Amphiphiles

Counterions Control Whether Self-Assembly Leads to Formation of Stable and Well-Defined Unilamellar Nanotubes or Nanoribbons and Nanorods

Dong Shi, Christian Schwall, George Sfintes, Erling Thyrhaug, Peter Hammershøj, Marite Cárdenas, Jens B. Simonsen, and Bo W. Laursen*^[a]

In memory of George Sfintes

Abstract: Self-assembly of the amphiphilic π -conjugated carbenium ion ATOTA-1⁺ in aqueous solution selectively leads to discrete and highly stable nanotubes or nanoribbons and nanorods, depending on the nature of the counterion (Cl⁻ vs. PF₆⁻, respectively). The nanotubes formed by the Cl⁻ salt illustrate an exceptional example of a structural well-defined (29 ± 2 nm in outer diameter) unilamellar tubular morphology featuring π -conjugated functionality and high stability and flexibility, in aqueous solution.

Self-assembly of π -conjugated discotic (disc-like) molecules to form materials and nanostructures containing columnar π stacks is of great interest for supramolecular optoelectronics. The columnar stacks of π -systems make up a fundamental supramolecular structure element, and provide a one-dimensional pathway for charge or exciton transport.^[1] Discotics equipped with a symmetric corona of flexible alkyl chains dominate the field of columnar liquid crystals and have successfully been applied in various thin-film devices.^[2] However, asymmetric discotics with alkyl chains on only one side of the disc and no chains or polar groups on the opposite side of the rim obtain amphiphilic properties and tend to organize the columnar aggregates in bilayer structures, which may lead to nanostructures, such as fibers and tubes.^[3] The increased complexity of self-assembled nanotubes, compared to the most common self-assembled structures, such as micelles, vesicles, and lyotropic liquid crystals, offers both an academic challenge and possibilities for more advanced structural and optoelectronic functions.^[3b,4] Aida and co-workers have shown that an amphiphilic variant of the molecular analog to graphite; hexabenzocorenene forms nanotubes in organic solution.^[3c] Müllen and co-workers demonstrated that tuning the size and struc-

 [a] Dr. D. Shi, C. Schwall, G. Sfintes, Dr. E. Thyrhaug, Dr. P. Hammershøj, Dr. M. Cárdenas, Dr. J. B. Simonsen, Dr. B. W. Laursen Nano-Science Center & Department of Chemistry University of Copenhagen, Universitetsparken 5 2100 Copenhagen (Denmark) E-mail: bwl@nano.ku.dk
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ture of the counterion of the cationic discotic molecule offers new opportunities to control aggregate structures^[3e,5] forming, for example, stable planar aggregates. The supramolecular aggregates mentioned above were formed in either THF or 50 to 100% methanol solutions. Recently, Shao et al. showed how the variation of the hydrophilic headgroup of an amphiphilic discotic leads to the formation of either uniform sized (diameter of ca. 10 nm) unilamellar or multilamellar nanotubes in aqueous solution.^[6] However, the compound forming the unilamellar tubes was completely insoluble at neutral pH.

Herein, we combine π -conjugated discotics, carbocationic charge, and tunability of counterions to form either uniform 29 nm wide and highly stable unilamellar nanotubes, or multi-layer nanoribbons and nanorods in aqueous solution. We demonstrate how the interaction between bilayers of the amphiphilic cationic discotic dye in aqueous solution can be tuned from attractive to repulsive by choice of anion, leading to these distinct and complex nanostructures.

Previously, we reported the synthesis and columnar self-assembly of dodecyl-aminobisdimethylaminotrioxatriangulenium hexafluoro-phosphate (ATOTA-1·PF₆, Figure 1) in Langmuir films at the air/water interface,^[7] and in solid multilayer Langmuir–Blodgett (LB) films.^[8]

The ATOTA-1·Cl and ATOTA-1·PF₆ were synthesized (see the Supporting Information) to study the three-dimensional self-assembly of this discotic amphiphile in aqueous solution, and the role of the associated counterions. The ATOTA-1⁺-based nanostructures were obtained by dilution of the ATOTA-1⁺ salt dissolved in acetonitrile (MeCN) with 10- to 100-fold of water (see the Supporting Information). The acetonitrile stock solu-



Figure 1. Molecular structure of the amphiphilic amino-trioxatriangulenium dye ATOTA-1+; $X^-\!=\!PF_6^-$ or Cl $^-$.

