

A Cavity-Tailored Metal-Organic Tetrahedral Nanocage and Gas Adsorption Property

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1. The characterization of L, Cage 1

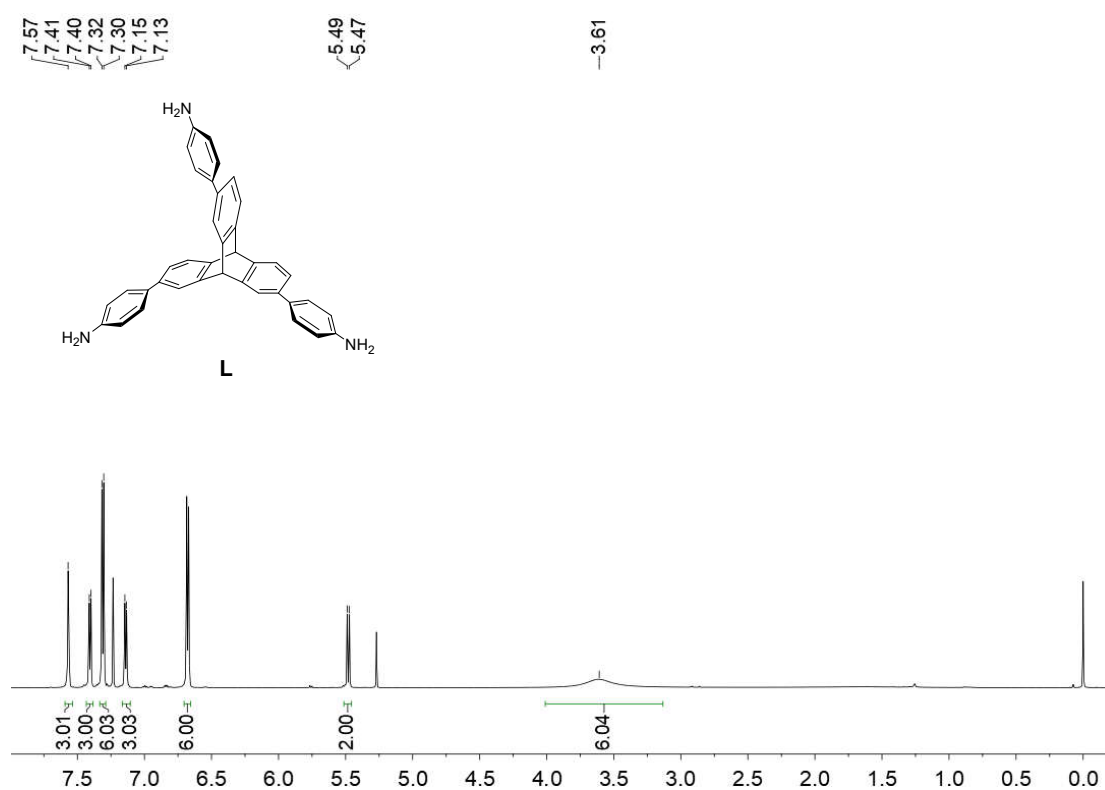


Figure S1. ¹H NMR (600 MHz, CDCl₃) spectrum of L.

