

Extraordinary Acceleration of Cogwheel Helical Self-Organization of Dendronized Perylene Bisimides by the Dendron Sequence Encoding Their Tertiary Structure

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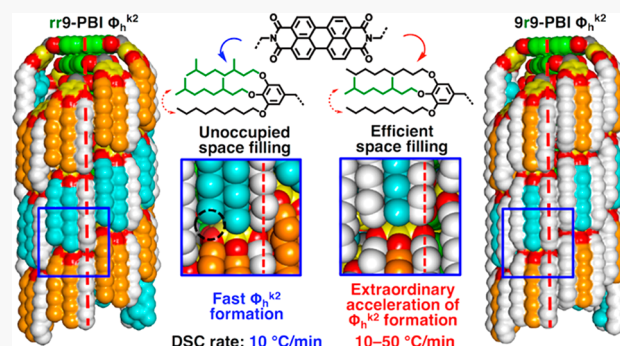


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ABSTRACT: The cogwheel model of hierarchical self-organization provides a route to highly ordered crystalline helical columnar hexagonal arrays of perylene bisimides (PBIs) conjugated to (3,4,5)-dimethyloctyl (racemic dm8*, *r*) minidendrons. Cogwheel PBIs assemble with identical structural order irrespective of molecular chirality to generate helical columns jacketed with an alkyl coat with length equal to half the helical pitch, exhibiting helical deracemization in the crystal state. These assemblies were accessible only via annealing or cooling and reheating at 1 °C/min. Recently it was discovered that hybrid **rr8** sequence-defined dendrons with *r* and linear *n*-octyl (8) chains enabled the formation of the cogwheel phase at 10 °C/min upon heating but not cooling. Here we report four libraries of hybrid PBIs with sequence-defined dendrons containing *r* and *n*-alkyl (C_nH_{2n+1}) chains with *n* = 6, 7, 9, and 10. Structural analysis of these libraries by fiber X-ray diffraction and differential scanning calorimetry reveals that the **9r9** sequence enables an extraordinary acceleration of cogwheel assembly at rates of up to 50 °C/min on heating and cooling, providing, to the best of our knowledge, the fastest crystallizing supramolecular or covalent macromolecule known. Solid-state NMR studies help to elucidate this unexpected and unprecedented extraordinary acceleration of hierarchical self-organization, which arises from a combination of crystal packing of the ideal tertiary structure and alkyl chain dynamics. This general model raises questions about the use of achiral motifs to achieve high structural order in chiral systems and the need for disorder to create order in complex biological and bioinspired synthetic systems.



INTRODUCTION

Function in natural systems arises from the hierarchical transfer of structural information encoded in a primary structure, such as DNA or an amino acid sequence, and expressed by a tertiary structure, such as the folded state of a protein.¹ These structures are often helical² and are invariably homochiral, the origin of which remains one of the greatest unsolved fundamental questions within the natural sciences.³ The emergence of homochiral life necessitates a means to resolve chirality within racemic mixtures, by enriching a statistical chiral imbalance⁴ or by separating racemates into enantiopure domains.⁵ This separation—known as deracemization—was demonstrated for the first time in the solution state by Pasteur in the 1840s.⁶

Supramolecular polymers⁷ provide a tunable platform for exploring helical assembly,⁸ responsive materials,⁹ and the role of chirality in generating order.¹⁰ Deracemization in the crystal state of supramolecular systems was first observed recently for racemic mixtures of hat-shaped dendronized molecules¹¹ and was driven by the demand of the hexagonal unit cell of the columnar crystal that all columns be identical, exhibiting the same helical sense, within each crystal domain. The mechanism

of deracemization, which depended on weak interactions between individual molecules, could only be understood using solid-state NMR.¹² Supramolecular deracemization does not occur in systems with strong intermolecular interactions, such as chiral dendritic dipeptides,¹³ which instead give lower order assemblies when not enantiopure.¹⁴ Indeed, incomplete deracemization of mixtures of hat-shaped molecules containing inseparable, diastereomeric combinations of stereocenters gave reduced order in the crystal state. This observation is analogous to the amorphous nature of atactic poly(propylene) compared to the crystallinity of its isotactic counterpart.¹⁵

Subsequently a perylene bisimide (PBI)¹⁶ with two chiral minidendrons¹⁷ that assembles into 3D helical columnar

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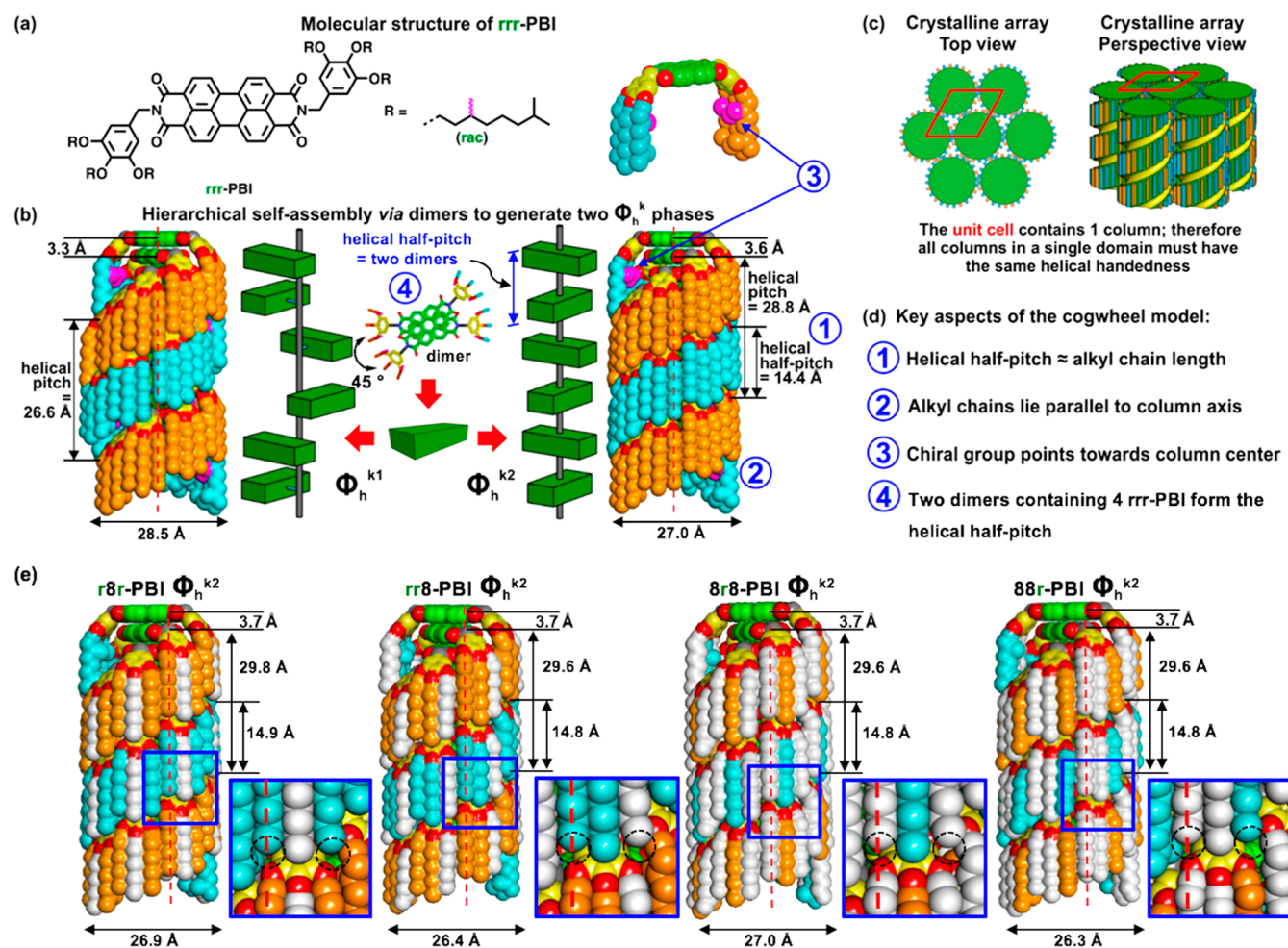


