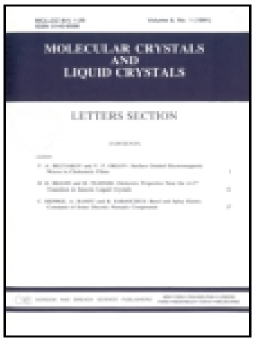

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Synthesis and characterization of new nematic liquid crystalline compounds-based thiophene units

Ying-Gang Jia, Dong Su, Zhi-Hao Guo, and Jian-She Hu

Center for Molecular Science and Engineering, College of Science, Northeastern University, Shenyang, P. R. China

ABSTRACT

Four new liquid crystalline thiophene compounds (**M1–M4**) with a long flexible spacer were prepared. Their structures were characterized by Fourier transform infrared and proton nuclear magnetic resonance. The mesomorphism and thermal stability were investigated with differential scanning calorimetry, polarizing optical microscopy, and thermogravimetric analysis. The photo-physical properties were evaluated using ultraviolet/visible spectroscopy and photoluminescence. **M1–M4** all showed thermotropic mesogenic properties with excellent thermal stability, and exhibited nematic threaded texture, droplet texture, and Schlieren texture on heating and cooling cycles. The effect of flexible spacer and terminal groups on mesomorphic and spectroscopic property is discussed. The experimental results demonstrated that the tendency toward melting temperature (Tm) decreased, while isotropic temperature (Ti) increased with increasing the flexible spacer length. In $CHCl_3$ solution, these thiophene compounds displayed an intense broad absorption band peaking within 230–340 nm and a maximum fluorescent emission wavelength at 426–439 nm.

KEYWORDS

Liquid crystalline; photoluminescence; synthesis; thiophene

1. Introduction

In recent year, the organic conjugated materials have attracted considerable interest due to their excellent electrical and optoelectric properties [1–7], and many important potential applications in various areas such as organic thin-film transistors [8], solar cells [9], organic light-emitting diodes [10], sensor arrays [11], large-area plastic displays [12], and power transmission devices [13]. Today, the thiophene derivatives occupy an important position in the study of organic conjugated materials. Functionalized thiophene derivatives are being shown to be the potential candidates for high-end applications. [14–20] As known, liquid crystalline (LC) materials combine order and mobility, form well self-organized assemblies that exhibit a variety of physical properties, and have been widely used in many fields. [21, 22] From a scientific and industrial point of view, the LC thiophene derivatives are fascinating because they combine the electrical properties of thiophene with the optical properties of conventional LC materials [23–32]. These properties are expected to be controllable through the spontaneous orientation of mesogenic core to enhance the co-planarity of thiophene units.

CONTACT Jian-She Hu ✉ hujs@mail.neu.edu.cn Center for Molecular Science and Engineering, College of Science, Northeastern University, Shenyang 110004, P. R. China.

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In the present work, we aimed to design and synthesize novel nematic LC thiophene compounds containing long flexible spacer length between thiophene unit and mesogenic unit. The phase behavior and mesomorphism of these obtained thiophene compounds were characterized using differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The thermal stability was measured with thermogravimetric analysis (TGA). The optical and photoluminescence properties were investigated by ultraviolet visible (UV/Vis) spectroscopy and fluorescence spectroscopy.

2. Experimental

2.1. *Materials*

All chemicals were obtained from the indicated sources. 3-Methylthiophene (Shanghai, China), *N*-bromosuccinimide (Shenyang, China), benzoyl peroxide (Shenyang, China), hexamethylenetetramine (Tianjing, China), malonic acid (Shenyang, China), 4,4′-dihydroxybiphenyl (Sigma-Aldrich, Shenyang, China), 1,4-dibromobuiane (Shenyang, China), 1,6-dibromohexane (Shenyang, China), 4-ethoxybenzoic acid (Beijing, China), and 4-pentylbenzoic acid (Yantai, China) were used as received. All other solvents and reagents used were purified by standard methods.

