Electronic Supplementary Information

Iridium(III) Complex Functionalized ZIF-8 as Novel POD-like Nanozyme for Visual Assay of Triazine Pesticides

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1. Chemical Regents and apparatus

Zinc nitrate hexahydrate ($Zn(NO_3)_2$•$6H_2O$), 2-Methylimidazole (Hmim) and 2 aminobenzimidazole (2-amBzIM) were purchased from Aladdin (Shanghai, China). Dimethyl sulfoxide (DMSO), 2-ethoxyethanol, dichloromethane, methanol and acetonitrile were all brought from Jiangsu Qiangsheng Functional Chemistry Co., Ltd. Acetic acid (HAc) was purchased from Nanjing reagent (Nanjing, China) and sodium acetate (NaAc) was purchased from Bide Pharmatech Ltd (Shanghai, China). Iridium(III) solvent complex (IrppyMeCN) was prepared by our laboratory and its synthesis was reported in our previous literature.[1] 3,3',5,5'-Tetramethyl-benzyl (TMB) were purchased from Energy Chemical Inc. (Shanghai, China). Atraton , glufosinates-ammonium and atrazine were procured from Energy Chemical Inc. (Shanghai, China). Pymetrozine metamitron, thiamethoxam and nitenpyram were procured from J&K Scientific (Hebei, China). Test sheets was purchased from Baisi Biotechnology Co., Ltd (Hangzhou, China).

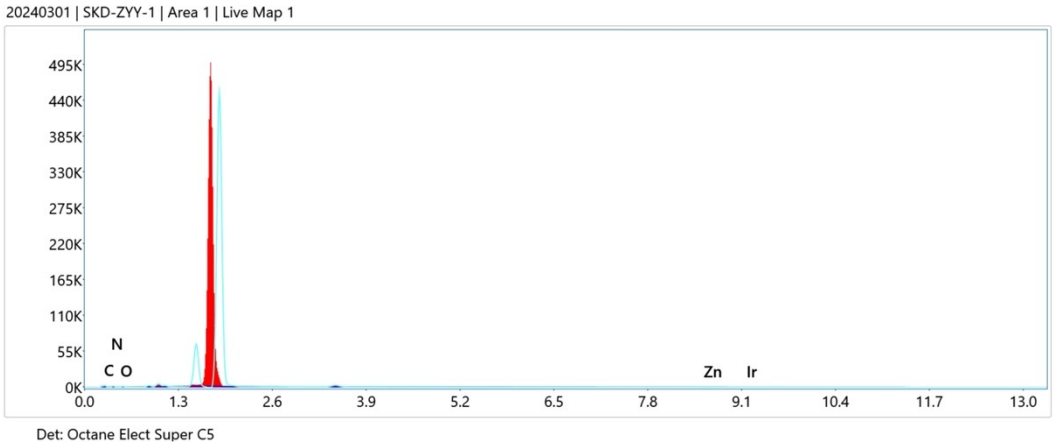
The morphology and size of the obtained products were studied using a Regulus 8100 scanning electron microscope with an operating voltage of 20 kV. The powder X ray diffraction (PXRD) patterns were obtained using a Bruker D8 Advance X-ray diffractometer with Cu Kα radiation source (40 kV, 40 mA) over a 2θ range of 5-50°. Fourier-transform infrared (FT-IR) spectra were recorded using a JASCO FT/IR-430 spectrometer in the wavenumber range of 500-4000 cm-1. TOF mass spectrum were measured on Bruker ultrafleXtreme. X-ray photoelectron spectroscopic (XPS) analysis was performed on Thermo Kalpha Xray photoelectron spectrometer (Thermo Fisher Scientific, America). UV-vis spectrophotometer was recorded on a UV-vis spectrophotometer S3 (TU-1950, Beijing Purkinje General Instrument Co., Ltd, Beijing, China)

2. Experimental section

Preparation of TMB+H_2O_2 chromogenic substrate solution

First, 20 mM of NaAc and 20 mM of HAc were added to 100 mL of deionized water, and then 18 mL of NaAc solution and 82 mL of HAc solution were mixed to make a buffer. Second, 10 mmol TMB was dissolved in 1 mL DMSO, and the volume was fixed to 100mL with NaAc-HAc buffer, then 1 mmol H_2O_2 was added, and the prepared solution was sealed and stored at 3℃ away from light.

