

Electronic Supplementary Materials

Towards robust porous coordination polymer: the inhibition of mutual movement between interpenetrating sub-networks by introduction of multiple C-H••• π interactions

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Experimental section:

Materials

The ligand H₄MTB^{S1} and [NiL¹⁻²](ClO₄)₂^{S2-S3} were prepared according to the literature methods. The XRD patterns of powder samples were measured on a Bruker D8 ADVANCE X-ray diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). Elemental analyses of those compounds were measured by Vario ELIII CHNS/O elemental analyzer. Thermogravimetric analyses (TGA) were obtained on a Boyuan DTU-2A equipment with a heating rate of 10°C·min⁻¹ in air atmosphere. IR spectra were performed on a RAYLEIGH WQF-510A Fourier Transform Infrared spectrometer by using KBr pellets. All gases (CO₂ and N₂) sorption and desorption were measured on ASAP-2020M adsorption equipment.

Synthesis of compound 1.

To a solution of [NiL¹](ClO₄)₂ (0.100 g, 0.2 mmol) in 10 ml DMF solution, a solution of H₄MTB (0.050 g, 0.1 mmol) and NaOH (0.016 g, 0.4 mmol) in 10 ml of aqueous solution was added with stirring, filtration and slow evaporation of the resulting solution gave purple crystals in two weeks. Yield: 105 mg, 79% based on H₄MTB. Anal. Calc. For C₅₆H₉₁N₁₃Ni₂O₁₇: C, 50.35; H, 6.87; N, 13.63%. Found: C, 50.17; H, 6.76; N, 13.89%. IR: 3402(s), 3146(s), 2931(s), 2850(s), 2829(w), 1667(s), 1595(s), 1537(s), 1470(m), 1378(s), 837(m), 778(m).

Synthesis of compound 2.

[NiL²](ClO₄)₂ (0.109 g, 0.2 mmol) in 10 ml acetonitrile/DMF solution layered on H₄MTB (0.050 g, 0.1 mmol) and NaOH (0.016 g, 0.4 mmol) in 10 ml of aqueous solution, giving purple crystals in a week. Yield: 90 mg, 66% based on H₄MTB. Anal. Calc. For C₅₇H₉₆N₁₂Ni₂O₁₈: C, 50.53; H, 7.14; N, 12.41%. Found: C, 50.84; H, 6.79; N, 12.22%. IR: 3440(s), 2903(w), 2866(w), 1602(s), 1551(s), 1470(m), 1381(s), 1285(w), 985(m), 778(m).

Crystallography

Single crystal X-ray diffraction data for compounds were collected on a Bruker Apex CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 100 K. The structures were solved by direct methods using the SHELXS-2014 program and refined with full-matrix least squares on F² using the SHELXL-2014 program.^{S4} All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Because of the highly disordered solvent molecules in compound **1**, attempts to locate and model the highly disordered solvent molecules in the pores were unsuccessful. Therefore, the SQUEEZE routine of PLATON was used to remove the diffraction contribution from these solvents to produce a set of solvent free diffraction intensities.^{S5} Final formulas were derived from crystallographic data combined with elemental and thermogravimetric analyses data. Details of the crystal parameters, data collection and refinements for compounds **1-2** are summarized in Table S1.

References

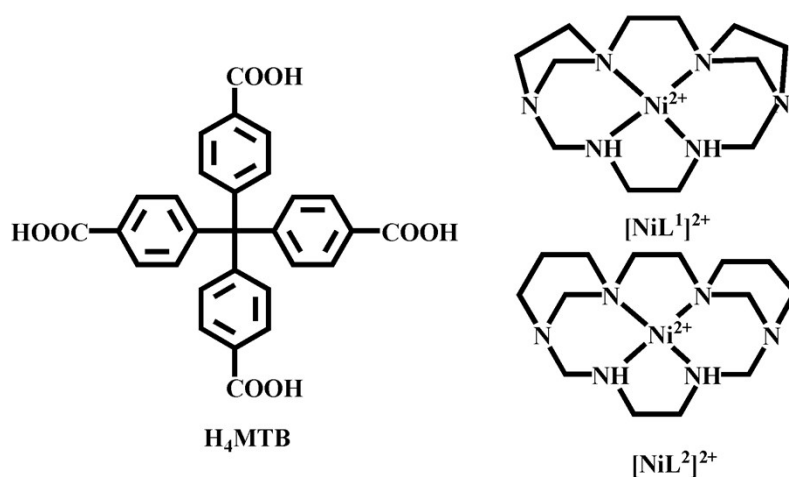
- [S1] (a) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, 1990, **112**, 1546; (b) M. Grimm, B. Kirste and H. Kurreck, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1097.
[S2] M. P. Suh, S. G. Kang, V. L. Goddard and S. Park, *Inorg. Chem.*, 1991, **30**, 365.

