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# Synthesis of liquid crystalline benzothiazole based derivatives: A study of their optical and electrical properties

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# ABSTRACT

Two new donor–acceptor type liquid crystalline semiconductors based on benzothiazole have been synthesized. Their structural, photophysical and electronic properties were investigated using X-ray diffraction, atomic force microscopy, cyclic voltammetry, UV–Vis, photoluminescence, and Raman spectroscopy. The liquid crystalline behaviour of the molecules was thoroughly examined by differential scanning calorimetry (DSC) and optical polarizing microscope. The DSC and thermogravimetric analysis (TGA) show that these materials posses excellent thermal stability and have decomposition temperatures in excess of 300 °C. Beyond 160 °C both molecules show a smectic A liquid crystalline phase that exists till about 240 °C. Field-effect transistors were fabricated by vacuum evaporating the semiconductor layer using standard bottom gate/top contact geometry. The devices exhibit p-channel behaviour with hole mobilities of 10<sup>-2</sup> cm<sup>2</sup>/Vs.

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# 1. Introduction

 $\pi$ -Conjugated organic materials have been the subject of recent research work due to their optical, electronic properties as well as their applications in many fields such as organic light-emitting diodes (OLED) [1–3], photovoltaic cells [4–7], thin film organic field-effect transistors (OFETs) [8-13]. The organic molecules used in electronic and optoelectronic devices are generally divided into two groups: small molecules and polymers. For field-effect transistors, small organic molecules and oligomers are extensively used rather than polymeric materials. The most notable examples include pentacene [14-16], rubrene [17-20] and oligothiophene derivatives [21-24]. In the best cases, the room temperature mobility of crystalline organic semiconductors can reach the value of around 0.1-20 cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup> [25]. A majority of these organic molecules are hole conductors although ambipolar and *n*-type materials are also known [26-32]. The major challenge in device fabrication is to achieve favourable alignment of molecules between source and drain contacts enabling efficient charge transport through the semiconducting medium [33,34]. In this context, liquid crystalline materials are promising candidates as active semiconductor layers in organic electronics [35-43]. Supramolecular organization of the organic semiconductor in a thin film can be enhanced through the utilization of the liquid crystalline material [44-50]. Liquid crystalline phase can induce highly ordered, closely packed structures, leading to high mobilities within the domain boundaries [51,52]. Introduction of  $\pi$ conjugated moieties into a liquid crystalline material gives many advantages in charge transport properties arising from their self-assembling nature [53-58]. They must contain a rigid, conjugated core, which is responsible for the semiconducting behaviour of the molecule. In the past few years, considerable efforts have been made to design, synthesize, and characterize such type of  $\pi$ -conjugated liquid crystalline materials [59-62]. In particular; smectic liquid crystalline materials because of their spontaneous alignment are good candidates for such applications. Their

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Fig. 1. Chemical structures of compounds a and b.

self-assembling property produces multidomain films with no physical grain boundaries between the domains thus facilitating hopping of charge carriers more easily.

In our search for organic semiconductors for OFET application we focused on benzothiazole based organic molecules (Fig. 1) because of their liquid crystalline properties. We have designed and synthesized two donor-acceptor (D-A) type benzothiazole based molecules showing interesting liquid crystalline and semiconducting properties. In both molecules, the core benzothiazole ring acts as an electron acceptor unit because of the presence of sulphur and nitrogen atoms and alkyl substituted thiophene ring as a donor because of its high electron donating ability and charge carrier mobilities. These molecules show a smectic A liquid crystalline phase above the melting temperature, which results in a good alignment and packing of the molecule in the solid state. Also, the materials exhibit p-type FET behaviour with hole mobility of  $10^{-2}$  cm<sup>2</sup>/Vs and on/off current ratio of  $1 \times 10^3$ . With additional surface modification of the gate dielectric layer, it is conceivable that the transport properties of OFETs may further improve. The AFM studies of the annealed samples show a dewetting of the surface with smooth morphology.

