This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A nitro-decorated tetracarboxylate ligand has been used to construct a highly porous metal-organic framework with NbO topology. This MOF exhibits a high BET surface area of 2383 m$^2$ g$^{-1}$, good adsorption selectivity of CO$_2$/CH$_4$ (6.5) and CO$_2$/N$_2$ (20.8), at 298 K and 1 bar, high excess unsaturation CO$_2$ uptake (94.0 wt%) at 273 K and 20 bar, a high methane total uptake of 184 cm$^3$ cm$^{-3}$ at 290 K and 35 bar that surpasses the old DOE target.
A nitro-decorated NbO-type metal-organic framework with highly selective CO$_2$ uptake and CH$_4$ storage capacity

Mingxing Zhang$^{a}$, Qian Wang$^{a}$, Zhiyong Lu$^{a}$, Huiyan Liu$^{a}$, Wenlong Liu$^{*b}$ and Junfeng Bai$^{*a}$

A nitro-decorated NbO-type metal-organic framework, Cu$_2$NTPTB (NJU-Bai 14; H$_4$NTPTB = 2'-nitro-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylic acid) was synthesized and structurally characterized. It exhibits high permanent porosity with the BET surface area of 2384 m$^2$ g$^{-1}$, improved adsorption selectivity of CO$_2$/CH$_4$ (6.5) and CO$_2$/N$_2$ (20.8) at 298 K and 1 bar, high excess unsaturation CO$_2$ uptake (94.0 wt%) at 273 K and 20 bar, a high methane total uptake of 184 cm$^3$ cm$^{-3}$ at 290 K and 35 bar.

The past two decades have witnessed the rapid development of metal-organic frameworks (MOFs). More interestingly, compared with zeolites and porous carbons, they have been considered as promising materials for CO$_2$ capture and CH$_4$ storage in terms of properties and exhibit the fine-tuning of pore shape, size, hydrophobicity and hydrophilicity, in terms of structures, which can be adjusted by the rich incorporation of different organic linkers and inorganic building blocks. In our previous work, we have successfully inserted -CONH- groups into rh- and agw-type MOFs and shifted coordination sites of ligands to fine-tune pore size and polarized the inner surface with uncoordinated nitrogen atoms of the (3,6) net MOF, in which their adsorption properties of CO$_2$ have been greatly improved.

The MOFs with NbO topologies, which were pioneered by Chen and Schröder, also named as MOF 505 and NOTT-10X series respectively, are of great importance. A number of related NbO-type MOFs constructed by a variety of tetracarboxylates have been investigated. Herein, we report a nitro-decorated tetracarboxylate ligand, H$_4$NTPTB 2'-nitro-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylic acid (Fig. 1a) and a nitro-decorated NbO-type metal–organic framework [Cu$_2$(NTPTB)(H$_2$O)]$_2$·6H$_2$O·2DMF (NJU-Bai 14, NJU-Bai for Nanjing University Bai’s group) based upon this ligand. NJU-Bai 14 is the first nitro-decorated MOF-505 analog and exhibits high apparent BET surface of 2383 m$^2$ g$^{-1}$ with good adsorption selectivity of CO$_2$/CH$_4$ (8) and CO$_2$/N$_2$ (24) at 273 K and 1 bar, CO$_2$/CH$_4$ (6.5) and CO$_2$/N$_2$ (20.8) at 298 K and 1 bar, large adsorption capacity of CO$_2$ at 20 bar and 273 K. Meanwhile the total methane uptake at 35 bar and 290 K is 184 cm$^3$ cm$^{-3}$, that surpasses the old DOE target.

Fig. 1 a-b) Nitro-decorated tetracarboxylate linker NTPTB$^4$ and [Cu$_4$(COO)$_4$]$_2$ paddlewheel cluster; c-d) The shuttle and spherical shaped cages. Cu, blue-green; C, black; O, red; N, blue. Water molecules and H atoms have been omitted for clarity.

