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Synthesis and properties of high birefringence liquid crystals: thiophenylacetylene and benzothiazolylacetylene derivatives

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We have synthesized and evaluated the physical properties of thiophenylacetylene and benzothiazolylacetylene derivatives in order to obtain higher Δn liquid crystals as compared with analogous phenylacetylene-based compounds. These new materials had poorer liquid crystallinity than the phenylacetylene derivatives. Exchanging the phenyl ring for a benzothiazole ring was effective in increasing Δn , whereas a thiophene ring decreased Δn because of the associated reduction in the anisotropic polarizability. These conjugated hetero rings shifted the UV absorption spectra into the visible region such that they are yellow or brownish in colour.

1. Introduction

High birefringence (Δn) liquid crystals are useful in not only conventional display devices like STN-LCDs, but also in scattering type displays such as PDLCs, in spatial light modulators, and in compensation films for the viewing angle, reflectors and polarizers. A number of materials have been studied for these purposes [1–3]. Most of these nematic compounds, including those being used, contain only carbon, hydrogen, oxygen and fluorine atoms. Recently, liquid crystalline compounds containing heterocyclic groups have been studied, not for use in displays but for other applications. Thiophenyl-based liquid crystalline compounds were developed as non-linear optic materials [4] and benzothiazolyl-based compounds have been studied as photoconductive materials [5, 6]. However, their optical properties, such as refractive index, have received little attention.

We have developed stable high Δn liquid crystals containing phenylacetylene which are highly conjugated along the molecular long axis [7, 8]. As expected, they exhibited high Δn values of over 0.4. To obtain higher Δn liquid crystals, heterocyclic groups were introduced to the phenylacetyl core. In this study, we have synthesized and evaluated the physical properties of thiophenylacetylene and benzothiazolylacetylene-based compounds in order to investigate the effect of these hetero-rings on the optical properties.

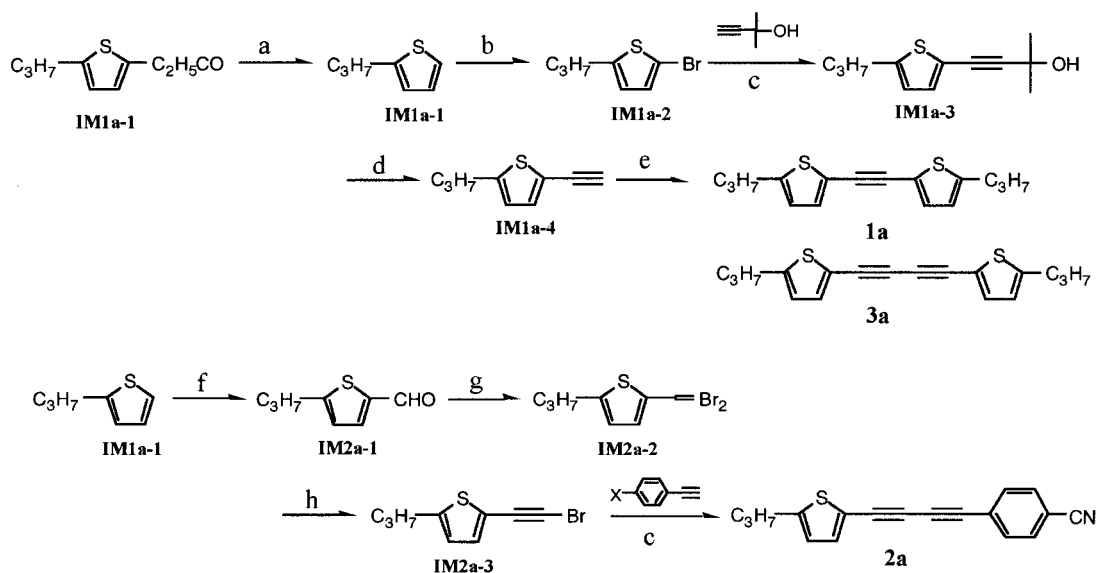
2. Experimental

The preparative routes for the thiophenylacetylene and benzothiazolylacetylene derivatives are shown in schemes 1 and 2, respectively. The main synthetic procedures are described in §5. The structures of the final compounds and various synthetic intermediates were characterized by ^1H NMR spectroscopy. All spectra were recorded in CDCl_3 with TMS as internal standard. The ^1H NMR spectra (UNITY300, Varian 300 MHz) were in agreement with the proposed structures. Mass spectra (SX102, Jeol) were also measured and the predicted molecular weights found. All the compounds in these series were of greater than 99% purity as measured using HPLC (ODS A-212 column, Sumika Chemical Analysis Service).

