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Perspective

Discotic liquid crystals 45 years later. Dendronized discs and crowns increase liquid crystal complexity to columnar from spheres, cubic Frank-Kasper, liquid quasicrystals and memory-effect induced columnar-bundles ☆

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In 1977 Chandrasekhar laboratory reported the first examples of a new class of thermotropic liquid crystals self-organized from planar disc-like molecules substituted with alkyl groups. X-ray analysis demonstrated that these disc-like molecules stack on top of each other at irregular spacing in columns located in the paraffin melt of their alkyl groups. These supramolecular columns self-organize in a hexagonal array defined as the new thermotropic discotic or columnar hexagonal liquid crystal phase. This new thermotropic liquid crystal phase has translational periodicity in two dimensions and liquid-like disorder in the third one, along the column axis. In 2002 Bushby and Lozman dedicated a brief review article to the 25 anniversary of discotic liquid crystals. This review also included a brief discussion of supramolecular discs and columns self-organized from self-assembling dendrons and dendrimers. The current publication is not another review but a brief perspective on new liquid crystal phases self-organized from dendronized rigid planar and conformationally flexible discs as well as from crown-like molecules. Crown-like molecules are the most stable conformation of a transient unstable disc. All dendronized disc-like and crown molecules adopt a crown conformation that self-assemble helical columns and spherical helices. A large diversity of new liquid crystalline phases self-organize from these helical columns and spherical helices. They include helical columnar hexagonal phases from crowns and from supramolecular spheres, Frank-Kasper A15 (known as cubic phase of space group $Pm\bar{3}n$), σ phase (also known as tetragonal of space group $P4_2/mnm$), 12-fold quasi liquid crystals (QLC) and supramolecular orientational memory (SOM) derived complex bundles of supramolecular columnar hexagonal arrays that are not yet completely elucidated. The impact of Chandrasekhar on the discovery of self-assembling dendrons and dendrimers *via* his biaxial nematic liquid crystal concept will also be discussed. This perspective is dedicated to the 45 anniversary of the discovery of discotic liquid crystals and to the memory of Professor Sivaramakrishna Chandrasekhar, a modest, respectful and great scientist.

☆ Dedicated to the 45th Anniversary of the Discovery of Discotic Liquid Crystals and to the Memory of Professor S. Chandrasekhar

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Introduction

In 1977 a landmark publication by Chandrasekhar, Sadashiva and Suresh [1] reported that hexa *n*-alkanoates of hexahydroxy benzene containing six to nine carbons in their alkyl groups provided the first examples of thermotropic mesomorphism in pure, single-component systems of two-dimensional (2D) plate-like or disc-like molecules. These 2D disc-like molecules differ from one-dimensional (1D) rod-like molecules or mesogens forming conventional thermotropic nematic and smectic liquid crystals [2] Chandrasekhar laboratory demonstrated by X-ray analysis that these disc-like molecules are stacked on top of each other at irregular spacings in the melt state of their alkyl groups to form columnar arrays self-organized in a hexagonal arrangement. Therefore, this new assembly has translational periodicity in two dimensions and liquid-like disorder in the third one. The title of the 1977 paper stated the name of this new thermotropic mesomorphic state: "liquid crystals of disc-like molecules." This mesophase is also known under the name of "discotic liquid crystals," or under the more general name of "columnar liquid crystals." At the time the 1977 paper was written [1], Chandrasekhar knew that mesophases of large plate-like molecules form during the carbonization of graphitizable substances, such as petroleum or coal tar pitches at very high temperatures but these complex materials did not provide single-component liquid crystal phases and were not accessible as models to understand the principles of this new concept [5]. An explosive development of the field of discotic liquid crystals followed immediately. This was driven by the elegance and by the structural diversity of the discotic molecules forming discotic liquid crystals. These disc-like molecules were ranging from planar-rigid [6–14] to conformationaly flexible [15–29] and to conical, that for reasons that we will explain later we named them crown [15–30]. Potential applications as organic electronic materials with high charge carrier mobility [14], photoconductivity [30], and their architectural diversity ranging from helical columnar [12–14] to pyramidal columnar [15–21,26–28] increased the interest in this field. Numerous review articles were published on covalent and supramolecular discotic liquid crystals [31–60]. Expansion of planar disc-like molecules to the size and properties of graphene represents one of the most recent developments in this field [39,40,50–52]. The 25th anniversary of discotic liquid crystals was celebrated by Bushby and Lozman with a review article [30]. The goal of the current article is not to provide an additional review of discotic liquid crystals but to demonstrate how the bridge between conformationally rigid and conformationally flexible disc-like molecules as well as of crown-like molecules with self-assembling dendrons, produced a large diversity of new liquid crystals mediated by disc-like molecules that were not originally predicted by Chandrasekhar [1]. The names of the molecules giving this bridge are "*dendronized discs and dendronized crowns*." The goal of this paper is not to provide a review, even of this very new field, but rather to demonstrate some of its capabilities and hopefully inspire other laboratories to approach and develop new concepts in this field.

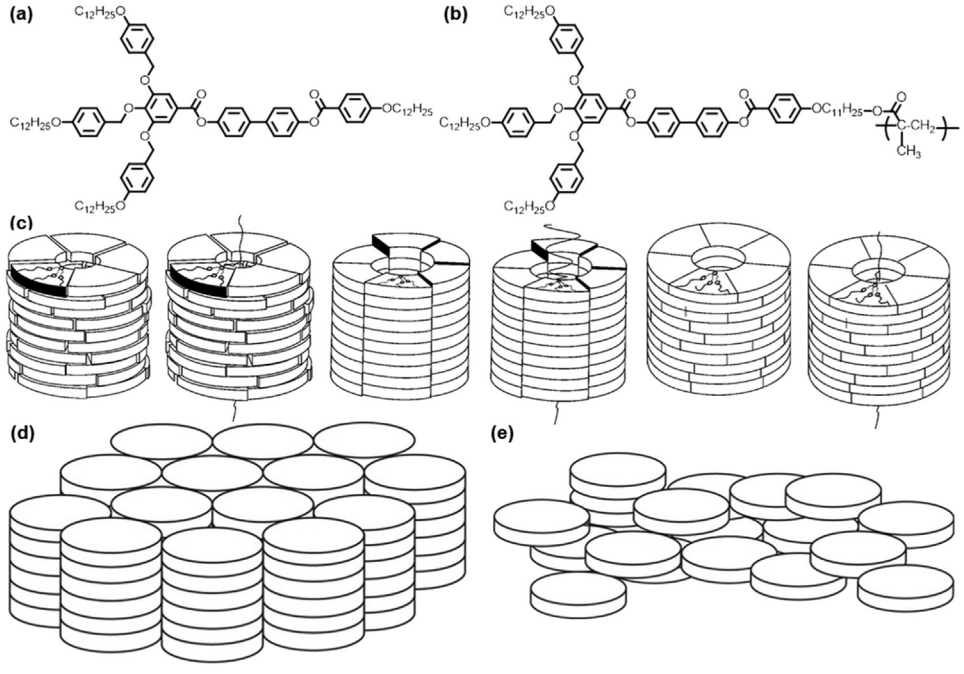

Fig. 1

Self-organization of half-disc combined with rod-like molecule of Malthete (a) and of its polymer (b) expected originally to form a biaxial nematic phase, into supramolecular columnar dendrimers or supramolecular columnar polymers (c) that inspired the development of self-assembling dendrons, self-assembling dendrimers and self-assembling dendronized polymers providing models of rod-like and icosahedral viruses, compared with the classic columnar hexagonal discotic (d) and nematic discotic (e) liquid crystals. Fig 1a and 1b were redrawn from reference 73. Fig. 1c was adapted and modified from reference 44. Figs. 1d and 1e were redrawn and rearranged with inspiration from reference 7 that shows a columnar hexagonal liquid crystal lattice (d) and discotic nematic liquid crystal (e).

Discussions

The Role of the Biaxial Nematic Liquid Crystal Concept of Chandrasekhar in the Discovery of Self-Assembling Dendrons, Dendrimers and Dendronized Polymers

For a number of years our laboratory was interested in the elaboration of a molecular strategy to self-assemble with synthetic building blocks supramolecular structures resembling those of rod-like and icosahedral viruses [54,55,60–65]. We did not have a good idea on how to approach this problem before the following event. During the summer of 1987 Professor Alfred Saupe from the Institute of Liquid Crystals of Kent State University came to my office, at the recommendation of Professor Helmut Ringsdorf from the University of Mainz, to discuss two publications and seek my help to solve a fundamental scientific problem. The first paper was one of his own reporting the discovery of the first biaxial nematic lyotropic liquid crystal [66]. The second was a brief communication by Malthete and Levelut [67] claiming the first monotropic biaxial nematic liquid crystal designed by a molecular concept elaborated by Chandrasekhar [49]. The Chandrasekhar concept involved a combination of half of a disc-like molecule attached to one end of a rod-like molecule [49] that will eliminate the rotation along the rod-like axis in the nematic phase to create a thermotropic biaxial nematic. Professor Saupe would have liked an enantiotropic thermotropic biaxial nematic liquid crystal phase in a range of temperatures accessible for physical measurements, and Ringsdorf advised him that I could help

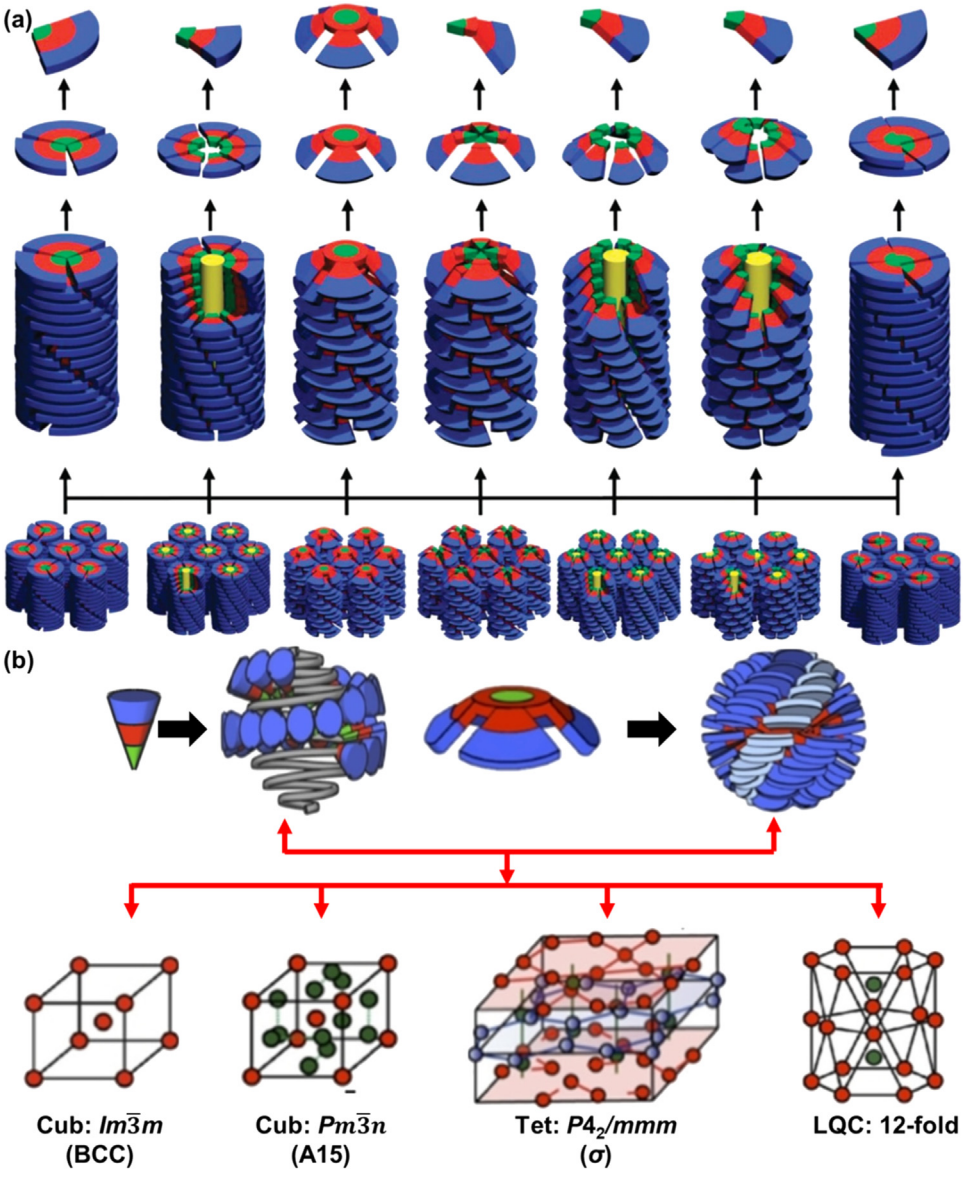

Fig. 2

Mechanism of self-organization of helical and helical pyramidal supramolecular columns (left to right) from tapered dendrons forming disc-like nonhollow, hollow and supramolecular crown, hollow supramolecular crown, hollow helicene-like and nonhollow helicene column cross-sections and their hexagonal arrays (a); mechanism of self-organization of spherical helix from conical and crown conformations and their BCC, Frank-Kasper A15 and σ, and 12 fold LQC assemblies (b). Fig. 2a was adapted from reference 44 and combined with Fig. 2b that was adapted and modified from reference 215.

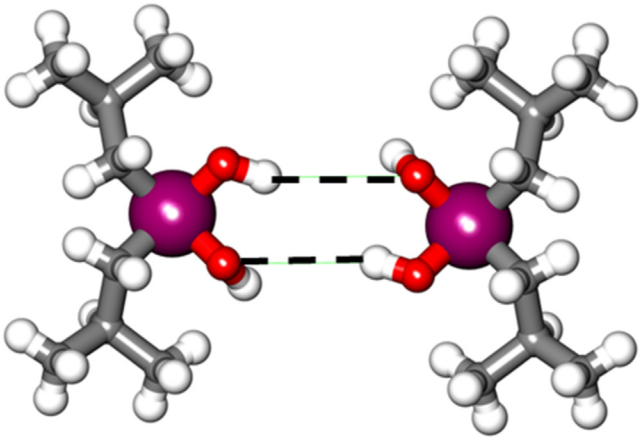

Fig. 3

The *di*isobutylsilanediol dimer, forming the first thermotropic columnar hexagonal liquid crystal phase. Details of supramolecular column structure are not yet known.

him with this transformation. Indeed, I considered that this would represent a very simple experiment and I asked my junior graduate student Jim Heck to attach a polymer backbone to the Malthete-Levelut monotropic biaxial nematic liquid crystal molecule. Fig. 1a shows the Malthete-Levelut monotropic biaxial nematic phase forming molecule while Fig. 1b illustrates the polymer expected to transform its monotropic biaxial nematic phase into an enantiotropic one by the polymer effect [68]. This and numerous additional related experiments failed to generate the enantiotropic biaxial nematic phase. Many other molecules that were variants of Fig. 1a,b were designed. None of them provided the expected enantiotropic biaxial nematic phase originally estimated by optical polarized microscopy in Malthete-Levelut paper [67]. Instead of a biaxial nematic phase the supramolecular columns shown in Fig. 1c were suggested to self-organize, as supported originally by optical polarized microscopy of their columnar hexagonal liquid crystal phase and subsequently by X-ray diffraction experiments.

The supramolecular structures from Fig. 1c demonstrated the failure to transform the expected monotropic biaxial nematic

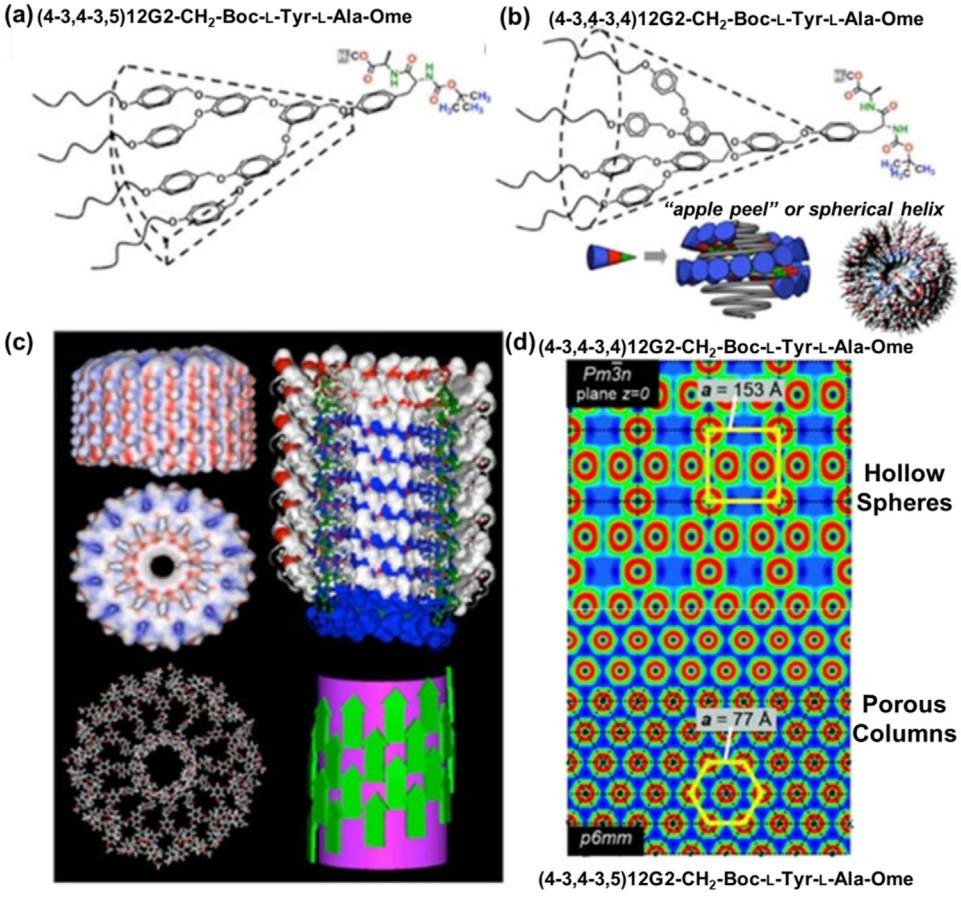

Fig. 4

Self-organization of constitutional isomeric tapered dendritic dipeptide (a) and conical dendritic dipeptide (b); an Aquaporin channel-like porous columnar structure is self-organized from the tapered dendritic dipeptide (c); the self-organization of a hollow spherical helix from the conical dendritic dipeptide is also shown in (b); a comparison of the electron density maps of the A15 Frank-Kasper phase of *Pm3n* symmetry assembled from hollow spheres with the *p6mm* columnar hexagonal phase generated from porous columns illustrating identical diameters of hollow spheres and columns is shown in (d). Reproduced with permission from reference 56. Copyright 2021 Wiley-VCH GmbH.

phase, which as shown later also by other laboratories, was not biaxial nematic [69–72]. These unsuccessful experiments led to the discovery of self-assembling dendrons, dendrimers and dendronized polymers that provided supramolecular disc-like assemblies and supramolecular columns resembling those of the Chandrasekhar 1977 publication [1]. Being disappointed by this failure we did not realize the complete significance of this discovery and therefore, this work of Jim Heck was not published in the most prestigious journals [71–109]. In respect for the creative and hard work of Jim Heck, most of his refereed papers and American Chemical Society Preprints, are cited here [71–109]. A more detailed story of this discovery with numerous examples of structures is available in several other publications [43–47,53–59,62].

