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Insights into the reaction of *trans*-diarylethenes with thionyl chloride: a practical synthesis of chlorobenzo[*b*]thiophenes

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ABSTRACT

The reactivity of a variety of *trans*-1,2-diarylethenes with thionyl chloride has been investigated. All the substrates could readily afford 3-chlorobenzo[*b*]thiophenes in moderate yields and a pair of *threo*- and *erythro*-1,2-dichloro-1,2-diarylethanes as the minor products under mild condition. The diastereoisomers of 1,2-dichloro-1,2-diarylethanes with a methoxy group on the benzene ring were found for the first time to be also converted into cholobenzo[*b*]thiophenes under treatment of thionyl chloride. The chemical transformations have been mechanistically rationalized and successfully applied to a one-pot synthesis of novel fluorescent liquid crystalline compounds containing benzo[*b*]thiophene and 1,3,4-oxadiazole units. Their spectroscopic and mesogenic behaviours are also described.

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1. Introduction

Benzo[*b*]thiophene and its related derivatives have been extensively documented as bioactive substances[1] as well as optoelectronic materials.[2] To date, much work has been done to develop new and convenient synthetic approaches to benzo[*b*]thiophenes.[3,4] These approaches may be categorized into two major types according to the source of sulfur: one is from organic sulfur source; the other is from inorganic sulfur source. As for the former, many kinds of sulfur-containing precursors, such as *ortho* sulfur-containing arylalkynes[5] and styrene,[4b,6] 2-mercaptobenzaldehydes,[7] 2-methylsulfanyl benzamides,[8] polarized ketene dithioacetals,[9] methylthiobenzene,[10] and thio-ketones[11] have been used for syntheses of various benzo[*b*]thiophenes. Although most of the methods are quite efficient, they usually suffer from certain drawbacks: (1) most of the reaction precursors are not commercially available, and should be prepared via multi-step procedures using unpleasant organic sulfur-containing reagents; (2) these synthetic methods often use expensive transition metal-catalysts, and the reactions should be carried out under rigid conditions, such as anhydrous and free of oxygen. In contrast, examples of syntheses of benzo[*b*]thiophenes using inorganic sulfur sources are relatively limited in literature. Inorganic sulfur sources include elemental sulfur,[7b,12] thionyl chloride,[13] sulfur dichloride[14] and sodium sulfide.[15] The common merits of these methods include that the reaction precursors are readily available, and most of the synthetic routes are very short, practical and free of expensive transition metal-catalyst.

Thionyl chloride, as one of the inorganic sulfur precursors, was first used to prepare 3-chlorobenzo[*b*]thiophenes by Krubsack,[13] and the procedure was subsequently investigated by several other research groups. The reported substrates are limited to cinnamic acid,[16] phenylpropanoic acid,[13,17] phenyl propynoic,[18,19] and *trans*-*p*-nitrostilbene as the only example of 1,2-diarylethenes.[17b] This methodology has not been properly investigated in detail, and its application in synthesis of functional organic compounds is very scarce.[20] To develop convenient one-pot routes to prepare novel fluorescent liquid crystalline compounds containing benzo[*b*]thiophene and 1,3,4-oxadiazole moieties, we re-investigated the reaction of *trans*-diarylethenes with thionyl chloride and gained some interesting insights into the relevant chemistry. Herein, we wish to report the results from such investigation.

2. Results and discussion

Our initial efforts focused on the synthesis of 3-chloro-2-(4-methoxy)phenyl-6-methoxybenzo[*b*]thiophene **2a** by the reaction of readily available (*E*)-1,2-bis(4′-methoxyphenyl)ethene **1a** with thionyl chloride (Scheme 1). The first attempt was carried out by treatment of (*E*)-1,2-bis(4′-methoxyphenyl)ethene **1a** (4.2 mmol) with excess of thionyl chloride without catalyst at room temperature. We were pleased to observe that the reaction occurred smoothly to yield the desired product **2a** in 42% yield after 24 h.

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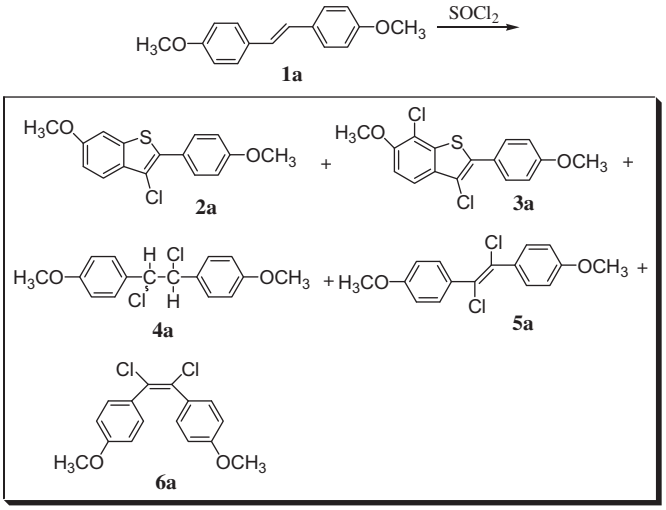
Interestingly, a pair of diastereoisomers of 1,2-dichloro-1,2-bis(4-methoxyphenyl)ethane **4a** (the *erythro*- and *threo*-isomers with the ratio of 4:1) and a pair of *E*/*Z* isomers of 1,2-dichloro-1,2-bis(4-methoxyphenyl)ethenes (**5a** and **6a**) were separated as side products in 23% and 4% yield, respectively. Elongation of reaction time to 48 h led to slight increase of the yields of **2a**, **4a** and **6a** with the ratio of *erythro*-**4a** and *threo*-**4a** changed from 4:1 into 2:1 (Table 1, entry2). When the reaction was carried out at reflux, the reaction time could be shortened to 4 h, furnishing products **2a**, **4a** (with a ratio of 2:1 for *erythro*-**4a** and *threo*-**4a**), **5a** and **6a** 37%, 11%, 3%, and 12% yields, respectively (Table 1, entry3). However, when the reaction time was prolonged to 24 h, both **2a** and **4a** disappeared completely, and a new product dichlorobenzo[*b*]thiophene **3a** was obtained in 41% yield, accompanied by compounds **5a** and **6a** in 4% and 12% yields, respectively (Table 1, entry 4). The structure of **3a** was unambiguously determined by single crystal X-ray analysis[21] as shown in Fig. 1. In order to elucidate the relationship between **2a** and **3a**, a solution of isolated **2a** in thionyl chloride was refluxed for 24 h, giving **3a** in 84% yield. This result indicated that monochlorobenzo[*b*]thiophene **2a** could be chlorinated by thionyl chloride to transform into dichlorobenzo[*b*]thiophene **3a** in good yield.



