

# Long time CO<sub>2</sub> storage under ambient condition in isolated voids of a porous coordination network facilitated by the “magic door” mechanism

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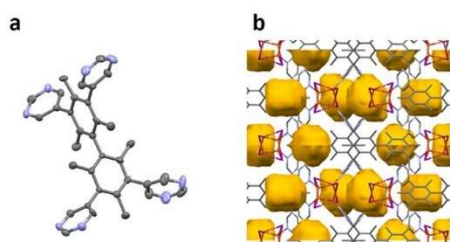
Despite the lack of accessibility, CO<sub>2</sub> was selectively adsorbed into these pores at 298 K and then retained for more than one week while exposed to atmosphere. CO<sub>2</sub> entered the isolated voids through transient channels, termed “magic doors”, which can momentarily appear within the structure. Once inside the voids, CO<sub>2</sub> remained locked in limiting its escape. This mechanism was facilitated by the flexibility of organic ligands and the pivot motion of cluster units. The uncovered CO<sub>2</sub> sorption and retention ability paves the way for the design of sorbents based on isolated voids.

## 1 Introduction

To achieve a carbon-neutral society, there is an urgent need to develop materials for CO<sub>2</sub> capture and storage. Porous coordination networks (PCNs) have attracted attention as promising candidates because of their readily modifiable structures and tunable pore environments. Although there has been a considerable progress in improving CO<sub>2</sub> uptake capacities and selectivity, the possibility of its long-term storage inside PCNs under ambient conditions has received comparatively less attention since the interactions.

## 2 Experiment

A ligand (**L**) based on a pseudo-tetrahedral bimesityl skeleton decorated with four pyrimidine groups was synthesized by Suzuki-Miyaura coupling reaction (Fig 1a). Reaction of **L** with CuI in the presence of KI and PPh<sub>3</sub> in the CH<sub>3</sub>CN/H<sub>2</sub>O/EtOH solvent mixture yielded two distinct crystal morphologies, yellow plates and prisms. The prisms were  $\{[(\text{Cu}_4\text{I}_4)(\text{L})]\cdot\text{solvent}\}_n$  (**1**), with a three dimensional interpenetrated structure (network **1**). The pure **1** could be obtained by the density separation method.

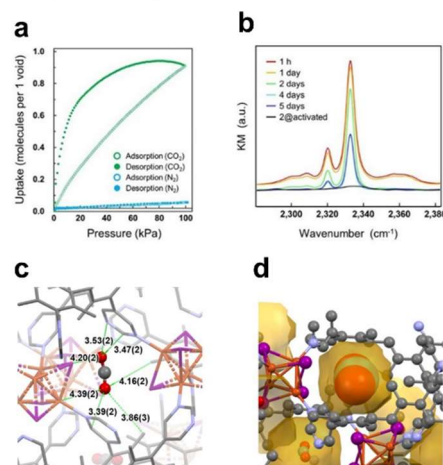


**Fig 1.** (a) Single crystal structure of **L**. (b) The structure of network **1**, showing the voids outlined in dark yellow. C – grey, N – blue, Cu – orange, and I – purple, hydrogen atoms were omitted for clarity.

## 3 Results and Discussion

**1** possessed closed pores with dimensions of  $5.2 \times 4.9 \times 4.9$  Å. However, the size of maximum aperture between each pore was only  $2.4 \times 1.5$  Å, which was too small for any molecule to pass through. Nevertheless, acetonitrile molecules were present in the pores of the as-synthesized crystal of **1**, which could be removed by heating at 473 K for 12 h under vacuum without loss of crystallinity,

suggesting that some diffusion pathways could exist for the guest escape to occur. This fact prompted us to investigate the possibility of encapsulating different gasses into the activated crystals of **1** (**activated 1**). First, N<sub>2</sub> isotherms measured at 298 K showed no uptake. In contrast, the CO<sub>2</sub> adsorption isotherm showed hysteresis between adsorption and desorption branches, suggesting some degree of guest trapping. To test this hypothesis, IR spectroscopy measurement was performed. The IR spectrum of CO<sub>2</sub>@**1** showed a strong absorption band at 2340 cm<sup>-1</sup>, indicating the presence of physisorbed CO<sub>2</sub>. CO<sub>2</sub>@**1** were left in the air while monitoring changes in the IR peak over time. Remarkably, the IR signal was still present after 1 week, only gradually decreasing in intensity (Figure 2b). To elucidate the structural changes accompanying the CO<sub>2</sub> adsorption and visualize the encapsulated gas molecules, SCXRD analysis was performed.



**Fig 2.** (a) Adsorption and desorption isotherms of N<sub>2</sub> and CO<sub>2</sub> for **activated 1** measured at 298 K. (b) Time-dependent IR spectra of CO<sub>2</sub>@**1** left in the air, (c) crystal structure of CO<sub>2</sub>@**1** (d) CO<sub>2</sub> orientation inside the pore.

## Research Achievements

The crystallographic Society of Japan poster award in 2021

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