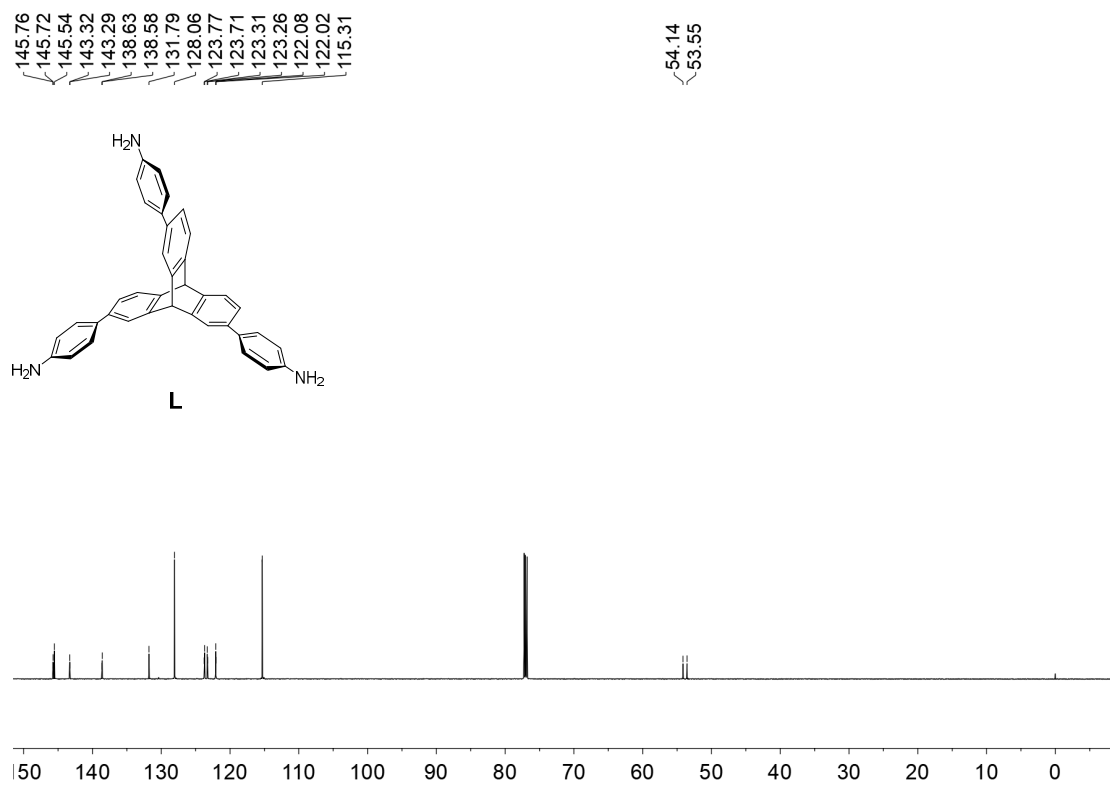


Figure S2. ^{13}C NMR (151 MHz, CDCl_3) spectrum of **L**.

