

Electronic Supplementary Information

A Paper-Based Chemosensor for Highly Specific, Ultrasensitive, and Instantaneous Visual Detection of Toxic Phosgene

Lintao Zeng,^{*a,c} Hongyan Zeng,^c Shuangfei Wang,^a Shan Wang,^b Ji-Ting Hou^{*b} and Juyoung Yoon^{*d}

^a College of Light Industry and Food Engineering, Guangxi University, Nanning 530004, PR China. E-mail: zlt1981@126.com. (L. Zeng)

^b College of Chemistry and Chemical Engineering, Xinyang Normal University, Xinyang 464000, PR China. E-mail: hujiting2206@163.com. (J.-T. Hou)

^c Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, Tianjin University of Technology, Tianjin 300384, PR China.

^d Department of Chemistry and Nanoscience, Ewha Womans University, Seoul 03760, Korea. E-mail: jyoon@ewha.ac.kr. (J. Yoon)

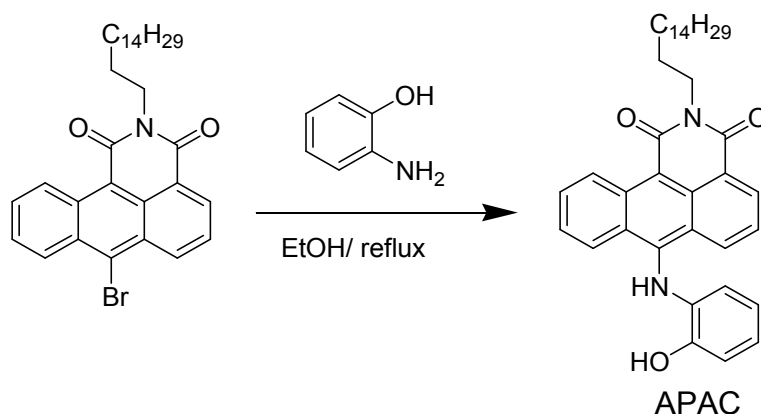
Table of Contents

| | |
|---|----|
| 1. Materials and General Methods | S2 |
| 2. Synthesis of chemosensor APAC | S2 |
| 3. Preparation of sample solutions for spectral measurements..... | S3 |
| 4. Determination of the detection limit | S3 |
| 5. Spectral responses of APAC towards various analytes | S5 |
| 6. Spectral responses of APAC towards HNO ₂ | S5 |
| 7. Exploration of Reaction Mechanism..... | S5 |
| 8. Preparation of Flexible Paper-Based Chemosensor | S6 |
| 9. Detection of Phosgene Vapor with Paper-Based Chemosensor | S6 |
| 10. NMR and HR-MS spectra..... | S7 |

1. Materials and General Methods

Unless otherwise mentioned, all reagents were purchased from Sigma-Aldrich and used directly without further purifications. ^1H and ^{13}C NMR spectra were measured on a Bruker AV spectrometer by using tetramethylsilane (TMS) as the internal standard. High-resolution mass spectra (HRMS) were recorded on a HP-1100 LC-MS spectrometer. UV-vis absorption and fluorescence spectra were measured with a Hitachi UV-3310 spectrometer and a FL-4500 fluorometer, respectively. Relative fluorescence quantum yields were determined by using rhodamine B ($\Phi = 0.65$ in ethanol) and fluorescein ($\Phi = 0.92$ in 0.1 M NaOH) as references.^[1]

2. Synthesis of chemosensor APAC



Under a nitrogen atmosphere, a mixture of 10-bromo-anthracene hexadecyl carboxyimide^[2] (164 mg, 0.3 mmol), 2-aminophenol (165 mg, 1.5 mmol) and NEt_3 (61 mg, 0.6 mmol) in 15 ml anhydrous EtOH was stirred at 80°C for 5 h. Then the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography using $\text{CH}_2\text{Cl}_2/\text{EtOH} = 40/1$ (v/v) as the eluent to afford APAC as a brick red solid (47 mg, 40%). ^1H NMR (400 MHz, Chloroform-*d*) δ /ppm 10.11 (d, $J = 9.2$ Hz, 1H), 8.74 (d, $J = 6.8$ Hz, 1H), 8.45 (d, $J = 8.4$ Hz, 1H), 8.25 (d, $J = 8.8$ Hz, 1H), 7.82 (t, $J = 7.8$ Hz, 1H), 7.60 – 7.53 (m, 2H), 7.03 (d, $J = 7.6$ Hz, 1H),