Figure 1. Cogwheel model of self-organization. (a) Molecular structure of **rrr-PBI** where **r** stands for racemic **dm8***. The chiral methyl group is indicated in pink. (b) The two crystalline columnar hexagonal (Φ_h^k) phases are generated via hierarchical self-organization of PBI dimers rotated around the column axis being offset from the column axis in Φ_h^{k1} and centered on the column axis in Φ_h^{k2} . Due to its columnar shape and the absence of alkyl groups perpendicular or tilted to the long axes of the column, intercolumnar interdigitation of alkyl chains is absent, and therefore, we denote Φ_h^{k2} as the “cogwheel” assembly. (c) Formation of a Φ_h^k array with only one helical column in the unit cell drives helical deracemization between columns. (d) Key aspects of the cogwheel model. (e) Supramolecular columns assembled from **r8r-PBI**, **rr8-PBI**, **8r8-PBI**, and **88r-PBI**,¹⁹ where 8 represents the *n*-octyl group, and insets illustrating the incomplete space filling by the alkyl ends from the 3- and 5- positions of the dendron. Dashed circles in insets indicate empty space on the column periphery. Panels (a)–(d) are adapted from ref 19.

hexagonal (Φ_h) arrays with identical single-crystal-like order irrespective of molecular chirality was discovered (Figure 1a).¹⁸ The Φ_h array exhibited helical deracemization, whereby even statistical mixtures of all possible diastereomers generated crystalline domains with a single helical sense.

This chirality-invariant structural order was rationalized using a model in which alkyl chains on the periphery of the supramolecular column act like the “teeth” of a cogwheel, covering the exterior of a column assembled from molecular dimers (Figure 1b). X-ray diffraction (XRD) and variable rate differential scanning calorimetry (DSC) experiments confirmed that the cogwheel phase (denoted Φ_h^{k2}), which was discovered by chance during XRD annealing studies, is formed only by annealing at 100 °C or upon slow cooling and reheating at 1 °C/min.

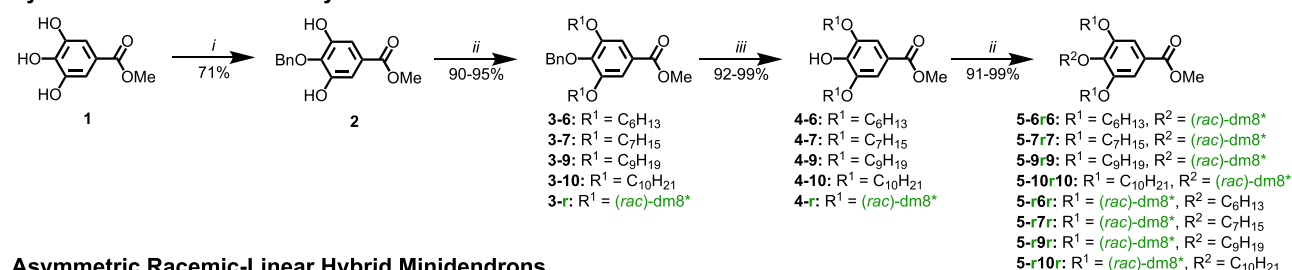
This cogwheel model had not been observed in assemblies of PBIs with exclusively linear *n*-alkyl chains that interdigitate,²⁰ likely because the key attributes of the cogwheel model (Figure 1d) not only demand peripheral alkyl chains that lie parallel to the column axis and are of approximately equal length to the half-pitch of the helical column, but also depend on the chiral

methyl group of the dimethyloctyl (**dm8***) chain to efficiently fill space within the center of the column and adopt an appropriate secondary structure that may disfavor intercolumnar interdigitation²¹ of chains (Figure 1a). Therefore, PBIs with sequence-defined hybrid dendrons containing mixtures of linear *n*-octyl and **dm8*** chains were investigated, leading both to the discovery that linear alkyls can be tolerated together with dimethyloctyl by the cogwheel assembly and to a hybrid sequence of **dm8***/linear chains that forms the cogwheel Φ_h^{k2} phase under relatively fast heating and cooling at 10 °C/min with the phase transition being observed only on heating (Figure 1e).¹⁹ However, the role of the linear alkyl chain in accelerating the formation of the cogwheel Φ_h^{k2} phase remained unclear and raised the question: how do linear *n*-alkyl chains affect assembly via the cogwheel model?

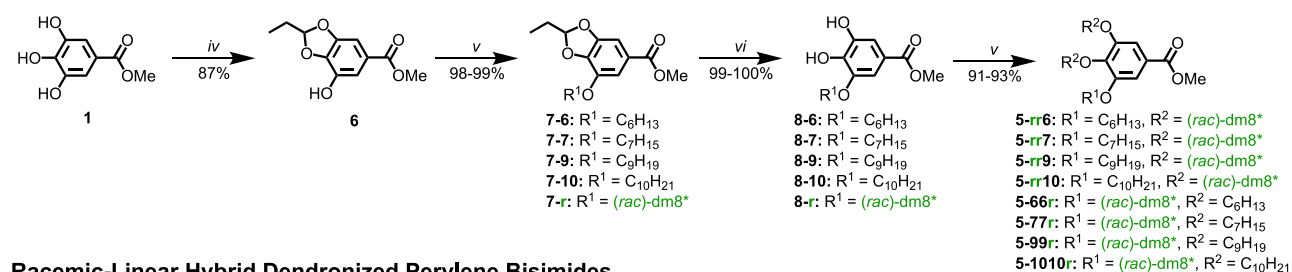
To answer this question, this study reports the investigation of four libraries of hybrid PBIs with sequence-defined mixtures of racemic **dm8***, **r**, chains, and linear *n*-alkyl (C_nH_{2n+1}) chains with *n* = 6, 7, 9, and 10 carbons in the alkyl group. Structural and retrostructural analysis of these libraries by XRD and DSC reveals a dendron sequence that enables an extraordinary

Scheme 1. Synthesis of PBIs with Sequence-Defined Linear–Racemic Hybrid Minidendrons^a

