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Toward Nanodevices: Synthesis and Characterization of the Nanoporous Surfactant-Encapsulated Keplerate $(DODA)_{40}(NH_4)_2[(H_2O)_n\subset Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$

Dirk Volkmer,*,[†] Alexander Du Chesne,[‡] Dirk G. Kurth,*,[§] Heimo Schnablegger,[§] Pit Lehmann,[§] Michael J. Koop,[†] and Achim Müller[†]

Contribution from the Department of Inorganic Chemistry 1, University of Bielefeld, P.O. Box 100 131, D-33501 Bielefeld, Germany, the Max-Planck-Institute for Polymer Research, P.O. Box 3148, D-55021 Mainz, Germany, and the Max-Planck-Institute of Colloids and Interfaces, D-14424 Potsdam, Germany

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Abstract: We describe the spontaneous self-assembly and the superstructure of a discrete surfactant-encapsulated cluster, $(DODA)_{40}(NH_4)_2[(H_2O)_n\subset Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ (**2**, $n \approx 50$), which consists of a hollow giant isopolyoxomolybdate core covered by a hydrophobic shell of dimethyldioctadecylammonium (DODA) cations. The structural characterization of these nanoporous core−shell particles is based on small-angle X-ray scattering (SAXS) data on solutions of the encapsulated clusters, TEM investigations, FT-IR and UV−vis spectroscopy, as well as determination of the molecular area of **2** by Langmuir film investigations. Computer modeling of the solvent-accessible surface of the encapsulated cluster yields a central cavity with a volume of 1.5 nm^3 that is occupied by approximately 50 H_2O molecules. The cluster bears (Mo−O) 9-ring openings with an average diameter of 0.43 nm. The covered surface area of 84 Å^2/DODA indicates a rather tight packing of the amphiphile at the cluster surface. Due to the unique supramolecular architecture of **2** as well as its high solubility in common organic solvents, this compound shows promising perspectives for future applications in host−guest chemistry and homogeneous size-selective catalysis.

Introduction

The future design of functional nanodevices will most likely rely on the principles of molecular self-organization.[1] Current approaches to this ambitious task focus on supramolecular model systems which self-assemble according to a manageable set of combination principles from a limited number of building blocks. Discrete supramolecular structures have been assembled from suitably designed organic building blocks exploiting ligand−metal ion interactions,[2] $\pi-\pi$ interactions,[3] or hydrogen-bonding mediated recognition processes.[4] With the recent discovery of self-assembling, discrete and nanosized polyoxomolybdates ("giant wheels",[5] "Keplerates"[6]), novel inorganic components are now available, allowing access to the construction of advanced nanodevices such as nanoreactors or sensors. A crucial point for POM applications that require further processing steps is the ability to control the surface properties and the grade of dispersion of the preferentially water-soluble clusters. This problem may be alleviated by encapsulating the inorganic clusters with a solubilizing protective shell of organic molecules, as we have recently shown in detail for the partially reduced heteropolyoxomolybdate $[H_3Mo_{57}V_6(NO)_6O_{183}(H_2O)_{18}]^{21-}$.[7]

Here we report on the synthesis and preliminary characterization of a novel type of partially reduced isopolyoxomolybdate, namely the surfactant-encapsulated Keplerate $(DODA)_{40}(NH_4)_2[(H_2O)_n\subset Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ (**2**, $n \approx 50$). Compound **2** was prepared from $(NH_4)_{42}[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]\cdot$ca. 300 $H_2O\cdot$ ca. 10 CH_3COONH_4 (**1**), the structure and synthesis of which have been described previously (ref 6).

Results and Discussion

For the surfactant-encapsulated cluster (SEC) **2**, we propose the following structure (compare Figure 1a): a single anionic Keplerate cluster **1** resides in a hydrophobic shell of 40 DODA molecules, leading to a discrete, nearly spherical particle. The cationic headgroups of the surfactant molecules point toward the negatively charged surface of the cluster core **1**, which itself possesses an average diameter of 3.0 nm, as derived from the crystal structure of **1** (ref 6). To determine the solvent-accessible surface (SAS) of **1**, we assumed a surface probe radius of 0.28

[†] University of Bielefeld.