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tions (10^{-3} to 10^{-4} m) showed the characteristic absorption and fluorescence spectra of the fully dissolved and non-aggregated ATOTA⁺ cation.^[9] The addition of water resulted in blueshift of the absorption and redshift of the fluorescence indicating the presence of columnar co-facial $\pi - \pi$ aggregates^[7–8] (Figures S1 and S2 in the Supporting Information). The absorption spectra of the ATOTA-1⁺ salts in aqueous solution were concentration independent in the measured range from $10^{-4}\ to\ 10^{-7}\, \textrm{m},$ and showed no variation with the acetonitrile content between 1 to 10 vol%. The data described below are based on the 10 vol % MeCN aqueous solution. No significant differences in absorption and fluorescence were found between the aggregates formed by Cl^- and PF_6^- salts. Dynamic light scattering (DLS) showed in both cases two modes with no linear dependence with the scattering angle, typical for large and elongated aggregates (Figure S3 in the Supporting Information).^[10]

The ATOTA-1·PF₆ (10^{-4} M) aggregates in water (with 10 vol% MeCN) were studied by cryo-transmission electron microscopy (cryo-TEM). Two types of nanostructures were observed (Figure 2 A). The dominant structure was 60 to 100 nm wide nanoribbons (1), whereas larger periodical twisting rods (2) with a diameter of approximately 150 nm were also present. It was difficult to determine the exact length of these structures. However, nanorods of several microns were in general observed (Figure S4 in the Supporting Information).

The nanoribbons were characterized by uniform density and straight edges, except for areas, in which occasional twists of the ribbons occurred (Figure 2B). The flat-ribbon structure could indicate a simple lamella packing of layers. However,



Figure 2. Cryo-TEM micrographs (A–E) and WAXS data (F) of ATOTA-1-PF₆ nanostructures formed in water (10 vol% MeCN). A) Nanoribbons labeled 1, and twisted nanorods labeled 2. B) Single kink on nanoribbon. C) Cross-section of nanoribbon in B. D) Enlarged twisted nanorod. E) Cross-section analysis of the gray scale along the yellow line in D. F) The presented data is background subtracted.

close inspection of the ribbons revealed in several cases regular fine structures at the edge as shown by the cross-section in Figure 2C. An equal numbers of layers were observed on both sides of the ribbon, indicating that the ribbon is a closed structure, rather than just an elongated assembly of layers. A uniform repeated thickness of 40 Å was found for all the observed layers. For the larger twisting rods (2) similar 40 Å layers occurred across the entire width of the rod (Figure 2D). The cross-section (Figure 2D and E) and the fast Fourier transform analysis (Figure S5 in the Supporting Information) confirmed that the 40 Å layer is a fundamental structural element in both the ribbons and the rods. In addition, atomic force microscopy (AFM) and X-ray diffraction studies of dried samples showed similar features (Figures S6 and S7 in the Supporting Information). AFM analysis of the twisting rods (2) showed uniform kink angles and periodicity along the rods (Figures S8-S10 in the Supporting Information), leading to the conclusion that the each twisting rod is made up by a single ribbon (1) twisting around itself.

The largest observed width of the untwisted ribbons (1) is 100-120 nm, indicating that the folding into rods (2) occurs as the ribbons reach a certain critical size, close to 100 nm. Twisting super-structures are observed for many self-assembled nanoribbons and fibers and may be driven by internal strain and solvophobic interactions.[11] Wide-angle X-ray scattering (WAXS) from an aqueous solution (10 vol% MeCN) of ATOTA-1.PF₆ showed two pronounced Bragg peaks corresponding to a repeat distances of 3.5 and 39.2 Å (Figure 2F). The 39.2 Å peak confirms the lamella structure observed by TEM and AFM, whereas the 3.5 Å corresponds to a characteristic cofacial π - π packing distance and confirms that a columnar π stacking motif is certainly is present in these multilayer nanostructures. A smaller peak at approximately 3.3 Å (also observed in the dry samples, Figure S7 in the Supporting Information) might be an indication of the co-existence of a more densely packed and crystalline π -stack,^[12] for example, in the twisting rods.

Although UV/Vis spectroscopy and DLS did not provide proof of any significant differences between the PF_6^- and the Cl⁻ salts, cryo-TEM data indeed did. Figure 3 shows cryo-TEM micrographs of a 10^{-4} m solution of ATOTA-1·Cl prepared in the



Figure 3. Cryo-TEM micrographs of ATOTA-1·Cl aggregates. A), B) ATOTA-1·Cl (10^{-4} M) in water (10 vol% MeCN). C) ATOTA-1·Cl (10^{-4} M) in pure water (vortexed).

