SUPPLEMENTARY INFORMATION

Fluorescence Detection of Volatile Amines using an Indanonalkene Platform

Peng Zhang,[a] Tianhong Wu,[a] Hui Cao,[d] Jie Zhang,[b,*] Tony D. James,[c,e*] and Xiaolong Sun[a,*]

[a]The Key Laboratory of Biomedical Information Engineering of Ministry of Education, School of Life Science and Technology, Xi’an Jiaotong University, Xi’an, 710049, P. R. China.

[b]The Fourth Military Medical University,169 Changle Xi Road, Xi'an Shannxi, 710032, P. R. China.

[c]Department of Chemistry, University of Bath, Bath, BA2 7AY, U.K.

[d]The State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi’an Jiaotong University, Xi’an 710049, China.

[e]School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, China.

Corresponding Authors:

zhangjie78@fmmu.edu.cn (J. Z); t.d.james@bath.ac.uk (T. D. J); x.l.sun86@xjtu.edu.cn (X. L. S)

Content:

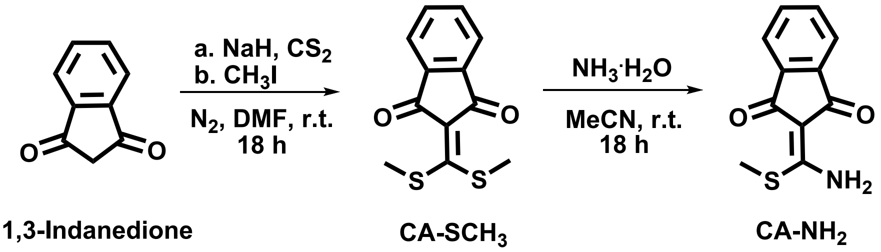
Materials and methods

Materials and instruments

All chemical reagents were purchased from Meryer, Aladdin Chemical Industry, and Energy Chemical, unless otherwise noted, and used without further purification. Phosphate buffers were prepared using distilled water. All cuvettes made by fused quartz were purchased from Starna Cells with standard screw and septum top. Silica gel from Qingdaohaiyang Chemical Company with 200-300 mesh was used for column chromatography.

^{1}H and ^{13}C NMR spectra were recorded on 400 MHz JEOL NMR spectrometer. High-resolution mass spectroscopic (HRMS) analysis was conducted by the WATERS I-Class VION IMS QTof mass spectrometer. The UV-vis absorbance spectra and molar extinction coefficient in water were obtained using a Cary 3500 UV-vis spectrophotometer from Agilent Technology. Concentration titrations and fluorescence spectra in different solvents were measured on a HITACHI F-7100 fluorescence spectrometer. Fluorescence spectra of powder were measured on and Edinburgh FLS980 fluorescence spectrometer. All fluorescence photographs were taken with a Canon EOS600D digital camera under a portable ultraviolet lamp (365 nm).

Synthesis of CA-SCH_3 and CA-NH_2



CA-SCH_3 was synthesized and purified according to the literature.[39] The production was obtained as yellow solid (90% yield).

For the synthesis of CA-NH_2, CA-SCH_3 (80 mg, 0.32 mmol, 1 eq.) was dissolved in MeCN (10 mL), followed by addition of $NH_3 \cdot H_2O$ (25% ammonia content, 1 mL, 6.5mmol, 20 eq.). The mixture was left to react overnight with constant stirring at room temperature. Then the mixture precipitated. The precipitates (CA-NH_2) was then filtered off and washed with water and light petroleum to give 37.6 mg (54%) as yellow crystals. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (m, 2H), 7.57 (t, *J* = 3.2, 2.76 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 171.63, 138.98, 133.60, 121.31, 12.18. HRMS(ES+) m/z: calcd for

$C_{11}H_9NO_2S$ $[M+H]^+$ 220.04268 found 220.04289. The NMR and HRMS spectra are shown in Figure S7, S8, S9.

