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Novel high birefringence dibenzothiophenylacetylene liquid crystals

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We have designed, synthesized and evaluated dibenzothiophenylacetylene homologues as new heterocyclic molecules which were expected to have high $\Delta\alpha$ values and short wavelength UV absorption spectra. The dibenzothiophenyl acetylene homologues exhibited wide nematic phase ranges and had very high extrapolated Δn of over 0.6 and directly measured values of 0.5. The compounds with two dibenzothiophenyl rings were colourless, so that we have succeeded in obtaining colourless super-high Δn liquid crystals. We have also analysed the contribution of the transition band to the refractive indices and the birefringence. From the analysis, the main origins of Δn for compounds **1** and **2** are lower MOs than the HOMO and this results in the compatibility of large Δn and lack of colour. The dibenzothiophenylacetylene compounds behaved according to our design expectations.

1. Introduction

High birefringence (Δn) liquid crystals have various uses in the field of display technology, for example, in addition to conventional display devices like STN LCDs, in bright reflective displays including PD LCDs [1, 2], cholesteric displays [3], holographic switching devices [4] and directional reflectors [5, 6]. Besides display applications, such materials are thought to be applicable to laser beam steering [7] and infrared spatial modulators [8].

A number of high Δn liquid crystalline compounds have been studied [9–12] and representative studies have been reviewed in detail [13]. We have also developed new high Δn liquid crystals containing the phenylacetylene unit and succeeded in obtaining compounds which exhibit high Δn values of about 0.5, wide or practical nematic temperature ranges, good stabilities and lack of colour [14–17]. In our recent work [18], liquid crystalline compounds containing thiophenylacetylene and dibenzothiophenylacetylene moieties were investigated to obtain even higher Δn than the phenylacetylene homologues which are without hetero atoms in their frameworks. Some of them exhibited high Δn as expected, but they were coloured. Introduction of hetero atoms is thought to induce a red shift of the UV-Vis absorption spectra because the HOMO level is raised. Therefore it is important to restrain the decrease in the HOMO-LUMO gap in the design of high Δn liquid crystalline compounds with heterocyclic rings.

In this paper, we have designed and synthesized dibenzothiophenylacetylene compounds and evaluated their physical properties.

2. Molecular designs

Refractive index is decided by polarizability and number density as expressed by the Vuks equation [19]. Increasing the polarizability along the molecular long axis is effective for increasing Δn. We have introduced dibenzothiophenyl rings with larger Δn than a phenyl ring because this was expected to cut the conjugation system in the molecule because of the different HOMO level from that of the phenyl ring. Before synthesis started, anisotropy of polarizability and UV-Vis absorption spectra had been calculated [20]. From the results of the calculations (see table 1), it was predicted that the dibenzothiophenyl series would exhibit larger $\Delta\alpha$ and almost the same absorption edge as 3-ring and 4-ring acetylenes.

The molecular orbital HOMO and HOMO-2, which is the next-but-one lower level of HOMO, of model 1 are shown in figure 1. HOMO-2 is the next-but-one

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Table 1. Calculation of polarizability and absorption wavelength of model molecules.

Model molecules	Δα/a.u.[a]	Abs./nm[b]
	755	348
	819	354
	808	348
R1 	426	350
	681	349

[a] Calculated by MOPAC93 (revision number 2).

[b] Calculated by MOPAC-RPA program, single CI [20].

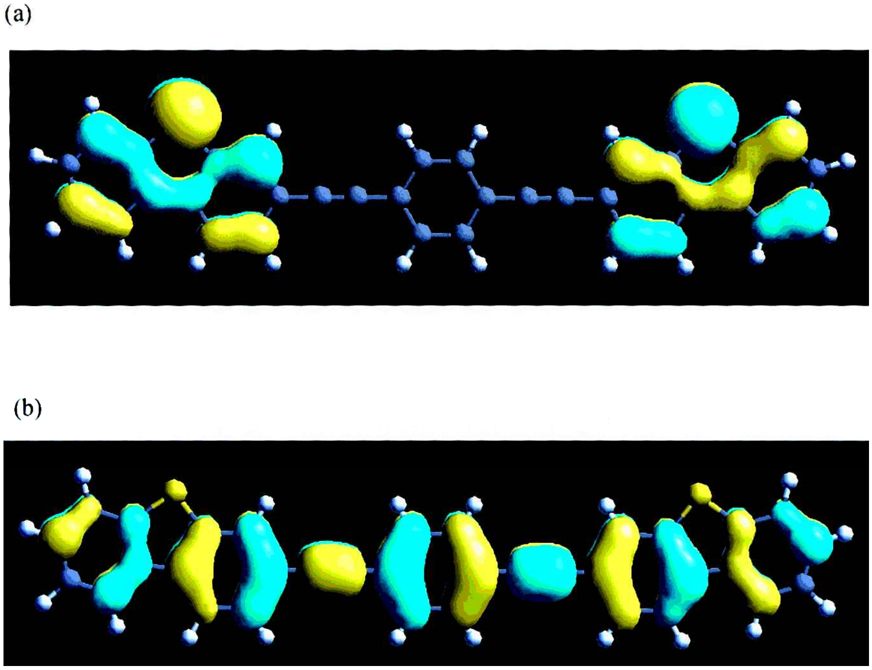
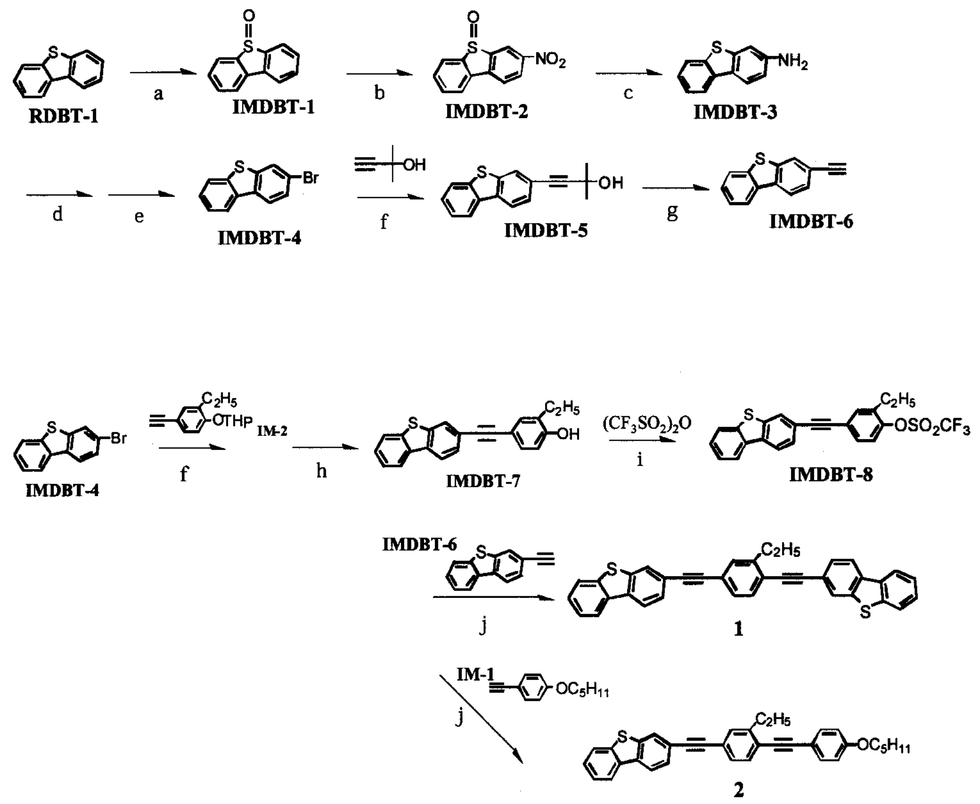


Figure 1. Image of MOs of the model molecule 1: (*a*) HOMO (*b*) HOMO-2.

lower energy level because of degeneration of HOMO and the next lower HOMO. The HOMO is localized at the dibenzothiophenyl rings. On the other hand, HOMO-2 is delocalized over the whole molecule. It might be speculated that the dibenzothiophenyl series exhibit high Δα because of the conjugated nature of HOMO-2 and short wavelength absorption because of the localized HOMO.

