Surface Interactions and Quantum Kinetic Molecular Sieving for H_2 and D_2 Adsorption on a Mixed-Metal-Organic Framework Material

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Supporting Information

Treatments of Errors

Error propagation was treated by standard methods using the following equations

Standard deviations for $z_1 = y_2 - y_1$ and $z_2 = y_2 + y_1$

The following equations were used

$$(SDz_1)^2 = (SD(y_2 - y_1))^2 = (SDy_2)^2 + (SDy_1)^2 \quad \text{(S1)}$$

$$(SDz_2)^2 = (SD(y_2 + y_1))^2 = (SDy_2)^2 + (SDy_1)^2 \quad \text{(S2)}$$

where z_1, z_2, y_2 and y_1 are the values, SDz_1, SDz_2, SDy_2 and SDy_1 are the standard deviations in z_1, z_2, y_2 and y_1, respectively, $SD(y_2\text{-}y_1)$ is the standard deviation for $y_2 - y_1$ and $SD(y_2+y_1)$ is the standard deviation for $y_2 + y_1$.

Standard deviations for $z_3 = x/y$ and $z_4 = xy$

$$\left(\frac{SDz_3}{z_3}\right)^2 = \left(\frac{SD(x/y)}{(x/y)}\right)^2 = \left(\frac{SDy}{y}\right)^2 + \left(\frac{SDx}{x}\right)^2 \quad \text{(S3)}$$

$$\left(\frac{SDz_4}{z_4}\right)^2 = \left(\frac{SD(xy)}{(xy)}\right)^2 = \left(\frac{SDy}{y}\right)^2 + \left(\frac{SDx}{x}\right)^2 \quad \text{(S4)}$$

where z_3, z_4, y_2 and y_1 are the values, SDz_3, SDz_4, SDy_2 and SDy_1 are the standard deviations in z_3, z_4, y_2 and y_1, respectively, $SD(y_2\text{-}y_1)$ is the standard deviation for $y_2 - y_1$ and $SD(y_2+y_1)$ is the standard deviation for $y_2 + y_1$.

Isotherm points

The averages for 3 independent measurements were taken and the standard deviation was calculated using the following equation;

$$SD = \sqrt{\frac{1}{(n-1)}\sum_{i=1}^{n}(x_i - \vec{x})^2} \qquad \text{(S5)}$$

where SD is the standard deviation, $x_i - \vec{x}$ is the difference of the value from the mean and n is the number of measurements.

The isotherm data and calculations for the average for the isotherm points are given in Tables 1 and S1-S4.

The nD$_2$/nH$_2$ ratios in Tables S1-S4 were calculated from the average values and the standard deviation determined by standard error propagation methods described above.

Virial Parameters

The standard deviations for the virial parameters in Table 1 were obtained by standard linear regression analysis. The average values were calculated and the standard deviation determined by standard error propagation methods described above.

Kinetic measurements

The averages for 3 independent measurements were taken for each pressure increment and the standard deviation was calculated using equation S5. These results are given in Tables S5-S8.

Isosteric Enthalpies of Adsorption

Comparison of Methods used for Determining the Isosteric Enthalpies of Adsorption

Models were used for interpolating isotherm pressure values at specific amount adsorbed from isotherm data. The following models were used for calculating the isosteric enthalpies of adsorption.

1) **Virial Method 1**

This method uses the following virial equation:

$$\ln(n/p) = A_0 + A_1 n \text{ -----} \quad \text{(S6)}$$

where n is the amount adsorbed, p is the pressure and A_0 and A_1 are constants. The model fitted the data for amounts adsorbed upto 4 mmol g^{-1} for adsorption at 77.3 K. The isotherm data at 87.3 K was described using equations for 0 – 2 mmol g^{-1} and 2 - 4 mmol g^{-1}. These equations were used interpolate between isotherm points to obtain pressures for specific amounts adsorbed. The van't Hoff isochore was used to determine the isosteric enthalpy of adsorption at specific surface coverages. The isosteric enthalpies of adsorption at zero surface coverage were obtained from the A_0 values.

2) **Virial Method 2**

The method uses the following virial equation:

$$\ln(p) = \ln(n) + (1/T)\sum_{i=0}^{m} a_i n^i + \sum_{j=0}^{n} b_j n^j \quad \text{(S7)}$$

$$\text{and } Q_{st} = -R\sum_{i=0}^{m} a_i n^i \quad \text{(S8)}$$

to determine the isosteric enthalpy of adsorption (Q_{st})

3) Langmuir-Freundlich equation

The Langmuir-Freundlich equation is as follows:

$$\left(\frac{n}{n_L}\right)=\left(\frac{kp^{1/m}}{1+kp^{1/m}}\right) \qquad \text{(S9)}$$

where n_L is the maximum amount adsorbed, p is the pressure, m and k are constants. The isotherm data were fitted using the above equation and a modified method of the Clausius-Clapeyron equation.

It was found that comparison of regression coefficients was not sufficient to distinguish unambiguously between the accuracy of the models. Therefore, the standard deviations expressed as a % of the amount adsorbed for all isotherm points which were in the range of values used (0 – 4 mmol g^{-1}) were compared with prediction of the model (predicted value – isotherm amount adsorbed)x 100/ (isotherm amount adsorbed) (%). The comparisons of the 3 models with the isotherm data including uncertainties for the data for H_2 and D_2 adsorption at 77.3 and 87.3 K are shown in Figures S12. These figures show that the model predictions for the virial methods are better than the Langmuir – Freundlich model for H_2 and D_2 adsorption on M'MOF **1.** The average deviations of the models are given in Table S9. Virial method 1 has the highest accuracy for H_2 and D_2 adsorption isotherms at 77.3 and 87.3 K as shown in Table S9. Both virial methods give accurate predictions to within ~ 1 standard deviation with virial method 1 being slightly better. The maximum deviation of virial method 1 from the experimental data was 3.87 %. The maximum standard deviation of the experimental data was 3.05%. The average error in the Langmuir-Freundlich method was substantially higher due to the poorer predictions at low pressure.

Zero surface coverage

The A_0 values and corresponding standard deviations for individual isotherms were obtained from linear regression analysis of the virial graphs(equation (3)). The standard deviations $SDA_0(77)$ and $SDA_0(87)$ obtained from linear regression analysis are quoted for individual datasets. The average values and standard deviations for this A_0 average value were calculated using the method used for isotherm points (equation S5). These values were used to calculate the standard deviation ($SD\Delta A_0$) of the difference ($\Delta A_0 = A_0(77) - A_0(87)$). The standard deviation was calculated using the error propagation methods described above.

The difference between liquid nitrogen and liquid argon temperatures is ~ 10 K. The boiling points of cryogenic fluids vary slightly with changes in atmospheric pressure. The average pressure for the complete measurement period for the series of experiments was 101.08 ± 0.88 kPa. This is not significantly different from standard atmospheric pressure (101.325 kPa). The uncertainty associated with the temperature of the cryogenic fluid was calculated using the following equations derived from data in the CRC Handbook for the variation of B. Pt. with pressure.

Nitrogen: $\ln(pN_2/kPa) = -704.10(1/T) + 13.717$ ($R^2 = 0.999988$) (S10)

Argon: $\ln(pAr/kPa) = -797.97\ (1/T) + 13.760$ ($R^2 = 0.999993$) (S11)

These uncertainties of 0.262 and 0.215 K, for nitrogen and argon temperatures were used to calculate the standard deviation ($SD\Delta T$) for the temperature difference (ΔT) using the error propagation equations described above.

The standard deviation of the gradient ($\Delta H/R$) of the A_0 versus 1/T graph was calculated from SDΔA0 and SDΔT using the equations for propagation of errors described above.

Activation Energies

Zero Surface Coverage

The $\ln(k_0)$ values and corresponding standard deviations were obtained from linear regression analysis of the ln(k) versus amount adsorbed (n) graphs. The activation energies for each kinetic parameter were calculated using the Arrhenius equation. These standard deviations, together with the standard deviations for the temperatures, were used in the calculation of the errors in activation energies using similar methods for the propagation of errors as described for enthalpies of adsorption. The results are given in Table 3.

Supporting Information

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Supporting Information

Tables

Table S1. Repeatability of H_2 and D_2 adsorption isotherm points and nD_2/nH_2 ratios for M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$) at 77.3 K.

P/kPa	Amount adsorbed on MOF $Zn_3(BDC)_3.Cu(Pyen)$ at 77.3 K/ mmol g^{-1}								nD_2/nH_2
	H_2				D_2				
	Run1	Run2	Run3	Average	Run1	Run2	Run3	Average	
0.5	1.149	1.151	1.190	1.163±0.023	1.332	1.299	1.342	1.324±0.023	1.139±0.030
1	1.576	1.609	1.606	1.597±0.018	1.792	1.7499	1.784	1.775±0.022	1.112±0.019
2	2.032	2.063	2.054	2.050±0.016	2.263	2.234	2.265	2.254±0.018	1.100±0.012
5	2.623	2.661	2.622	2.636±0.022	2.901	2.885	2.915	2.901±0.015	1.101±0.011
10	3.091	3.100	3.094	3.095±0.005	3.413	3.392	3.420	3.408±0.015	1.101±0.005
15	3.379	3.420	3.394	3.398±0.021	3.739	3.703	3.731	3.725±0.019	1.096±0.009
20	3.589	3.625	3.606	3.607±0.018	3.963	3.922	3.952	3.946±0.021	1.094±0.008
30	3.889	3.929	3.908	3.909±0.020	4.281	4.226	4.258	4.255±0.027	1.089±0.009
40	4.089	4.133	4.113	4.112±0.022	4.497	4.439	4.470	4.468±0.029	1.087±0.009
50	4.255	4.293	4.277	4.275±0.019	4.661	4.605	4.632	4.633±0.028	1.084±0.008
60	4.380	4.429	4.413	4.407±0.025	4.795	4.739	4.764	4.766±0.028	1.081±0.009
70	4.490	4.537	4.522	4.516±0.024	4.907	4.868	4.883	4.886±0.020	1.082±0.007
80	4.589	4.625	4.615	4.610±0.019	5.002	4.962	4.978	4.981±0.020	1.081±0.006
90	4.666	4.707	4.696	4.690±0.021	5.086	5.061	5.061	5.070±0.015	1.081±0.006
100	4.736	4.783	4.769	4.763±0.023	5.161	5.141	5.146	5.150±0.010	1.081±0.006

Table S2. Repeatability of H_2 and D_2 adsorption isotherm points and nD_2/nH_2 ratios for M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$) at 87.3 K.

