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Polarised luminescent films containing fluorene cross-linkers obtained by in situ photo-polymerisation

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Abstract

The paper describes the synthesis of several direactive compounds with luminescent properties based on the fluorene moiety. These difunctionalised compounds have been incorporated as cross-linking agents on liquid crystalline reactive mixtures to be used for the preparation of anisotropic films by the in situ polymerisation technique. The generation of polarised luminescence on the oriented films has been investigated.

Keywords: Fluorenes; Liquid crystals; In situ polymerisation; Photo-luminescence; Polarised emission

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1. Introduction

Luminescent conjugated polymers have gained an unquestionable position in different electro-optical applications [1–4]. In particular, organic luminescent devices based on oriented polymers that emit polarised light can be especially useful as backlights for conventional liquid crystal displays (LCDs) [5]. LCD technology is based on the manipulation of polarised light that is generated by a combination of absorbing polarisers and filters. The use of polarised light-emitting devices as a light source would allow the removal of the normal backlight, polarisers and colour filters combination improving the overall efficiency of the display.

One approach to constructing films that emit linearly polarised light is the uniaxial alignment of the emitting moieties, with the films having a high degree of molecular alignment as one of the main requirements. In principle, orientation can be induced by several methods including mechanical alignment by application of uniaxial stress, rubbing or shear, and Langmuir–Blodgett technique. In addition, one of the most attractive approaches is to use liquid crystalline polymers that can organise themselves into a monodomain on suitable alignment layers [6].

From the investigated polymers, polyfluorenes have evolved as one of the most promising classes of luminescent polymers [7,8]. A variety of polyfluorene derivatives have been tested in different electro-optical devices with a good correspondence between solution and solid-state fluorescence spectra as well as between fluorescence and electroluminescence spectra. They are a particularly suitable class of materials because of their extremely high photo-luminescence efficiencies, their exceptional chemical and physical versatility, and their photo- and thermal stability that is found to be better than those of phenylene vinylene derivatives [9]. Furthermore, the fluorene moiety also represents a favourable building block for obtaining liquid crystalline properties [10]. Therefore, the feasibility of liquid crystal polyfluorenes for polarised emitting layers with high dichroic ratios of absorption or a highly polarised photo- or electroluminescence has been demonstrated with homo- and copolymers or oligomers uniaxially aligned [11–13].

The alignment of liquid crystal polyfluorenes can be achieved with the help of conventional rubbed polyimide layers or even photo-aligned surfaces created on photo-addressable polymers. However, in general terms, polymers posses some disadvantages when compared to low molecular weight liquid crystal such as their high viscosity. For this

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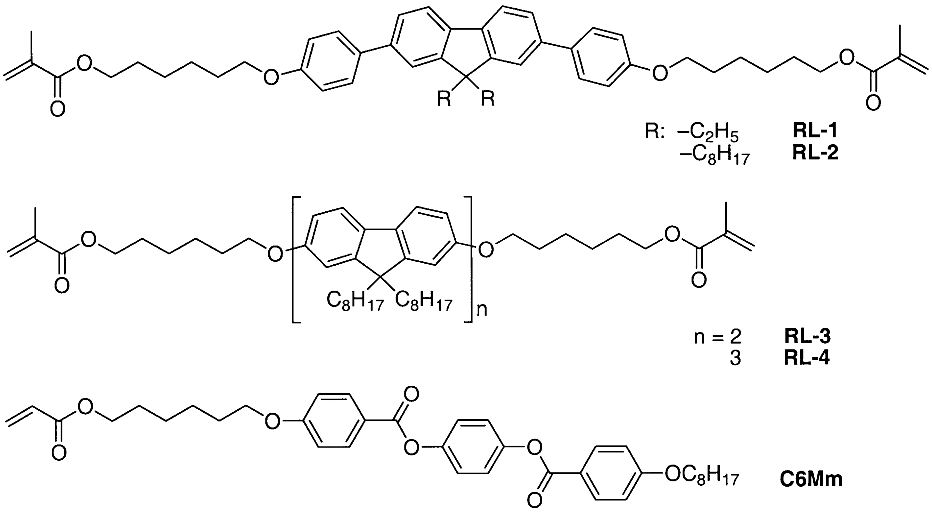

Fig. 1. Chemical structure of reactive fluorenes and liquid crystal host.

reason, they might require of long annealing times at high temperatures to achieve a satisfactory macroscopic alignment. It has been shown that a way to overcome the problem is to produce anisotropic polymeric networks by in situ photo-polymerisation of reactive liquid crystals. Therefore, by irradiating a macroscopically oriented photo-reactive mixture at the mesophase temperature a polymeric material, where the liquid crystalline order is frozen, is obtained. The incorporation of some degree of cross-linking within it would stabilise the ordered structure and also, impart a high degree of mechanical, thermal and chemical stability [14]. There are several examples of inducing polarised luminescence using this approach where chromophores are either dispersed or bonded to the polymer network [15–20].