2.2. *Measurements*

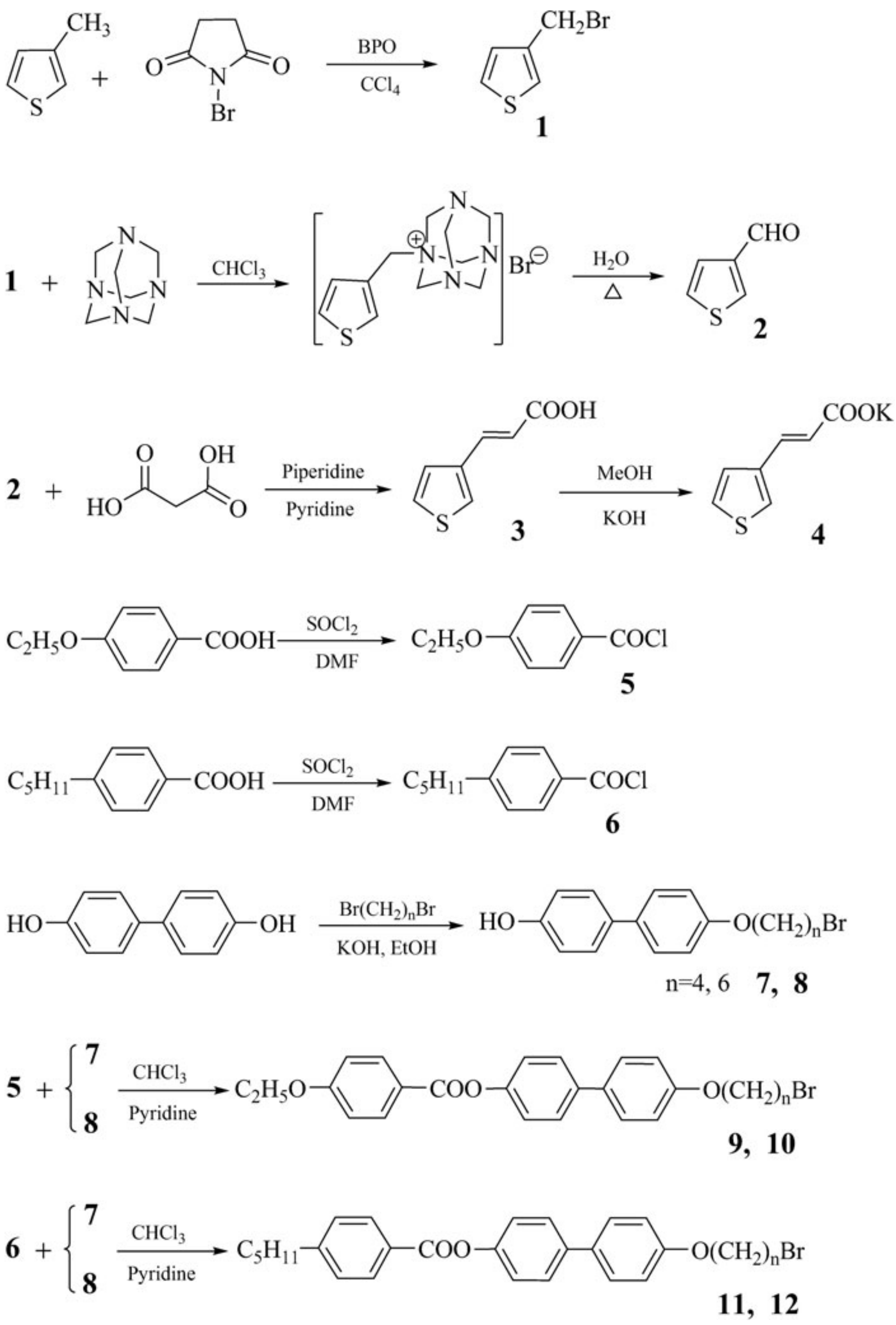
Fourier Transform Infrared (FTIR) spectra were measured on a PerkinElmer spectrum One (B) spectrometer (PerkinElmer, Foster City, CA). ^{1}H Nuclear Magnetic Resonance (NMR) spectra were obtained using a Bruker ARX 600 (Bruker, Fällanden, Swiss) high-resolution NMR spectrometer, and chemical shifts were reported in ppm with tetramethylsilane (TMS) as an internal standard. The thermal properties were determined with a Netzsch DSC 204 (Netzsch, Hanau, Germany) equipped with a cooling system. The thermal stability was measured with a Netzsch TGA 209C thermogravimetric analyzer. The optical texture was observed with a Leica DMRX POM (Leica, Wetzlar, Germany) equipped with a Linkam THMSE-600 (Linkam, London, UK) cool and hot stages. UV/Vis absorption spectra were recorded with a TU-1901 spectrophotometer (Purkinje, Beijing, China) using a quartz cuvette with a 1.0-cm path length. The photoluminescence studies were carried out on an F-7000 fluorescence spectrophotometer (Hitachi, Japan) equipped with a 0.2-cm quartz cuvette. Both excitation and emission slits were set at 5.0 nm, with a scan voltage of 700 V and scan speed of 1200 nm min^{-1}.

2.3. *Synthesis of intermediate compounds*

The synthetic route of intermediate compounds **1–12** is shown in Scheme 1. 3-(Bromomethyl)thiophene (**1**), thiophene-3-carboxaldehyde (**2**), (*E*)-3-(3-thiophenyl)acrylic acid (**3**), 4-(4-bromobutoxy)biphenyl-4’-ol (**7**), and 4-(6-bromohexyloxy)biphenyl-4’-ol (**8**) were synthesized as described in the literature. [33–36]

2.3.1. *Potassium (E)-3-(3-thiophenyl)acrylate (4)*

(*E*)-3-(3-Thiophenyl)acrylic acid (15.4 g, 0.1 mol) was dissolved in 50 mL of methanol, and then potassium hydroxide (5.6 g, 0.1 mol) in 10 mL of methanol was added drop-wise to the above solution under quick stirring. The mixture was reacted at room temperature for 2 h.



Scheme 1. Synthetic route of compounds 1–12.

After the evaporation of solvent, the crude product was recrystallized by methanol. Yield: 85%.

IR (KBr, cm^{-1}): 1641 (C=C); 1562 (C=O); 1516–1486 (thiophene ring); 1152 (C=S).

