Adsorption 9: 235–241, 2003

A Surprising Drop of the Diffusivities of Benzene in a Mesoporous Material of Type MCM-41 at Medium Pore Filling Factors

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Abstract. Pulsed Field Gradient (PFG) NMR is applied to study molecular diffusion of benzene in a commercial sample of MCM-41. Over a very small concentration range at medium pore filling factors the diffusivity is found to sharply drop by up to one order of magnitude, while it remains essentially constant over the total remaining range from vanishing concentrations up to over-saturation. Similarly extreme deviations from monotonous concentration patterns have so far not been described in the literature. The observed effect may be rationalised as a consequence of the onset of capillary condensation in the transport pores in the hyper-structure of the MCM-41 particles under study.

Keywords: self-diffusion, mesoporous materials, MCM-41, benzene, pulsed field gradient NMR

1. Introduction

With the advent of ordered mesoporous materials (Beck et al., 1992), adsorption science and technology has been accomplished by a further most attractive subject. Interestingly enough, among the numerous studies devoted to this novel field of research (Kärger et al., 1997; Bonneviot et al., 2001), only very few deal with the investigation of the transport properties of these new materials. This is mainly due to the fact that—unlike their nanoporous crystalline counterparts, the zeolites—ordered mesoporous materials are generally not available as well-shaped particles. Therefore, the application of macroscopic techniques of diffusion measurement like transient adsorption/desorption techniques (Ruthven, 1984; Kärger and Ruthven, 1992; Bülow and Micke, 1995), the frequency response method (Rees and Shen, 1990) or the Zero Length Column (ZLC) technique (Ruthven and Brandani, 2000) suffers from the lack of accuracy in defining the appropriate boundary conditions. It is not unexpected, therefore, that most of the diffusion measurements with ordered mesoporous materials so far have been carried out by pulsed field gradient (PFG) NMR (Kärger et al., 1998b; Matthae et al., 1998; Hansen et al., 1998; Courivaud et al., 2000a, 2000b; Stallmach et al., 2000, 2001). As a microscopic technique, PFG NMR is able to follow the diffusion paths of the diffusants under study, yielding their root mean square displacement $\langle r^2(t)\rangle^{1/2}$ during the observation time as the directly accessible quantity (Ruthven, 1984; Kärger and Ruthven, 1992; Kärger et al., 1998a; Stallmach and Kärger, 1999). It is true, however, that even PFG NMR is only able to determine genuine intraparticle diffusivities, if the particles are big enough—and of a sufficiently homogeneous structure—so that the molecules remain within one particle during the whole observation time and—moreover—their interference with the external surface of the particles is negligibly small. So far, owing to the ideal morphology of the MCM-41 particles applied (Pophal and Fuess, 1999), only in Stallmach et al. (2000), a convincing correlation between the mean diffusion paths observed by PFG NMR and the external shape of the adsorbent particles could be derived.

Earlier PFG NMR studies of self-diffusion in MCM-41 showed different concentration dependencies. While in Kärger et al. (1998b), for *n*-hexadecane a slightly decreasing self-diffusivity with increasing loading was observed, similar studies with *n*-hexane showed the indication of a maximum in the diffusivity at a loading of about 20% of the inner pore volume (Courivaud et al., 2000b). Finally, in the PFG NMR measurements of Matthae et al. (1998), the concentration dependence of the diffusivities hasn't been considered at all. In the present paper we communicate the results of PFG NMR measurements of diffusion in MCM-41, where for the first time the diffusivities of guest molecules in MCM-41 are found to depend dramatically on their concentration. In fact, covering as much as one order of magnitude within concentration intervals of less than one tenth of the saturation capacity, the observed concentration dependence is more pronounced than observed so far in any adsorbate-adsorbent system. We dedicate this work to Douglas M. Ruthven in recognition of his enormous contributions to the elucidation of the elementary processes constituting mass transfer in adsorbate-adsorbent systems.

2. Experimental

The samples of MCM-41 leading to the anomalous concentration dependence of diffusion were kindly provided by Mobil Oil. Figures 1(a) and (b) show scanning electron micrographs of the samples under study. It appears that the adsorbent grains contain some free space between the individual MCM-41 particles. The specific surface was determined to be 753 m^2/g by the BET method from the analysis of the nitrogen adsorption isotherms at 77 K (Spange et al., 1999, 2001a, 2001b).

