A new meso-porous coordination polymer: synthesis, structure, and gas adsorption studies

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General Information. All the reagents and solvents were commercially available and used as received. The IR spectra were recorded in the range of 4000-400 cm⁻¹ on a Nicolet ID5 ATR spectrometer. The elemental analysis was carried out with a Perkin-Elmer 240C elemental analyzer. Thermal analyses were performed on a Rigaku TG8120 instrument from room temperature to 600 °C at a heating rate of 5 °C/min under flowing nitrogen. Powder X-ray diffraction was obtained using a Rigaku RINT powder diffractometer with Cu Kα anode. The simulated PXRD spectra were acquired by the diffraction-crystal module of the Mercury program based on the single-crystal data. The program is available free of charge via the Internet at http://www.iucr.org.

Synthesis of the organic building block. 1,3,5-Tri(6-hydroxycarbonylnaphthalen-2-yl)benzene (H₃BTN) was synthesized according to our previous work¹.

Synthesis of NJTU-1. H₃BTN (6 mg, 0.01 mmol), Cu(NO₃)₂·3H₂O (15 mg, 0.062 mmol), DMF/H₂O = 5:1 (1 mL), and concentrated HNO₃ (30 µL) were mixed and stirred for a few minutes in air and then the clear solution was transferred into an autoclave Teflon-line stainless vessel (4 mL). The vessel was sealed and heated at 65
°C for 2 days and then cooled to room temperature. Green block crystals of NJTU-1 were obtained and then washed by DMF (yield: ~60% based on ligand). Anal. Calcd. C_{26}H_{14}CuO_{4}: C, 68.79; H, 3.11%. Found: C, 67.21; H, 2.95%.

**Single Crystal X-ray Study.** Single-crystal X-ray diffraction data were measured on a Bruker Smart Apex CCD diffractometer at 223 K using graphite monochromated Mo/Kα radiation (λ = 0.71073 Å). Data reduction was made with the Bruker Saint program. The structure was solved by direct methods and refined using the full-matrix least squares technique using the SHELXTL package. Nonhydrogen atoms were refined with anisotropic displacement parameters during the final cycles. Organic hydrogen atoms were placed in calculated positions with isotropic displacement parameters set to 1.2Ueq of the attached atom. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules and, thereby, to produce a set of solvent-free diffraction intensities; the structure was then refined again using the data generated.

**Sample Activation.** Before the supercritical CO\(_2\) treatment, as-synthesized samples were soaked in absolute DMF, replacing the soaking solution every 24 h for 3 days. After exchanging, the DMF-containing samples were placed inside the supercritical CO\(_2\) dryer and the DMF was exchanged with CO\(_2\) over a period of 4 h. During this time the liquid CO\(_2\) was vented under positive pressure for five minutes every two hours. The rate of venting of CO\(_2\) was always kept below the rate of filling so as to maintain a full drying chamber. Following venting, the chamber was sealed and the temperature was raised to 40 °C, at which time the chamber was slowly vented over the course of 15 h. The color of the NJTU-1 changed from green to blue. The collected sample was transferred into the sample tube and activated under a dynamic high vacuum at room temperature for a overnight to obtain the desolvated sample.

**Adsorption Experiments.** In the low pressure gas sorption measurement, ultra-high-purity grade were used throughout the adsorption experiments. Gas adsorption isotherms were obtained using a Belsorp-mini volumetric adsorption instrument from BEL Japan Inc. using the volumetric technique. A part of the N\(_2\) sorption isotherm at
77 K in the P/P₀ range 0.02-0.08 was fitted to the BET equation to estimate the BET surface area, and the Langmuir surface area calculation was performed using all data points. The pore-size distribution was obtained from the DFT model (assuming split pore geometry) based on the N₂ sorption isotherm. High pressure adsorption of CO₂, CH₄, C₂H₄ and C₂H₆ were measured by using a Belsorp-HP adsorption instrument at 273 and 298 K, respectively. The total high-pressure gas uptake was calculated by 
\[ N_{total} = N_{excess} + \rho_{bulk}V_{pore}, \]
where \( \rho_{bulk} \) is the density of compressed gas at the measured temperature and \( V_{pore} \) (1.0635 cm³·g⁻¹) is the pore volume of the sample that was obtained from the N₂ isotherm at 77 K.

