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High gas storage capacities and stepwise adsorption in a UiO type metal–organic framework incorporating Lewis basic bipyridyl sites†

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A UiO type MOF with Lewis basic bipyridyl sites was synthesized and structurally characterized. After being activated by Soxhlet-extraction, this MOF exhibits high storage capacities for H_2, CH_4 and CO_2, and shows unusual stepwise adsorption for liquid CO_2 and solvents, indicating a sequential filling mechanism on different adsorption sites.

Developing an effective system for carbon dioxide capture from anthropogenic emissions and finding appropriate mediums for energy gas (*i.e.*, H_2 and CH_4) storage have been long term challenges, and will be increasingly urgent in future.[1] Physical sorption using solid state absorbents provides efficient alternatives owing to fast kinetics and high energy efficiency.[2] Indeed, some pilot plants for carbon dioxide capture and methane storage using solid state absorbents have been realized by some research groups.[3]

Established as a new class of crystalline porous materials, metal–organic frameworks (MOFs) provide ideal platforms for such applications due to their intriguing structures, high surface area and tuneable functional pore environments.[4] In order to achieve high gas storage capacities or high selectivity, extensive efforts have been devoted to increase the affinity of frameworks with gas molecules, such as generating open metal sites[5] or tuning pore environments by immobilizing functional groups on the pore surface.[6] Immobilizing functional groups appears to be a promising strategy to tune the adsorption properties, especially for enhancing CO_2 binding strength by incorporating Lewis basic sites. However, the conventional strategy of anchoring the functional groups has some drawbacks. Along with the modification of the pore environments, the space occupation or blockage of functional groups always decreases the pore volume as well as specific surface areas significantly, which contrariwise lower the gas uptake capacities.[7] In this respect, the N-heterocyclic ligands are more attractive due to their benefits of constructing isomorphic MOFs and incorporating functional Lewis basic sites into the pore surface without declining their original pore spaces.[8]

The UiO types of MOFs are an emerging class of MOFs that attract broad interest.[9] The highly porous structures and excellent stability of these types of MOFs allow them to be promising materials for the targets of CO_2 capture and energy gas storage. Up to now, extensive studies have been conducted based on UiO MOFs and their derivatives synthesized by functionalization/modification on organic linkers.[10] Nevertheless, the gas sorption studies on UiO type MOFs incorporating Lewis basic pyridyl sites have never been investigated so far. The outstanding structural characteristics and excellent stability of UiO type MOFs motivate us to incorporate the pyridyl moieties into the frameworks, with the anticipation that it would further enhance the gas uptake capacities by anchoring the Lewis basic sites onto the pore surface but without sacrificing its original high porosity and exceptional robustness. Herein, we synthesized a UiO MOF, $Zr_6(\mu^3\text{-O})_4(OH)_4(bpdc)_{12}$ (termed as UiO(bpdc) in this communication), by using a N-heterocyclic carboxylate ligand: 2,2-bipyridine-5,5′-dicarboxylate (bpdc), in which the bipyridyl moieties were incorporated as free Lewis basic sites. Upon being activated by Soxhlet-extraction, the adsorption properties of N_2, H_2, D_2, CO_2 and CH_4 were examined. Afterwards, the sorption behaviours towards CO_2 at 195 K and organic solvents at room temperature on UiO(bpdc) were investigated, and the adsorption mechanism was discussed.

UiO(bpdc) is prepared from the solvothermal reaction of the bpdc ligand with $ZrCl_4$ *via* a modulated method (see experimental details in ESI,† S2), and a pure phase of octahedral shaped crystals were obtained. Single crystal analysis reveals that UiO(bpdc) crystallizes in *cubic* space group $Fm\bar{3}$ which has a lower symmetry in contrast to the commonly encountered $Fm\bar{3}m$ space group in UiO series MOFs,[11] because the inclusion of hetero N atoms in bpdc linkers lowers the symmetry of the crystal system. As expected, a six-nuclear 12-connected SBU: $Zr_6O_4(OH)_4(CO_2)_{12}$, is formed by the assembly of six zirconium atoms with eight μ^3-O or μ^3-OH bridged oxygen atoms and twelve carboxylate groups (as shown in Fig. 1a). Due to the oxo-philic nature of the early transition

