

Supporting Information

A Rhodamine-TPE Scaffold-Based Fluorescent Probe for Visualizing Phosgene with a Portable Smartphone via Test TLC Strips

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Additional spectroscopic data

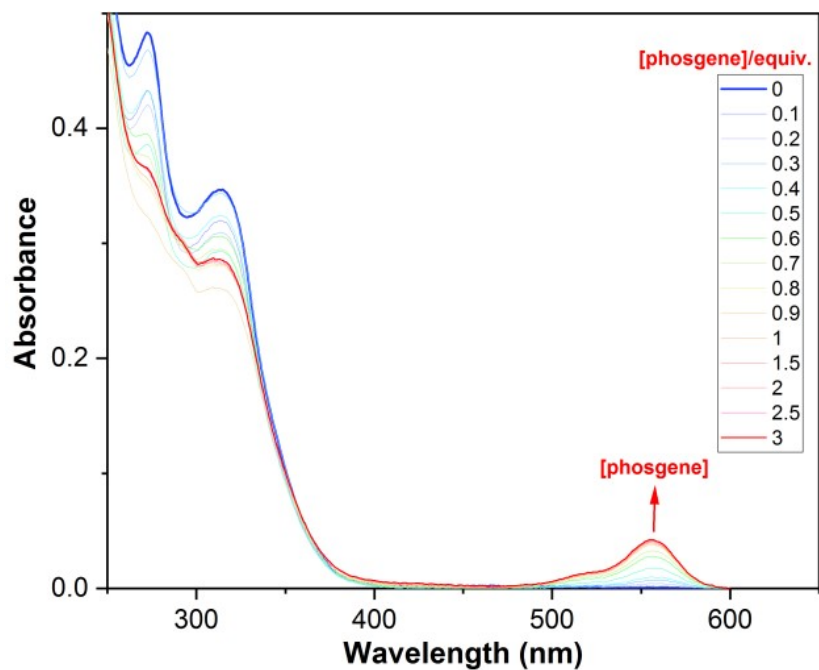


Fig. S1 UV-Vis absorption spectra of TPE-RhodEA (10.0 μM) in CH₃CN solution (containing 1% TEA) in the presence of different concentrations of phosgene (0-3.0 equiv.).

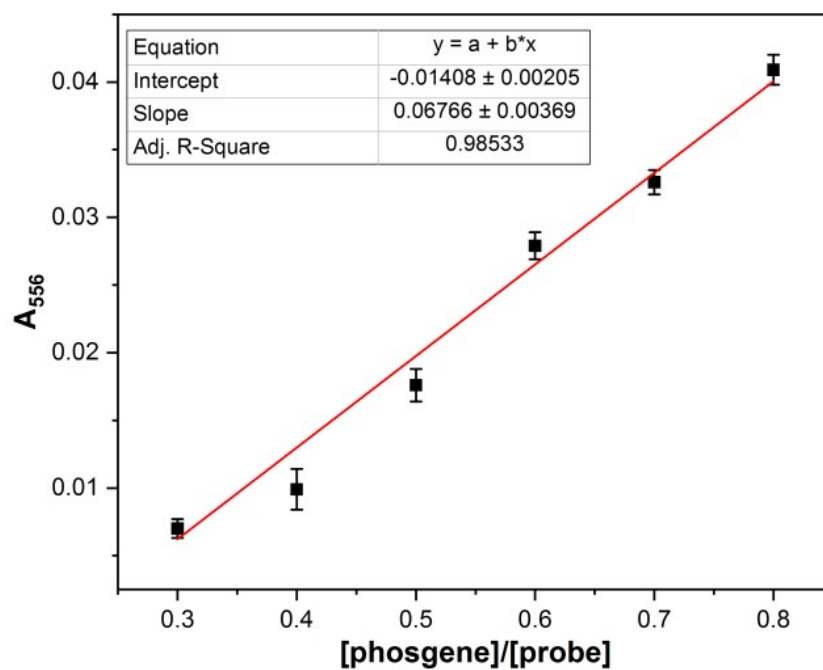


Fig. S2 The absorbance of UV-Vis absorption spectra of **TPE-RhodEA** (10.0 μM) at 556 nm (A_{556}) as a function of phosgene concentration (0.3-0.8 equiv.) in CH_3CN solution (containing 1% TEA).

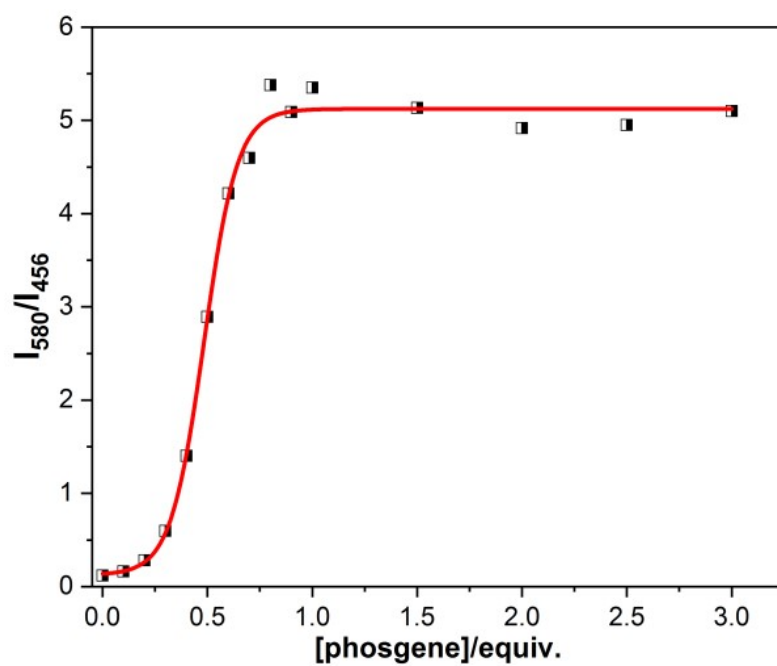


Fig. S3 The ratio of the fluorescent intensity of **TPE-RhodEA** (10.0 μ M) at 456 nm (I_{456}) and 580 nm (I_{580}), I_{580}/I_{456} , as a function of phosgene concentration (0-3.0 equiv.) under the same condition as the phosgene titration.

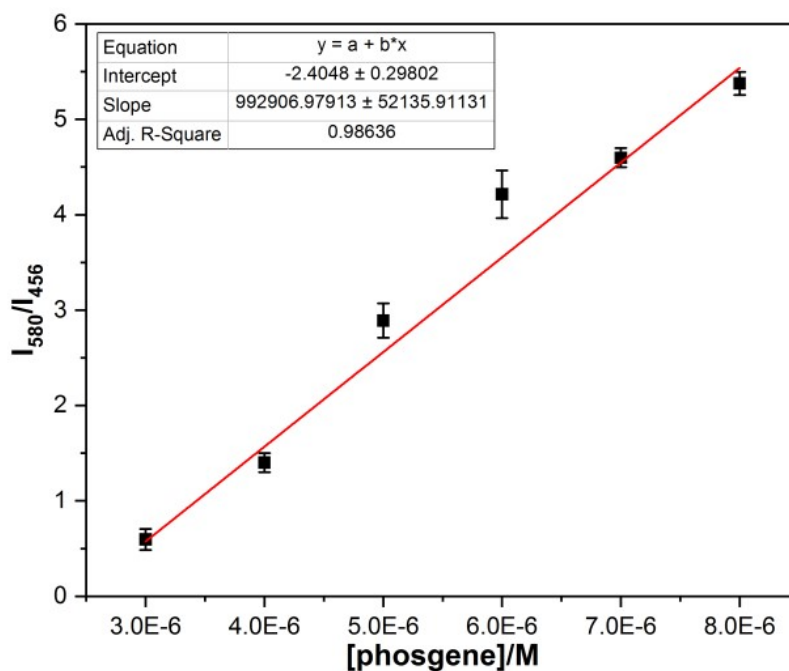


Fig. S4 The change of the ratio of the fluorescent intensity of **TPE-RhodeA** at 456 nm and 580 nm, I_{580}/I_{456} , as a function of phosgene concentration (0.3-0.8 equiv.) under the same condition as the phosgene titration.

The detection limit (DL) of phosgene using **TPE-RhodeA** was determined from the following equation: ¹

$$DL = 3 \cdot \sigma / K$$

Where σ is the standard deviation of the blank solution; K is the slope of the calibration curve.

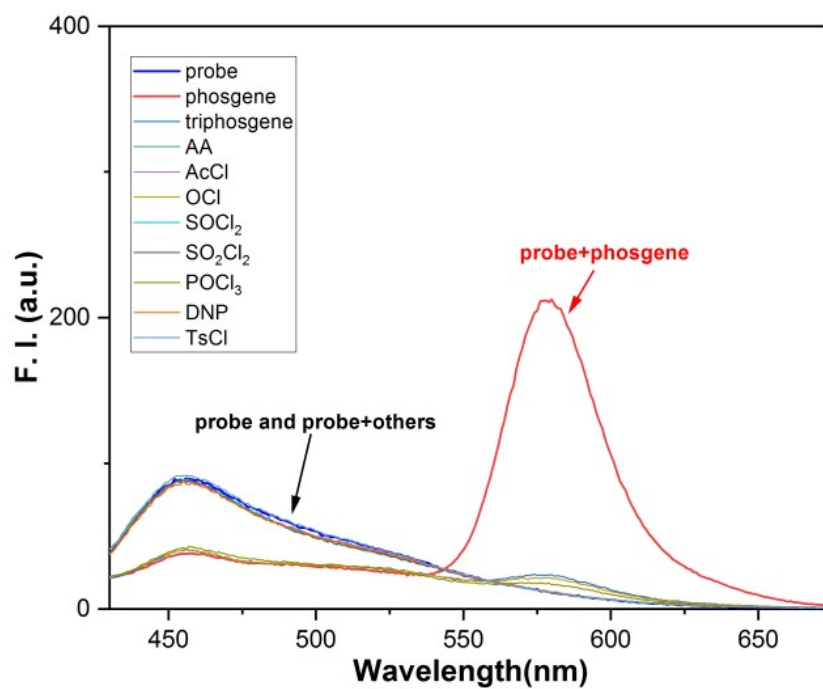


Fig. S5 Fluorescence spectra of **TPE-RhodEA** (10.0 μM) before and after addition of various analytes (including acetic anhydride (AA), acetyl chloride (AcCl), oxalyl chloride (OCl), thionyl chloride (SOCl_2), sulfone chloride (SO_2Cl_2), phosphorus oxychloride (POCl_3), diethyl chlorophosphate (DCP), *p*-toluenesulfonyl chloride (TsCl), triphosgene, and phosgene, (in CH_3CN solution, containing 1% TEA, $\lambda_{\text{ex}} = 400 \text{ nm}$).