**Selectivity prediction for binary mixture adsorption.** Ideal adsorbed solution theory (IAST) was used to predict binary mixture adsorption from the experimental pure-gas isotherms. In order to perform the integrations required by IAST, the single-component isotherms should be fitted by a proper model. There is no restriction on the choice of the model to fit the adsorption isotherm, but data over the pressure range under study should be fitted very precisely. Several isotherm models were tested to fit the experimental pure isotherms for CH₄, C₂H₄, C₂H₆ and CO₂ of NJTU-1, and the dual-site Langmuir-Freundlich equation were found to best fit the experimental data:

\[ q = q_{m1} \cdot \frac{b_1 \cdot P^{1/n_1}}{1 + b_1 \cdot P^{1/n_1}} + q_{m2} \cdot \frac{b_2 \cdot P^{1/n_2}}{1 + b_2 \cdot P^{1/n_2}} \]

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), \( q_{m1} \) and \( q_{m2} \) are the saturation capacities of sites 1 and 2 (mol/kg), \( b_1 \) and \( b_2 \) are the affinity coefficients of sites NJTU-1 (1/kPa), and \( n_1 \) and \( n_2 \) represent the deviations from an ideal homogeneous surface. Figure 4 shows that the dual-site Langmuir-Freundlich equation fits the single-component isotherms extremely well. The \( R^2 \) values for all the fitted isotherms were over 0.9998. Hence, the fitted isotherm parameters were applied to perform the necessary integrations in IAST.

**Estimation of the isosteric heats of gas adsorption.** A virial-type expression comprising the temperature-independent parameters \( a_i \) and \( b_i \) was employed to
calculate the enthalpies of adsorption for CO$_2$ (at 273 and 298 K) on NJTU-1. The
data were fitted using the equation:

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N_i + \sum_{i=0}^{n} b_i N_i$$  \hspace{1cm} (1)

Here, $P$ is the pressure expressed in Torr, $N$ is the amount adsorbed in mmol/g,
$T$ is the temperature in K, $a_i$ and $b_i$ are virial coefficients, and $m$, $n$ represent
the number of coefficients required to adequately describe the isotherms ($m$ and $n$
were gradually increased until the contribution of extra added $a$ and $b$ coefficients
was deemed to be statistically insignificant towards the overall fit, and the average
value of the squared deviations from the experimental values was minimized).

$$Q_{st} = -R \sum_{i=0}^{m} a_i N_i$$  \hspace{1cm} (2)

Here, $Q_{st}$ is the coverage-dependent isosteric heat of adsorption and $R$ is the
universal gas constant. In addition, the determination of the $Q_{st}$ on MgMOF-74,
NiMOF-74, Cu-TDPAT, CuBTC, and NaX zeolite is based on other reported
paper$^6$.

**Calculations of adsorption selectivity.** 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

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2}$$  \hspace{1cm} (3)

In equation (3), $q_1$ and $q_2$ are the *absolute* component loadings of the adsorbed
phase in the mixture. In all the calculations to be presented below, the calculations of
$S_{ads}$ are based on the use of the Ideal Adsorbed Solution Theory of Myers and
Prausnitz$^7$. 
Figure S1. TG of NJTU-1: as-synthesized samples (black) and completely activated samples (red).

Figure S2. The PXRD patterns of NJTU-1.
Figure S3. The results of Le Bail analysis for the PXRD of activated NJTU-1 by S-CO$_2$. Refined parameters and reliability factors are as follows: space group: Im-3, $a = 33.3895$ Å; $R_p = 0.03892$ and $R_{wp} = 0.08044$.

Figure S4. Photographic images of NJTU-1. (a): as-synthesized; (b) Activated samples by S-CO$_2$. 
**Figure S5.** Infrared spectra of the ligand, as-synthesized and degassed form of NJTU-1.

**Figure S6.** ORTEP View of the asymmetric unit for NJTU-1.
Figure S7. Three types of interpenetrated cage in NJTU-1.

Figure S8. The packing of three types of interpenetrated cage in NJTU-1.
Figure S9. The Connolly surface diagram displays the large three dimensional cross-linking tunnels in NJTU-1 (inner surfaces: yellow, outer surfaces: grey).

Figure S10. The sqc topology of NJTU-1.
Figure S11. The upper figure shows the consistency plot to determine the pressure range for BET fitting, and the bottom is the calculated BET plot from N\textsubscript{2} isotherm of NJTU-1.
Figure S12. Series gases adsorption isotherm of NJTU-1 at 273, respectively.

Figure S13. Series gases adsorption isotherm of NJTU-1 at 298, respectively.
Figure S14. The calculated virial equation isotherms parameters fit to the experimental CO$_2$ data of NJTU-1.

Figure S15. The isosteric heat of adsorption for CO$_2$ in series PCPs.
**Figure S16.** The calculated virial equation isotherms parameters fit to the experimental C$_2$H$_4$ data of NJTU-1.

**Figure S17.** The calculated virial equation isotherms parameters fit to the experimental CH$_4$ data of NJTU-1.
Figure S18. The calculated virial equation isotherms parameters fit to the experimental $C_2H_6$ data of NJTU-1.

Figure S19. The isosteric heat of series gases in NJTU-1.
Figure S20. The isosteric heat of CO\textsubscript{2} in MOF-14.

Figure S21. The calculated virial equation isotherms parameters fit to the experimental CO\textsubscript{2} data of MOF-14.
Reference


