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Dense Packing of Xenon in an Ultra-Microporous Metal–Organic Framework for Benchmark Xenon Capture and Separation

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ABSTRACT

For adsorptive separation of xenon/krypton mixture, it still remains a daunting challenge to target both high Xe adsorption and selectivity in a single adsorbent because of their close size and inert nature. Herein, we report an ultra-microporous alkyl Cu-based MOF (MOF-11) with suitable pore architecture for benchmark Xe capture and separation. MOF-11 features small pore channels (4.4 Å) close to the kinetic diameter of Xe atom, in which a large number of oppositely adjacent open Cu-metal sites and alkyl cavities are densely arranged along the pore channels in staggered mode. Such unique pore system can not only introduce strong binding affinity with Xe, but also enable the dense packing of Xe inside the pores. This material thus shows the highest Xe storage density of 2826 g L⁻¹ at ambient conditions, record-high Xe uptake of 4.0 mmol g⁻¹ (at 0.2 bar and 298 K) and one of the highest Xe/Kr selectivity (19.1), significantly higher than most top-performing materials reported so far. The Xe molecules trapped within MOF-11 were visually identified by single-crystal X-ray diffraction experiment, which unveils the dense packing mechanism of Xe within the pores accountable for the record Xe capture capacity. The breakthrough experiments confirm that MOF-11 exhibits the exceptional separation performance for 20/80 Xe/Kr mixture with both record-high Xe uptake capacity (3.46 mmol g⁻¹) and Kr productivity (350 cm³ g⁻¹).

INTRODUCTION

Highly efficient and energy-saving separation of noble gases such as xenon (Xe) and krypton (Kr) is a very important but challenging process in the production of high-purity noble gases

(Xe and Kr) and the pollution control of their radioactive isotopes. High-purity Xe and Kr are commercially valuable and widely used in many applications including spacecraft propellants, insulation, lighting, medical imaging and gas lasers¹. The main available resources of Xe and Kr come from the Earth atmosphere with the extremely low concentrations (0.087 ppmv for Xe and 1.14 ppmv for Kr)². Generally, commercial Xe and Kr gas are produced by cryogenic distillation from an approximately 20/80 (v/v) Xe/Kr gas mixture, which is obtained as a by-product during air separation industry². In addition, the radioactive ¹²⁷Xe and ⁸⁵Kr isotopes are generated in nuclear fission and can enter the atmosphere during the used nuclear fuel (UNF) reprocessing, which must be separated and sequestered safely to prevent the radioactive contamination since they are both hazardous and ⁸⁵Kr has a long half-life of 10.8 years³⁻⁵. Traditional cryogenic distillation is by far the most mature technology to separate Xe and Kr from air or the off-gas streams during the UNF reprocessing, which is excessively costly and energy-intensive⁴. To reduce energy consumption, the development of more efficient separation technologies is highly desired for Xe/Kr separations.

Adsorptive separation using solid porous adsorbents has been considered as a more energy-efficient alternative due to the potential of greatly cutting energy consumption and operating costs⁶. In this regard, porous metal-organic frameworks (MOFs)⁷⁻¹³, also known as porous coordination polymers (PCPs), have emerged as a new class of promising adsorbents for various gas separations owing to their highly tunable pore structures and functionalities¹⁴⁻²⁴. While a number of MOFs have been developed for efficient Xe/Kr separation²⁵⁻⁵¹, it still remains a grand challenge to target ultrahigh separation performance, since Xe and Kr are inert atomic gases with no dipole or quadrupole moments. Typically, there exists an obvious trade-

