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Communication

Designing Highly Ordered Helical and Nonhelical Porous Crystalline and Disordered Nonhelical Columnar Liquid Crystalline Self-Organizations

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ABSTRACT: Helical self-organizations are equilibrium structures responsible for the assembly of nonequilibrium and equilibrium living and synthetic systems. Racemic helical columnar systems transform into one-handed systems with the help of enantiomerically rich or pure components. Racemic, enantiomerically rich, and enantiomerically pure helical periodic arrays of columns are analyzed by oriented fiber X-ray diffraction (XRD). With few exceptions, highly ordered helical 3-D organizations as generated from homochiral columns cannot be obtained from achiral, racemic, or enantiomerically rich helical columns. Here, we report an unprecedented class of nonhelical porous ordered, disordered nonhelical columnar liquid crystalline (LC) self-organizations and columnar liquids constructed from AB_4 to AB_9 isomeric terphenyls by molecular design unwinding of a 3-D helical organization. A library of 16 nonhelical porous ordered, disordered columnar and four liquids was designed by employing as a model a closely related achiral AB_4 *meta*-terphenyl, which self-organizes one of the most perfect synthetic ordered columnar hexagonal helices known. A general molecular mechanism to unwind highly ordered 3-D helices into nonhelical porous columnar ordered LCs and liquids was elaborated to design this transformation, which provided unprecedented nonequilibrium synthetic systems. This methodology is expected to be general for transformation of helical macromolecular and supramolecular organizations into nonhelical crystals, LCs, and liquids.

The α-helix of the peptides advanced by Pauling et al.[1] and demonstrated by Crick et al.[2] and Perutz,[3] the incorrect triple helix of DNA,[4] the double helix of DNA,[4,5] and the helical viruses[6] are the main scientific events that pioneered the field of helical self-organizations in biological systems. These successes were accompanied by similarly spectacular failures in some of the most renown laboratories.[4,7] They also led to historical statements like the one of Sir Lawrence Bragg, "*the greatest failure of my scientific carrier*," when he, together with future Nobel laureates Kendrew and Perutz, misinterpreted the α-helix of peptides,[6a,7,8] and "*among the most beautiful X-way photographs ever taken*" of J. D. Bernal when referring to the "*photo 51*" of Rosalind Franklin.[6a] These successes and failures contributed equally to the development of biological and synthetic helical self-organizations.[6b,8,9] The helical peptides forming fibrous but also globular proteins[1a,b] and the double helix of DNA are equilibrium structures[1c] that are key components of the nonequilibrium self-organized living matter.[10] Brief discussions on the development of helical macromolecules[8,9a,11] and of helical supramolecular assemblies are available and, with the exception of several publications on highly ordered helical self-organizations including some obtained by deracemization in bulk state,[12] will not be repeated here. Substantial progress has been made on the design of helical macromolecules and of columnar and spherical helical self-organizations.[12] However, to our knowledge, no rational approach to the design and synthesis of nonhelical columnar nonequilibrium assemblies, including three-dimensional (3-D), crystalline, liquid crystalline (LC), and liquid by molecular design unwinding of a columnar helix into a nonhelical column, is known. Here, we report an unprecedented class of 3-D-ordered nonhelical porous, nonhelical columnar LC, and even columnar liquid self-organizations constructed from AB_4 to AB_9 dendrons. Nineteen of them are constitutional isomers, which due to their molecular design unwinding cannot be switched back into equilibrium helical self-organizations. This unwinding process is reversible only by synthesis. A closely related achiral AB_4 *meta*-terphenyl dendron, which self-organizes into one of the most perfect synthetic helical columns and periodic arrays known,[12d] was used as a model to elaborate the principles employed to design a library containing one 3-D-ordered nonhelical porous columnar, 15 nonhelical columnar LC, and four columnar liquid self-organizations. We will start this discussion with the design of the achiral AB_4 dendron V_d (Figure 1a−e). Its synthesis and helical self-organization were reported,[12d] but its mechanism of self-organization and design principles were not yet established in the previous publication, and therefore, they will be reported here. The apex of V_d is based on an AB_4 *meta*-terphenyl phenolic acid, which because of its sp^2−sp^2 bonds, exhibits a rigid taper angle of about