6.85 (t, $J = 7.6$ Hz, 1H), 6.65 (t, $J = 7.6$ Hz, 1H), 6.30 (d, $J = 7.6$ Hz, 1H), 5.87 (s, 1H), 4.33 – 4.28 (m, 2H), 1.86 – 1.79 (m, 2H), 1.52 – 1.27 (m, 26H), 0.90 (t, $J = 6.6$ Hz, 3H). ^{13}C NMR (150 MHz, DMSO- d_6) δ /ppm 167.4, 164.3, 163.4, 148.5, 135.1, 134.4, 133.8, 132.2, 132.1, 131.5, 130.0, 129.1, 126.7, 125.8, 125.2, 124.0, 123.4, 122.3, 122.2, 120.2, 120.0, 116.3, 67.9, 38.5, 31.7, 30.3, 29.5, 29.4, 29.2, 28.8, 28.0, 27.1, 23.7, 22.9, 22.6, 14.4, 11.3. HR-MS (ESI): calculated for $[\text{C}_{38}\text{H}_{46}\text{N}_2\text{O}_3 + \text{H}]^+$ 579.3581, found 579.3579.

3. Preparation of sample solutions for spectral measurements

Since phosgene is a high toxic gas, a nonvolatile and less toxic precursor triphosgene instead of phosgene gas was employed to in situ produce phosgene in chloroform. Stock solution of the APAC (1 mM) was diluted to 10 μM in chloroform (HPLC grade) as the test solution. Stock solutions (1 mM) of triphosgene, toluenesulfonyl chloride (TsCl), benzoyl chloride (BzCl), SOCl_2 , POCl_3 , acetyl chloride (AC), chloroacetyl chloride (CAC), oxalyl chloride (OC), diethyl cyanophosphonate (DECP), dimethyl methylphosphonate (DMMP), diethyl chlorophosphate (DCP) were prepared in chloroform. All spectroscopic experiments were carried out at room temperature.

4. Determination of the detection limit

The detection limit was calculated according to fluorescence titration of APAC at low concentration (1 μM). Fluorescence intensity F_{484} was linearly fitted to the triphosgene concentration in the range of 0 - 4 μM . According to the equation: detection limit (LOD) = $3 \times \sigma/k$, where σ represents the standard deviation of the fluorescence intensity of APAC (1 μM) in the absence of triphosgene, k is the slope of the curve equation. The detection limit of APAC for triphosgene was calculated to be 4.6 nM.

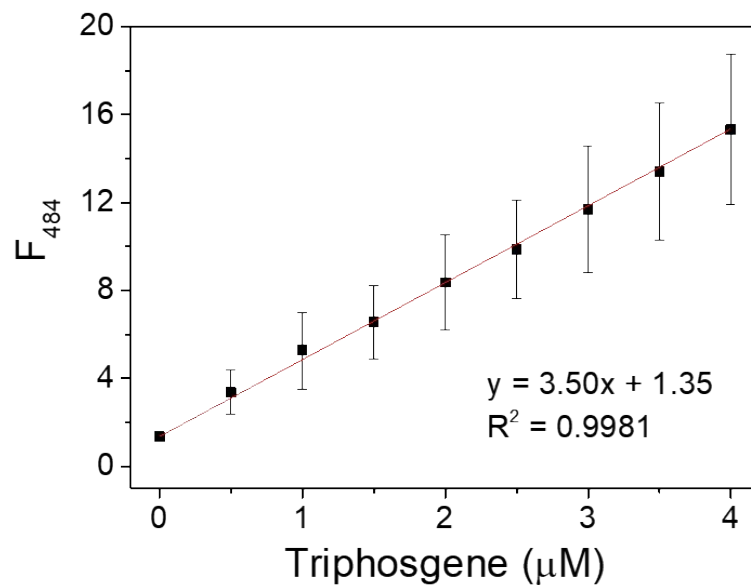


Figure S1. Linear relationships of fluorescence intensity (F_{484}) of APAC (1 μM) versus concentrations of triphosgene in CHCl_3 (containing 0.1% TEA). $\lambda_{\text{ex}} = 432 \text{ nm}$, slits: 2.5 nm/2.5 nm. Error bars are $\pm \text{SD}$ $n = 3$.