off between adsorption uptake and gas selectivity for Xe/Kr separation²⁷. For example, some large-pore MOFs (e.g., PCN-14 and HKUST)^{25,35} exhibit high Xe adsorption capacity at 1 bar but weak Xe binding affinity that cannot efficiently discriminate the two molecules, thus resulting in low Xe/Kr selectivity. On the other hand, some ultra-microporous MOFs with tailor-made pore size that is slightly larger than the kinetic diameter of Xe (4.047 Å), usually exhibit the strong Xe binding affinity due to the pore confinement effect induced by the overlap of van der Waals potentials, leading to the record high Xe/Kr selectivity reported so far. However, their small pore volumes or low surface areas prone to result in relatively low Xe uptake capacities, as exemplified by SBMOF-1³¹ and Co-squarate³². To overcome this trade-off limitation, a better design is to construct suitable pore confinement densely decorated with strong binding sites in ultra-microporous MOFs, enabling highly selective recognition and efficient packing of targeted Xe molecules inside the pores. Thus, the strong binding sites can strengthen the recognition of Xe over Kr and thus improve Xe/Kr selectivity; meanwhile, the dense packing of the preferred Xe molecules is able to fully make use of pore spaces for high Xe uptake density. This strategy has been well exemplified in the MOFs of SIFSIX-1-Cu¹⁴ and UTSA-16²³ for C₂H₂ or CO₂ capture and separation, wherein the suitable pore confinement enables the formation of gas clusters inside the pores to result in the dense packing of gas molecules for targeting simultaneously high gas uptake and selectivity. However, compared with those gases with dipole or quadrupole moments (e.g., CO₂, SO₂, and C₂H₂), inert atomic Xe gas usually shows weak host-guest or guest-guest interactions during the adsorption process, making the achievement of dense packing of Xe inside the pores more difficult and challenging. Therefore, such dense packing strategy has not been realized yet for Xe/Kr separation.

To achieve the desired dense packing of Xe within porous materials, an ideal material would have an appropriate pore system that densely and orderly arranges a large number of strong binding sites (e.g., polar groups or open metal centers) combined with an optimal pore size close to the kinetic diameter of Xe. We target this matter herein in an ultra-microporous alkyl Cu-based MOF-11 (also called ATC-Cu)^{13,24} that achieves the dense packing of Xe molecules for benchmark Xe capture and separation. We discovered that MOF-11 features small pore channels with suitable pore dimensions (4.4 Å) close to the kinetic diameter of Xe atom (4.047 Å), in which a large number of oppositely adjacent open Cu-metal sites and alkyl cavities are densely arranged along the channels in staggered mode to provide dense and strong adsorption sites for Xe capture (Fig. 1). Single-crystal X-ray diffraction studies on Xe loaded MOF-11 crystals (Xe@MOF-11) identified that this unique pore system can not only introduce the strong Xe-framework interactions, but also enable the dense packing of Xe atoms within the pores due to the efficient Xe···Xe interactions. MOF-11 thereby exhibits the highest Xe storage density of 2826 g L⁻¹ at 1 bar and 298 K, the record-high Xe uptake of 4.0 mmol g⁻¹ at 0.2 bar and 298 K, and very high Xe/Kr selectivity of 19.1 among all the reported materials at the same conditions. Dynamic breakthrough experiments confirm the benchmark separation performance of MOF-11 on Xe/Kr (20/80) gas mixtures, affording both the unprecedentedly high Xe adsorption capacity (3.46 mmol g⁻¹) and Kr productivity (350 cm³ g⁻¹).

RESULTS

Synthesis and characterisation. The MOF-11 crystal sample was simply prepared from the hydrothermal reaction of H₄ATC (1,3,5,7-adamantane tetracarboxylic acid) and copper nitrate trihydrate [Cu(NO₃)₂·3H₂O] according to the previous literatures with slight modification^{13,24}.

The phase purity of bulk MOF-11 sample was confirmed by matching the experimental and simulated powder X-ray diffraction patterns (PXRD; Supplementary Fig. 2). The dehydrated crystal structure of MOF-11 is depicted in Fig. 1. The framework of MOF-11 consists of paddle-wheel dinuclear $\text{Cu}_2(\text{COO})_4$ secondary building units (SBUs) linked by the ATC^{4-} organic linkers to form three-dimensional (3D) network, in which each ATC^{4-} ligand binds with four SBUs and one SBU is bridged by four ATC linkers (Fig. 1a). As a result, MOF-11 exhibits a (4,4)-connected *PtS* structure topology (Supplementary Fig. 1). As depicted in Fig. 1b and 1c, MOF-11 possesses two types of pore channels: one square-shaped pore channel with a diameter of 4.4 Å along the *c* axis, and one rhombic channel with a diameter of 4.4×5.4 Å (after subtracting van der Waals radius) along the *a* and *b* axis. Both of pore channels are constructed by four SBUs and four ATC^{4-} linkers to connect with each other. Most importantly, we found that two Cu-paddlewheel units are oppositely adjacent to each other along two pore channels. The Cu–Cu distance between neighboring open copper(II) centers is only 4.4 Å after subtracting van der Waals radius, thereby providing a considerable dual Coulombic interaction within the pores and potentially offering a strong binding site for Xe (Fig. 1b). In addition, there exist two kinds of aliphatic hydrocarbon cavities (cavity II and cavity III) constructed by four enclosed ATC linkers, as shown in Fig. 1b and 1c. Eight or twelve hydrogen atoms originated from four ATC linkers point toward the center of the aliphatic hydrocarbon cavities. The average distance between these hydrogen atoms and center of the cavity is only 3.7 Å and 3.5 Å, respectively, which provide potential adsorption sites for Xe capture. Most importantly, we found that cavity I and cavity II are staggered with each other along the *a* and *b* axis, and