Transition temperatures and phase sequences were measured using a Mettler FP82 hot stage and control unit in conjunction with an optical microscope (Optiphot2-POL, Nikon) and these were confirmed using differential scanning calorimetry (DSC-200, Seiko Instruments Inc.).

Refractive indices was evaluated as extrapolated values from mixtures containing 10 wt% of each test compound in MJ931381 (Merck, Japan). An Abbe refractometer (2T, Atago) was used to measure the refractive indices of the mixtures at 20°C. A sodium lamp was used to provide the light source at 589 nm. UV and visible spectra were measured using a U-3500 Hitachi spectrometer. The samples were prepared by

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Scheme 1. a $\text{NH}_2\text{NH}_2/\text{KOH}$; b $\text{Br}_2/\text{methanol}$; c $\text{CuI}/\text{PdCl}_2(\text{PPh}_3)_2/\text{triethylamine}$; d $\text{KOH}/\text{toluene}$; e $\text{CuI}/\text{PdCl}_2(\text{PPh}_3)_2, \text{air}/\text{NH}_4\text{OH}/\text{ethanol}$; f DMF/POCl_3 ; g $\text{Zn}/\text{PPh}_3/\text{CBr}_4/\text{CH}_2\text{Cl}_2$; h $\text{NaOH}/\text{PEG-400}$.

dissolving each compound (about 0.1 mg) in DMF (10 ml, spectroscopy grade). A 1 cm thick quartz cell was used for this measurement.

3. Results and discussion

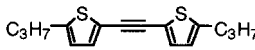
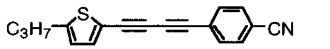
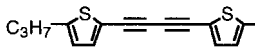
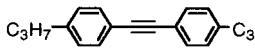
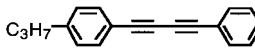
3.1. Physical properties of the thiophenylacetylene derivatives

The phase transition temperatures, associated enthalpies and refractive indices of the thiophenylacetylene derivatives are listed in table 1. Analogous phenylacetylene derivatives

(\mathbf{R}_1 and \mathbf{R}_2) are included for comparison. The thiophenylacetylene-based compounds are poorer liquid crystals than the corresponding phenylacetylene-based compounds. Compounds **1a** and **3a** did not exhibit liquid crystallinity while **2a** showed only a monotropic nematic phase. The melting points of the thiophenylacetylene series are lower than corresponding phenylacetylenes and; they exhibit good solubility in other nematic mixtures.

