

## Supplementary Materials

### **Lysine-modulated synthesis of enzyme-embedded hydrogen-bonded organic frameworks for efficient carbon dioxide fixation**

**Boyu Zhang<sup>1</sup>, Jiafu Shi<sup>1,2,3,\*</sup>, Ziyi Chu<sup>1</sup>, Jiayu Zhang<sup>1</sup>, Zhenhua Wu<sup>1</sup>, Dong Yang<sup>1</sup>, Hong Wu<sup>2,4</sup>, Zhongyi Jiang<sup>2,4,\*</sup>**

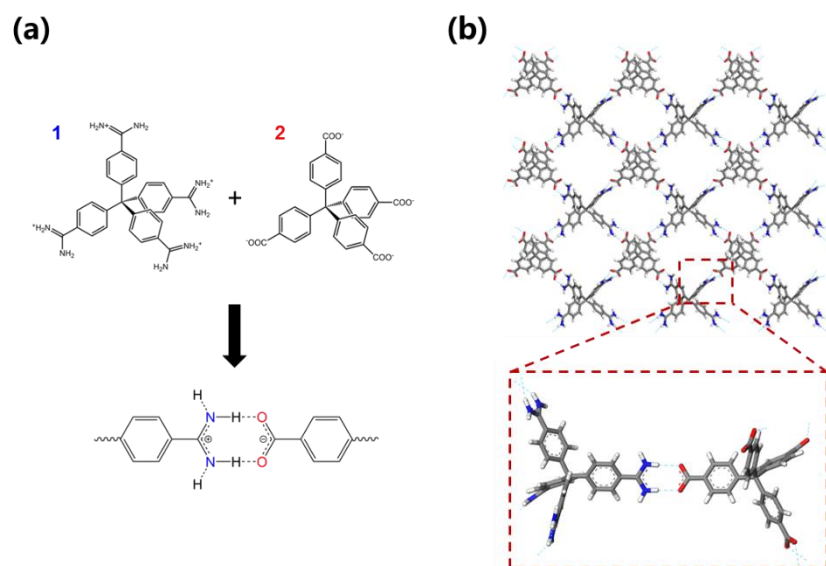
<sup>1</sup>School of Environmental Science & Engineering, Tianjin University, Tianjin 300072, China.

<sup>2</sup>Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China.

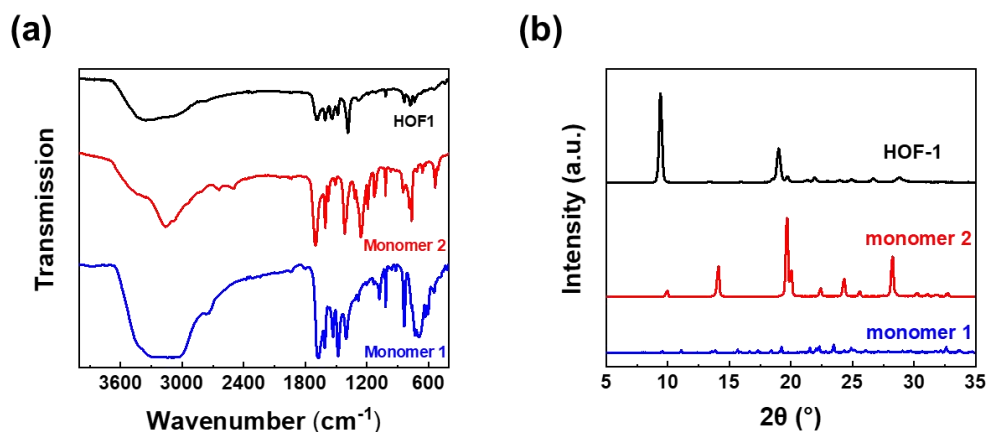
<sup>3</sup>State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Beijing 10090, China.

<sup>4</sup>Key Laboratory for Green Chemical Technology of Ministry of Education, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China.

