Synthesis and properties of highly birefringent liquid crystalline materials: 2,5-bis(5-alkyl-2-butadinylthiophene-yl) styrene monomers

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Synthesis and properties of highly birefringent liquid crystalline materials: 2,5-bis(5-alkyl-2-butadinylthiophene-yl) styrene monomers

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In order to obtain liquid crystals with high birefringence (Δn), a series of new liquid crystals monomers incorporating styrene, a 2,5-disubstituted thiophene ring and diacetylenes, which were highly conjugated along the molecular long axis, were synthesized. Their physical properties were evaluated. As expected, they exhibited high Δn values of 0.4–0.7 and a low melting point and were of potential use for polymer-dispersed liquid crystal displays (PDLCDs), cholesteric displays and laser beam steering applications.

Keywords: high birefringence; liquid crystals; styrene monomer

1. Introduction

Highly birefringent (Δn) liquid crystals (LCs) are useful not only in conventional display devices, such as super-twisted nematic liquid crystal displays (STNLCDs), but also in scattering-type polymer-dispersed liquid crystal displays (PDLCDs) as reflective liquid crystal displays (LCDs) and in spatial light modulators. They are also of great interest as one component of LCDs, for example, compensation films for improving viewing angles, reflectors and polarisers [1–4].

It is well known that high Δn values can be achieved by increasing the molecular conjugation length [5]; a considerable number of π-conjugated compounds have been developed as high Δn LCs. Molecules that contain highly polarisable groups with high electron density, such as benzene rings, thiophene rings or acetylene linking groups, will therefore have large optical anisotropies. Bistolane LCs show birefringences greater than 0.3 in the visible spectral region and as a result have attracted particular attention [6–14]. The 2,5-disubstituted thiophene ring is a potentially useful element of the molecular structure of new nematic LCs due to a number of factors [15, 16]: it is aromatic and rigid in nature; the electron-rich sulfur atom in the thiophene ring results in a dipole moment perpendicular to the long molecular axis of the molecule, i.e. the apolar derivatives are potentially of negative dielectric anisotropy; the non-collinear nature of the 2,5-disubstituted thiophene ring and the lower symmetry generally result in a low melting point for thiophene derivatives.

Liquid crystalline polymers (LCPs) have attracted longstanding attention for their outstanding applications in engineering plastics and optic, electroptic and non-linear optic devices, and light-emitting materials, etc. [17]. In 1987, Zhou *et al.* [18] reported the first example of a mesogen-jacketed LC polymer (MJLCP). During recent decades, the work in our research group has been dedicated to the structure–property relationship of MJLCPs [19–24].

With this background, in the present work, our objective is to obtain monomers with high Δn values, which could be used for the preparation of MJLCPs with high Δn values. We report the design, synthetic procedures and physical properties of monomers containing styrene and 2,5-disubstituted thiophene ring moieties linked by diacetylenes units (Scheme 1). It is expected that high birefringent values can be obtained by this kind of structure due to its high aspect ratio, large linear conjugation length and high electron density. The influence of the substituted alkyl chains at the C-5 position of the thiophene ring on the properties of the compounds was also studied. The polymerisation of these compounds and the birefringence properties of the resulting polymers will be described in forthcoming publications.

2. Synthesis

The synthesis of the target compounds is outlined in Scheme 2. All homologues were prepared using the same method and therefore the general experimental

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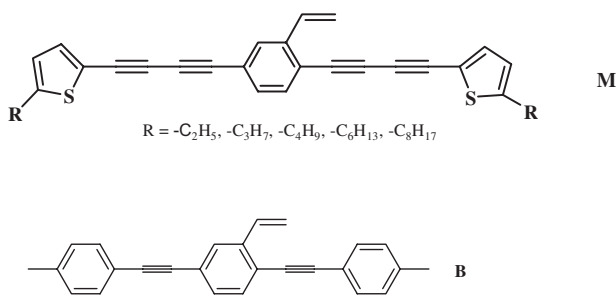
Scheme 1. Structure of the target compounds **M** and **B**.

procedures are illustrated using compounds **M3** as an example. These target compounds were synthesized through the coupling of intermediate molecules **5** and **10**. At first, 2,5-dibromostyrene was synthesized using a similar method to that reported previously [25] and a transparent, viscous liquid, which was very unstable, was obtained through purification by column chromatography. The introduction of the protected triple-bonded chain was straightforward and was achieved by a coupling between the 2,5-dibromostyrene and 2-methyl-3-butyn-2-ol (MEBYNOL) using Sonogashira conditions to give 2,5-bis(3-hydroxy-3-methyl-1-butynyl) styrene **9**. The removal of the protecting group from the acetylenes was carried out using the same method as reported earlier [12]. Our approach converted the aldehyde to dibromoolefin, which then dehydrobrominated to the bromoacetylene and the pale yellow liquid product **5** was successfully obtained [12]. It should be noted that the acetylene intermediates in this work were sensitive to light and heat and every effort needs to be made to protect these materials from light and heat. As shown in Scheme 2, the coupling of styrene fragment **10** with the bromoacetylene fragment **5** was carried out using Sonogashira conditions. However, each fragment can also self couple to form the respective dimers under the same conditions. The poor yields of **M** were attributed to these accompanying self-coupling reactions.

