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Trapping Metal-Organic Framework Nanocrystals: An *in-Situ* Time-Resolved Light Scattering Study on the Crystal Growth of MOF-5 in Solution

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Metal−organic open frameworks (MOFs) attract widespread interest in both academia and industry. Extraordinary gas-storage capacities for hydrogen and hydrocarbons were reported and other applications are emerging as well, including gas-separation, gas-sensing, and catalysis.[1−3] MOFs are based on the Werner-type coordination chemistry of metal cations M^{n+} ($n = 2, 3$) with oligofunctional organic spacer ligands leading to more or less complex 2D and 3D zeolite-like networks of perfect translational symmetry. MOFs exhibit cavities and/or channels for the adsorption of guest molecules,[4] imbedding of nanoclusters,[5] or more generally for the anchoring of functional species within the framework.[6] A key issue is the rational design and the precise control of the formation of the particular network. The so-called reticular synthesis refers to the self-organized assembly of suitable metal-ion-containing secondary building units (SBUs), by well chosen organic linkers.[7] Recently, a first direct evidence was provided for the persistence of such a molecularly defined SBU during the formation of MIL-89 by an ex-situ EXAFS study of the mother solutions of the hydrothermal synthesis.[8] Looking beyond the use of MOFs as bulk (powder) materials it is obvious that the integration of MOFs as novel building-blocks and functional units for bottom-up nanotechnology requires precise control over the crystallization process of MOFs in solution. For example, the addition of polyvinylsulfonic acid (sodium salt) to the mother solution significantly affects the nucleation of $[\{Cu_2(pzdc)_2(pyz)\}_n]$ (pzdc = pyrazine-2,3-dicarboxylate, pyz = pyrazine), which determines the crystal size in the range of 1−100 μm.[9] Likewise, the growth of thin films of MOFs at surfaces can be directed by applying microcontact printing of self-assembled organic monolayers.[10]

We investigated the homogeneous nucleation and crystal growth of $[Zn_4O(bdc)_3]$ (bdc = 1,4-benzenedicarboxylate; MOF-5, resp. IRMOF-1) in diethylformamide (DEF) at variable conditions and in the presence of certain additives using time-resolved static light scattering (TLS).[11] Standard mother solutions for MOF-5 in DEF[12] were prepared at 25 °C and then heated to 60 °C for 72 h (T_1, t_1). Under these conditions, the Zn^{2+} catalyzed decomposition of DEF is too slow to yield significant amounts of diethylamine as Brønsted base for the deprotonation of terephthalic acid. Nucleation was initiated by a temperature jump for a certain period of time (T_2, t_2). After the time period t_2, the solutions were filtered (0.2 μm syringe prefilter) into the scattering cells while cooling to 25 °C and were studied by TLS. Figure 1 shows the excess Rayleigh scattering of the growing particles as a function of the aggregation time for the three samples (Table 1). As expected, initiation at $T_2 = 105$ °C ($t_2 = 1.5$ h) is most effective. An almost linear growth over a period of a few minutes ($t < 10$ min) was observed at 25 °C. Eventually, the solution became turbid and macroscopic crystallites with sizes significantly above 350 nm began to deposit and were identified as authentic MOF-5 by X-ray diffraction.[4,12]

Table 1. Pretreatment of MOF-5 Mother Solutions[a]

sample	T_1 [°C]	t_1 [h]	T_2 [h]	t_2 [h]	ΔT [°C]
1	60	72	60	1.5	35
2	60	72	75	1.5	50
3	60	72	105	1.5	80

[a] Incubation, T_1, t_1; initiation, T_2, t_2; ΔT, difference between T_2 and growth temperature (25 °C).

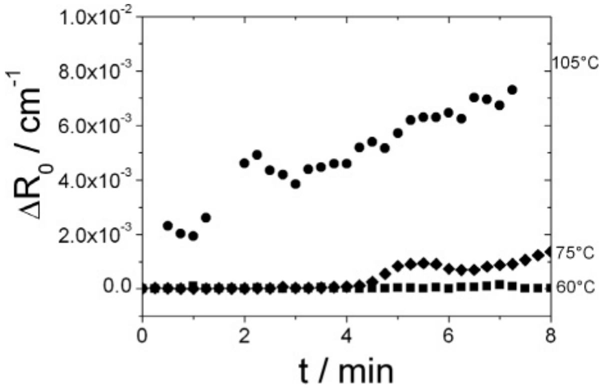

Figure 1. Growth of MOF-5 particles depending on different pretreatments (Table 1). (■) $T_2 = 60$ °C; (◆) $T_2 = 75$ °C; (●) $T_2 = 105$ °C. The excess Rayleigh scattering extrapolated to $q = 0$, ΔR_0, is used as a relative measure for the aggregate mass.

