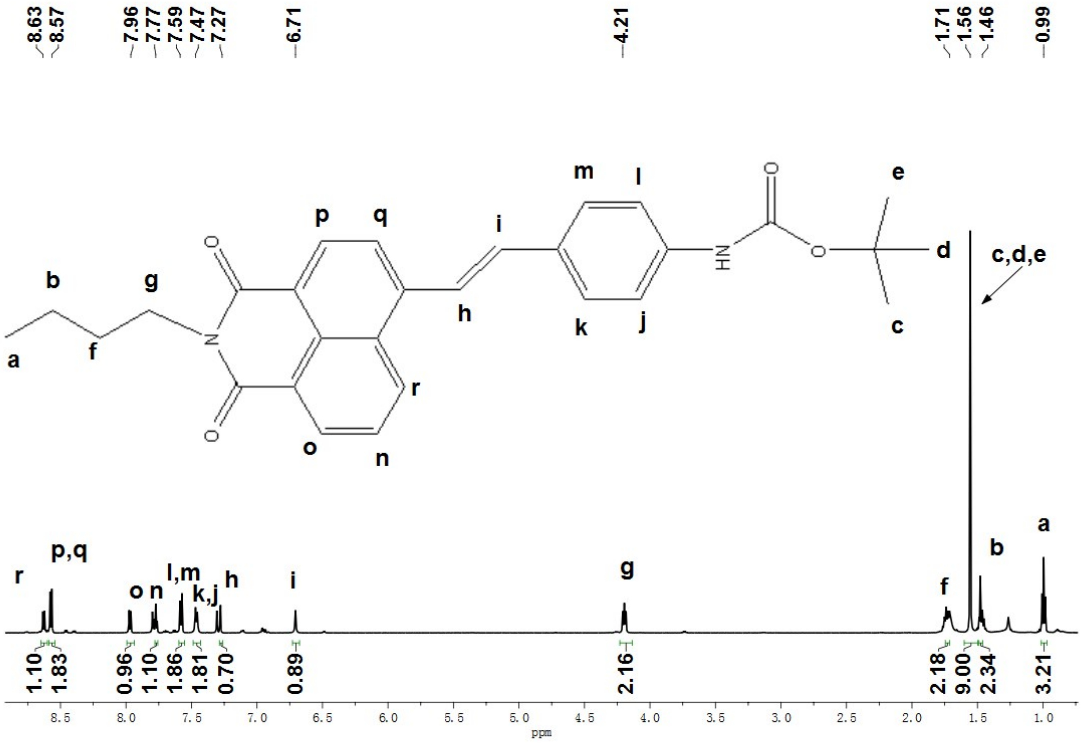


Fig. S7 ^{1}H NMR spectrum of Compound 3.

