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Liquid Crystals

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Oligo (p -phenylene)s substituted with long alkoxy chains I. Thermotropic liquid crystalline properties and UV absorption/emission characteristics

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Oligo(*p*-phenylene)s substituted with long alkoxy chains

I. Thermotropic liquid crystalline properties and UV absorption/emission characteristics

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A series of linear oligo(*p*-phenylene)s containing three, five and seven phenylene groups, modified with short lateral and long terminal alkoxy chains, were synthesized via Palladium complex-catalysed cross-coupling reactions. The thermotropic liquid crystalline and UV absorption/emission properties of these compounds were studied. It was observed that tri(*p*-phenylene)s develop a rich mesomorphism including tilted smectic type mesophases (SmC and SmF/SmI) and the nematic phase, whereas penta- and hepta-(*p*-phenylene)s substituted with short lateral chains develop only the nematic phase. From these observations it is clear that the short lateral chains hinder the layered molecular packing typical of smectic phases and promote the formation of the less ordered liquid-like nematic phase. Mesophases appeared at lower temperatures when longer end chains were used. The optical properties studied by UV-Vis and emission spectroscopy indicate that these systems are promising candidates for blue-emitting layers in electroluminescent devices.

1. Introduction

Since the discovery of the light emitting properties of poly(*p*-phenylenevinylene) (PPV) [1], a large number of reports describing new organic materials suitable for the fabrication of high performance light emitting diodes (LEDs), has been published [2]. Most studies concern main chain π -conjugated polymers containing vinylene (or ethynylene) and aryl (or heterocyclic) groups modified with alkyl chains or other organic radicals. Some examples of such polymers are derivatives of PPV [3], poly(*p*-phenylene) (PPP) [4], poly(phenylene-ethynylene) (PPE) [5] and poly(thiophene) [6]. Conjugated oligomers are interesting alternative candidates for this application, since they show similar conducting and emitting properties to those of their polymeric analogues [7]. An important advantage of conjugated oligomers is the control of their chemical

structure that can be strictly designed by chemical methods (step by step procedures), contrasting with the existing polymerization procedures normally used to prepare conjugated polymers. Also, oligomers tend to be more soluble and less viscous than polymers, which is advantageous in both the preparation of thin films and the orientation of molecular emitters.

The preparation of thin films seems to be of primary importance in obtaining light emission with specific features. In this respect, let us consider more specifically the case of thin films with unidirectional oriented molecules required for a linearly polarized light emission. Films with aligned emitters can be prepared by simple methods like rubbing [8] or by stretching [9]. Also, by means of a more sophisticated technique like the Langmuir–Blodgett deposition, it is possible to obtain thin films (mono- and multi-layers) with regular molecular assemblies [10]. An interesting approach is the use of rigid rod-like thermotropic liquid crystalline (LC) materials, which can be aligned, for instance, upon cooling from a smectic or a nematic phase [11, 12].

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The LC materials possess a unique capability for spontaneous molecular self-organization, which is particularly useful for integrating specific optical features into molecular films. Moreover, LC materials based on conjugated systems seem to be promising for linearly polarized light emission, and therefore for their use in LC displays as back-light emitters by eliminating one polarizer. In this respect, Lüssem *et al.* [13, 14] have prepared a series of main chain polymers containing arylvinylene units connected by flexible spacers of different length. These polymers showed a smectic A (SmA) phase, which is characterized by superposed molecular layered structures, with the molecules oriented on average perpendicular to the smectic plane. Taking advantage of the fluid SmA phase, the arylvinylene emitters were reported to be easily aligned by using a conventional deposition method. The photoluminescence (PL) measured with materials oriented by rubbing showed a substantial anisotropy between the directions parallel and perpendicular to the rubbing direction. In a similar approach, Hamaguchi and Yoshino [15] reported a PPV modified with nonoxy groups, which exhibits a nematic (N) phase at *c.* 230°C. UV absorption experiments carried out on this polymer have shown differences between oriented and non-oriented films.

Grell *et al.* [16] reported electroluminescence (EL) properties of poly(dioctylfluorene), which is a spacerless conjugated LC polymer. In spite of the relatively high emission anisotropy observed in quenched films of this polymer, no details were given on the characteristics of the observed thermotropic mesophases. Weder and Wrighton [5] and more recently Arias-Marín [17] have observed a spontaneous molecular arrangement in phenylene-ethynylene polymers; these were demonstrated to be efficient light emitting materials. By means of X-ray investigations they concluded that a molecular layered structure of the smectic type is formed.

An interesting class of materials showing a rich thermotropic polymorphism [18] and luminescent properties in the blue region [19, 20] is that of the oligo(*p*-phenylene)s and PPP derivatives. Thermal transitions and molecular structure determination have been reported for these materials [21, 22]; however, the determination of their precise liquid crystalline nature as well as their potential application in linearly polarized light emitting diodes have not yet been investigated.

In this study, we describe the synthesis, thermotropic liquid crystalline properties and UV absorption/emission characteristics of a series of oligo(*p*-phenylene)s (see the scheme) containing three, five and seven phenylene groups substituted with short lateral and long terminal alkoxy chains. Similar compounds have been synthesized previously [18] but as far as we are aware, their LC properties have not yet been investigated in detail. The

materials described here are potential organic materials for the preparation of thin films that may contain highly oriented molecules.