2.1. EDS analysis of as-prepared MOF-based nanocomposite Irppy-ZIF-8.



Element	Weight %	Atomic %
C K	43.19	51.63
N K	31.75	32.53
O K	15.86	14.23
Zn K	6.39	1.40
Ir L	2.81	0.21

Fig. S1. EDS analysis of as-prepared MOF-based nanocomposite Irppy-ZIF-8.

2.2. FI-IR spectra of as prepared IrppyMeCN and Irppy-ZIF-8

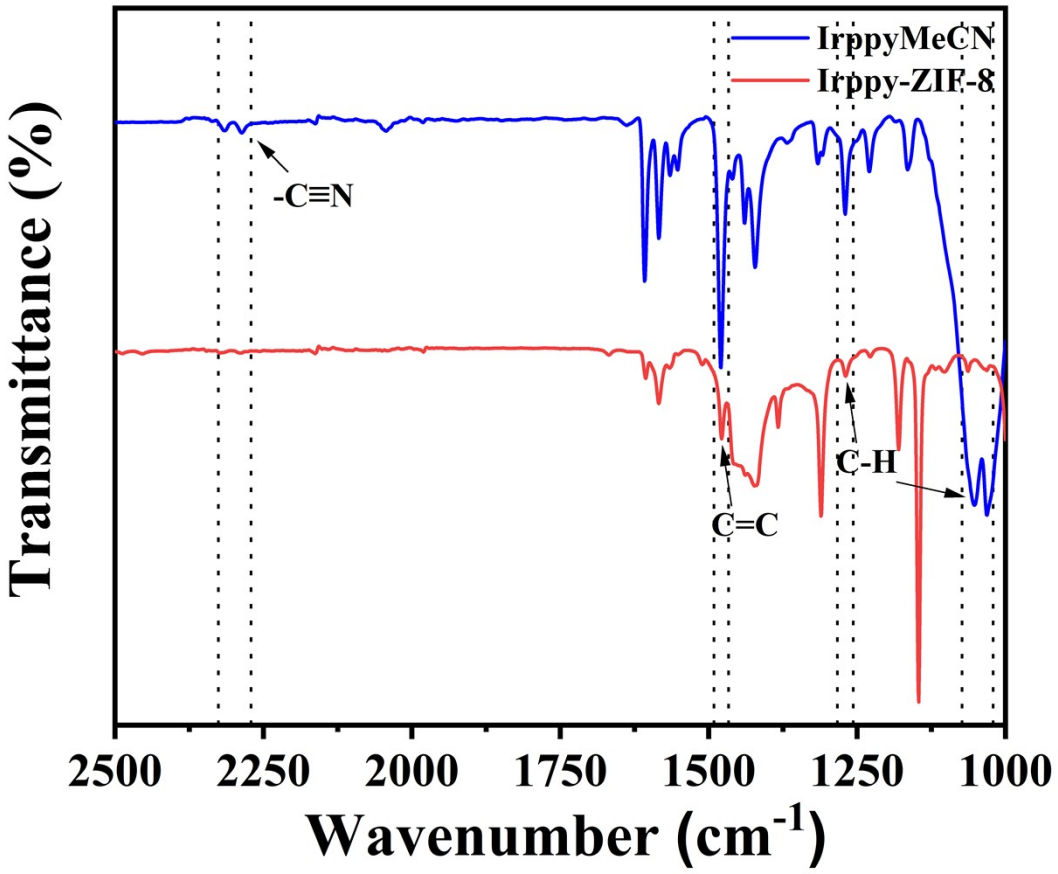


Fig. S2. FI-IR spectra of as prepared IrppyMeCN and Irppy-ZIF.

