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Mesogenic and optical properties of α,α' -bis(4-alkoxyphenylethynyl)oligothiophenes

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Mesogenic and optical properties of α,α' -bis(4-alkoxyphenylethynyl)oligothiophenes

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Liquid crystalline α,α' -bis(4-alkoxyphenylethynyl)oligothiophenes (bi- and ter-thiophene) have been synthesized and their mesogenic behaviour and optical properties investigated. They all exhibited a nematic mesophase, and compounds with long alkoxy chains also showed lamellar phases. Increasing the number of thiophene units increased both the transition temperatures and the mesophase ranges. As for their optical properties, incorporating more thiophene units results in red-shifted absorption and emission spectra, slightly enhanced quantum efficiency, and a larger Stoke's shift. Most importantly, in terms of the absorption and emission maxima, the incorporation of one 4-alkoxyphenylethynyl moiety was found to be equivalent to adding one thiophene ring.

1. Introduction

Oligomeric materials based on π -conjugated systems are of great interest for their potential application in optoelectronic devices such as field effect transistors (FETs) [1] and light emitting diodes (LEDs) [2]. Well defined π -conjugated oligomers possess precise chemical structures and conjugation lengths that can lead to well defined functional properties. A further advantage of oligomers is their convenient synthesis which allows for easy and systematic tuning of their electrical and optical properties.

Molecular ordering in π -conjugated oligomers has been shown to be an important factor governing the performance of devices such as LEDs and FETs [3]. For example, the performance of a sexithiophene-based FET can be enhanced by a factor of *c.* 50 by increasing the intermolecular ordering [4]. Inter-chain interactions have also been shown to play an important role in affecting the quantum efficiency of light emitting devices [3*a*]. In addition, polarized electroluminescence can be achieved using well oriented thin films that show strong anisotropy [5]. Thus, achieving fine control of the interchain correlations is of importance for manipulating the properties of these materials and hence enhancing the performances of devices.

The self-organizing ability of liquid crystals could provide a way to control the intermolecular correlations. Indeed, it has been shown that high mobilities in liquid crystal polymers can be achieved when they are annealed in their mesophase [6]. There have been many reports devoted to the study of mesogenic properties of compounds derived from oligothiophene [7]. In recent years, hybridized oligomeric materials comprising thiophenes and other arenes, especially phenylenes, have emerged as a new class of materials [6, 8]. Investigation of the liquid crystal behaviour of these co-oligomers could provide better control of the performance of devices for which molecular order is of importance. Thus, here we have chosen to focus on the systems 5,5'-bis(4-alkoxyphenylethynyl)-[2,2']bithiophenes (**1**) and 5,5''-bis(4-alkoxyphenylethynyl)-[2,2';5',2'']terthiophenes (**2**) (see the scheme). These two series, taken together with the analogous monothiophenyl mesogens reported by Swager *et al* [9], provide information about the influence of varying the size of the oligothiophene moiety on the liquid crystal properties. In these systems, an acetylene unit is inserted into each phenylene/thiophene pair to remove steric interactions between them and allow better conjugation. Attaching alkoxy chains to the phenyl rings should lead to higher molecular order [10] and may lead to the formation of liquid crystalline phases; in addition, these may improve the solubility of the compounds for possible film casting from solution. In this work, the synthesis of the bithienyls **1** and

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the terthienyl analogues **2** are reported and their mesogenic and optical properties are presented.

