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A Supramolecular Helix that Disregards Chirality

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Functions of complex crystalline systems derived from natural and synthetic macromolecules emerge from homochiral programmed primary structures via first principles involving secondary, tertiary and quaternary structures. Heterochiral and racemic compounds yield disordered crystals, amorphous solids or liquids. Supramolecular biological and nonbiological assemblies follow the same principles. Here we report the self-organization of a supramolecular helix that forms columnar hexagonal crystals with similar precision to biological systems. This high crystalline order is generated via a cogwheel mechanism that disregards the chirality of the self-assembling building blocks. We show that both homochiral and racemic compounds, including a mixture of 21 diastereomers that cannot be deracemized at the molecular level, self-organize to form single-handed helical assemblies with identical single crystal-like order. We anticipate that this new mechanism will facilitate access to previously inaccessible complex crystalline systems from racemic and homochiral building blocks.

The origin of biological homochirality remains a fundamental question of natural science,¹⁻⁵ even though the most advanced functions of biological and nonbiological systems emerge from homochiral primary structures. Classic examples are the helical structure of proteins,⁶ carbohydrates,⁷ isotactic polypropylene,^{8,9} carbon nanotubes¹⁰⁻¹² and the double helix of DNA.¹³⁻¹⁵ These secondary structures, together with other local conformations, are responsible for the creation of tertiary and quaternary crystalline structures^{15,16} and functions. Heterochiral primary structures such as syndiotactic polypropylene^{8,17} yield lower order crystals than their homochiral counterparts while racemic or atactic polymers generate amorphous solids or liquids.⁸ Since Pasteur's seminal experiment,¹⁸ chiral self-sorting, or spontaneous deracemization, of conglomerates during crystallization from solution¹⁸⁻²⁵ has been employed to generate homochirality at the single crystal

1 scale but not at the macroscopic level. This was demonstrated by conglomerates having lower melting
2 points than crystals of the corresponding pure enantiomers.²¹ Spontaneous deracemization of helical
3 assemblies produced from achiral molecules in thermotropic liquid crystals translated deracemization from
4 solution^{18–25} to bulk liquid crystal state.^{26–28} This advance enabled access to monodomains of
5 enantiomerically pure liquid crystals by spontaneous deracemization in melt liquid crystal states.^{26–28} The
6 same homochiral principles have been demonstrated during self-organization of supramolecular biological
7 assemblies, such as tobacco mosaic virus,^{29,30} and non-biological assemblies.^{31–41} A study of all
8 stereochemical permutations of self-assembling dendritic dipeptides, including homochiral, heterochiral
9 and various racemic variants in solution and bulk state, demonstrated that the highest degree of
10 stereochemical purity, enantiopure homochiral, exhibited the most thermodynamically favored self-
11 assembly process in solution, corresponding to the greatest degree of order in the crystal state.^{31–34} These
12 results showed that enantiomerically rich, racemic and achiral assemblies may undergo deracemization
13 even in sufficiently mobile crystal states, when the transfer of a molecule between neighboring assemblies
14 is thermodynamically and kinetically allowed. Supramolecular assemblies of dendritic dipeptides held
15 together via strong noncovalent interactions approaching the strength of a covalent bond precluded
16 deracemization due to prohibited disassembly.³² Therefore, their homochiral assemblies could crystallize
17 while their racemic assemblies could not.³² A recent study of the self-assembly of a family of weakly
18 interacting, dynamic cyclotrimeratrylene crowns substituted with 12 branched alkyl chains of various chiral
19 compositions demonstrated the first example of deracemization in the crystalline state.²¹ The driving force
20 for deracemization was formation of a columnar hexagonal crystal, whose lattice symmetry demands
21 identical single-handed helical columns in a crystal lattice whose unit cell contains fragments of four
22 separate columns representing a single column.²¹ This was possible due to the weak supramolecular
23 interactions between crowns. Homochiral and “racemic by mixture” samples were shown to deracemize at
24 the molecular level to generate crystalline order after annealing. However, a “racemic by synthesis” sample,
25 which intrinsically cannot deracemize at the molecular level, was unable to generate high crystalline order
26 and instead yielded poorly ordered columnar hexagonal crystals upon deracemization, with a much lower
27 melting temperature than the corresponding enantiopure forms.²¹ This study also demonstrated that
28 deracemization at the supramolecular level occurs between enantiomerically pure or enantiomerically rich
29 supramolecular columns rather than within a column.

30 Here we report the discovery of a family of perylene bisimide (PBI) derivatives containing six chiral side
31 chains in various stereochemical permutations including homochiral, “racemic by mixing” and “racemic by
32 synthesis” that self-assembles into single-handed supramolecular columns to yield identical single-handed
33 columnar hexagonal crystalline domains likely due to deracemization at the molecular and supramolecular

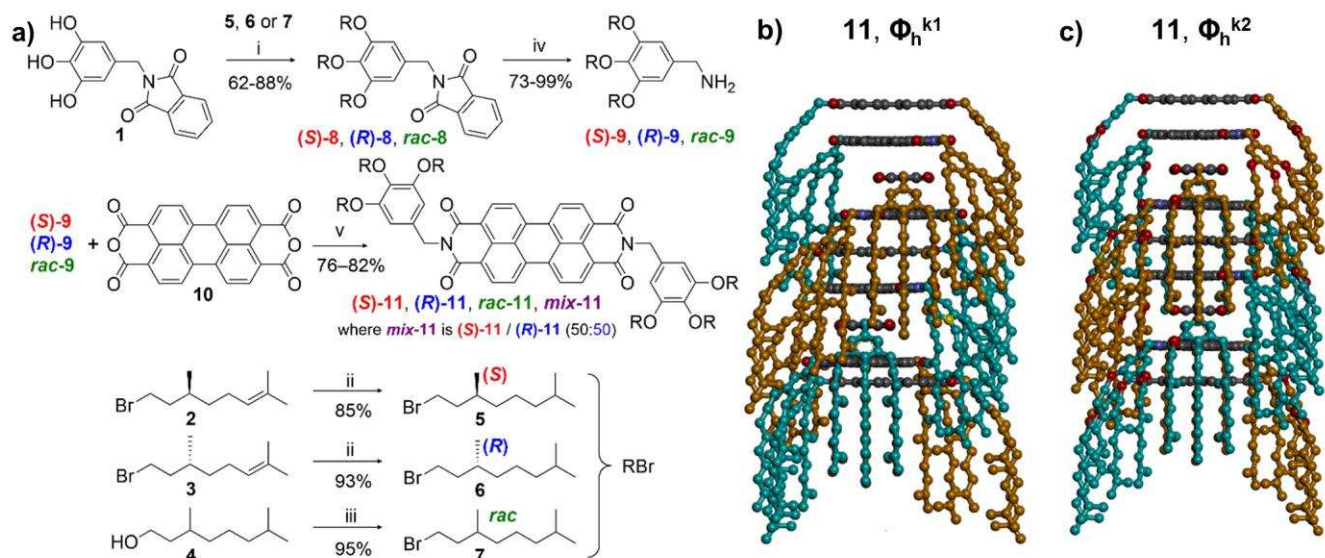
1 levels, irrespective of chiral composition. A cogwheel model of crystallization was proposed to facilitate
2 this process and to explain the very high degree of order even at the interface between single-handed
3 crystalline monodomains. A library of chiral PBI derivatives was screened in order to discover the
4 compounds reported here. This cogwheel mechanism responsible for the generation of single crystal-like
5 order from racemic compounds is expected to enable prediction of libraries of building blocks that follow
6 the same self-organization principles, via the design of other self-assembling molecules with structural
7 parameters congruent with the present PBI derivatives.

8 **Results and Discussion**

9 **Synthesis of building blocks and their self-organization in bulk.** The synthesis of four PBI derivatives
10 substituted with two identical benzyl rings bearing three chiral dimethyloctyloxy chains in either
11 enantiopure ((**R**)-**11** and (**S**)-**11**) or racemic form (**rac-11** and **mix-11**) is outlined in Fig. 1a. The two helical
12 models of the supramolecular columns formed by **11** are shown in Fig. 1b, c (Supporting Sections S19 and
13 S20). An overview of previously reported helical assemblies of PBI is in Supplementary Section S4.