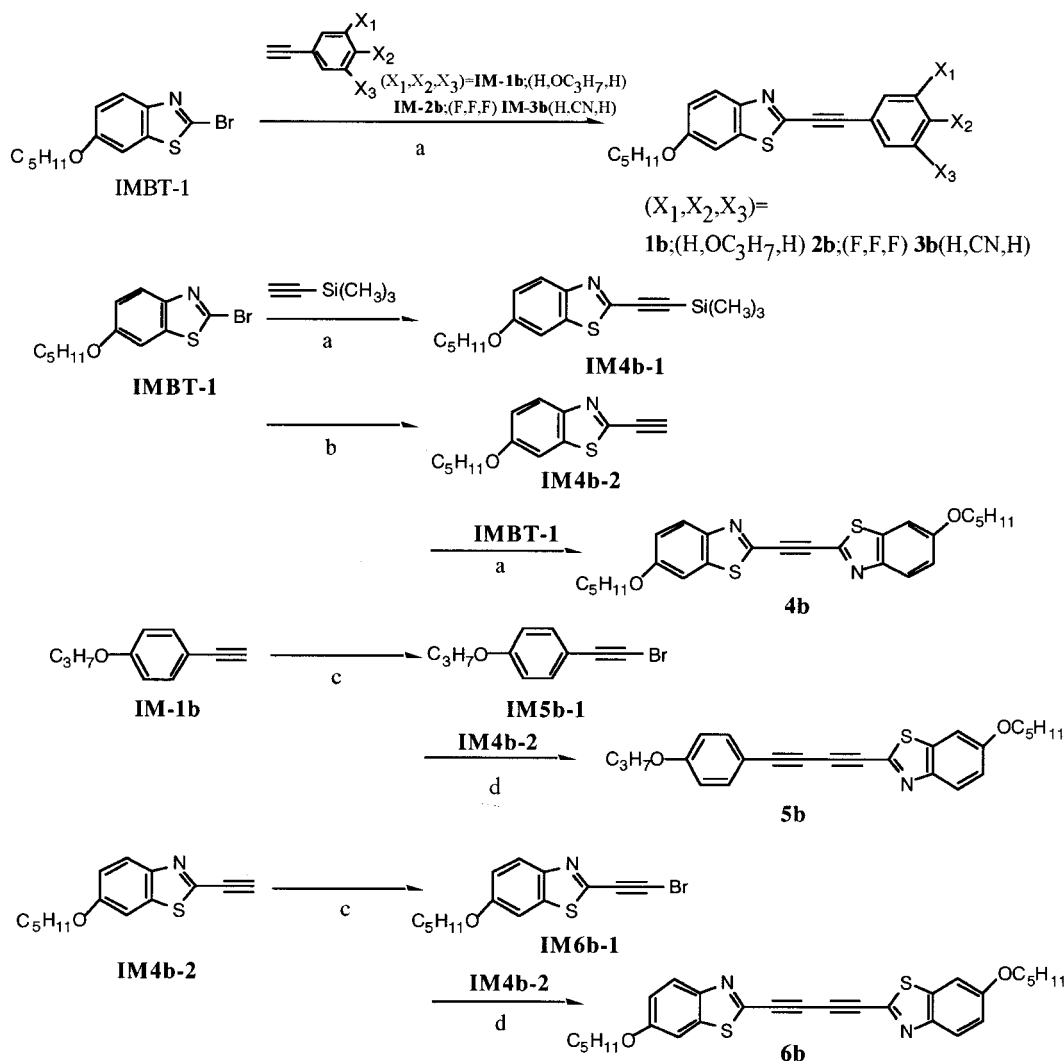
The values of Δn for the thiophenylacetylene series were around 0.3, which is moderately high. Δn was

Table 1. Physical properties of the thiophenylacetylene derivatives. (•) Denote a monotropic transition, Cr = crystal, N = nematic phase, I = isotropic.

Compound	Transition temperatures ($^{\circ}\text{C}$) and enthalpies (in square brackets, kJ mol^{-1})				n_e^a	n_o^a	Δn^a	$\Delta\alpha^b$
	Cr	N	I					
1a 	•	7[22.9]		•	1.732	1.575	0.157	241
2a 	•	114[37.9]	(• 107[0.1])	•	2.078	1.560	0.518	401
3a 	•	12[23.4]		•	1.911	1.584	0.327	363
\mathbf{R}_1 	•	73[20.2]		•	1.518	1.781	0.264	251
\mathbf{R}_2 	•	108[25.4]	• 133[1.4]	•	1.526	1.935	0.410	368

^a Optical properties (at 20°C and $\lambda = 589 \text{ nm}$) were extrapolated values of the mixture: liquid crystal (10 wt %) and MJ931381 (90 wt %).

^b Anisotropy of polarizability calculated by MOPAC 93. $\Delta\alpha = \alpha_x - (\alpha_y + \alpha_z)/2$; α_x = polarizability along molecule long axis; α_y, α_z = polarizability along molecular short axis.



Scheme 2. a PdCl₂(PPh₃)₂PPh₃/CuI/triethylamine; b K₂CO₃/methanol; c KOH, Br₂; d CuCl/NH₂OH·HCl/CH₃NH₂/methanol.

reduced by exchanging the phenyl group for a thiophenyl ring because of the reduction in the polarizability. As shown in table 1, the anisotropic polarizabilities of the thiophenylacetylene homologues are lower than those of phenylacetylene homologues.

