A NbO-type metal–organic framework derived from a polyyne-coupled di-isophthalate linker formed *in situ*†

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A NbO-type metal–organic framework, PCN-46, was constructed based on a polyyne-coupled di-isophthalate linker formed *in situ*. Its lasting porosity was confirmed by N_2 adsorption isotherm, and its H_2, CH_4 and CO_2 adsorption capacity was examined at 77 K and 298 K over a wide pressure range (0–110 bar).

Metal–organic frameworks (MOFs) have emerged as a new type of porous materials.[1] Their large surface area, high pore volume, uniform yet controllable pore size, and pore geometry make them good adsorbents for gases, such as H_2, CH_4, and CO_2.[2] Their gravimetric gas adsorption capacity, especially in the high pressure range, is directly related to the specific surface area and pore volume.[2d,3] The NbO-type MOFs, which consist of 4-connected di-isophthalate ligands and 4-connected secondary building units (SBU) (typically dicopper paddlewheel), have shown excellent framework stability, porosity, and gas adsorption capacity.[2f,2g,4] On the other hand, their hydrogen adsorption capacity at room temperature is relatively low because of weak framework–hydrogen interactions. In our continuing exploration of MOFs as a hydrogen storage medium, aligned open metal sites have been shown to have an impact on the heat of hydrogen adsorption.[5] In addition, double bonds[2g] and aromatic rings[6] were also studied as possible hydrogen-framework interacting sites. However, prior to this work, carbon–carbon triple bonds, especially polyyne chains, have not been systematically studied for gas adsorption purposes in MOFs. In this contribution, we report an NbO-type MOF that is constructed based on a polyyne-coupled di-isophthalate ligand formed *in situ*. The ensuing MOF has permanent porosity after the removal of guest molecules, and exhibits excellent H_2, CH_4 and CO_2 adsorption capacity.

The *in situ* ligand reactions under solvothermal conditions are well documented in the literature.[7] Herein our goal is to apply this versatile method to simplify the MOF synthesis by combining the ligand preparation, purification, and MOF synthesis into one simple step. It is hoped that the formation of the MOF will drive the ligand formation to completion; therefore, the purification of the ligand becomes unnecessary.

Copper(I)-catalyzed oxidative coupling of terminal acetylenes was found as early as 1869 and has been developed into a versatile synthetic tool for 1,3-diyne compounds.[8] We reason that by combining isophthalate ligand bearing terminal acetylene with a slight excess of copper(II) salt, which can be readily reduced to copper(I) under solvothermal reaction conditions, a homocoupling product di-isophthalate can be generated. Subsequently, the di-isophthalate linker reacts with the Cu(II) salts giving rise to a NbO MOF.

The ligand precursor used herein is 5-ethynylisophthalic acid (H_2ei), which contains both isophthalic moieties and terminal acetylene suitable for the coupling reaction. As expected, every two of the H_2ei were coupled into one 5,5′-(buta-1,3-diyne-1,4-diyl)diisophthalic acid (H_4bdi) under the catalysis of Cu(I), which came from the reduction of cupric acetate. In addition, the *in situ* formed 4-connected ligand bdi^{4-} was linked *via* the 4-connected dicopper paddlewheel SBU to form a NbO-type MOF, PCN-46 (PCN stands for porous coordination network) (Fig. 1) in 77% of yield (based on H_2ei).‡

It must be pointed out that the exact chronological sequence of events such as the coupling of the precursor molecules, the deprotonation of the di-isophthalic acid, and the formation of the MOF has not been deciphered. However, the high overall yield of the procedure implies that the coupling reaction benefits from the consumption of the tetracarboxylic acid by MOF formation.

Calculated using the PLATON routine, PCN-46 has a solvent accessible volume of 73.8%. This high porosity prompts us to examine its gas adsorption property. The phase purity of the bulk sample was confirmed by powder X-ray diffraction (PXRD), and the framework retains its crystallinity after the removal of guest molecules (Fig. S2, ESI†). Its permanent porosity was confirmed by both N_2 (77 K) and Ar (77 and 87 K) sorption isotherms (Fig. 2 and Fig. S3, ESI†). The isotherms show type-I sorption behavior, which is typical for microporous materials. Based on the N_2 sorption isotherm, PCN-46 has a BET surface area of 2500 m^2 g^{-1}

