Supporting Information

Unified mesopore and dense Cu^{2+} site in porous coordination polymers for high efficient gas storage and separation

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General Procedures and Materials

All the reagents and solvents were commercially available and used as received. Powder synchrotron X-ray diffraction patterns were collected at SPring-8 BL02B2 beamline. Simulated powder patterns from single-crystal X-ray diffraction data were generated using Mercury 1.4.2 software. For *in-situ* infrared spectroscopy, the samples were evacuated at 333 K for 6 h, and final activation was performed under a high vacuum by heating to 393 K for another 12h. IR was collected using a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a cryogenic detector with the sample compartment modified to accommodate the cryogenic head. The final spectra were recorded at the resolution of 0.125 cm^{-1}.

PCP synthesis

PCP-31 and PCP-32 were synthesized according to our previous work. Synthesis of PCP-31: copper(II) nitrate (25 mg), H_3L, 10 mg) and HNO_3 (80 μL)were mixed with 3 mL of DMF/1,4-dioxane/H_2O(4:1:1) in a 4 mL glass container and tightly capped with a Teflon vial and heated at 50°C for two days. After cooling to room temperature, the vials were heated at 60 °C for another two days and then decrease the temperature to room temperature. The resulting high yield green polyhedral crystals were harvested and washed with DMF. Synthesis of PCP-32: copper(II) nitrate (13 mg), H_3L, 6 mg) and HNO_3 (20 μL) were mixed with 1 mL of DMF/1,4-dioxane/H_2O (4:2:0.5) in a 4 mL glass container and tightly capped with a Teflon vial and heated at 65°C for two days. After cooling to room temperature, the resulting high yield green crystals were harvested and washed with DMF.

Adsorption experiments

Before the measurement, the solvent-exchanged sample was prepared by immersing the as-synthesized samples in dehydrated acetone for two days to remove the nonvolatile solvents, and the extract was decanted every 8 h and fresh acetone was replaced. The completely activated sample was obtained by heating the solvent-exchanged sample at room temperature for 6 h, 60°C for 6 h and then120°C for 24h under a dynamic high vacuum. In the gas sorption measurement, ultra-high-purity grade were used throughout the adsorption experiments. Gas adsorption isotherms were obtained using a Belsorpvolumetric adsorption instrument from BEL Japan Inc. using the volumetric technique. High pressure adsorption of H_2 (77K), CO_2, C_2H_4 and C_2H_6 were measured by using a Belsorp-HP adsorption instrument at 273 and 298 K, respectively. The total high-pressure gas uptake was calculated by $N_{\mathrm{total}} = N_{\mathrm{excess}} + \rho_{\mathrm{bulk}} V_{\mathrm{pore}}$, where ρ_{bulk} is the density of compressed gas at the measured temperature and V_{pore} is the pore volume of the sample that was obtained from the N_2 isotherm at 77 K.

Co-sorption measurements

Mixed gas adsorptions were carried out using a multicomponent gas adsorption apparatus, Belsorp-VC (MicrotracBEL Corp.). In this apparatus, the total adsorbed amount was calculated by a constant volume method, and the composition ratio of mixed gases was determined using an Agilent 490 Micro gas chromatographic system equipped with a thermal conductive detector. From these data, we calculated adsorbed amounts and partial pressures for each gas.

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 H_2 (at 77 and 87 K) on PCP-31 and PCP-32. In each case, the data were fitted using the equation:

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

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).

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i \qquad (2)$$

Here, Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant.

From these results, the Henry's constant (K_H) is calculated from where T is temperature.

$$K_H = \exp(-b_0) \exp(-a_0 / T) \qquad (3)$$

The Henry's Law selectivity for gas component i over j at 273 and 298 K were calculated based on Eq. **4**.

$$S_{ij} = K_{Hi}/K_{HJ} \qquad (4)$$

Estimation of the isosteric heats by temperature-dependent IR

The equations we used for the calculation of enthalpy and entropy[2]:

Langmuir isotherm:

$$Q = A / A_M = K(T)p / [1+K(T)p] \qquad (5)$$

where q is the coverage, A is the intensity of the IR adsorption band and A_M stands for the intensity correspoding to full coverage (q =1). K is adsorption equilibrium constant and p is the equilibrium pressure.

Vant't Hoff equation:

$$K(T) = \exp(-DH^{o}/RT) \exp(DS^{o}/R) \qquad (6)$$

the combination of the vant't Hoff and Langmuir equations lead to the VTIR equation:

$$ln[A/(A_M-A)p] = (-DH^o/RT)+(DS^o/R) \qquad (7)$$

Plot the left-hand side of Equation (7) against the reciprocal of the temperature.

In addition, three assumptions, the Lambert-Beer law is valid; the adsorption process is an ideal Langmuir-type process; both ΔH^0 and ΔS^0 are temperature independent, should be taken into the considerations.

Isotherm models

In order to evaluate the adsorption equilibrium selectivity and predict adsorption of gas mixture from pure component isotherms, the Henry's law linear isotherm equation and the Langmuir model were used to correlate the C_2H_2, C_2H_4, C_2H_6 and CO_2 adsorption on PCP-31 and PCP-32. The Henry's isotherm equation is

$$q = KP \qquad (8)$$

where q is the adsorbed amount per unit weight of adsorbent(cm^3 g^{-1}), P is the adsorbate gas pressure at equilibrium (torr), and K is the Henry's law constant (cm^3 g^{-1} torr^{-1}).

The Langmuir isotherm is formulated as:

$$q = q_m bp / (1+bp) \qquad (9)$$

where q_m (cm^3 g^{-1}) and b (torr^{-1}) are the Langmuir isotherm equation parameters. The values of q_m and b were determined can be determined from the slope and intercept of a linear Langmuir plot of ($1/q$) versus ($1/P$).