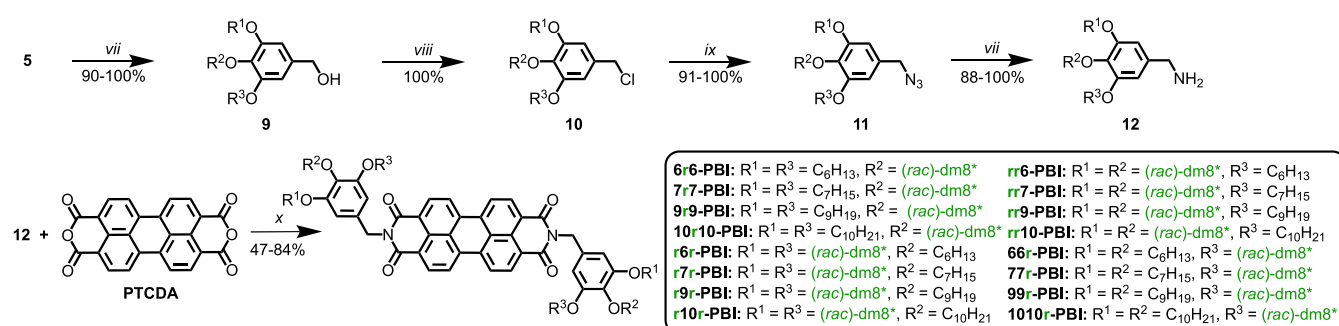
Symmetric Racemic-Linear Hybrid Minidendrons



Asymmetric Racemic-Linear Hybrid Minidendrons



Racemic-Linear Hybrid Dendronized Perylene Bisimides



^aReagents and conditions: (i) BnCl , KHCO_3 , DMF, 60 °C, 24 h; (ii) RBr , K_2CO_3 , DMF, 120 °C, 3.5–12 h; (iii) H_2 , Pd/C , $\text{CH}_2\text{Cl}_2/\text{MeOH}$, 23 °C, 24 h; (iv) triethyl orthoformate, Amberlyst-15(H), toluene, reflux, 6 h; (v) RBr , K_2CO_3 , DMF, 65–70 °C, 4 h; (vi) HCl , methanol, 60 °C, 7 h; (vii) LiAlH_4 , THF, 23 °C, 1 h; (viii) SOCl_2 , cat. DMF, 23 °C, CH_2Cl_2 , 0.5 h; (ix) NaN_3 , DMF, 23 °C, 9 h; (x) PTCDA, $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, imidazole, 180 °C, 6 h.

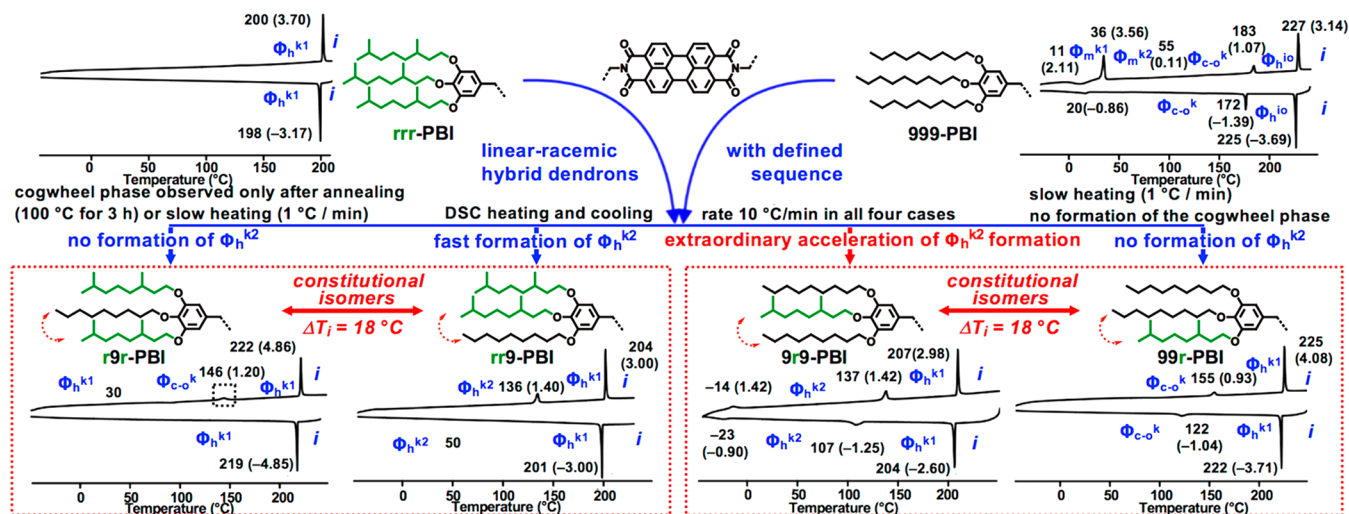


Figure 2. DSC traces of PBIs with sequence-defined hybrid *r/n*-nonyl dendrons recorded upon second heating and first cooling at 10 °C/min. Phases determined by fiber XRD, transition temperatures (in °C), and associated enthalpy changes (in parentheses, in kcal/mol) are indicated. Phase notation: $\Phi_{\text{h}}^{\text{k}1}$, columnar hexagonal crystal with offset dimers; $\Phi_{\text{h}}^{\text{k}2}$, columnar hexagonal crystal with cogwheel assembly; $\Phi_{\text{c-o}}^{\text{k}}$, columnar centered orthorhombic crystal; $\Phi_{\text{m}}^{\text{k}}$, columnar monoclinic crystal, *i*, isotropic liquid.

acceleration of the formation of the cogwheel Φ_h^{k2} phase at rates of up to 50 °C/min. *This is the highest rate that any current*

instrumentation including DSC and XRD can use for quantitative, temperature-dependent structural analysis in conventional research

