Electronic Supplementary Information (ESI) for

A ratiometric fluorescent chemosensor for selective and visual detection of phosgene in solutions and in gas phase

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1. Materials and Methods

Unless otherwise stated, all reagents for synthesis were purchased from commercial suppliers and used without further purification. The solvents, 1,2-dichloroethane (DCE) and triethylamine (TEA), were purified by conventional methods before use. All synthesis was carried out under N_2, magnetically stirred, and monitored by thin-layer chromatography (TLC). Flash chromatography was performed using silica gel (200-300 mesh). NMR spectra were recorded in $CDCl_3$ on Bruker AV spectrometer (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR). High resolution mass spectrometry (HRMS) data were obtained from a FTMS spectrometer or a LC−TOF MS spectrometer. UV/vis absorption spectra and fluorescence spectra were recorded at room temperature on a UV/vis spectrometer and a spectrofluorophotometer, respectively.

2. Details of Assay Experiments

In order to avoid handling volatile phosgene during the titration experiments, we employed nonvolatile and less toxic counterpart triphosgene ($CCl_3OC(O)OCCl_3$), which is a well-known precursor that generates phosgene in the presence of tertiary amines in solutions. For all measurements in solutions, dichloroethylane (DCE) was employed as the solvent.

Measurement of the detection limit.

The detection limit was calculated based on the fluorescence titration. The fluorescence intensity ratio (I_{442}/I_{511}) change was fitted linearly with the increasing concentrations of triphosgene over a range of 0-10 μM. From the plot, the slope (k) was obtained to be 0.206 μM^{-1} (Adj. R-Square 0.9988), shown in Fig. I right. The detection limit of Phos-1 toward triphosgene was calculated to be 1.3 nM in term of the formula ($3\sigma/k$). The value of σ was obtained from Fig. I left and Table I.

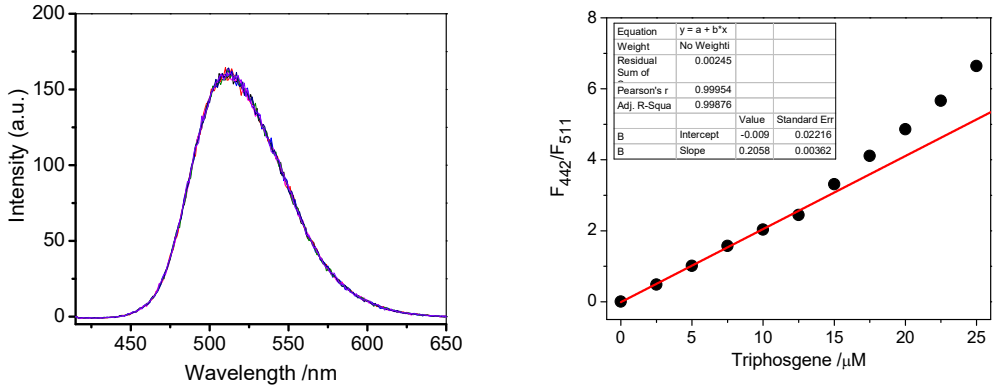


Fig. I. Left: Multi-recorded fluorescence spectra of the solution of 5μM Phos-1. Right: Calibration curve of fluorescence ratio (F_{442}/F_{511}) of 5μM Phos-1 solutions as a function of triphosgene concentration, λ_{ex} = 410 nm.

Table I. The data for standard deviation (σ) of blank measurement from Fig. I

I_{442}	I_{511}	I_{442}/I_{511}	σ (I_{442}/I_{511})
-0.043	157.337	-2.73E-04	
-0.025	156.08	-1.60E-04	
-0.053	158.519	-3.34E-04	
-0.037	159.455	-2.32E-04	8.98E-05
-0.037	162.304	-2.28E-04	
-0.027	163.248	-1.65E-04	
-0.009	160.844	-5.60E-05	

Selectivity experiments in solutions.

Phosgene: 12.5 μL of Triphosgene stock solution (5 mM) was added into 5 μM Phos-1 solution containing 125 μM TEA (2.5 mL), giving a final concentrations of triphosgene, 25 μM, after 20 min, the fluorescence spectrum was recorded.

Triphosgene: 12.5 μL of Triphosgene stock solution (5 mM) was added into 5 μM Phos-1 solution (2.5 mL), giving a final concentrations of triphosgene, 25 μM. After additions for 20 min, the fluorescence spectrum was recorded.

Other analytes, including CH_3COCl, $SOCl_2$, SO_2Cl_2, DCP, DCNP, $POCl_3$, TosCl. Various analytes stock solutions were added into 5 μM Phos-1 solutions (2.5 mL), giving a final concentrations, 250 μM, respectively. After additions for 20 min, the fluorescence spectra were recorded.

