View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: A. N. Gowda, L. Jacob, N. Joy, R. Philip, P. R and S. Kumar, *New J. Chem.*, 2018, DOI: 10.1039/C7NJ04807F.



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 <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, 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.



rsc.li/njc

Thermal and nonlinear optical studies of newly synthesized EDOT based bent-core and hockey-stick like liquid crystals

Ashwathanarayana Gowda, Litwin Jacob, Nithin Joy, Reji Philip, Pratibha R & Sandeep Kumar*

Raman Research Institute, C.V. Raman Avenue, Sadashivanagar, Bangalore - 560 080, India

Phone: +91 80 23610122, Fax: +91 80 23610492, E-mail: skumar@rri.res.in

Keywords: EDOT, bent core, hockey-stick liquid crystal, Sonogashira coupling reaction

Abstract

Novel EDOT based bent core and hockey-stick shaped mesogens bearing terminal alkyl chains and alkoxy terminal chains, respectively have been designed and synthesized via Sonogashira coupling reaction. Molecular structures of these new compounds were determined by using spectral and elemental analysis. The mesomorphic behaviour of all the novel compounds was primarily investigated by a combination of polarising optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction studies (XRD). All the compounds exhibit enantiotropic nematic phase in lower homolog. However, a smectic A phase at lower temperature along with the high temperature nematic phase was observed in higher homologue of BC and hockey-stick LCs. The density functional theory study has been carried out to investigate the stable configuration. The bent angle of these molecules was intermediate between calamitic LCs and banana LCs. The photophysical properties of all the compounds were studied in anhydrous chloroform solvent and shows absorption patterns around 370-395 nm and emission between 418–465 nm. We have also reported large effective two-photon absorption in these novel compounds when measured under excitation by nanosecond laser pulses at 532 nm. All the mesogenic compounds are nonlinear materials, which make them suitable candidates for optical limiting applications.

1. Introduction

Published on 03 January 2018. Downloaded by Fudan University on 03/01/2018 18:11:07.

Liquid crystalline state is the unique state of soft matter with the combination of order and mobility, i.e. anisotropic properties from crystals and mobility from the isotropic liquid. Thereby liquid crystals (LCs) adapt various degrees of orientational order, positional long range order and molecular mobility.¹ Among the many practical applications, this combination is essential key factor for biological self-assembly. LCs with bent molecular shape are called bent core liquid crystal or banana-shaped liquid crystals (BC LCs). In 1929, several bent-shaped molecules were synthesised and their mesogenic properties were reported by Vorländer² but that time they were just considered as "bad calamitic" LCs. After 60 years, the rebirth of BC liquid crystal research by Matsunaga and coworkers³⁻⁶ rehabilitated the synthesis of achiral compound consists of Schiff base bent-core molecules with five benzene rings in 1991 and further, the detail mesomorphic characterisation of one of the molecules, 1,3-phenylene bis[4-(4- noctyloxyphenyliminomethyl) benzoate] was reinvestigated by Niori et al. in 1996.⁷ It opened a new era of liquid crystal research all over the world. Eventually, studies reveal unique features of ferroelectric switching in these achiral molecules. Subsequent studies have also shown that subtle variation in the structure of BC LCs compounds results in the significant changes in the type of mesophases.⁸⁻¹⁶ A majority of BC LCs described up to now contains five, six and seven phenyl rings.^{9,10,17-19} Very recently bent core mesogens exhibiting nematic phase at room temperature have been reported by Pal et al.²⁰ Several hundred BC LCs derived from different central cores such as benzene, resorcinol, naphthalene, oxazole, oxadiazole, triazole, thiazole, thiadiazole, thiophene, ethylenedioxythiophene, benzothiophene, benzodithiophene, pyridine-2,6-dicarbaldehyde, pyrazabole, fluorenone etc. have been realized.²¹⁻²²

Shorting of one 'arm' in bent-core mesogens leads to hockey-stick shape compounds. The asymmetric shape anisotropy of the molecules often exhibit unusual mesomorphic properties resulting between bent core and calamitic mesogens.^{23,24} BC and hockey-stick LCs containing heterocyclic rings are of great importance as a core unit in thermotropic liquid crystals because the presence of hetero atoms (N, O and S) can strongly influence lateral or longitudinal dipole, mesomorphism, polarisability, polarity, dielectric, luminescence, phase transition and molecular geometry.^{5,25–34} Incorporation of five membered heterocyclic rings as a central core widens the bend angle and shows extensive mesomorphic behaviour.²¹⁻³⁵ LC mesogens derived from

thiophene central core have significantly helped to contribute to physical parameters such as increased lateral dipole moments, optical anisotropy, elevation of negative dielectric anisotropy, reduction in the melting point, fast switching response,^{36,37} and stability of mesophase, which promote advance technological promising materials.^{38–44}

Among all thiophene derivatives, 3,4-ethylenedioxythiophene (EDOT) represents electron rich unique building block for designing various molecular π - conjugated polymeric materials. They have been widely studied over the past decade because the presence of EDOT moiety, which results in a smaller intrinsic band gap in polymers, enhances electron donor ability, gives high thermal stability and improved electro optical properties.^{45–48} EDOT undergoes rapid polymerization at room temperature, which finds significant potential applications in the fabrication of various electronic and optoelectronic devices such as, field effect transistors, solar cells, non-linear optical materials, light emitting diodes, and molecular switches.^{49–53} Several LCs derived from thiophene central core are known in the literature.^{36–44} Recently we have reported the synthesis and mesomorphic characterisation of BC LCs derived from novel EDOT central core.^{54,55} Herein, we report the synthesis and mesomorphic characterization of some new BC and hockey-stick LCs derived from EDOT central unit.

2. Results and Discussions

2.1. Density functional theory studies

Density functional theory (DFT) based quantum chemical calculation has been performed in gaseous phase to calculated the related molecular parameters such as, bend angle, molecular length, dihedral angle etc., using Gaussian 16 computational package at the level of 6-311 G(d) basis set, Becke's three-parameter functional and Lee-Yang-Parr correlation functional (B3LYP). The internal coordinates of the molecular system, which is used as input for Gaussian 16 computational program was generated by the Gauss View 06 program.⁵⁶ The absence of any imaginary frequency in the calculated vibrational frequencies ensure that the optimized geometry corresponds to a true energy minimum. DFT computational calculations reveal the energy and the length of fully extended bent-core mesogen 9b to be -6,113,866.99 kJ mol⁻¹ and 40.64 Å respectively (Fig.1a). The dihedral angle between first phenyl ring and second phenyl ring with

acetylene ring, the central EDOT core and first phenyl ring is ~180° and~170°, respectively. Similarly, the energy and length of fully extended hockey-stick shaped mesogen 10d were found to be -12,260,268.33 kJ mol⁻¹ and 35.45 Å respectively, (Fig. 1b). The dihedral angle between first *p*-bromo-phenyl ring and central EDOT core, the second phenyl ring and central EDOT core, second phenyl ring and third phenyl ring with acetylene linkage is ~170°, 170° and 179.2°, respectively (Fig.S1). The bending angle or bent angle (θ) is calculated by (θ) = ($\theta_1 + \theta_2$)/2 as shown in Fig.1. The DFT computational analysis (Table 1) indicates that, the bend angle is 151.5° in bent-core mesogens 9b and 152.2° in hockey-stick like mesogens 10d respectively.⁵⁷



Fig. 1 DFT optimized molecular structures: (a) bent-core mesogen 9b and (b) hockey-stick like mesogen 10d. The bent angles are 151.5° and 152.2° respectively.

