Supporting Information

Electron Donating and Withdrawing Effect Discriminate the Fluorometric Sensing of Phosgene

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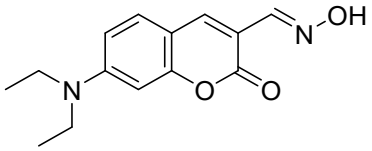
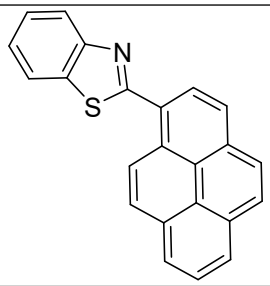
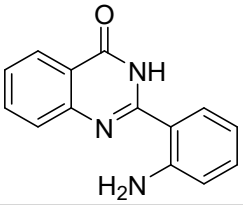
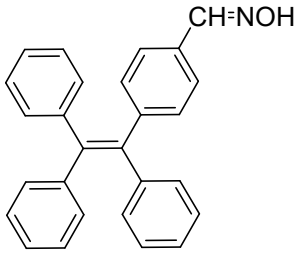
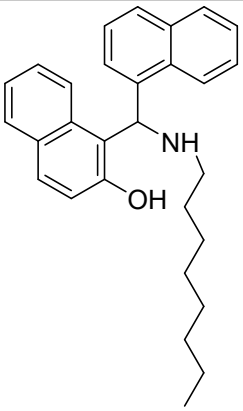
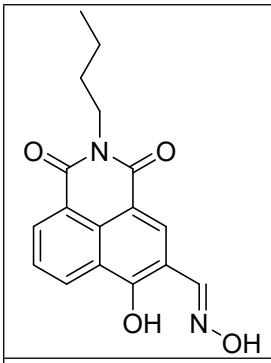
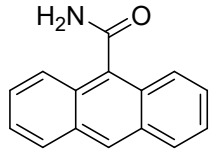
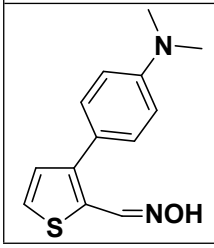
Table S1: Comparison between previously reported probe and this work

Structure of the probe	Solvent	Mode of sensing	Application	LOD	Response time	Ref
	Acetonitrile-water (1:1)	ICT	Paper-Strip	0.12 µM		1
	$CHCl_3$–acetone (1: 1)	PET & ICT	Paper-Strip	1.54 nM	<50 seconds	2
	CH_3CN	ESIPT	Paper-Strip	0.16 ppm	20 s	3
	Water/acetonitrile solution	AIE	Paper-Strip	9.3 nM	<30 s	4
	CH_3CN	PET	Paper-Strip	0.40 µM	<1 min	5

	CH_3CN	ESIPT	Vapour phase detection, SEM	0.087 ppm		6
	$CHCl_3$		Paper-Strip	5.56 nm	<1.5 min	7
	CH_3CN/H_2O	ICT & RIR	Paper-Strip	51 nm	< 20 s	This Work

2. Theoretical Calculations:

Table S2: Selected electronic excitation energies (eV), oscillator strengths (f), main configurations, and CI Coefficients of all the complexes. The data were calculated by TDDFT//M062X/6-31+G(*d,p*) based on the optimized ground state geometries.

Molecules	Electronic Transition	Excitation Energy[a]	f	Composition[b]	(composition) %
TCAO	$S_0 \rightarrow S_1$	4.3991 eV 281.84 nm	0.6242	H → L	88.9
TCAO-phos	$S_0 \rightarrow S_1$	3.8184 eV 324.70 nm	0.5460	H → L	94.8
HMBT	S0 → S1	4.4444 eV 278.97 nm	0.4808	H → L	93.9
	S0 → S2	4.8245 eV 256.99 nm	0.4011	H-1 → L	83.4
HMBT-phos	S0 → S1	4.5934 eV 269.92 nm	0.5896	H → L	96.6
	S0 → S2	4.9439 eV 250.78 nm	0.2779	H-2 → L	87.9

[a] Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. [b] H stands for HOMO and L stands for LUMO.