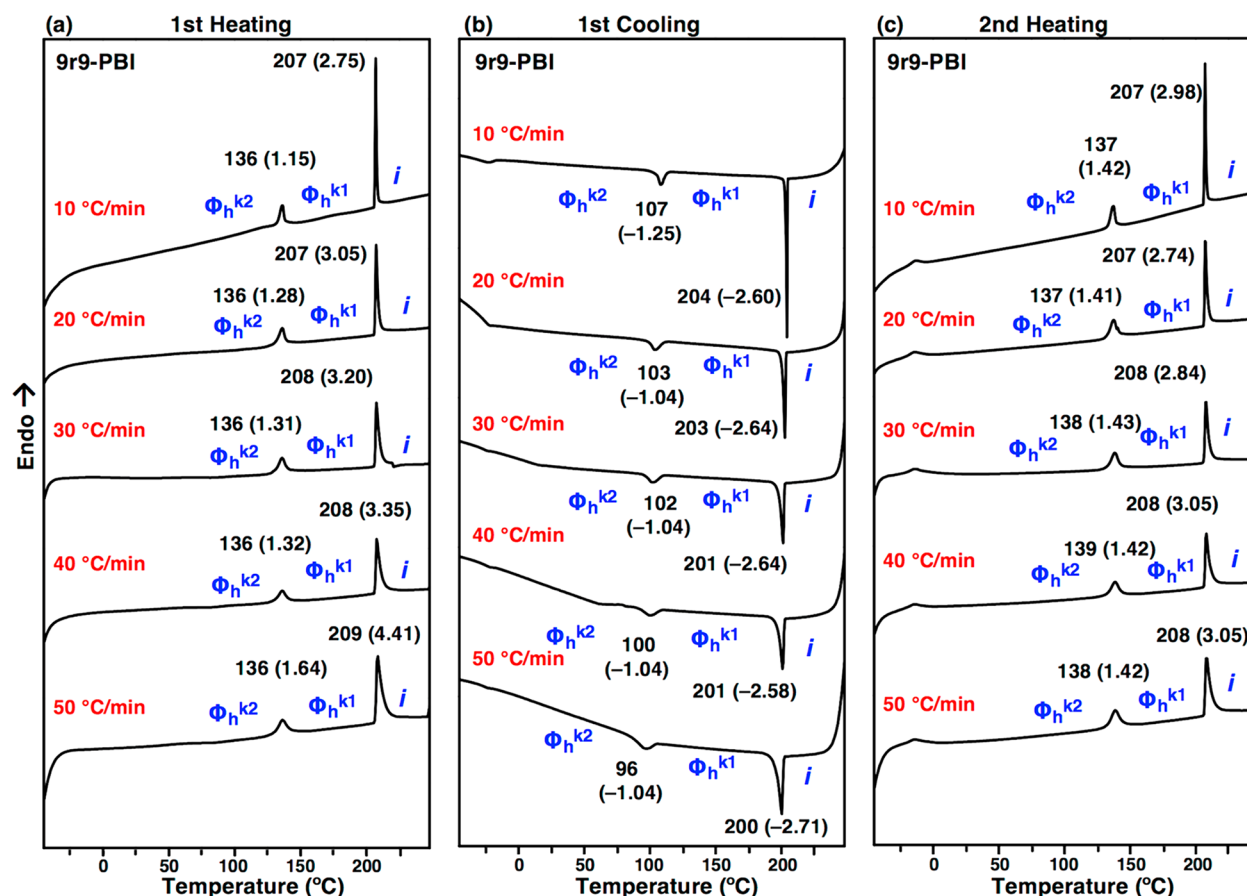


Figure 3. DSC traces of **9r9-PBI** assemblies measured upon heating and cooling at 10 to 50 °C/min during (a) first heating, (b) first cooling, and (c) second heating. Phases determined by fiber XRD, transition temperatures (in °C), and associated enthalpy changes (in parentheses, in kcal/mol) are indicated. Phase notation: Φ_h^{k1} , columnar hexagonal crystal with offset dimers; Φ_h^{k2} , columnar hexagonal crystal with cogwheel assembly; Φ_{c-o}^k , columnar centered orthorhombic crystal; Φ_m^k , columnar monoclinic crystal; *i*, isotropic liquid.

laboratories. Together with solid-state NMR and previous work with *r/n*-octyl dendrons,¹⁹ this extraordinary acceleration of the rate of Φ_h^{k2} formation relies on a complex interplay of crystal packing and chain dynamics. These findings raise questions about the role of nonchiral building blocks in achieving a high degree of structural order in chiral systems, support the power of constitutional isomerism to dictate self-assembly,^{19,22} and provide insights into the design of highly ordered assemblies with extraordinary acceleration of their formation and bulk helical deracemization.

RESULTS AND DISCUSSION

Synthesis of Libraries of PBIs Containing Sequence-Defined Hybrid Dendrons. Defining the sequence²³ of biological and bioinspired molecules is a powerful means to control supramolecular assembly²⁴ and elucidate fundamental biological concepts such as protein–carbohydrate binding.²⁵ Here, 16 sequence-defined hybrid dendronized PBIs were synthesized using an iterative methodology elaborated in a previous communication (Scheme 1).¹⁹

The nomenclature for these PBIs is dictated by the alkylation pattern on the (3,4,5)-minidendron, using *r* to denote the *r* chain and *n* to denote a linear *n*-alkyl, C_nH_{2n+1} , where *n* = 6, 7, 9, or 10. This functionalization pattern, or sequence of alkyl chains on the dendron periphery, is uniquely defined during synthesis. Sequence-defined dendrons **5** were prepared from either symmetrically protected methyl gallate derivative **2** (for *rrn*-

and *nrn*-PBI) or its asymmetrically protected analogue **6** (for *rrn*- and *nrn*-PBI). These four sequences should not be interconverted just like in the case of proteins and are independent of each other irrespective of dendron rotation. Alkylation with an initial alkyl chain, followed by deprotection and a second alkylation, provided dendrons **5**. Functional group manipulation of the benzyl esters **5** to benzyl amines **12**, and subsequent imidation of perylene tetracarboxylic dianhydride (PTCDA) per procedures elaborated in our laboratory,^{20a} gave PBIs with sequence-defined dendrons (Figures S1–S48).

The Discovery of the Extraordinary Acceleration of the Cogwheel Self-Organization. The thermal analysis of the 16 PBIs with hybrid dendrons (*n* = 6, 7, 9, 10), as well as fully racemic *rrr*-PBI, fully linear *nnn*-PBI (*n* = 6–10),^{20c} and hybrid *rac*-dm8*/*n*-octyl dendrons,¹⁹ was determined by DSC (Figures 2, 3, and S49–S57 and Supporting Table ST1).

Phases were assigned by XRD and will be discussed later. Whereas the cogwheel Φ_h^{k2} phase was observed for all four hybrid PBIs with *n*-octyl chains upon both heating and cooling (Figures S51 and S56), changing the length of the alkyl chain to *n* = 6, 7, or 10 eliminates the Φ_h^{k2} phase from all hybrid dendron sequences except *rrn*-PBI, for which Φ_h^{k2} is observed only upon heating (Figures S49, S50, and S53). Changing the alkyl chain to *n*-nonyl also generates the Φ_h^{k2} cogwheel phase in *rr9*-PBI and in *9r9*-PBI (Figures 2 and S52). This observation suggests that (1) there is something inherent in the *rrn*-sequence that tolerates different alkyl chain lengths, and (2) alkyl chains that