2.3. Image of chromogenic reaction: left TMB+H_2O_2+Irppy-ZIF-8 and right TMB+H_2O_2

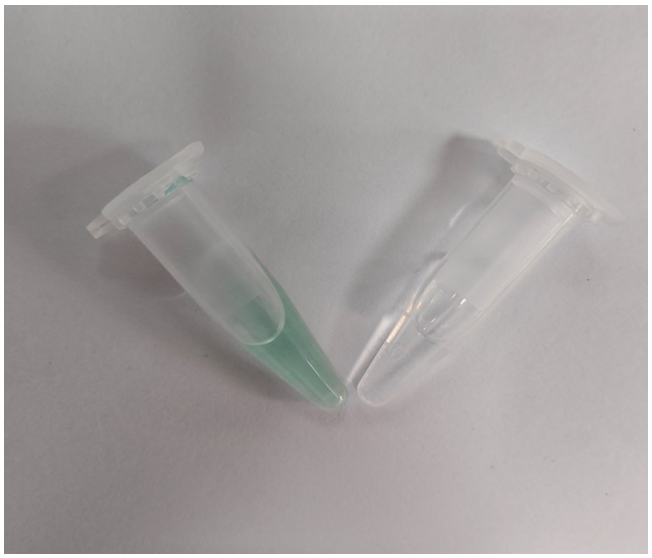


Fig. S3. Image of chromogenic reaction: left TMB+H_2O_2+Irppy-ZIF-8 and right TMB+H_2O_2.

2.4. UV absorption spectra of Irppy-ZIF-8+H_2O_2+TMB, Irppy-ZIF-8+TMB and H_2O_2+TMB.

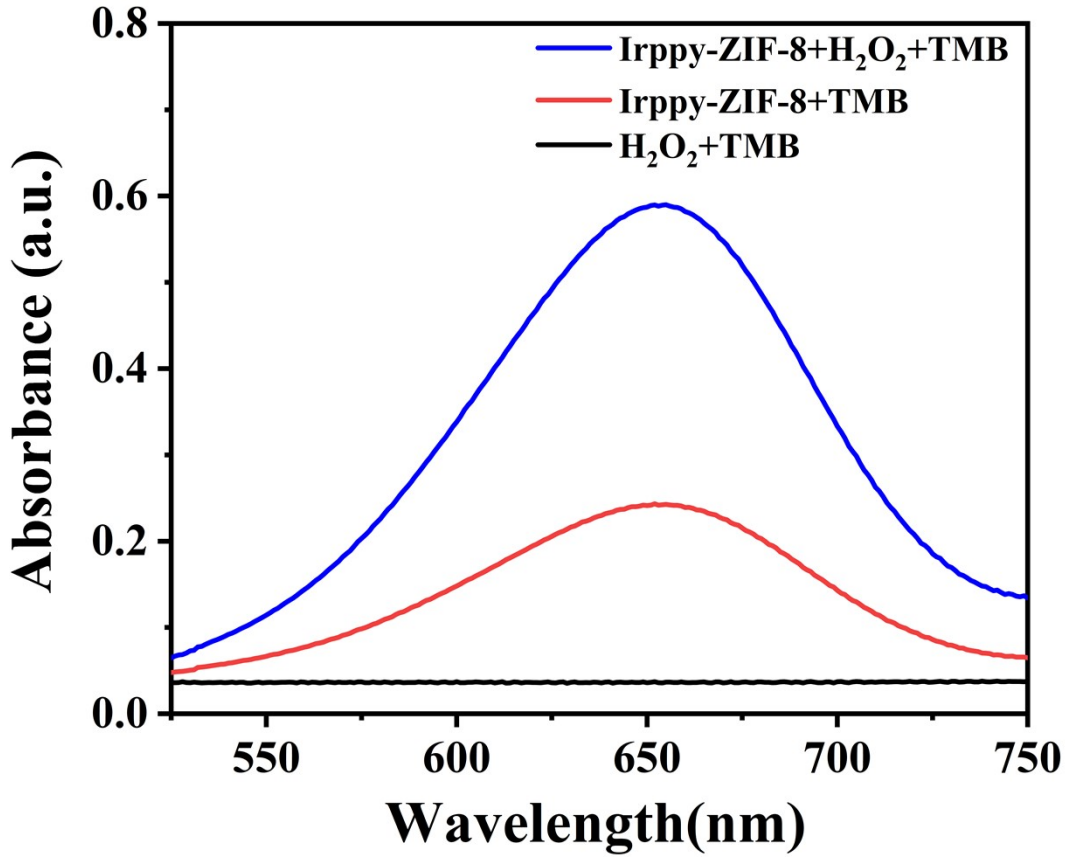


Fig. S4. UV absorption spectra of Irppy-ZIF-8+H_2O_2+TMB, Irppy-ZIF-8+TMB and H_2O_2+TMB.