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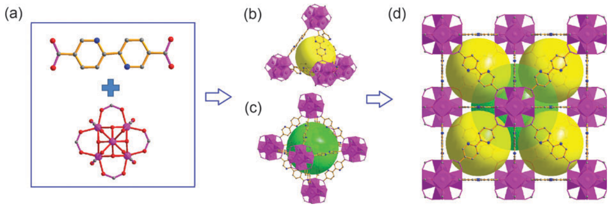

Fig. 1 (a) Ball and stick representation of the bpdc ligand and SBU: [$Zr_6(\mu^3\text{-}O)_3(OH)_3(COO)_{12}$] (gray: C; red: O; blue: N; purple: Zr); (b) the tetrahedral cage; (c) the octahedral cage; (d) packing of two types of cages.

elements, the Zr(IV) ions are preferably coordinated to the oxygen donor atoms of the carboxylate groups in bpdc, while the 2,2′-bipyridine moieties are left free, which could act as the Lewis basic sites. Then, each vertex of the 12-connected SBUs is bridged by the bpdc linkers through the carboxylate groups, forming a three-dimensional network with the *fcu* topology. The formula of UiO(bpdc) can be determined to be $Zr_6(\mu^3\text{-}O)_4(OH)_4(bpdc)_{12}$ on the basis of single crystal X-ray analysis and elemental analysis. Two types of cages, the octahedral cages with a diameter of 1.6 nm and the tetrahedral cages with a diameter of 1.2 nm, are formed by the assembly of the SBUs and linkers (as illustrated in Fig. 1b and c). The theoretical void ratio of the framework is 68.5%, with a crystallographic density of 0.765 g cm^{-3}.

The as synthesized sample prepared in this work is of high purity, as confirmed by good match between the simulated and experimental PXRD patterns (as shown in ESI,† S4). TGA analysis reveals that UiO(bpdc) is stable up to 512 °C under an N_2 atmosphere (see TGA curves in ESI,† S5), which is comparable with UiO-66 and its analogues,[7b] indicating its excellent thermal stability. The unvaried PXRD patterns of the samples exposed to moisture and treated by soaking in common solvents also show good chemical stability for this MOF (see PXRD patterns in ESI,† S4). To fully activate the as synthesized sample, we employed Soxhlet-extraction to extract the high boiling point solvents and other compounds involved in the framework, using ethanol as the extraction agent. Then, the guest molecules were removed by heating the extracted sample under ultrahigh vacuum before adsorption measurements.

The N_2 isotherm measured at 77 K of UiO(bpdc) shows a reversible typical type-I isotherm with a pore volume of 1.057 cm^3 g^{-1}. The Brunauer–Emmett–Teller (BET) and Langmuir surface areas are 2646 m^2 g^{-1} and 2965 m^2 g^{-1}, respectively (see the calculation process in ESI,† S7). These values are significantly higher than that of UiO-67 (BET surface area: 1877 m^2 g^{-1},[9a] 1575 m^2 g^{-1} (ref. 9*b*)). It is noteworthy that the experimental pore volume of UiO(bpdc) is identical to the theoretical value of UiO-67 (1.05 cm^3 g^{-1})[9b] which has almost the same ligand length and SBUs, demonstrating that UiO(bpdc) is fully activated and the Soxhlet-extraction is of great help for completely extracting the guest compounds involved in the framework.