P/kPa	Amount adsorbed on MOF $Zn_3(BDC)_3.Cu(Pyen)$ at 87.3 K/ mmol g^{-1}								nD_2/nH_2
	H_2				D_2				
	Run1	Run2	Run3	Average	Run1	Run2	Run3	Average	
0.5	0.364	0.369	0.373	0.369±0.005	0.415	0.404	0.413	0.411±0.006	1.113±0.017
1	0.587	0.585	0.565	0.579±0.012	0.680	0.676	0.686	0.680±0.005	1.176±0.019
2	0.915	0.906	0.912	0.911±0.005	1.087	1.0276	1.037	1.050±0.032	1.153±0.020
5	1.475	1.461	1.457	1.464±0.010	1.672	1.6486	1.663	1.661±0.012	1.134±0.009
10	1.935	1.928	1.925	1.930±0.005	2.163	2.170	2.151	2.161±0.009	1.120±0.005
15	2.227	2.202	2.202	2.210±0.014	2.455	2.459	2.447	2.451±0.006	1.110±0.006
20	2.422	2.399	2.399	2.407±0.014	2.667	2.670	2.662	2.666±0.004	1.108±0.005
30	2.700	2.675	2.678	2.684±0.014	2.971	2.967	2.965	2.968±0.003	1.106±0.005
40	2.903	2.878	2.882	2.888±0.013	3.191	3.186	3.184	3.187±0.003	1.104±0.004
50	3.065	3.036	3.046	3.049±0.014	3.363	3.356	3.357	3.359±0.003	1.102±0.004
60	3.194	3.166	3.178	3.179±0.014	3.506	3.499	3.499	3.501±0.004	1.101±0.004
70	3.307	3.280	3.292	3.293±0.013	3.626	3.619	3.620	3.622±0.003	1.100±0.004
80	3.404	3.383	3.391	3.393±0.011	3.731	3.723	3.725	3.726±0.004	1.098±0.003
90	3.494	3.470	3.481	3.482±0.012	3.825	3.814	3.820	3.820±0.005	1.097±0.003
100	3.570	3.546	3.559	3.558±0.012	3.908	3.896	3.903	3.903±0.006	1.097±0.003

Table S3. Virial parameters for H_2 and D_2 adsorption on M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$) at 77.3 K from low pressure isotherms (0.1 – 5 kPa) used for kinetic measurements.

Adsorbent	T/K	Adso-rbate	Run No	K_H/ mol g^{-1} Pa^{-1}	A_0/ ln(mol $g^{-1}Pa^{-1}$)	A_1/ G mol^{-1}	P Range/ kPa
MOF CuZn	77	H_2	1	$9.464x10^{-6}$	-11.568±0.019	-1115.4±11.0	0.1 - 5
			2	$9.003x10^{-6}$	-11.618±0.016	-1094.5±9.5	
			3	$9.540x10^{-6}$	-11.560±0.019	-1080.3±10.8	
			Average	$9.323x10^{-6}$	-11.583±0.031	-1096.7±17.7	
		D_2	1	$1.049x10^{-5}$	-11.465±0.026	-1024.4±14.1	0.1 - 5
			2	$1.051x10^{-5}$	-11.463±0.027	-1025.3±14.2	
			3	$1.043x10^{-5}$	-11.471±0.026	-1019.2±13.6	
			Average	$1.048x10^{-5}$	-11.466±0.026	-1023.0±14.0	

† Errors for individual isotherms were obtained from the corresponding virial graphs.
Errors for the averages were calculated from the A_0 and A_1 values for individual isotherms.

Table S4. Repeatability of isotherm points and nD_2/nH_2 ratios for H_2 and D_2 adsorption on $Zn_3(BDC)_3Cu(Pyen)$ at 77.3 K for low pressure isotherms (0.1 - 5 kPa) used for kinetic measurements.

P/kPa	Amount adsorbed / mmol g^{-1} on MOF $Zn_3(BDC)_3.Cu(Pyen)$ at 77.3 K								nD_2/nH_2
	H_2/ mmol g^{-1}				D_2 / mmol g^{-1}				
	Run1	Run2	Run3	Average	Run1	Run2	Run3	Average	
0.1	0.537	0.523	0.534	0.531±0.007	0.595	0.591	0.587	0.591±0.004	1.113±0.013
0.2	0.772	0.766	0.778	0.772±0.006	0.844	0.842	0.841	0.842±0.001	1.091±0.007
0.4	1.098	1.076	1.094	1.089±0.011	1.197	1.201	1.204	1.201±0.004	1.103±0.010
0.7	1.392	1.380	1.396	1.389±0.008	1.530	1.543	1.546	1.539±0.008	1.108±0.007
1.2	1.707	1.691	1.721	1.707±0.015	1.878	1.882	1.883	1.881±0.003	1.102±0.008
2.0	2.021	2.014	2.046	2.027±0.017	2.216	2.212	2.216	2.215±0.003	1.093±0.008
3.5	2.365	2.369	2.400	2.378±0.019	2.588	2.584	2.591	2.588±0.003	1.088±0.007
5.0	2.598	2.602	2.642	2.614±0.025	2.834	2.829	2.833	2.832±0.003	1.083±0.009

Table S5. Kinetic parameters (s^{-1}) obtained from the Double Exponential Model for H_2 adsorption on M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$)at 77.3 K. Pressure range 0.1 – 5 kPa.

P/kPa	n/ mmol g^{-1}	Run1		Run2		Run3		Average	
		k_1x10^3	k_2x10^3	k_1x10^3	k_2x10^3	k_1x10^3	K_2x10^3	k_1x10^3	k_2x10^3
0.01 – 0.1	0.531±0.007	0.3460	2.690	0.3843	2.449	0.4314	2.566	0.3872±0.043	2.570±0.121
0.1 – 0.2	0.772±0.006	0.4401	3.070	0.4683	3.043	0.4892	2.745	0.4659±0.025	2.953±0.180
0.2 -0,4	1.089±0.011	0.6616	3.870	0.6339	3.625	0.6770	3.804	0.6575±0.028	3.766±0.127
0.4 – 0.7	1.389±0.008	0.8889	4.831	0.9208	4.786	0.8880	4.600	0.8992±0.019	4.739±0.123
0.7 – 1.2	1.707±0.015	1.243	6.321	1.246	6.188	1.317	6.128	1.268±0.042	6.212±0.099
1.2 – 2.0	2.027±0.017	1.777	7.564	1.817	7.573	1.768	7.226	1.787±0.026	7.454±0.198
2.0 – 3.5	2.378±0.019	2.370	9.933	2.615	9.375	2.764	8.505	2.583±0.020	9.271±0.720
3.5 – 5.0	2.614±0.025	2.883	10.98	3.143	10.28	3.254	10.99	3.093±0.019	10.75±0.407

Table S6. Kinetic parameters (s^{-1}) obtained from the Double Exponential Model for D_2 adsorption on M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$) at 77.3 K. Pressure range 0.1 – 5 kPa.

P/ kPa	n/ mmol g^{-1}	Run1		Run2		Run3		Average	
		K_1x10^3	k_2x10^3	k_1x10^3	k_2x10^3	k_1x10^3	K_2x10^3	k_1x10^3	K_2x10^3
0.01 – 0.1	0.591±0.004	0.6397	3.618	0.6057	3.410	0.5696	3.639	0.6050±0.035	3.556±0.127
0.1 – 0.2	0.842±0.001	0.7724	3.984	0.7686	4.225	0.7811	4.078	0.7740±0.006	4.096±0.121
0.2 – 0.4	1.201±0.004	1.039	5.375	1.144	5.324	1.073	5.422	1.085±0.054	5.374±0.049
0.4 – 0.7	1.539±0.008	1.503	6.948	1.519	6.890	1.577	6.723	1.533±0.039	6.854±0.117
0.7 – 1.2	1.881±0.003	2.078	8.534	2.159	8.503	2.135	8.355	2.124±0.041	8.464±0.096
1.2 – 2.0	2.215±0.003	2.844	9.820	2.872	10.58	2.946	9.614	2.887±0.053	10.01±0.509
2.0 – 3.5	2.588±0.003	3.837	12.68	3.830	12.86	4.003	12.10	3.890±0.098	12.55±0.400
3.5 – 5.0	2.832±0.003	4.536	14.63	4.813	14.16	5.140	14.18	4.830±0.302	14.32±0.263

Table S7. Kinetic parameters (s^{-1}) obtained from the Double Exponential Model for H_2 adsorption on M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$) at 87.3 K. Pressure range 0.2 – 10 kPa.

P/ kPa	n/ mmol g^{-1}	Run1		Run2		Run3		Average	
		k_1x10^3	k_2x10^3	k_1x10^3	k_2x10^3	k_1x10^3	k_2x10^3	k_1x10^3	k_2x10^3
0.2 – 0.5	0.369±0.005	2.993	9.401	3.087	9.922	2.794	9.468	2.958±0.149	9.597±0.284
0.5 – 1.0	0.579±0.012	3.509	11.19	3.620	10.96	3.842	11.73	3.657±0.169	11.29±0.396
1.0- 2.0	0.911±0.005	4.415	13.98	4.941	14.28	4.434	13.29	4.596±0.299	13.85±0.511
2.0 – 5.0	1.460±0.010	7.561	16.25	7.453	17.44	7.356	16.90	7.456±0.103	16.86±0.598
5.0 – 10.0	1.930±0.005	10.15	21.75	10.93	22.15	11.24	22.29	10.77±0.565	22.06±0.276

Table S8. Kinetic parameters (s^{-1}) obtained from the Double Exponential Model for D_2 adsorption on M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$) at 87.3 K. Pressure range 0.2 – 10 kPa.

P/ kPa	n/ mmol g^{-1}	Run1		Run2		Run3		Average	
		k_1x10^3	k_2x10^3	k_1x10^3	k_2x10^3	k_1x10^3	k_2x10^3	k_1x10^3	k_2x10^3
0.2 – 0.5	0.411±0.006	4.110	12.41	3.910	11.74	3.867	11.73	3.962±0.130	11.96±0.388
0.5 – 1.0	0.680±0.005	4.950	14.53	5.068	14.10	5.080	13.09	5.033±0.072	13.91±0.740
1.0- 2.0	1.050±0.032	6.480	17.25	6.520	17.11	6.332	16.54	6.444±0.099	16.97±0.387
2.0 – 5.0	1.661±0.012	10.26	20.10	9.712	20.58	9.240	21.07	9.737±0.510	20.58±0.485
5.0 – 10.0	2.161±0.009	13.06	24.17	12.15	25.68	12.71	25.08	12.64±0.462	24.97±0.759

Table S9. Comparison of Average Experimental Standard Deviations for Isotherm data for H_2 and D_2 adsorption on M'MOF **1** and Isotherm Model predictions based on Virial and Langmuir Freundlich Isotherm Models.

