Supporting Information

A Metal-Calixarene Coordination Nanotube with 5-(pyrimidin-5-yl)isophthalic acid

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I. Experimental Section

Materials and Measurements. 5-(pyrimidin-5-yl) isophthalic acid was synthesized in single steps from commercially available reactants via Pd-catalyzed Suzuki coupling reactions.[1] *p*-*tert*-Butylthiacalix[4]arene (H_4TC4A) was synthesized by literature method[2] and other reagents were purchased and used as received. FT-IR spectra using KBr pellets were taken on a Bruker Vertex 70 Spectrometer. TGA was performed on a NETZSCH STA449F3. CHN elemental analysis was recorded on a VarioEL instrument.

Synthesis of CIAC-124. Yellow block crystals of **CIAC-124** were obtained from solvothermal reaction of the mixture of *p*-*tert*-butylthiacalix[4]arene (H_4TC4A, 0.1 g, 0.14 mmol), $NiCl_2 \cdot 6H_2O$ (0.1 g, 0.42 mmol), 5-(pyrimidin-5-yl) isophthalic acid (L, 0.05 g, 0.2 mmol), methanol (MeOH, 5 ml), N,N-dimethylformamide (DMF, 5 ml) and tetramethylammonium hydroxide solution (25%, 0.5 ml), in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at 4 $°C \cdot h^{-1}$. The crystals were isolated by filtration and then slowly washed with 1:1 MeOH-DMF and dry in air. Yield: ca. 50% with respect to H_4TC4A. Elemental analysis (%) for $\{Ni_{18.8}Cl_4(C_{40}H_{44}S_4O_4)_4(C_{12}H_6N_2O_4)_8(OH)_{1.6}(H_2O)_{5.2}\} \cdot 23(C_3H_7NO) \cdot 7CH_3OH$: calculated C 49.34 H 5.26 N 6.76; found C 49.13 H 5.15 N 6.71.

Synthesis of CIAC-125. Green block crystals of **CIAC-125** were obtained from solvothermal reaction of H_4TC4A (0.1 g, 0.14 mmol), $NiCl_2 \cdot 6H_2O$ (0.1 g, 0.42 mmol), $NiSO_4 \cdot 6H_2O$ (0.011 g, 0.04 mmol), L (0.05 g, 0.2 mmol), MeOH (5 ml), DMF (5 ml) and tetramethylammonium hydroxide solution (25%, 0.5 ml) in a 20 ml Teflon-lined autoclave which was kept at 130 °C for 3 days and then slowly cooled to 20 °C at 4 $°C \cdot h^{-1}$. The crystals were isolated by filtration and then slowly washed with 1:1 MeOH-DMF and dry in air. Yield: ca. 25% with respect to H_4TC4A. Elemental analysis (%) for $\{Ni_4(C_{40}H_{44}S_4O_4)(SO_4)(C_{12}H_6N_2O_4)(C_2H_7N)(C_3H_7NO)_2\} \cdot 2(C_3H_7NO)_2 \cdot 0.5(CH_3OH)$: calculated C 48.64 H 5.59 N 6.99; found C 48.72 H 5.52 N 7.05.

II. Crystallographic Analysis

The intensity data of **CIAC-124** and **CIAC-125** were recorded on a Bruker APEX-II with Mo-Kα radiation (λ= 0.71073 Å) and a Bruker D8 QUEST system with Cu-Kα radiation (λ = 1.54178 Å), respectively. The crystal structures were solved by means of Direct Methods and refined employing full-matrix least squares on F^2 (SHELXTL-97).[3] All non-hydrogen atoms except the butyl carbon atoms were refined anisotropically, and hydrogen atoms of the organic ligands were generated theoretically onto the specific atoms and refined isotropically with fixed thermal factors. Since the crystals do not diffract very well due to the structure disorder, the *R* factors in the final structure refinement are relatively large, but typical in such system. The diffraction data were treated by the "SQUEEZE" method as implemented in PLATON[4] to remove the contributions of the highly disordered solvent molecules. The SQUEEZE results for both structures are listed below. CCDC 1562140-1562141 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