The self-assembling dendrons providing the supramolecular columns of Fig. 1c were named "*tapered*." Scanning through generational libraries of self-assembling dendrons with the help of helical diffraction theory [110] we discovered different tapered shapes that form supramolecular discs, hollow discs, crowns, supramolecular crown, hollow supramolecular crowns, tilted helicenes and other helical fragments of column, all self-organizing columnar hexagonal arrays (Fig. 2a).

We did not know at that time that *di*isobutylsilanediol dimerizes into a disc-like molecule (Fig. 3) forming columnar hexagonal liquid crystals [111–113]. Most probably *di*isobutylsilanediol represents one of the first if not the first supramolecular polymer [111–113].

Jim Heck also predicted that higher generation dendrons will adopt "*conical*" conformations that will self-assemble into supramolecular spheres (Fig. 2b). Analysis by X-ray diffraction and electron density maps [114] together with transmission electron microscopy (TEM) [115], isomorphic replacement [115,116], AFM and STM [117], solid state NMR [118], and theoretical together with simulation work [119,120] led to the discovery of the first Frank-Kasper A15 cubic phase (space group $Pm\bar{3}n$) in supramolecular dendrimers and in soft matter (Fig. 2) This finding

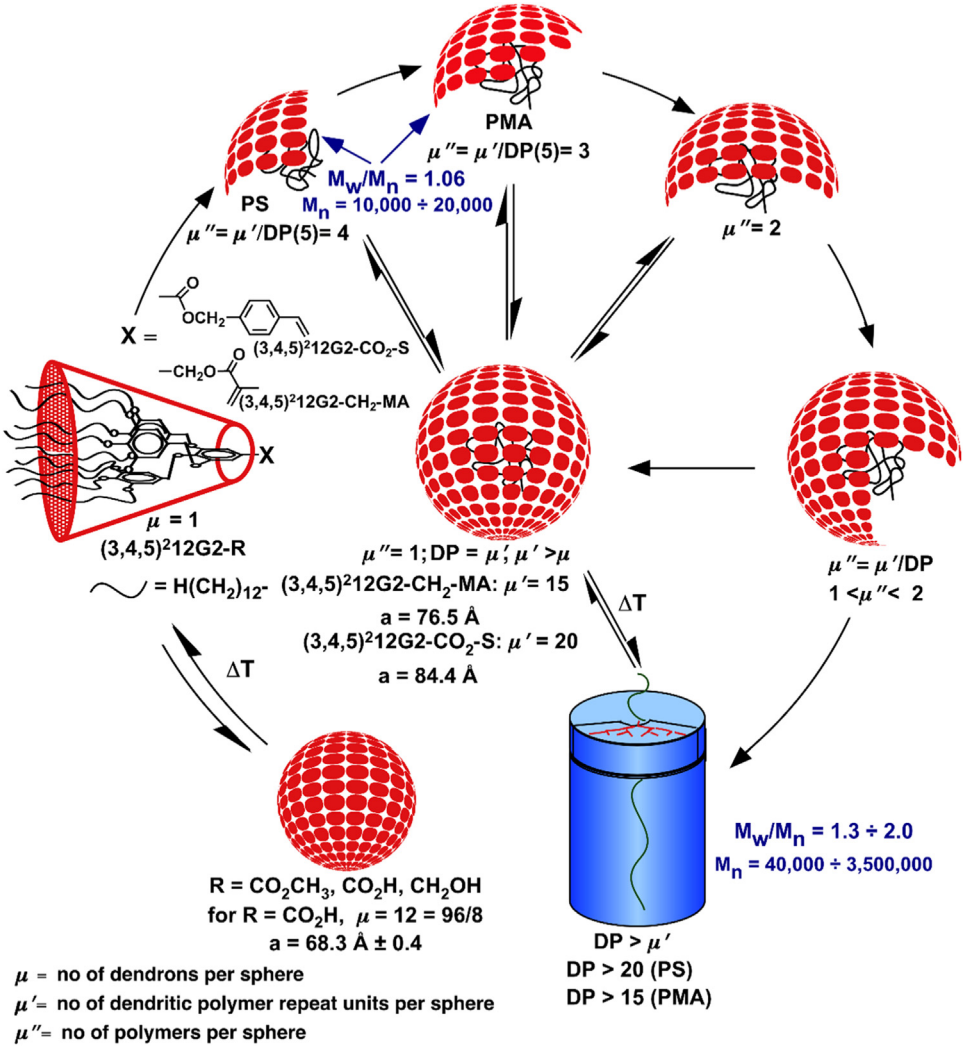

Fig. 5

Conventional radical polymerizations of quasi-equivalent conical dendronized monomers and the structure and shape of the resulting polymers in dilute solution by self-interrupted polymerization (SIP) and in self-assembled stated by self-accelerated polymerization (SAP). Reproduced with permission from reference 174 and transformed from black and white into colored. Copyright 1998, Macmillan Magazines Ltd.

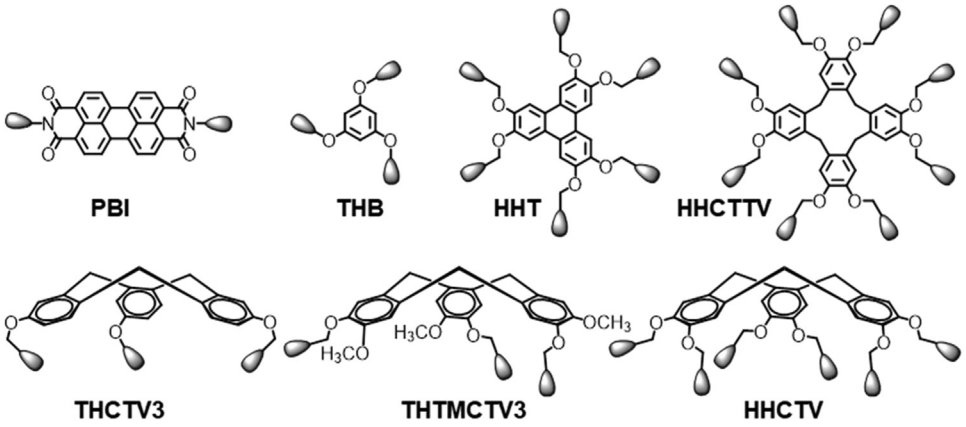

Fig. 6

Disc-like and crown-like molecules employed to prepare dendronized discs and crowns: perylenebisimide (PBI) 1,3,5-trihyhdroxybenzene (THB) hexahydroxytriphenylene (HHT) hexahydroxy-CTTV (HHCTTV), trihydroxy-CTV-3 (THCTV3), trihydroxytrimethoxy-CTV-3 (THTMCTV-3) and hexahydroxy-CTV (HHCTV).

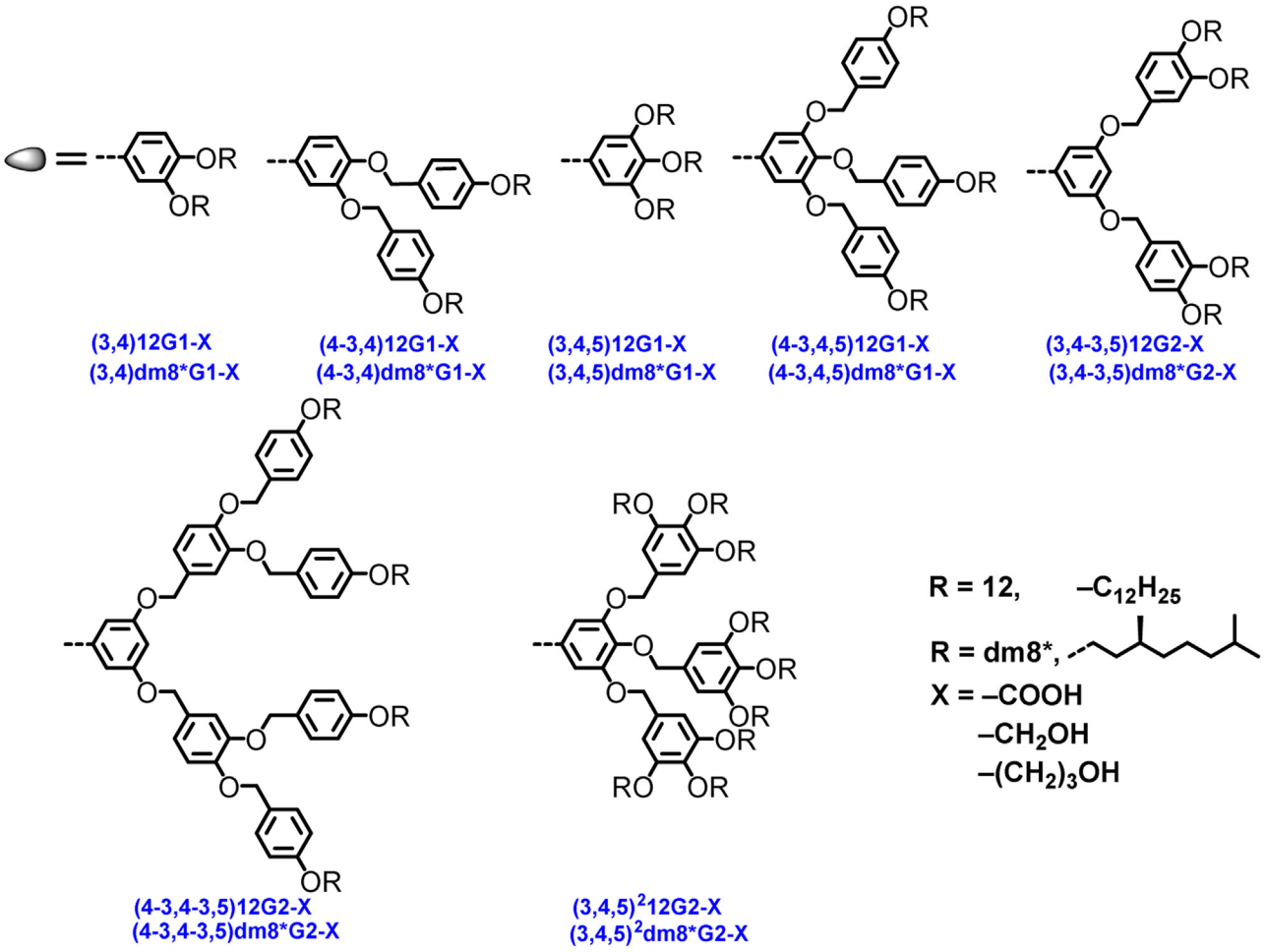

Fig. 7

List of self-assembling dendrons employed to dendronize the discs and crowns from Fig. 6.

was rapidly followed by the discovery of the Frank-Kasper σ phase (also known as tetragonal of space group $P4_2/mnm$) [121] and of the 12-fold quasi liquid crystals (QLC) [122] (Fig. 2b) in supramolecular dendrimers and dendronized polymers. Screening through generational [110,115, 123–158,114] and deconstruction [129] and other more complex libraries [158–188] of self-assembling dendrons and self-assembling hybrid dendrons synthesized by accelerated modular-orthogonal methodologies led to fundamental correlations between the primary structure of the dendrons and the tertiary structure of the resulting self-organizations. This provided the first Nano-Periodic-Table of supramolecular dendrimers [127].

The quasi-equivalence of self-assembling dendrons and their constitutional isomerism

In order to explain the self-assembly of icosahedral viruses from proteins with identical primary structure Casper and Klug elaborated in 1962 he concept of quasi-equivalence [190–192].

Quasi-equivalence was defined as being "Purposeful switching between more stable, unsociable, and less stable, associable, conformations of proteins during self-assembly of icosahedral viruses." Constitutional isomerism of self-assembling dendrons changes their secondary structure from tapered to conical and their self-organization from columnar hexagonal to cubic or Frank-Kasper A15 (Fig 2a,b). This is best illustrated with dendritic dipeptide constitutional isomers that self-organize either a columnar hexagonal LC from porous columns that mimic the Aquaporin channels or form hollow globular supramolecular assemblies self-organizing the cubic A15 Frank-Kasper phase (Fig. 4) [56,168].

Temperature and degree of polymerization in the case of covalent dendronized polymers (Fig. 5) [174] or strength of the interactions in the case of supramolecular dendronized polymers [160] provide the other mechanisms that change in a systematic and reversible way the shape of conical dendron in a tapered one, thus demonstrating their quasi-equivalence [47].

Why dendronized crown and discs?

The very simple question is: why dendronized crowns and discs when all new LC phases including Frank-Kasper and liquid quasicrystals were already discovered with self-assembling dendrons and dendrimers? There were numerous reasons we became interested in dendronizing crown-like and disc-like molecules with self-assembling dendrons. First, a disc-like or a crown molecule provides access to the core of a dendrimer or supramolecular dendrimer with a multiplicity at its core equal

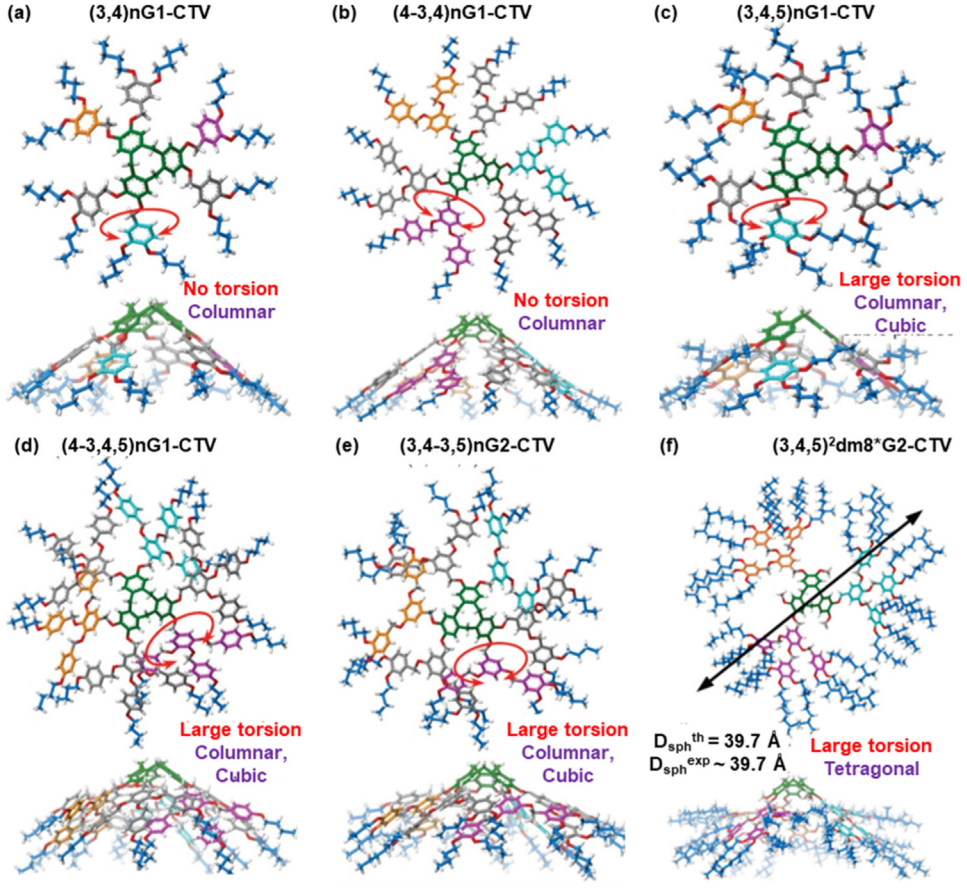

Fig. 8

Molecular models of a library of dendronized CTV crowns. The direct correlation between the presence of a columnar hexagonal, A15 cubic and σ tetragonal Frank-Kasper phases and dendron architecture is illustrated by the marked torsion angle required to fit the conformer in the supramolecular structure determined by XRD (a to f). Molecular model and detail of the aromatic core packing of $(3,4,5)^2$dm8*G2-CTV-3. Fig. 8 was adapted, combined and modified from various Figs of reference 159.

to the degree of substitution of the disc or crown but at the same time a preference towards certain self-organization by comparison with simple sp^3 based branching points. This can be 2, 3, 6, and 8, as it will be shown in the next subchapter. Can this increase the complexity of the supramolecular structure in one step reaction with a low generation dendron provide assemblies similar to those of higher generation dendrons and dendrimers? Second, hexasubstituted CTV was shown to form a pyramidal columnar LC that exhibited helical conformation even in its own melted alkyl groups [15–17,19–21,28,177,193]. Since helical *cis*-cisoidal and *cis*-transoidal polyphenylacetylene (PPA) and other arylacetylenes induce helicity in their dendronized state [171,194–199] providing a molecular machine [171–173] we asked if dendronizing molecular crowns with supramolecular dendrons would not provide an even simpler access to related helical chirality-based concepts already observed with dendronized helical stereoisomers of PPA and other polymers. Third, a crown inversion was observed in the pyramidal columnar LC phase of CTV [16,19]. Will this crown inversion be observed in the dendronized CTV? And if the answer is yes, what new concepts will be provided by it? Fourth, a helical conformation was observed in the liquid columnar crystal state of hexa *n*-alkylthio substituted triphenylene while the hexa-n-alkyloxy-substituted triphenylene provided non-helical columnar hexagonal LC only [10–14]. This small difference between the larger sulfur vs smaller oxygen prompted us to ask the question if replacing *n*-alkoxy groups with achiral self-assembling dendrons will not provide a similar effect with that of replacing oxygen with sulfur since dendrons are larger than alkyl groups? Fifth, CTTV is the conformationally flexible tetramer of the trimer crown-like CTV [22–26]. Will its dendronized structure provide similar structures with those of dendronized CTV? Sixth, any new classes of self-assembling building block have the probability to provide new unpredictable discoveries and we relied on this challenge hoping to discover new concepts with the help of self-assembling dendrimers.

