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Self-Assembly

Toroidal Nanoobjects from Rosette Assemblies of Melamine-Linked Oligo(*p*-phenyleneethynylene)s and Cyanurates**

Shiki Yagai, Sankarapillai Mahesh, Yoshihiro Kikkawa, Kanako Unoike, Takashi Karatsu, Akihide Kitamura, and Ayyappanpillai Ajayaghosh**

Spontaneous organization of small molecular building blocks into complex superstructures by concerted action of various noncovalent interactions is abundant in nature. The precision, elegance, complexity, and functions of these structures pose significant challenge to scientists. The quest to translate the salient features of nature's self-assembly principles has lead to the design of a variety of artificial objects useful in the field of advanced materials research.[1] In this context, the fabrication of well-defined, discrete nanoobjects of photonically and electronically active molecular components with controlled size, shape, and function is of paramount importance.[2] A major focus on this area is the self-assembly of linear π-conjugated molecules because of their inherent optical and electronic properties, which are vulnerable to intermolecular interactions.[3] Such interactions can be controlled by directional multiple hydrogen-bonding modules, leading to supramolecular objects of various dimensionalities.[4]

Among various multiple H-bonding modules, the complementary interaction between melamines and cyanurates has been of great value for chemists to the design of rosette (macrocyclic) and tape-like (linear or crinkled) architectures.[5] Reports on superstructures hierarchically organized from cyclic supramolecular assemblies are limited to extended columnar architectures.[6,7] Herein we report an unprecedented self-organization of hydrogen-bonded rosette assemblies of oligo(*p*-phenyleneethynylene) (OPE)[8] attached melamine **1** and the cyanurate **2** in aliphatic solvent, leading to the formation of toroidal objects of nanometer dimension (Figure 1).[9–11]

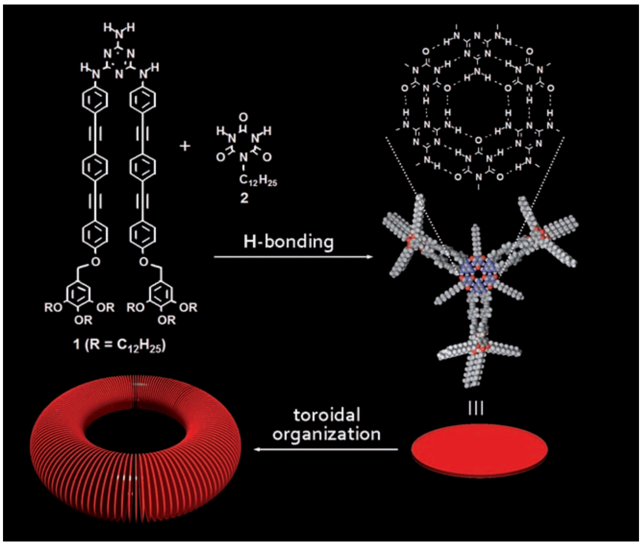

Figure 1. Self-assembly of melamine-linked OPE **1** and cyanurate **2**.

The melamine-linked OPE derivative **1** was prepared by Sonogashira coupling[12a] of *N*,*N'*-di(*p*-iodophenyl)triaminotriazine with 3,4,5-tridodecyloxybenzyloxy-substituted ethynyltolan, which was characterized by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry.[13] Coassembly of **1** with the cyanurate **2**[12b] resulted in discrete rosettes ($\mathbf{1}_3\cdot\mathbf{2}_3$). The ^{1}H NMR spectrum of an equimolar mixture of **1** and **2** ($[\mathbf{1}] = [\mathbf{2}] = 5\times10^{-3}$ M) in $CDCl_3$ showed resonances of the hydrogen-bonded imide protons of **2** at $\delta = 14.3$ ppm and the secondary amino protons of **1** at $\delta = 9.58$ ppm. Such values are characteristic of the formation of well-defined rosette assemblies.[13,14] The absorption spectrum of the equimolar mixture of **1** and **2** in $CHCl_3$ (1×10^{-2} M) showed a maximum at $\lambda =$ 334 nm, which is slightly blue-shifted from that of **1** alone in $CHCl_3$ ($\lambda_{max} = 339$ nm).[13] This indicates H-type aggregation of OPE segments upon conformational fixation of **1** to form a H-bonded rosette assembly with **2**.[8] The emission of the OPE coassembly showed a red shift of ca. 30 nm compared to that