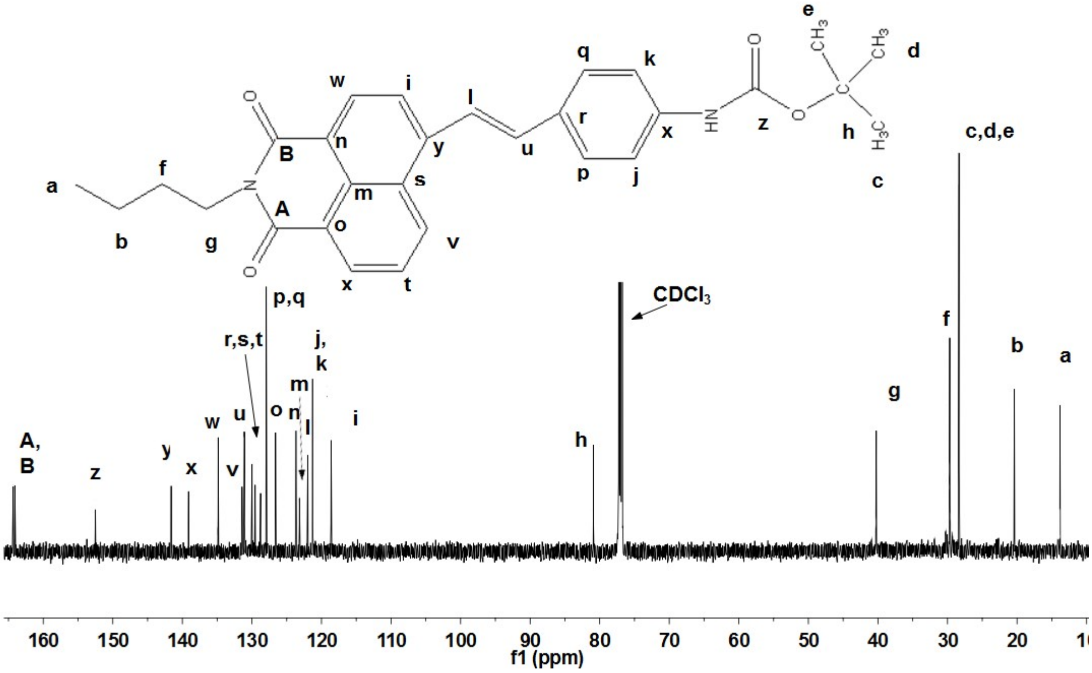


Fig. S8 ^{13}C NMR spectrum of Compound 3.

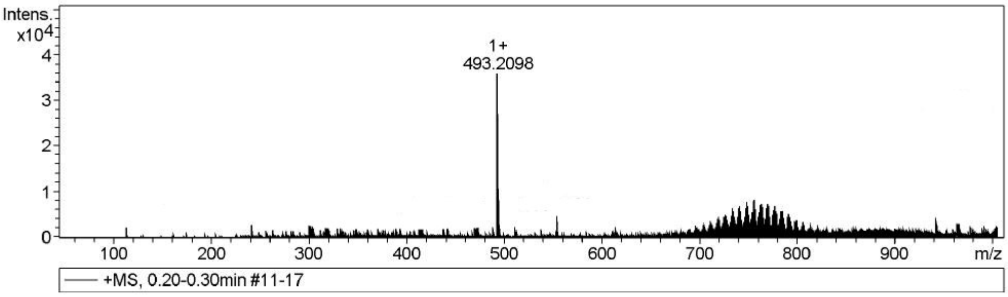


Fig. S9 HRMS spectrum of Compound 3.

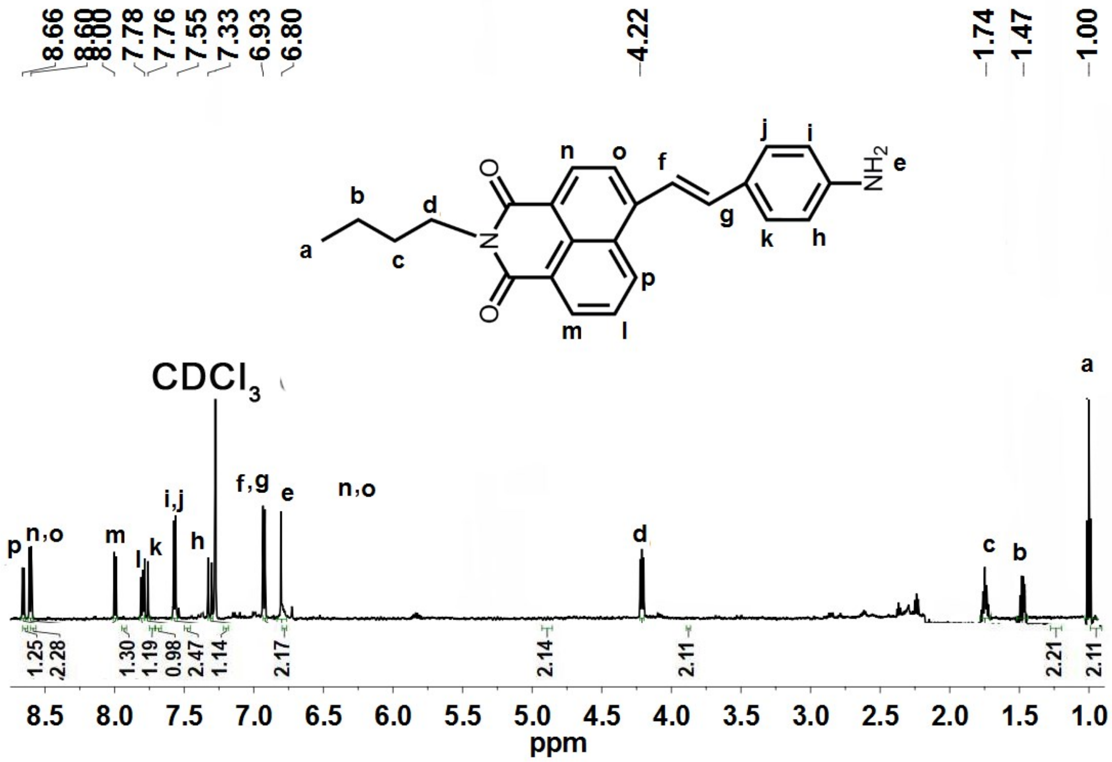


Fig. S10 ^{1}H NMR spectrum of Compound 4 (probe).

