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A Simple Phenazine Derivative Fluorescence Sensor for Detecting Formaldehyde

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Key words: Phenazine, Crystal, Fluorescent detection, VOCs.

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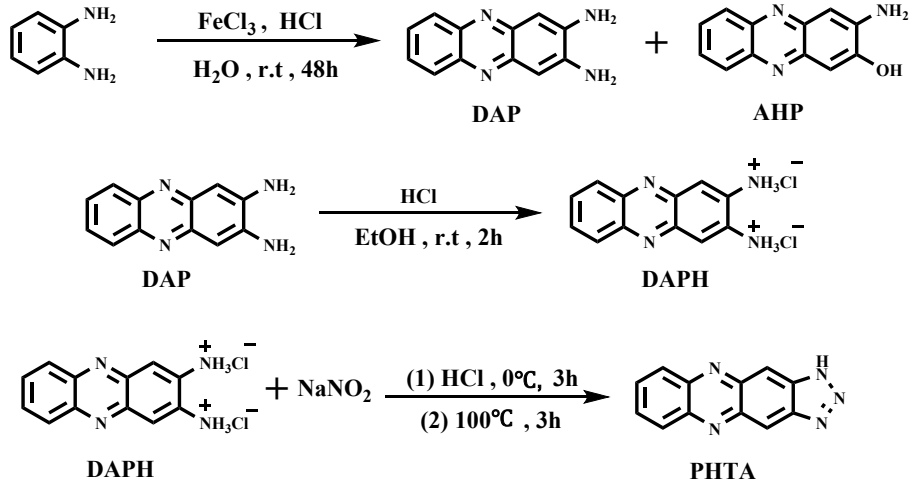
Table S1: Comparison of LOD and Response Time of Sensor for HCHO with Previously Reported HCHO Sensors

Table S2: Crystal date of **PHTA-HCHO**

Synthesis of **PHTA**

Diluted hydrochloric acid (6 mol/L) was added slowly to O-pheny-lenediamine (5.40 g, 50mmol) in round-bottom flask (500 mL). The resulting solution was stirred at room temperature until the o-pheny- lenediamine completely dissolved. 53.0g $FeCl_3 \cdot 6H_2O$ was dissolved in distilled water (75 mL) and trickled slowly into the round-bottom flask with a constant pressure funnel. With the addition of $FeCl_3 \cdot 6H_2O$, a red solid gradually formed. Produced mixture was stirred for 24 h, then removed and filtered, the red solid was washed with 6mol/L diluted hydrochloric acid for 3 to 5 times. Put red solid in hot distilled water at 100 °C and added 75ml NaOH (2 mol/L) into it, then a yellow solid was formed immediately. Continue to stir for 30–35 min and let it stand for 12h, after the suction filtration had tan solid was produced which was 2,3-diaminophenazine (**DAP**) (Yield: 41.5%. m.p > 300 °C). An orange precipitate was formed gradually after the addition of hydrochloric acid to the filtrate drop by drop. Then, adjusted the appropriate pH (pH =4~5) for precipitate and washed with distilled water. The obtained orange-red solid after drying was 2-amino-3-hydroxyphenazine (**AHP**)(Yield: 52.7%. m.p > 300 °C).

To dissolve 2, 3-diaminophenazine (0.4205 g, 2 mmol) in 20 mL of EtOH, and take 3 mL concentrated hydrochloric acid, diluted with EtOH to 10 mL. The diluted hydrochloric acid was added dropwise to the dissolved 2, 3-diaminophenazine solution and stirred the above solution fully at room temperature. By filtration and drying, the reserved solids are end-product **DAPH**. **DAPH** as dark brown solid and had a good solubility in distilled water. ^1H NMR (D_2O, 600 MHz) δ: 7.61 (s, 4H); 7.51 (s, 2H); 6.51 (s, 6H). ESI-MS calcd for $C_{12}H_{12}N_4^{2+}$ 212.1051, found 212.1010.



Scheme S1: Synthesis of **PHTA**

Crystal culture

PHTA (22 mg, 0.1 mmol) dissolved in DMSO, 0.5 formaldehyde solution was added. Sealed and stood for two days to precipitate dark yellow crystals in the container.

