Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Carbon Dioxide Adsorption by Physisorption and Chemisorption Interactions in Piperazine-Grafted Ni_2(dobdc) (dobdc = 1,4-dioxido-2,5-benzenedicarboxylate)

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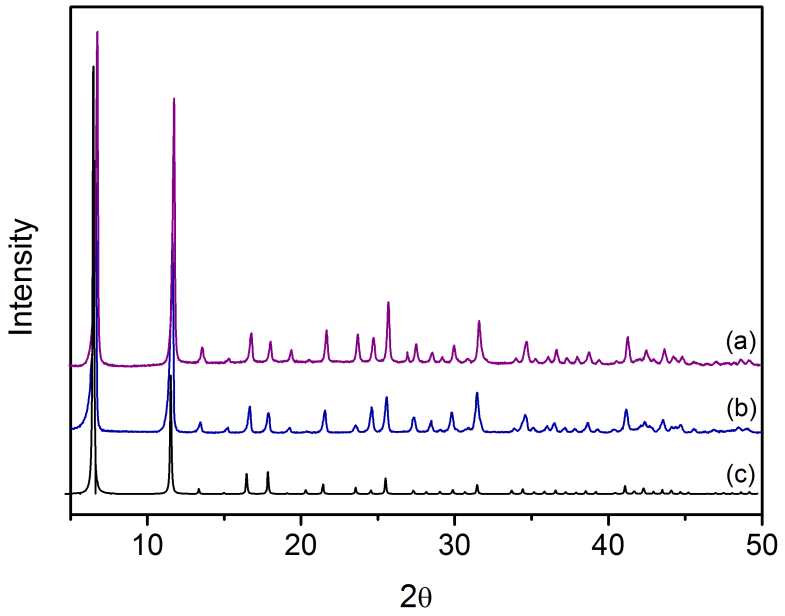

Figure S1 PXRD patterns of (a) pip-CPO-27-Ni, (b) experimental CPO-27-Ni and (c) simulated CPO-27-Ni

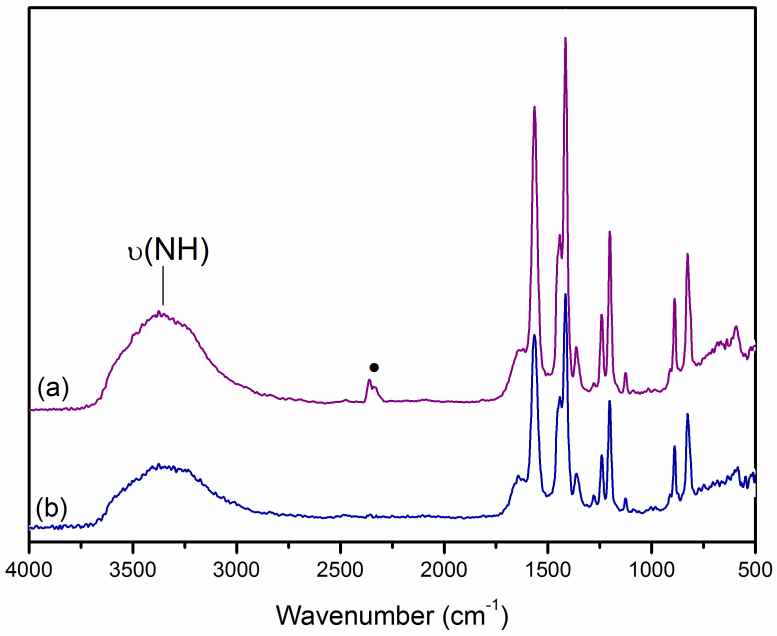

Figure S2 FTIR spectra of (a) pip-CPO-27-Ni and (b) CPO-27-Ni. Peaks denoted • represent uncompensated CO_2 peaks from air that were not removed during the background scan. The broad band at 3400 cm^{-1} is assigned to water that could not be removed entirely in the *ex-situ* experiment.

