We present a crystal engineering strategy to fine tune the pore chemistry and CH$_4$ storage performance of a family of isomorphic MOFs based upon PCN-14. These MOFs exhibit similar pore size, pore surface, and surface area (around 3000 m$^2$ g$^{-1}$) and were prepared with the goal to enhance CH$_4$ working capacity. [Cu$_2$(L2)(H$_2$O)$_5$]$_n$ (NJU-Bai 41: NJU-Bai for Nanjing University Bai’s group), [Cu$_2$(L3)(H$_2$O)$_5$]$_n$ (NJU-Bai 42), and [Cu$_2$(L4)(DMF)$_5$]$_n$ (NJU-Bai 43) were prepared and we observed that the CH$_4$ volumetric working capacity and volumetric uptake values are influenced by subtle changes in structure and chemistry. In particular, the CH$_4$ working capacity of NJU-Bai 43 reaches 198 cm$^3$ (STP: 273.15 K, 1 atm) cm$^{-3}$ at 298 K and 65 bar, which is amongst the highest reported for MOFs under these conditions and is much higher than the corresponding value for PCN-14 (157 cm$^3$ (STP) cm$^{-3}$).

Natural gas, primarily composed of CH$_4$, is an increasingly important energy source thanks to its relatively benign environmental footprint, its high natural abundance, and its inherent economic advantages. However, the widespread use of natural gas for mass vehicular transport remains hindered by its low energy density under ambient conditions even when compressed at pressures as high as 250 atm (CNG). Adsorptive gas storage (ANG) offers a promising solution by affording higher energy density at much lower pressures, such as 35–65 atm. Amongst the diverse range of porous adsorbents that have been studied with respect to ANG, metal–organic frameworks (MOFs) have emerged as particularly promising materials because they can exhibit extra-large surface areas and their modularity facilitates structural fine-tuning to enhance specific properties. Since the pioneering work of Kitagawa’s group, many MOFs with high volumetric methane uptake have been synthesized and characterized. However, it is the volumetric working capacity, the CH$_4$ uptake between storage and deliverable pressure, that is considered the crucial parameter for evaluating the practical utility of adsorbents for ANG. This is especially the case for light-duty vehicles with little space available for on-board fuel storage.

The uptake at storage pressures is determined largely by the gravimetric surface area and pore diameter of the adsorbent with optimal values typically between 2500–3000 m$^2$ g$^{-1}$ and approximately 8 Å, respectively. Low-pressure volumetric uptake is controlled by the strength of interactions, $Q_s$, between the surface of the adsorbent and CH$_4$, which is in turn affected by pore size and pore chemistry unless the adsorbent in question is flexible and exhibits no uptake at low pressure. High $Q_s$ in MOFs is generally undesirable in the context of gas storage in general, and ANG in particular, since it typically leads to relatively high uptake at low pressure, thereby reducing working capacity. Herein, we present a crystal-engineering strategy to fine tune the pore chemistry of a family of isomorphic MOFs with similar pore size, pore surface properties, and surface area (around 3000 m$^2$ g$^{-1}$). We thereby gain insight into the structure–property relationships of these and related MOFs in such a manner that we enable a decrease in low-pressure CH$_4$ uptake coupled with an increase in high-pressure uptake.
PCN-14 is a member of the MOF-505 family that exhibits high volumetric CH$_4$ uptake and it is a good target for fine tuning of pore size and chemistry in order to improve CH$_4$ storage performance because of the nature of its organic ligands. Previously, we finely tuned MOF-505 variants with respect to enhancing their performance for C$_2$H$_2$ storage.$^{[10]}$ Herein, we target PCN-14 variants in order to address its CH$_4$ working capacity. [Cu$_2$(L2)(H$_2$O)$_2$]$_n$ (NJU-Bai 41: NJU-Bai for Nanjing University Bai’s group), [Cu$_2$(L3)(H$_2$O)$_2$]$_n$ (NJU-Bai 42) and [Cu$_2$(L4)(DMF)$_2$]$_n$ (NJU-Bai 43; for L2–L4 see Scheme 1) were prepared in order to tune pore sizes, pore surface and surface area. Interestingly, we observed that the CH$_4$ volumetric working capacity and volumetric uptake values were impacted by the subtle changes we imposed in structure and chemistry. In particular, the CH$_4$ working capacity of NJU-Bai 43 can reach 198 cm$^3$(STP:2 73.15 K, 1 atm) cm$^{-3}$ at 298 K and 65 bar, which is amongst the highest reported for MOFs under these conditions and is much higher than the corresponding value for PCN-14 (157 cm$^3$ (STP) cm$^{-3}$).

To understand these results it is necessary to address the structure of PCN-14, which is composed of large spherical cages and shuttle-shaped cages alternately stacked in a 1:1 ratio in a manner similar to that of MOF-505 (Figure S1 in the Supporting Information).$^{[11]}$ The major difference between PCN-14 and MOF-505 is that the anthracene group of PCN-14 divides the shuttle-shaped cage into three sub cages with diameters of about 6, 10, and 6 Å, offering an opportunity to optimize pore structure through ligand “slimming”. NJU-Bai 41 was obtained by substituting anthracene with naphthalene. As revealed by Figure 1, the naphthalene rings are perpendicular to the phenylisophthalate rings, expanding the corresponding three sub cages into three parts with optimized diameters of about 8, 12, and 8 Å, that are close to multiples of the CH$_4$ kinetic diameter (3.8 Å).

To decrease the interaction of the framework walls with CH$_4$, we polarized the pore surface and enlarged the smaller sub cages. The slender oxamide group afforded NJU-Bai 42 with a partition-less shuttle-shaped cage (13 X 27 Å). The pyridyl moiety was introduced to replace half of the oxamide, leading to NJU-Bai 43, which exhibits a larger shuttle-shaped cage of 13x30 Å. Calculations conducted using Materials Studio with a probe radius of 1.2 Å indicate that NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43 have accessible pore volume of 69.7%, 74.2% and 76.8%, respectively.

The permanent porosities of NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43 were confirmed by the N$_2$ sorption isotherms at 77 K (Figure S8–S10), which exhibit type-I character with saturated uptakes of 628, 692, and 786 cm$^3$g$^{-1}$, respectively. The total pore volumes calculated from the N$_2$ adsorption isotherms were 0.92, 1.07, and 1.22 cm$^2$g$^{-1}$. The Brunauer-Emmett-Teller (BET) surface areas were calculated to be

![Scheme 1. Schematic structures of the organic ligands used to construct MOF-505 (H$_4$L), PCN-14 (H$_4$L1), NJU-Bai 41 (H$_4$L2), NJU-Bai 42 (H$_4$L3), and NJU-Bai 43 (H$_4$L4).](image)

![Figure 1. The development from PCN-14 to NJU-Bai 43. The organic linkers, cage size, pore surface properties, and the gravimetric surface area are optimized in a systematic manner.](image)
2370, 2830, and 3090 m² g⁻¹, respectively. The structural integrity of these activated MOFs was confirmed by PXRD data (Figure S2–S4).

To systematically evaluate the effects of the changing pore size, the pore surface and surface area on adsorption of CH₄, high-pressure adsorption measurements were performed using a Sieverts-type instrument developed at NIST (National Institute of Standards and Technology, USA). [12] Compared with PCN-14, NJU-Bai 41 exhibits improved volumetric uptake capacity (245 for NJU-Bai 41 vs. 230 cm³ (STP) cm⁻³ for PCN-14, Figure 2) and enhanced working capacity (172 vs. 157 cm³ (STP) cm⁻³, 5 bar as the minimum desorption pressure) and higher gravimetric storage capacity (0.236 g g⁻¹ vs. 0.193 g g⁻¹), at 65 bar and 298 K. We attribute this improvement in uptake and working capacity to the optimized pore size of NJU-Bai 41, which enables highly efficient space utilization. [6,7,8] Specifically, NJU-Bai 41 exhibits pore sizes of about 8 and 12 Å, suitable for two and three CH₄ molecules to be closely packed, respectively.

