

Cogwheel Mechanism of Helical Self-Organization is Thermodynamically Controlled, Self-Repairing, and Universal

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Cite This: <https://doi.org/10.1021/jacs.4c07428>

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ABSTRACT: The cogwheel mechanism of helical self-organization, reported by us, generates columns with the alkyl chains of their components parallel to the column axis. This mechanism disregards the enantiomeric purity of constituents and, under suitable design, provides the fastest rate of helical self-organization. Here, we investigate the supramolecular structure of a thermodynamically controlled helical self-organization system. Unexpectedly, we found that this system follows a cogwheel mechanism of helical self-organization that does not contain the two key parameters of the cogwheel mechanism: the length of the alkyl group of the self-assembling dendron identical to the helical half-pitch (hhp) of the column and the presence of chiral branches pointing toward the column center. Unpredictably, we uncovered that the presence of chiral branching points and strict alkyl chain lengths is not a requirement of the cogwheel mechanism. A self-repairing process provides access to a constant hhp via a shorter and longer alkyl chain length than the originally exact demanded value, which together with the lack of branching point(s) demonstrates the universality of the cogwheel mechanism of helical self-organization. Applications derived from this concept are envisioned.

Helical self-organizations, including homochiral, have been known in nature for billions of years.¹ Natural helical self-organizations, such as hurricanes, tornados, typhoons, tropical cyclones, whirlpools, and many others, have inspired art, architecture, and machines. As early as 234 BC, Archimedes constructed the first helical machine used even today and known as the Archimedes' screw. In 1485, Leonardo da Vinci built the aerial screw that follows the principles of today's helicopters.¹ It took over 2000 years from Archimedes' screw to the discovery of helical self-organizations at the molecular level.² The α -helix of peptides elaborated by Pauling et al.³ and the helical diffraction theory developed by Crick et al.,⁴ which were followed by the double helix of DNA,⁵ the globular tertiary structure of proteins assembled from helices,⁶ and helical viruses,⁷ facilitated the rapid development of synthetic helical macromolecules and assemblies.⁸ Five mechanisms of helical self-organization that most frequently self-organize helical columns containing repeat units equal to the cross-section of the column have been elucidated by us by using oriented fiber X-ray diffraction (XRD). Only these are discussed here.⁸ Examples of such components are planar disclike,⁹ crownlike,¹⁰ hatshaped,¹¹ cogwheel,¹² and chiral supramolecular spherical helices¹³ (Figure 1). The cogwheel mechanism places the alkyl groups of the self-assembling elements in a parallel arrangement to the column axis. This arrangement provides the smallest column diameter of all assemblies from Figure 1. Under suitable design, the cogwheel mechanism generates the fastest thermodynamically controlled and the highest ordered helical self-organization known.^{12c} The cogwheel mechanism demands that the alkyl group length of constituents is equal to its helical half-pitch (hhp), and a small stereocenter pointing toward the column center determines the distance from the inner part of the column to the cogwheel coat.^{12a,d} The cogwheel mechanism of helical self-organization has been shown to disregard the chirality of the

branching point located on the alkyl groups of its components and, therefore, provides the same helical column regardless of its enantiomeric purity.^{12a} The deracemization mechanism during cogwheel helical self-organization has not yet been elucidated. However, if shown to be universal, the cogwheel mechanism of helical self-organization could be employed to engineer unprecedented helical functions and may provide an alternative pathway to elucidate the origins of homochirality.¹⁴ In order to elucidate the thermodynamically controlled self-organization process reported previously,^{15a} we determined the 3D structure of dendronized perylene 3,4:9,10-tetracarboxylic acid bisimide (PBI), (3,4,5)*n*G1-1-PBI, with the number of carbons in their *n*-alkyl groups ranging from *n* = 6 to 12 (Figure 2), which was employed earlier to discover the transformation from kinetically into thermodynamically controlled self-organization.^{15a} Number 1 between generation-1 (G1) and PBI refers to a single methylenic unit between the self-assembling dendron and PBI. The alkyl groups employed in these experiments are shorter, equal, and longer than the hhp of the columns and do not contain any branching point(s). Unexpectedly, the thermodynamically controlled self-organization process of (3,4,5)*n*G1-1-PBI was found to be induced by an unprecedented cogwheel mechanism of helical self-organization that does not demand the two key structural parameters required by this mechanism: (a) the strict length of the alkyl groups equal to the hhp of the helical