Compounds	Selected bond length (Å)	Selected dihedral angle (°)	Selected bond angle (°)	Bent angle (°)
9Ъ	1.47 (O6-C7; O9-C8) 1.40 (O9-C3; O6-C2) 1.83 (C4-S5; C1-S5) 1.22(C22=C24; C23=C25)	Ring 1-Ring 2 = 180.0 Ring 2-Ring 3 = 170.6 Ring 3-Ring 4 = 170.6 Ring 4-Ring 5 = 179.8	C1-S5-C4 = 91.7 C2-O6-C7 = 114.2 C3-O9-C8 = 114.2	151.5°
10d	1.95 (C19-Br23) 1.47 (O6-C7; O9-C8) 1.40 (O9-C3; O6-C2) 1.83 (C4-S5; C1-S5) 1.22 (C22≡C24) 1.39 (C28-O31)	Ring 1-Ring 2 = 169.7 Ring 2-Ring 3 = 170.0 Ring 3-Ring 4 = 179.2	C1-S5-C4 = 91.6 C2-O6-C7 = 114.2 C3-O9-C8 = 114.2	152.2°

Table 1. The DFT quantum chemical calculations data of representative bent-core and hockeystick like mesogens (9b and 10d).

2.2. Synthesis

The synthesis of these BC and hockey-stick LCs is shown in Scheme 1. Compounds 8a and 8b were purchased from a commercial source. O-alkylation of 4-iodophenol 1 with an alkyl halide in the presence of dry potassium carbonate and dry DMF solvent under reflux condition gives 1-alkoxy-4-iodobenzene 2. Sonogashira coupling reaction between compound 2 with 2-methyl-3-butyn-2-ol in the presence of palladium and copper catalyst gives compound 3. The intermediate compound 4 was obtained by refluxing compound 3 in sodium hydroxide and toluene solvent. The palladium-catalyzed C–H bond arylations⁵⁸ of EDOT 5 with bromobenzene gives diarlylated EDOT 6 in good yield which on bromination gives the key intermediate compound 7. The final compounds were obtained by the Sonogashira coupling reaction between key intermediated compounds 7 with 4-alkyl (8 and 4) or 4-alkoxy phenyl acetylene (9 & 10) in good yield.



Scheme 1. Synthesis of novel bent-core and hockey-stick compounds: (i) alkyl halide, anhydrous K_2CO_3 , dry DMF, reflux, 24 h; (ii) 2-methyl-3-butyn-2-ol, bis(triphenylphosphine)palladium (II) dichloride (PdCl₂(PPh₃)₂), copper (I) iodide (CuI), triethylamine (TEA), reflux, 24 h; (iii) NaOH, toluene, reflux, 3 h; (iv) bromobenzene, palladium acetate (Pd(OAc)₂), triphenylphosphine (PPh₃), cesium carbonate (Cs₂CO₃), toluene, 110 °C, 24 h; (v) Br₂, dry. DCM, 6 h, r.t; (vi) 1-ethynyl-4-alkylbenzene, PdCl₂(PPh₃)₂, CuI, TEA, reflux, 24 h; (vii) 1-ethynyl-4-alkoxybenzene, PdCl₂(PPh₃)₂, CuI, TEA, reflux, 24 h.

3. Mesomorphic properties:

The thermotropic behaviour of all the synthesised compounds was first investigated by polarising optical microscopy. The exact phase transition temperature and associated enthalpy values were determined by differential scanning calorimetry on heating and cooling scans and the thermal behaviour is summarized in the Table 2. The onset temperatures are given in °C and the numbers in parentheses indicate the transition enthalpy (Δ H) in kJ mol⁻¹. The five membered bent core compounds 9a–9b exhibit wide range enantiotropic nematic phase along with SmA for 9b compound at lower temperature. Similarly, homologous series of compounds with hockey-stick

like molecules 10a–10e exhibit exclusively wide range enantiotropic nematic phase along with SmA phase for longer alkyl chain compounds, respectively.

Table 2. Phase transition temperature (peak in DSC, °C, on heating scan) and enthalpy of phase transition (Δ H, kJ mol⁻¹, in parentheses) of bent-core and hockey-stick like molecules (**9a–9b** & **10a–10e**).

	Phase transition			
Compounds	Peak temperature (°C); (Δ H, kJ mol ⁻¹)	Peak temperature (°C); (Δ H, kJ mol ⁻¹)		
	on second heating scan	on second cooling scan		
9a	Cr 181.3 (68.2) N 249.5 (1.7) I	I 233 (-1.4) N 170 (-24.1) Cr		
9b	Cr ₁ 135 (4.4) Cr ₂ 143.4 (22.0) SmA	I 256.4 (-0.6) N 188.9 (-0.3) SmA		
	191.3 (0.1) N 257.9 (0.6) I	122.5 (-24.3) Cr ₂ 78.6 (-2.7) Cr ₁		
10a	Cr 159.2 (34.9) N 190.8 (0.3) I	I 189.8 (-0.3) N 129.9 (-31.2) Cr		
10b	Cr 146.1 (40.4) N 180.3 (0.3) I	I 179.7 (-0.3) N 131.4 (-38.2) Cr		
10c	Cr ₁ 137.4 (6.6) Cr ₂ 144.9 (37.4) N	I 171.3 (-0.4) N 121.2 (-41.6) Cr		
	171.8 (0.4) I			
10d	Cr ₁ 81.6 (8.5) Cr ₂ 133.8 (39.8) SmA	I 163.2 (-0.4) N 152.2 (-0.3) SmA		
	153 (0.3) N 163.9 (0.4) I	104.7 (-35.0) Cr		
10e	Cr 129 (52.0) SmA 154.5 (1.8) I	I 153.6 (-1.5) SmA 112.6 (-53.3) Cr		

