Amino-Functionalized Bimetallic MOF Nanozyme via Solvent-Assisted Ligand Exchange for Interference-Free Phenolic Detection

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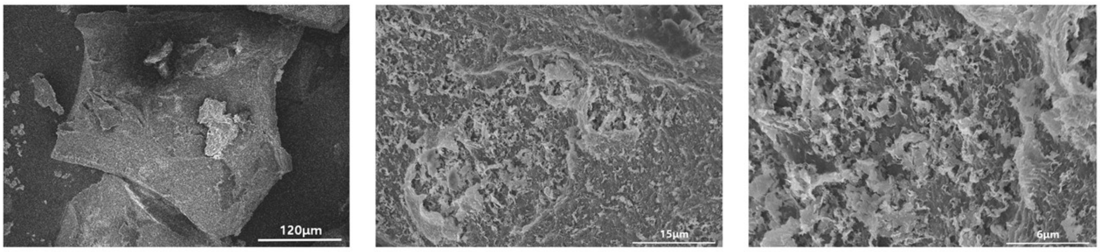

Fig. S1. SEM image of Cu-Mn-BDC-NH_2.

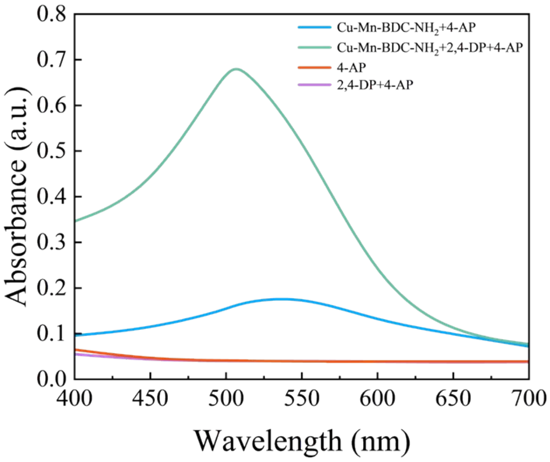

Fig. S2. Absorbance at 510 nm for different reaction systems.

Note: For comparison, a direct one-pot synthesis was performed. The procedure was identical to the synthesis of the Cu-Mn MOF precursor, except that the amino-functionalized ligand (NH_2-BDC) was directly added into the initial reaction mixture instead of the unfunctionalized BDC ligand, while the subsequent heating and washing procedures remained unchanged. As shown in Fig. S1, the resulting structure lacks a regular polyhedral morphology, indicating that the competitive coordination of amino groups interferes with crystal growth during the initial self-assembly. Furthermore, this direct-synthesized material exhibited autoxidation towards 4-AP even in the absence of the target analyte 2,4-DP (Fig. S2), demonstrating a loss of catalytic selectivity. These combined results support the use of the decoupled SALE strategy.

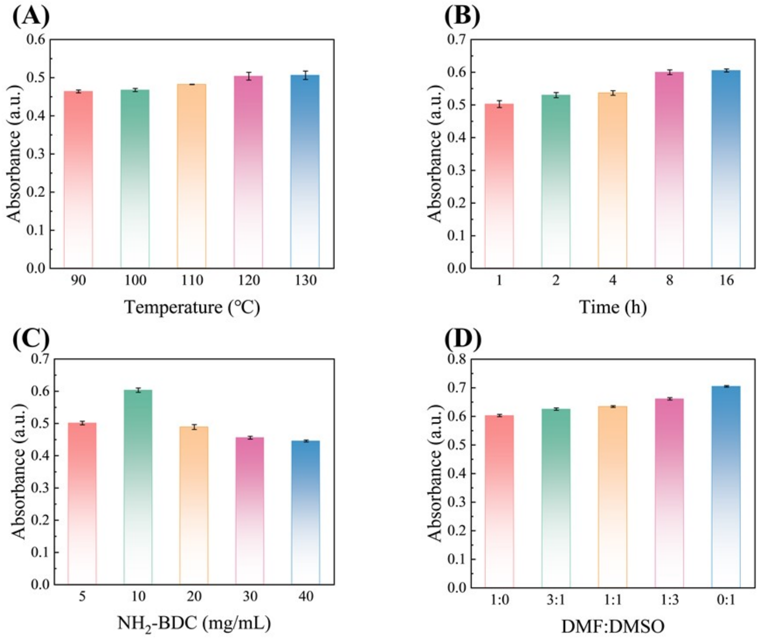

Fig. S3. Optimization of the preparation process of Cu-Mn NMOF.

