Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

A novel single-fluorophore-based ratiometric fluorescent probe for direct detection of isocyanates in air

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Experimental Section

Chemicals and Materials

N,N-Dimethylethylenediamine, 9-bromoanthracene, acetic anhydride, oxalyl chloride, n-butylamine, Oxone, Diethylnitrosamine (DEN), sodium methylate, $CuSO_4 \cdot 5H_2O$, HI aqueous solution, K_2CO_3, DMSO and MeOH were purchased from Aladdin Reagents. 2-chloroethyl isocyanate (CEI), 4,4-methylenediisocyanate (MDI), phenyl isocyanate (PI), 2,4-toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), Ethyl alcohol, ethyl acetate, methanol, dichloromethane, hexane, carbondisulfide (CS_2), anhydrous sodium sulfate, $AlC1_3$, sodium chloride and sodium hydroxide were of analytical grade reagents. In the experiments the water used was the triple-distilled water which was further treated by ion exchange columns.

Synthesis of 1 (6-bromoaceanthrylene-1,2-dione)

To a stirred solution of 9-bromoanthracene (1.03 g, 4 mmol) and oxalyl chloride (1.92 mL, 10 mmol) in CS_2 (10 mL) at 0 °C under a nitrogen, and then anhydrous $AlC1_3$ (0.81 g, 6 mmol) was added. After 2 h, additional CS_2 (10 mL) and $AlC1_3$ (0.64 g, 4.8 mmol) were added, and kept stirring for another 2 h at 0 °C, then back to the room temperature and reacted overnight. Afterwards 60 mL HCl aqueous solution (2 M) was added under stirring, and heated to 50 °C for 10 min. Then the precipitate was collected by filtration, washed ordinally with water, 5% NaOH aqueous solution and water. The solids dried under vacuum at 50 °C for 48 h to obtain compound 1 as a light brown power (0.93 g, 75%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): 7.82-7.92 (m, 3H), 8.12 (d, J = 6.6 Hz, 1H), 8.63 (d, J = 6.0 Hz, 1H), 8.71 (d, J = 6.0 Hz, 1H), 9.27 (d, J = 6.6 Hz, 1H). MS(ESI): m/z = 310.1 $[M+H]^+$.

Synthesis of 2 (6-bromo-l,2-anthracene dicarboxylic acid anhydride)

Under a nitrogen atmosphere, a stirred solution of compound **1** (0.93 g, 3 mmol) and oxone (2.31 g, 15 mmol) in methanol (60 mL) was heated to 72 °C and refluxed for 72 h. Then cooled down to the room temperature, and water was added and the suspension was collected by filtration and purified by column chromatography on silica gel (hexane: dichloromethane = 1: 3 in v/v). The product was dried under vacuum at 40 °C overnight to obtain compound **2** as a brown power (0.86 g, 85%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): 7.85 (t, J = 6.0 Hz, 1H), 7.92 (t, J = 6.6 Hz, 1H), 7.96 (t, J = 5.4 Hz, 1H), 8.79 (d, J = 6.6 Hz, 1H), 8.84 (d, J = 6.0 Hz, 1H), 9.06 (d, J = 7.2 Hz, 1H), 9.85 (d, J = 7.8 Hz, 1H). MS(ESI): m/z = 325.0 $[M-H]^-$.

Synthesis of 3 (N-(n-butyl)-6-bromo-anthracenecarboximide)

Under a nitrogen atmosphere, n-butylamine (986 μL, 10 mmol) and compound **2** (0.82 g, 2.5 mmol) were dissolved in ethyl alcohol and stirred for 10 min, then refluxed for 8 h. The mixture was concentrated and extracted with CH_2Cl_2/H_2O for several times. The organic phase was collected and purified by a silica gel column (dichloromethane) to obtain compound **3** as a brown power (0.46 g, 48%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): 1.00 (t, J = 5.4 Hz, 3H), 1.50 (m, 2H), 1.77 (m, 2H), 4.26 (t, J = 6.0 Hz, 2H), 7.73 (t, J = 7.2 Hz, 1H), 7.79-7.85 (m, 2H), 8.70 (d, J = 6.0 Hz, 1H), 8.79 (d, J = 6.6 Hz, 1H), 8.91 (d, J = 7.2Hz, 1H), 10.07 (d, J = 7.2 Hz, 1H). MS(ESI): m/z = 380.7 $[M]^-$.

Synthesis of 4 (N-(n-butyl)-6-methoxyl-anthracenecarboximide)

A solution of the above-obtained compound **3** (0.46 g, 1.2 mmol), sodium methylate (0.44 g, 8 mmol) and $CuSO_4 \cdot 5H_2O$ (14mg, 0.06 mmol) in methyl alcohol under a nitrogen atmosphere stirred for 10 min, then heated to 70°C and refluxed overnight. After being cooled down, the mixture was concentrated and extracted with CH_2Cl_2/H_2O for three times. Then the organic phase was collected and purified by a silica gel column (dichloromethane: methylalcohol= 10: 1 in v/v) to obtain compound **4** as a yellow power (0.34 g, 85%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): 1.01 (t, J = 6.0 Hz, 3H), 1.50 (m, 2H), 1.78 (m, 2H), 4.23 (s, 3H), 4.28 (t, J = 6.6 Hz, 2H),7.66 (t, J = 6.6 Hz, 1H), 7.74 (t, J = 6.6 Hz, 1H),7.84 (t, J = 7.2 Hz, 1H), 8.46 (d, J = 6.6 Hz, 1H), 8.65 (d, J = 6.6Hz, 1H), 8.77 (d, J = 6.0 Hz, 1H), 10.08 (d, J = 6.0 Hz, 1H). MS(ESI): m/z = 333.0 $[M]^-$.

Synthesis of 5 (N-(n-butyl)-6-hydroxy-anthracenecarboximide)

Under a nitrogen atmosphere, compound **4** (0.34 g, 1.0 mmol) was added into10 mL HI aqueous solution (57%), then heated to 132 °C and refluxed overnight. After being cooled down, the mixture was adjusted to be faintly acid with 2M NaOH aqueous solution. The precipitate was collected by filtration and washed with water for several times. The residue was purified by a silica gel column (dichloromethane: methylalcohol= 7: 1 in v/v) to obtain compound **5** as a red power (0.16 g, 52%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): 1.02 (t, J = 5.4 Hz, 3H), 1.51 (m, 2H), 1.79 (m, 2H), 4.23 (t, J = 6.6 Hz, 2H), 7.66 (t, J = 6.6 Hz, 1H), 7.70-7.78 (m, 2H), 8.57 (d, J = 6.6 Hz, 1H), 8.71 (d, J = 6.0 Hz, 1H), 8.79 (d, J = 6.6 Hz, 1H), 9.98 (d, J = 6.0 Hz, 1H). ^{13}C NMR (CD_3OD, 600 MHz, ppm): 14.01, 20.52, 30.1, 39.66, 114.85, 120.25, 122.86, 125.67, 126.78, 129.21, 130.75, 153.86, 162.65, 167.18. MS(ESI): m/z = 317.1 $[M-H]^-$.

