Supplementary information for

Interaction of hydrogen with accessible metal sites in the metal-organic frameworks M_2(dhtp) (CPO-27-M; M=Ni, Co, Mg)

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Experimental details

The inelastic neutron scattering experiments require gram amounts of material, which were obtained in single batches by using scaled-up synthetic procedures. The ease with which this was possible indicates that the materials are in all likelihood facile to produce on an industrial scale.

Synthesis of CPO-27-Ni ($Ni(C_4HO_3)(H_2O)\cdot 4H_2O$). A solution of 2,5-dihydroxyterephthalic acid (2.972 g, 15 mmol) in THF (50 mL) and a solution of nickel(II) acetate tetrahydrate (7.466 g, 30 mml) in water (50 mL) were combined in the Teflon lined inlet of an autoclave with a volume of 200 mL. The autoclave was sealed and heated in a pre-heated oven at 110°C for 3 days. The yellow fine crystalline product was recovered by filtration and washed with copious amounts of water. Yield: 6.461 g (28.1 mmol, 94%).

Synthesis of CPO-27-Co ($Co(C_4HO_3)(H_2O)\cdot 4H_2O$). A solution of 2,5-dihydroxyterephthalic acid (0.743 g, 3.75 mmol) in THF (50 mL) and a solution of cobalt(II) acetate tetrahydrate (1.868 g, 7.5 mml) in water (25 mL) were combined in the Teflon lined inlet of an autoclave with a volume of 200 mL. The autoclave was sealed and heated in a pre-heated oven at 110°C for 3 days. The orange-red fine crystalline product was recovered by filtration and washed with copious amounts of water. Yield: 1.558 g (6.3 mmol, 84%).

Synthesis of CPO-27-Mg ($Mg(C_4HO_3)(H_2O)\cdot 4H_2O$). Magnesium acetate tetrahydrate (3.216 g, 15 mmol) and 2,5-dihydroxyterephthalic acid (1.486 g, 7.5 mmol) are put into the Teflon lined inlet of an autoclave with 200 mL volume. N-Methylpyrrolidone (90 mL) and water (10 mL) are added. The mixture is homogenized and the autoclave sealed. The autoclave is heated in a pre-heated oven at 120°C for 24 h. A bright yellow fine crystalline substance was obtained by filtration. The product was washed with copious amounts of methanol. Yield: 1.502 g (minimum of 7.1 mmol, 47%, because the methanol treatment has possibly removed some of the water in the channels).

The identity of the materials was ascertained by comparison with the known powder X-ray diffraction patterns. Accessibility of the void volume was tested by nitrogen gas adsorption. It should be noted that the individual CPO-27 materials show significant differences in the activation procedure required to enable optimum access to the pore volume. The as-synthesized CPO-27-Ni material can be handled in ambient atmosphere and the full surface area is accessible after activation in a dynamic vacuum at temperatures as low as 110°C. In contrast, we obtained the high surface area of CPO-27-Mg reported herein only by handling of the material in inert atmosphere after synthesis, solvent exchange in methanol, and application of temperatures above 200°C in dynamic vacuum.

Gas adsorption measurements

Nitrogen and hydrogen adsorption isotherms up to 102 kPa were measured with a BELSORP-max instrument which is equipped with a low pressure transducer and a turbomolecular pump, enabling adsorption measurements from extremely low pressures ($p/p_0 = 10^{-8}$). Prior to measurement the samples were activated in a dynamic vacuum, serially using an external pre-treatment station and a furnace to treat the sample at the sample port of the instrument. Maximum pre-treatment temperatures vary in dependence of the sample. CPO-27-Ni and CPO-27-Co were treated at 150°C, and CPO-27-Mg was treated at 200°C.

Nitrogen gas sorption at 77 K was performed to ascertain the successful activation of the materials (Figure S1). Values for Langmuir surface area, BET surface area and pore volume are listed in Table S1. They correspond closely to the results of a calculation of the area assuming a plain cylinder shape along the *c* axis of the empty crystal structure and to pore volumes calculated from crystallographic data of the desolvated structures, indicating that the materials have indeed been fully activated (see Table S1).

