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# Efficient capture of trace benzene vapor by metal–organic frameworks modified with macrocyclic pyridyl ligands

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The capture of trace benzene vapor is an important and huge challenge due to its serious toxicity. Physisorbents usually exhibit weak interactions especially in the presence of trace concentrations, thus possessing poor removal performance. Herein, an efficient post-synthetic modification strategy with various mono-, bi-, and tri-pyridyl derivative ligands was performed on the parent [$Fe_3(\mu_3$-O)(OH)($H_2O)_2$(pet)] (**NU-1500(Fe)**, $H_6$pet = peripherally extended triptycene, 4,4′,4″,4‴,4‴,4‴-(9,10-dihydro-9,10-[1,2]benzenoanthracene-2,3,6,7,14,15-hexayl)hexabenzoic acid) with large hexagonal pores (14 × 19 Å$^2$) and modifiable metal sites. Remarkably, these MOFs can regulate the performance of trace adsorption of benzene. Among them, the tri-pyridyl ligand modified [$Fe_3(\mu_3$-O)(pet)(tph)] (**WYU-107**, Htph = 2,5,8-tri-(4-pyridyl)-1,3,4,6,7,9-hexaazaphenalene) reaches an uptake of 6.21 mmol g$^{-1}$ at 298 K and $P/P_0$ = 0.01 by virtue of the significant interactions between the pore partitioned host-framework and benzene molecules, which shows a capture performance exceeding that of most of the reported porous materials. At the same time, breakthrough experiments revealed that **WYU-107** can capture trace benzene in the air, and *in situ* variable-pressure PXRD indicates the reversible deformation behavior during the adsorption process. Theoretical calculations and *in situ* single-crystal structure reveal that the significant interactions are closely related to the insertion of the functional tph ligand, facilitating the capture of benzene vapor at trace levels.

## Introduction

According to the World Health Organization, benzene is a highly toxic carcinogen, which seriously endangers human health even at trace levels.[1] Therefore, it is necessary to develop functional materials to realize efficient benzene vapor capture, especially at trace concentrations. Current methods to remove benzene vapor from indoor air include oxidation and adsorption by functional porous materials. However, high energy consumption and low adsorption efficiency (weak interactions between the host-framework and benzene molecules) limit the application.[2–6]

As a booming sort of porous material, metal–organic frameworks (MOFs) are well-known for their highly designable, tunable structures and pore surfaces, which play important roles in numerous applications,[7,8] such as gas storage/capture,[9] selective separation and molecular sensing.[10–12] Recently, a few MOFs have demonstrated huge potential in the removal of saturated benzene vapor even at trace levels. For example, the unique double-walled MOF, [Co(dpn)] (BUT-54(Co), $H_2$dpn = 2,7-di(1*H*-pyrazol-4-yl)naphthalene) achieved a benzene vapor uptake of 4.31 mmol g$^{-1}$ at $P/P_0$ = 0.01 due to the multiple C–H⋯π interactions between dpn$^{2-}$ ligands and benzene molecules.[11] Similarly, the benzene vapor uptake of [Al(μ-O)$_2$(μ-OH)(dbp)] (ZJU-520(Al), $H_2$dbp = 4,6-di(4-carboxyphenyl)pyrimidine) reaches 5.98 mmol g$^{-1}$ at 298 K and $P/P_0$ = 0.01 based on the strong Al⋯π interactions between $AlO_6$ clusters and benzene molecules.[13] Besides, single-atom(Zn) sites in defective-MIL-125, [$Ti_8O_8(\mu$-OH)$_4$(bdc)$_6$] ($H_2$bdc = 1,4-benzenedicarboxylic acid), can serve as potential sites toward benzene molecules, achieving the record high benzene uptake (7.63 mmol g$^{-1}$) at 298 K and 1.2 mbar.[14] These results clearly demonstrate that enhancing the interaction between the host-framework and benzene molecules is the key to achieving efficient capture of benzene vapor.[15,16] Despite the progress in trace adsorption of benzene vapor, the efficient capture based on directional assembly remains a huge challenge. In principle, the introduction of aromatic macrocyclic groups into MOF frameworks is an effective approach to improve the adsorption of