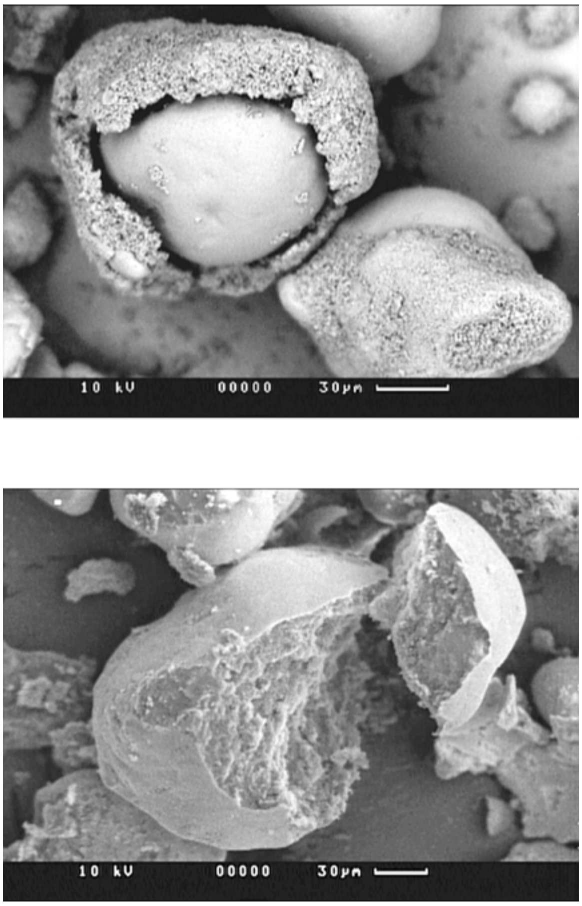


Figure 1. Electron micrographs of the investigated MCM-41 material.

Prior to the PFG NMR diffusion studies, the MCM-41 specimens were introduced into specially designed 7.5 mm o.d. glass tubes (Bär et al., 1995) to a filling height of about 10 mm. Under continuous evacuation, these samples have been heated at a rate of 10 K/h to a final temperature of 673 K. Under continued evacuation the samples have been kept over 24 h, until the pressure over the sample was less than <1 Pa. Subsequently, the guest molecules (benzene) were taken from the gas phase of well-defined pressure in a calibrated volume and introduced into the sample by chilling with liquid nitrogen.

For better mutual comparison of the PFG NMR samples, their loading is represented by relative pore filling factors θ. They are referred to the specific volume of the channels, which results to be 868 μl/g for the micropore volume, determined by nitrogen adsorption. Pore filling factors $\theta > 1$ indicate that the samples contain a correspondingly larger amount of sorbate than the micro- and mesoporous space may accommodate.

The diffusion measurements have been carried out at temperatures of 208 K, 258 K and 298 K with an accuracy of ±1 K by means of the home-built PFG NMR spectrometer FEGRIS 400 NT (Galvosas et al., 2001), operating at a proton resonance frequency of 400 MHz. The $\pi/2 - \tau_1 - \pi/2 - \tau_2 - \pi/2 - \tau_1$—stimulated echo pulse sequence was applied (Kärger and Ruthven, 1992; Bülow and Micke, 1995). For selected samples, also comparative measurements with the 13-interval pulse sequence have been carried out (Cotts et al., 1989; Galvosas et al., 2001). The stimulated echo and the 13-interval pulse sequence differ in particular in the fact that the latter—by using pairs of alternating gradient pulses—cares for an extinction of a possibly disturbing influence of internal magnetic field gradients on the diffusion measurements. Since in both types of measurement essentially identical diffusion properties have been observed, any substantial influence of internal gradients on the observed diffusion behaviour may be ruled out.