**\*Correspondence to:** Prof. Jiafu Shi, School of Environmental Science & Engineering, Tianjin University, 92 Weijin Road, Tianjin 300072, China. E-mail: shijiafu@tju.edu.cn; Prof. Zhongyi Jiang, School of Chemical Engineering & Technology, Tianjin University, 92 Weijin Road, Tianjin 300072, China. E-mail: zhyjiang@tju.edu.cn

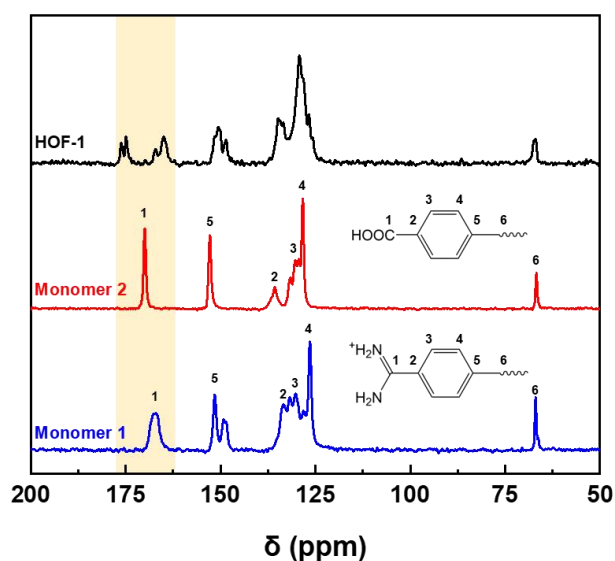


**Supplementary Figure 1.** (a) Hydrogen bond formation mechanism of HOF-1 and (b) simulated HOF-1 lattice.



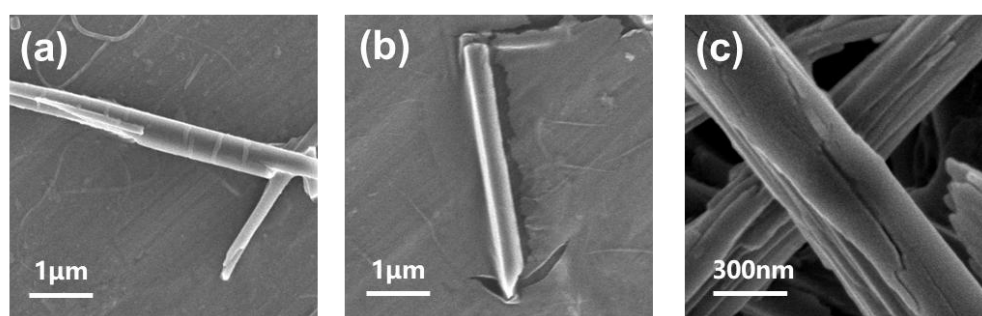
**Supplementary Figure 2.** (a) FTIR spectra and (b) XRD patterns of monomers and HOF-1.

FTIR spectra showed that the absorption bands at  $1190\text{ cm}^{-1}$  for the amino group and  $920\text{ cm}^{-1}$  for the carboxyl group of two monomers were weakened after synthesis, validating the formation of hydrogen bonds in HOF-1 [Supplementary Figure 2a]. Inspection of the XRD pattern showed peaks characteristic of HOF-1 at  $2\theta$  values of  $8.6^\circ$  and  $17.4^\circ$ , which also indicated the successful preparation of HOF-1 [Supplementary Figure 2b].

