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

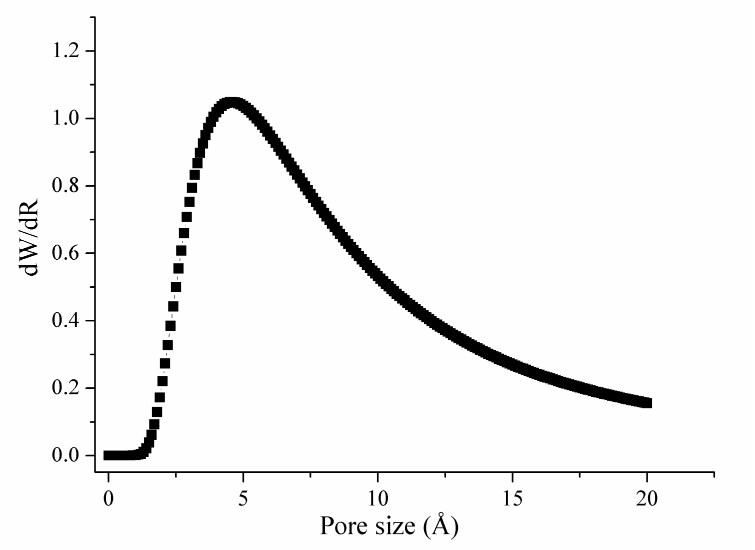


Figure S1: Pore size distribution for desolvated {[Zn_2(L)].

2. Derivation of the Isosteric 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.

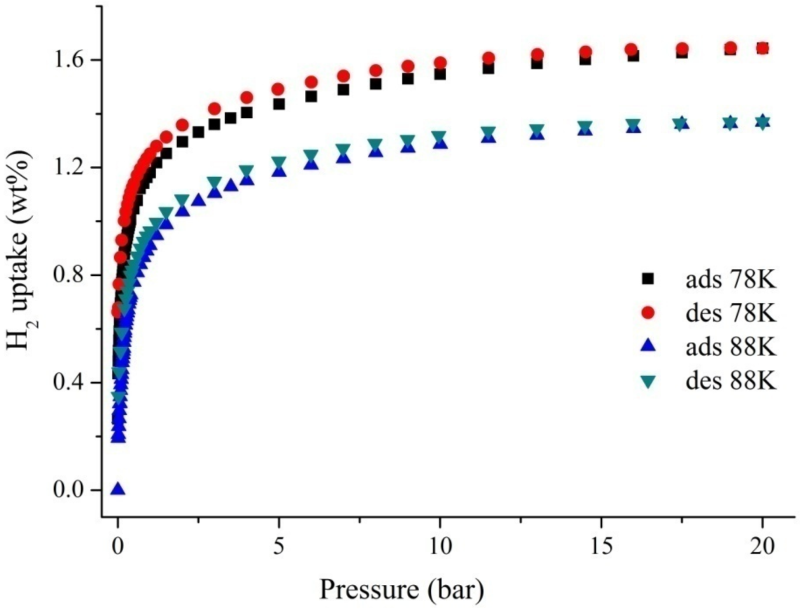


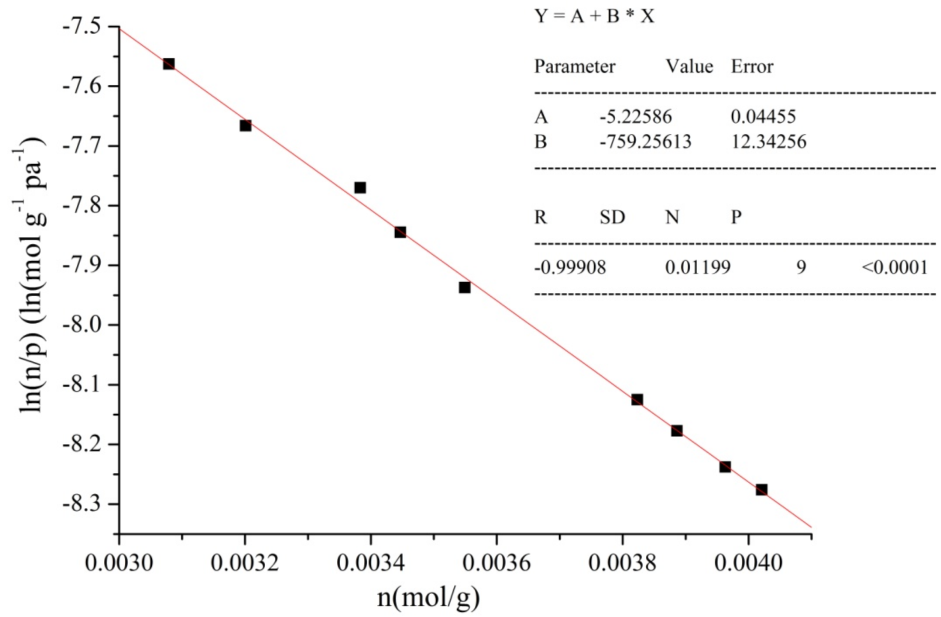
Figure S2: H_2 isotherms up to 20 bar for desolvated [Zn_2(L)] at 77 and 87 K.

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]

$$ln(n/p) = A_0 + A_1n + A_2n^2\ldots \qquad (1)$$

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_2 adsorption at 77 and 87 K for desolvated [Zn_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_2-surface interaction. The isosteric enthalpy for H_2 adsorption on desolvated [Zn_2(L)] was calculated as a function of surface coverage. The estimated error in the measured isosteric enthalpy is 0.1 kJ/mol.