Scheme 1. Reaction of **1a** with thionyl chloride.

Table 1
Reaction of the **1a** with thionyl chloride

Entry	Temp	Time (h)	**2a** (%)	**3a** (%)	**4a** (%)[b] (ratio)[c]	**5a**	**6a**
1	rt	24	42	0	23 (4:1)	Trace	4
2	rt	48	43	0	27 (2:1)	Trace	6
3	Reflux[a]	4	37	0	11 (2:1)	3	12
4	Reflux[a]	24	0	41	0 (/)	4	10

[a] The temperature of the oil bath is 90–95 °C.
[b] Isolated yields.
[c] Calculated by ^{1}H NMR spectroscopy of the crude products.

On the basis of the above results, a probable pathway leading to products **2a**–**6a** from **1a** is outlined in Scheme 2. The initial step of the reaction is an electrophilic addition of thionyl chloride across the double bond of **1a** to form sulfinyl chloride **i**. Intermediate **i** undergoes a thermolysis process to form the isomers **4a** (Path A), and competitively **i** undertakes a typical Pummerer reaction with thionyl chloride to form intermediate **ii** (Path B).[22] The sulfenyl chloride **ii** subsequently undergoes a concerted elimination–cyclization process, namely, loss of hydrogen chloride from the benzylic carbon and the sulfur simultaneously, to form intermediate **iii**

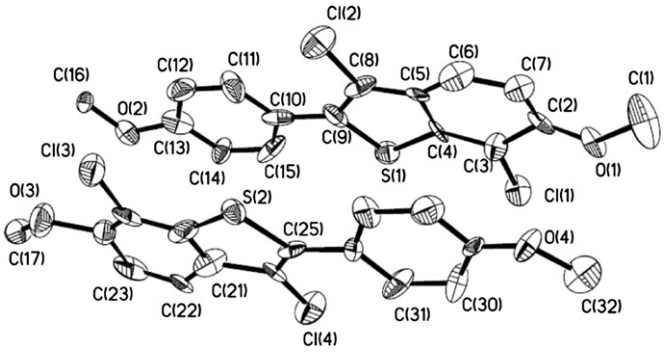


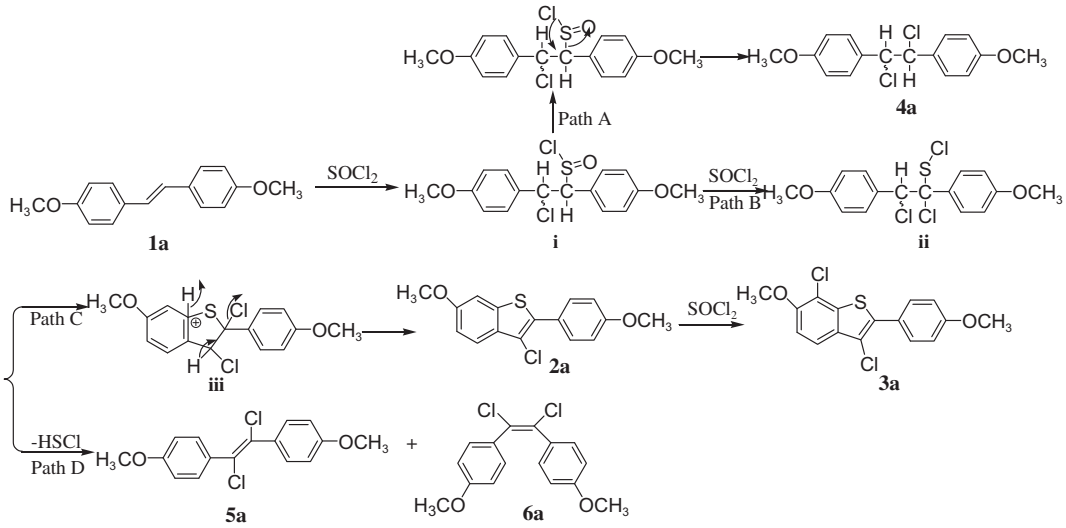
Fig. 1. The crystal structure of **3a**.

(Path C), which further expels another molecule of hydrogen chloride by a 1,4-elimination process to give rise to monochlorobenzo[*b*]thiophene **2a**. As observed in this work, compound **2a** can be chlorinated by thionyl chloride at the C7 position to furnish the dichlorobenzo[*b*]thiophene **3a**. In addition, the intermediate **ii** could be converted into the isomeric (*E*)- and (*Z*)-1,2-dichloro-1,2-bis(4-methoxyphenyl) ethene (**5a** and **6a**) by elimination of one molecule of HSCl (Path D), which decomposes into hydrogen chloride and sulfur, as evidenced by the observation of elemental sulfur in the reaction.

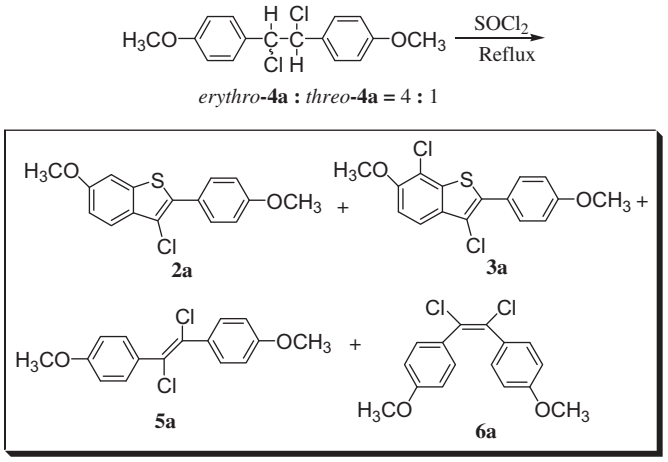
It's worthy to note that thionyl chloride could be used as a chlorinating agent to transform *trans*-1,2-di(4-methoxyphenyl) ethene **1a** into 1,2-dichloro-1,2-di(4-methoxyphenyl)ethane **4a** in moderate yields at room temperature or reflux (Table 1, entries 1–3). However, **4a** disappeared upon refluxing for prolonged time (Table 1, entry 4). In order to better understand the reaction pathway, a solution of isolated **4a** in thionyl chloride was refluxed and monitored by TLC. The results were shown in Scheme 3 and Table 2. When the reaction mixture was refluxed for 4 h, products **2a**, **5a** and **6a** were afforded in 12%, 6%, and 15% yield, respectively. When refluxed for 24 h, dichlorobenzo[*b*]thiophene **3a** emerged and was obtained in 15% yield, as well as compounds **2a** (10%), **5a** (8%) and **6a** (48%). Further elongation of the reaction time to 40 h, resulted in the disappearance of **4a** and **2a**, and afforded products **3a**, **5a** and **6a** in 21%, 18% and 61% yields, respectively. It's found that the reactions of **1a** and **4a** with thionyl chloride afforded the same products, but with different ratios.

