Hierarchical Preferences of Hydroxylated Oxanorbornane-Based Achiral Amphiphiles

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Supporting Information

ABSTRACT: Achiral amphiphiles with hydroxylated oxanorbornane headgroups showed specific morphological characteristics and hierarchical preferences depending upon the nature of lipophilic units. Detailed scanning electron microscopic (SEM) studies showed that twisted ribbonlike aggregates are characteristic of monoalkoxyaryl lipids with hydrocarbon chain length in the range C10–C13; these systems also had a preference toward lamellar arrangement. Asymmetric packing of these lipids is a unique occurrence and shows that the presence of molecular chirality is not an absolute requirement for curvature effects in their supramolecular assemblies. Aryl units in these systems were found to be important for the observed morphological preferences, which became evident from comparative studies involving simple long chain esters without this moiety. Single-crystal X-ray diffraction analysis of one of the lipids from the latter



group gave finer details of strong and weak secondary interactions, which operate during their assembly process. Introduction of more than one alkyl chain on the aromatic ring caused a notable shift in the packing propensity toward columnar arrangement. Most of these cone-shaped molecules were found to give doughnut-shaped aggregates from acetone solution through the intermediary of fibrous structures, which was confirmed through SEM, transmission electron microscopic, and atomic force microscopic studies.

■ INTRODUCTION

Formation of higher-order structures through molecular selforganization and their development into new functional materials is one of the hottest areas of research today.¹⁻³ The nature and directionality of secondary interactions involved and the orientation of interacting groups with respect to each other play decisive roles in such processes. A predictive power on these aspects would help us to design properties through appropriate choice of component(s). For this, a thorough understanding on the preference profiles in supramolecular architectures is necessary. Although networks based solely on hydrogen bonds are abundant, a great deal of attention is also being placed on using this in conjunction with hydrophobic clustering and π -stacking possibilities to create new organic materials of well-defined nano- and microscale structures.4-6 Concerted efforts have given insight into the organizational preferences of not only small organic molecules but also more complex systems such as polymers, dendrimers, and metallomesogens, which culminate in special properties with applications in diverse areas such as optoelectronics,^{7,8} data storage,⁹ soft magnetic systems, stimuli-responsive materials, and so forth.¹⁰⁻¹⁴

We have recently shown that polyhydroxylated oxanorbornane scaffolds can be used as a "sugar surrogate" to create structural mimics of glycolipids.¹⁵ Their self-assembly and aggregation characteristics were comparable to that of natural analogs reported in the literature.^{16,17} In continuation of this, we have synthesized a new series of hydroxylated oxanorbornenyl imides connected to the long chain alkoxy aryl units through an ethanolamine spacer. Favorable orientation of hydroxyl groups for hydrogen bonded assembly, flexibility of the linker for proper packing, and the possibility of varying the number of alkyl chains on the aromatic ring are the attractive features of this design. Systematic studies involving this class of compounds have shown that chirality in an individual lipid is not an absolute requirement for hierarchical preferences like twisted ribbons during their self-assembly. This has significance from both design and mechanistic standpoints and highlights the influence of headgroup tilt and conformational bias in dictating the assembly profile. Formation of doughnut-shaped assemblies from acetone solutions of di- and trialkyl lipids and an insight into their development are other important highlights of this work.

EXPERIMENTAL SECTION

Amphiphiles studied here were prepared in 4–6 synthetic steps, which started with Diels–Alder reaction of furan with maleic anhydride, treatment of the resulting adduct with ethanolamine to get an imide intermediate, its esterification with appropriate alkoxy benzoic acids (or long chain carboxylic acids), and a final

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cis-dihydroxylation using osmium tetroxide (Supporting Information Schemes S1 and S2). The alkoxy benzoic acids used in esterifications were separately prepared by alkylation of various hydroxy benzoates and hydrolysis of the ester group using alcoholic KOH. Their coupling with the imide intermediate was carried out under EDCI/HOBt/DIPEA conditions. Long chain carboxylic acid esters used for comparative studies were prepared by reaction of the corresponding acid chloride with the imide intermediate. We have presented the synthetic details of imide intermediate and the alkoxy benzoates in the Supporting Information. Specific information on the esterification and dihydroxylation steps are presented below.