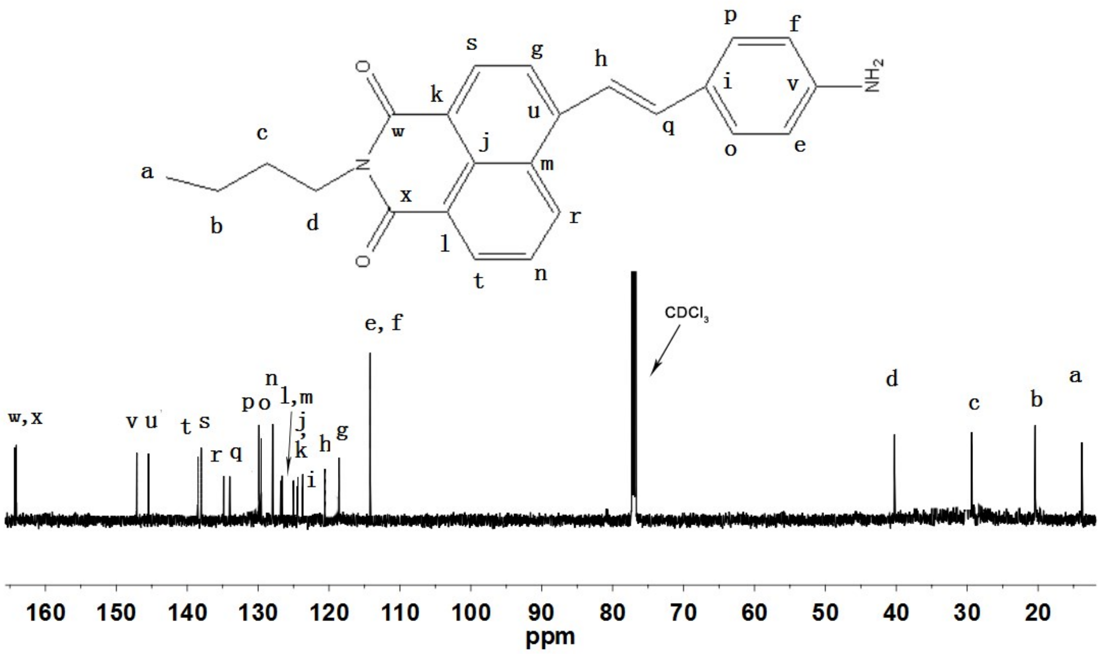


Fig. S11 ^{13}C NMR spectrum of Compound 4 (probe).

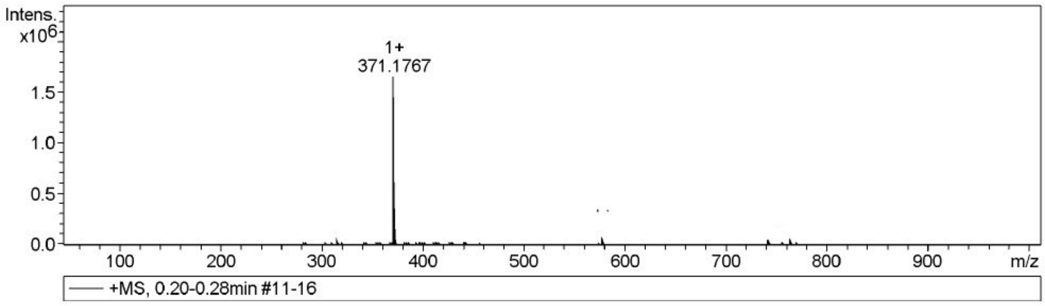


Fig. S12 HRMS spectrum of Compound 4 (probe).