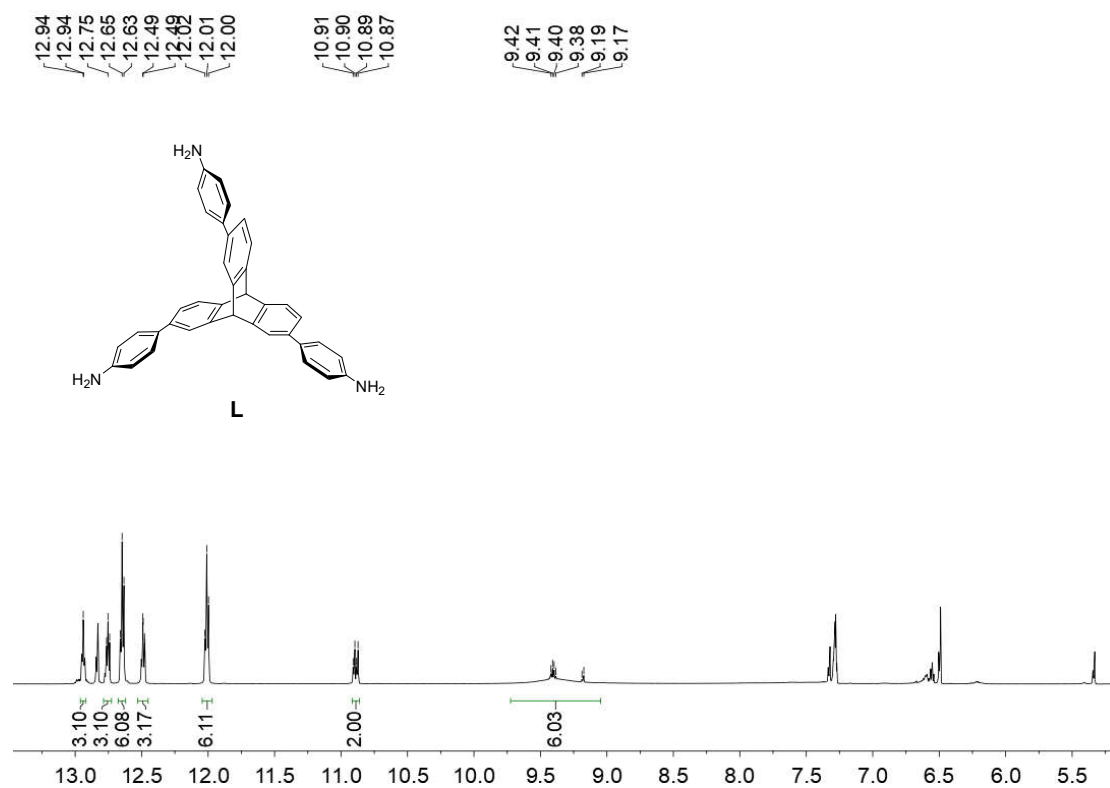


Figure S3. ^{13}C NMR (151 MHz, $\text{CDCl}_3/\text{CD}_3\text{CN}$ 1:1) spectrum of **L**.

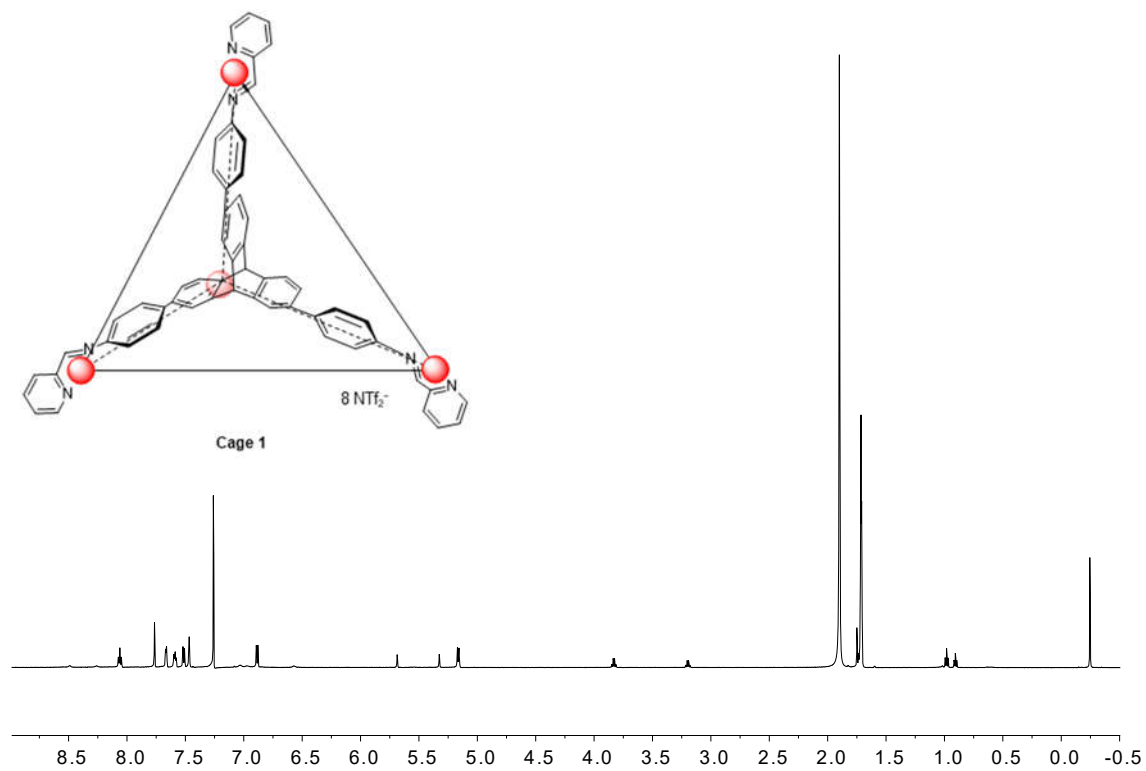


Figure S4. ¹H NMR (151 MHz, CDCl₃/CD₃CN 1:1) spectrum of **Cage 1**.