3. Experimental

The preparative routes for the dibenzothiophenylacetylene derivatives including some intermediates are shown in schemes 1 and 2; the main synthetic procedures are described in §6. The structures of the final compounds and the various synthetic intermediates were characterized by ^{1}H NMR spectroscopy; all spectra were recorded using $CDCl_3$ as solvent with TMS as internal



Scheme 1. a Cl_2/H_2O, b $HNO_3/H_2SO_4/CH_3COOH$, c $SnCl_2/HCl$, d $NaN0_2/H_2SO_4$, e CuBr/HBr, f $PdCl_2(PPh_3)_2/PPh_3/CuI$/ triethylamine, g KOH/toluene, h *p*-toluene sulphonic acid/methanol, i 4-pyrrolidin-1-yl-pyridine/pyridine, j $PdCl_2(PPh_3)_2/PPh_3/CuI/DMF$.

standard. All ^1H NMR spectra (UNITY300, Varian 300 MHz) were in accordance with the proposed structures. Mass spectra (SX102, JEOL) were also measured and identified the predicted molecular masses. The purity of each compound was checked by HPLC analysis (ODS A-212 column, Sumika Chemical Analysis Service) and all compounds were >99% pure.

Transition temperatures and phase sequences were measured using a Mettler FP82 hot stage and control unit in conjunction with polarizing optical microscopy (OPTIPHOT2-POL, Nikon) and the results were confirmed using DSC (DSC-200, Seiko Instruments Inc.). Refractive indices were obtained as extrapolated values from solutions containing 10 wt % of each test compound in MJ931381 (Merck Japan); error estimated as less than ±1%. 5 wt % solutions were used, estimated error of about ±1.5%, in cases of lower solubility. An Abbé refractometer (2T, ATAGO) with a sodium lamp (589 nm) was used to measure the refractive indices of the mixtures at 20°C. The birefringence of single compounds was also measured using the hollow prism method [21]. A He-Ne laser ($\lambda = 633$ nm) was used as the light source.

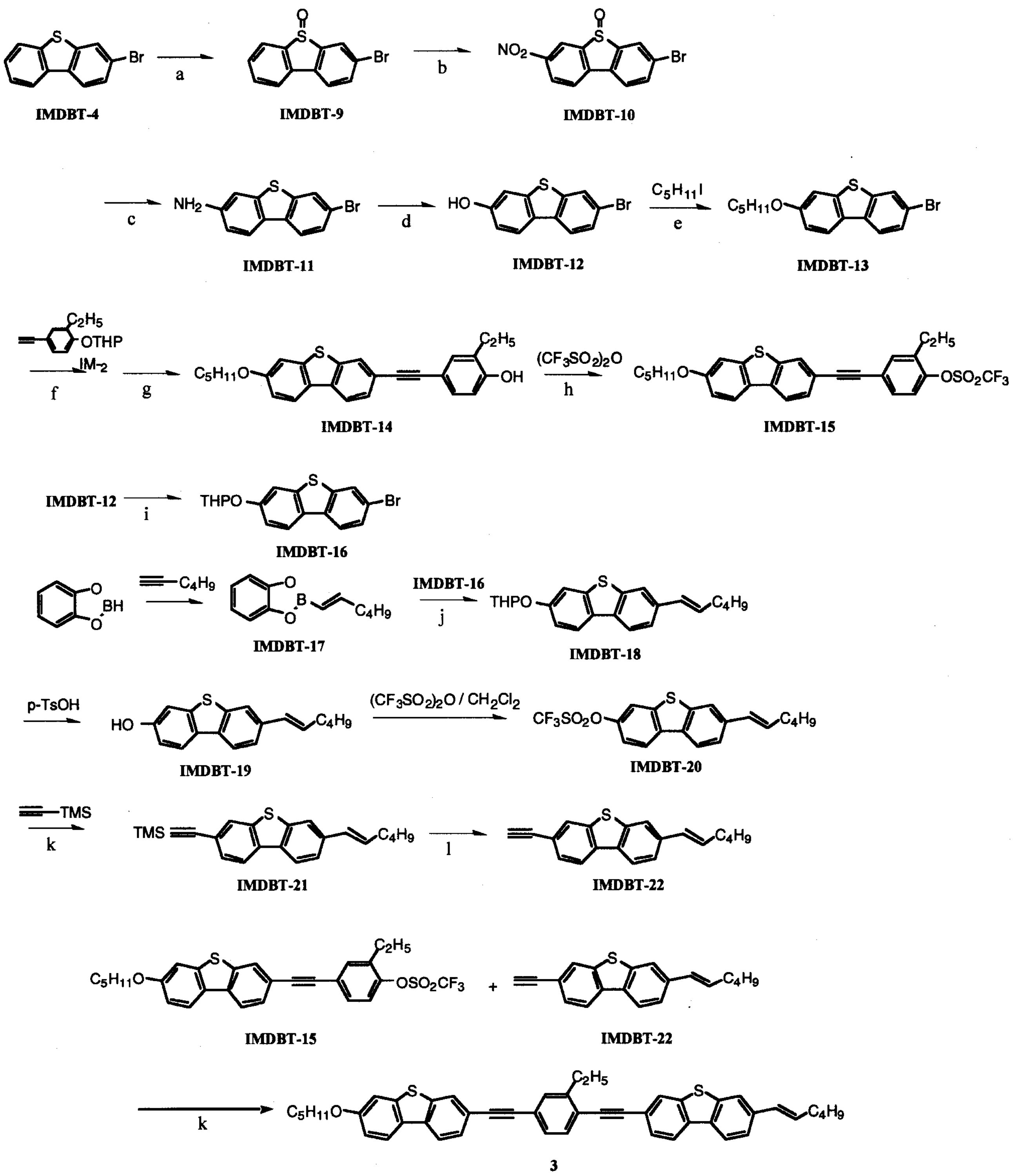
Order parameters were estimated by measuring polarized IR absorption spectra (FTIR, Magna860, Nicolet). 10 µm thick homogeneously aligned cells were prepared for such measurements; the substrates were CaF_2 plates coated with polyimide (LX-1800, Hitachi Chemical Co) and rubbed in one direction. Order parameters were calculated from the dichroic ratio of the acetylene C≡C stretching absorption peak at around 2220 cm^{-1}, according to the equation $S = (D-1)/(D+2)$, where D is the dichroic ratio and S is the order parameter [22].

UV and visible spectra were measured with a U-3500 (HITACHI) spectrometer. Solutions of samples were prepared by adding each compound (about 0.1 mg) to DMF (10 ml, spectroscopy grade). A quartz cell with 1 cm thickness was used for these measurements.