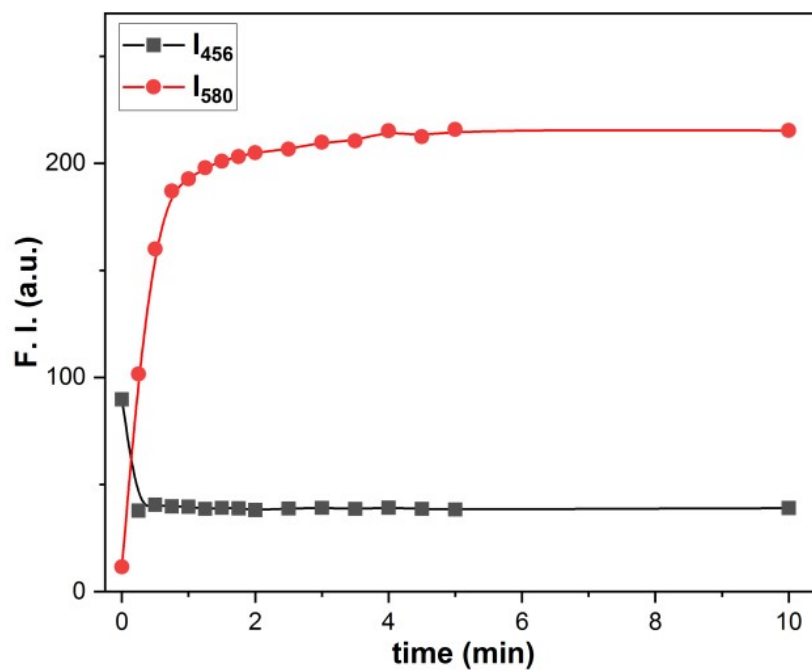
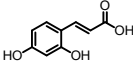
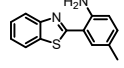
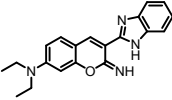
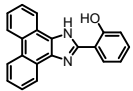
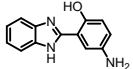
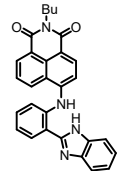
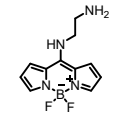
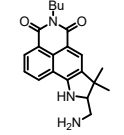
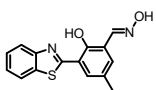
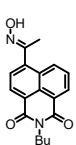
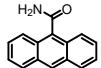
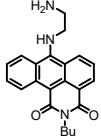
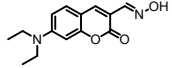
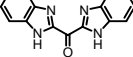
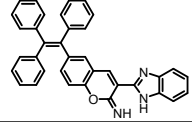
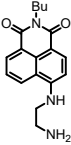
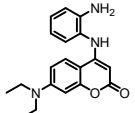
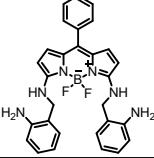
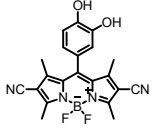
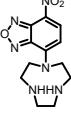
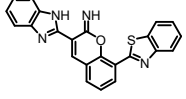
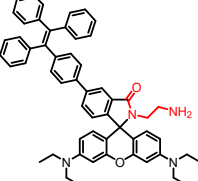


Fig. S6 The change of the fluorescent intensity of TPE-RhodEA ($10.0 \mu\text{M}$) in the present of 1 equiv. of phosgene at 456 nm (I_{456}) and 580 nm (I_{580}), respectively, as a function of reaction time (0-10 min) under the same condition as the phosgene titration.

Table S1 The performance comparison of the probe with other reported phosgene sensors.

Structures	Response type	LOD	Time (in solution)	Time (in gas phase)	Refs
	off-on	18 nM	-	-	2
	ratiometric	0.14 ppm	4 min	10 min	3
	ratiometric	27 nM	2 min	10 min	4
	ratiometric	0.14 μM	30 s	5 min	5
	ratiometric	5.3 nM	50 s	10 min	6
	ratiometric	6.7 nM	200 s	1 min	7
	ratiometric	12 nM	1.5 s	1 min	8
	off-on	0.3 nM	60 s	1 s	9
	off-on	0.48 nM	20 min	20 min	10
	off-on	6.3 nM	15 min	5 min	11
	off-on	5.56 nM	1.5 min	10 min	12
	ratiometric	0.09 nM	20 s	1 min	13
	off-on	0.12 μM	1 min	10 s	14
	off-on	3.3 nM	30 s	10 min	15

	ratiometric	0.36 μM	6 s	2 min	16
	ratiometric	4.9 nM	12 min	5 min	17
	off-on	3 nM	30 s	5 min	18
	ratiometric	2.36 nM	2 min	30 s	19
	off-on	24 ppm	3 s	30 s	20
	off-on	1.2 nM	20 s	5 min	21
	off-on	1.65 nM	200 s	5 min	22
	ratiometric	0.54 ppm	2 min	2 min	This work

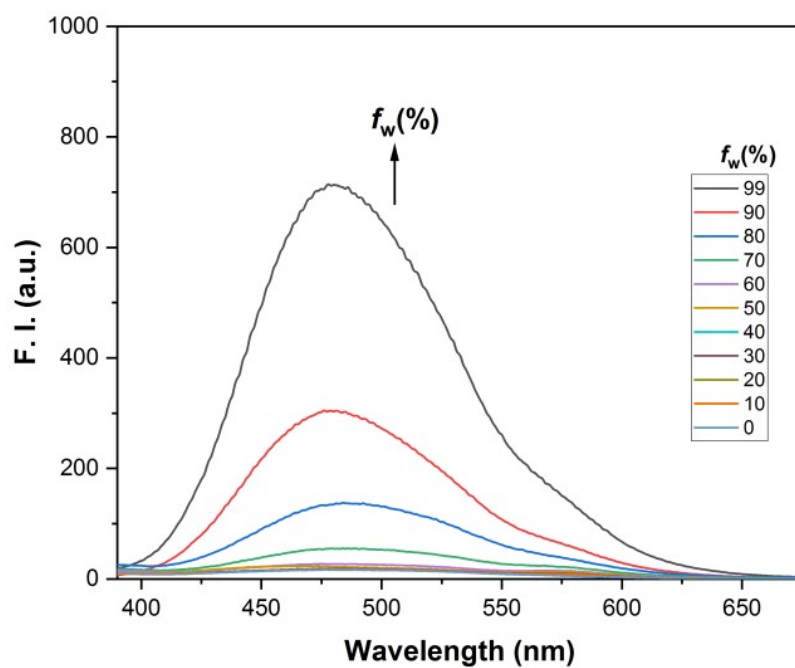


Fig. S7 Fluorescence spectra of **TPE-RhodEA** in THF and THF/water mixtures with different water fractions ($f_w\%$); $[\text{TPE-RhodEA}] = 10 \mu\text{M}$; $\lambda_{\text{ex}} = 365 \text{ nm}$.

