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A Porous Cobalt-based MOF with High CO₂ Selectivity and Uptake Capacity

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A porous cobalt-based metal-organic framework [CoL²⁻]ₙ (L= 5-(pyrimidin-5-yl) isophthalic acid) (termed as NJFU-2), has been designed by self-assembling [Co₂(COO)₄] paddlewheel SBUs and a novel trigonal hetero-functional ligand. 10 **Moreover, the activated sample NJFU-2a exhibits a moderate BET surface area of 1223 m² g⁻¹, large CO₂ uptake (6.14 wt% at 0.15 bar and 298 K) and high selectivity for CO₂ over CH₄ and N₂ at room temperature, estimated by the Ideal Adsorbed Solution Theory (IAST).**

15   Metal-Organic Frameworks (MOFs) are a new type of porous materials constructed by metal clusters and organic ligands through coordination bonds.[1] With high surface areas and tunable pore geometries, MOFs are widely regarded as a promising material for gas storage and separation. Thousands of MOFs with 20 diverse topologies and excellent gas-adsorption properties have been reported.[2] Nevertheless, when CO₂ separation is concerned, the high selectivity of CO₂ towards other gases as well as high uptake capacity of CO₂ ought to be achieved simultaneously in the same material. Under this consideration, only a few MOFs 25 can get the balance, such as Mg-MOF-74[3], mmen-CuBTTri[4] and et al..

To obtain high-performance porous MOFs for CO₂ selectivity, two main strategies in structural design usually can be followed, namely 1) introducing molecular sieving effect, that means, 30 MOFs with suitable pore size and geometry may permit gas molecules only up to a certain kinetic diameter to diffuse into the pores; 2) optimizing the inner surface environment that prefered by CO₂ molecules. Meanwhile, for retaining or elevating the uptake capacity of CO₂, obvious surface area loss should not be 35 caused in the material when improving its CO₂ selectivity[5]. One of the successful examples is NJU-Bai7 and NJU-Bai8[6a], reported

in our previous work, that achieved high CO₂ selectivity as well as high CO₂ uptake capacity by shifting the coordination sites and incorporating uncoordinated nitrogen atoms without causing any 40 decrease in BET surface area and pore volume. Another typical example that satisfies the criteria mentioned above is the MOF-74 family[3]. By altering the metals, Mg-MOF-74[3] exhibits the highest CO₂ adsorption capacity and selectivity among the family. Inspired by this case, we used cobalt ions instead of copper ions 45 and successfully obtained the isostructual MOF with NJU-Bai8[6a] under similar condition, [CoL²⁻]ₙ (L= 5-(pyrimidin-5-yl) isophthalic acid), termed NJFU-2 (NJFU denotes Nanjing Forestry University). The activated sample NJFU-2a exhibits a moderate BET surface area of 1223 m² g⁻¹, large CO₂ uptake 50 capacity (6.14 wt% at 0.15 bar and 298 K) and high selectivity of CO₂ over CH₄ and N₂. At 1 bar, the CO₂/CH₄ selectivity of NJFU-2a is 26.1 at 298 K (CO₂ and CH₄ mixtures in a 50:50 molar ratio) and CO₂/N₂ selectivity is 195.1 at 298 K (CO₂ and N₂ mixtures in a 15:85 molar ratio).