According to the results, a possible pathway for the reaction of **4a** with thionyl chloride is shown in Scheme 4. Initially, compound **4a** undergoes a C-sulfinylation reaction[23] to give the sulfinyl chloride **iv**, which is subsequently converted to sulfenyl chloride **ii** by a Pummerer-like reaction. Products **2a**, **5a** and **6a** are formed from **ii** by a process depicted in Scheme 3. The ratio of **2a**, **5a** and **6a** from **4a** is different from that from **1a**. This difference may be ascribed to the different ratios of isomeric intermediate **ii**, although an exact reason is not clear at present.

Under the optimized conditions, a series of *trans*-1,2-diarylethenes **1b**–**e** were examined to explore the scope of the cyclization reaction (Scheme 5). The results were summarized in Table 3. Substrates **1b** and **1c** with an electron-donating methoxy group readily afforded the corresponding monochlorobenzo[*b*]thiophenes (**2b**,**c**) and isomers of 1,2-diaryl-1,2-dichloroethanes (**4b**,**c**) in moderate yields after refluxed in thionyl chloride for 3–6 h (Table 3, entries 1, 5 and 6). When the reaction was refluxed for 48 h (Table 3, entries 4 and 8), both the monochlorobenzo[*b*]thiophenes (**2b**,**c**) and the 1,2-diaryl-1,2-dichloroethanes (**4b**,**c**) were transformed into the corresponding dichlorobenzo[*b*]thiophenes (**3b**,**c**). For the substrate **1d**, no benzo[*b*]thiophene derivatives were detected upon refluxing for 24 h, with only a minor of 1,2-dichloro-1,2-diphenylethanes **4d** isolated. With addition of a catalytic amount of pyridine, however, the reaction of **1d** could



Scheme 2. Probable pathway for the reaction of **1a** with thionyl chloride.



Scheme 3. Reaction of **4a** with thionyl chloride.

Table 2
Reaction of the **4a** with thionyl chloride[a]

Entry	Time (h)	**2a** ([b]/%)	**3a** ([b]/%)	**5a** ([b]/%)	**6a** ([b]/%)
1	4	12	0	6	15
2	24	10	15	8	48
3	40	0	21	18	61

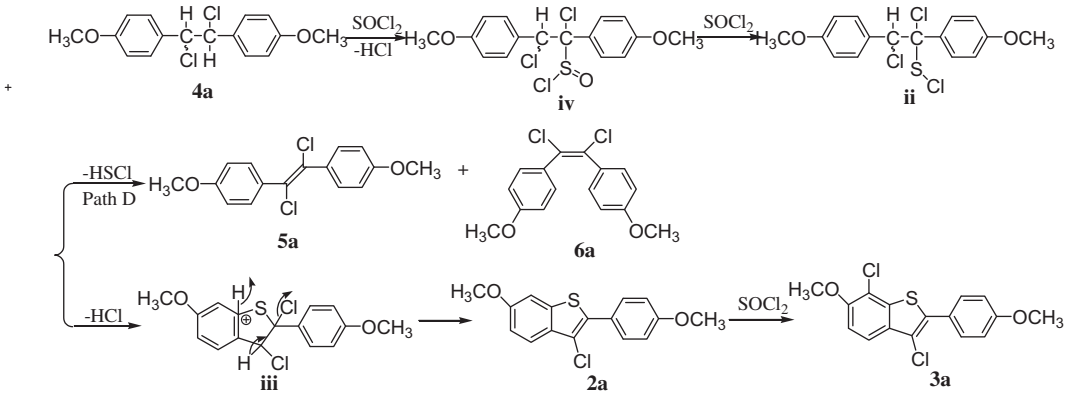
[a] The *erythro*/*threo* ratio is 4:1.
[b] Yields determined by ^{1}H NMR.

afford 3-chloro-2-phenylbenzo[*b*]thiophene **2d** and 1,2-diaryl-1,2-dichloroethanes **4d** in 42% and 12% yields, respectively. Further elongation of the reaction time to 48 h resulted in no apparent change in the yields of **2d** and **4d**, and no formation of diclorobenzo [*b*]thiophene **3d**. This result implicated that compounds **2d** and **4d** could not be further transformed into **3d** as observed in the cases of **1a**–**c**. To confirm this speculation, the isolated **2d** and **4d** were treated with refluxing thionyl chloride for 24 h, respectively, and no reactions happened as expected. As for the substrate **1e** bearing an ester group, similar results were observed to those of **1d**. (Table 3, entries 12–14).

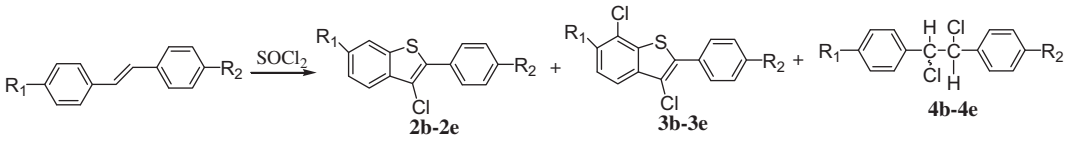
On the basis on the established methodology for construction of benzo[*b*]thiophenes, we then turn our attention to develop benzo [*b*]-thiophene based optoelectronic materials. A series of novel light-emitting liquid crystal compounds **9a**,**b** and **10a**,**10b** containing benzo[*b*]thiophene and 1,3,4-oxadiazole units have been synthesized by a simple and efficient one-pot procedure as shown in Scheme 6. Thionyl chloride plays a critical role in construction of both benzo[*b*]thiophene and 1,3,4-oxadiazole units. 1,3,4-Oxadiazole unit was selected as a mesogenic core, for this structural moiety has become an important synthon in design and synthesis of various liquid crystals with interesting properties,[24] and the 1,3,4-oxadiazole derivatives have also enjoyed widespread use as electron-transporting materials and emitting layers in electroluminescent diodes due to their electron-deficiency, high photoluminescence quantum yield and good thermal and chemical stability.[25] The combination of the unique feature of self-assembly and intrinsic light emitting capabilities may find potential application in the field of emissive LC displays and anisotropic OLEDs.

