This is a repository copy of Chirality induction through nano-phase separation: Alternating network gyroid (I4132) phase by thermotropic self-assembly of X-shaped bolapolyphiles.

White Rose Research Online URL for this paper:
http://eprints.whiterose.ac.uk/154805/

Version: Published Version

Article:
Chen, C., Kieffer, R., Ebert, H. et al. (6 more authors) (2019) Chirality induction through nano-phase separation: Alternating network gyroid (I4132) phase by thermotropic self-assembly of X-shaped bolapolyphiles. Angewandte Chemie International Edition.
ISSN 1433-7851

https://doi.org/10.1002/anie.201911245

Reuse
This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here:
https://creativecommons.org/licenses/

Takedown
If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.
Abstract: The single gyroid phase as well as the alternating double network gyroid, composed of two alternating single gyroid networks, hold a significant place in ordered nanoscale morphologies for their potential applications as photonic crystals, metamaterials and templates for porous ceramics and metals. Here, we report the first alternating network cubic liquid crystals. They form through self-assembly of X-shaped polyphilic molecules, where glycerol-capped terphenyl rods lie on the gyroid surface while semiperfluorinated and aliphatic side-chains fill their respective separate channel networks. This new self-assembly mode can be considered as a two-color symmetry-broken double gyroid morphology, providing a tailored way to fabricate novel chiral structures with sub-10 nm periodicities using achiral compounds.

New routes to chirality from initially achiral systems are of particular contemporary interest for obtaining chiral templates in asymmetric synthesis and catalysis.[1] This is important for the use in different fields of material- and nanoscience[2] as well as for the understanding of fundamental principles of the emergence of biological homochirality.[3] Creating chirality in liquids and liquid crystals (LCs), having no fixed positions of individual molecules, is especially challenging.[4,5] Nevertheless, it was recently achieved by mirror symmetry breaking through synchronization and locking-in of transient chiral conformations and configuration.[6] Here we report a new approach to spontaneous generation of chirality based on nano-phase segregation. In the reported case, breaking the inherent mirror symmetry of the double gyroid cubic phase (Ia3d, Q230), known from lyotropic[7] and thermotropic liquid crystals (LCs)[8] (Figure 1a), is achieved by self-assembly of X-shaped polyphilic molecules with two different chains at opposite sides of a rod-like molecular core.[8b] The cores arrange along the gyroid minimal surface, forming a wall that separates the two enantiomeric infinite networks involving these chains. Nano-phase separation of the two poorly compatible semiperfluorinated and aliphatic side-chains, into their own networks (blue and red in Figure 1b), gives rise to a gyroid cubic phase with two chemically non-equivalent networks (the “single gyroid” I4,32, Q214). This structure has broken mirror symmetry and represents the first alternating network gyroid cubic LC, and the first LC with chirality solely based on phase separation. Previous attempts to produce a single gyroid structure were based on replication from butterfly wings,[9] lithography[10] and templating.[11] The alternating double network gyroid was found in narrow composition ranges of multiblock copolymer blends,[11,12] leading to structures in the > 100 nm range in all cases. The new concept reported herein provides a tailored way to fabricate chiral structures with much smaller sub-10 nm periodicities, which are of great potential in nano-templating and as enantiospecific membranes for use in enantiomer separation.

Figure 1. a) The double-network gyroid Ia3d cubic phase and b) the alternating double gyroid cubic phase involving two networks comprising different components separated by the G minimal surface (this work).
Table 1: Structure information, phase transitions (transition temperatures and associated enthalpy changes), and lattice parameters of X-shaped molecules 1—3.

| Comp. | $R_{ni}$ | $n$ | $R_{t}$ | Phase transitions$^{[a]}$ | Lattice parameter [nm]$^{[b]}$ | Volume fraction of side chains$^{[c]}$ [%] |
|-------|---------|-----|---------|-----------------|-----------------|-----------------|
| 1a    | -C$_{20}$H$_{40}$ | 6   | -C$_{15}$F$_{30}$ | Cr$_{I}$ [18] Cr$_{I}$ [35] Col$_{w}$/p6mm $^{[81]}$ iso | 6.89 | 62.7 |
| 1b    | -C$_{20}$H$_{40}$ | 6   | -C$_{10}$F$_{21}$ | G $^{[24]}$ Cub/4,32 $^{[88]}$ iso | 9.19 | 64.5 |
| 1c    | -C$_{20}$H$_{40}$ | 6   | -C$_{7}$F$_{15}$ | Cr $^{[106]}$ (Cr$_{I}$ $^{[103]}$ iso 2.0 | 6.32 | 66.2 |
| 2     | -C$_{20}$H$_{40}$ | 4   | -C$_{7}$F$_{15}$ | Cr $^{[104]}$ Cub/4,32 $^{[110]}$ iso 11.4 | 8.70 | 64.9 |
| 3     | -C$_{20}$H$_{40}$ | 4   | -C$_{10}$F$_{21}$ | Cr $^{[35]}$ Cub/4,32 $^{[102]}$ iso 16.0 | 8.88 | 64.0 |