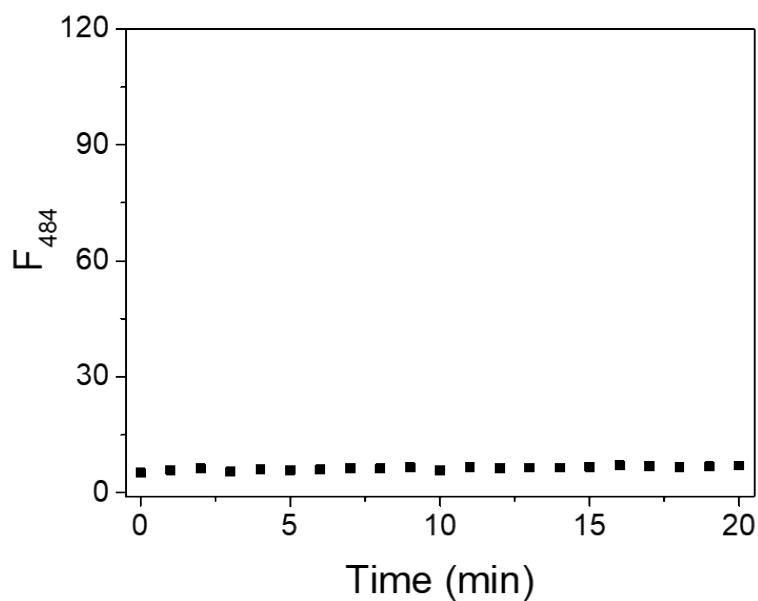


Figure S2. Time-dependent fluorescence response of APAC (10 μM) to triphosgene (30 μM) in CHCl_3 . $\lambda_{\text{ex}} = 432 \text{ nm}$, slits: 2.5 nm/2.5 nm.

5. Spectral responses of APAC towards various analytes

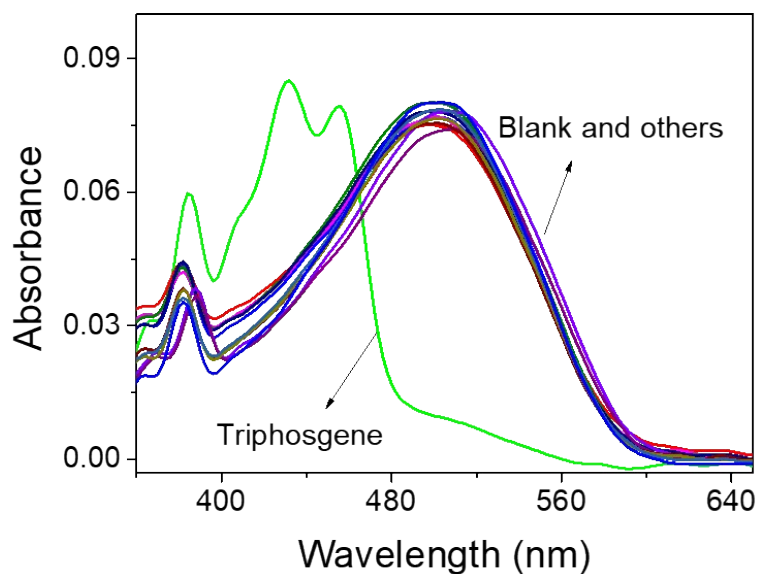


Figure S3. UV-vis absorption spectra response of APAC (10 μM) toward triphosgene (3 equiv)/TEA (0.1%) and other analytes (30 μM) in CH_3Cl .

6. Spectral responses of APAC towards HNO_2

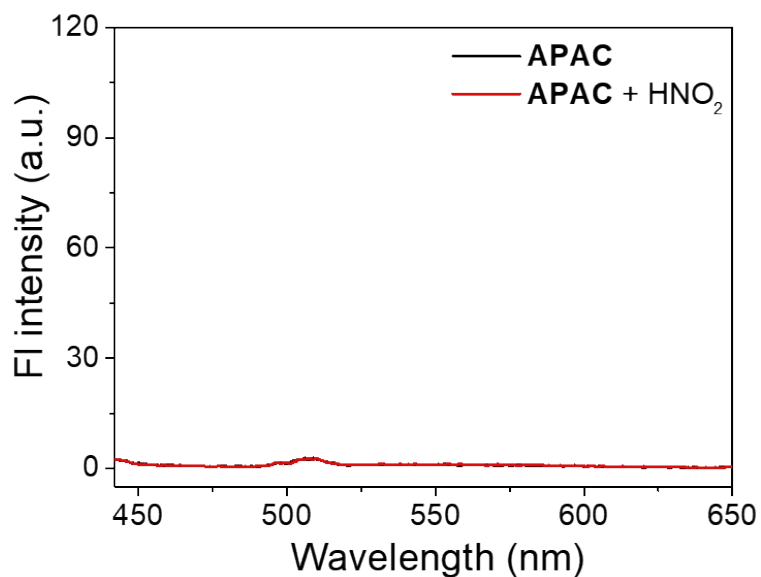


Figure S4. Fluorescence spectral changes of APAC (10 μM) after the addition of HNO_2 (100 μM) in an EtOH/HCl solution ($v/v = 1/4$, $\text{pH} = 1$). $\lambda_{\text{ex}} = 432$ nm, slits: 2.5 nm/2.5 nm.