55   NJFU-2 was obtained by solvothermal synthesis from Co(NO₃)₂·6H₂O and H₂L (L = 5-(pyrimidin-5-yl) isophthalic acid) in DMA/MeOH solution at 90 ℃ for 72 hours. The single crystal X-ray structure reveals that NJFU-2 crystallizes in space group P2₁/c. In the asymmetric unit, there are one cobalt(II) cation and 60 one ligand. Two Co(II) ions are bridged by four carboxylate groups to give a paddle-wheel-shaped secondary building unit with a Co···Co distance of 2.7816(9) Å and Co—O bond lengths in the range of 2.003(3) − 2.107(3) Å. The axial site of the paddle-wheel is occupied by pyrimidinyl N donors with a Co—N 65 distance of 2.063(3) Å. In the structure of NJFU-2, the isophthalate moieties with the angle of 120° are involved in the formation of 2D sql-lattices layers[7] based on the paddlewheel clusters. The sql-lattices 2D layers are further pillared by the pyrimidinyl moieties of L²⁻ ligand, resulting in a porous 3D 70 frameworks (Fig. 1). Considering the paddle-wheel clusters as six-connected nodes and ligands as three-connected nodes, NJFU-2 can be simplified as a (3,6)-connected net with the point (Schläfli) symbol of $(4\ 6^2)_2(4^2\ 6^{10}\ 8^3)$ calculated by TOPOS, which is usually recoginzed as a rtl-type network. NJFU-2 is iso- 75 structural with NJU-Bai8, but with a less distorted coordination mode around the metal ion owing to Jahn-Teller distortion, which results in smaller channels than NJU-Bai8[6a] (3.1×3.1 Å² vs 4×3.3 Å²). The calculated total potential solvent accessible volume for NJFU-2 calculated by PLATON[8], upon removal of guest solvent

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† Electronic supplementary information (ESI) available: Experimental details, TGA plots, PXRD patterns, heat of adsorption of CO₂, sorption selectivity calculations. CCDC 1020952. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

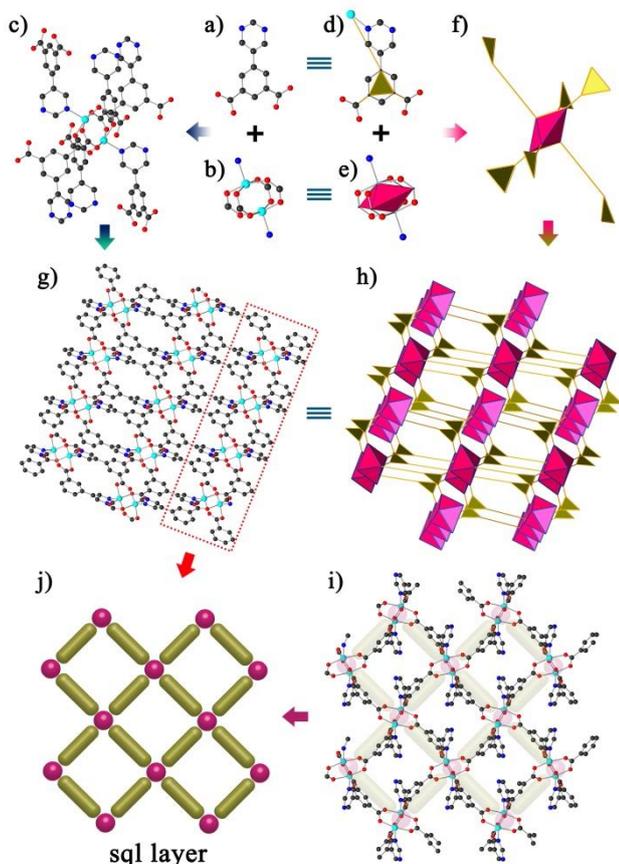molecules, was estimated to be 751.0 $Å^3$ per unit cell volume (1716.3 $Å^3$) or 43.8%.

Fig. 1 a) H_2L ligand; b) Cobalt paddlewheel cluster; c) coordination
5 mode of paddlewheel cluster and ligands; d) ligand simplified as 3-connected node; e) paddlewheel cluster simplified as 6-connected node; f) connection between 3-connected nodes and 6-connected node; g) network viewed along *b* direction (sql layer included); h) rtl-type topology of NJFU-2; i) channels viewed along *a* direction; j) sql layer extracted from
10 NJFU-2. H atoms have been omitted for clarity.