# 2. Results and discussion

# 2.1. Synthesis and characterization

The synthetic route to compounds (a) and (b) are summarized in the Scheme 1. Benzothiazole core were synthesized according to method described in literature [63] and bithiophene derivatives were synthesized by reported procedure [64,65]. The final derivatives were synthesized by Wittig reaction and Stille cross coupling and purified by column chromatography [66,67].

#### 2.2. Optical and electrochemical properties of the compounds

The optical and electrochemical properties of the compounds are summarized in the Table 1. The photophysical properties of these two derivatives were investigated using UV-Vis and photoluminescence spectroscopy. The absorption and emission spectra of these two compounds in solution (CHCl<sub>3</sub>) and solid state are depicted in Fig. 2. Compound (a) shows two strong absorption peaks at 318 nm and 395 nm in solution and photoluminescence peak at around 504 nm (in solution) and 587 nm (in solid state). The absorption peak at 318 nm belongs to the  $\pi$ - $\pi$ \* transition and the absorption peak at 395 nm corresponds to a charge transfer band of the donor-acceptor system [68]. Compound (b), on the other hand predominantly shows only one strong absorption peak at 390 nm in solution which belongs to the charge transfer band; the photoluminescence is observed at ~462 nm in solution and 550 nm in solid state. In case of compound (a) the donor and acceptor units are linked through a vinyl bond which inhibits a charge transfer process from the donor thiophene ring to acceptor benzothiazole ring. As a consequence both  $\pi - \pi^{T}$  transition and charge transfer bands are observed in the absorption spectrum. In compound



Scheme 1. Synthesis routes to a and b.

Table 1	
Optical and electrochemical	properties of the compounds.

Compounds	Film		Solution		CV	CV		
	$\lambda_{abs}$ (nm)	$\lambda_{\rm em} ({\rm nm})$	$\lambda_{abs}$ (nm)	$\lambda_{\rm em}  ({\rm nm})$	$E_g (eV)$	$E_{ox}^{onset}$ (V)	$E_{\rm HOMO}~({\rm eV})$	LUMO (eV)
a b	318 325	587 550	395 390	504 462	2.6 2.8	0.35 0.37	-5.17 -5.19	-2.57 -2.39



Fig. 2. UV-Vis absorption and photoluminescence spectra of compounds a and b.

(b) the donor and acceptor units are directly linked allowing a strong charge transfer process, and as a result only one peak is observed in the absorption spectrum. For both the molecules there is no sharp absorption peak in the solid state due to aggregation. The emission maxima in the solid state were observed at longer wavelengths than those in solution (80-90 nm red shift) indicating the presence of a strong interaction between the molecules (packing effect) [69] in the solid state, which is essential for good device performance. The optical band gaps,  $E_g$ , were approximated from the onset of the low energy side of the absorption spectra ( $\lambda_{onset}$ , solution) to the baseline. Further, the HOMO-LUMO energy levels were calculated by cyclic voltammetry measurements. The oxidation onset for the compound (a) and (b) were 0.35 and 0.37 eV, respectively, and their corresponding HOMO energy levels are -5.17 and -5.19 eV (Table 1). HOMO energy levels have been calculated by using equation HOMO =  $-(E_{\alpha x}^{onset} + 4.8)$  (eV). The LUMO levels were estimated from HOMO values and values of optical band gaps according to the equation: LUMO = HOMO +  $E_{\alpha}^{opt}$  (eV). These results show that the introduction of vinyl linkage between benzothiazole and bithiophene unit inhibits donor-acceptor charge transfer and increases the effective conjugation length, thus lowering the band gap by about 0.2 eV.

