Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information to the Article: "Vapour Pressure Dependence and Thermodynamics of Cylindrical Metal-Organic Framework Mesoparticles: an ESEM Study"

Torsten K. Sievers, Caroline Genre*, Florent Bonnefond, Thomas Demars, Daniel Meyer, Renaud Podor.

Institut de Chimie Séparative de Marcoule; UMR 5257 CEA/CNRS/UM2/ENSCM; BP 17171; 30207 Bagnols-sur-Cèze Cedex, France.
*To whom correspondence should be addressed.

Email: caroline.genre@cea.fr

This file includes:

- IR spectra of DHBQ and Nd-DHBQ
- TGA/TDA curves for Nd-DHBQ
- Crystal structure of Nd-DHBQ MOF (3 figures)
- High resolution SEM image and small angle x-ray scattering
- Structure change due to reduced water vapour pressure at 12°C and 5°C
- Fitting procedure and fitting equation
- Relative humidity vs. temperature and pressure vs. temperature curves

Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

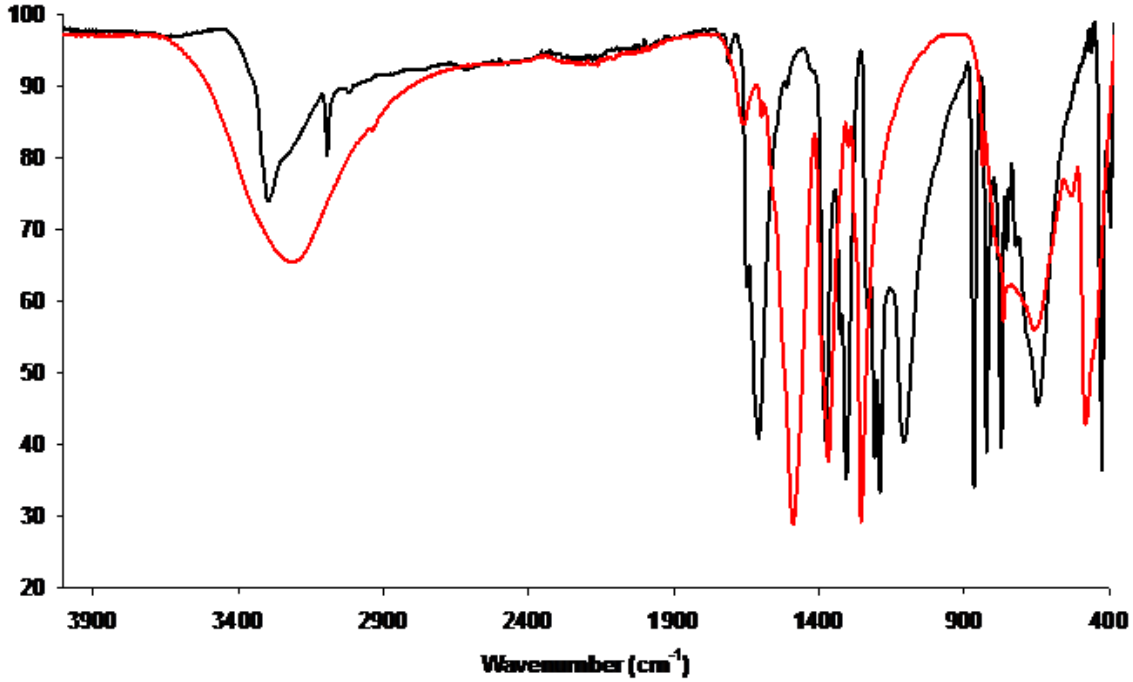

Figure S1. IR spectra of DHBQ (black) and $[Nd_2(DHBQ)_3(H_2O)_6] \cdot 18H_2O$ (red)