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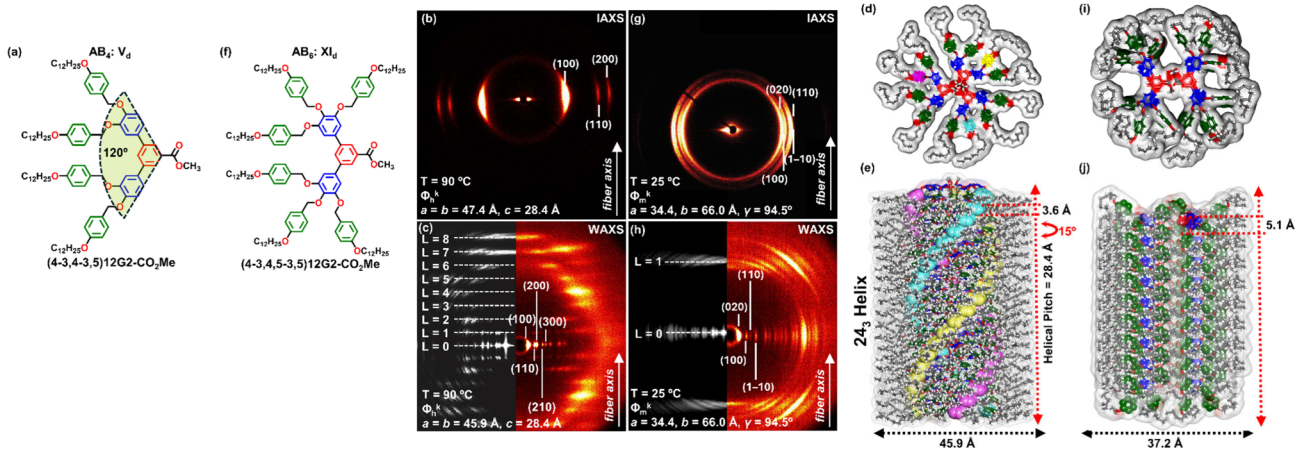

Figure 1. Molecular structures, oriented-fiber IAXS and WAXS, and supramolecular organizations of V_d (a–e) and XI_d (f–j); (d,i,j) show transparent potential surfaces of the supramolecular columns.

