Supplementary Material (ESI) for Chemical Communications

Reversible hydrogen gas uptake in nanoporous Prussian Blue analogues

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SUPPLEMENTARY INFORMATION

Supplementary Material (ESI) for Chemical Communications

Syntheses

$\mathbf{A'_M}$: Aqueous solutions of $M(NO_3)_2.xH_2O$ (0.75 mmol) and $K_3Co(CN)_6$ (0.5 mmol, 0.17 g) were allowed to diffuse through water in an H-shaped tube over 2 weeks to precipitate $M^{II}_3[Co^{III}(CN)_6]_2[H_2O]_6.x\{H_2O\}$ (**$\mathbf{A'_M}$**, x = 6 - 8) as single crystals and/or crystalline powders. The products were filtered off, washed with water and dried in air.

Single crystal structural studies of the as synthesised and dehydrated phases, **$\mathbf{A'_M}$** and **$\mathbf{A_M}$**, will be reported elsewhere.

$\mathbf{B_{Cd}}.x\mathbf{H_2O}$: Aqueous solutions of $Cd(NO_3)_2.xH_2O$ (0.5 mmol, 0.23 g) and $K_2Pt(CN)_6$ (0.5 mmol, 1.29 g) were allowed to diffuse in a test tube over 2 weeks to crystallise $Cd^{II}Pt^{IV}(CN)_6.xH_2O$ (**$\mathbf{B_{Cd}}$**.xH_2O, x = 2) as colourless cubic crystals. The crystals were filtered off, washed with water and dried in air.

H-ZSM-5: Powdered sample was synthesised according to a standard procedure available at http://www.iza-synthesis.org/. The hydrogen form was produced by ion-exchange in 0.2 M NH_4NO_3, followed by calcination at 540 °C for 12 h to give H-ZSM-5 (Al/Si = 7/89) as a white powder. The phase purity at each stage was verified by x-ray powder diffraction.

Thermogravimetry

Thermogravimetric analyses (TGA) were carried out using a TA instruments H-Res TGA 2950 Analyser in a nitrogen gas atmosphere and the data analysed using the TA instruments Universal Analysis 2000 program. Samples (10 - 20 mg) were heated at 1 $Kmin^{-1}$ from ambient temperature to decomposition at *ca.* 700 K.

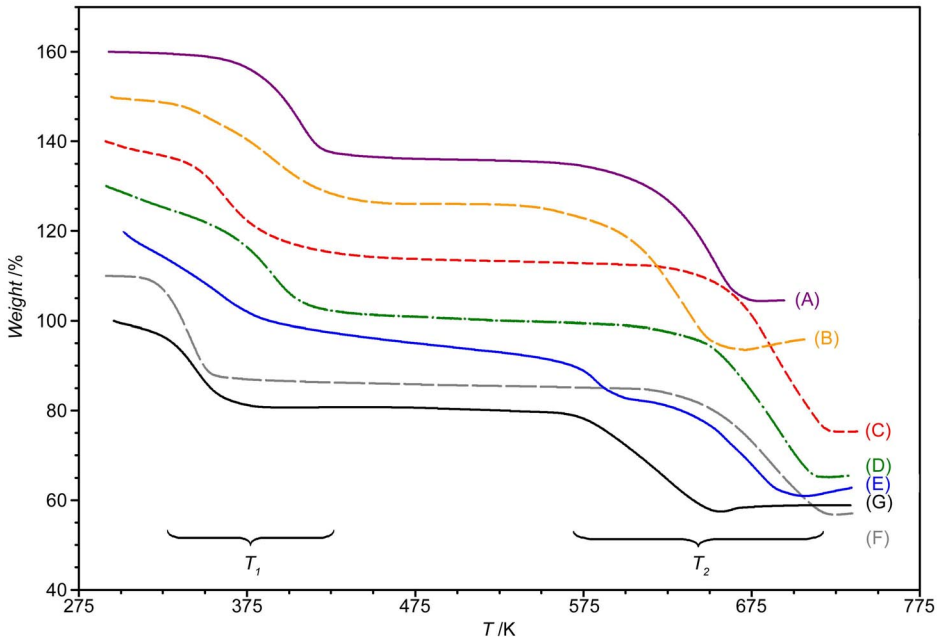

Fig. S1 TGA profiles for thermal decomposition of $\mathbf{A'_M}$, M = Mn, Fe, Co, Ni, Cu, Zn, Cd, (A)-(G). Profiles are offset by 10% for clarity.

