Abstract: Chiral segregation of enantiomers or chiral conformers of achiral molecules during self-assembly in well-ordered crystalline superstructures has fascinated chemists since Pasteur. Here we report spontaneous mirror-symmetry breaking in cubic phases formed by achiral multichain-terminated diphenyl-2,2’-bithiophenes. It was found that stochastic symmetry breaking is a general phenomenon observed in bicontinuous cubic liquid crystal phases of achiral rod-like compounds. In all compounds studied the Im3m cubic phase is always chiral, while the Ia3d phase is achiral. These intriguing observations are explained by propagation of homochiral helical twist across the entire networks through helix matching at network junctions. In the Ia3d phase the opposing chiralities of the two networks cancel, but not so in the three-networks Im3m phase. The high twist in the Im3m phase explains its previously unrecognized chirality, as well as the origin of this complex structure and the transitions between the different cubic phases.

Design and investigation of chiral self-assembled superstructures represents a fascinating field of contemporary research which provides numerous potential applications. Beside enantiomeric mixtures of molecules, segregation of chiral supermolecular aggregates\textsuperscript{[1,2,3]} and chiral molecular conformations were also found as sources of macroscopic chirality in the crystalline state and at surfaces.\textsuperscript{[4]} In recent years interest in mirror-symmetry breaking extended to soft matter systems. Special progress in this field was made with liquid crystalline phases formed by bent-core molecules and bent-mesogenic dimers showing symmetry breaking in their lamellar\textsuperscript{[5–11]} and nematic phases, respectively.\textsuperscript{[12,13]}

Spontaneous formation of helical superstructures was also observed in soft columnar crystals at reduced temperature where packing density is increased and the mobility of the aromatic segments is reduced.\textsuperscript{[14–17]} The lateral coupling between columns is much weaker than the longitudinal, therefore macroscopic chiral segregation is usually not observed, except for one case.\textsuperscript{[10]} Though, there is one report about spontaneous stochastic symmetry breaking in a thermotropic cubic phase, the structure of this cubic phase and the possible origin of macroscopic chirality are not clear in this case.\textsuperscript{[18]}

Herein we report that stochastic symmetry breaking is a general phenomenon typically observed in the bicontinuous cubic phases of achiral rod-like and polycatenar (multichain-terminated) liquid crystalline (LC) compounds.\textsuperscript{[19]} We show that optical activity and circular dichroism (CD) develop spontaneously whenever the cubic phase is of the triple-network type with Im3m symmetry\textsuperscript{[20,21]} whereas, in contrast, the “double gyroid” Ia3d cubic phase always remains achiral. These observations are explained by the action of two newly recognized phenomena: a) the correlated helical twist of molecular axis in the segments of the infinite interpenetrating networks, and b) the percolation through mm-sized domains of uniform helical sense carried across the network through matching of molecular orientation twist sense at network junctions. The current findings also bring the understanding of thermotropic cubic phases to a qualitatively new level and contribute to the general appreciation of symmetry breaking in LCs of achiral molecules.

The compounds under investigation (compounds 1, see Table 1) represent polycatenar rod-like molecules based on
Table 1: Chemical structures, phase transitions (heating top lines, cooling bottom lines) and cubic lattice parameters of the compounds of series 1

| Compd. | n | R | Phase transitions on heating/cooling (T/°C) | \(a_{cub}\) [nm] |
|--------|---|---|--------------------------------------------|----------------|
| 1a     | 10| H | Cr 114 [39.7] Cub/Ia{3d} 162 [2.3] Iso_{11}  | 10.8          |
| 1b     | 10| 4-OCH₃ | Cr 119 [55.3] Cub/Ia{3d} 192 [1.5] Iso_{11}  | 11.4          |
| 1c     | 10| 3,4-(OCH₃)₂ | Cr 137 [44.6] Cub/Ia{3d} 183 [3.3] Iso_{11}  | 11.1          |
| 1d     | 6 | 4-OCH₃H₃ | Cr 139 [55.2] M 171 [1] Cub/Ia{3d} 205 [1.2] Iso_{11} ²¹ | 10.3          |
| 1e     | 10| 4-OCH₃H₅ | Cr 134 [49.9] Cub¹/Im3m 183 [2.2] Iso_{11}  | 17.9          |
| 1f     | 10| 3-OCH₃H₃ | Cr 100 [27.8] Cub²/Im3m 130 [3.1] Iso_{11}  | 15.7          |
| 1g     | 10| 3,4-(OCH₃)₃H₃ | Cr 110 [70.2] Cub²/Im3m 127 [2.9] Iso_{11}  | 15.4          |