Table S1. The photophysical data of **APAC** and **APAC-Phos**.

| | $\lambda_{\text{abs}}/\text{nm}$ | $\lambda_{\text{em}}/\text{nm}$ | $\Delta\lambda/\text{nm}$ | $\epsilon/\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ | Φ_f |
|-----------|----------------------------------|---------------------------------|---------------------------|--|----------|
| APAC | 510 | / | / | 9014 | 0.06% |
| APAC-Phos | 432 | 484 | 52 | 7300 | 56.4% |

7. Exploration of Reaction Mechanism

Probe **APAC** (30 mg, 52 μmol), triphosgene (46 mg, 156 μmol) and 20 ml of chloroform solution were placed in a two-necked flask, then 20 μL of triethylamine was added to the flask. The reaction mixture was stirred at room temperature for 30 min. After the reaction was completed, the solvent was removed under reduced pressure. The product was isolated by column chromatography to afford a yellow solid **APAC-Phos** (24 mg, 76%). ^1H NMR (400 MHz, Chloroform-*d*) δ /ppm 10.23 (d, $J = 9.2$ Hz, 1H), 8.85 (d, $J = 6.0$ Hz, 1H), 8.13 (d, $J = 7.6$ Hz, 1H), 7.88 (d, $J = 8.8$ Hz, 1H), 7.83 – 7.78 (m, 1H), 7.75 – 7.67 (m, 2H), 7.57 – 7.50 (m, 2H), 7.12 (t, $J = 7.2$ Hz, 1H), 6.42 (d, $J = 8.0$ Hz, 1H), 4.35 – 4.31 (m, 2H), 1.86 – 1.71 (m, 4H), 1.49 – 1.28 (m, 24H), 0.90 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ /ppm 167.7, 164.6, 163.2, 153.1, 143.1, 134.1, 133.6, 132.8, 131.9, 131.3, 130.9, 129.8, 128.9, 128.6, 127.9, 127.5, 126.5, 124.6, 123.9, 123.4, 123.2, 118.2, 110.8, 109.6, 65.6, 41.0, 31.9, 29.7, 29.6, 29.4, 28.2, 27.3, 22.7, 19.2, 14.1, 13.7. HR-MS (ESI): calculated for $[\text{C}_{39}\text{H}_{44}\text{N}_2\text{O}_4 + \text{H}]^+$ 605.3374, found 605.3371.

8. Preparation of Flexible Paper-Based Chemosensor

2 mg of **APAC** and 1 g of poly(ethylene oxide) were dissolved in 20 mL chloroform, and they were stirred for 10 min to completely disperse. Filter paper was cut to the size of 0.5×2 cm, and immersed into the above solution for 5 min. Then, the paper stripes were taken out and dried in air. Finally, the paper stripes with chemosensor **APAC** serve as the flexible paper-based chemosensor for detection of phosgene in the gas phase.

9. Detection of Phosgene Vapor with Paper-Based Chemosensor

Phosgene vapors at various concentrations were prepared according to literature procedures.^[3,4] Five concentrations of triphosgene solutions (6.75, 33.75, 67.5, 135 and 270 mM) were prepared in CHCl_3 , and 10 μL of each solution were deposited into a 5 mL centrifuge tubes, respectively, followed by the addition of 10 μL of chloroform containing 0.1% TEA to each tube. Then, a test strip was put into the tube and the lid was immediately shut. 1 min later, the fluorescence color of the test strip was recorded under a 365 nm UV lamp.

