

Supporting Information

Organic-inorganic hybrid nanoflower of copper phosphate coated with tetra imidazolyl-phenanthroline derivatized calix[4]arene: Synthesis, characterization and its application as peroxidase mimic catalyst

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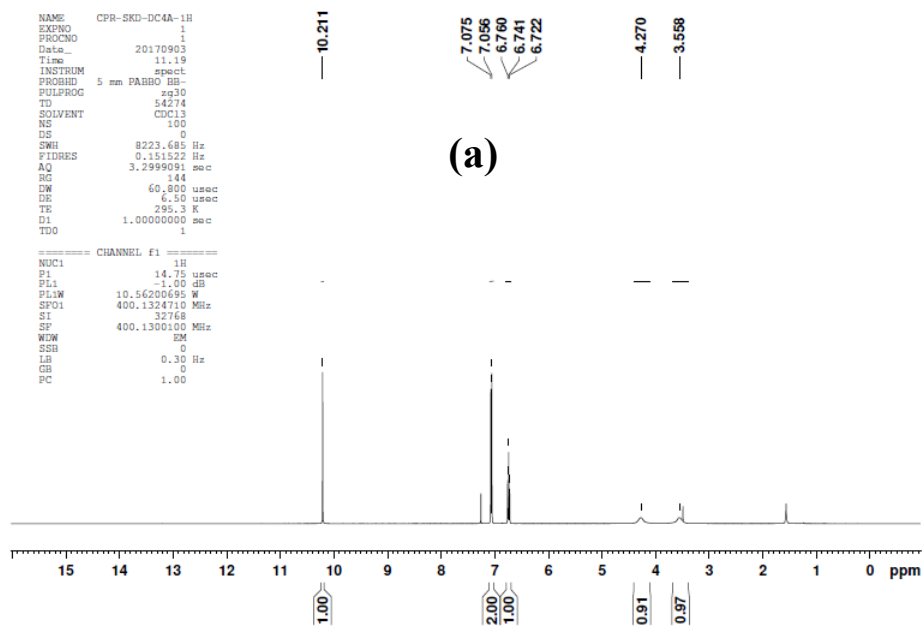
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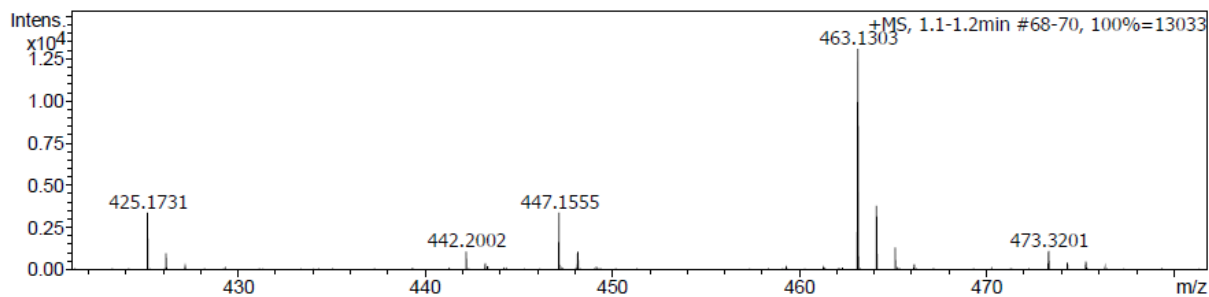
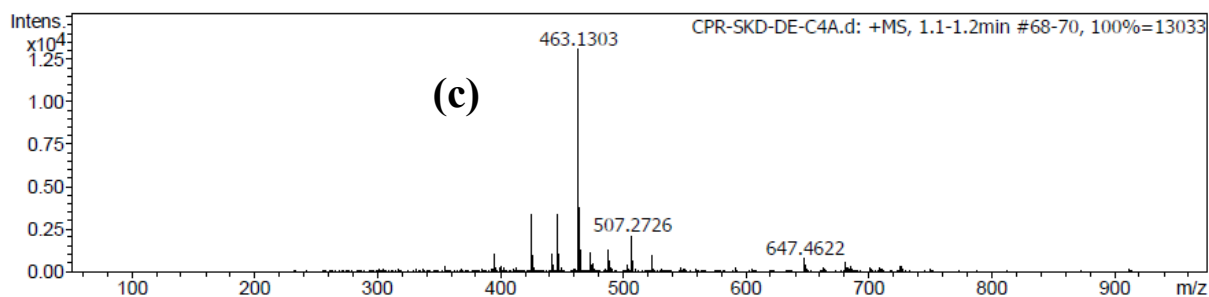
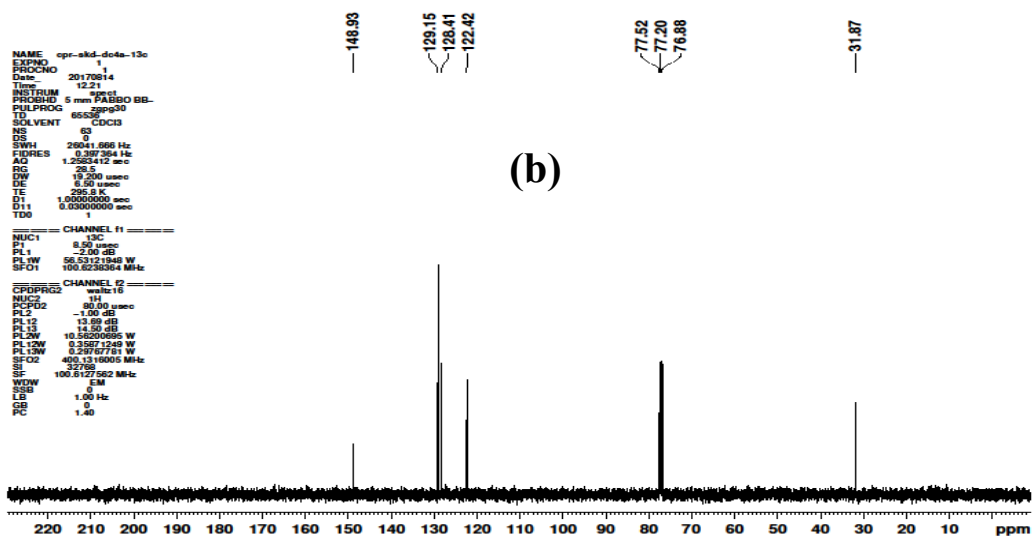
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S1. Characterization Data of P₂