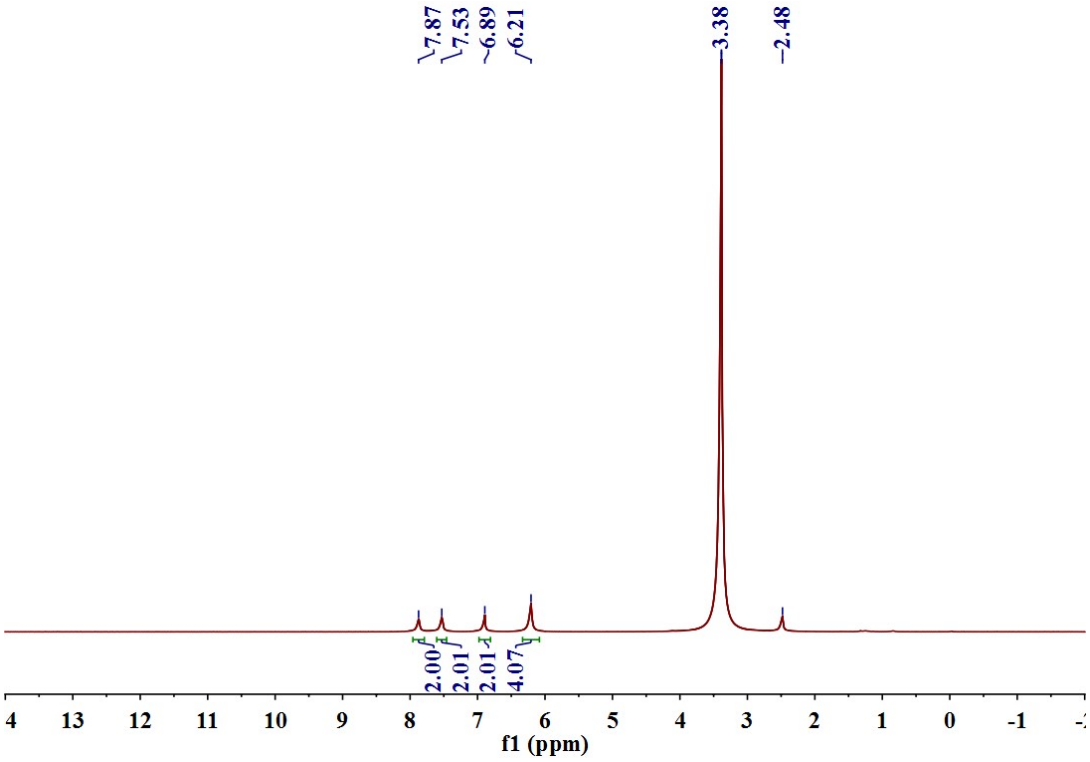


Figure S1: [1]H–NMR spectrum of 2, 3-diaminophenazine (**DAP**) in DMSO-d_6.

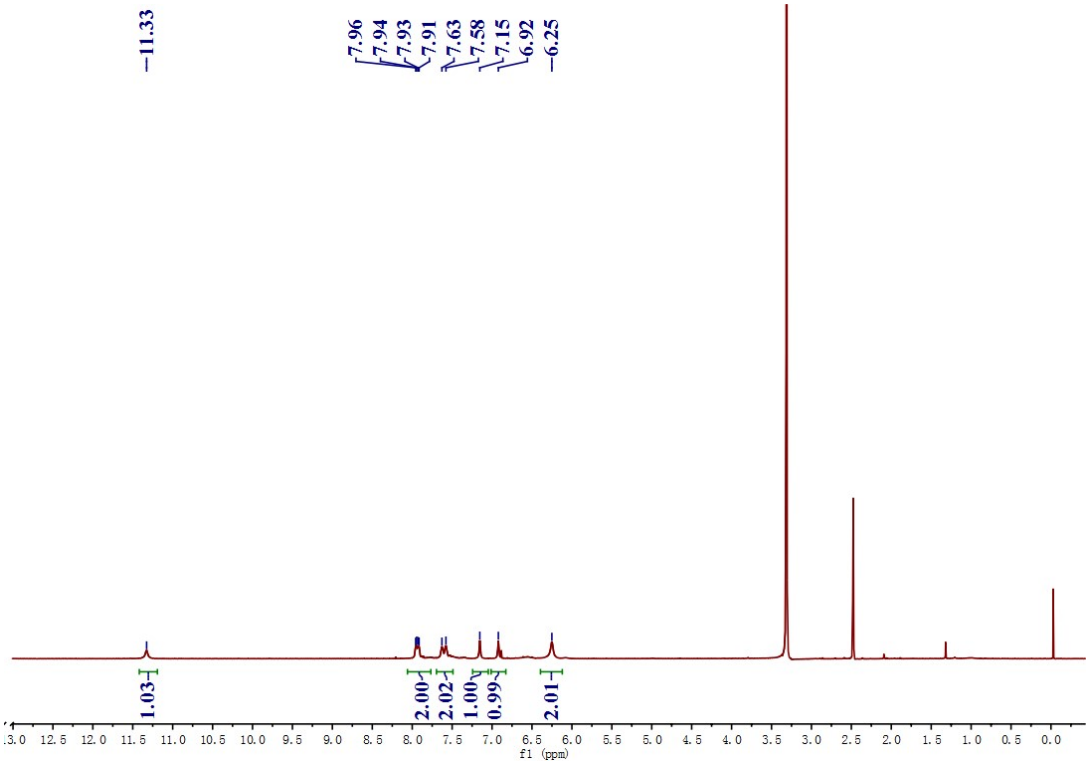


Figure S2: [1]H–NMR spectrum of 2-amino-3-hydroxyphenazine (**AHP**) in DMSO-d_6

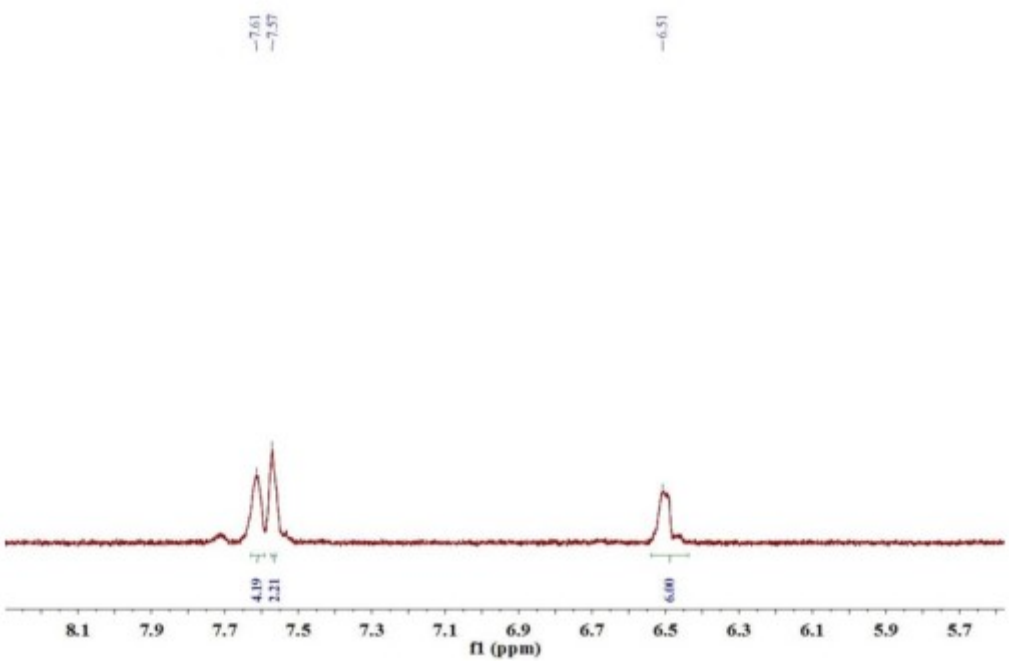


Figure S3: [1]H–NMR spectrum of **DAPH** in DMSO-d_6.