Selecting the disc-like and crown-like molecules to prepare dendronized discs and crowns

Commercial availability, simple synthesis, different multiplicity and flexibility and lack of steric restrictions of the substitution pattern were the main criteria for the selection of the rigid perylenebisimide (PBI) 1,3,5-trihyhdroxybenzene (THB) hexahydroxytriphenylene (HHT) and flexible hexahydroxy-CTTV, (HHCTTV) disc-like, as well as of trihydroxy-CTV-3 (THCTV-3) and hexahydroxy-CTV (HHCTV) crown building blocks illustrated in Fig. 6.

Self-organizations from dendronized CTVs

We will start our discussion with the dendronized crown CTV [159] since the structures resulted from these experiments made the biggest impact on this topic and were also used as model compounds for all other dendronized disc-like molecules. Two CTV derivatives were employed in these experiments. A trisubstituted, THCTV-3 and THTMCTV3 and a hexasubstituted, HHCTV, (Fig. 7). A large diversity of first

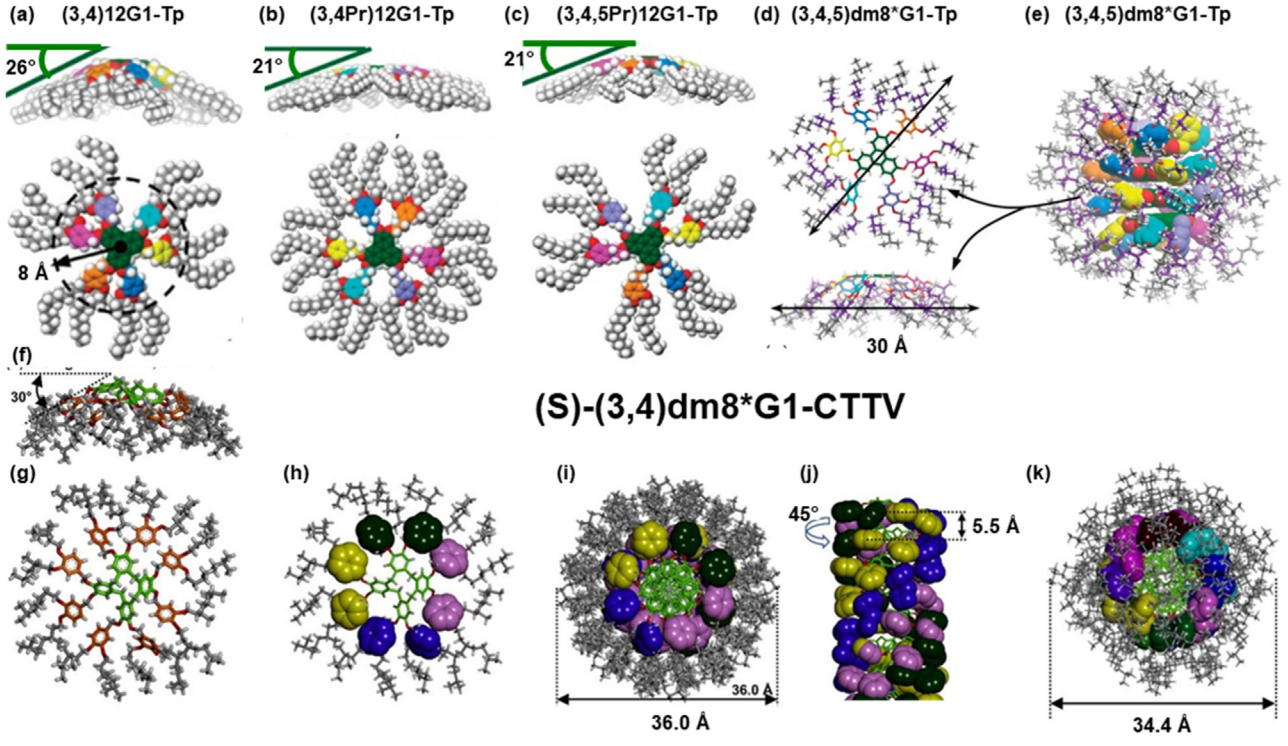

Fig. 9

Molecular models of (a) (3,4)12G1-Tp, (b) (3,4Pr)12G1-Tp, (c) (3,4,5Pr)12G1-Tp, (d) (3,4,5Pr)dm8*G1-Tp, (e) (3,4,5)dm8*G1-Tp. (f–k) Molecular models of (S)-(3,4)dm8*G1-CTTV, (f) Side view, (g) Top view, (h) Top view, (i) Column (Top view), Column (Side view), (k) Spherical structure of the hexagonal phase. Fig. 9a–e was adapted and modified from reference 166. Fig. 9f–k was adapted and modified from reference 28.

generation self-assembling dendrons attached to HHCTV such as (3,4)12G1, (3,4)dm8*G1, (4-3,4)G1, (4-3,4)dm8*G1 (Fig. 7 self-organize helical columnar hexagonal LCs while (3,4,5)12G1, (3,4,5)dm8*G1, (4-3,4,5)12G1, (4-3,4,5)dm8*G1 and (3,4-3,5)12G2 self-organize helical columnar LCss and cubic Frank-Kasper A15 LC phases, the last obtained from spherical helices. (3,4-3,5)dm8*G2-CTV self-organizes only the cubic A15 phase. The lower multiplicity CTV crown THCTV-3 requires second generation dendrons such as (4-3,4-3,5)12G2 and (4-3,4-3,5)dm8*G2 to self-organize helical columnar hexagonal LCs while $(3,4,5)^2$12G2-CTV-3 and $(3,4,5)^2$dm8*G2-CTV-3 self-organize only tetragonal σ Frank-Kasper phase. The mechanism of self-organization of helical columnar hexagonal and of cubic A15 phases is illustrated in Fig. 2b [159]. The spherical helices and helical columns forming these two LC phases mediate *via* temperature a crown inversion. This is a much simple mechanism than the one required to interconvert spheres from conical dendrons into columns from tapered self-assembling dendrons [193], as it will be discussed in even more details later. The experiments with dendronized CTVs set the principles and rules that will be followed by all other dendronized disc-like molecules.

A library of dendronized CTV with the conformation of the dendronized molecule and the phases in which it self-organizes as determined by X-ray analysis is shown in Fig. 8 [159]. Increasing generation number provides an enhanced torsion angle of the dendron repeat unites from the periphery. This enhanced torsion angle required to accommodate the dendron in a certain conformation, increases the probability to transit the hierarchical self-organization from helical pyramidal columns to columns and spheres and only to spheres. This is a general and very simple molecular design principle for the construction of Frank-Kasper cubic and tetragonal phases from first principles [159]. As it will be shown later this concept applies also to dendronized rigid discs such as HHT and flexible discs such as HHCTTV (Fig. 6) [160]. The directionality provided by the flexible benzyl ether repeat units of the self-assembling dendron is also a very important molecular design parameter that is not available in the melted state of the alkyl groups from classic discotic molecules in their discotic columnar liquid crystal state [1].

Self-organizations from dendronized HHT and HHCTTV

To our surprise dendronized HHT also self-organize helical columnar hexagonal LCs, A15 and σ Frank-Kasper as well as LQC phases [160,200].

Both the helical columns of the helical columnar hexagonal LCs and the helical spheres forming A15, σ and LQC phases

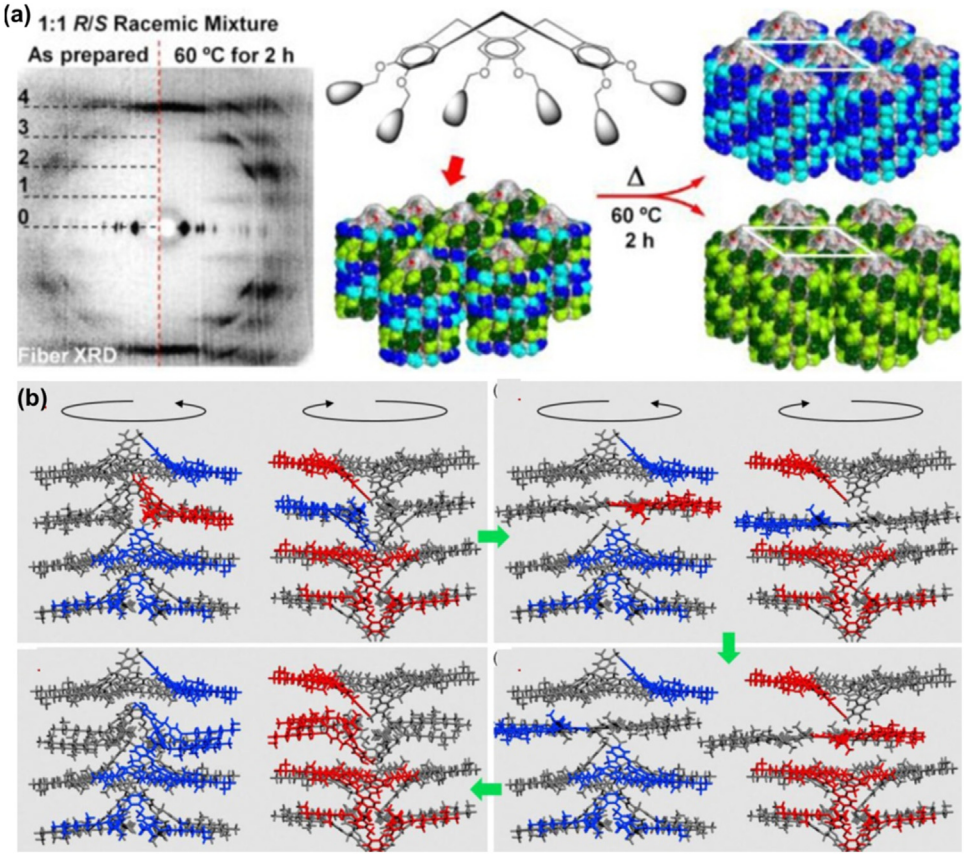

Fig. 10

X-Ray diffractograms before and after annealing of the columnar assembly self-organized from the racemic hat-shape CTV dendronized with the self-assembling (4-3,4)12G1CH_2OH displaying deracemization accompanied by crystallization of the dynamic racemic supramolecular columnar polymer into homochiral columnar hexagonal polymer; the columnar hexagonal crystal provides the driving force for this process (a); (b) the mechanism of deracemization by stereo-sequence rearrangement of dynamic racemic polymers in their semicrystalline liquid crystal state is shown in part (b) where the hat-crown inversion via a transient disc that transfers between columns provides the deracemization process. Fig. 10 was adapted and modified from reference 177.

are assembled from crown-like conformations of the dendronized triphenylene and CTTV [160,200,201]. As in the case of dendronized CTV [158] first generation self-assembling dendrons such as (3,4)12G1, (3,4Pr)12G1, (3,4,5Pr)12G1, (4-3,4)12G1 and (4-3,4,5)12G1 attached to triphenylenes form only hexagonal columnar arrays while (3,4,5)12G1, (3,4,5)dm8*G1, (4-3,4-3,5)12G2 and (3,4-3,5)12G2 self-organize helical columnar hexagonal and A15, σ and LQC phases. In all cases, temperature can change in a reversible way spheres into columns. It is also remarkable that in the case of the triphenylene helical columns complexation with electron-acceptor compounds can also transform spheres into columns [160]. This is due to an enhancement of the bond strength of the short supramolecular spheres columns due to the similarity of the helical column and spherical helices that are both organized from crown-like conformers [159]. Fig. 9 provides selected examples of dendronized HHT and HHCTTV, shown in Fig. 7, and the corresponding resulted dendronized disc conformation as obtained from X-ray diffraction experiments [28,160,200]. It is remarkable to observe from

Fig. 9 shows how the molecular design principles induced by self-assembling dendron generation number apply not only to HHCTV but also to flexible and rigid discotic molecules. Access via flexible and rigid discs to this self-organization process provides an entrance to designed dynamics of self-assembly and self-organization of identical tertiary structures. This is one of the most important concepts that requires elucidation in order to generate complex soft matter with the same level of precision to that of single crystals produced from few low molar mass atoms [53,54,56].

*A racemic (R+S) (3,4)dm8*G1 Dendronized CTV displays a hat-shape that self-organizes columnar hexagonal LCs undergoing deracemization accompanied by crystallization of homochiral columns*

Homochiral and racemic (3,4)dm8*G1-CTV adopt a hat-shaped conformation that self-organizes helical columnar hexagonal LCs and crystals [177]. Racemic (3,4)dm8*G1-CTV obtained from an equimolar ratio of their *R* and *S* enantiomers self-organize a helical columnar hexagonal LC phase that upon annealing undergoes deracemization into pure *R* and *S* domains of columns. The enantiomerically pure homochiral domains undergo fast crystallization forming highly ordered columnar hexagonal crystals. Deracemization of racemic columns is mediated by inversion of configuration of the CTV-hat and exchange between the supramolecular columns as illustrated in Fig. 10. A combination of X-ray diffraction, NMR and CD in solid state were used to demonstrate this concept that is similar to deracemization in solution accomplished by Pasteur in 1848 [202] except that the current example represents the

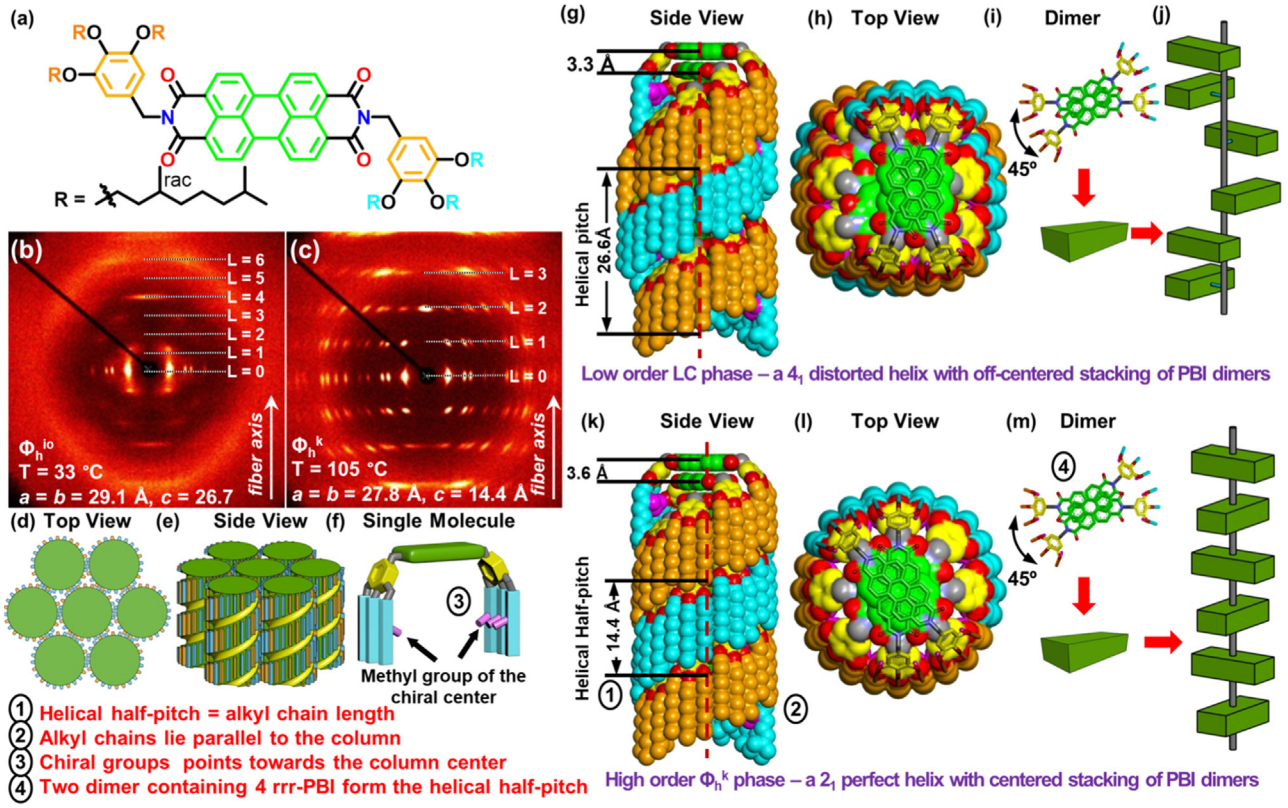

Fig. 11

Molecular structure of dendronized PBI (a); (b) wide-angle X-ray diffraction (WAXS) pattern in the Φ_h^{io} phase (b) and wide-angle X-ray diffraction (WAXS) pattern in Φ_h^{k} phase (c). The cogwheel model of helical self-organization accompanied by deracemization that disregards chirality (d to m). Fig. 11 was adapted and modified from reference 178.

first deracemization in the bulk state. The driving force for this deracemization and crystallization is the helical columnar hexagonal crystal state that provides the highest degree of order with homochiral single-handed helical columns (Fig. 10) [177]. It is remarkable to observe (Fig. 10b) how the hat conformer obtained by dendronizing CTV undergoes, as demonstrated by solid state NMR, crown inversion withing the supramolecular column. The transient disc-like conformation of the CTV-crown exits the column and enters in a neighboring column providing the mechanism responsible for the deracemization that is demanded for crystallization of homochiral columns. Since columnar hexagonal unit cell contains four quarters of a column (see top right column in Fig. 10a), single handedness is required to crystallize a helical columnar hexagonal crystal. In this particular case, single handedness is obtained by deracemization. Since these supramolecular columns are in fact supramolecular polymers we can consider this deracemization to be similar to a stereo-sequence rearrangement of a heterochiral, atactic or syndiotactic polymer into an isotactic homochiral polymer. This is a remarkable new concept with numerous potential applications [177].