Purification of the primary product resulted from the reaction between the probe and 2-chloroethyl isocyanate (CEI)

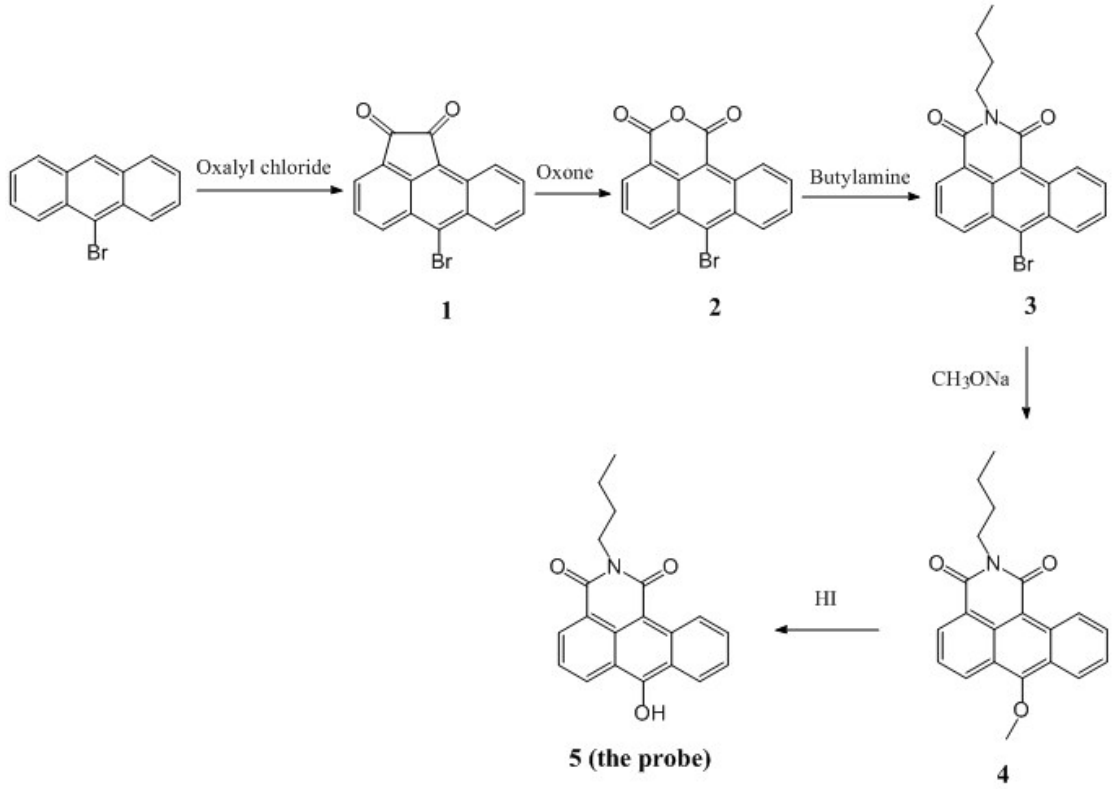
A solution of the probe (32 mg, 0.1 mmol) and CEI (42 μL, 0.5mmol) in 5 mL methanol was stirred for 10 min at the room temperature. Then the solvent was evaporated and purified by a silica gel column (dichloromethane: methylalcohol= 10: 1 in v/v) to obtain the primary product as a light yellow solid (yield: 81%). ^{1}H NMR ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): 0.98 (t, J = 6.6 Hz, 3H), 1.32 (m, 2H), 1.56 (m, 2H), 3.16 (t, J = 6.6 Hz, 2H), 3.25 (t, J = 6.0 Hz, 2H), 3.65 (t, J = 5.4 Hz, 2H), 7.57-7.66 (m, 3H), 8.01 (d, J = 7.2 Hz, 1H), 8.25 (d, J = 6.0 Hz, 1H), 8.38 (d, J = 6.6 Hz, 1H), 9.78 (d, J = 6.6 Hz, 1H). MS(ESI): m/z 440.1 $[M+OH]^-$.

Preparation of the test paper

The rectangular scrip (1 x 4 cm) was obtained from filter paper, and then the double of scrip were painted full with the probe methanol solution (1 mM) by disposable plastic dropper. After drying at the room temperature for 15 min, the carmine test paper was obtained with red emission under a hand-held UV lamp (365 nm).

Measurements

^{1}H NMR spectra were recorded on a Bruker Avance 600 MHz NMR spectrometer. Mass spectra were obtained through a Bruker Esquire HCT Plus mass spectrometer. UV-vis spectra were recorded on a Hitachi U-3010 UV-vis spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. HPLC data were acquired from an Agilent 1200 Infinity liquid chromatograph (Diode Array Detector). FTIR spectra were recorded with a NEXUS 670 spectrometer (Thermo Nicolet Corporation, Madison, WI)



Scheme S1. Synthetic route for the probe.

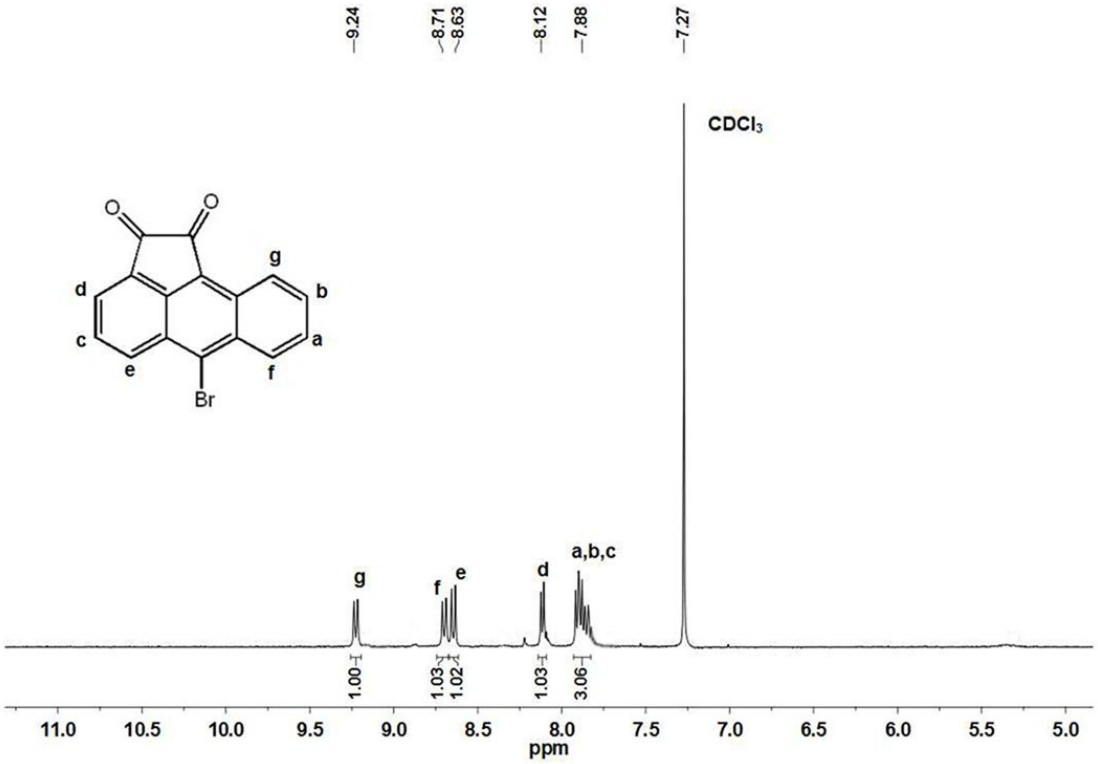


Figure S1.[1]H-NMR spectrum of **1** (in $CDCl_3$).

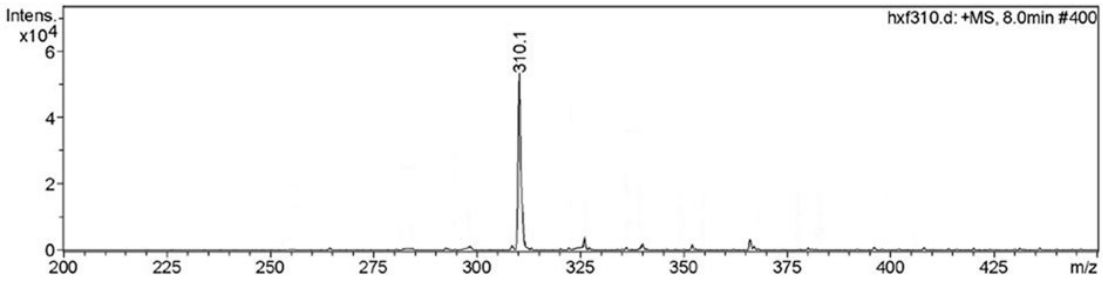


Figure S2. Mass spectrum of **1**. MS(ESI): m/z 310.1 $[M+H]^+$.