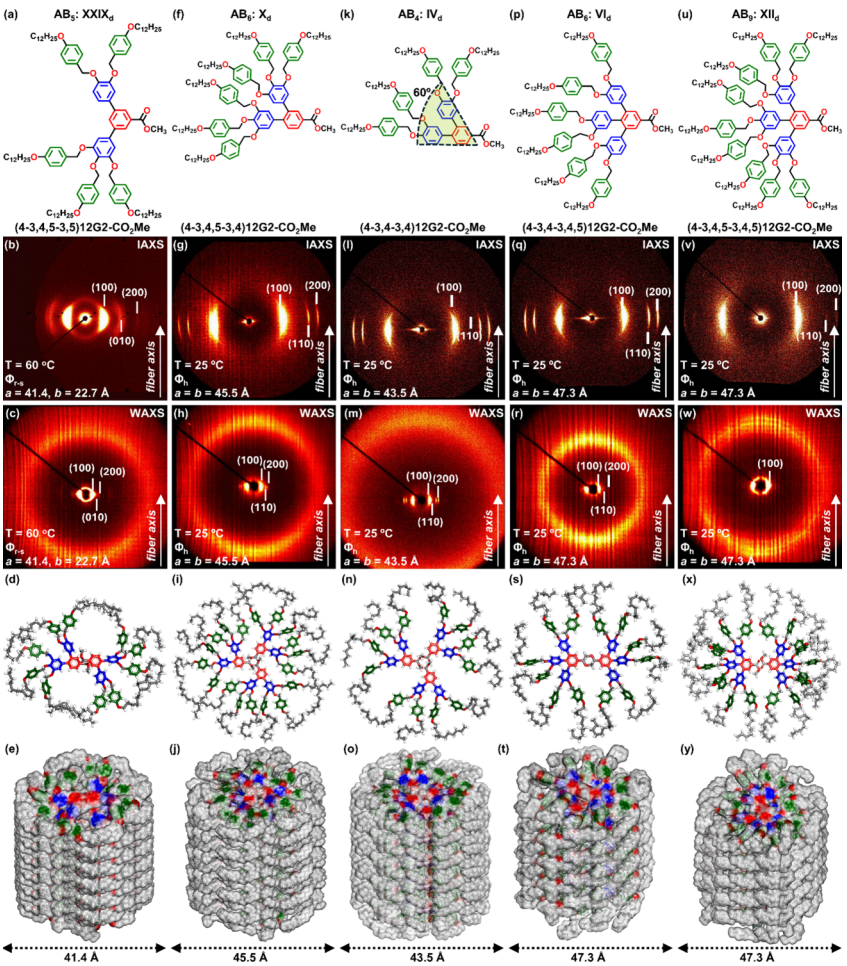

Figure 2. Molecular structures, oriented-fiber IAXS and WAXS, and supramolecular LC organizations of $XXIX_d$ (a–e), X_d (f–j), IV_d (k–o), VI_d (p–t), and XII_d (u–y); potential surface images of tilted supramolecular nonhelical disordered columns are shown in (e,j,o,t,y).

120°[12d,13] even after the substitution of its phenols with 4-*n*-dodecyloxobenzyloxy groups. Therefore, three V_d atoms form the cross-section of its supramolecular column. This cross-section resembles a crown or hat conformation that allows free rotation around column axis to impart the mechanism required to fill the space through helical self-organization. This generates a 24_3 triple helix (Figure 1e), which self-organizes a columnar, hexagonal, 3-D-ordered, crystalline (Φ_h^k) lattice (Figure 1b,c, Figure S1, and Table S1).[12n]

Reconstruction of the oriented fiber intermediary-angle (IAXS) and wide-angle X-ray scattering (WAXS) data by conventional methodologies used in our laboratory[14] provides diffractograms that agree with the experimental results shown on the left side of Figure 1c and Figure S2. Incorporation of an additional *n*-dodecyloxybenzyloxy group in V_d generates XI_d