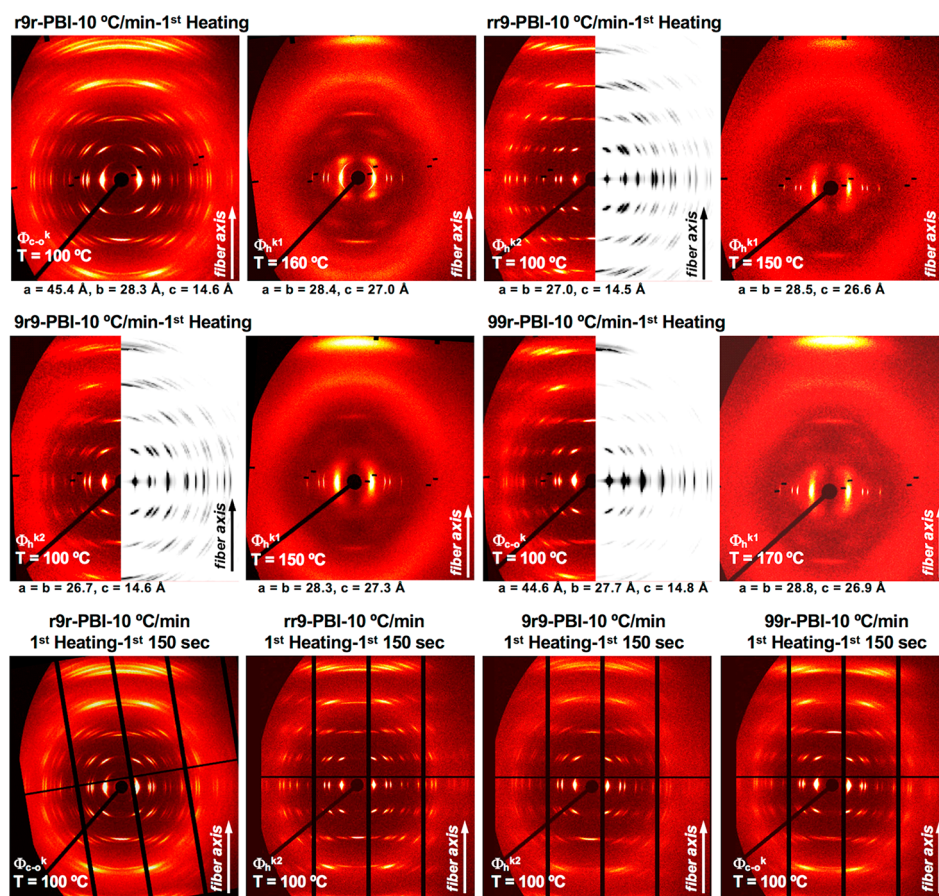


Figure 4. Fiber XRD of 9r9-PBI assemblies measured upon heating and cooling at 10 °C/min (red scale, left) and XRD simulated from the models in Figure 5 (gray scale, right). Phases, lattice parameters, and temperatures (in °C) are indicated. The time employed to record each XRD is 5 min. The 5 min scan consists of two 2.5 min XRD scans. In a single 2.5 min scan, gaps between eight individual panels in the detector (Pilatus 1M, Dectris) are recorded as black stripes with no data. The detector is moved for a subsequent 2.5 min scan, which collects data in the previously unrecorded areas. The combination of the two 2.5 min scans provides a 5 min scan in which the black stripes are mostly eliminated.

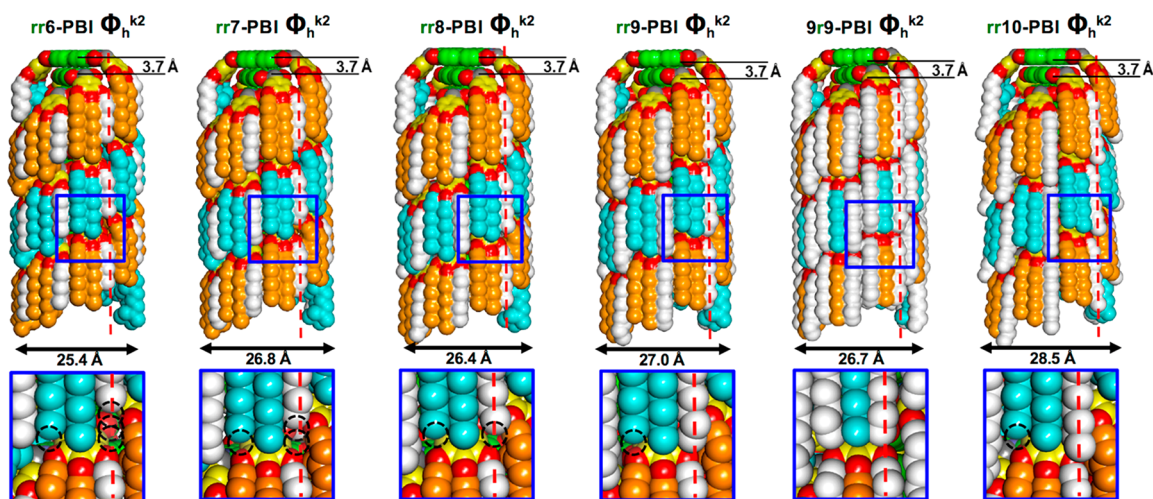


Figure 5. Models of the cogwheel columns of Φ_h^{k2} self-organized from rr6-, rr7-, rr8-, rr9-, 9r9-, and rr10-PBI. Intramolecular spacing and column diameter are indicated. Insets illustrate the space filling by the alkyl ends from the 3- and 5-positions of the dendron as a function of their length and sequence. Dashed circles in insets indicate empty space on the column periphery.

are 8 or 9 carbons in linear length (i.e., dimethyloctyl, *n*-octyl, and *n*-nonyl) are best tolerated by the cogwheel model in other dendron sequences.

The DSC traces of *rrn*-PBI (*n* = 6–9; Figures S49–S52) all exhibit an endothermic peak at about 140 °C upon heating,

assigned to the first-order transition from the cogwheel Φ_h^{k2} phase to a lower order columnar hexagonal phase, Φ_h^{k1} (Figure 1b, left). A corresponding exothermic crystallization peak upon cooling is not observed, suggesting that crystallization into the Φ_h^{k2} phase is a continuous, very slow process occurring under

kinetic control. By contrast, the DSC trace of **9r9-PBI** upon cooling (Figures 2 and S52) shows a distinct crystallization exotherm at 107 °C, suggesting that the transition from low-order Φ_h^{k1} to high-order cogwheel Φ_h^{k2} is well-defined, even upon fast cooling (10 °C/min).

To probe the kinetics of the Φ_h^{k1} – Φ_h^{k2} transition in **9r9-PBI**-based assemblies, DSC traces were measured at rates from 10 to 50 °C/min (Figure 3). Unexpectedly, a discrete exothermic crystallization peak is observed at the transition between Φ_h^{k1} and Φ_h^{k2} upon cooling at all rates. The enthalpy of the transition (1.04 kcal/mol) does not vary for cooling rates from 20 to 50 °C/min, although the transition temperature decreases from 103 °C at 20 °C/min to 96 °C/min at 50 °C/min. It should be noted that 11 °C of extra supercooling necessary to form the Φ_h^{k2} phase at 50 vs 10 °C/min (compare T_{onset} of 96 and 107 °C) represents only a 15 s delay in the onset of the phase transition at 50 °C/min. These data suggest that the Φ_h^{k1} – Φ_h^{k2} transition for **9r9-PBI** assemblies was extraordinarily accelerated and is much faster than has been observed for any other cogwheel assembly including homochiral.

Structural and Retrostructural Analysis by XRD Confirms High-Order Helical Cogwheel Assembly Irrespective of Rate. The phases annotated on all DSC traces were determined by XRD of oriented fibers.^{25,26} Fiber XRD diffractograms for PBIs with hybrid *r/n*-nonyl dendrons are shown in Figure 4. In each case, a higher order phase is observed at low temperature (columnar centered orthorhombic, Φ_{c-o}^k , for **r9r**- and **99r-PBI**; cogwheel Φ_h^{k2} for **rr9**- and **9r9-PBI**), and the lower order Φ_h^{k1} phase is observed at higher temperature (Supporting Tables ST2–ST4). The XRD data for **rr9**- and **9r9-PBI** are both consistent with the cogwheel Φ_h^{k2} and lower order Φ_h^{k1} phases observed previously.^{18,19}

Reconstruction of the XRD by the molecular models depicted in Figure 5 support the description of the higher order phases as cogwheel phases (Figure 4, grayscale images on right). The Φ_{c-o}^k phase observed for **r9r**- and **99r-PBI** is a pseudohexagonal phase that represents a distortion of a hexagonal array along the *a*- or *b*-direction of the unit cell. The ratio of *b/a* for a Φ_{c-o}^k unit cell that is equivalent to a perfect Φ_h^k cell would be 1.73 (= $\sqrt{3}$). For **r9r**- and **99r-PBI** this ratio is 1.60 and 1.61, respectively, suggesting a consistent deviation from a hexagonal array as dictated by the cogwheel model. However, the high number of sharp, bright off-axis features supports a high degree of order in these Φ_{c-o}^k arrays rivaling that of the cogwheel phase.