Table S1. Selected Crystal Data for Compounds **CIAC-124** and **CIAC-125**

	CIAC-124	**CIAC-125**
Formula*	$C_{256}H_{236}Cl_4N_{16}Ni_{18.8}O_{54.8}S_{16}$	$C_{60}H_{68}N_5Ni_4O_{14}S_5$
Formula Weight*	6171.90	1478.33
Crystal System	tetragonal	monoclinic
Space Group (no.)	$I4/m$	$P2_1$/n
a (Å)	30.0460(12)	13.2812(6)
b (Å)	30.0460(12)	22.1310(9)
c (Å)	21.8685(18)	27.4033(12)
α (°)	90	90
β (°)	90	103.714(2)
γ (°)	90	90
V (Å^3)	19742(2)	7824.9(6)
Z	2	4
D_c (g cm^{-3})	1.038	1.255
μ (mm^{-1})	1.037	2.783
F(000)	6346	3068
Total Data	9043	6169
Unique Data	5729	5297
R_{int}	0.1053	0.0391
GOF	1.024	1.097
R_1[a] [$I > 2\sigma(I)$]	0.0546	0.0604
wR_2[b] (all data)	0.1825	0.1726

[a] $R_1 = \Sigma ||F_o|-|F_c|| / \Sigma |F_o|$; [b] $wR_2 = \{\Sigma [w(F_o^2-F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$

* The formula is based on the contents without the unidentified disordered solvent molecules and/or counterions.

SQUEEZE Result for CIAC-124

```
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
   1  0.000  0.000  0.500        849        192 ' '
   2  0.000  0.500  0.062       3216       1084 ' '
   3  0.500  0.000 -0.050       3208       1084 ' '
   4  0.161  0.157  0.246         13          1 ' '
   5  0.161  0.157  0.754         13          1 ' '
   6  0.157  0.839  0.246         13          1 ' '
   7  0.157  0.839  0.754         13          1 ' '
   8  0.339  0.343  0.254         13          1 ' '
   9  0.339  0.343  0.746         13          1 ' '
  10  0.343  0.661  0.254         13          1 ' '
  11  0.343  0.661  0.746         13          1 ' '
  12  0.500  0.500  0.000        849        192 ' '
  13  0.657  0.339  0.254         13          1 ' '
  14  0.657  0.339  0.746         13          1 ' '
  15  0.661  0.657  0.254         13          1 ' '
  16  0.661  0.657  0.746         13          1 ' '
  17  0.839  0.843  0.246         13          1 ' '
  18  0.839  0.843  0.754         13          1 ' '
  19  0.843  0.161  0.246         13          1 ' '
  20  0.843  0.161  0.754         13          1 ' '
```

When all the results of SQUEEZE, TG and element analysis are considered, the appropriate chemical formula can be proposed as $\{Ni_{18.8}Cl_4(C_{40}H_{44}S_4O_4)_4(C_{12}H_6N_2O_4)_8(OH)_{1.6}(H_2O)_{5.2}\}\cdot 23(C_3H_7NO)\cdot 7CH_3OH$.

SQUEEZE Result for CIAC-125

```
loop_
  _platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
  1 -0.092  0.408  0.000        964        199 ' '
```

```
  2   0.037   0.463   0.500           964            199 ' '
```

398 electrons per unit cell in total, estimated by the PLATON/SQUEEZE program, belong to the contributions of the disordered species in the voids. There are 4 formula units per cell and the structure refinement revealed a neutral motif with the formula of $C_{60}H_{71}N_5Ni_4O_{14}S_5$. All the 398 e^- correspond to about 9 DMF molecules (C_3H_7NO, 40 e) and 2 CH_3OH molecules (18 e^-). When all the results of SQUEEZE, TG and element analysis are considered, the appropriate chemical formula can be proposed as $\{Ni_4(C_{40}H_{44}S_4O_4)(SO_4)(C_{12}H_6N_2O_4)\ (C_2H_7N)(C_3H_7NO)_2\}\ \cdot 2\ (C_3H_7NO)_2\} \cdot 0.5(CH_3OH)$