However, a high amount of CH₄ is adsorbed (73 cm³ (STP) cm⁻³) at 5 bar and 298 K (Figure 2), so NJU-Bai 41 exhibits a relatively poor working capacity of 172 cm³ (STP) cm⁻³ vs. HKUST-1 (190 cm³ (STP) cm⁻³) and MAF-38 (187 cm³ (STP) cm⁻³). [6,7] Given that low-pressure uptake is mainly controlled by sorbent-sorbate interactions, [7,8] it is reasonable to assert that smaller pore size and aromatic rings may be the reason for the high CH₄ binding energy of PCN-14 and NJU-Bai 41. We therefore created a hydrophilic cage with larger pore size to decrease CH₄-framework interactions by introducing slender oxamide moieties into the framework, NJU-Bai 42 (previously we reported as HNUST-3). [13] A larger shuttle-shaped cage decorated with polar amide moieties was thereby formed and the gravimetric storage capacity improved from 0.236 g g⁻¹ (NJU-Bai 41) to 0.254 g g⁻¹ (NJU-Bai 42). Interestingly, the amount of CH₄ adsorbed at 5 bar decreases from 73 to 53 cm³ (STP) cm⁻³ whereas the CH₄ uptake at 65 bar increases to 247 cm³ (STP) cm⁻³ (355.5 cm³ g⁻¹). NJU-Bai 42 therefore exhibits a high volumetric methane working capacity of 193 cm³ (STP) cm⁻³. This value is higher than that of HKUST-1 and most other MOFs and is only slightly lower than UTSA-76 and Co(bdp) under the same conditions (Table S2). That the optimal gravimetric surface area for CH₄ storage is around 3000 m² g⁻¹ prompted us to further expand NJU-Bai 42 by replacing one amide moiety with a pyridine ring to afford NJU-Bai 43. [8]

At 65 bar and 298 K, the NJU-Bai 43 was observed to exhibit high volumetric storage capacity of 254 cm³ (STP) cm⁻³ (Figure 2; 397.5 cm³ g⁻¹), which corresponds to the amount of methane stored in a CNG tank at 235 bar. Thus, NJU-Bai 43 effectively reduces the pressure required for CNG by a factor of 3.6 down to 65 bar. Furthermore, at 65 bar and room temperature, a tank filled with NJU-Bai 43 would deliver almost four times more methane than the same tank just filled with methane. From 35 to 65 bar, the uptake capacity of NJU-Bai 43 increases by 52 cm³ (STP) cm⁻³, while that of NJU-Bai 42 is 44 cm³ (STP) cm⁻³ (Table 1). The volumetric working capacity of NJU-Bai 43 at 298 K is 198 cm³ (STP) cm⁻³ for adsorption between 65 and 5 bar, which is among the highest values of CH₄ working capacity yet reported in the context of ANG.

A recent theoretical analysis of a database utilizing over 650000 MOFs predicted that theoretical-maximum 65 bar working capacity is unlikely to exceed 200 cm³ (STP) cm⁻³. [8] Though the volumetric working capacities of UTSA-76 and Co(bdp) can reach 197 cm³ (STP) cm⁻³ at 65 bar and 298 K, the gravimetric working capacity of NJU-Bai 43 is at least 10% higher than that of UTSA-76 and Co(bdp) (0.221 g g⁻¹ vs. 0.201 and 0.196 g g⁻¹ in UTSA-76 and Co(bdp), respectively). [6,7] The gravimetric storage capacity of NJU-Bai 43 (0.283 g g⁻¹) also surpasses three of the currently best performing MOFs for CH₄ storage, HKUST-1 (0.216 g g⁻¹), [6d] MAF-38 (0.247 g g⁻¹), and MOF-519 (0.172 g g⁻¹). [6d] but is lower than several MOFs with low crystal densities and large pore volumes, such as MOF-177 and NU-111. [6l,14] These values for gravimetric and volumetric working CH₄ storage performance place NJU-Bai 43 among the best performing MOFs for ANG and reveal how fine-tuning of pore chemistry and structure can be an effective strategy for boosting the volumetric and gravimetric CH₄ uptakes as well as working capacity.

Further analysis of the volumetric CH₄ adsorption isotherms of the three MOFs studied herein revealed interesting temperature effects (Table 1). [8,15] Specifically, the volumetric CH₄ storage working capacity for NJU-Bai 41 decreases from 172 cm³ (STP) cm⁻³ to 161 cm³ (STP) cm⁻³ when temperature is decreased from 298 to 273 K at working pressures between 65 bar and 5 bar. For NJU-Bai 42, the data is almost unchanged whereas for NJU-Bai 43 working capacity increases from 198 cm³ (STP) cm⁻³ to 205 cm³ (STP) cm⁻³. We attribute this apparent inconsistency with the smaller pore volume and smaller pore size of NJU-Bai 41 causing the CH₄ uptake to be higher in the 5 bar range and saturated close to 65 bar at 273 K. The opposite is NJU-Bai 43 because of its higher pore volume and larger internal surface. Its uptake is therefore relatively less at 5 bar versus 65 bar, leading to enhanced working capacity when the temperature is decreased. This rare behavior may increase the application

![Figure 2](https://example.com/figure2.png)

**Figure 2.** The experimental total volumetric methane-storage capacities at 65 bar and 298 K of the investigated MOFs and PCN-14.
range of NJU-Bai 43 unlike HKUST-1 and other MOFs including UTSA-76 (Table S3).\[6d\]

To obtain a better insight into the origin of the enhanced CH₄ storage performance we examined the Qₑ from the temperature-dependent isotherms (Figure S23). The zero-coverage CH₄ adsorption enthalpies of NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43 were calculated to be 17.77, 14.49 and 14.45 kJ mol⁻¹, respectively. CH₄ affinity is decreased after sub cage elimination and pore polarization. Indeed, the 5 bar CH₄ uptake of NJU-Bai 42 is the smallest compared to NbO-net MOFs with similar pore volume and framework density (Table S4). Considering larger pore size, higher pore volume and low open Cu density, we supposed that NJU-Bai 43 would exhibit smaller CH₄ Qₑ and lower uptake at 5 bar. However, the Qₑ of NJU-Bai 43 is similar to that of NJU-Bai 42 and falls into the range of 12–15 kJ mol⁻¹ that is expected for MOFs without strong CH₄ binding sites.\[6] The 5 bar uptake in NJU-Bai 43 is slightly increased (56 cm³(STP) cm⁻³ for NJU-Bai 43 vs. 53 cm³(STP) cm⁻³ for NJU-Bai 42). Conversely, under high pressure, surface area becomes a more important factor in CH₄ uptake\[6c] as exemplified by NJU-Bai 43.

To gain further insight, we simulated CH₄ adsorption in all three materials and found that the trend in the uptake at 298 K and 5 atm is NJU-Bai 41 > NJU-Bai 43 > NJU-Bai 42. The simulated volumetric adsorption isotherms for all three MOFs are given in Figure S26. The theoretical volumetric working capacities (from 5–35 atm and 5–65 atm) at 298 K based on GCMC simulations of CH₄ adsorption are summarized in Table S6. These working capacities are comparable to the corresponding experimental values shown in Table 1. In addition, the theoretical working capacities from both 5–35 atm and 5–65 atm display the same overall trend as experiment, which is NJU-Bai 43 > NJU-Bai 42 > NJU-Bai 41. Simulated annealing calculations for a single CH₄ molecule within NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43 reveal that the most favorable CH₄ binding site in all three MOFs is located within a triangular region enclosed by three isophthalate groups (Figure S26). Canonical Monte Carlo (CMC) simulations suggest that the trend in the MOF-CH₄ interaction at low loading is the following: NJU-Bai 41 > NJU-Bai 43 > NJU-Bai 42. The interaction energy for the adsorption of CH₄ about the triangular region is slightly higher for NJU-Bai 43 relative to NJU-Bai 42; this could be due to the fact that the space within the neck of the shuttle-shaped cage (i.e., the region of the cage enclosed by three linkers) is extended and narrower for NJU-Bai 43 (see Figure S33), which allows for the CH₄ molecules to interact with more atoms of the framework simultaneously, leading to slightly increased MOF-CH₄ interactions. CMC simulations in all three MOFs at higher pressures also reveal the same trend in the MOF-CH₄ interaction (Table S6). Under these conditions, the CH₄ molecules essentially crowd into the void space of each MOF as revealed by our simulations (see Figures S34–S36).