2. Experimental

2.1. Characterization

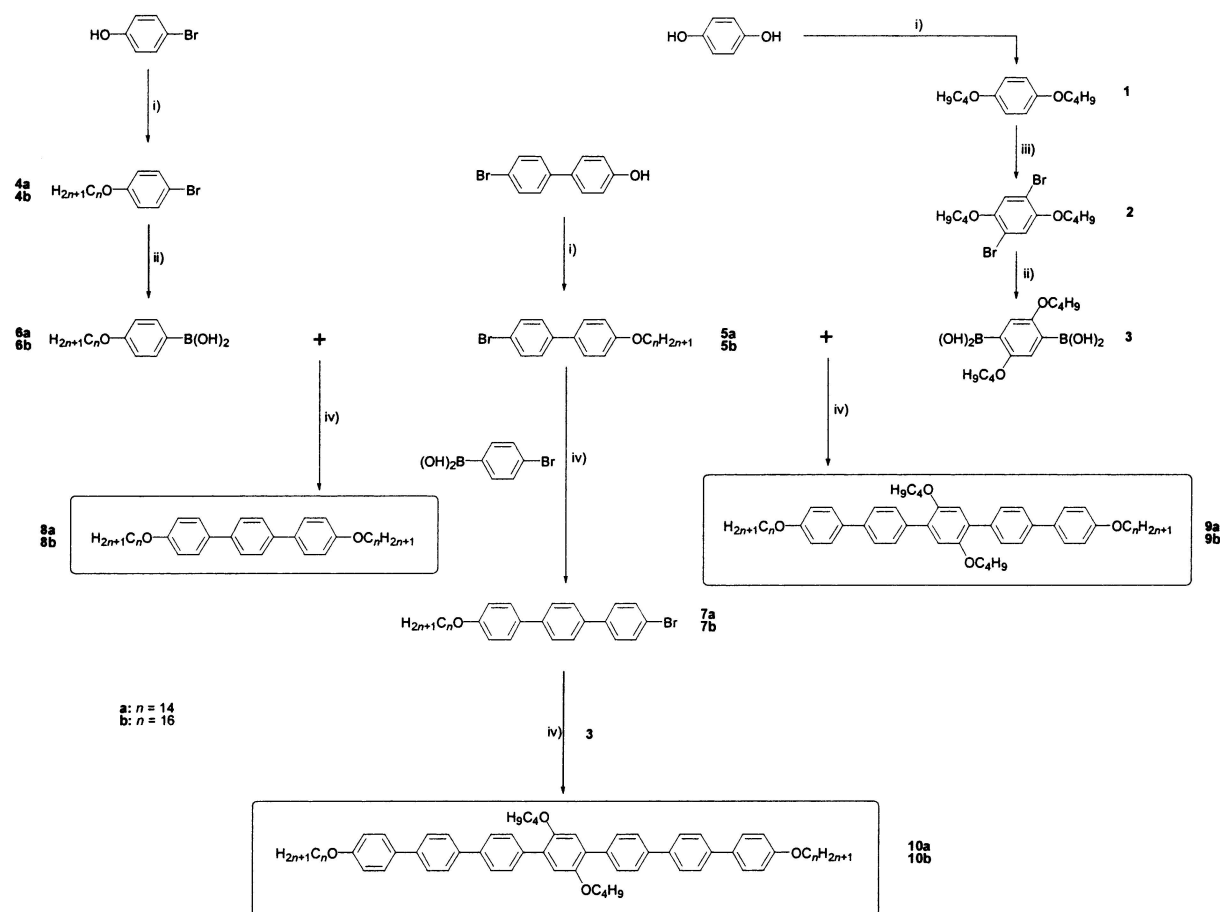
¹H NMR spectra were recorded with a Bruker 200 MHz (solvents, CDCl₃ and THF-d₈) at room temperature. Elemental analysis (C and H) was performed in a Carlo-Erba (1106) instrument at the Charles Sadron Institute, Strasbourg, France. Differential scanning calorimetry (DSC) was performed by using a Dupont Thermal Analyser (TA 210S) at heating and cooling rates of 5°C min⁻¹. Optical textures of mesophases and melting points of all intermediates were obtained by polarizing optical microscopy (POM) (Leitz Orthoplan) coupled with a Mettler FP82 hot stage. The X-ray diffraction (XRD) patterns were recorded with a Guinier focusing camera, using a bent quartz monochromator, K_{α1} copper radiation from a Philips PW 1009 X-ray generator, and a home-made electrical oven.

The UV-Vis spectra were recorded on a HP 8452 A spectrophotometer (190–820 nm) while the emission spectra were observed using a Perkin Elmer LS 50B spectrofluorimeter. All the solutions were prepared in spectroscopic grade chloroform at concentrations of around 10⁻⁴ g l⁻¹. All of the oligomers except the trimers were found to be soluble. For the latter, it was necessary to filter the solution through a 0.2 μm Millipore filter to obtain a clear and homogeneous solution. Films were prepared by spin-coating chloroform solutions with a Clay Adams spin-coater at 1500 rpm. For the substrates, glass slides were used, previously treated as follows: the slides were immersed for at least one day in a sulphochromic solution, then rinsed with water, soaked in an ultrasonic water bath and finally dried in an oven at 60°C.

2.2. Synthesis

All solvents were distilled before use. 4-Bromophenol (99%), 4-(4'-bromophenyl)phenol (97%), hydroquinone (99%), butyllithium 1.6M (in hexanes), triisopropyl borate (98%) ($\delta = 0.815$), tetrakis(triphenylphosphine)-palladium(0) (99%), 4-bromophenyl boronic acid, 1-bromobutane (99%), 1-bromotetradecane (97%) and 1-bromohexadecane (97%), all from Aldrich, were used as received.

The oligomers were synthesized from simple commercial compounds including hydroquinone, 4-bromophenol, 4-(4-bromophenyl)phenol, bromoalkanes, bromine and bromophenyl boronic acid (see the scheme). Although the number of reaction steps involved in the synthesis of the oligomers depends on the length of the final molecules (**8**, **9**, **10**), only three or four basic reactions



Scheme. Synthesis route for the preparation of the oligo(*p*-phenylene)s **8a**, **8b**, **9a**, **9b**, **10a** and **10b**. (i) NaOH/DMF/RBr, (ii) BuLi/THF; B[OCH(CH₃)₂]₃; HCl 2M, (iii) Br₂/CCl₄, (iv) Pd(PPh₃)₄/C₆H₆/Na₂CO₃ 2M.

were used. A classical Williamson reaction [23] (i) was used to introduce one or two alkyl chains into the 4-(4-bromophenyl)phenol, 4-bromophenol and hydroquinone. The following step (ii) involved the formation of aryl boronic acids from some of the bromoaryl intermediates [24] (**2** and **4**). Note that prior to step (ii), an additional bromination (iii) of the dialkoxybenzene (**1**) was necessary, which was normally conducted with bromine in CCl₄ under reflux. In this case a maximum of two bromine atoms could be introduced due to steric hindrance effects, also occurring in the *para*-positions. The final products were obtained by a Suzuki coupling reaction (iv) between the aryl boronic acids and the bromoaryl derivatives, catalyzed with Pd(0) [25]. The use of boronic acids as intermediates is highly convenient because these compounds tolerate a wide range of functional groups and are highly efficient in the Pd complex-catalysed coupling reactions which proceed under relatively mild conditions [26, 27]. It should be pointed out that the solubility of the intermediates is probably the main limiting parameter for obtaining oligomers with more than seven conjugated

phenyl groups. Intermediates **1**, **2**, **3**, **4a,b**, **5a,b** and **6a,b** were synthesized according to known procedures [24–27].