The P₂ has been synthesized according to the literature reported procedure.¹[C. D. Gutsche, J. A. Levine, P. K. Sujeeth, Functionalized Calixarenes: The Claisen Rearrangement Route, *J. Org. Chem.* 1985, **50**, 5802– 5806] ¹H NMR (400 MHz, CDCl₃) δ(ppm): 10.2 (s, 4H), 7.06 (d, *J*= 7.6 Hz, 8H), 6.74 (t, *J* = 7.6 Hz, 4H), 4.27 (br s, 4H), 3.55 (br s, 4H); ¹³C NMR (100 MHz, CDCl₃) δ: 148.9, 129.1, 128.4, 122.4, 31.8; ESI-MS (HRMS): Chemical formula C₂₈H₂₄O₄, [M+K]⁺ calculated m/z at 463.1303, observed m/z at 463.1306.



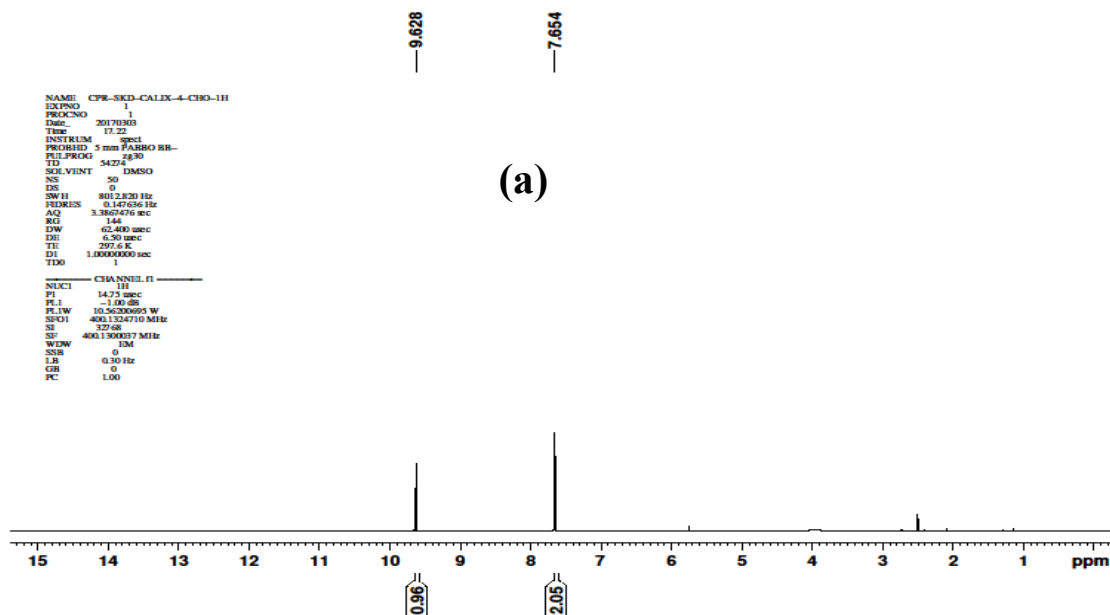


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e ⁻ Conf	N-Rule
463.1303	1	C28H24KO4	463.1306	0.6	14.6	1	100.00	16.5	even	ok