The liquid crystal properties of compounds **9a**,**b** and **10a**,**b** were investigated by means of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The mesophases are identified according to the classification system reported by Dierking.[26] All the DSC thermograms show clear-cut peaks both in the heating and cooling runs, which are well consistent with the respective observations of textures under the polarizing optical microscopy. The phase transitions and associated enthalpies of these products are summarized in Table 4, and the selected POM images are shown in Fig. 2. All compounds display thermotropic liquid crystalline properties with different mesophases, which are determined by the terminal and lateral groups. Compounds **9a** and **10a** exhibit smectic A phase with wide temperature range due to the terminal cyano group, while **9b** and **10b** with an end methoxy group tend to display nematic phase with relatively narrow temperature range. Compared to **9a** and **10a**, the corresponding analogues **9b** and **10b** facilitate to produce nematic phase with suppression of the smectic A phase due to the lateral chlorine, which may broaden the core of the mesogen, and the mesophases can show a decrease in range or even disappear.[27]

The UV–vis absorption and photoluminescence properties for **9a**,**b** in CH_2Cl_2 were investigated as shown in Fig. 3. Both **9a** and **9b** exhibit an intense absorption band peaking at 352 and 346 nm with high molar absorptivity (1.88×10^4 L mol^{-1} cm^{-1} for **9a** and 2.05×10^4 L mol^{-1} cm^{-1} for **9b**), respectively, and display an intense emission with moderate photoluminescence quantum yields (16% for **9a** and 46% for **9b**). The Stokes shifts for **9a** and **9b** are 3382 and



Scheme 4. Probable pathway for the reaction of **4a** with thionyl chloride.



1b-**4b**: $R_1 = CH_3O$, $R_2 = H$; **1c**, **2c**, **4c**: $R_1 = CH_3O$, $R_2 = CO_2CH_3$; **1d**,**2d**, **4d**: $R_1 = R_2 = H$; **1e**, **2e**, **4e**: $R_1 = H$, $R_2 = CO_2CH_3$.

Scheme 5. Reaction of **1b**–**e** with thionyl chloride.

Table 3
Reaction of **1b**–**e** with thionyl chloride

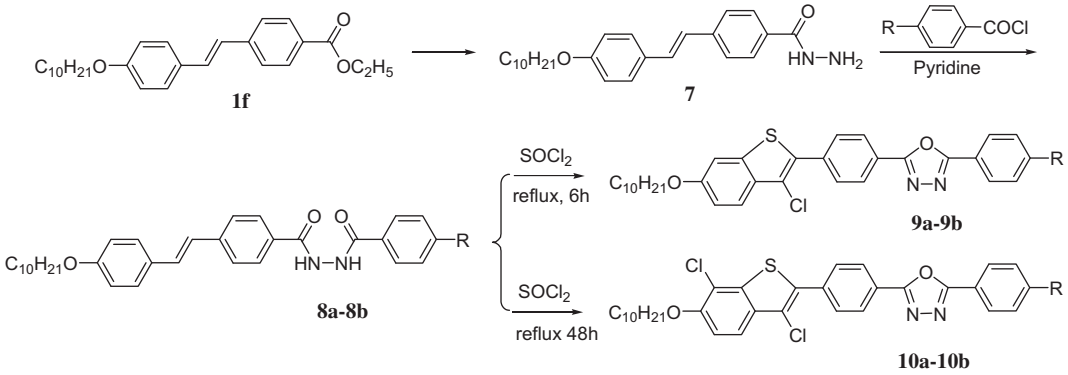
Entry	Substrate	Time (h) [a]	**2** (%)[b]	**3** (%)[b]	**4** (%) [b] (ratio)[c]
1	**1b**	4	45	0	4 (1.6:1)
2	**1b**	8	38	5	21 (1.6:1)
3	**1b**	24	25	15	0 (/)
4	**1b**	48	0	48	0 (/)
5	**1c**	3	26	0	Trace (/)
6	**1c**	6	42	0	0 (/)
7	**1c**	24	26	28	0 (/)
8	**1c**	48	0	45	0 (/)
9	**1d**	24	0	0	7 (4.8:1)
10[d]	**1d**	24	42	0	12 (2.4:1)
11[d]	**1d**	48	44	0	12 (1.8:1)
12	**1e**	24	0	0	Trace (/)
13[d]	**1e**	24	15	0	6 (1.7:1)
14[d]	**1e**	48	18	0	9 (1.5:1)

[a] The temperature of the oil bath is 90–95 °C.
[b] Isolated yields.
[c] The *erythro*-**4**/*threo*-**4** ratio was determined by ^{1}H NMR of the crude products.
[d] With 0.1 equiv of pyridine.

2603 cm^{-1}, respectively, which are comparable to those of the reported 1,3,4-oxadiazole derivatives.[28] Compared to **9b**, compound **9a** showed a larger red shift of absorption and a longer photoluminescent emission wavelength due to the elongated conjugation length of the cyano group in conjunction with the mesogenic core. According to the emission energy and quantum yields, the photoluminescence of the mesogens **9a**,**b** may be attributed to spin-allowed π–π* fluorescence.

3. Conclusions

The reactions between *trans*-1,2-diaylethenes and thionyl chloride have been systematically investigated, and new insights have been made. The main results are summarized as following: (1) the reactivity is affected greatly by the electronic nature of the substituents on the phenyl rings, the substrates bearing a methoxy group can react readily with thionyl chloride to provide monochlorobenzo[*b*]thiophenes, which may be further chlorinated by thionyl chloride to afford the dichlorobenzo[*b*]thiophenes. While



Scheme 6. One-pot preparation of the mesogenic compounds **9a**,**b** and **10a**,**b**.

Table 4
Phase transitions and enthalpies of **9a**,**b** and **10a**,**b**

Compds	Phase transitions[a] T[°C](ΔH [kJ mol^{-1}])
9a	Cr_1 121.9 (−15.6) $Cr_2$183.3 (34.1) SmA 242.3 (3.2) Iso
	Iso 240.3 (−3.1) SmA 154.5 (−12.7) Cr_2 128.3 (−5.0) Cr_1
9b	Cr 166.7 (46.3) N 172.0[b] Iso
	Iso 168.7 (−0.6) N 145.8 (−49.8) Cr
10a	Cr 179.5 (49.4) SmA 218.5 (0.9) N 224.1 (0.8) Iso
	Iso 222.4 (−1.0) N 216.8 (−1.1) SmA 138.3 (−51.5) Cr
10b	Cr 170.6[b] Iso
	Iso 160.5[b] N 135[b] Cr

[a] Cr or Cr_n=crystal phases (nth); SmA=smectic A; N=nematic phase; Iso=isotropic.
[b] Optical microscopy data.