2.2.1. 1-(4-Tetradecyloxyphenyl)-4-(4-bromophenyl)-benzene (**7a**)

In a 500 ml two-neck round-bottom flask, equipped with magnetic stirring and an inert gas inlet (argon), 20 mmol of **5a** (8.9 g), 100 ml of benzene, 3.45 mol % of [C₆H₅]₃P]₄Pd (0.8 g) and 14 ml of an aqueous solution of Na₂CO₃ were introduced. The mixture was degassed, vigorously stirred and heated to 80°C. A solution containing 12 mmol of 4-bromophenyl boronic acid (2.4 g) in 20 ml of ethyl alcohol was added dropwise to the mixture and the reaction allowed to proceed for 3 h. The solution was then filtered and the solid washed three times with water. The solid was added to 20 ml of CCl₄ and the resulting solution heated at 75°C. After cooling to room temperature, a white solid remained in the upper part of the solution; this was recovered by filtration and dried under vacuum; yield 33% (3.44 g), m.p. 280°C. ¹H NMR (CDCl₃): δ = 0.85–0.95 (t, 3H,

CH₃), 1.2–1.6 (m, 22H, (CH₂)₁₁), 1.75–1.90 (m, 2H, CH₂CH₂O), 4.0–4.1 (t, 2H, CH₂O), 6.95–7.75 (1d + 1m, 12H, Ar). C₃₂H₄₁BrO (521.58). Elemental analysis: calcd C 73.69, H 7.92; found C 73.53, H 7.34%.

2.2.2. 1-(4-Hexadecyloxyphenyl)-4(4-bromophenyl)-benzene (**7b**)

A similar procedure as for **7a** was used, employing 5 mmol of **5b** (2.36 g), 100 ml of benzene, 3.45 mol % of [C₆H₅]₃P]₄Pd (0.2 g) and 14 ml of an aqueous solution of Na₂CO₃, 4.8 mmol of 4-bromophenyl boronic acid (0.964 g) in 20 ml of ethyl alcohol; yield 45.5% (1.25 g), m.p. >300°C. ¹H NMR (CDCl₃): δ = 0.85–0.95 (t, 3H, CH₃), 1.2–1.6 (m, 26H, (CH₂)₁₃), 1.75–1.90 (m, 2H, CH₂CH₂O), 4.0–4.1 (t, 2H, CH₂O), 6.95–7.75 (1d + 1m, 12H, Ar). Elemental analysis for C₃₄H₄₅BrO (549.63): calcd C 74.30, H 8.25; found C 73.95, H 7.87%.

2.2.3. 1,4-Bis(4-tetradecyloxyphenyl)benzene (**8a**)

1.34 mmol of **5a** (0.6 g), 20 ml of dimethoxyethane, 15 mg of Pd(PPh₃)₄ and 6.7 ml of Na₂CO₃ 2M were charged in a 100 ml round-bottom flask; the mixture was degassed and then maintained under an argon atmosphere. In a second flask, 1.49 mmol of **6a** (0.5 g) was dissolved in a degassed mixture of DME/ethyl alcohol (5/2). The first mixture was vigorously stirred and heated to 90°C, and the second solution added dropwise. The reaction was allowed to proceed for 20 h. Compound **8a** was extracted into ether, washed three times with water, and purified by crystallization from hot dioxane; yield 62% (0.53 g). ¹H NMR (CDCl₃): δ = 0.85–1.0 (t, 6H, 2CH₃), 1.2–1.6 (m, 44H, 2 (CH₂)₁₁), 1.6–1.95 (m, 4H, 2 CH₂CH₂O), 4.0–4.1 (m, 4H, 2CH₂O), 6.95–7.65 (2 m, 12H, Ar). Elemental analysis for C₄₆H₇₀O₂ (655.06): calcd C 84.34, H 10.77; found C 84.35, H 10.64%.

2.2.4. 1,4-Bis(4-hexadecyloxyphenyl)benzene (**8b**)

This was prepared by the same procedure as for **8a**, using 2.1 mmol of **5b** (1 g), 20 ml of dimethoxyethane, 50 mg of Pd(PPh₃)₄, 10.5 ml of Na₂CO₃ 2M and 2.32 mmol of **6b** (0.84 g); yield 71.8%. ¹H NMR (CDCl₃): δ = 0.85–1.0 (t, 6H, 2CH₃), 1.2–1.6 (m, 52H, 2 (CH₂)₁₃), 1.6–1.95 (m, 4H, 2 CH₂CH₂O), 4.0–4.1 (m, 4H, 2CH₂O), 6.95–7.65 (2 m, 12H, Ar). C₅₀H₇₈O₂ (711.17). Elemental analysis: calcd C 84.45, H 11.05; found C 84.63, H 11.12%.

2.2.5. 1,4-Bis(4'-tetradecyloxybiphenyl)-2,5-dibutoxybenzene (**9a**)

This used the same procedure as for **8a**. The first solution contained 5 mmol of **5a** (2.23 g), 100 ml of benzene, 4 mol % of [C₆H₅]₃P]₄Pd and 25 ml of an aqueous solution of Na₂CO₃ 2M. The second solution

contained 2.1 mmol of **3** (0.65 g) in benzene/ethyl alcohol (1/1). The product was purified by extraction in diethyl ether, washing three times with water, and finally by flash chromatography (SiO₂, CCl₄/heptane 2/1, and CH₂Cl₂). It was precipitated by addition of ethyl alcohol and filtered; yield 21% (1 g). ¹H NMR (CDCl₃): δ = 0.85–1.05 (t, 12H, 4CH₃), 1.2–1.6 (m, 48H, 2 (CH₂)₁₁ + 2 CH₂CH₂CH₂O), 1.65–1.95 (m, 8H, 4 CH₂CH₂O), 3.95–4.1 (m, 8H, 4 CH₂O), 6.9–7.7 (2 m, 18H, Ar). Elemental analysis for C₆₆H₉₄O₄ (951.47): calcd C 83.32, H 9.96; found C 83.15, H 9.93%.

2.2.6. 1,4-Bis(4'-hexadecyloxybiphenyl)-2,5-dibutoxybenzene (**9b**)

The same procedure as for **8a** was used. The first solution contained 4.1 mmol of **5b** (1.95 g), 100 ml of benzene, 4 mol % of [C₆H₅]₃P]₄Pd and 20 ml of an aqueous solution of Na₂CO₃ 2M. The second solution consisted of 1.7 mmol of **3** (0.53 g) in benzene/ethyl alcohol (1/1). Purification was by extraction in diethyl ether, washing three times with water, and flash chromatography (SiO₂, CCl₄/heptane 2/1, and CH₂Cl₂). The product was finally precipitated by addition of ethyl alcohol and filtered; yield 42.3% (1.75 g). ¹H NMR (CDCl₃): δ = 0.8–1.0 (t, 12H, 4 CH₃), 1.15–1.6 (m, 56H, 2 (CH₂)₁₃ + 2 CH₂CH₂CH₂O), 1.65–1.90 (m, 8H, 4 CH₂CH₂O), 3.95–4.1 (m, 8H, 4 CH₂O), 6.95–7.75 (2m, 18H, Ar). Elemental analysis for C₇₀H₁₀₂O₄ (1007.77): calcd C 83.44, H 10.20; found C 83.35, H 10.22%.

