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Pore space partition of a fragile Ag(1)-carboxylate framework via post-synthetic linker insertion†

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The pore space partition approach via post-synthetic linker insertion was used to modulate the porosity of a fragile Ag(ı)-carboxylate framework with potentially large pore space. The resulting Ag(ı)-MOFs with partitioned pores showed enhanced permanent porosity compared with a nonpartitioned Ag(ı)-carboxylate framework.

Metal-organic frameworks (MOFs) are porous crystalline networks primarily composed of coordination bonds between metal ions and organic ligands.1 Their structural diversity represents a significant advantage for many applications based on the intrinsic properties of the constituent metals and functionalized ligands.2 After surveying metal ions for novel porous architectures, silver(1) has become a promising candidate due to its tolerance for a multitude of coordination numbers and geometries.³ Over the past decades, significant efforts have been devoted to preparing porous Ag(1)-based MOFs, but only a few have been investigated for their gas sorption properties⁴ because of the relatively weak Ag(1)-ligand bonds. These weak bonds often result in framework collapse during the activation process. Therefore, the synthesis of Ag(1)-based MOFs with permanent porosity remains a challenge in the expansion of MOF diversity and the utilization of silver. Recently, a pore space partition (PSP) strategy⁵ has been developed as a tool for improving the structural stability⁶ and gas separation abilities of MOFs.⁷ PSP utilizes the division of large pore spaces into smaller segments by using secondary metal8 or ligand insertion.9 However, most MOFs with partitioned pore space are obtained via one-pot synthesis using all framework building blocks including pore partitioning agents.

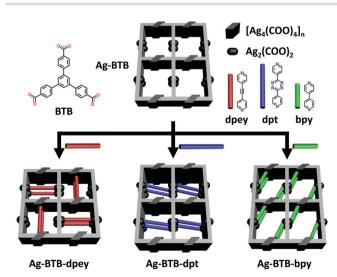
Herein, a rare example of permanently microporous Ag(1)-MOFs achieved by the PSP approach via post-synthetic insertion¹⁰ of auxiliary linkers is reported. The parent Ag(1)-carboxylate framework

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(AgBTB) contains a large one-dimensional (1D) solvent channel. However, AgBTB is fragile and practically nonporous for gas sorption. After partitioning the 1D channel via post-synthetic insertion of dipyridyl linkers, the resulting Ag(1)-MOFs showed improved structural stability upon guest molecule removal. In addition, the framework porosity could be adjusted by the amount and type of linkers added (Scheme 1).

The solvothermal reaction of AgNO₃ with 4,4',4"-benzene-1,3,5-triyl-tri-benzoic acid (H₃BTB) afforded AgBTB crystals. A three-dimensional (3D) coordination network was formed based on a finite [Ag₂(COO)₂] dinuclear cluster and an infinite $[Ag_4(COO)_4]_n$ 1D ribbon with inorganic nodes and BTB as an organic linker (Fig. 1 and Fig. S1, ESI†). Ag1 of the finite [Ag₂(COO)₂] secondary building unit (SBU) adopted a square planar geometry with two syn-syn bridging bidentate carboxylate oxygen atoms in a trans-configuration, an Ag atom of an inter-silver bond, and a ligated water molecule. Ag2 and Ag3 of the infinite $[Ag_4(COO)_4]_n$ structure adopted distorted square



Scheme 1 Pore space partition of AgBTB via post-synthetic insertion of dipyridyl linkers.