$^{[a]}$ Recorded from first DSC heating at 10 K min$^{-1}$ (see Figure S1) and POM; brackets mean metastable phase (only observed upon heating); transition temperatures $T$ (°C) are given in square brackets, associated enthalpy changes $\Delta H$ (kJ mol$^{-1}$) are given in lower lines in italics; $^{[b]}$ Determined by synchrotron powder small angle X-ray scattering; $^{[c]}$ Volume fraction of side chains measured using Material Studio. Abbreviations: Cr, Cr$_{I}$, Cr$_{I}$ = crystalline solid; G = glassy solid; Col$_{w}$/p6mm = Hexagonal columnar phase with p6mm symmetry; Cub/4,32 = alternating double network gyroid cubic phase with 4,32 symmetry; Col$_{I}$ = lamellar soft crystal phase; iso = isotropic liquid. * Partial crystallization.

To this end, a series of X-shaped molecules has been specifically designed and synthesized. These molecules are based on a p-terphenyl core terminated by two hydrogen-bonded polar glycerol groups, and bearing two laterally attached incompatible chains, that is, an aliphatic hydrocarbon chain ($R_{ni}$) and a semiperfluorinated chain ($R_{t}$) containing a short -(CH$_2$)$_n$- spacer and a long perfluorinated end segment -C$_{15}$F$_{30}$ (see Table 1). For details on synthesis and experimental procedures, see the Supporting Information. Most compounds form enantiotropic LC phases, except for compound 1a, which only exhibits a monotropic soft crystal phase (see Table 1). Here, compounds 1b, 2 and 3 are of main focus, all forming a novel alternating double network gyroid phase with lattice parameters below 10 nm upon both heating and cooling.

As the length of the perfluorinated side chain is increased, compounds 1a-c exhibit a phase sequence Col$_{w}$/p6mm—Cub/4,32—Cr$_{I}$ $^{[32]}$ (Table 1 and Figure 2a–c). Compound 1a, bearing the shortest semiperfluorinated chain, is found to form a hexagonal columnar phase showing a birefringent fan-like texture interspersed with black homeotropic regions (Figure S2a, Supporting Information). The sharp Bragg reflections in small angle X-ray scattering (SAXS) are indexed on a 2D hexagonal lattice with unit cell parameter $a_{hex} = 6.89$ nm, showing only diffuse scattering in the wide angle region, characteristic of a LC (Figures 2a, S3 and Tables 1, S1). The lattice parameter corresponding to about three times the molecular length ($L_{max} = 2.3–2.6$ nm measured between the two terminal polar groups). The electron density map reconstructed based on $p6mm$ symmetry (Figure S10) shows a partly segregated two-color tiling composed of a lower-density (alkyl) column and two higher density (mixed) columns. The analysis of the two-color Col$_{hex}$ phase is described in Section 5 of the Supporting Information. The aromatic cores make up the walls between the columns with glycerol groups forming the hydrogen bonding networks at cell edges (Figure 4g).