5

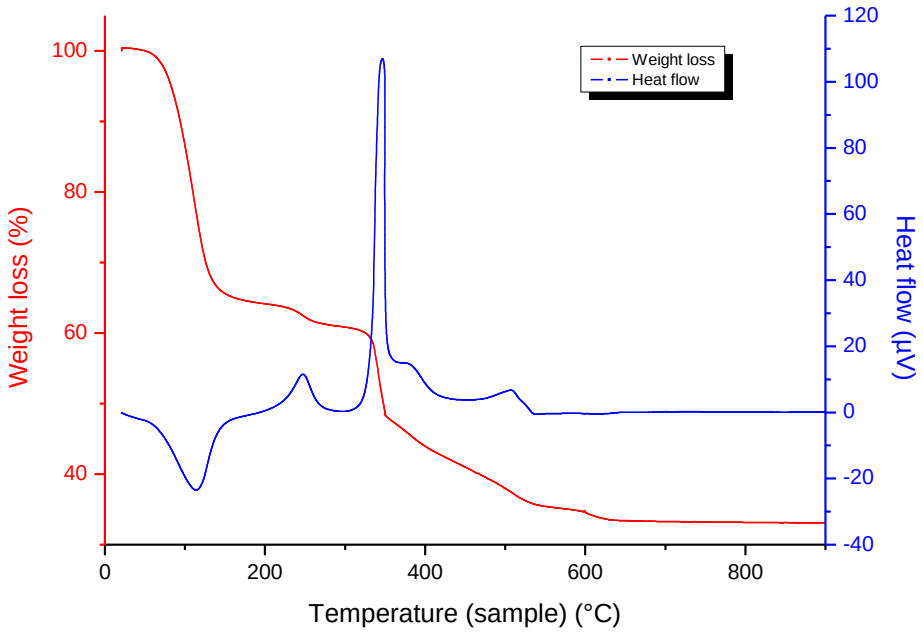

Figure S2. TGA/TDA curves of Nd-DHBQ with a heating rate of 5°C min-1 in a flowing air atmosphere

Crystal structure of $[Nd_2(DHBQ)_3(H_2O)_6] \cdot 18H_2O$ (Nd-DHBQ)

The crystal structure of the Nd-DHBQ compound presented in the article was derived from x-ray diffraction (XRD) patterns of the Nd-DHBQ powder and comparison of these XRD patterns with previously published data on similar compounds. The XRD patterns show a very strong similarity to the ones published by Abrahams et al. for the rhombohedral La, Ce, Gd, Y, Yb, and Lu-DHBQ crystal structures (*Chem. Comm.* 1996, 603-604 and *J. Chem. Soc.-Dalton Trans.* 2002, 1586-1594). Therefore, we assumed the Nd-DHBQ to be isostructural with Abrahams's compounds and calculated the size of the unit cell from our data accordingly. Due to the assumed isostructural relationship between the different materials, we have to maintain the same number of atoms in the unit cell and adjust their position only with respect to the size of the unit cell. Thus, we obtained a rhombohedra crystal structure for the Nd-DHBQ. To verify our hypothesis, we calculated the corresponding XRD powder pattern for the x-ray wavelength in the measurement, $\lambda = 1.54178$ Å. The measured and the simulated XRD powder patterns are shown together with the assignment of the major peaks in Figure S1.