Fig. 1 Crystal structure of MOF-11. **a** The ATC^{4-} linker and $Cu_2(COO)_4$ paddle-wheel building unit. **b** and **c** Two kinds of pore channels view along with a or c axis, in which three types of pore cavities are around the pore channels. **d** Cavity I and Cavity III are staggered with each other along the c axis. **e** Cavity I and Cavity II are staggered with each other along the a and b axis.

cavity I and cavity III show a staggered arrangement inside the pore channel along the c axis. These staggered arrangement features of oppositely adjacent open metal sites and aliphatic hydrocarbon cavities has the great potential to not only afford the ultrahigh Xe binding affinity but also enable the dense packing of Xe molecules within the pore channels, thus affording concurrently high Xe adsorption and selectivity. The permanent porosity of activated MOF-11 sample was confirmed by nitrogen (N_2) adsorption isotherms at 77 K. MOF-11 exhibits a typical type-I adsorption behavior with a N_2 uptake of $144 \text{ cm}^3 \text{ g}^{-1}$, implying its microporous nature (Supplementary Fig. 4). The Brunauer–Emmett–Teller (BET) surface area and pore volume of activated MOF-11 samples are evaluated to be $602.8 \text{ m}^2 \text{ g}^{-1}$ and $0.23 \text{ cm}^3 \text{ g}^{-1}$ respectively, which are comparable to the values reported in the previous literatures²⁴.

Gas adsorption measurements. The appropriate pore structure with dense binding sites and close pore size (~ 4.4 Å) with the diameter of Xe atom encouraged us to investigate the Xe and Kr adsorption performance of MOF-11. Single-component Xe, Kr, Ar, N₂ and O₂ sorption isotherms for activated MOF-11 were measured at different temperatures. As shown in Fig. 2a, MOF-11 displays extremely steep variable temperature adsorption isotherms at very low pressure, and almost saturation at around 0.2 bar and 298 K, indicating its strong affinity for Xe molecule. The total Xe uptake at 298 K and 1 bar can reach up to 4.95 mmol g⁻¹, which is notably higher than most of porous materials such as Ag-MOF-303 (3.25 mmol g⁻¹)³⁷, CC3 (2.44 mmol g⁻¹)⁵³, SBMOF-1 (1.4 mmol g⁻¹)³¹, and Co-squarate (1.34 mmol g⁻¹)³². At 0.2 bar, which is an indicator of the Xe capture ability of adsorbents from a 20/80 Xe/Kr mixture, MOF-11 exhibits a record high Xe uptake of 4.0 mmol g⁻¹ at 298 K, significantly higher than all the reported benchmark materials including MOF-74-Co (2.57 mmol g⁻¹)⁴², Ag-MOF-303 (2.06 mmol g⁻¹)³⁷, SBMOF-1 (1.27 mmol g⁻¹)³¹ and Co-squarate (1.18 mmol g⁻¹)³², setting a new benchmark for Xe capture uptake at 0.2 bar. Considering the relatively low BET surface areas (602.8 m² g⁻¹) and pore volume (0.23 cm³ g⁻¹), the density of adsorbed Xe inside MOF-11 was calculated to be ultrahigh of 2826 g L⁻¹ at 298K and 1 bar, which is 480 times larger than the density of gaseous Xe (5.89 g L⁻¹ at 1 bar and 273K) and just slightly lower than the liquid Xe density (3058 g L⁻¹ at 1 bar and 165 K). To the best of our knowledge, this value is the highest among all the reported materials so far, notably higher than that of SBMOF-1 (2042 g L⁻¹)³¹, SIFSIX-3-Ni (1830 g L⁻¹)⁴⁴, Co-squarate (1769 g L⁻¹)³² and Co-MOF-74 (1641 g L⁻¹)⁴², indicating the most highly efficient packing of Xe molecules inside the pores of MOF-11 (Fig. 2c). On the contrary, MOF-11 shows significantly low Kr, Ar, N₂ and O₂ uptakes at 1 bar and