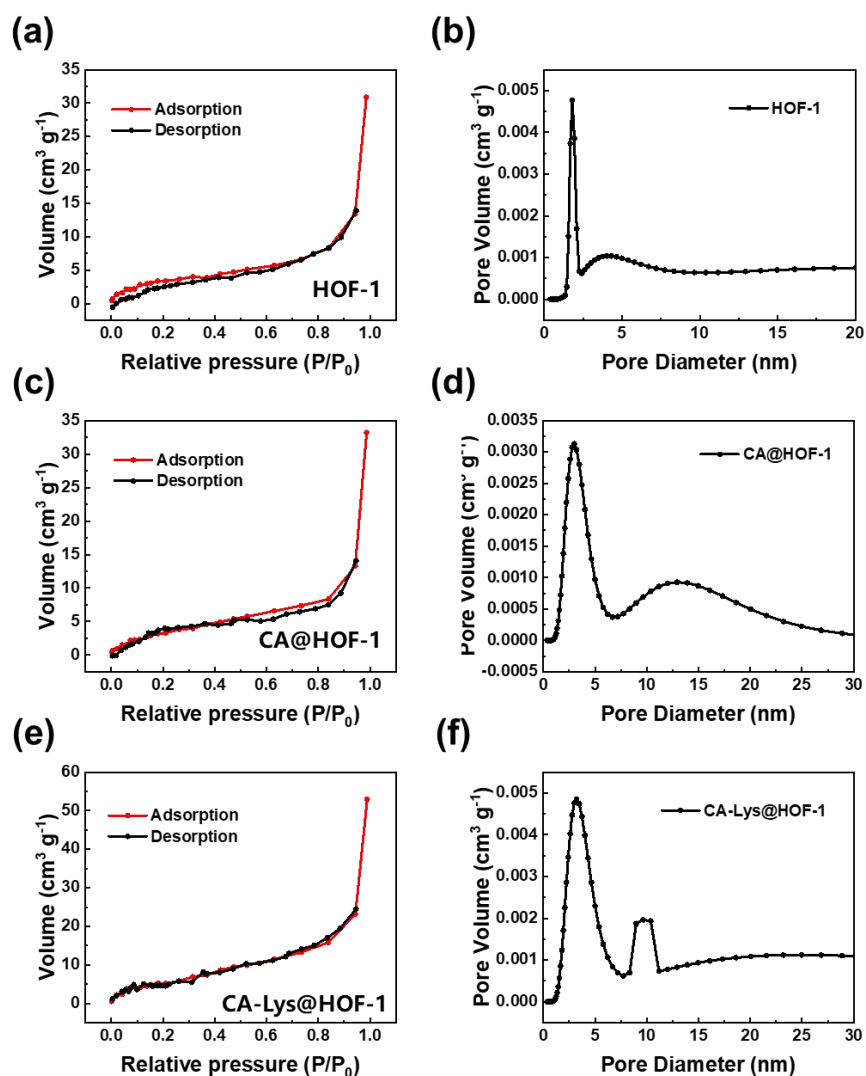


**Supplementary Figure 3.**  $^{13}\text{C}$ -NMR of HOF-1 and two monomers.

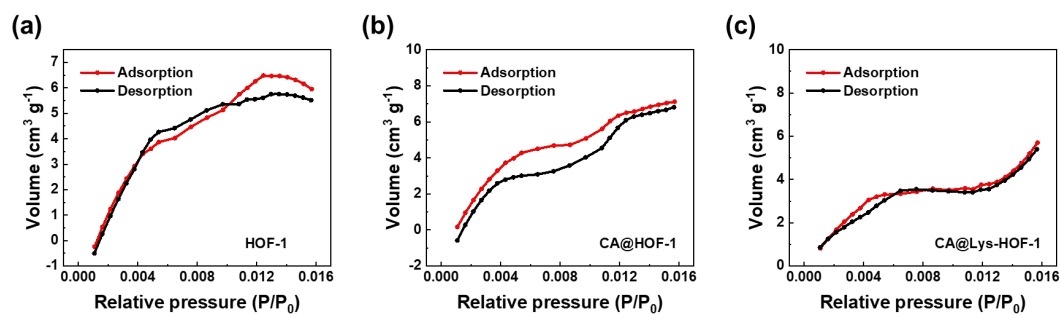
The various carbons in the monomers were numbered as shown in the figure and their corresponding peaks were indicated. From the results of the spectra, it can be seen that the peaks corresponding to the carbons 2-6 of the two monomers are basically unshifted after binding. Instead, a significant shift in the peaks of the carbon closest to the amino group in monomer 1 and the carbon on the carboxyl group in monomer 2 can be observed. This is due to the fact that the hydrogen bond in the HOF-1 structure is formed between the amino and carboxyl groups. The carbon atoms at the outermost ends of the two monomers are closest to the hydrogen bonding site and therefore are affected by the hydrogen bonding interactions and the  $\delta$  values are shifted. This further confirms the successful synthesis of HOF-1 material.



