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Liquid Crystals

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Bireactive calamitic liquid crystals derived from fluorene ester linkage

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New thermotropic liquid crystalline monomer esters, containing fluorene in their mesogenic core with luminescent properties, were synthesized and characterized. The monomers studied exhibited a broad mesomorphic range and a nematic phase was identified by differential scanning calorimetry and polarized optical microscopy. Absorption and photoluminescence spectra studied in solution indicated that these compounds possess good optical stability. Linearly polarized light emission was observed in oriented thin films prepared by an in-situ photopolymerization technique. The preparation of oriented thin films shows a preferential emission direction necessary for application in linearly polarized blue light-emitting diodes.

1. Introduction

Since the first observations of conjugated polymers based on poly(*p*-phenylenevinylene) for the development of photo- and electroluminescent devices such as organic light-emitting diodes (OLEDs), a large number of investigations has been carried out to make possible the preparation of efficient devices that are able to emit polarized light of the three primary colours essential for full visible range displays [1–7]. However, the capability of the polymer to emit in the blue portion of the visible spectrum does not yet meet the requirements for commercial applications in OLEDs [8]. In this context, polyfluorenes have emerged as a very attractive class of materials for linearly polarized blue light emission, due to that fact these materials are characterized by high quantum efficiencies, chemical and thermal stability and liquid crystalline properties indispensable for the performance of polarized LEDs [9–13]. Nevertheless, the general problem presented by the polyfluorenes is their tendency to form aggregates and excimers in the solid state, which leads to fluorescence quenching [14–17].

Recently, conjugated low molar mass liquid crystalline bireactives have received considerable interest as linearly polarized LEDs due to their ability of self-organization, which is particularly useful for the control of the state of polarization of the light emitted [18–23]. Also, these molecules possess important advantages compared to their polymeric analogues, such as the control of the chemical structure, solubility and preparation of oriented luminescent thin films by simple methods [24–28]. An interesting method for the production of oriented luminescent films is the in-situ photopolymerization technique [29–31]. This technique has been studied for several years now, involving the macroscopic alignment of liquid crystals (LC) bireactives followed by irradiation with light [32–34].

In this paper, we describe the synthesis and thermotropic behaviour of new liquid crystalline diacrylate esters based on fluorene (see scheme 1), as well as their optical properties. Preliminary results concerning these molecules show a potential for the preparation of oriented thin films that can be used as linearly polarized light-emitting devices.

2. Results and discussion

2.1. *Synthesis and characterization*

The LC monomers were synthesized according to scheme 2. The syntheses of the monomers was accomplished in several steps starting from 2,7-dibromofluorene. To facilitate functionalization at the C-9 position of the fluorene group, two alkyl groups were incorporated at this position in order to increase the solubility of the system, and influence mesomorphic properties of the monomers. Alkylation at the C-9 position was effected by a catalytic phase transfer process. Incorporation of a phenyl ring on both side of the fluorene segment at the 2 and 7 positions was achieved by a Suzuki coupling reaction between the 4-methoxyphenylboronic acid (previously prepared from 4-methoxybromobenzene

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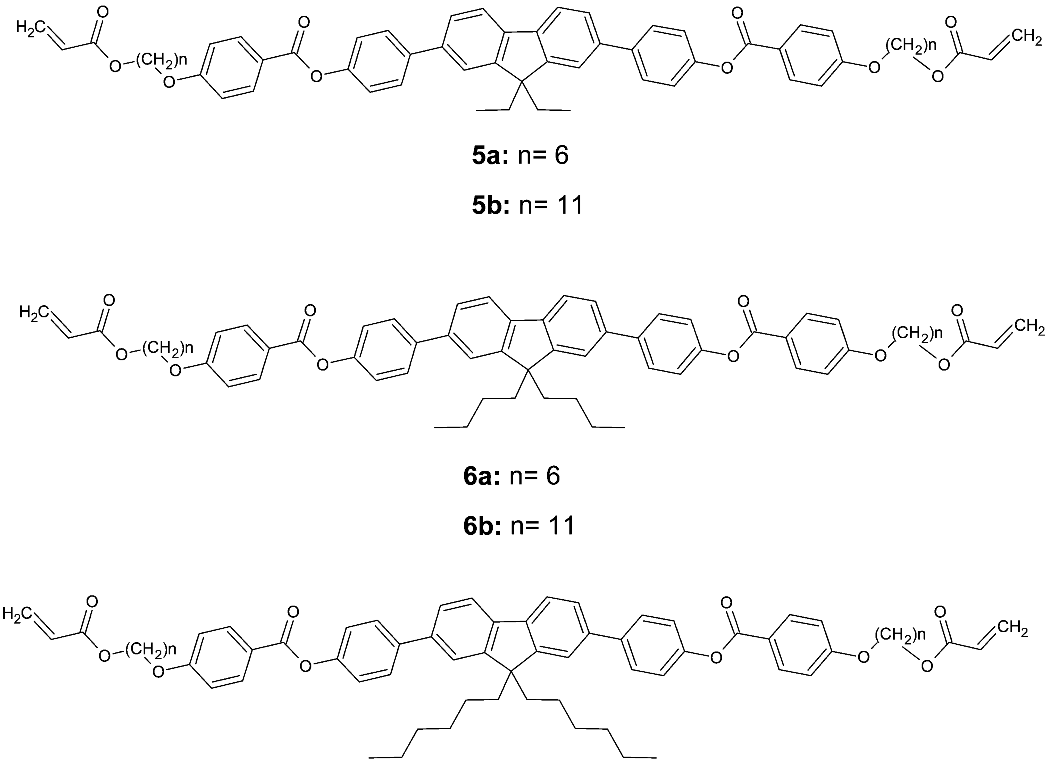


5a: n= 6

5b: n= 11

6a: n= 6

6b: n= 11

7a: n= 6

7b: n= 11

Scheme 1. Molecular structure of monomers investigated.

and triisopropyl borate) and 2,7-dibromo-9,9′-dialkylfluorene. The deprotection of the methoxy group was realized using boron tribromide 2.5M, enabling high yields of 2,7-bis(4-hydroxyphenyl)-9,9-dialkylfluorene (**3**).

