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# Structural characterization of vanillin derivatives with long alkyl chain and investigation of their electrochemical and thermal properties



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### ABSTRACT

This manuscript describes the synthesis, characterization and thermal properties of the two vanillin derivatives containing a long alkyl chain. Two vanillin derivatives 4-(heptyloxy)-3methoxybenzaldehyde  $(L^1)$  and 4-(decyloxy)-3-methoxybenzaldehyde  $(L^2)$  were obtained from the reaction of the vanillin with 1-bromoheptane or 1-bromodecane in DMF reaction media, respectively. The vanillin derivatives  $L^1$  and  $L^2$  have been characterized by the  ${}^{1}H-{}^{13}C$  NMR, FTIR and mass spectral techniques. Single crystals suitable for X-ray diffraction studies were grown by recrystallization of a chloroform solutions of the compounds. There are phenyl-phenyl stacking (edge to edge) interactions within the structures. Thermal analysis data (DSC) revealed that compounds do not show any liquid crystalline character. The electrochemical behaviours of the organic compounds  $L^1$  and  $L^2$  were investigated and all redox processes in the 100-1000 mV/s scan rates are irreversible.

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#### 1. Introduction

Vanilla has processed as a flavour a kind of pre-Columbian Mesoamerican community. In Central America, people have been used the vanilla as a flavour in chocolate. The people's of Europe discovered both chocolate and vanilla in the 1520s [1]. Previously, the natural vanillin has been extracted from the seeds of the Vanilla planifolia plant. But nowadays, Madagascar, an African country, is the largest producer of natural vanillin. The vanillin compound is widely used in many areas. These are in the producing of pharmaceuticals, cosmetics, and other fine chemicals [2]. In addition, vanillin is also used in perfumes, flavor and aromatic masking in medicines, miscellaneous user and cleaning products, and livestock foods [3]. Vanillin is a aromatic aldehyde, and it contains the aldehyde, hydroxyl, and ether functional groups on the phenylene ring. Several ether derivatives containing aliphatic long chains of the vanillin have been synthesised and characterized [4,5]. In these studies, the hexyloxy-, heptyloxy- and many other long chain containing vanillin based on ether compounds were obtained and their properties were investigated. In another study, the liquid crystalline properties of the unsymmetrical compounds based on

Corresponding author. E-mail address: ftumer@ksu.edu.tr (F. Tümer). chalcones containing the alkyloxy vanillin ether derivatives have been investigated and it has been found that the stability and the range of the mesophases increased with the length of the chain in the compounds [6].

Some substances have the intermediate state of matter with molecular arrangement in among that of the traditional crystalline solid and isotropic liquid phases. These substances are called liquid crystal (LC) or mesomorphic state. This state of the matter is an anisotropic liquid. Molecular shape of the materials has a preponderant effect on the presence of the liquid crystalline properties. The materials having LC properties are beneficial in the electronic apparatus (LCDs), medical thermographic devices, photoconductors and semiconductor materials, pharmaceutical preparedness and the textile industry [7]. The beginning necessity to stimulate the liquid crystalline properties in a material are the molecular stiffness and flexibility [8-11].

In this paper, two vanillin derivatives 4-(heptyloxy)-3methoxybenzaldehyde 4-(decyloxy)-3- $(L^1)$ and methoxybenzaldehyde  $(L^2)$  were obtained and characterized by the analytical and spectroscopic techniques. Thermal stabilities and phase transitions of the compounds  $L^1$  and  $L^2$  were investigated by the thermogravimetry (TGA) and differential scanning calorimetry (DSC). The molecular structures of the  $L^1$  and  $L^2$  were determined by the single crystal X-ray diffraction studies. The redox and photophysical properties of the compounds were investigated.







