

Supramolecular Architectures from Bent-Core Dendritic Molecules**

Miguel Cano, Antoni Sánchez-Ferrer, José Luis Serrano, Nélida Gimeno,* and M. Blanca Ros**

Abstract: Control of the self-assembly of small molecules to generate architectures with diverse shapes and dimensions is a challenging research field. We report unprecedented results on the ability of ionic, bent dendritic molecules to aggregate in water. A range of analytical techniques (TEM, SEM, SAED, and XRD) provide evidence of the formation of rods, spheres, fibers, helical ribbons, or tubules from achiral molecules. The compact packing of the bent-core structures, which promotes the bent-core mesophases, also occurs in the presence of a poor solvent to provide products ranging from single objects to supramolecular gels. The subtle balance of molecule/solvent interactions and appropriate molecular designs also allows the transfer of molecular conformational chirality to morphological chirality in the overall superstructure. Functional motifs and controlled morphologies can be combined, thereby opening up new prospects for the generation of nanostructured materials through a bottom-up strategy.

Bent molecules are the origin of bent-core liquid crystals (BCLCs), which have properties different to those of classical mesophases.^[1] Their molecular geometry forces the molecules to adopt a compact packing, which restricts their rotational freedom and leads to novel and intriguing polar mesophases. A distinctive feature of this class of mesogen is the possibility of the formation of mesophases with spontaneous macroscopic chirality from achiral molecules.^[1e,f,1,2] Their formation mechanisms are still under debate,^[1e,f,2a,b,d,3,4] but potential

applications such as chiral resolution, nonlinear optics, and photovoltaics are claimed.^[4g-i,5] Thus, in addition to the stated functional properties,^[5] BCLCs offer high potential in both supramolecular chemistry and materials science.

Interestingly, Ho, Hsu, and co-workers^[6] reported the ability of bent-core molecules to promote supramolecular chirality by self-assembly in a solvent. Thus, an achiral bent-core molecule formed hierarchical helical superstructures in a THF/water solution.^[6a] They proposed the molecular conformational chirality as the origin of such superstructures.

Control over the self-assembly of small molecules to generate architectures with diverse shapes and dimensions by supramolecular chemistry is still a topical, challenging, and dynamic research field.^[7,8] Systems ranging from the nano- and micrometer scales to macroscopic dimensions, along with diverse morphologies with shapes and structures that can influence the physical properties, are considered in this field, with applications in nanotechnology to biotechnology.^[7,8]

However, many such systems are still difficult to synthesize, especially in the case of aqueous systems, which could give rise to breakthroughs in biological, medical, and materials science. The prediction of structural features from noncovalent interactions is still in its infancy and, despite interest in new approaches, systematic studies on the self-assembly of bent-core molecules in solution have not been published to date, despite their mesomorphic abilities. Herein, we report major advances in the potential of the bent-core packing to generate controlled aggregates in water.

The choice of ionic bent-core/PPI-based (PPI = polypropyleneimine molecules) to achieve this target arose not only because they form BCLCs,^[9] but also because their inherent amphiphilicity could favor segregation effects in solvents, including water.^[10] Thus, we explored how pathways to create aggregates of bent-core molecules affected their final supramolecular structure by changing the molecular design. The effect of changing the length of the flexible tails, either in an inner (m : 4, 10) or an outer (n : 8, 14) position was evaluated initially with first generation dendrimers PPI1-B1- m - n (Scheme 1). We then extended our research to further ionic dendrimers by incorporating intrinsic chirality into the molecules (PPI1-B1-4-7* and PPI1-B1-4-8*) with the aim of controlling the supramolecular chirality. Furthermore, an isomeric rod-core dendrimer (PPI1-C1-4-8) was studied to demonstrate the exclusivity of the bent-core design to induce supramolecular chirality (Scheme 1).