2. Results and discussion

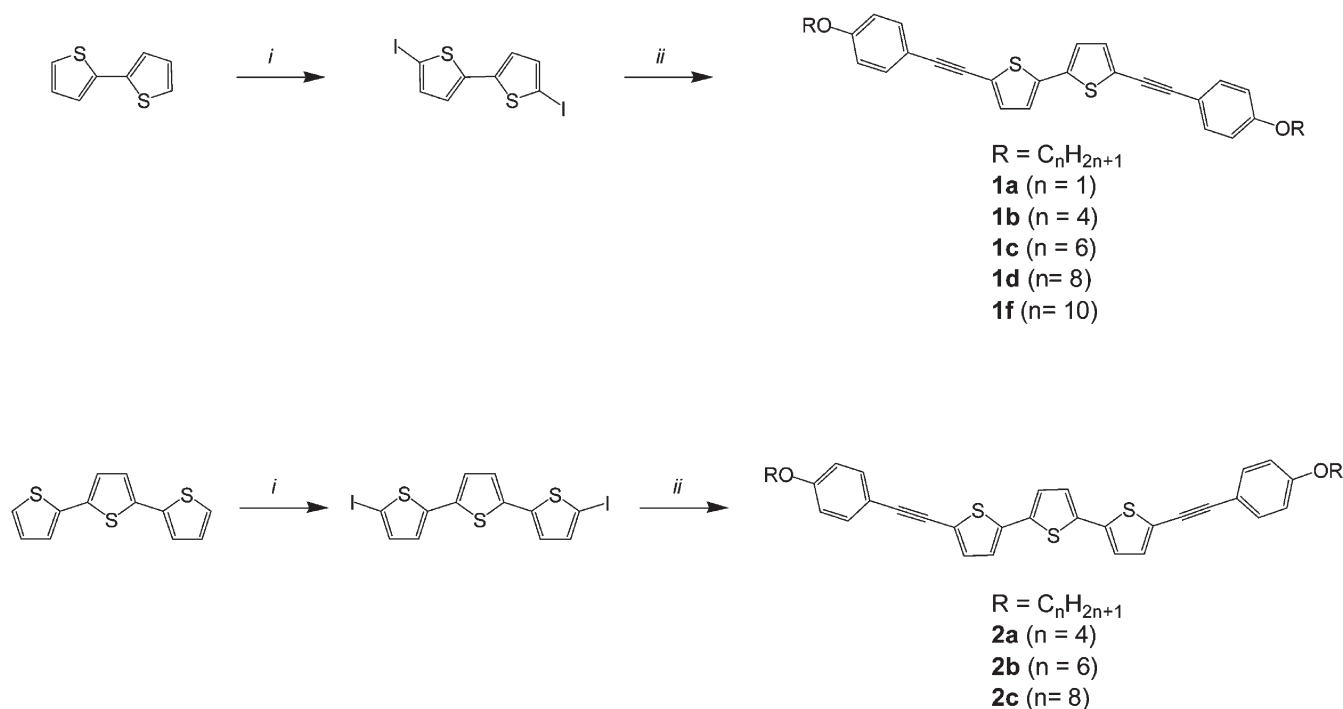
2.1. Synthesis

The scheme outlines the synthesis of the bithiophene- and terthiophene-based mesogenic materials, compounds **1a–1f** and **2a–2c**. The synthesis is straightforward and their purification is simple, making these materials attractive for property studies and device fabrication. The 5,5'-positions of 2,2'-bithiophene and the 5,5'-positions of 2,2';5',2''-terthiophene were iodinated in the presence of mercury acetate. Thereafter, the diiodooligothiophenes were coupled with alkoxy-derivatized ethynylbenzenes to afford the desired oligothiophene-containing compounds, the 5,5'-bis(4-alkoxyphenylethynyl)-[2,2']bithiophenes (**1a–1f**), and 5,5''-bis(4-alkoxyphenylethynyl)-[2,2';5',2'']terthiophenes (**2a–2c**). Series **1** exhibited moderate solubility in dichloromethane while the terthienyl series **2** only partially dissolved in dichloromethane, but better solubility was achieved in tetrahydrofuran.

2.2. Mesomorphic behaviour

The thermal behaviour of the bithienyl and terthienyl mesogens was investigated using polarizing optical

microscopy (POM) and differential scanning calorimetry (DSC) and is summarized in the table. Severe thermal decomposition indicated by the formation of a reddish orange area at 250°C was observed for **1a** and thus its thermal transition data were reported for the first heating run. As the chain length increases, the thermal decomposition is suppressed to partial decomposition for **1b** ($n=4$) while no thermal decomposition was observed for the longer chain derivatives **1c–1f** on heating to 250°C. All the terthienyl analogues, compounds **2a–2c**, showed partial decomposition on heating to their relatively higher clearing temperatures ($>260^\circ\text{C}$). The methoxy derivative **1a** showed a nematic texture prior to the aforementioned severe decomposition at the clearing point. For all other bithienyl compounds, **1b–1f**, on cooling from the isotropic melt, schlieren or marbled textures characteristic of the nematic phase were observed, as shown in figure 1. On further cooling, the longer chain analogues, **1e** ($n=10$) and **1f** ($n=12$), exhibited two additional mesophases, an enantiotropic smectic C phase indicated by a blurred schlieren texture, figure 1(b), and a monotropic smectic B phase assigned using mosaic textures, figure 1(c). In the terthienyl system, only a nematic phase was observed for the shortest chain derivative **2a** ($n=4$) while both nematic and smectic C phases were detected enantiotropically for the longer chain derivatives, **2b** and **2c**.



