

Supplementary Materials

A 3D ordered hierarchical crystalline porous organic salt for large-sized enzyme immobilization

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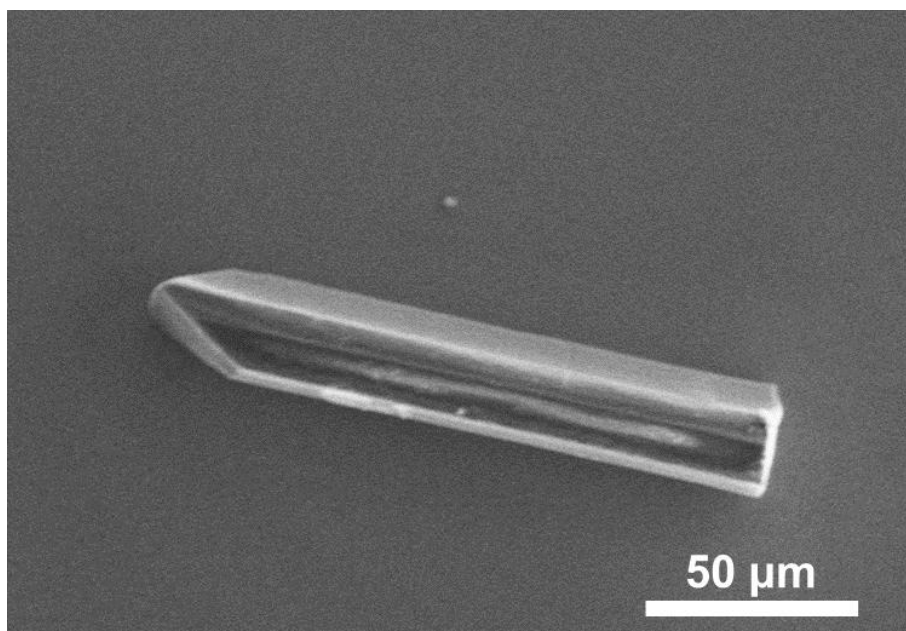
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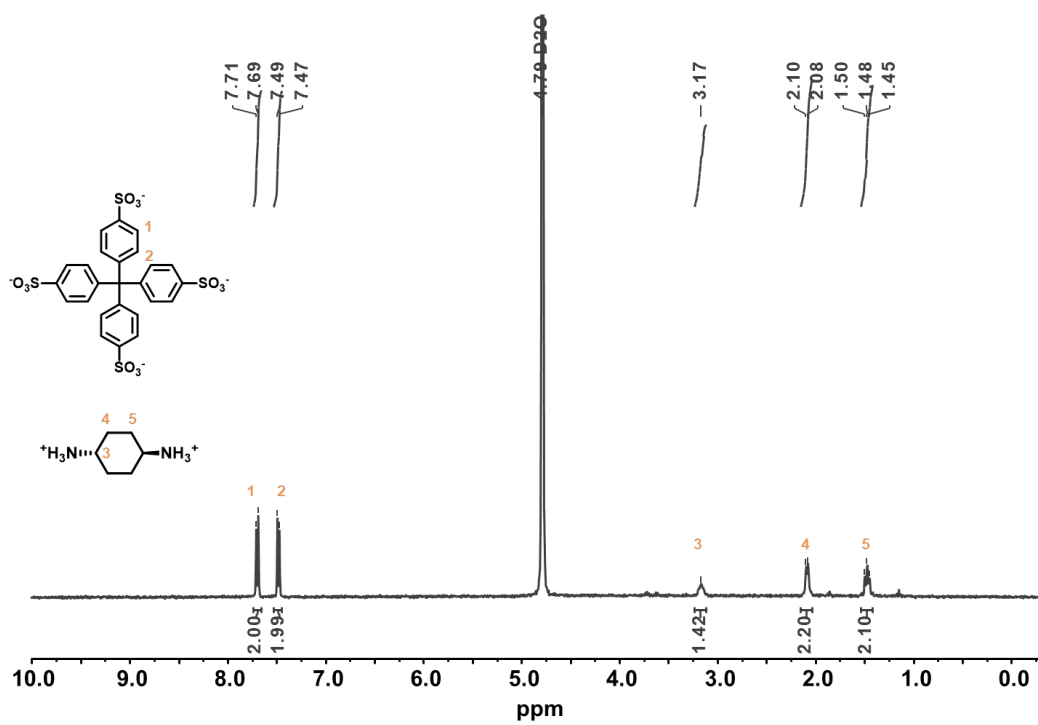
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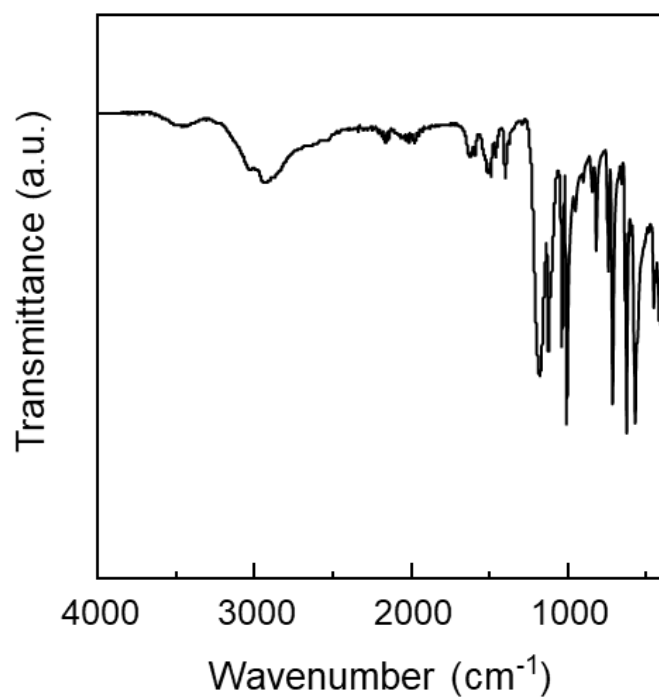
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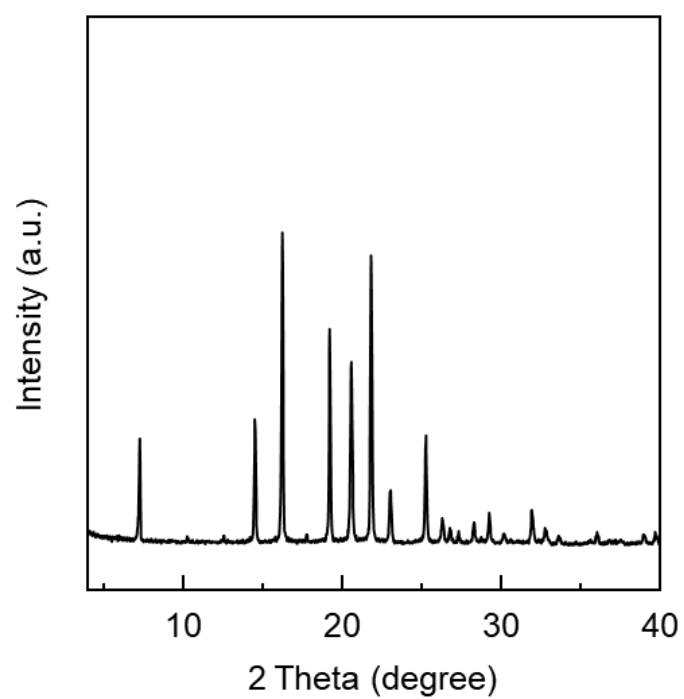
Supplementary Figure 1. SEM image of CPOS-1-Cryst.