[‡] Max-Planck-Institute for Polymer Research.

[§] Max-Planck-Institute of Colloids and Interfaces.

(1) Lehn, J.-M. *Supramolecular Chemistry*; VCH: Weinheim 1995; pp 139−197.

(2) Stang, P. J.; Olenyuk, B. *Acc. Chem. Res.* **1997**, *30*, 502−518.

(3) Claessens, C. G.; Stoddart, J. F. *J. Phys Org. Chem.* **1997**, *10*, 254−272.

(4) (a) Whitesides, G. M.; Simanek, E. E.; Mathias, J. P.; Seto, C. T.; Chin, D. N.; Mammen, M.; Gordon, D. M. *Acc. Chem. Res.* **1995**, *28*, 37−44. (b) Rebek, J. *Acc. Chem. Res.* **1999**, *32*, 278−286.

(5) (a) Müller, A.; Krickemeyer, E.; Meyer, J.; Bögge, H.; Peters, F.; Plass, W.; Diemann, E.; Dillinger, S.; Nonnenbruch, F.; Randerath, M.; Menke, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2122−2124. (b) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Beugholt, C.; Kögerler, P.; Lu, C. Z. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1220−1223. (c) Müller, A.; Das, S. K.; Fedin, V. P.; Krickemeyer, E.; Beugholt, C.; Bögge, H.; Schmidtmann, M.; Hauptfleisch, B. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1187−1192. (d) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Beugholt, C.; Das, S. K.; Peters, F. *Chem. Eur. J.* **1999**, *5*, 1496−1502. (e) Müller, A.; Kögerler, P.; Kuhlmann, C. *Chem. Commun.* **1999**, 1347−1358.

(6) Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Peters, F. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3360−3363.

(7) Kurth, D. G.; Lehmann, P.; Volkmer, D.; Cölfen, H.; Koop, M. J.; Müller, A.; Du Chesne, A. *Chem. Eur. J.* **2000**, *6*, 385−393.