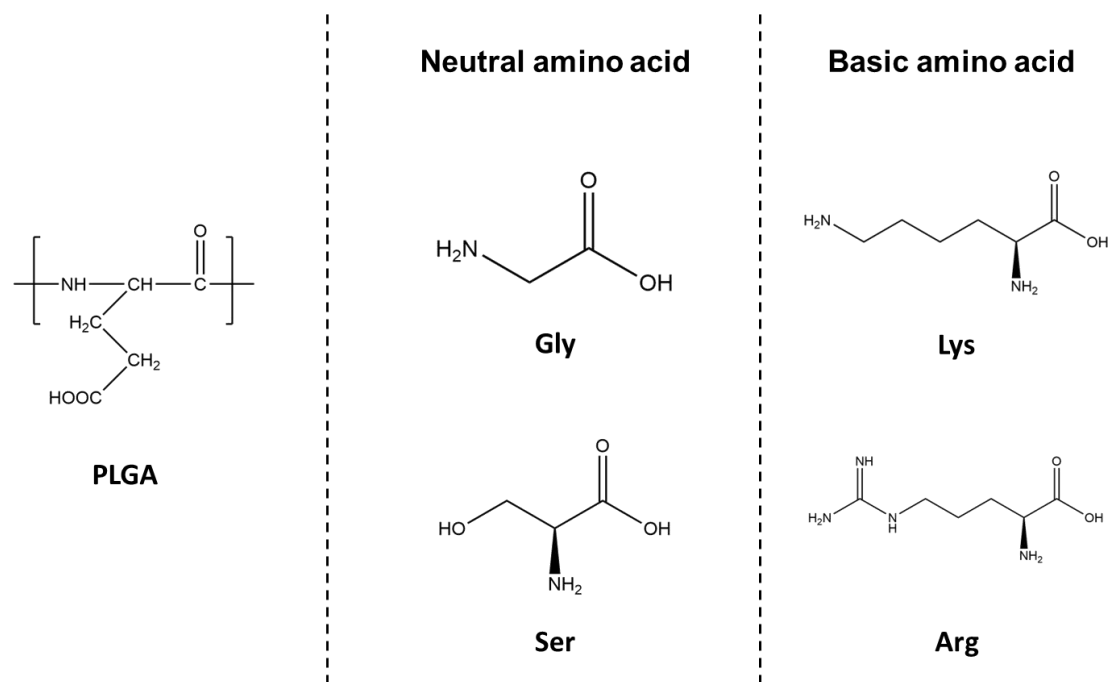
**Supplementary Figure 4.** SEM images of (a) HOF-1, (b) CA@HOF-1, and (c) CA@Lys-HOF-1.



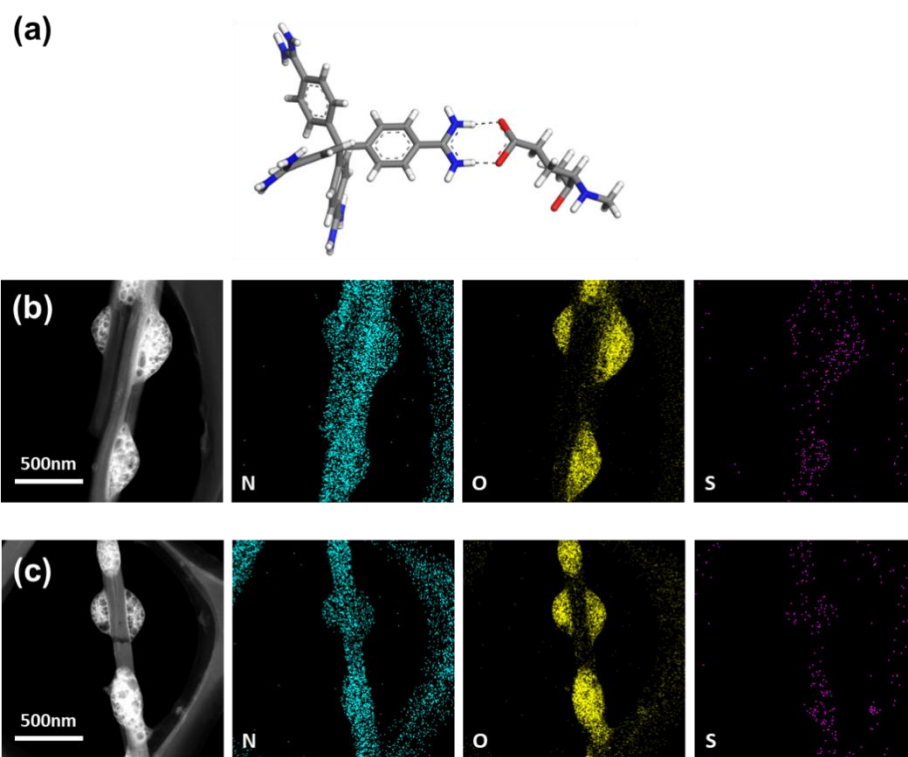
**Supplementary Figure 5.** Nitrogen sorption isotherms and pore-size distributions of (a, b) HOF-1, (c, d) CA@HOF-1, and (e, f) CA@Lys-HOF-1.