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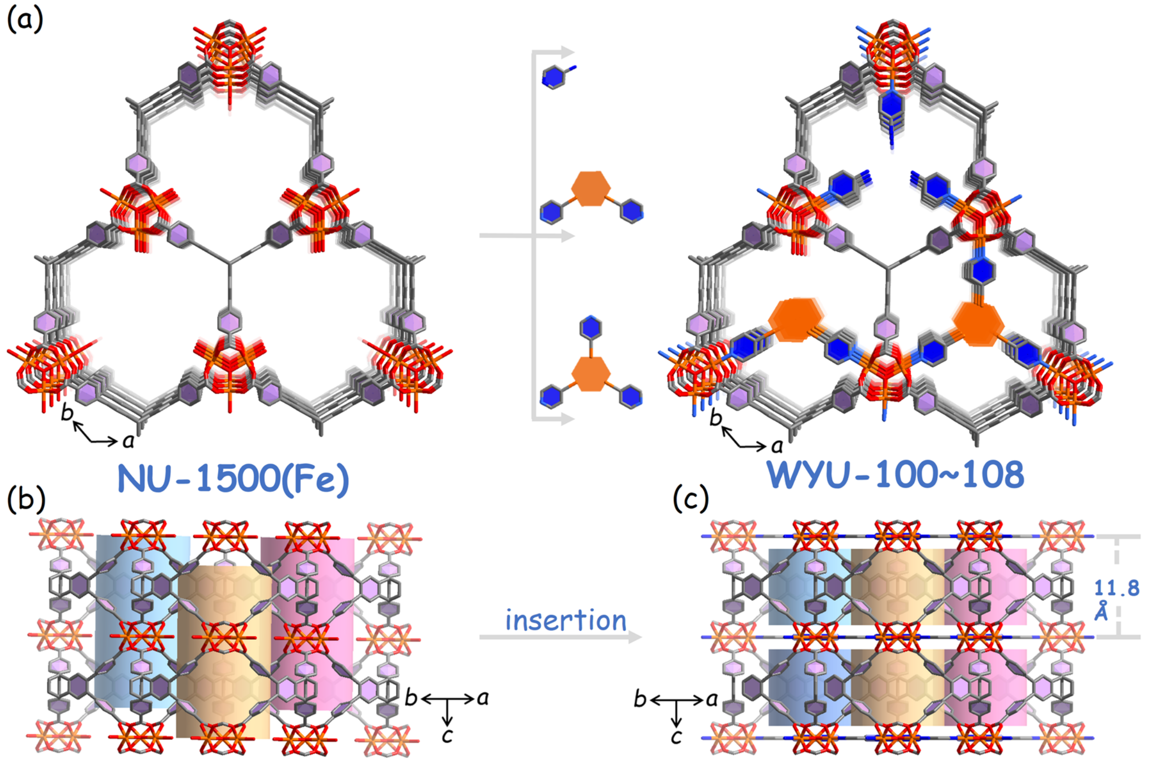


Fig. 1 (a) The post-modification strategy of various pyridyl derivative ligands based on the prototype **NU-1500(Fe)**. The comparison of pore void between (b) **NU-1500(Fe)** and (c) post-modification **WYU-107**.

benzene vapor by virtue of the strong interaction between aromatic macrocyclic ligands and benzene molecules. For example, $[Sr_2(bindi)(DMF)(H_2O)]$ (**WYU-61**, $H_4$bindi = *N*,*N*′-bis(5-isophthalic acid)-naphthalenediimide, DMF = *N*,*N*-dimethylformamide), a MOF with aromatic macrocyclic bindi ligands, exhibits the unique "bilateral π–π stacking" host–guest interaction between benzene molecules and the macrocyclic ligands, realizing the adsorption and detection of trace benzene vapor.[17] However, the poor solubility of macrocyclic derivative ligands and unpredictability of the direct synthetic method, as well as the low porosity of host-frameworks lead to difficulty in orientated construction of MOFs. In contrast, the insertion of aromatic macrocyclic ligands into the parent MOFs by post-synthetic modification (PSM) is an effective strategy, and the key is the compatibility of the parent MOFs and inserted ligands.[18–21]

Here, we report a series of MOFs (**WYU-100–108**, WYU = Wuyi University), synthesized by PSM of $[Fe_3(\mu_3\text{-}O)(OH)(H_2O)_2(pet)]$ (**NU-1500(Fe)**,[22] $H_6$pet = peripherally extended triptycene, 4,4′,4″,4‴,4⁗,4′′′′′-(9,10-dihydro-9,10-[1,2]benzenoanthracene-2,3,6,7,14,15-hexayl)hexabenzoic acid) with large hexagonal pores (14 × 19 Å$^2$) and various modifiable metal sites for insertion of various pyridyl ligands (Fig. 1a).

Interestingly, the insertion is not only feasible for smaller mono-pyridyl derivative ligands but also for bi-pyridyl derivative ligands, and even for larger tri-pyridyl derivative ligands, compared with the limited porosity MOFs, such as $[Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(OH)_4(H_2O)_4(ettc)_2]$ (WSU-5, $H_4$ettc = 4′,4‴,4′′′′′,4′′′′′′′-(ethene-1,1,2,2-tetrayl)tetrakis([1,1′-biphenyl]-4-carboxylic acid)) and $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(HCOO)_4(tcpe)_2$ ($H_4$tcpe = 1,1,2,2-tetra(4-carboxylphenyl)ethylene).[23,24] The saturation uptake of benzene vapor, stepped pressure, and the trace adsorption can be regulated by the insertion of different types of pyridyl derivative ligands based on the various host–guest interactions. Notably, $[Fe_3(\mu_3\text{-}O)(pet)(tph)]$ (**WYU-107**) containing the tri-pyridyl derivative ligand 2,5,8-tri-(4-pyridyl)-1,3,4,6,7,9-hexaazaphenalene (Htph) achieves an exceptional benzene uptake of 6.21 mmol g$^{-1}$ by virtue of the strong interactions between the larger conjugated hexaazaphenalene-based ligand and benzene molecules at $P/P_0 = 0.01$, which is three times that of the parent **NU-1500(Fe)** (2.12 mmol g$^{-1}$).[25] As far as we know, **WYU-107** is the first post-synthetic modified MOF showing highly efficient capture of benzene vapor at trace levels, being superior to most of the reported porous materials, and only next to the defective-MIL-125-X (X = Mn, Co, Ni, Cu, Zn). Furthermore, breakthrough experiments further demonstrate that **WYU-107** has excellent potential for trace benzene capture. The combination of *in situ* single-crystal X-ray diffraction (SCXRD) and theoretical calculations demonstrates that the large aromatic tph ligand is conducive to the benzene vapor adsorption under low pressure.