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same way as the solutions of the PF_6^- salt. Contrary to the PF_6^- salt, the CI^- salt of ATOTA-1⁺ formed unilamellar tubes.

The tubes showed an extremely uniform width of 29 ± 2 nm and a wall thickness of approximately 4 nm, corresponding very well to the bilayer dimension found in ATOTA-1·PF₆ LB films,^[8] and the layered structure observed in the rods and ribbons of the PF₆⁻ salt. The high similarity of the optical features and identical bilayer arrangement between the nanoribbons/ rods and the nanotubes confirmed that a similar π -stacking motif is present in the tubes. The tubes differ from the relatively rigid PF₆⁻ aggregates by showing a high flexibility, for example, by making a full 180° turn in less than 100 nm (Figure 3 A).

Interestingly, we were also able to form the 29 nm nanotubes by vigorously shaking ATOTA-1-Cl powder in pure water for 24 h at 40 °C (Figure 3 C). However, in this case, the most abundant feature was a twisting nanoribbon with a contrast in the range expected for a single bilayer wall of the tube structures. Several groups have shown that twisted ribbons are a potential precursor to formation of supramolecular nanotubes,^[13] including some amphiphilic π -conjugated discotics.^[6] The shaking experiment in 100% water indicates that MeCN during the dilution with water is promoting nanotube formation rather than playing a crucial role in stabilizing the tubular morphology in the water based solutions (1–10 vol% MeCN).

The nanotubes do not agglomerate, fuse, or form multilamellars over time, and are well-separated, even in regions with a high density of tubes. The long-term stability of the tubes was also indirectly confirmed by showing no sign of precipitation upon storage for months at ambient conditions. In contrast, the ATOTA-1.PF₆ aggregates precipitated over time in aqueous solution. Precipitation is a common behavior of π conjugated amphiphilic discotics that form nanotube, rod, and ribbon morphologies in organic-based solutions.^[3c, 14]

A transition from the unilamellar Cl⁻ nanotubes to the multilamellar morphologies could be induced by adding equal molar amounts of KPF₆ to a stabile solution of ATOTA-1·Cl nanotubes (Figure S11 in the Supporting Information). This demonstrates how specific ion effects may be used for postmodification of ionic self-assembled nanostructures, in this case, from unilamellar tubes to multilamellar rods/ribbons.

Based on the observed wall and layer dimensions within the Cl^- nanotubes and PF_6^- rods/ribbons, it became clear that the first level of self-assembly common to both structures is a bilayer formed from the amphiphilic columnar ATOTA-1⁺ aggregates as schematized in Figure 4B and C. This structure is very similar to Langmuir and LB films formed by ATOTA-1.PF₆ at the air/water interface.^[7-8] Comprehensive structural studies of these films based on compression isotherms and in situ X-ray scattering established the molecular footprint or surface area of each ATOTA-1⁺ unit in the columnar aggregates to be 58 Å² (Figure 4 A).^[7] On the other hand, densely packed alkyl chains each takes up an area of close to 20 $Å^{2}$.^[7] For ATOTA-1⁺ with its two *n*-decyl chains this corresponds to 40 Å². For simple amphiphiles, such asymmetry in the space-filling requirements of the hydrophilic and hydrophobic parts agree well with formation of flexible bilayers.^[15] The details of the next level of self-assembly of the chloride salt towards formation of nano-



Figure 4. Schematic outline of the molecular dimensions of the ATOTA-1⁺ amphiphile (A), the columnar stack (B) and cross-section of the bilayer (C).

tubes are not assigned. Nevertheless, the co-existence of twisted nanoribbons and tubes in the sample prepared by shaking ATOTA-1·Cl powder in pure water (Figure 3C), indicates that these single bilayer nanoribbons may be precursors for the tubes.^[13]

In the case of the ATOTA-1-PF₆ salt, the multilayer ribbons have a structure that in principle can be constructed by wrapping multiple bilayers around a flat ribbon or a flattened/collapsed tube. The twisting rods are assigned as higher-order structures formed by twisting/folding of the multilayer ribbons.