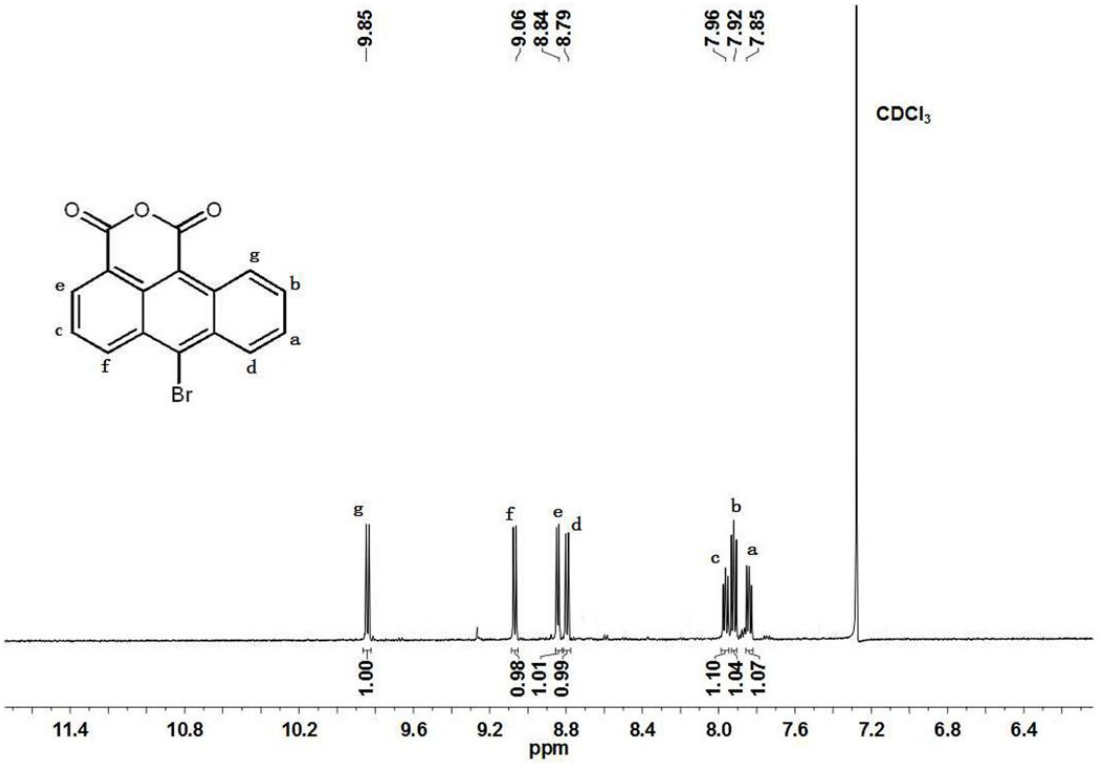


Figure S3.[1]H-NMR spectrum of **2** (in $CDCl_3$).

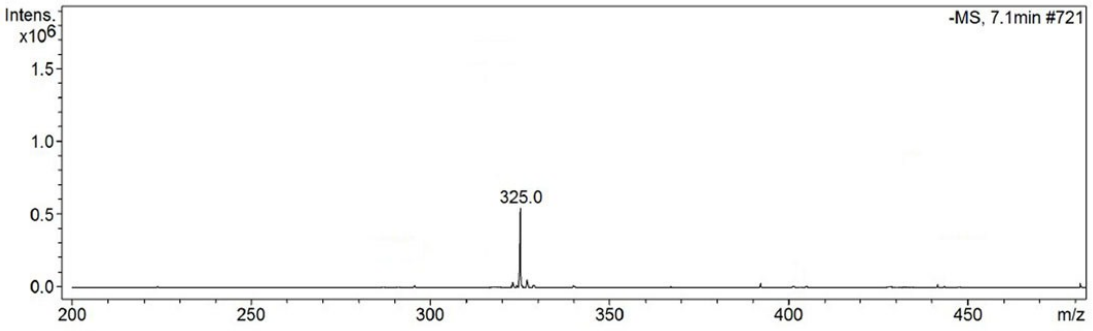


Figure S4. Mass spectrum of **2**. MS(ESI): m/z 325.0 $[M-H]^-$.

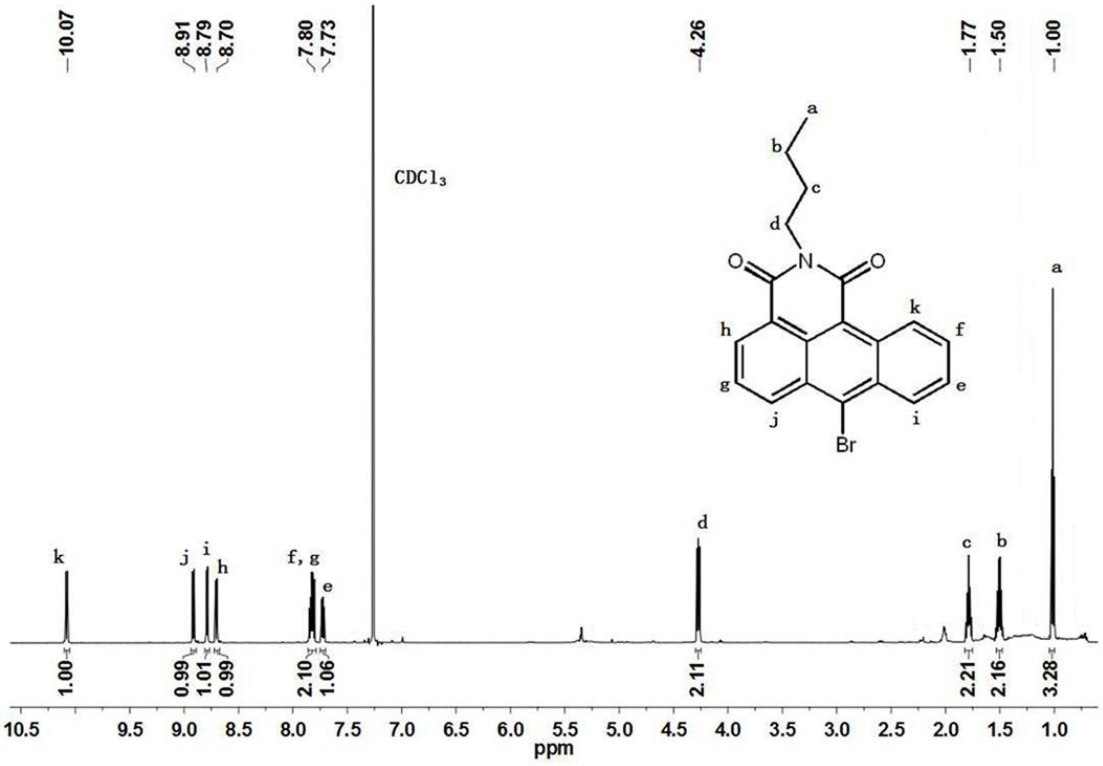


Figure S5.[1]H-NMR spectrum of **3** (in $CDCl_3$).