3.   Result and discussion

3.1   *Phase transitions and mesomorphic properties*

The differential scanning calorimetry (DSC) curves of these compounds are shown in Figure 1(a)–(c) and the associated data are listed in Table 1. All monomers were crystals at room temperature. **M2**, **M3**, **M4** and **M6** formed a nematic phase after melting. Two endothermic peaks appeared when the compounds **M2**, **M3**, **M4** and **M6** were heated, which corresponded to the transformation from the crystalline (Cr) phase to a liquid Cr phase and that from the LC to the isotropic (I) liquid, respectively. There were two exothermic

peaks in the DSC cooling curves of **M3**, **M4** and **M6**, which corresponded to the transformation from the I state to the liquid Cr state and that from LC state to Cr state. The transformation from the liquid Cr state to the I state for **M2** was not observed, possibly because the enthalpy was too small. However, there was only one endothermic peak during heating and one exothermic peak during cooling for the compound **M8**, which corresponded to the melting and crystallisation of the monomers. The DSC results showed that **M3**, **M4** and **M6** exhibited enantiotropic thermotropic liquid Cr behaviour with only one liquid Cr phase. For compound **B**, there was only one endothermic peak during heating and two exothermic peaks during cooling, which indicated that **B** exhibited monotropic liquid Cr behaviour. In the **M** series, the melting points showed an odd–even effect with the increase of the carbon numbers, while the clearing temperatures and liquid Cr temperature range were decreased.
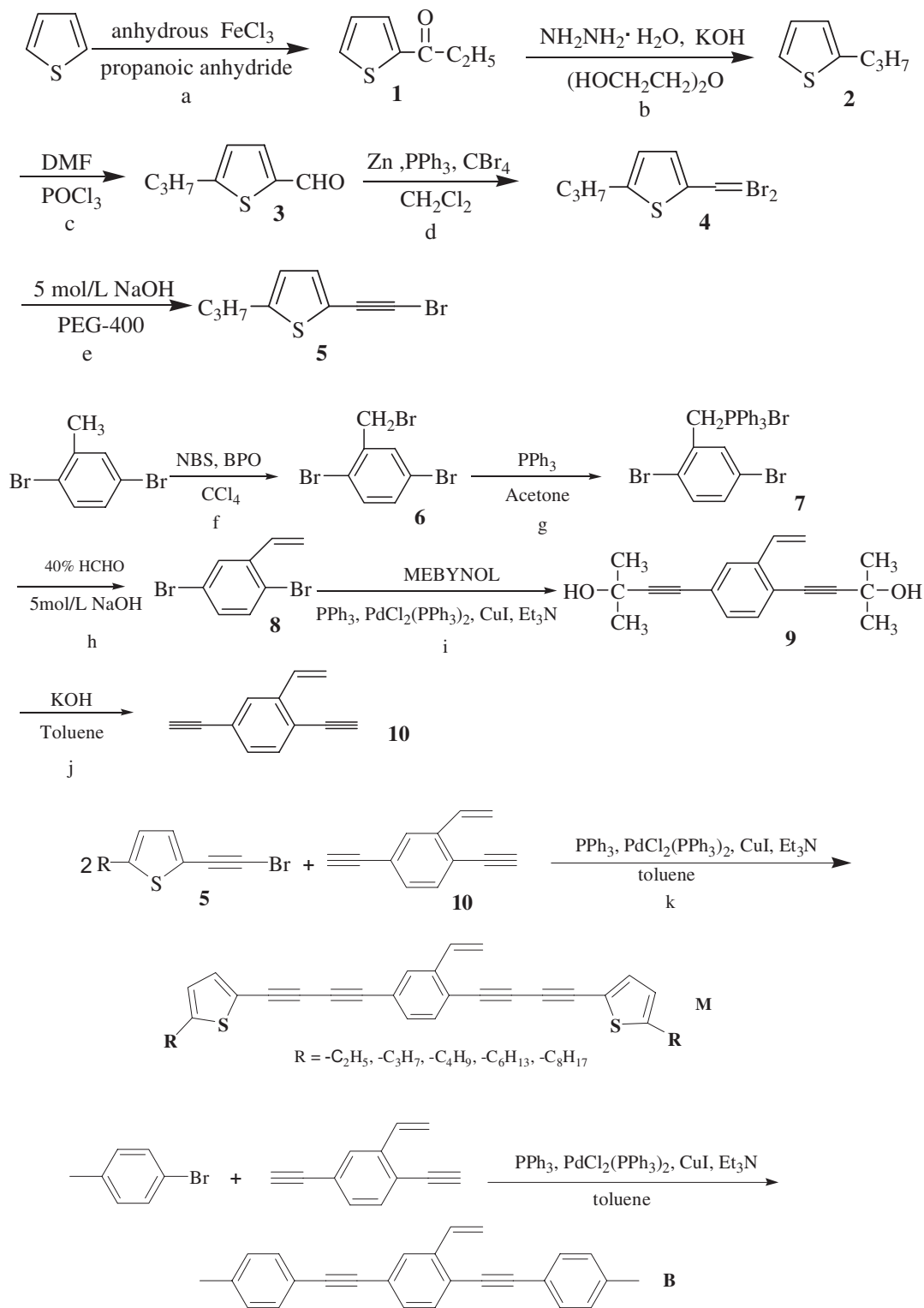
In order to further confirm the above DSC results, the textures of the liquid Cr phase of each compound were observed using polarised light microscopy (PLM). All four compounds **M2**, **M3** (Figure 2(a)), **M4** and **M6** developed the liquid Cr state at the first phase-transition temperature shown in the DSC curve, and a bright, colourful and fluidic schlieren texture could be observed. Upon further heating, the compounds entered into the I state and the field of view finally turned dark. When cooled from the I state, all of the compounds developed a liquid Cr state again and then started to crystallise. The observations above indicated that they showed enantiotropic phase behaviour with the existence of a nematic phase between the crystal and the I liquid, which were consistent with the DSC results. Compounds **M8** (Figure 2(b)) and **B** (Figure 2(c)) could not form a liquid Cr phase after melting, but a liquid Cr phase was observed during cooling. When cooled to 72.3°C, the schlieren texture of **M8** was observed, but crystallisation occurred quickly. The behaviour of **M8** observed by PLM was not consistent with the DSC result, probably because the enthalpy was too small to be detected by DSC.