Detection of gaseous phase with the testing paper.

Detection of phosgene gas in various concentrations. Four concentrations of triphosgene solutions (in DCE) were prepared, 1 g/L, 2 g/L, 3 g/L and 4 g/L. Using a PLC injection needle, 10 μL above solutions were removed to four centrifuge tubes, and then added 15 μL 0.4‰ TEA (DCE solution) into these tubes, finally quickly close the lid, respectively. After 10 min, the color and fluorescence of these tubes together with a blank tube were taken a picture under 365 nm light.

For the concentration of phosgene gas in the caption of Fig. 5 and Fig. S7, as an example, 10 μL of triphosgene solution (4 g/L) was added into 10-mL centrifuge tube, and followed by the supplementary addition of 15 μL DCE containing 0.4‰ v/v TEA, thus, the concentration of phosgene gas was calculated to be 4 mg/L in this case.

Selective detection of phosgene gas over vapor of other analytes. DCE solutions of triphosgene (80 mg/mL), TosCl (80 g/L) and other analytes (4%, v/v) containing CH_3COCl, $SOCl_2$, SO_2Cl_2, DCP, DCNP, $POCl_3$ were prepared. Using a PLC injection needle, 25 μL of above solutions was removed into 10-mL centrifuge tubes, respectively. The values in the caption of Fig. 6 and Fig. S8 are the volume or the weight of the analyte in the solution added, and not the volume or the weight of vapor for analytes.

3. Synthesis and Characterization of Phos-1 and Compound 2

2-(2-ethoxyethyl)-6,7-bis((2-ethoxyethyl)amino)-1H-benzo[de]isoquinoline-1,3(2H)-dione (Phos-1): K_2CO_3 (2.07 g, 15.0 mmol) was added into a solution of compound **1**[1] (966 mg, 3.0 mmol) and 2-ethoxyethylamine (2.67 g, 30.0 mmol) in 1,4-dioxane (50 mL). After being refluxed for 24 h under N_2, the mixture was allowed to cool to room temperature, added water (150 mL) and extracted with dichloromethane (50 mL×3). The organic extracts were collected, washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtrated and evaporated to give the crude material. The crude product was purified by column chromatography to give the target product Phos-1 (590 mg, yellow solid, 44 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.42 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 4.39 (t, *J* = 6.6 Hz, 2H), 3.77 (t, *J* = 5.2 Hz, 4H), 3.73 (t, *J* = 6.5 Hz, 2H), 3.58 (m, 6H), 3.41 (t, *J* = 5.2 Hz, 4H), 1.26 (t, *J* = 7.0 Hz, 6H), 1.18 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ= 164.55, 152.52, 133.62, 132.30, 112.09, 111.85, 107.26, 68.04, 67.33, 66.57, 66.16, 44.32, 38.84, 15.29, 15.21 ppm. TOFMS (ESI) calcd for $[M+H]^+$: 444.2493, found 444.2500.

1,3,7-tris(2-ethoxyethyl)pyrido[3,4,5-gh]perimidine-2,6,8(1H,3H,7H)-trione (**2**): Phos-1 (385 mg, 0.87 mmol) and triphosgene (128 mg, 0.43 mmol) were added in dichloromethane (100 mL) containing triethylamine (0.05 equivalents) at -5 °C. The mixture was stirred at −5° C for 1 h under N_2, then treated with NaOH solution (1.0 N, 25 mL) and stirred for 0.5 h, and extracted with dichloromethane (20 mL×3). The organic extracts were collected, washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtrated and evaporated to give the crude material. The crude product was purified by column chromatography to give the product **2** (344 mg, yellow solid, 84 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.53 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.6 Hz, 2H), 4.42 (t, *J* = 6.4 Hz, 2H), 4.35 (t, *J* = 5.9 Hz, 4H), 3.81 (t, *J* = 5.8 Hz, 4H), 3.74 (t, *J* = 6.4 Hz, 2H), 3.58 (q, *J* = 14.0 Hz, 2H), 3.53 (q, *J* = 14.0 Hz, 4H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ= 163.85, 149.97, 143.02, 134.25, 129.69, 114.12, 111.87, 106.47, 67.20, 67.16, 66.83, 66.19, 44.58, 39.13, 15.16, 15.12 ppm. TOFMS (ESI) calcd for $[M+Na]^+$: 492.2105, found 492.2112.