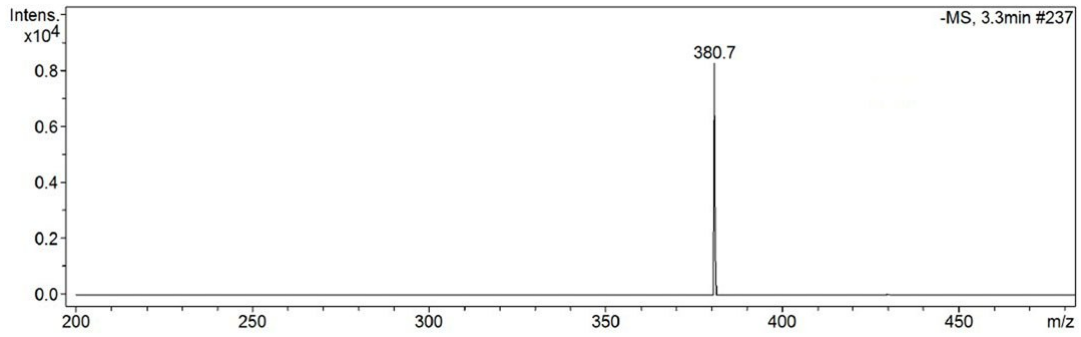


Figure S6. Mass spectrum of **3**. MS(ESI): m/z 380.7 $[M]^-$.

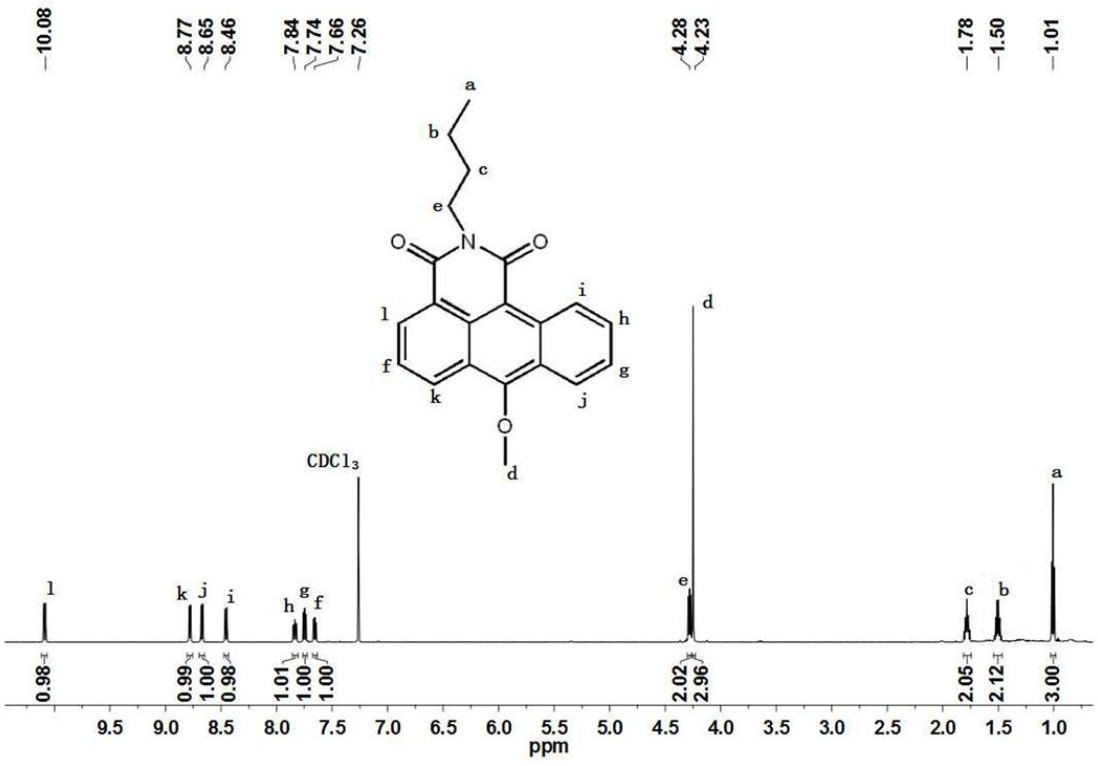


Figure S7.[1]H-NMR spectrum of **4** (in $CDCl_3$).

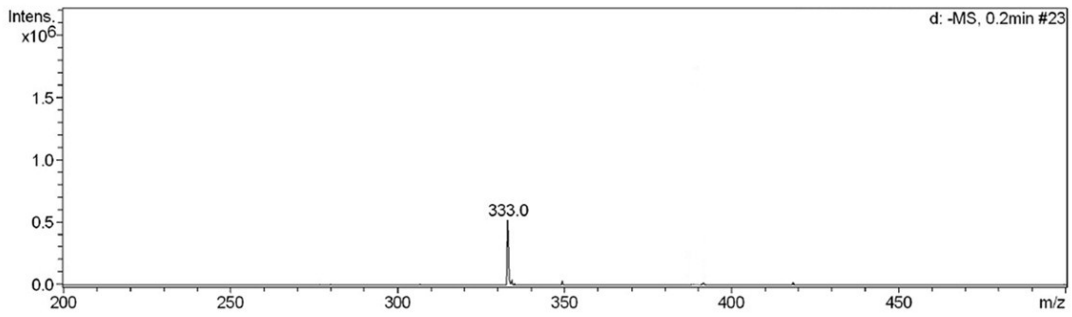


Figure S8. Mass spectrum of **4**. MS(ESI): m/z 333.0 $[M]^-$.

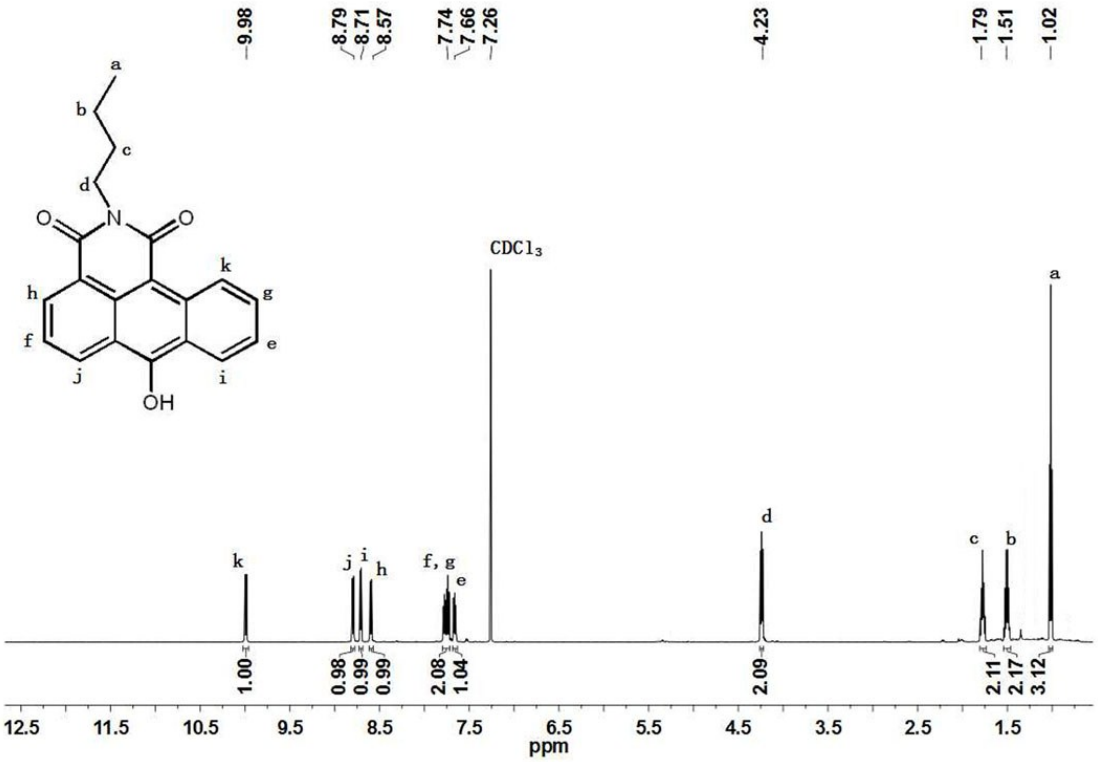


Figure S9.[1]H-NMR spectrum of **5** (in $CDCl_3$).