2.3.2. *4-(4-Bromobutoxy)biphenyl-4′-ethoxybenzoate (9)*

4-Ethoxybenzoyl chloride **5** was obtained through the reaction of 4-ethoxybenzoic acid with excess thionyl chloride. Then compound **5** (9.2 g, 0.05 mol), dissolved in 10 mL of dry chloroform, was added drop-wise to a stirred solution of compound **7** (16.0 g, 0.05 mol) in 150 mL of chloroform and 4 mL of dry pyridine. The mixture was reacted for 2 h at room temperature, refluxed for 24 h, and cooled to ambient temperature. After the evaporation of solvent, the crude product was precipitated by adding methanol to the residue, and recrystallized with ethanol/acetone (1:1). Yield: 73%, mp: 153°C.

IR (KBr, cm^{-1}): 2977, 2849 (CH_3–, –CH_2–); 1726 (C=O); 1605–1495 (Ar–); 1257 (C–O–C); 518 (Br–). ^{1}H NMR (δ, ppm from TMS in $CDCl_3$): 1.45–1.49 (t, 3H, $-C\underline{H}_3$); 1.88–1.95 [m, 4H, $-OCH_2(C\underline{H}_2)_2CH_2Br$]; 3.56–3.60 [t, 2H, $-OCH_2(CH_2)_2C\underline{H}_2Br$]; 4.11–4.17 (m, 2H, $-OC\underline{H}_2CH_3$); 4.27–4.31 [t, 2H, $-OC\underline{H}_2(CH_2)_2C\underline{H}_2Br$]; 7.01–8.20 (m, 12H, Ar$-\underline{H}$).

2.3.3. *4-(6-Bromohexyloxy)biphenyl-4′-ethoxybenzoate (10)*

The synthesis of **10** is similar to that for **9** as described above. Recrystallization from ethanol/acetone (1:1). Yield: 74%, mp: 126°C.

IR (KBr, cm^{-1}): 2977, 2856 (CH_3–, –CH_2–); 1727 (C=O); 1605–1496 (Ar–); 1258 (C–O–C); 519 (Br–). ^{1}H NMR (δ, ppm from TMS in $CDCl_3$): 1.33–1.90 [m, 11H, $-C\underline{H}_3$, and $-OCH_2(C\underline{H}_2)_4CH_2Br$]; 3.55–3.60 [t, 2H, $-OCH_2(CH_2)_4C\underline{H}_2Br$]; 4.12–4.18 (m, 2H, $-OC\underline{H}_2CH_3$); 4.20–4.26 [t, 2H, $-OC\underline{H}_2(CH_2)_4CH_2Br$]; 6.99–8.21 (m, 12H, Ar$-\underline{H}$).

2.3.4. *4-(4-Bromobutoxy)biphenyl-4′-pentylbenzoate (11)*

The synthesis of **11** is similar to that for **9** as described above. Recrystallization from ethanol/acetone (2:1). Yield: 75%, mp: 128°C.

IR (KBr, cm^{-1}): 2924, 2856 (CH_3–, –CH_2–); 1732 (C=O); 1606–1495 (Ar–); 1268 (C–O–C); 516 (Br–). ^{1}H NMR (δ, ppm from TMS in $CDCl_3$): 0.90–0.94 (t, 3H, $-C\underline{H}_3$); 1.32–1.96 [m, 10H, $-CH_2(C\underline{H}_2)_3CH_3$, and $-OCH_2(C\underline{H}_2)_2CH_2Br$]; 2.68–2.74 [t, 2H, $-C\underline{H}_2(CH_2)_3CH_3$]; 3.55–3.60 [t, 2H, $-OCH_2(CH_2)_2C\underline{H}_2Br$]; 4.26–4.33 [t, 2H, $-OC\underline{H}_2(CH_2)_2CH_2Br$]; 6.96–8.17 (m, 12H, Ar$-\underline{H}$).

2.3.5. *4-(6-Bromohexyloxy)biphenyl-4′-pentylbenzoate (12)*

The synthesis of **12** is similar to that for **9** as described above. Recrystallization from ethanol/acetone (2:1). Yield: 74%, mp: 115°C.