The TGA profile indicates the presence of two distinct phenomena: the loss of coordinated and uncoordinated water at temperatures up to *ca.* 425 K (T_1) and the decomposition of the framework at temperatures greater than *ca.* 550 K (T_2).

Table S1 Summary of thermogravimetric results for $\mathbf{A'_M}$.

Compound	m_1	m_2	x H_2O	T_1 /K	T_2 /K
$\mathbf{A'_{Mn}}$	24.2%	32.4%	4.9	375-425	575
$\mathbf{A'_{Fe}}$	23.7%	32.9%	4.7	350-425	550
$\mathbf{A'_{Co}}$	26.5%	40.0%	6.1	340-390	600
$\mathbf{A'_{Ni}}$	29.2%	36.3%	7.3	350-415	600
$\mathbf{A'_{Cu}}$	24.1%	35.6%	5.2	350-380	550
$\mathbf{A'_{Zn}}$	24.4%	30.0%	5.4	325-350	600
$\mathbf{A'_{Cd}}$	21.9%	38.0%	6.0	300-375	575

Initial mass loss is approximately consistent with that expected for hydrated phase of composition $M^{II}_3[Co^{III}(CN)_6]_2[H_2O]_6.x\{H_2O\}$ for $x \approx 6$ - 8. The deviation in degrees of hydration arises from variations in humidity and sample storage.

Adsorption Measurements

Hydrogen (99.999%) and nitrogen (99.99%) adsorption experiments at 77 K were performed in a static vacuum volumetric apparatus (Quantachrome Autosorb 1). The adsorption and desorption was measured at 12 - 16 points in the partial pressure range 0.0 – 1.0, referenced to atmospheric pressure, P_o, which varied in the range 0.988 and 1.016 standard atmospheres for the reported isotherms (see Fig. S2, Table S2 - S23). Before adsorption, the samples were dehydrated at temperatures at 373 - 443 K for 16 h under vacuum. Replicate measurements on fresh and reused samples agree within *ca.* 10%.

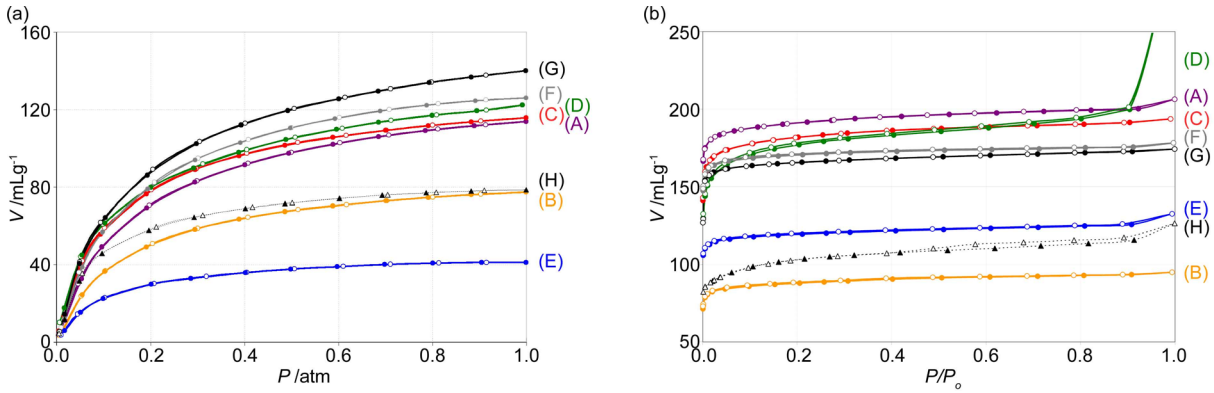

Fig. S2 Sorption (closed circles) and desorption (open circles) isotherms in nanoporous Prussian Blue analogues $\mathbf{A_M}$, M = Mn, Fe, Co, Ni, Cu, Zn, Cd (A-G), at 77 K for hydrogen (a) and nitrogen (b). Data collected on the high surface area zeolite H-ZSM-5 (H) are shown for comparison.

A large apparent increase in the adsorbed N_2 volume was observed at $P \rightarrow P_o$ due to N_2 condensation. The adsorbed volume of N_2 at 0.9 P/P_o, therefore, provides a more reliable figure for comparison of final uptakes.

BET plots were constructed for the nitrogen sorption isotherms. Nominal 'surface areas' were determined using a linear section over the range $P_o/P = 0.005$ - 0.1. The nitrogen micropore capacities were evaluated by extrapolation to $P_o/P = 0$.