2.5. Comparison of absorbance intensities of molar ratios between 2-methylimidazole and IrppyMeCN

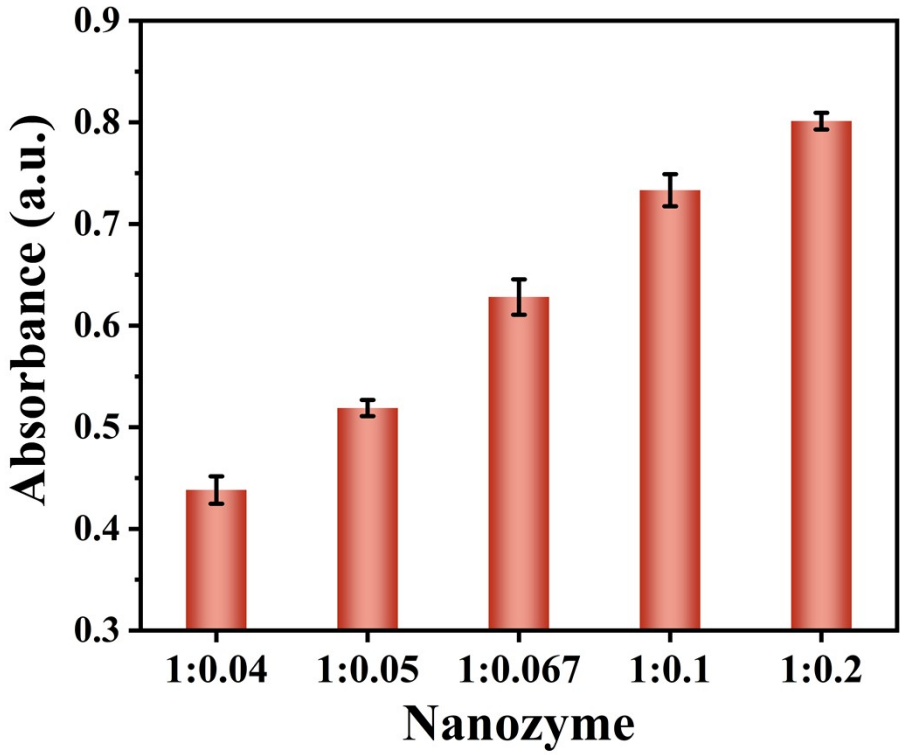


Figure S5. Comparison of absorbance intensities of molar ratios between 2-methylimidazole and IrppyMeCN