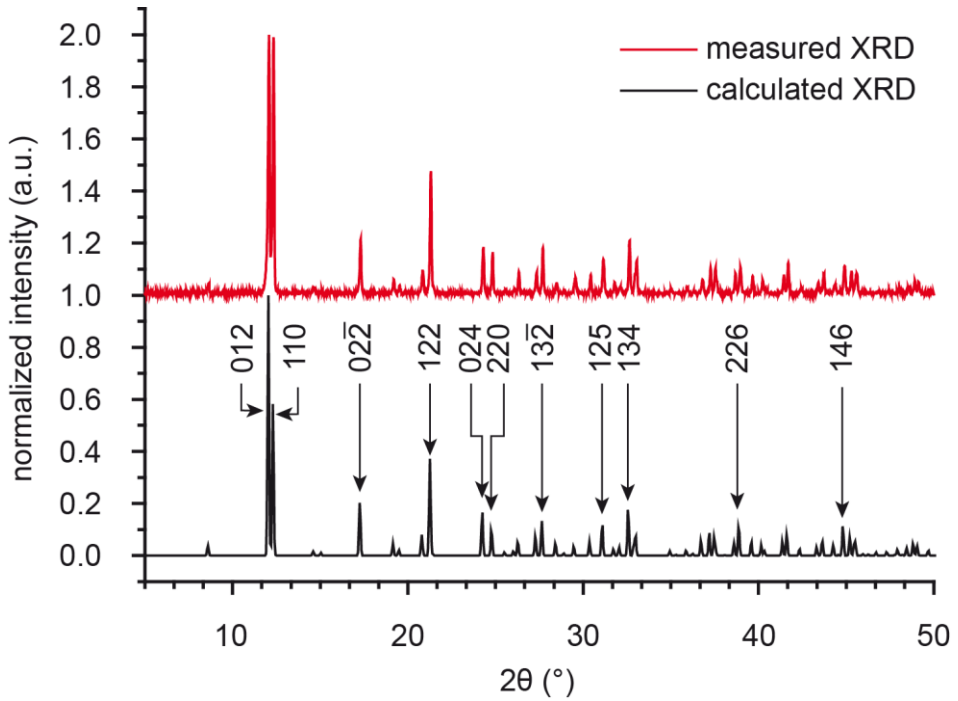

Figure S3. Calculated (black) and measured (red) X-ray diffraction (XRD) patterns of a powder of Nd-DHBQ are shown. The measured XRD pattern was obtained from a sample directly after drying under ambient condition, and the cell parameters were obtained through refinement with the APCM method. The calculated pattern was obtained from the crystal structure given above. In the measurement and the calculation we used Cu K_α ($\lambda = 1.54178$ Å) radiation. Unit cell parameters for Nd-DHBQ: Formula: $C_{18}H_{54}Nd_2O_{36}$; M: 1135.1 g/mol; T: 293(2) K; crystal system: trigonal; space group: R-3; a: 14.3510(18) Å; b: 14.3510(18) Å; c: 18.162(3) Å; α: 90°; β: 90°; γ: 120°;V: 3239.3(7) Å^3; ρ: 1.746 g/cm^3;