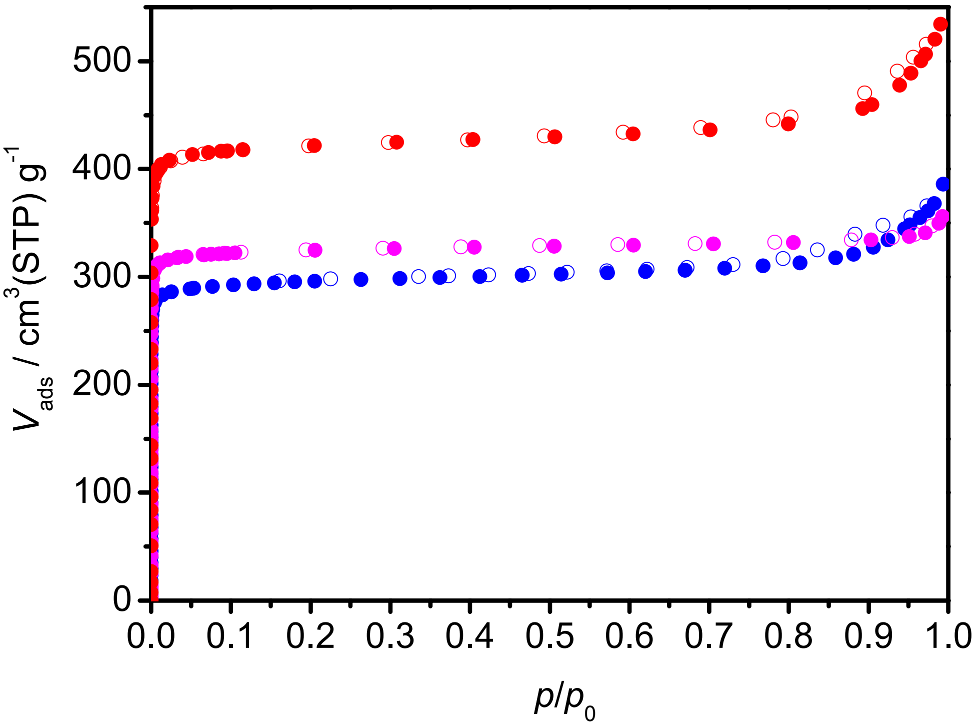


Figure S1. Nitrogen sorption isotherms of Mg_2(dhtp) (red), Co_2(dhtp) (magenta), and Ni_2(dhtp) (blue) at 77 K. Adsorption: closed symbols, desorption: open symbols.

The hydrogen adsorption measurements at 77.35 K and 87.3 K (Figure S2) were performed in low pressure mode in which the externally pre-treated samples were heated at 150°C (CPO-27-Ni) or 220°C (CPO-27-Co and Mg) in dynamic vacuum at the instrument until the leak rate was below $5 \cdot 10^{-3}$ Pa min^{-1}. All measurements were performed using a third, empty sample cell as dead volume reference cell to correct for the change in level of liquid nitrogen (or argon).

