Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting information

Increasing Nuclearity of Secondary Building Units in Porous Cobalt(II) Metal-Organic Frameworks: Variation in Structure and H_2 Adsorption

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Characterization

Powder X-ray diffraction

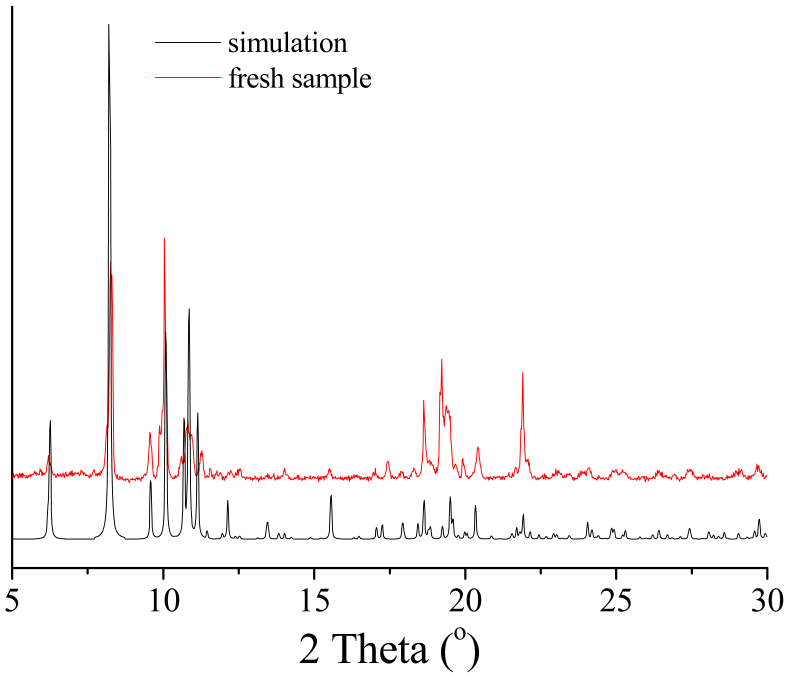

Figure SI-1. Simulated and experimental PXRD patterns for **1**

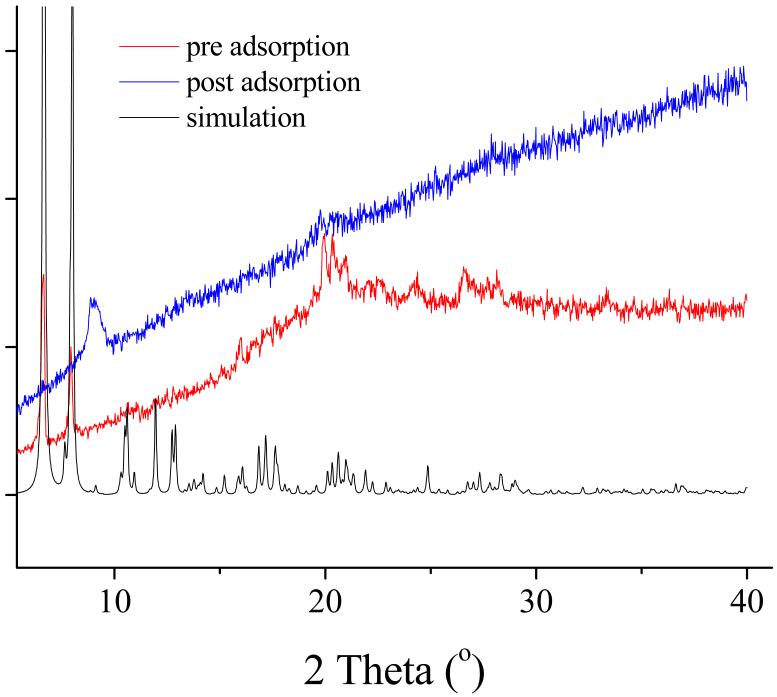

Figure SI-2. Simulated and experimental PXRD patterns for **3**

Thermal gravimetric analysis

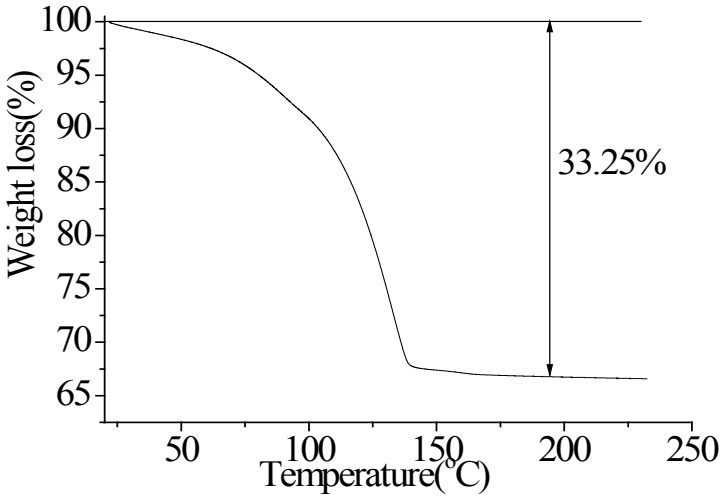

Figure SI-3. TGA analysis for **1**.

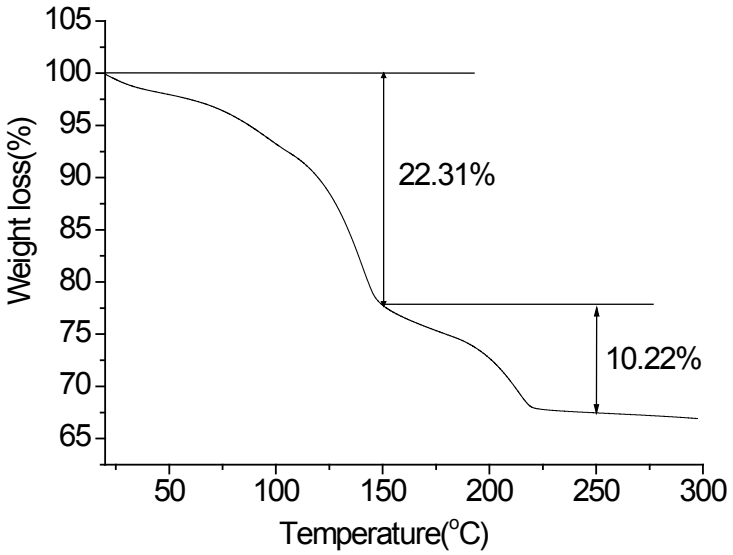

Figure SI-4. TGA analysis for **2**.

Derivation of the Isosteric Heats of Adsorption.

Gravimetric H_2 adsorption was measured from 0-20 bar at 78 and 88 K for **1** and **3**. All data were strictly corrected for the buoyancy of system, samples and adsorbates. All the H_2 sorption isotherms show good reversibility and absence of hysteresis. The H_2 adsorption kinetic data confirm that equilibrium is achieved within *ca*. 3 mins of the isotherm pressure step. These suggest a typical H_2 adsorption and exclude any significant effect due to the presence of impurities. The isosteric heats of adsorption were determined by fitting a virial-type equation to both 78 and 88 K adsorption isotherms. The $\ln(n/p)$ values for a given amount adsorbed (n) were calculated from the linear regressions from the viral equation analysis using the following viral equation:

$$\ln(n/p) = A_0 + A_{1n} + A_2n^2 \quad (1)$$

where p is pressure, n is amount adsorbed and A_0, A_1 etc. are viral coefficients. A_0 is related to adsorbate-adsorbent interactions, while A_1 describes adsorbate-adsorbate

interactions. At low surface coverage, A_2 and higher terms can be ignored. Then, a graph of ln (n/p) versus n should give a straight line at low surface coverage.

The simulation data for H_2 adsorption at 78 and 88 K for **1** and **3** between 50 and 400 mbar using equation (1) are presented in Figures SI-4 to SI-7. All the regression coefficients were larger than 0.998, confirming that the model fits the data very well. The virial method based on equation (1) is preferred at low pressure because the linearity in the low pressure part of the isotherm provides direct confirmation of the accuracy of the interpolations. Also, the intercept of the graph gives A_0, where the Henry's Law constant $K_H = \exp(A_0)$ and this is a measure of the H_2 to surface interaction. The isosteric enthalpies for H_2 adsorption on **1** and **3** were calculated as a function of surface coverage. The estimated error in the measured isosteric enthalpies is 0.1 kJ/mol.