To correlate the DSC traces from Figure 3 with the structure of **9r9-PBI**, diffractograms of the cogwheel Φ_h^{k2} phase were measured at 100 °C upon first heating and cooling at rates of 10 to 40 °C/min (Figure S58). The XRD data shown in Figure 4 were recorded at 100 °C, heated at 10 °C/min, and with 2 × 2.5 min recording time. The time it takes to record XRD patterns with reasonable signal/noise ratio means that we were not able to monitor the formation of the Φ_h^{k2} phase in real time by XRD at high heating/cooling rates. However, pleasingly, near-identical XRD patterns are observed at 100 °C, irrespective of heating and cooling rate (Figure S58). This demonstrates the extraordinary acceleration of the formation of the cogwheel Φ_h^{k2} of **9r9-PBI**.

To illustrate the practical implication of this rate acceleration, we consider how long it would take to obtain a macroscopic fiber of the cogwheel Φ_h^{k2} phase of **rrr-PBI**,¹⁸ **rr8-PBI**,¹⁹ and **9r9-PBI** at 25 °C. Starting with a freshly extruded macroscopic fiber at 25 °C, **rrr**- and **rr8-PBI** require heating to 100 °C (i.e., 7.5 min at 10 °C/min), followed by annealing for 3 h and 30 min,

respectively. After cooling to 25 °C at 10 °C/min (7.5 min), fibers of Φ_h^{k2} would have been prepared in ~3 h and 15 min for **rrr-PBI** and ~45 min for **rr8-PBI**. In contrast, Figure 4 shows that **9r9-PBI** transforms into Φ_h^{k2} within 150 s at 100 °C. Therefore, including heating and cooling at 50 °C/min (90 s between 25 and 100 °C) the total time is only 330 s, i.e., 5.5 min. Reducing the processing time from over 3 h for **rrr-PBI**¹⁸ to ~5 min for **9r9-PBI** represents substantial time savings that demonstrate how molecular design can affect both fundamentally and industrially relevant time-saving material parameters.

Structural Basis for Accelerated Cogwheel Formation in Assemblies of 9r9-PBI. To gain insight into the structural basis for the rapid formation of the cogwheel Φ_h^{k2} by **9r9-PBI**, molecular models of supramolecular assemblies were generated using an iterative methodology described previously.^{26,27} Diffraction features and lattice parameters were determined from fiber XRD data using Datasqueeze²⁸ and analyzed using helical diffraction theory.^{2a,26,29} An initial molecular model consistent both with XRD data and with the experimental density of the macroscopic fiber was constructed using Accelrys Materials Studio software (version 5.0).^{17c,26} Geometry optimization was performed using the VAMP module. The fiber XRD pattern expected from this model was simulated using Accelrys Cerius2 run on a Silicon Graphics (SGI) Tezro workstation.^{11,17c} The simulated and experimental XRD patterns were compared,¹¹ the molecular model was refined, and the XRD pattern was simulated again. This iterative process continued until the level of agreement between simulated and experimental XRD patterns was agreeable and no substantial improvement was observed upon further iteration.

Models of Φ_h^{k2} phases observed in **rrn-PBI** (*n* = 6–10) and **9r9-PBI** reveal subtle differences in the alkyl chain periphery of their supramolecular columns (Figure 5). The column diameters of **rrn-PBI** generally increase with increasing linear alkyl chain length, from 25.4 Å (**rr6-PBI**) to 28.5 Å (**rr10-PBI**). The diameter of ultrafast **9r9-PBI** (26.7 Å) lies between that of **rr8**- (26.4 Å) and **rr9-PBI** (27.0 Å), suggesting that this diameter falls within a particularly preferable range accessible only to hybrids of *r* with *n*-octyl and *n*-nonyl chains. In all cases, the intracolumnar π – π distance is 3.7 Å.

One of the key requirements of the cogwheel model (Figure 1d) is the alkyl chain coat length being almost equal to the helical half-pitch of 14.8 Å (= 4 × 3.7 Å). Both previous studies of the cogwheel model have utilized homochiral dm8*¹⁸ or dm8* (*r*)-*n*-octyl hybrids,¹⁹ with a linear length of 8 carbons. This length forms a coat that almost covers the entire column periphery, leaving small gaps between the end of the alkyl chains of the *i*th molecule without steric hindrance from the (*i* + 4)th molecule in the column (see inset for **rr8-PBI** in Figure 5). Shorter alkyl chains do not adequately cover the column exterior (see inset for **rr6-PBI** and dashed circular marks denoting empty space in Figure 5), whereas longer alkyl chains lead to steric hindrance and an unfavorable tilting of the alkyl chain away from the column axis (such as for **rr10-PBI**). The small degree of unoccupied space in *r/n*-octyl hybrids is sufficient to accommodate a ninth carbon in the alkyl chain without significant steric penalties; hence **rr9**- and especially **9r9-PBI** most efficiently fill the column periphery with aliphatic chains. A close inspection of the structures of the cogwheel columns of **rr9**- and **9r9-PBI** (Figure 5) demonstrates a perfect tertiary structure for **9r9-PBI** assembly and a small imperfection in the column derived from **rr9-PBI** (see dashed circle in the 3-position) due to the shorter *r* group at the 3-position of the

dendron. Therefore, the ideal place for the *r* group is in the 4-position of the dendron, while the ideal places for the *g* groups are in the 3- and 5-positions. This conclusion is also supported by solid-state NMR experiments to be discussed in a later subsection. The $\Phi_h^{k1}-\Phi_h^{k2}$ transitions are observed on heating and cooling for **9r9-PBI** and are present irrespective of the heating and cooling rate (Figure 3b). However, **rr9-PBI** assembly does not show the first-order transition on cooling at 107 °C that the **9r9-PBI** assembly shows (Figure 2) upon cooling at 10 °C/min. It is tempting to attribute such observations to the perfect **9r9-PBI** sequence that provides the ideal tertiary structure. However, DSC studies of **rr9-PBI** and **9r9-PBI** (Figure 2) provide near-identical $\Phi_h^{k1}-\Phi_h^{k2}$ transition temperatures (136 and 137 °C, respectively) and enthalpies (1.40 and 1.42 kcal/mol) upon heating, suggesting that the thermodynamic driving force for Φ_h^{k2} formation is very close for **rr9-PBI** and **9r9-PBI**. Since the rate of formation of the Φ_h^{k2} phase transition is almost independent of the heating and cooling rate (Figure 3 and Figure 4), we can conclude that the formation of a cogwheel assembly in **9r9-PBI** is extraordinarily accelerated versus that of **rr9-PBI**, and all other sequence-defined assemblies, although both assemblies have almost identical thermodynamic driving forces (*vide infra*, Figure 2). Hence the observed difference in the rate of Φ_h^{k2} formation must be due to kinetic effects.