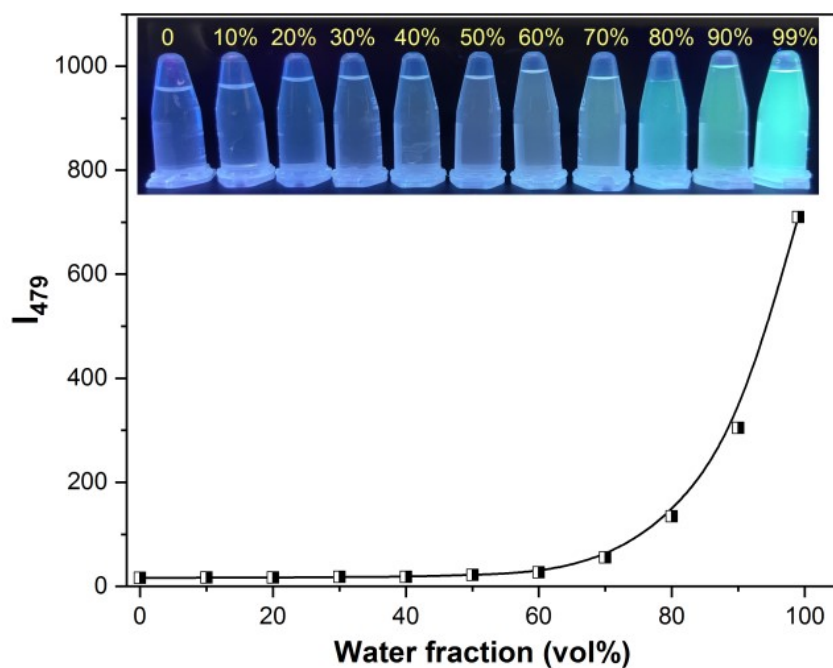


Fig. S8 Plot of relative fluorescence intensity of **TPE-RhodEA** at 479 nm versus the solvent composition of THF/water mixture. Inset: Photographs of **TPE-RhodEA** in different water fractions of H₂O/ THF (from 0 to 99%, v/v) taken under UV light (365 nm).

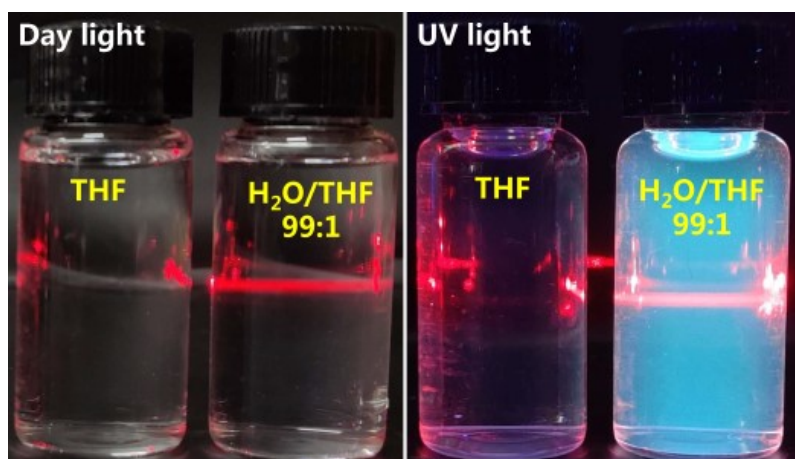


Fig. S9 Tyndall effect test of TPE-RhodEA in THF and H₂O/THF (99 : 1, v/v).

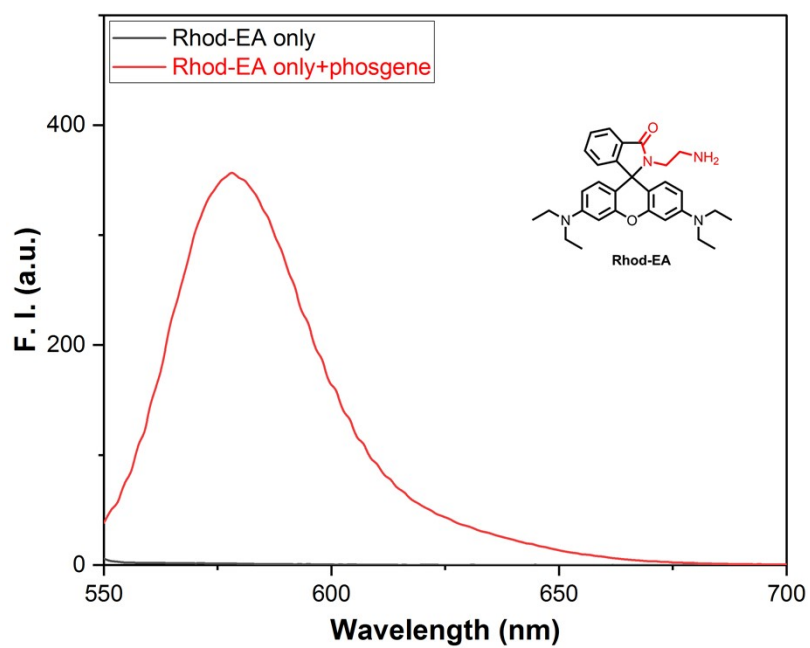


Fig. S10 Fluorescence spectra of **Rhod-EA** (10.0 μM) in CH_3CN solution (containing 1% TEA)