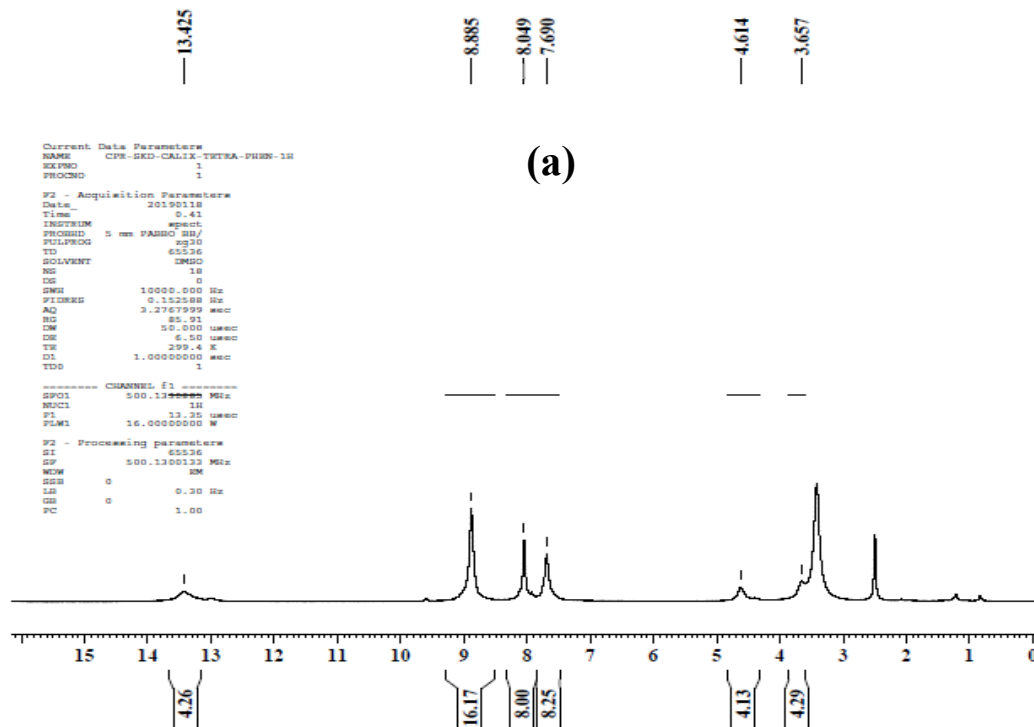
Fig. S1. Spectral data of **P₂**: (a) ¹H NMR in CDCl₃, (b) ¹³C NMR in CDCl₃ and (c) ESI-MS (HRMS)

S2. Characterization Data of P₃

The P₃ has been synthesized according to the literature reported procedure.² [K. Samanta, and C. P. Rao, A Bifunctional Thioether Linked Coumarin Appended Calix[4]arene Acquires Selectivity Toward Cu²⁺ Sensing on Going from Solution to SAM on Gold, *ACS Appl. Mater. Interfaces*, 2016, **8**, 3135] ¹H NMR (400 MHz, DMSO-d₆) δ(ppm): 9.6 (s, 4H), 7.65 (s, 8H); ¹³C NMR (100 MHz, DMSO-d₆) δ: 190.6, 160.5, 130.7, 129.7, 127.9 and 31.2; ESI-MS (HRMS): Chemical formula C₃₂H₂₄O₈ [M+H]⁺ calculated m/z at 537.1540, observed m/z at 537.1544.