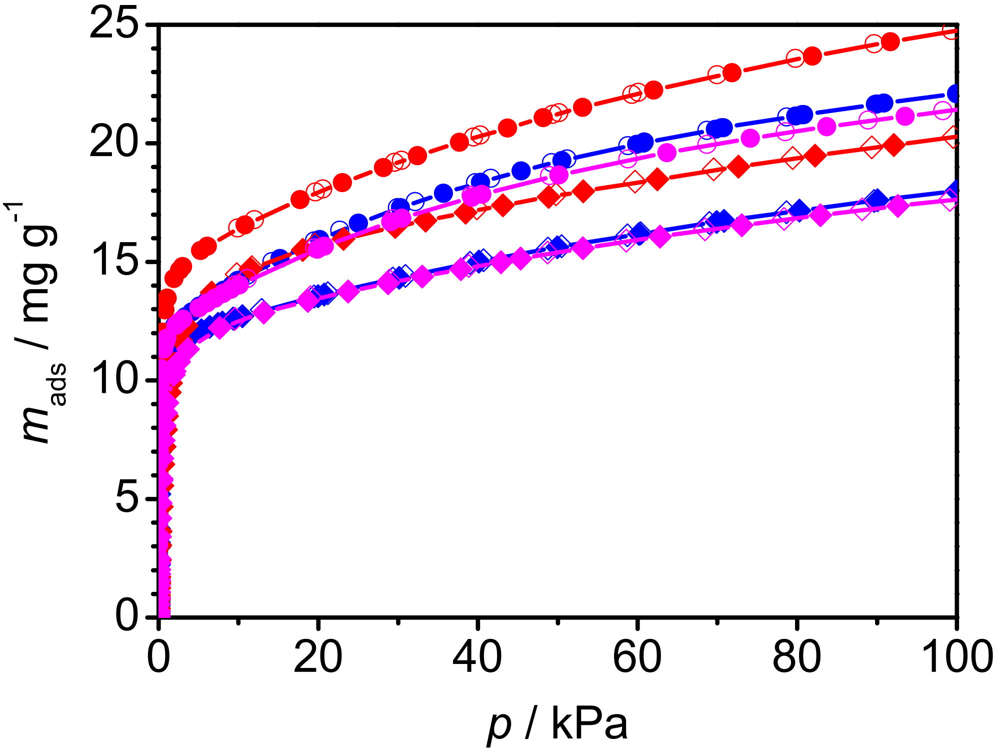
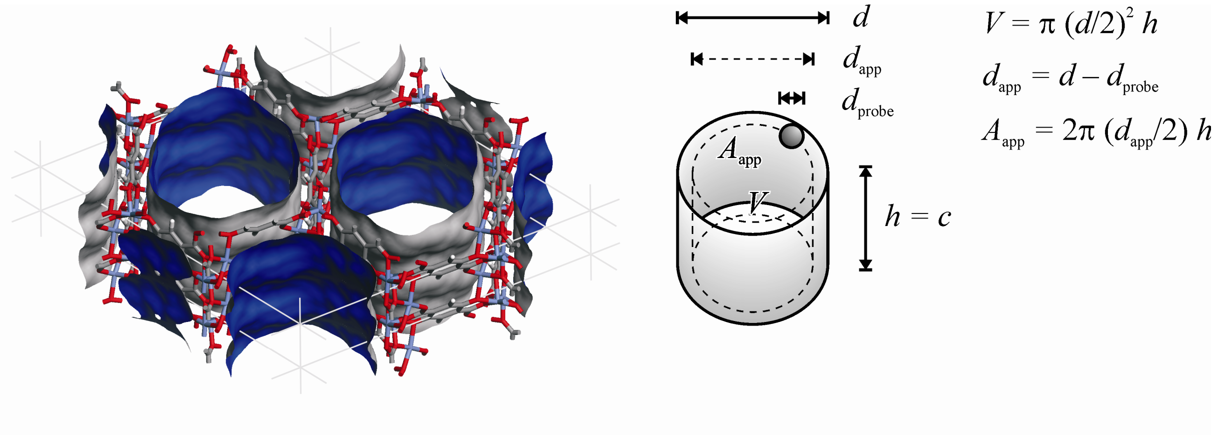


Figure S2. Hydrogen adsorption isotherms at 77 (circles) and 87 K (diamonds) of CPO-27-Ni (blue), CPO-27-Co (magenta) and CPO-27-Mg (red). Adsorption curve: filled symbols, desorption curves: open symbols.

Approximate deduction of the pore diameter and surface area

The pores of the CPO-27 materials are channels with a corrugated surface. They can be approximated by a cylinder with height of the *c* axis of the unit cell. There are three channels per unit cell. The volume of each therefore is 1/3 of the total void volume calculated with the help of PLATON on basis of the crystal structure determination of the activated compound (for CPO-27-Ni and Co) or the as-synthesized structure after hypothetical removal of the solvent molecules (for CPO-27-Mg). From the pore volume the pore diameter d can be calculated with the help of the formula in Figure S3. The apparent diameter d_{app} can be derived from d by subtraction of the diameter of the probe molecule d_{probe}. Finally, the surface area of the curved cylinder wall can be calculated. Comparison with the experimental values reveals a good agreement (Table S1), most importantly for the pore volume which was calculated using crystal structure data.



$$V = \pi\,(d/2)^2\,h$$
$$d_{\text{app}} = d - d_{\text{probe}}$$
$$A_{\text{app}} = 2\pi\,(d_{\text{app}}/2)\,h$$

Figure S3. Calculation of pore diameter and surface area using a cylindrical approximation for the pore shape in CPO-27.

Table S1. Calculated and experimental values describing the texture of CPO-27-M (M = Ni, Co, and Mg).