14 The length of the dimethyloctyl chains and the alkyl spacer between PBI and benzyl ring were selected to
15 achieve a thermodynamically controlled crystallization of their assemblies as discovered previously with
16 linear achiral alkyloxy groups.⁴² (**S**)-**8** and (**R**)-**8** are enantiomerically pure, whereas the racemic **rac-8** is a
17 mixture of 6 diastereomers with different chiralities of the side chains at the 3-, 4- and 5-positions of the
18 benzyl ring. Consequently, (**S**)-**11** and (**R**)-**11** are enantiomerically pure, while **rac-11**, named also
19 “racemic by synthesis”, contains 21 diastereomers whose chirality is statistically scrambled. **rac-11** differs
20 from “racemic by mixing” **mix-11**, which is a 50:50 mixture of the homochiral enantiomers (**S**)-**11** and
21 (**R**)-**11**.

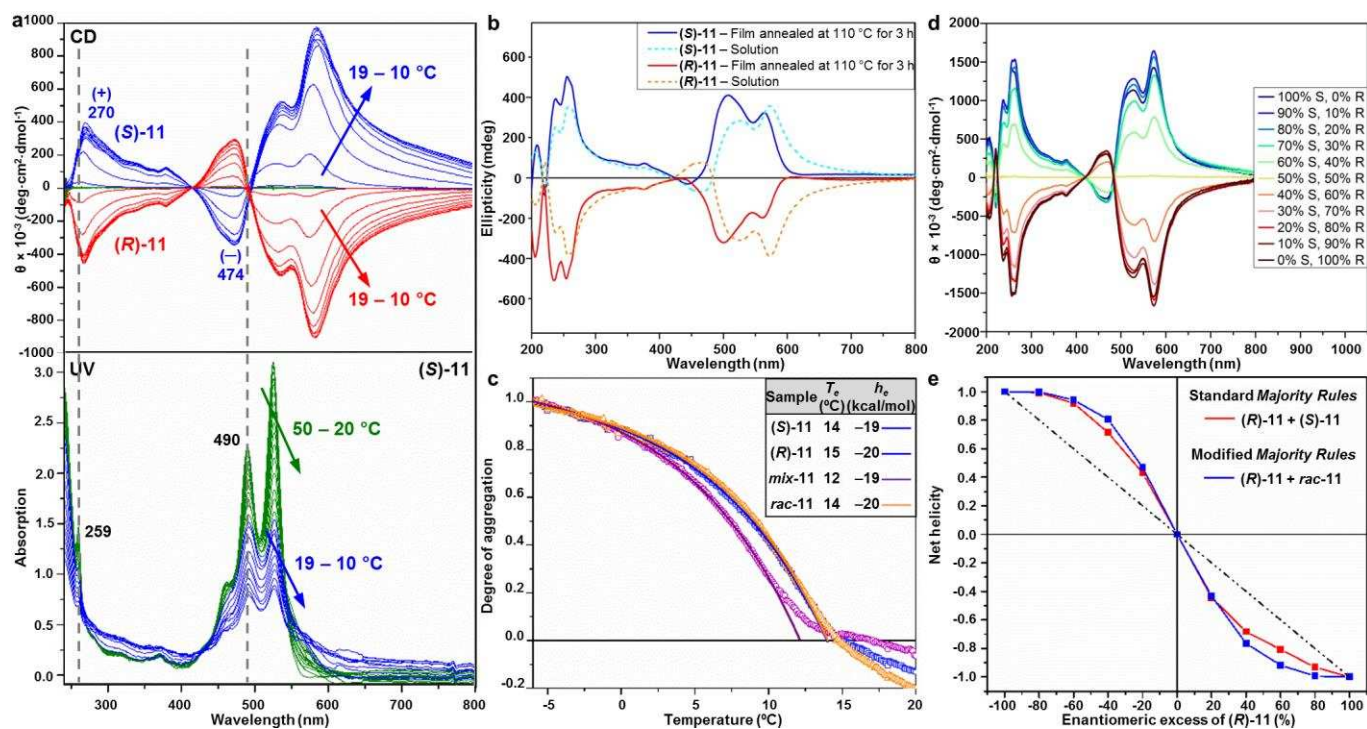
22 Differential scanning calorimetry (DSC) (Supplementary Fig. S2) combined with X-ray diffraction (XRD)
23 experiments (to be discussed later) demonstrated unexpected behavior of the assemblies obtained from the
24 enantiopure ((**S**)-**11**, (**R**)-**11**) and racemic (**rac-11**, **mix-11**) compounds. All assemblies exhibit a columnar
25 hexagonal crystalline phase, Φ_h^{k1} , formed under thermodynamic control,⁴² which melts at 200 °C with
26 almost no hysteresis; it crystallizes at 198 °C and 199 °C with cooling rates of 10 °C/min and 1 °C/min,
27 respectively. Low order Φ_h^{k1} is metastable at low temperature; high order Φ_h^{k2} , formed under kinetic
28 control, can be detected only by special thermal treatment such as (i) slow heating and reheating (1 °C/min)
29 via an exotherm at ~105 °C observed upon heating (Supplementary Figs S2 and S10), (ii) rapid heating (10
30 °C/min) followed by annealing at 110 °C for 3 h (Supplementary Fig. S2) or (iii) an extended period of
31 annealing at 23 °C (Supplementary Fig. S12). Upon heating, Φ_h^{k2} transforms into Φ_h^{k1} at 128–130 °C.



1
 2 **Figure 1. Synthesis and supramolecular structure of PBI derivatives.** a, Synthesis of chiral PBI
 3 derivatives **(S)-11** and **(R)-11**, “racemic by synthesis” **(rac)-11**, which is a statistical mixture of all possible
 4 diastereomers synthesized from racemic bromide **7**, and “racemic by mixing” **(mix)-11**, which is a 50:50
 5 mixture of the two enantiomers **(S)-11** and **(R)-11**. Reagents and conditions: (i) K_2CO_3 , DMF, 70 °C; (ii)
 6 H_2 , PtO_2 , EtOAc, 25 °C; (iii) HBr, H_2SO_4 (cat.), 120 °C; (iv) $NH_2NH_2 \cdot H_2O$, graphite, EtOH, reflux; (v)
 7 $Zn(OAc)_2 \cdot 2H_2O$, quinoline, 180 °C. **b**, **c**, Comparison of the helical structures of **b**, **11** in the low order
 8 Φ_h^{k1} phase and **c**, **11** in the high order Φ_h^{k2} phase. The supramolecular helix in the low order Φ_h^{k1}
 9 is slightly distorted, resulting in a wavy surface on the exterior of the supramolecular column. In contrast, the
 10 supramolecular columns in the high order Φ_h^{k2} phase are crystallographically perfect helices with a straight
 11 surface along the length of the column.

12 **Analysis of self-assembly in solution by CD and UV-vis.** Circular dichroism (CD) and UV-vis spectra of
 13 solutions of **(S)-11** and **(R)-11** in n-butanol/methylcyclohexane (85:15 v/v) recorded upon cooling from
 14 50 °C to 10 °C demonstrate that self-assembly of **11** proceeds via two distinct stages (Fig. 2a). In the first
 15 stage, from 50 °C to 20 °C, **(S)-11** and **(R)-11** are CD-silent. However, a significant decrease in the
 16 intensity of their UV-vis absorbance is observed. This suggests that **(S)-11** and **(R)-11** are molecularly
 17 dissolved at 50 °C and form short disordered stacks, such as dimers or trimers, upon cooling to 20 °C. The
 18 absence of Cotton effects between 50 °C and 20 °C excludes the formation of long, ordered helical
 19 assemblies. In the second stage, from 20 °C to 10 °C, an intense Cotton effect emerges in the CD spectra,
 20 evidencing the formation of an extended helical assembly (Fig. 2a, top). The spectra of **(S)-11** are mirror
 21 images of those of **(R)-11**, confirming that the chirality of the peripheral alkyl chains selects the handedness
 22 of the helical assemblies. The intense Cotton effects in the visible region confirm the transfer and
 23 amplification of chirality from the dimethyloctyl chains to the aromatic core of the assembly. The positive
 24 exciton coupling of **(R)-11** implies formation of a right-handed helix, while the negative exciton coupling
 25 of **(S)-11** indicates a left-handed helix (Supplementary Section S7). The first stage of self-assembly, from
 26 50 °C to 20 °C, observed only by UV-vis but not by CD, is associated with a nucleation process, while the

1 second part, from 20 °C to 10 °C, active in both CD and UV-vis, is associated with growth of the helix via
 2 a supramolecular helical polymerization mechanism.^{21,30,43–45} CD experiments in thin film and in solution
 3 (solid and broken lines, respectively, in Fig. 2b) indicate persistence of a similar helical structure in both
 4 states.