Scheme. Synthesis of series **1** and **2** compounds. Reagents and conditions: (i) I_2 , $\text{Hg}(\text{OAc})_2$; (ii) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, PPh_3 , CuI , $(i\text{Pr})_2\text{NH}$.

Table. Phase behaviour of compounds **1a–1f** and **2a–2c**. The transition temperatures (°C) and enthalpies (in parentheses/kJ mol⁻¹) were determined by DSC at 10°C min⁻¹. Cr, Cr1, and Cr2, crystalline phases; SmA, smectic A phase; SmB, smectic B phase; SmC, smectic C phase; N, nematic phase; I, isotropic liquid. *n* denotes the length of the alkoxy chains.

Compound	Behavior
1a , <i>n</i> = 1	Cr $\xrightleftharpoons[169.8 (-41.12)]{193.4 (47.26)}$ N $\xrightleftharpoons[220.0^a]{265.9^a}$ I _{decomp.}
1b , <i>n</i> = 4	Cr1 $\xrightleftharpoons[167.5 (-35.39)]{153.4 (41.53)}$ Cr2 $\xrightleftharpoons[178.9 (41.53)]{178.9 (41.53)}$ N $\xrightleftharpoons[248.2 (-1.23)]{258.1 (2.57)}$ I _{partial decomp.}
1c , <i>n</i> = 6	Cr $\xrightleftharpoons[147.8 (-37.86)]{160.0 (41.60)}$ N $\xrightleftharpoons[220.2 (-1.55)]{223.0 (2.04)}$ I
1d , <i>n</i> = 8	Cr1 $\xrightleftharpoons[145.0 (-46.22)]{155.0 (46.73)}$ N $\xrightleftharpoons[202.4 (-2.11)]{203.8 (2.74)}$ I
1e , <i>n</i> = 10	Cr1 $\xrightleftharpoons[83.0 (-3.75)]{95.1 (16.42)}$ Cr2 $\xrightleftharpoons[140.3 (-37.94)]{146.1 (39.77)}$ SmB $\xrightleftharpoons[140.9^b]{140.9^b}$ SmC $\xrightleftharpoons[159.1 (-2.51)]{160.2 (2.55)}$ N $\xrightleftharpoons[191.3 (-1.99)]{192.1 (2.12)}$ I
1f , <i>n</i> = 12	Cr1 $\xrightleftharpoons[77.7 (-22.33)]{111.7 (26.72)}$ Cr2 $\xrightleftharpoons[133.3 (-29.47)]{140.5 (42.62)}$ SmB $\xrightleftharpoons[136.6 (-5.67)]{136.6 (-5.67)}$ SmC $\xrightleftharpoons[166.2 (-3.86)]{167.6 (3.99)}$ N $\xrightleftharpoons[180.3 (-2.51)]{181.3 (2.62)}$ I
2a , <i>n</i> = 4	Cr1 $\xrightleftharpoons[146.4 (-5.53)]{175.6 (11.71)}$ Cr2 $\xrightleftharpoons[176.4 (-12.00)]{187.8 (10.04)}$ Cr3 $\xrightleftharpoons[189.9 (28.87)]{189.9 (28.87)}$ N $\xrightarrow{281.0^a}$ I _{partial decomp.}
2b , <i>n</i> = 6	Cr $\xrightleftharpoons[187.9 (-16.06)]{189.8 (16.33)}$ SmC $\xrightleftharpoons[197.0 (-0.84)]{198.1 (0.92)}$ N $\xrightarrow{280.0^a}$ I _{partial decomp.}
2c , <i>n</i> = 8	Cr $\xrightleftharpoons[188.2 (-17.12)]{191.1 (19.57)}$ SmC $\xrightleftharpoons[214.7 (-1.73)]{223.0 (1.79)}$ N $\xrightleftharpoons[259.9 (-1.33)]{266.6 (1.92)}$ I _{partial decomp.}

^a Determined by POM. ^b Overlapped with the transition at 140.3°C.