Compound[a]	$Ni(C_4HO_3)$	$Co(C_4HO_3)$	$Mg(C_4HO_3)$
M / g mol^{-1}	155.7	156.0	121.4
c / Å	6.770	6.806	6.759
Z / formula units per unit cell	18	18	18
Unit cell volume / Å^3	3898	3965	3964
Density / g cm^{-3}	1.19	1.18	0.92
Pore volume / Å^3 [b]	2240	2359	2370
Pore volume / cm^3 g^{-1} [c]	0.48	0.51	0.65
d / Å [d]	11.85	12.13	12.20
d_{app} / Å [d]	8.25	8.53	8.60
Calculated surface area / m^2 g^{-1} [e]	1131	1173	1509
Experimental BET surface area / m^2 g^{-1}	1218	1341	1743
Exp. Langmuir surface area / m^2 g^{-1}	1312	1432	1876
Exp. BET pore volume (p/p_0 = 0.5) / cm^3 g^{-1}	0.47	0.51	0.66

a) Crystallographic data from ref. 1 for CPO-27-Ni, ref. 2 for CPO-27-Co, and ref. 3 for CPO-27-Mg. b) Calculated by PLATON.[4] c) Calculated from the pore volume and the mass per unit cell. d) Calculated using the equation in Figure S2. e) Calculated using the equation for A_{app} in Figure S2 and transformed to the given units.

Reversibility of hydrogen adsorption in CPO-27-Ni

The reversibility studies of hydrogen adsorption were performed on a BELSORP-HP instrument equipped with an additional precision pressure transducer for the pressure range below 100 kPa. The experimental setup of this instrument allows performing consecutive adsorption measurement without intermittent warming of the sample, which would desorb the residual adsorbed hydrogen gas. Ultrahigh purity grade hydrogen (99.9995%) and helium (99.9999%) were used. The dead volume of the empty sample cell was determined using helium at 298 K and 77 K. The dead volume of the sample cell with sample was determined using helium gas at 298 K after activation of the sample. The CPO-27-Ni material was activated in a dynamic vacuum overnight at 200. The difference in volume and the sample mass was used to calculate the skeletal density of the activated sample. For the measurements at 77 K, the dead volume was calculated from the dead volume of the empty sample cell and the skeletal density and sample mass and a temperature correction factor.

There is no visible hysteresis between adsorption and desorption isotherm in Figure S2, which is commonly interpreted to mean that the hydrogen adsorption is easily reversible. However, in this case it is due to the fact that the measurement of the desorption curve is customarily stopped at pressures at which the metal site is still fully occupied. We found that it is, in fact, difficult to remove the final hydrogen molecule at 77 K. Even extended application of vacuum for 16 h did not fully restore the capacity of the material. For this, intermittent warming of the sample was necessary.

The reversibility of hydrogen adsorption was checked by running subsequent measurements with intermittent application of vacuum at the measurement temperature. This revealed that hydrogen cannot be removed quickly in this way (Figure S4). Evacuation for 20 min at 77 K appears to be insufficient to remove most of the hydrogen adsorbed on the metal. Even after evacuation for 16 h at 77K, the capacity is still less than 50% than in the first run, when the material was fully evacuated. Warming of the sample will recover the full surface area.

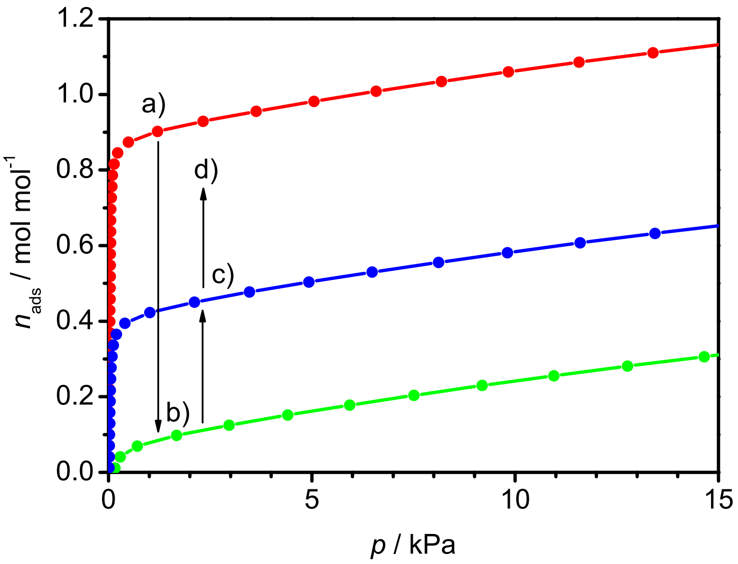


Figure S4. Variation in hydrogen adsorption in Ni$_2$(dhtp) at 77 K after

a) pre-treatment at 473 K for 1 h (sample had been activated before),
b) evacuation of sample from a) for 20 min. at 77 K, and
c) evacuation of sample from b) for 16 h at 77 K.
d) The surface area of the sample is fully recovered by removing occluded guest molecules by warming up as attested to by subsequent nitrogen adsorption (not shown).