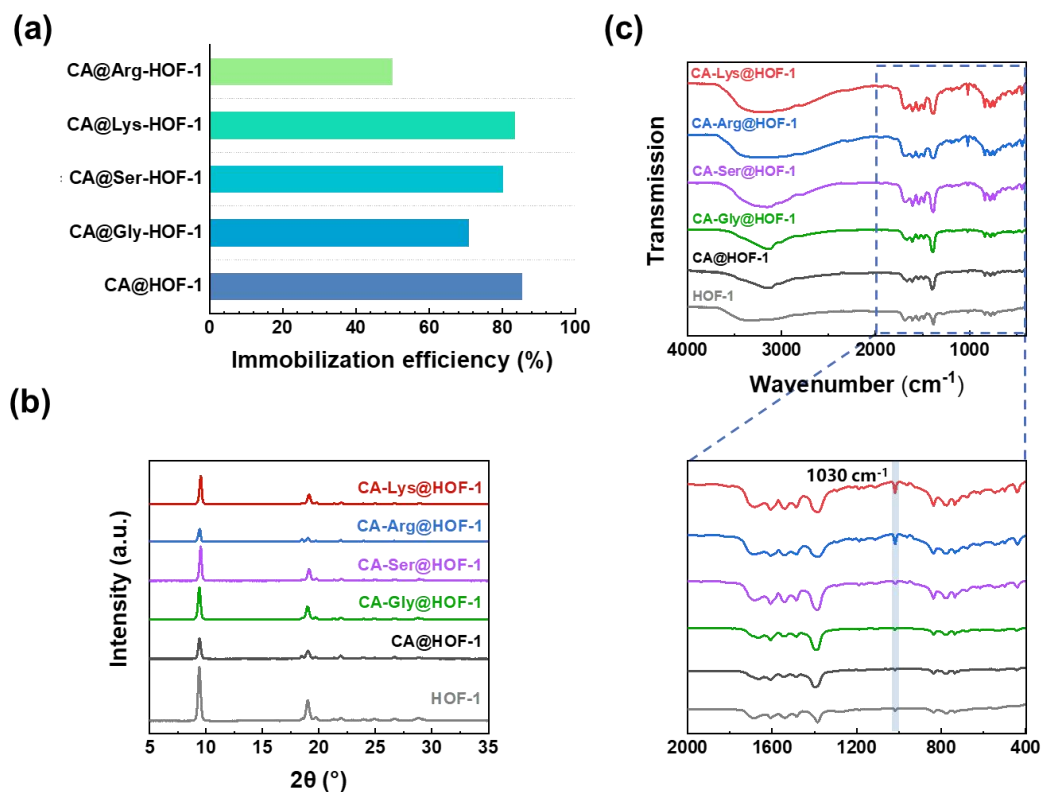
**Supplementary Figure 6.** CO<sub>2</sub> sorption isotherms of (a) HOF-1, (b) CA@HOF-1, and (c) CA@Lys-HOF-1.