Note: The solvent-assisted ligand exchange (SALE) parameters were optimized by evaluating the catalytic absorbance under various conditions (Fig. S3). The catalytic activity increased with temperature and time, reaching a plateau at 120 ℃ (Fig. S3A) and 8 h (Fig. S3B). For ligand concentration, 10 mg/mL NH_2-BDC yielded the highest activity (Fig. S3C); higher concentrations might cause pore blockage. Lastly, pure DMSO was found to be the most effective solvent (Fig. S3D). Therefore, the optimal SALE conditions were determined as: 120 ℃, 8 h, 10 mg/mL NH_2-BDC, and pure DMSO.

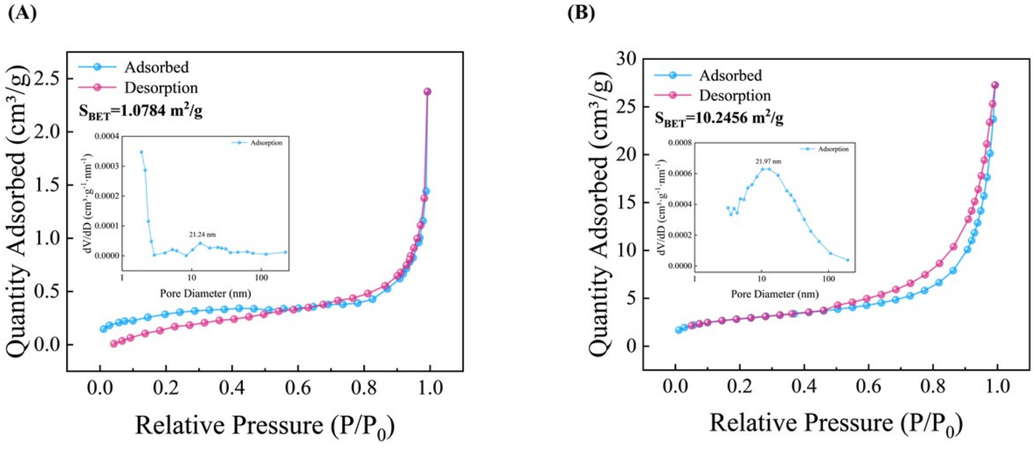

Fig. S4. Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curve of (A)Cu-Mn MOF and (B)Cu-Mn NMOF.

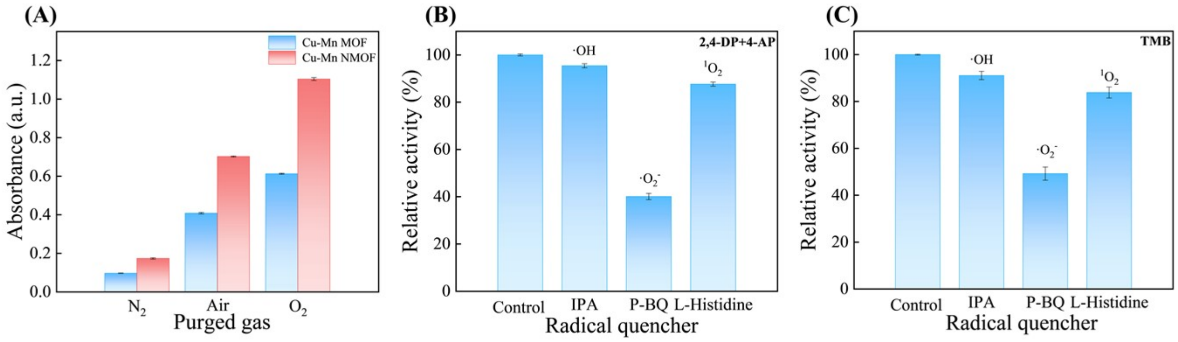

Fig. S5. (A) Catalytic activity under different gas atmospheres. Effects of radical scavengers on the (B) 2,4-DP/4-AP and (C) TMB systems.

