Electronic Supplementary Information

An AIE-Based Fluorescent Test Strip for Portable Detection of Gaseous Phosgene

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Experimental

Reagents and Materials: 4-Bromobenzophenone, zinc powder, titanium tetrachloride (TiCl₄), tetrahydrofuran (THF for HPLC), potassium carbonate, tetrabutylammonium bromide (TBAB for AR), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄), pyridine (for HPLC), acetic acid (CH₃COOH), malononitrile, o-phenylenediamine, tris(dibenzylideneacetone)dipalladium (Pd₂(dba)₃), sodium tert-butoxide (t-BuONa), tri-tert-butylphosphine (P(t-Bu)), triethylamine, triphosgene and 4-bromotriphenylamine were purchased from Aladdin and used as received. Diethyl chlorophosphate (DCP) were purchased from Sigma-Aldrich. Thionyl chloride (SOCl₂), oxalyl chloride ((COCl)₂), sulfuryl chloride(SO₂Cl₂), phosphorus oxychloride(POCl₃), acetyl chloride (CH₃COCl) and tosyl chloride (TsCl) were purchased from Xiya Reagent. 4-Formylphenylboronic acid was purchased from TCI. The Whatman qualitative filter paper (Grade 2 1002-070) was purchased from Hangzhou Wohua Co., Ltd. All solvents were analytically pure reagents and distilled before use.

Synthesis of 1,2-bis(4-bromophenyl)-1,2-diphenylethene (Br-TPE-Br). In a dry nitrogen atmosphere, 4-bromobenzophenone (7.83 g, 30 mmol) was dissolved with 125 mL THF in a 250 mL two-neck round-bottom flask. Zinc dust (5.85 g, 90 mmol) was subsequently added to the flask, followed by cooling down with an ice bath. TiCl₄ (6.74mL, 67.5 mmol) was added into the mixture dropwise with an injector. The reaction was then refluxed at 70 °C overnight under nitrogen. After the solution was cooled to room temperature, THF was evaporated under reduced pressure. Saturated sodium bicarbonate solution was added to the mixture until no bubbles came out. The mixture was then extracted with dichloromethane and dried with anhydrous sodium sulfate. The crude product was purified using silica column chromatography, using hexane and dichloromethane (25 : 1 v/v), affording a white solid (6.31 g, 85.8% yield) ¹H NMR (600 MHz, CDCl₃, δ ppm): 7.19-7.25 (m, 4H), 7.09-7.14 (m, 6H), 6.96-7.01 (m, 4H), 6.85-6.91 (m, 4H).

Synthesis of 4'-(2-(4-bromophenyl)-1,2-diphenylethyl)-[1,1'-biphenyl]-4-carbaldehyde (Br-TPE-Py-CHO). Br-TPE-Br (490 mg, 1 mmol) was dissolved in 15mL toluene in a 50 mL two-neck round-bottom flask followed by addition of the prepared aqueous solution of potassium carbonate (4 mL, 2mol/L). Then tetrabutylammonium bromide (50 mg, 0.15 mmol) and 4-formylphenylboronic acid (180 mg, 1.2 mmol) was added into the flask and stirred for 30min at room temperature. After that, tetrakis(triphenylphosphine)palladium(0) (5 mg, 8.7 µmol) was added. The flask was vacuumed and purged with nitrogen three times immediately and then heated to 90 °C for 24 h. After the solution was cooled to room temperature, the mixture was poured into ethyl acetate and washed three times with brine. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent under reduced pressure, was purified by silica gel column chromatography by
using hexane / dichloromethane (3:1 v/v) as eluent to give a white solid (327 mg, 63.5% yield). $^1$H NMR (600 MHz, CDCl$_3$, $\delta$ ppm): 10.02-10.04 (d, $J = 6$ Hz, 1H), 7.89-7.93 (m, 2H), 7.69-7.74 (m, 2H), 7.37-7.44 (m, 4H), 7.11-7.16 (m, 8H), 7.03-7.07 (m, 4H), 6.88-6.96 (m, 2H). MS (ESI): m/z 514.1 [M]$^+$. 