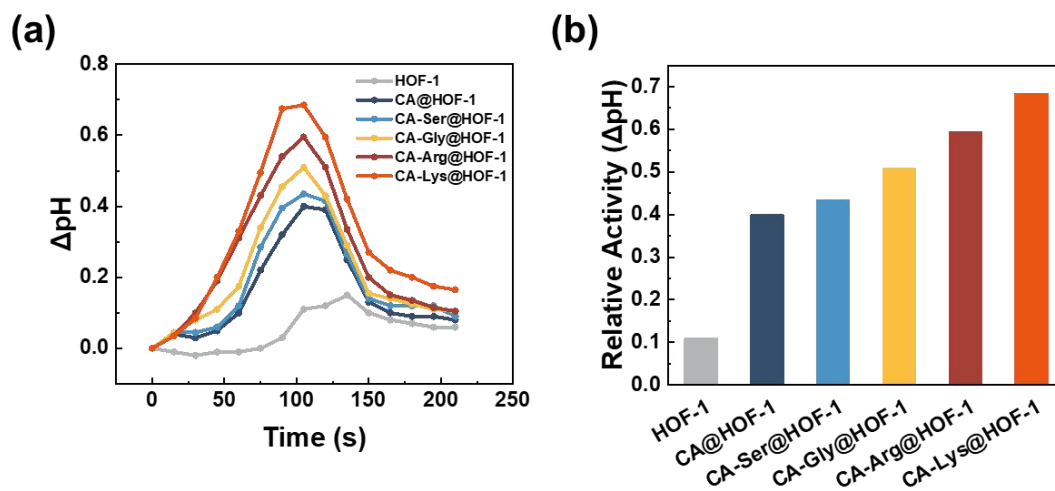
**Supplementary Figure 7.** The amino acids selected as modulators in this study.



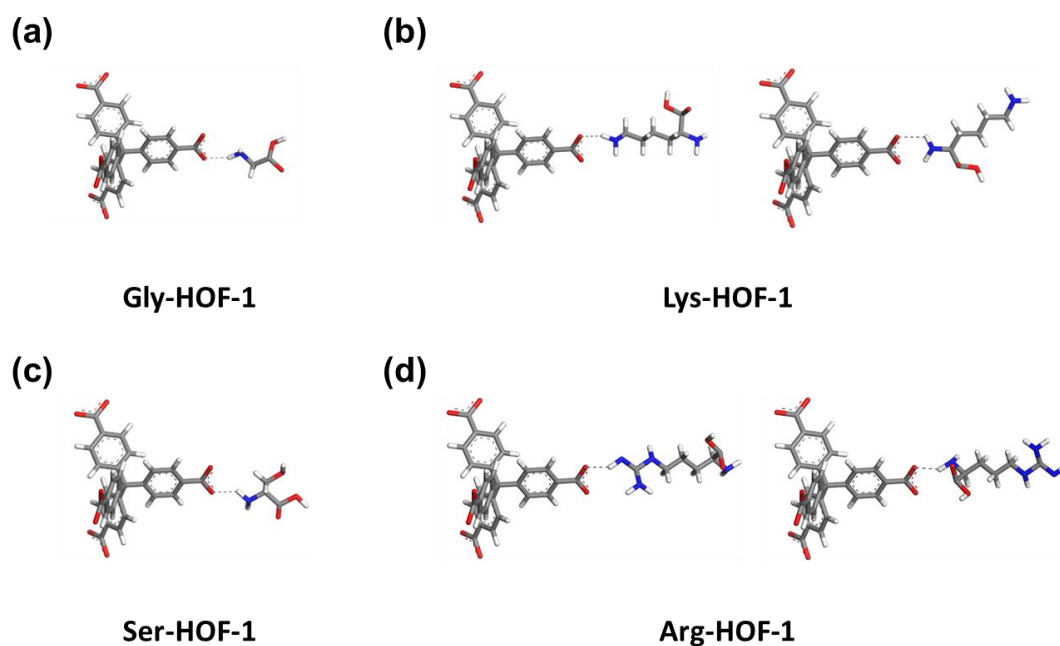
**Supplementary Figure 8.** (a) Possible ligation of PLGA to monomer 1 and (b, c) TEM images of the resulting immobilized enzyme