10. NMR and HR-MS spectra

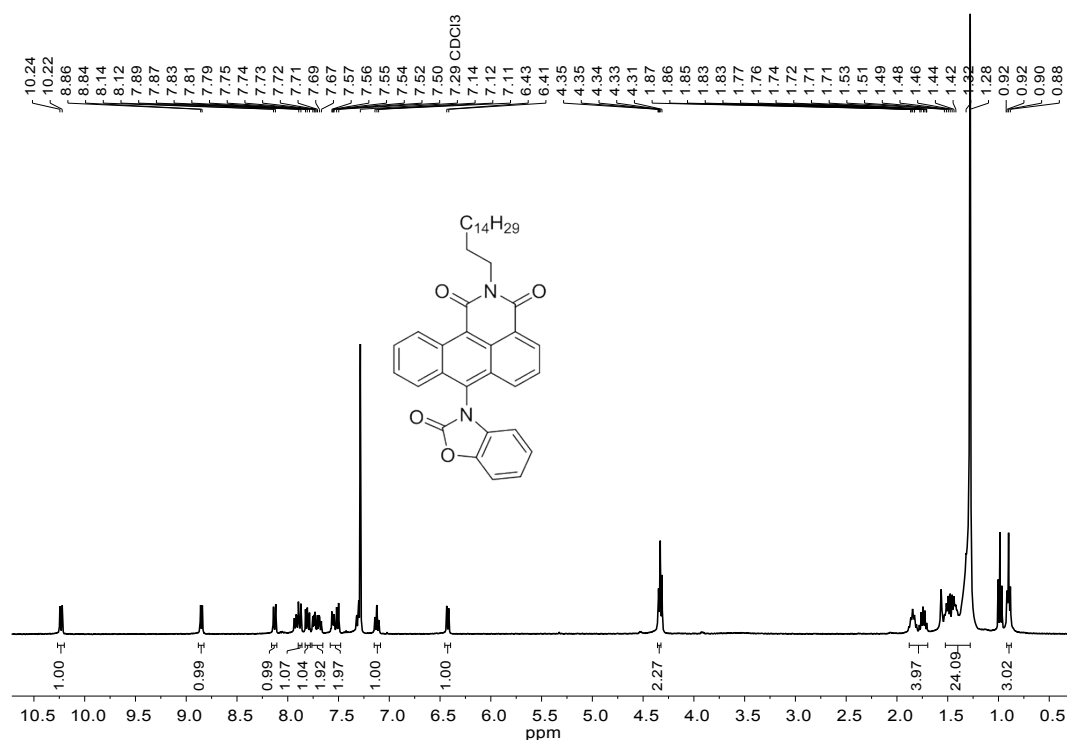


Figure S5. ^1H NMR spectrum of APAC-Phos in CDCl_3 (400 MHz).

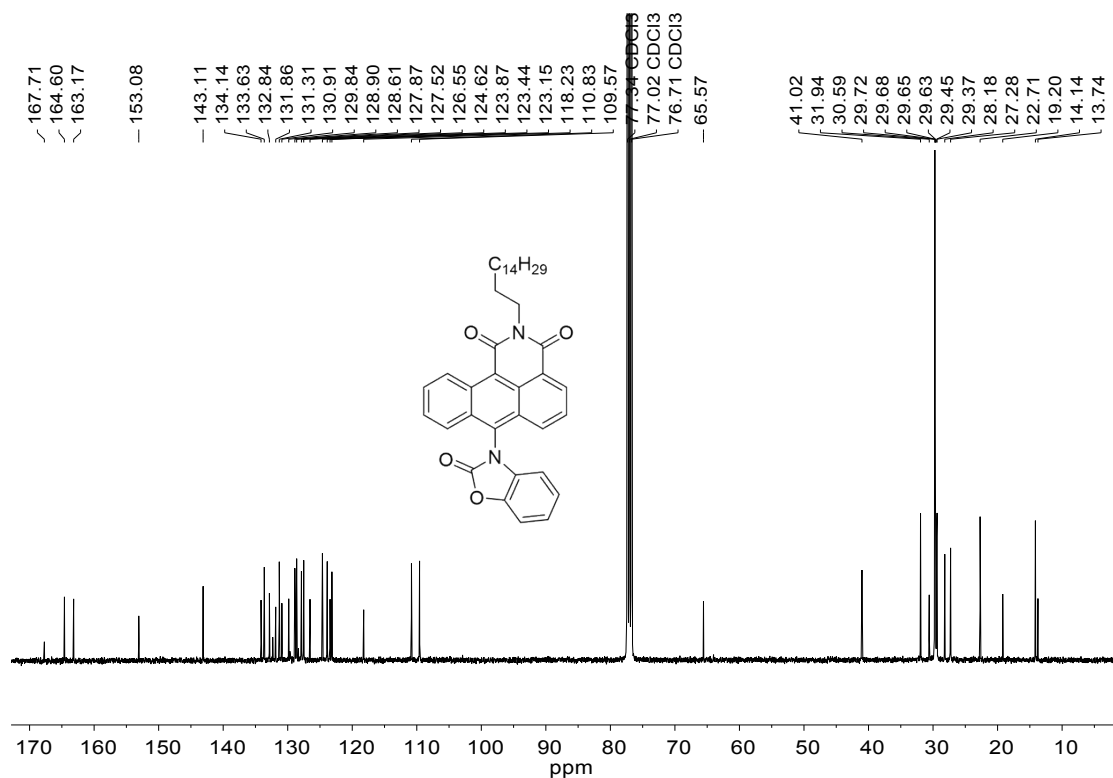


Figure S6. ^{13}C NMR spectrum of APAC-Phos in CDCl_3 (100 MHz).

