Identification of single photoswitchable molecules in nanopores of silica xerogels using powder diffraction

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Single photoswitchable molecules of $(\text{CN}_3\text{H}_6)_2[\text{Fe}(\text{CN})_5\text{NO}]$ (GuNP) are embedded into nanopores of an SiO_2 xerogel. It is shown that it is possible to identify the structural motif ('fingerprint') of the embedded complex by analyzing neutron powder diffraction data in a limited Q range ($Q < 37 \text{ nm}^{-1}$) using the Debye approach. The structural study reveals that the pores are occupied by GuNP monomers with a fill factor of 60–80%. The mutual arrangement of the anion and cations in the GuNP monomer is slightly changed ($\sim 1\%$ elongation), while the bond lengths within the anion and cation are changed by less than 0.2% with respect to the single-crystalline form of GuNP.

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1. Introduction

The embedding of functional molecules in nanostructured host matrices such as sol–gel materials offers several advantages; for example, sol–gel processing facilitates the scaling up to large quantities for industrial production, while the control of the interaction between host and guest on the nanoscale enables a targeted functionalization of the embedded molecule. For medical applications, such as the slow release of drugs from the nanopores of xerogels, the structural integrity of the embedded drug is important for the fulfillment of its medical functionality (Rose & Mascharak, 2008; Ahola *et al.*, 2001; Ferreira *et al.*, 2006); for example, the building of hydrogen bonds with the host could hinder the drug release (Ahola *et al.*, 2001) such that the release of NO for cancer reduction occurs only if the NO ligand of the active complex does not bind to or react with the host network (Ferreira *et al.*, 2006). For optical applications the light-triggered manipulation of the embedded complex – such as the switching of the NO ligand in $[\text{ML}_5\text{NO}]$ molecules, which is at the origin of their photorefractive response (Imlau *et al.*, 1999; Schaniel *et al.*, 2007) – needs to be retained. Thus the structure determination of the embedded complex reveals whether the functional groups interact with the host and whether there is enough space for the fulfillment of their functionality. However, the fundamental problem of structure determination of single complexes in amorphous host matrices is the loss of the periodicity of the motif, *i.e.* the translational symmetry as present in single-crystalline materials is missing. Therefore

the scattering of X-rays or neutrons does not yield sharp Bragg peaks, which are normally used for direct structure determination. We present here a scattering method that allows the identification of the molecular structure of single complexes (structural fingerprint) in a host material by separating the scattered intensities of the host and guest materials. Knowing the molecular structure at least roughly, for example from previous single-crystal studies, it is possible to evaluate the diffraction pattern of the embedded substance *via* the Debye (1915) equation and to obtain information on the structural arrangement of the embedded molecules: (1) the number of complexes embedded in a single nanopore, (2) the average pore size, (3) the distance to the host network and (4) the fill factor (= fraction of loaded pores). We use as an example $(\text{CN}_3\text{H}_6)_2[\text{Fe}(\text{CN})_5\text{NO}]$ (GuNP; Retzlaff *et al.*, 1989) embedded in a silica xerogel, since the total scattering length (Sears, 1992) of GuNP for neutrons is 129.3 fm, while for the SiO_2 xerogel it is 15.8 fm. GuNP is a relative of sodium nitroprusside and exhibits the same optical switchability of the NO ligand (Schaniel *et al.*, 2006) from $\text{Fe}=\text{N}-\text{O}$ to $\text{Fe}-\text{O}-\text{N}$ by rotation of 180° . As was shown by Schuy *et al.* (2009) using infrared spectroscopy, this functionality is retained for GuNP complexes embedded in silica xerogels. On the other hand these experiments demonstrated an enhanced photo-switching efficiency in xerogels compared to crystalline powder as well as an enhanced photostability of the complexes with respect to solutions of GuNP. In order to understand these differences it is necessary to study the structure of the GuNP complexes in the nanopores of the xerogel.