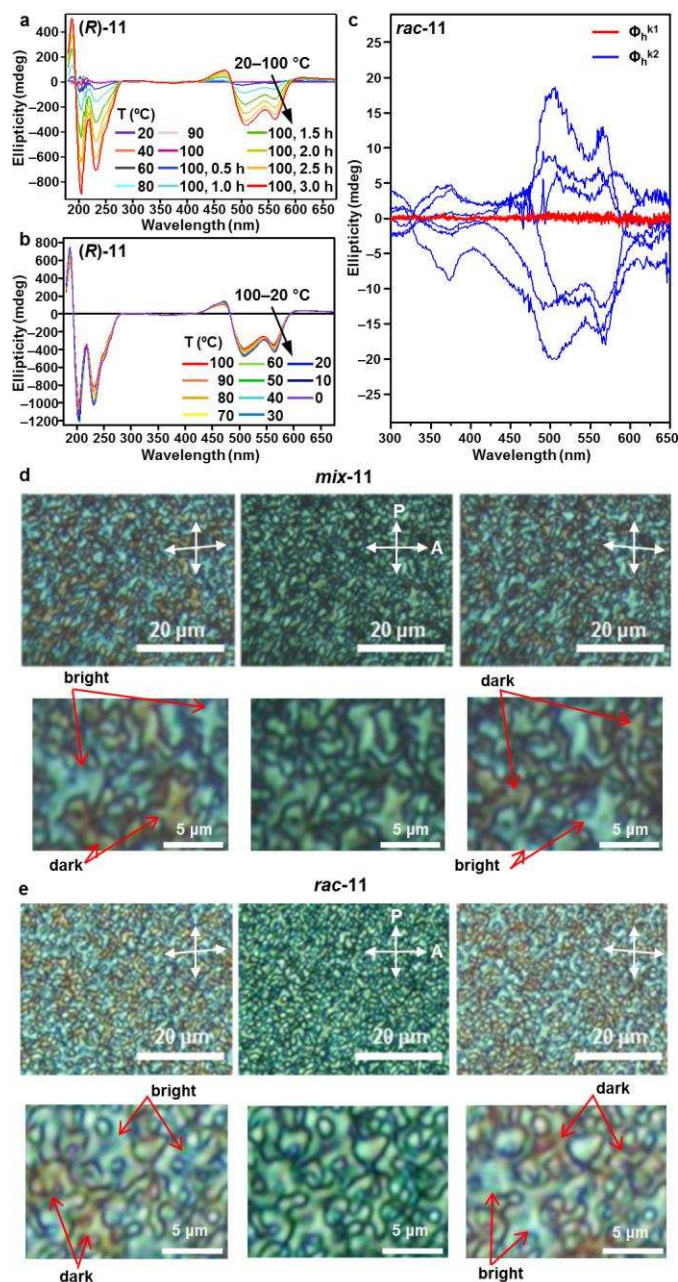


5 **Figure 2. Solution CD and UV-vis experiments.** a, Solution CD and UV-vis spectra of (S)-11 and (R)-11
 6 upon cooling. (S)-11: green (50 to 20 °C) and blue (19 to 10 °C); (R)-11: red (19 to 10 °C). UV spectra for
 7 (R)-11 and (S)-11 are identical. b, CD spectra of thin films (solid lines) of (S)-11 (blue) and (R)-11 (red)
 8 (collected at 23 °C). Solution spectra are also given (broken lines). c, Degree of aggregation of (S)-11
 9 (blue), (R)-11 omitted for clarity, mix-11 (purple), and rac-11 (orange) calculated from UV-vis data upon
 10 cooling, and fitting with the cooperative elongation model (solid lines). Calculated⁴⁶ values for the
 11 elongation enthalpy, h_e and elongation temperature, T_e are tabulated in the inset. d, e, Majority rules
 12 experiments; d, CD spectra collected from mixtures of (R)-11 and (S)-11. e, Net helicity dependence on the
 13 enantiomeric excess in mixtures of (R)-11 and (S)-11 (red) and (R)- or (S)-11 and rac-11 (blue). These
 14 experiments demonstrate not only that (R)-11 and (S)-11 generate supramolecular assemblies of opposite
 15 handedness in solution, but also that these structures show some disregard for chirality during self-
 16 assembly in solution.

18 Variable temperature CD/UV-vis experiments in solution performed on all variants of **11** demonstrate a
 19 cooperative nucleation mechanism for their helical supramolecular polymerization (Fig. 2c).^{21,30,32,34,43–45}
 20 Quantitative thermodynamic analysis from UV-vis data demonstrated, within experimental error, identical
 21 values for the elongation enthalpy, h_e , and elongation temperature, T_e , irrespective of enantiomeric
 22 composition (inset, Fig. 2c). The elongation enthalpy, h_e , represents the net enthalpy change upon
 23 elongation of the supramolecular column, while the elongation temperature, T_e , represents the temperature

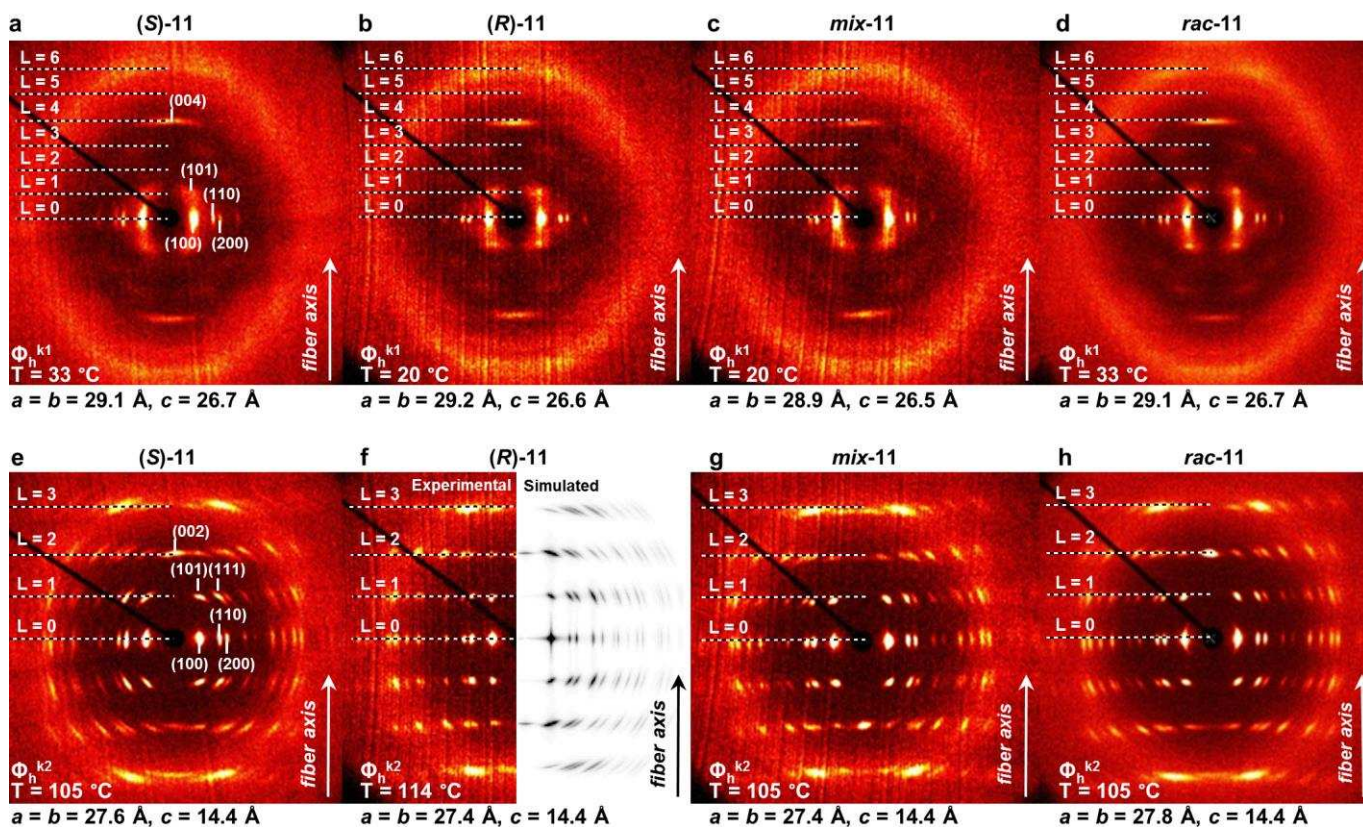
1 at which the nucleating assemblies begin to elongate to form extended helical segments.⁴⁶ The slightly
2 lower T_c of **mix-11** may be due to heterogeneous nucleation mediated by the mismatched enantiomer
3 impurity acting as a seed.³² The negative sign of h_e confirms that self-assembly is enthalpically driven.
4 These results agree with X-ray data (to be discussed later); which reveal identical structures in all cases and
5 suggest that the enthalpic energy gained by addition of a PBI molecule to the supramolecular structure is
6 almost invariant to the chirality of the molecule being added. In other words, addition of a matching or a
7 mismatching monomer to a helical column are similarly favorable and the calculated enthalpy is an average
8 value. The elongation enthalpy, h_e , should reflect the non-zero mismatch penalty (0.6 kcal/mol;
9 Supplementary Table S2) but experimental uncertainty in the value of h_e (± 1 kcal/mol) obscures its
10 influence. Therefore, in contrast to previous studies,²¹ h_e shows that the thermodynamic stability and the
11 supramolecular structure of homochiral and racemic compounds do not strongly depend, at least in
12 solution, on the enantiomeric purity of their side chains.