The mesophase textures of all the liquid crystalline compounds were viewed under optical microscopy with crossed polarisers which display characteristic defect textures. The microscopic textures were recorded by placing small amount of compounds on a normal glass slide and covered with a cover slip. Five membered bent core compound 9a exhibits exclusively enantiotropic nematic phase with wide temperature range. The early growing nematic droplets and four brush nematic textures of compounds 9a are shown in Fig. 2a and 2b respectively. Compound 9b shows SmA phase along with a nematic phase at lower temperature. To investigate the nature of smectic phase, we used polyimide- coated cells with approximately 9 µm thickness for planer alignment in the mesophase. The compound 9b was filled uniformly in

the LC cell at isotropic temperature. Upon slow cooling from the nematic phase, focal conic texture of smectic A phase appears as shown in Fig. 2c. The series of compounds in hockey-stick like molecules 10a-10e display enantiotropic nematic phase with broad temperature ranges followed by the appearance of SmA phase at a lower temperature for compounds 10d as shown in Fig. 2d. Compound 10e exhibits an enantiotropic SmA phase only. Compound 9a melts at 182 °C and become isotropic liquid at 250 °C; the nematic texture observed on slow cooling from the isotropic liquid (Fig. 2a and 2b). Compound 9b melts at 143 °C to a SmA phase but prior to that it exhibits a crystal-crystal transition at 135 °C. On further heating it shows a nematic phase at about 192 °C that goes to the isotropic phase at 258 °C. The nematic droplets were observed on slow cooling from the isotropic liquid and SmA phase observed at 172 °C (Fig. 2c) which crystallizes at 122 °C. The hockey-stick like compound 10a melts at 159 °C and become isotropic liquid at 191 °C. The nematic phase observed on slow cooling from isotropic liquid. The next homologue of the series, 10b, becomes isotropic liquid at 180 °C and the nematic textures were observed on cooling from isotropic liquid. Upon heating, compound 10c endures with the crystal-crystal transition at 137 °C and melts at 145 °C to a nematic phase that becomes clear liquid at 172 °C. Nematic droplets were observed on slow cooling from the isotropic melt. Compounds 10d and 10e show significant changes in texture from schlieren texture to the fanlike texture of smectic phase at low temperature. Compound 10d goes through crystal- crystal transition at 82 °C and melts at 134 °C and becomes isotropic liquid at 164 °C. On slow cooling, the nematic phase appears at about 163 °C that changes to a SmA phase at 152 °C (Fig. 2d). Compound 10e melts at about 129 °C and transforms to the isotropic liquid at 155 °C. On cooling, SmA phase appears at about 153 °C that crystallises at 112 °C.



Fig. 2 Polarising optical microscopy textures, for compounds 9a: (a) early growing nematic droplets after cooling from the isotropic liquid at 233 °C, (b) growing of nematic schlieren texture on further cooling to 198 °C, for compounds 9b: (c) SmA focal conic texture observed at 172 °C, for compounds 10d: (d) SmA texture observed at 152 °C. All the POM textures were viewed at 200X magnification.

The thermal behaviour of all the mesogenic compounds were also further investigated with DSC measurements on both heating and cooling scan rate of 10 °C min⁻¹ and recorded under a nitrogen atmosphere. The phase transition temperatures obtained in DSC agree very well with POM observations. The bent core compound 9a exhibits enantiotropic nematic phase over broad temperature range with two types of endothermic phase transition. The peak temperature at 181.3 °C, with phase transition enthalpy (Δ H) 68.2 kJ mol⁻¹ is attributed to crystalline phase to N phase while the peak at 249.5 °C with a lower enthalpy (Δ H = 1.7 kJ mol⁻¹) corresponds N phase to isotropic phase transition. On the other hand, compound 9b exhibited Cr to SmA phase at lower temperature 143.4 °C (Δ H = 22.0 kJ mol⁻¹); a weak phase transition at 257.9 °C (Δ H = 0.6 kJ mol⁻¹). Similarly, hockey-stick compounds 10a–10c shows two types of endothermic phase

transition from crystal to nematic phase at a lower temperature and nematic phase to isotropic phase at higher temperature. The compound 10a shows Cr to N phase at 159.2 °C (Δ H = 34.9 kJ mol⁻¹) and N phase to isotropic phase at 190.8 °C (Δ H = 0.3 kJ mol⁻¹). Compound 10b and 10c exhibited N phase at 146.1 °C (Δ H = 40.4 kJ mol⁻¹) and 144.9 °C (Δ H = 37.4 kJ mol⁻¹) respectively and transition from N phase to isotropic phase at 180.3 °C (Δ H = 0.3 kJ mol⁻¹), 171.8 °C (Δ H = 0.4 kJ mol⁻¹) respectively. However, on heating and cooling scans, compounds 10d exhibit additional enantiotropic SmA phase transition in between crystalline phase and nematic phase. It displayed Cr to SmA phase at 133.8 °C (Δ H = 39.8 kJ mol⁻¹); SmA to N phase and N phase to isotropic phase at 153 °C (Δ H = 0.3 kJ mol⁻¹) and 163.9 °C (Δ H = 0.4 kJ mol⁻¹) respectively. Compound 10e exhibit only a smectic phase. The crystalline compound melts to SmA phase at 129 °C, with transition enthalpy 52.0 kJ mol⁻¹ which goes to the isotropic phase at 154.5 °C (Δ H = 1.8 kJ mol⁻¹). As representative example, the DSC of compound 10d is shown in Fig. 3



Fig. 3 DSC thermograms obtained for the hockey-stick mesogen 10d showing phase transitions on heating and cooling cycles at a scan rate of 10 $^{\circ}$ C min⁻¹. Vertical arrow indicates phase transition point.

3.1. X-ray scattering measurements

The liquid crystalline behaviour of both the novel BC LCs (9a and 9b) and hockey-stick liquid crystals (10a–10e) was further examined by X-ray scattering studies of unoriented samples filled in Lindemann capillaries. A representative and typical diffraction pattern obtained for BC compound 9b at 210 °C in the nematic phase and at 160 °C for the SmA phase are shown in Fig. 4 (a) and (b), respectively. The XRD pattern for nematic phase at 210 °C shows diffuse peak at small angle region and a diffuse wide angle maxima at d = 4.48 Å, which corresponds to typical nematic phase as shown in Fig. 4 (a). However, the XRD pattern at 160 °C shows a sharp reflection in the small angle regime with *d*- spacings 37.37 Å as shown in the Fig. 4 (b). Based on POM observation and calculated molecular length (35.45 Å), this phase was deduced as a SmA phase. The diffuse peak at wide angle maxima at 4.46 Å responsible for fluid like correlation of the molecules in the layers.

New Journal of Chemistry Accepted Manuscript



Fig. 4 XRD patterns recorded for BC LCs compound 9b on cooling from isotropic temperature: (a) nematic phase at 210 °C; (b) smectic A phase at 160 °C respectively.

3.2. Thermogravimetric analysis

Published on 03 January 2018. Downloaded by Fudan University on 03/01/2018 18:11:07.

The thermal stability of all the liquid crystalline compounds was investigated by thermogravimetric analysis (TGA). All the samples (9a–9b and 10a–10e) are subjected to heat

scan of 10 °C min⁻¹ under a nitrogen atmosphere. All the mesogenic compounds show no weight loss till about 350 °C as shown in Fig. 5. The five membered bent core compounds 9a–9b initiate weight loss at about 380 °C–400 °C and decompose at 520 °C. Similarly, hockey-stick like compounds 10a–10e initiates weight loss at about 350 °C and the whole process was completed at about 500 °C. The decomposition temperature of hockey-stick like compounds decreases with increasing terminal alkyl chain length. The thermal stability of five membered bent core compounds was higher than hockey-stick like compounds. The decomposition temperatures for all the compounds were much higher than isotropic temperature. It concludes that all the mesogenic compounds possess good thermal stability.



Fig. 5. The thermogravimetric analysis of compounds 9a–9b and 10a–10e.