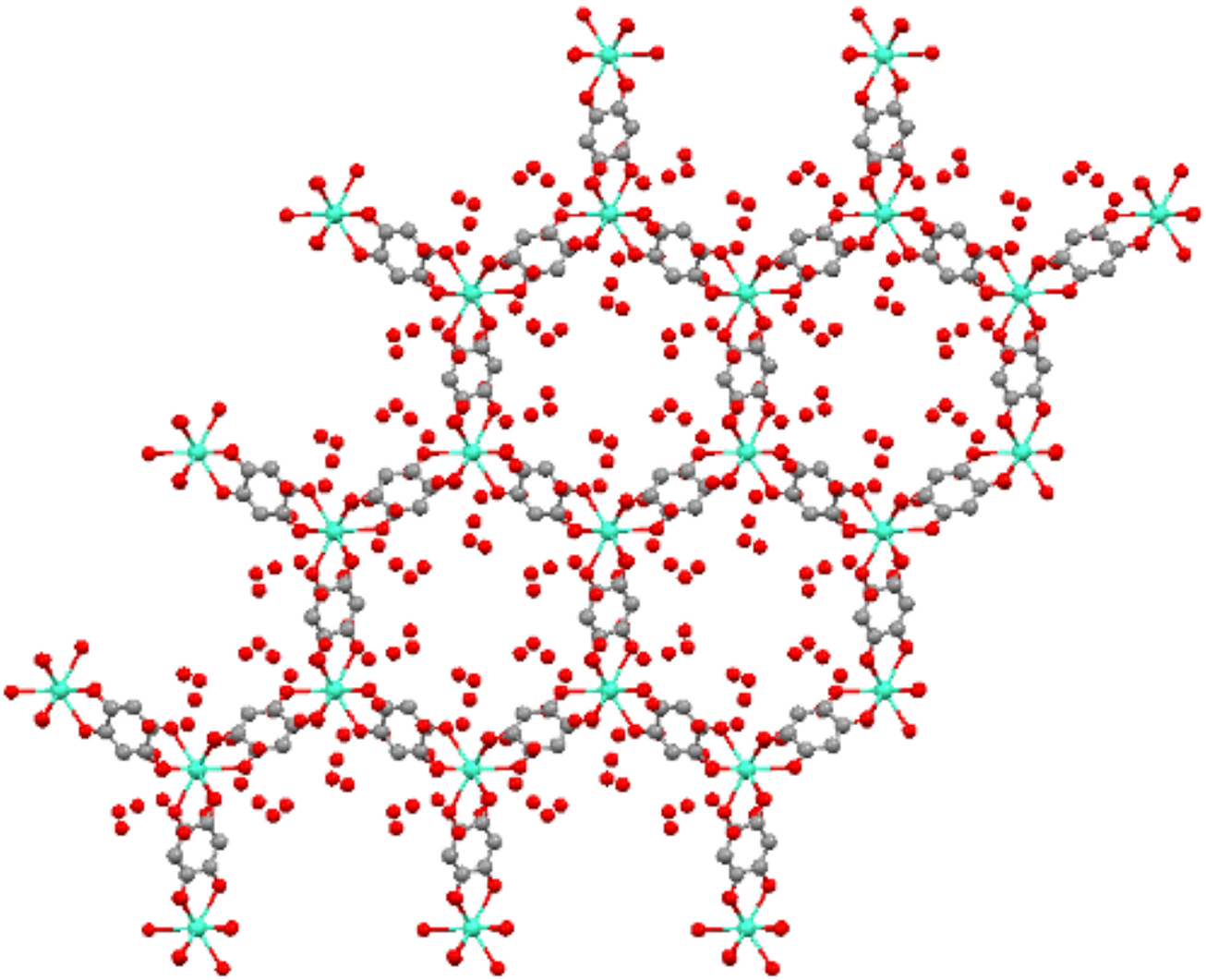

Figure S4. A view of the structure of $[Nd_2(DHBQ)_3(H_2O)_6]\cdot 18H_2O$ in the (001) plane, showing a polymeric sheet made of Nd ions and DHBQ ligands as well as water molecules laying underneath it. The hydrogen atoms are omitted for clarity.