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[*] Dr. S. Yagai, K. Unoike, Prof. Dr. T. Karatsu, Prof. Dr. A. Kitamura
Department of Applied Chemistry and Biotechnology
Faculty of Engineering, Chiba University
1-33 Yayoi-cho, Inage-ku, Chiba 263-8522 (Japan)
Fax: (+81) 43-290-3039
http://www.eng.chiba-u.ac.jp/outProfile.tsv?no=1228
E-mail: yagai@faculty.chiba-u.jp

S. Mahesh, Dr. A. Ajayaghosh
Photosciences and Photonics Group
Chemical Science and Technology Division
National Institute for Interdisciplinary Science and Technology (NIIST)
Trivandrum-695019 (India)
Fax: (+91) 471-249-0186
http://w3rrlt.csir.res.in/photo/people/draajayaghosh/Homepage.htm
E-mail: ajayaghosh62@gmail.com

Dr. Y. Kikkawa
Nanoarchitectonics Research Center
National Institute of Advanced Industrial Science and Technology (AIST)
1-1-1 Higashi, Tsukuba, Ibaraki 305-8562 (Japan)

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of the monomer ($\lambda_{em-max} = 378$ to 407 nm), which is in good agreement with the H-type excitonic coupling.

Dynamic light scattering (DLS) experiments with solutions of equimolar mixtures of **1** and **2** in chloroform and decane are shown in Figure 2. In chloroform, aggregates with an average hydrodynamic diameter of 8 nm were obtained. This size is in line with the gyration diameter of rosette assemblies with extended alkyl chains.[13] However, in decane (5×10^{-5} to 5×10^{-4} M) large aggregate species with average hydrodynamic diameter of 50 nm were obtained, indicating the formation of nanoobjects hierarchically organized from rosettes. Such nanoobjects seem to have a discrete shape, as the hydrodynamic diameter does not change over the above concentration regime. The optical properties of the mixture in decane (1×10^{-5} M) revealed a further excitonic interaction of the OPE segments. The absorption maximum emerged at 324 nm, whereas the fluorescence maximum appeared at 436 nm. These maxima are blue- and red-shifted from the mixture in $CHCl_3$ (1×10^{-2} M, see above), respectively.[13] Thus, further extended H-type aggregation of OPE segments takes place in nonpolar solvent, which drives hierarchical organization of rosettes. Remarkably, both spectra showed only marginal changes upon heating the solution up to 70 °C.[13] Accordingly, the rosette–rosette interaction as well as the hydrogen bonding interaction within rosette are significantly strong, which may render the hierarchically-organized assemblies considerably stable.

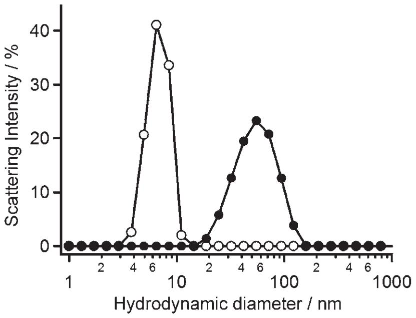

Figure 2. Dynamic light scattering analysis of an equimolar mixture of **1** and **2** in $CHCl_3$ (○ 1×10^{-3} M) and in decane (● 5×10^{-5} M).