General Procedure for the Coupling of Imide Intermediate with Alkoxy Benzoic Acids. To a stirred solution containing a mixture of alkoxy benzoic acid (1 equiv) and 1-hydroxybenzotriazole (HOBt, 1 equiv) in dry dichloromethane at 0 °C was added Pr2NEt (1.2 equiv) and 1-ethyl-3-[3-(dimethylamino)propyl]carbodiimide hydrochloride (EDCI, 1.1 equiv). The reaction mixture was stirred at 0 °C for 10 min, to which the imide intermediate (5, Supporting Information) was added, and the mixture was allowed to stir at 0 °C for 30 min and then at room temperature for 24 h. After completion of the reaction, the mixture was diluted with dichloromethane and washed with water (30 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel using 30-40% EtOAc/Hexanes to get the esters in 60-94% yield. Spectroscopic details of the resulting compounds are shown in the Supporting Information.

General Procedure for the Preparation of Aliphatic Esters. To a stirred solution of the imide intermediate (5, 1.0 equiv) and Et₃N (1.5 equiv) in dry dichloromethane was added the appropriate acid chloride (1.1 equiv) at 0 °C under N₂ atmosphere. The reaction mixture was warmed to room temperature and allowed to stir for 2 h. After completion of the reaction, the mixture was washed with water and extracted with dichloromethane. The organic layer was dried using anhydrous Na₂SO₄ and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using 20–30% EtOAc/Hexanes. Yields and spectroscopic details of resulting compounds are shown in the Supporting Information.

General Procedure for cis-Dihydroxylation: Preparation of Amphiphiles 1a-j, 2a-c, and 3a-c. To a stirred solution containing a mixture of the oxanorbornene derivative (1.0 equiv), N-methyl morpholine N-oxide (2.4 equiv) and pyridine (30 μ L for 100 mg of the alkene) in t-BuOH/H₂O (3:1) was added osmium tetroxide (0.02 M solution in t-BuOH, 0.01 equiv), and the solution was heated at 80 °C for 7-8 h. After completion of the reaction, the mixture was cooled to room temperature, treated with 15% Na₂SO₃(aq) (1 mL), and allowed to stir for 5-10 min. After removing the solvents under reduced pressure, the crude mixture was diluted with dichloromethane, dried using anhydrous Na2SO4, filtered, evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel using EtOAc-DCM-MeOH in a gradient mode to get the products as colorless solids. Yields and spectroscopic details of the resulting compounds are shown in the Supporting Information.

Preparation of Samples. To prepare samples for scanning electron microscopic (SEM) and atomic force microscopic (AFM) studies, the compound (1 mg) was dissolved in 1.5 mL

of appropriate solvent, sonicated, and drop-casted on silica or HOPG (highly ordered pyrolytic graphite) substrates. It was allowed to dry at ambient temperature in a desiccator overnight and then was used for imaging. To prepare the sample for transmission electron microscopic (TEM) studies, a solution of the compound in the desired solvent (1 mg/1.5 mL) was dropcasted onto a carbon coated copper TEM grid and allowed to dry in a desiccator as mentioned above. For studies involving amino acid as a chiral additive (Figure 6), 1 equiv of amino acid was dissolved in 0.1 mL of water and added to a methanolic solution of the sample (1 mg/1.4 mL). After sonication, a drop of the mixture was placed on silica substrate and allowed to dry under the conditions mentioned above before imaging.