- [S3] M. P. Suh, W. Shin, S.-G. Kang, M. S. Lah and T.-M. Chung, *Inorg. Chem.*, 1989, **28**, 1602
 [S4] Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
 [S5] PLATON program: Spek, A. L. *Acta Crystallogr., Sect. A*, 1990, **46**, 194.

Table S1. Crystallographic Parameters of Compounds **1-2**

	1	2
Temperature (K)	100	100
Space group	<i>P-4b2</i>	<i>P-4b2</i>
<i>a</i> (Å)	16.7806(6)	17.173(5)
<i>b</i> (Å)	16.7806(6)	17.173(5)
<i>c</i> (Å)	12.2501(13)	11.406(5)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume (Å ³)	3449.5(4)	3364(2)
<i>Z</i>	2	2
<i>GOF</i>	0.983	1.064
Final R indices [<i>I</i> >2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0438	<i>R</i> ₁ = 0.0546,
R indices (all data)	<i>wR</i> ₂ = 0.0901	<i>wR</i> ₂ = 0.1590

$$\text{GOF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}; R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$



Scheme S1: The molecular structure of H₄MTB, [NiL¹]²⁺ and [NiL²]²⁺.

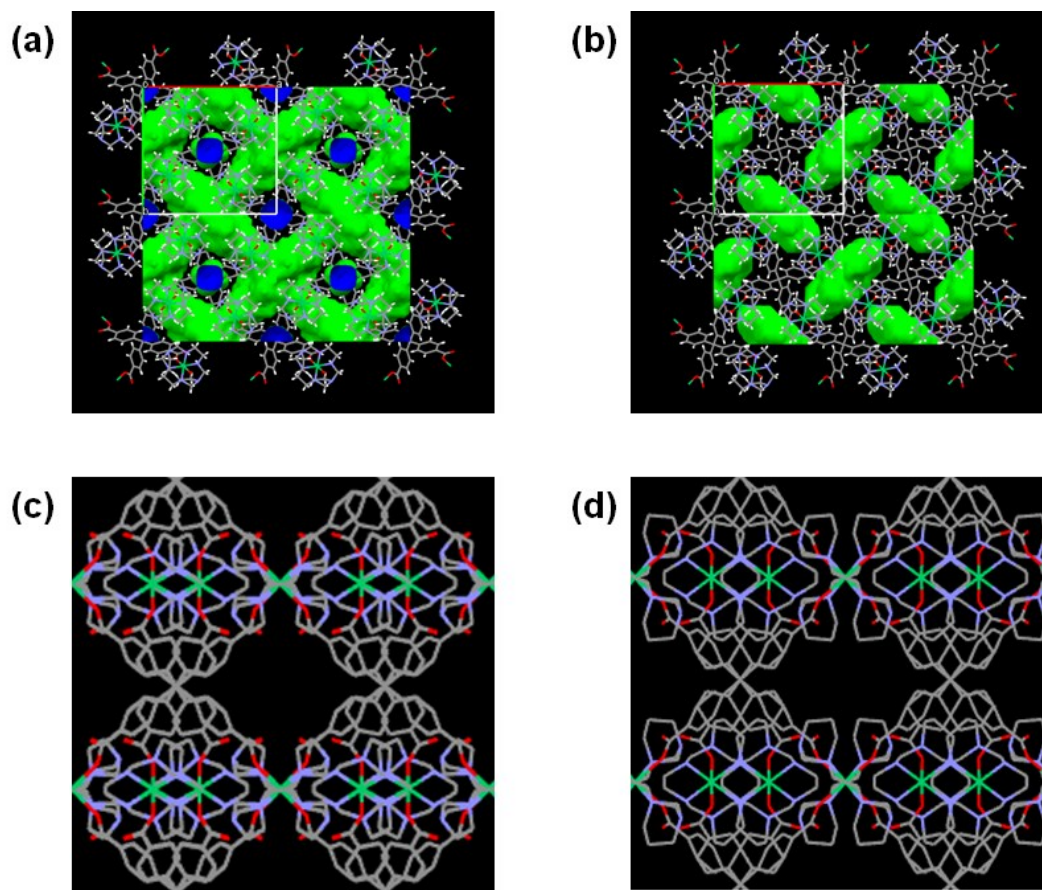


Fig. S1: Porous channels of compound **1** (a) and **2** (b) (the probe is 1.2 Å). The apertures of compound **1** (c) and compound **2** (d). The 2D channel was shrunk by extra -CH₂- group on L² in the compound **2**.