Adsorption Models

As the sorption is being measured far from critical conditions for hydrogen, sorption beyond a monolayer is exceedingly unlikely, and, therefore, the hydrogen sorption can be considered as monolayer adsorption on the pore surface. A number of simple physisorption models were fitted to the hydrogen adsorption data using a least squares method. All three models provided an adequate fit to the data with the generalised-Freundlich model providing a more consistent fit to the hydrogen adsorption over all phases.

Langmuir Isotherm

This model,[1] described by equation (1), considers monolayer adsorption in which adsorption at all sites is equivalent and independent of adsorption at neighbouring sites.

$$x(p) = x_L\left[\frac{bp}{1+bp}\right] \qquad (1)$$

Where x_L is a constant representing limiting adsorption capacity,[†] and b is a constant exponentially related to the positive value of the adsorption energy.

Generalised-Freundlich Isotherm

This model,[2] described by equation (2), is a combination of the Langmuir model with the Freundlich equation which allows a logarithmic fall in the enthalpy of adsorption with surface coverage.

$$x(p) = x_L\left[\frac{(bp)^{1/m}}{[1+(bp)^{1/m}]}\right] \qquad (2)$$

Where x_L is a constant representing limiting adsorption capacity, b is a constant exponentially related to the positive value of the adsorption energy and m is a constant related to the fall off in adsorption enthalpy.

[†] For the ease of visualisation and direct comparison with the number of mole of guest water (non-coordinative) in the hydrated phase $\mathbf{A'_M}$, the amount adsorbed, x, and the limiting adsorption capacities, x_L, in the fitting of these physisorption models have been expressed in terms of number of molecules per formula unit of framework, that is, $\mathbf{A_M}.x\{H_2\}$.

[1] I. Langmuir, *J. Am. Chem. Soc.*, 1916, **38**, 2221.
[2] R. Sips, *J Chem. Phys.*, 1948, **16**, 490.

Toth Isotherm

This model,[3] described by equation (3), is another variant of the Langmuir model assuming a logarithmic fall in the enthalpy of adsorption with surface coverage.

$$x(p) = x_L\left[\frac{p}{(k + p^m)^{1/m}}\right] \qquad (3)$$

Where x_L is a constant representing limiting adsorption capacity, k is a constant exponentially related to the positive value of the adsorption energy and m is a constant related to the fall off in adsorption enthalpy.

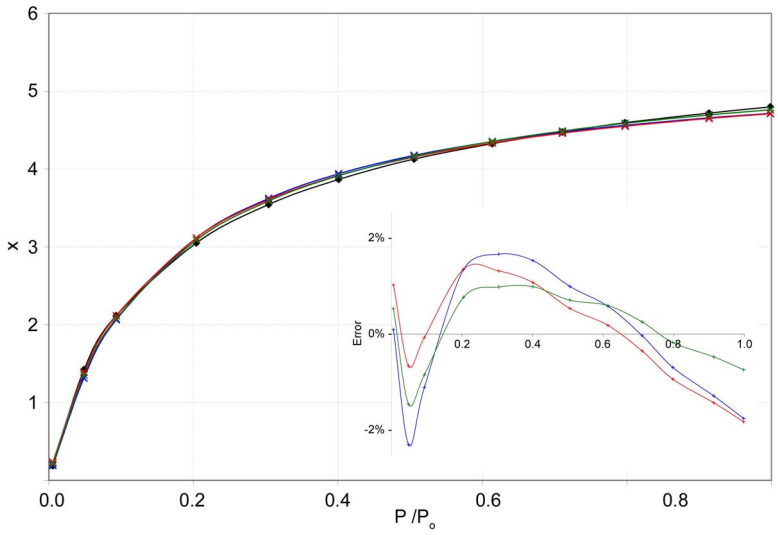

Fig. S3 Hydrogen adsorption isotherms for $\mathbf{A_{Cd}}$ as measured (black) and fitted Langmuir (blue), generalised-Freundlich (red) and Toth (green) isotherms. The insert shows errors in the fitted isotherms as a percentage of maximum uptake.

[3] J. Toth, *Acta. Chim. Acad. Sci. Hung.*, 1962, **35**, 416.

Table S2. Summary of hydrogen sorption data for $\mathbf{A_M}$ and H-ZSM-5 at 77 K.