Adsorption equilibrium selectivity

In order to evaluate the efficacy of an adsorbent for gas separation and purification such as removal/separation of $C_2H_{2/4}$ from their CO_2 mixtures by adsorption, it is necessary to know the adsorbent selectivity. The adsorption equilibrium selectivity (S) between components 1 and 2 is defined as

$$S = (X_1/X_2) \times (Y_1/Y_2) = K_1/K_2 = (q_{m1}b_1) / (q_{m2}b_2) \qquad (10)$$

where component 1 is the stronger adsorbate and 2 is the weaker adsorbate. X_1 and X_2 are the molar fractions of components 1 and 2 on the adsorbent surface (or in the adsorbed phase), Y_1 and Y_2 are the molar fractions of components 1 and 2 in the gas phase. q_{m1} and q_{m2} and b_1 and b_2 are the Langmuir equation constants for components 1 and 2. K_1 and K_2 are the Henry's constants for components 1 and 2. The Henry's constants and the equilibrium selectivity for different gases on the two PCPs are listed in Table 1.

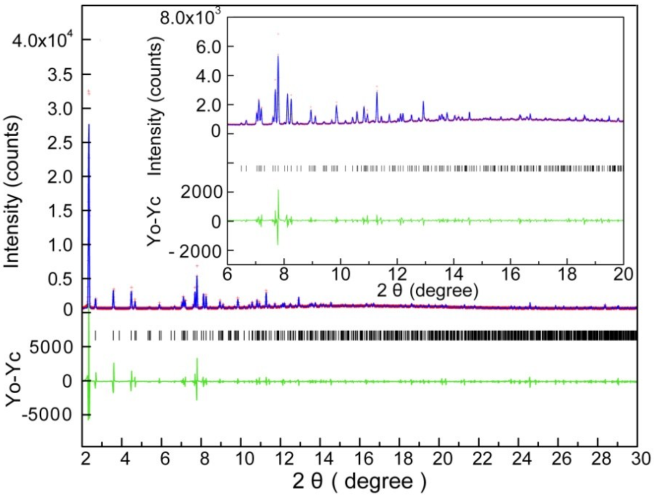

Figure S1. The results of Le Bail analysis for the PXRD of PCP-31. The wavelength of an incident X-ray is 1.0 Å. Refined parameters and reliability factors are as follows: *a* = 42.130(27) Å, *c* = 31.958(27) Å, R_p = 0.0445 and R_{wp} = 0.0886.

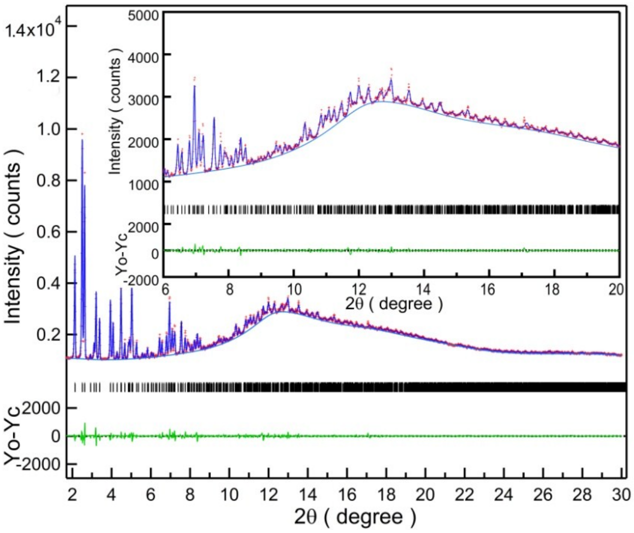

Figure S2. The result of Le Bail analysis for the PXRD of PCP-32. The wavelength of an incident X-ray is 1.0 Å. Refined parameters and reliability factors are as follows: *a* = 36.856(3) Å, *b* = 39.124(3) Å *c* = 43.598(3) Å, R_p = 0.01811 and R_{wp} = 0.03067.

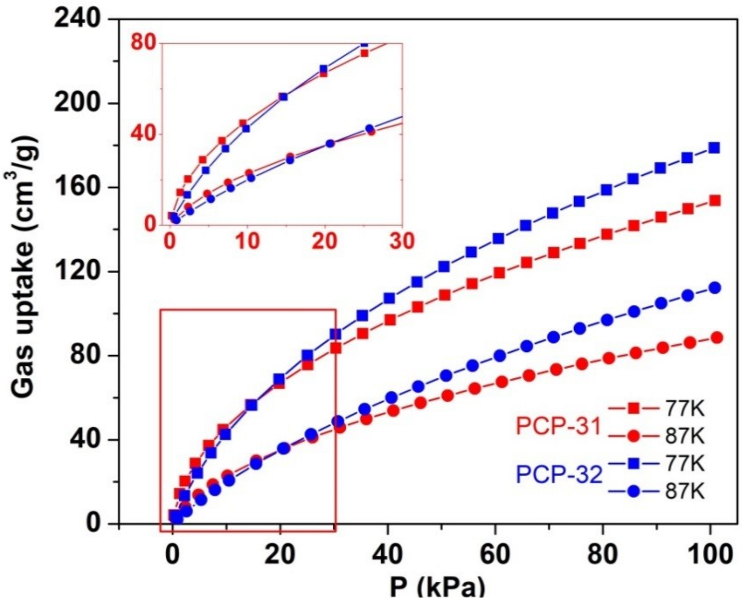

Figure S3. Hydrogen uptakes of PCP-31 and PCP-32 at 77 and 87K. Inset is the gas uptakes before 30 kPa.