RESULTS AND DISCUSSION

Structures of amphiphiles with alkoxy aryl lipophilic units used in the present study are shown in Figure 1. They can be placed



Figure 1. Hydroxylated oxanorbornane-based lipids used in the study.

into three groups based on the number of alkyl groups present on the aromatic ring. Compounds 1a-g form one group with a single alkyl chain at the 4-position but individually differ in the number of methylene units in the chain. At the same time 2a-cand 3a-c have two and three alkyl chains at 3,5 or 3,4,5positions, respectively. Differences in the hydrophilic-hydrophobic ratios were expected to affect their self-assembly profiles and morphological characteristics. To understand this, scanning electron microscopic (SEM) examination of samples prepared by directly drop-casting their methanol solutions on silica substrate was initially carried out.

In general, they were found to form fibrous or ribbonlike aggregates, which were discrete in the case of mono alkyl systems, interlinked in dialkyl series, and highly cross-linked in the trialkyl derivatives; the only exception was the globular assembly in the case of 3a. SEM images of aggregates from 1a, 1b, 2a, and 2b are shown in Figure 2 and those from other compounds are given in the Supporting Information (Figure S1).

One of the most astonishing observations was the presence of twisted ribbonlike aggregates in the sample of **1b** having the C12 alkyl chain. Because a change from fibrous to twisted ribbonlike morphology happened on increasing the chain length to C12, other homologues in this series with C10, C11, C13, and C14 alkyl chains (1d-g) were also synthesized and included in the study to understand the structural requirements for the observed hierarchical assembly. Of these, lipids 1d-fwith C10, C11, and C13 alkyl chains also gave twisted ribbons as that of **1b**. However, compound **1g** having a C14 alkyl chain gave spherical aggregates of more or less uniform sizes under this condition (Figure 3D), suggesting that there is an optimal



Figure 2. SEM images of the samples of (A) 1a, (B) 2a, (C) 1b, and (D) 2b prepared by directly drop-casting their methanol solutions (1 mg/1.5 mL) on silica substrate.



Figure 3. SEM images of samples of (A) 1d, (B) 1e, (C) 1f, and (D) 1g prepared by directly drop-casting their methanol solutions (1 mg/1.5 mL) on silica substrate.

chain-length requirement for the observed supramolecular chirality. Widths of these twisted ribbons ranged between 135 and 230 nm. Their pitches, however, were not uniform. Interestingly, they remained in either left-handed or righthanded forms. Unlike most of the known glycolipids that exhibit such morphologies, the amphiphiles studied here are achiral in nature, which makes the chiral preference during supramolecular organization significant.

Although the formation of globular aggregates from 1g having just an extra methylene unit compared to 1f was surprising, detailed SEM analysis showed regions having continuous linear array of these spherical assemblies (Figure 4A,B), which suggests that they probably originate from fibrous or ribbonlike aggregates through a pearlinglike phenomena that has been reported in the case of tubular vesicles from stearoyloleoyl-phosphatidyl-choline in the presence of alkyl chain modified dextran.¹⁸ A dynamic light scattering (DLS) study of 1g in MeOH showed the average diameter of these spherical aggregates as 825 nm (Figure 4C).

To get an insight into the assembly, samples of 1a-f were initially subjected to powder X-ray diffraction (PXRD) analysis. Diffraction patterns of 1a-b and d-g were nearly identical with d_1 , d_2 and d_3 in the ratio 1:1/2:1/3, which suggested lamellar arrangements. The PXRD profile of 1b, a representative example, is presented in Figure 9A and those of others are included in the Supporting Information. The data for 1a, 1b, 1d, and 1e supported a bilayer arrangement with d_1 being approximately equal to twice the molecular length. A tendency toward interdigitation was however observed in 1f and 1ghaving longer chains; d_1 in these cases were slightly less than 2l, l being the molecular length, measured from structures minimized using Chem3D. Unlike other compounds in this



Figure 4. (A) SEM images of a sample of 1g (B, enlarged view) prepared by drop-casting its MeOH solution (1 mg/1.5 mL) directly on silica substrate. (C) DLS histogram of 1g in MeOH.

series, the lattice parameters of 1c with a 16 carbon chain (a = 100 Å, b = 42 Å) supported a rectangular columnar arrangement.