Preparation of Paper-Based Sensor and Soft CA-PEG Gel

A volume of 40 μL of CH_2Cl_2 stock solution of the CA-SCH_3 (10 mM) was drop-casted onto the Whatman filter paper. The paper-based sensor CA-SCH_3 was prepared when the solvent evaporated dry.

CA-SCH_3 (2 eq.) and one equivalent of 4-arm PEG thiol (M_n ~ 5.0 kDa, 1 eq.) were mixed together in DMSO (100 μL). Triethylamine (0.01 eq.) was then added and vortexing was continued to obtain a solution. The solution was transferred to different shaped polytetrafluoroethylene templates and after 3 h the CA-PEG gel was formed. The hydrogel was swollen in acetonitrile to remove small molecules and dried for storage.

UV-Vis Absorbance Spectra

The UV-vis absorbance spectra in water was obtained using a Cary 3500 UV-vis spectrophotometer from Agilent Technology. The spectra were run in Cary WinUV software. The synthesized compounds CA-SCH_3 and CA-NH_2 were dissolved in DMSO as stock solutions (10 mM), which were subsequently diluted to 10 μM with MeCN for UV-vis experiments. Time-dependent UV-vis spectra of reaction between CA-SCH_3 and ammonia was carried out in a 1% aqueous system.

Fluorescence Spectra

The synthesized compounds CA-SCH_3 and CA-NH_2 were diluted to 10 μM with MeCN for fluorescent spectra experiments. Concentration titrations and fluorescence spectra in different solvents were measured on a HITACHI F-7100 fluorescence spectrometer. Time-dependent fluorescent spectra between CA-SCH_3 and ammonia was carried out in a 1% aqueous system. Paper-based CA-SCH_3 sensor and CA-PEG gel were exposed to various concentrations of amine vapors (0 - 624 ppm) produced by various concentrations of $NH_3 \cdot H_2O$, and then, fluorescence spectra of powder and paper-based sensors were measured on and Edinburgh FLS980 fluorescence spectrometer.

Detection of Amine Vapors Generated from Rotten Food

We evaluated the paper-based CA-SCH_3 sensor for food spoilage evaluation. Two sealed boxes each containing 100 g of cod fillet stored at 4 °C and 25 °C for 5 days. The sensor CA-SCH_3 was then placed in the box for 2 hours. Then, fluorescence photographs were taken under a portable ultraviolet lamp (365 nm).

Supplementary figures

Fluorescence images for the reaction

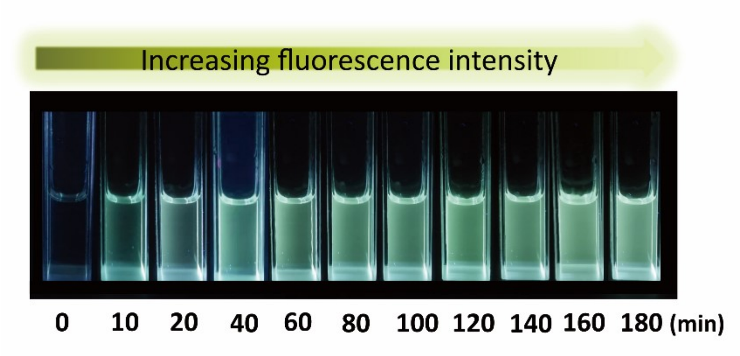


Figure S1. The images of **CA-SCH$_3$** fluorescence changes taken under UV light (365 nm) with increasing NH$_3$·H$_2$O titration time.

DFT calculations

DFT theoretical calculations were carried out using the Gaussian 09 program package. All the geometries of compounds were optimized at B3LYP/6-31+G(d) level without CPCM solvation model. The molecular orbital (MO) plots and MO energy levels were computed at the same level of theory.