2.2.7. 1,4-Bis(4''-tetradecyloxyterphenyl)-2,5-dibutoxybenzene (**10a**)

Same procedure as for **8a**: the first solution contained 4 mmol of **7a** (2.08 g), 150 ml of benzene, 3.4 mol % of [C₆H₅]₃P]₄Pd and 20 ml of an aqueous solution of Na₂CO₃ 2M. The second solution consisted of 2.0 mmol of **3** (0.6 g) in benzene/ethyl alcohol (1/1). Purification was as before. ¹H NMR (CDCl₃): δ = 0.8–1.0 (t, 12H, 4CH₃), 1.2–1.6 (m, 48H, 2 (CH₂)₁₁ + 2 CH₂CH₂CH₂O), 1.65–1.95 (m, 8H, 4 CH₂CH₂O), 3.95–4.1 (m, 8H, 4 CH₂O), 6.95–7.85 (2 m, 26H, Ar). Elemental analysis for C₇₈H₁₀₂O₄ (1103.67): calcd C 84.89, H 9.32; found C 84.84, H 9.46%.

2.2.8. 1,4-Bis(4''-hexadecyloxyterphenyl)-2,5-dibutoxybenzene (**10b**)

Same procedure as for **8a**: the first solution contained 1.35 mmol of **7b** (0.74 g), 100 ml of benzene, 3 mol % of [C₆H₅]₃P]₄Pd and 7 ml of an aqueous solution of Na₂CO₃ 2M. The second solution contained 0.6 mmol of **3** (0.186 g) in benzene/ethyl alcohol (1/1). Purification was as before. ¹H NMR (CDCl₃) δ (ppm): 0.8–1.0 (t, 12H,

4CH₃), 1.2–1.6 (m, 56H, 2 (CH₂)₁₃ + 2 CH₂CH₂CH₂O), 1.65–1.95 (m, 8H, 4 CH₂CH₂O), 3.95–4.1 (m, 8H, 4 CH₂O), 6.95–7.85 (2 m, 26H, Ar).

3. Thermotropic behaviour

The multiple thermal transitions exhibited by the oligomers **8a,b**, **9a,b** and **10a,b** were first determined by DSC. The optical texture and structure of each mesophase were then studied by POM and powder XRD, respectively.

DSC thermograms presented in figures 1 to 6 show that these oligomers exhibit a polymorphic behaviour. Among the oligomers studied, **8a** and **8b** exhibit the richest polymorphism, although it should be pointed out that these trimers are more linear or rod-like in nature than the longer oligomers that contain two short lateral chains in the central phenylene group. The substitution by such chains was necessary, firstly to facilitate the synthetic procedures, and secondly to obtain molecules that melt before degradation. In this respect, a penta- (*p*-phenylene) compound modified at both molecular ends with tetradecyloxy groups and with no lateral chains has been prepared. This compound was insoluble in all solvents, and when heated (285°C) decomposed before melting.

From figures 1 to 6, one can see differences in the DSC traces and in the temperatures at which the thermal transitions occur. The trimers show sharp peaks and the heptamers develop complex broad peaks, whereas the pentamers show an intermediate behaviour. The clearing temperatures of the trimers occur near 180–190°C,

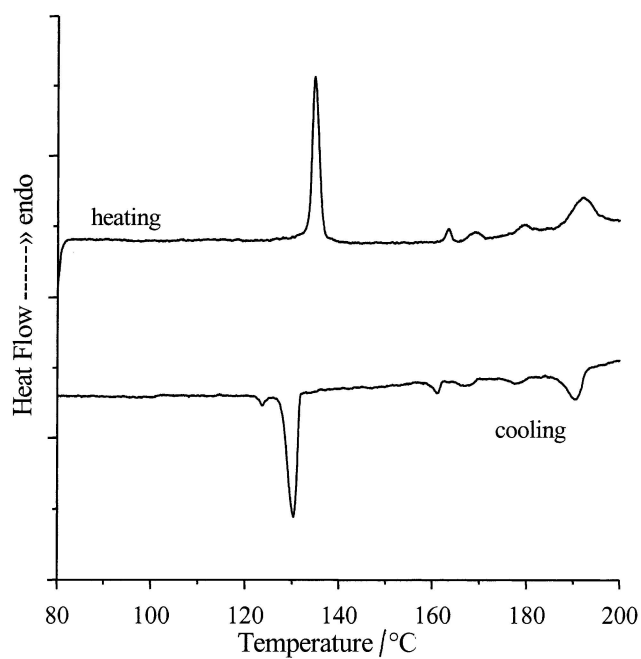


Figure 1. Heating and cooling DSC traces for compound **8a**.

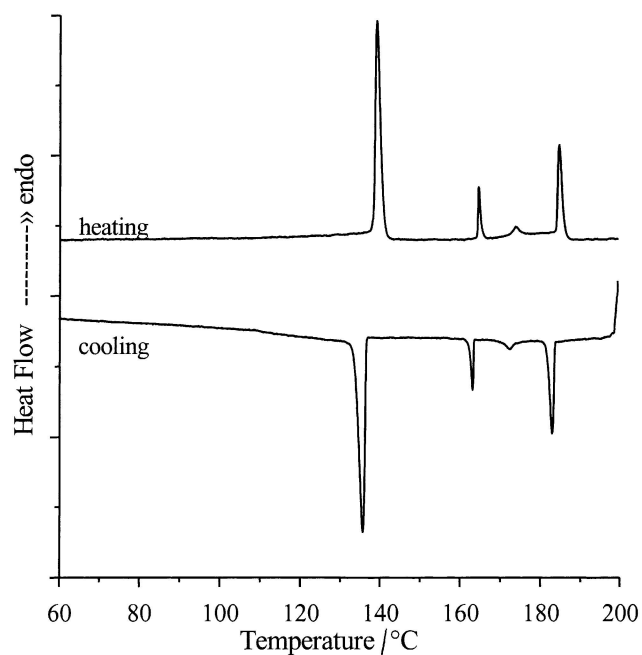


Figure 2. Heating and cooling DSC traces for compound **8b**.