3.2. Benzothiazolylacetylene derivatives

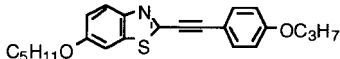
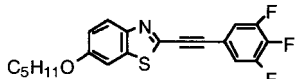
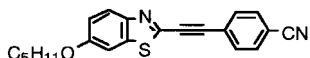
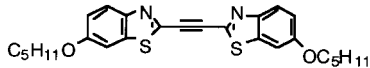
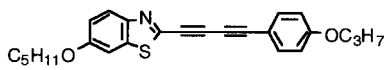

The physical properties of the benzothiazolylacetylene homologues are listed in table 2. They exhibit higher melting points and lower liquid crystal phase transition temperatures than the phenylacetylene and thiophenylacetylene homologues. Compounds **1b** to **4b** and **6b** did not exhibit liquid crystal phases. The transition enthalpies were larger than those of the reference compounds. The condensed ring increases the interaction area of the cores giving higher melting points and reduced liquid

crystalline behaviour. **5b** shows an enantiotropic nematic phase, but decomposes at 159°C; **6b** decomposes at 158°C prior to melting. The compounds containing a diacetylene fragment were less thermally stable than those having an acetylene linkage (**1b–4b**).

Δn was increased by exchanging the phenyl group for a benzothiazole ring. The fluorine-substituted compound (**2b**) showed a low Δn , while alkoxy substituents gave high Δn values of 0.3–0.5. As $\Delta\alpha$ increased on adding the benzothiazole ring, so did Δn . Compounds **3b** and **4b** showed poor solubility in the host nematic, and thus, their Δn values could not be estimated.

The benzothiazolylacetylene and thiophenylacetylene derivatives were yellow or brownish in colour. The absorption spectra of these series had longer absorption edges than that of even the colourless three-ring phenyl acetylene compound which has a higher Δn value of

Table 2. Physical properties of the benzothiazolylacetylene derivatives. Cr = crystal, N = nematic phase, I = isotropic.

Compound	Transition temperatures (°C) and enthalpies (in square brackets, kJ mol ⁻¹)			n_e^a	n_o^a	Δn^a	$\Delta\alpha^b$	
	Cr	N	I					
1b 	•	115[43.2]	•	1.878	1.543	0.335	395	
2b 	•	97[31.9]	•	1.780	1.540	0.240	351	
3b 	•	162[50.2]	•	—	—	—	—	
4b 	•	176[65.9]	•	—	—	—	—	
5b 	•	116[39.6]	•	decomposed at 159°C	1.554	2.057	0.503	530
6b 		decomposed at 158°C		1.537	2.015	0.478	636	

^a See footnote ^a to table 1.

^b See footnote ^b to table 1.

0.43 [9], see figure 1. It was considered that the conjugated hetero rings raise the HOMO level; indeed, the calculated HOMO levels of these compounds are -8.40 eV (**1a**) and -8.47 eV (**1b**), which are higher, than that of **R₁** (-8.56 eV). Therefore, the absorption spectra shifts to longer wavelengths on substituting the phenyl ring with a hetero ring.

4. Conclusions

We have synthesized new thiophenylacetylene and benzothiazolylacetylene homologues, and have evaluated their thermal and optical properties, in comparison with the analogous phenylacetylene homologues. These new series show poorer liquid crystalline behaviour than

the analogous phenylacetylene materials. The conjugated hetero ring systems shifted the UV absorption spectra into the visible region; as a result they are yellow or brownish in colour.

The thiophenylacetylenes exhibited low melting points and poor liquid crystallinity. Δn was also lower because of the reduced anisotropic polarizability. Exchanging the phenyl ring with a benzothiazole ring was effective in increasing Δn , but it decreased the liquid crystalline behaviour. Indeed, the benzothiazole-based compounds did not exhibit liquid crystalline behaviour except for one containing a diacetylene unit. Also, these materials decomposed at around 150°C. Thus further research to improve the liquid crystallinity, thermal stability and colour is needed if heterocyclic rings are to be incorporated into the conjugated core.

5. Synthesis

5.1. Bis(5-*n*-propylthiophene-2-yl)ethyne, **1a**

A solution of propionylthiophene (50 g) and hydrazine hydrate (71.4 g) in ethylene glycol (250 g) was degassed with nitrogen and then stirred at 131°C for 1 h. After adding potassium hydroxide (80 g) at 51°C, it was stirred again at 120°C for 4 h. The products were distilled and the distillate was extracted with ethanol, washed with water and 3% hydrochloric acid. After the water was removed using magnesium sulfate, it was dried to give **IM1a-1**; yield 41.5 g (92.2%).