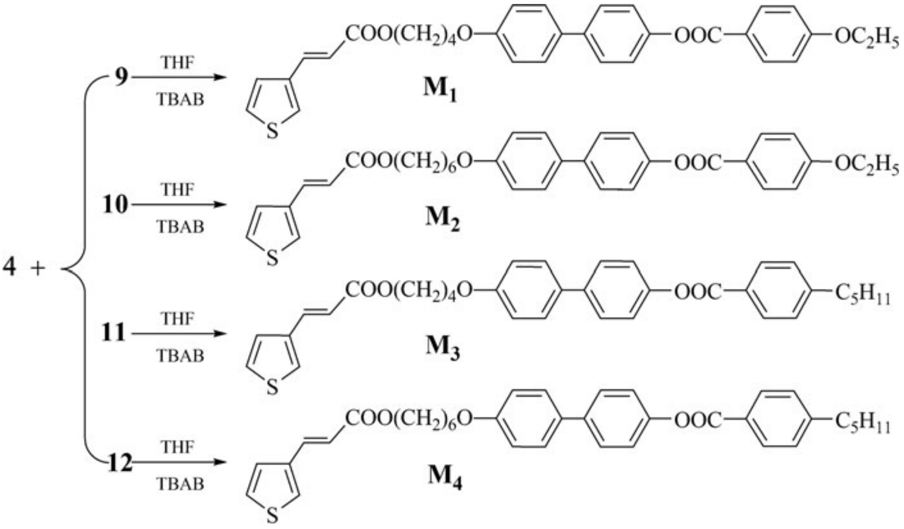
IR (KBr, cm^{-1}): 2926, 2856 (CH_3–, –CH_2–); 1732 (C=O); 1606–1495 (Ar–); 1270 (C–O–C); 516 (Br–). ^{1}H NMR (δ, ppm from TMS in $CDCl_3$): 0.90–0.95 (t, 3H, $-C\underline{H}_3$); 1.32–1.75 [m, 14H, $-CH_2(C\underline{H}_2)_3CH_3$, and $-OCH_2(C\underline{H}_2)_4CH_2Br$]; 2.66–2.73 [t, 2H, $-C\underline{H}_2(CH_2)_3CH_3$]; 3.57–3.61 [t, 2H, $-OCH_2(CH_2)_4C\underline{H}_2Br$]; 4.18–4.23 [t, 2H, $-OC\underline{H}_2(CH_2)_4CH_2Br$]; 6.97–8.17 (m, 12H, Ar$-\underline{H}$).

2.4. *Synthesis of thiophene compounds*

The synthetic route of $\mathbf{M_1}$–$\mathbf{M_4}$ is shown in Scheme 2. These thiophene compounds were prepared using the same method. As an example, the experimental details of $\mathbf{M_1}$ are described as follows.

2.4.1. *(E)-4-(4-(3-(Thiophen-3-yl)acryloyloxy)butoxy)biphenyl-4′-ethoxybenzoate (M_1)*

Compounds **4** (1.92 g, 0.01 mol), **9** (4.68 g, 0.01 mol), and tetrabutyl ammonium bromide (0.2 g) were dissolved in 80 mL of tetrahydrofuran (THF). The mixture was reacted for 48 h at 60°C. After the evaporation of solvent under reduced pressure, the residue was poured into cold water, and the precipitate was filtered. The crude product was recrystallized from acetone and purified by silica gel column chromatography (acetone/hexane = 1/1). Yield: 45%. mp: 121°C.



Scheme 2. Synthetic route of thiophene compounds M_1—M_4.

IR (KBr, cm^{-1}): 2952, 2854 (CH_3–, –CH_2–); 1728, 1715 (C=O); 1633 (C=C); 1605–1497 (thiophene and aromatic ring); 1257 (C–O–C); 1168 (C=S). ^{1}H NMR (δ, ppm from TMS in $CDCl_3$): 1.46–1.50 (t, 3H, $-C\underline{H}_3$); 1.89–1.97 [m, 4H, $-CH_2(C\underline{H}_2)_2CH_2-$]; 4.08–4.10 (t, 2H, $-COOC\underline{H}_2-$); 4.12–4.17 (m, 2H, $-OC\underline{H}_2CH_3$); 4.29–4.32 [t, 2H, $-CH_2(CH_2)_2C\underline{H}_2O-$]; 6.24–6.29 (d, 1H, $-CH{=}C\underline{H}COO-$); 7.65–7.70 (d, 1H, $-C\underline{H}{=}CHCOO-$); 6.97–7.01 (d, 4H, Ar-H); 7.23–7.27 (d, 2H, Ar-H); 7.28–7.49 (m, 3H, thiophene-H); 7.50–7.60 (d, 4H, Ar-H); 8.16–8.20 (d, 2H, Ar-H).

2.4.2. *(E)-4-(6-(3-(Thiophen-3-yl)acryloyloxy)hexyloxy)biphenyl-4′-ethoxybenzoate (M_2)*

Yield: 46%. mp: 94°C. IR (KBr, cm^{-1}): 2974, 2856 (CH_3–, –CH_2–); 1728, 1710 (C=O); 1635 (C=C); 1604–1495 (thiophene and aromatic ring); 1258 (C–O–C); 1169 (C=S). ^{1}H NMR (δ, ppm from TMS in $CDCl_3$): 1.46–1.51 (t, 3H, $-C\underline{H}_3$); 1.54–1.59 [m, 8H, $-CH_2(C\underline{H}_2)_4CH_2-$]; 4.01–4.06 (t, 2H, $-COOC\underline{H}_2-$); 4.13–4.18 (m, 2H, $-OC\underline{H}_2CH_3$); 4.22–4.27 [t, 2H, $-CH_2(CH_2)_4C\underline{H}_2O-$]; 6.26–6.32 (d, 1H, $-CH{=}C\underline{H}COO-$); 7.67–7.71 (d, 1H, $-C\underline{H}{=}CHCOO-$); 6.98–7.01 (d, 4H, Ar-H); 7.23–7.27 (d, 2H, Ar-H); 7.28–7.48 (m, 3H, thiophene-H); 7.50–7.61 (d, 4H, Ar-H); 8.17–8.19 (d, 2H, Ar-H).