2. Experimental and computational details

2.1. Sample description

GuNP–silica hybrids with pore sizes of 1–3 nm were prepared and characterized as described elsewhere (Schuy *et al.*, 2009). Fig. 1 schematically illustrates the embedding of the GuNP complexes in the SiO₂ xerogel. Possible hydrogen bonds to the network are indicated with dotted lines. The [Fe(CN)₅NO]^{2−} anion is octahedrally coordinated with five CN ligands and one NO ligand with almost 4mm symmetry. The two CN₃H₆⁺ cations are arranged in a coplanar manner as indicated in Fig. 1. The C–O–C angle between the guanidinium C atoms and the nitroprusside O atom is 151° (Retzlaff *et al.*, 1989). The xerogel consists of colloidal particles of diameter 1–10 nm, which are built from SiO₂ and SiOH groups. Depending on the preparation conditions the colloidal particles aggregate in a network forming pores of size 1–5 nm (Brinker & Scherrer, 1990), in which guest molecules can be embedded. The whole GuNP complex can be included in a circle of diameter $d = 1.4$ nm (the dimensions of the coplanar form are 1.4 nm length and 0.7 nm width and height). While the mutual arrangement between the cations and anion of GuNP might well change when the salt is adsorbed in the pores, it is expected that the anion and cation structure should remain the same or close to that found in the GuNP crystal.

The photoswitching properties of the embedded GuNP complexes were verified using infrared spectroscopy as described in detail by Schuy *et al.* (2009), showing that 15% can be transferred from Fe–N–O to the inverted configuration Fe–O–N. Thus the NO ligand retains its desired flexibility in this porous environment.

2.2. Defining the Q range

Depending on the average size of isolated atomic clusters of the embedded substance, an appropriate experimental Q range can be determined ($Q = 4\pi \sin \theta / \lambda$, where λ is the wavelength of the incident radiation and θ is half the scattering angle). For small clusters of one or two GuNP mol-

ecules, with a diameter of about 1–1.5 nm, it is best to choose $Q_{\min} \simeq 2\pi/D$ and $Q_{\max} \simeq 2\pi/d$, where D is the cluster diameter and d the nearest-neighbor distance. For GuNP, $Q_{\min} \simeq 5 \text{ nm}^{-1}$ and $Q_{\max} \simeq 60 \text{ nm}^{-1}$ using $D \simeq 1.25 \text{ nm}$ for the cluster size and $d \simeq 0.1 \text{ nm}$ for the nearest-neighbor distance. However, the range $Q < Q_{\min}$ contains valuable information on the substrate pore size, while it can be convenient to restrict $Q_{\max}$ in order to neglect the substrate–guest chemical bonds. So $Q_{\min} \simeq 1$ and $Q_{\max} \simeq 30 \text{ nm}^{-1}$ is, in this case, a valid choice. Consequently it is sufficient to perform the diffraction measurement at low Q values, which allows the use of standard neutron powder diffraction or in-house X-ray sources, in contrast to the PDF method (atomic pair distribution function), which relies on acquisition of high- Q data (Billinge, 2004).

2.3. Neutron diffraction

Neutron powder diffraction patterns were recorded with both samples enclosed in vanadium containers, at a wavelength $\lambda = 0.246 \text{ nm}$ in a 2θ range from 3 to 93° corresponding to $1.3 \leq Q \leq 37 \text{ nm}^{-1}$ with collection times of *ca* 24 h, at the DMC cold neutron diffraction beamline at the Swiss spallation neutron source SINQ (Paul Scherrer Institute, Villigen, Switzerland). After normalizing the patterns to the SiO₂ mass effectively in the beam, the difference pattern $I_{\text{GuNP}}(Q)$ in the region $Q > 14 \text{ nm}^{-1}$ was fitted. The calculations were performed using the Debye formula (Debye, 1915; Guinier, 1963; Cervellino *et al.*, 2003, 2006)

$$I_{\text{GuNP}}(Q) = I_{\text{inc}} + \sum_{j=1}^N b_j^2 + 2 \sum_{j>k=1}^N b_j b_k T_j(Q) T_k(Q) \frac{\sin(Qr_{jk})}{Qr_{jk}}, \quad (1)$$

with N the number of atoms (in our case $N = 33$ for a monomer and $N = 66$ for a dimer), b_j the scattering lengths, $T_j(Q)$ the Debye–Waller factors, r_{jk} the interatomic pair distances and I_{inc} the incoherent scattering contribution (mainly from hydrogen), which is to a good approximation a constant with a small negative slope towards higher Q . The distances r_{jk} were calculated from the known crystal structure (Retzlaff *et al.*, 1989), allowing for only the following changes: (a) a small isotropic expansion/contraction of the whole molecule, (b) a small change of the Gu–NP distances and (c) a small change of the Gu–NP–Gu dihedral angle. Debye–Waller factors have been taken from Retzlaff *et al.* (1989).