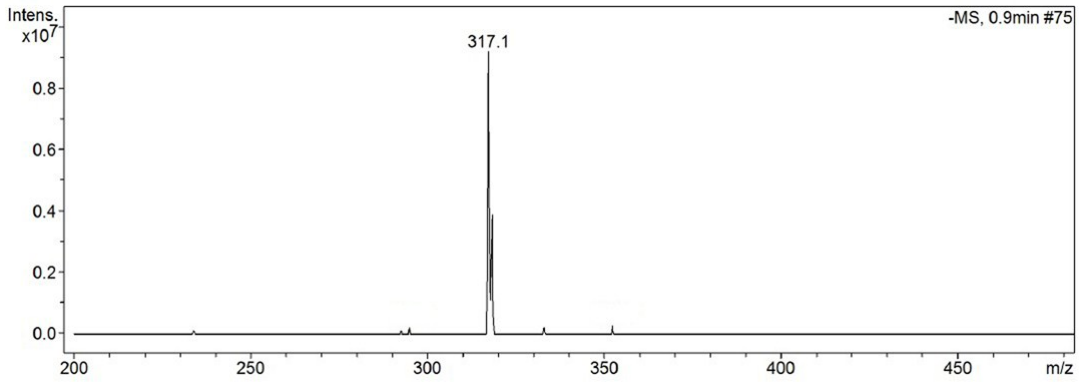


Figure S10. Mass spectrum of **5**. MS(ESI): m/z 317.1 $[M-H]^-$.

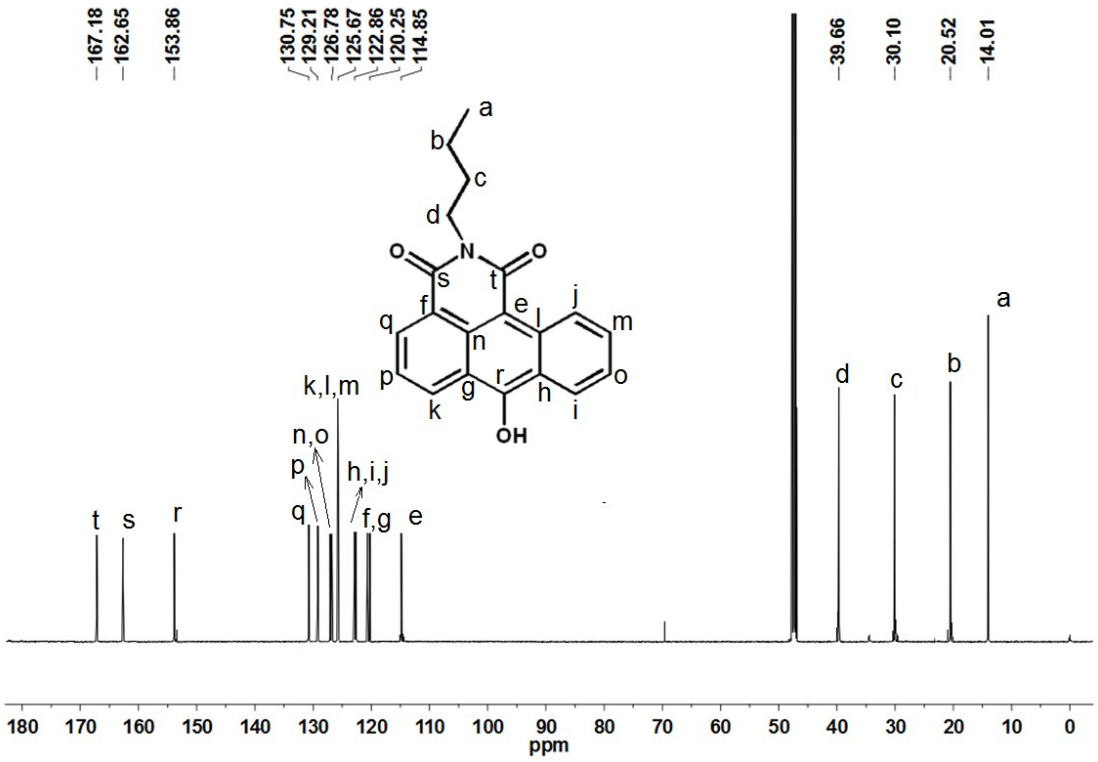


Figure S11. ^{13}C-NMR spectrum of **5** (in CD_3OD).

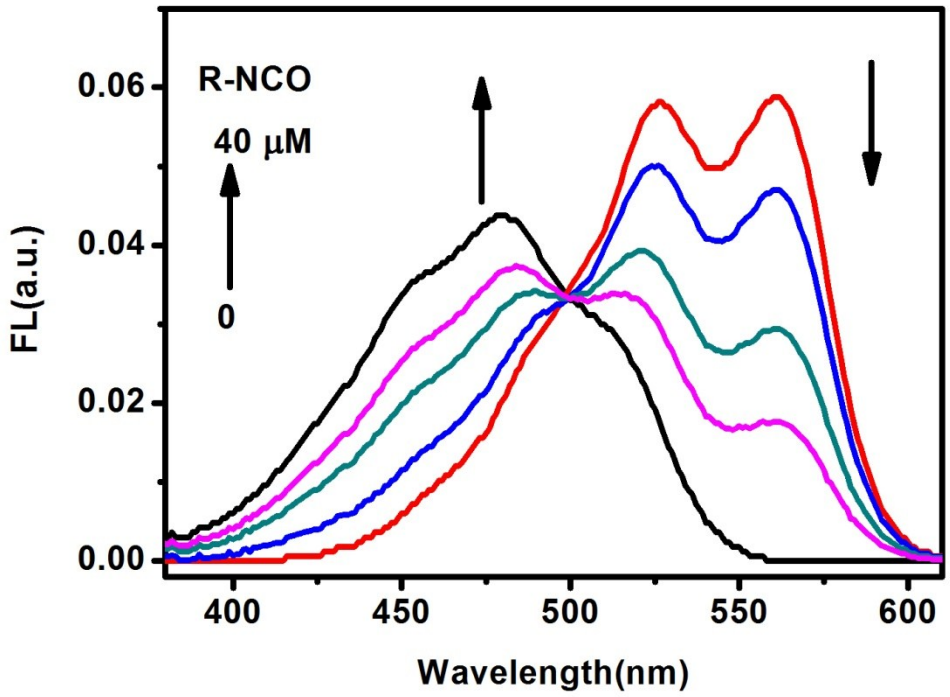


Figure S12. Absorption spectra of the probe in the presence of different concentrations of 2-chloroethyl isocyanate (CEI) in methanol.

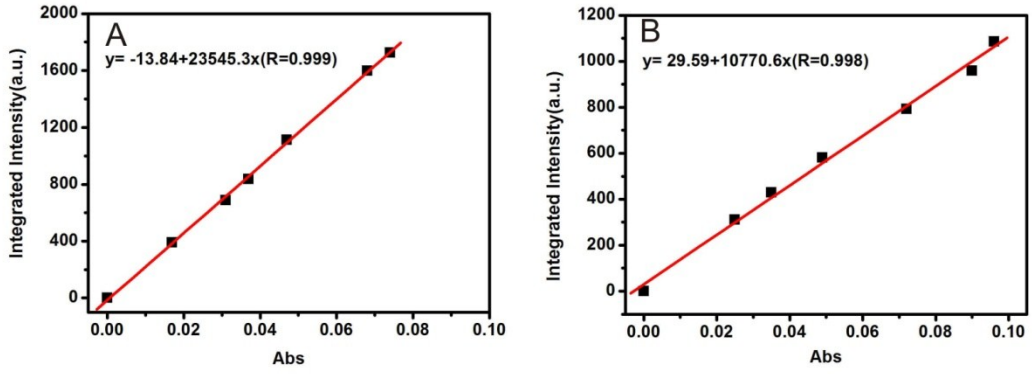


Figure S13. Plot of integrated fluorescence intensity versus absorbance for the quinine sulfate standard solution (A) and the probe solution(B).The quantum yield of this probe is determined to be 24.8%.