3.3. Raman spectroscopy

The molecular structures of novel liquid crystalline compounds were further investigated by Raman spectroscopy. Raman spectra were recorded using Horiba Jobin Yvon T6400 Micro Raman using He–Ne laser operating at $\lambda = 632.8$ nm. The laser power at 1.8 mW was kept constant throughout measurement. The Raman spectral data obtained at an optical resolution of $50 \times$ objective lenses and accumulated at 10 s to obtained data with sufficiently high signal-tonoise ratio at room temperature as shown in Fig. 6. All the solid samples were placed in a normal glass slide and covered with a cover slip. Theoretical Raman values were compared with experimentally obtained values are represented in Table 3. The peaks at lower regions at 919–1193 cm⁻¹, correspond to aliphatic chains vibrations. The intense peak at 1142 cm⁻¹ is for the central heteroaromatic EDOT ring v (C-S). The vibrational peaks at 1437–1597 cm⁻¹ are obtained for aromatic and hetero aromatic rings. The intense prominent vibrational peak at 2213 cm⁻¹ is responsible for alkyne linking group in all the mesogenic derivatives. All experimentally obtained Raman shift (wavenumbers, cm⁻¹) values were matching with the respective functional groups as shown in Table 3.



Fig. 6 Raman data of all the mesogenic compounds (9a–9b) and (10a–10e).

Table. 3. Comparison of experimental Raman shift values of all the mesogens (9a–9b and 10a–10e) with theoretical Raman shift values.

Compounds	Theoretical	Experimental	Functional
	Raman shift (cm^{-1})	Raman shift (cm^{-1})	group/vibration
	800–950	919	υ (C-O-C)
	1080–1100	1142	υ (C-S) aromatic
9a–9b &	1060–1150	1193	υ (C-O-C) asym
10a-10e	1450–1505	1437, 1476	υ (C-C) aromatic
	1550–1610	1597	υ (C-C) hetero ring
	2100–2250	2213	υ (C≡ C)

3.4. Photophysical properties:

The photophysical properties of novel compounds were investigated by Perkin-Elmer UV-vis lambda 35 double-beam spectrometer absorption spectra. The UV absorption properties of all the compounds (9a-9b & 10a-10e) were studied in anhydrous chloroform solvent (10⁻⁵ M) recorded at room temperature to know absorption maxima as presented in Fig. 7 (a) and the values were summarized in Table 4. The bent-core compounds (9a-9b) exhibit maximum absorption band at $\lambda_{max} = 392$ nm. Similarly, hockey-stick compounds (10a–10e) exhibit maximum absorption at $\lambda_{max} = 375-378$ nm. The highly delocalized electronic systems and π - π * transitions in the heteroaromatic portion (central EDOT), phenyl rings and acetylene linking group, and high molar absorption coefficient ($\varepsilon = 6.5-11.2 \times 10^6 \text{ Lmol}^{-1}\text{cm}^{-1}$) attributed to the maximum absorption in these compounds. Generally, the extent of light absorption and intensity of peak in the absorption spectrum largely depends on the number of molecules that absorb light of a given wavelength. It is also known that extended conjugation in bent-core mesogens (9a–9b) causes bathochromic shift (longer wavelength) with respect to hockey-stick like liquid crystalline compounds (10a-10e). Photoluminescence spectra of all the mesogens (9a–9b & 10a–10e) were recorded using a spectrofluorometer (Flurolog-3, Horiba Jobin Yvon), the emission spectra were recorded with a slit size of 2 nm in dilute anhydrous chloroform solution at room temperature and all the compounds are excited at λ_{ex}

= 390 nm. The bent-core mesogens (9a–9b) exhibit strong dual emission bands at 442 nm and 464 nm along with negligible shoulder peak at 490 nm as shown in Fig. 7 (b). Similarly, emission spectra of hockey-stick compounds (10a–10e) exhibits strong dual emission bands at 418–423 nm and 440 nm along with shoulder peak at 468 nm. The photoluminescence mechanism of bent-core mesogens (9a–9b) and hockey-stick compounds (10a–10e) involves two strong stable emission bands and one shoulder emission peak which attributed to the electronic transition from lowest unoccupied molecular orbital (LUMO) to the highest occupied molecular orbital (HOMO) and occupied molecular orbitals below HOMO (H-1, H-2) respectively. No appreciable changes were observed on increasing number of methylene group in the terminal chains.





Fig. 7 (a) UV-Visible absorption spectrum, (b) fluorescence emission spectrum of all the novel mesogens.

Table. 4. Photophysical properties of the bent-core and hockey-stick like mesogens recorded in the anhydrous chloroform (10^{-5} M) solution.

Compounds	Absorption λ_{abs}/nm	Emission λ_{em}/nm
	$(\varepsilon/10^6 \text{ Lmol}^{-1} \text{cm}^{-1})$	
9a	392 (11.2)	442, 463
9b	392 (9.1)	443, 464
10a	377 (6.5)	423, 441
10b	375 (8.2)	419, 441
10c	378 (6.6)	418, 440
10d	377 (11.1)	421, 441
10e	376 (7.1)	419, 441

3.5. Nonlinear optical transmission measurements

Published on 03 January 2018. Downloaded by Fudan University on 03/01/2018 18:11:07

Liquid crystals are known to exhibit large optical nonlinearities which have been the subject of considerable research interest in recent years, from both experimental and theoretical point of view. Since LC molecules typically have extended delocalized π -electrons and geometrical configuration, they are believed to be potential source of fast and large nonlinearities. In this open aperture Z-scan technique (Fig. S2), the transmission of all the samples is measured as a function of the input laser fluence. For varying the laser fluence the beam was focused using a plano-convex lens of 9.5 cm focal length, and the transmission was measured at different positions (z-axis) with respect to the beam focus. All the compounds were dissolved in anhydrous chloroform solvent and taken in a 1 mm path length cuvette to have linear transmission of 89% at 532 nm excitation wavelength. The samples experiences different fluences at different z, with a maximum at the focal point (z = 0). The laser pulse energy was 100 μ J and the transmitted energy was measured using a pyro electric energy detector (Laser probe, RJP-735). A curve can be obtained by plotting the normalized transmittance, T_{norm} (where the linear transmission is taken as unity) with z position, which is called the Z scan curve as shown in Fig. 8



Fig. 8 (a) Z-scan measurement of novel mesogenic compounds (9a–9b) and (10a–10e) respectively. The experimental measurements were carried out at room temperature with very

high dilute anhydrous chloroform solvent. (b) Normalized transmission as a function of input laser fluence, calculated from open aperture Z-scan measurements recorded at laser pulse energy of 100 micro Joules respectively.

For a spatially filtered Gaussian beam, the fluence (Fin (z)) at any position z can be obtained from the relation,

$$Fin(z) = 4(ln2)^{\frac{1}{2}} Ein/\pi^{\frac{3}{2}}\omega(z)^{2}$$

Where the beam radius $\omega(z)$ is given by

$$\omega(z) = \omega_0 (1 + \left(\frac{z}{z_0}\right)^2)^{\frac{1}{2}}$$

 ω_0 is the focal spot size and z_0 is the Rayleigh length given by $z_0 = \pi \omega_0^2 / \lambda$. We find that the nonlinear transmission has contributions from both reverse saturable absorption (RSA, sometimes referred to as effective two-photon absorption (2PA) in literature)^{59,60} and saturable absorption (SA).⁶¹ The nonlinear absorption coefficient is given by,

$$\alpha(I) = \frac{\alpha_0}{1 + \frac{I}{I_s}} + \beta I$$

Where I_s is the saturation intensity (in W/m^2) and β is the reverse saturable absorption coefficient (in m/W). I_s and β can be obtained by numerically fitting the pulse propagation equation to the measured transmission data. The obtained values are tabulated in Table 5. The presence high electron conjugation imparts nonlinear optical properties to these molecules. This can be attributed due to strong dipole moment and polarization of the molecules.

$$\frac{dI}{dx} = -\left[\frac{\alpha_0}{1+\frac{1}{I_s}} + \beta I\right]I$$

Table 5. RSA coefficient (β) and saturation intensity (I_s) calculated for the samples from the data given in Fig. 8

Compounds	Liner Transmission (%)	Beta (β) (X 10 ⁻¹¹ m/W)	$(X 10^{11} \\ W/m^2)$	Omega zero ω ₀ (X 10 ⁻⁶ m)	Energy (uJ)
9a	89	5.6	9.8	22	100
9b	89	3.3	58	20	100
10a	89	1.9	45	19	100
10b	89	1.3	50	22	100
10c	89	2.3	50	18	100
10d	89	1.5	25	20	100
10e	89	1.5	9	22	100

We believe that the 2PA observed in the present samples originates from excited state absorption. In bent-core mesogens (9a–9b), the acetylene (-C=C-) linking group acts as the conjugating spacer between central heteroaromatic EDOT ring and phenyl group with flexible alkoxy chain entities. These compounds is expected to be higher extended delocalized π electronic conjugation and geometrical shape of the molecules, which further enhance the high nonlinearities. Similarly, unsymmetrical molecular structure and electron acceptor bromo group at one end of the molecule and electron donor ability of phenyl acetylene group through central heteroaromatic EDOT in hockey-stick like liquid crystals (10a–10e) enhance the nonlinear optical properties.

4. Experimental section

4.1. General procedure for the synthesis of intermediate and final compounds.

The compounds 1-alkoxy-4-iodobenzene, 4-(4-alkoxyphenyl)-2-methylbut-3-yn-2-ol and 1ethynyl-4-alkoxybenzene were synthesised as reported⁶² and confirmed by spectral and elemental analysis.

4.1.1. Synthesis of 5,7-Diphenyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (6)

In a two neck-flak containing palladium (II) acetate (Pd(OAc)₂) (5 mol %), PPh₃ (10 mol %) ligand, Cs₂CO₃ (2.4 mmol) in toluene solvent (50 mL) was added EDOT (1.0 mmol) and bromobenzene (2.2 mmol) under argon atmosphere. The reaction mixture was heated at 110 °C for 24 h under argon. After completion of the reaction, the reaction mixture was cooled to room temperature, an excess of water was added. The aqueous layer was extracted with ethyl acetate (3× 100 mL) and the combined organic layers were dried over Na₂SO₄ and concentrated under vacuum. The crude compound was further purified by column chromatography using silica gel. gel (*n*-hexane/ ethyl acetate 9:1) gives desired pure product. Recrystallization of the pure compound with a mixture of DCM: hexane (1:9) gives light green solid **6**. Yield: 75 %. IR (film) v_{max} : 2912, 2872, 2852, 1597, 1518, 1454, 1359 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.76–7.73 (m, 4 H), 7.38–7.34 (m, 4 H), 7.24–7.19 (m, 2 H), 4.34 ppm (s, 4 H); ¹³C NMR (125 MHz, CDCl₃): δ = 138.61, 132.96, 128.65, 126.62, 126.11.15.39, 64.59 ppm; elemental analysis: C₁₈H₁₄O₂S; calculated (%): C 73.44, H 4.78, S 10.87; found: C 73.51, H 4.84, S 10.91.

4.1.2. Synthesis of 5,7-bis(4-bromophenyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (7)

A solution of bromine (5.43 g, 33.97 mmol) in dry chloroform (20 mL) was added drop wise to a stirring solution of compound **6** (5g, 16.98 mmol) in dry chloroform (75 mL) at 0 °C, and slowly allowed to room temperature. The resulting reaction mixture was stirred for 6 h at room temperature. After completion of the reaction, the reaction mixture was successfully washed with 3% aqueous NaOH, saturated NaHSO₃ and excess of water. The aqueous layer was extracted with chloroform (3 × 75 mL) and the combined organic layers were dried over Na₂SO₄ and

concentrated under vacuum. The crude compound was purified from column chromatography using silica gel (*n*-hexane/ ethyl acetate 8:2) gives desired pure compound 7. Recrystallization of pure compound from hexane afford off-white solid. Yield: 90%. IR (film) v_{max} : 2922, 2911, 2854, 1591, 1454, 1373, 1085 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.60 (d, *J* = 8.8 Hz, 4 H), 7.48 (d, *J* = 8.8 Hz, 4 H), 4.36 ppm (s, 4 H); ¹³C NMR (125 MHz, CDCl₃): δ = 138.97, 131.72, 127.49, 120.35, 114.50, 64.58 ppm; elemental analysis: C₁₈H₁₄O₂S; calculated (%): C 47.81, H 2.67, S 7.07; found: C 47.86, H 2.71, S 7.11.

4.1.3. Synthesis of final bent core and hockey-stick mesogenic compounds.

Published on 03 January 2018. Downloaded by Fudan University on 03/01/2018 18:11:07

All the mesogenic derivatives were prepared by Sonogashira C–C coupling reaction between 5,7-bis(4-bromophenyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxine 7 with 1-ethynyl-4-alkylbenzene or 1-ethynyl-4-alkoxybenzene in the presence of PdCl₂(PPh₃)₂ and CuI in anhydrous triethylamine solvent. The general method is described as follows.

In a three-neck flask, deoxygenated solution of compound 7 (1 eq), $PdCl_2(PPh_3)_2$ (0.04 eq) and CuI (0.05 eq) in 75 mL anhydrous triethylamine solvent was allowed to stir at room temperature under argon atmosphere for 10 minutes. To this, added 1-ethynyl-4-alkylbenzene (2.5 eq) or 1-ethynyl-4-alkoxybenzene (2.5 eq) in triethylamine (50 mL) solvent. The resulted reaction mixture was heated 72 °C for 24 h. After cooled to room temperature, the reaction mixture was diluted with diethyl ether and filtered through celite bed. The filtrate was then extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under vacuum. The crude compound was purified through silica gel (*n*-hexane/ethyl acetate 7:3) gives desired pure compound. Recrystallization of pure compound with cold ethanol gives pale green colour compound. Yield: 55–60 %.