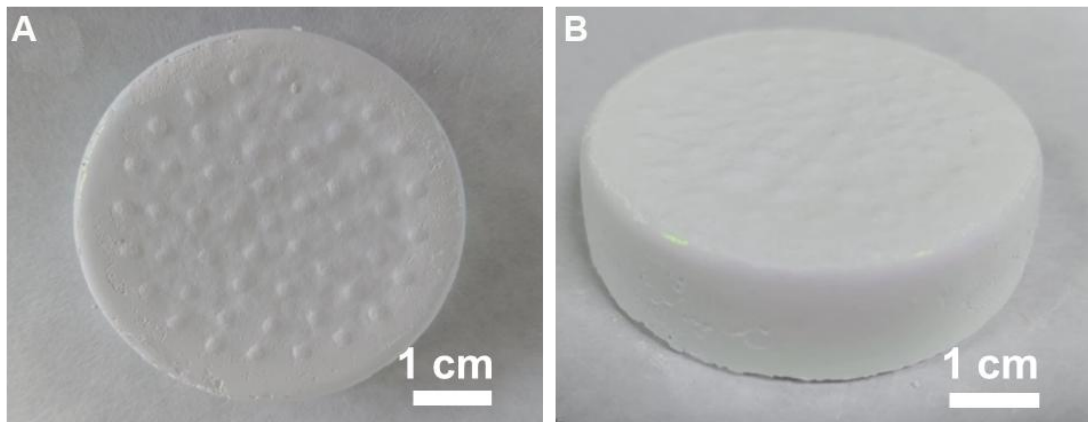
Supplementary Figure 2. ^1H NMR spectrum of CPOS-1-Cryst.



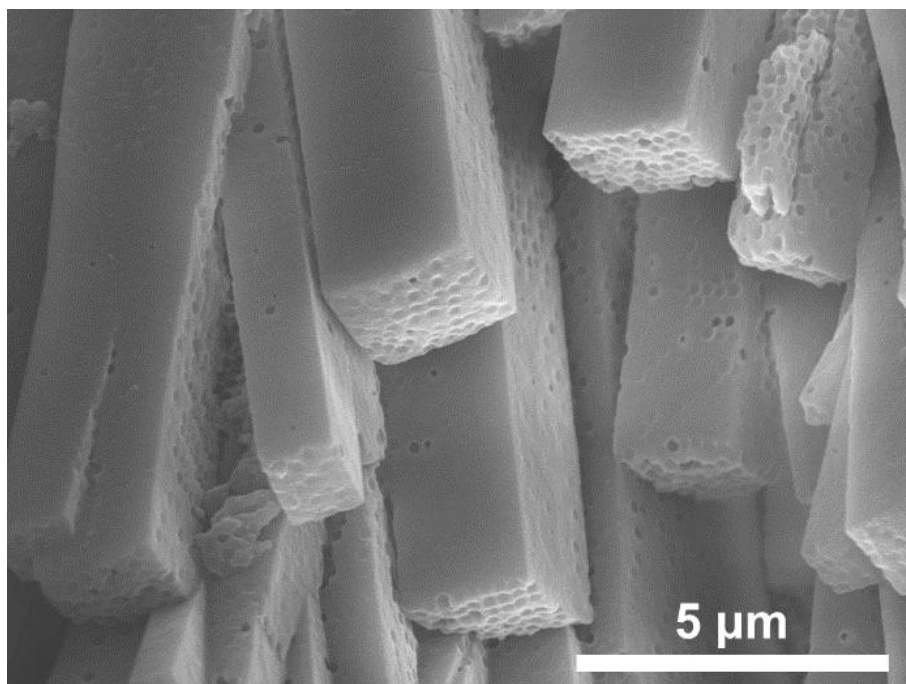
Supplementary Figure 3. FT-IR spectrum of CPOS-1-Cryst.