3. Results

Neutron powder diffraction patterns (see Fig. 2a) of a pure silica gel and a xerogel loaded with GuNP were recorded. Both samples show a clear small-angle rise. The series of small broad peaks apparent in both patterns is an electronic artefact due to the detector architecture (arrangement of anodes and cathodes). However, since this artefact is the same in both measurements, it cancels during normalization and subtraction of the data sets. Because of the presence of some content of water in the pores, the incoherent background of the

Figure 1
Schematic drawing of silica network with embedded GuNP complexes.

unloaded sample is increased, which is taken into account by adding a linearly decreasing background of $I_{\text{inc}} = 45000(1 - 0.022Q)$ counts. Normalizing both patterns to the SiO_2 mass and subtracting the unloaded from the loaded pattern results in the displayed difference pattern, which can be attributed to the GuNP complex diffraction. For evaluation we partition the diffraction pattern into a wide-angle region ($37 \geq Q \geq 15 \text{ nm}^{-1}$), a small-angle region ($Q \leq 2.2 \text{ nm}^{-1}$) and an intermediate region ($2.2 \leq Q \leq 15 \text{ nm}^{-1}$). In this manner we can obtain information about the number and structure of the GuNP molecules in the nanopores of the xerogel (wide-angle region), about the mean diameter of the nanopores and the fill factor (small-angle region), and about the mean distance between an atom of the pore wall and an atom of GuNP (intermediate-angle region).

3.1. Wide-angle region – fingerprint of the molecule

Fig. 2(b) shows the subtracted and corrected scattered intensity in the wide-angle region, together with two different calculated patterns (solid lines) as well as the corresponding residua. The calculated pattern labeled ‘monomer’ is based on the assumption that only one of the GuNP complexes, *i.e.* one $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ anion and two CN_3H_6^+ cations in the coplanar arrangement as illustrated schematically in Fig. 1, is incorporated into each nanopore. The second calculated pattern considers the incorporation of a GuNP dimer into each nanopore, which is formed by suitable clustering of two monomers. The description of the data with a monomer filling of the pores is substantially better than that using dimers, which is also evident from the goodness of fit (GoF) of 1.29 for the monomer filling compared to the GoF of 1.39 for the dimer filling. However the description with 100% monomers of the coplanar type is not perfect. A more detailed analysis shows that a combination of 80% coplanar monomers together with 20% monomers exhibiting a C–O–C angle of 101° between the guanidinium C atoms and nitroprusside O atom fits the measured data better, with a GoF of 1.24 (fit not shown in Fig. 2). Further, we find no detectable dilation of all molecular bonds ($< 0.2\%$) but an elongation of $\sim 1\%$ of the Gu–NP distance. Thus the molecules retain their structure in agreement with the retained functionality (Schuy *et al.*, 2009).

In view of the rather astonishing fact that we are able to distinguish between monomer and dimer filling as well as the more subtle structural details between cation and anion, we add a few words on the details of the data analysis. Fig. 3 shows the GoF for the different structural models of the GuNP complex as a function of the truncation value used for Q_{min} . Thus each GoF value at a truncation value Q_{min} in Fig. 3 corresponds to the GoF of a fit using the measured diffraction pattern from the indicated value of Q_{min} up to $Q_{\text{max}} = 37 \text{ nm}^{-1}$. The configurations of the monomers ‘alpha’ and ‘beta’ as well as the dimer ‘alpha–beta’ are indicated in the top panel of the figure. Clearly, the fits using a truncation value below $Q_{\text{min}} \simeq 10 \text{ nm}^{-1}$, *i.e.* including data below $\sim 10 \text{ nm}^{-1}$, are influenced by the scattering in the intermediate range. This angular range includes scattering caused by the interaction

between embedded complexes and host matrix and thus leads to higher GoF values with respect to the analysis of the pure molecular structure (‘fingerprint’). Nevertheless the smooth behavior of the GoF for all model structures as a function of the truncation value indicates that the fits are not hampered by arbitrary fluctuations or ancillary minima in the GoF landscape. The bottom panel of Fig. 3 shows a zoom into the region $11 < Q_{\text{min}} < 19 \text{ nm}^{-1}$. Clearly, the monomer fit based on the model ‘alpha’ (planar form of the GuNP complex) is better than the fit using a dimer based on two ‘alpha’ monomers. The monomer of type ‘beta’ (nonplanar form of GuNP) fits the data significantly worse (GoF of 1.56), as does the combination of ‘alpha–beta’ in a dimer (GoF of 1.63). A slight improvement with respect to the ‘alpha’ model is obtained when combining 80% monomers of type ‘alpha’ and 20% monomers of type ‘beta’ (labeled as ‘refined mix’). Interestingly the fit quality for the ‘alpha–alpha’ dimer is almost independent of the truncation value Q_{min} , with a GoF of about 1.39. This insensitivity