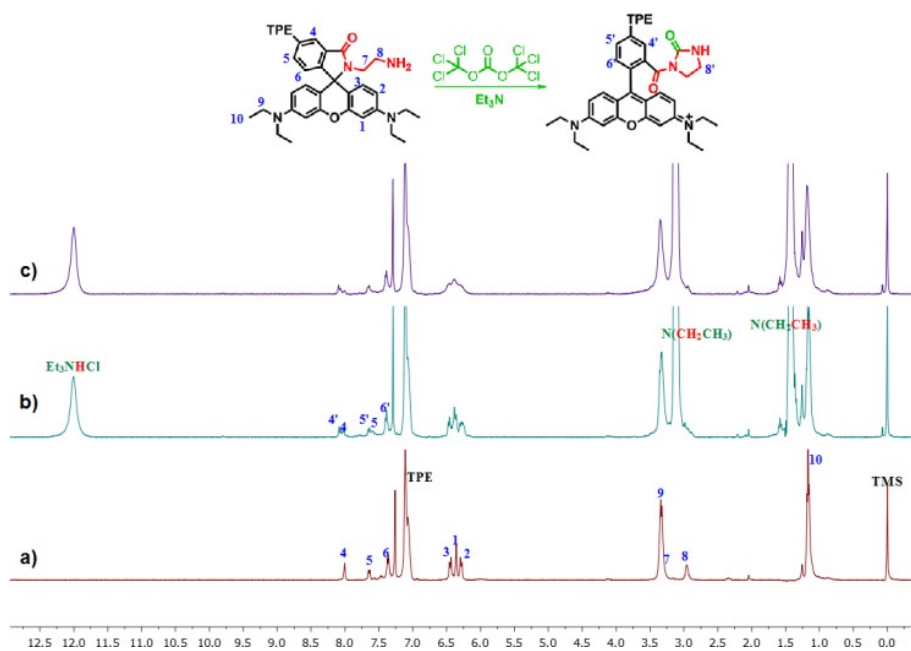


Fig. S11 In situ ¹H NMR titration experiments of the probe in the presence of phosgene in CDCl₃.
a) The probe alone; b) Add 1 equivalent of phosgene to the probe solution after 1 minute; c) Add 1 equivalent of phosgene to the probe solution after 10 minutes.

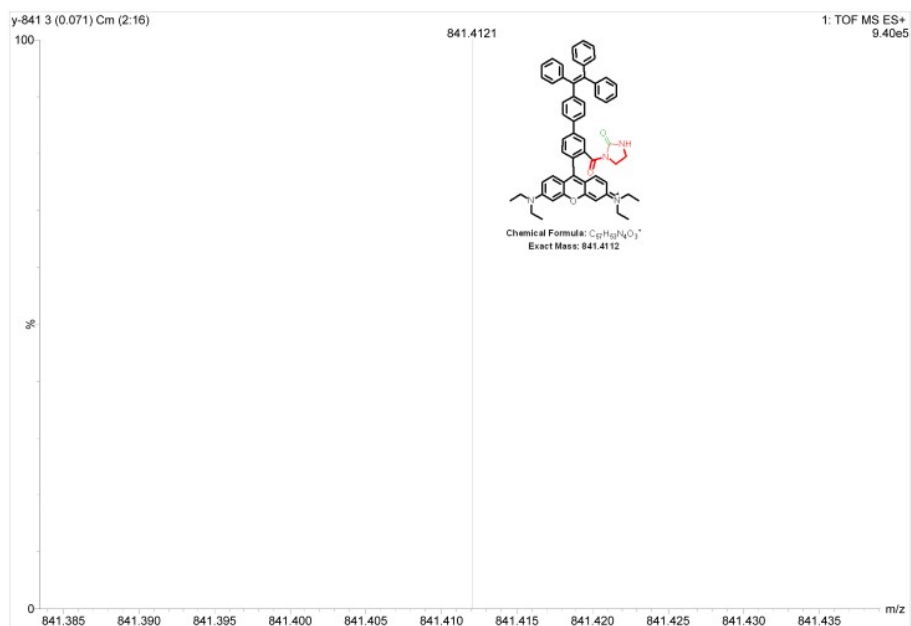


Fig. S12 The HR-MS spectrum of TPE-RhodEA-phosgene mixture solution.