As the side chain length is increased, the honeycomb is replaced by new mesophases. The mesophase in compound 1b, having a slightly longer semiperfluorinated chain, grows with a completely dark texture under crossed polarizers (Figure S2b). This isotropic mesophase has high viscosity, which is typical of a cubic phase. The reciprocal $d$-spacings from the SAXS reflections are in the ratio $2^{1/2}$:$6^{1/2}$:$8^{1/2}$:$14^{1/2}$:$22^{1/2}$:$26^{1/2}$:$30^{1/2}$:$34^{1/2}$:$36^{1/2}$:$38^{1/2}$:$42^{1/2}$ and could be indexed on a body-centered cubic lattice (for Miller indices see Figure 2b). Alternative indexing on a primitive Bravais lattice, with the first reflection as (100) instead of (110), would have had the $a/d$ of the $4^{th}$ reflection equal to $7^{1/2}$ instead of $14^{1/2}$, a $(h^2+k^2+l^2)^{1/2}$ value unobtainable for any combination of Miller indices. Thus, a primitive lattice is excluded. Furthermore, due to the clear absence of the (200) reflection ($a/d = 4^{1/2}$), only one space group, I4,32, satisfies the observed extinction conditions, which include the 4, screw axis condition 00l: $l = 4n$. Note that the 9th peak can be indexed as either (600) or (442), hence its presence in powder SAXS does not violate the screw-axis condition. Just to safeguard ourselves against the remote possibility that the absence of (200) is coincidental, we constructed the electron density map using $Im3m$ symmetry. However, in this case we obtain a body centered micellar structure with the fluorinated chains forming the micelles (Figure S11a); the high curvature of the micelles is unlikely considering the molecular structure, volume fractions and dimensions. Accordingly, the mesophase in compound 1b is assigned as a bicontinuous cubic with symmetry I4,32 (Figures 2d–g and S11b). Thus, we have the first documented case of a I4,32 cubic phase in liquid crystals, thermo- or lyotropic.
Figure 2. a–c) Synchrotron SAXS diffractograms of the mesophases of compounds 1a–c at given temperatures. d–g) Reconstructed electron density maps in 2 × 2 × 2 unit cell. The boundaries are estimated by the volume fractions of each segment: d) network formed by semiperfluorinated chains; e) gyroid minimal surface formed by molecular cores; f) network composed of the aliphatic chains; g) overall view of the electron density map (purple = perfluorinated chains, cyan = rod-like cores of aromatic and polar segments, red = alkyl chains). h,j) Views along a right-handed (h) and a left-handed (j) 4/32 phase, illustrating the opposite chirality of the two networks.

Since the intensities of all remaining reflections are smaller than 1% of the strongest (110) reflection (Tables S2, S4 and S5), the electron density map is dominated by that reflection, whose phase is either +π/2 or −π/2 rad. The map constructed using one of these phases is simply the reverse of that obtained using the other, meaning that the maps are identical except for a change of origin. Different representations of the map are shown in Figure 2d–g, where purple color indicates the regions of high, and red the regions of low electron density. The cyan intermediate density region follows the familiar gyroid surface of minimum curvature. The map is closely related to those of the double gyroid phase, except that in the latter case the color of the regions on both sides of the minimum surface would be the same, as both networks in the 1a3d phase have either lower or higher density than the minimal surface, depending on the compound. Thus, we can conclude that, as in the double gyroid, in our 4/32 phase there are two infinite networks with 3-way branched channels separated by the gyroid surface. Only here one network contains the high-density Rf and the other the low-density Rh chains (Figure 2d,f, respectively). In fact, the high-density network is of a core–shell type, with the perfluorinated chain ends in the center of the channels surrounded by the short aliphatic spacers. The gyroid surface is composed of the glycerol-terminated cores lying within it (Figure 2e,g).

The distance between the two 3D networks is $a_{\text{up}} \times 3^{1/2}/4 = 4.0 \text{ nm}$, which is the same as the distance between the columns (the prismatic honeycomb cells) of the hexagonal phase of compound 1a, which is $a_{\text{up}} \times 3^{1/2} = 4.0 \text{ nm}$ (Figures S10 and S12). This equivalence is to be expected, as in both cases we have an “inverse” thermotropic LC phase in which columns of flexible chains are surrounded by “walls” of rigid aromatic-glycerol rods; in the columnar case these are the honeycomb cell walls and in the cubic case the wall is the minimal surface of the same constitution.

To confirm our structure assignment in real space, compound 3 was imaged at temperatures of the cubic phase by atomic force microscopy (AFM). Images of two different crystallographic planes, (110) and (111), are shown in Figure 3a,c. Phase contrast is due to the difference in shear modulus between the stiffer Rf chains (dark) and the softer Rh chains (light). A comparison with the corresponding cuts through the electron density map (Figure 3b,d) confirms the general correspondence in geometry of the ED slices and the AFM images, the two methods agreeing in spacings and angles within 3%. The measured distance between the rows of motifs in the (111) plane is 11.2 nm (Figure 3c) while the value calculated from SAXS is $a/6/2 = 10.9 \text{ nm}$, with the rows inclined by exactly 60°; the measured distance between the rows in the (110) plane of 7.0 nm (Figure 3a) and the angle of 75° also compares well with the values of 6.8 nm and 73° measured from the (110) section through the map in Figures 3b and S14. However, while the position of the dark Rf spots on the triangular lattice in Figure 3c matches well with those of the centers of the 3-arm stars in Figure 3d, the star-like feature is absent in the AFM image. We attribute this discrepancy to surface reconstruction, as broken network segments at the surface coalesce in blobs (white domes in Figure 3e) to minimize their surface energy.