4. Results and discussion

4.1. *Physical properties of dibenzothiophenylacetylene derivatives*

Chemical structures and thermal properties of the dibenzothiophenylacetylene homologues are listed in table 2.



Scheme 2. a Cl_2/H_2O, b $HNO_3/H_2SO_4/CH_3COOH$, c $SnCl_2/HCl$, d $NaNO_2/H_2SO_4$, e K_2CO_3/methyl ethyl ketone, f $PdCl_2(PPh_3)_2/PPh_3/CuI$/triethylamine, g *p*-toluene sulphonic acid/methanol, h 4-pyrrolidin-1-yl-pyridine/pyridine/dichloromethane, i DHP/*p*-TsOH, j $PdCl_2(PPh_3)_2/Na_2CO_3$, k $PdCl_2(PPh_3)_2$/triethylamine, l K_2CO_3/methanol/THF.

Compound **1** containing two dibenzothiophenyl rings exhibited a high melting point and a wide range enantiotropic nematic phase. In the measurement by DSC, only the transition from the crystal to the nematic phase was observed on the heating cycle from room temperature to 330°C. Compound **2** with one dibenzothiophenyl ring

Table 2. Transition temperatures of dibenzothiophenyl derivatives.

Compound	Transition temperatures/°C
	Cr ● 277 ● N >300
	Cr ● 134 ● N ● 253 ● I
	Cr ● 255 ● SmX ● >300

exhibited a lower melting point of 134°C and a wide nematic phase range. Compound **3** with an alkenyl group connected directly to the core part exhibited a high melting point like compound **1** and had a smectic phase. This phase was thought to be highly ordered, but could not properly be assigned simply by observation of the texture using the polarizing microscope.

Extrapolated Δn values of the dibenzothiophenyl homologues were very high according to expectations (see table 3); compounds **1** and **3** had values of over 0.6. When E9 was used as host mixture (E9 has a higher T_{NI} than MJ931381), the extrapolated Δn of compound **1** was over 0.7. Refractive indices for compounds **2** and **1** were measured using the single compounds as shown in figure 2. They also exhibited very high Δn as single pure compounds, especially compound **1** with Δn over 0.5. The calculated $\Delta\alpha$ are increased by exchanging a phenyl ring for a dibenzothiophenyl ring (see table 4). The order parameter of dibenzothiophenyl compound **2** was slightly larger than that of the simple phenyl diacetylene compound **2r** (see figure 3), but the difference was so small that the increase in $\Delta\alpha$ must contribute mainly to the increase in Δn. Compound **3** also exhibited a high Δn over 0.6, but the alkenyl group apparently did not contribute an increase in Δn.

Absorption spectra of compounds **1**, **2** and reference compound **1r** are shown in figure 4. The spectral edges are all shorter than 400 nm, the shortest limit of the visible range. Compound **1** with two benzothiophenyl rings was colourless.

4.2. *Analysis of the contribution to birefringence*

Some semi-empirical models exist for describing the refractive index dispersions of liquid crystals [23]. Three absorption bands (one $\sigma \rightarrow \sigma^*$ and two $\pi \rightarrow \pi^*$ transition bands) have been correlated with the refractive indices

Table 3. Optical properties of dibenzothiophenyl derivatives and reference compound **1r**.

Compound	n_e[a]	n_o[a]	Δn[a]	n_e[b]	n_o[b]	Δn[b]
	2.223	1.590	0.633	2.332	1.589	0.743
	2.093	1.563	0.530	2.158	1.541	0.617
	2.181	1.551	0.631			
	—[c]	—[c]	—[c]	2.128	1.534	0.594

[a] Optical properties (at 20°C and $\lambda = 589$ nm) were extrapolated values from the mixture [liquid crystal (5 wt %) and MJ931381 (95 wt %)].

[b] Optical properties (at 20°C and $\lambda = 589$ nm) were extrapolated values from the mixture [liquid crystal (5 wt %) and E9 (95 wt %)].

[c] Insoluble in the host mixture.

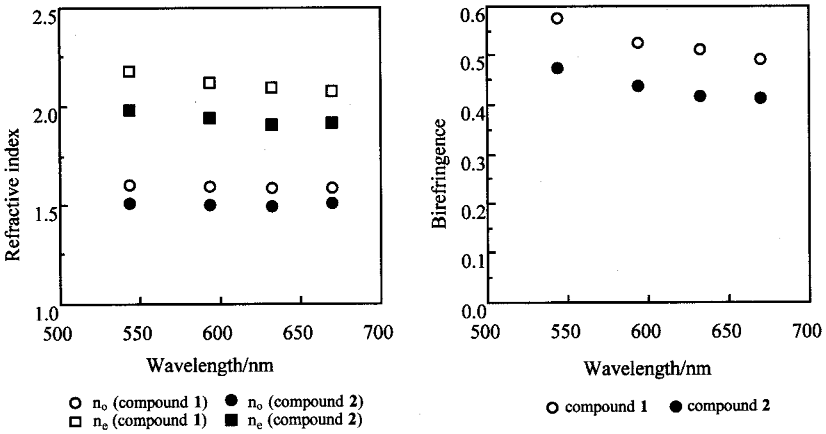


Figure 2. Refractive indices and birefringence values of compound **1** at 230°C and compound **2** at 150°C, measured by the hollow prism method.

Table 4. Calculated polarizabilities of dibenzothiophenyl derivatives and reference compound **2r**.

Compound	α_{xx}[a]	α_{yy}[b]	α_{zz}[b]	$\Delta\alpha$[c]
1	977	380	68	753
2	870	338	98	652
3	1251	456	146	950
2r	692	288	118	489

[a] α_{xx} = polarizability along the molecular long axis.
[b] α_{yy}, α_{zz} = polarizability along the molecular short axis.
[c] $\Delta\alpha = \alpha_{xx} - (\alpha_{yy} + \alpha_{zz})/2$.

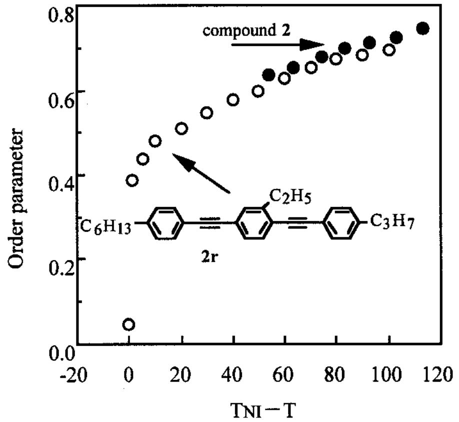


Figure 3. Order parameter of compound **2** and reference compound **2r**.

to identify the physical origins responsible for the observed values. In this section, the dependence of the refractive indices on the absorption wavelengths of compounds **2** and **1** were measured and analysed in order to confirm the origins of the physical features of the dibenzothiophenylacetylenes, which exhibited very high Δn and were colourless.