#### 2. Experimental

#### 2.1. Materials and measurements

All reagents and solvents were of reagent-grade quality and obtained from commercial suppliers (Aldrich or Merck). Elemental analyses (C.H.N) were performed using a LECO CHNS 932. Infrared spectra were obtained using KBr disc  $(4000-400 \text{ cm}^{-1})$  on a PerkinElmer Spectrum 100 FT-IR. The electronic spectra in the 200-900 nm range were obtained on a PerkinElmer Lambda 45 spectrophotometer. Mass spectra of the ligands were recorded on a LC/MS APCI AGILENT 1100 MSD spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker 400 MHz instrument. TMS was used as internal standard and CDCl<sub>3</sub> as solvent. The thermal analysis studies of the compounds were performed on a PerkinElmer STA 6000 simultaneous Thermal Analyzer under nitrogen atmosphere at a heating rate of 10 °C/min. The DSC analysis of the synthesised compounds were performed on DSC (PerkinElmer DSC-8000) using continuous heating and cooling under a pure nitrogen  $(N_2)$  atmosphere. The samples (about 2 mg) are accurately weighed by using a precision balance and the weighed samples were sealed in aluminium pans. The samples were heated up to the estimated clearing temperature at heating rate of 10 °C/min and stayed at its isotropic temperature for 4 min to reach thermal stability.

The single-photon fluorescence spectra of the vanillin based compounds L<sup>1</sup> and L<sup>2</sup> were collected on a PerkinElmer LS55 luminescence spectrometer. All samples were prepared in spectrophotometric grade solvents and analysed in a 1 cm optical path quartz cuvette. The solutions of ligands ( $1.0 \times 10^{-3} \text{ mol L}^{-1}$ ) were prepared in DMF solvent.

A stock solution in the  $1 \times 10^{-3}$  M concentration of the vanillin based compounds L<sup>1</sup> and L<sup>2</sup> was prepared in DMF for electrochemical studies. Cyclic voltammograms were recorded on a Iviumstat Electrochemical workstation equipped with a low current module (BAS PA-1) recorder. The electrochemical cell was equipped with a BAS glassy carbon working electrode (area 4,6 mm<sup>2</sup>), a platinum coil auxiliary electrode and a  $Ag^+/AgCl$ reference electrode filled with tetrabutylammonium tetrafloroborate (0.1 M) in DMF and DMF solution and adjusted to 0.00 V vs SCE. Cyclic voltammetric measurements were made at room temperature in an undivided cell (BAS model C-3 cell stand) with a platinum counter electrode and an Ag<sup>+</sup>/AgCl reference electrode (BAS). All potentials are reported with respect to Ag<sup>+</sup>/AgCl. The solutions were deoxygenated by passing dry nitrogen through the solution for 30 min prior to the experiments, and during the experiments the flow was maintained over the solution. Digital simulations were performed using DigiSim 3.0 for windows (BAS, Inc.). Experimental cyclic voltammograms used for the fitting process had the background subtracted and were corrected electronically for ohmic drop. Mettler Toledo MP 220 pH meters was used for the pH measurements using a combined electrode (glass electrode reference electrode) with an accuracy of  $\pm 0.05$  pH.

Eclipse E200, Nikon Japan Polarised optical microscope (POM) equipped with the digital camera was used. Temperature of sample was controlled with heating stage LTS 120, with PE95 LinkPad accuracy of 0.1 C from LinkamScientific Instrument, Ltd., England. POM studies carried out not only to observe the morphological texture of prepared samples but also to monitor phase transitions.

# 2.2. X-ray crystallography for compounds $L^1$ and $L^2$

Data were collected on a Bruker ApexII CCD diffractometer using Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å). Data reduction was performed using Bruker SAINT [12]. SHELXTL was used to solve and refine the

structures [13]. Crystallographic diffraction data for  $L^1$  were obtained at 150(2) K. A single crystal of  $L^2$  was mounted on a fiber and nitrogen cryostream was adjusted to 150(2) K. However, the crystal lost crystallinity and became white powder at this temperature. Therefore, the data for  $L^2$  were collected at room temperature with no problem. The structures were solved by direct methods and refined on  $F^2$  using all the reflections [13]. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon atoms were inserted at calculated positions using a riding model. Details of the crystal data and refinement are given in Table 1. Bond distances and angles for compounds are given in the supplementary documents (Tables S1 and S2).