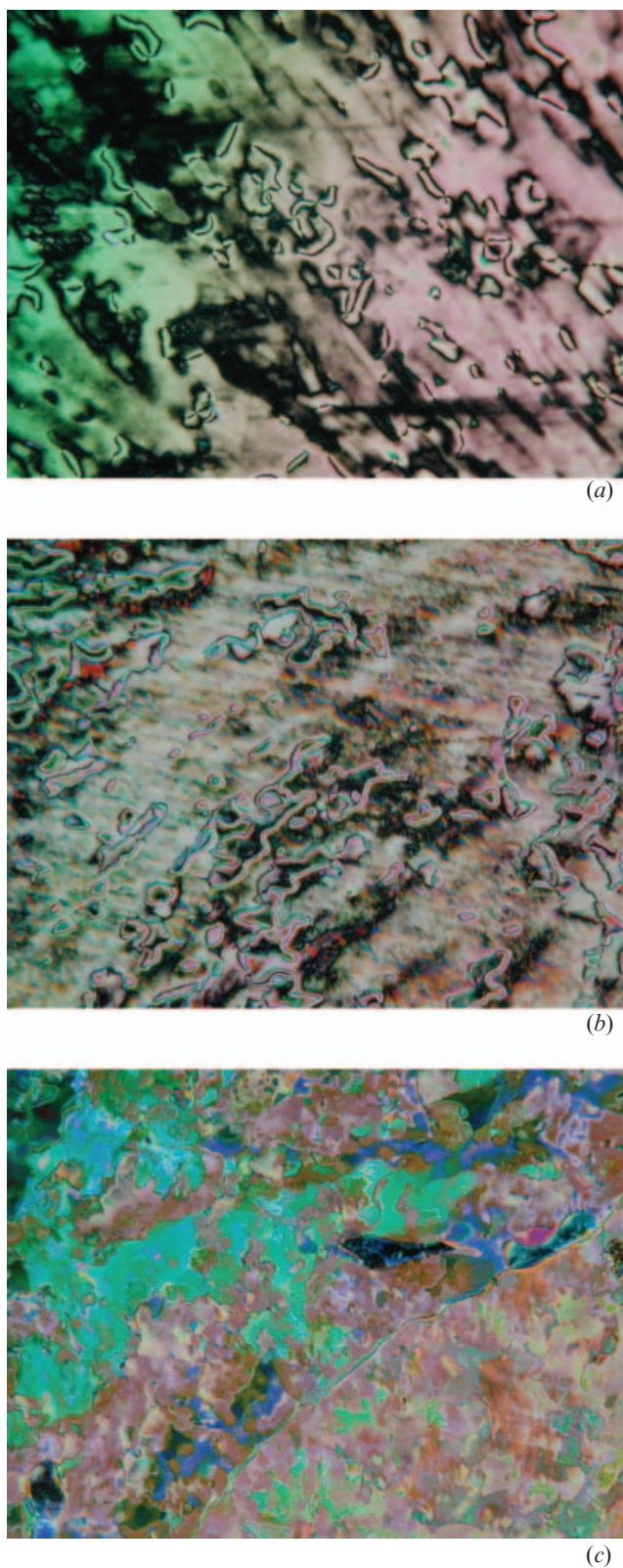


Figure 1. Polarizing micrographs of (a) nematic schlieren, (b) smectic C blurred schlieren, and (c) smectic B mosaic textures ($200\times$ magnification) of **1e** at 190, 157, and 140.5°C , respectively, on cooling.

Varying the alkoxy chain length influences the transition temperatures of the bithienyl series **1** and the terthienyl series **2** differently. For compounds **1a–1e**, both the melting and clearing temperatures were found to fall with increasing chain length. The mesophase ranges first increased from 57°C for **1a** to 79°C for **1b**, then decreased with increasing chain length. For compounds **2a–2c**, lengthening the terminal chains lowers the clearing temperatures but slightly increased the melting points.