Adsorption Isotherm for M'MOF **1**	Average Experimental Standard Deviation for isotherm /%	Virial Method 1, Equation 3/ %	Virial Method 2, Equation 5 /%	Langmuir-Freundlich Model (Equation 7) / %
H_2 at 77.3 K	0.827	0.717	0.816	3.07
H_2 at 87.3 K	0.627	0.424	0.685	2.23
D_2 at 77.3 K	0.552	0.810	0.950	2.86
D_2 at 87.3 K	0.510	0.147	0.308	2.47
Average Error /%	0.629	0.523	0.688	2.67

Isotherm Range 0 – 4 mmol g^{-1}

Adsorption data for virial method 1: 77.3 K uses equation 3; 87.3 K uses equation 3 in two parts 0 - 2 mmol g^{-1} and 2 - 4 mmol g^{-1}

Table S10. Virial Parameters for H_2 and D_2 adsorption on M'MOF **1** obtained from Equation S7 in Virial Method 2

H_2	77.3 K	87.3 K		Virial Parameters		
A_0/	11.6515	13.888	a_0	-1509.50	b_0	31.1793
A_1/	1048.32	709.559	a_1	228606	b_1	-1909.07
A_2/	8384.64	59199.1	a_2	-3.42847E7	b_2	451979
D_2						
A_0/	11.5518	13.7401	a_0	-1476.78	b_0	30.6563
A_1/	932.734	625.203	a_1	207531	b_1	-1752.01
A_2/	15283.4	58764.1	a_2	-2.93420E7	b_2	394869

A_0, A_1 and A_2 are derived from the graphs of ln(p) versus ln(n). The values of a_0 and b_0 were obtained from the equation $A_0 = a_0/T + b_0$ while the values of a_1 and b_1 were obtained from the equation $A_1 = a_1/T + b_1$ and those of a_2 and b_2 were obtained from the equation $A_2 = a_2/T + b_2$.

Supporting Information

List of Figures

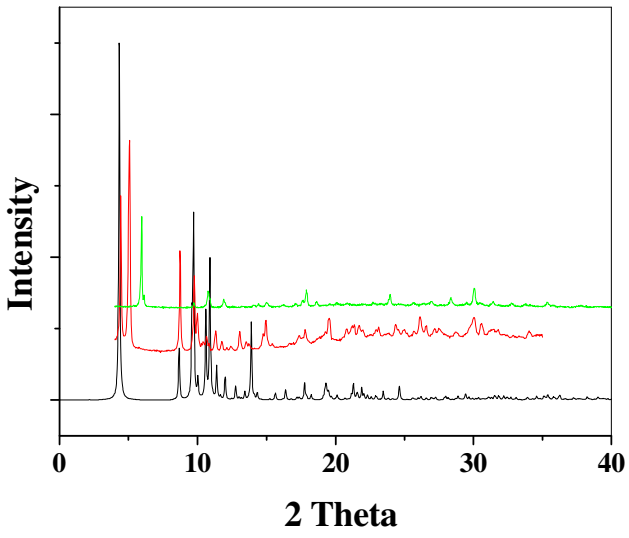


Figure S1 Powder X-ray diffraction (PXRD) patterns of the simulated M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$) (black), as-synthesized M'MOF **1** (red) and desolvated M'MOF **1** (green).

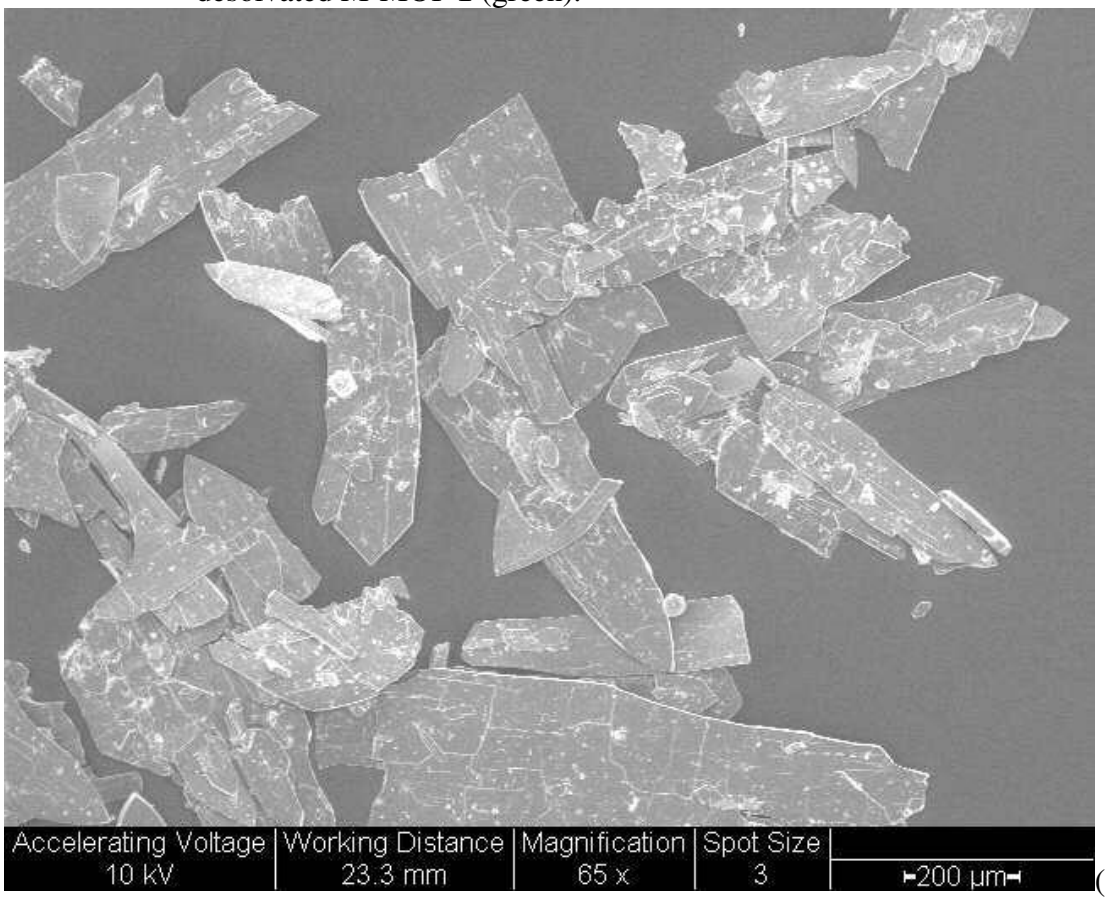


Figure S2. Scanning Electron Micrograph (65x) of M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$).

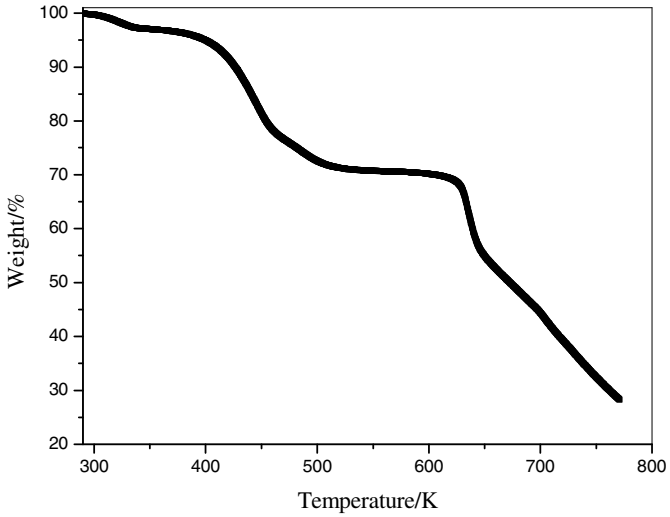
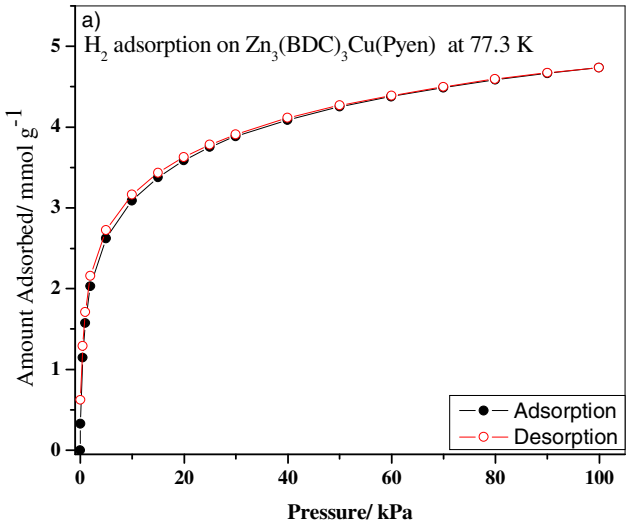
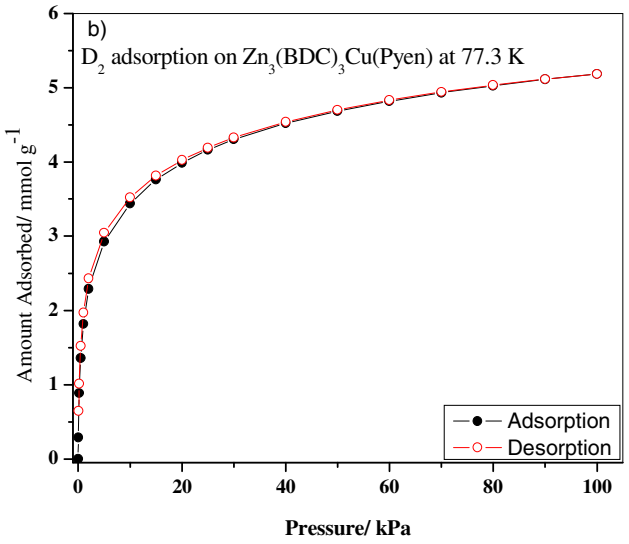


Figure S3 Thermogravimetric analysis profile of air-dried M'MOF **1** ($Zn_3(BDC)_3.Cu(Pyen)$): Heating rate 5 K min^{-1}, Nitrogen atmosphere


a)
H2 adsorption on Zn3(BDC)3Cu(Pyen) at 77.3 K
Amount Adsorbed/ mmol g-1
Pressure/ kPa
Adsorption
Desorption
0
1
2
3
4
5
0
20
40
60
80
100


b)
D2 adsorption on Zn3(BDC)3Cu(Pyen) at 77.3 K
Amount Adsorbed/ mmol g-1
Pressure/ kPa
Adsorption
Desorption
0
1
2
3
4
5
6
0
20
40
60
80
100

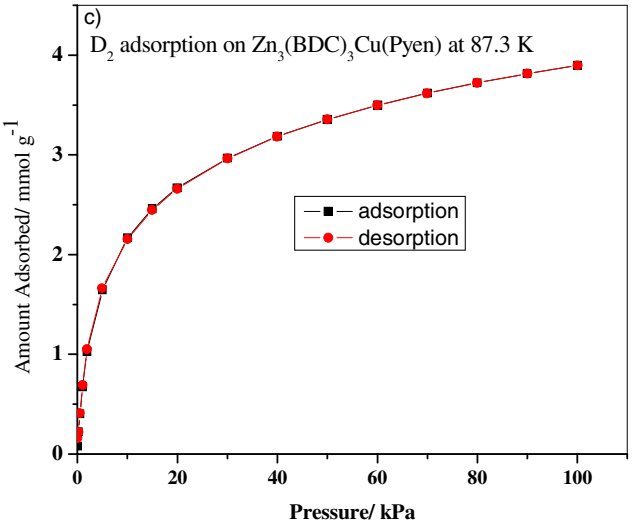


Figure S4 H_2 and D_2 adsorption/ desorption for $Zn_3(BDC)_3Cu(Pyen)$ a) H_2 at 77.3 K; b) D_2 at 77.3 K; c) D_2 at 87.3 K.