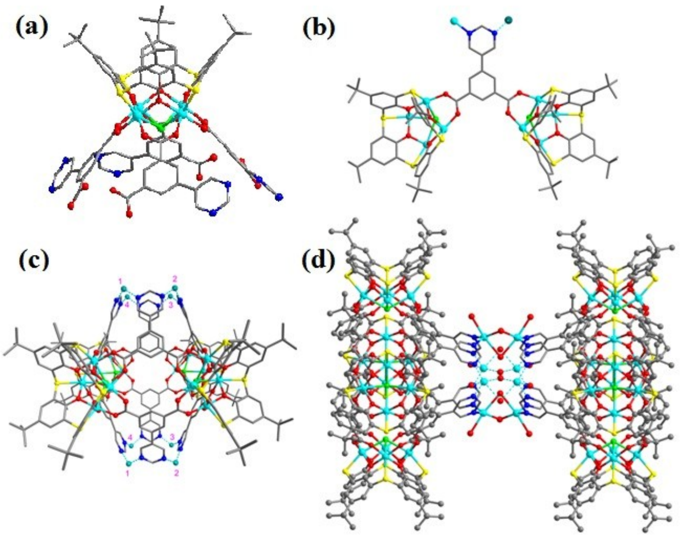


Figure S1 (a, b) Coordination mode of the Ni_4-TC4A SBU and **L**; (c, d) the arrangements of the truncated octahedral cage and oxygen atom bridges.

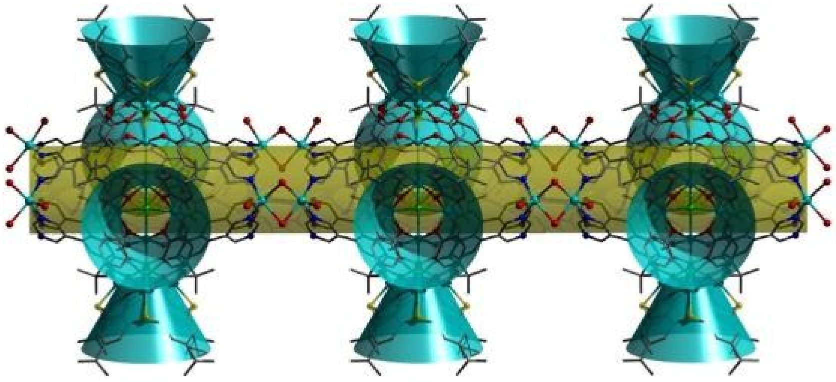


Figure S2 Coordination tube in **CIAC-124** (oxygen atom bridges lie in 1, 2 sites).

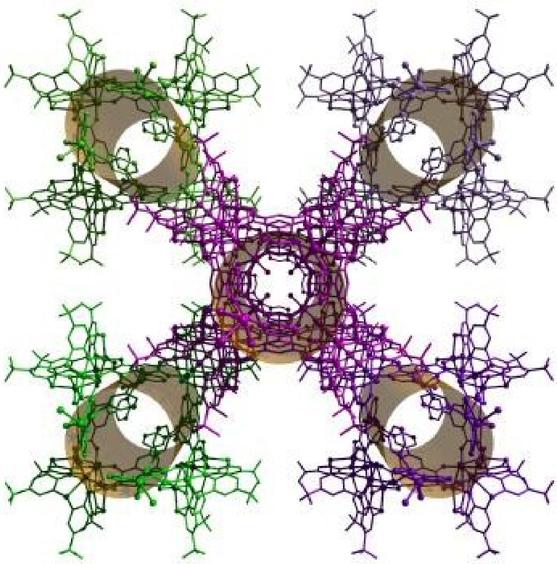


Figure S3 Packing diagram of the nanotubes in **CIAC-124**.

