

† Electronic Supplementary Information (ESI)

Immobilization of *bacillus subtilis* lipase on a Cu-BTC based hierarchically porous metal-organic framework material: biocatalyst for esterification

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Experimental section

Materials.

The benzene-1, 3, 5 tricarboxylic acid (H₃BTC) ligand was obtained from Sigma-Aldrich. Copper nitrate, ethanol, acetic acid, trimethylamine (TEA), isooctane, lauric acid and benzyl alcohol were purchased from Beijing Chemical Co. Inc. All materials were used as received without further purification.

Measurements.

Powder X-ray diffraction (PXRD) patterns of the materials were recorded using a Rigaku D/max-2550 diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 50 KV and 200 mA. The morphologies of the obtained Cu-BTC product were recorded on a Field-emission scanning electron microscopy (FESEM) by using a Magellan 400, FEI microscope. Transmission electron microscopy (TEM) was obtained on an FEI Tecnai G² F20 s-twin D573 field emission transmission electron microscope with an accelerating voltage of 200 kV. N₂ adsorption-desorption isotherms were measured at 77 K by using a Micromeritics ASAP 2420 instrument. Prior to the sorption analysis, the samples were degassed at 120 °C for 12 hours. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data in a relative pressure ranging from 0.05 to 0.3. The pore size distributions were estimated by using Barrett-Joyner-Halenda (BJH) method from adsorption branch of N₂ isotherm. The total pore

volume was determined from the amount adsorbed at a relative pressure of about 0.99. The mesopore pore volume was obtained from BJH cumulative specific adsorption volume. The enzymatic activity of the BSL2@Cu-BTC hierarchical material was detected by gas chromatography (GC-2014) with flame ionization detector (FID).

Preparation of Cu-BTC hierarchically porous MOF

Briefly, a mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.435 g, 1.8 mmol), acetic acid (0.62 mL, 10.8 mmol), 0.50 mL TEA and 12 mL ethanol was stirred at room temperature. After 1 hour, H_3BTC (0.210 g, 1.0 mmol) was added into the dark blue solution. The mixture was stirred for an additional 2 hours to form a homogenous solution. Then the mixture was transferred into a Teflon-lined autoclave. The mixture was heated at 85 °C for 24 hours. The solid was recovered by centrifugation, washed with fresh ethanol for three times. Finally, the product was treated with ethanol at 65 °C for 12 hours. After drying at 65 °C overnight, the product of Cu-BTC hierarchically porous MOF was obtained.

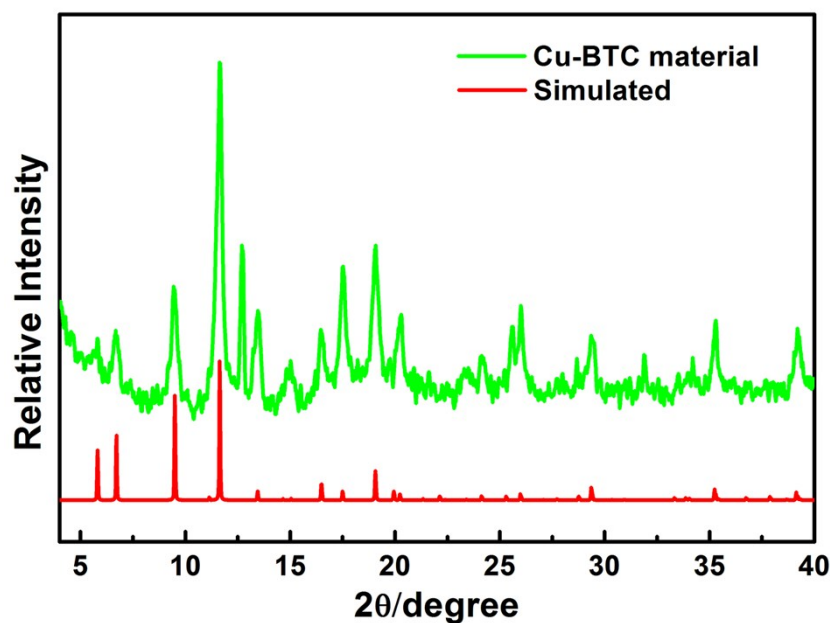


Fig. S1 PXRD pattern of Cu-BTC hierarchically porous MOF material and the simulated PXRD pattern of HKUST-1.