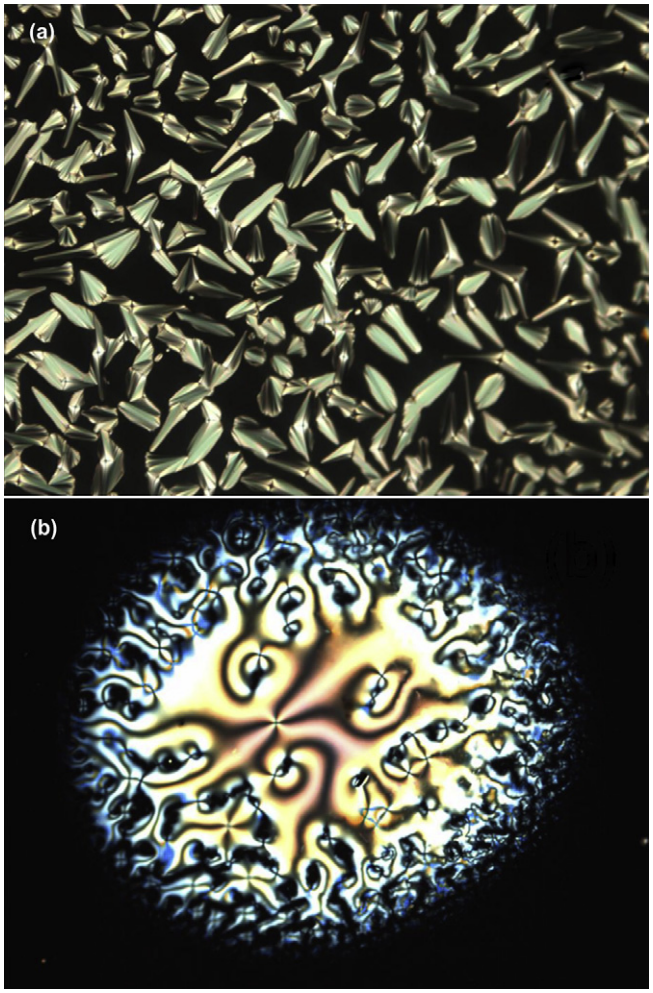


Fig. 2. Optical photomicrographs (200×) in the cooling cycle: (a) the bâtonnets and fan-shaped texture of SmA phase for **9a** at 228 °C; (b) the schilieren texture of N phase for **9b** at 169 °C isotropic.

the reaction between the stilbene derivatives with an electron-withdrawing group must be carried out with addition of catalytic pyridine at reflux temperature, and the corresponding monochlorobenzo[*b*]thiophenes can not been chlorinated with thionyl chloride; (2) for the first time, we found that thionyl chloride can work as a chlorinating reagent to transform 1,2-diarylethene into 1,2-dichloro-1,2-diarylethanes in moderate yields, and the isomeric 1,2-dichloro-1,2-diarylethanes with methoxy group can further react with thionyl chloride to give benzo[*b*]thiophenes; and (3) owing to the accessibility of the precursors and the easy experimental operation, this effective methodology has been applied to synthesize novel fluorescent liquid crystals containing benzo[*b*]thiophene and 1,3,4-oxadiazole units.

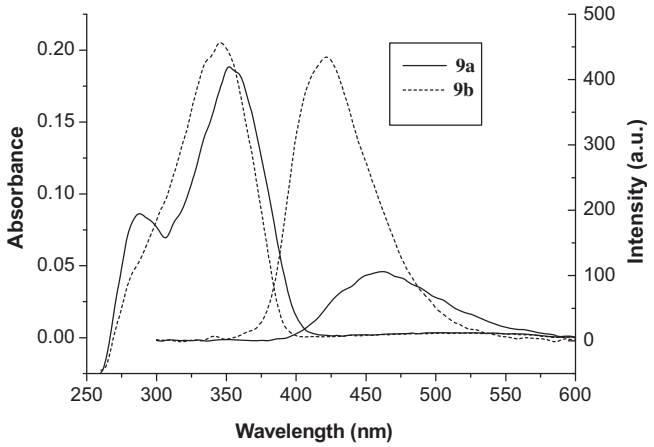


Fig. 3. Normalized UV–vis absorption and emission spectra of **9a** and **9b** in CH_2Cl_2 at 298 K (concentration=1×10^{-5} mol dm^{-3}).

4. Experimental

4.1. General

Melting points were determined with an X-4 digital melting point apparatus with thermometer uncorrected. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AV400 instrument. Elemental analyses were performed on an Elementar Vario EL apparatus. ESI-MS were recorded on a Finnigan LCQ Advantage spectrometer.

The single crystals of **3a** suitable for X-ray diffraction determination were obtained from slowly grown in CH_2Cl_2 at room temperature. Data for single X-ray structure were collected using Rigaku diffractometer with graphite monochromatized Mo Kα X-ray radiation (λ=0.71073) and Saturn CCD area detector. The X-ray crystal structure was solved by direct method and expanded using Fourier syntheses technique. The non-hydrogen atoms were refined using riding model. Structural refinement based on full-matrix least-squares refinement on $|F|^2$ was performed by using Crystal Structure of SHELXL97 suite program.[29]

The phase transition temperatures and enthalpy changes were measured on a NETZSCH DSC 204 differential scanning calorimeter with a heating rate of 5 °C/min and calibrated with a pure indium sample. The optical textures were observed on an optical polarized microscopy (OLYMPUS BX51) equipped with a heating stage. UV–vis absorption spectra were recorded with a Cary 300 spectrophotometer. Steady-state emission spectra were recorded with an SPEX 1681 Fluorolog-2 series F111AI spectrophotometer. The emission quantum yields were determined using the method of Demas and Crosby with quinine sulfate in degassed 1 N sulfuric acid as a standard reference solution (φ_r=0.546).[30]

Methyl (*E*)-[2-(4-methoxyphenyl)ethenyl]benzoate **1c**, Methyl 4-[(*E*)-2-phenylethenyl]benzoate **1e** and methyl (*E*)-[2-(4-decanoxyphenyl)ethenyl]benzoate **1f** were prepared according to the literature procedure.[31] Other starting materials were commercially available. Thionyl chloride was purified according to the standard method.[32] Dichloromethane used for photophysical studies was washed with concentrated sulfuric acid, 10% sodium hydrogencarbonate and water, dried with calcium chloride, and distilled from calcium hydride. All other solvents were of analytical grade used as received.