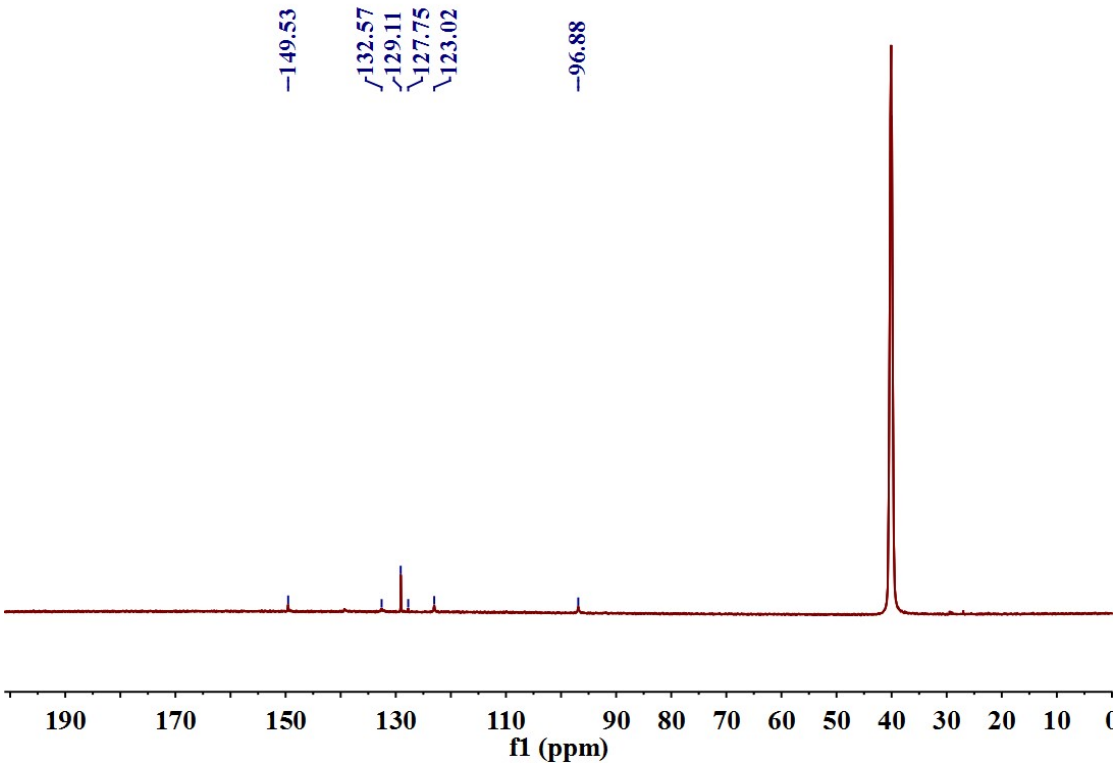


Figure S4: [13]C–NMR spectrum of **DAPH** in DMSO-d_6.