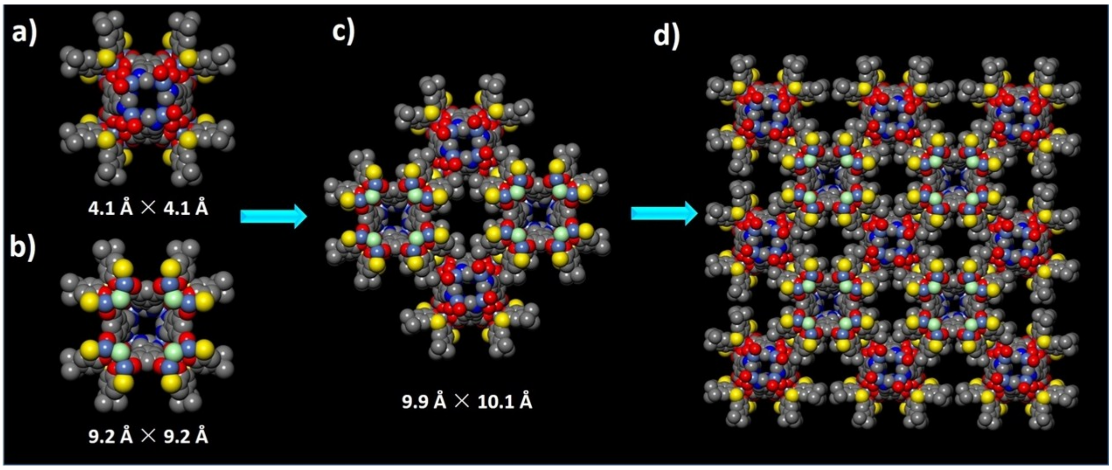


Figure S4 Space-filling model along the [110] direction of **CIAC-124**.

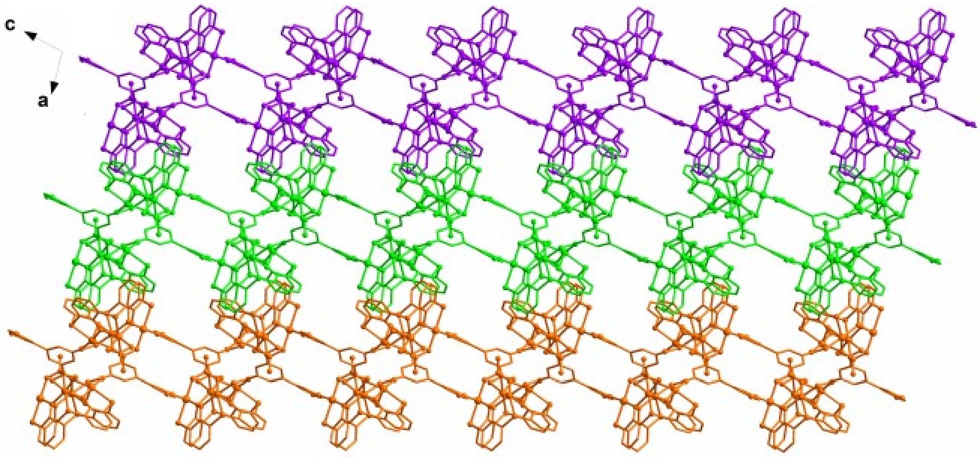
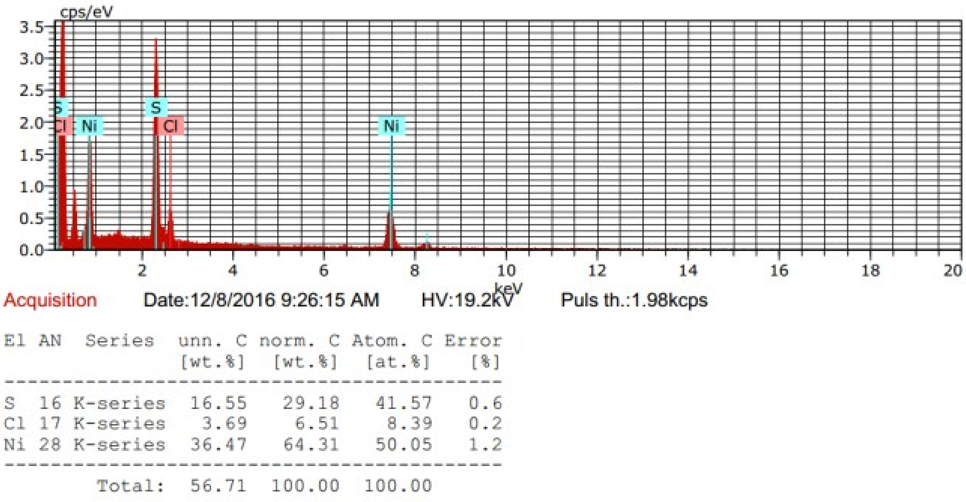


Figure S5 Packing diagram of the layer networks in **CIAC-125**.