Compound		$\mathbf{A_{Mn}}$	$\mathbf{A_{Fe}}$	$\mathbf{A_{Co}}$	$\mathbf{A_{Ni}}$	$\mathbf{A_{Cu}}$	$\mathbf{A_{Zn}}$	$\mathbf{A_{Cd}}$	**H-ZSM-5**
Molar Mass		594.9	597.6	606.9	606.2	620.7	626.2	767.3	5767.8
Dehydration Temperature / K		423	428	393	413	373	373	373	443
Analysis Mass /g		0.2396	0.2206	0.1450	0.1437	0.1907	0.2117	0.1505	0.2296
Measured Uptake	/mLg^{-1}	113.8	77.4	115.8	122.3	41.2	126.0	140.1	78.59
	/x	3.02	2.07	3.14	3.31	1.14	3.52	4.80	-
	/wt%	1.01%	0.69%	1.03%	1.09%	0.37%	1.12%	1.24%	0.70%
Langmuir†	/mLg^{-1}	132.3	87.5	128.7	133.4	47.7	145.7	159.1	-
	/x_L	3.51	2.34	3.49	3.61	1.32	4.07	5.45	-
	/wt%$_L$	1.17%	0.78%	1.15%	1.19%	0.43%	1.29%	1.41%	-
	/b	5.98	6.96	8.06	8.15	7.73	6.44	6.48	-
Generalised -Freundlich†	/mLg^{-1}	143.9	101.0	146.8	160.0	58.9	150.0	172.8	-
	/x_L	3.82	2.70	3.98	4.33	1.63	4.19	5.92	-
	/wt%$_L$	1.28%	0.90%	1.30%	1.42%	0.53%	1.33%	1.53%	-
	/b	4.7	4.8	5.8	5.0	4.4	6.0	5.3	-
	/m	1.15	1.28	1.31	1.39	1.52	1.06	1.16	-
Toth†	/mLg^{-1}	156.8	109.6	150.5	188.4	84.2	156.8	182.1	-
	/x_L	4.16	2.93	4.08	5.10	2.33	4.38	6.24	-
	/wt%$_L$	1.39%	0.98%	1.34%	1.67%	0.75%	1.39%	1.61%	-
	/k	0.241	0.226	0.189	0.240	0.289	0.190	0.215	-
	/m	0.697	0.593	0.674	0.499	0.385	0.825	0.735	-
GOOF‡$_{Langmuir}$		2.2	1	3.6	85.7	1	1.8	10.3	-
GOOF$_{GeneralisedFreundlich}$		1.5	6.4	3.4	4	1.5	1	2.4	-
GOOF$_{Toth}$		1	9.1	1	1	2.4	1.1	1	-

† Fitted values relate to values of pressure given in atm.

‡ A measure of the relative goodness-of-fit (GOOF) of the models for each compound was obtained by normalised sum of the square deviation of the experimental and fitted data.

Table S3. Summary of nitrogen sorption data for $\mathbf{A_M}$ and H-ZSM-5 at 77 K.

Compound		$\mathbf{A_{Mn}}$	$\mathbf{A_{Fe}}$	$\mathbf{A_{Co}}$	$\mathbf{A_{Ni}}$	$\mathbf{A_{Cu}}$	$\mathbf{A_{Zn}}$	$\mathbf{A_{Cd}}$	**H-ZSM-5**
Molar Mass		594.9	597.6	606.9	606.2	620.7	626.2	767.3	5767.8
Dehydration Temperature / K		423	428	393	413	373	373	373	443
Analysis Mass /g		0.077	0.2068	0.142	0.081	0.101	0.096	0.119	0.103
Measured Uptake at 0.9 P/P$_o$	/mLg^{-1}	200.1	93.34	191.3	199.7	125.7	175.0	172.6	116
	/x	5.32	2.49	5.18	5.40	3.48	4.90	5.91	-
	/wt%	20.0%	10.5%	19.31%	19.99%	13.59%	20.31%	17.75%	12.7%
N_2 Micropore capacity	/mLg^{-1}	190	89.6	181	172	119	178	164	101
	/x	5.06	2.39	4.91	4.66	3.29	4.80	5.60	-
	/wt%	19.2%	10.1%	18.5%	17.7%	13.0%	17.7%	17.0%	11.2%
Calculated Surface Area /m$_2$g^{-1}		756	350	719	668	478	697	667	385

Table S4. Hydrogen sorption data for $\mathbf{A_{Mn}}$ at 77 K and fitted model isotherms.