TLS does not only yield the particle size and molar mass. If the particles are larger than 100 nm, TLS provides information about the shape of the particles, too. The logarithm of the scattered intensity $I(q)$ in its normalized version $P(q) = I(q)/I(q = 0)$ displays characteristic oscillation, that is, minima for $P(q)$ in the case of high symmetry (spheres, cubes, rods) and very narrow size distribution.[13] In Figure 2, an example is shown for particles of a typical size of 320 nm prepared in a similar manner to sample 3 of Table 1. Our measurement clearly shows a first minimum around $q = 0.01$ nm^{-1}, and a second one around $q = 0.02$ nm^{-1} is indicated as well. This observation strongly substantiates the obvious conjecture that MOF-5 grows in the shape of perfect cubes from the very beginning. Nucleation and growth seem to be quite effectively separated at our conditions, since the characteristic features of $P(q)$ are only observed at almost monodisperse samples.

The growth of nanoparticles in colloidal solution is modified by the addition of surfactants and/or so-called capping groups, which bind to the surface of the particles.[14] We decided to use *p*-

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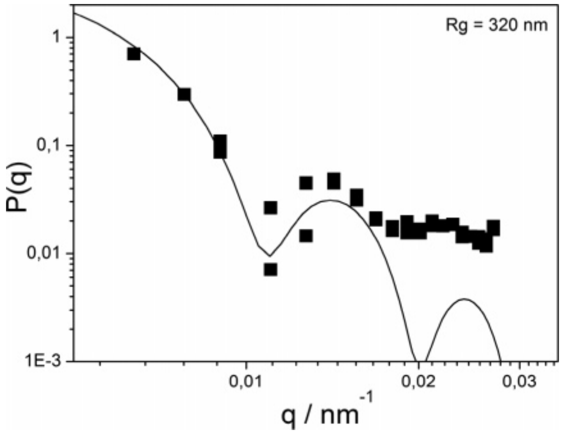

Figure 2. Particle scattering factor of MOF-5 nanocrystals ($T_2 = 95-100$ °C). The radius of gyration of the crystals is 320 nm.

perfluoromethylbenzenecarboxylate (pfmbc), which is likely to bind to vacant edges of surface-exposed Zn_4O sites. The compound $[Zn_4O(pfmbc)_6]$ (**1**) was synthesized as a model for this anticipated surface capping of nano-MOF-5.[15] The growth solutions were prepared according Table 1 and *p*-perfluoro-methylbenzoic acid (pfmbcH) was added at 25 °C in various molar ratios with respect to bdc and with a certain delay after initiating the growth as described above. Figure 3 shows the development of the radius of gyration R_g obtained by TLS as a function of the aggregation time. At a ratio of bdc to pfmbc of 1:2, that is, twofold excess of pfmbc added after 63 min, the growth stabilizes around 100 nm. In the case of a larger excess of pfmbc (1:5) added after 14 min, the particle size decreases and then stabilizes at 150 nm. Evidently, pfmbc competes with bdc for coordination to the $[Zn_4O]^{6+}$ units. The pfmbc seem to act as an etching agent, possibly yielding molecular species similar to **1** as the degradation products of the initial nano-MOF-5 crystals. These colloids proved to be quite stable at 25 °C in contrast to the uncapped case, where sedimentation occurred by the time. The pfmbc capped particles were deposited at a COOH terminated SAM on a Au substrate.[10] X-ray diffraction showed weak broadened peaks, but matching the MOF-5 pattern. SEM and AFM imaging revealed particles of 100−200 nm in size.

Hence, TLS can effectively be applied to study in situ the growth of MOF-5 crystals as a typical example of metal-organic frameworks. A procedure has been developed where nucleation as a fast step precedes the slower step of particle growth, in analogy to the anionic polymerization process. Addition of *p*-perfluoroethylbenzoic acid as capping reagent yields stable size-selected MOF-5 colloids and suggests a general concept for controlled particle formation of carboxylic acid based MOFs in solution.

Experimental. Samples of 3.14 g of $Zn(NO_3)_2 \cdot 4\ H_2O$ and 0.665 g of terepthalic acid were solved in 100 mL of pure DEF (Merck) and pretreated as described (Table 1). Time-resolved static light scattering experiments were performed with a home-built multiangle goniometer equipped with a HeNe Laser (35 mW, $\lambda = 632.8$ nm). The detector system is based on 38 light guides installed at 2 × 18 different angles θ, with $25.4° < \theta < 143.8°$. The scattering intensity $I(q)$ is recorded in a regime of 6.26×10^{-3} nm^{-1} $< q <$ 2.71×10^{-2} nm^{-1} with $q = (4n\pi/\lambda)\sin(\theta/2)$, and $n = 1.434$ as the refractive index of DEF.