Insight into the morphology of the hierarchical structures formed from the rosette $\mathbf{1}_3{\cdot}\mathbf{2}_3$ in decane is obtained from tapping-mode AFM images. To our surprise, AFM images of a decane solution (5×10^{-5} M), spin-coated (3000 rpm) onto freshly cleaved highly-oriented pyrolytic graphite (HOPG), displayed a large number of toroidal nanoobjects (Figure 3 a). The outer diameters of toroids (c in Figure 3 c) are uniform at around 40 nm, which is in line with D_h detected by DLS. The average cross-sectional diameter a is 20 nm, whereas the height a' is (3.2 ± 0.3) nm. The actual cross-sectional diameter was estimated to be (8 ± 2) nm after subtracting the tip broadening parameters.[15] This value matches the gyration diameter of a rosette from molecular modeling, implying that toroids are formed by the stacking of the individual rosettes. The discrepancy between the AFM height and the diameter of rosette might be caused by the tilting of rosettes on the substrate and/or the deformation of the aliphatic chains by high local forces exerted by the AFM tip. The body-to-body distance (b in Figure 3 c) given by cross-sectional analysis is (21 ± 2) nm (Figure 3 b), thus the circumference of toroids is ca. 67 nm. Assuming that the periodic distance of rosettes is in the range of 3.5–5 Å,[6b] the number of rosettes in a single toroid and the angle of inclination between the adjacent rosette disks are estimated to be 191–134 and 1.9–2.7°, respectively.

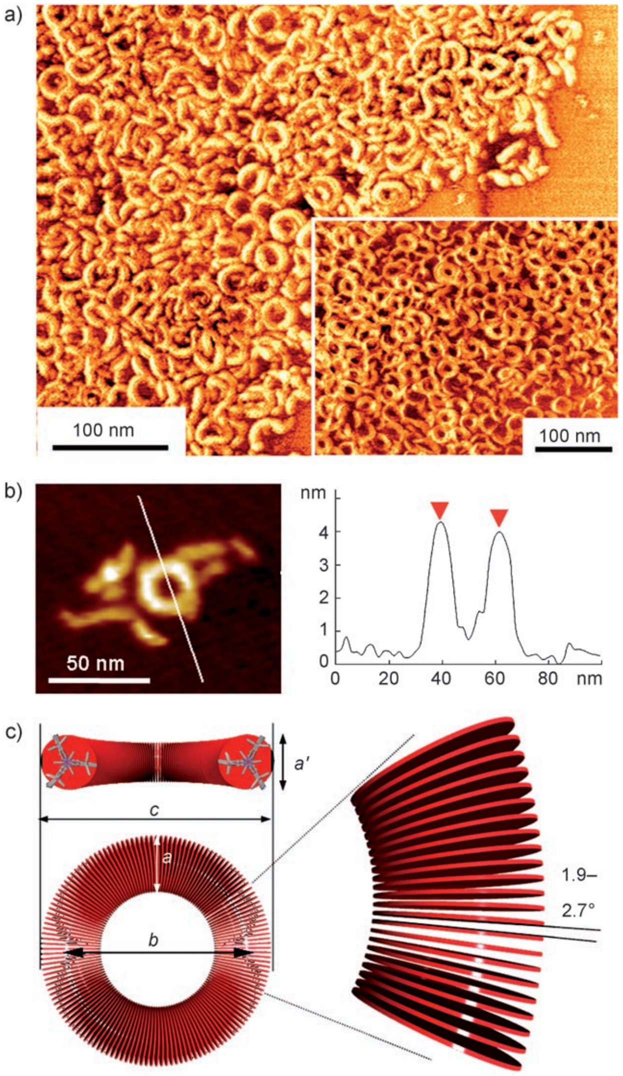

Figure 3. a) AFM phase image of an equimolar mixture of **1** and **2** spin-coated from decane solution (5×10^{-5} M) on HOPG. Inset: image obtained by low tapping force.[13] b) Cross-sectional analysis of an isolated toroid. Red arrows show the body-to-body distance b. c) Representation of the toroidal organization of rosettes (red disks).