Reference

1 L. Liu, C. Zhang and J. Zhao, *Dalton Trans.*, 2014, **43**, 13434-13444.

4. Spectral Response to Phosgene

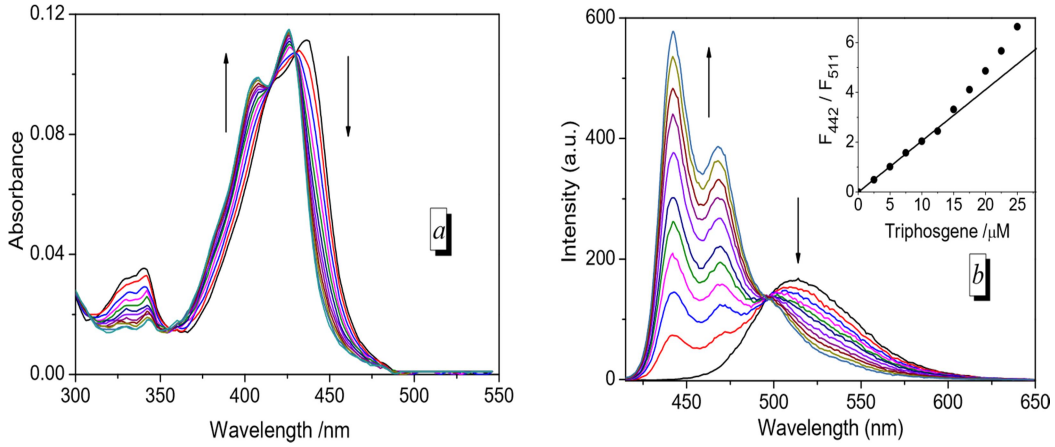


Fig. S1 UV/vis absorption (a) and fluorescence (b) spectra of Phos-1 (5 μM) in DCE containing TEA in the presence of different concentrations of triphosgene ranging from 0 to 25 μM, (molar ratio of TEA/triphosgene is 5:1) recorded after 0.5 h. λ_{ex} = 410 nm. Inset: Plot of fluorescence ratio of F_{442}/F_{511} *vs* the concentration of triphosgene.

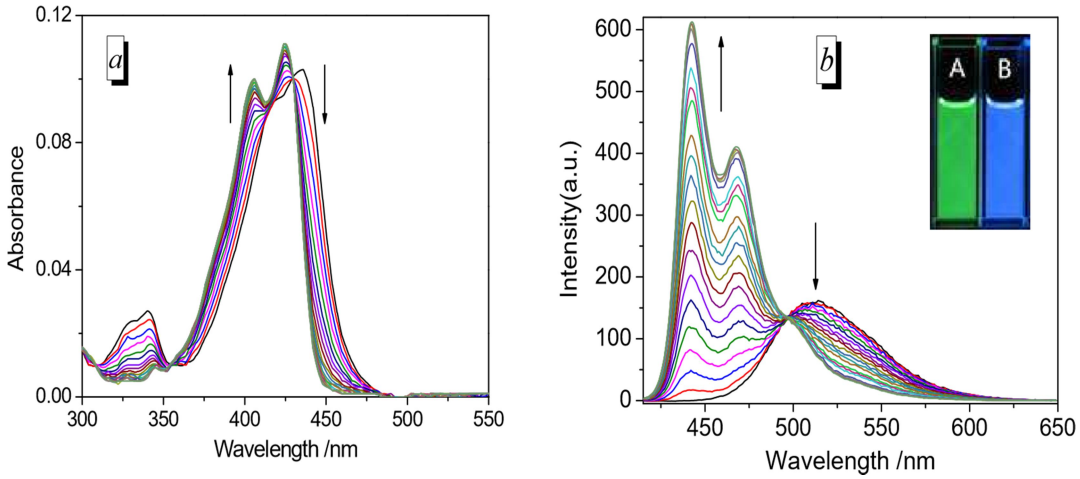


Fig. S2 Time-dependent UV/vis absorption (left) and fluorescence (right) spectra of Phos-1 (5 μM) in the presence of triphosgene (25 μM) in DCE containing TEA (250 μM). Data were recorded over 20 min, λ_{ex} = 410 nm. Inset: photos of above solutions of Phos-1 before (A) and after (B) under 365 nm light.

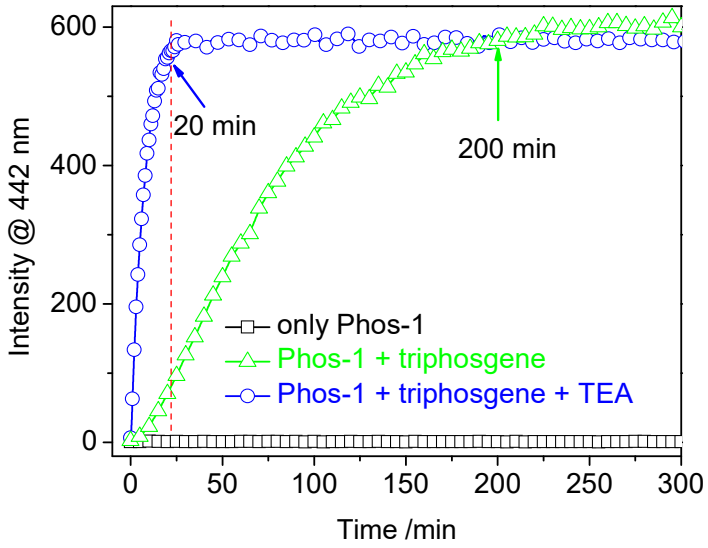


Fig. S3 Time-dependent fluorescence intensity of 5 μM Phos-1 (black) DCE solutions in the presence of 25 μM triphosgene without (green) or with 250 μM TEA (blue), excitation at 410 nm.

5. HRMS Evidence for the Sensing Mechanism

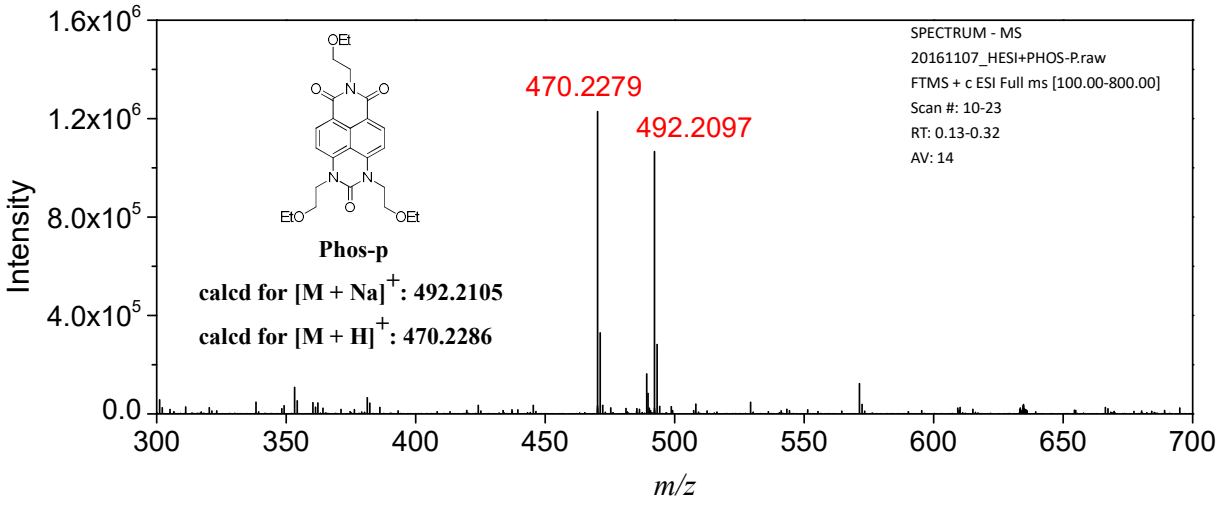


Fig. S4 HRMS for the reaction mixture of 5 μM Phos-1 solution with 25 μM triphosgene and 250 μM TEA.

6. Spectral Response of Phos-1 to NO

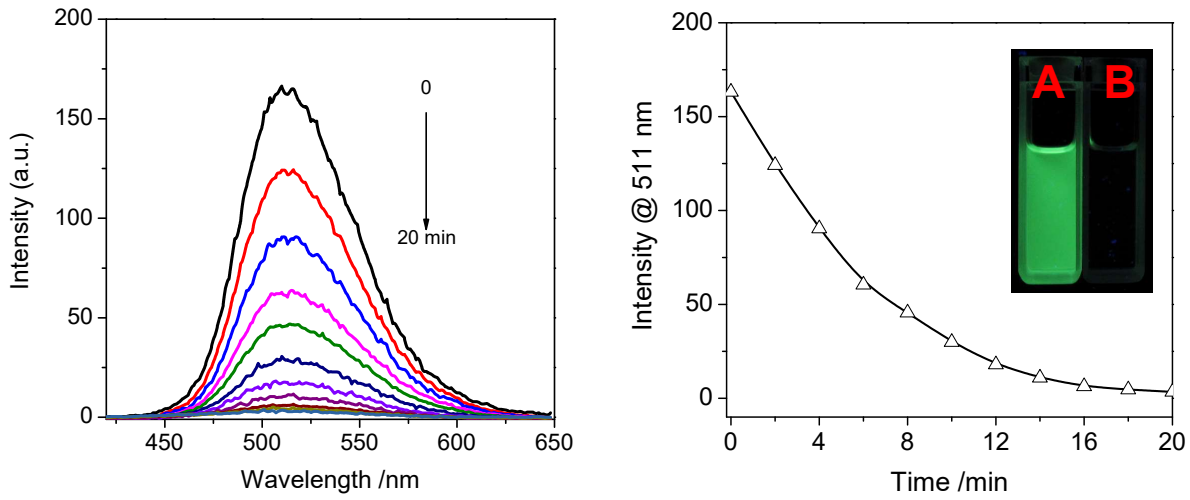


Fig. S5 Left: Time-dependent fluorescence spectra of Phos-1 (5 μM) DCE solution after bubbled a NO bubble, recorded over 20 min, λ_{ex} = 410 nm. Right: Plot of fluorescence intensity at 511 nm vs. time. Inset: fluorescence images of above solutions before (A) and after (B) under 365 nm light.

7. Preparation and Detection of the Test Paper with Phos-1

Phos-1 (2.0 mg) and polyethylene oxide (2.5 g) were dissolved in dichloromethane (100 mL). A filter paper was immersed in the solution, and then taken out to dry in air. Finally, the paper with Phos-1 was cut into strips in the size of 1.8 cm×0.5 cm for detection of phosgene in gas phase.

To assess its function, the test paper was exposed to phosgene gas or vapor of other analyte in a seal centrifuge tube (10 mL) (Fig. S6). First, the test paper was fixed at the inside of the centrifuge tube, then, the sample solution was removed to the bottom of the tube with a HPLC injection needle, and quickly close the lid, after 10 min, the color and fluorescence of the device was taken a picture.

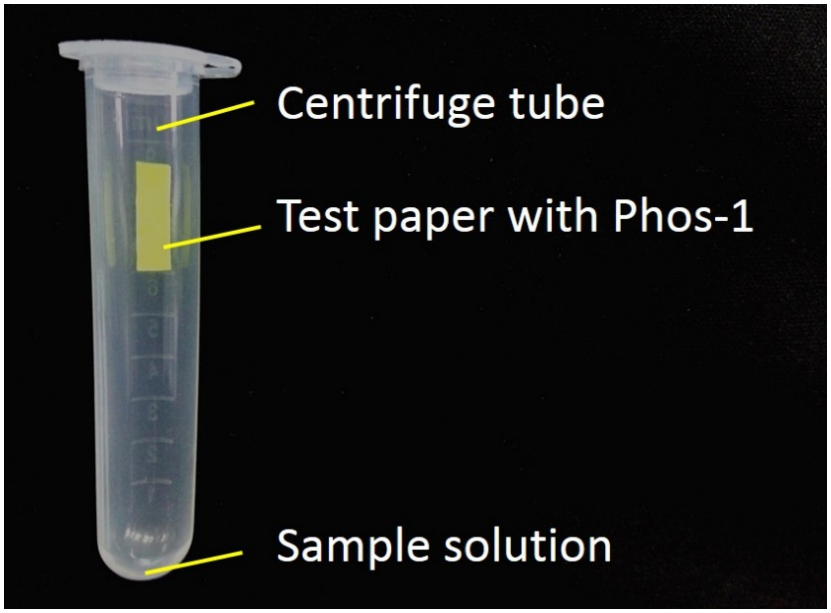


Fig. S6 Schematic diagram of detection device of phosgene gas and other sample vapor.

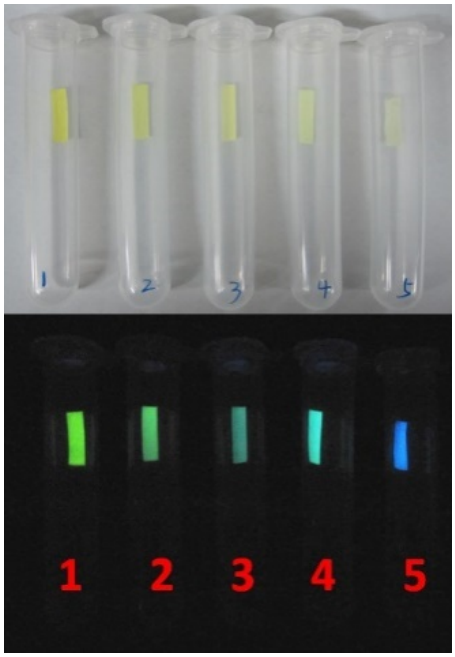


Fig. S7 Photograph of color (up) and fluorescence (down) response of the Phos-1 test papers upon exposure to vapor of various amounts of triphosgene. (1): 0 mg/L, (2): 1 mg/L, (3): 2 mg/L, (4): 3 mg/L, (5): 4 mg/L, in 25 μL DCE solution containing 0.4 ‰ v/v TEA.

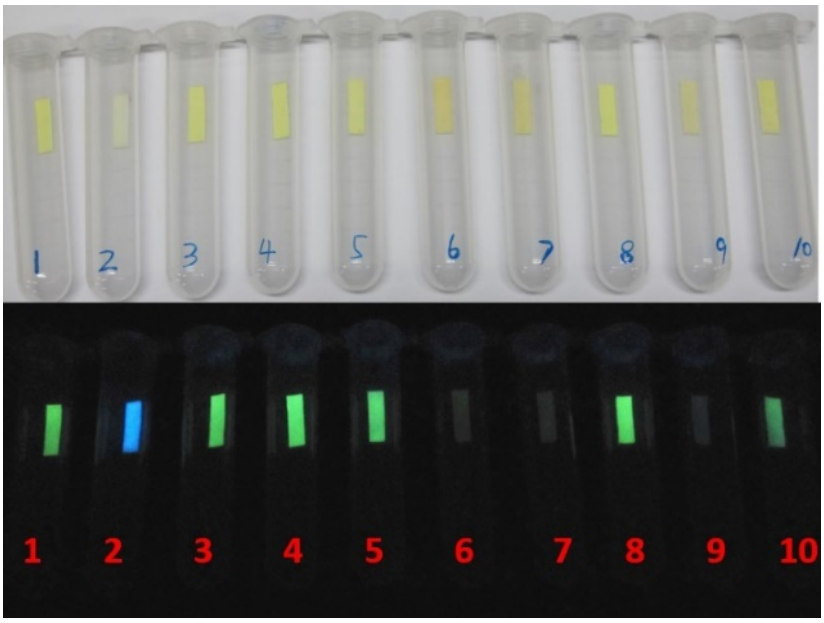
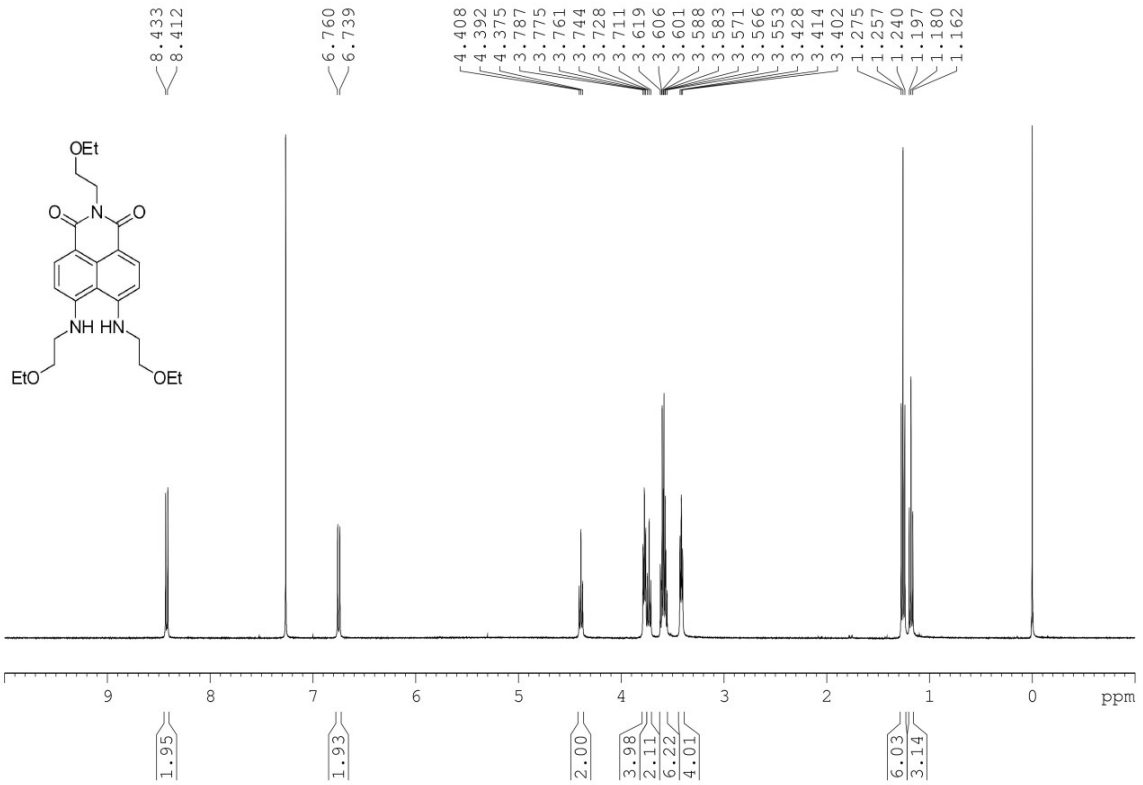
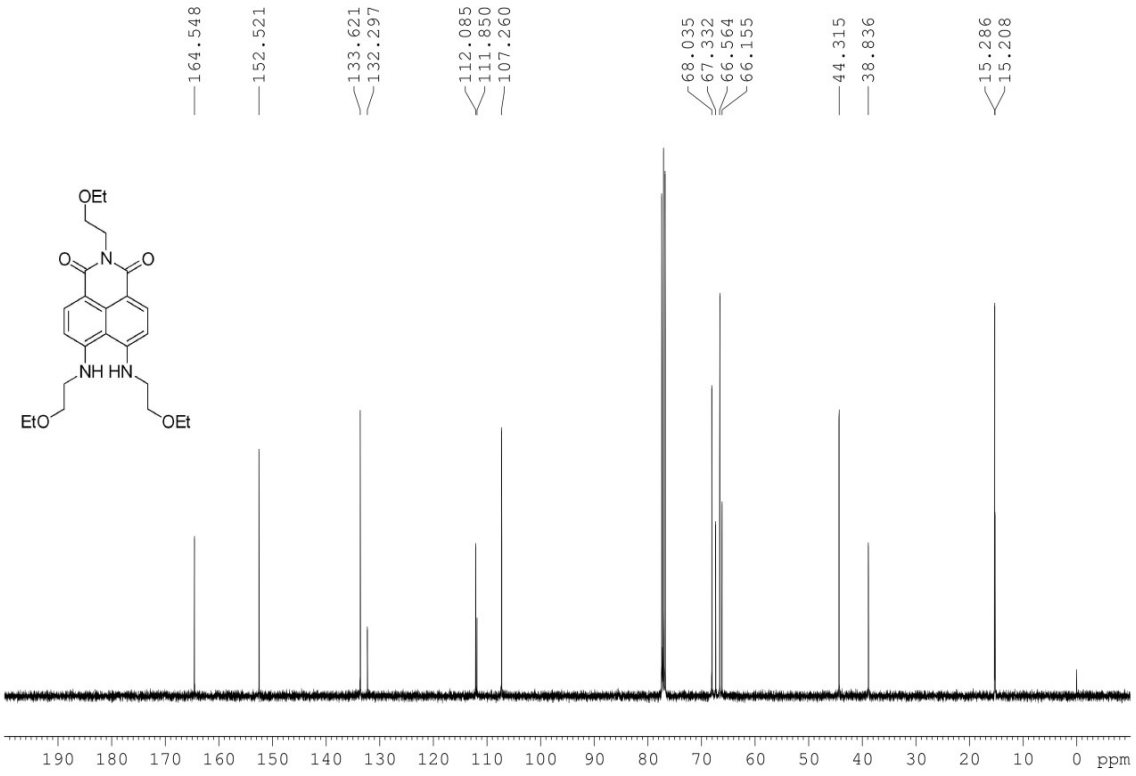
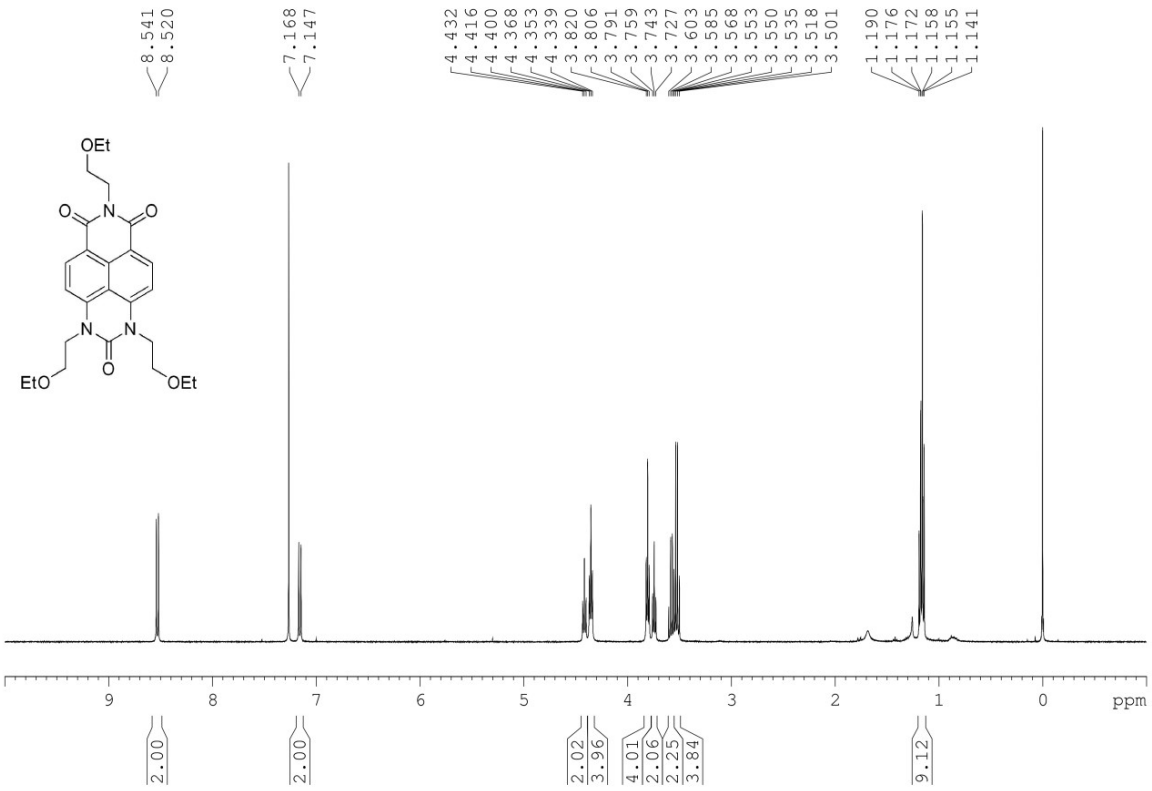


Fig. S8 Photograph of color (up) and fluorescence (down) response of Phos-1 test papers upon exposure to vapor of phosgene or various analytes after 10 min. (1) blank; (2) triphosgene (0.1 mg)/TEA(0.4 ‰ v/v); (3) DCP (1.0 μL); (4) DCNP (1.0 μL); (5) CH_3COCl (1.0 μL); (6) $SOCl_2$ (1.0 μL); (7) SO_2Cl_2 (1.0 μL); (8) TosCl (2.0 mg); (9) $POCl_3$ (1.0 μL); (10) triphosgene (2.0 mg), in 25 μL DCE solitions.

8. Copies for NMR spectra of Phos-1 and Compound 2



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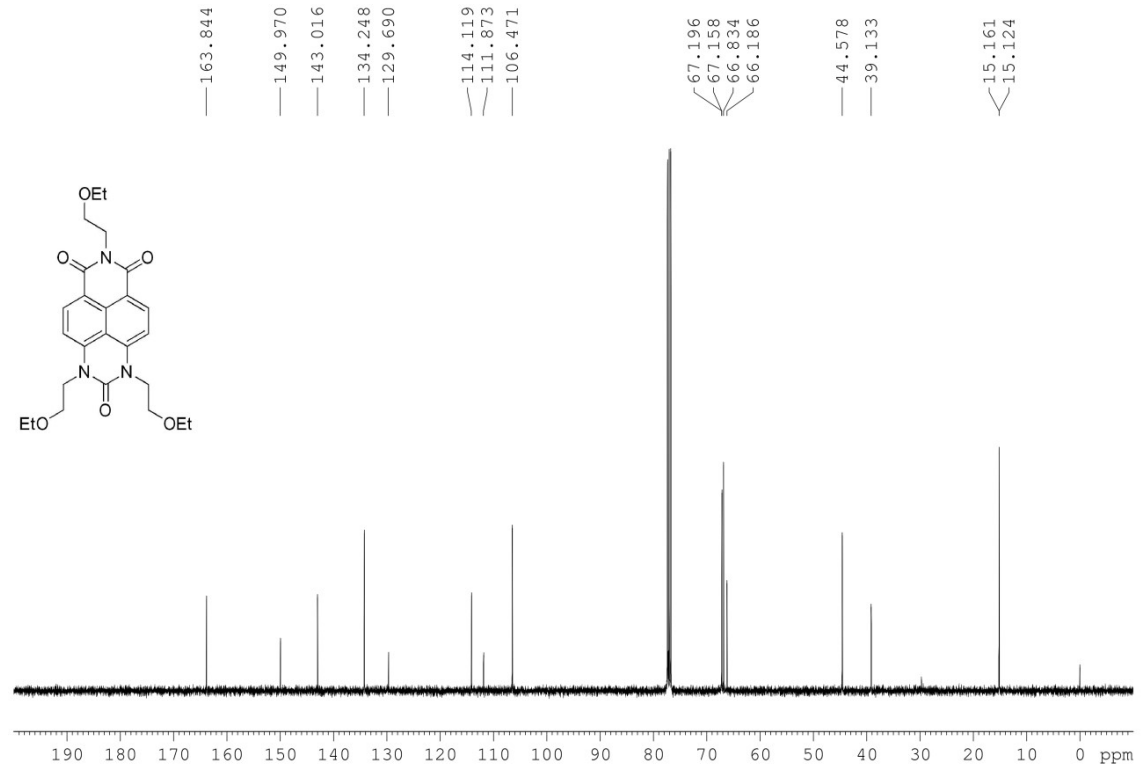
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