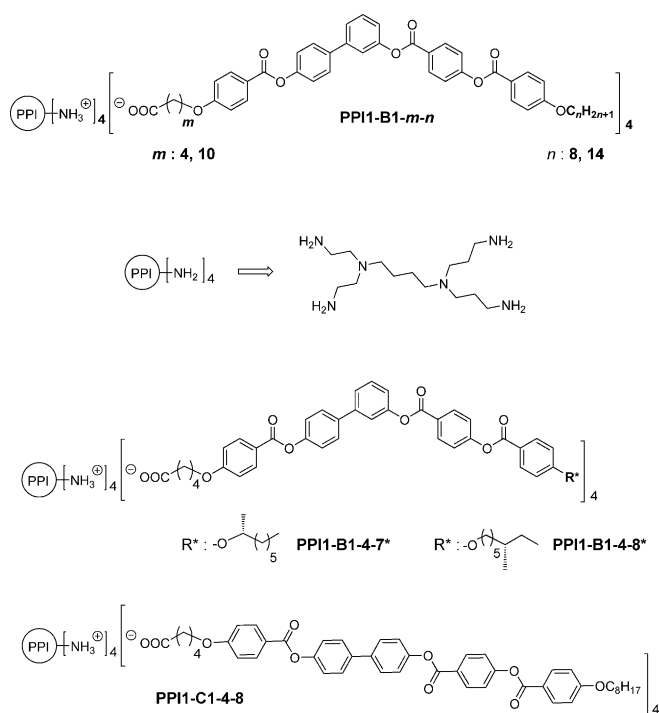
It is demonstrated here that these ionic dendrimers are suitable molecules not only to obtain different bent-core mesophases, but that they also aggregate to form a variety of useful architectures in water. However, the presence of a bent-core structure alone is not sufficient to provide either aggregates or similar morphologies, including helical structures.

[*] Dr. M. Cano, Dr. N. Gimeno, Prof. Dr. M. B. Ros
Instituto de Ciencia de Materiales de Aragón
Departamento de Química Orgánica. Facultad de Ciencias
Universidad de Zaragoza-CSIC
Campus San Francisco. 50009-Zaragoza (Spain)
E-mail: bros@unizar.es

Dr. A. Sánchez-Ferrer
ETH Zurich
Department of Health Sciences and Technology, IFNH
Schmelzbergstrasse 9, LFO, E29, 8092 Zurich (Switzerland)
Prof. Dr. J. L. Serrano
Instituto de Nanociencia de Aragón
Departamento de Química Orgánica
Facultad de Ciencias, Universidad de Zaragoza
Campus San Francisco, 50009-Zaragoza (Spain)

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Scheme 1. Chemical structure and nomenclature of the ionic bent-core dendrimers.

The new PPI-based dendrimers were synthesized and characterized according to previously published methods^[9] (see the Supporting Information) and they were used in aggregation studies together with the dendrimer PPI1-B1-10-14 previously reported by us.^[9] Self-assembly of these dendrimers in the bulk (see Table S1 in the Supporting Information) was investigated by a range of analytical techniques (POM, DSC, TGA, and XRD; see the Supporting Information). The materials with a long terminal chain and a flexible spacer (n : 14 or m : 10) form a lamellar mesophase, assigned as an SmCP phase, and this is consistent with previous results.^[9] However, the dendrimer with short flexible chains (n : 8 and m : 4) arranges into a Col_r liquid-crystal phase, as evident by X-ray diffraction (XRD) studies.^[9]

The aggregation of the ionic dendrimers in solution (THF and water) was carried out according to published procedures.^[10,11] These studies provided convincing evidence of the formation of different aggregates (the results are summarized in Table S1 in the Supporting Information).

These dendrimers, which incorporate four bent-core structures, are suitable molecules for self-organization upon the addition of water (poor solvent) to give different supramolecular morphologies, depending on the chemical structure of the ionic molecule (see Figure S6 in the Supporting Information). The presence of long hydrocarbon tails, as in PPI1-B1-10-14, induces the formation of small rods ($< 1 \mu\text{m}$ in length and 100 nm in width) (Figure 1 A and see Figure S6 in the Supporting Information). However, this is not the case for compounds with shorter terminal chains (n : 8). In this case, TEM results showed that PPI1-B1-10-8 forms long fibrillar aggregates (several micrometers), which have a width of around 30 nm. These aggregates coil to form small

