

Electronic Supplementary Information (ESI)

## Solution scattering studies of the hierarchical assembly of porphyrin trimers based on benzene triscarboxamide

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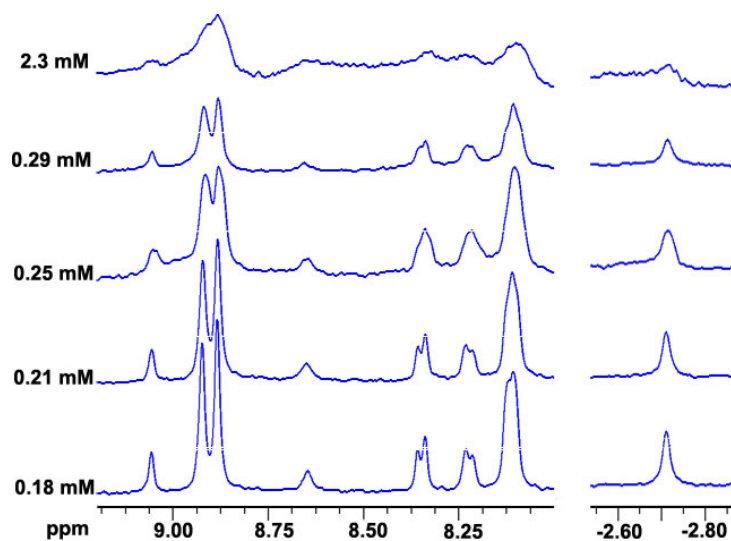
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Critical aggregation constant determination of compound **2**.



**Figure S1** Critical aggregation constant (c.a.c) determination of compound **2**.  $^1\text{H-NMR}$  spectra in  $\text{CDCl}_3$  of the aromatic region and the region of the pyrrole NH protons as a function of concentration. The c.a.c. value was determined to be  $0.2 \pm 0.05$  mM.

**SANS experiments.** SANS experiments on **1** were performed at the KWS1 spectrometer at the FRJ-2 Dido Reactor at Jülich, Germany.<sup>1)</sup> The SANS experiments on **2** in *n*-hexane-D14 were performed at 293 K at the small angle scattering instrument D11 at the Institute of Laue-Langevin in Grenoble,<sup>2)</sup> France, which has been described in the literature before.<sup>3)</sup>

**SANS theoretical model.** If a theoretical model for the scattering particle can be assumed, the absolute intensity which is measured experimentally can be calculated and checked. Parameters entering in the model can then be fitted and optimised in order to achieve the best agreement. The scattering cross-section of a collection of  $n$  particles can be written as:<sup>4)</sup>

$$\frac{d\Sigma}{d\Omega}(Q) = n\Delta\rho^2V^2P(Q)S(Q) + B_{gr}$$

where  $\Delta\rho$  is the difference in scattering length densities between the particles and solvent,  $V$  is the volume of the particles,  $P(Q)$  is the particle form factor,  $S(Q)$  the structure factor and  $B_{gr}$  is the incoherent background from solvent and solutes. The form factor describes the shape of the molecules, while the structure factor describes the interference of scattering of different particles and can give information on the interaction between the particles. In diluted systems this term can be neglected. As such, the differential scattering cross-section becomes:

$$\frac{d\Sigma}{d\Omega}(Q) = n\Delta\rho^2V^2P(Q) + B_{gr}$$

In case of spherical particles the scattering cross-section becomes:

$$\frac{d\Sigma}{d\Omega}(Q) = \phi_N V_S \Delta\rho^2 \left[ 3 \frac{\sin(QR_S) - QR_S \cos(QR_S)}{(QR_S)^3} \right]^2 + B_{gr}$$

where  $\phi_N$  is the volume fraction of the particles,  $V_S$  is the volume of the sphere ( $V_S = \frac{4}{3} \pi R_S^3$ ) and  $R_S$  is the radius of the sphere. In case the particles exhibit a cylindrical shape and are randomly oriented, the differential scattering cross-section becomes:<sup>5)</sup>

$$\frac{d\Sigma}{d\Omega}(Q) = \phi_N V_C \Delta\rho \int_0^{\frac{\pi}{2}} \left[ \frac{2J_1(QR_c \sin \alpha)}{QR_c \sin \alpha} \frac{\sin(\frac{1}{2} QL_c \cos(\alpha))}{\frac{1}{2} QL_c \cos(\alpha)} \right]^2 \sin \alpha d\alpha + B_{gr}$$

With  $V_C$  being the volume of the cylinder ( $V_C = \pi R_C^2 L_C$ ),  $R_C$  the radius and  $L_C$  the length, and  $\alpha$  the angle between the rod axis and the  $Q$ -vector.

In order to account for the upturn at low  $Q$ , we followed the approach of Pezron et al.,<sup>6)</sup> who demonstrated that it is possible to make an approximation of the structural parameters of solutes in a mesh, by taking into account the so-called screening length ( $\xi$ ), which is related to  $Q$  and the particle form factor  $P$  by the following equation:

$$P(Q) = \frac{P(0)}{1 + Q^2 \cdot \xi^2}$$

With this  $\xi$ -value it is possible to express the structural parameters of solutes in a mesh as a function of those in a dilute solution. In a good solvent for the rods, the  $\xi$ -value represents the average mesh-size in a transient network of chains.

The errors quoted on SANS-derived dimensions are fitting errors; the resolution of SANS is never below 1 Å.

## References

- 1) [http://www.fz-juelich.de/jcns/DE/Leistungen/Instruments2/Structures/KWS1/\\_node.html](http://www.fz-juelich.de/jcns/DE/Leistungen/Instruments2/Structures/KWS1/_node.html)
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- 4) J. S. Pedersen, *Modelling of Small-Angle Scattering Data from colloids and Polymer Systems in: Neutrons, X-rays and light: scattering methods applied to soft condensed matter*. (eds. Lindner, P. & Zemb, T.) (Elsevier Science B.V., Amsterdam, 2002 pp. 391-420)
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