We propose that the $\Phi_h^{k1}-\Phi_h^{k2}$ transition is so fast in **9r9-PBI** because there are many more local fluctuations of the favorable cogwheel Φ_h^{k2} structure within the Φ_h^{k1} phase below, and perhaps even above, the transition temperature, compared to **rr9-PBI**. Due to the increased degree of branching in **rr9-PBI**, such fluctuations are expected to have higher free energy and thus are less favorable. This is linked to the higher entropy that involves disorder, and hence mobility, of the linear chains compared to branched ones.³⁰ More Φ_h^{k2} fluctuations increase the probability that a fluctuation reaches critical nucleus size, thereby dramatically accelerating the nucleation of the Φ_h^{k2} and leading to an extraordinarily accelerated rate of self-organization and crystallization. The lack of cogwheel phases in PBIs dendronized with all *n*-alkyl chains^{20c} suggests that the methyl branch of the *r* chain is required for cogwheel packing, and the ideal length and position of the *n*-nonyl chains in **9r9-PBI** unpredictably lead to the formation of the cogwheel phase being kinetically accessible even at very fast heating and cooling rates.

Solid-State NMR Probes Distribution of Local Chain Conformations and Molecular Fluctuations. The formation of columnar arrays with long-range order is affected not only by the $\pi-\pi$ stacking of the PBI cores but also by the local conformations of the aliphatic side chains, in particular if the volume locally available for molecular fluctuations changes in amount or shape. Solid-state ¹³C NMR chemical shifts are very sensitive to local intracolumnar packing arrangements, acting as probes for local conformational distributions¹² and thus nicely augmenting the information available from XRD and DSC. ¹³C cross-polarization magic angle spinning (CP-MAS) experiments on hybrid PBIs with *r/n*-nonyl dendrons show that the conformational distribution is largely determined by the attachment site at the phenyl ring (Figure 6).

Dimethyloctyl (*r*) chains in the 3- and 5-positions (Figure 6a) show a broad chemical shift distribution resulting from a broad conformational distribution of the CH₂ groups next to the chiral center (green) and the chiral methyl group (yellow), whereas *r* chains in the 4-position (**9r9-PBI** spectrum in Figure 6b) exhibit sharp peaks for those sites. The narrower conformational

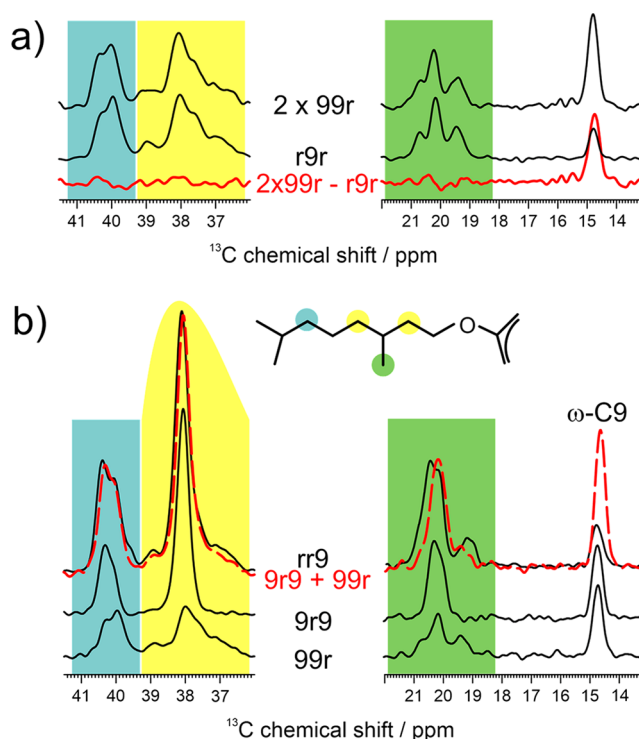


Figure 6. ¹³C CP-MAS NMR spectra of hybrid PBIs with dm8*/*n*-nonyl dendrons. (a) The NMR spectra of **99r**- and **r9r**-PBI differ only at the 14.7 ppm signal assigned to the chain end of the linear *n*-nonyl chains, as seen in the red difference spectrum. (b) Superimposing the NMR spectra of dm8* chains in *meta*- (**99r**-PBI) and *para*-position (**9r9**-PBI) provides the NMR spectrum for **rr9**-PBI for the main chain sites (yellow and blue). Green region denotes the chiral methyl group.

distribution of 4- vs 3- or 5-*r* chains is hardly affected by neighboring chains (Figure 6b), general for all hybrid *r/n*-alkyl dendrons with *n* = 6–10 (Figure S60), and invariant to temperature (Figure S61). In addition, the sum spectrum of **9r9**- and **99r**-PBI (broken red line, Figure 6b) is significantly narrower in the region of the chiral methyl group (green) than **rr9**-PBI (solid black line). This suggests a higher local mobility of the chiral methyl groups in **9r9**- and **99r**-PBI, more efficiently averaging different packing arrangements of the methyl group within the supramolecular column. This higher local mobility may be aided by the presence of two, more dynamic, linear *n*-nonyl chains in **9r9**- and **99r**-PBI compared to the single *n*-nonyl chain in **rr9**-PBI.

General Design Principles for Cogwheel Assembly beyond the Current System. The discovery of ultrafast cogwheel assembly for **9r9**-PBI enhances our understanding of the role of alkyl chain design in the cogwheel mechanism of self-assembly. This mechanism provides a route to highly ordered arrays of homochiral helical supramolecular columns irrespective of molecular chirality, a structure of potential interest for numerous applications and fundamental studies on complex systems. To date, this model has been demonstrated only with dendronized PBIs, but cogwheel assembly is applicable to a broader range of molecular cores.

To facilitate this process, we propose three criteria that must be satisfied for cogwheel assembly (Figure 7). The acceleration of cogwheel formation for **9r9**-PBI demonstrates that complete space-filling is needed to achieve the kinetically most favorable crystallization. First, the length of the alkyl chain coat jacketing the supramolecular column must match the helical half-pitch