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 methanol (refractive index:1.329). 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 maintainedunder 0.1 at the excitation wavelength. Excitation and emission slit widths were set at 5.0 nm when their fluorescence spectra were recorded.

$$\Phi = 0.546\left(\frac{10770.6}{23545.3}\right)\left(\frac{1.329^2}{1.333^2}\right)=0.248$$

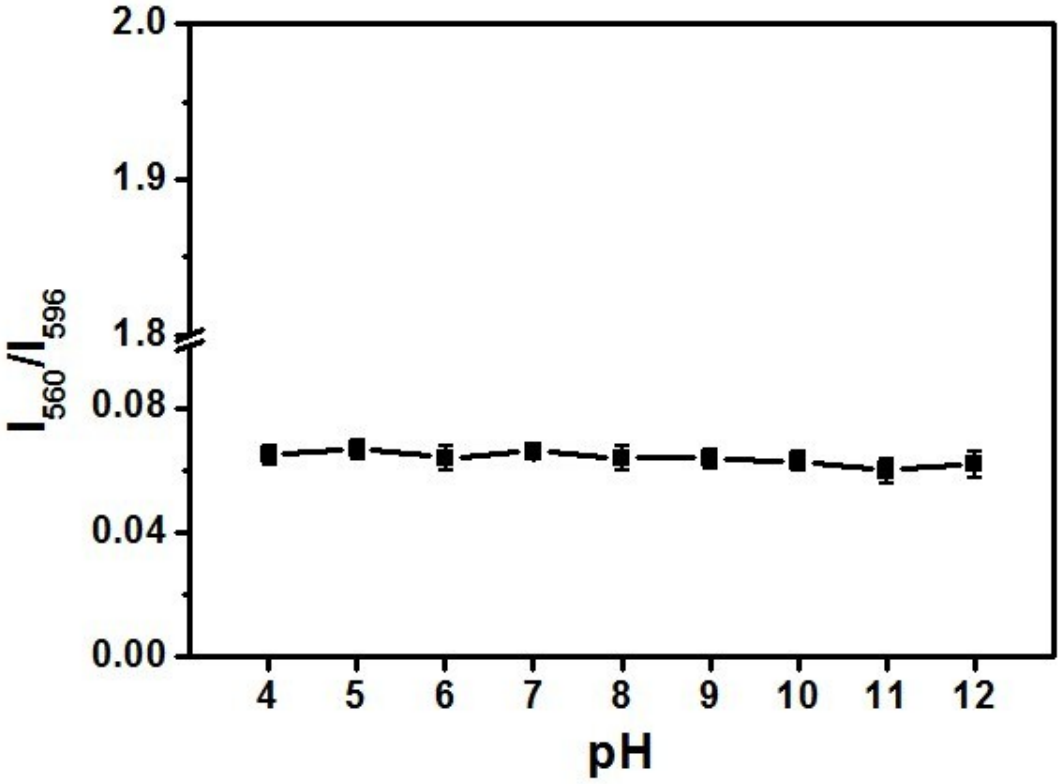


Figure S14. Stability of the probe under different pH values. The fluorescence ratio (I_{560}/I_{596}) of the probe treated with different pH buffer containing 20% methanol.

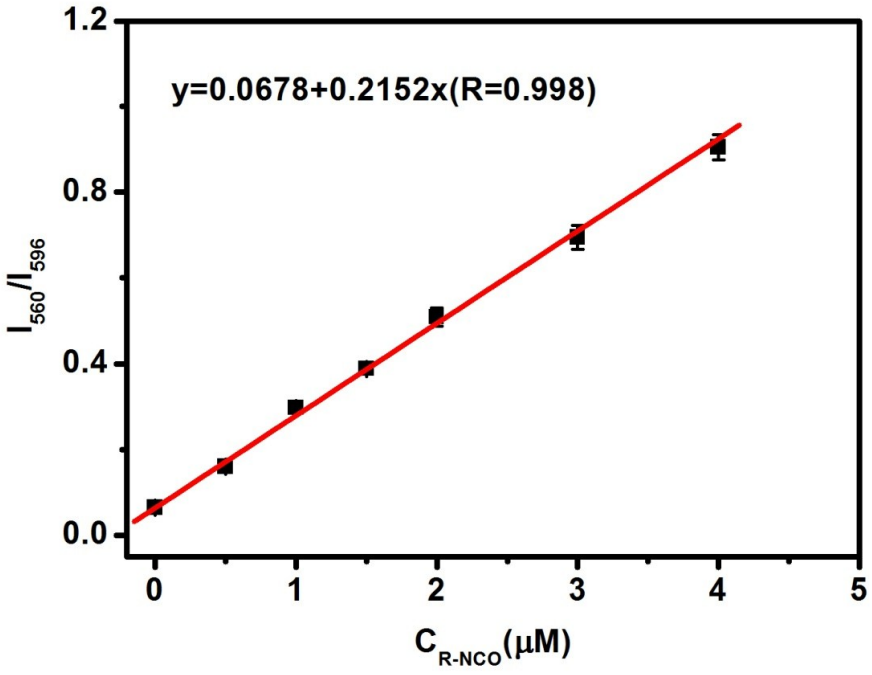


Figure S15. Fluorescence intensity ratio for the probe (4 μM) in as a function of $C_{R\text{-}NCO}$ upon the reaction time of 30 s. Excitation wavelength: 522 nm.

Determination of the detection limit:

First the calibration curve was obtained from the plot of fluorescence intensity ratio (I_{560}/I_{596}) as a function of the analyte concentration (R-NCO). 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 standarddeviation for the fluorescence intensity ratio of the probe in the absence of AFU.

I_{560}/I_{596} = 0.0687 +0.2152× [R-NCO] (R = 0.998)

LOD = 3 × 0.0069 / 0.2152 = 96 nM

References:

V. Thomsen, D. Schatzlein and D. Mercuro, Spectroscopy, 2003, 18, 112-114.

A. D. McNaught and A. Wilkinson, IUPAC Compendium of Chemical Terminology, 1997.

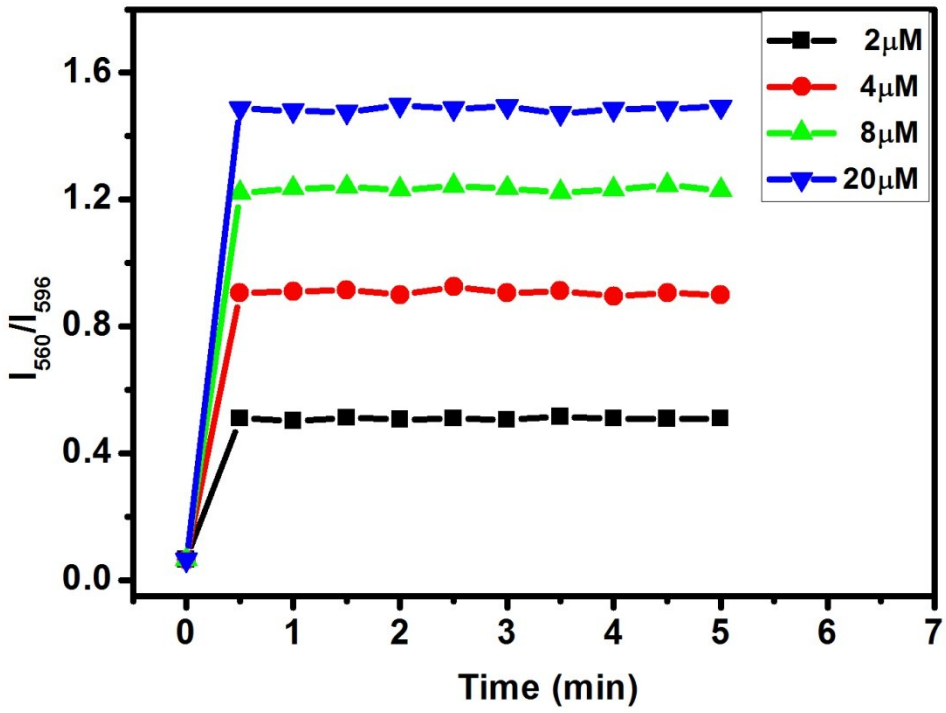


Figure S16. Fluorescence intensity ratio (I_{560}/I_{596}) as a function of time for the probe methanol solution with the addition of different concentrations of CEI.