The effect of extending the central thienyl oligomeric unit on mesogenic behavior can be elucidated by comparing mono- [9], bi-, and ter-thienyl analogues having the same alkoxy chains. For the mono-, bi-, and ter-thiophene analogues with terminal butyloxy chains, the melting points are 94, 179, and 189°C while the clearing temperatures are 140, 258, and 281°C , respectively. It is clear that increasing the number of central thienyl units initially increases both the melting and clearing temperatures significantly; however, the increase is significantly reduced on further incorporation of thiophene units. As the number of central thienyl units increases, their mesophase ranges are also affected. The mesophase ranges for the butyloxy analogues of the mono-, bi- (**1b**), and ter-thienyl (**2a**) derivatives were calculated to be 67, 79, and 91°C respectively. Incorporating more thiophene units not only promotes liquid crystallinity but also results in a higher tendency for the formation of the more ordered lamellar phases due to stronger intermolecular interactions.

For **2a**, the closest analogue, 5,5''-bis(5-butyl-2-thiophen-2-ylethynyl)-[2,2':5',2'']terthiophene, was reported to show a nematic phase at 101°C and isotropic liquid at 194°C on heating [11]. On cooling, in addition to a nematic phase, a smectic B phase was detected in the range $90\text{--}54^{\circ}\text{C}$. Replacing the outer 5-butylthienyl groups with 4-butyloxyphenyl moieties, as seen in **2a**, has little influence on the mesophase range but has considerably increased the transition temperatures.

2.3. Optical properties

The absorption and emission properties of series **1** and **2** compounds were studied in dichloromethane solution. The UV-vis and photoluminescence spectra of compounds **1a** and **2a** are shown in figure 2. For both series **1** and **2**, the absorption and emission maxima were independent of the chain lengths. The absorption maxima for series **1** and **2** compounds are at 392 and 418 nm, respectively. The emission peaks of series **1** compounds are located at 448 and 475 nm, while series **2** compounds show emission peaks centered at 482 and 514 nm.

