

Supplementary

Tailoring diacid carbon chain of precursor to boost peroxidase activity of carbon dots nanozymes for dual-mode glyphosate detection

Xiaomei Li ^{a,b,#}, Yi Feng ^{a,#}, Xue Huang ^a, Wencai Jiang ^a, Guilin Zou ^a, Shiyu Long ^a, Zhibo Hou ^{c,*}, Yan Zhao ^{a,*}, Guoqi Zhang ^{a,d,*}

^a Department of Chemistry, School of Science, Xihua University, Chengdu, 610039, China

^b School of Food and Bioengineering, Xihua University, Chengdu 610039, China

^c Department of Mathematics, School of Science, Xihua University, Chengdu 610039, PR China

^d Sichuan Provincial Engineering Research Center of Molecular Targeted Diagnostic & Therapeutic Drugs, Xihua University, Chengdu 610039, PR China

[#] Xiao-mei Li and Yi-Feng contributed equally to this work

*Corresponding authors:houzhibo@mail.xhu.edu.cn (Z.B.Hou);zhao518yan@163.com (Y.Zhao); guoqizhang@mail.xhu.edu.cn (G.-Q.Zhang).

1. Supplemental experimental details

Text S1. Computational details

Density functional theory (DFT) calculations were conducted with the Gaussian 16 software package. The B3LYP functional and the 6-31G(d) basis set were employed for geometry optimization and property calculations on the CDszymes models. The SMD implicit solvation model was applied to simulate the aqueous environment. HOMO and LUMO energy levels were extracted from the converged Kohn-Sham orbitals. The absence of imaginary frequencies in the vibrational analysis confirmed the stability of all optimized structures.

Text S2. Electrochemical Impedance Spectroscopy Test Method

The AC impedance measurement was conducted in an electrochemical workstation using a three-electrode system immersed in a 0.1 M KCl electrolyte solution containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$. The three electrodes consisted of carbon paper, platinum, and Ag/AgCl (in saturated KCl electrolyte), which served as the working electrode, counter electrode, and reference electrode, respectively. A mixture was prepared by combining 20 μL of CDs stock solution with 40 μL of Nafion solution (0.5 wt%), 240 μL of deionized water, and 720 μL of anhydrous ethanol. Subsequently, 20 μL of this mixture was deposited onto a 1.5 cm \times 1.5 cm piece of carbon paper. After allowing it to air-dry naturally, electrochemical impedance analysis was performed on the electrochemical workstation.

