Modulated Formation of MOF-5 Nano-particles – a SANS Analysis

Nayuk, R.[a] ; Zacher, D,[b] ; Schweins, R.[c] ; Wiktor, C.[b]; Fischer, R. A.[b] van Tendeloo, G.[d] and Huber, K.[a]**

[a]Chemistry Department, Universität Paderborn, Warburger Straße100, D-33098 Paderborn
[b] Faculty of Chemistry and Biochemistry, Inorganic Chemistry, Ruhr-Universität Bochum, Universitätsstraße 150, D-44801 Bochum
[c]Institut Laue-Langevin, LSS Group, B.P. 156, 6, rue Jules Horowitz, F-38042 Grenoble CEDEX 9
[d]Electron Microscopy for Materials Research (EMAT), University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerpen

E-mail: klaus.huber@upb.de

Supporting Information

1. Reference Experiments on Pure 4n-decylbencoic acid Solutions in DMF

In order to prove, that DBA itself does not form aggregates, a static light scattering experiment together with a SANS experiment was performed of pure DBA in DMF.

The **light scattering experiment** was carried out at a concentration of 0.872 g/L ($3.33*10^{-3}$ mol/L) corresponding to twice the amount of BDC for the experiments with a SBU:BDC molar ratio of 1:1. The resulting signal was within experimental uncertainty indistinguishable from the poor solvent signal (see Figure SI1). The very low excess scattering level at $q < 1x10^{-7}$ m^{-1} partially stems from the jump of refractive index at the boundary of DMF (scattering cell) / toluene (sample bath) and cannot be considered to be significant. An extremely low excess signal also at the four lowest scattering angles can be attributed to low amounts of dust or insignificant amounts of large DBA formations. However, this weak excess signal restricted to the lowest scattering angles only excludes formation of a significant amount of DBA nano-particles or micelles and thus suggests the use of DBA as suitable for further scattering experiments on MOF-5 formation.

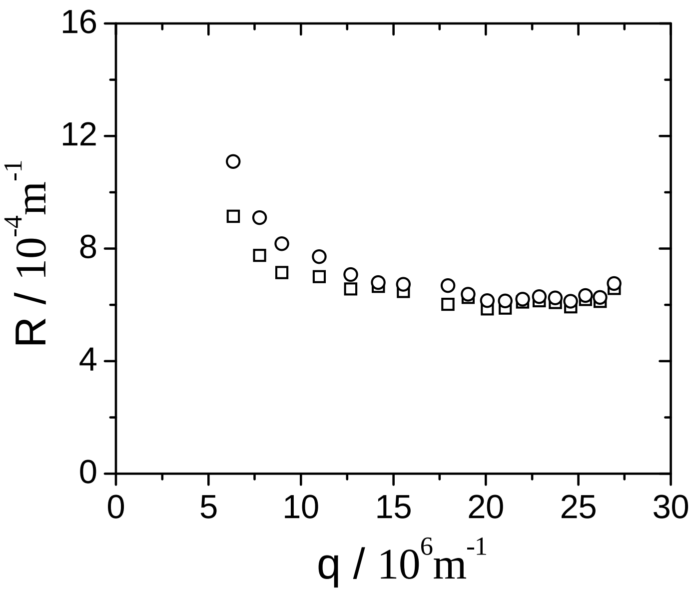

Figure SI1. Scattering signals expressed as the Rayleigh ratios of pure DMF (☐) and of DBA in DMF (○). The concentration of DBA was 0.872 g/L ($3.33*10^{-3}$ mol/L).

A second reference measurement of pure hydrogenated DBA was performed with **SANS** at a sample-to-detector distances of 8 m and 1.2 m for a solution having a concentration of 16.7*10^{-3}mol/L in D_7-DMF. Experimental data were treated according to equations (8) - (10) of the manuscript. Results are summarized in Figure SI2, revealing an angular independent scattering signal for q < 2 nm^{-1}. Hence, the formation of DBA nano-particles or micelles which might interfere with the scattering signal from MOF-5 particles can be excluded. This is in line with the obtained light scattering results.

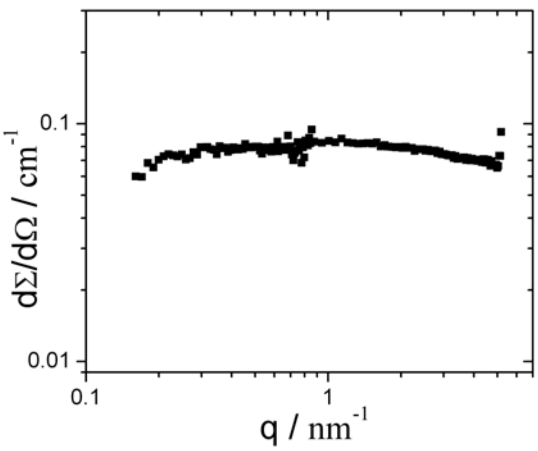

Figure S2. SANS measurement of DBA in D_7-DMF at a concentration of 16.7*10^{-3}mol/L.

2. Estimation of the Match-point for the Neutron Scattering Contrast of a H_7-DMF/D_7-DMF Solvent Mixture with MOF-5

The solvent composition for the first type of experiments (core is matched) was designed in order to render *ΔL* in eq(SI1) equal to 0. The difference *ΔL* of the scattering lengths per mass for MOF-5 ({$Zn_4O(BDC)_3$}) with respect to the solvent components was estimated according to

$$\Delta L = \frac{L_0}{m_0} - \sum_S n_S \overline{v_0} \rho_S \frac{L_S}{m_S} \qquad \text{(SI1)}$$

In eq. (SI1) the index i = 0 refers to MOF-5 and $i = s$ to either solvent component H_7-DMF ($s=1$) or D_7-DMF ($s=2$). The parameter m_i is the mass of species i with the scattering length L_i referring to $Zn_4O(BDC)_3$ ($i = 0$) and to H_7-DMF or D_7-DMF as solvent component ($i = s$). The parameter ρ_S is the density of s^{th} solvent component, $\overline{v_0}$ is the specific volume of suspended MOF-5 particles, n_S is the mole fraction of s-th solvent in the solvent mixture and.

$$L_i = \left(\sum_j^l b_j \right)_i \qquad \text{(SI2)}$$

In eq(SI2) b_j is the bound coherent scattering length of the j-th atom in species i with the total number of atoms l. The specific volume of MOF-5 particles $\overline{v_0}$ in DMF was estimated utilizing the following procedure. Four samples of MOF-5 suspension at different concentrations were prepared and measured 12 h after preparation. The density of these suspensions ρ_{susp} was measured using a DMA 02 D density meter from Anton Paar (Graz, Austria). The obtained values were plotted as a function of MOF-5 concentration C_{MOF-5} and fitted by $\rho_{susp} = C_{MOF-5}(1 - \overline{v_0}\rho_{DMF}) + \rho_{DMF}$ with ρ_{DMF} the density of pure solvent. The slope of the curve resulted in a specific volume of $\overline{v_0} = 1.054\, L/g$ for the MOF-5 particles, which was was treated as the inverse skeleton density of MOF-5 particles. Values of the density for H_7-DMF $\rho_{H7-DMF} = 0.944$ g/mL and for D_7-DMF $\rho_{D7-DMF} = 1.039$ g/mL were determined with the same density meter and used for further calculations. Based on these results a solvent composition of 66 mol% H_7-DMF and 34 mol% D_7-DMF was estimated to exhibit a contrast-matching point ($\Delta L = 0$) with MOF-5 particles.