All the final products were fully characterized with spectroscopic analyses and combustion elemental analysis. Compound **3a** was further confirmed by single X-ray crystallography. The isomeric ratios of the *threo*- and *erythro*-1,2-dichloro-1,2-diarylethanes **4a**–**e** were identified and determined by ^{1}H NMR spectroscopy

by the chemical shifts of the methane protons, which were earlier used for identification of chlorination products of *trans*-1,2-diarylethenes.[33]

4.2. Typical procedure for the reaction of 1a with thionyl chloride

Compound **1a** (1 g, 4.2 mmol) was added to $SOCl_2$ (15 mL), and the reaction mixture was refluxed under a nitrogen atmosphere for 4 h. Then, the excessive thionyl chloride was removed by vacuum distillation. The crude solid was purified to afford the products **2a** and a mixture of the isomeric *erythro*-**4a** and *threo*-**4a** in sequence by silica gel column chromatography using petroleum ether/dichloromethane (1:1 in volume) as eluent. The isomers of **4a** were further recrystallized from ethanol to afford the pure *erythro*-**4a**. In another run, the products **3a**, **5a** and **6a** were afforded upon refluxing the reaction mixture for 24 h under the same procedure and workup as above.

4.2.1. 3-Chloro-2-(4-methoxy)phenyl-6-methoxybenzo[b]thiophene ***2a***[34]. White solid, yield, 37%. Mp 90–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.67 (m, 3H), 7.26 (d, J=1.5 Hz, 1H), 7.08 (dd, J=8.7, 1.5 Hz, 1H), 7.00 (d, J=8.6 Hz, 2H), 3.90 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.70, 158.15, 137.81, 133.43, 131.96, 130.36, 124.96, 122.79, 115.31, 114.92, 114.12, 104.86, 55.69, 55.38; EI-MS: m/z: 304.0; Anal. Calcd for $C_{16}H_{12}Cl_2O_2S$: C, 63.05; H, 4.30. Found C, 63.35; H 4.36.

4.2.2. 3,7-Dichloro-2-(4-methoxy)phenyl-6-methoxybenzo[b]thiophene ***3a***. White crystals, yield, 41%. Mp 128–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J=8.7 Hz, 2H), 7.68 (d, J=8.7 Hz, 1H), 7.14 (d, J=8.8 Hz, 1H), 7.00 (d, J=8.7 Hz, 2H), 4.00 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.96, 152.93, 137.36, 135.32, 132.74, 130.38, 124.52, 120.84, 115.39, 114.94, 114.20, 111.24, 56.98, 55.38; EI-MS: m/z: 338.0; Anal. Calcd for $C_{16}H_{12}Cl_2OS$: C, 56.65; H 3.57. Found C, 56.51; H 3.59.

4.2.3. erythro-1,2-Dichloro-1,2-bis(4-methoxyphenyl)ethane erythro- ***4a***[35]. Yield, 11%. Mp 192–194 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J=8.5 Hz, 4H), 6.91 (d, J=8.5 Hz, 4H), 5.19 (s, 2H), 3.83 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=159.91, 130.70, 129.27, 113.86, 65.93, 55.32; EI-MS: m/z: 309.9; Anal. Calcd for $C_{16}H_{16}Cl_2O_2$: C, 61.75; H, 5.18. Found C, 61.78; H, 5.30.

4.2.4. (E)-1,2-Dichloro-1,2-bis(4-methoxyphenyl)ethene ***5a***[36]. Mp 166–168 °C, yield, 3%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J=8.7 Hz, 4H), 6.94 (d, J=8.7 Hz, 4H), 3.86 (s, 6H); EI-MS: m/z: 308.0.

4.2.5. (Z)-1,2-Dichloro-1,2-bis(4-methoxyphenyl)ethene ***6a***[37]. Mp 62–64 °C, yield, 12%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J=8.5 Hz, 4H), 6.71 (d, J=8.5 Hz, 4H), 3.76 (s, 6H); EI-MS: m/z: 308.0.

The procedures for the reaction of **1b**–**e** with thionyl chloride are similar to that of **1a**, and the characterization data are listed in the following.

4.2.6. 2-Phenyl-3-chloro-6-methoxybenzo[b]thiophene ***2b***. Mp 82–84 °C, yield, 45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J=7.7 Hz, 2H), 7.71 (d, J=8.8 Hz, 1H), 7.44 (t, J=7.5 Hz, 2H), 7.36 (t, J=7.2 Hz, 1H), 7.22 (d, J=2.2 Hz, 1H), 7.05 (dd, J=8.8, 2.2 Hz, 1H), 3.84 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ158.36, 138.17, 133.48, 132.57, 131.91, 129.11, 128.68, 128.39, 123.03, 116.21, 115.09, 104.82, 55.70; EI-MS: m/z: 274.1; EI-MS: m/z: 274.1; Anal. Calcd for $C_{15}H_{11}ClOS$: C, 65.57; H, 4.04. Found C, 65.44; H 4.13.

4.2.7. 2-Phenyl-3,7-dichloro-6-methoxybenzo[b]thiophene ***3b***. Mp 130–132 °C, yield, 15%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J=7.3 Hz, 2H), 7.72 (d, J=8.7 Hz, 1H), 7.49 (t, J=7.4 Hz, 2H), 7.42 (t, J=7.4 Hz, 1H,), 7.17 (d, J=8.8 Hz, 1H), 4.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.07, 137.66, 135.31, 132.58, 132.12, 129.09, 128.75, 128.73, 121.09, 116.30, 114.89, 111.23, 56.94; EI-MS: m/z: 307.9; Anal. Calcd for $C_{15}H_{10}Cl_2OS$: C, 58.26; H, 3.26. Found C, 58.11; H 3.40.

4.2.8. erythro-1,2-Dichloro-1-phenyl-2-(4-methoxyphenyl)ethane ***4b***. Mp 142–144 °C, yield, 4%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.31 (m, 7H), 6.91 (d, J=8.6 Hz, 2H), 5.20 (s, 2H, Note: the signal is not split.), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.98, 138.52, 130.45, 129.32, 128.96, 128.55, 128.07, 113.91, 66.05, 65.69, 55.34; EI-MS: m/z: 280.1; Anal. Calcd for $C_{15}H_{14}Cl_2O$: C, 64.07; H, 5.02. Found C, 63.97; H, 5.07.

4.2.9. Methyl 4-(3-chloro-6-methoxybenzo[b]thiophen-2-yl) benzoate ***2c***. Mp 176–177 °C. yield, 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J=8.2 Hz, 2H), 7.87 (d, J=8.2 Hz, 2H), 7.77 (d, J=8.8 Hz, 1H), 7.28 (d, J=2.2 Hz, 1H), 7.10 (dd, J=8.8, 2.2 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.64, 158.71, 138.40, 137.05, 132.09, 131.82, 129.87, 129.57, 128.83, 123.31, 117.53, 115.39, 104.74, 55.72, 52.25; EI-MS: m/z: 322.1; Anal. Calcd for $C_{17}H_{13}ClO_3S$: C, 61.35; H 3.94. Found C, 61.65; H 4.02.