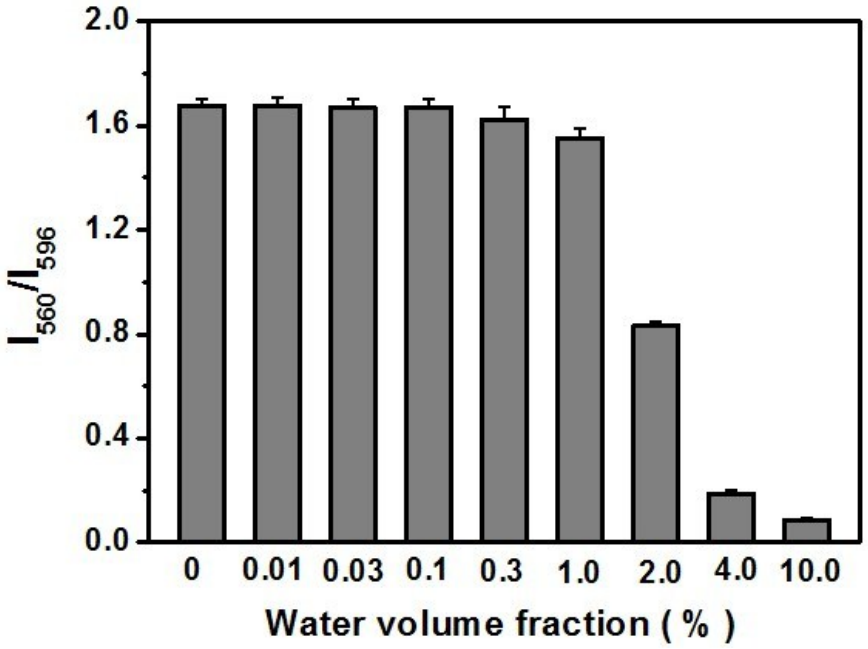


Figure S17. The probe's(4 μM) fluorescent response to isocyanates(40 μM) in methanol solutions containing different volume fraction of water.

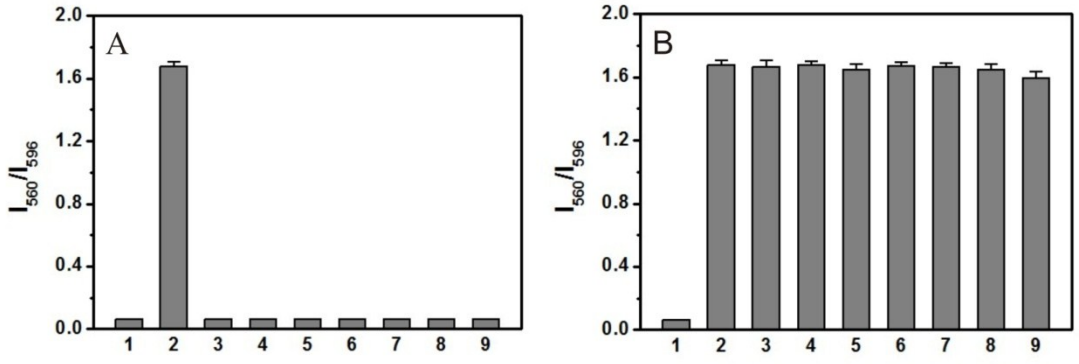


Figure S18. (A) Fluorescence response of 4 μM probe in the presence of common volatile organic compounds in methanol solution. (B) Fluorescence response of 4 μM probe in the presence of 40 μM CEI and with the addition of different volatile organic compounds respectively in methanol solution. Concentrations of the volatile organic compounds are 100 μM. 1-9 is blank, CEI, acetone, methylbenzene, chloroform, diethyl ether, ethyl acetate, propylene and formaldehyde respectively.

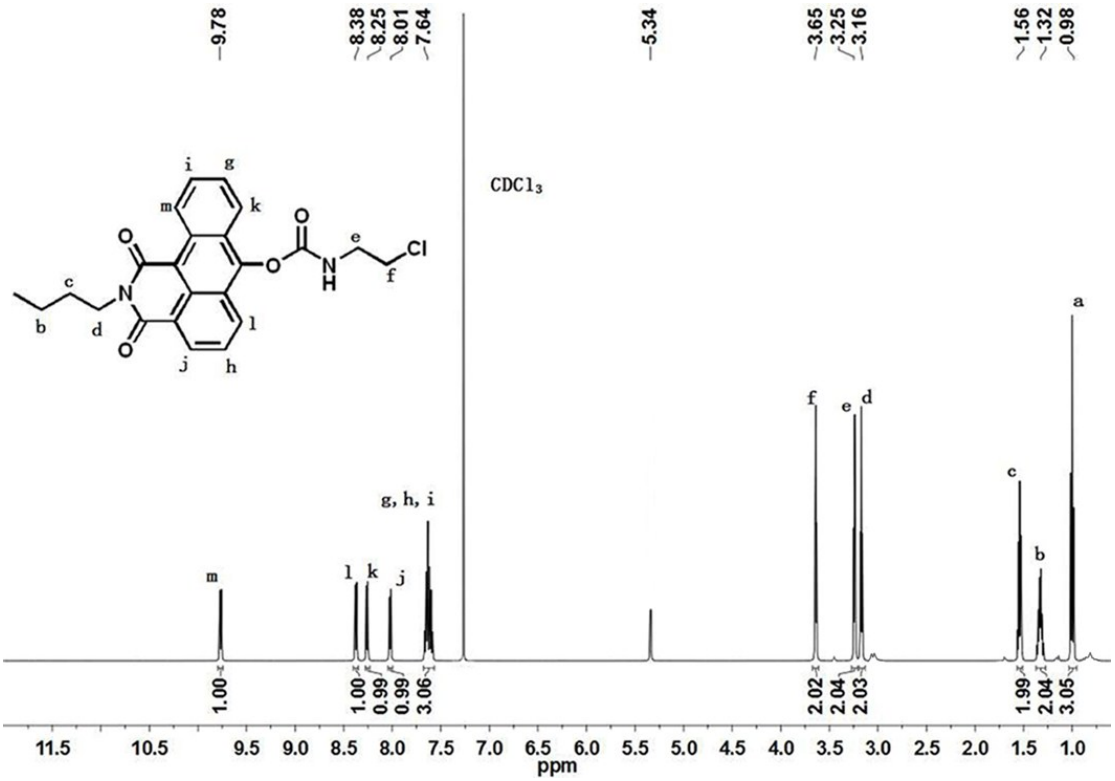


Figure S19. ^{1}H-NMR spectrum of the primary product separated from the reaction solution (in $CDCl_3$).