10.1021/ja992350v CCC: $19.00

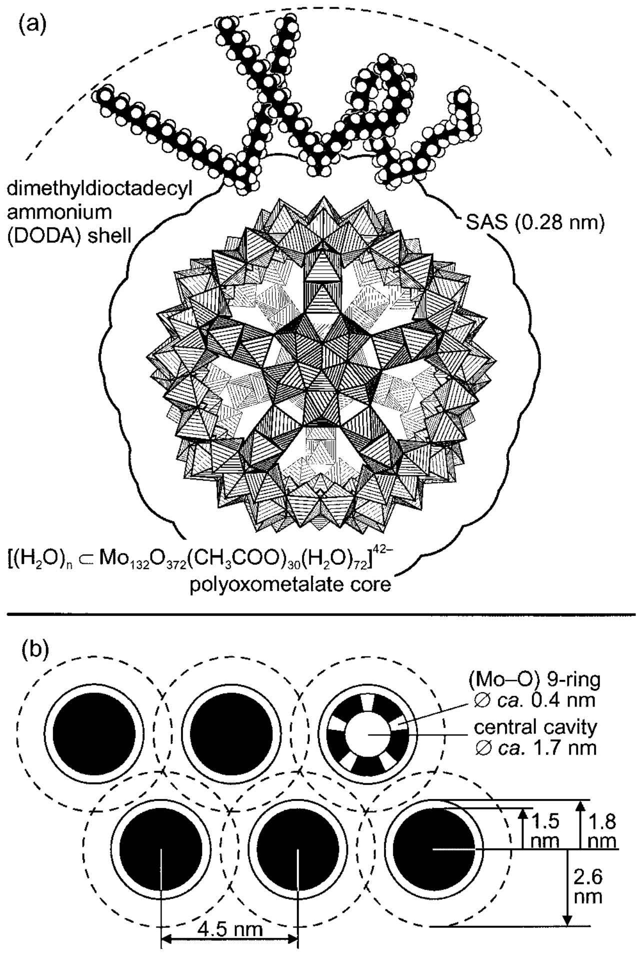

Figure 1. (a) Schematic representation of the surfactant-encapsulated cluster (SEC) **2**. The Mo−O framework of the Keplerate **1** is shown as a fused-polyhedral model. The DODA amphiphiles, only a fraction of which are represented in the scheme, form a hydrophobic shell around the cluster. Molecular dynamics simulations of a single SEC **2** placed within a periodic solvent-filled ($CHCl_3$) box indicate that in solution the relative density of the appending C_{18} chains decreases as the radial distance from the cluster increases. Due to the conformational flexibility of the C_{18} chains, the external boundary of the SEC (represented by the broken line) is not sharply defined. (b) Schematic representation of a single layer of **2** in accordance with TEM data and molecular models. The SECs arrange on a 2D lattice to form a closest packing. Surfactant shells of neighboring SECs locally interpenetrate one another. One of the SECs is displayed cross-sectioned to further highlight the supramolecular architecture.

nm, which refers to the estimated van der Waals radius of the tetramethylammonium cation that we considered as a model for the headgroup of DODA. Modeling the SAS of **1** yields a value of 33.4 nm^2.[8] Within the given range of uncertainty, this corresponds reasonably well to the empirical value of 32 (±8) nm^2 for the complete surface area of 40 DODA molecules.[9] Geometric matching of the two juxtaposed ionic surfaces may be a critical point for driving the self-encapsulation process to completeness. The surface charge density of the cluster anion **1** is such that all DODA molecules find sufficient space to form a single layer at a van der Waals distance to the cluster surface. The covered surface area of a 0.84 nm^2/DODA molecule furthermore suggests a rather tight packing of the amphiphile at the cluster surface. The SAS of **1** for a 0.28 nm probe displays a continuous spherically shaped surface which indicates that the DODA cations cannot penetrate the large central cavity of the Keplerate. In contrast, the SAS of **1** for a 0.14 nm probe, which is often referred to as the water-accessible (Connolly) surface,[10] extends into the central cavity through each of the 20 noncircular (Mo−O) 9-ring openings (ring aperture 0.30−0.56 nm). The 30 coordinated acetate ligands of **1** point with their methyl groups toward the center of the cluster, rendering the inner surface of the Keplerate partly hydrophobic. Nevertheless, the remaining internal cavity is quite large: from the crystal structure of **1** we determined a void volume of approximately 1.5(±0.3) nm^3. For a specific H_2O density of 1 g/cm^3 (=33.5 H_2O molecules/nm^3), we conclude that as many as 50(±15) H_2O molecules reside within the central cavity of **1**.[11]

Experimental evidence for the proposed structural model thus far is deduced from spectroscopic investigations, small-angle X-ray scattering (SAXS), and electron microscopy.

The UV−vis and IR spectra of **2** show the characteristic features of the Keplerate cluster (Experimental Section). Small-angle X-ray scattering (SAXS) studies were performed on solutions of **2** in toluene and on solutions of **1** in 1 M aqueous NH_4Cl, respectively. As a sensitive probe for electron-density differences in the scattering medium, the pair−distance distribution function (PDDF) obtained from SAXS provides information on the maximum dimension of the particle and its radius of gyration. In diluted systems where interparticle interferences can be neglected, the PDDF profile is characteristic for the shape and internal structure of the particles.[12] From the PDDF of **2** in toluene (and of **1** in aqueous solution, respectively; compare Figure 2a) the particle diameters are estimated to be 2.8 ± 0.2 nm, which is in excellent agreement with the crystallographic data of **1**. (The small negative oscillation in the PDDF of **1** at large radial distances is caused presumably by residual contributions of interparticle interferences that could not be avoided completely although NH_4Cl electrolyte was added to the aqueous solution of **1** to screen long-range Coulomb interactions.) The PDDFs of **2** in toluene and of **1** in aqueous solution (Figure 2a) are both asymmetric in shape and bent toward large radial distances, which is a characteristic feature of hollow spheres. In particular, the slope of the graph for $2.5 < r < 3.0$ nm