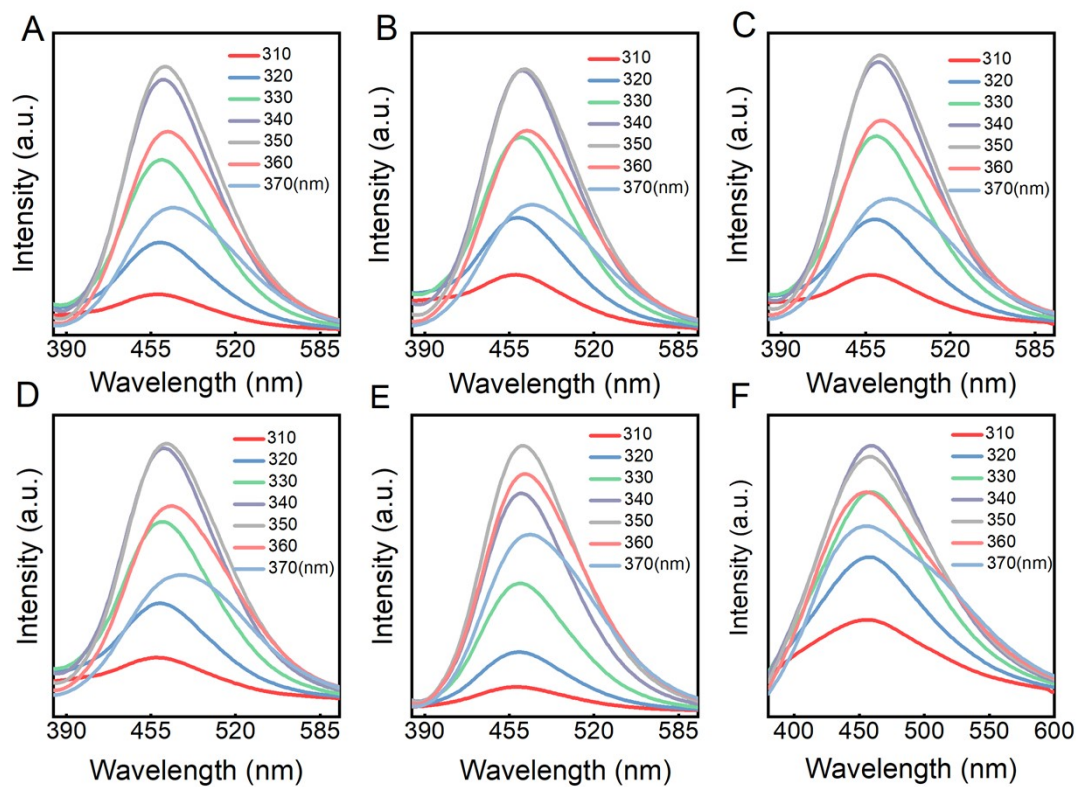


Figure S1. Fluorescence spectra of CDszymes-2, CDszymes-3, CDszymes-4, CDszymes-5, CDszymes-6, CDszymes-7.

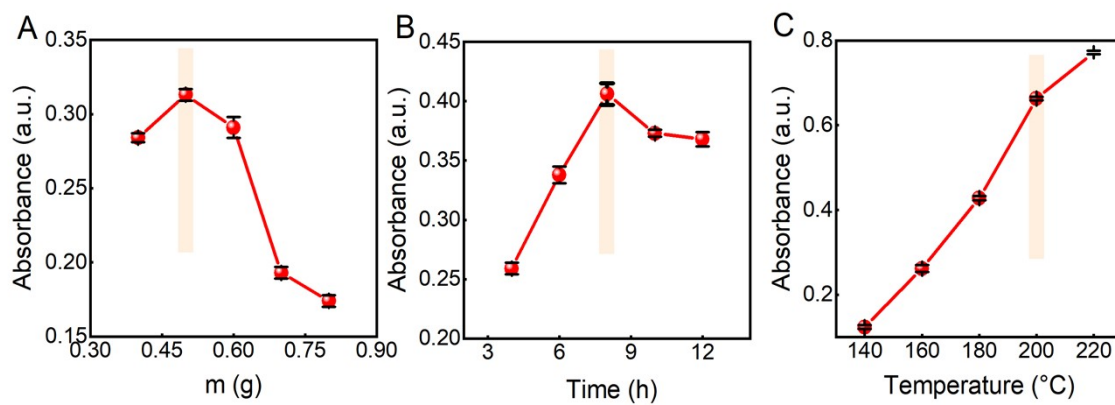


Figure S2. (A) ethanedioic acid mass; (B) synthesis time; (C) synthesis temperature.

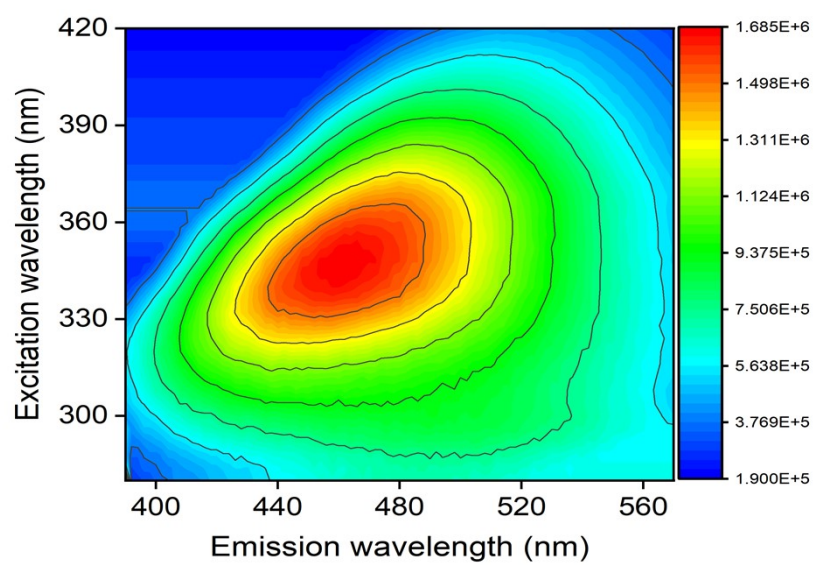


Figure S3. Three-dimensional fluorescence spectrum of CDszymes-2.