Dendronized PBI provides a cogwheel mechanism to self-organize helical columnar hexagonal LCs and crystals

The self-organization of a large diversity of dendronized perylenebisimides [177–180,203–210] naphthalenebisimides [210] and other related molecules [205] was investigated before the cogwheel mechanism of helical self-organization was discovered and reported in 2016 [178]. The structures of dendronized PBIs self-organizing by a cogwheel mechanism helical columns are showed in Fig. 9 The cogwheel mechanism of self-organization is illustrated in Fig. 9. Two dendronized PBI molecules form a supramolecular crown. A disordered, originally assigned crystal phase (k1) that in fact is a helical columnar hexagonal liquid crystal phase with intracolumnar order, forms at high temperature and a highly ordered helical columnar hexagonal crystal phase (k2) forms at low temperature [178]. In the liquid crystal phase the supramolecular crowns are "on" and "off" the column axis while in the crystal state they are all "on" the column axis. The length of the alkyl groups of the self-assembling dendron must be strictly equal to the half-pitch of the column. The alkyl groups must contain methyl substituents that will end-up facing inner

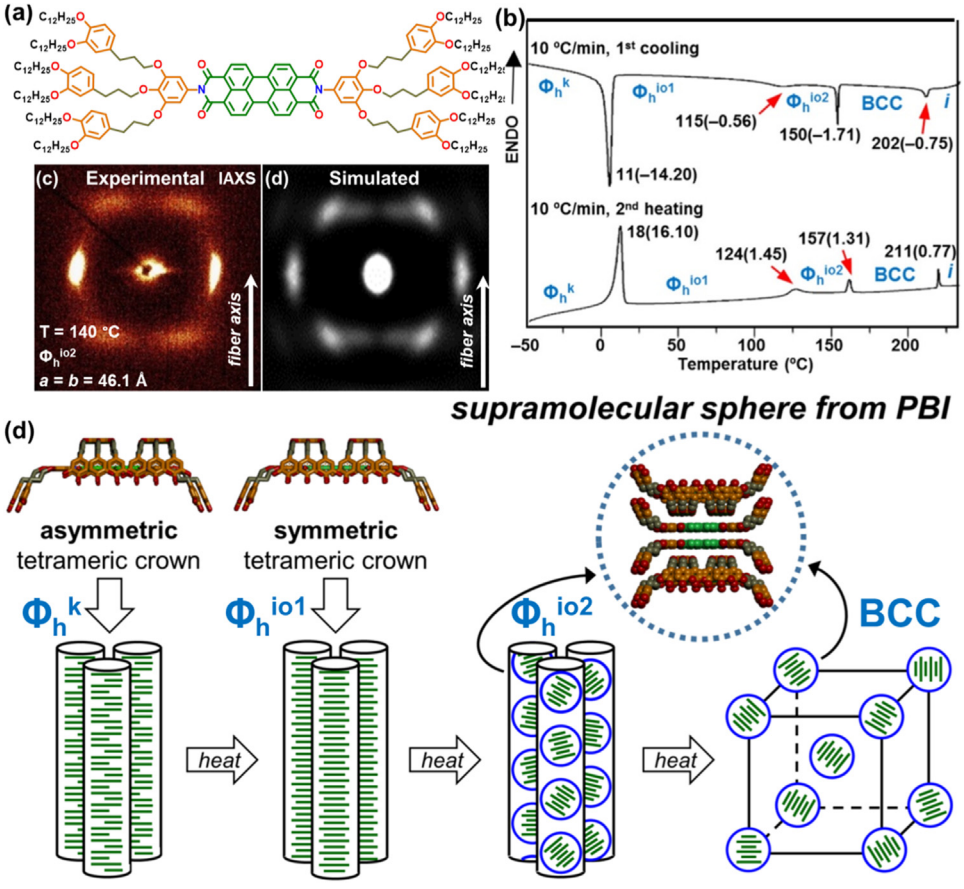

Fig. 12

Molecular structure of dendronized PBI, G2-PBI (a); DSC traces of G2-PBI recorded with heating and cooling rates of 10°C/min upon first cooling, and second heating phases determined by XRD (defined in main text) transition temperatures (in°C) and associated enthalpy changes (in parentheses in kcal/mol) are indicated (b); columnar hexagonal phase assembled from supramolecular spheres determined by experimental (c) and simulated (d) XRDs, and schematic models of the four phases of G2-PBI with phase notation: Φ_h^k, 3D crystalline columnar hexagonal phase; Φ_h^{io1}, low temperature 2D liquid crystalline columnar hexagonal phase with intracolumnar order; Φ_h^{io2}, high temperature 2D liquid crystalline columnar hexagonal phase with intracolumnar order; body-centered cubic phase (BCC) of space symmetry $Im\bar{3}m$ (d). Fig. 12 was adapted and modified from reference 205.

part of the column. Introducing a sequence-defined combination of alkyl groups in the dendron can provide an extraordinary acceleration of the extremely slow transition from the columnar hexagonal LC to its corresponding crystal [179,180].

Supramolecular columns assembled from supramolecular spheres self-organize columnar hexagonal liquid crystals

A PBI dendronized with the second generation self-assembling dendron (3,4Pr-3,4,5)12G2 forms a tetrameric supramolecular crown that self-organizes supramolecular spheres arranged in a supramolecular column self-organizing a columnar hexagonal LC phase [205]. This unusual columnar structure occurs above a columnar hexagonal phase assembled from supramolecular discs and below a cubic BCC periodic array generated also from supramolecular spheres (Fig. 10). It is required that supramolecular columns assembled from crowns display a transient state of columns generated from spheres before entering the BCC phase [212–215]. However, it was unexpected that this intermediate columnar hexagonal liquid crystal state containing columns assembled from spheres would be stable, as in this case, over a range 23 °C [205]. A chiral dendronized CTTV dendronized with (3,4)dm8*G1 was demonstrated to self-organize in supramolecular columns constructed from supramolecular spheres, with no subsequent transition to a cubic phase [28].

This columnar hexagonal phase constructed from chiral spheres was enantiotropically stable over a range of 23 °C on heating and on cooling. As in the previous case the supramolecular spheres forming the column are generated from crown conformations of the dendronized flexible CTTV in this case. An additional example of supramolecular columns from spheres forming columnar hexagonal LC phase was observed from C60 dendronized with (4-3,4,5)12G1 self-assembling dendrons (Fig. 13) [211].

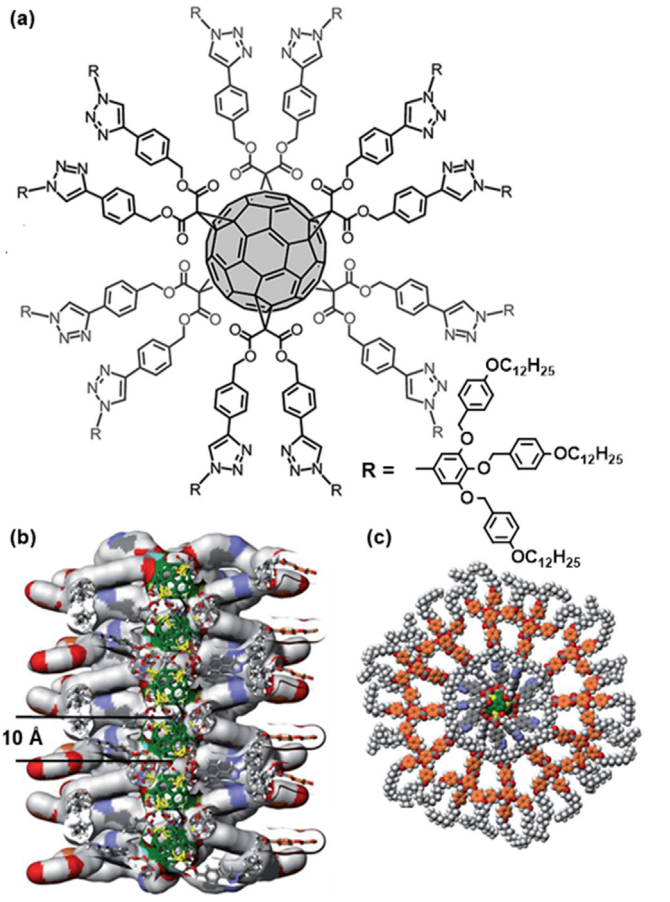

Fig. 13

(a) Molecular structure of dendronized fullerene with (4-3,4,5)12G1 self-assembling dendron (a); molecular model of column's side view (b) and top view of the column (c). Fig. 13 was adapted and modified from reference 211.

Hierarchical self-organization of new bundles and arrays of columnar hexagonal liquid crystals by supramolecular orientational memory effect

Hierarchical self-organization of a diversity of new arrays of columnar hexagonal fragments and bundles was accomplished by the supramolecular orientational memory effect (SOM).

SOM induced by an epitaxial nucleation mediated by the close contact spheres of cubic and tetragonal phases, emerged as a pathway to engineer complex nanoscale soft matter of helical and nonhelical columnar hexagonal arrays. SOM preserves the crystallographic directions of close contact supramolecular sphered upon cooling from a cubic to a columnar hexagonal periodic array. So far, SOM was observed at the transition from Frank-Kasper A15, BCC and Frank-Kasper σ phases to the columnar hexagonal arrays only when the column and spheres were self-organized from dendronized crowns, supramolecular crowns assembled from dendronized planar molecules and from supramolecular dendritic crowns assembled *via* H-bonding (Fig. 14) [193,212–215]. Orthogonal [193], tetrahedral [212,158], dodecahedral [213], rhombitruncated cuboctahedral [214], and rectangular bipyramidal [215] arrangements of hexagonal columns were so far discovered (Fig. 14 [215]). When the same cubic phases are self-organized from supramolecular spheres assembled from conical dendrons no SOM effect was observed so far [213]. Only the orthogonal arrangements of columnar hexagonal arrays were analyzed in complete details including histograms of all orthogonal orientations [193]. For all other arrays, only the new architectural structure induced by SOM was elucidated but no detailed analysis of its concentration and arrangement, as determined in great details for the case of the orthogonal array, is available at this time.

Discrimination between cone vs crown mechanism of self-assembly of supramolecular spheres via the SOM effect

Fig. 15 illustrates the self-assembly of a supramolecular sphere from the AB9-COOH self-assembling dendron showed in Fig. 15a [158]. Ten conical (Fig. 15c) or ten half-crown conformations of the AB9-COOH forming five crown conformations (Fig. 15b) self-assemble into the strictly identical supramolecular spheres from Figs. 15f and 15d self-organizing a BCC lattice. X-ray analysis could not discriminate between these two mechanisms of self-assembly and self-organization [158]. A SOM effect generating an orthogonal arrangement of bundles of columns occurs at the transition from BCC to the columnar hexagonal phase. Since only crown conformations forming spheres and columns provide the SOM effect, in this particular case, it is the SOM effect that

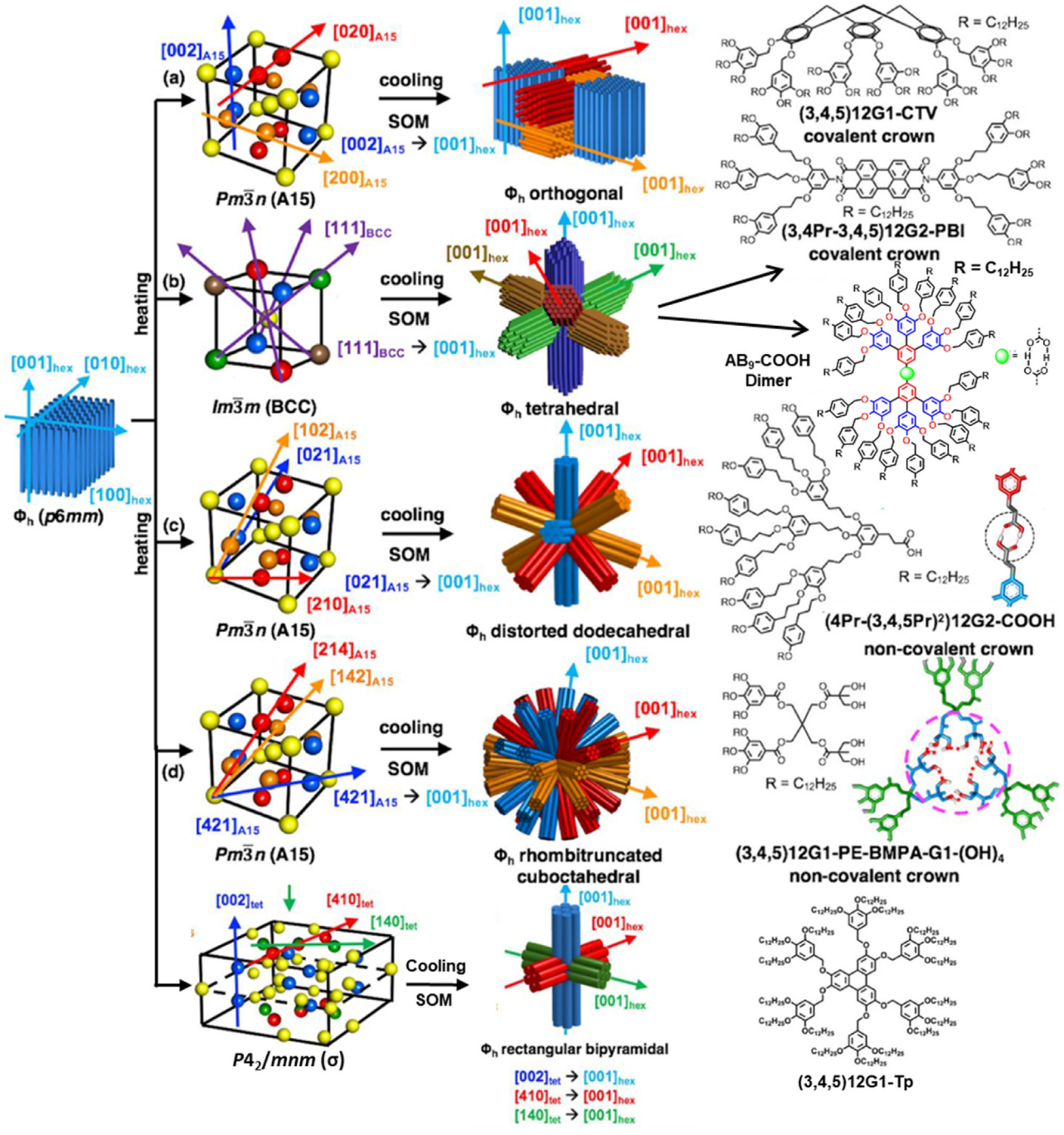

Fig. 14

Summary of the supramolecular orientational memory effect with selected examples of new bundles of columnar arrays and molecular structures generating them. Fig. 14 was adapted and modified from references 236 and 158.

discriminated between these two mechanisms demonstrating that both columns and sphere from Fig. 15 are self-organized from the supramolecular crowns and discs shown in Fig, 15 b,e [158].

Conclusions

A brief discussion of the discovery and development of molecular design principles for a large diversity of liquid crystal phases self-organized from self-assembling dendronized discs and crowns was briefly presented. These liquid crystal phases were not predictable when Chandrasekhar laboratory discovered and reported discotic liquid crystals in 1977 [1]. Thermotropic Frank-Kasper phases started to be discovered in soft condensed matter 20 years later, in 1997 in our laboratory, with the help of self-assembling dendrons [114,115]. Prior to 1997 the A15 Frank-Kasper phase was known only in the lyotropic state of lipids [216]. In the mean-time Frank-Kasper phases were also discovered in block copolymers [217] and giant molecules [218] to create a very active new field of research that will not be discussed here since

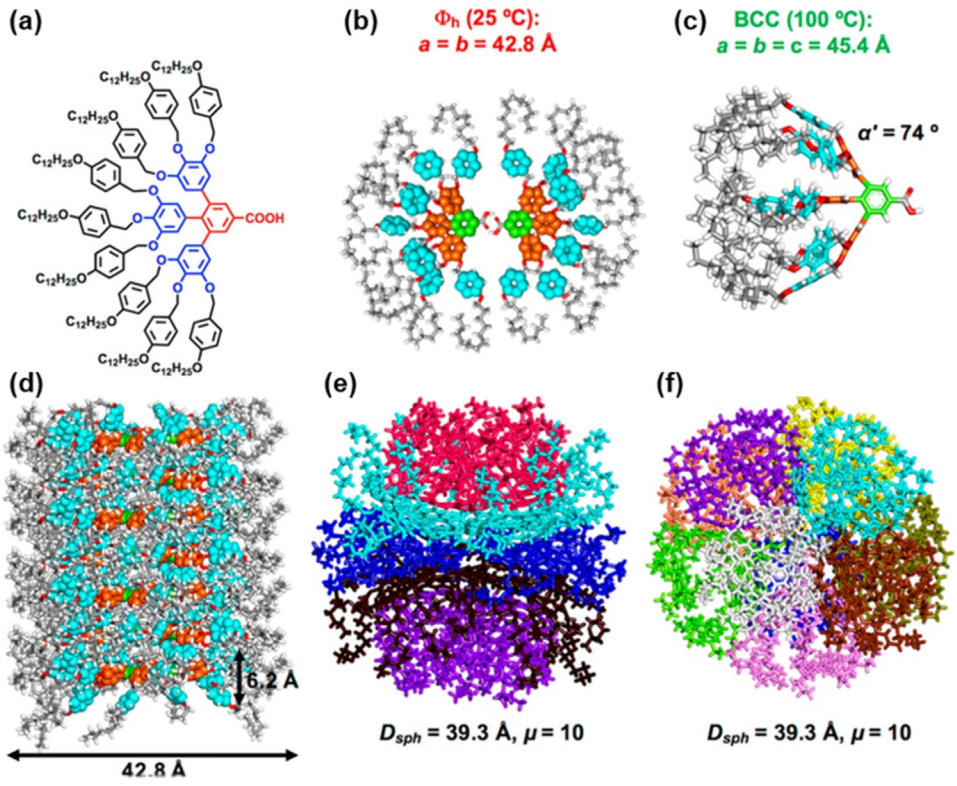

Fig. 15

Molecular structure of AB9–COOH self-assembling dendron (a); top view of the single layer of the supramolecular disc assembling the supramolecular columns forming the columnar hexagonal phase (b); the conical conformation of AB9-COOH (c); the side view of the supramolecular column (d) assembled from the discs shown in (b); supramolecular sphere (e) assembled from five crown dimeric conformers consisting of ten AB9-COOH dendrons assembled from distorting the discs from (b); the structure the supramolecular sphere (f) assembled from ten conical conformers of AB9-COOH shown in part (c). Fig. 15 was adapted and modified from reference 158.

it is not related to discotic liquid crystals. The topic of Frank-Kasper and quasicrystal phases in block copolymers should and will be discussed in an independent Perspective. Publications discussing the history of the first 100 years of research in liquid crystals and soon after are available [2–4,219]. However, the biaxial nematic thermotropic liquid crystal phase predicted by Chandrasekhar [49] is not yet solved. A thermotropic cyclic main chain polyether based on conformational isomerism seems to be the least debated biaxial nematic liquid crystal [220]. Research in the discovery and perfection of 1D, 2D and 3D self-organizations, their mechanism, functions and applications is in our opinion in its early stage of development. One of my preferred applications that will have a great impact on our society is purification of water with the same level of perfection as that of Aquaporins [163,201]. All these developments are and will be impacted by quantitative and simple synthetic methods accessible to any synthetic and nonsynthetic laboratory including simple click chemistry developed in our laboratory [24,26,27,49–51,158,221–236]. We hope that this perspective will inspire and help future developments in this field. This perspective is dedicated to the 45th anniversary of the discovery of discotic liquid crystals by Chandrasekhar laboratory [1] and to the memory of Professor Chandrasekhar. He was a great scientist and a modest and respectful person. As soon as our laboratory discovered dendritic liquid crystals, I started to be invited by him to give plenary and invited lectures at Symposia organized by him. I remember with great pleasure the lecture "From discotic liquid-crystals to dendritic liquid-crystals" presented as an invited lecture at the International Conference on Discotic Liquid Crystals organized by him, 20 years ago, at the International Center for Theoretical Physics in Trieste, Italy, on November 25 to 29, 2002. I will never forgive myself since I had to cancel my trip to present, at his invitation, the opening lecture during the inauguration of the Center for Liquid Crystals in Bangalore in 1991.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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References

[1] S. Chandrasekhar, B.K. Sadashiva, K.A. Suresh, Liquid crystals of disc-like molecules, Pramana - J Phys 9 (1977) 471–480, doi:10.1007/BF02846252.