4.2.1. *Three-band model*

A semi-empirical formula correlating the microscopic molecular polarizabilities ($\alpha_{e,o}$) of a liquid crystal with the macroscopic refractive indices was obtained from the Vuks equation and the semi-empirical relationship between n_e and n_o [24]:

$$n_e = M\alpha_e + [1 + (M\alpha_e)(M\alpha_o)]^{1/2} \qquad (1\,a)$$

$$n_o = M\alpha_o + [1 + (M\alpha_o)(M\alpha_e)]^{1/2} \qquad (1\,b)$$

where $M = 1.4(4\pi N/3)$ and N is the number of molecules per unit volume. Equations (1) can be expanded by a power series to the first order since both $M\alpha_e$ and $M\alpha_o$ are less than unity

$$n_e \cong 1 + M\alpha_e\left(1 + \frac{1}{2}M\alpha_o + \ldots\right) \qquad (2\,a)$$

$$n_o \cong 1 + M\alpha_o\left(1 + \frac{1}{2}M\alpha_e + \ldots\right) \qquad (2\,b)$$

At the off-resonance region, the molecular polarizability ($\alpha_{e,o}$) is related to the resonance absorption wavelength λ_i and the associated oscillator strength $(f_{e,o})_i$ as

$$\alpha_{e,o}(\lambda) \approx \sum_i (f_{e,o})_i \frac{\lambda^2 \lambda_i^2}{\lambda^2 - \lambda_i^2} \qquad (3)$$

In the three-band model, one $\sigma \rightarrow \sigma^*$ transition (designated as the λ_0 band and two $\pi \rightarrow \pi^*$ transitions (designated as the λ_1 and λ_2 bands with $\lambda_2 > \lambda_1$) are considered. The λ_0 band appears in the vacuum UV region; its actual wavelength has not been measured, but is expected to be located at around 120 nm. There are many σ-electrons available in a liquid crystal molecule, so that the transition intensity should be very strong. The λ_1 band of several conjugated liquid crystal molecules occurs at about 200 nm; it consists of two closely overlapped bands.

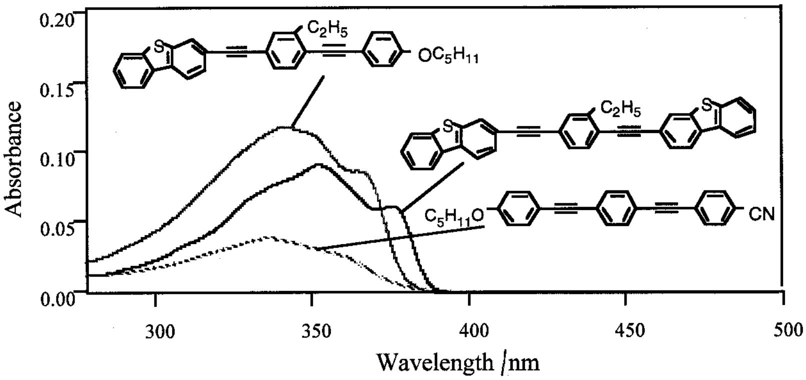


Figure 4. The effect of the dibenzothiophenyl ring on the UV-Vis absorption spectra.

Considering all three bands, we derive the following expressions for the refractive indices:

$$n_e \cong 1 + g_{0,e}\frac{\lambda^2\lambda_0^2}{\lambda^2-\lambda_0^2} + g_{1,e}\frac{\lambda^2\lambda_1^2}{\lambda^2-\lambda_1^2} + g_{2,e}\frac{\lambda^2\lambda_2^2}{\lambda^2-\lambda_2^2} \qquad (4a)$$

$$n_o \cong 1 + g_{0,o}\frac{\lambda^2\lambda_0^2}{\lambda^2-\lambda_0^2} + g_{1,o}\frac{\lambda^2\lambda_1^2}{\lambda^2-\lambda_1^2} + g_{2,o}\frac{\lambda^2\lambda_2^2}{\lambda^2-\lambda_2^2} \qquad (4b)$$

where the $g_i \sim Nz_i f_i$ are proportionality constants; Z_0 is the number of responsible σ-electrons, and $Z_1 = Z_2$ is the number of π-electrons in the molecule of a liquid crystal compound. The g_i determine the temperature effect on the refractive indices. In the visible region, $\lambda \gg \lambda_0$ so that the second terms in the equations (4) are reduced to constants: $n_{oe} = g_{0e}\lambda_{02}$ and $n_{oo} = g_{0o}\lambda_{20}$ which are independent of wavelength, but dependent on temperature. Furthermore, the ratio $g_{2e}/g_{1e} = m_e$ and $g_{2o}/g_{1o} = m_o$ for a liquid crystal can be obtained from the measured polarized absorption spectrum. Therefore, equations (4) are simplified to

$$n_e \cong 1 + n_{0,e} + g_{1,e}\left(\frac{\lambda^2\lambda_1^2}{\lambda^2-\lambda_1^2} + m_e\frac{\lambda^2\lambda_2^2}{\lambda^2-\lambda_2^2}\right) \qquad (5a)$$

$$n_o \cong 1 + n_{0,o} + g_{1,o}\left(\frac{\lambda^2\lambda_1^2}{\lambda^2-\lambda_1^2} + m_o\frac{\lambda^2\lambda_2^2}{\lambda^2-\lambda_2^2}\right) \qquad (5b)$$

The three-band model as described in equations (5) also involves two parameters (n_{0e} and g_{1e} for n_e, and n_{0o} and g_{1o} for n_o). These two parameters can be evaluated by simply measuring the refractive indices of a liquid crystal at two different wavelengths. Once these two unknowns are obtained, the wavelength dependent refractive indices of the liquid crystal can be calculated and the contribution of each band to the overall refractive index can be evaluated quantitatively.

4.2.2. *Analysis of refractive indices*

The data used for the analysis are listed in table 5. The parameters m_e and m_o are calculated from the polarized absorption spectra as shown in figures 5 and 6. These data were measured by mixing 1 wt % of each compound in a host liquid crystal mixture A at room

Table 5. Refractive indices and dichroic ratios of polarized UV spectra of dibenzothiophenyl derivatives and reference compound **3r**.

	Compound **1** (at 230°C)			Compound **2** (at 150°C)			Compound **3r**[a] (at 90°C)		
Wavelength/nm	n_o	n_e	Δn	n_o	n_e	Δn	n_o	n_e	Δn
670	1.581	2.073	0.492	1.536	1.959	0.422	1.499	1.870	0.372
632.8	1.584	2.096	0.512	1.538	1.974	0.436	1.501	1.880	0.380
594	1.590	2.116	0.526	1.540	1.997	0.457	1.502	1.896	0.395
543.5	1.602	2.178	0.577	1.551	2.041	0.490	1.509	1.930	0.421
m_o		0.65			0.65			0.83	
m_e		0.81			0.85			0.91	

[a]

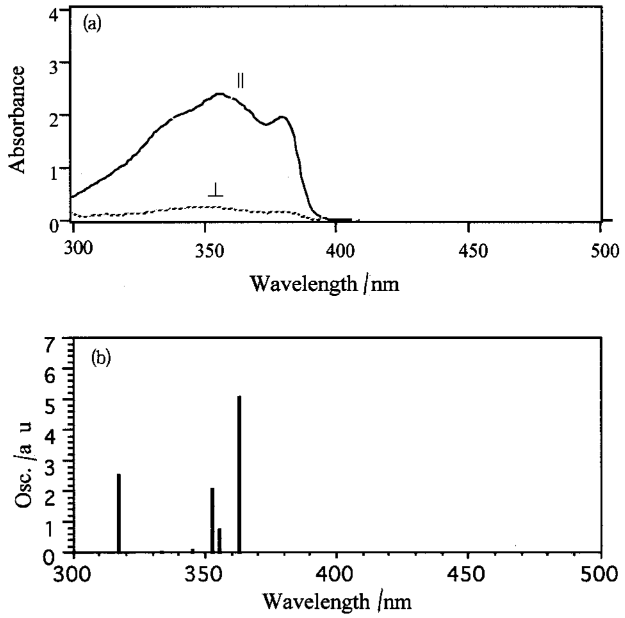


Figure 5. Absorption spectra of compound **1**. (*a*) Polarized spectra of compound **1** in mixture A (table 6); (*b*) calculated spectrum.