In PFG NMR, information about the intrinsic diffusivities is deduced from an analysis of the ratio Ψ between the signal intensities with and without field gradients applied. In the case of normal diffusion, one has (Ruthven, 1984; Kärger and Ruthven, 1992; Kärger et al., 1998a; Stallmach and Kärger, 1999).

$$\psi(\Delta, g\delta) = \exp(-\gamma^2\delta^2 g^2 D\Delta) \tag{1}$$

with D and γ denoting, respectively, the coefficient of self-diffusion (the diffusivity) and the gyromagnetic ratio (=$2.675 \cdot 10^8$ T^{-1} s^{-1} for protons). In the stimulated-echo technique, δ, g and Δ denote the duration, amplitude and separation of the gradient pulses, where generally the narrow-pulse approximation ($\delta \ll \Delta$) is supposed to be valid. The observation time $\Delta = \tau_1 + \tau_2$ covered a range from 2 ms up to 500 ms. The duration of the field gradient pulses was $\delta = 400$ μs. In the 13-interval pulse sequence, δ stands for the total duration of each pair of alternating gradient pulses. Since diffusivity D and observation time Δ are interrelated with the mean square displacement in a given direction (here in the direction of the applied field gradient) by the Einstein equation (Ruthven, 1984; Kärger and Ruthven, 1992; Kärger et al., 1998a; Stallmach and Kärger, 1999)

$$\langle z^2(\Delta)\rangle = 2D\Delta, \tag{2}$$

Equation (1) may as well be written as

$$\Psi(\Delta, g\delta) = \exp(-\gamma^2\delta^2 g^2 \langle z^2(\Delta)\rangle/2). \tag{3}$$

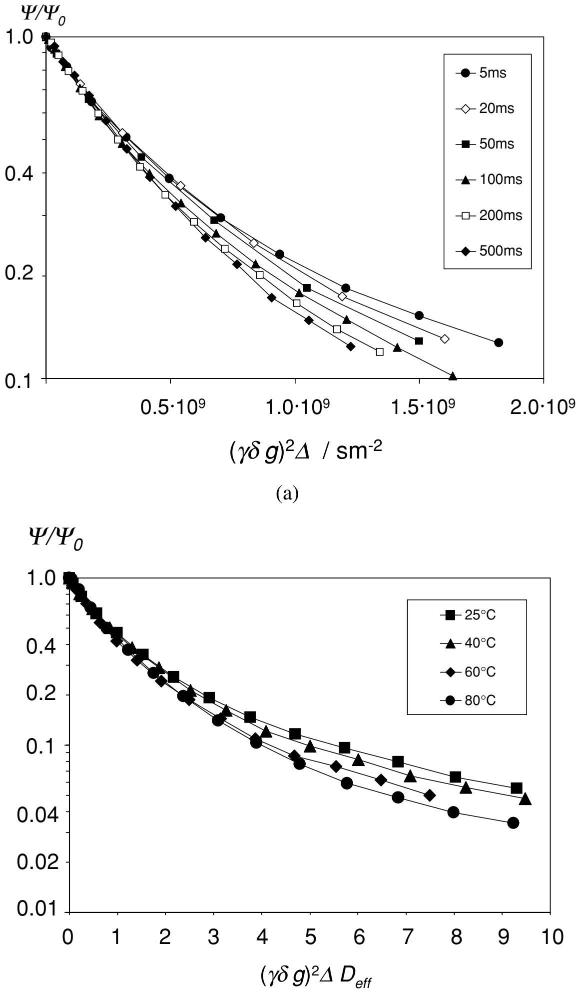
In general, Eq. (3) represents a satisfactory representation of the observed attenuation behaviour, even if molecular transport deviates from normal diffusion. If, in a broader sense, Eq. (2) is understood as the definition of an effective diffusivity, which (viz. in the case of anomalous diffusion) may become time-dependent, also Eq. (1) provides a reasonable approach even beyond the case of normal diffusion.

The isotherms of benzene adsorption on two different MCM-41 samples at 298 K reported in Section 3.3. have been measured by means of a commercial volumetric nitrogen sorption device SORPTOMATIC 1990 (FISONS). Prior to the benzene adsorption experiments the MCM-41 samples were outgassed in vacuum at a temperature of 498 K for several hours. For the special purpose of the benzene adsorption measurements the sorption device was modified slightly by the addition of a flask which contains liquid benzene under its own vapour pressure. This flask acts as a benzene vapour reservoir. The benzene adsorption isotherms were measured by subsequent dosing of small portions of benzene vapour to the samples and monitoring the resulting equilibrium pressure.