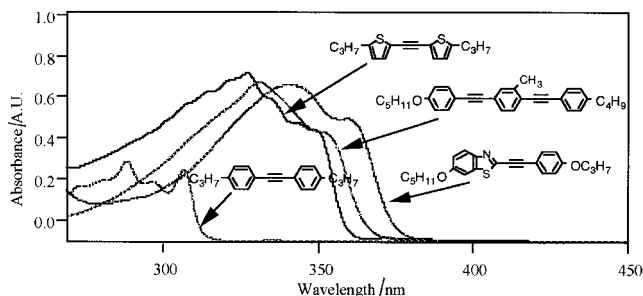


Figure 1. The effect of heterocyclic groups on the UV-Vis absorption spectra.

A solution of **IM1a-1** (20 g) in methanol (100 g) was degassed with nitrogen; methanol solution of bromine was added to it at -25°C and the mixture stirred for 1 h. Water and ether were added and the product extracted. The organic layer was washed with water and 1% aqueous NaHCO. After the water was removed using magnesium sulfate, it was dried to give **IM1a-2**; yield 27.7 g (57.9%).

A solution of **IM1a-2** (25.38 g), dichlorobis(triphenylphosphine)palladium ($\text{PdCl}_2(\text{PPh}_3)_2$, 1.27 g), triphenylphosphine (PPh_3 , 1.27 g), copper(I) iodide (0.51 g) and triethylamine (TEA, 50.1 g) 100 g was degassed with nitrogen; 1,2-dimethyl-3,1-butyn-2-ol (15.61 g) was added at 75°C and the mixture stirred for 1.5 h. After cooling to room temperature, the products was filtered. The filtrate was washed with toluene, concentrated and purified by column chromatography (silica gel, *n*-hexane/ethyl acetate, 8/1) to give **IM1a-3**; yield 20.3 g (72.6%).

A solution of **IM1a-3** (20.3 g) and potassium hydroxide (0.8 g) in toluene (101.5 g) was degassed with nitrogen and stirred at 93°C for 1 h. The reaction mixture was washed with water, concentrated and purified by column chromatography (silica gel, *n*-hexane with 0.1% triethylamine) to give **IM1a-4**; yield 4.6 g (77.7%).

A solution of **IM1a-2** (4.59 g), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.23 g), PPh_3 (0.23 g), copper(I) iodide (0.09 g) and TEA (11.3 g) in toluene (23 g) was degassed with nitrogen. A solution of **IM1a-4** (2.8 g) in toluene (11.2 g) was added at 80°C and the mixture stirred for 0.5 h. The product was filtered at room temperature, washed and concentrated. It was purified by column chromatography (silica gel, *n*-hexane) and recrystallized to give **1a**; yield 1.89 g (37.0%). $^1\text{H NMR}$ (δ): 0.97 (6H, t), 1.69 (4H, tq), 2.76 (4H, t), 6.66 (2H, d), 7.06 (2H, d). IR (CaF₂ cell) ν_{max} : 3072, 2960, 2930, 2871, 2191, 1718, 1485, 1456, 1379, 1339, 1280, 1227 cm^{-1} . MS m/z 274 (M^+).

5.2. 4-Nitrile-(5-*n*-propylthiophene-2-*y* l)-butadienylbenzene, **2a**

A solution of **IM1a-1** (12.62 g) in DMF (14.62 g) was degassed with nitrogen; POCl_3 (18.4 g) was added and the mixture heated to 80°C . After cooling to room temperature, sodium acetate was added to stop the reaction. The product was extracted with ether, and washed with water and 5% aqueous sodium carbonate. Water was removed by adding magnesium sulfate and **IM2a-1** was obtained by distillation; yield 13.75 g (91.0%).