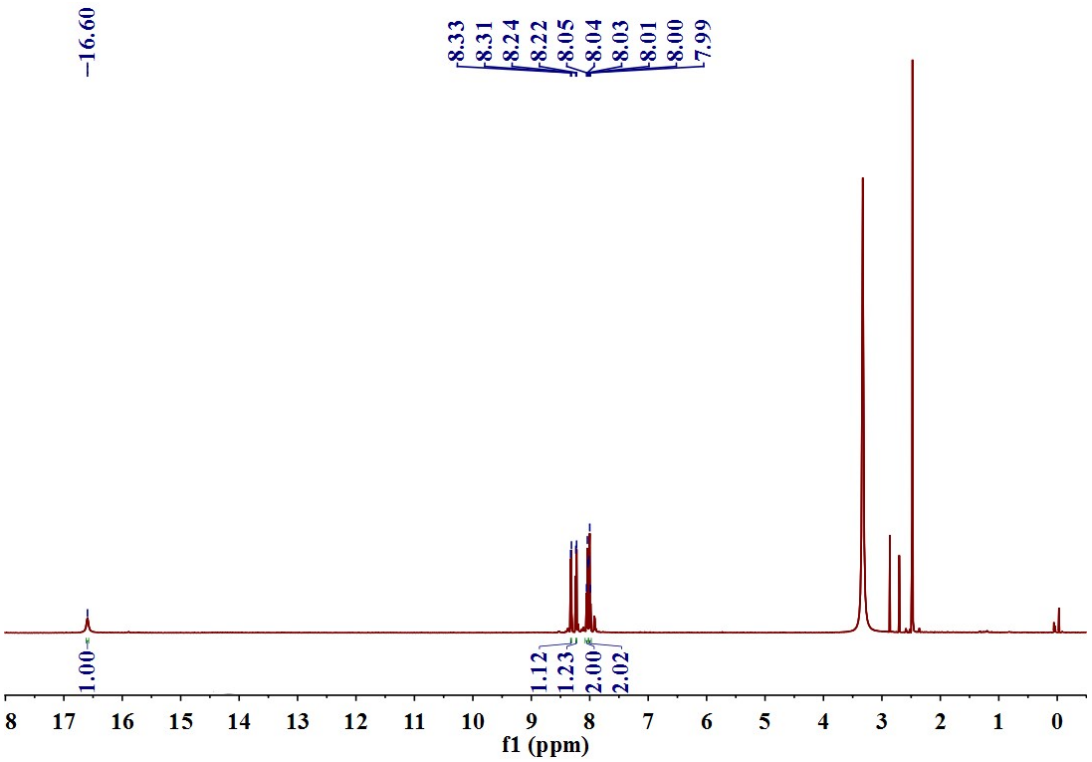


Figure S5: ^{1}H–NMR spectrum of **PHTA** in DMSO-$d_{6.}$

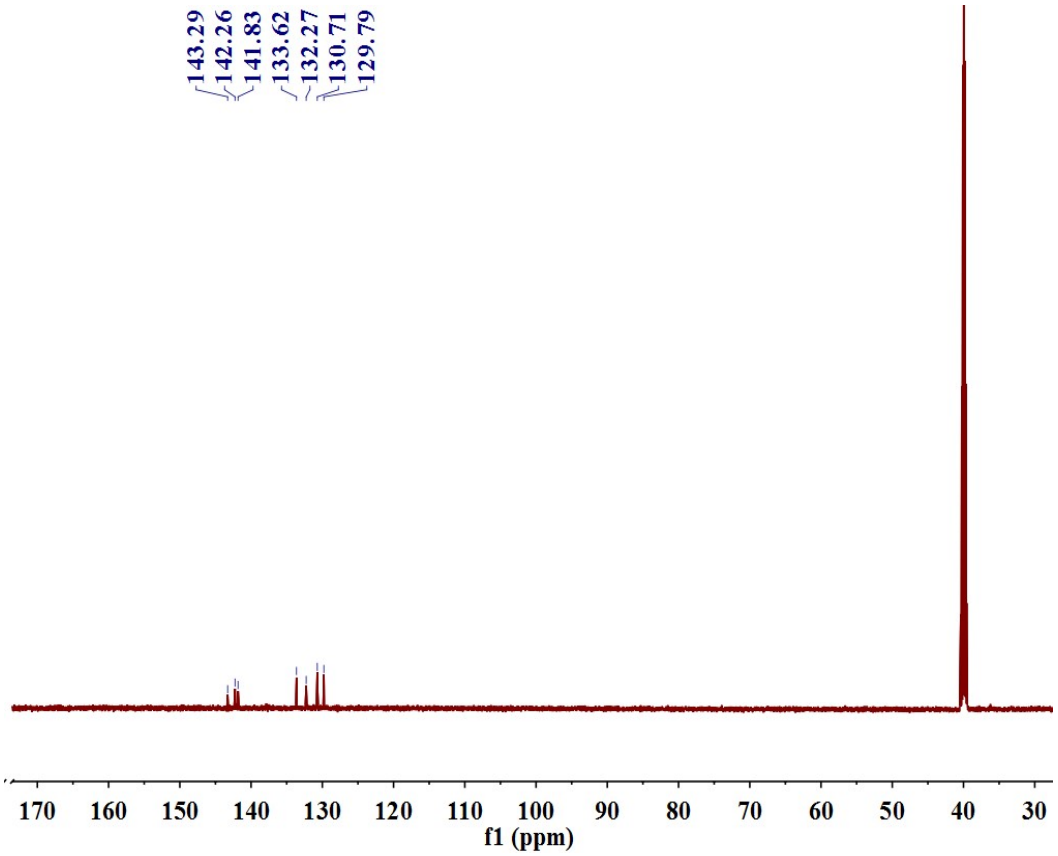


Figure S6: ^{13}C–NMR spectrum of **PHTA** in DMSO-$d_{6.}$

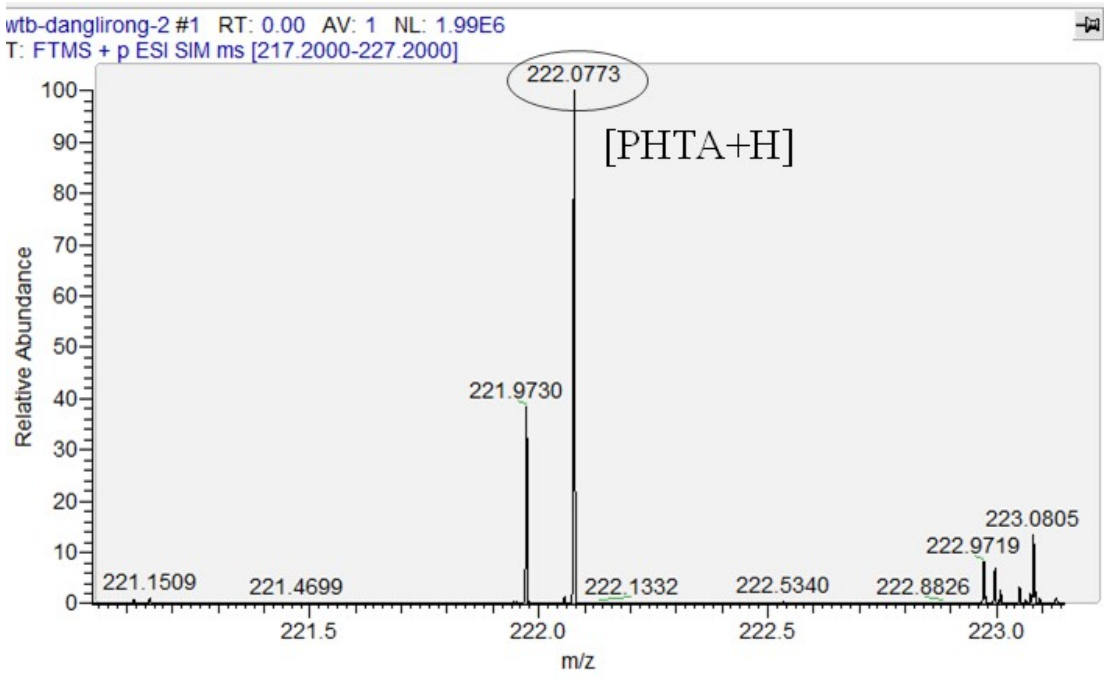


Figure S7: The ESI/MS of **PHTA**.