Table S3: Energies of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)

Species	E_{HOMO} (a.u)	E_{LUMO}(a.u)	ΔE(a.u)	ΔE(eV)	ΔE(kcal mol^{-1})
TCAO	-0.24354	-0.01186	0.23168	6.3043	145.4
TCAO-phos	-0.24434	-0.03697	0.20737	5.6428	130.1
HMBT	-0.29212	-0.05210	0.24002	6.5313	150.6
HMBT-phos	-0.30195	-0.05635	0.2456	6.6831	154.1

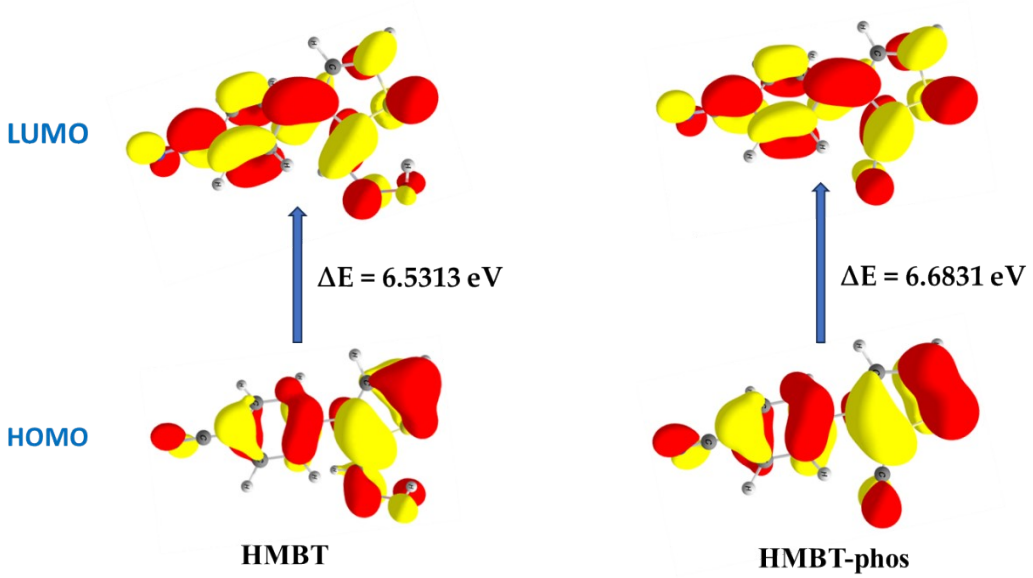


Figure S2: Frontier MO diagram with HOMO-LUMO energy gap of HMBT and HMBT-phos.

3. UV-Vis and fluorescence study of the control compound HMBT.

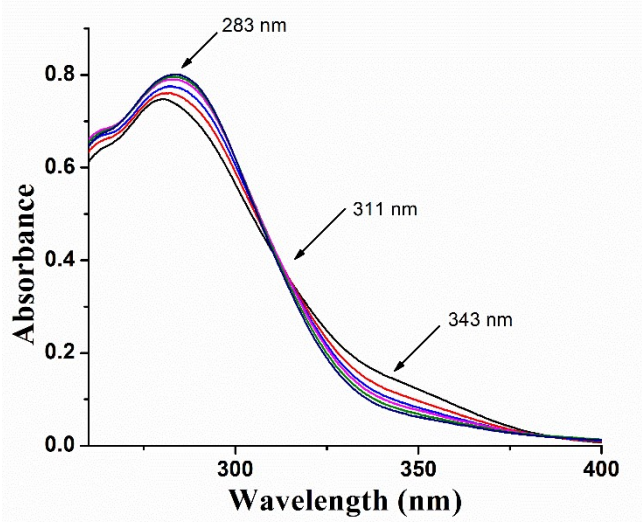


Figure S3: UV-Vis absorption spectra of the probe **HMBT** (1×10^{-5} M) in the solvent CH_3CN /H_2O (1:1, v/v).

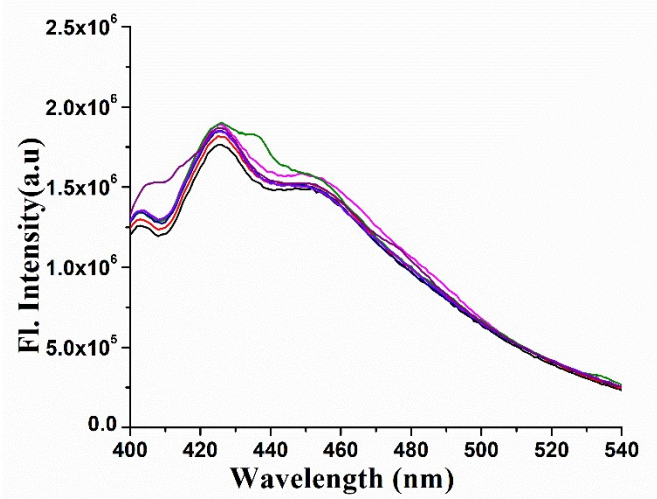


Figure S4: Fluorescence spectra of **HMBT** (1×10^{-5} M) in the solvent CH_3CN /H_2O (1:1, v/v) in the presence of phosgene.