3.2   *Optical anisotropy*

The Δn value, defined as the difference between the two principal refractive indices of a uniaxial material, was estimated by a guest–host method. The Δn value of a guest–host system can be approximated from the following equation:

$$(\Delta n)_{gh} = x(\Delta n)_g + (1 - x)(\Delta n)_h,$$

where the subscripts g, h and gh denote guest, host, and guest–host cells, respectively; x is the concentration

Scheme 2. Synthetic routes of the target compounds. The compound **M3** (R = −C$_3$H$_7$) was synthesized from **a** to **e**, and the other compounds **M2**, **M4**, **M6** and **M8** (R = −C$_2$H$_5$, −C$_4$H$_9$, −C$_6$H$_{13}$, −C$_8$H$_{17}$) were synthesized from **c** to **e**.

Table 1. Transition temperatures (°C), associated enthalpy changes (J g^{-1}) in square brackets for the **M** and **B** compounds. The parentheses denote a monotropic transition. Cr = crystal, N = nematic phase, I = isotropic.

Monomer	Phase transition temperature °C
M2	Cr 103.4 [70.91] N 129.9 [2.43] I
M3	Cr2 76 [2.95] Cr1 82 [63.49] N 125.3 [2.74] I
M4	Cr2 84.9 [31.26] Cr1 86.3 [23.24] N 99.9 [2.48] I
M6	Cr 78.3 [61.38] N 82 [1.12] I
M8	Cr 75 [89.51] N (72.3)[a] I
B	Cr 127.6 [94.03] N (102.7) [0.61] I

[a]The temperature was determined by PLM.

The Δn values of synthetic compounds are listed in Table 2. It can be seen that the Δn values of these compounds were in the range between 0.4 and 0.7, which was higher than that for the LC containing phenylacetylene and thiophenylacetylene [6]. That is because the structures of these compounds containing a 2,5-disubstituted thiophene ring, a diacetylenes unit and styrene had a more extended electron conjugation. It has been proven that a highly conjugated structure is beneficial to improve the Δn value. From these results, we can also conclude that the substitutions affected the Δn values of this series of compounds significantly. The Δn values decreased gradually with the increasing length of the end-substituted alkyl chain. Compound **M2** has the highest birefringence value of 0.732 among the **M** series compounds, because of the molecular packing density effect, and is expected to be useful for PDLCDs, cholesteric displays and laser beam steering applications. The Δn value of compound **B** was 0.462, which was lower than those of the **M** series. The reason was that the molecular conjugation length of **B** was shorter than that of the **M** compounds.