To investigate the permanent porosity of NJFU-2, traditional activation method of solvent exchange and then vacuum treatment was tried, but no obvious porous behavior was observed. Thus, the as-synthesized sample was treated with
15 supercritical carbon dioxide (SCD) and then degassed under high vacuum at room temperature for 12 h to obtain the fully desolvated sample (NJFU-2a), as is characterized by IR (see Fig. S1 in the Electronic Supplementary Information). The powder X-ray diffraction (PXRD) patterns demonstrate that the framework
20 is flexible and its crystallinity can be retained but some peaks shift to the high degree after activation (Fig. S2). Then we performed the low-pressure N_2 adsorption measurement of NJFU-2a at 77 K. The N_2 adsorption for NJFU-2a at 77 K exhibits a typical type-I curve (Fig. 2), a characteristic of
25 microporous materials, which is coincidental with the crystal structure. At 1 bar, NJFU-2a can take up 291 cm^3 g^{-1} of N_2, featuring an apparent Brunauer-Emmett-Teller (BET) surface area of ca. 1223 m^2 g^{-1} and a Langmuir surface area of ca. 1240 m^2 g^{-1}. Based on the N_2 adsorption isotherm, the total
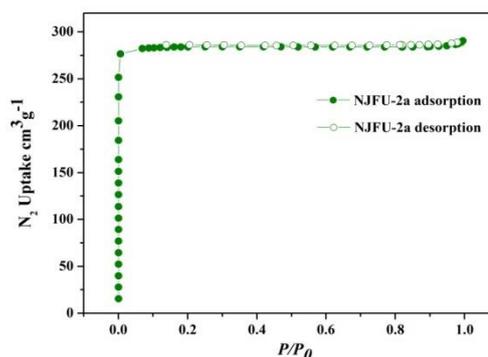30 pore volume of NJFU-2a was measured to be 0.44 cm^3 g^{-1}.

Fig. 2 Nitrogen adsorption isotherm of NJFU-2a at 77 K.
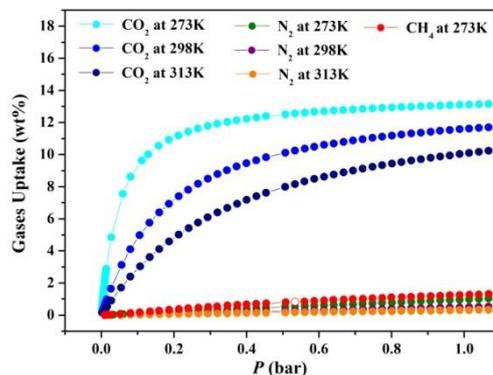

Fig. 3 Gas sorption properties of NJFU-2a under low pressure range (0~1
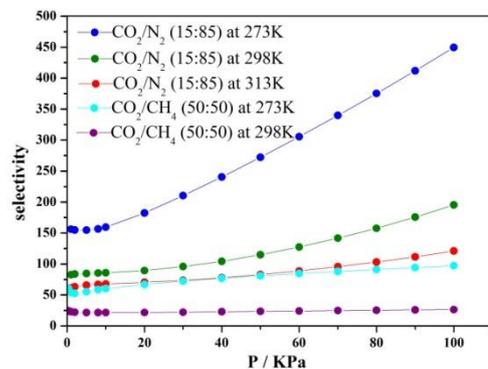35 bar) at different temperatures.

Fig. 4 IAST-predicted selectivity for CO_2/CH_4 and CO_2/N_2 adsorption based on observed adsorption isotherms of pure gases for NJFU-2a.

The gas adsorption/separation capacity of NJFU-2a was
40 evaluated by the adsorption of CO_2, CH_4, and N_2. As depicted by Fig. 3, NJFU-2a performs much better CO_2 uptake-capacity than many well-known MOFs with open metal sites or functional groups (6.14 wt% for NJFU-2a vs. 5.71 wt% for bio-MOF-11[10a,5d], 3.6 wt% for ZIF-78[5d,9], and 0.66 wt% for MOF-177[3b,5d])
45 at a relatively low pressure (~0.15 bar) at 298 K. This CO_2 adsorption capacity surpassed the iso-structural NJU-Bai8[6a] (5.4 wt%, BET: 1103 m^2 g^{-1}). Likewise, a high CO_2 uptake of 13.1, 11.6 and 10.1 wt% is observed under 1 bar at 273 K, 298 K and 313 K, respectively. Although the amount of absorbed CO_2 is
50 moderate compared with those of the best performing MOFs such as M-MOF-74[3] and bio-MOF-11[10a], NJFU-2a still surpasses some well-known MOFs with open metal sites or functional groups,