2.4.3. *(E)-4-(4-(3-(Thiophen-3-yl)acryloyloxy)butoxy)biphenyl-4′-pentylbenzoate (M_3)*

Yield: 44%. mp: 123°C. IR (KBr, cm^{-1}): 2952, 2855 (CH_3–, –CH_2–); 1727, 1708 (C=O); 1631 (C=C); 1606–1497 (thiophene and aromatic ring); 1282 (C–O–C); 1168 (C=S). ^{1}H NMR (δ, ppm from TMS in $CDCl_3$): 0.90–0.94 (t, 3H, $-C\underline{H}_3$); 1.33–1.71 [m, 6H, $-CH_2(C\underline{H}_2)_3CH_3$]; 1.91–1.99 [m, 4H, $-CH_2(C\underline{H}_2)_2CH_2-$]; 2.69–2.74 [t, 2H, $-C\underline{H}_2(CH_2)_3CH_3$]; 4.06–4.11 (t, 2H, $-COOC\underline{H}_2-$); 4.27–4.33 [t, 2H, $-CH_2(CH_2)_2C\underline{H}_2O-$]; 6.24–6.29 (d, 1H, $-CH{=}C\underline{H}COO-$); 7.65–7.71 (d, 1H, $-C\underline{H}{=}CHCOO-$); 6.96–7.01 (d, 2H, Ar-H); 7.24–7.28 (d, 2H, Ar-H); 7.29–7.50 (m, 3H, thiophene-H); 7.31–7.36 (d, 2H, Ar-H); 7.51–7.61 (d, 4H, Ar-H); 8.12–8.16 (d, 2H, Ar-H).

2.4.4. *(E)-4-(6-(3-(Thiophen-3-yl)acryloyloxy)hexyloxy)biphenyl-4′-pentylbenzoate (M_4)*

Yield: 47%. mp: 93°C. IR (KBr, cm^{-1}): 2925, 2855 (CH_3–, –CH_2–); 1734, 1703 (C=O); 1635 (C=C); 1608–1499 (thiophene and aromatic ring); 1283 (C–O–C); 1178

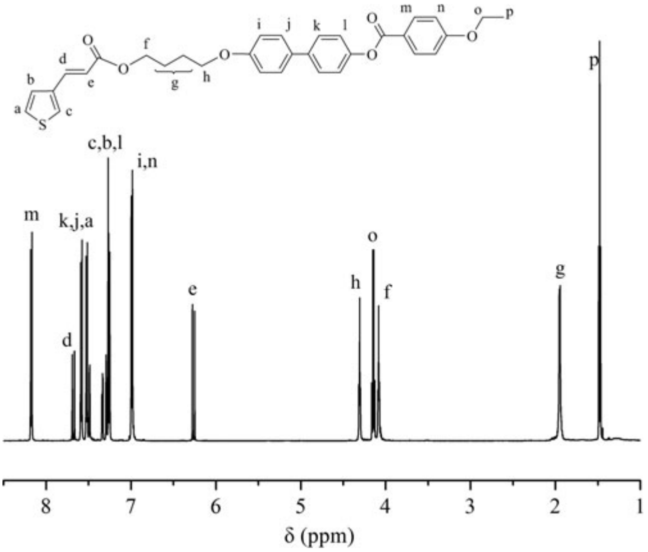


Figure 1. ^{1}H NMR spectrum of $\mathbf{M_1}$.

(C=S). ^{1}H NMR (δ, ppm from TMS in $CDCl_3$): 0.90–0.95 (t, 3H, $-C\underline{H}_3$); 1.33–1.38 [m, 4H, $-CH_2CH_2(C\underline{H}_2)_2CH_3$]; 1.55–1.59 [m, 4H, $-CH_2CH_2(C\underline{H}_2)_2CH_2CH_2-$]; 1.64–1.71 [m, 2H, $-CH_2C\underline{H}_2(CH_2)_2CH_3$]; 1.73–1.89 [m, 4H, $-CH_2C\underline{H}_2(CH_2)_2C\underline{H}_2CH_2-$]; 2.68–2.74 [t, 2H, $-C\underline{H}_2(CH_2)_3CH_3$]; 4.01–4.05 (t, 2H, $-COOC\underline{H}_2-$); 4.20–4.26 [t, 2H, $-CH_2(CH_2)_4C\underline{H}_2O-$]; 6.25–6.31 (d, 1H, $-CH=C\underline{H}COO-$); 7.65–7.71 (d, 1H, $-C\underline{H}=CHCOO-$); 6.96–7.01 (d, 2H, Ar-H); 7.22–7.28 (d, 2H, Ar-H); 7.29–7.51 (m, 3H, thiophene-H); 7.32–7.37 (d, 2H, Ar-H); 7.52–7.62 (d, 4H, Ar-H); 8.12–8.16 (d, 2H, Ar-H).