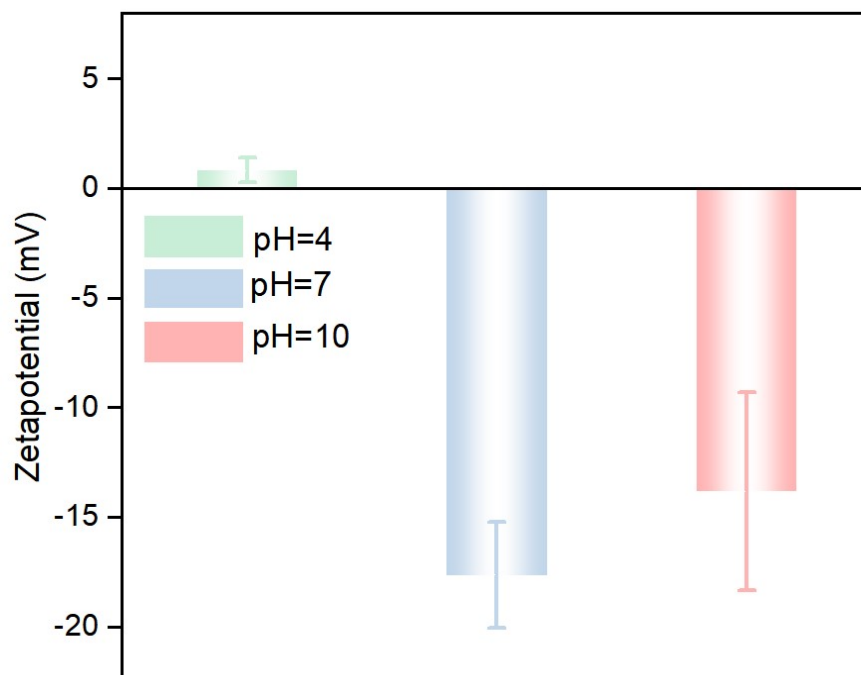


Figure S4. CDszymes-2 zeta potentials at different PHs.