[a] Abbreviations: Cr = crystalline solid. Cub/Ia{3d} = bicontinuous cubic phase with Ia{3d} lattice (achiral). Cub²/Im3m = cubic chiral conglomerate cubic phase with Im3m lattice; Iso_{11}²¹ = chiral isotropic liquid phase formed by a conglomerate of domains with opposite handedness; Iso_{11} = achiral isotropic liquid phase.

a 5,5'-diphenylbithiophene core (for synthesis, see the Supporting Information (SI)).

Crystalline phases of compounds 1 melt between 110 and 139°C and form optically isotropic and highly viscous mesophases which, based on X-ray diffraction (XRD) evidence (see below), are cubic LC phases, and which on further rising temperature transform to isotropic liquids. In some cases, an additional liquid-liquid transition (LLT) is observed and the liquid phase occurring between the cubic and the “ordinary” isotropic liquid is labelled here Iso_{11}. The liquid phase at higher temperature as Iso_{11}. Iso_{11} phases have previously been found as intermediate phases at Cub-Iso transitions (labelled Iso_{11}) and have recently been found to be chiral in some cases, representing a conglomerate of two segregated enantiomeric liquids (Iso_{11}{¹}). This chiral Iso_{11} is denoted here as Iso_{11}{¹}. While Iso_{11}{¹} appears in 1d both on heating and cooling in 1b and 1e it occurs only on cooling (monotropic phase). Compounds 1a, 1c, 1f and 1g form the cubic phases directly from the achiral Iso_{11}. Sharp DSC peaks accompany Cub-Iso transitions on heating and Iso_{11}Cub transitions on cooling, but the Iso_{11}Cub exotherm is broad and is better described as a heat capacity anomaly rather than a first-order transition (see Figure 3c,d, Table 1 and Figures S1–S9 in the SI).

Cubic space groups were determined by powder small-angle XRD and grazing-incidence diffraction as shown in the SI (Figures S11, S12, and Tables S2–S8). Two cubic phases were observed, the double-network “gyroid”, with Ia{3d} symmetry (Figure 1a), and the triple-network phase with Im3m symmetry (Figure 1b). The lattice parameters of the cubic phases are in the typical ranges around \(a_{cub}=11\) nm for the Ia{3d} phase and \(a_{cub}=15–18\) nm for the Im3m phase.

Symmetry breaking is observed in some of the cubic phases by polarized microscopy if the analyzer is rotated by a small angle out of the 90° crossed position with respect to the polarizer. In this way the polarizing microscope can be used as a polarimeter with the additional advantage of spatial resolution. Remarkably, all Ia{3d} cubic phases of the investigated compounds are optically inactive, whereas for all Im3m phases darker and brighter domains become visible between slightly uncrossed polarizers, which exchange their contrast if the rotation of the analyzer is reversed (Figure 2a,b). Rotating the sample between the polarizers does not change the contrast. This means that the Im3m phase represents a conglomerate of chiral domains with opposite handedness. Thus this cubic phase is denoted Cub²/Im3m.

Microbeam circular dichroism (CD) spectroscopy confirmed the presence of chiral domains in the Im3m phase. Figure 3a shows the CD evolution with temperature during heating a bulk film of 1g from the Cub¹/Im3m (120–125°C) to the Iso_{11} phase (130–140°C), and then cooling back to the Cub²/Im3m (120–125°C, dashed curves). As can be seen, there is strong CD in the cubic phase, disappearing in the isotropic Iso_{11} liquid and reappearing in the Cub²/Im3m, this time either with the same or with reversed chirality. In contrast, on no occasion did the Cub/Ia{3d} phase give any measurable CD.

