Check for updates

View Article Online
View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. K. Pal, V. Punjani, G. Mohiuddin, S. Kaur, R. K. Khan and S. Ghosh, *Chem. Commun.*, 2018, DOI: 10.1039/C7CC08885J.

Volume 52 | Number 1 | 4 January 2016 | Pages 1–216

ChemComm

Chemical Communications
www.rsc.org/chemcomm

ISSN 1359-7345

ROYAL SOCIETY OF CHEMISTRY

COMMUNICATION
Marilyn M. Olmstead, Alan L. Balch, Josep M. Poblet, Luis Echegoyen *et al.*
Reactivity differences of $Sc_3N@C_{2n}$ ($2n$ = 68 and 80). Synthesis of the first methanofullerene derivatives of $Sc_3N@D_{5h}$-C_{80}

175 YEARS

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/chemcomm

View Article Online
DOI: 10.1039/C7CC08885J

Journal Name

COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Observation of polar order and thermochromic behaviour in a chiral bent-core system exhibiting exotic mesophases by superstructural frustration

Vidhika Punjani,[a‡] Golam Mohiuddin,[a‡] Supreet Kaur,[a] Raj Kumar Khan,[b] Sharmistha Ghosh,[b] and Santanu Kumar Pal*[a]

A new approach accompanied by superstructural frustration is reported by attaching a cholesterol moiety directly to the central bent-core system that displayed exotic BPIII, BPII/I, N_{cyb}*, TGBA phases including $SmAP_A$, SmA and SmX phases as derived by X-ray scattering results. While higher homologue of the series exhibited spontaneous formation of polar order (Ps ~ 61 nC/cm^2) upon applied voltage, the lower homologues showed thermochromic behaviour which can also be trapped *via* temperature quenching.

Frustration, in particular for a molecular system, is important. Originated due to the presence of chirality in molecules, the frustration encourages to develop different complex structures with complicated spatial organization including a rich variety of transitions between differently ordered phases like ripple phases of phospholipids, Langmuir-Blodgett films, quasi-crystal of rapid cool alloys etc.[1-2] The role of molecular chirality has become ever more important in realization of the frustration and their many fold applications viz., pharmaceuticals, food additives, electro-optic devices, and liquid-crystal display technologies etc.[1] Chirality driven helical superstructure in cholesteric liquid crystals (CLCs), a potential 1D photonic bandgap material, allows the selective light reflection due to variation in helical pitch length (λ = np, where p is the pitch length of the helical structure and n is the average refraction index of the LC material). In recent years, CLC based superstructural switching have come into prominence in different field of applications like optical switching, displays, information storage, soft actuators, optic fibre-based temperature sensors and molecular motors.[3-16]

Blue phases (BP) and twist grain boundary (TGB) phases are ideally ubiquitous exhibition of frustration in LC systems. BPs, classified into three categories, namely, a body-centered-cubic BP (BPI), simple cubic BP (BPII) and amorphous BP (BPIII) in order of increasing transition temperature, are considered as the next-generation electro-optic materials with an advantage over slow (~ms) response of nematic LCs used in contemporary displays.[17] Bent-core (BC) LCs are realized as efficient candidates for stabilizing BPs upon suitably doped with different chiral dopant.[17-20] But reports on single component bent-core mesogens exhibiting BPs are very limited.[21-23] The complex TGB structures, arises due to the competition between chiral packing requirements to form spiral macrostructure and the requirement for the formation of a stable lamellar structure, are generally found in between isotropic or chiral nematic (N*) to smectic A (SmA) or smectic C (SmC) phases over a narrow temperature range.[2,24-28] TGB structures are also known as LC analogue of the Abrikosov vortex state in type-II superconductors.[27]

Herein, for the first time we present a series of smart bent-core materials (Scheme 1) that consist of a cholesterol moiety at one arm and 4-*n*-alkoxy-2-hydroxybenzaldehyde at another arm of the central core, exhibiting frustrated structures in the homologous series along with observation of high polar order and thermochromism. A variety of phases such as BPIII, BPII/I, N_{cyb}*, TGBA, $SmAP_A$, SmA and SmX mesophases were observed by varying end alkoxy chain (*n*) of these compounds. Unlike previous reports,[16,21,27] the absence of the spacer unit in between rigid cholesterol moiety and the central benzene core promote stiffness in the molecular architecture which is responsible for the realization of different frustrated phases of these newly synthesized compounds. Further, presence of an *ortho*-OH moiety to the imine linkage encourages the formation of intra-molecular H-bonding that stabilizes the Schiff's base linkage in these materials. Although the first observation of TGB structures was observed in bent-core systems previously, the present report is differentiated from the earlier one by the observation of TGB phase in much wider temperature range, high polar order and by attaching a chiral moiety directly to the central bent-core unit.[28]

The lower homologues of the compounds were found to exhibit different iridescent colours upon cooling the isotropic

---

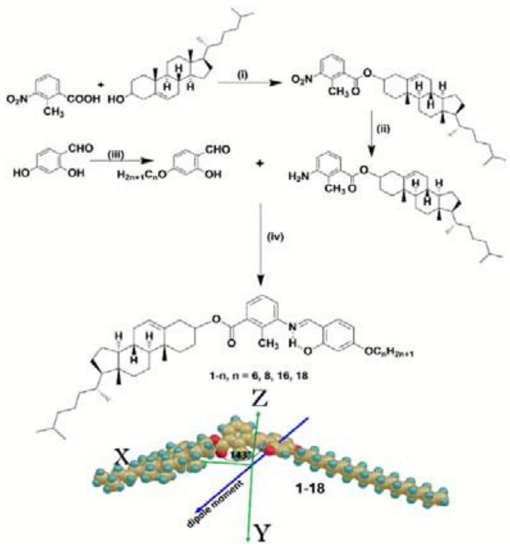
[a] Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector-81, Knowledge City, Manauli 140306 (India).
[b] Department of Physics, University of Calcutta, 92 Acharyya Prafulla Chandra Road, Kolkata-700009. E-mail: skpal@iisermohali.ac.in and santanupal.20@gmail.com

‡ Joint first author

† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/C7CC08885J

thin film which can also be trapped via temperature quenching that might be useful for various device point of view. The higher homologue of the series (n = 18) displayed spontaneous polarization upon applied voltage in the orthogonal phase (SmAP$_A$ phase). The synthetic approach of these cholesterol based BC compounds is sketched in Scheme 1 and the detailed experimental procedures and molecular characterizations are described in the ESI (Fig. S1-21). Density functional theory (DFT) calculations on the molecular architecture leads to realize the bent shape with bent angle 143° (Scheme 1) of the synthesized molecules with various important molecular parameters i.e. dihedral angle, dipole moments, molecular polarizability, HOMO-LUMO energy gap etc. which are presented in ESI (Fig. S39-S41).



Scheme 1. Synthetic details. Reagents and conditions: (i) DCC, dry DCM, DMAP, stirring 12 h; (ii) 5 wt% Pd/C, H_2, EtOAc, stirring 6 h; (iii) Dry acetone, $KHCO_3$, $C_nH_{2n+1}Br$, KI, reflux 12 h; (iv) Abs EtOH, AcOH, reflux 3 h and DFT optimized (at level of B3LYP/6-311G (d,p)) bent molecular geometry of **1-18**.

The observed mesophases, transition temperatures and associated enthalpies are summarized in Table 1 as observed from differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). All the compounds exhibited enantiotropic mesomorphism. Upon cooling the sample **1-8** from the isotropic liquid a foggy bluish texture appeared indicating the formation of amorphous BP at 172.0 °C (Fig. 1a) which turns into cubic BP at 171.7 °C (Fig. 1b). Upon further cooling at 170.8 °C a typical focal conic texture of chiral nematic (N$_{cyb}$*) phase was developed with an enthalpy value 0.16 kJ/mol that turns into cholesteric oily-streak texture (Fig. S22 c,d) upon shearing. At 103.7 °C the mesophase turned into crystalline (enthalpy 20.8 kJ/mol) state. Compound **1-6** exhibited similar behaviour under microscope with BPIII and BPII/I range 0.7 °C and 1.4 °C, respectively (Fig. S22 a,b). However compound **1-18** exhibited an ensemble of four mesophases that nucleate sequentially upon cooling the sample from isotropic liquid. The textural appearances of the compounds (**1-18** and **1-16**) are strongly dependent on the surface alignment of the glass substrate. In an unaligned glass substrate below short lived N$_{cyb}$* phase a transient thread-like texture appeared gradually turns into homeotropic (Fig. S25 a-c) and remain alike until crystallization. In a planar anchoring cell (PI-coated ITO cell, 4.8 µm) appearance of Grandejean-Cano lines (GC lines) of N$_{cyb}$* phase was observed (Fig. 1c) at 144.7 °C (enthalpy 0.41 kJ/mol) which gradually changes to a planar texture composed of differently coloured areas (Fig. 1d) at 141.2 °C (enthalpy 1.03 kJ/mol) resembling the LC analogue of Abrikosov flux phase i.e. TGB phase. The presence of differently coloured areas represents different twisted regions. Upon cooling, this typical texture changes to blurred texture of TGBA phase (Fig. S25 d-f) retained upon further cooling until it changes to a polar antiferroelectric mesophase of SmAP$_A$ at 112.0 °C (confirmed by electro-optic study) with sharp fan-like texture having uniformly coloured areas (Fig. 1e). Below this polar mesophase another unidentified tilted non-polar mesophase (SmX) appeared at 92.5 °C that needs detailed investigation (Fig. 1f) and the re-entrant phenomena in this context cannot be ignored completely. In homeotropic anchoring cell (cell gap 3.3 µm) a transient Schlieren texture of N$_{cyb}$* appeared at 144.7 °C from isotropic liquid which promptly turned to uniformly dark region until crystallization at 70.7 °C, (Fig. S25 g,h) indicating the optically uniaxial nature of the sample, contrary to the normal observed phenomena of TGBA structure.[29] Similar observation was also found for **1-16** (Fig. S28-30) however polar switching was absent.

Table 1. Phase transition temperatures (peak temperature, °C) and enthalpies of transition (ΔH, kJ mol^{-1}, in parentheses) determined by DSC (scan rate 10 °C min^{-1}) and by POM.

Comp	Phase transitions
1-6	**Heating**: Cr 154.7 [25.33] N$_{cyb}$* 181.2 [0.21] Iso **Cooling**: Iso (181.0 BPIII 180.3 BPII/I) 178.9 [0.34] N$_{cyb}$* 81.9 [13.3] Cr
1-8	**Heating**: Cr 155.4 [36.0] N$_{cyb}$* 172.1 [0.20] Iso **Cooling**: Iso (172.0 BPIII 171.7 BPII/I) 170.8 [-0.16] N$_{cyb}$* 103.8 [20.8] Cr
1-16	**Heating**: Cr 125.3 [29.3] TGBA 143.5 [0.43] N$_{cyb}$* 150.0 [0.19] Iso **Cooling**: Iso 148.9 [0.33] N$_{cyb}$* 142.3 [0.54] TGBA 110.6 (SmA 92.2) SmX 88.3 [17.5] Cr
1-18	**Heating**: Cr 121.7 [35.9] TGBA 142.5 [0.96] N$_{cyb}$* 145.9 [0.35] Iso **Cooling**: Iso 144.7 [0.41] N$_{cyb}$* 141.2 [1.03] TGBA 112.0 (SmAP$_A$ 92.5) SmX 70.69 [18.9] Cr

[a]Round brackets for monotropic phases; abbreviations: Cr = crystal; Iso = isotropic; N$_{cyb}$* = chiral nematic phase composed of Sm clusters; SmAP$_A$ = orthogonal smectic structure with layer polarization antiparallel; TGBA = twisted grain boundary phase; for DSC thermograms see Fig. S26 (ESI).

Detailed X-ray diffraction (XRD) measurements were carried out to investigate the phase structure for all the four compounds at a slow cooling rate from the isotropic liquid. The X-ray diffractogram of compound **1-8** (Fig. 2a) is composed of two diffused signals in small angle (d ~ 38.8 Å) and wide angle (d ~ 5.94 Å) region indicate the presence of nematic ordering. The small angle signal is relatively sharper than observed for normal nematic phases and also the intensity exceeding the wide angle signal and continuously becoming sharper with lowering the temperature (Fig. 2b) and thus confirming the cybotactic nature of nematic phase.[28,30] The correlation length (ξ) and d- spacing also increases with decrease in temperature along the whole nematic range (Fig. 2 c) implying cybotactic ordering (N$_{cyb}$*). Similar observation was also found for compound **1-6** (Fig. S27 a-c, S34).

View Article Online
DOI: 10.1039/C7CC08885J

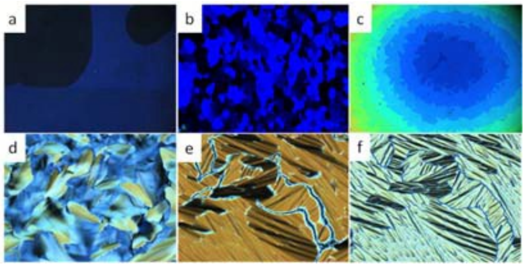


Fig. 1 Microphotograph of (a) BPIII at T = 172.0 °C of **1-8**; (b) BPII/I at T = 171.7 °C of **1-8**; (c) G-C lines of N_{cyb}* at T = 144.7 °C of **1-18**; (d) TGBA phase at T = 141.2 °C of **1-18**; (e) $SmAP_A$ at T= 109.1 °C of **1-18**; (f) SmX at T= 80.1 °C of 1-18 (c, d, e, f are taken in polyimide-coated ITO cell, cell gap 4.8 μm).

In compound **1-18** the chronological order of four different mesophases has been confirmed by the observed XRD pattern during cooling (Fig. S28). The recorded X-ray diffractogram of compound **1-18** at 143 °C is composed of two diffuse signals in small angle (d = 37.6 Å) and wide angle (d = 5.79 Å) region indicating the presence of N_{cyb}* phase (Fig. S29 a-c). Upon further cooling at 139 °C the diffuse small angle signal get sharper indicating the presence of long range order of the cholesteric molecules in the mesophase which is designated as TGBA phase via complementary textural investigation and DSC. The d-value gradually increases upon decreasing temperature until TGBA structure transform to $SmAP_A$ phase (d/L = 0.95, Table S1) which upon further cooling transform to another unidentified nonpolar SmX phase with decrease in d-value which continued until crystallization at 70.7 °C. The d = f (T) plot of compound **1-18** elucidate the variation of layer ordering during phase transition (Fig. 2d) and also point towards the re-entrant phenomenon for TGB phase.[31] The transformation of polar orthogonal mesophase to nonpolar tilted mesophase ($SmAP_A$–SmX) is of much interest and needs further investigation. Compound **1-16** also exhibit similar observation in XRD (Fig. S30-33).

CLCs are widely considered as thermochromic materials due to their Braggs type scattering of the incident light that found various device applications. In the present study compound **1-6** and **1-8** corroborated with N_{cyb}* phase exhibiting thermochromic behaviour upon cooling the isotropic thin film. The yellow colour of isotropic thin film (Fig. 3a) of the compound **1-8** transform to bluish colour (Fig. 3b) during cooling which further transform to greenish appearance (Fig. 3c) and crystallizes subsequently (Fig. 3d). This phenomenon of selective visible light reflection can be attributed to continuous change in the pitch length of CLCs during cooling. The colour of the thin film of the compounds has also been captured by vitrifying it in ice bath (Fig. S35-38) that can be considered to be a good candidate for colour recording.

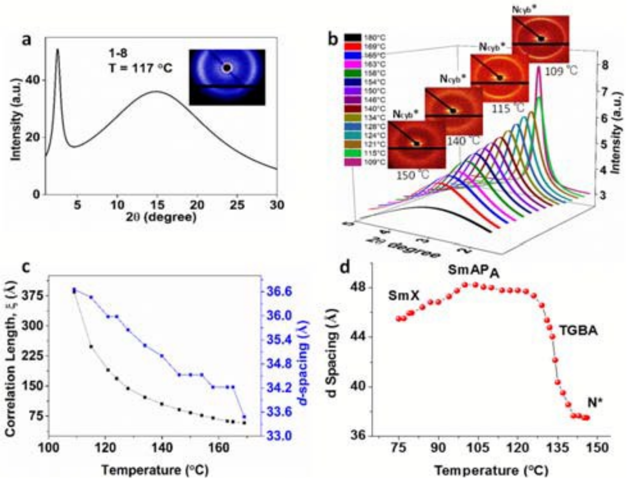


Fig. 2 X-ray diffractogram of (a) Intensity vs 2θ plot of N_{cyb}* phase of compound **1-8**; Comparative plot of intensity vs 2θ in small angle region at different temperatures with 2D-diffraction images (b) in the nematic range of compound **1-8**,(c) Variation of correlation length (ξ) and d-spacing corresponding to the small angle peak with temperature for **1-8**; (d) d = f (T) plot of compound **1-18**.

In order to study the relaxation dynamics of the samples we employed dielectric spectroscopy in the frequency range 20 Hz -10 MHz by using an impedance gain analyser E4990A (Keysight technologies). Different phase transition temperatures and the nature of the mesophases can be identified precisely from the dielectric study. For a representative compound **1-18**, three distinct relaxation modes are observed in all mesophases in planar geometry (10 μm planar cells with antiparallel rubbing) (Fig. 4a). The low frequency (~100-800 Hz) peak P1 has the highest dielectric strength ($\Delta\varepsilon_R$) and strong temperature dependence. In TGBA phase the relaxation frequency (f_R) of this mode decreases linearly upon cooling, suggesting soft-mode like behaviour. $\Delta\varepsilon_R$ is low in TGBA phase but builds-up as the compound enters in to smectic phase, attains a maximum and then decreases (Fig. 4b). As the temperature is reduced beyond $SmAP_A$-SmX transition $\Delta\varepsilon_R$ becomes lower. The possibility of this relaxation process to be a Gold-stone mode is ruled out by application of bias voltage. The peak is not suppressed upon applying a high (40V) bias voltage but only shifts to higher frequency side (Fig. S42) as observed earlier for polar organizations of the molecules in SmAP phases.[32-33] The peak P2 at intermediate frequency range (~8 kHz) is independent of bias and can be attributed to a molecular mode arising from rotation of the molecules along their short axis. The highest frequency peak P3 (3 MHz) does not have any temperature dependence and can be assigned to ITO relaxation mode. Results of the dielectric investigations on **1-8** and **1-16** are given in ESI (Fig. S42).

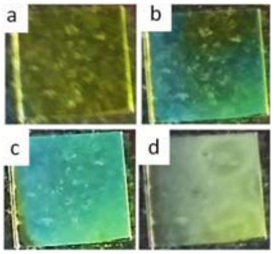


Fig. 3 Photograph displaying thermochromism of thin films of **1-8** during cooling from Iso (a) isotropic liquid; (b) transition to mesophase; (c) mesophase; (d) crystal (the white spots observed in the colored films are due to the background).