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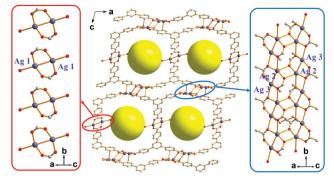


Fig. 1 The framework structure of **AgBTB** with an array of finite $[Ag_2(COO)_2]$ dinuclear clusters and an infinite $[Ag_4(COO)_4]_n$ 1D ribbon.

pyramidal geometries and were interconnected via two carboxylates to form a 1D ribbon along the crystallographic b-axis. **AgBTB** contained large 1D solvent channels that were 10.4 \times 13.0 Å^2 in size along the crystallographic *b*-axis. The total pore volume of AgBTB calculated by PLATON¹¹ was determined to be 3,508 Å³ per unit cell, corresponding to 45.4% of the total unit cell volume. Dye adsorption results show that the AgBTB can absorb dye molecules such as methylene blue and Nile red in ethanol solutions, which suggests the void space of the AgBTB is well preserved in liquid medium (Fig. S2, ESI†). However, the N2 adsorption experiment of activated AgBTB showed no N2 uptake at 77 K. This nonporous behavior is due to pore collapse upon solvent removal from the channel. Interestingly, at least six potential linkage sites of three different categories existed between the Ag atoms in the framework (Fig. 2). Moderatelength linkage sites 1 and 2 of the first category could interconnect in-plane Ag1-Ag1 (~14.7 Å) and off-plane Ag1-Ag1 $(\sim 15.8 \text{ Å})$, respectively, in the dinuclear Ag clusters facing each

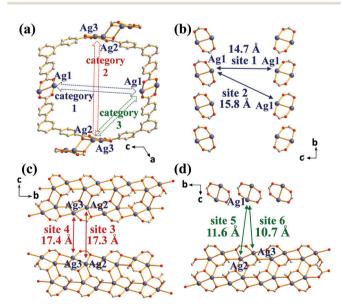


Fig. 2 (a) Potential linkages across the 1D solvent channel in **AgBTB**. Inter-silver distances (b) between dinuclear clusters, (c) between tetranuclear clusters of the 1D ribbons and (d) between the dinuclear and tetranuclear clusters of the 1D ribbon.

other across the 1D channel. However, the longer linkage sites 3 and 4 of the second category interconnect Ag2–Ag2 (\sim 17.3 Å) and Ag3–Ag3 (\sim 17.4 Å), respectively, in the tetranuclear Ag clusters. The short linkage sites 5 and 6 of the third category interconnect Ag1–Ag2 (\sim 11.6 Å) and Ag1–Ag3 (\sim 10.7 Å), respectively, in the AgBTB framework.

Given the above information, the PSP strategy was used to rationally partition the original 1D channel into smaller channels, leading to improved porosity. The PSP was achieved via post-synthetic insertion of carefully selected dipyridyl linkers, 1,2-di(pyridin-4-yl)ethyne (dpey), 3,6-di(pyridin-4-yl)-1,2,4,5tetrazine (dpt), and 4,4'-bipyridine (bpy), with lengths approximately matching those of the potential linkage sites (Fig. S3, ESI†). Powder X-ray diffraction (PXRD) patterns of the resulting crystals indicated that the dpey linker induced significant reorganization of the AgBTB framework (Fig. S4, ESI†). In contrast, dpt and bpy linkers resulted in only moderate structural changes. Single-crystal structural analyses revealed that the inserted dipyridyl linkers acted as pore-partition agents that interconnect the potential linkage sites in the AgBTB framework (Fig. 3 and Fig. S5-S7, ESI†). The insertion and partitioning modes of the dipyridyl linkers depend on their length. For **AgBTB-dpey**, since the length of dpey ($\sim 14.6 \text{ Å}$, including two 2.4 Å Ag-N bonds) matches with the potential linkage site 1 (\sim 14.7 Å), the fit into linkage site 1 was expected. Interestingly, insertions of dpey occurred at the preferred linkage site 1 and at the long linkage site 3 (Ag2-Ag2 pair; Fig. 3b and Fig. S5, ESI†). The original 1D channels $(10.4 \times 13.0 \text{ Å}^2)$ along the crystallographic b axis in **AgBTB** were partitioned by the dpey with horizontal and vertical modes, affording two rectangular 1D solvent channels (types **A** and **B**; Fig. 3b). Channel **A** (3.7 \times 11.6 Å²) was generated by the insertion of dpey into linkage site 1, resulting in horizontally partitioned channels. In contrast, the vertically partitioned channel **B** (3.8 \times 9.8 \mathring{A}^2) was created by embedding dpey in linkage site 3. Notably, embedding of the length-mismatched dpey linker at linkage site 3