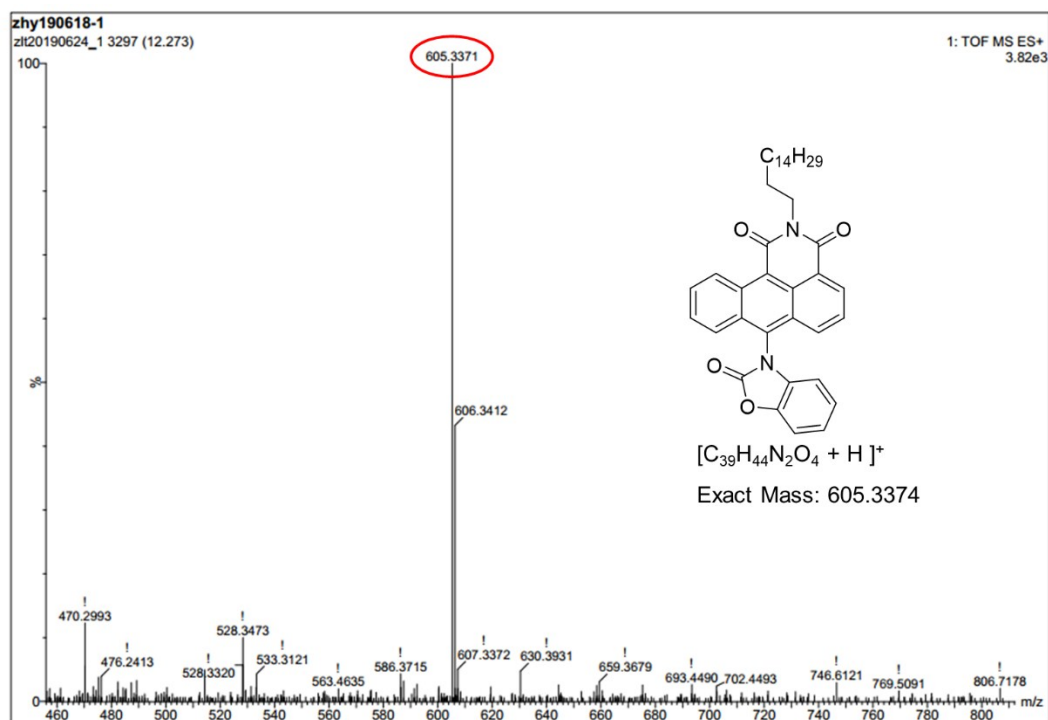


Figure S7. HR-MS (ESI) spectrum of APAC-Phos.

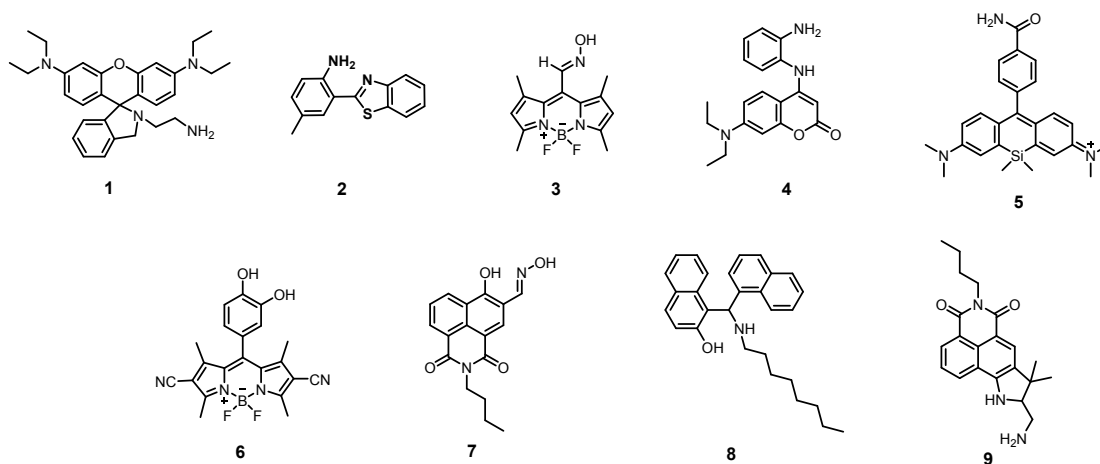


Figure S8. Chemical structures of some previously reported fluorescence probes for phosgene.