Inelastic neutron scattering (INS) measurements

Samples of pre-activated CPO-27-Ni, CPO-27-Mg and CPO-27-Co were loaded in Al-scattering cells inside a He-filled glove bag and attached to appropriate centre sticks equipped with gas capillaries through which the materials were additionally degassed first at room temperatures until the pressure in each case reached values below 10^{-6} mbar using a turbomolecular pumping unit. The temperatures were then stepwise raised to 200°C for the Mg and Ni-samples and 220°C for the Co-sample. At these temperatures, degassing was carried out for about 6 hours resulting in residual pressures below 10^{-6} mbar at the pressure gauge of the pump. After cooling of the samples down to room temperature, INS spectra of the bare samples (without H_2) were taken at 1.5 K for the Ni and Mg-analogues, using the hybrid spectrometer FOCUS [5] at the SINQ facility, Switzerland. Incident wavelength of 2.0 Å was selected using the [004] reflection of a pyrolitic graphite monochromator. The Co-CPO material was measured on the time-of-flight chopper spectrometer TOFTOF [6] at the FRM II neutron source in Germany using incident neutrons with a wavelength of 2.1 Å. Hydrogen gas in situ dosing was performed using a previously described gas handling rig [7]. Various hydrogen loadings were accomplished and equilibrated at near 70 K. Then the samples were cooled down and the corresponding INS spectra measured. INS spectra taken with $1H_2$ per metal centre in the three CPO-27-analogs are shown in Figure S5. Figures S6 and S7 display spectra of the Ni- and Mg-analogues, respectively, measured at different temperatures and at a hydrogen loading of about 1 H_2 molecule per metal atom. The temperature dependence of the peak intensities on the energy gain side of the spectra clearly indicate the rotational nature of these excitations. The higher ortho-para conversion activity of the CPO-27-Ni as compared to the Mg-analogue is also clearly visible in Figs. S6 and S7.

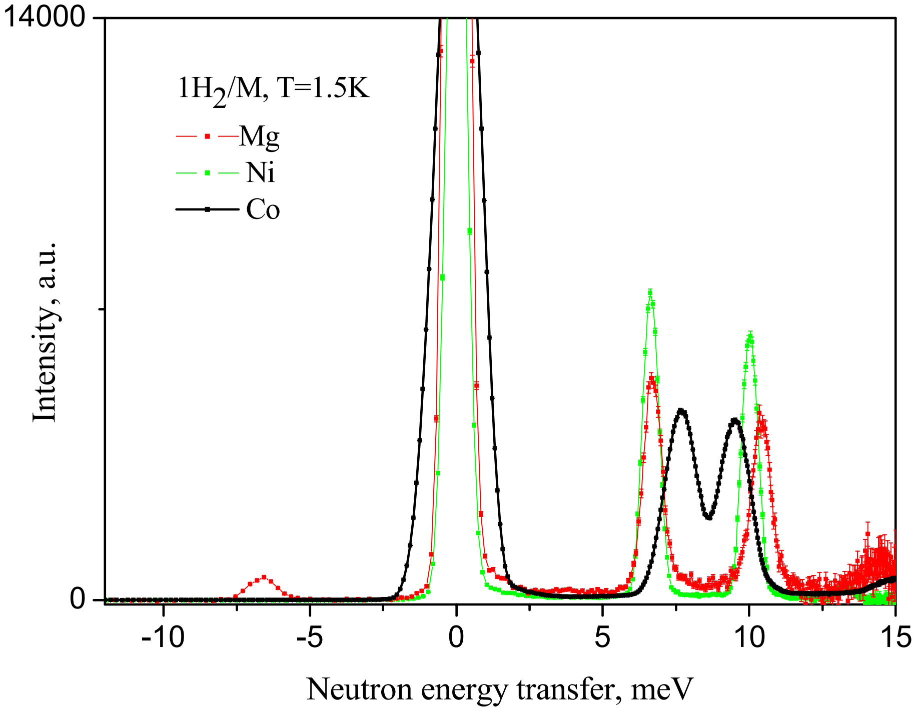


Figure S5. INS spectra for 0.5 H_2 per metal site in the Ni(green), Mg(red) and Co(black)-analogues of CPO-27. Spectra were collected at T = 1.5K. Positive values correspond to neutron energy loss.