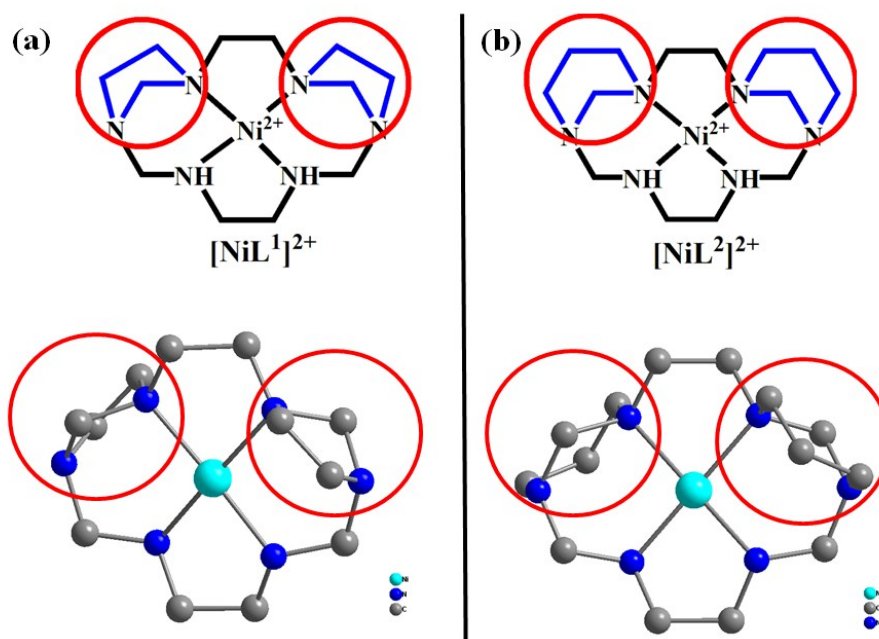


Fig. S2: Five-membered ring and its spatial position on L¹ (a); six-membered ring and its spatial position on L² (b).