2.3. General procedure for the synthesis of 4-(heptyloxy)-3methoxybenzaldehyde ( $L^1$ ) and 4-(decyloxy)-3methoxybenzaldehyde ( $L^2$ )

A mixture of 4-hydroxy-3-methoxybenzaldehyde (1 mmol), 1bromoheptane (1 mmol) and  $K_2CO_3$  (3 mmol) in N,N-dimethyl formamide (25 mL) was stirred at room temperature for 4 h. The reaction was monitored by TLC. After the completion of reaction, the product was extracted into ether layer and it was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> to obtain 4-(heptyloxy)-3methoxybenzaldehyde (L<sup>1</sup>). Similar procedure except using 1bromodecane rather than 1-bromoheptane was followed up to obtain 4-(decyloxy)-3-methoxybenzaldehyde (L<sup>2</sup>).

**L**<sup>1</sup>: C<sub>15</sub>H<sub>22</sub>O<sub>3</sub>: Yield: 98%, color: Dirty white, melting point: 38–40 °C. Elemental Analysis (%): Found (Calcd.): C, 72.02 (71.97%); H, 8.81 (8.86%). <sup>1</sup>H NMR ( $\delta$ , ppm; CDCl<sub>3</sub>): 9.85 (1H, *s*, –HC=O), 7.43–7.45 (1H, *dd* (*j*: 1.8, 8.1 Hz), Ar–H), 7.41 (1H, *d* (*j*: 1.8 Hz), Ar–H), 6.96–6.98 (1H, *d* (*j*: 8.1 Hz), Ar–H), 4.12 (2H, *t*, O–CH<sub>2</sub>-), 3.93 (3H, *s*, O–CH<sub>3</sub>), 1.92 (2H, *p*, O–C–CH<sub>2</sub>-), 1.49–1.32 (8H, *m*, aliphatic-CH<sub>2</sub>), 0.88(3H, *t*, –CH<sub>3</sub>). <sup>13</sup>C NMR ( $\delta$ , ppm; CDCl<sub>3</sub>): 14.05–31.71 (Aliphatic -<u>C</u>H<sub>2</sub>-, -<u>C</u>H<sub>3</sub>), 56.02 (O<u>C</u>H<sub>3</sub>), 68.99 (O<u>C</u>H<sub>2</sub>-), 109.18–154.30 (Ar–C), 190.70 (-HC=O). FTIR (KBr, cm<sup>-1</sup>): 2927  $\nu$ (C–H)<sub>alph</sub>, 1677  $\nu$ (C=O), 1393  $\nu$ (C–O)<sub>phenolic</sub>, 781  $\nu$ (out of plane C–H).

**L<sup>2</sup>:** C<sub>18</sub>H<sub>28</sub>O<sub>3</sub>: Yield: 82%, color: Dirty white, melting point: 52–55 °C. Elemental Analysis (%): Found (Calcd.): C, 73.97 (73.93); H, 9.68 (9.65%). <sup>1</sup>H NMR ( $\delta$ , ppm; CDCl<sub>3</sub>): 9.86 (1H, *s*, –HC=O), 7.44 (1H, *dd* (*j*: 1.8, 8.1 Hz), Ar–H), 7.43 (1H, *d* (*j*: 1.8 Hz), Ar–H), 6.99 (1H,

Table 1	
Crystallographic data for the compounds.	