In the AFM image of the assemblies (Figure 3 a), short wormlike and "opened" objects are also visualized, which might arise from deformation of the toroids by AFM tip force. Imaging with lower tapping force allowed almost all the nanoobjects to retain the toroidal shape (inset in Figure 3 a). The fragile nature of toroids is more pronounced in sparse regions than in crowded regions, making visualization of isolated toroids by AFM difficult.[13] Spontaneous formation of the toroidal nanostructures on different substrates was confirmed by AFM measurements on HOPG, mica, and silicon substrates,[13] which all showed the same nanostructures.[6c]

The toroidal nature of the supramolecular assembly of $\mathbf{1}_3{\cdot}\mathbf{2}_3$ was further confirmed by transmission electron microscopy (TEM) measurements. Figure 4 shows the TEM image of a dip-coated sample from a decane solution at a concentration of 5×10^{-5} M after negative staining by RuO_4 vapor. Isolated toroids are clearly seen with sizes of around 40 nm, which is in good agreement with those of the AFM images. The cross-sectional diameter (*a* in Figure 3 c) is approximately 10 nm, which is close to the diameter of rosettes from molecular modeling (8 nm). These results highlight the stability of toroids, which remain intact with staining, subsequent vacuum drying, and noncontact imaging processes. Furthermore, DLS and AFM analyses showed no evidence of morphological transformation in decane dispersions over a year, or after heating to 70 °C implying that the toroids are the thermodynamically stable product.

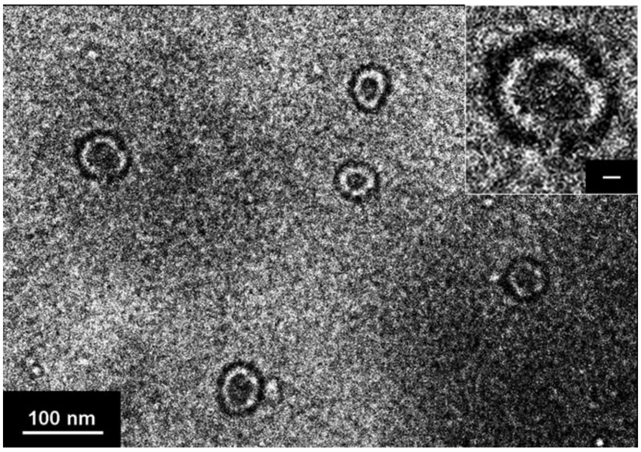

Figure 4. TEM image of an equimolar mixture of **1** and **2** from decane with concentration 5×10^{-5} M and stained by RuO_4. Inset (scale bar 10 nm) shows an enlarged view of the upper-left toroid in the main image.

The above observations unveil a unique property of the rosette $\mathbf{1}_3{\cdot}\mathbf{2}_3$ hierarchically organizing into discrete toroidal nanostructures in decane. However, the end-to-end binding of a short columnar nanostructure with persistent length of 67 nm (average circumference of toroids, see above) seems to be energetically disfavored because of the stiffness of such columns consisting of stacked disk-shaped supramolecules. Accordingly, a unique stacking property might be evolved for the present rosette, for which OPE π-electronic segments play an important role. As shown by the absorption measurements, a major driving force for the association of rosettes is H-type aggregation between OPE segments. Molecular modeling shows, however, that OPE π planes are rotated out of the hydrogen-bonded plane by 45°.[13] This structural feature indicates that inter-rosette face-to-face stacking (H-type aggregation) between OPE segments does not occur if the rosette stack on top of each other without tilting. Thus, biased H-type aggregation of OPE segments occurs for each adjacent rosettes by tilting their planes. Extended association of rosettes with such a tilted stacking fashion could lead to the formation of columns with a curvature, and eventually to the formation of toroidal architectures in solution.

The results shown herein are remarkable, as toroidal nanoobjects, hierarchically constructed from small molecular building blocks by discrete cyclic supramolecules, were hitherto unknown. This result is in contrast to the previously-reported toroidal nanostructures that are directly formed from building blocks, such as amphiphilic polymers,[9a,c,f] dumbbell-shaped molecules,[9b,d,g] proteins,[9e] DNA, or biopolymers.[10] The present assembly is novel as π-electronic segments are spatially arranged in closed circular structures, which is reminiscent of the light-harvesting systems of purple photosynthetic bacteria, in which the circular arrays of chlorophyll pigments are crucial for efficient excitation energy migration.[16] Therefore, intriguing applications, such as the creation of artificial light-harvesting nanodevices with ring-shape morphology, might be possible based on the present system.

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