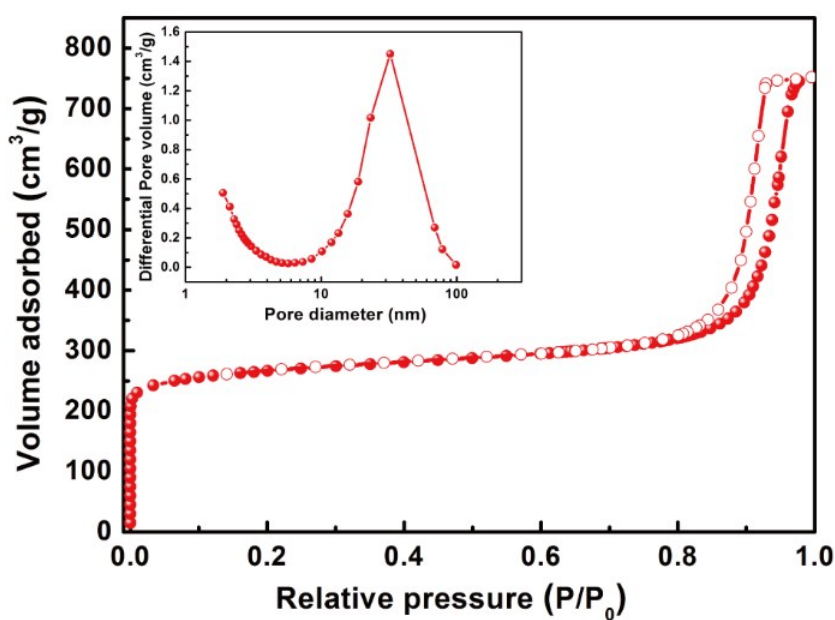


Fig. S2 N_2 adsorption-desorption isotherm of Cu-BTC hierarchically porous MOF material measured at 77 K. The inset shows the corresponding pore size distribution curve calculated by BJH method.

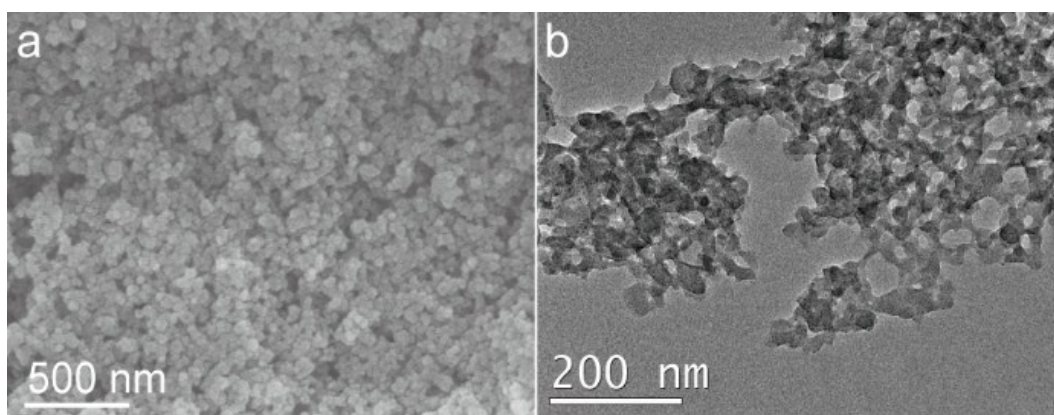


Fig. S3 (a) SEM image and (b) TEM image of the Cu-BTC hierarchically porous MOF material.