In conclusion, fine-tuning of MOF-505 analogues has enabled decreased low-pressure CH₄ uptake combined with increased high-pressure CH₄ uptake and resulted in enhancement of the performance of PCN-14 in terms of the volumetric CH₄ uptake and working capacity. NJU-Bai 43 is currently among the best-performing MOFs for CH₄ storage, with a working capacity of 198 cm³(STP) cm⁻³ at 65 bar and 298 K. NJU-Bai 43 also exhibits a high gravimetric storage capacity, indeed the highest amongst MOFs with volumetric working capacity above 190 cm³(STP) cm⁻³ between 65 bar and 5 bar at 298 K.

**Acknowledgements**

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** amide ligands · copper · metal–organic frameworks · methane storage · MOF-505 analogues

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Table 1: Methane adsorption characteristics of the investigated MOFs.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>S_{BET}^{[4]} cm⁻² g⁻¹</th>
<th>V_{ tot}^{[4]} cm³ g⁻¹</th>
<th>Q_{e}^{[4]} cm³ cm⁻³ [298 K]</th>
<th>Total uptake⁴ at 65 [35] bar cm³ cm⁻³ [298 K]</th>
<th>Working capacity⁴ at 65 bar cm³ cm⁻³ [298 K]</th>
<th>Qₑ cm⁻³ [273 K] cm³ cm⁻³ [298 K]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCN-14</td>
<td>2170</td>
<td>0.85</td>
<td>0.829</td>
<td>0.193 (0.163)</td>
<td>230 (195)</td>
<td>140</td>
<td>157</td>
</tr>
<tr>
<td>NJU-Bai 41</td>
<td>2370</td>
<td>0.92</td>
<td>0.741</td>
<td>0.236 (0.196)</td>
<td>245 (204)</td>
<td>161</td>
<td>172</td>
</tr>
<tr>
<td>NJU-Bai 42</td>
<td>2830</td>
<td>1.07</td>
<td>0.693</td>
<td>0.254 (0.209)</td>
<td>247 (203)</td>
<td>192</td>
<td>193</td>
</tr>
<tr>
<td>NJU-Bai 43</td>
<td>3090</td>
<td>1.22</td>
<td>0.639</td>
<td>0.283 (0.225)</td>
<td>254 (202)</td>
<td>205</td>
<td>198</td>
</tr>
<tr>
<td>NU-111</td>
<td>4930</td>
<td>2.09</td>
<td>0.409</td>
<td>0.360 (0.241)</td>
<td>206 (138)</td>
<td>239</td>
<td>179</td>
</tr>
<tr>
<td>MOF-177</td>
<td>4700</td>
<td>1.83</td>
<td>0.427</td>
<td>0.311 (0.292)</td>
<td>186 (125)</td>
<td>–</td>
<td>167[3]</td>
</tr>
<tr>
<td>Co(bdp)</td>
<td>2911</td>
<td>0.652</td>
<td>0.716</td>
<td>(0.144)</td>
<td>203 (161)</td>
<td>–</td>
<td>197</td>
</tr>
</tbody>
</table>

[a] BET surface areas calculated from N₂ isotherms at 77 K. [b] Pore volumes calculated from the maximum amounts of N₂ adsorbed. [c] Framework densities without guest molecules and terminal molecules. [d] At 298 K and 65 (35) bar. [e] Defined as the difference of the amount of methane adsorbed between 65 bar and 5 bar.
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Supporting Information

Fine Tuning of MOF-505 Analogues to Reduce Low-Pressure Methane Uptake and Enhance Methane Working Capacity

Mingxing Zhang, Wei Zhou, Tony Pham, Katherine A. Forrest, Wenlong Liu, Yabing He, Hui Wu, Taner Yildirim, Banglin Chen, Brian Space, Yi Pan, Michael J. Zaworotko, and Junfeng Bai*

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S1. Materials and Instrumentation

Commercially available reagents were used as received without further purification. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240 analyzer. The IR spectra were obtained on a VECTOR TM 22 spectrometer with KBr pellets in the 4000–400 cm$^{-1}$ region. $^1$H NMR spectra were recorded on a Bruker DRX-500 spectrometer with tetramethylsilane as an internal reference. Thermogravimetric analyses (TGA) were performed under N$_2$ atmosphere (100 mL/min) with a heating rate of 5 °C/min using a 2960 SDT thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected over the 2θ range 5 ~ 40° on a Bruker axs D8 Advance diffractometer using Cu Kα radiation (λ = 1.5418 Å) with a routine power of 1600 W (40 kV, 40 mA) in a scan speed of 0.2 deg/s at room temperature. A Micromeritics ASAP 2020 was used to measure gas adsorption isotherms. High-pressure CH$_4$ adsorption isotherms were collected using a Sieverts-type apparatus developed at NIST. Selected samples were further measured using a commercial Rubotherm ISOSERP-HyGpra+V instrument at NJU for additional confirmation.
S2. Ligand Synthesis

Synthetic routes to the organic linker H₄L₂

![Synthetic routes diagram]

5,5’-(naphthalene-1,5-diyl)diisophthalic acid (H₄L₂)

1,5-diiodonaphthalene (1.9 g, 5 mmol), (3,5-bis(methoxycarbonyl)phenyl)boronic acid (2.62 g, 11 mmol), CsF (3.04g, 20 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.3 g, 0.26 mmol) were dissolved in dimethoxyethane (60 mL) under N₂ atmosphere. The mixture was stirred at 343 K for two days. The reaction was cooled to room temperature then diluted with CH₂Cl₂ and filtered. The filtrate was washed with water and organic layer dried with MgSO₄ and concentrated. The concentrate was purified by column chromatography to obtain tetramethyl 5,5’-(naphthalene-1,5-diyl)diisophthalate. Yield: 70% (1.8 g).

Then, the tetramethyl 5,5’-(naphthalene-1,5-diyl)diisophthalate was suspended in 60 mL of THF/methanol mixed solvent, to which 30 mL 1M LiOH aqueous solution was added. After this mixture was stirred at 343 K for 24 hours, solvents were removed under vacuum, and diluted hydrochloric acid was added to the remaining aqueous solution until it became acidic (pH = 2). The precipitate was collected by filtration, washed with water and dried under vacuum at 353 K to give H₄L₂ as white solid. Yield: 87% (1.3 g).¹H NMR (DMSO-d₆, δ ppm): 13.442 (broad peak, COOH), 8.603 (s, 4H, ArH), 8.253 (s, 2H, ArH), 7.823 (d, 2H, ArH), 7.650 (t, 2H, ArH), 7.596 (d, 2H, ArH). MS (ESI) m/z [M+Na]⁺: 480.00.
Synthetic routes for the organic linker H₄L₃

![Synthetic routes diagram for H₄L₃]

5,5′-(oxalylbis(azanediyl))diisophthalic acid (H₄L₃)

In a dried 500 mL round bottom flask was added 5-aminoisophthalic acid (29 g, 160 mmol) and dry DMA (200 mL). The mixture was stirred under N₂ atmosphere at 273 K, then 40 mL oxalyl chloride in methylene chloride was added dropwise. The resulting mixture was stirred for 12 hours at room temperature under N₂ atmosphere. The precipitated solid was isolated by filtration and washed with 2 M hydrochloric acid followed by water to obtain H₄L₃ (25 g, 75%) after overnight drying under vacuum. ¹H NMR (DMSO-d₆, δ ppm): 13.315 (broad peak, COOH), 11.258 (s, 2H, CONH), 8.725 (s, 4H, ArH), 8.277 (d, 2H, ArH).

Synthetic routes for the organic linker H₄L₄

![Synthetic routes diagram for H₄L₄]

5-(5-((3,5-dicarboxyphenyl)carbamoyl)pyridin-2-yl)isophthalic acid (H₄L₄)
In a 100 mL round-bottomed flask was added 6-bromonicotinic acid (2.02 g, 10.0 mmol) and SOCl₂ (40.0 mL, 0.55 mol). DMF (3 drops) was carefully added dropwise, and the mixture was stirred and heated at 50 °C for 6 h under N₂ atmosphere. The excess SOCl₂ was removed under vacuum in a well-ventilated hood. The residual 6-bromonicotinoyl chloride was used without further purification and dissolved in anhydrous CH₂Cl₂ (20 mL) and added dropwise to a solution of 5-aminoisophthalic acid (2.09 g, 10.0 mmol) in CH₂Cl₂ (20 mL). The resulting mixture was stirred at room temperature for 12 h and then refluxed for 1 h. The excess CH₂Cl₂ was removed under vacuum and the obtained white solid was washed with 2 M hydrochloric acid followed by Na₂CO₃ solution and water. After the recrystallization in a mixed solvent consisting of methanol and ethanol, the white solid was dried under vacuum to obtain dimethyl 5-(6-bromonicotinamido)isophthalate (3.2 g, 81% yield). 1H NMR (DMSO-d₆, δ ppm): 11.203 (s, 1H, CONH), 8.891 (s, 1H, ArH), 8.849 (d, 2H, ArH), 8.995 (s, 1H), 8.248 (s, 1H), 8.106 (s, 1H), 3.921 (s, 6H).