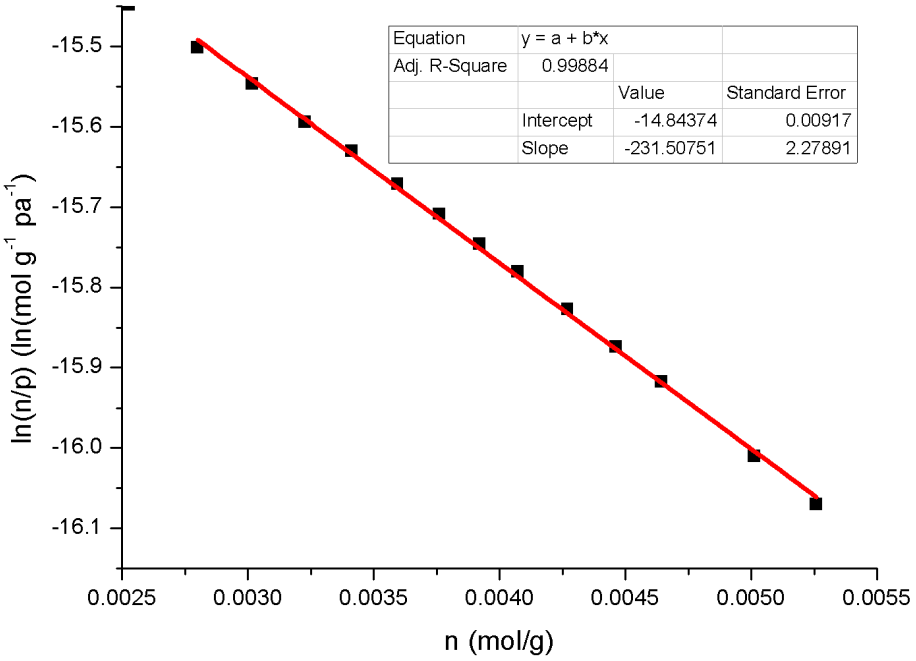

Figure SI-5. Virial plot for the adsorption of H_2 on **1** at 78 K

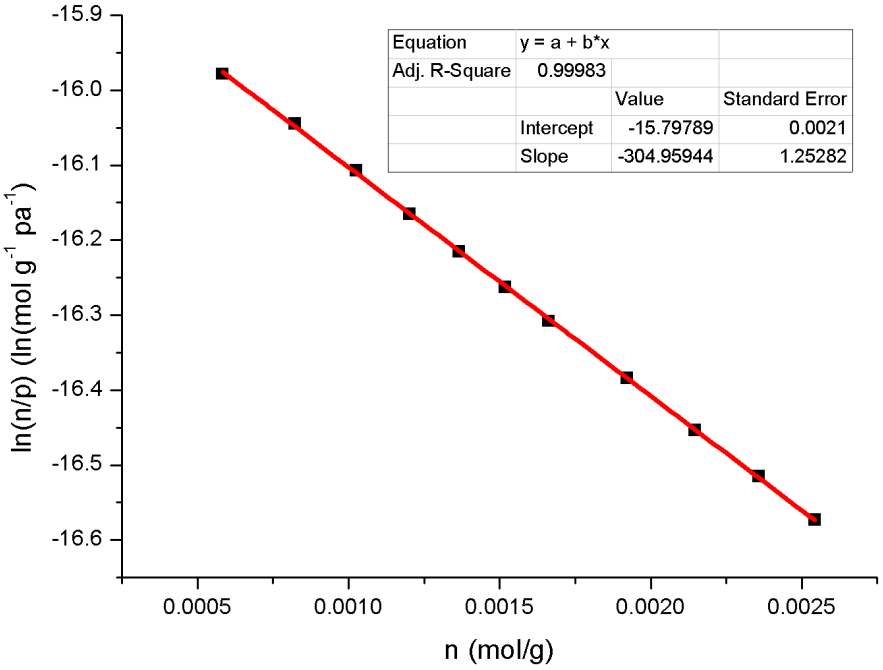

Figure SI-6. Virial plot for the adsorption of H_2 on **1** at 88 K