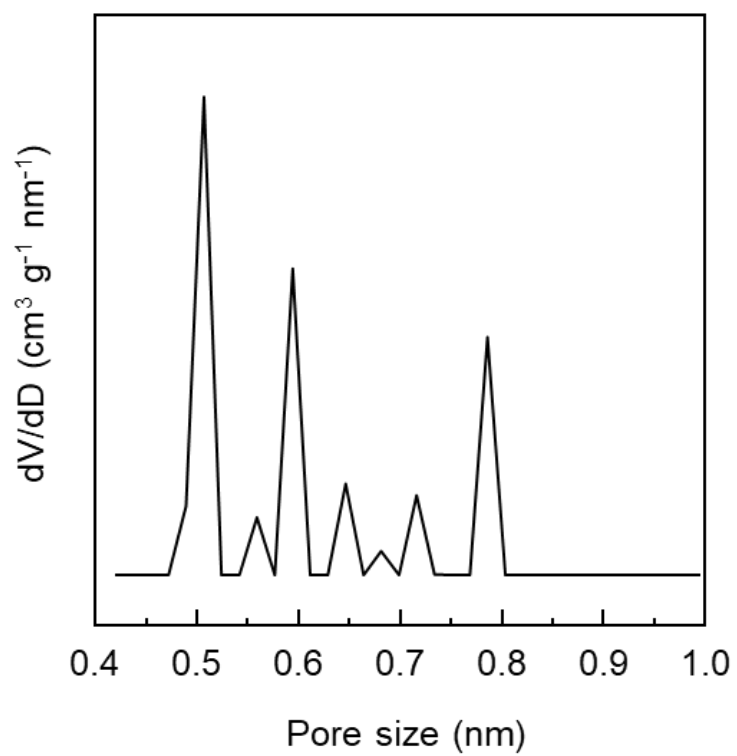
Supplementary Figure 4. PXRD pattern of CPOS-1-Cryst.



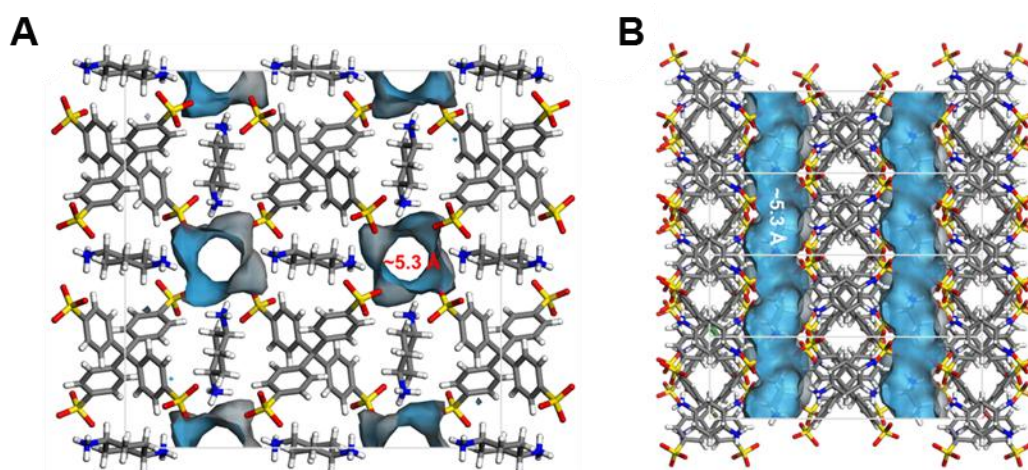
Supplementary Figure 5. Photographs of 3D ordered PS colloidal crystal template.



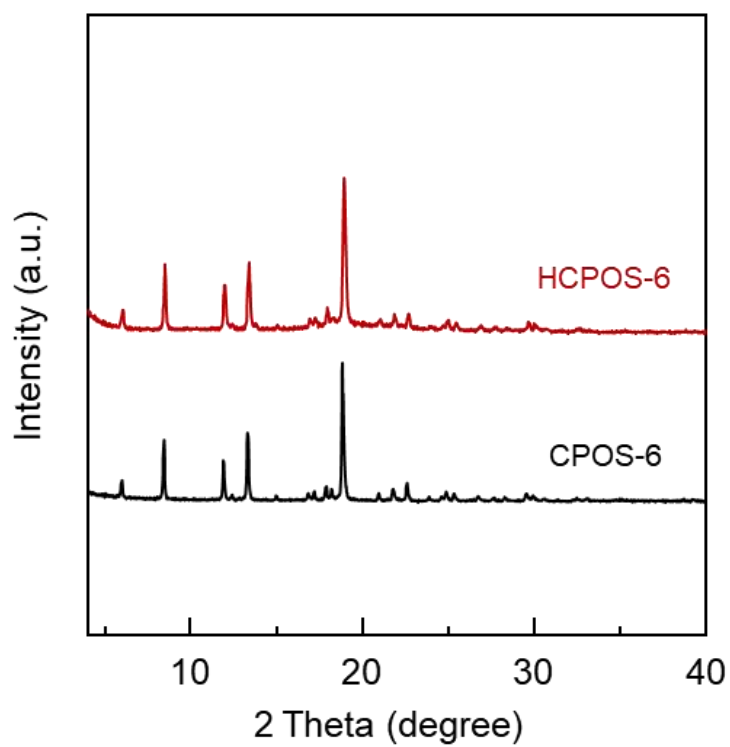
Supplementary Figure 6. SEM image of CPOS-1 with discrete macropore on the surface.