[2] G.W. Gray, J.W. Goodby, H. Kelker, History of liquid crystals, Mol. Cryst. Liq. Cryst. 21 (1973) 1–48, doi:10.1080/15421407308083312.

[3] D. Demus, Plenary Lecture, One hundred years of liquid-crystal chemistry: thermotropic liquid crystals with conventional and unconventional molecular structure, Liq. Cryst. 5 (1989) 75–110, doi:10.1080/02678289908026353.

[4] V. Percec, What are the new concepts used in the design of molecular, macromolecular and supramolecular liquid crystals? Macromol. Symp. 117 (1997) 267–273, doi:10.1002/masy.19971170130.

[5] J. Brooks, G. Taylor, Formation of graphitizing carbons from the liquid phase, Nature 206 (1965) 697–699, doi:10.1038/206697a0.

[6] J. Billard, J.C. Dubois, N.H. Tinh, A. Zann, Mesophase of disc-like molecules, Nouv. J. Chim. 2 (1978) 535–540.

[7] N.H. Tinh, C. Destrade, H. Gasparoux Destrade, Nematic disc-like liquid crystals, Phys. Lett. A 72A (1979) 251–254, doi:10.1016/0375-9601(79)90019-7.

[8] A.M. Levelut, Structure of a disk-like mesophase, J. Phys. Lett. 40 (1979) L81–L84, doi:10.1051/jphyslet:0197900400408100.

[9] A.M. Levelut, Structures of mesophases of disc-like molecules, J. Chim. Phys. 80 (1983) 149–161, doi:10.1051/jcp/1983800149.

[10] A.M. Levelut, P. Oswald, A. Ghanem, Structure of the 2 columnar phases of a chiral triphenylene ester, 45 (1984) 745–754, doi:10.1051/jphys:01984004504074500.

[11] B. Kohne, W. Poules, K. Praefcke, 1st Liquid-Crystalline hexakis(alkylthio)triphenylene, 108 (1984) 113–113.

[12] E. Fontes, P.A. Heiney, WH de Jeu, Liquid-crystalline and helical order in a discotic mesophase, Phys. Rev. Lett. 61 (1988) 1202–1205, doi:10.1103/PhysRevLett.61.1202.

[13] E. Fontes, P.A. Heiney, Molecular disorder in columnar-phase of discotic liquid-crystal strands, Phys. Rev. A. 37 (1988) 1329–1334, doi:10.1103/PhysRevA.37.1329.

[14] D. Adam, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K.H. Etzbachi, H. Ringsdorf, D. Haarer, Fast photoconduction in the highly ordered columnar phase of a discotic liquid crystal, Nature 371 (1994) 141–143, doi:10.1038/371141a0.

[15] H. Zimmermann, R. Poupko, Z. Luz, J. Billard, Pyramidic Mesophases, Z. Naturforsch (1985) 149–160 40a, doi:10.1515/zna-1985-0208.

[16] H. Zimmermann, R. Poupko, Z. Luz, J. Billard, Temperature dependent sign reversal of the optical anisotropy in pyramidic mesophases, Z. Naturforsch 41a (1986) 1137–1140, doi:10.1515/zna-1986-0908.

[17] Z. Luz, R. Poupko, E.J. Wachtela, H. Zimmermann, Mesomorphic properties of the neat enantiomers of a chiral pyramidic liquid crystal, Phys. Chem. Chem. Phys. 11 (2009) 9562–9568, doi:10.1039/B908029P.

[18] H. Zimmermann, R. Poupko, Z. Luz, J. Billard, Tetrabenzocyclododecatetraene a new core for mesogens exhibiting columnar mesophases, Liq. Cryst. 3 (1988) 759–770, doi:10.1080/02678298808086532.

[19] H. Zimmermann, R. Poupko, Z. Luz, J. Billard, Temperature dependent sign reversal of the optical anisotropy in pyramidic mesophases, Z. Naturforsch 41 (1986) 1137–1140, doi:10.1515/zna-1986-0908.

[20] A.M. Levelut, J. Malthête, A. Collet, X-ray structural study of the mesophases of some cone-shaped molecules, J. Phys. 47 (1986) 351–357, doi:10.1051/jphys:01986004702035100.

[21] J. Malthete, A. Collet, Inversion of the cyclotribenzylene cone in a columnar mesophase: a potential way to ferroelectric materials, J. Am. Chem. Soc. 109 (1987) 7544–7545, doi:10.1021/ja00258a057.

[22] N. Spielberg, M. Sarkar, Z. Luz, R. Poupko, J. Billard, H. Zimmermann, The discotic mesophases of octaalkyloxy-and octaalkanoyloxyorthocyclophanes, Liq. Cryst. 15 (1993) 311–330, doi:10.1080/02678299308029134.

[23] W. Kranig, H.W. Spiess, H. Zimmermann, Substituted tetrabenzocyclophanes as mesogenic units of new polycondensates exhibiting columnar mesophases, Liq. Cryst. 7 (1989) 123–129, doi:10.1080/02678299008029199.

[24] V. Percec, C.G. Cho, C. Pugh, D. Tomazos, Synthesis and characterization of branched liquid-crystalline polyethers containing cyclotetraveratrylene-based disk-like mesogens, Macromolecules 25 (1992) 1164–1176, doi:10.1021/ma00029a025.

[25] V. Percec, C.G. Cho, C. Pugh, Alkyloxy-substituted CTTV derivatives that exhibit columnar mesophases, J. Mater. Chem. 1 (1991) 217–222, doi:10.1039/JM9910100217.

[26] V. Percec, C.G. Cho, C. Pugh, Cyclotrimerization versus cyclotetramerization in the electrophilic oligomerization of 3,4-bis(methyloxy)benzyl derivatives, Macromolecules 24 (1991) 3227–3234, doi:10.1021/ma00011a029.

[27] T. Yamato, C. Hideshima, G.K. Surya Prakash, G.A. Olah, Solid superacid-catalyzed organic synthesis. 4. Perfluorinated resinsulfonic acid (Nafion-H) catalyzed Friedel-Crafts benzylation of benzene and substituted benzenes, J. Org. Chem. 56 (1991) 2089–2091, doi:10.1021/jo00006a023.

[28] D. Sahoo, M.R. Imam, M. Peterca, B.E. Partridge, D.A. Wilson, X. Zeng, G. Ungar, P.A. Heiney, V. Percec, Hierarchical self-organization of chiral columns from chiral supramolecular spheres, J. Am. Chem. Soc. 140 (2018) 13478–13487, doi:10.1021/jacs.8b09174.

[29] D. Sahoo, M. Peterca, M.R. Imam, B.E. Partridge, Q. Xiao, V. Percec, Conformationally flexible dendronized cyclotetraveratrylenes (CTTV)s self-organize a large diversity of chiral columnar, Frank-Kasper and quasicrystal phases, Giant 10 (2022) 100096, doi:10.1016/j.giant.2022.100096.

[30] R.J. Bushby, O.R. Lozman, Discotic liquid crystals 25 years on, Curr. Opin. Coll. Interf. Sci. 7 (2002) 343–354, doi:10.1016/S1359-0294(02)00085-7.

[31] S. Kumar, Self-organization of disc-like molecules: chemical aspects, Chem. Soc. Rev. 35 (2006) 83–109, doi:10.1039/B506619K.

[32] S. Kumar, Triphenylene-based discotic liquid crystal dimers, oligomers and polymers, 32 (2005) 1089–1113, doi: 10.1080/02678290500117415.

[33] S. Kumar, in: Chemistry of Discotic Liquid Crystals: From Monomers to Polymers, 1st Ed., Pub. Location: Boca Raton CRC Press, 2011, pp. 1–519, doi:10.1201/B10457.

[34] H. Ringsdorf, B. Schlarb, J. Venzmer, Molecular architecture and function of polymeric oriented systems: models for the study of organization, surface recognition, and dynamics of biomembrane, Angew. Chem. Int. Ed. Engl. 27 (1988) 113–158, doi:10.1002/anie.198801131.

[35] S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel, M. Tosoni, Discotic liquid crystals: from tailor-made synthesis to plastic electronics, Angew. Chem. Int. Ed. 46 (2007) 4832–4887, doi:10.1002/anie.200604203.

[36] T. Wöhrle, I. Wurzbach, J. Kirres, A. Kostidou, N. Kapernaum, J. Litterscheidt, J.C. Haenle, P. Staffeld, A. Baro, F. Giesselmann, S. Laschat, Discotic liquid crystals, Chem. Rev. 116 (2016) 1139–1241, doi:10.1021/acs.chemrev.5b00190.

[37] S. Kumar, Functional discotic liquid crystals, Isr. J. Chem. 52 (2012) 820–829, doi:10.1002/ijch.201200035.

[38] S. Kumar, Playing with discs, Liq. Cryst. 36 (2009) 607–638, doi:10.1080/02678290902755549.

[39] X. Feng, W. Pisula, K. Müllen, Large polycyclic aromatic hydrocarbons: synthesis and discotic organization, Pure Appl. Chem. 81 (2009) 2203–2224, doi:10.1351/PAC-CON-09-07-07.

[40] W. Pisula, X. Feng, K. Mullen, Charge-carrier transporting graphene-type molecules, Chem. Mater. 23 (2011) 554–567, doi:10.1021/cm102252w.

[41] M. Kumar, S. Varshney, S. Kumar, Emerging nanoscience with discotic liquid crystals, Polym. J. 53 (2021) 283–297, doi:10.1038/s41428-020-00414-6.

[42] F. Würthner, C.R. Saha-Möller, B. Fimmel, S. Ogi, P. Leowanawat, D. Schmidt, Perylene bisimide dye assemblies as archetype functional supramolecular materials, Chem. Rev. 116 (2016) 962–1052, doi:10.1021/acs.chemrev.5b00188.

[43] R.J. Bushby, K. Kawata, Liquid crystals that affected the world: discotic liquid crystals, Liq. Cryst. 38 (2011) 1415–1426, doi:10.1080/02678292.2011.603262.

[44] B.M. Rosen, C.J. Wilson, D.A. Wilson, M. Peterca, M.R. Imam, V. Percec, Dendron-mediated self-assembly, disassembly, and self-organization of complex systems, Chem. Rev. 109 (2009) 6275–6540, doi:10.1021/cr900157q.

[45] V. Percec, G. Johansson, From liquid crystal polymers containing crown ethers to tapered building blocks containing crown ethers which self-assemble into tubular supermolecules, Macromol. Symp. 96 (1995) 173–184, doi:10.1002/masy.19950960117.

[46] V. Percec, G. Johansson, D. Schlueter, J.C. Ronda, G. Ungar, Molecular recognition directed self-assembly of tubular supramolecular architectures from building blocks containing monodendrons as exo-receptors and crown- or pseudo-crown-ethers as endo-receptors, Macromol. Symp. 101 (1996) 43–60, doi:10.1002/masy.19961010107.

[47] V. Percec, C.-H. Ahn, W.-D. Cho, G. Johansson, D. Schlueter, Design of new macromolecular architectures by using quasi-equivalent monodendrons as building blocks, Macromol. Symp. 118 (1997) 33–43, doi:10.1002/masy.19971180106.

[48] S. Chandrasekhar, B.K. Sadashiva, K.A. Suresh, N.V. Madhusudana, S. Kumar, R. Shashidhar, G. Venkatesh, Disc-like mesogens, J. Phys. Colloques 40 (1979) C3-120–C3-124, doi:10.1051/jphyscol:1979325.

[49] S. Chandrasekhar, Relation between Molecular Structure and Liquid Crystalline Properties, Mol. Cryst. Liq. Cryst. 124 (1985) 1–20, doi:10.1080/00268948508079461.

[50] J. Wu, W. Pisula, K. Müllen, Graphenes as Potential Material for Electronics, Chem. Rev. 107 (2007) 718–747, doi:10.1021/cr068010r.

[51] A.J. Berresheim, M. Müller, K. Müllen, Polyphenylene nanostructures, Chem. Rev. 99 (1999) 1747–1786 +, doi:10.1021/cr970073.

[52] M.D. Watson, A. Fechtenkötter, K. Müllen, Big is beautiful—"aromaticity" revisited from the viewpoint of macromolecular and supramolecular benzene chemistry, Chem. Rev. 101 (2001) 1267–1300, doi:10.1021/cr990322p.

[53] V. Percec, Merging macromolecular and supramolecular chemistry into bioinspired synthesis of complex systems, Isr. J. Chem. 60 (2020) 48–66, doi:10.1002/ijch.202000004.

[54] V. Percec, Q. Xiao, Helical self-organizations and emerging functions in architectures, biological and synthetic macromolecules, Bull. Chem. Soc. Jpn. 94 (2021) 900–928, doi:10.1246/bcsj.20210015.

[55] C. Roche, V. Percec, Complex adaptable systems based on self-assembling dendrimers and dendrons: Toward dynamic materials, Isr. J. Chem. 53 (2013) 30–44, doi:10.1002/ijch.201200099.

[56] V. Percec, Q. Xiao, Helical chirality of supramolecular columns and spheres self-organizes complex liquid crystals, crystals, and quasicrystals, Isr. J. Chem. 61 (2021) 530–565, doi:10.1002/ijch.202100057.

[57] V. Percec, G. Ungar, Self-Assembly in Action, Science 313 (2006) 55–56, doi:10.1126/science.1129512.

[58] H.-J. Sun, S. Zhang, V. Percec, From structure to function via complex supramolecular dendrimer systems, Chem. Soc. Rev. 44 (2015) 3900–3923, doi:10.1039/C4CS00249K.

[59] V. Percec, Q. Xiao, G. Lligadas, M.J. Monteiro, Perfecting self-organization of covalent and supramolecular mega macromolecules via sequence-defined and monodisperse components, Polymer 211 (2020) 123252, doi:10.1016/j.polymer.2020.123252.

[60] A. Klug, From macromolecules to biological assemblies (Nobel lecture) Angew, Chem. Int. Ed 95 (1983) 579–596, doi:10.1002/anie.198305653.

[61] V. Percec, Q. Xiao, The legacy of Rosalind E. Franklin: landmark contributions to two Nobel Prizes, Chem 7 (2021) 529–536, doi:10.1016/j.chempr.2021.02.020.

[62] V. Percec, Bioinspired supramolecular liquid crystals, Phil. Trans. R. Soc. A. 364 (2006) 2709–2719, doi:10.1098/rsta.2006.1848.

[63] V. Percec, Q. Xiao, Helical chirality of supramolecular columns and spheres self-organizes complex liquid crystals, Crystals, and Quasicrystals, Isr. J. Chem. 61 (2021) 530–556, doi:10.1002/ijch.202100057.

[64] J.G. Rudick, V. Percec, Helical chirality in dendronized in dendronized polyarylacetylenes, New J. Chem 31 (2007) 1083–1096, doi:10.1039/B616449H.

[65] J.G. Rudick, V. Percec, Induced Helical Backbone conformations of self-organizable dendronized polymers, Acc. Chem. Res. 41 (2008) 1641–1652 10,1021/ar800086w.

[66] L.J. Yu, A. Saupe, Observation of a biaxial nematic phase in potassium laurate-1-decanol-water mixtures, Phys. Rev. Lett. 45 (1980) 1000–1003, doi:10.1103/PhysRevLett.45.1000.

[67] J. Malthete, L. Liebert, A. Levelut, Y. Galerne, Thermotropic biaxial nematic, Compt. Rend. Acad. Sci. Ser II 303 (1986) 1073–1076, doi:10.1080/00268948508079461.

[68] V. Percec, A. Keller, A thermodynamic interpretation of polymer molecular weight effect on the phase transitions of main-chain and side-chain liquid-crystal polymers, Macromolecules 23 (1990) 4347–4350, doi:10.1021/ma00222a003.

[69] J.R. Hughes, G. Kothe, G.R. Luckhurst, J. Malthête, M.E. Neubert, I. Shenouda, B.A. Timimi, M. Tittelbach, A deuterium nuclear magnetic resonance investigation of the symmetry and orientational order of the nematic phase of 4-[3,4,5-tris(4-dodecyloxybenzyloxy)benzoyloxy]-4′- (4-dodecyloxybenzoyloxy)-1,1′-biphenyl. A biaxial nematic? J. Chem. Phys. 107 (1997) 9252–9997, doi:10.1063/1.475318.

[70] G. Shenouda, I. Shi, M.E. Neubert, Mesomorphic properties of 4-[3′,4′,5′-tri(p-n−dodecyloxybenzyloxy)]-benzoyloxy-4‴-p-n−dodecyloxybenzyloxybi phenyl, Mol. Cryst. Liq. Cryst. Lett. 257 (1994) 209–218, doi:10.1080/10587259408033777.

[71] J. Malthête, P. Davidson, Mesogens based on one flexible triangular DOBOB unit, Bull. Soc. Chim. Fr. 131 (1994) 812.

[72] V. Percec, J. Heck, G. Johansson, D. Tomazos, G. Ungar, Towards tobacco mosaic virus-like self-assembled supramolecular architectures, 77 (1994) 237–265, doi:10.1002/masy.19940770127.

[73] V. Percec, J. Heck, Abstr. Pap, Am. Chem. Soc. 198 (1989) 135 –Poly.

[74] V. Percec, J. Heck, Side-chain liquid-crystal polymers containing mesogenic units based on 1/2 disk and rod-like moieties, ACS Polym. Prepr. 30 (1989) 450.

[75] V. Percec, J. Heck, Liquid crystalline polymers containing mesogenic units based on half-disc and rod-like moieties, Polym. Bull. 24 (1990) 255–262, doi:10.1007/BF00306572.