The outstanding characteristics of structures and pore environments of UiO(bpdc) enable it to possess high uptake capacities for H_2, CO_2 and CH_4. As shown in Fig. 2b, it adsorbs 5.7 wt% of H_2 at 77 K and 20 bar, which has not reached saturation yet. It should be pointed out that this uptake is among the top ranks of the hydrogen uptakes on MOF materials, comparable to the uptakes on NOTT-102[12] and $Be_{12}(OH)_{12}(BTB)_4$.[13] This uptake is also 26.6% higher than that on UiO-67[9a] (4.5 wt% at 77 K and 20 bar). D_2 isotherm for UiO(bpdc) upto 1 bar at 77 K (see inset in Fig. 2b) shows a similar shape to H_2 with D_2/H_2 ratios (mol ratio) of about 1.05 times that are the reasonable uptake ratios of D_2 to H_2, confirming the reliability of the above H_2 adsorption measurements.[14] Moreover, the uptake ratio of D_2 to H_2 shows an increasing trend with the decreasing pressure and reaches a maximum ratio of 1.19 at 20 mbar (as shown in Fig. S5 in ESI,† S8). Former studies revealed that the quantum effects of D_2 and H_2 adsorption in confined nano-porous structures led to the difference in their adsorption properties.[14] As for UiO(bpdc), the fine structure of nano-corners around SBUs might attribute to the different adsorption isotherms of D_2 and H_2 at low pressures. At 293 K and 20 bar, it absorbs 79.7 wt% of CO_2 (as shown in Fig. 2b), corresponding to 310 v(STP)/v (using a crystallographic density of 0.765 g cm^{-3}). This value is the among the top uptakes of CO_2 on MOF materials, comparable to the uptakes on MOF-177[15] and MIL-101(Cr)[16] under the similar conditions, and is also larger than the experimental or theoretical CO_2 uptake capacities on UiO-67 and UiO-68.[9b] Considering the almost identical configurations as well as theoretical pore volumes of UiO-67, the significant enhancement of CO_2 uptakes on UiO(bpdc) could be attributed to the combinational benefits of high surface area and Lewis basic bipyridyl sites. The CO_2 uptakes at 0.15 and 1 bar are 1.5 and 8.0 wt%, respectively. These values are higher than those on MIL-101[16b] and MOF-177[15b] under similar conditions, but are lower than those on MOFs with narrower pore size, high dense open metal sites or $-NH_2$ functional groups,[17] indicating the different roles of surface chemistry and surface area in gas adsorption. The methane isotherms for UiO(bpdc) measured at room temperature show nearly linear trends up to 20 bar, indicating the promise of high working capacity under practical conditions (as shown in Fig. 2d). At 293 K and 20 bar, the adsorbed amount of CH_4 is 12.2 wt% (7.63 mmol g^{-1}), which is far from saturation. The methane isotherms fit well with the Langmuir equation at a higher pressure

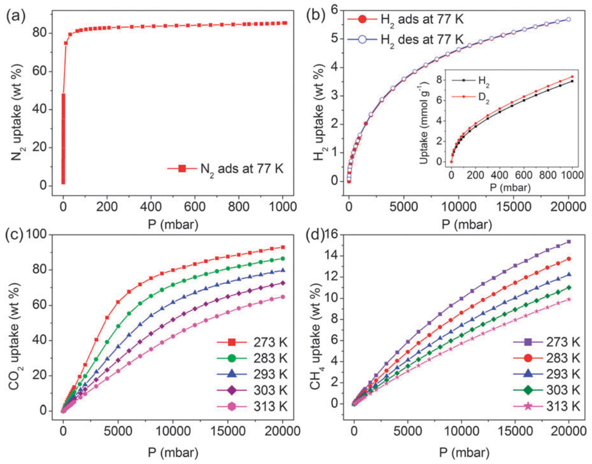

Fig. 2 Adsorption isotherms for UiO(bpdc). (a) N_2 (77 K); (b) H_2 (77 K) (excess) and D_2 (77 K) (inset); (c) CO_2 (273, 283, 293, 303 and 313 K) (excess); (d) CH_4 (273, 283, 293, 303 and 313 K) (excess).