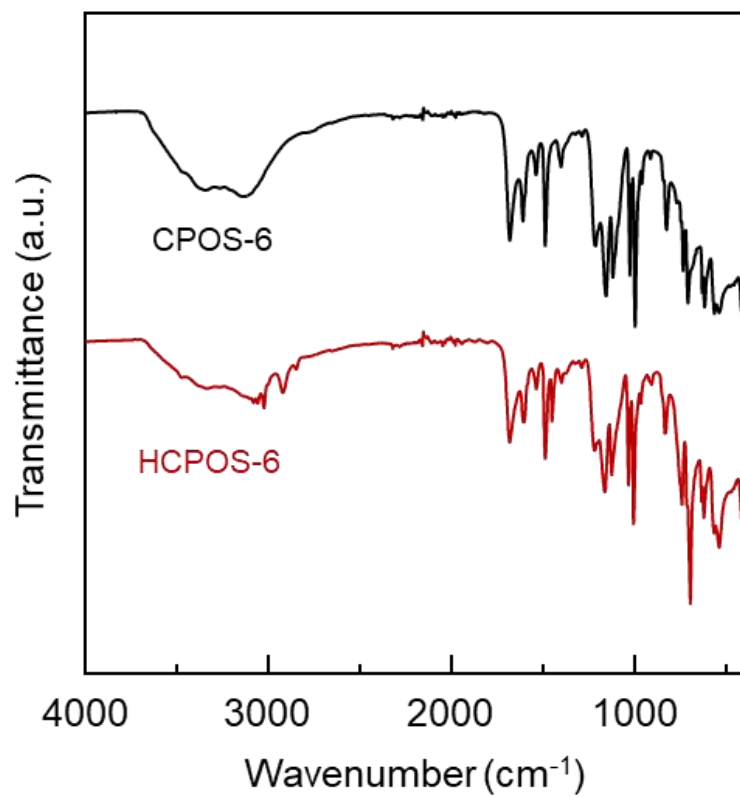
Supplementary Figure 7. Pore size distribution of HCPOS-1.



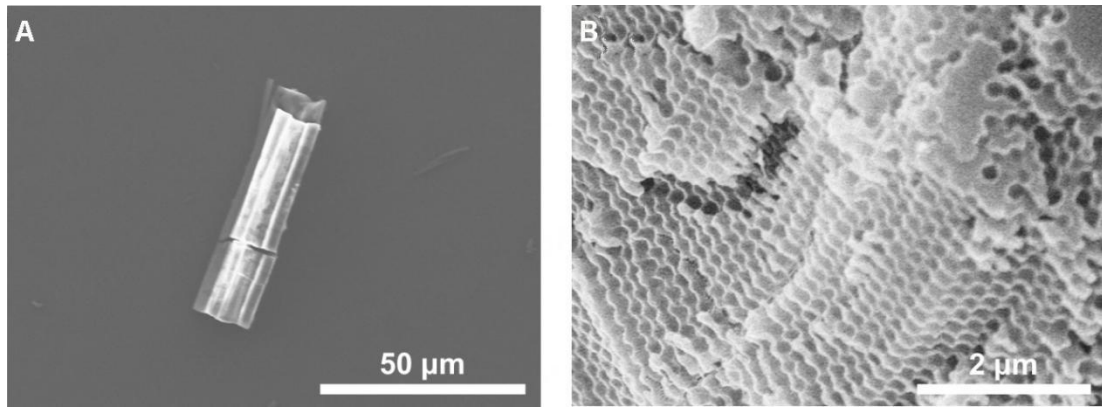
Supplementary Figure 8. (A) The top view and (B) the side view of CPOS-1 structure.



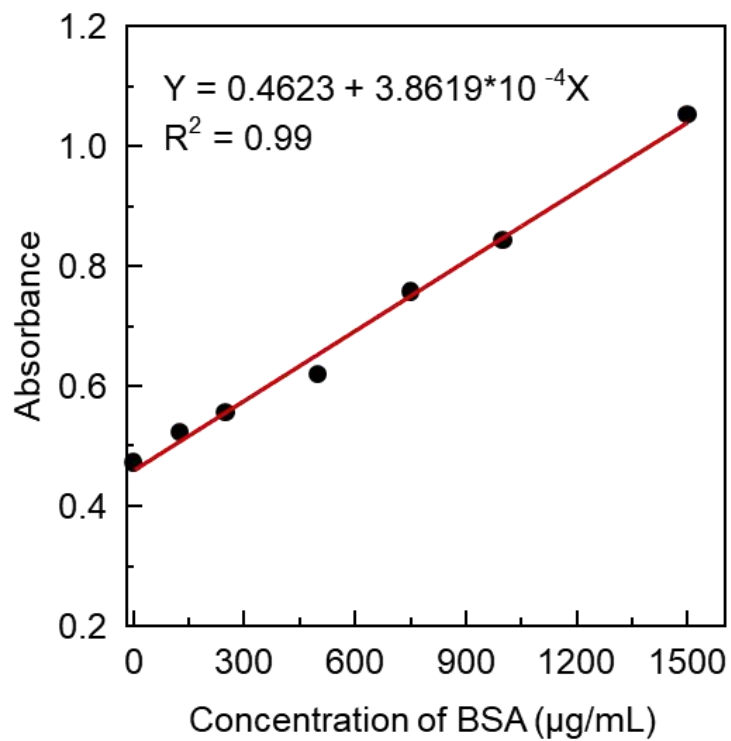
Supplementary Figure 9. PXRD patterns of CPOS-6 and HCPOS-6.