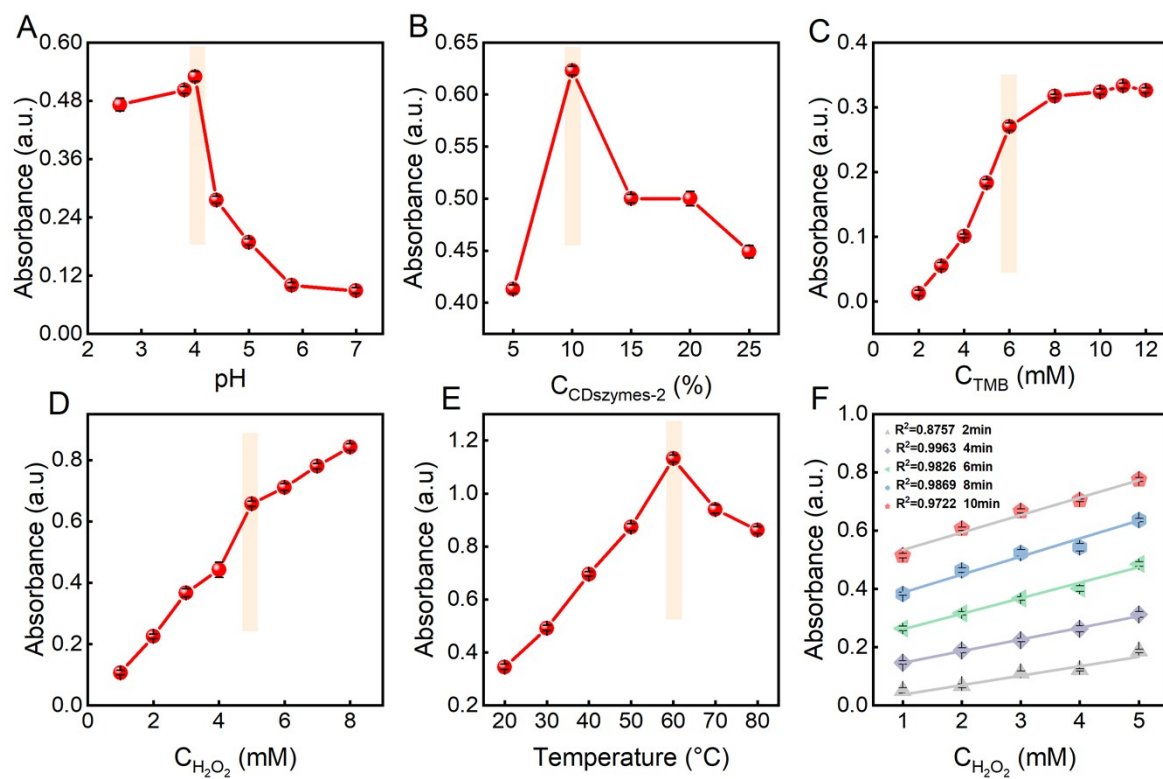


Figure S5: The POD activity of CDszyme-2 under varying (A) pH, (B) CDszyme-2 concentration, (C) TMB concentration, (D) H_2O_2 concentration, (E) temperature, and (F) reaction time.

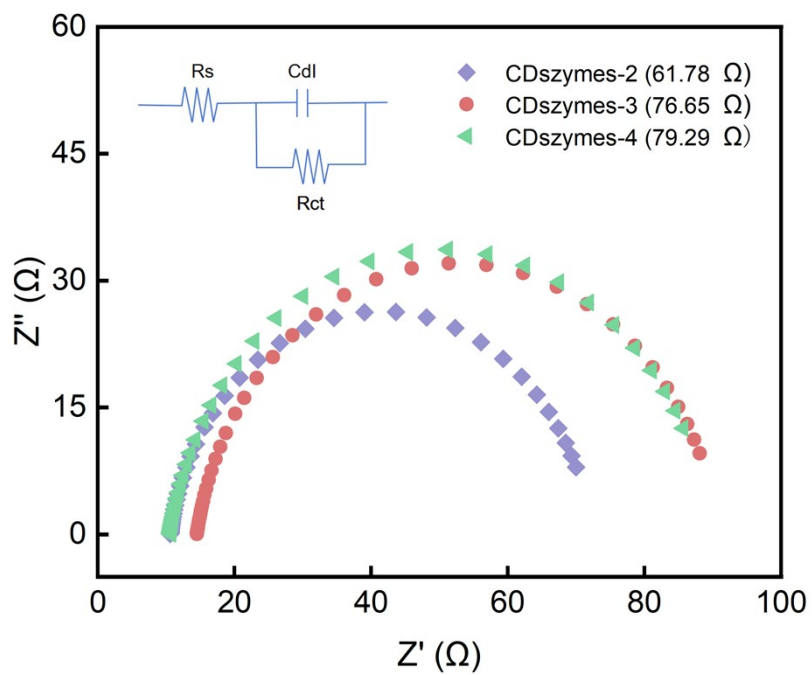


Figure S6: EIS of CDszymes-2, CDszymes-3, CDszymes-4.

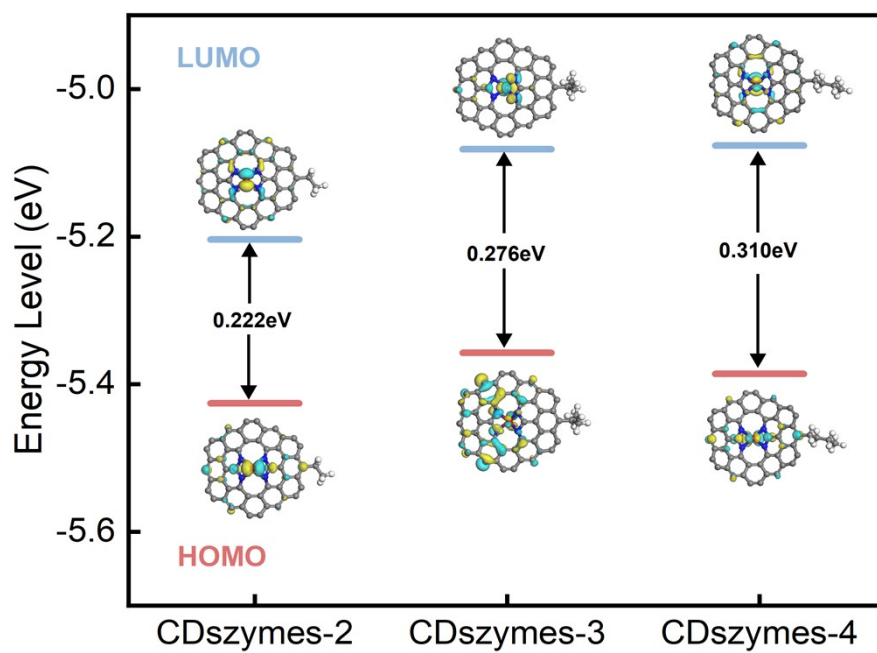


Figure S7: EIS of CDszymes-2, CDszymes-3, CDszymes-4.