Figure 2

Neutron powder diffraction patterns. (a) Pure SiO_2 xerogel (unloaded), SiO_2 xerogel loaded with GuNP (loaded), and scattered intensity after subtraction (loaded – unloaded) and scaling. (b) Observed difference (loaded – unloaded) in the wide-angle region. The red line is a fit using the GuNP monomer in the coplanar configuration, while the green curve shows the fit when using a GuNP dimer. The curves below show the corresponding residua.

indicates that a study as a function of the truncation value can be used to eliminate models that exhibit equal GoF for a chosen $Q_{\min}$. However, this indicates also that the analysis has to be made carefully, especially with respect to the chosen limits of $Q_{\min}$ and $Q_{\max}$. Furthermore, the two distinct steps in

the GoF, around 2.5 and 10 nm⁻¹, validate our segmentation into the three ranges wide angle, intermediate angle and small angle for the detailed analysis.

3.2. Small-angle region – pore size and fill factor

Although a real small-angle scattering experiment with appropriate instrumentation would be needed to obtain a more precise evaluation, a coarse but effective analysis – meant as a reality check – could be successfully performed. In particular, comparison of $\log I(Q)$ versus Q^2 in the small-angle region shows that the slopes for the unloaded and loaded sample coincide. From the value of the slope we obtain a rough estimate – for spherical cavities – to a pore diameter of 1.0 (1) nm in both cases. Assuming an elliptical shape of the pores results in pore diameters of 0.7 (1) nm (width) and 1.4 (1) nm (length). As shown in Fig. 1 the GuNP complex in the coplanar form has dimensions of about 0.7 nm (width) and 1.4 nm (length) such that the found pore size is sufficient for embedding the whole GuNP complex without disturbing its structure significantly.

Further, the value of $\log I(Q)$ versus Q^2 at $Q = 0$ is proportional to the square of the average density contrast and hence to the fraction of loaded pores. In our case it is about a factor of two times smaller for the loaded sample. Neglecting the effect of water because the total coherent scattering length of a water molecule is small (1.675 fm), and making reasonable assumptions on the baseline as a result of the incoherent scattering of the water in the unloaded sample, we find that in the loaded sample the pore–matrix contrast is about 40–45% smaller than that of pure silica gel. On the other hand, the total scattering length for GuNP of 129.2 fm corresponds to a scattering length density of 247 fm nm⁻³ in a 1.0 nm sphere. The mass density for SiO₂ gel ranges from 1.8 to 2.1 g cm⁻³, and the corresponding scattering length density is in the range 280–330 fm nm⁻³. Therefore the scattering length density contrast (sum of scattering lengths of all atoms enclosed in a given volume divided by the volume) of a GuNP-filled 1 nm pore shows only 13–26% contrast with respect to an empty pore. In order to reach 40–45%, the fill factor in the loaded sample may be estimated to 60–80%. For details of the calculation and definition of scattering density contrast see Appendix A.

3.3. Intermediate-angle region – host–guest interaction

There are also interference terms between the molecule and the pore as a result of the short distances from Si, O or H atoms of the host network to atoms of the embedded GuNP complex. These are manifested especially in the $2.2 < Q < 15$ nm⁻¹ range. Without setting up a model of the atoms on the surface of the pore and their distance to the atoms of the GuNP complex, we simply plot – on a linear–logarithmic scale – the absolute value of the difference of the corrected observed intensity $I_{\text{loaded}} - I_{\text{unloaded}}$ (Fig. 2) and the calculated intensity I_{GuNP} , as illustrated in Fig. 4. This shows a characteristic oscillation with the first zero at $Q \simeq 10$ nm⁻¹. Assuming a dominating distance between one atom at the

Figure 3 Monomer and dimer configurations in GuNP (top) and corresponding dependence of the fit quality (GoF) on the truncation value of $Q_{\min}$: full range $1.3 < Q_{\min} < 19$ nm⁻¹ (middle) and zoom in the region $11 < Q_{\min} < 19$ nm⁻¹ (bottom). In both cases the smooth behavior indicates the reliability of the fitting approach and the possibility of distinguishing monomer and dimer models.

pore wall and one atom of GuNP, having distance R , the oscillation represents the $\sin(QR)/(QR)$ contribution to the total pattern of this mixed pair. Having the first zero at $Q \simeq 10 \text{ nm}^{-1}$, we can evaluate the distance as $R \simeq 0.31 \text{ nm}$. This points to a sort of anchoring point of GuNP to the pore walls, which has to be investigated further.