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(8) To model the SAS, cluster **1** was placed by its crystallographic coordinates into the center of a water model (TIP3P, equilibrated at 300 K and 1 atm) kept within a cubic solvent box of 4.0 × 4.0 × 4.0 nm dimensions (HyperChem Release 5.02, HyperCube Inc. 1997). A critical minimal distance of 0.23 nm was taken to remove H_2O molecules from the vicinity of the inserted cluster. Of the 2114 initially generated H_2O molecules, 489 were automatically removed after inserting cluster **1**. The water-box model thereafter was edited manually, to discriminate between internal and external H_2O molecules. The final model displayed 50 internal H_2O molecules hosted by the Keplerate **1**. The model does not consider specific adsorption of H_2O molecules to the internal surface of the cluster. The displayed SAS value was finally calculated with the program WebLab Viewer Pro 3.20 (Molecular Simulation Inc., 1998), based on the suggested default van der Waals radii: O, 1.35 Å; C, 1.55 Å; and H, 1.10 Å.

(9) The molecular surface area of a single DODA cation as determined from the lamellar arrangement of DODA cations in the single-crystal structure of the compound DODA·Br (monohydrate), CSD entry code CIYWOW20, is 56.7 Å^2. Okuyama, K.; Soboi, Y.; Iijima, N.; Hirabayashi, K.; Kunitake, T.; Kajiyama, T. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1485−1490. Empirical values for the molecular surface area of a single DODA cation have been frequently determined from the Langmuir isotherms of compressed DODA monolayers spread at the air−water interface. The reported values range from 60 to 100 Å^2/DODA molecule, depending on the chemical nature of counteranions within the aqueous subphase. See: (a) Marra, J. *J. Phys. Chem.* **1986**, *90*, 2145−2150. (b) Clemente-León, M.; Agricole, B.; Mingotaud, C.; Gómez-García, C. J.; Coronado, E.; Delhaes, P. *Langmuir* **1997**, *13*, 2340−2347.

(10) Connolly, M. L. *Science* **1983**, *221*, 709−713.

(11) Keplerates with coordinated formate anions which possess a more hydrophilic inner surface have been described very recently. In this case, the positions of approximately 60 H_2O molecules residing within the Keplerate cavity could be determined directly by X-ray crystallography. Müller, A.; Fedin, V. P.; Kuhlmann, C.; Bögge, H.; Schmidtmann, M. *Chem. Commun.* **1999**, 927−928.

(12) Glatter, O. *J. Appl. Crystallogr.* **1979**, *12*, 166−175.

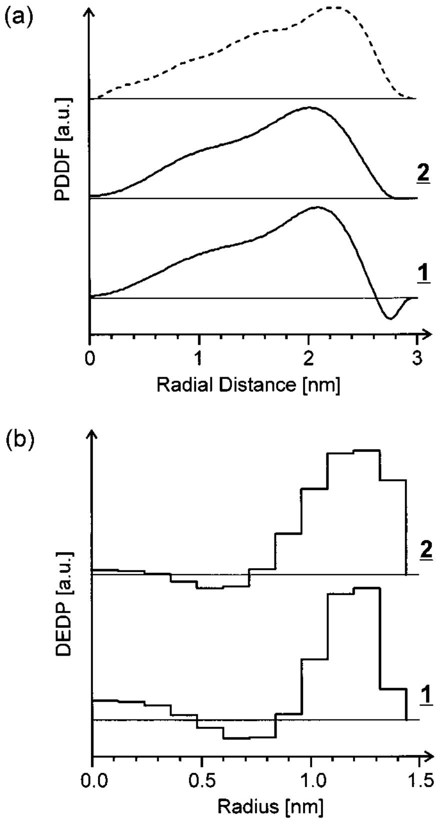

Figure 2. Small-angle X-ray scattering data. (a) Experimental pair-distance distribution functions (PDDFs) of the cluster anion **1** (bottom) and of the SEC **2** (middle). The dashed curve at the top represents a simulated PDDF, based on the crystallographic atomic positions of **1**. The PDDFs are asymmetrically bent toward large radial distances, which is indicative of a hollow sphere structure of the scattering particles. The mean particle diameter for **2** (and **1**, respectively) is 2.8 ± 0.2 nm, which is in excellent agreement with the molecular dimensions of **1** (av diameter: 3.0 nm). (b) Calculated difference electron-density profiles (DEDP) of **2** (top) and **1** (bottom) showing sharp maximums at a radius of 1.3 nm which may be ascribed to an electron-dense shell of Mo centers.