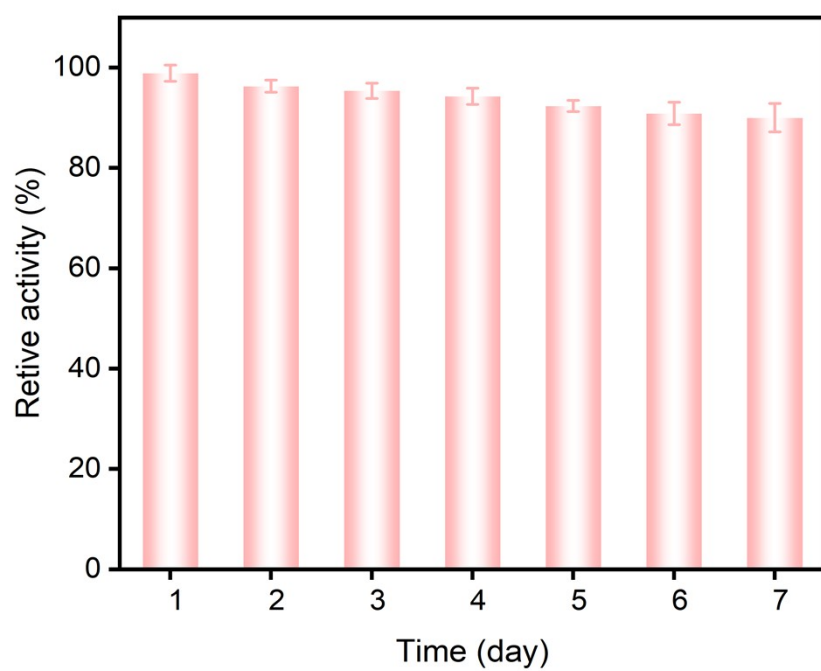


Figure S8: Storage stability of CDszymes.

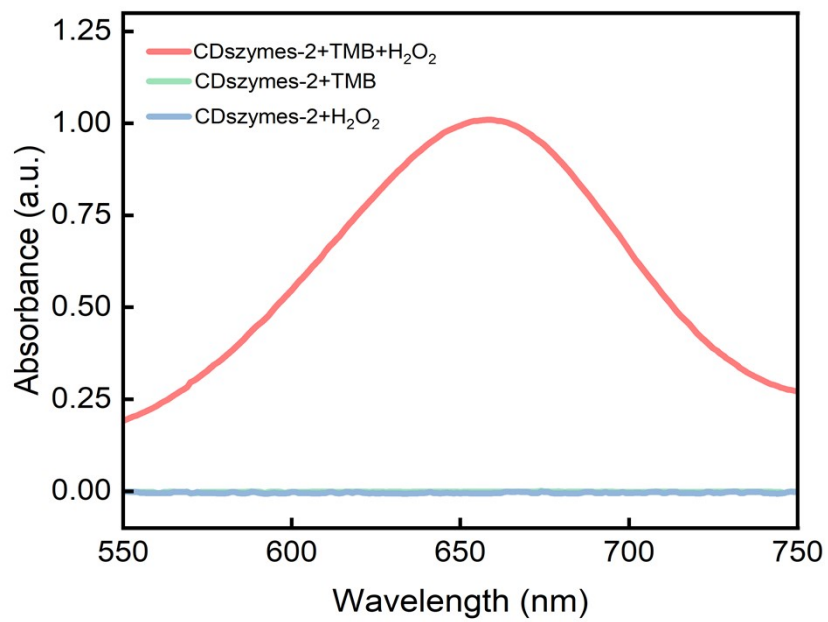


Figure S9: UV-visible absorption spectra of CDszymes-2 in different reaction systems.