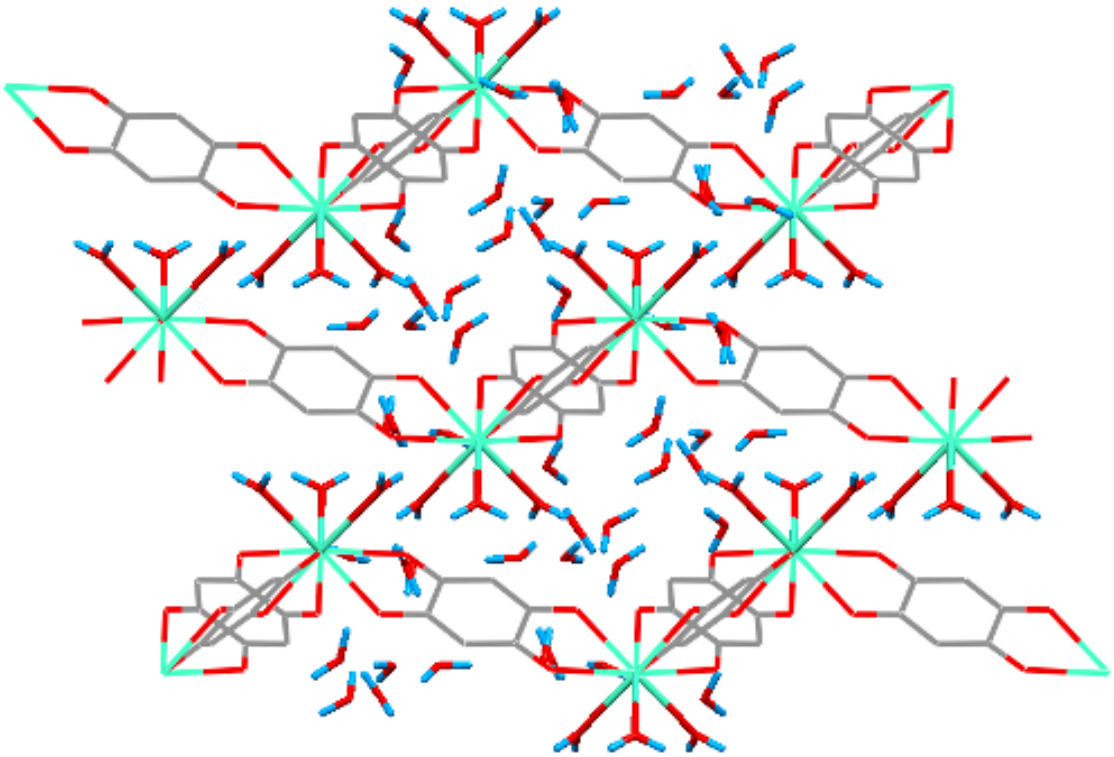

Figure S5. A view of the structure of $[Nd_2(DHBQ)_3(H_2O)_6]\cdot 18H_2O$ in the (100) plane, showing the water molecules lying between the polymeric sheets. The hydrogen atoms are represented in blue.

High resolution SEM image and small angle x-ray scattering

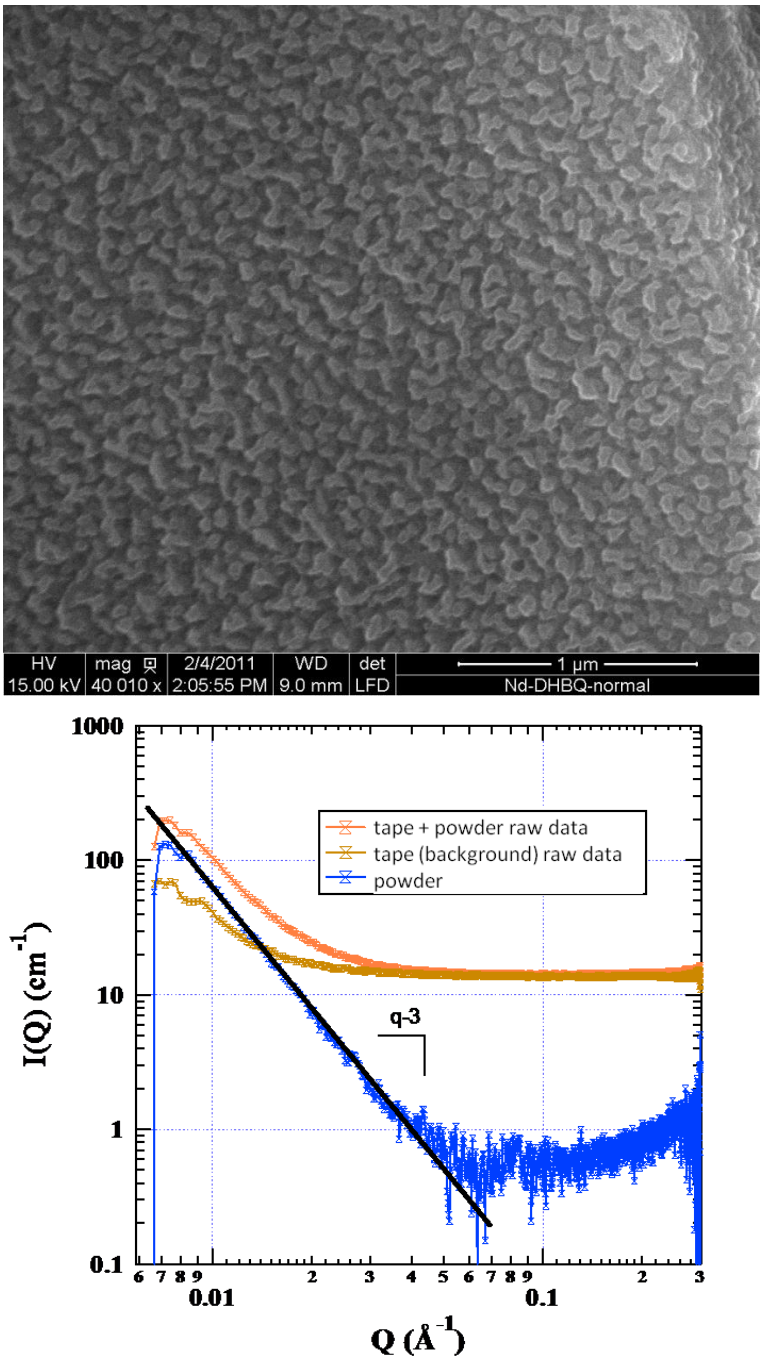

Figure S6. What is the substructure of Nd-DHBQ micro particles? SEM (left) and small angle x-ray scattering (right) suggest that the particles are composed of grains of several 10 nanometres.