4. Conclusion

In summary we have shown that monomeric GuNP complexes incorporated into the nanopores of an SiO_2 xerogel retain their structural integrity. This example demonstrates that the structure of single molecules in nanopores and their distance to nearest neighbors of the host network can be analyzed using a standard neutron powder diffractometer with limited Q range. From the analysis of the small-angle range one obtains an estimate for the average pore size and the fill factor of pores with embedded complexes. The distance between atoms of the host network and the guest complexes can be determined from the intermediate scattering range. Assuming a sufficient scattering contrast between host and guest this method can be extended to the X-ray case, such that these experiments can be performed on laboratory X-ray sources. Hence we have shown that such nanostructured materials can be characterized using standard powder diffraction sources.

APPENDIX A

Average density contrast and fill factor

A sphere with volume V and average scattering length density ρ_b in a medium with average scattering length density ρ_b^0 will scatter at $Q \rightarrow 0$ an intensity

$$I(Q \rightarrow 0) = (\Delta\rho_b V)^2, \quad (2)$$

where $\Delta\rho_b = \rho_b - \rho_b^0$.

$$C = (\rho_b - \rho_b^0)/\rho_b^0 \quad (3)$$

Figure 4

Absolute difference (log scale) of the scattered intensity of the GuNP compounds given by $(I_{\text{loaded}} - I_{\text{unloaded}})$ and the calculated intensity for the complex I_{GuNP} . The first minimum at $Q = 10 \text{ nm}^{-1}$ corresponds to a GuNP–silica distance of about 0.31 nm.

is the definition of scattering length density contrast. Note that if the pores are empty then simply $\rho_b = 0$. Filling pores with something else, the scattering length density ρ_b will become ρ'_b . In that case,

$$I'(Q \rightarrow 0) = (\Delta\rho'_b V)^2 = [(\rho'_b - \rho_b^0)V]^2, \quad (4)$$

so

$$\begin{aligned} \frac{I'(Q \rightarrow 0)}{I(Q \rightarrow 0)} &= \frac{(\Delta\rho'_b V)^2}{(\Delta\rho_b V)^2} = \frac{(\rho'_b - \rho_b^0)^2}{(\rho_b - \rho_b^0)^2} \\ &= \frac{[(\rho'_b - \rho_b^0)/\rho_b^0]^2}{[(\rho_b - \rho_b^0)/\rho_b^0]^2} = \left(\frac{C'}{C}\right)^2. \end{aligned} \quad (5)$$

For N atoms in a volume V the scattering length density is

$$\rho_b = \frac{\sum_{j=1}^N b_j}{V}, \quad (6)$$

where b_j is the scattering length of the j th atom. We are considering pores of diameter $D = 1 \text{ nm}$, so

$$V = (\pi/6)D^3 = 0.5236 \text{ nm}^3. \quad (7)$$

If a molecule of GuNP is in the hole, as in this case

$$\sum_{j=1}^N b_j = 129.2 \text{ fm}, \quad (8)$$

the scattering length density will be $\rho_b^{\text{GuNP}} = 247 \text{ fm nm}^{-3}$. The substrate is SiO_2 with mass density $m = 1.8\text{--}2.1 \text{ g cm}^{-3}$, or

$$m = 1800 + 300x \text{ kg m}^{-3}, \quad 0 \leq x \leq 1. \quad (9)$$

Since 1 kmol of SiO_2 weighs $M = 60 \text{ kg}$, in a 1 nm^3 volume we have

$$n = 10^{-27} N_A m M \simeq 18 + 3x \quad (10)$$

molecules of SiO_2 (N_A being Avogadro's number). Each SiO_2 unit has a total scattering length of $b_{\text{SiO}_2} = 15.755 \text{ fm}$. Therefore, the summed scattering length density for the substrate is

$$\rho_b^{\text{SiO}_2} = n b_{\text{SiO}_2} = 284.6 + 47.4x \text{ fm nm}^{-3}. \quad (11)$$

To evaluate the density contrast of a GuNP-filled pore, we evaluate

$$C_{\text{GuNP}} = \frac{\rho_b^{\text{SiO}_2} - \rho_b^{\text{GuNP}}}{\rho_b^{\text{SiO}_2}} = 0.132, \dots, 0.256 \quad \text{for } x = 0, \dots, 1, \quad (12)$$

while for an empty pore, the same quantity is

$$C_{\text{empty}} = \frac{\rho_b^{\text{SiO}_2} - 0}{\rho_b^{\text{SiO}_2}} = 1. \quad (13)$$

Therefore the density contrast of a GuNP-filled pore is only 13–26% of that of an empty pore.

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