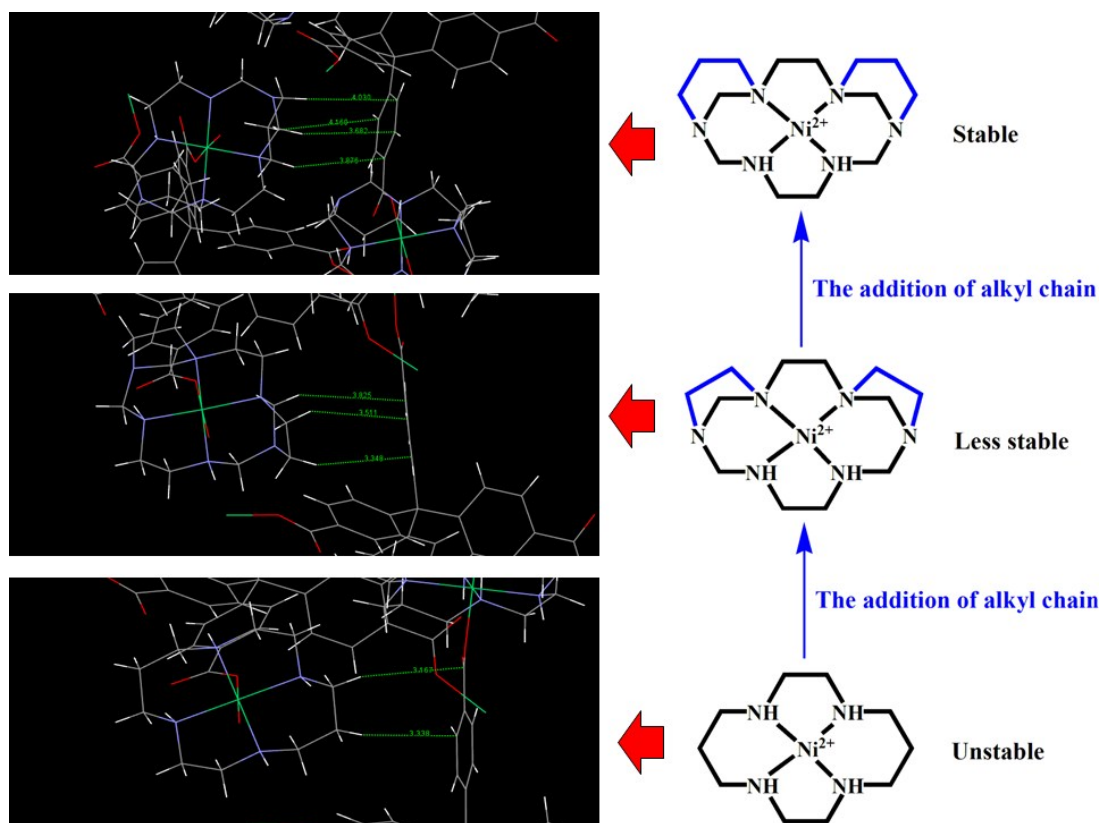


Fig. S3: C-H... π interaction in compounds **1-3**. The distance of C-H... π interaction within the scope of high level *ab initio* calculations. The comparison demonstrated that the mutual movement of diamonded sub-nets can be inhibited by introduction of multiple C-H... π , thus giving rise to robust PCP. It is worth mentioning that similar rule was observed very recently in our lab by using a flexible ligand tetrakis[4-(carboxyphenyl)oxamethyl]methane acid and several macrocyclic metallic tectons. However, the flexible ligand can't rule out the influence of ligand. Herein, MTB⁴⁺ ligand is rigid enough. Hence, the stability of desolvated compound is related to multiple C-H... π interactions exclusively.

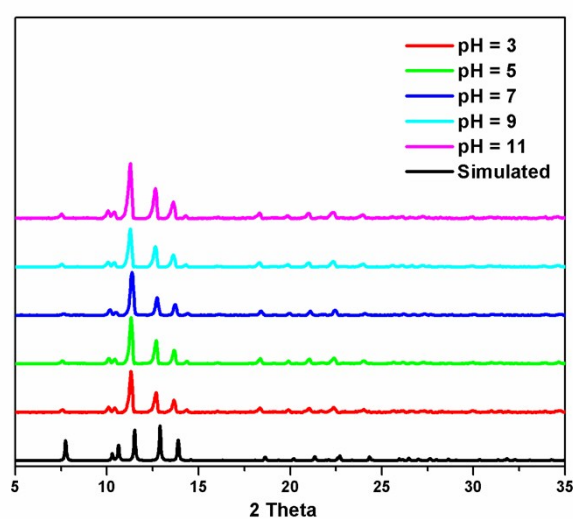


Fig. S4: XRD patterns of compound **2** in pH range of 3-11. The samples were collected by immersing as-synthesized compound in different pH solution for 12 h.

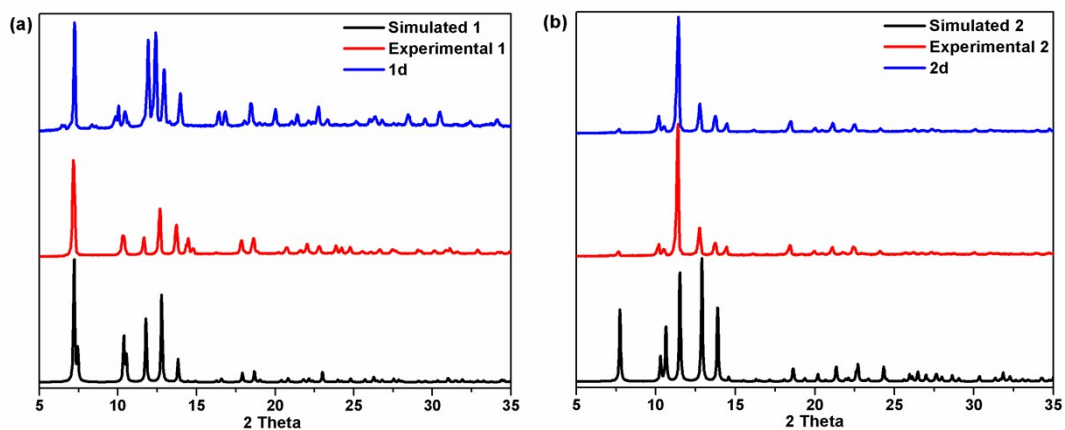


Fig. S5: XRD patterns of compound **1** (a) and compound **2** (b) for as-synthesized and desolvated samples.

