Highly sensitive and selective detection of triphosgene with a 2-(2'-hydroxyphenyl)benzimidazole derived fluorescent probe

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1. Optimization of triethylamine for the generation of phosgene

Figure S1 a) Fluorescence spectra of 10 µM 4-AHBI solutions containing triethylamine (TEA) (0-1 µM) upon addition of triphosgene (3.5 µM), λ(ex) = 357 nm, slit width = 2.5/2.5 nm; b) Fluorescence intensities @386 nm vs concentration of TEA.

2. Investigation of the effect of solvents

Figure S2 The fluorescence spectra of 4-AHBI (10 µM) in different solvents without (black) and with (red) triphosgene (3.5 µM). a: CH₂Cl₂ (λ(ex) = 357 nm, λ(em) = 386 nm), b: CHCl₃ (λ(ex) = 343 nm, λ(em) = 440 nm), c: MeOH (λ(ex) = 330 nm, λ(em) = 377 nm), d: EtOH (λ(ex) = 339 nm, λ(em) = 425 nm), e: MeCN (λ(ex) = 357 nm, λ(em) = 386 nm), f: acetone (λ(ex) = 357 nm, λ(em) = 383 nm), g: EtOAc (λ(ex) = 357 nm, λ(em) = 386 nm), h: DMF (λ(ex) = 346 nm, λ(em) = 444 nm), i: DMSO (λ(ex) = 346 nm, λ(em) = 441 nm). Slit width = 2.5/2.5 nm.
3. Measurement of the fluorescence quantum yield

**Figure S3** Measurement of the fluorescence quantum yields (Φf) of 4-AHBI. 4-AHBI were determined in CH$_2$Cl$_2$ with solvent refractive index correction. Quinine sulfate in 1.0 M H$_2$SO$_4$ was used as the reference (Φf = 54%) at an excitation wavelength of 340 nm. The fluorescence quantum yield was calculated by the following equation: Φ$_x$ = Φ$_s$ (F$_x$/F$_s$)(A$_s$/A$_x$)(n$_x$/n$_s$)$^2$. Where x and s indicate the 4-AHBI and quinine sulfate, respectively, F is the area of the fluorescence peak, A is the optical density at the excitation wavelength and n is the refractive index of the solvent.

4. Measurement of the LoD for 4-AHBI

**Figure S4** Measurement of the LoD for 4-AHBI to triphosgene. a) The emission intensities at 386 nm vs triphosgene concentration. Equation: y = 2416.7x-40.195, R$^2$ = 0.9948; b) Ten times of the blank experiment to evaluate the standard deviation σ (0.06728). The triphosgene detection limit was determined to be 0.08 nM (LoD = 3σ/k, where σ is the standard deviation of the blank experiment, and k is the slope of the relationship between the emission intensities and triphosgene concentration.)
5. Fluorescence spectra of 4-AHBI with triphosgene in the presence of interfering compounds

![Fluorescence spectra](image)

Figure S5 Fluorescence spectra of 4-AHBI (10 µM) in CH$_2$Cl$_2$ with triphosgene (3.5 µM) in the presence of various analytes (5 µM). $\lambda_{ex}$ = 357 nm.

6. Table S1 Determination of triphosgene in the presence of interfering compounds

<table>
<thead>
<tr>
<th>Interferents compounds (µM)</th>
<th>Triphosgene added (µM)</th>
<th>Triphosgene found (µM)</th>
<th>Recovery</th>
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<td>(COCl)$_2$</td>
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<tr>
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<tr>
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<td>88.6%</td>
</tr>
</tbody>
</table>

7. Exploration of the sensing mechanism

The reaction mixture was analysed by HPLC with a High-resolution mass spectra (HRMS) on Agilent Technologies 6530 Accurate mass Q-TOF LC/MS using ESI as ion source. A minor peak at 1.959 min corresponded with the remnant 4-AHBI (HRMS: [M+H]$^+$: calcd for C$_{13}$H$_{12}$N$_3$O: 226.0975, found: 226.0975.). A major peak at 3.812 min was obviously obtained and the HRMS spectrum showed the m/z 252.0776, which should be the single sensing product 4-AHBI-CO (for C$_{14}$H$_{10}$N$_3$O$_2$: M+H$^+$: calculated 252.0768).

The sensing product 4-AHBI-CO was synthesized as follows: 4-AHBI (0.113 g, 0.5 mmol) was stirred and dissolved in dry CH$_2$Cl$_2$ (25 mL) at 0 °C, then triphosgene (0.15 g,
0.5 mmol) in dry CH₂Cl₂ (10 mL) was added over a period of 10 min. Then the mixture was continually stirred at 0 °C until the completion of the reaction. Saturated NaHCO₃ aqueous solution was added into the mixture and extracted with CH₂Cl₂ (20 mL × 2). The organic phase was collected, dried over anhydrous Na₂SO₄ and evaporated to give the crude product. The crude product was further purified by column chromatography (ethyl acetate : petroleum ether = 1 : 5) to give the sensing product (0.096 g, yield 78%) as a white solid.

Figure S6 HPLC chromatogram of the reaction mixture (up) and HRMS spectrum of the peak at 1.959 min (middle) and 3.812 min (down).
Figure S7 $^1$H NMR of 4-AHBI-CO.

Figure S8 HRMS copy of 4-AHBI-CO.
8. $^1$H NMR, $^{13}$C NMR and HRMS copies of 4-AHBI

Figure S9 $^1$H NMR copy of 4-AHBI

Figure S10 $^{13}$C NMR copy of 4-AHBI
Figure S11 HRMS copy of 4-AHBI