Structure change due to reduced water vapour pressure

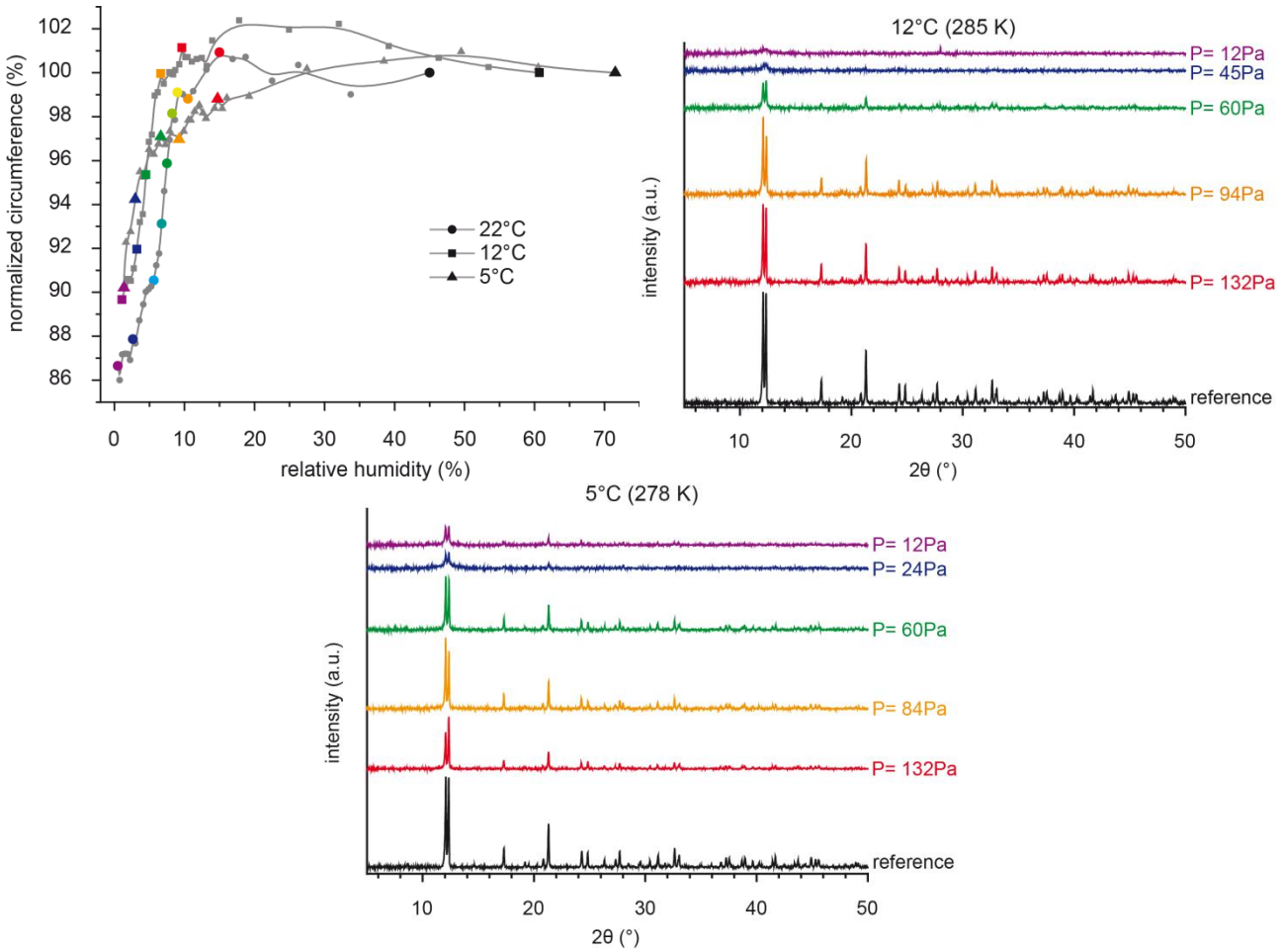

Figure S7. Top left: A change in circumference occurs during water vapour pressure reduction at 22, 12, and 5°C displayed by triangular, square and round symbols, respectively. The coloured symbols mark the relative humidity/water vapour pressure, at which samples were taken for XRD analysis. The resulting XRD patterns and the symbols have the same colour. The X-ray diffraction patterns are shown in the top left and at the bottom for the pressure reductions and 12 and 5°C, respectively. In both cases with reduced water vapour pressure, crystallinity is lost. The starting point and the end point of this loss depend on temperature.