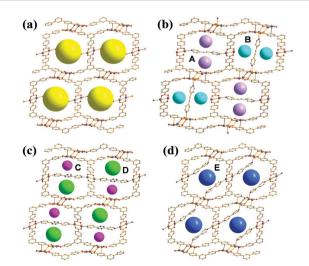


Fig. 3 (a) 1D channels of **AgBTB** and the PSPs through the insertions of the dipyridyl linkers in (b) **AgBTB-dpey**. (c) **AgBTB-dpt**, and (d) **AgBTB-bpy**.

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induced a significant contraction in the unit cell along the c-axis and a $\sim 5\%$ reduction in **AgBTB-dpey** unit cell volume compared to that of **AgBTB** (Table S1, ESI†). It should be noted that the total amount of dpey inserted was $\sim 75\%$ of the maximum amount. While linkage site 1 was almost fully occupied, only 55% of linkage site 3 was occupied in the single crystal structure. The inserted dpey linker content in the **AgBTB-dpey** framework was estimated to be $\sim 74\%$ from the ¹H NMR spectrum of the digested sample (Fig. S8, ESI†). This value is in good agreement with the average site occupancy of the dpey linkers in the single crystal structure.

The length of dpt is \sim 16.0 Å (with two \sim 2.4 Å Ag–N bonds); thus, it was expected that linkage site 2 would be the preferred insertion site. Structural analysis of **AgBTB-dpt** revealed that post-synthetic insertion of the dpt linker occurred exclusively at linkage site 2 with a site occupancy of 0.74 (Fig. 3c and Fig. S6, ESI†). In contrast to **AgBTB-dpey**, insertion of the dpt linker into linkage site 2 showed little effect on the unit cell parameters and volume of **AgBTB-dpt** (Table S1, ESI†). The inserted dpt linker partitioned the original 1D channel into two 1D rectangular channels—3.6 \times 11.9 and 5.2 \times 12.3 Ų in size for channels C and D, respectively. The ¹H NMR spectrum of digested **AgBTB-dpt** suggested that the inserted dpt linker content was as high as 63% of the theoretical maximum, slightly lower than the site occupancy of dpt linkers determined via single crystal structure refinement (Fig. S9, ESI†).

The length of bpy (\sim 12.0 Å, including two 2.4 Å Ag–N bonds) is well-matched with the short-length linkage site 5 (\sim 11.6 Å). As expected, the insertion of bpy was found to occur only at linkage site 5 with a site occupancy of \sim 0.8 (Fig. 3d and Fig. S7, ESI†). The insertion of bpy linkers into all linkage site 5 locations within the 1D channel of **AgBTB** formed the 1D channel **E** with dimensions of 5.2 \times 12.6 Å². Similar to dpt insertion, bpy induced no significant rearrangement of the framework. Therefore, the unit cell parameters and volume of the **AgBTB-bpy** single crystal were very similar to those of **AgBTB** (Table S1, ESI†). The bpy content estimated from the ¹H NMR spectrum of digested **AgBTB-bpy** was \sim 1.06 (Fig. S10, ESI†), indicating that all the linkage sites were fully occupied by bpy linkers, as determined *via* crystal structure analysis.

It should be noted that the length of the inserted linker is essential for framework rearrangement during linker insertion. As demonstrated, only the dpey linker causes significant contraction of the 1D channel and subsequent reorganization of the framework due to insertion of the length-mismatched linker into linkage site 3 (Table S1 and Fig. S5b, ESI†). In contrast, both dpt and bpy linkers localized to length-matched linkage sites in the framework, exerting negligible effects on the structure reorganization.