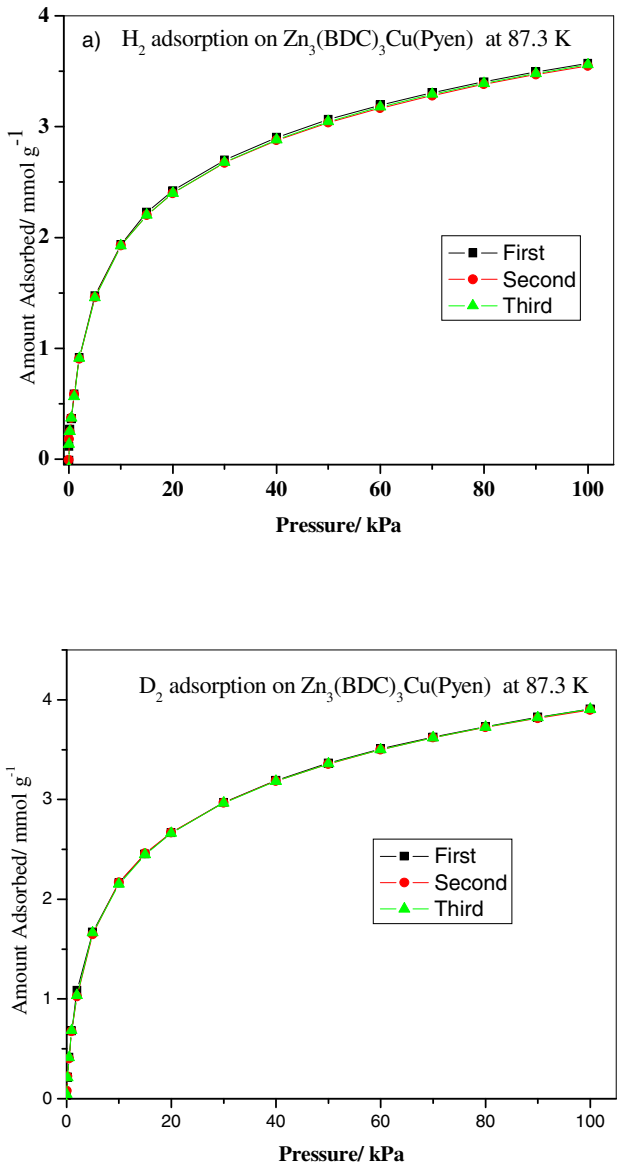
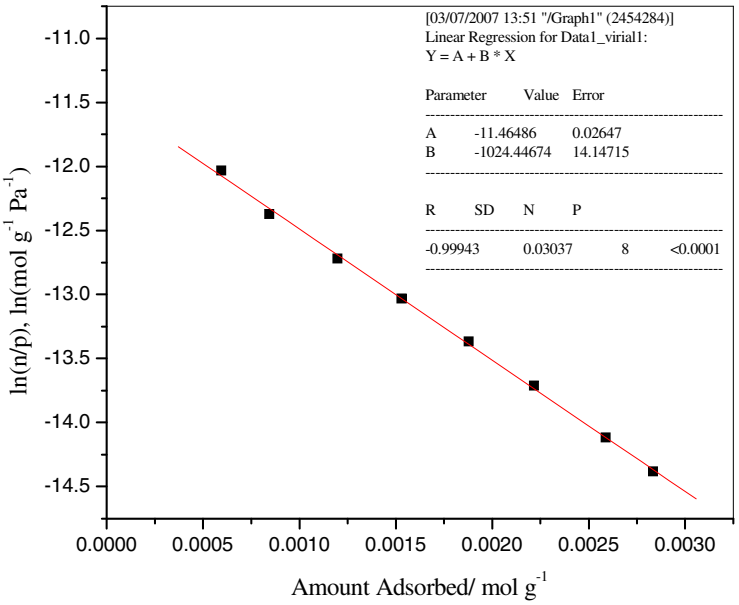
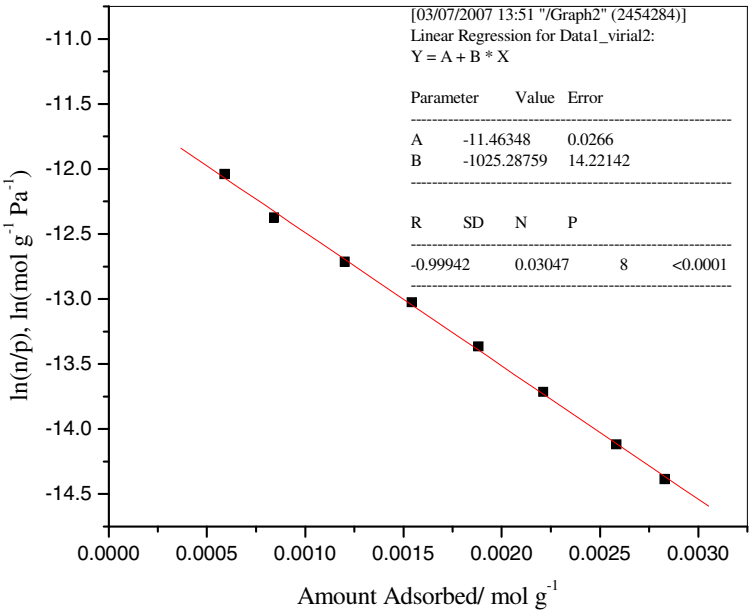


Figure S5. Adsorption isotherm repeatabilities for $Zn_3(BDC)_3Cu(Pyen)$ at 87.3 K a) H_2 ; b) D_2.

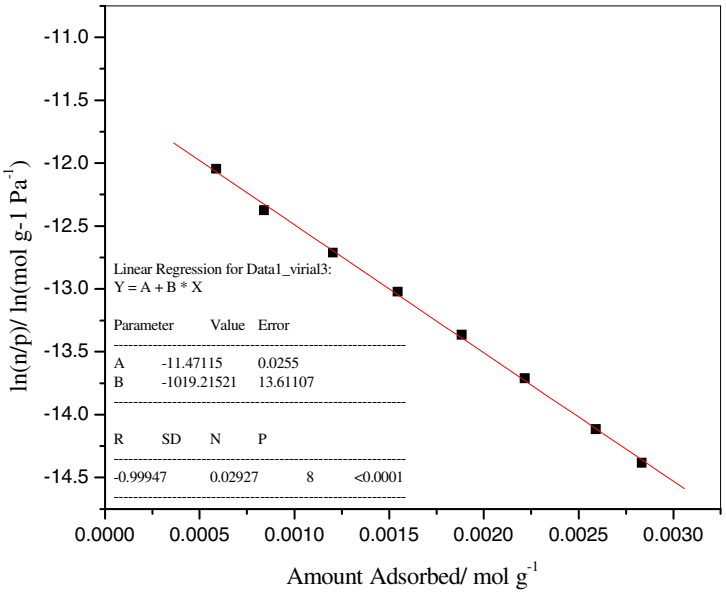
a)


[03/07/2007 13:51 "/Graph1" (2454284)]
Linear Regression for Data1_virial1:
Y = A + B * X
Parameter Value Error
A -11.46486 0.02647
B -1024.44674 14.14715
R SD N P
-0.99943 0.03037 8 <0.0001
ln(n/p), ln(mol g-1 Pa-1)
Amount Adsorbed/ mol g-1
-11.0
-11.5
-12.0
-12.5
-13.0
-13.5
-14.0
-14.5
0.0000
0.0005
0.0010
0.0015
0.0020
0.0025
0.0030

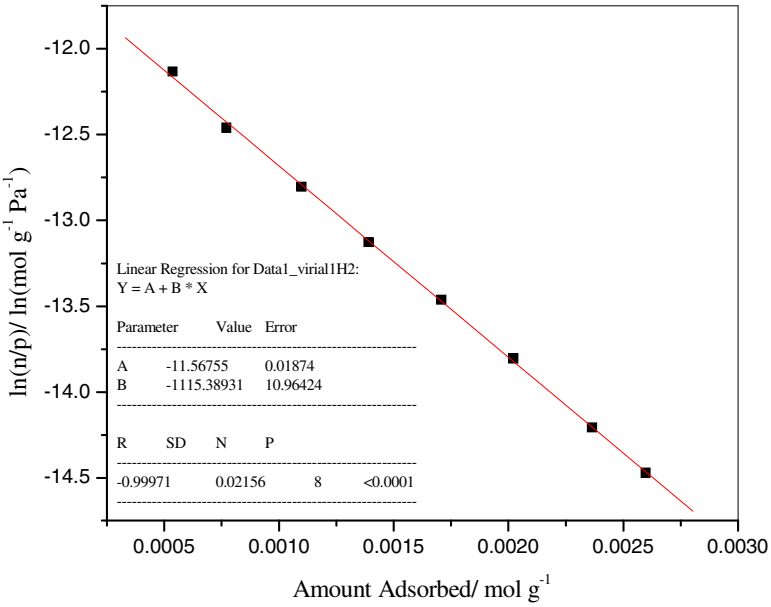
b)


[03/07/2007 13:51 "/Graph2" (2454284)]
Linear Regression for Data1_virial2:
Y = A + B * X
Parameter Value Error
A -11.46348 0.0266
B -1025.28759 14.22142
R SD N P
-0.99942 0.03047 8 <0.0001
ln(n/p), ln(mol g-1 Pa-1)
Amount Adsorbed/ mol g-1
-11.0
-11.5
-12.0
-12.5
-13.0
-13.5
-14.0
-14.5
0.0000
0.0005
0.0010
0.0015
0.0020
0.0025
0.0030

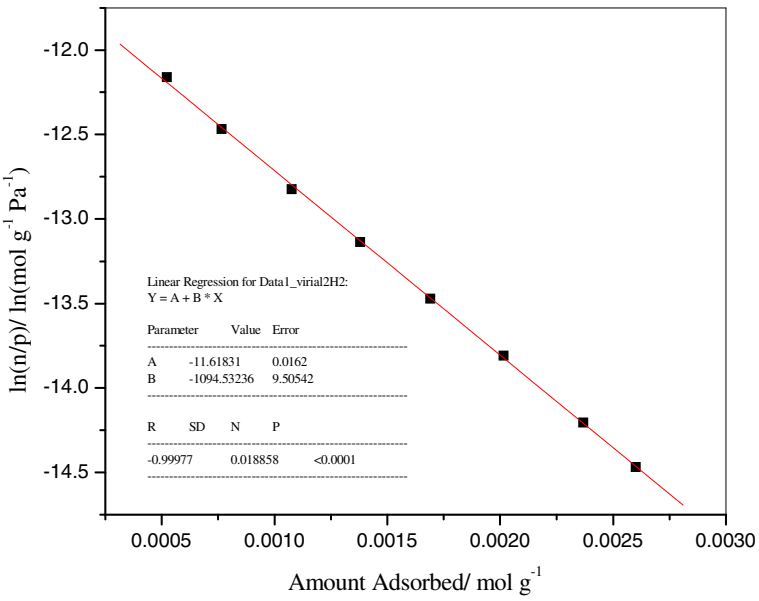
c)