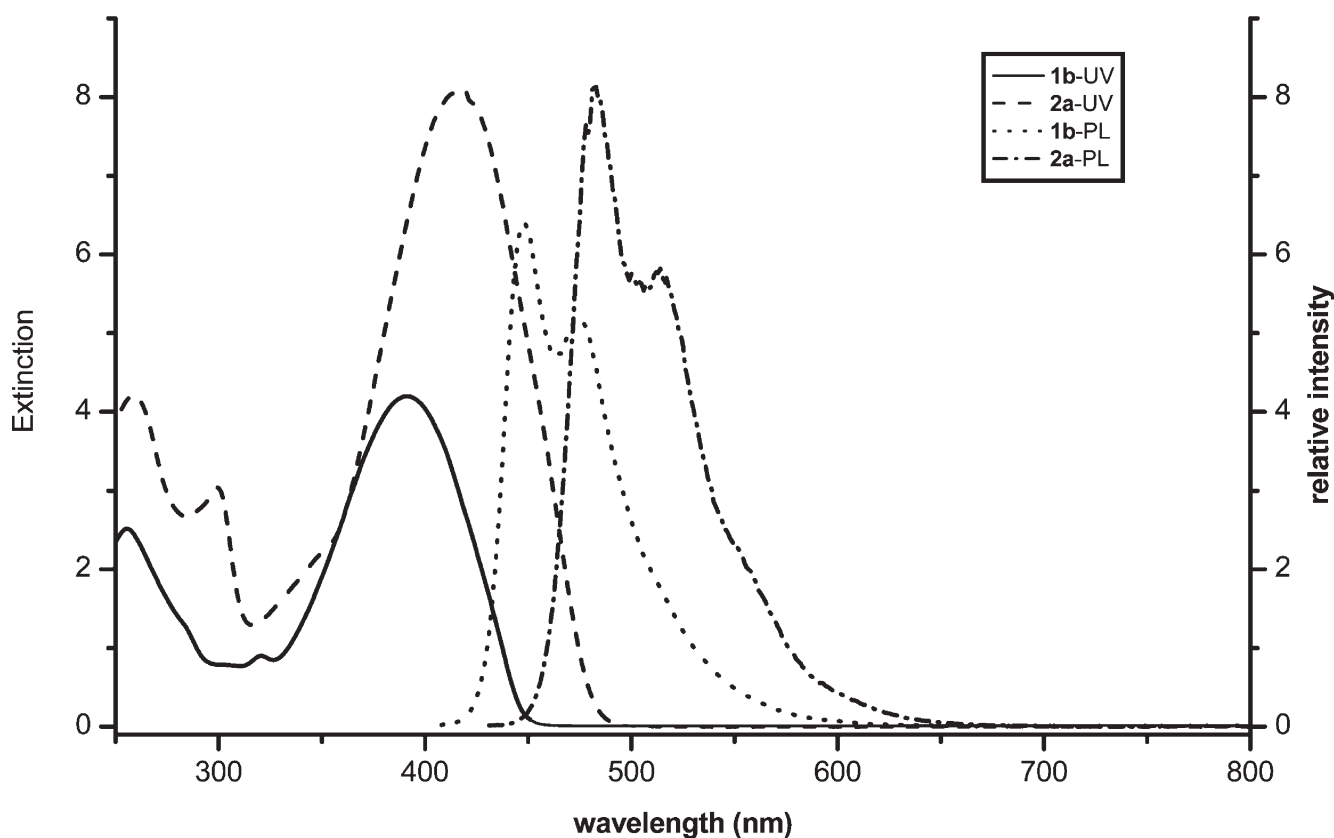


Figure 2. The absorption and emission spectra of **1b** and **2a** in dichloromethane. Extinction unit: $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

The optical properties of compounds **1** and **2** may be compared with those of α -oligothiophenes. For absorption spectra, the bithienyl derivative of **1a** showed a red shift of 90 nm when compared with α -bithiophene (λ_{abs} : 302 nm) [12] and a smaller red shift of 63 nm was found for the terthienyl derivative of **2a** when compared with α -terthiophene (λ_{abs} : 355 nm) [12]. The large red shifts together with high extinction coefficients of **1** and **2** indicates good conjugation of the phenyl and thienyl rings, as expected due to the reduction in steric interactions arising from the insertion of ethynyl bridges. It is noted that the absorption maxima of **1** and **2** are almost identical to those of α -quarterthiophene (390 nm) and α -quinquethiophene (416 nm) [12], respectively. This suggests the contribution of a 4-alkoxyphenylethyne moiety to the conjugation length is equivalent to that of a thiophene unit. Without the ethynyl bridges, as in 5,5'-bis(4-*n*-hexylphenyl)-2,2'-bithiophene (abs. maximum at 373 nm) [3*b*] and 5,5'-bis(4-*n*-hexyl-phenyl)-[2,2':5',2'']terthiophene (abs. maximum at 408 nm) [3*b*], twisting of the backbone due to the steric interactions between the phenylene and adjacent thiophene rings resulted in weaker conjugation, shifting the absorption maxima to lower wavelengths.

Comparing series **1** and **2**, the terthiophenyl series **2** reveals a red shift of 26 nm in their UV-vis spectra and a more significant red shift of 34 nm in the fluorescence spectra. The red shift in the absorption spectra can be accounted for by the extended conjugation length including the additional thiophene unit in **2**. However, the larger Stoke's shift of 64 nm for **2** compared with 56 nm for **1** implies a more significant conformational change between ground and excited states in **2**. Since both series **1** and **2** share the same end groups, 4-alkoxyphenylethyne, the difference in their Stoke's shifts is not likely to originate from the phenylethyne units. Hence, the central oligothiophenyl units are responsible for the difference in Stoke's shifts of **1** and **2**. This view is supported by the similar absorption and emission properties of **2a** and its analogue containing outer 5-butyl-2-thienylethyne groups (absorption maximum at 422.5 nm; emission peaks at 491 and 523 nm). Both compounds share the same α, α' -biethynylterthiophene unit but differ at the two terminals, i.e. alkoxyphenyl and alkylthienyl groups. However, the absorption maxima, emission maxima, and Stoke's shifts are found to be similar for these two.