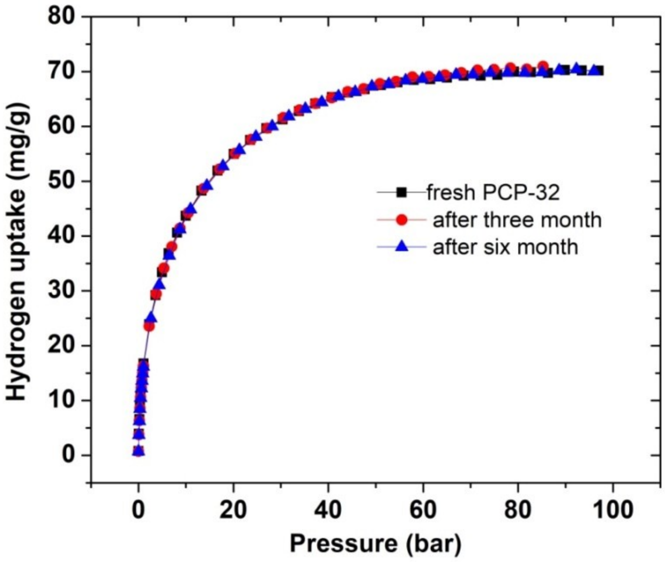

Figure S4. Repeated H_2 adsorption of PCP-32 at 77K. The sample was stored in dry environment.

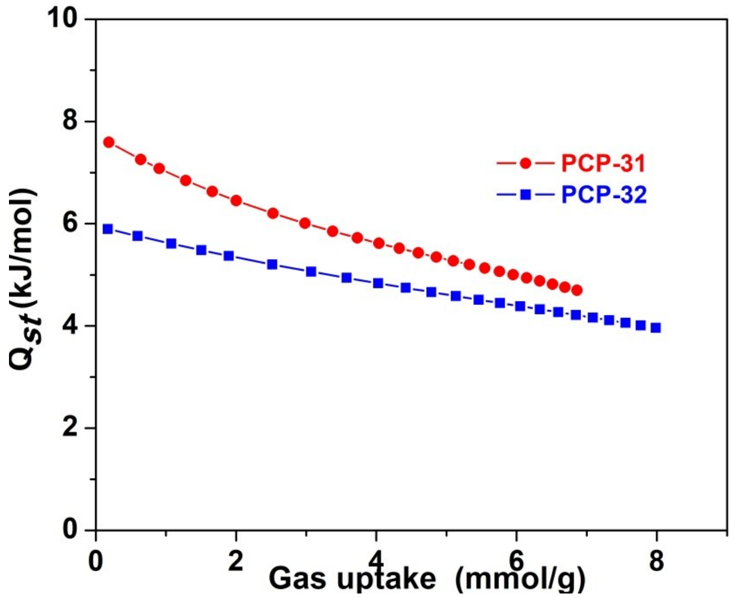

Figure S5. Calculated H_2 adsorption heat of PCP-31 and PCP-32.

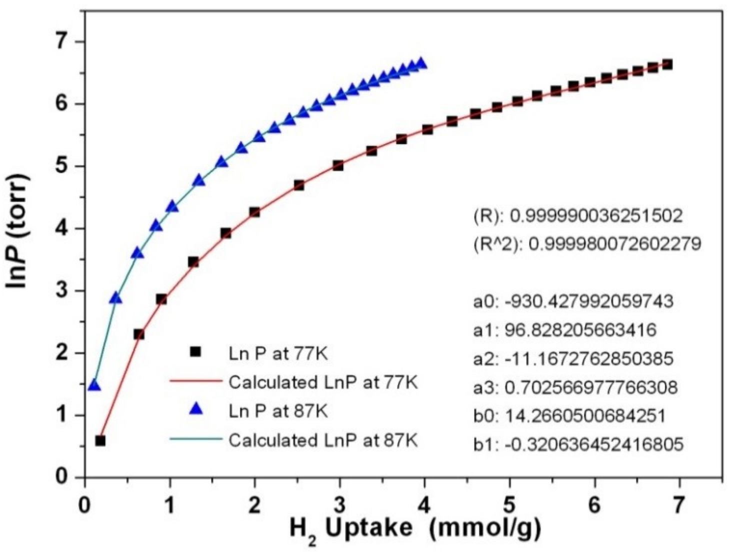

Figure S6. The calculated virial equation isotherms fit to the experimental H_2 data of PCP-31.

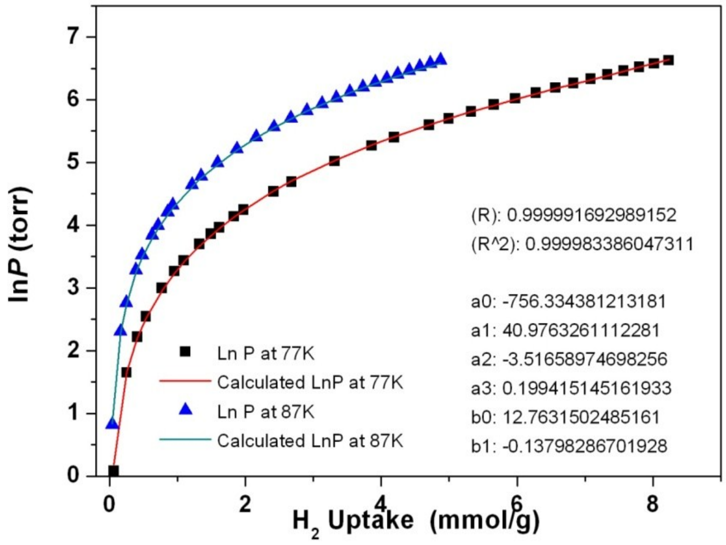

Figure S7. The calculated virial equation isotherms fit to the experimental H_2 data of PCP-32.