Table S2. Detection performance of fluorescence probes for phosgene.

| Probe | Excitation | Emission | Limit of detection | Detection system | Response time | Application | Reference |
|-------------|------------|----------|--------------------|--------------------|---------------|------------------------|-----------|
| 1 | 560 nm | 590 nm | 50 nM | DMF | Not mentioned | Test paper | [5] |
| 2 | 375 nm | 495 nm | 0.14 ppm | CHCl ₃ | 5 min | Test paper | [6] |
| 3 | 530 nm | 570 nm | 0.31 nM | CH ₃ CN | 10 s | TLC plate | [7] |
| 4 | 368 nm | 446 nm | 3 nM | CH ₃ Cl | 20 s | Test paper | [8] |
| 5 | 653 nm | 679 nm | 8.9 nM | CH ₃ CN | 4 min | Test paper | [9] |
| 6 | 480 nm | 516 nm | 2.4 ng/L | CH ₃ CN | 3 s | TLC plate | [10] |
| 7 | 382 nm | 577 nm | 0.09 nM | AcCN | 2 s | PCL nanober composite | [11] |
| 8 | 350 nm | 430 nm | 0.4 μM | CH ₃ CN | < 1.0 min | TLC test strip | [12] |
| 9 | 400 nm | 488 nm | 0.3 nM | CH ₃ CN | 60 s | Nanofibrous test strip | [13] |
| APAC | 432 nm | 484 nm | 4.6 nM | CHCl ₃ | 15 s | Test paper | This work |

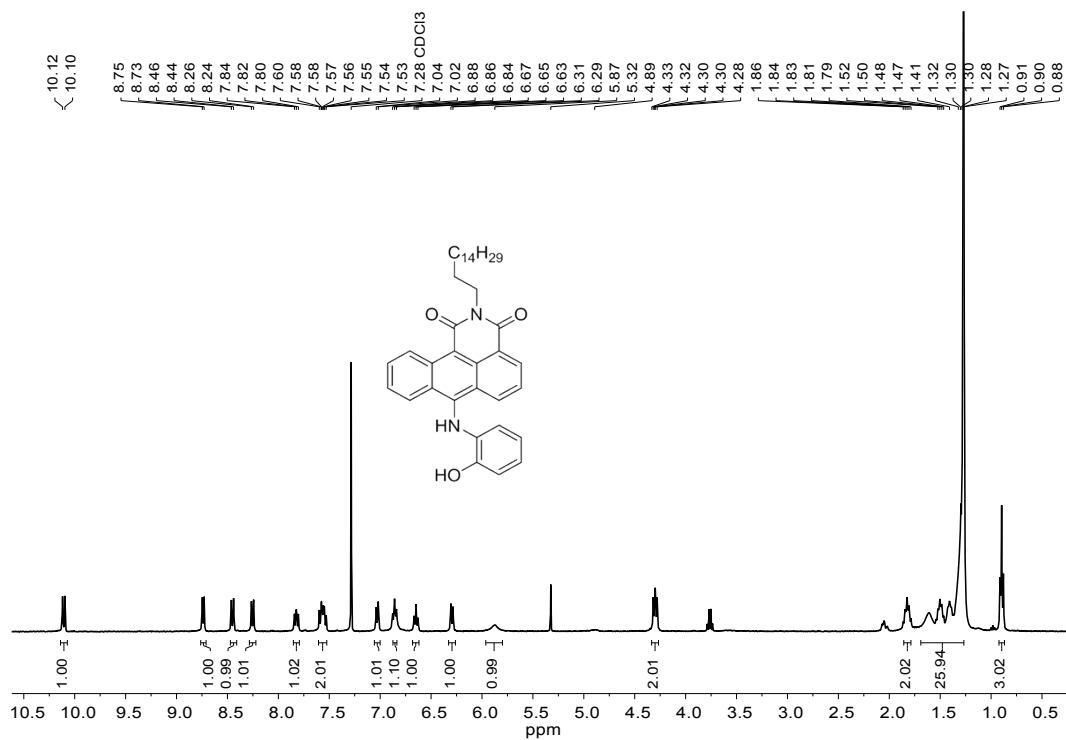


Figure S9. ¹H NMR spectrum of APAC in CDCl₃ (400 MHz).