As shown in scheme 2, the mesogens were prepared by an esterification reaction between 4-(ω-acryloyloxyalkyloxy)benzoic acid **(4)** and 2,7-bis(4-hydroxyphenyl)-9,9-dialkylfluorene **(3)** using *N*,*N*′-dicyclohexylcarbodiimide, *N*,*N*-dimethylaminopyridine in dry dichloromethane. The overall yields are between 45 and 70%. Synthesis and characterization of intermediates **1a**, **2a**, **3a**, **4a** and **4b** have been previously reported in the literature [35, 36].

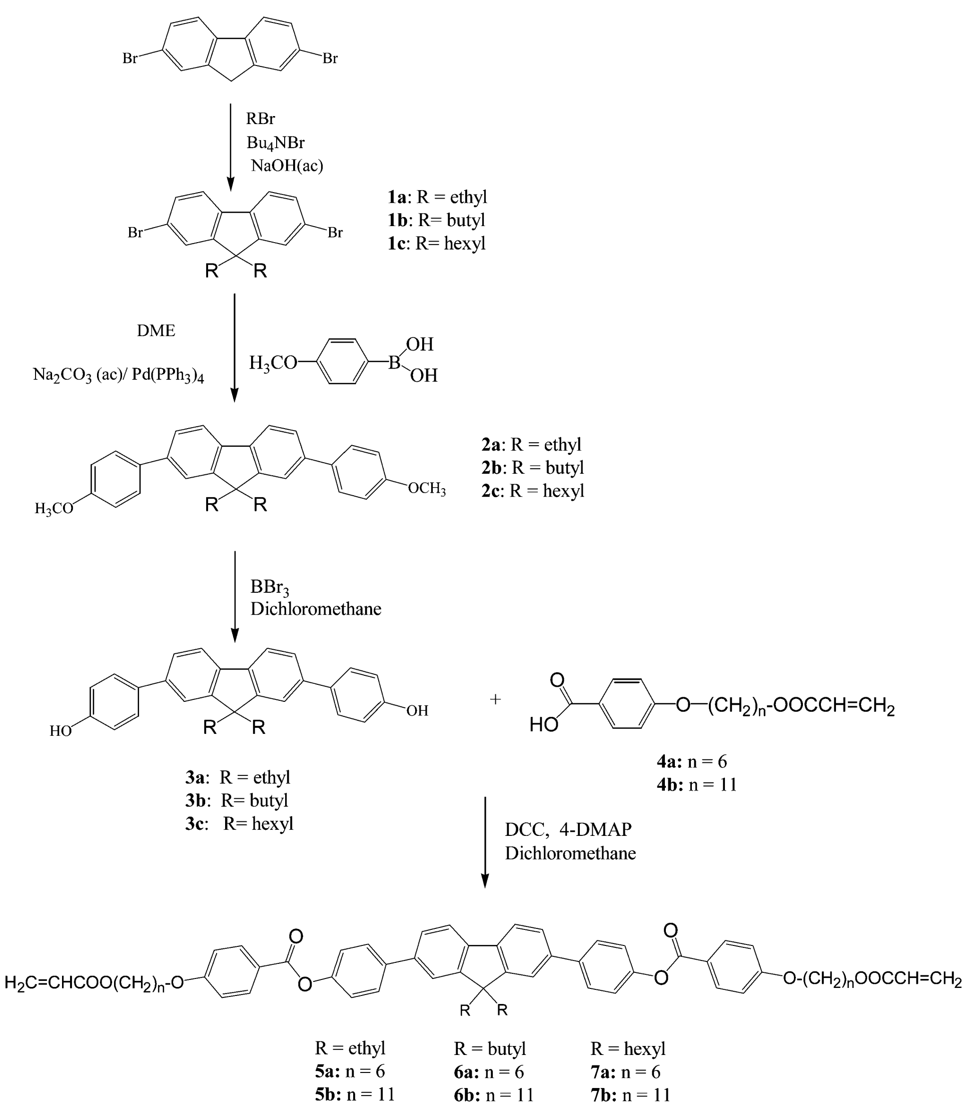
In FT-IR spectra, characteristic absorption bands of the ester were observed at 1721 cm^{-1}, C–O–C at 1267 cm^{-1}, C=C at 1632 cm^{-1} and CH stretching at 2845–2998 cm^{-1}. Furthermore, the ^{1}H and ^{13}C NMR spectra (figure 1) support the formation of the monomers.

The monomers were polymerized by the in-situ photopolymerization technique [37]. Monomer **5b** was photopolymerized using a photoinitiator (2,2-dimethoxy-2-phenylacetophenone) and thermal inhibitor (2,6-di-*tert*-butyl-4-methylphenol) yielding transparent network **8b** with a macroscopic orientation. The reaction was verified by IR measurements, proving the disappearance of the vinyl group.

2.2. *Mesomorphic behaviour*

The liquid crystalline properties of the monomers were evaluated by differential scanning calorimetry (DSC) measurements and texture characterization between crossed polarizers using polarized optical microscopy (POM). The transition temperatures are listed in table 1. All the compounds exhibited a nematic mesophase according to the POM and DSC measurements.

As indicated in table 1, the monomers have different transition temperatures. Compounds **5a** and **5b** possess a broad mesomorphic range (~130°C). A different behaviour is observed in compounds with lateral chains of four and six carbon atoms; compounds **6** and **7** possess smaller ranges of around 60°C. Enthalpies of melting and clearing points of the monomers are consistent with those of the transitions, except for **6a** where the clearing point peak was not determined



Scheme 2. Synthetic scheme employed for the preparation of LC bireactive fluorene-based monomers.