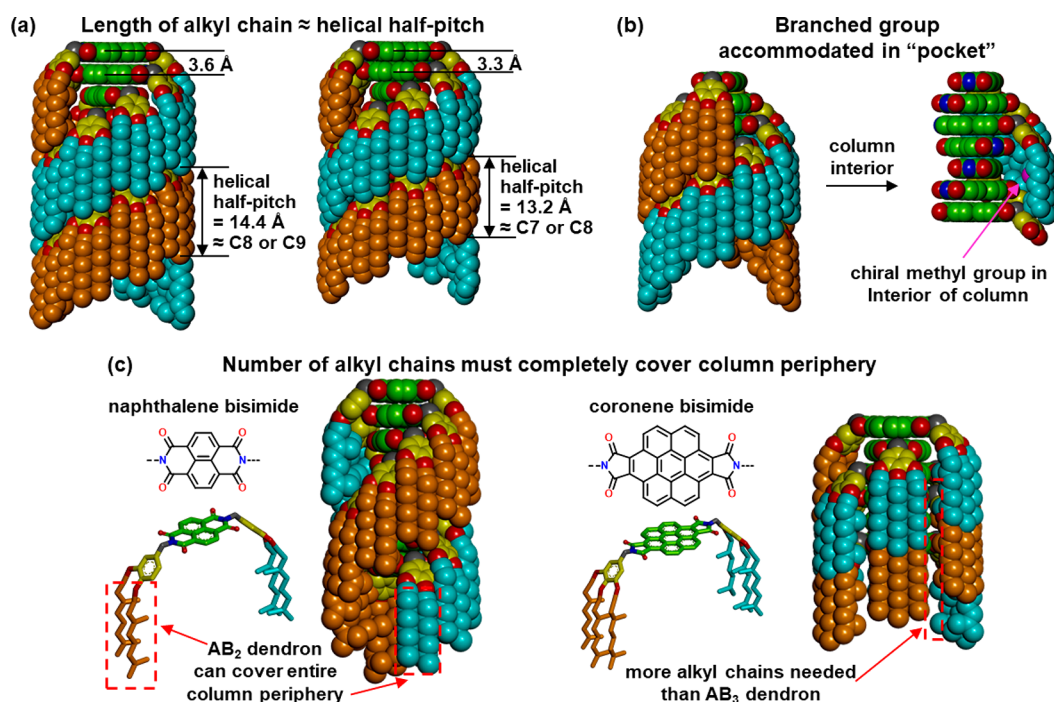


Figure 7. Design principles for the translation of the cogwheel model to other systems. (a) The length of the alkyl chain must match the helical half-pitch, which is dictated by intermolecular π – π stacking distance. (b) There must be a “pocket” of available space in which the branch group (i.e., a chiral methyl group in dm8*) can be accommodated. (c) The alkyl chain jacket on the column periphery must be continuous. (Left) Cores smaller than PBI, e.g., naphthalene bisimide, need fewer alkyl chains for complete jacketing, whereas (right) cores larger than PBI, e.g., coronene bisimide, need more alkyl chains.

and, most preferably, completely fill all available space on the column exterior. Molecules of **9r9-PBI** are stacked with a π – π distance of 3.6 Å, giving a helical half-pitch of 14.4 Å ($= 4 \times 3.6$ Å, Figure 7a). The shortest distance for close-contact planar aromatic cores is 3.3 Å³¹ (i.e., helical half-pitch of 13.2 Å), corresponding to an ideal alkyl chain length of between 7 and 8 carbons (Figure 7a). In contrast, increasing the spacing between aromatic cores, such as with nonplanar 1,6,7,12-tetrachloroperylene bisimide (Cl₄-PBI),³² would require a longer alkyl chain to cover the column exterior.

The second criterion, established previously,¹⁹ is that the minidendron must contain at least one branched alkyl chain to prevent column interdigitation with alkyl tails being perpendicular rather than parallel to the long axis of the column. The methyl branch in **9r9-PBI** is accommodated in a pocket defined by adjacent PBIs in the supramolecular column (Figure 7b). Most likely, the cogwheel model will tolerate alternative branching point positions, if space is available to accommodate the chiral group without disrupting the column periphery. Geometric considerations suggest that the methyl group should be closer to the dendron phenyl ring rather than the free end of the alkyl chain.

Finally, the number of alkyl chains must be modified to fill the entire periphery of the column for different core sizes, to account for differences in column diameter and intermolecular rotation. This intermolecular rotation, and thus helical pitch, will vary depending on size and shape of the aromatic core; for the current PBIs, 45° is favorable (Figure 1b). A compound with a different aromatic core may have a different minimum energy rotation angle that would favor a helix with a different pitch. It is then necessary to match both the length and the number of the pendant chains to the half-pitch of that helix. For example (Figure 7c), smaller cores (e.g., naphthalene bisimide,³³ NBI)

may require fewer, longer alkyl chains than **9r9-PBI**, whereas larger cores (e.g., coronenes³⁴) may require more, potentially shorter chains. Dendrons provide a particularly powerful tool to precisely modulate alkyl chain number and length, ranging from AB₂ to AB₅ in a single dendron generation.³⁵ Higher numbers of alkyl chains may require multigeneration dendron designs^{22a–d} or new methodologies to program first-degeneration AB_{*n*} self-assembling dendrons with *n* larger than 3.

CONCLUSIONS

Taken together, the combination of DSC, XRD, and solid-state NMR presented here suggests that the extraordinary acceleration of the self-organization of the cogwheel Φ_h^{k2} phase in **9r9-PBI** is a result of both favorable crystal packing and local chain dynamics. The results show that even just one branched chain out of three on a dendron is sufficient to disfavor intercolumnar interdigitation and instead favor axial chain alignment. The second condition for cogwheel assembly is matching the chain length to the half-pitch length of the helix. DSC and XRD (Figures 2–4 and S49–S57) suggest that the optimal chain length satisfying this condition is 8 and especially 9 carbons. More specifically, molecular modeling and reconstruction of fiber XRD by molecular models (Figures 4 and 5) indicate that the periphery of the supramolecular column is incompletely filled by linear and branched octyl chains, but that incorporation of *n*-nonyl chains can be tolerated and leads to better occupation of the aliphatic column periphery. Hence a mixture of **r** and **9** best in **9r9** sequence is most favorable for filling space within the crystalline assemblies of the cogwheel Φ_h^{k2} phase. Solid-state NMR (Figure 6) has further demonstrated a higher mobility of linear compared to the branched chains, supporting the increased Φ_h^{k1} – Φ_h^{k2} transition rate of **9r9**- and **99r-PBI** compared to that of **rr9**- and **r9r-PBI**.

NMR results also show that the presence of an **r** chain in the 4-position of the (3,4,5)-minidendron experiences a narrower distribution of conformations within the columnar array, likely indicating that the tertiary structure necessary for the cogwheel model is preferentially accessible to dendrons with 4-**r** substitution. Therefore, the **9r9** sequence represents the ideal dendron to cover the column periphery, enabling rapid formation of the highly ordered Φ_h^{k2} crystal. To the best of our knowledge the formation of the Φ_h^{k2} crystal represents the fastest self-organizing and crystallizing supramolecular or covalent natural or synthetic macromolecule known to date. This substantial acceleration in self-organization could not be predicted, neither from our previous knowledge of the cogwheel model nor from our preliminary experiments reported in the previous communication.¹⁹

These insights provide design guidelines for highly ordered, self-healing, and rapidly forming columnar structures, properties that are highly desirable in stable, fast-switching, fast-forming, and thermoresponsive defect-free functional materials. The methodology described here, relying on not just XRD but also DSC and solid-state NMR, may bring new insights for other complex soft matter.³⁶ Indeed, the presently employed *n*-semiconducting PBI core¹⁶ is only one option (Figure 7), replaceable with other core moieties forming similar Φ_h^{k2} -type structures. The precise design of aliphatic chains may have relevance not just for the directed supramolecular assembly of columnar assemblies but also for even more complex assemblies self-organized from spheres such as the Frank–Kasper phases assembled from supramolecular dendrimers and from self-organizable dendronized polymers,³⁷ and as synthetic cells generated from amphiphilic including sequence-defined Janus-dendrimers and Janus-glycodendrimers.^{24,38}

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c03353>.

Experimental methods, synthetic procedures with complete characterization data, structural and thermal analysis parameters, additional DSC, XRD, and solid-state NMR data, and associated discussion (PDF)

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Notes

The authors declare no competing financial interest.

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