Although the internal π -stacking columnar bilayer structure is proposed to be the same for the Cl⁻ and PF₆⁻ aggregates, two major differences are observed: 1) The Cl⁻ salt forms strictly unilamellar tubes, and the PF₆⁻ salt—solid multilamellar structures; 2) The PF₆⁻ nanoribbons show size distribution (60– 100 nm), form higher-order aggregates and precipitates over time, whereas the Cl⁻ tubes are very uniform (29±2 nm), highly flexible, and stable in aqueous solution.

We propose that these significant counterion effects largely can be explained by the differences in solvent interactions and the resulting Coulomb interactions between the ionic superstructures. Although the outer surface of the ATOTA-1⁺ bilayers have a relative high charge density (+1 e/ \approx 60 Å²), the ATOTA⁺ ions are large and extremely polarizable,^[9a, 12, 16] interacting only weakly with water. The same is true for the PF₆⁻ ion known to be a soft anion extreme in studies of ion-specific effects (Hofmeister series).^[17] The weakly bound water is easily expelled when the soft PF_6^- ion forms close ion pairs with the likewise soft ATOTA-1⁺ bilayer surface.^[18] For this neutralized and weakly solvated surface, there will be a large hydrophobic effect towards formation of multilayers. Further surface minimization occurs in the larger ribbons by folding into twisted rods. For the ATOTA-1·Cl salt the situation is reverse as the electrostatic interactions between the soft cationic bilayer and the hard Cl⁻ ions cannot break the strong hydration of the Cl⁻ ions. Overall, the bilayer is stabilized and adapts a tubular structure with all anions solvated in the water phase and no hydrophobic parts of ATOTA-1⁺ exposed to water. The tubes will be further stabilized by the surrounding corona of negatively charged Cl⁻ anions providing electrostatic repulsion towards other tubes or other parts of the same tube.

As was mentioned above, addition of PF_6^- ions to such stable solutions of CI^- tubes breaks this special bilayer stabilization and results in formation of multilayer aggregates similar

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to those formed directly from ATOTA-1·PF₆. Thus, PF_6^- ions may be applied as glue between the bilayers due to their favorable interaction with the soft ATOTA-1⁺ bilayer surface.

Recently, Chen et al. showed the ability to control the formation of either rigid multilayer tubular nanostructures or rigid nanoribbons comprised of a cationic pyrene based amphiphile by using monovalent or bivalent anions, respectively.^[19] Wu et al. have demonstrated that going from Cl⁻ to BF₄⁻ counterions changes the self-assembly morphology of an amphiphilic discotic π -conjugated cation in methanol from a ribbon structure to a mixture of coiled and tubular nanostructures, respectively.^[14] But in these cases, the morphology changes result from packing effects in the crystalline multilayer structures related to size and valency of the anion rather than their hard/ soft property or solvent interactions.

In summary, the self-assembly of cationic amphiphilic amino-triangulenium salts with Cl^- and PF_6^- counterions was investigated. In both salts bilayers featuring columnar π -stacks were formed. We demonstrated how the interaction between these positively charged bilayers can be tuned from attractive to repulsive by soft and hard anions, leading to rather well-defined multilayer nanoribbons and nanorods, or to highly uniform 29 nm unilamellar nanotubes that are very flexible and stable in aqueous solution. In particular, the combination of a highly charged polarizable surface of the self-assembled nanostructures (bilayers) and hard highly water coordinated (chloride) anions turn out to be a promising recipe for stabilization of discrete π -conjugated nanostructures in aqueous media. This study empathize the great potential of ionic building blocks and electrostatic interactions for nanostructure engineering via the counterions.

Experimental Section

ATOTA-1·PF₆ was synthesized according to literature procedures.^[7] The new chloride salt (ATOTA-1·Cl) was synthesized analogously from tris(2,4,6-trimethoxyphenyl)carbenium chloride.^[12] Experimental details and full spectroscopic characterization are given in the Supporting Information. Experimental details for aggregates formation, electronic absorption, emission, DLS, AFM, Cryo-TEM, and XRD measurements are also given in Supporting Information along with additional data/Figures S1–S11.

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COMMUNICATION



Specific-ion effects: Self-assembly of the amphiphilic π -conjugated carbenium ion dodecyl-aminobisdimethylaminotrioxatriangulenium hexafluoro-phosphate (ATOTA-1⁺) in aqueous solution

CI⁻ Hard anion Soft cation



selectively leads to discrete and highly stable nanotubes or nanoribbons and nanorods, depending on the nature of the counterion (CI^- vs. PF_6^- , respectively; see scheme).

Amphiphiles

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