4. Conclusion

A series of 2,5-bis(5-alkyl-2-butadinylthiophene-yl) styrenes with novel super high Δn LCs were designed and synthesized. [1]H nuclear magnetic resonance (NMR) spectra, elemental analysis and mass spectrometry (MS) were used to characterise their structures. These compounds exhibited low melting points. DSC and PLM indicated that all of the compounds had a nematic phase and that their liquid Cr properties were related to the length of the end group. Compounds **M2**, **M3**, **M4** and **M6** were enantiotropic thermally induced LCs. **M8** and **B** were monotropic LCs. The clearing temperatures and LC temperature range decreased gradually with the increase of the length of the end-substituted alkyl chain. The Δn values of these compounds were high (0.4–0.7). **M2** had the highest
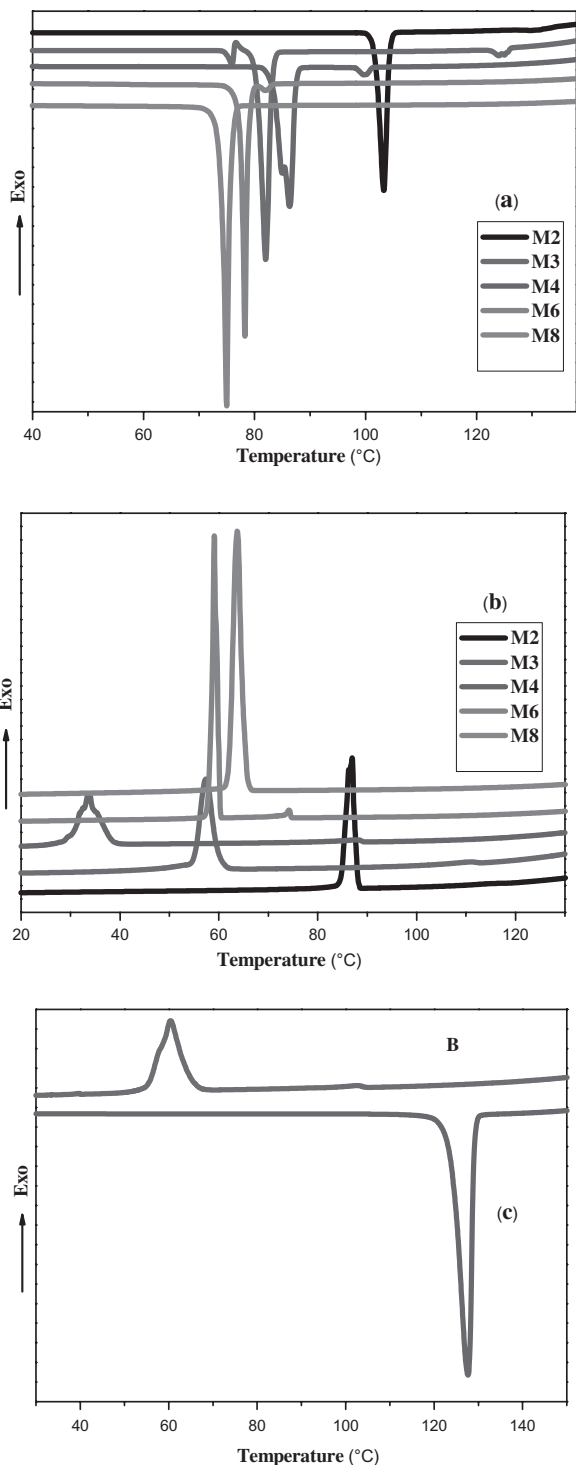
Figure 1. DSC curves of compounds **M** during heating (a), cooling (b) and compound **B** during heating and cooling (c) with a scanning rate of 5°C min^{-1} under a N$_2$ atmosphere.