## Results and discussion

**NU-1500(Fe)** with **acs** topology is constructed from pet ligands and trinuclear $[Fe_3(\mu_3\text{-}O)(H_2O)_2(OH)(RCOO)_6]$ clusters. There are large hexagonal channels (14 × 19 Å$^2$) in the framework along the *c*-axis, and the pore ratio reaches 74.8%. More importantly, there are two terminal $H_2O$ and one $OH^-$ ligands in the cluster, which can serve as perfect sites for ligand replacement by PSM. On the other hand, the compatibility of the substituting ligand and the spatial arrangement of the modifiable sites are also significant factors. Compared to **NU-1500(Fe)**, other parent MOFs, such as $[Co_2(dobdc)]$ (MOF-74(Co), $H_4dobdc$ = 2,5-dihydroxyl-1,4-benzenedicarboxylic acid,[26] $[Fe_3(\mu_3\text{-}O)(tba)_3(OH)(H_2O)_2]$ (MIL-88A(Fe), $H_2tba$ = *trans*-2-butenedioic acid) and $[Zr_{12}(\mu\text{-}O)_8(\mu\text{-}OH)_8(CH_3COO)_{12}(\text{tcpb-Br}_2)_3]$ (NU-600, $H_4\text{tcpb-Br}_2$ = 4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene), exhibit more restricted pore sizes and modifiable sites. Their inherent limitations hinder accommodation of the extended or bulky organic ligands.[27,28] As far as we know, few MOFs can achieve various types of ligand insertion, not to mention macrocyclic ligands with large molecular sizes. Fortunately, the combination of large pore size and three modifiable sites in the parent **NU-1500(Fe)** allows for modifications of not only smaller mono-pyridyl derivative ligands but also larger bi-pyridyl and even tri-pyridyl derivative ligands (Fig. S1). In principle, the insertion is feasible as long as the ligand length of $L_1$ (mono-pyridyl ligand) is shorter than the pore size, or the shapes and sizes of $L_2$ (bi-pyridyl ligand) and $L_3$ (tri-pyridyl ligand) are adaptable to two and three modifiable sites, respectively (Fig. S2).

The PSM strategy was proved by single-crystal X-ray diffraction (SCXRD) (Tables S2–S5), as well as $^1H$ NMR spectra. The ratio of $H_6pet:L_1$ (apy, ina, pyb) is close to 1 : 3 (Fig. S3–S5), suggesting that the three terminal $H_2O/OH^-$ ligands in a $[Fe_3(\mu_3\text{-}O)(H_2O)_2(OH)(RCOO)_6]$ cluster can be replaced by mono-pyridyl ligands to give the corresponding modified $[Fe_3(\mu_3\text{-}O)(apy)_3(pet)]$ *x* (**WYU-100**, apy = 4-aminopyridine, *x* = counter anions), which crystallizes in the hexagonal $P\bar{6}m2$ space group. There are three apy ligands inserted into each trinuclear cluster of the parent **NU-1500(Fe)** since the length of the ligand (4.6 Å) is less than $d_1$ (Fig. S2). Furthermore, similar mono-pyridyl ligands (ina = isonicotinic acid, pyb = pyridine-4-boronic acid) can also be used to modify **NU-1500(Fe)** into $[Fe_3(\mu_3\text{-}O)(ina)_3(pet)]$ *x* (**WYU-101**) and $[Fe_3(\mu_3\text{-}O)(pyb)_3(pet)]$ *x* **(WYU-102)**, respectively. However, the orientations of apy and ina ligands in the frameworks of **WYU-100** and **WYU-101** are vertical, while that of the pyb ligand in **WYU-102** is parallel, to the trinuclear core (Fig. S12).

Considering the distribution of trinuclear clusters in the hexagonal pore, bi-pyridyl ligands with the length close to 12.6 Å (the distance between two $Fe^{3+}$ ions in adjacent trinuclear clusters, Fig. S2) can also modify **NU-1500(Fe)**. The larger $N^1$,$N^3$-di(pyridine-4-yl)isophthalamide (bpipa) ligand with functional amide groups was then inserted into it to furnish a new MOF, $[Fe_3(\mu_3\text{-}O)(OH)(pet)(bpipa)]$ (**WYU-103**). The ratio of $H_6pet:L_2$ ($L_2$ = bpipa, dpyc, or dpyn) is close to 1 : 1 based on $^1H$ NMR spectra measurements (Fig. S6–S8), suggesting that two terminal $H_2O$ molecules in each trinuclear cluster can be replaced by pyridyl derivative ligands, transforming the 6-connected **NU-1500(Fe)** into the 8-connected **WYU-103**. Consequently, the hexagonal channel is partitioned into two smaller ones.[15] Similarly, other bi-pyridyl ligands featuring larger bending angles (103.5°) and longer lengths (11.95 Å), such as 3,6-di(pyridin-4-yl)-9*H*-carbazole (dpyc) and 2,7-di(4-pyridyl) naphthalene (dpyn), can also facilitate the assembly of similar 8-connected $[Fe_3(\mu_3\text{-}O)(OH)(pet)(dpyc)]$ (**WYU-104**) and $[Fe_3(\mu_3\text{-}O)(OH)(pet)(dpyn)]$ (**WYU-105**). These results further demonstrate the high adaptability of **NU-1500(Fe)** to diverse ligand modifications.