298 K (Fig. 2b), affording the obviously preferred adsorption of Xe over Kr, Ar, N₂ and O₂.

These adsorption differences between these gases and the dense packing of Xe molecules can be partially explained by the experimental isosteric heat of adsorption (Q_{st}), calculated based on adsorption isotherms at different temperatures. As shown in Fig. 2d, Supplementary Fig. 12, 16 and 17, the initial Q_{st} value of Xe (29.4 kJ mol⁻¹) is much higher than that of Kr (23.5 kJ mol⁻¹), Ar (13.9 kJ mol⁻¹), N₂ (18.4 kJ mol⁻¹) and O₂ (11.9 kJ mol⁻¹), indicating a much stronger binding affinity of Xe. With the increase of Xe loading, the Q_{st} value can be gradually increased to 34.9 kJ mol⁻¹ for Xe. This implies that the Xe adsorption process at high loadings benefits from intermolecular interactions among the adsorbates²², probably leading to the efficient packing of Xe molecules inside the pores. Such similar Q_{st} increase on gas adsorption was also observed in SIFSIX-1-Cu¹⁴ and CAU-10-H²², which has been proved to show the efficient packing of gas molecules to form gas clusters. Owing to the efficient packing of Xe, MOF-11 exhibits a moderate Q_{st} value of Xe but achieves the highest Xe storage density compared with all the reported MOFs, as evidenced in Supplementary Table 5 and Fig. 18.

Fig. 2 Experimental characterization of Xe and Kr adsorption in MOF-11. **a** Xe sorption isotherms of MOF-11 at different temperatures. Filled and open circles represent adsorption and desorption data. **b** Xe, Kr, Ar, N₂ and O₂ adsorption isotherms of MOF-11 at 298 K. **c** Comparison of Xe storage density at 1 bar and 298 K for MOF-11 and other top-performing MOFs. **d** Isothermic heat of adsorption (Q_{st}) for Xe and Kr of MOF-11. **e** Calculated IAST selectivity of MOF-11 for Xe/Kr (20/80, v/v), Xe/N₂ (1/99), Xe/O₂ (1/99) and Xe/Ar (1/99) at 298 K. **f** Comparison of Xe uptake at 0.2 bar and 298 K and IAST selectivity of MOF-11 and other top-performing materials.

The Xe/Kr selectivity of MOF-11 for a 20/80 binary gas mixture were predicted using ideal adsorbed solution theory (IAST) based on the experimental gas adsorption isotherms. As shown in Fig. 2e, MOF-11 exhibits a significantly high Xe/Kr selectivity of ~ 19.1 at 298 K and 1 bar, which is comparable to that of the best-performing CROFOUR-1-Ni (22)²⁹ and SBMOF-1 (16)³¹, but higher than Ag-MOF-303 (10.4)³⁷ and MOF-74-Co (11.8)⁴². For 20/80 Xe/Kr separation, high Xe uptake capacity is also very important to determine the final separation performance. In this regard, MOF-11 exhibits a record high Xe adsorption capacity of 4.0 mmol g⁻¹ at 298 K and 0.2 bar, much higher than that of all the reported porous materials including MOF-74-Co (2.57 mmol g⁻¹)⁴², Ag-MOF-303 (2.06 mmol g⁻¹)³⁷, SBMOF-1 (1.27 mmol g⁻¹)³¹ and Co-squarate (1.18 mmol g⁻¹)³². As shown in Fig. 2f, we present a comprehensive comparison of MOF-11 with the top-performing MOFs in light of 0.2 bar Xe uptake and Xe/Kr selectivity as concurrent objectives. Most of MOF materials show both lower Xe uptake capacity and Xe/Kr selectivity than those of MOF-11. While Co-squarate³² and CROFOUR-1-Ni²⁹ exhibit higher Xe/Kr selectivity than MOF-11, they show extremely lower Xe uptakes at 0.2 bar due to their low pore volumes. Evidently, MOF-11 achieves the benchmark balance with simultaneously high Xe uptake and Xe/Kr selectivity among all the reported MOFs so far. To evaluate the intrinsic interaction between adsorbents and adsorbed gas at very low pressure,