Having established the structure of the new cubic LC, it is important to note that 4/32 is a chiral space group, and the phase is therefore chiral, even though the compounds forming it are achiral. The chirality comes from the fact that the two enantiomorphous networks are chemically different (see Figure 2h, i) which breaks the mirror symmetry. In contrast, the achiral double gyroid Ia3d phase, having two identical but...
These are not the final page numbers!
mesophases are of the “inverse” thermotropic kind. The present molecules could be regarded as having a tapered shape, but with the chain ends located on average near the narrow end and the rigid rod spanning the wide end of the wedge—see Figure 4a–c. This is the opposite of the usual case of wedge-shaped mesogens, where the aromatic is at the apex and the multiple attached chains fan out at the wide end.[20]

For such “normal” wedges it has been shown that a key determinant of the adopted phase type is the dV/dr function, describing how volume increases as one moves along r from the apex (r = 0) toward the wide end of the wedge.[21] The same principle can be applied to the present inverse wedges. As a first approximation, the cross-section area A of the wedge is A(r) ∝ dV/dr ∝ r². Here q ≈ 1 (slice or triangle shape) suits a columnar phase (Figure 4a), q ≈ 0 (rectangle, matching aromatic and aliphatic cross-sections) suits a lamellar phase (Figure 4c), while 0 < q < 1 (shield shape) is most likely to adopt a C₂₅₂ phase (Figure 4b).[22] It is worth noting that a network of branched columns in a C₂₅₂ phase is an intermediate between straight columns and layers, as depicted in Figure 4d,e. A more detailed schematic of the molecular arrangement in the three phase types in the present compounds is given in Figure 4f–i.

In conclusion, we present the first I₄,3₂ alternating double network gyroid cubic LC. The work demonstrates a novel way of inducing chirality through phase separation in chemically non-chiral systems. The network segments reported here are on the scale of only a few nm between junctions, which is of great potential in nano-templating[12d] for example as enantiomer-specific membranes[8] for use in enantiomer separation and production and manipulation of circularly polarized light, chirality switching through thermally, chemically or light-induced mesophase transitions.[23] Moreover, the present study shows how the principle of self-assembled multicolor tiling can be extended from two dimensions (columnar) to three dimensions (cubic),[13,24] providing a new way to fabricate complex nano-architectures.

Acknowledgements

The work is supported by the National Natural Science Foundation of China (Nos. 21761132033, 21374086, 21674099), the Deutsche Forschungsgemeinschaft (392435074) and EPSRC (EP-K034308, EP-P002250). The authors thank 111 Project 2.0 (BP2018008) for the financial support and Station I22, Diamond Light Source and Beamline BL16B1 at SSRF (Shanghai Synchrotron Radiation Facility, China) for providing the beamtimes.

Conflict of interest

The authors declare no conflict of interest.

Keywords: chirality - liquid crystals - mirror symmetry breaking - single gyroid - soft matter