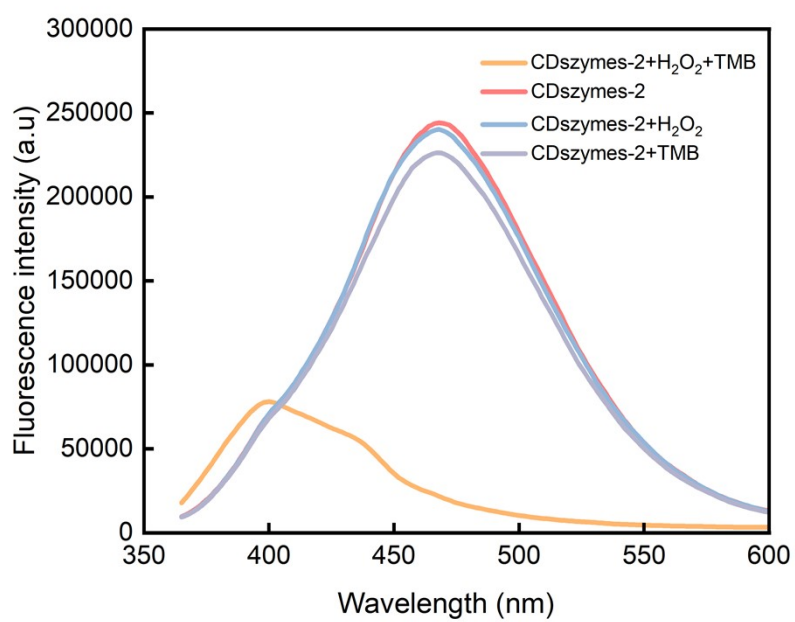


Figure S10: Fluorescence spectra of CDszymes-2 in different reaction systems.

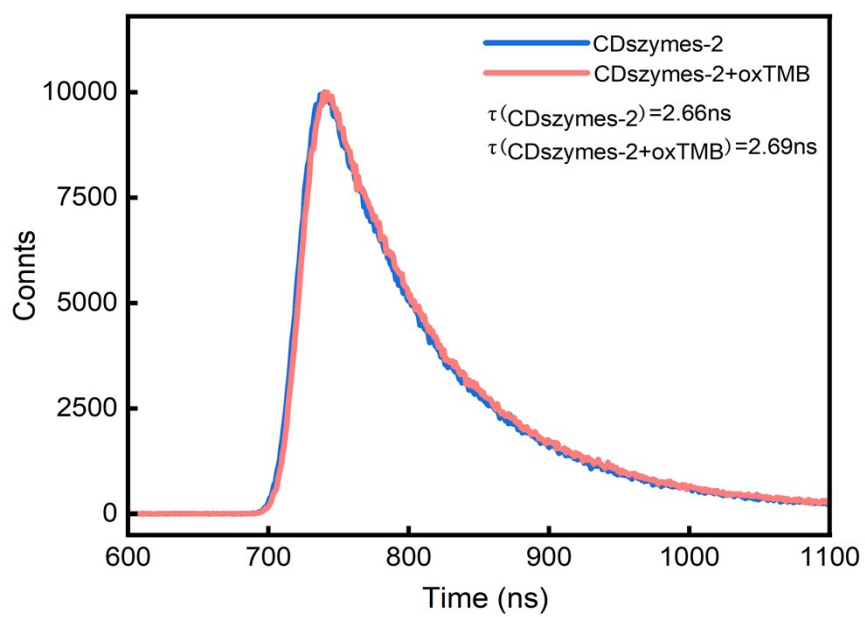


Figure S11:Fluorescence quenching spectra of CDszymes-2 and CDszymes-2 + oxTMB.