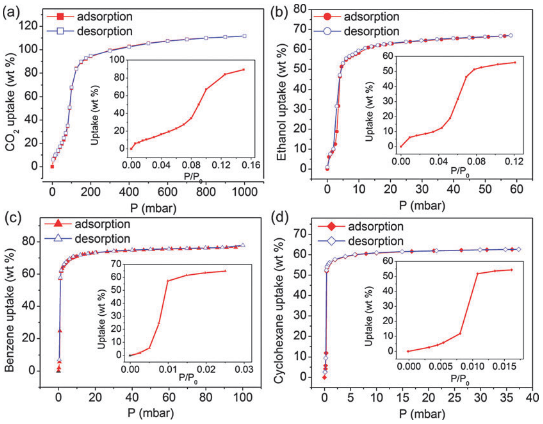

Fig. 3 (a) CO_2 isotherm at 195 K; (b) ethanol isotherm at 293 K; (c) benzene isotherm at 293 K; (d) cyclohexane isotherm at 293 K.

range (see details in ESI,† S10). The predicated methane storage capacity from Langmuir simulation is 10.52 mmol g^{-1} at 293 K and 35 bar, corresponding to 180 v(STP)/v. This value reached the DOE target of 180 v(STP)/v for methane storage at ambient temperature and 35 bar, making UiO(bpdc) one of the few MOFs that meet the DOE target. Compared to the benchmark MOFs with high methane capacities, such as PCN-14,[18] USTA-20[5] and MOF-74[19] *etc.*, UiO(bpdc) exhibits better thermal and chemical stability owing to the inclusion of the $Zr_6O_4(OH)_4(CO_2)_{12}$ SBUs. The high capacity and excellent stability make it a very attractive material for methane storage applications. The isosteric adsorption enthalpy (Q_{st}) of CO_2 and CH_4 on UiO(bpdc) lies in the range of 18.5–24.0 and 12.6–15 kJ mol^{-1}, respectively. These values suggest the moderate interaction strength of gas molecules with the framework, which is lower than that of MIL-101[16] but higher than that of MOF-177.[15b]

Other than high uptake capacities, UiO(bpdc) exhibits unusual reversible stepwise isotherms for CO_2 adsorption at 195 K and organic solvent (ethanol, cyclohexane and benzene) adsorption at room temperature (as shown in Fig. 3). Clear or obscure two-step reversible isotherms are observed for these sorbates at the low pressure range, which cannot be interpreted by simple multi-layer adsorption. It could also not be caused by pore expansion and contraction which is well documented in MIL-53[20] and TetZB,[21] based on the factors, UiO(bpdc)'s network rigidity combined with non-hysteretic isotherms and identical PXRD patterns (see PXRD patterns in ESI,† S4). The stepwise isotherms for UiO(bpdc) could be attributed to the sequential adsorption of sorbates on different adsorption sites. The first step may be ascribed to the adsorption of sorbates on the preferred adsorption sites such as nano-corners near metal atoms because of the higher adsorption potential, while the larger second step in isotherms could be attributed to the pore filling of the rest of the pore volume. With such a sequential adsorption process, the Q_{st} of CO_2 undergoes a two-step transformation. The first decrease in Q_{st} of CO_2 at low loadings indicates that preferable adsorption sites are occupied firstly, while the following gradual increase of Q_{st} at the higher loading could be ascribed to the larger CO_2–CO_2 interactions when filling the rest of the spaces. No evident stepwise adsorption is observed for CH_4 isotherms and the Q_{st} plot of CH_4 is relatively normal, indicating that the sequential filling mechanism is much related to the dipole moments of the sorbates.

In conclusion, a UiO type MOF with incorporated Lewis basic bipyridyl sites was synthesized by the solvothermal reaction of bpdc with Zr salts. The Soxhlet-extraction activation allows UiO(bpdc) to be fully evacuated. The highly porous structure combined with Lewis basic sites incorporated on the pore surface enables UiO(bpdc) to possess high uptake capacity for H_2, CO_2 and CH_4. The exceptional stability and excellent adsorption capacities make this MOF a very promising material for CO_2 capture and energy gas storage. Furthermore, the stepwise isotherms observed at low pressure for adsorption of CO_2 at 195 K and adsorption of organic solvents at room temperatures reveal a sequential filling mechanism of adsorbates on different adsorption sites.

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