## 2.3. Structure and morphology

To study the crystallinity of the materials, X-ray diffraction studies were performed from drop cast films that were annealed at 120 °C (Fig. 3). From the diffraction pattern it seems that both the materials are crystalline. Compound (a) exhibits distinct diffraction peaks at  $2\theta = 5.7^{\circ}$  and  $8.3^{\circ}$  with d-spacings of 15.2 Å and 10.5 Å corresponds to intermolecular distances. Similarly, compound (b) shows two sharp diffraction peaks at  $2\theta = 6.0^{\circ}$  and  $8.7^{\circ}$  with d-spacings of 14.6 Å and 10.0 Å corresponds to intermolecular distances. For both the compounds, several reflections in the wide-angle regions (between 7.6 Å and 3.6 Å), occur because of the organization within the 3D lattice and the reflections at around 3.6 Å may be due to  $\pi$ - $\pi$  stacking of mesogens [40].

Raman scattering is particularly informative on chemical composition, segmental orientation, conformational distribution and phase identification in organic semiconductors. Fig. 4 shows the Raman spectra of as-is powder samples for both compounds. They were measured in a perfect backscattering geometry with less than 2 mW incident laser power on a 50  $\mu$ m<sup>2</sup> area of the sample. The 1620 cm<sup>-1</sup> Raman peak in compound (a) originates from the C=C stretch motion of the vinyl group [70], which is absent in compound (b). The Raman peaks in the 1600 cm<sup>-1</sup> region in both compounds are from the intraring C-C stretch motion (ring breathing) of the phenyl group [71]. The 1564/1560 cm<sup>-1</sup> peak arises from a C=C stretch motion of the phenyl ring. The Raman peaks in the 1470–1490 cm<sup>-1</sup> region in both compounds are attributed to the benzothiazole unit [72]. These peaks arise from C-H bending and C-N stretch motions. The C-N stretch mode is usually an infrared active mode that may become Raman active due a lowering of the symmetry of the molecule. In compound (a) the 1487  $\mbox{cm}^{-1}$  peak is seen only as a shoulder. The 1447 cm<sup>-1</sup> Raman frequency in both compounds are from the C=C ring stretch motion of the thiophene unit. In thiophene-based polymers the 1447 cm<sup>-1</sup> appears as an intense peak in the Raman spectrum [73]. Future Raman scattering studies from biased OFET struc-



Fig. 3. Room temperature powder XRD of thin films of compounds a and b.



Fig. 4. Raman spectra of compounds a and b.

tures of both compounds will yield information on the nature of electron-phonon coupling associated with charge transport mechanism in such devices.

## 2.4. Thermal and liquid crystalline properties

The thermal stability of the compounds (a) and (b) were investigated using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Both the compounds have an excellent thermal stability, with decomposition temperatures of 320 °C (compound a) and 300 °C (compound b) as shown in Fig. 5. At temperature around 158 °C compound (a) starts melting and a liquid crystalline phase appears. This liquid crystalline phase exist up to 240 °C and a new nematic phase appears between 240 °C and 253 °C before it turns into a completely isotropic phase at around 260 °C. The existence of the nematic phase for compound (a) has been confirmed from a clear transition at 240 °C in DSC (Fig. 6). The optical polarizing images of the nematic and smectic A phase are shown in Fig. 7. Compound (b), on the other hand, starts to melt at around 177 °C and forms a smectic A phase existing up to 239 °C, beyond which it becomes a completely isotropic phase at



Fig. 5. TGA of compounds a and b.

250 °C as shown in DSC (Fig. 6). The optical polarizing images of smectic A phase and crystalline phase were given in Fig. 7. All the phase transition temperatures including their change of enthalpy are given in the Table 2.

#### 2.5. AFM analysis

A thin film of compound (a) was evaporated on cleaned Si wafers under vacuum evaporation  $(10^{-6} \text{ mbar})$ . The thickness of the films ranged from 60 to 80 nm. Two films were utilized for the AFM studies: one as-is and the other thermally annealed. The latter was placed in an oven (under nitrogen atmosphere) and slowly heated to 120 °C and kept at this temperature for a few hours. It was then heated to 160 °C, left at this temperature for a few hours and then slowly brought back to room temperature. These temperatures were chosen to match the changes in the crystalline phase with temperature. We simultaneously recorded AFM topography and phase images. Fig. 8 shows the topography and phase images of the as-grown [(a) and (b)] and annealed sample [(c) and (d)]. The annealed samples clearly show a dewetting of the surface but with a very smooth morphology. The rms roughness of the two samples for  $1 \,\mu m \times 1 \,\mu m$  area decreased from



Fig. 6. DSC of compounds a and b (scan rate is 10 °C/min under N<sub>2</sub>).