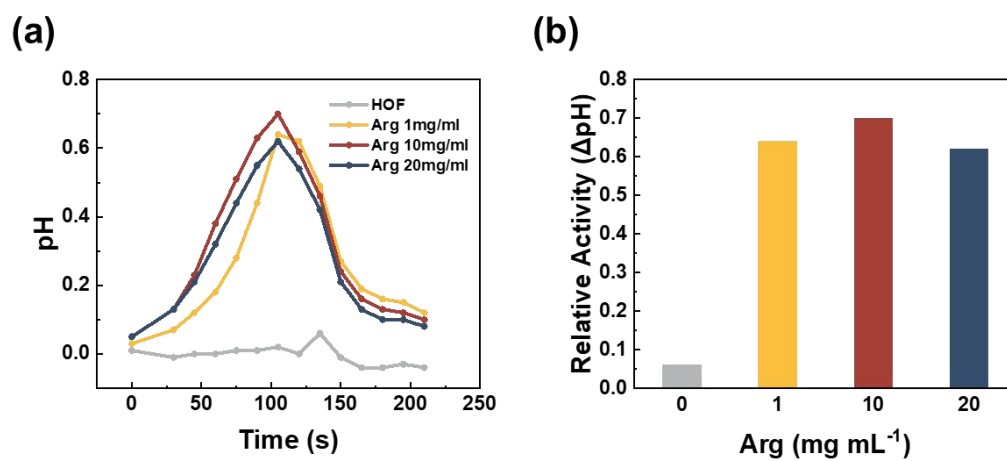
**Supplementary Figure 9.** (a) The immobilization efficiency of CA by amino acid-modulated HOF-1, and their (b) XRD patterns and (c) FTIR spectra.



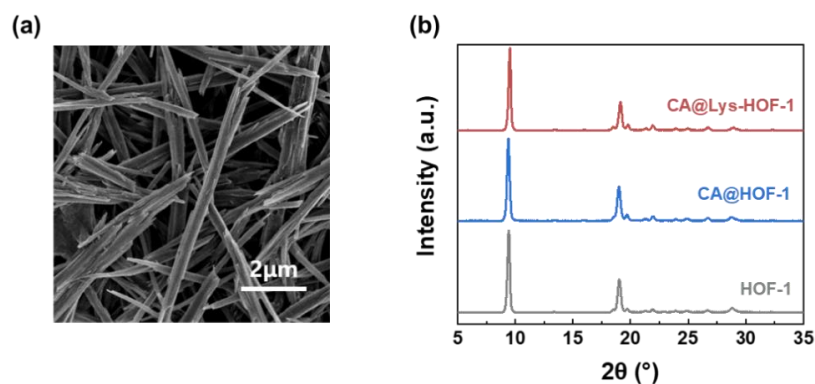
**Supplementary Figure 10.** Catalytic activity of CA@HOF-1 modulated by different types of amino acids.



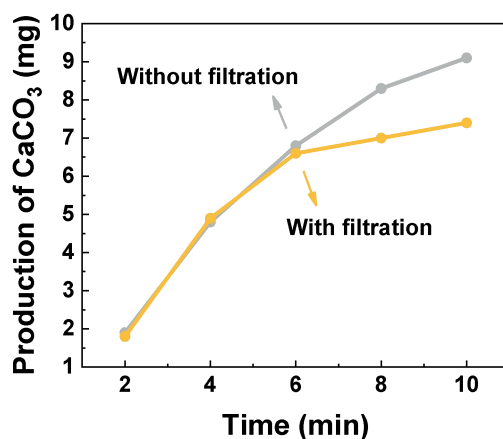
**Supplementary Figure 11.** Possible ligation of (a) Gly, (b) Lys, (c) Ser, (d) Arg to monomer 2.



**Supplementary Figure 12.** Catalytic activity of CA@HOF-1 modulated by different concentrations of Arg.



**Supplementary Figure 13.** (a) SEM image of CA@Lys-HOF-1 and (b) XRD patterns of catalysts after the 8th cycle of the reaction.



**Supplementary Figure 14.** The hot filtration test<sup>[1]</sup> of CA@Lys-HOF-1. The catalyst is filtrated by centrifugation after 6 min.

A hot filtration experiment was performed over CA@Lys-HOF-1 for the CO<sub>2</sub> mineralization. As shown in Supplementary Figure 14, no more increment in the production of CaCO<sub>3</sub> is observed after the filtration process, suggesting the heterogeneous nature of our catalytic system.

## REFERENCES

1. Qin Z, Li H, Yang X, et al. Heterogenizing homogeneous cocatalysts by well-designed hollow MOF-based nanoreactors for efficient and size-selective CO<sub>2</sub> fixation. *Appl Catal B Environ* 2022;307:121163. [DOI: 10.1016/j.apcatb.2022.121163]