The aim of this work is the preparation of anisotropic luminescent films by in situ photo-polymerisation of reactive liquid crystal mixtures. In order to achieve this aim, fluorene-based luminophores with two reactive terminal groups have been synthesised where the reactive functional group is attached via a flexible methylenic spacer in order to uncouple the movement of the rigid and reactive parts of the molecule. The structure of the target reactive luminophores (RL) is described in Fig. 1. Both, their thermal and optical properties in solution have been investigated. These fluorene-based dimethacrylates have been used as luminescent cross-linkers in photo-reactive liquid crystalline mixtures. In order to do that, a non-emissive reactive liquid crystal host identified as C6Mm (see Fig. 1) has been doped with a 5% (molar ratio) of the luminescent fluorene. Therefore, thermal properties and the in situ photo-polymerisation of the mixtures have been studied. Finally, oriented films have been produced by light induced polymerisation using conventional liquid crystal cells for planar alignment. The anisotropy of the absorption and emission has been studied by polarised UV-Vis and fluorescence spectroscopy.

2. Experimental

2.1. *Synthesis of reactive compounds*

The synthesis of RL-1 and RL-2, and the liquid crystal C6Mm is described elsewhere [21]. The synthesis of RL-3 and RL-4 is outlined in Fig. 2.

2.1.1. *Synthesis of compound* ***1***

A 50% NaOH aqueous solution (80 ml) was added to a mixture of 2-bromofluorene (42.8 mmol), tetrabutylammonium bromide (2.1 mmol) in toluene (80 ml). Afterwards, 1-bromooctane (97 mmol) in toluene (20 ml) was added and the reaction mixture was vigorously stirred overnight at 60 °C. The organic phase was separated, washed with water, dried over magnesium sulphate and the solvent evaporated. The unreacted 1-bromoundecane was removed under reduced pressure and the residue purified by flash column chromatography on silica gel using hexane as eluant to afford the desired compound as a pale yellow liquid (62%). ^1H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.64 (m, 1H), 7.54 (dd, $J = 7.3$, 1.5 Hz, 1H), 7.43 (dd, $J = 7.0$, 1.1 Hz, 2H), 7.31 (m, 3H), 2.00–1.80 (m, 4H), 1.24–1.03 (m, 20H), 0.81 (t, $J = 7.3$ Hz, 6H), 0.58 (m, 4H).

2.1.2. *Synthesis of compound* ***2***

A mixture of nickel(II) chloride (0.5 mmol), zinc (15.0 mmol), triphenylphosphine (2.6 mmol) and bipyridine (0.5 mmol) in dry DMF (200 ml) was purged with nitrogen and then heated at 65 °C. When the mixture turned dark brown, the compound **1** (4.9 mmol) was slowly added via syringe. The reaction mixture was heated at 70 °C for 10 h and then filtered. Ethyl acetate was added to the solution, which was then washed twice with water, dried over magnesium sulphate and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel

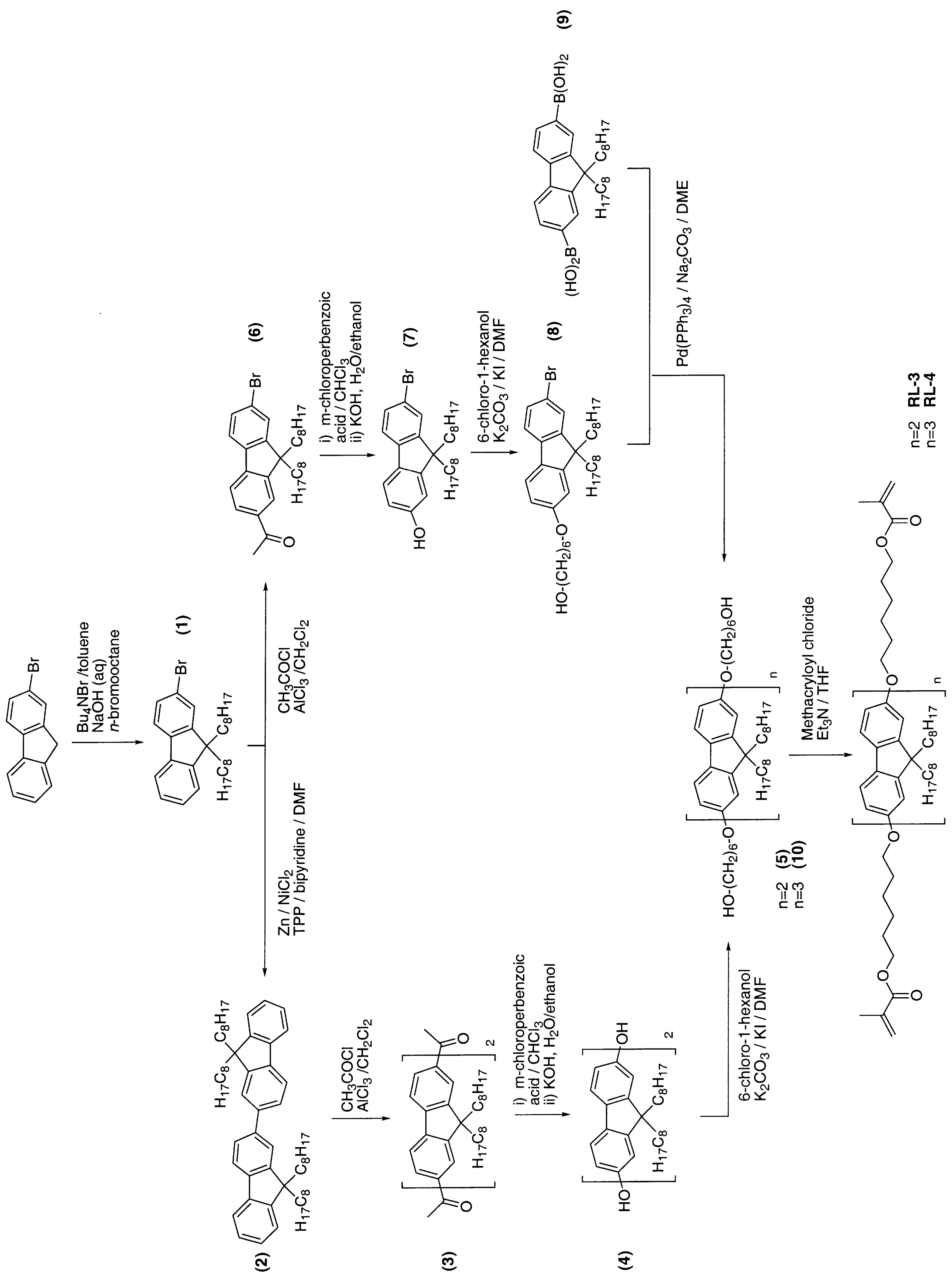

Fig. 2. Synthetic scheme for preparing RL-3 and RL-4.

using hexane as eluant (53%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.77–7.71 (m, 4H), 7.64–7.60 (m, 4H), 7.34–7.31 (m, 6H), 2.04–1.99 (m, 8H), 1.30–1.00 (m, 40H), 0.79 (t, $J = 7.3$ Hz, 12H), 0.76–0.59 (m, 8H).

2.1.3. *Synthesis of compounds **3** and **6***

In the preparation of these compounds to a suspension of the appropriate fluorene and $AlCl_3$ (2 equiv.) in dry dichloromethane under argon atmosphere at 0 °C, acetyl chloride (2 equiv.) was added dropwise (10 min) while vigorously stirring. The reaction mixture was then warmed to room temperature and stirred for an additional 48 h. The reaction mixture was washed with H_2O/HCl, water and brine, dried over magnesium sulphate and rotary evaporated. The crude product was recrystallised from ethanol to afford **3** (66%) or **6** (84%) as a white solid. Characterisation of **3** ^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.98–7.96 (m, 4H), 7.68–7.62 (m, 4H), 7.68–7.62 (m, 4H), 2.67 (s, 6H), 2.06 (t, $J = 8.1$ Hz, 8H), 1.23–0.89 (m, 40H), 0.78 (t, $J = 7.0$ Hz, 12H), 0.70–0.50 (m, 8H). Characterisation data of **6**: ^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.95 (d, $J = 7.3$, 1.5 Hz, 2H), 7.71 (d, $J = 7.3$, 1.5 Hz, 1H), 7.60 (dd, $J = 7.0$, 1.8 Hz, 1H), 7.47 (dd, $J = 7.0$, 1.8 Hz, 2H), 2.65 (s, 3H), 1.95 (m, 4H), 1.25–0.95 (m, 20H), 0.80 (t, $J = 7.3$ Hz, 6H), 0.55 (m, 4H).