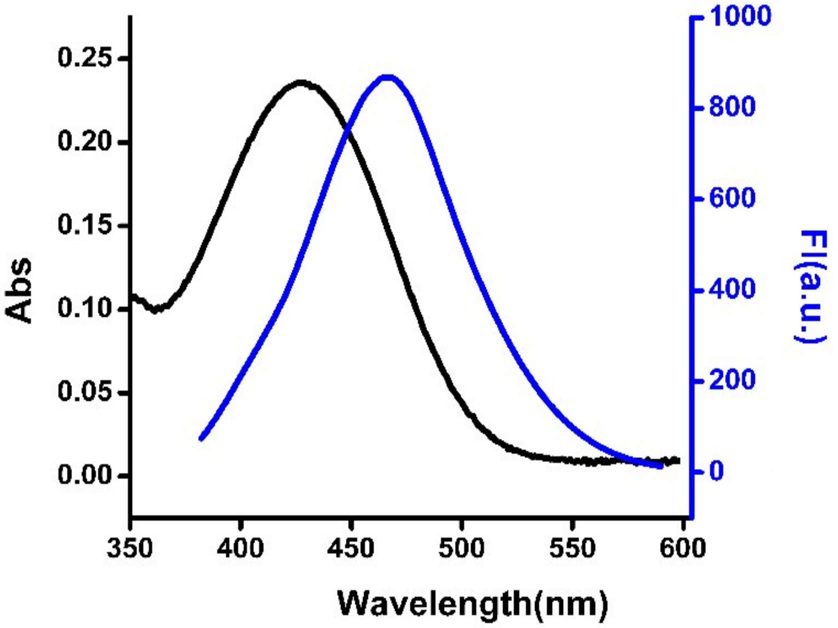


Fig. S13 Absorption spectrum (black) and fluorescence spectrum(blue) of pretreated probe in mixed solution (same volume of ethyl acetate and dichloromethane).

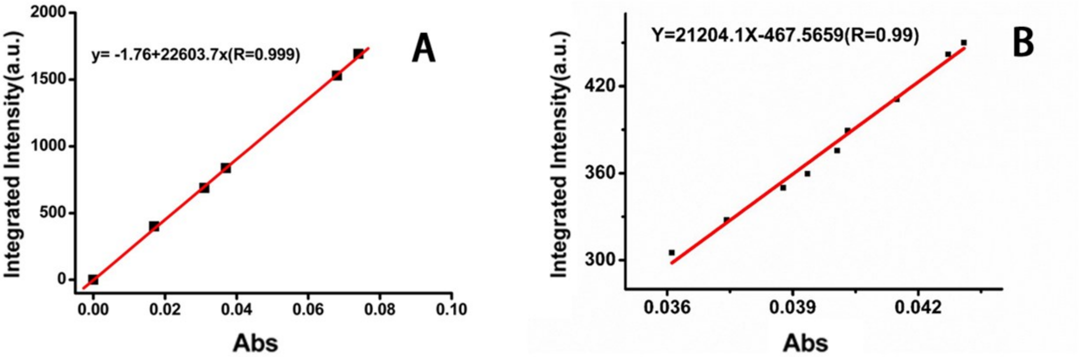


Fig. S14 (A) Plot of integrated fluorescence intensity versus absorbance for the quinine sulfate standard solution (B) Plot of integrated fluorescence intensity versus absorbance for the probe solution.

Quantum yield determination:

The quantum yield (Φ) of the probe was calculated by comparing their integrated fluorescence intensities and absorbance values with those of quinine sulfate. Quinine sulfate (Φ_{ST}= 0.546) was dissolved in 0.1 M H_2SO_4 (refractive index:1.333) and the probe were dissolved in ethyl acetate (refractive index:1.371). Quantum yield can be calculated according to the following equation:

$$\Phi = \Phi_{ST}\left(\frac{Grad}{Grad_{ST}}\right)\left(\frac{\eta^2}{\eta_{ST}^2}\right)$$

Where Φ is the fluorescence quantum yield, Grad is the slope of the plot of integrated fluorescence intensity versus absorbance, and η is the refractive index of the solvent. The subscript ST refers to the reference fluorophore, quinine sulfate solution. In order to minimize the re-absorption effects, absorbance values in the 10 mm fluorescence cuvettes should be maintained under 0.1 at the excitation wavelength. Excitation and emission slit widths were set at 5.0 nm when their fluorescence spectra were recorded.

$$0.546 \times \frac{21204.1}{22603.7} \times \frac{1.371^2}{1.333^2} = 0.54a^2$$