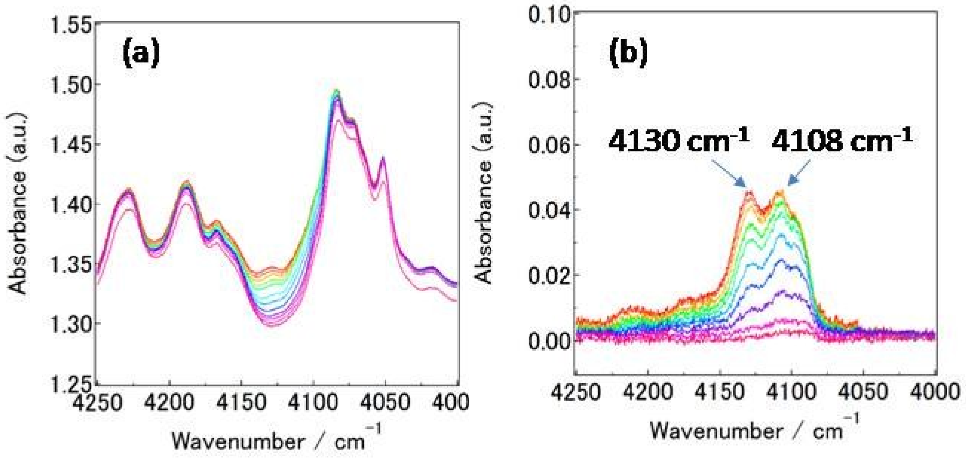

Figure S8. Pressure-dependent IR (0-5 bar) for H_2 binding within PCP-31 at 102 K (a, raw; b differential), the spectra represents a resolution of 0.125 cm^{-1} with an average collecting of 128 times. The max pressure is 5 bar.

Figure S9. Temperature-dependent IR (102-172 K) for H_2 binding within PCP-31 at 1 bar (a, raw; b differential), the spectra represents a resolution of 0.125 cm^{-1} with an average collecting of 128 times.

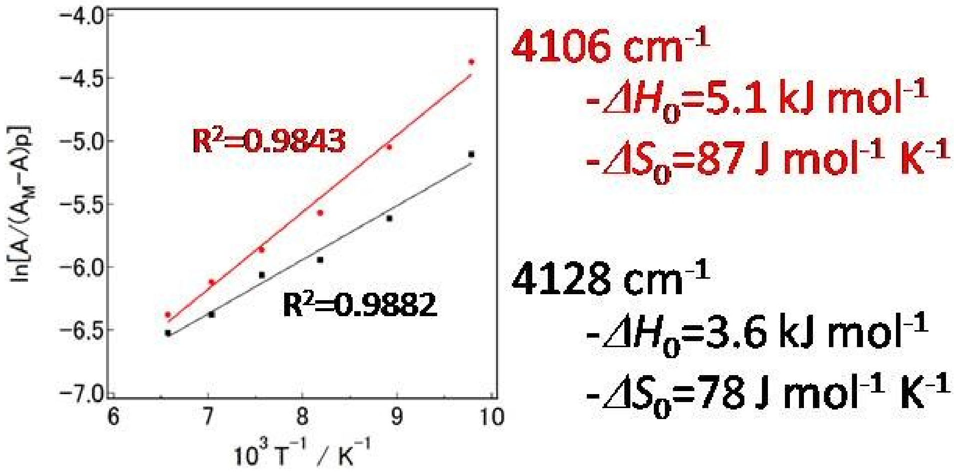

Figure S10. An Van't Hoff plot derived from the integral of absorption band corresponding to the binding site for PCP-31. The solid lines represent the line of best fit to each set of data.

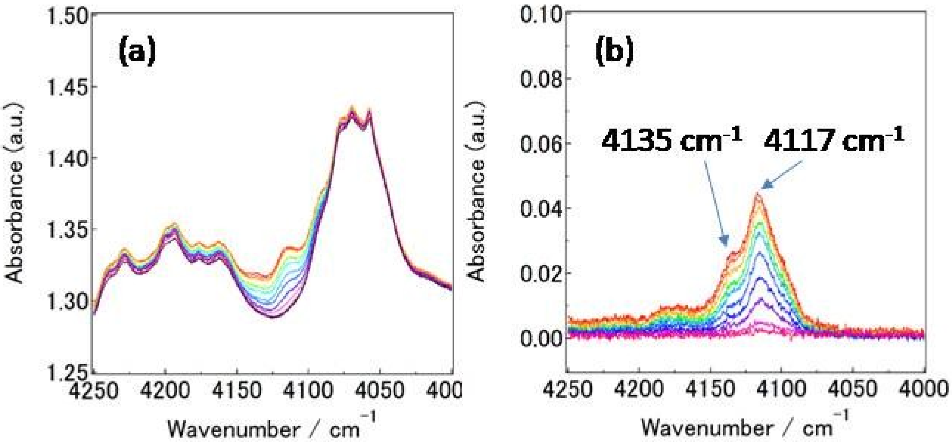

Figure S11. Pressure-dependent IR (0-5 bar) for H_2 binding within PCP-32 at 102 K (a, raw; b differential), the spectra represents a resolution of 0.125 cm^{-1} with an average collecting of 128 times. The max pressure is 5 bar.