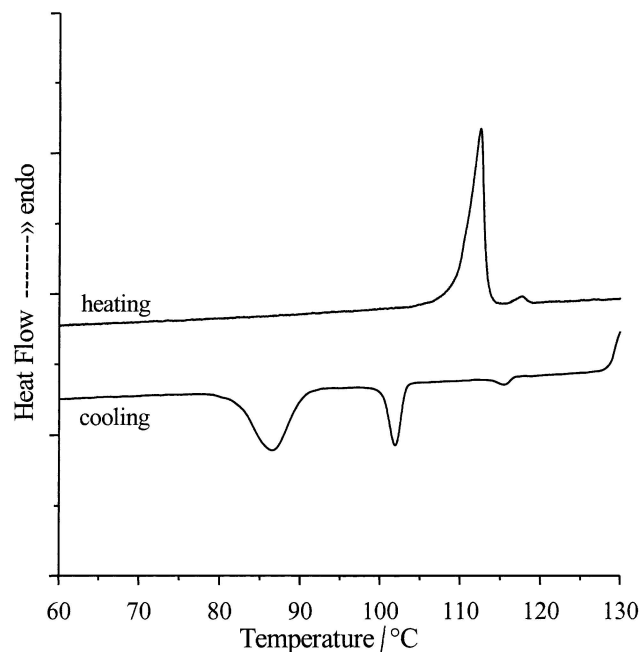
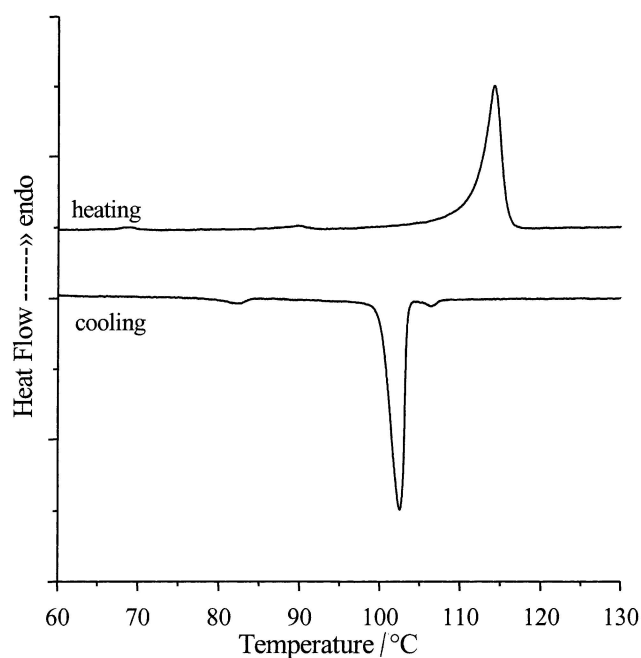
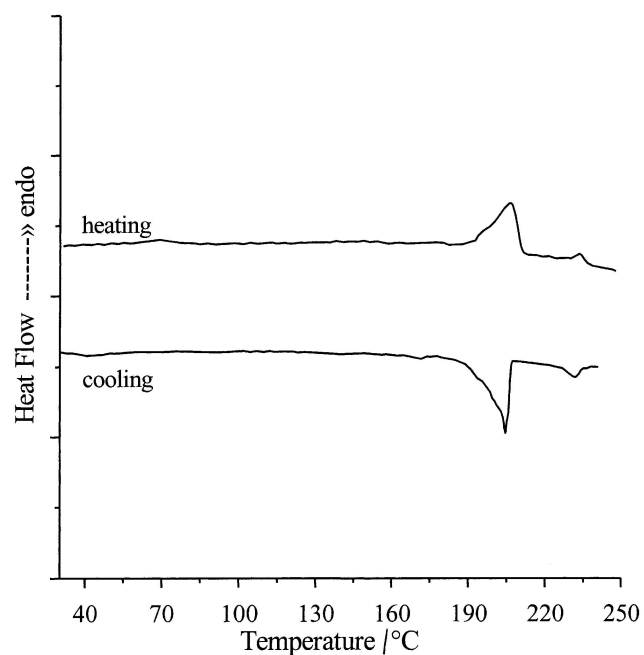
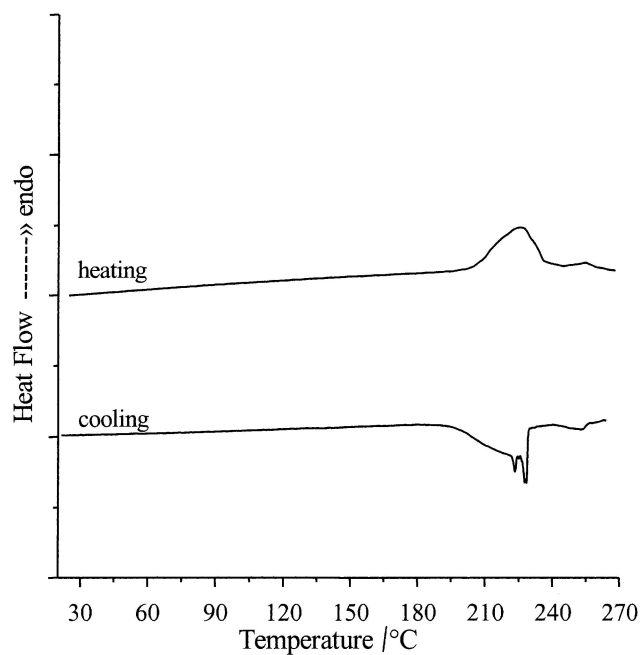


Figure 3. Heating and cooling DSC traces for compound **9a**.

whereas those of penta- and hepta-mers occur in the range 110–120 and 230–250°C, respectively. These data clearly indicate the antagonistic effect produced by the lateral chains and the conjugated phenylene groups on the thermal transitions. The lateral chains significantly reduce the clearing temperatures, whereas the length of phenylene conjugation rapidly increases this transition temperature up to a point where the oligomers tend to

Figure 4. Heating and cooling DSC traces for compound **9b**.Figure 6. Heating and cooling DSC traces for compound **10b**.Figure 5. Heating and cooling DSC traces for compound **10a**.

become infusible. This behaviour occurs for compounds having a rather reduced number of aryl groups, even for molecules substituted with lateral and long terminal alkyl chains. This is one of the reasons why this study is limited to oligomers no longer than seven conjugated phenyl rings. Nevertheless, longer oligomers of this kind could be prepared but the length and the number of substituted alkyl chains must be increased.

The transition temperatures determined by DSC and described above were used as reference for recording the observation of optical textures of all mesophases, which were sequentially obtained upon cooling from the isotropic state. Regarding the trimers, only **8a** showed a nematic phase. Then on further cooling, **8a** and **8b** showed concurrently a schlieren and a focal-conic fan textures typical of a smectic C (SmC) phase [28], see figure 7(a). On subsequent cooling, a change in the texture, namely a banded focal-conic fan texture was observed, figure 7(b). On the basis of this texture only, it was not possible to identify the mesophase.