(in wt%) of the guest compound. By comparing the measured results for the guest–host mixtures with those of the host mixture, the Δn values of the guest compounds can be extrapolated.
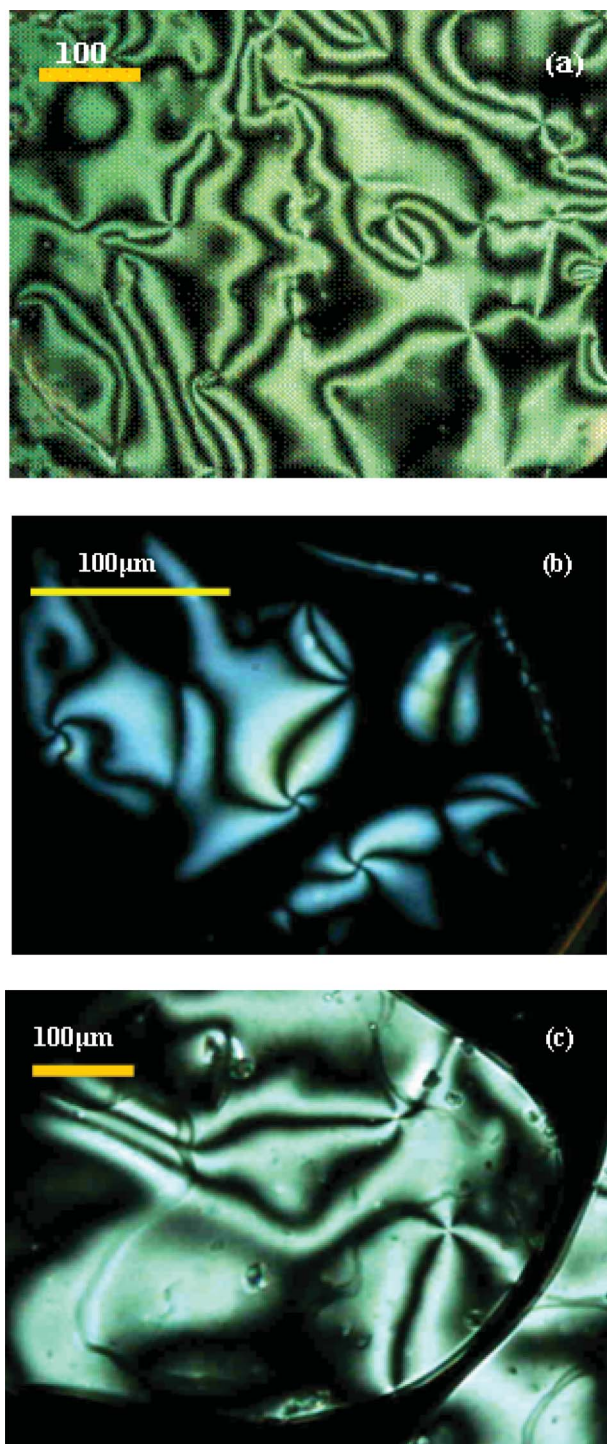
Figure 2. Polarising light microscopy images of the monomer. (a) **M3**: schlieren texture of the nematic phase at 100°C. (b) **M8**: schlieren texture of nematic phase at 72.3°C. (c) **B**: schlieren texture of nematic phase at 121.7°C.

birefringence value of 0.732. The Δn values also decreased gradually along with the increase of the length of the end-substituted alkyl chain. It was proved that a highly conjugated structure is beneficial

for improving the Δn values. In addition, these compounds as materials are probably limited in display-type applications because of the poor yields of these compounds (except **B**), unless the yield can be improved. The studies of the stability, viscosity and electro-optical properties of these compounds are in progress. The polymerisation of these compounds and the birefringence properties of the prepared polymers will be described in forthcoming publications.
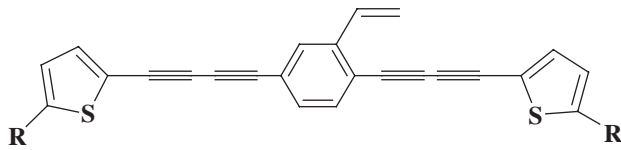
5. Experimental

5.1 Measurements

The structures of the intermediates and the final products were confirmed by a variety of spectral methods. ^{1}H NMR spectra with tetramethylsilane (TMS) as the internal standard were recorded on a BRUKER ARX400 MHz spectrometer at room temperature in chloroform-*d*. Elemental analysis was carried out with an Elementar Vario EL instrument. The mass spectra were recorded with a Finnigan-MAT ZAB-HS mass spectrometer, with electron impact ionisation (EI) as the ionisation resource. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q600 instrument at a heating rate of $10°C \, min^{-1}$ in N_2. The DSC examination was carried out on a TA DSC Q100 calorimeter with a programmed heating procedure $(5°C \, min^{-1})$ in nitrogen. The sample size was about 2–3 mg, and the sample was encapsulated in hermetically sealed aluminium pans, whose weights were kept constant. The PLM observation was performed on a Leitz Laborlux 12 microscope with a Leitz 350 hot stage. A conventional guest–host method was applied to extrapolate the Δn value. An Abbe refractometer (NAR-4T, ATAGO) with a sodium lamp (589 nm) was used to measure the refractive indices at 20°C of the mixtures with 5 wt% of the compound being dissolved in a LC host (SLC069015 with $\Delta n = 0.214$).

5.2 Synthesis

2-Propionylthiophene 1. Thiophene (96.6 mL, 1.22 mol) was added slowly to a rapidly stirred mixture of anhydrous $FeCl_3$ (120.0 g, 0.74 mol) and propanoic anhydride (113.6 g, 1.35 mol) in a water and ice bath. Then the reaction mixture was stirred at room temperature for 5 h before being diluted with water (300 mL). The crude product was extracted into ether, washed with 10% Na_2CO_3 solution and water until free of acid and dried with $MgSO_4$. The drying agent was filtered off and the solvent removed in vacuum before the residue was distilled to give a colourless liquid **1**. Yield: 134.9 g (79.0%). ^{1}H NMR (CDCl_3) (δ, ppm): 1.20–1.27 (t, 3H),

Table 2. Δn value of each compound. Data were calculated from guest–host systems.