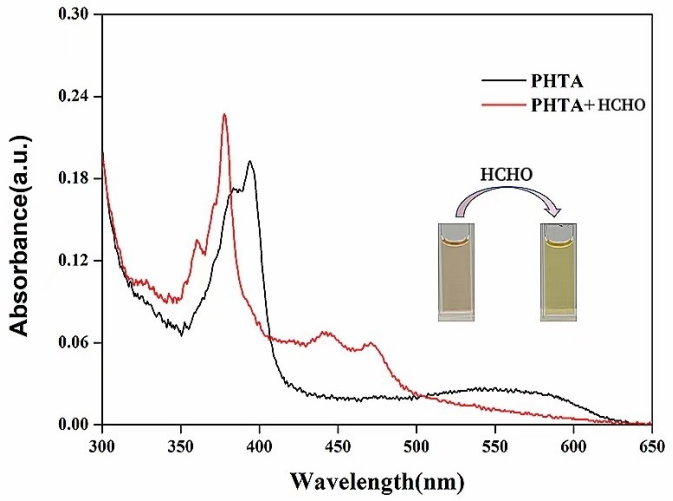


Figure S8: UV absorption spectra of **PHTA** and **PHTA+HCHO**

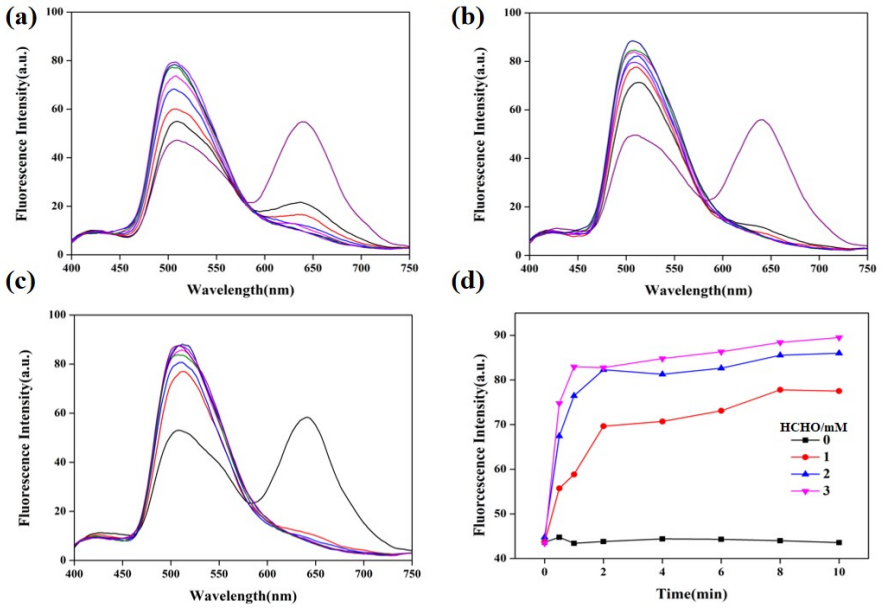


Figure S9: Fluorescence emission spectra of (a): n_{HCHO}= 1mM; (b): n_{HCHO}= 2mM; (c): n_{HCHO}= 3mM was added to **PHTA** (C=2.0 × 10^{-5}); (d)Fluorescence emission scatter diagram with HCHO added in **PHTA** within 10 min(λ_{ex} = 395nm).

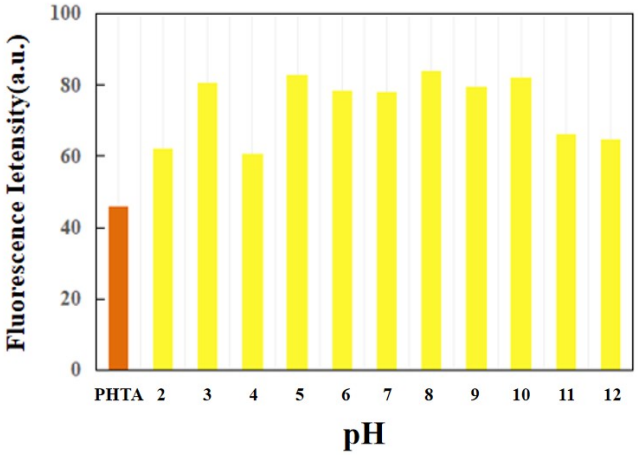


Figure S10: Fluorescent intensity change of **PHTA** added to HCHO in different PH systems(λ_{ex} = 395nm).