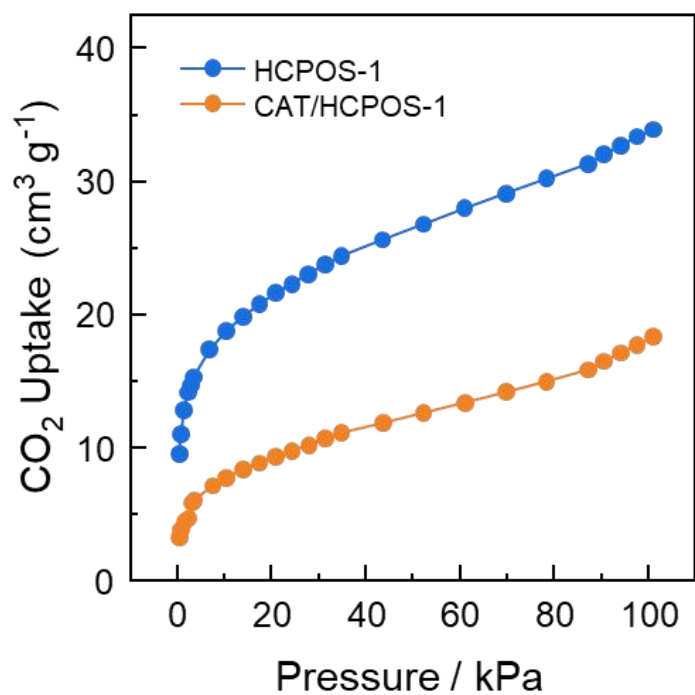
Supplementary Figure 10. IR spectra of CPOS-6 and HCPOS-6.



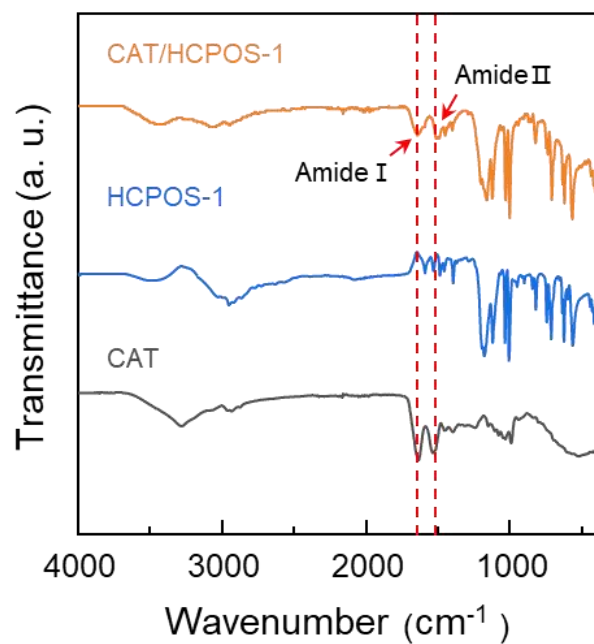
Supplementary Figure 11. SEM images of (A) CPOS-6 and (B) HCPOS-6.



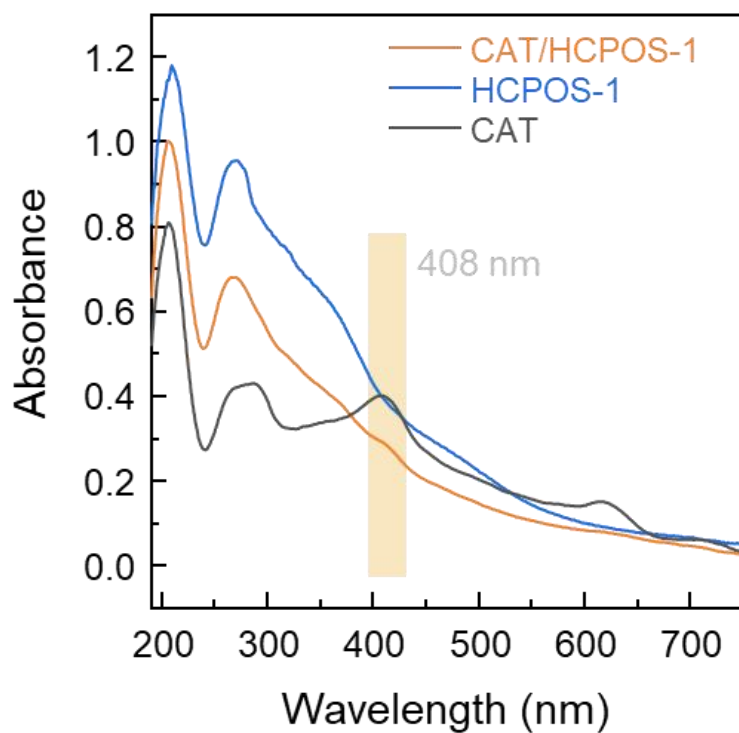
Supplementary Figure 12. The calibration curve of BSA concentration based on Bradford assay.



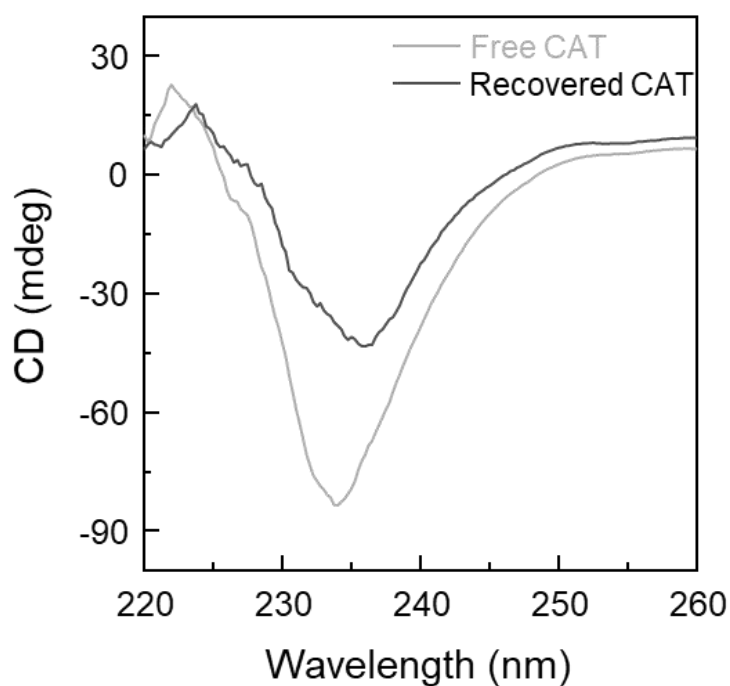
Supplementary Figure 13. CO₂ sorption isotherms of CAT/HCPOS-1 and HCPOS-1 at 273 K.