Because there is no internal element to induce chirality, the observed "handedness" is likely arising from curvature in lamellar arrangement brought about by uniform tilting of headgroups when molecules assemble. In the case of lipids 1b and 1d-1f, this is probably happening over a long-range, which gives rise to the twisted structure. A pictorial representation of this using the bilayer formed through a head—head interaction of the lipid 1b is presented in Figure 5.



Figure 5. Cartoon representation showing a possible mode of self-assembly of 1b (A) that could result in supramolecular chirality (B).

As can be anticipated, flexibility associated with the linker connecting the headgroup could allow the system to change the curvature and hence the nature of the twisting. This is probably responsible for the formation of both left- and right-handed twisted ribbons during the aggregation of **1b** and **1d–f**. To understand the effect of chiral additives, samples of **1b** from MeOH containing serine, tartaric acid, or arginine (1 equiv) were prepared and used in SEM studies. These molecules were expected to associate with the polar belt in between the alkyl chains by interacting with the headgroups and exerting additional influence on supramolecular chirality. Both D- and L-isomers of serine and tartaric acids were used to understand the difference, if any, in the nature of the aggregates. As evident

from Figure 6, presence of L-serine and D-(-)-tartaric acid promoted the formation of left-handed twisted ribbons



Figure 6. Effect of additives on the aggregation of 1b from methanol; images show morphologies of samples prepared in the presence of 1 equiv each of L-serine (a), L-arginine (b and c), D-serine (d and e), D-(-)-tartaric acid (f), and L-(+)-tartaric acid (g); M and P in these images refer to left-handed and right-handed twisted ribbons.

preponderantly. However, samples containing D-serine and L-(+)-tartaric acid had both left- and right-handed twists. They formed separate dendritic domains, suggesting that chiral preference during nucleation has a direct effect on subsequent supramolecular organization. Unlike L-serine, L-arginine facilitated the formation of both left- and right-handed twists and the profile was comparable with that of the sample with Dserine.

A notable increase in the number of right-handed twisted ribbons in the presence of D-serine, L-tartaric, and L-arginine suggests that the flexibility they impart to the lipid assembly is different compared to that from other additives examined here. Although a molecular level picture on this is currently lacking, it is reasonable to assume that the ability of diastereomeric complexes of **1b** with these chiral systems to assume different curvatures is contributing to the formation of left- and/or righthanded twists.

Apart from being a point of attachment for alkyl chains, the aromatic rings in 1a-g seem to play an important role in directing their assembly toward fibrous/ribbonlike structures. This became evident when the aggregation of lipids 1h-j (Figure 7) was studied under identical conditions. SEM analysis of their samples, drop-casted from methanol (1 mg/1.5 mL) on silica substrate, showed continuous sheetlike morphologies as shown in Figure 7A–C. Their PXRD spectra had peaks corresponding to d_1 , d_2 , and d_3 of 34, 17, and 8.8 Å (1h); 33, 17, and 8.7 Å (1i); 43, 22, and 14 Å (1j) in the ratio 1:1/2:1/4 (for 1h and 1i) and 1:1/2:1/3 (for 1j), indicating lamellar arrangements.

Gratifyingly, we could secure crystals of 1i by slow evaporation of its solution in a MeOH-DCM mixture (1:4).

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1h R=C7H15

Figure 7. SEM images of samples of 1h (A), 1i (B), and 1j (C) prepared by drop-casting their MeOH solution (1 mg/1.5 mL) on silica substrate.