Pale-blue block-shaped crystals of NJU-Bai14 were obtained by solvothermal reaction of H$_4$NTPTB and Cu(NO$_3$)$_3$·3H$_2$O in DMF (N,N'-dimethylformamide)/H$_2$O solvents at 85 °C for 24 hours. Single-crystal X-ray structural analysis reveals that like other NbO type MOFs, NJU-Bai14 is also constructed from paddlewheel [Cu$_4$(COO)$_4$]$_2$ secondary building units (SBUs), further bridged by NTPTB$^4$ to form a 3D non-interpenetrated (4,4)-connected net. Each Cu$^{2+}$ ion shows square-pyramidal geometry, with four oxygen atoms...
from four different NTPTB⁺ units and a water molecule coordinated at the axial position of the paddlewheel unit (Fig. 1b). In the crystal structure, there exist two types of cages which are alternately stacked in a 1:1 ratio with the formation of 3D framework along the c axis. The small cage of about 10 Å in diameter is surrounded by six Cu²⁺ paddle wheel SBU{s (Fig. 1d), while the large shuttle-shaped cage of about 9 × 20 Å with twelve Cu₆(COO)₄ clusters occupying the vertices and 6 NTPTB⁺ ligands occupying the faces (Fig. 1c). Compared with the prototype NOTT-101, a smaller void space is created in NJU-Bai14 due to the nitro substituents in the organic ligands which extend into the pores of the framework. The accessible pore volume of NJU-Bai14 is 60.9% (6984 Å³ per unit cell volume, after removal of the coordinated water) as calculated upon the single crystal structure using the PLATON program, while the NOTT 101 is 67.4% (7801 Å³ out of the 11569 Å³ per unit cell volume).

To confirm the permanent porosity of NJU-Bai14, the as synthesized sample was treated with dry methanol for 3 days and then degassed under high vacuum at 373 K for 24 hours to obtain the evacuated framework. The phase purity of the bulk sample was determined by powder X-ray diffraction, and the framework retains its crystallinity after removal of the guest molecules (Fig. S1). Accompanied with this, a color change was observed from pale blue to deep purple-blue, similar to those of other frameworks in which open Cu²⁺ sites can be generated. As expected, NJU-Bai14 exhibits a reversible type-I adsorption isotherm and take up large amount of N₂ at 77 K (598 cm³ g⁻¹ at 1 bar), featured by a moderate Brunauer-Emmett-Teller (BET) surface area and Langmuir surface area of ca.2383 m² g⁻¹ and 2594 m² g⁻¹, respectively (Fig. S3).

To investigate its performances for CO₂ capture, low-pressure CO₂ sorption measurement of NJU-Bai14 was initially measured at 273 and 298 K. The high CO₂ uptake of 187 and 100 cm³ g⁻¹ can be observed under 1 bar at 273 and 298 K, respectively, which is higher than those of NOTT 101 (164 cm³ g⁻¹ at 273 K and 86 cm³ g⁻¹ at 298 K, Fig. 2b), MOF-505 (74.0 cm³ g⁻¹ at 1 bar and 298 K) and PCN-305 isosstructural MOFs. In contrast to CO₂ adsorption, only limited amounts of CH₄ and N₂ can be adsorbed in NJU-Bai14 (33 cm³ g⁻¹ at 273 K and 1 bar for CH₄, and 7.0 cm³ g⁻¹ at 273 K and 1 bar for N₂, respectively) (Fig. 2a). This phenomenon indicates that NJU-Bai14 may be potentially used to selectively adsorb CO₂ over CH₄ or N₂. In addition, the separation ratios of CO₂/N₂ and CO₂/CH₄ are calculated as 28 and 8, respectively, higher than that of NOTT 101 (Fig. S4) but much higher than the corresponding value of typical MOF-177 (17.5, 4.4).
In order to understand these observations, the coverage-dependent CO$_2$ adsorption enthalpies of NJU-Bai 14 were calculated by the virial method from fits of the adsorption isotherms collected at 273 and 298 K. As shown in Fig. 56, the adsorption enthalpy of CO$_2$ is 24.5 kJ·mol$^{-1}$ at zero coverage. Compared with NOTT-101, there is no significant difference in the heat of adsorption, this phenomenon was also observed in other MOFs. With CO$_2$ loading increasing, $Q_a$ slightly decreases and approaches a value of 23.0 at 4.9 mmol·g$^{-1}$ which might be due to the nitro-decorated small cage and the incorporated –NO$_2$ group, whereas $Q_a$ of NOTT 101 sharply decreases. According to our previous research, surface polarization will bring larger $Q_a$ of CO$_2$, but this polar group –NO$_2$ decorated MOF bring strange $Q_a$ (small than NOTT-101). This point needs further understanding after much work has been done although it is unusual and very interesting.