Zn (9.81 g) and PPh_3 (39.34 g) in dichloromethane (120 g) was degassed with nitrogen. A solution of CBr_4 (49.74 g) in dichloromethane (249.74 g) was added and the reaction mixture stirred for 21 h at room temperature. A solution of **IM2a-1** (13.7 g) in dichloromethane (36.7 g) was added to the reaction mixture and this

stirred for 17 h. The product was filtered and the filtrate washed with dichloromethane and concentrated. The product was extracted using ethyl acetate; the solution was concentrated and purified by column chromatography (silica gel, *n*-hexane) to give **IM2a-2**; yield 23.1 g (89.6%).

5N sodium hydroxide solution (200 g) and PEG-400 400 g were degassed with nitrogen and stirred at room temperature. A solution of **IM2a-2** (23.1 g), PEG-400 (69.3 g) was added and the mixture stirred for 12 h. The product was extracted with water and ether; the ether layer was then washed with water. Water was removed by adding magnesium sulfate and the ether removed by distillation. The product was purified by column chromatography (silica gel, *n*-hexane) to give **IM2a-3** (14.3 g).

A solution of **IM2a-3** (5.96 g), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.3 g), PPh_3 (0.03 g), copper(I) iodide (0.12 g) and TEA (12.1 g) in toluene (24.3 g) was degassed with nitrogen. A solution of 4-ethynylbenzotrile (7.54 g) in toluene was added at 50°C , followed by stirring for 2 h. The product was filtered and the filtrate washed with toluene and concentrated. The wet cake was washed with *n*-hexane and purified by column chromatography (silica gel, *n*-hexane/ethylacetate 5/1, with 0.1% triethylamine) to give **2a**; yield 2.2 g (39.9%). $^1\text{H NMR}$ (δ): 0.98 (3H, t), 1.70 (2H, tq), 2.78 (2H, t), 6.69 (1H, d), 7.22 (2H, m), 7.55–7.64 (4H, m). IR (CaF₂ cell) ν_{max} : 2965, 2932, 2906, 2873, 2224, 2195, 2138, 1918, 1669, 1599, 1532, 1497, 1458, 1428, 1403, 1380, 1353, 1304, 1283, 1270, 1225 cm^{-1} . MS m/z 275 (M^+).

5.3. Bis(5-*n*-propyl-thiophene-2-*y* l)ethyne, **3a**

A solution of **IM1a-4** (5.68 g), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.28 g), copper(I) iodide (0.57 g) 28% aqueous ammonia (5.7 g) in ethanol (56.8 g) was degassed with nitrogen. It was stirred for 6 h with air bubbling. The product was filtered, washed with ethyl acetate and concentrated. It was purified by recrystallization and column chromatography (silica gel, *n*-hexane) to give **3a**; yield 4.2 g (75.4%). $^1\text{H NMR}$ (δ): 0.97 (6H, t), 1.69 (4H, tq), 2.76 (4H, t), 6.66 (2H, d), 7.15 (2H, d). IR (CaF₂ cell) ν_{max} : 2961, 2930, 2871, 2136, 1718, 1526, 1451, 1379, 1339, 1269, 1239, 1209 cm^{-1} . MS m/z 298 (M^+).

5.4. 4-*n*-Methoxy-(6-*n*-pentoxy-3,1-benzothiazolyl-2-*y* l)-2-ethynylbenzene, **1b**

A solution of **IMBT-1** (3.60 g), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.14 g), copper(I) iodide (0.07 g), PPh_3 (0.14 g) and TEA (10.2 g) in ethyl acetate (20.4 g) was degassed with nitrogen. A solution of **IM-1b** (1.6 g) in ethyl acetate (4.8 g) was added at 57°C and the mixture stirred at 55°C for 4 h. The product was filtered and washed with ethyl acetate. The filtrate was concentrated and purified by column chromatography (silica gel, *n*-hexane/chloroform 2/1)

and recrystallization from ethylacetate to give **1b**; yield 1.2 g (29.2%). $^1\text{H NMR}$ (δ): 0.95 (3H, t), 1.05 (3H, t), 1.34–1.52 (4H, m), 1.76–1.86 (4H, m), 3.95 (2H, t), 4.02 (2H, t), 6.90 (2H, d), 7.10 (1H, dd), 7.28 (1H, t), 7.55 (2H, d), 7.55 (2H, d), 7.91 (1H, d). IR (CaF₂ cell) ν_{max} : 3077, 3051, 2959, 2933, 2872, 2205, 1890, 1751, 1600, 1553, 1516, 1483, 1416, 1392, 1379, 1306, 1283, 1252, 1226 cm⁻¹. MS m/z 379 (M⁺).