Received: June 4, 2024

Revised: July 2, 2024

Accepted: July 3, 2024

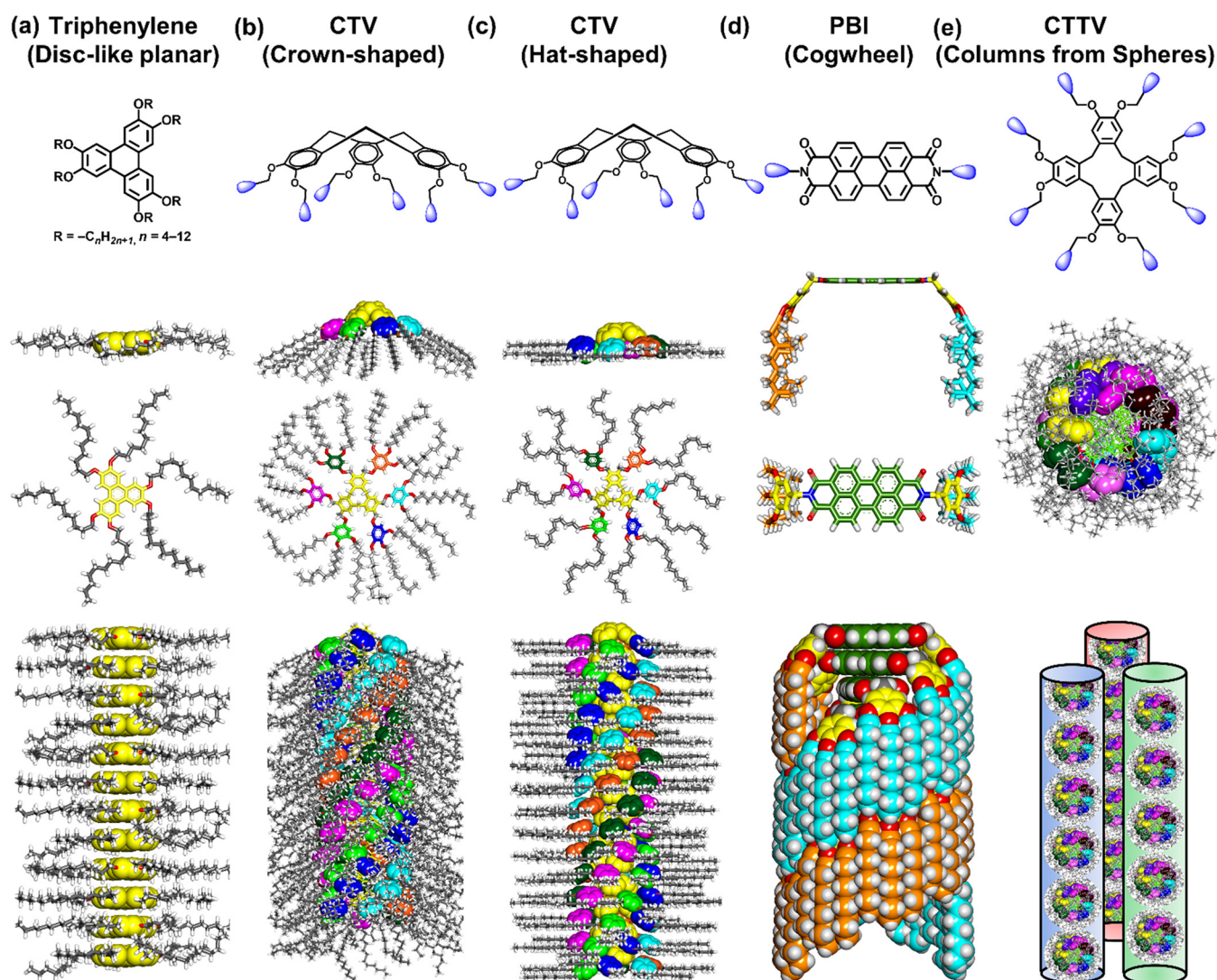


Figure 1. Selected helical self-organization mechanisms elucidated in our laboratory. (a) Helical supramolecular columns from disc-like triphenylene-based planar structures.⁹ (b) Helical columns from the crown shape produced from dendronized cyclotrivenatrylene (CTV);^{4c,10a} (c) helical columns from hat-shaped structures generated from dendronized CTV;¹¹ (d) the cogwheel mechanism;^{12a} and (e) helical columns from spherical helices assembled from dendronized cyclotrivenatrylene (CTTV).^{10d}