the Xe Henry coefficient for MOF-11 is calculated based on Xe adsorption isotherms at low pressure range (0–5 kPa) and 298 K. MOF-11 displays the second largest Henry coefficient value of 69.5 mmol g⁻¹ bar⁻¹ for Xe and a high thermodynamic Xe/Kr selectivity of 15.9 among all the reported top-performing MOFs²⁶. This indicates that MOF-11 is also placed among the most promising candidates for Xe capture and separation under dilute conditions. In addition, MOF-11 also exhibits an ultrahigh selectivity for 1/99 Xe/Ar (120), Xe/N₂ (76), or Xe/O₂ (131) binary gas mixtures (Fig. 2e), respectively.

Single-crystal diffraction studies on Xe-loaded MOF-11. To gain better insight into the record-high Xe storage density and capture capacity observed in MOF-11, we performed single-crystal X-ray diffraction (SCXRD) measurements on activated MOF-11 crystals filled with Xe. After the as-synthesized MOF-11 crystals in the capillary glass tube were activated at 150 °C under vacuum, the capillary glass tube was filled by pure Xe gas to 1 bar at 298K and sealed. Single-crystal X-ray diffraction data collected at room temperature revealed the crystal structure of Xe@MOF-11 with a formula of Cu₂(C₁₄H₁₂O₈)Xe₃. As shown in Fig. 3, MOF-11 was found to exhibit three binding sites (site-1, site-2 and site-3) for Xe molecules. Fig. 3a shows that Xe atom is located in the middle of the two oppositely Cu-paddle wheels (site-1), which dually interacts with the two metal sites with a short Xe···Cu distance of 2.950 Å. This value is much shorter than the metal–Xe interaction distance found in MOF-74-Co (Xe···Co, 3.22(3) Å)⁴² and MOF-74-Ni (Xe···Ni, 3.17(4) Å)⁴², indicating a much stronger Xe binding affinity of MOF-11. The Xe binding site-2 is located in the center of eight H atoms from four ATC linkers in rectangular channels with a Xe···H distances of 3.678 Å (Fig. 3b). As depicted in Fig. 3c, the Xe binding site-3 is in the center of aliphatic hydrocarbon cavity of rhombic

channels, in which Xe atom (Xe3) is surrounded by twelve H atoms from four enclosed ATC linkers with the Xe $\cdots$ H distances range from 3.477 Å to 3.988 Å. Due to the staggered arrangement of site-1 and site-2 along the *a* and *b* axis, the adsorbed Xe atom in site-2 interacts with two adjacent Xe atoms in site-1 with a Xe1 $\cdots$ Xe2 distance of 4.221 Å along the *a* or *b* axis (Fig. 3d). In addition, Xe atom in site-3 also strongly interacts with Xe atom in site-I with

Fig. 3 Illustration of the adsorbed Xe atoms in MOF-11 as determined by single-crystal X-ray diffraction.

a The Xe binding site-1 (Xe1) located in the center of the two adjacent open Cu-metal sites from oppositely Cu₂(COO)₄ paddle-wheels with a Xe $\cdots$ Cu distance of 2.950 Å. **b** The Xe binding site-2 (Xe2) in the aliphatic hydrocarbon cavity II. **c** The Xe binding site-3 (Xe3) in the aliphatic hydrocarbon cavity III. **d** The intermolecular interactions between Xe1 and Xe2 with the dense packing of Xe molecules along the *a* or *b* axis, and the intermolecular interactions between Xe1 and Xe3 with the dense packing of Xe molecules along the *c* axis. **e** The dense packing of Xe in the whole pore structure of MOF-11, viewed along the *c* axis.