Identification cod	e	L <sup>1</sup>	L <sup>2</sup>
Empirical formula Formula weight Temperature(K) Crystal system Space group	3	C <sub>15</sub> H <sub>22</sub> O <sub>3</sub> 250.33 150(2) <i>Triclinic</i> <i>P</i> T	C <sub>18</sub> H <sub>28</sub> O <sub>3</sub> 292.40 293(2) Monoclinic P2(1)/c
Unit cell Volume (Å <sup>3</sup> )	a (Å) b (Å) c (Å) α (°) β (°) γ (°)	8.4137 (18) 9.939 (2) 17.509 (4) 102.404 (3) 94.736 (3) 101.260 (3) 1390.6 (5)	22.131 (3) 9.3398 (13) 8.5515 (12) 90 93.341 (2) 90 1764.6 (4)
Z Calculated densit Abs. coeff. ( $mm^{-1}$ Refl. collected R1, wR2 [I > 2 $\sigma$ (I R1, wR2 (all data) Goodness-of-fit o CCDC	y(g/cm <sup>3</sup> ) ) )] n <i>F</i> <sup>2</sup>	4 1.196 0.082 5756 0.0472,0.1339 0.0889,0.1641 0.762 1062277	4 1.101 0.073 15312 0.0419,0.1216 0.0818,0.1527 1.008 1062278

*d* (*j*: 8.1 Hz), Ar–H), 4.13 (2H, *t*, O–CH<sub>2</sub>-), 3.94 (3H, *s*, O–CH<sub>3</sub>), 1.93 (2H, *p*, O–C–CH<sub>2</sub>-), 1.50–1.29 (14H, *m*, aliphatic-CH<sub>2</sub>), 0.91(3H, *t*, –CH<sub>3</sub>). <sup>13</sup>C NMR ( $\delta$ , ppm; CDCl<sub>3</sub>): 14.09–31.73 (Aliphatic -<u>C</u>H<sub>2</sub>-, -<u>C</u>H<sub>3</sub>), 56.03 (O<u>C</u>H<sub>3</sub>), 69.20 (O<u>C</u>H<sub>2</sub>-), 109.20–154.30 (Ar–C), 190.89 (-HC=O). FTIR (KBr, cm<sup>-1</sup>): 2928 *ν*(C–H)<sub>alph</sub>, 1682 *ν*(C=O), 1402 *ν*(C–O)<sub>phenolic</sub>, 804 *ν*(out of plane C–H).

#### 3. Results and discussion

In this paper, two vanillin-based ether compounds (Scheme 1)  $L^1$  and  $L^2$  have obtained and characterized by using the elemental analyses, <sup>1</sup>H–<sup>13</sup>C NMR, FTIR, UV–Vis., emission and mass spectra. The compounds [4-(heptyloxy)-3-methoxybenzaldehyde ( $L^1$ ) and

4-(decyloxy)-3-methoxybenzaldehyde  $(L^2)$ ] were synthesised by the reaction of vanillin and 1-bromoheptane or 1-bromodecane in DMF. The electrochemical and thermal properties of the compounds have been investigated. Also, single crystals of both compounds were grown from slow evaporation of CHCl<sub>3</sub> solution of the compounds. The solubility of the compounds is very high in the polar and apolar organic solvents.

All spectroscopic data for the compounds  $L^1$  and  $L^2$  have been given in the experimental section. The FTIR spectra of the compound  $L^1$  and  $L^2$  are presented in Fig. 1 &S1. The aliphatic  $\nu$ (C–H) vibration bands resulting from long chains in the compounds are observed at about 2927 cm<sup>-1</sup> as a sharp peak. The bands at 1677 for  $L^1$  and 1682 cm<sup>-1</sup> for  $L^2$  come from the vibration  $\nu$ (C=O) of the carbonyl group on the vanillin ring. The presence of characteristic



# **R-X:** 1-Bromoheptane (C<sub>7</sub>H<sub>15</sub>Br) and 1-bromodecane (C<sub>10</sub>H<sub>21</sub>Br)

**Scheme 1.** The synthesis reaction of the compounds  $L^1$  and  $L^2$ .



Fig. 1. FTIR spectrum of the compound 4-(heptyloxy)-3-methoxybenzaldehyde (L<sup>1</sup>).