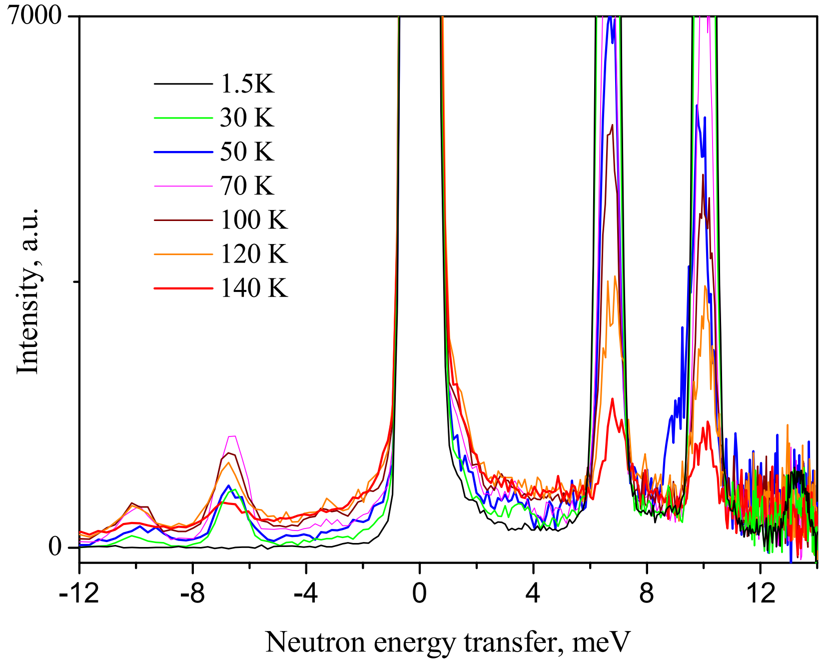


Figure S6. INS spectra of approximately $1H_2$ per metal center in CPO-27-Ni measured at different temperatures as indicated in the figure legend. At 1.5K, all of the adsorbed hydrogen is converted to the para ground state, J=0.

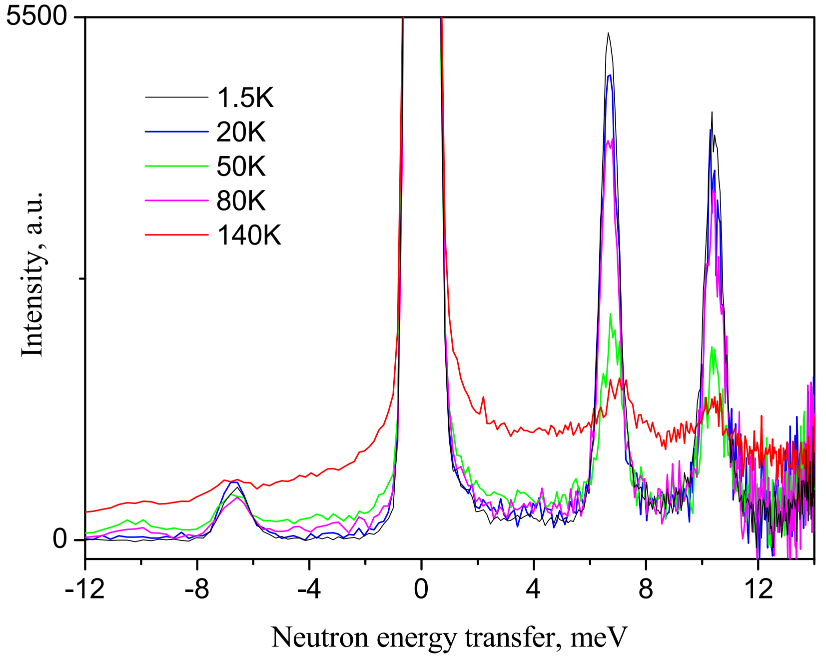


Figure S7. INS spectra of approximately $1H_2$ per metal center in CPO-27-Mg measured at different temperatures as indicated in the figure legend. Even at the lowest temperature, 1.5K, the adsorbed hydrogen, presumably on the Mg-site, remains trapped in the triplet ortho-J=1 state.

References

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