3. Results and discussion

3.1. *Synthesis and characterization*

As shown in Scheme 2, the target thiophene compounds containing different long spacer were successfully synthesized by the mucleophilic substitution reaction of potassium (*E*)-3-(3-thiophenyl)acrylate and the compounds **9**, **10**, **11**, and **12**, respectively, in THF at 60°C. All the intermediates and final products were thoroughly purified and characterized by FTIR and ^{1}H NMR, and the satisfactory analysis data corresponding to their expected molecular structures were obtained. A typical example of the ^{1}H NMR spectra of $\mathbf{M_1}$ is shown in Fig. 1. The aromatic and thiophene H resonance peaks appeared in the low magnetic region ($\delta = 8.2-7.0$), substituted acrylate-based 3-thiophenyl olefinic H resonance peaks also in low magnetic region ($\delta = 7.7-6.2$), whereas the aliphatic H resonance peaks in the high magnetic region ($\delta = 2.0-1.5$) except the peaks of the near-neighboring aliphatic H to the $-O-$ or $-COO-$ shifted to the middle region (4.3–4.0).

3.2. *DSC analysis*

The thermal behavior of the thiophene compounds $\mathbf{M_1}-\mathbf{M_4}$ was investigated with DSC at a heating and cooling rate of 10°C min^{-1} under nitrogen atmosphere. The DSC data, obtained on second heating and cooling scans, are summarized in Table 1. Representative DSC thermographs of $\mathbf{M_1}$ are presented in Fig. 2.

Table 1. The phase transition temperatures and mesophase of thiophene compounds.

	Mesophase, phase transition temperature (°C), and enthalpy changes (J·g^{-1})	
Thiophene compounds	Heating cycle	Cooling cycle
M_1	Cr120.5 (59.8) N171.2 (0.8)I	I167.8 (0.7) N80.5 (50.0)Cr
M_2	Cr94.2 (34.9) N176.2 (0.6)I	I173.4 (0.7) N71.7 (32.2)Cr
M_3	Cr127.3 (78.5) N134.2 (0.3)I	I132.7 (0.6) N78.7 (47.8)Cr
M_4	Cr96.3 (51.4) N136.1 (0.8)I	I133.2 (0.5) N69.5 (29.7)Cr

Note: Cr = crystal; N = nematic phase; I = isotropic.

According to DSC curves on heating cycle, $\mathbf{M_1}$−$\mathbf{M_4}$ showed two endothermal peaks, indicating a melting transition at low temperature and a nematic to isotropic phase transition at high temperature. On cooling cycle, two exothermal peaks occurred and these represented an isotropic to nematic phase transition and a crystallization transition. As seen in Table 1, the molecular structure of $\mathbf{M_1}$−$\mathbf{M_4}$ had an obvious influence on their phase transition temperatures. For $\mathbf{M_1}$ and $\mathbf{M_2}$, because of the same terminal groups and mesogenic core, the flexible spacer length affected the melting temperature (T_m) and the isotropic temperature (T_i). When the methylene number between thiophene unit and mesogenic core increased from 4 to 6, T_m decreased from 120.5°C for $\mathbf{M_1}$ to 94.2°C for $\mathbf{M_2}$**;** however, the corresponding T_i tended to increase from 171.2°C for $\mathbf{M_1}$ to 176.2°C for $\mathbf{M_2}$, so the mesophase temperature range widened from 50.7°C for $\mathbf{M_1}$ to 82.0°C for $\mathbf{M_2}$. Similar results could also be seen for $\mathbf{M_3}$ and $\mathbf{M_4}$.

3.3. *TGA analysis*

The thermal stability of $\mathbf{M_1}$−$\mathbf{M_4}$ was investigated with TGA at a heating rate of 20°C min^{-1} under nitrogen atmosphere. Their TGA curves are shown in Fig. 3. The corresponding thermal decomposition data are listed in Table 2. Temperatures at which 5% weight loss (T_d) of $\mathbf{M_1}$−$\mathbf{M_4}$ occurred were above 365°C, indicating that four thiophene compounds had high thermal stability because the existence of a biphenyl segment and thiophene unit may cause intermolecular π–π interaction. In addition, T_d decreased with increasing the methylene number between thiophene unit and mesogenic core.

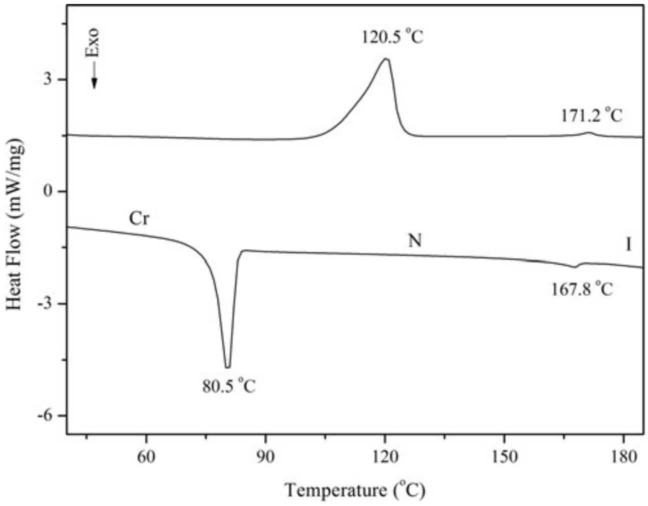


Figure 2. DSC curves of $\mathbf{M_1}$.