III. EDS and TGA Analysis



```
Acquisition     Date:12/8/2016 9:26:15 AM     HV:19.2kV     Puls th.:1.98kcps

El AN  Series   unn. C norm. C Atom. C Error
                [wt.%]  [wt.%]  [at.%]   [%]
--------------------------------------------
S  16 K-series  16.55   29.18   41.57   0.6
Cl 17 K-series   3.69    6.51    8.39   0.2
Ni 28 K-series  36.47   64.31   50.05   1.2
--------------------------------------------
        Total:  56.71  100.00  100.00
```

Figure S6 EDS analysis on the samples of **CIAC-124**.

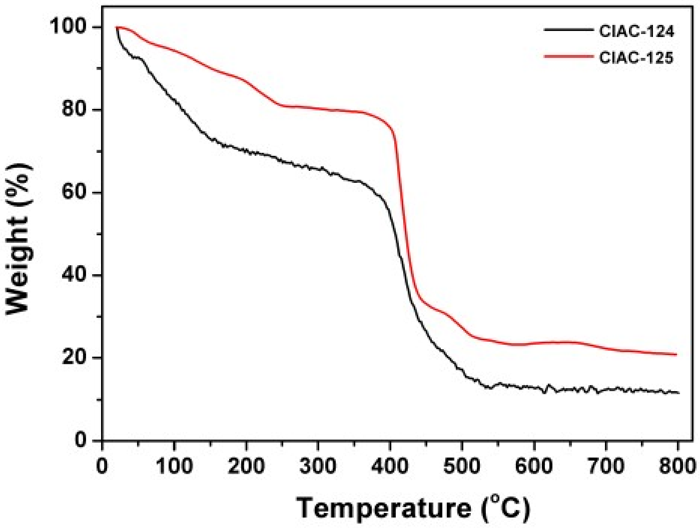


Figure S7 TGA of compounds **CIAC-124** and **CIAC-125** (in air).

IV. Gas Adsorption Analysis

Activation of Cages. As-synthesized samples of **CIAC-124** and **CIAC-125** were immersed in the methanol solution for 3 days, respectively, during which the solution was decanted and freshly replenished three times. Obtained samples were degassed under dynamic vacuum at 80 °C for 10 hours, yielding activated samples.

Low-Pressure Gas Sorption Measurements. Low-pressure gas sorption experiments were carried out on a Micromeritics ASAP-2420M and a ASAP 2020M automatic volumetric instrument. The N_2 and H_2 isotherms were measured using a liquid nitrogen bath (77 K) while that of CO_2, CH_4, C_2H_6 and C_3H_8 at 273 K and 298 K. The specific surface areas were determined using the Brunauer-Emmett-Teller (BET) and the Langmuire quation from the N_2 sorption data.

Langmuir-Freundlich Fitting of Pure Component Isotherms. The measured experimental data is excess loadings (q^{ex}) of the pure components CO_2, CH_4, C_2H_6 and C_3H_8 for **CIAC-124**, which should be converted to absolute loadings (q) firstly.

$$q = q^{ex} + \frac{pV_{pore}}{ZRT}$$

Here Z is the compressibility factor. The Peng-Robinson equation was used to estimate the value of compressibility factor to obtain the absolute loading, while the measure pore volume 0.648 cm^3 g^{-1} is also necessary.