[76] V. Percec, J. Heck, Liquid-crystalline polymers containing mesogenic units based on half-disk and rod-like moieties. 3. Synthesis and characterization of polymethylsiloxanes and copolymethyl-siloxanes based on 4-[3,4,5-tri(p-N-dodecan-1-yloxybenzyloxy)benzoate]-4-(p-allyloxybenzoate)biphenyl and 4-[3,4,5-tri(p-N-dodecan-1-yloxy-benzyloxy)benzoate]-4-(p-allyloxybenzo ate)thiodiphenyl side groups, Polym. Bull. 25 (1991) 55–62, doi:10.1007/BF00338899.

[77] V. Percec, J. Heck, Liquid crystalline polymers containing mesogenic units based on half-disc and rod-like moieties, Polym. Bull. 25 (1991) 431–438, doi:10.1007/BF00310233.

[78] V. Percec, J. Heck, Liquid crystalline polymers containing mesogenic units based on half-disc and rod-like moieties. I. Synthesis and characterization of 4-(11-undecan-1-yloxy)-4-[3,4,5-tri(p-n-dodecan-1-yloxybenzyloxy)benzoate]biphenyl side groups, J. Polym. Sci. Part A: Polym. Chem. 29 (1991) 591–597, doi:10.1002/pola.1991.080290416.

[79] V. Percec, J. Heck, G. Ungar, Liquid-crystalline polymers containing mesogenic units based on half-disk and rodlike moieties. 5. Side-chain liquid-crystalline poly(methylsiloxanes) containing hemiphasmidic mesogens based on 4-[[3,4,5-tris(alkan-1-yloxy)benzoyl]oxy]-4-[[p-(propan-1-yloxy)benzoyl]oxy]biphenyl groups, Macromolecules 24 (1991) 4957–4962, doi:10.1021/ma00017a036.

[80] J. A. Heck, PhD Thesis, Case Western Reserve University, 1995.

[81] V. Percec, J. Heck, M. Lee, G. Ungar, A. Alvarez-Castillo, Poly{2-vinyloxyethyl 3,4,5-tris[4-(n-dodecanyloxy)benzyloxy]benzoate}: a self-assembled supramolecular polymer similar to tobacco mosaic virus, J. Mater. Chem. 2 (1992) 1033–1039, doi:10.1039/JM9920201033.

[82] V. Percec, M. Lee, J. Heck, H.E. Blackwell, G. Ungar, A. Alvarez-Castillo, Re-entrant isotropic phase in a supramolecular disc-like oligomer of 4-[3,4,5-tris(n-dodecanyloxy)benzoyloxy]-4-[(2-vinyloxy)ethoxy]biphenyl, J. Mater. Chem. 2 (1992) 931–938, doi:10.1039/JM9920200931.

[83] V. Percec, G. Johansson, J. Heck, G. Ungar, S.V. Batty, Molecular recognition directed self-assembly of supramolecular cylindrical channel-like architectures from 6,7,9,10,12,13,15,16-octahydro-1,4,7,10,13-pentaoxabenzocyclopentadecen-2-ylmethyl 3,4,5-tris(p-dodecyloxybenzyloxy) benzoate, J. Chem. Soc., Perkin Trans. 1 (1993) 1411–1420 , doi:10.1039/P19930001411.

[84] V. Percec, J. Heck, D. Tomazos, F. Falkenberg, H. Blackwell, G. Ungar, Self-assembly of taper-shaped monoesters of oligo(ethylene oxide) with 3,4,5-tris(p-dodecyloxybenzyloxy)benzoic acid and of their polymethacrylates into tubular supramolecular architectures displaying a columnar mesophase, J. Chem. Soc., Perkin Trans. 1 (1993) 2799–2811, doi:10.1039/P19930002799.

[85] V. Percec, J.A. Heck, D. Tomazos, G. Ungar, The influence of the complexation of sodium and lithium triflate on the self-assembly of tubular-supramolecular architectures displaying a columnar mesophase based on taper-shaped monoesters of oligoethylene oxide with 3,4,5-tris[p-(n-dodecan-1-yloxy)benzyloxy]benzoic acid and of their polymethacrylates, J. Chem. Soc., Perkin Trans. 2 (1993) 2381–2388, doi:10.1039/P29930002381.

[86] V. Percec, D. Tomazos, J. Heck, H. Blackwell, G. Ungar, Self-assembly of taper-shaped monoesters of oligo(ethylene oxide) with 3,4,5-tris(n-dodecan-1-yloxy)benzoic acid and of their polymethacrylates into tubular supramolecular architectures displaying a columnar hexagonal mesophase, J. Chem. Soc., Perkin Trans. 2 (1994) 31–44, doi:10.1039/P29940000031.

[87] V. Percec, D. Schlueter, G. Ungar, S.Z.D. Cheng, A. Zhang, Hierarchical control of internal superstructure, diameter, and stability of supramolecular and macromolecular columns generated from tapered monodendritic building blocks, Macromolecules 31 (1998) 1745–1762, doi:10.1021/ma971459p.

[88] Y.K. Kwon, S. Chvalun, A.-I. Schneider, J. Blackwell, V. Percec, J.A. Heck, Supramolecular tubular structures of a polymethacrylate with tapered side groups in aligned hexagonal phases, Macromolecules 27 (1994) 6129–6132, doi:10.1021/ma00099a029.

[89] Y.K. Kwon, S.N. Chvalun, J. Blackwell, V. Percec, J.A. Heck, Effect of temperature on the supramolecular tubular structure in oriented fibers of a poly(methacrylate) with tapered side groups, Macromolecules 28 (1995) 1552–1558, doi:10.1021/ma00109a029.

[90] V. Percec, D. Schlueter, Y.K. Kwon, J. Blackwell, M. Moeller, P.J. Slangen, Dramatic stabilization of a hexagonal columnar mesophase generated from supramolecular and macromolecular columns by the semifluorination of the alkyl groups of their tapered building blocks, Macromolecules 28 (1995) 8807–8818, doi:10.1021/ma00130a013.

[91] V. Percec, D. Schlueter, J.C. Ronda, G. Johansson, G. Ungar, J.P. Zhou, Tubular architectures from polymers with tapered side groups. Assembly of side groups via a rigid helical chain conformation and flexible helical chain conformation induced via assembly of side groups, Macromolecules 29 (1996) 1464–1472, doi:10.1021/ma951244k.

[92] V. Percec, D. Schlueter, Mechanistic investigations on the formation of supramolecular cylindrical shaped oligomers and polymers by living ring opening metathesis polymerization of a 7-oxanorbornene monomer substituted with two tapered monodendrons, Macromolecules 30 (1997) 5783–5790 10.1021/ma970157k.

[93] V. Percec, J. Heck, G. Johansson, D. Tomazos, M. Kawasumi, G. Ungar, Molecular-recognition-directed self-assembly of supramolecular polymers, J. Macromol. Sci, Part A. Pure Appl. Chem. 31 (1994) 1031–1070, doi:10.1080/10601329409349776.

[94] V. Percec, J. Heck, Liquid-crystalline polymers containing mesogenic units based on half-disk and rod-like moieties. 1. Synthesis And Characterization OF 4-(11-Undecan-1-yloxy)-4′-[3,4,5-tri(para-normal-dodecan-1-yloxybenzyloxy)benzoate]biphenyl Side Groups, J. Polym. Sci., Part A-1: Polym. Chem 29 (1991) 591–597, doi:10.1002/pola.1991.080290416.

[95] V. Percec, J. Heck, Liquid-crystalline polymers containing mesogenic units based on half-disk and rod-like moieties .4. side-chain liquid-crystalline polymethylsiloxanes containing hemiphasmidic mesogens based on 4-[3,4,5-tri-(alkan-1-yloxy)benzoate]biphenyl groups, Polym. Bull. 25 (1991) 431–438, doi:10.1007/BF00310233.

[96] V. Percec, J. Heck, Side-chain liquid-crystalline polymers containing hemiphasmidic mesogens, Abstr. Pap. Am. Chem. Soc. 201 (1991) 201 –Poly.

[97] V. Percec, J. Heck, Molecular recognition directed supramolecular polymer architectures, Abstr. Pap. Am. Chem. Soc. 202 (1991) 299 -Poly.

[98] V. Percec, J. Heck, Towards tobacco mosaic virus-like supramolecular synthetic-polymers, Abstr. Pap. Am. Chem. Soc. 203 (1992) 6 –Poly.

[99] V. Percec, J. Heck, Molecular design of externally regulated self-assembled supramolecular ionic channels, Abstr. Pap. Am. Chem. Soc. 203 (1992) 402 –Poly.

[100] V. Percec, J. Heck, G. Johansson, G. Ungar, Towards tobacco mosaic virus-like self-assembled supramolecular architectures, Abstr. Pap. Am. Chem. Soc. Volume: 205 (1993) 235 -Poly.

[101] V. Percec, J. Heck, G. Johansson, D. Tomazos, M. Kawasumi, G. Ungar, Molecular-recognition-directed self-assembly of supramolecular solymers, J. Macromol. Sci. - Pure Appl. Chem. A31 (1994) 1031–1070.

[102] V. Percec, J. Heck, G. Johansson, D. Tomazos, M. Kawasumi, P. Chu, G. Ungar, Molecular recognition directed self-assembly of supramolecular architectures, J. Macromol. Sci. - Pure Appl. Chem. A31 (1994) 1719–1758, doi:10.1080/10601329408545879.

[103] Y.K. Kwon, C. Danko, S. Chvalun, J. Blackwell, J.A. Heck, V. Percec, Comparison of the supramolecular structures formed by a polymethacrylate with a highly tapered side-chain and its monomeric precursor, Macromol. Symp. 87 (1994) 103–114, doi:10.1002/masy.19940870113.

[104] J. Blackwell, Y.K. Kwon, S. Chvalun, V. Percec, J.A. Heck, Effect of temperature on the supramolecular tubular structure in oriented fibers of a poly(methacrylate) with tapered side-groups, 209 (1995) 242–PMSE.

[105] G. Ungar, D. Abramic, V. Percec, J.A. Heck, Self-assembly of twin tapered bisamides into supramolecular columns exhibiting hexagonal columnar mesophases. Structural evidence for a microsegregated model of the supramolecular column, Liq. Cryst. 21 (1996) 73–86, doi:10.1080/02678299608033797.

[106] J. Blackwell, S.N. Chvalun, J.D. Cho, Y.K. Kwon, V. Percec, J.A. Heck, X-ray analyses of the supramolecular structures formed by polymers with highly tapered side groups, Abstr. Pap. Am. Chem. Soc. 214 (1997) 32 –Poly.

[107] S.N. Chvalun, J. Blackwell, J.D. Cho, Y.K. Kwon, V. Percec, X-ray analysis of the internal rearrangement of the self-assembling columnar structure formed by a highly tapered molecule, Polymer 39 (1998) 4515–4522, doi:10.1016/S0032-3861(97)10131-8.

[108] G. Ungar, V. Percec, M.N. Holerca, G. Johansson, J.A. Heck, Heat-shrinking spherical and columnar supramolecular dendrimers: Their interconversion and dependence of their shape on molecular taper angle, Eur. J. Chem. 6 (2000) 1258–1266, doi:10.1002/(SICI)1521-3765(20000403).

[109] S.N. Chvalun, J. Blackwell, Y.K. Kwon, V. Percec, Small angle x-ray analysis of the effect of temperature on the self-assembling columnar structures formed by a polymethacrylate with highly tapered side groups and by one of its low molar mass precursors, Macromol. Symp. 118 (1997) 663–675, doi:10.1002/masy.19971180186.

[110] M. Peterca, V. Percec, M.R. Imam, P. Leowanawat, K. Morimitsu, Molecular structure of helical supramolecular dendrimers, J. Am. Chem. Soc. 130 (2008) 14840–14852, doi:10.1021/ja806524m.

[111] C. Eabor, Organosilicon compounds. Part III. Some sterically hindered compounds, J. Chem. Soc. (1952) 2840–2846, doi:10.1039/JR9520002840.

[112] C. Eaborn, N.H. Hartshorne, The mesomorphism of *di*isobutylsilanediol, J. Chem. Soc. (1955) 549–555, doi:10.1039/JR9550000549.

[113] J.D. Bunning, J.W. Goodby, G.W. Gray, J.E. Lydon, The classification of the mesophase of di-i-butylsilanediol, in: Proc. Int. Conf. Liq. Cryst. of One- and Two-Dimensional Order, Garmisch-Partenkirchen, 1980, pp. 397–402. ed. W. Helfrich & G. Heppke.

[114] V.S.K. Balagurusamy, G. Ungar, V. Percec, G. Johansson, Rational design of the first spherical supramolecular dendrimers self-organized in a novel thermotropic cubic liquid-crystalline phase and the determination of their shape by x-ray analysis, J. Am. Chem. Soc. 119 (1997) 1539–1555, doi:10.1021/ja963295i.

[115] S.D. Hudson, H.-T. Jung, V. Percec, W.-D. Cho, G. Johansson, G. Ungar, V.S.K. Balagurusamy, Direct visualization of individual cylindrical and spherical supramolecular dendrimers, Science 278 (1997) 449–452, doi:10.1126/science.278.5337.449.

[116] D.R. Dukeson, G. Ungar, V.S.K. Balagurusamy, V. Percec, G.A. Johansson, M. Glodde, Application of isomorphous replacement in the structure determination of a cubic liquid crystal phase and location of the counterions, J. Am. Chem. Soc. 125 (2003) 15974–15980, doi:10.1021/ja037380.

[117] V. Percec, C.-H. Ahn, W.-D. Cho, A.M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M. Möller, S.A. Prokhorova, S.S. Sheiko, S.Z.D. Cheng, A. Zhang, G. Ungar, D.J.P. Yeardley, Visualizable cylindrical macromolecules with controlled stiffness from backbones containing libraries of self-assembling dendritic side groups, J. Am. Chem. Soc. 120 (1998) 8619–8631, doi:10.1021/ja981211v.

[118] A. Rapp, I. Schnell, D. Sebastiani, S.P. Brown, V. Percec, H.W. Spiess, Supramolecular assembly of dendritic polymers elucidated by 1H and 13C solid-state MAS NMR spectroscopy, J. Am. Chem. Soc. 43 (2003) 13284–13297, doi:10.1021/ja035127d.

[119] Y. Li, S.-T. Lin, W.A. Goddard, Efficiency of various lattices from hard ball to soft ball: theoretical study of thermodynamic properties of dendrimer liquid crystal from atomistic simulation, J. Am. Chem. Soc. 126 (2004) 1872–1885, doi:10.1021/ja038617e.

[120] P. Ziherl, R.D. Kamien, Maximizing entropy by minimizing area: towards a new principle of self-organization J, Phys. Chem. B 105 (2001) 10147–10158, doi:10.1021/jp010944q.

[121] G. Ungar, Y.S. Liu, X.B. Zeng, V. Percec, W.D. Cho, Giant supramolecular liquid crystal lattice, Science 299 (2003) 1208–1211, doi:10.1126/science.1078849.

[122] X. Zeng, G. Ungar, Y. Liu, V. Percec, A.E. Dulcey, J.K. Hobbs, Supramolecular dendritic liquid quasicrystals, Nature 428 (2004) 157–160, doi:10.1038/nature02368.

[123] V. Percec, W.-D. Cho, G. Ungar, D.J.P. Yeardley, Synthesis and structural analysis of two constitutional isomeric libraries of AB 2 -based monodendrons and supramolecular dendrimers, J. Am. Chem. Soc. 123 (2001) 1302–1315, doi:10.1021/ja0037771.

[124] V. Percec, C.M. Mitchell, W.-D. Cho, S. Uchida, M. Glodde, G. Ungar, X. Zeng, Y. Liu, V.S.K. Balagurusamy, P.A. Heiney, Designing libraries of first generation AB 3 and AB 2 self-assembling dendrons via the primary structure generated from combinations of (AB) y −AB 3 and (AB) y −AB 2 building blocks, J. Am. Chem. Soc. 126 (2004) 6078–6094, doi:10.1021/ja049846j.

[125] V. Percec, M. Peterca, M.J. Sienkowska, M.A. Ilies, E. Aqad, J. Smidrkal, P.A. Heiney, Synthesis and retrostructural analysis of libraries of AB3 and constitutional isomeric AB2 phenylpropyl ether-based supramolecular dendrimers, J. Am. Chem. Soc. 128 (2006) 3324–3334, doi:10.1021/ja060062a.

[126] V. Percec, M.N. Holerca, S. Nummelin, J.J. Morrison, M. Glodde, J. Smidrkal, M. Peterca, B.M. Rosen, S. Uchida, V.S.K. Balagurusamy, M.J. Sienkowska, P.A. Heiney, Exploring and expanding the structural diversity of self-assembling dendrons through combinations of AB, constitutional isomeric AB 2, and AB 3 biphenyl-4-methyl ether building blocks, Chem. Eur. J. 12 (2006) 6216–6241, doi:10.1002/chem.200600178.

[127] B.M. Rosen, D.A. Wilson, C.J. Wilson, M. Peterca, B.C. Won, C. Huang, L.R. Lipski, X. Zeng, G. Ungar, P.A. Heiney, V. Percec, Predicting the structure of supramolecular dendrimers via the analysis of libraries of AB 3 and constitutional isomeric AB 2 biphenylpropyl ether self-assembling dendrons, J. Am. Chem. Soc. 131 (2009) 17500–17521, doi:10.1021/ja907882n.

[128] V. Percec, J.G. Rudick, M. Peterca, M.E. Yurchenko, J. Smidrkal, P.A. Heiney, Supramolecular structural diversity among first-generation hybrid dendrimers and twin dendrons, Chem. Eur. J. 14 (2008) 3355–3362, doi:10.1002/chem.200701658.

[129] B.M. Rosen, M. Peterca, C. Huang, X. Zeng, G. Ungar, V. Percec, Deconstruction as a strategy for the design of libraries of self-assembling dendrons, Angew. Chem. Int. Ed. 49 (2010) 7002–7005, doi:10.1002/anie.201002514.

[130] V. Percec, W.-D. Cho, G. Ungar, D.J.P. Yeardley, Synthesis and NaOTf mediated self-assembly of monodendritic crown ethers, Chem. Eur. J. 8 (2002) 2011–2025 10.1002/1521-3765(20020503)8:9(2011::AID- CHEM2011>3.0.CO;2-3.

[131] V. Percec, T.K. Bera, M. Glodde, Q. Fu, V.S.K. Balagurusamy, P.A. Heiney, Hierarchical self-assembly, coassembly, and self-organization of novel liquid crystalline lattices and superlattices from a twin-tapered dendritic benzamide and its four-cylinder-bundle supramolecular polymer, Chem. Eur. J. 9 (2003) 921–935, doi:10.1002/chem.200390114.