Linear Regression for Data1_virial3:
Y = A + B * X
Parameter Value Error
A -11.47115 0.0255
B -1019.21521 13.61107
R SD N P
-0.99947 0.02927 8 <0.0001
ln(n/p)/ ln(mol g-1 Pa-1)
Amount Adsorbed/ mol g-1

d)


Linear Regression for Data1_virial1H2:
Y = A + B * X
Parameter Value Error
A -11.56755 0.01874
B -1115.38931 10.96424
R SD N P
-0.99971 0.02156 8 <0.0001
ln(n/p)/ ln(mol g-1 Pa-1)
Amount Adsorbed/ mol g-1

e)



f)

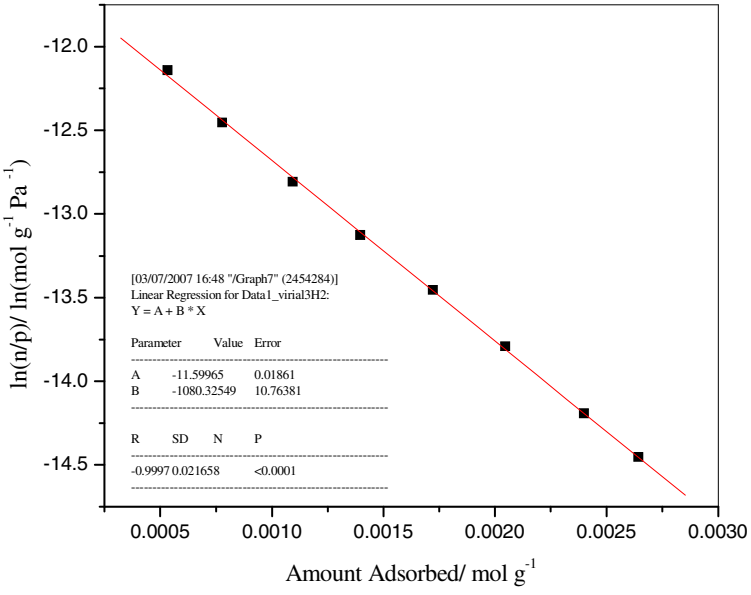
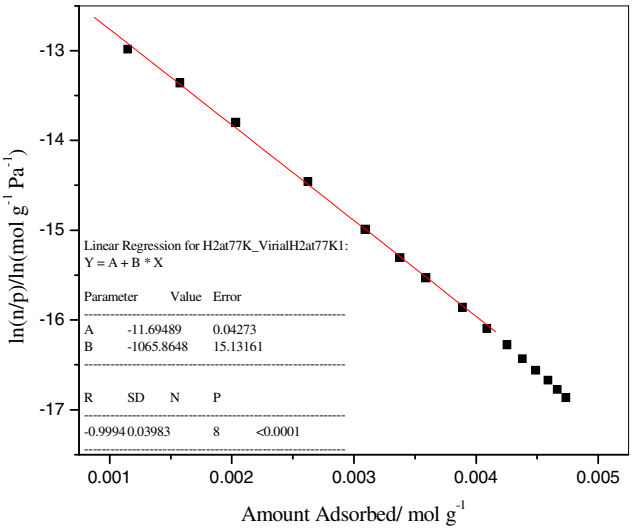
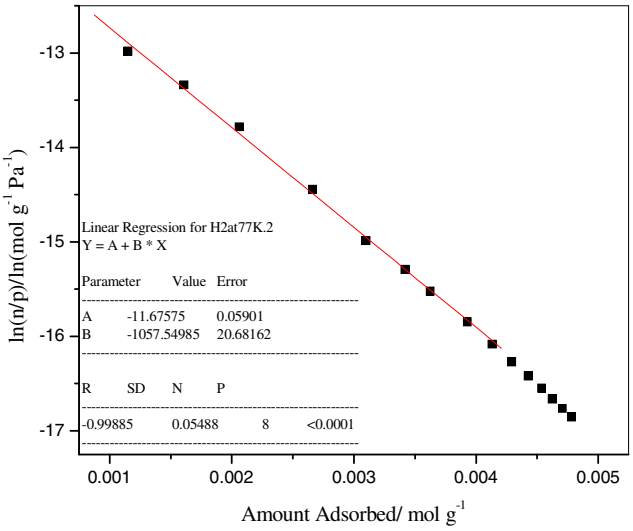


Figure S6. Virial graphs for high resolution isotherm data for adsorption of H_2 and D_2 on M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$) at 77.3 K. a) D_2 Run 1; b) D_2 Run 2; c) D_2 Run 3; d) H_2 Run 1; e) H_2 Run 2; f) H_2 Run 3.

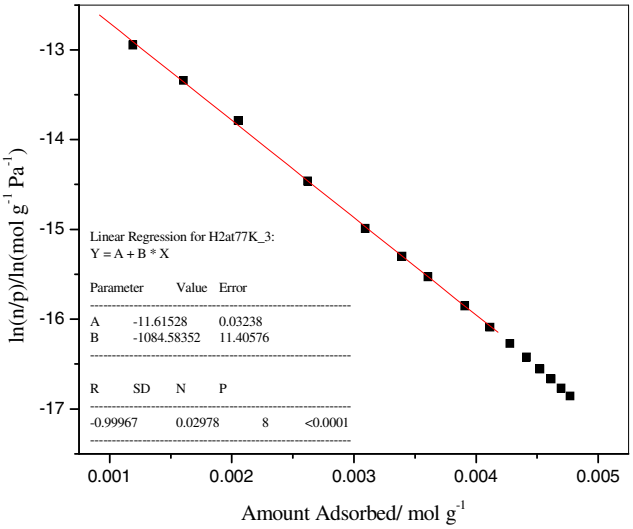
a)


Linear Regression for H2at77K_VirialH2at77K1:
Y = A + B * X
Parameter Value Error
A -11.69489 0.04273
B -1065.8648 15.13161
R SD N P
-0.9994 0.03983 8 <0.0001
ln(n/p)/ln(mol g-1 Pa-1)
Amount Adsorbed/ mol g-1
-13
-14
-15
-16
-17
0.001
0.002
0.003
0.004
0.005

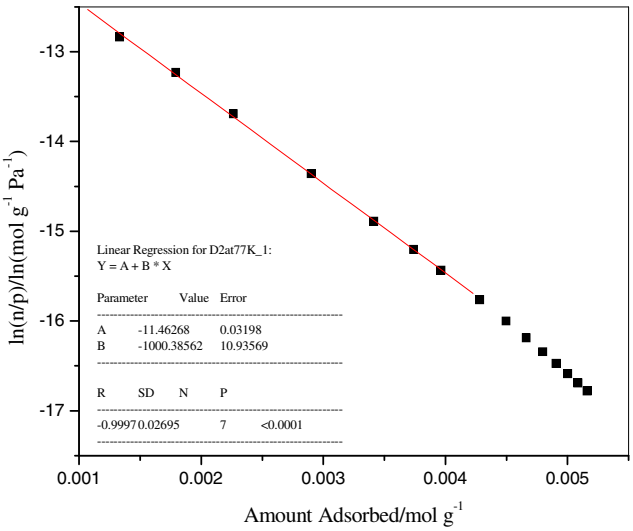
b)


Linear Regression for H2at77K.2
Y = A + B * X
Parameter Value Error
A -11.67575 0.05901
B -1057.54985 20.68162
R SD N P
-0.99885 0.05488 8 <0.0001
ln(n/p)/ln(mol g-1 Pa-1)
Amount Adsorbed/ mol g-1
-13
-14
-15
-16
-17
0.001
0.002
0.003
0.004
0.005

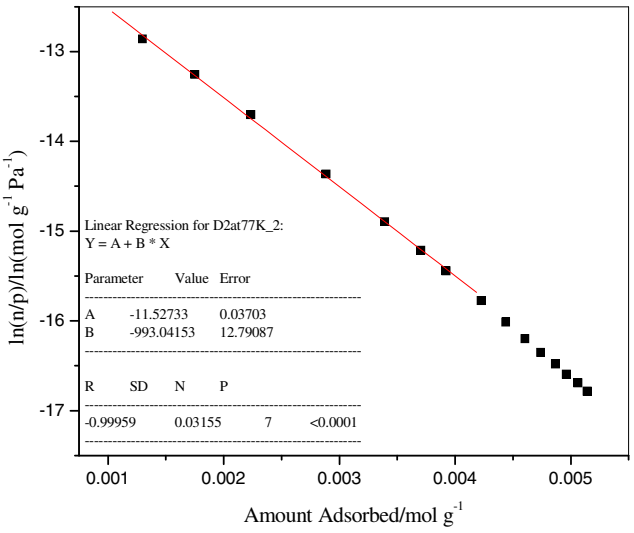
c)


Linear Regression for H2at77K_3:
Y = A + B * X
Parameter Value Error
A -11.61528 0.03238
B -1084.58352 11.40576
R SD N P
-0.99967 0.02978 8 <0.0001
ln(n/p)/ln(mol g-1 Pa-1)
Amount Adsorbed/ mol g-1

d)


Linear Regression for D2at77K_1:
Y = A + B * X
Parameter Value Error
A -11.46268 0.03198
B -1000.38562 10.93569
R SD N P
-0.9997 0.02695 7 <0.0001
ln(n/p)/ln(mol g-1 Pa-1)
Amount Adsorbed/mol g-1

e)



f)

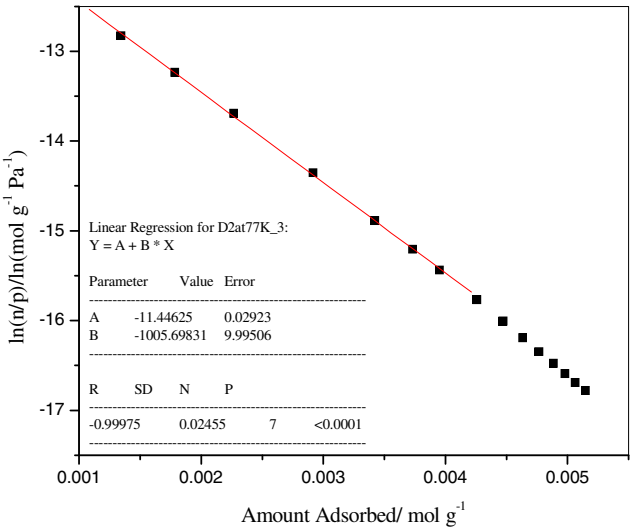
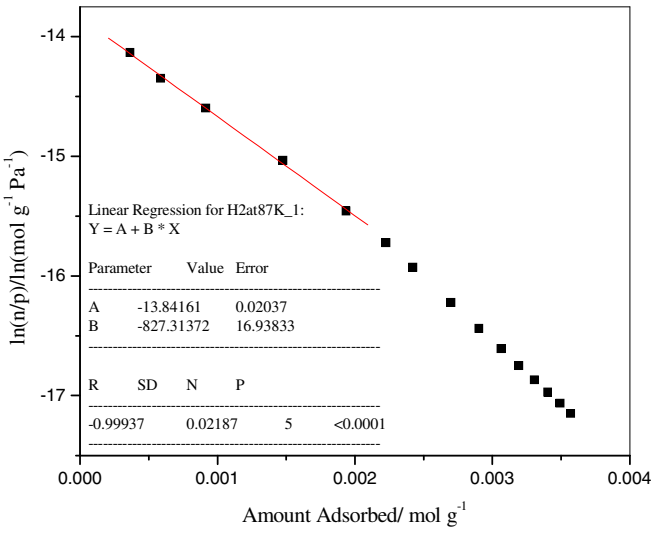
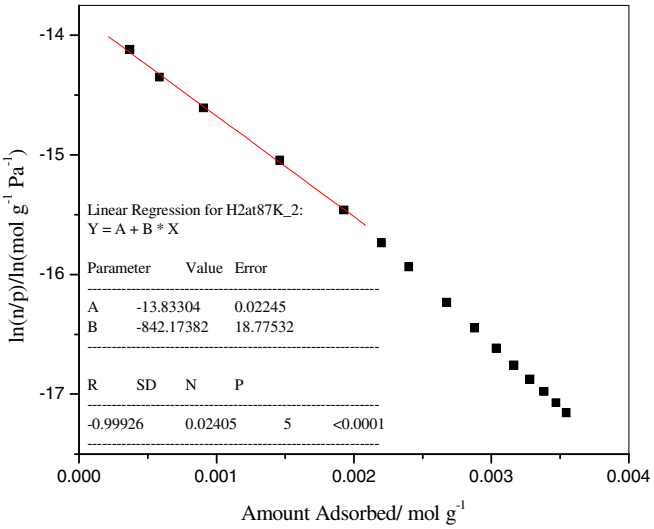