3. Results and Discussion

3.1. *Shape of the PFG NMR Signal Attenuation Curves*

Figure 2 provides a typical example of the PFG NMR signal attenuation curves observed with the MCM-41 specimens under study. There is, obviously, a substantial deviation from the exponential interdependence between the signal attenuation Ψ and the squared gradient pulse intensity, $g^2\delta^2$, as required on the basis of Eqs. (1) or (3). In fact, such deviations have to be expected in the case of powder samples, where the diffusivities in the individual crystallites undergo anisotropic diffusion (Stallmach and Kärger, 1999). In Stallmach et al. (2000), such deviations have been used to determine the mean diffusivities parallel and perpendicular to the



(a)

(b)

Figure 2. Examples of master plots of the PFG NMR spin echo attenuation for the MCM-41 sample under study at a loading of 0.34 g benzene per 1 g of activated MCM-41, plotted (a) as a function of $(\gamma\delta g)^2\Delta$ with increasing Δ, and (b) as a function of $(\gamma\delta g)^2\Delta D_{\text{eff}}$ in the temperature range between 293 and 353 K and for $\Delta = 10$ ms.

channel direction in long-range ordered specimens of MCM-41. Having in mind that the mean diffusion paths covered in the present study are on the order of several micrometers, inspection of the micrographs presented in Fig. 1 clearly reveals that in the given case this interpretation is not applicable: the diameters of the regions in which uniform channel orientations may be expected are much smaller than the observed displacements. One is therefore measuring an averaged diffusivity taken over all (ordered) regions traversed by the diffusants during the observation time.

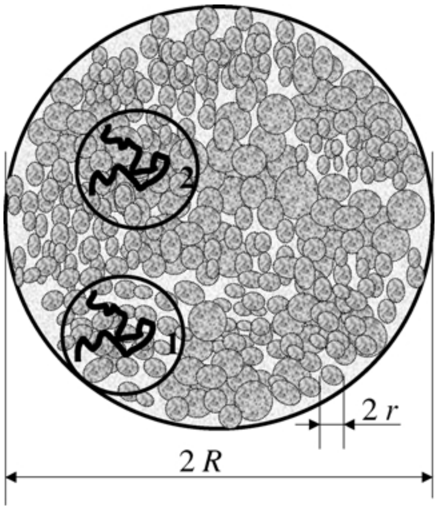


Figure 3. Schematic representation of possible diffusion paths in grains of the MCM-41 material. The regions of ordered mesoporous structure (diameter $2r$) are much smaller than the grain diameters ($2R$).

As schematically indicated in Fig. 3, deviations from a simple mono-exponential decay of PFG NMR signal attenuation are therefore most likely to be explained by different fine-structures within the adsorbent grains, probably mainly differing between the inner core and the outer shell as suggested by the micrographs in Fig. 1. The ranges of averaging on the diffusion paths of the individual molecules obviously increase with increasing observation times. As a consequence, the differences in the main diffusivities of the individual diffusants should decrease. This tendency is in fact reflected by Fig. 2(a), where the deviation from a simple exponential becomes less pronounced with increasing observation time. Figure 2(b) demonstrates that evolution towards a monoexponential PFG NMR signal attenuation with increasing observation time becomes even more easily visible with increasing temperatures, since the latter ensures that still larger regions within the adsorbent grain are covered by the diffusants.

Being determined by the mean value of the diffusivities over the whole sample, in the chosen ln Ψ-vs.- $g^2\delta^2\Delta$ plots, the first, steep decay of the PFG NMR signal attenuation curves has to remain unaffected by the observation time. Such a behaviour is shown in Fig. 2(a) and was in fact observed in all PFG NMR measurements carried out during this studies. It are the mean diffusivities resulting from these steep decays, which shall be exclusively considered in the following.