**b)** Emission ( $\lambda_{exc}$ : 390 nm) and excitation ( $\lambda_{em}$ : 422 nm) for L<sup>1</sup>.



c) Emission ( $\lambda_{exc}$ : 395 nm) and excitation ( $\lambda_{em}$ : 428 nm) for L<sup>2</sup>.

Fig. 2. The UV-vis, emission and excitation spectra of the compounds  $L^1$  and  $L^2$  in the  $1.0 \times 10^{-3}$  M DMF solution.









Fig. 4. The cv curves of the compounds  $L^1$  and  $L^2$  in the  $1.0 \times 10^{-3}$  M DMF solution and 100-1000 mV/s scan rates.

bands in the FTIR spectra of the compounds confirms their structure.

The UV-Vis., emission and excitation properties of the compounds  $L^1$  and  $L^2$  were investigated in DMF solution ( $10^{-3}$  M) and their spectra are given in Fig. 2. The compounds showed similar absorption bands in DMF. In the UV-vis spectra of the compounds. there are two absorption bands in the 340-250 nm range. While the bands at the longer wavelengths are result from the  $n-\pi^*$  transitions, the bands at 290-250 nm range are due to the  $\pi$ - $\pi$ \* transitions. It can be seen from the UV-Vis spectra that the length of the aliphatic chain does not have a significant effect in the absorption wavelengths, yet higher absorption intensities were observed for the longer aliphatic chain  $(L^2)$ . In the emission and excitation spectra of the compounds  $L^1$  and  $L^2$ , there are two bands and while the intensity of one of them is very low but another is high. It has been determined that the increasing of the aliphatic chain number has not changed the emission and excitation wavelengths of the compounds.

The  ${}^{1}\text{H}{-}{}^{13}\text{C}$  NMR spectra of the compounds were investigated and obtained spectral data are given in the experimental section. The  ${}^{1}\text{H}{-}{}^{13}\text{C}$  NMR spectra of the compound L<sup>2</sup> are shown in Fig. 3 and  ${}^{1}\text{H}{-}{}^{13}\text{C}$  NMR spectra of the compound L<sup>1</sup> is given in the supplementary documents (Fig. S2). In the  ${}^{1}\text{H}$  NMR spectra of the compounds L<sup>1</sup> and L<sup>2</sup>, the signals at 9.85 and 9.86 ppm can be attributed to the hydrogen atom of the carbonyl group (HC=O), respectively. The aromatic ring hydrogen atoms were seen in the 6.98–7.45 ppm range as multiplet. The hydrogen atoms of the methoxy group on the vanillin ring were observed at 3.93 for L<sup>1</sup> and 3.94 for L<sup>2</sup> ppm as a singlet signal. The aliphatic chain methyl and methylene ( $-CH_2-$ ,  $-CH_3$ ) hydrogen atoms were found in the 0.88–1.93 ppm range as multiplets. In the <sup>13</sup>C NMR spectra of the compounds L<sup>1</sup> and L<sup>2</sup>, the carbon atom signals of the carbonyl group was seen at 190.70 and 190.89 ppm, respectively. The signals in the 109.18–154.30 ppm range can be attributed to the aromatic ring carbon atoms. The signals of methoxy and methylenoxy carbon atoms were observed in the 56.02–69.20 ppm range. The signals of the aliphatic carbon atoms are in the 14.05–31.73 ppm range.

The electrochemical properties of the compounds  $L^1$  and  $L^2$ were investigated by using  $1.0 \times 10^{-3}$  M DMF solution and in the range 100-1000 mV/s scan rates. The cyclic voltammograms (cv) of the compounds have been given in Fig. 4. In the cv curve of the L<sup>1</sup>, a very weak cathodic peak at -0.70 V arises from the reduction of the aldehyde group to the alcohol group. In the L<sup>2</sup>, this reduction peak has become more apparent and shown at about 0.25 V. Depending on the number of the chain long in the L<sup>2</sup> compound, the reduction process was more difficult than the L<sup>1</sup>. In the anodic scanning, the L<sup>1</sup> compound has three oxidation processes in the -1.90-0.75 V range. These reactions are the oxidation from the alcohol to aldehyde and etheric oxygens to ketones (Fig. 5) [14,15]. Similar redox reactions were also observed in the  $L^2$  compound. However, the anodic peak values in this compound are in the range -1.0-0.28 V. Depending on the increasing of the scan rate, although the peak potential values did not change, the peak current values increased.



