

Electronic Supplementary Information to:

Self-assembly of porphyrin hexamers via bidentate metal-ligand coordination

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1 Theoretical considerations for the SANS evaluations

1.1 Model for the SANS experiments

Neutron scattering can be considered as the ideal method to resolve the characteristics of objects in solution, since it is sensitive to both structural and volumetric parameters, as well as sizes with length scales between 1 and 1000 Å. It is similar to light scattering, however with increased sensitivity to the internal structure of the objects. If a theoretical model for the scattering particle is available, the absolute intensity which can be measured experimentally in a small angle (neutron or X-ray) experiment if the scattering is compared to a pre-calibrated standard, can be calculated and checked against the assumptions of it. The structural parameters that then enter in the model can then be refined and optimised in order to achieve the best agreement for the shape and size of the particle. In the following sections, we shortly summarize the main formulas which apply to the underlying manuscript and we refer to the specialized literature and text books for further details.¹ We will assume that the concentration of the particles is strongly dilute and that particle-particle interactions which are typically treated in a virial expansion can be neglected.

The intensity scattered from a dilute sample containing well-defined scattering objects is given as function of the scattering vector q and is defined in general as in equation (1).¹

$$\frac{d\Sigma}{d\Omega}(q) = \frac{N}{V} \langle f(q)f^*(q) \rangle + B_{gr} \quad (1)$$

This macroscopic differential scattering cross-section is abbreviated further as the intensity of the solution of scatterers and depends on the scattering vector q with $q=(4\pi/\lambda)\sin(\theta/2)$ where θ is the scattering angle and λ the wavelength. The coherent angle-dependence of scattering is determined by the form factor f^2 of the particles. An additional incoherent

structure-independent background B_{gr} is present as well and must be subtracted before model computations can be compared. The form factor $\langle f(q)f(q)^* \rangle = f^2$ yields the amplitude of the scattering and can be calculated from the geometry. N/V is the number density of the scattering objects, which can be estimated from the weighed concentration (yielding the number of molecules N) and the dimensions of the molecules as predicted by molecular modeling calculations (yielding the volume of the particles). The form factor is typically abbreviated as $P(q)$ and thus describes the shape of the particle from the intra-molecular correlations only. It is the Fourier-transform of the scattering length density distribution over the particle. It is clear that, depending on this, the form factors may differ largely. In this supplementary section which is not intended to review these, we restrict ourselves to the applicable ones in the interest of the particular manuscript. From the chemical construction and indirect spectroscopic investigations, spherical as well as elongated aggregates may be found. As the most detailed, a core-shell-shell structure may be identified from which further simplifications can be derived.

1.2 Core-shell cylinder

Considering the construction of the porphyrin hexamers, a model that assumes the presence of core-shell or even core-shell-shell cylindrical aggregates seems the most appropriate, although other structures may be equally well possible.^{2,3} If these differ strongly enough in their scattering length density (SLD, for neutrons) or electron density (for X-rays), the relative dimensions of the core and the shell structures, based on information from chemistry and molecular modeling and complying with theoretical contrast conditions, can be determined. The assumptions to be able to do this base on a massive and spatial independence of the scattering length distribution inside each component *i.e.* core and shell. This is a hard restriction and if this approach does not yield a satisfactory description, the core-shell model can be further simplified to a model based on a homogenous cylinder with the same length but averaged SLD irrespective of the core or former shells. This case is especially true for solutions of associated species in which no dense, no massive components can be identified but instead a thorough intermixing of shells and the embedding medium occurs.

With respect to this, the porphyrin hexamers can be considered to comprise three such segments: (i) a core, (ii) a shell of porphyrin moieties, and (iii) a shell of alkyl tails (Figure S1). The scattering intensity of a core-shell cylinder in a solvent as a 3-component system has been reported previously.¹⁻³ To apply this, the number of components is to be reduced to 3 for a core, a shell and the solvent. The number of segments describing the porphyrin cylinders in the present case needs to be reduced to two: one core segment and one shell. For a random orientation of dilute cylinders, equation (1) can be specified to yield equation (2), which was used as the basis for our curve fitting.

$$I(q) = \frac{\phi}{V_{shell}} \int_0^{\pi/2} f^2(q, \alpha) \sin \alpha d\alpha + B_{gr} \quad (2)$$

In equation (2) the intensity $I(q)$ includes the more complicated definition of the form factor amplitude f as a function of q and α , the angle of the scattering vector q with the cylinder axis. The full description is given by equation (3), which can be simplified at a later stage,

if necessary.