4. Calculation of Limit of detection

The limit of detection (LOD) of TCAO for phosgene was calculated utilizing the general equation DL = K × Sb1/S

Where K = 2 or 3 (we take 2 in this case) and Sb1, obtained as 0.033349 is the standard deviation of the blank solution and S is the slope of the calibration curve

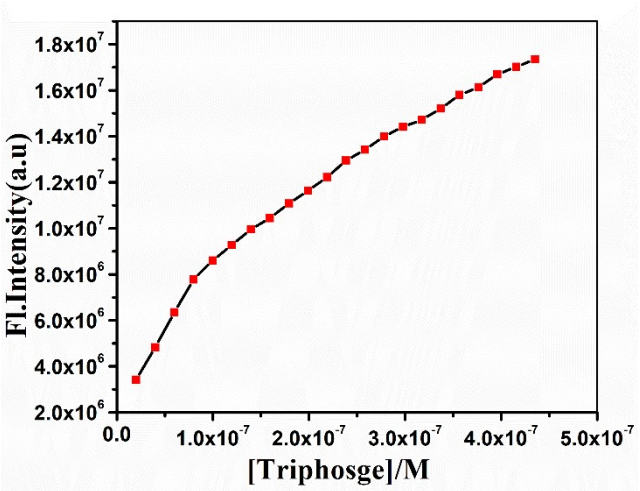


Figure S5: Plot of fluorescence intensity vs molar concentration of triphosgene

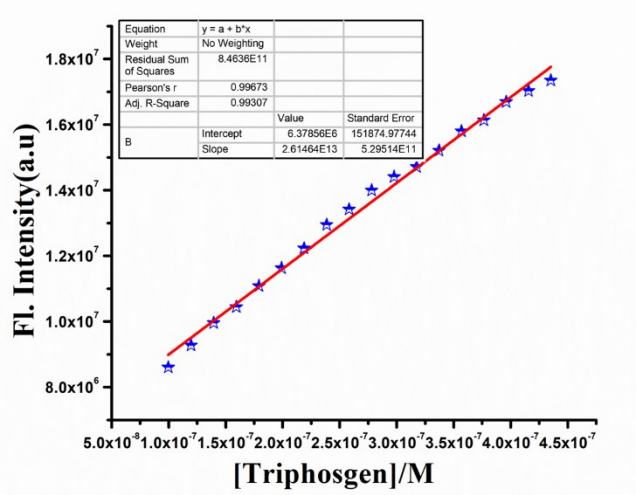


Figure S6: Fluorescence linear fit (496 nm) plot in the concentration region 0.1-0.45 µM for estimation of limit of detection.