Compound		$n_e{}^a$	$n_o{}^a$	Δn^a
	R = –C_2H_5	2.334	1.602	0.732
	R = –C_3H_7	2.283	1.596	0.687
	R = –C_4H_9	2.216	1.596	0.620
	R = –C_6H_{13}	2.136	1.583	0.553
	R = –C_8H_{17}	2.069	1.570	0.499
		2.044	1.582	0.462

[a]Refractive indices (at 20°C and 589 nm) were extrapolated values of the mixtures from 5 wt% liquid Cr compounds to be determined and 95 wt% SLC069015 with $\Delta n = 0.214$.

2.89–3.00 (q, 2H), 7.11–7.15 (dd, 1H), 7.61–7.64 (dd, 1H), 7.71–7.73 (dd, 1H).

2-Propylthiophene 2. A mixture of 2-propionylthiophene (60.0 g, 0.43 mol), hydrazine hydrate NH_2NH_2·H_2O (62 mL, 85%) and 400 mL diethylene glycol was heated at 140°C. After 2 h, the mixture was cooled to below 60°C and KOH pellets (72.6 g, 1.30 mol) were added. The mixture was heated for 3–4 h, then the product, water and the excess of NH_2NH_2·H_2O was distilled off. Finally, the mixture was heated at 195–200°C for 20 min, then it was cooled. The distilled mixture was extracted into ether, washed with 6 mol L^{-1} HCL and water until pH = 7 and dried with $MgSO_4$. The drying agent was filtered off and the solvent removed in a vacuum before the residue was distilled to give a colourless liquid **2**. Yield: 43.3 g (80.0%). b.p. 152–153°C at 760 mmHg. ^{1}H NMR $(CDCl_3)$ (δ, ppm): 0.93–1.00 (t, 3H), 1.72–1.76 (sextet, 2H), 2.82–2.89 (t, 2H), 6.77–6.79 (dd, 1H), 6.89–6.94 (dd, 1H), 7.09–7.12 (dd, 1H).

2-Formyl-5-propylthiophene 3 [26]. A solution of **2** (40.0 g, 0.32 mol) in dimethylformamide (DMF) (57 mL, 53.7 g, 0.74 mol) was stirred in water and an ice bath. $POCl_3$ (73.6 g, 0.48 mol) was slowly added and the temperature of the mixture was controlled to be below 20°C. The mixture was stirred at 20°C for 1 h and then heated to 80°C for 4 h. After it cooled to room temperature, 100 g ice was slowly added. 5 mol L^{-1} NaOH was added to adjust the pH = 6. The product was extracted with ether and washed with 10% aqueous Na_2CO_3 and water. The water was removed by adding magnesium sulfate and colourless liquid **3** was obtained by distillation in a vacuum. Yield: 45.3 g (92.0%). ^{1}H NMR $(CDCl_3)$ (δ, ppm): 0.95–1.03 (t, 3H), 1.69–1.72 (sextet, 2H), 2.82–2.89 (t, 2H), 6.90–6.92 (d, 1H), 6.89–6.94 (d, 1H), 9.83 (s, 1H).

2-(2,2-Dibromoethenyl)-5-propylthiophene 4 [26]. Zn dust (16.0 g, 0.24 mol) and PPh_3 (44.0 g, 0.17 mol) in dichloromethane (50 mL) were degassed with Ar. The reaction mixture was cooled to 0°C and a solution of carbon tetrabromide (50.0 g, 0.15 mol) in dichloromethane (180 mL) was added slowly. The reaction

mixture was then stirred for 21 h at room temperature. A solution of **3** (10.7 g, 0.075 mol) in dichloromethane (20 mL) CH_2Cl_2 was added dropwise to the reaction mixture, which was brought to room temperature. It was stirred until the completion of the reaction, which was confirmed by thin layer chromatography (TLC) analysis (7 h). The product was filtered and the filtrate was washed with CH_2Cl_2 and concentrated. The product was purified by column chromatography (silica gel) using petroleum ether as an eluent to give **4** as a pale yellow liquid. Yield: 21.3 g (91.7%). TLC (petroleum ether), $R_f = 0.56$. ^{1}H NMR $(CDCl_3)$ (δ, ppm): 0.93–1.01 (t, 3H), 1.62–1.79 (sextet, 2H), 2.72–2.79 (t, 2H), 6.69–6.71 (d, 1H), 7.04–7.06 (d, 1H), 7.50 (s, 1H).

2-Bromoethynyl-5-propylthiophene 5 [26]. 140 mL 5 mol L^{-1} NaOH and 200 mL PEG-400 were degassed with Ar and stirred at room temperature. A solution of **4** (12 g, 0.038 mol) in 50 mL PEG-400 was added. The mixture was stirred for 5 h. The product was extracted with water and ether, and the ether layer was then washed with water. The water was removed by adding magnesium sulfate and the ether was removed when concentrated. The product was purified by column chromatography (silica gel, petroleum ether) to give **5** as a pale yellow liquid. Yield: 7.3 g (84.0%). TLC (petroleum ether), $R_f = 0.67$. ^{1}H NMR $(CDCl_3)$ (δ, ppm): 0.92–1.00 (t, 3H), 1.62–1.79 (sextet, 2H), 2.70–2.78 (t, 2H), 6.62–6.4 (d, 1H), 7.05–7.07 (d, 1H), 7.50 (s, 1H).

2,5-Dibromostyrene 8. 2, 5-dibromotoluene (25.0 g, 0.10 mol), N-Bromosuccinimide (NBS) (36.6 g, 0.10 mol) and benzoyl peroxide (BPO) (0.6 g, 2.60 mmol) were dissolved in 200 mL of CCl_4 and refluxed. The reaction ended when a large amount of the floating succinimide was produced. The succinimide was filtrated off and the filtrate was evaporated. Then the residue was boiled with 26.5 g (0.10 mol) of triphenylphosphine in 150 mL of acetone for 3 h and the phosphonium salt was obtained. Finally, 100 mL of 5 mol L^{-1} NaOH aqueous solution was added slowly to 100 mL of 40% formaldehyde containing 24.0 g (0.04 mol) of the phosphonium salt. The mixture was stirred for

24 h at room temperature. The product was extracted with CH_2Cl_2 and the water was removed by adding magnesium sulfate and the CH_2Cl_2 was removed when concentrated. The product was purified by column chromatography (silica gel, petroleum ether: CH_2Cl_2 (v:v) = 3:1) to give **8** as a colourless liquid. Yield: 14.0 g (76.3%). TLC (petroleum ether), $R_f =$ 0.7. ^{1}H NMR (CDCl$_3$) (δ, ppm): 5.39–5.45 (dd, 1H), 5.67–5.76 (dd, 1H), 6.91–7.02 (q, 1H), 7.21–7.67 (m, 3H).

2,5-Bis(3-hydroxy-3-methyl-1-butynyl)styrene 9. Triphenylphosphine (0.3 g, 1.20 mmol), cuprous iodide (0.1 g, 0.46 mmol) and dichlorobis(triphenylphosphine) palladium (0.1 g, 0.12 mmol) in 100 mL of dry triethylamine was degassed with Ar. Then MEBYNOL (16.0 g, 0.19 mol) was added and refluxed for 17 h. The mixture was cooled to room temperature and filtered to remove the insoluble salt (triethylamine hydrobromide) formed during the reaction. The filtrate was washed with ether. After it was concentrated, the product was purified by column chromatography (silica gel, petroleum ether: ethyl acetate (v:v) =3:1) to give **9** as a pale yellow viscosity liquid. Yield: 9.0 g (88.0%). TLC (petroleum ether: ethyl acetate (v:v) =3:1), $R_f =$ 0.27. ^{1}H NMR (CDCl$_3$) (δ, ppm): 1.62–1.64 (d, 12H), 2.04 (d, 2H), 5.35–5.40 (dd, 1H), 5.78–5.86 (dd, 1H), 7.01–7.16 (q, 1H), 7.21–7.62 (m, 3H).

2,5-Diethynylstyrene 10. The deprotection procedure for **9** is detailed below as an example of the reaction conditions. A solution of **9** (8.0 g, 0.03 mol) in 350 mL toluene was heated to reflux and sodium hydroxide (3.4 g, 0.03 mol) was added at once. The mixture was heated at reflux for 3 h. The solvent was evaporated after filtering. The product was purified by column chromatography (silica gel, petroleum ether) to give **10** as a pale yellow liquid. Yield: 2.3 g (50.0%). TLC (petroleum ether), $R_f =$ 0.43. ^{1}H NMR (CDCl$_3$) (δ, ppm): 3.17 (s, 1H), 3.40 (s, 1H), 5.38–5.44 (dd, 1H), 5.79–5.88 (dd, 1H), 7.10–7.21 (q, 1H), 7.31–7.71 (m, 3H).