$$\begin{aligned}
 f(q, \alpha) = & 2(\rho_{core} - \rho_{shell})V_{core}j_0(q \frac{1}{2}L \cos \alpha) \frac{J_1(qr \sin \alpha)}{qr \sin \alpha} \\
 & + 2(\rho_{shell} - \rho_{solvent})V_{shell}j_0(q(\frac{1}{2}L + t) \cos \alpha) \frac{J_1(q(r+t) \sin \alpha)}{q(r+t) \sin \alpha}
 \end{aligned} \tag{3}$$

In equation (3), r is the radius of the core of the cylinder, while the ‘shell thickness’ is represented by the variable t and L is the full length of the cylinder. $J_1(x)$ is the first order Bessel function and $j_0(x) = \sin(x)/x$. V_{core} and V_{shell} are determined by $\pi r^2 L$ and $\pi(r+t)^2 L$, respectively. Note that we changed the notation from N/V to ϕ/V_p where ϕ is the volume fraction and V_p the volume of the scattering particle. In solution, integration over all contributions from all angles is performed to account for the averaging over all possible orientations of the cylindrical object. This integral in Eq. 2 is done numerically. The parameter ρ in the above formulas is defined as the scattering length density (SLD), which is obtained from summing up all coherent scattering lengths ‘b’ (tabulated values)⁴ per volume of a scattering component and we occasionally switch between the notations. In the present study where the bruto formulas are known from chemistry, the SLD values are estimated from the molar mass and the bulk density of similar compounds. As can be recognized, if the shell and solvent cannot be distinguished, the scattering is only due to the core whereas if the solvent matches the core, then a hollow particle results and the shell is measured. Likewise, if core and shell have the same SLD, the first term in Eq 3 cancels and the 2nd term leads to the homogenous case of a cylinder in a solution. As a further approximation it can be seen experimentally that a short cylinder of which the length is twice its radius can hardly be distinguished from that of a spherical particle which yields

$$f(q) = (\rho_{core} - \rho_{solvent}) \frac{4\pi}{3} r^3 \left(3 \frac{(\sin(qr) - qr \cos(qr))}{(qr)^3} \right) \tag{4}$$

and can be inserted in the former orientation-average which of course is angle-independent.

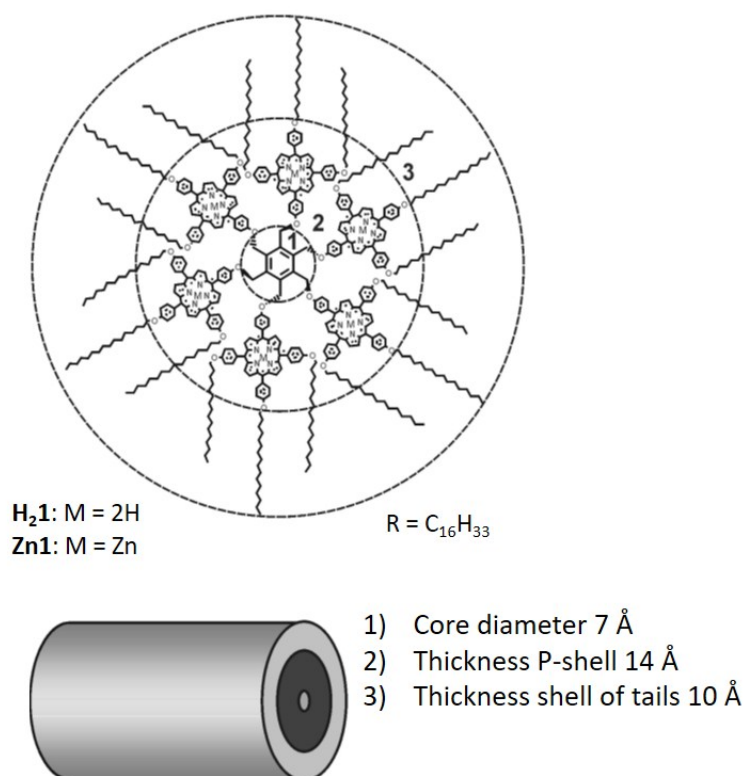


Figure S1 Definition of core and shell segments of porphyrin hexamers, and schematic representation of the core-shell cylindrical structure of the aggregates.