Figure S7. Virial graphs for adsorption of H_2 and D_2 on M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$) at 77.3 K as in Table 1. a) H_2 Run 1; b) H_2 Run 2; c) H_2 Run 3; d) D_2 Run 1; e) D_2 Run 2; f) D_2 Run 3.

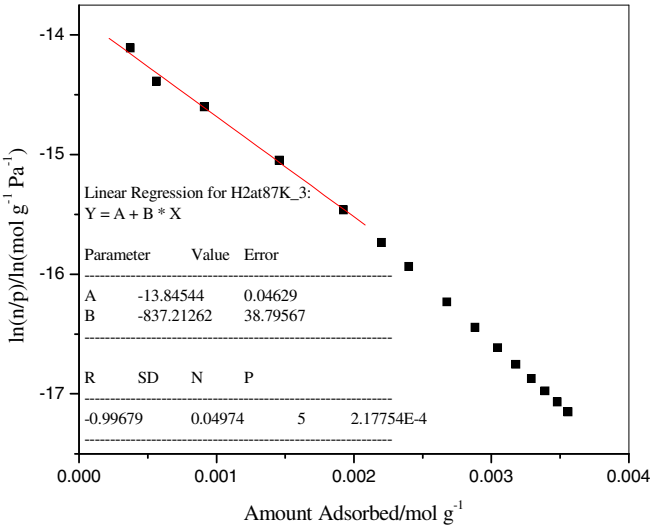
a)


Linear Regression for H2at87K_1:
Y = A + B * X
Parameter Value Error
A -13.84161 0.02037
B -827.31372 16.93833
R SD N P
-0.99937 0.02187 5 <0.0001
ln(n/p)/ln(mol g-1 Pa-1)
Amount Adsorbed/ mol g-1
-14
-15
-16
-17
0.000
0.001
0.002
0.003
0.004

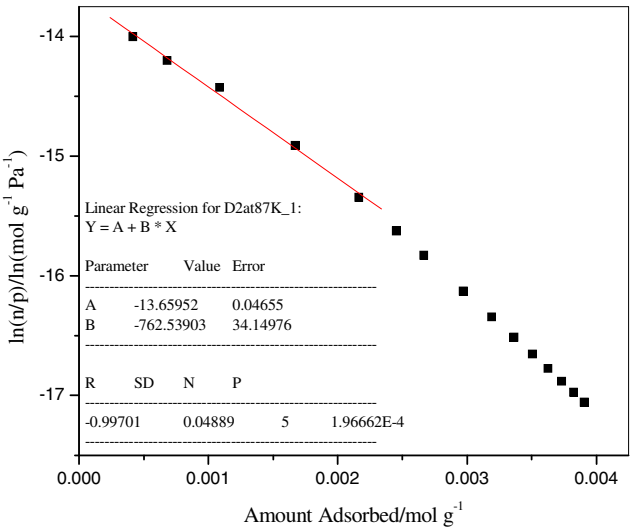
b)


Linear Regression for H2at87K_2:
Y = A + B * X
Parameter Value Error
A -13.83304 0.02245
B -842.17382 18.77532
R SD N P
-0.99926 0.02405 5 <0.0001
ln(n/p)/ln(mol g-1 Pa-1)
Amount Adsorbed/ mol g-1
-14
-15
-16
-17
0.000
0.001
0.002
0.003
0.004

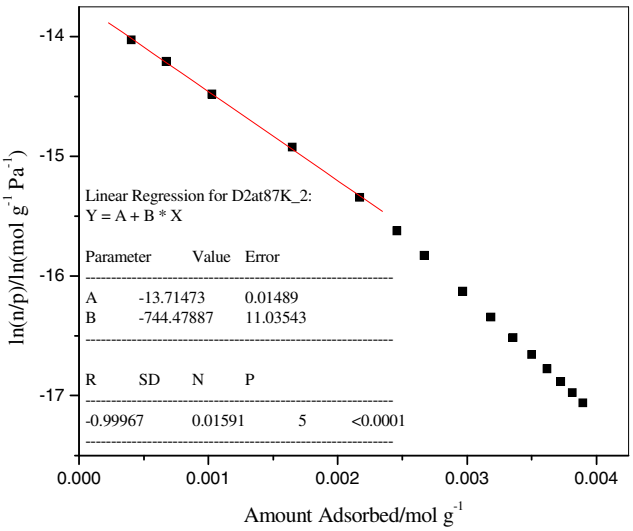
c)


Linear Regression for H2at87K_3:
Y = A + B * X
Parameter Value Error
A -13.84544 0.04629
B -837.21262 38.79567
R SD N P
-0.99679 0.04974 5 2.17754E-4
ln(n/p)/ln(mol g-1 Pa-1)
Amount Adsorbed/mol g-1
-14
-15
-16
-17
0.000
0.001
0.002
0.003
0.004

d)


Linear Regression for D2at87K_1:
Y = A + B * X
Parameter Value Error
A -13.65952 0.04655
B -762.53903 34.14976
R SD N P
-0.99701 0.04889 5 1.96662E-4
ln(n/p)/ln(mol g-1 Pa-1)
Amount Adsorbed/mol g-1
-14
-15
-16
-17
0.000
0.001
0.002
0.003
0.004

e)



f)

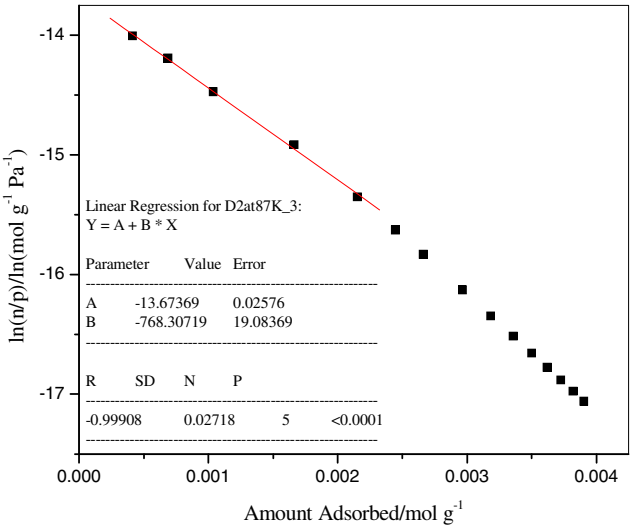
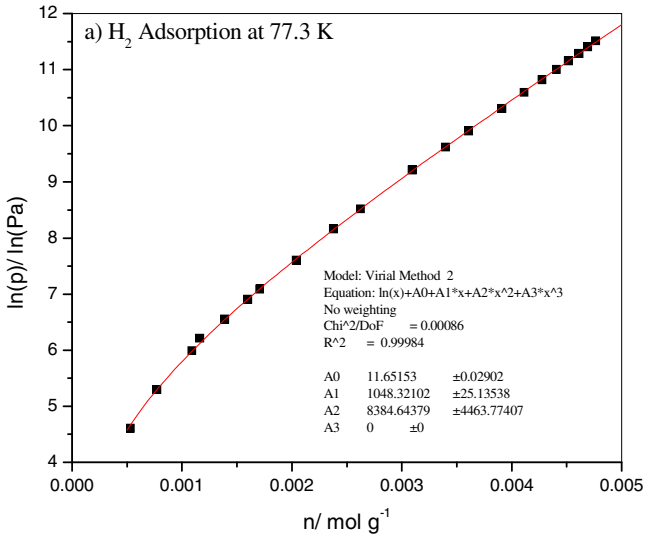
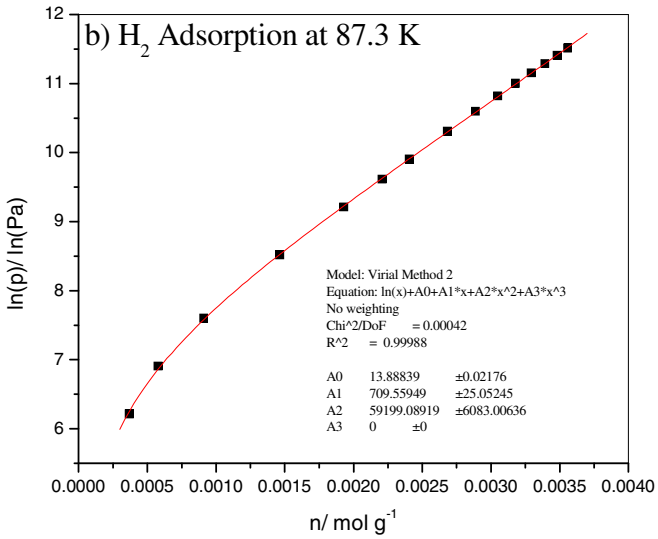


Figure S8. Virial graphs for adsorption of H_2 and D_2 on M'MOF **1** ($Zn_3(BDC)_3Cu(Pyen)$) at 87.3 K as in Table 1. a) H_2 Run 1; b) H_2 Run 2; c) H_2 Run 3; d) D_2 Run 1; e) D_2 Run 2; f) D_2 Run 3.


a) H2 Adsorption at 77.3 K
ln(p)/ ln(Pa)
n/ mol g-1
Model: Virial Method 2
Equation: ln(x)+A0+A1*x+A2*x^2+A3*x^3
No weighting
Chi^2/DoF = 0.00086
R^2 = 0.99984
A0 11.65153 ±0.02902
A1 1048.32102 ±25.13538
A2 8384.64379 ±4463.77407
A3 0 ±0


b) H2 Adsorption at 87.3 K
ln(p)/ ln(Pa)
n/ mol g-1
Model: Virial Method 2
Equation: ln(x)+A0+A1*x+A2*x^2+A3*x^3
No weighting
Chi^2/DoF = 0.00042
R^2 = 0.99988
A0 13.88839 ±0.02176
A1 709.55949 ±25.05245
A2 59199.08919 ±6083.00636
A3 0 ±0