2. ESI-MS spectrum of **Cage 1**

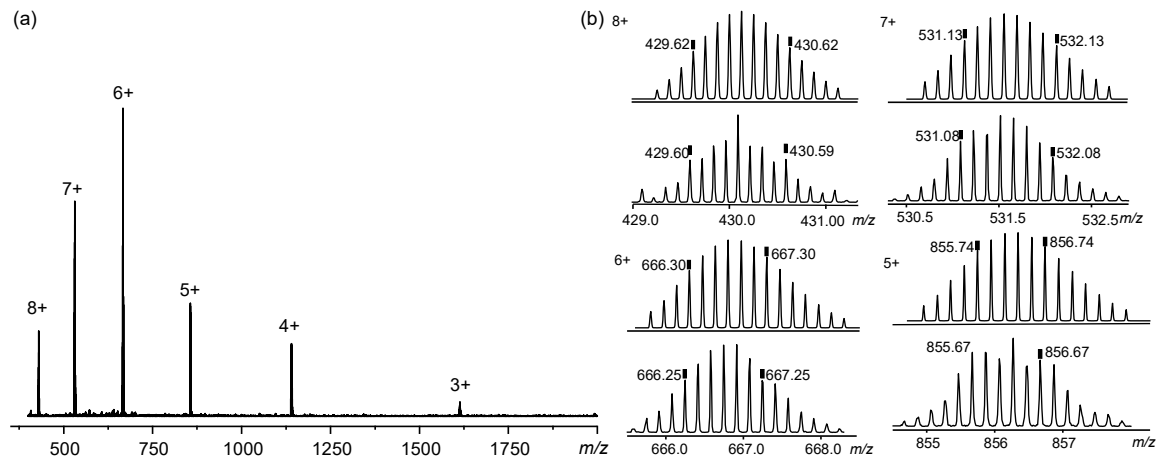


Figure S5. (a) and (b) ESI-MS spectrum of **Cage 1**. Theoretical (top) and experimental (bottom) isotopic patterns for different charge states observed from **Cage 1** (NTf₂⁻ as the counterion).

3. Generation of the molecular model of Cage 1

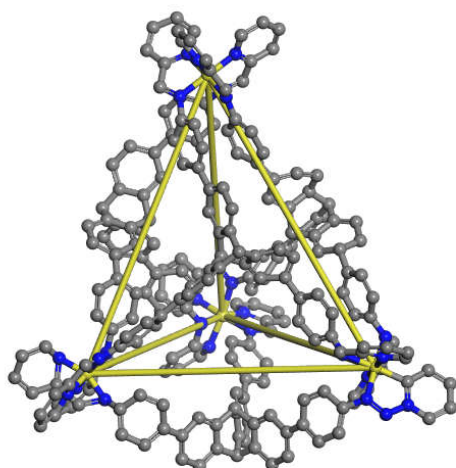


Figure S6. Energy-minimized molecular model of **Cage 1**. (Zn, yellow; N, blue; C, gray). Hydrogens and counter anions are omitted for clarity.

5. Gas adsorption properties of Cage 1

Orange powder **Cage 1** was obtained through direct precipitation of **Cage 1** from its acetonitrile solution after self-assembly by adding diethyl ether. The solid was dried under vacuum overnight. Prior to each measurement below, the sample was treated following the description in Materials and instrumentation [1].