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Y = A + B * X

Parameter        Value      Error
------------------------------------------------------------
A          -5.22586         0.04455
B          -759.25613       12.34256
------------------------------------------------------------

R         SD        N         P
------------------------------------------------------------
-0.99908        0.01199         9         <0.0001
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Figure S3: Virial plot for the adsorption of H_2 on desolvated [Zn_2(L)] at 77 K.

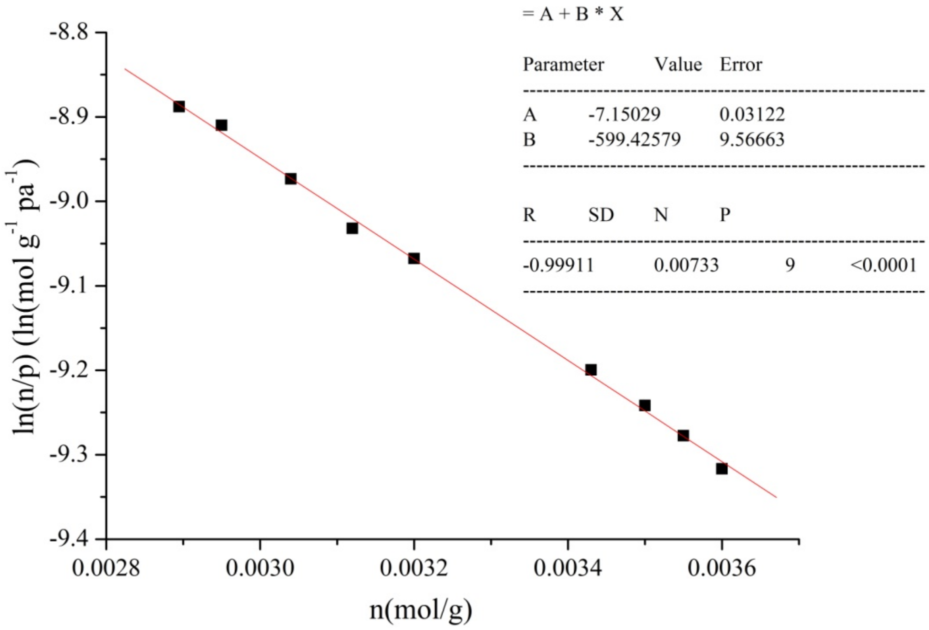

Figure S4: Virial plot for the adsorption of H_2 on desolvated $[Zn_2(L)]$at 87 K.

3. Reaction of $Zn(NO_3)_2$ with (H_4L) at two different temperatures

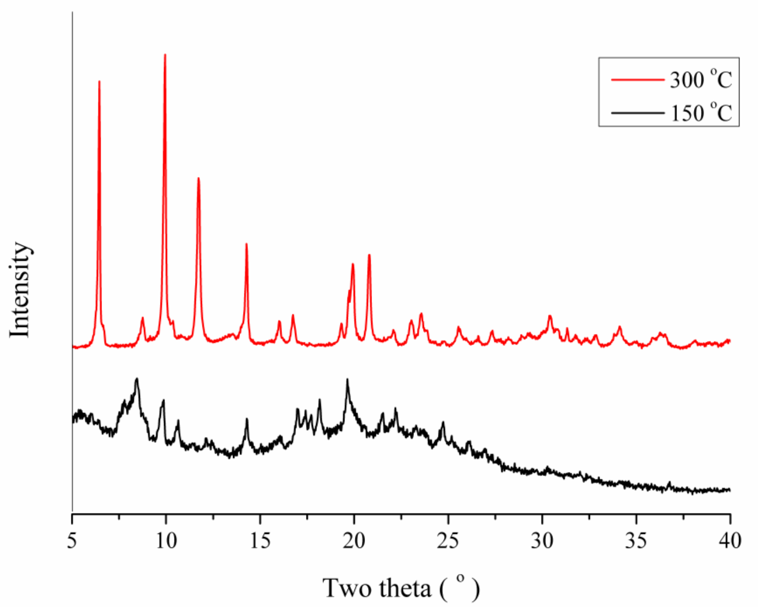

Figure S5: Experimental PXRD patterns of reaction of $Zn(NO_3)_2$ with H_4L at 150 °C (black pattern) and 300 °C (red pattern); the latter was confirmed to be $\{[Zn_2(L)]\cdot(H_2O)_3\}_\infty$.

References:

1. X. B. Zhao, S. Villar-Rodil, A. J. Fletcher and K. M. Thomas, *J. Phys. Chem. B*, 2006, **110**, 9947; X. B. Zhao, B. Xiao, A. J. Fletcher and K. M. Thomas, *J. Phys. Chem. B*, 2005, **109**, 8880; I. P. Okoye, M. Benham and K. M. Thomas, *Langmuir*, 1997, **13**, 4054; C. R. Reid and K. M. Thomas, *Langmuir*, 1999, **15**, 3206; C. R. Reid, I. P. O'Koye and K. M. Thomas, *Langmuir*, 1998, **14**, 2415; C. R. Reid and K. M. Thomas, *J. Phys. Chem. B*, 2001, **105**, 10619.
2. J. H. Cole, D. H. Everett, C. T. Marshall, A. R. Paniego, J. C. Powl and F. Rodrigue, *J. Chem. Soc., Faraday Trans. I*, 1974, **70**, 2154.