such as HKUST-1[11](6.6 wt% at 1 bar and 313 K), MIL-53(Cr) (8.9 wt% at 1 bar and 298 K)[12]. The zero-coverage adsorption enthalpy (Q_{st}) of CO_2 in NJFU-2a is 38.2 kJ mol^{-1}, as shown in Fig. S6, indicating strong interactions between CO_2 molecules and the framework, which is quite comparable with the reported data for NJU-Bai8 (37.7 kJ mol^{-1})[6a], SIFSIX-3-Zn (45 kJ mol^{-1})[13]. This strong interaction should be mainly attributed to the uncoordinated nitrogen atoms decorated along the inner wall of the framework. The interaction between the localized dipoles of the N-containing group and the quadrupole moment of CO_2 molecule induces the dispersion and electrostatic forces to enhance CO_2 adsorption. As for CH_4, NJFU-2a exhibits a weaker CH_4 binding affinity than CO_2 throughout the adsorption process, and as well a limited uptake amount of CH_4 (17.1 and 13.9 cm^3 g^{-1}) under 1 bar at 273 and 298K. These results demonstrate that NJFU-2a has the ability of selective adsorption of CO_2 over CH_4 and N_2 (Fig. 3).

To better illustrate the gas adsorption preference of NJFU-2a, we used Ideal Adsorption Solution Theory (IAST)[14] to predict the CO_2/N_2 and CO_2/CH_4 selectivity at different temperatures, and the results are presented in Fig. 4. Remarkably, NJFU-2a shows exceptionally high CO_2/N_2 selectivity in the binary mixture of CO_2 and N_2, with the ratio of 15:85 (S = 449.6, at 273 K; S = 195.1, at 298 K and S = 120.6, at 313 K), which is quite comparable with the high selectivity of CO_2 over N_2 in reported compounds of MAF-66 (S = 403, at 273 K; S = 225, at 298 K)[14f] and UTSA-49a (S = 193.7, at 273 K; S = 93.5, at 298 K)[14g] under similar condition. At 1 bar, the predicted selectivity of NJFU-2a for CO_2 over CH_4 in CO_2/CH_4 equimolar mixture at 273 K and 298 K are 96.8 and 26.1, respectively. The high CO_2 selectivity over CH_4 and N_2 of NJFU-2a could be attributed to the synergistic effect of Lewis bases (the uncoordinated N atoms from pyrimidine rings) and narrow pore size.

In summary, we have successfully designed and synthesized a sql-pillared rtl-type metal-organic framework with cobalt ions (NJFU-2). The activated NJFU-2a exhibits a moderate BET surface area of 1240 m^2 g^{-1}, large CO_2 uptake (6.14 wt% at 0.15 bar and 298 K) and high selectivity for CO_2 over CH_4 (26.1) and N_2 (195.1) at 298K, indicating that NJFU-2a may be a promising adsorbent in the process of CO_2/N_2 and CO_2/CH_4 separation, respectively required for post-combustion CO_2 capture and natural gases purification. Future efforts will address such sql-pillared MOF materials with other metal ions/clusters to further improve the CO_2 adsorption capacity and selectivity.

Acknowledgements

Notes and references

‡ Crystal data for NJFU-2: $C_{12}H_6CoN_2O_4$ x(solv), M = 301.12, Monoclinic, P 21/c, a = 10.8161(13) Å, b = 12.6809(15) Å, c = 13.4170(16) Å, β = 111.147(2) °, V = 1716.3(4) Å^3, Z = 4, D_c = 1.165 g cm^{-3}, GOF = 1.033 based on F^2, final R_1 = 0.0381, wR_2 = 0.1075 [for 3012 data $I > 2\sigma(I)$]; data for structure was treated with squeeze[15].

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