References

[1] Y. Nagata, R. Takeda, M. Sugimome, ACS Cent. Sci. 2019, 5, 1235–1240.
[2] M. Liu, L. Zhang, T. Wang, Chem. Rev. 2015, 115, 7304–7397.
[3] D. G. Blackmond, Cold Spring Harbor Perspect. Biol. 2010, 2, a002147.
[4] a) K. V. Le, H. Takezoe, F. Araoka, Adv. Mater. 2017, 29, 1602737; b) C. Tschieck, Liq. Cryst. 2018, 45, 2221–2252.
[5] C. Dressel, T. Reppe, M. Prehm, M. Brautzsch, C. Tschieck, Nat. Chem. 2014, 6, 971–977.
[6] C. Tschieck, G. Ungar, ChemPhysChem 2016, 17, 9–26.
[7] a) V. Luzatti, P. A. Spegt, Nature 1967, 215, 701–704; b) J. F. Sadoc, J. Charvolin, J. Phys. (Paris) 1996, 47, 685–691.
[8] a) G. Ungar, F. Liu, X. Zeng, Handbook of Liquid Crystals, 2nd ed., Wiley-VCH, Weinheim, 2014, pp. 363–436; b) C. Tschieck, Angew. Chem. Int. Ed. 2013, 52, 8828–8878; Angew. Chem. 2013, 125, 8992–9047; c) T. Kato, J. Uchida, T. Ichikawa, T. Sakamoto, Angew. Chem. Int. Ed. 2018, 57, 4355–4371; Angew. Chem. 2018, 130, 4438–4455; d) S. Kutsunizum, Isr. J. Chem. 2012, 52, 844–853.
[9] C. Mille, E. C. Ty rode, W. R. Corkery, Chem. Commun. 2011, 47, 9873–9875.
[10] C. K. Ullal, M. Mal dov an, M. Wohl gemuth, E. L. Thomas, J. Opt. Soc. Am. A 2003, 20, 948–954.
[11] Q. Zhang, F. Matsuoka, H. S. Suh, P. A. Bea uca geo, S. S. Xiong, D. M. Smig lies, K. W. Tan, J. G. Werner, P. F. Nealey, U. B. Wiesen, ACS Nano 2018, 12, 347–358.
[12] a) M. Seki, J. Suzuk i, T. Matushita, J. Appl. Crystallogr. 2000, 33, 285–290; b) T. H. Epps, E. W. Cochr an, T. S. Bailey, R. S. Wa letzko, C. M. Hardy, F. S. Bates, Macromolecules 2004, 37, 8325–8341; c) J. Chatterjee, S. Jain, F. S. Bates, Macromol. Chem. Phys. 2007, 40, 2882–2896; d) X. Cao, W. T. Mao, Y. Y. Mai, L. Han, S. Che, Macromolecules 2018, 51, 4381–4396.
[13] a) X. Zeng, R. Kieffer, B. Glettner, C. Nürnber ge, F. Liu, K. Pelz, M. Prehm, U. Baumeister, H. Hahn, H. Lang, G. A. Gehring, C. H. M. Weber, J. K. Hobbs, C. Tschieck, G. Ungar, Science 2011, 331, 1302–1306; b) S. George, C. Bentham, X. B. Zeng, G. Ungar, A. G. Gehring, Phys. Rev. E 2017, 95, 062126.
[14] C. Tschieck, J. Mater. Chem. 2001, 11, 2647–2671.
[15] C. Dressel, F. Liu, M. Prehm, X. Zeng, G. Ungar, C. Tschieck, Angew. Chem. Int. Ed. 2014, 53, 13115–13120; Angew. Chem. 2014, 126, 13331–13336.
[16] K. Mislow, P. Bickart, Isr. J. Chem. 1976, 15, 1–6.
[17] M. Saba, B. D. Wilts, J. Hielcher, G. E. Schröder-Turk, Mater. Today Proc. 2014, 1, 193–208.
[18] G. Ungar, Polymer 1993, 34, 2050–2059.
[19] E. S. Clark, L. T. Nuus, Z. Kristallogr. 1962, 117, 119–127.
[20] K. Borirsch, C. Tschieck, P. Goring, S. Diele, Chem. Commun. 1998, 2711–2712.
[21] a) X. Zeng, G. Ungar, M. Impéror-Clerc, Nat. Mater. 2005, 4, 562–567; b) X. Zeng, S. Poppe, A. Lehmann, M. Prehm, C. Chen, F. Liu, H. Lu, G. Ungar, C. Tschieck, Angew. Chem. Int. Ed. 2019, 58, 7375–7379; Angew. Chem. 2019, 131, 7453–7457.
[22] Y.-X. Li, F.-F. Fan, J. Wang, L. Csch, M. Xie, X.-B. Zeng, G. Ungar, Chem. Eur. J. 2019, Chem. Eur. J. 2019, 25, 13739–13747.
[23] Photonic Functional Soft Materials: Preparation, Properties, and Applications (Ed.: Q. Li), Wiley-VCH, Weinheim, 2019.
[24] J. J. K. Kirkensgaard, M. E. Evans, L. de Campo, S. T. Hyde, Proc. Natl. Acad. Sci. USA 2014, 111, 1271–1276.

Manuscript received: September 3, 2019
Revised manuscript received: November 24, 2019
Accepted manuscript online: November 25, 2019
Version of record online: [link]

These are not the final page numbers!
Chirality Induction through Nano-Phase Separation: Alternating Network Gyroid Phase by Thermotropic Self-Assembly of X-Shaped Bolapolyphiles

Self-sorting of the two poorly compatible side-chains of X-shaped polyphiles into their own networks gives rise to a chiral gyroid cubic phase (the "single gyroid" I4;32) with two chemically non-equal networks. This is the first alternating network gyroid cubic liquid crystal, and the first liquid crystal with chirality solely based on phase separation, allowing the self-assembly of chiral structures with sub-10 nm periodicities.