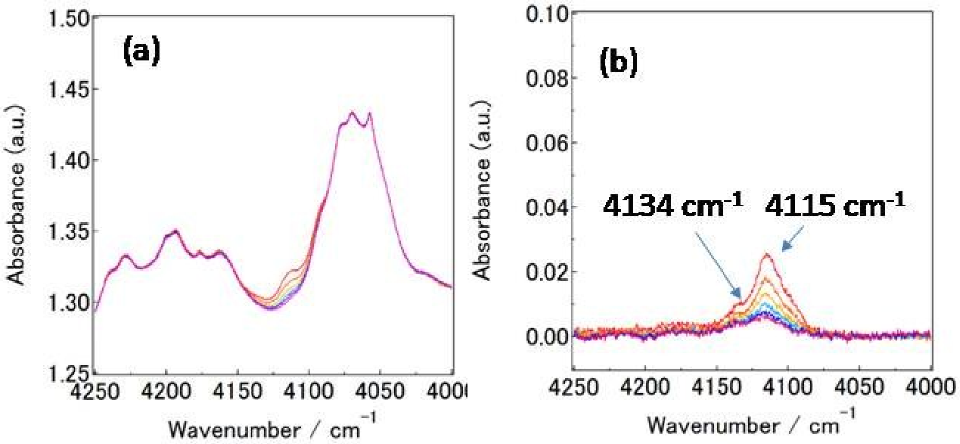

Figure S12. Temperature-dependent IR (102-172 K) for H_2 binding within PCP-32 at 1 bar (a, raw; b differential), the spectra represents a resolution of 0.125 cm^{-1} with an average collecting of 128 times.

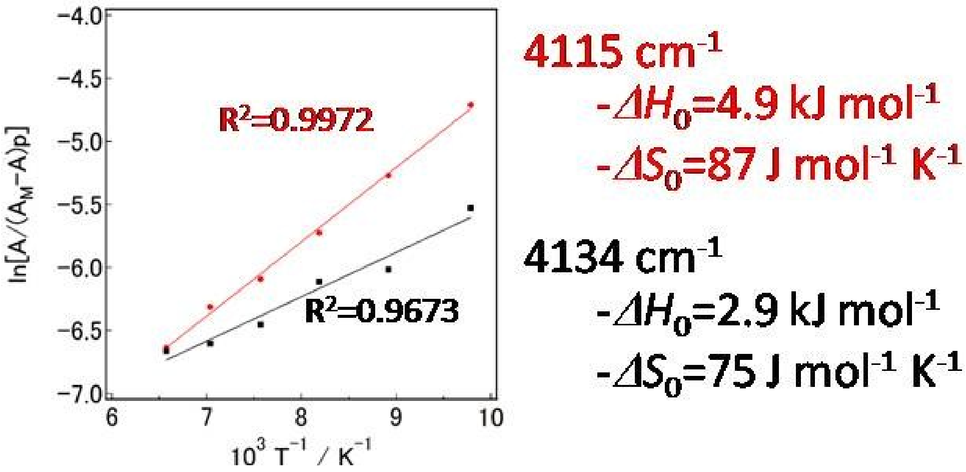

Figure S13. An Van't Hoff plot derived from the integral of absorption band corresponding to the binding site for PCP-32. The solid lines represent the line of best fit to each set of data.

Table S1. List of physical parameters for the adsorbate molecules.

	C_2H_2	C_2H_4	C_2H_6	CO_2
Kinetic Diameter / Å	3.3	3.9	3.9	3.3
Boiling Point / K	189	170	184	195

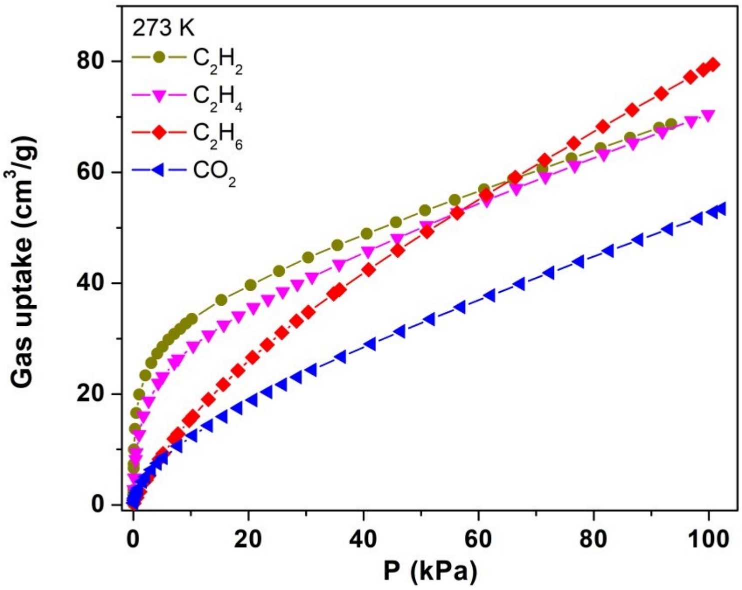

Figure S14. C2-hydrocarbons and CO_2 gas adsorption at 273 K in PCP-31.