Optical property for CA-SCH$_3$ and CA-NH$_2$

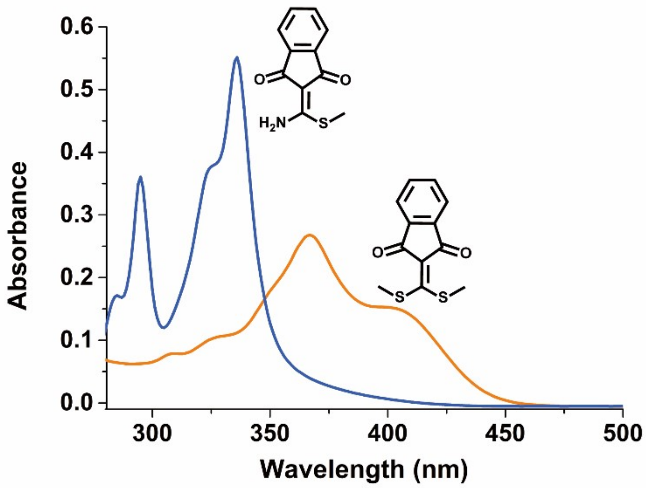


Figure S2. Absorbance spectra of **CA-SCH$_3$** (10 μM) and **CA-NH$_2$** (10 μM) in MeCN.

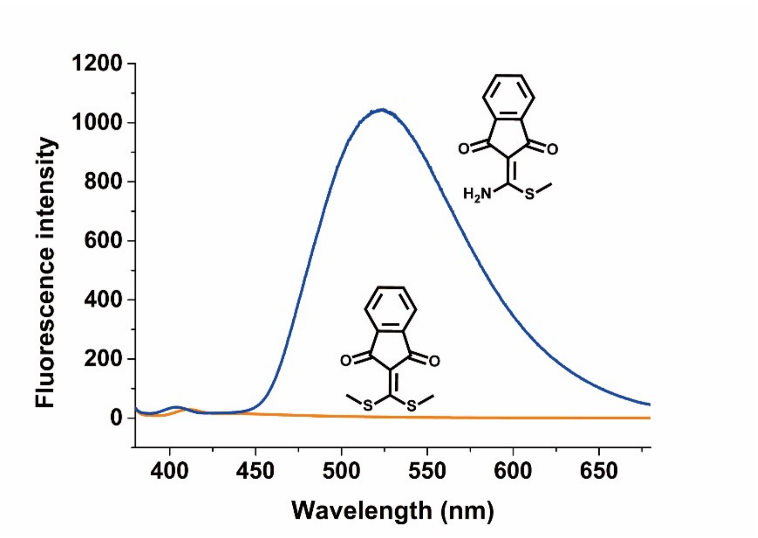


Figure S3. Emission spectra of **CA-SCH$_3$** (10 μM) and **CA-NH$_2$** (10 μM) in MeCN under excitation at 336 nm.

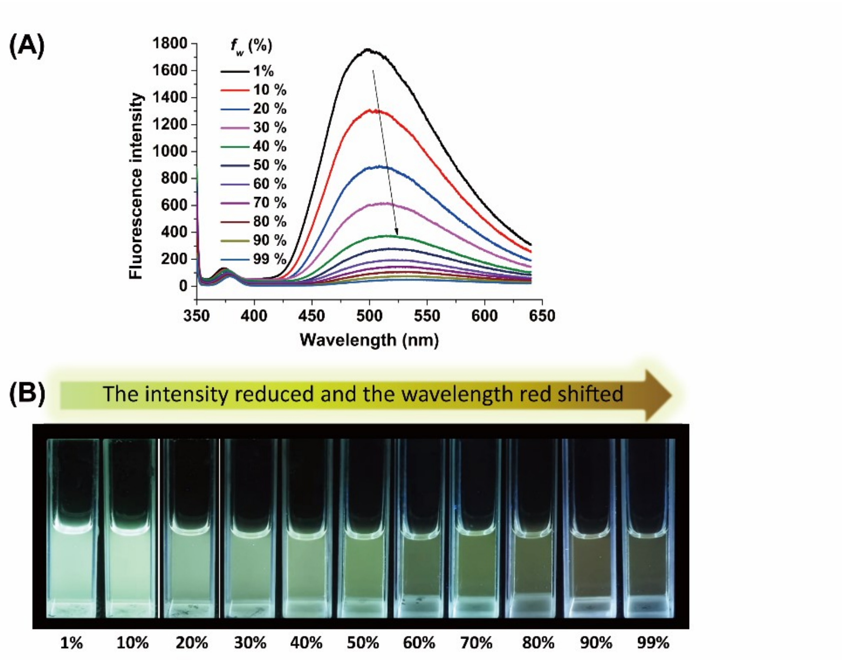


Figure S4. (A) Fluorescence spectra of **CA-SCH$_3$** (10 μM) and $NH_3·H_2O$ (0.0125%) in different proportions of H_2O / DMSO for 30 min. (B) **CA-SCH$_3$** fluorescence changes taken under UV light (365 nm) with the increased water fraction.