Fitting procedure and fitting equation

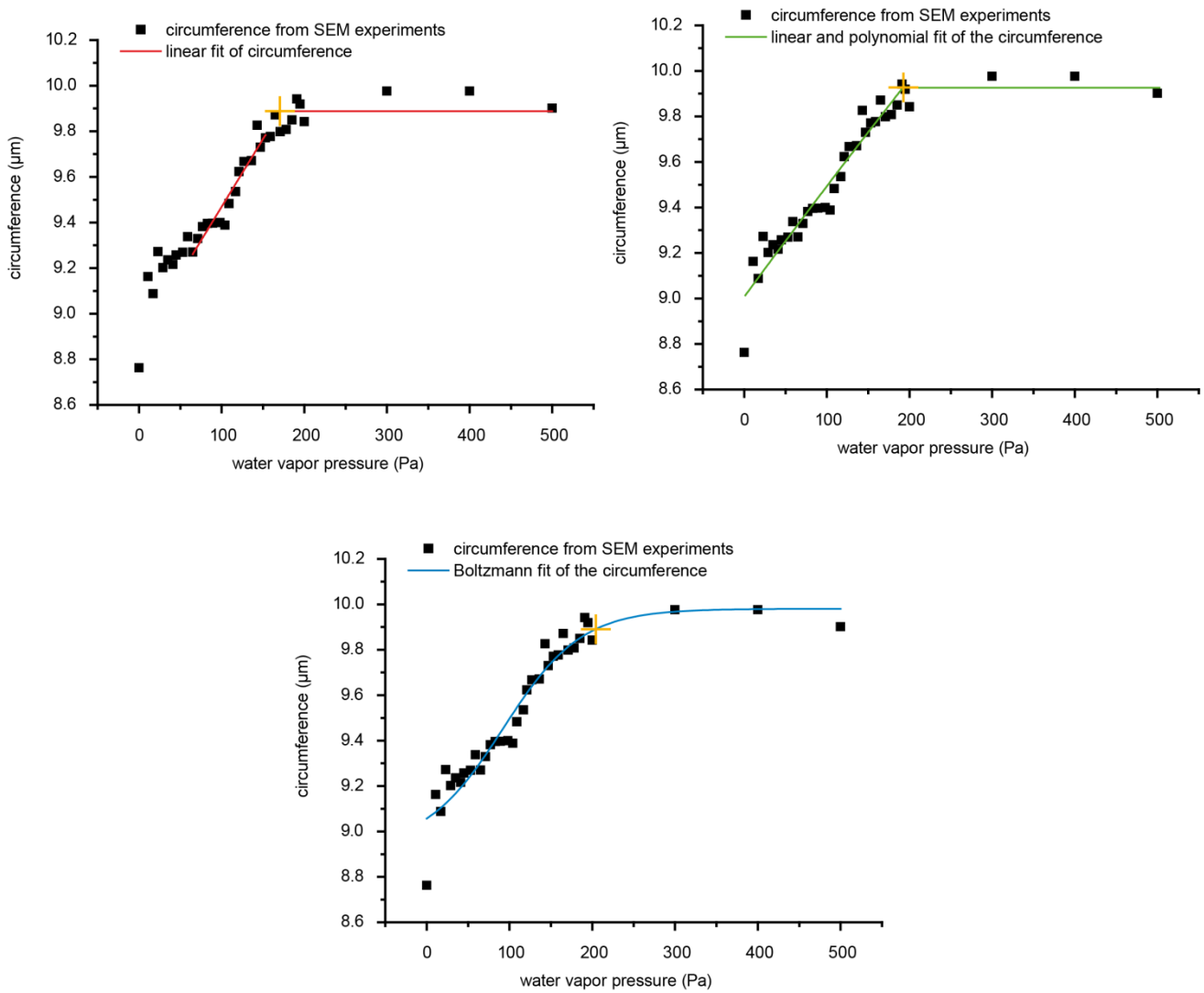

Figure S8. Three methods were applied to fit the particle size vs. pressure curve. Top left: two linear functions, one for the plateau region an one for the decrease. The starting point for the size change was determined from the intersection of the two functions. Top right: a linear function and a parabola are applied to fit the two regimes of the curve, plateau and size decrease, respectively. The starting point for the size change was determined from the left intersection of the two functions. Bottom: The sigmoid Boltzmann function (**eq. 1**) was used to fit the data and the transient pressure was determined by finding the point of the fit curve, at which 10% of the overall size change has occurred. In all graphs the transient pressure is marked by a yellow cross.

The following sigmoid Boltzmann function was used to fit the particle size vs. pressure curves:

$$y = A + \frac{(B-A)}{1+e^{\frac{(x-x0)}{dx}}}, \qquad \textbf{(1)}$$

with A being the lower plateau, B being the upper plateau, x0 being x value to the point exactly in the middle between the two plateaus and with dx being the slope in this point.

Relative humidity *vs.* temperature and pressure *vs.* temperature

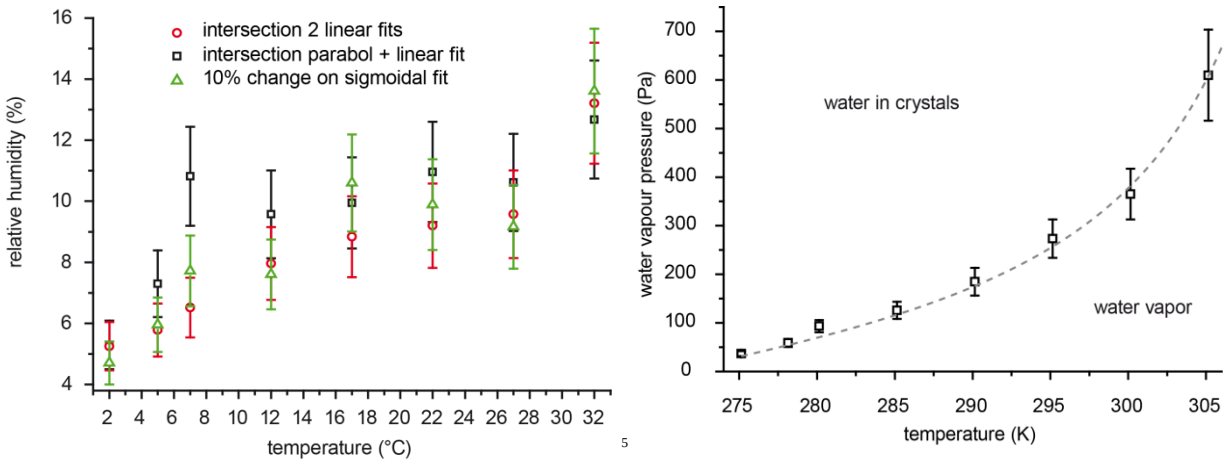

Figure S9. The fitting of the pressure vs. temperature curves by three different fitting routines (two linear fits, parabola and linear fit, sigmoid fit) gave for each curve three transient pressures at which particle size starts to change. If these transient pressures are plotted individually as relative humidity (left) or as an average pressure (right) versus temperature, we obtained a linear or exponential relationship, respectively. In the right figure, the coexistence curve from Clausius-Clapeyron equation is also shown.