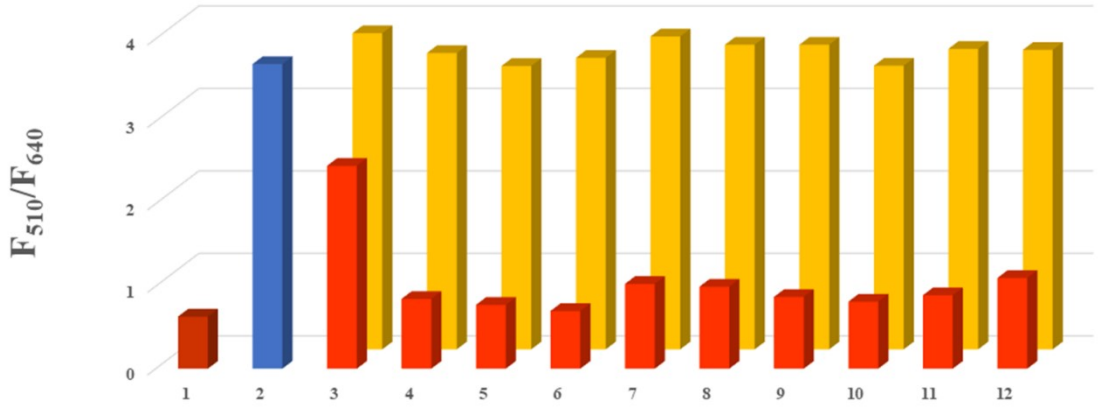
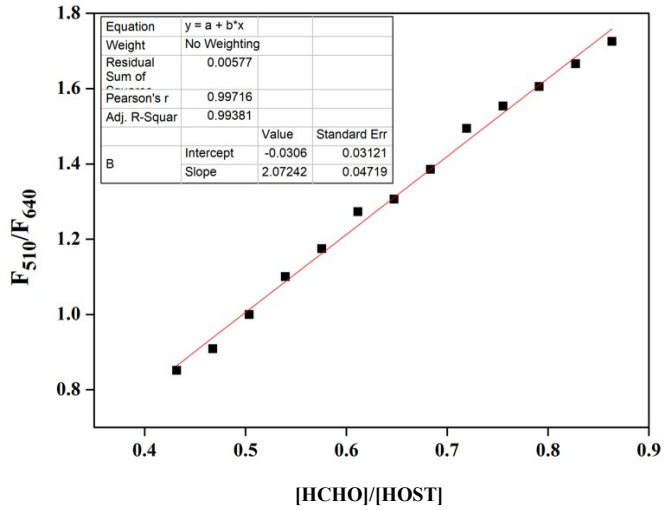


Figure S11: Fluorescence spectra of the target compound PHTA-HCHO(2.0×10^{-4} M) in the DMSO solution in the presence of HCHO and other VOCs.



Linear Equation: $Y = 2.07242X - 0.0306$ $R^2 = 0.99381$

$$S = 2.07242\times10^{6} \quad \delta = \sqrt{\frac{\sum (F_i - F_0)^2}{N-1}} = 0.010738 \ (N = 20) \quad K = 3$$

$$LOD = K \times \delta / S = 1.5544\times10^{-8}\ M$$

Figure S12: The fluorescence spectral intensity linear range for HCHO

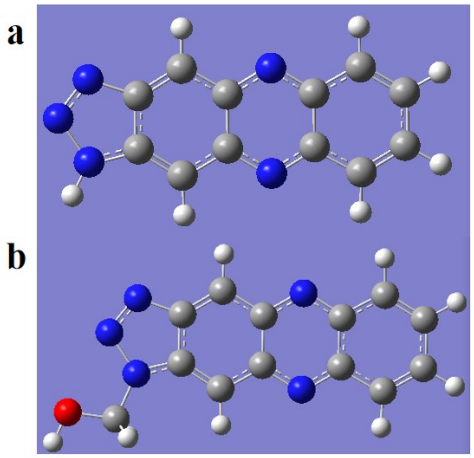
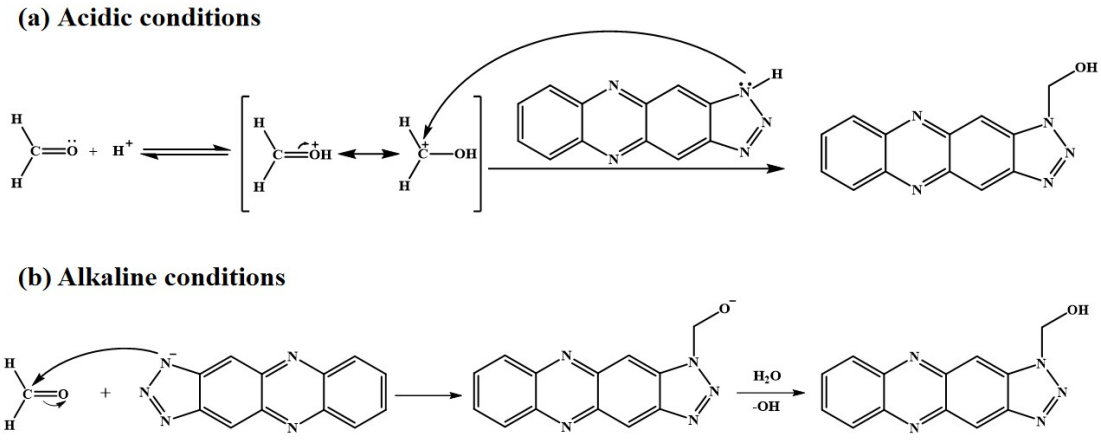


Figure S13. Energy-minimized structure of chemosensor (a)**PHTA** and (b)**PHTA-HCHO**.



Scheme S2: The reaction mechanism and synthesis route of **PHTA-HCHO** (a) acidic conditions and (b) alkaline conditions**.**