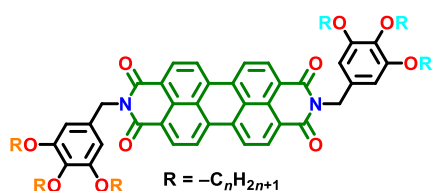


Figure 2. Molecular structure of (3,4,5) n G1-1-PBI, with $n = 6-12$.

column and (b) the presence of branching points in alkyl tails pointing toward the inner part of the column.^{12a}

However, the structure of helical columns and of their periodic arrays self-organized from (3,4,5) n G1-1-PBI was not elucidated.^{15a} The synthesis of (3,4,5) n G1-1-PBI with $n = 6-12$, outlined in Scheme S1, and phase transitions of the resulting assemblies determined by differential scanning calorimetry with heating and cooling rates ranging from 1 to 10 °C/min combined with oriented fiber XRD experiments were reported.^{15a} Table S1 summarizes the structural analysis of helical columnar-centered orthorhombic crystalline (Φ_{c-o}^k) and columnar hexagonal with intracolumnar-order liquid crystalline

(Φ_h^{io}) self-organizations (Figures 3h,i and S1) to be discussed here. We inform that the Φ_{c-o}^k periodic array is pseudohexagonal, being a slightly distorted hexagonal crystal. For simplicity, Figure 3 illustrates the helical cogwheel self-organization mediated with dimethyloctyl (dm8*) groups. The dm8* contains two methyl groups, which form the chiral and achiral branching points. Figure 3b–e shows the formation of the helical columns by the cogwheel mechanism of (3,4,5)dm8*G1-1-PBI.^{12a,c,d} It is notable (Table S1) that (3,4,5) n G1-1-PBI with $n = 6$ and 7 self-organizes helical columns exhibiting only the Φ_{c-o}^k phase, while those with $n = 8-11$ generate helical columns displaying both Φ_{c-o}^k and Φ_h^{io} arrays (Figures S1 and S2). (3,4,5)12G1-1-PBI self-organizes only the Φ_h^{io} phases. The original discovery of the cogwheel concept was made with chiral and racemic dm8*.^{12a} The side view of the helical cogwheel column is shown in Figure 3e–g, while the unit cells of Φ_{c-o}^k and Φ_h^{io} are revealed in Figure 3 h,i. As shown in Figure 3 f,g, in order to coat completely the helical column, the hhp of column must be strictly equal to that of the alkyl chain length attached to (3,4,5)dm8*G1-1-PBI.