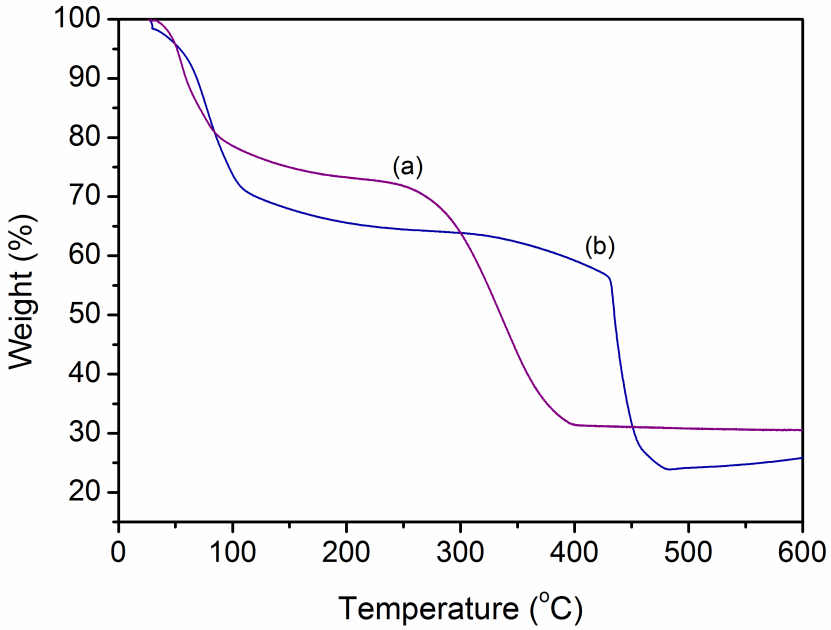

Figure S3 TGA of (a) pip-CPO-27-Ni and (b) CPO-27-Ni.

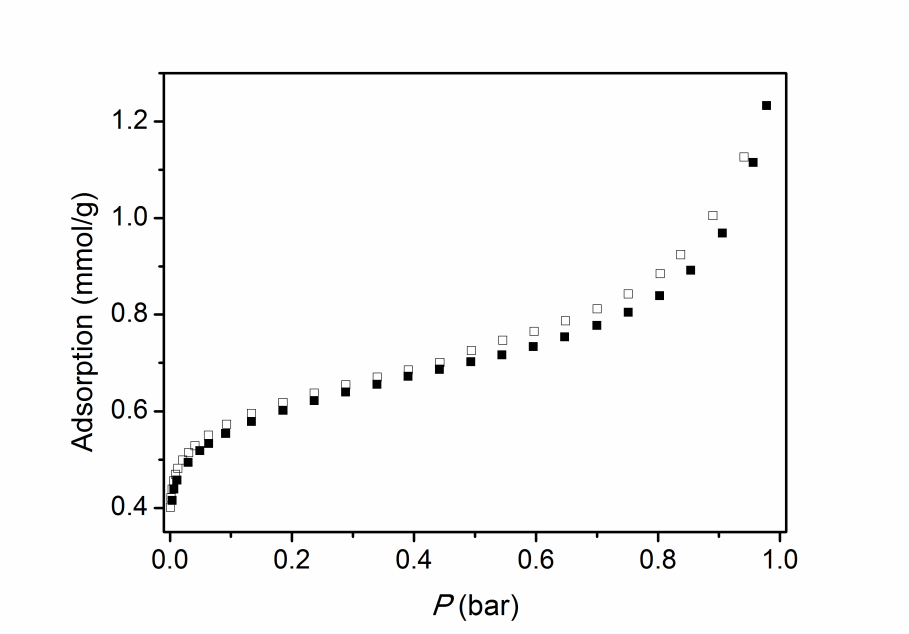

Figure S4 N_2 adsorption (filled squares) and desorption (open squares) isotherms at 77 K for pip-CPO-27-Ni.