(possible thermal polymerization). The DSC traces of the monomers **5a** and **5b** are illustrated in figure 2.

In the case of monomer **5a**, thermal polymerization occurs after melting. In order to establish the mesophase small amounts of thermal inhibitor (2,6-di-*tert*-butyl-4-methylphenol) were added. The study of this sample by POM confirmed the mesophase and revealed that isotropization takes place at around 240°C.

The monomer **5b** exhibits a larger enthalpy phase transition at 73°C and a small transition to the isotropic phase at 201°C on the second heating scan. On the cooling cycle, the compound revealed a very low tendency to crystallize. Nevertheless, the crystallization can be induced on extreme cooling or standing for prolonged periods at room temperature. On cooling the samples to 0°C, the DSC curves reveal a mesophase–crystal transition at 8°C.

When viewed between crossed polarizers under POM, a nematic phase was observed for all the compounds. The phase was recognized by typical schlieren texture, being characterized by singularities with two and four brushes. The polarizing microphotograph of monomer **5b** is presented in figure 3.

2.3. *Optical properties*

The optical properties of the monomers in THF solution were investigated. Figure 4 shows the absorbance and photoluminescence spectra of the mesogens **5a** and **5b**. The absorption maximum is observed at 329 nm for all mesogens; it is based on the π–π* transition of the mesogenic core. In the photoluminescence spectra, blue light emissions were observed at around 401 nm. Optical measurements did not reveal

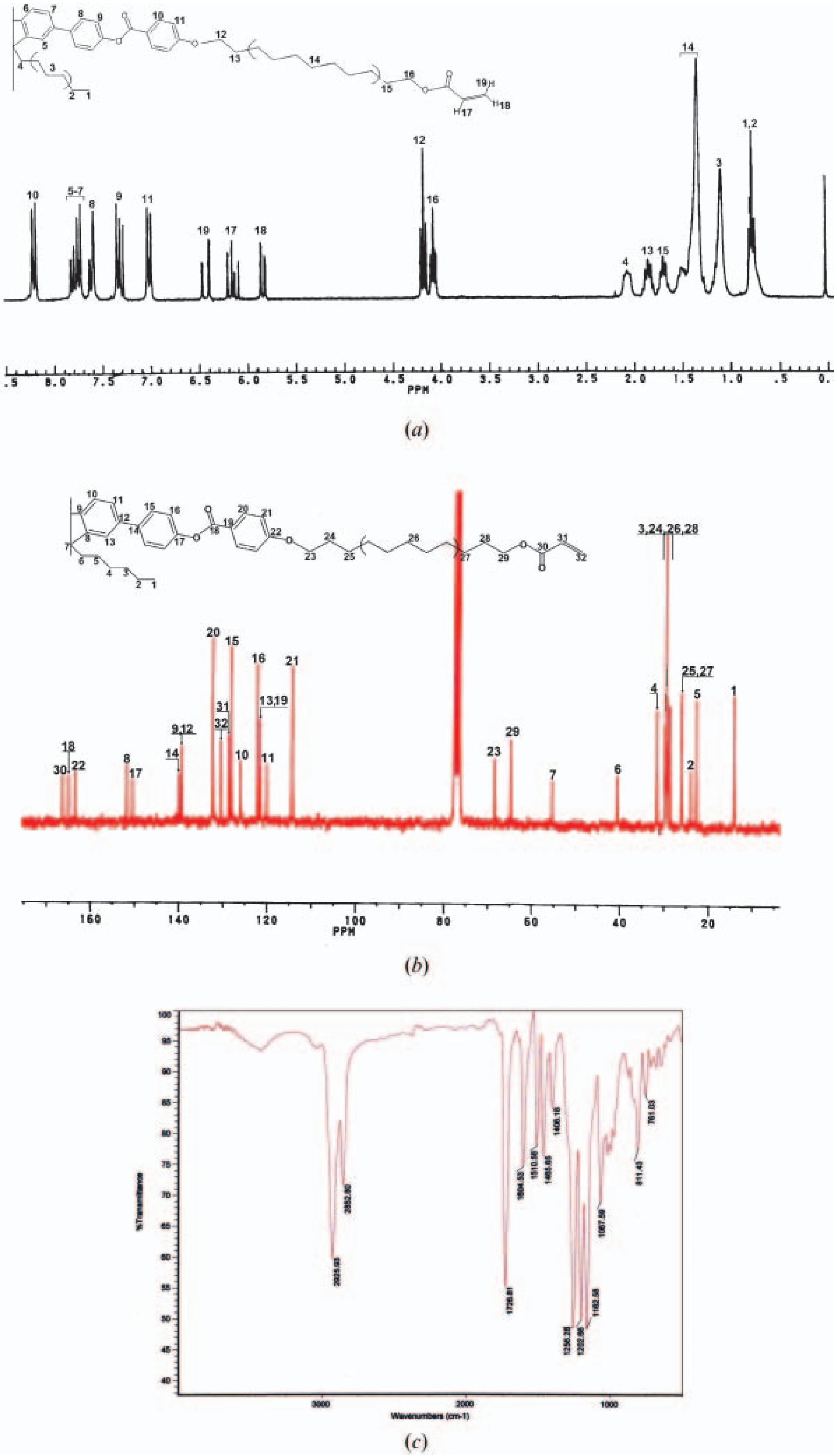


Figure 1. (a) ^{1}H NMR, (b) ^{13}C NMR and (c) FT-IR spectra of compound **7b**.

Table 1. Phase transition temperatures and enthalpies of the monomers.