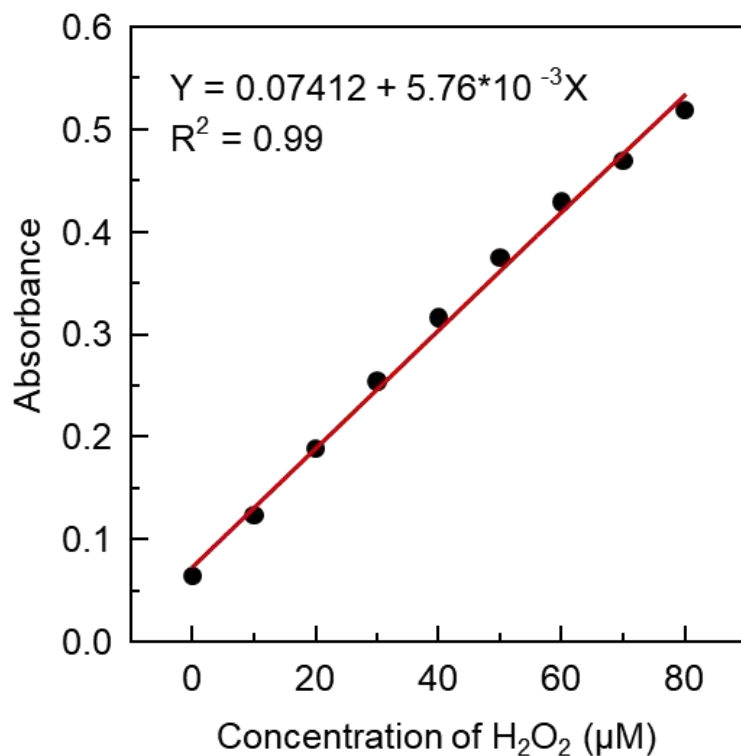
Supplementary Figure 14. FT-IR spectra of CAT/HCPOS-1, HCPOS-1 and CAT.



Supplementary Figure 15. Solid-state UV-Visible spectra of CAT/HCPOS-1, HCPOS-1 and CAT.

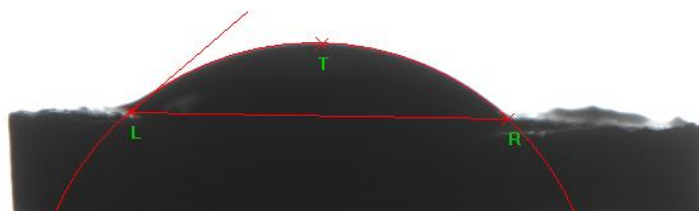


Supplementary Figure 16. CD spectra of free CAT and recovered CAT from CAT@HCPOS-1. Directly putting CAT@HCPOS-1 into PBS buffer (pH = 7.4, 3 mM) to get recovered CAT.

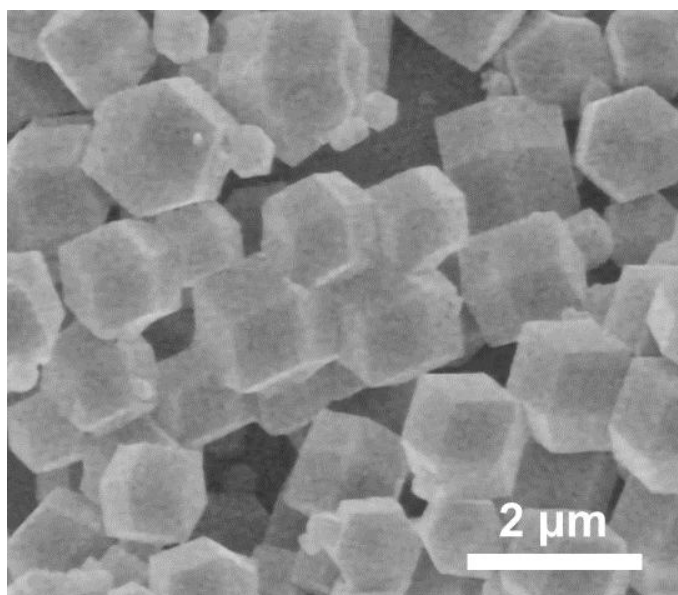


Supplementary Figure 17. The calibration curve of H₂O₂ concentration based on FOX (Ferrous Oxidation in Xylenol orange) assay. Briefly, H₂O₂ standard solutions (50 µL) at various concentrations were mixed with the FOX reagent (composed of 250 µM ammonium ferrous sulfate, 100 µM xylenol orange, and 100 mM sorbitol in 25 mM H₂SO₄; 950 µL) and incubated for 30 min at room temperature before reading absorbance at 560 nm.