4.2.10. Methyl 4-(3,7-dichloro-6-methoxybenzo[b]thiophen-2-yl) benzoate ***3c***. Mp 185–186 °C, yield, 45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J=8.2 Hz, 2H), 7.88 (d, J=8.2 Hz, 2H), 7.74 (d, J=8.8 Hz, 1H), 7.18 (d, J=8.8 Hz, 1H), 4.02 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.54, 153.40, 137.86, 136.53, 133.92, 132.43, 129.91, 128.84, 121.40, 117.58, 114.87, 111.39, 56.92, 52.31; EI-MS: m/z: 366.0; Anal. Calcd for $C_{17}H_{12}Cl_2O_3S$: C, 55.60; H, 3.29. Found C, 55.70; H, 3.30.

4.2.11. 2-Phenyl-3-chlorobenzo[b]thiophene ***2d***[5e,34]. Mp 64–65 °C. yield, 42%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, J=8.0 Hz, 2H), 7.83–7.79 (m, 3H), 7.54–7.46 (m, 3H), 7.46–7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.82, 136.76, 136.29, 132.34, 129.28, 128.67, 126.50, 125.46, 125.06, 122.27, 122.24, 116.64; EI-MS: m/z: 244.0; Anal. Calcd for $C_{14}H_9ClS$: C, 68.71; H, 3.71. Found C, 69.35; H 4.07.

4.2.12. erythro-1,2-Dichloro-1,2-diphenylethane ***4d***[35]. Mp 193–195 °C, yield, 12%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.33 (m, 10H), 5.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.36, 129.01, 128.56, 128.06, 65.75; EI-MS: m/z: 250.0; Anal. Calcd for $C_{14}H_{12}Cl_2$: C, 72.56; H, 5.22. Found C, 66.65; H, 4.85.

4.2.13. Methyl 4-(3-chlorobenzo[b]thiophen-2-yl)benzoate ***2e***. Mp 120–122 °C, yield, 15%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J=7.9 Hz, 2H), 7.93–7.86 (m, 3H), 7.83 (d, J=7.9 Hz, 1H), 7.50 (t, J=7.5 Hz, 1H), 7.44 (t, J=7.5 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.60, 137.75, 136.94, 136.82, 134.96, 129.96, 129.90, 129.13, 125.98, 125.29, 122.52, 122.36, 117.88, 52.31; EI-MS: m/z: 302.0; Anal. Calcd for $C_{16}H_{11}Cl_2O_2S$: C, 63.47; H, 3.66. Found C, 63.93; H, 3.76.

4.2.14. erythro-Methyl 4-(1,2-dichloro-2-phenylethyl)benzoate ***4e***. Mp 157–159 °C, yield, 6%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J=8.1 Hz, 2H), 7.50 (d, J=8.1 Hz, 2H), 7.47–7.36 (m, 5H), 5.24 (d, J=9.2 Hz, 1H), 5.20 (d, J=9.2 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.51, 143.02, 137.86, 130.67, 129.81, 129.17, 128.63, 128.23, 128.03, 65.45, 64.98, 52.30; EI-MS: m/z: 308.0; Anal. Calcd for $C_{16}H_{14}Cl_2O_2$: C, 62.15; H, 4.56. Found C, 61.88; H, 4.71.

4.3. Synthesis of (*E*)-*N*-[2-(4-decanoxyphenyl)vinyl]benzoyl hydrazide 7

A suspension of **1f** (12 g, 30 mmol) in 20 mL of hydrazine monohydrate (80%) was dissolved in 150 mL of methanol and

100 mL of toluene, and the mixture was refluxed for 72 h. After cooling, the reaction mixture was poured in water and the crude solid was recrystallized from ethanol to afford **7** as white needle crystals. Yield, 83%. ^{1}H NMR ($CDCl_3$, 400 M): δ 9.65 (s, 1H), 7.80 (d, J=8.0 Hz, 2H), 7.59 (d, J=8.0 Hz, 2H), 7.52 (d, J=7.6 Hz, 2H), 7.26 (d, J=16.4 Hz, 1H), 7.09 (d, J=16.4 Hz, 1H), 6.92 (d, J=8.4 Hz, 2H), 4.48 (s, 2H), 3.97 (t, J=6.0 Hz, 2H), 3.92 (s, 3H), 1.76–1.63 (m, 2H), 1.46–1.11 (m, 14H), 0.84 (t, J=6.4 Hz).

4.4. Synthesis of (*E*)-[2-(4-decanoxyphenyl)vinyl] benzoic acid *N*-(4-cyanobenzoyl)hydrazide 8a

To a round-bottomed flask was added 4-cyanobenzoic acid (330 mg, 2.2 mmol), 10 mL of thionyl chloride, and the mixture was refluxed for 8 h. After cooling, the excess of thionyl chloride was removed at reduced pressure to give the 4-fluorobenzoyl chloride, which was added to a solution of compound **7** (790 mg, 2 mmol) in 10 mL of pyridine. The reaction mixture was stirred for 2 h at 90 °C and then poured into water. The solid was filtered and crystallized from ethanol to give **8a** as white crystals; yield, 76%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.78 (s, 1H), 10.58 (s, 1H), 8.05 (d, J=8.5 Hz, 2H), 8.02 (d, J=8.5 Hz, 2H), 7.90 (d, J=8.3 Hz, 2H), 7.68 (d, J=8.3 Hz, 2H), 7.55 (d, J=8.6 Hz, 2H), 7.35 (d, J=16.4 Hz, 1H), 7.15 (d, J=16.4 Hz, 1H), 6.94 (d, J=8.6 Hz, 2H), 3.96 (t, J=6.4 Hz, 2H), 2.36 (s, 3H), 1.68 (quintet, 2H), 1.38 (quintet, 2H), 1.33–1.18 (m, 12H,), 0.83 (t, J=6.8 Hz, 3H).

4.4.1. (E)-[2-(4-Decanoxyphenyl)vinyl]benzoic acid N-(4-methoxybenzoyl)hydrazide ***8b***. Compound **8b** was prepared according to the procedure as **8a**. Yield, 78%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.40 (s, 1H), 10.34 (s, 1H), 7.89 (d, J=8.4 Hz, 4H), 7.67 (d, J=8.4 Hz, 2H), 7.54 (d, J=8.8 Hz, 2H), 7.34 (d, J=16.4 Hz, 1H), 7.14 (d, J=16.4 Hz, 1H), 7.04 (d, J=8.8 Hz, 2H), 6.93 (d, J=8.8 Hz, 2H), 3.96 (t, J=6.4 Hz, 2H), 3.81 (s, 3H), 1.68 (quintet, 2H), 1.38 (quintet, 2H), 1.34–1.14 (m, 12H), 0.83 (t, J=6.8 Hz, 3H).