1.3 Scattering length densities

As the former scattering models already lead us to suspect, the detailed shape of the curves, is strictly correlated to the scattering length densities (SLDs) of all three components.² It is crucial to estimate the SLD-values of core, shell and solvent as accurately as possible because small differences in the theoretical SLDs may lead to huge discrepancies in the resulting relative dimensions found by curve fitting. In the case of ideal core-shell cylindrical particles, there should be sufficient contrast between all different segments in order to elucidate the core radius and shell thickness. If the SLD-values of core and shell are identical, only the part, which contains the contrast with the solvent remains, corresponding with a solid or homogeneously filled cylinder. On the other hand, if the SLD of the solvent is chosen to match the SLD of the core the measured scattering is that of a hollow cylinder. If the shell is equally scattering as the solvent, only the part which describes the core remains, and the core radius can be determined.

In practice, intermixing can occur between core and shell and/or solvent is taken up in any or both of the components. In such cases, the individual contributions of core and shell become inseparable, making it necessary to reconsider the average SLD of core and shell, taking into account the density profile of the solvent inside the aggregate.⁵ With the simplification for a homogeneous cylinder, equation (2) is modified to equation (5):

$$I(q) = \frac{\phi}{V_{cyl}} \int_0^{\pi/2} 4(\rho_{cyl} - \rho_{solvent})^2 V_{cyl}^2 j_0^2(q/2 L \cos \alpha) \frac{J_1^2(qr \sin \alpha)}{(qr \sin \alpha)^2} \sin \alpha d\alpha + B_{gr} \quad (5)$$

In this equation the unknowns are $V_{cyl}(r,L)$, the volume fraction ϕ and the contrast factor $(\Delta\rho)^2$, which scales with the difference between the SLD values of cylinder and solvent. The product of all three variables yields the prefactor and at the same time the intensity at $q = 0$ as the structure is normalized to 1. The volume parameter is obtained intrinsically from the q -dependence through r and L by $V = \pi R^2 L$ but can be corroborated from the extrapolated intensity at $q = 0$. This leaves ϕ and $(\Delta\rho)^2$ as remaining decisive parameters. Since they cannot be determined separately, the calculated volume fraction (based on the amount of material in the dispersion) can be used as input to obtain the contrast factor from curve fitting. Since the measured intensity should scale with dilution due to its dependency on ϕ , the effect of dilution on the intensity at $q = 0$ provides an independent control to remove remaining uncertainties.

1.4 Determination of the radius

In the calculation of model intensities it is assumed that radii as well as lengths in the scattering object are monodisperse. Polydispersity in the radius of the core will affect mainly the high q -region, smearing the minima whereas a distribution of lengths will result in a loss of resolution at low q .⁶ Since no distribution model for the cylinder length is known and in view of the rather pronounced low q -Guinier behavior, the cylinder is taken in good approximation monodisperse.

As far as this hypothesis can be kept and as shown from the data, the first minimum in the oscillation of the form factor provides direct information about the radius of the object. In addition, it allows one to discriminate between cylinders and spherical objects. For a cylinder the term $(J_1(x)/x)^2$ ($x = qr$) shows its first minimum at $x = 3.83$, *i.e.* r is obtained as $3.83/q_{\min}$, while for a sphere this minimum shifts to $x = 4.49$; q_{\min} here is the value of q at the minimum. This means that, for a constant radius, spherical objects (nonaggregated disks or very short rods) should have their first minimum at approximately 17% higher scattering vector values than cylinder-shaped objects, which is a significant difference. In the case of spherical objects, the single disks have to be modeled as simple spherical units of which the volume, contrast with the solvent, and radius can be determined. The intensity is then described by the more simple equation (6) for spherical objects. We add here also the incoherent background B_{gr} to yield from equation (4)

$$I(q) = \phi V_{sph} (\rho_{sph} - \rho_{solvent})^2 \left[3 \frac{\sin(qr) - (qr) \cos(qr)}{(qr)^3} \right]^2 + B_{gr} \quad (6)$$

V_{sph} is the volume of the sphere ($4/3\pi r^3$). The radius is not expected to differ from the value used in the cylinder case. Again, no polydispersity is assumed in the radius and therefore no volume polydispersity is to be expected.

1.5 Geometric information derived from the shape of the scattering profile

A typical scattering profile as measured for **Zn1** + DABCO can be depicted by plotting the experimental scattering intensity I versus the scattering vector q on a log-log scale (Figure S2). The scattering is determined at 4 different distances of the sample with respect to the

detector. For the present system, there is a perfect overlap of the intensity profiles measured at different positions (covering different q -ranges).