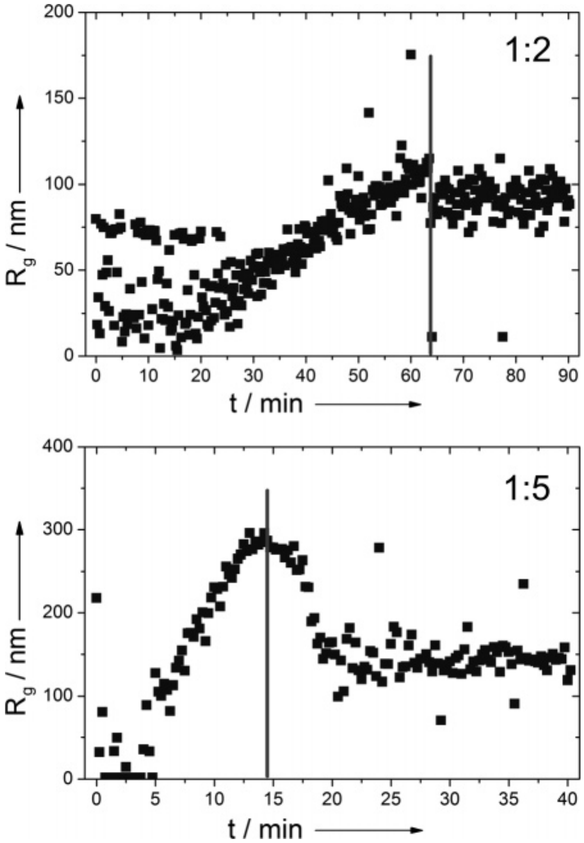

Figure 3. Growth of MOF-5 colloids ($T_2 = 95-100$ °C) terminated by the addition of pfmbc at the time indicated by the vertical lines. The molar ratios of bdc to pfmbc were 1:2 (above) and 1:5 (below).

Supporting Information Available: Experimental detail, scattering curves, XRD, SEM, AFM, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem*. **2004**, *116*, 2388.
(2) Kaskel, S. *Nachr. Chem*. **2005**, *53*, 394.
(3) Matsuda, R.; Kitaura, R.; Kitagawa, S.; Kubota, Y.; Kobayashi, T. C.; Horike, S.; Takata, M. *J. Am. Chem. Soc*. **2004**, *126*, 14063.
(4) Hermes, S.; Schröder, F.; Amirjalayer, S.; Schmid, R.; Fischer, R. A. *J. Mater. Chem*. **2006**, *16*, 2464.
(5) Hermes, S.; Schröter, M.-K.; Schmid, R.; Khodeir, L.; Muhler, M.; Tissler, A.; Fischer, R. W.; Fischer, R. A. *Angew. Chem., Int. Ed*. **2005**, *44*, 6237.
(6) Cho, S.-H.; Ma, B.; Nguyen, S. T.; Hupp, J. T.; Albrecht-Schmitt, T. E. *Chem. Commun*. **2006**, 2563.
(7) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
(8) Surblé, S.; Millange, F.; Serre, C.; Férey, G.; Walton, R. I. *Chem. Commun*. **2006**, 1518.
(9) Uemura, T.; Hoshino, Y.; Kitagawa, S.; Yoshida, K.; Isoda, S. *Chem. Mater*. **2006**, *18*, 992.
(10) Hermes, S.; Schröder, F.; Chelmowski, R.; Wöll, C.; Fischer, R. A. *J. Am. Chem. Soc*. **2005**, *127*, 13744.
(11) Becker, A.; Schmidt, M. *Macromol. Chem., Macromol. Symp*. **1991**, *50*, 249.
(12) Yaghi, O. M.; Eddaoudi, M.; Li, H.; Kim, J.; Rosi, N. The Regents of the University of Michigan, WO 02/088148 A1, 2002.
(13) Rayleigh, L. *Proc. R. Soc. London, Ser. A* **1914**, *90*, 219. Mittelbach, P.; Porod, G. *Acta Phys. Austr*. **1961**, *14*, 185.
(14) Uemura, T.; Kitagawa, S. *Chem. Lett*. **2005**, *34*, 132.
(15) Clegg, W.; Harbron, D. R.; Homan, C. D.; Hunt, P. A.; Little, I. R.; Straughan, B. P. *Inorg. Chim. Acta* **1991**, *186*, 51.

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