 $<sup>\</sup>mathbf{R}$ = Heptyl- (L<sup>1</sup>), decyl (L<sup>2</sup>).

## 3.1. X-ray structures of $L^1 \& L^2$

Single crystals of the compounds were obtained from slow evaporation of chloroform solutions of the compounds. Molecular structures of two vanillin derivatives are closely similar differing only in the number of carbon atoms in the alkyl chain; L<sup>1</sup> contains seven carbon atoms (heptyl) in the chain while L<sup>2</sup> has ten carbon atoms (decyl) in the alkyl chain. Molecular structures of the

compounds  $L^1 \& L^2$  are shown in Fig. 6a and b. Asymmetric unit of  $L^1$  contains two independent molecules differing by the position of the aldehyde group, the aldehyde oxygen(O3) atom in molecule B is disordered with respect to C13 and it was modelled as 70:30 (O3:O3') occupancy over the two positions. In both compounds, the formyl group bond distances are within the range of C=O bond distances.

In the structure of L<sup>1</sup>, two independent molecules in the



**Fig. 6. a)** Asymmetric unit of L<sup>1</sup> with thermal ellipsoid (30% probability), the aldehyde oxygen atom in molecule A is disordered and it was modelled 70:30 (O3:O3') occupancy over the two positions. **b)** Asymmetric unit of L<sup>2</sup> with thermal ellipsoid (30% probability).



Fig. 7. Packing plot of L<sup>2</sup> viewing down c axis showing interdigitation in the decyl chain of the molecules. Hydrogen atoms are omitted for clarity.

asymmetric unit are linked by weak hydrogen bond type  $CH_{phe-nyl} \cdots O_{aldeyhde}$  interactions (Fig. 6a). In structure of  $L^2$ , the alkyl chain is in *trans* conformation except for the bond from the carbon atom connected to the phenol unit and the second carbon of the alkyl chains. In  $L^1$ , the heptyl group of two molecules is interdigitated (head to tail) forming a non-polar region (Fig. S3). The heptyl group of the molecule is aligned to phenyl group of an adjacent

molecule which restricts cycle stacking between the phenyl rings. However, the extension of the alkyl chain from seven to ten (compound  $L^2$ ) results in fully interdigitation of the alkyl chains (head to tail) forming a non-polar domain. The phenyl ring of two neighbouring molecules showed phenyl-phenyl stacking interactions resulting in zipper-like chains along the *c* axis (Fig. 7).

Hirshfeld surfaces for the compounds L<sup>1</sup> and L<sup>2</sup> were drawn to



Fig. 9. Relative contribution of different intermolecular contacts to overall stability of the crystal structures of L<sup>1</sup> and L<sup>2</sup>.

elucidate the intermolecular interactions of the polar and nonpolar moieties of the molecules with their neighbouring molecules. Hirshfeld surface analysis represent a clear visualization of potential van der Waals interactions between the alkyl group of adjacent molecules which may form an interdigitation in the crystal packing  $(H \cdots H \text{ contacts})$ . As shown in Fig. 8, the 2D fingerprint plots of the compounds  $L^1$  and  $L^2$  are very similar and indicated high intensities for di and de values between 1.2 and 1.8 Å, indicating the high degree of hydrophobic interactions. The relative contribution of intermolecular contacts for both compounds is given in Fig. 9. The main contribution for both compounds comes from H ···· H contacts followed by  $O \cdots H/H \cdots O$  and  $C \cdots H/H \cdots C$  contacts. The longer carbon chain in compound L<sup>2</sup> resulted in higher degree of hydrophobic interactions  $(H \cdots H)$  between the molecules. In both structures, the closer intermolecular  $O \cdots H/H \cdots O$  contacts were observed as red-spots in the d<sub>n</sub> surfaces of the compounds (Fig. S4). Fully interdigitation of decyl chain in L<sup>2</sup> allowed phenyl-phenyl stacking interactions (Fig. S5).