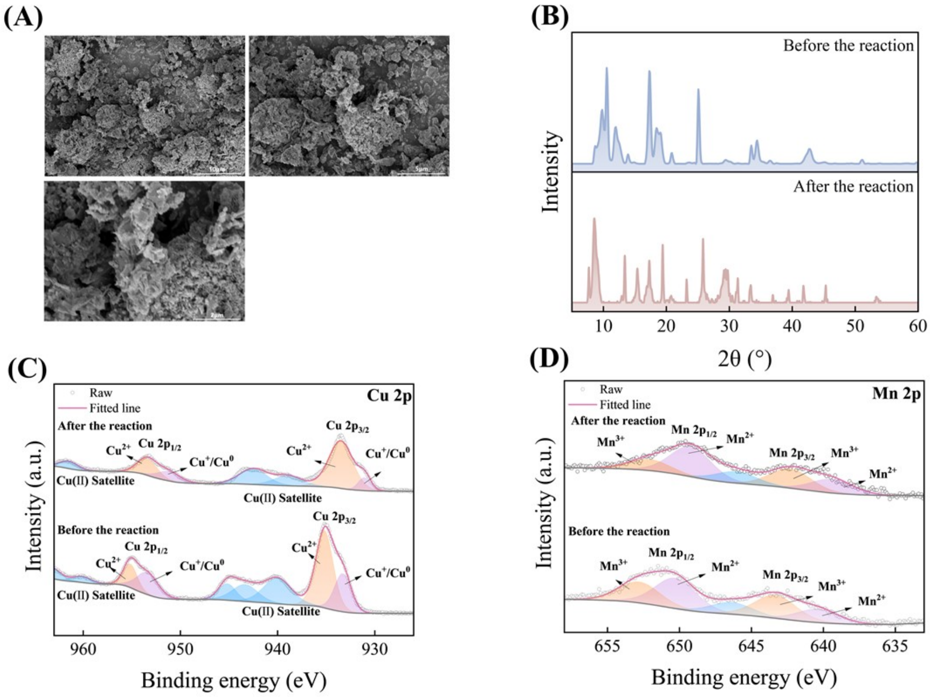

Fig. S6. (A) SEM images of the Cu-Mn NMOF after the catalytic reaction; (B) XRD patterns and high-resolution XPS spectra of (C) Cu 2p and (D) Mn 2p for the Cu-Mn NMOF before and after the reaction.

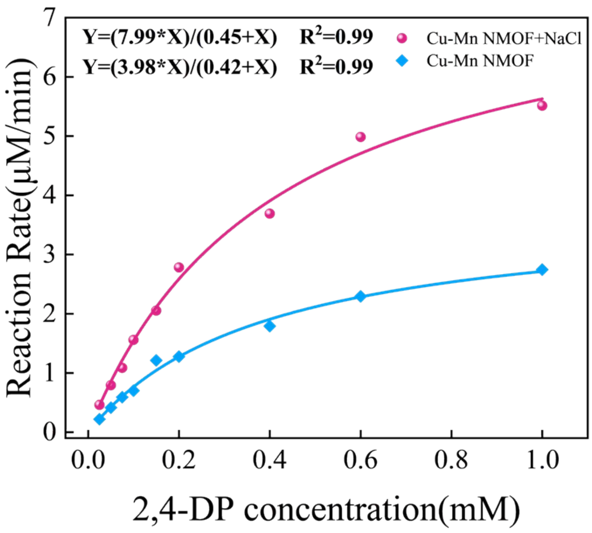

Fig. S7. Steady-state kinetic assays of the Cu-Mn NMOF for the oxidation of 2,4-DP in the absence and presence of 400 mM NaCl.