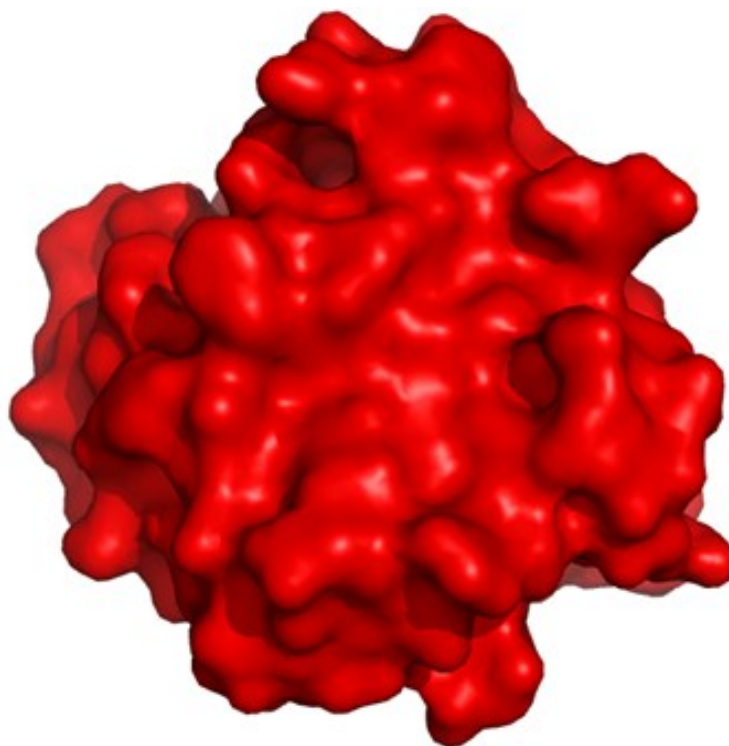


Fig. S4 A representation of the structure of *Bacillus subtilis* Lipase (Lip A), from PyMOL v0.99.

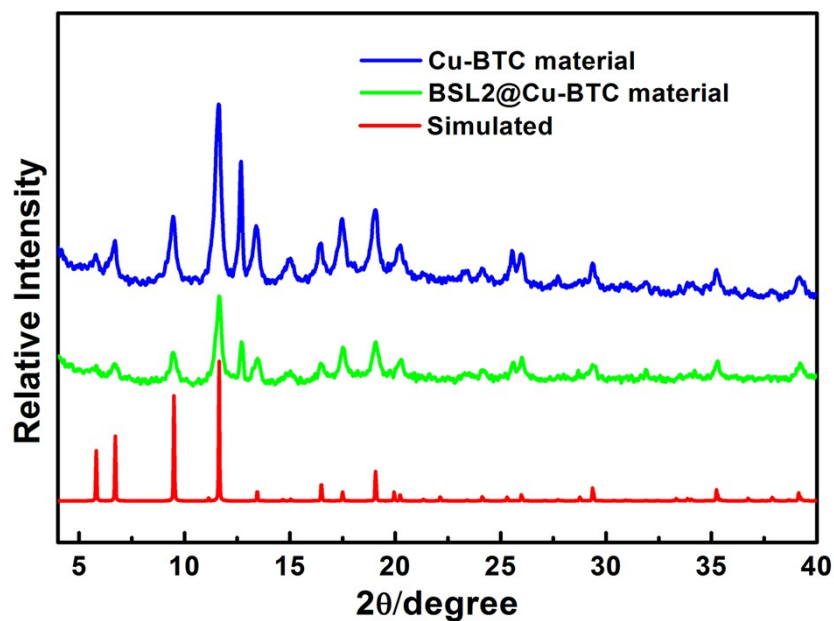


Fig. S5 PXRD pattern of Cu-BTC hierarchically porous MOF material and BSL2@Cu-BTC hierarchically porous MOF, and the simulated PXRD pattern of HKUST-1.

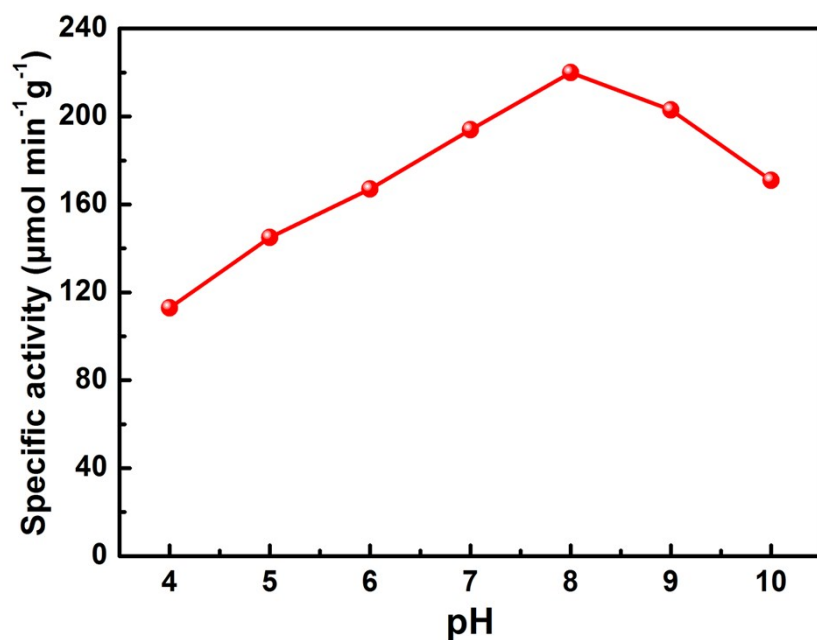


Fig. S6 Effect of aqueous pH in the preparation of surfactant-BSL2 complexes on specific activity.