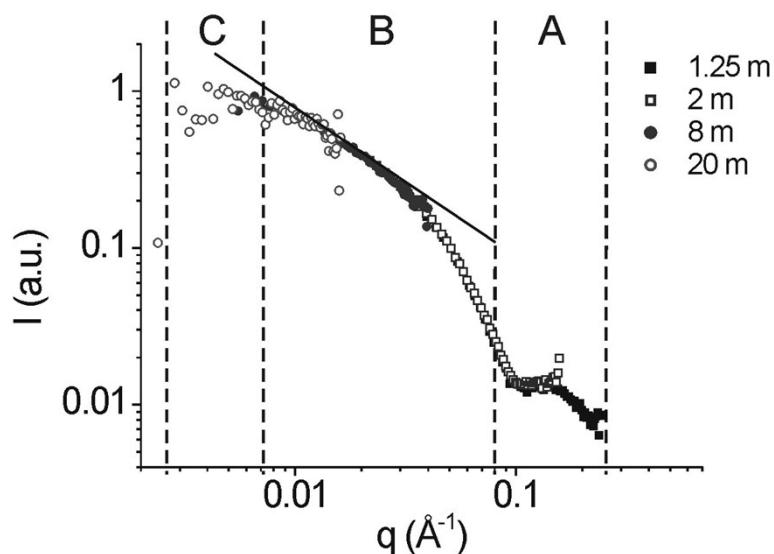


Figure S2 Experimental scattering profile measured for **Zn1** + DABCO ($[\text{Zn1}] = 2.8 \text{ mM}$) at 4 different positions from the detector. Information about the geometry and size of the scattering object can be derived from different q -regions, denoted as A, B and C (see text).

The right-hand side of the curve (high q) holds information about the core-shell character of the scattering particles. The length scales at this region are of the order $2\pi/q$, corresponding to ~ 5 to 10 \AA . In simulated curves where the relative dimensions of the core and shell are used as input (with realistic SLD-values), there can be very clear modulations. In practice, however, they are mostly not perfectly resolved due to a wavelength spread, experimental pixel size and polydispersity.⁷

The middle part of the curve (intermediate q) may provide information about the rodlike character of the aggregates. From mathematical simplifications of the cylindrical structure factor a q^{-1} behavior is expected for rodlike scatterers,^{1-3,8} Such q^{-1} behavior can be recognized in normal log–log plots as a part of the curve where the slope is constant over a certain range of q and is approximately -1 (experimentally, deviations from -1 are possible due to the contribution of other terms). In Figure S2, such a linear relation is present (the straight line is drawn to guide the eye). Theoretically, in the case of cylinders with a length L going to infinity, the structure factor seems to split in a very good approximation to $I(q) \sim \pi/(qL) \cdot (2J_1(qr)/qr)^2$. Plotting the scattering curves as qI vs q , which is often seen in literature,^{9,10} this results in a q -independent line and the graphical proof of the cylinder. The transition between the 2 regimes leads to a kink (which can be seen) and occurs around the q value corresponding to the reciprocal radius.

From region C (low q) the overall size of the cylindrical aggregates can be derived. In the case of rods, for which a so-called Guinier or Zimm plateau is visible^{31,3,8} at the lowest q -range, the intensity can be described (like in light scattering) by equation (7), yielding a first estimate of the radius of gyration R_g .¹¹

$$\ln I = \ln I(q=0) - \frac{qR_g^2}{3} \quad (7)$$

For very thin rods, L and R_g are related as $R_g = \sqrt{(1/12)L}$. Practically, if the curve levels off at low q , extrapolation of the intensity at $q = 0$ thus leads to a simple estimate of the length of the rods. On the other hand, if the curve does not reach a plateau at low q , the existence of even larger scattering objects than $R_g \sim 1000 \text{ \AA}$ cannot be excluded.