Crystalline phase at 166 °C

Smectic A phase at 222 °C

Compound b

Fig. 7. Optical polarizing microscopic images of compounds a and b.

#### Table 2

Phase transition temperatures and their corresponding Enthalpy changes.

Compounds	$T_{\rm t}$ (Cr– $S_{\rm A}$ )	$\Delta H(Cr-S_A)$ (J/gm)	$T_{\rm t} \left( S_{\rm A} - N \right)$	$\Delta H(S_A - N) (J/gm)$	$T_{\rm t} (N-I)$	$\Delta H(N-I)$ (J/gm)
a	158 °C	18.40	239	1.85	250	1.08
b	177 °C	30.35	-	-	234	15.91

Transition temperatures and enthalpies determined by DSC at scan rate = 10 °C/min. (Cr = crystalline phase,  $S_A$  = smectic A phase, N = nematic phase and I = isotropic phase,  $T_t$  is transition temperature and  $\Delta H$  = enthalpy change.)

 ${\sim}3.2$  nm in the as-grown sample to  ${\sim}0.7$  nm in the annealed sample. At this point it is not clear if the dewetting

of the annealed sample may be avoided by treating the Si surface differently. We are currently exploring different



Fig. 8. AFM images of as-grown and annealed samples of compound a.

chemical treatments of Si and  $Si/SiO_2$  interfaces for thin film growth of such liquid crystalline molecules since the small rms roughness of annealed films is extremely beneficial from the device aspect if the film coverage were better. Due to the issues with the annealed films all devices were fabricated with as-is evaporated films of compounds (a).

# 2.6. Field-effect transistor performance

Thin film transistors were fabricated by vacuum deposition of compound (a). The devices were fabricated using a top-contact bottom gate structure. In this work no surface modification of the Si/SiO<sub>2</sub> layers were done and all organic films were grown at room temperature. The devices exhibit p-channel performance. Although the output transistor characteristics from FETs fabricated with compound (b) were similar to compound (a), the former exhibited large leakage currents. It is not clear whether the leakage current in compound (b) mainly originates from the morphology of the film owing to grain boundaries and whether this can be circumvented using different gate dielectric layers. Systematic studies for improving FET characteristics using different surface modification and gate dielectrics from both compounds are in progress.

Fig. 9 shows the transfer characteristics for a forward and reverse sweep from an OFET using compound (a); the inset shows the output characteristics where the



Fig. 9. The transfer characteristics for a forward and reverse sweep and output characteristics (inset) from an OFET fabricated using compound a.

drain-source voltages were swept from 0 to -20 V. The highest hole mobility, calculated from the saturation regime ( $V_{\text{DS}} = -60$  V), was estimated as 0.01 cm<sup>2</sup>/Vs. The on/off ratio was obtained as  $10^3$  from  $I_{\text{DS}}$  at  $V_{\text{GS}} = 0$  V and  $V_{\text{GS}} = -60$  V; the threshold voltages were relatively low at

 $\sim$ 7 V. We point out that there is a lot of room for improvement for device performance. It is well established that surface modification by octyltrichlorosilane (OTS) or hexamethyldisilazane (HMDS) self-assembled monolayers can improve charge carrier mobilities and on/off ratios by more than an order of magnitude [67]. The results presented here are a proof of concept that the liquid crystalline benzothiazole compounds are excellent candidates for application in organic electronics.

# 3. Conclusions

Two new liquid crystalline donor-acceptor type benzothiazole derivatives have been synthesized by simple synthetic methods and characterized by optical absorption and photoluminescence spectroscopies, Raman scattering, differential scanning calorimetry, and thermogravimetric analysis. The field-effect transistor performance of one of the benzothiazole compounds shows that these materials have a great potential for future application in organic devices.

