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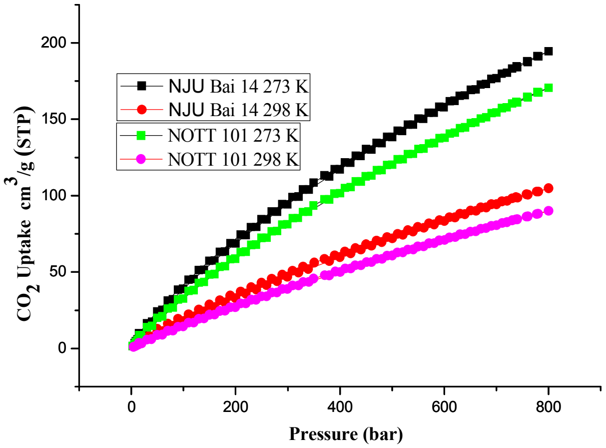
A nitro-decorated tetracarboxylate ligand has been used to construct a highly porous metal-organic framework with *NbO* topology. This MOF exhibits a high BET surface area of 2383m^2 g^{-1}, good adsorption selectivity of CO_2/CH_4 (6.5) and CO_2/N_2 (20.8), at 298 K and 1 bar, high excess unsaturation CO2 uptake (94.0 wt%) at 273 K and 20 bar, a high methane total uptake of 184 cm3 cm-3 at 290 K and 35 bar that surpasses the old DOE target.



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A nitro-decorated *NbO*-type metal-organic framework with highly selective CO_2 uptake and CH_4 storage capacity

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A nitro-decorated *NbO*-type metal–organic framework, Cu_2NTPTB (NJU-Bai 14; H_4NTPTB = 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[1] 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[2]. In our previous work, we have successfully inserted -CONH- groups into *rht*-type and *agw*-type MOFs [3]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[2a].

The MOFs with *NbO* topologies, which were pioneered by Chen and Schröder[4], 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[1x, 5]. Herein, we report a nitro-decorated tetracarboxylate ligand, H_4NTPTB 2'-nitro-[1,1':4',1''-terphenyl]-3,3'',5,5''-tetracarboxylic acid (Fig. 1a) and a nitro-decorated *NbO*-type metal–organic framework $\{Cu_2(NTPTB)\cdot(H_2O)_2\}\cdot 6H_2O\cdot 2DMF$ (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.

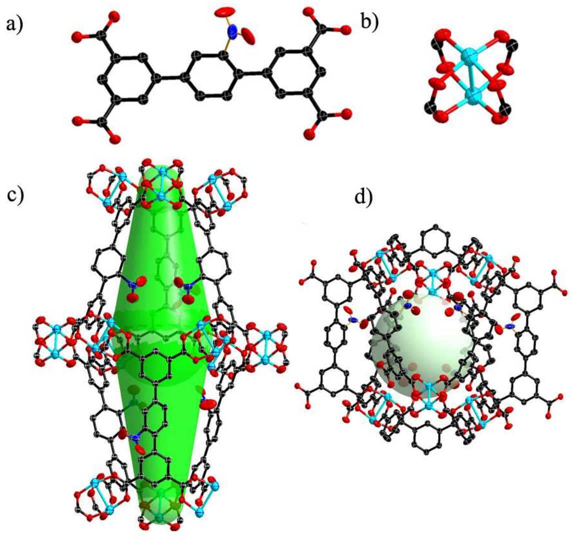

Fig.1 a-b) Nitro-decorated tetracarboxylate linker $NTPTB^{4-}$ and $[Cu_2(COO)_4]$ paddlewheel cluster; c-d) The shuttle and spherical shaped cages. Cu, blue-green; C, black; O, red; N, blue. Water molecules and H atoms have been omitted for clarity.

Pale-blue block-shaped crystals of NJU-Bai14 were obtained by solvothermal reaction of H_4NTPTB and $Cu(NO_3)\cdot 3H_2O$ in DMF (N,N'-dimethylformamide)/H_2O 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 $[Cu_2(COO)_4]$ 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^{4-} 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 Cu^{2+} paddle wheel SBUs (Fig. 1d), while the large shuttle-shaped cage of about 9 × 20 Å with twelve $Cu_2(COO)_4$ clusters occupying the vertices and 6 NTPTB^{4-} 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 Å^3 out of the 11465 Å^3 per unit cell volume, after remove of the coordinated water) as calculated upon the single crystal structure using the PLATON[6] program, while the NOTT 101 is 67.4% (7801 Å^3 out of the 11569 Å^3 per unit cell volume).

