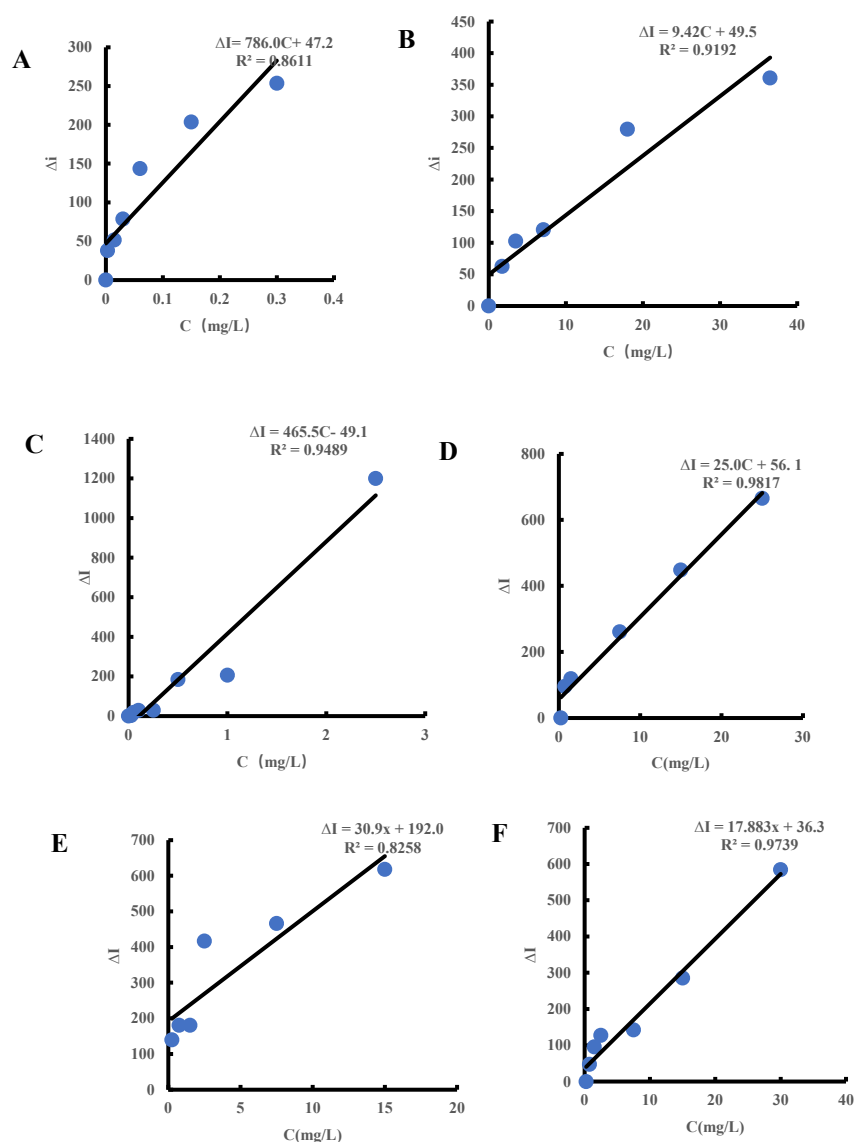
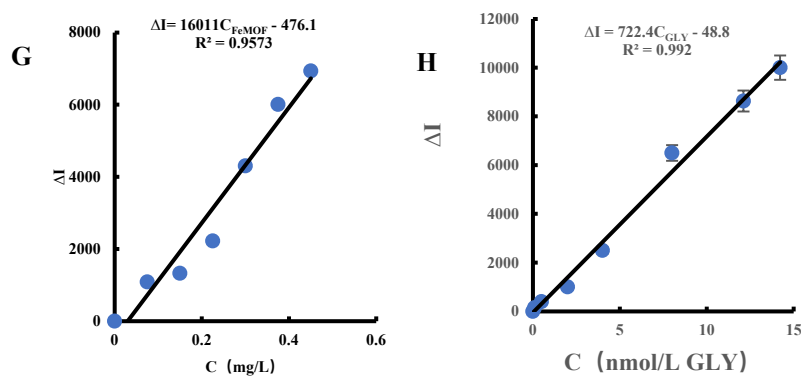