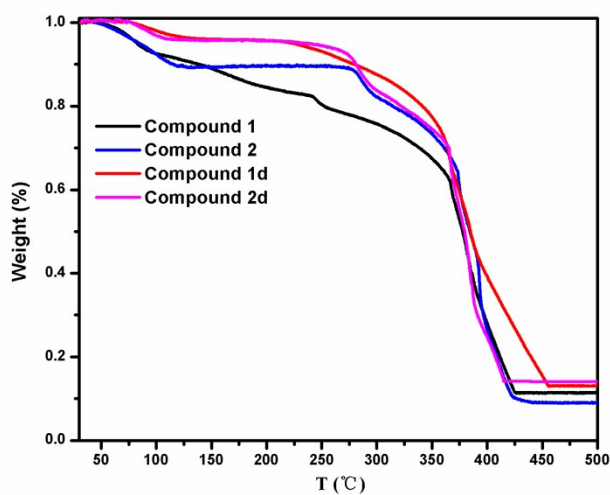


Fig. S6: TGA of compounds **1**, **2**, **1d** and **2d**.

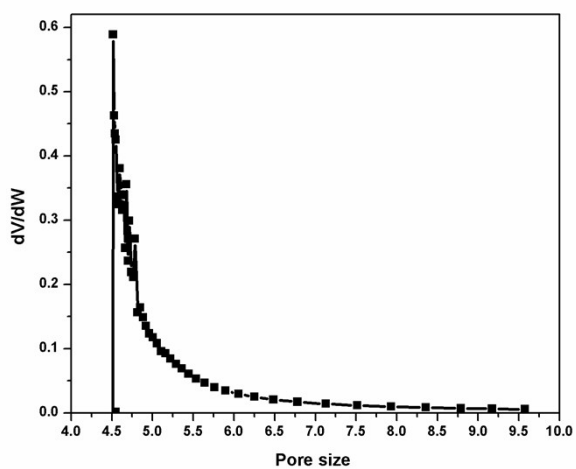
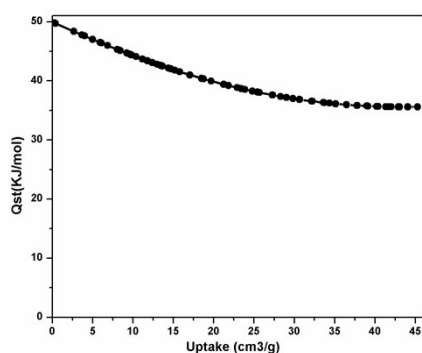


Fig. S7: Pore size distribution of compound **1d**.

(a)



(b)

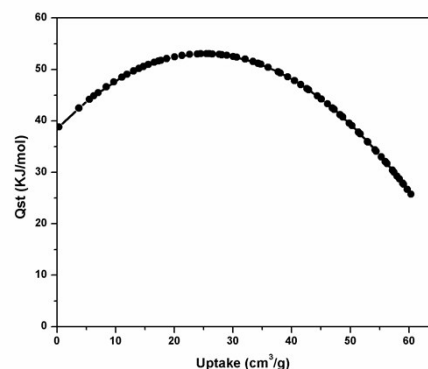


Fig. S8: Q_{st} for compounds **1d** and **2d**.

Calculation of sorption heat for CO₂ uptake using Virial 2 model

$$\ln P = \ln N + 1/T \sum_{i=0}^m a_i N^i + \sum_{i=0}^n b_i N^i \quad Q_{st} = -R \sum_{i=0}^m a_i N^i$$

The above virial expression was used to fit the combined isotherm data for **1d** and **2d** at 273 and 293 K, where P is the pressure, N is the adsorbed amount, T is the temperature, a_i and b_i are virial coefficients, and m and N are the number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.