Single-crystal X-ray diffraction analysis showed the compound (Figure 8A) as belonging to a monoclinic system with a $P2_1/c$ space group. The solved structure showed 2-fold positional disorder for the alkyl side chain with relative occupancies of 58:42. The disordered components were located through successive difference Fourior synthesis. The components were partitioned and refined with the sum of their occupancies restrained at 1. A detailed examination of the lattice showed the involvement of an array of weak and strong hydrogen bonding interactions in maintaining the assembly (bond length and bond angle details are presented in the Table S3 of the Supporting Information). Prominent among these are H2A… O3 and H3A…O2 hydrogen bonding (H2A…O3, 2.044 Å; H3A…O2, 2.032 Å; ∠O2−H2A…O3 = 151.43°, ∠O3−H3A… $O2 = 151.93^{\circ}$), which link molecules along the *b*-axis as shown in Figure 8C. In addition to these, the bridge-head oxygen was found to maintain weak C-H-O hydrogen bonds with H1 and H2 of another one to give additional stabilization to the stacking (Figure 8C). Laterally, there were weak C-H--O interactions between O3 and H3 of each molecule with the corresponding atoms on the adjacent one to give a $R_2^2(8)$ motif. Apart from these, the imide C=O acted as a trifurcated donor to form weak hydrogen bonds with H1 and H7 of the adjacent molecule in the same layer and H8 of another one diagonally above it, which is presented in Figure 8B. The overall arrangement of molecules in the lattice, stabilized by a combination of hydrogen bonding interactions and hydrophobic clustering, is presented in Figure 8D.

An increase in the number of alkyl chains in 2a-c and 3a-c was reflected in their PXRD pattern. Although the bis-hexyl derivative 2a was lamellar with $d_1 = 41.2$ Å corresponding to bimolecular thickness, the C12 and C16 derivatives 2b and 2c gave peaks in the low angle region with d_1 , d_2 , and d_3 of 30.2, 19.6, and 13.2 Å and 31.3, 22.1, and 15.7 Å, respectively in the ratio 1:0.707:0.5, indicative of tetragonal columnar arrangement. Similarly, the trialkyl derivatives 3a and 3b had peaks corresponding to d_1 , d_2 , and d_3 of 34, 27.5, and 18 Å and 42.4, 36.5, and 22.4 Å, respectively.

The PXRD graphs of representative compounds (**1b**, **2b**, and **3b**) are presented in Figure 9 and those of others are shown in the Supporting Information (Table S1 and Graphs S1–12). The lattice parameters a = 68 Å, b = 32 Å for **3a** and a = 84.8 Å, b = 40.5 Å for **3b** are suggestive of rectangular columnar organization in these systems. Being nonionic with a fairly wide lipophilic surface, the compounds **2b**, **2c**, **3a**, and **3b** are likely forming inverted columns with alkyl groups dispersed radially outward. Unlike these, the lipid **3c** with three C16 alkyl chains had peaks corresponding to d_1 , d_2 , and d_3 of 58.1, 32.6, and 19.7



Figure 8. (A) X-ray crystal structure of 1i. (B) Weak hydrogen bonding interactions at the imide carbonyl. (C) Hydrogen bonding network involving head-head interactions. (D) Hydrogen bonding network involving head-head interactions and hydrophobic clustering in the crystal system.

Å, respectively, in the ratio 1:1/2:1/3, indicating a lamellar arrangement.

As with the aggregates from methanol, morphologies of samples from other solvents such as ethanol, *t*-BuOH, trifluoroethanol, tetrahydrofuran, and acetonitrile–water were also found to originate from fibrous primary aggregates

(Supporting Information, Figure S2). A consistent and unique preference was however observed in the case of samples of 2a, 2b, and 3a-c drop-casted from acetone. SEM and TEM images of samples from 2b presented in Figure 10 clearly show that an increase in the number of alkyl chains has resulted in a markedly different morphology. The aggregates were dough-



Figure 9. Powder XRD profiles of 1b (A), 2b (B), and 3b (C).