View Article Online
DOI: 10.1039/C7CC08885J

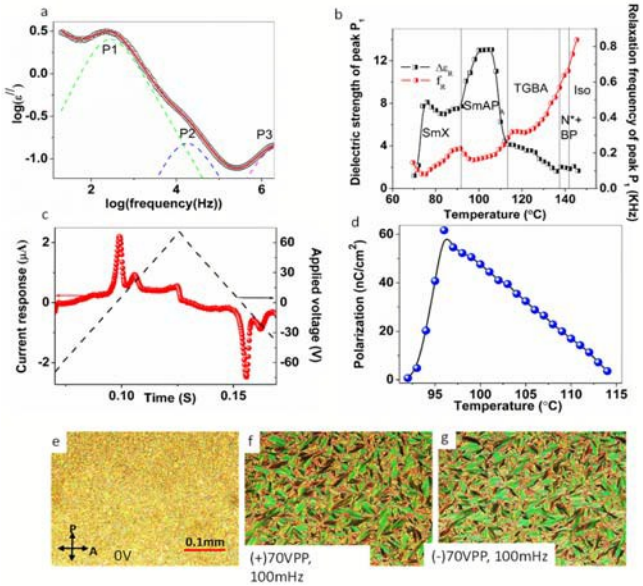


Fig. 4 Dielectric and electro-optic investigations of compound **1-18** in a 10 µm planar cell: (a) Typical dielectric spectra at 110 °C revealing three relaxation peaks; (b) Temperature dependence of dielectric strength ($\Delta\varepsilon_R$) and relaxation frequency (f_R); (c) Current response at 105 °C applying triangular wave voltage $70V_{PP}$, 10 Hz; (d) Polarization as function of temperature as measured on applying a triangular wave field (10 Hz) at 100 V_{PP}; Texture of $SmAP_A$ at 105 °C (e) without any field (f,g) after applying field (±70 V).

The switching current response was investigated using the triangular wave technique for the compounds **1-8**, **1-16** and **1-18**. The existence of polar switching was observed only for the compound **1-18**. As the sample was cooled from isotropic phase, no current peak was obtained until 115 °C. Below this temperature two current peaks per half cycle started appearing indicating the antiferroelectric ground state structure of the phase (Fig. 4c) until 92 °C. Hence the mesophase is identified as $SmAP_A$ in accordance with the XRD data. The maximum value of spontaneous polarization was measured to be ~61 nC/cm^2 at 96 °C (Fig. 4d). In SmX phase the polar switching was vanished signifying non-polar nature of the phase. Dependence of the switching current peak on applied voltage and frequency is given in ESI (Fig. S43).

In summary, the first observation of exceptionally high polar order and exotic frustrated mesophases in chiral bent-core system showing thermochromism has been reported. The novelty in the design of the molecular structure of the chiral bent core system encourages the realization of long range enantiotropic TGB structures accompanied by formation of spontaneous polarization.

GM acknowledges DST-SERB, India for NPDF (NPDF/2016/000560) and Prof. NVS Rao. IISER Mohali has been acknowledged for SAXS-WAXS facility and PhD fellowship. SKP acknowledges CSIR Project File No. 02(0311)/17/EMR-II. SG is grateful to the DST, India for INSPIRE Faculty Award (IFA-13, PH-60) scheme.