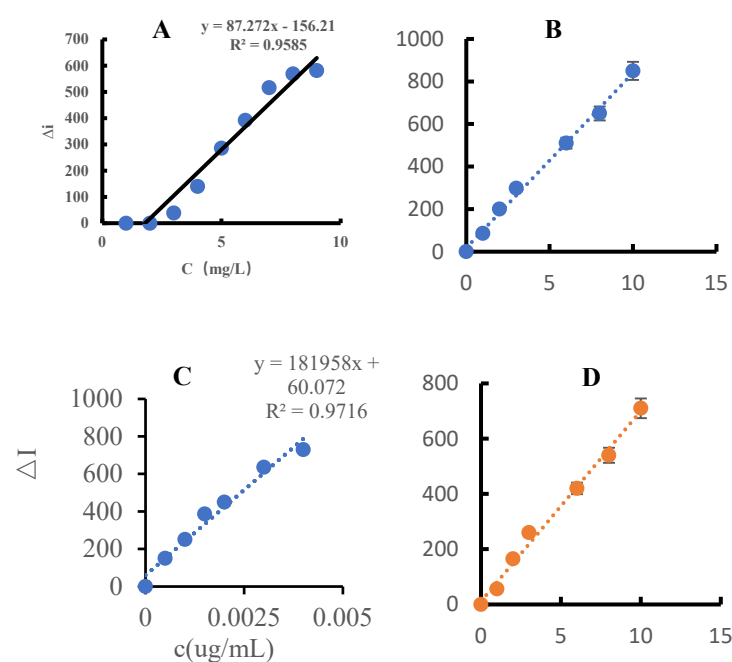
supplementary

# Aptamer Trimode Biosensor for Trace Glyphosate Based on FeMOF Catalytic Oxidation of Tetramethylbenzidine

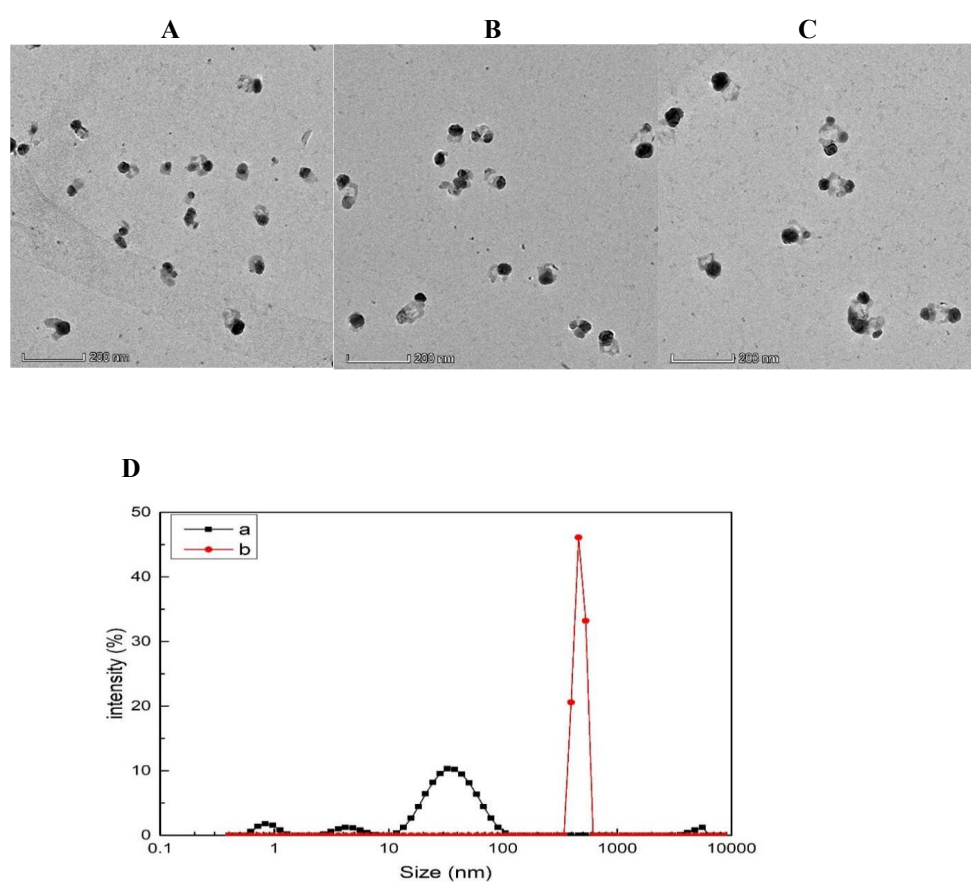




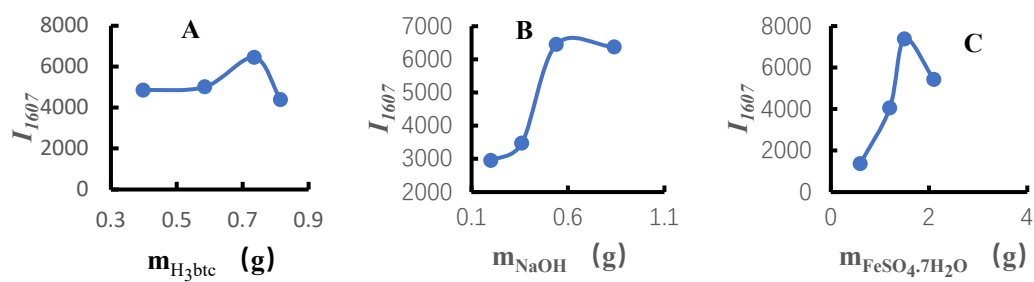
**Figure S1.** The relationship between SERS peak intensity and catalyst/GLY concentration. **A:** a: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mmol/L TMB + 11.6 mg/L AgNPs; b: a+ 0.003 mg/L AuNPs; c: a+0.015 mg/L AuNPs; d: a+0.03mg/L AuNPs; e: a+0.06 mg/L AuNPs; f: a+0.15 mg/L AuNPs; g: a+0.3 mg/L AuNPs; **B:** a: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mmol/L TMB + 11.6 mg/L AgNPs; b: a+ 1.725 mg/L AgNPs; c: a+3.5 mg/L AgNPs; d: a+7.1 mg/L AgNPs; e: a+18 mg/L AgNPs; f: a+36 mg/L AgNPs. **C:** a: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mmol/L TMB + 11.6 mg/L AgNPs; b: a+ 0.025 g/L HPR; c: a+0.05 mg/L HPR; d: a+0.1 mg/L HPR; e: a+0.25 mg/L HPR; f: a+0.5 mg/L HPR; g: a+1 mg/L HPR; h: a+2.5 mg/L HPR. **D:** a: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mol/L TMB + 11.6 mg/L AgNPs; b: a+ 0.25 mg/L CoMOF; c: a+0.75 mg/L CoMOF; d: a+1.5 mg/L CoMOF; e: a+7.5 mg/L CoMOF; f: a+0.015 g/L CoMOF; g: a+0.025g/L CoMOF. **E:** a: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mol/L TMB + 11.6 mg/L AgNPs; b: a+ 0.25 mg/L CuMOF; c: a+0.75 mg/L CuMOF; d: a+1.5 mg/L CuMOF; e: a+2.5 mg/L CuMOF; f: a+7.5 mg/L CuMOF; g: a+0.015 g/L CuMOF; **F:** a: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mol/L TMB + 11.6 mg/L AgNPs; b: a+ 0.25 mg/L NiMOF; c: a+0.75 mg/L NiMOF; d: a+1.5 mg/L NiMOF; e: a+2.5 mg/L NiMOF; f: a+7.5 mg/L NiMOF; g: a+0.015 g/L NiMOF; f: a+0.03 g/L NiMOF; **G:** a: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mmol/L TMB + 11.6 mg/L AgNPs; b: a+ 0.25 mg/L FeMOF; c: a+0.75 mg/L FeMOF; d: a+1.5 mg/L FeMOF; e: a+2.5 mg/L FeMOF; f: a+7.5 mg/L FeMOF; g: a+0.015 g/L FeMOF; h: a+0.025g/L FeMOF; i: a+0.05g/L FeMOF; **H:** a: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mmol/L TMB+7.5mg/L FeMOF + 0.01  $\mu\text{mol/L}$  Apt<sub>GLY</sub> + 11.6 mg/L AgNPs; b: a+ 0.1 nmol/L GLY; c: a+ 0.5 nmol/L GLY; d: a+2 nmol/L GLY; e: a+4 nmol/L GLY; f: a+8  $\mu\text{mol/L}$  GLY; g: a+10  $\mu\text{mol/L}$  GLY; h: a+14.22 nmol/L GLY.