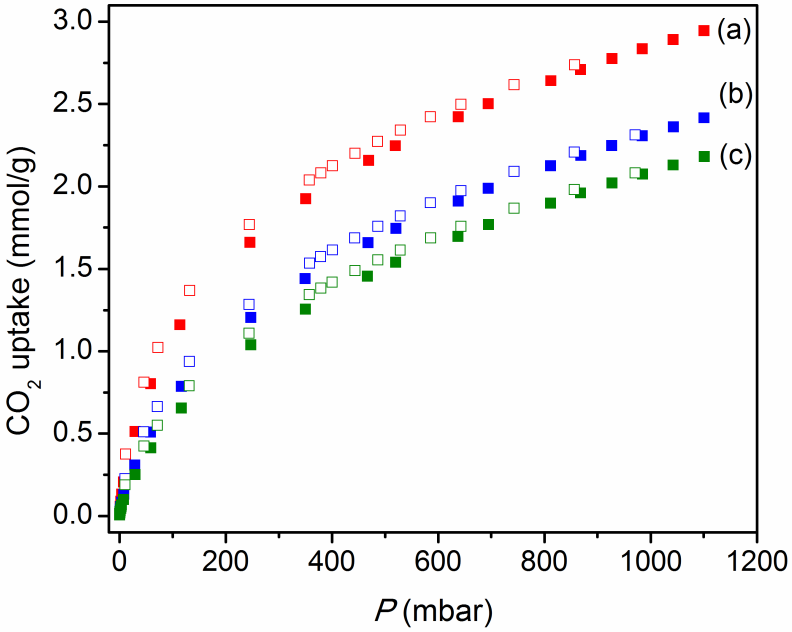

Figure S5 Adsorption isotherms at (a) 298.15, (b) 308.15 and (c) 318.15 K for pip-CPO-27-Ni.

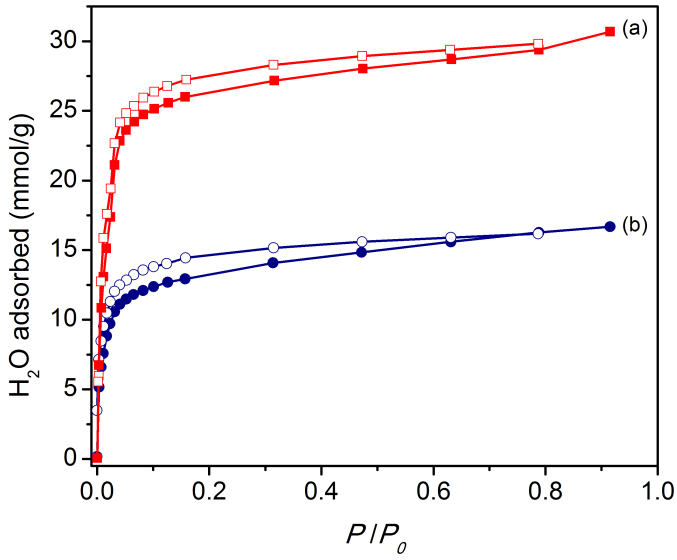

Figure S6 Water adsorption isotherms at 25 °C for (a) CPO-27-Ni (red squares) and (b) pip-CPO-27-Ni (blue circles). Solid and open symbols represent adsorption and desorption, respectively.

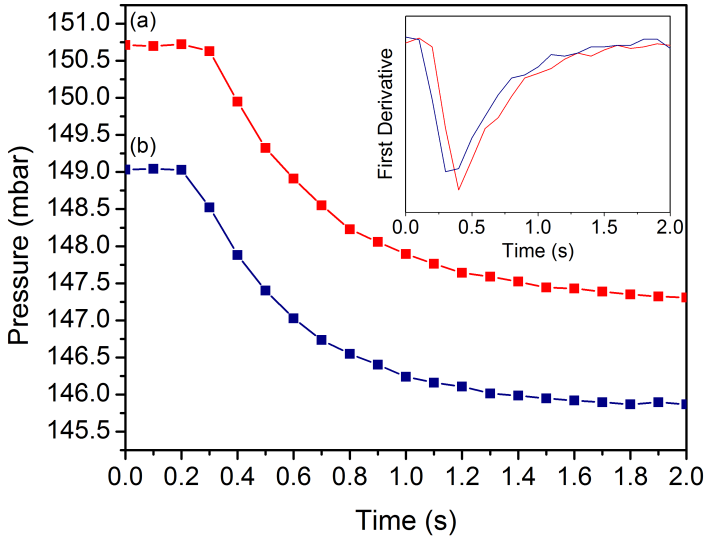

Figure S7 Kinetics data at *ca.* 0.15 bar for (a) CPO-27-Ni (red squares) and (b) pip-CPO-27-Ni (blue squares). The inset shows the first derivative of the raw data indicating a slightly faster rate of adsorption in CPO-27-Ni.