Based on the above results, PSMs with larger tri-pyridyl derivative ligands (tpybtc = *N*,*N*′,*N*″-tris(4-pyridinyl)-1,3,5-benzenetricarboxamide, Htph = (2,5,8-tri-(4-pyridyl)-1,3,4,6,7,9-hexaazaphenalene, tpvb = 1,3,5-tris((*E*)-2-(pyridin-4-yl)vinyl)benzene) were further performed to verify the feasibility of this strategy.[29] SCXRD reveals that three terminal $H_2O/OH^-$ ligands on the trinuclear cluster can be completely replaced by the tri-pyridyl ligands to achieve 9-connected MOFs, $[Fe_3(\mu_3\text{-}O)(pet)(tpybtc)]$ *x* **(WYU-106)**, $[Fe_3(\mu_3\text{-}O)(pet)(tph)]$ **(WYU-107)** and $[Fe_3(\mu_3\text{-}O)(pet)(tpvb)]$ *x* **(WYU-108)**. $^1H$ NMR spectral measurements further verified that the ratio of $H_6pet:L_3$ ($L_3$ = tpybtc, tph, tpvb) is close to 1 : 1 (Fig. S9–S11). The replaced groups in the ligands derived from **WYU-106–108** were further confirmed by FT-IR spectra (Fig. S15). As the terminal $OH^-$ ligand is replaced by the deprotonated tph ligand, **WYU-107** becomes a neutral framework. In contrast, there are counter anions accommodated in **WYU-106** and **WYU-108**, although these anions cannot be clearly determined by SCXRD due to their serious disorder. Interestingly, the symmetries of **WYU-106–108** are maintained after the ligand insertion of tpybtc, Htph and tpvb due to the geometric compatibility of the ligands and the rigidity of the parent framework. It is worth noting that the large 3D pore in **NU-1500(Fe)** is partitioned into three smaller ones after the above modification. Notably, the porosity decreased from 74.8% of **NU-1500(Fe)** to 69% of **WYU-100–102** with mono-pyridyl ligands, to 67% of **WYU-103–105** with bi-pyridyl ligands, and finally to 66% of **WYU-106–108** with tri-pyridyl ligands. More importantly, the functional N and O sites are successfully introduced into the host-framework upon modification. For example, the anionic tph ligand contains a large hexaazaphenalene moiety with six nitrogen atoms, which is conducive to the formation of multiple hydrogen bonds between the macrocycle moiety and guest molecules. In other words, various types of pyridyl ligands can be inserted into the host-framework to regulate the functionality.

The purities of as-synthesized **NU-1500(Fe)** and **WYU-100–108** were checked by powder X-ray diffraction (PXRD) patterns, which are consistent with the simulated ones, indicating the high purity and crystallinity (Fig. S13 and S14). TG curves of as-synthesized **WYU-100–108** showed large weight loss from room temperature to 350 °C due to the removal of the free guest and coordination solvent molecules within the pore, and the remaining host framework decomposed above 400 °C (Fig. S16 and S17). The porosities of **WYU-100–108** were measured by $N_2$ sorption isotherms at 77 K, which showed typical type-I curves (Fig. 2a). The adsorption capacities of these frameworks are lower than those of the parent **NU-1500(Fe)** attributed to the insertion of various ligands. Specifically, the pore volumes of **NU-1500(Fe)**, **WYU-100**, **WYU-105** and **WYU-107** can be calculated to be 1.25, 1.07, 0.99 and 0.93 $cm^3\ g^{-1}$, respectively, which

