Supplementary Information

High and selective CO_2 uptake in a nitrogen-rich pillar-layered metal organic framework

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Material synthesis: Co(Imda) (4, 4'-bpy) was synthesized referring to the method of Li et al..[13] A mixture of NaOH (1.50 mmol) in H_2O (5.0 ml), 4, 5-imidazole dicarboxylic acid (1.0 mmol) and 4, 4'-bipyridyl (1.0 mmol) was added to an aqueous solution (5.0 ml) of $Co(NO_3)_2 \cdot 6H_2O$ (1.5 mmol) and stirred. The resulting solution was kept statically under autogenous pressure at 180 °C for 3 days in a teflon-lined autoclave. The resultant solid was isolated by filtration and washed with deionized water.

Characterization methods: Powder X-ray powder diffraction (XRD) measurement was conducted using $CuK\alpha$ (λ=1.54 Å) radiation on a Rigaku diffractometer. The N_2 adsorption-desorption measurements were carried out on a BEL adsorption instrument (BELsorp(II)-Max) at 77 K. The surface areas of the samples were calculated using the Brunauer–Emmett–Teller (BET) method. Thermogravimetric analysis (TGA) was carried out on a SCINCO thermal gravimeter S-1000. Scanning electron microscopy (SEM) was carried out using a Hitachi S-4200 instrument to observe particle morphologies.

CO_2 or N_2 adsorption-desorption measurements: Equilibrium CO_2 and N_2 adsorption isotherms at 298 K were obtained using a BEL adsorption instrument (BELsorp(II)-mini) using ultra high purity gases (U-Sung, 99.999%). The samples were pretreated under high vacuum at 150 °C overnight before the measurement.

The TGA unit was used to perform the cyclic CO_2 adsorption-desorption runs. High purity CO_2 (99.999%, U-Sung) and 15% CO_2 (85% N_2 as balance gas, U-Sung) were used as adsorption gases, while argon (Ultra high purity, 99.999%, U-Sung) was used as purge gas in the desorption process. The feed gas flow rate was maintained to 30 mL/min using a mass flow controller. Both adsorption and desorption experiments were carried out at 298 K.

CO_2/N_2 selectivity calculation: CO_2/N_2 selectivity was calculated using Ideal Adsorbed Solution Theory (IAST) method [19,20]. The absolute CO_2 loading was fitted with a dual–site Langmuir model, while the N_2 loading was fitted with a single–site Langmuir model. Both adjusted R2 values of fitting exceed 0.9998. The single–site Langmuir model can be defined as,

$$q = q_{sat}bp/(1+bp)$$

The dual–site Langmuir model can be defined as,

$$q = q_A+q_B = q_{sat,A}b_Ap/(1+b_Ap) + q_{sat,B}b_Bp/(1+b_Bp)$$

Where, q is molar loading of adsorbate; q_{sat} is saturation loading; b is parameter in the pure component Langmuir adsorption isotherm, A and B is referring to two different sites. The IAST selectivity for the CO_2:N_2 (0.15:0.85) gas mixture was calculated using following equation,