Calculation of detection limit

The detection limit (3*δ/S*) for ammonia vapor was calculated by the signal-to-noise ratio method.

$$\mathrm{LOD} = 3\delta/S$$

δ: Standard deviation of fluorescence intensity of 10 blank probes; S: The slope of the analysis calibration curve in the low concentration range.

Synthesis of hydrogel

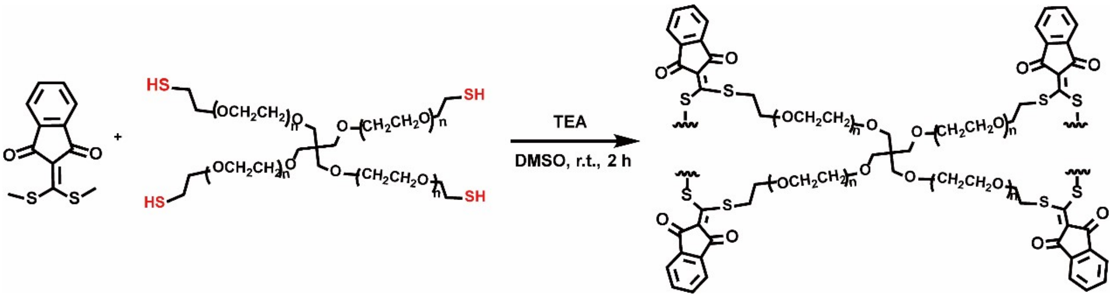


Figure S5. Schematic diagram of **CA-PEG** hydrogel synthesis.

Scanning electron microscope (SEM) image of CA-PEG gel

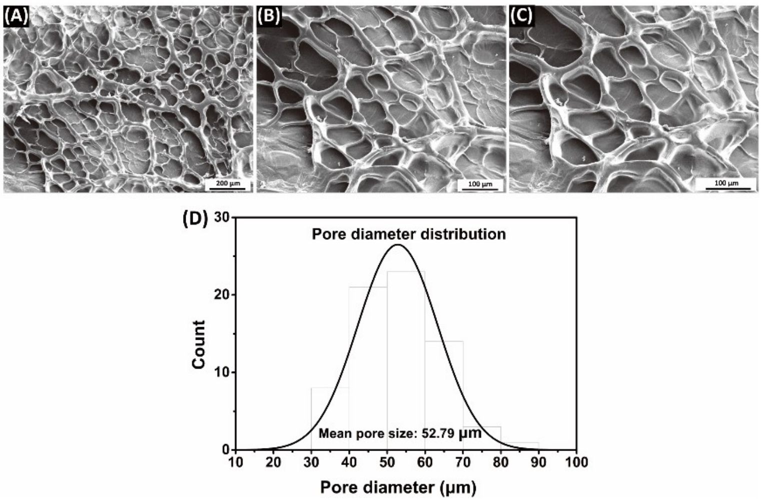


Figure S6. SEM images of **CA-PEG** gel. Picture (A), (B) and (C) are 200×, 400×, and 500× magnified images under 10kV voltage conditions, respectively. (D) Pore diameter distribution map obtained by aperture analysis software. The mean pore size of **CA-PEG** is about 52.79 µm.