5. NMR Spectra: 1H NMR, 13C NMR:

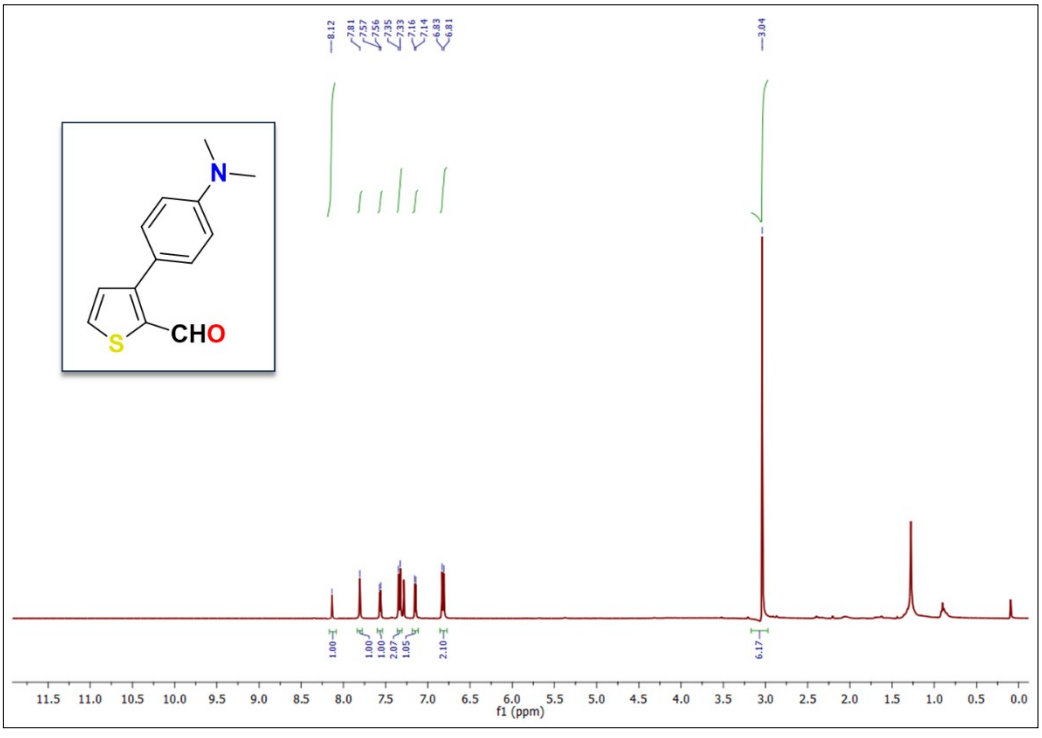


Figure S7: ^{1}H NMR of TCA.

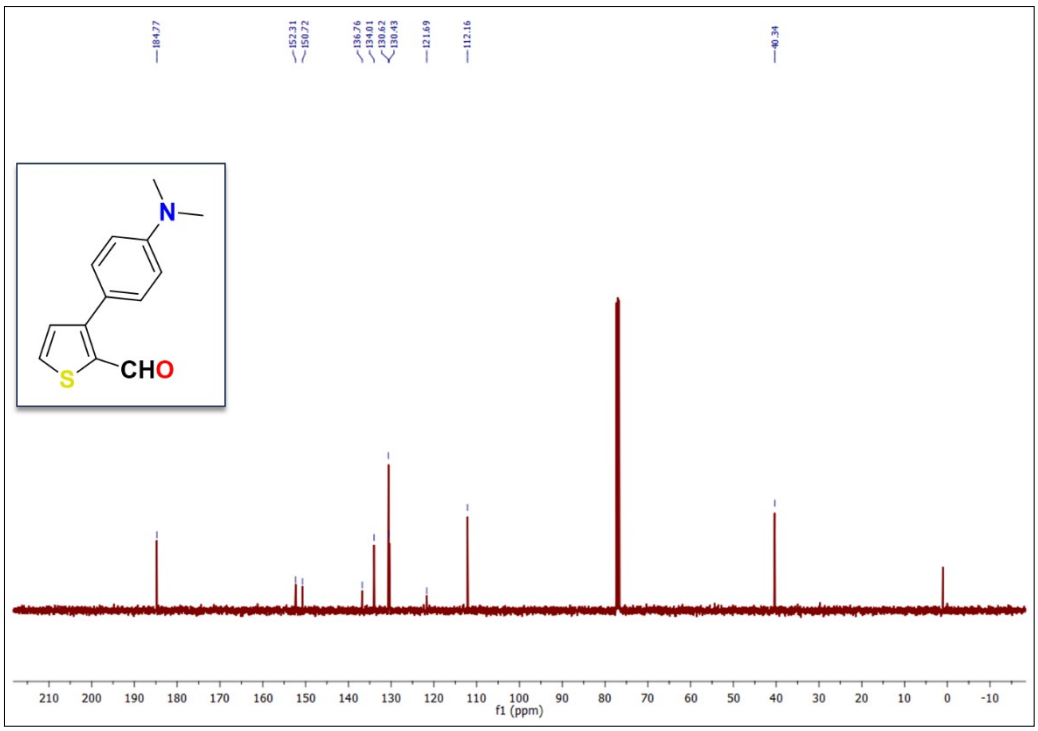


Figure S8: ^{13}C NMR of TCA.