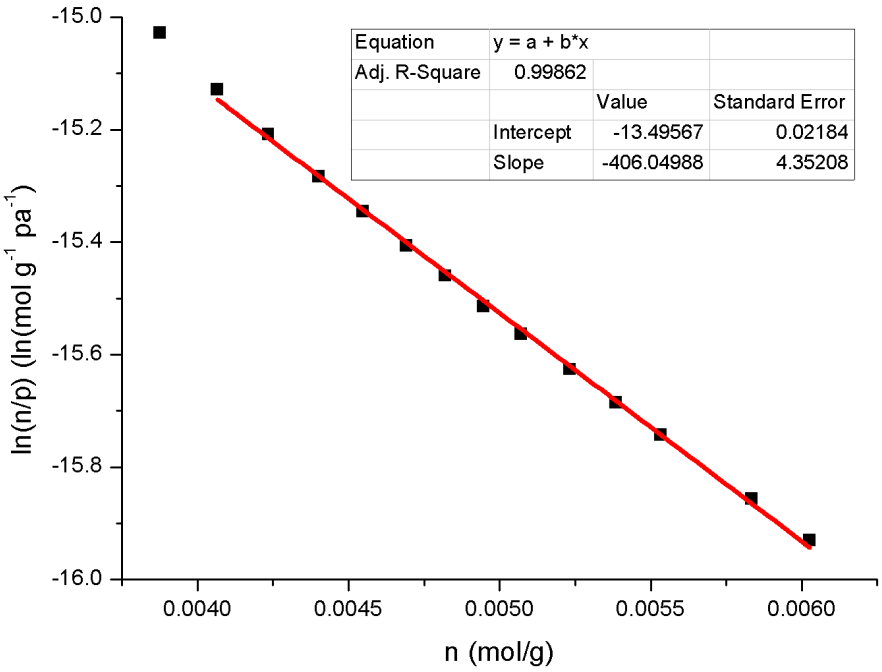

Figure SI-7. Virial plot for the adsorption of H_2 on **3** at 78 K

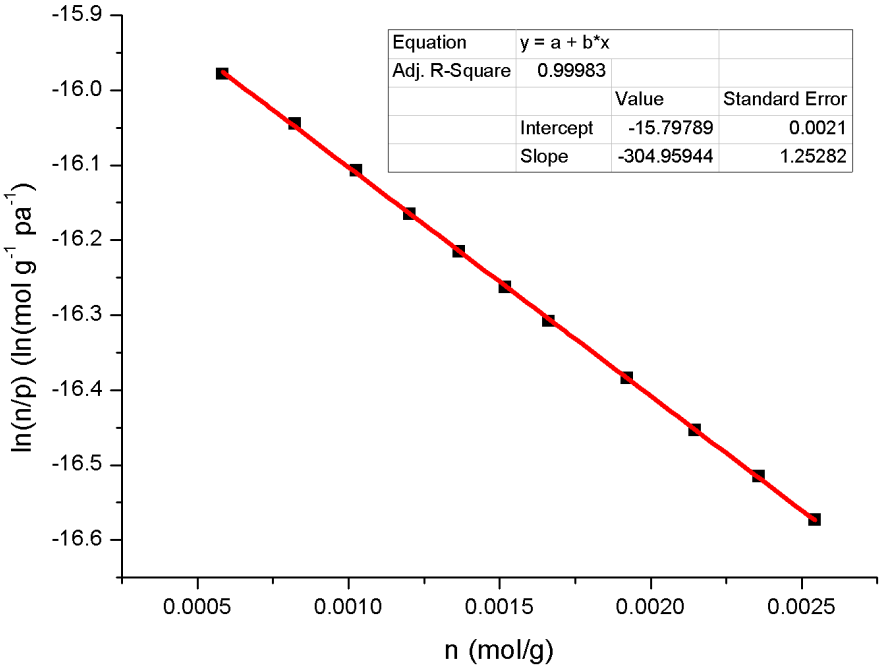

Figure SI-8. Virial plot for the adsorption of H_2 on **3** at 88 K