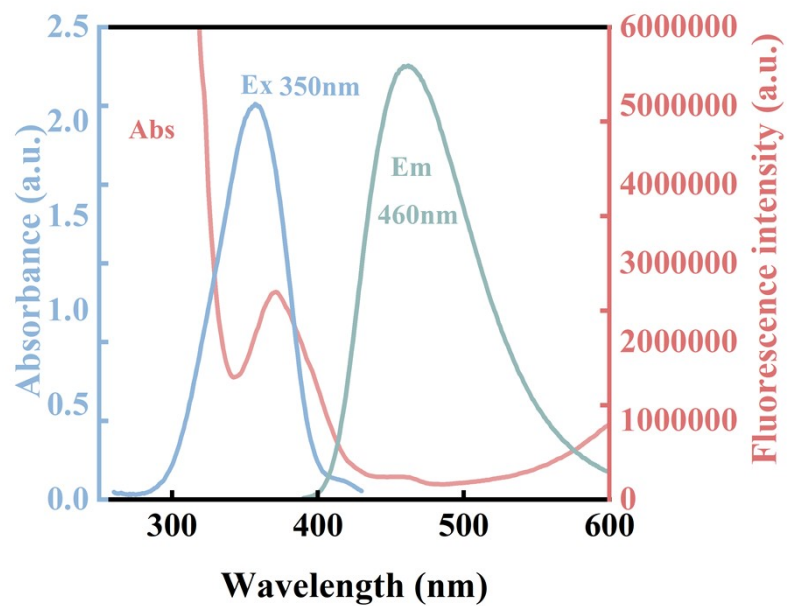


Figure S12: UV-vis absorption spectrum of oxTMB, and fluorescence excitation and emission spectra of CDszymes-2.

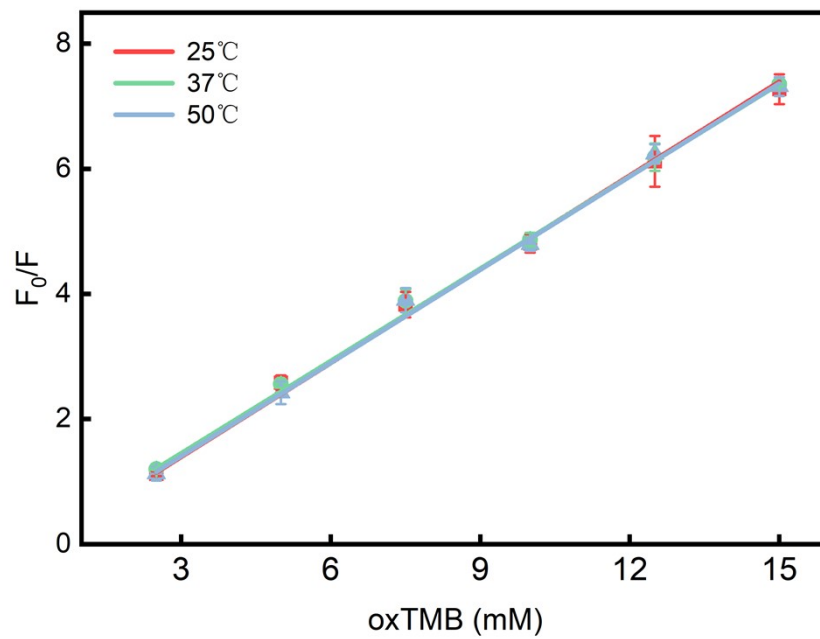


Figure S13: Stern-Volmer plots at different temperatures with error bars (n = 3)

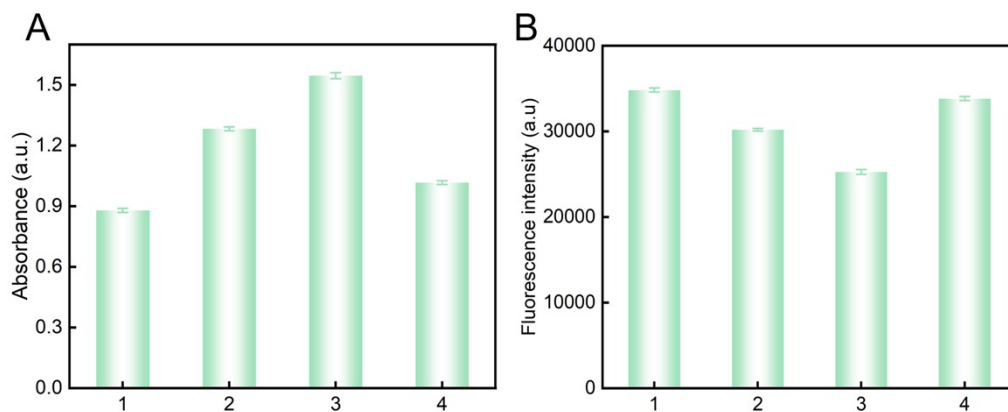


Figure S14:(A) Colorimetric interference; (B) Fluorescence interference. (,Note: 1-4: blank experiment, carbofuran, chlorpyrifos, lambda-cyhalothrin; GLY concentration is 500 ng/mL, interferent concentration is 50 μ g/mL).