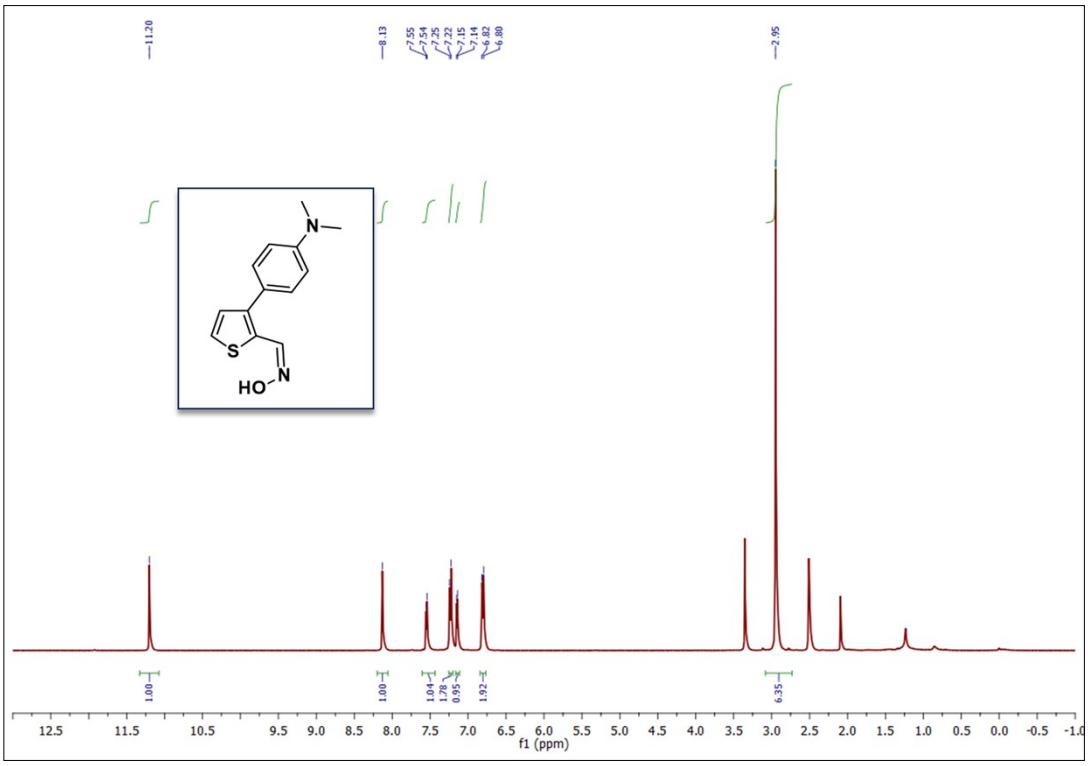


Figure S9: ^{1}H NMR of TCAO.

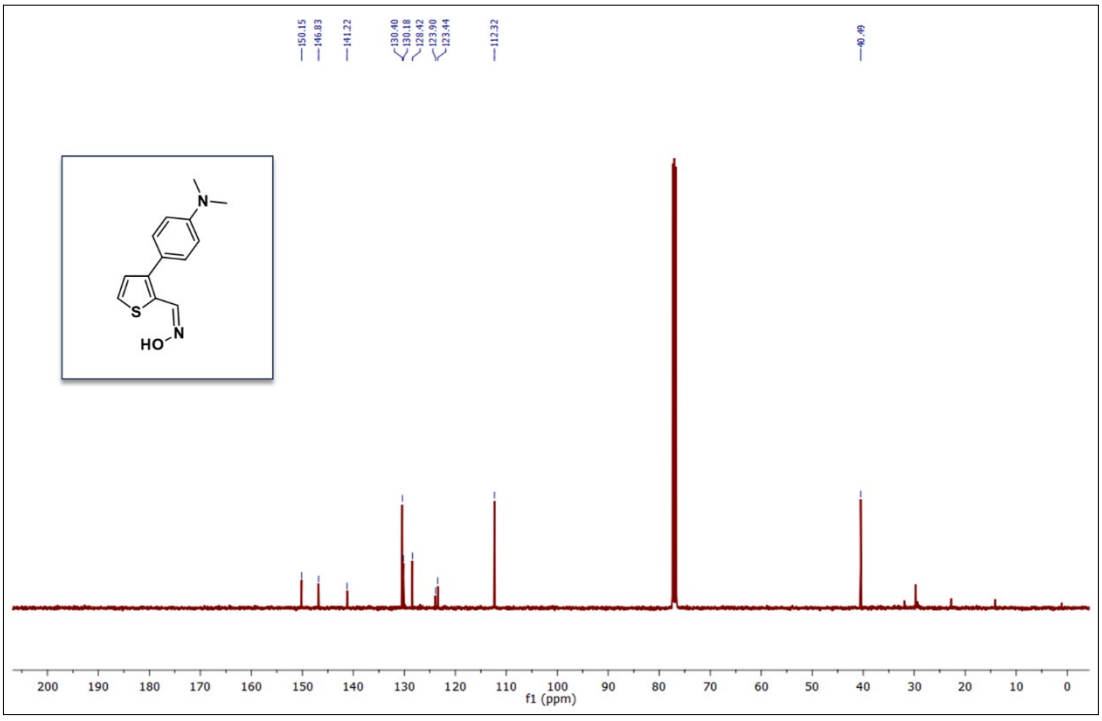


Figure S10: ^{13}C NMR of TCAO.