**Synthesis of 2-((4'-(2-(4-bromophenyl)-1,2-diphenylvinyl)-[1,1'-biphenyl]-4-yl) methylene)malononitrile (Br-TPE-Py-2CN).** Br-TPE-Py-CHO (200 mg, 0.39 mmol) was dissolved in 30 mL pyridine in a 250 mL single-neck round-bottom flask. Subsequently, malononitrile (0.025 mL, 0.39 mmol) was added to the flask. After acetic acid (0.11 ml, 0.62 mmol) was put in last, the flask was vacuum purged with nitrogen gas three times. The reaction mixture was stirred at 40 °C for 24h. After cooling to room temperature, the reaction mixture was poured into ethyl acetate, washed three times with hydrochloric acid solution (1 mol/L). The organic layer was then separated and dried over anhydrous sodium sulfate. The solvent was removed by evaporation and the residue was purified by silica gel column chromatography using hexane / dichloromethane (2 : 1 v/v). Orange solid was obtained (216 mg, 98.5% yield) after dried. $^1$H NMR (600 MHz, (CD$_3$)$_2$SO, $\delta$ ppm): 8.53-8.56 (m, 1H), 8.00-8.03 (m, 2H), 7.90-7.95 (m, 2H), 7.62-7.68 (m, 2H), 7.33-7.39 (m, 2H), 7.06-7.28 (m, 10H), 6.97-7.05 (m, 4H). MS (ESI): m/z 585.1 [M]$^+$. 

**Synthesis of 2-((4'-(2-(4-((2-aminophenyl)amino)phenyl)-1,2-diphenylvinyl)-[1,1'-biphenyl]-4-yl)methylene)malononitrile (OPD-TPE-Py-2CN).** A 50ml two-necked round-bottom flask with a reflux condenser was purged with dry nitrogen and Br-TPE-Py-2CN (25 mg, 0.044 mmol) was added and dissolved in dried toluene (25 ml). o-Phenylenediamine (6.2 mg, 0.058 mmol), tris(dibenzylideneacetone)dipalladium (0.6 mg, 0.66 µmol), tri-tert-butylphosphine (0.14 mg, 0.69 µmol) and sodium tert-butoxide (5.5mg, 0.058mmol) were added subsequently. Afterwards, the reaction was stirred for 24h at 110 °C. After completion, the solvent was removed by evaporation. Silica column chromatography using hexane / dichloromethane (1 : 2 v/v) was carried out to remove the impurities. Yellow solid was obtained (23 mg, 88.6% yield) after dried. $^1$H NMR (600 MHz, (CD$_3$)$_2$SO, $\delta$ ppm): 8.23-8.24 (s, 1H), 8.22-8.23 (s, 1H), 7.83-7.87 (d, $J = 12$ Hz, 2H), 7.59-7.61 (d, $J = 12$ Hz, 2H), 6.98-7.26 (m, 22H), 3.15-3.19 (s, 2H). MS (ESI): m/z 591.5 [M]$^+$. 

**Characterization**

$^1$H NMR spectra were measured with a Bruker Avance 600 MHz NMR Spectrometer. Mass spectra were obtained using a Bruker Esquire HCT Plus mass spectrometer. Fluorescence spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. UV-vis spectra were measured on a Hitachi U-3010 UV-vis spectrophotometer. The fluorescence lifetime data were obtained by using an Edinburgh Instrument FLS920 fluorescence spectrometer. 

**Preparation of OPD-TPE-Py-2CN loaded test strips**

A volume of 10 µL tetrahydrofuran stock solution of OPD-TPE-Py-2CN (10$^{-3}$ M) was
dropped on a Whatman filter paper and permeated naturally. After dried in the air, a portable test strip for phosgene detection was obtained. The test strips are saved in a dry and cool place after preparation.

**Fluorometric analysis**

Phosgene was prepared according to the reported method.\(^1\) Different concentrations of triphosgene solutions were prepared with dichloromethane as solvent. 10 μL of the solutions were placed at the bottom of a bottle, and the test paper was hanged and fixed above the solution inside the bottle, afterwards the addition of 10 μL of dichloromethane containing 0.1% TEA into the solution was conducted; after that, the lid was closed immediately. Fluorescence changes of OPD-TPE-Py-2CN loaded test strips with exposure to different concentrations of phosgene for 2 min were recorded on a fluorimeter (excitation wavelength: 365 nm). The test strips were exposed to phosgene or other analytes in the selectivity experiments.
Scheme S1. Synthesis and structure of OPD-TPE-Py-2CN.
Fig. S1 $^1$H NMR spectrum of Br-TPE-Br in CDCl$_3$. 
**Fig. S2** $^1$H NMR spectrum of Br-TPE-Py-CHO in CDCl$_3$.