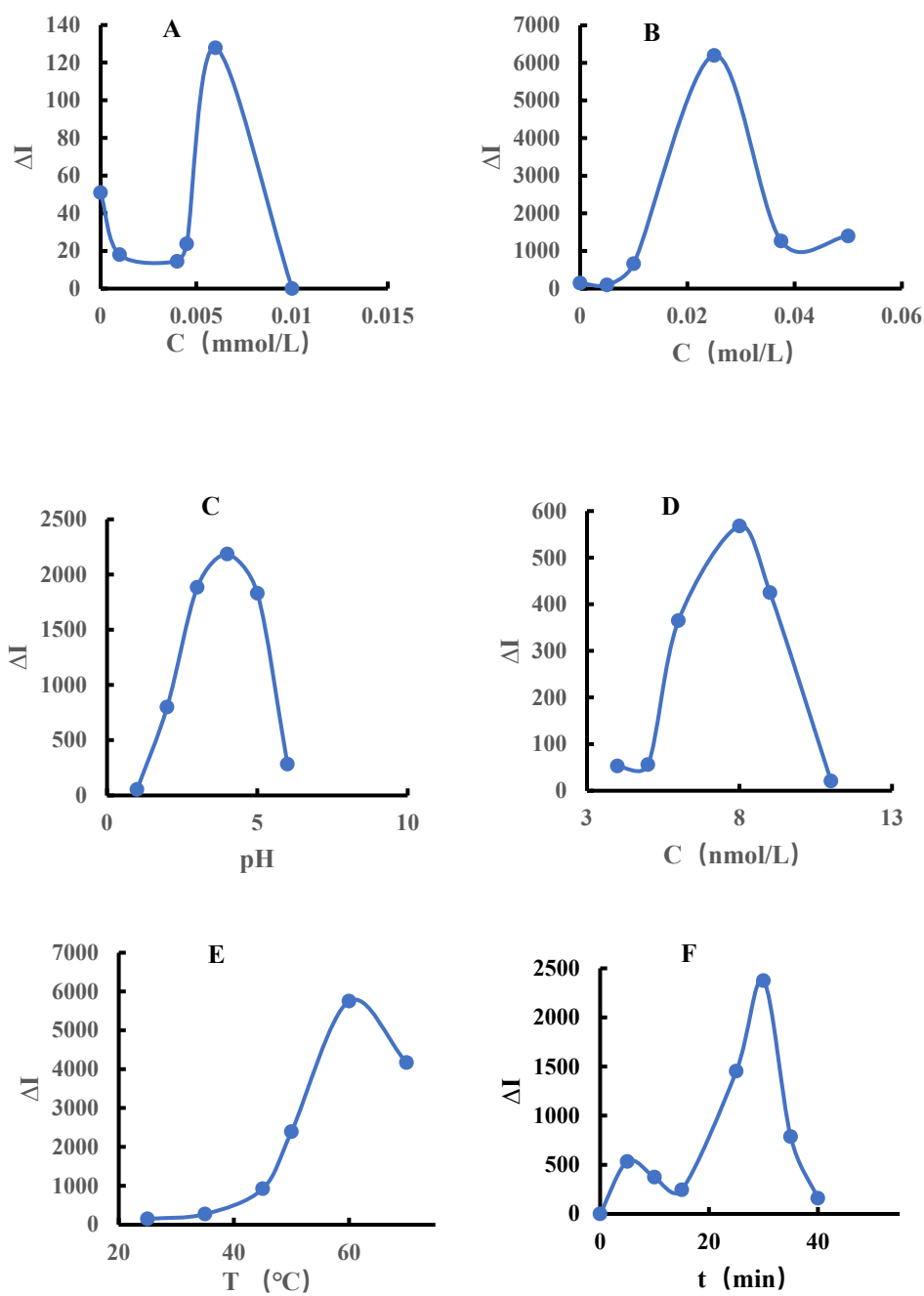
**Figure S2.** The relationship between RRS/fluorescence intensity and FeMOF/GLY. A: RRS, a: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mmol/L TMB + 11.6 mg/L AgNPs; b: a+ 0.25 mg/L FeMOF; c: a+0.75 mg/L FeMOF; d: a+1.5 mg/L FeMOF; e: a+2.5 mg/L FeMOF; f: a+7.5 mg/L FeMOF; g: a+0.015 g/L FeMOF; h: a+0.025g/L FeMOF; i: a+0.05g/L FeMOF; B: RRS, a: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mmol/L TMB+7.5mg/L FeMOF + 0.01  $\mu\text{mol/L}$  Apt<sub>GLY</sub> + 11.6 mg/L AgNPs; b: a+ 1 nmol/L GLY; c: a+2 nmol/L GLY; d: a+73 nmol/L GLY; e: a+6 nmol/L GLY; f: a+8 nmol/L GLY; g: a+10 nmol/L GLY. C: Fluorescence, with excitation wavelength of 300 nm,  $2.5 \times 10^{-4}$  mol/L TMB +  $5 \times 10^{-4}$  mol/L  $\text{H}_2\text{O}_2$ + 0.45 mmol/L Tris-HCl + FeMOF (a~g: 0,  $5 \times 10^{-4}$ ,  $1 \times 10^{-3}$ ,  $1.5 \times 10^{-3}$ ,  $2 \times 10^{-3}$ ,  $3 \times 10^{-3}$ ,  $4 \times 10^{-3}$  g/L FeMOF). F: Fluorescence,  $2.5 \times 10^{-4}$  mol/L TMB +  $5 \times 10^{-4}$  mol/L  $\text{H}_2\text{O}_2$ +0.45 mmol/L Tris-HCl + 1 nmol/L Apt<sub>GLY</sub>+xGLY (0, 1, 2, 3, 6, 8, 10 nmol/L GLY).