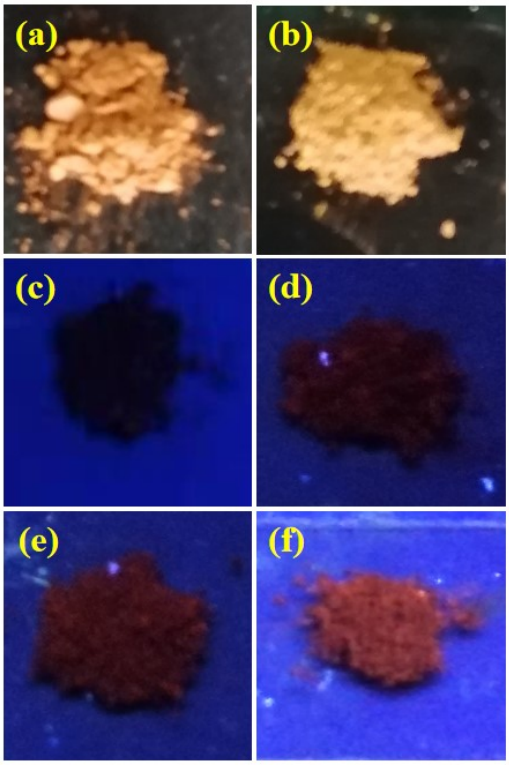


Figure S14: (a)Host compound PHTA at nature light; (b)After 24h of exposure to formaldehyde gas at nature light; (c)Host compound PHTA under UV-lamp (λ_{ex}=365 nm); (d)After 6h of exposure to formaldehyde gas under UV-lamp (λ_{ex}=365 nm); (e)After 24h of exposure to formaldehyde gas under UV-lamp(λ_{ex}=365 nm); (f)After 48h of exposure to formaldehyde gas under UV-lamp(λ_{ex}=365 nm)

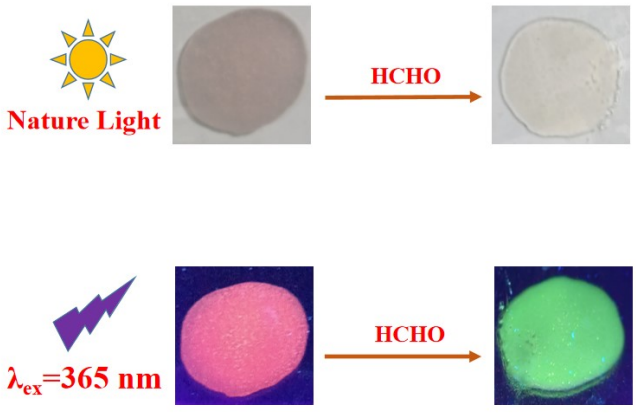


Figure S15: Fluorescence color change (under the UV-lamp, λ_{ex} = 365 nm) of silica gel plate treated by **PTHA** after addition HCHO .

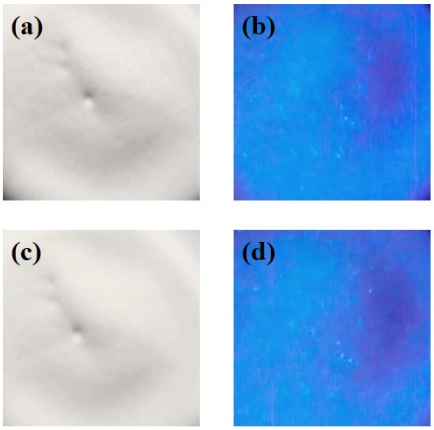


Figure S16: Fluorescence color (under the UV lamp, at λ ex = 365 nm) of silica gel plate after addition HCHO (Control experiment with figure S13).

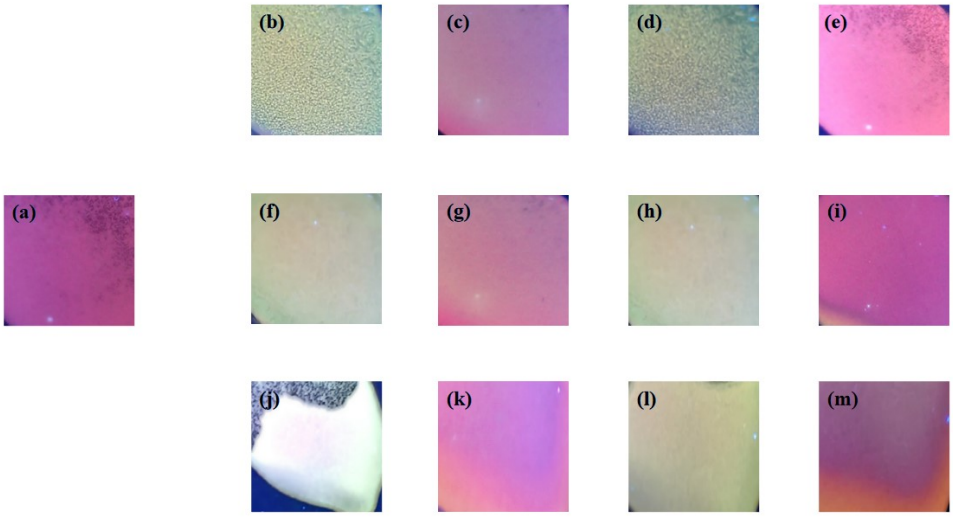


Figure S17: Fluorescence color change (under the UV lamp, at λ ex = 365 nm) of silica gel plate treated by **PTHA** after exposion HCHO and heat.

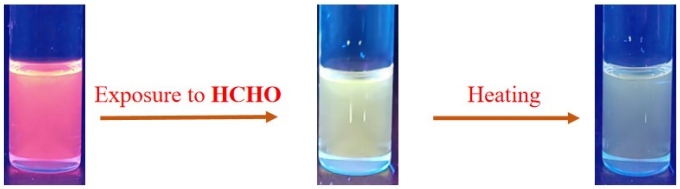


Figure S18: Fluorescence color change (under the UV lamp, at λ ex = 365 nm) of **PTHA** solution after exposion HCHO and heat.