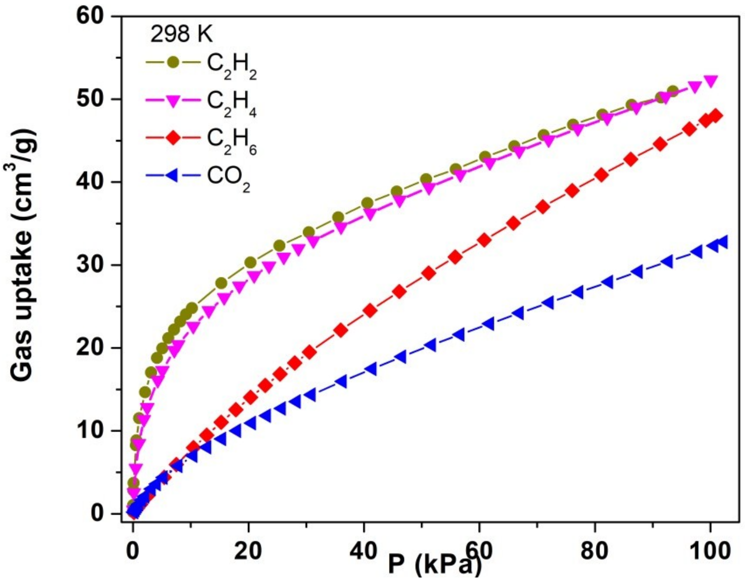

Figure S15. C2-hydrocarbons and CO_2 gas adsorption at 298 K in PCP-31.

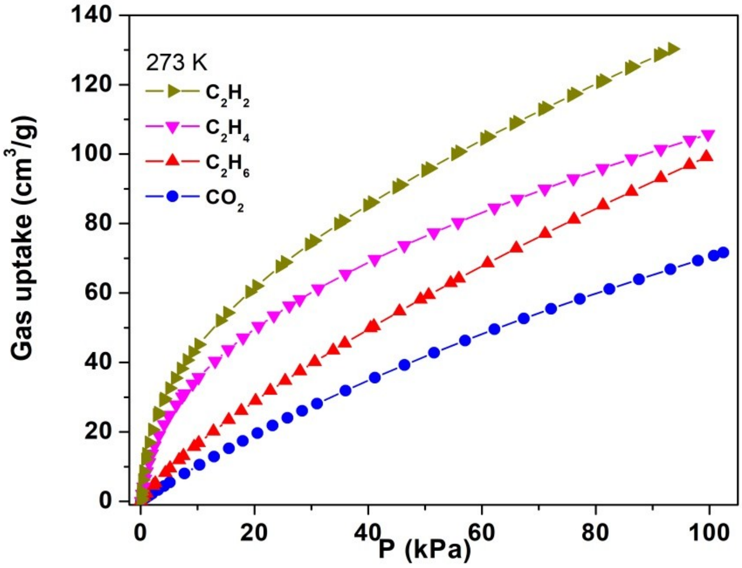

Figure S16. C2-hydrocarbons and CO_2 gas adsorption at 273 K in PCP-32.

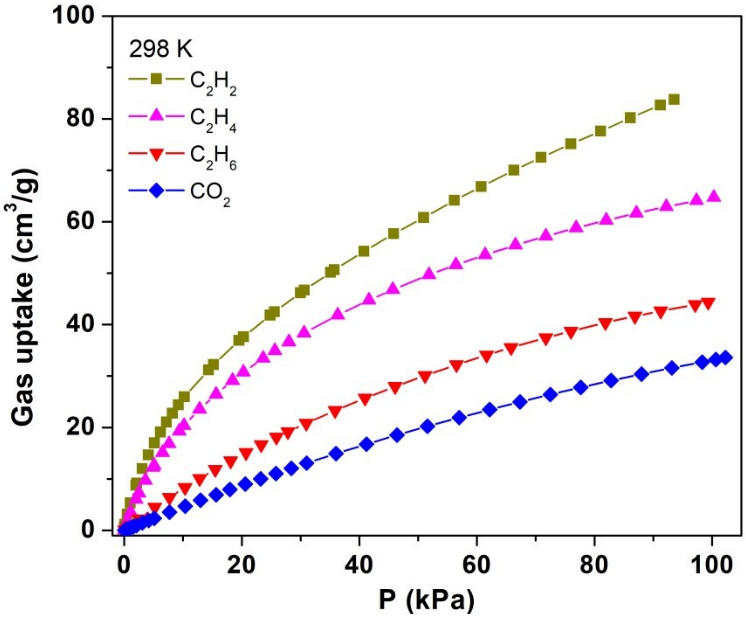

Figure S17. C2-hydrocarbons and CO_2 gas adsorption at 298 K in PCP-32.

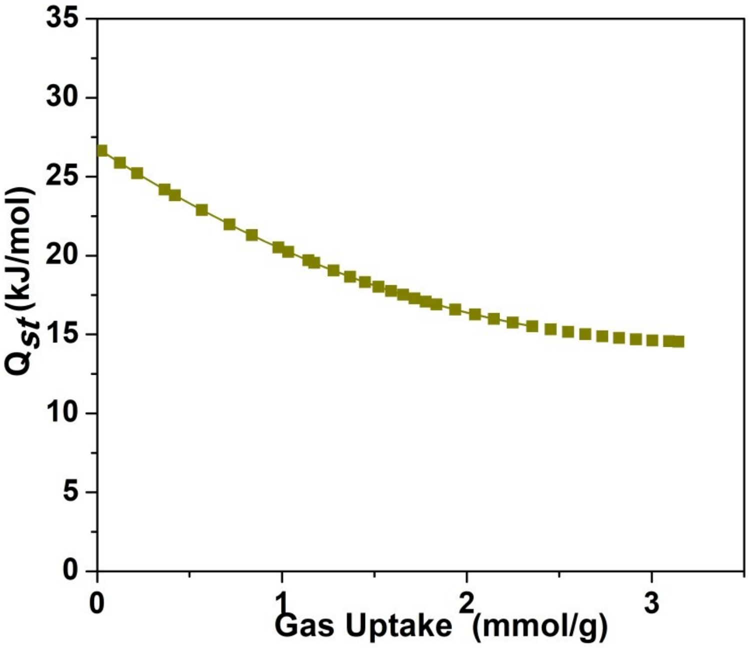

Figure S18. Calculated C_2H_4 adsorption heat of PCP-31.