S3. Characterization Data of L



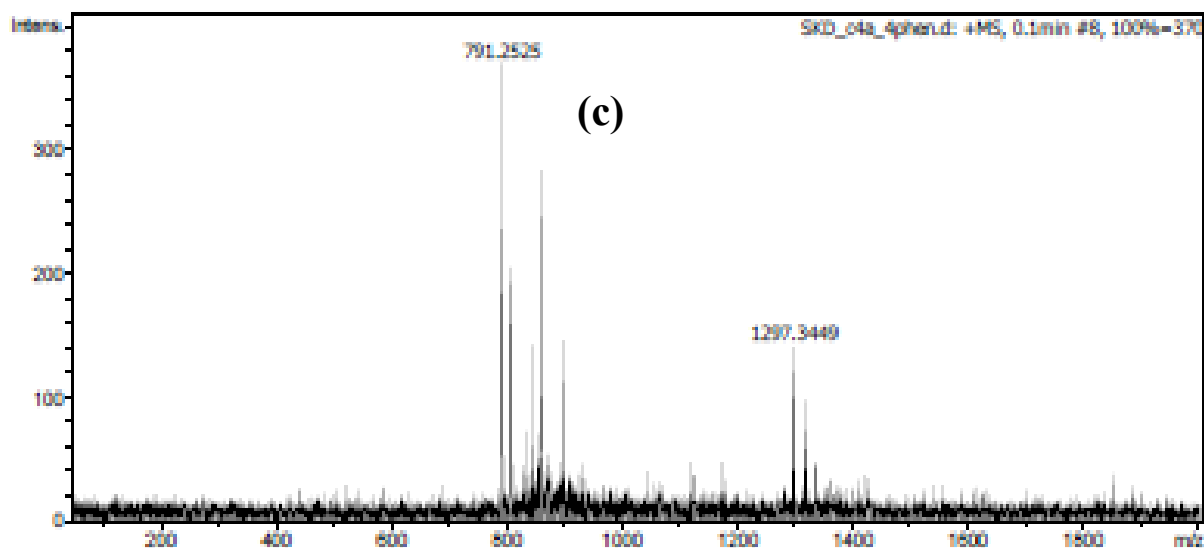
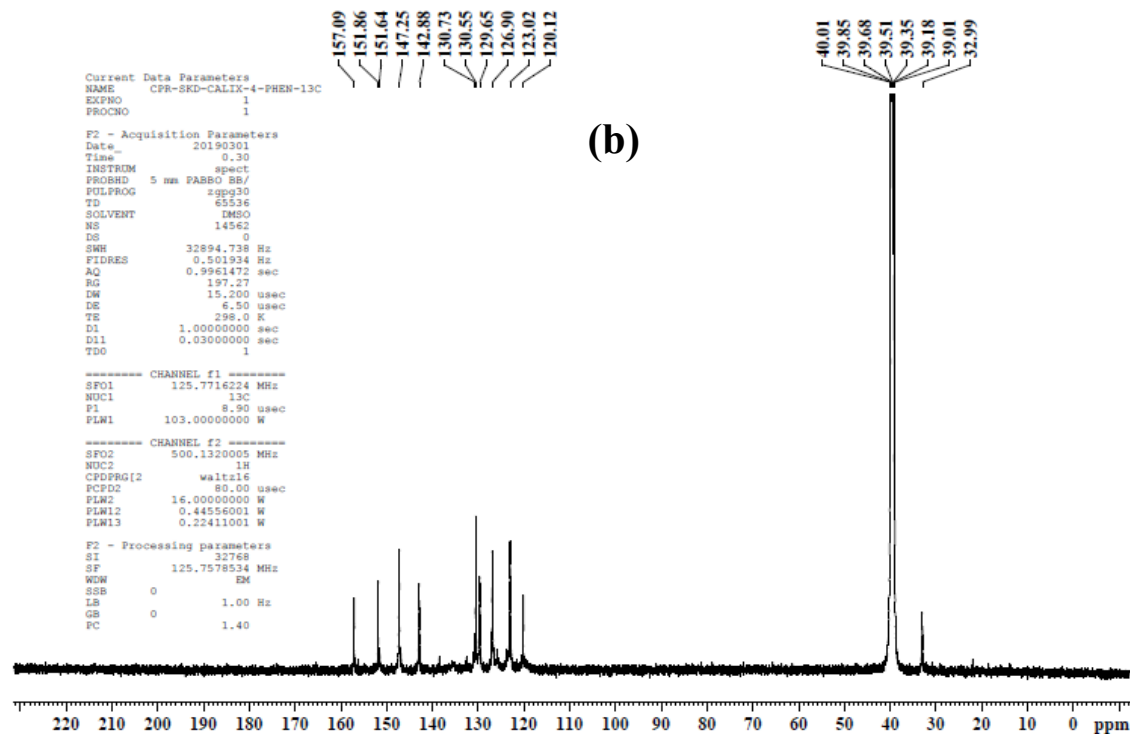


Fig. S3. Spectral data for **L** (a) ^1H NMR in DMSO-d_6 (500 MHz); (b) ^{13}C NMR in DMSO-d_6 (125 MHz) and (c) ESI-MS.