NMR spectra and HRMS of CA-NH_2

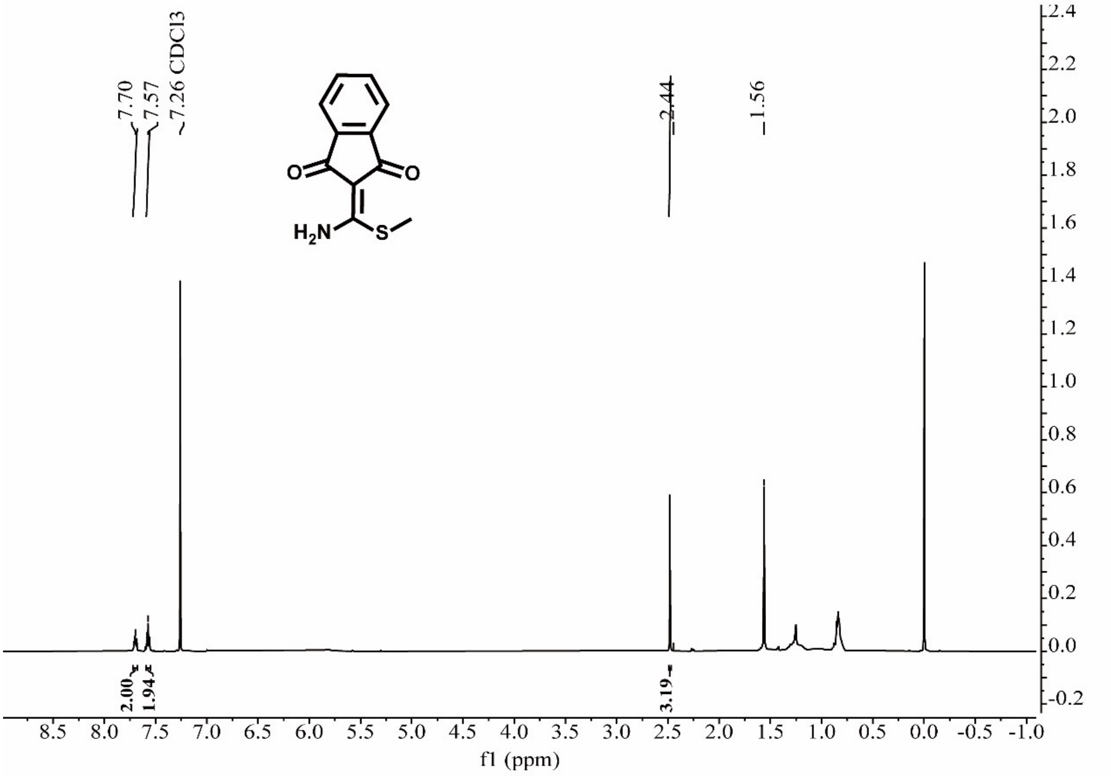


Figure S7. ^{1}H NMR spectra for compound **CA-NH$_2$** in CDCl$_3$.