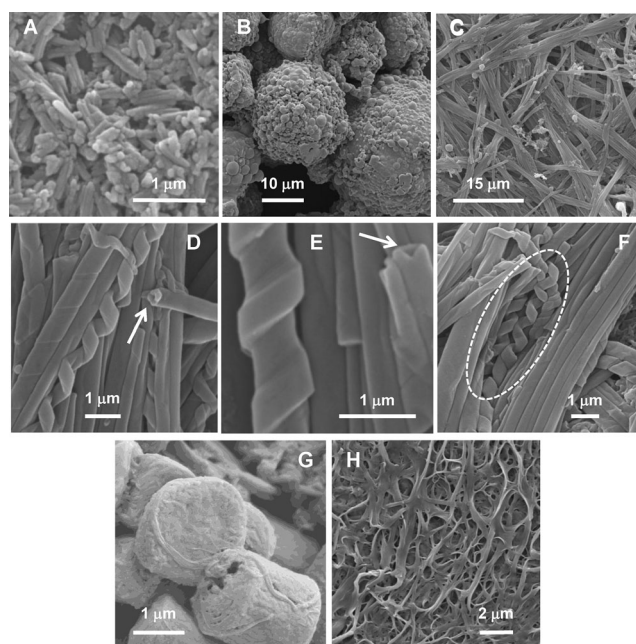


Figure 1. Scanning electron microscopy (SEM) images of dialyzed aqueous solutions of PPI1-B1-10-14 (A), PPI1-B1-10-8 (B), PPI1-B1-4-8 (C–F), PPI1-B1-4-8* (G), and PPI1-C1-4-8 (H).

spheres that aggregate into circular objects (diameters of 20–60 μm ; Figure 1 B and see Figure S6 in the Supporting Information).

Remarkable differences were observed in the case of aggregates formed from dendrimers with a short inner spacer (m : 4). PPI1-B1-4-14 and PPI1-B1-4-8 both form helical aggregates, which are new chiral arrangements formed from achiral units.^[8d] Very long twisted tapes (several micrometers in length and around 30 nm in width) with a pitch in the range of 110 nm are generated by the self-assembly of PPI1-B1-4-14 (see TEM and FESEM images in Figure 2 A–D and Figure S6 in the Supporting Information). Interestingly, the entangled fibrillar nanostructure immobilizes THF, as evident by the test-tube method (Figure 2 E). This observation is reminiscent of the rare recent reports of organogels based on a bent-core organized gelator,^[4g,12] and thus relates to the active field of molecular gels in general.^[13]

For PPI1-B1-4-8, with the shortest outer and inner flexible tails (m : 4, n : 8), TEM and SEM studies indicate the formation of long helical ribbons and empty nanotubes (tubules) that are several micrometers in length (Figure 1 C–F and Figure 3) with polydisperse diameters (ca. 400–600 nm diameter) as a result of multiple wrappings (Figure 1 E); tubules have attracted great interest in nanotechnology for the preparation of functional materials.^[14] However, gel formation was not detected in this case.

The formation of tubules was studied by ^1H NMR spectroscopy and SEM. Starting from a $[\text{D}_8]\text{THF}$ solution, the signals of the aromatic protons were shifted upfield in the NMR spectra on increasing the amount of D_2O , an observation that supports the existence of a solvent effect (see Figure S4 in the Supporting Information). Cast samples for SEM studies showed that small twisted ribbons are formed at

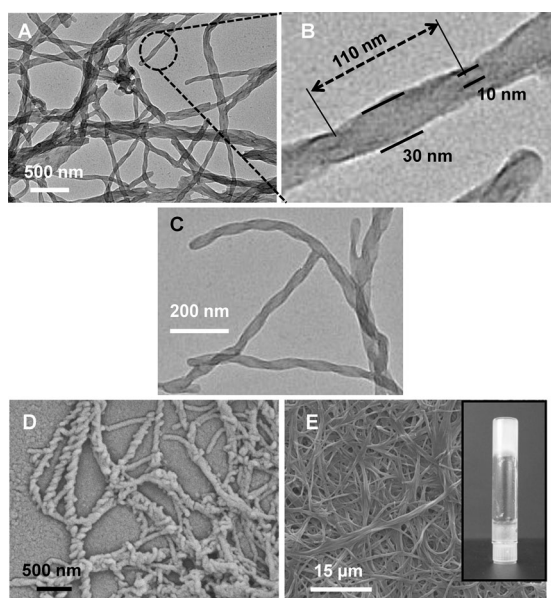


Figure 2. Transmission electron microscopy (TEM; A–C), field-emission scanning electron microscopy (FE-SEM; D), and SEM (E) images of PPI1-B1-4-14 from dialyzed aqueous solutions and formation of an organogel (test-tube method, inset in (E)).