The penta- and hepta-(*p*-phenylene)s showed the typical schlieren texture of a nematic phase only (figure 8), as could have been expected for compounds with this molecular structure [29]. The phase was recognized by its typical schlieren texture with 2- and 4-brush point defects (figure 8). It should be mentioned that upon heating, the nematic texture of **9a** was observed in a quite limited temperature interval, *c.* 5°C, whereas for **10a** and **10b**, this mesophase was observed over slightly larger temperature intervals, *i.e.* 230–250 and 210–225°C, respectively. Upon cooling, **9a** showed a marked hysteresis (see figure 3). Such hysteresis resulted in a larger temperature range (around 12°C) for the nematic phase. For this pentamer, a nematic-solid transition at 105°C and a solid-solid transition at around 85°C were observed. **9b** displayed a monotropic nematic phase on cooling recognized on the basis of its optical texture.

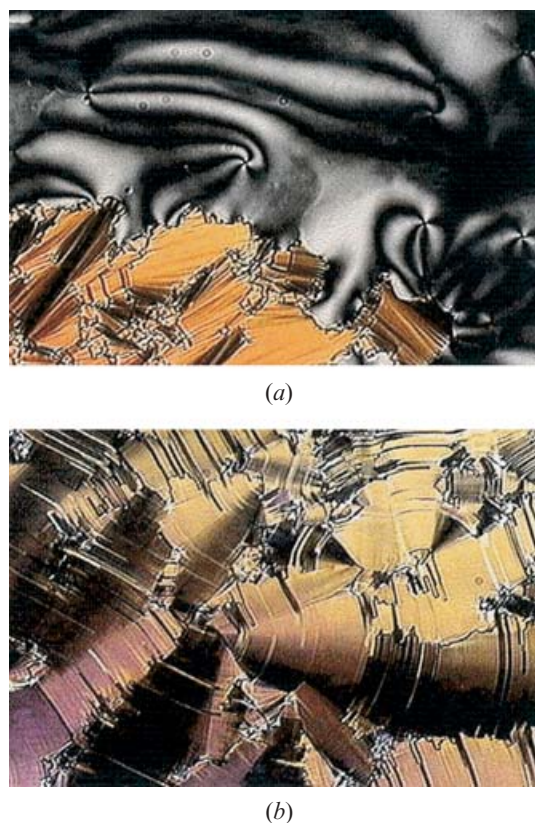


Figure 7. Optical texture of compound **8b** at (a) 170°C and (b) 137°C obtained on cooling.

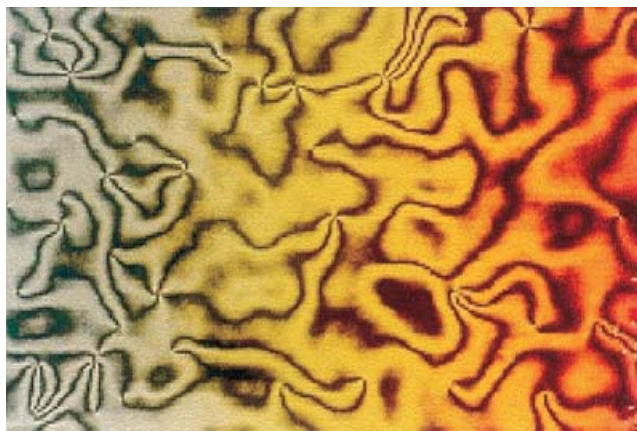


Figure 8. Optical texture of compound **10b** at 224°C obtained on cooling.

4. Structure of the liquid crystalline phases

XRD analysis allowed for a complementary assessment of the nature of the phases observed by DSC and POM, giving in additional information about their structural parameters.

Let us first consider the trimers **8a,b**. Only **8a** exhibits a nematic phase, characterized by diffuse signals in both the small and wide angle regions. It is interesting to

note the existence of cybotactic groups, as revealed by the strong intensity of the small angle signal. At lower temperature, both compounds exhibit the same smectic behaviour. The smectic nature of mesophases observed at high temperature for **8a,b** was characterized in the XRD pattern by the presence of two or more sharp equidistant small angle reflections at low angles. These reflections correspond to the stacking period of the smectic layers. This periodicity (d_{001}) measured experimentally was compared with the calculated length L of the oligomers in their most stretched conformation (see table 1). The molecular length was calculated using molecular modelling software (Insight) from Biosym. A comparison between d_{001} and L immediately suggests that the molecules are tilted with respect to the normal of the smectic planes. The calculated average tilt angle, θ ($\cos \theta = d_{001}/L$), of the molecules in the SmC phase of **8a** and **8b** is *c.* 45°. Similar large tilt angle values have already been reported for smectic C phases which transform directly into a nematic or isotropic phase on increasing temperature [30].

The symmetry change of the mesophases was monitored by the number and shape of the scattering signals in the wide angle region of the XRD pattern (figures 9 and 10). At higher temperature, the phase was characterized by the presence of one broad diffuse band, which is typical of the liquid-like ordering of the molecules within the layers [28]. On cooling from the SmC phase, the layer spacing increased slightly but still remained smaller than L . This indicates that the tilt angle decreased gently (less than 5°) with decreasing temperature. At the same time the diffuse signal in the wide angle region became sharper, indicating a hexatic-type ordering of the molecules within the smectic layers, similar to that

Table 1. Experimental stacking period d_{001} of smectic layers measured at temperature T , and calculated length L of oligomers in their most extended conformation.

Compound	$T/^\circ\text{C}$	Mesophase	$L/\text{Å}$	$d_{001}/\text{Å}$	Tilt angle/ $^\circ$
8a	180	N	—	—	—
	170	SmC	48.9	38.3	38
	165	SmF or SmI	—	40.8	33
	150	SmX	—	40.8	33
8b	190	I	—	—	—
	180	SmC	54.0	40.3	41
	170	SmF or SmI	—	42.5	38
	160	SmX	—	43.3	37
9a	110	N	57.1	—	—
9b	105	N	62.2	—	—
10a	240	N	65.5	—	—
10b	220	N	70.6	—	—

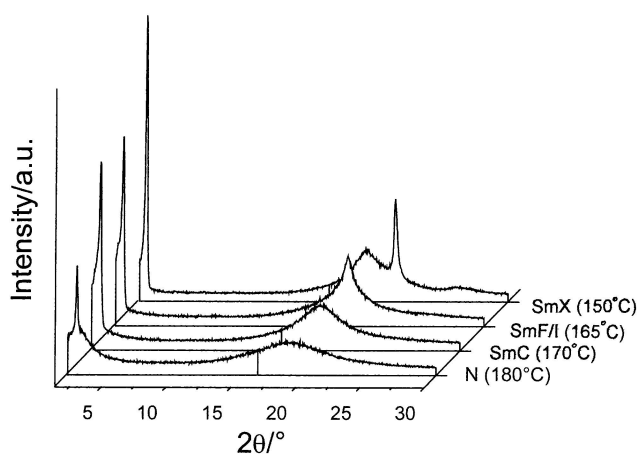


Figure 9. XRD pattern of compound **8a** at four different temperatures.