#### 3.2. Thermal properties

Thermal properties of the compounds  $L^1$  and  $L^2$  have investigated by using thermogravimetric (TG) and differential thermal analysis (DTA) methods in the 25–900 °C temperature range under nitrogen atmosphere at a heating rate of 10 °C/min. TGA and DTA curves of the compounds  $L^1$  and  $L^2$  have been given in Fig. 10. The compounds show the different decomposition processes. The compound  $L^1$  undergoes to mass loss in only one step. In 170–240 °C range, the compound showed a sharp mass los and 93% of the total mass was lost. The rest of the organic moiety was lost up to the higher temperatures leaving no residue in the samples. In DTG curve of the  $L^1$ , this mass loss corresponds to the endothermic peak (T<sub>max</sub>: 242 °C). Compound L<sup>2</sup> has shown two thermal decomposition steps. The mass loss of the compound starts at around 100 °C. In the first decomposition step, ~10% of the total mass was removed from sample in the 100–170 °C followed by an endothermic peak at 147 °C (T<sub>max</sub>). In the second step, rest of the organic moiety of the compound decomposed at 170–290 °C leaving no residue.

The mesomorphic behaviours of the synthesised two vanillin derivatives [4-(heptyloxy)-3-methoxybenzaldehyde (L<sup>1</sup>) and 4-(decyloxy)-3-methoxybenzaldehyde (L<sup>2</sup>)] were investigated by differential scanning calorimetry (DSC) and polarizing optical microscope via a heating/cooling stage. The DSC thermograms for the compounds are shown in Fig. 11. On the DSC measurement, compound L<sup>1</sup> an endothermal peak at 38 °C and this peak is assigned to the melting of the compound. The melting of L<sup>1</sup> can be clearly seen by polarizing optic microscopy (POM) in which the compound melted to isotropic liquid at 38 °C. The melting peak of L<sup>1</sup> is narrow with the enthalpy change of 22.37 J/g showing a clear crystalline state [16]. In the cooling scan of DSC measurement indicated that compound L<sup>1</sup> crystallized directly from the isotropic liquid at 11.9 °C. Both DSC measurements and polarizing optic microscopy showed no mesophase transition on the heating or cooling cycle for compound L<sup>1</sup>. On the heating cycle, compound L<sup>2</sup> showed one endothermal peak at 52.88  $^{\circ}$ C (T<sub>max</sub>) which was due to the melting of the compound which can be seen in POM image given in Fig. S6. The melting of the compound was accompanied by an enthalpy change of 323.86 J/g. On the cooling scan, isotropic liquid  $\rightarrow$  crystallisation peak was observed in the 0–10 °C. The increasing the alkoxy chain of the compound  $L^2$  has caused an increase in the melting point of the compound. This may be due to fully interdigitation of the alkoxy chain resulting in higher lattice energy [17]. The interdigitation of the alkyl chains in  $L^2$  was confirmed by single



**Fig. 10.** Thermal curves for  $L^1$  and  $L^2$ .



Fig. 11. DSC thermograms of  $L^1$  and  $L^2$  on heating/cooling stage.

crystal X-ray crystallography.

## 4. Conclusion

In this work, two vanillin derivatives containing heptyloxy or

decyloxy groups have been prepared. The solid-state structures of the compounds were investigated by single crystal X-ray diffraction studies. The X-ray data revealed that fully interdigitation occurred when decyloxy group present in the structure of L<sup>2</sup>. Thermal behaviours of the compounds were investigated under inert

atmosphere by TG and DSC measurements. There was not liquid crystalline behaviour shown by the compounds. The melting point of the compounds increased with increasing alkyl chain length.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.molstruc.2019.127018.

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