Furthermore, the high-pressure CO$_2$ gravimetric sorption measurements of NJU-Bai 14 were also carried out at 273 and 298 K in the pressure range of 0 – 20 bar (Fig. 3a). The gravimetric excess CO$_2$ isotherms of NJU-Bai 14 are not saturated at 273 and 298 K, and the storage capacity climbs to 94.0 wt% (21.59 mmol·g$^{-1}$) at 50 bar, NU-100$_{13b}$ 46.4 mmol·g$^{-1}$ at 40 bar and MIL-101$_{14}$, 40 mmol·g$^{-1}$ at 50 bar, but still comparable to most of the other high CO$_2$ uptake MOFs (e.g. MIL-100$_{12}$, 18 mmol·g$^{-1}$ at 30 bar and Mg-MOF-74 15.7 mmol·g$^{-1}$ at 36 bar), suggesting that NJU-Bai 14 may serve as a good CO$_2$ adsorbent.

The large surface area and pore volume of NJU-Bai 14 prompted us to further measure its CH$_4$ storage capacity. Adsorption data were collected up to 70 bar at 290 K and 298 K for CH$_4$. As shown in Fig. 3b, the CH$_4$ isotherm is not fully saturated when the pressure reaches up to 70 bar and NJU-Bai 14 shows an excess CH$_4$ uptake of 215 cm$^3$ g$^{-1}$ and a total uptake amount of 245 cm$^3$ g$^{-1}$. When the crystal density being considered, the volumetric methane total uptake of NJU-Bai 14 is 184 cm$^3$ g$^{-1}$, much smaller than that of the famous PCN-14 (230 cm$^3$ g$^{-1}$), nevertheless, it still surpass the old DOE target (180 cm$^3$ g$^{-1}$) for methane storage at room temperature and 35 bar. Compared with NOTT-101, NJU-Bai 14 takes up smaller amount of CH$_4$ at 298 K (173 cm$^3$ g$^{-1}$ vs 194 cm$^3$ g$^{-1}$). NO$_2$ decorated MOF is about 20 cm$^3$ g$^{-1}$ lower than NOTT-107 (decorated with methyl, 193 cm$^3$ g$^{-1}$ at 298 K and 35 bar), this may indicate that such bulky substituent groups will bring dead space for CH$_4$ storage. However, $Q_a$ of CH$_4$ adsorption in NJU-Bai 14 (16.6 kJ·mol$^{-1}$) is slightly higher than that of NOTT-101. As shown in Fig. 56, $Q_a$ of CH$_4$ adsorption first slowly decreases and then increases gradually with the CH$_4$ loading. This indicates that the methane – methane interaction becomes dominant in the adsorption process after high-concentration methane loadings. In contrast, $Q_a$ of NOTT 101 linearly decrease. Apparently, the open metal sites as well as nitro-decorated small cage also enable their moderately strong interaction with methane molecules at low pressures.

In summary, by incorporating a nitro-decorated tetracarboxylate ligand within a framework of NbO topology, we have successfully synthesized a highly porous MOF, NJU-Bai 14, which shows a high BET surface area of 2383 m$^2$ g$^{-1}$, improved selectivity of CO$_2$/CH$_4$ (8) and CO$_2$/N$_2$ (28) at 273 K and 1 bar, CO$_2$/CH$_4$ (6.5) and CO$_2$/N$_2$ (20.8) at 298 K and 1 bar and an excellent uptake capacity for CO$_2$ at 20 bar (94.0 wt% 273 K and 83.2 wt% 298 K). In addition, NJU-Bai 14 exhibits a large total CH$_4$ uptake of 184 cm$^3$ g$^{-1}$ at 35 bar and 290 K. This work further enrich our research of fine-tuning MOFs toward high performance.

This work was supported by the Major State Basic Research Development Programs (2011CB808704), National Natural Science Foundation of China (21371150 and 21371091)

Notes and references