2.1.4. *Synthesis of compounds **4** and **7***

In the preparation of these compounds in a blackened flask the adequate acetylfluorene was dissolved in chloroform. *m*-Chloroperbenzoic acid (50% excess over the stoichiometric amount) was portionwise added at 0 °C under argon atmosphere while stirring. The reaction mixture was then warmed to room temperature and stirred for 3 days. The resulting brown solution was successively washed with a $NaHCO_3$ saturated solution, water and brine, dried over magnesium sulphate and then evaporated to dryness. The residue was purified by flash column chromatography on silica using hexane/dichloromethane (3:7) as eluant to yield an oil. The oil was taken up in water/ethanol (2:5) and a large excess of KOH in water was added. The reaction was heated at reflux temperature for 16 h. The reaction was cooled to room temperature, neutralised by adding concentrated HCl and the residue extracted with diethyl ether. The organic extracts were combined, washed with brine and dried over magnesium sulphate. The solvent was evaporated under vacuum and the residue purified by flash column chromatography on silica gel using dichloromethane/hexane (4:1) as eluant to yield **4** as an oil (80%) and **7** as a pale yellow solid (53%). Characterisation data of **4**: ^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.67–7.54 (m, 8H), 6.84–6.80 (m, 4H), 1.91 (m, 8H), 1.24–1.03 (m, 40H), 0.81 (t, $J = 7.0$ Hz, 12H), 0.66–0.49 (m, 8H). Characterisation data of **7**: ^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.49 (dd, $J = 5.1$, 3.7 Hz, 1H), 7.41 (m, 3H), 6.77 (dd, $J = 5.9$, 2.2 Hz, 2H), 4.83 (s, 1H), 1.86 (m, 4H), 1.25–1.03 (m, 20H), 0.81 (t, $J = 7.0$ Hz, 6H), 0.57 (m, 4H).

2.1.5. *Synthesis of compounds **5** and **8***

Synthesis of compounds was carried out according to the procedures reported in the literature [22]. Characterisation data of **5**: ^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.67–7.54 (m, 8H), 6.92–6.84 (m, 4H), 4.16 (t, $J = 6.6$ Hz, 4H), 4.03 (t, $J = 6.6$ Hz, 4H), 2.03–1.60 (m, 16H), 1.55–1.48 (m, 8H), 1.24–0.83 (m, 40H), 0.81–0.58 (m, 20H). Characterisation data of **8**: ^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.47 (br, 1H), 7.35 (m, 3H), 6.80 (br, 2H), 3.95 (t, $J = 6.6$ Hz, 2H), 3.62 (t, $J = 6.6$ Hz, 2H), 1.83 (m, 6H), 1.57–1.44 (m, 6H), 1.25–0.98 (m, 20H), 0.76 (t, $J = 7.3$ Hz, 6H), 0.54 (m, 4H).

2.1.6. *Synthesis of compound **10***

A mixture of compounds **8** (3.3 mmol) and **9** (prepared as described in [23]) (1.4 mmol), triphenylphosphine (0.2 mmol), 2 M sodium carbonate (37 ml) and dimethoxyethane (80 ml) was heated at reflux temperature while stirring for 3 days. Then, the reaction was cooled to room temperature and extracted with diethyl ether. The combined organic extracts were washed with water, dried over magnesium sulphate and evaporated to dryness. The crude product was purified by flash column chromatography on silica gel using hexane/ethyl acetate (9:2) as eluant to afford the desired product (51%). ^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.83–7.52 (m, 10H), 7.49–7.21 (m, 4H), 6.91–6.82 (m, 4H), 4.01 (t, $J = 6.6$ Hz, 4H), 3.66 (t, $J = 6.7$ Hz, 4H), 2.22–1.64 (m, 16H), 1.62–1.27 (m, 12H), 1.26–0.98 (m, 60H), 0.88–0.50 (m, 30H).