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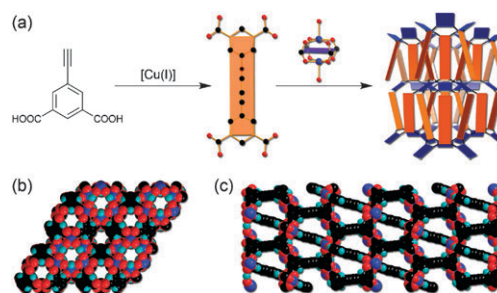
Fig. 1 (a) *In situ* formed ligand bdi^{4-} and the formation of NbO-type framework; (b) atomic packing of PCN-46, viewed through [0 0 1] direction; (c) atomic packing of PCN-46, viewed through [1 0 0] direction.
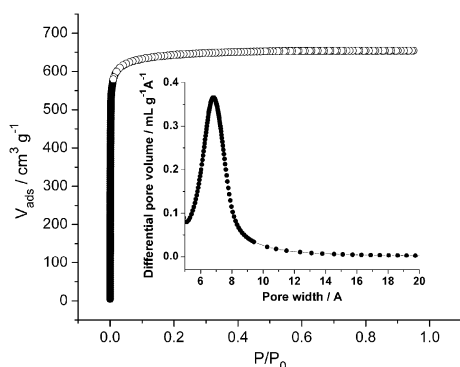
Fig. 2 The N_2 sorption isotherm at 77 K (solid symbols, adsorption; open symbols, desorption) and pore size distribution of PCN-46.

(Langmuir surface area: 2800 m^2 g^{-1}) and a total pore volume of 1.012 cm^3 g^{-1}. It has a uniform pore size around 6.8 Å based on the Horvath–Kawazoe model in the Micromeritics ASAP2020 software package (assuming cylinder pore geometry).[9]

The high porosity and stable framework make PCN-46 a good candidate for gas storage. In 2009, the U.S. Department of Energy (DOE) reset the gravimetric and volumetric storage targets for on-board hydrogen storage for 2010 (4.5 wt%, 28 g L^{-1}) and 2015 (5.5 wt%, 40 g L^{-1}).[10] At 77 K and 760 Torr, PCN-46 can reversibly adsorb 1.95 wt% of H_2 (Fig. 3). Under high pressure range, the saturated excess gravimetric H_2 uptake is 5.31 wt% (56.1 mg g^{-1}) at 32 bar. Taking the gaseous H_2 compressed within the void pore at 77 K into consideration, the total gravimetric H_2 uptake can reach as high as 6.88 wt% (73.9 mg g^{-1}) at 97 bar. Calculated from the crystal density of the activated form (0.6185 g cm^{-3}), PCN-46 has an excess volumetric H_2 uptake of 34.7 g L^{-1} (32 bar) and a total volumetric uptake of 45.7 g L^{-1} (97 bar).

Theoretical studies reveal that given the same MOF structural type, the longer the ligand, the higher the specific surface area, and accordingly the higher the gravimetric H_2 uptake would be.[11] This is further confirmed by the comparison of PCN-46 and the NOTT series NbO-type MOFs.[4b] As can be seen from Table 1, when the length of ligand increases, the surface area, pore volume, and high pressure hydrogen uptake of the MOFs also increase, but not the heat of adsorption.

Based on a variant of the Clausium–Clapeyron equation, the H_2 isosteric adsorption enthalpy of PCN-46 reaches 7.20 kJ mol^{-1} at low coverage, and decreased to 4.06 kJ mol^{-1} at medium coverage (Fig. S4).[12] The increased heat of hydrogen
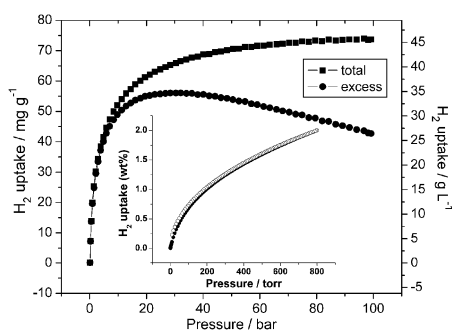

Fig. 3 Gravimetric and volumetric H_2 uptake in PCN-46 at 77 K (solid symbols, adsorption; open symbols, desorption).

Table 1 Ligand length, porosity and H_2 uptake of selected NbO-type MOFs

tpta⁴⁻ in NOTT-101   bdi⁴⁻ in PCN-46   qpta⁴⁻ in NOTT-102

MOFs	Ligand length/Å[a]	BET surface area/m² g⁻¹	Pore volume/ cm³ g⁻¹[b]	H₂ uptake/ mg g⁻¹[c] 60bar	Q_{st} at low coverage/ kJ mol⁻¹
NOTT-101	5.773	2316	0.886	66.0	< 5.5
PCN-46	6.484	2500	1.012	71.6	7.20
NOTT-102	10.098	2942	1.138	72.0	< 5.5

[a] Distance between 5-position of two isophthalate moieties. [b] Calculated from N_2 isotherms at 77 K. [c] Total uptake at 77 K.