a Xe3 $\cdots$ Xe1 distance of 3.620 Å, affording the staggered packing of Xe along the *c* axis (Fig. 3d). It should be noted that the observed Xe $\cdots$ Xe contact distance between site-1 and site-3

(3.620 Å) are notably shorter than that found in the Xe-loaded crystal structures of Xe@SBMOF-1 (5.567 Å)³¹, Xe@SBMOF-2 (5.181 Å)⁴⁵, Xe@MOF-74-Co (4.42 Å)⁴² and Xe@MOF-74-Ni (~ 4.50 Å)⁴² collected at 200K. This distance is even much shorter than the Xe···Xe distance in the crystal structure of pure Xe gas (~ 4.34 Å) collected at 26 K, as well as the van der Waals diameter of Xe atom (4.32 Å)⁵⁴. Evidently, the suitable pore architecture of MOF-11 enables the unprecedentedly dense packing of Xe molecules within the pore channels (Fig. 3e), thus accounting for the record-high Xe adsorption capacity and storage density observed in MOF-11. The SCXRD data indicates that the adsorbed Xe amount in site-1, site-2 and site-3 corresponds to 2.2, 2.2 and 2.2 mmol g⁻¹ gas uptake, wherein the total value of 6.6 mmol g⁻¹ is very close to the experimentally Xe uptake (5.28 mmol g⁻¹) at 273 K and 1 bar.

Column breakthrough experiments. To verify the practical applicability of MOF-11 for Xe/Kr separation, dynamic breakthrough experiments were carried out on the column packed with activated MOF-11 at 298 K for a representative Xe/Kr (20/80) gas mixture that mimics the feedstock generated from cryogenic process in air separation. As shown in Fig. 4a, a very clean Xe/Kr separation was accomplished by MOF-11. Pure Kr broke through immediately at ~ 28 min g⁻¹ for MOF-11 after the injection of Xe-Kr gas mixture into columns, while Xe retained in the column for a much longer retention time of 152 min g⁻¹. According to the breakthrough curves, the Xe/Kr selectivity of MOF-11 was calculated up to 16.6, which is

Fig. 4 Column breakthrough experiments using MOF-11 at room temperature and 1 bar. **a** Experimental column breakthrough curves for Xe/Kr (20/80) gas mixture adsorbed on MOF-11 at 1 bar and 298 K under a flow rate of 2.5 mL min^{-1} . **b** The signals of desorbed Xe and Kr during the regeneration process under 1.25 mL min^{-1} He flow at 298 K. **c** Comparison of the amount of Xe capture during the column breakthrough for MOF-11 with other top-performing porous materials at 298K. **d** Comparison of high-purity Kr productivity during the column breakthrough for MOF-11 with other promising porous materials at 298K. **e** Experiment breakthrough curves of MOF-11 at low concentrations using a gas-mixture (400 ppm Xe and 40 ppm Kr in dry air) at 298 K under a flow rate of 2.5 mL min^{-1} .

higher than the most top-performing MOFs reported such as MOF-Cu-H, Ag-MOF-303 and MOF-74-Co. During this dynamic separation process, MOF-11 exhibits the record high Xe adsorption capacity of 3.46 mmol g^{-1} and the highest productivity of high-purity Kr ($> 99.9\%$) of $350 \text{ cm}^3 \text{ g}^{-1}$ obtained from the outlet effluent. These values are significantly higher than those of all the reported porous materials so far, including MOF-Cu-H (2.09 mmol g^{-1} and $73 \text{ cm}^3 \text{ g}^{-1}$)³³, Ag-MOF-303 (1.64 mmol g^{-1} and $93 \text{ cm}^3 \text{ g}^{-1}$)³⁷, CROFOUR-2-Ni (1.91 mmol g^{-1} and $101 \text{ cm}^3 \text{ g}^{-1}$)²⁹ and ZJU-62 (2.88 mmol g^{-1} and $206 \text{ cm}^3 \text{ g}^{-1}$ at 273 K)²⁸. MOF-11 can be easily regenerated by vacuum or purging with helium for around 60 min at 298 K due to its

relatively low Q_{st} value of Xe and Kr (29.4 kJ mol⁻¹ and 23.5 kJ mol⁻¹). During the desorption process, high-purity Xe (99%) could be produced with a high productivity of 66.8 cm³ cm⁻³ (a recovery rate of ~ 61.5% for all the desorbed Xe). Multiple breakthrough tests for Xe/Kr mixtures confirmed that MOF-11 maintains the excellent Xe adsorption capacity and separation performance within three continuous cycles, indicating its good recyclability for Xe/Kr separation (Supplementary Fig. 19).