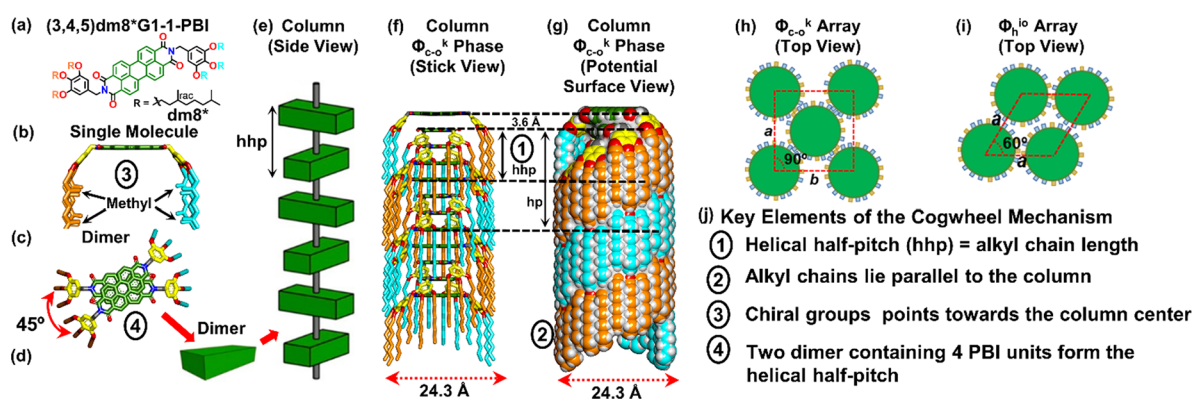


Figure 3. Schematic of the cogwheel mechanism of helical self-organization of columnar-centered orthorhombic crystal (Φ_{c-o}^k) and columnar hexagonal with intracolumnar order ($\Phi_{h^{io}}$) phases. (a) Molecular structure of (3,4,5)8G1-1-PBI; (b) conformation of (3,4,5)8G1-1-PBI forming Φ_{c-o}^k and $\Phi_{h^{io}}$ phases (side view); (c) dimer of (3,4,5)8G1-1-PBI (top view); (d) schematic of dimer; (e) schematic of helical column assembled from dimers; (f) side view of helical column in Φ_{c-o}^k phase; (g) potential surface view of helical column in Φ_{c-o}^k phase; (h) top view of helical column in $\Phi_{h^{io}}$ phase (CPK model); and (i) key requirements of cogwheel model (hp = helical pitch, hhp = helical half-pitch).

A sequence-defined arrangement of two *n*-nonyl groups in the 3,5-positions combined with dm8* in the 4-position of the self-assembling dendron, (3,4,5)dm8*,9,dm8*G1-1-PBI, demonstrated the fastest thermodynamically controlled self-organization process encountered in bulk for the cogwheel helix or for any other self-organization.^{12d} This fast self-organization was accomplished by a proper helical coat design. Figure 4a–e shows in red the oriented fiber XRDs of the Φ_{c-o}^k arrays of (3,4,5)*n*G1-1-PBI with *n* = 6–10. The black parts in Figure 4 illustrate the reconstructed oriented fiber XRDs of the same assemblies generated by the periodicities constructed from the supramolecular columns shown in Figure 4k. Comparing the red and black oriented fiber diffractograms from Figure 4a–e demonstrates that the helical columns from Figure 4k validate the cogwheel model of helical self-organization. This is in spite of the absence of the two methyl branching points of dm8* and of different lengths of their *n*-alkyl groups. The ideal length of the *n*-alkyl group coating the helical column is *n*-nonyl for 3,5-positions and *n*-octyl for the 4-position of the dendron.^{12d} Nevertheless, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-decyl, and *n*-undecyl tolerate the cogwheel model, although they are shorter and longer than the ideal value. Decreasing the length of *n*-nonyl and *n*-octyl to *n*-heptyl and *n*-hexyl provides a shorter column coat that uncovers the yellow aromatic part of the (3,4,5)*n*G1 dendron. Therefore, in Φ_{c-o}^k , both the absence of the two branched methyl groups of dm8* and shorter, as well as longer, *n*-alkyl groups than ideal are sustained by the cogwheel model of helical self-organization. The red parts of the oriented fiber XRDs from Figure 4f–j show the experimental oriented fiber XRDs obtained in the $\Phi_{h^{io}}$ array. The black parts illustrate the reconstructed XRDs obtained by using the molecular models from Figure 4l. The agreement between experimental and reconstructed oriented fiber XRDs supports the helical columns self-organized by the cogwheel models illustrated in Figure 4l. Since the $\Phi_{h^{io}}$ periodic array is liquid crystalline, the *n*-alkyl groups are partially disordered (Figure 4l), although at shorter *n*-alkyls for *n* = 6 and 7, they uncover parts of the yellow-colored benzyl group of the dendron, just as in the case of the Φ_{c-o}^k columns (Figure 4k). In both Φ_{c-o}^k and $\Phi_{h^{io}}$ columns, hhp is not strictly equal to the length of the *n*-alkyl chains. The *c* parameters of the columnar phases were calculated from the experimental oriented fiber XRDs along the fiber *z*-axis. The bright diffraction spot along the fiber axis (*L* = 4) shows the π – π stacking distance