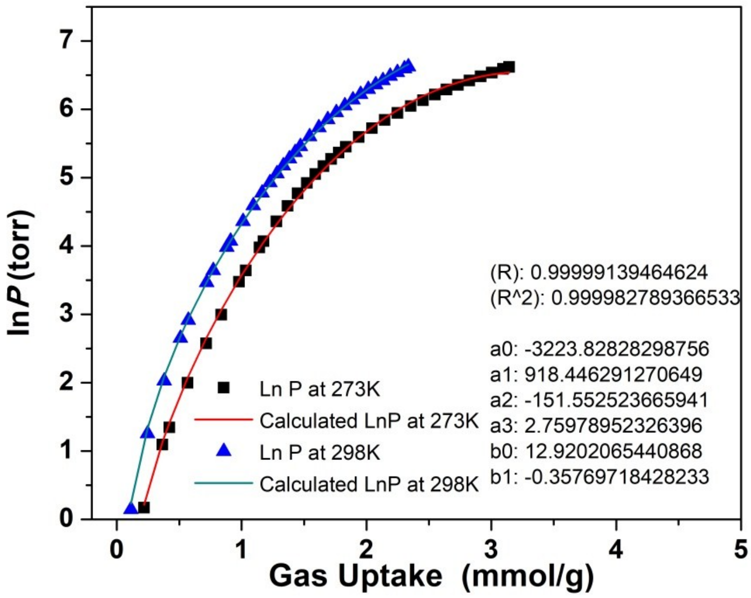

Figure S19. The calculated virial equation isotherms fit to the experimental C_2H_4 data of PCP-31.

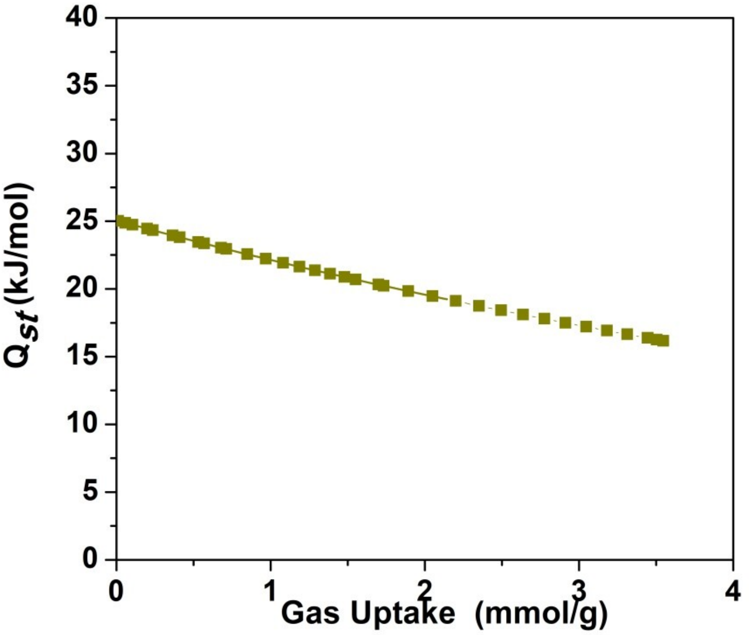

Figure S20. Calculated C_2H_6 adsorption heat of PCP-31.

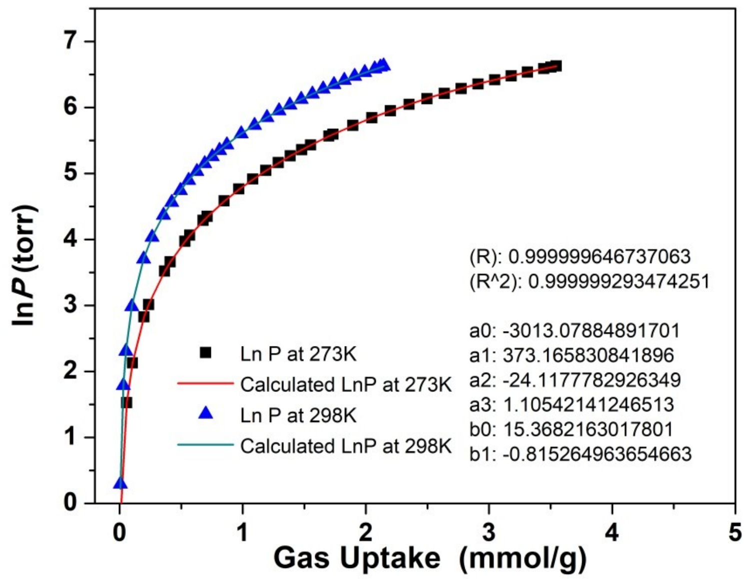

Figure S21. The calculated virial equation isotherms fit to the experimental C_2H_6 data of PCP-31.