2,5-Bis(2-butadinyl-5-propylthiophene-yl)styrene M3. Triphenylphosphine (0.3 g, 1.20 mmol), cuprous iodide (0.1 g, 0.42 mmol), dichlorobis(triphenylphosphine) palladium (0.1 g, 0.20 mmol) and **10** (1.0 g, 6.60 mmol) in 75 mL of dry triethylamine and 75 mL of toluene were degassed with Ar. Then **5** (5.0 g, 22.00 mmol) was added and heated at 50°C for 21 h. The mixture was cooled to room temperature and filtered to remove the insoluble salt (triethylamine hydrobromide) formed during the reaction. The filtrate was washed with ether. After it was concentrated, the product was purified by column chromatography (silica gel, petroleum ether) and recrystallised to give **M3** as a yellow crystal. Yield: 0.3 g (10.0%). TLC (petroleum ether), $R_f =$ 0.24. ^{1}H NMR (CDCl$_3$) (δ, ppm): 0.96–0.99 (t, 6H), 1.66–1.75 (sextet, 4H), 2.76–2.79 (t, 4H), 5.43–5.46 (dd, 1H), 5.83–5.87 (dd, 1H), 6.67–6.68 (d, 2H), 7.09–7.17 (q, 1H), 7.19–7.20 (d, 2H), 7.31–7.71 (m, 3H). Elemental analysis: calc. for $C_{30}H_{24}S_2$, C 80.31%, H 5.39%, S 14.29%; found, C 80.26%, H 5.44%, S 14.21%. MS m/z ([M]$^+$): 448.

The other compounds **M2**, **M4**, **M6**, **M8** and **B** were prepared in the same manner as described for **M3**.

M2, a yellow crystal. TLC (petroleum ether), $R_f =$ 0.24. ^{1}H NMR (CDCl$_3$) (δ, ppm): 1.30–1.34 (t, 6H), 2.82–2.87 (t, 4H), 5.43–5.46 (dd, 1H), 5.83–5.87 (dd, 1H), 6.68–6.70 (d, 2H), 7.10–7.17 (q, 1H), 7.19–7.21 (d, 2H), 7.32–7.71 (m, 3H). Elemental analysis: calc. for $C_{28}H_{20}S_2$, C 79.96%, H 4.79%, S 15.25%; found, C 79.61%, H 4.87%, S 14.85%. MS m/z ([M]$^+$): 420.

M4, a yellow crystal. TLC (petroleum ether), $R_f =$ 0.37. ^{1}H NMR (CDCl$_3$) (δ, ppm): 0.92–0.96 (t, 6H), 1.34–1.44 (sextet, 4H), 1.62–1.69 (quintet, 4H), 2.78–2.82 (t, 4H), 5.42–5.45 (dd, 1H), 5.82–5.87 (dd, 1H), 6.67–6.69 (d, 2H), 7.09–7.17 (q, 1H), 7.19–7.20 (d, 2H), 7.31–7.71 (m, 3H). Elemental analysis: calc. for $C_{32}H_{28}S_2$, C 80.63%, H 5.92%, S 13.45%; found, C 80.55%, H 5.92%, S 13.33%. MS m/z ([M]$^+$): 476.

M6, a yellow crystal. TLC (petroleum ether), $R_f =$ 0.38. ^{1}H NMR (CDCl$_3$) (δ, ppm): 0.88–0.91 (t, 6H), 1.28–1.32 (m, 12H), 1.63–1.70 (quintet, 4H), 5.43–5.46 (dd, 1H), 5.83–5.87 (dd, 1H), 6.67–6.68 (d, 2H), 7.09–7.17 (q, 1H), 7.19–7.20 (d, 2H), 7.32–7.71 (m, 3H). Elemental analysis: calc. for $C_{36}H_{36}S_2$, C 81.15%, H 6.81%, S 12.04%; found, C 80.99%, H 6.76%, S 11.93%. MS m/z ([M]$^+$): 532.

M8, a yellow crystal. TLC (petroleum ether), $R_f =$ 0.5. ^{1}H NMR (CDCl$_3$) (δ, ppm): 0.87–0.90 (t, 6H), 1.28–1.32 (m, 20H), 1.63–1.70 (quintet, 4H), 2.77–2.81 (t, 4H), 5.43–5.46 (dd, 1H), 5.83–5.87 (dd, 1H), 6.67–6.68 (d, 2H), 7.09–7.17 (q, 1H), 7.19–7.20 (d, 2H), 7.31–7.71 (m, 3H). Elemental analysis: calc. for $C_{40}H_{44}S_2$, C 81.58%, H 7.53%, S 10.89%; found, C 81.52%, H 7.40%, S 10.86%. MS m/z ([M]$^+$): 588.

B, a pale yellow crystal. TLC (petroleum ether), $R_f =$ 0.24. ^{1}H NMR (CDCl$_3$) (δ, ppm): 2.38 (s, 6H), 5.41–5.43 (dd, 1H), 5.87–5.92 (dd, 1H), 7.16–7.18 (d, 4H), 7.27–7.30 (q, 1H), 7.36–7.75 (m, 7H). Elemental analysis: calc. for $C_{26}H_{20}$, C 93.94%, H 6.06%; found, C 93.75%, H 6.14%. MS m/z ([M]$^+$): 332.

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