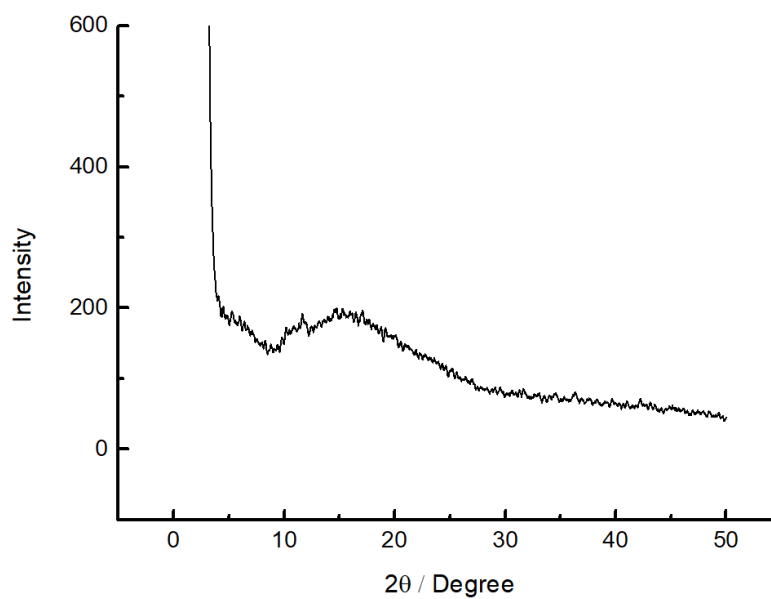


Figure S7. Experimental PXRD pattern of **Cage 1**.

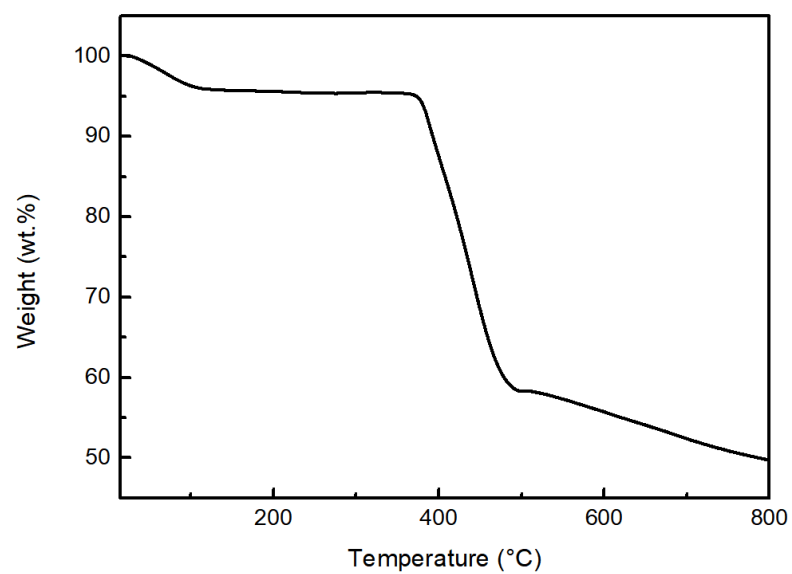
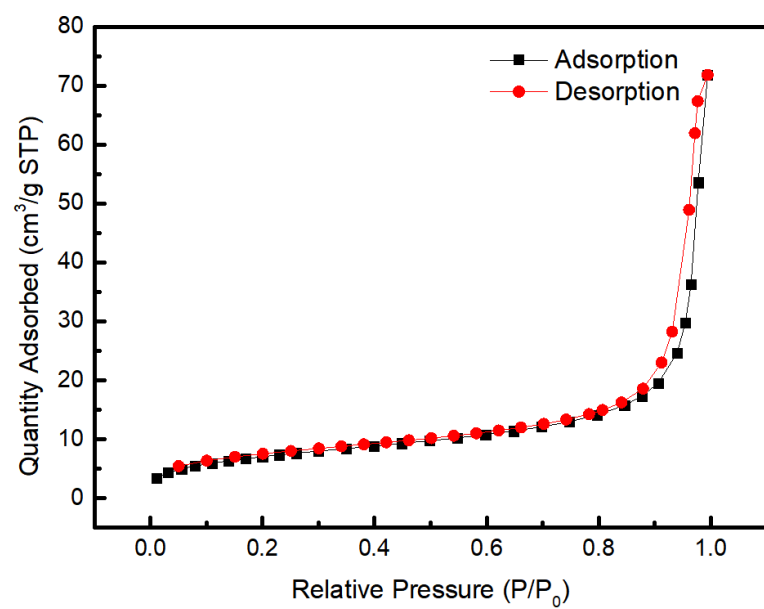


Figure S8. TGA plot of solid **Cage 1** under N₂.