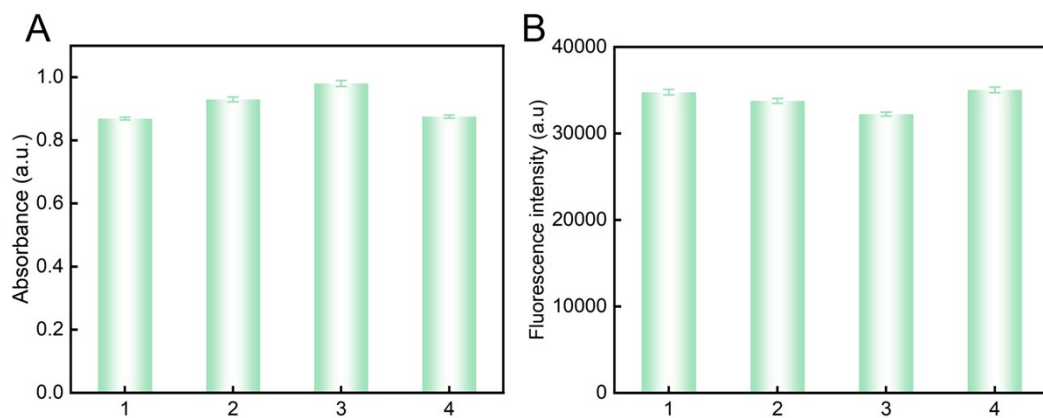


Figure S15: Colorimetric interference; (B) Fluorescence interference. (Note: 1-4: blank experiment, carbofuran, chlorpyrifos, lambda-cyhalothrin; GLY concentration is 500 ng/mL, interferent concentration is 0.1 $\mu\text{g/mL}$).

Table S1. Table 1. HOMO/LUMO energy levels and HOMO-LUMO gaps of CDszymes with different carbon chain lengths

Sample	HOMO (eV)	LUMO (eV)	能隙 (eV)
CDszymes -2	-5.426	-5.2043	0.222
CDszymes -3	-5.3579	-5.0818	0.276
CDszymes -4	-5.3864	-5.0768	0.310

Table S2. Comparative analysis of enzymatic kinetic parameters between CDszymes-X and other nanozymes.

Nanozymes	$K_m(\text{mM})$		$V_{\max}(\text{Ms}^{-1})$		Re.f
	TMB	H_2O_2	TMB	H_2O_2	
CDszymes-2	0.72	0.47	217.4×10^{-5}	332.2×10^{-5}	This work
CDszymes-3	0.99	0.95	177.3×10^{-5}	125.2×10^{-5}	This work
CDszymes-4	2.13	1.49	131.4×10^{-5}	166.9×10^{-5}	This work
ZnCo-ZIFs@MIL-101 (Fe)	1.90	1.96	4.10×10^{-8}	10.36×10^{-8}	[1]
Fe-CDs	8.56	6.72	2.04×10^{-5}	2.82×10^{-5}	[2]
CoCDs	1.542	1.746	3.54×10^{-8}	22.05×10^{-8}	[3]
CDs-Fe	3.30	4.71	6.68×10^{-7}	3.00×10^{-7}	[4]

Table S3. Comparison of GLP measurement methods

Response model	Sensor	Linear range ($\mu\text{g/mL}$)	LOD ($\mu\text{g/mL}$)	Ref.
Colorimetry	CDszymes-2	0.1-0.8	0.013	This work
Fluorometry	CDszymes-2	0.1-0.8	0.007	
Fluorometry	2D MOF-Calix	0.42-7.6	0.38	[5]
Colorimetry	UCNP-Cu(II)	5.0-125	1.0	[6]
Fluorescence	CdTe QDs	1.7-20.0	0.52	[7]
Fluorescence	Fe₃O₄@SiO₂@U iO-67	0.1-40	0.093	[8]
Fluorescence	Fe-MOFs	0.50–15.00	0.36	[9]
Colorimetry	Zn-MOFs	1.00–30.00	0.95	[10]
Fluorescence		0.50–20.00	0.46	

References

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