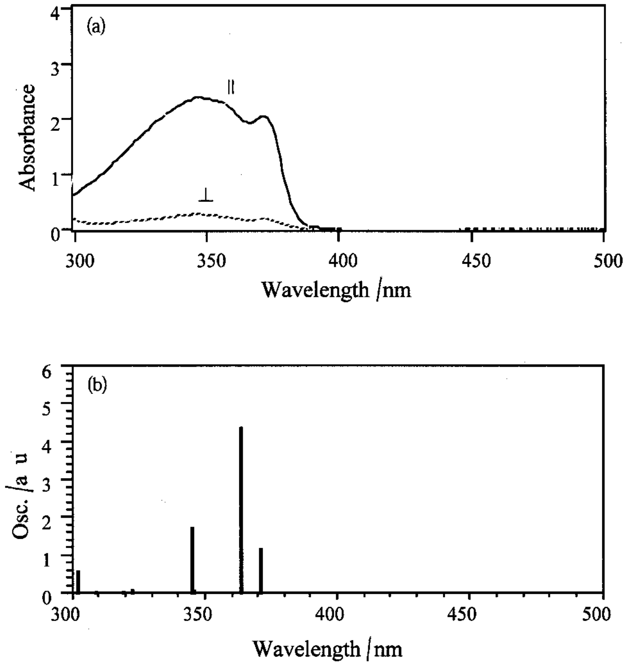
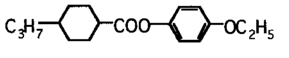
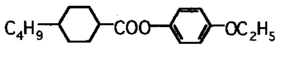
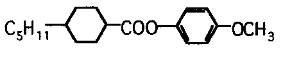
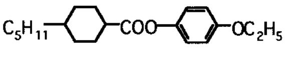
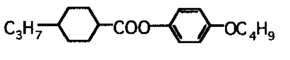


Figure 6. Absorption spectra of compound **2**. (*a*) Polarized spectra of compound **2** in mixture A (table 6); (*b*) calculated spectrum.

temperature. The compositions of the mixture A are shown in table 6. In this study, the ratio of m_e and m_o was treated as constant for simplicity [24].

Once m_e and m_o are known, the number of adjustable parameters of the three-band model is reduced to two.

Table 6. Constituents and physical properties of mixture A.

Constituents	Concentration/mol %
	18.3
	21.0
	20.9
	13.3
	26.5
Physical properties	
$\mathrm{Cr} \xrightarrow{2} \mathrm{N} \xrightarrow{75} \mathrm{I}$ (°C)	
$\Delta n = 0.088$ (20°C, 633 nm)	

Figures 7 and 8 show, respectively, the fittings of the experimental results for compound **2** at 150°C and compound **1** at 230°C to the three-band model; the fittings were very good. The contributions of each band, defined as in equations (5), to the total refractive indices of the compounds were evaluated by using the fitting parameters of $n_{\mathrm{ie,o}}$ and $g_{\mathrm{ie,o}}$. From the results, the λ_0 band makes a greater contribution to the refractive indices than the sum of the λ_1 and λ_2 bands. The contribution of λ_1 band to n_o was slightly larger than that of λ_2. Contrary to this, the λ_2 band makes more contribution to n_e and Δn than λ_1. The contribution of λ_2 to Δn of compound **1** was smaller than that of compound **2**.

The contribution of each MO to Δn was estimated by using the assignment of the calculated transitions [20]. The calculated transitions are listed in table 7. The MO numbers of the HOMO of compounds **2** and **1** were 91 and 89, respectively. The transitions from the HOMO mainly contributed to the λ_2 transition with respect to compound **2**.

However, in the case of compound **1**, the contribution of the transition from the MO lower than HOMO was the largest. The contribution rates of each MO to Δn at 600 nm are summarized in table 8. Compound **3r**, which is a three-ring phenylacetylene, was analysed in the same way for comparison. The main origins of Δn for compounds **1** and **2** were MOs lower than the HOMO and this resulted in the combination of large Δn and lack of colour. In contrast to this, compound **3r** which is a simple π-conjugated compound showed a main contribution from the HOMO.

From the analysis of the contribution of each band to Δn, it has been confirmed that the molecular design involving the combination of the dibenzothiophenyl ring

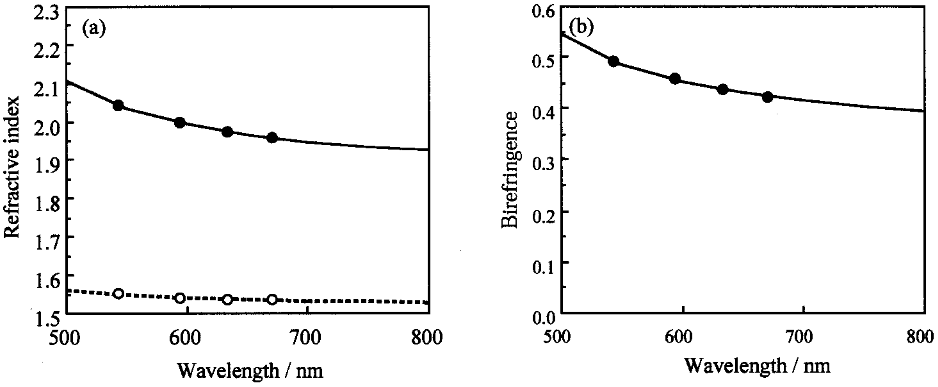


Figure 7. Wavelength dependence of the refractive indices and birefringence of compound **2** at 150°C. Circles are experimental data; solid or dashed lines are the fitting curves, equation (5).

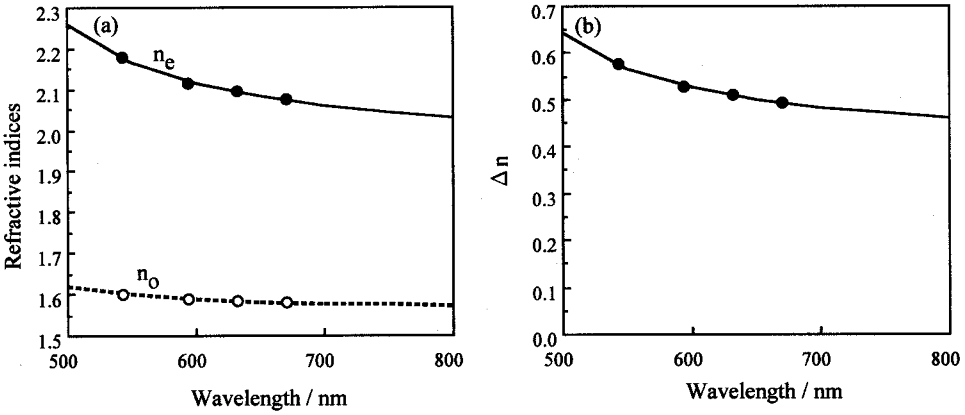


Figure 8. Wavelength dependence of refractive indices and birefringence of compound **1** at 230°C. Circles are experimental data; solid or dashed lines are the fitting curves, equation (5).

and the ethynyl group has been successful in increasing Δ*n*, while restraining the red-shift of the UV absorption spectra.