S4. UV-Visible spectra of peroxidase mimetic activity of L with different substrates

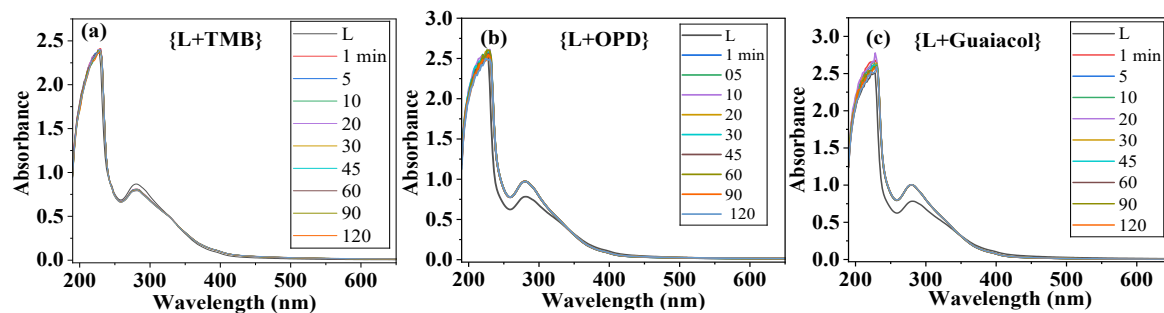


Fig. S4. UV-Visible spectra of peroxidase mimetic activity of (a) TMB, (b) OPD and (c) Guaiacol (0.2 mM) in the presence of H_2O_2 (2 mM) and L (0.1 g/ml) at different time intervals in PBS buffer (10 mM, pH 5.0).