13 Majority rules experiments probe whether a system exhibits chiral amplification.^{21,24,32–34,47–49} In a system
14 with no chiral amplification, the net ellipticity of a mixture of two enantiomers changes linearly with
15 enantiomeric excess (Fig. 2e, broken black line). In contrast, a deviation from linearity suggests that the
16 enantiomer in excess has a disproportionate impact upon the handedness of the supramolecular assemblies
17 generated, as observed in majority rules experiments with **(R)-11** and **(S)-11** (Fig. 2e, red) and with **(R)-** or
18 **(S)-11** and **rac-11** (Fig. 2e, blue). This moderate non-linear effect suggests that—the enantiomers can co-
19 assemble into a single column in solution and that the majority enantiomer dictates the helical sense of the
20 column. The similarity of the deviation from linearity in both majority rules experiments suggests that
21 elongation of a helical column with a monomer of the non-preferred chirality is only slightly less
22 unfavorable for a monomer with all six stereocenters of the non-preferred chirality (i.e. **(R)-** or **(S)-11**) as it
23 is for a monomer with as little as one stereocenter of the non-preferred chirality (**rac-11**). Hence a disregard
24 for chirality is evident in the assembly of helical supramolecular columns in solution.



1
 2 **Figure 3. Thin film CD and optical polarized microscopy studies.** **a, b,** Thin film CD spectra of **(R)-11**
 3 during **a,** heating from 20 to 100 °C followed by annealing at 100 °C and **b,** cooling from 100 °C after
 4 annealing. **c,** Thin film micro-spot CD spectra of **rac-11** in the (red) Φ_h^{k1} and (blue) Φ_h^{k2} phases. Each
 5 spectrum was obtained from a different spot on the film at 23 °C. Thin film micro-spot CD spectra of
 6 racemic by mixing **mix-11** and enantiopure **(S)-** and **(R)-11** are in Supplementary Figs S7 and S8. **d, e,**
 7 Optical polarized micrographs of **d, mix-11** and **e, rac-11** in the Φ_h^{k2} phase, from the same films used for
 8 micro-spot CD. The analyzer was rotated $\pm 5^\circ$ from the crossed position in the right and left micrographs,
 9 respectively. Bright and dark areas (blue and brown, respectively) are indicated. The directions of polarizer
 10 (P) and analyzer (A) are shown denoted by arrows (top). The emergence of distinct positive and negative
 11 CD signals in a film of **rac-11** demonstrates segregation into microdomains of supramolecular columns of a
 12 single handedness. Optical polarized micrographs show these microdomains as distinct areas, the contrast
 13 of which changes from bright to dark, or vice versa, upon rotating an analyzer in different directions.

1 **Analysis of the self-assembly in bulk by CD, micro-spot CD and optical polarized microscopy.** The
2 helicity of assemblies in Φ_h^{k1} and Φ_h^{k2} was investigated in a thin film of **(R)-11** monitored by CD during
3 annealing (Fig. 3a, b). No Cotton effect was observed in the as prepared film at temperatures lower than
4 100 °C, indicating that assemblies in Φ_h^{k1} either have no well-defined handedness or exist as an equal
5 mixture of right- and left-handed columns (Fig. 3a). Heating and annealing at 100 °C transformed Φ_h^{k1} into
6 Φ_h^{k2} and the Cotton effect increased dramatically, demonstrating that assemblies in Φ_h^{k2} exhibit a well-
7 defined helical structure that is stable upon cooling to 20 °C (Fig. 3b). Neither **rac-11** nor **mix-11** exhibit a
8 CD signal in solution or in a thin film annealed under the same conditions as for **(R)-11**, suggesting that
9 both racemic samples contain a mixture of either an equal number of helical columns with opposite
10 handednesses (racemic between columns) or columns with a helix inversion and an equal amount of right-
11 and left-handed helical segments (racemic within a column). Micro-spot CD experiments on films of
12 **rac-11** (Fig. 3c) and **mix-11** (Supplementary Figure S7) in the Φ_h^{k1} and Φ_h^{k2} phases were performed to
13 discriminate between these two possibilities.²¹ The birefringence of these films was confirmed to be
14 negligibly small (Supplementary Section S11), as also supported by thin film micro-spot CD spectra of
15 enantiopure **(S)-** and **(R)-11** (Supplementary Fig. S8). Micro-spot CD experiments demonstrated that Φ_h^{k2}
16 of **mix-11** (Supplementary Figure S7) and surprisingly also **rac-11** (Fig. 3c, blue) consists of domains
17 containing columns of a single handedness. A control experiment on Φ_h^{k1} of **rac-11** (Fig. 3c, red) shows no
18 deracemization in the low order Φ_h^{k1} phase. Therefore, deracemization takes place between left- and
19 right-handed homochiral supramolecular columns in the crystal state, as demonstrated for the first time
20 recently.²¹ Optical segregation of enantiopure domains was also identified by uncrossing the polarizers of
21 an optical polarized microscope. Enantiomeric domains are distinguished as bright and dark regions that
22 interchange by rotating the analyzer clockwise or counterclockwise (Fig. 3d, e). These experiments support
23 a chiral self-sorting or deracemization process^{18,21} occurring for assemblies of **mix-11** and **rac-11** during the
24 transition to the columnar hexagonal crystal phase, Φ_h^{k2} . A control experiment with homochiral **(S)-** and
25 **(R)-11** (Supplementary Figure S9) shows no relative change in the contrast of individual microdomains, but
26 rather an overall change across the entire film. This indicates the presence of microdomains of a single
27 handedness throughout Φ_h^{k2} , as expected from homochiral samples. We conclude that in Φ_h^{k2} the
28 supramolecular columns generated from all four homochiral and racemic compounds are single-handed and
29 homochiral.