The averaged quantum yield for **1a**–**1f** in dichloromethane solution is calculated to be 28%, while a

slightly higher averaged value of 33% is obtained for **2a–2f**. These values are considerably higher than those for α -bithiophene (1%) and α -terthiophene (6%) [13], in dichloromethane solutions. With comparable conjugation lengths, series **1** compounds show significantly higher quantum yields than that of α -quarterthiophene (18%) [13]. On the other hand, series **2** compounds exhibit similar quantum efficiency to that of α -quintethiophene (32%) [13]. It is noteworthy that although the absorption and emission positions of **2a** and its analogous compound with outer butylthienyl groups (quantum yield: 17%) [11] are very similar, the quantum yield of **2a** is almost doubled.

3. Conclusion

Liquid crystals based on oligomeric thiophenes and containing one phenylethynyl moiety at each end have been prepared. The resulting bi- and ter-thiophene-based thiophene/phenylene co-oligomers exhibited a nematic mesophase and those possessing long alkoxy chains also showed additional lamellar phases. Increasing the number of thiophene units in the oligothiophene fragment increased both the transition temperatures and mesophase ranges. Extending the central bithiophene to terthiophene results in red-shifted absorption and emission spectra, slightly enhanced quantum efficiency, and a larger Stoke's shift. We also note that the introduction of one phenylethynyl unit onto an oligothiophene moiety is equivalent to the inclusion of one more thiophene ring where absorption and emission maxima are concerned. Hence, the incorporation of a phenylethynyl moiety can be used as an alternative way of adding more thiophene units to extended oligothiophene backbones if optical properties are to be considered. Moreover, the phenylene can be modified independently before being attached to the oligothiophene backbone, and the diverse chemistry exhibited by the phenyl ring will allow the preparation of various derivatives showing different physical properties, e.g. high solubility for easy processing.

4. Experimental

4.1. General

All chemicals and solvents were of reagent grade (Aldrich Chemical Co.) and used without further purification. 1-Ethynyl-4-alkoxybenzene [14], 5,5'-diiodo-2,2'-bithiophene [15], and 5,5'-diiodo-2,2';5',2'-terthiophene [16] were synthesized following literature procedures. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer. Chemical shifts are reported in ppm relative to residual CHCl_3 ($\delta=7.26$, ^1H ; 77.0, ^{13}C). Multiplicities are given as s (singlet), d

(doublet), t (triplet), q (quartet), and m (multiplet). DSC was performed using a Perkin-Elmer Pyris1 instrument with heating and cooling rates of $10^\circ\text{C min}^{-1}$. Optical microscopy was carried out on a Nikon Eclipse E600 POL with a Mettler FP90/FP82HT hot stage system. Mass spectra were obtained on a Finnigan MAT-95XL and elemental analyses were carried out on a Heraeus CHN-O-Rapid Analyzer at the NSC Regional Instrumental Center at National Chiao Tung University, Hsinchu, Taiwan and at National Cheng Kung University, Tainan, Taiwan.

4.2. Synthesis of 5,5'-bis(4-alkoxyphenylethynyl)-[2,2']bithiophenes

To a 100 ml Schlenk flask with a nitrogen inlet, containing 5,5'-diiodo-2,2'-bithiophene (700 mg, 1.67 mmol), copper(I) iodide (35 mg, 0.184 mmol), and triphenylphosphine (88 mg, 0.336 mmol), was added $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (26 mg, 0.037 mmol) and (*i*-Pr) $_2\text{NH}$ (40 ml) under nitrogen. The mixture was heated to 60°C and 1-ethynyl-4-alkoxybenzene (4.389 mmol) in 5 ml THF was added dropwise over 10 min. After the addition, the reaction mixture was heated at 60°C for two hours. It was cooled to room temperature and dichloromethane (50 ml) was added. The solution was then washed with $\text{NH}_4\text{Cl}_{(\text{aq})}$ (3×200 ml) and H_2O (3×200 ml). The organic phase was dried with MgSO_4 , evaporated, and the residue recrystallized from dichloromethane to afford yellow powders of products **1a–1f**.