low D₂O proportions and these undergo fusion to form helical nanoribbons that progressively close into nanotubes (tubules; see Figure S5a,b in the Supporting Information). Heating the solution up to 50 °C results in the tubular aggregates opening and breaking to form ribbons (see Figure S5c in the Supporting Information). Cooling the mixture to room temperature causes these ribbons to fuse together to give high-quality large tubules through a sort of self-healing process (see Figure S5d in the Supporting Information).

TEM data and SAED reflections from samples of PPI1-B1-4-8 revealed an inner lamellar nanostructured organization in the helical ribbons with a *d*-spacing of 4.4 nm. Based on these data, the molecular size of PPI1-B1-4-8 (length of the bent-core acid: 4.6 nm), and the ability of the bent core to form tilted structures (as in the SmCP mesophase),^[1f,2c] we propose the packing model shown in Figure 3. Folded dendrimers, which are partially exposed to the water, arrange in layers with the aromatic cores compacted within and the ionic parts facing upwards towards the water to form twisted ribbons. Progressive lateral growth steps will guide this arrangement to form helical ribbons, which eventually close to give tubules.

Despite the complexity of the molecules, the self-assembled structures described here show several similarities with the topologies of other supramolecular aggregates based on chiral surfactants or peptides,^[7c,14,15] thus suggesting a common mechanism for the formation of tubules by the helical coiling of tapelike aggregates. Furthermore, the stacking of twisted layers to form strands resembles models proposed for the formation of helical nanofilaments through a local saddle splay deformation, which generates the B4 helical nanofilament phase^[4] reported in bent-core molecules. This chiral mesophase has great potential^[4g–i] and has strong

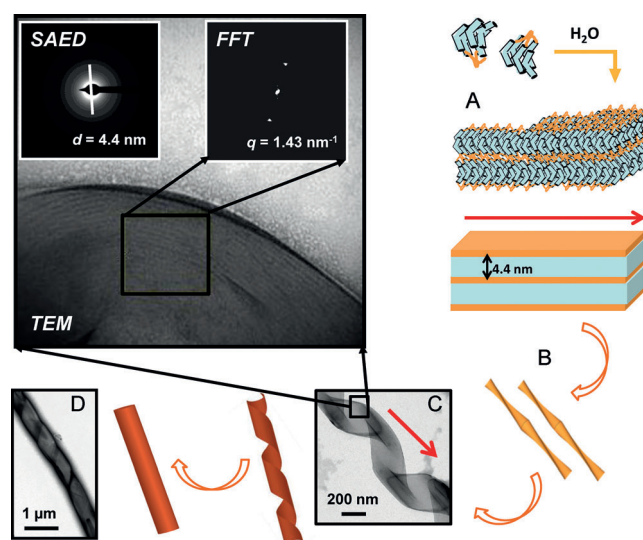


Figure 3. TEM image of PPI1-B1-4-8 showing a lamellar arrangement (insets: selected-area electron diffraction (SAED) and fast Fourier transform (FFT) images) in the helical ribbons and tubes. Proposed mechanism for the hierarchical self-assembly of the ionic dendrimers in the presence of water (A–D).

optical activity, despite the fact that it is formed from achiral molecules.

SAXS and WAXS experiments on dry powder samples of different aggregates (see Figure S8 in the Supporting Information) also supported the molecular lamellar disposition when assembled in water. Sub-micrometer lamellar-like structures are suggested in all cases, which evolve from seeding filaments to different morphologies depending on the chemical structure.

Besides the possibility of achieving different nanostructured architectures by selecting the appropriate ionic bent-core dendrimers, the exclusive possibility of inducing chiral structures attracted our attention. Why do only some dendrimers induce supramolecular chirality? And why are two different chiral architectures built?

