Dual-mode sensing platform for electron spin resonance and UV-vis
 detection of alkaline phosphatase based on Cu-based metal-organic
 frameworks

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42 Figure S1. Variation of the catalytic activity of Cu-MOFs as peroxidase mimic with43 temperature (a) and the pH of the reaction solution (b).



46 Figure S2. Variation of the ESR signal of ABTS<sup>++</sup> with the concentration of PPi (a),
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**Figure S3.** The stability of the ESR signal of ABTS<sup>++</sup>. Cu-MOFs,  $6 \mu g m L^{-1}$ ; H<sub>2</sub>O<sub>2</sub>, 6 62 mmol L<sup>-1</sup>; ABTS, 4 mmol L<sup>-1</sup>. To prevent the further generation of new ABTS<sup>++</sup> by 63 the catalysis of Cu-MOFs, the sample was kept in the ice bath before ESR 64 measurement.



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Figure S4. UV-vis signals at 740 nm in the presence of interfering substances ( $PO_4^{3-}$ , 83  $HPO_4^{2-}$  and  $H_2PO_4^{-}$ , 250 mmol L<sup>-1</sup>; Cl<sup>-</sup>,  $CO_3^{2-}$  and  $SO_4^{2-}$ , 100 mmol L<sup>-1</sup>; BSA, 100 84 nmol L<sup>-1</sup>; GOx and ChOx, 3000 U L<sup>-1</sup>).

Catalyst	Substrate	K <sub>m</sub> (mmol L <sup>-1</sup> )	V <sub>max</sub> (10 <sup>-7</sup> mol L <sup>-1</sup> s <sup>-1</sup> )	Ref.
	ABTS	71.53	36.5	1
$Au_1Ag_1Pd_1$	$H_2O_2$	0.011	0.123	
	ABTS	0.14	1.254	1
MgFe <sub>2</sub> O4	$H_2O_2$	4.61	1.346	
	ABTS	0.15	1.61	2
Cys–MoS <sub>2</sub>	$H_2O_2$	8.06	9.92	
	ABTS	0.97	0.63	
raw MoS <sub>2</sub>	$H_2O_2$	6.74	1.92	2
	ABTS	3.07	149	3
HRP	$H_2O_2$	0.342	54.6	
G . 1 ( 0 F	ABTS	4.38	0.713	
Cu-MOFs	$H_2O_2$	2.38	4.79	This work

87 **Table S1.** Comparison of two kinetic parameters ( $K_{\rm m}$  and  $V_{\rm max}$ ) of the synthesized Cu-88 MOFs with HRP and nanoenzymes reported in the literatures.

## 91 **References:**

- 92 1. J. Kong, J. Zheng, Li Z., J. Huang, F. Cao, Q. Zeng and F. Li, Anal. Bioanal. Chem.,
- 93 2021, **413**, 5383-5393.
- 94 2. J. Yu, D. Ma, L. Mei, Q. Gao, W. Yin, X. Zhang, L. Yan, Z. Gu, X. Ma and Y.
- 95 Zhao, J. Mat. Chem. B, 2018, 6, 487-498.
- 96 3. R. Li, Y. Zhou, L. Zou, S. Li, J. Wang, C. Shu, C. Wang, J. Ge and L. Ling, Sens.
- 97 Actuator B-Chem., 2017, 245, 656-664.