Figure 10. A-C respectively show SEM, TEM, and AFM images of samples of 2b prepared by drop-casting its acetone solution (1 mg/1.5 mL) on silica substrates for SEM and AFM, and on a carbon coated copper grid for TEM.

nut-shaped with inner and outer diameters in ranges 1–320 nm and 200 nm–3 μ m, respectively. A sample of **2b** for AFM imaging was prepared by drop-casting its acetone solution (1 mg/1.5 mL) on silica substrate. The outcome from this study was also in accordance with the results from SEM and TEM experiments. Generally, central pores in these assemblies were found to disappear over time to give the morphology shown in Figure 10C.

In the SEM image of **2b**, there were isolated regions containing coiled fibers and partially formed "doughnuts" (Figure 11), suggesting that they could be the precursors



Figure 11. Selected areas from the SEM images of sample from 2b (A and B) showing the intermediary of coiled fibers during the development of doughnut-shaped aggregates (C).

during the formation of doughnuts. Transition from fibrous to the final morphology appears to happen during solvent evaporation and is likely facilitated by mixing of hydrophobic domains.

As mentioned, the tendency to form doughnut-shaped structures was also seen in trialkyl lipids. The SEM and AFM images of samples from **3b** are presented in Figure 12 and those of **2a**, **2c**, **3a**, and **3c** are included in the Supporting Information (Figure S20). Although the central pores in compound **3b**



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Figure 12. (A and B) SEM and 3-D AFM images of the samples of 3b from acetone (1 mg/1.5 mL); (C) coiled fibers en route to doughnutshaped assemblies. The cross-sectional height profile of aggregates of 3b along the line shown in panel D is displayed in panel E.

appear to be wider compared to those in 2b, no consistency could be observed to correlate this with the number of alkyl chains. AFM images of 3b were comparable to those of 2b

(Figure 10). Here again, fibers seem to be the probable precursors for the formation of doughnuts, which is evident from the image shown in Figure 12C.

Because the SEM images presented above were taken on silica substrate, it became important to see whether its hydrophilic nature is contributing to the morphological preference. To test this, experiments involving the lipids 1b, 1g, 2b, and 3b were repeated using hydrophobic HOPG (highly ordered pyrolytic graphite) as the substrate, and the results are presented in Figure 13. Twisted ribbonlike



Figure 13. SEM images of samples of (A) 1b, (B) 1g, (C) 2b, and (D) 3b prepared by directly drop-casting their solutions (1b and 1g from methanol and 2b and 3b from acetone; 1 mg/1.5 mL) on HOPG substrate.

aggregates from the methanol solution of 1b, formation of spherical aggregates and pearlinglike phenomena from the methanol solution of 1g (Supporting Information, Figure S30), and doughnut-shaped aggregates from acetone solutions of 2b and 3b were observed under this condition also, which suggests that the solid support does not significantly influence their assembly profile.

Aggregation profiles of lipids presented here, when viewed in light of current developments in this area, prompts us to present two important points for detailed discussion. First one is on the origin of "handedness" during the self-assembly of 1b and 1d-f. Such supramolecular chirality has in fact been observed with a number of ionic and nonionic lipids, but these systems invariably possess a chiral center either as part of the main lipid or as part of the counterion. Although packing of chiral headgroups in principle could induce curvature in lamellar structures, the nature and length of a lipid chain also have been found detrimental in getting stable twists.¹⁹ Control of supramolecular chirality by using chiral counterions in gemini surfactants reported by Oda et al., 20,21 time-dependent development of twisted ribbons, helical ribbons, and nanotubes from lysine-based amphiphile reported by Ziserman and coworkers,²² and generation of helical aggregates from sugar based amphiphiles²³ are some interesting examples. Such hierarchical preferences have also been found with mixtures of lipids like 1,2-bis(tricosa-10,12-diynoyl)-sn-glycero-3-phosphocholine (DC8,9PC) and 1,2-bis(dinonanoyl)-sn-glycero-3phosphocholine (DNPC), which not only show new avenues in material design but also highlight the remarkable ways in which amphiphiles can pack to give three-dimensional order.²⁴ Recent theoretical studies on curvature formation in lamellar structures have taken into account the free energy of the system with contributions from the bending and surface tension.²⁵ Conformational preferences of individual lipids, their tilt with respect to the layer normal, solvation effects, and secondary interactions are some of the specific factors that determine the energy state of the assembly and hence the observed hierarchical preference.²⁶ In the absence of a chiral center, the curvature could result if there is asymmetric packing over a long-range with adequate stability. Most of the known reports on supramolecular chirality from achiral systems are based on compounds having tendency to stack one above the other in a spiral fashion; initially formed fibrils in these cases develop in to nano- or microscale assemblies through further aggregation.²⁷ In comparison, the lipids studied here are achiral and also do not have any unsaturation on the alkyl chain to control its orientation. Preferential formation of left-handed twisted ribbons in presence of L-serine and D-(-)-tartaric acid, and a notable increase in right-handed twisted assemblies in the presence of D-serine, L-tartaric, and L-arginine tend to suggest that the stabilities and accessible curvatures of their diastereomeric complexes with 1b are different.