From consideration of the chiral aggregates of PPI1-B1-4-14 and PPI1-B1-4-8, it appears that the small flexible spacer (*m*: 4 versus *m*: 10) connecting the hydrophilic and bent-core parts of the dendrimer controls the twisting ability of the lamellar assembly. This causes adjacent ester groups to rotate at different angles relative to each other, thereby resulting in the formation of the optimum molecular geometry with a molecular twist.^[3d,6,16] Furthermore, this molecular conformational chirality can successfully be transferred from the molecular level into supramolecular chirality through self-assembly, both in the mesophase^[3d,16] and in the presence of a solvent.^[6,12] Interestingly, in the case of our aggregates in water, this transfer only occurs when a short chain is present to link the hydrophobic and hydrophilic structures.

Concerning the second question, the TEM images clearly show that helical ribbons and tubules are only formed by PPI1-B1-4-8. The mechanism and pathway for tubule formation have motivated both experimental and theoretical studies,^[15] and the reason why some ribbons have a cylindrical

curvature, which leads to tubes, whereas others have a saddle-like shape, is still a matter of debate. The formation of twisted versus helical ribbons is proposed to be related to the lateral assembly width of the tapes, which is typically—but not always—influenced by the length of the alkyl tails which form the membranes that control the fluid or crystalline organizations.^[15c,d] Thus, the presence of longer chains favors twisted ribbons.^[15a,f] In our case, the terminal chains of the dendrimer seem to exert this control (ca. 30 nm versus ca. 300 nm for PPI1-B1-4-14 and PPI1-B1-4-8, respectively) to afford the two chiral supramolecular structures.

TEM and SEM studies on PPI1-B1-4-14 and PPI1-B1-4-8 showed the formation of both left- and right-handed helical strands (Figures 1F and 2C,D), although specific optical activity was not detected by CD measurements. Nanostructures with precise chirality could offer many advantages,^[17] and attempts to direct the screw-sense of the helical assemblies of our systems were investigated by the incorporation of intrinsic chirality. Regrettably, neither PPI1-B1-4-7*, bearing a terminal tail that was successfully used by Ho, Hsu, and co-workers,^[6b] nor PPI1-B1-4-8* provided evidence of pure twisted aggregates (Figure 1G, and see the Supporting Information). The stereogenic centers are probably too far from the origin of the scrolling collective process to have any influence, but unsuitable molecular packing for conformational chirality transfer cannot be ruled out.

Finally, concerning the key role of rigid-core designs to promote helical supramolecular structures, it can be stated that PPI1-C1-4-8, a linear isomer of PPI1-B1-4-8, forms long nontwisted fibers (Figure 1H and see the Supporting Information). Thus, the molecular packing is of particular importance for the expression of the conformational chirality, which is induced by the presence of a molecular kink in the bent-core molecules, and to the morphological chirality in the overall superstructure; but other structural requirements should also be fixed in the molecule to achieve this goal.

In conclusion, ionic bent-core dendrimers are suitable molecules both to obtain different bent-core mesophases and to allow their assembly in water to provide useful materials. Rods, spheres, nontwisted or twisted fibers, helical ribbons, and tubules can be obtained by using these achiral molecules. The compact packing that characterizes bent-core structures and induces the attractive bent-core mesophases can be achieved in the presence of water, thereby providing systems ranging from specific single objects to supramolecular gel structures. Nevertheless, a subtle balance between molecule/solvent interactions, which can be controlled through suitable molecular design, is a crucial parameter to control the morphology of the aggregation.

These results open up very broad and attractive possibilities for the design of new molecular and nanostructured materials in a bottom-up strategy, with interest for nanotechnology and advanced materials applications. Many functional motifs compatible with the assembly of bent-core structures,^[2c] controlled morphologies, different processing approaches, as well as the properties reported for BCLCs^[5] could be combined in these new supramolecular systems. Likewise, some of the fibrous supramolecular architectures could be considered as alternatives to the attractive filaments

of the B4-like phase,^[3e,4] in this case also suitable for processing from solution. Finally, our results raise new questions and offer new prospects in terms of both theoretical and experimental approaches for understanding the parameters that govern the induction of supramolecular chirality from achiral molecules.

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