[132] V. Percec, M. Peterca, T. Tadjiev, X. Zeng, G. Ungar, P. Leowanawat, E. Aqad, M.R. Imam, B.M. Rosen, U. Akbey, R. Graf, S. Sekharan, D. Sebastiani, H.W. Spiess, P.A. Heiney, S.D. Hudson, Self-assembly of dendronized perylene bisimides into complex helical columns, J. Am. Chem. Soc. 133 (2011) 12197–12219, doi:10.1021/ja204366b.

[133] V. Percec, W.-D. Cho, G. Ungar, Increasing the diameter of cylindrical and spherical supramolecular dendrimers by decreasing the solid angle of their monodendrons via periphery functionalization, J. Am. Chem. Soc. 122 (2000) 10273–10281, doi:10.1021/ja0024643.

[134] V. Percec, M.R. Imam, T.K. Bera, V.S.K. Balagurusamy, M. Peterca, P.A. Heiney, Self-assembly of semifluorinated Janus-dendritic benzamides into bilayered pyramidal columns, Angew. Chem. Int. Ed. 44 (2005) 4739–4745, doi:10.1002/anie.200501254.

[135] V. Percec, M. Glodde, G. Johansson, V.S.K. Balagurusamy, P.A. Heiney, Transformation of a spherical supramolecular dendrimer into a pyramidal columnar supramolecular dendrimer mediated by the fluorophobic effect, Angew. Chem. Int. Ed. 42 (2003) 4338–4342, doi:10.1002/anie.200351804.

[136] V. Percec, B.C. Won, M. Peterca, P.A. Heiney, Expanding the structural diversity of self-assembling dendrons and supramolecular dendrimers via complex building blocks, J. Am. Chem. Soc. 129 (2007) 11265–11278, doi:10.1021/ja073714j.

[137] G. Ungar, V. Percec, M.N. Holerca, G. Johansson, J.A. Heck, Heat-shrinking spherical and columnar supramolecular dendrimers: Their interconversion and dependence of their shape on molecular taper angle, Chem. Eur. J. 6 (2000) 1258–1266, doi:10.1002/(SICI)1521-3765(20000403)6:7(1258::AID- CHEM1258)3.0.CO;2-O.

[138] V. Percec, M.N. Holerca, S. Uchida, W.-D. Cho, G. Ungar, Y. Lee, D.J.P. Yeardley, Exploring and expanding the three-dimensional structural diversity of supramolecular dendrimers with the aid of libraries of alkali metals of their AB 3 minidendritic carboxylates, Chem. Eur. J. 8 (2002) 1106–1117, doi:10.1002/1521-3765(20020301)8:5(1106::AID-CHEM1106)3.0.CO;2-G.

[139] V. Percec, W.-D. Cho, P.E. Mosier, G. Ungar, D.J.P. Yeardley, Structural analysis of cylindrical and spherical supramolecular dendrimers quantifies the concept of monodendron shape control by generation number, J. Am. Chem. Soc. 120 (1998) 11061–11070, doi:10.1021/ja9819007.

[140] V. Percec, W.-D. Cho, M. Möller, S.A. Prokhorova, G. Ungar, D.J.P. Yeardley, Design and structural analysis of the first spherical monodendron self-organizable in a cubic lattice, J. Am. Chem. Soc. 122 (2000) 4249–4250, doi:10.1021/ja9943400.

[141] D.J.P. Yeardley, G. Ungar, V. Percec, M.N. Holerca, G. Johansson, Spherical Supramolecular minidendrimers self-organized in an "inverse micellar"-like thermotropic body-centered cubic liquid crystalline phase, J. Am. Chem. Soc. 122 (2000) 1684–1689, doi:10.1021/ja993915q.

[142] V. Percec, E. Aqad, M. Peterca, J.G. Rudick, L. Lemon, J.C. Ronda, B.B. De, P.A. Heiney, E.W. Meijer, Steric communication of chiral information observed in dendronized polyacetylenes, J. Am. Chem. Soc. 128 (2006) 16365–16372, doi:10.1021/ja0665848.

[143] V. Percec, C.-H. Ahn, T.K. Bera, G. Ungar, D.J.P. Yeardley, Coassembly of a hexagonal columnar liquid crystalline superlattice from polymer(s) coated with a three-cylindrical bundle supramolecular dendrimer, Chem. Eur. J. 5 (1999) 1070–1083, doi:10.1002/(SICI)1521-3765(19990301)5:3(1070::AID-CHEM1070)3.0.CO;2-9.

[144] V. Percec, M.N. Holerca, S.N. Magonov, D.J.P. Yeardley, G. Ungar, H. Duan, S.D. Hudson, Poly(oxazolines)s with tapered minidendritic side groups. The simplest cylindrical models to investigate the formation of two-dimensional and three-dimensional order by direct visualization, Biomacromolecules 2 (2001) 706–728, doi:10.1021/bm015550j.

[145] V. Percec, M.N. Holerca, S. Uchida, D.J.P. Yeardley, G. Ungar, Poly(oxazoline)s with tapered minidendritic side groups as models for the design of synthetic macromolecules with tertiary structure. A demonstration of the limitations of living polymerization in the design of 3-D structures based on single polymer chains, Biomacromolecules 2 (2001) 729–740, doi:10.1021/bm015559l.

[146] V. Percec, M.N. Holerca, Detecting the shape change of complex macromolecules during their synthesis with the aid of kinetics. A new lesson from biology, Biomacromolecules 1 (2000) 6–16, doi:10.1021/bm005507g.

[147] M.N. Holerca, D. Sahoo, M. Peterca, B.E. Partridge, P.A. Heiney, V. Percec, A tetragonal phase self-organized from unimolecular spheres assembled from a substituted poly(2-oxazoline, Macromolecules 50 (2017) 375–385, doi:10.1021/acs.macromol.6b02298.

[148] M.N. Holerca, D. Sahoo, B.E. Partridge, M. Peterca, X. Zeng, G. Ungar, V. Percec, Dendronized poly(2-oxazoline) displays within only five monomer repeat units liquid quasicrystal, A15 and σ Frank–Kasper phases, J. Am. Chem. Soc. 140 (2018) 16941–16947, doi:10.1021/jacs.8b11103.

[149] G. Ungar, Y. Liu, X. Zeng, V. Percec, W.-D. Cho, Giant supramolecular liquid crystal lattice, Science 299 (2003) 1208–1211, doi:10.1126/science.1078849.

[150] M.R. Imam, M. Peterca, U. Edlund, V.S.K. Balagurusamy, V. Percec, Dendronized supramolecular polymers self-assembled from dendritic ionic liquids, J. Polym. Sci. Part A: Polym. Chem. 47 (2009) 4165–4193, doi:10.1002/pola.23523.

[151] V. Percec, W.-D. Cho, G. Ungar, D.J.P. Yeardley, From molecular flat tapers, discs, and cones to supramolecular cylinders and spheres using Fréchet-type monodendrons modified on their periphery, Angew. Chem. Int. Ed. 39 (2000) 1597–1602, doi:10.1002/(SICI)1521-3773(20000502)39:9(1597::AID-ANIE1597)3.0.CO;2-I.

[152] A. Rapp, I. Schnell, D. Sebastiani, S.P. Brown, V. Percec, H.W. Spiess, Supramolecular assembly of dendritic polymers elucidated by 1 H and 13 C solid-state MAS NMR spectroscopy, J. Am. Chem. Soc. 125 (2003) 13284–13297, doi:10.1021/ja035127d.

[153] M. Peterca, M.R. Imam, P. Leowanawat, B.M. Rosen, D.A. Wilson, C.J. Wilson, X. Zeng, G. Ungar, P.A. Heiney, V. Percec, Self-assembly of hybrid dendrons into doubly segregated supramolecular polyhedral columns and vesicles, J. Am. Chem. Soc. 132 (2010) 11288–11305, doi:10.1021/ja104432d.

[154] V. Percec, M. Peterca, Y. Tsuda, B.M. Rosen, S. Uchida, M.R. Imam, G. Ungar, P.A. Heiney, Elucidating the structure of the Pm3n cubic phase of supramolecular dendrimers through the modification of their aliphatic to aromatic volume ratio, Chem. Eur. J. 15 (2009) 8994–9004, doi:10.1002/chem.200901324.

[155] G. Ungar, V. Percec, X. Zeng, P. Leowanawat, Liquid quasicrystals, Isr. J. Chem. 51 (2011) 1206–1215, doi:10.1002/ijch.201100151.

[156] V. Percec, M.R. Imam, M. Peterca, W.-D. Cho, P.A. Heiney, Self-assembling dendronized dendrimers, Isr. J. Chem. 49 (2009) 55–70, doi:10.1560/IJC.49.1.55.

[157] V. Percec, S.D. Hudson, M. Peterca, P. Leowanawat, E. Aqad, R. Graf, H.W. Spiess, X. Zeng, G. Ungar, P.A. Heiney, Self-repairing complex helical columns generated via kinetically controlled self-assembly of dendronized perylene bisimides, J. Am. Chem. Soc. 133 (2011) 18479–18494, doi:10.1021/ja208501d.

[158] V. Percec, S. Wang, N. Huang, B.E. Partridge, X. Wang, D. Sahoo, D.J. Hoffman, J. Malineni, M. Peterca, R.L. Jezorek, N. Zhang, H. Daud, P.D. Sung, E.R. McClure, S.L. Song, An accelerated modular-orthogonal Ni-catalyzed methodology to symmetric and nonsymmetric constitutional isomeric AB 2 to AB 9 dendrons exhibiting unprecedented self-organizing principles, J. Am. Chem. Soc. 143 (2021) 17724–17743, doi:10.1021/jacs.1c08502.

[159] V. Percec, M.R. Imam, M. Peterca, D.A. Wilson, P.A. Heiney, Self-assembly of dendritic crowns into chiral supramolecular spheres, J. Am. Chem. Soc. 131 (2009) 1294–1304, doi:10.1021/ja8087778.

[160] V. Percec, M.R. Imam, M. Peterca, D.A. Wilson, R. Graf, H.W. Spiess, V.S.K. Balagurusamy, P.A. Heiney, Self-assembly of dendronized triphenylenes into helical pyramidal columns and chiral spheres, J. Am. Chem. Soc. 131 (2009) 7662–7677, doi:10.1021/ja8094944.

[161] V. Percec, M. Glodde, T.K. Bera, Y. Miura, I. Shiyanovskaya, K.D. Singer, V.S.K. Balagurusamy, P.A. Heiney, I. Schnell, A. Rapp, H.-W. Spiess, S.D. Hudson, H. Duan, Self-organization of supramolecular helical dendrimers into complex electronic materials, Nature 419 (2002) 384–387, doi:10.1038/nature01072.

[162] V. Percec, A.E. Dulcey, M. Peterca, M. Ilies, S. Nummelin, M.J. Sienkowska, P.A. Heiney, Principles of self-assembly of helical pores from dendritic dipeptides, Proc. Natl. Acad. Sci. U.S.A. 103 (2006) 2518–2523, doi:10.1073/pnas.0509676103.

[163] M.S. Kaucher, M. Peterca, A.E. Dulcey, A.J. Kim, S.A. Vinogradov, D.A. Hammer, P.A. Heiney, V. Percec, Selective transport of water mediated by porous dendritic dipeptides, J. Am. Chem. Soc. 129 (2007) 11698–11699, doi:10.1021/ja076066c.

[164] V. Percec, A.E. Dulcey, M. Peterca, P. Adelman, R. Samant, V.S.K. Balagurusamy, P.A. Heiney, Helical pores self-assembled from homochiral dendritic dipeptides based on L-Tyr and nonpolar alpha-amino acids, J. Am. Chem. Soc. 129 (2007) 5992–6002, doi:10.1021/ja071088k.

[165] V. Percec, J. Smidrkal, M. Peterca, C.M. Mitchell, S. Nummelin, A.E. Dulcey, M.J. Sienkowska, P.A. Heiney, Self-assembly of hybrid dendrons with complex primary structure into functional helical pores, Chem. A Eur. J. 13 (2007) 3989–4007, doi:10.1002/chem.200601582.

[166] M. Peterca, V. Percec, A.E. Dulcey, S. Nummelin, S. Korey, M. Ilies, P.A. Heiney, Self-assembly, structural, and retrostructural analysis of dendritic dipeptide pores undergoing reversible circular to elliptical shape change, J. Am. Chem. Soc. 128 (2006) 6713–6720, doi:10.1021/ja0611902.

[167] B.M. Rosen, M. Peterca, K. Morimitsu, A.E. Dulcey, P. Leowanawat, A.-M. Resmerita, M.R. Imam, V. Percec, Programming the supramolecular helical polymerization of dendritic dipeptides via the stereochemical information of the dipeptide, J. Am. Chem. Soc. 133 (2011) 5135–5151, doi:10.1021/ja200280h.

[168] V. Percec, M. Peterca, A.E. Dulcey, M.R. Imam, S.D. Hudson, S. Nummelin, P. Adelman, P.A. Heiney, Hollow spherical supramolecular dendrimers, J. Am. Chem. Soc. 130 (2008) 13079–13094, doi:10.1021/ja8034703.

[169] V. Percec, A.E. Dulcey, M. Peterca, M. Ilies, J. Ladislaw, B.M. Rosen, U. Edlund, P.A. Heiney, The internal structure of helical pores self-assembled from dendritic dipeptides is stereochemically programmed and allosterically regulated, Angew. Chem. Int. Ed. 44 (2005) 6516–6521, doi:10.1002/anie.200501331.

[170] V. Percec, A. Dulcey, M. Peterca, M. Ilies, Y. Miura, U. Edlund, P.A. Heiney, V. Percec, A. Dulcey, M. Peterca, M. Ilies, Y. Miura, U. Edlund, P.A. Heiney, Helical porous protein mimics self-assembled from amphiphilic dendritic dipeptides, Aust. J. Chem. 58 (2005) 472–482, doi:10.1071/CH05092.

[171] V. Percec, J.G. Rudick, M. Peterca, P.A. Heiney, Nanomechanical function from self-organizable dendronized helical polyphenylacetylenes, J. Am. Chem. Soc. 130 (2008) 7503–7508, doi:10.1021/ja801863e.

[172] V. Percec, M.R. Imam, M. Peterca, P. Leowanawat, Self-organizable vesicular columns assembled from polymers dendronized with semifluorinated Janus dendrimers act as reverse thermal actuators, J. Am. Chem. Soc. 134 (2012) 4408–4420, doi:10.1021/ja2118267.

[173] K.A. Andreopoulou, M. Peterca, D.A. Wilson, B.E. Partridge, P.A. Heiney, V. Percec, Demonstrating the 8_1-helicity and nanomechanical function of self-organizable dendronized polymethacrylates and polyacrylates, macromolecules 50 (2017) 5271–5284, doi:10.1021/acs.macromol.7b01216.

[174] V. Percec, C.-H. Ahn, G. Ungar, D.J.P. Yeardley, M. Möller, S.S. Sheiko, Controlling polymer shape through the self-assembly of dendritic side-groups, Nature 391 (1998) 161–164, doi:10.1038/34384.

[175] V. Percec, C.-H. Ahn, W.-D. Cho, A.M. Jamieson, J. Kim, T. Leman, M. Schmidt, M. Gerle, M Möller, S.A. Prokhorova, S.S. Sheiko, S.Z.D. Cheng, A. Zhang, G. Ungar, D.J.P. Yeardley, Visualizable cylindrical macromolecules with controlled stiffness from backbones containing libraries of self-assembling dendritic side groups, J. Am. Chem. Soc. 120 (1998) 8619–8631, doi:10.1021/ja981211v.

[176] M.N. Holerca, M. Peterca, B.E. Partridge, Q. Xiao, G. Lligadas, M.J. Monteiro, V. Percec, Monodisperse macromolecules by self-interrupted living polymerization, J. Am. Chem. Soc. 142 (2020) 15265–15270, doi:10.1021/jacs.0c07912.

[177] C. Roche, H.-J. Sun, M.E. Prendergast, P. Leowanawat, B.E. Partridge, P.A. Heiney, F. Araoka, R. Graf, H.W. Spiess, X. Zeng, G. Ungar, V. Percec, Homochiral columns constructed by chiral self-sorting during supramolecular helical organization of hat-shaped molecules, J. Am. Chem. Soc. 136 (2014) 7169–7185, doi:10.1021/ja5035107.

[178] C. Roche, H.-J. Sun, P. Leowanawat, F. Araoka, B.E. Partridge, M. Peterca, D.A. Wilson, M.E. Prendergast, P.A. Heiney, R. Graf, H.W. Spiess, X. Zeng, G. Ungar, V. Percec, A supramolecular helix that disregards chirality, Nat. Chem. 8 (2016) 80–89, doi:10.1038/nchem.2397.

[179] B.E. Partridge, L. Wang, D. Sahoo, J.T. Olsen, P. Leowanawat, C. Roche, H. Ferreira, K.J. Reilly, X. Zeng, G. Ungar, P.A. Heiney, R. Graf, H.W. Spiess, V. Percec, Sequence-defined dendrons dictate supramolecular cogwheel assembly of dendronized perylene bisimides, J. Am. Chem. Soc. 141 (2019) 15761–15766, doi:10.1021/jacs.9b08714.

[180] L. Wang, B.E. Partridge, N. Huang, J.T. Olsen, D. Sahoo, X. Zeng, G. Ungar, R. Graf, H.W. Spiess, V. Percec, Extraordinary acceleration of cogwheel helical self-organization of dendronized perylene bisimides by the dendron sequence encoding their tertiary structure, J. Am. Chem. Soc. 142 (2020) 9525–9536, doi:10.1021/jacs.0c03353.

[181] V. Percec, M. Lee, Molecular engineering of liquid crystal polymers by living polymerization. XXIII. Synthesis and characterization of AB block copolymers based on ω-[(4-cyano-4 -biphenyl)-oxy]alkyl vinyl ether, 1H, 1H, 2H, 2H-perfluorodecyl vinyl ether, and 2-(4-biphenyloxy)ethyl vinyl ether with 1H, 1H, 2H, 2H-perfluorodecyl vinyl ether, J. Macromol. Sci., Part A. Pure Appl. Chem. 29 (1992) 723–740, doi:10.1080/10601329208054112.

[182] V. Percec, G. Johansson, G. Ungar, J. Zhou, Fluorophobic effect induces the self-assembly of semifluorinated tapered monodendrons containing crown ethers into supramolecular columnar dendrimers which exhibit a homeotropic hexagonal columnar liquid crystalline phase, J. Am. Chem. Soc. 118 (1996) 9855–9866, doi:10.1021/ja9615738.