AgBTB-dpey, **AgBTB-dpt**, and **AgBTB-bpy** prepared in N,N-dimethylformamide (DMF) released substantial amounts of dipyridyl linkers during solvent exchange with methylene chloride. Therefore, **AgBTB-dpey(x)**, **AgBTB-dpt(x)**, and **AgBTB-bpy(x)** crystals were obtained via immersing **AgBTB** crystals into x mL of either 1 or 2 mM methylene chloride solution containing the dipyridyl linkers, where x denotes the volume of methylene

chloride solution. It should be noted that the amounts of inserted linkers were lower than those of crystals prepared in DMF (Fig. S11, ESI†). Interestingly, the PXRD pattern of AgBTBdpey(40) differs from that of AgBTB-dpey prepared in DMF (Fig. S4, ESI†). This structural discrepancy may be attributed to the lower site occupancies of the linkage sites 1 and 3 in AgBTBdpey(40). Because the total amount of the dpey inserted in AgBTB-dpey(40) is much smaller than that of AgBTB-dpey, both linkage sites 1 and 3 on AgBTB-dpey(40) are likely to have lower site occupancies. In particular, the low site occupancy of lengthmismatched linkage site 3 did not cause the framework contraction, resulting in a PXRD pattern similar to that of the parent framework AgBTB. Meanwhile, the AgBTB-dpt(40) and AgBTB-bpy(40) PXRD patterns are similar to those prepared in DMF. For the gas sorption experiments, activated AgBTBdpey(x)a, AgBTB-dpt(x)a, and AgBTB-bpy(x)a were prepared in vacuum at 298 K for 1 day to minimize pore collapse.

Activated AgBTB (AgBTB-a) showed no N2 uptake at 77 K and minor CO₂ uptake (up to $\sim 10 \text{ cm}^3 \text{ g}^{-1}$) at 195 K (Fig. S12, ESI†). Meanwhile, the N_2 uptake of **AgBTB-dpey(10)a** with $\sim 25\%$ site occupancy was $\sim 98 \text{ cm}^3 \text{ g}^{-1}$ at relative pressure $P/P_0 = 1$, reaching ~ 137 cm³ g⁻¹ for **AgBTB-dpey(40)a** with $\sim 48\%$ site occupancy (Fig. 4a). The BET specific surface areas were calculated as 503 and 342 m² g⁻¹ for AgBTB-dpey(40)a and AgBTBdpey(10)a, respectively. At 195 K, the CO2 isotherms exhibited stepwise adsorption and hysteresis during desorption, which becomes evident for AgBTB-dpey(40)a (Fig. 4b). The CO₂ adsorption amounts at 1 bar increased from ~ 118 cm³ g⁻¹ for AgBTB-dpey(10)a to $\sim 160 \text{ cm}^3 \text{ g}^{-1}$ for AgBTB-dpey(40)a. However, at 273 and 298 K the CO₂ isotherms exhibited neither stepwise adsorption nor hysteresis (Fig. S13, ESI†). The stepwise adsorption is likely due to stability differences between partitioned channels A and B in the AgBTB-dpey framework. Highly populated dpey linkers in channel A effectively prevented pore collapse during activation to a larger extent than the less populated dpey linkers in channel B. The stepwise

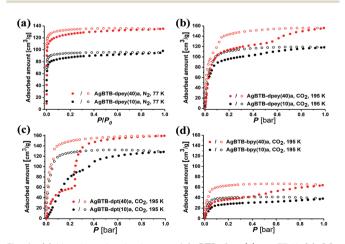


Fig. 4 (a) N_2 adsorption isotherms of **AgBTB-dpey(x)a** at 77 K. (b) CO_2 adsorption isotherms of **AgBTB-dpey(x)a**, (c) **AgBTB-dpt(x)a**, and (d) **AgBTB-bpy(x)a** at 195 K (filled circles: adsorption; empty circles: desorption).

