Electronic Supplementary Information

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

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1. Materials and General Methods

Unless otherwise mentioned, all reagents were purchased from Sigma-Aldrich and used directly without further purifications. $^1$H 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

![Chemical structure of APAC](image)

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 CH$_2$Cl$_2$/EtOH = 40/1 (v/v) as the eluent to afford **APAC** as a brick red solid (47 mg, 40%).$^1$H 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 \([C_{38}H_{46}N_2O_3 + H]^+\)
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. Stoke 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 × \(\sigma/k\), where \(\sigma\) 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). $\lambda_{ex}$ = 432 nm, slits: 2.5 nm/2.5 nm. Error bars are ± SD n = 3.

Figure S2. Time-dependent fluorescence response of APAC (10 μM) to triphosgene (30 μM) in CHCl$_3$. $\lambda_{ex}$ = 432 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\textsubscript{3}Cl.

6. Spectral responses of APAC towards HNO\textsubscript{2}

Figure S4. Fluorescence spectral changes of APAC (10 µM) after the addition of HNO\textsubscript{2} (100 µM) in an EtOH/HCl solution (v/v = 1/4, pH = 1). λ\textsubscript{ex} = 432 nm, slits: 2.5 nm/2.5 nm.
Table S1. The photophysical data of APAC and APAC-Phos.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{abs}}$/nm</th>
<th>$\lambda_{\text{em}}$/nm</th>
<th>$\Delta\lambda$/nm</th>
<th>$\varepsilon$/L·mol⁻¹·cm⁻¹</th>
<th>$\Phi_f$</th>
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<tbody>
<tr>
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<td>/</td>
<td>/</td>
<td>9014</td>
<td>0.06%</td>
</tr>
<tr>
<td>APAC-Phos</td>
<td>432</td>
<td>484</td>
<td>52</td>
<td>7300</td>
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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%). $^1$H 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 [C$_{39}$H$_{44}$N$_2$O$_4$ + 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 was 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 CHCl₃, 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

![NMR spectrum](image)

**Figure S5.** ¹H NMR spectrum of APAC-Phos in CDCl₃ (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.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Excitation</th>
<th>Emission</th>
<th>Limit of detection</th>
<th>Detection system</th>
<th>Response time</th>
<th>Application</th>
<th>Reference</th>
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<td>3 nM</td>
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<td>[8]</td>
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<tr>
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<td>[9]</td>
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<td>[10]</td>
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<td>2 s</td>
<td>PCL nanober composite</td>
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<td>CH₂CN</td>
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<td>CHCl₃</td>
<td>15 s</td>
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</table>

APAC
Figure S9. $^1$H NMR spectrum of APAC in CDCl$_3$ (400 MHz).

Figure S10. $^{13}$C NMR spectrum of the APAC in DMSO-$d_6$ (150 MHz).
Figure S11. HR-MS (ESI) spectrum of APAC.
References