descends faster in comparison to the hypothetical PDDF corresponding to a solution of homogeneous but polydisperse spherical particles with a PDDF maximum at the same radial distance. The topmost curve in Figure 2a shows the theoretical PDDF, computed with a particle model based on the crystallographic coordinates of **1**, which is very similar to the experimental PDDFs. The correspondence between the experimental and the theoretical PDDFs may be regarded as a strong indication for the fact that the structural integrity of the Keplerate clusters is preserved within the SEC during and after the preparation procedure. Figure 2b shows the calculated difference electron-density profile (DEDP) as a function of the particle radius. Clearly, the electron density is smaller at the center of the sphere than on the periphery, in accordance with the hollow sphere structure of **1**. For small radii the DEDPs oscillate around zero, which is more pronounced for the aqueous solution of compound **1** compared with the toluene solution of compound **2**. This behavior may also be due to the residual influence of interparticle interferences.

Discrete clusters as in **2** have been directly imaged by transmission electron microscopy. Figure 3a shows a thin film originally cast onto a water surface. The inorganic cores of **2** appear as dark spots embedded in a bright matrix of surfactant molecules. Both the diameter of the dark objects (ca. 3 nm) as well as the average distance between them (ca. 4.5 nm) match the film structure depicted in Figure 1b. The image shows monolayer regions, regions consisting of a bilayer (darker) and the uncovered substrate (brighter). Small domains exhibit hexagonal arrays of SECs corresponding to a two-dimensional dense packing of spherical particles (arrows). In thicker films, the order improves and becomes three-dimensional. An ordered region is shown in Figure 3b; the related electron diffraction pattern (insert) clearly reveals long-range order (spots rather than rings) and a 3-fold symmetry for the pattern of reflections corresponding to a spacing of 4.2 nm. Due to the local appearance of 4-fold symmetry projections it can be assumed that the SECs are arranged on a fcc lattice with the most dense (111) planes preferentially oriented parallel to the substrate, as is the case for latex films.[13] We conclude, therefore, that the diffraction pattern reflects the reciprocal structure from the triangular array of particles in a (111) plane at normal orientation

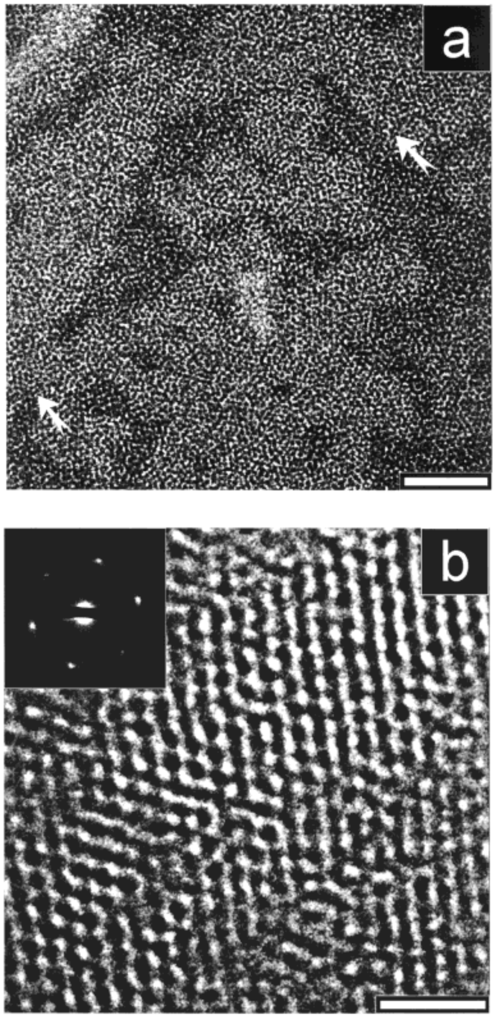

Figure 3. (a) TEM micrograph of a thin film of **2** (scale bar 50 nm). Extended monolayers, interspersed with holes and doublelayer regions, are visible. Arrows mark some regions of apparent hexagonal order. (b) TEM micrograph of an ordered region of a thicker film at high magnification (scale bar 20 nm). The insert shows a low-angle electron diffraction pattern (elastically filtered) recorded from a larger area (5 μm^2) containing the region shown.