2.1.7. *Synthesis of RL-3 and RL-4*

This was carried out according to the procedures reported in the literature [22]. Characterisation of RL-3: IR (NaCl, cm^{-1}) ν: 2933, 2859, 1716, 1637, 1607, 1516, 1464, 1320, 1296, 1247, 1175, 817. ^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.67–7.54 (m, 8H), 6.92–6.84 (m, 4H), 6.10 (s, 2H), 5.53 (s, 2H), 4.16 (t, $J = 6.2$ Hz, 4H), 4.02 (t, $J = 6.2$ Hz, 4H), 2.03–1.60 (m, 22H), 1.55–1.48 (m, 8H), 1.24–0.83 (m, 40H), 0.81–0.58 (m, 20H). ^{13}C NMR ($CDCl_3$, 300 MHz, δ (ppm)): 167.5, 159.0, 153.0, 150.9, 140.1, 139.4, 136.5, 133.8, 125.9, 125.2, 121.2, 120.3, 118.9, 112.7, 109.6, 68.0, 64.6, 55.3, 40.5, 31.8, 30.0, 29.7, 29.3, 29.2, 28.6, 25.9, 23.7, 22.6, 18.3, 14.0. Characterisation of RL-4: IR (NaCl, cm^{-1}) ν: 2924–2852, 1721, 1638, 1608, 1582, 1295, 1103, 939, 885. ^{1}H NMR ($CDCl_3$, 300 MHz, δ (ppm)): 7.84–7.26 (m, 14H), 6.91–6.79 (m, 4H), 6.12 (s, 2H), 5.57 (s, 2H), 4.19 (t, $J = 6.2$ Hz, 4H), 4.04 (t, $J = 6.2$ Hz, 4H), 2.12–1.82 (m, 22H), 1.64–1.43 (m, 12H), 1.28–0.98 (m, 60H), 0.88–0.58 (m, 30H). ^{13}C NMR ($CDCl_3$, 300 MHz, δ (ppm)): 159.1, 153.0, 151.7, 151.0, 140.5, 140.3, 139.9, 139.3, 133.8, 126.0, 121.4, 121.2, 120.4, 119.8, 118.0, 112.8, 109.3, 77.7, 77.6, 77.4, 77.2, 77.0, 76.6, 68.2, 62.9, 55.2, 40.5, 40.4, 32.7, 32.1, 31.8, 30.2, 30.0, 29.7, 22.6, 14.1.

2.2. Photo-polymerisable mixtures

Reactive liquid crystalline mixtures were prepared by dissolving C6Mm and the corresponding fluorene-based dimethacrylate (95:5 molar ratio) in freshly distilled dichloromethane together with the photo-initiator Irgacure 784-DC (1 wt.%) and the thermal inhibitor 2,6-di-*tert*-butyl-4-methylphenol (200 ppm). The solvent was evaporated first at room temperature and then at 30 °C under vacuum.

2.3. Preparation of anisotropic films by in situ photo-polymerisation

Light-induced photo-polymerisation was carried out by irradiation of the molten samples in commercial LC cells for planar alignment (Linkam 5 μm). The monomeric mixture was introduced by capillarity at 100 °C and cooled down to the polymerisation temperature. Uniaxial orientation was checked by optical microscopy. The irradiation process was performed using an OSRAM Ultravitalux 300 W lamp using a 400 nm long pass filter between the lamp and the sample. Irradiation was maintained for 10 min while the lamp was kept at 20 cm from the cell.

2.4. Techniques

IR spectra were measured on an ATI-Matsson Genesis Series FTIR from nujol mulls between NaCl disks. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unit-300 spectrometer operating at 300 MHz.

Mesogenic behaviour and transition temperatures were determined using an Olympus BH-2 polarising microscope equipped with a Linkam THMS hot-stage central processor and a CS196 cooling system. Differential scanning calorimetry (DSC) was performed using a DSC 2910 from TA Instruments with samples sealed in aluminium pans and a scanning rate of 10 °C/min under nitrogen atmosphere. Temperatures were read at the onset of the peak after previous heating of the sample to the isotropic liquid and cooling to 0 °C. In situ photo-polymerisation was studied by DSC using a Perkin-Elmer 7 apparatus modified for light irradiation [24]. The sample (2–4 mg) was placed in an unsealed aluminium pan that was irradiated under a nitrogen atmosphere using an OSRAM Ultravitalux lamp. A 400 nm long pass filter and water to filter the IR radiation were placed between the sample and the light source. The lamp was kept at 30 cm from the sampler holder.