1.6 Dimensions of core and shell

The observation of modulations at high q suggest that at least the average radius and possibly also the relative dimensions of the core and the shell can be fitted, using as input values the weighted average of the scattering length densities (SLDs) that were calculated for the constituting core and shells of the hexamer structures (regions 1, resp. 2 and 3 in Figure S1 and Table S1). It should be noted that, the expected form factor would be that of a 4-component mixture (core, 2 shells and solvent. The different SLDs for the regions 1-3 should yield contrast with the solvent CDCl_3 ($\text{SLD} = 3.16 \times 10^{10} \text{ cm}^{-2}$). As can be seen from Table 1, the largest contrast with the solvent is expected from the alkyl tails in shell 3, for which the SLD is even negative; it should be noted, however, that the alkyl tails do not completely fill this shell, and that the empty space is taken up by solvent molecules, which on average reduce the contrast. The SLDs of shell 2 corresponding to the porphyrin moieties are very similar to the SLD of the solvent, and apparently the contrast predicted by these calculations are not influenced much by the metallation of the porphyrins, nor by the presence of the DABCO ligand. The weighing factors are the volume fractions of each ring using the estimated dimensions of the molecules as derived from molecular modelling.

Table S1. Calculated SLDs (cm^{-2}) of molecular segments based on bruto formulae. For the definition of regions (1)-(3), see Figure S1.

Compound	Core (1)	Porphyrin shell (2)	Alkyl tail shell (3)
H₂1	1.2×10^{10}	2.97×10^{10}	-3.52×10^9
Zn1	1.2×10^{10}	2.85×10^{10}	-3.52×10^9
Zn1 + DABCO	1.2×10^{10}	2.72×10^{10}	-3.52×10^9

For example, for the free base hexamer **H₂1**, the volume of the porphyrin shell is $V = \pi(17.5^2 - 3.5^2)L$, whereas the total volume taken by the alkyl tails is $V = \pi(27.5^2 - 17.5^2)L$, yielding a ratio of 0.4 for porphyrins/(porphyrins + tails). If the core-shell cylinder is considered to have region 1 as the core (radius = 3.5 Å, $\text{SLD} = 1.12 \times 10^{10} \text{ cm}^{-2}$) and ring 2 and 3 together as shell (thickness = 24 Å), the SLDs of rings 2 and 3 must be weighed by 0.4 and 0.6, respectively. This yields a new SLD for the shell of $0.99 \times 10^{10} \text{ cm}^{-2}$. Obviously, the SLDs of the core and shell become almost identical, corresponding to a solid homogeneous cylinder.

Taking region 1 and ring 2 together as the core and the alkyl tails as shell requires weighing the SLDs of regions 1 and 2 by 0.04 and 0.96, respectively. The small contribution of ring 1 to the total volume only slightly decreases the SLD of the porphyrin shell; the new SLD for the core is still $2.8 \times 10^{10} \text{ cm}^{-2}$, thus the contrast with the solvent is very small. In principle, the alkyl tails that contain many hydrogen atoms would provide the largest contrast with deuterated solvents. As discussed above, however, the outer shell is hairy and comprises a lot of empty space that is filled up with solvent; for example, the mixing in of 50% of CDCl_3 solvent molecules changes the SLD of region 3 effectively into $1.4 \times 10^{10} \text{ cm}^{-2}$.

Thus, employing either of the approaches of defining a core and a shell, the calculated contrasts between core and shell and with the solvent are decreased or modified in such a way that no distinction can be easily made between core and shell. It must be concluded that the most realistic contrast between the particles and the solvent can be obtained when the model assuming a homogenous cylinder is applied. This approach to assume one average SLD for the cylinder as a whole is valid, and often used if the individual SLDs of core and shells cannot be assigned unambiguously or if the object is interpenetrated with the solvent. In spite of this necessary simplifying approximation, the resulting parameters were observed to fit the experimental data very accurately (*vide infra*). We take the stock solutions of which the concentrations are well defined, as the reference from which the SLD of the average cylinder/spherical aggregate can be obtained from the refinement. For the **Zn1**-DABCO combination, the SLD of the aggregate is $2.53 \times 10^{10} \text{ cm}^{-2}$ whereas for **H₂1** a value of $2.69 \times 10^{10} \text{ cm}^{-2}$ is derived. Independent of the morphology these values sufficiently corroborate the assumption above where the outer shell is 'annihilated' or invisible in the chloroform. The description of the samples diluted *in situ* was achieved assuming this effective SLD of the aggregate and allowed the dilution degree to be verified experimentally from SANS. Within experimental error, the latter values are fully in line with the envisaged ones. While detailed information on the internal construction of the rod cannot be derived in this approach, these results can be nevertheless considered confidently as proof of the assembly of disks into rodlike aggregates.

2. References

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11. The exact form in terms of R and L can be obtained from Taylor expansion of the above given structure factors (equations 1, 2, 4 and 5). The above approximation is therefore only valid up to $qR_g = 1-2$.