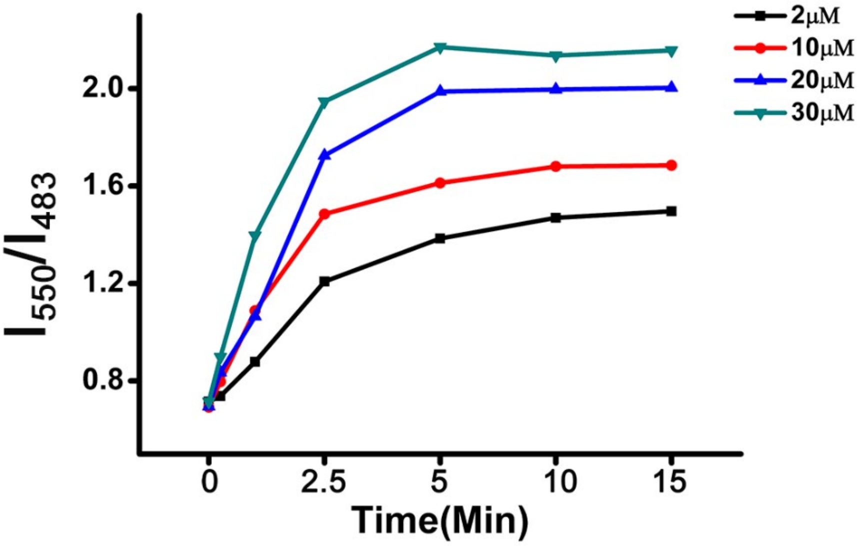


Fig. S15 Fluorescence intensity ratio values (I_{550}/I_{483}) of pretreated probe solutions containing different styrene at different time.

$+ b^2 =$

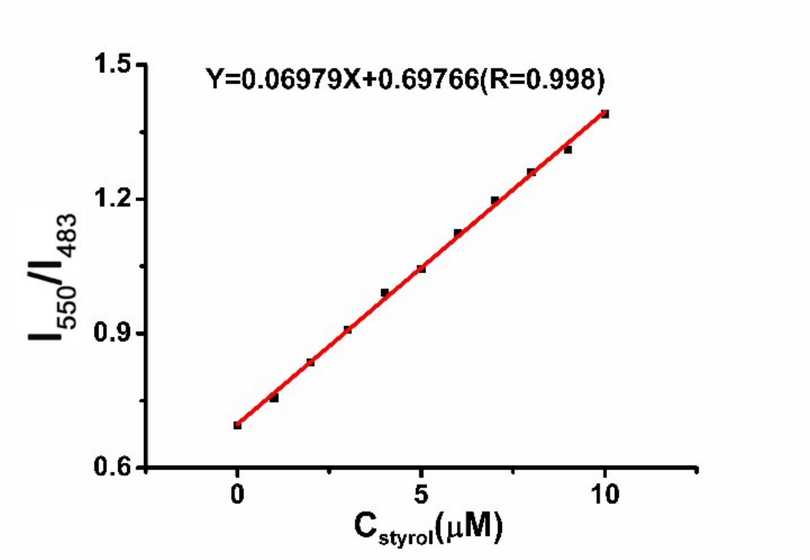


Fig. S16 Fluorescence intensity ratio for the probe (5 μM) in as a function of styrene upon the reaction time of 5 min.

Determination of the detection limit:

First the calibration curve was obtained from the plot of fluorescence intensity ratio (I_{550}/I_{483}) as a function of the analyte concentration (styrene). The regression curve equation was then obtained for the lower concentration part.

The detection limit = 3 × S.D./k

where k is the slope of the curve equation, and S.D. represents the standard deviation for the fluorescence intensity ratio of the probe in the absence of styrene.