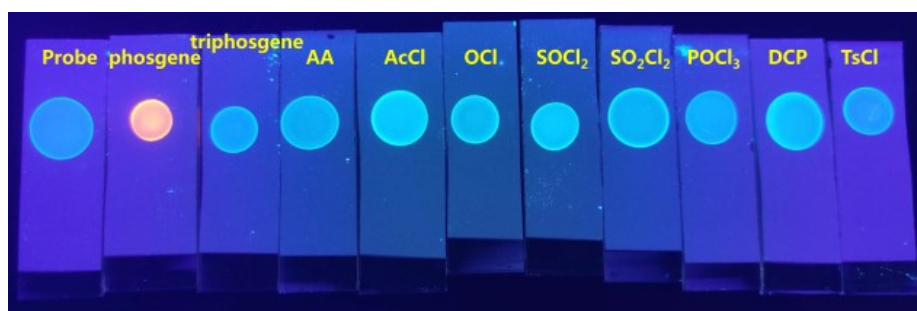
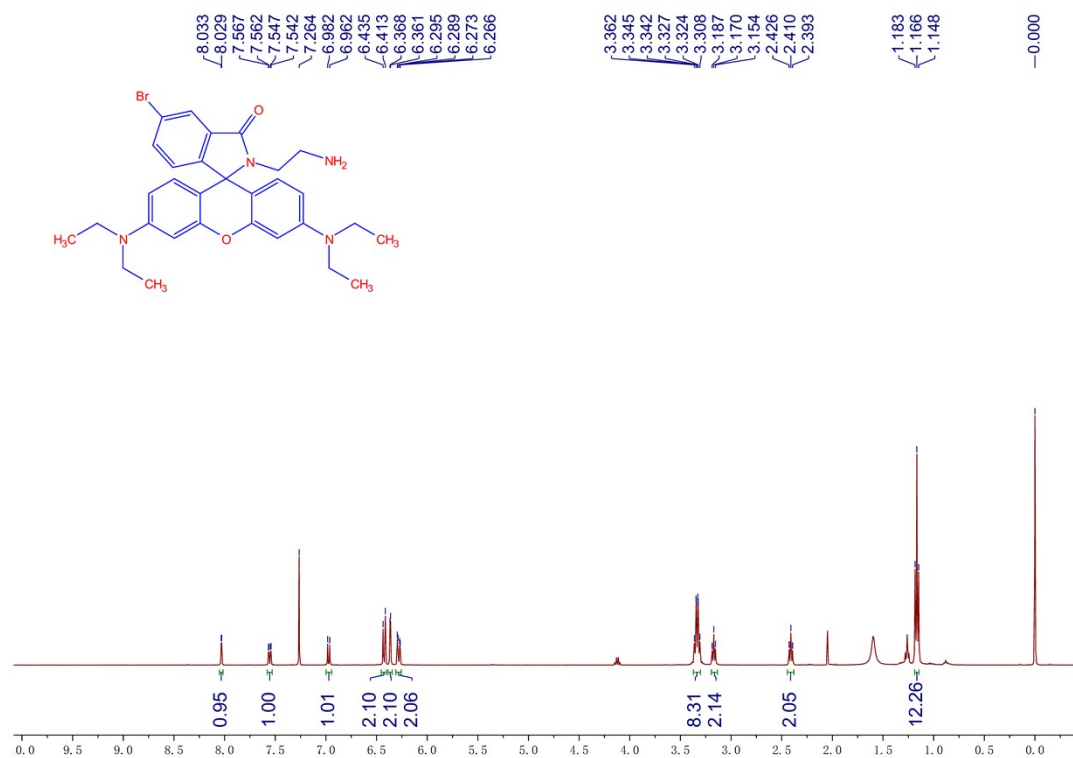


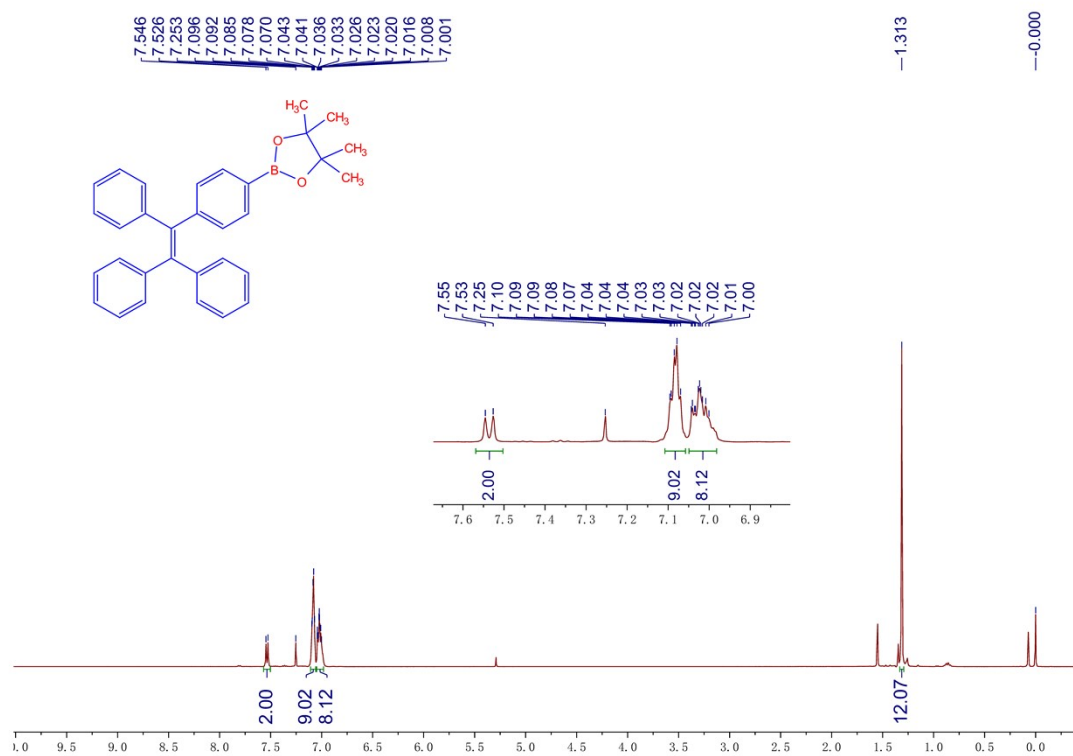
Fig. S13 The probe-loaded TLC test strips response for various analytes (including acetic anhydride (AA), acetyl chloride (AcCl), oxalyl chloride (OCl), thionyl chloride (SOCl₂), sulfone chloride (SO₂Cl₂), phosphorus oxychloride (POCl₃), diethyl chlorophosphate (DCP), p-toluenesulfonyl chloride (TsCl), triphosgene, and phosgene) (the photo was taken using a smartphone under a 365 nm hand-held UV lamp).