2.6. Optimal incubation time of the colorimetric sensor to detect TRZ

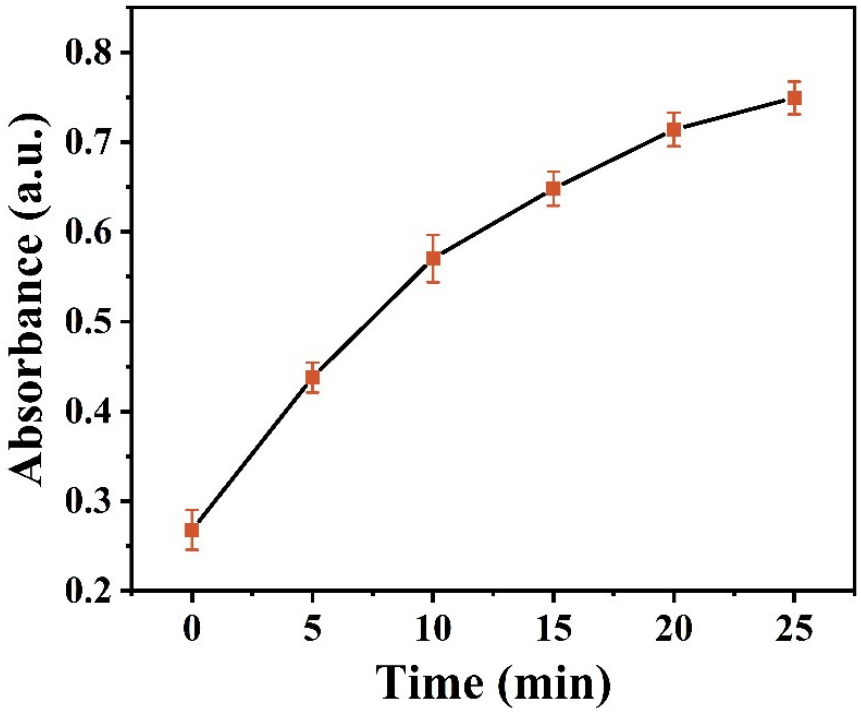


Figure S6. Optimal incubation time of the colorimetric sensor to detect TRZ.

2.7. Reaction–time curves of Irppy-ZIF-8+H_2O_2+TMB colorimetric reaction catalyzed by different concentrations of H_2O_2 and TMB

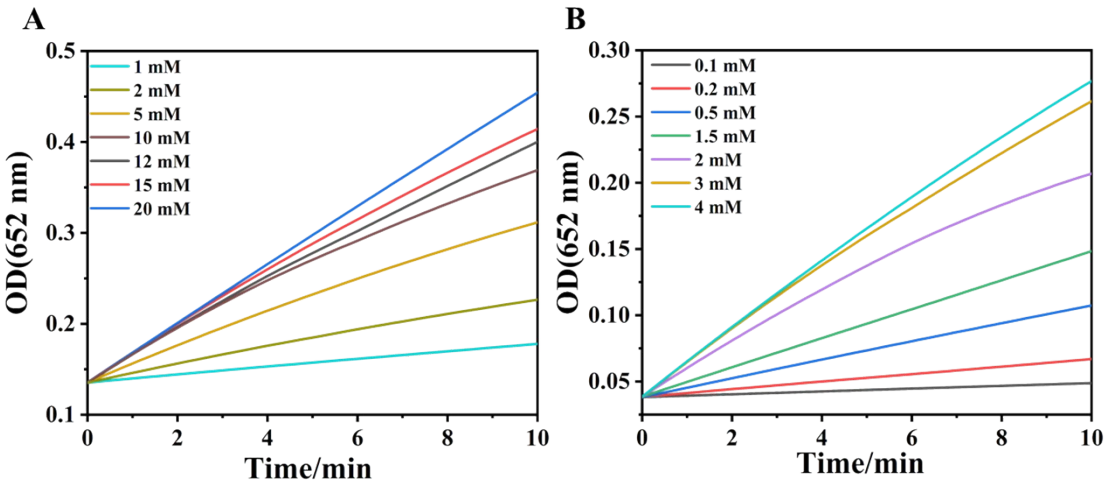


Fig. S7. (A) Reaction–time curves of Irppy-ZIF-8+H_2O_2+TMB colorimetric reaction catalyzed by different concentrations of H_2O_2. (B) Reaction–time curves of Irppy-ZIF-8+H_2O_2+TMB colorimetric reaction catalyzed by different concentrations of TMB.