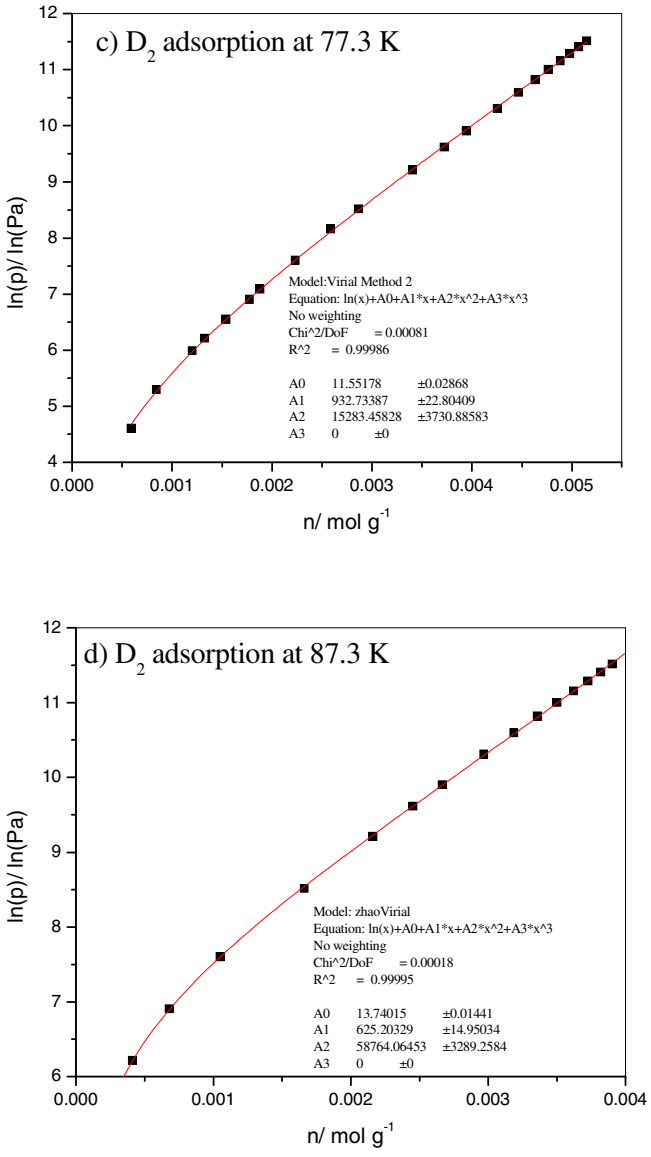


Figure S9 Adsorption isotherm for M'MOF 1 at 77 K fitted using a three parameter virial equation (5) a) H_2 at 77.3 K b) H_2 at 87.3 K c) D_2 at 77.3 K d) D_2 at 87.3 K

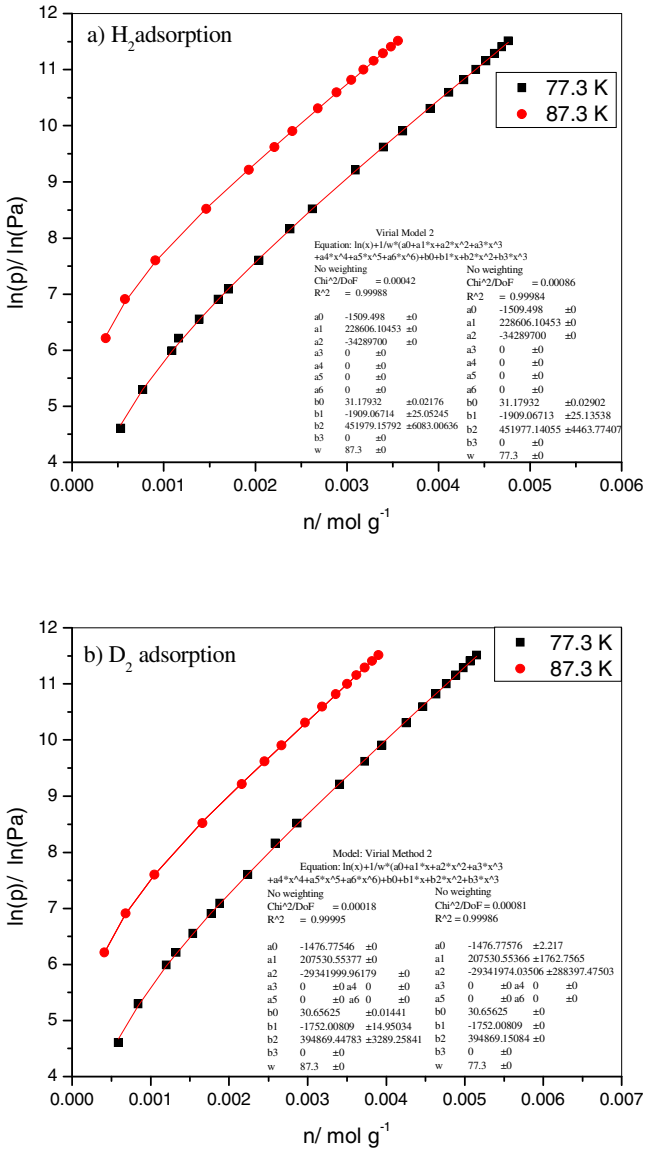


Figure S10. H_2 and D_2 adsorption isotherms for M'MOF **1** with fitting by Virial method 2 using a_0, a_1, a_2, b_0, b_1, b_2 a) H_2 and b) D_2.

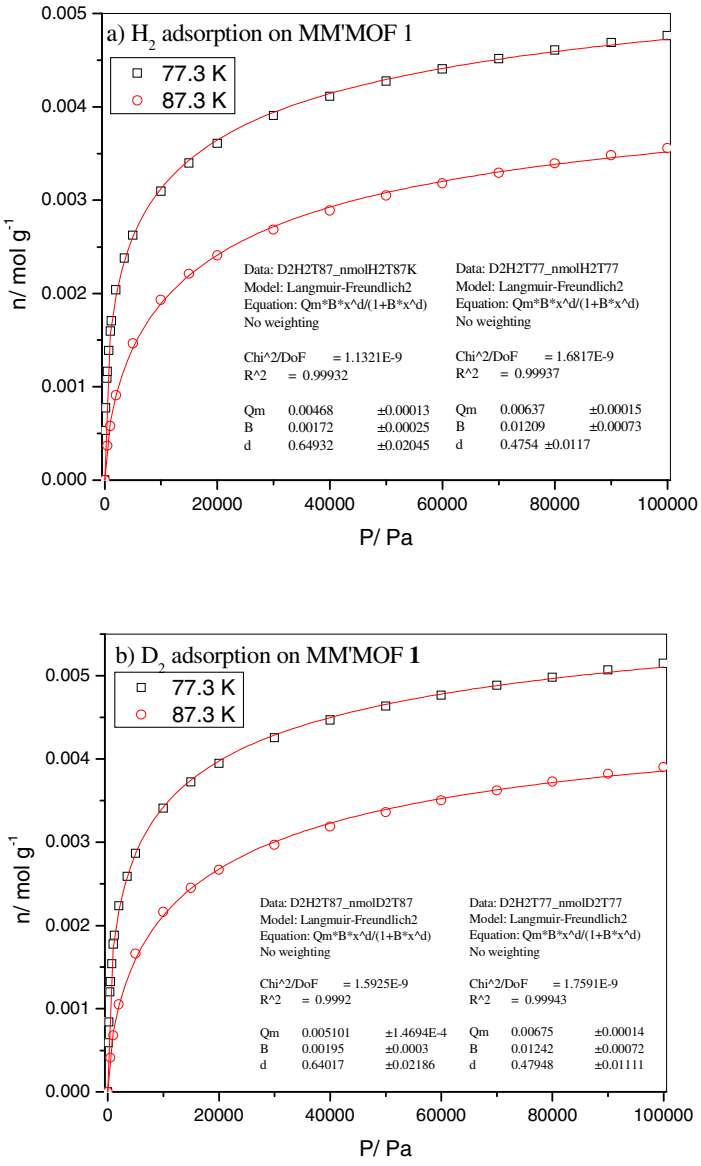
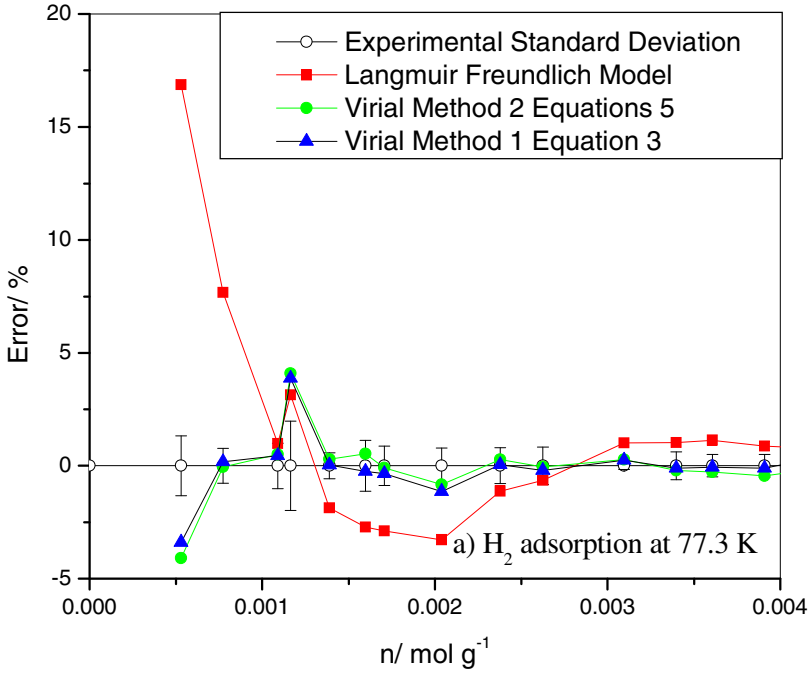
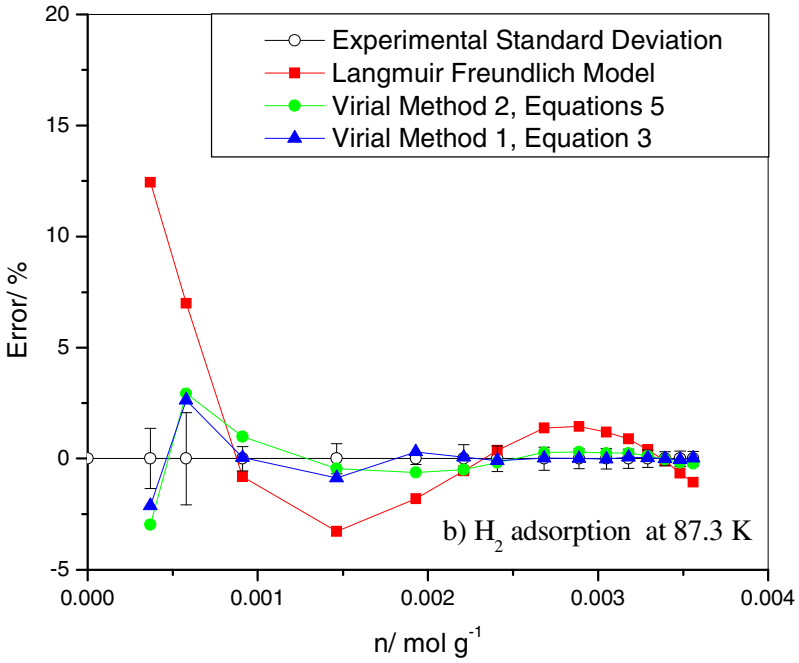
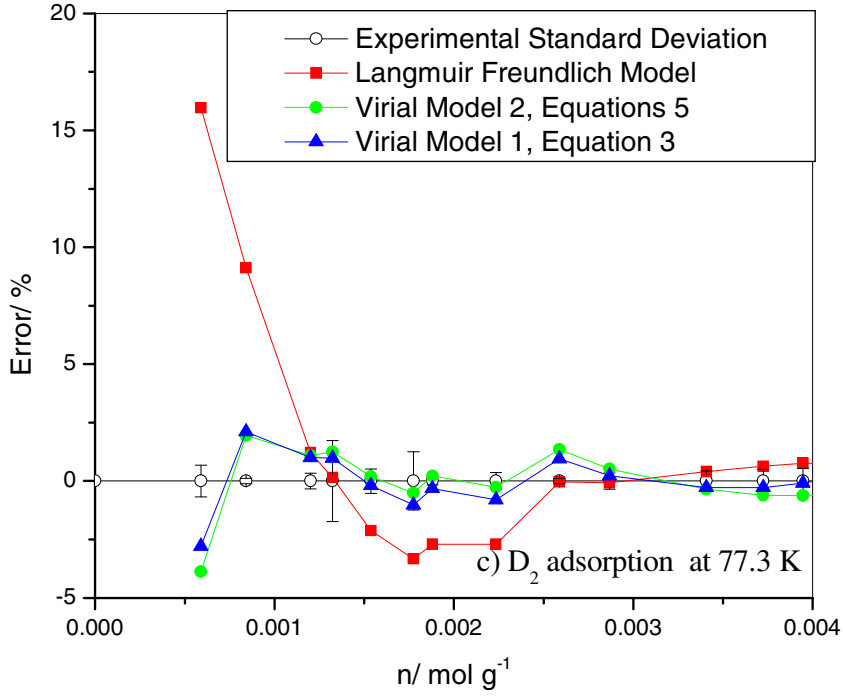