The characterization data of TPE-RhodEA

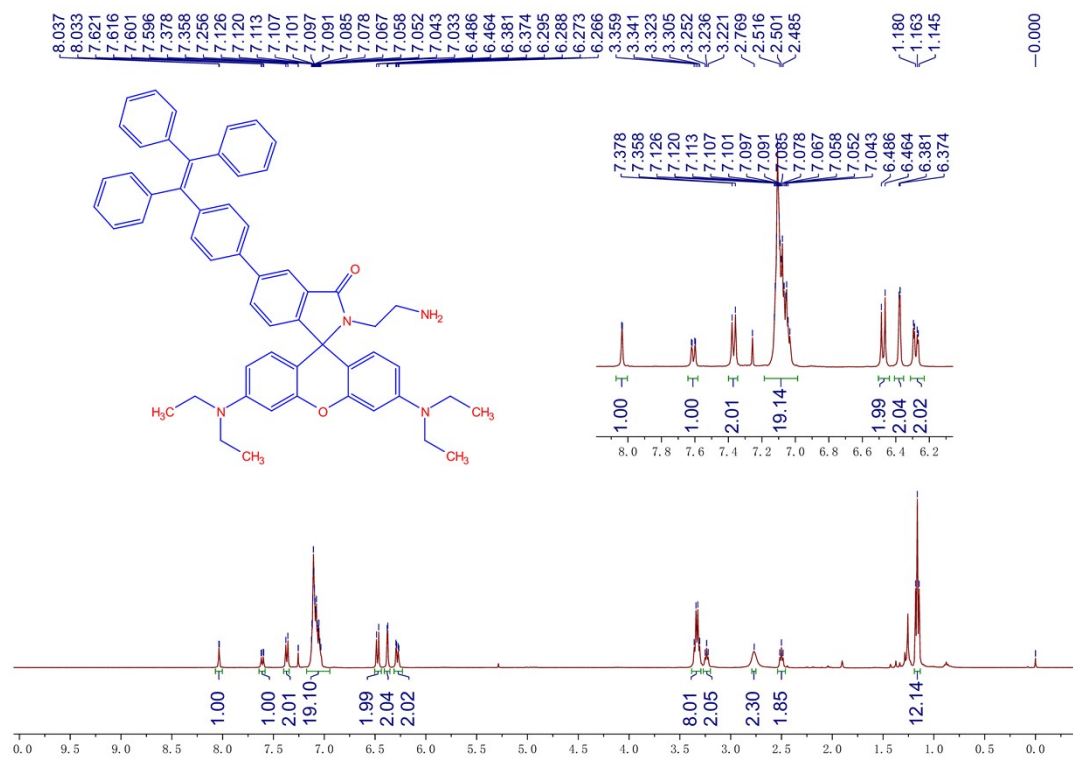
¹H NMR of 1 (RhodBr-EA)



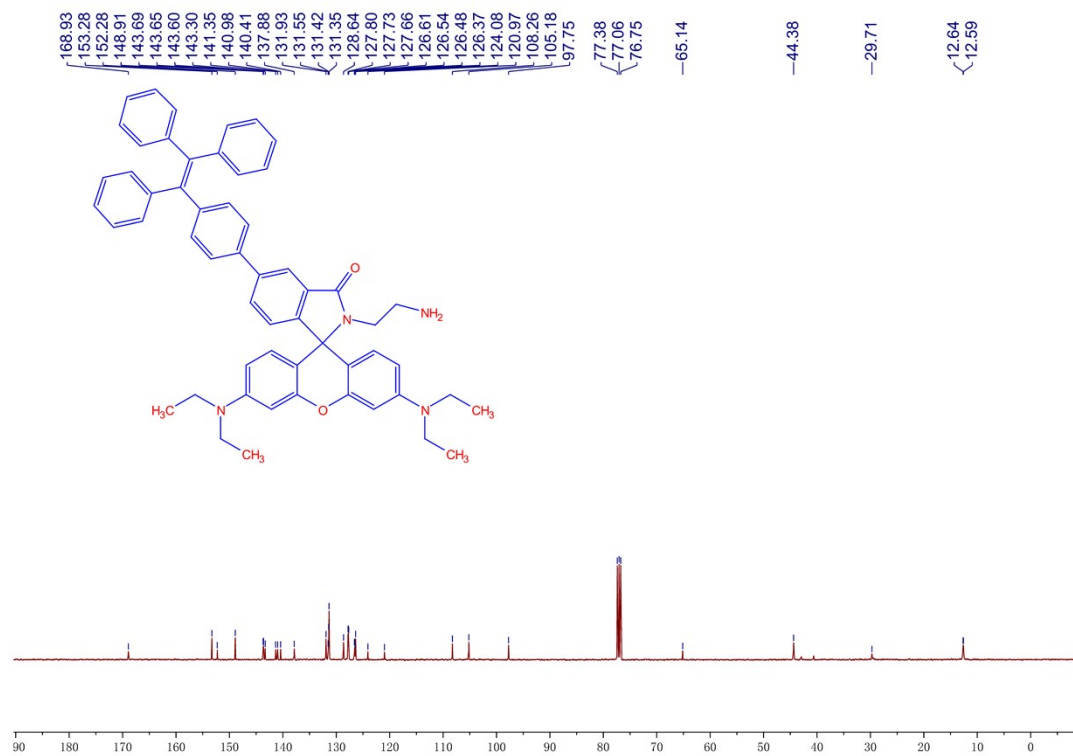
¹H NMR of 3 (4,4,5,5-tetramethyl-2-(4-(1,2,2-triphenylvinyl)phenyl)-1,3,2-dioxaborolane)



