ELECTRONIC SUPPLEMENTARY INFORMATION

Near-Critical Water, a Cleaner Solvent for the Synthesis of a Metal-Organic Framework


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1. Pore Size Distribution Analysis

![Figure S1: Pore size distribution for desolvated \([Zn_2(L)]\).](image)

2. Derivation of the Isothermic Heats of Adsorption

Gravimetric H\(_2\) adsorption was measured from 0-20 bar at 77 K and 87 K for [Zn\(_2\)(L)]. All data were strictly corrected for the buoyancy of system, samples and absorbates. All the H\(_2\) sorption isotherms show good reversibility (Figure S2). 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.
Figure S2: H$_2$ isotherms up to 20 bar for desolvated [Zn$_2$(L)] at 77 and 87 K.

The isosteric heat of adsorption was determined by fitting a Virial-type equation to both 77 and 87 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:$^{1,2}$

$$\ln(n/p) = A_0 + A_1n + A_2n^2 \ldots$$  \hfill (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.$^2$ Henry’s Law constant ($K_H$) is equal to $\exp(A_0)$, and at low surface coverage, $A_2$ and higher terms can be ignored. A plot of $\ln(n/p)$ versus $n$ should thus give a straight line at low surface coverage.
The simulation of data for H\textsubscript{2} adsorption at 77 and 87 K for desolvated [Zn\textsubscript{2}(L)] between 50 and 400 mbar using equation (1) are presented in Figures S3 and S4. All regression coefficients were larger than 0.999, corroborating 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\textsubscript{2}-surface interaction. The isosteric enthalpy for H\textsubscript{2} adsorption on desolvated [Zn\textsubscript{2}(L)] was calculated as a function of surface coverage. The estimated error in the measured isosteric enthalpy is 0.1 kJ/mol.

![Figure S3: Virial plot for the adsorption of H\textsubscript{2} on desolvated [Zn\textsubscript{2}(L)] at 77 K.](image-url)
**Figure S4:** Virial plot for the adsorption of H₂ on desolvated [Zn₂(L)] at 87 K.

1. Reaction of Zn(NO₃)₂ with (H₄L) at two different temperatures

**Figure S5:** Experimental PXRD patterns of reaction of Zn(NO₃)₂ with H₄L at 150 °C (black pattern) and 300 °C (red pattern); the latter was confirmed to be \{[Zn₂(L)]·(H₂O)₃\}_∞.
References:
