Exceptionally Wide Thermal Range Enantiotropic Existence of a Highly Complex Twist Grain Boundary Phase in a Pure, Single-Component Liquid Crystal Chiral Dimer

Madhu Babu Kanakala and Channabasaveshwar V. Yelamaggad*

ABSTRACT: Twist grain boundary (TGB) phases exhibiting highly frustrated and complex liquid crystal structures have aroused enormous interest because of their close resemblance to superconductors. The remarkable experimental demonstration of their occurrence by Goodby and co-workers paved the way for developing new research endeavors. However, of the several genuine concerns associated with these intriguing structures, their temperature range has been challenging. In this communication, we report the occurrence of the TGB phase with smectic C* blocks (TGBC*) over a vast, unprecedented thermal range of ∼170 °C in a newly synthesized chiral dimer derived from cholesterol. Detailed investigations covering synthesis, characterization, and evaluation of liquid crystallinity with the aid of optical, calorimetric, and X-ray diffraction are presented.

I. INTRODUCTION

The diverse manifestations of chirality (handedness) in the universe from the microscopic level to mesoscopic scales have inspired the design and development of a wide variety of chiral materials, including supramolecular self-complimenting systems. Such investigations have led to the discovery of novel chiral materials displaying complex helical superstructures originating from the manifestation of molecular chirality via self-assembly or self-organization or packing of the constituent functional chiral molecules. For instance, the twist grain boundary (TGB) phases, which have been known since 1988, represent one of the fascinating soft-matter phases where the striking manifestations of chirality persist vividly, involving fluidity, order, frustration, and a regular array of defects. They have been considered as the chiral LC analogs of the Abrikosov vortex lattice phase of type-II superconductors in an external magnetic field. Generally, they exist over a short thermal span between the isotropic (I)/N* short-pitch chiral nematic LCs at the thermotropic phase transition from the isotropic (I)/N* phases. The helix and the smectic layers is not feasible. However, the co-existence of these two different orderings is attained by forming a defect structure. That is, the continuous structure (TGB phase) is formed by small blocks (slabs) of mesogens with a local smectic order that are rotated with respect to each other via sets of screw dislocations situated at their interface leading to a helical superstructure. Accordingly, several TGB phases differing in the local smectic order have been theoretically predicted and found experimentally in short-pitch chiral nematic LCs at the thermotropic phase transition from the isotropic (I)/N* and SmA or SmC or SmC* phases over a short temperature width of a few degrees Celsius. Of these, the TGBC* phase has received considerable attention not only due to the structural complexity and the exhibition of fascinating defect textural patterns but also because it responds to the applied electrical field. Interestingly, it shows the striking square or hexagonal grid texture superimposed on the homogeneously aligned textural pattern. Unlike other TGB phases, it is characterized by a hierarchical structure where the director (n), the direction of the orientation, of all the mesogens is twisted in directions perpendicular to the TGB layer helix axis. In other words, in the TGBC* phase, the piled-up helislabs, the smectic (SmC*) helilayers with the helical pitch P ≈ 2 μm.
superimpose on a stack of smectic slabs present in the form of density waves. Accordingly, it shows a wide range of variable length scales, which includes the layer thickness of the smectic blocks, periodicity of the TGB helix, the spacing of the square grid texture, etc.\textsuperscript{49} Therefore, there have been constant explorations to design and synthesize new chiral LCs (single-component systems) or realize mixtures capable of displaying the TGBC* phase over a wide thermal span.\textsuperscript{31−44} However, the literature indicates that it is highly challenging to discover the exact molecular structural parameters/compositions required for chiral mesogens or appropriate LC mixtures competent at displaying the TGBC* phase with a wide temperature range. In this communication, we report the occurrence of the TGBC* phase over an unparalleled, extensive temperature range of 170 °C in a novel, non-symmetric liquid crystalline dimer MBC-253 (Figure 1c) formed by covalently binding the natural cholesterol with a three-ring salicylaldehyde core through an oxybutanoyloxy (even-parity) spacer. This particular molecular design stemmed from the previous reports that the cholesterol-based dimers comprising either a three- or four-ring core favor the thermodynamic stabilization of the TGBC* phase over an extended thermal range.\textsuperscript{41,42}

II. RESULTS AND DISCUSSION

The novel chiral LC dimer MBC-253 was synthesized in quantitative yield (94%) by reacting equimolar amounts of 4-formyl-3-hydroxyphenyl 4-(dodecyl oxy)benzoate (P1) and cholesteryl 4-(4-aminophenoxy)butanoate (P2) (Figure 1) in refluxing ethanol along with a mild acid catalyst (acetic acid) (see the Supporting Information for details) and fully characterized with the aid of data derived from UV−Vis (Figure S1), FTIR (Figure S2), and \textsuperscript{1}H & \textsuperscript{13}C NMR (Figure S3) and microanalytical data (see the Supporting Information). The dimer MBC-253 and the corresponding precursors showed characterization data consistent with their chemical structure. The thermotropic mesomorphism of the newly synthesized chiral dimer was studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and powder X-ray diffraction (XRD). The phase sequence, transition temperatures, and enthalpies of the transitions derived from POM and DSC studies are presented in Table 1. The DSC thermograms recorded for the first heating–

| Phase | Heating Temperature (°C) | Cooling Temperature (°C) | Delta Entropy (kJ mol\textsuperscript{-1}) | Delta Enthalpy (kJ mol\textsuperscript{-1}) |
|-------|--------------------------|--------------------------|------------------------------------------|------------------------------------------|
| Cr    | 134.8 (50.7)             | 87.9 (21.3)              | 0.5                                       | 0.7                                       |
| TGBC* | 264                      | 258.4                    | 0.7                                       | 0.5                                       |
| N*    | 274.6 (0.7)              | 269.7 (0.5)              |                                           |                                           |

\textsuperscript{0} Transition temperatures determined by both polarizing optical microscope (POM) and DSC traces; peak values of the DSC traces during the first heating/cooling cycles at a 5 °C/min rate are given.\textsuperscript{1} The thermotropic phase transitions were seen under POM, but they were too weak to be detected by DSC.\textsuperscript{**} = Enantiotropic phase. Cr: Crystal. TGBC*: Twist grain boundary phase with chiral smectic C (SmC*) blocks. N*: Chiral nematic phase. I: Isotropic liquid state. The thermal width of the TGBC* phase occurrence.

The dimer MBC-253 and the corresponding precursors were characterized with the aid of data derived from UV−Vis (Figure S1), FTIR (Figure S2), and \textsuperscript{1}H & \textsuperscript{13}C NMR (Figure S3) and microanalytical data (see the Supporting Information). The dimer MBC-253 and the corresponding precursors showed characterization data consistent with their chemical structure. The thermotropic mesomorphism of the newly synthesized chiral dimer was studied by polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and powder X-ray diffraction (XRD). The phase sequence, transition temperatures, and enthalpies of the transitions derived from POM and DSC studies are presented in Table 1. The DSC thermograms recorded for the first heating–

cooling cycles at a 5 °C/min rate are illustrated in Figure 2a (Table 1). The heating trace comprises two endothermic peaks at about 134 °C (ΔH = 50.7 kJ mol\textsuperscript{-1}) and 274 °C (ΔH = 0.7 kJ mol\textsuperscript{-1}) originating from the crystal melting and LC-to-isotropic liquid state phase transitions of the sample, respectively. In the cooling flow curve, the corresponding exothermic signals occurred at ~270 °C (ΔH = 0.5 kJ mol\textsuperscript{-1}) and ~87 °C (ΔH = 21 kJ mol\textsuperscript{-1}), as expected. The DSC traces obtained for the subsequent heating−cooling cycles were found to be nearly similar (Figure S4) to that obtained for first cycles, implying that the dimer is thermally stable. To corroborate this observation, thermogravimetric analysis (TGA) was performed. As shown in Figure 2b, the TGA curve recorded for the pristine (as synthesized, purified) sample from room temperature to 800 °C in the presence of...
nitrogen supports the results of DSC experiments. For the optical textural study, the dimer was placed between a glass slide and a coverslip and heated to its clearing temperature to obtain a thin film of the liquid sample. On cooling from the isotropic liquid state, the typical pseudo-focal-conic texture of the N* phase appears from the dark surroundings (Figure S5a) where the helix axis of the structure has a randomly varying spatial distribution with respect to the glass surface normal. When this texture was subjected to mechanical shearing, it transformed instantly to a Grandjean planar texture having oily streaks (Figure S5b) in which the mesogens are arranged parallel to the glass substrate and the helical axis remains perpendicular to the glass plates (along the viewing direction). Further cooling of the sample resulted in another LC phase, which remains unaltered until the crystallization of the sample appears. Depending upon the surface anchoring conditions (the alignment of mesogens), this mesophase existing below the N* phase displayed some striking textural patterns that were found to be characteristic of the TGBC* phase. When the sample is cooled from the focal-conic pattern of the N* phase, the TGBC* phase comes into existence with the growth of tiny chiral lines on the focal conics that eventually coalesce to yield columnar- or cone-like domains (Figure S5c). If the sample is cooled from the Grandjean planar texture of the N* phase, the TGBC* phase appears exhibiting a distinct square grid pattern texture superimposed on the planar texture (Figure S5d–f) that remains intact until the sample crystallizes at ~87 °C. Notably, in some regions of the cell, especially near the edges where the mesogens are aligned homeotropically, the TGBC* phase exhibited a filament texture with an undulatory pattern occurring over a dull grayish texture (Figure S5g); the periodicity of this structure is roughly the same as that of the spacing in the aforesaid grid pattern. As expected, the filament texture remains unmoved down to 87 °C.

The sample was further examined using glass plates pretreated with polyimide and unidirectionally rubbed so that the director, n, orients homogeneously. Upon cooling from the isotropic phase, the Grandjean plane texture, which is
a characteristic of the N* phase, appears. This pattern evidences that the helix axis is along the viewing direction. On further cooling, at the second transition, the planar texture of the N* phase sharply changes into a well-aligned square grid pattern (Figure 3a), which remains up until 87 °C (Figure 3b) where it transforms into a solid. To reveal that the grid pattern registered is genuinely due to the TGBC* structure and not because of the instabilities in the SmC* phase, the dimer was examined in a wedge-shaped cell where the thickness varies from one end to another. Such a cell was fabricated using glass substrates pretreated for the homogeneous anchoring. On cooling the sample from the isotropic liquid, an array of Grandjean−Cano lines appears due to the N* phase; here, the helix direction remains normal to the glass substrates. On lowering the temperature further, the above pattern transforms to a square grid pattern developing over these dislocation lines. As shown in Figure 3c, the TGBC* phase shows the Cano lines superposed on the square grid pattern, as expected. The Grandjean−Cano lines imply the presence of the TGB helical superstructure (twist axis normal to the substrate), whereas the grid patterns stem from the two-dimensional director modulation in the plane of the anchor, mostly due to the pitch of the SmC* phase. According to the model suggested by Galerne,50 the square grid structure originates from the helislabs separated by disclination lines; the appearance of such a pattern has also been attributed to the undulation of the smectic slabs.36 When the sample was examined on glass substrates treated to give a homeotropic alignment, a filament texture with an undulatory structure is visualized (Figure 3d); the undulated filaments’ growth was abundantly seen when the sample was heated toward the N* phase (Figure S5h−l).

As noted earlier, the TGBC* phase consists of smectic blocks featuring SmC* orientation of the constituent mesogens, and naturally, it possesses the lamellar ordering. Thus, to ascertain the existence of long-range smectic order in TGBC* phase, XRD measurements were performed with Xenocs, Genix Cu MAR345 apparatus using Cu-Kα (1.5418 Å) radiation. The powder (non-oriented) sample was prepared by heating it to the isotropic liquid state and filling in the 0.7 mm-diameter Lindemann capillary. Both the ends of the capillary were flame sealed carefully. The diffraction patterns were recorded as a function of temperature in the cooling mode covering both the mesophases. The XRD profile was recorded in the N* phase for comparison. The one-dimensional (1D) intensity profiles as a function of the scattering angle 2θ, recorded for the N* phase at 260 °C and TGBC* phase at 140, 150, and 160 °C, are depicted in Figures 4a,b, respectively. Table 2 gives the low- and wide-angle peak positions, spacings d (d1 and d2) corresponding to the low-angle reflections, and d1/L ratio derived from the XRD profiles of the N* and TGBC* Phases Exhibited by LC Dimer MBC-253

| mesogen (molecular length L ([Å]) LC phase temperature (°C) low-angle peak position (Å) (spacings: d1, d2) wide-angle peak position (Å) d1/L tilt angle Φ |
|---|---|---|---|---|---|---|
| MBC-253 (58) N* 260 | 16.1 | 4.8 |
| | TGBC* 160 | 43.0 (d1), 21.8 (d2) | 4.8 | 0.74 | 42 |
| | 150 | 41.9 (d1), 21.1 (d2) | 0.72 | 43.7 |
| | 140 | 40.8 (d1), 20.6 (d2) | 0.71 | 45 |

L is the all-trans molecular length (Å) of the LC dimer. Φ = cos−1d1/L.

Figure 4. 1D intensity vs 2θ profiles obtained for the N* phase at 260 °C (a) and the TGBC* phase at 140, 150, and 160 °C (b).

Table 2. Low- and Wide-Angle Peak Positions, Spacings d (d1 and d2) Corresponding to the Low-Angle Reflections, and d1/L Ratio Derived from the XRD Profiles of the N* and TGBC* Phases Exhibited by LC Dimer MBC-253

https://doi.org/10.1021/acsomega.1c00768
ACS Omega 2021, 6, 11556−11562
11559
molecular length ($\text{\AA}$) of the LC dimer MBC-253, which is 58 Å.

As can be seen in Figure 4a, the XRD profile of the N* phase consists of a peak in the small-angle region ($0 < 2\theta < 5^\circ$) centered at $2\theta \approx 5^\circ$ ($d_1 \approx 16.1$ Å) as well as a diffuse reflection in the wide-angle region ($2\theta \approx 20^\circ$); the occurrence of the latter diffuse peak indicates the liquid-like ordering of the constituent LC dimeric molecules in the direction normal to the N* director. The presence of the less intense peak in the low-angle region suggests the presence of a short-range order. It is immediately apparent from Figure 4b that the diffractogram patterns registered at three different temperatures within the thermal range of the TGBC* phase are nearly identical. Seemingly, all the three 1D intensity vs 2$\theta$ plots comprise two low-angle reflections, with $d$ values of 43 Å ($d_1$; intense) and 21.8 Å ($d_2$; weak) (at 160 °C), 41.9 Å ($d_1$) and 21.1 Å ($d_2$) (at 150 °C), and 40.8 Å ($d_1$) and 20.6 Å ($d_2$) (at 140 °C); additionally, they consist of a diffuse peak at wide angles centered at 4.8 Å, which is indicative of a liquid-like order within the smectic layer. The spacing ($d_1$) of the small-angle Bragg reflection observed in all the profiles corresponds to the smectic layer thickness in the TGBC* phase. The second reflection with the spacing $d_2 = 21.8$ Å, which is approximately half of the all-trans molecular length of the dimer, may occur from the combination of different segments of the molecular core. Such a feature has been generally encountered for many dimers derived from cholesterol. There is also a possibility that this reflection would emerge from the Fourier Transform of non-sinusoidal electron density variation of the layer as this kind of harmonics occurs in various smectic phases formed by different LC molecules. Above all, the layer spacing $d_1$ is lower than the theoretical all-trans molecular length ($L$) of the mesogen, and consequently, the $d_1/L$ ratio is less than one, implying the tilted organization of the molecules within the smectic layers with a tilt angle of $\approx 42^\circ$; as can be seen, the $d_1$ value decreases progressively upon cooling the TGBC* phase meaning that the tilt angle of the mesogens within the smectic layers, with respect to the layer normal, increases on decreasing the temperature. Thus, XRD results clearly suggest that the slabs of the TGBC* phase are composed of the smectic layers where the constituent mesogens within an individual layer are tilted at an angle to the layer normal. In essence, the combined results of the POM textural and XRD studies support the presence of the TGBC* phase.

III. CONCLUSIONS

A newly synthesized, chiral (cholesterol-based) LC dimer displays a highly frustrated LC structure characterized by modulations in all the three dimensions, namely, the TGBA phase having SmC* slabs (the TGBC* phase), over an extensive thermal range of 170 °C, which is evidenced unequivocally by optical microscopic, calorimetric, and XRD studies. To our knowledge, the temperature range of the TGBC* phase observed in this study is the highest ever reported hitherto. It is essential to mention here that the experimental TGBC phase stability width is characteristically lower than the TGBA phase range, although both ranges are expected to be comparable theoretically; the same logic can be extended to the TGBC* phase. Thus, this result poses challenges to both theorists and experimentalists to rationally investigate for a better understanding of the physical properties of the TGBC* phase and figure out whether the properties of phase can be exploited in technological endeavors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00768.

General information, synthetic procedure, molecular structural characterization data, UV-vis spectrum, FTIR spectrum, $^1$H and $^{13}$C NMR spectra; DSC trances, textural photomicrographs; DSC thermograms; microphotographs of the defect textures (PDF).

AUTHOR INFORMATION

Corresponding Author

Channabasaveshwar V. Yelamaggad – Centre for Nano and Soft Matter Sciences (CeNS) Arkavathi Campus, Bangalore 562162, India; * orcid.org/0000-0003-3098-8358; Email: yelamaggad@cens.res.in, yelamaggad@gmail.com

Author

Madhu Babu Kanakala – Centre for Nano and Soft Matter Sciences (CeNS) Arkavathi Campus, Bangalore 562162, India; Department of Chemistry, Mangalore University, Mangalore 574199, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00768

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project has been funded by Science and Engineering Research Board Established (SERB), Department of Science & Technology (DST), Government of India, through a grant (No CRG/2020/001779); C.V.Y. gratefully acknowledges and expresses his profound gratitude to SERB for the same reasons. The authors thank Dr. D. S. Shankar Rao and Dr. S. K. Prasad for helpful discussion and their keen interest in the work. They also thank Ms. Rekha Hegde for her help in obtaining the XRD data.

REFERENCES

(1) Hegstrom, R. A.; Kondepudi, D. K. The Handedness of the Universe. Sci. Am. 1990, 262, 108–115.
(2) Avnir, D. Critical Review of Chirality Indicators of Extraterrestrial Life. New Astron. Rev. 2021, 92, 101596.
(3) Wagnière, G. H. On Chirality and the Universal Asymmetry: Reflections on Image and Mirror Image; Wiley-VCH: Weinheim, 2008.
(4) Liu, M.; Zhang, L.; Wang, T. Supramolecular Chirality in Self-Assembled Systems. Chem. Rev. 2015, 115, 7304–7397.
(5) Yashima, E.; Oussaka, N.; Taura, D.; Shimomura, K.; Ikai, T.; Maeda, K. Supramolecular Helical Systems: Helical Assemblies of Small Molecules, Foldamers, and Polymers with Chiral Amplification and Their Functions. Chem. Rev. 2016, 116, 13752–13990.
(6) Morrow, S. M.; Bissette, A. J.; Fletcher, S. P. Transmission of Chirality through Space and across Length Scales. Nat. Nanotechnol. 2017, 12, 410–419.
(7) Whitesides, G. M.; Grzybowski, B. Self-Assembly at All Scales. Science 2002, 295, 2418–2421.
(8) Yang, Y.; Liang, J.; Pan, F.; Wang, Z.; Zhang, J.; Amin, K.; Fang, J.; Zou, W.; Chen, Y.; Shi, X.; Wei, Z. Macroscopic Helical Chirality and Self-Motion of Hierarchical Self-Assemblies Induced by Enantiomeric Small Molecules. Nat. Commun. 2018, 9, 3808.
(9) Wang, L.; Urbas, A. M.; Li, Q. Nature-Inspired Emerging Chiral Liquid Crystal Nanostructures: From Molecular Self-Assembly to DNA Mesophase and Nanocolloids. *Adv. Mater.* 2020, 32, 1801335.