To evaluate the performance of MOF-11 on capture and separation of Xe and Kr from the off-gases in UNF reprocessing, we further carried out the breakthrough experiments using a low Xe-Kr concentration gas mixture (400 ppm Xe, 40 ppm Kr balanced with dry air). After initially purging with He for 5 min, the target gas mixture was injected into the column. As shown in Fig. 4e, N₂, O₂ and Kr broke through almost immediately after the gas-mixture injection. While Xe was retained much longer in the column with a retention time of about 100 min, in comparison with N₂, O₂ and Kr, suggesting the high performance of MOF-11 on Xe capture and Xe/Kr separation at dynamic dilute condition. Under these dilute conditions, the Xe adsorption capacity of MOF-11 was calculated to be 24.5 mmol kg⁻¹ at 298 K. This value is extremely higher than that of all the benchmark materials reported so far, such as SBMOF-1 (13.2 mmol kg⁻¹)³¹, CC3 (11 mmol kg⁻¹)⁵³, Ni-MOF-74 (4.8 mmol kg⁻¹)⁴ and MOF-Cu-H (13.0 mmol kg⁻¹)³³. These results prove the best separation performance of MOF-11 for both Xe/Kr separation from Xe/Kr binary gas mixture and Xe capture from off-gas mixture under UNF reprocessing conditions.

Conclusions

In summary, we have realized an ultra-microporous MOF (MOF-11) with dense packing of Xe inside the pores for highly efficient Xe capture and separation. The Xe loaded SCXRD studies identified that the dense and staggered arrangement of the oppositely adjacent open Cu^{2+} -metal sites and alkyl cavities along the small channels can not only provide strong binding affinity with Xe but also enable the dense packing of Xe inside the pores, thus simultaneously optimizing the Xe adsorption uptake and Xe/Kr selectivity. This material thereby achieves the highest Xe storage density at ambient conditions, record-high Xe adsorption capacity at 0.2 bar and 298 K and concurrently high Xe/Kr selectivity reported so far. The breakthrough experiments affirmed that MOF-11 can efficiently separate Kr from Xe/Kr (20/80) mixtures with both the highest Xe uptake capacity and Kr productivity, making it as a new benchmark material for highly efficient Xe/Kr separation. This work may provide a new strategy of designing porous MOFs with dense packing of Xe inside the pores to achieve excellent Xe/Kr separation performance.

Methods

Synthesis of MOF-11. The MOF-11 crystal sample was simply prepared according to the previously reported literature with slight modification.^{13,24} H_4ATC (0.070 g, 0.22 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.532 g, 0.47 mmol) were dissolved in the aqueous NaOH solution (15 M, 15 mL). The reactants were added into a Teflon-lined autoclave and heated at 573 K for 18 hours. The green crystals of MOF-11 were obtained at the bottom of the vial. The as-synthesized samples were filtrated and washed with methanol, and then exchanged with methanol for 2 days prior to activation.

Characterization. A X'Pert PRO PANalytical diffractometer (Cu K α , 45 kV and 40 mA) was applied to obtain the powder X-ray diffraction (PXRD) patterns ($2\theta = 5\sim 50^\circ$). Thermogravimetric analysis (TGA) was performed on a TGA-550 (TA instrument) analyzer under N₂ gas flow from 30 °C to 800 °C in an aluminum crucible with a heating rate of 10 °C min⁻¹ using 3~6 mg of products..

Gas adsorption measurements. The gas sorption isotherms were measured using a surface characterization analyzer (Micromeritics 3Flex). The as-synthesized MOF-11 samples were degassed at 150 °C for 18 hours to yield guest-free phase before sorption measurements. The N₂ sorption isotherms at 77 K were measured using a liquid nitrogen bath. The gas sorption isotherms at different temperatures were collected using a Micromeritics's ISO Controller (Thermoelectric Cooled Dewar) to maintain the temperatures.