P	**Volume**		**Experimental Uptake**			**Langmuir**		**Generalised-Freundlich**		**Toth**	
atm	mL	mLg^{-1}	$mmolg^{-1}$	*x*	wt%	*x*	wt%	*x*	wt%	*x*	wt%
0.004643	0.850941	3.552	0.16	0.09	0.03%	0.09	0.03%	0.13	0.05%	0.13	0.04%
0.044968	7.20226	30.060	1.34	0.80	0.27%	0.74	0.25%	0.79	0.27%	0.83	0.28%
0.095695	11.7780	49.157	2.19	1.31	0.44%	1.28	0.43%	1.27	0.43%	1.31	0.44%
0.196987	16.9206	70.620	3.15	1.88	0.63%	1.90	0.64%	1.84	0.62%	1.87	0.63%
0.298184	19.9159	83.121	3.71	2.21	0.74%	2.25	0.76%	2.18	0.73%	2.20	0.74%
0.407207	22.0802	92.154	4.11	2.45	0.82%	2.49	0.84%	2.43	0.82%	2.44	0.82%
0.499663	23.4456	97.853	4.37	2.60	0.87%	2.63	0.88%	2.58	0.87%	2.60	0.87%
0.602746	24.6227	102.766	4.59	2.73	0.92%	2.75	0.92%	2.71	0.91%	2.73	0.92%
0.707239	25.5863	106.788	4.77	2.84	0.95%	2.84	0.95%	2.82	0.95%	2.84	0.95%
0.811621	26.3290	109.887	4.91	2.92	0.98%	2.91	0.98%	2.90	0.97%	2.93	0.98%
0.913537	26.8710	112.149	5.01	2.98	1.00%	2.96	0.99%	2.97	1.00%	3.00	1.01%
0.999400	27.2667	113.801	5.08	3.02	1.01%	3.00	1.01%	3.02	1.01%	3.06	1.03%
0.888919	26.7337	111.576	4.98	2.96	0.99%						
0.784963	26.1336	109.072	4.87	2.90	0.97%						
0.685467	25.3748	105.905	4.73	2.81	0.94%						
0.588368	24.4330	101.974	4.55	2.71	0.91%						
0.493638	23.3309	97.374	4.35	2.59	0.87%						
0.400091	21.9128	91.456	4.08	2.43	0.82%						
0.293944	19.7515	82.435	3.68	2.19	0.74%						
0.191428	16.5820	69.207	3.09	1.84	0.62%						
0.095978	11.7477	49.030	2.19	1.30	0.44%						
0.052795	7.84303	32.734	1.46	0.87	0.29%						
0.016914	2.6942	11.245	0.50	0.30	0.10%						

Table S5. Hydrogen sorption data for $\mathbf{A_{Fe}}$ at 77 K and fitted model isotherms.

P	**Volume**		**Experimental Uptake**			**Langmuir**		**Generalised-Freundlich**		**Toth**	
atm	mL	mLg^{-1}	$mmolg^{-1}$	*x*	wt%	*x*	wt%	*x*	wt%	*x*	wt%
0.006402	0.773546	3.507	0.16	0.09	0.03%	0.10	0.03%	0.17	0.06%	0.16	0.06%
0.051653	5.25701	23.831	1.06	0.64	0.21%	0.62	0.21%	0.68	0.23%	0.71	0.24%
0.102991	8.12058	36.811	1.64	0.98	0.33%	0.98	0.33%	0.99	0.33%	1.02	0.34%
0.203774	11.2423	50.962	2.28	1.36	0.46%	1.37	0.46%	1.34	0.45%	1.35	0.45%
0.300060	12.9595	58.747	2.62	1.57	0.53%	1.58	0.53%	1.54	0.52%	1.55	0.52%
0.406831	14.2163	64.444	2.88	1.72	0.58%	1.73	0.58%	1.70	0.57%	1.69	0.57%
0.513835	15.0880	68.395	3.05	1.82	0.61%	1.83	0.61%	1.81	0.61%	1.80	0.60%
0.616641	15.6594	70.985	3.17	1.89	0.63%	1.90	0.64%	1.89	0.63%	1.88	0.63%
0.700854	16.0832	72.907	3.25	1.95	0.65%	1.94	0.65%	1.95	0.65%	1.94	0.65%
0.800488	16.4991	74.792	3.34	2.00	0.67%	1.99	0.67%	2.00	0.67%	1.99	0.67%
0.902870	16.8282	76.284	3.41	2.04	0.68%	2.02	0.68%	2.05	0.69%	2.04	0.68%
0.999400	17.0807	77.428	3.46	2.07	0.69%	2.05	0.69%	2.09	0.70%	2.08	0.70%
0.882485	16.7611	75.980	3.39	2.03	0.68%						
0.791303	16.4614	74.621	3.33	1.99	0.67%						
0.702482	16.0921	72.947	3.26	1.95	0.65%						
0.587678	15.5025	70.274	3.14	1.87	0.63%						
0.486026	14.8591	67.358	3.01	1.80	0.60%						
0.388203	13.9913	63.424	2.83	1.69	0.57%						
0.294183	12.8528	58.263	2.60	1.55	0.52%						
0.190794	10.8407	49.142	2.19	1.31	0.44%						
0.101751	8.03761	36.435	1.63	0.97	0.33%						
0.054290	5.38677	24.419	1.09	0.65	0.22%						
0.014258	1.5257	6.916	0.31	0.18	0.06%						

Table S6. Hydrogen sorption data for $\mathbf{A_{Co}}$ at 77 K and fitted model isotherms.