Compound	Transition temperatures/°C (ΔH/kJ mol^{-1})				
5a	Cr	108 (57.0)	N	240 (1.7)	I
5b	Cr	73 (53.1)	N	201 (2.0)	I
6a	Cr	140 (84.5)	N	177 (n.d.)	I
6b	Cr	107 (83.6)	N	146 (2.1)	I
7a	Cr	96 (106.7)	N	158 (2.1)	I
7b	Cr	85 (119.8)	N	120 (1.4)	I

n.d.=not determined. Cr=crystal. N=nematic phase. I=isotropic liquid.

any significant shift for the compounds that differ only in the number of alkoxy groups; this is due to the fact that the effective conjugation length is not influenced by alkoxy chains.

The emission spectrum of **8b** was compared to the spectra observed in solution. The emission spectra of the films exhibited a slight red-shift (416 nm) because of higher interactions of the molecule in the solid state. This situation can be related to an increase of the planar structure in the excited state and the consequent increase of the effective conjugation length [33].

Polarized emission spectra (for an excitation wavelength of 329 nm) of the film **8b** were recorded at room temperature. For instance, figure 5 shows the emission spectra of the oriented film measured parallel and perpendicular to the rubbing direction of the cell. The difference between the spectra recorded parallel and perpendicular to the rubbing direction shows that there is a preferential orientation for emission.

The photoluminescence dichroic ratio ($R=I_{//}/I_{\perp}$) between maximal and minimal intensity of emission was calculated being about of 11 times larger in the direction of the molecular orientation, indicating a substantial difference in the intensity of rubbing (parallel) direction and perpendicular to it, respectively, demonstrating the high anisotropy of film.

Finally, the intensity of emission the oriented film was also measured as a function of optical bleaching exposed to light at 330 nm at room temperature during different periods of time. We have found that the luminescence of the film is stable under illumination; changes of the emission behaviour were not observed.

3. Conclusions

New LC ester monomers with luminescent properties have been synthesized. The mesomorphic behaviour can be explained because a phenyl ring is connected to both ends of the mesogenic core connected with an ester group, stabilizing the formation of the mesophase due to the higher polarizability in the molecule.

Monomer **5b** was oriented and photopolymerized in a commercial cell; the emission was eleven times higher in the direction of molecular orientation. The preparation of oriented thin films by in-situ photopolymerization shows a preferential emission direction necessary for application in linearly polarized blue light-emitting diodes.

4. Experiment

4.1. *Materials*

All reactions were performed under nitrogen atmosphere. Solvents such as dichloromethane and dimethoxyethane (DME) were dried before use. All chemicals, such as *N*,*N*′-dicyclohexylcarbodiimide and N,N-(dimethylamino)pyridine, were purchased from Aldrich Chemical Co and were used as received.

4.2. *Measurements*

^{1}H and ^{13}CNMR spectra were recorded on a Bruker CA (250, 300 and 400 MHz) spectrometer. Chemical shifts were referenced to tetramethylsilane (TMS). Infrared measurements were carried out using a Nicolet Magma-IR$^{\mathrm{TM}}$550-Fourier.

DSC traces were obtained using a STA 625 from Polymer Laboratories. All heating and cooling rates were 10°C min^{-1} under nitrogen.

Leitz Ortholux II Pol-BK, an optical polarized microscope equipped with a hot stage, was used to observe thermal transitions and anisotropic textures.

UV–visible and photoluminescence spectra were obtained using a Shimadzu UV–visible 3100 spectrometer and a Perkin-Elmer LS50B spectrofluorimeter, respectively.

4.3. *Synthesis*

4.3.1. 2,7-dibromo-9,9-dialkylfluorenes (1). A 50% KOH aqueous solution (30 ml) was added to a mixture of 2,7-dibromofluorene (15.43 mmol) and tetrabutylammonium bromide (0.76 mmol) under a nitrogen atmosphere and heated at 60°C. Afterwards, 1-bromoalkane (92.58 mmol) was added and the reaction mixture was vigorously stirred overnight at 60°C. The mixture was diluted with water and ethyl acetate. The organic phase was separated and washed with water, dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure.

For 2,7-dibromo-9,9-dibutylfluorene (**1b**), the yellow residue was recrystallized from 1-propanol to give a white solid. Yield 71%. IR (KBr) $\nu_{\max}$/cm^{-1}: 2916–2852, 1452, 1411, 810. ^{1}H NMR (250 MHz, CDCl$_3$) δ (ppm): 7.53–7.42 (m, 6H), 1.90 (m, 4H), 1.07 (m, 4H), 0.67 (t,