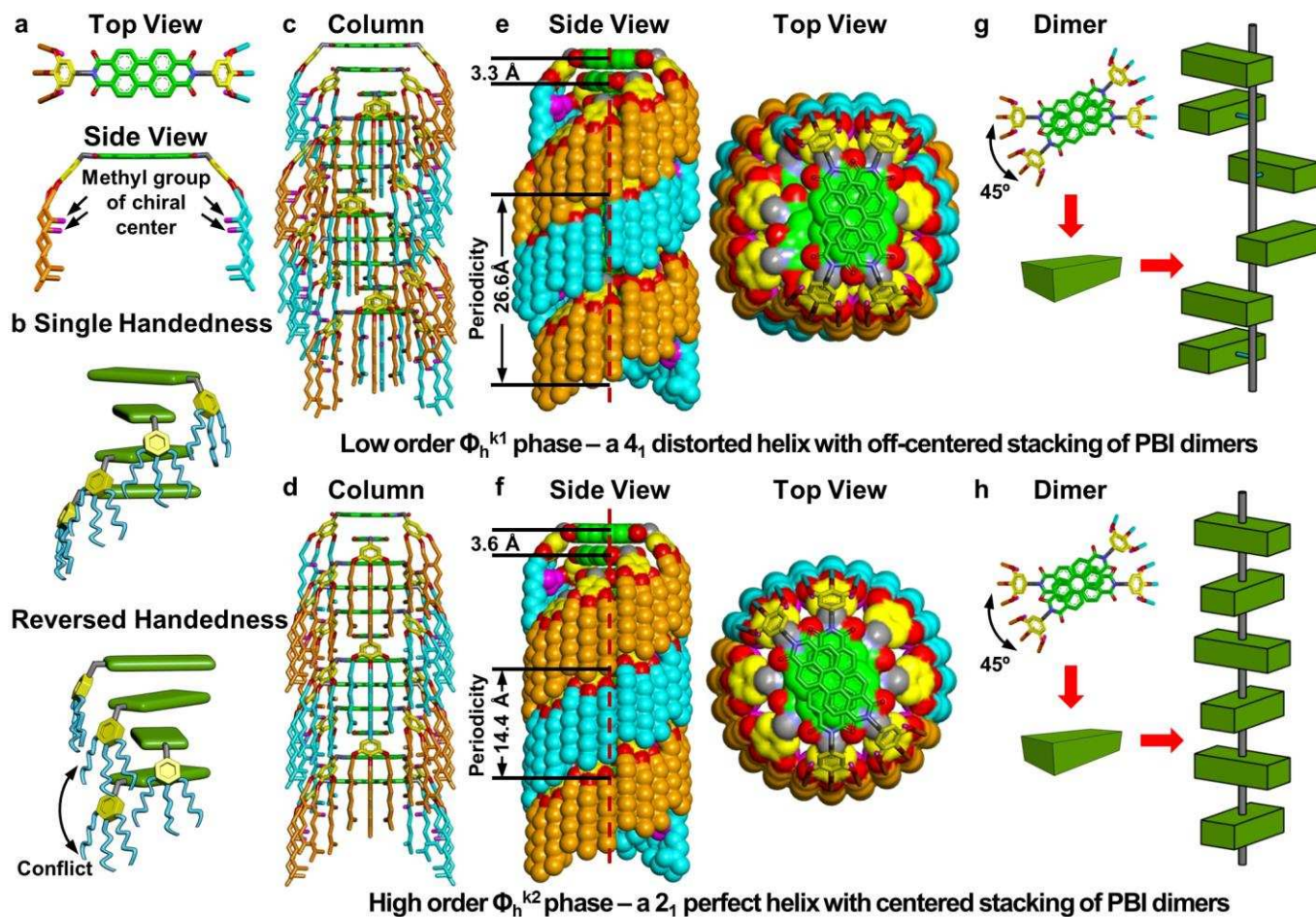
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2 **Figure 4. Oriented fiber X-ray diffraction (XRD).** XRD patterns collected from oriented fibers of **a, e**,
3 **(S)-11**; **b, f, (R)-11**; **c, g, mix-11**; and **d, h, rac-11** in the **a–d, Φ_h^{k1}** and **e–h, Φ_h^{k2}** phases, respectively. **f**,
4 right, Comparison of experimental XRD pattern with XRD pattern simulated from molecular model of **(R)-**
5 **11** presented in Fig. 5d, f. Fiber axis, temperature, phase, and lattice parameters ($a = b = D$, where D is the
6 column diameter, Supplementary Table S1) are indicated. Fully indexed patterns for **(R)-11** (b, f) showing
7 $L = 8$ and $L = 4$ layer lines are in Supplementary Fig. S12. The XRD patterns of the Φ_h^{k1} and Φ_h^{k2} phases
8 are, respectively, identical irrespective of the chiral composition of **11**. These patterns demonstrate that
9 homochiral **(S)-** and **(R)-11** and both racemic derivatives, **mix-** and **rac-11**, self-assemble to give identical
10 supramolecular structure with low order in the Φ_h^{k1} phase and high order in the Φ_h^{k2} phase. The cross-like
11 pattern of diffraction peaks in all diffraction patterns indicates that the assembled structures are helical.

12 **Structural analysis of supramolecular assemblies by X-ray diffraction.** X-ray fiber patterns of Φ_h^{k1} of
13 all chiral compositions of **11** were collected from oriented fibers extruded⁴¹ from non-annealed powders
14 (Fig. 4a–d). Annealing for more than 12 days at 23 °C or for shorter times at higher temperatures
15 transformed Φ_h^{k1} into Φ_h^{k2} (Fig. 4e–h, Supplementary Figs. S10–S12). Crystallographic layer lines, $L = 1$,
16 are labelled in Fig. 4 and selected reflections are identified in Fig. 4a, e. Irrespective of the chiral
17 composition and as suggested by the DSC data (Supplementary Fig. S2), Φ_h^{k1} and Φ_h^{k2} are identical in all
18 samples of **11** (Fig. 4). Sharp reflections on layer line $L = 0$ of Φ_h^{k1} (Fig. 4a–d) indicate well-ordered
19 columns arranged on the projection of the 3D hexagonal lattice along the c -axis (ab -plane of the 3D unit
20 cell, Supplementary Fig. S12). Diffuse streaks extending from the meridian and quadrants demonstrate a
21 helical arrangement of the columns.^{13,14,21} The lattice parameters of Φ_h^{k1} and Φ_h^{k2} are listed in Fig. 4 and

1 Supplementary Table S1. The c-axis length in $\Phi_{\text{h}}^{\text{k1}}$ is almost double that in $\Phi_{\text{h}}^{\text{k2}}$ (26.6 Å vs 14.4 Å). Unit
2 cell dimensions and experimental density (1.05 g/cm³) indicate that eight molecules form the unit cell of
3 $\Phi_{\text{h}}^{\text{k1}}$ and only four form the unit cell of $\Phi_{\text{h}}^{\text{k2}}$. The (008) reflection of $\Phi_{\text{h}}^{\text{k1}}$ (Supplementary Fig. S12)
4 corresponds to a 3.3 Å π - π stacking distance between successive PBI units. The meridional (004) reflection
5 suggests a 4-fold repeat stacking along the c-axis in $\Phi_{\text{h}}^{\text{k1}}$. The presence of the (101) reflection at L = 1 in
6 $\Phi_{\text{h}}^{\text{k1}}$ suggests a certain degree of intercolumnar crystalline order. However, the lack of other off-meridional
7 reflections indicates that this intercolumnar order is weak and therefore $\Phi_{\text{h}}^{\text{k1}}$ has only short-range helical
8 order, in line with CD (Fig. 3c) and NMR (Fig. 6 and Supplementary Section S10) experiments. In contrast,
9 $\Phi_{\text{h}}^{\text{k2}}$ is a highly ordered columnar hexagonal crystal with long range intra- and intercolumnar order, as
10 evidenced by numerous sharp reflections in its XRD pattern (Fig. 4e-h) and solid state NMR analysis (Fig.
11 6). The absence of (001) coupled with the observation of a nonzero (002) reflection in $\Phi_{\text{h}}^{\text{k2}}$ indicates that
12 the PBI molecules may be dimerized, as supported by CD and UV-vis experiments (Fig. 2), and that this
13 aggregation consists at least in part of distortions along the c-axis.

14 The diameter of the $\Phi_{\text{h}}^{\text{k1}}$ column is only slightly larger than that of the $\Phi_{\text{h}}^{\text{k2}}$ column (29.2 Å vs 27.4 Å).
15 Modeling shows that a supramolecular column assembled from **11** with alkyl chains extended
16 perpendicular to the column has a maximum diameter of 44 Å (Supplementary Fig. S15b, c). The
17 experimental column diameter (27.4 Å) can only be explained by the model of $\Phi_{\text{h}}^{\text{k2}}$ from Fig. 5d, f with
18 diameter of 27.7 Å (Supplementary Fig. S15a), in which the alkyl groups are extended parallel to the
19 column axis. Polarized infrared (IR) experiments in aligned films of **rac-11** in the $\Phi_{\text{h}}^{\text{k2}}$ phase support the
20 arrangement of alkyl chains parallel to the column axis (Supplementary Section S24).