The dual-site Langmuir-Freundlich equation is used for fitting the isotherm data at 298K.

$$q = q_{m_1} \times \frac{b_1 \times p^{1/n_1}}{1 + b_1 \times p^{1/n_1}} + q_{m_2} \times \frac{b_2 \times p^{1/n_2}}{1 + b_2 \times p^{1/n_2}}$$

Here p is the pressure of the bulk gas at equilibrium with the adsorbed phase (kPa), q is the adsorbed amount per mass of adsorbent (mol kg^{-1}), q_{m1} and q_{m2} are the saturation capacities of sites 1 and 2 (mol kg^{-1}), b_1 and b_2 are the affinity coefficients of sites 1 and 2 (1/kPa), n_1 and n_2 are the deviations from an ideal homogeneous surface.

The selectivity of preferential adsorption of component 1 over component 2 in a mixture containing 1 and 2, perhaps in the presence of other components too, can be formally defined as

$$S = \frac{q_1/q_2}{p_1/p_2}$$

q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2

using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz. [5]

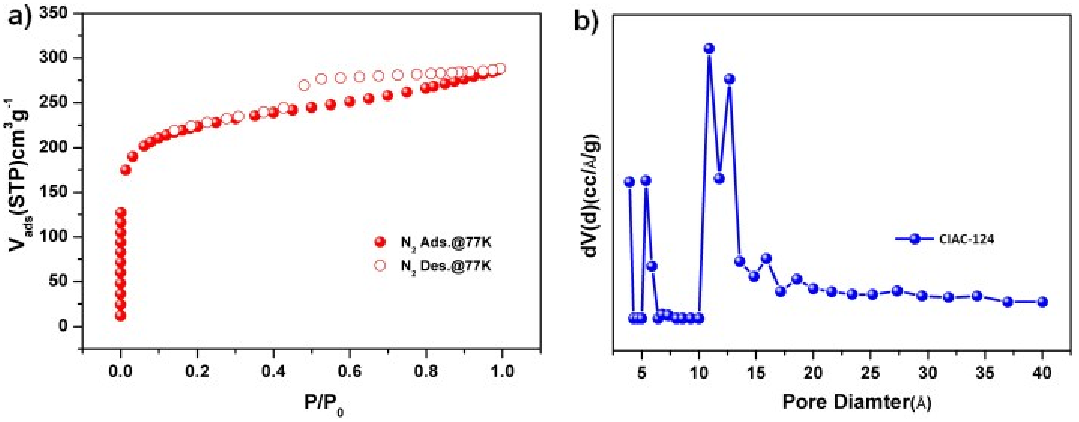


Figure S8 a) Nitrogen sorption isotherms on **CIAC-124** at 77 K (Adsorption: closed; desorption: open, respectively); b) The pore size distribution calculated by the DFT method.