P	Volume		Experimental Uptake			Langmuir		Generalised-Freundlich		Toth	
atm	mL	mLg^{-1}	$mmolg^{-1}$	*x*	wt%	*x*	wt%	*x*	wt%	*x*	wt%
0.005101	0.831117	5.732	0.26	0.16	0.05%	0.14	0.05%	0.25	0.08%	0.20	0.07%
0.053929	6.08717	41.980	1.87	1.14	0.38%	1.06	0.35%	1.16	0.38%	1.15	0.38%
0.101654	8.56682	59.082	2.64	1.60	0.53%	1.57	0.52%	1.60	0.53%	1.60	0.53%
0.201091	11.3874	78.534	3.51	2.13	0.70%	2.16	0.71%	2.11	0.70%	2.12	0.70%
0.296975	12.9618	89.392	3.99	2.42	0.80%	2.46	0.81%	2.40	0.79%	2.40	0.79%
0.404231	14.1145	97.341	4.35	2.64	0.87%	2.67	0.88%	2.62	0.86%	2.62	0.86%
0.512903	14.9264	102.941	4.60	2.79	0.92%	2.81	0.92%	2.78	0.91%	2.78	0.91%
0.616223	15.4572	106.601	4.76	2.89	0.95%	2.90	0.96%	2.89	0.95%	2.89	0.95%
0.700293	15.8444	109.272	4.88	2.96	0.97%	2.96	0.97%	2.97	0.98%	2.96	0.98%
0.800176	16.2265	111.907	5.00	3.03	1.00%	3.02	0.99%	3.04	1.00%	3.04	1.00%
0.902770	16.5376	114.052	5.09	3.09	1.02%	3.07	1.01%	3.11	1.02%	3.10	1.02%
0.999400	16.7838	115.750	5.17	3.14	1.03%	3.10	1.02%	3.16	1.04%	3.16	1.04%
0.882305	16.4724	113.603	5.07	3.08	1.01%						
0.790867	16.1862	111.629	4.98	3.02	0.99%						
0.701223	15.8445	109.272	4.88	2.96	0.97%						
0.587707	15.3088	105.578	4.71	2.86	0.94%						
0.485628	14.7134	101.472	4.53	2.75	0.90%						
0.387899	13.9211	96.008	4.29	2.60	0.86%						
0.294312	12.9005	88.969	3.97	2.41	0.79%						
0.190729	11.0762	76.388	3.41	2.07	0.68%						
0.092693	8.07692	55.703	2.49	1.51	0.50%						
0.050903	5.70183	39.323	1.76	1.07	0.35%						
0.015448	1.9043	13.133	0.59	0.36	0.12%						

Table S7. Hydrogen sorption data for $\mathbf{A_{Ni}}$ at 77 K and fitted model isotherms.