S5. ESI-MS Spectrum of oxidized product of TMB

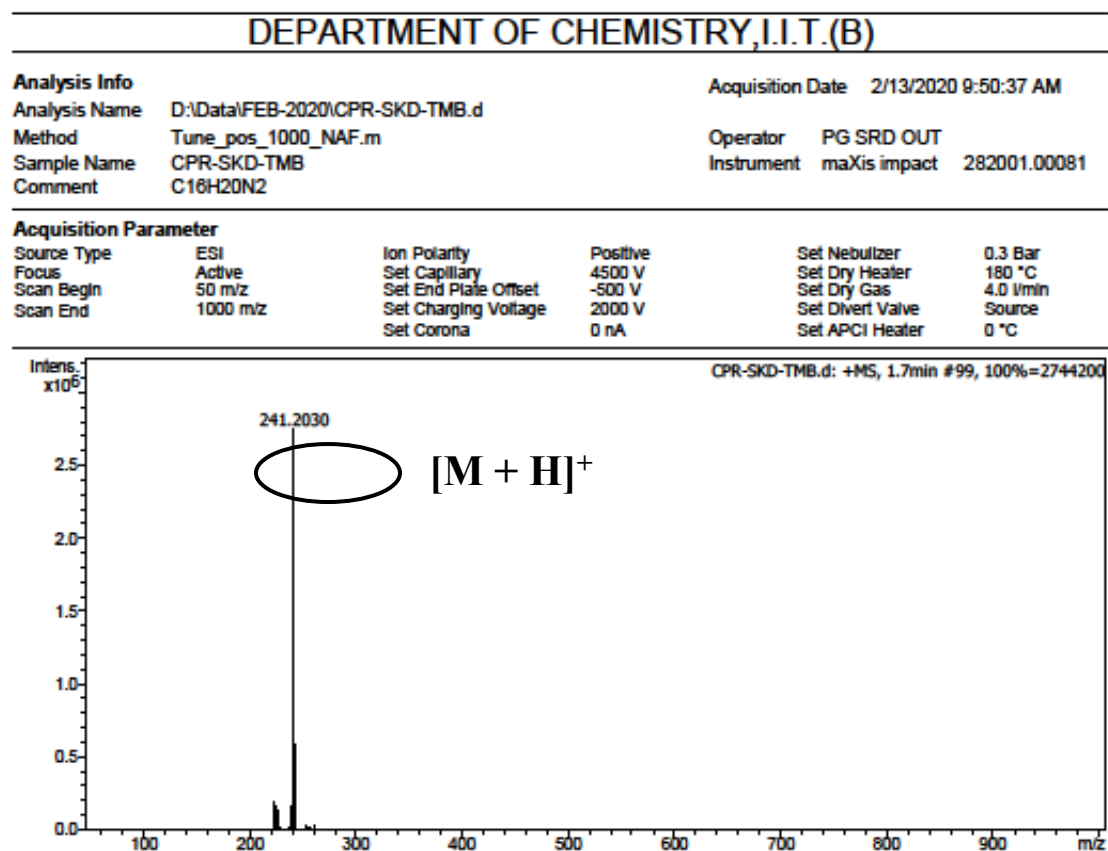


Fig. S5. ESI-MS Spectrum of oxidized product of TMB

S6. ESI-MS Spectrum of oxidized product of OPD

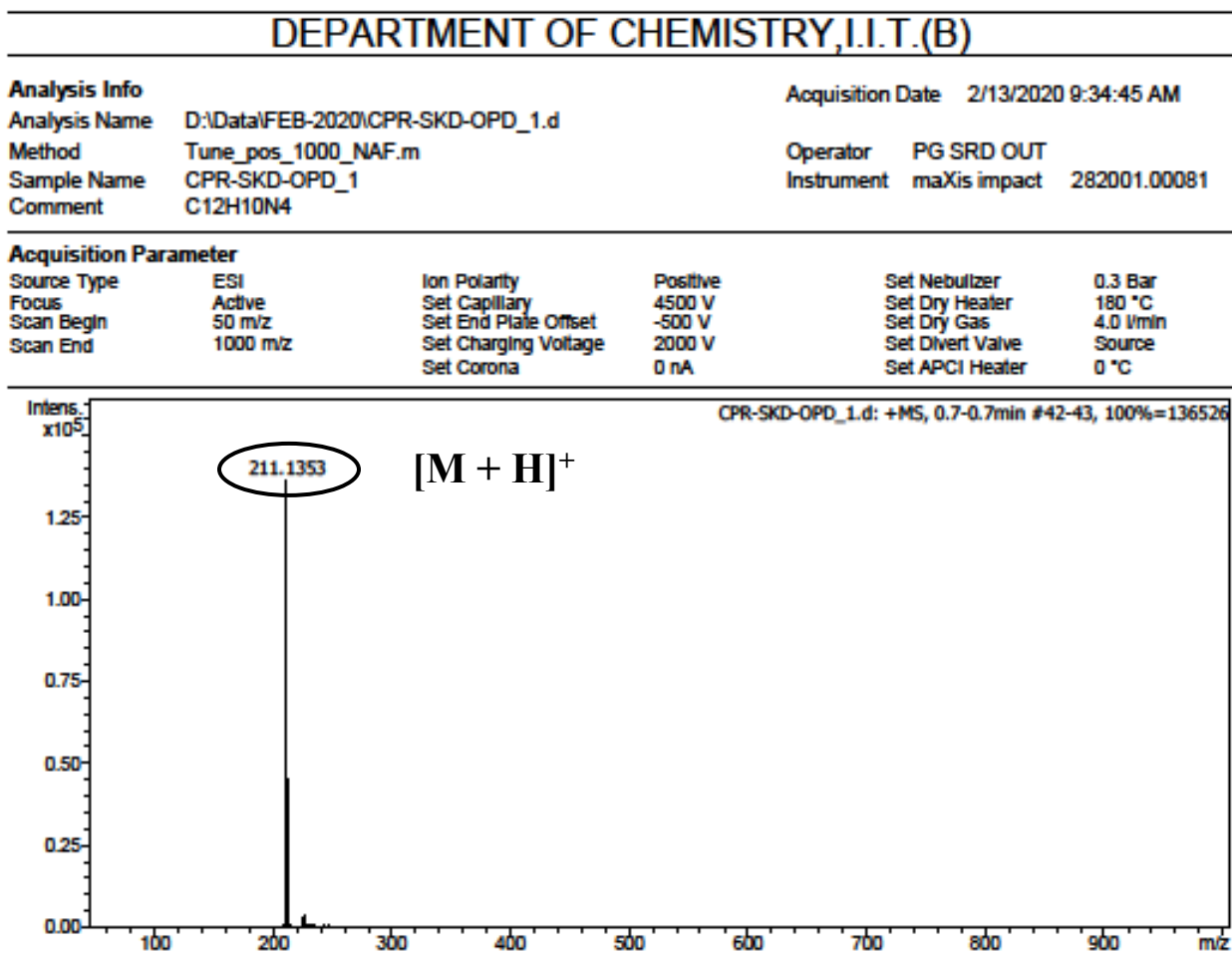


Fig. S6. ESI-MS Spectrum of oxidized product of OPD