5.5. *3,4,5-Trifluoro-(6-n-pentoxy-3,1-benzothiazolyl-2-yl)-2-ethynylbenzene, 2b*

2b was obtained by the same method as **1b** using **IM-2b** instead of **IM-1b**; yield 56.5%. $^1\text{H NMR}$ (δ): 0.95 (3H, t), 1.05 (3H, t), 1.34–1.52 (4H, m), 1.76–1.86 (4H, m), 3.95 (2H, t), 4.02 (2H, t), 6.90 (2H, d), 7.19 (1H, dd), 7.28 (1H, t), 7.55 (2H, d), 7.91 (1H, d). IR (CaF₂ cell) ν_{max} : 3074, 2958, 2935, 2873, 2574, 2214, 1890, 1601, 1552, 1526, 1489, 1451, 1429, 1388, 1363, 1312, 1260, 1242, 1226, 1211 cm⁻¹. MS m/z 375 (M⁺).

5.6. *4-Nitrile-(6-n-pentoxy-3,1-benzothiazolyl-2-yl)-2-ethynylbenzene, 3b*

3b was obtained by the same method as **1b** using **IM-3b** instead of **IM-1b**; yield 45.7%. $^1\text{H NMR}$ (δ): 0.95 (3H, t), 1.34–1.53 (4H, m), 1.79–1.89 (2H, m), 4.03 (2H, t), 7.14 (1H, dd), 7.39 (1H, d), 7.65–7.74 (4H, m), 7.96 (1H, d). IR (CaF₂ cell) ν_{max} : 3066, 2956, 2934, 2871, 2579, 2227, 1917, 1596, 1551, 1513, 1479, 1449, 1405, 1388, 1311, 1287, 1226, 1213 cm⁻¹. MS m/z 346 (M⁺).

5.7. *Bis(6-n-pentoxy-3,1-benzothiazolyl-2-yl)ethyne, 4b*

A solution of **IMBT-1** (21.01 g), PdCl₂(PPh₃)₂ (0.84 g), copper(I) iodide (0.42 g), PPh₃ (0.84 g) and TEA (28.3 g) in ethyl acetate (28.3 g) was degassed with nitrogen. Trimethylsilyl ethyne (10.31 g) was added at 58°C and the mixture stirred for 1 h. The product was washed with ethyl acetate and the filtrate concentrated. The wet cake was purified by column chromatography (silica gel, *n*-hexane/ethylacetate 10/1 with 0.1% triethylamine) to give **IM4b-1**; yield 13.24 g (59.6%).

A solution of **IM4b-1** (13.2 g) in methanol (66.0 g) was degassed with nitrogen. Potassium carbonate (0.1 g) was added at 22°C and the mixture stirred for 1 h. The product was concentrated and purified by column chromatography (silica gel, *n*-hexane/ethyl acetate 10/1 with 0.1% triethylamine) to give **IM4b-2**; yield 6.52 g (63.9%).

A solution of **IMBT-1** (3.85 g), PdCl₂(PPh₃)₂ (0.3 g), copper(I) iodide (0.18 g), PPh₃ (0.15 g) and TEA (13.0 g) in ethyl acetate (26.0 g) was degassed with nitrogen. A solution of **IM4b-2** (4.20 g) in ethyl acetate (10.5 g) was added at 56°C and the mixture stirred for 17 h. The product was filtered and washed with ethyl acetate. The wet cake was purified by column chromatography (silica

gel, *n*-hexane/chloroform 1.5/1 with 0.1% triethylamine) to give **4b**; yield 1.83 g (23.0%). $^1\text{H NMR}$ (δ): 0.95 (6H, t), 1.34–1.53 (8H, m), 1.79–1.89 (4H, m), 4.03 (4H, t), 7.15 (2H, dd), 7.31 (2H, d), 7.98 (2H, d). IR (CaF₂ cell) ν_{max} : 3076, 3054, 2957, 2929, 2871, 2201, 2034, 1886, 1734, 1598, 1553, 1508, 1456, 1417, 1392, 1313, 1283, 1228 cm⁻¹. MS m/z 464 (M⁺).