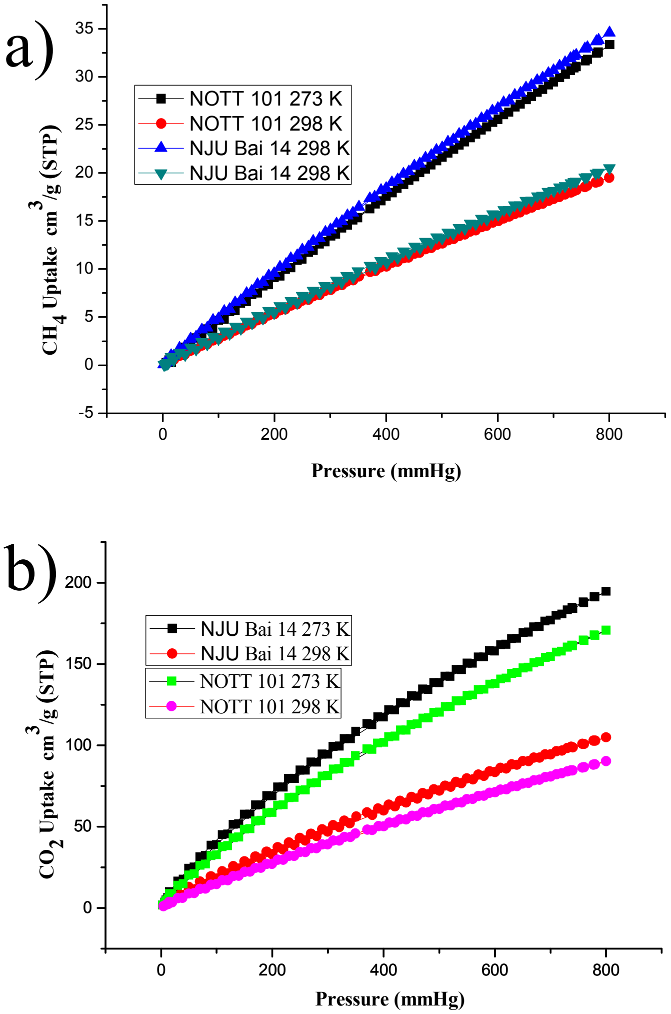

Fig.2. a) Low-pressure volumetric CH_4 isotherms at 273 and 298 K of NJU-Bai 14 and NOTT-10 . b) Low-pressure volumetric CO_2 isotherms at 273 and 298 K of NJU-Bai 14 and NOTT-101.

To confirm the permanent porosity of NJU-Bai 14, 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 confirmed 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 Cu^{2+} sites can be generated. As expected, NJU-Bai14 exhibits a reversible type-I adsorption isotherm and take up large amount of N_2 at 77 K (598 cm^3 g^{-1} at 1 bar), featured by a moderate Brunauer-Emmett-Teller (BET) surface area and Langmuir surface area of ca.2383 m^2 g^{-1} and 2594 m^2 g^{-1}, respectively (Fig. *S3*).

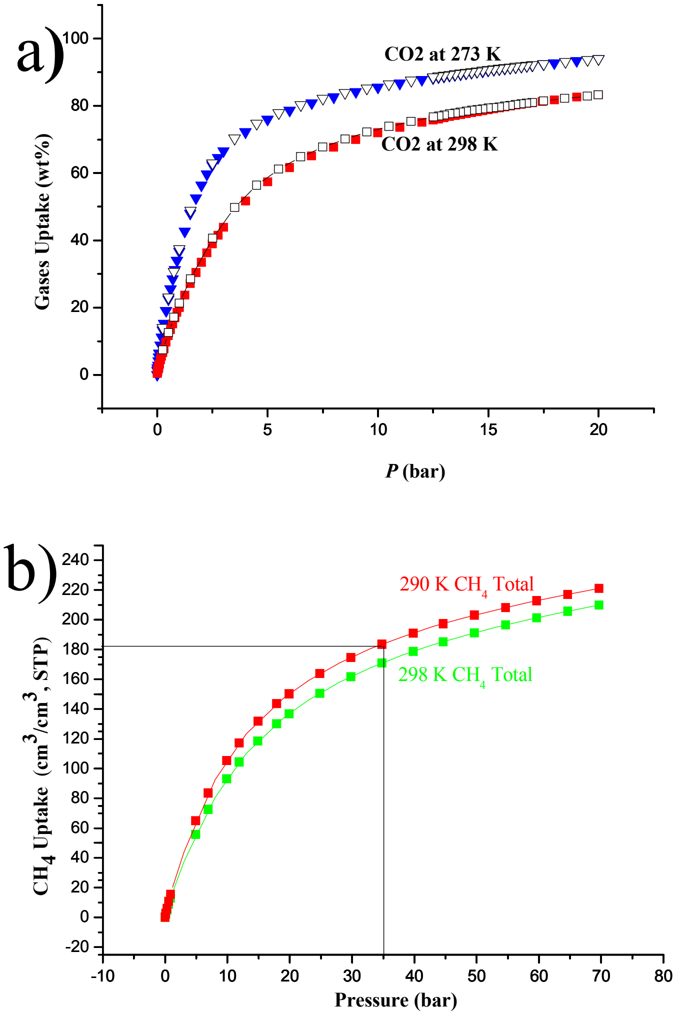

Fig.3. a) High-pressure gravimetric excess CO_2 isotherms collected at 273 and 298 K for NJU-Bai 14. b)High-pressure total CH_4 isotherms collected at 290 and 298 K for NJU-Bai 14.