S7. ESI-MS Spectrum of oxidized product of Guaiacol

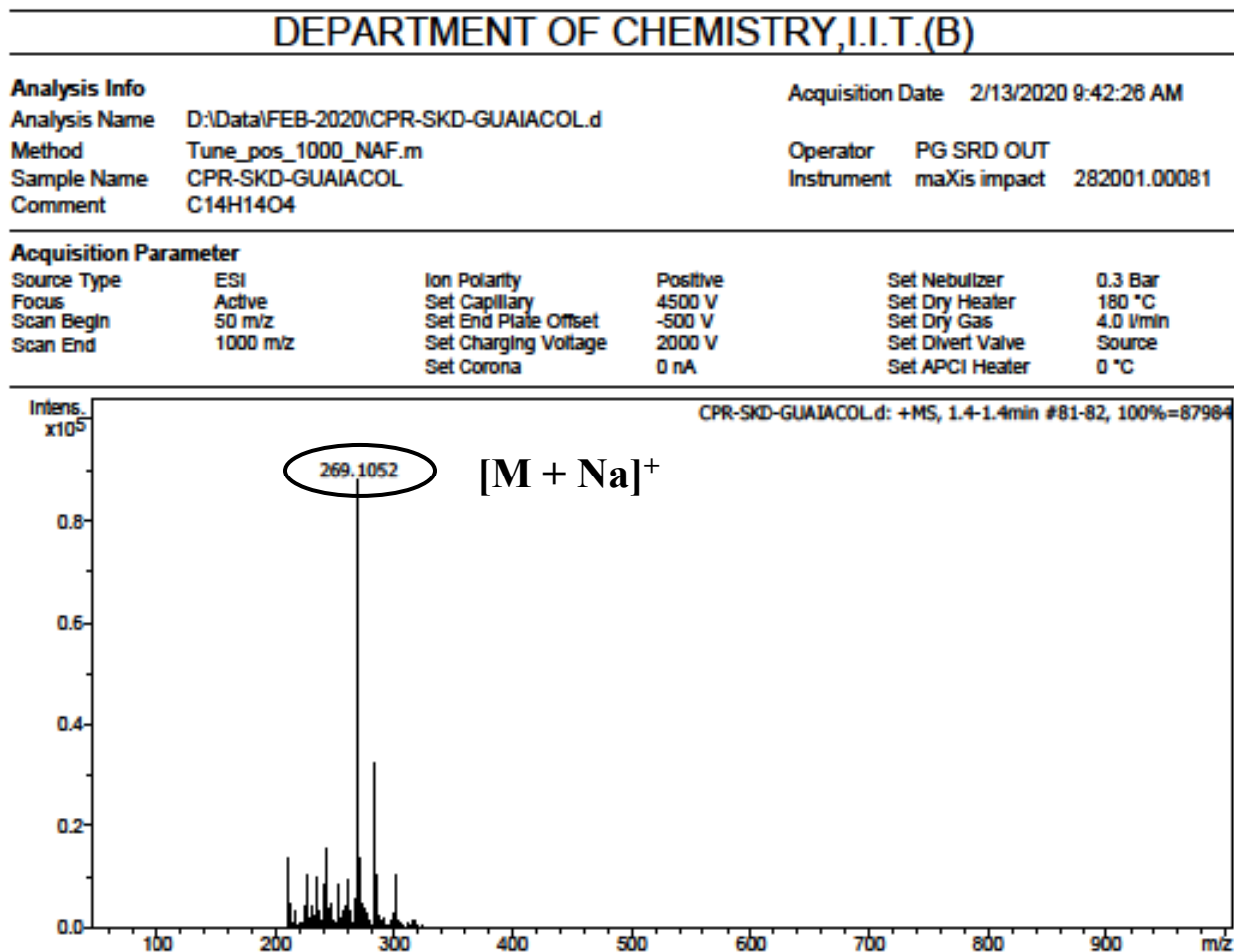


Fig. S7. ESI-MS Spectrum of oxidized product of guaiacol

S8. Table S1: Data pertinent to the literature reported copper phosphate nanoflower based peroxidase mimics