LOD = 3 × 0.0028 / 0.06979 = 120 nM

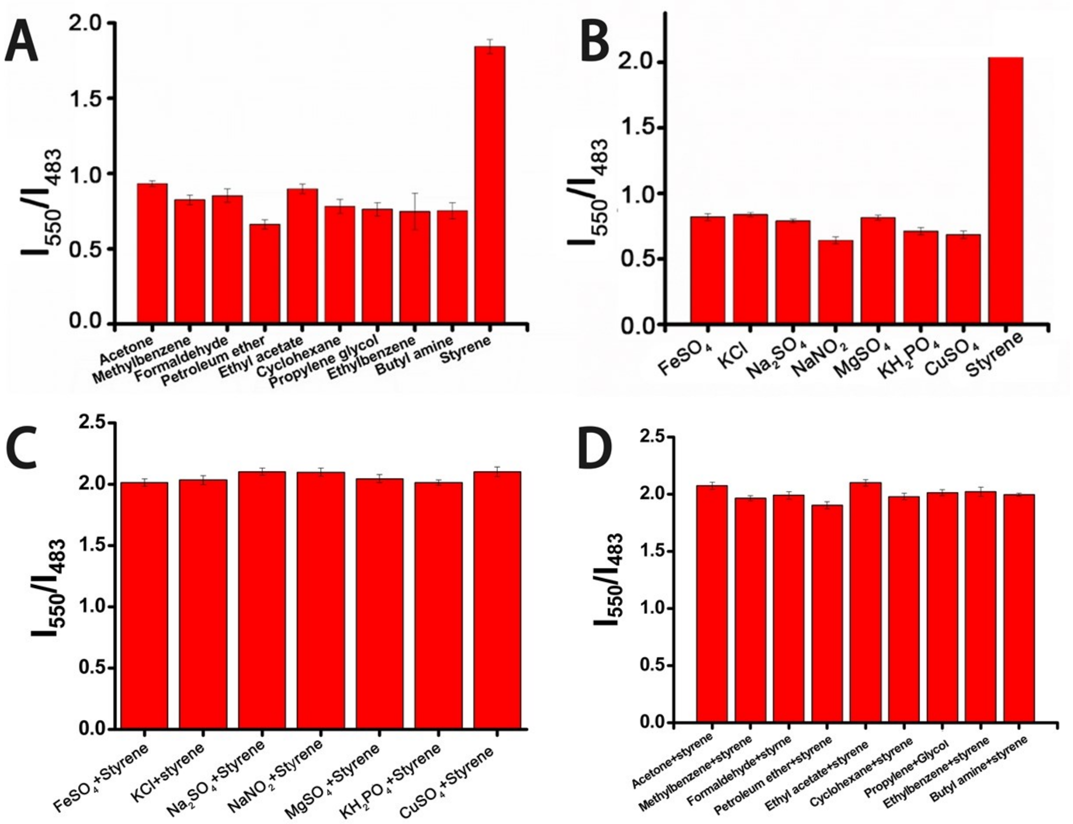


Fig. S17 Fluorescence intensity ratio of probe (5 μM) solution containing different volatile organic compounds (30 μM) (A) and metal salts (30 μM) (B). Fluorescence response of pretreated probe toward styrene in the presence of metal salts (30 μM) (C) and different volatile organic compounds (30 μM) (D).