Dimethyl 5-(6-bromonicotinamido)isophthalate (1.96 g, 5 mmol), K₂CO₃ (4.14 g, 30 mmol), (3,5-bis(ethoxycarbonyl)phenyl)boronic acid (2.0 g, 7.5 mmol) and tetrakis(triphenylphosphine) palladium(0) (0.3 g, 0.26 mmol) were dissolved in tetrahydrofuran (60 mL) and water (30 mL) under N₂ atmosphere. The mixture was stirred at 343 K for two days. After that, the precipitate was collected by filtration, washed with tetrahydrofuran and methanol for several times, and then recrystallized in toluene and methanol to obtain the diethyl 5-(5-(3,5-bis(methoxycarbonyl)phenyl) carbamoyl)pyridin-2-yl)isophthalate. Yield: 51.3% (1.3 g). 1H NMR (CDCl₃, δ ppm): 9.311 (s, 1H, ArH), 8.872 (s, 2H, ArH), 8.804 (s, 1H, ArH), 8.748 (s, 1H, ArH), 8.608 (s, 2H, ArH), 8.469 (s, 1H, ArH), 8.416 (d, 1H, ArH), 7.976 (d, 1H, ArH), 3.996 (s, 6H, -CH₃), 3.947 (s, 6H, -CH₃).

Then, the diethyl 5-(5-(3,5-bis(methoxycarbonyl)phenyl) carbamoyl)pyridin-2-yl)-isophthalate was suspended in 40 mL of tetrahydrofuran/methanol mixed solvent, to which 20 mL 1M LiOH aqueous solution was added. After this mixture was stirred at 343 K for 24 hours, solvents were removed under vacuum, and diluted hydrochloric
acid was added to the remaining aqueous solution until it became acidic (pH = 2). The precipitate was collected by filtration, washed with water and dried under vacuum at 353 K to give **H_{4}L_{4}** as yellow solid. Yield: 90% (1.0 g). ¹H NMR (DMSO-δ, δ ppm): 13.582 (broad peak, COOH), 10.916 (s, 1H, CONH), 9.312 (s, 1H, ArH), 8.950 (s, 2H, ArH), 8.712 (s, 2H, ArH), 8.582 (s, 1H, ArH), 8.578 (d, 1H, ArH), 8.372 (d, 1H, ArH), 8.248 (s, 1H, ArH). MS (ESI) m/z [M+Na⁺]: 477.17.

**S3. MOF Synthesis**

**Synthesis of NJU-Bai 41**

H_{4}L_{2} (10.0 mg) and Cu(NO_{3})_{2}·3H_{2}O (20 mg) were dissolved in 2.8 mL solvent of DMF/Water (5:2) in a vessel, to which 0.04 mL hydrochloric acid were added. The vessel was sealed and heated to 85 °C for 1 days and then cooled to room temperature at a rate of 5 °C/hour. Blue block crystals of **NJU-Bai 41** were filtered and washed with DMF. Yield 10.6 mg. Selected IR (cm⁻¹): 3396 (br, s), 1655(m), 1583 (vs), 1435 (m), 1390 (m), 1369 (w), 1252(m), 1097 (m), 1046 (m). Anal. Found: C, 46.72; H, 5.16; N, 4.80 %.

**Synthesis of NJU-Bai 42**

H_{4}L_{3} (10.0 mg) and Cu(NO_{3})_{2}·3H_{2}O (15 mg) were dissolved in 1.6 mL solvent of DMF/EtOH/Water/DMF (10:1:3:2) in a vessel, to which 0.15 mL HNO_{3} were added. The vessel was sealed and heated to 75 °C for 1 days and then cooled to room temperature at a rate of 5 °C/hour. Blue block crystals of NJU-Bai 41 were filtered and washed with DMF. Yield 8.5 mg. Selected IR (cm⁻¹): 3359 (br, s), 3082 (br, s), 2929 (br, s), 2807 (br, s), 2475 (br, s), 2360 (m), 1965 (vs), 1846 (m), 1635 (m), 1529 (w), 1373(m). Anal. Found: C, 36.81; H, 4.36; N, 8.53 %.
Synthesis of NJU-Bai 43

H$_4$L$_4$ (10.0 mg) and Cu(NO$_3$)$_2$·3H$_2$O (20 mg) were dissolved in 1.4 mL solvent of DMF/EtOH/Water (5:1:1) in a vessel, to which 0.06 mL HNO$_3$ were added. The vessel was sealed and heated to 85 °C for 1 days and then cooled to room temperature at a rate of 5 °C/hour. Blue block crystals of NJU-Bai 43 were filtered and washed with DMF. Yield 8.8 mg. Selected IR (cm$^{-1}$): 3394 (br, s), 2928 (m), 2492 (vs), 2360 (m), 1868 (m), 1654 (w), 1558(m), 1493 (m), 1436 (m), 1414 (m), 1101 (m). Anal. Found: C, 42.21; H, 4.41; N, 8.31%.

S4. Single Crystal X-Ray Crystallography

Single-crystal X-ray diffraction data were measured on a Bruker Apex II CCD diffractometer using graphite monochromated Mo/Kα radiation ($\lambda = 0.71073$ Å). Data reduction was made with the Bruker SAINT program. The structures were solved by direct methods and refined with full-matrix least squares technique using the SHELXTL package. Non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2 × $U_{eq}$ of the attached atom. The hydrogen atoms of the ligated water molecules could not be located. The unit cell includes a large region of disordered solvent molecules, which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE$^{[1]}$ to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; structures were then refined again using the data generated.

In the structure of NJU-Bai 43, the middle amide-phen moiety in the ligand is disordered over two positions. CCDC 1534097, 1534099 and 1534098 contain the supplementary crystallographic data for NJU-Bai 41, NJU-Bai 42 and NJU-Bai 43, respectively. The data can be obtained free of charge at
Table S1. Crystallographic data and structure refinement results for NJU-Bai 41, NJU-Bai 42 and NJU-Bai 43.

<table>
<thead>
<tr>
<th></th>
<th>NJU-Bai 41</th>
<th>NJU-Bai 42</th>
<th>NJU-Bai 43</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C$<em>{1}$H$</em>{6}$CuN$<em>{2}$O$</em>{2}$</td>
<td>C$<em>{54}$H$</em>{24}$Cu$<em>{6}$N$</em>{6}$O$_{36}$</td>
<td>C$<em>{22}$H$</em>{10}$Cu$<em>{2}$N$</em>{2}$O$_{11}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>305.73</td>
<td>1714.09</td>
<td>605.42</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>123</td>
<td>123</td>
<td>123</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Trigonal</td>
<td>Monoclinic</td>
<td>Trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>R-3m</td>
<td>P21/c</td>
<td>R-3m</td>
</tr>
<tr>
<td>a (Å)</td>
<td>18.4973(14)</td>
<td>28.1588(12)</td>
<td>18.484(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>18.4973(14)</td>
<td>18.5342(8)</td>
<td>18.484(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>39.459(6)</td>
<td>32.102(2)</td>
<td>45.277 A</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>90</td>
<td>112.335(5)</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>120</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>V (Å$^3$)</td>
<td>11692</td>
<td>15497.1(15)</td>
<td>13397(4)</td>
</tr>
<tr>
<td>Z</td>
<td>18</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>D$_{calc}$ (g cm$^{-3}$)</td>
<td>0.782</td>
<td>0.735</td>
<td>0.675</td>
</tr>
<tr>
<td>F(000)</td>
<td>2754</td>
<td>3408</td>
<td>2718</td>
</tr>
<tr>
<td>GOF</td>
<td>1.081</td>
<td>1.096</td>
<td>1.225</td>
</tr>
<tr>
<td>Rs</td>
<td>0.1197</td>
<td>0.1967</td>
<td>0.2794</td>
</tr>
<tr>
<td>R$<em>{1}$, wR$</em>{2}$: [I&gt;=2σ (I)]</td>
<td>0.0711, 0.2345</td>
<td>0.0834, 0.1900</td>
<td>0.1162, 0.3169</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e Å$^{-3}$)</td>
<td>0.639 and -0.431</td>
<td>2.671 and -1.217</td>
<td>1.027 and -0.875</td>
</tr>
</tbody>
</table>

S5. Gas Sorption Measurements

The solvent-exchanged sample was prepared by immersing the as-synthesized samples in dry acetone for 3 days to remove the nonvolatile solvates, and the extract was decanted every 8 hours and fresh acetone was replaced. The completely activated sample was obtained by heating the solvent-exchanged sample at 100 °C under a
dynamic high vacuum for 24 hours. During this time, the pale blue sample changed to a deep purple-blue color indicative of the presence of unsaturated metal Cu\textsuperscript{II} sites. The similar color change upon activation was observed for other frameworks that constructed from copper paddlewheel clusters\cite{2}. The activated samples are sensitive to the moisture. The color will be changed from deep purple-blue to light green, which indicates the collapse of the frameworks.