5,7-bis(4-((4-butylphenyl)ethynyl)phenyl)-2,3-dihydrothieno[3,4-b][1,4]dioxine (9a):

IR (film) v_{max} : 2953, 2926, 2852, 2210, 1606, 1541, 1454, 1354, 1120, 1082 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.73 (d, *J* = 8 Hz, 4 H), 7.51 (d, *J* = 8 Hz, 4 H), 7.44 (d, *J* = 8 Hz, 4 H), 7.16 (d, *J* = 8 Hz, 4 H), 4.36 (s, 4 H), 2.62 (t, *J* = 7.5 Hz, 4 H), 1.63–1.58 (m, 4 H), 1.39–1.32 (m, 4 H), 0.93 ppm (t, *J* = 7 Hz, 6 H); ¹³C NMR (125 MHz, CDCl₃): δ = 143.38, 139.23, 132.57, 131.77, 131.50, 128.48, 125.72, 121.49, 120.46, 115.56, 90.39, 89, 64.60, 35.61, 33.38, 22.31,

13.91 ppm; elemental analysis: $C_{42}H_{38}O_2S$; calculated (%): C 83.13, H 6.30, S 5.27; found: C 83.20, H 6.38, S 5.31. ¹H NMR and ¹³C NMR spectrum showed in supplementary information Fig. S3

5,*7*-*bis*(*4*-((*4*-*hexylphenyl*)*ethynyl*)*phenyl*)-*2*,*3*-*dihydrothieno*[*3*,*4*-*b*][*1*,*4*]*dioxine* (**9b**):

IR (film) v_{max} : 2955, 2924, 2852, 2220, 1604, 1577, 1454, 1361, 1222, 1082 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): $\delta = 7.73$ (d, J = 8.5 Hz, 4 H), 7.51 (d, J = 8 Hz, 4 H), 7.45 (d, J = 8 Hz, 4 H), 7.16 (d, J = 8 Hz, 4 H), 4.39 (s, 4 H), 2.61 (t, J = 7.5 Hz, 4 H), 1.64–1.58 (m, 4 H), 1.36–1.25 (m, 12 H), 0.88 ppm (t, J = 6 Hz, 6 H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 143.43$, 139.22, 132.57, 131.77, 131.49, 128.47, 125.72, 121.49, 120.44, 115.56, 90.39, 88.99, 64.60, 35.92, 31.69, 31.19, 28.91, 22.58, 14.06 ppm; elemental analysis: C₄₆H₄₆O₂S; calculated (%): C 83.34, H 6.98, S 4.82; found: C 83.39, H 7.03, S 4.89. ¹H NMR and ¹³C NMR spectrum showed in supplementary information Fig. S4

5-(4-bromophenyl)-7-(4-((4-(hexyloxy)phenyl)ethynyl)phenyl)-2,3-dihydrothieno[3,4-

b][1,4]*dioxine* (**10a**): IR (film) v_{max} : 2955, 2924, 2854, 2206, 1604, 1519, 1454, 1377, 1249, 1085 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.71 (d, *J* = 8 Hz, 2 H, 7.61 (d, *J* = 8.5 Hz, 2 H), 7.50–7.45 (m, 6 H), 6.86 (d, *J* = 8.5 Hz, 2 H), 4.37 (s, 4 H), 3.97 (t, *J* = 6.5 Hz, 2 H), 1.81–1.75 (m, 2 H), 1.49–1.43 (m, 6 H), 0.91 ppm (t, *J* = 6.5 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ = 159.26, 139.11, 139.03, 133.01, 132.31, 131.81, 131.70, 131.66, 127.50, 125.71, 121.71, 120.30, 115.37, 115.16, 114.67, 114.57, 90.31, 88.21, 68.11, 64.59, 31.57, 29.17, 25.69, 22.58, 14.01 ppm; elemental analysis: C₃₂H₂₉BrO₃S; calculated (%): C 67.01, H 5.09, S 5.57; found: C 67.09, H 5.14, S 5.61. ¹H NMR and ¹³C NMR spectrum showed in supplementary information Fig. S5

5-(4-bromophenyl)-7-(4-((4-(octyloxy)phenyl)ethynyl)phenyl)-2,3-dihydrothieno[3,4-

b][1,4]*dioxine* (**10b**): IR (film) v_{max} : 2953, 2922, 2852, 2210, 1608, 1521, 1454, 1359, 1255, 1085 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.71 (d, *J* = 8.5 Hz, 2 H), 7.62 (d, *J* = 8.5 Hz, 2 H), 7.50–7.45 (m, 6 H), 6.86 (d, *J* = 9 Hz, 2 H), 4.38 (s, 4 H), 3.97 (t, *J* = 6.5 Hz, 2 H), 1.81–1.76 (m, 2 H), 1.47–1.42 (m, 2 H), 1.34–1.25 (m, 8 H), 0.89 ppm (t, *J* = 6.5 Hz, 3 H); ¹³C NMR

(125 MHz, CDCl₃): δ = 159.26, 139.03, 139, 133.01, 132.31, 131.70, 131.66, 127.50, 125.71, 121.68, 120.30, 115.40, 115.15, 114.68, 114.57, 90.30, 88.21, 68.12, 64.59, 31.80, 29.20, 26.02, 22.64, 14.07 ppm; elemental analysis: C₃₄H₃₃BrO₃S; calculated (%): C 67.88, H 5.52, S 5.31; found: C 67.92, H 5.59, S 5.35. ¹H NMR and ¹³C NMR spectrum showed in supplementary information Fig. S6

5-(4-bromophenyl)-7-(4-((4-(decyloxy)phenyl)ethynyl)phenyl)-2,3-dihydrothieno[3,4-

Published on 03 January 2018. Downloaded by Fudan University on 03/01/2018 18:11:07

b][1,4]*dioxine* (**10c**): IR (film) v_{max} : 2953, 2924, 2852, 2212, 1606, 1541, 1454, 1377, 1253, 1084 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): $\delta = 7.71$ (d, J = 8.5 Hz, 2 H), 7.61 (d, J = 8.5 Hz, 2 H), 7.49–7.44 (m, 6 H), 6.86 (d, J = 8.5 Hz, 2 H), 4.36 (s, 4 H), 3.96 (t, J = 6.5 Hz, 2 H), 1.81–1.75 (m, 2 H), 1.48–1.42 (m, 2 H), 1.34–1.27 (m, 12 H), 0.88 ppm (t, J = 7 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 159.26$, 139.11, 139.03, 133.01, 132.31, 131.81, 131.70, 131.66, 127.50, 125.70, 121.71, 120.30, 115.37, 114.67, 114.57, 90.32, 88.22, 68.12, 64.58, 31.90, 29.57, 29.55, 29.31, 29.21, 26.02, 22.68, 14.10 ppm; elemental analysis: C₃₆H₃₇BrO₃S; calculated (%): C 68.67, H 5.91, S 5.08; found: C 68.72, H 5.96, S 5.13. ¹H NMR and ¹³C NMR spectrum showed in supplementary information Fig. S7