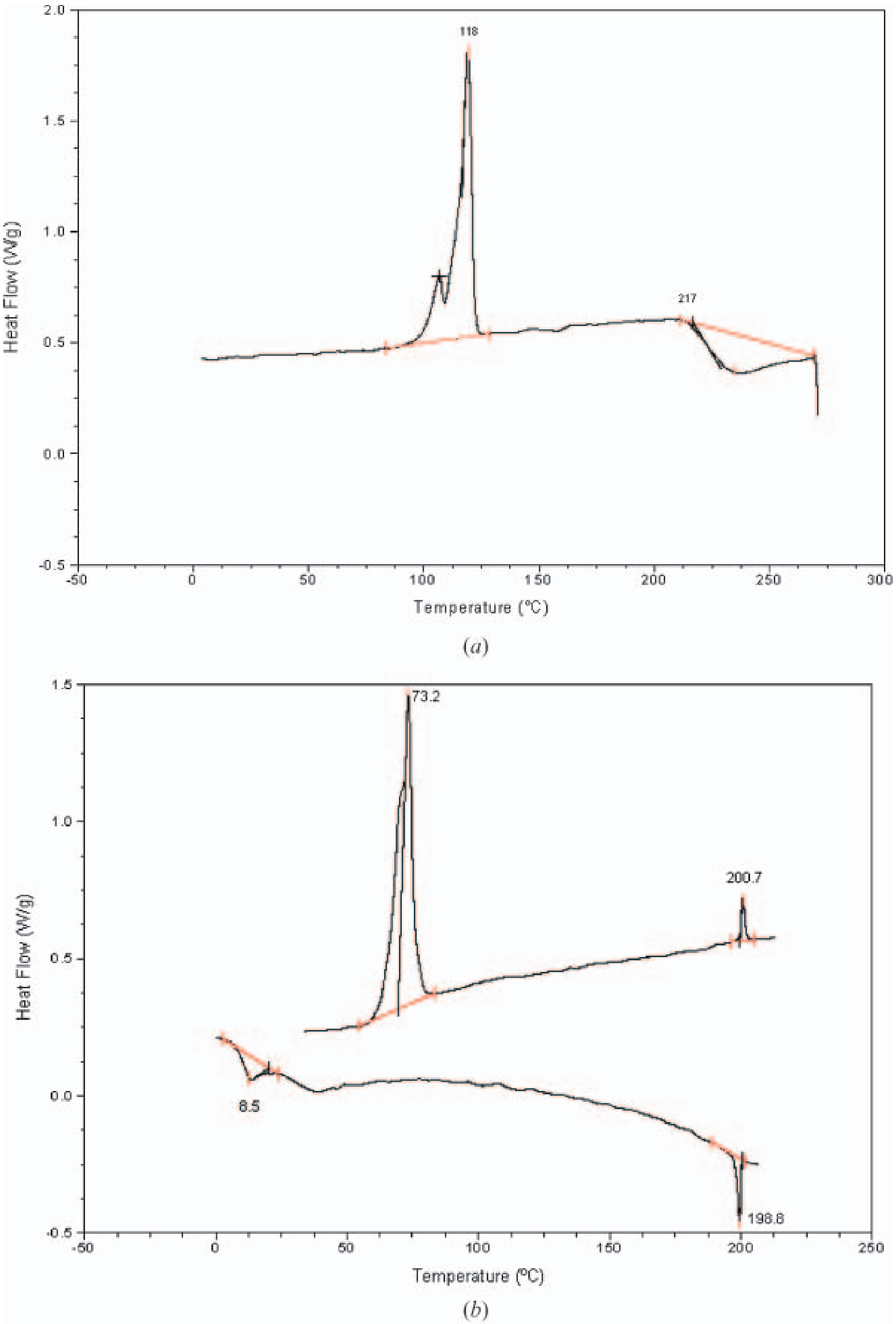


Figure 2. (a) DSC thermogram obtained on heating for compound **5a**; (b) DSC thermogram obtained on heating and cooling for compound **5b**.

6H, $J{=}6.2\,\mathrm{Hz}$), 0.59 (m, 4H). ^{13}C NMR (250 MHz, $CDCl_3$) δ (ppm): 152.52, 139.05, 130.14, 126.15, 121.47, 121.11, 55.58, 40.01, 25.80, 22.93, 13.75.

For 2,7-dibromo-9,9-dihexylfluorene (**1c**), the residue yellow was recrystallized from 1-propanol to give a white solid. Yield 85%. IR (KBr) ν_{max}/cm^{-1}: 2923–2858, 1457, 1404, 812. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.53–7.47 (m, 6H), 1.92 (m, 4H), 1.17–1.06 (m, 12H), 0.78 (t, 6H, $J{=}6.8\,\mathrm{Hz}$), 0.60 (m, 4H). ^{13}C NMR (250 MHz, $CDCl_3$) δ (ppm): 152.52, 139.05, 130.14,

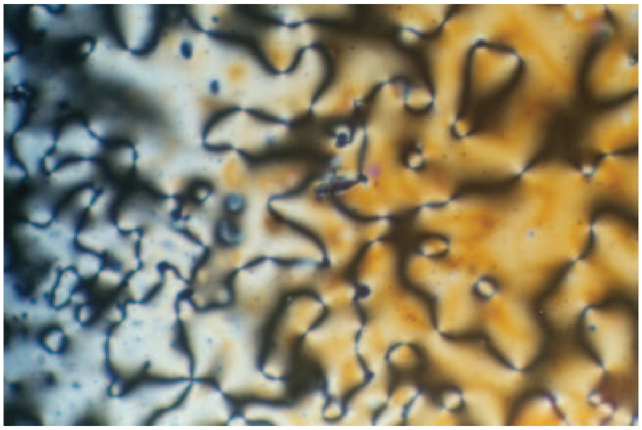


Figure 3. Optical texture of the mesophase of compound **5b** at 80°C, obtaining on cooling. (magnification: ×250)

126.15, 121.47, 121.11, 55.58, 40.46, 31.43, 29.70, 23.77, 22.56, 13.97.

4.3.2. 2,7-Bis(4-methoxyphenyl)-9,9-dialkylfluorene (2).

A mixture of **1** (2.44 mmol), sodium carbonate (14.9 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.2 mmol) was dissolved in DME (50 ml) and water (10 ml). The reaction was heated to 60°C and 4-methoxyphenylboronic acid (7.2 mmol) was added dropwise while stirring at this temperature for 24 h. Toluene was added and the reaction maintained for 12 h. The reaction mixture was cooled and 2N HCl (100 ml) was added. The product was extracted with diethyl ether and dried over anhydrous sodium sulfate. After solvent removal, the residue was subjected to purification by column chromatography.