(10) Green, M. M.; Nolte, R. J. M.; Meijer, E. W. (Eds). *Materials Chirality: Volume 24 of Topics in Stereochemistry*; ed John Wiley & Sons Inc.; New Jersey, 2003.

(11) Lewandowski, W.; Vaupotič, N.; Pociecha, D.; Görgek, E.; Liz-Marzán, L. M. Chirality of Liquid Crystals Formed from Achiral Molecules Revealed by Resonant X-Ray Scattering. *Adv. Mater.* 2020, 32, 1905591.

(12) Zheng, Z.-G.; Li, Y.; Bisoi, H. K.; Wang, L.; Bunning, T. J.; Li, Q. Three-dimensional control of the helical axis of a chiral nematic liquid crystal by light. *Nature* 2016, 531, 352.

(13) Goodby, J. W.; Collings, P. J.; Kato, T.; Tschierva, C.; Gleeson, H.; Raynes, P. (Editors). *Handbook of Liquid Crystals*; Volume 1: Fundamentals of Liquid Crystals. Part-II: Symmetry and Chirality in Liquid Crystals; 2nd Edition, Wiley-VCH: Weinheim, 2014.

(14) Kitzerow, H. S. Twist Grain Boundary Phases. Kitzerow, H. S.; Bahr, C. (eds.). *Chirality in Liquid Crystals*; Springer-Verlag: Berlin, 2001, pp. 296–354 and references cited therein.

(15) Dierking, I. Chiral Liquid Crystals: Structures, Phases, Effects. *Symmetry* 2014, 6, 444–472.

(16) Fernsler, J.; Hough, L.; Shao, R.-F.; Maclennan, J. E.; Navailles, L.; Brunet, M.; Madhusudana, N. V.; Mondain-Monval, O.; Boyer, C.; Zasadzinski, J.; Rege, J. A.; Walba, D. M.; Clark, N. A. From The Cover: Giant-Block Twist Grain Boundary Smectic Phases. *Proc. Natl. Acad. Sci.* 2005, 102, 14191–14196.

(17) Goodby, J. W.; Waugh, M. A.; Stein, S. M.; Chin, E.; Pindak, R.; Patel, J. S. Characterization of a New Helical Smectic Liquid Crystal. *Nature* 1989, 337, 449–452.

(18) Goodby, J. W.; Waugh, M. A.; Stein, S. M.; Chin, E.; Pindak, R.; Patel, J. S. A New Molecular Ordering in Helical Liquid Crystals. *J. Am. Chem. Soc.* 1989, 111, 8119–8125.

(19) Goodby, J. W. Twist Grain Boundary and Frustrated Liquid Crystal Phases. *Curr. Opin. Colloid Interface Sci.* 2002, 7, 326–332.

(20) Goodby, J. W. Twist Grain Boundary (TGB) Phases. In *Liquid Crystals II*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2007; pp. 83–147.

(21) Dhar, R. Twisted-Grain-Boundary (TGB) Phases: Nanostructured Liquid-Crystal Analogues of Abrikosov Vortex Lattices. *Phys. Rev. Lett.* 2006, 99, 175–199, and references therein.

(22) Shankar Rao, D. S.; Krishna Prasad, S.; Prajapati, A. K. Frustrated Liquid Crystals: Structures, Phases, Effects. *Adv. Mater.* 2006, 18, 1076–1078.

(23) Yelamaggad, C. V.; Achalkumar, A. S.; Bonde, N. L.; Prasad, S. K. S. Unsymmetrical Trimesogens Exhibiting the Undulated Twist Grain Boundary (UTGBC*) Mesophase. *Liquid Cryst.* 2001, 28, 1581–1583.