Notes and References

1 R. D. Kamien and J. V. Selinger, *J. Phys.: Condens Matter*, 2001, **13**, R1.
2 K. J. Ihn, J. A. N. Zasadzinski, R. Pindak, A. J. Slaney and J. Goodby, *Science*, 1992, **258**, 275.
3 V. I. Kopp, B. Fan, H. K. M. Vithana and A. Z. Genack, *Opt. Lett.*, 1998, **23**, 1707.
4 J. Xiang, S. V. Shiyanovskii, C. Imrie and O. D. Lavrentovich, *Phys. Rev. Lett.*, 2014, **112**, 217801.
5 C. P. J. Schubert, M. G. Tamba and G. H. Mehl, *Chem. Commun.*, 2012, **48**, 6851.
6 R. Alvarez and G. H. Mehl, *Mol. Cryst. Liq. Cryst.,* 2005, **439**, 259.
7 M. F. Moreira, I. C. S. Carvalho, W. Cao, C. Bailey, B. Taheri and P. Palffy-Muhoray, *Appl. Phys. Lett.*, 2004, **85**, 2691.
8 J. Xiang, A. Varanytsia, F. Minkowski, D. A. Paterson, J. M. D. Storey, C. T. Imrie, O. D. Lavrentovich and P. Palffy-Muhoray, *Proc. Natl. Acad. Sci. USA*, 2016, **113**, 12925.
9 H. Finkelmann, S. T. Kim, A. Munoz, P. Palffy-Muhoray and B. Taheri, *Adv. Mater.*, 2001, **13**, 1069.
10 Y. Fuchigami, T. Takigawa and K. Urayama, *ACS Macro Lett.*, 2014, **3**, 813.
11 S. J. Aβhoff, S. Sukas, T. Yamaguchi, C. A. Hommersom, S. L. Gac and N. Katsonis, *Sci. Rep.*, 2015, **5**, 14183.
12 T. J. White, M. E. McConney and T. J. Bunning, *J. Mater. Chem*., 2010, **20**, 9832.
13 S. S. Lee, B. Kim, S. K. Kim, J. C. Won, Y. H. Kim and S.-H. Kim, *Adv. Mater.*, 2015, **27**, 627.
14 M. Mitov, *Adv. Mater.*, 2012, **24**, 6260.
15 S. S. Choi, S. M. Morris, W. T. S. Huck and H. J. Coles, *Adv. Mater.*, 2009, **21**, 3915.
16 N. Tamaoki, *Adv. Mater*., 2001, 13, 1135.
17 Y. Hisakado, H. Kikuchi,T. Nagamura and T. Kajiyama, *Adv. Mater.*, 2005, **17**, 96.
18 H. Iwamochi and A. Yoshizawa, *Mol. Cryst. Liq. Cryst.*, 2009, **509**, 223.
19 H. Iwamochi, T. Hirose, Y. Kogawa and A. Yoshizawa, *Chem. Lett.*, 2010, **39**, 170.
20 K.-W. Park, M.-J.Gim, S. Kim, S.-T. Hur and S.-W. Choi, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8025.
21 C. V. Yelamaggad, I. S. Shashikala, G. Liao, D. S. S. Rao, S. K. Prasad, Q. Li and A. Jakli, *Chem. Mater.*, 2006, **18**, 6100.
22 I-H. Chiang, C.-J.Long, H.-C.Lin, W.-T.Chuang, J.-J.Lee and H.-C. Lin, *ACS Appl. Mater. Interfaces*, 2014, **6**, 228.
23 H. Ocak, B. Bilgin-Eran, M. Prehm, S. Schymura, J. P. F. Lagerwall and C. Tschierske, *Soft Matter*, 2011, **7**, 8266-8280.
24 J. W. Goodby, M. A. Waugh, S. M. Stein, E. Chin, R. Pindak and J. S. Patel, *Nature*, 1989, **337**, 449.
25 J. W. Goodby, *Curr. Opin. Colloid Interface Sci*., 2002, **7**, 326.
26 C. V. Yelamaggad, A. S. Achalkumar, N. L. Bonde and A. K. Prajapati, *Chem. Mater.*, 2006, **18**, 1076.
27 S. R. Renn and T. C. Lubensky, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 2132.
28 H. Ocak, B. Bilgin-Eran, D. Guzeller, M. Prehm and C. Tschierske, *Chem. Commun*., 2015, **51**, 7512.
29 C. V. Yelamaggad, G. Shanker, U. S. Hiremath and S. K. Prasad, *J. Mater. Chem*., 2008, **18**, 2927.
30 G. Shanker, M. Nagaraj, AntoniKocot, J. K. Vij, M. Prehm and C. Tschierske, *Adv. Funct. Mater*., 2012, **22**, 1671.
31 D. S. S. Rao, S. K. Prasad, V. N. Raja, C. V. Yelamaggad, and S. A. Nagamani, *Phys. Rev. Lett.*, 2001, **87**, 085504.
32 L. Guo, K. Gomola, E. Gorecka, D. Pociecha, S. Dhara, F. Araoka, K. Ishikawa and H. Takezoe, *Soft Matter*, 2011, **7**, 2895.
33 J.-K. Song, U. Manna, A. Fukuda and J. K. Vij, *Appl. Phys. Lett.*, 2008, **93**, 142903.

View Article Online
DOI: 10.1039/C7CC08885J