Optical absorption spectra were recorded with an UV-Vis spectrophotometer UV4-200 from ATI-Unicam for THF solutions. Polarised UV-Vis measurements were recorded with the same equipment using a Glan-Thomson polariser. Luminescence measurements were performed using a Perkin-Elmer LS50B spectrofluorimeter. Spectra of the pure RL compounds were recorded in 10^{-6} to 10^{-7} M THF solutions under excitation in the absorption maximum [22]. Fluorescence quantum yields were determined by comparing the integrated photo-luminescence of a ca. 0.01 optical density THF solution of the compound with that of a reference with a known quantum yield. 9,10-Diphenylanthracene (99%, Acros Organics) in cyclohexane (quantum yield 0.90) was used as reference. Polarised luminescence measurements were recorded in the same equipment with a sample holder designed to measure LC cells [16] using 1% attenuation to avoid saturation of the detector. The measurements were taken with the excitation beam polarised in parallel to the rubbing direction of the cell and the detection polariser either parallel or perpendicular, these two experimental configurations are noted as vvv or vvh, respectively.

3. Results and discussion

3.1. Synthesis, thermal and optical properties of fluorene compounds

The structure of the fluorene direactive compounds and the host liquid crystalline compound are presented in Fig. 1. Two types of fluorene derivatives were prepared. The first type (RL-1 and RL-2) contain a 9,9-dialkylfluorene unit in the centre of the potentially mesogenic core that it is elongated by a phenyl ring at both second and seventh positions of the fluorene. The compounds would be, at least formally, related to tetraphenyl derivatives. The synthesis and thermal properties of these compounds have already been published elsewhere [21]. The second type of fluorenes (RL-3 and RL-4) contains an aromatic core composed of two or three 9,9-dialkylated fluorene units bonded at the second and seventh positions. The synthesis of RL-3 and RL-4 is depicted in Fig. 2. Both reactive compounds were prepared starting from a common precursor, 2-bromo-9,9-dioctylfluorene (**1**), and the methacrylate reactive moiety was incorporated in the last step of the reaction sequence in order to avoid undesired lateral reactions involving it. Compound RL-3 was prepared by self-coupling of **1** to render the desired aromatic core which was subsequently hydroxy-functionalised in two steps: a Friedel–Crafts acylation; followed by one-pot Bayer–Villager oxidation and hydrolysis of the intermediate ester. The prepared dihydroxybifluorene (**5**) was alkylated with 6-chloro-1-hexanol before formation of the methacrylic ester. To the preparation of compound RL-4, compound **1** was also hydroxy-functionalised in two steps, as mentioned above and then alkylated. The resulting compound **8** was reacted with bromofluorene in a Suzuki cross-coupling reaction to yield the aromatic core bearing the flexible tails. In the last step of the reaction sequence, the photo-reactive terminal groups were incorporated to give the target compounds.

The thermal properties of the fluorene compounds are gathered in Tables 1 and 2. The 2,2-diethylfluorene derivative, RL-1 melts at 65 °C. On cooling, a mesophase develops that, when viewed through crossed polarisers, exhibits the typical appearance of an SmC phase. The transition SmC-I

Table 1
Thermal and optical properties of the reactive fluorenes

Compounds	Thermal transitions	λ_{abs} (nm)	λ_{em} (nm)	Φ_{fl}
RL-1	K 65 (SmC 22)[a] I[b]	335	370, 389	0.66
RL-2	K 42 I[b]	336	371, 388	0.65
RL-3	K 60 I[c]	340	378, 397	0.55
RL-4	K 36 I[c]	357	403, 422	0.75

[a] Thermal transition recorded on a second heating scan with an associated enthalpy of 0.85 kJ mol^{-1}.

[b] Melting temperatures determined on a first heating of the sample.

[c] Melting temperatures determined after cooling the sample below −50 °C.

temperature was determined by DSC to be at 22 °C. However, the 9,9-dioctylfluorene homologue RL-2 has a lower melting temperature, 42 °C, but the longer lateral chains destabilise the formation of liquid crystalline phases. This can be attributed to steric effects due to an increase of the intermolecular distance and therefore, the weakening of the intermolecular interactions. On cooling both compounds show a very low tendency to crystallise. A comparison with analogous reported compounds proves that lengthening the aromatic core will be required to promote liquid crystalline behaviour, however, this would occur with an increase of the transition temperatures [19].