Note: As shown in Fig. S7, upon the addition of 400 mM NaCl, the maximum reaction velocity (V_{max}) increased from 3.98 μM/min to 7.99 μM/min, whereas the Michaelis constant (K_m) remained essentially unchanged (0.42 mM vs. 0.45 mM). The near-constant K_m indicates that the high concentration of electrolytes does not induce competitive binding at the active sites nor disrupt the substrate-catalyst affinity. The two-fold increase in V_{max} can be attributed to the primary kinetic salt effect and the compression of the electrical double layer at the solid-liquid interface. These physicochemical effects lower the activation energy barrier for the rate-determining electron-transfer step, thereby accelerating the catalytic turnover without altering the binding behavior.

Table S1

Surface elemental composition of Cu-Mn MOF and Cu-Mn NMOF determined by XPS analysis.

Sample	C (at%)	O (at%)	N (at%)	Cu (at%)	Mn (at%)
Cu-Mn MOF	63.16	26.43	4.28	4.47	1.66
Cu-Mn NMOF	61.67	26.71	5.51	4.45	1.67

Note: The surface ligand exchange efficiency was semi-quantitatively estimated based on the XPS elemental composition, utilizing the total metal content (Cu and Mn) as an internal reference. For a straightforward estimation, we assume an average simplified stoichiometric ratio of 1:1 between the organic ligands and the metal centers on the MOF surface. The calculation formula is simplified as:

$Exchange\ Efficiency = \Delta N / M_{total} \times 100\%$

Where ΔN represents the net increase in the nitrogen atomic percentage after the SALE process (5.51% - 4.28% = 1.23%), corresponding to the newly incorporated NH_2-BDC ligands (containing one N atom per molecule). M_{total} is the total atomic percentage of the metal centers determined by XPS (Cu + Mn = 4.45% + 1.67% = 6.12%). This estimated efficiency of ~20.1% suggests a successful and moderate partial ligand exchange, which introduces catalytic primary amine sites while maintaining the structural stability of the framework.

Table S2

Analytical precision, repeatability, and reproducibility profiles of the Cu-Mn NMOF for different phenolic substrates.

Substrates	Intra-day repeatability(n = 5)		Inter-day precision(n = 3 days)		Batch-to-batch reproducibility(n = 4 batches)	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
2,4-DP	99.08	3.16	98.35	4.82	103.82	7.65
Phenol	101.45	2.64	100.73	4.08	95.41	8.33
Catechol	98.14	3.43	97.48	5.17	93.86	8.12

Table S3

Analytical results for the determination of phenolic pollutants in real water samples using the proposed colorimetric method and standard HPLC method (n=3).

Samples		Spiked (μM)	Proposed method			HPLC method		RE (%)
			Found (μM)	Recovery (%)	RSD (%)	Found (μM)	RSD (%)	
Lake water	2,4-DP	20	18.46	92.30	4.85	-	-	-
		60	57.34	95.57	4.01	-	-	-
		80	81.63	102.04	3.37	77.13	2.47	5.83
	Phenol	20	21.85	109.25	4.04	-	-	-
		60	65.17	108.62	5.01	61.51	3.89	5.95
		80	77.37	96.71	4.76	-	-	-
	Catechol	20	22.75	113.75	6.82	21.39	4.61	6.36
		60	55.21	92.02	4.16	-	-	-
		80	75.43	94.29	3.82	-	-	-
Tap water	2,4-DP	20	18.84	94.20	3.67	-	-	-
		60	61.71	102.85	3.24	-	-	-
		80	76.48	95.60	4.13	78.67	3.95	2.78
	Phenol	20	18.77	93.85	3.33	-	-	-
		60	64.12	106.87	2.95	61.95	2.45	3.50
		80	78.38	97.98	2.67	-	-	-
	Catechol	20	18.41	92.05	4.11	19.23	2.36	4.26
		60	57.66	96.10	3.41	-	-	-
		80	77.85	97.31	3.14	-	-	-