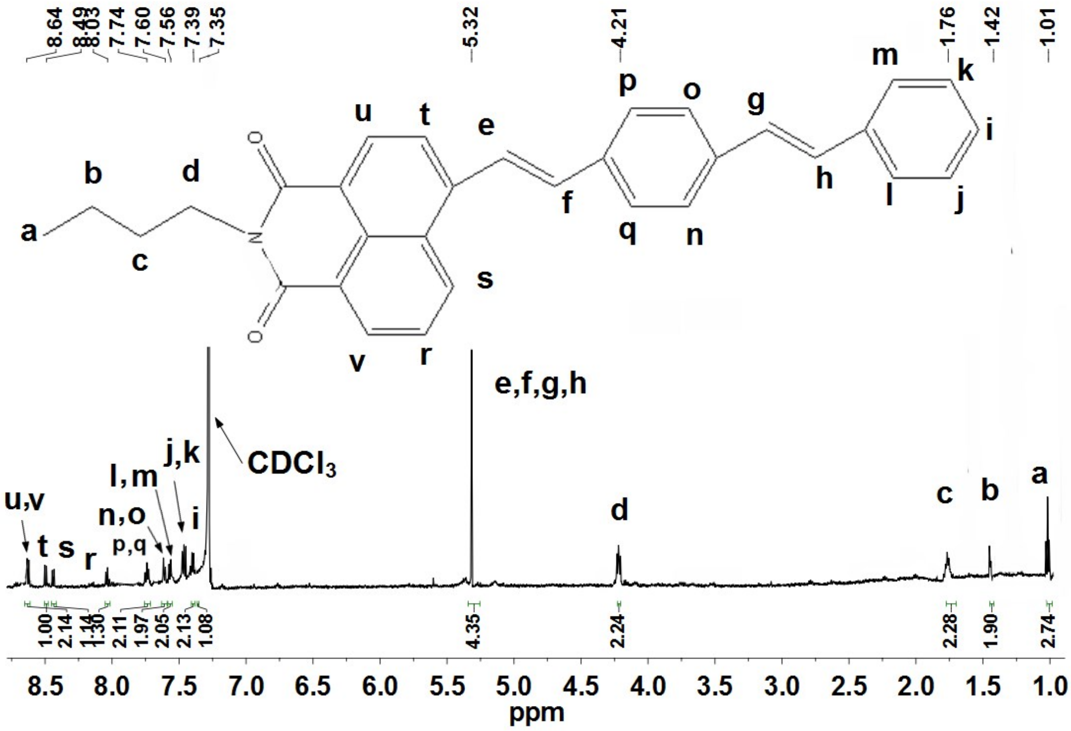


Fig. S18 ^{1}H NMR spectrum of the primary product of sensing reaction between styrene and pretreated probe.

^{1}H NMR($CDCl_3$, 600MHz, ppm): 1.01(t, J=6Hz, 3H), 1.42(m, 2H), 1.76(m, 2H), 4.21(t, J=12Hz, 2H), 5.32(s, 4H), 7.35(t, J=6Hz, 1H), 7.39(t, J=6Hz, 2H), 7.56(t, J=6Hz, 2H), 7.60(d, J=6Hz, 2H), 7.74(d, J=6Hz, 2H), 8.03(t, J=12Hz, 1H), 8.40(d, J=6Hz, 1H), 8.49(d, J=6Hz, 1H), 8.64(d, J=6Hz, 2H).

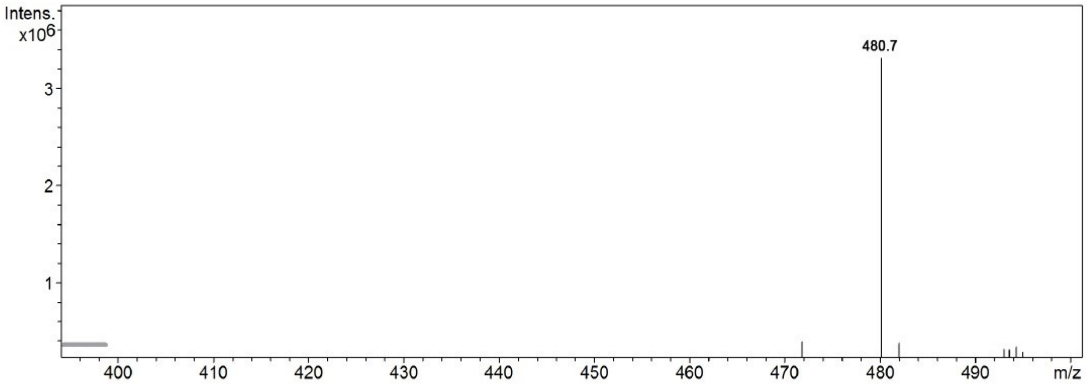


Fig. S19 ESI-MASS spectrum of the primary product of sensing reaction between styrene and pretreated probe. MS(ESI): m/z=480.7[M+Na]$^+$.

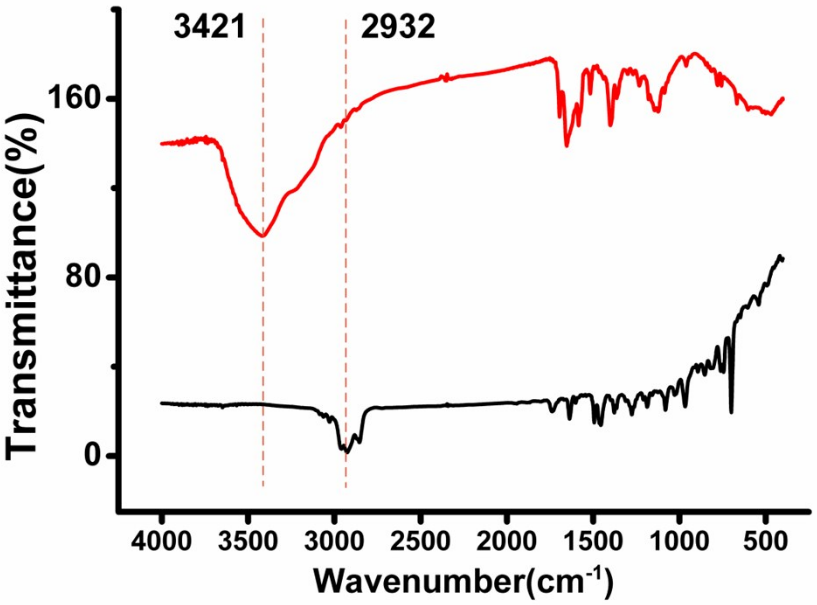


Fig. S20 FT-IR spectra of probe (red) and the primary product (black).