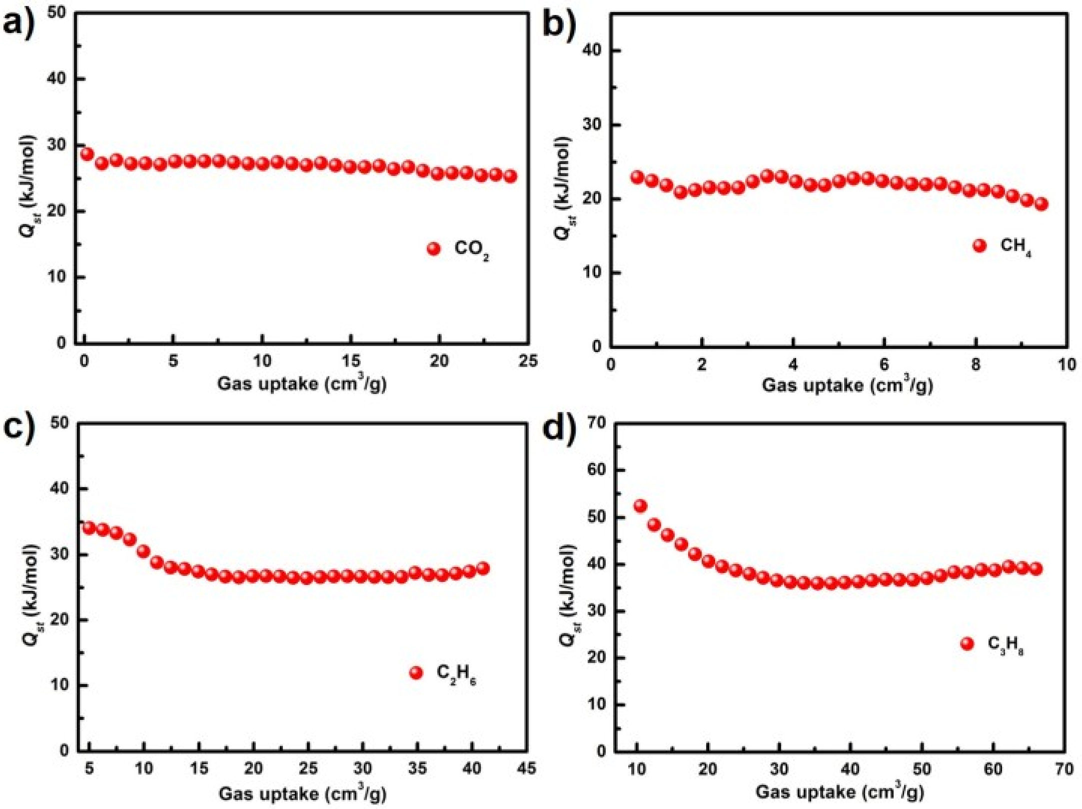


Figure S9 Isosteric heat of CO_2 (a), CH_4 (b), C_2H_6 (c) and C_3H_8 (d) for **CIAC-124**.

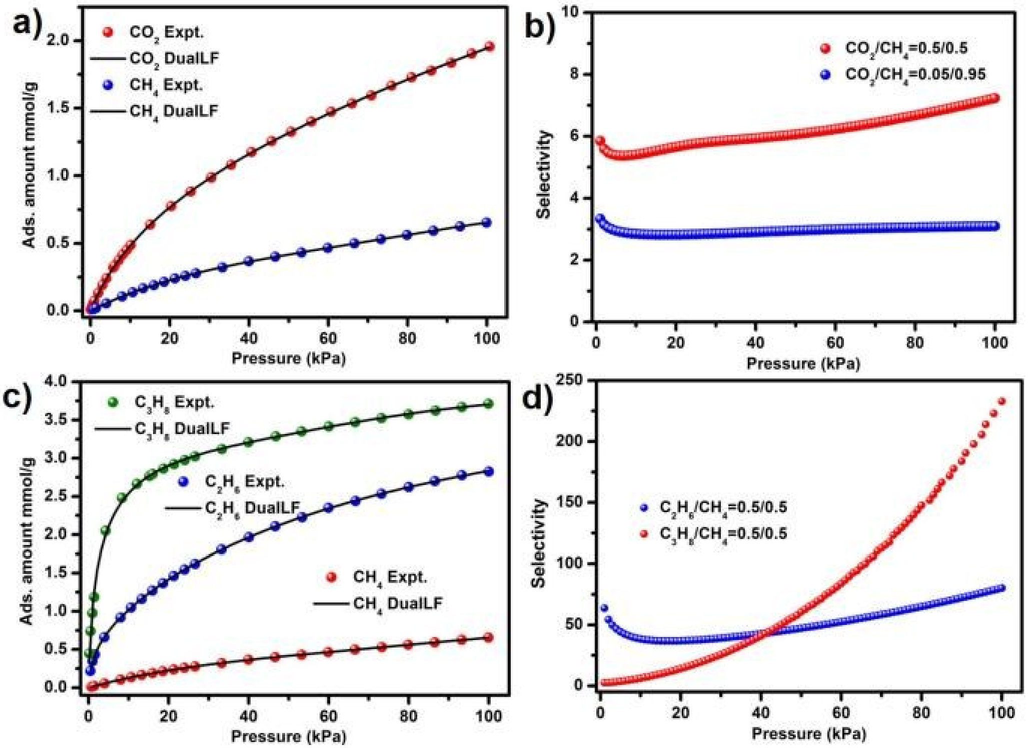


Figure S10 CO_2, CH_4, C_2H_6 and C_3H_8 adsorption isotherms at 273 K along with the Dual-Site Langmuir Freundich (DSLF) fits (a, c); Gas mixture adsorption selectivity is predicted by IAST at 273 K and up to 100 kPa (= 1 bar) for **CIAC-124** (b, d).