Single-crystal diffraction and structure determination. A single crystal of MOF-11 was selected and putted into a capillary glass tube with a 0.1mm inner diameter. This capillary glass tube was activated at 150 °C under vacuum for 24 hours. And then the capillary glass tube was filled by pure Xe gas up to 1 bar at 298K and then sealed. The single-crystal data on the Xe-loaded activated MOF-11 crystal were collected using an Agilent Supernova CCD diffractometer equipped with graphite-monochromatic enhanced Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The datasets were corrected by empirical absorption correction using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods and refined by full matrix least-squares methods with the SHELX-97 program package.⁵⁵ The crystal data are summarized in Supplementary Table 4.

Breakthrough measurements. The breakthrough experiments were performed in a home-built

dynamic gas breakthrough equipment (Supplementary Fig. 20). The activated MOF-11 sample (~210 mg) was packed into a steel column (the steel column is about 12 cm long with a 4-mm inner and 6.4-mm outer diameter) with silica wool filling the void space. The column was activated by heating at 423 K under vacuum for 12 h and then purged by helium gas with a flow rate of (2.5 mL min⁻¹) for 2 h before the column temperature was decreased to 298 K. A circulator bath was used to maintain the columns at 298 K. The flow of helium gas was stopped while target gas mixtures (a 20/80 Xe/Kr binary gas mixture or 400 ppmv Xe 40 ppmv, Kr balanced with dry air) were fed to the column with a flow rate of 2.5 mL min⁻¹. The flow of helium and targeted gas mixture was controlled by two mass flow controllers. The downstream was monitored by a Hiden mass spectrometer (HPR 20). The desorption test of MOF-11 was carried out using the same dynamic gas breakthrough equipment, while the downstream was monitored by a gas chromatography (SCION GC-450) with thermal conductivity detector (TCD, detection limit 0.1 ppm). The standard gases were used to calibrate the concentration of the outlet gas. After the breakthrough tests, MOF-11 samples in the steel column can be readily generated by sweeping He gas (10 mL min⁻¹) at room temperature for 40 min or in high vacuum at room temperature for 60 min.

The adsorption capacity was estimated from the breakthrough curves using the following equation:

$$n_{\text{ads}} = FC_i t_i \quad (1)$$

Where n_{ads} is the adsorption capacity of the gas i , F is the total molar flow, C_i is the concentration of the gas i entering the column and the t_i is the time corresponding to the gas i , which is estimated from the breakthrough profile.

The selectivity was then calculated according to the equation:

$$S_{A/B} = \frac{X_A/X_B}{Y_A/Y_B} \quad (2)$$

Where X_A and X_B are the mole fractions of the gases A and B in the adsorbed phase and Y_A and Y_B are the mole fractions of the gases A and B in the bulk phase.

Data availability

All data involved in this work are included in this article and the corresponding supplementary information. Additional graphics, TG curves, PXRD diffractograms, multiple cycle breakthrough experiments, dual site Langmuir-freundlich isotherm model fitting, isosteric heat of adsorption calculations, IAST calculations of adsorption selectivities and column breakthrough test setup are available as Supplementary Information. The crystal structure data of Xe-loaded MOF-11 have been deposited at CCDC under the deposition numbers CCDC: 2130314. These data can be obtained free of charge from the CCDC database via www.ccdc.cam.ac.uk.

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538

539 **Author contributions**

540 Y.-L.P. designed the experiments, Q.L. synthesized MOF-11, and performed the activation and single-
541 component gas-adsorption experiments. B. L. and Y. G. performed column breakthrough experiments.
542 H.-M. W. and J. P. performed single-crystal X-ray diffraction studies. Q. L. and H.-M. wrote the original
543 draft of the manuscript; S.X., B.L. and X.W. conceived the project and Review & Editing the manuscript.
544

545 **Competing interests**

546 The authors declare no competing interests.
547

Dense Packing of Xenon in an Ultra-Microporous Metal–Organic Framework for Benchmark Xenon Capture and Separation

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