# Electronic Supplementary Information (ESI)

# Hierarchically porous metal-organic frameworks with single–crystal structure and their enhanced catalytic properties

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## Experimental section

### Solvothermal method synthesis of conventional Cu-BTC

In a typical synthesis,[1] 0.525 g of 1, 3, 5-benzenetricarboxylic acid ($H_3BTC$) was dissolved in 15 mL ethanol (denoted as solution A). 1.093 g of copper nitrate trihydrate ($Cu(NO_3)\cdot 3H_2O$) was added to 15 mL of deionized water (denoted as solution B). Then, solution A was added to solution B, and the mixture was stirred for 30 min. The final mixture was transferred into Teflon-lined stainless steel autoclave stewing and heated at 120°C for 12 h. After cooling to room temperature, the blue product was filtered and washed, and then activated using ethanol at for 48 h (four times). The obtained product was filtered and dried in a vacuum oven at 150 °C for 12 h. The resulting product is denoted as C-Cu-BTC.

## Simulation section

**Simulation parameters:** the repulsion beads relative to the interaction energy of beads of like species. The value of the repulsion parameter can be derived from Flory-Huggins parameter $\chi_{ij}$. $\chi_{ij}$ between bead $i$ and bead $j$ used in this paper, which was calculated by the Blends module of the Materials Studio software package.[2, 3] As shown in Table S1, the smaller $\chi_{ij}$ value means the stronger affinity between the two beads, while the larger $\chi_{ij}$ indicates the stronger repulsion.[4] The small value of $\chi_{ij}$ between E bead and B or A bead reflects that the ethanol can dissolve the Benzene and the alkyl. As we all know, both the Benzene and the alkyl can hardly be dissolved in the water, so the calculated $\chi_{ij}$ value between the W bead and B or A bead is large. In the

experiment, the positively charged copper ions form a complex with the carboxyl group on the $H_3BTC$, and there is electrostatic attraction between the copper ions and the sulfonic group on the template.[5] In order to reflect the attraction between complexes and sulfonic groups, the χ between O and S is set as 0.8.

**Table S1.** Flory-Huggins interaction parameter $\chi_{ij}$ between beads.

| Bead | A | C | S | O | E | W |
|---|---|---|---|---|---|---|
| A | 0.00 | 2.40 | 5.78 | 13.6 | 3.68 | 10.6 |
| C | | 0 | 1.52 | 1.62 | 3.03 | 9.08 |
| S | | | | 0.8 | 1.49 | 1.4 |
| O | | | | 0 | 3.53 | 3.5 |
| E | | | | | 0 | 0.06 |
| W | | | | | | 0 |

**Simulation process:** the simulation was carried out by the MesoDyn module of the Materials Studio software package.[4] The bond length between beads $d = ah^{-1} = 1.1543$ (where $a$ is Gaussian bond length, $h$ is grid size). Diffusion coefficient was set as $10^{-7} cm^2 s^{-1}$ and the system's noise coefficient $\Omega = V' h^3 = 75.019$ (where *V* is the volume of bead).[4] The size of the simulated box was set as $32\ nm \times 32\ nm \times 32\ nm$. In the simulation of the sodium dodecyl benzene sulfonate system, the volume fraction of SDBS, complexs ($H_3BTC$-$Cu^{2+}$), E and W beads are 8.33%, 8.33%, 16.7%, 66.7%, respectively. In order to simulate the mixing environment during the synthetic process, a constant shear effect was introduced into the simulation system after 0.25 ms. The *X* axis is the direction of velocity, and the *Y* axis is the direction of velocity gradient. The *Z* axis is the neutral axis. The program achieves stable shear, that is, the velocity gradient is uniform: $\partial v_x / \partial v_y = \hat{U}_\gamma$ keeps constant and the shear rate $\gamma = 5 \times 10^5 s^{-1}$. The simulated time step $\Delta\tau = 50\ ns$, and the total simulation time is 1.0 ms (20000 steps in total).[4]

**Table S2.** Leaching test analysis of the recycling experiments.

| Entry | Leaching of Cu(II)* (ppm) |
|---|---|
| run 1 | 11.1 |
| run 2 | 14.0 |
| run 4 | 11.2 |

*The leached Cu content was determined by inductively coupled plasma optical emission spectroscopy Optima 5300 DV.