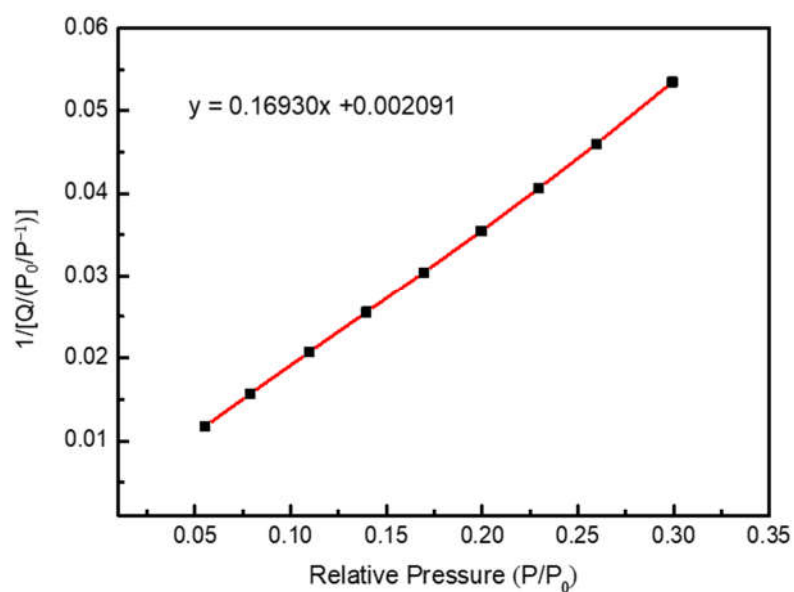


Figure S9. N₂ sorption isotherms of activated **Cage 1** measured at 77 K (upper) and plot of the linear region of the BET equation for **Cage 1** (bottom). $S_{BET} = \frac{VmNA\sigma}{22400W} = \frac{6.022 \times 10^{23} \times [1/(0.169310 + 0.002910)] \times 1.62 \times 10^{-17}}{22400} = 25.3955 \text{ m}^2/\text{g}$

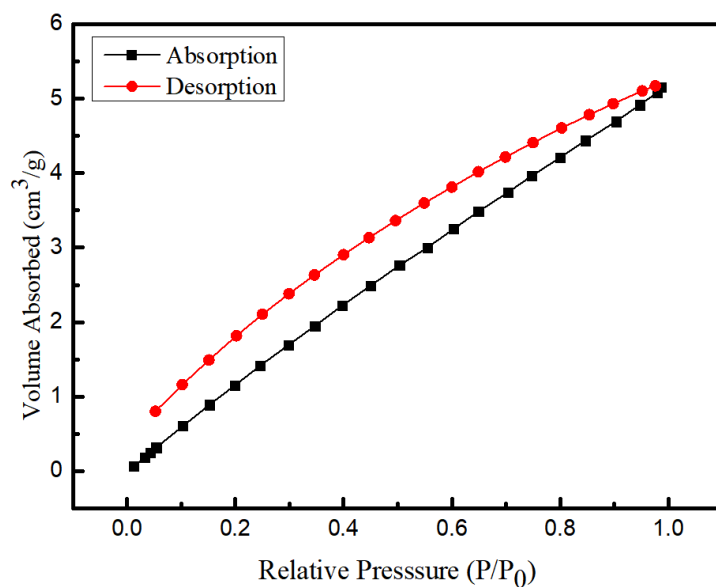


Figure S10. CO₂ adsorption/desorption isotherms of activated **Cage 1** at 298 K.

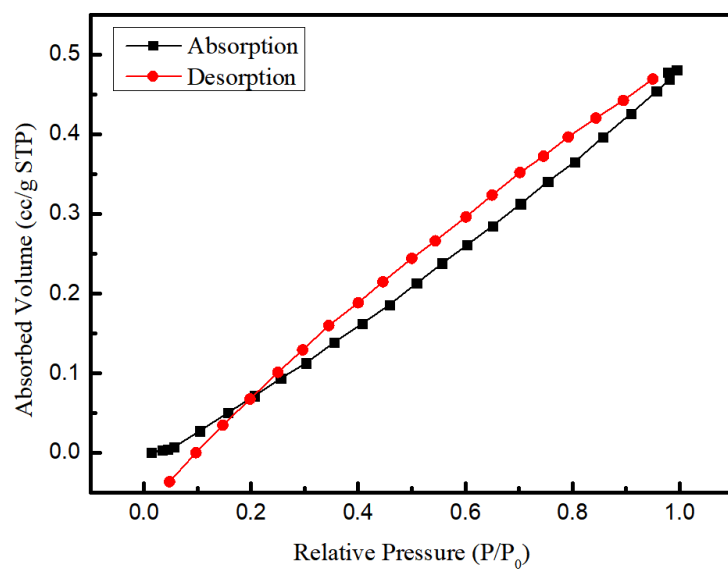


Figure S11. O_2 adsorption/desorption isotherms of activated **Cage 1** at 298 K.