In relation to compounds RL-3 and RL-4, they were obtained as waxy solids with no great tendency to crystallise. Nevertheless, crystallisation can be induced on extreme cooling or standing for prolonged periods of time at room temperature. Melting temperatures of RL-3 and RL-4 were 60 and 36 °C, respectively, as determined by DSC after cooling the samples below −50 °C. When viewed between crossed polarisers, there was no evidence of mesophase formation. These results are in accordance with former papers on 9,9-dialkyloligofluorenes [20,25,26]. Oligofluorenes are in general amorphous materials. Nevertheless, investigations on related chiral 9,9-dialkyloligofluorenes show oligomers longer than four fluorenes units are inherently mesomorphic.

The absorption and emission spectra of the compounds were recorded in THF. The results are summarised in Table 1. It has been established that the alkyl side chains strongly influence the liquid crystal behaviour, however, their structure and length do not significantly vary the optical and electronic properties of polyfluorenes in dilute solutions [8]. Accordingly, absorption and emission spectra of RL-1 and RL-2 are almost identical because of the coincidence on their conjugated core. They present an unstructured absorption band centred about 336 nm. Emission spectra, when excited at the maximum absorption, show a weak vibronic structure with two maxima of approximately the same intensity at about 370 and 388 nm. Relative quantum yields have the same values 0.65–0.66. Differences are encountered when comparisons are established with RL-3 and RL-4. The absorption of RL-3, 340 nm, is slightly red-shifted when compared to RL-1 or RL-2, which are π-isolectronic. The same situation is reproduced on comparing the emission spectra but being the emission efficiency lower. When the length of the conjugated core is enlarged with an additional fluorene unit, RL-4, the bathochromic displacement of absorption and emission is increased. In this case the emission efficiency is also larger, 0.75 for the fluorescence quantum yield measured in solution. Results obtained for RL-3 and RL-4 are in accordance to those of related fluorene oligomers [26].

Table 2
Optical properties of anisotropic films

Film compositions	λ_{em} (nm)	I_{vvv}/I_{vvh}
RL-1/C6Mm	378^{sh}, 395	6.5
RL-2/C6Mm	379^{sh}, 395	5.7
RL-3/C6Mm	384, 402	4.7
RL-4/C6Mm	408, 425	5.6

3.2. Preparation and study of fluorene-containing oriented films

As it was stated, reactive mixtures were prepared dissolving the fluorene in the non-luminescent reactive liquid crystal host C6Mm. This monoacrylate C6Mm shows a N phase between 86 and 116 °C. The prepared samples contain 5% (molar ratio) of fluorene, 1% (w/w ratio) of a photo-initiator and 200 ppm of a thermal inhibitor. Acrylate and methacrylate functions are the most common reactive groups used in the in situ photo-polymerisation of reactive liquid crystals because they undergo a rapid and efficient polymerisation. This light activated process involves the generation of radicals by photolysis of an initiator by action of light and subsequent radical polymerisation of the monomeric mixture. The polymerisation was carried out using a photo-initiator of the titanocene type, Irgacure 784DC® from Ciba-Geigy, which shows a broad absorbance in the visible region of the spectrum, and a visible light source in combination with a 400 nm long pass filter. Under these conditions, the absorbance of the polymerisable mixture is extremely low and excitation of the fluorene chromophore is minimal, therefore light induced polymerisation is optimally performed.

In situ photo-polymerisation is carried out isothermally at the temperature of the N mesophase. However, spontaneous generation of radicals can occur at the mesophase temperature. In order to avoid the undesired thermal polymerisation a small amount of a thermal inhibitor (200 ppm) is added to the reactive mixture.

On using these concentrations, the samples were completely miscible. The DSC and optical microscopy studies, show that the samples melt around 60 °C into a N mesophase, that it is stable up to approximately 120 °C. On cooling they have a very low tendency to crystallise and maintain the mesophase at room temperature. On a subsequent heating they exhibit a cold crystallisation processes at about 15–30 °C. Thermally induced polymerisation was detected only in the isotropic liquid phase, above 150–200 °C.