Low-pressure gases (N\textsubscript{2}, CH\textsubscript{4}) sorption isotherms (up to 1 bar) were performed on Micromeritics ASAP 2020 surface area and pore size analyzer. Before gases sorption measurements, about 200 mg samples were activated by using the “outgas” function of the surface area analyzer. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity). A part of the N\textsubscript{2} sorption isotherm at 77 K in the P/P\textsubscript{0} range 0.001–0.03 was fitted to the BET equation to estimate the BET surface area and the Langmuir surface area calculation was performed using all data points. The pore size distribution (PSD) was obtained from the DFT model in the Micromeritics ASAP 2020 software package (assuming cylinder pore geometry) based on the N\textsubscript{2} sorption isotherm. DFT kernel used: N\textsubscript{2}@77 K, Carbon Cylinder Pores, NLDFT.

High-pressure CH\textsubscript{4} sorption isotherms were measured using a Sieverts-type apparatus at NIST (National Institute of Standards and Technology, USA) lab. A detailed description of the experimental setup, calibration, and the isotherm can be found in a previous publication.\textsuperscript{3}

A virial-type expression comprising the temperature-independent parameters $a_i$ and $b_j$ was employed to calculate the enthalpies of adsorption for CH\textsubscript{4} (at 273 and 298 K). In each case, the data were fitted using the equation:

$$
\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j
$$

Here, $P$ is the pressure expressed in Torr, $N$ is the amount adsorbed in mmol/g, $T$ is the temperature in K, $a_i$ and $b_j$ are virial coefficients, and $m$, $n$ represent the number of
coefficients required to adequately describe the isotherms ($m$ and $n$ were gradually increased until the contribution of extra added $a$ and $b$ coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients $a_0$ through $a_m$ were then used to calculate the isosteric heat of adsorption using the following expression.

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

$Q_{st}$ is the coverage-dependent isosteric heat of adsorption and $R$ is the universal gas constant. The heat of CH$_4$ sorptions in the manuscript is determined by using the low pressure gas sorption data measured in the pressure range from 0-1 bar (273, 288 and 298 K).
### S6. Methane Sorption Data Comparisons (Table S2-S4)

**Table S2.** MOFs with high methane storage working capacities reported at 65 bar and room-temperature.

<table>
<thead>
<tr>
<th>MOFs</th>
<th>BET ( m^2 \text{ cm}^{-3} )</th>
<th>( D_c ) ( m^2 \text{ g}^{-1} )</th>
<th>Total uptake at 35/65Bar ( \text{cm}^3 \text{ cm}^{-3} )</th>
<th>Working capacity for 35/65 bar ( \text{g} \text{ cm}^{-3} )</th>
<th>( Q_s ) ( \text{ KJ mol}^{-1} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NJU-Bai 43</td>
<td>1974</td>
<td>3090</td>
<td>0.639</td>
<td>202/254</td>
<td>0.225/0.283</td>
<td>14.45 This work</td>
</tr>
<tr>
<td>NJU-Bai 42</td>
<td>1961</td>
<td>2830</td>
<td>0.693</td>
<td>203/247</td>
<td>0.209/0.254</td>
<td>14.49 This work</td>
</tr>
<tr>
<td>Cu(dbp)</td>
<td>2084</td>
<td>2911</td>
<td>0.716</td>
<td>161/203</td>
<td>0.144/0.179</td>
<td>13 9</td>
</tr>
<tr>
<td>UTSA-76</td>
<td>1971</td>
<td>2820</td>
<td>0.699</td>
<td>211/257</td>
<td>0.216/0.263</td>
<td>15.4 6h</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>1634</td>
<td>1850</td>
<td>0.883</td>
<td>227/267</td>
<td>0.184/0.216</td>
<td>15.4 6d</td>
</tr>
<tr>
<td>MAF-38</td>
<td>1539</td>
<td>2022</td>
<td>0.761</td>
<td>226/263</td>
<td>0.212/0.247</td>
<td>21.6 6f</td>
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<td>MOF-520</td>
<td>1928</td>
<td>3290</td>
<td>0.586</td>
<td>162/215</td>
<td>0.197/0.262</td>
<td>13.6 6i</td>
</tr>
<tr>
<td>Ni-MOF-74</td>
<td>1628</td>
<td>1350</td>
<td>1.206</td>
<td>230/260</td>
<td>0.136/0.154</td>
<td>20.6 6d</td>
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<tr>
<td>PCN-14</td>
<td>1658</td>
<td>2000</td>
<td>0.829</td>
<td>230/260</td>
<td>0.174/0.206</td>
<td>17.6 6d</td>
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<tr>
<td>Al-soc-MOF-1</td>
<td>2111</td>
<td>5585</td>
<td>0.378</td>
<td>121/197</td>
<td>0.267/0.412</td>
<td>11 6j</td>
</tr>
<tr>
<td>Cu-tbo-MOF-5</td>
<td>2363</td>
<td>3971</td>
<td>0.595</td>
<td>151/199</td>
<td>0.181/0.238</td>
<td>20.4 6k</td>
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</tbody>
</table>
Table S3. Total methane uptakes and volumetric working capacities in the 5-65 bar pressure ranges in comparison to the best microporous MOFs.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$Q_a$</th>
<th>T (K)</th>
<th>Uptake at 65 bar cm$^3$ cm$^{-3}$</th>
<th>Working capacity (5-65 bar) cm$^3$ cm$^{-3}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ mol$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NJU-Bai 41</td>
<td>17.8</td>
<td>273</td>
<td>266</td>
<td>161</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>245</td>
<td>172</td>
<td></td>
</tr>
<tr>
<td>NJU-Bai 42</td>
<td>14.5</td>
<td>273</td>
<td>270</td>
<td>192</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>247</td>
<td>193</td>
<td></td>
</tr>
<tr>
<td>NJU-Bai 43</td>
<td>14.5</td>
<td>273</td>
<td>286</td>
<td>205</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>254</td>
<td>198</td>
<td></td>
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<tr>
<td>Al-soc-MOF-1</td>
<td>11</td>
<td>273</td>
<td>241.7</td>
<td>213</td>
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<tr>
<td></td>
<td></td>
<td>298</td>
<td>196.9</td>
<td>176</td>
<td></td>
</tr>
<tr>
<td>UTSA-76</td>
<td>15.4</td>
<td>270</td>
<td>300</td>
<td>200</td>
<td>6h</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>257</td>
<td>197</td>
<td></td>
</tr>
<tr>
<td>HKUST-1</td>
<td>17</td>
<td>270</td>
<td>300</td>
<td>155</td>
<td>6d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>267</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>Ni-MOF-74</td>
<td>20.6</td>
<td>270</td>
<td>275</td>
<td>95</td>
<td>6d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>251</td>
<td>129</td>
<td></td>
</tr>
<tr>
<td>PCN-14</td>
<td>17.6</td>
<td>273</td>
<td>260</td>
<td>140</td>
<td>6d</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298</td>
<td>230</td>
<td>157</td>
<td></td>
</tr>
<tr>
<td>NU-111</td>
<td>14.2</td>
<td>273</td>
<td>284</td>
<td>177</td>
<td>14</td>
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<td></td>
<td></td>
<td>298</td>
<td>205</td>
<td>177</td>
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</table>
Table S4. The 5 bar CH₄ uptakes of some NbO type MOFs with similar pore volume, framework density and BET surface area at room-temperature.