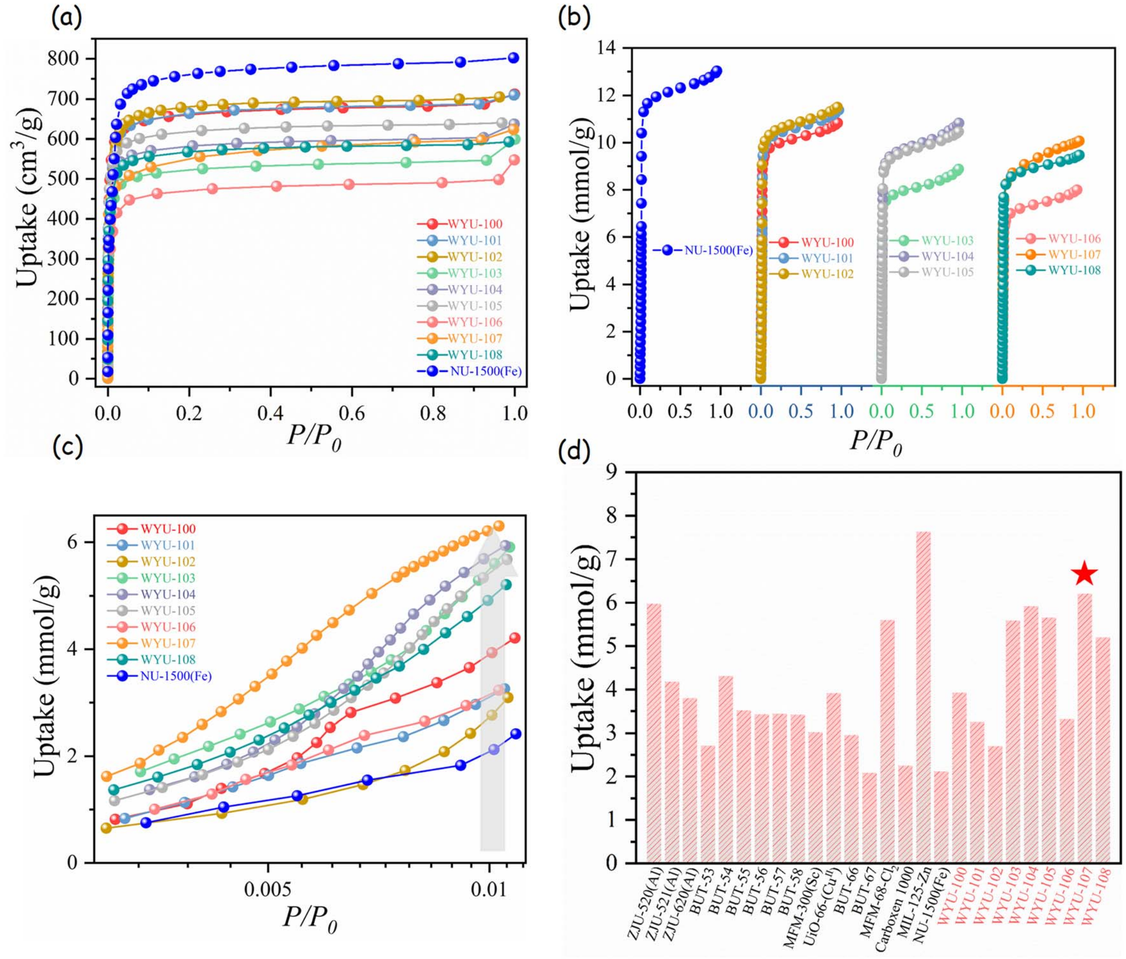


Fig. 2 (a) $N_2$ sorption isotherms at 77 K and (b) benzene vapor adsorption isotherms at 298 K for **WYU-100–108** and **NU-1500(Fe)**. (c) Logarithmic-scale plots of $P/P_0 = 0.01$ to view the adsorption of benzene at low partial pressures. (d) The performance comparison of trace benzene vapor uptakes for various MOFs at $P/P_0 = 0.01$.

are close to their theoretical values (1.40, 1.19, 1.13 and 0.97 $cm^3\ g^{-1}$). Fitting the adsorption isotherms of **NU-1500(Fe)**, **WYU-100**, **WYU-105** and **WYU-107** using the Brunauer–Emmett–Teller (BET) model gave the surface areas of 2900, 2690, 2480 and 2070 $m^2\ g^{-1}$, respectively. As expected, the insertion of different sized ligands ($L_1$ to $L_3$) can regulate the pore size of the host-framework.

Nonlocal Density Functional Theory (NLDFT) calculations gave a broad pore size distribution centered from 8.3 to 12 Å (Fig. S18), which is smaller than that of the parent **NU-1500(Fe)** (14 Å) due to the insertion of various pyridyl ligands. Interestingly, the pore window of **WYU-107** was partitioned into three triangular channels (7.8 × 6.9 $Å^2$), being consistent with the value from the pore size distribution. This pore size compatibility with molecules significantly promotes the host–guest interaction, which is conducive to improving the capture performance. In addition, these MOFs retain their frameworks after being exposed to air or immersed in aqueous solutions in a wide pH range from 3 to 10 for one year (Fig. S19–S21). Moreover, $^1$H NMR measurement of **WYU-100–108** after post-treatment (the desorbed MOFs were exposed to air for one year, and washed with DMF and acetone for several times) further verified the stability of the inserted pyridyl ligand (Fig. S3–S11). However, 77 K $N_2$ adsorption measurements of **WYU-100–108** after being exposed to air for one year revealed a decline in saturation uptake. Among them, the uptake of tri-pyridyl modified MOFs (**WYU-107** and **WYU-108**) displayed a marginally smaller decline than bi-pyridyl and mono-pyridyl modified MOFs (Fig. S22). This trend was further corroborated by the result obtained from **WYU-107** after immersion at pH = 3 and pH = 10. These observations can be attributed to the higher structural connectivity, which is more conducive to the stability of the framework (Fig. S23).

As the pore sizes and functional ligands inserted in the host-framework have a significant impact on the host–guest interactions, benzene vapor sorption isotherms at 298 K were measured, which showed typical type-I curves (Fig. 2b) and verified the significant interaction between the guest benzene and host-framework. Obviously, the saturated benzene adsorption capacities of **WYU-MOF** correlate with pore volumes, as well as the pore sizes, whose capacity order gradually decreases from mono-pyridyl to tri-pyridyl ligand insertion with increase in the size of the pyridyl ligand. Specifically, the uptakes of mono-pyridyl ligand modified **WYU-100** (10.83 mmol $g^{-1}$), **WYU-101** (11.37 mmol $g^{-1}$) and **WYU-102** (11.50 mmol $g^{-1}$) are lower than that of the parent **NU-1500(Fe)** (13.02 mmol $g^{-1}$), due to the reduction of pore volume after the insertion of mono-pyridyl ligands. Similarly, the uptakes of bi-pyridyl ligand modified **WYU-104** (10.50 mmol $g^{-1}$) and **WYU-105** (10.46 mmol $g^{-1}$) are higher than those of tri-pyridyl ligands modified **WYU-107** (10.07 mmol $g^{-1}$) and **WYU-108** (9.47 mmol $g^{-1}$). It is worth noting that MOFs modified with ligands of amide groups, **WYU-103** (8.88 mmol $g^{-1}$) and **WYU-106** (7.99 mmol $g^{-1}$), exhibit poor benzene vapor uptakes, probably because the charge density and distribution of ligand are not conducive to interacting with the benzene molecule. The saturation uptakes of **WYU-100–108** are not superior compared to those of the reported MOFs, $[Zn_{12}(\mu\text{-}O)_3(BTB)_4(MPTDC)_9]$ (NENU-513, $H_3BTB$ = benzene-1,3,5-tribenzoic acid, $H_2MPTDC$ = 3-methyl-4-phenylthieno [2,3-*b*]thiophene-2,5-dicarboxylic acid) (21.62 mmol $g^{-1}$), MIL-101(Cr) (15.84 mmol $g^{-1}$) and ZJU-520 (12.07 mmol $g^{-1}$) (Table S1).[13,30,31]