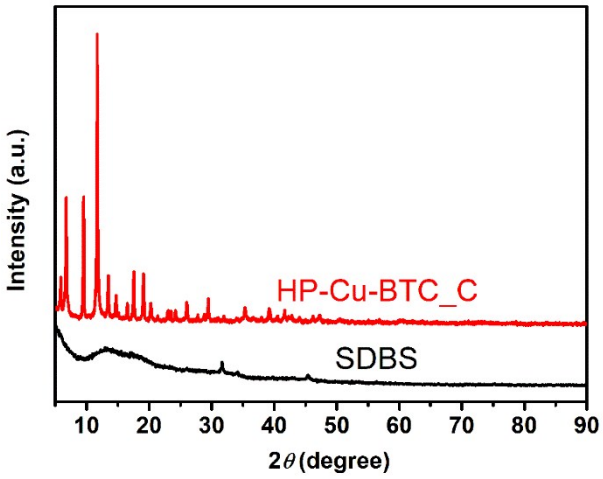


**Figure S1.** (a) Powder XRD patterns of hierarchical porous Cu-BTC_C (HP- Cu-BTC_C), and (b) surfactant sodium dodecylbenzenesulphonate (SDBS).

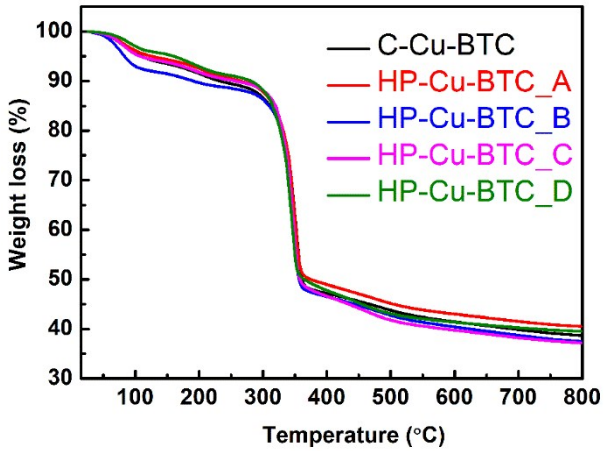


**Figure S2.** The thermogravimetric analysis (TGA) of HP-Cu-BTC_*X* (*X* = A, B, C, D) and C-Cu-BTC.

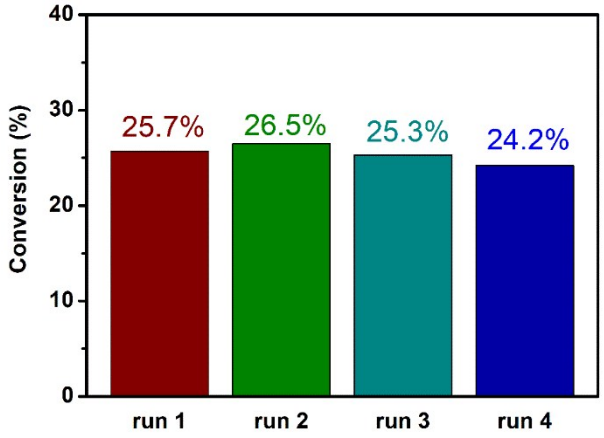


**Figure S3.** Conversion as a function of the number of recycle runs with Cu-BTC_C as the catalyst.

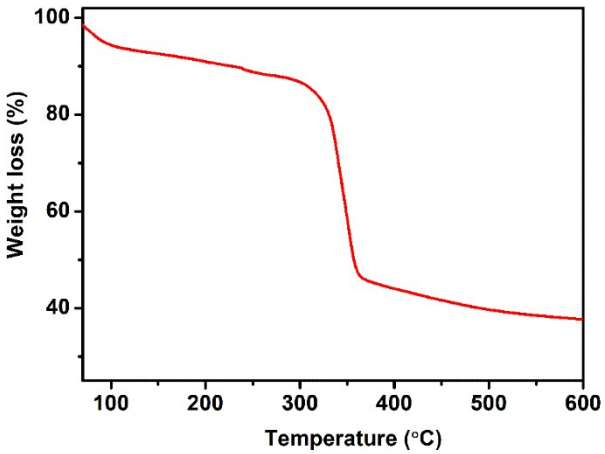


**Figure S4.** TGA of the Cu-BTC_C HP-MOFs after catalytic cycles.

**References**

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