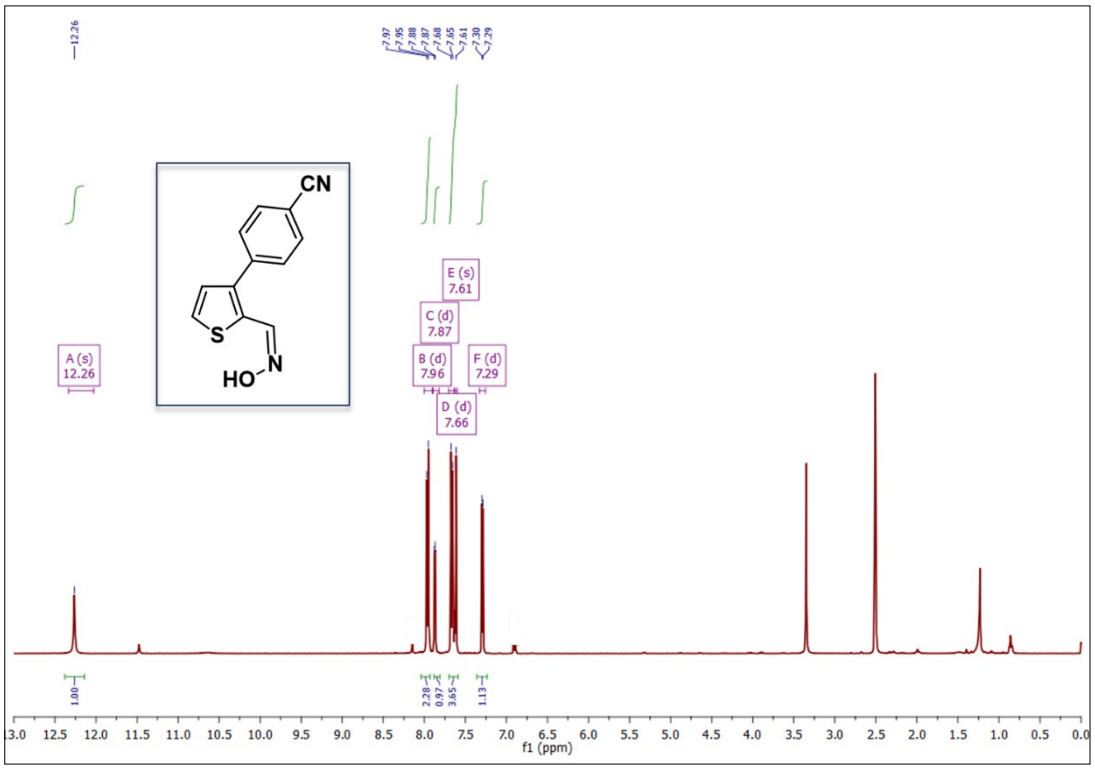


Figure S11. ^{1}H NMR of the HMBT**.**

6. Mass Spectroscopy:

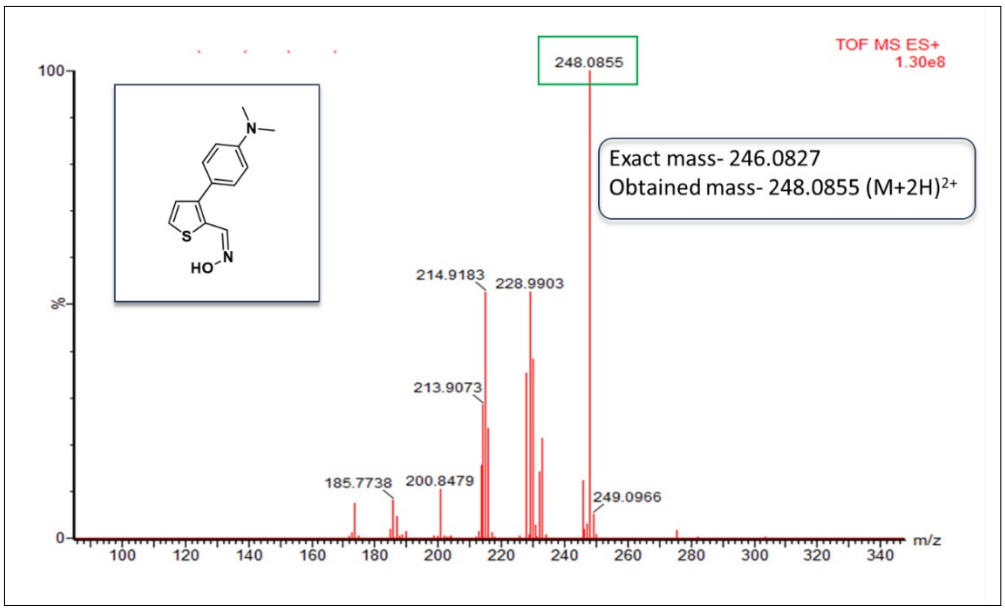


Figure S12: HRMS mass spectra of the probe TCAO.