Interestingly, further analysis shows that the frameworks modified with various pyridyl ligands exhibit exceptional benzene adsorption behaviors at relatively low pressures. Specifically, **WYU-100–108** exhibit significantly steep increases at low pressures, indicating the great potential for the capture of benzene vapor at trace levels. According to the literature, the capture of benzene at low concentrations, especially at low pressure ($P/P_0$ < 0.01), is critically important as it directly correlates with the challenging scenario of adsorption of highly diluted pollutants from air.[11,32–34] This value corresponds to a partial benzene pressure of ∼127 Pa, and equates to a benzene concentration of approximately 1250 ppm. Although benzene is present in polluted air or industrial settings at concentrations of parts-per-billion (ppb) and lower levels (parts-per-million (ppm)), $P/P_0$ = 0.01 is usually used to simulate the trace conditions in the laboratory for investigating the capture performance of benzene.

For example, **WYU-100**, **WYU-101** and **WYU-102** show benzene uptakes of 3.93, 3.25 and 2.76 mmol $g^{-1}$ at $P/P_0 = 0.01$, respectively, which are significantly higher than that (2.12 mmol $g^{-1}$) of their parent **NU-1500(Fe)**. At the same time, those of **WYU-103**, **WYU-104** and **WYU-105** are 5.59, 5.92 and 5.66 mmol $g^{-1}$, respectively, while those of **WYU-106**, **WYU-107** and **WYU-108** reach 3.23 mmol $g^{-1}$, 6.21 mmol $g^{-1}$ and 5.20 mmol $g^{-1}$, respectively (Fig. 2c). Notably, the uptake of **WYU-107** modified with tph ligand is about three times higher than that of **NU-1500(Fe)**. As far as we know, the trace adsorption capacity of **WYU-107** exceeds that of most porous materials, and is only below that of the defective-MIL-125-X (7.63 mmol $g^{-1}$, X = Mn, Co, Ni, Cu, Zn) (Fig. 2d).[11,13,31,33–35] In short, the pore volume is conducive to the saturation uptake of benzene, while the adsorption performance of trace benzene uptake is related to the sizes and structures of the inserted ligands in the framework, which govern the host–guest interaction. Consequently, the uptakes of trace benzene vapor gradually increase from mono-pyridyl **WYU-100** to bi-pyridyl **WYU-105** to tri-pyridyl **WYU-107**. In addition, the benzene vapor uptake for **WYU-107** showed negligible decline after multiple cycles, suggesting the significant reproducibility for **WYU-107** (Fig. S24). In order to verify the structural distortions of the framework during the adsorption process, *in situ* variable-pressure PXRD spectra of activated **WYU-107** were collected, which show that a new diffraction peak (the highlighted zone) occurred with the pressure increase of benzene vapor. At the same time, the PXRD pattern of desorption at 120 °C was consistent with that of as-synthesized **WYU-107**, which may be attributed to the deformation behaviour during the adsorption process (Fig. 3a).

To evaluate the efficiency of **WYU-107** for the capture of trace benzene at different humidity levels (RH = 0% and 40%), dynamic breakthrough experiments of **WYU-107** were performed. The results indicated that benzene vapor started to breakthrough the column of ∼3750 min $g^{-1}$ under dry conditions (RH = 0%), corresponding to a dynamic adsorption capacity of 6.64 mmol $g^{-1}$. However, the adsorption capacity reduced to 1.22 mmol $g^{-1}$ (∼652 min $g^{-1}$) under the humidity level (RH) of 40% due to the competitive adsorption of water (Fig. 3b and S25–S26). At the same time, adsorption kinetic experiments of benzene vapor were performed on **WYU-100**, **WYU-105** and **WYU-107** as examples at $P/P_0 = 0.01$. The results show that there were 12 minutes more for adsorption equilibrium to be reach in the case of **WYU-100**, while there were only 2 minutes for **WYU-107** in the case of the macrocyclic ligands. Meanwhile, the adsorption uptake (5.90 mmol $g^{-1}$) of **WYU-107** is close to the value (6.21 mmol $g^{-1}$) from the adsorption isotherm at $P/P_0 = 0.01$. These results indicate that the PSM of macrocyclic ligands into **NU-1500(Fe)** can significantly enhance the host–guest interaction, which is conducive to the enhanced rate of adsorption of benzene vapor (Fig. S27).

To gain insight into the interaction mechanism between the framework of **WYU-107** and benzene molecules, **$C_6H_6$@WYU-107** was characterized by SCXRD, showing clearly the positions of benzene molecules in the pores (Fig. 4). There are three binding sites (I, II and III) for $C_6H_6$ in **$C_6H_6$@WYU-107**. Specifically, sites I and II are located in the cavities enclosed by a pair of triptycence moieties and a pair of trinuclear clusters, respectively. The benzene molecule in site I is bound to the triptycence moieties through C–H···π interactions ($d$ = 3.7 to 4.4 Å), while that in site II is stabilized by C–H···π interactions ($d$ = 4.2–4.5 Å),[36–39] as well as strong C–H···O interactions with carboxylate groups (2.9–3.3 Å). Notably, a pair of benzene molecules are tightly encapsulated in site III enclosed by a pair of tph ligands, where each benzene molecule simultaneously interacts with the hexaazaphenalene moiety in a face-to-face fashion at a short distance of *ca.* 3.4 Å and with the other benzene molecule at a distance of *ca.* 4.8 Å through special π–π stacking interactions.[40] Such strong host–guest interactions obviously contribute to the remarkable benzene uptake of **WYU-107** at low pressures compared to the parent **NU-1500(Fe)**, demonstrating the crucial role of macrocyclic tph in enhancing the binding interactions with benzene molecules. At the same time, the results of theoretical calculations for **$C_6H_6$@WYU-107** and **NU-1500(Fe)** demonstrate that the interaction sites are in substantial accordance with the *in situ* SCXRD.[41–43]