[183] V. Percec, M. Glodde, M. Peterca, A. Rapp, I. Schnell, H.W. Spiess, T.K. Bera, Y. Miura, V.S.K. Balagurusamy, E. Aqad, P.A. Heiney, Self-assembly of semifluorinated dendrons attached to electron-donor groups mediates their π-stacking via a helical pyramidal column, Chem. Eur. J. 12 (2006) 6298–6314, doi:10.1002/chem.200501195.

[184] G. Johansson, V. Percec, G. Ungar, J.P. Zhou, Fluorophobic effect in the self-assembly of polymers and model compounds containing tapered groups into supramolecular columns, Macromolecules 29 (1996) 646–660, doi:10.1021/ma9511558.

[185] D.R. Dukeson, G. Ungar, V.S.K. Balagurusamy, V. Percec, G.A. Johansson, M. Glodde, Application of isomorphous replacement in the structure determination of a cubic liquid crystal phase and location of counterions, J. Am. Chem. Soc. 125 (2003) 15974–15980, doi:10.1021/ja037380j.

[186] V. Percec, D. Tomazos, A.E. Feiring, Semifluorinated polymers: 1. Synthesis and characterization of side chain liquid crystalline polymers containing semifluorinated oligooxyethylene based flexible spacers, Polymer 32 (1991) 1897–1908, doi:10.1016/0032-3861(91)90382-S.

[187] G. Johansson, V. Percec, G. Ungar, K. Smith, Fluorophobic effect generates a systematic approach to the synthesis of the simplest class of rodlike liquid crystals containing a single benzene unit, Chem. Mater. 9 (1997) 164–175, doi:10.1021/cm960267q.

[188] V. Percec, E. Aqad, M. Peterca, M.R. Imam, M. Glodde, T.K. Bera, Y. Miura, V.S.K. Balagurusamy, P.C. Ewbank, F. Würthner, P.A. Heiney, Self-assembly of semifluorinated minidendrons attached to electron-acceptor groups into pyramidal columns, Chem. Eur. J. 13 (2007) 3330–3345, doi:10.1002/chem.200600901.

[189] I. Shiyanovskaya, K.D. Singer, V. Percec, T.K. Bera, Y. Miura, M. Glodde, Charge transport in hexagonal columnar liquid crystals self-organized from supramolecular cylinders based on acene-functionalized dendrons, Phys. Rev. B. 67 (2003) 035204, doi:10.1103/PhysRevB.67.035204.

[190] D.L. Caspar, A. Klug, Physical principles in the construction of regular viruses, Cold spring Harb. Symp. Quant. Biol. 27 (1962) 1–24, doi:10.1101/SQB.1962.027.001.005.

[191] D.L. Caspar, Movement and self-control in protein assemblies. Quasi-equivalence revisited, Biophys. J. 32 (1980) 103–138, doi:10.1016/S0006-3495(80)84929-0.

[192] W. Jentzen, J.G. Ma, J.A. Shelnutt, Conservation of the conformation of the porphyrin macrocycle in hemoproteins, Biophys. J. 74 (1998) 753–763, doi:10.1016/S0006-3495(98)74000-7.

[193] M. Peterca, M.R. Imam, S.D. Hudson, B.E. Partridge, D. Sahoo, P.A. Heiney, M.L. Klein, V. Percec, Complex arrangement of orthogonal nanoscale columns *via* a supramolecular orientational memory effect, ACS Nano 10 (2016) 10480–10488, doi:10.1021/acsnano.6b06419.

[194] V. Percec, J.G. Rudick, M. Peterca, M. Wagner, M. Obata, C.M. Mitchell, W.-D. Cho, V.S.K. Balagurusamy, P.A. Heiney, Thermoreversible cis−cisoidal to cis−transoidal isomerization of helical dendronized polyphenylacetylenes, J. Am. Chem. Soc. 127 (2005) 15257–15264, doi:10.1021/ja055406w.

[195] J.G. Rudick, V. Percec, Helical chirality in dendronized polyarylacetylenes, New J. Chem. 31 (2007) 1083–1096, doi:10.1039/B616449H.

[196] V. Percec, J.G. Rudick, E. Aqad, Diminished helical character in para-substituted cis-transoidal polyphenylacetylenes due to intramolecular cyclization, Macromolecules 38 (17) (2005) 7205–7206, doi:10.1021/ma051536d.

[197] V. Percec, J.G. Rudick, Independent electrocyclization and oxidative chain cleavage along the backbone of cis-poly(phenylacetylene), Macromolecules 38 (17) (2005) 7241–7250, doi:10.1021/ma051060y.

[198] V. Percec, J.G. Rudick, Nanomechanical Function Made Possible by suppressing structural transformations of polyarylacetylenes, J. Polym. Sci., Part A-1: Polym. Chem 209 (2008) 1759–1768, doi:10.1002/macp.200800271Ci.

[199] V. Percec, J.G. Rudick, P. Nombel, W. Buchowicz, Dramatic decrease of the cis content and molecular weight of cis-transoidal polyphenylacetylene at 23°C in solutions prepared in air, J. Polym. Sci., Part A-1: Polym. Chem 40 (2002) 3212–3220, doi:10.1002/pola.10421.

[200] M.R. Imam, M. Peterca, Q. Xiao, V. Percec, Enhancing conformational flexibility of dendronized triphenylene via diethylene glycol linkers lowers transitions of helical columnar, Frank-Kasper, and quasicrystal phases, Giant 10 (2022) 100098, doi:10.1016/j.giant.2022.100098.

[201] V. Percec, A.E. Dulcey, V.S.K. Balagurusamy, Y. Miura, J. Smidrkal, M. Peterca, S. Nummelin, U. Edlund, S.D. Hudson, P.A. Heiney, H. Duan, S.N. Magonov, S.A. Vinogradov, Self-assembly of dendritic dipeptides into helical pores, Nature 430 (2004) 764–768, doi:10.1038/nature02770.

[202] L. Pasteur, Memoires sur la relation qui peut exister entre la forme crystalline et al composition chimique, et sur la cause de la polarization rotatoire, C. R. Acad. Sci. 26 (1848) 535–538.

[203] V. Percec, M. Peterca, T. Tadjiev, X. Zeng, G. Ungar, P. Leowanawat, E. Aqad, M.R. Imam, B.M. Rosen, U. Akbey, R. Graf, S. Sekharan, D. Sebastiani, H.W. Spiess, P.A. Heiney, Steven D. Hudson, Self-assembly of dendronized perylene bisimides into complex helical columns, J. Am. Chem. Soc. 133 (2011) 12197–12219, doi:10.1021/ja204366b.

[204] V. Percec, H.-J. Sun, P. Leowanawat, M. Peterca, R. Graf, H.W. Spiess, X. Zeng, G. Ungar, P.A. Heiney, Transformation from kinetically into thermodynamically controlled self-organization of complex helical columns with 3D periodicity assembled from dendronized perylene bisimides, J. Am. Chem. Soc. 135 (2013) 4129–4148, doi:10.1021/ja400639q.

[205] D. Sahoo, M. Peterca, E. Aqad, B.E. Partridge, P.A. Heiney, R. Graf, H.W. Spiess, X. Zeng, V. Percec, Hierarchical self-organization of perylene bisimides into supramolecular spheres and periodic arrays thereof, J. Am. Chem. Soc. 138 (44) (2016) 14798–14807, doi:10.1021/jacs.6b09986.

[206] B.E. Partridge, P. Leowanawat, E. Aqad, M.R. Imam, H.-J. Sun, M. Peterca, P.A. Heiney, R. Graf, H.W. Spiess, X. Zeng, G. Ungar, V. Percec, Increasing 3D supramolecular order by decreasing molecular order. a comparative study of helical assemblies of dendronized nonchlorinated and tetrachlorinated perylene bisimides, J. Am. Chem. Soc. 137 (15) (2015) 5210–5224, doi:10.1021/jacs.5b02147.

[207] Y.-C. Wu, P. Leowanawat, H.-J. Sun, B.E. Partridge, M. Peterca, R. Graf, H.W. Spiess, X. Zeng, G. Ungar, C.-S. Hsu, P.A. Heiney, V. Percec, Complex columnar hexagonal polymorphism in supramolecular assemblies of a semifluorinated electron-accepting naphthalene bisimide, J. Am. Chem. Soc. 137 (2015) 807–819, doi:10.1021/ja510643b.

[208] B.E. Partridge, L. Wang, D. Sahoo, J.T. Olsen, P. Leowanawat, C. Roche, H. Ferreira, K.J. Reilly, X. Zeng, G. Ungar, P.A. Heiney, R. Graf, H.W. Spiess, V. Percec, Sequence-defined dendrons dictate supramolecular cogwheel assembly of dendronized perylene bisimides, J. Am. Chem. Soc. 141 (40) (2019) 15761–15766, doi:10.1021/jacs.9b08714.

[209] D. Sahoo, M. Peterca, E. Aqad, B.E. Partridge, M.L. Klein, V. Percec, Losing supramolecular orientational memory via self-organization of a misfolded secondary structure, Polym. Chem. 9 (2018) 2370–2381, doi:10.1039/C8PY00187A.

[210] M.-S. Ho, B.E. Partridge, H.-J. Sun, D. Sahoo, P. Leowanawat, M. Peterca, R. Graf, H.W. Spiess, X. Zeng, G. Ungar, P.A. Heiney, C.-S. Hsu, V. Percec, Screening libraries of semifluorinated arylene bisimides to discover and predict thermodynamically controlled helical crystallization, ACS Comb. Sci. 18 (12) (2016) 723–739, doi:10.1021/acscombsci.6b00143.

[211] S. Guerra, J. Iehl, M. Holler, M. Peterca, D.A. Wilson, B.E. Partridge, S. Zhang, R. Deschenaux, J.-F. Nierengarten, V. Percec, Self-organisation of dodeca-dendronized fullerene into supramolecular discs and helical columns containing a nanowire-like core, Chem. Sci. 6 (2015) 3393–3401, doi:10.1039/C5SC00449G.

[212] D. Sahoo, M. Peterca, Emad Aqad, B.E. Partridge, P.A. Heiney, R. Graf, H.W. Spiess, X. Zeng, V. Percec, Tetrahedral arrangements of perylene bisimide columns via supramolecular orientational memory, ACS Nano 11 (2017) 983–991, doi:10.1021/acsnano.6b07599.

[213] N. Huang, M.R. Imam, M.J. Sienkowskaa, M. Peterca, M.N. Holerca, D.A. Wilson, B.M. Rosen, B.E. Partridge, Q. Xiao, V. Percec, Supramolecular spheres assembled from covalent and supramolecular dendritic crowns dictate the supramolecular orientational memory effect mediated by Frank–Kasper phases, Giant 1 (2020) 100001, doi:10.1016/j.giant.2020.100001.

[214] N. Huang, Q. Xiao, M.Peterca Icon, X. Zeng, V. Percec, Self-organisation of rhombitruncated cuboctahedral hexagonal columns from an amphiphilic Janus dendrimer, Mol. Phys. 119 (2021) e1902586, doi:10.1080/00268976.2021.1902586.

[215] V. Percec, N. Huang, Q. Xiao, B.E. Partridge, D. Sahoo, M.R. Imam, M. Peterca, R. Graf, H.-W. Spiess, X. Zeng, G. Ungar, Self-organization of rectangular bipyramidal helical columns by supramolecular orientational memory epitaxially nucleated from a Frank-Kasper σ phase, Giant 9 (2022) 100084, doi:10.1016/j.giant.2021.100084.

[216] H. Delacroix, T. Gulik-Krzywicki, P. Mariani, V. Luzzati, Freeze-fracture electron microscope study of lipid systems: the cubic phase of space group Pm3n, J. Mol. Biol. 229 (1993) 526–539, doi:10.1006/jmbi.1993.1052.

[217] M. Peterca, V. Percec, Recasting metal alloy phases with block copolymers, Science 330 (2010) 333–334, doi:10.1126/science.1196698.

[218] K. Yuea, M. Huanga, R.L. Marsonb, J. Hec, J. Huanga, Z. Zhoua, J. Wanga, C. Liua, X. Yanc, K. Wua, Z. Guod, H. Liua, W. Zhanga, P. Nic, C. Wesdemiotisa, W.-B. Zhange, S.C. Glotzerb, S.Z.D. Cheng, Geometry induced sequence of nanoscale Frank–Kasper and quasicrystal mesophases in giant surfactants, Proc. Natl. Acad. Sci. U.S.A. 113 (2016) 14195–14200, doi:10.1073/pnas.1609422113.

[219] V. Percec, Molecular design of novel liquid crystalline polymers with complex architecture: Macrocyclics and dendrimers, Pure Appl. Chem. (67) (1995) 2031–2038, doi:10.1351/pac199567122031.

[220] J.F. Li, V. Percec, C. Rosenblatt, O. Lavrentovich, Biaxiality in a cyclic thermotropic nematic liquid crystal, Europhys. Lett. 25 (1994) 199–204, doi:10.1209/0295-5075/25/3/008.

[221] Zhang N, S.R. Samanta, B.M. Rosen, V. Percec, Single electron transfer in radical ion and radical mediated organic, materials and polymer synthesis, Chem. Rev. 114 (2014) 5848–5958, doi:10.1021/cr400689s.

[222] M. Peterca, D. Sahoo, M.R. Imam, Q. Xiao, V. Percec, Searching for the simplest self-assembling dendron to study helical self-organization and supramolecular polymerization, Giant 12 (2022) 100118, doi:10.1016/j.giant.2022.100118.

[223] B.M. Rosen, G. Lligadas, C. Hahn, V. Percec, Synthesis of dendrimers through divergent iterative thio-bromo "Click" chemistry, J. Polym. Sci. 15 (2009) 3931–3939, doi:10.1002/pola.23519.

[224] B.M. Rosen, G. Lligadas, C. Hahn, V. Percec, Synthesis of dendritic macromolecules through divergent iterative thio-bromo "Click" chemistry and SET-LRP, J. Polym. Sci. 15 (2009) 3940–3948, doi:10.1002/pola.23518.

[225] B.M. Rosen, C. Huang, V. Percec, Sequential Ni-catalyzed borylation and cross-coupling of aryl halides via in situ prepared neopentylglycolborane, Org. Lett. 10 (2008) 2597–2600, doi:10.1021/ol800832n.

[226] R.L. Jezorek, N. Zhang, P. Leowanawat, M.H. Bunner, N. Gutsche, A.K.R. Pesti, J.T. Olsen, V. Percec, Air-stable nickel precatalysts for fast and quantitative cross-coupling of aryl sulfamates with aryl neopentylglycolboronates at room temperature, Org. Lett. 16 (2014) 6326–6329, doi:10.1021/ol503061c.

[227] D.A. Wilson, C.J. Wilson, C. Moldoveanu, A.-M. Resmerita, P. Corcoran, L.M. Hoang, B.M. Rosen, V. Percec, Neopentylglycolborylation of aryl mesylates and tosylates catalyzed by Ni-based mixed-ligand systems activated with Zn, J. Am. Chem. Soc. 132 (2010) 1800–1801, doi:10.1021/ja910808x.

[228] X. Jiang, B.M. Rosen, V. Percec, Mimicking "nascent" Cu(0) mediated SET-LRP of methyl acrylate in DMSO leads to complete conversion in several minutes, J. Polym. Sci., Part A: Polym. Chem. 48 (2010) 403–409, doi:10.1002/pola.23797.

[229] S. Zhang, H.-J. Sun, A.D. Hughes, R.-O. Moussodia, A. Bertin, Y. Chen, D.J. Pochan, P.A. Heiney, M.L. Klein, V. Percec, Self-assembly of amphiphilic Janus dendrimers into uniform onion-like dendrimersomes with predictable size and number of bilayers, Proc. Natl. Acad. Sci. U.S.A. 111 (2014) 9058–9063, doi:10.1073/pnas.1402858111.

[230] A. Joseph, A.M. Wagner, M. Garay-Sarmiento, M. Aleksanyan, T. Haraszti, D. Söder, V.N. Georgiev, R. Dimova, V. Percec, C. Rodriguez-Emmenegger, Zwitterionic dendrimersomes: a closer xenobiotic mimic of cell membranes, Adv. Mater. (2022) 2206288, doi:10.1002/adma.202206288.

[231] V. Percec, G. Johansson, D. Schlueter, J.C. Ronda, G. Ungar, Molecular recognition directed self-assembly of tubular supramolecular architectures from building blocks containing monodendrons as exoreceptors and crown- or pseudo-crown-ethers as endo-receptors, Macromol. Symp. 101 (1996) 43–60, doi:10.1002/masy.19961010107.

[232] A. Moreno, J.C. Ronda, V. Cádiz, M. Galià, G. Lligadas, V. Percec, SET-LRP from programmed difunctional initiators encoded with double single-cleavage and double dual-cleavage groups, Biomacromolecules 20 (2019) 3200–3210, doi:10.1021/acs.biomac.9b00892.

[233] D.S. Maurya, A. Malik, X. Feng, N. Bensabeh, G. Lligadas, V. Percec, Me6-TREN/TREN mixed-ligand effect during SET-LRP in the catalytically active DMSO revitalizes TREN into an excellent ligand, Biomacromolecules 21 (2020) 1902–1919, doi:10.1021/acs.biomac.9b01765.

[234] V. Percec, P. Leowanawat, H.-J. Sun, O. Kulikov, C.D. Nusbaum, T.M. Tran, A. Bertin, D.A. Wilson, M. Peterca, S. Zhang, N.P. Kamat, K. Vargo, D. Moock, E.D. Johnston, D.A. Hammer, D.J. Pochan, Y. Chen, Y.M. Chabre, T.C. Shiao, M. Bergeron-Brlek, S. André, R. Roy, H.-J. Gabius, P.A. Heiney, Modular Synthesis of Amphiphilic Janus Glycodendrimers and Their Self-Assembly into Glycodendrimersomes and Other Complex Architectures with Bioactivity to Biomedically Relevant Lectins, J. Am. Chem. Soc. 135 (2013) 9055–9077, doi:10.1021/ja403323y.

[235] B.M. Rosen, K.W. Quasdorf, D.A. Wilson, N. Zhang, A.-M. Resmerita, N.K. Garg, V. Percec, Nickel-Catalyzed Cross-Couplings Involving Carbon−Oxygen Bonds, Chem. Rev. 111 (2011) 1346–1416, doi:10.1021/cr100259t.

[236] S.E. Sherman, Q. Xiao, V. Percec, Mimicking Complex Biological Membranes and Their Programmable Glycan Ligands with Dendrimersomes and Glycodendrimersomes, Chem. Rev. 117 (2017) 6538–6631, doi:10.1021/acs.chemrev.7b00097.