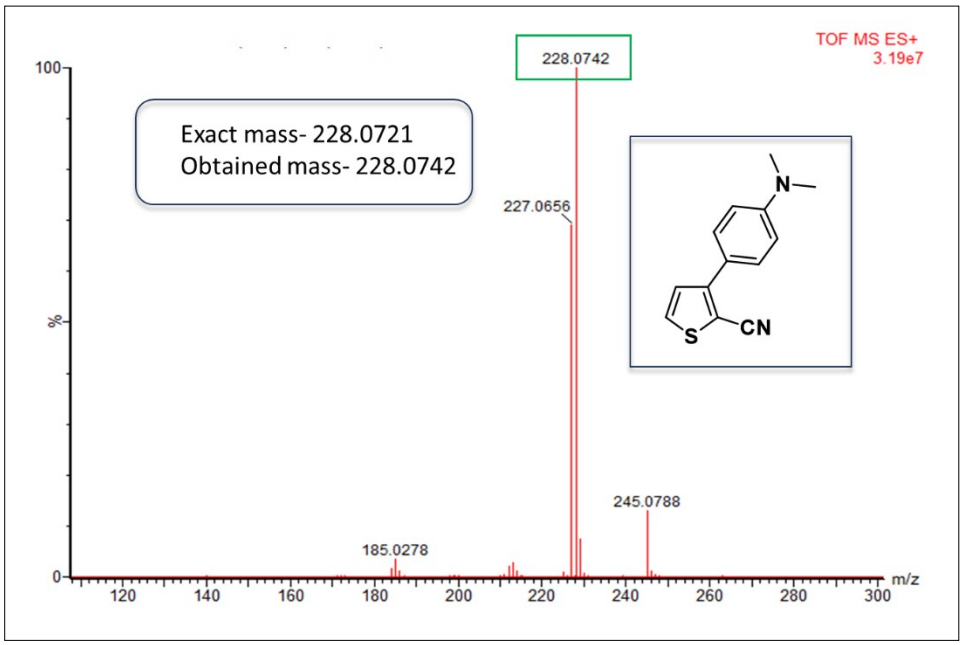


Figure S13: HRMS mass spectra of the adduct TCAO-phos.

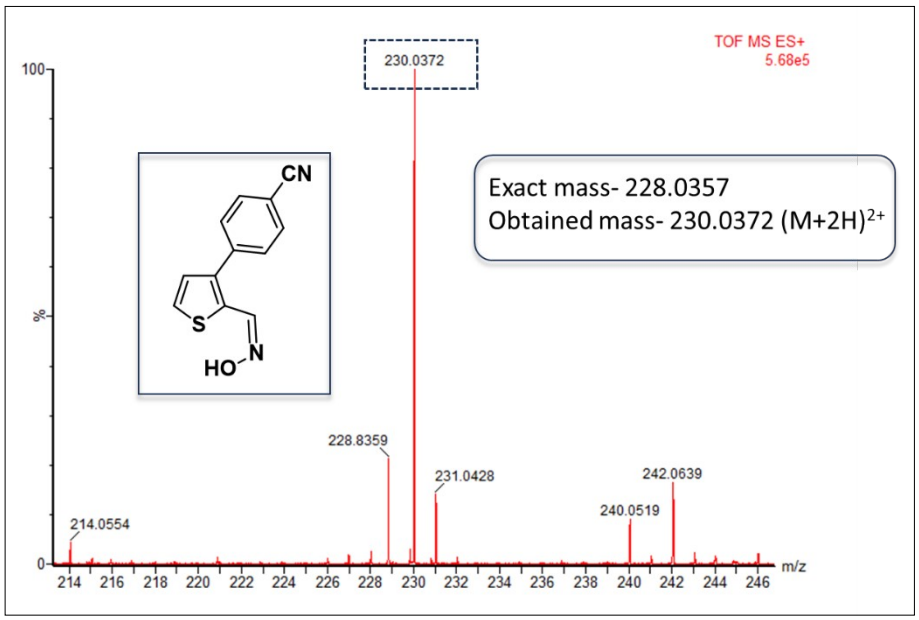


Figure S14: HRMS mass spectra of the HMBT.