While both, optical activity and CD, are strongly affected by helical order, CD is highly sensitive to molecular conformation. It is suggested that the chiral chromophore mainly responsible for the CD is the slightly twisted 5,5’-diphenyl-2,2’-bithiophene unit (Figure 3b) which has its UV absorption maximum at the inflection point of the CD curves at 374 nm (Figure S10).

As mentioned above, there are two different types of transitions from the achiral Iso_{11} liquid to the Cub²/Im3m phase, either directly (compounds 1f and 1g, Figure 2a,b) or via the chiral Iso_{11}{¹} phase (compounds 1e and 2, Figure 2c,d). The chirality of the Iso_{11}{¹} phase, a conglomerate of chiral domains, is indicated by optical investigations in the same way as described for the cubic phases (see Figure 2c).
IsoLT domains of the IsoLT closely the curved borders between the enantiomeric liquid
However, when the boundaries reflecting crystallographic facets (Figure 2a,b).

Other than by XRD, the direct transition IsoHT-Cub/ (compounds 1a and 1b).

Where the transition takes place directly from the achiral IsoLT phase the resulting chiral domains have mainly straight

and c) typical chemical structures of representative compounds forming

these phases (compounds 2-4 were newly synthesized, as
described in the SI, and compounds 5 and 6 were known from
literature, see Table S1 and Figures S7–S9, S13, S14, S17–S22 for
details.[19] a) The double-network Im3m (“gyroid”) phase; b) the triple-

network Im3m phase. Each of the infinite networks is coloured
differently. In (b) the red and blue are the identical “inner” and “outer”

networks, mutually related by a (1/2, 1/2, 0) translation; yellow is the
“middle” network. Equivalent figures with the added minimum surface
are shown in SI.

Figure 1. a, b) Framework models of a unit cell of the two cubic
structures discussed in this work[20] (see also Figures S15 and S16)
and c) typical chemical structures of representative compounds form-
ing these phases (compounds 2-4 were newly synthesized, as
described in the SI, and compounds 5 and 6 were known from
literature, see Table S1 and Figures S7–S9, S13, S14, S17–S22 for
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“middle” network. Equivalent figures with the added minimum surface
are shown in SI.

The transition to the Im3m phase can also occur in two
ways. Other than by XRD, the direct transition IsoLT-Cub/
Ia3d is only detectable by a marked increase in viscosity
(compounds 1a and 1c). In this case investigation between
uncrossed polarizers give no evidence of chirality. What is
more, where the Ia3d phase is formed from the chiral IsoLT[21]

Figure 2. Photomicrographs of chiral domains (dark/bright), observed
between slightly uncrossed polarizers. The orientations of polarizer (P)
and analyzer (A) are indicated by arrows. a,b) Im3m phase of
compound 1f at T = 112 °C as obtained on cooling from the achiral
IsoLT phase; c) IsoLT[21] phase of compound 1e (T = 177 °C) and
d) Im3m phase (T = 175 °C) as observed after transition from the
IsoLT[21] phase; note that the domain boundaries between the chiral
domains are slightly shifted. e,f) Growth of the domains of the Ia3d
phase at the IsoLT[21]-Ia3d transition as observed for compound 1b at
T = 160 °C (white arrow indicates a seed of the Ia3d phase); note that
during formation of the cubic phase the chirality of the IsoLT[21] phase
is completely extinguished (see also videos in SI).

(compounds 1b and 1d), the chirality is completely erased
(see Figure 2e,f).

Similar IsoLT[21]-Cub[21]/Im3m transition behavior as for
compound 1e, was also observed for compound 2, having
a shorter bithiophene unit and for the tetracatenar com-
ounds 3 and 4 without the bithiophene units. 5 (ANBC-n)
and 6 (BABH-n) are members of the two best investigated
homologous series of cubic phase forming compounds (see
Table S1 and Figures 1, S7–S9, S13, S14, S17–S22).[19,20]