5.8. *4-n-Propoxyl-(6-n-pentoxy-3,1-benzothiazolyl-2-yl)-2-butadinybenzene, 5b*

A solution of **IM4b-2** (0.79 g), NH₂OH·HCl (10.8 g), water (2.57 g), 70% ethylamine (11.9 g) and copper(I) chloride (0.16 g) in methanol (23.7 g) was degassed with nitrogen. A solution of **IM5b-1** (0.64 g) in methanol (9.6 g) was added and stirred. The product was filtered and washed with methanol. The filtrate was concentrated and purified by column chromatography (silica gel, *n*-hexane/chloroform 1.5/1) to give **5b**; yield 0.26 g (26.2%). $^1\text{H NMR}$ (δ): 0.94 (3H, t), 1.04 (3H, t), 1.33–1.52 (4H, m), 1.75–1.88 (4H, m), 3.94 (2H, t), 4.01 (2H, t), 6.86 (2H, d), 7.11 (1H, dd), 7.26 (1H, d), 7.49 (2H, d), 7.92 (1H, d). IR (CaF₂ cell) ν_{max} : 3069, 2959, 2935, 2873, 2199, 2138, 1889, 1600, 1551, 1510, 1485, 1465, 1449, 1416, 1390, 1321, 1395, 1252, 1227 cm⁻¹. MS m/z 403 (M⁺).

5.9. *Bis(6-n-pentoxy-3,1-benzothiazolyl-2-yl)ethyne, 6b*

A solution of **IM6b-1** (1.29 g), **IM4b-2** (1.18 g), PdCl₂(PPh₃)₂ (0.1 g), copper(I) iodide (0.05 g) and PPh₃ (0.1 g), in ethyl acetate (11.8 g) was degassed with nitrogen. A solution of TEA (0.5 g) in ethyl acetate (5.0 g) was added and the mixture stirred for 1 h. The product was concentrated and the wet cake purified by column chromatography (silica gel, *n*-hexane/chloroform 2/1 with 0.1% triethylamine) to give **6b**; yield 0.68 g (27.9%). $^1\text{H NMR}$ (δ): 0.95 (6H, t), 1.34–1.53 (8H, m), 1.79–1.89 (4H, m), 4.03 (4H, t), 7.15 (2H, dd), 7.28 (2H, d), 7.96 (2H, d). IR (KBr) ν_{max} : 3085, 3048, 2958, 2923, 2869, 2632, 2513, 2291, 2048, 1891, 1744, 1601, 1549, 1468, 1413, 1393, 1358, 1315, 1292, 1267, 1234 cm⁻¹. MS m/z 488 (M⁺), 440.

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References

- [1] MENG, H. H. B., DALTON, L. R., and WU, S. T., 1994, *Mol. Cryst. liq. Cryst.*, **259**, 303.
- [2] WU, S. T., MARGERUM, J. D., HO, M. S., FUNG, M., HSU, C. S., CHEN, S. M., and TSAI, K. T., 1995, *Mol. Cryst. liq. Cryst.*, **261**, 79.
- [3] HSU, C. S., TSAY, K. T., CHANG, A. C., WANG, S. R., and WU, S. T., 1995, *Liq. Cryst. Mol. Cryst. liq. Cryst.*, **19**, 4,409.

- [4] MCEWAN, K. J., DAY, S., MACDONNEL, D. G., and HARRISON, K. J., 1992, *Proc. SPIE*, **1692**, 118.
- [5] FUNAHASHI, M., and HANNA, J., 1996, *Jpn. J. appl. Phys.*, **35**, L703.
- [6] FUNAHASHI, M., and HANNA, J., 1997, *Phys. Rev. Lett.*, **78**, 2184.
- [7] SEKINE, C., FUJISAWA, K., KONYA, N., and MINAI, M., 1998, JP 98-43 289.
- [8] SEKINE, C., FUJISAWA, K., KONYA, N., and MINAI, M., 1999, *Mol. Cryst. liq. Cryst.*, **332**, 235.
- [9] SEKINE, C., FUJISAWA, K., IWAKURA, K., and MINAI, M., *Mol. Cryst. liq. Cryst.* (in the press).