(Table S1). The value of the *c* parameter represents the hhp of the column(s). Inspecting the trend of hhp of columns for (3,4,5)*n*G1-1-PBI (*n* = 6–12) and comparing it with the hhp of (3,4,5)6G1-1-PBI and (3,4,5)7G1-1-PBI, we observe that is constant and equal to 14.7 Å for the Φ_{c-o}^k columns. Unexpectedly, hhp values of (3,4,5)8G1-1-PBI, (3,4,5)9G1-1-PBI, (3,4,5)10G1-1-PBI, and (3,4,5)11G1-1-PBI assemblies containing longer *n*-alkyl groups are shorter than (3,4,5)6G1-1-PBI and (3,4,5)7G1-1-PBI columns showing values between 14.2 and 14.5 Å. The higher hhp of (3,4,5)6G1-1-PBI and (3,4,5)7G1-1-PBI is also unexpected since the helical coat is constructed from a shorter *n*-alkyl chain length. Shorter chain lengths of *n* = 6 and 7 cannot fulfill the required length for a perfect cogwheel assembly. As a result, the packing of the molecules is less compact compared with the perfect cogwheel model observed for *n* = 8, 9, and even for 10, and therefore, for *n* = 6 and 7, we see a slightly longer hhp. This longer hhp induces the small gap between the two consecutive hhp, which uncovers the yellow benzyl parts of the dendron (Figure 4k), thereby generating a less perfect coat. By contrast, an almost perfect coat is observed in the case of (3,4,5)8G1-1-PBI, (3,4,5)9G1-1-PBI, and (3,4,5)10G1-1-PBI, as the chain length of the alkyl groups provides a more perfect coat. Therefore, in these cases, we observe a tighter packing between two PBI and dendritic layers and a slightly shorter hhp. These results demonstrate a self-repairing process of the cogwheel helical coat that could not be predicted during the discovery process of the helical cogwheel self-organization.^{12a,c,d} It is remarkable that this self-repairing helical cogwheel coat process occurs both in the crystal state of the Φ_{c-o}^k periodic array and in the liquid crystal state of $\Phi_{h^{io}}$.

A brief inspection of the supramolecular helical columns from Figure 4l displays a self-repairing process in the $\Phi_{h^{io}}$ liquid crystalline periodic array. In this case, the fluidity of the *n*-alkyl groups facilitates a constant hhp of 14.0 Å regardless of the number of carbons in the *n*-alkyl group. All helical cogwheel coats from Figure 4l exhibit the same hhp values for *n* = 6 to 11. The last two columns in Table S1 summarize the length (*L*) of the *n*-alkyl groups employed in these experiments and the difference between the values of hhp and *L* (hhp–*L*). Unexpectedly, they demonstrated that one of the two major requirements of the original cogwheel model, i.e., hhp equal to alkyl chain length, is not demanded since it is accomplished by self-repairing of its helical coat. The self-repairing process relaxes