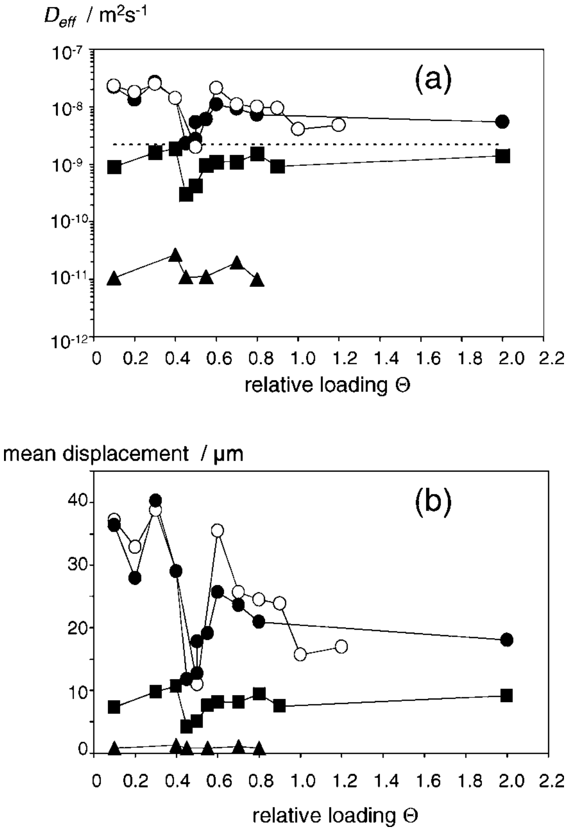


Figure 4. Concentration dependence of benzene diffusivity in MCM-41. (a) Effective diffusion coefficients versus relative loading ($\Theta = 1.0$ refers to complete occupation of the channel pores) at 298 K (○, ●), 258 K (■) and 208 K (▲), dashed line: diffusivity of the benzene liquid at 298 K; (b) corresponding mean displacements of the benzene molecules versus relative loading at 298 K (○, ●), 258 K (■) and 208 K (▲), calculated for an observation time Δ of 10 ms. Open and filled symbols (○, ●) refer to two different sets of samples.

3.2. Concentration Dependence of the Mean Diffusivities

Figure 4(a) gives a survey of the measured diffusivities of benzene in the MCM-41 sample under study. The temperatures under consideration were 298 K, 258 K and 208 K, respectively. The broken line represents the value of the bulk diffusivity of benzene at 298 K. Over the total range of observation times considered (3 ms $\leq \Delta \leq$ 50 ms) within an interval of about $\pm 5\%$ the diffusivities remained essentially constant. At a temperature of 298 K, these diffusivities exceed that of the bulk liquid by about one order of magnitude. Only around medium pore filling factors the diffusivities are found to sharply decrease.

After the measurements with a first set of samples have been accomplished, a second set has been prepared. The measurements of these samples (results included in Fig. 4 as a second set of samples) completely reproduced the remarkable drop in the diffusivities. For an alternative visualization of the effect, Fig. 4(b) shows the root mean square displacements, corresponding to the effective diffusivities shown in Fig. 4(a) on the basis of Eq. (2) for an observation time of $\Delta = 10$ ms.

3.3. Discussion of the Observed Concentration Dependence

Diffusivities in adsorbate-adsorbent systems exceeding those of the bulk liquid are generally referred to the possibility of fast molecular propagation through the free space in the gas phase of the pore system (Tabony and Cosgrove, 1979; Kärger, 1981; Kärger and Ruthven, 1992). In this case the effective diffusivity as observable by PFG NMR may be represented as the sum of two constituents

$$D_{\text{eff}} = D_{\text{surface}} + p_{\text{inter}} D_{\text{inter}} \qquad (4)$$

where p_{inter} and D_{inter} denote, respectively, the relative amount of molecules in the gas phase and their diffusivity, while the remaining contribution to molecular transportation is summarized in the term D_{surface}. Though p_{inter} is clearly much smaller than 1, depending on the free volume of the pore system, D_{inter} attains values, which may significantly exceed all the other contributions to mass transfer, so that $p_{\text{inter}} D_{\text{inter}}$ becomes the dominant term, possibly even exceeding the diffusivity in the bulk liquid.

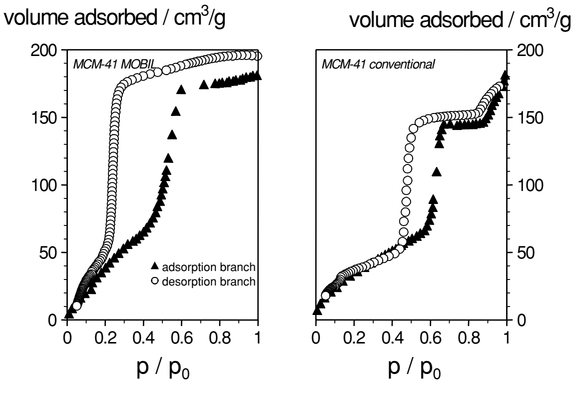
Close to sorbate concentrations corresponding to a filling of about one half of the MCM-channel system, however, the effective diffusivities drop by one order of magnitude, attaining at 298 K values close to the diffusivities in the bulk liquid. This behaviour is observed for two different temperatures and could be reproduced with a second set of samples. Not unexpectedly, at the lowest temperature of 208 K, the diffusivities are not subject anymore to a similarly steep drop. This is due to the fact that p_{inter} is decreasing with decreasing temperatures so that the influence of $p_{\text{inter}} D_{\text{inter}}$ in comparison with D_{surface} is also decreasing.