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(13) Joanicot, M.; Wong, K.; Maquet, J.; Chevalier, Y.; Pichot, C.; Graillat, C.; Lindner, P.; Rios, L.; Cabane, B. *Prog. Colloid Polym. Sci.* **1990,** *81,* 175−183.

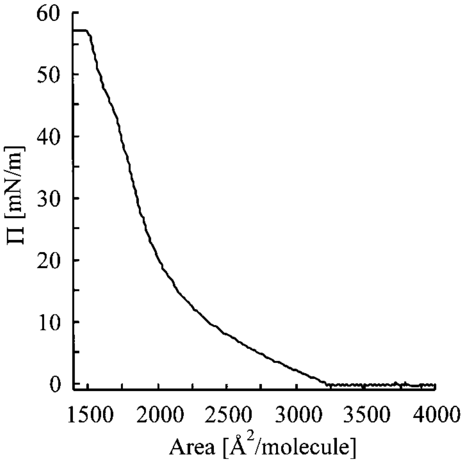

Figure 4. Surface pressure−area (π−A) isotherm of **2** at the air−water interface.

to the beam, and that the packing of the SECs is best described within a fcc lattice with a cubic unit cell axis of approximately 6 nm.

One of the characteristic features of the SEC **2** is that it spreads at the air−water interface. We used this property to measure the molecular area of **2**. From the compression isotherm of a monolayer of **2**, shown in Figure 4, we determined a molecular area of 15 nm^2 at the collapse point, which corresponds to the most dense possible packing.

Assuming a void-free monolayer in which the inorganic cluster cores are packed in a hexagonal array as suggested in Figure 1b, a core-to-core distance of 4.2 nm is obtained, which is in excellent agreement with the TEM data. The molecular area for noninteracting SECs determined at the onset of the isotherm ($\pi = 0$) is 32 nm^2, corresponding to a diameter (of the spherical projection) of 6.4 nm.

Summary and Outlook

In summary, we provide experimental evidence for the formation of a surfactant-encapsulated Keplerate $(DODA)_{40}(NH_4)_2[(H_2O)_n \subset Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ (**2**, $n \approx 50$). Compound **2** is prepared by a stepwise self-assembly process, starting from simple commercially available compounds, and finally leading to a discrete supramolecular architecture composed of at least 2300 non-hydrogen atoms and with a molecular mass of roughly 45 kDa. Future studies will concentrate on the molecular dynamic behavior of **2** in different organic solvents. The nanoporous structure of **1** suggests the use of surfactant-encapsulated Keplerates **2** as nanoreactors in homogeneous solutions. Since **1** possesses uniform apertures, a zeolite-like shape-selective loading of the cluster cavity may be achieved. This, together with the well-known catalytic properties of polyoxomolybdate clusters, would certainly represent a completely novel type of supramolecular catalyst and host−guest system from which functional nanodevices may evolve.

Experimental Section

Synthesis of 2. A freshly prepared aqueous solution of $(NH_4)_{42}[Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]\cdot$ca. 300 $H_2O\cdot$ca. 10 CH_3COONH_4 (**1**) was treated with a trichloromethane solution of the surfactant dimethyldioctadecylammonium bromide (DODA·Br). The initial ratio of DODA to **1** was 38:1, and the amount of surfactant was gradually increased until the aqueous phase became almost colorless. From the organic phase, a brownish material was isolated which corresponds to the tentative formula **2:** $(DODA)_{40}(NH_4)_2[(H_2O)_{50} \subset Mo_{132}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$. A sample of **2** was dried for 5 days at room temperature (3 mbar). Anal. Calcd for $C_{1580}H_{3542}Mo_{132}N_{42}O_{554}$: C, 42.49; H, 7.99; N, 1.32; Mo, 28.35. Found: C, 42.67; H, 7.51; N, 1.12; Mo, 29.9.