To investigate its performances for CO_2 capture, low-pressure CO_2 sorption measurement of NJU-Bai 14 was initially measured at 273 and 298 K. The high CO_2 uptake of 187 and 100 cm^3 g^{-1} can be observed under 1 bar at 273 and 298 K, respectively, which is higher than those of NOTT 101 (164 cm^3 g^{-1} at 273 K and 86 cm^3 g^{-1} at 298 K, Fig. 2b), MOF-505 (74.0 cm^3 g^{-1} at 1 bar and 298 K) and PCN-305[7] isostructural MOFs. In contrast to CO_2 adsorption, only limited amounts of CH_4 and N_2 can be adsorbed in NJU-Bai 14 (33 cm^3 g^{-1} at 273 K and 1 bar for CH_4, and 7.0 cm^3 g^{-1} at 273 K and 1 bar for N_2, respectively) (Fig. 2a). This phenomenon indicates that NJU-Bai 14 may be potentially used to selectively adsorb CO_2 over CH_4 or N_2. In addition, the separation ratios of CO_2/N_2 and CO_2/CH_4 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[8] (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. *S6*, the adsorption enthalpy of CO_2 is 24.5 $kJ\cdot mol^{-1}$ 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[7]. With CO_2 loading increasing, Q_{st} slightly decreases and approaches a value of 23.0 at 4.9 $mmol\cdot g^{-1}$ which might be due to the nitro-decorated small cage and the incorporated $–NO_2$ group, whereas Q_{st} of NOTT 101 sharply decreases. According to our previous research, surface polarization will bring larger Q_{st} of CO_2, but this polar group $–NO_2$ decorated MOF bring strange Q_{st} (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 $mmol\cdot g^{-1}$), 83.2 wt% (18.9 $mmol\cdot g^{-1}$), respectively. This CO_2 storage capacity at 298 K is below some famous MOFs, such as MOF-210[9], 54.5 $mmol\cdot g^{-1}$ at 50 bar, NU-100[10] 46.4 $mmol\cdot g^{-1}$ at 40 bar and MIL-101[11], 40 $mmol\cdot g^{-1}$ at 50 bar, but still comparable to most of the other high CO_2 uptake MOFs (e.g. MIL-100[12], 18 $mmol\cdot g^{-1}$ at 30 bar and Mg-MOF-74 15.7 $mmol\cdot g^{-1}$ 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 $cm^3\ cm^{-3}$, much smaller than that of the famous PCN-14 (230 $cm^3\ cm^{-3}$), nevertheless, it still surpass the old DOE target (180 $cm^3\ cm^{-3}$) 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 $cm^3\ cm^{-3}$ *vs* 194 $cm^3\ cm^{-3}$). NO_2 decorated MOF is about 20cm^3/cm^3 lower than NOTT-107 (decorated with methyl, 193 $cm^3\ cm^{-3}$ at 298 K and 35 bar), this may indicate that such bulky substituent groups will bring dead space for CH_4 storage. However, Q_{st} of CH_4 adsorption in NJU-Bai 14(16.6 $kJ\cdot mol^{-1}$) is slightly higher than that of NOTT-101. As shown in Fig *S6*, Q_{st} 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.[11, 23] In contrast, Q_{st} 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[13].

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 $cm^3\ cm^{-3}$ at 35 bar and 290 K. This work further enrich our research of fine-tuning MOFs toward high performance.

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Notes and references

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†Crystal data for NJU-Bai 14, $[Cu_2(NTPTB^{4-})]_n$: $C_{22}H_{13}Cu_2NO_{12}$ (guest molecules removed with PLATON SQUEEZE[9]), M_r = 606.4, rhombohedral, *R-3m*, $a = b$ = 18.4898 (11) Å, c =38.7266(19) Å, $\alpha = \beta$ = 90, γ =120, V = 11465.8 (17) Å^3, Z = 9, D_c = 0.790 $g\cdot cm^{-3}$, F_{000} = 2718, T = 150 (2) K, 9426 reflections collected 2089 independent reflections (R_{int} = 0.392), R_1 = 0.1208, wR_2 = 0.3522 for $[I > 2\sigma(I)]$ and GOF = 1.449. CCDC: 981572.

Electronic supplementary information (ESI) available: Experimental details, TGA plots, PXRD patterns, IR spectra, heat of adsorption of CO_2 and CH_4, sorption selectivity calculations. CCDC: 981572. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c00000000x.

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