Remarkably, also for these compounds in all cases the
Ia3d phase is achiral (compounds 5a, b and 6a, b) whereas the
Im3m phase appears as chiral conglomerate (compounds 2, 5b, c and 6c). For the 3’-nitro-4’-alkoxybiphenyl carboxylic
acids 5 there is an additional enantiotropic (i.e. reversible)
IsoLT-IsoLT transition; however in this case the IsoLT phase is
for all investigated compounds achiral. Nevertheless, chirality
evolves for 5c (n = 20) at the transition to the Cub[21]/Im3m
phase (see Table S1 and Figure S20e,f). For 5b (n = 18) an
achiral Ia3d phase is formed on cooling, but on heating an
in all these diverse non-chiral polycatenar compounds, without exception, while the Cub/Ia\(_{3d}\) was non-chiral, also without exception. Hence, chirality of the Im\(_3m\) phases appears to be a general phenomenon, already present in long known systems, but surprisingly not previously recognized.\\[26\\] Chirality in the Cub\(_{3l}^*/\text{Im}3m\) phase has thus been seen to develop in four different ways, either 1) directly from the achiral isotropic liquid Iso\(_{\text{LT}}\), via Iso\(_{\text{HT}}\) phases which can be either 2) chiral (Iso\(_{\text{LT}}^{+}\)) or 3) achiral (Iso\(_{\text{LT}}^{-}\)), or 4) from the achiral Cub/Ia\(_{3d}\) phase.

For the understanding of the development of chirality in the cubic phase it must be recalled that the molecules have liquid like local order, with no hint of any Bragg-like X-ray reflection in the wide-angle range. Therefore, the classical approach of achiral symmetry breaking, where the formation of a more or less ordered crystalline phase energetically favors one chiral conformer over another,\\[1,3,7\\] cannot be applied here. Considering that the observed “static symmetry breaking” leads to a significant entropy penalty, there is a compelling mode of self-assembly that compensates for the entropy loss, yet does not involve crystallization at any level (“dynamic symmetry breaking”), as introduced recently as the underlying process for mirror-symmetry breaking in isotropic liquids.\\[23\\] The model must also explain why all Cub/Im\(_3m\) phases are chiral and all Cub/Ia\(_{3d}\) ones are not.

In soft-crystal columns of short hexacatenar hydrazine rods\\[27\\] or broader board-like perylene bisimides\\[28\\] it was found that molecular pairs stack on top of one another with a nearly 90° twist. In this way the molten alkyls spread around the column while effective core-core π-stacking is still maintained. For long thin rods with less than six chains, as studied here, a smaller twist angle would be sufficient to alleviate the crowding of the alkyls\\[19,29\\] thus allowing the development of helical twist. Without any degree of 3D positional order of achiral molecules, as in the “disordered” hexagonal columnar LC phase, there is no long-range helical order (LRHO). However, the superstructural twist couples with the helical twist of the chiral molecular conformations, thus biasing each other and collectively favoring the helical superstructure in the fluid columns.\\[23\\] Thus, the preorganization in columns favors conformational segregation and vice versa. But even in this case, in 1D columns, without intercolumnar correlation, a helix reversal defect has no way of being corrected, so that macroscopic chirality cannot be observed in fluid columnar LC phases.

However, in the bicontinuous cubic phases we also must consider the network junctions. At the 3-fold junctions the three twisting “ribbons” that may be used to represent the network segments, must merge into one another smoothly. In an optimal junction the aromatic rods arrive parallel to each other and with a synchronized twist where the helices lock-in together as they approach each other—for the Ia\(_{3d}\) network junction (see Figure 4b,c). The junction itself then effectively becomes a small triangular platelet, approximately normal to the molecular axis.\\[19,23\\] We calculate that there is a distance of 0.345 nm between the junctions, which accommodates about 9 molecular triplets spaced at 0.45 nm. As the twist between the Ia\(_{3d}\) junctions is \(\phi = \pm 70.5°\), there is an average rotation of ±8° between adjacent molecules. For
concentrate here only on the middle (yellow) network, as it is the simplest of the three and, like in the \( Ia\overline{3}d \) phase, contains only 3-way junctions. The key assumption is, as with the \( Ia\overline{3}d \) phase, that at the junctions, in order to interlock smoothly, the molecules twist with the same sense. As an example, a portion of the middle network forming a closed loop of 6 junctions is shown in the ribbon representation in Figure 4f. There are three “perfect” (I) and three “imperfect” (II) junctions in that loop, detailed in Figures 4g,h and i,j, respectively. In junctions I all ribbons merge perfectly smoothly, while in junctions II the blue and red ribbons merge smoothly but the green comes at an angle. We note that the latter defect is of little consequence because even if all green segments were disconnected, the remaining network would still remain connected and percolating the entire domain of the phase. The full extent of the middle network within the unit cell is shown in Figures 4d,e, with the Schwartz \( P \) minimum surface added in Figure 4d. A calculation similar to that for the \( Ia\overline{3}d \) phase (details in SI) gives the average twist angle between adjacent molecules as 30–35°, that is, significantly higher than the value for the \( Ia\overline{3}d \) phase, and in line with the expectation.