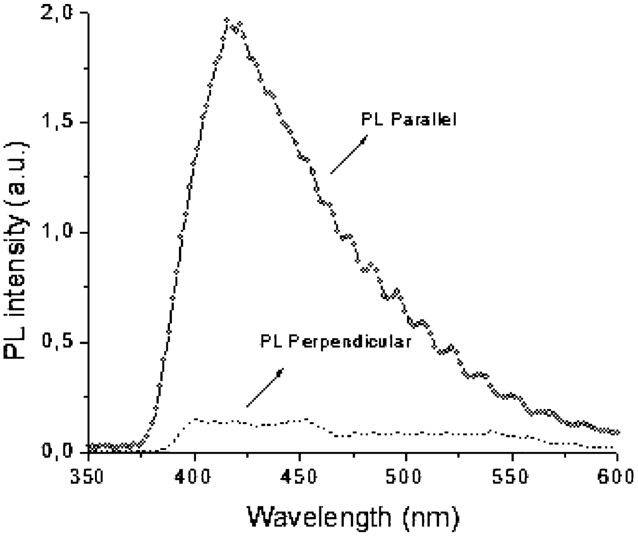


Figure 5. Linearly polarized photoluminescence spectra of oriented film (**8b**) on a cell (Linkam) of 5 μm thickness.

For 2,7-bis(4-methoxyphenyl)-9,9-dibutylfluorene (**2b**), the residue was purified on silica gel with hexane/ethyl acetate (9/3) as eluent to give the required product as a white solid. Yield 51%. IR (KBr) ν_{max}/cm^{-1}: 2924–2854, 1605, 1512, 1460, 1250, 1032. ^{1}H NMR (250 MHz, CDCl$_3$) δ (ppm) : 7.70 (d, 2H, J=7.8 Hz), 7.49–7.63 (m, 8H),7.01 (d, 4H, J=8.8 Hz), 3.87 (s, 6H), 2.00 (m, 4H), 1.06 (s, 4H), 0.82–0.76 (m, 10H). ^{13}C NMR (250 MHz, CDCl$_3$) δ (ppm): 159.04, 151.57, 139.52, 134.31, 128.17, 125.52, 121.06, 119.81, 114.20, 55.39, 55.39, 40.43, 30.02, 22.57, 14.05.

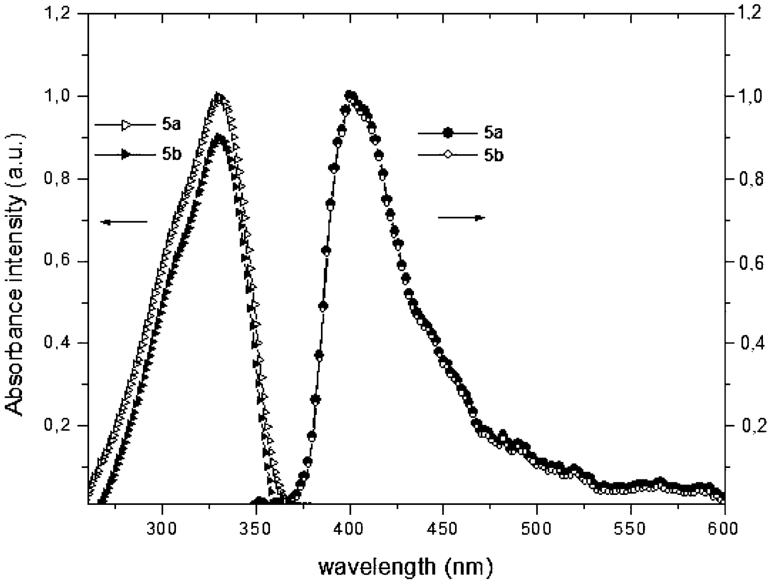


Figure 4. Absorption and photoluminescence spectra for the compounds in THF solution.

For 2,7-bis(4-methoxyphenyl)-9,9-dihexylfluorene (**2c**), the residue was purified on silica gel with hexane/ethyl acetate (9/3) as eluent to give the required product as a white solid. Yield 62%. IR (KBr) ν_{max}/cm^{-1}: 2925–2850, 1604, 1513, 1463, 1246, 1031, 811. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm) : 7.74 (d, 2H, J=8.4 Hz), 7.63–7.51 (m, 8H),7.03 (d, 4H, J=8.8 Hz), 3.86 (s, 6H), 2.04 (m, 4H), 1.09–1.06 (m, 12H), 0.75 (m, 10H). ^{13}C NMR (250 MHz, $CDCl_3$) δ (ppm): 159.02, 151.55, 139.49, 134.27, 128.14, 125.52, 121.02, 119.81, 114.19, 55.35, 55.15, 40.46, 31.43, 29.70, 23.77, 22.56, 13.97.

4.3.3. 2,7-Bis(4-hydroxyphenyl)-9,9-dialkylfluorene (3). The equipment consisted of a 250 ml three-necked flask equipped with a magnetic stirrer, and septum, nitrogen atmosphere and light protection. To the flask was added compound **2** (1.12 mmol) and dry dichloromethane (100ml) before cooling to 0°C with water/ice/brine. Under these conditions, BBr_3 (1M, 3.36 ml) was added dropwise and the reaction was stirred overnight at room temperature. The mixture was poured slowly into water (100 ml) and stirred for 1 h. The organic phase was extracted twice with dichloromethane, the resulting organic phase were washed with Na_2CO_3 (1M, 50 ml), dried with Na_2SO_4, and the solvent removed under reduced pressure.

For 2,7-bis(4-hydroxyphenyl)-9,9-dibutylfluorene (3b), the crude product was purified by flash column chromatography on silica gel using ethyl acetate/hexane (3/7) as eluent to give the desired product as a white solid. Yield 95%. ^{1}H NMR (250 MHz], $CDCl_3$) δ (ppm): 7.73 (d, 2H, J=8.5 Hz), 7.58–7.50 (m, 8H), 6.97 (d, 4H, J=7.5 Hz), 5.56 (s, 2H), 2.05–1.99 (m, 4H), 1.13–1.04 (m, 4H), 0.67 (m, 10H). ^{13}C NMR (250 MHz, $CDCl_3$) δ (ppm): 154.94, 151.55, 139.57, 139.44, 134.43, 128.39, 125.51, 120.97, 119.84, 115.69, 55.09, 40.27, 25.98, 23.05, 13.79.