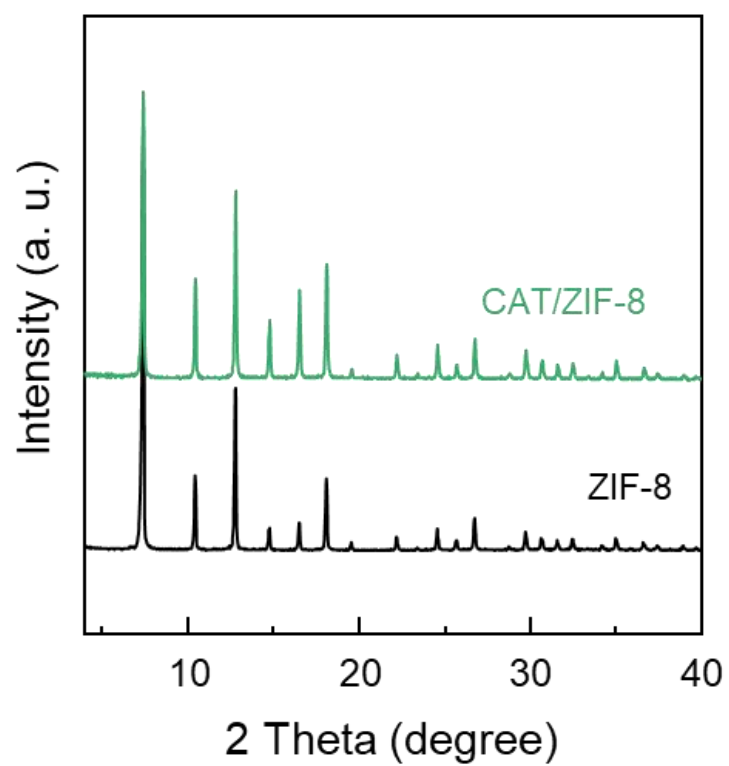
CA = 41.698



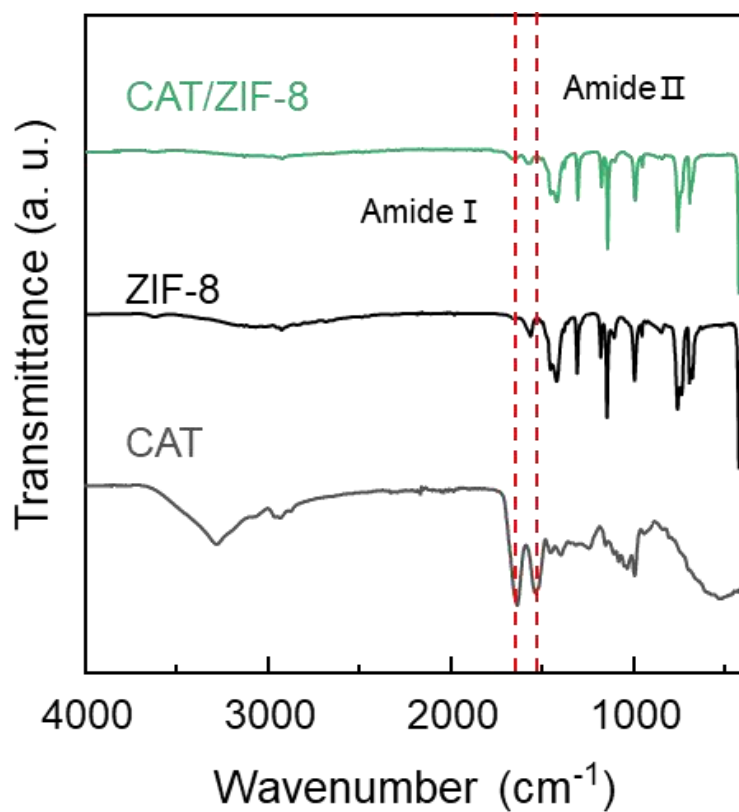
Supplementary Figure 18. Water contact angle of HCPOS-1.



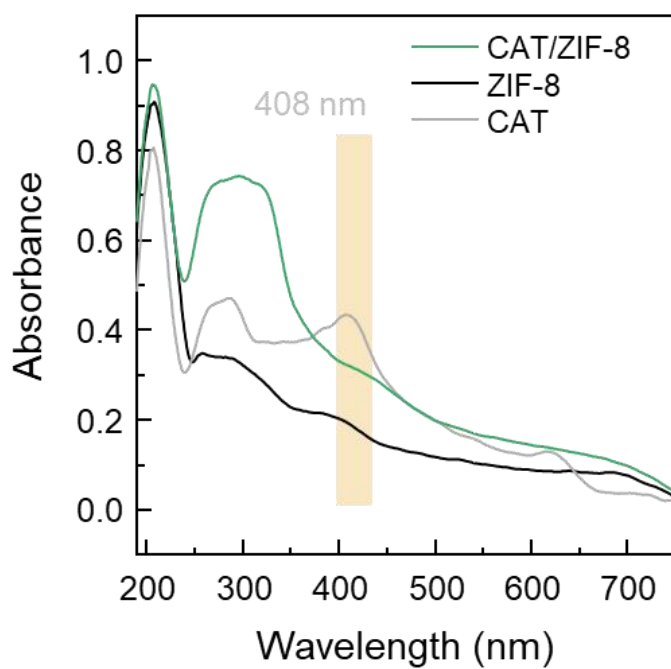
Supplementary Figure 19. SEM image of ZIF-8.



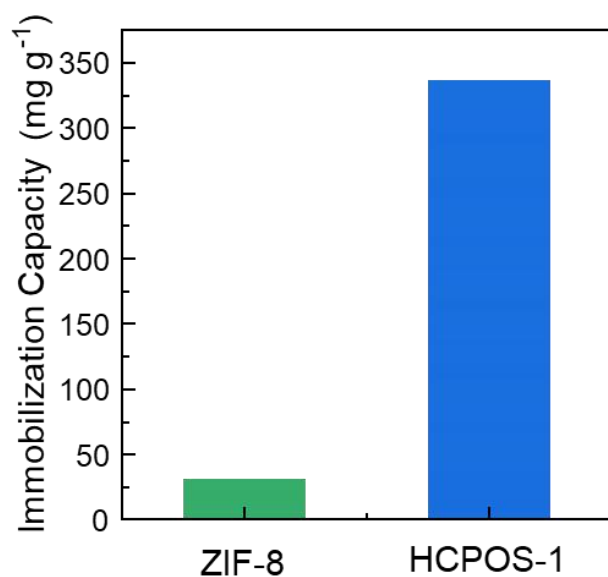
Supplementary Figure 20. PXRD patterns of CAT/ZIF-8 and ZIF-8.