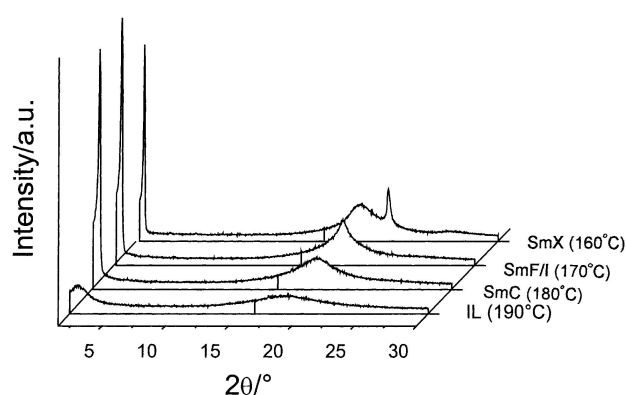


Figure 10. XRD pattern of compound **8b** at four different temperatures.

found for the smectic F (SmF) or smectic I (SmI) phases of terephthal-bis-4-*n*-alkylaniline derivatives [31]. The structural difference between these two smectic F and I phases is essentially the tilt direction of molecules with respect to the 2D hexagonal lattice. In the SmF phase molecules are tilted towards the edge, whereas in the SmI phase molecules are tilted towards the apex [28].

On cooling further from this hexatic phase, the presence of several equidistant Bragg reflections in the low angle region indicates the existence of a well developed layered

molecular stacking of the smectic type. However, in the high angle region the X-ray pattern changes completely, showing two main signals: a more or less broad band and a sharp signal. These two signals are probably an indication of a two-dimensional ordering of the molecules within the smectic layers. However, a deeper analysis is necessary to ascertain the exact nature of this mesophase and this is now under investigation. In addition, it is worth noting the presence of a very diffuse scattering at about 3.5 Å indicating the existence of π - π interactions between phenyl rings of the conjugated oligomers.

The nematic nature of the liquid crystalline phase observed at high temperature in both the pentamers and heptamers was confirmed by XRD with the presence of two diffuse halos, one in the small angle and the other in the wide angle region. The diffuse band observed in the wide angle region is indicative of the liquid-like ordering of the molecules within the nematic phase, while that at low angle is of the order of the molecular length. At room temperature, the crystalline nature of all oligomers was demonstrated by the presence of many sharp Bragg reflections in both low and wide angles.

A summary of these observations, the exact phase sequences and the transition enthalpies are gathered in table 2.

5. UV absorption and emission

The optical properties of solutions and films of the oligomers were studied. The absorption and emission maxima and their corresponding absorption coefficients in solution ϵ are collected in table 3. For the oligomers **8a** and **8b** it was not possible to obtain reliable ϵ values due to solubility problems. In order to complete the ϵ values of the homologous series 1,4-bis(4-tetradecyloxyphenyl)-2,5-dibutoxybenzene (**8c**) was synthesized and its absorption coefficient in solution measured. Details on the synthesis and characterization of this oligomer will be reported elsewhere.

The spectroscopic features of the pentamers and heptamers are quite independent of the length of either the main conjugated backbone or the alkoxy substituents. In dilute solution ($\sim 10^{-4} \text{ g l}^{-1}$) the absorption spectra exhibit two main peaks at around 300 and 330 nm

Table 2. Transition temperatures and enthalpy changes of oligomers.

Compound	Transition temperature $T/^\circ\text{C}$ [Enthalpy change, $\Delta H/\text{kJ mol}^{-1}$]
8a	Cr 133.4 [47.7] SmX 162.0 [2.7] SmF/I 166.4 [3.5] SmC 176.7 [3.1] N 187.2 [19.4] I
8b	Cr 138.3 [49.5] SmX 164.3 [5.8] SmF/I 171.9 [1.8] SmC 183.9 [16.6] I
9a	Cr 109.4 [87.0] N 115.9 [1.5] I
9b	Cr 66.4 [1.1] Cr' 84.4 [1.8] Cr'' 111.3 [105.8] I I 107.7 [2.3] N 104.4 [9.7] Cr'' 83.4 [2.5] Cr'
10a	Cr 205.1 [38.6] N 245.5 [1.6] I
10b	Cr 58.2 [1.5] Cr' 190.3 [23.4] N 226.1 [1.8] I

Table 3. Optical properties of oligomers.

Compound	Solution		Film	
	$\lambda_{\text{abs}}(\epsilon)/\text{nm}$ ($1 \text{ g}^{-1} \text{ cm}^{-1}$)	$\lambda_{\text{emis}}/\text{nm}$	$\lambda_{\text{abs}}/\text{nm}$	$\lambda_{\text{emis}}/\text{nm}$
8a	268	366	a	a
8b	268	364	a	a
8c	272 (18.8)	b	c	c
9a	292 (36.4), 332 (31.8)	404	302, 360	403, 422 ^d
9b	294 (30.2), 330 (26.4)	404	301, 355	403, 422 ^d
10a	306 (52.7), 334 (52.6)	409	302, 359	418, 439 ^d
10b	304 (81.8), 332 (72.1)	410	c	c

^a Non-homogeneous films can be prepared.

^b The emission in solution was not measured.

^c No films were prepared.

^d Shoulder.

(figure 11), the intensity of the first band being higher than that of the second. Based on previous studies on unsubstituted poly(phenylene)s the two absorption bands can be attributed to the transitions between localized orbitals (at low wavelength) and as a result of phenylene ring conjugation (high wavelength band) [32]. On changing from the pentamer to the heptamer, the two peaks undergo a bathochromic shift of a few nanometers. From the pentamer to the heptamer, the conjugation slightly increases as expected since the chain is growing, even if the effect on the UV absorption is less marked than that measured for other conjugated oligomers as oligo(phenylethynylene)s [33]. This is presumably due to the less important contribution of an additional phenyl group with respect to the phenylethynyl moieties in the overall electronic delocalization.

The value of the absorption maximum at around 330 nm is in agreement with the maximum observed by Vahlenkamp and Wegner [26] for a (2,5-dialkoxy-*p*-

phenylene) heptamer (λ_{max} in chloroform 333 nm). The fact that there is no significant difference in the wavelengths measured for the oligomers with the C₁₄ or C₁₆ substituents confirms that these long chains have no effect on the conjugation; they only help in increasing the solubility of the systems. In the emission spectra, the increase in the wavelength is less pronounced. However, it has to be pointed out that the rather large breadth of the emission band impedes a net assignment of the maximum. The large Stokes shift calculated from the absorption and emission spectra (about 70 nm) indicates that the geometries of the ground and excited states are different. A possible explanation could be given by taking into account a change of the torsion angle between adjacent phenyl rings due to excitation [26].