Volumetric Capacity Calculations

The crystallite volumetric capacities of CPO-27-Ni and pip-CPO-27-Ni were determined from unit cell densities. Only slight changes to the unit cell were apparent from the PXRD diffraction patterns upon addition of piperazine to the Ni^{2+} open metal sites of CPO-27-Ni. For both samples, a unit cell volume of V = 3884.67 $Å^3$ were used for density calculations. The molecular weight of pip-CPO-27-Ni was calculated with 0.25 piperazine molecules for every one Ni^{2+} centre in accordance with the characterisation data obtained from elemental analysis. The molecular weight of desolvated CPO-27-Ni was calculated to be 311.47 g/mol. Gas sorption data was converted from mmol/g to mmol/cm^3 with the following densities:

Density of CPO-27-Ni: $\rho = 0.1332$ g/cm^3

Density of pip-CPO-27-Ni: $\rho = 0.1516$ g/cm^3

Heat of adsorption calculations

Isotherm pressure values at specific amounts adsorbed was interpolated from the isotherm data according to the following methods:

Method 1: Linear interpolation

This method involves the generation of an interpolated curve by linear interpolation of data points. The model was used to fit data for adsorption isotherms at 298, 308 and 318 K. The Clausius-Clapeyron equation was then used to determine the isosteric enthalpy of adsorption at specific surface coverages. The heat of adsorption profile resulting from this method is provided in Figure S8.

Method 2: Spline interpolation

This method involves the generation of an interpolated curve by spline interpolation of data points using ASAP2020 software. The model was used to fit data for adsorption isotherms at 298, 308 and 318 K. The Clausius-Clapeyron equation was then used to determine the isosteric enthalpy of adsorption at specific surface coverages. The heat of adsorption profile resulting from this method is provided in Figure S8.

Method 3: Virial fit

This method uses the following virial equation:

$$\ln\left(\frac{n}{p}\right) = \sum_{i=0}^{N} A_i n^i = A_0 + A_1 n + A_2 n^2 + \cdots$$

where n is the amount adsorbed, p is the pressure and A0, A1, A2 etc. are constants.

The model was fitted to the data for amount adsorbed up to 0.20 mmol/g for adsorption isotherms at 298, 308 and 318 K. These equations were used interpolate between isotherm points to obtain pressures for specific amounts adsorbed. The Clausius-Clapeyron equation was then used to determine the isosteric enthalpy of adsorption at specific surface coverages. The heat of adsorption profile resulting from this method is provided in Figure S8.

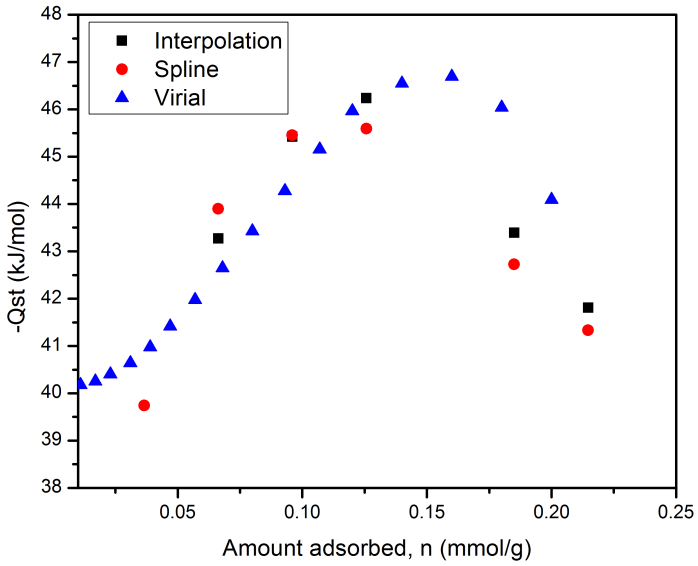

Figure S8 Heat of adsorption calculations of isotherms at 298, 308 and 318 K using the Clausius-Clapeyron equation and fitting the isotherms through simple interpolation, a spline fit and a virial model at low coverage