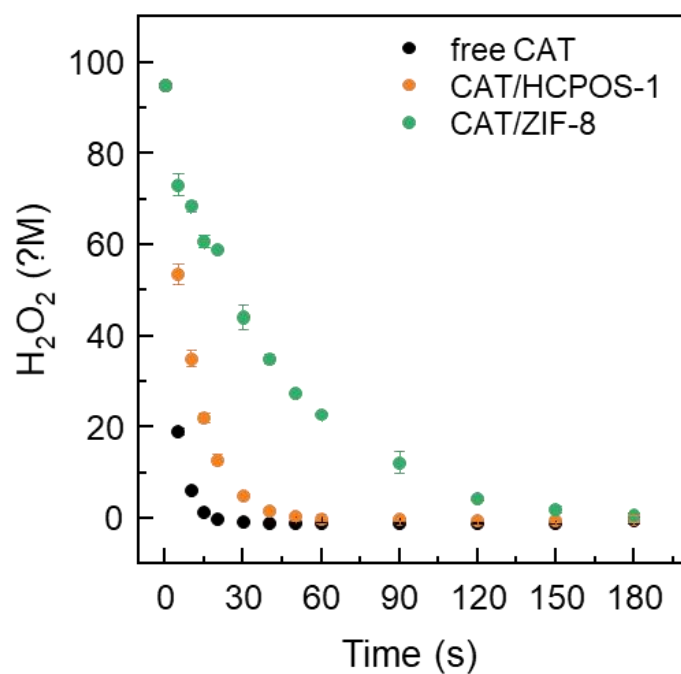
Supplementary Figure 21. FT-IR spectra of CAT/ZIF-8, ZIF-8 and CAT.



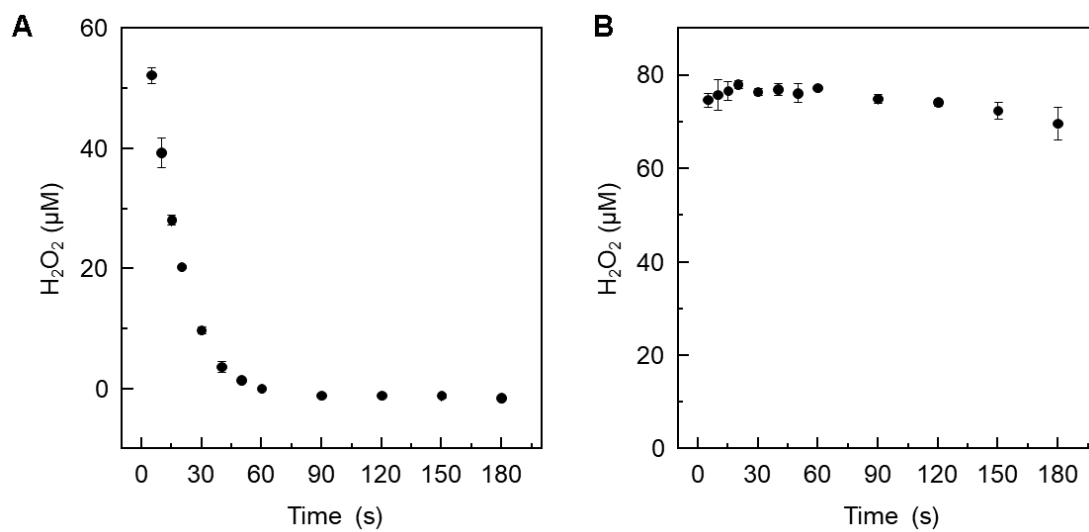
Supplementary Figure 22. Solid-state UV-visible spectra of CAT/ZIF-8, ZIF-8 and CAT.



Supplementary Figure 23. The enzyme immobilization capacities of ZIF-8 and HCPOS-1.



Supplementary Figure 24. Catalytic performance of CAT/HCPOS-1 and CAT/ZIF-8. The assay was performed in Tris-HCl buffer (pH 8, 50 mM) with H₂O₂ (0.095 mM) and encapsulated CAT that determined by Bradford assay (50 µg).



Supplementary Figure 25. The catalytic stability of CAT/HCPOS-1. (A) first cycle and (B) second cycle.

Supplementary Table 1. Comparison of immobilization capacity of HCPOS-1 with reported porous organic frameworks

Enzyme	Materials	Immobilization method	Immobilization capacity (mg g ⁻¹)	Ref.
CAT	mNMZIF-8	Covalent binding and cross-linking	1000.0	[1]
GOx	MOF-545(Fe)	Pore encapsulation	296.0	[2]
CAT	MAF-7	Physical adsorption	5.0	[3]
CAT	MAF-7	<i>In situ</i> encapsulation	9.1	[3]
CAT	BioHOF-1	<i>In situ</i> encapsulation	60.0	[4]
GDH	ZIF-67	Physical adsorption	110.4	[5]
GDH	ZIF-8	Physical adsorption	88.3	[5]
Trypsin	UiO-66(Zr)	Physical adsorption	80.2	[6]
	CYCU-4(Al)	Physical adsorption	163.4	[6]
Cyt <i>c</i>	ZIF-8	Physical adsorption	71.0	[7]
CAT	Zr-fcu-azo/sti-30%	Pore encapsulation	210.0	[8]
GOx	PCN-888-en	Pore encapsulation	1000.0	[9]
HRP	PCN-888-en	Pore encapsulation	2000.0	[9]
Z-DAAO	BioHOF-1	<i>In situ</i> encapsulation	500.0	[10]
CAT	HCPOS-1	Physical adsorption	336.9	This work
CAT	CPOS-1	Physical adsorption	163.3	This work
CAT	ZIF-8	Physical adsorption	31.7	This work

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