21 Each unit cell of $\Phi_{\text{h}}^{\text{k2}}$ contains only one column (Fig. 7b, brown area). Since the unit cell repeats itself
22 three-dimensionally across the entire crystal, this implies that every column in the crystal must be identical
23 with the same helical handedness in order to form a perfect hexagonal crystal.²¹ This is true even for **rac-11**
24 and **mix-11**. The $\Phi_{\text{h}}^{\text{k2}}$ crystal of the racemic compounds show no CD signal in thin film but exhibit signals
25 in micro-spot CD experiments (Fig. 3c and Supplementary Fig. S7). These micro-spot CD data, in
26 combination with changes in contrast in the optical polarized micrographs (Fig. 3d, e) and the identical
27 patterns and $\Phi_{\text{h}}^{\text{k2}}$ lattice symmetry evidenced by fiber XRD (Fig. 4g, h), provide three complementary
28 techniques that demonstrate that chiral self-sorting or deracemization occurs at the supramolecular level
29 during or after assembly of **mix-11** and **rac-11** to produce hexagonal crystals containing enantiopure
30 domains of single-handed columns. This high order in $\Phi_{\text{h}}^{\text{k2}}$ is unexpected since only low crystalline order²¹
31 or no crystallization was previously observed in related assemblies comprising single-handed
32 monodomains produced from non-deracemizing racemic building blocks.^{32,34}



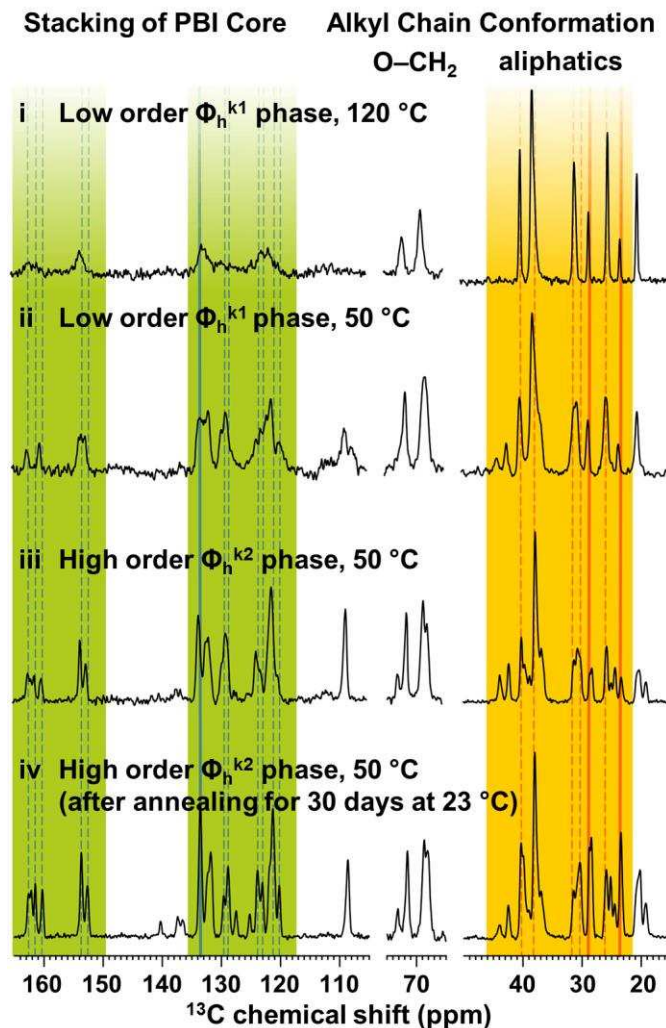
1
 2 **Figure 5. Model of supramolecular packing in the Φ_h^{k1} and Φ_h^{k2} phases.** a, Single molecular
 3 conformation in Φ_h^{k2} of (**R**)-**11** from top and side views. b, Simplified models of four molecules (two
 4 dimers) stacked in a column with single handedness (top) and reversed handedness (bottom) showing
 5 conflict between periphery alkyl chains. c, d, Side views of stick column models and e, f, space filling
 6 models for Φ_h^{k1} and Φ_h^{k2} . g, h, Schematic intracolumnar arrangement of dimers in the two phases. The
 7 high steric interaction between alkyl groups upon helix reversal ensures that an assembling column
 8 maintains the same helicity along its entire length. Molecules of **11** organize into dimers, which then
 9 aggregate to form the supramolecular column in both the Φ_h^{k1} and Φ_h^{k2} phases. The dimers in both phases
 10 are identical, but their relative arrangement defines the difference between the two phases: in the low order
 11 Φ_h^{k1} phase, the dimers are arranged off-axis, leading to a staggered surface on the exterior of the column;
 12 in the high order Φ_h^{k2} phase, the dimers are arranged co-axially generating a smooth column exterior and
 13 mediating higher order packing of the supramolecular columns.

14 Models of supramolecular single-handed helical columns forming the low order Φ_h^{k1} and high order Φ_h^{k2}
 15 crystals are shown in Fig. 5. In columns of both phases, two neighboring molecules are stacked and rotated
 16 by 45° with respect to each other to form dimers (Fig. 5g, h). In Φ_h^{k2} , the helical axis corresponds to the
 17 center of each column, whereas the axis is off-center in the columns comprising Φ_h^{k1} . Consequently, in
 18 Φ_h^{k1} , a 4_1 -helix with a pitch of 26.6 \AA is formed, and in Φ_h^{k2} , a 2_1 -helix with a pitch of 14.4 \AA is formed.

1 This structure can also be crystallographically defined as a double helix that is different from that of DNA,
2 whose strands are covalent, while here they are supramolecular (Supplementary Section S19).

3 The sense of the 45° rotation between neighboring molecules is selected by their chirality. The rotation of
4 racemic dimers is also single-handed but statistically forms racemic crystals with large single-handed
5 domains. The alkyl chains extend parallel to the column axis with the methyl stereocenters pointing into
6 internal gaps defined by the rotation of the supramolecular helical backbone of PBI cores (Fig. 5a–d). This
7 arrangement, demonstrated by the column diameter (Fig. 4 and Supplementary Fig. S15), by the simulation
8 of XRD²¹ (Fig. 4f) of the supramolecular model from Fig. 5d, f, by UV analysis in solution (Fig. 2a,
9 bottom) and thin film in Φ_h^{k2} (Fig. 3c), and by solid state NMR (Fig. 6), explains the mechanism by which
10 the chirality of mismatched enantiomers or racemic molecules neither affects neighboring columns (Fig.
11 7f) nor distorts the highly-ordered hexagonal crystal structure (Fig. 5a, c–f). The length of the alkyl chains
12 matches perfectly with the half-pitch of the helix, thus optimizing organization into helices and providing a
13 principle for the design of additional building blocks following the same self-assembly and crystallization
14 mechanisms.