For 2,7-bis(4-hydroxyphenyl)-9,9-dihexylfluorene (3c), the crude product was used in the next step without further purification.

4.3.4. 2,7-bis[4′-{4-(ω-acryloyloxyalkyloxy)benzoyloxy}-phenyl]-9,9-dialkylfluorenes (5). To a mixture of the corresponding 4-(ω-acryloyloxyalkyloxy)benzoic acid (21 mmol), 2,7-bis(4-hydroxyphenyl)-9,9-dialkylfluorene (**3**) (9.1 mmol), *N*,*N*-dimethylaminopyridine (catalytic amount) and 2,6-di-*tert*-butyl-4-methylphenol (0.50 g) as thermal inhibitor in 80 ml of CH_2Cl_2, *N*,*N*′-dicyclohexylcarbodiimide (22 mmol) was added. The mixture was stirred at room temperature for three days in darkness. The dicyclohexylurea was filtered off and washed with CH_2Cl_2. Then the organic layer was washed with 2N HCl (2 × 50 ml), 2N $NaHCO_3$ (2 × 50 ml), water (2 × 50 ml), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue was subjected to purification by column chromatography.

For 2,7-bis[4′-{4-(6-acryloyloxyhexyloxy)benzoyloxy}-phenyl]-9,9-diethylfluorene (**5a**), the residue was purified by column chromatography on silica gel using ethyl acetate/dichloromethane/hexane (2/1/7) as eluent. Finally the product was washed in absolute ethanol to give the compound as a white solid. Yield 70%. IR (KBr) ν_{max}/cm^{-1}: 2845–2998, 1721, 1632, 1584, 1267. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.12 (d, 4H, J=8.6 Hz), 7.83–7.23 (m, 14H), 6.95 (d, 4H, J=8.8 Hz), 6.42 (dd, 2H, J=10.6 Hz), 6.12 (dd, 2H, J=17.6 Hz), 5.80 (dd, 2H, J=17.4 Hz), 4.20 (t, J=6.4 Hz, 4H), 4.05 (t, 4H, J=6.2 Hz), 2.02 (q, 4H, J=6.7 Hz), 1.82 (m, 4H), 1.63 (m, 4H), 1.36–1.27 (m, 8H), 0.43 (t, 6H, J=7.1 Hz).^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) : 167.41, 154.51, 150.65, 139.92, 139.21, 136.54, 134.07, 128.10, 125.22, 125.55, 121.07, 119.77, 114.76, 68.30, 64.72, 56.33, 31.24, 29.57, 28.56, 25.96, 8.69.

For 2,7-bis[4′-{4-(11-acryloyloxyundecyloxy)benzoyloxy}phenyl]-9,9-diethyl-fluorene (**5b**), the product was purified with column chromatography on silica gel using ethyl acetate/dichloromethane/hexane (2/2/6) and washed in absolute ethanol to give the compound as a white solid. Yield 65%. IR (KBr) ν_{max}/cm^{-1}: 2998–2845, 1721, 1632, 1582, 1267. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.19 (d, 4H, J=8.5 Hz), 7.80–7.30 (m, 14H), 6.95 (d, 4H, J=8.5 Hz), 6.42 (dd, 2H, J=10.5 Hz), 6.12 (dd, 2H, J=17.4 Hz), 5.80 (dd, 2H, J=17.4 Hz), 4.16 (t, 4H, J=6.5 Hz), 4.05 (t, 4H, J=6.4 Hz), 2.02 (q, 4H, J=6.6 Hz), 1.86–1.31 (m, 32H), 0.41 (t, 6H, J=7.1 Hz). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm)]: 167.51, 154.52, 150.65, 139.92, 139.21, 136.54, 134.07, 128.10, 125.55, 125.22, 121.07, 119.77, 114.76, 68.30, 64.72, 56.33, 31.24, 29.53, 29.50, 29.36, 28.62, 26.00, 25.93, 8.69.

For 2,7-bis[4′-{4-(6-acryloyloxyhexyloxy)benzoyloxy}-phenyl]-9,9-dibutylfluorene (**6a**), the product was purified with column chromatography on silica gel using ethyl acetate/hexane (3/7) and washed in absolute ethanol to give the compound as a white solid. Yield 45%. IR (KBr) ν_{max}/cm^{-1}: 2936–2862, 1724, 1604, 1511, 1259. ^{1}H NMR (250 MHz $CDCl_3$) δ (ppm): 8.19 (d, 4H, J=8.75 Hz), 7.81–7.71 (m, 6H), 7.61 (d, 4H, J=9 Hz), 7.31 (d, 4H, J=8.75 Hz), 6.99 (d, 4H, J=8.75 Hz), 6.42 (dd, 2H, J_1=17.3 Hz, J_2=1.8 Hz), 6.13 (dd, 2H, J_1=17.2 Hz, J_2=10.5 Hz), 5.83 (dd, 2H, J_1=10.3, J_2=1.8 Hz), 4.19 (t, 4H, J=6.75 Hz), 4.07 (t, 4H, J=6.5 Hz), 2.05 (m, 4H), 1.86 (m, 4H), 1.74 (m, 4H), 1.50 (m, 8H), 1.14 (m, 4H), 0.70 (t, 10H, J=7.2 Hz).^{13}C NMR ($CDCl_3$, 250 MHz) δ (ppm): 166.32, 164.99, 163.44, 151.68, 150.38, 140.02, 139.70, 132.31, 130.37, 128.53, 128.16, 126.00, 122.07, 121.49, 120.02, 114.26, 68.23, 64.68, 55.24, 40.41, 28.54, 28.52, 25.68, 25.70, 23.05, 13.81.