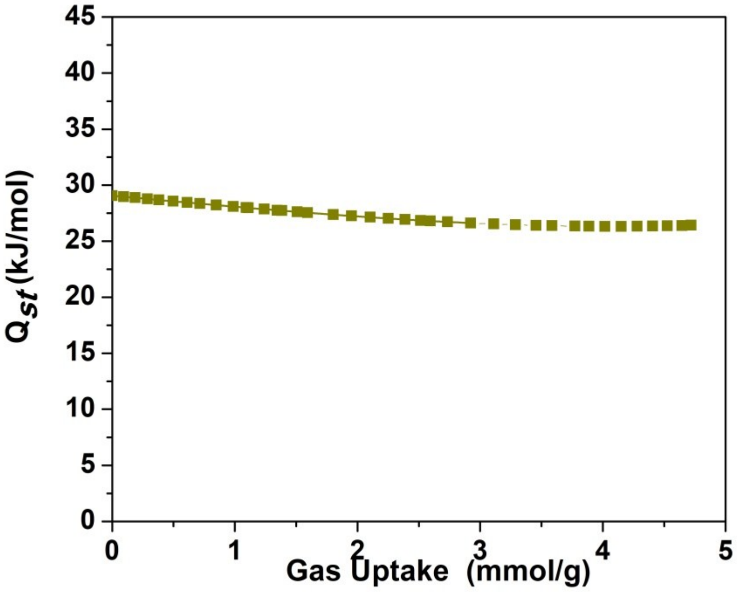

Figure S22. Calculated C_2H_4 adsorption heat of PCP-32.

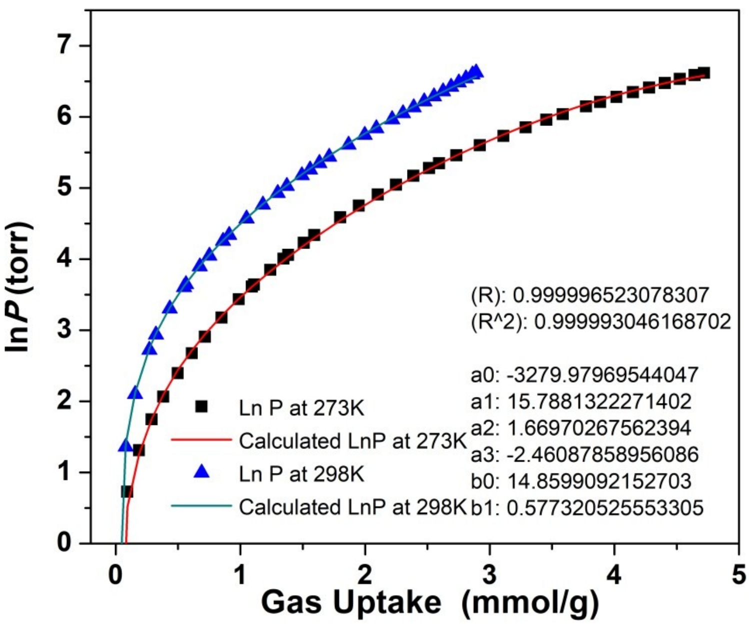

Figure S23. The calculated virial equation isotherms fit to the experimental C_2H_4 data of PCP-32.

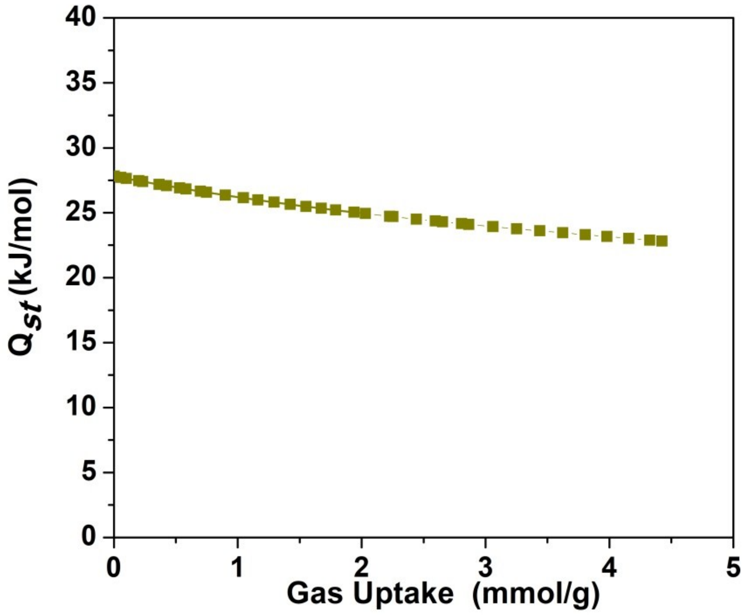

Figure S24. Calculated C_2H_6 adsorption heat of PCP-32.

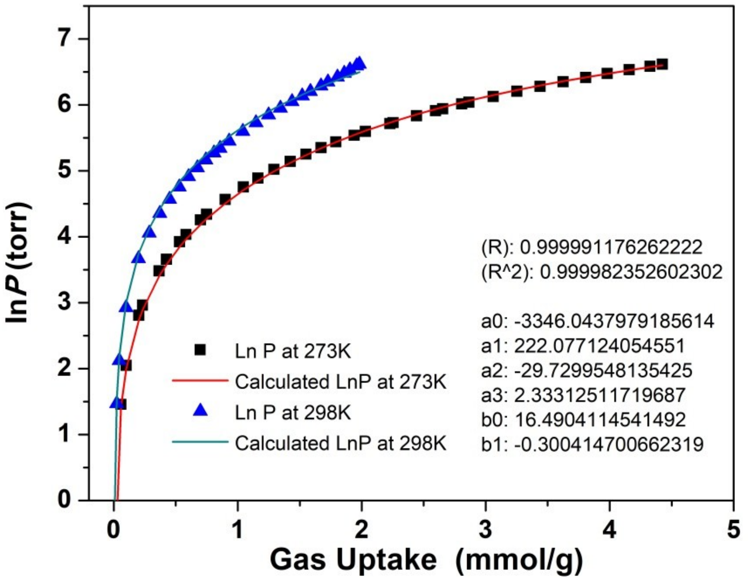

Figure S25. The calculated virial equation isotherms fit to the experimental C_2H_6 data of PCP-32.