adsorption in PCN-46, compared to those of other NbO type MOFs shown in Table 1, can be attributed to the interaction between dihydrogen molecules and the exposed and delocalized π electrons in the polyyne unit in bdi⁴⁻, which is evidently stronger than that for the phenyl rings in tpta⁴⁻ and qpta⁴⁻. A strong interaction between acetylene and a NbO-type MOF containing alkyne unit was also discovered, in which the high acetylene affinity towards the framework was partially attributed to the π–π interaction.[4f] In addition, the replacement of phenyl rings by polyyne chain leads to a boost of pore volume and hydrogen uptake. As Table 1 shows, the bdi⁴⁻ ligand is much shorter than qpta⁴⁻, but the pore volumes and hydrogen uptakes of PCN-46 and NOTT-102 are very close. Furthermore, in the absence of a catalyst, the hydrogen addition reaction on the polyyne unit has not been observed even at high pressure, as shown by the reversible hydrogen sorption isotherms of PCN-46, validating the stability of the MOF under hydrogen storage conditions.

Methane is another candidate as an on-board fuel. However, it also suffers from a lack of reliable storage. The DOE methane storage target has a volumetric basis: 180 v(STP) v^{-1} at 35 bar.[13] With high surface area and high pore volume, MOFs have proved reliable due to their high methane uptake capacity.[2e–g] The high pressure methane adsorption in PCN-46 at 298 K was also examined. As can be seen from Fig. 4, the gravimetric excess CH_4 uptake in PCN-46 reaches saturation at 12 mmol g^{-1} (60 bar) (total: 17.2 mmol g^{-1}, 110 bar). At 35 bar, the volumetric excess CH_4 uptake in PCN-46 is 150 v v^{-1} (total: 172 v v^{-1}).

The capture and sequestration of CO_2 is considered to be an effective way for the control of greenhouse gas emissions. Most of the capture processes in large scale operation nowadays are based on amine-based wet scrubbing systems, which have high energy and resource consumption.[14] MOFs have proven to be good adsorbents for CO_2 at ambient temperature.[2i,j] As can be seen in Fig. 5, the saturation excess CO_2 uptake in PCN-46 is 21.0 mmol g^{-1} (30 bar).

In summary, a NbO-type MOF, PCN-46, was synthesized based on an *in situ* formed polyyne-coupled di-isophthalate ligand by the copper(I)-catalyzed oxidative coupling of terminal
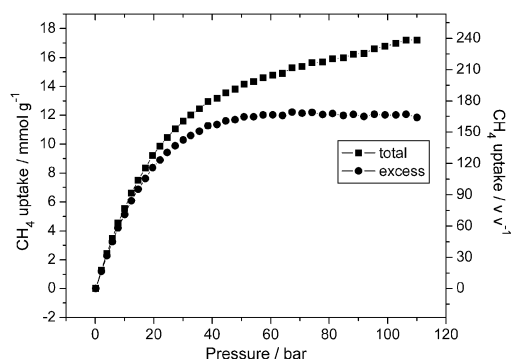
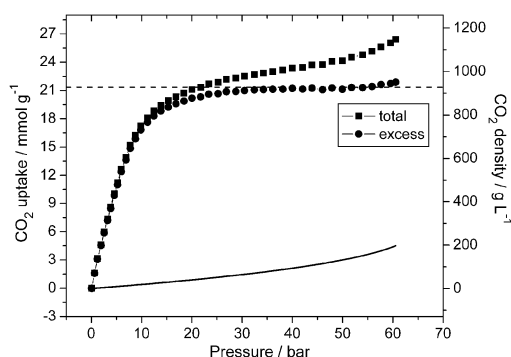**Fig. 4** Gravimetric and volumetric CH_4 uptake in PCN-46 at 298 K.

Fig. 5 Gravimetric CO_2 uptake and density in PCN-46 at 298 K. Solid line, density of compressed CO_2 at 298 K; dashed line, density of liquid CO_2 at 273 K (928 g L^{-1}).[15]

acetylenes. The polyyne units in the MOF exhibit high heat of hydrogen adsorption, high pore volume, and excellent stability under high pressure hydrogen. The hydrogen, methane, and carbon dioxide adsorption uptakes of the MOF are also impressive. Research in further extending the polyyne chain in MOFs is currently underway in our laboratory.

Notes and references

‡ X-Ray crystal data for PCN-46: $C_{10}H_5CuO_5$, $M = 268.68$, trigonal, space group $R\bar{3}m$, $a = b = 18.2386(8)$, $c = 42.049(2)$ Å, $V = 12113.4(9)$ Å^3, $Z = 18$, $D_c = 0.663$ g cm^{-3}, $F_{000} = 2412$, synchrotron radiation, $\lambda = 0.41328$ Å, $T = 173(2)$ K, $2\theta_{max} = 30.0°$, 68 838 reflections collected, 3022 unique ($R_{int} = 0.1069$). Final $GooF = 1.055$, $R_1 = 0.0747$, w$R_2 = 0.2042$, 82 parameters. CCDC 747535.

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