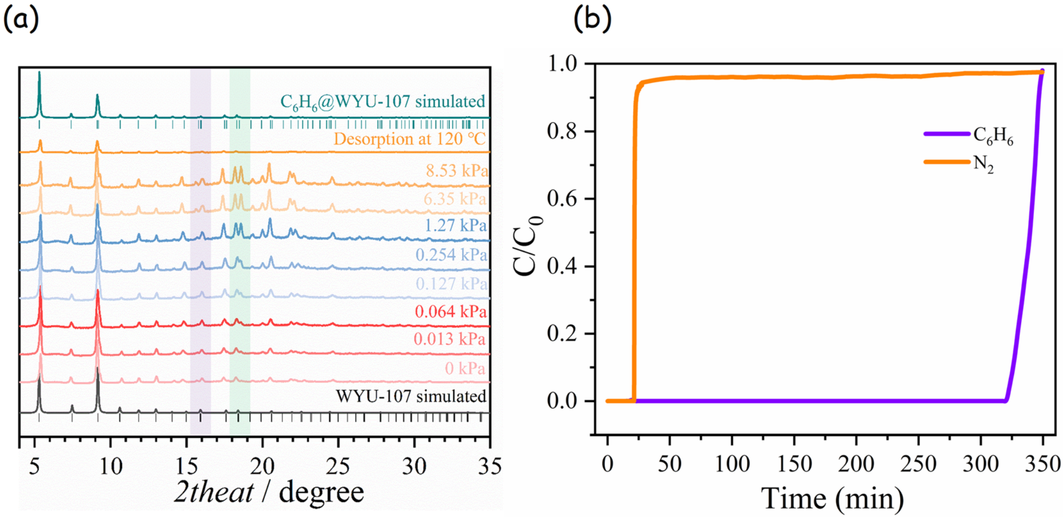


Fig. 3 (a) *In situ* variable-pressure PXRD patterns of **WYU-107**, collected under benzene vapor pressure from 0 to 8.53 kPa (guest-free to $C_6H_6$@**WYU-107**) and desorption at 120 °C after the adsorption process. (b) Benzene breakthrough curves for **WYU-107** in air at 298 K.

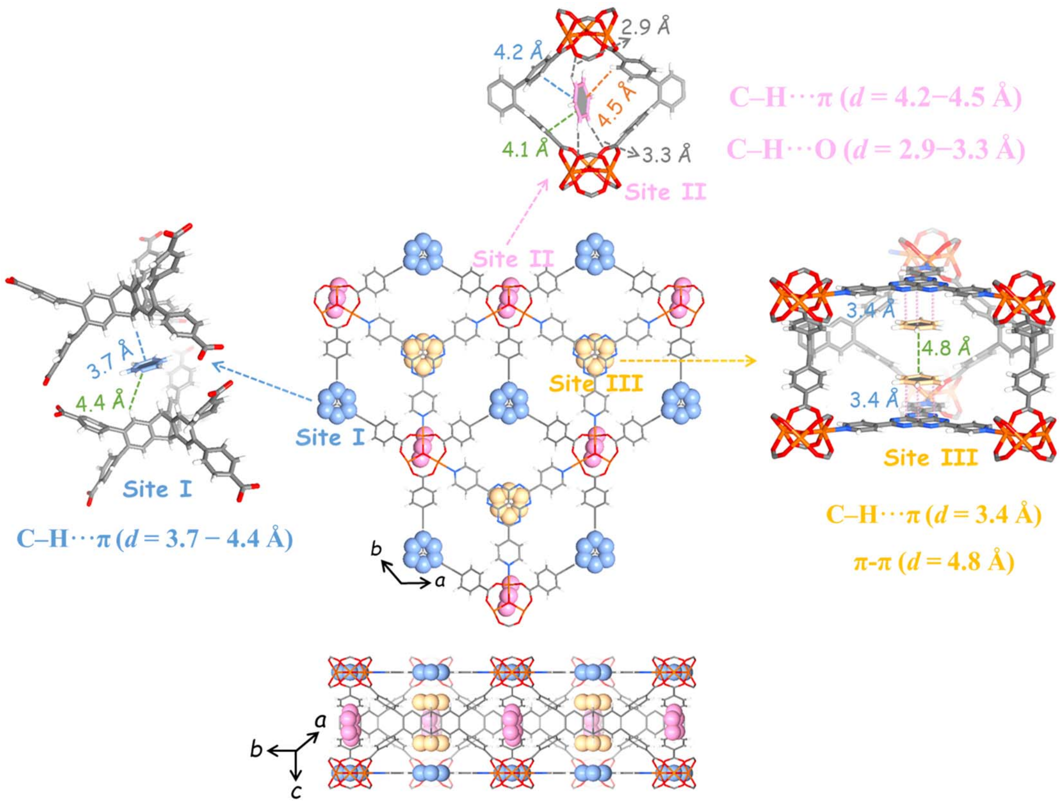


Fig. 4 The adsorption sites of $C_6H_6$@**WYU-107** characterized by single-crystal X-ray diffraction.