4.5. Synthesis of compounds 9a and 9b

Compound **8a** (524 mg, 1 mmol) was added to $SOCl_2$ (15 mL), and the reaction mixture was refluxed under a nitrogen atmosphere for 12 h. Then, the excessive thionyl chloride was removed by vacuum distillation. The crude solid was purified to afford the products **9a** and **9b** in sequence by silica gel column chromatography using dichloromethane as eluent.

4.5.1. (E)-2-(4-Cyanophenyl)-5-[4-(3-chloro-6-decyloxy benzo[b] thiophene-2-yl)phenyl]-1,3,4-oxadiazole ***9a***. Yield, 29%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J=8.3 Hz, 2H), 8.23 (d, J=8.3 Hz, 2H), 7.99 (d, J=8.3 Hz, 2H), 7.86 (d, J=8.3 Hz, 2H), 7.77 (d, J=8.9 Hz, 1H), 7.28 (d, J=2.0 Hz, 1H), 7.11 (dd, J=8.9, 2.0 Hz, 1H), 4.05 (t, J=6.5 Hz, 2H), 1.84 (quintet, 2H), 1.49 (quintet, 2H), 1.44–1.20 (m, 12H), 0.89 (t, J=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.03, 163.18, 158.41, 138.37, 136.60, 132.94, 131.65, 131.49, 129.58, 127.75, 127.40, 127.33, 123.33, 122.68, 117.90, 117.80, 115.93, 115.27, 105.48, 68.63, 31.91, 29.57, 29.40, 29.33, 29.22, 26.06, 22.69, 14.13; EI-MS: m/z: 569.2; Anal. Calcd for $C_{33}H_{32}ClN_3O_2S$: C, 69.52; H, 5.66; N, 7.37. Found C, 69.40; H, 5.61; N 7.35.

4.5.2. (E)-2-(4-Cyanophenyl)-5-[4-(3,7-dichloro-6-decyloxy benzo [b]thiophene-2-yl)phenyl]-1,3,4-oxadiazole ***9b***. Yield, 17%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J=8.3 Hz, 2H), 8.24 (d, J=8.4 Hz, 2H), 8.00 (d, J=8.4 Hz, 2H), 7.86 (d, J=8.3 Hz, 2H), 7.73 (d, J=8.8 Hz, 1H), 7.17 (d, J=8.9 Hz, 1H), 4.16 (t, J=6.5 Hz, 2H), 1.88 (quintet, 2H), 1.53 (quintet, 2H), 1.45–1.20 (m, 12H), 0.89 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.94, 163.23, 153.26, 137.89, 136.12, 133.43, 132.94, 132.31, 129.64, 127.70, 127.40, 123.07, 121.42, 117.89, 115.55, 115.30, 113.01, 70.26, 31.91, 29.56, 29.34, 29.24, 25.93, 22.69, 14.13; EI-MS: m/z: 603.1; Anal. Calcd for $C_{33}H_{31}Cl_2N_3O_2S$: C, 65.56; H, 5.17; N, 6.95. Found C, 65.47; H, 5.08; N, 7.07.

Compounds **10a** and **10b** were prepared according to the same procedure as that of **9a** and **9b**.

4.5.3. (E)-2-(4-Methoxyphenyl)-5-[4-(3-chloro-6-decyloxybenzo [b] thiophene-2-yl)phenyl]-1,3,4-oxadiazole ***10a***. Yield, 45%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J=8.5 Hz, 2H), 8.11 (d, J=8.9, 5.2 Hz, 2H), 7.96 (d, J=8.5 Hz, 2H), 7.76 (d, J=8.8 Hz, 1H), 7.28 (d, J=2.2 Hz, 1H), 7.10 (dd, J=8.9, 2.2 Hz, 1H), 7.06 (d, J=8.8 Hz, 2H), 4.05 (t, J=6.5 Hz, 2H), 3.91 (s, 3H), 1.84 (quintet, 2H), 1.49 (quintet, 2H), 1.44–1.23 (m, 12H), 0.89 (t, J=6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.69, 163.79, 162.44, 158.30, 138.32, 135.79, 131.82, 131.69, 129.44, 128.77, 127.02, 123.51, 123.24, 117.49, 116.41, 115.82, 114.57, 105.51, 68.62, 55.49, 31.89, 29.56, 29.39, 29.32, 29.22, 26.05, 22.68, 14.11; EI-MS: m/z: 574.2; Anal. Calcd for $C_{33}H_{35}ClN_2O_3S$: C, 68.91; H, 6.13; N, 4.87. Found C, 68.80; H, 6.17; N, 4.91.

4.5.4. (E)-2-(4-Methoxyphenyl)-5-[4-(3,7-dichloro-6-decyloxy benzo [b]thiophene-2-yl)phenyl]-1,3,4-oxadiazole ***10b***. Yield, 23%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J=8.5 Hz, 2H), 8.11 (d, J=8.9 Hz, 2H), 7.98 (d, J=8.6 Hz, 2H), 7.73 (d, J=8.8 Hz, 1H), 7.17 (d, J=8.8 Hz, 1H), 7.06 (d, J=8.9 Hz, 2H), 4.16 (t, J=6.6 Hz, 2H), 3.91 (s, 3H), 1.88 (quintet, 2H), 1.53 (quintet, 2H), 1.43–1.20 (m, 12H), 0.89 (t, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.73, 163.68, 162.47, 153.16, 137.85, 135.32, 133.78, 132.40, 129.49, 128.78, 127.07, 123.91, 121.31, 117.61, 116.39, 114.58, 113.02, 70.30, 55.50, 31.92, 29.56, 29.34, 29.27, 25.95, 22.69, 14.11; EI-MS: m/z: 608.1; Anal. Calcd for $C_{33}H_{34}Cl_2N_2O_3S$: C, 65.02; H, 5.62; N, 4.60. Found C, 65.05; H, 5.42; N, 4.73.

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Supplementary data

Supplementary data (proton NMR and carbon NMR for **2a**, **3a**, **3b**, *erythro*-**4b**, **2c**, **2d**, *erythro*-**4d**, **2e**, *erythro*-**4e**, **9a**, **9b**, **10**a, and **10b**). Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.09.060. These data include MOL files and InChiKeys of the most important compounds described in this article.

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