Formation of doughnut-shaped assemblies from 2a, 2b, and **3a**–**c** is another noteworthy observation from the present work. The question of whether the overall shape originates spontaneously or from other simpler structures is pertinent here. The results from SEM and AFM analysis of 2b and 3b presented in Figures 11 and 12 rule out the likelihood of the former mechanism and point toward a pathway involving fibrous aggregates as intermediates. Nanometer-sized torroidal structures have been reported from block copolymers,²⁸ peptides,^{29–31} dendrimers,³² and also from melamine-oligo(p-phenylenevinylene) supramolecular complexes.²⁷ The mode of assembly that results in such superstructures could vary from one system to another and depend on the nature and shape of amphiphiles. For example, torroidal aggregates from dumbbellshaped amphiphilic system reported by Kim et al. is believed to develop through coalescence of initially formed spherical micelles having hydrophobic cores and hydrophilic peripheries.³³ A similar structure has also been obtained from coneshaped amphiphilic peptide Ac-GAVILRR-NH₂, and the initially formed spherical micellar aggregates in this case seem to transform to nanopipelike intermediates. Bending of these nanopipes and fusion of ends then result in final morphologies.³¹ Results from our studies involving 1a-g, 2a-c, and 3ac suggest that the molecular structure, hydrophilicity-hydrophobicity ratio, and the overall molecular shape have profound influence on final morphologies. Notably, aggregates from cone-shaped systems 2a, 2b, and 3a-c, though fibrous initially, show a tendency to transform to doughnut-shaped structures through coiling and domain mixing during curing stages.

CONCLUSIONS

The aggregation behavior of a new class of oxanorbornanebased amphiphiles and morphological characteristics of their samples were systematically studied using a combination of SEM, TEM, AFM, single-crystal XRD, and PXRD techniques. Although formation of fibrous or ribbonlike structures from alcoholic solvents is seen as a common characteristic, some of the cone-shaped lipids with two and three alkyl chains were

found to give doughnut-shaped assemblies from acetone through the intermediary of fibers. This shape-dependent selfprocessing of lipid assemblies is remarkable and could be useful in the future design of new nano- or micrometer-sized molecular aggregates for diverse applications. Formation of twisted ribbons from some of the achiral lipids with alkyl chain lengths in the range C10–C13 is another unique finding and indicates that chirality in individual lipids is not an absolute requirement for getting supramolecular chirality in this class of compounds. Most of the existing reports on hierarchical preferences of lipids make use of chiral component either as part of the lipid, counterion or as additives. The findings reported here show that asymmetric packing of achiral systems also can give curvature effects in their assemblies.

ASSOCIATED CONTENT

S Supporting Information

Synthetic schemes and spectral data of the amphiphiles, plots of PXRD data, large area views of SEM images, single-crystal XRD data, and ¹H and ¹³C NMR spectra of all compounds. This material is available free of charge via the Internet at http:// pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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