2.8. UV absorption spectra of PTZ, MTT, ATO, ATZ, NPM, TTX, GA ,TB and CB.

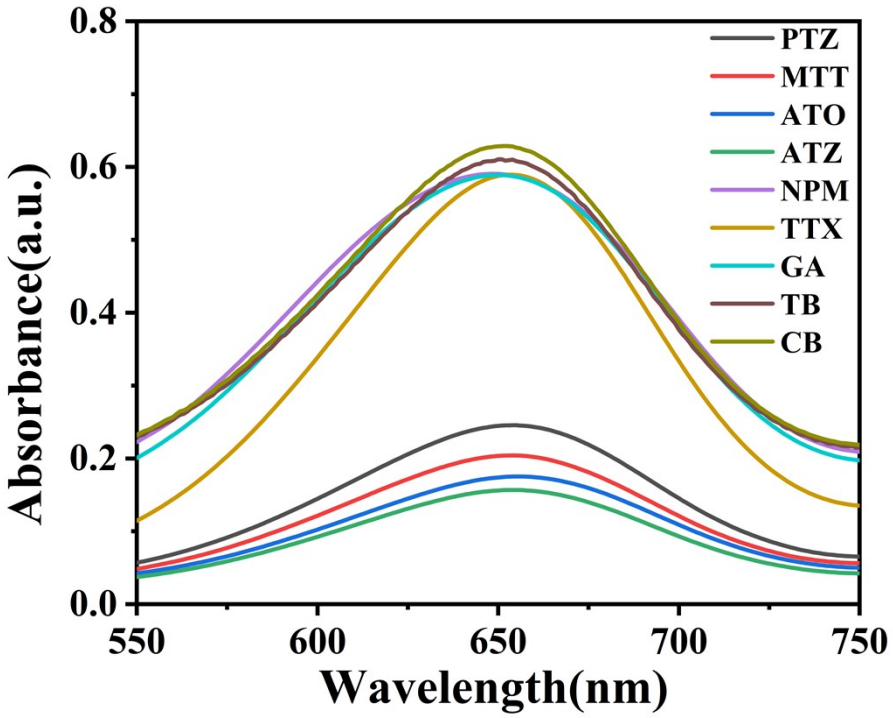


Fig. S8. UV absorption spectra of PTZ, MTT, ATO, ATZ, NPM, TTX, GA ,TB and CB.

2.9. The curve of atrazine RGB colorimetric mediated sensor using the (R+B)/2G formula.

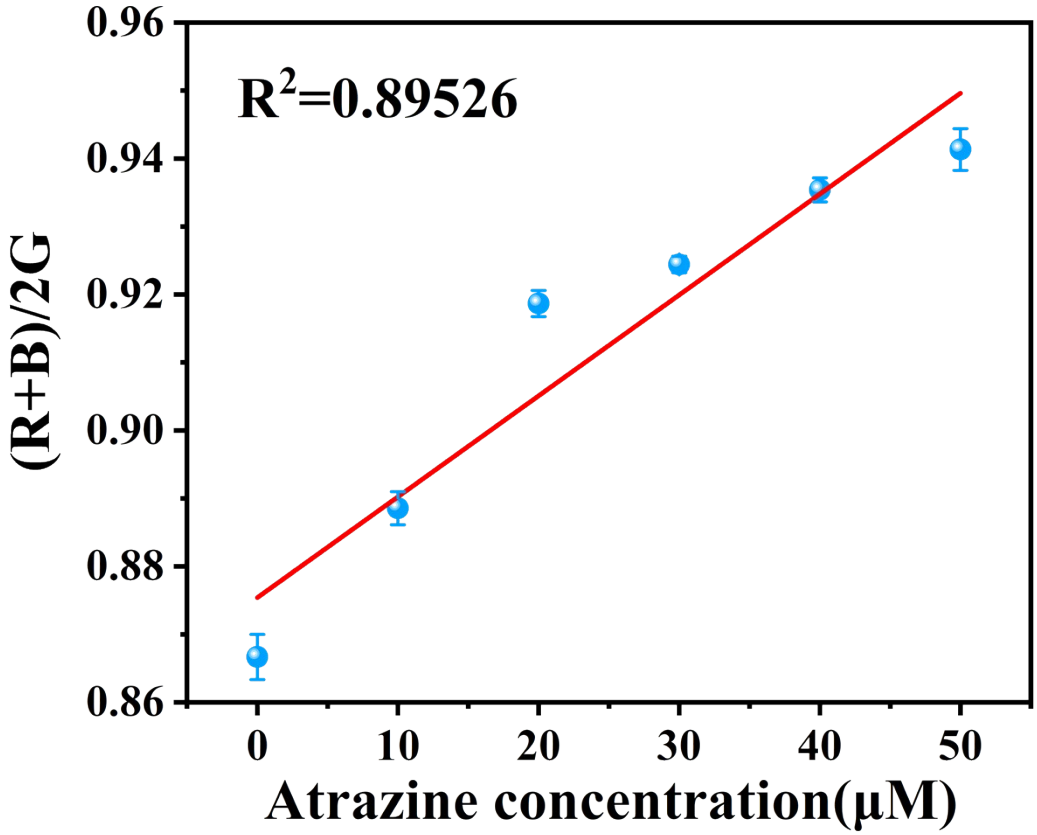


Fig. S9. The curve of atrazine RGB colorimetric mediated sensor using the (R+B)/2G formula.