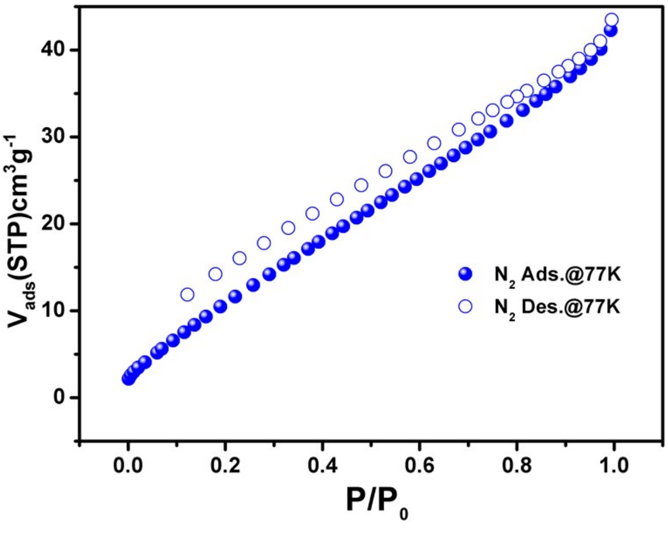


Figure S11 Nitrogen sorption isotherms on **CIAC-125** at 77 K (Adsorption: closed; desorption: open, respectively).

V. FT-IR Spectra

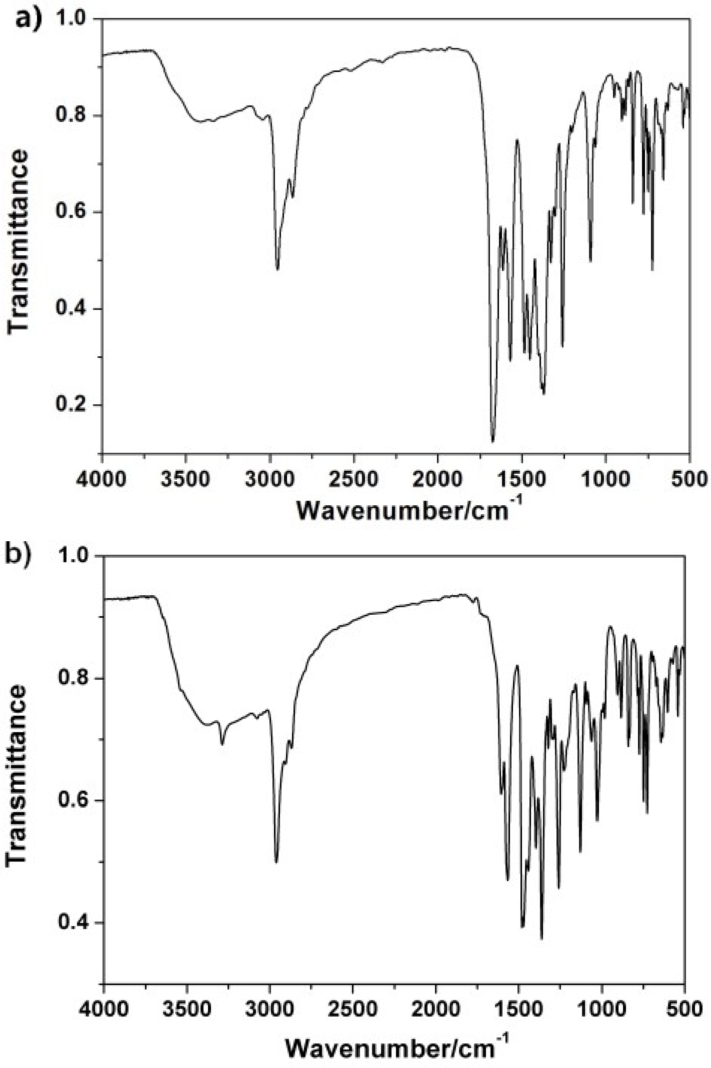


Figure S12 FT-IR spectra of compounds **CIAC-124** (a) and **CIAC-125** (b).

VI. References

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