(24) Dierking, I. Chiral Dopant Induced Twist Grain Boundary Phases. *Liq. Cryst.* 2001, 28, 165–170.

(25) Cha, S. W.; Jin, J. I.; Achard, M. F.; Hardouin, F. Anomalies of Periodicity in TGB Phases in New Liquid Crystal Dimers. *Liq. Cryst.* 2002, 29, 755–763.

(26) Yelamaggad, C. V.; Achalkumar, A. S.; Bonde, N. L.; Prajapati, A. K. Liquid Crystal Abrikosov Flux Phase: The Exclusive Wide Thermal Range Enantiotropic Occurrence. *Chem. Mater.* 2006, 18, 2463–2472.

(27) Majumdar, K. C.; Shyam, P. K.; Rao, D. S. S.; Prasad, S. K. Occurrence of Unusually Wide Thermal Range Enantiotropic Twist Grain Boundary TGB* Phases in Unsymmetrical Cholesterol and Oxadiazole Based Liquid Crystalline Dimers. *J. Mater. Chem.* 2011, 21, 556–561.

(28) Hiremath, U. S.; Sonar, G. M.; Rao, D. S. S.; Yelamaggad, C. V. Wide Thermal Range Frustrated Liquid Crystal Phase in Chiral Dimers. *J. Mater. Chem.* 2011, 21, 4064–4067.

(29) Geetha, G. N.; Prasad, S. K.; Yelamaggad, C. V. Effect of Electric Field on the TGB* Phase. *Ferroelectrics* 2002, 277, 117.

(30) Pandey, M. B.; Dhar, R.; Achalkumar, A. S.; Yelamaggad, C. V. Characteristic Dielectric Behaviour of the Wide Temperature Range Twist Grain Boundary Phases of Unsymmetrical Liquid Crystal Dimers. *J. Phys. Condens. Matter* 2007, 19, 436219.

(31) Majumdar, K. C.; Shyam, P. K.; Rao, D. S. S.; Prasad, S. K. Frequency and Temperature Dependence of the Dielectric Parameters of Wide Temperature Range TGB and TGB* Phases of Unsymmetrical Liquid Crystal Dimers. *Phase Transitions* 2008, 81, 449–458.

(32) Sahoo, R.; Rao, D. S. S.; Hiremath, U. S.; Yelamaggad, C. V.; Shinde, P.; Prasad, B. L. V.; Prasad, S. K. Influence of Gold Nanorods on the Structure and Photonic Bandgap in a Twist Grain Boundary Phase with Smectic C* Blocks. *J. Mol. Liq.* 2020, 299, 112117.

(33) Galerne, Y.; Developable Domains and Commensurate Structures in the Twist Grain Boundary Phases. *J. Phys. II* 1994, 4, 1699–1711.

(34) Veerabhadraswamy, B. N.; Bhat, S. A.; Hiremath, U. S.; Yelamaggad, C. V. Light-Emitting Chiral Nematic Dimers with Anomalous Odd-Even Effect. *ChemPhysChem.* 2019, 20, 2836–2851.
(52) Nayak, R. A.; Bhat, S. A.; Rao, D. S. S.; Yelamaggad, C. V. Wide thermal Range, Exclusive Occurrence of Technically Significant Chiral Nematic Phase: Synthesis and Mesomorphism of Cholesterol-Based Nonsymmetric Dimers. Bull. Mater. Sci. 2020, 43, 188.

(53) Yelamaggad, C. V.; Shanker, G.; Hiremath, U. S.; Prasad, S. K. Cholesterol-Based Nonsymmetric Liquid Crystal Dimers: An Overview. J. Mater. Chem. 2008, 18, 2927–2949.

(54) Nayak, R. A.; Bhat, S. A.; Shanker, G.; Rao, D. S. S.; Yelamaggad, C. V. Highly Frustrated Liquid Crystal Phases in Optically Active Dimers: Synthesis and Rich Phase Transitional Behavior. New J. Chem. 2019, 43, 2148–2162.