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adsorption observed at \sim 0.6 bar is likely a result of the recovery of the partially collapsed pore upon CO₂ adsorption. The N₂ and CO₂ adsorption results demonstrated that the PSP approach accomplished *via* post-synthetic dpey insertion enhanced the structural stability of **AgBTB-dpey(x)a** over that of **AgBTB**.

For AgBTB-dpt(x)a, neither AgBTB-dpt(10)a nor AgBTBdpt(40)a showed any N2 uptake at 77 K (Fig. S14, ESI†). Even though the site occupancies of the dpt linkers, $\sim 35\%$ and $\sim 48\%$ for AgBTB-dpt(10)a and AgBTB-dpt(40)a, respectively (Fig. S11, ESI†), are comparable to those of the corresponding **AgBTB-dpey**(x)**a** moieties, the frameworks were not sufficiently stable upon activation. The site 2 linkage between the off-plane Ag1-Ag1 pair across the 1D channel resulted in inefficient partitioning of the 1D channel, leading to pore collapse in AgBTB-dpt(x) during activation. However, at 195 K AgBTBdpt(x) exhibited stepwise CO_2 adsorption behavior with hysteresis, which is pronounced for AgBTB-dpt(40)a (Fig. 4c). The CO₂ adsorption at 1 bar increased from $\sim 130 \text{ cm}^3 \text{ g}^{-1}$ for AgBTBdpt(10)a to ~160 cm³ g⁻¹ for AgBTB-dpt(40)a. This stepwise adsorption can be attributed to the degree of recovery of the collapsed channels. The smaller channel C (3.6 \times 11.9 Å²) is likely restored at lower CO2 pressures, followed by the recovery of the larger channel **D** (5.2 \times 12.3 Å²) at higher CO₂ pressures. At 273 and 298 K, the recovery of both channels is ineffective, and CO_2 uptakes were ~ 35 and 17 cm³ g⁻¹ at 273 and 298 K, respectively, for AgBTB-dpt(40)a (Fig. S15, ESI†).

Similarly, the bpy linkers in AgBTB-bpy(10)a and AgBTBbpv(40)a occupied 22% to 36% of the potential linkage sites, showing no N2 uptake at 77 K (Fig. S16, ESI†). The CO2 adsorption of AgBTB-bpy(10)a measured at 195 K exhibited a type I isotherm curve, with total CO₂ uptake of ~ 40 cm³ g⁻¹ (Fig. 4d). The total CO2 uptake for AgBTB-bpy(40)a reached \sim 65 cm³ g⁻¹ due to the increased linkage site occupancy of the bpy linkers. Stepwise adsorption was observed along with hysteresis, which can be rationalized using the same argument discussed earlier. The presence of the bpy linker in the framework of AgBTB-bpy(40)a allowed for initial CO₂ adsorption up to ~ 0.35 bar. At pressure of > 0.35 bar, recovery of the collapsed solvent channels can occur. At 273 and 298 K, gradually increasing CO2 uptake is observed with increasing amounts of bpy linkers. The maximum CO2 uptakes for AgBTB**bpy(40)a** were ~ 15 and 10 cm³ g⁻¹ at 273 and 298 K, respectively (Fig. S17, ESI†).

In summary, rare examples of permanently porous Ag(1)-based MOFs were prepared herein using the PSP approach *via* post-synthetic insertion of auxiliary dipyridyl linkers. The dipyridyl linkers determined the partitioning modes of the original 1D channel in the parent **AgBTB** framework and enhanced framework stability. Consequently, permanent porosities of the prepared MOFs (**AgBTB-dpey**, **AgBTB-dpt**, and **AgBTB-bpy**) were

achieved. The stability and porosity of the frameworks could be adjusted by the amount and type of linkers added.

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Conflicts of interest

There are no conflicts to declare.

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