Characterization results for **1a**: yield=59%. ^1H NMR (CDCl_3 , 300 MHz): δ 7.46 (d, $J=8.7$ Hz, 4H), 7.14 (d, $J=3.3$ Hz, 2H), 7.06 (d, $J=3.6$ Hz, 2H), 6.88 (d, $J=9.3$ Hz, 4H), 3.84 (s, 6H). ^{13}C NMR ($\text{CDCl}_3/\text{CS}_2(1/1)$, 75 MHz): δ 159.9, 137.7, 133.0, 132.3, 123.8, 123.0, 114.9, 114.1, 94.6, 81.3, 55.3. HRMS (EI) calcd for $\text{C}_{26}\text{H}_{18}\text{O}_2\text{S}_2$ 426.0748, found 426.0753. Anal. calcd for $\text{C}_{26}\text{H}_{18}\text{O}_2\text{S}_2$, C 73.21, H 4.25; found, C 73.13, H 4.68%.

Characterization results for **1f**: yield=57%. ^1H NMR (CDCl_3 , 300 MHz): δ 7.44 (d, $J=8.4$ Hz, 4H), 7.13 (d, $J=3.9$ Hz, 2H), 7.05 (d, $J=3.6$ Hz, 2H), 6.87 (d, $J=8.7$ Hz, 4H), 3.97 (t, $J=6.9$ Hz, 4H), 1.78 (m, 4H), 1.60–1.20 (m, 36H), 0.88 (t, $J=6.0$ Hz, 6H). ^{13}C NMR (CDCl_3 , 75 MHz): δ 160.7, 138.5, 133.7, 133.2, 125.0, 124.2, 115.5, 96.1, 82.2, 68.9, 33.1, 30.8, 30.61, 30.55, 30.4, 27.2, 23.9, 14.9. HRMS for $\text{C}_{48}\text{H}_{62}\text{O}_2\text{S}_2$ 734.4191, found 734.4202. Anal. calcd for $\text{C}_{48}\text{H}_{62}\text{O}_2\text{S}_2$, C 78.42, H 8.50; found, C 78.24, H 8.61%.

4.3. Synthesis of 5,5''-bis(4-alkoxyphenylethynyl)-[2,2';5',2'']terthiophenes

To a 100 ml Schlenk flask with a nitrogen inlet, containing 5,5'-diiodo-2,2'-bithiophene (500 mg,

1.00 mmol), copper(I) iodide (22 mg, 0.116 mmol), and triphenylphosphine (56 mg, 0.214 mmol), was added Pd(PPh₃)₂Cl₂ (72 mg, 0.102 mmol) and (*i*-Pr)₂NH/THF (15/15 ml) under nitrogen. The mixture was heated to 60°C and 1-ethynyl-4-alkoxybenzene (2.134 mmol) in THF (5 ml) was added dropwise over 10 min. After the addition, the reaction mixture was heated at 60°C for a further one hour. The reaction solution was cooled to room temperature and dichloromethane (50 ml) was added. The solution was then washed with NH₄Cl_(aq) (3 × 200 ml) and H₂O (3 × 200 ml). The organic phase was dried with MgSO₄ and recrystallized from dichloromethane to afford yellow powders of compounds **2a–2c**.

Characterization results for **2a**: yield=52%. ¹H NMR (CDCl₃/CS₂(1/1), 300 MHz): δ 7.41 (d, *J*=8.7 Hz, 4H), 7.11 (d, *J*=4.1 Hz, 2H), 7.08 (s, 2H), 7.04 (d, *J*=4.1 Hz, 2H), 6.85 (d, *J*=8.7 Hz, 4H), 3.98 (t, *J*=6.6 Hz, 4H), 1.79 (m, 4H), 1.51 (m, 4H), 1.01 (t, *J*=7.4 Hz, 6H). ¹³C NMR (CDCl₃/CS₂(1/1), 75 MHz): δ 159.4 (2C), 137.7 (2C), 136.1 (2C), 132.8 (4C), 132.2 (2C), 124.7 (2C), 123.5 (2C), 122.9 (2C), 114.6 (2C), 114.5 (4C), 94.9 (2C), 81.4 (2C), 67.7 (2C), 31.3 (2C), 19.3 (2C), 13.9 (2C). HRMS for C₃₆H₃₂O₂S₃ 592.1564, found 592.1575.

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