<table>
<thead>
<tr>
<th>MOF</th>
<th>5 bar uptake at 298 K cm³ cm⁻³</th>
<th>Pore volume cm³ g⁻¹</th>
<th>Density g cm⁻³</th>
<th>( S_{\text{BET}} ) m² g⁻¹</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOTT-101</td>
<td>56</td>
<td>1.08</td>
<td>0.688</td>
<td>2805</td>
<td>6h</td>
</tr>
<tr>
<td>UTSA-75</td>
<td>59</td>
<td>1.06</td>
<td>0.698</td>
<td>2838</td>
<td>6m</td>
</tr>
<tr>
<td>UTSA-76</td>
<td>60</td>
<td>1.09</td>
<td>0.699</td>
<td>2820</td>
<td>6h</td>
</tr>
<tr>
<td>ZJU-5</td>
<td>61</td>
<td>1.08</td>
<td>0.679</td>
<td>2829</td>
<td>6m</td>
</tr>
<tr>
<td>NJU-Bai 42</td>
<td>53</td>
<td>1.07</td>
<td>0.693</td>
<td>2830</td>
<td>This work</td>
</tr>
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</table>
S7. The Structures of MOF-505 and PCN-14

Figure S1. a) The shuttle-shaped cages and big spherical cages are interconnected in an alternating fashion in MOF-505 and PCN-14. b) The big spherical cages in PCN-14, NJU-Bai 41, NJU-Bai 42 and NJU-Bai 43. The hydrogen atoms are omitted for clarity.
S8. Powder X-ray Diffraction

**Figure S2.** The PXRD patterns of **NJU-Bai 41**. A simulated PXRD pattern from the single-crystal structure; as-synthesized and activated samples, respectively.

**Figure S3.** The PXRD patterns of **NJU-Bai 42**. A simulated PXRD pattern from the single-crystal structure; as-synthesized and activated samples, respectively.
Figure S4. The PXRD patterns of NJU-Bai 43. A simulated PXRD pattern from the single-crystal structure; as-synthesized and activated samples, respectively.

S7. Thermogravimetric Analysis

Figure S5. TGA data of as-synthesized NJU-Bai 41.
Figure S6. TGA data of as-synthesized NJU-Bai 42.

Figure S7. TGA data of as-synthesized NJU-Bai 43.
S10. N\textsubscript{2} Sorption Isotherms

Figure S8. N\textsubscript{2} sorption isotherms of NJU-Bai 41 at 77K (filled symbols: adsorption; open symbols: desorption); inset: pore size distribution analysed by NLDFT method.

Figure S9. N\textsubscript{2} sorption isotherms of NJU-Bai 42 at 77K (filled symbols: adsorption; open symbols: desorption); inset: pore size distribution analysed by NLDFT method.
Figure S10. N\textsubscript{2} sorption isotherms of \textbf{NJU-Bai 43} at 77K (filled symbols: adsorption; open symbols: desorption); inset: pore size distribution analysed by NLDFT method.

Figure S11. The BET plots for \textbf{NJU-Bai 41} in the chosen range ($P/P_0 = 0.001–0.03$). This range was chosen according to two major criteria: The pressure range selected should have values of $Q(P_0-P)$ increasing with $P/P_0$. Inset: The y intercept of the linear region must be positive to yield a meaningful value of the $c$ parameter, which should be greater than zero.
**Figure S12.** The BET plots for **NJU-Bai 42** in the chosen range \(\frac{P}{P_0} = 0.001–0.03\). This range was chosen according to two major criteria: The pressure range selected should have values of \(Q(P_0-P)\) increasing with \(\frac{P}{P_0}\). Inset: The y intercept of the linear region must be positive to yield a meaningful value of the \(c\) parameter, which should be greater than zero.

**Figure S13.** The BET plots for **NJU-Bai 43** in the chosen range \(\frac{P}{P_0} = 0.001–0.03\). This range was chosen according to two major criteria: The pressure range selected should have values of \(Q(P_0-P)\) increasing with \(\frac{P}{P_0}\). Inset: The y intercept of the linear region must be positive to yield a meaningful value of the \(c\) parameter, which should be greater than zero.
S11. Methane Sorption Isotherms

*Figure S14.* Total CH₄ sorption isotherms of **NJU-Bai 41** at 273 K, 283 K and 298 K under 1 bar.

*Figure S15.* Total CH₄ sorption isotherms of **NJU-Bai 42** at 273 K, 283 K and 298 K under 1 bar.
Figure S16. Total CH$_4$ sorption isotherms of NJU-Bai 43 at 273 K, 283 K and 298 K under 1 bar.

Figure S17. Excess volumetric CH$_4$ adsorption isotherms of NJU-Bai 41 at 273 K and 298 K.
Figure S18. Excess volumetric CH₄ adsorption isotherms of NJU-Bai 42 at 273 K and 298 K.

Figure S19. Excess volumetric CH₄ adsorption isotherms of NJU-Bai 43 at 273 K and 298 K.
Figure S20. Repeated measurements of excess methane uptake isotherms for NJU-Bai42 at 298 K. Run1 was performed on a Sieverts-type apparatus at NIST and run2 was tested on Rubotherm ISOSORP-HyGpra+V instrument.

Figure S21. Repeated measurements of excess methane uptake isotherms for NJU-Bai43 at 298 K. Run1 was performed on a Sieverts-type apparatus at NIST and run2 was tested on Rubotherm ISOSORP-HyGpra+V instrument.
S12. Calculations of Adsorption Isoëstéric Heats

Figure S22. Details of virial equation (solid lines) fitting to the experimental CH₄ Adsorption data (symbols) for NJU-Bai 41 collected at 273 K, 283 K and 298 K.

Figure S23. Details of virial equation (solid lines) fitting to the experimental CH₄ Adsorption data (symbols) for NJU-Bai 42 collected at 273 K, 283 K and 298 K.
Chi-Square: 1.65190783370328E-6
R^2 = 0.999999924574045
a0 = -1737.739571
a1 = 45.87427269
a2 = -24.63084174
b0 = 8.63346203
b1 = 12.6067709
NJU-Bai 43 at 273 K
NJU-Bai 43 at 283 K
NJU-Bai 43 at 298 K

Figure S24. Details of virial equation (solid lines) fitting to the experimental CH₄ Adsorption data (symbols) for **NJU-Bai 43** collected at 273 K, 283 K and 298 K.

**Figure S25.** The $Q_{st}$ for CH₄ adsorption of **NJU-Bai 41**, **NJU-Bai 42** and **NJU-Bai 43**. a) calculated by low-pressure isotherms b) calculated by high-pressure isotherms.
S13. Modeling

The single X-ray crystallographic structures that were obtained for NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43 herein were used for the parametrizations and simulations. For parametrizing the three MOFs, all atoms of the adsorbent were given Lennard-Jones 12–6 parameters and point partial charges to model repulsion/dispersion and permanent electrostatic interactions, respectively. The Lennard-Jones 12–6 parameters were taken from the Universal Force Field (UFF).4 The point partial charges for the atoms in all three MOFs were calculated using the extended charge equilibration (EQeq) method.5 We note that simulations including explicit many-body polarization6 in these MOFs did not significantly alter the results. In addition, the theoretical results described here for NJU-Bai 43 are based on simulations within a configuration of the MOF in which (1) the amide groups are oriented identically in the crystallographic c direction and (2) the amide oxygen atoms of the linkers are pointing in the same direction around the three sides of the cage. Simulations within a configuration consisting of random orientations of the amide groups produced very similar results to the previously described configuration.