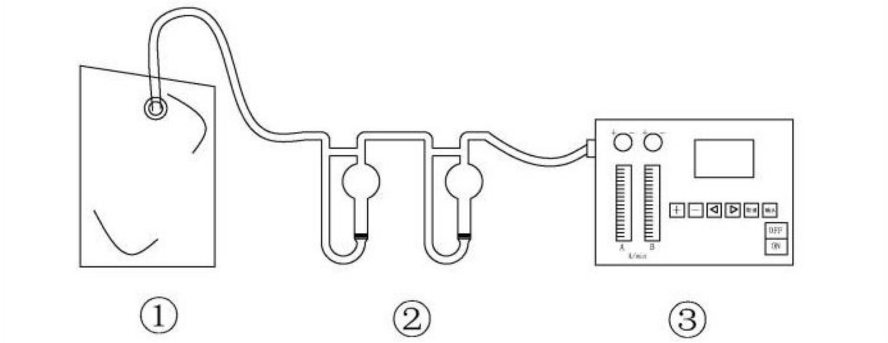


Fig. S21 Schematic diagram of sampling system

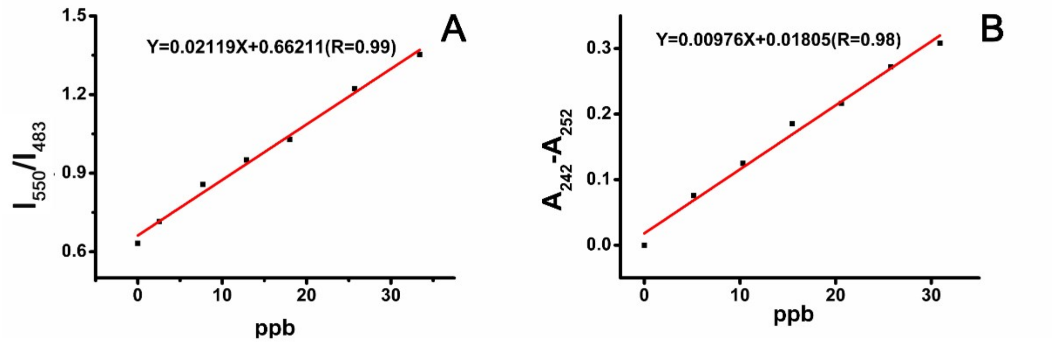


Fig. S22 Working curves for fluorescence absorption method (A) and double wavelength UV spectrum method (B).

Probe solution absorption method

6 standard air samples of styrene (known concentration) were made by volatilizing certain amount of styrene into air sampling bags (30 L), then those standard samples were sampled by the sampling system (Fig. S21) with probe solution (air flow 0.5 L/min, 60 min). Fluorescence spectra of probe absorption solution were record. And the standard curve (Fig. S22 A) was built by plotting the fluorescence emission ratio (I_{550}/I_{483}) of those samples versus the concentration of styrene.

Double wavelength UV spectrum method

Standard samples were collected by collecting system (the absorption solution is dichloromethane) with air flow 0.5L/min for 60min. Absorbance of absorption solution at 242 nm and 252 nm was measured. And standard curve (Fig. S22 B) was built by plotting the difference between A242 and A252 versus the concentration of styrene.

Reference:

S. Fu, S. Shen, C. Liu, W. Wang. *Chemical Industry Times*, 2007, **21**, 28-30.

Table S1 Selectivity of probe solution absorption method.

Samples	Acetone	Methylbenzene	Formaldehyde	Petroleum ether	Ethyl acetate	Styrene
$C_{Styrene}$ (ppb)	-	-	-	-	-	48.90

Table S2 Anti-interference of probe solution absorption method.

Mixed Samples	Acetone	Methylbenzene	Formaldehyde	Petroleum ether	Ethyl acetate
$C_{Styrene}$(ppb)	49.12	48.96	49.3	48.59	49.42