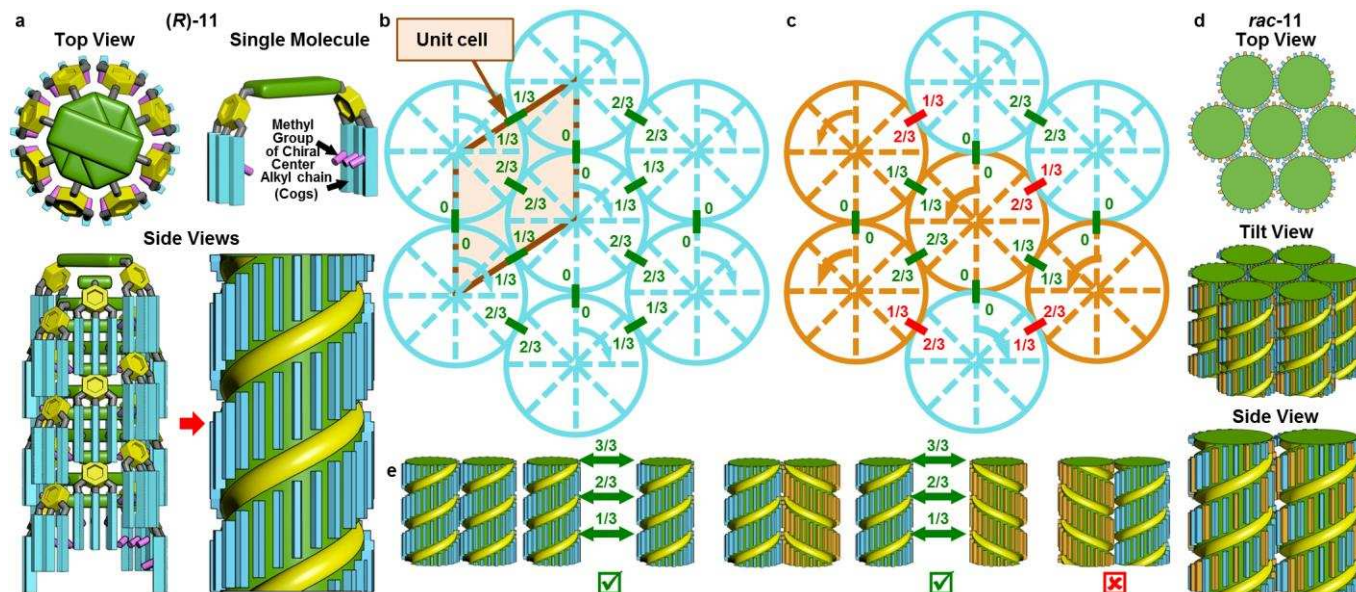
15 This model resembles a cogwheel (Fig. 5c–f and Fig. 7), with 24 alkyl chains on the periphery of the
16 column forming teeth. Slight interlocking (0.3 Å) with adjacent single-handed columns reduces the column
17 diameter from a theoretical value of 27.7 Å (Supplementary Fig. S15) to the experimental value of 27.4 Å
18 (Fig. 4e–h) and thus generates the high order observed in the Φ_h^{k2} crystal. Theoretical and experimental
19 values for the column diameter in Φ_h^{k1} are 28.9 and 29.1 Å, respectively. The diameters of the columns as
20 modeled are supported by X-ray data (Fig. 4 and Supplementary Fig. S15). The helix reversal penalty
21 (1.5 kcal/mol, Supplementary Table S2) is higher than the chiral mismatch penalty (0.6 kcal/mol,
22 Supplementary Table S2), that is, the energetic penalty for a chiral monomer to add to a helix of its non-
23 preferred handedness (compare bottom and top, Fig. 5b). This provides the mechanism by which a
24 monomer with non-preferred chirality or even mixed chiral character is incorporated in a single-handed
25 helix. The handedness of all dimers is the same within a column (Fig. 5b), and therefore crystals of racemic
26 compounds have a racemic mixture of left- and right-handed columns, segregated into crystalline domains
27 of single handedness columns (Figs 3c and 7). This allows the generation of columns with indistinguishable
28 cogwheel shapes from non-deracemizing **rac-11** and the formation of hexagonal crystals with as high a
29 degree of order as those formed from enantiomerically pure compounds (Fig. 7).



1
2 **Figure 6.** ¹³C Cross-Polarization Magic Angle Spinning (CP-MAS) solid state NMR studies. ¹³C
3 CP-MAS solid state NMR spectra of **rac-11** in **i**, low order Φ_h^{k1} phase at 120 °C; **ii**, low order Φ_h^{k1} phase at
4 50 °C; **iii**, high order Φ_h^{k2} phase at 50 °C; **iv**, high order Φ_h^{k2} phase at 50 °C after annealing the sample for
5 30 days at 23 °C. Green highlighted areas correspond to signals arising from the PBI core. Yellow
6 highlighted areas correspond to signals arising from the aliphatic chains at the periphery of the structure.
7 The broad aromatic peaks in the low order Φ_h^{k1} phase at high temperature sharpen significantly upon
8 cooling the Φ_h^{k1} phase, in the Φ_h^{k2} phase and, unexpectedly, by allowing the Φ_h^{k2} phase to anneal at 23 °C
9 for 30 days. This indicates that the optimal molecular packing is very well defined for **rac-11**, and that even
10 in the high order phase, sufficient molecular fluctuations are present in order to refine and improve the
11 supramolecular structure of the crystal on very long time scales.

12 **Solid state NMR experiments.** Solid state NMR experiments of assemblies of **11** support the structure
13 determined by XRD (Fig. 6 and Supplementary Figs S4 and S5). ¹³C Cross-Polarization (CP) MAS spectra
14 of Φ_h^{k1} of **rac-11** exhibit broadening of the aromatic signals on cooling to 120 °C and 50 °C due to
15 molecular motions mediated by the irregular packing of the PBI core (Fig. 6i, ii). In contrast, well resolved
16 signals are obtained in Φ_h^{k2} at 50 °C, indicating a regular packing of the aromatic part of the PBI (Fig. 6iii).
17 The -CH₂O- and aliphatic chain signals follow the same trend with respect to order, indicating a liquid-like
18 molecular motion in Φ_h^{k1} and almost perfect conformational order in Φ_h^{k2} that is unexpected for the short

1 and branched dimethyloctyl chains.⁵⁰ Repeating the CP-MAS experiment with **rac-11** after extended
 2 annealing at ambient temperature (30 days, 23 °C) improves the spectral resolution due to substantially
 3 improved packing in the aromatic and aliphatic side chains (Fig. 6iv). This indicates that very well defined
 4 packing of the alkyl groups in the highly ordered Φ_h^{k2} phase of **rac-11** is achieved due to sufficient
 5 molecular fluctuations that refine and improve the molecular structure of the periodic array on very long
 6 time scales. 2D $^{13}\text{C}\{^1\text{H}\}$ heteronuclear Lee-Goldburg Cross-Polarization (LGCP) correlation experiments
 7 and additional CP-MAS experiments with **(R)-11** and **rac-11** provide further details on these observations
 8 (Supplementary Section S10).



9
 10 **Figure 7. Cogwheel model of self-assembly and its role in generating microdomains of single-handed**
 11 **supramolecular columns.** **a**, Schematic representation of a right-handed column produced by **(R)-11** from
 12 top and side views. The supramolecular column (left) can be considered as a cogwheel (right).
 13 Conformation of a single molecule within the column is also shown. **b**, **c**, Schematic packing of helical
 14 columns with **b**, single handedness and **c**, mixture of two handednesses (Supplementary Section S21).
 15 Right- and left-handed helical columns are denoted in blue and orange, respectively. The relative heights of
 16 the grooves at the interfaces between adjacent columns are indicated as a fraction of column length (0, 1/3,
 17 2/3). Grooves with matching and mismatching interfacial heights are presented in green and red,
 18 respectively. In **b**, the unit cell of Φ_h^{k2} lattice containing a single helical column is marked in brown. **d**,
 19 Columns of **rac-11** packed in a right-handed crystal domain from top and side views. **e**, Schematic
 20 representations of the alignment of the grooves of neighboring columns: (left) matching between columns
 21 of the same handedness; (center) matching between columns of different handedness; (right) mismatching
 22 between columns of different handedness. In **d–e**, blue and orange teeth represent chiral alkyl chains with
 23 different chiralities.

24 The proposed cogwheel model (Fig. 7a) requires the helical packing of molecules with alkyl chains parallel
 25 to the column axis and methyl groups pointed toward the center of the column. Within each supramolecular
 26 column, the teeth (alkyl chains, Fig. 7a, bottom right) are hydrophobic while the grooves are more polar
 27 due to the ether linkages between the alkyl chains and aromatic rings. During self-assembly, the columns

1 seek to maximize the intercolumnar electrostatic and hydrophobic interactions by vertically aligning the
2 alkyl chains at the interface between columns. Only packing with the same handedness columns can
3 simultaneously optimize the interactions with all neighbors ~~at the same time~~ by positioning the grooves of
4 neighboring columns at the same height (Fig. 7b, c, e and Supplementary Information). The grooves of
5 columns of the same handedness (Fig. 7e, left) will always align in all directions. In contrast, the grooves of
6 columns of different handedness will align in some instances (Fig. 7e, center) but not in others (Fig. 7e,
7 right; see also Fig. 7c). It is a requirement of Φ_h^{k2} that all columns have the same handedness, as there is
8 only one column in the crystallographic unit cell (Fig. 7b). Aligning the grooves and teeth of adjacent
9 columns provide a mechanism through which only columns with the same handedness pack together to
10 form highly ordered crystals, even in fully racemized; **rac-11** (Fig. 7d).