**Figure S3.** Transmission electron microscopy and laser scattering of FeMOF analytical system. A:  $4.0 \times 10^{-4}$  mol/L AgNPs; B: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mmol/L TMB+7.5mg/L FeMOF + 0.01  $\mu\text{mol/L}$  Apt<sub>GLY</sub>+0.16  $\mu\text{mol/L}$  AgNPs; C: 0.45 mmol/L Tris-HCl +  $4.5 \times 10^{-6}$  mol/L  $\text{H}_2\text{O}_2$  + 0.025 mmol/L TMB+7.5mg/L FeMOF + 0.01  $\mu\text{mol/L}$  Apt<sub>GLY</sub>+2.5 ng/L GLY+0.16  $\mu\text{mol/L}$  AgNPs; D: Laser light scattering; a: Blank system; b: FeMOF analysis system.



**Figure. S4** Effect of preparation conditions on FeMOF.



**Figure S5.** Influence of the analysis conditions. A: H<sub>2</sub>O<sub>2</sub> concentration, 0.45 mmol/L Tris-HCl + 0.025 mmol/L TMB+7.5 mg/L FeMOF+0.1 µmol/L Apt<sub>GLY</sub>+21.1 nmol/L GLY+ H<sub>2</sub>O<sub>2</sub>+ 11.6 mg/L AgNPs; B: TMB concentration, 0.45 mmol/L Tris-HCl + 4.5×10<sup>-6</sup> mol/L H<sub>2</sub>O<sub>2</sub> + 7.5 mg/L FeMOF+1.25 ng/L Apt<sub>GLY</sub>+21.1 nmol/L GLY + TMB+ 11.6 mg/L AgNPs; C: Tris-HCl concentration, 0.1 µmol/L Apt<sub>Co</sub> + 0.025 mmol/L TMB+7.5 mg/L FeMOF+ 4.5×10<sup>-6</sup> mol/L Apt<sub>GLY</sub>+21.1 nmol/L + Tris-HCl+ 11.6 mg/L AgNPs; D: Apt<sub>GLY</sub> concentration, 0.45 mmol/L Tris-HCl + 0.025 mmol/L TMB+7.5 mg/L FeMOF+ 4.5×10<sup>-6</sup> mol/L H<sub>2</sub>O<sub>2</sub> +21.1 mol/L GLY+ Apt<sub>GLY</sub>+ 11.6 mg/L AgNPs; E: Reaction time, 0.45 mmol/L Tris-HCl + 0.025 mmol/L TMB+7.5 mg/L FeMOF+0.1 µmol/L Apt<sub>Co</sub>+0.1nmol/L CoCl<sub>2</sub>+ 4.5×10<sup>-6</sup> mol/L H<sub>2</sub>O<sub>2</sub>+ 11.6 mg/L AgNPs; F: Reaction temperature, 0.45 mmol/L Tris-HCl + 0.025 mmol/L TMB+7.5 mg/L FeMOF+0.1 µmol/L Apt<sub>Co</sub>+0.1 nmol/L CoCl<sub>2</sub>+ 4.5×10<sup>-6</sup> mol/L H<sub>2</sub>O<sub>2</sub>+ 11.6 mg/L AgNPs.

**Table S1.** Effect of coexistence substance on the SERS determination of GLY.

Coexisting substance	Relative multiples	Relative error (%)	Coexisting substance	Relative multiples	Relative error (%)
PO <sub>4</sub> <sup>-</sup>	100	1.08	NH <sub>4</sub> <sup>+</sup>	100	-6.92
P <sub>2</sub> O <sub>7</sub> <sup>-</sup>	50	5.6	NO <sub>3</sub> <sup>-</sup>	100	3.59
IO <sub>3</sub> <sup>-</sup>	100	3.29	Ba <sup>2+</sup>	50	6.82
Br <sup>-</sup>	100	-6.64	SiO <sub>3</sub> <sup>-</sup>	100	0.76
CO <sub>3</sub> <sup>2-</sup>	100	0.56	Al <sup>3+</sup>	100	1.92
Mg <sup>2+</sup>	100	-9.16	Fe <sup>3+</sup>	50	-3.76
Sanmate	100	4.8	Phosphoramidothionate	100	3.9
Dipterex	100	5.6	BSA	100	4.2

**Table S2.** SERS results of GLY in wastewater samples.

Sample	Mean value (µmol/L, n=5)	Added GLY (µmol/L)	Found (µmol/L)	Recovery (%)	RSD (%)	Content (µmol/L)	Ref results (µmol/L)
1	0.382	0.169	0.385	93.6	3.6	0.764	0.750
2	0.226	0.169	0.537	92.1	8.7	0.0760	0.0712
3	0.338	0.169	0.527	97.5	6.3	0.0720	0.0686
4	0.196	0.169	0.356	94.6	5.4	0.0420	0.0401
5	0.113	0.169	0.275	96.1	4.8	0.0240	0.0280