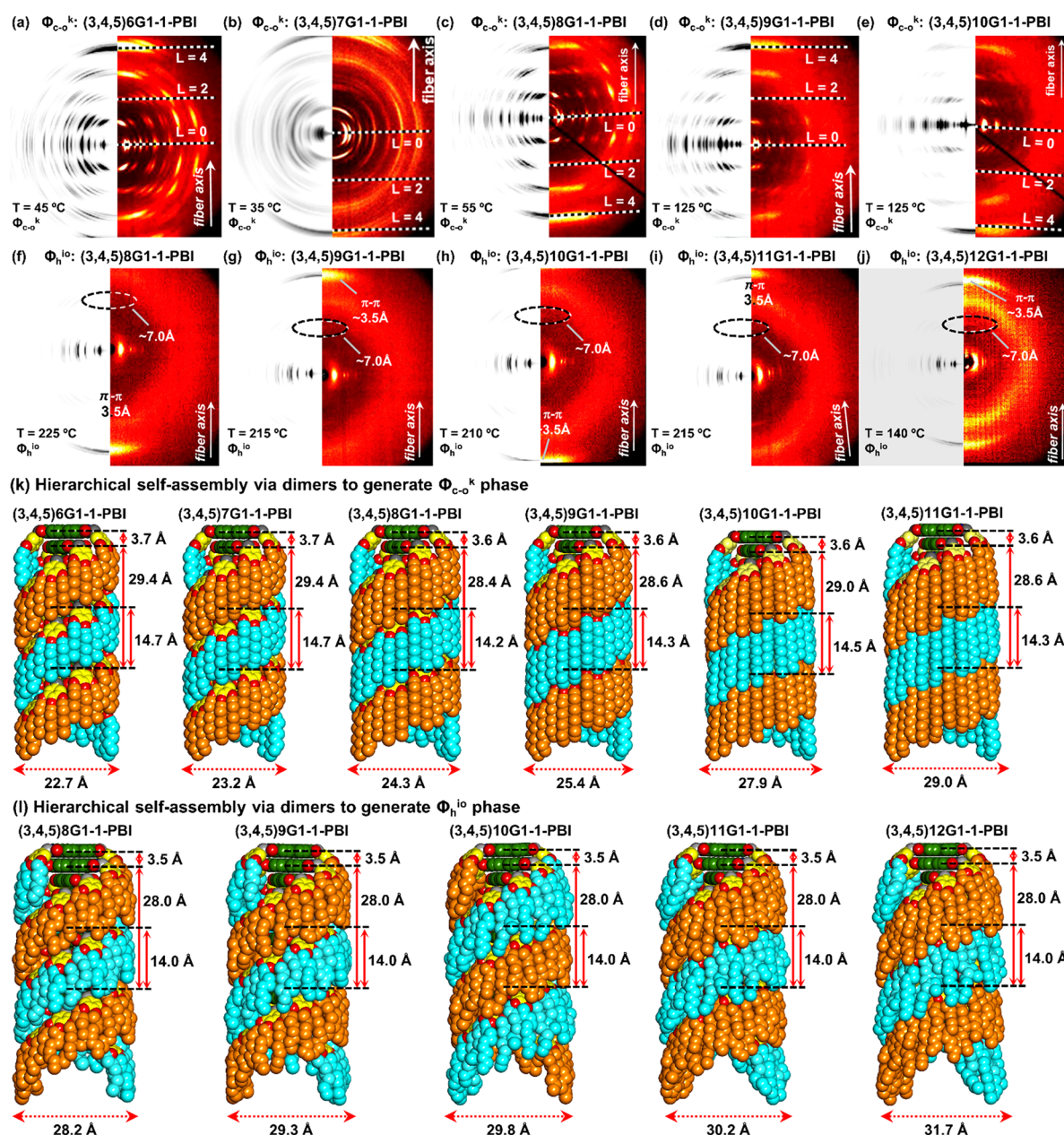


Figure 4. Experimental and simulated oriented fiber XRDs of Φ_{c-o}^k (a–e) and Φ_h^{io} phases (f–j); side views of the cogwheel helical columns assembling Φ_{c-o}^k phases from (3,4,5)6G1-1-PBI, (3,4,5)7G1-1-PBI, (3,4,5)8G1-1-PBI, (3,4,5)9G1-1-PBI, (3,4,5)10G1-1-PBI, and (3,4,5)11G1-1-PBI (k); and Φ_h^{io} phases of (3,4,5)8G1-1-PBI, (3,4,5)9G1-1-PBI, (3,4,5)10G1-1-PBI, (3,4,5)11G1-1-PBI, and (3,4,5)12G1-1-PBI (l).

this strict requirement. Is the difference between various hhp values observed in the Φ_{c-o}^k phase (Figure 4 and Table S1) due to the different temperatures at which the XRD was performed? The plot of the hhp versus temperature in the Φ_{c-o}^k phase demonstrates that within experimental error, the hhp values from Table S1 and Figures 4 and S3 are constant as they are in the case of the Φ_h^{io} array. In conclusion, no alkyls equal in length with hhp of cogwheel helical column and branched alkyl groups that must point toward the center of the column are demanded. These relaxed structural requirements of the helical cogwheel mechanism of thermodynamically controlled self-organization explain why a perfluoroether containing only six atoms forms a helical cogwheel.^{12b} This opens opportunities to functionalize the helical coat of columns with a diversity of functions equipped with unprecedented potential applications, including fast

molecular electronics^{15b–d} and pathways to origins of biological homochirality to be reported soon.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c07428>.

Methods for synthesis and structural analysis by DSC and XRD (PDF)

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Funding

This work was supported by National Science Foundation Grants DMR-2104554, the P. Roy Vagelos Chair at the University of Pennsylvania, and the Alexander von Humboldt Foundation (all to V.P.).

Notes

The authors declare no competing financial interest.

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