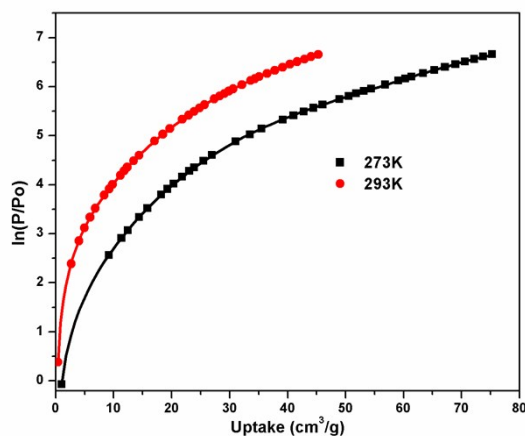


Fig. S9. CO₂ adsorption isotherms for compound **1d** with fitting by Virial 2 model. Fitting results: $a_0 = -6008.19938$, $a_1 = 73.45073$, $a_2 = -0.2391$, $a_3 = -0.02332$, $a_4 = 3.36247E-4$, $a_5 = -1.63603E-6$, $b_0 = 21.84093$, $b_1 = -0.22299$, $b_2 = 0.00271$; $R^2 = 0.99998$.

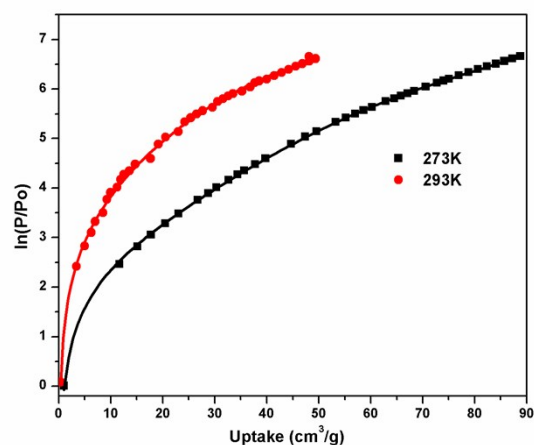


Fig. S10. CO₂ adsorption isotherms for compound **2d** with fitting by Virial 2 model. Fitting results: $a_0 = -4625.91082$, $a_1 = -160.29114$, $a_2 = 2.82093$, $a_3 = -5.21313E-5$, $a_4 = -3.35514E-5$, $a_5 = 2.24906E-7$, $b_0 = 16.86947$, $b_1 = 0.59244$, $b_2 = -0.0097$; $R^2 = 0.99900$.

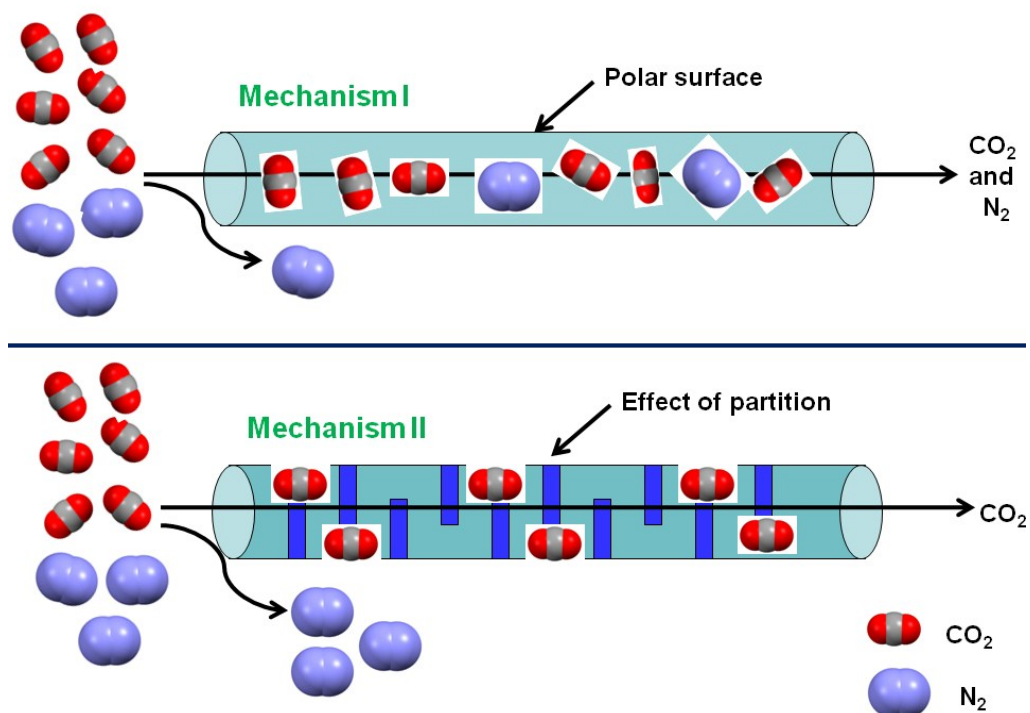


Fig. S11: The mechanism for the selectivity of CO₂ over N₂.