**Fig. S3** Mass spectrum of Br-TPE-Py-CHO. MS (ESI): $m/z$ 514.1 [M]$^+$
Fig. S4 $^1$H NMR spectrum of Br-TPE-Py-2CN in (CD$_3$)$_2$SO.

Fig. S5 Mass spectrum of Br-TPE-Py-2CN. MS (ESI): $m/z$ 585.1 [M$^+$.]
Fig. S6 $^1$H NMR spectrum of OPD-TPE-Py-2CN in (CD$_3$)$_2$SO.

Fig. S7 Mass spectrum of OPD-TPE-Py-2CN. MS (ESI): $m/z$ 591.5 [M]$^+$
**Fig. S8** Normalized UV-vis absorption spectra of OPD-TPE-Py-2CN (black) and the final reaction product of OPD-TPE-Py-2CN with phosgene vapor (red).

**Fig. S9** (a) Fluorescence spectra of OPD-TPE-Py-2CN (10^{-3} M) in THF and OPD-TPE-Py-2CN loaded test strip; λex = 365 nm; (b) Fluorescence spectra of 4-bromotriphenylamine (10^{-3} M) in THF and 4-bromotriphenylamine loaded test strip under 365 nm excitation. Insets: photographs of solutions and test strips were taken under hand-held UV lamp (365 nm)
**Fig. S10** Fluorescence spectra of OPD-TPE-Py-2CN (10⁻³ M) in THF and OPD-TPE-Py-2CN loaded test strip after reaction with phosgene; λex = 365 nm. Insets: photographs of solutions and test strips were taken under hand-held UV lamp (365 nm).

**Fig. S11** Stability of OPD-TPE-Py-2CN loaded test strips under continuous illumination of daylight. \( I_0 \) is the original maximum fluorescence intensity excited at 365 nm before light irradiation and \( I_t \) is the fluorescence intensity (recorded at the same wavelength as \( I_0 \)) excited at 365 nm after t-day light irradiation. The ratio \( I_t/I_0 \) was calculated to be representative of the magnitude of change in fluorescence intensity.
**Fig. S12** (a) Five different places throughout the dried aggregation spot on Whatman filter paper after exposure to phosgene (64 ppm) (b) the fluorescence intensity ratio ($I_{496}/I_{435}$) of these five places.

**Fig. S13** Fluorescence intensity ratio as a function of phosgene level.

**Determination of the detection limit**:  
The calibration curve was first obtained from the plot of fluorescence ratio $I_{496}/I_{435}$ as a function of phosgene vapor level. The regression curve equation was obtained for the lower concentration part.  
The detection limit = $3 \times \text{S.D.} / k$  
where $k$ is the slope of the curve equation, and S.D. represents the standard deviation for the fluorescence intensity of OPD-TPE-Py-2CN in the absence of phosgene.  
$I_{496}/I_{435} = 1.9641 + 0.0924 \times \text{[Phosgene]}$ ($R^2 = 0.998$)  
LOD = $3 \times 0.05760 / 0.0924 = 1.87$ ppm (83 nM)
Fig. S14 (a) Fluorescence spectra of OPD-TPE-Py-2CN loaded test strips in the absence and in the presence of 1.87 ppm phosgene for 2 min. Excitation wavelength: 365 nm. (b) Photographs of OPD-TPE-Py-2CN loaded test strips treated with different phosgene concentrations for 2 min at 25 ºC taken under a 365 nm handheld UV lamp.

Fig. S15 Fluorescence intensity ratio ($I_{496}/I_{435}$) of OPD-TPE-Py-2CN loaded test strips (a) upon exposure to 12.8 ppm phosgene or DCP, SOCl$_2$, (COCl)$_2$, SO$_2$Cl$_2$, POCl$_3$, CH$_3$COCl, TsCl at equal amount respectively; and (b) exposure to 12.8 ppm phosgene, simultaneously in the presence of DCP, SOCl$_2$, (COCl)$_2$, SO$_2$Cl$_2$, POCl$_3$, CH$_3$COCl or TsCl respectively. The fluorescence intensities were measured 2 min after exposure. Excitation wavelength: 365 nm. (Phos in this figure represents phosgene).
**Fig. S16** Mass spectrum of the reaction product from the reaction between OPD-TPE-Py-2CN and phosgene. MS (ESI): m/z 617.1 [M]+