5-(4-bromophenyl)-7-(4-((4-(dodecyloxy)phenyl)ethynyl)phenyl)-2,3-dihydrothieno[3,4-

b][1,4]*dioxine* (**10d**): IR (film) v_{max} : 2953, 2922, 2852, 2210, 1608, 1519, 1438, 1377, 1247, 1085 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): $\delta = 7.71$ (d, J = 8 Hz, 2 H), 7.61 (d, J = 8.5 Hz, 2 H), 7.50–7.44 (m, 6 H), 6.86 (d, J = 8.5 Hz, 2 H), 4.37 (s, 4 H), 3.96 (t, J = 6.5Hz, 2 H), 1.81–1.75 (m, 2 H), 1.48–1.42 (m, 2 H), 1.35–1.26 (m, 18 H), 0.88 ppm (t, J = 7 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): $\delta = 159.26$, 139.10, 139.03, 133.01, 132.30, 131.81, 131.70, 131.65, 127.50, 125.70, 121.71, 120.30, 115.15, 114.67, 114.57, 90.31, 88.21, 68.12, 64.58, 31.91, 30.89, 29.65, 29.63, 29.56, 29.38, 29.34, 29.20, 26.01, 22.68. 14.09 ppm; elemental analysis: C₃₈H₄₁BrO₃S; calculated (%): C 69.39, H 6.27, S 4.86; found: C 69.45, H 6.32, S 4.92. ¹H NMR and ¹³C NMR spectrum showed in supplementary information Fig. S8

5-(4-bromophenyl)-7-(4-((4-(tetradecyloxy)phenyl)ethynyl)phenyl)-2,3-dihydrothieno[3,4b][1,4]dioxine (**10e**): IR (film) ν_{max}: 2955, 2920, 2852, 2214, 1606, 1508, 1454, 1377,

1242, 1082 cm⁻¹; ¹H NMR (500 MHz, CDCl₃): δ = 7.64 (d, *J* = 8 Hz, 2 H), 7.54 (d, *J* = 8.5 Hz, 2 H), 7.42–7.37 (m, 6 H), 6.79 (d, *J* = 8.5 Hz, 2 H), 4.29 (s, 4 H), 3.89 (t, *J* = 6.5 Hz, 2 H), 1.73–1.68 (m, 2 H), 1.48 (br, 2 H), 1.39–1.35 (m, 2 H), 1.27–1.19 (m, 22 H), 0.81 (t, *J* = 6.5 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃): δ = 158.25, 138.10, 138.02, 132, 131.29, 130.80, 130.69, 130.64, 126.48, 126.69, 120.70, 119.28, 114.36, 114.14, 113.66, 113.56, 89.31, 87.20, 67.10, 63.57, 30.91, 28.67, 28.66, 28.64, 28.58, 28.55, 28.37, 28.34, 28.20, 25.01, 21.67, 13.09 ppm; elemental analysis: C₄₀H₄₅BrO₃S; calculated (%): C 70.06, H 6.60, S 4.66; found: C 70.11, H 6.64, S 4.72. ¹H NMR and ¹³C NMR spectrum showed in supplementary information Fig. S9

5. Conclusions

Two new series of BC and hockey-stick like liquid crystals from central EDOT core were synthesized and characterized. The BC LCs exhibits wide range of enantiotropic nematic phase for lower homologues and SmA phase for higher homologues at lower temperature. Similarly, hockey-stick compounds exhibit wide range enantiotropic nematic phase for lower homologues, while SmA phase obtained from higher homologues at lower temperature respectively. DFT calculations revealed that the bent angle of these compounds is around $151^{\circ}-153^{\circ}$. All the compounds exhibits strong photoluminescence in chloroform solvent under excitation wavelength of 390 nm. The presence of extended delocalized π -electron conjugations in these novel mesogens exhibit large optical nonlinear properties which make them potential candidates for technological applications.

Supplementary Information

The general methods, DFT calculations, NLO experimental set up and NMR spectra (¹H and ¹³ NMR) of all the mesogens are provided.

Acknowledgements

The author thanks Dr. Vijayaragavan for recording NMR spectra. Dr. Srinivas HT, Ms. Vasuda for their technical support. Mr. Yathendran for Raman studies.

Reference:

- D. Demus, J. W. Goodby, G. Gray, and H. W. Spiess, Low Molecular Weight Liquid Crystals I. Wiley-VCH: Weinheim; New York, 1998; Vol. 2A.
- [2] D. Vorlander, Ber, Dtsch. Chem. Ges., 1929, 62, 2831.
- [3] M. Kuboshita, Y. Matsunaga and H. Matsuzaki, Mol. Cryst. Liq. Cryst., 1991, 199, 319.
- [4] T. Matsuda and Y. Matsunga, Bull. Chem. Soc. Jpn., 1991, 64, 2192.
- [5] H. Matsuzaki and Y. Matsunaga, Liq. Cryst., 1993, 14, 105.
- [6] T. Akutagawa, Y. Matsunaga and K. Yasuhara, Liq. Cryst., 1994, 17, 659.
- [7] T. Niori, T. Sekine, J. Watanabe, T. Furukawa, H. Takezoe, J. Mater. Chem., 1996, 6, 1231.
- [8] D. R. Link, G. Natale, R. Shao, J. E. Maclennan, N. A. Clark, E. Korblova, D. M. Walba, *Science.*, 1997, 278, 1924.
- [9] G. Pelzl, S. Diele, W. Weissflog, Adv. Mater., 1999, 11, 707.
- [10] W. Weissflog, H. Nádasi, U. Dunemann, G. Pelzl, S. Diele, A. Eremin, H. Kresse, J. Mater. Chem., 2001, 11, 2748.
- [11] A. Jakli, *Liq. Cryst. Rev.*, 2013, **1**, 65–82.
- [12] W. Weissflog, H.N.S. Murthy, S. Diele, G. Pelzl, *Phil. Trans. R. Soc. A.*, 2006, 364, 2657.
- [13] R. A. Reddy, C. Tschierske, J. Mater. Chem., 2006, 16, 907.
- [14] H. Takezoe, Y. Takanishi, Jpn. J. Appl. Phys., 2006, 45, 597.
- [15] H. F. Gleeson, S. Kaur, V. Gortz, A. Belaissaoui, S. Cowling, J. W. Goodby, *ChemPhysChem.*, 2014, 15, 1251.
- [16] M. B. Ros, J. L. Serrano, M.R. Fuente, C. L. Folcia, J. Mater. Chem., 2005, 15, 5093.
- [17] D. Shen, A. Pegenau, S. Diele, I. Wirth and C. Tschierske, J. Am. Chem. Soc., 2000, 122, 1593.
- [18] D. Shen, S. Diele, G. Pelzl, I. Wirth and C. Tschierske, *J. Mater. Chem.*, 1999, 9, 661. 15
- [19] B. K. Sadashiva, H. N. S. Murthy and S. Dhara, *Liq. Cryst.*, 2001, 28, 483.
- [20] G. Mohiuddin, V. Punjani, S. K. Pal, *ChemPhysChem.*, 2015, 16, 2739.
- [21] S. Kumar, A. N. Gowda, *Liq. Cryst. Rev.*, 2015, **3**, 99.