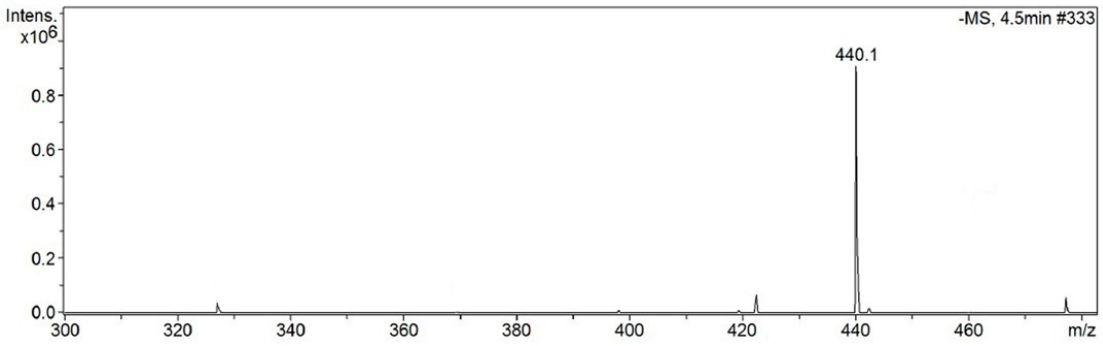


Figure S20. Mass spectrum of the primary product separated from the reaction solution. MS(ESI): m/z 440.1 $[M+OH]^-$.

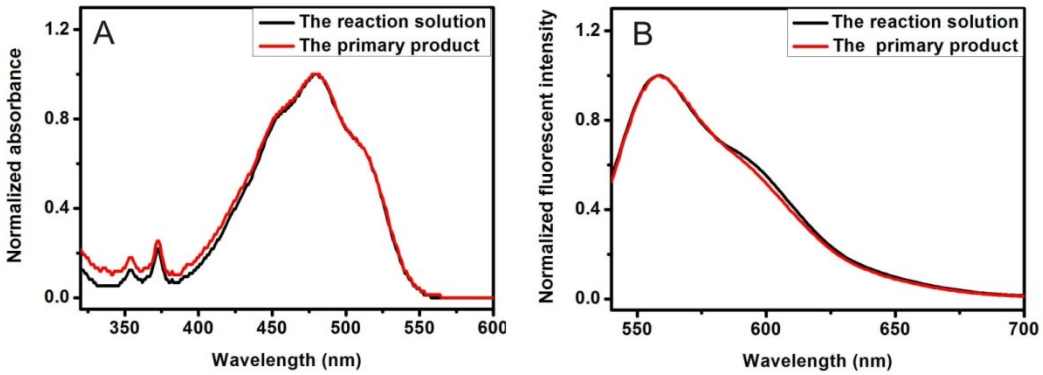


Figure S21. UV-vis absorption spectra (A) and fluorescence emission spectra (b) of the reaction solutions (black line) (containing 4 μM probe and 20 μM CEI) and the primary product (red line) (N-(n-butyl)-6-(2-chloroethylcarbamate)-anthracene carboximide) in methanol solutions.

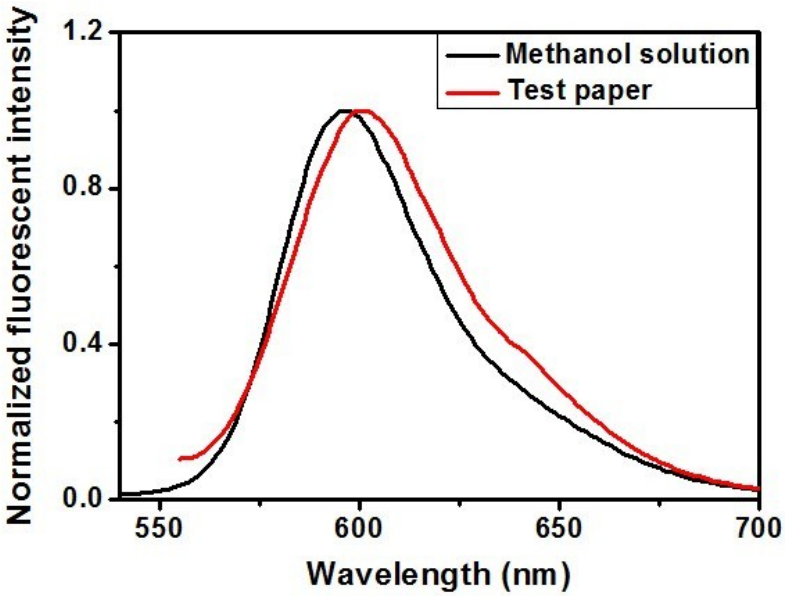


Figure S22. Normalized fluorescence spectra of probe methanol solution (black line) and test paper (red line). Excitation wavelength: 522 nm.

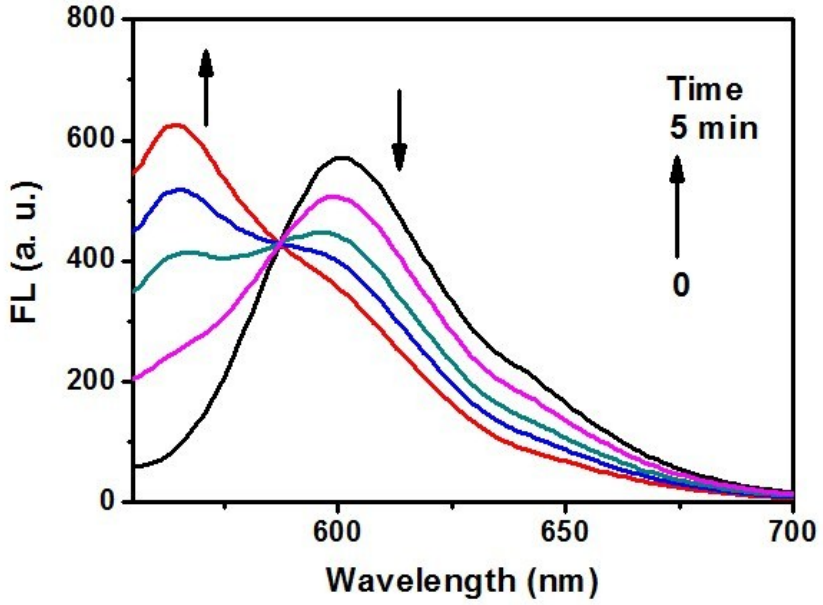


Figure S23. Time course of fluorescence spectra for the test paper upon exposure to CEI vapor.

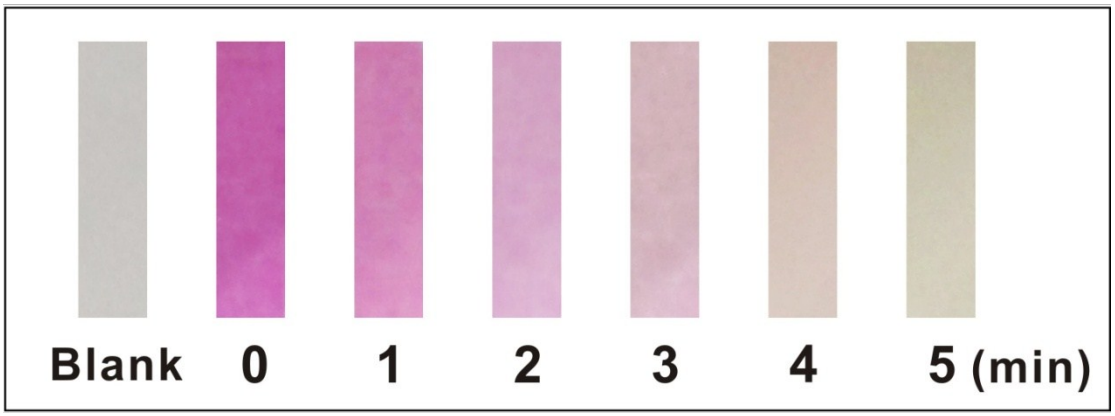


Figure S24. Photographs of test papers exposed to CEI vapor in different time under light field. The blank is for the untreated filter paper.