Simulations of CH4 adsorption were performed in NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43 using grand canonical Monte Carlo (GCMC) methods7 in a single unit cell of the respective MOFs. A macroscopic crystalline environment was approximated by periodic boundary conditions. A spherical cut-off distance corresponding to half the shortest unit cell dimension length was used for the simulations in all three MOFs. A nine-site electrostatic potential that was developed previously for CH4 was used for the simulations in this work.8 The parameters for this model are given in Table S5. The total potential energy of the MOF–CH4 system was calculated through the sum of the Lennard-Jones 12–6 and Coulomb potentials. For the former, the interactions between unlike species were governed by the Lorentz-Bertholet mixing rules.9 Permanent electrostatic interactions were calculated through Ewald summation10 of the point partial charges. The chemical potential for
CH$_4$ was determined for a range of temperatures and pressures through the BACK equation of state.$^{11}$ All MOF atoms were held fixed throughout the simulations. All simulations were performed using the Massively Parallel Monte Carlo (MPMC) code.$^{12}$ For all state points considered (pressures ranging from 0.01–80 atm at 298 K), the simulations consisted of $1.5 \times 10^6$ Monte Carlo steps to guarantee equilibration, followed by an additional $1.5 \times 10^6$ steps to sample the desired thermodynamic properties.

Simulated annealing calculations$^{13}$ within the canonical ensemble (i.e., constant particle number, volume, and temperature) were performed for a single CH$_4$ molecule localized within the unit cell of NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43. This was done in order to identify the most favorable CH$_4$ binding site in the respective MOFs. The initial CH$_4$ molecule position in these MOFs was chosen to be arbitrary. The simulated annealing calculations started at an initial temperature of 500 K and this temperature was scaled by a factor of 0.99999 after every $1.0 \times 10^3$ Monte Carlo steps. The simulations continued until the temperature of the system dropped below 5.0 K.

Next, canonical Monte Carlo (CMC) simulations were performed for a CH$_4$ molecule positioned at the global minimum in all three MOFs. This was done in order to evaluate the averaged classical potential energy for the CH$_4$ molecule about the equilibrium position in the respective MOFs. As with the GCMC simulations and simulated annealing calculations, the CMC simulations were executed within the rigid unit cell of the individual MOFs. These simulations were performed at a temperature of 298 K and a pressure of 0.10 atm. Such CMC simulations were also executed on the MOF–CH$_4$ system that was obtained from GCMC simulations at 298 K and 65 atm for NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43. In order to estimate the CH$_4$ adsorption energy at high pressures for each MOF, the total averaged classical potential energy of the system was divided by the number of adsorbate molecules in the MOF. All CMC simulations ran for a total of $1.0 \times 10^6$ Monte Carlo steps to ensure reasonable ensemble averages for the total potential energy of the system.
Table S5. Parameters for the nine–site electrostatic CH$_4$ potential used in this work. OS refers to the off-atomic sites and $r$ corresponds to the distance from the center-of-mass.

<table>
<thead>
<tr>
<th>Site</th>
<th>$r$ (Å)</th>
<th>$\varepsilon$ (K)</th>
<th>$\sigma$ (Å)</th>
<th>$q$ ($e^-$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.000</td>
<td>58.53869</td>
<td>2.22416</td>
<td>$-0.5868$</td>
</tr>
<tr>
<td>H</td>
<td>1.099</td>
<td>0.00000</td>
<td>0.00000</td>
<td>+0.1467</td>
</tr>
<tr>
<td>OS</td>
<td>0.816</td>
<td>16.85422</td>
<td>2.96286</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

Summary of Modeling Results

The simulated CH$_4$ adsorption isotherms that were generated herein for NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43 at 298 K and pressures up to 80 atm are shown in Figure S26. It can be observed that the trend in the volumetric CH$_4$ uptake at low pressures is NJU-Bai 41 > NJU-Bai 43 > NJU-Bai 42, with calculated uptakes of 131.1, 68.5, and 94.7 cm$^3$ (STP) cm$^{-3}$ for NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43, respectively, at 298 K and 5 atm. Although this trend is consistent with what was observed experimentally, these uptakes are higher than the measured values for the corresponding MOFs under the same condition (73, 53, and 56 cm$^3$ (STP) cm$^{-3}$, respectively). At 298 K and 35/65 atm, the calculated CH$_4$ uptakes for NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43 are 260.6/289.5, 220.1/260.7, and 257.5/294.9 cm$^3$ (STP) cm$^{-3}$, respectively, whereas the matching experimental quantities are 204/245, 203/247, and 202/254 cm$^3$ (STP) cm$^{-3}$. The simulated volumetric uptakes for NJU-Bai 42 are the lowest for all pressures considered. This could be due to the weak interactions that are captured between the CH$_4$ molecules and the pore walls of the neck of the shuttle-shaped cage; this region contains a wider void space in NJU-Bai 42 compared to the other two MOFs. In general, larger pore sizes result in weaker interactions between the adsorbate molecules and the framework, and therefore less uptake.

The deviation from the experimental and simulated uptakes for all three MOFs...
could be due to the fact that a perfect crystal is utilized in simulation or inaccuracies in the present simulation model. However, the overestimation of the simulated uptakes relative to experiment is consistent across all pressures for the individual MOFs such it provides theoretical working capacities that are comparable to the corresponding experimental results. Further, we believe that our findings of the modeled CH₄ adsorption sites and energies at low and high pressures (see below) are valid despite the difference in the experimental and simulated adsorption isotherms. This is because these results are still consistent with the experimental expectations of the CH₄ binding sites that are described in the manuscript.

The theoretical volumetric working capacities (from 5–35 atm and 5–65 atm) at 298 K based on GCMC simulations of CH₄ adsorption in **NJU-Bai 41**, **NJU-Bai 42**, and **NJU-Bai 43** are summarized in **Table S6**. These working capacities are comparable to the corresponding experimental values shown in **Table 1**. In addition, the theoretical working capacities from both 5–35 atm and 5–65 atm display the same overall trend as experiment, which is **NJU-Bai 43 > NJU-Bai 42 > NJU-Bai 41**.

Simulated annealing calculations for a single CH₄ molecule within **NJU-Bai 41**, **NJU-Bai 42**, and **NJU-Bai 43** reveal that the most favorable CH₄ binding site in all three MOFs is located within a triangular region enclosed by three isophthalate groups. A molecular illustration of this site in **NJU-Bai 43** is shown in **Figure S27**. The averaged classical potential energies for CH₄ localized about this region in all three MOFs according to CMC simulations are listed in **Table S6**. The simulations suggest that the trend in the MOF–CH₄ interaction at low loading is the following: **NJU-Bai 41 > NJU-Bai 43 > NJU-Bai 42**.

The orientation of the naphthalene rings on the linkers in **NJU-Bai 41** allows for the existence of a small cage within the MOF, which is formed by three [Cu₂(O₂CR)₄] units and three L1 linkers. This small cage is not observed in either **NJU-Bai 42** and **NJU-Bai 43** since the decorated components are slimmer in these MOFs. As the CH₄ molecule is adsorbed within the region enclosed by three isophthalate groups in **NJU-Bai 41**, it can also travel further down the “basket” and interact with the naphthalene rings. An illustration depicting these sites as captured from the MC
adsorption history is shown in Figure S28. The interaction between CH$_4$ and the naphthalene rings within the confined cage in NJU-Bai 41 is very favorable and explains why analogue exhibits higher CH$_4$ uptake at low loadings, and hence greater MOF–CH$_4$ interactions under such conditions, compared to NJU-Bai 42 and NJU-Bai 43. We note that this site within the “basket” of NJU-Bai 41 is consistent with what was observed for CH$_4$ and H$_2$ in PCN-14 in earlier theoretical studies.$^{14}$

Figures S29, S30, and S31 display the sites of CH$_4$ occupancy within 5.0 Å of the Cu$^{2+}$ ions in the modeled unit cells of NJU-Bai 41, NJU-Bai 42, NJU-Bai 43, respectively, according to GCMC simulations at 298 K and 5 atm. As highlighted in Figure S29, a considerable quantity of CH$_4$ molecules was found to adsorb within the vicinity of the naphthalene rings of the linkers in NJU-Bai 41. This is in contrast to what was observed in NJU-Bai 42 and NJU Bai 43, as there is less occupancy about the decorated components of the linkers in these MOFs at this thermodynamic condition (Figures S30 and S31). Furthermore, the radial distribution function (g(r)) was evaluated about the Cu$^{2+}$ ions in all three MOFs at 298 K and 5 atm and the resulting plots are shown in Figure S32. It can be observed that the magnitudes of the nearest-neighbor peaks are larger for NJU-Bai 41 relative to the other two analogues, which further indicates that this MOF displays a greater population of CH$_4$ molecules within the triangular regions at low loadings.