- [22] A. N. Gowda, A. Roy, S. Kumar, *Liq. Cryst.*, 2016, **43**, 175.
- [23] M. Monika, V. Prasad and N. G. Nagaveni, *Liq. Cryst.*, 2015, **42**, 1490.
- [24] A. Chakraborty, M. K. Das, B. Das, U. Baumeister and W. Weissflog, J. Mater. Chem C., 2013, 1, 7418.
- [25] S. K. Sahaa, J. Debb, U. Sarkarb and M. K. Paul, *Liq. Cryst.*, 2017, 44, 2203.
- [26] P. Tuzimoto, D. M. P. O. Santos, T. dos S. Moreira, R. Cristiano, I. H. Bechtold & H. Gallardo, *Liq. Cryst.*, 2014, 41, 1097.
- [27] E. Girotto, I. H. Bechtold and H. Gallardo, *Liq. Cryst.*, 2016, **43**, 1768.
- [28] H. Gallardo, R. Cristiano, A. A. Vieira, R. A. W. N. Filho, R. M. Srivastava & I. H. Bechtold, *Liq. Cryst.*, 2008, 35, 857.
- [29] M. Subrao, D. M. Potukuchi, G. S. Ramachandra, P. Bhagavath, S. G. Bhat, S. Maddasani, *Beilstein J. Org. Chem.*, 2015, 11, 233.
- [30] R. Cristiano, A. A. Vieira, F. Ely & H. Gallardo, *Liq. Cryst.*, 2006, 33, 381.
- [31] I.-H. Chiang, C.-J. Long, H.-C. Lin, W.-T. Chuang, J.-J. Lee, H.-C. Lin, ACS *Appl. Mater. Interfaces.*, 2014, **6**, 228.
- [32] F. Speetjens, J. Lindborg, T. Tauscher, N. LaFemina, J. Nguyen, E.T. Samulski,
 F. Vita, O. Francescangeli, E. Scharrer, *J. Mater. Chem.*, 2012, 22, 22558.
- [33] G. Shanker, M. Prehm, C. Tschierske, *Beilstein J. Org. Chem.*, 2012, **8**, 472.
- [34] A. J. Seed, K. J. Toyne, J. W. Goodby, J. Mater. Chem., 1995, 5, 653.
- [35] K. Kishikawa, M. C. Harris, T. M. Swager, *Chem. Mater.*, 1999, **11**, 867.
- [36] S. H. Eichhorn, A. J. Paraskos, K. Kishikawa, T. M. Swager, J. Am. Chem. Soc., 2002, 124, 12742.
- [37] A. J. Paraskos, T. M. Swager, *Chem. Mater.*, 2002, 14, 4543.
- [38] J. Herman, O. Chojnowska, P. Harmata, R. Dąbrowski, B.W. Klus, P. Kula, *Liq. Cryst.*, 2014, **41**, 1647.
- [39] V. Kozmík, T. Hodík, J. Svoboda, V. Novotna, D. Pociecha, E. Gorecka, *Liq. Cryst.*, 2016, 43, 839.
- [40] E. Girotto, I. H. Bechtold, H. Gallardo, *Liq. Cryst.*, 2015, **42**, 1798.
- [41] A. Kovarová, M. Kohout, J. Svoboda, V. Novotna, *Liq. Cryst.*, 2014, **41**, 1703.
- [42] W. Zhang, W. He, C. Di, X. Wang, Z. Yang, D. Wang, H. Cao, D. Yang, H. Yang, *Liq. Cryst.*, 2016, 43, 524.

- [43] N. L. Campbell, W. L. Duffy, G. I. Thomas, J. H. Wild, S. M. Kelly, K. Bartle, M. O'Neill, V. Minter, R. P. Tuffin, *J. Mater. Chem.*, 2002, 12, 2706.
- [44] A. J. Seed, G. J. Cross, K. J. Toyne, J. W. Goodby, *Liq. Cryst.*, 2003, **30**, 1089.
- [45] J. J. Apperloo, L. B. Groenendaal, H. Verheyen, M. Jayakannan, R. A. J. Janssen,

A. Dkhissi, D. Beljonne, R. Lazzaroni, J. L. Bredas, Chem. Eur. J., 2002, 8, 2384.

- [46] S. Akoudad, P. Frere, N. Mercier, J. Roncali, J. Org. Chem., 1999, 64, 4267.
- [47] A. Kumar, J. R. Reynolds, *Macromolecules.*, 1996, **29**, 7629.
- [48] B. Sankaran, J. R. Reynolds, *Macromolecules.*, 1997, **30**, 2582.
- [49] C. D. Dimitrakopoulos, P. R. L. Malenfant, Adv. Mater., 2002, 14, 99.
- [50] J. F. Hulvat, S. I. Stupp, Angew. Chem. Int. Ed., 2003, 42, 778.
- [51] R. de Bettignies, Y. Nicolas, P. Blanchard, E. Levillain, J.-M. Nunzi, J. Roncali, Adv. Mater., 2003, 15, 1939.
- [52] D. Wohrle, D. Meissner, *Adv. Mater.*, 1991, **3**, 129.

- [53] U. Mitschke, P. Bäuerle, J. Mater. Chem., 2000, 10, 1471.
- [54] A. Gowda, A. Roy, S. Kumar, J. Mol. Liq., 2017, 225, 840.
- [55] A. N. Gowda & S. Kumar, *Liq. Cryst.*, 2016, **43**, 1721.
- [56] M. J. Frisch et al., Gaussian 16, Gaussian, Inc., Wallingford, CT, 2017.
- [57] S. A. R. Krishnan, W. Weissflog, G. Pelzl, S. Diele, H. Kresse, Z. Vakhovskaya and R. Friedemann, *Phys. Chem. Chem. Phys.*, 2006, 8, 1170.
- [58] C.-Y. Liu, H. Zhao, and H.-h. Yu, Org. Lett., 2011, 13, 4068.
- [59] R. L. Sutherland in Handbook of Nonlinear Optics, Dekker, New York, 2nd ed.
 1996
- [60] A. N. Gowda, M. Kumar, A. R. Thomas, R. Philip, and S. Kumar. ChemistrySelect., 2016, 1, 1361.
- [61] R. Philip, G. R. Kumar, N. Sandhyarani, T. Pradeep, *Phys. Rev. B.*, 2000, 62, 13160.
- [62] Y. Arakawa, S. Nakajima, R. Ishige, M. Uchimura, S. Kang, G.-i. Konishi and J. Watanabe, *J. Mater. Chem.*, 2012, 22, 8394.

Graphical abstract

Thermal and nonlinear optical studies of newly synthesized EDOT based bent-core and hockey-stick like liquid crystals

Ashwathanarayana Gowda, Litwin Jacob, Nithin Joy, Reji Philip, Pratibha R & Sandeep Kumar* Raman Research Institute, C.V. Raman Avenue, Sadashivanagar, Bangalore - 560 080, India Phone: +91 80 23610122, Fax: +91 80 23610492, E-mail: skumar@rri.res.in



The synthesis and characterisation of some novel bent-core and hockey-stick like liquid crystals from EDOT are reported. All the compounds exhibit enantiotropic mesophase with wide temperature range. These mesogens shows good photophysical and nonlinear optical properties.