<i>Oxidation of 3,3,5,5-tetramethylbenzidine (TMB)</i>					
Sr. no	Composite hybrid	Size (μm)	Reaction conditions	Reaction time (min)	Reference
1	ChOx@HRP hybrid nanoflowers	20	PBS buffer, pH=7.4, 37°C	10	<i>J. Nanosci. Nanotechnol.</i> 2018, 18 , 6555–6561
2	AuNPs@PMo12 Nanohybrid	19.8	pH=3, 37°C	5	<i>RSC Adv.</i> , 2020, 10 , 35949–35956
3	GOx@Mn ₃ (PO ₄) ₂ hybrid	NA	20 mM KMnO ₄ & 1mM H ₂ O ₂ ,	30	<i>RSC Adv.</i> , 2019, 9 , 1889–1894
4	Calix[4]arene conjugate @CuPNF	8-12	PBS (10 mM, pH 5.0), 0.1mM H ₂ O ₂ , 37°C	10	Present study
<i>Oxidation of ortho-phenylenediamine (OPD)</i>					
5	Pyrenyl@CuPNF	93	H ₂ O ₂ =50 mM, PBS at pH=7.4, 37°C	30	<i>J. Mater. Chem. B</i> , 2021, 9 , 3523–3532
6	POM-Calix hybrid	40	100mM H ₂ O ₂ , 37°C	15	<i>Inorg. Chim. Acta</i> , 2018, 483 , 337–342
7	RuNPs		3mM H ₂ O ₂ , PBS=7.4, 37°C	35	<i>RSC Adv.</i> , 2017, 7 , 52210–52217
8	Calix[4]arene conjugate @CuPNF	8-12	PBS (10 mM, pH 5.0), 0.1mM H ₂ O ₂ , 37°C	25	Present study
<i>Oxidation of Guaiacol</i>					
9	LPO–Copper phosphate HNFs	15	22 mM H ₂ O ₂ , PBS (pH 4, 0.1 M KH ₂ PO ₄ , 25 °C)	60	<i>Int. J. Biol. Macromol.</i> , 2016, 84 , 402–409
10	HRP–Cu ²⁺ hybrid nanoflowers	10	22 mM H ₂ O ₂ , pH 6.8, 0.1 M KH ₂ PO ₄ , 25°C	45	<i>Dalton Trans.</i> , 2015, 44 , 13845–13852
11	Amino acid-copper hybrid nanoflowers	09	22 mM H ₂ O ₂ , PBS, pH 7, 35°C	130	<i>Chem Biodivers.</i> 2023, 20(8) , e202300743
12	Calix[4]arene conjugate @CuPNF	8-12 μm	PBS (10 mM, pH 5.0), 0.1mM H ₂ O ₂ , 37°C	50 min	Present study

S9. UV-Visible spectra of peroxidase mimetic activity of different substrates with copper precursors

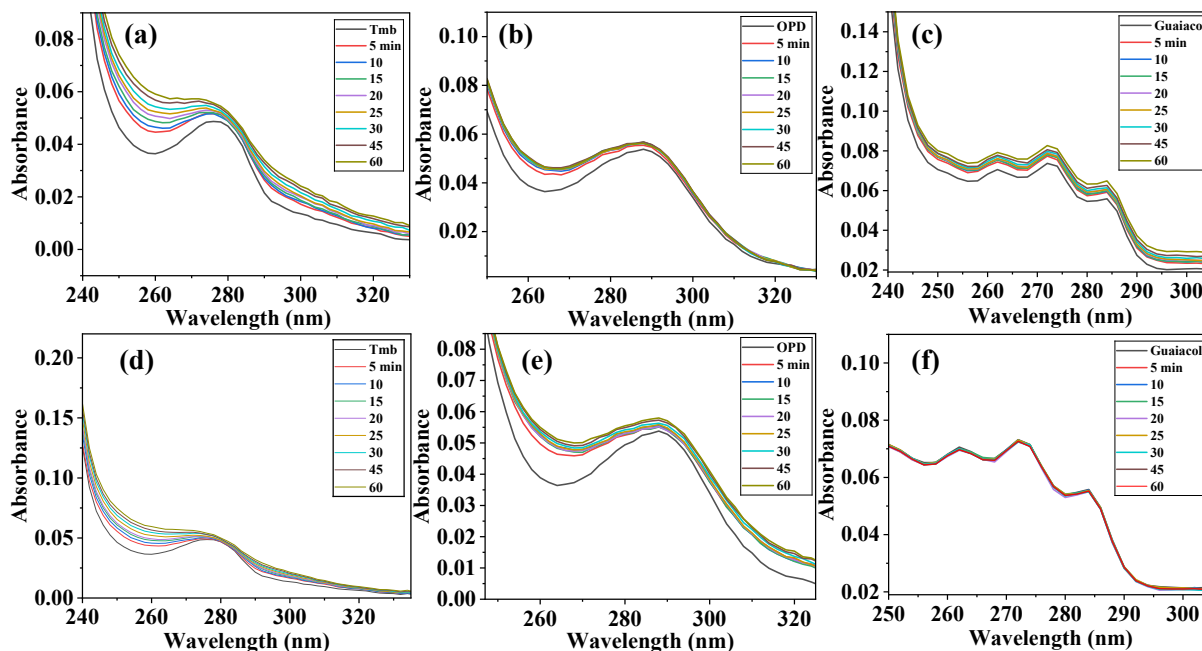


Fig. S9. UV-Visible spectra of peroxidase mimetic activity of (a) TMB, (b) OPD and (c) Guaiacol with CuSO_4 and (d) TMB (e) OPD and (f) Guaiacol with $\text{Cu}(\text{acac})_2$ in the presence of H_2O_2 at different time intervals in PBS buffer (10 mM, pH 5.0).