Obviously, the sharp decrease of D_{eff} with increasing loading for effective pore filling factors close to 0.5 has to be associated with a dramatic drop of p_{inter} and/or

D_{inter}. Since p_{inter} is proportional to the sorbate pressure divided by the total amount adsorbed, an increase in the relative loading of about 10% cannot give rise to a decrease of p_{inter} by one order of magnitude. The dramatic decrease in D_{eff} has to be explained, therefore, by a corresponding decrease in D_{inter}. As the most likely explanation of the observed behaviour, one has to assume that in the given range of concentrations, with increasing loading and hence with increasing sorbate pressure, there shall be an onset of capillary condensation in pore throats of the MCM-41 hyper-structure connecting the free space relevant for the large values of D_{inter} at smaller concentrations. Blocking these formerly free passages may in fact be expected to lead to the observed dramatic slowing down of the averaged diffusivities. The subsequent increase of D_{eff} with further increasing loading might in turn be attributed to a corresponding increase in the value of p_{inter}.

For effective pore filling factors exceeding one, the primary MCM-41 pores shall be filled and, subsequently, the free volumes within the adsorbed particles as well as the space between them shall be filled too. Owing to the remaining free space, the resulting effective diffusivities may still slightly exceed the value of the bulk liquid.

As a first independent piece of evidence for the validity of the suggested explanation of the steep drop in the diffusivities around $\theta \approx 0.5$, Fig. 5 compares the adsorption isotherms of benzene on the sample under study with a reference sample of conventional MCM-41, whose intra-particle pore volume does exclusively consist of the hexagonally arranged channels of the genuine MCM-41 structure. It turns out that capillary condensation as revealed by the hystereses between the adsorption and desorption branches is much more pronounced in the MCM-41 sample under study.



(a) (b)

Figure 5. Branches of the adsorption-desorption isotherms of benzene in the MCM-41 sample under study at 298 K (a) in comparison with an MCM-41 specimen without secondary pore space (b).

4. Conclusion

Using PFG NMR, the self-diffusion of benzene in conglomerated MCM-41 particles is studied. In these measurements, for the first time in adsorbate-adsorbent systems over a relatively small interval of concentrations a steep drop in the effective diffusivities is observed. The effect is explained by the onset of capillary condensation in pore throats, suppressing fast exchange of the diffusants between regions of high molecular mobility within the secondary pore system of the adsorbent particles. As a first independent support of this explanation, capillary condensation in the system under study is found to be much more pronounced than in MCM-41 specimens without secondary pore systems. Comparative measurements of the PFG NMR diffusivities including benzene and other guest molecules as well as of the corresponding adsorption isotherms are in progress.

Nomenclature

D	Coefficient of self-diffusion (diffusivity)
D_{eff}	Effective diffusivity
D_{inter}	Diffusivity in the intercrystalline space
g	Amplitude of field gradient pulses
p_{inter}	Relative amount of diffusants in the intercrystalline space
$r(t)$	Molecular displacement during time t
z	Molecular displacement in z direction

Greek Letters

γ	Gyromagnetic ratio
δ	Width of field gradient pulses
Δ	Separation of field gradient pulses
Θ	Pore filling factor
$\tau_{1(2)}$	Separation if the rf pulses in the stimulated-echo sequence
Ψ	Signal attenuation in PFG NMR

Acknowledgment

We are obliged to Douglas M. Ruthven for his continuous interest in the development of PFG NMR and his personal engagement in numerous problems of the application of this technique to zeolite science and technology. Financial support by Deutsche Forschungsgemeinschaft (Schwerpunktprogramm 467 "Nanostrukturierte Wirt/Gast-Systeme", SFB 294) and Fonds der Chemischen Industrie is gratefully acknowledged.

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