Nevertheless, because the naphthalene rings of the linkers protrude into the pore in NJU-Bai 41, this results in less space for the CH$_4$ molecules to occupy at higher pressures. As a consequence, the CH$_4$ adsorption capacity in this MOF is limited under these conditions. On the other hand, due to the slender nature of the oxamide and pyridyl amide moieties in NJU-Bai 42 and NJU-Bai 43, respectively, this allows for the formation of an undivided shuttle-shaped cage in these MOFs. This cage has a large accessible volume in both MOFs, which can be used to store a significant amount of CH$_4$ molecules at high pressures. This could explain why NJU-Bai 42 and NJU-Bai 43 have improved experimental and theoretical working capacities compared to NJU-Bai 41. Substitution of one amide group in the oxamide moiety with pyridine results in a larger shuttle-shaped cage. This leads to NJU-Bai 43 having
greater CH$_4$ uptake at high pressures than NJU-Bai 42. In addition, the interaction energy for the adsorption of CH$_4$ about the triangular region is slightly higher for NJU-Bai 43 relative to NJU-Bai 42 (see Table S6). This could be due to the fact that the space within the neck of the shuttle-shaped cage (i.e., the region of the cage enclosed by three linkers) is extended and narrower for NJU-Bai 43 (see Figure S33), which allows for the CH$_4$ molecules to interact with more atoms of the framework simultaneously, leading to slightly increased MOF–CH$_4$ interactions. Thus, the elongation of the neck and attendant reduction of the aperture results in greater CH$_4$ uptake in NJU-Bai 43 for virtually all pressures considered.

At higher pressures, the CH$_4$ molecules are essentially crowding into the void space of each MOF. Figures S34, S35, and S36 show the modeled packing of CH$_4$ within the shuttle-shaped cages of NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43, respectively, as observed from GCMC simulations at 298 K and 65 atm. According to the simulations, up to 2 and 7 CH$_4$ molecules can occupy the small cage and the larger sub cage connecting the two small cages, respectively. In addition, the undivided shuttle-shaped cage in NJU-Bai 42 and NJU-Bai 43 can adsorb approximately 26 and 33 CH$_4$ molecules, respectively, under the conditions considered. The averaged classical potential energies per particle within the adsorbent–adsorbate system that was obtained from GCMC simulations at 298 K and 65 atm for the respective MOFs are presented in Table S6. These results indicate that the magnitude of the potential energy for CH$_4$ adsorption decreases at higher pressures. However, consistent with what was observed at low loadings, the simulations suggest that the trend in the MOF–CH$_4$ interaction at higher loadings is: NJU-Bai 41 > NJU-Bai 43 > NJU-Bai 42.
Table S6. Summary of theoretical results for simulations of CH₄ adsorption in NJU-Bai 41, NJU-Bai 42, and NJU-Bai 43.

<table>
<thead>
<tr>
<th>MOF</th>
<th>Working Capacity 5–35 atm (cm³ cm⁻³)</th>
<th>Working Capacity 5–65 atm (cm³ cm⁻³)</th>
<th>&lt;U&gt; at Global Minimum (kJ mol⁻¹)</th>
<th>&lt;U&gt; at 298 K/65 atm (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NJU-Bai 41</td>
<td>129.5</td>
<td>158.4</td>
<td>20.1</td>
<td>17.5</td>
</tr>
<tr>
<td>NJU-Bai 42</td>
<td>151.5</td>
<td>192.2</td>
<td>15.8</td>
<td>13.4</td>
</tr>
<tr>
<td>NJU-Bai 43</td>
<td>162.7</td>
<td>200.2</td>
<td>18.1</td>
<td>14.5</td>
</tr>
</tbody>
</table>

Figure S26. Simulated volumetric CH₄ adsorption isotherms for NJU-Bai 41 (blue), NJU-Bai 42 (green), and NJU-Bai 43 (red) at 298 K and pressures up to 80 atm.
Figure S27. Molecular illustration of a CH\textsubscript{4} molecule adsorbed within a region enclosed by three isophthalate groups in NJU-Bai 43 as determined from simulated annealing calculations. A graphically similar picture of this site can be observed for NJU-Bai 41 (see Figure S28) and NJU-Bai 42. Atom colors: C(MOF) = cyan, C(CH\textsubscript{4}) = orange, H = white, N = blue, O = red, Cu = gold.

Figure S28. Molecular illustration of CH\textsubscript{4} molecules adsorbed within the small cage that is formed by three [Cu\textsubscript{2}(O\textsubscript{2}CR)\textsubscript{4}] units and three L1 linkers in NJU-Bai 41. The CH\textsubscript{4} molecule shown in orange corresponds to the simulated annealing position, while the adsorbate shown in blue represents a CH\textsubscript{4} molecule that moved further down the “basket” to interact with the naphthalene rings. (a) shows the downward view of the small cage whereas (b) shows the side view. Atom colors: C(MOF) = cyan, C(CH\textsubscript{4}) = orange/blue, H = white, O = red, Cu = gold.
Figure S29. (a) Orthographic c-axis view and (b) b-axis view of the modeled unit cell of \textbf{NJU-Bai 41} showing the sites of CH$_4$ occupancy (orange) within 5.0 Å of the Cu$^{2+}$ ions at 298 K and 5 atm. The magenta circles indicate that significant occupancy was observed near the naphthalene rings of the linkers, which in contrast to what was observed about the decorated components of the linkers in \textbf{NJU-Bai 42} and \textbf{NJU-Bai 43} (see Figures S30 and S31). Atom colors: C = cyan, H = white, O = red, Cu = gold.
Figure S30. (a) Orthographic c-axis view and (b) b-axis view of the modeled unit cell of NJU-Bai 42 showing the sites of CH₄ occupancy (orange) within 5.0 Å of the Cu²⁺ ions at 298 K and 5 atm. Atom colors: C = cyan, H = white, N = blue, O = red, Cu = gold.
Figure S31. (a) Orthographic $c$-axis view and (b) $b$-axis view of the modeled unit cell of \textbf{NJU-Bai 43} showing the sites of CH$_4$ occupancy (orange) within 5.0 Å of the Cu$^{2+}$ ions at 298 K and 5 atm. Atom colors: C = cyan, H = white, N = blue, O = red, Cu = gold.
Figure S32. Radial distribution function (g(r)) of CH$_4$ carbon atoms about the Cu$^{2+}$ ions in NJU-Bai 41 (blue), NJU-Bai 42 (green), and NJU-Bai 43 (red) from GCMC simulations at 298 K and 5.0 atm. The g(r) plots shown are normalized for volume and number of configurations over the distance examined.

Figure S33. Molecular illustration of CH$_4$ molecules adsorbing within the neck of the shuttle-shaped cages (the region of the cage surrounded by three linkers) in (a) NJU-Bai 42 and (b) NJU-Bai 43 as determined from the simulations. The extension and narrowing of the neck in NJU-Bai 43 allows for greater accommodation of CH$_4$ molecules. Atom colors: C(MOF) = cyan, C(CH$_4$) = orange, H = white, N = blue, O = red, Cu = gold.
Figure S34. Molecular illustration of CH$_4$ molecules occupying the sub cages of the shuttle-shaped cage in NJU-Bai 41 as observed from GCMC simulations at 298 K and 65 atm. The numbers shown indicate the maximum number of CH$_4$ molecules that can adsorb within each sub cage according to the simulations. Atom colors: C(MOF) = cyan, C(CH$_4$) = orange, H = white, O = red, Cu = gold.
Figure S35. Molecular illustration of CH$_4$ molecules occupying the undivided shuttle-shaped cage in NJU-Bai 42 as observed from GCMC simulations at 298 K and 65 atm. The number shown indicates the approximate number of CH$_4$ molecules that are adsorbed within the shuttle-shaped cage according to the simulations at the state point considered. Atom colors: C(MOF) = cyan, C(CH$_4$) = orange, H = white, N = blue, O = red, Cu = gold.
Figure S36. Molecular illustration of CH₄ molecules occupying the undivided shuttle-shaped cage in NJU-Bai 43 as observed from GCMC simulations at 298 K and 65 atm. The number shown indicates the approximate number of CH₄ molecules that are adsorbed within the shuttle-shaped cage according to the simulations at the state point considered. Atom colors: C(MOF) = cyan, C(CH₄) = orange, H = white, N = blue, O = red, Cu = gold.
S16. References