$$S = (q_1/q_2)/(p_1/p_2)$$

Where, S is the selectivity factor, q_1 and q_2 represent the adsorbed amount of CO_2 and N_2, and p_1 and p_2 represents the partial pressure of CO_2 and N_2.
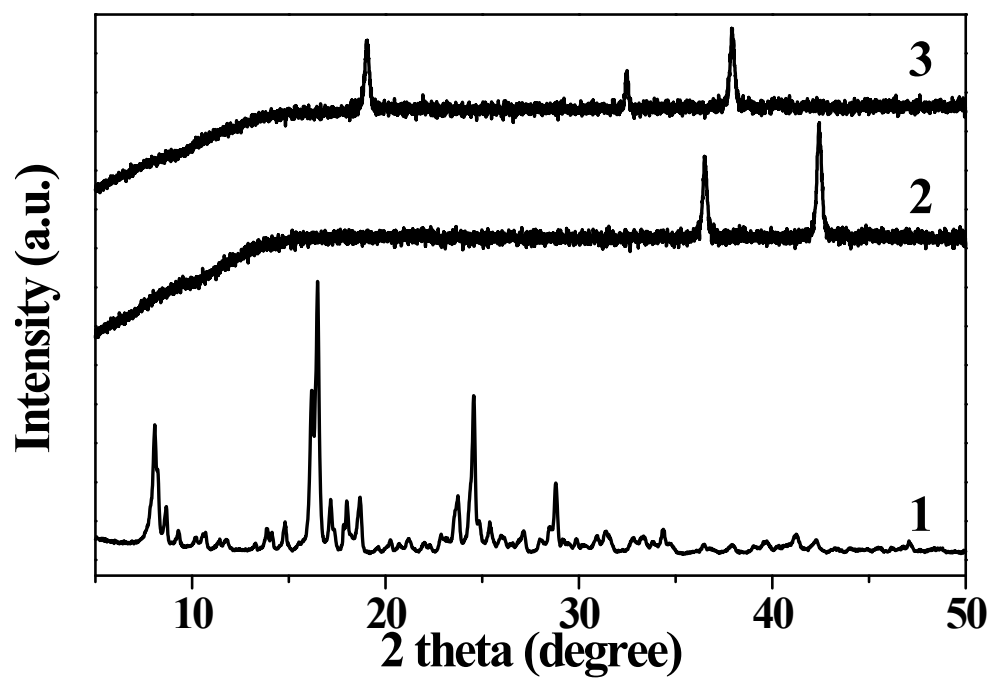
Fig. S1: A comparison of XRD patterns of 1) Co(Imda) (4, 4'-bpy), 2) CoO, and 3) Co(OH)$_2$.
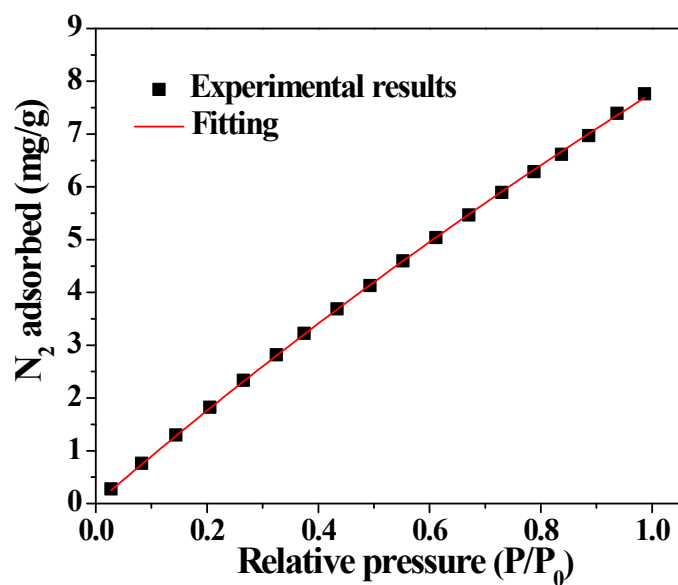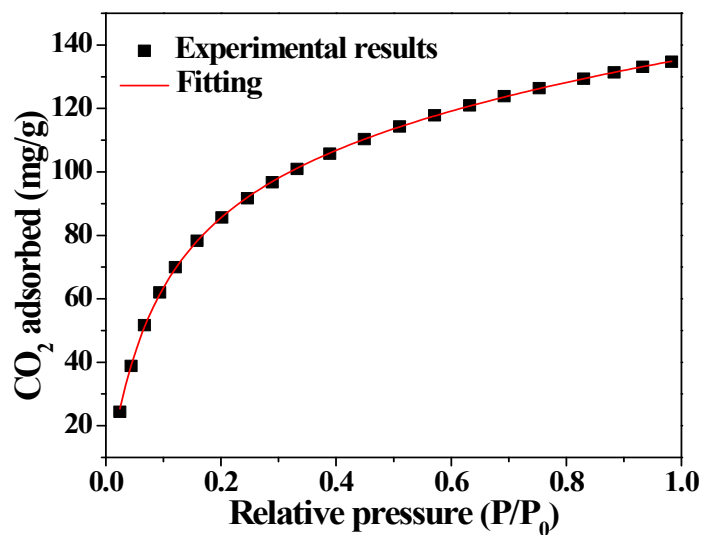
Fig. S2: CO_2 and N_2 adsorption isotherms were fitted by dual-site Langmuir model and single-site Langmuir model respectively for IAST CO_2/N_2 selectivity calculation of Co(Imda) (4, 4'-bpy).