For 2,7-bis[4′-{4-(11-acryloyloxyundecyloxy)benzoyloxy}phenyl]-9,9-dibutyl-fluorene (**6b**), the product was purified with column chromatography on silica gel using ethyl acetate/hexane (3/7) and washed in absolute ethanol to give the compound as a white solid. Yield 52%. IR (KBr) ν_{max}/cm^{-1}: 2930–2858, 1724, 1604, 1510, 1256. ^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.23 (d, 4H, J=6.5 Hz), 7.84–7.76 (m, 6H), 7.64 (d, 4H, J=7.5 Hz), 7.36 (d, 4H, J=5 Hz), 7.04 (d, 4H, J=6.5 Hz), 6.44 (dd, 2H, J_1=20 Hz, J_2=1.6 Hz), 6.17 (dd, 2H, J_1=17.2 Hz, J_2=6.8 Hz), 5.86 (dd, 2H, J_1=10.4 Hz, J_2=1.2 Hz), 4.20 (t, 4H, J=8.8 Hz), 4.01 (t, 4H, J=8.0 Hz), 2.11 (m, 4H), 1.88 (m, 4H), 1.71 (m, 4H), 1.60–1.22 (m, 28H), 1.17 (m, 4H), 0.75 (t, 10H, J=4.5 Hz). ^{13}C NMR (400 MHz, CDCl$_3$) δ (ppm): 166.34, 165.01, 163.61, 151.76, 150.50, 140.09, 139.05, 132.34, 130.37, 128.71, 128.19, 126.06, 122.11, 121.64, 121.57, 120.06, 114.36, 68.37, 64.71, 55.26, 40.28, 29.72, 29.53, 29.50, 29.37, 29.25, 29.14, 28.66, 26.11, 26.02, 25.94, 23.10, 13.83.

For 2,7-bis[4′-{4-(6-acryloyloxyhexyloxy)benzoyloxy}phenyl]-9,9-dihexylfluorene (**7a**), the product was purified with column chromatography on silica gel using ethyl acetate/hexane (3/7) and washed in absolute ethanol to give the compound as a white solid. Yield 68%. IR (KBr) ν_{max}/cm^{-1}: 2929–2859, 1720, 1605, 1511, 1474, 1260. ^{1}H NMR (250 MHz], CDCl$_3$) δ (ppm): 8.19 (d, 4H, J=7.5 Hz), 7.80–7.71 (m, 6H), 7.59 (d, 4H, J=7.5 Hz), 7.32 (d, 4H, J=7.5 Hz), 6.99 (d, 4H, J=7.5 Hz), 6.42 (dd, 2H, J_1=17.5 Hz, J_2=1 Hz), 6.13 (dd, 2H, J_1=17.3 Hz, J_2=10.4 Hz), 5.83 (dd, 2H, J_1=10.0 Hz, J_2=1.1 Hz), 4.19 (t, 4H, J=6.6 Hz), 4.06 (t, 4H, J=6.3 Hz), 2.12 (m, 4H), 1.86 (m, 4H), 1.75 (m, 4H), 1.52 (m, 8H), 1.16 (m, 12H), 0.77 (m, 10H). ^{13}C NMR (250 MHz, CDCl$_3$) δ (ppm): 166.28, 164.97, 163.42, 151.68, 150.36, 140.00, 139.27, 132.30, 130.55, 128.52, 128.14, 125.98, 122.05, 121.58, 121.50, 120.00, 114.25, 68.04, 64.43, 55.24, 40.40, 31.42, 29.65, 28.96, 28.51, 25.68, 23.78, 22.54, 13.96.

For 2,7-bis[4′-{4-(11-acryloyloxyundecyloxy)benzoyloxy}phenyl]-9,9-dihexyl-fluorene (**7b**), the product was purified with column chromatography on silica gel using ethyl acetate/hexane (3/7) and washed in absolute ethanol to give the compound as a white solid. Yield 52%. IR (KBr) ν_{max}/cm^{-1}: 2926–2853, 1727, 1604, 1511, 1466, 1256. ^{1}H NMR (250 MHz, CDCl$_3$) δ (ppm): 8.18 (d, 4H, J=8.8 Hz), 7.80–7.70 (m, 6H), 7.64 (d, 4H, J=9.2 Hz), 7.31 (d, 4H, J=8.5 Hz), 6.99 (d, 4H, J=8.8 Hz), 6.41 (dd, 2H, J_1=17.5 Hz, J_2=1.4 Hz), 6.13 (dd, 2H, J_1=17.2 Hz, J_2=10.3 Hz), 5.82 (dd, 2H, J_1=10.2 Hz, J_2=1.5 Hz), 4.16 (t, 4H, J=6.8 Hz), 4.06 (t, 4H, J=6.4 Hz), 2.05 (m, 4H), 1.84 (m, 4H), 1.68 (m, 4H), 1.32 (m, 28H), 1.14 (m, 12H), 0.77 (m, 10H). ^{13}C NMR (250 MHz, CDCl$_3$) δ (ppm): 166.34, 165.82, 163.54, 151.71, 150.36, 140.02, 139.31, 132.31, 130.42, 128.64, 128.17, 126.00, 122.08, 121.53, 120.02, 114.30, 68.31, 64.69, 55.10, 31.45, 29.47, 29.33, 29.22, 28.69, 25.90, 23.80, 22.56, 13.98.

4.3.5. Network anisotropic luminescent (8b). Monomer **5b** (25 mg), photoinitiator Irgacure 784-DC (1 wt%) and thermal inhibitor 2,6-di-*tert*-butyl-4-methylphenol (200 ppm) were dissolved in dichloromethane and afterwards evaporated at room temperature for 12 h and then under vacuum for 4 h. The reaction mixture was introduced by capillarity into commercial LC cells for planar alignment (Linkam 5 μm) and carried out isothermally at the temperature of the mesophase (90°C). The irradiation was performed using an Ultravitalux 300 W lamp. Irradiation was maintained for 5 min, yielding transparent network (**8b**) with a macroscopic orientation. The reaction was verified by IR measurements, showing disappearance of the vinyl group.

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