5. Conclusions

We synthesized new dibenzothiophenylacetylene homologues, and evaluated their thermal and optical properties for comparison with phenylacetylene homologues. The dibenzothiophenylacetylene homologues exhibited wide nematic phase ranges and very high extrapolated Δ*n* of over 0.6 and values of 0.5 by direct measurement. The compounds with two dibenzothiophenyl rings were colourless, so that we have succeeded in obtaining colourless super-high Δ*n* liquid crystals. We also analysed the contribution of the transition band to the refractive indices and birefringence.

6. Synthesis

6.1. *Bis[1,4-(4-dibenzothiophenyl)ethynyl]-3-ethyl-benzene (1)*

A solution of RDBT-1 (27.64 g) in carbon tetrachloride (276.4 g) was degassed with nitrogen, and Cl_2 gas was bubbled through at 2°C for 5 h. The solution was poured into ice water (400 g) and the mixture stirred for 50 min. The mixture was filtered and the insolubles were washed with water. The filtrate was concentrated and shaken with toluene/*n*-hexane 1/1 to give IMDBT-1. Yield 18.53 g (59.9%), purity 97.1%.

Glacial acetic acid (164.5 g) was degassed with nitrogen and cooled to 5°C. After adding sulphuric acid (549.3 g), IMDBT-1 was added at 23°C; 70% nitric acid was then added at 6°C and the mixture stirred for 2 h. The product was filtered off and washed with water; the dry filter cake was triturated with ethanol to give IMDBT-2. Yield 69 g (85.6%), purity 95.6%.

IMDBT-2 (69.0 g) and glacial acetic acid (690 g) were degassed with nitrogen. A solution of $SnCl_2$ (320.1 g) in concentrated hydrochloric acid (439.5 g) was added at 24 to 33°C and stirred for 12 h. The product was filtered off and washed with glacial acetic acid/concentrated hydrochloric acid 1/1. Aqueous 10% NaOH (600 g) was added and the product was extracted into ethyl acetate. After washing with water and concentration, the residue was purified by column chromatography (silica gel,

Table 7. Transition energy and contribution of compounds **1** and **2**.

Compound **1**				Compound **2**			
Transition energy/nm		Contribution		Transition energy/nm		Contribution	
Obs.	Calc.	MO number	%	Obs.	Calc.	MO number	%
380	363	87→90	40.0	372	371	91→92	46.7
		86→91	14.5			91→93	15.1
		89→90	10.9			89→94	10.7
		88→91	7.9			90→93	8.1
		85→92	4.9			90→94	5.7
		88→90	4.5			91→95	1.9
		89→91	2.5			89→93	1.8
		86→93	2.4			84→98	1.8
		89→92	2.1			88→94	1.7
		87→92	2.0			89→92	1.3
		87→94	1.6				
		85→94	1.2	347	364	90→92	52.7
		88→93	1.1			89→93	12.0
		84→95	1.0			91→93	7.2
						91→94	6.3
356	353	87→90	22.9			89→92	5.9
		88→91	21.1			88→95	3.2
		89→90	9.7			88→93	1.8
		86→93	6.2			89→94	1.7
		86→91	5.9			87→97	1.2
		89→91	5.9				
		89→92	5.3				
		88→90	4.9				
		87→94	3.9				
		85→92	2.8				
		88→92	2.5				
		89→94	1.7				
		85→94	1.4				

Table 8. Contribution rates of each MO to Δn at 600 nm.

MO level[a]	Contribution rate (%) Compound **1**	Compound **2**	Compound **3r**
HOMO	11.3	13.0	22.9
HOMO-1	11.1	19.9	4.8
HOMO-2	20.1	10.2	12.3
HOMO-3	8.8	2.0	2.1
HOMO-4	3.1	0.4	3.2
HOMO-5	0.3	0.0	0.5

[a] HOMO-X: X is the MO number below the HOMO (e.g. HOMO-1 is the second HOMO).

chloroform) to give IMDBT-3. Yield 48.0 g (87.4%), purity 97.7%.

A solution of $NaNO_2$ (18.28 g) in 98% sulphuric acid was degassed with nitrogen and cooled to 2°C. A solution of IMDBT-3 (48.0 g) in glacial acetic acid (576 g) was added and the mixture stirred at 5 to 8°C for 1.5 h. Ether (500 ml) was added at 5 to −5°C and stirring continued for 0.5 h. The product was filtered off and washed with ether. The wet filter cake was added to a solution of CuBr (51.84 g) in 48% aqueous HBr (1037 g), stirred at 25 to 64°C for 0.5 h, under reflux at 64°C for 2 h and then filtered off and washed with water. After drying, the product was purified by column chromatography (silica gel, *n*-hexane) to give IMDBT-4. Yield 41.8 g (65.9%), purity 97.4%.

A mixture of IMDBT-4 (10.53 g), $PdCl_2(PPh_3)_2$, 0.21 g, PPh_3 (0.21 g), CuI (0.11 g) and triethylamine (40.5 g) was degassed with nitrogen. A solution of propargyl alcohol (5.05 g) in ethyl acetate (2.5 g) was added at 76°C and the mixture stirred for 2 h. The reaction mixture was filtered, the insoluble materials were washed with ethyl acetate and the filtrates concentrated. Purification of the residue by column chromatography (silica gel, *n*-hexane/ethyl acetate = 5/1 with 0.1% triethylamine) gave IMDBT-5. Yield 9.75 g (92.9%), purity 98.5%.

A solution of IMDBT-5 (9.75 g) and potassium hydroxide (0.4 g) in toluene (48.8 g) was degassed with nitrogen gas and stirred at 95°C for 3.5 h. The mixture was concentrated and the residue purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) to give IMDBT-6. Yield 6.6 g (86.6%), purity 99.6%. ^{1}H NMR ($CDCl_3$, δ): 3.15 (s, 1H), 7.43–7.46 (m, 2H), 7.53–7.56 (m, 1H), 7.81–7.84 (m, 1H), 7.97–8.11 (m, 3H).

A solution of IMDBT-4 (18.95 g), $PdCl_2(PPh_3)_2$, 0.387 g, PPh_3 (0.38 g), CuI (0.19 g) and triethylamine (72.9 g) was degassed with nitrogen. A solution of IMDBT-2 (17.41 g) in ethyl acetate (9.1 g) was added at 76 to 80°C and the mixture stirred for 5 h. The reaction mixture was filtered, the insolubles were washed with ethyl acetate and the filtrate was concentrated. Methanol (129.6 g), *p*-toluene sulphonic acid (0.32 g) and THF (129.6 g) were added and the whole stirred at 23 to 40°C for 2 h. Triethylamine (2 g) was added and the mixture concentrated. Purification by column chromatography (silica gel, *n*-hexane/ethyl acetate = 10/1 with 0.1% triethylamine) gave IMDBT-7. Yield 14.1 g (59.6%), purity 95.1%.

IMDBT-7 (14.1 g) was degassed with nitrogen. A solution of pyridine (28.1 g) and 4-pyrrolidin-1-yl-pyridine (0.28 g) in toluene (70.5 g) was added and the mixture stirred at 2°C. A solution of trifluoromethanesulphonic anhydride (18.17 g) in toluene was added and the whole stirred at 0 to 2°C for 1.5 h. Ethyl acetate and water were added and the product was extracted into the organic layer. It was purified by column chromatography (silica gel, *n*-hexane/chloroform = 20/1) to give IMDBT-8. Yield 18.62 g (94.3%), purity 97.5%. ^{1}H NMR ($CDCl_3$, δ): 1.29 (t, 3H, $J = 7.5$ Hz), 2.75 (q, 2H, $J = 7.5$ Hz), 7.20–7.26 (m, 1H), 7.40–7.60 (m, 5H), 7.81–7.89 (m, 1H), 8.01–8.18 (m, 3H).

A solution of IMDBT-8 (5.53 g), $PdCl_2(PPh_3)_2$ (0.11 g), PPh_3 (0.38 g) and triethylamine (3.64 g) in DMF (33.2 g) was degassed with nitrogen. A solution of IMDBT-6 (4.50 g) in DMF (6.8 g) was added at 63 to 68°C and stirred for 7 h. The reaction mixture was filtered, the filtrate was shaken with ethyl acetate and the extract concentrated. Purification by column chromatography (silica gel, *n*-hexane/chloroform = 5/1 with 0.1% triethylamine) and recrystallization from chloroform gave compound **1**. Yield 2.86 g (69.1%), purity 99.5%. ^{1}H NMR ($CDCl_3$, δ): 1.38 (t, 3H, $J = 7$ Hz), 2.95 (q, 2H), 7.37–7.58 (m, 7H), 7.58–7.69 (m, 2H), 7.83–7.90 (m, 2H), 8.02–8.08 (m, 2H), 8.11–8.20 (m, 4H). IR (CaF_2 cell) ν_{max}: 3052, 3022, 2965, 2590, 2191, 1931, 1862, 1770, 1586, 1558, 1492, 1448, 1393, 1307, 1288, 1253, 1224, 1155, 1070, 1021 cm^{-1}. MS *m/z* 518 (M^+).

6.2. *1-(4-dibenzothiophenyl)ethynyl-3-ethyl-4-4-n-pentoxyphenylethynylbenzene (2)* see scheme 1

A solution of IMDBT-8 (5.53 g), $PdCl_2(PPh_3)_2$ (0.17 g) and triethylamine (3.64 g) in DMF (33.2 g) was degassed with nitrogen. A solution of IM-1 (4-*n*-pentoxyphenylacetylene, 3.84 g) in DMF (4.3 g) was added at 64 to 68°C and the mixture stirred for 10 h. The product was filtered off, washed with ethyl acetate and the extracts concentrated. Purification by column chromatography (silica gel, chloroform with 0.1% triethylamine), gave a product which was redissolved in ethyl acetate and again column chromatographed (silica gel, *n*-hexane/chloroform = 10/1 with 0.1% triethylamine) to give compound **2**. Yield 4.18 g (69.8%), purity 100%. ^{1}H NMR ($CDCl_3$, δ): 0.94 (t, 3H, $J = 7.5$ Hz), 1.33 (t, 3H, $J = 7.5$ Hz), 1.38–1.49 (m, 4H), 1.75–1.85 (m, 2H), 2.90 (q, 2H, $J = 7.5$ Hz), 3.97 (t, 2H, $J = 7.5$ Hz), 6.86–6.90 (m, 2H), 7.37–7.63 (m, 8H), 7.85–8.37 (m, 4H). IR (CaF_2 cell) ν_{max}: 3054, 2961, 2932, 2871, 2202, 1734, 1653, 1602, 1588, 1560, 1509, 1471, 1450, 1388, 1307, 1280, 1245, 1172, 1152, 1103, 1071, 1021 cm^{-1}. MS *m/z* 498 (M^+).

6.3. *1-[4-(7-n-Pentoxy)dibenzothiophenylethynyl]-3-ethyl-4-{4-[7-(2-heptenyl)]dibenzothiophenylethynyl}-benzene (3)*

A solution of IMDBT-4 (44.1 g) in carbon tetrachloride (441 g) was degassed with nitrogen and chlorine gas bubbled through at −7 to 12°C for 5 h. The solution was poured into ice water (1000 g) and stirred for 40 min. The product was filtered off and washed with carbon tetrachloride; the crystals were dried to give IMDBT-9. Yield 31.9 g (59.6%), purity 92.9%.

A solution of IMDBT-9 (27.9 g) in glacial acetic acid (69.8 g) was degassed with nitrogen and cooled to 10°C. After adding sulphuric acid (239.8 g), 70% nitric acid (72.0 g) was added at −2 to 8°C and the mixture stirred for 2 h. The product was filtered off and washed with water; the dry filter cake was washed with ethanol to give IMDBT-10. Yield 31.9 g (98.5%), purity 88.5%.

IMDBT-10 (26.98 g) and glacial acetic acid (269.8 g) were degassed with nitrogen. A solution of $SnCl_2$ (112.7 g) in concentrated hydrochloric acid (158 g) was added at 14 to 18°C and the mixture stirred for 12 h. The product was filtered off and washed with glacial acetic acid/concentrated hydrochloric acid = 1/1. Aqueous 7% NaOH (1100 g) was added and the product was extracted into ethyl acetate. After washing with water and concentration of the organic layer, the residue, was purified by column chromatography (silica gel, *n*-hexane/chloroform = 1/1 with 0.1% triethylamine) to give IMDBT-11. Yield 17.31 g (74.8%), purity 91.9%.

A solution of $NaNO_2$ (8.93 g) in concentrated sulphuric acid (209.3 g) was degassed with nitrogen and cooled to 2°C. IMDBT-11 (24.0 g) was added and the mixture stirred at 2 to 4°C for 3 h. The organic materials were added to 65% sulphuric acid (348.7 g, 80°C) and water (99.8 g) and stirred at 80 to 85°C for 5 h. The product was filtered off, extracted into ethyl acetate

(300 ml) and the solution concentrated. The residue was purified by column chromatography (silica gel, chloroform) to give IMDBT-12. Yield 7.11 g (29.5%), purity 91.1%. ^{1}H NMR ($CDCl_3$, δ): 4.98 (s, 1H), 6.95–7.00 (m, 1H), 7.25–7.27 (m, 1H), 7.50–7.54 (m, 1H), 7.84–7.88 (m, 1H), 7.91–7.93 (m, 1H), 7.93–7.97 (m, 1H).

A solution of IMDBT-12 (3.16 g), K_2CO_3 (3.91 g) and 1-iodopentane (5.6 g) in methyl ethyl ketone (16.8 g) was degassed with nitrogen and stirred at 80 to 85°C for 4 h. The solids were filtered off at room temperature, washed with ethyl acetate (100 ml) and the filtrate concentrated. The residue was purified by chromatography (silica gel, *n*-hexane) to give IMDBT-13. Yield 3.31 g (85.5%), purity 92.4%. ^{1}H NMR ($CDCl_3$, δ): 0.95 (t, 3H, $J = 6$ Hz), 1.39–1.51 (m, 4H), 1.84 (tt, 2H, $J = 6$ Hz, 6 Hz), 4.05 (t, 2H, $J = 6$ Hz), 7.03–7.06 (m, 1H), 7.26–7.29 (m, 2H), 7.50–7.53 (m, 1H), 7.85–7.98 (m, 3H).

A solution of IMDBT-13 (3.30 g), $PdCl_2(PPh_3)_2$ (0.03 g), PPh_3 (0.06 g), CuI (0.03 g) and triethylamine (18.9 ml) was degassed with nitrogen. A solution of IM-2 (3.30 g) in triethylamine (2 g) was added at 60°C and the whole was stirred at 70°C for 7 h. The solids were filtered off, washed with ethyl acetate (100 ml) and the extract concentrated. Methanol (20 ml) and *p*-toluene sulphonic acid (0.10 g) were added and the mixture was stirred at room temperature for 4 h. After adding triethylamine (1.3 ml), the mixture was concentrated and the residue purified by chromatography (silica gel, *n*-hexane/ethyl acetate = 10/1 with 0.1% triethylamine) to give IMDBT-14. Yield 4.30 g (98.9%), purity 89.7%.

A solution of IMDBT-14 (3.92 g), pyridine (15.1 ml) and 4-pyrrolidin-1-yl-pyridine (0.4 g) in dichloromethane (37.8 ml) was degassed with nitrogen. A solution of trifluoromethanesulphonic anhydride (3.5 g) in dichloromethane (10 ml) was added and the mixture stirred at 1 to 3°C for 4 h. Ethyl acetate (200 ml) and water (50 ml) were added and the product was extracted into the organic phase. After separation and concentration, the product was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 10/1) to give IMDBT-15. Yield 4.10 g (78.8%), purity 98.4%. ^{1}H NMR ($CDCl_3$, δ): 0.95 (t, 3H, $J = 6$ Hz), 1.30 (t, 3H, $J = 6$ Hz), 1.40–1.54 (m, 4H), 1.85 (tt, 2H, $J = 6$ Hz, 6 Hz), 2.76 (q, 2H, $J = 6$ Hz), 4.06 (t, 2H, $J = 6$ Hz), 7.05–7.08 (m, 1H), 7.23–7.32 (m, 2H), 7.43–7.58 (m, 3H), 7.97–8.02 (m, 3H).

A solution of IMDBT-12 (5.2 g) and *p*-toluene sulphonic acid (0.0007 g) in chloroform (150 ml) was degassed with nitrogen. Dihydropyran (4.8 g) was added at 1°C and the mixture was stirred for 6 h. After adding triethylamine (3 ml), the mixture was concentrated and the residue purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 13/1 with 0.1% triethylamine) to give IMDBT-16. Yield 6.42 g (14.3%), purity 89.9%.

A solution of 1-hexyne (3.5 ml) in THF (5 ml) was degassed with nitrogen. A solution of RDBT-2—see scheme 2—in THF (1 mol l^{-1}, 36 ml) was added and the mixture stirred at 68°C for 8 h; it was then concentrated and used in the next step without isolation. The residue (IMDBT-17), IMDBT-16 (5.0 g), tetrakis-(triphenylphosphine)palladium(0) (1.6 g), toluene (26 ml) and ethanol (40 ml) were degassed with nitrogen. 2M aqueous Na_2CO_3 (11 ml) was added and the mixture heated at 73°C under reflux for 4 h. Ethyl acetate and water were added at room temperature and the product was extracted into the organic phase which was then concentrated. The residue (IMDBT-18), methanol (41 ml) and *p*-toluene sulphonic acid (0.5 g) were degassed with nitrogen and stirred for 3 h. Triethylamine (2 ml) was added and the mixture concentrated. The residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 8/1 with 0.1% triethylamine) to give IMDBT-19. Yield 3.5 g (65.3%), purity 95.8%.

A solution of IMDBT-19 (3.8 g), pyridine (22 ml) and 4-pyrrolidin-1-yl-pyridine (0.6 g) in dichloromethane (54 ml) was degassed with nitrogen. A solution of trifluoromethanesulphonic anhydride (2.6 ml) in dichloromethane (8 ml) was added and the mixture stirred at 1.3°C for 4 h. Dichloromethane (80 ml) and water (50 ml) were added and the product was extracted. After concentration of the organic phase, the residue was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 5/1 with 0.1% triethylamine) to give IMDBT-20. Yield 4.4 g (96.9%), purity 99.7%. ^{1}H NMR ($CDCl_3$, δ): 0.95 (t, 3H, $J = 6$ Hz), 1.36–1.52 (m, 4H, $J = 6$ Hz), 2.29 (dt, 2H, Jd = 6 Hz, Jt = 6 Hz), 6.35 (dt, 1H, Jd = 15 Hz, Jt = 6 Hz), 6.50 (d, 1H, $J = 15$ Hz), 7.31–7.35 (m, 1H), 7.47–7.50 (m, 1H), 7.72–7.78 (m, 2H), 8.00–8.11 (m, 2H).

A solution of IMDBT-20 (3.0 g), $PdCl_2(PPh_3)_2$, (0.2 g) and triethylamine (1.5 ml) in DMF (29 ml) was degassed with nitrogen. A solution of trimethylsilylacetylene (2 ml) was added at 45°C and the whole was stirred for 4 h. Diethyl ether (50 ml) and water (20 ml) were added at room temperature and the product was extracted into the organic phase which was concentrated and the residue purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 20/1 with 0.1% triethylamine) to give IMDBT-21. Yield 2.60 g (63.6%), purity 88.8%.

A solution of IMDBT-21 (2.60 g), K_2CO_3 (0.3 g) and methanol (70 ml) in THF (35 ml) was degassed with nitrogen and stirred at room temperature for 2 h. Ethyl acetate was added, the mixture was filtered and the solids washed with the solvent. After concentration, the product was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 20/1 with 0.1% triethylamine) to give IMDBT-22. Yield 1.57 g (68.8%), purity 92.4%. ^{1}H NMR ($CDCl_3$, δ): 0.94 (t, 3H, $J = 6$ Hz), 1.35–1.53 (m, 4H), 2.26 (dt, 2H, Jd = 6 Hz, Jt = 6 Hz), 3.17 (s, 1H), 6.34 (dt, 1H, Jd = 15 Hz, Jt = 6 Hz), 6.49 (d, 1H, J = 15 Hz), 7.43–7.46 (m, 1H), 7.51–7.55 (m, 1H), 7.76–7.77 (m, 1H), 7.94–8.11 (m, 3H).

A solution of IMDBT-15 (1.90 g), $PdCl_2(PPh_3)_2$ (0.07 g) and triethylamine (0.7 ml) in DMF (14 ml) was degassed with nitrogen. A solution of IMDBT-22 (1.60 g) in DMF (4 ml) was added at 60°C and the mixture stirred for 2 h. Diethyl ether (20 ml) and water (10 ml) were added and the product was extracted into the organic phase. After washing this with water and concentration, the product was purified by column chromatography (silica gel, *n*-hexane/chloroform = 10/1 with 0.1% triethylamine) to give compound **3**. Yield 0.12 g (5%), purity 97.7%. ^{1}H NMR ($CDCl_3$, δ): 0.95 (t, 3H, J = 6 Hz), 0.96 (t, 3H, J = 6 Hz), 1.34–1.4 (m, 11H), 1.85 (tt, 2H, J = 6 Hz, 6 Hz), 2.26 (dt, 2H, Jd = 6 Hz, Jt = 6 Hz), 2.93 (q, 2H, J = 6 Hz), 4.06 (t, 2H, J = 6 Hz), 6.34 (dt, 1H, Jd = 15 Hz, Jt = 6 Hz), 6.51 (d, 1H, J = 15 Hz), 7.05–7.09 (m, 1H), 7.31–7.61 (m, 7H), 7.79–7.80 (m, 1H), 7.98–8.09 (m, 6H). IR (CaF_2 cell) ν_{max}: 3049, 2959, 2930, 2871, 2202, 1902, 1729, 1650, 1589, 1562, 1537, 1494, 1461, 1393, 1322, 1260, 1247, 1217, 1144, 1058, 1028 cm^{-1}. MS m/z 687 (M^+).

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