**Fig. S17.** $^1$H NMR spectra for comparison of OPD-TPE-Py-2CN and its reaction product in (CD$_3$)$_2$SO. I: OPD-TPE-Py-2CN; II: reaction product.
Fig. S18 (a) Fluorescence decay curve for the OPD-TPE-Py-2CN loaded test strips (recording 10000 photons measured at 365 nm excitation and 475 nm emission), Fit = A + B_1\exp(-t/\tau_1) + B_2\exp(-t/\tau_2) (\tau_1 = 0.90 \text{ ns}, \tau_2 = 2.85 \text{ ns}). (b) Fluorescence decay curve for the OPD-TPE-Py-2CN loaded test strip upon exposure to phosgene vapor ([phosgene] = 64 ppm, recording 10000 photons at 365 nm excitation and 496 nm emission), Fit = A + B_1\exp(-t/\tau_1) + B_2\exp(-t/\tau_2) (\tau_1 = 0.85 \text{ ns}, \tau_2 = 3.25 \text{ ns}).
Table S1. Comparison of the chemical structures and characteristics of the probe system herein with other reported probes for phosgene.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Mechanism of fluorophore</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure 1" /></td>
<td>ACQ</td>
<td>Turn-on</td>
</tr>
<tr>
<td><img src="image2" alt="Chemical Structure 2" /></td>
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<td>ACS Appl. Mater. Interfaces 2016, 8, 22246–22252</td>
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<tr>
<td><img src="image4" alt="Chemical Structure 4" /></td>
<td>ACQ</td>
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<tr>
<td><img src="image5" alt="Chemical Structure 5" /></td>
<td>ACQ</td>
<td>Turn-on</td>
</tr>
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</table>
Our probe
Table S2. Comparison of properties of the probe system herein with other reported probes for phosgene.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Concentration range</th>
<th>Detection limit</th>
<th>Response time</th>
<th>Specificity</th>
<th>Applicability</th>
</tr>
</thead>
<tbody>
<tr>
<td>PY-OPD</td>
<td>0-20 µM[s] 0-20 ppm[g]</td>
<td>20 nM[s]</td>
<td>2 min[s]</td>
<td>Can distinguish phosgene from other mimics (including chlorides and chloroacetyl chloride)[s]</td>
<td>in solutions and partly in gas phase</td>
</tr>
<tr>
<td>NAP-OPD</td>
<td>0-10 µM[s] 0.8mg/L[l]</td>
<td>2.8 ppb[s]</td>
<td>&gt; 5 min[s]</td>
<td>/</td>
<td>in solutions</td>
</tr>
<tr>
<td>dRB-EDA</td>
<td>0-1 µM[s] 0-4 mg/L[g]</td>
<td>50 nM[s]</td>
<td>Immediately[s]</td>
<td>Can distinguish phosgene from formaldehyde[s]</td>
<td>in solutions and partly in gas phase</td>
</tr>
<tr>
<td>Phos-1</td>
<td>0-25 µM[s] 0-4 mg/L[g]</td>
<td>1.3 nM[s]</td>
<td>20 min[s]</td>
<td>Can distinguish phosgene from triphosgene, CH$_3$COCl, SOCl$_2$, SO$_2$Cl$_2$, DCP, DCNP, POCl$_3$, TosCl[g]</td>
<td>in solutions and partly in gas phase</td>
</tr>
<tr>
<td>o-Pac</td>
<td>0-50 µM[s] 0-40 ppm[g]</td>
<td>3 nM[s]</td>
<td>1 min[g]</td>
<td>Can distinguish phosgene from DCP, DCNP, (COCl)$_2$, SOCl$_2$, SO$_2$Cl$_2$, CH$_3$COCl, POCl$_3$, TosCl, triphosgene[s][g]</td>
<td>in solutions and partly in gas phase</td>
</tr>
<tr>
<td>Our probe</td>
<td>0-64ppm[g]</td>
<td>1.87ppm[g]</td>
<td>2min[g]</td>
<td>Can distinguish phosgene from DCP, (COCl)$_2$, SOCl$_2$, SO$_2$Cl$_2$, CH$_3$COCl, POCl$_3$, TosCl[g]</td>
<td>Completely in gas phase</td>
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Note: [s] here means the detection experiments were conducted in solutions by using the solution-
based detection system; [g] here means the experiments were conducted in gas phase by using the solid detection system.
References: