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Supporting Information

A Portable Chromogenic and Fluorogenic Membrane Sensor for Ultrasensitive, Specific and Instantaneous Visualizing Lethal Phosgene

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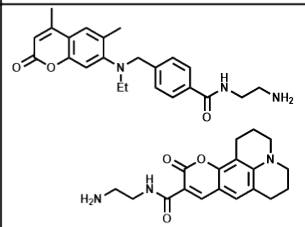
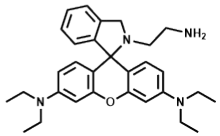
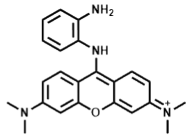
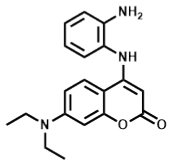
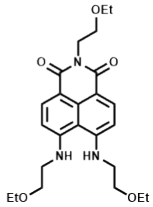
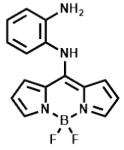
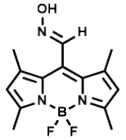
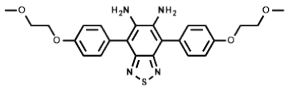
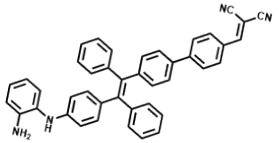
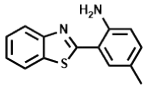
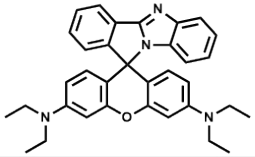
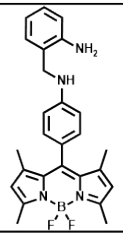
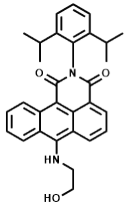
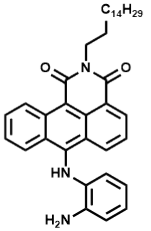
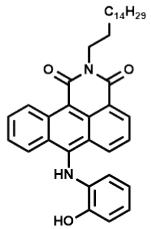
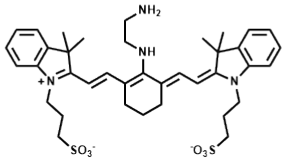
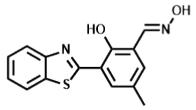
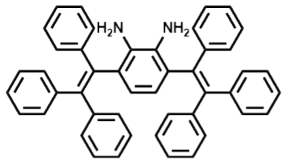
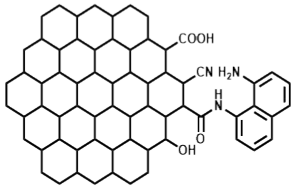
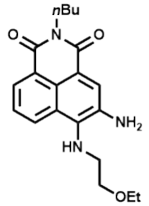
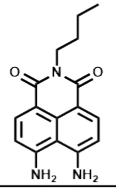
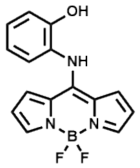
Contents

1. Table S1. Summary of fluorescent chemosensors for phosgene.

Entry	Structures	LOD	Response time	Response mode	RGB pattern analysis	Practical application of gas leakage detection	References[1-21]
1		50 mM	--	--	--	--	Chem. Commun. 2007, 1238-1239.
2		50 nM	seconds	Turn-on	--	--	Chem. Commun. 2012, 48, 1895-1897.
3		20 nM	2 min	Turn-on	--	--	Angew. Chem. Int. Ed. 2016, 55, 4729-4733.
4		3 nM	20 s	Turn-on	--	--	ACS Sens. 2017, 2, 178-182.
5		1.3 nM	20 min	Ratiometric fluorescence	--	--	Chem. Commun. 2017, 53, 1530-1533.

6		2.7 nM	15 s	Turn-on	--	--	Anal. Chem. 2017, 89, 4192-4197.
7		0.31 nM	10 s	Turn-on	--	--	Anal. Chem. 2017, 89, 12837-12842.
8		20 nM	20 min	Turn-on	--	--	Org. Chem. Front. 2017, 4, 1719-1725
9		--	--	Turn-on	--	--	Chem. Commun. 2017, 53, 9813-9816.
10		1.4 nM	4 min	Ratiometric fluorescence	--	--	Anal. Chem. 2017, 89, 12596-12601.
11		32 nM	2 min	Ratiometric fluorescence	--	--	Anal. Chem. 2018, 90, 3382-3386.
12		179 nM	30 s	Turn-on	--	--	Chem. Eur. J. 2018, 24, 3136-3140.

13		2.3 nM	5 min	Ratiometric fluorescence	--	--	Anal. Chem. 2018, 90, 8686-8691.
14		72 nM	2 min	Turn-on	--	--	Anal. Chem. 2019, 91, 12070−12076
15		4.6 nM	15 s	Turn-on	--	--	Chem. Commun. 2019, 55, 13753--13756
16		0.79 nM	seconds	Turn-on	--	--	Angew.Chem.In. Ed. 2020, 59, 695-699.
17		0.48 nM	20 min	Turn-on	--	--	Dyes Pigm. 2019, 163, 483-488

18		21 nM	2 min	Turn-on	--	--	ACS Omega 2019, 4, 22557−22561
19		2.33 ppb	< 1 min	Turn-on	--	--	ACS Appl. Mater. Interfaces 2019, 11, 19339−19349
20		0.2 nM	6 min	Turn-on	--	--	Chem. Eur.J. 2018, 24,5652 – 5658
21		2.25 μM	20 min	Ratiometric fluorescence	--	--	J Chin Chem Soc. 2020, 67, 1213-1218
22		0.22 nM	~ 2 s	Turn-on	yes	yes	This work

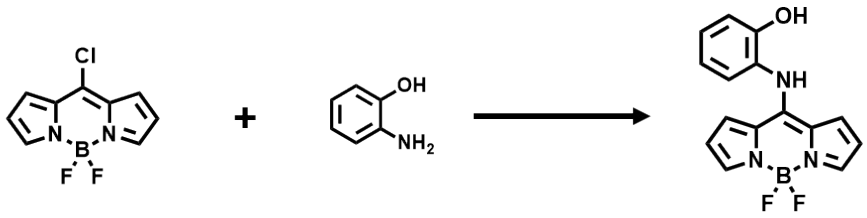
"- -" Not reported

2. Experimental section.

2.1 Materials and apparatus.

All reagents were purchased from Sigma-Aldrich and used directly without further purification. ^{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 obtained by a Hitachi UV-3310 spectrometer and a FL-4500 fluorometer, respectively. Scanning electron microscope (SEM) images were acquired by ZEISS MERLIN compact (Germany). Atom Force microscope (AFM) images were acquired by Bruker Dimension Icon with ScanAsyst® (Germany). Relative fluorescence quantum yields were determined by using fluorescein (Φ = 0.92 in 0.1 M NaOH) as references.[22]

2.2 Synthesis of BODIPY-OHA.



Scheme S1. Synthesis of BODIPY-OHA.

Under N_2 atmosphere, 8-chloro-BODIPY[23] (200 mg, 883.2 μmol), 2-aminophenol (144 mg, 1.32 mmol), triethylamine (123 μL, 883.2 μmol) and 15 ml of anhydrous ethanol were heated at 80 °C for 5 h. After the reaction mixture was cooled down to room temperature, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (CH_2Cl_2/ethanol 20:1, v/v) to give **BODIPY-OHA** (210 mg, 80%) as yellow solid. ^{1}H-NMR (400

MHz, DMSO-d_6) δ 11.11 (s, 1H, O*H*), 10.22 (s, 1H, N*H*), 7.70 (s, 1H, pyrrole-*H*), 7.48-7.47 (d, *J* = 4.0 Hz, 2H, pyrrole-*H*), 7.42-7.39 (t, *J* = 6.0 Hz, 1H, *meta*-Ph-*H*), 7.36-7.35 (d, *J* = 4.0 Hz, 1H, *ortho*-Ph-*H*), 7.12-7.10 (d, *J* = 8.0 Hz, 1H, *meta*-Ph-*H*), 7.04-7.01 (t, *J* = 6.0 Hz, 1H, *para*-Ph-H), 6.45-6.43 (d, *J* = 8.0 Hz, 1H, pyrrole-*H*), 6.27-6.25 (d, *J* = 8.0 Hz, 1H, pyrrole-*H*), 5.77(s, 1H, pyrrole-*H*). ^{13}C-NMR (100 MHz, DMSO-d_6) δ/ppm 153.5 (C_1), 149.3 (C_6), 133.8 (C_7), 132.6 ($C_{10,11}$), 131.1 ($C_{14,15}$), 128.8 (C_2), 125.5 (C_3), 120.7 (C_4), 118.7 ($C_{8,9}$), 117.7 (C_5), 114.2 ($C_{12,13}$). HR-MS (ESI): calculated for $[C_{35}H_{48}N_2O_3 + H]^+$ 545.3738, found 545.3745.

2.3 Colorimetric and fluorimetric assays for phosgene.

To avoid use of highly toxic volatile phosgene, we utilized a nonvolatile and less toxic counterpart triphosgene as a precursor to *in-situ* yield phosgene under the catalysis of triethylamine (TEA). Assays were carried out by titrating aliquots of triphosgene (0−10 μM) into **BODIPY-OHA** solution (10 μM) containing TEA (100 μM) at 25 °C. Fluorescence time-lapse images were recorded after addition of TEA into **BODIPY-OHA** solution (10 μM) containing triphosgene (20 μM). The images were recorded by using a mobile phone camera under 365 nm UV light. We also studied the colorimetric and fluorimetric responses of **BODIPY-OHA** to *p*-toluenesulfonyl chloride (TsCl), benzoyl chloride (BzCl), $SOCl_2$, $POCl_3$, acetyl chloride (AC), formaldehyde, HCl, oxalyl chloride (OC), and some nerve agent simulants including diethyl cyanophosphonate (DECP), diethyl chlorophosphate (DCP). The UV-vis absorption and fluorescence spectra (λ_{ex} = 452 nm) change of sensor were measured at room temperature.

2.4 Time-resolved fluorescence response of BODIPY-OHA towards phosgene.

BODIPY-OHA solution (10 μM) containing 100 μM TEA was placed in a 1 cm quartz cell with cover. Then, triphosgene (20 μM) in $CHCl_3$ was added to the above solution, and the fluorescence intensity at 530 nm was recorded at time interval of 2 s. Finally, the fluorescence intensity of BODIPY-OHA at 530 nm was plotted as the function of time.

Fluorescence time-lapse video was performed as following: **BODIPY-OHA** solution (10 μM) containing triphosgene (20 μM) was place in a glass tube, then a pipette loaded with 5 μL TEA (0.02 M) was set below the level of solution. At the same time, a video about time-lapse fluorescence image was recorded by a mobile phone camera under 365 nm UV light.

2.5 BODIPY-OHA-loaded membrane strips for sensing phosgene.

BODIPY-OHA (5 mg) was completely dissolved in 30 mL of anhydrous dichloromethane, and then polystyrene (2.5 g) was added. The mixture was stirred to form a homogeneous pale yellow solution. The above solution was poured into rectangular glass containers (L: 5 cm; W: 3 cm; D: 2 mm) until the surface of the plate was covered, then it was placed in the fume hood and dried at ambient condition. Finally, the **BODIPY-OHA** polymeric membrane was cut into some pieces of strips.

BODIPY-OHA-loaded membrane strips were used to determine phosgene and some other analyte vapors including TsCl, BzCl, $SOCl_2$, $POCl_3$, AC, HCl, OC, DECP, formaldehyde, DCP. Firstly, the test strips were stuck inside the bottle caps, and a predetermined amount of other analytes (100 ppm) were separately placed in some bottles (10 mL). Then, these bottles were immediately closed with the above bottle caps to allow test strips soak in the vapor of analytes for 5 min at room temperature. Investigation of sensing ability of these membrane strips for phosgene (0-10 ppm) were carried out in the similar manner, and all photos were taken by using a mobile phone camera under daylight and UV irradiation (365 nm). The time-lapsed fluorescence images of **BODIPY-OHA** membrane test strips were recorded as following: the membrane strip was placed in a 10 mL test tube containing triphosgene solution (10 μL, 135 μM). The test tube was sealed with a rubber stopper, followed by the addition of 10 μL of $CHCl_3$ containing 0.1% TEA by using a HPLC injection needle. At the same time, fluorescence images were recorded by a mobile phone camera under 365 nm UV light. 10 μL of triphosgene (135 μM) and 100 μM of TEA solution in 10 mL test tube can yield 10 ppm of phosgene.

3. Linear relationship and determination of the detection limit.

The calibration curve was first obtained from the plot of fluorescence F_{530} as a function of Triphosgene level. The regression curve equation was obtained for the lower concentration part.

$$\text{Detection limit (LOD)} = 3 \times \sigma/k$$

where k is the slope of the curve equation, and σ represents the standard deviation for the fluorescence intensity of the probe in the absence of triphosgene. $F_{530} = -9.0400 + 682.7986 \times$ [Trihposgene] ($R^2 = 0.9979$)

$$\text{Detection limit (LOD:Triphosgene)} = 3 \times 0.017/682.7986 = 0.000074\ \mu M = 0.074\ nM$$

According to the principle that one molecule of triphosgene can be decomposed into three molecules of phosgene:

$$\text{Detection limit (LOD:Phosgene)} = 3 \times \text{(LOD:Triphosgene)} = 3 \times 0.000074\ \mu M = 0.22\ nM$$

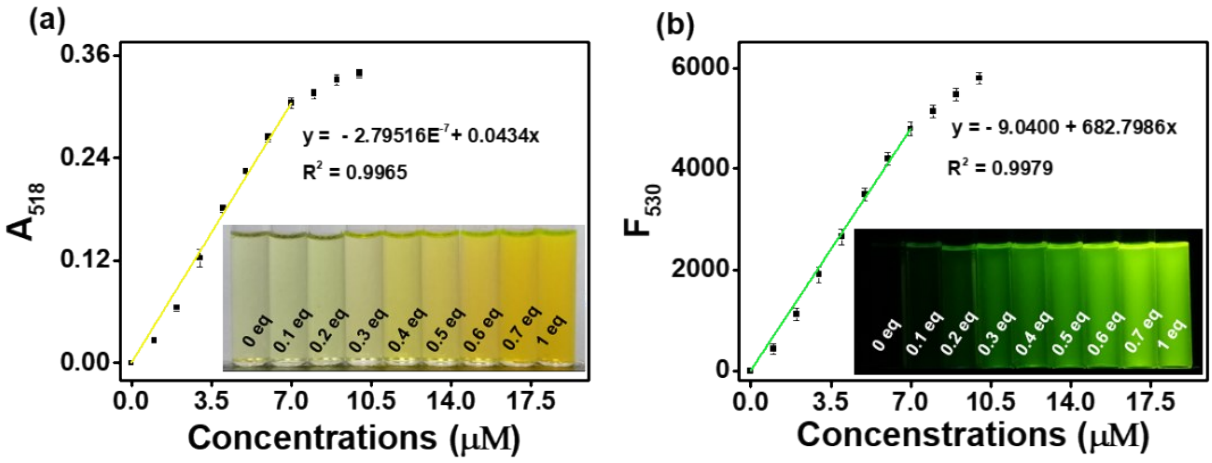


Fig. S1 (a) Absorbance and (b) fluorescence intensity linear correlation between **BODIPY-OHA** (10 μM) and concentrations of triphosgene (0-10 μM)/TEA (100 μM) in $CHCl_3$. Inset: The color and fluorescence of **BODIPY-OHA** solution (10 μM) in the presence of triphosgene (0-10 μM)/TEA (100 μM) under daylight and 365 nm UV light. (λ_{ex} = 452 nm, λ_{em} = 530 nm, slits:2.5 nm/5.0 nm, error bars are ± SD, n=3)

4. Selectivity of BODIPY-OHA.

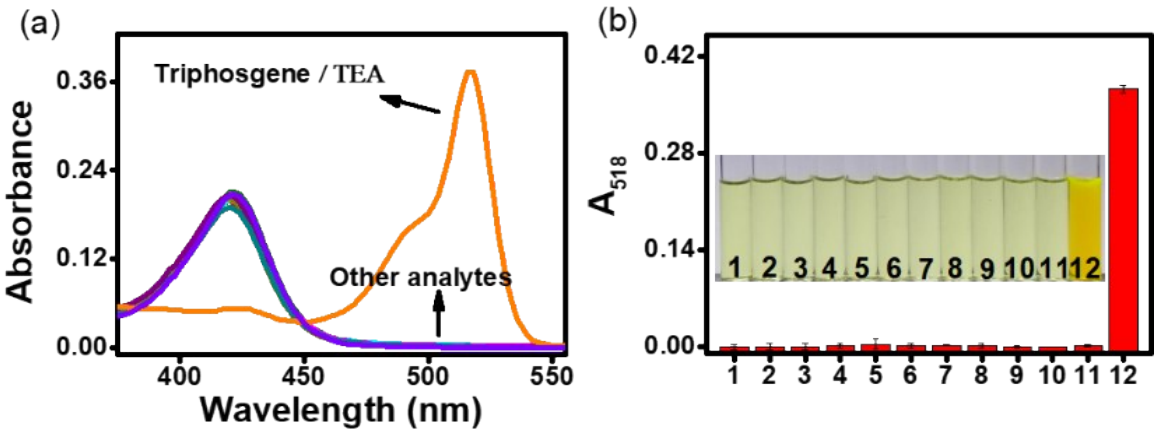


Fig. S2 (a) UV-vis absorption spectra and (b) absorbance (A_{518}) changes of **BODIPY-OHA** (10 μM) in the presence of triphosgene (10 μM)/TEA((100 μM)) and analytes (100 μM) at 25 °C. Insert: photos of the color of **BODIPY-OHA** in the presence of various analytes: (1) blank, (2) TsCl, (3) BzCl, (4) $SOCl_2$, (5) $POCl_3$, (6) AC, (7) HCl, (8) OC, (9) DECP, (10) formaldehyde, (11) DCP, (12) phosgene. All fluorescence photos of the sensor were obtained under a 365 nm lamp. (λ_{ex} = 452 nm, λ_{em} =530 nm, slits: 2.5 nm/5 nm, Error bars are ± SD, n=3).

5.The response of BODIPY-OHA for triphosgene and diphosgene.

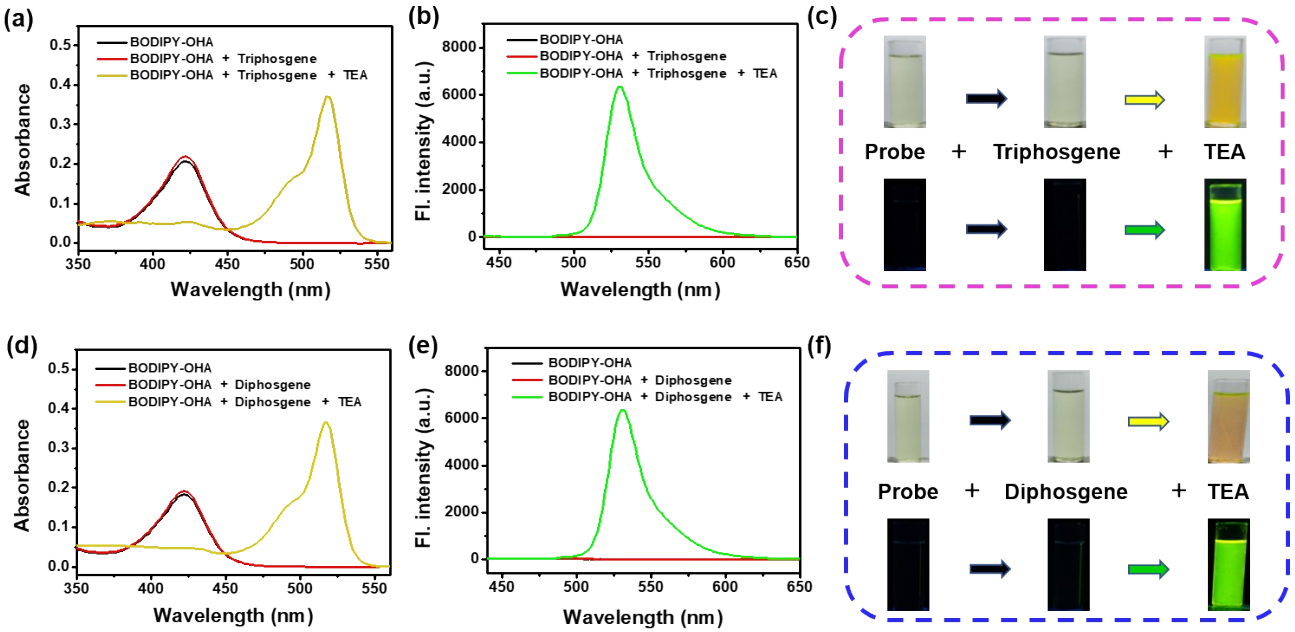


Fig. S3 (a) UV-vis absorption and (b) Fluorescence spectra of **BODIPY-OHA** solution (10 μM) before/after treatment with triphosgene (20 μM) and TEA (100 μM). **BODIPY-OHA** solution was firstly incubated with triphosgene (20 μM) at 25 °C, and then TEA (100 μM) was added to the **BODIPY-OHA** solution. (c) The color and fluorescence images of **BODIPY-OHA** solution (10 μM) before/after treatment with triphosgene (20 μM) and TEA (100 μM). (d) UV-vis absorption and (e) Fluorescence spectra of **BODIPY-OHA** solution (10 μM) before/after treatment with diphosgene (20 μM) and TEA (100 μM). **BODIPY-OHA** solution was firstly incubated with diphosgene (20 μM) at 25 °C, and then TEA (100 μM) was added to the **BODIPY-OHA** solution. (f) The color and fluorescence images of **BODIPY-OHA** solution (10 μM) before/after treatment with diphosgene (20 μM) and TEA (100 μM). λ_{ex} = 452 nm, λ_{em} = 530 nm, slits: 2.5 nm/5.0 nm.

6. Investigation of sensing mechanism.

BODIPY-OHA (40 mg, 134 μmol), triphosgene (119 mg, 401 μmol) and 10 mL chloroform were placed in a round bottom flask. The mixture was stirred for 30 min at room temperature. Then the solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography using CH_2Cl_2/ethanol (80:1, v/v) as eluent to give **BODIPY-OAC** as peacock blue solid (41mg, 94%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.25 (s, 2H, pyrrole-*H*), 7.55-7.53 (d, *J* = 8.0 Hz, 1H, *ortho*-Ph-*H*), 7.51-7.50 (d, *J* = 4.0 Hz, 2H, pyrrole-*H*), 7.30-7.26 (t, *J* = 8.0 Hz, 1H, *meta*-Ph-*H*), 7.23-7.19 (t, *J* = 8.0 Hz, 1H, *para*-Ph-*H*),7.13-7.11 (d, *J* = 8.0 Hz, 1H, *meta*-Ph-*H*), 6.71-6.70 (d, *J* = 8.0 Hz, 2H, pyrrole-*H*), ^{13}C NMR (100 MHz, DMSO-d_6) δ/ppm 152.1 (C_1), 147.9 (C_2), 143.2 (C_7),134.2 (C_8), 132.7 (C_{15}), 132.5 (C_{16}), 131.0 ($C_{11,12}$), 124.8 ($C_{4,5}$), 124.4 ($C_{9,10}$), 120.4 ($C_{3,6}$), 110.8(C_{13}), 110.6(C_{14}). HR-MS (ESI): calculated for $[C_{16}H_{10}BF_2N_3O_2 + H]^+$ 326.0912, found 326.0957.

7. Gaussian calculation summary.

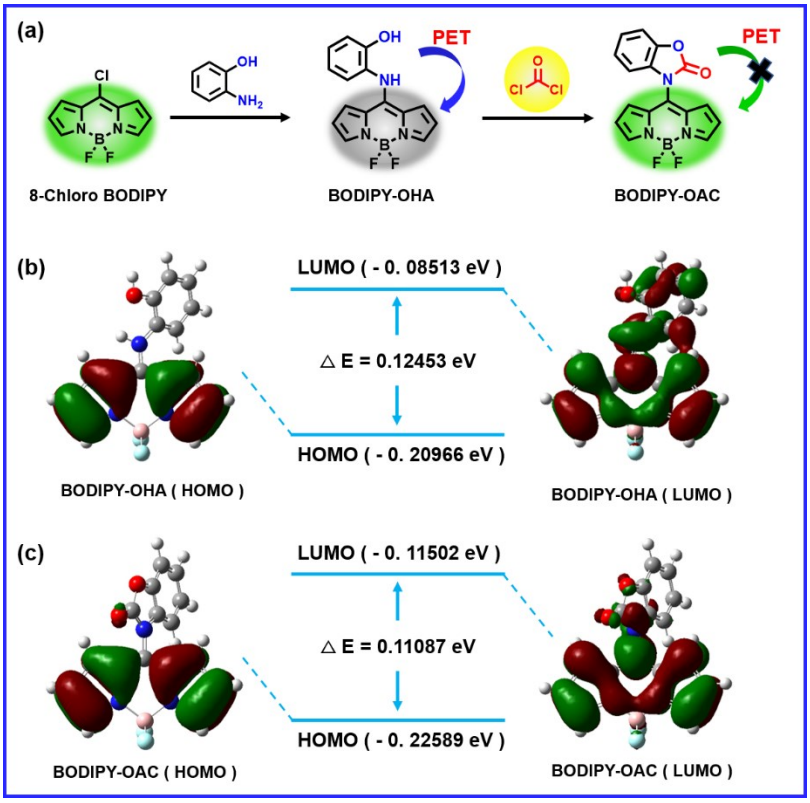


Fig. S4 (a)The design strategy of BODIPY-OHA. Molecular amplitude plots the HOMO and LUMO of (b) BODIPY-OHA and (c) BODIPY-OAC using the B3LYP/6-31G* basis set.

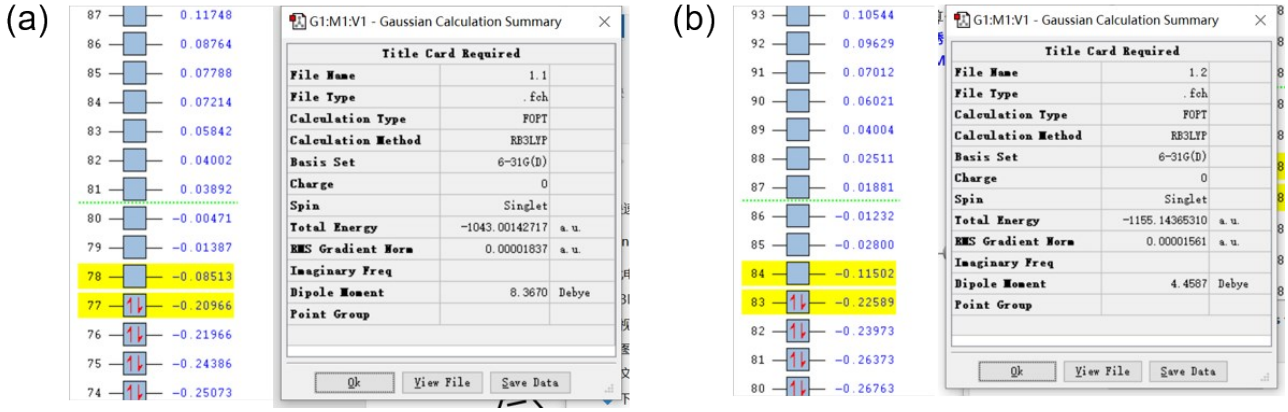


Fig. S5 Gaussian calculation summary of (a) **BODIPY-OHA** and (b) **BODIPY-OAC.**

8. Fluorescence response of BODIPY-OHA-loaded strip towards phosgene.

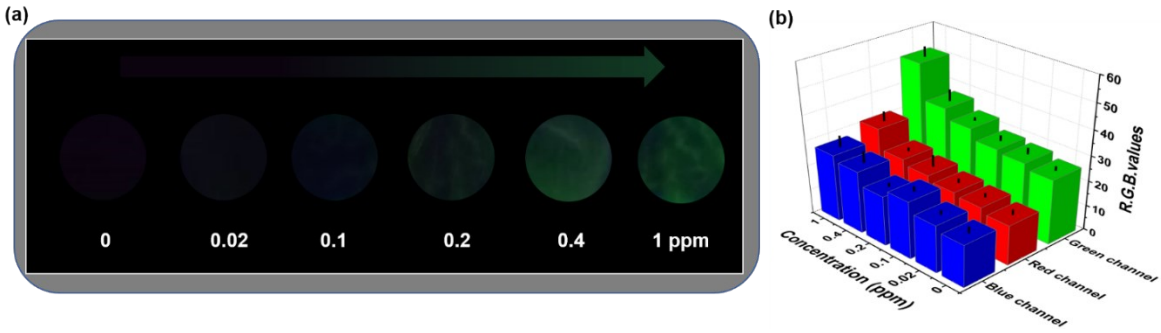


Fig. S6 (a) Fluorescence images and (b) RGB values of **BODIPY-OHA**-loaded strips after exposure to different levels of phosgene vapor: 0, 0.02, 0.10, 0.20, 0.40, 1.00 ppm.

9. Cytotoxicity assay.

The cytotoxicity of **BODIPY-OHA** in L929 normal cells was evaluated by using the Cell Counting Kit-8 (Shanghai Biyuntian Bio-Technology Co., Ltd.). L929 cells were grown in 96-well plates (Corning) at 5000 cells per well. After the cells completely attached to the plates for 24 h, each well was washed with 100 μL PBS, and then incubated with various concentrations of **BODIPY-OHA** (2.5, 5, 10, 15, 20, and 25 μM) for 24 h. Afterwards, each well was washed with 100 μL PBS and added 100 μL serum-free DMEM containing 10% CCK-8, and further incubated for 1 h, Finally, the absorbance at 450 nm was determined by a plate reader (BioTek: Gene Co., Ltd).

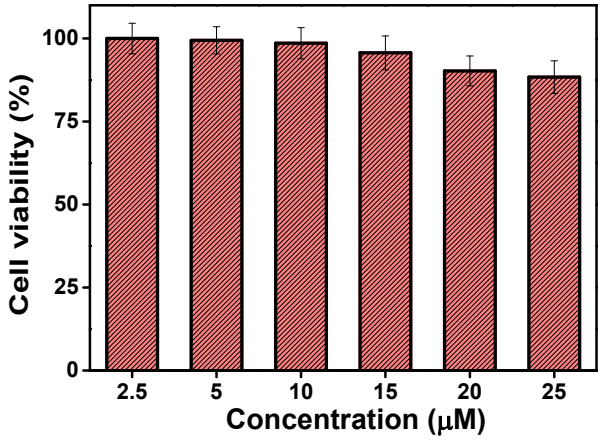


Fig. S7. The L929 cells viability after incubation with various concentrations of **BODIPY-OHA** (0 – 25 μM) for 24 h. (error bars are ± SD n = 5)

10. Fluorescence response of test strips to phosgene in the presence of interfering species.

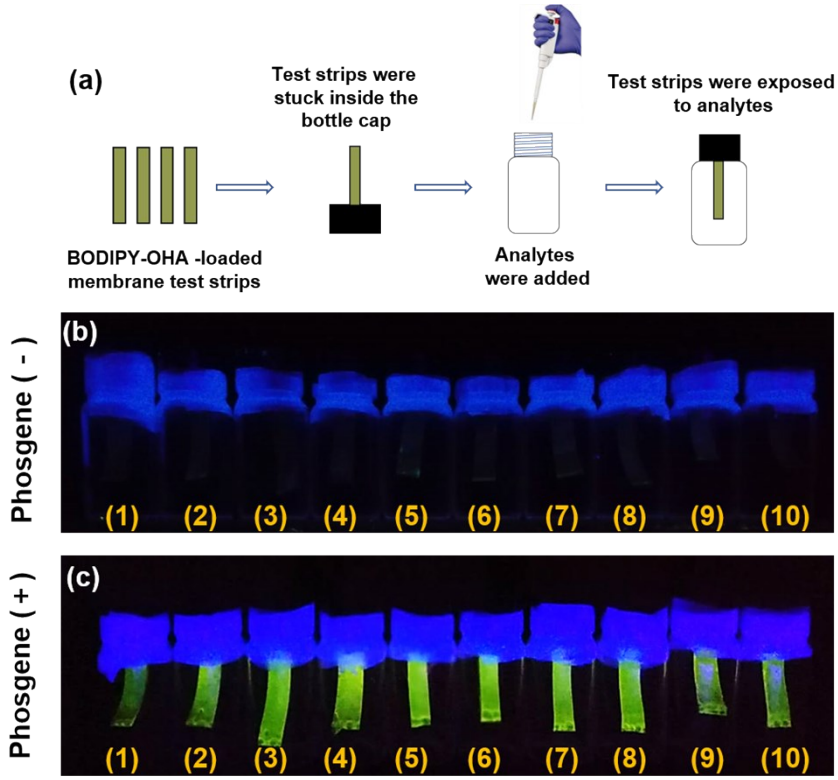


Fig. S8 (a) The schematic procedure to detect phosgene and other analyte vapors by using **BODIPY-OHA**-loaded polystyrene membrane strips. (b) Fluorescence photos of test strips that were exposed to 100 ppm of various nerve-gas mimics, acyl chlorides and formaldehyde for 5 min, respectively. (c) Fluorescence photos of test strips that were exposed to phosgene gas (10 ppm) under coexistence of 100 ppm acyl chlorides, some nerve agent mimics and formaldehyde, respectively. (1) TsCl, (2) BzCl, (3) $SOCl_2$, (4) $POCl_3$, (5) AC, (6) HCl, (7) OC, (8) DECP, (9) formaldehyde, (10) DCP.

11. Fluorescence responses of BODIPY-OHA-loaded strips towards phosgene at different conditions.

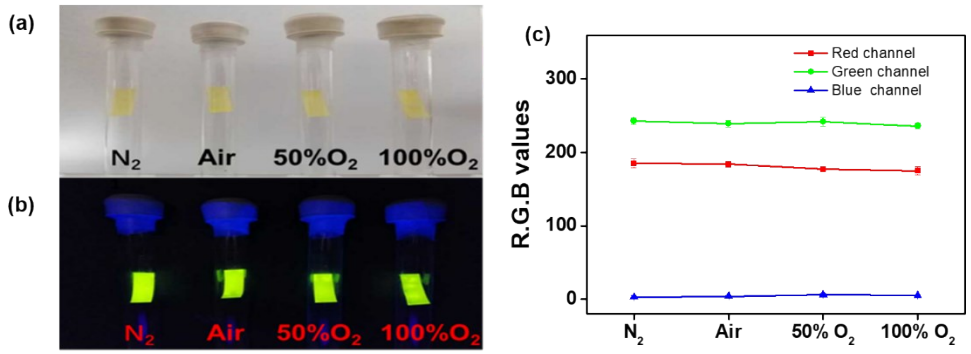


Fig. S9 Photos of (a) color and (b) fluorescence of **BODIPY-OHA**-loaded test strips that was firstly exposed to different oxygen contents for 7 days at room temperature, then exposed to 10 ppm of phosgene. (c) RGB values of each fluorescence image. All fluorescence photos of the sensor were obtained under a 365 nm lamp.

12. Structure characterization.

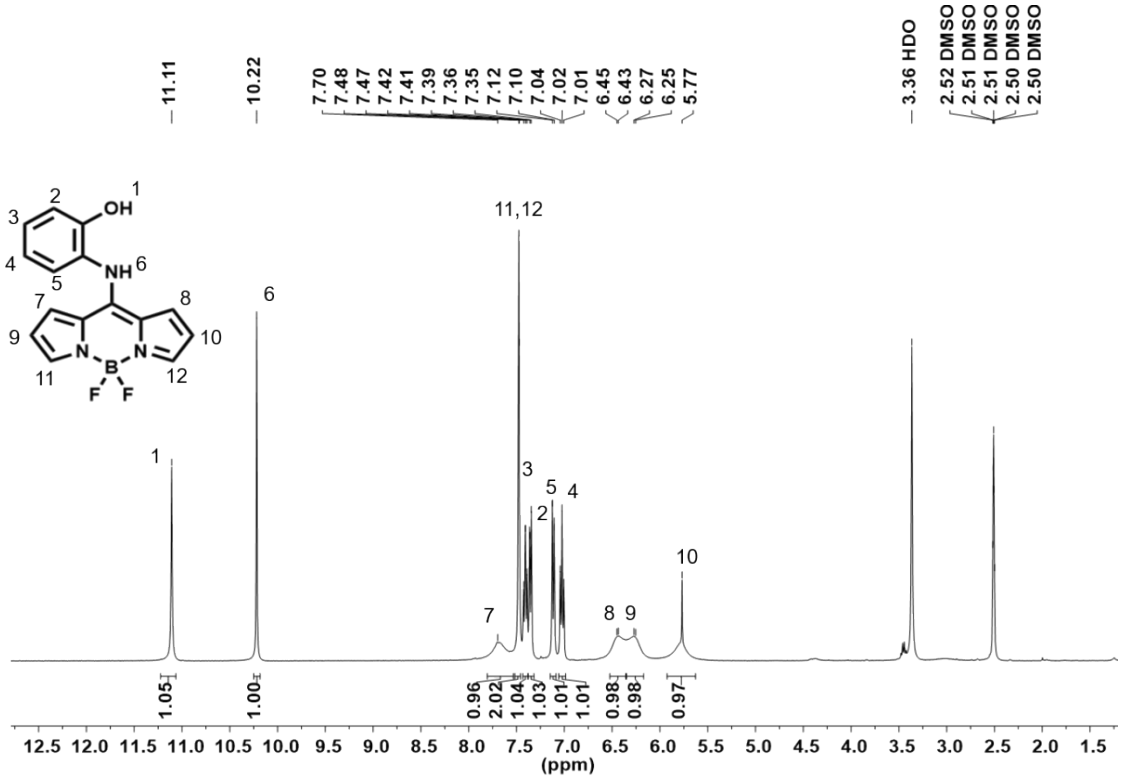


Fig. S10 ^{1}H NMR spectrum of **BODIPY-OHA** in DMSO-d_6 (400 MHz).

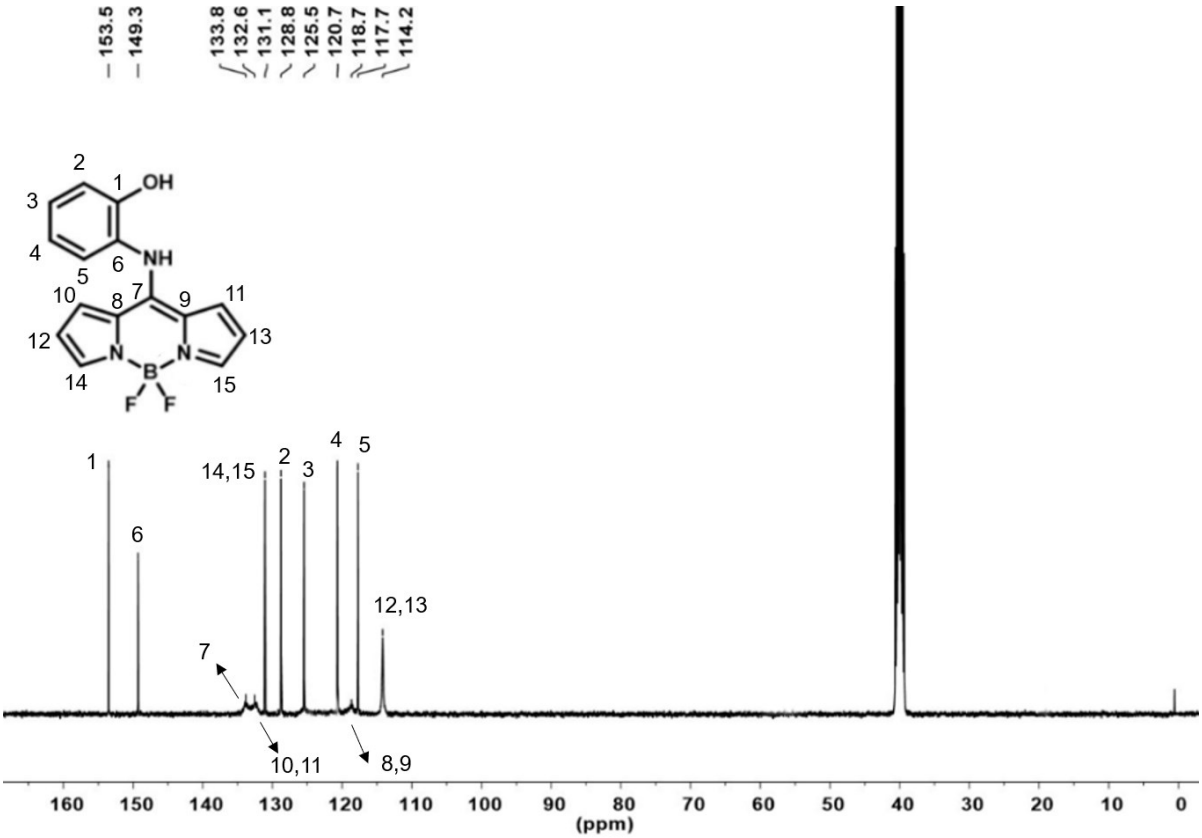


Fig. S11 ^{13}C NMR spectrum of **BODIPY-OHA** in DMSO-d_6 (100 MHz).

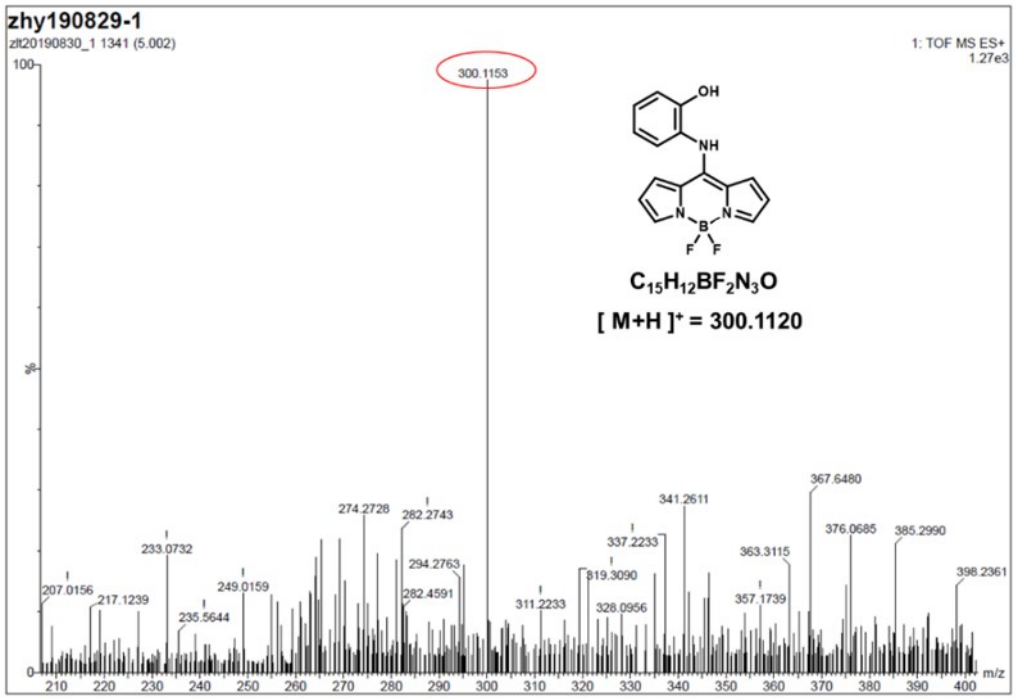


Fig. S12 HR-MS spectra of **BODIPY-OHA**.

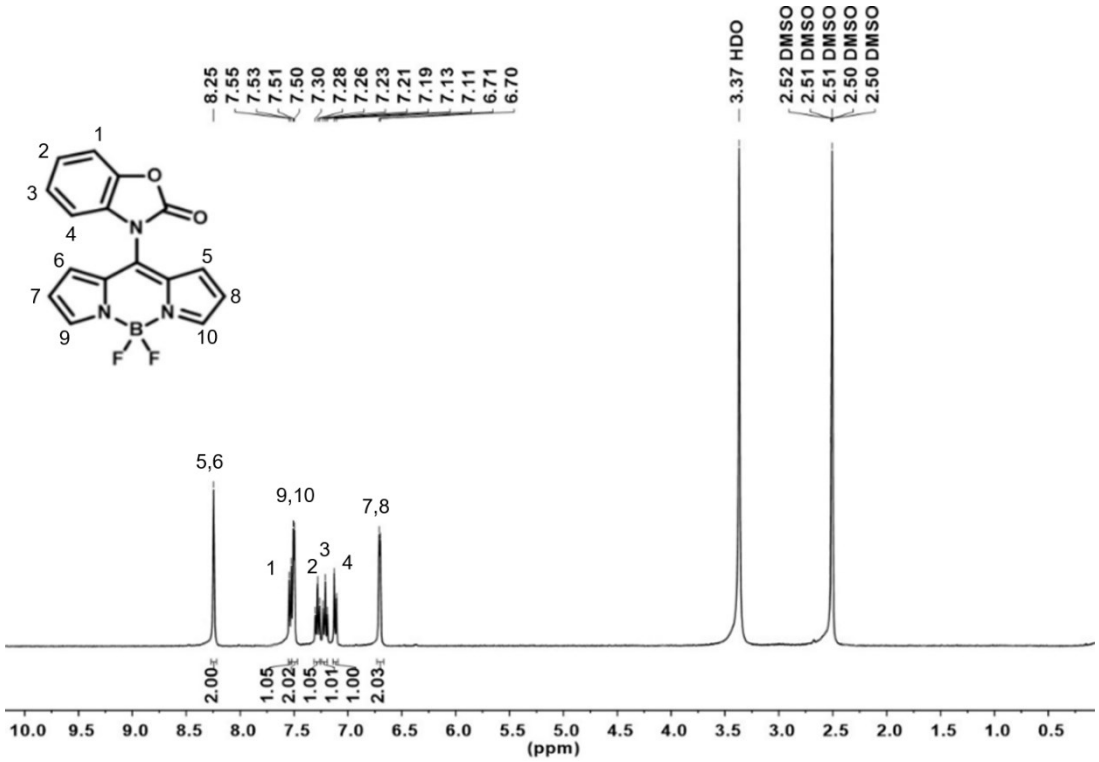


Fig. S13 ^{1}H NMR spectrum of **BODIPY-OAC** in DMSO-d_6 (400 MHz).

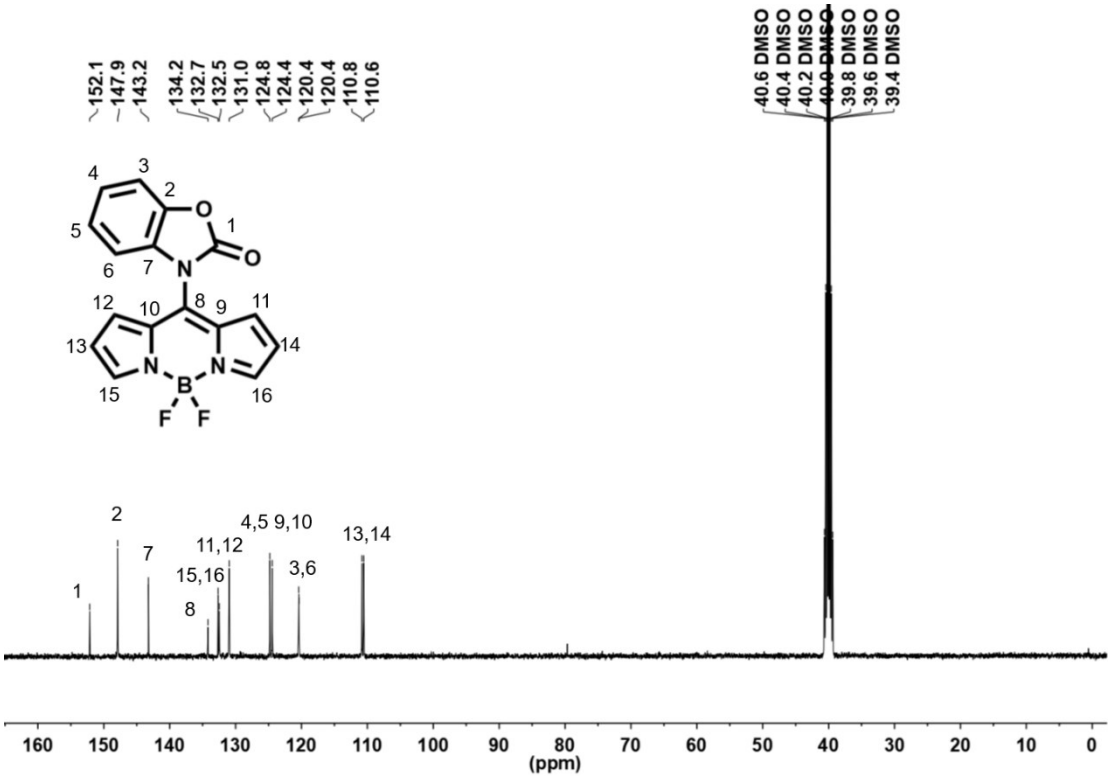


Fig. S14 ^{13}C NMR spectrum of **BODIPY-OAC** in DMSO-d_6 (100 MHz).

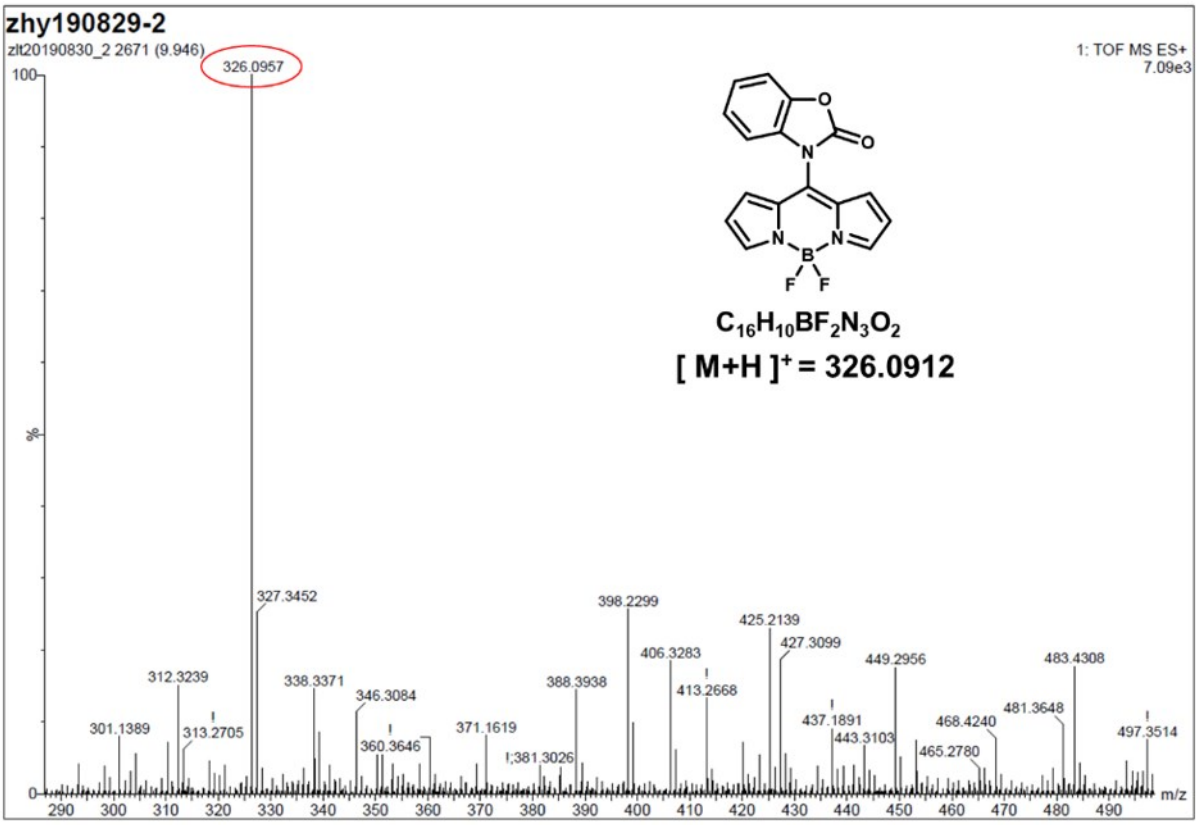


Fig. S15 HR-MS spectra of **BODIPY-OAC**.

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