# 4. Experimental details

# 4.1. Synthesis

All chemicals were purchased from S.D. Fine Chemicals Ltd.; Mumbai, India and Spectrochem Pvt. Ltd.; Mumbai, India, except tributyltinchloride, Pd(PPh<sub>3</sub>)<sub>4</sub> and potassium tert-butoxide which were bought from Sigma Aldrich.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using Bruker 400 MHz. Chemical shifts were given in parts per million and coupling constants (J) in Hertz.

# 4.1.1. Synthesis of 2-(4-((E)-2-(5-(5-decylthiophen-2-yl)thiophen-2-yl)vinyl)phenyl)benzo[d] thiazole (a)

To a solution of 5-(5-decylthiophen-2-yl)thiophene-2carbaldehyde (1) (0.617 g, 1.08 mmol) and Wittig salt (2) (0.347 g, 1.03 mmol) in dry CHCl<sub>3</sub> was added t-BuO<sup>-</sup>K<sup>+</sup> (0.139 g, 1.2 mmol) in ethanol at room temperature. After allowing the mixture refluxing for 4 h, water was added and extracted with CHCl<sub>3</sub>. The organic phase was dried over sodium sulphate. After removal of the solvent, the residue was purified by silica gel column chromatography with 30% chloroform and hexane as the eluent. Yield 67%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.02–8.00 (m, 3H), 7.85– 7.83 (d, J = 8 Hz, 1H), 7.51–7.49 (d, J = 8 Hz, 2H), 7.45– 7.41 (dt, 1H), 7.34–7.30 (dt, 1H), 7.23–7.19 (d, J = 16 Hz, 1H), 6.95–6.39 (m, 3H), 6.84–6.80 (d, J = 16 Hz, 1H), 6.62– 6.60 (d, J = 8 Hz, 1H), 2.75–2.71 (t, J = 8 Hz, 2H), 1.63–1.53 (m, 4H), 1.30–1.18 (m, 12H), 0.83–0.80 (t, J = 8 Hz, 3H).

 $^{13}$ C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  146.00, 140.71, 137.63, 129.53, 128.10, 127.95, 127.72, 126.40, 125.20, 124.90, 123.47, 123.44, 123.41, 121.61, 31.88, 31.58, 30.19, 29.55, 29.32, 29.06, 22.67, 14.10.

ESIMS [Found: m/z 542.1 [M+H]<sup>+</sup>, Calcd. for C<sub>33</sub>H<sub>35</sub>NS<sub>3</sub> [M+H]<sup>+</sup>: 541.19.

Anal. Calcd. for C<sub>33</sub>H<sub>35</sub>NS<sub>3</sub>: C, 73.15; H, 6.51; N, 2.59; S, 17.75. Found C, 71.84; H, 6.19; N, 3.64; S, 16.10.

4.1.2. Synthesis of 2-(4-(5-(5-decylthiophen-2-yl)thiophen-2-yl)phenyl)benzo[d]thiazole (b)

Tributyl(5-(5-decylthiophen-2-yl)thiophen-2-yl)stannane (3) (0.515 gm, 0.86 mmol) and 2-(4-bromophenyl)benzo[d]thiazole (4) (0.250 g, 0.86 mmol) were dissolved in 25 ml of dry DMF.  $Pd(PPh_3)_4$  (50 mg, 0.04 mmol) was added and the mixture was stirred for 16 h at 95 °C. After cooling to room temperature the solvent was removed in rotavapor and the yellow color solid compound was purified by column chromatography (SiO<sub>2</sub>/ chloroform:Hexane (v:v 1:1)) to give b as a yellow solid. Yield 65%.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.11–8.045 (m, 3H), 7.93– 7.91 (d, *J* = 8 Hz, 1H), 7.72–7.70 (d, *J* = 8.3 Hz, 2H), 7.52– 7.49 (dt, 1H), 7.41–7.38 (dt, 1H), 7.33–7.32 (d, *J* = 3.7, 1H), 7.11–7.10 (d, *J* = 3.7 Hz, 1H), 7.05–7.04 (d, *J* = 3.5 Hz, 1H), 6.71–6.70 (d, *J* = 3.4 Hz, 1H), 2.82–2.79 (t, *J* = 8 Hz., 2H), 1.71–1.66 (m, 4H), 1.36–1.19 (m, 12H), 0.89–0.86 (t, *J* = 6.9 Hz, 3H).

 $^{13}$ C NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  146.32, 140.94, 138.79, 136.37, 134.22, 128.15, 126.45, 125.75, 125.26, 124.76, 124.00, 123.68, 123.12, 121.61, 31.90, 31.59, 30.21, 29.55, 29.34, 29.08, 22.67, 14.09.

ESIMS [Found: m/z 516.2 [M+H]<sup>+</sup>, Calcd for  $C_{31}H_{33}NS_3[M+H]^+$ : 515.17.

Anal, Calcd. for C<sub>31</sub>H<sub>33</sub>NS<sub>3</sub>:C, 72.19; H, 6.45; N, 2.72; S, 18.65. Found C, 72.26; H, 6.29; N, 3.33; S, 18.21.

# 4.2. Instrumental analysis

Thermal properties were studied under nitrogen atmosphere on Mettler DSC-1 instrument. Thermal gravimetric analysis (TGA) was conducted on Mettler Toledo TGA/SDTA 851e (temperature rate 10° C/min under N<sub>2</sub>). The electrochemical properties of both the molecules were examined by using cyclic voltammetry (CH instrument). The electrolyte solution employed were 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/THF solution using platinum as working electrode and Ag/Ag+ as the reference electrode at a scan rate of 100 mVs<sup>-1</sup> under Argon atmosphere.

Absorption spectra were recorded on Perkin Elmer (Lambda 35) UV–Vis Spectrometer and fluorescence emission spectra were recorded by using Perkin Elmer Spectro-fluorophotometer (LS 50B) for both solution as well as solid state. Films of the two molecules were fabricated on quartz substrate from orthodichlorobenzene solution by spin casting. The absorption and fluorescence spectra of solution state were taken in chloroform (conc.  $1 \times 10^{-5}$  mol/L). Optical polarizing microscopic images of liquid crystalline phase were taken by Olympus-BX-51 polarizing microscope.

The AFM measurement was performed with a Nanoscope IIIa (Veeco Instruments, Inc.) operating in the tapping mode. Commercial ultra-sharp, rectangular silicon cantilevers made by Micromasch ( $250 \times 35 \times 1.7 \ \mu m^3$ ) were used having a nominal spring constant of ~0.35 N/m and a resonance frequency of ~33 kHz.

The Raman spectra were collected using an Invia Renishaw spectrometer attached to a confocal microscope with  $a \times 50$  long working distance objective and a 785 nm line of a diode laser as the excitation wavelength. Typical laser power was a few mW on the sample.

OFET Fabrication: The devices were fabricated using a top-contact bottom gate structure with gold source and drain electrodes. A heavily p-doped silicon (100) wafer was used as the gate electrode with 200 nm bare SiO<sub>2</sub> layer as the gate dielectric insulator. Thin films (100 nm) of compound (a) were deposited on SiO<sub>2</sub> by vacuum sublimation at a rate of 0.2 Å/s under a pressure of  $10^{-6}$  mbar. The substrate was kept at room temperature. Patterned Au layers of thickness 60 nm were deposited for the source (S)-drain (D) contacts. Typical S–D channel length (L) and width (W) for OFETs were 500 µm and 5 mm, respectively. The device characteristics were measured at room temperature with two source meters, Keithley 2400 and Keithley 236, configured together using a program written in LabView. The source-drain current and the source-gate leakage currents were measured with Keithley 236, which has a resolution of 10 fA.

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