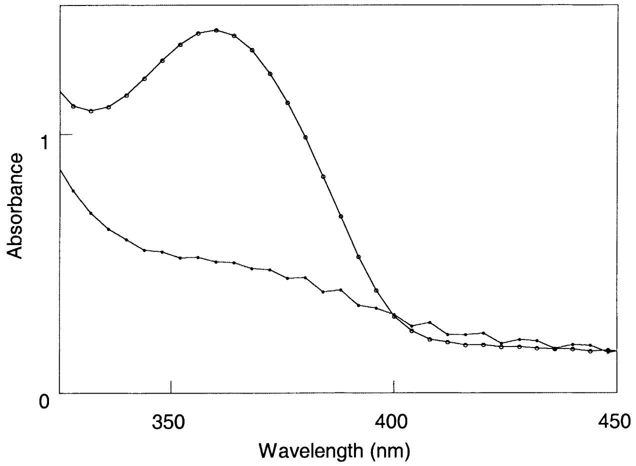

Fig. 3. Polarised UV-Vis absorption of RL-4/C6Mm film. Spectra recorded parallel (above) and perpendicular (below) to the molecular orientation direction.

Photo-DSC studies on the polymerisation of the mixtures revealed that polymerisation takes place at high rates, achieving conversions higher than 90%. A previous study of a sample containing 10% of RL-2 at different temperatures showed that the polymerisation rate decreases on increasing temperature indicating a higher influence of the polymerisation temperature in comparison to phase ordering.[2] For that reason, polymerisation was performed at 50 °C in the N phase, in order to combine a suitable polymerisation rate and control of the temperature.

Oriented films were obtained in commercial cells for planar alignment. The cells are formed by two parallel glass plates whose inner faces are coated with an ITO and a polyimide film, which has been uniaxially rubbed. This produces an alignment of the molecules along the rubbing direction. In all cases, optically transparent films were produced after irradiation, indicating their amorphous character.

Polarised UV-Vis absorption and photo-luminescence spectra of the films were taken at room temperature. Representative data is collected in Fig. 3. Polarised UV-Vis spectra were measured with the rubbing direction of the cell parallel to the transmission direction of the polariser and perpendicular to it. Because of the low wavelength absorption, there is some overlapping between the low energy absorption band of the film and absorption of the glass substrate of the cell. Therefore, an accurate measurement of the absorption wavelength and the absorbance is difficult. Nevertheless, the dichroism on the absorption is evident as it is can be seen from Fig. 3. The difference between the spectra taken parallel and perpendicular to the rubbing direction shows that there is a preferential orientation of the chromophore.

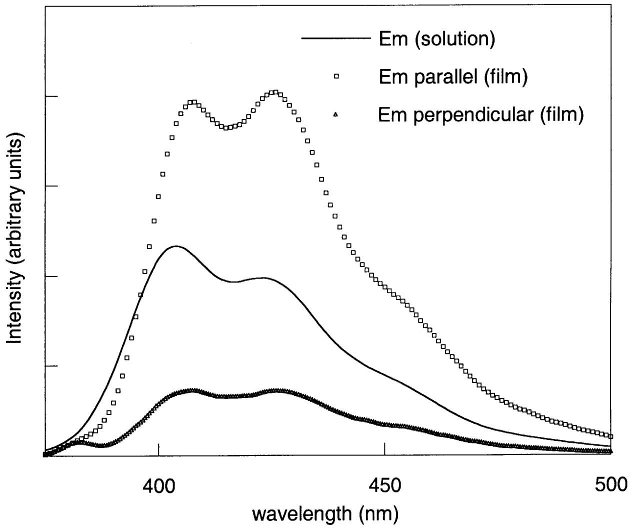

Fig. 4. Emission spectrum of RL-4 in THF and emission spectra of RL-4/C6Mm film taken parallel and perpendicular to the molecular orientation direction as described in the experimental section.

Emission spectra of the solid films were compared to the spectra taken in solution (see Fig. 4). In all cases, the emission spectra of the films are qualitatively identical to the spectra taken in solution. Furthermore, a slight red-shift on the emission wavelength was observed. This situation has already been observed and related to a more planar structure of the excited state for the film [26]. As it has been reported, the estimation of the order parameter from polarised photo-luminescence measurements is not evident [16]. However, from the relationship between the maximum intensity of the emission bands ($I_{\mathrm{vvv}}/I_{\mathrm{vvh}}$) a preferential direction for emission is inferred, being about five-to-six times larger in the direction of the molecular orientation.

4. Conclusions

Novel luminescent cross-linking agents have been prepared that can be incorporated into reactive mixtures. Preparation of anisotropic films form these reactive blends is possible by in situ photo-polymerisation of uniaxially oriented samples. The films show a preferential emission direction due to their anisotropic absorption.

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