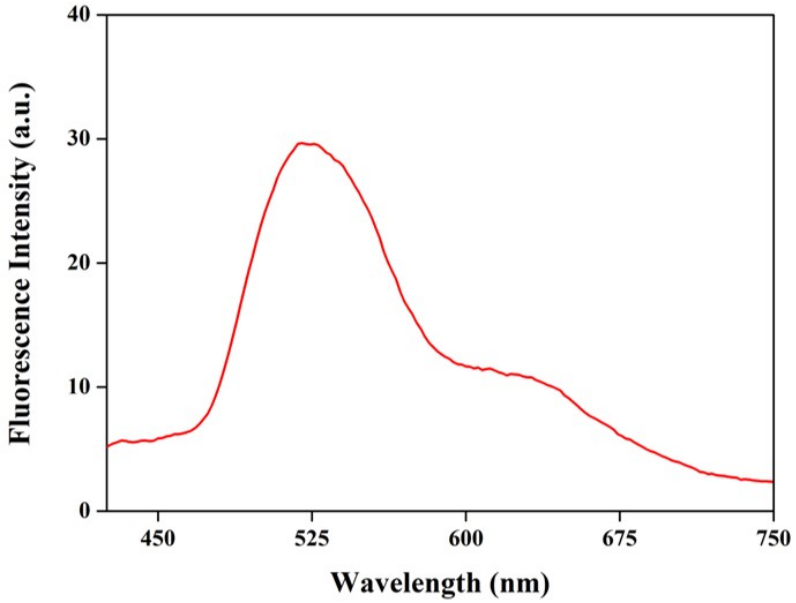
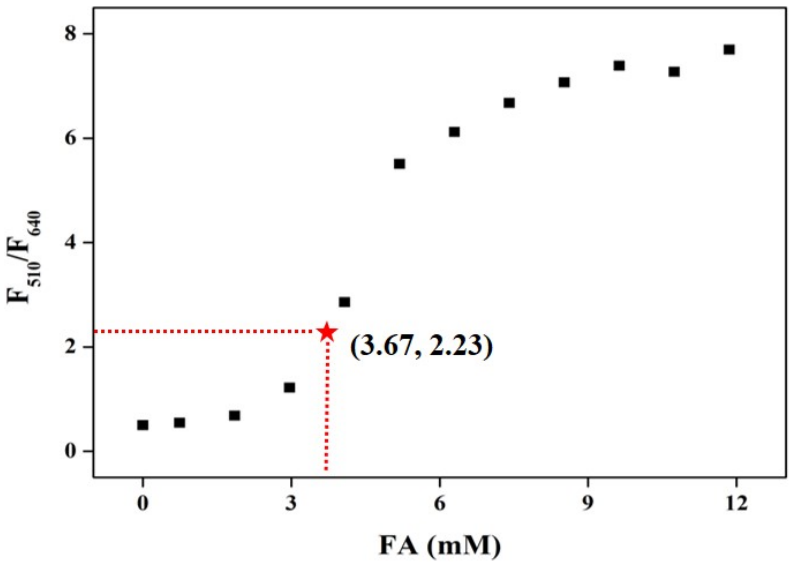


Figure S19: The fluorescence spectrum of **PHTA-HCHO** (C=1.0 × 10^{-3})in food(λ_{ex} = 395nm).



$$N_{PHTA\text{-}HCHO} = 3.67\ mM$$

$$m_s = 100\ g$$

$$n_{PHTA\text{-}HCHO}/m_s = 3.67 \times 10^{-5}\ M/g$$

$$m_{PHTA\text{-}HCHO}/m_s = 0.0011\ g/g$$

Figure S20: Determination of HCHO content in food.

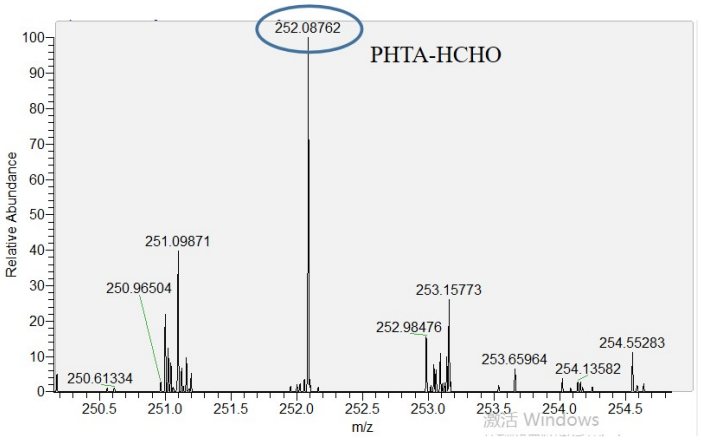


Figure S21: The ESI-MS of **PHTA-HCHO** in food.

Table S1: Comparison of LOD and Response Time of Sensor for FA with Previously Reported HCHO Sensors

Refs	Response Time	Catalyst	LOD
1	60 min	No	0.036 mg/m^3
2	90 min	Yes	0.96 μM
3	300 s	No	0.25 ppm
4	-	Yes	19.8 nM
5	90 s	Yes	-
6	7.5 s	Yes	3.27×10^{-9} M
7	46 s	Yes	6.67×10^{-7} M
8	-	No	7.7×10^{-7} M
Our work	5 min	No	1.55×10^{-8} M

Table S2: Crystal date of **PMTA-HCHO**

Compound	**PHTA-HCHO**
Structural formula	$C_{13}H_9N_5O$
Molecular mass (g mol $^{-1}$)	251.250
Data collection temp. (K)	293K
Crystal colour	clear dark yellow
Crystal system	triclinic
Space group	P -1
Hall group	-P 1

a (Å)	6.1526(7)
b (Å)	7,2932(8)
c (Å)	12.3335(16)
a (°)	88.687(10)
b (°)	82.045(10)
g (°)	84.959(9)
Volume ($Å^3$)	546.27(11)
Crystal F 000	260.0
Z	2
D_c , calc density (g cm^{-3})	1.528
Absorption coefficient (mm^{-1})	0.858
θrange	10.1520-69.2970
Reflections collected	2024
No data I > 2 sigma (I)	1562
Final R indices [I >2 sigma (I)]	R_1=0.0426; wR_2=0,1122
R indices (all data)	R_1=0.0551; wR_2=0,1250
CCDC	2041062

Notes and references

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