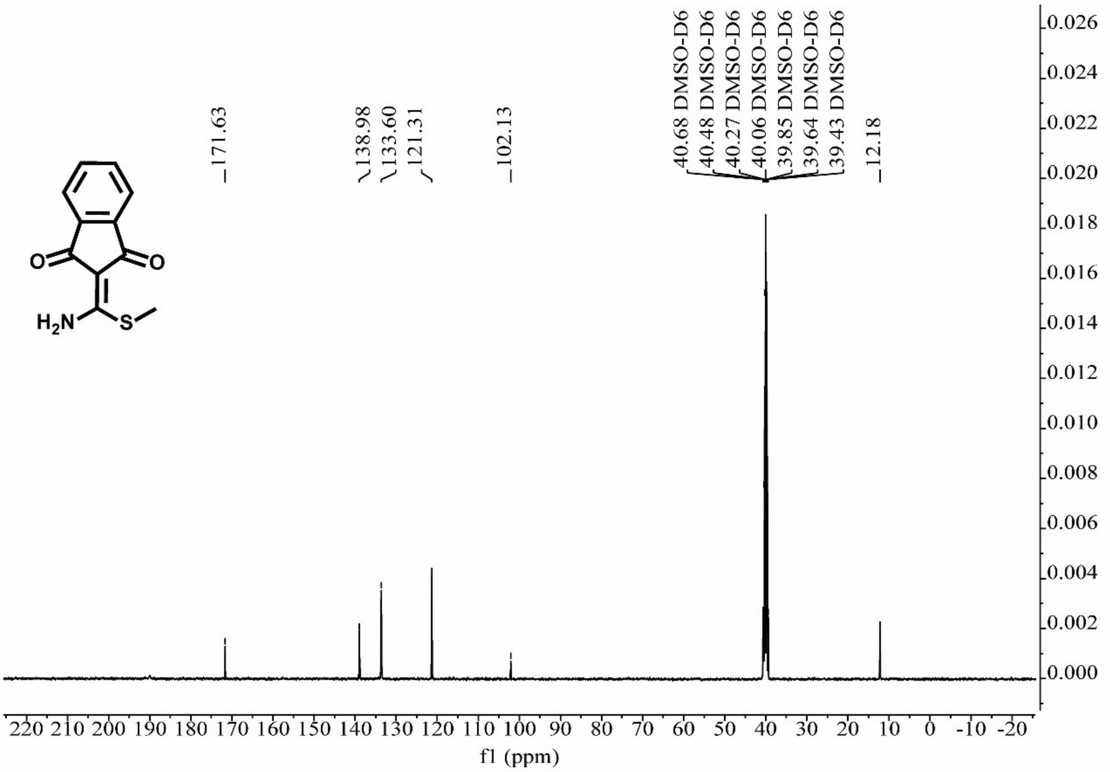


Figure S8. ^{13}C NMR spectra for compound **CA-NH$_2$** in DMSO-*d*6.

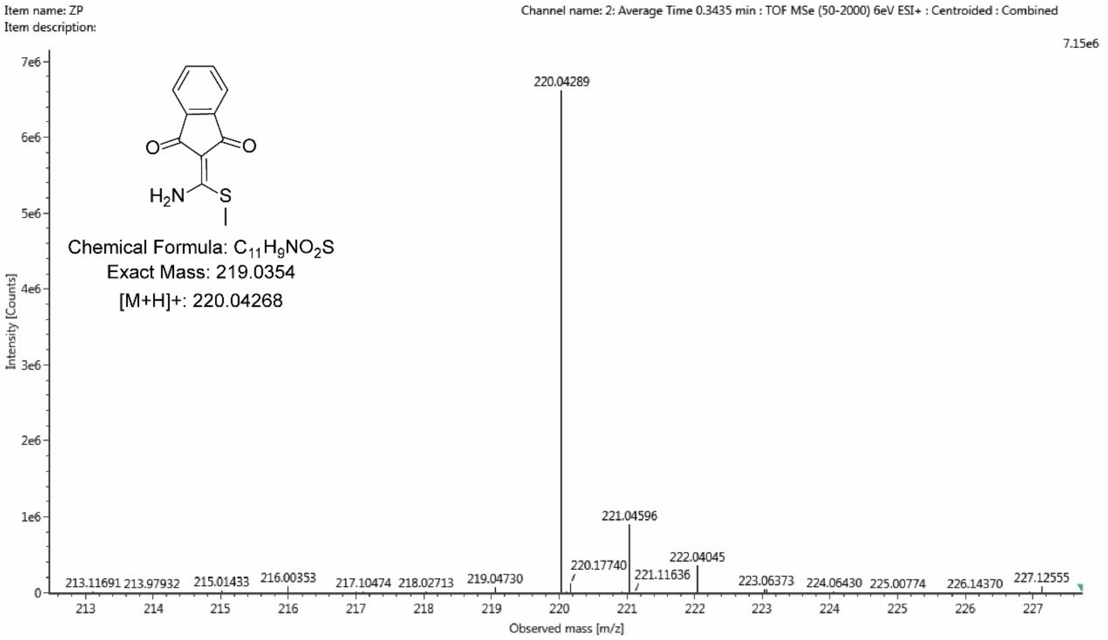


Figure S9. Quadrupole–time-of-flight mass spectra (Q-TOF-MS) of **CA-NH$_2$**.