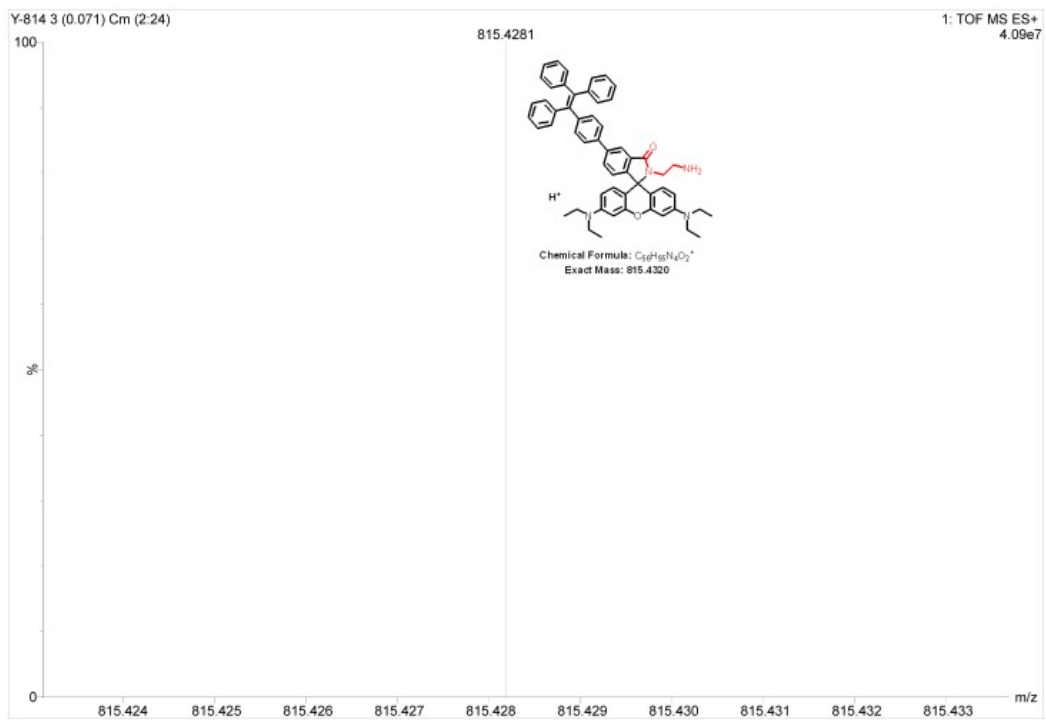
¹H NMR of 4 (TPE-RhodEA)



¹³C NMR of 4 (TPE-RhodEA)



HR-MS of 4 (TPE-RhodEA)



References

- 1 (a) J. T. Yeh, P. Venkatesan and S. P. Wu, *New J. Chem.*, 2014, **38**, 6198-6204. (b) A. Roy, D. Kand, T. Saha and P. Talukdar, *Chem. Commun.*, 2014, **50**, 5510-5513.
- 2 P. Kundu, K. C. Hwang, *Anal. Chem.*, 2012, **84**, 4594-4597.
- 3 L. Chen, D. Wu, J. M. Kim, et al., *Anal. Chem.*, 2017, **89**, 12596-12601.
- 4 W. Feng, S. Gong, E. Zhou, et al., *Anal. Chim. Acta*, 2018, **1029**, 97-103.
- 5 C. Wu, H. Xu, Y. Li, et al., *Talanta*, 2019, **200**, 78-83.
- 6 Z. J. Li, W. J. Zhang, W. Z. Bi, et al., *RSC Adv.*, 2021, **11**, 10836-10841.
- 7 J. Y. Ni, D. L. Qian, R. Sun, et al., *Talanta*, 2022, **236**, 122826.
- 8 Y. Zhang, A. Peng, X. Jie, et al., *ACS Appl. Mater. Inter.*, 2017, **9**, 13920-13927.
- 9 S. L. Wang, C. L. Zhang, Q. H. Song, *J. Mater. Chem. C*, 2019, **7**, 1510-1517.
- 10 L. Bai, W. Feng, G. Feng, *Dyes Pigment.*, 2019, **163**, 483-488.
- 11 Y. L. Huang, W. Ye, Y. T. Su, et al., *Dyes Pigment.*, 2020, **173**, 107854-107860.
- 12 A. Gangopadhyay, S. S. Ali, A. K. Mahapatra, *ChemistrySelect*, 2019, **4**, 8968-8972.
- 13 P. Liu, N. Liu, C. Liu, et al., *Dyes Pigment.*, 2019, **163**, 489-495.
- 14 S. Paul, P. Ghosh, P. Roy, *New J. Chem.*, 2020, **44**, 5784-5791.
- 15 L. Yang, F. Wang, Z. Sun, et al., *Anal. Method.*, 2020, **12**, 3123-3129.
- 16 Q. Hu, Q. Huang, K. Liang, et al., *Dyes Pigment.*, 2020, **176**, 108229-108237.
- 17 Z. Xu, Y. Luo, Y. Hong, et al., *Spectrochim. Acta A: Mol. Biomol. Spectrosc.*, 2022, **269**, 120789-120795.
- 18 H. C. Xia, X. H. Xu, Q. H. Song, *ACS Sens.*, 2017, **2**, 178-182.
- 19 T. Cao, D. Gong, L. Zheng, et al., *Anal. Chim. Acta*, 2019, **1078**, 168-175.
- 20 T. I. Kim, D. Kim, J. Bouffard, et al., *Sens. Actuat. B Chem.*, 2019, **283**, 458-462.
- 21 L. Yang, Z. Sun, Z. Li, et al., *Anal. Method.*, 2019, **11**, 4600-4608.
- 22 L. Patra, K. Aich, S. Gharami, et al., *Sens. Actuat. B Chem.*, 2021, **326**, 128837-128843.