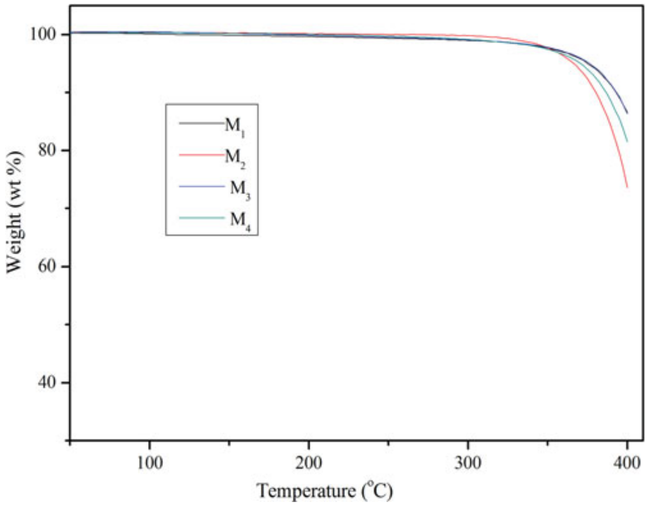


Figure 3. TGA curves of **M1—M4**.

3.4. *POM analysis*

In general, LC compounds containing achiral unit show either nematic phase or smectic phase; this mainly depends on relative strength of molecular transverse attractive force and terminal attractive force. If the molecular transverse attractive force is predominant, only smectic phase can be seen. Conversely, these LC materials show nematic phase. However, when the strength of these two kinds of force is about equal, both smectic and nematic phase appear. Under POM observation, $\mathbf{M_1}$—$\mathbf{M_4}$ showed typical nematic texture on heating and cooling cycles. As an example, the mesomorphism and texture of $\mathbf{M_1}$ were observed and recorded in detail as follows. When $\mathbf{M_1}$ was heated to 119.3°C, the sample started to melt and mesomorphism appeared; heating continued, the thread-like texture of nematic phase was observed, and the texture disappeared at 176.5°C. On cooling the samples from the isotropic melt, the droplet texture appeared at 175.2°C, cooling continued, the droplet texture grew up gradually and transformed to schlieren texture, and crystallized at 88.6°C. The optical texture of **M1** is shown in Figs. 4(a and b).

3.5. *UV/Vis analysis*

Figure 5 shows the UV/Vis absorption spectra of $CHCl_3$ solutions of the selected compounds $\mathbf{M_1}$–$\mathbf{M_4}$. All these compounds exhibited an intense broad absorption band peaking within 230–340 nm. Owing to the same conjugated core of thiophene and phenyl rings, four compounds $\mathbf{M_1}$–$\mathbf{M_4}$ had the similar absorption bands, and the absorption spectra were nearly identical in shape, which are attributed to the π–$\pi*$ bands.

3.6. *Fluorescence analysis*

Four thiophene derivatives had good fluorescence optical properties. Figure 6 shows representative 2D fluorescence topographical maps of $\mathbf{M_1}$ and $\mathbf{M_3}$ in $CHCl_3$ solution at a concentration of 15 mg mL^{-1} and a scan voltage of 700 V. Due to the same conjugated core, the corresponding 2D fluorescence topographical maps were nearly identical in shape. As seen in Fig. 6, $\mathbf{M_1}$ exhibited a maximum excitation wavelength at 366 nm and emission wavelength at

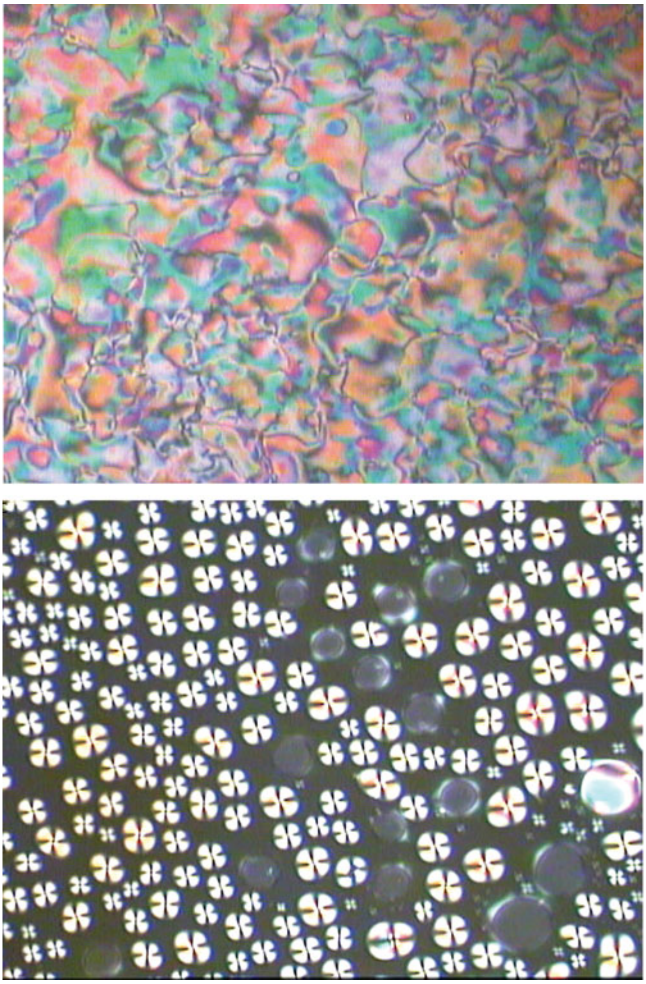


Figure 4. Optical textures of **M$_1$** (200×) (a) nematic threaded texture at 126°C; (b) nematic droplet texture at 174°C.