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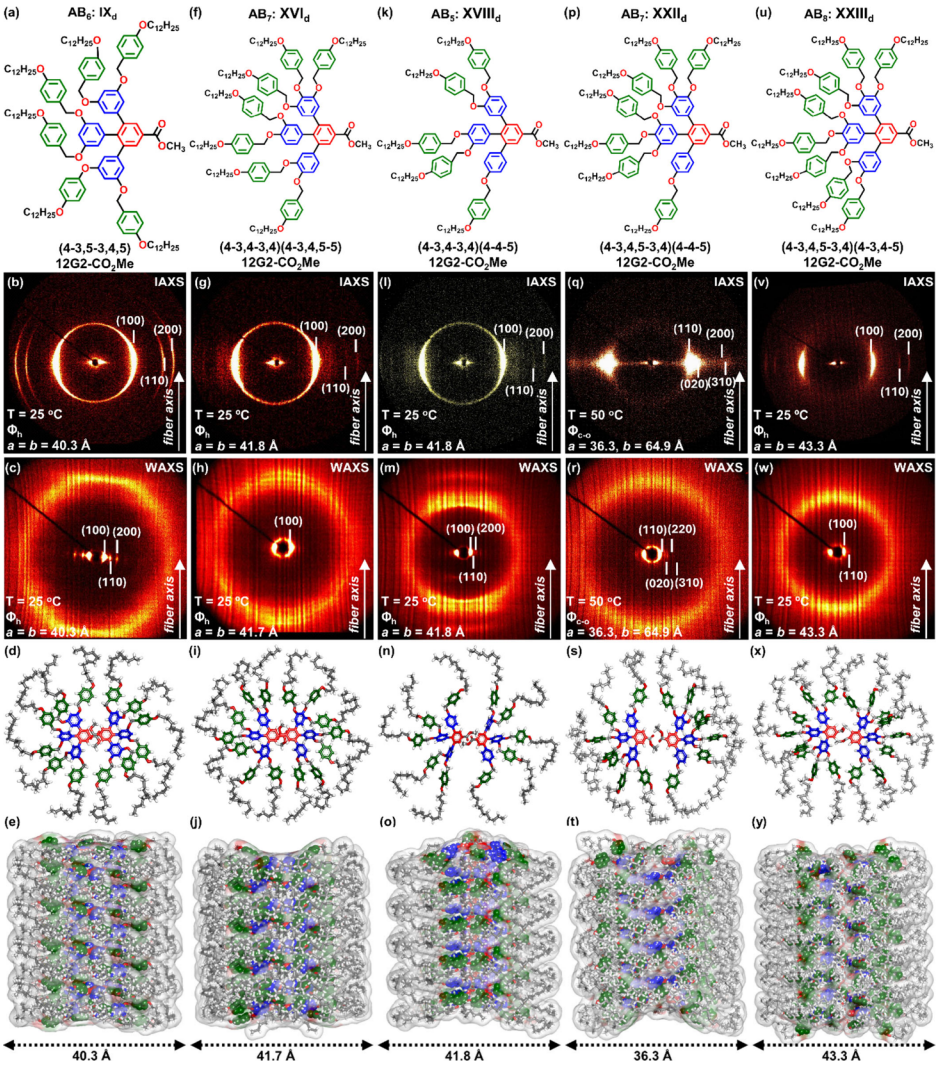

Figure 3. Molecular structures, oriented-fiber IAXS and WAXS, and supramolecular LC organizations of IX_d (a–e), XVI_d (f–j), $XVIII_d$ (k–o), XXI_d (p–t), and $XXIII_d$ (u–y); transparent potential surface images of supramolecular nonhelical disordered columns are shown in e,j,o,t,y.

(Figure 1f). The transition from V_d to XI_d eliminates the helical self-organization, although it continues to provide a 3-D-ordered, crystalline nonhelical columnar monoclinic periodic array (Φ_m^k) (Figure 1g–j, Figure S1). The nonhelical crystalline columns self-organized from XI_d contain four pores parallel to the column axis (Figure 1i). An inspection of Figure 1a,d,f,i reveals that although the parent *meta*-terphenyl building blocks of V_d and XI_d contains a rigid taper angle of about 120°, only the taper angle of V_d in its supramolecular column matches its rigid taper angle of 120°, while the rigid taper angle of XI_d increases its experimental taper angle to about 180°. The adjustment of the taper angle at the transition from V_d to XI_d is mediated by the change in the pattern and degree of substitution with *n*-dodecyloxybenzyloxy groups from 3,4-disubstituted to 3,4,5-trisubstituted. This modification continues to facilitate the self-organization of XI_d into the 3-D-ordered column and periodic array Φ_m^k but eliminates the helicity of the supramolecular column of V_d. The transition from XI_d to $XXIX_d$ (Figure 2a) is attained by combining the disubstitution of V_d and trisubstitution of XI_d in the 3- and 5-positions of $XXIX_d$. This modifies the structure of the self-organizable dendron from symmetric V_d and XI_d to nonsymmetric $XXIX_d$. Surprisingly, the transition from symmetric V_d and XI_d to nonsymmetric $XXIX_d$ is accompanied by a change from 3-D-ordered, crystalline helical Φ_h^k or porous nonhelical Φ_m^k to a disordered nonhelical nonporous columnar simple rectangular ($\Phi_{r\text{-}s}$) LC (Figure 2b–e). This transition maintains the taper angle of 180° of XI_d in $XXIX_d$ (Figures 1i and 2d). What is the mechanism of these transformations? In the cross section of the supramolecular column of XI_d, its dimer is missing the free rotation around the column axis, which is required to transit from nonhelical to helical. This prohibited free rotation is mediated by some orthogonal arrangements of the benzyl ethers and is close to orthogonal, 35°, of the phenyl groups of the biphenyl parts of the *meta*-terphenyl groups of XI_d and $XXIX_d$. The nonsymmetric arrangement of $XXIX_d$ eliminates crystallization forming the $\Phi_{r\text{-}s}$ LC. Dendron nonsymmetry was also introduced by the transition from *meta*- to *ortho*-terphenyl, as shown by X_d and IV_d in Figure 2f–o and Figure S3. Both IV_d and X_d exhibit theoretical rigid taper angles of about 60° (Figure 2f,k), which experimentally convert to about 120° (Figure 2i,n). The high degree of substitution on the periphery of IV_d and X_d makes them disregard their rigid taper angle of 60°. Both IV_d and X_d adopt a taper angle of 120° (Figure 2i,n) and, via orthogonal or close to orthogonal placement of