P	**Volume**		**Experimental Uptake**			**Langmuir**		**Generalised-Freundlich**		**Toth**	
atm	mL	mLg^{-1}	$mmolg^{-1}$	*x*	wt%	*x*	wt%	*x*	wt%	*x*	wt%
0.005737	1.45836	10.149	0.45	0.27	0.09%	0.16	0.05%	0.31	0.10%	0.29	0.10%
0.050404	6.34303	44.141	1.97	1.19	0.40%	1.05	0.35%	1.17	0.39%	1.19	0.39%
0.098261	8.73808	60.808	2.71	1.65	0.54%	1.61	0.53%	1.62	0.54%	1.64	0.54%
0.199396	11.4609	79.756	3.56	2.16	0.71%	2.24	0.74%	2.16	0.71%	2.16	0.71%
0.310551	13.1988	91.850	4.10	2.49	0.82%	2.59	0.85%	2.51	0.83%	2.49	0.82%
0.404666	14.2634	99.258	4.43	2.69	0.89%	2.77	0.91%	2.70	0.89%	2.69	0.89%
0.507626	15.1840	105.665	4.72	2.86	0.94%	2.91	0.96%	2.86	0.94%	2.85	0.94%
0.607858	15.8429	110.250	4.92	2.98	0.98%	3.00	0.99%	2.99	0.98%	2.98	0.98%
0.711564	16.4371	114.385	5.11	3.10	1.02%	3.08	1.01%	3.09	1.02%	3.09	1.02%
0.808938	16.8510	117.265	5.24	3.17	1.04%	3.14	1.03%	3.17	1.04%	3.17	1.04%
0.914814	17.2099	119.763	5.35	3.24	1.07%	3.18	1.05%	3.24	1.07%	3.26	1.07%
0.991395	17.5682	122.256	5.46	3.31	1.09%	3.21	1.06%	3.29	1.08%	3.31	1.09%
0.894350	17.1388	119.268	5.32	3.23	1.06%						
0.798893	16.8098	116.978	5.22	3.17	1.04%						
0.685241	16.2907	113.366	5.06	3.07	1.01%						
0.595889	15.7655	109.711	4.90	2.97	0.98%						
0.487716	15.0062	104.427	4.66	2.83	0.93%						
0.387613	14.0684	97.901	4.37	2.65	0.87%						
0.291309	12.8972	89.751	4.01	2.43	0.80%						
0.200116	11.4703	79.821	3.56	2.16	0.71%						
0.102218	8.83820	61.505	2.75	1.66	0.55%						
0.053136	6.45694	44.933	2.01	1.22	0.40%						
0.016020	2.53707	17.655	0.79	0.48	0.16%						

Table S8. Hydrogen sorption data for $\mathbf{A_{Cu}}$ at 77 K and fitted model isotherms.

P	Volume		Experimental Uptake			Langmuir		Generalised-Freundlich		Toth	
atm	mL	mLg^{-1}	$mmolg^{-1}$	*x*	wt%	*x*	wt%	*x*	wt%	*x*	wt%
0.008714	0.688383	3.610	0.16	0.10	0.03%	0.08	0.03%	0.17	0.06%	0.16	0.05%
0.043897	2.75075	14.424	0.64	0.40	0.13%	0.34	0.11%	0.41	0.13%	0.40	0.13%
0.102075	4.3763	22.949	1.02	0.64	0.21%	0.58	0.19%	0.61	0.20%	0.59	0.19%
0.206912	5.7757	30.287	1.35	0.84	0.27%	0.81	0.26%	0.79	0.26%	0.77	0.25%
0.318593	6.47509	33.954	1.52	0.94	0.30%	0.94	0.30%	0.91	0.29%	0.89	0.29%
0.404528	6.86110	35.979	1.61	1.00	0.32%	1.00	0.32%	0.97	0.31%	0.95	0.31%
0.505916	7.21787	37.849	1.69	1.05	0.34%	1.05	0.34%	1.03	0.33%	1.01	0.33%
0.609769	7.46770	39.159	1.75	1.09	0.35%	1.09	0.35%	1.07	0.35%	1.07	0.35%
0.710264	7.67353	40.239	1.80	1.12	0.36%	1.12	0.36%	1.11	0.36%	1.11	0.36%
0.813366	7.79942	40.899	1.83	1.13	0.37%	1.14	0.37%	1.14	0.37%	1.15	0.37%
0.914971	7.86061	41.220	1.84	1.14	0.37%	1.16	0.38%	1.17	0.38%	1.18	0.38%
0.999400	7.85237	41.177	1.84	1.14	0.37%	1.17	0.38%	1.18	0.38%	1.20	0.39%
0.904752	7.85477	41.189	1.84	1.14	0.37%						
0.800621	7.78422	40.819	1.82	1.13	0.37%						
0.697955	7.64995	40.115	1.79	1.11	0.36%						
0.596995	7.43798	39.004	1.74	1.08	0.35%						
0.498176	7.19301	37.719	1.68	1.05	0.34%						
0.401565	6.84778	35.909	1.60	1.00	0.32%						
0.285272	6.26563	32.856	1.47	0.91	0.29%						
0.200787	5.69352	29.856	1.33	0.83	0.27%						
0.098731	4.28011	22.444	1.00	0.62	0.20%						
0.050255	2.92252	15.325	0.68	0.42	0.14%						
0.016697	1.14327	5.995	0.27	0.17	0.05%						

Table S9. Hydrogen sorption data for $\mathbf{A_{Zn}}$ at 77 K and fitted model isotherms.