7. FT-IR Spectroscopy:

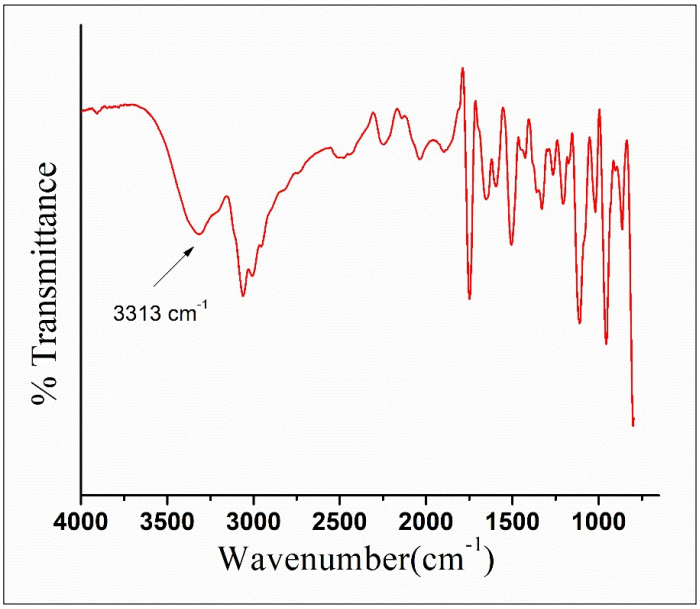


Figure S15: FT-IR spectroscopy of TCAO**.**

8. Calculation of quantum yield of TCAO in the absence and presence of phosgene.

Here, the fluorescence quantum yield Φ was calculated by using the following equation:

$\Phi_x = \Phi_s (F_x / F_s) (A_s/A_x) (\eta_x^2/ \eta_s^2)$

Where, X and S indicate the unknown and standard solution respectively, Φ = quantum yield

F = Area under the emission curve, A= Absorbance at the excitation wavelength,

η = Refractive index of solvent. Here Φ measurements were performed using fluorescein in ethanol as standard [Φ = 0.79]

η_s = 1.36 (for ethanol); η_x = 1.34 (for acetonitrile)

In the absence of phosgene, the calculated quantum yield (Φ_x) for probe TCAO = 0.043.

where, Φs = 0.79, $F_x = 4.71\times10^8$, $F_s = 4.34\times10^8$, A_s = 0.008, A_x = 0.151.

In the presence of phosgene, the calculated quantum yield (Φ_x) for adduct TCAO-phos = 0.155.

Where, Φ_s = 0.79, F_x =1.38×109, $F_s = 2.00\times10^9$, A_s = 0.008, A_x = 0.178.

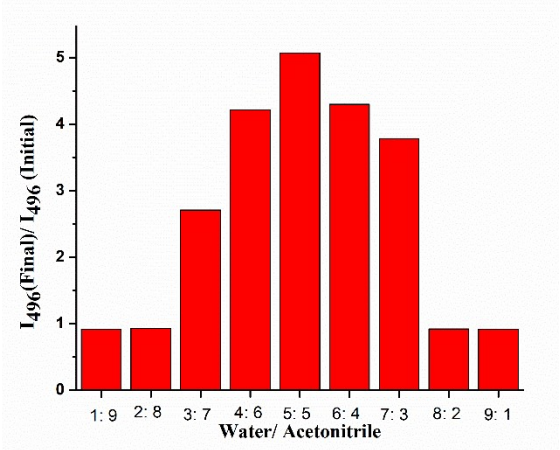


Figure S16: Fluorescence intensity ratio of Final to Initial emission at 496 nm with the addition of excess phosgene in the different solvent ratio.

8. References

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2. A. Gangopadhyay, and A.K. Mahapatra, *New Journal of Chemistry*, 2019, ***43***, 14991-14996.

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