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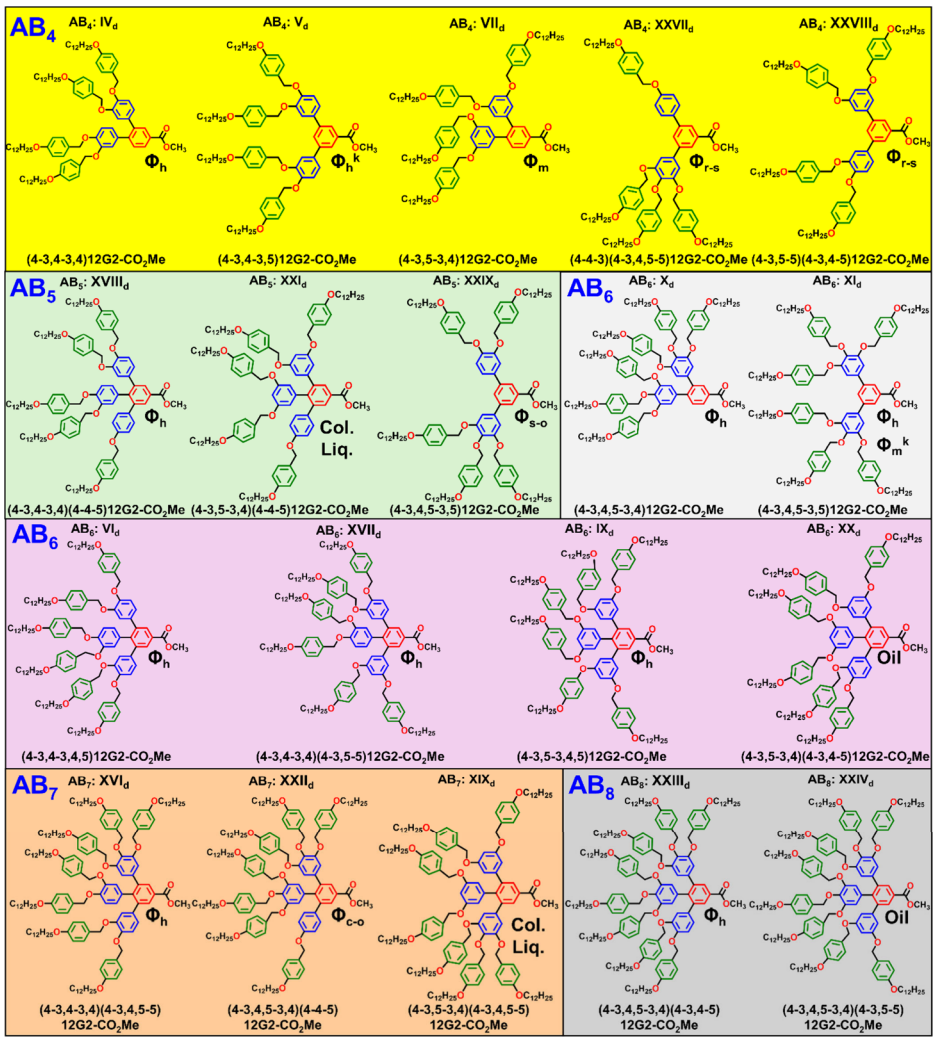