2.10. The curve of atraton RGB colorimetric mediated sensor using the (R+B)/2G formula.

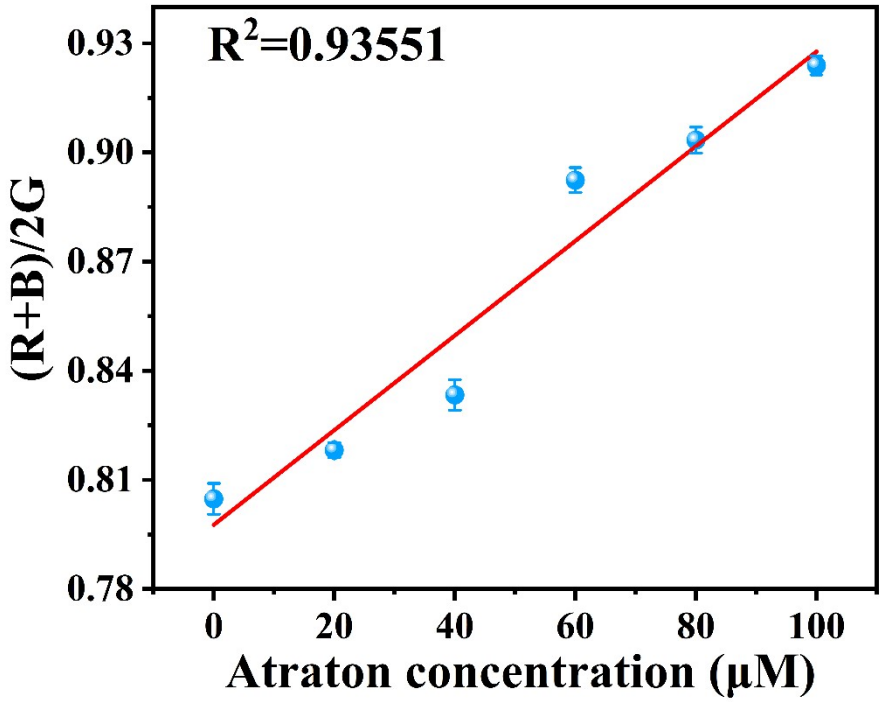


Fig. S10. The curve of atraton RGB colorimetric mediated sensor using the (R+B)/2G formula

2.11. Table S1. Comparison of Km and Vmax between Irppy-ZIF-8 with other catalysts.

Catalyst	Substrate	Km (mM)	Vmax (10^{-8} M s^{-1})	Reference
Irppy-ZIF-8	TMB	0.4997	1.2382	This work
	H_2O_2	16.5344	3.3164	
ZIF-8	TMB	0.224	10.66	2
	H_2O_2	40.16	12.15	
Fe_3O_4	TMB	0.098	3.44	3
	H_2O_2	154	9.78	
CeO_2	TMB	0.67	0.38	4
	H_2O_2	2.5	16.67	
HRP	TMB	0.434	10	3
	H_2O_2	3.7	8.71	

2.12. Table S2. Determination of triazine pesticide residues at different concentration levels in two kinds of vegetables by UV and colorimetric detection

Methods		UV Detection			RGB Detection		
Samples	Pesticides	Added (μmol L^{-1})	Recovery (%)	RSD (%)	Added (μmol L^{-1})	Recovery (%)	RSD (%)
pakchoi cabbage	ATZ	0	ND	/	0	ND	/
		10	104.5	2.7	10	103.9	3.2
		20	101.1	1.4	20	98.4	1.8
		50	86.5	3.1	50	89.1	1.9
	ATO	0	ND	/	0	ND	/
		50	97.5	3.6	50	102.9	1.9
		100	106.1	2.1	100	104.3	2.4
celery cabbage	ATZ	0	ND	/	0	ND	/
		10	98.9	4.1	10	99.6	1.5
		20	87.2	1.6	20	86.3	3.1
		50	97.6	2.1	50	94.9	3.0
	ATO	0	ND	/	0	ND	/
		50	102.4	3.3	50	101.5	2.6
		100	94.1	2.6	100	93.3	4.2

3. References

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