11 **Conclusion**

12 The cogwheel columnar model from Figs 5 and 7 and its role in enabling deracemization in supramolecular
13 assemblies is demonstrated herein by three key complementary techniques: variable temperature XRD of
14 oriented fibers (Fig. 4 and Supplementary Figs S10–S12 and S16), microspot CD of thin films (Fig. 3c and
15 Supplementary Figs S7 and S8) and optical polarized microscopy (Fig. 3d, e), as well as a diversity of other
16 supporting techniques including solid state NMR (Fig. 6 and Supplementary Section S10), solution CD
17 (Fig. 2), DSC (Supplementary Fig. S2), molecular modeling (Supplementary Fig. S15), IR (Supplementary
18 Fig. S17) and UV analysis (Supplementary Fig. S4). This cogwheel model provides a mechanism for
19 perfect packing of single-handed columns irrespective of the chirality of their molecular building blocks
20 (Fig. 7b), as well as near-perfect packing for helical columns with different handednesses (Fig. 7d). We
21 anticipate that the principle of matching the helical half-pitch with the length of the side chains will give
22 access to extended libraries of compounds with similar helical structures. This packing mechanism yields a
23 higher level of hexagonal crystal order in the assemblies of homochiral, racemic, and irreversibly
24 racemized building blocks than any homochiral biological or non-biological single or double helix. The
25 findings reported here challenge the established requirement that highly ordered crystalline systems are
26 achievable only with enantiopure building blocks, and hence provide new access to high order assemblies
27 of chiral PBIs, which have higher charge carrier mobility than achiral counterparts.³⁵ We therefore envisage
28 that the cogwheel mechanism of self-assembly and self-organization described here will find practical
29 applications in the design of functions in complex materials.

30

1 **Methods**

2 Synthesis, materials, characterization data and methods for MALDI-TOF, micro-spot CD, POM and
3 density measurements are described in Supplementary Section S2.

4 **Differential scanning calorimetry (DSC).** Thermal transitions were determined on a TA Instruments
5 Q100 differential scanning calorimeter equipped with a refrigerated cooling system with 10 °C/min and
6 1 °C/min heating and cooling rates. Indium was used as a calibration standard. The transition temperatures
7 were calculated as the maxima and minima of their endothermic and exothermic peaks. An Olympus BX51
8 optical microscope (100× magnification) equipped with a Mettler FP82HT hot stage and a Mettler Toledo
9 FP90 Central Processor was used to verify thermal transitions.

10 **Circular dichroism (CD) spectroscopy in solution.** Circular dichroism and UV-vis spectroscopy
11 measurements were carried out on a Jasco J-720 Spectropolarimeter. The temperature was controlled by a
12 Peltier temperature controller (Jasco PTC-423). Methylcyclohexane, cyclohexane (both 99%,
13 spectrophotometric grade, Aldrich) and 1-butanol (99.5%, spectrophotometric grade, Aldrich) were used as
14 solvents. Solution spectra were recorded in 10-mm quartz cuvettes stirred at 1000 rpm with a small
15 magnetic stirring bar, and corrected by subtracting the spectrum of the pure solvent at the same
16 temperature. A scan rate of 100 nm/min with a response time of 1 s and a bandwidth of 1 nm was used to
17 measure the CD spectra, which were recorded in low sensitivity mode between 800 and 200 nm
18 (3 accumulations). Further details are provided in Supplementary Section S2.3.

19 **CD spectroscopy in thin film.** Thin film CD/UV experiments were conducted as follows. A 2% w/v
20 solution of **11** in n-butanol/methylcyclohexane (85:15 v/v) was prepared by heating 2 mg of sample in
21 100 µL of solvent until dissolved. The hot solution was spin-coated on a round quartz plate (22 mm
22 diameter) at 2500 rpm for 6 s and 7000 rpm for 30 s, using a Chemat Technology Spin Coater KW-4A. The
23 thin film was then annealed at 110 °C for 3 h and cooled to room temperature, whereupon measurements
24 were recorded. CD/UV spectra of thin films were recorded using the same parameters as those used for
25 solution experiments, and the spectra were corrected by subtracting spectra of the quartz plate recorded
26 before spin-coating. The presence of linear dichroism was negated by recording CD spectra of the thin film
27 at various rotations perpendicular to the beam and ensuring that the CD spectra was the same, irrespective
28 of rotation.

29 **X-ray diffraction (XRD).** X-ray diffraction measurements were performed using Cu-K_{α1} radiation
30 ($\lambda = 1.542 \text{ \AA}$) on a Bruker-Nonius FR-591 rotating anode X-ray source equipped with a $0.2 \times 0.2 \text{ mm}^2$

1 filament and operated at 3.4 kW. The Cu radiation beam was collimated and focused by a single bent
2 mirror and sagittally focused through a Si(111) monochromator, generating a $0.3 \times 0.4 \text{ mm}^2$ spot on a
3 Bruker-AXS Hi-Star multiwire area detector. To minimize attenuation and background scattering, an
4 integral vacuum was maintained along the length of the flight tube and within the sample chamber.
5 Samples were held in quartz capillaries (0.7–1.0 mm in diameter), mounted in a temperature-controlled
6 oven (temperature precision: $\pm 0.1 \text{ }^\circ\text{C}$, temperature range from $-120 \text{ }^\circ\text{C}$ to $270 \text{ }^\circ\text{C}$). Further details are
7 provided in Supplementary Section S2.5.

8 **Preparation of aligned fibers for XRD.** Aligned samples for fiber XRD experiments were prepared using
9 a custom-made extrusion device.⁴¹ The powdered sample ($\sim 10 \text{ mg}$) was placed inside the extrusion device
10 and the fiber was extruded in the as prepared state ($\Phi_{\text{h}}^{\text{kl}}$ phase) at room temperature without any heat
11 treatment. Typically, the aligned fiber samples have a thickness of 0.3–0.7 mm and a length of 3–7 mm. All
12 XRD measurements were done with the aligned sample axis perpendicular to the beam direction.

13 **Solid state NMR spectroscopy.** Variable temperature $^{13}\text{C}\{^1\text{H}\}$ Cross-Polarization-Magic Angle Spinning
14 (CP-MAS) NMR spectra (Fig. 6) were recorded with a Bruker Avance III console operating at 700.23 MHz
15 ^1H Larmor frequency (176.1 MHz ^{13}C Larmor frequency) using a commercial double resonance probe
16 supporting zirconia rotors with 2.5mm outer diameter. Measurements were performed at 25 kHz MAS
17 spinning frequency using a CP contact time of 1 ms. An rf nutation frequency of 100 kHz was used on both
18 the ^1H and ^{13}C channels, as well as for ^1H heteronuclear decoupling during acquisition using the SPINAL64
19 scheme. The given temperatures have been corrected for known deviations due to frictional heating under
20 fast spinning conditions based on the temperature dependent chemical shift of lead nitrate. In order to
21 compare the temperature dependence of the CP-MAS signal intensities, spectra with 5120 transients and
22 identical experimental parameters were recorded in the temperature range from 40 to $100 \text{ }^\circ\text{C}$. 2D $^{13}\text{C}\{^1\text{H}\}$
23 heteronuclear Lee-Goldburg Cross-Polarization (LGCP) correlation experiments (Supplementary Fig. S4)
24 were recorded at 18 kHz MAS and 850 MHz ^1H Larmor frequency using an LGCP contact time of 0.2 ms
25 and 102 kHz FSLG multi pulse decoupling for line narrowing in the ^1H dimension.

26

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8 B.E.P., D.A.W. and M.E.P. performed solution state CD and UV-vis analysis; F.A. performed micro-spot
9 CD analysis; H.-J.S., M.P. and B.E.P. collected and processed X-ray diffraction data; X.Z., H.-J.S., P.A.H.
10 and G.U. generated the molecular model; H.-J.S. and B.E.P. simulated X-ray data; R.G. and H.W.S.
11 performed solid state NMR analysis; V.P. designed the study; V.P., B.E.P., C.R., and H.-J.S. analyzed data
12 and prepared the manuscript. All authors discussed the results and commented on the manuscript.

13 **Additional information** Supplementary information and chemical compound information are available in
14 the online version of the paper. Reprints and permissions information is available at
15 www.nature.com/reprints. Correspondence and requests for materials should be addressed to V.P.

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