Figure 4. Molecular structures of the five AB_4 constitutional isomers, three AB_5 constitutional isomers, two AB_6 constitutional isomers, three AB_7 constitutional isomers, and two AB_8 constitutional isomers and their self-organized supramolecular structures. Col. Liq. indicates a columnar liquid.

aromatic groups, eliminate rotation around the column axis and helicity, which results in a nonhelical columnar hexagonal (Φ_h) LC array (Figure 2h,m and Figure S1). The nonsymmetric substitution and the crowding arrangement of aromatic groups do not allow helicity and crystallinity, which provides a general method to design disordered nonhelical nonporous columns by molecular unwinding.

It is interesting to observe that IV_d and V_d have identical chemical compositions but are constitutional isomers. XI_d and X_d are also constitutional isomers. Constitutional isomers are expected to display completely different physical properties, although they have identical chemical composition but different arrangement of their atoms.[14] An additional concept that produces disordered nonhelical self-organizations is presented in Figures 2p–y and 3a–y and Figures S3 and S4. This concept involves the incorporation of an additional trisubstituted, disubstituted, or monosubstituted phenolic acid in the *meta*-position of the *meta*-terphenyl part of the dendron. Structures VI_d and XII_d (Figure 2p,u) and IX_d, XVI_d, $XVII_d$, $XVIII_d$, $XXII_d$, and $XXIII_d$ (Figure 3a–y) demonstrate this concept. Interestingly, both symmetrically substituted XII_d (Figure 2u–y) and IX_d (Figure 3a–e) and nonsymetrically substituted VI_d (Figure 2p–t), XVI_d, $XVIII_d$, $XXII_d$, $XXIII_d$, $XXIII_d$ (Figure 3f–y), VII_d, and $XVII_d$ (Figure S1f–o) yield disordered nonhelical columnar liquid crystal self-organizations exhibiting Φ_h and columnar centered orthorhombic $\Phi_{c\text{-}o}$ LC (Figure S1) periodic arrays. Four of the structures investigated, XXI_d, XX_d, XI_d, and $XXIV_d$ (Figure S5), are liquids at room temperature.

However, they exhibit phase transitions below room temperature, and therefore, by analogy with the other structures, we expect that they are columnar liquid crystals below room temperature and "columnar liquids" at and above room temperature (Figure S6).

Nineteen of these building blocks are constitutional isomers (Figure 4) supporting the idea that their physical properties must be different. In conclusion, the results reported here demonstrate a general methodology to transform by changing the primary structure, self-organizing supramolecular helical columnar crystals (Figure 1a–e) into nonhelical nonequilibrium porous 3-D-ordered columns (Figure 1f–j) and nonporous nonhelical columnar LCs (Figures 2,3) and columnar liquids. The design of porous columnar 3-D-ordered columns presented here is complementary to other methodologies that mimic aquaporin and provides biologically inspired channels for fast transport of water across cell membranes, and for water purification.[15] This general methodology establishes an unprecedented molecular design

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approach to irreversible helical unwinding maintaining a columnar structure, which is expected to provide numerous and unparalleled applications in the fields of macromolecular and supramolecular sciences. The role of the functional group from the apex of the building block on its taper angle and on the self-organization process will be reported in a future publication.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c09127.

Methods for synthesis and structural analysis by XRD (PDF)

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Notes

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