A similar calculation can be performed on the other two networks; however because of their complexity we shall not discuss them here. The important point to make, however, is that the chirality of the middle network will undoubtedly affect the chirality of the inner and outer networks. Because of their crystallographic equivalence, the helical sense of the inner and outer (red and blue) network will be the same. Whether it will be the same or opposite of that of the middle network, we cannot tell with certainty. However, what is certain is that, in the general case, there will always be at least a residual chirality in the cubic \( Im\overline{3}m \) phase, as indeed observed.

The above model implies that each of the cubic structures is the solution best suited to accommodate a certain range of required molecular twist angles. It is not suggested that the \( Im\overline{3}m \) provides a general solution for any situation that requires high twist. In fact experiments on the homologous series of compounds 5 and 6 have shown that as the terminal chains become very long, the \( Im\overline{3}m \) is again replaced by the \( Ia\overline{3}d \). It would thus appear that such molecules require a twist exceeding the range covered by the \( Im\overline{3}m \) structure. In fact, one can speculate that for an intermolecular twist above 40° the exact match between the helical pitch and segment length ceases to dominate the choice of the phase, and the simpler \( Ia\overline{3}d \) wins once again. Furthermore, due to lateral thermal expansion of the terminal chains, the twist is expected to increase on heating. This would explain the different temperature sequences observed for some homologues, where for the short chain compound an \( Ia\overline{3}d-Im\overline{3}m \) sequence is observed on heating, whereas for the long homologues this sequence is reversed (series of compounds 6).

A closer look at the \( Is\overline{4}m \)-Cub transitions indicates that the germs of the achiral \( Ia\overline{3}d \) phase emerge always at the interface between the domains with opposite handedness. This appears to be favorable for the formation of this superstructure composed of two enantiomorphic networks (see Figure 2e and Video 1b). In contrast, the germs of the \( Im\overline{3}m \) phase are not bound to the domain boundaries. The
The chiral sense of the nuclei once formed is retained and growth takes place preferentially within the same domain. But there is also a slower growth into domains with opposite chirality, leading to a change of the relative areas of the different domains (compare Figure 2c,d, see also Video 1e). This means, that the growing Cub\textsuperscript{[3]}/Im\textsubscript{3}m\textsubscript{3} phase completely overgrows the chirality of the liquid domains if required, although this causes a notable growth retardation.

In summary, we have discovered that, in spite of appearing in achiral compounds, the Im\textsubscript{3}m cubic LC phase is chiral in all compounds studied, while the Ia\textsubscript{3}d phase is invariably achiral.\textsuperscript{[3]}

This previously unrecognized features have led us to propose a model of the two phases based on networks with helical segments where the twist sense propagates in 3D across macroscopic domains through matching twist at network junctions. While the opposing chiralities of the two networks of the Ia\textsubscript{3}d phase cancel, this cannot happen in the triple network Im\textsubscript{3}m phase. This model also offers, for the first time, a feasible explanation for the existence of the complex Im\textsubscript{3}m phase, and for the observed Ia\textsubscript{3}d–Im\textsubscript{3}m phase sequences as a function of chain length and temperature. The structural insight acquired herein promises to end one of the longest persisting mysteries in the liquid crystal field, that started with the discovery of the “smectic-D” phase over half a century ago.\textsuperscript{[3,3]}

But the importance of this finding goes far beyond the systems discussed herein and contributes to the general understanding of symmetry breaking in soft condensed matter.

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