Based on the accuracy of elemental analysis, we estimate a margin of error for the DODA/NH$_4$ ratio of **2** in the range of 38:4 to 42:0.

Spectral Data of 2. UV−vis (CHCl$_3$): 470 nm, ϵ 3.40 × 10^5 M^{-1} cm^{-1}. (A nonbuffered aqueous solution of **1** displayed similar spectral properties, UV−vis (H$_2$O): 470 nm, ϵ 3.16 × 10^5 M^{-1} cm^{-1}.) IR (KBr, cm^{-1}): 2955, 2922, 2872, 2852, 1557, 1466, 1401, 1024, 981, 956, 859, 804, 735, 630, 574.

Small-Angle X-ray Scattering (SAXS). Compound **1** was dissolved in aqueous 1.0 N NH$_4$Cl at a concentration of 20.45 g/L; compound **2** was dissolved in toluene at a concentration of 20.59 g/L. The solutions were directly filtered into capillaries using 20 nm pore-size filters. The scattering experiments were done with a Kratky compact camera system that was equipped with a stepping motor and a counting tube with an impulse-height discriminator. The light source was a conventional X-ray tube with fixed copper target operating at 40 mA and 30 kV (Cu $K\alpha$ = 0.154 nm). No monochromator (except the built-in impulse-height discriminator of the detector) was used. Instead, the K_b contributions were numerically accounted for in the subsequent desmearing procedure which is included in the program ITP that transforms the scattering data into pair−distance distribution functions (PDDF).[14] The blank-scattering contributions of the solvents, sample holder, and incoherent (Compton) scattering were subtracted prior to any calculations. The theoretical relationship between the scattering function $I(q)$ and the PDDF $p(r)$ is

$$I(q) = 4\pi \int_{r=0}^{\infty} p(r) \frac{\sin(qr)}{qr}\,\mathrm{d}r$$

where r is the radial distance, $q = (4\pi/l)\sin(\theta/2)$, λ is the wavelength of the X-rays, and θ is the detection angle. The actual calculations dealing with the experimental scattering curves $I_{\exp}(q)$ accounted for the finite beam dimensions and the wavelength profile by using

$$\int_{\lambda'=0}^{\infty} \int_{t=-\infty}^{\infty} \int_{x=-\infty}^{\infty} Q(x)\,P(t)\,W(\lambda')I[\sqrt{(q-x)^2 + t^2}/\lambda']\,\mathrm{d}\lambda'\,\mathrm{d}t\,\mathrm{d}x$$

where $Q(x)$ is the beam-width profile, $P(t)$ is the beam-length profile, $\lambda' = \lambda/\lambda o$, and $W(\lambda)$ is the wavelength distribution centered at the reference wavelength λo.

The radial difference electron-density profiles (DEDP) were calculated by deconvoluting the PDDFs with the program DECON.[15] This program applies

$$p(r) = \int_{s=-\infty}^{\infty} \rho(s)\,\rho(s-r)\,\mathrm{d}s$$

where $\rho(r)$ is the radial DEDP. For details of the involved calculations the reader is referred to the cited literature.

TEM. Thin films of **2** were prepared by evaporating a trichloromethane solution of **2** cast onto a water surface and transferred to thin (6 nm) carbon film coated TEM grids. Thicker films were directly cast onto such grids. Specimens were investigated in a Leo EM 912 Ω at 120 kV using the elastic filtering mode. Images and diffraction patterns were recorded with a slow scan CCD camera (1024 × 1024 pixels, 14 bits graylevels).

Langmuir Films. Langmuir films of **2** were prepared with a Lauda film balance. A 20.55 mg sample of **2** was dissolved in 10 mL of CHCl$_3$ (c 4.82 × 10^{-5} M) and 100 μL of the solution was spread over distilled H$_2$O (Milli-Q H$_2$O with a resistance higher than 18.2 MΩ cm) at 18 °C.

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(14) (a) Glatter, O. *Acta Phys. Aust.* **1977**, *47*, 83−102. (b) Glatter, O. *J. Appl. Crystallogr.* **1977**, *10*, 415−421.

(15) Glatter, O. *J. Appl. Crystallogr.* **1981**, *14*, 101−108.