P	**Volume**		**Experimental Uptake**			**Langmuir**		**Generalised-Freundlich**		**Toth**	
atm	mL	mLg^{-1}	$mmolg^{-1}$	*x*	wt%	*x*	wt%	*x*	wt%	*x*	wt%
0.009239	1.60158	7.565	0.34	0.21	0.07%	0.23	0.07%	0.26	0.08%	0.27	0.09%
0.047320	7.6259	36.022	1.61	1.01	0.32%	0.95	0.31%	0.98	0.31%	1.01	0.32%
0.097017	12.0199	56.778	2.53	1.59	0.51%	1.57	0.50%	1.57	0.50%	1.59	0.51%
0.207557	17.4367	82.365	3.68	2.30	0.74%	2.33	0.74%	2.31	0.74%	2.31	0.74%
0.300429	20.0707	94.807	4.23	2.65	0.85%	2.68	0.86%	2.66	0.85%	2.65	0.85%
0.407523	22.1085	104.433	4.66	2.92	0.93%	2.95	0.94%	2.93	0.93%	2.92	0.93%
0.499239	23.4044	110.555	4.94	3.09	0.99%	3.11	0.99%	3.09	0.99%	3.08	0.98%
0.601915	24.5190	115.820	5.17	3.24	1.03%	3.24	1.03%	3.23	1.03%	3.22	1.03%
0.707916	25.4033	119.997	5.36	3.35	1.07%	3.34	1.06%	3.34	1.06%	3.33	1.06%
0.812140	26.0233	122.925	5.49	3.44	1.09%	3.42	1.09%	3.42	1.09%	3.42	1.09%
0.913774	26.4505	124.943	5.58	3.49	1.11%	3.48	1.11%	3.49	1.11%	3.49	1.11%
0.999400	26.6827	126.040	5.63	3.52	1.12%	3.52	1.12%	3.54	1.13%	3.55	1.13%
0.891426	26.3587	124.510	5.56	3.48	1.11%						
0.787854	25.8787	122.242	5.46	3.42	1.09%						
0.688360	25.2359	119.206	5.32	3.33	1.06%						
0.592335	24.4075	115.293	5.15	3.22	1.03%						
0.497525	23.3766	110.423	4.93	3.09	0.98%						
0.390712	21.7811	102.887	4.59	2.88	0.92%						
0.294321	19.8824	93.918	4.19	2.63	0.84%						
0.193727	16.7358	79.054	3.53	2.21	0.71%						
0.098115	12.0637	56.985	2.54	1.59	0.51%						
0.054310	8.19542	38.712	1.73	1.08	0.35%						
0.016386	2.65742	12.553	0.56	0.35	0.11%						

Table S11. Hydrogen sorption data for $\mathbf{A_{Cd}}$ at 77 K and fitted model isotherms.

P	**Volume**		**Experimental Uptake**			**Langmuir**		**Generalised-Freundlich**		**Toth**	
atm	mL	mLg^{-1}	$mmolg^{-1}$	*x*	wt%	*x*	wt%	*x*	wt%	*x*	wt%
0.005544	0.82125	5.457	0.24	0.19	0.05%	0.19	0.05%	0.27	0.07%	0.25	0.06%
0.048455	6.2503	41.530	1.85	1.42	0.37%	1.30	0.34%	1.40	0.37%	1.41	0.37%
0.093187	9.3059	61.833	2.76	2.12	0.55%	2.05	0.54%	2.08	0.54%	2.10	0.55%
0.204210	13.4062	89.078	3.98	3.05	0.80%	3.10	0.81%	3.06	0.80%	3.06	0.80%
0.304227	15.5721	103.469	4.62	3.54	0.92%	3.62	0.94%	3.56	0.93%	3.55	0.92%
0.400865	16.9894	112.886	5.04	3.87	1.01%	3.94	1.02%	3.88	1.01%	3.87	1.01%
0.505401	18.1440	120.558	5.38	4.13	1.07%	4.18	1.09%	4.14	1.08%	4.13	1.07%
0.613675	19.0098	126.311	5.64	4.33	1.12%	4.36	1.13%	4.34	1.13%	4.34	1.13%
0.710745	19.6701	130.698	5.83	4.48	1.16%	4.48	1.16%	4.48	1.16%	4.48	1.16%
0.797490	20.1914	134.162	5.99	4.60	1.19%	4.57	1.19%	4.59	1.19%	4.59	1.19%
0.913701	20.7315	137.751	6.15	4.72	1.22%	4.66	1.21%	4.71	1.22%	4.71	1.22%
0.998458	21.0799	140.066	6.25	4.80	1.24%	4.72	1.23%	4.78	1.24%	4.79	1.24%
0.882748	20.5877	136.795	6.11	4.69	1.22%						