Figure S11 Adsorption isotherms and fitting to Langmuir-Freundlich model for H_2 and D_2 Adsorption on M'MOF 1 a) H_2 and b) D_2.


Experimental Standard Deviation
Langmuir Freundlich Model
Virial Method 2 Equations 5
Virial Method 1 Equation 3
Error/ %
n/ mol g-1
a) H2 adsorption at 77.3 K
20
15
10
5
0
-5
0.000
0.001
0.002
0.003
0.004


Experimental Standard Deviation
Langmuir Freundlich Model
Virial Method 2, Equations 5
Virial Method 1, Equation 3
Error/ %
n/ mol g-1
b) H2 adsorption at 87.3 K
20
15
10
5
0
-5
0.000
0.001
0.002
0.003
0.004



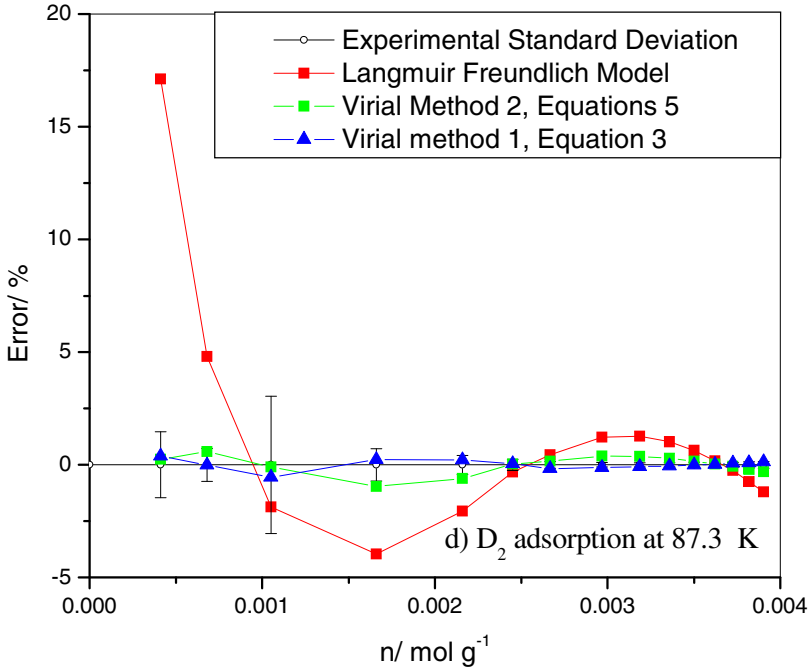


Figure S12. Comparison of experimental standard deviation and (model predicted value – isotherm amount adsorbed)x 100/ isotherm amount adsorbed) for Virial and Langmuir-Freundlich isotherms models for determining isosteric enthalpies of adsorption of H_2 and D_2 on M'MOF **1**, a) H_2 adsorption at 77.3 K b) H_2 adsorption at 87.3 K, c) D_2 adsorption at 77.3 K d) D_2 adsorption at 87.3 K.

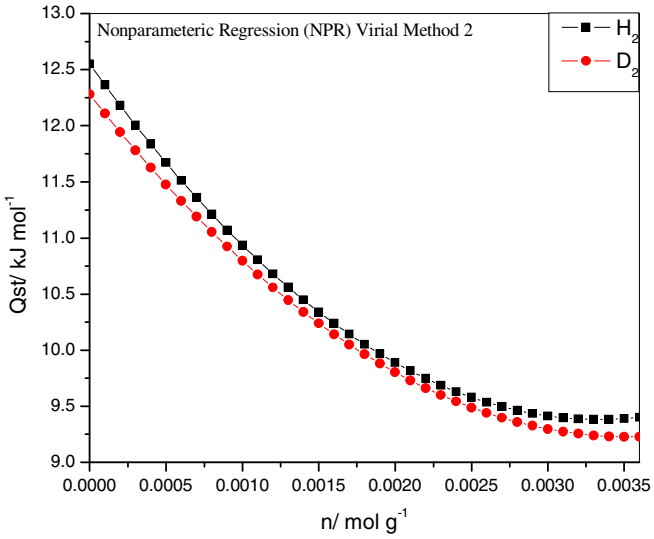


Figure S13. Variation of isosteric enthalpy of adsorption (Q_{st}), calculated using virial method 2 for estimating pressure for specific amounts adsorbed, with amount adsorbed for H_2 and D_2 adsorption on MM'MOF 1

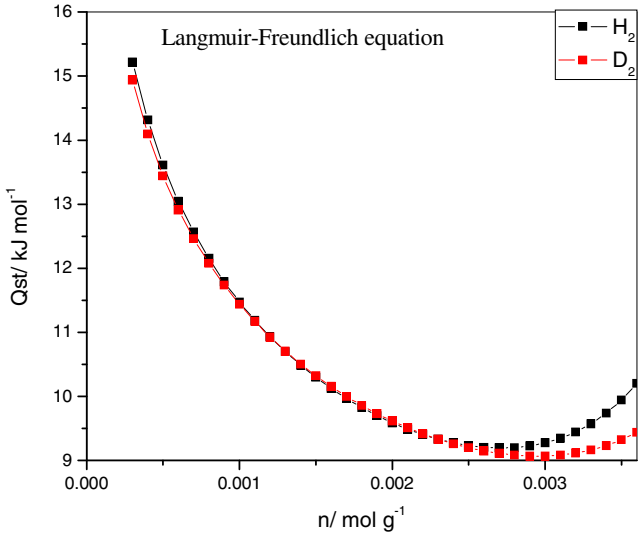


Figure S14. Variation of isosteric enthalpy of adsorption (Q_{st}), calculated using Langmuir-Freundlich equation for estimating pressure for specific amounts adsorbed, with amount adsorbed for H_2 and D_2 adsorption on M'MOF **1**

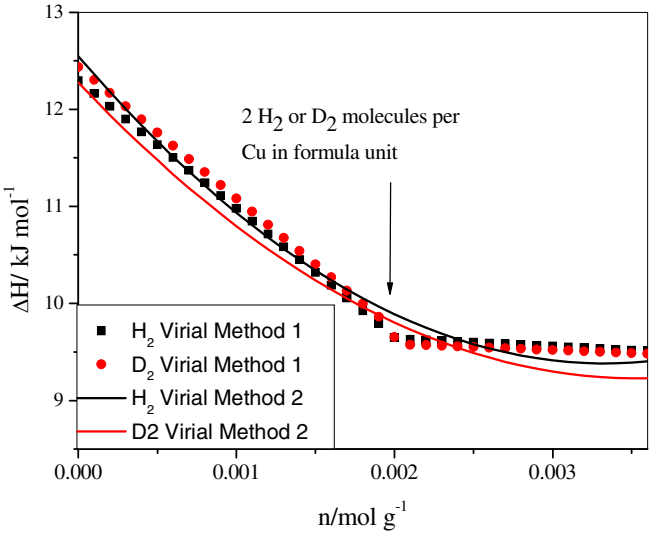


Figure S15. Comparison of isosteric enthalpies of adsorption (Q_{st}) calculated using virial methods for H_2 and D_2 adsorption on M'MOF **1**.

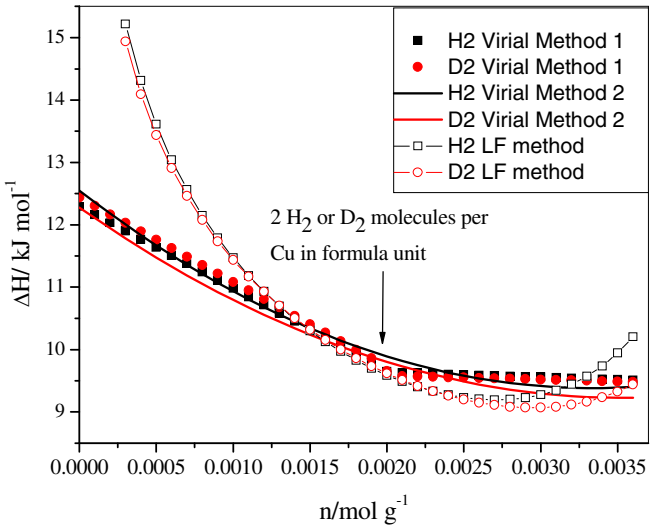


Figure S16. Comparison of isosteric enthalpies of adsorption (Q_{st}) calculated using virial methods and Langmuir Freundlich methods for H_2 and D_2 adsorption on M'MOF **1**.