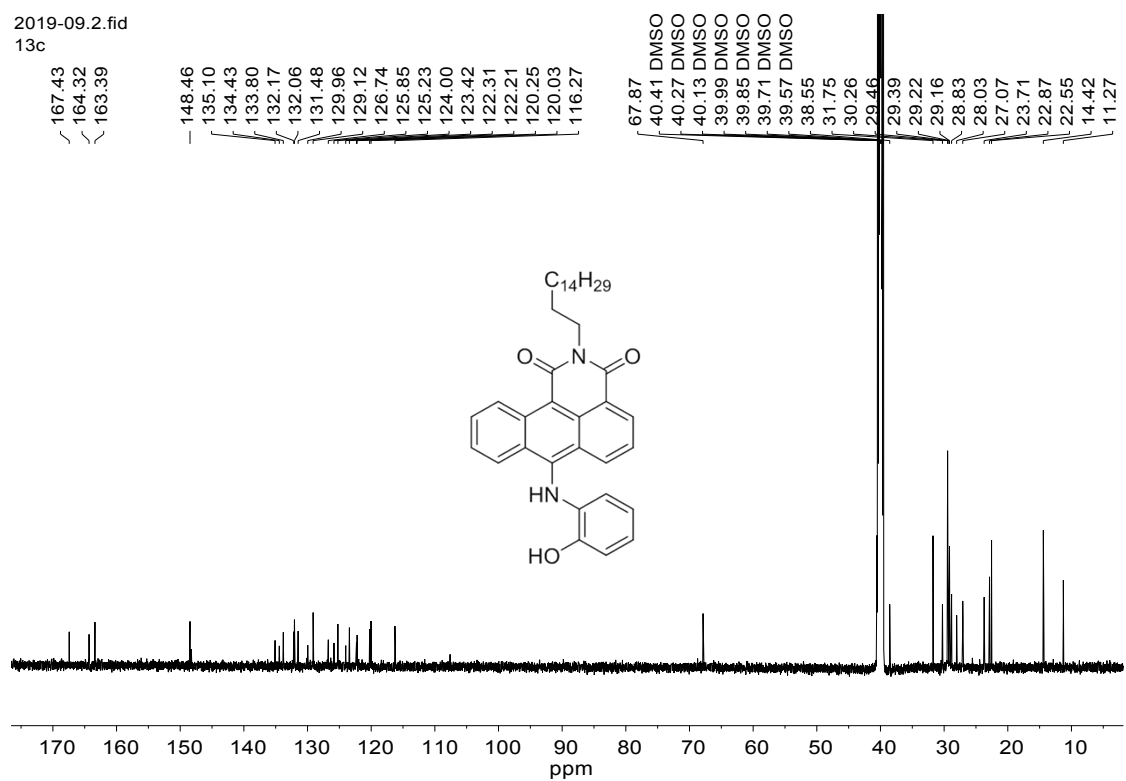


Figure S10. ¹³C NMR spectrum of the APAC in DMSO-*d*₆ (150 MHz).

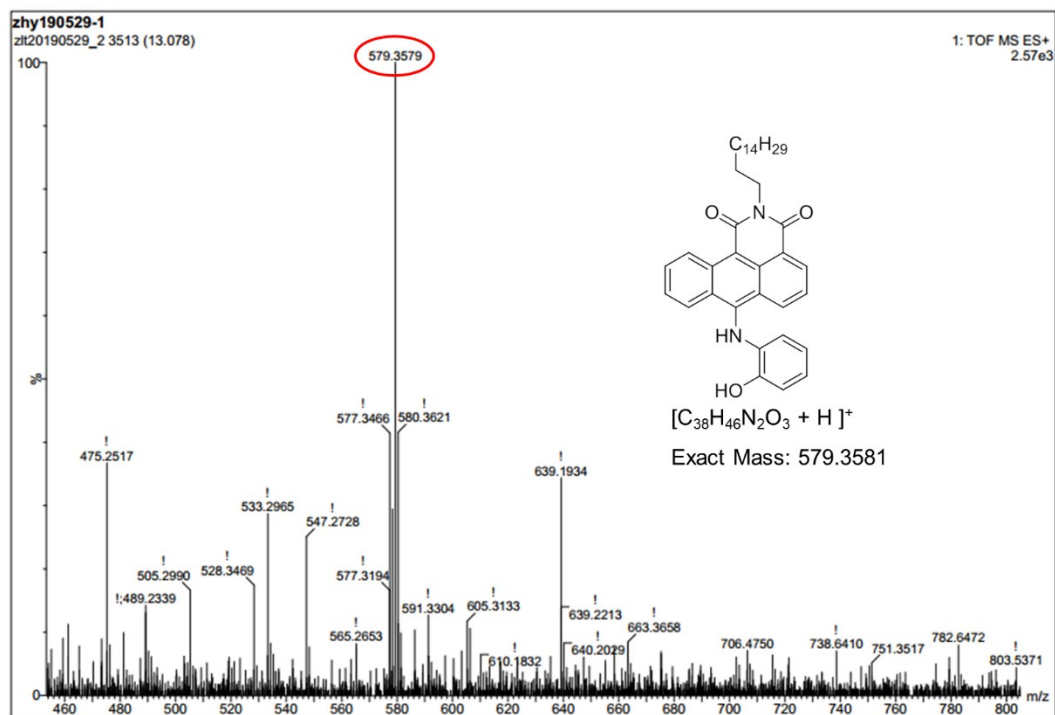


Figure S11. HR-MS (ESI) spectrum of APAC.

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