Furthermore, the calculations of electrostatic potential (ESP) indicated that there are significant dispersion forces between benzene molecules and multiple adjacent atoms within the host-framework at site I, due to the close distances, while strong induction and orientation forces were present at site II due to the electrostatic interaction between hydrogen atoms (positive charge) of benzene and oxygen atoms (negative charge) of carboxylate groups. Specifically, the calculated binding energy of the benzene molecule in the parent **NU-1500(Fe)** at site II is −58.01 kJ mol$^{-1}$, which is slightly higher than that at site I of −57.23 kJ mol$^{-1}$ (Fig. 5a and b). In contrast, **WYU-107** possesses not only two adsorption sites (site I and II) similar to those of **NU-1500(Fe)**, with the calculated binding energies being −46.40 kJ mol$^{-1}$ and −71.78 kJ mol$^{-1}$ (Fig. 5c and d), respectively, but

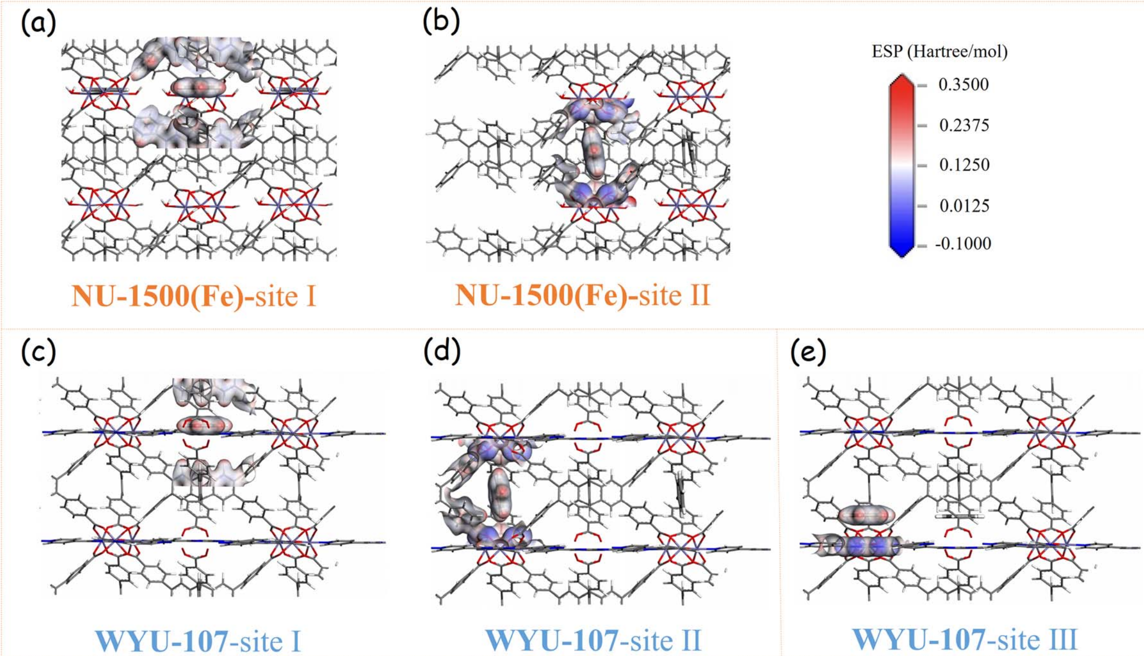


Fig. 5 The ESP of adsorption binding sites in **NU-1500(Fe)** (a and b) and **WYU-107** (c–e).

also an additional site III with a calculated binding energy of −33.71 kJ mol$^{-1}$ (Fig. 5e). In other words, the insertion of macrocyclic ligands induces structural deformation, resulting in the enhancement of host–guest interactions at site II, and introducing an extra site III in **WYU-107** at the same time. Consequently, such multiple effects result in the significantly enhanced capture of trace benzene.

## Conclusions

In summary, various pyridyl derivative ligands were successfully integrated into **NU-1500(Fe)** by a post-synthetic modification strategy, allowing the regulation of host–guest interaction. Particularly, **WYU-107** modified with a tri-pyridyl ligand of functional macrocyclic moiety exhibits significant interaction for benzene molecules by virtue of the combination of π–π, C–H⋯π and C–H⋯O interactions, enabling the capture performance surpassing most reported porous materials. These results demonstrate that the enhancement of the host–guest interactions by post-synthetic modification of functional macrocyclic ligand insertion in large pores of MOFs is effective for the capture of trace benzene vapor, which may inspire the molecular design of porous materials to achieve higher capture efficiency.

## Author contributions

Gang Liang: investigation, data curation, writing – original draft. De-Jian Chen: methodology, data curation, resources. Zhu-Jun Long: methodology, data curation, resources. Hao Zhou: resources, methodology. Xiao-Feng Zhong, Xiong-Hai Chen and Huai-Yu Shao: review & editing. Zong-Wen Mo: project administration, funding acquisition, writing – original draft, writing – review & editing, formal analysis. Xiao-Ming Chen: supervision, project administration, funding acquisition.

## Conflicts of interest

The authors declare no competing financial interest.

## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

CCDC 2424097–2424106 contain the supplementary crystallographic data for this paper.[44a–j]

Supplementary information: Experimental details , theoretical calculation methods, PXRD patterns, thermogravimetric analysis (TGA) data, and crystallographic data (PDF). See DOI: https://doi.org/10.1039/d5sc05093f.

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