426 nm. However, **M$_3$** exhibited a maximum excitation wavelength at 367 nm and emission wavelength at 436 nm. This indicated that the terminal groups also had effects on photoluminescent properties. Since the electron donating effect of pentyl group was stronger than that of ethoxy group, fluorescence strength and photoluminescence quantum yields of **M$_3$** were greater than that of **M$_1$**.

Table 2. TGA data of thiophene compounds.

Sample	T_d[a] (°C)	Weight loss (%) 350°C	Weight loss (%) 400°C
M$_1$	375	2.3	13.4
M$_2$	366	2.3	26.4
M$_3$	376	2.2	13.7
M$_4$	371	2.5	18.5

Note: [a]Temperature at which 5% weight loss occurred.

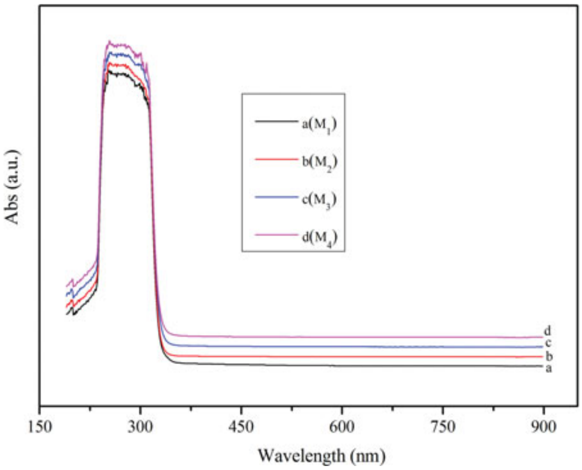
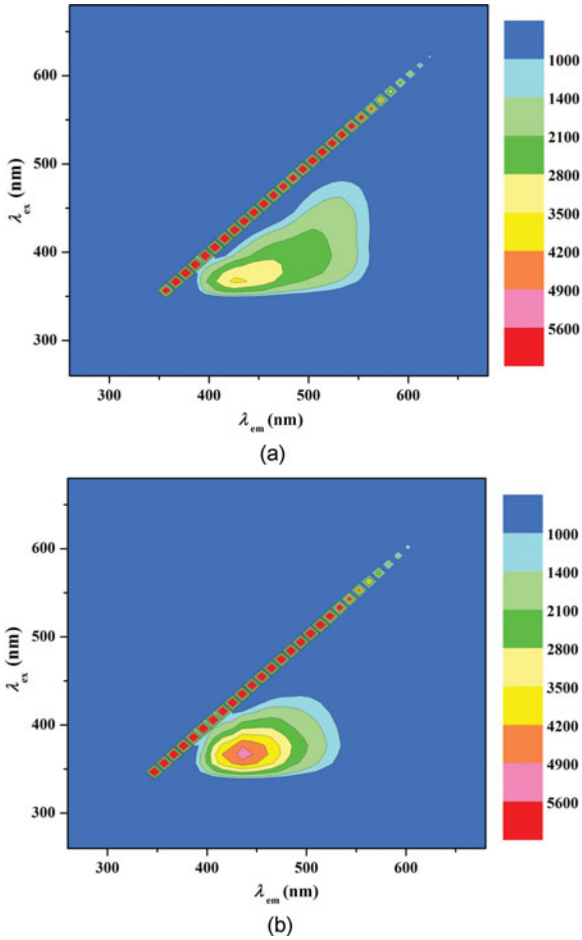


Figure 5. UV/Vis absorption spectra of **M_1**—**M_4** in $CHCl_{3.}$



(a)

(b)

Figure 6. 2D-fluorescence topographical map of $CHCl_3$ solution: (a) **M_1**, (b) **M_3**.

4. Conclusions

In this work, four new mesogenic thiophene derivatives were designed, synthesized, and characterized. They all showed thermotropic nematic phase with high thermal stability. With increasing the flexible spacer length, the corresponding T_m decreased, while T_i increased, and the mesophase range widened. In $CHCl_3$ solution, four thiophene compounds had the similar broad absorption bands within 230–340 nm, and the absorption spectra were nearly identical in shape. Moreover, they all had good fluorescence properties, and showed a maximum fluorescent emission wavelength at 426–439 nm. The fluorescence strength and photoluminescence quantum yields of thiophene compounds (**M_3** and **M_4**) with terminal pentyl groups were greater than that of thiophene compounds (**M_1** and **M_2**) with terminal ethoxy groups.

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