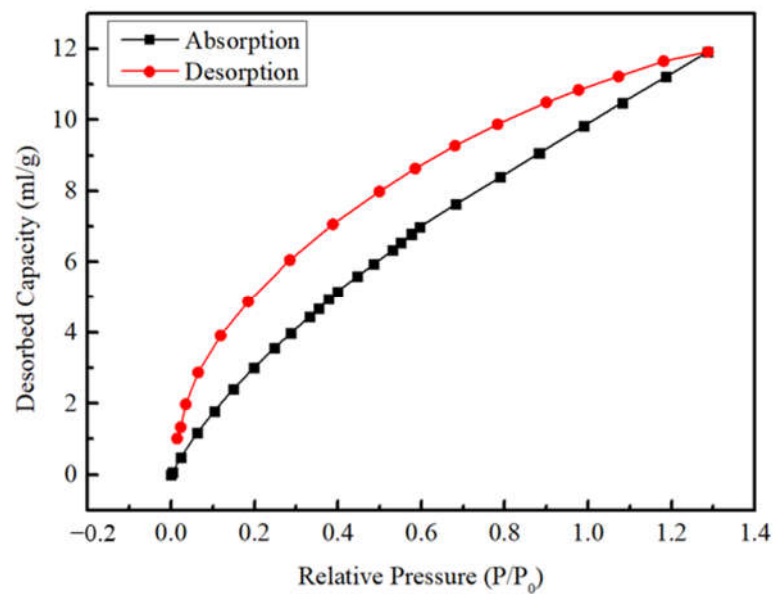


Figure S12. C_2H_2 adsorption/desorption isotherms of activated **Cage 1** at 298 K.

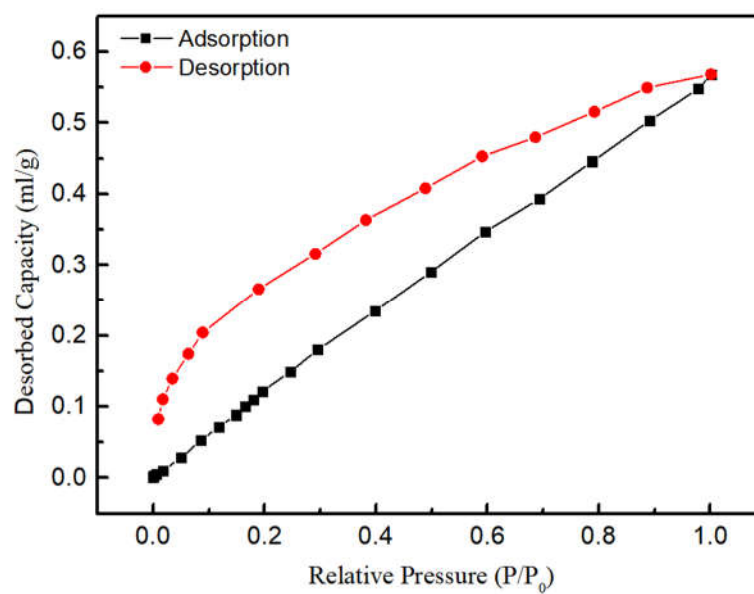


Figure S13. N₂ adsorption/desorption isotherms of activated **Cage 1** at 298 K.

References

1. Zhu, J.L.; Zhang, D.; Ronson, T.K.; Wang, W.; Xu, L.; Yang, H.B.; Nitschke, J.R. A Cavity-Tailored Metal-Organic Cage Entraps Gases Selectively in Solution and the Amorphous Solid State. *Angew. Chem. Int. Ed.* **2021**, *60*, 11789–11792. <https://doi.org/10.1002/anie.202102095>.