The situation for the trimers is quite different. The absorption and emission spectra of **8a** in chloroform solution are shown in figure 12. Due to the poor solubility of **8a** and **8b**, a clear and stable solution can

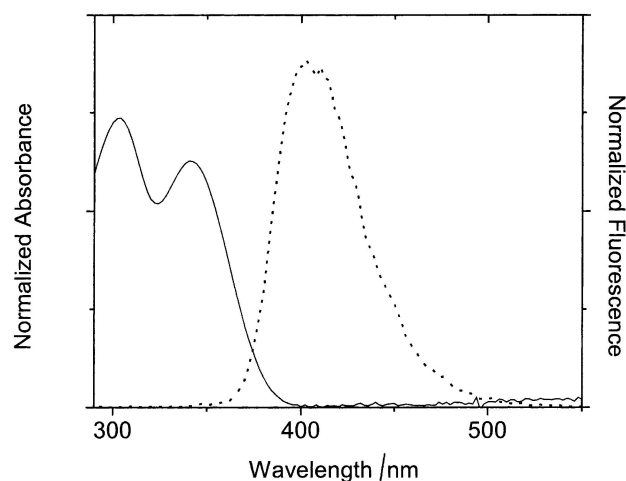


Figure 11. Absorption (solid line) and emission (dashed line) of chloroform solution of **9a**.

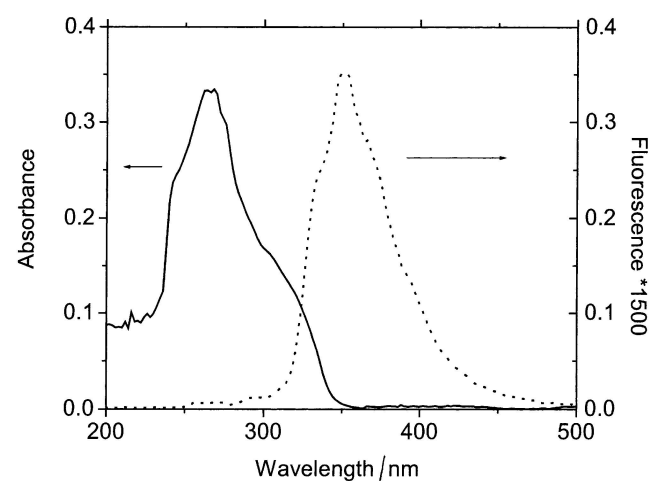


Figure 12. Absorption (solid line) and emission (dashed line) of chloroform solution of **8a**.

be obtained only after filtration. As mentioned, this limitation impedes the measurement of a precise value of the absorption coefficient and also prevents preparation of good homogeneous films. The absorption spectra of these oligomers were characterized by a broad band centred at 268 nm, similar to that reported for related terphenyl derivatives [34]. The Stokes shift is also large (about 100 nm), even higher than those observed for the other oligomers. The optical properties of **8c** are similar to those of its higher homologous, with two peaks centered at wavelengths slightly shorter than those of **9a** and **10a** in agreement with its lower conjugation.

In order to test the potential use of these new oligomers in light emitting diodes, the optical properties in thin films have been studied. The absorption spectra, quite similar to the spectra in solution, show two peaks, slightly red-shifted because of the higher π - π interactions of the molecules in the solid state as already observed for analogous systems [32]. The emission peaks, centred for all the oligomers at about 400 nm, highlight the fact that these systems can be used as blue emitting layers for electroluminescent devices. Figure 13 shows the absorption and emission spectra of a thin film of **9a**. From the absorption and emission peaks, the Stokes shifts of the films prove to be smaller by about 40 nm than in solution.

6. Conclusion

Oligo(*p*-phenylene)s substituted with lateral and terminal alkoxy chains were prepared by palladium-catalysed Suzuki cross-coupling reactions between aryl boronic acids and bromoaryl derivatives. The final oligomers and intermediates were obtained in good yields, although the poor solubility of some intermediates reduces the yields and limits the synthesis of oligomers

containing more than seven conjugated phenyl groups. All the synthesized oligomers showed thermotropic liquid crystalline properties. The tri(*p*-phenylene)s display smectic phases (SmC and SmF/SmI type) and a nematic phase for **8a**, whereas the penta- and hepta- (*p*-phenylene)s, substituted with short lateral chains, exhibit only a nematic phase, monotropic for **9b**. The short lateral chains substituted in the central phenylene alter the mesomorphic range by hindering the layered molecular packing of smectic phases, and thus favour the formation of the less ordered liquid-like nematic phase. Mesophases were observed systematically at lower temperatures for oligomers substituted with the longer end chains (C₁₆).

UV measurements have shown that solutions of pentamers and heptamers exhibit two peaks: one attributed to transitions between localized orbitals (near 300 nm), the other to the conjugation of phenylene rings (near 330 nm). Trimers exhibit only one broad band centred at 268 nm. On the other hand, absorption peaks of thin films were red-shifted compared with solutions, although the emission peaks were located at almost the same wavelength. UV-Vis and emission spectra indicate that the alkoxy chains, which increase the solubility of the oligomers and decrease the temperature for the formation of the liquid crystalline mesophases, do not affect the conjugation of the systems. The emission peak of all the oligomers is centred at about 400 nm. Even if further work might be carried out to reduce transition temperatures and to increase the solubility of the systems in order to get good optical quality of the films, the results obtained in this work open up the possibility to use this kind of oligo(phenylene)s as linearly polarized blue light emitters in LED devices, by using for example **9a** and **9b** in a highly oriented nematic phase.

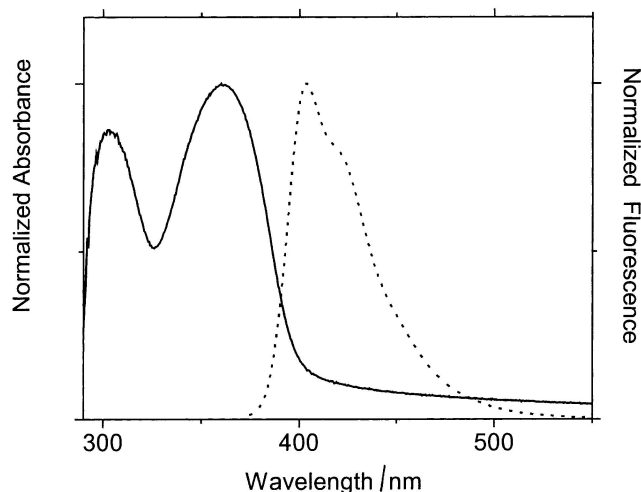


Figure 13. Absorption (solid line) and emission (dashed line) of a spin-coated film of **9a**.

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